



**LEVELS OF SELECTED GASEOUS POLLUTANTS IN AMBIENT AIR IN THE
VICINITY OF A CHEMICAL INDUSTRY, KWEKWE, ZIMBABWE**

by

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TABLE OF CONTENT

DECLARATION	iv
ABSTRACT.....	v
ACKNOWLEDGEMENTS	vii
DEDICATION.....	viii
LIST OF FIGURES	ix
LIST OF TABLES.....	ix
APPENDICES.....	x
CLARIFICATION OF BASIC TERMS AND CONCEPTS.....	xi
LIST OF ABBREVIATIONS.....	xiii
CHAPTER ONE	1
INTRODUCTION	1
1.1 Background.....	1
1.2 Air Pollution: Health and Environmental problems/consequences.....	2
1.3 Arable Soil Fertility in Zimbabwe and the Sable Chemical Industry	3
1.4 Research scope.....	4
1.5 Objectives of this research study	4
CHAPTER TWO	6
LITERATURE REVIEW.....	6
2.1 Air pollution.....	6
2.2 Occurrences of air pollutants in the environment	7
2.2.1 Sources of air pollutants	7
2.2.2 Distribution and transport of air pollutants.....	8
2.3 Transformation of air pollutants.....	9
2.4 Impacts of air pollution (human and environmental damage)	9
2.4.1 Health Impacts.....	10
2.4.2 Effects of pollution on ecological systems.....	12
2.4.3 Air pollution and global warming	15
2.4.4 Impacts on buildings and material.....	16
2.4.5 Economic influences of poor air quality	16
2.5 Environmental Impacts of selected gaseous pollutants NH ₃ , SO ₂ and NO ₂	17

2.5.1	Ammonia (NH ₃)	17
2.5.2	Sulphur dioxide (SO ₂).....	19
2.5.3	Nitrogen dioxide (NO ₂).....	20
2.6	Gaseous pollutants from fertilizers	21
2.6.1	Emission from chemical and fertilizer production	23
2.7	An overview of past research studies on air pollution.....	24
2.8	Air monitoring Techniques	28
2.8.1	Passive sampling method	29
2.8.2	Active samplers	30
2.8.3	Biomonitoring of air pollutants.....	30
2.8.4	Environmental law on biomonitoring and bioaccumulation	31
2.8.5	Environmental Law in Zimbabwe	31
2.8.6	Air quality guidelines	32
CHAPTER THREE.....		34
RESEARCH DESIGN AND METHODOLOGY		34
3.1	Description of study location	34
3.2	Topography.....	35
3.3	Vegetation and plant geography	36
3.4	Fauna and flora population	36
3.5	Delineation of assessment study area.....	37
3.6	Sampling frequency and study duration	37
3.7	Sampling stations	37
3.8	Data acquisition (Measuring Principle)	40
CHAPTER FOUR.....		41
RESULTS AND DISCUSSION.....		41
4.1	Instrument calibration and validation	41
4.2	Concentration levels of NH ₃ , SO ₂ and NO ₂ around vicinity of Sable Chemical Industry	41
4.2.1	Ammonia (NH ₃)	42
4.2.2	Sulphur dioxide (SO ₂).....	43
4.2.3	Nitrogen dioxide (NO ₂).....	43
4.3	Distribution of NH ₃ , SO ₂ and NO ₂ around the vicinity of Sable Chemical Industry	44
4.3.1	Levels and distribution of NH ₃ around the vicinity of Sable Chemical Industry	45

4.3.2	Distribution of NO ₂ around the vicinity of Sable Chemical Industry.....	46
4.3.3	Distribution of SO ₂ around the vicinity of Sable Chemical Industry.....	47
4.4	Comparative isokinetic (results) and dissipation studies	48
4.5	Evaluation of ambient levels of NH ₃ , NO ₂ and SO ₂ : Environment and Health implication	50
4.5.1	NH ₃ in the environment: source apportionment, levels, and distribution (Distribution and apportionment of source levels of NH ₃)	50
4.5.2	Exposure evaluation of NO ₂	52
4.5.3	Exposure evaluation for SO ₂	53
CHAPTER FIVE.....		56
CONCLUSION AND RECOMMENDATIONS.....		56
5.1	Conclusion.....	56
5.2	Recommendations	57
REFERENCES		58
APPENDICES.....		70

DECLARATION

I **Joseph Simbi**, declare that the content of this dissertation represent my own unaided work, and has not previously been submitted for academic examination towards any other qualification at any University. Furthermore, it represents my own opinion and not necessarily that of the Cape Peninsula University of Technology.

Signed

Date

ABSTRACT

The integrity of natural air has been compromised due to the deposition of chemical, biological and particulate substances from natural and anthropogenic sources. Adverse health consequences arising from the exposure of plants, animals and human to elevated atmospheric concentrations have been reported severally. The ambient baseline levels of many air contaminants in urban and industrial layouts of many Africa cities, especially Zimbabwe have not been fully characterized. Information on levels of these contaminants and their real time variability is therefore scarce and scanty.

In this study, the ambient air concentration levels of selected gaseous pollutants in the vicinity of a fertilizer production facility in Zimbabwe were investigated. Nine sampling stations were systematically and randomly identified for the measurement of selected air pollutants (SO_2 , NO_2 , and NH_3) the fertilizer production factory to capture air quality data on all wind directions. The electrochemical Drager Sensors which rely on electrochemical measuring transducer for measuring concentration of gases under atmospheric conditions was used for the measurement of NH_3 , SO_2 , and NO_2 . The ambient air monitored was allowed to diffuse through a membrane into the sensor liquid electrolytes, containing a sensing electrode, a counter electrode, a reference electrode, and an electronic potentiostat-circuit which ensures constant electrical voltage between the sensing electrode and the reference electrode. The flow of electrons, generated by the reaction is proportional to the concentration of the measured gas. The observed concentrations of NH_3 , SO_2 , and NO_2 measured within and around the study site were very variable.

Levels of NH_3 ranged between 0.36 - 7.36 ppm; corresponding values for SO_2 and NO_2 were 0.02 - 84.61 ppm and 0.61 - 34.78 ppm respectively. These concentrations were significantly higher ($p < 0.05$) than measured (NH_3 ; 0.01 - 0.05 ppm; SO_2 ; 0.03 - 0.18 ppm; NO_2 ; 0.17 - 1.30 ppm) at the control sampling station about 5 km from the industry. Isokinetic and dissipation of the measured gases, governed by the processes of molecular diffusion and convection, confirmed a common pattern of distance dissipation. Thus, the cloud concentrations of NH_3 , SO_2 , and NO_2 within the facility were higher than observed distances away from the fertilizer factory. The variability in the concentrations of each parameter measured within the

plant may be connected with hotspots such as the ammonia loop, valve leakage areas as well as the prevailing meteorological conditions at the time of measurement.

Keywords

Ammonia, fertilizer production, nitrogen dioxide, pollution, sulphur dioxide, Zimbabwe

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DEDICATION

I dedicate this dissertation to my wife Shamiso and our children, my supervisor and lecturer Prof Beatrice Olutoyin Opeolu and Sable Chemical Industry staff.

LIST OF FIGURES

Figure 1: Health effects of air pollution	10
Figure 2: Presents general mechanism of cardiovascular disease	12
Figure 3: Impact of acid rain on forest nutrient cycles.....	13
Figure 4: Acid tolerance ranges of common freshwater organisms (Courtesy United States)....	14
Figure 5: Fertilizer production stages	22
Figure 6: Map of Zimbabwe showing the location of Kwekwe and the Sable Chemical Industry Position of (S.C.I) in Zimbabwe (<i>Adapted from: Zimbabwe district map, 2012</i>)	34
Figure 7: Geo-references of Kwekwe and Sable Chemical Industry land boundary showing the 7km radius danger zone (<i>Adapted from: S.C.I Training Manual, 2011</i>)	35
Figure 8: Sable Chemical Industry Google Map showing the nine sampling points	38
Figure 9: The Drager X-am 5000 automatic multi gas monitor	39
Figure 10: Distribution of the mean monthly concentration of NH ₃ in the different sampling stations around S. C. I.....	46
Figure 11: Distribution of the mean monthly concentration of NO ₂ in the different sampling stations around Sable Chemical Industry	47
Figure 12: Distribution of the mean monthly concentration of SO ₂ in the different sampling stations around Sable Chemical Industry	48
Figure 13: Concentrations of SO _x and NO _x from the stack	49
Figure 14: Main Entrance of S.C.I	72
Figure 15: Fractional distillation plant at S.C. I	73
Figure 16: Ammonia plant (Loop) at S.C.I	74
Figure 17: Ammonia storage tanks at S.C.I.....	75
Figure 18: Nitric acid plant at S.C.I.....	76
Figure 19: Ammonium nitrate plant at S.C.I.....	77
Figure 20: Boiler plant at S.C.I	78
Figure 21: Impacts of air pollution on forest at S.C.I.....	79
Figure 22: Mr. Burger and his son Daniel working on their farm about a 1km from S.C.I.....	80
Figure 23: Mrs.Sibanda a newly resettled farmer at her new home	81

LIST OF TABLES

Table 1: Stack heights and diameter at S.C.I	32
Table 2: EPA and WHO guidelines for SO ₂ , NO ₂ and NH ₃	33
Table 3: Zimbabwe air quality standards for NH ₃ ,NO _x and SO ₂	33
Table 4: Concentrations of NH ₃ gas measured at the different sampling points.....	42
Table 5: Concentrations of SO ₂ gas measured at the different sampling points.....	43
Table 6: Concentrations of NO ₂ gas measured at the different sampling points.....	44
Table 7: Concentrations of SO _x and NO _x from the stack	49
Table 8: Guideline for NO ₂ in µg/m ³	53

APPENDICES

Appendix A	Letter of authority to carry out a research at Sable Chemical Industry	70
Appendix B	Air Sampling Record Sheet	71
Appendix C	Main Entrance of S.C.I	72
Appendix D	Fractional distillation plant at S.C.I	73
Appendix E	Ammonia plant (Loop) at S.C.I	74
Appendix F	Ammonia storage tanks at S.C.I	75
Appendix G	Nitric acid plant at S.C.I.....	76
Appendix H	Ammonium nitrate plant at S.C.I.....	77
Appendix I	Boiler plant at S.C.I.....	78
Appendix J	Impacts of air pollution on forest at S.C.I.....	79
Appendix K	Farmers within the 7 kilometre radius	80
Appendix L	Newly resettled Farmer	81
Appendix M	GLM Procedure (Class Level)	82
Appendix N	Analysed data using SPSS.....	89

CLARIFICATION OF BASIC TERMS AND CONCEPTS

TERM	DEFINITION
Air pollution	Introduction of substances or surplus energy as waste products of human activities into the atmosphere while directly or indirectly adversely alter or destroy the quality of the environment or cause undesirable effects on man, animals, vegetation or materials. These wastes may be gaseous or particulate emissions (Chipindu, 2009).
Ambient air	That portion of the atmosphere, external to buildings, to which the public has access (Martineau and Novello, 2004).
Anthropogenic	Made by humans, human caused. (The InviroLink Network, 2008).
Asthma	A chronic condition of the lung characterised by wheezing and difficulty in breathing (Diab, 2011).
Bronchitis	An inflammation of the mucous membrane of the bronchi or tubes leading to the lung. It causes a persistent cough that produces large amounts phlegm (Diab, 2011).
Chlorofluorocarbons (CFCs)	Also known as Freons. They were produced for a variety of commercial and industrial purposes, but currently are produced in small quantities because of the destruction of the protective ozone layer in earth's stratosphere. They also act as greenhouse gases and will remain in the atmosphere for several centuries to come (Grimsrud, 2012).
Carcinogen	A substance that causes cancer. (The InviroLink Network, 2008).
Cardiovascular	Relating to the heart and blood vessels. (The InviroLink Network, 2008).
Climate change	A change in the climate of a region over time due to natural forces or human activity. In the context of the UN Framework Convention on Climate Change, it is the change in climate caused by higher levels of greenhouse gases in the atmosphere due to human activities as well as natural climate changes (National Adult Literacy Agency, 2009).
Criteria pollutants	A group of air pollutants which are deemed to have human health and /or environmental effects and as such are regulated by the setting of air quality standards. In the United States, these include CO, NO _x , O ₃ , SO ₂ , Pb and PM (Diab, 2011).

TERM	DEFINITION
Emission	Pollutants discharged into the atmosphere from the range of stationary and mobile sources. These include smoke stacks, vents and surface areas of commercial and industrial facilities, residential sources, motor vehicles and other transport related sources (National Adult Literacy Agency, 2009).
Environment	Refers to the external surroundings including all of the biotic and abiotic factors that surround and affect the survival and development of an organism or population i.e. the sum total of water, air and land interrelationships among themselves and with the human beings, and other living organisms (Enger and Smith, 2010).
Global warming	The gradual increase in temperature of the Earth's surface caused by human activities that cause high levels of carbon dioxide and other gases to be released into the air (National Adult Literacy Agency, 2009).
Green Chemistry	Involves the design of chemical processes and products that reduce or eliminate the use and generation of hazardous substances in the manufacture and application of the products. By eliminating and reducing waste from chemical processes, green chemistry aims to develop a sustainable approach to a cleaner environment that is beneficial to both our society and the economy (School for Excellency, 2012).
Greenhouse gases (GHG)	Are gases in the atmosphere that absorbs and emits radiation within the thermal infrared range. The primary greenhouse gases in the earth's atmosphere are water vapour, carbon dioxide, methane, nitrous acid and ozone (Parker, 1980).
Hot Spot	Is a spot where long term mean concentrations of one or more air pollutants are consistently high compared with other areas of the same city (WHO, 2004).
Natural Sources	Pollution sources that are related to natural processes as opposed to those which are due to human activities (Diab, 2011).
Ozone	Is the harmful pollutant that causes biological damage to lung tissue and plants near the earth's surface where it has a chance to come in direct contact with live animals, plants and humans (Ogunseitan and Robbinson, 2011).

LIST OF ABBREVIATIONS

CHEMICAL SYMBOLS/ ABBREVIATIONS	MEANING
AEGLS	Acute exposure guideline levels
ATSDR	Agency for Toxic Substances and Disease Registry
AQS	Air Quality Strategies
CFCs	Chlorofluorocarbons
CH₄	Methane
E.M.A	Environmental Management Act
E.H.S	Environmental, Health and Safety
EFMA	European Fertilizer Manufacturing Association
E.H. & E	Environmental Health & Engineering
EPA	Environmental Protection Agency
G.H.G	Green House Gases
HNO₂	Nitrous acid
HNO₃	Nitric acid
N₂O	Nitrous oxide
NGO	Non-Governmental Organization
NH₃	Ammonia
NH₄NO₃	Ammonium nitrate
NO₂	Nitrogen dioxide
O₃	Ozone
Pb	Lead
PFCs	Perfluorocarbons
PM	Particulate matter
ppb	Parts per billion
ppm	Parts per million
S.C.I	Sable Chemical Industry
SE	School of Excellency
SF₆	Sulphur hexafluoride
SO₂	Sulphur dioxide
UNEP	United Nations Environmental Programme
VOC	Volatile organic compound
WBK	World Bank
WHO	World Health Organisation

CHAPTER ONE

INTRODUCTION

1.1 Background

The integrity of the natural composition of air has been compromised by the receipt of emissions such as chemicals, biological and particulates substances from diverse sources including natural and anthropogenic. This has resulted in the dynamics of changes in the cloud density of naturally occurring gases, bearing in it many airborne contaminants which are featured with aerodynamic characteristics. Although many of these contaminants may not persist in the atmosphere for a long time due to silting; while precipitation may bring contaminants cloud density to near zero.

Natural sources of air contaminants include volcanoes, magma degassing, weathering processes among others. Anthropogenic sources are mostly the result of human activities including domestic and industrial, with combustion of fossil fuels being a common source. Industrial processes involving time dependent unit operations in industries such as in chemical and petrochemical production and refinery, fertilizers manufacturing. may emit substantial quantity of atmospheric contaminants (CO, CO₂, SO₂, NO₂, NH₃, particulates) and other wastes (Daly, 2007; Hutton, 2011). Consequently, the purity of air over a given sphere may be variable and time dependent. This implies that the real time concentration of air pollutants is a function of the different emission sources within near and far distances, as well as climatic conditions.

Atmospheric contamination may be classified as indoor air pollution and ambient environmental air pollution; depending on whether the environment is concealed or open. This distinction arises from the context of atmospheric ambience and the immediate cloud concentration. Olatunji and Osibanjo (2013) reported that, the concentrations of low vapour density airborne contaminants in air shows distance disintegration from its hotspot. This is because of the buffer capacity of the atmosphere which allows for their rapid diffusion into air.

Clean air is considered to be a basic requirement of human health and well-being (WHO, 2005). However air pollution continues to pose a significant threat to health worldwide. High concentrations and presence of air contaminant gases and particulates poses a potential health hazard. The extent and magnitude of the impacts of air pollution on human and environmental health has been a subject of media reports and policy debate nationally and internationally. Adverse health consequences arising from the exposure of plants, animals and human to elevated atmospheric concentrations have been reported by different authors (Wood and Cowie, 2004; Ahlgren *et al.*, 2008; Motavalli *et al.*, 2008; Singh, 2009; Kirova-Yordanova, 2010; E. H. & E., 2011; Prajapati and Singhai, 2012; Subramani, 2012; Thakkar, 2013). Many of these air quality contaminants are harmful and can cause disease, death to humans, and damage to other living organisms such as food crops, or the natural or built environment. According to the 2014 WHO report, in 2012, air pollution caused the deaths of around 7 million people worldwide. Ambient air pollution is responsible for 1.4 % of all deaths, 0.8 % of disability and 2 % of all cardiopulmonary diseases (WHO, 2004).

1.2 Air Pollution: Health and Environmental problems/consequences

Since the industrial revolution, many manufacturing companies have added toxic and hazardous wastes into the atmosphere, land, and water (UNEP, 2005). The chief culprits are thermal power stations, chemical industries, cement factories and the transport sector (UNEP, 2005). This has resulted in negative impacts on ecosystems (Obire *et al.*, 2008). Evidence of these impacts has been gathered through numerous studies conducted by different scientists (Wood and Cowie, 2004; Singh, 2009; Subramani, 2012; Thakkar, 2013). The global impact of toxic and hazardous industrial waste cannot be overemphasized. The health impacts of toxic pollutants such as NH₃, NO₂, SO₂, CO and other gases emitted into the atmosphere has gained attention from governments and the scientific community over years (Brook *et al.*, 2003). This has resulted in the several conventions and protocols developed to abate air pollution challenges in an endeavour to improve environmental and human health and livelihood.

Many chemical/petrochemical industries uses coal for powering boilers, thereby producing pollutant emissions such as CO₂, NO₂, NO_x, NH₃, H₂S, particulates (EFMA, 2000). Agrochemical industries such as fertilizer producing plants have also been reported to release similar

pollutants into the environment (Wood and Cowie, 2004; Tsimakuridze, 2005; von Blottnitz *et al.*, 2007; Subramani, 2012; Thakkar, 2013).

Unfortunately, ambient baseline levels of many air contaminants in environments of both urban and industrial layouts in many Africa cities, especially Zimbabwe have not been fully characterized. Thus, information concerning the levels of many gaseous contaminants, and their real time variability is scarce and scanty. Knowledge of the identity, ambient concentrations and fate of these pollutants is of prime concern, as high levels in the air may have negative effects on plants, animals and the exposed human population (Mujuru *et al.*, 2012). Thus this study intends to assess levels of selected gaseous pollutants in the vicinity of an agrochemical and fertilizer production industry in Zimbabwe. The concentration levels of these pollutants with respect to distance from their source points will be determined.

1.3 Arable Soil Fertility in Zimbabwe and the Sable Chemical Industry

Fertilization originated from observations on the effects of natural organic manure on growth of plants. The Romans increased soil fertility by use of human excreta, ashes and waste oil press. In England, they used acidulated bones as phosphorus source. Then, in 1840, Justus Von Liebig came up with the theory of, "Organic Chemistry and its Application and Physiology". This theory led to the emergence of fertilizer production in Europe in the 19th century. The first nitrogen fertilizer was introduced in Germany in 1840 (Gorecki, 2002).

In Zimbabwe, the expansion of the agricultural industry increased the demand for ammonium nitrate within the country. The purchased and importation of the needed ammonium nitrate stock and other types of fertilizers from foreign companies was seen as a drain on the country's foreign exchange (Ndamba, 1999). To curtail this problem, Sable Chemical Industry (S.C.I) was established in March 1969, at 16 km north of the Midlands town of Kwekwe, with a production capacity of 220 000 tons of ammonium nitrate per annum. Production operation of this company results in the release of substantial amount of gaseous emission. Hence pollutants are emitted almost throughout the year. In Morocco for example, a similar company burns one million tonnes of fossil fuel per year, generating two million tonnes of carbon dioxide (Godson *et al.*, 2005, UNEP, 2005).

Currently the impacts of pollution and loss of ambient air quality in locations around S.C.I are visible. Visual inspection showed that many trees and other plants have lost their greens and exhibited stunted growth during before winter in April. The odour of NH_3 can be perceived around the manufacturing plant. According to Zvirime (2011), people exposed to coal boiler emission coupled with other sources suffer health effects such as inflammation of the nasal passage and airways, respiratory disorders, altered lung function, tissue damage and exacerbated heart diseases. It is against this background that this study was carried out around S.C.I.

1.4 Research scope

This study focuses on Sable Chemical Industry, in Kwekwe, Zimbabwe being an industry capable of exacerbating the levels of noxious air contaminants in the environment; with the aim of creating an inventory for the baseline levels for NH_3 , SO_2 and NO_2 in the atmospheric blankets of the environment around Sable Chemical Industry production circles.

Ambient air in selected locations within and around the immediate vicinity of Sable chemical industry at Kwekwe Zimbabwe, were sampled in order to determine the levels of ammonia gas (NH_3), sulphur dioxide gas (SO_2) and nitrogen dioxide gas (NO_2) available in the atmospheric blanket within this location as an indicator of their atmospheric environmental status.

1.5 Objectives of this research study

This research work investigates the ambient atmospheric status of selected noxious air contaminants NH_3 , SO_2 and NO_2 within and around Sable Chemical Industry with a view to determine their levels as a measure of their air composition and or enhancement as a result of anthropogenic activities such as the production of fertilizer and other chemicals. This is with the intent of defining current concentrations as a basis for evaluating their potential risk to human and environmental as a result of production operation, and to create benchmark for future environmental monitoring and the control of pollution that may be arising from production activities in order to facilitate sustainable environmental protection. This study was set to achieve the following objectives:

1. To ascertain the environmental quality of ambient air of the atmospheric blanket within S.C. I and its vicinity 5 km radius, with the view of generating and compiling baseline data set for contaminants such as NH_3 , SO_2 and NO_2 . This is with a view to assessing potential of the production operation of Sable Chemical Industry to cause atmospheric environmental pollution, and consequently health and environmental damage.
2. To determine the spatial distribution of NH_3 , SO_2 and NO_2 in ambient air and their degree of their bioavailability and possible effect on the environment and health of local people, animals and plant species, and to delineate the most heavily polluted areas for eventual environmental protection and remediation measures.
3. To establish transport of NH_3 , SO_2 and NO_2 through ecosystems, and to develop simple relationships to explain their spatial distribution across the sub-environments and the environment conditions associated with enhanced mobility.
- 4.

CHAPTER TWO

LITERATURE REVIEW

2.1 Air pollution

Past studies have reported that that most harm from air pollution was first experienced by humans when fires were built in poorly ventilated caves (Franek and DeRose, 2003; Grzywacz, 2006; Hutton, 2011; Mahwood, 2011). Humans have however continued to pollute more of the earth over time. Since the early 17th century, severe air pollution episode occurrences in the United Kingdom (UK) have been reported (Pope *et al.*, 2002; Chauhan and Johnston, 2003; Raghunandan *et al.*, 2008; Valavanidis *et al.*, 2008). Major industrial air pollution episodes were also reported in the United States and Belgium (Franek and DeRose, 2003; Valavanidis *et al.*, 2008). Air pollution episodes become even more severe and more frequent towards the 19th century in Europe and Asia as a result of the rapid industrialization and urbanization (Chauhan and Johnston, 2003; Franek and DeRose, 2003; Rani *et al.*, 2011).

The consequences of air pollution range from impairment of human physiology, metabolism, asphyxiation and death (Valavanidis *et al.*, 2008; E. H. & E., 2011; Balashanmugam, 2012). Chauhan and Johnston (2003) reported the death of several thousands, mostly among infants and elderly people in London during this period. Similarly physical disabilities such as otitis have been reported due to air pollutants (Brauer *et al.*, 2006).

The impact of air pollution on human and the environment underscores the need for legislation concerning the control of emissions and reduction of smoke from industry. Most of the early legislated acts were limited by challenges in implementation, thus there was very little improvement in air quality until the early 20th century (Chauhan and Johnston, 2003). Severe effect of pollution episodes on health have however increased public and parliamentary concerns, which led to effective legislation in the UK (Valavanidis *et al.*, 2008). The United States of America Clean Air Acts of 1956, 1968 and the 1970 were also promulgated in order to control and regulate emissions release into the atmosphere. This also triggered scientific research on air quality and pollution to date (Chauhan and Johnston, 2003; Brauer *et al.*, 2006).

2.2 Occurrences of air pollutants in the environment

Pre-industrial atmosphere is now completely different from the present day atmosphere in terms of chemical composition. The key players in this change are man in an attempt to improve their livelihood. This can be traced back from when man started burning fuels (Franek and DeRose, 2003; Daly and Zannetti, 2007). Before the 18th century, the chemical composition of air was as follows; N₂, O₂, Argon (Ar), Neon (Ne), Helium (He), Krypton (Kr), Xenon (Xe), CO₂, CH₄, Nitrous oxide (N₂O), and water (Harry Heimann, 1961; Daly and Zannetti, 2007). Currently the composition is mainly industrial mission gases the atmosphere also contains particulate matter such as dust, volcanic ash, rain, and snow (Egger, 2000).

The composition of air can be altered by either anthropogenic or natural emissions. The natural causes fall into geogenic and biogenic contributors to air pollution. Geogenic emissions are caused by the natural sources, such as volcanic emissions, sea-salt emissions and natural fires. Biogenic emissions come from the living world; such as volatile organic compound (VOC) emissions from forest and CH₄ emissions from swamps (Daly and Zannetti, 2007). The long term accumulation of CO₂, VOC and CH₄ in the atmosphere may lead to climate change, which then can be harmful to humans and the ecosystem (Holdren and Smith, 2002; Daly and Zannetti, 2007).

2.2.1 Sources of air pollutants

Hazardous air pollutants released from natural sources and anthropogenic sources influence environmental quality and health on local, regional and global scales (E. H. and E, 2011). Ambient air quality can be affected by both natural phenomena and anthropogenic activities. Natural sources include forest fires, volcanic eruptions, lightening, dust and storms and anthropogenic sources include transport industry, energy, manufacturing industries such as cement and fertilizer companies. Accidental fires, fireworks, burning tires, open dumping and wars or military demonstrations are also good examples (Harry Heimann, 1961; EPA, 2010).

Other sources of air pollutants include natural NH₃ emitted from livestock and poultry manure (EPA, 1995; Motavalli, 2007). Inorganic N₂ in the waste is emitted through volatilisation, nitrification, denitrification, leaching and run off, with NH₃ volatilisation generally the highest total

loss of this N. SO_2 is produced by volcanoes and various industrial processes e.g. fertilizer production. Further oxidation of SO_2 in the presence of NO_2 in the atmosphere forms H_2SO_4 . This is acid rain and can result in the destruction of buildings, forests as well as marine and aquatic organisms (UNEP, 2004; Singh, 2009; Rani *et al.*, 2011).

2.2.2 Distribution and transport of air pollutants

Pollutants which are either from natural or anthropogenic sources are carried by air currents, diluted and exposed to different environmental conditions or other substances in the atmosphere. These pollutants are then either chemically transformed or deposited on; and or water through dry or wet deposition processes. Depending on the distance from the emitting source which are determined by varying meteorological conditions such as wind direction, wind speed, wet or dry condition, pollutants can be deposited at varying distances and directions from the source (Medhavi and Manju, 2013; Franco and Philip, 2013). There are four types of scales depending on the distance from the emitting source, these are:

- Near-field phenomena (< 1 km from source)
- Short-range transport (< 10 km from source)
- Intermediate-range transport (between 10 – 100 km from source)
- Long-range transport (> 100 km from source) (Medhavi and Manju, 2013)

Further clarification was provided by Franco and Philip (2013), when air pollutants cross geopolitical boundaries or migrate across several geographic zones, the pollution is designated as transboundary even if the physical distance of the boundary from the emitting pollutant source is quite short. For example, the smelter in Trail, British Columbia, released SO_2 from a tall stack that impinged directly on sites in Washington State, USA. This issue generated negotiations between the two states from the 1930s to the 1950s until it was resolved in Budbury (Franco and Philip, 2013). There three main reasons which cause transboundary transport of pollutants; these are:

- Pollutants have low deposition velocities
- Pollutants might need an extended period of time for the pollutants to develop from the precursor compounds to secondary pollutants.
- Or go through a multi-hop pathway as in the case of persistent organic pollutants (POPs). (Franco and Philip, 2013).

2.3 Transformation of air pollutants

Air pollutants can be categorised as primary and secondary. Primary pollutants are those that can be directly emitted into the atmosphere from sources, whereas secondary pollutants are formed in the atmosphere from primary pollutants. The main primary pollutants are, CO, CO₂, CH₄, NO, N₂O, NH₃, SO₂, H₂S (Daly and Zannetti, 2007). It is important to stress that secondary air pollutants are not directly emitted from sources, but instead form from primary pollutants (precursors) discharged into the atmosphere. NO₂ and HNO₃ are secondary pollutants formed from NO_x while O₃ is formed from photochemical reactions of NO_x and VOCs. H₂SO₄ droplets are formed from SO₂ and HNO₃ droplets are from NO₂. NH₃ reacts with H₂SO₄ droplets and HNO₃ to form ammonium sulphate and ammonium nitrate respectively (UNEP, 2004; Daly and Zannetti, 2007; Saini *et al.*, 2008; Rani *et al.*, 2011).

2.4 Impacts of air pollution (human and environmental damage)

It has been proven that secondary pollutants have negative impacts on health and the ecosystems. In 2008 researchers from the University of Virginia proved that fragrance in flowers may be short-lived due O₃ a secondary air pollutant. The study showed that increasing levels of NO_x in the air react and degrade hydrocarbons responsible for fragrance in flowers. Hydrocarbons react with NO_x in the air to form O₃. This restricts the fragrance from travelling long distances to attract insects. This makes it difficult for insects to find flowers. Simulation studies showed that pre-industrial times when levels of air pollution were low, the fragrance of a flower could travel several kilometres. Air pollution therefore is posing a danger to flowering plants, due to the effect of reproductive success (Saini *et al.*, 2008; Rani *et al.*, 2011).

Air pollution has increasingly become a major health issue affecting both the developed and developing nations around the world (Simkhovich *et al.*, 2008). The major air pollutants from fertiliser industries are dust, soot, odours, SPM, GHG, NO_x, SO₂, trace metals e.g.(Mg, Pb), NH₃, CO_x (Gordon *et al.*, 2004; Wood and Cowie, 2004; Prajapati and Singhai, 2012; Thakkar, 2013; Algren *et al.*, 2014). These pollutants have also impacted on ecosystems, climate change, water quality and eutrophication, soil quality and infrastructure (Chipindu, 2009). Amann *et al.*,

(2010) noted that these pollutants are considered by experts to be damaging even in small concentrations.

2.4.1 Health Impacts

Humans can be exposed to contaminants in both ambient air and the indoor environment (Kumar *et al.*, 2005). Exposure to high levels of air pollutants can adversely affect human health (Ren and Tong, 2008). Early concerns about health related effects of air pollution arose after catastrophes such as the 1930 fog disaster in the Mouse Valley, Belgium, the 1948 Donora fluoride fog in Pennsylvania, USA, and the 1952 Great London Smog in the UK, which caused acute illness and premature deaths of over 4000 people (Pope *et al.*, 2002; Chauhan and Johnston, 2003; Raghunandan *et al.*, 2008; Valavanidis *et al.*, 2008). Although the effects of these pollution episodes remain a subject of debate, increase in morbidity and mortality from cardiopulmonary diseases provide clear evidence that extremely high concentrations of air pollution can have adverse effects on human health (Raghunandan *et al.*, 2008). Figure: 1 shows the pyramid of air pollution health effects, from simple to complex effects and until death.

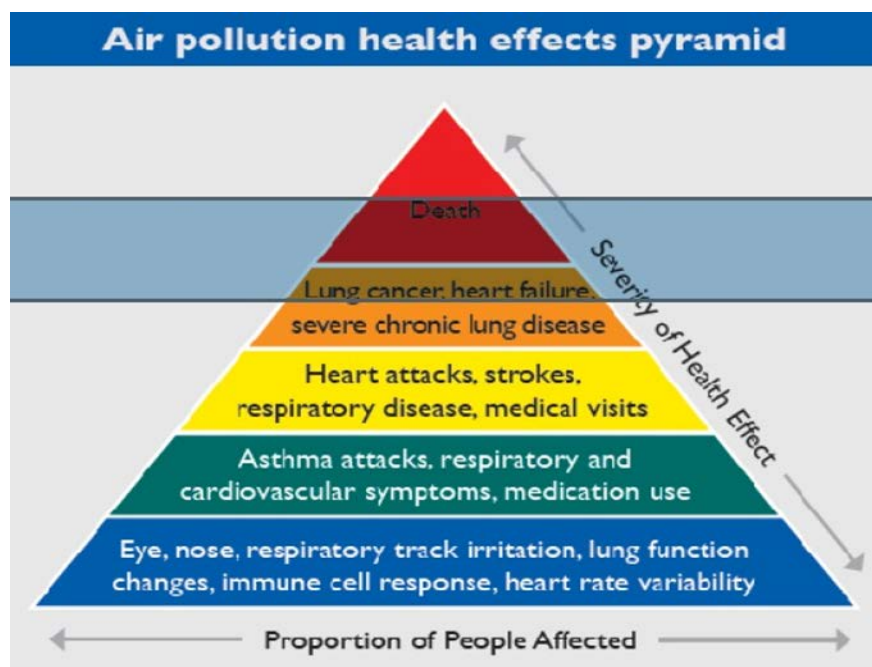


Figure 1: Health effects of air pollution
(Adapted from USEPA, 2010b)

Air pollution may affect humans and different organisms in different ways, depending on their sensitivity (Raghunandan *et al.*, 2008). Studies have shown that, the extent to which individuals

and other species are harmed by air pollution usually depends on the extent of their exposure to air pollutants. Healthy individuals may also be at risk in some cases (Chauhan and Johnston, 2003). Children and elderly people often suffer more from the effects of air pollution (Valavanidis *et al.*, 2008). Continued exposure to polluted air can have deleterious effects on the lungs of growing children, while it may complicate medical conditions of the elderly.

People with chronic health problems such as asthma, heart and lung diseases are more vulnerable when exposed to polluted air (Fullerton *et al.*, 2008). Long term health effects can include chronic respiratory diseases lung cancer, heart disease and even damage to the brain, nerves, liver or kidneys (Fullerton *et al.*, 2008). Short-term effects of air pollution include irritation of the eyes, nose, throat and upper respiratory infections. Other symptoms may include headache, nausea, confusion, body weakness, lack of concentration and allergic reactions (Chauhan and Johnston, 2003). Short-term exposure to air pollution can also aggravate the medical conditions of individuals with asthma and emphysema.

Particulate matter (PM) was reported to be an important environmental pollutant that results in different cardiopulmonary diseases and lung cancer (Valavanidis *et al.*, 2008). Numerous epidemiological studies showed that PM has short-term effects such as premature mortality and regular hospital admissions. The size of the airborne particles and their surface area determines the potential to elicit inflammatory injury, oxidative damage and other biological effects (Brook *et al.*, 2003; Pope and Dockery, 2006). These effects are stronger for fine and ultrafine particles because they can penetrate deeper into the airways of the respiratory tract and can reach the alveoli in which 50 % are retained in the lung parenchyma (Simkhovich *et al.*, 2008; Valavanidis *et al.*, 2008).

Inhaled air pollutants have serious impacts on human health and mainly target the respiratory and cardiovascular system. Human lungs have a large surface area and as such people inhale large volumes of air (20 000 litres per day), lungs therefore become the most significant site of interaction between air pollutants and the physiological system.

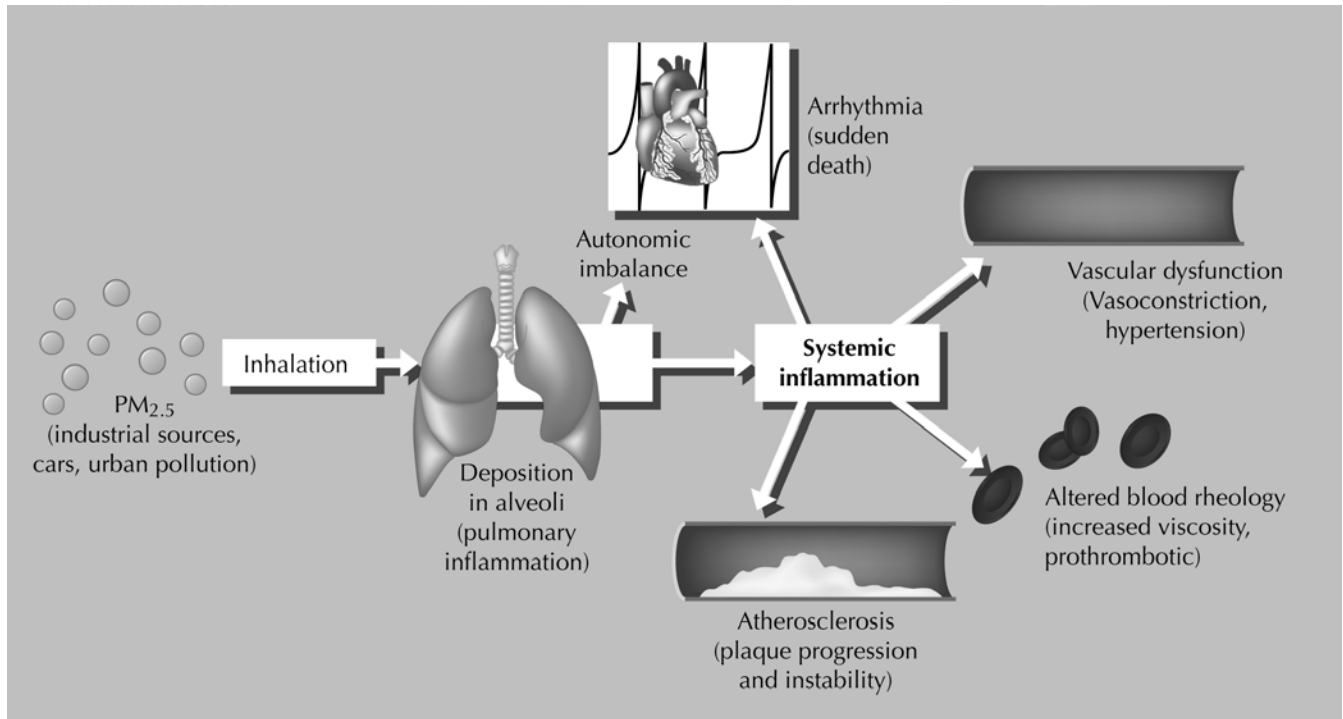


Figure 2: Possible health risk associated with air pollution
(Adapted from: Brook et al., 2003)

Blood also absorb pollutants especially heavy metals and circulates them in the body resulting in possible tissue and organ damage (Figure 2).

2.4.2 Effects of pollution on ecological systems

Air pollutants have been reported to cause damage to vegetation, water bodies and even certain animals (Matooane and Diab, 2011). SO₂, NO₂, O₃, PM and F are all known to be products of fossil fuel combustion and are well known to be the most important in terms of their ecological effects (Fenger, 2008; Amann, 2010; Matooane and Diab, 2011). Studies have also revealed that most ecological damage is caused by acid rain. The emitted NO₂, SO₂, CO₂ react with water vapour to form HNO₃, H₂SO₄ and H₂CO₃, respectively. Acid rain damages forest, crops, buildings, limestone rocks, changes the chemistry of the soil and causes streams and lakes to become acidic and unsuitable for aquatic organisms (Matooane and Diab, 2011).

2.4.2.1 Effects on vegetation

The damage to vegetation can be visible or invisible injury. Visible injury usually consists of discoloration on the leaf surface caused by internal damage to cells. The appearance of the leaf is affected and this can lead to reduced market value. Invisible injury results from pollutant impacts on plant physiology and this can lead to a reduction in growth, reduced crop yields and changes in the quality of agriculture crops (Fenger, 2008; Matoane and Diab, 2011).

According to Amann *et al.*, (2010) exposure to ground level ozone causes negative effects on forest trees such as reduced photosynthesis, premature leaf shedding and growth reduction. These effects have negative consequences for carbon sequestration, biodiversity and other ecosystem services provided by forests (e.g. reducing soil erosion and decreasing flooding and avalanches). In Europe, effects have been detected on forest. For example, reduced stem growth reported in Switzerland and leaf loss has been reported in Greece (Amann *et al.*, 2010). Figure 3 summarises the impacts of acid rain on forest.

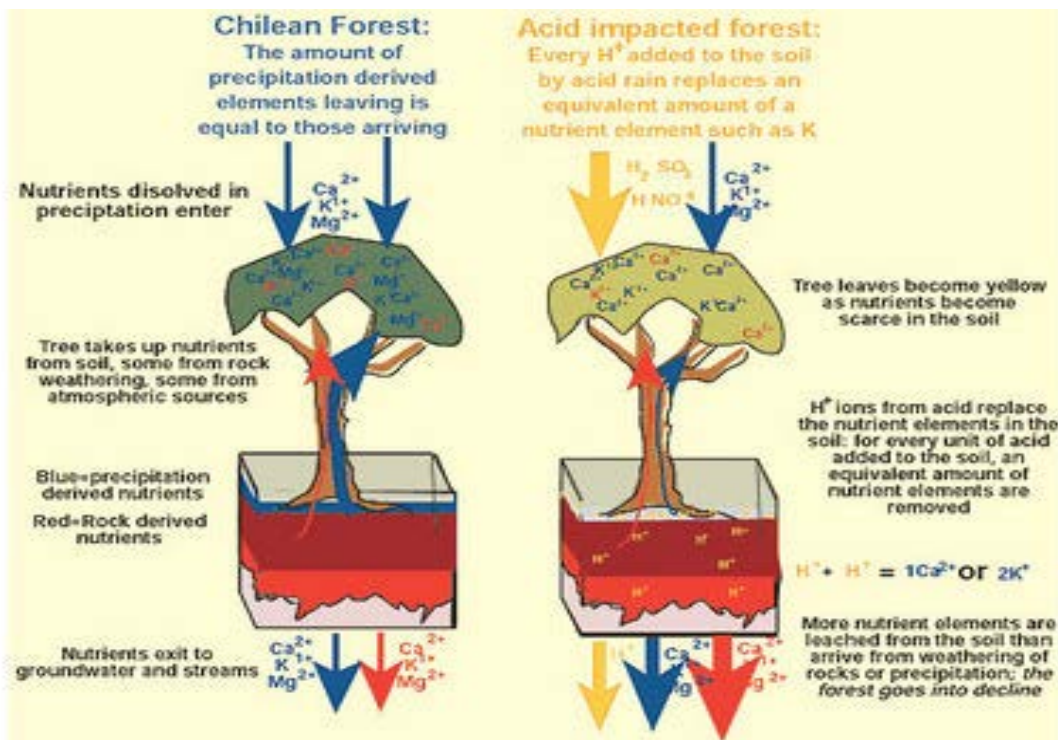


Figure 3: Impact of acid rain on forest nutrient cycles
(Adapted from: Martin Kennedy, 2007)

When pollutant absorption occurs, leaf response is determined by two factors, the internal concentration level of the pollutant and the biochemical threshold level of tolerance for the pollutant or its toxic derivatives (Malhotra and Hocking, 1976). If the internal concentration exceeds the threshold level, leaf damage is sustained. Different plant constituents (tissues, cells, molecules, etc.) may vary in their respective levels of biochemical tolerance (Malhotra, 1977); therefore, the same internal pollutant concentration may elicit variable strain depending on the affected constituent. This resistance mechanism is strain avoidance; the stress is absorbed by the leaf, but the potential consequence of the stress is not sustained. Strain tolerance is the other mechanism imparting stress tolerance.

2.4.2.2 Aquatic and Marine environments

Figure 4 show acidic tolerance levels for common aquatic organisms. Survival of more fish species is favoured in the higher pH ranges relative to the amphibians like salamanders which tend to adapt well with lower pH as observed. High acidity in lakes and rivers corrodes fishes' organic gill material and attacks their calcium carbonate skeletons. Figure 4 shows the acidity levels at which common freshwater organisms can live and reproduce successfully. Acid deposition also dissolves toxic metals such as aluminum in soil sediments, which can poison plants and animals that take the metals up.

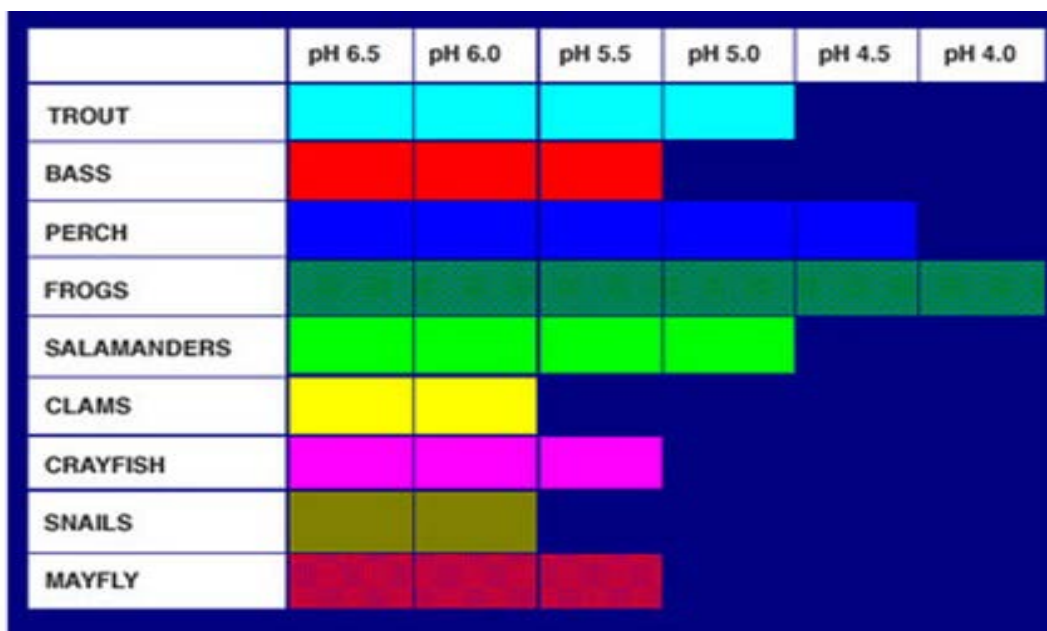


Figure 4: Acid tolerance ranges of common freshwater organisms (Courtesy United States)
 (Adapted from: Environmental Protection Agency, 2012)

2.4.3 Air pollution and global warming

Some air pollutants belonging to the group of greenhouse gases (G.H.G) can absorb infrared radiation emitted by the earth and in so doing prevents heat from escaping the atmosphere (Matookane and Diab, 2011). They include CO₂, CH₄, N₂O, FCs, HFC₅, PFCs and SF₆ (Fenger, 2008). CO₂ is assigned a global warming potential of one, while other (G.H.G) are measured against CO₂. Although PFCs and SF₆ are often emitted in small quantities, they have large global warming potentials and long atmospheric life that can be of significant concern (Allen and Shonnard, 2012). CO₂ is emitted in high levels, and arises mainly from the burning of fossil fuels, decomposition of waste, fermentation, among others. These gases traps heat on the earth's surface, exerting a thermal blanketing effect that keeps the planet's surface much warmer than it would otherwise be (Holdren and Smith, 2002). The increasing greenhouse effect and its impacts in the form of rising temperatures and sea level is sometimes depicted as the end of civilization and ultimately the end of life on earth (Fenger, 2008). This alarm has resulted in the most important international meeting on climate protection, held in Tokyo, Japan in 1997 (Kyoto Protocol). At this conference industrialized countries were advised to reduce their G.H.G to save the earth (Grubb *et al.*, 2002). Unfortunately, the Kyoto Protocol did not achieve much in limiting the build-up of G.H.G in the atmosphere. Levels of CO₂ are increasing at the rate of 0.5 % per year; atmospheric concentrations of other G.H.G have also risen. CH₄ has increased from 700 ppb to 1790 ppb in 2009 and N₂O rose from 275 to 320 ppb over the same period (Allen and Shonnard, 2012). N₂O is a powerful G.H.G and its global warming potential is about 310, meaning that 1 kg of N₂O causes as much warming as 310 kg of CO₂ (Von Blottnitz *et al.*, 2007).

Furthermore, CFCs are also causing damage to the ozone layer which absorbs ultraviolet radiation from the sun, protecting life on earth, from the harmful effects of the ultraviolet radiation. Destruction of the ozone layer may cause damage to plants and the reduction of plankton population in oceans (Matookane and Diab, 2011). The earth's average surface temperatures will increase from 15.0 to 17.5 °C annually. Some regions would have longer growing seasons and some will have droughts and freezing weather (Holdren and Smith, 2002). These climate changes including erratic rainfall are experienced in industrialized regions of the world (Chitongo, 2013; Masih *et al.*, 2014).

2.4.4 Impacts on buildings and material

The impacts of air pollution on buildings and materials include; acid corrosion of metallic materials, paints due to contact with SO₂, NO_x and ozone. Damage to polymeric materials, particularly natural rubbers, soiling of buildings and materials including both “utilitarian” and historic buildings have been reported.

These damages due to buildings are classified as economic damages because of the cost of cleaning amenities and restoration of acid impacts on materials of cultural merit (including stone, fine art, and medieval stained glass) (Hutton, 2011). Natural environmental effects and anthropogenic pollution leads to deterioration of buildings and corrosion of metallic structures. This shortens the life span and usefulness of these structures and demand for expensive materials. It also gives rise to higher cost of surface protection or replacement (Monemanova' *et al.*, 2007). Air pollution also has considerable effect on stone and concrete buildings in polluted industrial areas. Losses may occur when air pollution affects historical sites, stone statuary and other works of art. The damage is not only physical but also to the aesthetic appeal of the material surface (Monemanova' *et al.*, 2007). SO₂, O₃ and soot can damage stone buildings and monuments by accumulating on the exterior of building, changing their appearance, staining the building material and increasing cleaning cost (Matooane and Diab, 2011). Acid rain formed when these gaseous pollutants dissolves in rain water causes increased rate of oxidation of metals, in particular, copper and bronze (Amann *et al.*, 2010).

2.4.5 Economic influences of poor air quality

According to Matooane and Diab (2011), impacts of air pollution are not confined to health impacts, materials or vegetation only. It also has economic impacts, which are determined through a cost benefit analysis and willingness to pay techniques. The accumulative cost of drugs, loss of life, damage to building, climate change and destruction of forest could be very high and actually more expensive. The cost of buying air pollution control equipment in order to reduce all these impacts may however be a cheap way to mitigate or at least bring to minimum these effects. Therefore, there is need for agencies, NGOs, government and other stake holders to carry out a cost benefit analysis, value the impacts and develop a rational management procedures and legislations.

2.5 Environmental Impacts of selected gaseous pollutants NH₃, SO₂ and NO₂

Some air contaminants have been reported to show specific deleterious impact on humans, biotic and abiotic components of the environment. The impacts and characteristics of NH₃, SO₂ and NO₂ pollutants in air include:

2.5.1 Ammonia (NH₃)

Ammonia occurs naturally as a ring colourless, acrid-smelling gas (Krupa *et al.*, 2004). It is water soluble and volatile. Globally more than 99 % of the NH₃ present in the atmosphere is the result of natural processes, mainly biological degradation of organic matter, chemical and microbial degradation of animal wastes, in particular urine (Krupa *et al.*, 2004). Industrial emitters of NH₃ include chemical industries, coke manufacture industries, fertilizer manufacturing industries, fossil fuel combustion, livestock management and refrigeration industry (Phillips, 1995; Godson, 2005; Fenger, 2008; Shaheen *et al.*, 2010). According to Mroczkowski and Stuczynski (2006), sources of NH₃ in the atmosphere include industrial emission and volatilization from manures and fertilizers. High concentrations in the atmosphere are mostly a result of accidents upon the production, storage or transportation processes.

The primary route of exposure of humans and animals to NH₃ is via inhalation (Krupa *et al.*, 2004). According to Pritchard (2007), exposure can either be acute exposure or chronic exposure depending on air concentrations of NH₃. Exposure to concentrations ≥ 50 ppm may result in irritation of the upper respiratory tract, eyes and the skin, excessive salivation, burns to the mouth, throat and oesophagus. It can also result in burns in the oral cavity, nasopharynx, larynx and trachea (Krupa *et al.*, 2004; Pritchard, 2007). Chronic exposure results in increased cough, phlegm, wheeze and asthma. Substantial inhalation exposure to ammonia may cause long term health effects including persistent air way obstruction; cough exceptional dyspnoea, bronchiolitis, obliterans and bronchiectasis (Pritchard, 2007). At high concentrations, NH₃ can even cause death (ATSDR, 2004). Becker and Graves, (2004) highlighted that, accumulation of NH₃ within animal housing systems can have a negative impact on production and animal health. Colina *et al.* (2000) also reported that there was reduced final body weight in poultry in houses with indoor NH₃ pollution. However, Krupa *et al.*, (2004) argues that no significant

effects were observed in rats; rabbits, dogs and monkeys exposed to 50 ppm of NH_3 for 114 days.

Effects of NH_3 on plants may be positive and negative. At lower and more natural concentration levels, NH_3 add the extra nitrogen (N) input which results in a stimulation of photosynthesis and a higher biomass production. These positive effects coincide with changes in shoot, root and nutrient balance (Chen *et al.*, 2012). Exposure of plants to high atmospheric NH_3 concentration may be directly harmful to plants and negatively affect growth and result in direct toxic effects, although this may depend on the sensitivity of plants (Chen *et al.*, 2012). NH_3 , (both anthropogenic and natural NH_3 and NH_4^+ derived from air) can significantly affect vegetation by influencing the cycling of nitrogen in plants and the ecosystems (Krupa *et al.*, 2004).

Ammonia plays an important role in atmospheric chemistry, in that release of NH_3 into the atmosphere and its subsequent deposition into the ecosystem can lead to acidification of soils, eutrophication of water bodies, contribution to forest decline and a decrease in biological diversity (Von BobrutzkI *et al.*, 2010). Dammgen and Erisman (2005) noted that, high concentration of NH_3 in the vicinity of strong sources may result in direct damage of plants, which is related to increased pH in the plant tissue.

However forest decline has been attributed to complex interactions of both natural and anthropogenic stresses such as frost, droughts, pathogens and pests, air pollutants and possible global air climate change (Krupa *et al.*, 2004). Vacek *et al.*, (2013) reported that industrial pollution has eventually resulted in the decline of coniferous forest in Czech Republic and the entire Central European Region. The effect of an individual pollutant is difficult to separate from others.

Ammonia may however contribute to the damage of materials and buildings in several ways, but its role is not fully known yet (Krupa *et al.*, 2004). Marcela, (2008) argued that NH_3 reacts with water forming ammonium hydroxide ($\text{NH}_4(\text{OH})_2$). Ammonium Hydroxide reacts with calcium hydroxide ($\text{Ca}(\text{OH})_2$) which can react with concrete structures creating holes, especially concrete with less cement. According to Marcela (2008) alkaline substances act on concrete through exchangeable reactions with mineralogical components of cement and stone. Complex compounds formed from air pollutants affect protective coatings, discoloration, causes structural failure and loss of detail in carvings (Krupa *et al.*, 2004).

2.5.2 Sulphur dioxide (SO₂)

SO₂ is a non-flammable and colourless gas. The main anthropogenic source of SO₂ is combustion of fossil fuels like coal and petroleum products (Treissman *et al.*, 2003; Foxall, 2010). Other sources of SO₂ include non-ferrous smelters, iron ore smelters, steel mills and the pulp and paper industries (Riordan and Adeeb, 2004).

Acute exposures to SO₂ can cause irritation of the nose, eyes and throat, immediate bronchiole constriction, narrowing of the airways, nausea, vomiting, and stomach pain. Skin contact with SO₂ causes stinging pain, redness of skin and blisters. High concentrations can cause blindness (Foxall, 2010). The degree of these symptoms however, depends on concentrations (Treissman *et al.*, 2003; Riordan and Adeeb, 2004). Long-term exposure to SO₂ can aggravate existing pulmonary diseases like asthma, may impair lung function and reduced life span. Young people with tender organs are more vulnerable because their organs are very sensitive. However, it is not known whether SO₂ cause harm on unborn babies (Foxall, 2010; Treissman *et al.*, 2003).

In animals exposure to high concentration of SO₂ causes coughing, laboured breathing, rhinitis, eye irritation conjunctivitis and death (Treissman *et al.*, 2003). The most serious issue was presented by Campbell *et al.*, (2011) who proved that, exposure to SO₂ is associated with increased DNA damage in sperm cells of humans and animals. In female animals oestrous cycle; pregnancy frequency and offspring growth are also affected.

Sulphur dioxide dissolves in rain water forming acid rain. This can cover long distances and as a result can damage large forest, structures and ecosystems at large scale (Treissman *et al.*, 2003; Riordan & Adeeb, 2004; Staurup, 2005; Foxall, 2010). Acid rain directly attacks the protective coating of plants, acidifies lakes and soils which may result in the formation of substances that are toxic to plants and animals. This has resulted in forests being destroyed in Northern USA, Canada and Scandinavia (Staurup, 2005). Studies reveal that SO₂ affects nearby vegetation by causing leaf injury, decreasing plant growth and yields and reducing the number and variety of plant species (Hill & Baum, 2001). Acid rain can severely affect buildings made of marble, limestone and paint. Lakes and water sources have lost the ability to support life due to changing acid of the water (Riordan and Adeeb, 2004; Staurup, 2005).

2.5.3 Nitrogen dioxide (NO₂)

Nitrogen dioxide (NO₂) is a reddish-orange brown gas with a pungent smell. It is the most ubiquitous of the oxides of nitrogen. It is irritating, acrid, corrosive and oxidising agent (Brauer *et al.*, 2002; Kindzierski *et al.*, 2007). According Gillah (2011), NO₂ and NO are both oxides of nitrogen and together they are referred to as NO_x. All combustion processes produce NO_x emissions largely in the form of NO which is then converted in the atmosphere to NO₂. It is believed that nitrogen oxide compound occur from both natural and anthropogenic sources. The major anthropogenic sources are combustion of fossil fuels for heating, household appliances, power generation, fertilizer industry and motor vehicles (AEGLS, 2008). Natural sources of NO include the burning of biomass, organic decay and lightning (Brauer *et al.*, 2002). In the industry NO₂ is prepared by the oxidation of HNO₃ or as an intermediate in the oxidation of NH₃ to HNO₃ (Kindzierski *et al.*, 2007).

Among industrial emissions and G.H.G, NO₂ has the greatest impact on human health (AEGLS, 2008). Nitrogen dioxide may cause significant toxicity because of its ability to form HNO₃ with water in the eye, lung, mucus membranes and skin (DHSS, 2000). Low levels of NO_x in the air can irritate the eyes, nose, throat and lungs causing cough and shortness of breath, tiredness and nausea (ATSDR, 2002). Fluid build-up in the lungs may occur in human and animals 24-48 hours after severe exposure to NO₂.

Exposure to high concentration of NO can cause rapid burning spasms, swelling of tissues in the throat, upper respiratory tract, reduced oxygenation of body tissues due to swollen lungs and death (ATDSR, 2002). The New Jersey Department of Health and Senior Services, (2000) points out that, inhalation of high concentrations of NO may interfere with the oxygen carrying capacity of blood, causing headache, fatigue dizziness and a blue colour to the skin and lips (methemoglobinemia), while repeated exposure may lead to permanent lung damage. Studies have shown that NO₂ affects the lining of the lungs by directly causing inflammation and indirectly impairing immune defence mechanism. Asthmatics and people with chronic bronchitis are more vulnerable, coughing, wheezing and respiratory infections are more common in children especially those between 5-12 years (Ferrari, 1997). According to the Pollution Prevention and Abatement Handbook, (1998) studies with animals have found that if animals are exposed to NO₂ of concentration less than 1.88 µg/m³ they develop both reversible and

irreversible lung effects and biological changes. It has also been noted that if animals are exposed to NO_2 levels as low as $940 \mu\text{g}/\text{m}^3$ for six months they experience destruction of cilia, alveolar, tissues disruption, obstruction of the respiratory bronchioles and increased susceptibility to bacterial infection of the lungs and more severe tissue damage resembling emphysema experienced in rats and rabbits.

2.5.3.1 Effects on the ecosystem

Nitrogen Oxides (NO_2) are precursors of both acid precipitation and ozone (O_3), each of which is blamed for the injury to plants (Pollution Prevention and Abatement Handbook, 1998). The same source explains that, it is the NO_x that absorbs sunlight, initiating the photo-chemical process that produces HNO_3 . It is this HNO_3 which when deposited into freshwater streams and lakes damages the ecosystem. Acid deposition can lower the pH of the water with serious consequences for fish, animals and aquatic plants (Figure 4). Acidification also decreases the species diversity which is referred to as “Acid Pulses” (PPAH, 1998). It has also been proven that the atmospheric deposition of NO is a substantial source of nutrients that damage estuaries by causing algal blooms and anoxic conditions, United States Environmental Protection Agency (USEPA, 1998). Nitrogen oxides are a precursor of ground-level O_3 which is a serious problem, since it is the source of 90% plant damage in North America. Ozone can travel long distances from source and can contribute to the elevated O_3 concentrations hundreds of kilometres causing intense damage to the forest (USEPA, 1998). Acid can also cause deterioration of cars, buildings and historical monuments (USEPA, 1998).

2.6 Gaseous pollutants from fertilizers

Fertilizers are materials which supply plants' nutrients needed for growth and development and improve soil fertility (Gorecki, 2002). In modern agriculture NH_4NO_3 is an important synthetic nitrogenous fertilizer now used worldwide (Kirova–Yordanova, 2010). The use of fertilizer has improved agricultural produce, which in turn improved food supply for the human population (Davidson, 2012). It is estimated that about 40 to 60% of the current world 7 billion people depends upon crops grown using synthetic nitrogen fertilizer. Unfortunately, this impressive advancement in agricultural productivity and human nutrition has come at a high price of environmental degradation and human health risk from pollution. The release of air pollutants such as NH_3 , SO_2 and NO_2 , from fertilizer production plants is well reported (Wood and Cowie,

2004; Ahlgren *et al.*, 2008; Motavalli *et al.*, 2008; Singh 2009; Kirova Yordanova, 2010; E.H. & E., 2011).

Production stages of NH_4NO_3 are almost the same globally. This involves the production and use of basic elements hydrogen through electrolysis of water, nitrogen from fractional distillation of air, are then combined to produce NH_3 which is mixed with nitric acid (HNO_3) to form ammonium nitrate. According to Wood and Cowie (2004), ammonia production is largely based on modification of the Haber-Bosch process where NH_3 is synthesized from a 3:1 volume mixture of hydrogen and nitrogen at elevated temperature and pressure in the presence of an iron catalyst. Ammonia (NH_3) is then mixed with HNO_3 to produce NH_4NO_3 . The five major production facilities namely (i).air separation plant, (ii).electrolysis plant, (iii).ammonia synthesis plant, (iv).nitric acid plant and (v).ammonium nitrate plant as illustrated in Figure 5.

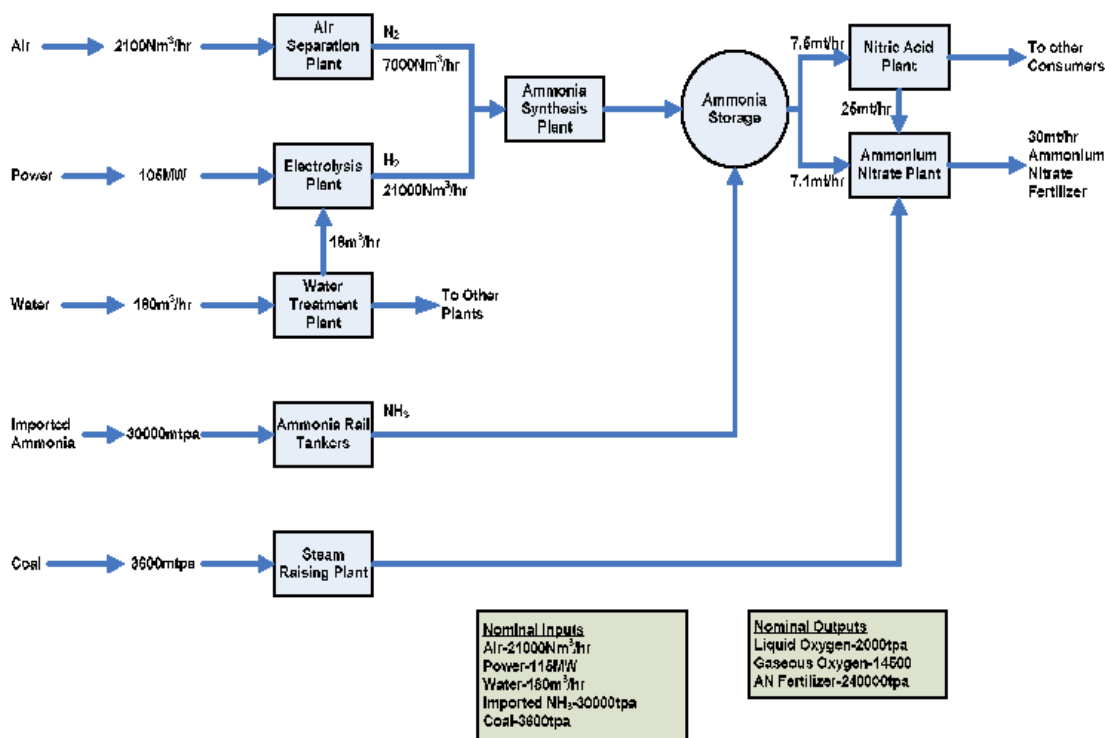


Figure 5: Fertilizer production stages
(Adapted from: S.C.I Training Manual, 2007)

During the different stages of production, a number of pollutants from fertilizers are produced and released into the atmosphere. As with other chemical industries, the production of fertilizers gives off emissions containing pollutants that may contribute to global environmental challenges such as global warming, eutrophication, climate change, acid rain and health impacts (Toan *et al.*, 2014). There is strong evidence that some of these pollutants cause detrimental effects due to the increasing amounts of reactive (-N-) released to the environment (UNEP, 2007). Increased activity in the use of fertilizers coupled with socio-economic activities contribute significantly to air pollution, which has gradually grown into a major environmental concern for African policy makers and gained prominence on the region's political agenda (UNEP, 2005).

2.6.1 Emission from chemical and fertilizer production

The process of fractional distillation precludes electrolysis to produce hydrogen utilizes clean dry air is a mixture of gases with different freezing points (Randall, 2010). This process do not have significant emission release because the gases freeze at different temperatures, while heat is removed from the incoming stream of air by passing it counter current to the outgoing cold gas streams in the heat exchangers. During the process of liquefaction, liquid air is separated into pure liquid and gaseous nitrogen and impure nitrogen. Traces of other gases in the air that are not condensing under the conditions of liquefaction in the column are vented to the atmosphere with the impure nitrogen stream.

In the NH_3 synthesis plant, H_2 gas from electrolysis of water and gaseous nitrogen from the air separation plant are chemically reacted over an activated iron catalyst to form NH_3 (Jim, 2002). It is however not possible to obtain complete conversion in one passage only; about 12-17% of the gases are converted on each occasion. The NH_3 produced in each passage through the converter is separated from the unconverted gases by condensation in an NH_3 cooler. The unconverted 'syngas' is returned to the converter with fresh make-up gas which continually replace the condensed ammonia gas as it is removed from the system. The re-circulation process may lead to some NH_3 gas leaks. In order to maintain the NH_3 in liquid form; the temperature and pressure have to be carefully controlled. This is achieved by removing NH_3 vapour given off by the liquid NH_3 in the atmospheres (Ahlgren *et al.*, 2008; Singh, 2009). Some degree of NH_3 vaporization may also occur from the liquid ammonia produced. Pollutants produced during ammonia production are ammonia vapour; NO_x , NH_3 , SO_x and CO.

The main gaseous emissions from the process of HNO_3 production (Ostwald process) include both NO and NO_2 gases, and they contribute to photochemical smog (SE, 2012). Careful attention is therefore required to minimize the amount of these gases emitted into the atmosphere. This is because the production of HNO_3 via the oxidation of ammonia to NO_x is associated with the release of NO_x (Ahlgren *et al.*, 2008). In the absorption column the NO is first oxidized to NO_2 by a stream of air supplied from the discharge of the centrifugal compressor. The NO_2 then flows up the column where it is dissolved in feed water flowing down the column to produce HNO_3 . The unabsorbed gases flow out through the top of the column as tail gas and gain heat as they pass through the heat exchangers counter current to the process gas.

The plant may also indirectly generate emissions of CO_2 and methane (CH_4). It has been proven beyond doubt that coal fired boilers are a major source of criteria air pollutants; these include SO_2 , CO ; NO_x ; and PM (Aneja *et al.*, 2001; E.H. & E., 2011). According to Wang and Mauzerall (2005), these pollutants from coal can cause health damages which, can be compared with the market price of coal. The current coal price does not include the external costs to health and the environment. Wang and Mauzerall (2005) believes that, if emissions from the use of other fuels other than coal is negligible, the value of damage from coal is equal to the total health damage costs from air pollution divided by the total tonnage of coal consumed.

2.7 An overview of past research studies on air pollution

Rani *et al.*, (2011) defines air pollution as, “the introduction of chemicals, particulates matter, or biological materials that cause harm or discomfort to humans or other living organisms or cause damage to the natural environment or built environment, into the atmosphere.” This definition covers it all; animals, plants and the built environment are equally affected by pollution. Rani *et al.*, (2011) goes further to highlight that air pollution from increasing vehicular traffic, cutting down of trees to build express highways, flyovers, agricultural land and the hazards from industrial effluent have sharply increased the incidence of a range of diseases, some of which are asthma, cancer, mental retardation, caused by heavy metals like lead and mercury, in the blood stream. Air pollution has become a devastating child killer throughout Asia. This becomes an issue of concern because Zimbabwe as a developing country, is affected by all these

mentioned above. According to Rani *et al.*, (2011) children under five years of age are more vulnerable to both indoor and outdoor air pollution.

Shaheen *et al.*, (2010) found out that employees and residents in the vicinity of a fertilizer factory had higher prevalence of asthma/rhinitis related symptoms. The study reported that the fertilizer industries release toxic waste and emit various noxious gases at high concentrations. In this study Shaheen used a cross sectional survey in residents and employees of a fertilizer company located in Multan city. A questionnaire on respiratory symptoms was circulated among residents and employees. The results were then analysed using a two tailed chi-square test using Statistical Package for the Social Sciences (SPSS). The results showed that residents living in the vicinity of the fertilizer factory had high prevalent symptoms of shortness of breath as compared to those living outside. This could be attributed to NH_3 , HNO_3 , CO , G.H.G and fine particulate matter that can clog the capillaries in the lungs causing respiratory infections (Shaheen *et al.*, 2010). However, this study did not measure the concentration of various pollutants for it was beyond its scope.

Tsimakuridze (2005) reported that the atmosphere around an ammonium nitrate industry is highly polluted with NH_3 , nitrous acid (HNO_2), NO_2 and SO_2 . The study also concluded that concentrations of toxic substances depends on the character of the technological process, high air temperature has bad effects on health during warm periods of the year, and that noise factor and general industrial vibration exceeds acceptable level in the majority of working area. The study proved that the morbidity of respiratory diseases, musculoskeletal, cardiovascular, neural, kidney and digestive systems are frequent and they amount to 76 % of all cases at a fertilizer company and its surroundings. In addition, the clinical examinations of workers with basic professions about production of NH_4NO_3 showed frequent cases of chronic bronchitis, radiculoneuropathy, damaged airways and myocardiodystrophy.

Godson *et al.*, (2005) conducted a research at a chemical fertilizer complex. Air samples were collected, cross sectionally from 7 points located at the ammonia plant using a wet test meter (Model 63115, Precision Scientific Inc., USA) to draw air into a double orifice fitted glass bottle containing a specially prepared medium of weakly bonded boric acid, known to loosely trap free ammonium molecules. This medium was then transferred to the laboratory for ammonia determination. The result revealed that NH_3 and particulate emissions constituted the major air pollutants. A health survey conducted with randomly selected workers showed that there were

66.1 % with respiratory problems and 22.6 % had eye problems. Those living further away from the complex experienced relatively low levels of ailments.

Mujuru *et al.*, (2012) monitored four pollutants (SO_2 , NO_2 , Pb and suspended particulate matter) at sites scattered throughout Harare for three months. Sulphur dioxide was determined by bubbling the air into a solution of hydrogen peroxide (H_2O_2) followed by titration. The result was that the highest SO_2 pollution of $8200 \mu\text{g}/\text{m}^3$ was in an industrial area. Nitrogen dioxide (NO_2) was sampled from the air by passive samplers followed by spectrophotometric determination. The highest NO_2 pollution was $46.14 \mu\text{g}/\text{m}^3$ at a site on a busy road. The total suspended particulate matter was determined as “black smoke” using the Soiling Index method. The highest total suspended particulate matter was $154.31 \mu\text{g}/\text{m}^3$ found in a suburb located near industries and the lowest was $9.54 \mu\text{g}/\text{m}^3$ in a low-density residential area far from pollution sources. Pb was determined by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) for each month for every site and ranged from 0.01- $0.72 \mu\text{g}/\text{m}^3$. These pollutants in the greater city were then linked to chronic health problems like cardiovascular and cardio-respiratory diseases in the population. The study shows high level of pollutants in the city which could be attributed to old technology and equipment used by the industries.

Manufacture of HNO_3 normally done at the site of a fertilizer plant is a source of NO and NO_2 , whilst production of NH_4NO_3 gives rise to the emission of NH_3 . Emission of SO_2 may occur from fossil fuel combustion (Harrison and McCartney, 1979). Air pollutants have been monitored by use of fast-response continuous gas analysers, 24h-average manual samplers and deposit gauges at an ammonium nitrate plant near Heysham for a period of 2.5 years. The results were that NO_2 had an average concentration of $100 \mu\text{g m}^{-3}$ at a site within the works boundary. SO_2 had an average concentration of $100 \mu\text{g m}^{-3}$ at a 4 km from the works. It was also concluded that this could have been attributed substantially by domestic fuel combustion. Concentrations of NO and NH_3 were not reported in this research.

The use of biomass fuel has proved to cause pollution. A study by Oguntoke *et al.*, (2010) monitored the concentrations of five G.H.G and examined health implications among the exposed rural residents. Fifteen villages were randomly selected in Ogun State (South Western Nigeria). A Gasman auto sampler was used to collect data in replicates over a period of three months. SO_2 , NO_2 , CO, H_2S and CH_4 , were found to be the main pollutants in the area. Respondents suffered from sneezing (44 %), nausea (34 %), headache (34 %), dizziness (31.1

%), eye irritation (23.3 %) and catarroh (24 %), among others. These health problems are largely consequences of human exposure to high concentrations of gaseous pollutants in the air.

Fertilizer industries cause serious harm to the environment. The major air pollutants from chemical industries are particulate matter, NO_x , SO_2 and trace metals (Thakkar, 2013). A study done around G.S.F.C (Gujarat State Fertilizer Company) Vadodara India from 2010-2013 using high volume sampler equipment measured different parameters and also analysed the effect of seasonal variation on various parameters. Samples were collected around the factory premises manually at regular intervals. The parameters were analysed in the laboratory. According to Thakkar, trace metals cause great damage to humans and animals since they suffer from respiratory diseases like lung cancer and asthma, throat infection etc. SO_2 and NO_x cause irritation in the respiratory system, eyes and also affect the mucous membrane. NO_x can damage the lung tissues and cause internal bleeding, oxygen deficiency, and nasal irritation. In this study, results were that the value for SO_2 was found between $19.40 \mu\text{g}/\text{m}^3$ - $56.12 \mu\text{g}/\text{m}^3$ and the value of NO_x was found between $21.48 \mu\text{g}/\text{m}^3$ - $62 \mu\text{g}/\text{m}^3$ for the four year testing in G.S.F.C. Trace metals were also found in this study (e.g. Zn, Pb, Ni, Cd, and Cr). Some of these are said to be carcinogenic.

While studies are being done to find pollutants, their concentrations and effects within centres of their production, research is also being done to mitigate them and protect the environment. A recent study by Hill and Bennett (2012) indicated that plants could play a very important role in pollutant uptake. Hill and Bennett used a typical vegetation canopy and chambers that were designed specifically for gaseous exchange studies. The data indicated that an alfalfa canopy removed gases from the atmosphere in the following order: Hydrogen fluoride (HF) > Sulphur dioxide (SO_2) > Chlorine (Cl_2) > Nitrogen dioxide (NO_2) > Ozone (O_3) > Peroxyacetyl nitrate (PAN) > Nitric oxide (NO) > Carbon monoxide (CO).

The absorption rate of NO was low, and no absorption of CO could be measured with the method used. Wind velocity above the plants, height of the canopy and light intensity were shown to affect the pollutant removal rate. The study concluded that vegetation might be an important sink for many gaseous air pollutants (USEPA, 1998).

Another study in United States seems to be having solutions to the problems. Simmons (2009) reported that coal-fired electricity generation is far cleaner today than ever before. The popular misconception that air quality is getting worse is wrong, as shown by the Environment Protection Agency's data (USEPA, 2010). Modern coal plants and those retrofitted with modern technologies to reduce pollution, are a success story and are currently providing about 51 % of the world's electricity. Institute for Energy Research (2009) stated that since 1970, the so-called criteria pollutants have declined significantly, even though the generation of electricity from coal-fired plants has increased by over 180 %. The "Criteria pollutants" are CO, lead (Pb), SO₂, NO₂, ground level ozone (O₃) and particulate matter (PM). These are called "criteria" pollutants because the Environmental Protection Agency sets the criteria for permissible levels (USEPA, 2010).

2.8 Air monitoring Techniques

Industrialisation and urbanisation has been increasing in most cities around the globe. The growth of these cities, increase of population, and use of vehicles has led to health and environmental damage around the world. This has resulted in contamination of the atmosphere and the need for air quality monitoring and management (Krupa and Legge, 1999; Wongniramaikul, 2012). In tandem with this the World Health Organisation (WHO) has been publishing and updating air quality guidelines for common air pollutants like PM, O₃, NO₂, and SO₂ since 1987 in order to provide information on how to reduce health impacts due to air pollution across the globe (Lin, *et al.*, 2011).

Air monitoring methodologies can be put into four major generic types according to their performance and cost. These are continuous analysers, active manual samplers', passive samplers and remote sensing devices (Chemical Engineering, 2014). Each type can be particularly useful in obtaining specific monitoring aims and objectives and hence it has its own advantages and disadvantages (Chemical Engineering, 2014) According to Wongniramaikul (2012) there are two methods which can be used to sample air, these are active and passive sampling. Each method is discussed here under. Advantages and disadvantages of each method will be highlighted.

2.8.1 Passive sampling method

It does not require active air movement from a pump. But air movement is due to diffusion through a static layer of air or membrane (Salter, 2005). It is one of the most important developments in air sampling technology in recent years. This method was first introduced to the health and safety profession in 1973 by Palmes and Gunnison, and since then the number and types of passive samplers have escalated (Salter, 2005; Lin, *et al.*, 2011). There are however two major passive samplers on the market today that operate on the principle of diffusion, these are samplers requiring laboratory analysis and the direct reading devices. Passive samplers that require laboratory analysis use a solid sorbent material or chemically treated paper to collect air borne pollutants. Direct-reading passive samplers are based on colorimetric techniques. The length of the colour band or the intensity of the colour changes is read on a scale or compared to a chart to determine concentration levels of gaseous pollutants (Salter, 2005).

According to Wongniramaikul (2012), passive sampling is the sampling technique that analyses molecules free flow from sampled media to collecting media due to the difference in their concentrations between two media following Fick's first law. Simple passive samplers are meant to be used for surveillance of time integrated gas concentrations. They are less expensive, hence no need for electrical connectivity, easy to handle and have an adequate overall precision and accuracy dependent upon the pollutant concentration level in question. It has been used in industrial areas urban and in rural areas to monitor NH_3 , SO_2 , NO_x , O_3 , HF, HCl and benzene-toluene-xylenes (BTX) (Krupa and Legge, 1999; Clemitshaw, 2011; Lin, *et al.*, 2011; Wongniramaikul, 2012; Chemical Engineering, 2014).

Passive samplers are good for saturation sampling, enabling in depth characterisation. They include diffusion tubes and badges, simple and can be deployed in large numbers without electrical connections. As a result they are suitable for screening studies, for mapping and for baseline studies. They are however labour intensive for their deployment and analysis, they are not proven for measuring concentrations of some pollutants and they provide monthly and weekly averages only. Passive samplers are also not suitable for measuring peak concentrations (Krupa and Legge, 1999; Salthammer and Uhde, 2009; Clemitshaw, 2011; Chemical Engineering, 2014).

2.8.2 Active samplers

This method involves the use of an air sampling pump to actively pull air with pollutants through a collection device as a filter for some specified time typically 24 hours. The collecting medium is then analysed and the pollutant concentration determined. So this method is faster than passive samplers (Salter, 2005; Clemitshaw, 2011). Active samplers are generally quite expensive because the active pump, flow meter and sampling media have to be bought. Power supply is needed for the pump so this means that it cannot be used in rural areas. Equipment also needs to be maintained. Active samplers can be used to monitor O₃, NO, NO₂, CO, SO₂, and hydrocarbons at a typical time interval of 1-60 minutes (Clemitshaw, 2011; Wongniramaikul, 2012).

The accuracy of the sample is determined by the sample volume, thus measuring the correct air volume is one of the most important quality issues for the whole analysis. Active sampling is also preferred when determining indoor air pollutants concentration (Salthammer and Uhde, 2009). Most ambient air pollutants involve the collection of grab samples and subsequent analysis using gas chromatography-mass spectrometry (GC-MS) or high performance liquid chromatography. Some of the active sampling methods used in United States of America are canister sampling, adsorbent tubes, absorption bottles, impregnated filter sampling, and high volume PUF-sampler to mention just a few (Chemical Engineering, 2014).

2.8.3 Biomonitoring of air pollutants

Biomonitoring is the technique based on use of organisms that have the ability to store and accumulate contaminants in their tissues, "bioaccumulation", under the control of several mechanisms of setting and transfer. This technique has become an attractive complement of traditional methods for measurements of air quality. The identification of pollution within sensitive organisms can also allow detection of air quality degradation before it severely affects the biota or humans. Sensitive plants can be real bioindicators of pollution. Urban vegetation can interact, directly and indirectly, with local and regional air quality by altering the urban atmospheric environment (Maatoug *et al.*, 2012). Trees can change local meteorology, alter pollution concentrations in urban areas, and remove gaseous air pollution or intercepting airborne particles.

2.8.4 Environmental law on biomonitoring and bioaccumulation

In the UK rapid population growth, urbanisation and the use of coal accounts for the increase in air pollution. The pollutant concentrations caused pollution episodes in the 17th and the 19th century (Chauhan and Johnston, 2003; Franek and DeRose, 2003). These air pollution episodes such as the Great Smog caused severe health impacts and great public concern leading to the Clean Air Act of 1956 and 1968 (Chauhan and Johnston, 2003; Kuklinska *et al.*, 2015). Since the Clean Air Act, the UK government has developed Statutory, Air Quality Strategies and a system of air quality management first published in 1997. UK AQS has set targets for eight air pollutants (e.g. CO, NO₂, O₃, PM₁₀, and SO₂ (Stone, 2000; Kuklinska *et al.*, 2015). In the United States air pollution gave government pressure by 1940 as a result of smog formed in Los Angeles, while other cities reported poor air quality and visibility (Franek and DeRose, 2003). In 1947 California passed air pollution regulation. In 1955 the Congress underpinned by strong public support passed its first environmental legislation, Environmental Protection Agency and an effective public policy the environment were instituted (Franek, 2003; Valavanidis *et al.*, 2008).

2.8.5 Environmental Law in Zimbabwe

Basically air pollution can be regulated in various ways, some of which are; stipulating emission standards, air quality standards, emission taxes and by cost benefit analysis (Fenger, 2008). Zimbabwe has Laws to control pollution from established and new companies. These are

1. Atmospheric Pollution Prevention Act Chapter 20:03 revised 1996
2. Environmental Management Act 92 of 2009 (EMA)

The Environmental Management Act (EMA) of Zimbabwe stipulates emission standards for motor vehicles, chimneys and the powers of environmental inspectors. Section 15 of this Act deals with height of chimneys, 15(1) state that, the chimney of every air-polluting appliance shall be 50 m above the ground or so designed as to allow adequate dispersion of the pollutants to the satisfaction of the Agency. Sable Chemical Industry stack heights are as follows:

Table 1: Stack heights and diameter at S.C.I

Plant	Diameter (m)	Height (m)	WHO standards column
Boiler stack	1.4	31	35.4
Nitric acid	0.30	30.48	
Ammonia plant	0.48	30	

All these stack heights are below the World Health Organisation standards (WHO) and as such causes the dispersion of pollutants far into the atmosphere difficult. This means they will release their emissions within the company premises thus affecting the workers and the farm dwellers .Section 15(3) states that, the Agency may require the owner or occupier of any premises in or on which an air polluting appliance with a chimney which does not conform to the requirements of subsection (1) to install, alter, or extend such chimney within a stated period at own cost. Sable Chemical Industry should revisit the issue of stack heights and comply with the laws of Zimbabwe.

2.8.6 Air quality guidelines

The creation of effective legislation in the UK and the clean air acts of 1970 in the United States helped in the creation of emission guidelines by the highest international body which deals with human health (World Health Organization, WHO). These guidelines are intended to support risk management and environmental policies in different contexts. As such standards set in each country will vary according to country's level of development, economic consideration and other political and social factors (WHO, 2005). However, World Health Organisation air quality guidelines provide a uniform scientific base for understanding the effects of air pollution.

The Blue, Green, Yellow and Red denotes the carbon tax the emitter should pay according the colour code of his/her emissions, for example Blue licence pays \$100, Green licence \$145, Yellow licence \$280 and Red licence \$555 (Zimbabwe, 2009) pollution on human health. Using these guidelines as a base local or national air quality standards can be developed for the management of air quality. There is growing evidence that there is adverse health effect at low

levels of exposure, and that researchers have been unable to identify a clear threshold or level below which there is no adverse effect to human, animal and ecological health (WHO, 2005).

Table 2: EPA and WHO guidelines for SO₂, NO₂ and NH₃

Parameter	Maximum Level /µg/m ³	EPA	WHO
SO₂	80(annual)	0.03 ppm (annual)	20µg/m ³ (24 hrs)
	12 (24hrs)	0.14ppm(24 hrs)	500µg/m ³ (10mins)
	350 (1 hr)	75ppb (1hr)	
NO₂	100 (annual)	53ppb (annual)	40 µg/m ³ (annual)
	150 (24hrs)	100 ppb(1 hr)	200 µg/m ³ (1 hr)
	200 (1 hr)		
NH₃	500 (24hrs)	50 (1 hr)	300 ppb (annual)
		141 ppb (24 hrs)	

United States Environmental Protection Agency (WHO, 2005; Zimbabwe, 2009; EPA, 2010)

Table 3: Zimbabwe air quality standards for NH₃,NO_x and SO₂

Parameter	Blue	Green	Yellow	Red
NH₃	<40mg/m ³	<60 mg/m ³	<80 mg/m ³	<100 mg/m ³
NO_x	<70mg/m ³	<100 mg/m ³	<130 mg/m ³	<150 mg/m ³
SO₂	<30mg/m ³	<40 mg/m ³	<45 mg/m ³	<50 mg/m ³

CHAPTER THREE

RESEARCH DESIGN AND METHODOLOGY

3.1 Description of study location

The study location consists of the peripherals of the industrial layout of Kwekwe with the Sable Chemical Industry as the epicentre (Figure 6). Kwekwe which sits within the Midlands Province is a small mining town situated approximate 220 km from Harare and 230 km from Bulawayo.

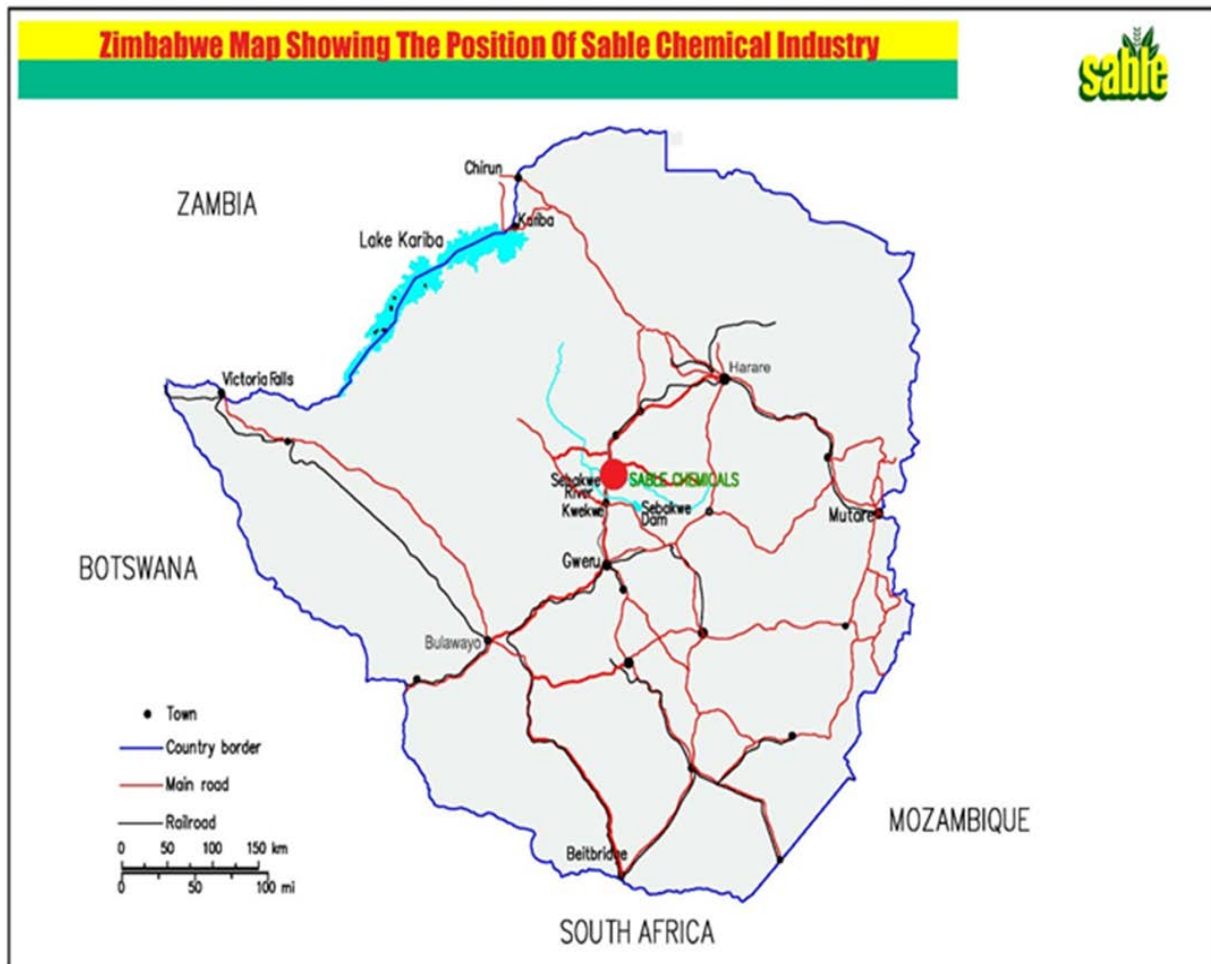


Figure 6: Map of Zimbabwe showing the location of Kwekwe and the Sable Chemical Industry Position of (S.C.I) in Zimbabwe (Adapted from: Zimbabwe district map, 2012)

The geo-reference co-ordinates of Kwekwe are in Figure 7 Sable Chemical Industry is surrounded mainly by commercial farms and the recently resettled farmers.

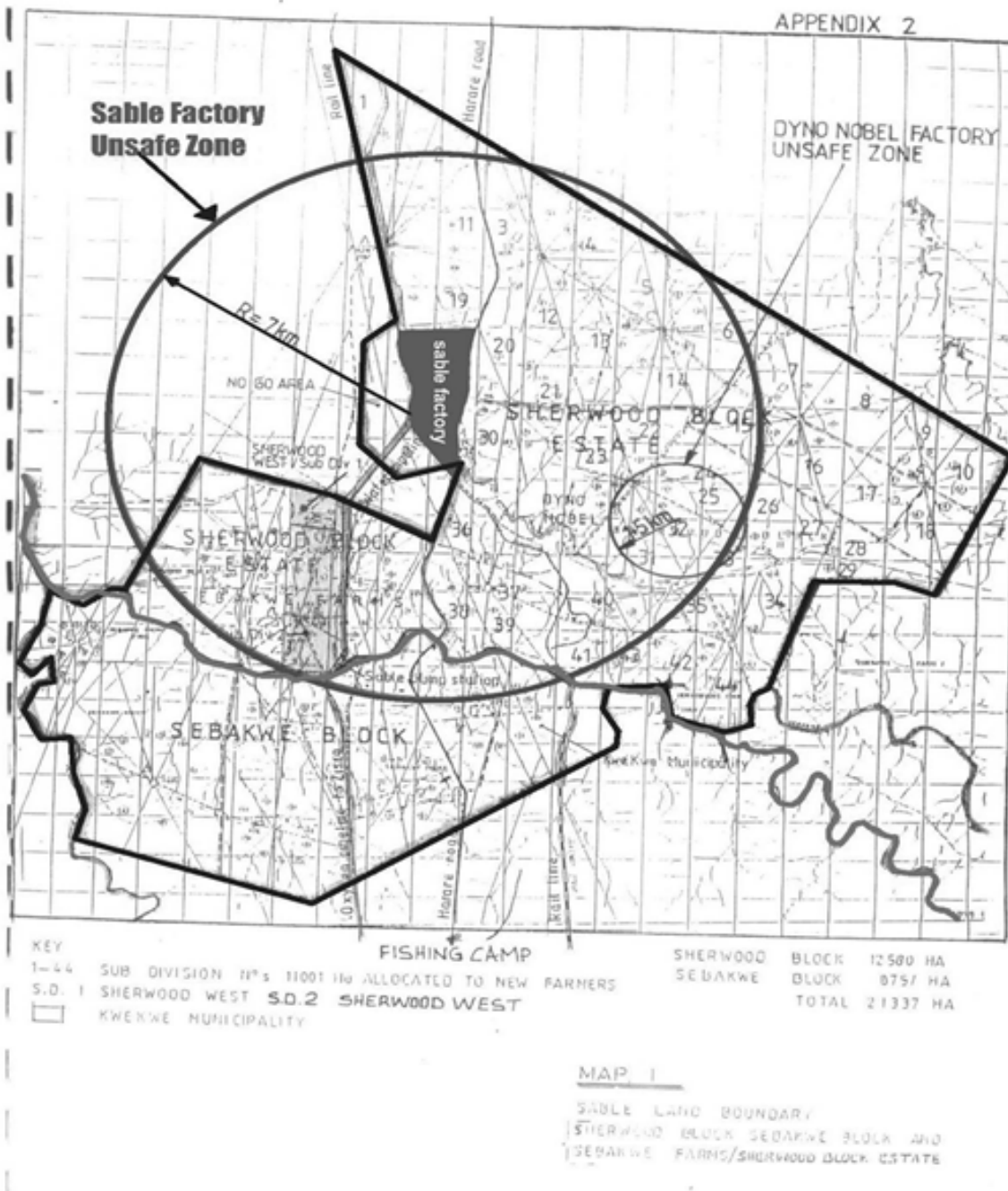


Figure 7: Geo-references of Kwekwe and Sable Chemical Industry land boundary showing the 7km radius danger zone (Adapted from: S.C.I Training Manual, 2011)

3.2 Topography

The co-ordinates of Kwekwe are: (18.9167° S; 29.8167° E) latitude: 19°, 0000; longitude: 29.7500). The area is characterised by flat or gently undulating topography (William and Smith, 1994). It is in the Highveld at an altitude of about 1,220 m above the sea level. District drainage is dominated by two north flowing rivers, the Kwekwe and the Sebakwe which join Munyati River about 8 km north of Kwekwe town (William and Smith, 1994). Agriculturally it lies in a region whose rainfall ranges from 650-700 mm per annum. The average annual temperature is 19°C, summers are long and temperatures depend on cloudiness and the amount of rainfall received. The climate is hot and wet during summer (November - March) and winters (May - August) are cool and dry with an average minimum temperature of 7 °C (Makaure and Makaka, 2013; Matsi, 2014). S.C.I. is surrounded mainly by commercial farms and the recently resettled farmers (Matsi, 2014). Figure 7 and 8 shows.

3.3 Vegetation and plant geography

Zimbabwe is mostly Savannah. The vegetation is characterised with short shrubs and tall grass. The *Brachystegia spiciformis* (msasa), *Julbernardia globiflora* (mnodo) and the mvunga shrubs are the common species in the Kwekwe area. *Hyparrhenia* spp. (grassveld) occurs in areas receiving between 750 mm and 1 125 mm at an altitude ranging from 1 200 m to 1 675 m. This is a high veld and has a grazing capacity of 1 LU: 2.5-3.5 ha. Common grasses include *Hyparrhenia filipendula*; *Hyperthelia dissoluta*; *Heteropogon contortus*; *Brachiaria brizantha*; *Digitaria milanjana*; *Eragrostis racemosa*; *Andropogon schinzii*; *Schizachyrium semiberbe*; *Skeneoides jeffreysii*; and *Aristida congesta*. *Hyparrhenia* species and *Themeda triandra* dominate on fertile red clays and clay loams. This veld type is relatively resistant to overgrazing (Gambiza and Nyama, 2006). There are also numerous flowers which include the spider lily, *Leonotus cassia*, *Tree wisteria* and (Matsi, 2014). However deforestation due to farming activities and population growth dombeya and poaching has reduced the amount of wildlife and plant species (Matsi, 2014).

3.4 Fauna and flora population

There are around 350 species of animals that are found in Zimbabwe. The vegetation and interspaced hills around Kwekwe provide habitat for animals such as warthogs (*Potamochoerus africanus*), monkeys (*Cercopithecus mitis* ssp. *albogularis*), kudu (*Tragelaphus strepsiceros*), elands (*Tragelaphus oryx*), impala (*Aepyceros melampus*), and spring hares. There are also many snakes and over 500 birds' species (Makaure and Makaka, 2013; Matsi, 2014).

3.5 Delineation of assessment study area

An air quality-monitoring network was established at S.C.I near Kwekwe in Zimbabwe from: July, August, and September 2012, to measure the concentration of NH₃, SO₂ and NO₂ within the industry's vicinity. The Dräger X-am 5000 automatic multi-gas monitor was used. Sampling was conducted in nine selected points. The points are, ammonia synthesis plant (loop), nitric acid plant, ammonium nitrate plant, boiler, samples were also taken 500 m from the centre of the ammonium plant towards the North South, East and West. A control sampling point was established about 5 km away from the centre of the ammonia synthesis plant (loop) towards the North-West. (i.e. the general windward direction in the area). All samples were collected from a height approximately 1.5 m above the ground (shoulder height).

3.6 Sampling frequency and study duration

Sampling was conducted in three months: July; August; September; 2012, three times a week. This means that 9 samples were collected per day, 27 samples per week and 108 per month. This will give a gross total of 324 samples collected for the whole period. All samples were collected during the day between 1000-1500 hrs.

3.7 Sampling stations

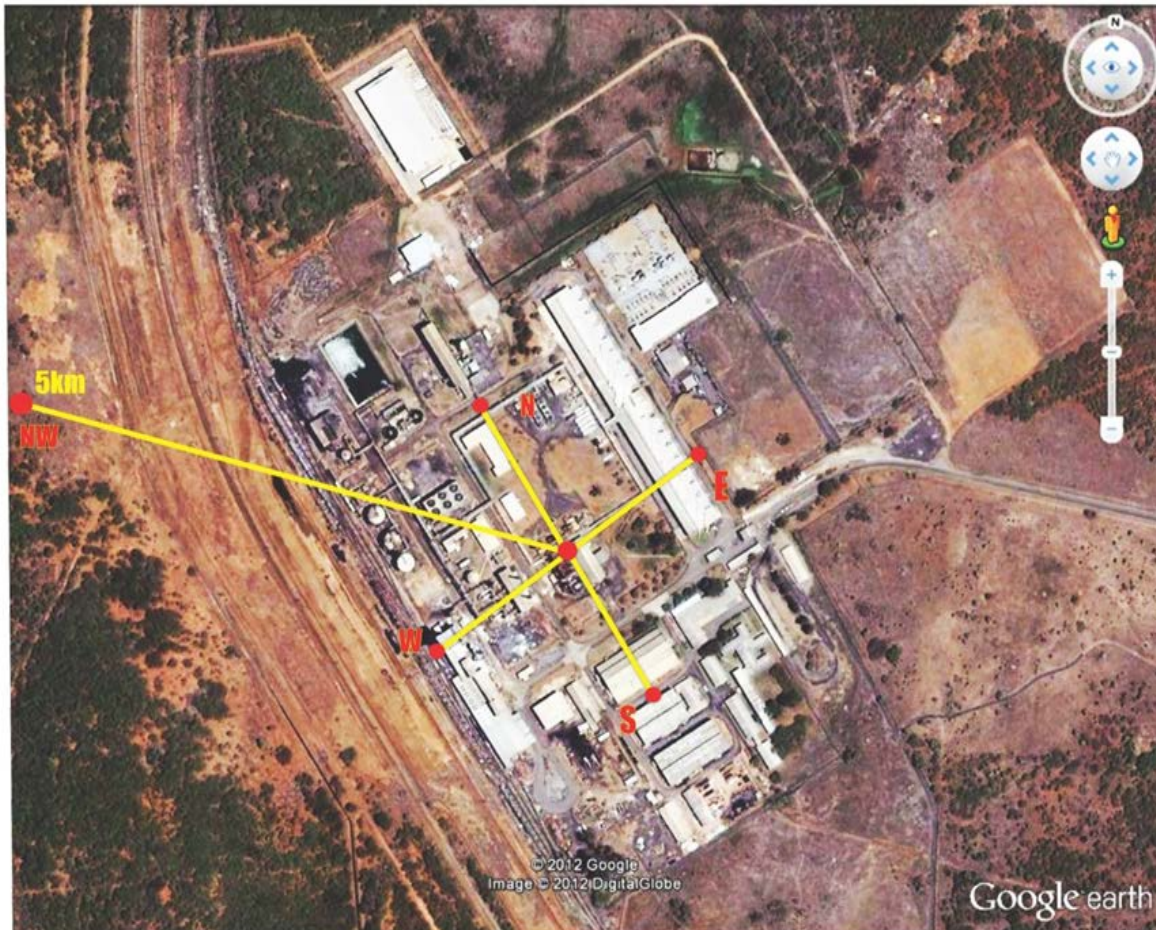


Figure 8: Sable Chemical Industry Google Map showing the nine sampling points
(Google maps: accessed 7 march 2012)

Nine sampling stations were randomly identified for the measurement of some air pollutants around Sable Chemical Industry (S.C.I) in Kwekwe (Figure: 8). The sampling stations were selected to capture air quality data on all wind directions.

The electrochemical Drager Sensors (Figure 9) which rely on electrochemical measuring transducers for measuring concentration of gases under atmospheric conditions were used for the measurement of NH_3 , SO_2 , NO_2 , CO , H_3S , CO_2 , Cl_2 , HCN , O_3 , COCl_2 , amines, odorants and organic vapours. The ambient air being monitored diffuses through a membrane into the liquid electrolyte in the sensor. The electrolyte contains a sensing electrode, a counter electrode and a reference electrode. An electronic potentiostate-circuit ensures a constant electrical voltage between sensing electrode and reference electrode. Voltage, electrolyte and electrode material are selected to suit the gas being monitored so that it is transformed electrochemically

on the sensing electrode. The flow of electrons generated by the reaction is the measure of the gas concentration. (Dräger Booklet, 2012).



Figure 9: The Dräger X-am 5000 automatic multi gas monitor
(Adapted from: Dräger Booklet, 2012)

3.8 Data acquisition (Measuring Principle)

Pollutants	Measuring range	Response Time	Accuracy	Temperature	Humidity	Pressure
NO ₂	0-50ppm of NO ₂	15s at 20°C	≤±2of the measure value	-30-50°C	10-90% r.h	700-1300hPa
NH ₃	0-300ppm NH ₃	20s at 20°C	≤±3 of the measured value	-40-50°C	10-90% r.h	700-1300hPa
SO ₂	0-100ppm SO ₂	15s at 20°C	≤±2 of the measured value	-30-50°C	10-90% r.h	700-1300hPa

(Source: Dräger Booklet, 2012).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Instrument calibration and validation

Air sampling was done using a modern automatic ambient air analyser (The Drager X-am 5000 automatic multi-gas monitor) consisting of electrodes (which contain sensing electrolytes for different gases), a counter electrode and a reference electrode. The NH₃, SO₂ and NO₂ electrochemical transducer sensors of the automatic multi-gas monitor (Drager X - am 5000) were calibrated prior to measurement and acquisition of data (for NH₃, SO₂ and NO₂) at the designated sampling stations. The sensor electrode for each of the parameters were referenced against a counter electrode and a reference electrode on an electronic potentiostate-circuit (which ensures a constant electrical voltage between sensing electrode and reference electrode), by allowing steady flow of gases to diffuse through a membrane into the liquid electrolyte in the sensor.

The electrode materials, and voltage applied is selected to suit the gas being monitored, such that it electrochemically transform the flowing gas concentration to sensor detectable electrons, which is then measured as the gas concentration. The accuracy of the machine at calibration was $\leq \pm 2\%$ for the measured value of NO₂; $\leq \pm 3\%$ for the measured value of NH₃, and $\leq \pm 2\%$ for the measured value of SO₂.

4.2 Concentration levels of NH₃, SO₂ and NO₂ around vicinity of Sable Chemical Industry

Toxic gases such as NH₃, SO₂ and NO₂ are emitted during different unit operations in chemical and fertiliser production plants (Singh, 2009). The levels of these gases were monitored at different sampling points within and around the vicinity of S.C.I in Kwekwe. The result showed that the concentration levels of NH₃, SO₂ and NO₂ detected in ambient air around the vicinity of S.C.I were variable, with sampling location, time of measurement and climatic factors. The concentrations of all three gases varied significantly ($P \leq 0.05$) over the climatic seasons, with the lowest and highest detection observed during late winter (August)

and springs (September), respectively. The distribution sequence of the abundance of the measured gases were in the order $\text{SO}_2 > \text{NO}_2 > \text{NH}_3$.

4.2.1 Ammonia (NH_3)

The concentration levels of NH_3 measured around the S.C.I are presented in Table 4. The levels of ammonia general ranged between 0.36 - 7.36 ppm in all sampling stations. The observed mean levels of NH_3 at the different sampling stations were ranged 2.78 – 7.36 ppm at the ammonia synthesis plant; 0.86 – 5.54 ppm at the nitric acid plant; 1.57 – 5.84 ppm at the ammonia nitrate plant; 2.03 – 7.07 ppm at the boiler; 0.36 – 0.64 ppm at 500 m from loop South; 2.00 – 7.61 ppm at 500 m loop west; 2.21 – 7.30 ppm at 500 m loop North; and 0.90 – 1.86 ppm at 500 m loop east. The least (0.36 ppm) and the highest (7.36 ppm) mean level of NH_3 were observed at the 500 m from the south loop during July, and by the NH_3 synthesis plant loop respectively, during August. These concentrations were significantly higher than measured at the control site (0.01 - 0.05 ppm).

The high mean value concentration of NH_3 detected near the ammonia plant (loop) is not unexpected due to the production of ammonia. The result is consistent with the findings of Godson (2005).

The sampling point is a key factor in gaseous concentrations value. The ammonia plant (loop) showed a high mean value concentration of NH_3 because that is where NH_3 is being produced (Godson, 2005). In this study the loop showed the highest mean value concentration of NH_3 14.5 ppm, followed by 500 m from the loop towards the North 4.5 ppm. This is the windward direction at S.C.I. 500 m towards the West recorded 3.8 ppm, the boiler 3.6 ppm and the control point had 0.03 ppm.

Table 4: Concentrations of NH_3 gas measured at the different sampling points

Sampling points	July	August	September	Mean±std dev
Ammonia synthesis plant (Loop)	2.78	7.36	5.84	5.33±2.33
Nitric acid plant	2.17	0.86	5.54	2.79±2.41
Ammonia nitrate plant	2.78	1.57	5.84	3.34±2.20
Boiler	2.03	2.07	7.07	3.65±2.90
500 M from loop South	0.36	0.64	0.49	0.50±0.14
500 M from loop West	2.31	2.00	7.61	3.89±3.15
500 M from loop North	4.44	2.21	7.30	4.59±2.55
500 M from loop East	1.86	1.64	0.90	1.49±0.50
Control	0.03	0.01	0.05	0.03±0.02
average SD	1.80			

4.2.2 Sulphur dioxide (SO₂)

SO₂ concentrations measured within and around the S.C.I are presented in Table 5. The measured mean concentrations of SO₂ at the different sampling stations were 0.17 – 69.32 ppm at the ammonia synthesis plant; 28.76 – 69.28 ppm at the nitric acid plant; 7.17 – 30.77 ppm at the ammonia nitrate plant; 7.28 – 84.61 ppm at the boiler; nd – 7.14 ppm at 500 m from loop South; 7.18 – 14.28 ppm at 500 m loop west; nd – 69.23 at 500 m loop North; and nd – 0.04 ppm at 500 m loop east. The least (0.02 ppm) and the highest (84.61 ppm) mean level of SO₂ were observed at 500 m from the loop east/south, and by the boiler plant respectively, during September. The levels of SO₂ generally ranged between 0.02 - 84.61 ppm in all sampling stations. These concentrations were significantly higher than measured at the control site, (0.03 - 0.18 ppm).

Table 5: Concentrations of SO₂ gas measured at the different sampling points

Sampling points	July	August	September	mean±std dev
Ammonia synthesis plant (Loop)	14.34	0.17	69.32	26.94±36.53
Nitric acid plant	42.88	28.76	69.28	46.43±20.57
Ammonia nitrate plant	7.17	28.6	30.77	21.97±13.04
Boiler	21.56	7.28	84.61	36.68±41.15
500 M from loop South	7.14	nd	0.02	2.45±4.12
500 M from loop West	7.18	14.28	7.71	9.78±3.96
500 M from loop North	21.54	nd	69.23	29.31±35.43
500 M from loop East	0.04	nd	0.02	0.02±0.02
Control	0.03	0.03	0.18	0.08±0.09
average sd	17.21			

The highest mean value concentration for SO₂ was observed at the nitric acid plant with 46.43 ppm followed by the boiler 36.68 ppm, 500 m north from the loop 29.31 ppm, the loop 26.94 ppm, ammonium nitrate plant 21.97 ppm and the control has 0 ppm. The results showed that, there is a high mean concentration value of SO₂ within the 500 m radius of S.C.I. This is a result of anthropogenic emission from combustion of coal in the boiler. Most SO₂ comes from coal which contains 0.5-7 % sulphur. SO₂ can be transported long distances if emitted by high stacks (Diab, 2011).

4.2.3 Nitrogen dioxide (NO₂)

The observed concentrations of NO₂ measured within and around the study site are very variable. The levels of NO₂ measured in all sampling stations ranged between 0.61 - 34.78 ppm (Table 6), with the least (0.61 ppm) observed at the ammonia synthesis and the ammonium nitrate plants during August and the highest (34.78 ppm) mean levels observed by the ammonia synthesis plant during September. The mean levels of NO₂ observed at the different sampling stations within and around the study site were ranged: ammonia synthesis

plant, 0.61 – 34.78 ppm; nitric acid plant, 1.24 – 23.86 ppm; ammonia nitrate plant, 0.61 – 1.43 ppm; boiler, 0.76 – 0.76 ppm; at 500 m from loop South, 0.73 – 0.77 ppm; at 500 m loop west, 0.71 – 0.79 ppm; at 500 m loop North, 0.70 – 0.78 ppm; and at 500 m loop east, 0.71 – 0.72 ppm. The detected concentrations were significantly higher ($p > 0.05$) than measured at the control site, (0.17 - 1.30 ppm).

Table 6: Concentrations of NO₂ gas measured at the different sampling points

Sampling points	July	August	September	mean±std dev
Ammonia synthesis plant (Loop)	4.23	0.61	34.78	12.68±18.77
Nitric acid plant	5.09	1.24	23.86	9.73±12.10
Ammonia nitrate plant	0.71	1.43	0.61	0.97±0.45
Boiler	0.76	0.76	0.76	0.76±0.00
500 M from loop South	0.73	0.76	0.77	0.75±0.02
500 M from loop West	0.79	0.71	0.75	0.75±0.04
500 M from loop North	0.74	0.70	0.78	0.74±0.04
500 M from loop East	0.72	0.71	0.71	0.72±0.01
Control	0.17	0.67	1.30	0.7±0.57
SD	1.79	0.29	12.87	
average SD	3.55			

The highest mean concentration value of 9.73 ppm was produced in the month September. The reason for this is as stated above. The average mean concentration values tend to decrease as we move outwards away from the plant. Ammonia synthesis plant (Loop) 9.73 ppm, Nitric acid plant 0.97 ppm, Boiler 0.75 ppm, 500 m from loop South 0.75 ppm, 500 m from loop West 0.74 ppm, 500 m from loop North 0.72 ppm, and lastly the Control 0 ppm. A survey by Lampard (2011) reported an average concentration of 0.49 ppm at a distance of 700 m towards the South. These results are consistent with what was found in this study. People within the 1 km radius of S.C.I may therefore be at high risk of respiratory disease, especially children under the age of 12 years (Lampard, 2011; Prajapati and Singhai, 2011, Thakkar, 2013).

4.3 Distribution of NH₃, SO₂ and NO₂ around the vicinity of Sable Chemical Industry

The observed concentration levels of the measured gases are in the order SO₂> NO₂> NH₃. The higher concentrations of the gases detected in the month of September may be as a result of the characteristics relatively calm and hot climate noted in September. An average temperature of 18 °C and an average wind speed of 17 km/h were reportedly captured during September in Zimbabwe by World Weather Online (2014). This could imply that the mean atmospheric pressure was relatively high. This could therefore result in slight elevation in the

release of gaseous emissions from different sources such as pipe jointing's, flanges, valves and nozzles, apart from designated release points in the plant. According to Godson (2005), potential sources of leaks in ammonia plants are the refrigeration loop, storage areas, flanges, valve packing and the pump and the compressor seals. Productivity may also be a factor.

During calm and hot climate such as this, some anthropogenic occurrences may interfere with natural processes atmospheric interaction. High atmospheric pressure may result in increase in gas leakages from different pipe units. The build-up of excess gases in the plants may consequently, result in pollution, poisoning and even explosions, on the one hand, while their levels around the plant may diminish via atmospheric deposition within the company premises (Tsimakuridze, 2005). The lower concentration levels of the gases observed in the month of August may however be the result of the generally cool and windy climate, with an average monthly temperature of 5 – 7 °C, and an average wind speed is 75 - 76 km/h (Weather on line, 2014). The high wind speed could also enhance the dispersal of emissions away from the plant. Thus, as observed, the concentration levels of the gases are expected to be low within the plant and the surrounding areas. This is consistent with the observation of Lampard (2011) who reported decreased concentration of gaseous pollutants with increase in distance from Chemical Industry's Plant.

4.3.1 Levels and distribution of NH₃ around the vicinity of Sable Chemical Industry

Activities at the different sampling point within and outside the chemical plant appeared to have an input in the gaseous concentration levels of the measured gases. For instance, a high mean concentration of NH₃ was detected at the ammonia plant (loop). Godson (2005) suggested in his study, that such high mean concentration levels of NH₃ may be as a result of subtle release, vis-a-vis leaks or pressure venting during production at the NH₃ plant loop.

In this study the loop showed the highest mean value concentration of NH₃ 14.5 ppm, followed by sampling station at about 500 m from the loop towards the North which measured 4.5 ppm (Figure 10). This is the windward direction at S.C.I. Five hundred metres towards the West recorded 3.8 ppm, the boiler 3.6 ppm and the control point had 0.03 ppm. The highest mean concentration values of NH₃ were observed in the month of September followed by August and lowest in July.

Apart from the differences in operational activities at different sites in the plant, the variations in levels of the measured gases may be associated with fluvial characteristics of gaseous and particulate substances. Thus, the dispersion of air pollutants from source area into the atmosphere is governed by the processes of molecular diffusion and convection (Pragati *et al.*, 2012; Lakshminarayananachari *et al.*, 2013), and this depends on climatic factors such as wind speed, temperature inversions, and dry deposition. It is also evident that NH_3 concentrations decreased with distance from the plant, as NH_3 gas was nearly at detection limit concentration quantities at the control point.

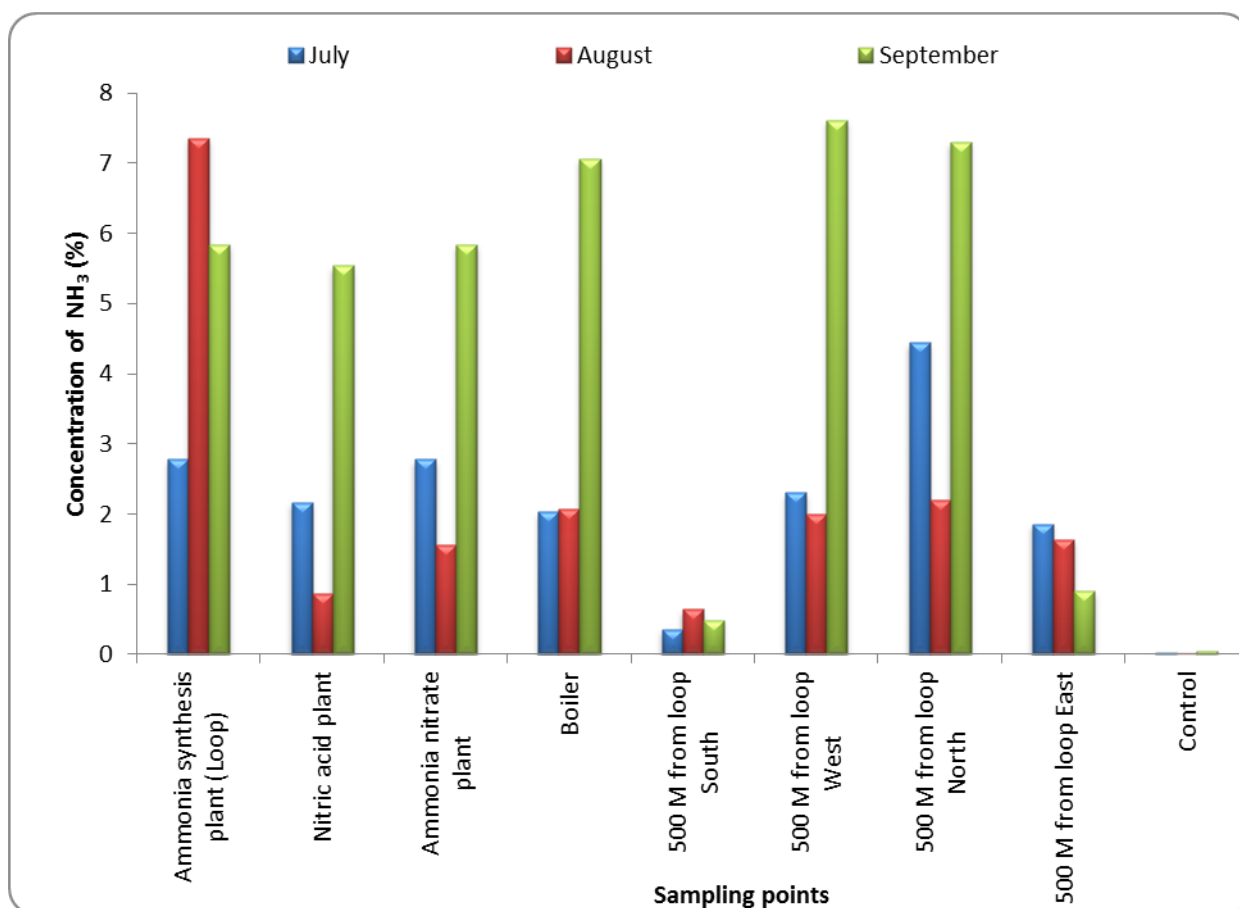


Figure 10: Distribution of the mean monthly concentration of NH_3 in the different sampling stations around S. C. I.

4.3.2 Distribution of NO_2 around the vicinity of Sable Chemical Industry

The highest mean concentration value of NO_2 was recorded in the ammonia synthesis plant (Loop) (Figure 11) in the month of September. The concentration decreases with distance from the plant. The lowest NO_2 concentrations were observed in the month of August. This may be because of the high winds (VALUES) observed during the period. Variations in the ambient air levels of NO_2 may also be as a result of chemical reactions in the atmosphere. According to Diab (2011), nitric oxide (NO) reaches a maximum levels in ambient air the

early hours of the day, after sunrise, after which NO is converted to NO₂, which results in the increase of NO₂ in the atmosphere. At the later hour in the day, ambient air NO₂ also declines due to photo dissociation, to form secondary pollutants such as O₃

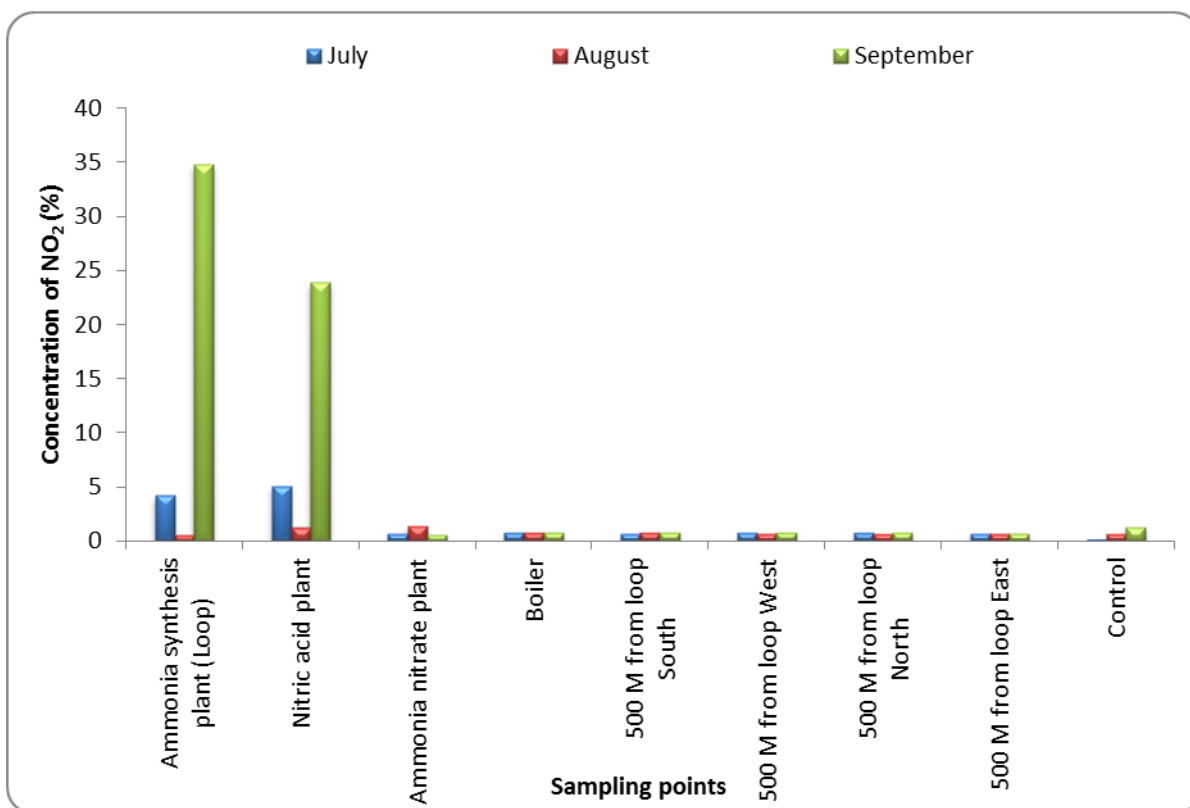


Figure 11: Distribution of the mean monthly concentration of NO₂ in the different sampling stations around Sable Chemical Industry

4.3.3 Distribution of SO₂ around the vicinity of Sable Chemical Industry

The mean concentration value of SO₂ detected by the boiler was the highest, measuring 36.68 ppm. This may be because the SO₂ plant is powered by the use of coal as energy source in the production of SO₂. The mean concentration values of SO₂ also decrease with distance from the plant.

Results from the study revealed that the mean concentration level of SO₂ was highest during the onset of summer (September). This was followed by the mean concentration levels of SO₂ during August and then July (Figure 12). This observation is however contrary to the findings of Thakkar (2013). Thakkar reported a higher value of gaseous pollutants (SO₂: 19.40 - 56.12 ppm; NO_x: 21.48 - 62.00 ppm) around the Gujarat State Fertilizer Company in India in winter than in summer.

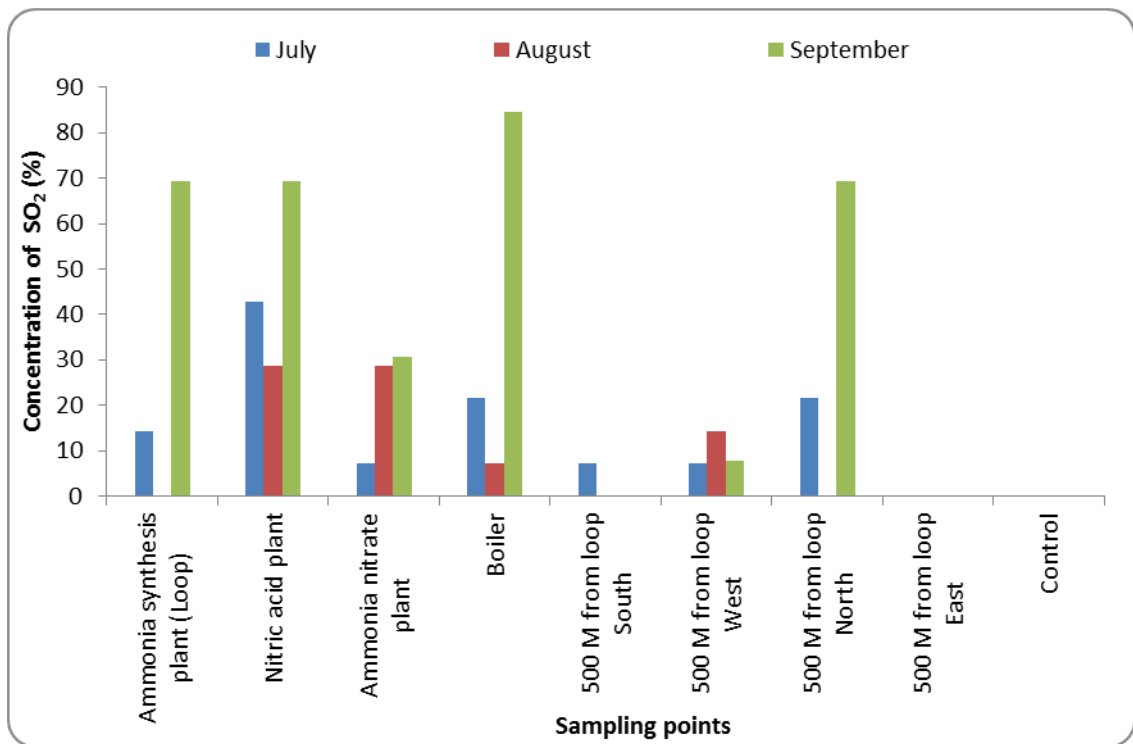


Figure 12: Distribution of the mean monthly concentration of SO₂ in the different sampling stations around Sable Chemical Industry

4.4 Comparative isokinetic (results) and dissipation studies

The evaluation of the isokinetic and dissipation of the measured gases, using an isokinetic sampling train over a distance of about 5 km away from S.C.I, with the epicentres defined by the different sampling station within (See Figure 7 Sable Land Boundary Map), confirmed a common pattern of distance dissipation. This may be due to rapid mixing/diffusion into the blanket of atmospheric gases. Samples were taken from the windward direction. The average wind speed was 4 knots.

The results showed that the concentrations of the measured gases decreased with distance from the plant (Table 7.x; Figure 13). The trend observed in this study is consistent with the findings of Lampard (2011). He reported that particulate matter showed the highest concentration followed by SO_x and then NO_x. Similar observations were noted by Lin *et al.*, 2011.

Table 7: Concentrations of SO_x and NO_x from the stack

Distance from the stack in m	800	1000	1500	2500	3500	5000
SO _x mg/m ³	0.030	0.024	0.014	0.006	0.003	0.002
NO _x mg/m ³	0.024	0.019	0.011	0.005	0.003	0.002
Particulates mg/m ³	0.126	0.100	0.057	0.025	0.014	0.007

X = number of atoms

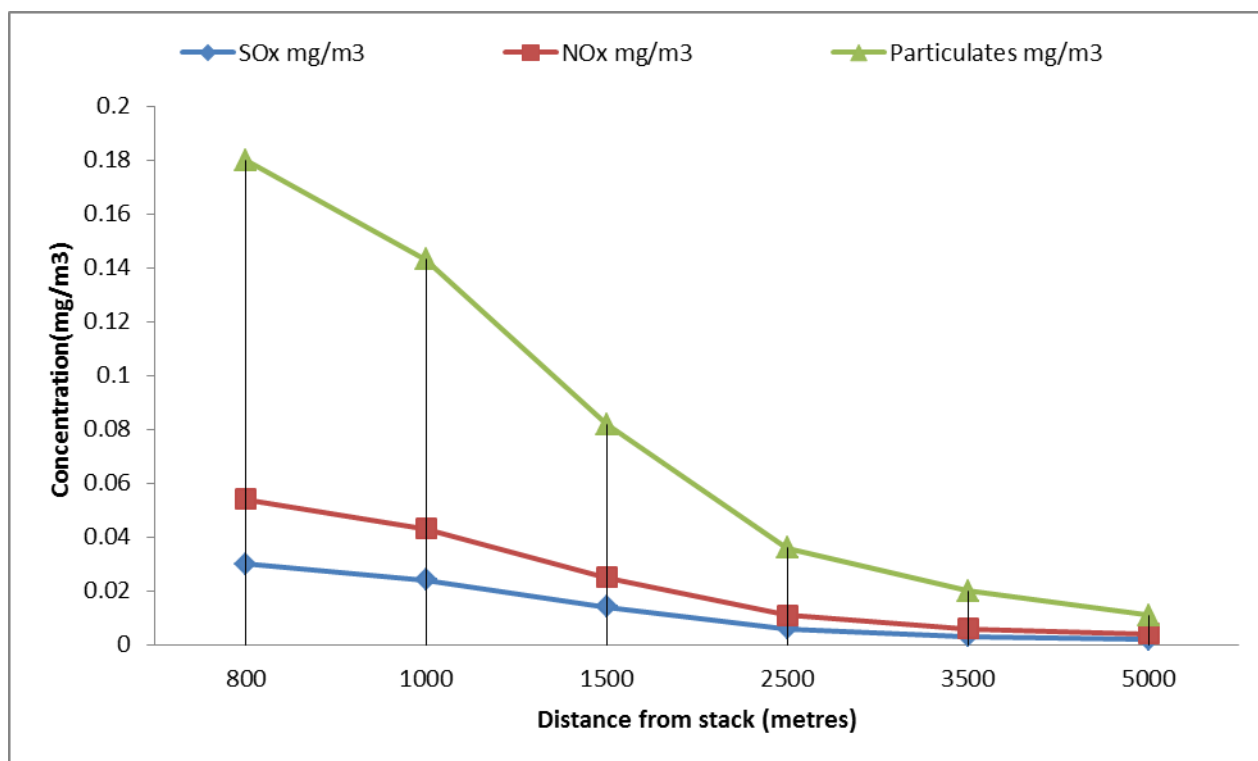


Figure 13: Concentrations of SO_x and NO_x from the stack

Lampard, (2011) noted with concern that children under 12 years at Sherwood primary school are the most vulnerable to respiratory diseases. Sherwood primary school is about 6 km from S.C.I and this school is within the danger zone of the company.

The survey recommendations from Lampard, (2011) were as follows:

1. Nitrogen oxides were too high, there is need to review the initial design of the nitric acid plant, and the Environmental Impact Assessment.
2. Sable Chemical Industry should revisit its stack heights and must comply with the Environmental Management Act (E M A).
3. Obtain emission licences and legal compliance on all stack heights (Sable Chemical Limited Survey Report, 2011).

4.5 Evaluation of ambient levels of NH₃, NO₂ and SO₂: Environment and Health implication

Ambient air quality can be impaired by emission from natural sources as well as from the domestic and industrial combustion of fossil fuels. There are inherent dangers associated with elevated concentrations of NH₃, NO₂, SO₂ and some other volatile materials in the atmosphere especially when in mixture with air (especially oxygen) in certain proportions (EPA, 1995).

4.5.1 NH₃ in the environment: source apportionment, levels, and distribution (Distribution and apportionment of source levels of NH₃)

Natural sources are mainly the result of chemical and microbial degradation of organic matter, such as dead plants and animals, animal wastes i.e. urine and faeces. Chemical industries including coke manufacturing, refrigeration, livestock management and fertilizer industry are major anthropogenic sources of NH₃ in the environment. The EPA reported that about 90 % of the atmospheric NH₃ is largely from fertilizer production and from livestock management (EPA 1995; WBK *et al.*, 2004). The mean concentration level of NH₃ detected within and around S.C.I during the study was 3.8 ppm. While the most intense perception of NH₃ odour was at the NH₃ synthesis plant loop (7.36 ppm), pungent smell of NH₃ is expected to be perceived at NH₃ concentrations of 50 ppm and above (EPA, 1995).

Short and long term exposure and effects

The average of the total concentration of ammonia in ambient air around the study locations (S.C.I) during study, revealed a mean concentration 3.53 ± 2.10 ppm. The observed concentration levels are low compared with levels (VALUE OF LEVELS) indicated for human and animal responses.

Human and animals may responds to exposure to different concentrations of NH₃ over a short or long period of time differently. Inhalation of low concentration of NH₃ can be tolerated for a very short time. This is because substantial proportion of the inhaled NH₃ gas may also be exhaled within 30 minutes of absorption. However, inhalation of about 500 ppm (348 mg/m³) NH₃ may lead to the dissolution of NH₃ in, or absorption in the mucous lining of the upper respiratory tract of human and animals (WBK *et al.*, 2004). Chronic exposure to relatively low concentrations, or acute exposure to concentrations greater than 500 ppm (348 mg/m³), may saturate the scrubbing ability of the upper respiratory system, and this may

result in adverse effects on distal portions of the lungs including chronic respiratory disease (WBK *et al.*, 2004). Experimental studies on the exposure of human and animals to different air concentration of NH₃ revealed zero mortality at concentration of 33.737 ppm (23.499 mg/m³) and lower, for 5 minutes. Human exposure to NH₃ concentrations of 9.2 ppm has no significant effect on pulmonary functions. No associations were made between changes in lung function and NH₃ concentration or length of exposure. However, inhalation exposure to air concentrations of NH₃ at greater than 5000 ppm (3483 mg/m³) for 30 minutes or more can be severely debilitating or lethal to both animals and humans.

Generally, acute health effect of humans and animals exposure to NH₃ include oral, nasal and eye irritation, respiratory tract irritation, decreased respiratory rate, increased respiratory depth, reduced body weight and lethargy. WBK *et al.*, (2004) reported that fatality from acute NH₃ inhalation arises from severe laryngeal edema, and obstruction, pulmonary edema, or extensive pneumonia complications, necropsy, cerebral haemorrhage and severe liver damage. Chronic relapsing sinusitis was reported in an individual exposed to NH₃ fumes as a result of a train spill (Pritchard, 2007). Severe chemical burns and inhalation injury can also occur. There are limited data on the chronic effects of ammonia in exposed populations (Pritchard, 2007).

The prevalence of self-reported symptoms was similar for unexposed controls and exposed workers although exposure to NH₃ was reported to precipitate, or increase cough, wheeze, nasal complaints, eye irritation and sore throat symptoms (WBK *et al.*, 2004).

Effect on flora and natural Environment

NH₃ may also affect vegetation by influencing the nitrogen cycle in the ecosystems. Depending on the type of vegetation under exposure NH₃ may be harmful to plants (WBK *et al.*, 2004). Both gaseous and particulate ammonia contribute to eutrophication of surface waters, soil acidification, fertilization of vegetation, changes in ecosystems, and smog and decreased visibility in cities and pristine areas.

4.5.2 Exposure evaluation of NO₂

NO₂ in the environment: source apportionment, levels, and distribution (Distribution and apportionment of source levels of NO₃)

Naturally levels of NO₂ vary widely because of a continuous baseline level present in the atmosphere. The annual mean concentrations of NO₂ range from 0.4 -9.4 µg/m³. At S.C.I the average mean concentration level was 3.1 ppm for a period of three months.

Short and long term exposure effects: Critical concentration

Results from animal experiments, revealed that exposure to NO₂ at concentrations less than 1880 µg/m³ (1 ppm) rarely results in acute toxicity (WHO, 2005). Exposure of healthy people at rest, or who undergo light exercise for less than 2 hours, to NO₂ concentrations greater than 4700 µg/m³ (2.5 ppm), may lead to pronounced decrease in pulmonary function (WHO, 2000; 2005). Animal toxicology experiments indicate that there are rarely effects of acute exposure to NO₂ concentrations of less than 1880 µg/m³ (1 ppm). It has been reported that normal healthy people exposed at rest or with light exercise for less than 2 hours to concentrations of more than 4700 µg/m³ (2.5 ppm) experience pronounced decrements in pulmonary function.

In a study reported by the World Health organisation (WHO, 2000), a 3.75 hr exposure to 560 µg/m³ (0.3 ppm) resulted in a slight effect on the lung function of people with chronic obstructive pulmonary disease. At lower concentrations the pulmonary function was not changed significantly. Asthmatics are most likely to be sensitive subjects to NO₂, although the health database is not certain. No observable effect was indicated in asthmatic patients' exposure to 7520 µg/m³ (4 ppm) for 75 min, whereas others showed decrease in FEV after 10 min of exercise at exposure levels of 560 µg/m³ (0.3 ppm). Hence, the lowest concentration capable of causing effects on pulmonary function was reported in patients with mild asthmatics exposed to 560 µg/m³ (0.3 ppm) for 10 - 30 minutes.

Thus human and animals exposed to such ambient air levels of NO₂ detected in the vicinity of S.C.I may be subject to NO₂ health risk. This is because the average concentration level observed is greater than the 1 ppm threshold for the manifest of acute toxicity. People exposed to NO₂ in location with air concentrations less than 1880 µg/m³ (1 ppm) around S.C.I may not experience acute toxic effect. However, the actual mechanisms of allergen challenges of NO₂ are not fully defined since NO₂ showed no effect at the lowest

concentration tested i.e. 190 $\mu\text{g}/\text{m}^3$ (0.1 ppm) (WHO, 2000). It is also not clear whether long term exposures to ambient NO_2 has any long term health effects in adults, but available results suggests respiratory effects in children exposed to an annual average NO_2 concentration of 50 - 70 $\mu\text{g}/\text{m}^3$ or higher.

It is important to note that NO_2 may cause a plethora of effects on lung, spleen, liver and blood (WHO, 2000). Both reversible and irreversible lung effects such as structural changes in cell types in the tracheobronchial and pulmonary regions to emphysema like effects have been reported. Biochemical changes often reflect cellular alterations at levels of 380 - 750 $\mu\text{g}/\text{m}^3$ (0.2 - 0.4 ppm). NO_2 levels as low as 940 $\mu\text{g}/\text{m}^3$ (0.5 ppm) also increase susceptibility to bacterial and viral infection of the lung.

NO_2 guidelines

NO_2 guidelines are complicated to come up with because of difficulties posed by the uncertainties in establishing an appropriate margin of protection. However epidemiological and animal toxicological studies have proved that NO_2 can cause infections and alter lung structure. Thus on these grounds it has been proposed that a long term guideline be established. An annual value of 40 $\mu\text{g}/\text{m}^3$ therefore has been proposed by the Environmental Health Criteria document as a standard guideline for NO_2 (WHO 2000; 2005). According to WHO, (2005) below are some of the guidelines for EU countries and South Africa;

Table 8: Guideline for NO_2 in $\mu\text{g}/\text{m}^3$

	1 year	24 hours	1 hour	10 minutes
WHO	40		200	
EU	40		200	
USA	100			
JAPAN		113		
SA	94	188	376	

4.5.3 Exposure evaluation for SO_2

SO_2 in the environment: source apportionment, levels, and distribution (Distribution and apportionment of source levels of NH_3)

The combustion of fossil fuels is one major source of release of SO_2 , with coal accounting for nearly 50% of the annual global SO_2 release, followed by oil accounting for between 25 – 30

% (WHO 2000; 2005). The average mean concentration value of SO₂ at S.C.I was 19.3 ppm. The annual mean concentrations of SO₂ in the atmosphere around Europe are now in the range of 20 - 60 µg/m³ (0.007 - 0.21 ppm) (WHO, 2005). This is as a result of the strict emission control on as well as changes in the pattern of fossil fuel use (WHO, 2000). In large cities where coal is still being used and with large traffic volumes SO₂ concentrations could be 5 - 10 times higher. Peak concentrations can reach 1000 - 2000 µg/m³ (0.35-0.70 ppm) or higher.

Short and long term exposure effects: Critical concentration

Effects of SO₂ exposure over an extended period of 24 hours were mainly derived from epidemiological studies. Symptoms of lung infection was reported to be exacerbated in selected sensitive patients, consistently exposed to SO₂ concentrations exceeding 250 µg/m³ (0.087 ppm), in the presence of PM. Recent studies also revealed the mortality effects of SO₂ exposure in industrial layouts, and in high vehicular traffic locations.

The annual average LOAEL of the sum of SO₂ and PM has been suggested to be 100 µg/m³ (0.035 ppm) (WHO, 2000; 2005). Although adverse health effects may occur at concentrations below this level; long term effects are liable to be affected by current conditions as well as the different qualitative and quantitative pollution of earlier years (WHO, 2000).

More specifically, exposure of asthmatics to SO₂ for as short as 10 minutes indicated that significant proportion experience changes in pulmonary function and respiratory symptoms. Other effects include reductions in forced expiratory volume (FEV), increases in specific airway resistance, and wheezing or shortness of breath. These effects are enhanced by exercise, which increases the volume of air intake thereby allowing the penetration of more SO₂ into the respiratory tract (WHO, 2000; 2005). Thus, people who exercise regularly are vulnerable because of the distribution of SO₂ along the conductive airways is not uniform as a result of the breathing volumes, types of air contaminants mix and the corrosive nature of SO₂ (WHO, 2000). Sulphur dioxide (SO₂) stimulates nerves in the lining of the nose, throat and lungs thereby irritating them. This causes reflex cough and chest tightness, which may lead to narrowing of the airways. This is a peculiar effect on asthmatics and people suffering from chronic lung diseases.

Based on empirical data a threshold SO₂ concentration value of 500 µg/m³ (0.175 ppm) was recommended not be exceeded over an average exposure periods of 10 minutes. Long term exposure threshold for SO₂ is associated with PM values which were suggested to be 125

$\mu\text{g}/\text{m}^3$ (0.04 ppm) (WHO, 2000). It is however not certain that adverse effects as a result of exposure to much lower concentrations of SO_2 may occur, but rather, a surrogate for SO_2 and PM (WHO, 2000). The World Health Organization (WHO, 2000), therefore recommends a concentration of $125 \mu\text{g}/\text{m}^3$ over a period of 24 hour, and an annual average concentration of $50 \mu\text{g}/\text{m}^3$.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The mean concentration levels observed for NH₃, SO₂ and NO₂ during study were ranged 3.8 ppm, 19.3 ppm and 3.1 ppm respectively. The emission levels of NH₃, SO₂ and NO₂ into the blanket of atmosphere around the Fertilizer and Chemical; production Industry were within the ambient levels considered to be safe according to the World Health Organization (WHO, 2002; 2005), the South Africa Air Quality Standards (SAAQS, 2012), and Chapter 20.27 of the Environmental Management Act of Zimbabwe (EMAZ, 2002). The concentration levels of the measured air pollutants at the control sampling station about 5 km from the industry were near zero. This may be as a result of air diffusion arising from the dispersion of contaminants through the air. Thus, the cloud concentrations of NH₃, SO₂ and NO₂ within the Fertilizer and Chemical; production facility of the Industry were higher than observed distances away from the Industry.

The variability in the concentrations of each parameter measured within the plant may be connected with some hotspots such as the ammonia loop, valve leakage areas as well as the prevailing meteorological conditions at the time of measurement. For instance, low surface wind speed, mixing height, temperature inversion, anticyclonic conditions, high pressure and poor maintenance within the plant could have resulted in high pollutants concentrations. In general, high pollutant concentrations were observed when the ambient air temperature was higher, than on a low ambient air temperature/cool days.

The relationship between emission pollutants and detected concentrations are non-linear. Thus, the complexity of environmental emissions and their attendant impacts on the environment and its associated biotic and non-biotic features is not clearly understood. This is because of the variation in the composition and chemical species released, and their atmospheric concentration levels. Pollutants may however not stay long in the atmosphere; they can be deposited onto land and water near or far distances, providing the relationship between air qualities, water quality and ecosystem health. While the mean concentration values of pollutants in this study appear to be fairly low, findings from earlier studies showed that air pollutants can be damaging even at low concentrations. This underscores the need to

consider and take issues of air quality seriously. This is because of their subtle and chronic ability to cause significant health and environmental damages and even death.

5.2 Recommendations

Although the observed ambient air concentrations of NH_3 , SO_2 and NO_2 were low, there are a number of suggested guideline and thresholds. There is need therefore to further reduce or attenuate release of air pollutants from production operation at S.C.I. This must be in accordance to the Environmental, Health and Safety Guidelines (EHSG, 2007), Hazardous Material management (2007); United States Environmental Protection Agency (USEPA, 2010), Environmental Health Engineering (E.H.E, 2011), and The School for Excellency (2012) recommendations for pollution reduction in Chemical Industries.

This may involve the designing of chemical processes and products that reduce or eliminate the use and generation of hazardous substances during production, and use of the products. Reduction and or elimination of wastes from the chemical processes, green chemistry aims at sustainable approach to cleaner environment, and this can be beneficial to economy and the society at large.

Also, the mechanism behind air pollution, impacts and diseases is not well understood, more so the present study did not investigate human and environmental health. This aspect need to be studied in order to find out if there is link between atmospheric chemical species and prevailing health and environmental condition of the populace within and around S.C.I. For instance NH_3 was reported may contribute to the damage of materials and buildings in several ways, but its role is not yet known. Further work may involve epidemiology study from the area.

However it needs to be stated that no temperature measurement where taken in this study. There is need for more research in this area where pollutant concentration is recorded against the environmental temperature. The rate of production and the time of the day when the pollutants are measured may also be an aspect to be looked into in future studies.

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APPENDICES

Appendix A Letter of authority to carry out a research at Sable Chemical Industry



Chemical Industries Limited

P O Box 561
KWEKWE
ZIMBABWE

when you call ask for:
Mr Musvipa

TEL: 263-(0)55-23601
FAX: 263-(0)55-22896
FAX: 263-(0) 55 20318

Ref : ZM/fm

Date : 14 February 2012

Mr Joseph Simbi
Ngezi Barracks Secondary School
P Bag 8004
KWEKWE

Dear Sir

RE : REQUEST TO DO AN MTECH RESEARCH AT SABLE CHEMICAL INDUSTRIES

Reference is made to your letter dated 24 January 2011 being a request to carry out a research on Environmental Management with the Company.

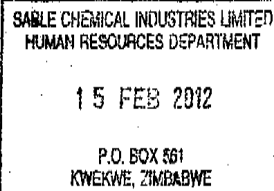
I am happy to advise that your request has been accepted under the following conditions:-

1. That the research shall be supervised by our SHEQ Manager who shall approve the methodology.
2. That the research will be wholly to your account and no costs shall be borne by Sable Chemical Industries Limited.
3. That the findings shall first be submitted to Sable Chemical Industries for approval before being submitted to the college or any other party.
4. Other conditions of secondment will be communicated to you by the Human Resources Officer on assumption of the research programme.

In this regard, you are requested to see our SHEQ Manager, Mr Leo Mukaro for further guidance. You shall also be asked to sign your consent to the above conditions before commencement of the research.

Yours sincerely

Z. Musvipa
Human Resources Manager



c.c. SHEQ Manager
Human Resources Officer
File Copy

DIRECTORS: S. Mutasa (Chairman), MS Kachere (Deputy Chairman), BP Nyajeka, Brigadier General G Chankira, A. Connolly, J. Chigwende, JP Murewa, NL Magado

Appendix B Air Sampling Record Sheet

Date	Time	Sampling sites	Pollutants	Concentrations ppm
		Ammonia synthesis Plant (loop)	<u>Centre</u> NH ₃	
			SO ₂	
			NO ₂	
		Nitric acid plant	<u>Centre</u> NH ₃	
			SO ₂	
			NO ₂	
		Ammonia nitrate Plant	<u>Centre</u> NH ₃	
			SO ₂	
			NO ₂	
		Boiler	<u>Centre</u> NH ₃	
			SO ₂	
			NO ₂	
		500m from the ammonia synthesis plant (loop)	<u>North</u> NH ₂	
			SO ₂	
			NO ₂	
		500m from the ammonia synthesis plant (loop)	<u>South</u> NH ₃	
			SO ₂	
			NO ₂	
		500m from the ammonia synthesis plant (loop)	<u>East</u>	
			NH ₃	
			SO ₂	
			NO ₂	
		500m from the ammonia synthesis plant (loop)B	<u>West</u> NH ₃	
			SO ₂	
			NO ₂	
		5Km away from the ammonia synthesis plant towards the North-West	NH ₃	
			SO ₂	
			NO ₂	

Samples collected by:

Signature:

Date:

Appendix C Main Entrance of S.C.I



Figure 14: Main Entrance of S.C.I
Date taken: 24 Sept 2012

Appendix D Fractional distillation plant at S.C.I



Figure 15: Fractional distillation plant at S.C. I
Date taken: 24 Sept 2012

Appendix E Ammonia plant (Loop) at S.C.I



Figure 16: Ammonia plant (Loop) at S.C.I
Date taken: 24 Sept 2012

Appendix F Ammonia storage tanks at S.C.I



Figure 17: Ammonia storage tanks at S.C.I
Date taken: 24 Sept 2012

Appendix G Nitric acid plant at S.C.I



Figure 18: Nitric acid plant at S.C.I
Date taken: 24Sept 2012

Appendix H Ammonium nitrate plant at S.C.I



Figure 19: Ammonium nitrate plant at S.C.I
Date taken: 24 Sept 2012

Appendix I Boiler plant at S.C.I



Figure 20: Boiler plant at S.C.I
Date taken: 24 Sept 2012

Appendix J Impacts of air pollution on forest at S.C.I



Figure 21: Impacts of air pollution on forest at S.C.I
Date taken: 24 Sept 2012

Appendix K Farmers within the 7 kilometre radius



Figure 22: Mr. Burger and his son Daniel working on their farm about a 1km from S.C.I
Date taken: 30 Sept 2012

Appendix L Newly resettled Farmer



Figure 23: Mrs.Sibanda a newly resettled farmer at her new home
Date taken: 30 Sept 2012

Appendix M GLM Procedure (Class Level)

17:36 Wednesday, November 21, 2012 1

The GLM Procedure
Class Level Information

Class	Levels	Values
SITES	9	500 M from loop East 500 M from loop North 500 M from loop South 500 M from loop West Ammonia nitrate plant Ammonia synthesis plant (Loop) Boiler
Control Nitric acid plant		

MONTHS	3	AUGUST JULY SEPTEMBER
		Number of observations 369
		The GLM Procedure

Dependent Variable: NH₃

	Source	DF	Sum of Squares	Mean Square	F Value	Pr >
F	Model	26	8434.83604	324.41677	11.92	
<.0001	Error	342	9306.32005	27.21146		
	Corrected Total	368	17741.15610			

	Source	DF	Type III SS	Mean Square	F Value	Pr >
F	MONTHS	2	1128.488326	564.244163	20.74	
<.0001	SITES	8	6212.003780	776.500473	28.54	
<.0001	SITES*MONTHS	16	1234.921863	77.182616	2.84	

The GLM Procedure

Dependent Variable: SO₂

	Source	DF	Sum of Squares	Mean Square	F Value	Pr >
F	Model	26	226395.4905	8707.5189	8.60	
<.0001	Error	342	346255.7052	1012.4436		
	Corrected Total	368	572651.1957			

	Source	DF	Type III SS	Mean Square	F Value	Pr >
F	MONTHS	2	53905.97640	26952.98820	26.62	
<.0001	SITES	8	99472.09045	12434.01131	12.28	
<.0001	SITES*MONTHS	16	77389.02819	4836.81426	4.78	

The GLM Procedure

Dependent Variable: NO₂

	Source	DF	Sum of Squares	Mean Square	F Value	Pr >
F	Model	26	20428.74296	785.72088	14.17	
<.0001						

Error	342	18961.26582	55.44230		
Corrected Total	368	39390.00878			
	R-Square	Coeff Var	Root MSE	NO ₂ Mean	
	0.518628	241.0139	7.445958	3.089431	
Source	DF	Type III SS	Mean Square	F Value	Pr >
MONTHS	2	2884.25967	1442.12984	26.01	
SITES	8	7719.81572	964.97696	17.41	
SITES*MONTHS	16	10422.71938	651.41996	11.75	

The GLM Procedure

Tukey's Studentized Range (HSD) Test for NH3

NOTE: This test controls the Type I experimentwise error rate.

Alpha 0.05
 Error Degrees of Freedom 342
 Error Mean Square 27.21146
 Critical Value of Studentized Range 3.32901

Comparisons significant at the 0.05 level are indicated by ***.

MONTHS Comparison	Difference		Simultaneous 95% Confidence Limits	
	Between Means			
SEPTEMBER - JULY	2.8382	1.2616	4.4147	***
SEPTEMBER - AUGUST	4.2485	2.6719	5.8250	***
JULY - SEPTEMBER	-2.8382	-4.4147	-1.2616	***
JULY - AUGUST	1.4103	-0.1367	2.9574	
AUGUST - SEPTEMBER	-4.2485	-5.8250	-2.6719	***
AUGUST - JULY	-1.4103	-2.9574	0.1367	

The GLM Procedure

Tukey's Studentized Range (HSD) Test for SO2

NOTE: This test controls the Type I experimentwise error rate.

Alpha 0.05
 Error Degrees of Freedom 342
 Error Mean Square 1012.444
 Critical Value of Studentized Range 3.32901

Comparisons significant at the 0.05 level are indicated by ***.

MONTHS Comparison	Difference		Simultaneous 95% Confidence Limits	
	Between Means			
SEPTEMBER - JULY	23.254	13.637	32.870	***
SEPTEMBER - AUGUST	28.005	18.388	37.621	***
JULY - SEPTEMBER	-23.254	-32.870	-13.637	***
JULY - AUGUST	4.751	-4.686	14.187	
AUGUST - SEPTEMBER	-28.005	-37.621	-18.388	***
AUGUST - JULY	-4.751	-14.187	4.686	

The GLM Procedure

Tukey's Studentized Range (HSD) Test for NO₂

NOTE: This test controls the Type I experimentwise error rate.

Alpha 0.05
 Error Degrees of Freedom 342
 Error Mean Square 55.4423
 Critical Value of Studentized Range 3.32901

Comparisons significant at the 0.05 level are indicated by ***.

MONTHS Comparison	Difference		Simultaneous 95% Confidence Limits	
	Between Means			
SEPTEMBER - JULY	5.5272	3.2769	7.7776	***
SEPTEMBER - AUGUST	6.3907	4.1404	8.6410	***

JULY	- SEPTEMBER	-5.5272	-7.7776	-3.2769	***
JULY	- AUGUST	0.8635	-1.3448	3.0718	
AUGUST	- SEPTEMBER	-6.3907	-8.6410	-4.1404	***
AUGUST	- JULY	-0.8635	-3.0718	1.3448	

The GLM Procedure

Tukey's Studentized Range (HSD) Test for NH₃

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II

error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	342
Error Mean Square	27.21146
Critical Value of Studentized Range	4.41487
Minimum Significant Difference	3.5967

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	SITES
A	14.561	41	Ammonia synthesis plant (Loop)
B	4.588	41	500 M from loop North
C B	3.885	41	500 M from loop West
C B	3.646	41	Boiler
C B D	3.341	41	Ammonia nitrate plant
C B D	2.790	41	Nitric acid plant
C B D	1.485	41	500 M from loop East
C D	0.500	41	500 M from loop South
D	0.032	41	Control

The GLM Procedure

Tukey's Studentized Range (HSD) Test for SO₂

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II

error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	342
Error Mean Square	1012.444
Critical Value of Studentized Range	4.41487
Minimum Significant Difference	21.939

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	SITES
A	46.429	41	Nitric acid plant
B A	36.678	41	Boiler
B A C	29.307	41	500 M from loop North
B A C	26.937	41	Ammonia synthesis plant (Loop)
B D C	21.971	41	Ammonia nitrate plant
E D C	9.778	41	500 M from loop West
E D	2.446	41	500 M from loop South
E D	0.078	41	Control
E	0.020	41	500 M from loop East

The GLM Procedure

Tukey's Studentized Range (HSD) Test for NO₂

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II

error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	342
Error Mean Square	55.4423
Critical Value of Studentized Range	4.41487
Minimum Significant Difference	5.1339

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	SITES
A	12.678	41	Ammonia synthesis plant (Loop)
A	9.729	41	Nitric acid plant
B	0.971	41	Ammonia nitrate plant

B	0.763	41	Boiler
B	0.754	41	500 M from loop South
B	0.751	41	500 M from loop West
B	0.739	41	500 M from loop North
B	0.717	41	500 M from loop East
B	0.702	41	Control

Breakdown of Means and Other Descriptive Statistics

1

----- Effect=MONTHS -----

Std.		Mean of	Std. Dev. of	Std. Error	Mean of
Dev. of SITES S02	MONTHS	NH3	NH3	of NH3	S02
28.3218	AUGUST	2.04127	4.34696	0.38726	8.7921
34.2805	JULY	3.45159	7.33952	0.65386	13.5429
48.3865	SEPTEMBER	6.28974	8.05000	0.74422	36.7966

SITES	MONTHS	Std. Error of S02	Mean of NO ₂	Std. Dev. of NO ₂	Std. Error of NO ₂
	AUGUST	2.52310	0.76825	0.3141	0.02798
	JULY	3.05395	1.63175	6.2487	0.55668
	SEPTEMBER	4.47333	7.15897	16.5083	1.52619

----- Effect=Overall -----

Std.		Mean of	Std. Dev. of	Std. Error	Mean of
Dev. of SITES S02	MONTHS	NH3	NH3	of NH3	S02
39.4477		3.86992	6.94332	0.36145	19.2938

SITES	MONTHS	Std. Error of S02	Mean of NO ₂	Std. Dev. of NO ₂	Std. Error of NO ₂
		2.05356	3.08943	10.3459	0.53859

----- Effect=SITES -----

Std.		Mean of	Std. Dev. of	Std. Error	Mean of
Dev. of SITES S02	MONTHS	NH3	NH3	of NH3	S02
0.0558	500 M from loop East	1.4854	2.9315	0.45783	0.0195
46.0396	500 M from loop North	4.5878	4.7282	0.73842	29.3073
15.6163	500 M from loop South	0.5000	1.4244	0.22246	2.4463
30.0335	500 M from loop West	3.8854	5.0203	0.78404	9.7780
41.8954	Ammonia nitrate plant	3.3415	3.5328	0.55173	21.9707
44.7922	Ammonia synthesis plant (Loop)	14.5610	13.6438	2.13080	26.9366

Std. Std. Std.

SITES	MONTHS	Error of SO ₂	Mean of NO ₂	Dev. of NO ₂	Error of NO ₂
500 M from loop East		0.00871	0.7171	0.0892	0.01393
500 M from loop North		7.19017	0.7390	0.0997	0.01557
500 M from loop South		2.43885	0.7537	0.1098	0.01714
500 M from loop West		4.69044	0.7512	0.1287	0.02010
Ammonia nitrate plant		6.54296	0.9707	1.4483	0.22619
Ammonia synthesis plant (Loop)		6.99536	12.6780	21.4621	3.35182

Breakdown of Means and Other Descriptive Statistics

2

----- Effect=SITES -----

(continued)

Std.	Mean of	Std.	Std.	Mean of
Dev. of SITES	MONTHS	NH ₃	Dev. of NH ₃	SO ₂
Boiler		3.64634	4.64231	36.6780
Control		0.03171	0.06870	0.0780
Nitric acid plant		2.79024	3.65676	46.4293
Std.	Mean of	Std.	Std.	Mean of
Dev. of SITES	MONTHS	Error of SO ₂	Dev. of NO ₂	Error of NO ₂
Boiler		7.60481	0.76341	0.01806
Control		0.01929	0.70244	0.11106
Nitric acid plant		7.87169	9.72927	2.89415

----- Effect=SITES*MONTHS -----

Std.	Mean of	Std.	Std.	Mean of
Dev. of SITES	MONTHS	NH ₃	Dev. of NH ₃	SO ₂
500 M from loop East	AUGUST	1.64286	2.81772	0.0000
500 M from loop East	JULY	1.86429	3.08036	0.0357
500 M from loop East	SEPTEMBER	0.90769	3.03438	0.0231
500 M from loop North	AUGUST	2.21429	2.69411	0.0000
500 M from loop North	JULY	4.43571	3.93947	21.5429
500 M from loop North	SEPTEMBER	7.30769	5.93555	69.2308
500 M from loop South	AUGUST	0.64286	1.64584	0.0000
500 M from loop South	JULY	0.36429	1.33452	7.1429
500 M from loop South	SEPTEMBER	0.49231	1.36165	0.0231
500 M from loop West	AUGUST	2.00000	3.03822	14.2857
500 M from loop West	JULY	2.30714	3.87863	7.1857
500 M from loop West	SEPTEMBER	7.61538	5.96571	7.7154
Ammonia nitrate plant	AUGUST	1.57143	2.87467	28.6000

SITES	MONTHS	Std. Error of SO ₂	Mean of NO ₂	Std. Dev. of NO ₂	Std. Error of NO ₂
500 M from loop East	AUGUST	0.0000	0.71429	0.06630	0.017719
500 M from loop East	JULY	0.0199	0.72143	0.08018	0.021429
500 M from loop East	SEPTEMBER	0.0166	0.71538	0.12142	0.033677
500 M from loop North	AUGUST	0.0000	0.70000	0.05547	0.014825
500 M from loop North	JULY	11.3641	0.74286	0.11579	0.030945
500 M from loop North	SEPTEMBER	13.3235	0.77692	0.10919	0.030285
500 M from loop South	AUGUST	0.0000	0.75714	0.06462	0.017271
500 M from loop South	JULY	7.1429	0.73571	0.12774	0.034141
500 M from loop South	SEPTEMBER	0.0231	0.76923	0.13156	0.036488
500 M from loop West	AUGUST	9.7052	0.70714	0.13281	0.035494
500 M from loop West	JULY	7.1397	0.79286	0.09972	0.026653
500 M from loop West	SEPTEMBER	7.6904	0.75385	0.14500	0.040216
Ammonia nitrate plant	AUGUST	12.5244	0.74286	0.05136	0.013725

Breakdown of Means and Other Descriptive Statistics

3

----- Effect=SITES*MONTHS -----

(continued)

Std. Dev. of SITES S02	MONTHS	Mean of NH3	Std. Dev. of NH3	Std. Error of NH3	Mean of S02
26.7180	JULY	2.7857	2.9399	0.78571	7.1714
48.0384	SEPTEMBER	5.8462	3.5319	0.97957	30.7692
0.2673	AUGUST	7.3571	9.5241	2.54543	0.1714
36.2896	JULY	15.0714	15.9010	4.24971	14.3429
47.8948	SEPTEMBER	21.7692	11.4539	3.17675	69.3231
26.6860	AUGUST	2.0714	3.4298	0.91666	7.2857
42.5132	JULY	2.0357	5.1750	1.38308	21.5571
37.5534	SEPTEMBER	7.0769	3.3779	0.93686	84.6154
0.0469	AUGUST	0.0143	0.0363	0.00971	0.0286
0.0611	JULY	0.0286	0.0825	0.02206	0.0286
0.1625	SEPTEMBER	0.0538	0.0776	0.02153	0.1846
46.7604	AUGUST	0.8571	2.2138	0.59167	28.7571
51.3361	JULY	2.1714	3.1631	0.84538	42.8786
47.9545	SEPTEMBER	5.5385	3.9289	1.08967	69.2846

SITES	MONTHS	Std. Error of S02	Mean of NO ₂	Std. Dev. of NO ₂	Std. Error of NO ₂
Ammonia nitrate plant	JULY	7.1407	1.4357	2.4663	0.65914
Ammonia nitrate plant	SEPTEMBER	13.3235	0.7154	0.1281	0.03553
Ammonia synthesis plant (Loop)	AUGUST	0.0714	0.6071	0.2018	0.05393
Ammonia synthesis plant (Loop)	JULY	9.6988	4.2286	13.1749	3.52114
Ammonia synthesis plant (Loop)	SEPTEMBER	13.2836	34.7769	23.7694	6.59244
Boiler	AUGUST	7.1321	0.7643	0.1151	0.03075

Boiler	JULY	11.3621	0.7643	0.0929	0.02482
Boiler	SEPTEMBER	10.4154	0.7615	0.1446	0.04009
Control	AUGUST	0.0125	0.6786	0.3142	0.08398
Control	JULY	0.0163	0.1714	0.3474	0.09284
Control	SEPTEMBER	0.0451	1.3000	0.8554	0.23724
Nitric acid plant	AUGUST	12.4972	1.2429	0.6869	0.18359
Nitric acid plant	JULY	13.7201	5.0929	12.9974	3.47371
Nitric acid plant	SEPTEMBER	13.3002	23.8615	25.2140	6.99310

Appendix N Analysed data using SPSS

Item		Months			Mean site
		August	July	September	
NH ₃	Ammonia synthesis plant (Loop)	7.36	2.78	5.84	14.561
	Nitric acid plant	0.86	2.17	5.54	2.79
	Ammonia nitrate plant	1.57	2.78	5.84	3.341
	Boiler	2.07	2.03	7.07	3.646
	500 M from loop South	0.64	0.36	0.49	0.5
	500 M from loop West	2	2.31	7.61	3.885
	500 M from loop North	2.21	4.44	7.3	4.588
	500 M from loop East	1.64	1.86	0.9	1.485
	Control	0.01	0.03	0.05	0.032
	Mean Months	2.04	3.45	6.29	
	Interaction		<.0001		<.0001
	P ≤ 0.05		<.0001		
	SO ₂	Ammonia synthesis plant (Loop)	0.17	14.34	69.32
Nitric acid plant		28.76	42.88	69.28	46.43
Ammonia nitrate plant		28.6	7.17	30.77	21.97
Boiler		7.28	21.56	84.61	36.68
500 M from loop South		0	7.14	0.02	2.45
500 M from loop West		14.28	7.18	7.71	9.78
500 M from loop North		0	21.54	69.23	29.31
500 M from loop East		0	0.04	0.02	0.02
Control		0.03	0.03	0.18	
Mean Months		8.79	13.54	36.80	
Interaction			<.0001		<.0001
P ≤ 0.05			<.0001		
NO ₂		Ammonia synthesis plant (Loop)	0.61	4.23	34.78
	Nitric acid plant	1.24	5.09	23.86	0.97
	Ammonia nitrate plant	1.43	0.71	0.61	0.11
	Boiler	0.76	0.76	0.76	0.75
	500 M from loop South	0.76	0.73	0.77	0.75
	500 M from loop West	0.71	0.79	0.75	0.74
	500 M from loop North	0.7	0.74	0.78	0.72
	500 M from loop East	0.71	0.72	0.71	0.7
	Control	0.67	0.17	1.3	
	Mean Months	0.78	1.63	7.15	
	Interaction		<.0001		<.0001
	P ≤ 0.05		<.0001		