Underground mine workers' respiratory exposure to selected gasses after the blasting process in a platinum mine

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AUTHOR'S CONTRIBUTIONS

This study was planned and executed by a team of researchers. The contributions of each of the researchers are depicted in the table below:

Name	Contribution
Mr C. Steyn	• Drafting of the research protocol; • Planning of the monitoring programme, calibration of sampling equipment and field work (sampling underground); • Literature research, statistical analysis and interpretation of the data; • Discussion of the results, recommendations and writing of the article.
Miss A. Franken	• Supervisor; • Assisted in the introduction, designing, planning and reporting of the study (mini-dissertation); • Approval of the protocol and acquired the funding for this study; • Professional input and recommendations; • Reviewing of the mini-dissertation and interpretation of the results.
Mr M.N. Van Aarde	• Co-Supervisor; • Assisted with the planning and design of the study as well as the approval of the protocol; • Reviewing of chapters 1 and 2 and professional input.
Mr C.J. Van der Merwe	• Co-Supervisor; • Reviewing of the mini-dissertation and assisted with the interpretation of the results.

The following is a statement from the above mentioned supervisors that confirms each individual's role in the study:

I certify that I have approved this article and that my role in the study as indicated above is representative of my actual contribution and that I hereby give my consent that it may be published as part of Cecil-Roux Steyn's MSc (Occupational Hygiene) mini-dissertation.

Miss A. Franken (Supervisor)	Mr M.N. Van Aarde (Co-Supervisor)	Mr C.J. Van der Merwe (Co-Supervisor)

PREFACE

In the mining industry, blasting gasses or the by-products formed from the detonation of ammonium nitrate-fuel oil (ANFO) explosives are generally referred to as blasting or nitrous fumes. For uniformity, the term blasting gasses as indicated in the title will be used throughout this mini-dissertation. This mini-dissertation will be presented in article format and written according to the requirements of the NWU postgraduate manual and Annals of Occupational Hygiene. As per the requirements of the Annals of Occupational Hygiene, references in text should be listed in the form of Jones (1995), or Jones and Brown (1995) or Jones *et al*. (1995). At the end of each Chapter, references are listed in alphabetical order by name of first author, using the Vancouver Style of punctuations and abbreviations. For uniformity this reference style will be used throughout the entire mini-dissertation. The Annals of Occupational Hygiene limits the word count of the article to 5000 words, excluding the abstract, references, tables and figures. The number of words in the article exceeded this number by 841 words due to an in depth discussion on the impact of environmental factors on the sampling media.

ABSTRACT

Ammonium Nitrate-Fuel Oil (ANFO) is the explosive generally used in the mining industry to blast ore from the rock face. The use and detonation of ANFO explosives in an underground mine is an intrinsically hazardous process. The by-products formed during blasting have been well studied over the years and modern mining techniques and methods have evolved to mitigate the inherent blasting and gas emission risks. However, there is insufficient research and quantitative data on mine workers' respiratory exposure to blasting gasses under realistic underground conditions. Aim: The objective of this study was to determine whether blasting gasses such as nitric oxide (NO), nitrogen dioxide (NO_2) and ammonia (NH_3) pose an inhalation health risk to underground mine workers cleaning at the blasting panels approximately three hours after the detonation of ANFO explosives. Scraper Winch Operators' (SWOs) respiratory exposure to selected blasting gasses was simultaneously sampled by means of active and passive sampling methodologies.

Method: Personal exposures to NO, NO_2 and NH_3 were measured and analysed in accordance with NIOSH methods 6014 and 6015. Along with the active air samplers, respiratory exposure to NO_2 and NH_3 were measured by means of radial symmetry diffusive samplers (Aquaria® RING). Measurements were taken over an 8-hour period, where this was not applicable; results were time weighed to an average 8-hour exposure concentration in order to compare the Scraper Winch Operators' (SWOs) respiratory exposure to the Occupational Exposure Limits (OELs) contained in the Regulations of the Mine Health and Safety Act (No. 29 of 1996).

Results: The active air sampling results indicated that the SWOs' respiratory exposure to NO, NO_2 and NH_3 complied with their respective OELs contained in the Regulations of the Mine Health and Safety Act (No. 29 of 1996). However, one of the SWOs had an exposure which exceeded the action level (50% of OEL) at which level the implementation of control measures are recommended to reduce the SWO's exposure. Based on the results of the Wilcoxon matched pairs test, statistical significant differences were observed between the exposure results of the two sampling methodologies for NO_2 ($p = 0.00078$) and NH_3 ($p = 0.044$), with the passive diffusive sampling technique under sampling when compared to the active sampling method. This was also confirmed by a Spearman rank order correlation which indicated a poor relationship between the two sampling methods for NO_2 ($r = -0.323$) and NH_3 ($r = 0.090$). Environmental conditions (i.e. temperature and humidity), as presented in an underground mine, may have been a major factor for the variation between the two sampling methods, mostly affecting the passive samplers.

Conclusion: It was established that engineering and administrative control measures implemented at the underground mine were effective to control SWOs' respiratory exposure to NO, NO_2 and NH_3 below their respective OELs. An acute health risk pertaining the inhalation of blasting gasses was, therefore, not presented to mine workers cleaning at the blasting panels approximately three hours after the detonation of ANFO explosives. However, long-term exposure to blasting gasses at low concentrations may present SWOs with a health risk if such exposures are not adequately controlled or mitigated. The dilution and production of blasting gasses also varied from one blasting level to another. Geological formation, explosive charge-up and loading practices, the amount of water vapour inside the stopes and ventilation parameters are among the factors that may have affected the amount of blasting gasses produced underground. In addition, a drop in the carbon monoxide levels as indicated by the mine's central gas monitoring system would not necessarily mean a lowering in other blasting gas concentrations (i.e. elevated ammonia gas concentrations as identified in the present study). The personal exposure levels between the active and passive sampling measurements also differed considerably. This may be ascribed to the impact underground mining conditions and processes had on the sampling media as well the complexities involved when sampling blasting gasses in general.

Keywords: blasting gasses, ANFO explosives, respiratory exposure, underground, sampling methodologies.

OPSOMMING

Ammoniumnitraat (ontploffings) brandstof, bekend as ANFO in engels, is die algemene plofstof wat in die myn industrie gebruik word om erts los te skiet vir die volgende fase van die myn proses. Die gebruik en ontploffing van sulke plofstowwe in ŉ ondergrondse myn is 'n inherente gevaarlike proses. Die byprodukte en gepaardgaande gevaarlike gasse wat gevorm word tydens die ontploffing is reeds noukeurig bestudeer en moderne myntegnieke en metodes is reeds dienooreenkomstig aangepas en verfyn om risiko's te bestuur. Die gebrek aan relevante kwantitatiewe navorsing op mynwerkers se respiratoriese blootstelling aan plofstofgasse in realistiese ondergrondse omstandighede het die basis gevorm van hierdie studie. Doel: Die doel van die studie was om vas te stel of die gasse soos stikstofoksied (NO), stikstofdioksied (NO_2) en ammoniak (NH_3), wat vrygestel word na afloop van die ontploffing, 'n moontlike respiratories gesondheidsrisiko inhou vir Skraper Hystoestel Operateurs (SHOs) wat verantwoordelik is vir die skoonmaak van die ontploffingspanele, drie ure na die ontploffing. SHOs se respiratoriese blootstelling aan ontploffingsgasse is gelyktydig aktief en passief volgens monsternemingsmetodes getoets.

Metode: Persoonlike blootstelling aan NO, NO_2 en NH_3 is aktief gemeet volgens NIOSH 6014 en 6015 analitiese metodes. Passiewe monsternemers, bekend as radiale simmetriese diffusie apparate (Aquiria® RING) is gebruik om blootstelling aan NO, NO_2 en NH_3 te meet. Die metings is geneem oor 'n 8 uur periode waar moontlik, met 8 uur-tydbeswaarde aanpassings waar dit nie moontlik was nie, om sodoende die mynwerkers se werklike respiratoriese blootstelling te vergelyk met die beroepsblootstellingsdrempels vervat in die Regulasies van die Wet op Myngesondheid en Veiligheid (No. 29 van 1996).

Resultate: Die aktiewe moniterings resultate het getoon dat die mynwerkers se respiratoriese blootstelling aan NO, NO_2 en NH_3 binne die blootstellingsdrempels was soos vervat in die Regulasies van die Wet op Myngesondheid en Veiligheid (No. 29 van 1996). Een van die SHOs se blootstelling het egter die aksievlak (50%) van die beroepsblootstellingsdrempel beduidend oorskry. In hierdie geval word voorgestel dat die implementering van beheermaatreëls oorweeg moet word om die mynwerkers se blootstelling te verminder. Volgens die Wilcoxon gepaste pare, was daar ook betekenisvolle statistiese verskille tussen die twee moniteringsmetodes vir die toets van NO_2 ($p = 0.00078$) en NH_3 ($p = 0.044$). Die aktiewe moniteringsmetode toon ŉ beduidende hoër blootstellingsresultaat in vergelyking met die passiewe navorsingsmetode. Die Spearman rangorde korrelasie toets het ook getoon dat daar ŉ swak korrelasie was tussen die twee blootstellingsmetodes vir NO_2 ($r = -0.323$) en NH_3 ($r = 0.090$). Omgewingsfaktore (bv. temperatuur en humiditeit), soos teenvoordig in ŉ ondergrondse myn, mag wel die beduidende verskil tussen die twee monsternemingsmetodes verklaar het met die faktore wat meestal die passiewe monsters beïnvloed het.

Gevolgtrekking: Daar is bevestig dat die ingenieurs- en administratiewe beheermaatreëls huidiglik geïmplementeer by die ondergrondse myn wel effektief was om die SHOs se respiratoriese blootstelling aan NO, NO_2 en NH_3 te beheer (verlaag) tot onder die aanvaarbare beroepsblootstellingsdrempels. Geen akute gesondheidsrisiko is dus teenwoordig tydens ondergrondse mynwerkers se blootstelling aan plofstofgasse in die drie ure na die ontploffings nie. Die moontlikheid bestaan dat langtermyn blootstelling aan plofstof gasse by lae konsentrasies wel 'n gesondheidsrisiko vir SHOs inhou, indien sodanige blootstelling nie beheer word nie. Daar was ook vasgestel dat die verdunning en produksie van plofstofgasse beduidend kan verskil ten opsigte van die diepte (vlakke) van die onderskeie ontploffings areas. Moontlike verklarings vir die verskille is die verskillende geologiese grondformasies, veranderende ontploffingsmetodes en prosesse, die hoeveelheid waterdamp teenwoordig ondergrond en die effektiwiteit van die ondergrondse ventilasie. Terselfdertyd sal 'n verlaging van koolstofmonoksied (CO), soos normaalweg waargeneem sou word deur die myn se sentrale gas moniteringstelsel, nie noodwendige die verlaging in ander ontploffingsgasse weerspieël nie (bv. verhoogde ammoniak gas konsentrasies soos geïdentifiseer in die huidige studie). Persoonlike blootstellingsvlakke tussen die aktiewe en passiewe moniteringsmetodes het ook merkbare verskille getoon. Bogenoemde variasies en verskille kan verklaar word aan die impak van wisselende omgewings kondisies op die monsternemers asook die inherente kompleksiteit betrokke by die monsterneming van plofstofgasse in 'n ondergrondse myn.

Sleutewoorde: Plofstofgasse, Ammoniumnitraat ontploffings brandstof (ANFO), respiratoriese blootstelling, ondergronds, meetmetodes.

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LIST OF ABBREVIATIONS

AEISG	Australian Explosives Industry Safety Group
ANFO	Ammonium Nitrate – Fuel Oil
CCOHS	Canadian Centre for Occupational Health and Safety
CO	Carbon Monoxide
CO_2	Carbon Dioxide
e.g.	As an example
FEV_1	Forced expiratory volume in one second
H_2O	Water
i.e.	That is
kg/m^3	Kilogram per cubic metre
MHSA	Mine Health and Safety Act
mg/m^3	Milligram per cubic metre
MSDS	Material Safety Data Sheet
N_2	Nitrogen
N_2O_3	Dinitrogen Trioxide
N_2O_4	Dinitrogen Tetraoxide
NH_3	Ammonia
NH_4NO_3	Ammonium Nitrate
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_x	Oxides of nitrogen
NOHb	Nitrosyl-Haemoglobin

NIOSH	National Institute for Occupational Safety and Health, USA
OELs	Occupational Exposure Limits
OEL – TWA	Occupational Exposure Limit – Time Weighted Average
OHS Act	Occupational Health and Safety Act
OSHA	Occupational Safety and Health Administration, USA
PGM	Platinum Group Metals
RADS	Reactive Airways Dysfunction Syndrome
SANAS	South African National Accreditation System
STEL	Short Term Exposure Limit
SWOs	Scraper Winch Operators
TLV	Threshold Limit Value
TWA	Time Weighted Average
WHO	World Health Organization
µm	Micrometre

CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

Harmful gasses produced by the detonation of explosives in an underground mining setup are among the most common and severe hazards presented to underground mine workers (De Souza and Katsabanis, 1991; Mainiero *et al*., 2007). Blasting operations in most mines result in up to several thousand tons of broken rock. During this process, large quantities of harmful gasses are released into the working environment (De Souza and Katsabanis, 1991, AEISG, 2011). During the aforesaid, mine workers who are required to remove this broken ore from underground mining excavations (stopes) may be exposed to these hazardous gasses, if such gasses areas are not adequately controlled (De Souza and Katsabanis, 1991; Bakke *et al*., 2001). Furthermore, the release of post blasting gasses may not only impact on the stope area where blasting takes place but also on the general underground area (De Souza and Katsabanis, 1991). According to Attalla *et al*. (2008), the blasting gasses generated from the detonation of blasting agents such as dynamite and Ammonium Nitrate-Fuel Oil (ANFO), generally consist of carbon monoxide (CO), the oxides of nitrogen (NO_x), carbon dioxide (CO_2) and ammonia (NH_3). Poisoning by nitrous oxides and carbon monoxide gasses is not uncommon in mines, where cases of gas poisoning have been noticed as far back as the early 1900's, where miners developed respiratory problems and fatalities were high (Irvine, 1916). Information on "gassing" and the inhalation of gasses remain limited, as no comprehensive occupational exposure data are available for blasting gasses in an underground mine in particular.

The explosive DDS™ Sensitised Emulsion also known as Gassed Ammonium Nitrate Emulsion is commonly used in the underground mining sector, such as the platinum industry (Sasol, 2012). Under conditions where ventilation and other health and safety measurements are difficult to implement, as in mines, these detonation products can present severe health hazards for the mine workers (Attalla *et al*., 2008).

Mine workers are frequently exposed to agents such as diesel exhaust, blasting fumes, oil mist and other gaseous compounds, with Bakke *et al*. (2001) concluding that this exposure may place the workers at increased risk of obstructive pulmonary disorders. Exposure concepts such as the composition of the gas, the gas concentration and duration of exposure all contribute to the total exposure of the miners to blasting gasses (Kampa and Castanas, 2008). Miners are also more prone to be exposed to a mixture of airborne pollutants than to a single substance, and as a result the effects of these mixtures on their health might be diverse (Bakke *et al*., 2001; Bakke *et al*., 2004). Effects can range from nausea, skin irritation and difficulty in breathing, to the development of cancer. Blasting gasses can also impair the functioning of the cardiovascular and respiratory system as well as other bodily functions (Kampa and Castanas, 2008).

Due to the health implications associated with exposure to blasting gasses, several engineering and administrative control measures, such as mechanical ventilation systems and re-entry periods, have been implemented over the years by the mining industry to control and to reduce mine workers' exposures (De Souza and Katsabanis, 1991; AEISG, 2011). Due to the lack of quantitative research data on mine workers exposures to blasting gasses, this study was required to determine the effectiveness of these control measures as well as to establish mine workers' respiratory exposure to NO (nitric oxide), NO_2 (nitrogen dioxide) and NH_3 several hours after the blasting process. Each of these selected blasting gasses will be required to be sampled by individually approved methods due to the absence of a means to test blasting gasses simultaneously.

The study will aim to address the following objectives:

1.2 Research Objective

The research objective can be divided into a general objective and specific objectives.

1.2.1 General Objective

The general objective is to determine the Time Weighted Average (TWA) respiratory exposure of underground mine workers to NO, NO_2 and NH_3 over an 8-hour period, in order to compare the results to the legislative occupational exposure limits.

1.2.2 Specific Objectives

- To determine the occupational exposure of underground nightshift workers several hours after the blasting process to NO, NO_2 and NH_3 formed as by-products during blasting.
- To compare the passive sampling measurements and the active sampling measurements for NO_2 and NH_3 by means of approved measurement methodologies.

1.3 Research Questions

Are mine workers cleaning at the blasting area approximately three hours after the blasting process exposed to NO, NO_2 and NH_3 at concentrations exceeding their respective OELs?

Will there be an association between the results of the simultaneous active and passive sampling measurements?

1.4 References

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CHAPTER 2: LITERATURE OVERVIEW

A literature study was conducted to investigate the occupational environment (i.e. mining industry, mining conditions, control measures, etc), circumstances, exposure to blasting gasses and the daily work activities present at an underground platinum mine.

Underground miners, specifically miners working at the blasting area, are exposed to different types of gasses and fumes liberated during the blasting process. Exposure to these blasting gasses can be highly dangerous and may produce different kinds of physiological disorders. Therefore, the blasting process, by-products produced during blasting and the physiological effects of these gasses on the respiratory system will be discussed.

Exposure to blasting gasses such as nitric oxide (NO), nitrogen dioxide (NO_2) and ammonia (NH_3) will be reviewed, as well as their effects on the respiratory system and other physiological effects mine workers might experience as a result of gas inhalation.

2.1 The mining sector: South Africa

The mining industry plays an important role in the world and in South Africa’s economy, creating thousands of job opportunities and contributing significantly to South Africa’s gross domestic product (GDP) and social development (Smit and Pistorius, 1998). Platinum’s unique chemical properties and wide variety of uses makes it a sought after component as an auto catalyst in motorcar exhaust systems, reducing the emission of harmful gasses into the atmosphere. Its resistance to corrosion and high melting point makes it an essential ingredient in numerous industrial processes and as a result the demand for platinum around the world has increased substantially (Jones, 2005).

South Africa is the world’s largest producer of the platinum group metals (PGM), owning more than three quarters of the world’s platinum reserves. Platinum ore in South Africa is commonly found in reefs, with the primary PGM-rich deposits located in the unique geological formation known as the Bushveld Complex (Jones, 2005). PGM’s are concentrated in three known layers in the Bushveld Complex, and they are known as the Merensky Reef, the Platreef and the UG2 chromitite layer. Each of the reefs have their own distinctive mineralogy which has been well described. South Africa’s PGM reserves are derived mainly from the Bushveld Complex, with a mere 0.1% coming from the gold deposit of the Witwatersrand and Free State, and the copper deposit in Phalaborwa (Vermaak, 1995; Van der Merwe *et al*., 1998; Jones, 2005). These PGM-rich deposits in the Bushveld Complex are known to be the largest layered igneous complex of its type in the world (Jones, 2005).

2.2 Mining process and conditions

Rutter (2009) defined mining as the removal (extraction) of minerals from the earth. Any substance that cannot be grown by agriculture or made by chemists must be mined, usually from areas deep within the earth's crust called ore bodies, veins, beds or seams (Rutter, 2009).

The mining industry can mainly be classified into two types of mining processes, namely opencast mining and narrow-stope mining. Opencast mines are surface mines, usually coal, quarries and base metal mines. For the purpose of this study narrow-stope, conventional mining is the main focus, which constitutes more than 75% of South Africa's blasting and detonator market (Smit and Pistorius, 1998).

One of the difficulties in an underground mine, is the extraction of platinum-rich ore. Due to the lack of space available for mine workers to perform their work, a large enough area must be blasted, which in return creates its own problems (Smit and Pistorius, 1998; Rutter, 2009).

The blasting area, or as referred to as stopes (underground excavations) is a channel in the order of one metre high which enables mine workers to slide or duck-walk through (Smit and Pistorius, 1998). Stoping operations are largely confined to narrow, tubular spaces making mechanisation extremely difficult. Miners are limited in terms of flexibility and stope width and so drilling occurs by means of handheld, pneumatic rock drills at the blasting panel inside the stope. Cleaning operations of fly rock (broken ore) are done by means of conventional methods, utilising scrapers and scraper winches. Conventional mining operations are not just costly in terms of labour intensity and mining processes but they also create a hazardous working environment to work in. Some of these risks involve the fall of ground, fires, blasting gasses and extreme heat exposures (Smit and Pistorius, 1998; Rutter, 2009).

The stope areas in a mine can be some of the harshest working conditions, with temperatures exceeding 35.8 °C and humidity levels reaching 100% (Smit and Pistorius, 1998). These conditions do not only impact on the health and well being of the mine workers, but they can also affect the reliability of various sampling media used underground to evaluate mine workers' exposures, which will be discussed in Chapter 3.

2.3 Explosives and blasting operations

Blasting operations occur on a daily basis. Before such blasting can take place, the number of stope blast holes required to be drilled into the rock face is calculated to achieve the desired blast distance. Once the number of stope blast holes has been determined, they are marked onto the rock face. The Drill Operators then enter the stope and drill the marked out areas with a depth of approximately one point six (1.6) metres by means of a pneumatic drill. After completion, the holes are then dewatered by means of compressed air hoses. The holes are dewatered due to the fact that water contaminated stope blast holes and ANFO explosives are known to increase the production of blasting gasses such as NO and NO_2

significantly (Rowland III and Mainiero, 2000). These dewatered holes are then filled with explosives (ammonium nitrate-fuel oil (ANFO) mixtures) and then interconnected with a series of detonators (AEISG, 2011).

ANFO is the explosive generally used in most open-cut and underground blasting activities, mostly because of its low cost. ANFO is a mixture between ammonium nitrate (94.6%) and fuel oil (5.4%). Aluminium powder is sometimes added to increase the power of the explosion (Rowland III and Mainiero, 2000). ANFO can either be in granule or cartridge form. Granules are mostly used when no moisture (H_2O) is present in the boreholes, while cartridges (emulsion explosives) are used when water is present in the boreholes (Martel *et al.*, 2004). In this study, DDS™ Sensitised Emulsion was used as blasting agent. It consists of ammonium nitrate (70-80%), gas oils "hydro treated" (2.50-5%), fuels/diesel gasoil (0.50-4%) and sodium nitrite (0.01-0.10%) (Sasol, 2012). After the charge up is completed, mine workers are removed from the mine, and may not re-enter the mine for a period of at least three hours after blasting, also known as the general re-entry period (Guild *et al.*, 2001). The explosives are then detonated by means of centralised blasting from the surface. The entire mine shaft must be evacuated and only then are the explosives set off one by one. After the detonation process, fly rock shears away from the stope face and is thrown into a gully where it is winched, transported and hoisted back up to the surface. By means of this rock removal process, the rock face can be advanced from as much as one metre per day, also known as the rate of face advance (Smit and Pistorius, 1998).

It is important to note that the quantity of toxic gasses produced by blasting operations can be affected by external factors such as the formulation of explosives, confinement, method of priming, length of charge and the oxygen content present in the underground atmosphere. The contamination of explosives with water or drill cutting is also known to affect blasting gas production (Martel *et al.*, 2004; Mainiero *et al.*, 2007).

Any of the above factors can affect the full decomposition of ammonium nitrate to its thermodynamic favoured end product, namely nitrogen, which could result in the formation of NO_x and CO (AEISG, 2011). Previous studies and theories have shown that by changing the fuel oil content of the ANFO composition may have a significant impact on NO_x, CO and NH_3 production. Detonating explosives when the fuel oil content is high will increase CO and NH_3 formation, while NO_2 levels will increase significantly when the fuel oil content is lower. The ANFO ratio between ammonium nitrate and fuel oil is regarded as optimum at 94%:6% to minimise toxic gas production (Rowland III and Mainiero, 2000).

As previously discussed, the presence of water inside the stope bore holes and ANFO explosives may result in excess nitrogen oxides production after detonation. According to Rowland III and Mainiero (2000), this effect on ammonia formation was inconclusive and that further research is required.

According to research, the oxygen content present during the time of detonation, can significantly increase or decrease blasting gas formation. Rowland III and Mainiero (2000) tested this theory inside a controlled test chamber. By increasing the oxygen content inside the chamber, they noticed a decrease in the CO and NH_3 concentrations. This decrease in the CO formation may be ascribed to the conversion of CO to CO_2 in the presence of oxygen. The production of nitrogen oxides increased in a rich oxygen environment (Rowland III and Mainiero, 2000). Ammonia production is known to increase as aluminium is added to ANFO to increase the velocity and energy output of the explosive (Mainiero *et al*., 2007).

2.4 Cleaning operations after blasting

Approximately three hours after blasting has occurred and once the Ventilation Officer on duty has given the all clear, the shaft is re-opened. During this re-entry period, the carbon monoxide concentrations are monitored at various levels underground by means of an electronic gas detection system from within the Control Room. Once the concentration levels drop below a safe level underground (approximately two hours and 30 minutes after blasting) the mine is re-opened. The mine workers (usually the cleanup crews) working the night shift (8pm – 6am) are then sent down to the different underground levels where blasting took place. The miners then enter the mine and make their way to the different sections and levels underground to their safe zones where they are then briefed by their Lead Hand (Supervisor). This process takes another two hours before the mine workers enter the blasting panels, which adds additional air changes to clear blasting gasses from the stopes. According to Guild *et al*. (2001), a re-entry period of roughly three hours will be sufficient for the dilution and removal of airborne contaminants at the blasting panels by means of the mine's mechanical ventilation system.

The purpose of this study was to evaluate the respiratory exposure of the highest potential exposed group to blasting gasses and, therefore, the Scraper Winch Operators (SWOs) who are the first occupational group to enter the stopes after blasting were selected to participate in this study. The cleanup crews consist of two teams of four SWOs each who are sent down to the stopes or blasting panels to perform the cleanup process. Two miners work at the panel, one at the gully and one at the centre gully (See Figure 1). The crews are supervised by a Lead Hand, whose first priority it is to secure the blasting area by implementing safety procedures such as the suppression of dust liberated during blasting, the removal of rock debris, determining the air quality and inserting temporary support platforms. The Lead Hand's responsibilities form part of an underground risk assessment to ensure the safety of his crew.

Conventional cleanup methods are used at the mine where the study took place. The cleaning crews or Scraper Winch Operators remove the debris by the rigging of scraper winches. Once the rigging has been completed the crew take safe distance. The winch used at the face is then operated from a winch operating station approximately 15 metres away (gully). The scraper is then pulled several times over the blasting debris, pulling the debris into the gully and from there into the ore chute or grizzly that is positioned above the locomotive. The debris containing the precious metals is then loaded into the hoppers of the locomotive and transported to the tipping area. Finally, the debris is tipped and the rock matter transported to the surface by means of conveyor belts and cages.

The panel and gully workers also perform lashing, removing the remainder of the debris by means of shovels. When transferring pieces of rock by means of lashing, winching or the transfer of rock form one conveyor belt to another or when it is dropped into the hoppers, trapped dust particles and toxic gasses are released into the mining environment (Unsted, 2001). Such tasks or activities may result in the respiratory exposure of mine workers. The following Figure is an illustration of the blasting area where the cleanup process took place and sampling was done. The illustration was drafted according to the manner in which the researcher perceived the workings inside the stope as well as field notes.

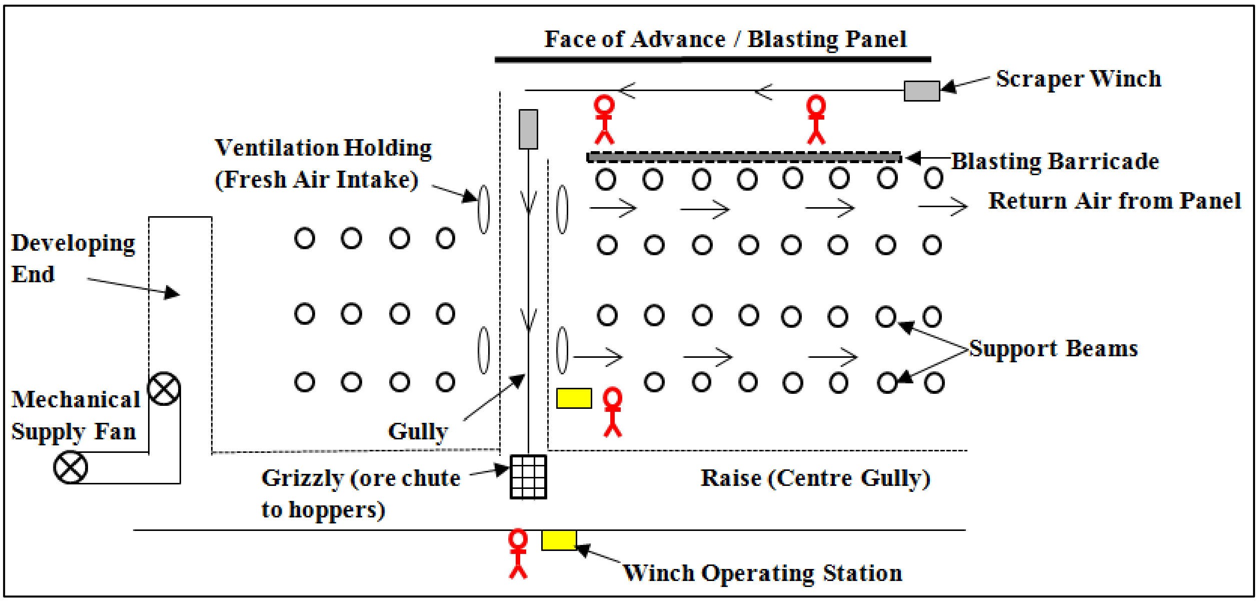

Figure 2.1: An illustration of a typical developing area where the clean-up crews work. The air flow from left to right (ventilation), winch operating stations, blasting panel and scraper winches are also indicated.

2.5 By-products formed from blasting

The potential hazards of gasses generated from blasting operations in underground mines have long been recognised. These hazards are produced when agents such as dynamite and ammonium nitrate-fuel oil (ANFO) mixtures are detonated. The condensed materials in the explosives are then transformed into gasses (Attalla *et al*., 2008). Under ideal conditions, the gaseous products expected to be found after the detonation of ammonium nitrate-based explosives will produce carbon dioxide (CO_2), water vapour (H_2O) and nitrogen (N_2). The detonation of ANFO explosives under ideal conditions may yield the following chemical reaction (Attalla *et al*., 2008; AEISG, 2011):

$$\mathbf{3NH_4NO_3 + CH_2 \rightarrow 3N_2 + CO_2 + 7H_2O}$$

Mine conditions are, however, seldom perfect and explosions following stoichiometric guidelines are rare. This may be due to changes in the material or in the atmosphere such as the contamination of the explosives or stope blast holes, presence of mineral matter, rock composition, oxygen balance in the atmosphere and other factors. This can lead to the formation of toxic gasses such as CO and NO, as indicated in the equations below (Attalla *et al*., 2008):

$$\mathbf{2NH_4NO_3 + CH_2 \rightarrow 2N_2 + CO + 5H_2O}$$
$$\mathbf{5NH_4NO_3 + CH_2 \rightarrow 4N_2 + 2NO + CO_2 + 7H_2O}$$

Additionally, some of the NO formed, may rapidly oxidise with oxygen to form an orange/red plume of NO_2 (Attalla *et al*., 2008; AEISG, 2011). According to Sasol's material safety data sheet (MSDS) on *DDS™ Sensitised Emulsion,* the gasses produced during combustion under ideal conditions are carbon oxides and nitrogen oxides (Sasol, 2012). The gasses emitted from ANFO explosives are lighter than atmospheric or underground air (1.19-1.20 kg/m³ at 20 °C and 1 atm) and the gasses produced will most likely tend to migrate vertically.

2.6 Underground ventilation

The stopes and developing areas in an underground platinum mine are confined and limited, and if airborne pollutants produced by mining operations are not adequately controlled or extracted to harmless levels, these contaminants may pose a health risk to mine workers. One of the main control measures to prevent or mitigate this build-up of blasting gasses, exhaust fumes and other pollutants from occurring is by means of mechanical ventilation. Once blasting has taken place underground, fresh outside air is drawn from the ventilation shafts and distributed or ducted towards the developing ends and stoping sections where blasting took place (Brady and Brown, 2004; Du Toit, 2007).

Ventilation piping in conjunction with auxiliary fans is used to convey air to and from the stope and blasting face. To prevent the short-circuiting of air through the blasting panels, brattices and ventilation curtains are erected in the travelling gullies and used ventilation holdings to direct the air to the working areas (Du Toit, 2007) (See Figure 2.2 below). These ventilation holdings or ventilation raises are excavated sections along the gullies of the stope to provide through ventilation for the workplace, and can also be modified for use as emergency escape routes (Brady and Brown, 2004). The air then travels through the gullies and ventilated holdings and through the blasting panels to facilitate the removal and dilution of blasting gasses. The return air from the stopes is then exhausted out of the workings. The mine is then re-opened once several air changes have occurred to lower airborne gas concentrations to an acceptable level (Du Toit, 2007).

One of the challenges in an underground mine is to direct the fresh air to the working areas inside the stope and secondly, to maintain the supply of fresh outside air to these rock removal areas (blasting panel) without it going to waste or escaping to the mined out areas (old madala sites) (Du Toit, 2007).

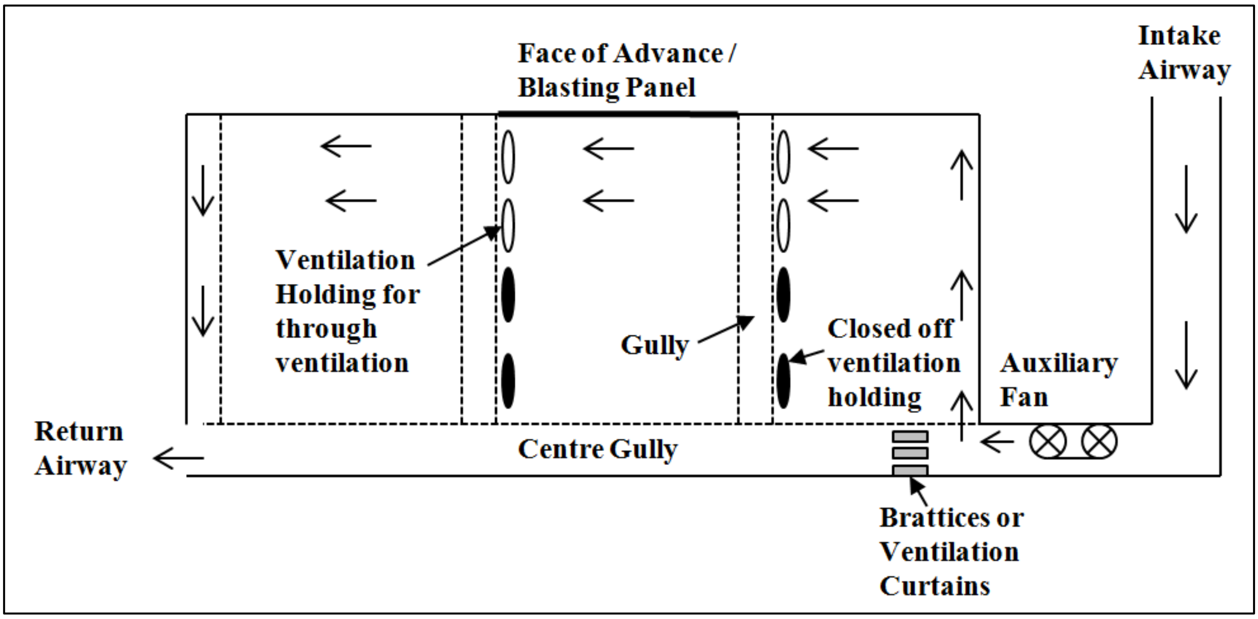

Figure 2.2: A typical ventilation working inside an underground stope used for the dilution and removal of blasting gasses (Du Toit, 2007).

2.7 Routes of exposure

In the mining occupation, the two principal modes of exposure are inhalation and dermal, while ingestion represents a minor route. Toxic substances mainly enter the body through the respiratory tract, skin or gastrointestinal tract. Inhalation exposure to gasses, vapours and aerosols are ever-present in environmental and occupational settings (Schaper and Bisesi, 2003; Kampa and Castanas, 2008).

2.8 Airborne pollutants present underground

Mine workers are exposed to various airborne contaminants while working underground. The inhalation of such pollutants including amongst others airborne dust, blasting gasses and exhaust fumes may pose a health risk to the mine workers if not adequately controlled.

2.8.1 Types of airborne pollutants

Airborne pollutants can mainly be classified into five groups, based on their physical properties and composition.

2.8.1.1 Dust

Dusts are usually generated during the handling, crushing, rapid impact and decrepitating of organic and inorganic substances such as rock, metal and coal. The particles are small and do not always move in the expected manner or direction i.e. downwards (Unsted, 2001).

2.8.1.2 Fumes

Fumes can be defined as the solid particles generated by the condensation from the gaseous state. This usually happens after the volatilisation of molten metals. In the processing of metals, they are usually coupled with oxidation, meaning that the metallic fumes present in the air, are partly in the form of an oxide. Fumes generally flocculate or coalesce (Unsted, 2001).

2.8.1.3 Mists

When mists are formed, they consist of small liquid droplets generated by the condensation of gasses or by the breaking-up of liquids, for example, splashing, foaming or atomising. Mists are usually suspended into air, for instances during spraying operations (Unsted, 2001).

2.8.1.4 Gasses

A substance can be considered a gas if at standard conditions of temperature and pressure (25^{o}C, 1 atm) its normal physical state is gaseous. Gasses are known to be completely airborne at room temperature (McDermott, 2004). The physical properties of a gas can be defined as a formless, diffusing fluid, which can completely fill a container in which it is released or kept. These gasses can transform to a liquid state only by combining the effects of pressure and temperature (Unsted, 2001). Examples are helium, oxygen, carbon monoxide, ammonia and nitrogen oxides.

2.8.1.5 Vapours

Vapours have the ability to completely diffuse in air or any other gas. Vapours are gaseous forms of substances that can be transformed to a liquid by either decreasing the temperature or increasing pressure (Unsted, 2001). Table 2.1 indicates the typical sizes of the different airborne contaminants.

Table 2.1: Types and sizes of airborne contaminants (Unsted, 2001)

Airborne material	Size range (µm*)
Dust (Airborne)	0.1 – 30.0
Mists	0.01 – 10.0
Fumes	0.001 – 1.0
Vapours	0.005
Gasses	0.0005

*micrometre

2.9 Specific entities

Most mine workers at a mine are potentially at risk to the exposure of blasting gasses, airborne respirable dust and other toxic exposures. This includes both the surface and underground hard rock workers. For the purpose of this study, the focus will be on the Scraper Winch Operators who are the first occupational group to enter the underground mine after the detonation of explosives when the blasting gas concentrations are expected to be the highest (Unsted, 2001).

2.9.1 Blasting gasses

Several oxides of nitrogen are usually found together in the same working environment and collectively they are known in mining circles as nitrous fumes (Unsted, 2001). Nitrogen oxides are commonly a combination and mixture of NO, NO_2, N_2O_4 with some possible N_2O_3. According to Attalla *et al*. (2008), the blasting gasses created from the detonation of ANFO explosives, mostly consist of the oxides of nitrogen (NO_x), carbon monoxide (CO) and carbon dioxide (CO_2) as previously discussed. The burning of such explosives produces significantly greater quantities of these gasses. These gasses are also present in the exhausts of diesel-powered engines and are also produced in small quantities of both oxy-acetylene gas cutting and arc welding (Unsted, 2001).

Table 2.2: Gas quantities produced by ANFO explosives (Unsted, 2001)

Gas	Volume (m^3)
Carbon monoxide	1.2 – 4.0
Carbon dioxide	10 – 27
Nitrogen oxides	0.6 – 4.4
Ammonia	0.03 – 0.3

A summary of the blasting agents encountered in mines, together with the sources are given in Table 2.3.

Table 2.3: Relevant properties and sources of gasses emitted from blasting operations (Unsted, 2001; Attalla *et al*., 2008)

Name	Chemical symbol	Sources
Carbon dioxide	CO_2	Breathing, oxidation, blasting, diesel exhaust, fires.
Carbon monoxide	CO	Blasting, diesel exhaust, fires.
Nitrogen oxides	NO, NO_2, etc.	Blasting, diesel exhaust, welding and burning of explosives.
Ammonia	NH_3	Cooling plants, ammonia-nitrate explosives (blasting).

For the purposes of this study, the selected gasses (NO, NO_2 and NH_3) identified as potential health risks for mine workers cleaning at the blasting panel and gullies, will now be discussed according to their physical and chemical properties.

2.10 Properties of specific blasting gasses

2.10.1 Nitrogen oxides (NO and NO_2)

NO and NO_2 are often found as the by-products formed from the detonation of ANFO explosives. NO is invisible, while NO_2 is generally responsible for the orange post-blast cloud as a result of the after burning process (Mainiero *et al*., 2007; AEISG, 2011). These post-detonation gasses have been associated with wet conditions and have not been viewed with alarm due to the rapid dispersion of these gasses into the atmosphere. The orange-reddish coloration is produced as a result of the secondary oxidation of NO to NO_2 as the cloud mixes with air (Kampa and Castanas, 2008).

2.10.1.1 Nitric oxide (NO)

NO is generally produced commercially by passing air through an electric arc or by the oxidation of ammonia over platinum gauze (Wagner and Millerick-May, 2008). Nitric oxide is a colourless gas with a faint smell and regarded as toxic (LD_{50} of 165 mg/m^3 / 4 hours). It is relatively soluble in water and is slightly heavier than air. In concentrated form, it combines with oxygen to form nitrogen dioxide as previously explained. This reaction is very slow when concentrations of NO and oxygen (O_2) are low, as in the case of an underground environment (Unsted, 2001).

2.10.1.2 Nitrogen dioxide (NO_2)

After the blasting process has taken place, a reddish-brown gas is released into the air. This is known as nitrogen dioxide (Unsted, 2001). Nitrogen dioxide is produced as a result of combustion (vehicle exhaust, burning oil, coal and explosives) or as result of the oxidation of nitric oxide (Wagner and

Millerick-May, 2008). This gas is toxic, LD_{50} of 1068 mg/m^3 / 4 hours, and has a distinct, pungent smell (Unsted, 2001).

2.10.2 Ammonia (NH_3)

Ammonia is a light, colourless gas and soluble in water with a distinct pungent smell. Ammonia is generally smelt after the detonation of ANFO explosives and is only considered dangerous in large concentrations for example from the leakage of cooling plants. Ammonia is very corrosive with irritant properties known to cause intense eye (caustic agent), nose and throat irritation above 35 mg/m^3 (Unsted, 2001). The Canadian Centre for Occupational Health and Safety (1998) has classed ammonia gas as a severe respiratory tract irritant and may cause pulmonary oedema for brief exposures above 1080 mg/m^3.

The above mentioned blasting gasses are generally produced and released into the atmosphere by mining operations such as blasting, scraping, barring, lashing and loading (Unsted, 2001, Attalla *et al*., 2008). For the purpose of this study, the focus will be at the lashing and scraping areas of the stope where cleaning tasks are generally conducted after the blasting process.

2.11 The respiratory system and toxicology

2.11.1 Respiratory system and its defence against blasting gasses

The respiratory system is the major route for the absorption and deposition of blasting gasses. This system is comprised of three regions; they are the nasal passages, the conducting airways and the gas exchange region, each performing its own important function during respiration as well as its defence against harmful substances. The first line of defence are the physical and mechanical barriers which include the nasal hairs, the mucus layer and impaction of particles at bends and bifurcations of airways (Wagner and Millerick-May, 2008). The nasal region acts as a scrubber site for water soluble gasses such as ammonia as well as the removal of inhaled particles greater than 5 µm (Klonne, 2003; Dwyer, 2008). This is achieved by the mucosa in the nasal area which is covered by a sticky semi-gel film of liquid that traps the air contaminants (Marieb and Hoehn, 2007).

The inhaled air is then directed from the atmosphere through the nasal passages and into the conducting airways. While this occurs, the air passes through the smell organs (olfactory epithelium) (Dwyer, 2008). The olfactory epithelium provides an early warning system with the ability to detect odours (Dwyer, 2008). As toxicants pass through these areas they stimulate these receptors which then promotes an acute, physiological constriction reflex of the pulmonary airways also known as the pulmonary irritant reflex. This response restricts the airflow into the deep lung and is usually followed by a cough reflex when lung irritants such as ammonia, ozone and nitrogen oxides are present in the trachea or bronchi (Marieb and Hoehn, 2007; Wagner and Millerick-May, 2008). The nasal tissues can also metabolise foreign substances by cytochrome P450 dependent mono-oxygenases, other oxidative (Phase 1) enzymes, conjugative (Phase II) enzymes, proteases and peptidases (Guyton and Hall, 2006).

The air then travels through the conductive airways which are comprised of the pharynx, larynx and trachea towards the gas exchange regions of the lung. The trachea bifurcates (splits) into the two bronchi, which directs the inhaled air into the lungs. The bronchi then branches out into bronchioles which terminate in acini. Each acinus is comprised of a terminal bronchiole, alveolar ducts and alveolar sacs. The alveolus (alveolar sacs) is the important site where gas exchange occurs (Guyton and Hall, 2006). The wall of each alveolus is very thin, facilitating gas exchange between capillaries of the pulmonary blood flow and the air spaces within the lungs (Dwyer, 2008).

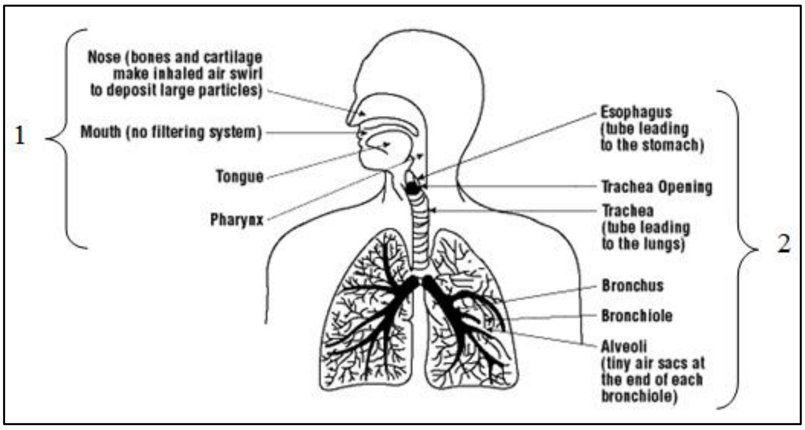

Figure 2.3: The upper(1) and lower(2) airway passages of the respiratory system (Guyton and Hall, 2006; CCOHS, 2012).

The gasses are then absorbed by simple diffusion driving the oxygen or insoluble gasses such as nitrogen dioxide from the alveoli into the pulmonary blood for the transport and distribution throughout the body. Simple diffusion also drives carbon dioxide from the pulmonary blood supply into the alveoli to be exhaled (Klonne, 2003; Guyton and Hall, 2006).

2.11.2 Occupational respiratory toxicants

Mine workers conducting cleaning operations inside the stopes may be exposed to blasting gasses and irritants. Pulmonary irritants are known to cause respiratory disorders with Bakke *et al*. (2001), concluding that tunnel workers exposed to ANFO explosives, dust and blasting gasses are at increased risk of obstructive pulmonary diseases and upper and lower airway inflammation. These irritants can be classified into primary and secondary irritants. Primary irritants exert their effect in the respiratory tract via direct contact, while secondary irritants give rise to systemic effects (Wagner and Millerick-May, 2008). Ammonia is a primary irritant, and overexposure could lead to throat irritation due to the chemical reaction taking place at the epithelium. Irritants can be classified either as engendering sensory irritation or pulmonary irritation (Wagner and Millerick-May, 2008). For the purpose of this study the focus will be on the pulmonary irritants and the effects they exert on the respiratory system. When a miner is exposed to pulmonary irritants, the receptors in the pulmonary conducting airways and alveoli are stimulated. This can induce several respiratory responses such as inflammation, oedema and mucus hypersecretion. As a group, irritants are extremely broad and are commonly found in the mining occupation, they include ammonia, volatile organic compounds, oxides of nitrogen and sulphur (Wagner and Millerick-May, 2008).

2.12 The toxicology of gasses

Miners are most likely to be exposed to toxicants through inhalation, while ingestion and dermal contact represent minor routes (Kampa and Castanas, 2008). These toxicants are then absorbed via the gastrointestinal and respiratory tract and transferred to all regions of the body (organs, tissues and cells) to exert their respective actions (Witschi and Last, 2003).

2.12.1 The absorption and distribution of toxicants

According to Witschi and Last (2003), the deposition site of a toxicant in the respiratory tract defines its pattern of toxicity. The amount of the gas molecules absorbed through the lungs depends on air contamination, the water solubility of the compound, the size of the particles and the respiratory rate of the worker (Shelnutt, 2008). Gas molecules (especially water soluble ones such as ammonia) may react with the nasal mucosa and not reach the airways as previously discussed. The critical factor that determines how deep gas molecules penetrate into the lung structure is water solubility (Witschi and Last, 2003).

Ammonia gas is highly soluble and is regarded as a primary irritant causing severe upper and lower respiratory tract irritation (CCOHS, 1998). Relative insoluble gasses such as NO_2 and ozone can penetrate deep into the lungs to reach smaller airways and the alveoli, where they can cause a toxic response (Witschi and Last, 2003). Upon exposure, NO is generally taken up in the body and is rapidly absorbed in the blood which then competes with the oxygen molecules for the binding site on haemoglobin. The NO molecules then bind to the haemoglobin due to its low partial pressures and an affinity greater to that of oxygen to form methaemoglobin which prohibits the oxygenation of blood for transport (Wagner and Millerick-May, 2008). As with NO, carbon monoxide (CO) also binds to haemoglobin in the pulmonary blood supply to be distributed throughout the body (Witschi and Last, 2003).

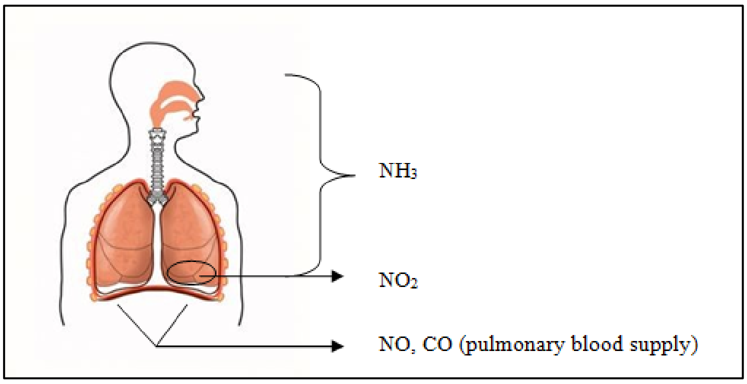

Figure 2.4: The deposition of selected gasses in the respiratory system (Shutterstock Inc, 2013; Witschi and Last, 2003).

Particle deposition occurs primarily through interception, impaction, sedimentation and diffusion. For the purpose of this study, these mechanisms will not be discussed, however, it is important to note that gas particles (such as NO, NO_2 and NH_3 included in this study) smaller than 0.5 µm have the tendency to deposit onto the lung walls by means of diffusion. It is one of the most important mechanisms for deposition into the small airways and alveoli (Chen, 2003). The elimination of these toxicants usually occurs by a degree of excretion (Kampa and Castanas, 2008) which will later be discussed.

Exposure to harmful gasses may not always result in toxicity. Before gasses can exert any actions, they must first enter the cells of the human body. The gas must first pass through the biological membranes, from an external environment to an internal environment, by means of absorption (Schaper and Bisesi, 2003). Cell membranes consist of a double layer of phospholipids with cholesterol and proteins embedded in between them. The structure of the layers will not be discussed, however, it is important to understand that the cell membranes play important roles to help maintain the structural integrity of the cells and to regulate the passage of elements and molecules into and out of the cell (Schaper and Bisesi, 2003; Widmaier *et al.*, 2004). In general, lipid soluble molecules (non-polar, hydrophibic, lipophilic) such as NO_2 have the ability to be readily absorbed through diffusion across cell membranes relative to polar (hydrophilic) molecules (Widmaier *et al.*, 2004).

2.12.2 The transport and biotransformation of toxicants

Once the toxicants have entered the body, and taken up into the bloodstream, they bind to plasma proteins such as albumin, ceruloplasmin and tranferrin. These proteins serve as carriers during transport in the circulatory system and when these contaminants are bound, they can be distributed to distal organ systems. This is essential for the toxicity of the contaminant. Two of the factors that greatly affect the distribution of the toxic compound are the affinity in an organ system and the perfusion via circulating blood through the organ systems. Organs (tissues) that are well-perfused such as the brain, liver and kidneys are more likely to be exposed to these chemicals than those that are not well-perfused. As these organs become affected, normal bodily functions then attempt to correct the problem by removing these foreign substances (toxicants) from the body through biotransformation or metabolism (Schaper and Bisesi, 2003).

This process converts the toxicants by reducing their non-polar characteristics (lipophilicity) and increasing their polar characteristics (hydrophilicity) (Schaper and Bisesi, 2003). These xenobotic biotransformation enzymes (cytochrome P450s) are found in the liver and are used to catalyse conversion reactions. By creating less toxic and more soluble metabolites, this process enhances the elimination of toxicants from the body (Seeley *et al*., 1998). However, in the case of some chemicals, when biotransformed they may yield end-products that tend to be more toxic than their parent compounds. After the biotransformation process has been completed, the metabolites are eliminated via excretion. The chemicals and their metabolites are then removed from the body (Seeley *et al*., 1998). According to Schaper and Bisesi (2003), the major routes of elimination are biliary (e.g. liver) and renal (e.g. kidney) while other chemicals simply pass through the blood-gas barrier and are expelled through exhalation (Schaper and Bisesi, 2003).

Low ammonia concentrations are generally dissolved by mucus of the upper respiratory tract where a large percentage of the ammonia gas is released back into the expired air. The remaining ammonia is then absorbed across the nasopharyngeal membranes and into the systemic circulation (ATSDR, 2004). This circulating ammonia gas is then metabolised in the liver through oxidative deamination. By removing the amine group of glutamic acid, to regenerate α-ketoglutaric acid. The ammonia molecules combine then with CO_2 to yield urea and water. The urea is then released into the bloodstream and removed via urine (Seeley *et al*., 1998). Other toxic gasses such as NO and NO_2 are also converted and excreted by means of urine. However, once NO is absorbed in the blood, it combines with haemoglobin with an affinity about 1000 times greater than that of CO. Methaemoglobin is produced and is rapidly restored to haemoglobin by methaemoglobin reductase which releases oxygen, nitrate and nitrite. Within a period of 48 hours, most of the inhaled NO is excreted in the form of nitrate or nitrogen dioxide in the urine (Kirkhorn and Garry, 2000; Dwyer, 2008).

2.13 Health effects associated with blasting gasses

Post blast gas exposure or gas poisoning generally occurs when miners return to the blasting area too soon. Initially, symptoms are slight but worsen as exposure continues (Kampa and Castanas, 2008). According to Bakke *et al*. (2001) and Bakke *et al*. (2004), exposure to blasting gasses can result in a significant decrease in lung function and FEV_1 (forced expiratory volume in one second) and, as a result, exposure to blasting gasses can cause severe health and respiratory problems.

A summary of the different types of blasting gasses as well as their health effects follows.

2.13.1 Nitrogen oxides (NO and NO_2)

Post blasting gasses such as NO and NO_2 create an irritant gas mixture, and when inhaled can cause severe irritation in the nasal and throat area and this could lead to several pulmonary disorders which can be fatal (Wagner and Millerick-May, 2008). Irritant injury of the lung parenchyma caused by deep lung irritants (i.e. oxides of nitrogen) can produce an intense inflammation reaction of the lower and upper airway structures with copious secretions flooding the alveoli known as pulmonary oedema (Carson and Delclos, 2003). This in turn leads to poor gas exchange and can cause severe shortness of breath. These gasses can be life threatening and can cause permanent anatomical defects and physiological impairment (Kirkhorn and Garry, 2000). Kirkhorn and Garry (2000) also stated that miners who are exposed to high levels of nitrous gasses may develop acute hemorrhagic pulmonary oedema and death. In some cases, massive irritant exposure to NO and NO_2 can lead to the development of irritant-induced occupational asthma (Carson and Delclos, 2003). Studies on animals have also indicated that exposure to NO_x may affect the humoral and cell-mediated defence systems, which interfere with the ability of the lungs to remove inhaled particles (Wolfe and Patz, 2002).

For the purpose of this study, the effects of NO and NO_2 on the respiratory system will be discussed separately.

2.13.1.1 Nitrogen dioxide (NO_2)

Once a miner is exposed, the inhaled nitrogen dioxide is rapidly absorbed in the lower respiratory tract due to its insoluble properties. As NO_2 is absorbed it binds to the respiratory tract tissues and causes severe respiratory problems (Wagner and Millerick-May, 2008).

NO_2 is known to produce irritation and burns to the skin or mucous membranes, while respiratory effects are more serious. Short term exposure to low concentrations of NO_2 will generally cause non-specific symptoms, these include coughing, dyspnea, headaches, nausea, vertigo, fatigue, eye irritation and some symptoms lasting longer than two weeks. As miners are exposed to higher concentrations of NO_2, they can experience spasms of the lung airways or larynx. After several hours, the exposed individuals may develop acute respiratory distress, which includes pulmonary oedema, accompanied with shallow breathing, cyanosis and productive coughing which usually progresses to anoxia (Wagner and Millerick-May, 2008).

The syndrome, acute respiratory distress, can further be characterised into two important phases. The first phase, within 1-7 days of exposure is characterised by pulmonary capillary congestion, endothelial swelling and microatelectasis. Other conditions include pulmonary oedema, fibrin deposition and the formation of hyaline membranes in the lungs. Hypoxemic respiratory failure follows a few days after exposure and the individual may require a ventilator. After 7 days, the fibroproliferative phase follows.

This phase is associated with stiffening of the lungs, increased blood CO_2 levels and diffused alveolar damage. Fatalities are known to be high in most cases (Wagner and Millerick-May, 2008). Survivors usually develop lifelong chronic pulmonary fibrosis. Research estimates that NO_2 concentrations of 560-940 mg/m³ are needed to produce fatal pulmonary oedema or asphyxia, and 47-140 mg/m³ for the development of bronchitis or pneumonia (Wolfe and Patz, 2002).

According to Wolfe and Patz (2002), NO_2 also acts as a strong oxidant and may lead to the toxification of the lung cells through peroxidation of membrane lipids or membrane proteins, each of which increases cell permeability, leading to injury and death. NO_2 also inhibits the bactericidal activity of the alveolar macrophages that are significant in preventing pneumonia. It can also increase the susceptibility to both bacterial and viral respiratory infections (Wolfe and Patz, 2002). Miners exposed to NO_2 who suffer from asthma are also more susceptible to increased bronchi-constriction, thus triggering an inflammatory response in the lung and increasing airway resistance and reduced diffusion capacity. Most studies show a stronger association between exposure and symptoms during prolonged exposure than immediately upon exposure (Wolfe and Patz, 2002).

Kubota *et al*. (1987) studied the effect of long-term NO_2 exposure at concentrations of 0.753 mg/m^3 and 7.527 mg/m^3 on rats. NO_2 exposure at 0.753 mg/m^3 revealed physical changes in the interstitial oedema of the alveolar walls as well as changes in the epithelium after an exposure period of 27 months. Exposure at 7.527 mg/m^3 showed various alterations to the lung function and interstitial tissue, which in turn led to fibrosis after 27 months. Studies regarding mine workers' long-term exposure to blasting gasses are also limited, however, it has been suggested that long-term exposure to low levels of NO_2 can present mine workers with adverse health effects such as obstructive respiratory disorders, especially those with asthmatic problems (Orehek *et al*., 1976). Bakke *et al*. (2004) also confirmed that long-term (6 years) exposure to NO_2 at low concentrations (1.88 mg/m^3) can result in the decrease in tunnel construction workers' respiratory functions (FEV_1).

2.13.1.2 Nitric oxide (NO)

Nitric oxide is relatively non-toxic at low concentrations and is frequently used in the clinical industry to treat pulmonary hypertension, pulmonary embolism and acute respiratory distress. Nitric oxide is synthesised by several cell types which mediates normal physiological actions such as neurotransmission and inhibition of platelet adhesion (Dwyer, 2008).

However, exposure to high concentrations of NO has produced cyanosis and death in animals (Dwyer, 2008). NO is also known to cause similar respiratory disorders and health problems to that of nitrogen dioxide (Wagner and Millerick-May, 2008). The Threshold Limit Value (TLV) for NO is, however, based on the formation of methaemoglobin and not on the health effects it may cause as is the case with NO_2 (Dwyer, 2008).

Nitric oxide is a primary lung irritant, causing irritation to the nasal and trachea regions. Inhaled NO combined with moisture in the lungs can result in scarring of the lung tissue and lead to bleeding and accumulation of moisture in the lungs (pulmonary oedema). Once the miner is affected by NO poising, if it is not recognised and treated correctly, the miner may eventually die from suffocation due to the filling of the alveoli (Unsted, 2001).

Yoshida and Kasama (1987) studied the effects that inhaled nitrogen oxide (NO) had on mice, and found that NO gasses are of low solubility, and when inhaled penetrates deep into the lower respiratory tract (Kirkhorn and Garry, 2000), most entering the blood through the alveoli and reacting with haemoglobin in erythrocytes to form NOHb (nitrosyl-haemoglobin), and these are then transferred to the serum. Emphysema-like lesions have also been observed in mice exposed to NO (Kampa and Castanas, 2008).

Emphysema can be distinguished by the permanent enlargement of the alveoli, accompanied by the destruction of the alveolar walls. This destruction of the alveolar walls has three important consequences; the first is the collapsing of the bronchioles during expiration, trapping large volumes of air in the alveoli. This hyper inflammation leads to the development of the permanently expanded "barrel chest" and flattens the diaphragm, reducing ventilation efficiency. Thus decreasing the ability of the lungs to recoil and expel air. Finally, damage to the pulmonary capillaries as the alveolar wall disintegrates increasing the resistance in the pulmonary circuit, leading to an enlarged right ventricle (Seeley *et al*.; 1998; Marieb and Hoehn, 2007).

2.13.2 Ammonia (NH_3)

Ammonia is a respiratory and mucous membrane irritant and at high concentrations, an exposed individual may experience respiratory distress (Kirkhorn and Garry, 2000). It can be associated with upper and lower airway irritation, sinusitis, chronic obstructive pulmonary conditions, and mucous membrane inflammation syndrome. After prolonged exposure to NH_3 gas, a miner may develop a tolerance, and this could lead to fewer irritant symptoms developing with greater pulmonary exposure. Prolonged exposure to NH_3 at levels below 17 mg/m^3 have been linked to adverse health effects. It has been suggested that long-term exposure to NH_3 of 2hr/day for six years can be associated with a variety of conditions such as sinusitis, chronic bronchitis, alveolar oedema and asthma (Kirkhorn and Garry, 2000). Studies have indicated that long-term exposure to ammonia at concentration between 1.2 mg/m^3 and 7.71 mg/m^3 may cause obstructive lung diseases including lung function impairment (Brautbar *et al.*, 2003). However, other studies have reported no significant changes in the pulmonary functions of workers exposed to ammonia concentrations at 6 mg/m^3 over a period of 12 years (Holness *et al.*, 1989).

Ammonia is also known to cause irritant induced asthma or Reactive Airways Dysfunction Syndrome (RADS). RADS differs from occupational asthma caused by sensitisation to a single substance in a mine, it represents a response to direct injury to the airways and the symptoms of airflow obstruction do not necessarily have any relationship to ongoing workplace exposure. RADS can develop into a long-lasting condition (White, 2001). Ammonia is also known as an eye irritant and may cause ocular damage by penetrating the ocular tissue, and causing damage to the cornea, adnexia, iris, ciliary body and lens (Fox and Boyes, 2003).

According to the CCOHS (1998), numerous cases of fatal ammonia exposure have been reported, however, actual exposure levels have not been documented. Long-term respiratory system and lung disorders have been observed following severe short-term exposure to ammonia (CCOHS, 1998).

2.14 Sampling methods for blasting gasses

Over the years, various organisations such as National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA) have researched and developed various methods for the individual sampling of blasting gasses. NIOSH 6014 and 6015 are such methods and were used for the monitoring of blasting gasses NO_x (NO and NO_2) and NH_3 respectively (NIOSH, 2003). However, the reliability of these methods are questionable since they have not been tested extensively in the harsh conditions of an underground mine.

Various studies have been carried out to determine the types of gas emissions and concentrations liberated from blasting activities as well as the techniques to measure and analyse such emissions (Mainero, 1997; Attalla *et al*., 2008). However, quantitative data regarding mine workers' respiratory exposure to blasting gasses in an underground mine remain limited. In one study, Bakke *et al*. (2001) determined the effect of blasting fumes exposure and short-term lung function changes in Tunnel Construction Workers. Their exposure to total and respirable dust, volatile organic compounds, oil mist, formaldehyde, nitrogen dioxide and carbon monoxide were assessed. The workers were required to clean the tunnel after the detonation of ANFO explosives (Bakke *et al*., 2001). The researchers measured the tunnel workers exposures to NO_2 and CO by means of a direct reading instrument (Neotox-al personal single gas monitor) during the cleaning and moving of blasted debris out of the tunnel. Results indicated that the tunnel workers mean exposures to NO_2 were less that 1.88 mg/m^3. It was also established that the tunnel construction workers' highest peak exposures were recorded during the moving and transporting of blasted rock (Bakke *et al*., 2001). This finding may also be relevant in an underground mine where rock removal activities take place on a daily basis.

In another study, Mainiero (1997) designed a chamber for the testing of ANFO explosives in a controlled environment, in order to determine a technique for measuring blasting gasses. NO_x and NH_3 were then retrieved from the chamber through a 0.6 cm Teflon or polyethylene tube for analysis. The vacutainer sample or sampling bags containing the gasses were then sent to a laboratory for analysis. It was determined that NO, NO_2 and NH_3 are not amenable for analysis by means of the vacutainer technique and were instead chemically absorbed via bubble trains. Bubble trains were accepted as a measuring technique for NO, NO_2 and NH_3 in the blasting cloud. However, due to the time constraints regarding this method, the researcher simplified the process by measuring blasting gasses by a series of Draeger electrochemical cells (Mainiero, 1997).

The methodologies developed by Mainiero (1997) for the testing of blasting gasses are of no relevance to this study since they cannot be used to determine mine workers' personal respiratory exposure over an 8-hour period. As a result, specific sampling methodologies were developed by institutions such as NIOSH and OSHA to measure the individual constituents of the blasting cloud. Whether these active and passive sampling methodologies are effective and reliable for the sampling of underground mine workers to post blasting gasses such as NO, NO_2 and NH_3 is unclear and further research is required. This is also one of the objectives of this study, to evaluate mine workers' respiratory exposure by means of active and passive sampling methodologies under realistic field conditions (underground) and to determine whether there will be an association between the parallel measurements. Valuable information will also be gathered from this study to determine whether active and passive sampling methods are user friendly and whether they are effective when measuring mine workers' respiratory exposure underground.

The mine under study uses various types of gas detection devices to monitor static as well as personal gas exposures. Static sampling usually refers to the central gas monitoring system which continuously monitors gas concentrations such as CO at various levels underground which is mostly used when establishing the re-entry period after centralised blasting at the mine. Direct reading instrumentation fitted with electronic sensors is generally used to measure gas concentrations in confined spaces. In addition, these devices are also used to evaluate mine workers' respiratory exposure to CO, NO, NO_2, NH_3, methane and oxygen underground, but on an infrequent and non-specific basis. Personal exposure sampling by means of electronic devices is considered relatively expensive due to the cost of the equipment as well as the maintenance and annual calibration of such equipment. For the purpose of this study, two other sampling methodologies were selected (i.e. active and passive sampling) to determine mine workers' respiratory exposure to blasting gasses and also to determine their effectiveness in an underground mining environment.

2.15 Legislation and Occupational Exposure Limits (OELs)

Occupational exposures to blasting gasses for miners working in platinum mines have long been recognised, however, exposure limits for these workers working at the face (panel) have not been well documented and researched. The Mine Health and Safety Act and Regulations (No. 29 of 1996) and the Occupational Health and Safety Act and Regulations (No. 85 of 1993) are two sources regarding the legislative requirements and recommendations for occupational exposure limits (OEL's) in the South African mining industry. These OEL's are set and developed with the main focus to protect the health of the miner in his/her occupation. Although the mine is obligated to use the MHSA, the Regulations for

Hazardous Chemical Substances (No.1179 of 1995) under the Occupational Health and Safety Act may also be used as legislative measure to determine OEL-TWA.

The primary gas exposures of occupational concern in this study include nitric oxide (NO), nitrogen dioxide (NO_2) and ammonia (NH_3). The OEL-TWA for these gasses according to the Hazardous Chemical Substances Regulation (1995) under the OHS Act (No. 85 of 1993) is the same as the Mine Health and Safety Regulations of the MHS Act (No. 29 of 1996) and is presented in Table 2.4.

Table 2.4: Time Weighted Average - Occupational Exposure Limits (TWA - OELs) for blasting gasses in an underground mine.

Source	**Ammonia**		**Nitric Oxide**		**Nitrogen Dioxide**	
	ppm	mg/m³	ppm	mg/m³	ppm	mg/m³
Hazardous Chemical Substances Regulations (1995), OHS Act No. 85 of 1993 & Regulation 22.9 of the MHS Act No. 29 of 1996	25	17	25	30	3	5

According to Section 9.2 (2) of the Mine Health and Safety Act (No. 29 of 1996) the employer of a mine must establish and maintain a system of occupational hygiene measurements where gasses such as NO, NO_2 and NH_3 as well as vapours equal or exceed 50% of the occupational exposure limit. For the purpose of this study, the occupational exposure levels measured during the project will be compared to the OEL's stated in Regulation 22.9 of the Mine Health and Safety Act (No. 29 of 1996).

Various Occupational Exposure Limits (OELs) have been set for toxic gasses such as NO, NO_2 and NH_3 to protect the health of underground mine workers. However, these set OELs do not always take into account that mine workers working inside the stopes may be exposed to more than one individual substance. Miners are, therefore, subject to mixed exposures. Some mixed exposures involve substances that act on different body tissues or organs, or by different toxicological mechanisms, these various effects being independent of each other. Other mixtures will include substances that act on the same organs, or by similar mechanisms, so that the effects reinforce each other and the substances are additive in their effect. Where there is reason to believe that the constituents are additive, the mixed exposure should be assessed since OELs are not assigned to mixed exposures such as in the case of blasting gasses (HCS Regulations, 1995).

This literature study provided valuable information on the workings and environmental conditions present to mine workers in an underground mine, as well as the physical and chemical properties of blasting gasses and their associated health risks. There were, however, limited research and studies relating to mine workers' respiratory exposure to blasting gasses after the detonation of ANFO explosives as well as approved techniques for the sampling of such gasses in an underground mining setup. This study was, therefore, motivated to address some of these limitations by quantifying mine workers' respiratory exposure to blasting gasses (i.e. NO, NO_2 and NH_3) after the detonation of ANFO explosives in an underground mine. The results are presented and discussed in Chapter 3.

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Underground mine workers' respiratory exposure to selected gasses after the blasting process in a platinum mine.

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3.1 Abstract

Ammonium Nitrate-Fuel Oil (ANFO) is generally the preferred explosive used in the mining industry for underground blasting operations. During the aforesaid, by-products or blasting gasses such as nitric oxide (NO), nitrogen dioxide (NO_2) and ammonia (NH_3) are liberated into the atmosphere, and when inhaled, may present mine workers with adverse health effects depending on the level of exposure. **Objectives:** The objectives of this study were to quantify Scraper Winch Operators (SWOs) respiratory exposure to selected blasting gasses approximately three hours after the detonation of ANFO explosives, as well as the association between the active and passive analytical methods. **Method:** One group of twenty African SWOs, at three different underground blasting levels, were selected for this study. SWOs' personal exposure to selected blasting gasses (NO, NO_2 and NH_3) over an 8-hour period were evaluated by means of active and passive sampling methodologies. Results were time weighed to an average 8-hour exposure level in order to compare the results to legislative occupational exposure limits. **Results:** The SWOs respiratory exposure to NO, NO_2 and NH_3 complied with their respective OELs. One SWO had an ammonia exposure level of 9.830 mg/m^3 which exceeded the action level. Blasting gas concentrations fluctuated between the three blasting levels, with the highest mean NO and NO_2 concentration recorded at Level 33-35 (represents one level), while Level 36 recorded the highest mean NH_3 concentration. There was a poor correlation between the exposure results of the active and passive sampling methods for NO_2 ($r = -0.323$) and NH_3 ($r = 0.090$). The passive samplers generally underestimated the SWOs personal exposures in comparison to the active air samplers. There was, however, one correlation ($r = 0.486$) of medium effect between blasting gasses NO (active) and NH_3 (active). **Conclusion:** Control measures implemented at the mine were adequate to control the SWOs respiratory exposure to NO, NO_2 and NH_3 to levels below their respective OELs. Health effects associated with acute blasting gas exposure is, therefore, not likely. Long-term exposure to blasting gasses at low concentrations may, however, present SWOs with a health risk. External factors such as geological formation, explosive composition, loading and charging of ANFO explosives as well as ventilation parameters inside the various blasting levels may affect blasting gas production. Therefore, any changes made to these external factors can result in higher blasting gas exposures. There was a significant difference between the active and passive sampling methods for NO_2 and NH_3. The most likely explanation for this variation between the two sampling methods may be ascribed to the hot and humid conditions underground that may have affected the passive diffusive samplers.

Keywords: blasting gasses, ANFO explosives, respiratory exposure, underground, sampling methodologies.

3.2 Introduction

Ammonium Nitrate-Fuel Oil (ANFO) explosives are generally used in the mining industry for the blasting of underground rock faces and excavation areas (Attalla *et al*., 2008). During the aforesaid blasting operations, by-products or blasting gasses such as oxides of nitrogen (NO_x), ammonia (NH_3), carbon dioxide (CO_2) and carbon monoxide (CO) are liberated into the atmosphere, and when inhaled, may result in the acute and chronic exposure of mine workers (De Souza and Katsabanis, 1991; Guild *et al*., 2001; Mainiero *et al*., 2007; Attalla *et al*., 2008). Poisoning by nitrogen oxides (NO_x) and carbon monoxide gasses is not uncommon in mines, where cases of gas poisoning date back as far as the early 1900's (Irvine, 1916). In the past decades, mines have implemented certain safety measures such as the monitoring of airborne gas concentrations, setting re-entry periods and the dilution of airborne pollutants through mechanical ventilation in order to improve underground mining conditions (Guild *et al*., 2001; AEISG, 2011). One of their concerns, however, is the lack of occupational data regarding the respiratory exposure of mine workers (Scraper Winch Operators) to blasting gasses after the re-entry period.

Blasting gasses are produced when agents such as dynamite and ammonium nitrate-fuel oil mixtures are detonated, and gasses such as NO, NO_2 and CO are released into the atmosphere (Attalla *et al*., 2008). The explosive DDS™ Sensitised Emulsion also known as Gassed Ammonium Nitrate Emulsion is commonly used in the underground mining sector in the Bushveld Complex of Rustenburg (Sasol, 2012). The by-products formed after the detonation of gassed ammonia nitrate emulsion products can present mine workers with adverse health effects if these blasting gasses are not adequately controlled or mitigated especially in stoping areas where ventilation and other health and safety measures are difficult to implement (De Souza and Katsabanis, 1991; Attalla *et al*., 2008; AEISG, 2011).

After the charge up and the detonation of explosives by means of centralised blasting, a re-entry period of approximately three hours is allowed for the dilution and removal of airborne contaminants at the blasting panels by means of mechanical ventilation (Guild *et al*., 2001). The re-entry period at the mine under study is determined through a central gas monitoring system which measures solely the background carbon monoxide concentrations at the various underground levels. Once the CO levels drop below a safe concentration, a Ventilation Officer on duty gives the all clear and re-opens the shaft for the night shift. Although the mine under study has conclusive data regarding mine workers' respiratory exposure to CO, it was also in the interest of the mine to determine the mine workers' respiratory exposure to other blasting gasses since these gasses are generally not measured and do not form part of the mine's re-entry period. It is also unclear whether long-term exposure at low concentrations as well as the additive effect of NO, NO_2 and NH_3 may pose a health risk to Scraper Winch Operators (SWOs) who are exposed to blasting gasses on a daily basis. Bakke *et al*. (2004) concluded that long-term exposure to blasting gasses in particular NO_2 may result in the decrease in lung function (FEV_1) of tunnel construction workers.

The SWOs are the first group to enter the stopes (underground excavations in the order of one metre high) after the re-entry period (Smit and Pistorius, 1998; Unsted, 2001; Rutter, 2009). The SWOs are required to clean and remove rock debris (containing the precious metal) from the face through the utilisation of conventional mining techniques (i.e. mechanical scraper winches) during which they may be exposed to high concentrations of NO, NO_2 and NH_3 which may be trapped within the broken ore and released during the scraping thereof (Unsted, 2001).

Respiratory irritants such as NO_2 and NH_3 are known to cause respiratory disorders with Bakke *et al.* (2001) concluding that workers exposed to dust and blasting gasses are at increased risk of obstructive pulmonary diseases and upper and lower airway inflammation. Blasting gasses can also impair the functionality of the cardiovascular system, respiratory system and other organ functions (Kampa and Castanas, 2008).

Based on the health effects as well as limited occupational exposure data in the South African mining sector, the aim of this study was to evaluate the 8-hour TWA exposure of mine workers to NO, NO_2 and NH_3 approximately three hours after the blasting process by means of personal air sampling. In addition, the aim was also to assist the mining industry in establishing the most effective and reliable means of measuring blasting gasses underground. Furthermore, the above findings will also indicate whether the control measures implemented at the mine and the set re-entry period of approximately three hours provide adequate protection against the inhalation of blasting gasses.

3.3 Methodology

3.3.1 Mine setting

This study was conducted at an underground platinum mine in the Rustenburg region of the North West Province. Ore containing platinum and other precious metals are extracted from the UG2 chromitite reef of the Bushveld Complex through conventional mining techniques. Mine workers entered the mine approximately three hours after the blasting process by means of a vertical shaft which lowered the mine workers to the various levels. The study was conducted at different blasting panels inside the stopes on Levels 33-35, 36 and 37. One group of mine workers was required to clean a blasting panel at Level 33 which also extends to Level 35. The remaining groups only conducted cleaning operations inside a stope on Levels 36 or 37.

3.3.2 Job description

Mine workers followed a sequence of rock drilling, charging of explosives, blasting, scraping and transporting of broken ore out of the mine. The group of mine workers, Scraper Winch Operators (SWOs), who participated in the study, were responsible for the removal of broken ore from the face and gullies by means of mechanical scraper winches inside the stopes and developing areas.

3.3.3 Sampling strategy

A quantitative research design was formulated to determine the 8-hour Time Weighted Average (TWA) exposure of SWOs to NO, NO_2 and NH_3 approximately three hours after the blasting process. Personal exposure measurements were performed by means of active and passive sampling techniques on 20 selected African male workers over a period of eight days. Three SWOs were evaluated per shift. The sampling period was, however, limited from 4 to 8 hours due to the variability of time in which the SWOs took to clear the gullies and blasting panels from broken ore. Once the SWOs had completed their work, they returned to the shaft. The remainder of the SWOs exposures were regarded as 0 mg/m^3 since blasting gas exposures are expected to be low at the fresh air intake shaft, which was then used to calculate their time weighted average exposure over an 8-hour period in order to compare the results to the Occupational Exposure Limits (OELs) stated in Regulation 22.9 of the Mine Health and Safety Act (No. 29 of 1996).

After a walkthrough survey and consultations with the occupational hygienist onsite, mine captains and ventilation experts it was established that the group of mine workers who are potentially exposed to the highest concentrations of blasting gasses are the SWOs. They are the first group of miners to enter the mine after blasting operations when blasting concentrations inside the stopes are regarded as the highest. The underground sampling levels and SWOs were randomly selected according to the mine's production and blasting schedules.

Each of the SWOs who participated in this study, were fitted with an active air sampling train for the sampling of NO, NO_2 and NH_3 as well as two passive diffusive air samplers for the sampling of NO_2 and NH_3. A total of 20 mine workers and 100 samples were collected and evaluated during the course of the study.

3.3.4 Sampling equipment and calibration

3.3.4.1 Active personal air sampling

Active personal air sampling measurements for NO, NO_2 and NH_3 were conducted in accordance with the National Institute for Occupational Safety and Health (NIOSH) methods. Personal exposure to NO_x (NO and NO_2) and NH_3 were measured by means of the NOISH 6014 and 6015 methods respectively (NIOSH, 2003). Each mine worker was fitted with a sampling train that consisted of a calibrated sampling pump (GilAir-3®), constant pressure flow controller (SKC® 224-26-CPC), flexible tubing, a dual adjustable low flow holder (SKC® 224-26-02) and sampling tubes.

NIOSH 6014 method

The sampling medium used for the sampling of NO and NO_2 was an oxidiser with two triethanolamine treated molecular sieves tubes (ST 226-40 SKC®). The tube series was arranged as follows: a pre-drying tube (226-44 SKC®) was fitted to the front of the NO_2 triethanolamine tube (ST 226-40 sampling series). Due to the high sensitivity of the NO_x sampling tubes to external factors (i.e. humidity and temperature), a sorbent (sodium sulphate) tube was used to remove the moisture in the air which may affect the chemical adsorption properties of the NO_x sampling tubes. The second tube, treated with triethanolamine was used for the collection of NO_2. The NO_2 and NO tubes were separated by an oxidiser which assisted with the oxidising of NO_2 to NO which was captured by the second triethanolamine tube.

After arranging, breaking the ends of the tubes and fitting the tubes by means of plastic tubing into series, the sampling train was inserted into the dual adjustable low flow holder and attached to the collar of the mine worker. Due to the added addition of the drying tube to the series, additional clip-on's were used to attach the long train of tubes to the mine workers breathing zone to prevent the tubes from dragging through the ground when mine workers crawled through the stopes.

NIOSH 6015 method

The NIOSH 6015 method was used to determine the respiratory exposure of each mine worker to ammonia. The media used consisted of a sulphuric acid treated silica gel tube (ST 226-10-06 SKC®) placed into a sorbent protective holder.

Calibration specifications of NIOSH methods 6014 and 6015

The flow rates for the sampling pump and multi sorbent tubes using the dual adjustable low flow holder were calibrated as follows: the pumps were switched on at least 5 minutes prior to calibration. The flow rates for NO_x (0.025 l/min) and NH_3 (0.2 l/min) as specified in accordance with the analytical methods were added together (NIOSH, 2003). The sampling pumps were then set to a flow rate greater than or equal to 15 % higher than the sum. The NO_x tube series were then inserted into one of the rubber sleeves of the dual adjustable flow holder, while the NH_3 tube was inserted into the other. The open end of the drying tube was then inserted into the tubing of the BIOS 510 calibrator. The flow rate was then adjusted on the tube holder to a flow rate of 0.025 l/min. Once the flow rate was recorded, the calibrator was disconnected and connected to the NH_3 tube. The NH_3 tube holder was then calibrated to a flow rate specification of 0.2 l/min. After sampling, the pumps were post calibrated in a similar way to verify whether the flow rates did not change by more than 5 %.

Transport of samples

After the completion of the rock removal process by the SWOs, the sampling train was removed, sealed with caps and placed into an ice container before being transported to the surface. From there on, the samples were secured in an ice container and finally transported to a SANAS accredited laboratory for analysis. The NO and NO_2 tubes were analysed according to the specifications of NIOSH 6014 method, by visible absorption spectrophotometry, while the NH_3 tubes were analysed according to the NIOSH 6016 method via the ion chromatography technique (NIOSH, 2003). Ammonia can be analysed by using either the NIOSH 6015 method or the NIOSH 6016 method.

3.3.4.2 Passive diffusive air sampling

Along with the active air samplers, the Scraper Winch Operators were also monitored for NO_2 and NH_3 exposure by means of radial symmetry diffusive samplers (RING) developed by Aquaria®. RING samplers are characterised by a cylindrical diffusive surface, an absorbent device, internal and coaxial to the surface diffusive, and a diffusive path parallel to the beam. The NO_2 (P702R) and NH_3 (P700R) cartridges were placed into a diffusive body (P502R), secured and then attached to a supporting plate (P500R) and labelled (i.e. sample number, time and date). The completed RING sampler was then attached to the collar of the mine worker. After sampling, the cartridges were removed from their diffusive bodies and placed into secure holders and labelled before being transported to the surface on ice. The samples were then secured (in an ice container) and transported to a SANAS accredited laboratory where the NO_2 and NH_3 cartridges were analysed and quantified by using visible absorption spectrophotometry according to NIOSH methods 6700 and 6015 (NIOSH, 2003).

3.3.5 Sampling procedure

Before the start of sampling, the mine workers were informed of the purpose of the study as well as the limitations and correct handling of the sampling media while working inside the stopes. The active sampling trains and passive diffusive samplers were placed in the respiratory zone of each worker. The sampling sheets were completed (i.e. date, start time, sample numbers, personal details, etc.). During the sampling process, the sampling devices were removed from the mine workers before the 8-hour period since a majority of the SWOs completed their work inside the stopes within 4 to 7 hours. After collecting the sampling equipment from the SWOs, they returned to the shaft. During this period, the mine workers' respiratory exposure to blasting gasses was regarded as 0 mg/m^3. The results were then time weighed to an 8-hour exposure value in order to compare the results to the OELs stated in Regulation 22.9 of the Mine Health and Safety Act (No. 29 of 1996). In addition, the results were also converted to a 1-hour exposure concentration to give an indication of their actual exposure level while cleaning inside the stopes. The 1-hour exposure concentration was calculated by using the following equation: (actual exposure (mg/m^3) / exposure time (min)) x 60 (min).

3.3.6 Statistical analysis

Statistical analysis was performed by means of Statistica version 11 (StatSoft, Inc., 2011). The data did not meet the assumption of normal distributed variables and, subsequently, the Wilcoxon matched pairs test was done in favour of the t-test due to the non-parametric distribution of dependent variables. Statistical analysis included basic descriptive statistics (means, maximum, minimum and standard deviation). A Wilcoxon matched pair test was performed to investigate whether there was any statistical significant difference between the active and passive sampling methods. Statistical significance was regarded as p-value ≤ 0.05. A Bland-Altman plot was compiled in order to determine the limits of agreement between the active and passive sampling methods and, finally, a Spearman Rank Order Correlation was performed to obtain the relationship (r-values) between the different measuring techniques and gasses. The following correlation values (r) were used to define the meaningfulness between two variables:

- $r = 0.1$ reflects a small effect (no significant correlation between two variables)
- $r = 0.3$ a medium effect (visible correlation)
- $r = 0.5$ a large effect (significant correlation) (Field, 2009).

3.4 Results

This article described and presented the results of mine workers' respiratory exposures to blasting gasses for the duration of their work activity inside the stopes as well as the performance of the active and passive diffusive samplers used in an underground mining setup. Table 3.1 depicts the descriptive results of the 8-hour Time Weighted Average (TWA) exposure of the Scraper Winch Operators (SWOs) to NO, NO_2 and NH_3 by means of active and passive diffusive air sampling methodologies.

Table 3.1: Scraper Winch Operators' 8-hour TWA respiratory exposures to selected gasses after the blasting process.

Variable	**n**	**Mean ± SD**	**Minimum (mg/m^3)**	**Maximum (mg/m^3)**
Active air monitoring				
Nitric Oxide (NO)	20	0.186 ± 0.183	0.011	0.649
Nitrogen Oxide (NO_2)	20	0.044 ± 0.049	0.001	0.233
Ammonia (NH_3)	20	2.669 ± 2.408	0.778	9.830
Passive air monitoring				
Nitrogen dioxide (NO_2)	20	0.010 ± 0.007	0.007	0.029
Ammonia (NH_3)	20	1.388 ± 0.545	0.144	2.168

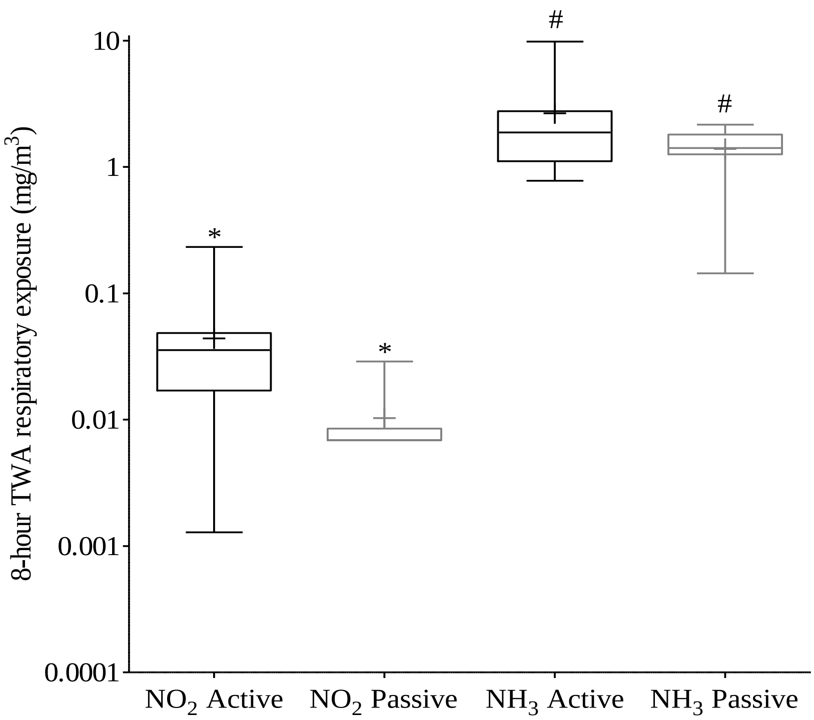
In Table 3.1 the 8-hour TWA exposure of all the Scraper Winch Operators (SWOs) to NO, NO_2 and NH_3 complied with their respective OELs of 30 mg/m^3, 5 mg/m^3 and 17 mg/m^3 (MHSA, 1996). One of the SWOs had an exposure to ammonia that was 9.830 mg/m^3, which exceeded the action level (50% of OEL). Results also indicated that the mean 8-hour TWA exposure level monitored by means of the active sampling method were higher when compared to the results of the passive sampling method.

Table 3.2 depicts the average 1-hour exposures of the Scraper Winch Operators while cleaning inside the stopes. SWOs' respiratory exposures were calculated for a 1-hour exposure concentration in order to give an indication of their actual exposure levels during the removal of blasted ore from the blasting panels and gullies. Results were averaged to a 1-hour exposure value since SWOs do not perform cleaning operations for the full 8-hour work shift. Results indicate that the highest NO_2 and NH_3 personal exposure concentrations were measured by means of the active air sampling method.

Table 3.2: Scraper Winch Operators actual 1-hour exposure levels to post blasting gasses.

Variable	n	Mean ± SD	Minimum (mg/m³)	Maximum (mg/m³)
Active air monitoring				
Nitric Oxide (NO)	20	0.063 ± 0.077	0.006	0.317
Nitrogen Oxide (NO_2)	20	0.017 ± 0.024	0.024	0.114
Ammonia (NH_3)	20	0.816 ± 0.519	0.227	2.272
Passive air monitoring				
Nitrogen dioxide (NO_2)	20	0.004 ± 0.004	0.001	0.016
Ammonia (NH_3)	20	0.504 ± 0.241	0.027	0.981

Figure 3.1 represents a Box-whiskers plot for the comparison of the 8-hour TWA exposures between NO_2 and NH_3 measured by active and passive diffusive air sampling methods. Included are the mean, median, 25% percentile, 75% percentile as well as the minimum and maximum concentrations for each of the variables. Figure 3.1 clearly illustrates that there were significant discrepancies between the sampling results (mean, min, max) of the active and passive methods for both NO_2 and NH_3. A Wilcoxon matched pairs test was also performed on the nonparametric variables and confirmed that there was a statistical significant difference between the two sampling methods.



* NO_2: p = 0.00078

\# NH_3: p = 0.044

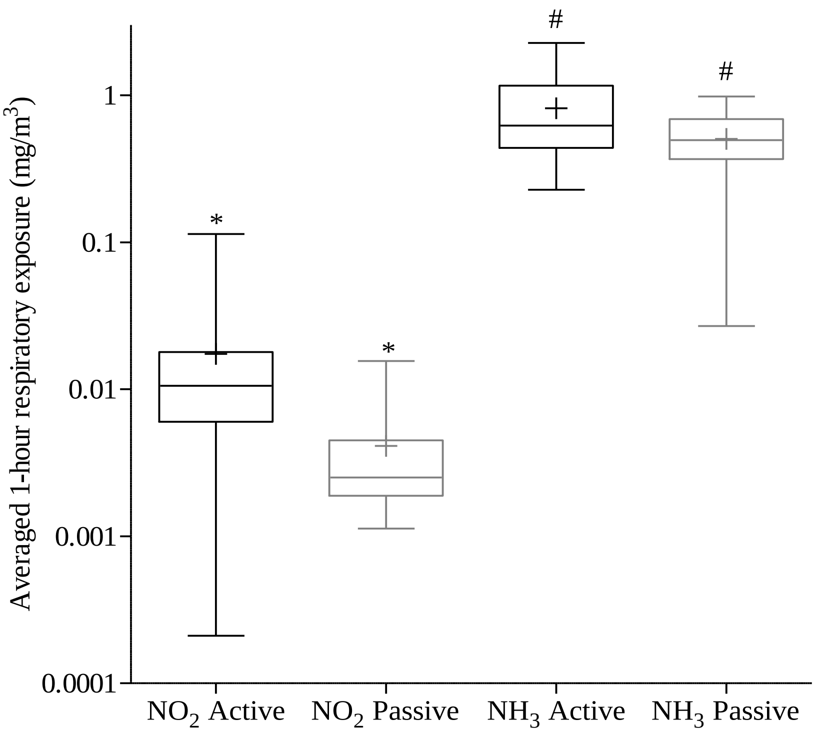
\+ Mean = NO_2 Active (0.044), NO_2 Passive (0.010), NH_3 Active (2.669), NH_3 Passive (1.388)

□ 25%-75% = NO_2 Active (0.017, 0.049), NO_2 Passive (0.007, 0.009), NH_3 Active (1.113, 2.767), NH_3 Passive (1.259, 1.809)

— Median: NO_2 Active (0.036), NO_2 Passive (0.007), NH_3 Active (1.882), NH_3 Passive (1.411)

Figure 3.1: Comparison of SWOs 8-hour TWA exposure for NO_2 and NH_3 measured by active and passive sampling methods.

Figure 3.2 illustrates the comparison between the SWOs average 1-hour exposure for NO_2 and NH_3 between the two sampling methods.



* NO_2: p = 0.00078
\# NH_3: p = 0.037
\+ Mean = NO_2 Active (0.017), NO_2 Passive (0.004), NH_3 Active (0.816), NH_3 Passive (0.504)
□ 25%-75% = NO_2 Active (0.006, 0.018), NO_2 Passive (0.002, 0.005), NH_3 Active (0.438, 1.162), NH_3 Passive (0.369, 0.689)
— Median: NO_2 Active (0.011), NO_2 Passive (0.003), NH_3 Active (0.623), NH_3 Passive (0.496)

Figure 3.2: Comparison of SWOs averaged 1-hour exposure levels for NO_2 and NH_3 measured by active and passive sampling methods.

Figures 3.3 and 3.4 reflect the SWOs 8-hour TWA exposures for NO_2 and NH_3. Bland-Altman plots were used to illustrate the percentage differences between the active and passive measurements (y-axis), as a function of the average (x-axis) of the two sampling measurements for each of the samples. The average bias (the average difference between an active and passive measurement) for NO_2 and NH_3 were in most instances above the zero line which indicated that the active sampling method produced higher results when compared to that of the passive sampling method (below zero line). The mean bias or the average of the differences between the active and passive sampling methods, for NO_2 and NH_3 were 91.1% and 36.1% respectively, in favour of the active sampling method.

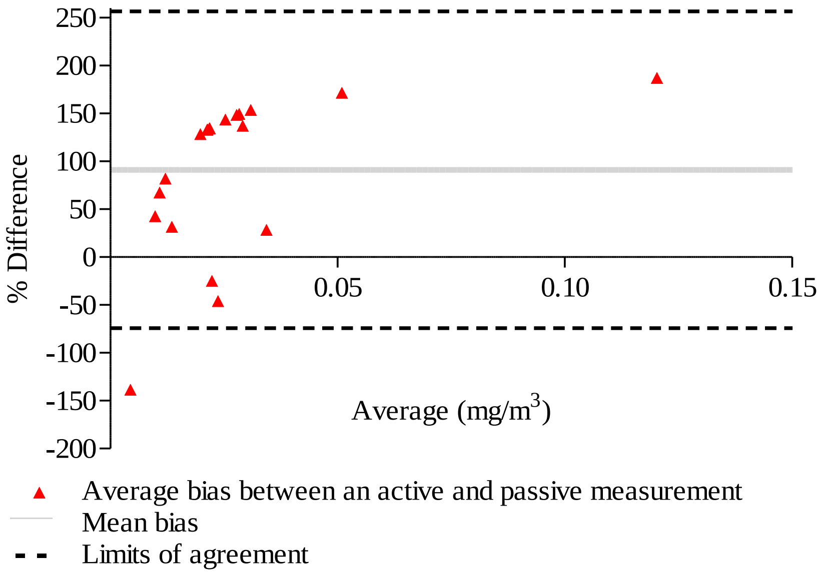


Figure 3.3: Bland-Altman plot illustrating the average bias between the active and passive sampling methods for NO_2.

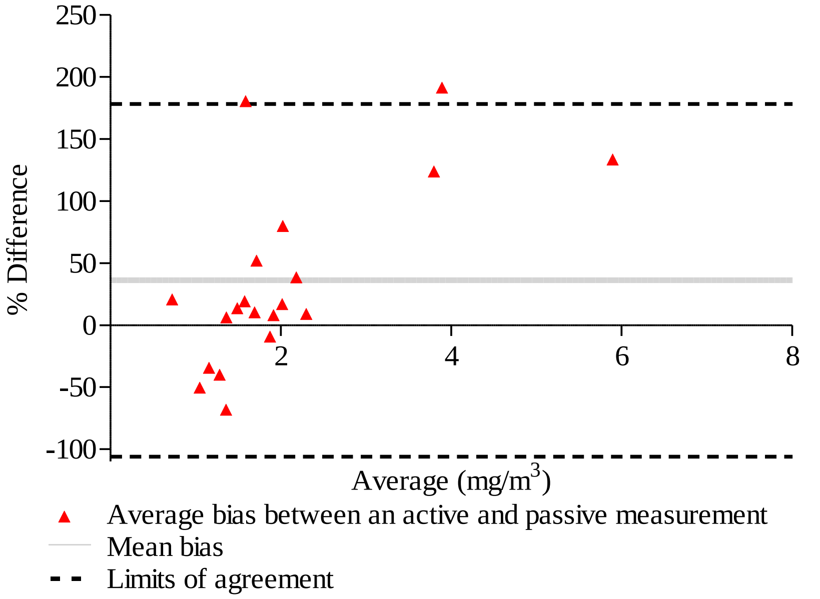


Figure 3.4: Bland-Altman plot illustrating the average bias between the active and passive sampling methods for NH_3.

Table 3.3 reports r-values as determined by a Spearman Rank Order Correlation, to determine the relationship between the two sampling methods as well as between exposure concentrations of the blasting gasses. The results indicate that there was a poor relationship between the active and passive diffusive air sampling methods for both NO_2 and NH_3. There was, however, a significant correlation with a large effect between the exposure measured for NO (active) and NH_3 (active) which indicates that a higher NO exposure may result in higher NH_3 exposure levels and *vice versa*.

Table 3.3: Spearman Rank Order Correlations, relationships between the active and passive diffusive sampling methods, as well as for the blasting gasses.

Variable	r-value
Methods	
NO_2 active vs NO_2 passive (TWA mean)	-0.323
NH_3 active vs NH_3 passive (TWA mean)	0.090
Blasting gasses	
NO_2 active vs NH_3 active (TWA mean)	0.186
NO_2 passive vs NH_3 passive (TWA mean)	-0.144
NO active vs NO_2 active (TWA mean)	0.139
NO active vs NH_3 active (TWA mean)	0.486

Table 3.4 depicts the Scraper Winch Operators' respiratory exposure levels at various locations where blasting and cleaning operations occurred. Level 33-35 indicated the highest NO (0.434 mg/m^3 ± 0.307) and NO_2 (0.099 mg/m^3 ± 0.118) mean TWA exposures compared to the other levels. The highest NH_3 mean TWA exposures were obtained on Level 36.

Table 3.4: Mine workers' exposure levels at blasting levels 33-35, 36 and 37.

Variable	**Level 33-35 (n = 3)**	**Level 36 (n = 8)**	**Level 37 (n = 9)**
Active air monitoring			
Nitric Oxide (NO)	0.434 ± 0.307	0.207 ± 0.125	0.084 ± 0.083
Nitrogen Oxide (NO_2)	0.099 ± 0.118	0.048 ± 0.020	0.022 ± 0.015
Ammonia (NH_3)	2.308 ± 0.248	3.893 ± 3.073	1.702 ± 1.703
Passive air monitoring			
Nitrogen dioxide (NO_2)	0.008 ± 0.001	0.007 ± <0.001	0.014 ± 0.010
Ammonia (NH_3)	1.603 ± 0.309	1.342 ± 0.801	1.358 ± 0.317

Values are arithmetic mean (mg/m^3) ± SD.

3.5 Discussion

From the results, it is confirmed that mine workers cleaning at the blasting panels approximately three hours after the detonation of explosives, are exposed to blasting gasses (i.e. NO, NO_2 and NH_3). Studies have indicated that high concentrations of toxic gasses are emitted during underground blasting operations and subsequently may result in the exposure of mine workers if not adequately controlled or managed (De Souza and Katsabanis, 1991; AEISG, 2011). Due to the lack of statistical and occupational data under realistic field conditions, the concentration of blasting gasses liberated from the detonation of ANFO explosives underground as well as the 8-hour respiratory exposure of mine workers is unknown. This study was, therefore, designed to determine the 8-hour TWA exposure levels of underground mine workers, the effectiveness of the mine's underground control measures as well as to establish a method for the sampling of blasting gasses underground.

The results obtained from the personal active air samples (Table 3.1), indicated that all of the mine workers (Scraper Winch Operators) had an 8-hour TWA exposure to NO, NO_2 and NH_3 that complied with their respective OELs of 30 mg/m^3, 5 mg/m^3 and 17 mg/m^3 (Regulation 22.9 of MHSA, 1996). It is apparent that the highest 8-hour TWA exposure level recorded during the course of the study was 0.649 mg/m^3 for NO, 0.233 mg/m^3 for NO_2 and 9.830 mg/m^3 for NH_3. The latter exceeding the action level (50 % of the OEL). The action level is the level at which it is recommended that management implement measures to reduce an employee's exposure to these blasting gasses. Mine workers' exposure to blasting gasses can be controlled through various control measures which include amongst others, correct loading practices, limiting the ingress of moisture into blasting holes as well as through effective mechanical ventilation for the dilution of blasting gasses (AEISG, 2011). The re-entry period currently in place at the mine under study is determined through the airborne monitoring of CO concentrations underground. A lowering in the carbon monoxide gas concentrations would not necessarily mean a drop in other blasting gasses as identified in the present study with elevated ammonia exposure levels. It is, therefore, recommended and good practice to consider other blasting gasses for example ammonia gas when establishing a re-entry period.

The results of the passive diffusive air samples reflected in Table 3.1 indicated that the SWOs had respiratory exposure levels to NO_2 and NH_3 that complied with their respective OELs in all instances. Furthermore, the mean TWA exposure level for NO_2 and NH_3 were 0.2 % and 8.16 % of their respective OELs. The mean TWA exposures of the passive diffusive samplers were 23 % (NO_2) and 52 % (NH_3) lower when compared to the results of the active air samplers. A health risk pertaining to the inhalation of blasting gasses when evaluated according to passive diffusive air methodologies was, therefore, not presented to the mine workers. This is in contradiction with the active air sampling results, where one of the SWOs had an exposure level of 9.830 mg/m^3 which exceeded the action level. This may indicate possible discrepancies between the two sampling methods, especially when measuring underground.

Table 3.2 is an indication of the SWO's 1-hour exposure to selected blasting gasses while performing cleaning operations within the stopes. The average 1-hour exposure results indicated that the active air sampling methods for NO_2 (24%) and NH_3 (62%) recorded higher results in comparison to the passive sampling methods. One of the SWOs had an average 1-hour exposure of 2.272 mg/m^3 which may have exceeded the 8-hour OEL of 17 mg/m^3 if the ammonia concentrations were to remain the same and if the mine worker was required to work for the full 8-hour duration within the stope.

The Scraper Winch Operators' general low exposures to blasting gasses may be ascribed to the re-entry period of approximately three hours implemented as a safety precaution at the mine to allow time for the dilution of gasses liberated during the blasting process through mechanical ventilation. By the time the mine workers enter the shaft and start cleaning at the blasting panels, another 90 to 120 minutes have passed which added additional air changes for the dilution of blasting gasses. Before the miners enter the face (blasting panels) they suppress dust and gas concentrations by means of sprayed water which is an effective control measure for water soluble gasses such as ammonia (Unsted, 2001). Effective loading practices of explosives as well as the type of primer and explosive used may all contribute to low post blast gas concentrations (AEISG, 2011).

The mine workers' low exposure to NO and NO_2 may also be ascribed to the oxidation of NO to NO_2 which gradually decreases the NO concentration in the underground atmosphere. The formed NO_2 is then rapidly absorbed in the moist underground mining environment, decreasing the NO_2 content in the air (Mainiero *et al*., 2006) and, subsequently, its uptake in the active and passive sampling media.

Although the SWOs' respiratory exposure to NO, NO_2 and NH_3 complied with their respective OELs, research has suggested that factors such as geological formation, control measures, the confinement of an explosive charge as well as the material (strata or type of explosive) being blasted may significantly impact blasting gas production or formation (Sapko *et al*,. 2002). As a result, personal exposure levels may vary from one mine to another and higher exposures are, therefore, likely. This was also evident in Table 3.4, where different mining levels registered different NO, NO_2 and NH_3 concentrations. The variation between one blasting level and the next may possibly be ascribed to changes in the geological formation or current ventilation parameters at that specific blasting level that may give rise to higher blasting gas concentrations.

Data suggest that mine workers cleaning underground after the detonation of ANFO explosives were exposed to blasting gasses at low concentrations. Research has indicated that acute and chronic exposure to blasting gasses may present mine workers with adverse health effects (De Souza and Katsabanis, 1991; Brautbar *et al*., 2003; Bakke *et al*. 2004). Bakke *et al*. (2004) concluded that mine workers' cumulative exposure to blasting gasses in particular NO_2 at low concentrations (1.882 mg/m^3) may result in a decrease of their respiratory functions (FEV_1). Various epidemiological studies on animals (rats) indicate that long-term NO_2 exposure at concentrations of 0.753 mg/m^3, may reveal changes in the interstitial oedema of the alveolar walls and epithelium (Kubota *et al*., 1987). Studies have also shown that chronic exposure to low ammonia concentrations between 1.2 to 7.71 mg/m^3 may cause obstructive pulmonary diseases (Brautbar *et al*., 2003). Research is, however, limited whether the additive effect of NO, NO_2 and NH_3 at low concentrations, as identified during this study, may pose a health risk to mine workers working underground.

One of the most prominent symptoms of NO_x exposure is red and irritated eyes. On contact, NO_x dissolves in the moisture of the eye to form nitric acid which can be irritating to the eyes (AEISG, 2011). These symptoms were observed amongst certain SWOs which could have been a result of the presence of NO_x in the ambient air. However, this was only an observation made as no data are available to substantiate this finding.

Figure 3.1 compared the NO_2 and NH_3 exposure levels between the active and passive sampling methods. From Table 3.1 and Figure 3.1, it is apparent that the highest mean TWA exposure levels for NO_2 and NH_3 were obtained from the active air sampling methods. A Wilcoxon matched pairs test also confirmed that there was a statistical significant difference between the results of the active and passive sampling methods for NO_2 ($p = 0.00078$) and NH_3 ($p = 0.044$) with the active method sampling higher than the passive method. From the results, it was conclusive (95% confidence) that the active air sampling methods recorded higher results in comparison to those of the passive method. Subsequently, the two sampling methods cannot be substituted for one another. In accordance with this study, other research has suggested that passive diffusive air samplers tend to underestimate exposure concentrations when compared to other sampling mediums, although field research is still limited to be conclusive (Hafkenscheid *et al*., 2009).

This discrepancy between the two methods was also confirmed by the Bland-Altman plots, Figures 3.3 and 3.4, which indicated a poor agreement between the active and passive air sampling methods for NO_2 and NH_3. The differences between the results (8-hour TWA exposure levels) of the active air sampling methods were 91.1% higher for NO_2 and 36.1% for NH_3 when compared to the results of the passive diffusive methods. The difference between the two sampling methods also tends to get larger as the average between the two methods increased. Several points on the Bland-Altman Plots were also scattered across the graph, above and below the zero, which suggested that there was no consistent bias of one method (approach) versus the other.

The difference between the two sampling methods may be ascribed to external environmental factors such as relative humidity, temperature and air movement within the sampling areas that could have affected the reliability of the sampling media, especially with regards to the passive diffusive samplers. According to Šerevičienė and Paliulis (2012), the effects of temperature and relative humidity can have a significant impact on passive diffusive samplers. They found that temperatures above 30 ^{o}C and humidity levels in excess of 75% may affect the accuracy of the passive samplers by 65% and 90% when compared to other methods (e.g. electronic gas analyser). This may be ascribed to the sampling rate of the samplers that are dependent to ambient temperature, because the temperature modifies the concentration of the water vapour that influences the efficiency of the NH_3 and NO_2 absorption through the diffusive cartridge (Šerevičienė and Paliulis, 2012). High humidity levels are also known to alter the absorption behaviour of the exposed outer diffusive body and inner cartridge, especially if condensation occurs (Brown, 2000; Hafkenscheid *et al*., 2009). The reliability of this sampling technique under varying environmental conditions may, therefore, be subject to controversy. It has also been established that the absorption of large quantities of water by the diffusive body and cartridge may also affect the passive sampler's performance and diffusion capabilities (Hafkenscheid *et al*., 2009). This study suggests that the moist underground conditions created by the perspiration of mine workers due to their hard physical labour as well as wetting methods used to suppress dust and gas concentrations may have affected the passive badges.

Results in Table 3.3, indicated that there was a poor relationship (r-values) between the two sampling methods as confirmed by the p-values of the Wilcoxon matched pairs test. The NO_2 ($r = -0.323$) and NH_3 ($r = 0.090$) recorded on the active and passive sampling media of the SWOs yielded no meaningful correlation between the two sampling methods. A possible explanation for the poor correlation between the active and passive sampling methods may be ascribed to the environmental factors that may have influenced the results of the passive samplers (Šerevičienė and Paliulis, 2012). The poor correlation may also be ascribed to the active air sampling methods that were recoding higher exposure results in comparison to that of the passive sampling methods for NO_2 and NH_3.

One correlation of medium effect as described by Field (2009) was obtained between NO (active) and NH_3 (active), as indicated in Table 3.3. There is extensive research available on the conversion of NO to NO_2 after the detonation of ANFO explosives, however, no information is presented on the blasting gas formation or relationship between NO and NH_3. The results, however, suggested that both NO and NH_3 will be liberated as by-products during the detonation of ANFO explosives under certain mining conditions. When both of these gasses are sampled, an increase in one of the gasses will result in an increase of the other due to the positive correlation ($r = 0.486$) between the gasses. There was also no significant correlation between the remaining blasting gasses. The poor correlation between NO (active) and NO_2 (active) may be ascribed to the formation of NO_2 through the oxidation of NO. The formation of NO_2 after blasting is greatly dependent on the NO and ozone concentrations present in the air (Düring *et al*., 2011). Generally the NO_2 concentration within the blasting area tends to be far lower than the NO concentration which may also be an indication of the lower NO_2 exposure levels detected during the study. Due to the poor correlation between NO_2 and the other blasting gasses (i.e. NO and NH_3) liberated during blasting, each of the gasses should be individually sampled by means of personal or static monitoring since there was no meaningful correlation.

Although passive sampling is a cost effective and an easy to use method for the sampling of respiratory exposure, this technique under varying circumstances and environmental conditions as presented underground is subject to controversy as found in this study and various other researches. The active air sampling methods appeared to be less affected by environmental conditions and on average sampled higher in comparison with the passive diffusive samplers.

3.6 Conclusion

A quantitative research design was carried out to evaluate the mine workers' respiratory exposure to blasting gasses emitted after the detonation of ANFO explosives and to indentify whether the control measures at the mine were adequate in the prevention of exposure. The mine workers' (Scraper Winch Operators) exposure to NO, NO_2 and NH_3 measured by means of an approved active air sampling methodology complied to their respective OELs (MHSA, 1996) in all instances. However, one of the Scraper Winch Operators had an ammonia gas exposure level of 9.830 mg/m^3 which exceeded the action level (50% of the OEL). The results of the passive diffusive samplers generally underestimated the respiratory exposure of the SWOs and, therefore, are considered unreliable for the sampling of blasting gasses in an underground environment. The actual exposure results of mine workers cleaning inside the stopes could also not be determined since the results had to be time weighed to an 8-hour TWA exposure level in order to compare them to the OELs of the Mine Health and Safety Act (No 29 of 1996). Therefore, short term exposure measurements (15 min STEL) may provide valuable information on the actual blasting gas concentrations (at different time periods) present in an underground mine during cleaning operations.

Results between the two sampling methodologies (active and passive diffusive samplers) indicate that there was a statistical significant difference between the two sampling methods. Results confirmed that the passive diffusive samplers tended to sample lower in comparison with the respiratory exposure concentrations of the active air samplers. A possible explanation for this occurrence may be ascribed to the effect environmental conditions such as humidity and temperature had on the passive samples. Active air sampling media was less affected by environmental conditions and should rather be used for future sampling underground. Further research should, however, be conducted using other sampling techniques to determine the effectiveness and accuracy of the active air sampling methods and to determine whether it is an effective means for the measurement of mine workers' exposure to blasting gasses in an underground platinum mine.

The engineering and administrative control measures implemented at the underground mine were regarded as adequate to control mine workers' respiratory exposures to NO, NO_2 and NH_3 below their respective OELs. However, elevated ammonia exposures were recorded during the course of the study. A lowering of the CO concentrations as reflected by the mine's electronic CO monitoring system may not reflect a lowering of other blasting gasses (i.e. ammonia gas). Subsequently, blasting gas concentrations such as NH_3 gas should be taken into account when setting a safe re-entry period, in order to allow adequate time for the dilution of blasting gasses.

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CHAPTER 4: CONCLUDING CHAPTER

4.1 Conclusion

One of the objectives of this study was to determine whether mine workers cleaning the blasting areas underground after the detonation of ANFO explosives are subject to respiratory exposure of post blasting gasses NO, NO_2 and NH_3. According to the literature, the expected gasses emitted during blasting are carbon monoxide and nitrogen oxides (Attalla *et al*., 2008; Sasol, 2012). Results indicated that mine workers cleaning underground approximately three hours after the blasting process are exposed to low concentrations of NO, NO_2 and NH_3.

Results indicated that the mine workers' (Scraper Winch Operators) TWA occupational exposure to NO, NO_2 and NH_3 measured by means of active air samplers complied with the OELs stated in Regulation 22.9 of the MHS Act (No. 29 of 1996). However, one of the SWOs had an ammonia respiratory exposure concentration of 9.830 mg/m^3, which exceeded the action level (50% of OEL). As a result, the mine should include the airborne monitoring of ammonia into their monitoring programme as stipulated in Section 9.2 (2) of the Mine Health and Safety Act (No. 29 of 1996). By including such measurements, a baseline may be established to determine whether a low concentration inhalation health risk is presented to the mine workers cleaning underground after the detonation of explosives. This will also provide valuable information whether control measures (i.e. engineering, administrative and personal protective equipment) should be improved or implemented to reduce mine workers' exposure to ammonia. Furthermore, the respiratory exposure results of the passive diffusive air samples for NO_2 and NH_3 also complied with their respective OELs. Results between the two sampling methodologies (active and passive diffusive samplers) indicate that there was a significant difference between the two sampling methods for NO_2 ($p = 0.00078$) and NH_3 ($p = 0.044$) with a 95% confidence level that active sampling methods will record higher personal exposure results when compared to passive sampling methods. The passive sampling technique was, therefore, unreliable to measure the personal exposure of mine workers in an underground environment. The poor performance of the passive samplers in comparison to the active air samplers may be ascribed to environmental factors such as temperature and humidity which may have affected the absorption properties of the passive samplers considerably (Šerevičienė and Paliulis, 2012).

In addition, exposure results also suggested that the administrative and engineering control measures implemented at the mine under study was sufficient to lower mine workers' respiratory exposure below the occupational exposure limits. Blasting gas concentrations were lowered to a safe level (below action level) by means of mechanical ventilation which assisted with the dilution and removal of airborne pollutants liberated during blasting operations. In addition, dust and gas suppression measures (i.e. water hoses) were also implemented to control mine workers' exposures further. Administrative control measures, in co-operation with engineering control measures, allowed for the adequate dilution of airborne contaminants through the setting of a re-entry period (approximately three hours). CO gas concentrations were continuously monitored by means of an electronic gas detection system. Once the CO concentrations reached a safe level at the various blasting levels, the mine was re-opened for the night shift. The period between the re-opening of the shaft until the mine workers started cleaning underground also allowed for additional air changes which contributed to lower NO, NO_2 and NH_3 exposures. Although CO concentrations dropped to a safe level, several mine workers were, however, exposed to elevated ammonia levels, one of them exceeding the action level. The cause of the elevated ammonia exposure should be investigate and rectified by improving current control measures such as the ventilation parameters in those specific stopes. Although personal exposure concentrations to NO, NO_2 and NH_3 complied with their respective OELs, a cumulative and long-term exposure health risk may still be presented to the mine workers' at low concentrations. Studies have shown that long-term exposure to ammonia and nitrogen dioxide at low concentrations (1.2 – 7.71 mg/m^3) may cause obstructive pulmonary diseases as well as lung function impairment (Brautbar *et al.*, 2003; Bakke *et al*. 2004). In another study, occupational exposures of around 12 years to low concentrations of ammonia (6 mg/m^3) showed no significant changes in the respiratory systems of a group of workers at a sodium bicarbonate factory (Holness *et al*., 1989). Research regarding the long-term health effects is limited and inconclusive to be certain of the cumulative and long-term health effects associated with blasting gas exposure. Mine workers' exposure to blasting gasses and other airborne pollutants should, therefore, be controlled and mitigated to as low as reasonably practical, to prevent any future diseases from occurring.

The low respiratory exposures may also be ascribed to the results that were time weighed to an average 8-hour exposure value in order to compare the result to the OELs of the Mine Health and Safety Act (No. 29 of 1996). The actual exposure levels of the mine workers could, however, not be determined due to the variance between the mine workers' general cleaning practices (lasting on average 298 minutes) as well as the fact that blasting gas concentrations liberated during blasting operations may vary from day to day. Blasting gas production is dependent on various factors such as the amount of ANFO explosives used, the composition of the explosives used, water vapour present in the stope blast holes, ventilation specifications at that specific stope, the re-entry period and many more. Short Term Exposure Limits (STEL) may, however, provide a better indication of the mine workers' actual exposure levels while cleaning at the blasting panel (face) within the first two hours when the highest gas exposures are expected.

Mine workers had mixed exposures to NO, NO_2, NH_3 and other blasting gasses, which may have an additive health effect on the respiratory system. Their mixed exposures to NO, NO_2 and NH_3 were determined and evaluated to the standard of 1 for exposures with an additive effect (HCS Regulations, 1995). All of the mine workers' had a mixed exposure below the standard of 1 and, therefore, a cumulative health risk was not presented. However, studies have shown that the cumulative exposure of tunnel construction workers to blasting gasses, airborne dust and other airborne pollutants can result in a decrease in lung function measured as forced expiratory volume in one second (FEV_1) (Bakke *et al*., 2004). Exposure to blasting gasses should, therefore, be mitigated and controlled to reduce mine workers' exposure since blasting gasses are not the only hazardous substances presented to underground mine workers. According to Unsted (2001), underground mine workers are also subject to mixed exposures which may include blasting gasses, respirable dust and exhaust fumes amongst others. Subsequently, the combined effect of these mixed exposures may present mine workers with adverse health effects.

The statistical results of the blasting gas concentrations at blasting levels 33-35 (n = 3), 36 (n = 8) and 37 (n = 9) were not significant due to a lack of quantitative data. However, it was noted that various blasting levels recorded higher NO and NH_3 concentrations when compared to the other levels which may be an indication of the ventilation specifications and parameters (i.e. fan size, the number of auxiliary fans, air flow, rate of fresh air supply, gullies diameters, etc.) that varied from one level to another. The ventilation parameters of these blasting panels and stopes should be re-assessed to ensure adequate ventilation and dilution of blasting gasses. In addition, factors such as wet stope blast holes, contamination of explosives, rock formation and the oxygen content present in the atmosphere may have been some factors also contributing to higher NO, NO_2 and NH_3 concentrations (Rowland III and Mainiero, 2000). Any external factor which may affect the full decomposition of ammonium nitrate into its thermodynamic favoured end products, may result in the formation of NH_3, NO_x and CO (AEISG, 2011). The formulation (fuel oils/ammonium nitrate ratio) specifications of the blasting agent (DDS^{TM} Sensitised Emulsion) used underground may also have contributed to higher NH_3 formation. According to Sasol's MSDS, the expected gasses to be liberated after the detonation of explosives in a controlled environment are nitrogen oxides and carbon monoxides (Sasol, 2012). The presence of ammonia in the atmosphere may also be as a result of the external and environmental factors present underground which may have affected the full decomposition of Sasol's blasting product (Rowland III and Mainiero, 2000).

The following research questions were asked at the beginning of this study (Chapter 1):

Firstly, are mine workers cleaning at the blasting area approximately three hours after the blasting process exposed to NO, NO_2 and NH_3 at concentrations exceeding their respective OELs?

The question can be answered: No, results indicated that all of the mine workers had personal exposure levels to NO, NO_2 and NH_3 that complied with (below) their respective OELs (stated in Regulation 22.9 of the Mine Health and Safety Act No. 29 of 1996).

Secondly, will there be an association between the results of the simultaneous active and passive sampling measurements?

The question can be answered: No, data indicated that there was no association between the results of the active and passive sampling measurements. It was established that the active air sampling method recorded significant higher exposure results in comparison to the passive sampling method. The passive diffusive samplers generally underestimated the SWOs exposures in comparison to that of the active air samplers.

4.2 Challenges sampling underground

Data capturing during the course of the study had several implications and limitations which will be discussed and addressed for future studies:

Sampling equipment and their limitations when sampling underground

- Various environmental factors such as humidity and temperature had a negative impact on sampling tubes and diffusive bodies/cartridges as previously explained which affected numerous samples during the course of study which had to be repeated. In some instances, even the addition of the de-humidifier tube in front of the NO_x sampling train was affected by the wet underground conditions. The added tube to the NO_x sorbent tube series made it impractical and difficult to attach it to the respirator zone of the mine worker. In addition, the long active sampling train hindered the mine worker's body movement in an already confined environment. Due to the length of the NO_x tube series, the front end dragged through the muddy surface during crawling tasks which blocked the opening of the tube with mud. Additional clip-on's were attached to the tubes to prevent this from occurring.

- Simultaneous measurements were conducted to determine whether there is a correlation between the active and passive sampling methodologies for NO_2 and NH_3. This was difficult due to the loss and possible tampering of samples. In some instances, the diffusive body and cartridge attached to the supporting plate were lost due to possible design flaws. The diffusive body was also contaminated by water vapour and dirt which may have affected the movement of air through the outer diffusive body into the inner absorption cartridge (Brown, 2000; Hafkenscheid *et al*., 2009). All contaminated and lost samples had to be repeated along with the active air samples, which could be a costly process. Due to the loss of passive diffusive samples in response to the environmental conditions on them, active air sampling methodologies should be used in favour of passive diffusive air sampling methodologies for future studies.

- The pre-drying tube also required specialised tubing since the diameter of the sulphate tube was smaller than those of the NO and NO_2 triethanolamine tubes. The tubing provided with the triethanolamine tubes was unsuitable to secure the pre-drying tube on the front end of the active sampling series. Tubing of a smaller diameter was required to rectify this problem.

- NIOSH method 6014 had detailed sampling specifications that had to be adhered to for the sampling of NO and NO_2. This method states that NO_x sampling should be conducted at a flow rate of 0.025 l/min over a 240 minute sampling period, in order to prevent a chemical breakthrough within the triethanolamine treated molecular sieve tubes. However, this was not always practical since a dual adjustable low flow holder was used for the simultaneous active sampling of NO, NO_2 and NH_3. By removing the NO_x tubes after 240 minutes from the dual adjustable low flow holder, the sampling rate within the NH_3 tube would have been affected. Subsequently, the NO_x tubes along with the remaining sampling equipment (i.e. NH_3 active and NO_2/NH_3 passive) were only removed once the mine workers had completed their cleanup work underground (on average 298 minutes per SWO). No NO_x breakthrough was observed within the tubes. NIOSH method 6014 was, therefore, impractical when sampling mine workers' respiratory exposure along with other blasting gas analytical methods.

- Although the Scraper Winch Operators' personal exposures were evaluated, they do not reflect the actual blasting gas concentrations present inside the stopes. During their normal working shift, mine workers do not clean for their full 8-hour shift. The use of static air monitoring for example direct reading instrumentation may provide more insightful data regarding the Short Term Exposure Limits (STEL), TWA exposures and peak concentration values detected underground.

- Direct reading instruments can be considered as an alternative method to evaluate mine workers' personal exposures to CO, NO, NO_2 and NH_3. However, the use of direct reading instruments were not considered due to the lack and shortage of calibrated equipment as well as a lack of devices fitted with all the necessary gas detection sensors for the sampling of CO, NO, NO_2 and NH_3.

- NIOSH methods 6014 and 6015 required the use of a low flow rate which would not have been possible without a constant pressure low flow controller (SKC® 224-26-CPC), a dual adjustable low flow holder and low flow calibrator. The calibration of the sampling pumps using the dual adjustable low flow holder at low sampling rates (0.025 l/min and 0.2 l/min) proved difficult and a time consuming process.

- Wearing of the active and passive sampling equipment may have interfered with the mine workers freedom of movement. Furthermore, sampling equipment in addition to heavy lamp batteries and rescue packs may also have increased the physical load on the workers. Subsequently, mine workers were generally hesitant to wear sampling equipment.

4.3 Future investigations

The following considerations should be taken into account for any future studies:

- Include a larger sampling group. The current sample size limited results as well as the statistical analysis thereof.

- Sampling methodologies such as active air sampling methods and direct reading instrumentation should be used and compared to one another to evaluate mine workers' respiratory exposures, to establish an effective means of determining mine workers' respiratory exposures underground. The testing should only be done if the correct electronic sensors are acquired and fitted to each of the devices for the simultaneous measurement of CO, NO, NO_2 and NH_3. Ensure that all direct reading instrumentation is calibrated and certified by the manufacturer or an approved SANAS accredited facility.

- If practical, electronic direct reading instrumentation may be used inside strategic locations within the stope to measure the blasting gas concentrations continuously during and after the detonation of explosives. This will provide valuable information regarding the formation of gasses for example NO oxidising to NO_2, concentration statistics (peaks, STEL etc) and the effectiveness of control measures. The results can also be used to compare the CO concentrations measured by means of the electronic direct reading instrument to that of the mine's central CO monitoring system used to establish the re-entry period.

- Short term exposure measurements (active or electronic) should be conducted to determine mine workers' respiratory exposure to blasting gasses within the first two hours of their work shift when gas concentrations are expected to be the highest.

- Finally investigate whether mine workers' cumulative exposure to blasting gasses can have a negative effect on their respiratory functions (FEV_1) through spirometry testing in a underground platinum mine (Bakke *et al*., 2004).

4.4 Recommended actions

The following actions are recommended to reduce and control mine workers' respiratory exposure and manage the health risks associated with blasting gas exposure:

4.4.1 Engineering control measures

4.4.1.1 Ventilation changes

The ventilation parameters at Blasting Level 36 should be re-assessed to ensure adequate fresh outside air supply to the relevant blasting panel for the removal and dilution of airborne pollutants. A re-assessment of the ventilation layout should include amongst others:

- The rate of fresh air supply to the blasting panel should be determined;
- Removal of any equipment (i.e. support beams) or broken ore which may hamper air flow within the stoping area;
- The layout and positioning of brattices or ventilation curtains may be repositioned within the gullies to improve air flow;
- Limit air flow movement to worked out areas by ensuring that old ventilation holdings and worked out areas are adequately sealed off;
- Install additional auxiliary fans to improve ventilation parameters inside the various sections of the stope.

4.4.1.2 Explosive formulation and quality assurance

The sources of blasting gas formation, especially ammonia gas, should be investigated to minimise the generation of ammonia gas amongst others and to mitigate this hazard. The following changes may be implemented to reduce the formation of post blasting gasses:

- Ensure that the stope blasting holes are completely dry with compressed air hoses before loading explosives, in order to limit the contamination of explosives with water vapour;
- Stope blast hole liners or gas bags may be used to prevent the ingress of water and moisture into the explosive column (stope blast holes);
- The practice of loading the low lying stope blast holes should be loaded last as water may seep into these areas during loading operations;
- Post blasting gasses can also be reduced by the correct formulation of explosives regarding oxygen, ammonia nitrate and fuel/oil content.

4.4.2 Administrative control measures

- Mine workers who are responsible for the loading and charge up of ANFO explosives should be trained in the correct handling, loading and charge up practices as well as the sources which may affect and increase the formation of blasting gasses during detonation operations;

- Mine workers cleaning at the blasting panel after the detonation of explosives should be informed on the health risks associated with blasting gas exposure as well as the use of control measures to reduce their exposure;

- Explosive manufactures should be informed of the importance to test their products in conditions similar to those present in an underground mine to establish the types and concentrations of blasting gasses liberated during detonation. MSDS should be updated accordingly;

- The sleep time between the loading and detonation of explosives should be reduced so as to limit the deterioration of the stope blast holes as well as the contamination of explosives with water;

- Personal air sampling of Scraper Winch Operators to ammonia gas should be included into the mines occupational hygiene monitoring programme;

- Ammonia concentrations along with the current CO concentrations should be taken into consideration when establishing the re-entry period.

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