Dermal exposure to arsenic and lead at a base metals refinery

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The larger and greater the support behind you, the closer you can get to your goal - Kakashi Hatake (Naruto Shippuden, TV TOKYO)

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SUMMARY

Title: Dermal exposure to arsenic and lead at a base metals refinery

Background: South Africa is the world's most prominent supplier of platinum group metals. The refining of platinum group metals consists of three main processes namely: smelting, base metal refining and precious metals refining. Dermal exposure to both arsenic and lead has been found to occur during the smelting process of precious metals (Gorman Ng *et al*., 2017). It is therefore anticipated that exposure to arsenic and lead could also possibly occur during base metals refining (BMR).

Objectives: To quantify and compare the dermal exposure of refinery workers to arsenic and lead in the various sampling areas with each other, to compare the exposure on the various anatomical areas with each other and to quantify arsenic and lead workplace surface contamination in order to identify potential sources of exposure.

Method: Wipe samples (Ghostwipes^{TM}) were collected from the palm, wrist and forehead of workers at various times during the working shift, in one administrative and two production areas within the refinery. In the administration area two workers gave consent to participate in this study. In each of the production areas, six workers gave their consent to participate in this study. Ten wipe samples were collected from each worker per day in the administrative area, only eight wipe samples were collected per worker per day in production area A and B. Additionally, surface wipes were collected to identify potential sources of contamination. A total of 132 wipe samples (112 dermal, 14 surface, 3 media blank and 3 field blanks) were collected during sampling. The collected samples were analysed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) by a South African National Accreditation System accredited laboratory for arsenic and lead.

Results: The analytical method used had a detection limit of 1 µg for arsenic and lead. None of the wipe samples contained arsenic at a detectable concentration. Additionally, 14% of the collected wipe samples contained lead at a detectable concentration. The palm received the highest exposure concentration (0.318 µg/cm^2) followed by the wrist and lastly by the forehead. Nine of the wipe samples collected from the palm of workers contained lead above the detection limit. Only one of the wrist and forehead wipes collected contained lead above the detection limit. Workers in production area A received higher lead exposure than those in production area B. Surface wipes collected in the administrative area, dirty change house and from the personal protective equipment used by the workers, was contaminated with lead.

Conclusion: During the refining process of base metals, workers were not exposed to an arsenic concentration above 1 µg and only six of the workers experienced lead exposure above 1µg. The palm of workers received the highest exposure to lead in both the production areas, which suggests that the palm is the primary area of exposure for the refinery workers. Surface and skin wipe samples indicated that surfaces can act as a source of additional exposure to lead. The control measures already implemented by the refinery prevents workers direct contact with these hazardous substances, which reduces workers' dermal exposure.

Keywords: arsenic, lead, base metals refinery, dermal exposure.

Words: 524

PREFACE

This mini-dissertation was written in article format in accordance with the specifications for the journal Annals of Work Exposures and Health. The author's instructions for this journal are located in the beginning of Chapter 3. This journal requires that references in the text should be in the form Jones (1995), or Jones and Brown (1995), or Jones *et al*. (1995) if there are more than two authors. References must be listed in alphabetical order by name of first author, using the Vancouver style of abbreviation and punctuation.

This mini-dissertation is written according to United Kingdom English spelling. An exception was made for the names and references used. The contributions of the listed co-authors are given in Table 1. Chapter 1 consists of a general introduction, problem statement related to base metal refining, research aim, objectives and hypotheses of the study. Chapter 2 comprises of a literature review. Chapter 3: Dermal exposure to arsenic and lead at a base metals refinery, written in a format that meets the journal Annals of Work Exposures and Health specifications. Chapter 4 includes a concluding chapter with recommendations, study limitations and future research suggestions. Appendix A: Declaration of language editing. Appendix B: Ethics approval document. Appendix C: Turn-it-in report.

Table 1: Authors contribution

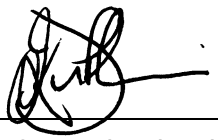
Author	**Contribution to the mini-dissertation**
Mnr. B Stofberg	• Study design, planning and data collection. • Conducting monitoring at the base metals refinery, data interpretation, writing of the article and formulation of recommendations. • Literature research. • Writing of the mini-dissertation.
Dr. S.J.L. Linde	• Supervisor. • Assisting with the study planning and design. • Approving the study protocol. • Professional guidance and recommendations. • Assisted with communication with the participating base metals refinery. • Assisted with interpretation of results. • Review of the mini-dissertation.
Prof. J.L. du Plessis	• Co-supervisor. • Assisting with the study planning and design. • Approving the study protocol. • Professional guidance and recommendations. • Assisted with interpretation of results. • Review of the mini-dissertation.

Table 1: Authors contribution continued

Author	Contribution to the mini-dissertation
Miss. M.M. Young	• Co-supervisor. • Assisting with the study planning and design. • Approving the study protocol. • Professional guidance and recommendations. • Assisted with interpretation of results. • Review of the mini-dissertation.

Mr. B. Stofberg

Dr. S.JL. Linde



Prof. J.L. du Plessis

Miss. M.M. Young

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

I declare that I have approved the 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 B Stofberg's MHSc (Occupational Hygiene) mini-dissertation.

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Units	Description
µg/cm²	Microgram per centimeter squared
%	Percentage
°C	Degrees Celsius
mg/m³	Milligram per cubic metre
µg/g creatinine	Microgram per gram of creatinine
cm²	Squared centimetres
ml	Millilitre
<	Smaller than
µg	Microgram
cm	Centimetre

LIST OF ABBREVIATIONS

Abbreviation	Description
√	Square root
ADP	Adenosine diphosphate
As	Elemental arsenic
As^{3+}	Arsenite
As^{5+}	Arsenate
ATSDR	Agency for Toxic Substances and Disease Registry
BDL	Below detection limit
BEI	Biological exposure indices
BMR	Base metals refinery (BMR)
Cu_2S	Chalcocite
Cu_5FeS_4	Bornite
DMA	Dimethylarsinic acid
DME	Department of Minerals and Energy
DNA	Deoxyribonucleic acid
DOL	Department of labour
e.g.	For example
et al.	And others
FeS	Trolite
FFP2	Free flight phase 2
G2/M	DNA damage checkpoint
HCS	Hazardous chemical substances
HREC	Health research ethics committee
IARC	International Agency for Research on Cancer
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
Inc	Incorporated
LOD	Limit of detection
MHSA	Mine Health and Safety Act
MMA	Monomethylarsonic acid
n	Number of samples
N/A	Not applicable
Ni_3S_2	Heazlewoodite
NIOSH	National Institute for Occupational Safety and Health
NIOSH 7303	Elements by ICP 7303 (Hot Block/hcl/HNO3 Digestion)
NMF	Natural moisturising factor
NWU	North-west university
OEL-CL	Occupational exposure limit – control limit
OEL-RL	Occupational exposure limit – recommended limit
OHHRI	Occupational Hygiene and Health Research Initiative
OHSA	Occupational Health and Safety Act
OSHA	Occupational Safety and Health Administration
OSHA ID-125G	Metal and metalloid particulates in workplace atmospheres
p21	Cyclin-dependent kinase inhibitor
p53	Suppressor protein
Pb	Lead
PGMs	Platinum group metals
PMR	Precious metals refinery
PPE	Personal protective equipment
SANAS	South African national accreditation system

SB	Stratum basale
SC	Stratum corneum
SG	Stratum granulosum
SIMRAC	Safety in Mines Research Advisory Committee
SK	Able to penetrate the intact skin and be absorbed into the body
SL	Stratum lucidum
SOD	Superoxide dismutase
SS	Stratum spinosum
TM	Trademark
TWA	Time weighted average
UV	Ultraviolet
WHO	World health organisation
β	Beta
δ	Delta

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CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

Platinum group metals (PGMs) consist of platinum, rhodium, palladium, iridium, osmium and ruthenium. The use of PGMs have increased since 1975, due to their corrosion resistance, catalytic qualities and high melting points (PricewaterhouseCoopers Inc., 2016; Fernandez, 2017). South Africa is the world's most prominent supplier of PGMs and was responsible for 73% of global platinum production, 82.4% of rhodium production and 38.9% of palladium production in 2017 (Chamber of Mines of South-Africa, 2018). The process of PGMs purification consists of three main processes namely: smelting, base metal refining and precious metals refining (Cramer, 2008). After ore rich in PGMs has been mined, the PGMs are isolated into a floatation concentrate that consists of nickel-copper-iron sulphides. This concentrate is then smelted and converted to a nickel-copper sulphide matte. After the matte has cooled, it is crushed to liberate the magnetic alloy platelets, which can then be removed by magnetic separation. The magnetic fraction is then treated in leaching steps and the resulting PGM concentrate is sent to the precious metals refinery (PMR) to be refined into individual PGMs (Crundwell *et al.,* 2011). The magnetic separation and leaching steps of the copper-nickel sulphide matte pose the greatest risk to workers due to the presence of various metals that are liberated during these processes.

PGMs occur naturally with major base metals such as cobalt, copper, iron and nickel as well as minor metals such as arsenic, lead and tellurium. During the refining of base metals, lead is removed from the floatation concentrate and this increases the workers' risk of potentially being exposed to lead (Phetla et al., 2010). However, it is unclear during which process of base metals refining workers may be exposed to arsenic. One possibility is that when the floatation concentrate is heated to a temperature of 480°C, arsenic turns from a solid into a gas and escape into the atmosphere (Sanders, 1926; Mpinga *et al*., 2015).

Cherrie *et al*. (2006) stated that in an occupational setting, inhalation exposure is considered to be the most important route in terms of toxicity, followed by dermal contact and lastly ingestion. The skin as a route of exposure has received some attention during exposure assessment of workers in occupational settings. Numerous studies have stated that the dermal route of exposure has been neglected and should receive more attention when determining the exposure of workers to hazardous chemicals (Fenske, 1993; van Hemmen and Brouwer, 1995; Soutar *et al*., 2000; Semple, 2004; Ouypornkochagorn and Feldmann, 2010; Flora *et al*., 2012; Behroozy, 2013; Anderson and Meade, 2014).

The released arsenic can settle on various surfaces, such as personal protective equipment or working surfaces, on workers clothing or on the skin of workers. Contaminants (such as arsenic and lead) that have settled on surface may in turn act as an additional source of dermal contamination or may be re-suspended into the air, which can then settle on additional surfaces, clothing or the skin of workers (Schneider *et al*., 1999; Schneider *et al*., 2000). Additionally, workers may also transfer the contaminants from their skin onto workplace surface when coming into contact with them, creating additional sources of contamination. Du Plessis *et al.* (2010) and Julander *et al.* (2010) indicated that workplace surfaces can be potential sources of exposure. This increases the workers risk of dermal exposure to arsenic. It is important to consider the influence that contaminated surfaces has on dermal exposure.

Workers' dermal exposure to metals such as arsenic, cobalt, chromium, lead, nickel and soluble platinum has previously been reported in various occupational settings (Lidén *et al*., 2006; Du Plessis *et al*., 2013; Gorman Ng *et al*., 2017; Linde *et al*., 2018). These studies investigated the dermal exposure of workers on the palm, back of the hand, the whole hand, wrist, lower arm, perioral area, neck and forehead. Lead has received much more attention than arsenic and a substantial number of occupational dermal exposure studies to lead exist (Hughson, 2005; Ouypornkochagorn and Feldmann, 2010; Koh *et al*., 2015; NIOSH, 2017).

Arsenic and lead pose a significant risk to the workers' health. Arsenic exposure may lead to the development of skin cancer (squamous cell carcinoma and basal cell carcinoma) as the skin is the most sensitive organ to arsenic exposure. Lead exposure may cause peripheral neuropathy (in adults), anaemia and immune system impairment (Goyer, 1990; SIMRAC, 2000; Yu *et al*., 2006; ATSDR, 2007; Rosin, 2009; Ouypornkochagorn and Feldman, 2010; Hong *et al*., 2014; Mason *et al*., 2014). Therefore, it is important to assess workers' dermal exposure to arsenic and lead.

As mentioned earlier, the purification of PGMs consists of three purification processes (smelting, base and precious metal refining) (Cramer, 2008). Only Gorman Ng *et al.* (2017) investigated the dermal exposure of workers to various contaminants, including arsenic and lead, during the smelting of precious metals. Gorman Ng *et al*. (2017) found that workers were exposed to both arsenic and lead during the smelting process of PGM purification. No other dermal exposure studies at a base metals refinery (BMR) or precious metals refinery (PMR) investigated the dermal exposure of workers to arsenic and/or lead.

This study investigated the arsenic and lead dermal exposure of workers at two production areas and one administrative area of a South African BMR. The administrative area served as a control area, due to workers not entering the production areas.

This study served as a means to indicate in which of the two production areas the highest dermal exposure occurred and also to indicate the anatomical area with the highest arsenic and lead exposure.

1.2 Aim and Objectives

The general aim of this study was to assess the dermal exposure of workers to arsenic and lead at a South African base metals refinery.

The specific objectives of this study were:

1. To quantify and compare the dermal exposure of base metals refinery workers in two production areas and one administrative area to arsenic and lead, through the use of skin wipe sampling.
2. To compare the dermal exposure on the various anatomical areas with each other for both arsenic and lead.
3. To quantify arsenic and lead workplace surface contamination in the three working areas in order to identify potential sources of exposure.

1.3 Hypothesis

Gorman Ng *et al.* (2017) indicated that workers' skin was exposed to both arsenic and lead during the smelting of precious metals. No other dermal exposure studies at a base metals refinery (BMR) or precious metals refinery (PMR) have investigated the dermal exposure of workers to arsenic and lead. Therefore, it is hypothesised that workers experience dermal exposure to arsenic and lead at detectable levels during the magnetic separation of PGMs from the base metals and subsequent leaching steps.

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CHAPTER 2: LITERATURE STUDY

2.1 Introduction

This chapter is divided into eight sections, namely an introduction to the refining of the platinum group metals (PGMs), the structure of the skin and its physiological function, the toxicology and health effects of arsenic and lead, the skin wipe sampling method, published literature on dermal exposure to arsenic and lead and the South African occupational health and safety regulations regulating exposure to arsenic and lead.

As stated in Chapter 1, the dermal route of exposure has been neglected when determining a worker's exposure to hazardous chemical substances (HCS) with only one study reporting dermal exposure to arsenic and lead at a precious metals smelter (Gorman Ng *et al.*, 2017). No other studies have determined whether refinery workers working at base metals refinery (BMR) or precious metals refinery (PMR) are being exposed to arsenic and/or lead. Data on occupational dermal exposure to arsenic is limited to a few studies, while numerous studies report the dermal exposure to lead in various occupations (refer to Table 2-1) (Hughson, 2005; Ouypornkochagorn and Feldmann, 2010; Koh *et al*., 2015; NIOSH, 2017).

2.2 Purification process of Platinum Group Metals

After the ore, rich in platinum-group metals (PGMs), has been mined and crushed, the PGMs are isolated into a floatation concentrate, rich in PGMs. The floatation concentrate is produced by (1) crushing and grinding the ore to liberate copper, iron, nickel, PGMs and sulphide, (2) separating the liberated minerals into a PGM rich concentrate by froth floating. This concentrate is then smelted and converted to remove iron, silica and sulphur, resulting in a sulphide matte rich in PGMs. An air-oxygen mixture is then blown through the resulting matte to oxidise the sulphur and iron in the matte. This is done to produce a matte that is low in sulphur and iron content (Crundwell *et al.,* 2011).

The PGMs is then separated from the base metals and associated sulphur by magnetic concentration. During this process the converted matte is allowed to cool over a period of several days. The converted matte consists of bornite (Cu_5FeS_4), chalcocite (Cu_2S), heazlewoodite (Ni_3S_2) and trolite (FeS). This allows large crystals of chalcocite, heazlewoodite and metal alloys to develop. PGMs concentrate in the alloy phase during the cooling phase. The PGMs is then separated from the base metals and associated sulphur by magnetic concentration. Copper, cobalt, iron and nickel (magnetic fraction) are then removed from the magnetic fraction by leaching steps. The resulting PGM concentrate is then sent to a precious metals refinery to be refined into individual PGMs (Crundwell *et al.,* 2011).

The refining into individual PGMs occurs in three separation stages: (1) primary separation, where the particular PGM is separated from the other PGMs and impurities, (2) secondary purification, where the resulting product is then purified, (3) reduction to metal, where the product of the primary separation and secondary purification remains as a metal salt that needs to be reduced to metal (Crundwell *et al.,* 2011).

2.3 Skin structure and physiological function

The skin acts as a barrier between the external environment and the human body and consists of three layers, an upper layer called the epidermis, an inner layer called the dermis and subcutaneous tissues (hypodermis). The epidermis and dermis are separated by a basement membrane (Benson, 2011). The structure of the epidermis, dermis and hypodermis and factors that influence the permeation of metals through the skin will be discussed in the following section.

2.3.1 Epidermis

The epidermis consists of five layers (from outside to inside): the stratum corneum (SC), the stratum lucidum (SL), stratum granulosum (SG), the stratum spinosum (SS) and the stratum basale (SB) (Oláh *et al*., 2012). The SC serves as the primary protective barrier against ultraviolet (UV) radiation, physical and mechanical injuries, percutaneous penetration of microbes and chemicals and also regulates water loss from the skin (transepidermal water loss) (Elias, 2005; Proksch *et al*., 2008; Desai *et al*., 2010; Benson, 2011). Corneocytes in the SC, lack cell organelles and a nucleus. Cells are compacted and flattened with keratinisation increasing as they migrate outward (Benson, 2011). The SG consists of keratinocytes at a different level of differentiation (Menon, 2002). The keratinocytes in the SG contain intracellular keratohyalin granules. These granules are composed of keratin, loricin, a cysteine rich protein and profillagrin. The alignment and aggregation of keratin filaments are promoted by the fillagrin subunits of the profillagrin. Cells ascending in the SG extrude their lamellar bodies (containing SC chymotryptic enzyme associated with the desquamation process) to the intracellular domains (Egelrud, 1993; Menon, 2002).

The SL is a layer that is present mainly in the soles of the feet and palms of the hand (not found in thin skin) and is composed of four to six rows of highly refractive eosinophilic cells (Gartner and Hiatt, 2000; Young *et al.,* 2006; Gartner and Hiatt, 2007; Mescher, 2010; Pawlina and Ross, 2011; Kierszenbaum and Tres, 2012; Arda *et al.,* 2014). The SS consists of between two to six rows of keratinocytes. These rows are directly above the SB, which is a single layer of columnar keratinocytes cells attached to the basement membrane by hemidesmosomes and is the only layer of the epidermis that can undergo cell division (Menon, 2002; Benson, 2011).

The keratinocytes of the SG possess an enlarged cytoplasm, which contain a higher number of organelles and keratin filaments in comparison to those of the SB, and their morphology also changes from columnar to polygonal (Menon, 2002; Benson, 2011).

Each of the five layers of the epidermis represents a different level of epidermal or cellular differentiation (Brown *et al*., 2006). The migration of the keratinocytes, from the SB to the SC, results in a change of their composition and structure (Bouwstra and Ponec, 2006). During migration, precursor lipids are synthesised in the SB, SS and SG. These precursor lipids are assembled in the SS and SG within lamellar bodies (lipid precursor carriers). The content of these lamellar bodies (polar lipids) are released, through exocytosis, at the SG-SC interface. These polar lipids undergo significant metabolic changes and are enzymatically converted into their non-polar counterparts and finally form lamellar structures around the corneocytes (Bonte *et al.,* 1997; Weerheim and Ponec, 2001; Loden, 2003; Bouwstra and Ponec, 2006). This migration causes the keratinocytes to mature (Bouwstra and Ponec, 2006). The cells that reach the SC are referred to as corneocytes (flattened dead cells filled with water and keratin) embedded in a lipid matrix and are known as the nonviable epidermis (Walters, 2002; Madison, 2003; Benson, 2011; Sahle *et al*., 2015). The skin is constantly renewed due to the continuous proliferation, differentiation and keratinisation of the keratinocytes (Brown *et al*., 2006).

The epidermis also contains various skin appendages (hair, sebaceous and sweat glands) and enzymes. The enzymes of the epidermis are involved with general homeostasis, natural moisturising factor (NMF) formation, metabolism of topically applied compounds, the desquamation process and keratinocyte maturation (Zeeuwen, 2004; Hachem *et al.*, 2005; Riviere, 2005).

2.3.2 Dermis

The dermis consists of a layer of connective tissue, primarily containing a cellular collagen/elastin matrix with fibroblasts embedded within and can be divided into the lower stratum reticulare and upper stratum papillare (according to collagen content and thickness). It also contains lymphatic channels, blood vessels (deep and superficial plexi) and sensory nerves (end corpuscles and free nerve endings). The lymphatic channels and blood vessels remove permeated substances. The sensory nerves include Meissner corpuscles, responsible for pressure and tactile sensation, and Pacinian corpuscles sensing vibration (Lai-Cheong and McGrath, 2009).

2.3.3 Hypodermis

The hypodermis, a loose layer of connective tissue is directly beneath the dermis and is composed of lipocytes that form fat lobules with interconnecting elastin and collagen fibres (Lai-Cheong and McGrath, 2009). Primary functions of the hypodermis include heat insulation, energy storage, protection against physical shocks and also aid in the attachment of the skin to the skeletal muscle and facia (Walters, 2002).

2.3.4 Permeation of metals through the skin and factors affecting their permeation.

Contaminants may be transported through the skin by means of transcellular absorption, intercellular absorption or by means of appendageal absorption (WHO, 2006; Larese Filon, 2018). Transcellular absorption involves the transfer of the contaminant through one cell membrane into the next, while intercellular absorption is the transport of the contaminant through the lipid-rich extracellular regions around the corneocytes. Appendageal absorption occurs when the contaminant enters the shunt of the sweat gland, hair follicles or sebaceous glands (WHO, 2006; Larese Filon, 2018).

Exogenous factors such as dose, protein reactivity, vehicle, molecular weight, valence state and the nature of chemical bonds and polarity of the metallic compound influence the permeation of metals through the skin (Hostýnek, 2003; Larese Filon, 2018).

An increased dose, may result in the increased permeation of the metal until a plateau value is reached and then decrease as the concentration increases further. However, the diffusion rate of certain transition metals is not proportional to the applied concentration. For other transitions metals, an increase in concentration results in a steady decrease in absorption. This may be due to electrophilic metals forming a secondary diffusion barrier as a result of stable bonds being formed with skin proteins, thus the electrophilic nature of the metal determines whether a depot will be formed. Protein reactivity of the metal and electrophilicity of an ion can be changed by changing the number of valence electrons, consequently influencing the diffusion of the metal (Hostýnek, 2003).

The size and counter ion of a metal compound correlates with the permeation of the compound through the skin (Hostýnek, 2003; Larese Filon, 2018). Smaller molecules (nanoparticles) penetrate and permeate the skin faster than larger molecules (macromolecules) (Larese Filon, 2018). A solvent (vehicle) can affect the permeation of a metal by influencing the rate at which the metal is released or by modifying the properties of the barrier (Hostýnek, 2003; Larese Filon, 2018). The lipophilic category, alkyl and aryl derivatives, of chemicals, poses a greater risk due to penetration (Hostýnek, 2003).

Several endogenous factors influence skin permeation such as the anatomical area where the contaminant comes into contact with the skin, age, hydration of the stratum corneum, gender, skin disorders and damage to the SC and desquamation rate (WHO, 2006; Vitorino *et al*., 2015).

The permeability of the different anatomical areas' may vary from each other due to differences in the functional characteristics and structure of the anatomical skin areas e.g. thinner facial skin is more permeable than the skin of the foot and palm (Feldmann and Maibach, 1967; Ngo *et al*., 2010). Thicker skin reduces the permeation of the contaminant through the skin, while the duration of skin contact can increase the permeation and penetration of the contaminant (Hostýnek *et al.,* 2001). Permeation in these areas may also be influenced by the presence of skin appendages such as hair follicles, sweat and sebaceous glands. These skin appendages may serve as an additional route of contaminant permeation (Otberg *et al*., 2004).

As the skin ages, the epidermis becomes thinner, the corneocytes become less adherent to each another and there is a change in the lipid composition and the dermis becomes relatively avascular, acellular and atrophic (Batisse *et al*., 2002). The reduced permeability of hydrophobic contaminants may be due to the lower hydration, lower surface lipid content and reduced blood flow of aging skin (Roskos *et al*., 1989; Walters, 2002). However, these factors may also reduce the barrier integrity of the skin (Hostýnek, 2003).

Differences in the permeation of contaminants between ethnic groups have been reported. However, some studies reports are inconsistent and suggest that the difference is much less profound (Darlenski and Fluhr, 2012; Vitorino *et al*., 2015). Several studies indicate that African skin is less permeable to certain contaminants than Caucasian skin (Wedig and Maibach, 1981; Berardesca and Maibach, 1990; Kompaore *et al.,* 1993). However, an *in vitro* study conducted by Franken *et al.* (2015) indicates that significantly more platinum permeated through African skin than through Caucasian skin.

Slight or no differences have been reported in the epidermal barrier between men and women (Tupker *et al*., 1989; Cua *et al*., 1990; Benson, 2011). Permeation may also be influenced by the state of the skin (diseased, abraded or normal). Diseases such as ichthyosis, eczema (dermatitis), psoriasis and acne vulgaris may result in the barrier function being compromised, causing increased permeation and allowing larger contaminants (that could previously not permeate through intact skin) to permeate the skin (Bouwstra and Ponec, 2006; Kezic and Nielsen, 2009; Benson, 2011). However, this may aid in the permeation of allergens and irritants, causing the barrier function to be degraded further and increasing the likelihood of sensitisation (Kezic and Nielsen, 2009).

2.4. Arsenic

Arsenic, a metalloid, is commonly found in either its neutral oxidation state as elemental arsenic (As), arsenite (As^{3+}) or as arsenate (As^{5+}) (Martinez *et al.,* 2011). Arsenic is mainly found in its inorganic form as arsenate, under aerobic conditions, and arsenite, under anaerobic conditions. Organic arsenic compounds are less toxic than inorganic arsenic compounds and arsenate is less toxic than arsenite (Sun *et al*., 2014). Both organic and inorganic arsenic compounds have been classified as human carcinogens according to IARC (Group 1) (IARC, 2018). Arsenic is used for medicine, in solders, herbicides, insecticides and as an alloying agent (ATSDR, 2007).

2.4.1 Toxicology

Possible exposure to arsenic can occur through inhalation, ingestion and dermal exposure (Anderson and Meade, 2014). Once arsenic has entered the body through either the gastrointestinal tract, lungs or skin, it is primarily distributed to the spleen, kidneys, liver, intestine, lungs, uterus and the skin. The skin is considered to be the most sensitive organ of all as exposure to arsenic can result in malignancies (ATSDR, 2007; Yu *et al.,* 2006). This may be due to the tendency of arsenic to accumulate in the dermis and epidermis following dermal exposure, which may result in skin cancer (squamous cell carcinoma and basal cell carcinoma) (Yu *et al*., 2006; Ouypornkochagorn and Feldman, 2010; Hong *et al*., 2014).

Bowen's disease, squamous cell carcinoma and basal cell carcinoma are considered the most common cancers induced by arsenic (Martinez *et al.,* 2011). Wollina (2015) defines Bowen's disease as a squamous cell carcinoma *in situ*, which may develop into a more invasive skin cancer. Both squamous cell carcinoma and basal cell carcinoma may develop as a result of arsenic-induced Bowen's disease. In both arsenic-induced Bowen's disease skin lesions in humans, and in cultured keratinocytes, DNA aneuploidy and G2/M cell cycle arrest are associated with arsenic exposure. These cellular abnormalities may lead to the development of cancer due to p53 dysfunction caused by arsenic (Yu *et al*., 2006). After a genotoxic agent has caused DNA damage, p53 transcriptionally induces the expression of p21. In turn p21 causes cell cycle arrest which allows the damaged DNA to be repaired before the cell cycle can continue. However, it was observed that following concomitant arsenic exposure there was a decreased expression of p21. This suggests that p53 function, following its poly (ADP-ribosy)ation, was inactivated by arsenite (Komissarova and Rossman, 2010). Arsenic may therefore, promote the mutation of several tumour suppressor genes, such as p53, through interferences with the DNA repair (Shibata *et al.,* 1994; Kelsey *et al.,* 2005). Shibata *et al.* (1994) and Kelsey *et al.* (2005) have reported that this may lead to an increased risk of developing bladder cancer.

Two metabolic pathways have been suggested for the metabolism of arsenic in the human body. In the first pathway, arsenate is reduced to arsenite with arsenite reductase. The second pathway involves oxidative methylation, in which arsenite is methylated, by using S-adenosyl methionine and glutathione as cofactors, resulting in the formation of mono- and dimethylarsinic acid (DMA^{5+}) (Sattar *et al*., 2016). It is thought that these methylated arsenicals are more toxic than inorganic arsenic (Thomas *et al*., 2007; Drobna *et al*., 2010).

Arsenate acts as an uncoupler of the mitochondrial oxidative phosphorylation. (Hong *et al*., 2014). The toxic effects of arsenic may also lead to: genomic instability and alterations in DNA methylation, oxidants and oxidative DNA damage, enhanced cell proliferation and impaired DNA repair (NRC, 2001; Rossman, 2003, Martinez *et al.,* 2011).

Arsenic that reaches the systemic circulation is primarily excreted in urine. Urinary excretion of arsenic is composed of 10 to 20% monomethylarsonic acid (MMA), 10 to 30% inorganic arsenicals and 55 to 76% dimethylarsinic acid (DMA) (NRC, 2001; IARC, 2011).

2.4.2 Short-term and chronic adverse health effects

Short-term adverse health effects of arsenic include a diffuse skin rash, acute psychosis, toxic cardiomyopathy, haematological abnormalities, pulmonary oedema, encephalopathy, seizures, peripheral neuropathy and respiratory and renal failure (Ratnaike, 2003; Khairul *et al*., 2017).

Chronic adverse health effects of arsenic exposure include: dermatological changes, i.e. palmar and solar keratosis, hyperpigmentation and skin lesions, malignant changes in the skin (squamous cell carcinoma and basal cell carcinoma), lungs, bladder, liver and prostate as well as leukaemia, increased risk of respiratory, cardiovascular and peripheral vascular disease, hepatotoxicity and nephrotoxicity (Ratnaike, 2003; Khairul *et al*., 2017).

2.5. Lead

Lead is a bluish-grey heavy metal that is commonly used because of its low melting temperature, corrosion resistance, its shape and malleability and it can be used to form alloys with other metals. Lead can be found, either in its organic or inorganic form, in batteries, weights, pipes, shot and ammunition, radiation shields and cable covers (ATSDR, 2007). According to IARC, organic lead compounds promoting carcinogenicity in humans are regarded as unclassifiable (Group 3) while inorganic lead compounds have been classified as a probable human carcinogen (Group 2A) (IARC, 2018).

2.5.1 Toxicology

Exposure to lead occurs via all three routes of exposure namely inhalation, ingestion and dermal exposure, with ingestion being the primary route of exposure (Fenga *et al*., 2017).

The gastrointestinal absorption of lead can occur either through diffusion of lead through the lumen of the gut or entrance of lead to the gut through pinocytosis. The absorption of ingested lead through the gastrointestinal tract ranges between 5 to 10% for adults. The gastrointestinal absorption of lead and can be increased by a diet low in calcium and iron (Ziegler *et al.,* 1978; Watson *et al*., 1986; Mushak, 1991).

Once lead enters the body, it is transported to soft tissue and organs, such as the heart, brain, kidneys, liver, spleen, muscles and lungs. The transport of lead in blood is performed primarily by erythrocytes, where it is bound to haemoglobin (ATSDR, 2007; Mason *et al*., 2014). The effect that lead has on the body is the same regardless of the route of entry into the body (ATSDR, 2007). The brain seems to be the primary target for lead toxicity in children while lead toxicity causes central nervous system damage and peripheral neuropathy in adults (Goyer, 1990; Mason *et al*., 2014).

The toxicity of lead, throughout body, is manifested through oxidative stress, which can occur either by generating reactive oxygen species or depleting antioxidant reserves (Flora *et al*., 2012). Lead forms a covalent bond with the antioxidant enzymes, leading to their inactivation (Flora *et al*., 2012). Lead inactivates enzymes such as glutathione, glutathione peroxidase, glutathione reductase, glutathione-S-transferase, δ-amino levulinic acid dehydratase, catalase and superoxide dismutase (SOD). This leads to further reduction of glutathione levels (Ahamed and Siddiqui, 2007). The reduction in SOD decreases superoxide radical removal (Flora *et al.,* 2007).

The majority of lead is excreted through urine and the remainder through faecal matter (one-third of total lead excretion) (ATSDR, 2007).

2.5.2 Short-term and chronic adverse health effects

Short-term adverse health effect of lead includes: vomiting, dyspepsia, constipation, abdominal colic, reversible renal damage, encephalopathy with confusion and peripheral neuropathies (SIMRAC, 2000; Rosin, 2009).

Chronic exposure results in renal failure, gastritis, anorexia, anaemia, interference with the synthesis of heme, steroid metabolism, increased blood pressure, brain damage, impaired peripheral nerve function, and impairment of the immune system (SIMRAC, 2000; Rosin, 2009).

2.6. Dermal exposure monitoring

Dermal exposure can be assessed by either removal methods, interception methods or the *in situ* detection method (Du Plessis *et al*., 2008; Behroozy, 2013).

Removal methods remove the contaminant from the skin by making use of an appropriate collection medium and consists of skin wipe sampling, tape stripping sampling, hand washing or rinsing methods and suction sampling (Du Plessis *et al*., 2008; Day *et al*., 2009; Behroozy, 2013). Skin wipe sampling was chosen for this study due to metals having low volatility, and thus remaining on the skin after exposure has occurred. The amount of contaminant removed from the skin indicates the concentration of the contaminants on the skin at the time the sample was taken and metals can be reliably analysed on wipes (Behroozy, 2013; Gorman Ng *et al*., 2017).

Dermal exposure may occur when contaminants that have settled on a surface become re-suspended into the air, consequently settling on additional surfaces, clothing or the skin of workers. Additionally, workers may also transfer the contaminants from their skin onto workplace surfaces when coming into contact with them, creating additional sources of contamination (Schneider *et al*., 1999). The workers' risk of dermal and respiratory exposure to arsenic and lead is increased. Du Plessis *et al.* (2010) and Julander *et al.* (2010) have indicated that workplace surfaces can be potential sources of exposure. Therefore, it is important to consider the influence that contaminated surfaces has on dermal exposure. Wipe sampling can also be used to assess the concentration of the contaminant on surfaces (Du Plessis *et al.,* 2010; Julander *et al.,* 2010).

2.6.1 Advantages and limitations of skin wipe sampling

The use of wipe sampling allows the researcher to determine workers' individual exposure to contaminants and also allows the comparison of the results obtained on different anatomical areas (Du Plessis *et al*., 2008; Behroozy, 2013). Wipe sampling provides an estimate of dermal loading, which can be used for risk assessments (Hughson, 2005). Skin wipe sampling has previously been used to assess the dermal exposure of workers to both arsenic and lead (Rodriguez and Aristeguieta, 2009; Gorman Ng *et al*., 2017).

The comparison between anatomical areas can only be made if the surface area sampled remains consistent (Du Plessis *et al*., 2008; Behroozy, 2013). Wipe samples are easily contaminated if the researcher does not change the gloves worn or template used after each sample has been collected. A standard protocol for the amount of force applied and the number of wipes needed during sampling is not available (Du Plessis *et al*., 2008; Behroozy, 2013).

2.7 Published dermal exposure data for arsenic and lead

Table 2-1 summarises the findings of previous studies regarding the dermal exposure to arsenic and lead in different occupational settings.

Results from previous exposure studies (Table 2-1) indicate that dermal exposure to arsenic and lead can be quantified through the use of wipe sampling. These studies also indicate that Ghostwipes^{TM} are an appropriate sampling medium to quantify the concentration of these contaminants on the skin. Various anatomical areas have been included to determine workers' occupational exposure to arsenic and lead by using skin wipe sampling techniques (Table 2-1).

Du Plessis *et al.* (2008) indicate in their study that the forehead, forearm and hands (palms and fingertips) have been the main anatomical areas considered when the dermal exposure of workers were quantified through the use of skin wipe sampling (Brouwer *et al.,* 2000; Day *et al.,* 2007). However, the study conducted by Hughson (2005) indicates that dermal exposure could also be quantified on other anatomical areas such as the chest and neck as well. The samples collected from the chest were used to investigate the degree of contamination underneath the work clothes. Hughson (2005) and Gorman Ng *et al.* (2017) collected samples from the perioral area to quantify the potential exposure of workers through inadvertent ingestion. These studies indicate that various anatomical areas can be used to quantify workers' exposure to contaminants and is not limited to only the neck, forehead, forearm and hands.

Wipe samples in these studies were collected using various different sampling procedures and materials. Sleeuwenhoek and Van Tongeren (2006) and Hughson (2005) indicate that the wipe samples of the various anatomical areas were obtained by three sequential wipes. Gorman Ng *et al.* (2017) and Rodriguez and Aristeguieta (2009) do not indicate the number of times the areas were wiped but only that the areas were wiped. Hughson (2005) and Gorman Ng *et al.* (2017) collected wipe samples from the workers at three different intervals. Hughson (2005) do not indicate at which interval the samples were collected during the working shift. Gorman Ng *et al.* (2017) indicated that samples were obtained at the beginning, during mid-break and at the end of the shift. Rodriguez and Aristeguieta (2009) only collected samples at the beginning and at the end of the working shift by wiping the area for 30 seconds. Only Hughson (2005) utilised a template, to demarcate the area to be wiped, during his study to collect wipe samples.

Sleeuwenhoek and Van Tongeren (2006) investigated the relationship between the pressure applied to an object over a period of time and the amount of dermal depositioning resulting from the contact. A procedure to simulate grasping or rubbing of a moving surface was included in the study. In the study the volunteers were asked to complete six tests, in which the volunteers held and rubbed lead objects. For the first three tests the volunteers applied pressure to the different objects and for the last three tests, the volunteers rubbed the object for different periods of time.

The study concludes that the surface loading of the hand increased with an increase in the number of contacts (Sleeuwenhoek and Van Tongeren, 2006).

Table 2-1: Overview of related data regarding arsenic and lead dermal sampling using wipes.

Exposure scenario	Sampling material	Anatomical area of exposure measurement		Exposure concentration (µg/cm^2)	Reference
Arsenic					
Glass beads blending and repacking	Moist towelette	Palm and back of the hand		6.5	Rodriguez and Aristeguieta, (2009)
Precious metals smelter	Ghost Wipe™	Left hand		0.008*	Gorman Ng *et al*. (2017)
		Right hand		0.009*	
		Perioral area		0.015*	
Lead					
Zinc/lead refinery	Moist wipes (Jeyes 'Sticky Fingers' Wet Ones)	Hands		21.3•	Hughson, (2005)
		Forearms		81.7•	
		Hands and arms		56.1•	
		Neck		123.0•	
		Forehead		14.8•	
		Chest		78.9•	
Lead chemical production plant	Moist wipes (Jeyes 'Sticky Fingers' Wet Ones)	Hands		16.9•	Hughson, (2005)
		Forearms		33.4•	
		Hands and arms		87.5•	
		Neck		5.5•	
		Face		105.9•	
		Chest		4.4•	
Laboratory experiments	Moist wipes (unspecified)	Hand (Palm and fingers after ten contacts)	Lead sheeting	1.96#	Sleeuwenhoek and Van Tongeren, (2006)
			Plastic pipe	2.24#	
			Lead ingot	1.38#	
Glass beads blending and repacking	Moist towelette	Palm and back of the hand		8.2+	Rodriguez and Aristeguieta, (2009)
Precious metals smelter	Ghost Wipe™	Left hand		0.061*	Gorman Ng *et al.* (2017)
		Right hand		0.062*	
		Perioral area		0.062*	

* = Geometric mean, ● = Arithmetic average exposure concentration, # = Individual measurement

As indicated in Table 2-1, more attention was previously paid to the dermal exposure to lead than to arsenic. A study conducted at a precious metals smelter, indicates that workers experienced dermal exposure to both arsenic and lead, but the dermal exposure to arsenic was less than to lead (Gorman Ng *et al.,* 2017). This study also indicates that the exposure was higher on the right hand than on the left hand for both arsenic and lead. Furthermore, the study conducted by Rodriguez and Aristeguiet (2009) indicates that the dermal exposure to arsenic was lower than that of lead.

However, this study was conducted at a glass beads blending and repacking facility and cannot be used to compare exposure values with those of Gorman Ng *et al.* (2017). Gorman Ng *et al.* (2017) found that workers involved in the smelting of precious metals experienced dermal exposure to a geometric mean of 0.009 µg/cm² of arsenic on their right hand and 0.008 µg/cm² of arsenic on their left hand. The workers were also exposed to a geometric mean of 0.062 µg/cm² of lead on their right hand and 0.061 µg/cm² on their left hand (Gorman Ng *et al*., 2017).

2.8 Regulations in South Africa

In South Africa, the exposure to HCSs in the workplace is regulated by the Mine Health and Safety Act 29 of 1996 (MHSA) and the Occupational Health and Safety Act 85 of 1993 (OHSA) (DOL, 1995; DME, 2002). Under the OHSA, the Hazardous Chemical Substance Regulations (1995), Lead Regulations (2002) and the Mine Health and Safety Regulations – Regulation 22.9 under the MHSA, provide occupational exposure levels and guidance in terms of workers' exposure to various HCS. The HCS Regulations of the OHSA (1995) place various HCS into three tables: Table 1 (of the HCS Regulations) lists all the HCS for which an inhalation occupational exposure limit – control limit (OEL-CL) has been assigned, Table 2 (of the HCS Regulations) lists all the HCS for which an inhalation occupational exposure limit – recommended limit (OEL-RL) has been given and Table 3 gives the biological exposure indices (BEI) for various HCSs. The values listed in Table 1 and Table 2 (of the HCS Regulations) provide exposure values for a shift (eight-hour Time Weighted Average (TWA) or for short periods of high exposure (Short-Term Exposure Limit is used). The HCS regulations do not include lead, as lead exposure is regulated by the Lead Regulations. Unlike the HCS Regulations of the OHSA, the Mine Health and Safety Regulations, Regulation 22.9 - 2006 Occupational Exposure Limits for Airborne Pollutants place HCS into one table. However, the HCS Regulations, Lead Regulations and the Mine Health and Safety Regulations, Regulation 22.9 provide exposure limits for respiratory exposure. HCSs that are able to penetrate the skin and be absorbed into the body is assigned a skin notation (SK) (DOL, 1995). The HCS Regulations (1995), Lead Regulations (2002) and the Mine Health and Safety Regulations – Regulation 22.9 do not provide guidance for the allowed concentration of HCSs on the skin or work surfaces.

Table 2-2: OHSA exposure values for exposure to arsenic and lead.

Substance	TWA OEL-CL (mg/m^3)	TWA OEL-RL (mg/m^3)	BEI (µg/g creatinine)	Notes
HCS Regulations				
Arsenic and compounds, except arsine (as As)	0.1	-	-	-
Arsine	-	0.2	50	-
Lead Regulations				
Lead (for tetra-ethyl lead)	0.1	-	-	-
Lead (other than tetra-ethyl lead)	0.15	-	-	-

-: no value or notation available

Table 2-3: MHSA exposure values for exposure to arsenic and lead.

Substance	TWA OEL	BEI (µg/g creatinine)	Notes
Arsenic and compounds, except arsine (as As)	0.01	-	-
Arsine	0.2	-	-
Lead, elemental, and inorganic compounds [as Pb]	0.1	-	-
Lead tetra- ethyl [as Pb]	0.1	-	SK
Lead tetra- methyl [as Pb]	0.15	-	SK

SK: able to penetrate the intact skin and be absorbed into the body; -: no value or notation available

2.9 Conclusion

Dermal exposure to arsenic and lead occurs during the smelting process of precious metals (Gorman Ng *et al*., 2017). Therefore, it is anticipated that exposure could also possibly occur at the base metals refinery (BMR) due the incomplete removal of arsenic and lead during the smelting phase. Both arsenic and lead may elicit significant short term and chronic health effects (that adversely affect the health of the workers), which may be significantly increased if co-exposure occurs simultaneously due their combined effect in reducing the glutathione levels (Vahter, 2002; Ahamed and Siddiqui, 2007; Flora *et al*., 2012). Several studies indicate that wipe sampling is an appropriate method for determining the dermal exposure to metals, including arsenic and lead. Finally, a brief overview of the OHSA and MHSA that regulate exposure to arsenic and lead was discussed.

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CHAPTER 3: ARTICLE

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Title, abstract and keywords*:* Titles should be constructed to succinctly describe the major issue or question examined by the paper and should not assert the research findings as a truth. Recognisable, searchable terms and keywords must be included to enable readers to more effectively find your paper. To optimise the visibility of your paper we advise you to make a list of the 10 most likely search terms that your intended readers will use to find your work, and to ensure that these appear in your title, the abstract and the keywords. The 'number one' search term from your list should appear somewhere in the paper's title. The 'top 5' search terms (including 'number one') should each appear at least once in the abstract, with the 'top 3' appearing more than once if possible. It is important that your abstract is written in a naturalistic and engaging style that will encourage readers to follow up by reading the full paper. The 'bottom 5' search terms can then be added as keywords.

Authorship: Persons should only be named as authors if they have made substantial contributions to the conception or design of the work, or the acquisition, analysis or

interpretation of data for the work AND have assisted with the drafting or revising of the paper for important intellectual content AND have final approval of the version to be published AND can take responsibility for the accuracy of the work. Other contributions may be recognised by acknowledgement at the end of submission.

Structure of paper*:* Papers should generally conform to the pattern: Introduction, Methods, Results, Discussion, and Conclusions, unless these are clearly inappropriate. A paper must be prefaced by an abstract of the argument and findings, which may also be arranged under the same headings.

Design and analysis: The quality of the data and analysis must always be good enough to justify the inferences and conclusions drawn. Particular attention should be given to design of sampling surveys, which should be planned using modern statistical principles, and to the treatment of results below the limit of detection.

Units and symbol*s:* SI units must be used, though their equivalent in other systems may be given as well.

Figures: These include photographs, diagrams and charts. The first submission should include good quality low resolution copies of Figures, and may be incorporated into the text or at the end of the manuscript.

Tables: Tables should be numbered consecutively and given a suitable caption. As with Figures, it is helpful to incorporate them into the text of the first submission, but in the revised version each table should be presented on a separate page. Footnotes to tables should be provided below the table and should be referred to by superscript lowercase letters.

References: References should only be included which are essential to the development of an argument or hypothesis, or which describe methods for which the original account is too long to be reproduced. References in the text should be in the form Jones (1995), or Jones and Brown (1995), or Jones *et al*. (1995) if there are more than two authors, and they should be incorporated naturally into the text.

Examples:

Jones and Brown (1995) and Hospath *et al.* (2006) observed total breakdown of control..., or

Total breakdown of control has sometimes been observed (Jones and Brown, 1995; Hospath *et al*., 2006).

At the end of the paper, references should be listed in alphabetical order by name of first author, using the Vancouver Style of abbreviation and punctuation. ISBNs should be given

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Examples:

Simpson AT, Groves JA, Unwin J, Piney M. (2000) Mineral oil metal working fluids (MWFs)—Development of practical criteria for mist sampling. Ann Occup Hyg; 44: 165–72.

Vincent JH. (1989) Aerosol sampling: science and practice. Chichester, UK: John Wiley. ISBN 0 471 92175 0.

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Dermal exposure to arsenic and lead at a base metals refinery

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3.1 Abstract

Title: Dermal exposure to arsenic and lead at a base metals refinery

Background: Arsenic and lead are toxic to humans and dermal exposure has been found to occur during the smelting process of precious metals. It is therefore, anticipated that exposure to arsenic and lead would also possibly occur at the base metals refinery (BMR).

Objectives: To quantify and compare the dermal exposure of refinery workers to arsenic and lead, to compare the exposure on the various anatomical areas with each other and to quantify arsenic and lead workplace surface contamination in order to identify potential sources of exposure.

Method: Wipe samples (Ghostwipes^{TM}) were collected from the palm, wrist and forehead of workers at various intervals during the working shift, in one administrative and two production areas within the refinery. Additionally, surface wipes were collected to identify potential sources of contamination. Wipe samples were collected from 14 workers and 14 surfaces in the refinery. A total of 132 wipe samples were collected during sampling and analysed using ICP-AES.

Results: None of the wipe samples contained arsenic at a detectable concentration. Additionally, 14% of the collected wipe samples contained lead at a detectable concentration. The palm received the highest exposure concentration (0.318 µg/cm^2) followed by the wrist and lastly the forehead. Only one of the wrist and forehead wipes collected indicated the presence of lead. Workers in production area A received higher lead exposure than those in production area B. Surface wipes collected indicated several surfaces, in the administrative area and dirty change house, along with wipe samples collected from the personal protective equipment used by the workers, were contaminated with lead.

Conclusion: During the refining process of base metals, workers were not exposed to an arsenic concentration above 1 µg and only six of the workers experienced lead exposure above 1 µg. The palm of workers received the highest exposure to lead in both the production areas which suggests that the palm is the primary area of exposure for the refinery workers. Surface and skin wipe samples indicated that surfaces can act as a source of additional exposure to lead. The control measures already implemented by the refinery prevents workers direct contact with these hazardous substances, which reduces workers' dermal exposure.

Keywords: arsenic, lead, base metals refinery, dermal exposure.

Words: 379

3.2 INTRODUCTION

Platinum along with rhodium, palladium, iridium, osmium and ruthenium form the platinum group metals (PGMs) (Fernandez, 2017). PGMs occur naturally with major base metals such as cobalt, copper, iron and nickel and minor metals such as arsenic, lead and tellurium (Phetla *et al.,* 2010). South Africa is the world's most prominent supplier of PGMs and was responsible for 73.2% of platinum, 82.2% of rhodium and 37.7% of palladium global production in 2018 (Chamber of Mines of South-Africa, 2019). Gorman Ng *et al*. (2017) investigated the dermal exposure of workers to various contaminants, including arsenic and lead, during the smelting of precious metals and indicated that workers experienced dermal exposure to both arsenic and lead. It is therefore, possible that workers may also experience dermal exposure to arsenic and lead during the refining of base metals. To date no other dermal exposure studies have investigated the dermal exposure of workers to arsenic and lead at a base metals refinery (BMR) or precious metals refinery (PMR).

The process of PGM purification consists of three main phases namely: smelting, base metal refining and precious metals refining (Cramer, 2008). During the smelting phase, a copper-nickel sulphide matte is produced, which is then allowed to cool over a period of three days (Crudwell *et al.,* 2011). After the matte has cooled, it is crushed to liberate the magnetic alloy platelets, which can then be removed by magnetic separation. The magnetic fraction is then treated in leaching steps and the resulting PGM concentrate is sent to the precious metals refinery (PMR) (Crudwell *et al.,* 2011). During the refining of base metals, lead is removed from the floatation concentrate and this increases the workers' risk of potentially being exposed to lead (Phetla *et al.,* 2010). Since arsenic also occurs with lead as one of the minor metals associated with base metal refining, workers can potentially be exposed to arsenic during the refining process. The magnetic separation and leaching steps of the copper-nickel sulphide matte pose the greatest risk to workers due to the presence of various metals that are liberated during these processes.

In an occupational setting, inhalation exposure is generally considered to be the most important route in terms of toxicity, followed by dermal contact and then ingestion (Cherrie *et al*., 2006). The skin as a route of exposure has received little attention during exposure assessment of workers in occupational settings and numerous studies have stated that the dermal route of exposure has been neglected and needs to receive more attention when determining the exposure of workers to hazardous chemicals (Fenske, 1993; van Hemmen and Brouwer, 1995; Soutar *et al*., 2000; Semple, 2004; Ouypornkochagorn and Feldmann, 2010; Flora *et al*., 2012; Behroozy, 2013; Anderson and Meade, 2014).

Information on the dermal exposure to arsenic is limited, whereas a substantial volume exists on occupational dermal lead exposure (Hughson, 2005; Ouypornkochagorn and Feldmann, 2010; Koh *et al*., 2015; NIOSH, 2017). The presence of arsenic on the skin has been reported at a concentration of between 0.008 µg/cm² and 0.015 µg/cm² during the smelting of precious metals, and at a higher concentration of 6.5 µg/cm² during the packaging of glass beads (Gorman Ng *et al.,* 2017; Rodriguez and Aristeguieta, 2009). Dermal exposure to lead has been reported to occur at concentrations ranging between 0.062 µg/cm² and 123 µg/cm², in a precious metals smelter, lead/zinc refinery and lead chemical production plant (Hughson, 2005; Gorman Ng *et al.,* 2017).

Metals remain on the skin after exposure has occurred and therefore, skin wipe sampling is an appropriate removal method to assess exposure (OSHA, 2002, Gorman Ng *et al.,* 2017). Skin wipe sampling provides a representation of the amount of contaminant on the skin at the time when the sample was collected and metals can be reliably analysed on wipes (OSHA, 2002; Behroozy, 2013; Gorman Ng *et al*., 2017).

The permeation of metals through the skin has generally been underestimated as the focus has been on the local effects such as allergic contact dermatitis caused by metals such as cobalt, chromium, nickel and palladium (Lidén *et al.,* 2008; Larese Filon *et al.,* 2007; Larese Filon, 2018). Metals' permeation through the skin is dependent on several factors, for example the molecular weight and valence state of the substances (Hostýnek, 2003; Larese Filon, 2018). Arsenic's permeation through the skin is dependent on the oxidation state of arsenic. Arsenite permeates the skin between 29 and 59 times faster that arsenate (Ouypornkochagorn and Feldmann, 2010). Inorganic lead's permeation through the skin is negligible when compared to that of organic lead, which can rapidly permeate through the skin (WHO, 2006, ATSDR, 2007; Wani *et al.,* 2015). The presence of contaminants on the skin pose the risk of inadvertent ingestion when the contaminant is transferred from the hand of the worker to the mouth of the worker, causing ingestion of the contaminant (Cherrie *et al.,* 2006). Therefore, workers may be exposed not only through the permeation of contaminants through the skin but also through the inadvertent ingestion of the contaminant.

Once arsenic and lead enter the body these metals may cause severe adverse health effects. Arsenic exposure may lead to the development of skin cancer (squamous cell carcinoma and basal cell carcinoma) as the skin is the most sensitive organ to arsenic exposure. Lead exposure may among others cause peripheral neuropathy (in adults), anaemia and immune system impairment (Goyer, 1990; SIMRAC, 2000; Yu *et al*., 2006; ATSDR, 2007; Rosin, 2009; Ouypornkochagorn and Feldman, 2010; Hong *et al*., 2014; Mason *et al*., 2014).

Dermal exposure may also be the result of workers coming into contact with contaminated surfaces. Du Plessis *et al.* (2010), Julander *et al.* (2010) and Linde *et al.* (2018) indicate that workplace surfaces can be potential sources of exposure. Surface contamination may be the result of the contaminant settling on the surface following emission from a source or the resuspension of contaminants from clothing, skin or other surfaces or from the direct transfer of substances between outer clothing, the skin and surfaces (Schneider *et al*., 1999; Schneider *et al*., 2000). Therefore, it is important to consider the influence of contaminated surfaces on dermal exposure.

This study aims to quantify and compare the dermal exposure of refinery workers to arsenic and lead in the various sampling areas with each other, to compare the exposure of the various anatomical areas with each other and to quantify arsenic and lead workplace surface contamination in order to identify potential sources of exposure.

3.3 Materials and Method

3.3.1 The recruitment of workers

Ethics approval for the study was obtained from the Health Research Ethics Committee (HREC) of the North-West University (NWU-00015-19-S1). According to the informed consent procedure, potential participants were informed of the details of the study and asked to complete informed consent forms if they agreed to participate. Wipe samples were collected from participants of three different working areas within the refinery. This included an administrative area and two production areas. In consultation with the occupational hygiene team on site, data from previous in-house surveys was used to identify the production areas where exposure was most likely to occur. In the administrative area, only two workers worked a full shift in the area without entering any production areas. These two workers agreed to participate in this study. Six workers in each of the two production areas (A and B), agreed to participate. In production area B a security guard was included due to the presence of the security guards in the production area for a full shift while production workers carry out their tasks. The dermal exposure of 14 workers (12 males and 2 female) was quantified and a total of 132 samples (112 dermal, 14 surface, 3 media blank and 3 field blanks) were collected.

3.3.2 The base metal refinery and process description

In production area A, the PGMs are separated from the converted matte by magnetic separation. This is achieved by allowing the converted matte to cool down over a period of three days, while the matte cools the PGMs concentrate in the alloy phase.

Table 3-1: Description of participating workers' activities performed and PPE worn during an 8 hour shift.

Location	Job	Description	PPE worn by the worker
Administrative area	Secretary	Administrative work.	No PPE worn.
	Human resources officer		
Production area A	Process operator 1	Removing the plates used in electrowinning with the in-house crane, packaging the processed material (magnetic fraction) into large containers that is sent to the precious metals refinery. Turning equipment on and off.	Full-face mask with forced air respirator, FFP2 dust mask, safety glasses, chemical resistant long sleeve gloves, safety shoes, disposable earplugs, disposable protective coveralls, hard hat, acid proof overalls.
	Process operator 2		
	Process operator 3		
	Process operator 4		
	Process operator 5		
	Security guard	Security worker in die process area.	FFP2 dust mask, safety glasses, safety shoes, disposable earplugs, acid proof overalls.
Production area B	Process operator 6	Workers place the process material into the autoclaves for leaching by using the in-house crane to move the buckets, containing the process material, and place them on top of the autoclave. After the bucket has been placed on top, the worker opens a chute that allows the material to pass into the autoclave. Turning equipment on and off.	FFP2 dust mask, safety glasses, chemical resistant long sleeve gloves, safety shoes, disposable earplugs, hard hat, acid proof overalls.
	Process operator 7		
	Process operator 8		
	Process operator 9		
	Process operator 10		
	Process operator 11		

PPE – personal protective equipment. FFP2 – free flight phase 2

The matte is then crushed to liberate the magnetic alloy platelets, which are then removed by magnetic separation. In production area B, the magnetic fraction is then treated to remove copper, iron and nickel through three leaching steps. The resulting material is then sent to the PMR to be refined into individual PGMs (Crundwell *et al.,* 2011). Table 3-1 describes the activities performed by the process workers in production areas A and B.

3.3.3 Dermal exposure wipe sample collection

Ghostwipes™ have been validated for lead and have also been used to assess workers' dermal exposure to arsenic, chromium, nickel and soluble platinum (OSHA, 2002; Gorman Ng *et al*., 2017; Cao *et al*., 2018; Linde *et al*., 2018). The sampling strategy that was used in this study was based on those used by Du Plessis *et al.* (2013) and Linde *et al*. (2018). The anatomical areas that were selected included the palm and wrist of the dominant arm as well as the forehead.

Table 3-2 indicates the anatomical area, intervals at which the sample was collected and the number of wipe samples collected from each worker in the specific areas of the refinery. Table 3-2 shows that, ten individual dermal exposure wipe samples were collected from each administrative worker, while eight wipe samples were collected from each production worker per shift. Workers in the production areas did not make use of their tea-break, therefore, samples were not collected before tea-break, reducing the number of wipe samples collected. The aim of the pre-shift wipe was firstly, to clean the anatomical area to ensure that the exposure measured was a result of exposure from the working area and secondly to quantify the possible dermal exposure from other sources such as the change house.

Table 3-2: Description of the anatomical area, sampling time and the number of samples collected from each worker.

Anatomical area	Sampling time	Number of samples collected per worker per shift	
		Administrative area	Production area A and B
Palm of the hand	Pre-shift	1	1
	Before tea-break	1	N/A
	Before lunch	1	1
	End of the shift	1	1
Wrist	Pre-shift	1	1
	Before tea-break	1	1
	Before lunch	1	N/A
	End of the shift	1	1
Forehead	Pre-shift	1	1
	Before tea-break	N/A	N/A
	Before lunch	N/A	N/A
	End of the shift	1	1
Total		10	8

N/A – Not applicable

Workers were informed to refrain from washing their hands before a wipe samples was collected. Samples were collected before workers' washed their hands in order to ensure that the contaminants were not removed from their skin (Du Plessis *et al.*, 2013; Linde *et al*., 2018). Before each sample was collected, the researcher donned a clean pair of disposable nitrile gloves in order to prevent contamination of the sample. Pre-made acetate paper templates, with a rectangular surface area of 24 cm² (6 cm x 4 cm), were used to demarcate the anatomical areas (Du Plessis *et al.*, 2013; Linde *et al*., 2018). This was done to keep the anatomical surface area sampled consistent throughout the wipe sampling process. A new wipe was removed from its packaging and the researcher's fingertips were used to hold the wipe in place when wiping the area inside the template while applying constant pressure. The area was then wiped in an overlapping 'S' pattern, using horisontal strokes, after which the wipe was folded inwards. The area was then wiped for a second time, using the same wipe, using vertical 'S'-strokes perpendicular to the first motion. After the area had been wiped for the second time, the wipe was again folded and used to wipe the area for a third time using vertical 'S'-strokes after which it was folded to wipe the area for a fourth time making use of horizontal 'S'-strokes. The area was, therefore, wiped four times with the same wipe (Du Plessis *et al.*, 2013; Linde *et al*., 2018).

The wipe was then deposited into a 50 ml digestion vial and stored for analysis. One field and media blank was collected per day for both dermal and surface sampling. The collected samples were sent to a South African National Accreditation System (SANAS) accredited laboratory to be analysed according to Occupational Safety and Health Administration (OSHA) ID-125G and National Institute for Occupational Safety and Health (NIOSH) 7303 using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for both arsenic and lead with a detection limit of 1 µg per sample (OSHA, 2002; NIOSH, 2003).

3.3.4 Surface wipe sample collection

Pre-made acetate paper templates, with a square surface area of 100 cm² (10 cm x 10 cm), were used to demarcate the surface areas to keep the surface area consistent throughout the wipe sampling process. The same method used for dermal wipe sampling was used to wipe the demarcated surfaces. The collected surface samples were sent to a SANAS accredited laboratory for analysis using ICP-AES. Surface wipe samples were collected from all three selected working areas within the refinery.

The number of surface wipe samples that were collected was limited due to strict rules for removing any material that may contain precious metals. Therefore, only two surface wipe samples were collected in the administrative area, production area A, production area B, dirty change house and clean change house, respectively.

Surface wipe samples were also collected from personal protective equipment (PPE) worn by the workers in the two production areas. A total of ten wipe samples were collected from surfaces that workers frequently come into contact with and four wipe samples were collected from PPE worn by workers.

3.4 Data processing and analysis

GraphPad Prism 8.0 (GrapPad Software, San Diego, California) was used for statistical analysis and to create graphs. Due to the majority (86.4%) of the measurements being below the analytical detection limit of 1 µg per sample, it was not possible to carry out statistical analyses. A β-substitution could not be used due to the low number of samples above the detection limit (Ganser and Hewett, 2010). A LOD/√2 substitution method was used for workers with one exposure value below the detection limit (1 µg) for the specific analytical method. The dermal exposure of the workers on the wrist and palm for a full 8-hour shift, was calculated as the sum of the before tea-break, before lunch and end of shift measurements. This concentration was used to represent the workers' cumulative exposure on the anatomical area for the shift.

3.5 Results

The aim of this study is to quantify and compare the dermal exposure of refinery workers to arsenic and lead, to compare the exposure on the various anatomical areas with each other and to quantify arsenic and lead workplace surface contamination in order to identify potential sources of exposure. Figure 3-1 indicates the percentage of collected samples that were below the detection limit of 1 µg per sample for arsenic and lead.

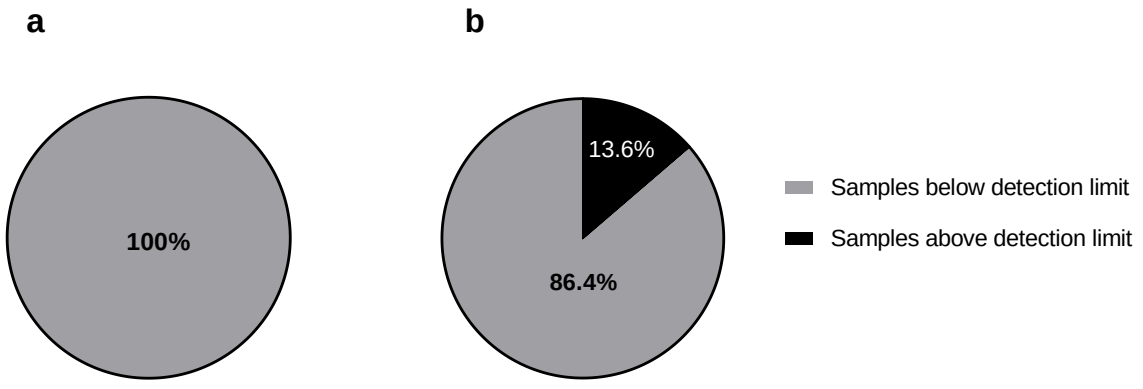

Figure 3-1: Percentage of samples below the detection limit for a) arsenic and b) lead.

Table 3-3: Dermal exposure concentrations of workers during a full shift in the administrative and production areas.

Work area	Worker	Lead concentration (µg/cm²)														
		Palm					Wrist					Forehead				
		Pre-shift	Before tea-break	Before lunch	End of shift	Total exposure	Pre-shift	Before tea-break	Before lunch	End of shift	Total exposure	Pre-shift	Before tea-break	Before lunch	End of shift	Total exposure
Administrative area	Administrative worker 1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Administrative worker 2	BDL	0.030*	0.030*	0.101	0.161	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Production area A	Process worker 1	BDL	-	0.030*	0.283	0.313	BDL	-	BDL	BDL	BDL	BDL	-	0.030*	0.142	0.172
	Process worker 2	BDL	-	0.131	0.187	0.318	BDL	-	0.162	0.030*	0.192	BDL	-	BDL	BDL	BDL
	Process worker 3	BDL	-	0.073	0.104	0.176	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL
	Process worker 4	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL
	Process worker 5	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL
	Security guard	BDL	-	0.064	0.204	0.268	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL
Production area B	Process worker 6	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL
	Process worker 7	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL
	Process worker 8	BDL	-	0.047	0.030*	0.077	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL
	Process worker 9	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL
	Process worker 10	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL
	Process worker 11	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL	BDL	-	BDL	BDL	BDL

* - Substituted concentrations [= (1/√2)/24]; BDL – Below detection limit; - = Not applicable (process workers did not make use of tea-break)

Table 3-4: Surface exposure concentrations and description of the surface from which the wipe sample was collected.

Location	Concentration of lead (µg/cm²)	Description of surface
Administrative area	0.012	Boardroom table where the safety meetings are held before workers start their shift in production areas A and B.
	BDL	Table in the kitchen where workers eat or make beverages such as coffee.
Dirty change house	0.017	Change house bench on which workers usually sit and stand when changing clothes.
	0.023	Shower tiles on the front sides of the shower. Workers push with both hands on the tiles to support themselves as they climb across the shower step.
Clean change house	BDL	Change bench on which workers usually sit and stand when changing clothes.
	BDL	Lockers in which workers place clothing and other objects before they enter the refinery.
Production area A	BDL	Monitor table in the control room.
	BDL	Table in the area designated for eating and drinking.
	0.020	PPE: The inside surface of a full face mask, powered air-purifying respirator.
	0.028	PPE: The inside surface of a full face mask, powered air-purifying respirator.
Production area B	BDL	Monitor table in the control room.
	BDL	Table in the area designated for eating and drinking.
	0.017	PPE: The outer rim of the hardhat worn by workers.
	0.028	PPE: The outer rim of the hardhat worn by workers.

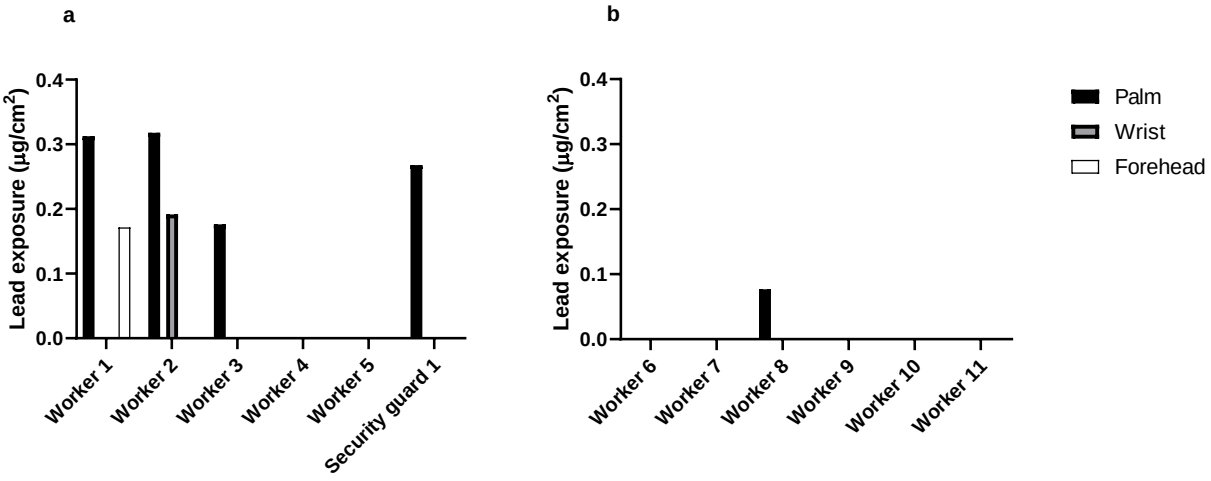

Figure 3-2: Total dermal exposure concentration for the entire shift on the palm, wrist and forehead of refinery workers in a) production area A and b) production area B.

Analysis of the collected samples revealed that 100% of the collected samples were below the LOD for arsenic and 86% of the samples were below the LOD for lead. Due to the limited number of exposure data, the geometric mean and geometric standard deviation were not calculated. Instead the results are only graphically represented (Figure 3-1 and 3-2). From the samples that were above the LOD, eleven were dermal exposure wipe samples and seven were surface wipe samples. Dermal exposure concentrations on individual anatomical positions to lead ranged between BDL (< 0.042 µg/cm²) and 0.318 µg/cm² for a full shift (Figure 3-2).

The highest dermal exposure was measured on the palm of process operator 2 (0.318 µg/cm²) for a full shift (refer to Table 3-3 and Figure 3-2) in production area A. From the wipe samples collected in the administrative area, only one wipe sample contained a lead concentration above the detection limit (palm, end of shift). The forehead wipe sample collected from process operator 2 was the only wipe sample from the forehead that contained a detectable concentration of lead. Only one of the wipe samples collected in production area B contained lead above the detection limit (palm, before lunch).

Surface wipe concentrations ranged between BDL (< 0.001 µg/cm²) and 0.028 µg/cm², with the highest concentrations measured on the hard hat of process worker 7 in production area B. None of the surface wipes in the clean change house contained lead.

3.6 Discussion

In this study, the dermal exposure of refinery workers to arsenic and lead was investigated within three areas of a South African BMR. Both arsenic and lead exposures were anticipated to occur at the BMR, since it was previously found to occur at detectable concentrations during the smelting of precious metals (Gorman Ng *et al.,* 2017).

However, none of the skin wipe samples collected contained levels of arsenic above 1 µg per sample and only 13.6% of the 132 samples contained detectable concentrations of lead, of which 8.3% (n=11) were dermal wipe samples and 5.3% (n=7) were surfaces wipe samples. None of the pre shift wipes indicated that workers experienced contamination before the start of their shift. Field blanks and media blanks collected during sampling indicated no background contamination.

Several studies that investigated dermal exposure to arsenic or lead did not indicate what the detection limit was, only that the samples were below the detection limit (Hughson, 2005; Gorman Ng *et al.,* 2017). Previous studies that reported their detection limit for the specific analytical method used, reported detection limits of 3 µg for arsenic and 1 µg for lead (Sleeuwenhoek and Van Tongeren, 2006; Rodriguez and Aristeguieta, 2009). However, in the study conducted by Gorman Ng *et al.* (2017) the detection limit was calculated to be 0.3 µg, which is lower than those used by Sleeuwenhoek and Van Tongeren (2006) and Rodriguez and Aristeguieta (2009). These studies utilised inductively coupled plasma atomic emission spectroscopy (ICP-AES) to analyse their wipe samples. The analytical method used in the present study had a detection limit of 1 µg per sample for both arsenic and lead, which is comparable to the detection limit used by previous studies (Sleeuwenhoek and Van Tongeren, 2006; Rodriguez and Aristeguieta; 2009).

Figures 3-2a and 3-2b indicate the dermal exposure experienced by refinery workers in the two production areas. The results indicate that the palm had the highest exposure concentration, followed by the wrist and lastly the forehead. Only process worker 1 experienced forehead exposure to lead. The results indicate that the process workers in production area A experienced higher dermal exposure to lead than those in production area B. This may be due to the measures already implemented by the refinery in production area B, namely to limit workers' direct contact with the process material. The production process in area B is a closed process, with the majority of the tasks being automated, only requiring workers to switch machinery on and off to complete their tasks. Extraction ventilation is present in all the areas (in both production areas A and B) where dry material is present or being handled. However, two of the workers still experienced exposure to lead. The exposure may be due to the transfer of lead from the outside of the containers and/or on the cables used to lift the buckets, to the hands of workers.

Workers in production area A come into contact with the process material when the plates used in electrowinning need to be changed and when the PGMs need to be packaged. This increases the workers contact with process material, resulting in higher exposure concentration as indicated by the wipe samples in production area A. The increased exposure of the palm of process workers in production area A may be due to workers touching the outside of the gloves with their hands when they remove them. Exposure may also occur when workers touch contaminated surfaces with their hands without wearing gloves.

One of the skin wipe samples indicated that the worker in the administrative area experienced lead exposure on the palm even though he did not enter the refinery itself. The worker experienced lead exposure at a higher concentration that the production worker in production area B. The cause of the worker's exposure may be the transfer of lead from the contaminated table (Table 3-4), used by the workers for their pre-shift meetings, to the workers' skin. The worker may also be exposed due to the transfer of lead from one worker's hand to the next such as when workers shake hands when greeting each other.

The results of this study indicate that workers' palm exposure to lead ranged between BDL (< 0.004 µg/cm²) and 0.318 µg/cm², which is higher than the reported dermal exposure of smelter workers by Gorman Ng *et al.* (2017), who reported workers' exposure to lead as ranging between 0.009 µg/cm² and 0.191 µg/cm² on the right hand and 0.013 µg/cm² and 0.248 µg/cm² on the left hand. The higher exposure suggests that workers involved with base metal refining can potentially experience higher dermal exposure to lead than those at a precious metals smelter. Hughson (2005) reports that workers in a zinc/lead refinery experienced dermal exposure at a higher concentration, with the hand of workers having an exposure concentration of up to 21.3 µg/cm². Exposure of BMR workers is therefore, not negligible but can be well controlled. Only one of the wrist wipe samples in production area A and one of the palm wipes in production area B indicates the presence of lead. This suggests that the coveralls and chemical resistant gloves worn by the workers' in these production areas aid in preventing dermal exposure.

Du Plessis *et al.* (2010) and Julander *et al.* (2010) suggest that surfaces may act as additional sources of exposure. This statement is supported by the presence of lead on some of the surfaces sampled in this study. Some of the surface wipe samples collected in the administrative area, dirty change house, production area A and B and personal protective equipment (PPE) indicated the presence of lead above the detection limit (Table 3-4). The results indicate that the wipe samples collected from the PPE worn by workers were contaminated with lead. The most notable of contamination of these surfaces is the contamination on the inside of the respirator worn by workers in production area A. The forehead wipe sample of the worker indicated the presence of lead. This shows that the respirator itself was contaminated and could possibly have caused contamination of the worker's forehead. Contamination may be the result of contaminants being transferred from the inside of the respirator onto the forehead of the worker. The hardhats worn by the workers may become contaminated when workers remove the hardhat while still wearing gloves. Contaminants may then be transferred to the hardhat causing the hardhat itself to become a source of contamination.

At the end of the workers' shifts, they shower and change clothes before exiting to the clean change house. The results indicated the presence of lead on tiles on the front sides of the shower and on a change bench in the dirty change house.

Workers frequently come into contact with these surfaces after they have showered and changed clothes and there is a possibility that lead may be transferred from these surfaces onto the hand of worker, causing exposure outside their working areas.

However, surface wipes collected in the clean change house did not indicate the presence of lead. This may be due to either worker's washing their hands before exiting the dirty change house, preventing the transfer of lead from workers hands to surfaces, or the cleaning of the clean change house after the workers have left the change room, consequently preventing the transfer of lead from these surfaces onto the skin of workers.

3.7 Conclusion

This study investigated the dermal exposure of 14 refinery workers to arsenic and lead, and found that only lead was present on the workers' skin at a quantifiable concentration. Workers may still experience arsenic and lead exposure at a concentration below that of the detection limit. The palm received the highest exposure to lead in both production areas A and B and the concentrations were comparable to a study conducted in a precious metals smelter. The results indicates that the palm of the hand is the primary area of exposure of the workers working in the refinery. Surface and skin wipe samples indicated that surfaces can act as a source of exposure to lead, as indicated by the contamination of the forehead of the worker wearing a respirator contaminated on the inside with lead. Measures already implemented by the refinery, such as a closed process, extraction ventilation and correct PPE, reduced the workers' exposure to arsenic and lead, by limiting workers direct contact with these hazardous substances. Extraction ventilation prevents the contaminants from settling on the skin of workers and on surfaces, which in turn can act as sources of contamination.

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CHAPTER 4: CONCLUDING CHAPTER

This chapter is divided into four sections, namely conclusions, recommendations for control measures, limitation and future studies. References are made to the aim, objectives and hypothesis stated in Chapter 1. Recommendations that could be implemented by the refinery to control workers' dermal exposure to lead are made and finally, the one limitation of this study and future studies are discussed.

4.1 Conclusions

The aim of this study was to assess the dermal exposure of workers to arsenic and lead at a South African base metals refinery and to identify sources of contamination. This was achieved by using wipe sampling to collect wipe samples from the workers to quantify their dermal exposure to arsenic and lead. The palm and wrist of the dominant arm as well as the forehead was wiped using Ghostwipes^{TM}. The results indicate that arsenic was not present, on the skin of workers and surfaces, during the refining process and that only 14% of the samples contained lead above the detection limit (1 µg) for the specific methods of analysis. Workers exposure to lead on the palm ranged between BDL (< 0.042 µg/cm²) and 0.318 µg/cm² for a full shift. Only one of the wipe samples collected from the wrist, indicated the presence of lead at a concentration of 0.192 µg/cm². One of the wipes collected from the forehead indicated the presence of lead at a concentration of 0.172 µg/cm². Gorman Ng *et al*. (2017) reported workers' exposure to lead as ranging between 0.009 µg/cm² and 0.191 µg/cm² on the right hand and 0.013 µg/cm² and 0.248 µg/cm² on the left hand in a precious metals smelter. These exposure concentrations was lower than those obtained in this study, which indicate that workers involved in the refining of base metals can possibly experience higher dermal exposure to lead. The exposure concentrations indicate that workers in production area A experienced the highest dermal exposure to lead, followed by the workers in the administrative area and workers in production area B experienced the lowest dermal exposure to lead (Objective 1). The palms of the workers received the highest exposure of the anatomical areas, with an exposure concentration of 0.318 µg/cm², followed by the wrist exposure (0.192 µg/cm²) and lastly the forehead (0.172 µg/cm²). Six of the workers experienced lead exposure on their palms. Only one worker experienced lead exposure on his wrist and one worker on his forehead. This suggests that the palm is the primary anatomical area of exposure for refinery workers (Objective 2).

Dermal exposure may also be the result of workers coming into contact with contaminated surfaces, resulting in the contaminants being transferred from the surface onto the skin of workers (Schneider *et al*., 1999; Du Plessis *et al.*, 2010; Julander *et al.,* 2010).

Therefore, surface wipes were also collected to identify contaminated surfaces. The surface wipe samples collected indicated that surfaces in the refinery were contaminated such as the boardroom table (0.012 µg/cm²) in the administrative area and shower tiles (0.023 µg/cm²) and benches (0.017 µg/cm²) in the clean change house. Wipe samples were also collected from personal protective equipment (PPE) worn by the workers in production area A and B. The wipe samples collected from the PPE indicated that the PPE used by workers were contaminated with lead (Objective 3). The wipe sample collected from the forehead of process worker 1 indicated the presence of lead. Lead was also found to occur on the inside of the respirators worn by the workers. This indicates that lead was transferred from the respirator onto the forehead of the workers and can be concluded that surfaces can act as sources of additional exposure. The three objectives of this study were all achieved.

In Chapter 1 it is hypothesised that workers experience dermal exposure to arsenic and lead at detectable levels during the magnetic separation and leaching of PGMs. The results indicated that arsenic was not present at a detectable concentration and only some of the workers were exposed to lead at a quantifiable concentration during the magnetic separation and leaching processes. Therefore, the hypothesis is partially accepted.

4.2 Recommendations

- Recommendation 1: The palms of workers recruited for this study received the highest exposure when compared to the wrist and forehead. Therefore, it is recommended that beneficial hygiene practice, such as hand washing, is strictly enforced and should be performed before workers enter the administrative area, dirty change house, before workers leave the dirty change house and before entering an area designated for the consumption of food and beverages.
- Recommendation 2: Some of the wipes collected from the PPE indicated the presence of lead, which indicates the PPE themselves are contaminated. PPE can become contaminated when workers deviate from proper donning and doffing of PPE (Kwon *et al*., 2017). It is recommended that workers are provided with information and training on the correct procedure to remove, store and use PPE and a schedule implemented for the cleaning of PPE. Workers need to be knowledgeable about the manner of contamination of PPE.
- Recommendation 3: Workers place their PPE (safety shoes, protective eye wear, earplugs and hard hats) inside their lockers at the end of their shift. Storing the PPE in the lockers where workers also store their dirty clothes may lead to contamination of the PPE. Wipe samples indicated the presence of lead on the hard hats used by workers. Therefore, it is recommended that workers store their PPE in separate lockers to prevent the transfer of contaminants.

- Recommendation 4: Lead was present in the dirty change house. It is recommended that a cleaning schedule is implemented in the dirty change house. The change house should be cleaned after a shift's workers have left the change house to prevent the transfer of contaminants from surfaces onto the skin of workers entering the change house at the onset of a shift.
- Recommendation 5: When the change houses are cleaned, different cloths needs to be used when cleaning different surfaces, such a separate cloth for cleaning the shower tiles, benches and washbasins respectively.
- Recommendation 6: Workers entering the dirty change house often bring food with them. It is recommended that signs are displayed, prohibiting the consumption of food and beverages in the dirty change house. Also, food brought into the change house should be in a container that can close properly to prevent toxins from contaminating their food.
- Recommendation 7: Workers often stand on top of the benches while wearing their safety shoes. In this way, contaminants, such as lead, are transferred onto the bench. These surfaces can then act as sources of contamination. It is recommended that signs are displayed, prohibiting workers from standing on top of these benches. Workers should be made aware that they are contaminating the surface with their shoes, which in turn may cause contamination of their own or other workers' skin.
- Recommendation 8: Gorman Ng *et al.* (2017) concludes that workers' hand exposure was a determinant of inadvertent ingestion. Therefore, it is recommended that an inadvertent ingestion program is implemented reinforcing workers' awareness of the risk that inadvertent ingestion poses and to educate them on the importance of the maintenance of good hygiene.

4.3 Limitation

- The analytical method used in this study had a detection limit of 1 µg, which is higher than the detection limit of 0.3 µg for the analytical method used by Gorman Ng *et al.* (2017). This limited the study to concentrations of arsenic and lead above the detection limit of 1 µg. Concentrations of arsenic and lead below 1 µg could not be quantified.

4.4 Future studies

- When samples were collected from workers in the production areas, it was noted that their fingertips were darker than the rest of the hand. This observation indicates that the finger tips may receive more exposure than the palm. In future studies, the number of dermal samples collected from the workers should be increased to include additional areas such as the tips of fingers on the dominant hand.

- Gorman Ng *et al.* (2017) indicated that workers who wore respirators had higher perioral exposure compared to the workers who did not wear respirators. The wipe samples collected from the inside of respirators worn by the workers indicated that lead was present. Future studies can include wipe samples from the perioral area as well, to account for contamination caused by the respirator.
- Wipe sampling was used to quantify the dermal exposure of workers to arsenic and lead. However, respiratory exposure is considered to be the primary route of exposure and respiratory exposure to arsenic and lead may occur during the refining process when dry material is handled in the production areas (Cherrie *et al.,* 2006). Future studies can include respiratory exposure to provide a more accurate representation of the total exposure experienced by the workers during the refining process.
- Gorman Ng *et al.* (2017) indicated that workers involved in the smelting of precious metals experienced dermal exposure to both arsenic and lead. However, workers at the BMR did not experience any dermal exposure to arsenic. Only lead was found to occur during the refining process. A future study can be conducted at a precious metals smelter, to investigate whether arsenic is present during smelting and during which phase of smelting arsenic is removed.

4.5 References

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APPENDIX A

Woorde wat werk / Working Words

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BA Honns. HOD(G)
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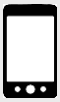
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LANGUAGE EDITING STATEMENT

2019 – 11 - 22

I, Jannetje Levina De Kock hereby declare that the mini-dissertation

Dermal exposure to arsenic and lead at a base metals refinery

by

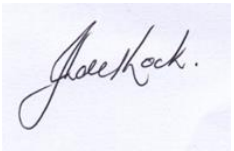
Barend Stofberg

for submission to the

the NWU
in the Niche area Occupational Hygiene and Health Research Initiative (OHHRI)

- has been edited for language correctness and spelling.
- has been edited for consistency (repetition, long sentences, logical flow)

No changes have been made to the document's substance and structure (nature of academic content and argument in the discipline, chapter and section structure and headings, order and balance of content, referencing style and quality).



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APPENDIX B

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Health Sciences Ethics Office for Research, Training and Support

North-West University Health Research Ethics Committee (NWU-HREC)
Tel: 018-285 2291
Email: Wayne.Towers@nwu.ac.za

Dr SJL Linde
Occupational Hygiene
OHHRI

05 August 2019

Dear Dr Linde

APPROVAL OF YOUR APPLICATION BY THE NORTH-WEST UNIVERSITY HEALTH RESEARCH ETHICS COMMITTEE (NWU-HREC) OF THE FACULTY OF HEALTH SCIENCES

Ethics number: NWU-00015-19-S1

Kindly use the ethics reference number provided above in all future correspondence or documents submitted to the administrative assistant of the North-West University Health Research Ethics Committee (NWU-HREC) secretariat.

Study title: Dermal exposure to arsenic and lead at a base metals refinery

Study leader: Dr SJL Linde

Student: B Stofberg-25095293

Application type: Single study

Risk level: Minimal (monitoring report required annually)

Expiry date: 31 August 2020 (monitoring report is due at the end of August annually until completion)

You are kindly informed that after review by the NWU-HREC, Faculty of Health Sciences, North-West University, your ethics approval application has been successful and was determined to fulfil all requirements for approval. Your study is approved for a year and may commence from 05/08/2019. Continuation of the study is dependent on receipt of the annual (or as otherwise stipulated) monitoring report and the concomitant issuing of a letter of continuation. A monitoring report should be submitted two months prior to the reporting dates as indicated i.e. annually for minimal risk studies, six-monthly for medium risk studies and three-monthly for high risk studies, to ensure timely renewal of the study. A final report must be provided at completion of the study or the NWU-HREC, Faculty of Health Sciences must be notified if the study is temporarily suspended or terminated. The monitoring report template is obtainable from the Faculty of Health Sciences Ethics Office for Research, Training and Support at Ethics-HRECMonitoring@nwu.ac.za. Annually, a number of studies may be randomly selected for an internal audit.

The NWU-HREC, Faculty of Health Sciences requires immediate reporting of any aspects that warrants a change of ethical approval. Any amendments, extensions or other modifications to the proposal or other associated documentation must be submitted to the NWU-HREC, Faculty of Health Sciences prior to implementing these changes. These requests should be submitted to Ethics-HRECApply@nwu.ac.za with a cover letter with a specific subject title indicating, "Amendment request: NWU-XXXXX-XX-XX". The letter should include the title of the approved study, the names of the researchers involved, the nature of the amendment/s being made (indicating what changes have been made as well as where they have been made), which documents have been attached and any further explanation to clarify the amendment request being submitted. The amendments made should be indicated in yellow highlight in the amended documents. The *e-mail*, to which you attach the documents that you send, should have a *specific subject line* indicating that it is

an amendment request e.g. "Amendment request: NWU-XXXXX-XX-XX". This e-mail should indicate the nature of the amendment. This submission will be handled via the expedited process.

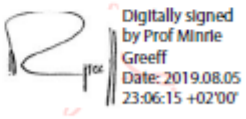
Any adverse/unexpected/unforeseen events or incidents must be reported on either an adverse event report form or incident report form to Ethics-HRECIncident-SAE@nwu.ac.za. The *e-mail*, to which you attach the documents that you send, should have a specific subject line indicating that it is a notification of a serious adverse event or incident in a specific project e.g. "SAE/Incident notification: NWU-XXXXX-XX-XX". Please note that the NWU-HREC, Faculty of Health Sciences has the prerogative and authority to ask further questions, seek additional information, require further modification or monitor the conduct of your research or the informed consent process.

The NWU-HREC, Faculty of Health Sciences complies with the South African National Health Act 61 (2003), the Regulations on Research with Human Participants (2014), the Ethics in Health Research: Principles, Structures and Processes (2015), the Belmont Report and the Declaration of Helsinki (2013).

We wish you the best as you conduct your research. If you have any questions or need further assistance, please contact the Faculty of Health Sciences Ethics Office for Research, Training and Support at Ethics-HRECApply@nwu.ac.za.

Yours sincerely

Prof Wayne Towers
Chairperson: NWU-HREC



Prof Minrie Greeff
Head of Health Sciences Ethics Office for Research, Training and Support

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30 April 2018

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APPENDIX C

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by STEFAN LINDE

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