Dermal exposure and skin barrier function of petrochemical workers exposed to polycyclic aromatic hydrocarbons

S.J.L. Linde

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Supervisor: Prof. J.L. du Plessis
Assistant Supervisor: Prof. F.C. Eloff
Assistant Supervisor: P.J. Jacobs

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This mini-dissertation is dedicated to my family, especially my mother and father, who supported me throughout my university career.

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Summary

Title - Dermal exposure and skin barrier function of petrochemical workers exposed to polycyclic aromatic hydrocarbons

Aims and Objectives – The aim of this study was the following: (1) to assess the dermal exposure of workers to PAH's during an entire eight hour work shift; (2) to assess the short term dermal exposure of workers to PAH's while performing certain identified tasks; (3) to identify the areas and occupations that poses the highest risk to the health of the workers; (4) to assess the skin barrier function of workers that may be exposed to PAH's by measuring TEWL, skin hydration and skin surface pH.

Methods – Workers from three different plants in a South African petrochemical factory participated in the study. Their dermal exposure was assessed during a single 8-hour shift by using dermal adhesive patches and during specific 30 minute tasks by means of dermal wipes. Their baseline skin barrier function was also determined at the beginning of the eight hour shift by measuring skin surface hydration, skin surface pH and the Transepidermal water loss (TEWL). Surface PAH-samples were also collected from various surfaces in two of the plants.

Results: Eight hour study- Cleaner 3 from the Solids Filtration Plant (SFP) experienced the highest average dermal exposure to total PAHs (759.6 ng/cm^2) as well as the highest total PAH-concentration on the outside of his clothing (28596.3 ng/cm^2). At the Tar Separation Plant (TSP) Cleaner 2 experienced the highest average dermal exposure (274.4 ng/cm^2). Cleaner 3 and Process controller at SFP as well as Truck loader 2 at TSP were all exposed to benzo[a]pyrene on the surface of their skin (37.20 ng/cm^2; 57.66 ng/cm^2 and 9.30 ng/cm^2 respectively). Statistical significant differences were seen between the skin surface hydration values (p=0.013) as well as the TEWL values (p = 0.033) of TSP and SFP workers.

Short term study- Slop pit cleaner 3 from TSP experienced the highest dermal exposure to total PAHs (1659.04 ng/cm^2). A splash of tar landed on Slop pit cleaner 3's cheek which contained 14871.45 ng/cm^2 total PAHs. The following workers were exposed to benzo[a]pyrene on various anatomical areas during their tasks: Truck loader 3 at TSP (2.7 ng/cm^2); Cleaner 6 at SFP (6.2 ng/cm^2 and 3.5 ng/cm^2); Slop pit cleaner 2 at TSP (20.8 ng/cm^2 and 12.8 ng/cm^2) and Slop pit cleaner 3 at TSP (72.8 ng/cm^2 and 108 ng/cm^2). Slop pit cleaner 3 at TSP was exposed to dibenz[a,h]anthracene (9.6 ng/cm^2 and 15.2 ng/cm^2)

The surface with the highest contamination is on top of the dirty lockers in the SFP (519.0 ng/cm^2).

Conclusions: In both studies, Cleaners were identified as the greatest exposed occupation. Cleaning the slop pit at TSP and cleaning the plant at SFP were identified as tasks with the highest potential exposure. Cleaners are probably the highest exposed workers because they come in direct contact with the tar more often. Workers exposed to benzo[a]pyrene or dibenz[a,h]anthracene face the greatest health risk as these substances are highly carcinogenic. SFP workers are in general exposed to higher concentrations of PAHs than workers in other areas. Workers at both SFP and TSP had high baseline TEWL and low baseline skin surface hydration values which indicated disrupted skin barrier function and may lead to an increase in their susceptibility to skin disorders. Dirty surfaces can also contain PAHs including benzo[a]pyrene and dibenz[a,h]anthracene.

Key words: Polycyclic aromatic hydrocarbons; Dermal exposure; Dermal patches; Skin barrier function; Tranepidermal water loss, Skin surface hydration; Skin surface pH; Petrochemical workers; Dermal wipes; Occupational exposure.

Opsomming

Titel- Dermale blootstelling en velkondisie van petrochemiese werkers wat aan polisilkiese aromatiese koolwaterstowwe (PAH's) blootgestel is

Doelstellings en doelwitte – Die teiken van hierdie studie was die volgende: (1) om die mate van dermale blootstelling van werkers aan PAH's gedurende 'n agtuurwerkskof te probeer vasstel; (2) om die korttermyn blootstelling aan PAH's van werkers te bepaal terwyl sekere vasgestelde take verrig word; (3) om areas en ambagte te identifiseer wat die hoogste gesondheidsrisiko vir werkers inhou; (4) om die velkondisie van werkers te bepaal wat moontlik aan PAH's blootgestel kan word deur transepidermale waterverlies (TEWL), veloppervlak hidrasie en die pH van die veloppervlak te meet.

Metodes – Werkers van drie verskillende aanlegte by 'n Suid Afrikaanse petrochemiese fabriek het aan die studie deelgeneem. Hulle dermale blootstelling is gedurende 'n enkele agtuurskof gemonitor deur gebruik te maak van dermale plakkers asook gedurende spesifieke dertigminutetake met behulp van dermale veelappies. Hul grondlynvelkondisie is aan die begin van die agtuurskof vasgestel deur die meet van die veloppervlakhidrasie, die pH van die veloppervlakte en die transepidermale waterverlies (TEWL). Monsters van die oppervlakte-PAH van verskeie oppervlaktes op die twee aanlegte is ook versamel.

Resultate: Agtuurstudie- Skoonmaker 3 van die Vastestoffiltrasieaanleg (SFP) het die hoogste gemiddelde dermale blootstelling aan totale PAH's (759.6 ng/cm^2) ervaar sowel as die hoogste totale PAH-konsentrasie aan die buitekant van sy kleredrag (28596.3 ng/cm^2). By die Teerskeidingsaanleg (TSP) het Skoonmaker 2 die hoogste gemiddelde dermale blootstelling (274.4 ng/cm^2) ervaar. Skoonmaker 3 en die Prosesbeheerder by SFP asook Vraglaaier 2 by TSP is almal aan benzo[a]pyrene op hul veloppervlaktes (37.20 ng/cm^2; 57.66 ng/cm^2 and 9.30 ng/cm^2 onderskeidelik) blootgestel. Statisties betekenisvolle verskille is opgemerk tussen die verlopppervlakhidrasiewaardes (p=0.013) asook die TEWL-waardes (p = 0.033) van die TSP- en SFP-werkers.

Korttermynstudie- Vuilwaterputskoonmaker 3 van TSP het die hoogste dermale blootstelling aan totale PAH's (1659.04 ng/cm^2) ervaar. 'n Spatsel teer, wat 14871.45 ng/cm^2 totale PAH's bevat, het op Vuilwaterputskoonmaker 3 se wang beland. Die volgende werkers is op verskillende anatomiese areas aan benzo[a]pyrene blootgestel gedurende die verrigting van hul take: Vraglaaier 3 by TSP (2.7 ng/cm^2); Skoonmaker 6 by SFP (6.2 ng/cm^2 en 3.5 ng/cm^2); Vuilwaterputskoonmaker 2 by TSP (20.8 ng/cm^2 en 12.8 ng/cm^2) en

Vuilwaterputskoonmaker 3 by TSP (72.8 ng/cm^2 en 108 ng/cm^2). Vuilwaterputskoonmaker 3 by TSP is aan dibenz[a,h]anthracene (9.6 ng/cm^2 en 15.2 ng/cm^2) blootgestel. Die oppervlakte met die hoogste besmetting is geidentifiseer as bo-op die vuil sluitkaste in die SFP (519.0 ng/cm^2).

Gevolgtrekkings: In beide studies is vasgestel dat Skoonmaak die ambag is met die hoogste blootstelling. Die skoonmaak van die vuilwaterput by TSP en die skoonmaak van die aanleg by SFP is as die take met potensiaal vir die grootste blootstelling geidentifiseer. Skoonmakers is waarskynlik die werkers wat die meeste blootstelling ervaar omdat hulle meer gereeld in kontak met die teer kom. Werkers wat aan benzo[a]pyrene of dibenz[a,h]anthracene blootgestel word staar die grootste gesondheidsrisiko's in die gesig aangesien hierdie stowwe hoogs karsinogenies is. SFP-werkers word oor die algemeen aan hoër konsentrasies PAH's blootgestel in vergelyking met werkers in ander areas. Werkers by beide SFP and TSP het hoë basislyn TEWL- en lae grondlyn velopppervlakhidrasiewaardes gehad wat dui op ontwrigte velkondisie. Dit kan lei tot 'n verhoogte vatbaarheid vir velafwykings. Op vuil oppervlaktes kan ook PAH's teenwoordig wees wat benzo[a]pyrene en dibenz[a,h]anthracene bevat.

Sleutelwoorde: Polisikliese aromatiese koolwaterstowwe; Dermale blootstelling; Dermale plakkers; Velkondisie; Transepidermale waterverlies, Veloopervlaktehidrasie; Veloppervlakte-pH; Petrochemiese werkers; Dermale veelappies; Beroepsblootstelling.

Author's contribution

This study was planned and carried out by a team of researches. The contribution of each researcher is given in Table 1.

Table 1. Research team

NAME	**CONTRIBUTION**
Mr. S.J.L. Linde	▪ Planning of the study and developing the protocol. ▪ Personal dermal exposure sampling and skin condition monitoring. ▪ Literature research and writing of the article.
Dr. J.L. Du Plessis	▪ Supervisor ▪ Assisted with the design and planning of the study, approval of the protocol used in the study, review of the dissertation and interpretation of the obtained results.
Prof. F. C. Eloff	▪ Assistant-supervisor ▪ Assisted with the planning and design of the study, with the approval of the protocol and review of the article.
Mr. P.J. Jacobs	▪ Assistant-supervisor ▪ Assisted with the design and planning of the study, as well as the execution of the sampling.

The following is a statement from the co-authors 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 a true reflection of my actual contribution and that I hereby give my consent that it may be published as part of S.J.L. Linde's M.Sc (Occupational Hygiene) dissertation.

Dr. J.L. Du Plessis	*Prof. F. C. Eloff*
(Supervisor)	*(Assistant-Supervisor)*

Mr. P.J. Jacobs
(Assistant-Supervisor)

Preface

The outline of this mini-dissertation is as follows:

- Chapter 1 – General introduction which gives a short background as well as the problem statement, hypothesis and aims of the study.
- Chapter 2 – Literature study which focuses on literature that is relevant to the study.
- Chapter 3 – Article of the full shift exposure study as well as the skin barrier function study.
- Chapter 4 – Article of short term exposure study.
- Chapter 5 – Provides conclusions on the study as well as recommendations, limitations, and prospects for future studies.
- The Vancouver Style of referencing was used as this is the preferred reference style of the Annals of Occupational Hygiene.
- Article format was used to in the writing of the Mini Dissertation.

Table of contents

Table of contents (continued...).

List of tables

Page

Chapter 2 – Literature study

Chapter 3 – Full shift exposure study

Chapter 3 Supplementary material

Chapter 4 – Short term exposure study

Chapter 4 - Supplementary material

Chapter 5– Conclusion

List of figures

Page

Chapter 3 – Full shift exposure study

Chapter 4 – Short term exposure study

List of Abbreviations

ATSDR	-Agency for Toxic Substances and Disease Registry
cm	-centimeter
EPA	- Environmental Protection agency
NIOSH	-National Institute for Occupational Safety and Health, United States of America
mg	- milligram
ng	- nanogram
OSHA	- Occupational Safety and Health Administration, United States of America
PAH	- Polycyclic Aromatic Hydrocarbon
pH	- negative logarithm of the H^+ concentration
PPE	- Personal Protective Equipment
POP's	- Persistent Organic Pollutants
OEL	- Occupational exposure Limit
SC	- Stratum Corneum
TEWL	- Transepidermal Water Loss

Chapter 1

General Introduction

1.1 Introduction

PAHs are becoming more of a problem in environmental as well as occupational settings: For example, benzo[a]pyrene has been recognised by the US Environmental Protection Agency as a priority pollutant and is known to be very carcinogenic (Bamforth and Singleton, 2005). PAHs derived from fossil fuels in lower trophic levels (invertebrates and fish) have increased 10 to 30 fold over the past 25 years and now dominate the summed POP burden (25 POPs, including 11 PAHs) in these biota (De Laender *et al*., 2011). In occupational settings, the number of workers potentially exposed to PAHs in countries like the UK may run into tens of thousands (Unwin *et al.,* 2006*)* and workers employed in the production of fuel from the destructive distillation of coal often experience high exposure to PAHs (Bofetta *et al.,* 1997).

From the destructive distillation of coal the viscous matter tar is derived. Tar contains several classes of organic compounds one of which being PAHs (Cirla *et al.,* 2007). The process of the destructive distillation of coal is commonly used in the production of petrol. Many PAHs are either known or suspected to be human carcinogens (McClean *et al.,* 2007). The development of cancer due to exposure to PAHs is a major concern as epidemiological studies point to increased cancer risks related to PAH exposures (Sodus *et al.,* 2009).

A growing number of studies have tried to determine the relationship between respiratory and dermal exposure and their various contributions to the total absorbed dose. These studies increasingly suggest that the route of dermal exposure is the primary route of PAH exposure in industrial settings (Fusinoni *et al.,* 2009).

Short term exposure to PAH-containing heavy fuel oils can cause skin irritation and defatting of the skin, which will result in dryness and cracking of the skin, as well as oil acne, dermatitis, hyperkeratosis, photo sensitivity and eye irritation (Christopher *et al.,* 2011, Baars, 2002). Short term exposure can also lead to allergic reactions on the skin and in the upper airways (Lubitz *et al.,* 2009).

The occupational exposure of asphalt and coke oven workers to PAHs has been associated with an increased risk for developing cancer of the lung, stomach, bladder, skin (including non-melanoma skin cancer) and blood (McClean *et al.,* 2004). According to the IARC classification, coal gasification and coal tar fumes (both rich in PAHs) are carcinogenic to humans (IARC, 1984). The PAH, benzo(a)pyrene is especially known for its carcinogenicity (Jongeneelen, 1997).

In contrast to inhalation exposure to hazardous chemicals not much literature is available on occupational dermal exposures to PAHs in South Africa and as a result there is no widely used occupational exposure limits (OEL's) available. This makes it very difficult to compare newly obtained dermal exposure data with existing data.

Factors that could contribute to differences in exposure level between workers include: smoking (Jongeneelen, 2001), type of personal protective clothing (PPE) used (Cirla *et al.,* 2007), work practice, equipment, varying weather conditions and other production characteristics (McClean *et al.,* 2004). Temperature and other environmental factors can also influence the skin barrier strength of healthy individuals (Muizzuddin *et al.,* 2010). The weather conditions and the type of protective clothing worn by the worker must therefore also be taken into account when assessing dermal exposure.

Dermal exposure to PAHs can occur in two ways: direct contact with contaminated surfaces or equipment, and from the settling of airborne particles or vapour on the skin (McClean *et al.,* 2004). This exposure can be assessed by using one of three techniques: Surrogate skin, removal techniques and fluorescent tracer techniques (Fenske, 1993). We used dermal patches (surrogate skin) and wipes (removal technique) to assess the dermal exposure of the workers at the petrochemical factory who are possibly exposed to PAHs which are present in the tar.

The skin is the primary barrier between a human being and the environment. It is very important to monitor the skin condition of workers as a reduced barrier function may lead to easier penetration of cemicals through the skin (Procksh *et al.,* 2008). To determine the effectiveness of the skin's function as a barrier certain factors such as Transepidermal water loss (TEWL), skin hydration and skin surface pH need to be quantified (Darlenski *et al.*, 2008).

The stratum corneum (SC) is the outer layer of the skin, is only 10-20 µm thick (Fluhr *et al.,* 2002) and comprises of pentagonal and/or hexagonal corneocytes in a lipid matrix (Hadgraft *et al.,* 2009).

TEWL is the physiological loss of water vapour from the skin in the absence of sweat gland activity. A disruption in the barrier function of the skin will lead to an increase in TEWL (Kezic *et al.,* 2009), whereas a lower TEWL value is characteristic of an intact skin barrier (Darlenski *et al.*, 2009).

Hydration of the skin is another important factor that must be determined when assessing the health of the human skin as failure of the SC to retain water (lower hydration) causes dryness and impairs the function of the skin barrier (Darlenski *et al.*, 2009).

An acidic environment is essential for skin barrier function. If the SC's acidity is neutralized, barrier function is inhibited because of a reduction in lipid-processing enzyme activity (Hachem *et al.,* 2005).

In the determination of a worker's total exposure to hazardous chemical substances the importance of dermal exposure is more often than not overlooked. Dermal exposures must, therefore, be incorporated into one's study if you are to accurately determine a worker's exposure.

1.2 Aims and objectives

The aims of this study are:

- To assess the dermal exposure of workers to PAHs during an entire 8 hour work shift.
- To assess the short term dermal exposure of workers to PAHs while performing certain identified tasks.
- To identify the areas and occupations that poses the highest risk to the health of the workers.
- To assess the skin barrier function of workers that may be exposed to PAHs by measuring TEWL, skin hydration and skin surface pH.

1.3 Hypothesis

- Workers at the petrochemical plant are exposed to a variety of PAHs via the dermal exposure route.
- The skin barrier function of these workers is impaired as a result of the exposure to PAHs.

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Chapter 2

Literature study

The literature presented in the following literature study will discuss the following: the chemical and physical characteristics of polycyclic aromatic hydrocarbons (PAHs), the negative health effects, in particular cancer, following exposure, a comparison between the influences that dermal and respiratory exposure respectively have on the total PAH load and different factors that influence exposure to PAHs. It will also focus on the skin barrier and factors that determine the permeability of the skin to PAHs as well as the factors that determine the integrity of the skin barrier.

2.1 The chemical and physical characteristics of PAHs

2.1.1 PAHs

PAHs is a class of organic compounds that consist of two or more fused benzene rings and/or pentacyclic molecules that are arranged in various structural conFigureurations (Bamforth and Singleton, 2005). PAHs can be present in a gaseous state or it can be bound to other particles in the air (Tsai *et al.,* 2001). There are several hundred types of known PAHs (Bofetta *et al.,* 1997), which are divided into two categories: high molecular weight compounds (202-278 g/mol) composed of four or more benzenic rings, for example benzo(a)pyrene and benzo(g,h,i)perylene, and low molecular weight compounds (128-166 g/ mol) composed of fewer than four rings, such as naphthalene, phenanthrene and fluorene (Sobus *et al.,* 2009). Normally, PAH molecules with three or less benzenic rings exist predominantly in the vapour phase, while PAH molecules with four rings exist in both vapour and particulate phases and PAH molecules with more than four rings exist only in the particulate phase (Cirla *et al.,* 2007). This is shown in a study by Elovaara *et al.* (1995) where naphthalene was abundant, while pyrene was absent in the air of workplaces where PAH-containing creosote is used. PAHs are highly lipophilic which allows them to move through the SC more readily (Poet and McDougal, 2002, Bamforth and Singleton, 2005). They are also thermodynamically stable (Angerer *et al.,* 1997) and can be broken down by reaction with sunlight and other chemicals in the air over a period of days or weeks (Mumtaz and George, 1995). PAHs do not dissolve easily in water. Instead they tend to attach to solid particles and settle on the bottom of lakes and rivers (Mumtaz and George, 1995).

Table1: Summary of the best known and most harmful PAH compounds and their respective molecular weights and number of aromatic rings according to Chen and Liao (2006) and (Fustinoni *et al.,* 2010).

Compound	**Abbreviation**	**Molecular weight (g mol^{-1})**	**Number of aromatic rings**
Naphthalene	Nap	128	2
Acenaphthylene	AcPy	152	3
Acenaphthene	AcP	154	3
Fluorene	Flu	165	3
Phenanthrene	PA	178	3
Anthracene	Ant	178	3
Fluoranthene	FL	202	4
Pyrene	Pyr	202	4
Cyclopenta[c,d]pyrene	CYC	228	4
Benzo[a]anthracene	BaA	228	4
Chrysene	CHR	228	4
Benzo[b]fluoranthene	BbF	252	5
Benzo[k]fluoranthene	BkF	252	5
Perylene	PER	252	5
Benz[e]pyrene	BeP	252	5
Benzo[a]pyrene	BaP	252	5
Indeno[1,2,3-c,d]pyrene	IND	276	6
Dibenz[a,h]anthracene	DBA	278	6
Benzo[b]chrycene	BbC	276	6
Benzo[g,h,i]perylene	BghiP	276	6
Coronene	COR	300	6

To date, the World Health Organisation has identified approximately 106 PAHs in pit coal tar, 280 PAHs in cigarette smoke and 146 PAHs in automobile exhaust emissions (Yadav *et al.,* 2010).

2.1.2. Sources

In the environment, PAHs are commonly present due to discharge from natural (volcanoes and forest fires), industrial (industrial plants) and urban (motor vehicle traffic, residential heating with fossil fuels, etc.) sources. Other sources include: tobacco smoke, chargrilled meats and smoked foods (Angerer *et al.,* 1997; Bamforth and Singleton, 2005; Cirla *et al.,* 2007). PAHs are also generated by the incomplete combustion of fuels, such as petrol, diesel and coal (Yadav *et al.,* 2009). Particulate extracts from diesel exhaust particles contain PAHs, in particular, nitro-PAHs such as nitro- and dinitro-pyrenes. Diesel engines emit 10 times more nitro-PAHs than petrol engines (Bofetta *et al.,* 1997).

In the industrial milieu, coal tar is formed during the gasification of coal which takes place during the production of fuels such as petrol and diesel (Cirla *et al.,* 2007). The composition of coal tar is very complex, which is apparent from the fact that over 200 compounds, including PAHs, have been isolated from it (IARC, 1985; Cirla *et al.,* 2007). Because of the variation in the source and composition of the coal and the manufacturing processes (different temperatures and times of gasification) used, no two coal tars are chemically identical (IARC, 1985). The concentration PAHs in the tar, heavily depend on these differences in coal composition, gasification temperature and manufacturing process (Väänänen *et al.,* 2005). Industries where PAH mixtures represent a significant amount of the risk for the worker's health include coal gasification, coke production and other industries where coal tars are used (Bofetta *et al.,* 1997).

Creosotes are obtained from the fractional distillation of coal and also contain significant quantities of PAHs (Bamforth and Singleton, 2005).

From the above mentioned sources it can be seen PAHs are abundant in the petrochemical industry and it is, therefore, very important to fully understand the way that PAHs affect workers in order to better control their exposure.

2.2 Toxicology

2.2.1. Metabolism

The metabolism of xenobiotics can usually be divided into three phases: phase 1 leads to the formation of reactive electrophilic intermediates, phase 2 most often leads to the deactivation of these reactive electrophiles by various conjugation reactions and phase 3 is the active transport of polar metabolites from the cell into the surrounding environment (Boström *et al.,* 2002).

After entering the body a PAH, for example pyrene, is metabolized to form 1-hydroxypyrene-glucuronide and is rapidly distributed and eliminated from the body in the urine (Jongeneelen, 2001). The metabolite most abundant in the body following exposure to pyrene, 1-hydroxypyrene (1-OHP), has a urinary excretion half-life of 18 hours in occupational exposed workers (Buchet *et al.,* 1992). In biological monitoring, the urinary excretion of 1-OHP is determined to assess the internal exposure to PAHs as individual exposure to pyrene is seen as an indicator of PAH exposure (Pastorelli *et al.,* 1999). Pyrene however does not add much to the carcinogenicity of PAH mixtures occurring in the workplace and the metabolites of more potent carcinogenic PAHs such as 1-, 2-, 3- and 4-hydroxyphenanthrene, 3-hydroxybenz(a)anthracene and 3-hydroxybenzo(a)pyrene can also be determined (Gündel *et al.,* 2000). In general, it is accepted that a greater number of benzene rings in the PAH molecule will lead to increased hydrophobicity and toxicity of the specific PAH molecule (Bamforth and Singleton, 2005). Biotransformation of pyrene into 1-HP by human liver preparations *in vitro* has shown large differences between people (Elovaara *et al.,* 1995).

2.3 Health effects

Occupational dermal exposure to PAHs can cause short term health effects, induce allergic reactions and may lead to the development of cancer.

2.3.1. Symptoms associated with short term exposure

Short term exposure to PAH-containing heavy fuel oils can cause skin irritation and defatting of the skin, which will result in dryness and cracking of the skin, as well as oil acne, dermatitis, hyperkeratosis and photo sensitivity (Christopher et al., 2011). Besides irritation of the skin, eye irritation was also observed in workers exposed to heavy fuel oils (Baars, 2002). Cirla et al. (2007) reported an increase in acute symptoms as asphalt workers' shifts progressed. The most frequently reported symptoms were eye irritation and coughing, although headaches, fatigue and throat irritation also occurred. These symptoms normally increase with an increase in the asphalt temperature and the concentration of asphalt fumes (Cirla et al., 2007).

2.3.2. PAHs as allergens

Certain PAHs may, following metabolism, induce inflammatory processes that can lead to allergic reactions (Boström *et al.,* 2002). *In vitro* studies have shown that PAHs originating from respiratory exposure to diesel exhaust particles can directly enhance IgE synthesis in human B cells and that they, as well as other single PAHs such as pyrene, anthracene,

fluoranthene and benzo(a)pyrene, can act as adjuvants for allergen-specific IgE production in the upper airways of humans (Lubitz *et al.,* 2009). Benzo[a]pyrene can also elicit an allergic contact hypersensitivity response when applied to the skin of animals (Mumtaz and George, 1995).

2.3.3. Cancer

The key event in the discovery of PAHs that cause tumors in humans was an observation by the British surgeon Sir Percival Pott in 1775, that scrotal cancer in chimney sweeps originated from occupational exposure to soot and in 1875 von Volkman reported elevated incidences of skin cancer in workers in the coal tar industry (Boström *et al.,* 2002). Workers employed in the destructive distillation of coal were among the first occupational groups included in studies which reported an increase in scrotal and other skin cancers linked to exposure to tar or pitch (Bofetta *et al.,* 1997).

The carcinogenicity of petroleum products such as fuel oils is a major cause of concern. It is generally accepted that the PAHs in these oils are the major culprit responsible for causing cancer following exposure to the oil (Baars, 2002) and it is suggested that PAHs from coal tar are the most plausible explanation for the increase of skin and scrotal cancer among coal gasification workers (Bofetta *et al.,* 1997). The occupational exposure of workers to PAHs has been associated with an increased risk for developing cancer of the lung, stomach, bladder, skin (including non-melanoma skin cancer) and blood (McClean *et al.,* 2004; Kammer *et al.,* 2011). Many PAHs are considered to be complete carcinogens, i.e. the compounds are tumour initiators and promoters/progressors (Boström *et al.,* 2002). The IARC classified coal tars and coal gasification as class 1 (carcinogenic to humans) and the single PAHs benzo[a]pyrene and dibenz[a,h]anthracene are classified as class 2A (probably carcinogenic to humans) (Bofetta *et al.,* 1997; IARC 1984). Benzo[a]pyrene is recognised as a priority pollutant by the US Environmental Protection Agency and is known to be one of the most carcinogenic of all known PAHs (Bamforth and Singleton, 2005).

The skin can be a target organ for carcinogens (Väänänen *et al.,* 2005). PAHs require metabolic activation to exert their biological, mutagenic and carcinogenic activities which are mediated through the formation of reactive metabolites that can cause DNA damage or form DNA covalent adducts (Yan *et al.,* 2004). An important property of PAHs is, therefore, their metabolic conversion to reactive electrophilic intermediates that can covalently bind nucleophilic targets in DNA, RNA and proteins (Boström *et al.,* 2002). Benzo(a)pyrene forms intermediary metabolites (epoxide-benzo(a)pyrene and dihydrodiol-epoxide-benzo(a)pyrene) that can covalently bind to nucleophilic sites in DNA to form benzo(a)pyrene-DNA-adducts. These intermediate metabolites are thought to be the carcinogenic form of benzo(a)pyrene

(Jongeneelen *et al.,* 1997) and interfere with transcription, DNA replication and protein synthesis (Boström *et al.,* 2002). Therefore, the genotoxic activity of a particular PAH requires metabolic activation to the ultimate active form and subsequent binding of these intermediates to critical positions in DNA (Boström *et al.,* 2002, Yadav *et al.,* 2010). The extent of this DNA binding in conjunction with the distribution of these adducts throughout the body and their structures are intimately associated with their mutagenic and carcinogenic potency (Boström *et al.,* 2002).

A study by Cavallo *et al.* (2005) on chronic occupational dermal exposure, showed early oxidative DNA damage in paving workers who had been chronically exposed to low doses of PAH mixtures and in an early mortality study in the UK, tar distillation workers were found to be at higher risk of contracting cancer (Bofetta *et al.,* 1997). Dermal exposure to PAHs not only results in local effects on the skin but also in systemic effects, which may lead to the formation of PAH-DNA adducts in the lung which may increase the risk of developing lung cancer (Jongeneelen *et al.,* 2001). Wester *et al.* (1990) found that ~24% of applied benzo(a)pyrene penetrated the skin and was therefore, able to enter the systemic circulation. Tsai *et al.* (2001) found that workers handling PAH-containing materials had a significant risk for developing skin cancer.

In addition to evidence of human carcinogenicity, tests performed on rats revealed maternal and foetal toxic effects following 19 days of dermal exposure to PAH containing heavy fuel oils (Baars, 2002). Another animal study done on rodents showed that benz[a]anthracene, benzo[a]pyrene, dibenz[a,h]anthracene and possibly other PAHs are carcinogenic when given in high oral doses (ATSDR, 1995).

Because of the multiple aromatic ring systems in PAHs, these compounds can absorb UVA light energy form reactive species in order to cause damage to cellular components. It has been shown that dermal exposure to PAHs and light can cause DNA single strand cleavage, oxidation of DNA bases and form DNA covalent adducts. PAHs can be activated by light irradiation without requiring metabolizing enzymes. Some PAHs are photomutagenic although they are not mutagenic in cells through normal metabolic activation (Yan *et al.,* 2004).

Occupational settings are the primary milieu where exposure to PAHs occur and it is, therefore, very important to understand the way in which these workers are exposed in order to better control their exposure.

2.4 Occupational dermal exposure to PAHs

Occupational exposure to PAHs is complicated by several factors: Firstly, PAHs occur mainly in mixtures whose composition depends on the type of raw material used and the combustion circumstances. Secondly, PAHs in occupational environments are often adsorbed to solid particles and thirdly, there are other non-occupational sources of PAHs such as tobacco smoke that can influence the exposure. It is therefore difficult to compare different studies conducted in the same industry and on different individuals as quantitative as well as qualitative differences in exposure may occur (Bofetta et al., 1997).

2.4.1. Dermal vs inhalation exposure

Previously in occupational hygiene, exposure via inhalation has been considered the most important route for occupational exposure to hazardous chemicals. During the past two decades however, there has been an increased interest in exposure via the dermal exposure route (Kammer *et al.,* 2011).

PAHs can enter the body through inhalation, ingestion and absorption through the skin. (Cirla *et al.,* 2007; Soutar *et al.,* 2000; Boström *et al.,* 2002). Most studies evaluating PAH exposure have predominantly focussed on inhalation exposure as methods for evaluating airborne contaminants are reasonably standardised. The assessment of dermal exposure on the other hand is much more difficult as there is no general agreement on the wide range of available procedures or their underlying assumptions (Fustinoni *et al.,* 2010). PAHs are non-polar substances which can easily penetrate through the lipoprotein layers of the skin. The lipophilic properties of PAHs increase with an increase in the complexity of its structure and, therefore, more complex PAHs will move through the skin more easily (Boström *et al.,* 2002). Dermal absorption of PAHs is, therefore, of great importance (Gündel *et al.,* 2000; McClean *et al.,* 2007).

Toxicological and epidemiological studies have shown that dermal penetration of PAHs is an important route of exposure and that quantitatively, dermal absorption could represent up to 90% of the total dose penetrating the body under specific conditions (Dor *et al.,* 2000). From the treatment of patients' skin with coal tar it is known that pyrene is readily absorbed and excreted as high urinary concentrations of 1-OHP (Elovaara *et al.,* 1995). According to Väänänen *et al.* (2005) skin contamination is the main determinant of internal PAH-dose and contributes on average 70% or more. For example, results from a study by Van Rooij *et al.* (1993) suggest that dermal absorption is the primary route of PAH exposure in coke oven

workers. After evaluating pyrene dermal and respiratory exposure data as well as urinary 1-OHP data, it was indicated that an estimated 75% of the total absorbed dose could be attributed to dermal exposure. In more recent studies Cirla *et al.* (2007) and McClean *et al.* (2004) established that the total body dermal exposure in a given time period amongst Italian asphalt workers was three times higher than their respiratory exposure for the same period of time. McClean *et al.* (2004) also determined that the effect of the dermal exposure to the asphalt vapours caused 8 times higher 1-OHP levels than that of the inhalation exposure. Furthermore, the effect of the inhalation exposure was apparent immediately after the shift, while that of the dermal exposure was still increasing 8 – 16 hours after the shift had ended. In a study by Jongeneelen *et al.* (1988) skin contamination of asphalt workers appeared to increase 10-fold when the asphalt contained coal tar, which is in accordance with the literature that coal tar is a major occupational source of PAHs (Boogaard and van Sittert, 1995). Christopher *et al.* (2011) also suggests that the emphasis for exposure to heavy fuel oils, which contain PAHs, should be on the dermal route. Dermal absorption is a major route of PAH uptake, therefore PAH determination in the air is not sufficient to estimate the health risk of the individual worker (Gündel *et al.,* 2000). Based on 1-OHP data, Elovaara *et al.* (1995) established that the major route for the uptake of carcinogenic PAHs in their study was via the skin. Dermal exposure is more important in maintenance workers than in operators as the maintenance workers have a greater risk of skin contact with the contaminant than the operators, who are more likely to be exposed to only airborne PAH (Boogaard and van Sittert, 1995). PAHs with smaller molecular structures such as naphthalene are more volatile and exposure usually takes place via inhalation, whereas larger PAHs such as pyrene and benzo[a]pyrene are more likely to settle on the surface of the skin (Elovaara *et al.,* 1995).

No quantitative occupational exposure limit values exist that may protect workers against adverse effects from uptake through dermal exposure (Bos *et al.,* 1998). Unlike inhalation exposure there are no occupational exposure limits (OEL's) for dermal exposure to different hazardous chemicals (Semple, 2004). The reason for this is that there are no standardised strategies for measuring and assessing skin exposure and, therefore, there cannot be standardised exposure limits (Väänänen *et al.,* 2005; Kammer *et al.,* 2011). Not many results for dermal exposures to PAHs have previously been reported and as a result of this, there is not a lot of dermal exposure data available for comparisons (Christopher *et al.,* 2011; Schneider *et al.,* 2000). Data regarding dermal PAH exposure to workers in South Arica is especially lacking. This makes it very difficult to compare newly obtained dermal exposure data with existing data. Although OEL's are predominantly focussed on the air concentrations of chemicals, some chemicals have received a skin notation to indicate that it

can enter the body through the skin (Väänänen *et al.,* 2005; Bos *et al.,* 1998). The purpose of this skin notation is to identify substances that can contribute substantially to the total body burden and have serious systemic health effects after being absorbed through unbroken skin (Semple, 2004). The German committee on MAK (maximum workplace concentration) has assigned a skin notation to bitumen fumes because it has been shown in animal studies that carcinogenic compounds, present in bitumen fumes, can penetrate the skin. PAHs on the other hand have no skin notation although many studies have concluded that skin absorption of PAHs can be considerable (Väänänen *et al.,* 2005).

Occupational exposure to PAHs should be controlled to levels that are as low as reasonably practical (Unwin *et al.,* 2006*)*.

2.4.2. Factors that affect exposure

Many factors such as personal hygiene, work practice, equipment, varying weather conditions and other production characteristics can influence the measurement of occupational exposure to PAHs and must be taken into consideration when assessing workers' exposure.

2.4.2.1. Smoking

Tobacco smoke contains numerous PAH compounds and there is approximately 10-50 ng of benzo[a]pyrene in the main stream smoke per cigarette, and the concentration is four times higher in side stream smoke (Kuljukka *et al.,* 1997). Elevated levels of PAH-DNA adducts are associated with smoking (Chan and Liao, 2005) and the level of 1-OHP in the urine is highly affected by the smoking of cigarettes (Jongeneelen, 2001; Cirla *et al.,* 2007) but also to a lesser extent by PAH pollution in the environment (Jongeneelen, 2001). McClean *et al.* (2007) found that the urinary 1-OHP levels in smoking asphalt roofing workers were twice as high when compared with that of non-smoking workers. This suggests that smoking plays a significant role in determining the overall PAH exposure.

2.4.2.2. Diet

Carcinogenic PAHs have also been identified in many food items such as grilled or smoked meat and fish (Kuljukka *et al.,* 1997) and even in whiskey (Kleinjans *et al.,* 1996). It has been estimated that dietary PAH exposure may contribute considerably to the total PAH load (Bofetta *et al.,* 1997, Kuljukka *et al.,* 1997, Cirla *et al.,* 2007).

2.4.2.3. Weather

Varying weather conditions can contribute to differences in the exposure level between workers in that it can affect the way that the PAH-molecules are distributed (McClean *et al.,* 2004). For example, in winter airborne pyrene levels reach a peak which can affect the exposure to PAHs considerably (Pastorelli *et al.,* 1999). Pastorelli *et al.* (1999) observed a significant seasonal difference in PAH exposure. Twenty four hour personal exposure monitoring data showed a 3-fold increase in pyrene levels in winter compared with summer. There was also a significant difference in 1-OHP excretion levels of the workers, where 1-OHP excretion was higher during winter than during the summer. In winter they also observed a larger difference between the exposure of smokers and non-smokers compared to this difference observed in summer. A reason for this could have been that the low ambient temperatures influenced the distribution and concentration of the PAH on particle matter (Pastorelli *et al.,* 1999). McClean *et al*. (2007) found that dermal exposure to pyrene and benzo[a]pyrene varied by relative humidity and wind speed. Relative humidity was positively associated with dermal exposure, while wind speed showed a negative association. The authors argued that the increased humidity decrease evaporation by means perspiration from the skin, which could increase the potential for dust to adhere to the skin and that the increased wind speed act as a natural ventilation system to reduce the potential for skin contact with airborne dust (Muizzuddin *et al.,* 2010). The joint effect of field variables such as a change in wind speed and direction and the presence of side exposure sources can sometimes provoke a 10-fold higher exposure level on one day compared to other days (Deygout *et al.,* 2011).

Temperature and other environmental factors such as humidity can also influence the skin barrier strength of healthy individuals (Muizziddin *et al.,* 2010) and can alter percutaneous penetration of chemicals. Studies have shown that working in hot and humid environments will increase dermal absorption and lead to the increased bioavailability of chemicals in the systemic circulation (Poet and McDougal, 2002).

Therefore, varying weather conditions can influence workers' dermal exposure from one day to the other by changing the concentration PAH-molecules in the air and by changing the penetration of the PAH-molecules through the skin.

2.4.2.4. Modus operandi

McClean *et al*. (2004) and McClean *et al*. (2007) reported a difference in exposures in different crews that do the same job, which suggest that *modus operandi* also plays an important role in exposure. Dirty clothes also cause additional exposure to the contaminant

as a result of direct contact (Fustinoni *et al.,* 2010). Simple hygienic operations can reduce skin contamination considerably (Väänänen *et al.,* (2005).

2.4.2.5. Molecular weight of PAH

Dermal exposure to PAHs can occur in two ways: direct contact with contaminated surfaces or equipment, and from the settling of airborne particles or vapour on the skin (McClean *et al.,* 2004). The deposition of vapours and the splashing of oils are common occurrences at workplaces (Sartorelli *et al* 1999). McClean *et al.* (2004) showed data suggesting that dermal exposure to PAHs are more likely to be to higher molecular weight compounds than PAHs with lower molecular weights, which are more likely to be inhaled. The reason for this could be that lower molecular weight compounds are more volatile and are, therefore, more likely to become airborne (Cirla *et al.,* 2007). Larger molecules, on the other hand, such as benzo[a]pyrene are more likely to settle on the skin (Elovaara *et al.,* 1995).

2.4.2.6. Clothing and personal protective equipment

Cirla *et al*. (2007) found no difference in the dermal exposure to PAHs between areas of the skin covered by clothing and areas not covered. In their study, workers wore cotton clothes, instead of protective PVC or Tyvek suits. Tsai *et al.* (2001) also found considerable dermal exposure to packaging workers in areas of the body covered by clothes. Boogaard and van Sittert (1995) reported two PAH exposure studies regarding personal protective clothing amongst ground workers working in PAH contaminated soil. In the first study the workers wore half-face masks with organic vapour cartridges, but no special measures were taken to protect them against dermal exposure and the results revealed significant dermal exposure to PAHs. In the second study however, a more strict application of dermal protection (impermeable PVC suits) were imposed that led to a substantial decrease in dermal exposure. The type of protective clothing worn by the worker must therefore also be taken into account when assessing dermal exposure. Coveralls may reduce contamination, but they also may increase the dermal absorption rate of contaminants due to the elevated temperature of the skin, humidity and physical stress (van Rooij *et al.,* 1993).

2.4.2.7. Inter-individual differences

Inter-individual differences in the enzyme/enzyme systems participating in the metabolism of PAHs are expected to play an important role in tumour susceptibility. Polymorphisms in these enzymes that participate in the activation of PAHs to their ultimate mutagens and the subsequent detoxification and elimination of these intermediates have been identified in humans (Boström *et al.,* 2002). Inter-individual variability in the capacity to activate or

deactivate potential genotoxic and carcinogenic PAHs may have an influence in the cancer susceptibility of each individual worker (Yadav *et al.,* 2010).

2.5 Method of occupational sampling

The measurement of dermal exposure resulting from contaminants being deposited directly onto the skin or from a worker's physical contact with a contaminated surface is important in the overall assessment of a worker's exposure (McArthur, 1992). Fenske (1993) has classified the methods of assessing dermal exposure into three groups: surrogate skin techniques, removal techniques and fluorescent tracer techniques. In this study we used two of these techniques, namely the surrogate skin and removal techniques.

2.5.1 Patch sampling

The objective of patch sampling is to estimate the amount of contaminant deposited on the skin during the entire work shift (Soutar *et al.,* 2000). The polypropylene pad method that was used in this study was successfully used in a collection of other PAH exposure studies, including Fustinoni *et al.* (2010), McClean *et al*. (2004), Väänänen *et al.* (2005), McClean *et al*. (2007), Cirla *et al.* (2007) and Sobus *et al.* (2009). A few advantages of this method are that it is user-friendly, cost-effective and that is easily applied and accepted by workers (Fustinoni *et al.,* 2010; Väänänen *et al.,* 2005). On the negative side though, when the contaminant is sprayed onto the skin and the patch is missed, the exposure can be underestimated, while when a few droplets land on the patch, exposure can be overestimated (Soutar *et al.,* 2000). The method assumes that the contamination is uniformly distributed over the whole area that is represented by the patch (Soutar *et al.,* 2000). Exposure may also be underestimated due to the fact that no absorption mechanism is involved in the process (Fustinoni *et al.,* 2010). The pad material differs from natural skin and PAH absorption into the pad therefore differs from PAH absorption into the skin (Väänänen *et al.,* 2005; Schneider *et al.,* 2000). Because of these disadvantages careful observation was needed throughout the shift in order to identify factors that could have compromised the potential of the patch to give an accurate representation of the exposure (Soutar *et al.,* 2000).

The location of the patches was carefully chosen in order to give an accurate measurement of the overall exposure (Väänänen *et al.,* 2005). Fustinoni *et al.* (2010) nominates the wrist as the best area to sample as it is in the closest proximity to the contaminated surfaces. The wrist is, therefore, expected to be the most contaminated area (Jongeneelen *et al.,* 1988). Another reason for choosing the wrist was that unlike that of the hand, the skin on the wrist

did not bend and twist while the worker was working. The presence of the patch did therefore not cause any discomfort to the worker.

2.5.2. Wipe sampling

Skin wiping is defined by Brouwer *et al.* (2000) as the removal of contaminants from the skin by providing a manual external force to a medium that equals or exceeds the force of adhesion over a defined surface area and it has the advantage of being cost effective and easy to use. Christopher *et al.* (2011) developed a skin wipe dermal sampling method which uses PAH compounds as markers in order to assess the dermal exposure to heavy fuel oils in occupational settings. This removal method uses pre-injection swabs that contain 70% isopropyl alcohol to remove the PAH containing heavy fuel oils from the skin. In testing they obtained a recovery efficiency of 95% to 106% from directly spiked samples and an overall sampling efficiency from pig skin that ranged from 88.9% (benzo(a)pyrene) to 100% (phenanthrene). Storage stability of the wipes allows for a 2-week window in which the samples can be stored. The authors concluded that this is a reliable and reproducible method for determining short term dermal exposure to PAH. This removal method was used in our study to determine short term task-specific exposure to PAHs. However, one of the disadvantages of this method is that it only measures the contaminant still present on the surface of the skin and does not account for the contaminant that has already been absorbed (Soutar *et al.,* 2000). The amount of chemical removed by the wipe technique represents the amount of chemical present on the skin at the time of the sampling (Brouwer *et al.,* 2000) and it is, therefore, ideal for task based monitoring (i.e. measuring short term exposure resulting from specific activities that only last approximately 15-30 minutes) because in all likelihood the majority of the contaminant will still be present on the skin.

Task based monitoring of exposures is an important tool in assessing the complete exposure of a worker to PAHs (McClean *et al.,* 2004). Task based monitoring done by McClean *et al.,* (2004) showed a consistency between dermal exposure experienced by asphalt workers and the degree to which each task required actual contact with contaminated surfaces and equipment. Task-based sampling is the most appropriate sampling strategy when exposure scenarios are generally of short duration and do not occur on a regular basis (Cristopher *et al.,* 2011). This strategy helped to determine the specific tasks that pose the biggest threat to the health of the worker.

2.6 The skin barrier

The skin is the primary barrier between a human being and the environment and protects against extensive water loss, the loss of proteins and plasma components from the organism as well as the invasion of harmful substances from the environment (Procksh *et al.,* 2008). Its major component, the stratum corneum (SC), is the rate-limiting unit that obstructs the penetration of exogenous substances through the skin (Darlenski *et al.*, 2008).

The SC is the outermost layer of the epidermis that consists of pentagonal and/or hexagonal corneocytes that are embedded in a lipid matrix (Rawlings *et al.,* 2008; Hadgraft and Lane*,* 2009) and has a thickness of approximately 10-20 µm (Fluhr *et al.,* 2002). It forms a continuous sheet of protein-enriched corneocytes that are connected by corneodesmosomes which are imbedded in an intercellular matrix enriched in non-polar lipids and organised as lamellar lipid layers (Procksh *et al.,* 2008). The predominant route of penetration of xenobiotics as well as water is through this complex mixture of lipids (Hadgraft and Lane*,* 2009).

The corneocytes and extracellular matrix in the SC have a “brick and mortar” appearance (Hadgraft and Lane*,* 2009) and the corneocytes on the top layer of the SC are constantly being replaced by younger cells (keratinocytes) from the deeper lying cellular layers of the epidermis. This process is known as desquamation (Harding *et al.,* 2001) and, under normal conditions, occurs every 14 days (Hadgraft and Lane*,* 2009).

The ability of the skin to act as a barrier result from the properties of the lipids and depends on the path length that the chemical needs to travel through the SC, which depends on number of layers of corneocytes, their size and their cohesion. The larger the corneocytes, the longer the path length will be and this will lead to lower penetration of the chemical through the SC (Hadgraft and Lane*,* 2009). Absorption rates of chemicals through skin, where the permeability barrier is in doubt can vary greatly (Levin and Maibach, 2005). Studies have shown that damaged skin is a less effective barrier against percutaneous penetration of chemicals than uncompromised skin (Nielsen *et al.,* 2007). A study by Nielsen *et al.* (2007) demonstrated that even limited damage to the skin barrier can significantly increase the absorption rate as well as the percutaneous penetration of chemicals through the skin, especially those compounds that, due to their physiochemical characteristics, have low penetration rates through intact skin. Chemical penetration through the skin is also influenced by the location on the body. On the face for example, the corneocytes are smaller, there are fewer layers and penetration is more rapid, whereas on the forearm there

are more corneocytes and cell layers and therefore less chemical penetration (Hadgraft and Lane, 2009).

In order to determine the effectiveness of the skin's function as a barrier certain factors such as Transepidermal Water Loss (TEWL), skin hydration and skin surface pH need to be quantified (Eberlein-König *et al.,* 2000, Darlenski *et al.*, 2008). These are non-invasive methods that can help to assess the skin barrier's function (Eberlein-König *et al.,* 2000) which is of great importance because a damaged skin barrier may lead to enhanced skin absorption of PAHs such as pyrene and benzo[a]pyrene through the skin (Kammer *et al.,* 2011).

Impairment of the skin barrier function is often demonstrated by an altered integrity of the SC and a consequential increase in TEWL. A decrease in skin barrier function often arises from direct damage followed by a breach in the SC and a decrease in or dysfunction of the SC lipids. Dry and flaky skin is caused by direct damage to the SC and by the impairment of corneocyte maturation and its desquamation together with a decrease in the water holding capacity of the SC (Rawlings *et al.,* 2008). Factors such as anatomical site, temperature, time of day, sex and age are also known to affect the barrier function of the skin (Breternitz *et al.,* 2006).

Non-invasive methods such as the determination of TEWL, skin hydration and skin surface pH can be used to assess the skin barrier function (Eberlein-König *et al.,* 2000).

2.6.1. TEWL

TEWL is the physiological loss of water vapour from the skin in the absence of sweat gland activity (Kezic and Nielsen 2009) and TEWL measurements are used to gauge skin barrier function (Levin and Maibach, 2005).

In the absence of sweat TEWL may be used as an indirect measurement of skin permeability and barrier function (Singh *et al.,* 2001). A disruption in the barrier function of the skin will lead to an increase in TEWL (Kezic and Nielsen 2009), whereas a lower TEWL value is characteristic of an intact skin barrier (Darlenski *et al.*, 2009). TEWL measurements allow for the discovery of disturbances in the protective barrier function of skin at an early stage (Mündlein *et al.,* 2005) as the impairment of the skin barrier function is often associated with a change in SC integrity, which leads to an increase in TEWL (Rawlings *et al.,* 2008) as well as an increase in the absorption of exogenous substances and toxins (Levin and Maibach, 2005). TEWL is increased in a variety of pathological and cosmetic conditions that involve abnormal barrier function and dry scaly skin (Rawlings *et al.,* 2008).

This is supported by studies that reported increased TEWL values in adult patients with atopic eczema (Eberlein-König *et al.,* 2000). A study done by Machado *et al.* (2010) showed TEWL data that was inversely correlated with the diffusional path length for water movement through the skin. This means that TEWL values will be lower in areas of the skin that has a thicker SC.

TEWL measurements can be affected by the anatomical site, sweating, skin surface temperature, inter- and intra-individual variation, air convection, ambient air temperature, ambient air humidity, and instrument related variations (Levin and Maibach, 2005). TEWL has been shown to vary directly with skin temperature (Singh *et al.,* 2001).

2.6.2. Skin hydration

Adequate hydration is essential for optimal skin functioning (Kezic and Nielsen, 2009). Failure of the SC to retain water (lower hydration) causes skin dryness and impairs the function of the skin barrier (Darlenski *et al.*, 2009). SC hydration drastically decreases with an increase in skin dryness (Eberlein-König *et al.,* 2000), therefore, measured hydration values will decrease with increasing skin dryness. Disturbed skin barrier function is often associated with low hydration of the SC and it is because of this that the application of moisturizers often improves skin barrier function (Procksh *et al.,* 2008).

Excessive hydration can also lead to reduced barrier function as it reduces the cohesiveness of the SC (Kezic and Nielsen, 2009). Increased hydration leads to weakened SC cohesion (Löffler *et al.,* 2004) and will cause disruption in the SC intercellular bi-layers as well as corneodesmosome degradation. Twenty four hours after the onset of the increased hydration the corneocytes will begin to dissociate (Warner *et al.,* 1999). Excessive hydration of the skin can occur following prolonged exposure to water or it can alternatively be caused by occlusion (i.e. the wearing of gloves) that prevent the normal evaporation of sweat from the hands (Kezic *et al.*, 2009).

2.6.3. TEWL vs skin hydration

An inverse relationship exists between SC hydration and TEWL (Procksh *et al.,* 2008*)*. A lower TEWL and normal hydration values are associated with normal healthy skin, whereas high TEWL and low hydration values are usually linked to damaged or diseased skin. The physical appearance of skin is also important as there is a greater chance that larger volumes of water will be lost through visibly dry and flaky skin (Darlenski *et al.*, 2008). If the skin's function as a barrier is compromised by chemical or physical damage, a high TEWL and a low hydration value is expected. Once the barrier is less effective it may become more

permeable to chemical substances, thus facilitating their systemic absorption (Kezic and Nielsen, 2009).

2.6.4. Skin surface pH

An acidic environment is essential for skin barrier function (Gunathilake, 2009). Studies have shown that several kinds of inflammation or trauma and dryness of the skin can cause an increase in skin surface pH (Eberlein-König *et al.,* 2000). If the SC's acidity is neutralized, barrier function is inhibited because of a reduction in lipid-processing enzyme activity. Acidification of the SC is a major stimulus for the expression of these enzymes (Hachem *et al.,* 2005). Exposure of perturbed skin sites to a neutral pH delays recovery of the permeability barrier following an injury. The SC pH regulates permeability barrier homeostasis, SC integrity and cohesion (Gunathilake, 2009) and acute alkalisation of the SC has been known to have negative effects on SC integrity and cohesion (Hachem *et al.,* 2005).

2.6.5. Ethnic differences

The workers in this study was mostly of African descent, while most of the previous research done on occupational dermal PAH exposure focussed on Caucasians. Because of this certain differences between black and Caucasian skin need to be taken into account. Black skin contains low levels of ceramide and high levels of protein cohesion in the uppermost layers of the SC. It is, therefore, characterised by a low baseline TEWL and a strong, well matured skin barrier with a high resistance to mechanical change (Muizzuddin *et al.,* 2010). Darker skin shows an increased integrity and superior permeability function as the skin barrier recovers faster after injury (Gunathilake, 2009). In comparison with Caucasian and East Asian skin, the uppermost layer of the SC of black skin contains low protease and high protein levels which suggests slower desquamation. This causes a thicker SC in black skin. This, combined with lower levels of ceramides in the SC may be the reason for the increased scaliness of black skin (Muizzuddin *et al.,* 2010). In general, black skin has a lower skin pH than lighter skin (Gunathilake, 2009). Although the differences between black and Caucasian skin is a very controversial issue it needs to be kept in mind when interpreting these results.

2.6.5. The use of barrier and skin creams

The use of skin barrier creams in occupational settings can help prevent the dermal absorption of industrial chemicals and can also help prevent the development of contact dermatitis and improve skin barrier function (Korinth *et al.,* 2003).

2.6.6. Differences between anatomical sites

A great deal of data clearly demonstrates anatomical site variability in dermal absorption (Poet and McDougal, 2002). This could be due to the fact that the SC in different anatomical sites varies in thickness, morphology and lipid composition (Fluhr *et al.,* 2002), and that various dermal appendages such as follicles act as shunts to modify dermal absorption. A third less popular theory is that differences in cutaneous blood flow affects the rate at which the chemical is absorbed into the systemic circulation. Of all these explanations, the composition of the SC is the most important variable for the difference in dermal absorption between the different anatomical sites (Poet and McDougal, 2002).

Using a tape stripping method to investigate SC physiology and corneocyte cohesion, Löffler *et al.* (2004) showed a significantly higher vulnerability to damage in the skin on the face and torso compared to the forearm. This may be due to a decreased number of cell layers in the SC of the face and torso. Furthermore, there are site-dependant differences in spontaneous desquamation and, therefore, possibly also SC cohesion, which may also account for the differences in SC integrity between the various sites (Löffler *et al.,* 2004).

There are a wide variety of factors that can affect dermal exposure of workers to PAHs in the petrochemical industry, such as the composition of the tar, the weather, side exposures, *modus operandi*, clothing and the use of personal protective equipment by the workers. Along with the fact no accepted exposure limits exist for dermal exposure to PAHs, it makes it very difficult to interpret and compare data. Therefore, all of these factors need to be taken into consideration when interpreting dermal exposure results.

2.7 References

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1. Chapter three in this study consists of more than 5000 words. This is done for examination purposes only.
2. The graphs in chapter three and chapter four are included in the text to make it easier to read for the examiners.
3. The names given to all the workers in chapter three and chapter four are given in such a way that the complete study can be observed as its entirety.

Chapter 3

Full shift exposure study

Full shift dermal exposure and skin barrier function of petrochemical workers exposed to polycyclic aromatic hydrocarbons

LINDE S.J.L, DU PLESSIS J.L, ELOFF F.C, JACOBS P.J.

School of Physiology, Nutrition and Consumer Sciences

North-West University, Potchefstroom Campus,

South Africa

Corresponding author

Prof. J.L. du Plessis

School of Physiology, Nutrition and Consumer Sciences

North-West University, Potchefstroom Campus

Private Bag X6001

Potchefstroom

2520

South Africa

Tel: 018 299 2437

Fax: 018 299 2433

Word count: 6213

ABSTRACT

Objectives: To determine the dermal exposure of petrochemical workers to 16 polycyclic aromatic hydrocarbons (PAHs) throughout an 8-hour shift, by applying polypropylene patches to six different sites on the skin's surface and one on the outside of the clothing. Also to determine the state of their baseline skin barrier function as a result of this exposure and to assess the health risk experienced by these workers.

Methods: 14 Workers from three different plants in a South African petrochemical factory were included in the study and their dermal exposure was assessed during a single 8-hour shift. Patches were placed on both wrists, both forearms, the neck, the ankle and on the outside of the clothing on the right forearm. The skin surface hydration, skin surface pH and the Transepidermal water loss (TEWL) were measured on the palm, wrist, forearm and neck at the beginning of the shift.

Results: Cleaner 3 from the Solids Filtration Plant (SFP) experienced the highest average dermal exposure to total PAHs (759.6 ng/cm^2) as well as the highest total PAH-concentration on the outside of his clothing (28596.3 ng/cm^2). At the Tar Separation Plant (TSP) Cleaner 2 experienced the highest average dermal exposure (274.4 ng/cm^2). Cleaner 3 and Process controller at SFP as well as Truck loader 2 at TSP were all exposed to benzo[a]pyrene on the surface of their skin (37.20 ng/cm^2; 57.66 ng/cm^2 and 9.30 ng/cm^2 respectively). Statistical significant differences were seen between the skin surface hydration values ($p=0.013$) as well as the TEWL values ($p = 0.033$) of TSP and SFP workers.

Conclusions: Cleaners were identified as the greatest exposed occupation. This is probably because they come in direct contact with the tar more often. In general, SFP workers experience higher dermal exposures than TSP workers to total PAHs. Workers exposed to benzo[a]pyrene or dibenz[a,h]anthracene face the greatest health risk as these substances are highly carcinogenic. Workers at both SFP and TSP had high TEWL and low skin surface hydration values which indicated disrupted skin barrier function and increases their susceptibility to skin disorders.

Key words: Polycyclic aromatic hydrocarbons; Dermal exposure; Dermal patches; Skin barrier function; Transepidermal water loss, Skin surface hydration; Skin surface pH; Petrochemical workers.

Introduction

PAHs is a class of organic compounds that consists of two or more fused benzene rings and/or pentacyclic molecules that are arranged in various structural conFigureurations (Bamforth and Singleton, 2005) and can be present in a gaseous state or can be bound to other particles in the air (Tsai *et al.,* 2001).

PAHs are generated by the incomplete combustion of fuels, such as petrol, diesel and coal (Yadav *et al.,* 2005). They are commonly present in the environment due to discharge from forest fires, motor vehicle traffic and the burning of fossil fuels. Other sources include: tobacco smoke, chargrilled meats and smoked foods (Angerer *et al.,* 1997; Bamforth and Singleton, 2005; Cirla *et al.,* 2007). Industries where PAH mixtures represent a significant amount of the risk to the worker's health, include chimney sweeping, coal gasification, coal-tar distillation, coke production, coal-tar pitches (paving and roofing) and aluminium production (Bofetta *et al.,* 1997). These mixtures were all confirmed as Group 1 carcinogens (carcinogenic to humans) by the International Agency for Research on Cancer (IARC). (IARC 2002; IARC 2010; IARC 2012). Benzo[a]pyrene, which is one of the most toxic and carcinogenic individual PAHs (Tsai *et al.,* 2001), is classified as carcinogenic to humans by the IARC (IARC 2012) and is recognised as a priority pollutant by the US Environmental Protection Agency (Bamforth and Singleton, 2005). A study by Cavallo *et al.* (2005) on chronic occupational dermal exposure, showed early oxidative DNA damage in paving workers who had been chronically exposed to low doses of PAH mixtures and Tsai *et al.* (2001) found that workers handling PAH-containing materials had a significant risk for developing skin cancer.

Some of the symptoms workers commonly experience following exposure to PAHs is skin irritation and defatting of the skin, which will lead to dryness and cracking of the skin, as well as oil acne, dermatitis hyperkeratosis and photo sensitivity (Christopher *et al.,* 2011). Other frequently reported symptoms include eye irritation, coughing, headaches, fatigue and throat irritation (Cirla *et al.,* 2007). PAHs such as benzo[a]pyrene can also act as allergens to produce allergic reactions on the skin of animals (Mumtaz and George, 1995).

During the past two decades in occupational hygiene, there has been an increased interest in exposure via the dermal exposure route (Kammer *et al.,* 2011). Because PAHs are non-polar substances, they can easily penetrate through the lipoprotein layers of the skin (Elovaara *et al.,* 1995) and a number of studies have shown that PAH absorption through the skin can contribute up to 75% of the total PAH load in the body (Van Rooij *et al.,* 1993; McClean *et al*., 2004; Väänänen *et al.,* 2005). Gündel *et al.,* (2000) and Väänänen *et al.*

(2005) also concluded that dermal absorption is a major route of PAH uptake and therefore, the determination of PAH-concentration in the air alone is not sufficient to accurately estimate the total health risk for the individual worker.

Unlike inhalation exposure there are no occupational exposure limits (OELs) for dermal exposure to different hazardous chemicals (Semple, 2004). The reason for this is that there are no standardised strategies for measuring and assessing skin exposure and, therefore, there cannot be standardised exposure limits (Väänänen *et al.,* 2005; Fustinoni *et al.,* 2010; Kammer *et al.,* 2011). Not many results for dermal exposure to PAHs have previously been reported and, therefore, there is not a lot of dermal exposure data available for comparisons (Schneider *et al.,* 2000; Christopher *et al.,* 2011). Data regarding dermal PAH exposure to workers in South Arica is especially lacking, which makes it very difficult to compare newly obtained dermal exposure data.

The skin is the primary barrier between a human being and the environment and protects against extensive water loss, the loss of proteins and plasma components from the organism as well as the invasion of harmful substances from the environment (Procksh *et al.,* 2008). The Stratum Corneum (SC), which is the outer layer of the skin, is only 15 µm thick and comprises of pentagonal and/or hexagonal corneocytes in a lipid matrix (Hadgraft *et al.,* 2009).

In order to determine the effectiveness of the skin's function as a barrier, certain factors such as Transepidermal Water Loss (TEWL), skin hydration and skin surface pH need to be quantified (Eberlein-König *et al.,* 2000; Darlenski *et al.*, 2009). These are non-invasive methods that can help to assess the skin barrier function (Eberlein-König *et al.,* 2000) which is of great importance because a damaged skin barrier may lead to enhanced skin absorption of PAHs such as pyrene and benzo[a]pyrene through the skin (Kammer *et al.,* 2011).

TEWL is the physiological loss of water vapour from the skin in the absence of sweat gland activity (Kezic and Nielsen, 2009) and may be used as an indirect measurement of skin permeability and barrier function (Singh *et al.,* 2001). A disruption in the barrier function of the skin will lead to an increase in TEWL (Kezic and Nielsen, 2009), whereas a lower TEWL value is characteristic of an intact skin barrier (Darlenski *et al.*, 2009). TEWL measurements can be affected by the anatomical site, sweating, skin surface temperature, inter- and intra-individual variation, air convection, ambient air temperature, ambient air humidity, and instrument related variations (Levin and Maibach, 2005). When measuring TEWL, the subject needs to be in a controlled environment where contamination by sweat can be prevented.

Adequate hydration is essential for optimal skin functioning (Kezic and Nielsen, 2009). Failure of the SC to retain water (lower hydration) causes skin dryness and impairs the function of the skin barrier (Darlenski *et al.*, 2009). Excessive hydration on the other hand can also lead to reduced barrier function as it reduces the cohesiveness of the SC (Kezic and Nielsen, 2009).

An acidic environment is also essential for skin barrier function (Gunathilake, 2009) and studies have shown that several kinds of inflammation or trauma and dryness of the skin can cause an increase in skin surface pH (Eberlein-König *et al.,* 2000).

The aim of this study was to determine the dermal exposure of workers at a South African petrochemical factory to PAHs, by measuring 8 hour-full shift exposure, as well as changes in the skin barrier function (TEWL, skin hydration and skin pH) of the workers throughout the shift.

Methods and materials

Study design

The full shift dermal exposure of workers to PAHs was studied at three different plants in a South African petrochemical factory during August and September of 2011. The different plants included: a tar separation plant (TSP), a solids filtration plant (SFP) and a coal mixing plant (CMP). These plants were open air plants and were, therefore, susceptible to ventilation by wind. The job descriptions of the workers at the different plants as well as the PPE that they wore are shown in Table 1 and Table 2 respectively. A total of 14 workers was included in the study.

Process description

At TSP, various gaseous, liquid and solid components are separated from the gaseous water streams that are obtained from the gasification of coal. This gaseous water contains by-products from coal carbonisation such as water vapour, tar, oil, naphtha, phenols, chlorine, fluorine and fatty acids. It also contains dissolved gasses (NH_3, CO_2 and H_2), a small amount of combustible gasses, coal dust and inorganic salts. A stream containing bulk free tar and some heavy oils is gravitated to primary tar separators where most of the tar and solids are separated from the oil and tarry water. In the secondary tar separator the oil and entrained tar/solids are separated from the tarry water. The recovered oil is then gravitated to an oil rundown tank. Tar and solids from the secondary tar separator are periodically drained to the slop pit, which is periodically cleaned by workers using shovels and buckets to

remove the tar and solids from the pit. The remaining hot tarry water from the secondary tar separator containing ammonia and hydrocarbons is then gravitated to a tank and after undergoing further purification processes to remove the ammonia, this hot tarry water is used by the cleaners to clean the plant.

The products of this separation process that may contain PAHs are oil, clean tar, heavy dusty tar and tarry water.

The separated tar from the primary tar separator is transported to SFP by tanker trucks where the solids are removed and the liquid tar is filtered. The filtered solids from the tar filtration plant are then transported by trucks to CMP where it is mixed with coal to serve as fuel for the gasification process.

TSP and CMP are both relatively open plants while SFP is a maze of pipes and other structures. SFP workers come in direct contact with tar from dirty structures much more often than on the other plants.

Table 1: Description of different jobs performed by the workers in the 8-hour exposure study.

Job	Location	Description	Duration
Process controller 1-3	TSP + SFP	Monitored the progress of the different processes, solved production problems and collected samples.	Plant visits lasted ~20 min – 40 min, 5-6 times per day.
Cleaner 1-3	TSP + SFP	Used hot tarry water at high pressure to clean the plant.	Up to 2 hours at a time, 2 times per shift.
Truck loader 1-2	TSP	Stood on a platform directly above the manhole opening of the tank of the truck and operated switches in order to load tar which poured into the tank of the truck from a pipe.	To load 1 tank took ~20 min Loads ~ 12 trucks per shift.
Truck offloader 1-2	SFP	Opened the outlet of the truck, scraped the solids that lay at the bottom of the tank into a tar pit and watched as the liquid tar poured into the tar pit.	To unload one tank took ~ 30 min. Unloads ~12 trucks per shift.
Truck attendant 1	SFP	Monitored the loading of the filtered solids onto a truck.	Plant visits last ~20 min. He visits the plant ~8 times per shift.
Mechanical operator 1-2	SFP	Built scaffolding and repaired filters and other mechanical equipment on the plant.	Was on the plant for long periods of time.
Cleaner 4	CMP	Plant did not function normally and the worker performed other small tasks which included cleaning of bathrooms and other parts of the plant.	Was on the plant for periods of 50 min at a time for ~6 times
Occupational hygiene assistant	Occupational hygiene office	Office work.	8 Hours.

TSP-Tar Separation Plant, SFP- Solids Filtration Plant, CMP- Coal mixing Plant

Sampling strategy

Dermal exposure patch sampling

In order to measure full shift dermal exposure of workers to PAHs, workers wore adhesive dermal patches on six different anatomical positions on their skin and one on the outside of their clothing. This method is a modification of a method described by Jongeneelen *et al.* (1988) and van Rooij *et al.* (1993). The adhesive patches consisted of Pall corporation® 47 mm polypropylene filters that were attached to the skin using Elastoplast® sportswrap plaster. A hole with the diameter of 37 mm was cut from the plaster in order to create a patch with an effective exposure surface area of 10.752 cm^2 on the filter. A piece of foil was laid between the skin and the filter to avoid contamination from sweating. These patches were attached to the ventral side of the wrists and forearms, the neck and the inside of the ankle on the dominant side of the body. A seventh patch was placed on the dorsal side of the right forearm on the outside of the clothing. Therefore, a total of 7 samples was collected from each worker. After the samples were collected they were placed in foil-wrapped Petri dishes, transported in coolers and stored at 20 °C.

One field blank and one media blank were analysed per sampling day to establish whether there had been any PAH-contamination other than worker exposure.

A total of 98 full shift exposure samples were collected from 14 workers. Of these 14 workers, six worked at TSP, six at SFP, one at CMP and one worked in an office away from the plant.

Skin barrier function measurements

Parallel with the dermal patch sampling, the change in skin barrier function of the workers for the duration of the shift, was determined by measuring TEWL, skin hydration and skin surface pH. TEWL was measured using a Delfin® Vapometer (Delfin Technologies Ltd). Skin hydration and skin surface pH were measured using a Mobile Skin Centre® (MSC 100) (Courage + Khazaka electronic) and its Corneometer® CM 825 and Skin-pH-Meter® pH 905 probes.

The TEWL, skin hydration and skin surface-pH were measured on four different anatomical positions on the body: 1) on the palm in the area between the index and middle fingers, and horizontally in line with the base of the thumb, 2) on the wrist in the area between the index and the middle finger, one finger width below the lowest part of the lunate hand bone, 3) on the neck, four finger widths below the underside of the ear, and 4) on the forearm on the ventral side in the middle of the forearm.

For TEWL measurements, each anatomical area was measured twice in each position, while skin-hydration and –pH were measured three times before calculating the average. TEWL is measured in $g/m^2/h^1$, while skin surface pH is measured in pH-units and skin surface hydration is measured in arbitrary units (a.u.) because no specific unit is specified by the manufacturer of the Corneometer® CM 825.

A validated questionnaire developed by Dalgard *et al*. (2003) was used to evaluate dermatological complaints of the workers. This questionnaire included questions on itching of the skin, skin rashes and on the use of skin creams. Basic worker information such as age, race and years of employment as well as additional information on smoking was also collected.

Method of analysis

All samples were analysed using the NIOSH 5515 method by an accredited SANAS laboratory (accreditation no. T 0361). This method uses a gas chromatograph to analyse for PAHs. Results of individual PAHs that were below the detection limit (BDL) were substantial. When calculating the total PAH concentration of the samples, these BDL values were taken as the detection limit/2. The total PAH concentration was calculated as the sum of all the individual PAH-concentrations. The percentage of PAH that penetrated through the clothing of the workers was calculated with the following formula:

$$\% \text{ PAH penetrating the PPE} = \frac{[PAH]_{Inside}}{[PAH]_{Outside}} X \frac{100}{1}$$

Where, $[PAH]_{Inside}$ = The PAH measurement on the right forearm, $[PAH]_{Outside}$ = the PAH measurement on the right forearm on the outside of the clothing.

In the determination of the barrier function of the workers, only baseline skin barrier measurements were taken because no suitable location could be found where the workers could acclimatise. The measurements would have been contaminated by sweat on the surface of the workers' skin.

Statistical analysis of results

The statistical analysis of the results included basic statistics (mean and standard deviation), t-tests and ANOVAs and was carried out using Statistica version 10 (Statsoft Inc.). One-way ANOVA with Bonferroni's post-tests were performed to establish whether there was a significant difference between the PAH exposure experienced by the different workers and whether there was a statistical significant difference between the different workers' barrier function measurements. Independent t-tests were performed to establish whether there were statistical significant differences between the barrier function measurements of the TSP workers and the SFP workers. Column and line graphs were drawn using GraphPad Prism version 4.00 for Windows (GraphPad Software).

Results

The full shift dermal exposures to PAHs of workers at a petrochemical plant were determined with dermal patches. Fourteen sets of full shift samples were collected. All field and media blanks that were collected and analysed were below the limit of detection for all individual PAHs. The skin barrier function of the workers was also determined through TEWL, skin hydration and skin pH measurements.

Figure 1 shows the total PAH exposure of workers at the TSP. Process controller 1 and Process controller 2 experienced approximately the same exposure on the different anatomical positions.

Truck loader 1 experienced significant exposure on his right wrist (365.5 ng/cm^2) and right forearm (361.8 ng/cm^2), while Truck loader 2 experienced substantial exposure on his right wrist (350.2 ng/cm^2) and left forearm (192.5 ng/cm^2). Both truck loaders also had considerable exposure on their ankles (Truck loader 1 – 163.2 ng/cm^2; Truck loader 2 – 161.4 ng/cm^2).

The highest exposure point on the skin of Cleaner 1 was on the ankle (201.8 ng/cm^2). All the other areas were moderately exposed. Cleaner 2 experienced his highest exposure on his wrists and forearms (ranging from 317.1 ng/cm^2 to 352.5 ng/cm^2). Compared to the other TSP workers Cleaner 2 also experienced high exposure on his neck (193.9 ng/cm^2).

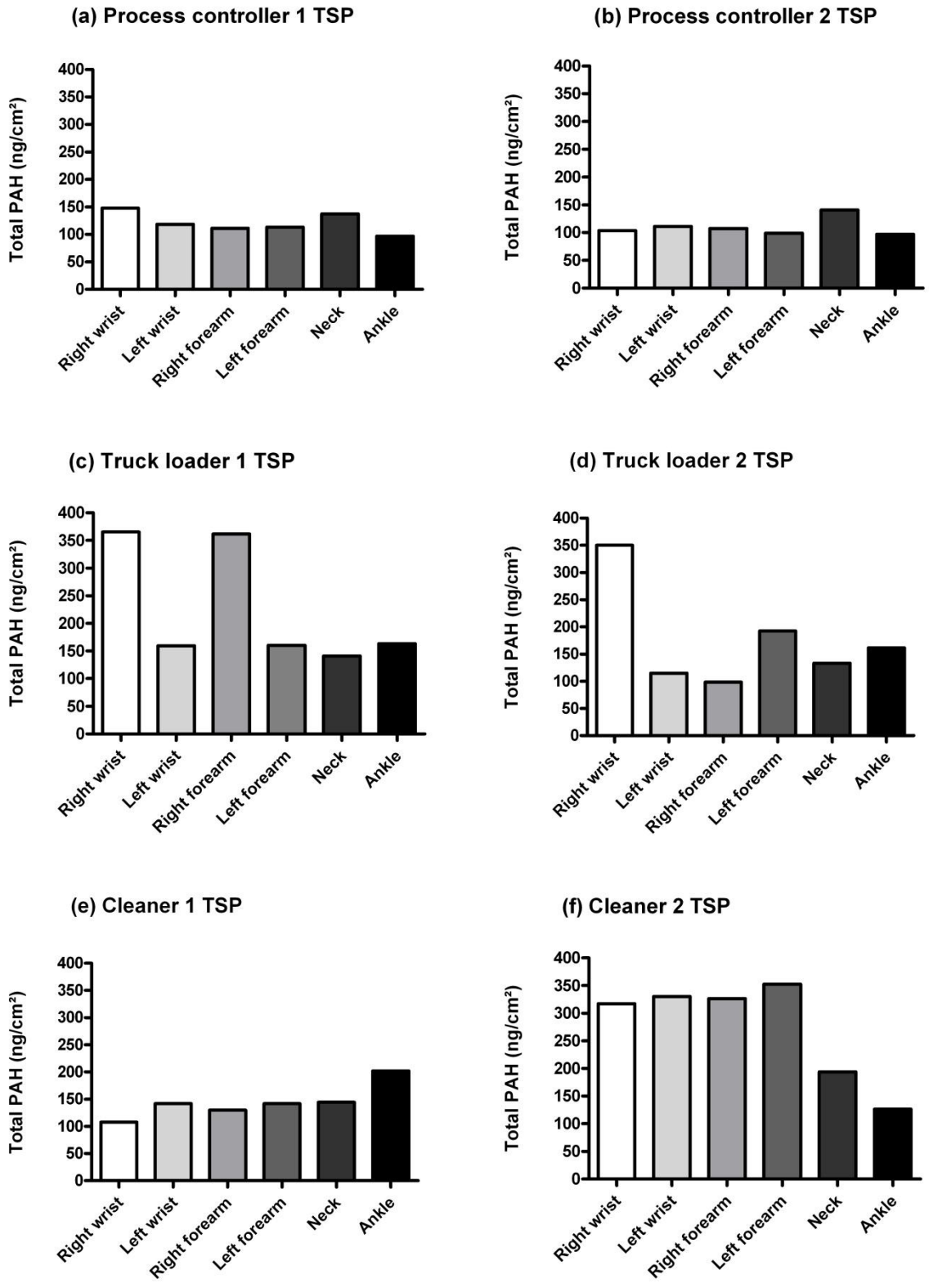

Figure 1: Total PAH exposure of TSP workers on different anatomical areas.

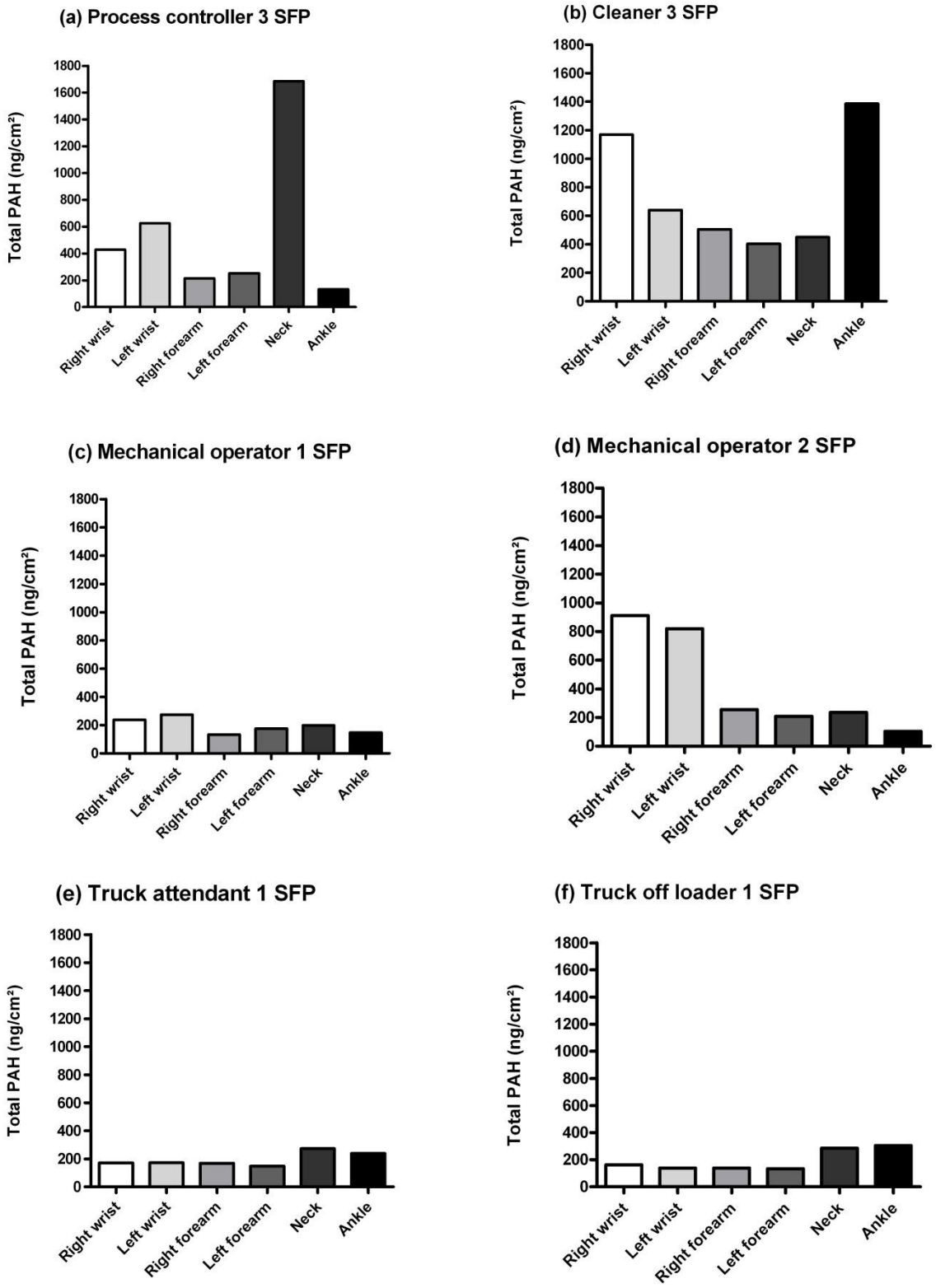

Figure 2: Total PAH exposure of SFP workers on different anatomical areas.

Figure 2 shows the total PAH exposure of SFP workers. The highest exposure experienced by Process controller 3 at SFP was on the neck (1685.3 ng/cm^2). Two tar smudges were observed on the neck filter where the worker came in contact with tar from one of the structures on the plant. He also experienced significant exposure on his left (624.5 ng/cm^2) and right (427.8 ng/cm^2) wrists.

Cleaner 3 experienced the highest PAH exposure of all the workers in this study. This worker was very highly exposed on the ankle (1385.3 ng/cm^2) and the right wrist (1170.0 ng/cm^2) and his Tyvek® suit was visibly dirty.

All the anatomical areas of Mechanical operator 1 were similarly exposed. His highest exposure was on the left wrist (274.8 ng/cm^2) but, Mechanical operator 2's wrists were exposed to much higher levels of PAH (right wrist 911.9 ng/cm^2 and left wrist 820.8 ng/cm^2). Mechanical operator 2 came in direct contact with tar more often and the tar marks from contact with dirty structures on the plant were visible on his hands.

The Truck attendant as well as the Truck loader at SFP experienced their highest exposures on their necks (Truck attendant 274.4 ng/cm^2 and Truck loader 285.5 ng/cm^2) and ankles (Truck attendant 238.6 ng/cm^2 and Truck loader- 304.1 ng/cm^2).

All the filters collected from the occupational hygiene assistant in the office were below the detection limit for individual PAHs.

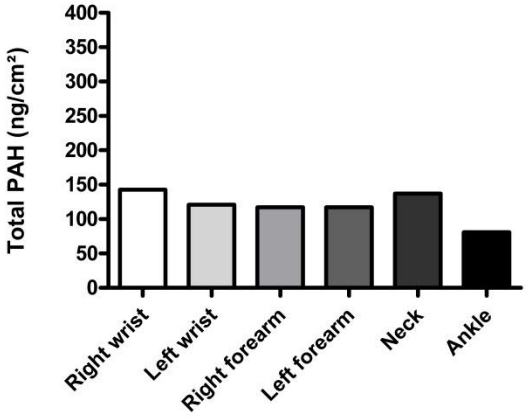

Figure 3: Total PAH exposure on different anatomical areas of cleaner 4 at CMP.

Figure 3 shows the total PAH exposure of Cleaner 4 at the CMP. The worker had PAH exposure of ~150 ng/cm^2 on all the anatomical areas except on the ankle, where it was below 100 ng/cm^2. The CMP plant was not functional on the day of monitoring but Cleaner 4 performed cleaning tasks on the plant.

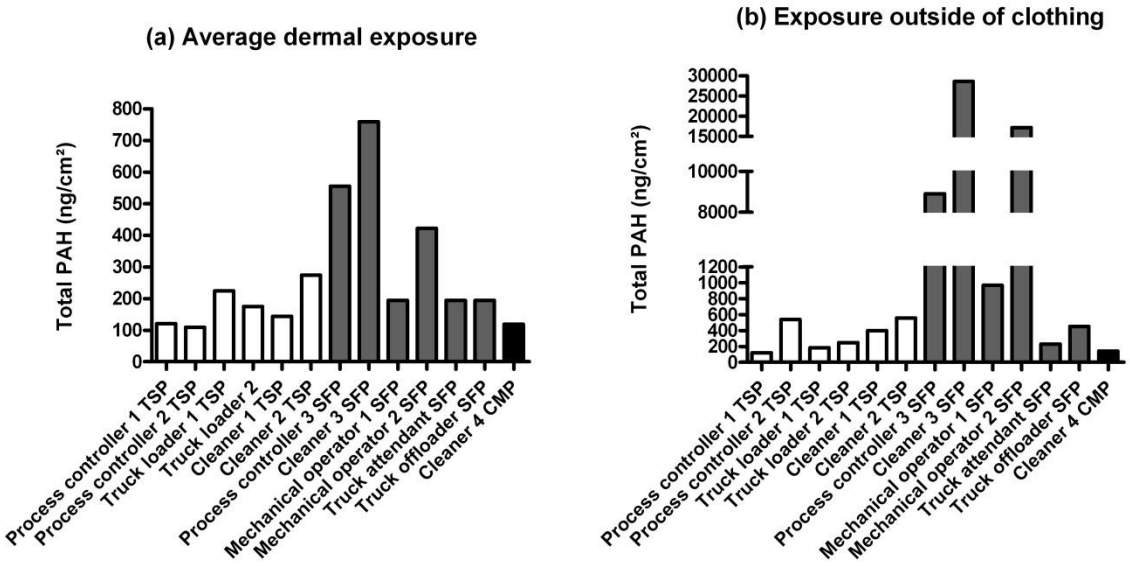

Figure 4: a) Average total dermal PAH exposure experienced by all the TSP workers (white), SFP workers (grey) and CMP worker (black) on the different anatomical areas. b) Total dermal PAH exposure experienced by all the TSP workers (white), SFP workers (grey) and CMP worker (black) on the outside of the clothing on the right forearm.

Figure 4 shows the average dermal PAH exposure measured on all the anatomical areas of the workers in the full shift exposure study as well as the PAH exposure measured on the outside of their clothing.

Cleaner 2 and Truck loader 1 experienced the highest average dermal PAH exposure of all the TSP workers (274.4 ng/cm^2 and 225.2 ng/cm^2 respectively), while Cleaner 3 (759.6 ng/cm^2), Process controller 3 (556.1 ng/cm^2) and Mechanical operator 2 (422.6 ng/cm^2) from SFP experienced the highest average dermal exposure of all the workers in the study.

Cleaner 2 and Process controller 2 experienced the highest levels of exposure of all the TSP workers on the outside of their clothing (557.6 ng/cm^2 and 540.8 ng/cm^2). At SFP, Cleaner 3 and Mechanical operator 2 were exposed to much higher levels of PAHs (28596.3 ng/cm^2

and 17225.9 ng/cm^2). This is not surprising as Cleaner 3's filter on the outside his clothing was totally covered in tarry water.

Table 2: Total PAH collected outside of the clothing and the percentage of PAH's that penetrated through PPE (Personal protective equipment).

Worker	Area	PPE	Total PAH outside of clothing (ng/cm^2)	Total PAH on right forearm (ng/cm^2)	Estimated % breakthrough
Process controller 1	TSP	Standard overall	124.2	111.1	**89.5**
Process controller 2	TSP	Tyvek® + Standard overall	540.8	107.4	19.9
Truck loader 1	TSP	Tyvek® + Standard overall	187.4	361.8	193.1*
Truck loader 2	TSP	Tyvek® + Standard overall	248.3	98.6	39.7
Cleaner 1 TSP	TSP	Dust suit + Standard overall	401.3	129.7	32.3
Cleaner 2	TSP	Dust suit + Standard overall	557.6	326.4	**58.5**
Process Controller 3	SFP	Tyvek® + Standard overall	8900.6	214.4	2.4
Cleaner 3	SFP	Tyvek® + Standard overall	28596.3	506.9	1.8
Mechanical operator 1	SFP	Tyvek®	969.6	133.0	13.7
Mechanical operator 2	SFP	Tyvek®	17225.9	254.8	1.5
Truck attendant 1	SFP	Standard overall	231.6	166.9	**72.1**
Truck offloader 1	SFP	Tyvek®	453.4	139.0	30.7
Cleaner 4	CMP	Standard overall	144.6	117.2	**81.0**
OH assistant	Office	Standard overall	BDL	BDL	-

BDL-Below Detection Limit, CMP-Coal Mixing Plant, SFP-Solids Filtration Plant, TSP-Tar Separation Plant, * Unusual results as a result of contamination that was not through the PPE but from contact with other sources. All the percentages above 50% are highlighted.

Table 2 shows the total PAH exposure experienced by TSP and SFP workers as well as the percentage PAHs that penetrated through the PPE. The outside patches were placed on the outside of the right forearm and the forearm patches were placed on the inside of the right forearm. These percentages, therefore, represent the percentage of the PAH concentration on the outside of the clothing that moved through the clothing and settled onto the skin. Process controller 1 and Cleaner 2 from TSP, Cleaner 4 from CMP and the truck attendant from SFP are the workers with the highest breakthrough percentages that ranged from 58.5% to 89.5%.

Skin barrier function measurements

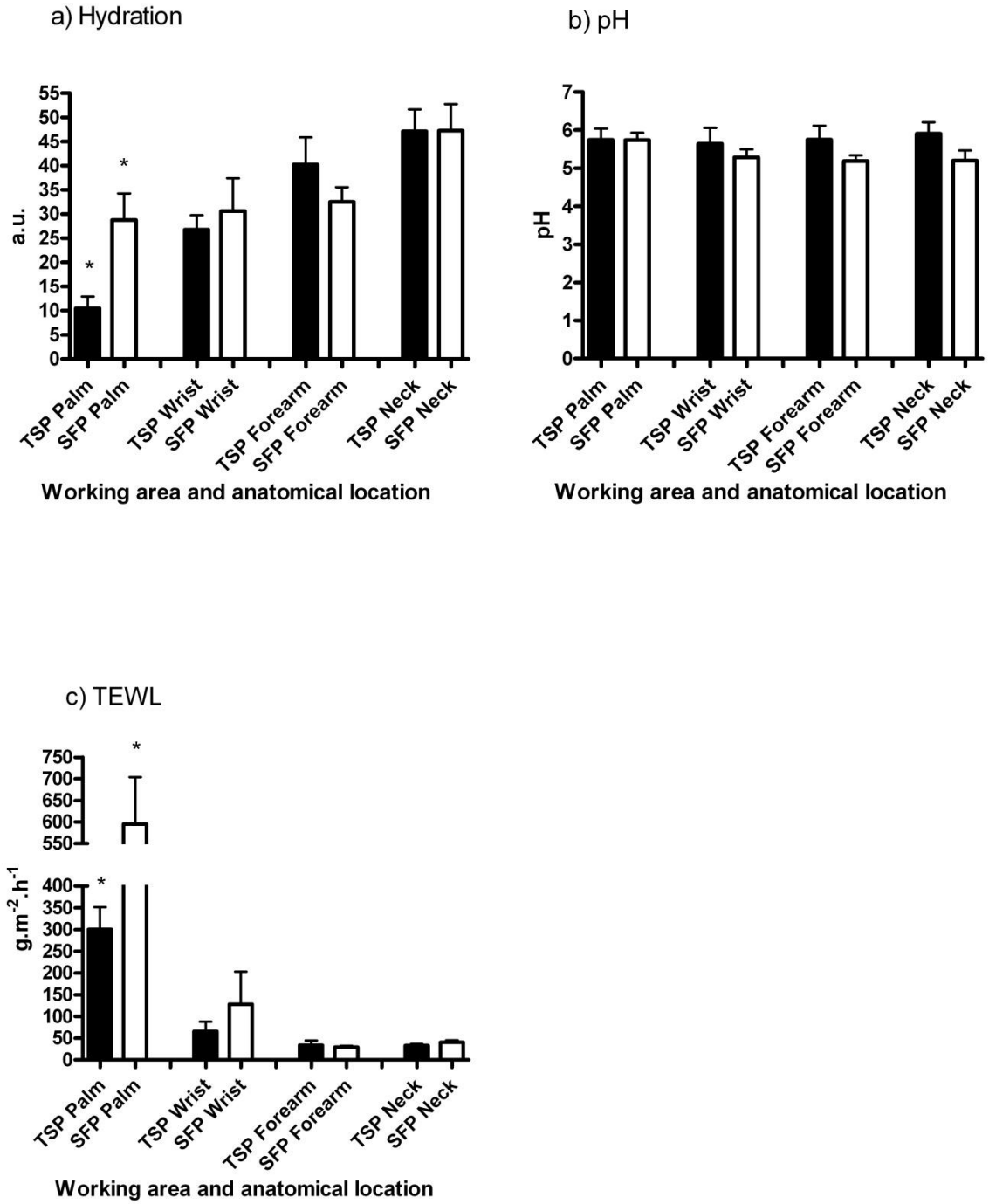

Figure 5: Baseline measurements of a) skin hydration, b) skin pH and c) TEWL taken at the beginning of each shift. * Statistical significant differences between the skin surface hydration (p=0.013) and TEWL (p = 0.033) values of TSP and SFP workers.

Skin barrier function measurements

A difference in skin surface hydration, skin surface pH and TEWL values were found between different anatomical areas which can be contributed to the fact that the SC in different anatomical sites varies in thickness, morphology and lipid composition.

Skin hydration measurements

Figure 5a shows the skin hydration measurements taken at the beginning of the shift. The palm measurements of the TSP workers show low skin hydration values, while the rest of the hydration measurements are in an acceptable range of above 30 a.u.. A notable statistical difference was seen between the palm surface hydration measurements of TSP and SFP workers ($p=0.013$). TSP workers showed much lower hydration values.

Skin surface pH measurements

Figure 5b shows the skin surface pH measurements taken at the beginning of the shift. All the average skin surface pH measurements are in the acceptable range of between 4 and 6.

TEWL measurements

Figure 5c shows the TEWL measurements taken at the beginning of the shift. Both the TSP and the SFP workers had extremely high palm TEWL values and on the wrists of both sets of workers, TEWL values were also increased. The forearm and neck measurements are in an acceptable range of fewer than 30 $g/m^2/h$. A notable statistical difference was seen between the palm TEWL measurements of TSP and SFP workers ($p=0.0333$). SFP workers showed much higher TEWL values.

Skin condition questionnaire

When questioned about the condition of their skin, five of the fourteen workers from all the plants complained about dry and itchy skin. At TSP, workers said that direct contact with the tarry water caused itching. Three of the six workers at SFP complained about dry and itchy skin. They experienced a chemical burning sensation after direct contact with the tar and some of these workers developed red spots on their thighs, arms and chests after they started employment at SFP. Process controller 3 at SFP complained of tiredness and body pains that develop during the middle of the week which do not occur during the weekend.

Discussion

Observations

Process controller 2 at TSP was exposed to 540.8 ng/cm^2 on the outside of his clothing and Process controller 1 to 124.2 ng/cm^2 (Figure 4b), while both of them experienced approximately the same exposure on the surface of the skin. A bigger fraction 89.5% (Table 3) of the PAHs penetrated through the clothing and deposited on the skin of Process controller 1, while only 19.9% penetrated through Process controller 2's clothing. Table 1 in the supplementary material shows that Process controller 1 only wore a standard overall, while Process controller 2 wore a standard overall as well as a Tyvek® classic suit, which in all likelihood caused the decreased PAH penetration through Process controller 2's clothing.

In comparison with the other TSP workers, Truck loaders 1 and 2 both experienced high exposure on the ankle. This is because the stations where the truck loaders operate the different switches are located directly above the outlets where the tar is poured into the trucks and as a result of this, vapour from the hot tar often surrounds the workers. They also had the highest right hand exposures in the TSP area because they removed their gloves during loading to shift their goggles into the correct position. Truck loader 1 had an unexpected high right forearm exposure on the surface of the skin which was 193.1% (Table 3) of the PAH concentration on the outside of his right arm. The cause of this unexpected exposure is unclear but cross contamination during the rolling up of his sleeves or direct contact with another source could have been the cause.

The highest exposure area on the skin of Cleaner 1 was on the ankle. The reason for this could be that this worker spent some time cleaning a trench that was below his feet with high pressure hot tarry water. A tremendous amount of the vapour was present in the area of his ankles during this activity. The vapour from the hot tarry water could, therefore, move through his clothing and socks to settle on his ankles. Cleaner 1 and Cleaner 2 at TSP wore normal safety boots instead of gumboots (Table S2). Cleaner 2 experienced higher PAH exposure on both his wrists and forearms than Cleaner 1. Cleaner 2 worked with very dirty gloves and this could have caused unnecessary contamination as a result of the chemical breakthrough through the gloves or contamination as a result of poor personal hygiene, improper use of PPE or working with dirty equipment. Cleaner 2 also experienced the highest neck and outside clothing exposure of all the workers at TSP. Cleaner 2 experienced the highest average PAH exposure of all the TSP workers and is the worker with the highest risk of dermal exposure to PAHs in this area.

The highest exposure experienced by Process controller 3 at SFP was on the neck. This was the highest individual exposure of any one anatomical area in this study. Two tar smudges were observed on the filter, which indicates that when the tar comes into contact with the skin, it transfers high concentrations of PAHs onto the skin's surface. This sample contained the highest benzo[a]pyrene concentration of all the samples in this study (57.7 ng/cm^2). When compared with the Process controllers at TSP (Figure 1), Process controller 3 was exposed to 8000 ng/cm^2 more PAH on the outside of his clothing. The PAH exposure on the wrists of Process controller 3 is also more than twice that of the Process controllers at TSP. These differences in exposure are present despite the fact that Process controller 1 and 2 spent 155 and 140 minutes on the plant respectively, while Process controller 3 only spent 82 minutes on the plant. The PAH exposure experienced by Process controller 3 on all anatomic areas was more than that experienced by Process controller 1 and 2 at TSP. When questioned about his skin condition, Process controller 3 complained about rashes on his skin, dry skin, tiredness, body pains and pimples on his thighs.

Cleaner 3 at SFP experienced the highest dermal exposure to PAHs of all the workers participating in this study. Despite wearing gumboots (Table S3), his ankles were the highest exposed area because he spent most of his time working in pools of tarry water. He cleaned for up to 3 hours at a time and was covered with tarry water up to his waist by the time he was finished. The Cleaners at SFP do not usually clean 3 hours on end without resting and cleaner 3's exposure can, therefore, be seen as a worst case scenario. The area Cleaner 3 cleaned was a maze of pipes and there was a lot of potential for contamination as a result of contact with the dirty structures. His right wrist was also highly exposed and a contributing factor to this could be that he occasionally removed his right glove in order to move his safety goggles into the correct position. All the cleaners used hot tarry water at high pressure to clean the plant and splatter occurred a lot as a result of the high pressure, especially in confined areas. As a result of the increased temperature of the tarry water, vapour was released that also contributed to the exposure. This vapour was very irritating to the eyes.

Mechanical operator 1 at SFP worked on the top as well as on the middle platforms of the plant. He never came into direct contact with tarry water or any other liquid but still experienced more PAH exposure on the outside of his clothing than any of the workers at TSP. The PAH exposure on his skin was low, compared to other SFP workers. In this case the Tyvek® suit seems to effectively prevent breakthrough of the PAH vapour through the clothing. This is because the Mechanical operator 1 was only exposed to vapour and not to tarry water or tar smudges.

Mechanical operator 2 replaced mechanical parts in the filters and was in close proximity to dirty structures. He had the second highest concentration of PAHs on the outside of his clothing of all the workers in this study. He did not wear a standard overall jacket under his Tyvek® suit as worn by the other workers and worked for periods with his sleeves rolled up to under the forearm patches. As a result of this both his wrists were highly exposed. This worker was quite dirty at the end of his shift. When questioned about his skin condition, he complained about pimples on his thighs and chest, dry skin and burning after the tar comes in contact with the skin. He also mentioned that the skin problems started when he started employment at SFP.

The Truck attendant only wore a standard overall. Because he did not wear a Tyvek® suit 72.1% (Table 3, page 70) of the chemical penetrated his clothing. He did not do a lot of physical work and, therefore, did not experience high levels of exposure on his wrists or forearms. Instead he experienced his highest exposure on his neck and ankle.

The Truck offloader at SFP experienced his highest exposure on the ankle and neck. The reason for the higher exposure on the ankle is that the tar he unloads from the truck gets drained into a pit that is located at his feet. As he scrapes the solids from the tanker, his neck is close to the opening. He spends the bulk of his shift in the area where the trucks are unloaded.

Penetration of PAHs through clothing

Table 3 shows the percentage PAHs that penetrated from the outside through the workers' clothing and onto their skin. The workers that experienced breakthrough percentages of > 70% all only wore standard overalls with no Tyvek® suits (Table 2). They experienced the lowest outside exposures of all the workers in the study (Table 2), which is probably the reason why they did not wear Tyvek® suits. Process controller 2 at TSP experienced higher PAH exposure than Process controller 1 on the the outside of his PPE but they both experienced the same right forearm exposure because Process controller 2 wore a Tyvek® suit and Process controller 1 did not. CMP, where cleaner 4 worked, did not function normally but 81.0% of PAHs still penetrated through his clothing. The truck attendant at SFP was exposed to the lowest outside exposure of all the workers in the plant but the highest percentage PAH (72.1%) penetrated through his overall. Cleaners 1 and 2 at TSP wore dust suits instead of Tyvek® suits. This also helped to protect against PAH penetration but still was not as effective as the Tyvek® suit. Cleaner 2 still experienced 58.5% penetration which was higher than any worker that wore a Tyvek® suit. Therefore, when compared to a standard overall, it appears that a Tyvek® suit does help to guard against penetration of

PAHs through clothing. The Tyvek suits also have elastic bands around the wrists and ankles that prevent vapour from reaching the skin.

Table 3: Ranking of workers according to total PAH exposure experienced on the skin.

Worker	Area	Total PAH outside of clothing. (ng/cm^2)	Total exposure on skin. (ng/cm^2)	Average exposure as used in Figure 4. (ng/cm^2)
Cleaner 3	SFP	28596.3	4557.7	759.6
Process Controller 3	SFP	8900.6	3336.6	556.1
Mechanical operator 2	SFP	17225.9	2535.3	422.6
Cleaner 2	TSP	557.6	1646.1	274.4
Truck loader 1	TSP	187.4	1351.4	225.2
Truck attendant 1	SFP	231.6	1171.4	195.2
Mechanical operator 1	SFP	969.6	1168.1	194.7
Truck offloader 1	SFP	453.4	1164.4	194.1
Truck loader 2	TSP	248.3	1051.0	175.2
Cleaner 1 TSP	TSP	401.3	867.7	144.6
Process Controller 1	TSP	124.2	724.5	120.8
Cleaner 4	CMP	144.6	716.1	127.7
Process Controller 2	TSP	540.8	659.4	109.9
OH assistant	Office	BDL	BDL	BDL

BDL-Below Detection Limit, CMP-Coal Mixing Plant, SFP-Solids Filtration Plant, TSP-Tar Separation Plant

PAH chemical structures

Table 3 in the Annexure (page 70) shows the exposure of all the workers to individual PAHs. The 3- and 4-ring PAHs dominate the exposures. TSP workers were exposed to 2-4 ring PAHs exclusively, while the SFP workers suffered more severe exposures to 2-6 ring PAHs. This result was expected as the SFP workers experienced more direct contact with tar in the solid phase, which contains more 4-6 ring PAHs. It was observed that filters with tar smudges contained more 4-6 ring PAHs (including benzo[a]pyrene. TSP workers are predominantly exposed to vapour that contains more volatile 2-4 ring PAHs (Sodus *et al*., 2010). In general, PAH structures with more benzene rings are more toxic to humans (Bamforth and Singleton, 2005) and PAHs with more than 4 benzene rings are also generally more carcinogenic (Cavallo *et al*., 2005). The SFP workers are, therefore, exposed to more harmful and carcinogenic PAHs than the TSP workers. Studies in laboratory animals

have demonstrated the ability of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, and indeno[l,2,3-c,d]pyrene to induce skin tumors (i.e., they are complete carcinogens) following intermediate dermal exposure. These PAHs all have four or more aromatic rings, whereas anthracene, fluoranthene, fluorene, phenanthrene, and pyrene on the other hand all have four or less aromatic rings and do not act as complete carcinogens (Mumtaz and George, 1995). Most of the SFP workers were exposed to higher concentrations PAHs outside of their clothing than TSP workers, which show that SFP is a higher risk area. It can, therefore, be suggested that SFP workers are at higher risk than TSP workers, to develop cancer.

Table 3 shows ranking of highly exposed workers. The highest exposed workers from each area were cleaners because they more often come in direct contact with tar and tarry water. The top three exposed workers worked at SFP and SFP workers are, therefore, at higher risk than TSP workers, to develop skin diseases as a result of dermal exposure to PAHs.

In accordance with symptoms reported in previous studies (Christopher *et al*., 2011) following exposure to PAHs, workers at SFP complained about eye and throat irritation, headaches, fatigue, itching as well as acne and skin rashes.

Skin condition measurements

The TEWL values on the palms of the SFP workers at the beginning of the shift were high in comparison with all the other areas measured. This indicates that the skin barrier function of the palms of the SFP workers is compromised. Workers from SFP also complained more of adverse skin conditions such as pimples and rashes than TSP workers as they come in direct contact with tar more often.

In a comparison between the TSP and SFP workers' palm hydration and palm TEWL values at the beginning of the shift, a significant statistical difference is observed (palm hydration $p=0.012892$; palm TEWL $p = 0.033295$). The SFP workers have much higher palm TEWL values before the shift starts, which indicates that the skin barrier of the palms of the SFP workers are significantly weaker than that of the palms of the TSP workers. Both sets of workers' TEWL values for their palms and wrists are above that of healthy skin (table 4).

It is clear from the literature that even a slight reduction in the integrity of the skin barrier may lead to an increase in the absorption of PAHs through the skin, which may lead to an increased susceptibility to local as well as systemic toxicity (Kezic and Nielsen, 2009).

Especially PAH-molecules that are highly lipophilic by nature will move even more easily through a compromised skin barrier (Poet and McDougal, 2002).

Cancer risk

There have been reports of skin tumours among individuals exposed to mixtures containing PAHs. Human studies have shown that individuals exposed to mixtures of PAHs can develop cancer and that mixtures of carcinogenic PAHs cause skin disorders in humans. For example, regressive verrucae (i.e., warts) were reported following up to 120 applications of 1% benzo[a]pyrene to human skin. Especially in persons with pre-existing skin disorders such as blisters, adverse dermal effects were observed following intermediate benzo[a]pyrene exposure (Mumtaz and George, 1995), which shows that workers with a weakened skin barrier are more susceptible to adverse dermal effects (i.e. cancer) as a result of dermal exposure to PAHs.

Benzo[a]pyrene is also classified as a group 1 carcinogen and along with dibenz[a,h]anthracene (that is classified as a group 2A carcinogen) they represent the two most carcinogenic PAHs (IARC, 2012). Workers exposed to them will have the highest risk of cancer (Tsai *et al*., 2001). Table 4 shows a summary of the workers that were exposed to benzo[a]pyrene and dibenzo[a,h]anthracene.

Table 4: Summary of patches that contained benzo[a]pyrene and dibenz[a,h]anthracene

Worker	**Area**	**Anatomical area**	**Benzo[a]pyrene**		**Dibenz[a,h]anthracene**	
			Outside concentration ng/cm^2)	**Concentration on skin surface (ng/cm^2)**	**Outside concentration (ng/cm^2)**	**Concentration on skin surface (ng/cm^2)**
Cleaner 3	SFP	Right wrist	1187.21	37.20	223.68	-
Cleaner 3	SFP	Left wrist	1187.21	9.30	223.68	-
Cleaner 3	SFP	Neck	1187.21	9.30	223.68	-
Process Controller 3	SFP	Neck	167.41	57.66	-	-
Mechanical operator 1	SFP	-	39.06	-	-	-
Mechanical operator 2	SFP	-	212.98	-	33.95	-
Truck loader 1	TSP	Right wrist	-	9.30	-	-

Table 5: Comparison between similar studies. Studies are arranged from highest to lowest exposures.

Reference, year	n	Number and type of workers (exposure source)	PYR on right wrist Geometric mean (ng/cm^2)	PYR on right wrist Median (ng/cm^2)	Range (ng/cm^2)	No. %> LOD
Van Rooij 1992	20	Aluminium workers	42.0-150.7	NS	37.4-192.4	100
Van Rooij 1993	10	Creosote impinging workers	NS	82	NS	100
This study at SFP	6	Petrochemical workers (exposed to coal tar)	42.472	21.391	< 3.255 - 119.047	67
This total study	14	Petrochemical workers (exposed to coal tar)	24.979	10.231	<3.255 - 119.047	53.
This study at TSP	6	Petrochemical workers (exposed to coal tar)	14.726	10.231	< 3.255 - 37.202	67
Jongeneelen 1988	40	Paving workers (exposed to coal tar)	12.43	NS	NS	70
McClean 2007	26	Roofers	11.0	NS	<2.4-221	NS
Van Rooij 1993	20	Coke oven workers	6.4	NS	0.7-31.2	100
McClean 2004	20	Road pavers (recycled asphalt)	NS	3.4	<2.3-28	61
Väänänen 2005	22	Road Pavers (recycled asphalt)	0.45 -2.9	NS	0.07-24	100
Fustinoni 2010	24	Asphalt workers	NS	0.527	0.023-2.516	100
Väänänen 2006	18	Road pavers (stone majestic asphalt)	0.12	NS	<0.09-0.48	NS

LOD- limit of detection; NS- not specified. PYR- pyrene.

In a comparison between the pyrene exposures on the right wrists of workers in similar studies where patch sampling was used, the average exposure for this study was the third highest. This study did not have as many participants as the other studies.

Toxicity of a chemical depends on both the external dose and the exposure time (McDougal and Boeniger, 2002). It is, therefore, necessary to reduce either the external dose (through engineering methods or PPE) or the exposure time (through administrative measures) in order to effectively reduce the exposure to the chemical.

Conclusion

The aim of this study was to determine whether workers at a South African petrochemical factory experience high dermal exposure to PAHs throughout an eight hour work shift and whether their skin barrier function is weakened as a result of this exposure.

PAHs can easily be absorbed through the skin and is a major route of PAH exposure in the workplace (Van Rooij *et al.,* 1993; Gündel *et al.,* 2000; McClean *et al*., 2004; Väänänen *et al.,* 2005).

Workers at SFP came in direct contact with the tar more often. As a result of this, higher average dermal exposures were seen in these workers. Direct contact of the filters with tar was associated with high concentrations PAHs, including benzo[a]pyrene and dibenz[a,h]anthracene. Benzo[a]pyrene and dibenz[a,h]anthracene are classified as Group 1 (human carcinogen) and Group 2A (Probable human carcinogen) respectively and are the most harmful individual PAHs. 66.7% (4/6) Workers at SFP were exposed to benzo[a]pyrene on the outside of their clothing and two of these experienced dermal exposure. At TSP none of the workers were exposed to benzo[a]pyrene or dibenz[a,h]anthracene on the outside of their clothing but one worker was exposed to benzo[a]pyrene on the surface of his skin. None of the workers in the study was exposed to dibenz[a,h]anthracene on the surface of their skin but two of the SFP workers were exposed to dibenz[a,h]anthracene on the outside of their clothing. Workers at SFP also complained more of skin rashes, pimples and itching.

There exists an uncertainty concerning the acceptable safe limit for dermal exposure. Knowing that a carcinogenic chemical might penetrate through the skin, is sufficient information to provide a warning that the chemical poses a threat for systemic carcinogenicity and any worker that is exposed to benzo[a]pyrene or dibenz[a,h]anthracene is at risk.

SFP workers experience higher average exposures to total PAHs than TSP workers. Most of the individual PAHs that TSP workers are exposed to, have 2-4 benzene ring structures which are not very harmful to humans. SFP workers come in direct contact with tar more often and are more exposed to individual PAH structures with 4-6 benzene ring structures that are in general more harmful to the health of humans. At both SFP and TSP, a cleaner experienced the highest exposure to total PAHs and this is, therefore the highest exposed occupation.

SFP workers are considerably more exposed to total PAHs as well as benzo[a]pyrene and dibenz[a,h]anthracene than TSP. TSP as well as SFP workers' palms and wrists show high baseline TEWL values which indicate weak skin barrier function. This also increases the risk of skin absorption of PAHs and the risk of developing cancer and other skin diseases. In general, SFP workers, and especially cleaners, are at greater risk of experiencing significant dermal exposure to PAHs.

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Supplementary material

Table S1: Description of specific PPE worn by different workers.

Job	Work area	PPE
Process Controller 1	TSP	Safety helmet. Standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Process Controller 2	TSP	Safety helmet. Tyvek® classic suit over standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Cleaner 1 + 2	TSP	Safety helmet. PVC gloves. Dust suit over standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Truck loader 1 + 2	TSP	Safety helmet. Leather gloves. Tyvek® classic suit over standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Cleaner 3	SFP	Safety helmet. Nitrile gloves. Tyvek® classic suit over standard overall. Gumboots. Dräger® half mask respirator. Safety glasses.
Mechanical operator 1	SFP	Safety helmet. Mechanical gloves. Tyvek® classic suit over standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Mechanical operator 2	SFP	Safety helmet. Nitrile gloves. Tyvek® classic suit over t-shirt and standard overall pants. Dräger® half mask respirator. Safety glasses. Safety boots.
Truck offloader 1	SFP	Safety helmet. PVC gloves. Tyvek® classic suit over standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Process Controller 3	SFP	Safety helmet. Ninja flex gloves. Tyvek® classic suit over standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Truck attendant 1	SFP	Safety helmet. Nitrile gloves. Standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Cleaner 4	CMP	Safety helmet. Nitrile gloves. Standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Occupational Hygiene Assistant 1	Occupational Hygiene office	Standard overall. Safety boots.

TSP-Tar Separation Plant, SFP- Solids Filtration Plant, CMP- Coal mixing Plant

Table S2: Exposure of Process controller 1 TSP to individual PAHs

Process controller 1 TSP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	-	-	-	-	-	-	-
Acenaphthylene	-	-	-	-	-	-	-
Acenaphthalene	-	-	-	-	-	-	-
Fluorene	16.74091	13.02071	14.88081	13.02071	18.60102	14.88081	18.60102
Phenanthrene	33.48183	22.32122	27.90152	24.18132	37.20203	14.88081	29.76163
Anthracene	16.74091	11.16061	11.16061	11.16061	16.74091	-	11.16061
Fluoranthene	13.02071	-	-	-	-	-	-
Pyrene	9.300508	-	-	-	-	-	-
Benz[a]anthracene	-	-	-	-	-	-	-
Chrysene	-	-	-	-	-	-	-
Benz[b]fluoranthene	-	-	-	-	-	-	-
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	-
Total PAHs	**147.8781**	**111.1411**	**118.5815**	**113.0012**	**137.1825**	**96.72528**	**124.1618**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S3: Exposure of Process controller 2 TSP to individual PAHs

Process controller 2 TSP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	-	-	-	-	-	-	9.300508
Acenaphthylene	-	-	-	-	-	-	9.300508
Acenaphthalene	-	-	-	-	-	-	16.74091
Fluorene	11.16061	14.88081	11.16061	13.02071	29.76163	16.74091	137.6475
Phenanthrene	18.60102	18.60102	24.18132	16.74091	31.62173	11.16061	137.6475
Anthracene	9.300508	9.300508	11.16061	-	14.88081	-	74.40406
Fluoranthene	-	-	-	-	-	-	39.06213
Pyrene	-	-	-	-	-	-	31.62173
Benz[a]anthracene	-	-	-	-	-	-	13.02071
Chrysene	-	-	-	-	-	-	11.16061
Benz[b]fluoranthene	-	-	-	-	-	-	18.60102
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	-
Total PAHs	**103.7007**	**107.4209**	**111.1411**	**99.05041**	**140.9027**	**97.19031**	**540.8245**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S4: Exposure of Process controller 3 SFP to individual PAHs

Process controller 3 SFP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	-	-	-	-	11.16061	-	18.60102
Acenaphthylene	-	-	-	-	11.16061	37.20203	100.4455
Acenaphthalene	9.300508	-	9.300508	-	9.300508	20.46112	119.0465
Fluorene	96.72528	59.52325	104.1657	37.20203	128.347	9.300508	1540.164
Phenanthrene	135.7874	55.80305	212.0516	83.70457	388.7612	-	2481.376
Anthracene	70.68386	27.90152	117.1864	40.92224	210.1915	-	1354.154
Fluoranthene	29.76163	9.300508	57.66315	18.60102	230.6526	-	978.4134
Pyrene	22.32122	-	42.78234	13.02071	193.4506	-	790.5432
Benz[a]anthracene	-	-	9.300508	-	102.3056	-	349.6991
Chrysene	-	-	11.16061	-	87.42478	-	282.7354
Benz[b]fluoranthene	9.300508	-	14.88081	-	156.2485	-	465.0254
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	57.66315	-	167.4091
Benzo[g,h,i]perylene	-	-	-	-	42.78234	-	133.9273
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	33.48183	-	96.72528
Total PAHs	**427.8234**	**214.3767**	**624.5291**	**252.0438**	**1685.252**	**132.5322**	**8900.586**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S5: Exposure of Truck loader 1 TSP to individual PAHs

Truck loader 1 TSP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	-	-	-	-	-	9.300508	7.440406
Acenaphthylene	-	-	-	-	-	-	-
Acenaphthalene	-	-	-	-	-	9.300508	-
Fluorene	122.7667	68.82376	39.06213	31.62173	31.62173	42.78234	57.66315
Phenanthrene	102.3056	87.42478	37.20203	39.06213	31.62173	27.90152	42.78234
Anthracene	53.94295	46.50254	18.60102	18.60102	13.02071	13.02071	16.74091
Fluoranthene	16.74091	57.66315	-	9.300508	-	-	-
Pyrene	11.16061	42.78234	-	-	-	-	-
Benz[a]anthracene	-	-	-	-	-	-	-
Chrysene	-	-	-	-	-	-	-
Benz[b]fluoranthene	-	-	-	-	-	-	-
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	-
Total PAHs	**365.51**	**361.7898**	**159.5037**	**160.4338**	**140.9027**	**163.2239**	**187.4052**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S6: Exposure of Truck loader 2 TSP to individual PAHs

Truck loader 2 TSP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	-	-	-	-	-	11.16061	9.300508
Acenaphthylene	-	-	-	-	-	-	-
Acenaphthalene	-	-	-	-	-	-	-
Fluorene	39.06213	16.74091	20.46112	53.94295	29.76163	37.20203	55.80305
Phenanthrene	76.26417	14.88081	20.46112	42.78234	27.90152	33.48183	59.52325
Anthracene	40.92224	-	9.300508	16.74091	11.16061	16.74091	29.76163
Fluoranthene	44.64244	-	-	11.16061	-	-	20.46112
Pyrene	37.20203	-	-	9.300508	-	-	16.74091
Benz[a]anthracene	16.74091	-	-	-	-	-	-
Chrysene	16.74091	-	-	-	-	-	-
Benz[b]fluoranthene	26.04142	-	-	-	-	-	-
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	9.300508	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	-
Total PAHs	**350.1641**	**98.58538**	**114.8613**	**192.5205**	**133.4623**	**161.3638**	**248.3236**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S7: Exposure of Cleaner 1 TSP to individual PAHs

Cleaner 1 TSP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	-	-	-	-	-	-	9.300508
Acenaphthylene	-	-	-	-	-	-	-
Acenaphthalene	-	-	-	-	-	-	9.300508
Fluorene	18.60102	18.60102	22.32122	20.46112	29.76163	40.92224	65.10356
Phenanthrene	22.32122	31.62173	33.48183	35.34193	35.34193	48.36264	98.58538
Anthracene	-	14.88081	14.88081	14.88081	14.88081	24.18132	50.22274
Fluoranthene	-	-	9.300508	9.300508	-	16.74091	40.92224
Pyrene	-	-	-	-	-	13.02071	33.48183
Benz[a]anthracene	-	-	-	-	-	-	13.02071
Chrysene	-	-	-	-	-	-	13.02071
Benz[b]fluoranthene	-	-	-	-	-	-	24.18132
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	-
Total PAHs	**107.8859**	**129.7421**	**141.8327**	**141.8327**	**144.6229**	**201.821**	**401.3169**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S8: Exposure of Cleaner 2 TSP to individual PAHs

Cleaner 2 TSP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	-	-	-	-	-	-	-
Acenaphthylene	-	-	-	-	-	-	-
Acenaphthalene	-	-	-	-	-	-	-
Fluorene	50.22274	48.36264	55.80305	44.64244	33.48183	13.02071	65.10356
Phenanthrene	100.4455	119.0465	122.7667	126.4869	57.66315	31.62173	184.1501
Anthracene	52.08284	61.38335	63.24345	66.96366	27.90152	16.74091	91.14498
Fluoranthene	31.62173	22.32122	16.74091	31.62173	13.02071	-	66.96366
Pyrene	24.18132	16.74091	13.02071	24.18132	-	-	50.22274
Benz[a]anthracene	-	-	-	-	-	-	14.88081
Chrysene	-	-	-	-	-	-	14.88081
Benz[b]fluoranthene	-	-	-	-	-	-	22.32122
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	-
Total PAHs	**317.1473**	**326.4478**	**330.168**	**352.4893**	**193.9156**	**126.0219**	**557.5655**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S9: Exposure of Cleaner 3 SFP to individual PAHs

Cleaner 3 SFP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	20.46112	14.88081	18.60102	11.16061	7.440406	20.46112	167.4091
Acenaphthylene	13.02071	9.300508	9.300508		9.300508	14.88081	377.6006
Acenaphthalene	14.88081	11.16061	13.02071	13.02071	11.16061	24.18132	418.0578
Fluorene	126.4869	87.42478	106.0258	76.26417	94.86518	219.492	3656.96
Phenanthrene	267.8546	152.5283	182.29	130.2071	113.4662	496.6471	5448.238
Anthracene	137.6475	76.26417	94.86518	65.10356	53.94295	273.4349	3061.727
Fluoranthene	141.3677	57.66315	59.52325	31.62173	40.92224	150.6682	3217.976
Pyrene	119.0465	44.64244	46.50254	22.32122	33.48183	111.6061	2760.391
Benz[a]anthracene	63.24345	-	18.60102	-	13.02071	11.16061	1834.06
Chrysene	53.94295	-	14.88081	-	11.16061	11.16061	1483.431
Benz[b]fluoranthene	100.4455	-	29.76163	-	14.88081	9.300508	2972.442
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	37.20203	-	9.300508	-	9.300508	-	1187.21
Benzo[g,h,i]perylene	29.76163	-	-	-	-	-	1012.36
Dibenz[a,h]anthracene	-	-	-	-	-	-	223.6772
Indeno[1,2,3-c,d]pyrene	22.32122	-	-	-	-	-	768.687
Total PAHs	**1170.004**	**506.8777**	**640.34**	**404.5721**	**450.6096**	**1385.311**	**28596.27**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S10: Exposure of Cleaner 4 CMP to individual PAHs

Cleaner 4 CMP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	11.16061	9.300508	9.300508	9.300508	7.440406	11.16061	-
Acenaphthylene	-	-	-	-	-	-	-
Acenaphthalene	-	-	-	-	-	-	-
Fluorene	33.48183	27.90152	33.48183	26.04142	31.62173	-	39.06213
Phenanthrene	24.18132	14.88081	13.02071	16.74091	24.18132	-	27.90152
Anthracene	11.16061	-	-	-	11.16061	-	13.02071
Fluoranthene	-	-	-	-	-	-	-
Pyrene	-	-	-	-	-	-	-
Benz[a]anthracene	-	-	-	-	-	-	-
Chrysene	-	-	-	-	-	-	-
Benz[b]fluoranthene	-	-	-	-	-	-	-
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	-
Total PAHs	**142.7628**	**117.1864**	**120.9066**	**117.1864**	**137.1825**	**80.91442**	**144.6229**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S11: Exposure of Mechanical operator 1 SFP to individual PAHs

Mechanical operator 1 SFP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	-	-	7.440406	-	-	-	11.16061
Acenaphthylene	-	-	-	-	-	-	-
Acenaphthalene	-	-	-	-	-	-	9.300508
Fluorene	37.20203	18.60102	39.06213	37.20203	29.76163	27.90152	91.14498
Phenanthrene	50.22274	26.04142	57.66315	39.06213	44.64244	27.90152	172.9894
Anthracene	22.32122	9.300508	24.18132	16.74091	22.32122	13.02071	79.98437
Fluoranthene	24.18132	11.16061	29.76163	13.02071	18.60102	11.16061	135.7874
Pyrene	20.46112	9.300508	24.18132	11.16061	14.88081	9.300508	115.3263
Benz[a]anthracene	9.300508	-	11.16061	-	-	-	65.10356
Chrysene	9.300508	-	13.02071	-	-	-	72.54396
Benz[b]fluoranthene	16.74091	-	22.32122	-	13.02071	-	137.6475
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	39.06213
Benzo[g,h,i]perylene	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	-
Total PAHs	**237.628**	**132.9973**	**274.83**	**175.7796**	**199.0309**	**147.8781**	**969.578**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S12: Exposure of Mechanical operator 2 SFP to individual PAHs

Mechanical operator 2 SFP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	6.510356	4.650254	18.60102	-	-	7.440406	279.9453
Acenaphthylene	12.09066	5.580305	9.300508	4.650254	-	-	481.7663
Acenaphthalene	15.81086	8.370457	9.300508	8.370457	-	6.510356	572.9113
Fluorene	156.2485	65.10356	97.65533	60.4533	47.43259	15.81086	3884.822
Phenanthrene	246.4635	56.7331	215.7718	42.78234	66.03361	10.23056	4165.698
Anthracene	133.9273	30.69168	118.1165	21.39117	36.27198	-	2384.65
Fluoranthene	105.0957	15.81086	108.8159	9.300508	14.88081	-	1746.635
Pyrene	86.49472	12.09066	88.35483	7.440406	12.09066	-	1416.467
Benz[a]anthracene	38.13208	-	40.92224	-	-	-	670.5666
Chrysene	30.69168	-	32.55178	-	-	-	514.3181
Benz[b]fluoranthene	38.13208	5.580305	39.06213	-	-	-	651.9656
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	212.9816
Benzo[g,h,i]perylene	-	-	-	-	-	-	104.6307
Dibenz[a,h]anthracene	-	-	-	-	-	-	33.94685
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	90.67995
Total PAHs	**911.9148**	**254.8339**	**820.7698**	**209.2614**	**235.3029**	**103.2356**	**17225.94**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S13: Exposure of Truck attendant 1 SFP to individual PAHs

Truck attendant 1 SFP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	-	-	-	-	-	-	-
Acenaphthylene	-	-	-	-	-	-	-
Acenaphthalene	-	-	-	-	9.300508	11.16061	-
Fluorene	42.78234	40.92224	48.36264	35.34193	72.54396	78.12427	59.52325
Phenanthrene	44.64244	42.78234	40.92224	35.34193	78.12427	55.80305	65.10356
Anthracene	18.60102	18.60102	18.60102	13.02071	29.76163	24.18132	27.90152
Fluoranthene	-	-	-	-	16.74091	9.300508	11.16061
Pyrene	-	-	-	-	11.16061	-	9.300508
Benz[a]anthracene	-	-	-	-	-	-	-
Chrysene	-	-	-	-	-	-	-
Benz[b]fluoranthene	-	-	-	-	-	-	-
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	-
Total PAHs	**170.6643**	**166.9441**	**172.5244**	**148.3431**	**274.365**	**238.558**	**231.5826**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S14: Exposure of Truck offloader 1 SFP to individual PAHs

Truck offloader 1 SFP							
Compound	Right wrist	Right forearm	Left wrist	Left forearm	Neck	Ankle	Outside clothing
Naphthalene	-	-	-	-	-	-	-
Acenaphthylene	-	-	-	-	-	-	-
Acenaphthalene	-	-	-	-	-	-	9.300508
Fluorene	44.64244	39.06213	37.20203	37.20203	11.16061	74.40406	115.3263
Phenanthrene	35.34193	24.18132	26.04142	22.32122	87.42478	76.26417	128.347
Anthracene	18.60102	11.16061	11.16061	9.300508	79.98437	40.92224	61.38335
Fluoranthene	-	-	-	-	39.06213	29.76163	31.62173
Pyrene	-	-	-	-	9.300508	24.18132	24.18132
Benz[a]anthracene	-	-	-	-	-	-	11.16061
Chrysene	-	-	-	-	-	-	9.300508
Benz[b]fluoranthene	-	-	-	-	-	-	16.74091
Benz[k]fluoranthene	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-	-	-
Total PAHs	**163.2239**	**139.0426**	**139.0426**	**133.4623**	**285.5256**	**304.1266**	**453.3998**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Chapter 4

Short term exposure study

Dermal exposure of petrochemical workers exposed to polycyclic aromatic hydrocarbons during specific tasks of short duration

LINDE S.J.L, DU PLESSIS J.L, ELOFF F.C, JACOBS P.J.

School of Physiology, Nutrition and Consumer Sciences

North-West University, Potchefstroom Campus,

South Africa

Corresponding author

Prof. J.L. du Plessis

School of Physiology, Nutrition and Consumer Sciences

North-West University, Potchefstroom Campus

Private Bag X6001

Potchefstroom

2520

South Africa

Tel: 018 299 2434

Fax: 018 299 1053

Word count: 4550

ABSTRACT

Objectives: To determine the dermal exposure of petrochemical workers to 16 polycyclic aromatic hydrocarbons (PAHs) during specific tasks, by wiping the surface of the skin with isopropanol alcohol swabs and to assess the health risk experienced by these workers as a result of the PAH exposure during the tasks.

Methods: Seven tasks on two different plants in a South African petrochemical factory were included in the study. Samples were collected from five different anatomical areas including: both palms, the wrist, forearm and neck on the dominant side of the body. Thirteen surface samples were also collected from various surfaces in both plants.

Results: Slop pit cleaner 3 from the Tar Separation Plant (TSP) experienced the highest dermal exposure to total PAHs (1659.04 ng/cm^2). A splash of tar landed on Slop pit cleaner 3's cheek which contained 14871.45 ng/cm^2 total PAHs. The following workers were exposed to benzo[a]pyrene during their tasks: Truck loader 3 at TSP (2.7 ng/cm^2); Cleaner 6 at SFP (6.2 ng/cm^2 and 3.5 ng/cm^2); Slop pit cleaner 2 at TSP (20.8 ng/cm^2 and 12.8 ng/cm^2) and Slop pit cleaner 3 at TSP (72.8 ng/cm^2 and 108 ng/cm^2). Slop pit cleaner 3 at TSP was exposed to dibenz[a,h]anthracene (9.6 ng/cm^2 and 15.2 ng/cm^2) The surface with the highest contamination is on top of the dirty lockers in the Solids Filtration Plant (SFP) (519.0 ng/cm^2).

Conclusions: Cleaning the slop pit at TSP and cleaning the plant at SFP were identified as the greatest exposed tasks. This is probably because workers frequently come in direct contact with tar during the tasks. Tasks where workers are exposed to benzo[a]pyrene or dibenz[a,h]anthracene pose the greatest health risk to workers as these substances are highly carcinogenic. Dirty surfaces can also contain PAHs including benzo[a]pyrene and dibenz[a,h]anthracene.

Key words: Polycyclic aromatic hydrocarbons; Dermal exposure; Dermal wipes; Occupational exposure; Petrochemical workers.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) include several hundred lipophilic, non-polar organic compounds, characterised by the presence of two or more fused benzene rings (Kammer *et al*., 2011) and can be present in a gaseous state or be bound to other particles in the air (Tsai *et al.,* 2001). PAHs are generated by the incomplete combustion of fuels, such as petrol, diesel and coal (Yadav *et al.,* 2005). They are commonly present in the environment due to discharge from forest fires, motor vehicle traffic and the burning of fossil fuels. Industries where PAH mixtures represent a significant amount of the risk to the worker's health include coal gasification, coke production and other industries where coal tars are used (Bofetta *et al.,* 1997).

Following exposure to PAHs workers commonly experience skin irritation and defatting of the skin, which will lead to dryness and cracking of the skin, as well as oil acne, dermatitis hyperkeratosis and photo sensitivity (Christopher *et al.,* 2011). Other frequently reported symptoms include eye irritation, coughing, headaches, fatigue and throat irritation (Cirla *et al.,* 2007). PAHs such as benzo[a]pyrene can also act as allergens to produce allergic reactions on the skin of animals (Mumtaz and George, 1995).

The International Agency for Research on Cancer (IARC) has classified several PAHs, including benzo[a]pyrene as carcinogenic to humans (Group 1) (Kammer *et al*., 2011). Tsai *et al.* (2001) found that workers handling PAH-containing materials had a significant risk of developing skin cancer and that mixtures of carcinogenic PAHs cause skin disorders in humans. For example, regressive verrucae (i.e., warts) were reported following up to 120 applications of 1% benzo[a]pyrene to human skin. Especially in persons with pre-existing skin disorders such as blisters, adverse dermal effects were observed following intermediate benzo[a]pyrene exposure (Mumtaz and George, 1995).

When it comes to occupational exposure to certain chemicals, the skin surface as a route of exposure has been overlooked (Du Plessis *et al*., 2010) but during the past two decades in occupational hygiene, there has been an increased interest in exposure via the dermal exposure route (Kammer *et al.,* 2011). PAHs are highly lipophilic, which allows them to move readily through the skin (Poet and McDougal, 2002; Bamforth and Singleton, 2005) and a number of studies have shown that PAH absorption through the skin can contribute up to 75% of the total PAH load in the body (Van Rooij *et al.,* 1993; Gündel *et al*., 2000; McClean *et al*., 2004). Väänänen *et al.* (2005) concluded that dermal absorption is a major route of PAH uptake and therefore, the measurement of PAH-concentration in the air alone is not sufficient to accurately estimate the total health risk for the individual worker.

It is essential to evaluate workplace factors, including tasks, work patterns and techniques, production processes, sources of direct skin contact, spilling, splashing, emission into the air, safety precautions and procedures (including personal protective equipment (PPE)) in order to gauge the potential for dermal exposure to the chemical agents (Schneider *et al*., 2000). Transfer, cleaning and maintenance tasks are typical situations during which dermal exposure to PAH can occur. The frequency and potential for direct contact with tar and other PAH-containing products during the tasks will be an important factor when describing workers' exposure and health risk (Christopher *et al*., 2011).

Wipe sampling can be used to assess dermal exposure and is recommended when workers are exposed to chemical compounds that have the potential for percutaneous absorption. Skin wipes can only collect substances that are present on the skin and cannot recover chemicals after they have already penetrated the skin (McArthur, 1992). This makes it an ideal method for collecting short term task based exposure samples.

Not many results for dermal exposures to PAHs have previously been reported and as a result of this there is not a lot of dermal exposure data available for comparisons (Schneider *et al.,* 2000; Christopher *et al.,* 2011). Data regarding dermal PAH exposure to workers in South Arica is especially lacking, which makes it very difficult to compare newly obtained dermal exposure data with existing data. The aim of this study was to determine the dermal exposure of workers at a South African petrochemical factory to PAHs, by measuring short term task specific exposure.

Methods and materials

Study design

The short term dermal exposure of workers to PAHs was studied at two different plants in a South African petrochemical factory during August and September of 2011. The different plants included: a tar separation plant (TSP) and a solids filtration plant (SFP). These plants were open air plants and were, therefore, susceptible to ventilation by wind. The descriptions of the tasks performed at the different plants as well as the PPE wore by the workers are shown in Table 1 and Table 2 respectively. A total of seven tasks was included in the study.

Process description

At TSP, various gaseous, liquid and solid components are separated from the gaseous water streams that are obtained from the gasification of coal. This gaseous water contains

by-products from coal carbonization such as water vapour, tar, oil, naphtha, phenols, chlorine, fluorine and fatty acids. It also contains dissolved gasses (NH_3, CO_2 and H_2), a small amount of combustible gasses, coal dust and inorganic salts. A stream containing bulk free tar and some heavy oils is gravitated to primary tar separators where most of the tar and solids are separated from the oil and tarry water. In the secondary tar separator the oil and entrained tar/solids are separated from the tarry water. The recovered oil is then gravitated to an oil rundown tank. Tar and solids from the secondary tar separator are periodically drained to the slop pit, which is periodically cleaned by workers using shovels and buckets to remove the tar and solids from the pit. The remaining hot tarry water from the secondary tar separator containing ammonia and hydrocarbons, is then gravitated to a tank and after undergoing further purification processes to remove the ammonia, this hot tarry water is used by the cleaners to clean the plant.

The products of this separation process that may contain PAHs are oil, clean tar, heavy dusty tar and tarry water.

The separated tar from the primary tar separator is transported to SFP by tanker trucks where the solids are removed and the liquid tar is filtered.

During a shutdown, some of the processes are stopped and the plant is cleaned. This happens approximately twice a year. The only shutdown activity featured in this study is the cleaning of the slop pit and the separator tank.

Table 1: Description of different tasks performed by the workers.

Job	Location	Description	Duration
Cleaner 5	TSP	Used hot tarry water at high pressure to clean the plant.	30 minutes at a time.
Truck loader 3	TSP	Stood on a platform directly above the manhole opening of the tank of the truck and operated switches in order to load tar which poured into the tank of the truck from a pipe.	Loading 1 tank took ~ 30 min.
Tank scaffold builder 1	TSP	Climbed into the primary tar separator tank to build scaffolding for cleaning purposes. The tank was rinsed with water before he climbed in.	30 minutes at a time.
Slop pit cleaner 1 + 2	TSP	Climbed into the slop pit and helped to remove buckets of tar slop from the pit.	30 minutes at a time.
Slop pit cleaner 3	TSP	Climbed into the slop pit and shovelled slop into a bucket.	30 minutes at a time.
Cleaner 6	SFP	Used hot tarry water at high pressure to clean the plant.	30 minutes at a time.
Truck offloader 3	SFP	Opened the outlet of the truck, scraped the solids at the bottom of the tank into a tar pit and watched as the liquid tar poured into the tar pit.	To unload one tank took ~ 30 min.

TSP-Tar Separation Plant, SFP- Solids Filtration Plant

Sampling strategy

Skin wipe sampling

In order to measure the short term dermal exposure to PAHs following tasks or activities that lasted approximately 30 minutes, the skin of the workers was wiped on five different anatomical positions on the body. This method was based on a wipe method developed by Christopher *et al.* (2011). In testing, Christopher *et al.* (2011) obtained a recovery efficiency of 95% to 106% from directly spiked samples and an overall sampling efficiency from pig skin that ranged from 88.9% (benzo(a)pyrene) to 100% (phenanthrene). Neosafe® 70% Isopropanol alcohol swabs (Neomedic Ltd®) were used to wipe the skin and a template was used to ensure that an area of 25 cm^2 was wiped. The wipe was folded in half after each wipe and each area was wiped three times. The area was wiped in a zig-zag motion, beginning at the one corner and ending at the corner on the opposite side of the square.

Skin wipe samples were collected from: 1) the middle of the palm on the right hand, 2) the middle of the palm on the left hand, 3) the wrist on the dominant side of the body, 4) the forearm on the dominant side of the body and 5) the neck on the dominant side of the body. One baseline and four repeats were collected per task and all repeats of the same task were collected on the same day. The baseline sample represented the PAH contamination experienced by the worker before performing the task and cleaned the area that had to be sampled. The four repeats were taken after the completion of specific tasks. Slop pit cleaner 2 and Slop pit cleaner 3 did not undergo baseline wipes as they were only later identified as being high risk workers. A total of 146 wipe samples were collected. Following the collection of the samples they were placed in foil-wrapped Petri dishes, transported in coolers and stored at 20 °C.

Surface wipe sampling

Thirteen surface samples were also collected from control and locker rooms at both the TSP and SFP. Most of these samples were taken on tables and other work surfaces in the control and locker rooms, but samples were also taken on surfaces where a lot of dust had settled or which workers might encounter on a daily basis.

All the surface samples were collected and handled in the same way as the skin wipes.

One field blank and one media blank were analysed per sampling day to establish whether there had been any PAH-contamination other than worker exposure.

Method of analysis

All samples were analysed using the NIOSH 5515 method by an accredited laboratory. This method uses a gas chromatograph to analyse for PAHs. When calculating the total PAH content of the samples, concentrations that were below the detection limits were taken as detection limit/2. The total PAH concentration was calculated as the sum of all the individual PAH-concentrations.

Statistical analysis of results

Box & whisker graphs were drawn using GraphPad Prism version 4.00 for Windows (GraphPad Software). In Figure 1 and 2 the data is presented in box and whisker graphs where the box represents the 5^{th} - 95^{th} percentiles, the horizontal line in the middle of the box is the mean and the two horizontal lines at the top and bottom of the graph represent the maximum and minimum. One of the repeat samples taken from the right palm of the Truck loader 3 at TSP was extraordinarily high (489,4 ng/m^2) and subsequently identified as an outlier because it was higher than the mean ± 3 (standard deviation). This value was excluded from the statistical analysis.

Results

Short term dermal exposure of workers to PAHs at a petrochemical plant was determined with dermal wipes. Short term samples from seven different tasks as well as 13 surface wipe samples were collected. All field and media blanks that were collected were below the limit of detection for PAHs.

Figure 1 shows the short term dermal exposure experienced by TSP workers on certain anatomical areas while performing specific tasks.

Truck loader 3 at TSP experienced the lowest mean neck exposure of all the TSP workers. There was a statistical significant difference between the total PAHs on his right palm and his forearm ($p = 0.017$) as well as between his right palm and his neck ($p = 0.010$), his wrist and his forearm ($p = 0.050$) and his wrist and his neck ($p = 0.027$). The highest total mean PAH concentration was observed on his right palm (~70 ng/cm^2). Cleaner 5's highest exposed area was on the neck. The other areas were all relatively equally exposed.

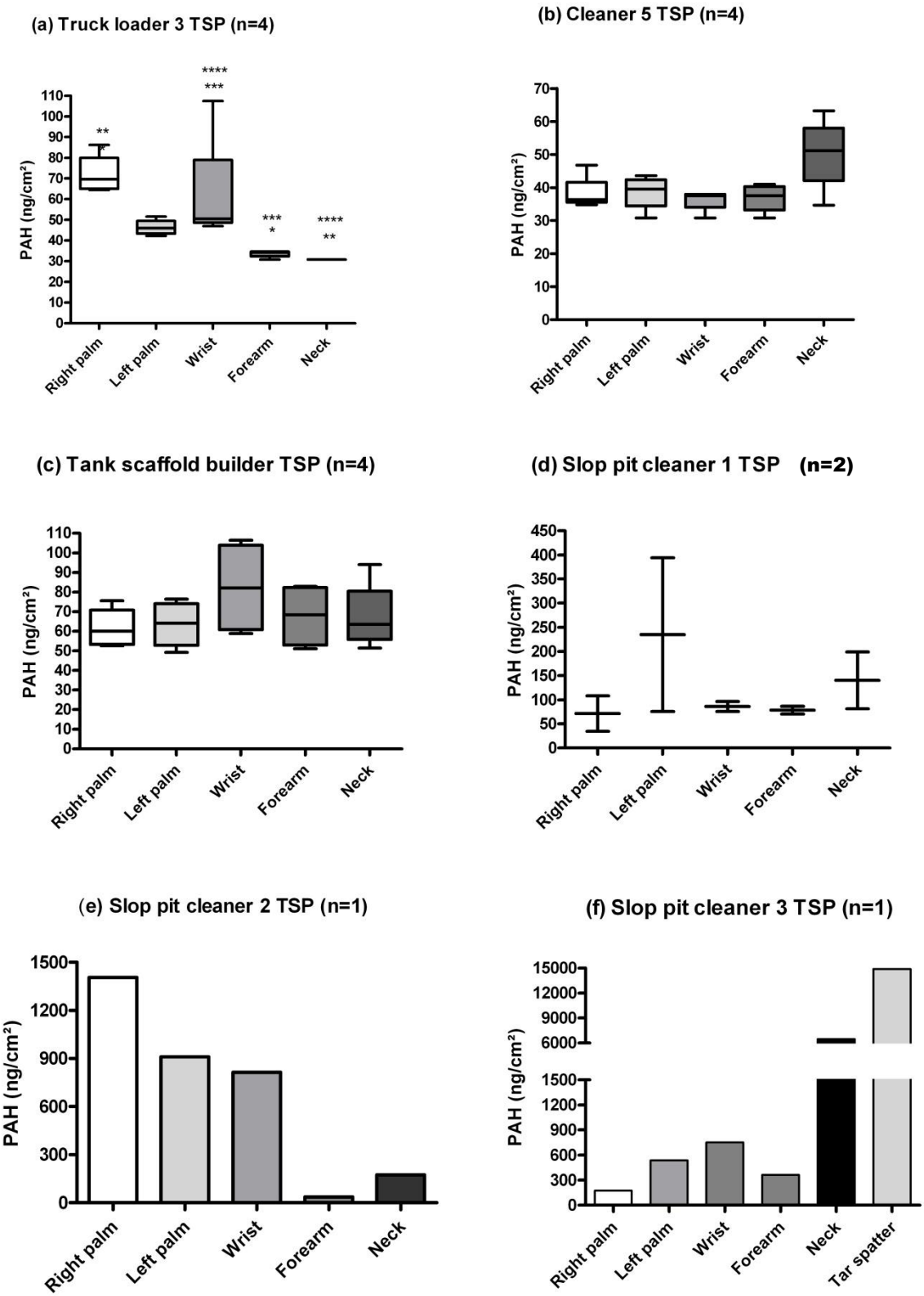

Figure 1: Box and whisker and column plots of short term PAH exposure of TSP workers.
* Indicates the presence of statistical differences between exposures at different anatomical sites. n=number of repeats. Note the differences in the Y-axis scale of the different graphs.

The Tank scaffold builder experienced a higher mean exposure than both Cleaner 5 and Truck loader 3. His highest exposed area was the wrist where the mean PAH concentration was ~ 85 ng/cm^2. The mean exposures on all the other areas were relatively equal.

Truck offloader 2's highest exposed area was his right wrist but overall he experienced low levels of exposure.

Slop pit cleaner 1 was the highest exposed worker at TSP. He was the only left handed worker in the study and it is, therefore, not surprising that his left palm was his highest exposed area. The mean exposure on his neck was also higher in comparison with that of his right palm, wrist and forearm.

Figure 1e and 1f show PAH concentrations for once off wipe samples collected from two Slop pit cleaners. Slop pit cleaner 2 experienced the highest exposure on the right palm (1405.6 ng/cm^2). He also had significant exposure on his left palm (910.4 ng/cm^2) and his wrist (814.2 ng/cm^2). A prominent spot of tar was present on the wiping area of his right palm. Slop pit cleaner 3 experienced the highest exposure on his neck (6467 ng/cm^2) where a spot of tar was present. The PAH contamination of the palms and wrist was lower compared to that of Slop pit cleaner 2. Also included in Figure 1f is a wipe of tar splatter that landed on the worker's face, which was removed with a wipe and analysed for PAHs (14871.45 ng/cm^2).

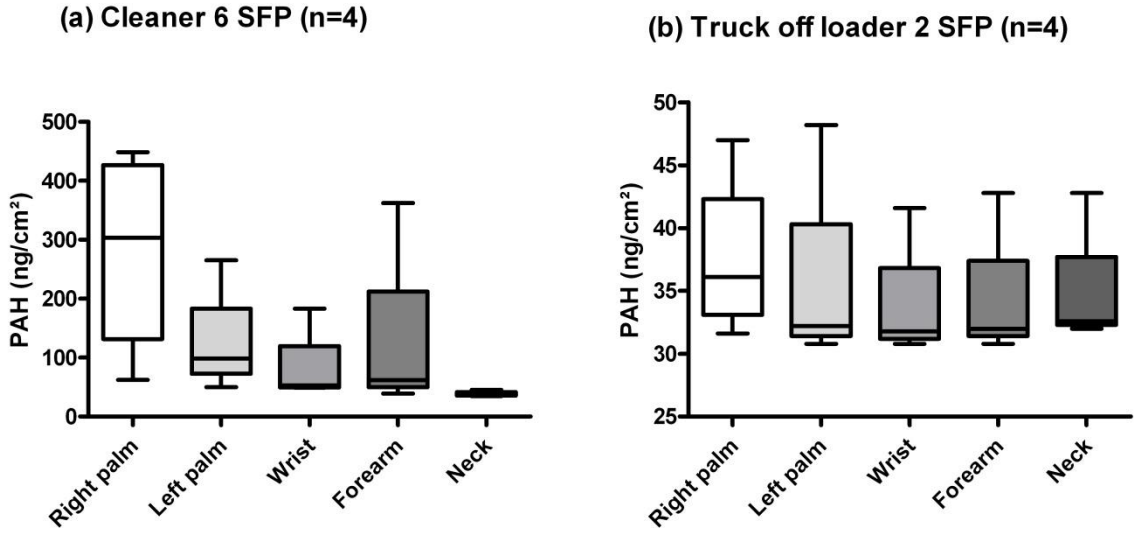

Figure 2: Box and whisker plots of SFP workers' short term exposure to total PAHs. n=number of repeats.

Figure 2 shows the short term exposure to total PAHs experienced by SFP workers on different anatomical areas. Cleaner 6 who worked at SFP experienced the highest mean

palm exposure of all the workers in the short term exposure study where repeat samples were taken. His right palm had a mean PAH concentration of ~300 ng/cm^2. The neck was his lowest exposed area.

Table 2: Total PAH contamination on workplace surfaces.

TSP areas	**PAH (ng/cm^2)**
Control room: Behind computer screen	318.0
Cleaners locker room: On top of front locker	272.8
Cleaners locker room: On top left locker	189.0
Control room: Front room plug box	159.8
Cleaners locker room: Inside locker	81.8
Control room (back room): On power box	40.2
SFP areas	
Cleaners locker room: On top dirty locker	519.0
Control room (back room): On top key chest	178.6
Control room (left room): On top of fridge	107.0
Control room (left room): Behind computer screen	49.2
Cleaners locker room: On top cleaner locker	43.6
Cleaners locker room: Inside locker	34.6
Control room (front room): Table work area	33.4

Table 2 shows the results of surface wipes from a variety of workplace surfaces in TSP and SFP. All the surface wipes collected at TSP and SFP contained PAHs. At TSP the highest PAH contamination was measured in the control room, behind a computer screen (318.0 ng/cm^2). The lowest contamination was measured in the back room (40.2 ng/cm^2). In the workers' changing room the highest contamination level was on top of the locker closest to the door (272.8 ng/cm^2) and the lowest, inside the locker (81.8 ng/cm^2). The sample inside this locker was collected from the dirtiest visible area in the locker.

At SFP the highest surface contamination was measured on top of a visibly dirty locker (519 ng/cm^2). The PAH contamination on top of a less dirty locker was considerably less (43.6 ng/cm^2) and the PAH contamination inside the locker was (34.6 ng/cm^2). In the control room, the highest contamination was measured in the places where it was very dusty (on top of the key chest- 178.6 ng/cm^2 and on top of the fridge- 107.0 ng/cm^2).

Discussion

Significantly lower amounts of PAHs were detected on the neck of Truck loader 3 at TSP (Figure1) which is most probably due to the fact that he wore a powered air purifying respirator (table 1 in supplementary material) that covered his neck and shielded it from PAH-containing vapours. As a result of this, a statistical significant difference in exposure occurred between the neck and the right palm as well as between the neck and the wrist. Significant differences in exposure also occurred between the wrist and the forearm and the right palm and the forearm. This means that the Truck loader was not uniformly exposed to PAHs, with the right palm and wrist having significantly higher exposure compared to his neck and forearm.

Cleaner 5 at TSP experienced relative uniform exposure on all anatomical areas except for his neck where his exposure was higher (Figure 1). A reason for this could be that the vapour from the hot tarry water that is used by the cleaners, settled on the neck of the worker. The Tyvek® suit worn by the worker does not completely cover the neck and exposure could have occurred as a result of this.

The Tank scaffold builder experienced higher exposure than both Cleaner 5 and Truck loader 3 at TSP (Figure 1). The Tank scaffold builder worked in the primary tar separator tank where PAH vapour could not be removed by natural ventilation and remained in close proximity to the worker for a longer period. His highest exposed area was the wrist. A reason for this is that he wore all-purpose gloves (Table 1 in Supplementary material) that only covered his hands up to his wrist. Vapour could have moved between his overall and the gloves and settled onto his wrists. The mean exposure on all the other areas was relatively equal.

Slop pit cleaner 1 experienced the highest exposure of all the workers in the repeat study at TSP (Figure 1). He is left handed, which explains why the highest exposure is on the left palm. He handled buckets filled with tar and some of the tar got onto his hands contributing to the increased exposure. The other anatomical areas of this worker were highly exposed when compared to the other TSP workers. His neck was highly exposed because he worked inside the pit and his neck was not covered by protective clothing. The Slop pit cleaners were in direct contact with tar more than the other TSP workers and it is because of this that they are the highest exposed workers in this area. Figure 1f shows the PAH concentration of a tar splatter that was wiped from the cheek of Slop pit cleaner 3. The PAH concentration of the tar is 14871.45 ng/cm^2 which confirms that direct contact with the tar will lead to an increase in dermal exposure to PAHs.

Slop pit cleaners 2 and 3 worked inside the slop pit and participated in the study only once after they were identified as high risk. Slop pit cleaner 2 carried buckets filled with tar in the pit and Slop pit cleaner 3 shovelled tar into the buckets at the bottom of the pit. Slop pit cleaner 2 experienced the highest exposure on the right palm, left palm and his wrist (Figure 1e). A prominent spot of tar was present on the wiping area of his right palm and as a result of this, a high PAH concentration was measured. The cause of this spot is unknown but PPE failure or other contamination due to unnecessary removal of the gloves could have resulted in this unnecessary exposure. Low dermal exposure on the forearm could be contributed to the worker wearing a PVC raincoat. Slop pit cleaner 3 experienced the highest exposure on his neck. A big tar spot was part of the area wiped on his neck. This worker also wore a PVC raincoat but the neck was exposed at the opening of the collar which caused the high exposure. The PAH contamination on his palms and wrists is lower compared to that of Slop pit cleaner 2. No tar spots were observed on these workers' palms, indicating either appropriate use of effective PPE and/or more effective personal hygiene practices of the worker. The Slop pit cleaners very often have direct contact with tar which causes very high exposures to PAHs. Workers also complain of a terrible chemical burning sensation on their skin following direct contact with the tar. The Slop pit is only cleaned two to three times per year so results represent the worst case scenario exposure for these workers.

Cleaner 6 at SFP experienced the highest exposure of all the workers in the repeated short term exposure study. A tar spot was part of the wiping area on his right hand and caused the high PAH concentration. His Tyvek® suit was also very dirty which could have caused exposure during donning or doffing. The extremely high maximum concentration on his forearm was caused by contamination from dirty PPE while he was pulling up his sleeves. He is also the only highly exposed worker that performed his job every day and not only two or three times a year. This is, therefore, a worker at high risk for dermal exposure to PAHs.

Truck offloader 3 did not experience high exposure because he works in a very open area. Despite this, high maximum PAH concentrations during one of the repeats were caused by other activities such as cleaning that occurred in his immediate environment.

All the workplace surface wipes collected at TSP and SFP contained PAHs. At TSP the highest PAH contamination was observed in the control room, behind a computer screen. This location is the nearest to the door in the office. The lowest contamination was observed in the back room which is the furthest from the door. The surface PAH contamination in the control room is higher close to the door and lower in the back room. In the workers' changing room, the highest contamination levels were on top of the locker closest to the door and the lowest, inside the locker. The sample inside this locker was taken on the dirtiest location in

the locker. Therefore, it can be presumed that surfaces closer to the door will be more contaminated as PAHs that have adsorbed to particles (i.e. dust) will settle on surfaces closest to the door. It is presumed that the outside part of the door will have the highest surface PAH contamination as it is constantly exposed to the external environment.

The highest surface contamination observed at SFP was on top of a dirty locker near the door. The PAH contamination on top of a cleaner locker at the back of the room was considerably less. In the control room, the highest contamination was observed in the places where it was very dusty (on top of the key chest and on top of the fridge). The dust, therefore, also contain PAHs and proper cleaning of the surfaces is required.

The cleaners' locker rooms at TSP and SFP contained very dirty surfaces that could lead to skin contamination. It is probable that additional contamination will occur as a result of the transfer of PAH contaminated particles from dirty clothes into surfaces and onto the skin. Dirty protective clothing is stored inside the dirty locker and eventually the PAH compounds will penetrate onto the inside of the clothing. Civilian clothing is put inside separate lockers but inside the same locker room. If workers put these clean clothes on top of the lockers they will also become contaminated.

Table 3: Average total PAH exposures (ng/cm^2) of workers during short tasks. Workers are shown from highest to lowest mean exposure.

		Concentration PAH (ng/cm^2)					
Task	n	Right palm	Left palm	Wrist	Forearm	Neck	**Ave per anatomical area**
Slop pit cleaner 3 TSP	1	175.8	537.4	751.2	363.8	6467	**1659.04**
Slop pit cleaner 2 TSP	1	1405.6	910.4	814.2	37.2	174.2	**668.32**
Cleaner 6 SFP	4	279.5	128.25	84.75	131.3	38.9	**132.54**
Slop pit cleaner 1 TSP	2	71.4	234.9	86	78.7	140.3	**122.26**
Tank scaffold builder TSP	4	62.05	63.4	82.3	67.6	68.1	**68.69**
Truck loader 3 TSP	4	63.05	46.4	63.8	33.45	30.8	**47.5**
Cleaner 5 TSP	4	38.6	38.4	36	36.75	50.05	**39.96**
Truck offloader 2 SFP	4	37.7	35.85	34	34.4	35	**35.39**

n = number of repeats

Table 3 shows the average of short term dermal PAH exposure experienced by workers per anatomical area during specific tasks that lasted ~ 30 minutes. It shows that all of the Slop

pit cleaners as well as the Cleaner at SFP are the workers with the highest risk for dermal exposure to PAHs. The reason for this is that they are the workers that come in direct contact with tar more often. It should however be noted that Slop pit cleaner 2 and Slop pit cleaner 3 were only wiped once each.

Cancer risk

According to the IARC (2012), both coal gasification and coal distillation are classified as group 1 carcinogenic processes and the application of coal-tar from gas works has been shown to induce a high number of papillomas and carcinomas in animals (IARC 2012).

Benzo[a]pyrene is also classified as a group 1 carcinogen and along with dibenz[a,h]anthracene (classified as a group 2A carcinogen) they represent the two most carcinogenic PAHs (IARC, 2012). Benzo[a]pyrene is also recognised as a priority pollutant by the environmental protection agency (EPA). In a study by Tsai *et al*. (2001) they used a series of toxic equivalent factors (TEFs) developed by Nisbet and LaGoy in 1992, who awarded a number to each PAH according to their carcinogenic toxicity relative to that of benzo[a]pyrene. Benzo[a]pyrene and dibenz[a,h]anthracene were identified as the most carcinogenic potent of the individual PAHs. In the past, several studies in which benzo[a]pyrene were applied to different strains of mice, benign and malignant skin tumours were observed and diben[a,h]anthracene has also been shown to exhibit significant carcinogenic activity (IARC 2010). As benzo[a]pyrene and dibenzo[a,h]anthracene have been shown to be the most carcinogenic PAHs, workers exposed to them will have the highest risk of cancer.

Table 4 shows a summary of the workers that were exposed to as well as surfaces that contained benzo[a]pyrene and dibenzo[a,h]anthracene.

Table 4: Summary of workers and surface wipes that contained benzo[a]pyrene and dibenz[a,h]anthracene

Worker	**Area**	**Anatomical Area**	**Concentration Benzo[a]pyrene (ng/cm^2)**	**Concentration Dibenz[a,h]anthracene (ng/cm^2)**
Truck loader 3	TSP	Wrist	2.7	-
Cleaner 6	SFP	Right palm	6.2	-
Cleaner 6	SFP	Forearm	3.5	-
Slop pit cleaner 2	TSP	Right palm	20.8	-
Slop pit cleaner 2	TSP	Left palm	12.8	-
Slop pit cleaner 3	TSP	Neck	72.8	9.6
Slop pit cleaner 3	TSP	Tar splatter on cheek	108	15.2
Surface	SFP	Behind computer screen in control room	10.4	-
Surface	SFP	On top front locker	6.8	-

In the SFP area, Cleaner 6 was exposed to benzo[a]pyrene on his right palm and forearm while he was cleaning the plant. In the TSP area, Truck loader 3 was exposed to benzo[a]pyrene on his right palm while Slop pit cleaner 1 was exposed to benzo[a]pyrene on his right and left palm and Slop pit cleaner 2 was exposed to both benzo[a]pyrene and dibenzo[a,h]anthracene on his neck. These workers all work directly with open tar and are at risk of developing cancer.

At SFP, benzo[a]pyrene was observed in the cleaners' locker room: on top of a dirty locker and at TSP, benzo[a]pyrene was found in the control room: on top of the fridge and behind the computer screen. This indicates that benzo[a]pyrene is present on dirty surfaces and that contact with these surfaces will increase the risk of cancer development. Therefore, all dirty surfaces need to be cleaned regularly in order to avoid this risk.

Many of the workers at SFP complained of skin diseases such as itching, pimples and rashes on their torsos, thighs and arms that started to appear after they started working at SFP. All the workers in the study (especially the Slop pit cleaner from who the tar splatter sample was collected) mentioned that the tar caused a chemical burning sensation after it came in contact with the skin.

It is clear that the highest dermal exposures to benzo[a]pyrene and dibenzo[a,h]anthracene in this study occurred as a result of excessive contact with tar, as can be seen in the tar splatter sample, where the tar contained 108 ng/cm^2 benzo[a]pyrene and 15.2 ng/cm^2 dibenzo[a,h]anthracene. This study agrees with Agostini *et al*. (2011) in that the transference of PAHs from contaminated surfaces to the hands is one of the most important routes of dermal exposure. These results along with those of Agostini *et al*. (2011) and Christopher *et al*. (2011) suggest that dermal exposure to PAHs is highly associated with the frequency of dermal contact with tar. It is recommended that workers avoid direct contact with the tar as much as possible and if contact occurs, that they wash it off as soon as possible. If the tar stays on the skin for a longer time period, higher concentrations of benzo[a]pyrene and dibenzo[a,h]anthracene can penetrate the skin and become systemically available. (Boström *et al.,* 2002).

Conclusion

The aim of this study was to determine whether workers at a South African petrochemical factory experience high dermal exposure to PAHs during specific tasks such as cleaning, truck loading and unloading and scaffold building.

Higher dermal exposure to PAHs during specific tasks was associated with direct skin contact with tar. The frequency of tasks with potential for contact with tar will clearly be an important factor when describing the workers' risk for exposure (Christopher *et al*., 2011). Tar contains large amounts of PAHs, including carcinogenic individual PAHs such as benzo[a]pyrene (Group 1) and dibenzo[a,h]anthracene (Group 2A) (IARC 2012). Direct skin contact with the tar occurred as a result of damaged PPE and bad work habits that resulted in high exposures to PAHs. Especially Cleaners and Slop pit cleaners are at high risk of dermal exposure as they work with contaminated surfaces and equipment. Dirty surfaces in locker rooms and control rooms also contain amounts of benzo[a]pyrene. Surfaces need to be kept as clean as possible to avoid unnecessary exposure. Therefore, if a specific task involves frequent contact of tar with the surface of the skin, then that worker will be at risk of developing cancer and other skin diseases.

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Supplementary material

Table S1: Description of specific PPE worn by different workers.

Job	Work area	PPE
Cleaner 5	TSP	Safety helmet. PVC gloves. Tyvek® suit over standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Truck loader 3	TSP	Safety helmet. Nugreen rubber gloves. Tyvek® classic suit over standard overall. Full face powered air purifying respirator. Safety glasses. Safety boots.
Tank scaffold builder 1	TSP	Safety helmet. Standard overall over a hoody jersey. All-purpose gloves. Dräger® half mask respirator. Safety glasses. Safety boots.
Slop pit cleaner 1	TSP	Safety helmet. PVC raincoat pants and dust suit jacket over standard overall. Nitrene gloves. Dräger® half mask respirator. Safety glasses. Safety boots.
Slop pit cleaner 2 + 3	TSP	Safety helmet. PVC raincoat suit over standard overall. Nitrene gloves. Dräger® half mask respirator. Safety glasses. Safety boots.
Cleaner 6	SFP	Safety helmet. PVC gloves. Tyvek® classic suit over standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.
Truck offloader 2	SFP	Safety helmet. One PVC and 1 nitrile glove. Tyvek® classic suit over standard overall. Dräger® half mask respirator. Safety glasses. Safety boots.

TSP-Tar Separation Plant, SFP- Solids Filtration Plant, CMP- Coal mixing Plant

Table S2: Exposure of Truck loader 3 TSP to individual PAHs

Truck loader 3 TSP					
Compound	Right palm	Left palm	Wrist	Forearm	Neck
Naphthalene	-	-	-	-	-
Acenaphthylene	-	-	-	-	-
Acenaphthalene	-	-	-	-	-
Fluorene	7.2	3.25	1.95	-	-
Phenanthrene	0	7.8	9.8	3.65	-
Anthracene	7.8	4.4	5.4	-	-
Fluoranthene	8.8	3.7	7.4	-	-
Pyrene	7.6	2.05	6.6	-	-
Benz[a]anthracene	3.4	-	3.8	-	-
Chrysene	2.35	-	2.55	-	-
Benz[b]fluoranthene	5.3	-	5	-	-
Benz[k]fluoranthene	-	-	-	-	-
Benzo[a]pyrene	-	-	2.7	-	-
Benzo[g,h,i]perylene	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-
Total PAHs	**63.05**	**46.4**	**63.8**	**33.45**	**30.8**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S3: Exposure of Cleaner 5 TSP to individual PAHs

Cleaner 5 TSP					
Compound	Right palm	Left palm	Wrist	Forearm	Neck
Naphthalene	8.6	8.4	6	6	11.6
Acenaphthylene	-	-	-	-	-
Acenaphthalene	-	-	-	-	-
Fluorene	-	-	-	-	5.05
Phenanthrene	-	-	-	1.75	4.45
Anthracene	-	-	-	-	1.95
Fluoranthene	-	-	-	-	-
Pyrene	-	-	-	-	-
Benz[a]anthracene	-	-	-	-	-
Chrysene	-	-	-	-	-
Benz[b]fluoranthene	-	-	-	-	-
Benz[k]fluoranthene	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-
Total PAHs	**38.6**	**38.4**	**36**	**36.75**	**50.05**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S4: Exposure of Cleaner 6 SFP to individual PAHs

Cleaner 6 SFP					
Compound	Right palm	Left palm	Wrist	Forearm	Neck
Naphthalene	42.8	18	8.1	18.6	6.2
Acenaphthylene	5.2	3.1	1.3	-	-
Acenaphthalene	5.3	3.9	-	2.7	-
Fluorene	42.3	23.5	7.5	15.4	2.15
Phenanthrene	48.6	21.3	12.7	19.5	2.35
Anthracene	26.4	11.3	6.6	10.05	1.45
Fluoranthene	23.9	8.9	8.8	12.8	-
Pyrene	20.25	7.65	7.7	10.85	-
Benz[a]anthracene	11.9	4.35	4.15	5.65	2.15
Chrysene	9.95	3.05	3.3	4.25	-
Benz[b]fluoranthene	17.9	5	5.6	9.4	-
Benz[k]fluoranthene	-	-	-	-	-
Benzo[a]pyrene	6.2	-	-	3.5	-
Benzo[g,h,i]perylene	6	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-
Total PAHs	**279.5**	**128.25**	**84.75**	**131.3**	**38.9**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S5: Exposure of Truck offloader 2 SFP to individual PAHs

Truck offloader 2 SFP					
Compound	Right palm	Left palm	Wrist	Forearm	Neck
Naphthalene	4.5	5.6	4	4.4	4.5
Acenaphthylene	-	-	-	-	-
Acenaphthalene	-	-	-	-	-
Fluorene	1.6	-	-	-	-
Phenanthrene	2.65	1.25	-	-	1.5
Anthracene	1.25	-	-	-	-
Fluoranthene	1.9	-	-	-	-
Pyrene	-	-	-	-	-
Benz[a]anthracene	-	-	-	-	-
Chrysene	-	-	-	-	-
Benz[b]fluoranthene	-	-	-	-	-
Benz[k]fluoranthene	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-
Total PAHs	**37.7**	**35.85**	**34**	**34.4**	**35**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S6: Exposure of Tank scaffold builder SFP to individual PAHs

Tank scaffold builder SFP					
Compound	Right palm	Left palm	Wrist	Forearm	Neck
Naphthalene	13	10.4	9.8	6	8.8
Acenaphthylene	-	-	-	-	-
Acenaphthalene	-	-	-	-	-
Fluorene	5.2	5.8	9.4	11.2	8.8
Phenanthrene	7.8	8.6	15.4	14.4	12
Anthracene	3.1	4.05	7.8	6.8	5.6
Fluoranthene	4.8	5.8	8.2	2.8	5.2
Pyrene	3.75	4.35	6.6	2	3.3
Benz[a]anthracene	-	-	-	-	-
Chrysene	-	-	-	-	-
Benz[b]fluoranthene	-	-	1.9	-	-
Benz[k]fluoranthene	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-
Total PAHs	**62.05**	**63.4**	**82.3**	**67.6**	**68.1**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S7: Exposure of Slop pit cleaner 1 TSP to individual PAHs

Slop pit cleaner 1 TSP					
Compound	Right palm	Left palm	Wrist	Forearm	Neck
Naphthalene	12.4	13.2	18	21.2	23.6
Acenaphthylene	-	11.6	-	-	3.2
Acenaphthalene	-	5.6	-	-	4
Fluorene	6.9	43.6	8.8	9.2	23.2
Phenanthrene	10.1	52.8	12.8	11.2	25.2
Anthracene	5.7	28.8	7.2	5.6	13.2
Fluoranthene	5.4	22.8	8	4.4	12
Pyrene	5.1	18.8	6.8	2.7	10.4
Benz[a]anthracene	-	7.2	-	-	3.6
Chrysene	-	5.7	-	-	2.5
Benz[b]fluoranthene	2.6	6.6	-	-	-
Benz[k]fluoranthene	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-
Total PAHs	**71.4**	**234.9**	**86**	**78.7**	**140.3**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S8: Exposure of Slop pit cleaner 2 SFP to individual PAHs

Slop pit cleaner 2 SFP					
Compound	Right palm	Left palm	Wrist	Forearm	Neck
Naphthalene	61.6	46.4	33.6	7.2	16
Acenaphthylene	29.6	18.4	14.4	-	-
Acenaphthalene	26.4	16	11.2	-	-
Fluorene	235.2	149.6	110.4	-	20.8
Phenanthrene	346.4	227.2	221.6	-	39.2
Anthracene	193.6	124.8	120	-	20.8
Fluoranthene	158.4	104.8	104	-	20
Pyrene	131.2	86.4	84.8	-	17.6
Benz[a]anthracene	58.4	36	33.6	-	7.2
Chrysene	48	29.6	27.2	-	5.6
Benz[b]fluoranthene	64	38.4	35.2	-	7.2
Benz[k]fluoranthene	-	-	-	-	-
Benzo[a]pyrene	20.8	12.8	-	-	-
Benzo[g,h,i]perylene	12.8	7.2	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	-	-
Total PAHs	**1405.6**	**910.4**	**814.2**	**37.2**	**174.2**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S9: Exposure of Slop pit cleaner 3 SFP to individual PAHs

Slop pit cleaner 3 SFP						
Compound	Right palm	Left palm	Wrist	Forearm	Neck	Tar spatter on cheek
Naphthalene	23.2	24.8	102.4	48	876	4037.6
Acenaphthylene	-	8	19.2	8.8	172.8	450.4
Acenaphthalene	-	4.8	20	9.6	189.6	540
Fluorene	20.8	50.4	120.8	61.6	1191.2	2825.6
Phenanthrene	35.2	136.8	165.6	80	1389.6	2612
Anthracene	20	76.8	91.2	42.4	787.2	1490.4
Fluoranthene	20	78.4	80	34.4	593.6	970.4
Pyrene	16.8	64.8	65.6	28.8	492	786.4
Benz[a]anthracene	7.2	27.2	26.4	11.2	216	338.4
Chrysene	5.6	21.6	22.4	9.6	169.6	261.6
Benz[b]fluoranthene	7.2	25.6	18.4	11.2	224.8	331.2
Benz[k]fluoranthene	-	-	7.2	-	-	-
Benzo[a]pyrene	-	-	-	-	72.8	108
Benzo[g,h,i]perylene	-	-	-	-	40.8	56
Dibenz[a,h]anthracene	-	-	-	-	9.6	15.2
Indeno[1,2,3-c,d]pyrene	-	-	-	-	35.2	48
Total PAHs	**175.8**	**537.4**	**751.2**	**363.8**	**6467**	**14877.4**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S10: Individual PAHs in surface samples at SFP

Surface SFP							
Compound	On top dirty locker	Inside locker	On top cleaner locker	Table in control room (front room)	On top key chest (CR) (back room)	Behind computer screem (CR) (left room)	On top frige (CR) (left room)
Naphthalene	10	3.6	2.8	1.6	7.6	4	7.6
Acenaphthylene	7.2	-	-	-	2	-	-
Acenaphthalene	1.6	-	-	-	-	-	-
Fluorene	15.2	-	2	-	8.8	2.4	5.6
Phenanthrene	48.8	2	4.8	2.8	30	6	17.2
Anthracene	41.2	-	2.4	-	17.2	2.8	9.6
Fluoranthene	69.6	-	4	-	26.8	4	13.6
Pyrene	60	-	3.2	-	22.8	3.2	11.2
Benz[a]anthracene	27.2	-	-	-	11.6	2.4	2.4
Chrysene	60.4	-	-	-	12	-	6.8
Benz[b]fluoranthene	111.6	-	-	-	20.8	3.6	13.2
Benz[k]fluoranthene	6.2	-	-	-	-	-	-
Benzo[a]pyrene	12.4	-	-	-	-	-	-
Benzo[g,h,i]perylene	25.2	-	-	-	-	-	-
Dibenz[a,h]anthracene	19.2	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	3.2	-	-	-	-	-	-
Total PAHs	**519**	**34.6**	**43.6**	**33.4**	**178.6**	**49.2**	**107**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Table S11: Individual PAHs in surface samples at TSP

Surface TSP						
Compound	Behind computer screen (CR)	On power box (CR) back room	Front room plug box (CR)	On top front locker	On top left locker	Inside locker
Naphthalene	2	-	5.2	7.2	4	3.6
Acenaphthylene	2.4	-	2	3.2	2	-
Acenaphthalene	-	-	-	-	-	-
Fluorene	9.2	-	5.2	8.4	6	5.6
Phenanthrene	62	4.4	23.2	28.8	22.4	9.6
Anthracene	37.2	2.4	14	20	14.4	6
Fluoranthene	44.4	4	28	42.8	31.2	8.4
Pyrene	37.2	3.2	23.2	35.6	26.4	6.8
Benz[a]anthracene	28.8	-	10	20.4	14.8	4.8
Chrysene	24	-	12	30	19.2	5.6
Benz[b]fluoranthene	39.2	-	18	45.6	29.6	11.6
Benz[k]fluoranthene	-	-	-	-	-	-
Benzo[a]pyrene	10.4	-	-	6.8	-	-
Benzo[g,h,i]perylene	7.6	-	-	7.2	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-
Indeno[1,2,3-c,d]pyrene	-	-	-	6.4	-	-
Total PAHs	**318**	**40.2**	**159.8**	**272.8**	**189**	**81.8**

– - Values below the detection limit. Values that were below the detection limit were taken as BDL/2.

Chapter 5

Conclusion

Conclusion

The dermal exposure to PAHs of workers in a South African petrochemical factory was determined during the full shift using adhesive dermal patches and during specific short tasks by using dermal wipes. The workers' baseline skin barrier function at the beginning of the shift was also determined.

Previously in occupational hygiene, exposure via inhalation has been considered the most important route for occupational exposure to hazardous chemicals. During the past two decades however, there has been an increased interest in exposure via the dermal exposure route (Kammer *et al.,* 2011).

PAHs are generated by the incomplete combustion of fuels, such as petrol, diesel and coal and are present in complex mixtures such as coal-tars (Yadav *et al.,* 2009). Dermal contact with PAHs can cause acute effects such as skin irritation, oil acne and defatting of the skin (Christopher *et al.,* 2011) and chronic exposure can cause cancer (benzo[a]pyrene and dibenz[a,h]anthracene are classified as Group 1 and Group 2A carcinogens respectively (IARC 2012).

The genotoxic mechanism of action of benzo(a)pyrene involves metabolism to highly reactive species that form covalent adducts to DNA which induces mutations in oncogenes and tumour suppressor genes. Other genotoxic effects include sister chromatid exchange, micronuclei, DNA damage and 8-oxo-deoxyguanosine which contribute to the carcinogenic effect of benzo(a)pyrene and benzo(a)pyrene-containing complex mixtures in exposed humans (IARC 2012).

Complex chemical mixtures in occupational settings are the primary milieu where exposures to PAHs occur and exposure to these mixtures is always a health concern whenever they contain PAHs (Elovaara *et al*., 1995). Occupational PAH exposure is complicated by several factors: PAHs occur mainly in mixtures the composition of which depends on the type of raw material used and the combustion circumstances. They are often adsorbed to solid particles and there are other non-occupational sources of PAHs such as tobacco smoke that can influence exposure. It is, therefore, difficult to compare different studies conducted in the same industry and on different individuals because quantitative as well as qualitative differences in exposure may occur (Bofetta *et al*., 1997). Many factors such as personal hygiene, work practice, equipment, varying weather conditions and other production characteristics can influence the measurement of occupational exposure to PAHs and must be taken into consideration when assessing workers' exposure. Especially day to day

changes in weather conditions and differences in the *modus operandi* of individual workers can cause inter-day and inter-worker variations in exposure. (Deygout *et al*., 2011).

This was also the case in this study. A variation in dermal exposure was seen between workers that performed the same job in the same area. For example, Cleaners 1 and 2 from TSP (Chapter 3) both cleaned the plant at the same time and both wore the same PPE, but their full shift dermal exposures were quite different. Another example is Process controllers 1 and 2 from TSP (Chapter 3) who both experienced approximately the same full shift dermal exposure despite Process controller 2 being exposed to more than three times as much PAHs outside of his clothing than Process controller 1. This difference in dermal exposure was caused because Process controller 2 wore a Tyvek® suit and Process controller 1 only wore a standard overall. There was also a visible difference in the dermal exposure of Truck loader 1 and 2 from TSP (Chapter 3). Inter-individual differences in exposure are caused by a range of factors:

1) *Modus operandi*. The way in which each worker performs his work is unique. For example, Cleaner 3 from SFP (Chapter 3) removed his right glove every few minutes to move his safety goggles into a more comfortable position while he was in a mist or vapour.

2) Personal hygiene. The ways in which the different workers practice personal hygiene differ. Cleaner 3 from SFP wore the same shirt to work three days in a row and some of the workers started work with dirty Tyvek® suits. Only a few of the workers used skin cream to improve the health of their skin.

3) Facilities. The Cleaners' facilities at SFP and TSP were very dirty and different surfaces that were wiped contained carcinogenic PAHs such as benzo[a]pyrene. It is plausible that some of the PAHs measured on the skin of some workers could have originated from dirty clothes and surfaces in the locker rooms of the workers.

4) PPE. The type of PPE worn by the different workers varied. For example, Cleaner 5 from TSP (Chapter 4) wore a powered air purifying respirator that resulted in him experiencing very little neck exposure. Some of the workers did not wear Tyvek® suits and this resulted in higher breakthrough percentages of PAHs through the clothing. The condition of the PPE is also important and the use of expired or damaged PPE can lead to skin contact with the tar. For example, Cleaner 6 from SFP (Chapter 4) had a large tar spot on his right hand that was probably caused by penetration of the tar through the glove and led to substantial dermal exposure. The correct use of the PPE is also important because Mechanical operator 2 from

SFP (Chapter 3) worked with his sleeves rolled up to his forearms as a result of the heat and both his wrists suffered substantial exposure.

5) Day to day tasks. The tasks of some of the workers vary from day to day. For example, the Mechanical operators only work when something needs to be repaired or replaced.

6) Environment. The other activities in the area of the worker often change. For example, one repeat measurement of Truck offloader 2 from SFP (Chapter 4) showed very high concentrations compared to the other repeats. This is because he was downwind from a cleaning activity which caused an increase in exposure.

Every measurement of every worker, therefore, needs to be looked at individually and all the possible contributors need to be taken into account. It is very difficult to accurately determine the source of a worker's dermal exposure to hazardous chemical substances because of variations in the way in which each worker performs his or her job and variations in the way each worker reacts to exposure to chemical substances. Certain assumptions and uncertainties are, therefore, unavoidable when interpreting dermal exposure results (McDougal and Boeniger, 2002).

Dermal exposure to PAHs can occur in two ways: direct contact with contaminated surfaces or equipment and from the settling of airborne particles or vapour on the skin (McClean *et al.,* 2004). In this study, it was clear that exposure through direct contact with tar had a more potent effect on the dermal exposure of workers. In all the wipes in the short term exposure study that contained benzo[a]pyrene, a quantity of tar was wiped as part of the wiping zone. In the full shift exposure study, the patches that contained benzo[a]pyrene and dibenz[a,h]anthracene all had visible marks of tar on them.

Agostini *et al*. (2011) as well as Christopher *et al.* (2011) has stressed the increased risk for dermal exposure in occupations where workers come in direct contact with contaminated surfaces and equipment. Both the short term and the full shift exposure studies confirmed that increased instances of direct contact with the tar will increase dermal exposure to PAHs. Cleaners are often high risk workers because they, by definition, work with dirty surfaces. In both the full shift as well as the short term exposure studies Cleaners were the highest exposed workers. The Slop pit cleaners in the short term study and the SFP Cleaner in the full shift exposure study experienced the most contact with the tar and, therefore, experienced the highest exposures in the two respective studies.

It remains difficult to compare the results from the present study with that of previous studies as there are not any exposure limits or standardised methods of reporting results. The only exposure limits that exist are skin notations that serve as a qualitative guideline to warn against harmful effects as a result of skin absorption and the criteria for awarding these skin notations vary between countries (Bos *et al*., 1998). The determination of safe contact with the skin is not nearly as easy as determining the safe amount of inhalable chemical, as there are almost an infinite number of possible ways in which a worker can have dermal contact with chemicals (i.e. contaminated surfaces, contaminated clothing and via the air) (McDougal and Boeniger, 2002). Therefore, a wide variety of factors add to the difficulty of reporting dermal exposure results. Especially when working with certain chemicals, such as PAHs which dermal absorption can contribute more than 75% of the internal dose, it is very necessary to be able to properly judge the severity of the dermal exposure. Knowing that a chemical might penetrate through the skin is sufficient information to provide a warning that the chemical poses a threat for systemic toxicity and chemicals that triple the biological exposure indexes when the dermal route is present should be assigned a skin notation (McDougal and Boeniger, 2002).

According to the IARC (2012), both coal gasification and coal distillation are classified as group 1 carcinogens. In six studies on mice and two on rabbits, the application of coal-tar from gas works induced a high number of papillomas and carcinomas in both animals (IARC 2010). Chronic dermal exposure of mice to tar condensate that contained several PAHs, in addition to other compounds, produced increased skin papillomas and carcinomas (Mumtaz and George, 1995).

There have been reports of skin tumours among human individuals exposed to mixtures containing PAHs. Human studies have shown that individuals exposed to mixtures of PAHs can develop cancer and that mixtures of carcinogenic PAHs cause skin disorders in humans. For example, regressive verrucae (i.e., warts) were reported following up to 120 applications of 1% benzo[a]pyrene to human skin. Especially in persons with pre-existing skin disorders such as blisters, adverse dermal effects were observed following intermediate benzo[a]pyrene exposure (Mumtaz and George, 1995). Therefore, workers with a disrupted skin barrier function are more susceptible to adverse dermal effects as a result of dermal exposure to PAHs. In this study it was found that TEWL values measured on the palms and wrists of both SFP and TSP workers were higher than that of healthy skin. This indicates that the skin barrier function of these workers is disrupted, which increases the risk of PAHs, such as benzo[a]pyrene, moving through the skin and into the body.

Benzo[a]pyrene is also classified as a group 1 carcinogen and along with dibenz[a,h]anthracene (that is classified as a group 2A carcinogen) they represent the two most carcinogenic PAHs (IARC, 2012). Benzo[a]pyrene is also recognised as a priority pollutant by the environmental protection agency (EPA). In a study by Tsai *et al*. (2001) they used a series of toxic equivalent factors (TEFs) developed by Nisbet and LaGoy in 1992, that awarded a number to each PAH according to their carcinogenic toxicity relative to that of benzo[a]pyrene. Benzo[a]pyrene and dibenz[a,h]anthracene were identified as the most carcinogenic potent of the individual PAHs. In the past, several studies in which benzo[a]pyrene was applied to different strains of mice, benign and malignant skin tumours were observed and diben[a,h]anthracene has also been shown to exhibit significant carcinogenic activity (IARC 2010). As benzo[a]pyrene and dibenzo[a,h]anthracene have been shown to be the most carcinogenic PAHs, workers exposed to them will have the highest risk of developing cancer. These two individual PAHs are the most potent carcinogenic of all the individual PAHs and both have been proven to move through the skin and into the body. Based on this and on the uncertainty surrounding threshold limits for dermal exposures, it is recommended that any detectable amount of benzo[a]pyrene or dibenz[a,h]anthracene on the surface of a worker's skin, irrespective of the anatomical site where it was measured, be considered as an indicator that that particular worker is at risk of adverse health effects due to dermal exposure to PAHs.

Table 1: Workers in the full shift exposure study exposed to benzo[a]pyrene or dibenz[a,h]anthracene on the surface of their skin. The workers are arranged from higher to lower exposures.

Worker	**Area**	**Anatomical area**	**Benzo[a]pyrene**		**Dibenz[a,h]anthracene**	
			Outside concentration ng/cm^2)	**Concentration on skin surface (ng/cm^2)**	**Outside concentration ng/cm^2)**	**Concentration on skin surface (ng/cm^2)**
Process controller 3	SFP	Neck	167.41	57.66	-	-
Cleaner 3	SFP	Right wrist	1187.21	37.20	223.68	-
Cleaner 3	SFP	Left wrist	1187.21	9.30	223.68	-
Cleaner 3	SFP	Neck	1187.21	9.30	223.68	-
Mechanical operator 2	SFP	-	212.98	-	33.95	-
Truck loader 1	TSP	Right wrist	-	9.30	-	-

Table 1 shows the ranking of workers in the full shift exposure study according to exposure to benzo[a]pyrene and dibenz[a,h]anthracene. It shows that the neck of Process controller 3 at SFP was the highest exposed area of any worker in the throughout the full shift study. This was due to tar smudges on his neck. Mechanical operator 2 was not exposed on the surface of his skin but was included in Table 1 because the patch on the outside of his clothing was covered in tar smudges which contained both benzo[a]pyrene and dibenz[a,h]anthracene. The same tar smudges were observed on his arms because he worked with his sleeves rolled up. It is presumed that these smudges also contain both benzo[a]pyrene and dibenz[a,h]anthracene.

Table 2: Workers in the short term exposure study exposed to benzo[a]pyrene or dibenz[a,h]anthracene on the surface of their skin and on the surface of other areas. The workers are arranged from the highest to the lowest exposures.

Worker	**Area**	**Anatomical Area**	**Concentration Benzo[a]pyrene (ng/cm^2)**	**Concentration Dibenz[a,h]anthracene (ng/cm^2)**
Slop pit cleaner 3	TSP	Tar splatter on cheeck	108	15.2
Slop pit cleaner 3	TSP	Neck	72.8	9.6
Slop pit cleaner 2	TSP	Right palm	20.8	-
Slop pit cleaner 2	TSP	Left palm	12.8	-
Cleaner 6	SFP	Right palm	6.2	-
Cleaner 6	SFP	Forearm	3.5	-
Truck loader 3	TSP	Wrist	2.7	-
Surface	SFP	Behind computer screen in control room	10.4	-
Surface	SFP	On top front locker	6.8	-

Table 2 shows the ranking of workers in the short term exposure study according to exposure to benzo[a]pyrene and dibenz[a,h]anthracene. The cheek and the neck of Slop pit cleaner 3 at TSP's was the worst exposed area during 30 minutes of exposure. This was exclusively due to direct contact with tar. Cleaner 6 at SFP had the highest exposure of the permanent workers who perform the same task daily.

Dermal exposure to benzo(a)pyrene was measured for 21.4% (3/14) of workers participating in the full shift exposure study and 57.1% (4/7) of tasks in the short-term task-based exposure study. It is clear from Tables 1 and 2 that Cleaners are the most at risk. They work around contaminated surfaces and come into contact with tar more often than other workers. Some surface in SFP (on top of a dirty locker and behind a computer screen) also contained amounts of benzo[a]pyrene which can easily come in contact with workers' skin.

In terms of exposure areas, SFP workers were generally more exposed than TSP workers. In the full shift exposure study, the four workers that experienced the highest PAH exposures on the outside of their clothing were all SFP workers (Chapter 3). Of all the workers that experienced exposure to benzo[a]pyrene and dibenz[a,h]anthracene either on the surface of their skin or on the outside of their clothing, four were from SFP and only one was from TSP. In the short term exposure study, benzo[a]pyrene and dibenz[a,h]anthracene were only found on SFP surfaces. Cleaning of the slop pit at TSP also produced high exposures to benzo[a]pyrene and dibenz[a,h]anthracene but this activity only takes place two to three times per year. Higher concentrations of benzo[a]pyrene and dibenz[a,h]anthracene are, therefore, present at SFP and these workers are at a higher risk of experiencing dermal exposure to PAHs. As conformation of this increased risk, workers at SFP complained of skin rashes, pimples and itching that started after they started working at SFP.

It can be concluded that workers in the petrochemical plant are exposed to PAHs, originating from the tar and other processes on the plant. The skin barrier function on the palms and wrists of these workers is also disrupted as a result of this exposure. Weak skin barrier function increases the risk of dermal absorption of PAHs such as benzo[a]pyrene and dibenz[a,h]anthracene. These individual PAHs are classified as Group 1 and Group 2A carcinogens respectively. The SFP area poses a higher risk to workers than the TSP area as higher concentrations of benzo[a]pyrene and dibenz[a,h]anthracene were detected in this area. Dermal exposure to benzo[a]pyrene and dibenz[a,h]anthracene increases the risk of developing cancer and any dermal exposure to these compounds will be potentially harmful to the health of workers. More frequent direct contact with tar in the SFP area caused exposure to benzo[a]pyrene and dibenz[a,h]anthracene and Cleaners are especially vulnerable to dermal PAH exposure as they come in contact with tar very often.

The hypothesis at the beginning of this study was that the workers at this petrochemical factory are dermally exposed to PAHs and have a disrupted skin barrier function as a result of this exposure. This hypothesis is accepted with the modification that these workers are exposed to PAHs but not all of them experience the same risk to their health as a result of this exposure. Only some workers are exposed to highly carcinogenic PAHs such as

benzo[a]pyrene and dibenz[a,h]anthracene which increase their risk of developing cancer. The results also show that the workers' palms and wrists have high baseline TEWL values. These are also the highest exposed anatomical areas which suggest that weak skin barrier function is as a result of their exposure.

Recommendations

Toxicity depends on both the external exposure dose and the exposure time (McDougal and Boeniger, 2002). It is, therefore, necessary to reduce either the external exposure dose (through engineering methods or personal protective equipment) or the exposure time (through administrative measures) in order to effectively reduce the exposure to the chemical.

When trying to reduce exposures of workers to hazardous chemicals, it is always the best option to implement engineering controls in order to eliminate the exposure as a whole. In this situation it would be best to try and reduce the number of open sources of tar, in order to reduce direct contact of workers' skin with the tar. There are currently a number of open sources of tar (i.e. loading and unloading of trucks; cleaning with tarry water and maintenance of filters and other equipment), especially in the SFP area. Enclosing these processes will help to reduce direct contact with the tar.

Administrative controls can also be put into place to help reduce the exposure time of individual workers. For example, the Cleaners can work in pairs, where the one Cleaner operates the hose and the other assists him. After a while they can swap places and the other Cleaner can then assist him. This way, one of the workers is not predominantly exposed all of the time.

The sample that contained the highest concentration of benzo[a]pyrene in this study had two clear tar stripes on it and it is evident that all the patches that had direct contact with the tar contained high concentrations of PAHs. Therefore, personal hygiene and education regarding the dangers of PAH-absorption through the skin is of utmost importance. Workers need to understand that if a tar smudge stays on their skin for a whole shift that it can be absorbed systemically and potentially cause cancer. They, therefore, need to clean their hands as soon as possible after they have come in contact with tar because the longer the tar stays on the skin, the longer it has to penetrate through the skin. This includes housekeeping and the way in which workers don and doff their clothes or PPE. Workers

need to ensure that contamination from dirty surfaces and dirty clothes does not get transferred onto their skin or clean clothes.

Personal protective equipment (PPE) can also help to protect against severe dermal exposure. A substantial decrease in urinary 1-hydroxypyrene concentrations was observed in workers working in PAH-contaminated soils after they were made to wear impermeable PVC suits instead of only facemasks (Boogard and van Sittert, 1995). Especially in activities such as cleaning and maintenance where direct contact with chemicals is the primary route of exposure, impermeable PVC suits can help to avoid unnecessary exposure through direct contact with tar. Cleaners often walk through puddles during which the bottom of their trousers gets wet and the tarry water can more easily come into contact with skin. The wearing of gumboots will prevent this. A lot of unnecessary exposure also occurs as a result of damaged gloves or the re-use of dirty Tyvek® suits. Dirty Tyvek® suits must not be used the following day as contaminants may still be able to move from the suit to the skin of the worker. Apart from workers wearing the correct type of PPE, it is also important that they use the PPE correctly. For example, Mechanical operator 2 at SFP rolled up the sleeves of his Tyvek® suit and as a result, experienced high exposure on his wrists. In the short term exposure study, Cleaner 6 from SFP experienced high exposure on his right palm because some tar most probably penetrated through his glove and Cleaner 2 in the full shift study worked with dirty gloves which increased his exposure. PPE that is not used correctly is practically useless. For example, Cleaner 3 at SFP as well as Truck loaders 1 and 2 at TSP in the full shift study, regularly removed one of their gloves in order to move their safety goggles into the correct position. A solution for this problem could be to provide them with safety goggles that fasten behind the head like ski goggles, then the goggles will not constantly move around on the face. Workers will also need to be trained in the correct ways in which to use PPE and when to replace it. A plan must be put into place in order to replace all PPE before it has reached its breakthrough point. The breakthrough time for PAHs through each particular type of PPE must be determined and PPE needs to be replaced as soon it has been used for that particular time period.

As discussed previously, the skin barrier function of both the TSP and the SFP workers is disrupted. Especially the palms and the wrists of the workers showed high values at the beginning of the shift, indicating unhealthy skin. In order to protect the integrity of the skin as a barrier, certain skin care products that accelerate regeneration of the SC will have positive effects to prevent dermal absorption of hazardous chemicals such as PAHs through the skin. At present only a handful of the workers use regular skin cream or Vaseline that does not properly repair the damage done to the skin throughout the shift. Workers can be provided

with skin barrier creams which they can apply to their hands and wrists before, during and after work. In field studies, a reduction in internal exposure was observed in workers who frequently used protective skin creams, while the internal exposure of workers who only wore gloves did not differ from those who did not (Drexler, 2003). The reason for this difference could either be that the cream enhances the regeneration of the physiological barrier or that the workers that apply the cream more often deal with the hazardous chemical substances more cautiously (Drexler, 2003).

As was seen in the short term exposure study, dusty surfaces in both TSP and SFP contain PAHs (including benzo[a]pyrene). Dirty and dusty surfaces in the control and locker rooms at TSP and SFP need to be cleaned on a regular basis in order to decrease contamination of clothes and workers' skin. Especially the Cleaners' locker rooms at SFP are extremely dirty and workers come in contact with these surfaces every day.

Research recommendations

It is recommended that the concentrations PAHs measured in this study be used to estimate the actual absorption of individual PAHs (benzo[a]pyrene and dibenz[a,h]anthracene) through the skin. This will reveal the fate of the chemical after it has been applied to the skin as well as what health risks are associated with what type of exposure (type of exposure is defined by time of exposure, variety of individual PAH and concentration PAH).

A number of studies have shown through dermal, inhalation and biological studies that PAH absorption through the skin can contribute up to 75% of the total PAH load in the body (Van Rooij *et al.,* 1993; McClean *et al*., 2004; Väänänen *et al.,* 2005). It will be ideal if future studies can incorporate all three of these types of sampling in order to more accurately study all aspects of a workers exposure. This will give a holistic view of the exposure and the main route of exposure will be determined more accurately.

The research conditions of this study did not allow for skin barrier function measurements to be taken during or at the end of the shift as no room was available where the environment could be controlled. It is recommended that future studies measure the skin barrier function during and at the end of the shift as this will give an indication of the change in skin barrier function throughout the shift. These measurements must be taken where workers can wait for 10 to 20 minutes in an air conditioned environment. This will cool them down and eliminate contamination of the measurements by sweat.

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Annexure: Dalgard skin questionnaire

The Dalgard questionnaire including translation into Setswana:

During the last week, have you had any of the following complaints?
Mo bekeng e e fetileng, a o kile wa nna le ngwe ya dingongorego tse?

	Yes, a little Ee. Go le gonnye.	**Yes, quite a lot** Ee. Gantsi.	**Yes, very much** Ee. Gantsi thata.	**No** Nnyaa
1. Itchy skin Go babelwa ga letlalo				
2. Dry/sore rash Boswata bo bo omeletseng/botlhoko				
3. Scaly skin Letlalo le le obogang				
4. Itchy rash on your hands Boswata bo bo babelang mo diatleng				
5. Pimples Dipeise				
6. Other rashes on your face Boswata mo sefatlhegong				
7. Warts Diso/dokgoto				
8. Troublesome sweating Go fufulelwa thata				
9. Loss of hair Go wa ga moriri				
10. Other skin problems Mathata a mangwe a letlalo				

If yes, when did the skin problem start? Mark one answer.
Fa karabo ya gago ele ee, bothata jwa letlalo bo simolotse leng? Ka kopo, tshwaya karabo e le ngwe.

During the last week Beke ee fetileng	
During the last month Kgwedi ee fetileng	
1-6 months ago Kgwedi ele ngwe go tse thataro (1-6)	
More than 6 months ago Go feta dikgwedi dile 6 tse di fetileng	