COAL TAR PITCH VOLATILES EXPOSURE IN A PETROCHEMICAL REFINERY PLANT – A TASK BASED EXPOSURE ASSESSMENT

A RESEARCH PROJECT REPORT
BY MICHAEL MAKGATHO
STUDENT NO 0406579M

IN PARTIAL FULFILMENT OF THE REQUIREMENT OF THE DEGREE
MASTER OF PUBLIC HEALTH - OCCUPATIONAL HYGIENE
SCHOOL OF PUBLIC HEALTH
FACULTY OF HEALTH SCIENCES

UNIVERSITY OF THE WITWATERSRAND
February 2008

ABSTRACT

This study describes tripper car operators' exposure to coal tar pitch volatiles at an operation at Coal Distribution Steam Plant that involves the use of coal tar mix to feed as fuel the steam generating boilers. A cross-sectional task-based exposure assessment approached was used. The objectives of this study were to monitor tripper car operators' exposures to coal tar pitch volatiles as benzene soluble fraction and to then compare the measured concentrations with the occupational exposure limit. The general aim of the study was to accumulate data about employee exposure to coal tar pitch volatiles in South African Petrochemical Refineries.

A total of 56 samples was collected and analyzed for coal tar pitch volatiles – benzene soluble fraction. Of the 56 samples, 41 were personal samples collected on the breathing zones of the workers and 15 samples were field blank samples. The method used for the collection of the samples was the United States Department of Labor, Occupational Safety & Health Administration Method 58.

In South Africa the available occupational exposure limit for coal tar pitch volatiles is the time weighted average occupational exposure limit – recommended limit for cyclohexane soluble fraction which is 0.14 mg/m^3. For the evaluation of personal exposure to compare with the occupational exposure limit, the UK Health & Safety Executive Method for the Determination of Hazardous Substances (MDHS) 68 was adopted in the past to monitor workplace air. This method was since withdrawn by the Health & Safety Executive after research conducted by the Health & Safety Laboratory revealed that unacceptable variability were introduced into the method due to the small mass changes involved and the difficulty in accurately weighing the filters before and after the cyclohexane extraction.

Due to the unavailability of a suitable and acceptable method to assess workers' exposure to coal tar pitch volatiles – cyclohexane soluble fraction to compare to the South African occupational exposure limit, the Occupational Safety & Health Administration Method Number 58 was used during this study for the collection of the samples. This is a validated method. This method follows a similar approach as the MDHS 68 however benzene is used instead of cyclohexane during sample extraction.

The Occupational Safety and Health Administration have the permissible exposure limit of 0.2 mg/m^3 for coal tar pitch volatiles – benzene soluble fraction to use when assessing worker exposure. This limit was used during this study for assessing tripper car exposure to coal tar pitch volatiles.

No coal tar pitch volatiles were detected on the samples collected during the study. The results revealed concentrations below detection limit of the test laboratory analytical method. The detection limit used thereof was 0.1 mg per sample. The tripper car operators were therefore exposed to coal tar pitch volatiles at concentrations that complied with the permissible exposure limit 0.2 mg/m^3.

The hypothesis of this study was that the tripper car operators at Coal Distribution Steam Plant are over exposed to coal tar pitch volatiles – benzene soluble fraction. This hypothesis is therefore rejected.

Based on the results derived from this study it is recommended that further research studies be conducted specifically with focus on different methods of exposure assessment to workers exposed to coal tar pitch volatiles in South African Petrochemical Refinery Plants.

Since the method used was limited to the particulate phase of the contaminant exposure, with the gaseous phase of exposure to coal tar pitch volatiles only looked at when the PEL is exceeded. A method that can measure both the gaseous and particulate phase of the contaminant must be investigated.

Acknowledgements

Special acknowledgement is made to the management of Occupational Hygiene Department and Coal Distribution Steam Plant for the funds and the opportunity for me to carry out the study at the area.

I'm also grateful to Prof AC Cantrell for the assistance and direction given.

To many other individuals and companies who have made specific contributions and have provided support, suggestions and constructive criticism, thank you.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW

In this chapter coal tar pitch volatiles (CTPV) are defined and the health effects associated with exposure reviewed. National and international occupational exposure standards are reviewed and methods of monitoring CTPV exposure are presented. Available data relating to CTPV exposure of workers in Petrochemical Refinery operations in South Africa are also reviewed. This chapter ends by stating the general aim, objectives and hypothesis of the study described in this Research Report.

Coal tar is a viscous liquid mixture of hydrocarbon compounds derived from destructive distillation of coal[1]**.** It's a black**,** shiny material that is solid and brittle at low temperatures and liquid at high temperature. It consists of high hydrocarbons such as benzene, toluene, phenol, styrene, cresol, naphthalene, etc. and numerous polycyclic aromatic hydrocarbons, which can become airborne when heated[2]. Polycyclic aromatic hydrocarbons can be divided into two categories, low molecular weight and high molecular weight. They are commonly found adhering to airborne particulate matter and a limited number are reported to be confirmed human carcinogens[3]. Coal tar itself may be subjected to fractional distillation, a process that separates certain groups of the more volatile components from others[1]. The resultant by-product of this is coal tar pitch sludge.

1.1 Review of health hazards associated with coal tar pitch volatiles

Processing of tar in recent years has led to the rising concerns on worker exposure to coal tar pitch volatiles and their component polycyclic aromatic hydrocarbons[3].

Polycyclic aromatic hydrocarbons are highly lipid soluble and are reported to be capable of being absorbed from the lungs, gastrointestinal tract and skin in animals. Coal tar pitch volatiles will have similar behaviour effects as they contain a percentage of polycyclic hydrocarbons[3].

Cancer-causing substances are called carcinogens. During the past decades, there has been a growing awareness of the presence of carcinogenic materials in the environment, both air and water.

The International Agency for Research on Cancer (IARC) is part of the World Health Organization. IARC's mission is to coordinate and conduct research on the causes of human cancer, the mechanisms of carcinogenesis, and to develop scientific strategies for cancer control. The Agency is involved in both epidemiological and laboratory research and disseminates scientific information through publications, meetings, courses, and fellowships.

IARC lists coal tar as a "Group One Carcinogen". "Group One" is the classification for substances known to cause cancer in humans, and includes asbestos and gamma radiation[4,5].

Coal tar pitch materials comprise largely of highly condensed aromatic hydrocarbons, including polycyclic aromatic hydrocarbons. A U.S Department of Health and Human Services report issued in August 1995 titled "Toxicological Profile for Polycyclic Aromatic Hydrocarbons" found that:

- individuals exposed by breathing or skin contact for long periods to mixtures that contain PAHs and other compounds can develop cancer.

- Adverse non-cancer respiratory effects, including bloody vomit, breathing problems, chest pains, chest and throat irritation, and abnormalities in chest X-rays have been reported in humans exposed PAHs
- The skin is susceptible to PAH-induced toxicity in both humans and animals
- Workers exposed to substances that contain PAHs experienced chronic dermatitis and hyperkeratosis.
- The PAH benzo(a)pyrene has been shown to markedly inhibit the immune system, especially T-cell dependent antibody production by lymphocytes
- There is potential for adverse reproductive effects to occur in humans exposed to benzo(a)pyrene in the workplace or at hazardous waste sites[6].

Major routes of coal tar pitch volatile exposure are dermal and inhalational. Diffuse erythema of exposed skin, with the sensation of burning and pruritus, may be temporarily disabling. Areas of folliculitis with comedones are common. Phototoxic keratoconjunctivitis occurs among roofers with coal tar pitch exposure. Keratoacanthomas (pitch warts) occur after prolonged exposure; some of these may develop into squamous cell carcinomas. Malignant skin lesions observed in coal tar pitch volatiles exposed workers are primarily squamous cell carcinomas, with only 2.5 % of malignant lesions being basal cell carcinomas in one series of 3,700 cases. A survey of pitch workers identified keratotic papillomas among 10 %, while more than 90 % of the same group had some form of acne form lesion[7].

Epidemiological evidence suggests that workers intimately exposed to coal tar pitch volatiles are at risk of cancer at many sites. These include cancer of the respiratory tract, kidney, bladder, and skin[8]. Components of coal tar pitch volatiles produce cutaneous photosensitization, skin eruptions that are limited to areas exposed to the sun or ultraviolet light. Coal tar may be associated with benzene, an agent suspected of causing leukemia and known to cause aplastic anemia[9]. Diffuse erythema of exposed skin, with the sensation of burning and pruritus, may be temporarily disabling.

Studies of coke oven workers have shown increased risk of mortality from cancer of the lung, trachea and bronchus; cancer of the kidney; cancer of the prostate; and cancer of all sites combined. In animals, extracts and condensates of coke oven emissions were found to be carcinogenic in both inhalation studies and skin-painting bioassys. The mutagenicity of whole extracts and condensates, as well as their individual components, provides supportive evidence for carcinogenicity[10].

Chronic exposure to pitch dust has been found to cause deep staining of the cornea in the palpebral fissure, conjunctival discoloration and irritation, and deformities of the lower lid. In one case a peripheral, brownish annular discoloration of the cornea was found to be associated with subepithelial pigmented granules[11].

The skin of the face and back of the neck is most frequently affected and presents erythema, burning and itching sometimes accompanied by desquamation. The eyes may suffer from blepharoconjunctivitis sometimes combined with superficial, punctatekeratitis. Signs and symptoms appear rapidly and may be intensified by exposure to the weather; ultraviolet radiation in sunlight increase pruritus and burning and often leads to photophobia; wind may have similar effects. Symptoms usually disappear within 3-5 days of removal from exposure, although eye lesions may persist for several months. Benign neoplasms may take the form of papillomata, usually found on the eyelids and area around eyes[12].

1.2 Review of occupational exposure standards and methods

Occupational exposure limits exist to serve one main purpose: protect workers from excessive exposure to toxic chemicals in the workplace. They are designed for healthy adults, usually for exposure duration of a day's work shift of 8 hours. They are not meant to be used for protection of the public, since the general public includes sensitive groups such as the very young and very old, people with respiratory diseases and other illnesses, and people who are hypersensitive to some chemicals. Occupational exposure limits are also not designed to compare toxicity of chemicals, or to be the fine line between "safe" and "unsafe." This section will briefly review the main occupational exposure limits[13].

Countries in the world have occupational exposure limits for toxic chemicals and below are some of the well known occupational exposure limits.

1.2.1 IDLH (Immediately Dangerous to Life and Health)

Defined as conditions that pose immediate danger to life or health, or conditions that pose a threat of severe exposure. IDLH limits are created mainly to assist in making decisions regarding respirator use: above the IDLH only supplied air respirators should be used, below the IDLH, air purifying respirators may be used, if appropriate. Two factors were considered when establishing the IDLH limits:

1. Workers must be able to escape such environment without suffering permanent health damage.
2. Workers must be able to escape without severe eye or respiratory tract irritation or other conditions that might impair their escape.

Until the last revision in 1994, exposure duration of 30 minutes was associated with the IDLH. This is no longer the case. The current definition has no exposure duration associated with it. Workers should not be in an IDLH environment for any length of time unless they are equipped and protected to be in that environment. IDLH values were determined based on animal and human data[13].

1.2.2 TWA (Time-Weighted Average)

Unless otherwise defined, TWA is the airborne concentration of contaminants over an 8-hour period. It is determined by sampling the breathing zone of the worker for 8 hours. Mathematically, it is expressed as follows when a series of successive samples has been taken:

$$TWA = \sum_i (C_i * t_i) / \sum t_i$$

where t_i is the period of time during which one sample is taken, and C_i is the average concentration over time period t_i.

To determine the level of exposure, the TWA reading is compared with a standard such as the threshold limit value (TLV; described below) or permissible exposure limit (PEL). If the reading exceeds the standard, overexposure occurred[13].

1.2.3 STEL (Short-Term Exposure Limit)

It is a 15-minute TWA concentration that may not be exceeded, even if the 8-hour TWA is within the standard. TWA-STEL are given for contaminants for which short-term hazards are known. For the rest, an excursion factor of 3 often has been used: STEL should not exceed 3 times the TWA limit. STEL concentrations also may not occur more than 4 times in an 8 hour workday with at least 60 minutes between excursions.

1.2.4 Ceiling Limit

It is that concentration that should not be exceeded at any time. Note that both TWA and STEL permit limited excursion if, in the end, the average is below the exposure limit. The ceiling value, however, may not be exceeded at any given time. Figure 1 describes these terms. Note that excursions above the TWA line are compensated by periods of low exposure. The ceiling value is not exceeded[13].

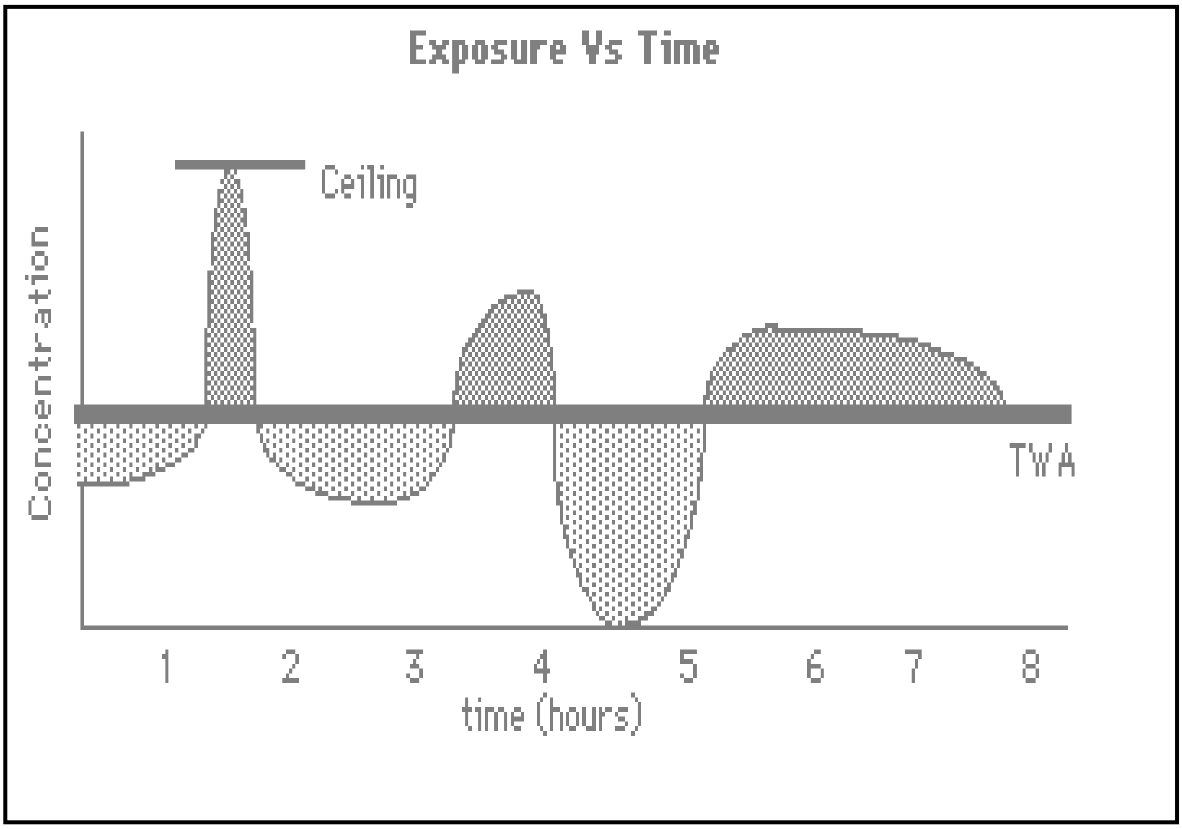

Fig 1: Concentration during an 8-hour day at a hypothetical workplace. During this day, the TLV and ceiling values were not exceeded: excursions of concentration above the TWA line were balanced out by periods when concentrations were below the line, and while the ceiling value was reached, it was never exceeded[13].

1.2.5 TLV (Threshold Limit Value)

It is an exposure standard set by the technical committee of the American Conference of Governmental Industrial Hygienist (ACGIH). This committee, with the aid of unpaid consultants (mostly from private industry), meets regularly to update existing values and set new ones. The TLVs are published annually in a booklet containing exposure guidelines for many commonly used substances. The guidelines are based on available animal and human exposure studies, epidemiological evidence, modeling and anecdotal reports. The rationale for setting the TLVs is given in a publication called "Documentation of the TLVs." The ACGIH committee is independent and flexible, can incorporate new data rapidly, and is relatively free of bureaucratic constrains that slow down official government agencies. It is important to remember that the TLVs are recommended values, not legal limits. They do not guarantee protection to all workers and are not intended to be used for community exposure. They are not the fine line between safe and unsafe; rather, TLVs are values that should not be exceeded. The goal is to minimize workers' exposure to hazardous concentrations as much as possible[13].

1.2.6 REL (Recommended Exposure Limits)

These are those limits set by the National Institute for Occupational Safety and Health (NIOSH) which is part of the U.S Department of Health and Human Services. NIOSH scientists recommend exposure limits to OSHA, based on animal and human studies. NIOSH RELs are often more conservative than the TLV, and NIOSH's consideration of available research and studies is regarded as thorough. In addition, NIOSH publishes criteria documents that include the data related to each standard, as well as sampling techniques and control measures[13].

1.2.7 PEL (Permissible Exposure Limits)

These limits are set by the U.S Occupational Safety and Health Administration (OSHA) and are the law of the land in the United States. Workers' exposure may not exceed these standards and OSHA has the power to warn, cite, and fine violators. The OSHA Act required OSHA to set standards that will provide safe working conditions, but required it to set its permanent standard by negotiation and consensus. As a result, only about 25 permanent standards have been set since 1973[13].

To protect workers in the meantime, OSHA was allowed to adopt existing standards or develop Emergency Temporary Standards (ETS). OSHA adopted the ACGIH TLV as the interim standard, giving legal status to what was meant to serve as recommended limits. The permanent standards are thorough and reflect the extensive effort invested in their preparation. They include action levels that are typically half the TWA exposure limits. When the action limit is exceeded, several steps must be taken such as medical monitoring, air sampling, and control measures. Each permanent standard includes recommendations for air sampling procedures, regulations for record keeping, engineering control methods, labeling and warning, and other pertinent regulations. The PELs are published in 29 Code of Federal Regulation 1910.1000[13].

In South Africa the Chief Inspector, on the recommendation of the Advisory Council for Occupational Health and Safety, sets "Occupational Exposure Limits" or concentrations of substances in the air at or below which exposure control is considered to be adequate.

These occupational exposure limits are listed in the Occupational Health and Safety Act, (Act 85 of 1993) - Hazardous Chemical Substances Regulations (1995) Tables 1 and 2.

The difference between occupational exposure limits in Tables 1 and 2 in the Hazardous Chemical Substances Regulations (1995) is that in Table 1, hazardous chemical substances with Occupational Exposure Limits – Control Limits (OEL-CL) are tabulated whilst in Table 2 hazardous chemical substances with Occupational Exposure Limits – Recommended Limits (OEL-RL) are located. An OEL-CL is the maximum concentration of an airborne substance, averaged over a reference period, to which employees may be exposed by inhalation under any circumstances. An OEL-RL is the concentration of an airborne substance, averaged over a reference period, at which, according to current knowledge, there is no evidence that it is likely to be injurious to employees if they are exposed by inhalation, day after day, to that concentration[14].

A fundamental requirement of the Hazardous Chemical Substances Regulations is that the exposure of employees to such hazardous substances should be prevented, or, where this is not reasonably practicable, adequately controlled[14]. Exposure to harmful materials can occur by inhalation, by ingestion or by absorption through the skin but inhalation is usually the main route of entry into the body.

Internationally the exposure standard for most jurisdictions for coal tar pitch volatiles is 0.2 mg/m^3 for an eight-hour exposure such jurisdictions includes British Columbia Workers' Compensation Board – Occupational Health and Safety Regulations, Alberta Workplace Health and Safety – Chemical Hazards Regulation, Saskatchewan Labour – occupational Health and Safety Regulations, Northwest Territories – General Safety Regulations etc[3]. The American Conference of Governmental Industrial Hygienists (ACGIH) has an 8h threshold limit value of 0.2 mg/m^3 as benzene soluble aerosol[15].

In South Africa the Department of Labour (DoL) adopted the United Kingdom Health and Safety Executive occupational exposure limit for coal tar pitch volatile as cyclohexane soluble fraction (CTPV-CSF) which is the time weighted average occupational exposure limit - recommended limit of 0.14 mg/m^3. Although IARC has classified CTPVs as human carcinogen, the occupational exposure limit in the Hazardous Chemical Substances Regulations has since not be reviewed nor updated in cognizance of the latest information available regarding coal tar pitch volatiles effects to health[14].

To assess occupational exposures, CTPV-CFS was assessed by measuring the cyclohexane soluble matter that is extracted from inhalable particulates, collected on filters, as described in Coal Tar Pitch Volatiles: Measurement of particulates and cyclohexane soluble material in workplace air, Laboratory method using filters and gravimetric estimation, Method for the Determination of Hazardous Substance (MDHS) Number 68.This method was adopted from the United Kingdom Health & Safety Executive, Methods for the Determination of Hazardous Substances[16].

However, the Health & Safety Executive has since withdrawn this method, because of seen unacceptable variability introduced into the method due to the small mass changes involved and the difficulty in accurately weighing the filters before and after the cyclohexane extraction[17]. The Health & Safety Executive in an effort to improve the quality of the results arrived at using this method, contracted the Health & Safety Laboratory to conduct research into establishing an improved method for the determination of coal tar pitch volatiles in air. The aim of the study was to review the procedure set out in MDHS 68 and to establish an analytical method with greater sensitivity and accuracy than that described in MDHS 68[17]. Therefore, for the South African occupational exposure limit for CTPV-CSF, no method was available that one can use to be able to assess exposure to compare with the standard.

The outcome of the HSL study mentioned resulted in the rejection of the then MDHS 68 analytical procedure for measuring coal tar pitch volatiles. During the study other methods such as UV analysis and evaporative light scattering detection were also evaluated and rejected[17].

Health & Safety Laboratory proposed that the way forward to assess exposure to CTPV was to measure pyrene, as a marker, or those individual polycyclic aromatic hydrocarbons, chosen for their carcinogenicity, should be quantified as an indication of exposure[17].

Although MDHS Number 68 was recommended by DoL for the assessment of workers' exposure to CTPV, the DoL does not require, or mandate, the use of a particular sampling method. Rather, one must insure that the method to be used meet specific criteria set forth for the accuracy and precision of sampling and analytical methods. The assessor is therefore obligated to select a method that meets these criteria, relative to their specific sampling conditions. Typically, these criteria for sampling at the permissible exposure limit must be within approximately 25% of the true value, at a 95% confidence level. Alternative methods, with supporting validation data to demonstrate the accuracy and precision of the methods, are acceptable for compliance monitoring[3].

A variety of sample collection and analytical methods exists in the literature for the determination of coal tar pitch volatiles. The most common sampling method employed for coal tar pitch volatiles is the use of a sampling pump to draw air through a 37 mm diameter glass fibre or polytetrafluoroethylene filter. Coal tar pitch volatiles are most commonly sampled using either open or closed faced 37 mm cassette. These types of sampling methods are mainly designed to collect only the particulate phase of the fume generated.

In the collection of coal tar pitch volatiles samples there are various international governmental and non-governmental agencies that have a list of chemical monitoring methods. Such institutions include OHSA, HSE and NIOSH[3].

For monitoring CTPVs NIOSH has a Manual of Analytical Methods with methods such as Method 5042: Benzene-soluble fraction and total particulate, and method 5515: polynuclear aromatic hydrocarbons by gas chromatography, capillary column, FID. These methods mentioned above are used for the collection and analysis of the samples to compare with a threshold value. There are as yet only partially evaluated hence were not utilized in this study. Partially evaluated method implies a sampling and analytical procedure for which an in-depth evaluation has not been performed. The evaluation of these methods is often performed rapidly in order to meet the immediate need of field personnel when established methodology does not exist[18].

The U.S Department of Labor, Occupational Safety and Health Administration (OSHA), has a permissible exposure limit for coal tar pitch volatiles, as a benzene soluble fraction also of 0.2 mg/m^3 [6]. There is also an OSHA evaluated method number 58, for the sampling and analysis of the samples that is evaluated. An evaluated method means the sampling and analytical methodology that has been thoroughly evaluated according to the evaluation guidelines as evaluated by the Methods Development Team, Industrial Hygiene Chemistry Division, OSHA Salt Lake Technical Center. This method requires that air samples be collected by drawing known amounts of air through cassettes containing glass fiber filters (GFF). The filters are then analyzed by extracting with benzene and gravimetrically determining the benzene-soluble fraction (BSF). If the BSF exceeds the appropriate permissible exposure limit (PEL), then the sample is analyzed by high performance liquid chromatography (HPLC) with a fluorescence (μL) or ultraviolet (UV) detector to determine the presence of selected polynuclear aromatic hydrocarbons (PAHs) [9].

The OSHA method number 58 was used during this study. The reason the method was selected was due to the ease of access to sampling media i.e. glass fiber filter, availability of sampling equipment and access to an accredited analytical laboratory after it was establish and confirmed with the laboratory that it has necessary equipment and competency capable of analyzing the samples as per specifications of the method. The South African occupational exposure limit of 0.14 mg/m^3 for CTPVs is lower than the OSHA permissible exposure limit of 0.2 mg/m^3. However the OSHA PEL was used to assess worker's exposure due to the availability of the comprehensive sampling method of which the results derived from it can be compared to the PEL.

1.3 Review of exposure data in South Africa

Currently limited data and in some spheres no data is available relating to exposure to coal tar pitch volatiles in petrochemical refinery operations. The exposure data that is available in most cases is for workers working in aluminum smelters, iron and steel workers, expansion joint making operations, coke production, asphalt industry etc. It is widely documented that coal tar pitch volatiles are carcinogenic. Petrochemical refineries where coal is liquefied to produce synthetic petrochemical products as well as heating of coal tar or coal tar pitch takes place in such settings it would not come as a surprise that coal tar pitch volatiles emissions are found. These emissions as they enter the workers' breathing space may be inhaled or come in contact with the skin, exposing the workers to possible short or long term health effects.

Studies have shown that the major health effects resulting from long-term repeated exposure to coal tar pitch volatiles (CTPV) are cancers of the lung, kidney, and skin[19]. The serious nature of the effects of exposure to coal tar pitch volatiles resulted in the need to quantify the extent of employee exposure in order to protect their health from ill effects associated with exposure. This brought about the interest to conduct this study. The general aim of this study was to create a coal tar pitch volatiles exposure database for employees working in petrochemical refineries, mainly looking at the section of the refinery were coal tar is handled by operations personnel. This study was restricted to assessment of inhalational exposure of the workers, with dermal exposure excluded.

1.4 Study Objectives

1.4.1 To measure airborne exposure of tripper car operators to coal tar pitch volatiles, as benzene soluble fraction, at a petrochemical refinery plant.

1.4.2 To determine whether tripper car operators' exposures to coal tar pitch volatiles, as benzene soluble fraction, exceed the Occupational Safety & Health Administration permissible exposure limit of 0.2 mg/m^3.

1.5 Statement of Hypothesis

Tripper car operators' exposure to coal tar pitch volatiles, as benzene soluble fraction, at the Coal Distribution Steam Plant exceeds the 8-hour time weighted average permissible exposure limit of 0.2 mg/m^3.

CHAPTER 2: METHODS

In this chapter the type of study design is described and explained, the workplace where the study was carried out is discussed, sampling strategy is outlined and data analysis method and data quality method used are explained. The protocol was submitted to the University of the Witwatersrand Ethics Committee where it gained approval.

2.1 Type of study and general design

This study was conducted as a cross-sectional exposure assessment survey. The study took the form of a compliance survey taken over a number of days to be able to have statistical adequate data. The survey was conducted at a Petrochemical Refinery Coal Distribution Steam Plant when the tripper car operators carried out their normal plant operating activities. Such activities included manning and controlling the tripper car, conducting observations and inspections on the plant which involved noting and reporting of any machinery defects on and around the tripper cars that may affect their usage as well as ensuring the plant is cleaned.

2.2 Scope of the study, sample selection and size, unit of analysis and observation, selection criteria

This study was performed at the Coal Distribution Steam Plant of the refinery. This workplace was selected as it was convenient and access into the plant already existed. In addition, it is the only plant in the refinery that workers in their operations include the use of coal tar sludge. Regulation 6 of the Hazardous Chemical Substances Regulations requires that where inhalation of a hazardous chemical substance is concerned, an employer shall ensure that there is a measurement programme of the airborne concentrations of the hazardous chemical substance to which an employee is exposed[14].

In compliance to Regulation 6, a monitoring programme for monitoring hazardous chemical substances has been established and implemented at the Coal Distribution Steam Plant. The scope of the monitoring programme was increased with approval from the Occupational Hygiene Department to accommodate this study, in terms of time allocation and the utilization of the department's resources such as sampling equipment, transportation, stationary etc.

The other factor that was an influence in selecting the workplace was that it is the only workplace at which fine coal is mixed with tar sludge and used as fuel to feed into the boilers for steam generation as well as the fact that once the coal tar blend is deposited into the open boiler bunker, and fugitive emissions from the blend continue to be emitted into the work environment of the workers until such time the blend is fed into the boiler.

The Coal Distribution Steam Plant is positioned at the top floor of the Steam Generating Plant where the bunkers or large bins feed fuel to the steam generating boilers. The plant building is constructed of corrugated iron panels. On the southern walls of the building blower fans are installed to encourage general dilution ventilation in the building.

The plant receives feed which is a blend of fine coal and coal tar sludge. Coal tar sludge, or tar decanter sludge, is the residue remaining from raw tar filtration after fine and coarse solids are removed. The sludge is obtained on a daily basis from the Tar Filtration Plant. The sludge is transported by tipper trucks from Tar Filtration Plant to the Mixing Plant. Blending occurs in an open concrete-lined pit used to store the sludge and is conducted through out the day. A screw conveyor, located in this area, is used to mix and convey the sludge-laden coal to the conveyor belts which transports it to the Coal Distribution Steam Plant[20] (Fig 2).

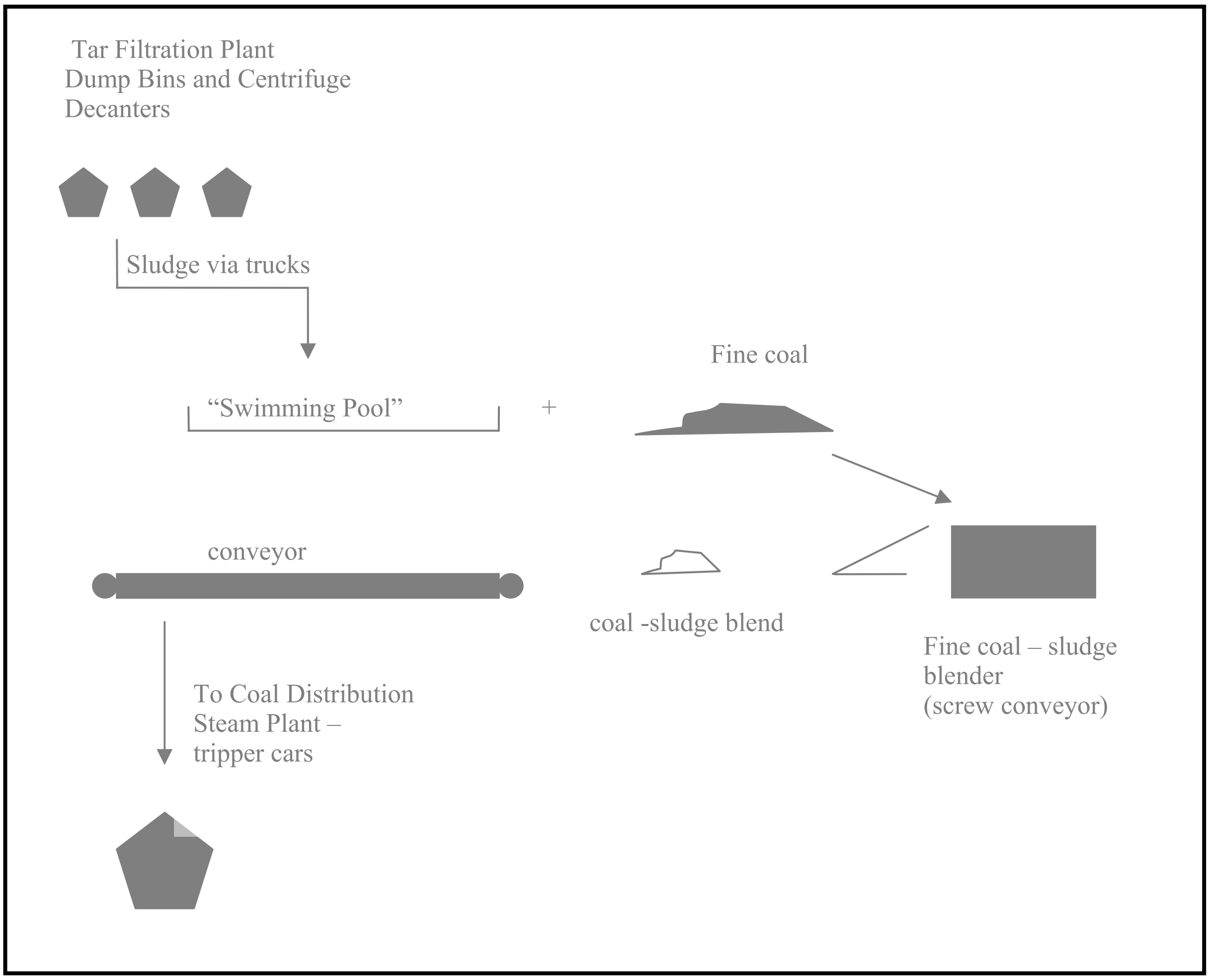

Fig 2: Coal – sludge process

At the Coal Distribution Steam Plant the sludge-laden coal is taken as the plant feed. At the discharging end of the conveyor belts from the Mixing Plant, there are trippers. Tripper cars are mechanical chutes used to position and empty the contents of the conveyor belts into the boiler bunkers. There are two tripper cars connected to each of two conveyor belts. The two conveyor belts run parallel to each other in the plant. Plate 1 and 2 give details of the plant. However, there are only two tripper cars operated at a time on the plant and as a result only two operators per 8 hours shift are available at any one time. On Mondays, however, there is an exception, 2 shifts of 12 hours are worked. From Tuesday to Sunday, three 8 hour shifts are worked. The study population included all the tripper car operators working at the Coal Distribution Steam on all the randomly selected days.

Plate 1: Tripper car

Plate 2: Tripper car operation

2.3 Sampling

2.3.1 Sampling equipment

The instrumentation that was used during the preparation and collection of personal breathing zone samples during the study was as follows:

- Sampling pumps, i.e. Gillian® constant flow sampling pumps, model 17G9 Gilair personal air sampler;
- High accuracy bubble flow calibration meter, make Sensidyne®, model Gilibrator™ primary 2 flow calibrator;
- Small flat screw driver to adjust calibration setting on the Gilair pumps;
- Sampling head, i.e. three-piece filter holding cassette fitted with a support pad and glass fiber filter for pump calibration (refer to Fig 3).

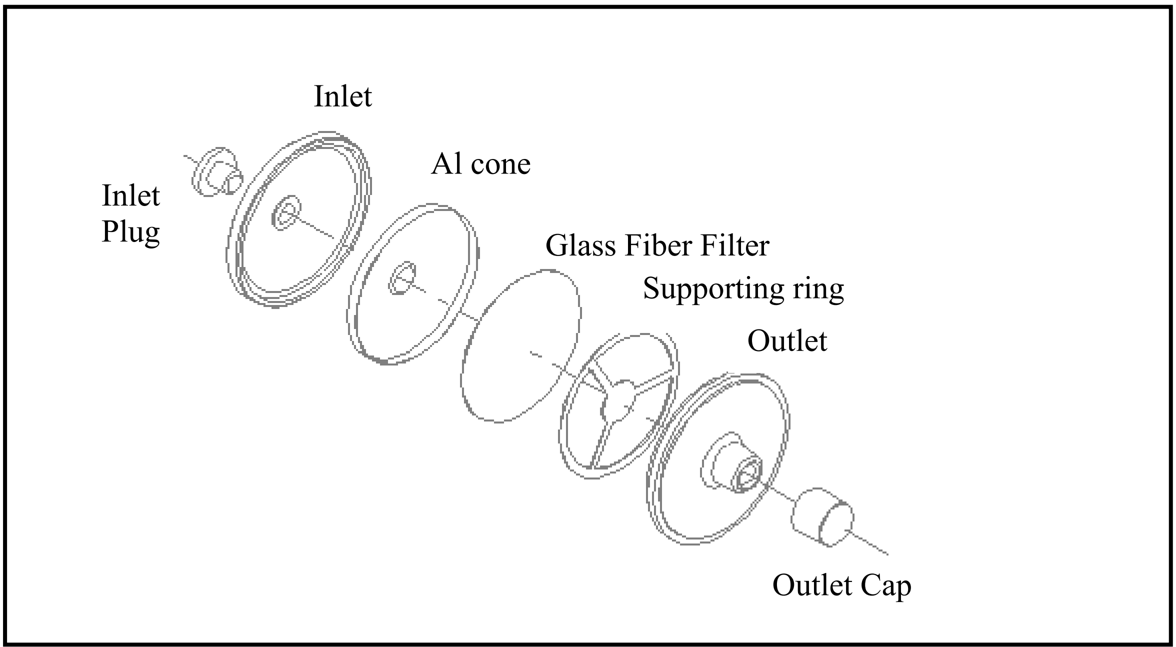

Fig 3: Three-piece cassette containing filter

- Tygon tubing to connect the sample cassette with the sampling pumps, the tubing was cut into pieces of 1.2 meters. The pieces were used to assemble the sampling train (refer to plate 3) together;

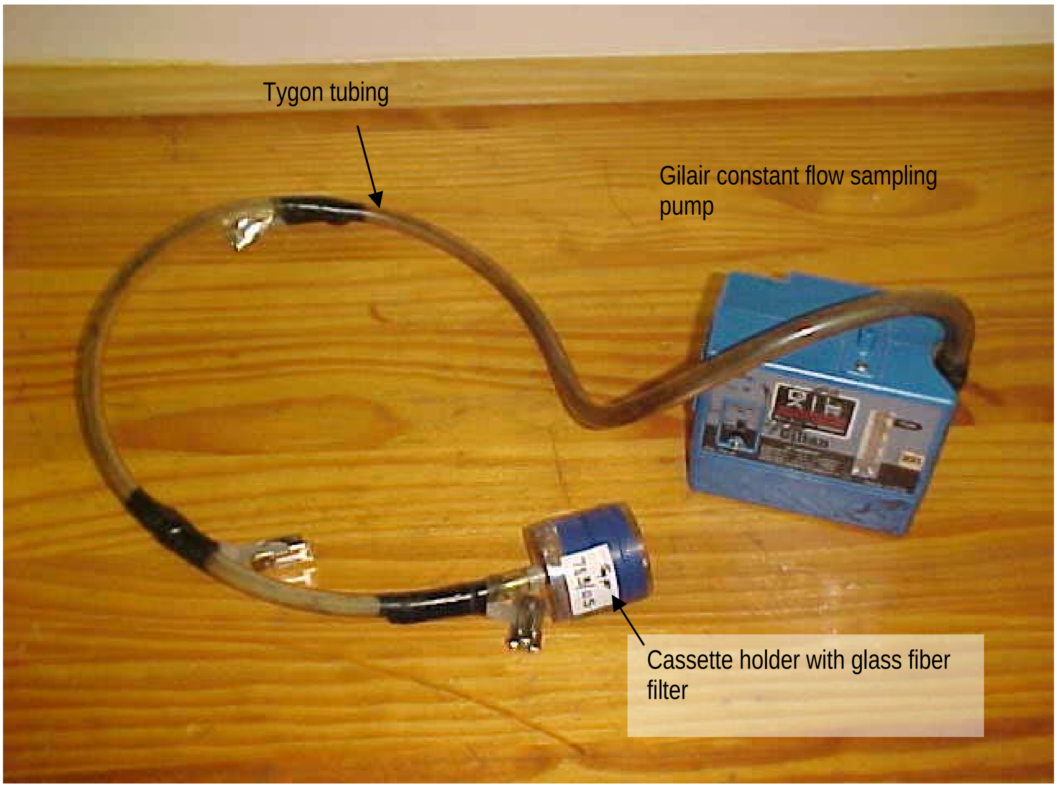

Plate 3: Sampling train

- Cooler box with ice packs to put the samples after collection prior storing them in the refrigerator;
- Refrigerator set at a temperature of approximately 4°C;
- Carry case to transport sample cassettes between site and laboratory.

2.3.2 Pump calibration

The pumps were calibrated with a secondary calibrator before monitoring at the plant. Secondary calibration is that form of calibration which is not based on natural physical measurements. It involves calibrating the pump flow against another flow meter that has been calibrated itself on a primary standard.

The procedure followed is detailed below.

2.3.2.1 Sampling train pre- and post-calibration:

- On the inlet of the sampling cassette, a tube was connected; this tube was then connected on to the high accuracy bubble flow calibration meter.
- The high accuracy bubble flow calibration meter is an electronic flow bubble meter. It has an electronic keypad and a small burette with soap at the base. It works on the principle that when the sampling train to be calibrated draws the air in the burette, electronically the flow rate of the pump is determined.
- If the flow is not the one required as per sampling method, there is an adjustment screw on the sampling pump to set the desired level, in this case 2.0 litres per minute.
- All the pumps that were used during the study were calibrated before the sampling was done and after the sampling completion, they were checked again.
- To ensure reliability of the results a deviation of no more than 5 percent between the pre-sample collection and post-sampling collection flow rate was allowed. During the study none of the pumps showed deviations. Had this occurred, the samples collected with such pumps would have been discarded and another set collected[21].
- The sampling pumps were calibrated at a recommended sampling rate of 2 l/min as per OSHA Method 58.

2.4 Sampling strategy

The Coal Distribution Steam Plant is building constructed of corrugated iron panels with conditions inside the plant taken to be constant through out the year.

No variability in ambient meteorological conditions that could affect the results of the study was expected hence none were taken into account during the study. However, the meteorological conditions that prevailed on the days the samples were collected were noted (refer to Table 3) for the sake of completeness of the data collected on the day. In the light of the result obtained the ambient meteorological conditions were not discussed in this report as an assumption was made that they were the same through the duration of the study and if there was any variability it would not have been significant so far as to could have affected the attained results in a negative manner.

The samples were collected by a registered and certified occupational hygiene technologist certified by the South African Institute of Occupational Hygiene (SAIOH). SAIOH is a member of the International Occupational Hygiene Association (IOHA) the international voice of the occupational hygiene profession. IOHA is officially recognized as a non-governmental organization by both the International Labour Organisation (ILO) and the World Health Organisation (WHO)[22]. While fitting the personal samplers on the workers, their role in doing the study was given and they were also informed that it was voluntary for them to take part in the study as well as that they were not going to be harmed in any way. It was explained that the only perceived negative impact might be the bulkiness of the sampling train that had to be worn on their persons for the duration of their shifts.

The number of samples taken ensured that sufficient data could be gathered and that the data collected would be adequate in terms of ensuring that one would be able to draw conclusions about the extend to which the worker have been exposed to coal tar pitch volatiles.

Sampling is known in most cases to be the largest source of error during the performance of research studies. This is said to be caused by many factors. Such factors include but are not limited to:

Environmental factors such as variability of temperature, relative humidity, barometric pressure and contaminant concentration;

Sample collection factors such as variability in sampler volumetric flow, sampling time and collection efficiency;

Human factors such as personnel being monitored intentionally or unintentionally interfering with sample collection and contamination of sampling materials[23].

To minimize sources of variability and errors during the sampling process, and to ensure that reliable data was obtained for the study, glass fiber filters that were used as samplers. They were bought pre-prepared from Ergosaf Occupational and Environmental Services cc. which is an Approved Inspection Authority (AIA) approved by the Chief Inspector of the South African Department of Labour at their gravimetric laboratory. The pre-prepared samplers were delivered in closed three-piece cassettes. The openings were closed with blue caps to indicate that they were not used and red plugs were put at the bottom of the cassette only to be used once the samples were drawn through the filter to indicate that the filter has been used. These were referred to as sampling heads. A walkthrough inspection was conducted at the premises of Ergosaf to observe the laboratory conditions, quality control system in place and to scrutinize the laboratory facility were the sampling heads were prepared. Upon receipt of the sampling heads from Ergosaf, arrangements were made for a temporary location to store them prior to use. The temporary location was arranged in an effort to ensure that the received samplers do not get contaminated before sampling is carried out. In the temporary storage room this was achieved by not removing the plugs on the filter cassettes holders, in addition access into the storage area was controlled.

Personal sampling was used during this study. In order to overcome the practical difficulties associated with measurements at the entrance of the nose, by common practice the sampler is located at an unspecified distance in front of the face or by attaching it at the worker's shirt collar or lapel area referred to commonly as breathing zone. Thus personal breathing zone samples were collected during the study. The breathing zone is an area within 15 cm of the nose from which air is inhaled. Blank control samples were also collected throughout the shift[24]. To counter any variability that could be as a result of human factors, participants in the study were informed of the purpose of the study, its aim and objectives. Furthermore, the participants were put under observation when they were busy performing their tasks.

The results of exposure sampling were intended for eventual comparison with some form of hygiene standard such as Occupational Exposure Limits, Threshold Limit Values of Permissible Exposure Limits. These standards have been developed usually from dose-effect relationship where the dose is the estimated body burden of the contaminant accumulated over a short time for a substance producing acute effects or over a long period for a substance giving rise to chronic effects. In order to predict the biological effects of exposure to a fast acting contaminant, it is necessary to sample for brief periods of time so as to detect the transient concentration peaks. Conversely if airborne substance only produces its effects in a long term after a build-up of a large body burden, then a series of measurements of atmospheric concentrations carried out over an extended time period will be appropriate. In this case coal tar pitch volatiles are said to produce long term effects[25]. In terms of sampling full period single samples were collected. This involves taking of a single sample for full period of standard. The standard used in during the study is for a continuous 8 hour shift.

The Coal Distribution Steam Plant is a small work area with only two workers operating the tripper cars at any given time during normal plant operation. In order to get sufficient results to present in this study, repeated monitoring had to be done. At the inception of the study a decision was taken to collect samples over five randomly selected days. To increase the reliability of the results obtained through the study an additional four days of sampling was added to the original five days planned for at the beginning of the study. Ultimately a total of 56 samples were collected to complete the study. These samples were collected on all the tripper operators over three shifts per day on five days. Sampling days were selected randomly. This selection was achieved by drawing the days out of a hat. The dates from January 1st to May 30th were written on a piece of paper and put into a hat from which five pieces were drawn and the dates written on them taken as the dates the surveys were to be carried out on.

On the day of sampling, the sample heads were processed by number tagging before going to working area. Once there, a field sheet was completed whilst putting the sampler on the workers. The information put on the field sheet (refer to Annexure I) included date, the location of the worker, instrument number (i.e. pump and sample number), type of sample (i.e. personal or strategic sample), sample type, pre-sampling flow rate, observations and sampling strategy as well as sampling time. The collected samples were thereafter stored in a refrigerator at approximately 4 ºC. Once the last set of samples on the last shift of the day in question was number tagged, the samples were dispatched to the analytical laboratory (Protechnik Laboratories in Centurion, Pretoria) by car.

The study was conducted on the period January to May 2006. The samples were collected during normal plant operation. For completeness meteorological conditions that prevailed at the time of monitoring were noted and recorded.

2.5 Sampling collection

Taking samples involves various activities from the assembling of sampling instruments to the transportation of the samples for chemical analysis. Quality is an integral and vital component of any sampling and analysis. The purpose of quality assurance and quality control procedures is to ensure that data collected represents actual conditions at the site for the time of sampling. Effective quality procedures are essential to ensure the validity of data and ultimately the decision. In scientific measurements, there are three main attributes that describe the quality of the resulting information: precision, bias, and accuracy. Precision is a measure of the degree of agreement among replicate analyses of a sample, usually expressed as the standard deviation, bias is the consistent deviation of measured values from the true value, caused by systematic errors in procedure and accuracy is a combination of bias and precision of an analytical procedure, which reflects the closeness of a measured value to a true value[23].

During this study a written and validated method was used to ensure quality and reliability of the results obtained. This was Occupational Health and Safety Administration Method Number 58 for CTPV, Coke Oven Emissions, and selected polynuclear aromatic hydrocarbons[9].

The sampling heads were attached to the lapels of the workers in the breathing zone. The rest of the sampling train was placed on the workers in a manner that it did not obstruct them from performing their tasks. The pumps were clipped on the workers belts and the tubing was pulled from behind the backs to the front, i.e. at the lapel.

Once the sampling train was attached on to the worker, the information regarding the details of the person sampled, date, and environmental conditions at the time and observations of how the person was performing the work were noted onto the field sheet (refer to Appendix I). Then the workers were allowed to return to their place of work whereby they were observed while performing their tasks. When the shift is completed while samples train still on the worker, the pump was switched off and the filter cassette holder inlet plugged with a red plastic cap indicating the cassette as used.

The cassette was then carefully detached from the tubing and placed inside a cooler box with ice packs and transported to the site office. At the office, the samples collected were transferred into the refrigerator that was running at a temperature of approximately 4 ºC. The OSHA 58 method requires that the collected samples be removed from the cassette in the field and placed in a glass vial which has to be sealed with a cap containing a polytetrafluoroethylene liner before shipment. During this study however, an arrangement was made with the analytical laboratory that the samples be shipped still in the holding cassettes and the laboratory personnel in charge of the analysis to the individual to remove the samples from the cassette and transfer them into the glass vials.

Field blank samples were collected to assess the extent to which actual samples have been contamination during the collection process. These samples were treated as though they were actual samples except that they were not exposed to the contaminated atmosphere. The samples accompanied the actual samples through every stage of the sampling process.

Analysis of the samples was done according to the method described in Occupational Safety and Health Administration Sampling and Analytical Methods, Method 58.

The method requires samples to be collected with glass fiber filters in three-piece polystyrene cassettes. The samples were collected as the method required. The sealed cassettes were shipped cold to the laboratory and, upon receipt, stored in a refrigerator until analyzed.

At the laboratory the glass fiber filters (samples) had to be placed in test tubes containing benzene and be sonicated for 20 min. The resulting solutions filtered with fine fritted glass filter funnels. The filters were then rinsed twice with benzene and the filtrate combined with the original extract. The benzene extracts were concentrated to 1ml. A 0.5 ml aliquot of each sample taken to dryness and the benzene soluble fraction determine gravimetrically. The other half of each sample saved to be analyzed by high performance liquid chromatography if the benzene soluble fraction is over the permissible exposure limit[9], this is as per the specification of the OSHA Method Number 58.

The South African National Accreditation System (SANAS) is recognized by the South African Government as the single National Accreditation Body that gives formal recognition that Laboratories, Certification Bodies, Inspection Bodies, Proficiency Testing Scheme Providers and Good Laboratory Practice (GLP) test facilities are competent to carry out specific tasks. Protechnik Laboratories is SANAS accredited for analyzing coal tar pitch volatiles hence it was used during this study[26].

The samples transported to the analytical laboratory were kept at 4 ºC to prevent samples loss and protected from UV light to prevent chemical decomposition. Constant communication with the laboratory was maintained to ensure quality. Method accuracy (defined as closeness to truth) can be evaluated through the use of control samples. Control samples include duplicate, split samples, spiked samples and blank samples[23].

During this study blank samples were taken. There are several types of blank samples that can be used as controls: field blanks, transport blanks, and reagent blanks. The type of control samples collected were field blanks. These were used to assess the extent to which the actual samples have been contaminated during the collection process. They were treated as though they were actual samples, except that they did not get exposed to the contaminated atmosphere[23]. The field blanks accompanied the actual samples through every stage of the sampling process. In an event that the mass of the contaminant was to be found on the field blank was going to be subtracted from that found on the actual samples before dividing by the air volume sampled in the determination of the mass concentration of the contaminant. Normally each sampling method has a limit on the mass of contaminant permissible on the field blank. A contaminant mass above this limit makes the airborne concentration of contaminant found on the actual samples represented by the field unacceptable.

2.6 Quality assurance issues

A written quality assurance plan is fundamental to the operation of any analytical laboratory as it spells out in details of the processes by which data generated by the laboratory will be evaluated, corrected if necessary and reported[23]**.** It is normally recommended that the following topics constitute the bare minimum quality plan. Protechnik laboratory have such a quality assurance system in terms of their SANAS accreditation certificate.

Quality policy

This is the management's written commitment to the production of data of highest quality.

Document control:

This is a procedure or protocol by which the quality assurance plan is updated and revised, and its distribution is controlled. While there are several systems in use, one such system includes labeling the top of each page in the quality assurance plan with the section number, revision number, revision date, and the page number. Such a table of revisions should be the first page of the QA manual. The table of revisions would normally include a list of all revisions by sections, revision number and date.

Organization

These are the job duties and responsibilities for each job category within the laboratory, together with the minimum qualifications, experience levels, and reporting relationship.

Training

In this section of the quality assurance (QA) manual required level of training for each job category is specified. There are two major types of training: on-the-job and formal. The minimum levels of training appropriate for each job category should be specified, together with an evaluative instrument for determining what the attendee learned as a result at such training.

Procurement

This section delineates the procedure(s) by which supplies, materials, and capital equipment are procured. Details of how as-received supplies, etc. will be tested to certify the specified quality of those materials should be included.

Calibration

The calibration section of the QA manual contains those elements required to be covered when discussing calibration for a specific sampling or analysis method. It should contain for example details of frequency of calibration, quality of standards used in calibration, record-keeping protocols and environmental conditions to be maintained.

Preventive maintenance

The laboratory is most efficient when sampling and analytical instrumentation are optimally functioning. To minimize variability and optimize "up-time" a cycle of pre-emptive down-time must be in place. Preventive maintenance reduces instrument "crashes" or unplanned down time.

Sample handling

This entails having specific written procedures for the handling of samples received into the laboratory. The procedures should include, as a minimum, the conditions under which samples are accepted and rejected as received, if accepted, how samples are logged in, how samples are stored prior to analysis, how samples are distributed to analysts, how samples are stored following analysis, how samples are distributed for reanalysis if such is required and how long samples are retained before being discarded.

Intra-laboratory and intra-laboratory testing

This is the section which the interlaboratory and intralaboratory Quality assurance program is found. The intralaboratory part it is were such topics as evaluation of precision and accuracy for within-analyst and between-analyst data, construction and use of control charts, and use of duplicate, replicate and/or spiked samples is found. In the interlaboratory section, such topics as selection of interlaboratory participants, selection of analyte, duration and frequency of interlaboratory testing, and statistical evaluation and reporting of test data is found.

Data validation

This is required before reporting test results. Data generated should go through some sort of data validation.

Audits

Every QA program needs to undergo periodic auditing with the question to be answered being "is the QA program effective in producing quality data". Audits are of two general types systems and performance. A system audit is essentially a paper audit. If a protocol or procedure calls for specific paperwork to be completed, is that paperwork completed for some randomly selected samples? A performance audit incorporates the qualitative evaluation of the data quality through the evaluation of data generated from the analysis of unknown samples.

Corrective action

These are the procedures for dealing with nonconformities found during an audit when an analytical system suddenly goes out of control. The corrective action should form a closed-loop system, that is corrective action should consist of identifying the problem, designation of a person or persons to correct the problem, identifying appropriate corrective action, instituting the corrective action, evaluating the correction and finally placing the previously nonconformity system back online with quality reports to management. Management should be kept updated routinely on the state of quality through short simple reports[23].

In the present study a day visit to the laboratory was undertaken during the delivery of the samples to observe the processes followed as well as to check and verify the information in their quality management systems.

Microsoft Excel provides a set of data analysis tools called Analysis ToolPak that could be used to save steps when developing complex statistical analyses. Descriptive Statistics analysis tool is one of such tools, it generates a report of univariate statistics for data in the input range, providing information about the central tendency and variability of data, thus it gives general statistical information about a set of data, such as the mean, median, standard deviation, maximum etc[27]. From the raw data received from the Analytical Laboratory after analysis the Microsoft Excel descriptive statistics analysis tool was to be used to compare the findings with the permissible exposure limits, however, no coal tar pitch volatiles were detected on any of the filters collected during the study period.

2.7 Ethics

This study was not expected to cause harm to the workers who participate in it. Permission was sought from Health Optimization Division of the Occupational Health Department and management of the area where the study was to be conducted. Participation by the workers was voluntary. First verbal consent from subjects was obtained.

Procedures were explained to each individual employee as outlined in Appendix II. Confidentiality and anonymity was guaranteed. The results of the study will be made available to the management of the area where the study was conducted first, before being made available to the plant operators, and the plant management.

2.8 Time line

Permission to go ahead with the study was given in September 2005. The commenced in January 2006 and was completed within a period of six months thus by the end of May 2006. The final report of the study was supposed to be compiled and submitted by November 2006; however, the analytical laboratory entrusted with the analysis of the collected samples had a back log in terms of releasing the results in time.

2.9 Budget

No extra funds were needed to be sourced for the study as all expenses that is from sample heads, stationery, the storage facility for the samples, and the vehicle for the transporting of the samples were borne against the monitoring programme developed by the company.

CHAPTER 3: RESULTS

In this chapter the results of personal air sampling conducted at Coal Distribution Steam Plant are shown in tables i.e. Table 1. Table 2 shows the results of the field blank samples collected during sampling as a means of Quality assurance. Table 3 shows the ambient meteorological conditions that existed on the days samples were collected.

Table 1: Coal tar pitch volatiles concentrations of tripper car operators at Coal Distribution Steam Plant. Secunda. 30 January – 25 May 2006.

No	Person Monitored	Sample Time (min)	Sample No.	Concentration Measured (ppm)
30 January				
1.	Operator 1	647	10600042	ND
2.	Operator 2	642	10600043	ND
3.	Operator 3	684	10600045	ND
4.	Operator 4	671	10600046	ND
01 February				
5	Operator 5	326	10600048	ND
6.	Operator 6	350	10600049	ND
7.	Operator 7	348	10600051	ND
8.	Operator 8	338	10600050	ND
06 February				
9.	Operator 5	681	10600053	ND
10.	Operator 6	615	10600052	ND
11.	Operator 2	548	10600097	ND
12.	Operator 1	612	10600098	ND
16 February				
13.	Operator 4	400	10600099	ND
14.	Operator 3	322	10600100	ND
15.	Operator 9	359	10600103	ND

No	Person Monitored	Sample Time (min)	Sample No.	Concentration Measured (ppm)
16.	Operator 2	319	10600104	ND
17.	Operator 6	426	10600102	ND
18.	Operator 5	420	10600101	ND
22 February				
19.	Operator 2	423	10600117	ND
20.	Operator 1	433	10600116	ND
21.	Operator 10	442	10600119	ND
22.	Operator 6	435	10600118	ND
23.	Operator 7	404	10600121	ND
24.	Operator 8	422	10600120	ND
16 May				
25.	Operator 11	406	10600308	ND
26.	Operator 12	424	10600307	ND
27.	Operator 13	412	10600314	ND
28.	Operator 14	437	10600313	ND
18 May				
29.	Operator 11	219	10600315	ND
30.	Operator 15	202	10600316	ND
31.	Operator 14	360	10600319	ND
32.	Operator 13	425	10600320	ND
33.	Operator 12	199	10600317	ND
23 May				
34.	Operator 13	334	10600325	ND
35.	Operator 14	270	10600327	ND
36.	Operator 16	240	10600329	ND
37.	Operator 15	428	10600331	ND

No	Person Monitored	Sample Time (min)	Sample No.	Concentration Measured (ppm)
25 May				
38.	Operator 14	441	10600332	ND
39.	Operator 16	240	10600337	ND
40.	Operator 13	292	10600334	ND
41.	Operator 15	300	10600336	ND

Table 2: Blank samples collected at Coal Distribution Steam Plant. Secunda. 30 January – 25 May 2006.

Date	Location	Sample Time (min)	Sample Number	Concentration Measured(ppm)
30 January	Boiler Bunker 3	627	10600044	ND
30 January	Boiler Bunker 5	724	10600047	ND
06 February	Boiler Bunker 9	576	10600096	ND
16 February	Boiler Bunker 8	360	10600105	ND
22 February	Boiler Bunker 4	428	10600115	ND
16 May	Boiler Bunker 5c	473	10600312	ND
16 May	Boiler Bunker 6a	419	10600310	ND
18 May	Boiler Bunker 5d	420	10600318	ND
23 May	Front of Control Room	420	10600330	ND
23 May	Tripper car 101C	481	10600328	ND
23 May	Tripper 101D	339	10600326	ND
23 May	Boiler Bunker 8b	395	10600324	ND
25 May	Tripper 101D	360	10600338	ND
25 May	Boiler Bunker 3	335	10600335	ND

Date	Location	Sample Time (min)	Sample Number	Concentration Measured(ppm)
25 May	Tripper 101D	437	10600333	ND

Table 3: Meteorological conditions at Coal Distribution Steam Plant. January 2006 – May 2006.

Parameter	Rainfall (mm)	Temperature (°C)	Wind speed (m/s)	Humidity (%)
30 January 2006				
Average	0.00	25.7	0.1	42.1
01 February				
Average	0.00	23.7	0.3	49.4
06 February 2006				
Average	0.00	25.2	0.1	42.2
16 February 2006				
Average	0.00	24.1	0.4	49.3
22 February 2006				
Average	0.00	23.9	0.5	42.1
16 May 2006				
Average	0.00	20.4	0.4	39.8
18 May 2006				
Average	0.00	22.0	0.2	38.1
23 May 2006				
Average	0.00	21.4	0.1	40.1
25 May 2006				
Average	0.00	20.4	0.2	40.3

CHAPTER 4. DISCUSSION OF RESULTS

In this Chapter all the aspects of the present study are critically evaluated. The strengths and weaknesses of the study design, methodology and results are discussed. The low exposure of workers to coal tar pitch volatiles is examined and further steps to fully understand their health risk and apply adequate controls are discussed.

4.1 Comparison of result with occupational exposure standards

To complete this study, a total of 56 samples were collected over a period of nine days and analyzed. These included 41 personal samples and 15 field blank samples. The samples were collected on pre-weighed 37 mm, 0.8 µm glass fiber filters. The filters were connected to constant air sampling pumps set at 2.0 ± 5% liters per minute using flexible tubing. Shift long task-based samples were collected for personal samples and blank samples were collected at a distance of approximately 10 meters from the tripper car operation. These measurements were collected during the task-based coal tar pitch volatiles exposure assessment of employees at Coal Distribution Steam Plant. None of the sampling pumps utilized had deviations between pre and post sampling calibrations.

The OSHA time weighted average permissible exposure limit for coal tar pitch volatiles is 0.2 mg/m^3. The OSHA Method Number 58 used has the detection limit of the analytical procedure as 6 µg per sample which is based on the precision of the analytical balance used. This is the weight which corresponds to twice the standard deviation of the precision data for a 50-mg weight, which is the approximate weight of an average PTFE cup. This detection limit also takes into account the dilution factor of 2[9]. The analytical laboratory on the other hand uses 0.1 mg per sample as the detection limit for OSHA Method Number 58 at their establishment. The detection limit referred on in this report therefore refers to the detection limit as given by the analytical laboratory[28].

The samples collected for the assessment of tripper car operators' exposure to coal tar pitch volatiles – benzene soluble fraction revealed exposure concentrations below the detection limit. Therefore the tripper car operators were exposed to coal tar pitch volatiles – benzene soluble fraction at levels that fall well within the permissible exposure limit of 0.2 mg/m^3. Health effects associated with exposure to high levels and/or continuous low levels of coal tar pitch volatiles should therefore not be expected in the tripper car operators. These concentrations revealed are therefore taken to be in compliance with the OSHA exposure standard. The results obtain during this study were accepted with the assumption that stringent laboratory quality control was in place and strictly adhered to by the Analytical Laboratory, which included for example analysis of spikes, repeat analysis, etc,

Absorption through the skin is another important route of exposure and was not accounted for during this study. Only airborne concentration measurements were done.

4.2 Controls in Place

4.2.1 Engineering Controls

Dilution ventilation is the dilution of contaminated air with uncontaminated air for the purpose of controlling potential airborne health hazards, fire and explosive conditions, odor, and nuisance type contaminants. Dilution ventilation also can include the control of airborne contaminants such as vapours, gases and particulates, generated in closed buildings[29]. At the Coal Distribution Steam Plant, dilution ventilation was used to control heat build-up as well as hazardous vapours in the area. This was achieved by installing on the southern side of the building blower fans that draw uncontaminated air from the outside and allow it to dissipate out of the building through structural openings. The effectiveness of the dilution ventilation was not measured during the study but was assumed to have been adequate in the light of the sampling results.

4.2.2 Personal protective equipment

Personnel at Coal Distribution Steam Plant were issued with **3M**™ 8247 P2 type free maintenance respirators. **3M** recommends this type of respirators for relief against nuisance levels of organic vapors. Nuisance level refers to concentrations not exceeding OSHA PEL or applicable government occupational exposure limit, which ever is low. However, compliance with the wearing of this respiratory protective equipment was not reliable as it was intermittent. But in those cases where respiratory protective equipment may have been worn at times during the shift, the operators would have been at even lower risk than personal sampling indicated.

4.3 Possible sources of errors and other factors that affected the study

4.3.1 Analytical laboratory quality control

During the collection of samples at the Plant, field quality control procedures were followed. However, it was assumed, but not confirmed, that quality control procedures were adequate in the analytical laboratory. Possible deviations from good laboratory practice may constitute a source of error. The scale of this error introduced by instrumentation, human and/or during data presentation can therefore not be ignored. Any of such error that could have been introduced during receiving, handling, analyzing to producing the results report, could have influenced the result. With an assumption that there could have been complacency when applying some of their in-house quality control procedures when handling the samples the results provided therefore could be somewhat skewed so much to the negative in representation of the conditions monitored at the plant as not harmful to the health of the workers while in fact they are harmful.

4.3.2 Analytical method detection limit

One other factor that could have influenced the results obtained is the analytical method detection limit. The detection limit is commonly understood to be the smallest concentration that can measured with a particular technique. In fact it is the point at which we can make a decision whether the element or compound is present or not. To be able to measure it one needs at least three times the detection limit. Three times the detection limit is often called the limit of determination. There are a number of different "detection limits" that are commonly used. These include the instrument detection limit (IDL), the lower level of detection (LLD), the method detection limit (MDL) and the level of quantitation (LOQ)[28].

The analytical laboratory used in this study has a “tested” detection limit used when following the OSHA Method Number 58 of 0.1 mg (100 μg) per sample. The OSHA method literature specifies the detection limit for the overall procedure of 6 μg per sample for CTPV-BSF, which is 17 times more sensitive than the laboratory achieved. By implication, the detection limit achieved by the analytical laboratory can only detect relatively higher concentrations. This may be attributed to the instrumentation used or other technical incompetence which rendered the laboratory unable to follow the OSHA methods to the letter. It must be borne in mind that at 0.1 mg per sample the concentration of contaminant to be detected is high. Due to the fact that CTPVs are carcinogenic, concentrations of below 0.1 mg could still cause irreparable health effects to individuals exposed. The high detection limit, i.e. 0.1 mg used by the analytical laboratory for CPTV determination could have not been sensitive enough in measuring lower levels. The detection limit could therefore presented the extent of exposure to CTPV by tripper car operators as non existent while in effect they could have been exposed to some concentrations of CTPV which were below the permissible exposure limit. It is known that exposure to carcinogenic substances even at concentrations below set national and international exposure standards does not imply the absence of health risk to the exposed individuals.

4.3.3 Sampling material and handling of samples

The method used in the sampling of CTPVs consisted of drawing air through a high-volume sample containing a circular fibrous glass fiber filter. Analysis consisted in weighing and extracting with warm benzene, reweighing the filters and reporting the resultant weigh loss as the benzene soluble fraction**.** Another assumption for the results of this study is that the analytes on the filter could have been lost during the handling and transportation of the samples to the laboratory. It was reported in 1967 that glass fiber filters were not suitable for personnel sampling of CTPVs because of the "relatively high blank filter weight losses, in some cases equaling the weight loss of extracted samples". Data was presented which indicated that silver membrane filters were more suitable for collection of CTPVs with personnel samplers[30].

In a more recent study NIOSH investigated the extent of exposure of coke oven workers to polycyclic aromatic hydrocarbons and evaluated methods of sampling and analysis for coke oven emissions. NIOSH's personnel who obtained the samples found that silver membrane filters used in personnel monitors tended to clog during periods of high emission or high moisture after a relatively short sampling time. After some experimenting, the NIOSH sampling team discovered that the problem could be eliminated by placing a glass fiber filter (without organic binder) ahead of the silver filter within the cassette. This sandwich of glass and silver filters supported by a cellulose filter pad thus became the standard media which NIOSH as well as OSHA used to collect CTPVs [30]. In this study however, the OSHA sampling and analytical method number 58 require only that after sampling, each glass fiber filter be transferred to a separate scintillation vial and the vial sealed with a PTFE-lined cap[9].

In transporting the filters still in the cassettes, the assumption was made that this would reduce any contamination in the field of the samples, which were handled by competent laboratory personnel only. As a result modification of the transportation of the samples from the plant to the refrigerator and then to the laboratory could have interfered with the recovery of analytes and thus produce in accurate results.

The results of the study must be evaluated in the light of the very low values observed, all of which were reported as Not Detectable (ND).

Could a more sensitive method have been used? One has to assume that OSHA method number 58 is internationally accepted as being sufficient to measure exposure that could be dangerous to the workers. As the detection limit is often at 10 fold margin of safety, it is more than adequate in the present study. No benefit would have been gained if another more sensitive method had been used.

4.3.4 Plant production changes

Why then were CTPVs concentrations so low in a workplace where higher levels could reasonably be expected? Coal Distribution Steam Plant receives its feed i.e. tar sludge blend, continuously for 24 hours. This study was initiated with the information received from the plant production personnel that tar sludge blend was made immediately upon the delivery by tipper trucks of tar sludge and that the blend was in the same activity transported via conveyor belts to Coal Distribution Steam Plant. The premise was that the tar decanter sludge was not allowed time in the “swimming pool” area (an open concrete-lined pit used to store the sludge) whereby the volatiles were allowed to evaporate[20]. This implied that the freshly prepared blend of tar decanter sludge and fine coal was utilized at

Coal Distribution Steam Plant whilst considerable high volumes of vapours are still being emitted by the blend. Based on that, one then expected the workers (i.e. tripper car operators) to be exposed to high concentrations of coal tar pitch volatile vapours emitted by the blend.

However, during the study, it was established that the way the feed to the plant is prepared has since been changed; specifically the way the blend was mixed was changed. The changes in the preparation of tar sludge blend came in where the sludge was not immediately mixed with the fine coal and conveyed to Coal Distribution Steam Plant. As tar decanter sludge was delivered by tipper trucks to the “swimming pool” area, it remained for some time (i.e. hours and in some instances days) in the “swimming pool” area before blending took place. This delay in mixing the blend could in some way have reduced the amount of vapour emitted compared to the previous blending method which meant preparation was done immediately after the sludge was dumped into the “swimming pool” area and thus not giving enough time for the vapours contained in the sludge to evaporate into the atmosphere.

Another process change that could have resulted in lower quantities of vapours being emitted from the feed exists. It became apparent that previously the tar sludge blend was done with equal parts fine coal and tar decanter sludge. This was however also changed to mix one part tar sludge with four parts fine coal. The higher proportion of fine coal used in the mixture may have in some way had a diluting effect on the intensity of coal tar pitch volatiles emissions from the tar sludge blend. This could result from the increased binding capacity for volatile compounds.

In the light of the present results, the decision to limit the scope of the study to measuring airborne concentration of CTPV, benzene soluble fraction needs to be discussed.

- Working in an environment heavily contaminated with CTPVs is known to be a risk occupation. Occupationa1 exposure to coal tar has been associated with cancer in target organs, including the lung, bladder, kidney and digestive tract. This has been shown in several epidemiological studies of workers exposed to coal tar pitches in coal gasification, coke production, aluminum and calcium carbide production[19].
- As only airborne concentrations are considered here, the possibility that skin absorption is contributing to the toxic dose should be included in any future study. Such future work should also consider whether the choice of benzene soluble fraction is an adequate measure of risky working procedures or whether the estimation should be made using specific marker compounds such as pyrene, anthracene or benzo(a)pyrene[3].

The study would be more robust if dermal absorption as a form of exposure were also considered. The sticky nature of CTPVs is such that contact with the skin on shift and possible skin–cleaning during and after shift could substantially increase the internal dose of CTPVs concentration in the workers, even at acceptable ambient concentrations. Therefore the question as to whether these workers are at risk or not requires that they may be subjected to regular biological monitoring to measure internal exposure of hydroxylated metabolites of pyrene in urine (1-hydroxypyrene, 1-OHP) and phenanthrene (1-, 2+9-, 3-, 4-hydroxyphenanthrene, 1-, 2+9-, 3-, 4-OHPhe)[31].

CHAPTER 5: CONCLUSION

Tripper operators are not exposed to coal tar pitch volatiles – benzene soluble fraction at concentrations above the Occupational Safety & Health Administration permissible exposure limit of 0.2 mg/m^3 not only this, but given the detection limit, there is a 10 times margin of safety.

5.1 Control measures

In light of the not detectable findings, the control measures are adequate. The Regulations for Hazardous Chemical Substances requires that the implementation of control measures in a particular hierarchy. This hierarchy starts with the elimination of hazards, engineering controls, administrative controls and the use of personal protective equipment as a last resort[14]. A discussion of control measures as observed at Coal Distribution Steam Plant follows below.

5.1.1 Engineering controls

Coal Distribution Steam Plant is provided with blower fans in the wall communicating with ambient atmospheric air to blow an adequate quantity of air with the aim of diluting any hazardous vapours present in the work environment air.

5.1.2 Administrative controls

There is a training system whereby every employee working in the plant goes through an intense training program. Training is also provided on an ongoing basis whereby employees are informed of the health risks associated with the chemicals that they work with. Work procedures also include standard working procedures which determine how to work safely with chemical substances. This includes the use of personal protective equipment.

Employees are also in a medical surveillance program whereby their health status is monitored on an ongoing process. Any deviation is noted and the reason thereof is investigated and control measures put in place. Workplace air monitoring and personal exposure monitoring is part of the occupational health and hygiene program

5.1.3 Personal protective equipment

For inhalational protection the tripper car operators provided were with and using 3M 8243 masks and for skin chemical resistant long sleeve overalls were utilized.

CHAPTER 6: RECOMMENDATIONS

a) Investigation of other exposure assessment methods should be carried out in the future to establish exposure data of tripper car operators. The sampling and analytical method to be selected should be capable to yield results that can be interpreted in a meaningful way. This is important when comparing to exposure standard. The other important factor is that the method should be a validated method for accuracy, precision and the concentration range for which the method is applicable[3].

b) Other measures to examine exposure to CTPVs such as medical surveillance records to see if there is an increased incidence of skin lesions, or other associated conditions over time since the plant was commissioned should be investigated.

c) Are there other job categories with increased risk at the refinery? Maybe the choise of tripper car operators was not ideal. Other job categories should be identified, measured and controlled. Only then, when confident that the whole workplace is safe with regard to CTPV exposure can another study of a different hazard conducted.

REFERENCES

1 Irwin, R.J. (1997) *Environmental Contaminants Encyclopedia Coal Tar Entry* [Internet] Fort Collins, Colorado. Available from: <http://www.nature.nps.gov/hazardssafety/toxic/coaltar.pdf> [Accessed 07 March 2005].

2 Kurtz, L.A., Verma, D.K., & Sahai, D. (2003) Coal Tar Pitch Volatiles and Polycyclic Aromatic Hydrocarbons Exposures in Expansion Joint-Making Operations on a Construction Site: A Case Study. *Applied Occupational and Environmental Hygiene*, Volume 18 (Number 12), December, pp.545-552.

3 B.C. Research Inc. and Certified Industrial Consulting Ltd., (2004) *Canadian Association of Petroleum Producers – Polycyclic Aromatic Hydrocarbons(PAH) Monitoring Protocol*, Publication No. 2005-0009. Alberta Canada.

4 International Agency for Research on Cancer (1987) *Monograph on the Evaluation of the Carcinogenic Risk to Humans,* Coal-Tar Pitches, Supplement 7 (p 174). Lyon, France.

5 International Agency for Research on Cancer (2004) Group 1: Carcinogenic to humans as evaluated in IARC Monographs Volumes 1 -88. *Overall Evaluations of Carcinogenicity to Human*. [Internet] January, Lyon. Available from: http://www-cie.iarc.fr/monoeval/crthall.html [Accessed 24 February 2005].

6 Fortifiber Building Systems Groups (2006) *Chinese building Paper with Coal Tar Presents a clear health hazard* [Internet], Reno, Nevada. Available from http://www.fortifiber.com_coal_tar.htm [accessed 10 October 2006].

7 Zenz, C. (1988) *Occupational Medicine-Principle and Practical Applications. Coal Tars*. 2nd ed.. St Louis, MO: Mosby-Yearbook.

8 National Institute for Occupational Safety and Health (1996) *Documentation for Immediately Dangerous to Life or Health Concentrations.* Coal Tar Pitch Volatiles [Internet] August Available from:http://www.cdc.gov/niosh/idlh/65996932.html [Accessed 17 February 2005].

9 Occupational Safety and Health Administration (1986) *Organic Method 58 – Coal tar Pitch Volatiles, Coke Oven emissions, Selected Polynuclear* Aromatic *Hydrocarbons*. OSHA Analytical Laboratory. Salt Lake City. Utah.

10 United States Environmental Protection Agency (1993) *Integrated Risk Information System on coke oven emissions* (CASRN 8007-45-2). [Internet] January, 0395. Available from :http://www.epa.gov/iris/subst/0395.htm [Accessed 09 September 2006].

11 Grant, W.M (1986) *Toxicology of the Eye*. 3rd ed. Springsfield, IL Charles C Thomas Publisher.

12 International Labour Office (1983) *Encyclopedia of Occupational Health and Safety,* Volumes I & II, pp 2148.

13 National Oceanic & Atmospheric Administration, U.S Department of Commerce (2006) *Occupational exposure limits* [Internet] United States, NOAA. Available from <http://www.archive.orr.noaa.gov/cameo/locs/worklims.html> [Accessed 09 January 2007].

14 Southern African Department of Labour (1993), *Occupational Health and Safety Act (Act no 85 of 1993) and its regulations*. Cape Town, Department of Labour.

15 American Conference of Governmental Industrial Hygienists, (2005). *TLVs® and BEIs® Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*. Cincinnati, OH.

16 Health & Safety Laboratory (1990) *Coal Tar Pitch Volatiles: Measurement of particulates and cyclohexane soluble material in air. Laboratory method using filters and gravimetric estimation* [Internet] February, United Kingdom Available from http://www.hsl.gov.uk/publications/mdhs_list.htm [Accessed 01 February 2006].

17 Gibby, E. (1997) Improved Methods for the determination of Coal tar pitch volatiles in air. *Mainstream Research News*. Issue 2. [Internet] September, United Kingdom Available from http://www.hse.gov.uk/RESEARCH/journals/mrn0297.htm#2. [Accessed 18 August 2006].

18 Occupational Safety and Health Administration, Methods Development Team (1999) *Evaluation guidelines for air sampling methods utilizing chromatographic analysis.* Industrial Hygiene Chemistry Division. OSHA Salt Lake Technical Center. Salt Lake City, OSHA.

19 Report on Carcinogens, Eleventh Edition, U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program.

20 National Institute for Occupational Safety and Health (1995) *Health Hazard Evaluation*, Hazard Evaluation and Technical Assistance Report No 94-0020-2483 (P3) AK Steel coke works, Ashland, Kentucky.

21 Occupational Safety and Health Administration, United States Department of Labor. *OR-OSHA Technical Manual. Section II - Sampling, Measurements Methods, and Instruments*. NW Washington DC.

22 SAIOH (2001) *Southern African Institute for Occupational Hygiene* [Internet]. Clubview. Available from: http://www.saioh.org/ [Accessed 06 June 2006].

23 Di Nardi, S.R. (2003) *Quality Control for Sampling and Laboratory Analysis.. The Occupational Environment: Its Evaluation, Control, and Management*, 2nd Edition. American Industrial Hygiene association, Fairfax, Virginia.

24 National Institute for Occupational Safety and Health.(2005) *Pocket Guide to Chemical Hazards*. Publication No 2005 – 149. United States Department of Health and Human Services. Cincinnati, OH.

25 Department of Occupational Safety & Health, Ministry of Human Resources (2000) Assessment of the Health Risks arising from the use of hazardous chemicals in the Workplace. *Chemical Health Risk Assessment Manual*. 2nd ed, Malaysia, Department of Occupational Safety & Health.

26 SANAS (2005) *The South African National Accreditation System* [Internet] Pretoria. Available from http://www.sana.co.za/ [Accessed 23 August 2006]

27 Microsoft Office Online (2006) *Microsoft Office Excel, About Statistical Analysis Tools* [Internet] United States. Available from: <http//wwwoffice.microsoft.com/en-us/excel/HP05203871033.aspx> [Accessed 20 September 2006].

28 The Spectroscopy Net. (2007)The Spectroscopy Net – Detection Limit [Internet] Paris, France. Available from :http://www.thespectroscopynet.com/Educational/Detection_limit.htm [Accessed 03 May 2007].

29 American Conference of Governmental Industrial Hygienist (1998) *Industrial Ventilation 20th Edition A Manual of Recommended Practice.* American Conference of Governmental Industrial Hygienist, Inc, Cincinnati, Ohio.

30 Siem H.J.,Hanneman, W.W., Barsotti .L.R, & Walker .T.J (1974) Determination of Pitch Volatiles in Airborne Particulates. *American Industrial Hygiene Association Journal.* Voume 35, Number 11 pp 718 – 723.

31 Strunk, P., Ortlepp, K., Heinz, H., Rossbach, B., & Angerer, J. (2002) Ambient and biological monitoring of coke plant workers – determination of exposure to polycyclic aromatic hydrocarbons. *International Archives of Occupational and Environmental Health.* Volume 75, Number , June, pp 354-358.

APPENDIX I

FIELD SHEET

Area Task:

Date	**Time** **On - off**	**Operator** **Monitored**	**Sample No.**	**Equipment No.**	**Comments/observations/RH/Temp.**

APPENDIX II

I am Michael Makgatho, working for the Occupational Hygiene Department. I am conducting a coal tar pitch volatiles exposure assessment trying to determine the amount of personal exposure during the distribution of coal-sludge blend into the bunkers. Your Supervisor told me that you have been made aware about this study. I therefore, will like you to participate in this study by wearing this sampling device which will collect coal tar pitch volatiles air sampling in your breathing zone.

You are not obliged to participate in this study; it is on voluntary basis. If you decide not to participate you will not be victimized in any manner and that will not be used against you.

The aim of this study is to determine coal tar pitch volatiles concentration when you operate the tripper car to feed the coal-sludge blend into the boiler bunkers. Vapours will collect on this sampling medium (medium will be shown) while you work and wear this sampling device for the duration of your shift, it will not harm you in any way and you are requested to continue with your job task as you normally you perform it. The results of this study will be used to improve on future monitoring strategies and therefore, assist to control employee exposure to coal tar pitch volatiles and other chemicals. The sampling device will be sent to the laboratory for analysis. I

I am available at the Medical Station, Office 3 and telephonically on 610 8418 should you have any questions relating to this study. If you participate you will not be harmed in any way and your participation in this study will not compromise your job or your position in the company. Participation is voluntary and you are free to withdraw your participation at any stage of the study.

Thank you,
PM Makgatho
Occupational Hygiene Technician