Monitoring exposure to total volatile organic compounds and particulate matter at a petrol-filling station

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I love You, Lord
Oh, Your mercy never failed me
And all my days, I've been held in Your hands
From the moment that I wake up
Until I lay my head
Oh, I will sing of the goodness of God

All my life, You have been faithful
All my life, You have been so, so good
With every breath that I am able
Oh, I will sing of the goodness of God

I love your voice
You have led me through the fire
In darkest night, You are close like no other
I've known You as a Father
I've known You as a Friend
Oh, I have lived in the goodness of God

All my life, You have been faithful
All my life, You have been so, so good
With every breath that I am able
Oh, I will sing of the goodness of God

Your goodness is running after, it's running after me
Your goodness is running after, it's running after me
With my life laid down, I'm surrendered now
I give You everything

You lead me and guide me, God
Faithful Father, floods my soul
Oh, and You are my anchor in the wind and the waves
You are my provider, oh, yeah
And You lead me and guide me by Your Spirit
And Your Word, I have never walked alone
My joy, my joy, every day

Oh, Shepherd of my soul, oh
What a joy to know You
Oh, the joy of knowing You, God
You're everything to me
So wonderful, in all Your ways, hey
All Your ways
Amen

-Bethel Music & Jenn Johnson

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AUTHOR CONTRIBUTIONS

This study was planned and completed by the following project team. The contribution of each is listed in the table below:

Contribution of team members

Name	Contribution
Miss EC van der Westhuizen (Student)	• Designed and planned the study. • Literature searches. • Data collection. • Statistical analysis and interpretation of data. • Wrote the dissertation.
Prof. SR Horn (Supervisor)	• Assisted with approval of the protocol and obtained ethics approval, interpretation of results, and documentation of the study. • Provided guidance on scientific aspects of the study. • Assisted with the planning and designing of the study. • Provided professional input and recommendations. • Reviewed the dissertation.
Prof. SJL Linde (Co-supervisor)	• Assisted with approval of the protocol, interpretation of results, and documentation of the study. • Provided guidance on scientific aspects of the study. • Assisted with the planning and designing of the study. • Provided professional input and recommendations. • Reviewed the dissertation.

DECLARATION

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

I declare that I have approved the dissertation and that my role in this study, as indicated above, is representative of my actual contribution and that I hereby give my consent that it may be submitted as EC van der Westhuizen's MHSc (Occupational Hygiene) dissertation.



Miss EC van der Westhuizen



Prof. SR Horn



Prof. SJL Linde

PREFACE

The dissertation is written according to the specifications of the Manual for Higher Degrees Studies (2020) of the North-West University (NWU). The NWU Harvard reference style was applied for referencing the sources used in the study. This dissertation is presented in article style. The main methods and findings of the study are contained in a manuscript in preparation to be submitted to a journal after examination of the dissertation (Chapter 3). The entire dissertation is written in Arial with a font size of 11 and in British English. The document has undergone professional language editing, and the corresponding certificate is provided in Annexure A. The outline of the dissertation is as follows:

- Chapter 1 – Introduction with the problem statement, aims, objectives and hypotheses of the study.
- Chapter 2 – Literature study relevant to the industry; hazardous chemical agents at petrol-filling stations; health risks associated with volatile organic compounds and diesel particulate matter, supported by case studies; legislation and regulatory framework and monitoring methods.
- Chapter 3 – Manuscript containing the main materials and methods; results; discussion and conclusion to be submitted to a scientific journal after refinement.
- Chapter 4 – Concluding chapter discussing the main findings and seven recommendations applicable to the study. Two study limitations, as well as five future studies, are also mentioned.
- Annexure A: Declaration of language editing.
- Annexure B: Calibration certificates of instruments
- Annexure C: Supplementary material.
- Annexure D: Ethics approval letter.

DISCLAIMER

As the NWU's senate's rules on the responsible and ethical use of artificial intelligence (AI) (2025) currently provide specific guidelines for referencing AI, this statement serves as a formal declaration that AI tools such as OpenAI. 2023 *ChatGPT* (GPT-5.1) [Large language model] https://chatgpt.com/chat and Gupta. R. 2017 *QuillBot* (v36.4.3) [Natural language processing, NLP, model] https://quillbot.com/ was responsibly used to improve learning outcomes. The dates of access for both tools are from February to November 2025. These tools were utilised in alignment with clear ethical standards and academic integrity principles. These tools aided in the aspects of paraphrasing and refining scientific language. AI was also used to assist in spelling, grammar, register, tone and improving style by structuring ideas by providing the author's (EC vd Westhuizen) own words (prompts).

EXECUTIVE SUMMARY

The petroleum industry is a major contributor to energy supply and employment in South Africa. However, petrol-filling stations present occupational health risks due to exposure to hazardous chemical agents (HCAs) associated with petrol and diesel handling. These fuels contain volatile organic compounds (VOCs), notably benzene, toluene, ethylbenzene and xylene (BTEX), which easily evaporate and pose inhalation risks. Chronic exposure to BTEX has been associated with systemic toxicity, neurological effects, blood disorders and cancer. Diesel particulate matter (DPM) including the gaseous and particle emissions, a component of vehicular exhaust, consists of ultrafine particles containing elemental carbon (EC), organic carbon (OC) and trace metals. Benzene and DPM are classified by the International Agency for Research on Cancer (IARC), as Group 1 carcinogens, while ethylbenzene is classified as a possible carcinogen (Group 2B) As DPM is a carcinogen the EC component is the main concern, not necessarily the OC component. Due to the carcinogenic nature of DPM and sub-micron particles (PM<1.0), DPM and exhaust-derived compounds have been linked to increased lung cancer risk.

Unlike many developed countries that operate self-service stations (SSS), South Africa predominantly retains full-service stations, where petrol-filling attendants are responsible for refuelling vehicles and assisting customers. These tasks may result in exposure to fuel vapours and exhaust emissions during their 12-hour shift.

This study aimed to assess occupational exposure of petrol-filling attendants to total volatile organic compounds (TVOCs) and particulate matter (PM) (PM <0.8 µm (as an estimate of DPM)) using real-time monitoring (RTM), as well as exposure to selected VOCs (BTEX) and DPM using conventional sampling methods. This study was conducted at a high-traffic petrol-filling station in South Africa, dispensing an average of 23 916 litres (L) of fuel per day. Personal and area monitoring was conducted over five consecutive 12-hour shifts (n=15 personal: n=5 area samples). Conventional sampling followed NIOSH methods 1500/1501 (BTEX) and 5040 (EC), while RTM instruments included the ppbRAE 3000 and TSI Sidepak™ AM 520. Ambient conditions were also recorded.

All 12-hour time-weighted average (TWA) concentrations for BTEX were below their respective occupational exposure limits (OELs) as stipulated in the Regulations for Hazardous Chemical Agents (RHCA, 2021). EC concentrations were below the Mine Health and Safety Act's (MHSA, 1998) adjusted 12-hour OEL of 0.07 mg/m^3 (8-hour TWA

for EC: 0.1 mg/m^3). No statistically significant differences were observed between personal and area concentrations or across sampling days. A very strong positive correlation (ρ= 0.975: $p<0.05$) was observed between personal benzene and the total volume of fuel dispensed, while no significant correlation was observed between EC and fuel volume, nor between BTEX and ambient conditions.

Real-time monitoring of TVOCs and PM indicated temporal exposure peaks during vehicle refuelling, underground tank deliveries and cigarette smoking. Smoking petrol-filling attendants experienced substantially higher short-term PM exposure compared to non-smokers.

Bland-Altman analysis comparing RTM (PM <0.8 µm) and NIOSH 5040 (EC) indicated a clear overestimation by the SidePak™ AM520 (mean bias 0.0557 mg/m^3), although a strong positive correlation (ρ= 0.7125; $p=0.0004$) was observed between the two methods. RTM cannot replace conventional methods but is valuable for identifying peak exposure and emission sources.

Although exposure concentrations complied with regulatory limits, activity-related peaks can motivate for control measures to reduce exposure. Implementation of vapour recovery systems (VRS), administrative controls, health surveillance and worker training is recommended. Future research should include seasonal variation, biological monitoring, and dermal exposure assessment to strengthen occupational health protection at petrol-filling stations.

Key terms: Petrol, diesel, hazardous chemical agents, volatile organic compounds, diesel particulate matter, health risks.

LIST OF SYMBOLS AND ABBREVIATIONS

Symbols

%	Percentage
°C	Degrees Celsius
<	Less than
>	Greater than
±	Plus-minus
µ	Micro
/	Per
=	Equal to
–	En dash
ρ	Greek letter Rho

Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
AI	Artificial Intelligence
AIA	Approved Inspection Authority
ALA	∂-Aminolevulinic acid
ALARP	As low as reasonably practicable
AML	Acute Myeloid Leukaemia
ANOVA	Analysis of variance
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
BP	British Petroleum
C	Ceiling limit
CARC	Carcinogen notation
CI	Compression-Ignition
CO_2	Carbon Dioxide
COPD	Chronic Obstructive Pulmonary Disease
DF	Standard deviation of the differences
DNA	Deoxyribonucleic acid
DPM	Diesel Particulate Matter
EC	Elemental Carbon
FEV1	Forced expiratory volume in the first second
FEF25-75	Forced expiratory flow

FID	Flame Ionisation Detector
FL	Florida
FVC	Forced vital capacity
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
HA	Hippuric acid
HCA	Hazardous Chemical Agent
HPLC	High-performance liquid chromatography
HREC	Health Research Ethics Committee
HSE	The Health and Safety Executive
HSL	Health and Safety Laboratory
H_2O	Water
IARC	International Agency for Research on Cancer
IMS	Ion mobility spectrometry
kW	Kilowatt
L	Litres
LOD	Limit of detection
NEF	National Empowerment Fund
NIOSH	National Institute for Occupational Safety and Health
NO	Nitric oxide
NO_2	Nitrogen dioxide
NRF	National Research Foundation
NWU	North-West University
MA	Mandelic acid
MDHS	Methods for the Determination of Hazardous Substances
MHA	Methyl hippuric acid
MHSA	Mine Health and Safety Act
MTBE	Methyl tert-butyl ether
MVV	Maximum Voluntary Ventilation
O_2	Oxygen
O_3	Ozone
OC	Organic Carbon
OEL	Occupational Exposure Limit
OEL-ML	Occupational Exposure Limit Maximum Limit
OEL-RL	Occupational Exposure Limit Restricted Limit

OHHRI	Occupational Hygiene and Health Research Initiative
OTO	Ototoxin
OTS	Outdoor tobacco smoke
OSHA	Occupational Safety and Health Administration from the USA
OSH Act	Occupational Health and Safety Act
PAHs	Polycyclic Aromatic Hydrocarbons
PAS	Photoelectric aerosol sensor
PBG	Porphobilinogen
PDR	Thermo Electron Personal DataRAM 1200
PEL	Permissible Exposure Limit
PEFR	Peak expiratory flow rate
PFT	Pulmonary Function Tests
PID	Photoionization Detector
PIXE	Particle-Induced X-ray emission
PM	Particulate Matter
PZB	Piezoelectric microbalance
REL	Recommended Exposure Limit
RF	Reduction Factor
RH	Relative humidity
RHCA	Regulations for Hazardous Chemical Agents
RTM	Real-Time Monitoring
SANAS	South African National Accreditation System
SD	Standard deviation
SEG	Similar exposure group
SKIN	Skin notation
SO_2	Sulphur dioxide
STEL	Short-term exposure limit
SOP	Standard Operating Procedure
SPMA	S-phenyl mercapturic acid
TC	Total carbon
TSI	TSI Incorporated (instrument brand)
tt-MA	Trans trans-mercapturic acid
TLV	Threshold limit values
TOR	Thermal-optical reflectance
TOT	Thermal-optical transmittance

TWA	Time weighted average
TVOC	Total Volatile Organic Compounds
UFPM	Ultrafine Particulate Matter
USA	United States of America
UV	Ultraviolet
v/v	Volume/Volume
VOC	Volatile Organic Compound
VRS	Vapour recovery system
WHO	World Health Organisation

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CHAPTER 1 INTRODUCTION

1.1 Background

1.1.1 The petroleum industry.

The petroleum industry is a necessity around the globe, as it supplies petrol-filling stations with fuel needed by consumers. According to estimations, petrol and diesel will remain the main energy sources for the transportation industry until 2050 (Wong *et al*., 2023:122099). As of 2020 to 2025, over 12.3 million vehicles were travelling on South African roads and due to the lack of public rail transport, these numbers increase every year (Statista Research Department, 2025). There are almost 6 000 fuel stations throughout South Africa. The locations of petrol-filling stations have a significant impact on fuel consumption, which correlates with demographic and geographic factors. Petrol-filling stations near primary routes have higher fuel sales due to frequent use by consumers and public travelling on the main roads. These petrol-filling stations provide more than 100 000 direct and indirect job opportunities in South Africa, which include petrol-filling attendant positions (NEF, 2020).

Petrol and diesel originate from crude oil, also known as petroleum. Crude oil is a naturally occurring liquid that forms beneath the earth's surface. Crude oil is a mixture of hydrocarbons like paraffin (alkanes), naphthene (cycloalkanes) and aromatics with varying molecular weights and a small number of organic compounds, whereas the olefins (alkenes) are formed after rough processing (Singh *et al.*, 2021). The elemental composition of crude oil by weight is carbon (80-90%), hydrogen (10-14%), oxygen (1-15%), nitrogen (<0.1-2%), and sulphur (0.2-3%). The crude oil is extracted through oil drilling and is thereafter separated through a distillation process based on their respective boiling points. Many refinery pathways lead to petrol or diesel, but in simple refineries, petrol is produced from light distillates and goes through additional refinement processes to enhance its quality, while diesel is produced from a medium-heavy distillate. Diesel fuel of a high environmental class (MK1) was introduced on the Swedish market in the early 1990s. There were significant differences between these two standard fuels, but since the European standard, EN 590, was introduced in the early 1990s, there was an increase in

environmental benefits and a decrease in, for example, sulphur content (Eriksson & Ahlgren, 2013). The main risks of petrol and diesel exposure are due to the impurities found in the raw materials and the product after processing, as well as chemicals released after combustion in an internal combustion engine, such as particulate matter (PM), sulphur compounds, nitrogen oxides (NOx), carbon monoxide (CO) and volatile organic compounds (VOCs). Benzene has been classified by the International Agency for Research on Cancer (IARC, 2007) as a Group 1 carcinogen, indicating sufficient evidence of carcinogenicity in humans. In contrast, toluene is classified as Group 3 (not classifiable as to its carcinogenicity to humans) due to inadequate evidence in both human and animal studies. Ethylbenzene is categorised as a Group 2B carcinogen (possibly carcinogenic to humans), while xylene has not been classified as carcinogenic by IARC. Although these by-products are reduced during refining processes to limit impurities in fuel products, residual concentrations remain and may pose health risks upon inhalation (Kaiser et al., 2007).

Similarly, diesel particulate matter (DPM) has been classified by IARC as a Group 1 carcinogen. It is important to note that for carcinogenic substances, no safe threshold of exposure has been established, as even low-level, chronic exposure may increase cancer risk. Therefore, although occupational exposure limits (OELs), such as the time-weighted average restricted limit (TWA-RL), are provided in legislation for regulatory and risk management purposes, these limits cannot be regarded as fully protective. In the case of DPM, compliance with the prescribed OEL does not eliminate carcinogenic risk but rather aims to reduce exposure to a level that is reasonably practicable within occupational settings. Petrol-filling attendants perform different activities at petrol-filling stations (Table 1) (Akram, 2018).

Table 1: Activities performed at a petrol-filling station.

Activity	Description	Performed by
Operation of fuel pumps	Attendants are trained to input the volume of fuel electronically into the pump as per consumer's request.	Petrol attendants.
Vehicle assistance services	Attendants perform additional services like checking and filling engine oil, checking tyre pressure, checking coolant and radiator water and cleaning the windscreen and mirrors.	Petrol attendants.
Cash and retail operations	Petrol attendants assist with card and cash transactions after the refuelling of vehicles.	Petrol attendants and cashiers.
Fuel tank deliveries	Tanker trucks deliver fuel from refineries to the underground storage tanks.	Fuel delivery personnel and petrol-filling station supervisor.
Maintenance and safety procedures	Examining nozzles, hoses, and dispensers for leaks. Underground tank inspections. General cleaning of fuel and oil spills.	Petrol attendants or station managers.

1.1.2 Hazardous chemical agents

In addition to the exposure of petrol-filling attendants to hazardous chemical agents (HCAs) during these activities (Table 1) and idling vehicles' emissions, the public is exposed when visiting the petrol-filling station. Although members of the public are exposed to VOCs and DPM spreading into the air of the environment, petrol attendants' 12-hour work shifts and the type of activities they perform increase their exposure.

VOCs are organic substances which are emitted in large quantities when fossil fuel is burned in automobiles and when fuel is dispensed into vehicles (Ge *et al.*, 2018). The combustion of fuel poses a significant health risk to those exposed by inhalation, even at parts per billion (ppb) or parts per million (ppm) concentrations (Soni *et al.*, 2018). The nature and impact of adverse health effects caused by the vapours are determined by the degree of airborne concentrations and the duration of exposure. VOCs have an inherent property of high volatility, mobility, and resistance to degradation. The respiratory system is the primary route by which VOCs enter the body. These VOCs can enter the bloodstream through the thin alveolar membranes and have detrimental effects on a variety of organs and tissues after entering the bloodstream. Adverse health effects caused by non-respiratory exposure (dermal exposure) is also a major cause of occupational health effects (Vo *et al.*, 1999).

Among the chemicals that could cause health risks during the handling and engine combustion of petrol and diesel are benzene, toluene, ethylbenzene and xylenes (BTEX), ethanol, isopropyl alcohol, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), polycyclic aromatic hydrocarbons (PAHs), naphthalene, formaldehyde, cyclohexane, nonane, decane, CO, cycloalkanes, sulphur, NOx, aldehydes, ketones and metals (Al-Harbi *et al*., 2020:241). Some of these constituents present a concern due to their carcinogenic potential. It has been established that benzene is a carcinogen which have been stated earlier. Leukaemia, especially acute myeloid leukaemia (AML), is highly associated with prolonged exposure to benzene (IARC, 2025; Zahed *et al*., 2024). Acute toluene exposure can result in headaches, light-headedness, and sleepiness. Excessive doses might cause narcosis and even death. Breathlessness and coughing can result from exposure to ethylene and ethylbenzene, which can irritate the throat and lungs. Chronic exposure to BTEX has been linked to kidney and liver damage (Saeedi *et al*., 2024:100459; Neghab *et al*., 2015).

Even while gaseous molecules make up most of the air we breathe (78% N_2 and 21% O_2), the presence of tiny amounts of suspended particles, or aerosols, in the air has a significant effect on human respiratory health. In the urban environment, vehicle emissions are the primary source of fine PM (PM2.5 refers to PM with an aerodynamic diameter of <2.5 μm). Aerosols are a complex combination of liquid and solid particles (PM suspended in a gas that contains many pollutants. Various particle constituent classes, including organics, sulphates, and elemental carbon (EC), as well as metallic ash, metal oxides, inorganic ions, and toxic substances like PAHs, reactive oxygen species (ROS), carbonyls, and quinones, all form part of the chemical composition of DPM (Ristovski *et al.*, 2012). Exposure to these emissions has been linked to several negative health outcomes, such as higher rates of mortality and morbidity (Sydbom *et al*., 2001). The primary source of EC in both urban settings and the atmosphere is thought to be diesel engines. It has been demonstrated that the optical characteristics of DPM directly impact the radiative balance of the atmosphere and decrease regional visibility. In every instance, the size and makeup of the diesel exhaust particles have a direct impact on the environment. Ultrafine PM is defined as particles with an aerodynamic diameter of 100 nanometres (nm) or less. Fine particulate matter is defined as particles with an aerodynamic diameter of less than 2.5 μm (Kittelson et al., 1999:63). Diesel exhaust particles predominantly occur in the

submicron size range, with elemental carbon (EC) forming a substantial component of particles typically smaller than 1 µm. Given that a large fraction of diesel-related particles falls within the ultrafine and submicron range, the TSI SidePak™ AM520 was set to measure PM <0.8 µm in this study. These measurements are used as an indicator of submicron particulate concentrations potentially associated with diesel emissions, but not as a direct equivalent or substitute for DPM or EC (TSI, 2015). Total carbon (TC) represents the combined mass of EC and organic carbon (OC) present in an aerosol. Elemental carbon is the refractory, graphite-like component generated primarily from incomplete combustion processes and is used as an indicator of DPM. In contrast, OC consist of a diverse mixture of volatile, semi-volatile and non-volatile organic compounds that originate from emissions and secondary atmospheric formation. The ratio and contribution of EC and OC within the TC fraction, provides insight into source identification and interpretation of chemical composition (Karanasiou *et al.*, 2015; Bae *et al.*, 2004; Kim *et al.*, 2000). As stated, combustion processes greatly increase the amount of PM and HCA released into the atmosphere (Zamanian *et al.*, 2018). It can be derived that exposure to a combination of these HCAs poses serious health risks to workers since DPM's ultrafine particles can enter the bloodstream and penetrate deep into the lungs (National Institute for Occupational Safety and Health [NIOSH], 2020). The IARC has classified DPM as a recognised human carcinogen (group 1) that mostly causes lung cancer (Pronk *et al.*, 2009).

Real-time monitoring (RTM) has appeared as an essential approach for understanding dynamic exposure patterns in occupational environments. Unlike conventional sampling methods that provide time-integrated results, RTM instruments measure rapid fluctuations in airborne contaminants as they occur. This provides critical insight into peak emissions, activity-related exposure and on-site hazard identification. This advantage of RTM is particularly insightful at petrol-filling stations, where petrol-filling attendants' tasks, fuel types, fuel volume (L) and environmental conditions change throughout the shift. RTM enhances exposure assessment and provides on-site risk management. (Barrett *et al.*, 2019; Goede *et al.*, 2021; Cauda *et al.*, 2021).

1.1.3Legislation

The Regulations for Hazardous Chemical Agents (RHCA) stipulates specific OELs for occupational exposure to various chemicals such as those found in petrol, diesel, and their emissions and require employers to monitor exposure to these chemicals every two years on a risk-based approach (Department of Employment and Labour, 2021:3). In 2021, the Minister of Employment and Labour promulgated the RHCA, which included the addition of DPM as a HCA which is generated by diesel engines during combustion, with an established TWA OEL-RL of 0.16 mg/m^3 for TC over eight hours. The Mine Health and Safety Act (MHSA, 1998) have an 8-hour TWA of 0.1 mg/m^3 for EC. Benzene has a TWA-OEL maximum limit (OEL-ML) of 1 ppm and a skin notation. Toluene and ethylbenzene both have a TWA-OEL restricted (OEL- RL) of 40 ppm and a skin notation. Furthermore, xylene has a TWA-OEL-RL of 200 ppm and a skin notation. Although there are specific standards and regulations for occupational health and safety, an important regulatory and scientific consideration arises in the classification of DPM. The IARC classifies DPM as a Group 1 carcinogen. In contrast, the South African RHCA does not explicitly categorise DPM as a carcinogen within its regulatory framework and instead assigns it an OEL-RL rather than an OEL-ML). When a substance is classified as a carcinogen, no safe threshold of exposure can be assumed, and exposure control should follow the principle of keeping concentrations as low as reasonably practicable (ALARP). Therefore, compliance with the prescribed OEL-RL for DPM cannot be interpreted as the absence of risk, but rather as a regulatory benchmark for exposure control.

The absence of a carcinogenic designation in the RHCA may reflect the relatively recent introduction of the DPM OEL and a cautious regulatory approach, allowing industry time to adapt to the new standard before potentially imposing a stricter maximum limit. The divergence between international scientific classification and national regulatory designation highlights the need for critical interpretation of legislation. Future regulatory revisions may consider aligning the RHCA more explicitly with international carcinogenic classifications and re-evaluating whether a maximum limit designation would be more appropriate for DPM. Such alignment would strengthen worker protection and better reflect the current scientific consensus regarding diesel exhaust exposure.

1.2 Problem statement

The majority of South Africa's petrol-filling stations are situated in densely trafficked urban and semi-urban regions characterised by high traffic volumes. At these facilities, petrol-filling attendants are routinely exposed to petrol and diesel emissions. Due to the full-service nature of fuel dispensing in South Africa, petrol-filling attendants are particularly vulnerable to long-term DPM and VOC exposure since they are frequently stationed outside, in close proximity to fuel pumps, and around idling vehicles. In addition, customers and convenience store visitors may experience incidental exposure; however, occupational exposure among petrol-filling attendants remains of primary concern. The absence of self-service stations in South Africa increases the duration and frequency of direct exposure compared to settings where customers refuel their own vehicles (Naidoo *et al.*, 2016). Furthermore, exposure monitoring in small- to medium-sized or informal enterprises is often limited or inconsistent, potentially resulting in inadequate characterisation of occupational risk. Extended working hours, commonly 12-hour shifts, further compound the risk by increasing cumulative exposure over time, which may lead to adverse health outcomes (Keretetse, 2007). In terms of regulatory requirements, the RHCA (2021) mandates that approved inspection authorities (AIA) assess and evaluate the concentrations of HCAs in the air to which workers may be exposed to. Despite this legislative framework, there is a lack of publicly available data regarding occupational exposure of petrol-filling attendants in South Africa. The proposed study aims to assess the extent of petrol-filling attendants' exposure to VOCs (specifically the BTEX group) and DPM during their routine work shifts. The study will include area and personal exposure monitoring to determine exposure to HCAs by using conventional sampling methods and RTM instruments, respectively to provide a comprehensive assessment of exposure to HCAs in this occupational setting.

1.3 Research aims and objectives

This study aims to conduct monitoring of exposure to VOCs and PM at a petrol-filling station, with a specific focus on how various work activities contribute to exposure.

Objective 1: To conduct personal exposure monitoring of petrol attendants to VOCs and DPM by using NIOSH 1500/1501 and 5040 methods, respectively, during a 12-hour work

shift and compare results to OELs.

Objective 2: To use real-time monitoring to determine petrol-filling attendants' exposure to TVOCs and PM (<0.8 µm as an estimate for DPM) while they are performing different activities during a 12-hour work shift with a ppbRAE 3000 and TSI SidePak™ AM520, respectively.

Objective 3: To compare monitoring methods for DPM by using the TSI Sidepak™ AM520 (using the particles <0.8 µm surrogate as an estimate for DPM) and the conventional sampling method NIOSH 5040 (EC) during side-by-side monitoring.

1.4 Hypothesis

Based on the objectives of the study, the following hypotheses are formulated:

- Previous studies have demonstrated that exposure to VOCs and DPM at petrol-filling stations are activity-dependant, with refuelling and fuel-handling tasks producing high short-term emission peaks (Hilpert *et al.,* 2015; Sairat *et al*., 2015; Özbakır., 2024; Jayaraj, & Shiva Nagendra., 2023; McDermott, & Vos., 1979). Based on the literature, it is hypothesised that the exposure to TVOCs and PM (<0.8 µm as an estimate for DPM) will be different for each activity, with higher concentrations observed during tasks involving fuel handling and vehicle refuelling.

- The application note by TSI (TSI, 2015) indicated that the TSI Sidepak™ AM520's PM<0.8µm is an effective surrogate for DPM even though it does not provide the exact same concentrations. Nabiwa *et al*. (2025) indicated that RTM data and conventional sampling results can be compared effectively through the application of the Bland-Altman analysis, linear regression and correlation analysis. It is therefore hypothesised that the RTM results for PM (<0.8 µm as an estimate for DPM) will agree with conventional sampling (EC as per NIOSH 5040) according to Bland-Altman, linear regression and correlation analysis.

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CHAPTER 2 LITERATURE REVIEW

2.1 The industry

Petroleum is used for a vast and continuously growing range of purposes, that are essential to our daily lives, and for which cost-effective substitutes are not yet available. The refined product fuels automobiles and aeroplanes, products to grease machinery, natural gas for heating and manufacturing products such as plastics, which are used to produce thousands of different materials. Access to oil is becoming increasingly difficult due to the challenges to discover new oil reserves and rising extraction costs (Bridge & Wood, 2010). Historically, engineers and entrepreneurs began deliberately drilling for petroleum in the 19th century. The main use for crude oil at that time was as a source of kerosene to replace scarce whale oil for lamps, but with the invention of the automobile, the industry shifted to producing transportation fuels. The development of thermal cracking increased the yield of fuel from a given quantity of crude oil, and in 1936, Eugune Houdry's catalytic cracking process increased both the yield and quality of fuel. This led to the transportation industry developing exponentially (Vassiliou, 2009). Unfortunately, fuel, being a complex combination of hydrocarbon resources, is limited, and will eventually be depleted (Grace, 2013).

Natural gas and oil are often processed at a refinery thereafter, crude oil is moved from the wellhead to the refinery facility through pipelines, railroads, trucks, and sea routes. The petroleum products developed at refinery facilities are often shipped to industries or domestic users by tankers, railroad tank cars, trucks, or pipelines. Typically used in pipelines. However, tankers are not recommended for transporting compressed natural gas due to the high pressure and higher potential risk of an explosion. Rather, it is transformed into liquefied natural gas (LNG) first, and then LNG tankers are used to transport it to the consumers (Ahmad *et al*., 2022).

Oil and gas companies are divided into upstream, downstream, and midstream sectors. Exploration, extraction, or production of raw materials, including crude oil from wells, are all part of the upstream service for oil and gas. The midstream industry includes (a)

transportation services for the safe transportation of natural gas and crude oil via pipelines, tanker trucks and heavy goods vehicles (HGV); (b) warehouse services for the short-term storage of crude oil at oil field terminals; and (c) processing and blending services for the terminal's preliminary processing of crude oil. In the downstream stage, crude oil that is transported from different oil production locations is refined at an oil refining facility to create marketable and usable products like petrol, diesel, and LNG. Oil and gas exploration and production are costly as processes like oil and gas searching and exploration, drilling, and production from the drilled wells are involved (Wang *et al*., 2022). The exploration phase involves geologists who mostly follow seismic techniques to search for the location of oil and gas reserves beneath the surface of the earth. Before the start of the production process, wells are drilled to test the quality and quantity of oil and gas reserves. The extraction process involves collecting the oil deposits from the well through the deployed infrastructure. These deposits are then processed to remove the impurities. The goal of petroleum refineries, bulk fuel storage depots, and retail petrol-filling stations are to use the highest concentration of reliability while operating safely. Presently, older oil and fuel facilities face considerable challenges in achieving this goal (Ghaithan *et al*., 2024:494).

In response to these increased challenges, oil-producing countries throughout Africa are reviewing their current oil and fuel control measures and policies in South Africa specifically the Petroleum Products Regulations (2006) to improve the efficiency of regulatory institutions and, ultimately, to guarantee that the government receives maximum revenue from the resources that could accelerate economic growth at a national level. This implementation can be seen in Kenya, Tanzania and Ghana, where their governments recently enacted new oil and fuel legislation. The actions by these governments also influence a country such as Nigeria. Firstly, regional regulatory benchmarking is established by these reforms. Higher standards are set in the African energy sector when nations like Kenya, Tanzania, and Ghana implement updated petroleum laws that emphasise governance, transparency, and environmental protection. Nigeria, which is Africa’s largest producer of crude oil after Libya, is under more pressure to conform its legal system to new continental standards in order to maintain its credibility and competitiveness (Nwapi, 2020). Secondly, investors may perceive these reforming states as lower-risk environments if they provide stronger environmental protections, more

transparent laws, and more transparent governance. Nigeria is under competitive pressure to improve its own petroleum governance systems in order to draw in and keep foreign direct investment. Thirdly, policies are being standardised and disseminated throughout Africa. Regulatory alignment is frequently promoted by continental initiatives and regional economic communities. Modernising petroleum laws in several African states helps to move the continent closer to uniform standards in fields like community involvement, occupational health, and environmental compliance (Nwapi, 2020). Globally, there are different goals for each government (economic growth, social welfare, global governance and good governance) and the distinct socioeconomic environment in which the petroleum industry functions in South Africa influences the way it provides different services. As part of the labour and consumer protection laws, South Africa requires the use of petrol attendants, in contrast to many other countries that shifted to self-service fuel stations (SSFS). However, even though SSFS are becoming increasingly popular in most developed countries, it is still unknown whether such innovations can be adopted in emerging economies such as South Africa (Ulta, 2015:3).

Four main fuel companies in South Africa supply both petrol and diesel to most petrol-filling stations. These are British Petroleum (BP), Shell, Engen and SASOL based on refining capacity, national distribution infrastructure, retail footprint and historical market dominance (Moolla, 2015). Fuel types in the country include unleaded petrol: 93-unleaded and 95-unleaded LRP: lead replacement petrol, for older vehicles; and three variants of diesel. It is important to distinguish between 93-octane and 95-octane unleaded petrol in this study because the two fuel types differ not only in octane rating, but also in formulation, geographic availability, and potentially in their emission profiles(93-unleaded petrol is only available in the interior of South Africa and not in coastal areas because it is crucial for maintaining the performance and efficiency of vehicles in areas with lower altitudes). These are ultra-low sulphur diesel (10 ppm), which was introduced in 2013; low sulphur diesel (50 ppm); and standard (heavy-end) diesel (500 ppm). Each of the different fuel companies enhances its fuel by adding specific additives, which further changes the composition of the fuel, making monitoring and regulation difficult, but imperative (Moolla, 2015). The distinction between petrol grades 93 and 95 is their octane ratings, which determine the performance of an engine or aviation fuel. Some kinds of emissions may be lessened by increased octane, which causes a more thorough burn. However, the overall

efficiency and design of the engine can also affect the type of emissions that could pollute the environment (Stone, 1999).

In highly populated cities, the emissions created by the incomplete combustion of fossil fuels during vehicle traffic contribute to air pollution, which has a significant effect on air quality. In developed countries petrol-filling stations frequently employ self-service systems in which customers refuel their own vehicles. At these self-service stations, fuel vapours are typically controlled by integrated vapour recovery systems (VRS) which limit consumer exposure to volatile organic compounds (VOCs) and reduce environmental emissions. In contrast, petrol pumps in South Africa are not yet equipped with VRS, placing petrol attendants at risk of exposure (Scheepers *et al*., 2019:108670). Many governmental organisations have realised the effects of fuel emissions on air quality, human and environmental health and have placed different restrictions on fuel. One such restriction has been imposed by the European Union (EU), where they have regulated the amount of benzene in petrol (Pavlova and Ivanova, 2003). As of 2010, only 1% (v/v) benzene is allowed in petrol (Karakitsios *et al*., 2007, Moolla, 2015). The main risks associated with petrol and diesel exposure arise from impurities present in the fuels themselves, as well as from by-products formed during processing and combustion in internal combustion engines. These include PM, sulphur compounds, nitrogen oxides (NOx), carbon monoxide (CO), and VOCs (Abdellatief *et al.,* 2021:120112).

In South Africa, it is estimated that more than 60 000 petrol attendants are employed nationwide, making the country one of the few in the world where full-service refuelling at petrol-filling stations remains standard practice. Petrol attendants generally work according to rotating shifts that may extend into early mornings, long daytime hours, evenings, or overnight duties, depending on the operating hours of the station. A typical shift lasts between 8 to 12 hours and is often characterised by limited opportunities for rest. This extended time spent on-site increases the duration and intensity of occupational exposure to fuel vapours and vehicle exhaust emissions (NEF, 2020). Over time, repeated exposure can heighten health risks. Considering the petroleum industry's introduction, it is critical to understand which fuel components, like benzene, constitute a risk to users and how they affect the environment and workers.

2.2 Hazardous chemical agents at petrol-filling stations

A hazardous chemical agent (HCA) is any chemical substance that has the potential to cause harm to human health or the environment after exposure. According to the Occupational Health and Safety Act (OHS Act no 85 of 1993) employers should detect, evaluate, and manage occupational exposure to HCAs in accordance with the Regulations for Hazardous Chemical Agents (RHCA, 2021). The World Health Organisation (WHO) defines VOCs as compounds with a boiling point below 250°C at normal atmospheric pressure of 101.3 kPa. These are the organic compounds with varying volatility and lipophilicity that readily evaporate at room temperature. The primary sources of VOCs in the environment are industrial processes and the burning or evaporation of petroleum-based products (Khan *et al*., 2021). Fuels handled by petrol-filling attendants are derived from petroleum, which also contains VOCs, many of which are classified as HCAs. Therefore, petrol-filling stations are a major source of occupational exposure to these harmful substances (Bruce *et al*., 2002).

Petrol is a mixture of hydrocarbons. Petrol vapour contains 95% aliphatic and cyclic compounds of which 2% are aromatic compounds. The main concern with VOCs in ambient air is that they can react photochemically with free radicals to produce secondary smog and ozone. Most people are unaware of the chemicals present in the air until they stop at a petrol station and smell the pungent odour (Jia *et al*., 2022). Fuel formulations include alkanes, aromatics, oxygenates, and anti-knocking compounds (Batterman *et al*., 2005). Certain aromatic chemicals found in petrol, such as benzene, toluene, ethylbenzene, and xylenes (BTEX) (Bolden *et al*., 2015), as well as oxygenating substances such as methyl tert-butyl ether (MTBE) (McGregor, 2006), have raised health concerns. Employees at the petrol-filling station and drivers of fuel tankers are more exposed compared to the public sitting in their vehicles. Fuel attendants refuel vehicles with petrol and diesel. However, because diesel has far less volatility than petrol, research has mostly concentrated on petrol emissions and the ensuing health impacts. As a result, diesel exposure to VOCs is thought to be significantly lower than that of petrol. However, continuous exposure to VOCs, especially in ‘hot spot’ areas where concentrations of VOCs may be augmented, such as diesel refuelling bays, may still be of concern (Moolla, 2015:4).

2.3 Health effects associated with VOCs and DPMs at a petrol-filling station

General health effects reported by petrol-filling attendants are migraines, weakness and throat irritation, which have been linked to exposure to fuel and its components (Kuburi *et al*., 2023). The BTEX group, in relation to other VOCs, have more severe health effects following chronic exposure. When fuel containing hydrocarbons burns completely in an internal combustion engine, the only by-products should be carbon dioxide (CO_2) and water (H_2O). Although compression-ignition (CI) engines are highly efficient (burning up to 98% of the fuel), small amounts of unburned fuel and lubricating oil remain. These residuals produce a variety of incomplete combustion by-products. Diesel particulate matter (DPM) is one of these by-products. The composition of DPM is influenced by several variables, including how much diesel composition is diluted and how the composition reacts in the atmosphere after being emitted. Other important factors include the engine's operating conditions (like speed and fuel injection strategies), the use of emission control technologies (such as diesel particulate filters), how well the engine is maintained, and the types of fuels and lubricants used. Spark-ignition engines, also known as petrol engines, and CI engines, also known as diesel engines, are the two primary internal combustion engine types that release chemicals contributing to air pollution. The particulate matter (PM) emissions from these two internal combustion engine types vary significantly, with diesel engines being particularly challenging to manage due to the heterogeneity of the combustion process. Therefore, as diesel engines emit more PM (in 2012 measured to be by a ratio of 10-100) than the petrol engine and even though most of the gases in the air we breathe (78% N_2 and 21% O_2) are gaseous, concentrations of suspended particles can have a significant effect on human respiratory health. An adult male generally breathes 10.8 m^3 of air per day (at rest), with the volume increasing during physical activity (Ristovski *et al*., 2012). This is important when assessing occupational exposure, as the gender ratio of petrol attendants in South Africa is unknown. Ugwu *et al*., (2021:207) examined female labour dominance in petrol-filling stations in the South-Eastern States of Nigeria. Consequently, the total inhaled volume of air and the potential inhalation of airborne contaminants such as VOCs and DPM of petrol attendants are critical for exposure assessment and evaluating potential health effects associated with a petrol-filling station.

Ultrafine PM (UFPM) is defined as particles with a diameter of less than 100 nm, PM2.5 as coarse particles with a diameter of 2.5-10 µm. Respiratory, cardiovascular, and neurological systems are targets for the adverse health impacts of PM. PM2.5 and UFPM are especially dangerous for brain health because these particles enter the brain through a number of different mechanisms. PM with a diameter of less than 2.5 µm can breach the alveolar-capillary barrier in the lungs, enter the bloodstream, and then pass across the blood-brain barrier. Additionally, PM can enter the brain directly through the olfactory system's nasal epithelial mucosa (Lee *et al*., 2023:115565). PM in this regard is composed of metallic components such as titanium, lead, arsenic, and iron, as well as organic carbon (OC), elemental carbon (EC), sulphate, and nitrates. DPM is emitted into the air of the petrol-filling station, where petrol attendants are exposed to inhalation of these particles (Schlesinger, 2007). At low temperatures (5-10°C), engines and vehicle emissions-control equipment function less efficiently and cause incomplete combustion, with the formation of CO in higher concentrations. An increase in temperature on the other hand, intensifies volatilisation, which results in higher emission rates. Therefore, it is important to include seasonal changes (Tabinda *et al*., 2019). Diesel engines generate DPM through the incomplete combustion of diesel fuel, a complex combination of liquid and solid particles that is often defined by high concentrations of metals, as mentioned above, polycyclic aromatic hydrocarbons (PAHs), and elemental carbon. IARC classified Diesel Engine Exhaust as a Group 1 carcinogen which includes the gaseous and particle emissions and not only the particulate fraction. (IARC, 2012).

In some instances, BTEX and DPM affect the same biological systems, as seen in Table 2; therefore, it can be derived that when an individual is exposed to a mixture of these chemicals, the risks become profound.

Table 2: Adverse health effects associated with exposure to benzene, toluene, ethylbenzene, xylene (BTEX), and diesel particulate matter (DPM)

Health effect	Benzene	Toluene	Ethylbenzene	Xylene	DPM
Carcinogenicity	Group 1, X[A, F]	Group 3, X[B, H]	Group 2B, X[B, G]	Group 3, X[B, H]	Group 1, X[B, C, I]
Hematological	X[B]		X[A]		
Neurological	X[E]	X[E]	X[E]	X[B]	X[C]
Reproductive	X[D]	X[D]		X[D]	
Respiratory effect	X[B]	X[B]	X[B]	X[A]	X[C]
Cardiovascular effect				X[B]	X[C]
Immune suppression	X[A]				X[C]
Renal toxicity		X[A, C]	X[C]	X[C]	
Skin and eye damage		X[J]		X[J]	

A: (Saeedi *et al*., 2024:100459); B: (Zahed *et al*., 2024); C: (Lee *et al.,* 2023:115565); D: (Suaidi *et al*., 2022:235); E: (Khan *et al*., 2021); F: Group 1 carcinogen (IARC, 2018); G: Group 2B carcinogen (IARC, 2018); H: Xylene and toluene have been classified as a Group 3 (not classifiable as to its carcinogenicity to humans); I: Group 1 carcinogen (IARC, 2018); J: (Olabisi. 2018).

2.4 Case studies reporting on the health effects of VOCs and DPMs

In Potchefstroom, South Africa, a pilot study was conducted to assess the concentration of exposure of petrol attendants to VOCs from fuel Researchers used sorbent tubes to measure personal exposure. The study found that the exposure concentrations of benzene, toluene, and xylene (BTX) were 0.65, 0.73 and 0.31 mg/m^3, respectively (Keretetse *et al*., 2008). The exposure effect on DNA damage and lymphocyte repair was also evaluated. The petrol attendants were found to be exposed to concentrations of petrol VOCs lower than the South African occupational exposure limit (OEL) for constituent chemicals. A significant relationship was found between the volume of petrol sold during the shift and the average concentrations of benzene, toluene and the total VOCs measured, and a strong correlation existed between the proximity to petrol-filling stations with elevated VOC concentrations (Keretetse *et al*., 2008). The results from Elsayyad *et al*. (2025) revealed that petrol-filling stations emerged as social spaces, particularly for young adults and examined their health and the environmental implications. The study highlights the importance of co-ordinated urban planning and public health policies to ensure a balance between the social value of petrol-filling stations and essential safety regulations, thereby promoting healthier and more sustainable environments. The study indicated that air-quality measurements exceeded the WHO-recommended safety thresholds near seating and gathering areas. These studies support the conclusion that there is a positive relationship between worker health problems and the presence of VOCs in the workplace (Eltahir *et al*., 2016).

The results on the pulmonary function parameters, monitored using a simple random sampling technique among 52 petrol-filling attendants and 20 office workers of the Hooghly District in West Bengal, India, observed a significant reduction ($p < 0.001$) in the spirometry parameters. These parameters included forced vital capacity (FVC), forced expiratory volume in the first second (FEV1), forced expiratory flow (FEF (25-75%)), and peak expiratory flow rate (PEFR) (Solanki *et al*., 2015). The odds ratios for various respiratory diseases ranged from 1.12-3.12, indicating an increased risk of developing phlegm, asthma, cough and skin diseases among petrol-filling attendants (Mandal & Mukherjee, 2020). Petrol-filling attendants are more likely to get chronic obstructive pulmonary disease (COPD) due to breathing petrol fumes and automobile exhaust for extended periods of time (Begum & Rathna, 2012).

Shahne *et al*. (2022:118303) assessed PM2.5 chemical composition and exhaust emissions in the Niyayesh tunnel in Tehran, Iran, at two sites: the inlet and outlet of the tunnel. The study concluded that vehicles were the primary source of particle OC and ambient PM. PM concentrations were higher during morning rush hours than at night, indicating significant effects of traffic volume. The daily average of EC and OC was observed to be 3.4 ± 1.5 μg/m^3 and 28.1 ± 6.2 μg/m^3 at the inlet site, respectively, and increased to 5.9 ± 2.2 μg/m^3 and 40.8 ± 5.4 μg/m^3 at the outlet site, respectively. The study indicates the importance of DPM's chemical and physical characteristics, especially its OC content, due to the adsorbed organic compounds which can cause respiratory damage (Ristovski *et al*., 2012).

The potential synergistic impact of these hazardous chemical agents, more specifically BTEX and DPM, in occupational settings such as petrol-filling stations highlights the urgent need for effective exposure monitoring. It becomes essential to examine the relevant legislative frameworks and regulatory standards that are in place.

2.5 Legislation and regulatory framework

In South Africa, the Occupational Health and Safety Act (OHSA) No. 85 of 1993 and the associated Regulations for Hazardous Chemical Agents (RHCA, 2021) serve as the primary legal framework governing chemical exposure, as seen in Table 3 with the occupational exposure limit (OEL) values and the agent's notation. DPM was specifically

included as a regulated hazardous chemical agent (HCA) with an 8-hour time-weighted average restricted limit (TWA-RL) stated as total carbon (TC), TWA-OEL-RL = 0.16 mg/m³, when the RHCA (promulgated in 2021) revised the list of hazardous chemical agents. The RHCA provides TWA-OELs as well as notations (skin, sensitiser and carcinogen). This was the first time DPM was included in the general hazardous chemical standards (Department of Employment and Labour, 2021:3). Guidelines for surface and underground mining activities are also provided under the Mine Health and Safety Act (MHSA) No. 29 of 1996, many of which are relevant to petrol-filling stations and underground mining due to similar exposure risks. The preferred metric for DPM is elemental carbon (EC) rather than total carbon (TC), and the recommended limits provide 0.1 mg/m³ EC as an OEL. Table 3 provides a comparison of exposure limits and values for BTEX as per the Occupational Safety and Health Administration (OSHA), National Institute for Occupational Safety and Health (NIOSH) and American Conference of Governmental Industrial Hygienists (ACGIH), which are lower than South Africa's TWA values (NIOSH, 2018; ACGIH, 2025; OSHA, 2025).

Table 3: Comparison of Regulations for Hazardous Chemical Agents (RHCA, 2021), occupational exposure limits (OEL), notations and global guidelines for benzene, toluene, ethylbenzene, xylene (BTEX) and DPM

Chemical agent	OSHA under the US Department of Labour, (as of 11/12/2021)	NIOSH US federal agency responsible for conducting research, (as of 11/15/2021)	ACGIH TLV, American charitable scientific organization,	RHCA, 2021
	8-hour TWA (ST) STEL (C) Ceiling	Up to 10-hour TWA (ST) STEL (C) Ceiling		
Benzene	1 ppm (ST) 5 ppm	Ca 0.1 ppm (ST) 1 ppm	TLV TWA, 0.02 ppm Skin A1-Confirmed human carcinogen	TWA OEL-ML: 1 ppm, CARC, SKIN
Toluene	10 ppm (ST) 150 ppm (C) 500 ppm	100 ppm (ST) 150 ppm	TLV TWA, 20 ppm OTO- Ototoxicant A4- Not classified as a human carcinogen	TWA OEL-RL: 40 ppm, SKIN
Ethylbenzene	5 ppm (ST) 30 ppm	100 ppm (ST) 125 ppm	TLV TWA, 20 ppm A3-Confirmed animal carcinogen with unknown relevance to humans	TWA OEL-RL: 40 ppm, CARC, SKIN
Xylene	100 ppm (ST) 150 ppm (C) 300 ppm	100 ppm (ST) 150 ppm	TLV TWA, 20 ppm A4- Not classified as a human carcinogen OTO- p-xylene and other isomers containing p-xylene	TWA OEL-RL: 200 ppm, SKIN
DPM	No PEL	No REL	20 µg/m^3 as elemental carbon	TWA OEL-RL: 0.16 mg/m^3 for total carbon over eight hours

***The empty spaces in the table indicate that there are no notatios or values for DPM, CARC: Carcinogen; C: Ceiling limit; Ca: Potential occupational carcinogens DPM: diesel particulate matter; mg/m3; milligrams per cubic meter; ppm; parts per million; SKIN; Skin notation; STEL: Short term exposure limit; TLV: Threshold Limit Value; TWA OEL-RL: Time weighted average occupational exposure limit, recommended limit; TWA OEL-ML: Time weighted average occupational exposure limit, maximum limit; OTO: Ototoxin; PEL: Permissible Exposure Limit; REL: Recommended Exposure Limit**

2.6 Monitoring methods

2.6.1 Conventional sampling of VOCs and DPM

The NIOSH 1500/1501 (VOCs) and NIOSH 5040 (DPM) (NIOSH, 1994) methods are the accepted standards and are viewed as the standard analytical procedure to determine VOC and DPM (Fiedler *et al*., 2010) exposure, respectively. The Mine Safety and Health Administration (MSHA) uses the NIOSH 5040 method for DPM compliance via EC determination in underground mining. Underground miners frequently have exposure concentrations up to ten times higher than those in other sectors. Petrol stations frequently lack regular exposure evaluations, in contrast to underground mines, where stringent

legislation may have led to better-established monitoring and control mechanisms (Khan, 2017). To guarantee that their health is sufficiently safeguarded and to guide the creation of suitable control mechanisms and policy interventions, like those used in mining contexts, it is imperative to assess the occupational exposure of petrol-filling station attendants to DPM and VOCs (Khan, 2017).

Conventional sampling of VOCs, procedures use passive or active sampling techniques and DPM only active sampling to gather airborne pollutants for a predetermined period, usually a complete work shift (8 or 12 hours). Passive sampling relies on the natural diffusion of airborne contaminants onto a sorbent medium without the use of a pump. The contaminant migrates along a concentration gradient and is collected on an adsorbent (activated charcoal for VOCs). Active sampling uses a calibrated personal sampling pump to draw a known volume of air through a collection medium (filter or sorbent tube). This allows for accurate calculation of airborne concentration based on sampled air volume. Passive sampling is generally selected for cost-effective, full-shift VOC monitoring where moderate sensitivity is acceptable. Active sampling is preferred when higher precision, lower detection limits, short-term measurements, or particulate contaminants (such as DPM) are involved. (Hayward *et al.,* 2010). By using the TraceAir® II organic vapor badges (Assay Technology, Inc., Livermore, California, USA) recommended by the SANAS accredited laboratory the samples are subjected to chemical analysis for the two NIOSH methods. NIOSH method 1500 (for aliphatic and aromatic hydrocarbons) and NIOSH method 1501 (for aromatic chemicals, including BTEX) (Chaiklieng *et al*., 2019) are the most generally used procedures for VOCs. These techniques gather air samples in the worker's breathing zone using sorbent tubes (active sampling) usually filled with activated charcoal, which are connected to calibrated low-flow pumps (passive sampling). Gas chromatography with flame ionisation detection (GC-FID) is used to analyse the substances that have been collected after they have been desorbed using a solvent such as carbon disulphide (HSE & HSL, 1997). In addition, gas chromatography–mass spectrometry (GC-MS) may be employed, particularly where enhanced compound identification and confirmation are required, as it provides greater specificity through mass spectral characterisation of individual analytes. The chemical analysis results provide concentrations; thereafter, the time-weighted average (TWA) concentrations can be calculated. The TWA is a metric used to assess worker exposure over an 8-hour shift and

they may be directly compared to OELs, in South Africa's Regulations for Hazardous Chemical Agents (2021). Their incapacity to identify brief or peak exposures that could happen during high-intensity activities is a significant drawback. This may be important in determining the health hazards connected to sporadic high-concentration exposures.

The NIOSH 5040 method is the method for DPM. This technique uses a 37 mm diameter quartz fibre filter media to measure total carbon (TC) and quantify elemental carbon (EC), the primary surrogate for DPM (Ayers, 2017). EC is considered the most specific marker for DPM because it is less influenced by non-diesel sources. Other organic aerosols (such as cigarette smoke, lubricating oils, and petrol fumes) may contribute to TC, which lowers specificity in mixed-exposure settings like petrol-filling stations. As a result, although the method measures TC, the preferred exposure metric for DPM reported in regulatory and research applications is usually EC. A respirable aluminium cyclone sampler actively draws air through it, filtering out bigger particles and concentrating on the respirable portion. After that, the samples are subjected to thermal-optical examination, usually using a method like thermal-optical reflectance (TOR) or thermal-optical transmittance (TOT). The technique is thought to be appropriate for both occupational and environmental situations and offers extremely sensitive and specific assessments of DPM exposure, especially in sectors like mining, transportation, and fuel distribution services where diesel-powered machinery is often utilised (Pretorius & Grové, 2011). Conventional sampling provides advantages such as:

- Standardised methods and validated outcomes that comply with both domestic and global regulatory standards.
- Calculations can be used based on formulas to provide the concentrations of TWA exposure.
- Provides historical information that may be utilised for compliance and trend research.

Nevertheless, conventional sampling is associated with several restrictions:

- Avoids recording peak or brief exposures that can have immediate negative health impacts.
- Laboratory services are required for the specific identification of individual total

volatile organic compounds (TVOCs).

- Specialised equipment is expensive.
- Qualified and skilled laboratory workers must be appointed to perform analysis.
- Results are only accessible upon sample transportation and laboratory analysis; therefore, feedback is delayed (Floeder *et al.,* 2025; Smith *et al*., 2002; Ashley *et al*., 2000).

2.6.2 Real-time monitoring (RTM)

An important development in occupational hygiene exposure evaluation is RTM. Unlike conventional sampling techniques, which calculates a TWA over the course of a shift. RTM technologies provide continuous real-time input on the amounts of airborne contaminants (Sheehan *et al*., 2022). Effective hazard detection, risk reduction, and process optimisation depend on rapid identification of high-risk activities, peak exposure occurrences, and temporal exposure patterns. In workplaces such as petrol-filling stations, where activities like vehicle refuelling and underground tank refuelling can cause intermittent emission surges. Chemical exposures fluctuate greatly throughout the work shift, and RTM is becoming more and more important (Vosburgh *et al*., 2022). Benefits of RTM include:

- The determination of exposure patterns associated with certain activities or environmental circumstances.
- Quantification of short-term peak exposures, which are often underestimated by conventional methods.
- Increase in risk assessments' precision, particularly for occupations requiring sporadic or high-frequency exposure.
- Serves as guidance to enable immediate intervention should concentrations exceed pre-determined thresholds or OELs.
- Provide educational feedback to workers and supervisors on high-exposure behaviours or locations (Evans *et al.,* 2023; Goede *et al*., 2021; Cauda *et al*., 2022; Barrett *et al*., 2019).

Noll & Janisko (2013) conducted underground monitoring at four metal and seven stone mines in the United States of America. The primary aim was to evaluate the accuracy and

reliability of a wearable real-time monitoring instrument, Airtec, and to determine if this real-time method could replace the standard NIOSH 5040 method. The Airtec monitor, a real-time EC monitor based on laser extinction, was tested against the NIOSH 5040 method, that uses quartz fiber filters and thermal-optical analysis to determine EC concentrations. Side-by-side sampling setups were used, where both instruments collected data under the same environmental conditions. Statistical tests including Mann-Whitney Rank Sum and Levene's Test for the bias between Airtec and NIOSH 5040 results, were performed by Noll & Janisko (2013). Airtec results showed strong agreement with NIOSH 5040, with an average bias of 3±3%, meeting NIOSH accuracy criteria. 96% of Airtec measurements were within ±25% of the standard method. At concentrations >40 µg/m³ EC, 95% were within ±16% reliability. Therefore, Airtec provided timely and reliable real-time data, enabling quicker interventions and ventilation adjustments compared to delayed lab-based (conventional) methods.

2.6.3 Examples of real-time monitoring (RTM) instruments

Real-time monitoring (RTM) technology combined with conventional sampling methods offers a comprehensive framework for evaluating occupational exposure to VOCs and DPM. Understanding how these methods are applied in real-world occupational environments enhances their practical value. These monitoring techniques have been effectively applied in several case studies from various sectors, including petroleum refuelling stations, mining operations, to assess worker exposure and guide management actions. Despite its many advantages, RTM devices have several drawbacks. The interpretation of chemical-specific exposure can be complicated by instruments such as the ppbRAE, which measure TVOCs rather than single specific chemicals. Since PID operate by ionising VOCs using ultraviolet (UV) light with a specific ionisation energy. Because PID response factors vary according to the ionisation potential and molecular structure of individual compounds, instruments are calibrated using isobutylene as a reference gas. Measured concentrations are therefore reported as isobutylene equivalents unless compound-specific correction factors are applied. Proper calibration involves zero calibration (using clean air or nitrogen), span calibration with a certified calibration gas at a known concentration, and routine bump testing to verify instrument response prior to use. RTM devices require regular maintenance and appropriately trained individuals for

proper application, calibration, and data interpretation. Variables including temperature, humidity, and airflow can affect instrument results (Zhang & Mo, 2009).

Spinelle *et al.* (2015) highlight that recent advancements in sensor technology have significantly enhanced sensitivity, enabling some systems to detect benzene concentrations at ppb and in rare cases, even sub-ppb. The sensors evaluated include a range of technologies such as metal oxide semiconductors, electrochemical cells, PIDs, ultraviolet spectrometers, micro gas chromatographs (GCs), and electronic noses. Despite these improvements, distinguishing between BTX remains challenging when using PIDs. Even with the lowest available lamp energy (e.g., xenon at 9.6 eV), these compounds cannot be individually resolved due to their ionisation potentials being lower than the lamp energy, resulting in overlapping responses. Several manufacturers offer portable instruments capable of real-time VOC monitoring, including models like the Dräger Multi-PID 2, Baseline-Mocon VOC Traq, GrayWolf AdvancedSense DirectSens, Ion Science Tiger Select, and RAE Systems UltraRAE 3000 and ppbRAE 3000. Detection limits typically range from 50 ppb (Dräger) to 10 ppb (Ion Science and RAE Systems). While OEM sensors, such as PIDs, metal oxide, and amperometric types, are often insufficiently selective or sensitive for ppb-level benzene detection. Portable PID instruments with benzene-specific enhancements may offer a viable alternative for field applications. The research's findings indicate that highly sensitive and selective technologies, such as portable GC or ion mobility spectrometry (IMS) remain expensive for the market of low-cost sensors (Spinelle *et al.,* 2015).

Honeywell's ppbRAE (photoionisation detector) series measures TVOC concentrations in parts per billion (ppb) by ionising VOC molecules with UV and quantifying the resulting electrical current. This instrument was selected for the study due to its high sensitivity and ability to identify a variety of VOCs such as BTEX, as well as aliphatic hydrocarbons and other fuel-related organic vapours, making it particularly suitable for task-based exposure evaluations in dynamic environments. Its portable and lightweight design allows for both personal and area monitoring, while its capacity to transmit data in real-time or store results for later retrieval enhances its utility for remote oversight and detailed activity-based exposure evaluation (RAE Systems by Honeywell, 2024).

For PM (including DPM Surrogate), the TSI SidePak™ AM520 is utilised, which is a laser photometer designed to measure the mass concentration of airborne particles in real time. It may be set up to monitor certain size fractions (such as PM2.5, PM10, or even <0.8 µm as an estimate of DPM) when equipped with a cyclone or impactor intake. Yu *et al*. (2015) conducted a controlled laboratory study to assess the performance of five real-time monitoring instruments, recognising that such devices can be influenced by varying environmental conditions. The instruments evaluated included the Airtec real-time DPM/EC Monitor, TSI SidePak AM520 (PM2.5), TSI Condensation Particle Counter 3007, microAeth AE51 Black Carbon Aethalometer, and the Langan T15n CO Monitor. Tests were conducted under different temperatures (55°, 70°, and 80°F), relative humidity (10, 40, and 80%) and two DPM concentrations (50 and 200 µg/m³), within a controlled exposure chamber. Among the instruments, the Airtec monitor demonstrated strong agreement with the NIOSH Method 5040 for EC (r^2 = 0.84; slope = 1.17±0.06; N = 27), although it tended to overestimate EC concentrations by approximately 17%. Importantly, variations in temperature, humidity, and DPM concentration did not significantly affect the 2-hour averaged EC readings from the Airtec compared to the reference method.Overall, the real-time monitors deviated by no more than 20% from the NIOSH reference values. Simultaneous monitoring of temperature and relative humidity is essential in field investigations to understand and adjust for environmental impacts on real-time monitoring data.

According to Shriwas and Pritchard (2020), there are three real-time DPM sensors commercially available: (1) the Pinssar READER, a laser-light scattering photometry, (2) the Sunset Laboratory Inc., Model 4 Organic Carbon and Elemental Carbon (OCEC) Field Analyzer, and (3) the Magee Aethalometer. The authors reviewed relevant papers and manufacturers' websites to evaluate these available monitoring and control components and applications used in Canadian, Australian, and United States mines. The objective was to define the current state of monitoring and control system technology and use, identify existing health and safety application gaps for future research, and analyse improved ventilation solutions that could result in a safer and healthier mine environment. The study concluded that current RTM technologies for DPM, silica and dust are not yet fully integrated into the mine monitoring systems, mostly because the instruments remain limited or prohibitively expensive. Although devices such as the Magee Aethalometer,

Sunset OCEC and Pinssar provide short-term or partial real-time capability, there is an industry need for durable, cost-effective instruments and integrating monitoring systems with ventilation models are essential for effective emergency planning and real-time insight into contaminant behaviour during critical events. The review also highlights a key insight: technology alone isn't enough. While hardware and software play a crucial role, human oversight and a direct connection to the ventilation system are essential for maintaining safe operations.

In a 2019 study conducted in the United States, by Parks *et al*. explored the potential of mid-infrared spectrometry as a more practical alternative to traditional thermo-optical methods for real-time, portable monitoring of DPM. Their research focused on developing a technique to measure both OC and EC across a wide range of OC/EC ratios. To validate their approach, they analysed diesel exhaust samples generated in the lab as well as in practice samples collected from two active mining sites. Using a Bruker Alpha FT-IR spectrometer with a diffuse reflection setup, alongside a Sunset Laboratory OCEC analyser (Model 5L) following the NIOSH 5040 method, they found a strong correlation with the standard method —achieving an r^2 of 0.96 for both OC and EC. These promising results suggest that FT-IR technology could provide portable, near-real-time device capable of accurately assessing DPM exposure in the field (Parks *et al*., 2019).

Miller *et al. (*2007) evaluated the feasibility of using a direct-reading photometer to estimate EC emissions directly from diesel engine tailpipes against the NIOSH Method 5040 as a reference. The photometer chosen for this evaluation was the Thermo Electron Personal DataRAM 1200 (PDR). A diesel generator powered by a 3-cylinder, 1.5 L Isuzu engine was used and operated at three loads (kilowatt): 0 kW, 2 kW, and 6 kW. The exhaust was sampled directly from the tailpipe. The initial readings from the PDR photometers displayed sinusoidal fluctuations, which were likely caused by temperature fluctuations in the engine. After relative humidity (RH) and calibration against the reference method, the PDR measurements correlated strongly with the EC values obtained from filter analysis; with an r^2 of 0.97 and a regression slope of 0.89. These results lead to the conclusion that direct-reading photometers like the PDR can reliably estimate EC emissions when properly calibrated and adjusted for RH.

The SidePak™ personal aerosol monitor was selected for this study due to its application note proving effectiveness in occupational hygiene applications, particularly for monitoring DPM and respirable dust and its ability to identify brief surges in exposure (TSI, 2015). Jiménez *et al*. (2011) compared the performance of the TSI Aerodynamic Particle Sizer (APS) and the TSI portable photometer SidePak™ to measure airborne oil mist particulate matter (PM) with aerodynamic diameters below 10 µm, 2.5 µm and 1 µm (PM10, PM2.5 and PM1). The study concluded that the TSI SidePak™ is a very useful instrument for personal monitoring in occupational hygiene due to its light weight and quiet pump. However, it may not be suitable for the measurement of particle concentrations from oil mist.

Real-time monitoring instruments are frequently employed in conjunction with conventional sampling techniques. Real-time risk management and compliance monitoring are made possible by this hybrid method (Noll & Janisko, 2013).

2.6.4 Case studies with a focus on different methods

The following case studies illustrate the application of different methods, providing evidence of effectiveness and challenges within different occupational contexts. Adebiyi *et al*. (2015) assessed size-segregated suspended particulate matter (PM2.5 and PM10-2.5) in ambient air quality at four major petroleum filling stations in Ile-Ife, Nigeria. A double-staged Gent stacked filter sampler collected size-segregated PM with Whatman polynuclepore filters. This was performed over 11-hour daily sampling periods for several weeks, and a Particle-Induced X-ray emission (PIXE) via a Tandetron accelerator were used as a method and for analysis. A total of 25 elements were analysed. The results indicated that PM10 values exceeded the WHO's 24-hour guideline of 50 µg/m³ at all stations, ranging from 82-130 µg/m³, while PM2.5 concentrations ranged from 16-46 µg/m³, exceeding the WHO's 25 µg/m³ limit at most stations.

Tabinda *et al*. (2019) performed a study at petrol-filling stations in Lahore, Pakistan. The study was done during the summer and winter seasons at 50 randomly selected petrol stations representing five major petroleum companies: PSO, Attock, Shell, TOTAL, and Caltex. During the study, TVOCs, CO, CO_2, NO, NO_2, SO_2, O_3, PM2.5, PM10, sound

levels, humidity, and temperature were measured with HAZ-Scanner (HIM 6000) for gas and particulate monitoring, sound meter, thermo-hygrometer and analysis using SPSS 19.0, with one-way ANOVA to identify significant seasonal and site-based differences. The results indicated that TVOCs were significantly higher in summer than in winter; PSO and TOTAL had the highest concentrations while Attock and Shell had acceptable levels. The results for CO & CO_2 were higher in winter, attributed to poor combustion in cold temperatures. All stations showed values above normal ambient limits. For NO & NO_2 the results showed NO was higher in winter, NO_2 was higher in summer, with some values exceeding international limits. For O_3 and SO_2 the results showed both higher during summer with SO_2 often exceeding permissible limits, likely due to sulphur in fuels. The results for PM2.5 and PM10 are both higher in winter, likely due to stagnant air and reduced dispersion. All exceeded the WHO's and national standards for ambient air quality.

Mukherjee *et al*. (2016) conducted a study in Kolkata City, India, a heavily populated metropolitan location with heavy traffic, on PM10 and VOCs, specifically BTEX compounds, by evaluating biomarker levels in urine, measuring the pulmonary function and examining the heme metabolism alterations because of such exposure. For PM10 and VOCs, they used 8-stage cascade impactors and sorbent tubes (per NIOSH standards). Urine samples were analysed for BTEX metabolites using high-performance liquid chromatography (HPLC). Biomarkers included trans trans-mercapturic acid (tt-MA), S-phenyl mercapturic acid (SPMA), hippuric acid (HA), mandelic acid (MA) and methyl hippuric acid (MHA) and the pulmonary function test (PFT) was measured spirometrically. ∂-Aminolevulinic acid (ALA) and porphobilinogen (PBG) in lymphocytes were measured spectrophotometrically following column chromatographic separation. Spirometry was utilised to assess PFT parameters such as forced vital capacity (FVC), forced expiratory volume in one second (FEV_1), and peak expiratory flow rate (PEFR). The statistical analysis was done by T-tests, linear regression (r^2), and correlation analysis using SPSS. The results indicated that PM10 levels exceeded national limits at both petrol pumps and traffic zones with the highest personal exposure to benzene among traffic police, and the highest toluene exposure among petrol workers. Significantly higher levels of tt-MA and SPMA were detected in the exposed groups vs. the control group. A strong correlation between benzene levels in air and biomarker levels in urine ($r^2 > 0.7$) was found.

Additionally, altered blood cell counts in exposed workers, including decreased platelets (suggestive of hematotoxicity from benzene) were noted. Reduced FVC and FEV_1 in petrol pump workers and traffic police were identified. The results indicated that 11.1% of petrol workers and 8.3% of traffic police had impaired lung function (restrictive and/or obstructive patterns). A greater decline in lung function correlated with increased years of exposure.

2.6.5 Summary

The petroleum industry remains important to global and South African economies, supplying fuel for transportation and providing work opportunities. The petroleum extraction, refining and distribution are divided into upstream, midstream and downstream operations, with petrol-filling stations being a downstream link between the industry and the public. South Africa still employs petrol-attendants, who manually refuel vehicles, placing the workers at continuous risk of exposure to HCA, particularly VOCs (from evaporative fuel emissions) and DPM (from engine combustion of idling vehicles in high-traffic environments).

Volatile organic compounds (VOCs), including the BTEX group, are all hydrocarbons derived from petroleum, which some are recognised for their carcinogenic and neurotoxic effects. An important factor to include is: DPM is classified by the IARC as a Group 1 carcinogen. Studies have indicated that exposure to these agents, even below the OELs, may cause genotoxicity, respiratory impairment and systemic toxicological effects among petrol-filling attendants. Because of this risk, exposure assessment and regular monitoring in the occupational setting of petrol-filling stations remain a focus.

Chemical exposure is governed, legislatively, through the Occupational Health and Safety Act (OSHA) and the Regulations for Hazardous Chemical Agents (RHCA, 2021). The 2021 update of the RHCA indicated that DPM is now a regulated agent with an TWA-OEL-RL of 0.16 mg/m^3 TC, while BTEX exposure limits are expressed in ppm. Compared to international standards (OSHA, NIOSH and ACGIH), South Africa's OELs are generally higher, indicating less stringent exposure limits.

The conventional sampling methods, such as NIOSH 1500/1501 and 5040, which are the

standardised analytical procedures, provide validated results, while RTM, like the ppbRAE 3000 and TSI SidePak™ AM520, allows dynamic exposure results during specific activities. The literature motivates the integration of both methods to provide a comprehensive understanding of exposure and risks.

Overall, the literature review and the studies referenced highlight the significance of this study on real-time, activity-based exposure to VOCs and DPM among South African petrol-filling attendants.

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CHAPTER 3 MANUSCRIPT FOR ARTICLE

The article is written in accordance with the guidelines of the Harvard Referencing Guide and follows the United Kingdom English spelling, with exceptions made for the names and references used.

General principles for referencing: The referencing list must start on a new page. All sources must be sorted into alphabetical order according to the author. “Bullets” or numbering must not be used, and the line spacing must be 1.5, and the spacing must be aligned and not justified. Journal names must be italicised, and all entries must have a full stop at the end except when a DOI, permanent internet link or hyperlinked URL is used.

Examples:

525 TraceAir® II Organic Vapor Monitor. 2025 Assay Technology. https://www.assaytech.com/product/525-traceair-organic-vapor-monitor Date of access: 18 Feb. 2025.

Acar, T.O. 2024.Comparing Measurement Reliability Estimation Techniques: Correlation Coefficient vs. Bland–Altman Plot, *Measurement: Interdisciplinary Research and Perspectives*, 22(4), pp. 5. https://doi.org/10.1080/15366367.2023.2266306

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Monitoring exposure of total volatile organic compounds and particulate matter at a petrol-filling station

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3.1 Abstract

Petrol-filling attendants in South Africa are occupationally exposed to hazardous chemical agents (HCAs), particularly volatile organic compounds (VOCs) associated with fuel handling and diesel particulate matter (DPM) generated from diesel-powered vehicle exhaust. In this context, it is important to distinguish clearly between these agents. Total volatile organic compounds (TVOCs) represent the aggregate concentration of multiple VOCs present in petrol vapours, whereas individual VOC constituents, such as benzene, toluene, ethylbenzene, and xylene (BTEX) are chemically distinct compounds with specific toxicological profiles. Similarly, diesel particulate matter (DPM) refers specifically to the submicron particles formed during diesel engine combustion, which differ in composition and health risk from general ambient particulate matter (PM). Exposure monitoring of three petrol attendants and one area was conducted during a 12-hour working shift over five consecutive days in a winter month (personal: n=15; area: n=5). BTEX and DPM were monitored by using conventional sampling methods in combination with real-time monitoring (RTM) of TVOCs and PM. Both personal and area monitoring of BTEX and DPM with results including elemental carbon (EC) and total carbon (TC) with the focus on EC were monitored by using NIOSH 1500/1501 and 5040, respectively and TVOCs and PM <0.8 µm (as an estimate of DPM) were monitored using RTM (ppbRAE 3000 and TSI Sidepak^{TM} AM520). No statistically significant difference was found between results for personal and area samples, nor between different days (personal monitoring), for BTEX and EC. However, a statistically significant very strong positive Spearman correlation (ρ = 0.975; p <0.05) was observed for personal benzene exposure and the amount of fuel dispensed. The exposure to TVOCs, while performing different activities, indicated a difference in exposure concentrations and peak concentrations up to 10 000 ppb while refuelling vehicles with petrol and lower peaks when refuelling vehicles with diesel. The lowest peaks were observed during vehicle assistant services and cash and retail operations. During the delivery of fuel and underground tank refuelling, petrol reached higher peaks, up to 7 000 ppb, than diesel, only up to 600 ppb. PM <0.8 µm (estimate of DPM) results of four different petrol attendants over a 12-hour shift indicated short-term peaks which were higher for smokers than non-smoking petrol attendants during the period of five minutes that they smoked. The comparison between the NIOSH 5040 and RTM methods for DPM indicated a strong agreement with minimal bias (personal: 0.050

mg/m^3 ± 0.058; area: EC 0.041 mg/m^3 ± 0.043). Although exposure concentrations were below the regulatory limits of the adjusted 12-hour time-weighted average (TWA) occupational exposure limit (OEL), petrol attendants experience continuous low concentrations of exposure, which may pose long-term adverse health effects.

3.2 Introduction

The petroleum industry plays an important role in supplying fuel to consumers in South Africa and worldwide, with over 10 million vehicles in South Africa relying on petrol and diesel as primary energy sources. Many petrol-filling stations are located along primary routes in South Africa and support over 100 000 job opportunities, including petrol attendants (NEF, 2020). Petrol and diesel, which are refined from crude oil, contain hazardous chemical agents (HCAs) such as hydrocarbons and other compounds. After combustion, HCAs such as particulate matter (PM) are released from the exhaust, while volatile organic compounds (VOCs) in fuel are released while performing tasks such as dispensing fuel, underground tank refuelling during delivery and assisting with vehicle maintenance, all of which increase the potential exposure to HCAs (Kaiser *et al*., 2007; Akram, 2018). VOCs such as benzene, toluene, ethylbenzene, and xylenes (BTEX) are emitted during refuelling of vehicles with petrol or diesel and can cause severe health effects after extended exposure times, even at low concentrations (Al-Harbi *et al*., 2020). The International Agency for Research on Cancer (IARC) classified benzene as a Group 1 carcinogen (sufficient evidence of carcinogenicity in humans), toluene as Group 3 (indicating insufficient evidence in both human and animal studies to determine carcinogenicity), ethylbenzene as a Group 2B carcinogen (possibly carcinogenic to humans), while xylene has not been classified (Soni *et al*., 2018). Diesel particulate matter (DPM), a form of ultrafine PM, contains elemental carbon, organic compounds, and trace metals, and is also classified as a Group 1 human carcinogen (IARC, 2025). The VOCs and DPM have been linked to respiratory diseases, cancer, and other systemic health impacts, with petrol attendants at particular risk due to prolonged shifts and constant proximity to emission sources (Zamanian *et al*., 2018). South Africa's Regulations for Hazardous Chemical Agents (RHCA) (2021) contains time-weighted average (TWA) 8-hour occupational exposure limits (OELs) for many fuel-related compounds (BTEX) and DPM (0.16 mg/m³ total carbon), which is a risk-based requirement (2-yearly) monitoring by approved inspection authorities (AIAs). The Mine Health and Safety Act's (MHSA, 1998) adjusted 12-hour OEL of 0.07 mg/m³ for EC was used as the RHCA does not have EC limits. Benzene has a TWA-OEL maximum limit (TWA OEL-ML) of 1 ppm and a skin notation. Toluene and ethylbenzene both have a TWA-OEL restricted limit (OEL-RL) of 40 ppm and a skin notation. Furthermore, xylene has a TWA-OEL-RL of 200 ppm and a skin

notation.

An important development in occupational hygiene exposure evaluation is real-time monitoring (RTM). Unlike conventional sampling techniques, which only give TWA concentrations over the course of a shift, RTM technologies provide continuous, near real-time data on the concentration of airborne contaminants (Sheehan *et al*., 2022). Effective hazard identification, risk reduction, and process optimisation depend on the ability to quickly identify high-risk activities, peak exposure occurrences, and temporal exposure patterns. In workplaces where chemical exposures fluctuate greatly throughout the work shift, such as petrol stations where different activities take place, RTM is proving to be increasingly valuable due to its robustness, workplace use, and price concerning return on investment (Vosburgh *et al*., 2022). The instruments offer several advantages, including short delay between measurements and the reporting of results, rapid detection and recording of fluctuations in concentration, providing both peak and TWA concentrations. Providing real-time exposure aids workers to adjust habits during work shifts and supports informed decision-making regarding control measures (Coffey *et al*., 2008). An RTM instrument, such as Honeywell's ppbRAE, can be useful to determine TVOC concentrations of task-based exposure evaluations in near real-time. Another RTM instrument of interest is the TSI SidePak™ AM520, a laser photometer that measures the mass concentration of airborne particles. This instrument can be used to monitor certain size fractions (such as PM2.5, PM10, or even <0.8 µm as an estimate of DPM) when equipped with a cyclone or impactor intake. The lack of publicly available data on HCA exposure at petrol-filling stations in South Africa highlights the need for studies that quantify personal exposure and area concentrations to VOCs that are emitted during vehicle refuelling and underground tank refuelling, providing recommendations for control measures to lower exposure, protect worker health and comply with legislation within this working environment. This study aimed to conduct monitoring of exposure to VOCs and PM at a petrol-filling station, with a specific focus on how various work activities contributed to exposure.

3.3 Materials and methods

3.3.1 Workplace description

This study was conducted at a petrol-filling station that was selected due to its high traffic load, with an average of 23 916 litres (L) of petrol and diesel being sold per day. The station has seven pumps, of which three supply only 10 ppm diesel, while the remaining pumps offer 93 or 95 ppm petrol as well as 10 ppm diesel (Figure 1).

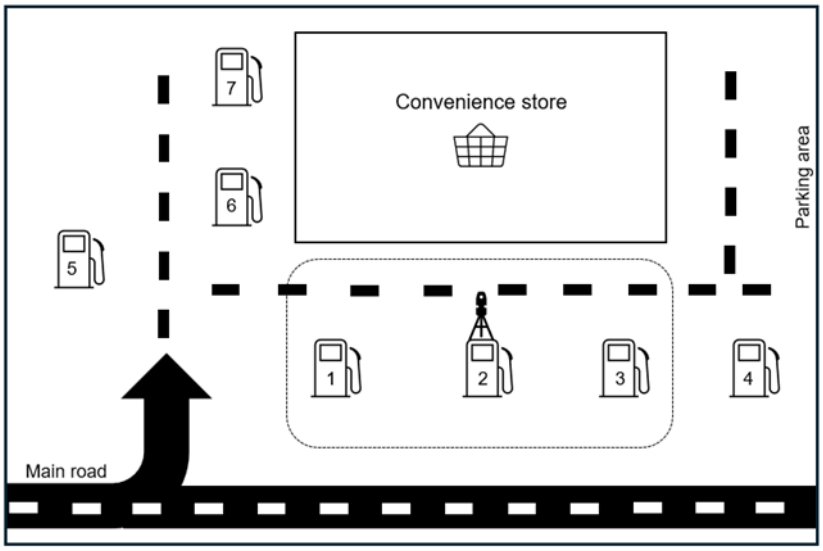


Figure 1: Petrol-filling station with seven dispensing pumps. Pumps 5-7 only supply diesel, while pumps 1-4 dispense petrol and diesel. The tripod for area sampling was positioned next to pump 2, closest to the convenience store.

Personal and area monitoring of VOCs were conducted using NIOSH 1500/1501, and for DPM using NIOSH 5040. RTM of personal exposure and area monitoring of TVOC and particles <0.8 µm were conducted as well. The exposure of three different petrol attendants was monitored per day over the course of five days (n=15) to achieve representable data, covering their entire 12-hour shifts. The sample size and number of measurements were determined based on occupational hygiene sampling principles, practical feasibility and due to instrument limitations. Three petrol-filling attendants were sampled to represent variability within the similar exposure group (SEG), and 15 total samples were collected to ensure sufficient repeated measurements to characterise exposure pattern and this amount is statistically acceptable (Waterman & Baxter, 2005). Different activities are performed at these petrol-filling stations. These activities include

refuelling of vehicles, the refuelling of underground tanks during fuel delivery, assisting with vehicle maintenance, including checking the tyre pressure and engine oil level and washing windows during or after refuelling. The duration of these activities depends on the amount of fuel being supplied (L). During the study, the following control measures or the lack thereof, were observed: no vapour recovery systems (VRS) were installed on the pumps, and the petrol attendants wore safety shoes and coveralls. An extensive, standardised safety control routine being performed by the driver of the fuel tank truck was also observed.

During the time of the study, there was a fuel shortage on day two and all diesel vehicles were diverted to pumps 5-7 (Figure 1) with only petrol vehicles being able to refuel at pumps 1-4 (Figure 1)

3.3.2 Volatile organic compound personal and area monitoring

This study used real-time monitoring instruments together with conventional methods to assess petrol attendants' exposure to VOCs during different activities. The ppbRAE 3000 (Honeywell, North Carolina, USA) was used for TVOC exposure measurements (ppb) at a flow rate of 450 ml/min with one-second logging intervals. One instrument was hand-held (for task-based spot measurements) and used to follow a petrol attendant during vehicle refuelling, underground tank refuelling during fuel delivery, vehicle assistant services and cash and retail operations to monitor TVOC exposure peaks in the breathing zone. A second instrument was mounted on a tripod at a height of 1.5 m to align with the standard breathing zone height (American Industrial Hygiene Association [AIHA], 2019). The tripod was positioned at the central pump, closest to the convenience store (Figure 1).

Both ppbRAEs were factory-calibrated by the manufacturer, and each instrument was supplied with a calibration certificate (Annexure B). To determine the instrument's baseline response in the absence of pollutants, zero calibration was carried out using clean, VOC-free air by attaching a charcoal (activated carbon) filter, supplied by the manufacturer, to the inlet of each instrument. The filter removes trace VOCs from ambient air, enabling the PID to stabilise at a true zero reading. Span calibration was carried out immediately afterwards to set the detector's response to a known concentration using a certified 100

ppm isobutylene calibration gas with the supplied calibration adaptor and flow rate regulator compatible with the gas cylinder. Span calibration enables the instrument to register a stable reading to match the reference concentration of isobutylene. At the end of each sampling day, both ppbRAEs were inspected to ensure no errors, alarms or instrument malfunction occurred during exposure monitoring, and the recorded data were downloaded using ProRAE Studio II software (Honeywell, North Carolina, USA).

Conventional personal exposure monitoring was conducted using TraceAir® II organic vapor badges (Assay Technology 525). This method was selected based on the recommendation of the accredited analytical laboratory that performed the sample analysis (Assay Technology, Inc., Livermore, California, USA). The Assay Technology 525 badges are designed for extended sampling durations, typically ranging from 8 to 24 hours, depending on the target analyte concentration and environmental conditions. Their uptake rate is predefined, allowing time-weighted average (TWA) concentrations to be calculated over extended shifts. Therefore, a 12-hour sampling period falls within the operational range specified by the manufacturer. While the badge itself may not constitute an accredited method in isolation, the analytical procedure performed by the accredited laboratory aligned with recognised methods such as NIOSH or OSHA equivalents. The selected sampler must, be compatible with validated analytical procedures, which was confirmed by the laboratory prior to use. The expected BTEX concentrations at petrol filling stations were considered, which are typically well below levels that would overload the sorbent during a 12-hour period to remain within the validated analytical range (King *et al*., 1982: Stefaniak *et al.,* 2019). The TraceAir® II badges were also used because petrol attendants were already wearing two sampling trains (NIOSH 5040 and the SidePak™ AM520), and it was determined that air movement occurred over the badge, allowing passive sampling to be an appropriate strategy. On the sampling day, badges were removed from their packaging, unique serial numbers corresponding to designated workers or sampling areas were assigned, and the badges were attached to the collars of the petrol attendants within the breathing zone (personal sampling). One badge was also attached to the tripod (area sampling) (Figure 1). No additional preparation was required. A total of 15 personal samples, five area samples, and three field blanks were collected during the study. The field blanks were included to detect any potential contamination that may have occurred during handling, transport, sampling train attachment or exposure to

the field environment. Additionally, three laboratory blanks were included to assess possible contamination introduced during sample preparation, storage, or analytical processing in the laboratory.

Following the sampling, the badges were sent to a SANAS-accredited laboratory for analysis of individual VOCs according to the methods for the determination of hazardous substances (MDHS) method number 88. Samples were analysed on an Agilent Technologies 7890A GC-FID system. The analysis method was a dual-column method (J&W DB-624 capillary gas chromatography column and J&W DB-WAX capillary gas chromatography column), with verification on an Agilent Technologies 7890A GC equipped with an Agilent Technologies 5975C VL MSD. Sorbents were soaked in carbon disulphide and left to stand for 30 minutes with intermittent agitation. An exact volume (1–3 µl) of the liquid was injected into a hot injector, where all compounds were volatilised and transferred in a constant flow of nitrogen carrier gas to two capillary columns at 35°C. A split injector was used. As each compound exited the column, it passed through a flame ionisation detector (FID). This signal was monitored and recorded as peaks corresponding to individual compounds. The instrument was calibrated using a set of standards prepared by adding measured amounts of each compound to volumetric flasks filled with carbon disulphide. The data station was programmed to calculate and directly report the concentrations of each compound from the peak areas within the calibration range. The limit of detection (LOD) for individual VOCs was 0.50 µg for each VOC.

3.3.3 Particulate matter personal and area monitoring

The SidePak™ AM520 (TSI Incorporated, Shoreview, Minnesota, USA), a light-scattering laser photometer equipped with a 0.8 µm cyclone attachment, was used to measure particles <0.8 µm (as an estimate of DPM). The instrument was calibrated at a flow rate of 1.7 L/min with a TSI primary calibrator 4146 (TSI Incorporated, Shoreview, Minnesota, USA). The sampling train was attached to the petrol attendants (three attendants per day over five days; except on day five, there were only two attendants; n=14) with the cyclone attached to the workers' collars within the breathing zone. The sampling train for area monitoring (n=5; one per day, over five days) was attached to the tripod, which was placed in the middle of the station (Figure 1). All SidePak™ AM520 units were factory-calibrated by the manufacturer. Each instrument was supplied with a calibration certificate (Annexure

B), zero calibrated with a zero filter and their flow rates were calibrated to 1.7 L/min before and verified after sampling according to the manufacturer's instructions by using a flowmeter and an established deviation of <5% between the before and after measurements. At the end of each sampling day, data were downloaded using TSI TrakPro 5 software (TSI Incorporated, Shoreview, Minnesota, USA). The SidePak™ AM520 logged the real-time data every second in $\mu g/m^3$ and calculated the 8h-TWA after each measurement.

Conventional personal exposure monitoring of DPM using the NIOSH 5040 method was conducted simultaneously (side-by-side monitoring) with the SidePak™ AM520. Particles were collected using a sampling train consisting of a sampling head (a cassette containing a 37 mm quartz fibre filter connected to an aluminium cyclone (with a 50% cut-point at 4 µm) attached with tubing to a GilAir® Plus sampling pump (Sensidyne, St. Petersburg, FL, USA) which was set at a flow rate of 2.5 L/min. On the sampling day, the sampling head and GilAir® Plus sampling pump (Sensidyne, St. Petersburg, FL, USA) were assigned unique serial numbers corresponding to designated workers and sampling areas. The sampling train was attached to the petrol attendants (n=15; three attendants per day, over five days) with the sampling head attached to the workers' collars within the breathing zone. The sampling train for area monitoring was attached to the tripod and was placed in the middle of the station (Figure 1) (n=5; one per day, over five days). The sampling pumps were calibrated to 2.5 L/min using a BIOS Defender 510 DryCal calibrator (MesaLabs, Lakewood, Colorado, USA). After sampling, the flow was verified, establishing the post flow rate that did not differ by >5% from the pre-sampling flow rate. Following the sampling period, all the filters (including three field blanks and three laboratory blanks) were sent to a SANAS-accredited laboratory for analysis of elemental carbon (EC) and organic carbon (OC). Analysis was performed according to the NIOSH 5040 method using a Sunset Laboratory Inc. Organic Carbon / Elemental Carbon (OCEC) Analyser (Sunset Laboratory Inc., Tigard, Washington County, Oregon, USA). A uniform portion was removed from each sample using a punch and inserted into a quartz oven. The oven was then purged with helium, and the temperature was programmed to increase to 870˚C. Organic compounds and pyrolysis products were thermally desorbed into manganese dioxide (MnO_2) in an oxidising oven. Here, the carbon fragments were quantitatively converted to CO_2 gas as they flowed through the MnO_2. The CO_2 was carried in the helium stream out

of the oxidising oven. Hydrogen gas was mixed with this stream, which then flowed through a heated nickel catalyst, where it was quantitatively converted to methane. The methane was measured by an FID, representing the OC measurement. A second temperature ramp in the oxidising gas stream allowed any elemental carbon to be oxidised from the filter into CO_2 gas and passed into the oxidising oven. Elemental carbon (EC) was detected in the same manner as OC. The OCEC analyser was also fitted with a fixed-volume loop to inject an external standard (5% methane in helium) at the end of every injection. Each sample was compared to its own standard, compensating for gradual drift or instrument fluctuation and resulting in increased stability (NIOSH, 2003). The method LOD for EC and OC was 0.002 mg. The results were reported as EC in mg/m^3.

3.3.4 Ambient conditions

The Q-Trak Indoor Air Quality Monitor 7575 (TSI Incorporated, Shoreview, Minnesota, USA), a handheld instrument, was used to measure ambient conditions such as relative humidity, dry-bulb temperature and carbon dioxide concentrations, in the area between the petrol pumps at three-hour intervals throughout the 12-hour shifts, resulting in a total of n=4 measurements per parameter day. Additionally, a Multi-Function Anemometer TA465 (TSI Incorporated, Shoreview, Minnesota, USA) was used to measure the airflow during the same period, resulting in a total of n=4 airflow measurements per day. During each measurement, the probes of the two instruments were allowed to stabilise. The Multi-Function Anemometer TA465 was held perpendicular to the direction of airflow. Both instruments were factory-calibrated by the manufacturer and each instrument was supplied with a calibration certificate (Annexure B). As recommended by TSI, the instruments were inspected for sensors, batteries and diagnostic malfunctions before usage. No additional on-site calibration was required, as both instruments incorporate built-in auto-zeroing functions, designed to verify sensor stability. All measurements were recorded on a field data sheet and transferred to Microsoft Excel®.

3.3.5 Data analysis

The data obtained from the SANAS-accredited laboratory and from the RTM instruments were entered into Microsoft Excel®. GraphPad Prism (version 10) was used to generate line and bar graphs and for statistical analyses.

The concentrations received from the laboratory were converted to 12-hour TWA by using the following equation:

$$\text{TWA} = \frac{\Sigma(Cn \times Tn)}{\text{T}_{\text{Total}}}$$

Where:

- C_n = Concentration of the substance during time period n (mg/m³ or ppm),
- T_n = Time duration of exposure at concentration Cn (in minutes),
- T_{Total} = Total time of exposure (in minutes).

Each 12-hour TWA concentration of BTEX obtained from personal sampling was compared to the adjusted 12h TWA-OEL (from 8 hours to 12 hours) of the RHCA, 2021. The 12-hour TWA calculated for EC was compared to the OEL for EC in the MHSA.

3.3.6 Statistical analysis

Descriptive statistics, including maximum, minimum, mean, median, and standard deviation, of results from the ambient conditions and exposure concentrations for BTEX and EC measured during the five-day monitoring period were calculated. Results below the LOD for each chemical were substituted with the DL/√2. The decision to use the DL/√2 approach was based on established occupational hygiene and environmental exposure assessment guidance for datasets with a relatively low proportion of censored values. The percentage of non-detects is low (generally <15–20%). The data are not heavily skewed by censoring, and the primary objective is estimation of summary statistics rather than complex distributional modelling (Hewett & Ganser, 2007). The Shapiro-Wilk test was used to investigate normality due to the sample size (n<50). The data were not normally distributed and non-parametric tests were subsequently used. To compare two means (area vs personal concentrations of BTEX and EC), the Mann-Whitney U test was performed in case of non-parametric data. A Spearman correlation test was used to investigate the relationship between the personal BTEX (TWA-12h) and ambient conditions (temperature, airflow, relative humidity and carbon dioxide). A Spearman correlation was also used to investigate the relationship between the volume of fuel supplied per day (L) and personal (BTEX and EC) or area (BTEX and EC) exposure monitoring results. Relationships of Spearman's rank correlation were considered to be

very strong when Rho (ρ <0.7), strong between 0.4–0.69, moderate at 0.3–0.39, weak at 0.2–0.29 and no relationship at 0.01–0.19. These values applied to both positive and negative relationships (Leclezio *et al*., 2015). The Kruskal-Wallis test with Dunn's multiple comparisons test was used to determine differences in personal exposure concentrations between each of the five monitoring days. Statistical significance was set at $p<0.05$.

The Bland-Altman test was used to assess the level of agreement between two methods to measure DPM. The 12-hour TWA (mg/m^3) for particles <0.8 µm from the SidePak™ AM520 and the 12-hour TWA EC concentrations (mg/m^3) derived from the conventional NIOSH 5040 method were used. For each paired measurement, the mean of the two methods ([A+B]/2) was plotted on the x-axis, and the difference between the two methods (B-A) was plotted on the y-axis. The mean difference (d) represents the average bias between the methods, while the limits of agreement (LoA) were calculated as:

d ± 1.96 × SD of the differences

These limits indicate the range within which most differences between the two methods are expected to fall. A mean difference close to zero suggests minimal systematic bias, whereas the LoA provide insight into the extent of random variability between the methods (Acar, 2024). A Spearman correlation and regression analysis were also performed on the method comparison between the 12-hour TWA concentration from the SidePak™ AM520 (PM <0.8 µm) and the conventional NIOSH 5040 method. On the fifth day of sampling, one of the SidePak™ AM520 instruments did not work, and therefore, those results for the one instrument are not included in the statistical analysis (n=14).

3.3.7 Ethics approval

All petrol-filling attendants at the station were invited to take part in this study; therefore, participants who participated in this research participated voluntarily. Fifteen different individuals participated, and no petrol attendants were measured during more than one shift. Each petrol attendant signed an informed consent document including all the project information as well as terms and conditions. This study was approved by the Health Research Ethics Committee of the North West University (approval number: NWU-00123-25-A1) (Annexure D).

3.4 Results

3.4.1 Ambient conditions

The data were descriptively examined, and the observed ranges indicated substantial day-to-day variations. The ambient conditions measured in a winter month, over five days, between airflow, temperature (refers to dry-bulb temperature), relative humidity and carbon dioxide concentrations are provided in Table 4. The highest mean airflow (1.1 ± 0.7 m/s) was observed on day two, despite day three having the highest maximum airflow (2.6 m/s). Temperature reached a minimum of 5.7°C (day one) and a maximum of 23.4°C (day two). Relative humidity ranged from 16.2%-67.7% with higher averages observed on cooler days. Brief rainfall occurred early on day three. Mean daily carbon dioxide concentrations ranged between 495.2-523.3 ppm with occasional peaks above 600 ppm. Table 4 provides the values of the ambient conditions measured for each day.

Table 4: Ambient conditions monitored over five days

	Airflow (m/s)	Temperature (°C)	Relative humidity (%)	Carbon dioxide (ppm)
Day1				
Mean	0.8 ± 0.7	16.6 ± 6.5	29.5 ± 17.7	523.3 ± 97.0
Minimum	0.3	5.7	16.2	459
Maximum	2.4	22.2	60.2	808
Day 2				
Mean	1.1 ± 0.7	18.2 ±5.2	24.9 ± 11.1	506.2 ± 52.0
Minimum	0.3	9.6	16.3	446
Maximum	2.3	23.4	46.8	610
Day 3				
Mean	0.8 ± 0.7	10.5 ±1.8	57.6 ± 5.8	495.2 ± 25.8
Minimum	0.2	7.9	49.3	463
Maximum	2.6	13.4	67.6	570
Day 4				
Mean	0.4 ± 0.5	14.5 ±3.4	51.1 ±13.5	502.3 ± 80.1
Minimum	0.2	8.8	33.3	422
Maximum	1.8	18.3	67.5	668
Day 5				
Mean	0.8 ± 0.8	15.1 ± 4.9	44.6 ± 10.0	504.4 ± 53.4
Minimum	0.1	7.8	34.3	432
Maximum	2.5	20.7	59.3	609

±: standard deviation; m/s: meter per second; °C: degree Celsius; %:percentage; ppm:parts per million.

3.4.2 Volatile organic compounds

The 12h TWAs for individual VOCs measured over five days were all below their adjusted 12-hour OELs. The results for BTEX are listed in Table 5 while other compounds targeted in the VOC analysis, including pentane, all isomers; acetone; hexane, all isomers; n-hexane; iso-octane; heptane, all isomers; n-octane; n-nonane; n-decane and white spirits can be found in the supporting material (Supplementary material 5.1). In this study, xylene was reported by the accredited laboratory as mixed isomers, rather than as individual isomer-specific concentrations (m-, p-, and o-xylene separately). This means that the reported concentration represents the combined total of all xylene isomers present in the sample. These compounds were detected at trace concentrations, in most cases near or below the analytical LOD.

Petrol-filling attendant referred to as worker three, monitored on day one, experienced the highest overall exposure to benzene, toluene and xylene at 0.04, 0.07 and 0.04 ppm, respectively (Table 5) (indicated in bold in Table 5). There was no statistically significant difference between the personal and area BTEX 12-hour TWA concentrations. Dunn's multiple comparisons test between the days also indicated no statistically significant differences. The highest total volumes of fuel dispensed were on day 1 (28 855 L) and the lowest was on day 2 (19 569 L) (Figure 2B). There was a statistically significant very strong positive correlation (ρ=0.975; $p < 0.05$) between personal benzene 12-hour TWA concentrations and the volume of fuel (L) sold at the station over the five-day monitoring period. The highest peak concentrations did not correspond with the same day the highest volume of fuel was sold.

3.4.3 Correlation between BTEX and ambient conditions

Spearman correlation analysis was conducted to assess the relationship between personal exposure concentrations and ambient conditions (temperature, airflow, RH and CO_2). For all comparisons, no statistically significant correlations were observed. Even though no correlation was statistically significant, the r-values are listed below indicating the direction in which the relationship between exposure and ambient conditions tended. Negligible to weak negative correlations were observed between benzene, toluene and

ethylbenzene with temperature, ρ = -0.051, -0.205, -0.112, respectively, and for benzene and toluene with airflow stronger relationship, ρ = -0.573, -0.688, respectively. Strong negative correlations were observed for ethylbenzene with CO_2 (ρ= - 0.447) and xylene with RH (ρ= - 0.791). Weak to strong positive correlations were observed between benzene, toluene and ethylbenzene with RH, ρ = 0.513, 0.201, 0.112 and for benzene, toluene and xylene with CO_2, ρ= 0.359, 0.201, 0.949, respectively. For ethylbenzene and xylene, a strong and very strong positive correlation was observed with airflow of ρ= 0.5 and ρ= 0.949, respectively.

Table 5: Calculated time weighted averages (TWA) and occupational exposure limits (OELs) of BTEX compounds

	Day 1	W1		W2		W3		Area	
	OEL 12h TWA (ppm)	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL
B	1	0.02	2.65	0.02	3.12	**0.04**	5.34	0.01	1.34
T	27	0.03	0.12	0.05	0.18	**0.07**	0.27	0.01	0.05
E	133	0.005*	0	0	0	0	0	0.005*	0
X	67	0.02	0.02	0.01	0.01	**0.04**	0.06	0.006*	0
	Day 2	**W4**		**W5**		**W6**		**Area**	
	OEL 12h TWA (ppm)	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL
B	1	0.006*	0	0.01	0.81	0.006*	0	0.006*	0
T	27	0.02	0.08	0.02	0.08	0.02	0.06	0.01	0.05
E	133	0.005*	0	0.005*	0	0.005*	0	0.005*	0
X	67	0.02	0.02	0.01	0.01	0.01	0.01	0.006*	0
	Day 3	**W7**		**W8**		**W9**		**Area**	
	OEL 12h TWA (ppm)	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL
B	1	0.02	3.64	0.02	3.25	0.01	1.34	0.02	2.74
T	27	0.05	0.18	0.04	0.16	0.02	0.09	0.05	0.19
E	133	0.005*	0	0.005*	0	0.005*	0	0.005*	0
X	67	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.03
	Day 4	**W10**		**W11**		**W12**		**Area**	
	OEL 12h TWA (ppm)	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL
B	1	0.01	1.84	0.03	4.38	0.02	2.44	0.01	1.57
T	27	0.04	0.14	0.06	0.22	0.04	0.14	0.03	0.09
E	133	0	0	0.005*	0	0.005*	0	0.005*	0
X	67	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01
	Day 5	**W13**		**W14**		**W15**		**Area**	
	OEL 12h TWA (ppm)	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL
B	1	0.02	3.67	0.03	4.06	0.01	0.97	0	0.63
T	27	0.05	0.2	0.05	0.17	0.01	0.06	0.01	0.05
E	133	0.005*	0	0.005*	0	0.005*	0	0.005*	0
X	67	0.02	0.04	0.01	0.02	0.01	0.01	0.01	0.01

*** Results below limit of detectionfor each chemical was substituted with DL/√2; Indicated in bold: Worker three, monitored on day one, the highest overall concentrations for BTX at 0.04, 0.07 and 0.04 ppm; %: percentage; TWA: time weighted average; OEL: occupational exposure limit; ppm: parts per million (RHCA,2021); W: worker.**

3.4.4 Particulate matter (PM) exposure results

The results obtained from the SANAS-accredited laboratory revealed high concentrations of OC in the samples collected at the petrol-filling station. The high OC concentrations were deemed to have originated from the fuel itself and not from the exhaust of vehicles. Therefore, it was decided to report EC concentrations in mg/m^3 as a measure of DPM exposure and not TC and discard the OC component.

The results over the five days indicated that all EC 12-hour TWA concentrations were below the MHSA's adjusted 12-hour OEL of 0.07 mg/m^3. No comparison to the RHCA was made since it does not contain an OEL for EC (Table 6). There was no statistical significant difference between personal EC exposure concentrations and area EC concentrations ($p<0.05$). Dunn's multiple comparisons test between days for worker personal exposure of EC 12-hour TWA concentrations indicated no statistically significant difference. Workers one, three and 14 as well as the area on day five showed the highest 12-hour TWA concentration of 0.003 mg/m^3 (indicated in bold in Table 6). The Spearman correlation indicated no statistically significant relationship between personal and area EC 12-hour TWA concentrations and the volume of fuel (L) sold per day ($\rho= 0.2$; $p>0.05$) (Figure 2B). Worker three, monitored on day one, had the highest PM <0.8 µm TWA of 0.13 mg/m^3 and worker 13, monitored on day five, experienced the second highest of 0.12 mg/m^3 (both petrol attendants were non-smokers). The RTM instrument (SidePak™ AM520) malfunctioned on day five and therefore there is no PM <0.8 µm TWA (mg/m^3) concentration listed for worker 15 in Table 6.

Table 6: 12-hour TWA of particulate matter (PM) (< 0.8µm) and elemental carbon (EC) as a measure of DPM

MHSA 12-hour OEL EC: 0.07 mg/m^3	Day 1			
	W1	**W2**	**W3**	**Area**
EC 12-hour TWA (mg/m^3)	**0.003**	0.002	**0.003**	0.0007*
% of OEL	4.29	2.85	4.29	0.1
PM (<0.8 µm) 12-hour TWA (mg/m^3)	0.09	0.03	0.13	0.08
	Day 2			
	W4	**W5**	**W6**	**Area**
EC 12-hour TWA (mg/m^3)	0.0007*	0.0007*	0.0007*	0.0007*
% of OEL	0.1	0.1	0.1	0.1
PM (<0.8 µm) 12-hour TWA (mg/m^3)	0.01	0.03	0.03	0.01
	Day 3			
	W7	**W8**	**W9**	**Area**
EC 12-hour TWA (mg/m^3)	0.0007*	0.0007*	0.0007*	0.0007*
% of OEL	0.1	0.1	0.1	0.1
PM (<0.8 µm) 12-hour TWA (mg/m^3)	0.01	0.01	0.02	0.01
	Day 4			
	W10	**W11**	**W12**	**Area**
EC 12-hour TWA (mg/m^3)	0.001	0.0007*	0.0007*	0.002
% of OEL	1.43	0.1	0.1	2.85
PM (<0.8 µm) 12-hour TWA (mg/m^3)	0.01	0.06	0.03	0.05
	Day 5			
	W13	**W14**	**W15**	**Area**
EC 12-hour TWA (mg/m^3)	0.002	**0.003**	0.002	**0.003**
% of OEL	2.85	4.29	2.85	4.29
PM (<0.8 µm) 12-hour TWA (mg/m^3)	0.12	0.1	E	0.1

* Results below the limit of detection for each value of elemental carbon (EC) were substituted with DL/√2; %: percentage; mg/m3: milligram per cubic meter; E: Sidepak malfunction; EC: elemental carbon; MHSA: Mine Health and Safety Act; OEL: occupational exposure limit; TWA: time weighted average; W: Worker.

3.4.5 Area monitoring of total volatile organic compounds (TVOCs)

Real-time monitoring of TVOCs over five consecutive days using the ppbRAE 3000 showed fluctuations in area TVOC concentrations during the 12 hours (Figure 2A). The highest peaks were observed between 07:00 and 08:00 (high volume of traffic before work) and between 12:00 and 13:00 (high volume of traffic in lunch period). Days 4 and 5 recorded the highest concentrations with a peak exceeding 16 000 ppb, while days 1 to 3 remained low throughout the shifts.

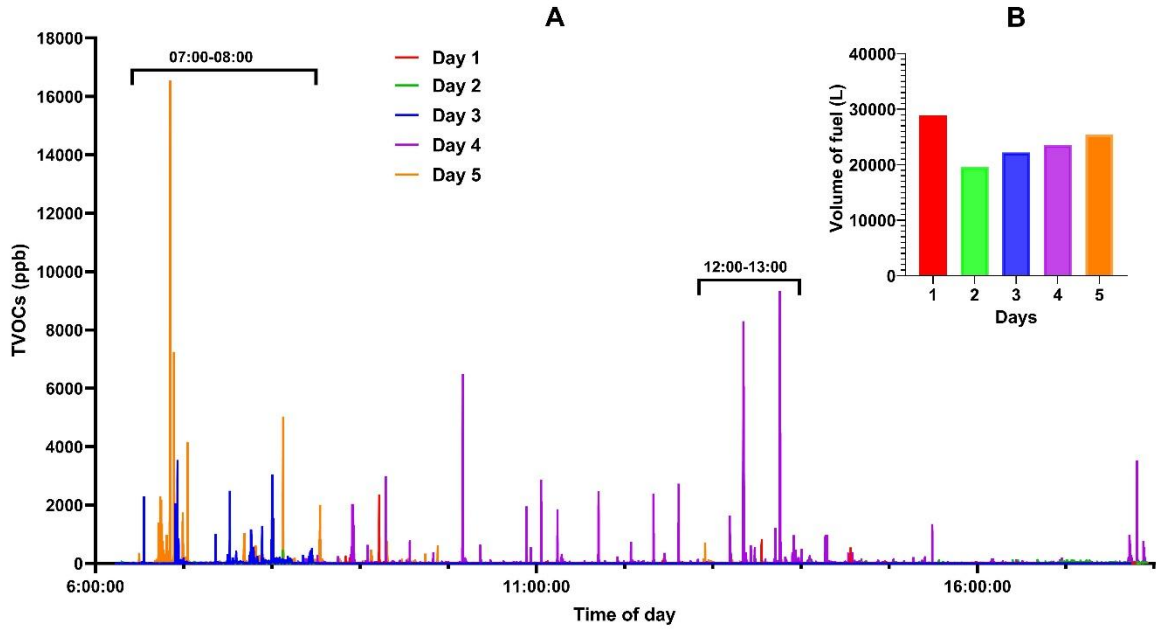


Figure 2: A: Area monitoring of total volatile organic compounds (TVOCs) (ppb) over five days. B: The amount of fuel supplied per day (L)

3.4.6 Personal monitoring of total volatile organic compounds (TVOCs)

Activities performed by petrol attendants were monitored with the ppbRAE 3000 in the breathing zone and indicated variations in exposure (Figure 3). Figures 3A and 3B illustrate the TVOC exposure of the petrol filling attendant while refuelling vehicles with petrol (A) and diesel (B), respectively. The highest peaks are associated with the volume of fuel dispensed and the duration of refuelling. The peak reached when refuelling vehicles with petrol (Figure 3A) is higher than that of vehicles refuelled with diesel (Figure 3B). Figure 3C illustrates the TVOC exposure of the petrol attendants during vehicle assistance services performed, such as checking oil and water levels and tyre pressure. Figure 3D illustrates exposure peaks when cash and retail operations with short-term exposure to TVOCs, associated with removing the pump's nozzle from the vehicle's fuel cap.

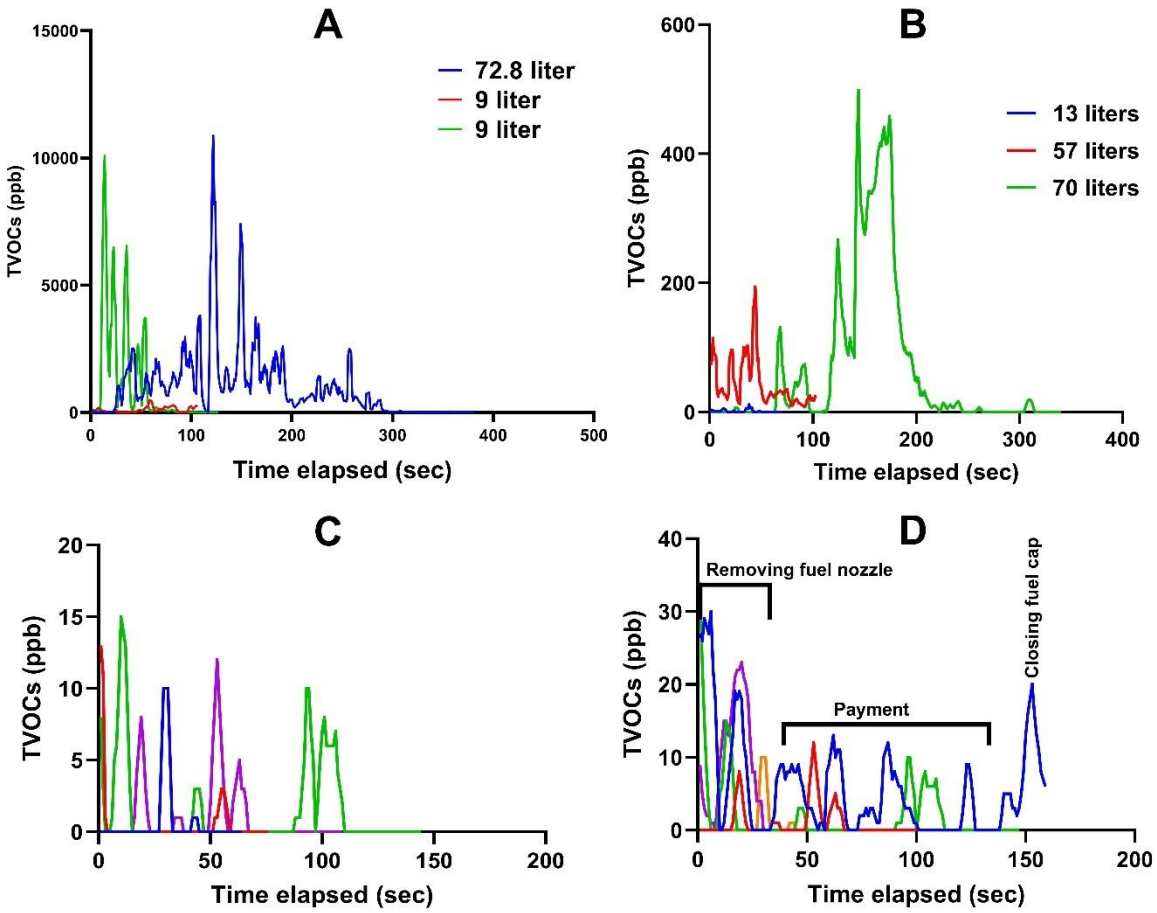


Figure 3: TVOC concentrations measured in the breathing zone of petrol attendants during refuelling vehicles with petrol (A) and diesel (B); vehicle assistant services (C); and cash and retail operations (D). The y-axes of the graphs were adjusted to accommodate different peak heights. The x-axes indicate the duration of the activities in seconds.

Activities performed by the tanker driver responsible for fuel delivery, were monitored with the ppbRAE 3000 in the breathing zone and indicated variations in exposure (Figure 4). The diesel tank refuelling was monitored for three repetitions and the petrol tank refuelling only once, over the course of five days. The petrol tank refuelling indicated higher peaks in comparison to the diesel tank refuelling.

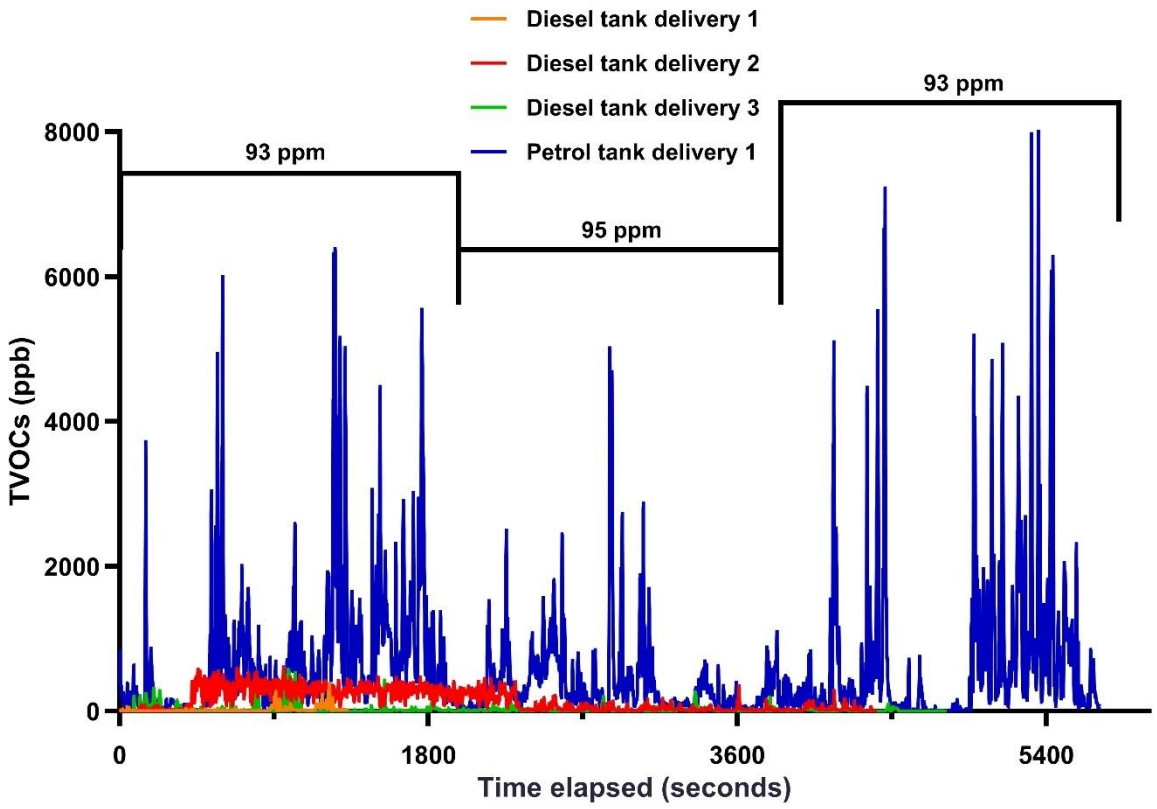


Figure 4: TVOC concentrations measured in the breathing zone of petrol attendants during delivery of fuel and underground tank refuelling with petrol (blue) and diesel (in triplicate) from a delivery truck.

Figure 5 shows the activity-based monitoring for personal exposure of TVOCs with the ppbRAE 3000, overlaid with the monitoring of PM <0.8 µm. Peaks in exposure to TVOCs and PM <0.8 µm during specific tasks are indicated (Figure 5). The TSI SidePak™ AM520 shows multiple fluctuations in PM <0.8 µm concentrations over the duration of the 12-hour shift, with a noticeable peak during cigarette smoking. Vehicle refuelling with both petrol and diesel generated peaks in TVOCs, indicating short-term exposure.

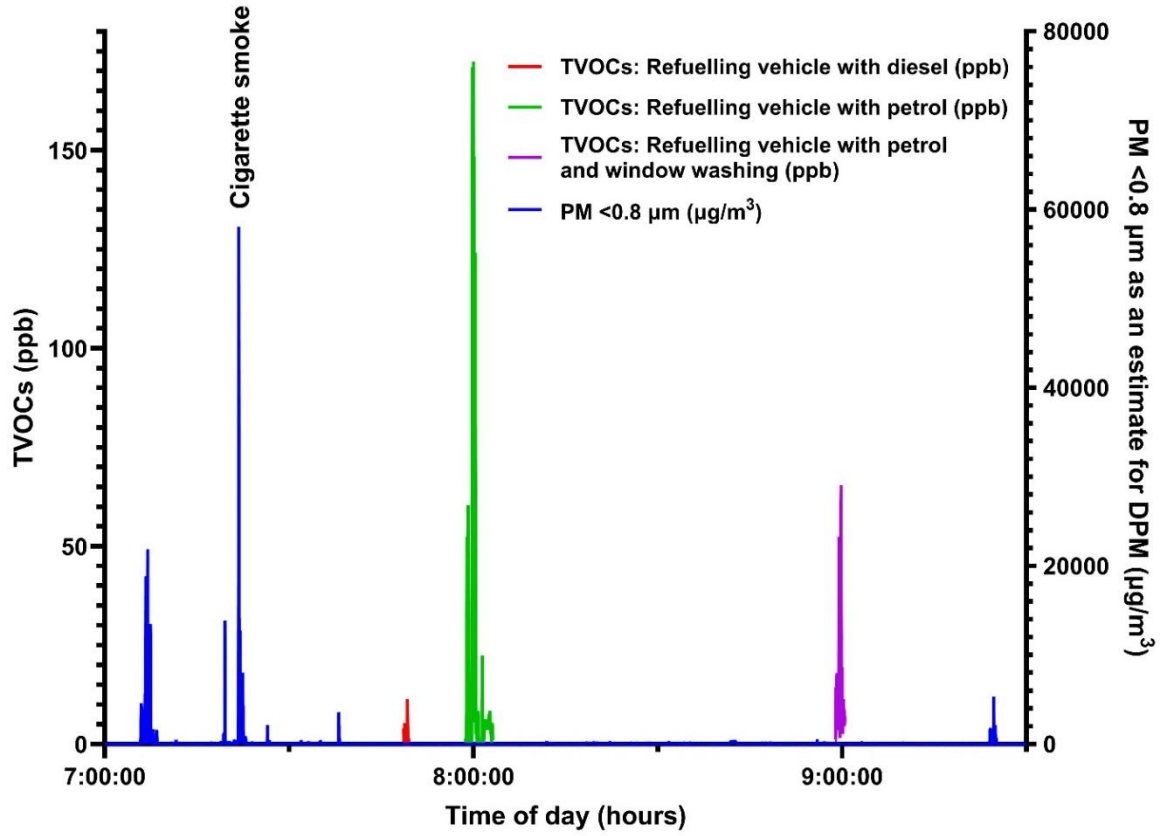


Figure 5: Personal exposure of one petrol filling attendant to particles <0.8 µm (estimate for diesel particulate matter (DPM)) and total volatile organic compounds (TVOC) (ppb) during various activities.

3.4.7 Area monitoring of particulate matter (PM) <0.8 µm

Area RTM (Figure 1) of PM <0.8 µm as an estimate for DPM over five consecutive days showed fluctuations in airborne concentrations during the 12-hour work shifts (Figure 6). On day 1, elevated levels were observed in the afternoon, while days 3 and 5 showed more increases during the morning and midday hours due to the amount of traffic observed. On day one, a nearby veld fire was observed around midday.

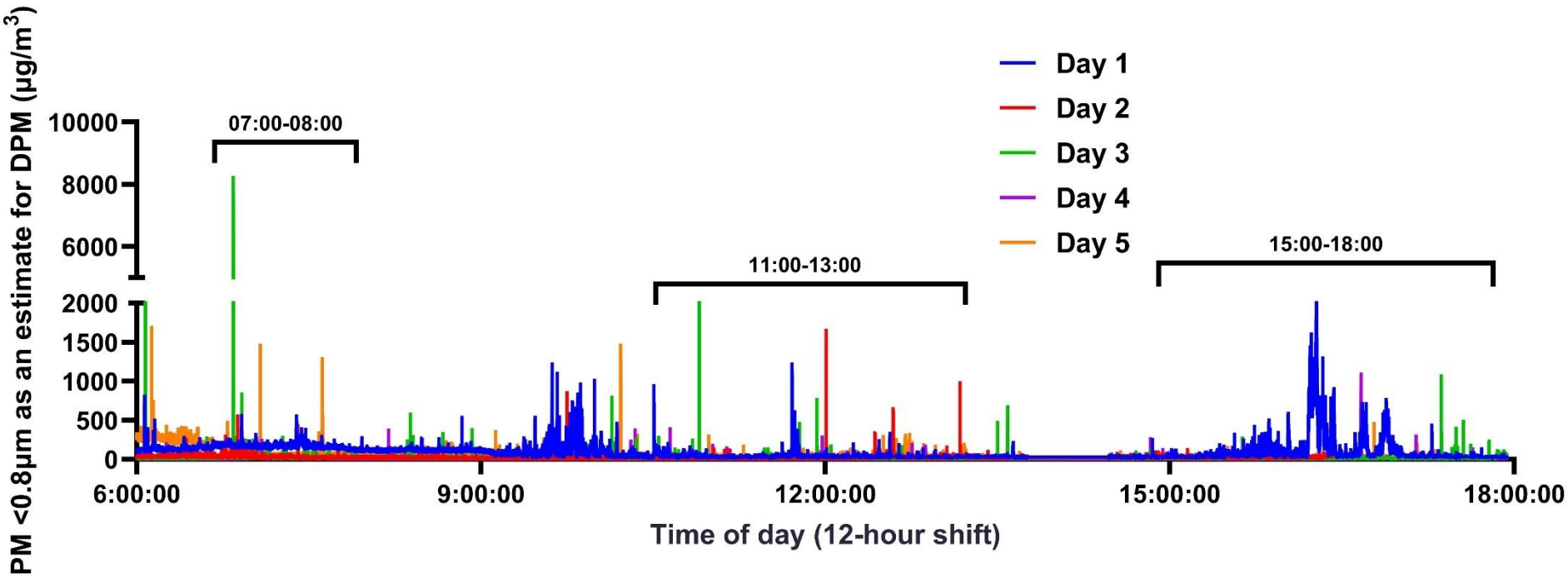


Figure 6: Particulate matter (PM) <0.8 µm (as an estimate of diesel particulate matter (DPM)) area monitoring over five days.

3.4.8 Personal monitoring of particulate matter (PM) <0.8 µm

Personal monitoring of petrol attendants using the TSI SidePak™ AM520 to measure PM <0.8 µm, indicated fluctuations in exposure concentrations for each individual based on activities performed (Figure 7). A maximum peak of 75 300 µg/m^3 and 100 000 µg/m^3 was detected due to cigarette smoking in Figure 7A and Figure 7B, respectively. In contrast, in Figure 7C and Figure 7D (non-smoking petrol attendants), the peak exposure remained below 2 500 µg/m^3, establishing a lower level of exposure to PM <0.8 µm compared to the smoking petrol attendants.

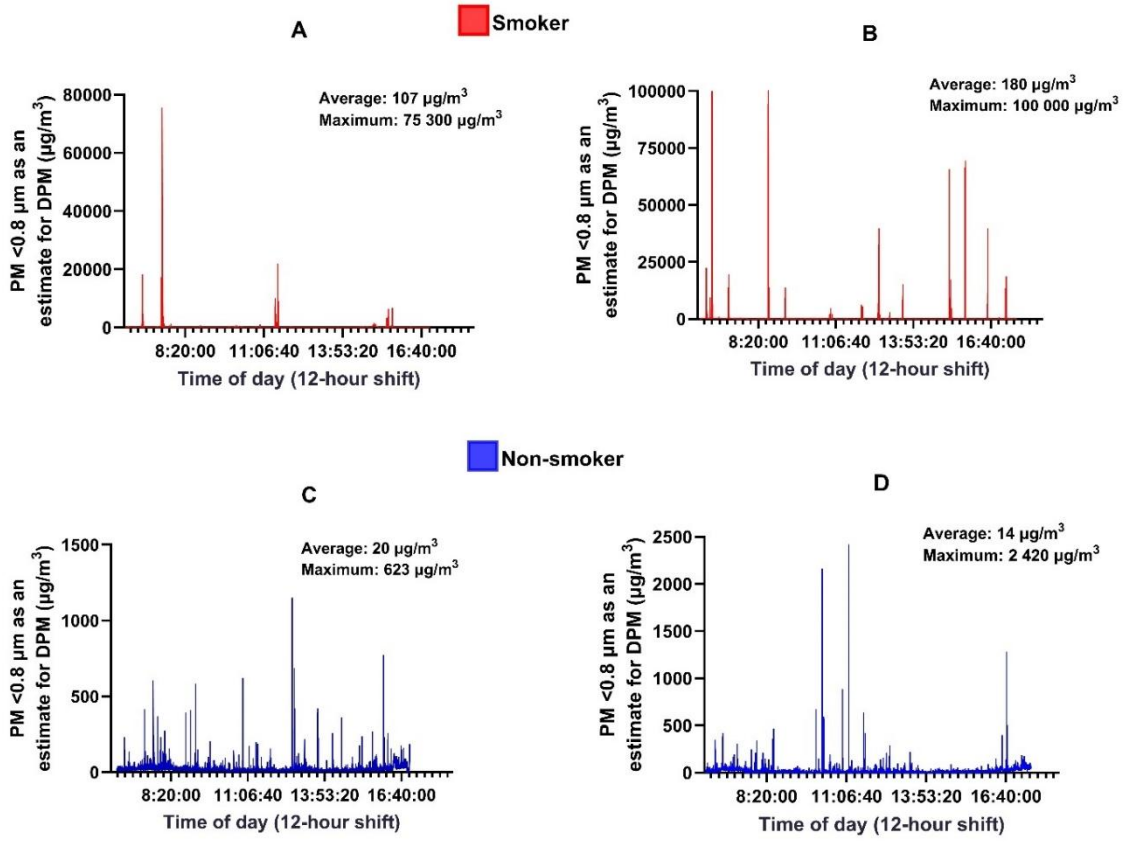


Figure 7: Particulate matter (PM) <0.8 µm as an estimate of diesel particulate matter (DPM) monitoring of four different petrol attendants over a 12-hour shift.

3.4.9 Comparison between real-time monitoring and conventional sampling methods

The Bland-Altman plot compared two methods for monitoring DPM exposure: 12-hour TWA PM<0.8 µm results from the SidePak™ AM520 and the NIOSH 5040 method's 12-hour EC TWA results for personal exposure (n=14) and area monitoring (n=5). The SidePak™ AM520 reported higher PM<0.8 µm 12-hour TWA concentrations in comparison with the NIOSH 5040 method's 12-hour TWA for EC. The method comparison had a bias of 0.0557 mg/m^3 SD of 0.0515, with a 95% limits of agreement ranging from -0.045-0.156 (Figure 8). Only 13 (of the 14) data points are visible in the plot due to overlapping measurements.

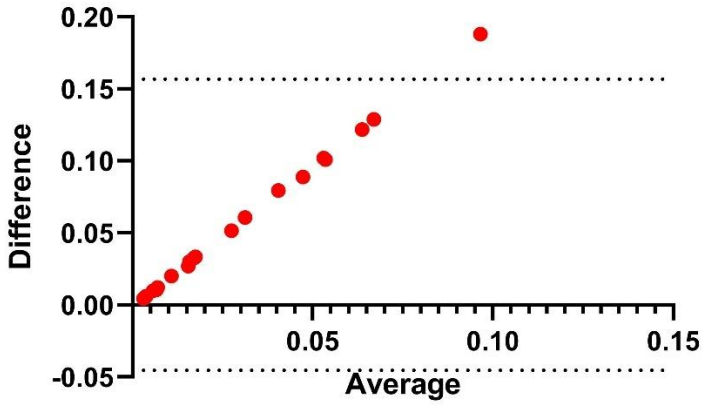


Figure 8: Bland-Altman comparison of real-time monitoring (RTM)(SidePak™ AM520) of particulate matter (PM) <0.8 µm as an estimate of diesel particulate matter (DPM) and the conventional NIOSH 5040 method for elemental carbon (EC) during personal and area exposure monitoring.

Correlation analysis was conducted on the EC and PM<0.8 µm concentration (mg/m^3) pairs. The dataset was not normally distributed, therefore Spearman's correlation coefficient was calculated. Spearman's correlation yielded a very strong positive correlation that is statistically significant (ρ= 0.7125; p=0.0004). The linear regression described the relationship between the concentrations reported by two methods. The simple linear regression indicated a slope significantly non-zero (p<0.0001) and equation of:

$$y = 46.72 * \mathrm{x} - 0.01142.$$

With y=predicted value of y, and x=slope (rate of increase/decrease of y for each unit increase of x).

3.5 Discussion

In order to determine how different work activities at petrol filling stations contribute to exposure, this study aimed to monitor the exposure of petrol-filling attendants to TVOCs and PM <0.8 µm, as an estimate of DPM using RTM. In addition, the conventional (NIOSH 5040 and 1500/1501) methods were used to compare the exposure to OELs as specified in the Regulations for Hazardous Chemical Agents (RHCA, 2021). The RHCA do not have an EC OEL for compliance; therefore, the adjusted (from 8h to 12h) Mine Health and Safety Act (MHSA, 1998) EC 12-hour OEL of 0.07 mg/m³ were used for comparisons.

3.5.1 Volatile organic compounds

The variety of emissions typical when handling fuel and incomplete combustion, as previously described by Kaiser *et al.* (2007), is confirmed in this study by the detection of various hydrocarbons, including BTEX chemicals, but this study also identified the activities associated with higher exposure. The 12-hour TWA for all petrol-attendants remained well below the RHCA (2021) OELs for benzene (<6% of the OEL) and for TEX (toluene <0.3%; ethylbenzene 0%; xylene <0.1% of the OEL). This finding aligns with Keretetse *et al.* (2008), who reported BTX concentrations of 0.31-0.73 mg/m^3 respiratory exposure in South African petrol-attendants, which were also well below legislative limits. Their study also concluded that, although compliant with legislation, the low exposures were sufficient to cause measurable DNA damage. Zahed *et al*. (2024) emphasised that sub-OEL exposure to BTEX may still cause genotoxic, neurotoxic and respiratory health effects through chronic low-dose accumulation. Therefore, although the measured BTEX concentrations indicate regulatory compliance, they do not eliminate potential health risks associated with prolonged exposure, specifically considering petrol attendants' 12-hour shifts and cumulative exposure (Akram, 2018). Identifying the specific activities that contribute to higher exposure can assist in implementing targeted interventions to further reduce exposure. Dunn's multiple comparisons test indicated no statistically significant difference between the days for personal exposure. A key influential factor was the daily volume of fuel sold. As illustrated in Figure 3, higher fuel volumes required longer refuelling

durations, which resulted in higher peak petrol and diesel exposure levels compared to shorter refuels. A statistically significant very strong, positive correlation (ρ =0.975; p <0.05) was observed between personal benzene 12-hour TWA concentrations and the volume of fuel (L) sold at the station over the five-day monitoring period. Keretetse *et al*. (2008) also found a significant relationship between the volume of petrol sold during the shift and the average concentrations of benzene, toluene and the total VOCs measured. A strong correlation existed between elevated VOC concentrations and the proximity to petrol-filling stations. In this study the environmental results indicate that variations in ambient conditions did not significantly influence personal exposure concentrations over the course of five days. In contrast, Tabinda *et al*. (2019) observed that increased temperature enhances volatilisation of hydrocarbons, thereby increasing environmental VOC concentration. It is argued that the fuel shortage on day 2 at the petrol filling station where the study was conducted, may have influenced exposure concentration.

3.5.2 Particulate matter

The EC concentration measured by the NIOSH 5040 method for personal and area monitoring varied from 0.001 to 0.003 mg/m³, corresponding to 0.1-4.295% of the adjusted 12-hour OEL of 0.07 mg/m^3 under the MHSA. All measured EC concentrations remained below the applicable OEL, indicating low levels of DPM exposure during the monitoring period. Organic carbon (OC) concentrations are influenced by the environmental presence of VOCs; therefore, EC was used as an indicator of exposure (Birch & Cary, 1996; Leotz-Gartziandia *et al*., 2000; Shen *et al*., 2021; Schauer, 2003). Over the course of five days of monitoring, no statistically significant differences were observed between personal and area EC concentrations, as confirmed by Dunn's multiple comparison tests (adjusted p >0.05). Workers one, three and 14, along with the area concentration on day five, indicated the highest 12-hour OEL TWA EC value of 0.003 mg/m^3, these concentrations are less than 5% of the OEL. Several concentrations were below the LOD and concentrations were calculated by using standard substitution methods (DL/√2). The Spearman correlation analysis revealed no significant relationship between the 12-hour concentrations of personal and area EC and the daily volume of fuel dispensed (with both personal and area weak correlations at ρ = 0.200). This indicates that daily variations in the volume of fuel sold did not influence EC exposure (Groves & Cain, 2000). Overall, the results indicate that EC are present in the area and personal work environment. The exposure was

produced by vehicle emissions and occasional environmental events, such as veld fires. The EC concentrations remained well below the OEL, and the enforcement of policies such as requiring vehicles to be switched off during refuelling demonstrates that the control measures are effective.

3.5.3 Real-time monitoring

TVOC concentrations measured in the breathing zones of petrol attendants indicated temporal and task-specific peak exposure variation, with the maximum exposures occurring during vehicle refuelling and when fuel is delivered to refuel the underground tank. These results corroborate observations in international and South African studies that identified fuel handling and refuelling as emission sources (Keretetse *et al*., 2008; Eltahir *et al*., 2016; Moolla, 2015).

The higher TVOC peaks observed during underground petrol tank refuelling compared with diesel tank refuelling can be attributed to the fundamental physicochemical differences between petrol and diesel (de Carvalho Rocha & Sheen, 2019). Petrol is a highly volatile fuel composed of low-molecular-weight hydrocarbons. These compounds have significantly higher vapour pressures compared to heavier, less volatile hydrocarbons present in diesel (Terrés *et al.,* 2010). As a result, even small disturbances during refilling or displacement of vapour within the underground tanks can lead to rapid volatilisation and short emission spikes as seen in the results (Figure 4). Operational conditions during the fuel delivery and underground tank refuelling may also have amplified petrol peaks due to higher transfer rates and could possibly influence results. The higher transfer rates lead to greater turbulence in the fill lines and petrol being forcefully expelled into the underground tank (Pshenin *et al*., 2019; Wongwises *et al.,*1997). Overall, the results highlight the increase in potential exposure associated with petrol refilling activities and reinforcement of control and operational strategies such as vapour recovery systems during underground tank refuelling (Chass *et al*.,1963).

The RTM, conducted by using the SidePak™ AM520, indicated measurable concentrations of PM<0.8 µm across personal and area monitoring. The detection of PM<0.8 µm in both personal and area samples aligns with literature, such as Ristovski *et al*. (2012), who reported that vehicle emissions are a primary contributor to fine PM

concentrations in urban environments. This supports the assumption that background traffic emissions, such as idling and moving cars, contributed to the measured PM concentrations at the petrol-filling station.

The results for personal exposure to PM<0.8 µm indicating the high peaks (75 300 µg/m^3 and 100 000 µg/m^3) for petrol attendants that smoked during the shift, align with the results of the study by Klepeis *et al.* (2007), who performed an RTM study on outdoor tobacco smoke (OTS). The RTM included a piezoelectric microbalance (PZB), a photoelectric aerosol sensor (PAS), and three light-scattering photometers: an integrating nephelometer (NEPH), a laser particle counter (GRIMM), and a laser diode photometer (Sidepak). Measurements were collected at 10 outdoor public places where active cigar and cigarette smokers were present, including parks, sidewalk cafés, and restaurant and pub patios in Stanford, California. The OTS caused sharp spikes in particle mass concentration during the study that sometimes exceeded 1 000 µg/m^3 at distances within 0.5 m of the source.

The fluctuations in area exposure levels of PM<0.8 µm during the 12-hour work shifts over the course of five days indicated elevated levels in the afternoon, while days 3 and 5 increased during morning and midday hours. An observational inference can therefore be drawn that these fluctuations are associated with increased vehicular traffic and the presence of idling vehicles in the area of the petrol-filling station. On day one, a nearby veld fire was observed around midday, resulting in temporary changes to PM <0.8 µm monitoring (Figure 6).

3.5.4 Method comparison for DPM exposure measurement

Nabiwa *et al*. (2025) used the Bland-Altman, linear regression and correlation analysis to compare an RTM instrument (Nanozen DustCount 9000Z1) with a conventional sampling technique (NIOSH 0600) for sampling respirable dust. Their analysis indicated that although the results from the two methods trend together the actual concentrations are not necessarily the same, especially at higher concentrations. Similar results were found for this study where the comparison between the SidePak™ AM520 RTM results and the conventional NIOSH 5040 method. There was a significant agreement between the method for PM <0.8µm and the method for EC which showed that the methods trended together. The Bland-Altman analysis indicated that the SidePak™ AM520 consistently

reported higher PM <0.8µm concentrations than the EC from the NIOSH 5040 method for both personal and area monitoring. Also, the mean bias of 0.0557 mg/m^3 (SD=0.0515) indicates a clear overestimation by the SidePak™ AM520, with the 95% limits of agreement ranging from -0.045-0.156. According to the TSI application note (TSI, 2015) on custom calibration factors for DPM, photometric instruments are factory calibrated using the International Standard Organisation's (ISO) 12103-1 A1 test dust, which differs substantially from real-world DPM in composition in terms of their optical properties. The document emphasises that photometric responses are different when the sampled PM do not match the calibration aerosol, leading to systematic over- or underestimation of true mass concentration. However, there was a systemic error found between the two methods which showed that the methods did not measure exactly the same concentrations. The SidePak™ AM520 overestimation mirrors the limitations described in the TSI application note, and the systematic error should be corrected for. The incorporation of the correction and calibration factors would improve agreement between these two methods, and therefore, the RTM/Sidepak cannot replace the NIOSH method, but could be used in conjunction to identify peak exposure sources.

The added benefits of real-time feedback to identify high-risk activities and facilitate immediate intervention aligns with Barrett *et al.* (2019) and Sheehan *et al.* (2022). Noll. & Janisko (2013) evaluated the accuracy and reliability of a wearable Airtec RTM instrument. They performed statistical tests, including the Mann-Whitney and Levene's tests to assess the bias between Airtec and NIOSH 5040 results. The RTM Airtec results showed strong agreement with NIOSH 5040, with an average bias of 3±3%, meeting NIOSH accuracy criteria. A high percentage, 96% of Airtec measurements were within ±25% of the standard method. At concentrations >40 µg/m³ EC, 95% were within ±16% reliability. The instrument met the NIOSH accuracy criteria and showed no statistical difference from the NIOSH 5040 method when evaluated using the Mann-Whitney and Levene's tests. The Bland-Altman method was selected to evaluate the agreement between the two methods and not to test for statistical differences between groups. This method provided a more appropriate and informative analysis for method comparison than the Mann-Whitney U-test.

3.6 Conclusion

No results for BTEX and EC were more than 6% of the respective 12-h OELs. Exposure is well below concern, but by identifying activities that contribute to exposure, the exposure can be reduced even further. Furthermore, the continuous low-level exposure, especially to compounds such as the carcinogens benzene and DPM, may contribute to health effects over time (Naidoo *et al*., 2016; Rahimi *et al*., 2020). Studies by Mandal & Mukherjee (2020), Begum & Rathna (2012) and Solanki *et al*. (2015) collectively demonstrate decreased pulmonary function that may occur among petrol-filling attendants, supporting the need for preventative control measures even at sub-threshold concentrations. Engineering interventions such as installation of vapour-recovery systems are recommended (Scheepers *et al*., 2019:108670). Administrative controls including enforcement of no-idling vehicle policies, rotation of attendants between higher- and lower-exposure tasks, periodic medical surveillance, pulmonary function tests and worker training on safe handling of fuel are recommended. As for sampling strategies, the integration of both RTM and conventional sampling remains the appropriate and best practice for comprehensive exposure assessment and compliance verification (Spinelle *et al*., 2015).

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CHAPTER 4 CONCLUDING CHAPTER

4.1 Findings

This study aimed to monitor the exposure to volatile organic compounds (VOCs), particulate matter (PM) <0.8 µm as an estimate for diesel particulate matter (DPM) at a petrol-filling station with a specific focus on how various work activities contribute to exposure. During this study, conventional methods for compliance and real-time monitoring (RTM) methods for activity exposure were applied during a 12-h work shift.

Overall, the study successfully met its aim to monitor petrol attendants' exposure to HCAs. Exposure to BTEX and EC remained well below the applicable OELs. However, the RTM results revealed distinct short-term peaks associated with specific activities such as petrol refuelling, underground tank refuelling during fuel delivery and periods of increased vehicular traffic. Collectively, these findings indicate that while exposure does not exceed regulatory compliance, integrating both compliance monitoring and RTM techniques for activity-based exposure will improve exposure assessment and contribute to proactive control strategies.

Objective 1:

The first objective was to conduct personal exposure monitoring of petrol attendants to VOCs and DPM by using NIOSH 1500/1501 and 5040 methods, respectively during a 12-hour work shift and compare results to OELs. The activities of three petrol attendants were monitored per day over the course of five days (n=15) according to the NIOSH 1500/1501 and NIOSH 5040 methods. The sampling train for area monitoring was attached to the tripod, which was placed in the middle of the station (n=5; one per day, over five days).

Petrol-filling stations are not required to comply with the MHSA, but using the EC OEL was deemed to be the best practice for the exposure scenario. No statistical significant difference was found between personal and area samples, nor between days, for BTEX and EC. However, a very strong, positive correlation (ρ= 0.975) was observed between personal benzene exposure and the volume of fuel supplied. It is noteworthy that exposure

is <6% of the OELs. The first objective was achieved.

Objective 2:

The second objective was to use RTM data to determine petrol attendants' exposure to TVOCs and PM (<0.8 µm as an estimate for DPM) with a ppbRAE 3000 and TSI SidePak™ AM520, respectively, while they are performing different activities during a 12-hour workshift.

For area monitoring, the highest peaks for TVOCs were observed between 07:00 and 08:00 (high volume of traffic before work) and between 12:00 and 13:00 (high volume of traffic in lunch period). Days 4 and 5 recorded the highest TVOC concentrations with a peak exceeding 16 000 ppb. The highest total volumes of fuel dispensed were on day 1 (28 855 L) and the lowest was on day 2 (19 569 L). The most prominent personal monitoring peaks for TVOCs were found during refuelling of vehicles with petrol. These peaks were higher than those found for refuelling of vehicles with diesel. The TVOC exposure of the petrol attendants during vehicle assistance services performed, such as checking oil and water levels, checking tyre pressure and performing cash and retail activities, indicated short-term low exposure to TVOCs linked to nozzle removal from the vehicle, payment transactions and closing of the fuel cap. The petrol tank refuelling indicated higher peaks in contrast to the diesel tank refuelling for the personal monitoring of the fuel tank operator. The highest TVOC exposure peaks were associated with high volumes of fuel dispensed for longer durations.

The area RTM of PM <0.8 µm as an estimate for DPM with the TSI SidePak™ AM520 showed fluctuations in exposure concentrations during the 12-hour work shift. Elevated concentrations were measured during day one and during days three and five in the morning and midday hours. This was explained by observing the volume of traffic during those periods. The PM <0.8 µm results of four different selected petrol attendants over a 12-hour shift (two that smoke and two that do not smoke) indicated short-term peaks which were higher for smokers than non-smoking petrol attendants.

The objective was therefore achieved and linked to the first hypothesis. The first hypothesis was accepted, that the exposure to TVOCs and PM (<0.8 µm as an estimate

for DPM) will be different for each activity, with higher concentrations observed during tasks involving fuel handling and vehicle refuelling.

Objective 3:

The third objective was to compare methods by using the TSI Sidepak™ AM520 (particles <0.8 µm as an estimate for DPM) and the conventional sampling method NIOSH 5040 for EC during side-by-side monitoring.

The SidePak™ AM520 consistently reported higher PM <0.8 µm (as a surrogate for DPM) concentrations relative to the NIOSH 5040 method for both personal exposure (n=14) and area (n=5) monitoring. The Bland-Altman analysis indicated a mean bias of 0.0557 mg/m^3 (SD = 0.0515), with 95% limits of agreement from -0.045 mg/m^3-0.156 mg/m^3, indicating a small but clear systematic overestimation by the SidePak™ AM520. Spearman's correlation yielded a very strong, positive correlation that is statistically significant (ρ= 0.7125; p=0.0004).

The observed systematic error is consistent with the TSI application note (TSI, 2015), which highlights that over- or underestimation when aerosol properties differ from calibration aerosol occurs. This explains that the SidePak™ AM520 that measures PM<0.8 µm, and a certain percentage of the PM are EC. This resulted in the overestimation of EC in comparison with the NIOSH 5040 method, and by correcting the calibration factor for PM<0.8 µm for EC would improve the agreement even more. The comparison demonstrated a statistically significant relationship between the methods, a predictable systematic bias and agreement sufficient for the combination of RTM and conventional sampling methods. The RTM devices remain valuable for identifying peak exposure and high-risk tasks, consistent with findings from Barrett *et al.* (2019) and Sheehan *et al*. (2022). Thus, objective three was achieved, and the results support the second hypothesis.

The second hypothesis that the RTM results for PM (<0.8 µm as an estimate for DPM) agree with conventional (EC as per NIOSH 5040) monitoring data for DPM, according to Bland-Altman, linear regression and correlation analysis, was accepted

Overall, the conclusion remains that although exposure was below the regulatory limits,

petrol attendants remain exposed to low levels of total VOCs and DPM that could contribute to long-term health effects. The side-by-side use of RTM and conventional sampling is a comprehensive way to monitor exposure; this dual method enables both compliance and proactive identification of exposure peaks.

4.2 Recommendations

The following recommendations are based on the hierarchy of control (Nix, 2011).

4.2.1 Engineering controls

It is recommended that where financially viable, employers, companies and stakeholders of petrol-filling stations should consider installing vapour recovery systems (VRS) at petrol-filling stations to lower VOC exposure during underground tank refuelling and vehicle refuelling. VRS are units that capture and recycle vapours released during industrial processes, specifically at fuel pumps, to reduce emissions and recover hydrocarbons. Although engineering controls are associated with a higher cost, the long-term effectiveness and sustainability in exposure reduction justify the investment to reduce exposure even more. While measured exposures were below 6% of the respective OELs, compliance with OELs does not necessarily equate to zero risk, particularly in the context of carcinogenic and potentially additive exposures. Evidence from the international study by Cruz-Núñez *et al*. (2003) supports the efficacy of such interventions. Cruz-Núñez *et al*. (2003) conducted a field study on the evaluation of VRS efficiency and personal exposure at petrol-filling stations in Mexico City. The results indicated that the installation of VRS in the Mexico City metropolitan area (MCMA) had remarkably contributed to the reduction of petrol-filling attendants' exposure to fuel vapour as measured with personal monitors. This finding was particularly important in the case of benzene. A comparison of benzene, toluene and xylene concentrations found a reduction of almost 99% in benzene concentrations, 68% in toluene concentrations and 57% in xylene concentrations in dispensing areas of service stations. The results for benzene reflect the combined effect of the VRS. Therefore, it is recommended that the South African petroleum sector explore the feasibility of adopting similar systems, as it is clear that in a developing country such as South Africa, self-service stations remain unlikely in the foreseeable future.

4.2.2 Administrative controls

Work rotation schedules are already implemented to reduce continuous exposure of attendants, as can be seen by the low exposure concentrations. To reduce exposure even more, petrol attendants assigned to highly exposed activities, such as delivery of fuel for underground tank refuelling and vehicle refuelling, could be given longer recovery times to minimise their total body burden. Scheepers *et al*. (2019:108670) emphasised that reducing long working hours provides workers with time to recover during regular periods of no exposure. This approach is considered the most effective way to reduce exposure from the body burden of BTX exposure at petrol-filling stations in Sri Lanka, Asia.

Under Regulation 5 and 6 of the Hazardous Chemical Agents Regulations, an exposure assessment must be carried out immediately and thereafter at intervals not exceeding two years, if such an assessment indicates that airborne HCAs are present at levels of potential risk, the employer must ensure that air monitoring is carried out at least every 24 months. Conducting risk assessments and based on the findings periodic occupational hygiene monitoring at least every two years, unless more frequent monitoring is required based on the outcome of the risk assessment, changes in process, or control measures. Using both RTM and conventional sampling is recommended. The choice of methods should align with internationally recognised occupational hygiene standards, the objectives of the assessment, and the requirements of Regulation 6, which requires that the measurement programme be representative of employee exposure.

In South Africa, medical surveillance of employees exposed to health hazards is not only good practice, but also a regulatory requirement under the Department of Employment and Labour's Occupational Health and Safety Act (OHSA) and associated regulations. Employers are legally obligated to provide and maintain a safe work environment that is without risk to health, which includes implementing appropriate medical surveillance programmes where occupational exposures exist It is therefore recommended to conduct annual medical surveillance and pulmonary function tests, if a risk assessment indicates exposure to hazardous substances that may adversely affect health and where valid medical tests are available to detect early effects. An occupational health practitioner must oversee these programmes. Employers must establish a documented medical surveillance system with initial, periodic, and exit medical examinations appropriate to the hazard and evaluated by an occupational health practitioner. Records of medical

surveillance, exposure assessments, and monitoring reports must be retained for at least 40 years (Mandal & Mukherjee, 2020; Begum & Rathna, 2012; Solanki *et al.,* 2015).

On the second day, it was observed that traffic was directed to certain pumps due to a fuel shortage. It is recommended to limit idling and queuing times by optimising traffic flow at the petrol-filling station even more, and while traffic is queued, implement a policy for engines to be switched off to prevent the increase of exhaust emissions.

Cruz-Núñez *et al*. (2003) indicated another source of exposure at petrol-filling stations: emissions from fuel spillage during refuelling of cars. During the monitoring over the course of five days, spillages were also observed; therefore, it is recommended that training and awareness programs should be implemented on exposure hazards, workplace practices, regular hand washing and overall personal hygiene.

Regularly inspect coveralls for damage and spills to ensure coveralls are washed, preventing dermal exposure.

4.3 Limitations

The study was conducted over a short period of time (five days). As a result, the data may not reflect variations in seasonal trends, traffic patterns, fuel demand (for petrol and diesel) and operational differences across this and other petrol-filling stations.

The petrol-filling station monitored in the study primarily dispenses a greater volume of diesel for agricultural purposes compared to petrol. However, the data obtained did not differentiate between the quantities of diesel and petrol dispensed. Consequently, there is no established distinction between the fuel types except for the RTM results indicating higher peaks of underground tank refuelling of petrol. The results can be different at petrol stations that dispense greater or equal volumes of petrol.

4.4 Future studies

It is recommended that future research on exposure to VOCs and PM at petrol-filling stations be conducted across different seasons and a variety of locations of petrol-filling stations to account for environmental and operational conditions. This will provide a more

comprehensive understanding of exposure trends, periods of elevated risks and reflect real-world seasonal variations throughout the year (Tabinda *et al*., 2019).

Post-implementation of VRS, research can be conducted to assess the efficiency and practicality within the South African petroleum sector. This will ensure evidence-based information on the reduction to VOC exposure of petrol-filling attendants and compliance with legislative standards.

To evaluate the possible health consequences of extended exposure to VOCs and PM, future studies should incorporate biological and physiological monitoring measuring urinary concentrations of BTEX metabolites. A more direct connection between environmental exposure and health consequences would be made possible by such monitoring, allowing the assessment of internal exposure levels and physiological reactions over time. Furthermore, retrospective health data of petrol attendants, particularly longitudinal records concerning the duration of their employment at petrol-filling stations, were not the primary focus. To gain a better understanding of the cumulative and long-term health effects of occupational exposure in the petroleum industry, it is highly recommended that future studies address this issue.

Due to petrol attendants working 12-hour shifts that deviated from the conventional 8-hour work shifts, adjusted OELs can be used for future studies to compare exposure for these extended work shifts by using three general formula models. These models include: the Brief and Scala, Occupational Health and Safety Administration (OSHA) and Québec adjustment models to calculate adjustment factors (RF) (Engelbrecht *et al*., 2024) (Table 7). The three models take different scenarios into account and adjust the OELs based on work shift (days on and off), resting time as well as the chemical characteristics of specific HCAs for a more holistic evaluation.

Table 7: Three models to calculate the adjusted OELs based on extended workshifts

Model	Equation
Brief and Scala	$RF_d = \frac{8}{h_d} \times \frac{24 - h_d}{16}$ $RF_w = \frac{40}{h_w} \times \frac{168 - h_w}{128}$

Occupational Health and Safety Administration (OSHA)	$RF_d = \frac{8}{h_d}$
Québec	$RF_w = \frac{40}{h_w}$

hd: hours worked per day (shift); hw: hours worked per week (full roster cycle/consecutive workdays); OSHA: Occupational Safety and Health Administration; RF: reduction factor; RFd: daily reduction factor; RFw: weekly reduction factor.

Future research should focus on the dermal exposure of petrol attendants resulting from fuel spillage during vehicle refuelling (Creta *et al.*, 2017). Additionally, an epidemiological survey can be conducted investigating the prevalence of any skin allergies, sensitivity and adverse health effects experienced by petrol-filling attendants.

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CHAPTER 5 ANNEXURES

ANNEXURE A Declaration of language editing.

WOORDE WAT WERK
WORKING WORDS

Venita de Kock
BA HONS. • PEG
084 588 5008
venita.dekock@gmail.com

2 December 2025

LANGUAGE EDITING STATEMENT

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

Monitoring exposure to total volatile organic compounds and particulate matter at a petrol-filling station

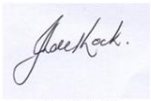
by

Lize van der Westhuizen
37548034

in fulfilment of the requirements for the degree
Master of Health Science in Occupational Hygiene
at the North-West University,

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

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



J L DE KOCK

ANNEXURE B Calibration certificates of instruments

Technology Solutions
Measurement Science Laboratory

Certificate of Calibration

ANSI National Accreditation Board (ANAB) is a member of the International Laboratory Accreditation Cooperation (ILAC) Mutual Recognition Agreement (MRA). This arrangement allows for the mutual recognition of technical test and calibration data by the member accreditation bodies worldwide. For more information on the arrangement please consult www.ilac.org. The accuracies of all measurements were traceable to the SI (International System of Units) through NIST, NMISA, PTB or International Measuring Standards, unless otherwise noted. The uncertainties of measurement were estimated for a coverage factor of k=2 which approximates to a 95% confidence level.

American Standard Calibration Laboratory
Measurement Science Laboratory

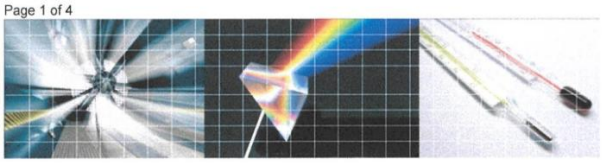
GOLDILUX

Certificate No	L97929	As Found/As Left	Rev 0
Manufacturer	TSI VelociCalc		
Description	Air Velocity Meter		
Model No	9545-A		
Serial No	9545A2316003		
Plant No	None		
Calibrated for	North West University		
Address	11 Hoffman Street, C1 Third Floor, Potchefstroom, 2531		
Temperature	(18.1 to 21.1) ± 2 °C		
Relative humidity	(47.9 to 54.8) ± 5 %rh		
Date of calibration	14 July 2025		
Expiry date	14 July 2026	Issue Date	15 July 2025
Calibrated by	C.M. Steyl	Digitally signed by Catharina Magdalena Steyl Date: 2025.07.15 07:16:31 +02'00'	

This certificate is issued without alteration, and in accordance with the conditions of accreditation granted by ANAB. Copyright of this certificate is owned by Technology Solutions & American Standard Calibration Laboratory and may not be reproduced other than in full, except with the prior written approval. It is a correct record of the measurements performed at the time of calibration.Subsequently the accuracy will depend on factors such as care exercised in handling the instrument and frequency of use. Recalibration should be performed after a period which has been chosen to ensure that, under normal circumstances, the instruments accuracy remains within the desired limits.The results relate to the device under calibration.

Technical Signatory V Oosthuizen Digitally signed by Visser Oosthuizen Date: 2025.07.15 07:41:09 +02'00'

Page 1 of 4



Hards Laboratories cc
T/A Technology Solutions
C3 Prospect Close
43 Regency Drive
R21 Corporate Park, Irene
Tel: +27 (0) 12 345 5358
Fax +27 (0) 12 345 3263

Technology Solutions
Measurement Science Laboratory

Certificate of Calibration

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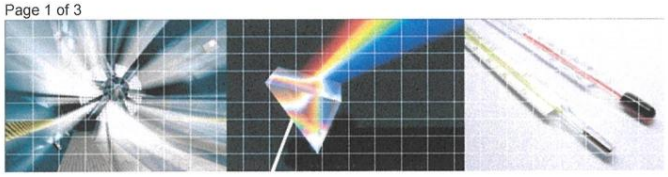
American Standard Calibration Laboratory
Measurement Science Laboratory

Certificate No	L97620	As Found/As Left	Rev 0
Manufacturer	MesaLabs		
Description	Primary Air Flow Calibrator		
Model No	Defender 510-M		
Serial No	166168		
Plant No	None		
Calibrated for	North West University		
Address	11 Hoffman Street, C1 Third Floor, Potchefstroom		
Temperature	(23.6 ± 2) °C		
Relative humidity	(18 ± 5) %rh		
Date of calibration	19 June 2025		
Expiry date	19 June 2026	Issue Date	19 June 2025

Calibrated by Pieter W Botha Digitally signed by Pieter Willem Botha Date: 2025.06.19 13:54:42 +02'00'

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Technical Signatory Pieter W Botha Digitally signed by Pieter Willem Botha Date: 2025.06.19 13:54:54 +02'00'



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Technology Solutions
Measurement Science Laboratory

Certificate of Calibration

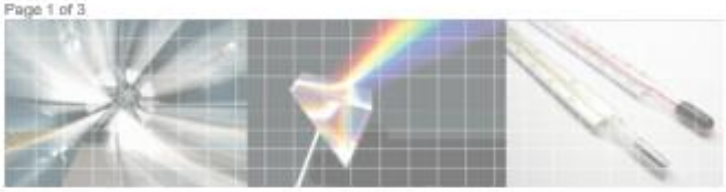
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American Standard Calibration Laboratory
Measurement Science Laboratory

Certificate No	L97941	As Found/As Left	Rev 0
Manufacturer	TSI Q-Trak		
Description	Indoor Air Quality Meter		
Model No	7575-X-NB		
Serial No	7575X1829002		
Plant No	None		
Calibrated for	North-West University		
Address	11 Hoffman Street, C1 Third Floor, Potchefstroom, 2531		
Temperature	18.1 °C ± 2 °C		
Relative humidity	50.4 % rh ± 5 % rh		
Date of calibration	17 July 2025		
Expiry date	17 July 2026	Issue Date	17 July 2025
Calibrated by	Y Cockshaw		

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Technical Signatory Y Cockshaw



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envirocon instrumentation
environmental and occupational hygiene instruments Pty Ltd
SABS ISO 9001
VAT Nr: 4210116291 Reg Nr: 2020/873056/07

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104 MISA Centre 12 Fir Drive Northcliff Johannesburg South Africa
Phone: +27 11 476 7323
sales@envirocon.co.za
www.envirocon.co.za

CALIBRATION CERTIFICATE

Customer: North West University

Instrument Serial Number: 594-913893

Product Name: PPB-Rae

Calibration Date: 05 June 2025

Reference Number: 2025-0386

CALIBRATION GASES

Standard Mixed Gases	Disposable Cylinder Gas Cylinder#	Lot/ Certificate/ Cylinder#
VOC	100ppm	WO208221-1

TEST RESULT

Sensors	VOC (ppm)
Zero Gas	0
Span Gas	100

This instrument has been calibrated using valid calibration gases and Instrument manual operation procedures.

T. Mieth

Approved by

envirocon instrumentation
environmental and occupational hygiene instruments Pty Ltd
SABS ISO 9001
VAT Nr: 4210116291 Reg Nr: 2020/873056/07

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CALIBRATION CERTIFICATE

Customer: North West University

Instrument Serial Number: 594-000245

Product Name: PPB-Rae

Calibration Date: 05 June 2025

Reference Number: 2025-0386

CALIBRATION GASES

Standard Mixed Gases	Disposable Cylinder Gas Cylinder#	Lot/ Certificate/ Cylinder#
VOC	100ppm	WO208221-1

TEST RESULT

Sensors	VOC (ppm)
Zero Gas	0
Span Gas	100

This instrument has been calibrated using valid calibration gases and Instrument manual operation procedures.

T. Muirhead

Approved by

envirocon instrumentation
environmental and occupational hygiene instruments Pty Ltd
SABS ISO 9001
VAT Nr: 4210116291 Reg Nr: 2020/873056/07

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Phone: +27 11 476 7323
sales@envirocon.co.za
www.envirocon.co.za

CALIBRATION CERTIFICATE

Customer: North West University

Instrument Serial Number: 7575X1904003

Product Name: Q-Trak

Calibration Date: 04 June 2025

Reference Number: 2025-0384

CALIBRATION GASES

Standard Mixed Gases Disposable Cylinder	Gas Cylinder#	Lot/ Certificate/ Cylinder#
CO	50ppm	110SG220523AB
CO2	1000ppm	

TEST RESULT

Sensors	CO (ppm)	CO2 (ppm)
Zero Gas	0	0
Span Gas	50	1000

This instrument has been calibrated using valid calibration gases and Instrument manual operation procedures.

T. Muirhead

Approved by

ANNEXURE C Supplementary material

Table 8: Time weighted averages (TWA) compared to occupational exposure limits (OELs) of total volatile organic compounds (TVOCs)

		Day 1							
		W1		W2		W3		Area	
	OEL 12-hour TWA (ppm)	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL
Pentane	1333	0.59	0.04	1.05	0.08	1.92	0.14	0.17	0.01
Acetone	333	0.35	0.11	0.007*	0.00	0.007*	0.00	0.007*	0.00
Hexane	667	0.10	0.01	0.15	0.02	0.24	0.04	0.04	0.01
n-Hexane	67	0.03	0.04	0.04	0.05	0.06	0.09	0.00	0.01
Benzene	1	0.02	2.65	0.02	3.12	0.04	5.34	0.01	1.34
Isooctane	200	0.02	0.01	0.02	0.01	0.04	0.02	0.005*	0.00
Heptane	533	0.04	0.01	0.04	0.01	0.07	0.01	0.006*	0.00
Toluene	27	0.03	0.12	0.05	0.18	0.07	0.27	0.01	0.05
Ethyl benzene	133	0.005*	0.00	0.00	0.00	0.00	0.00	0.005*	0.00
Xylene	67	0.02	0.02	0.01	0.01	0.04	0.06	0.006*	0.00
n-Octane	200	0.01	0.01	0.007*	0.00	0.02	0.01	0.007*	0.00
n-Nonane	133	0.006*	0.00	0.006*	0.00	0.006*	0.00	0.006*	0.00
n-Decane	133	0.005*	0.00	0.005*	0.00	0.005*	0.00	0.005*	0.00
White Spirits	67	0.37	0.56	0.56	0.84	1.09	1.63	0.06	0.09
		Day 2							
		W4		**W5**		**W6**		**Area**	
	OEL 12-hour TWA (ppm)	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL
Pentane	1333	0.11	0.01	0.19	0.01	0.21	0.02	0.007*	0.00
Acetone	333	0.007*	0.00	0.02	0.00	0.007*	0.00	0.007*	0.00
Hexane	667	0.03	0.00	0.05	0.01	0.05	0.01	0.006*	0.00
n-Hexane	67	0.01	0.01	0.01	0.01	0.01	0.01	0.007*	0.00
Benzene	1	0.006*	0.00	0.01	0.81	0.006*	0.00	0.006*	0.00
Isooctane	200	0.01	0.01	0.01	0.00	0.01	0.01	0.005*	0.00
Heptane	533	0.02	0.00	0.01	0.00	0.01	0.00	0.006*	0.00
Toluene	27	0.02	0.08	0.02	0.08	0.02	0.06	0.01	0.05
Ethyl benzene	133	0.005*	0.00	0.005*	0.00	0.005*	0.00	0.005*	0.00
Xylene	67	0.02	0.02	0.01	0.01	0.01	0.01	0.006*	0.00
n-Octane	200	0.007*	0.00	0.007*	0.00	0.007*	0.00	0.007*	0.00
n-Nonane	133	0.006*	0.00	0.006*	0.00	0.006*	0.00	0.006*	0.00

n-Decane	133	0.005*	0.00	0.005*	0.00	0.005*	0.00	0.005*	0.00
White Spirits	67	0.28	0.43	0.09	0.14	0.20	0.30	0.004*	0.01

Day 3

		W7		**W8**		**W9**		**Area**	
	OEL 12-hour TWA (ppm)	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL
Pentane	1333	1.38	0.10	1.01	0.08	0.01	0.00	0.69	0.05
Acetone	333	0.007*	0.00	0.007*	0.00	0.007*	0.00	0.007*	0.00
Hexane	667	0.19	0.03	0.14	0.02	0.06	0.01	0.12	0.02
n-Hexane	67	0.04	0.06	0.04	0.06	0.02	0.02	0.03	0.04
Benzene	1	0.02	3.64	0.02	3.25	0.01	1.34	0.02	2.74
Isooctane	200	0.03	0.01	0.02	0.01	0.01	0.00	0.02	0.01
Heptane	533	0.04	0.01	0.04	0.01	0.03	0.00	0.03	0.01
Toluene	27	0.05	0.18	0.04	0.16	0.02	0.09	0.05	0.19
Ethyl benzene	133	0.005*	0.00	0.005*	0.00	0.005*	0.00	0.005*	0.00
Xylene	67	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.03
n-Octane	200	0.007*	0.00	0.007*	0.00	0.01	0.00	0.007*	0.00
n-Nonane	133	0.006*	0.00	0.006*	0.00	0.006*	0.00	0.006*	0.00
n-Decane	133	0.005*	0.00	0.005*	0.00	0.005*	0.00	0.005*	0.00
White Spirits	67	0.64	0.96	0.47	0.71	0.23	0.35	0.34	0.51

Day 4

		W10		**W11**		**W12**		**Area**	
	OEL 12-hour TWA (ppm)	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL
Pentane	1333	0.57	0.04	1.56	0.12	0.83	0.06	0.40	0.03
Acetone	333	0.007*	0.00	0.007*	0.00	0.007*	0.00	0.007*	0.00
Hexane	667	0.09	0.01	0.23	0.03	0.13	0.02	0.07	0.01
n-Hexane	67	0.02	0.03	0.05	0.08	0.03	0.04	0.02	0.02
Benzene	1	0.01	1.84	0.03	4.38	0.02	2.44	0.01	1.57
Isooctane	200	0.02	0.01	0.03	0.02	0.02	0.01	0.01	0.00
Heptane	533	0.03	0.01	0.05	0.01	0.03	0.01	0.02	0.00
Toluene	27	0.04	0.14	0.06	0.22	0.04	0.14	0.03	0.09
Ethyl benzene	133	0.00	0.00	0.005*	0.00	0.005*	0.00	0.005*	0.00
Xylene	67	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01
n-Octane	200	0.007*	0.00	0.007*	0.00	0.007*	0.00	0.007*	0.00
n-Nonane	133	0.006*	0.00	0.006*	0.00	0.006*	0.00	0.006*	0.00
n-Decane	133	0.005*	0.00	0.005*	0.00	0.005*	0.00	0.005*	0.00
White Spirits	67	0.12	0.17	0.80	1.21	0.43	0.64	0.40	0.60

Day 5

	W13	**W14**	**W15**	**Area**

	OEL 12-hour TWA (ppm)	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL	12h-TWA (ppm)	% of OEL
Pentane	1333	1.14	0.09	1.39	0.10	0.24	0.02	0.18	0.01
Acetone	333	0.007*	0.00	0.03	0.01	0.007*	0.00	0.007*	0.00
Hexane	667	0.17	0.03	0.19	0.03	0.04	0.01	0.04	0.01
n-Hexane	67	0.05	0.07	0.04	0.07	0.01	0.01	0.01	0.01
Benzene	1	0.02	3.67	0.03	4.06	0.01	0.97	0.00	0.63
Isooctane	200	0.03	0.01	0.02	0.01	0.01	0.00	0.0054	0.00
Heptane	533	0.05	0.01	0.04	0.01	0.02	0.00	0.0062	0.00
Toluene	27	0.05	0.20	0.05	0.17	0.01	0.06	0.01	0.05
Ethyl benzene	133	0.005*	0.00	0.005*	0.00	0.005*	0.00	0.005*	0.00
Xylene	67	0.02	0.04	0.01	0.02	0.01	0.01	0.01	0.01
n-Octane	200	0.01	0.00	0.007*	0.00	0.007*	0.00	0.007*	0.00
n-Nonane	133	0.006*	0.00	0.006*	0.00	0.006*	0.00	0.006*	0.00
n-Decane	133	0.005*	0.00	0.005*	0.00	0.005*	0.00	0.005*	0.00
White Spirits	67	0.61	0.92	0.69	1.03	0.14	0.22	0.10	0.15

***** Results below the detection limit (BDL) for each value of elemantal carbon (EC) was substituted with DL/√2; %: percentage; mg/m3:milligram per cubic meter; EC; elemental carbon; MHSA: Mine Health and Safety Act; OEL:occupational exposure limit; TWA: time weighted average; W: Worker.

ANNEXURE D Ethics approval letter

Private Bag X1290, Potchefstroom
South Africa 2520

Tel: 086 016 9698
Web: http://www.nwu.ac.za/

North-West University Health Research Ethics Committee (NWU-HREC)

Tel: 018 299-1206
Email: Ethics-HRECApply@nwu.ac.za (for human studies)

9 July 2025

ETHICS APPROVAL LETTER OF STUDY

Based on approval by the North-West University Health Research Ethics Committee (NWU-HREC) on 09/07/2025, the NWU-HREC hereby approves your study as indicated below. This implies that the NWU-HREC grants its permission that, provided the general conditions specified below are met and pending any other authorisation that may be necessary, the study may be initiated, using the ethics number below.

Study title: Monitoring of exposure to total volatile organic compounds and particulate matter at a petrol-filling station
Principal Investigator/Study Supervisor/Researcher: Prof SR Horn
Student: EC van der Westhuizen - 37548034

Ethics number:

N	W	U	-	0	0	1	2	3	-	2	5	-	A	1
Institution				Study Number						Year			Status	

Status: S = Submission; R = Re-Submission; P = Provisional Authorisation; A = Authorisation

Application Type: Single study
Commencement date: 09/07/2025
Expiry date: 31/07/2026

Risk: **Minimal**

Approval of the study is provided for a year, after which continuation of the study is dependent on receipt and review of an annual monitoring report and the concomitant issuing of a letter of continuation. A monitoring report is due at the end of July annually until completion of the study.

General conditions:

While this ethics approval is subject to all declarations, undertakings and agreements incorporated and signed in the application form, the following general terms and conditions will apply:

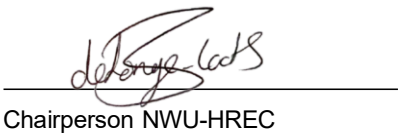
- *The principal investigator/study supervisor/researcher must report in the prescribed format to the NWU-HREC:*
  - *Annually on the monitoring of the study, whereby a letter of continuation will be provided annually, and upon completion of the study; and*
  - *without any delay in case of any adverse event or incident (or any matter that interrupts sound ethical principles) during the course of the study.*
- *The approval applies strictly to the proposal as stipulated in the application form. Should any amendments to the proposal be deemed necessary during the course of the study, the principal investigator/study supervisor/researcher must apply for approval of these amendments at the NWU-HREC, prior to implementation. Should there be any deviations from the study proposal without the necessary approval of such amendments, the ethics approval is immediately and automatically forfeited.*
- *Annually a number of studies may be randomly selected for active monitoring.*
- *The date of approval indicates the first date that the study may be started.*
- *In the interest of ethical responsibility, the NWU-HREC reserves the right to:*

- *request access to any information or data at any time during the course or after completion of the study;*
- *to ask further questions, seek additional information, require further modification or monitor the conduct of your research or the informed consent process;*
- *withdraw or postpone approval if:*
  - *any unethical principles or practices of the study are revealed or suspected;*
  - *it becomes apparent that any relevant information was withheld from the NWU-HREC or that information has been false or misrepresented;*
  - *submission of the annual monitoring report, the required amendments, or reporting of adverse events or incidents was not done in a timely manner and accurately; and/or*
  - *new institutional rules, national legislation or international conventions deem it necessary.*

- *NWU-HREC can be contacted for further information via Ethics-HRECApply@nwu.ac.za or 018 299 1206*

The NWU-HREC would like to remain at your service and wishes you well with your study. Please do not hesitate to contact the NWU-HREC for any further enquiries or requests for assistance.

Yours sincerely,



Chairperson NWU-HREC

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