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PHYSICOCHEMICAL PROPERTIES OF INDOOR AND OUTDOOR PARTICULATE MATTER IN RESIDENTIAL AREAS NEAR A FERROMANGANESE SMELTER



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Declaration

I, **Setlamorago Jackson Thobejane (student number: 2281450)** declare that the research project entitled *"Physicochemical Properties of Indoor and Outdoor Particulate matter in a Residential Area Near a Ferromanganese Smelter"* is my research work undertaken under the supervision of Dr Masilu Daniel Masekameni. The work is being submitted in partial fulfilment for the degree of Master of Medicine in the field of Exposure Science at the School of Public Health, University of the Witwatersrand, Johannesburg. This work has not been presented for examination at any other university. The author designed the study, conducted all field data collection, data analysis, and writing the research report. Parts of this research report have been planned to be published in peer-reviewed journals and presented at conferences. All the sources cited in this study have been acknowledged through comprehensive references. The senate plagiarism policy is signed and attached as Appendix A: Plagiarism Declaration Form.

Abstract submission

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3. Thobejane, SJ., Masekameni, MD. "Source apportionment of indoor and outdoor particulate matter in a residential area near a ferromanganese smelter using chemical mass balance and positive factorisation matrix"

Dedication

This research report is dedicated to my family for the endless support they have given me in good and bad times. I appreciate the support that my sisters (Melita, Mahlako, Mathodi, Refilwe, Thobejane, and Neria Mbazima) have given me and the encouragement that my brothers (Seremi and Bauba Thobejane) have I would also like to thank my partner Yonda Nokhwethu for the understanding and support that she has provided throughout the years and for having patience when I was a present but absent partner. Lastly, to my newborn child Atamelang, welcome to earth my son!

Abstract

Background

Approximately 90% of the world's population resides in areas where ambient air quality standards are exceeded. Particulate matter with an aerodynamic size of less than 2.5 µm ($PM_{2.5}$) has been identified as the leading contributor to indoor and outdoor air pollution. $PM_{2.5}$ can be released from natural and anthropogenic sources, however, anthropogenic sources such as ferromanganese smelters are among the major sources. Ferromanganese smelters tend to release Mn-bearing $PM_{2.5}$. Owing to their size, Mn-bearing $PM_{2.5}$ can remain suspended for longer periods and travel a greater distance from the emitting source and penetrate indoor environments. It is suggested that most people, especially vulnerable groups spend approximately 80%–90% of their time indoors. Chronic exposure to Mn-bearing $PM_{2.5}$ is associated with neurological disorders. Most of the evidence on the causal relationship between Mn exposure and neurological disorder was drawn from epidemiological studies that lacked exposure assessments.

Purpose

To systematically characterise the similarities between indoor and outdoor $PM_{2.5}$ airborne particles in residential areas within the vicinity of the smelter in Meyerton.

Methods

Indoor and outdoor airborne $PM_{2.5}$ were collected concurrently from selected households using two identical active samplers. A gravimetric sampling technique was used to sample $PM_{2.5}$ continuously over seven days from the 30 selected households. GilAir plus pumps were used to draw in air containing $PM_{2.5}$ into the sampling media at a flow rate of 2.75 L/min. The sampling media comprised of a 37 mm cassette, which was housed in a 37 mm polycarbonate filter. A 1.5 m long Teflon tubing was used to connect the sampling media outlet to the inlet of the pump. A total of 60 samples were collected over three months (August–November 2019) and comprised 30 indoor and 30 outdoor samples. $PM_{2.5}$ mass concentrations were obtained gravimetrically using a microbalance scale. The physicochemical properties were analysed using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). Inductively coupled plasma-mass spectrometry (ICP-MS) was used to analyse the elemental composition of indoor and outdoor $PM_{2.5}$. The difference between indoor and outdoor $PM_{2.5}$ mass concentration was

determined by calculating the indoor-outdoor ratio, where a ratio greater than 1 indicated that indoor $PM_{2.5}$ is less than the outdoor. Furthermore, statistical analysis for indoor and outdoor $PM_{2.5}$ was performed using an F-Test and a Student t-test. A P-value of <0.05 indicated a statistically significant difference between indoor and outdoor $PM_{2.5}$.

Results

Indoor $PM_{2.5}$ mass concentration ranged between 2.88 and 19.19 µg/m^3 with an average of 10.99 ± 5.10 µg/m^3 while outdoor concentration ranged between 11.68 and 40.44 µg/m^3 with an average of 24.97 ± 6.77 µg/m^3. Outdoor $PM_{2.5}$ mass concentration in Meyerton was 2.7 fold greater than the indoor. The I/O ratio of $PM_{2.5}$ was 0.44 indicating that indoor $PM_{2.5}$ was lower than the outdoor. The I/O ratio of less than 1 further indicated and that indoor $PM_{2.5}$ was influenced by PM from the outdoor environment. A statistically significant difference was found (P=5.8×10^{-13}) between indoor and outdoor $PM_{2.5}$ mass concentrations. SEM images showed that indoor $PM_{2.5}$ consisted of irregular and agglomerated particles ranging from 0.1 to 0.7 µm in diameter while $PM_{2.5}$ outdoor also consisted of irregular but single spherical particles ranging from 0.1 to 1.3 µm in diameter. SEM images showed similarities between indoor and outdoor particles suggesting that they are from the same or similar source. ICP-MS results indicated an abundance of elements in decreasing order of Si > Fe > Zn > Mn both on indoor and outdoor $PM_{2.5}$. However, outdoor $PM_{2.5}$ had the highest concentration of Mn, Zn, Si, and Fe relative to indoor $PM_{2.5}$. The average indoor and outdoor Mn concentration was 1.30 µg/m^3 and 5.36 µg/m^3, respectively.

Conclusion

This study investigated the similarities between the physicochemical properties of indoor and outdoor $PM_{2.5}$ sampled in residential areas near a ferromanganese smelter and found that most indoor $PM_{2.5}$ originated from an outdoor source. Moreover, indoor and outdoor $PM_{2.5}$ were enriched with Mn and other elements, which can lead to chronic health outcomes amongst vulnerable groups. Since Mn and the other elements found in this study are mainly released from ferromanganese smelters, the nearby smelter might be a major source of indoor and outdoor Mn-bearing $PM_{2.5}$ in Meyerton. However, further studies using advanced source apportionment techniques are recommended to verify the findings. Lessons drawn from this study suggest the need for integrated town planning and development where ferromanganese smelter are not supposed to be built near residential areas. Measures such as tree plantation may be introduced in such residential areas to reduce or trap airborne PM.

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Nomenclature

List of abbreviations

AG	Atkiengesellschaft
Al	Aluminium
Amcor	African Metals Cooperation Limited
As	Arsenic
ATSDR	Agency for Toxic Substances and disease registry
BSE	Back-scattered electron
Ca	Calcium
Cd	Cadmium
CNS	Central nervous system
Co	Cobalt
Cr	Chromium
Cu	Copper
EDX	Energy-dispersive X-ray spectroscopy
Fe	Iron
FeMn	Iron Manganese
FeSi	Ferrosilicon
FeTi	Ferrotitanium
FeW	Ferrotungsten
FL	Florida
GPS	Global positioning system
H_2O_2	Hydrogen peroxide
HCFeMn	High-carbon ferromanganese
HNO_3	Nitric acid
I/O	Indoor-outdoor ratio

ICP-MS	Inductively coupled plasma-mass spectrometry
K	Potassium
LCFeCr	Low-ferrochromium
LCSiMn	Low-carbon silicomanganese
LoD	Limit of detection
LoQ	Limit of quantification
MCFeCr	Medium-ferrochromium
MCFeMn	Medium-carbon ferromanganese
Mg	Magnesium
MMT	Methylcyclopentadienyl manganese tricarbonyl
Mn	Manganese
MnDPDP	Mangafodipir trisodium
MRI	Magnetic resonance imaging
Na	Sodium
Ni	Nickel
Pb	Lead
PCTE	Polycarbonate membrane
PD	Parkinson's disease
PM	Particulate matter
$PM_{2.5}$	Particulate matter less than 2.5 in diameter
S	Sulphur
SD	Standard deviation
SE	Secondary electron
SEM	Scanning electron microscopy
SEM-EDX	Scanning electron microscopy coupled with energy dispersive X-ray
Si	Silicon

SiMn	Silicomanganese
UK	United Kingdom
USA	United States of America
V	Vanadium
WHO	World Health Organization
Wt%	Weight percent
Zn	Zinc

SI units and symbols

%	Percent
ºC	Degree Celsius
µg	Microgram
µg/L	Microgram per litre
µg/m^3	Microgram per cubic metre
µm	Micrometer
C	Concentration
C_e	Element concentration
cm^2	Square centimetre
g	Gram
kg	Killogram
km	Kilometre
km/h	Kilometre per hour
km^2	Square kilometre
kV	Kilovolt
L/min	Litres per minute
m	Mass
m	Metre

m^3	Cubic metre
M_e	Element mass
mg/L	Milligram per litre
mg/m^3	Miligram per cubic metre
mL	Millilitres
mm	Millimeter
MVA	Mega volt-ampere
$M\Omega/cm^2$	Milliohm per square centimetre
nA	Nanoampere
ng/m^3	Nanogram per cubic metre
nm	Nanometre
V	Volume

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CHAPTER 1: INTRODUCTION

This chapter begins with an overview of particulate matter (PM) and its natural and anthropogenic sources and their impact on indoor and outdoor air quality. The release of Manganese-bearing PM from ferromanganese smelters is outlined and the chapter further describes Manganese as a trace element and micronutrient, its use, and the health outcomes associated with exposure to Mn-bearing PM. The problem statement and justification of the study are outlined and the chapter ends by presenting the study aim, hypothesis, and objectives.

1.1 Background

Particulate matter (PM) refers to a mixture of particles suspended in the air in a liquid or solid form which are often observed as dust, smoke, or haze (Brüske-Hohlfeld and Peters, 2010; Lowther *et al.*, 2019). PM is categorised into $PM_{0.1}$ (<0.1 μm), $PM_{2.5}$ (<2.5 μm), and PM_{10} (<10 μm) depending on the aerodynamic diameter (Brüske-Hohlfeld and Peters, 2010; Hoeflinger and Laminger, 2019). The World Health Organization (WHO), stated that approximately 90% of the global population has no access to clean air (World Health Organization, 2016).

The WHO further stated that most people reside in areas where ambient air quality standards are exceeded (World Health Organization, 2016) and $PM_{2.5}$ has been identified as the leading contributor to indoor and outdoor air pollution (Li *et al.*, 2017). $PM_{2.5}$ has been categorised as a criteria pollutant by the South African National Standards (Gholampour *et al.*, 2016) and it is used as an indicator of air pollution globally (Hänninen and Goodman, 2019).

$PM_{2.5}$ can be emitted from various sources (Pöschl, 2010), the sources are classified into two main categories, natural and anthropogenic sources (Ahmed, Guo and Zhao, 2017; Galvão *et al.*, 2018). Natural sources associated with the release of PM_2 include cyclones, earthquakes, and uranium decay (Mukherjee and Agrawal, 2017; Galvão *et al.*, 2018). Anthropogenic sources include industrial activities, residential areas, and automobiles, however, compelling literature highlights industrial activities as major sources of $PM_{2.5}$ (Galvão *et al.*, 2018).

Electricity generation, ferromanganese smelters, metal casting, and mining activities are among the leading sources in the industrial sector that contribute to $PM_{2.5}$ emissions with

different physicochemical properties (Sielicki *et al.*, 2011; Gonzalez-Castanedo *et al.*, 2014; Zhou *et al.*, 2019). Such activities operate at a high temperature and often release single particles with an aerodynamic diameter of 1 μm or less, also known as submicron PM (Valavanidis, Fiotakis and Thomas, 2008; Masekameni *et al.*, 2018).

Ferromanganese smelters are some of the industrial activities operated at temperatures between 100 and 1 400ºC (Marris *et al.*, 2012) resulting in the emission of submicron PM (Lighty, Veranth and Sarofim, 2000). Ferroalloy production processes such as raw material and product handling, sintering, smelting, tapping, and casting release Mn-bearing PM with different physicochemical properties (Davourie *et al.*, 2017; Hernández-Pellón *et al.*, 2017). The Mn-bearing PM may also have high concentrations of elements such as lead (Pb), Mercury (Hg), Cadmium (Cd), Nickel (Ni), Arsenic (As), and Chromium (Cr) (Mazzei *et al.*, 2008; Li *et al.*, 2017). These elements are commonly found in the environment and have similar neurotoxic effects (Popoola *et al.*, 2018).

Submicron PM has a higher resident time in the atmosphere and can be easily be transported over a greater distance from the initial source of release (Hernández-Pellón and Fernández-Olmo, 2019; Lowther *et al.*, 2019). During transportation, the particles tend to undergo a chemical and physical transformation and grow into larger particles with an aerodynamic diameter of 2.5 μm or less by the time they reach a residential area (Galvão *et al.*, 2018; Thompson, 2018).

The particles grow from nucleation or Aitken (0.0001–0.1 μm), accumulation mode (0.1–2.5 μm), and to course mode (2.5–10 μm) due to agglomeration, condensation, and accumulation (Riffault *et al.*, 2015; Rohra *et al.*, 2018), and they agglomerate based on their inherent chemical and physical characteristics (Setyan *et al.*, 2019; Zhou *et al.*, 2019). Furthermore, $PM_{2.5}$ moves and deposit through diffusion relative to larger particles (PM_{10}) that deposit through gravitational force (Morawska *et al.*, 2013).

The deposited PM can settle on a residential building and enter indoor environments through infiltration, filtration, foot tracking, open windows, and other openings. The indoor-outdoor (I/O) ratio can be used to determine the relationship between indoor and outdoor PM mass concentrations (Martins *et al.*, 2020). An I/O ratio of less than 1 indicates good indoor air quality and the absence of major indoor contributing sources (Chen and Zhao, 2011; Martins *et al.*, 2020) while an I/O ratio greater than 1 indicates a presence of significant indoor sources (Pallarés *et al.*, 2019). In the absence of major indoor sources, indoor air quality is directly linked to outdoor sources (Guo *et al.*, 2010).

Although the size and morphology determine the fate of the PM in the respiratory tract (Allen *et al.*, 2017), however, the elemental composition also affects health outcomes (Galvão *et al.*, 2018). Therefore, information and understanding of the physicochemical properties are needed to apportion the source and protect public health since atmospheric PM is a complex mixture and the elemental composition differs (Peters *et al.*, 2006; Rodríguez *et al.*, 2007; Park *et al.*, 2018). Due to the complexity of PM, elemental isolation within a mixture is necessary to determine the potential for source contribution and possible health effects (Genga *et al.*, 2018).

It is well established that ferromanganese smelters release a significant amount of Mn-bearing PM into the atmosphere (Bowler *et al.*, 2016). Due to the inherent risks associated with Mn exposure (Racette *et al.*, 2018), it is necessary to establish the relationship between indoor and outdoor PM levels using Mn as an indicator element.

1.2 Literature review

Mn exists in an organic and inorganic form and it is the fifth most abundant heavy metal and the twelfth most abundant trace element in the earth's crust (Horning *et al.*, 2015; O'Neal and Zheng, 2015). Mn comprises approximately 0.1% of the earth's crust and commonly exists as oxides, carbonates, and silicates (Chen, Culbreth and Aschner, 2016). It also occurs naturally in certain food products, however, it can be added as a nutritional supplement (Horning *et al.*, 2015). It can be found in food products such as legumes, rice, nuts, whole grains, seafood, and teas (Peres *et al.*, 2016). Levels between 2 and 5 mg/day and 9 and 11 mg/day are regarded as a sufficient daily intake for children and adults respectively (Aschner and Aschner, 2005; Miah *et al.*, 2020).

At an acceptable daily intake, Mn is essential for human physiological functions such as bone mineralization, metabolic regulation, and breakdown of cholesterol, carbohydrates, and proteins (Menezes-Filho *et al.*, 2014; Verenice Muñoz-Rocha *et al.*, 2018; dos Santos *et al.*, 2019). Due to its catalytic and regulatory functions, Mn is important in biochemical reactions of several enzymes including Mn-dependent superoxide dismutase (Michalke and Fernsebner, 2014). Also, Mn maintains the nervous and immune system and it is necessary for normal reproductive hormone function and the prevention of cellular oxidative stress (Hernández-Pellón *et al.*, 2017; Hernández-Pellón and Fernández-Olmo, 2019).

Countries rich with Mn reserves are Gabon, South Africa, China, and Ghana (Chen, Culbreth and Aschner, 2016). South Africa reserves 80% of the world's high-grade Mn and it is the

largest producer of high-quality manganese (Steenkamp and Basson, 2013; Coetsee, 2019). The Mn reserves in South Africa are found in the Kalahari Basin, Northern Cape Province and the Kalahari Basin reserves 90% Mn which consists of the Mamatwan and Wessels type (Steenkamp and Basson, 2013). In 2001, 50% of the Mn ore mined in the country was smelted locally and the numbers have remained constant over the years (Steenkamp *et al.*, 2018).

1.2.1 Use of manganese

Manganese and its compounds are used in various industries for the production of steel, welding rods, fireworks, dry cell batteries, and various Mn chemical products (Otero-Pregigueiro and Fernández-Olmo, 2018; Ou *et al.*, 2018). In steel and stainless industries, Mn is a common and important constituent that is used as a supplement to improve the quality of the steel (Davourie *et al.*, 2017; Coetsee, 2019). Mn is primarily used for the deoxidisation and desulphurisation of the steel and to control the morphology of the sulphides and improve the strength, toughness, and hardness of the steel (Steenkamp and Basson, 2013).

Approximately two tonnes of Mn are required to produce 1 tonne of ferromanganese (ATSDR, 2012). Approximately 90% of the Mn ferroalloys produced are in the steelmaking making industry at a consumption rate between 7.5 and 10 kg of Mn per tonne of steel (Steenkamp and Basson, 2013). The sintering step generates fine particles relative to the other steps involved in the processing of Mn (Sammut *et al.*, 2010). Other than the application in Mn ferroalloys, Mn is also used in the production of Cu, Al, and Silver-Cu alloys and other non-metallic applications such as fertilisers and dry cell batteries production (Steenkamp and Basson, 2013).

After the ban of Pb in the petroleum industry, methylcyclopentadienyl manganese tricarbonyl (MMT) which is an organic derivative of Mn has been used significantly as an additive to improve the octane level and anti-knock of petrol (Beaupré *et al.*, 2004; Finkelstein and Jerrett, 2007; Walsh, 2007). Mn is also used in the production of pesticides and fungicides such as Mn ethylene-bis-dithiocarbamate (maneb) and dithiocarbamate (mancozeb) (Crossgrove and Zheng, 2004; Chen, Culbreth and Aschner, 2016). Due to its paramagnetic nature, mangafodipir trisodium (MnDPDP) is used as a liver and pancreas-specific contrasting agent for MRI (Aschner *et al.*, 2009; Chen, Culbreth and Aschner, 2016).

1.2.2 Sources of Mn-bearing PM

The sources of Mn-bearing PM can be divided into natural and anthropogenic sources. Crustal rock is a major natural source of atmospheric Mn-bearing particles. Mn-bearing PM can be released during ocean spray, forest fires, volcanic eruptions, and vegetation activities such as ploughing (Malcolm, Wood and Kingdom, 2004; Omrani *et al.*, 2017). However, natural sources emit coarse Mn-bearing particles relative to anthropogenic sources (Martins *et al.*, 2020).

Anthropogenic sources of Mn include municipal wastewater discharges, sewage sludge, mining and mineral processing, the combustion of fossil fuels, automobiles, battery and pesticides manufacturing alloy, steel, and iron smelters (Malcolm, Wood and Kingdom, 2004; Omrani *et al.*, 2017; Popoola *et al.*, 2018). Studies investigating the formation and release of PM from automobiles have been conducted. Karagulian *et al.* (2015), Amato *et al.* (2016) and (2017) reported that automobiles are significant contributors to atmospheric PM concentration levels in urban areas.

Automobiles became a contributing source of Mn-bearing particles due to the use of MMT (Walsh, 2007). The combustion of MMT in automobile engines leads to the formation and release of Mn-bearing particles in the size range between 0.2 and 10 µm (Loranger and Zayed, 1995). Although fuel combustion in automobiles is the predominant way in which PM is formed and released, the mechanical abrasion and corrosion processes such as tyre, clutch, and brake wear, and road surface abrasion also contribute to the formation and release of PM (Viana, 2013; Liati *et al.*, 2016; Alves *et al.*, 2020). Both the mechanical and exhaust-formed PM will settle on the road surface and can be suspended or resuspended due to wind and or automobile-generated turbulence (Viana, 2013). These processes are suggested to contribute significantly to the atmospheric $PM_{2.5}$ concentration levels (Alves *et al.*, 2020).

1.2.3 Exposure to Mn

Exposure to Mn can occur through three common routes, which are ingestion, dermal, and inhalation (Carvalho *et al.*, 2018; Oberdörster and Kuhlbusch, 2018). Ingestion can occur through the direct consumption of water and food containing Mn (Horning *et al.*, 2015). The dermal route exposure can occur when bathing using water that is contaminated with Mn or through contact with Mn-bearing particles, however, direct contact with the Mn-bearing PM is considered less effective (Jin *et al.*, 2018; Thompson, 2018). The inhalation route is considered the most obvious, effective, and susceptible route of entry relative to the ingestion

and dermal route (Menezes-Filho *et al.*, 2009; Otero-Pregigueiro and Fernández-Olmo, 2018).

The uptake of Mn-bearing PM through the inhalation route is considered threatening because Mn-bearing PM can bypass normal biliary excretion mechanisms and directly enter the brain along the olfactory neurons before it can be metabolized by the liver (Haynes *et al.*, 2010; Hernández-Bonilla *et al.*, 2011; Fulk *et al.*, 2017). Moreover, inhaled Mn can directly enter the CNS and be absorbed more effectively (Lee *et al.*, 2017; Riediker *et al.*, 2019). Some of the Mn-bearing PM will be absorbed by macrophages and transported into the systemic circulation causing systematic effects (Andruska and Racette, 2015; Salma *et al.*, 2015).

Exposure to Mn-bearing PM can occur indoor or outdoor¸ however, it has been argued that exposure to airborne particles mainly occurs indoors (Monn, 2002). This is concerning since it is suggested that in modern society, residents spend approximately 80%–90% of their time indoors (Manigrasso *et al.*, 2018; Koivisto *et al.*, 2019). The elderly, sick, pregnant women, and children spend most of their time indoors (Pavilonis *et al.*, 2015; Delgado-Saborit, 2019) and they are considered vulnerable because of their higher duration of exposure and a weak or compromised immune system (Zota *et al.*, 2011; Morawska *et al.*, 2013).

Exposure to Mn-bearing PM has been associated with neurological disorders, premature death, and respiratory illnesses globally (Cortez-Lugo *et al.*, 2018). Furthermore, Mn-bearing $PM_{2.5}$ can be deposited in the bronchi and penetrate deeper into the alveoli during gaseous exchange (Andruska and Racette, 2015; Hu *et al.*, 2015). To better understand the potential exposure and health outcomes in residents living near a ferromanganese smelter, it is important to assess the similarities between indoor and outdoor PM concentrations and their physicochemical properties (Sajani *et al.*, 2015).

1.2.4 Health effects of Manganese

Although Mn plays a vital role in human physiological functions, exposure to excessive levels of Mn can result in adverse neurotoxic health effects (Fulk *et al.*, 2017; Kornblith *et al.*, 2018). Environmental exposure to Mn-bearing PM is associated with neurological health effects (Colledge *et al.*, 2015; Kornblith *et al.*, 2018). In addition, studies (Smith *et al.*, 2007; Menezes-Filho *et al.*, 2009; Cantone *et al.*, 2011; Nascimento *et al.*, 2016; Hernández-Pellón *et al.*, 2017; Rodrigues *et al.*, 2018) have confirmed and reported a consistent and significant association between exposure to airborne Mn-bearing PM and manganism and other

neurobehavioral deficits at low concentration levels in residential areas near ferromanganese smelters.

The biological mechanisms by which Mn exerts its toxicity on humans have not yet been fully understood, however, chronic exposure to Mn-bearing PM has been associated with CNS disorders (Rodrigues *et al.*, 2018). Mn accumulates in the brain and enters the CNS where it is absorbed more effectively. Once Mn is absorbed in the CNS, it causes adverse effects on the basal ganglia leading to a neurologic psychiatric disorder known as manganism which is similar to Parkinson's disease (PD) (Horning *et al.*, 2015; Ou *et al.*, 2018). Furthermore, excessive exposure to Mn can also lead to disruptions of the respiratory and reproductive systems (Menezes-Filho *et al.*, 2009; dos Santos *et al.*, 2019).

The toxicity and adverse health effects of exposure to Mn-bearing PM depend on individual characteristics such as breathing rate, duration of exposure, and concentration, and the size of the particles (Lucchini, Martin and Doney, 2009; Morawska *et al.*, 2013; Kim, Kabir and Kabir, 2015). Furthermore, the solubility of the PM is an important factor for systematic uptake (Hernández-Pellón *et al.*, 2017). Symptoms of manganism include decreased memory, concentration, fatigue, headache, vertigo, loss of equilibrium, insomnia, tinnitus, trembling of fingers, muscle cramp, and rigidity (Menezes-Filho *et al.*, 2009; Haynes *et al.*, 2010).

Although such symptoms have been documented from occupational studies, environmental studies investigating exposure to airborne Mn-bearing particles have reported similar pre-clinical neurological effects (Lucchini *et al.*, 2007; Solís-Vivanco *et al.*, 2009; Carvalho *et al.*, 2018). Bowler *et al.* (2016) reported a correlation of long-term chronic environmental Mn exposure with impairment in motor function. The study found a change in postural and bilaterality in tremors which are more frequent in manganism (Bowler *et al.*, 2016). The chronic health outcomes are due to a cumulative exposure effect relationship (Squizzato *et al.*, 2018). However, the studies were using epidemiological approaches, which lack exposure assessment data and do not provide information on the source(s) of emission (Yue *et al.*, 2008).

1.2.5 Studies investigating Mn-bearing $PM_{2.5}$ in residential areas

Although Mn-bearing PM is ubiquitous in the atmosphere, anthropogenic sources such as ferromanganese smelters have been linked with low and high atmospheric concentrations of Mn-bearing PM in residential areas. Several studies have investigated Mn-bearing PM in

residential areas and the highest concentration levels were reported in residential areas near ferromanganese smelters (Otero-Pregigueiro *et al.*, 2018).

A study by Lucchini *et al.* (2007) measured atmospheric Mn in the respirable fraction in six areas two km from a manganese alloy plant in Brescia, Italy. The study reported a geometric mean of 0.69 µg Mn/m^3 and a range of 0.2–1.8 µg Mn/m^3. In the same study, Mn concentrations were 0.08 µg Mn/m^3 and ranged between 0.05–0.3 50 km downwind of the smelter (Lucchini *et al.*, 2007). Menezes-Filho *et al.* (2009) measured atmospheric Mn-bearing $PM_{2.5}$ in residential areas 1.3 km from a ferromanganese smelter plant in Salvador, Brazil. The authors reported atmospheric Mn concentrations ranging from 0.011–0.439 $\mu g/m^3$.

In another study conducted near a ferro and silico-manganese smelter in two Ohio towns, total suspended particles atmospheric Mn sampled from 2003–2013 were between 0.11–0.39 in Marietta and 0.17–1.5 in East Liverpool $\mu g/m^3$ (Colledge *et al.*, 2015). In a recent study conducted in two residential areas near a ferromanganese smelter in the north of Spain, Cantabria, Hernández-Pellón *et al.* (2017) highest daily atmospheric Mn concentrations were found to be 1 279 ng/m^3 and 2 062 ng/m^3

The findings from previous studies suggest that ferromanganese smelters are a major contributor to atmospheric Mn-bearing PM in residential areas (Parmalee and Aschner, 2016; Parsons-White and Spitzer, 2018). Furthermore, Mn-bearing PM can settle in nearby residential buildings and infrastructure and impact the indoor air quality (Weisel *et al.*, 2005; Pavilonis *et al.*, 2015; Urso *et al.*, 2015; Hänninen and Goodman, 2019). Moreover, it is stated that 35%–70% of indoor $PM_{2.5}$ is from the outdoor environment (Allen *et al.*, 2012; Lv *et al.*, 2017). The outdoor particles can enter indoor environments through infiltration, ventilation, or filtration mechanisms (Hasheminassab *et al.*, 2014; Koivisto *et al.*, 2019) and through openings and improperly sealed windows (Bowler *et al.*, 2016). $PM_{2.5}$ can also enter the indoor microenvironment through foot tracking (Lee *et al.*, 2002).

1.3 Problem statement

In South Africa, several studies (Myers *et al.*, 2003; Young, Myers and Thompson, 2005) assessing exposure to Mn-bearing PM have been conducted, however, they were focused and confined to occupational settings with little focus on incidental exposures at a community level. Davourie *et al.* (2017) stated that exposure to airborne Mn-bearing particles in occupational settings has been sufficiently investigated, however, non-

occupational exposure remains a significant concern (Davourie *et al.*, 2017). Furthermore, occupational exposure to Mn-bearing particles is characterised by intermittent high concentrations while environmental exposure consists of low concentrations for a prolonged period through multiple exposure routes (Rodríguez-Agudelo *et al.*, 2006; Solís-Vivanco *et al.*, 2009; Kornblith *et al.*, 2018).

Despite several gaps in understanding source to receptor relationship, only one study (Batterman *et al.*, 2011) in South Africa has investigated the physicochemical properties of airborne Mn-bearing PM and exposure thereof. Therefore, there is limited data regarding the physicochemical properties of PM and exposure assessment data in residential areas near ferromanganese smelters in South Africa (Hermanus, 2000). Subsequently, epidemiological studies (Wild, Bourgkard and Paris, 2009) use occupational data due to limited data (Niu *et al.*, 2010; Sly *et al.*, 2016). The limited data is attributed to the reluctance to conduct studies due to anticipated low concentration levels in residential areas near ferromanganese smelters (Sly *et al.*, 2016).

Such studies often use ambient concentration levels obtained from fixed monitoring stations that are located far from the receptor, and the study population is allocated to the same exposure (Turpin *et al.*, 2007; Hasheminassab *et al.*, 2014). Diapouli *et al.* (2011) and Gozzi *et al.* (2016) argued that the concentration of airborne PM obtained from fixed monitoring stations does not represent the exposure at the receptor level. The lack of exposure assessment data subsequently leads to poor development of pollution inventory and establishment of strategies or policies to improve air quality in residential areas in the industrialised parts of the country. Therefore, a study of this kind that intends to link the source and hazard is necessary to develop effective control measures to protect public health.

1.4 Justification

Source apportionment studies have been conducted in South Africa, however, the studies lacked information on the elemental composition of the PM (Galvão *et al.*, 2018). Consequently, limited emission inventories on industrial processes exist in the country since the implementation of an emission inventory depends on the correct determination of the elemental composition of PM (GroundWork, 2016). Therefore, to improve the emission inventory for source control or mitigation, the correct identification of the chemical signature remains an important variable that must be analysed (Ahmed, Guo and Zhao, 2017).

The objective of various source apportionment techniques is to determine emission sources and quantify their contribution (Li *et al.*, 2017). Determining the physicochemical properties of PM is important in understanding their origin, formation, and transformation mechanisms and the processes that can occur at their surface (Crenn *et al.*, 2018). Furthermore, to implement interventions that will be effective and efficient in protecting both public health and the environment, information on the main contributing source(s) is important (Aldabe *et al.*, 2011; Dong *et al.*, 2015; Hopke, 2016).

This study is relevant in that it builds on the main study titled "exposure to manganese in an African community", ethical clearance certificate (M150466). The main study aims to associate exposure to Mn-bearing PM and adverse health outcomes and is targeting adults over 40 years due to a higher prevalence of manganism in this age group. To achieve this, BGI PQ-100 samplers are used to collect samples at the three selected residential areas and human samples such as nails, saliva, and hair are collected from the participants. Furthermore, the participants are taken for an MRI scan to check for any presence of Mn particles in the brain. Pilot studies reported a significant prevalence of Parkinsonism (18%), anxiety, and depressive symptoms. Therefore, the MRI scan is done to validate the association between exposure to Mn-bearing PM and the identified health outcomes.

Questionnaires will also be administered to obtain information on the participant's residential and occupational history, potential confounders, mood, and behaviour changes. A series of tests will also be done using various measurement tools to assess the cognitive, memory, and motor function of the participants. The measurement tools include the matrix reasoning subtest from the Wechsler Abbreviated Scale of Intelligence, Object-Go-No-Go test, Letter Number Sequencing, Grooved Pegboard, and Unified Parkinson's Disease Rating Scale 3.

The main study has limitations, it lacks exposure assessments in the near field of the receptors. The main study will only use outdoor concentrations despite that people spend 70–90% of their time indoors where they are likely to be exposed. The current study will address the limitations by sampling indoor and outdoor $PM_{2.5}$ at the level of the receptor to reduce the uncertainty. The study further provides information on the morphology and elemental composition of the sampled $PM_{2.5}$.

Results from this study may help identify the emission source(s), pathway, and transport media of the particles, which are important for source apportionment. The results will also provide insight into the morphology, chemical composition, and identity of particles that the Meyerton residents are potentially exposed to. Therefore, the findings from the study can be

used to strengthen epidemiological data sets in the main study and other future studies. Moreover, the characterisation of PM is fundamental in identifying the emitting source(s) and implementing effective interventions to prevent exposure. Findings from this study will also be useful in policy formulation and decision making, particularly during town planning and the development of industrial and residential areas.

1.5 Hypothesis

This study hypothesised that the Mn-bearing $PM_{2.5}$ concentration will be higher outdoor relative to indoor in the three selected residential areas near the ferromanganese smelter in Meyerton.

1.6 Study Aim

To systematically characterise the similarities between indoor and outdoor $PM_{2.5}$ in three residential areas near the ferromanganese smelter in Meyerton.

1.7 Objectives

To achieve the above aims the following objectives were set out:

1. To determine indoor and outdoor mass concentration of the sampled $PM_{2.5}$ in the three selected residential areas near the ferromanganese smelter in Meyerton;
2. To compare the indoor and outdoor mass concentration of the sampled $PM_{2.5}$ in the three selected residential areas near the ferromanganese smelter in Meyerton;
3. To determine the physical properties of the sampled indoor and outdoor $PM_{2.5}$ in the three selected residential areas near the ferromanganese smelter in Meyerton.
4. To determine the elemental composition of the sampled indoor and outdoor $PM_{2.5}$ in the three selected residential areas near the ferromanganese smelter in Meyerton.

CHAPTER 2: RESEARCH DESIGN AND METHODOLOGY

This chapter begins with a comprehensive description of the study area and the characterisation of the study parameters. A brief history of the ferromanganese smelter and products produced is given. The methods and materials used in the preparation of filters, sampling of particulate matter, and calculation of indoor and outdoor $PM_{2.5}$ mass concentration are outlined. The data analysis and statistical analysis used to determine the

I/O ratio and difference between indoor and outdoor $PM_{2.5}$ mass concentration are described. The chapter further describes the SEM-EDX used for studying the particle morphology and software used to convert particle size to particle number concentration of indoor and outdoor $PM_{2.5}$. The chapter ends by describing the ICP-MS used to study the elemental composition of the sampled indoor and outdoor $PM_{2.5}$.

2.1 Research design

This is a cross-sectional study that used a quantitative approach whereby we aimed to compare the physicochemical properties of indoor and outdoor Mn-bearing $PM_{2.5}$

2.2 Methods and materials

2.2.1 Description of the study area

The study was conducted in Meyerton which is located 15 kilometres north of Vereeniging, Gauteng Province with a global positioning system (GPS) coordinates 26.5854° S and 28.0069° E. Meyerton is under the Midvaal Municipality administration. The Midvaal is well known for its agricultural activities and it is surrounded by maize and dairy farmlands that supply most parts of Gauteng Province.

Meyerton has an area of 180.24 km² and a population size of 55 283 people consisting of 28 041 (50.72%) males and 27 242 (49.28%) females (Statistics South Africa, 2011). The area has an average temperature of 17 ºC, average rainfall of 34.4 mm, humidity 61%, and wind speeds of 6km/h. Approximately 22.7% of the population is between the ages of 0–14, 70% is between 15–64 and 7% is 65 years and above (Statistics South Africa, 2011). Approximately 77.5% of the households in Meyerton are formal dwellings while the remaining are informal settlements made mainly of corrugated iron and boards (Statistics South Africa, 2011).

Within Meyerton, three residential areas (Old Sicelo, New Sicelo, and Noldick) are located near and downwind of a ferromanganese smelter (Figure 1). Although these residential areas are in the same region, they have different characteristics and are at a different distance from the ferromanganese smelter. New Sicelo and Noldick are located near the smelter while Old Sicelo is located farther. Old and New Sicelo are the most densely populated residential areas relative to Noldick. Most of the dwellings in Noldick are constructed of cement blocks and they have ceilings. Most dwellings at New and Old Sicelo are predominantly shacks

constructed from corrugated Fe and boards. Such dwellings are naturally ventilated, thus allowing the outdoor PM to enter indoor environments through openings and cracks.

Most of the Noldick area is vegetated and paved relative to Old and New Sicelo, however, Old Sicelo has tree plantations compared to New Sicelo and Noldick. It has been proven that trees can help reduce the concentration of airborne particles through deposition (Xing and Brimblecombe, 2019). The lack of paving, vegetation, and tree plantations can influence the re-suspension of deposited dust during strong winds or other human activities. Old and New Sicelo are located west of the R59 which is one of Gauteng province's busiest freeways that connects to other neighbouring Provinces. The R551 and M61 roads pass through Noldick and New Sicelo and connect to neighbouring residential areas.

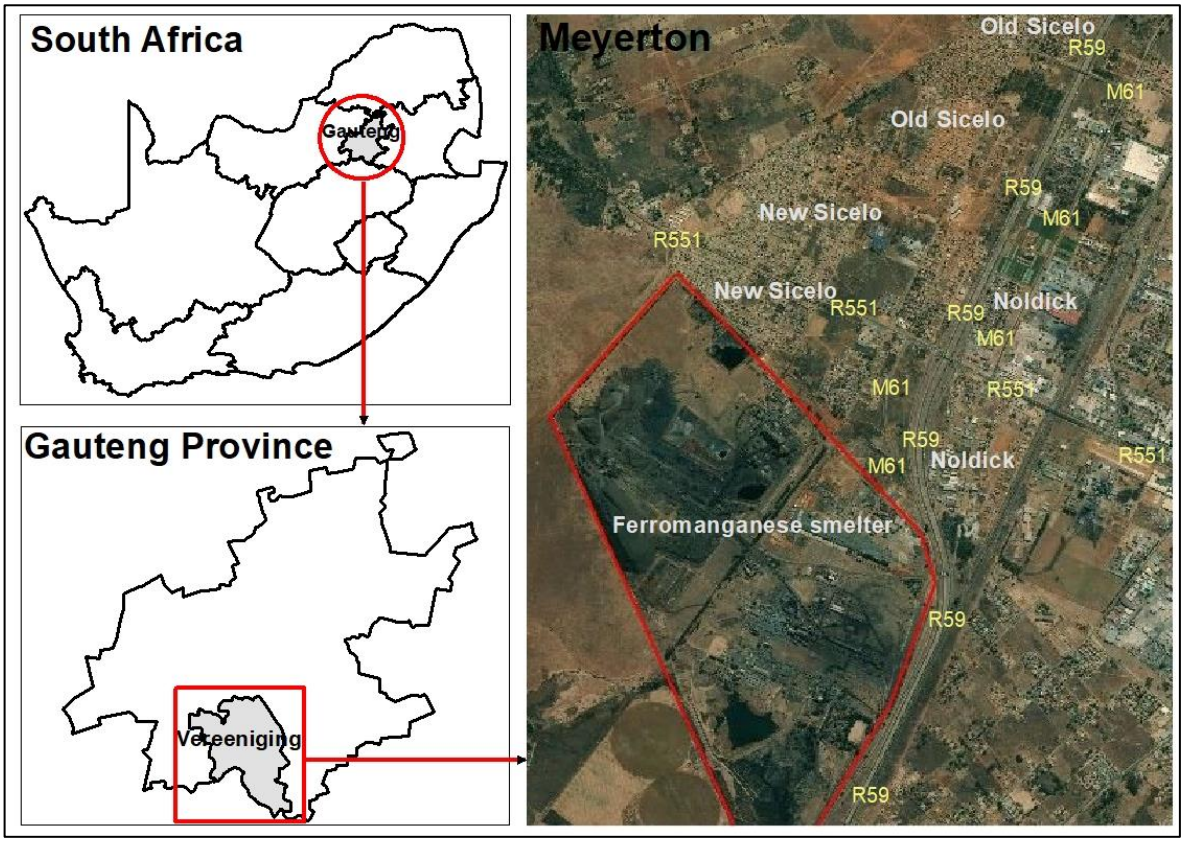


Figure 1: A geographical map of the study area (created Arcmap GIS and Google map)

The ferromanganese smelter was founded in 1939 by the late Dr. H.J van der Bijl who was a pioneer in the exploitation of minerals (Steenkamp and Basson, 2013). The smelter was initially built in the city of Vereeniging and named African Metals Cooperation Limited (Amcor) and produced HCFeMn and ferrosilicon (FeSi) using a three mega volt-ampere (MVA) furnace (Steenkamp and Basson, 2013). The production was expanded, and the company produced high-ferrochromium (HCFeCr), ferrotitanium (FeTi), medium

ferrochromium (MCFeCr), low ferrochromium (LCFeCr), ferrotungsten (FeW), Pb, and various types of stainless steel (Steenkamp and Basson, 2013).

In 1951, the Amcor smelter plant was renamed Samancor Manganese's Metalloys plant upon its relocation to Meyerton where it operates to date, however, the smelter has changed ownership from various companies in the past decades. The smelter is currently under the ownership of South32 which holds 60% of the shares while the remaining 40% is owned by Anglo American and it is called the South32 Metalloys alloy smelter. In 2012, Metalloys alloy ceased the production of SiMn and replaced it with HCFeMn (Steenkamp and Basson, 2013).

The Mn ore used by Metalloys alloy smelter is mined and transported from the Kalahari in the Northern Cape Province (Steenkamp and Basson, 2013). The Metalloys alloy smelter is one of the largest Mn smelters globally and produces HCFeMn (Creamer, 2013). In 2013, the Metalloys alloy smelter was installed with the biggest and distinctive furnace which would enable the company to beneficiate 30% of the Mn ore they produced locally (Creamer, 2013). The 81 MVA furnace can produce 120 000 tonnes of HCFeMn per year (Creamer, 2013). According to Creamer (2013), the production of MCFeMn and HCFeMn is approximately 60 and 480 kilotons annually, respectively. Steyn (2018), stated that the smelter can process more than one million tonnes of product annually.

2.2.2 Preparation of filters

Polycarbonate membrane (PCTE) filters (Zefon, Ocala, FL, USA) of 37 mm in diameter and pore size of 0.08 µm were conditioned in a controlled laboratory environment over 24 hours and pre-weighed gravimetrically in the occupational health laboratory at the University of the Witwatersrand. The weighing was done under ideal conditions (@ 21 ± 1˚C temperature and 35 ± 2% humidity) using a model CPA225D electronic microbalance scale (Sartorius, AG, Göttingen, Germany) that has a minimum resolution of 0.001 mg. The microbalance scale was calibrated internally by pressing the CAL button before weighing the filters. Before sampling, the filters were stored in a controlled laboratory environment with the temperature recorded at 22˚C and humidity 35%. Before and after sampling each filter was weighed three times and the average mass was used.

2.2.3 Sampling of indoor and outdoor $PM_{2.5}$

Sampling is a critical phase that can determine the success or failure of the experimental work, therefore the sampling equipment must be chosen carefully to achieve reliable results

(Galvão *et al.*, 2018). The sampling of airborne PM has been conventionally done using active samplers and the most used method of active sampling is by passing air through a filtering media using a pump (Elmes and Gasparon, 2017).

The active sampling technique ensures enough accumulation of PM on the filter for a statistically robust determination of the mass concentration thus providing reliable quantitative data (Elmes and Gasparon, 2017). It further allows accurate measurement of the air pumped through the filter so that the mass concentration can be calculated and reported as mass per cubic metre of air (Elmes and Gasparon, 2017).

The correct selection of a filter medium is critical to avoid misleading results, PCTE filters are suitable for microscopic analyses because they have a smooth surface area which makes it easier to detect single particles (Yue *et al.*, 2006; Genga *et al.*, 2018). PCTE filters are recommended for elemental analysis due to their low blank levels, inertness to gas adsorption, comprise of low impurities, low moisture absorption, high PM collection efficiency and they can withstand severe weather conditions (Izhar *et al.*, 2016; Genga *et al.*, 2018).

In this study, indoor and outdoor $PM_{2.5}$ was sampled concurrently using two identical Gilian GilAir 300plus pumps (Sensidyne, St Petersburg FL, USA) (Stanislawska *et al.*, 2017), connected to a Teflon tube that joins the pump and a 37 mm cassette (SKC Inc., Eighty-Four, PA, USA) fitted with a PCTE filter. The cassette was coupled with a 37 mm $PM_{2.5}$ Gs-3 multiple-inlet cyclone (SKC Inc., Eighty-Four, PA, USA) that separated the coarse and fine particles using centrifugal force (Boudissa *et al.*, 2006; Panda and Shiva Nagendra, 2018).

One pump was used to sample the outdoor $PM_{2.5}$ while the other pump was used to sample indoor $PM_{2.5}$ in the main activity room. Both pumps were placed indoors for security purposes and to protect the pumps from harsh environmental conditions such as rain and direct sunlight which can damage the pumps and affect their functionality. The samples were collected at a height of ~1.5 m, ~1 m away from walls, and ~1.2 m away from windows, doors, and ventilation inlets (Hoek *et al.*, 2008). Although the pumps are fitted with a battery with a life span of eight hours, they were connected to an electric charger as a backup. The pumps were continuously monitored to ensure that they are sampling effectively.

The airborne $PM_{2.5}$ was sampled at a constant flow rate of 2.75 L/min and the particles were deposited on the PCTE filters (Boudissa *et al.*, 2006) and the flow rate was checked before and after sampling using a Gilibrator (Sensidyne, St Petersburg FL, USA) for quality control.

The pumps provided the relapsed time in minutes and calculated the volume of air sampled. However, the volume was in litres per minute (L/min). Therefore, the volume was divided by a thousand to convert it into cubic metres (m^3).

Households sampled were those of participants that went the MRI scan as part of the main study. The houses were selected as part of the main study by drawing grids on the map of each residential area and two houses were selected from the grid. Thirty households were selected for the study and households sampled are those of the participants under the MRI scan for the main study.

Sampling was conducted from August to November 2019 and 60 samples consisting of 30 outdoor and 30 indoor $PM_{2.5}$ samples were collected. Indoor and outdoor $PM_{2.5}$ samples were collected concurrently at each household for ~24 hours and seven days a week. The 30 outdoor $PM_{2.5}$ samples comprised ten Old Sicelo, ten New Sicelo, and ten Noldick samples. Similarly, the 30 indoor samples comprised 10 Old Sicelo, 10, New Sicelo, and 10 Noldick $PM_{2.5}$ samples as shown in Table 1.

Table 1: Duration of the sampling campaigns and the number of houses sampled per residential area

Sampling campaign	Sampling period		Residential area		
	Start	End	Old Sicelo	New Sicelo	Noldick
Campaign 1	06 September	13 September	1	2	-
Campaign 2	13 September	20 September	1	1	-
Campaign 3	20 September	27 September	1	2	-
Campaign 4	27 September	04 October	1	1	-
Campaign 5	04 October	11 October	-	1	1
Campaign 6	11 October	18 October	-	2	1
Campaign 7	25 October	11 November	2	-	2
Campaign 8	01 November	08 November	1	-	2
Campaign 9	08 November	15 November	2	-	2
Campaign 10	16 November	21 November	1	1	2
Total sampled houses			**10**	**10**	**10**

2.2.4 Preparation of samples and analyses using scanning electron microscopy and energy-dispersive X-ray (SEM-EDX)

Electron microscopy techniques have been applied in several studies to characterise atmospheric particles for the past decades (Sielicki *et al.*, 2011; Riffault *et al.*, 2015). Relative to light microscopy, electron microscopes use a particle beam of electrons instead of visible light to illuminate the specimen and produce a magnified image (Ul-Hamid, 2018;

Kwiecińska, Pusz and Valentine, 2019). Electron microscopy can achieve resolutions of 0.05 nm and magnifications of up to 10 000 000× (Ul-Hamid, 2018; Kwiecińska, Pusz and Valentine, 2019). SEM creates magnified images thus providing microscopic information on the morphological properties of a sample (Zanetti-Ramos *et al.*, 2010).

SEM allows a focused electron beam to be scanned across the sample while under vacuum and collects the response of reflected electrons and photons to generate an image (Casuccio *et al.*, 2004; Kwiecińska, Pusz and Valentine, 2019). The ability of SEM to provide detailed information on the morphological and chemical properties of individual particles has made it the first choice method for identifying emitting sources affecting atmospheric air quality (Casuccio *et al.*, 2004; Li *et al.*, 2010).

During the analysis process, the specimens are exposed in SEM to the high-energy electron beam and provide information about the topography, morphology, and elemental composition (Brodusch, Demers and Gauvin, 2018). SEM is more helpful when characterising the morphological and elemental properties of single particles. (Moreno *et al.*, 2011). Therefore, SEM is a useful technique for distinguishing the origin of different particles based on their elemental composition and morphological properties (Satsangi and Yadav, 2014; Ul-Hamid, 2018).

The interaction of the electron beam with the sample produces various signals that can be monitored with suitable detectors (Casuccio *et al.*, 2004). The SEM analyses include the secondary electrons (SE), back-scattered electrons (BSE), Auger electrons and X-rays, and photons of different energies (Sielicki *et al.*, 2011; Ellingham, Thompson and Islam, 2018). However, SE and BSE are more significant and commonly used (Ul-Hamid, 2018). The SE yields an image with a three-dimensional view and a high-depth field while the BSE yields an image containing compositional information since the signal depends on the atomic number of the particle examined (Casuccio *et al.*, 2004).

In this study, the size and morphological properties of two indoor and two outdoor $PM_{2.5}$ samples were analysed using a Tescan Vega3 LMH SEM (Tescan, Brno, Czech Republic) at the University of Johannesburg (Stanislawska *et al.*, 2017). SEM was coupled with X-max 50 mm^2 energy-dispersive X-ray spectroscopy (EDX) (Oxford Instruments, Abingdon, Oxfordshire, UK) which was used for mapping and analysing the elemental composition of the $PM_{2.5}$. The EDX has a detection limit of 0.1 weight percent (Wt%).

EDX is the most commonly used X-ray detector in the SEM for analysing elements in high concentrations (Carvalho, 2018; Ul-Hamid, 2018). The interaction of the electron beam with the sample being analysed results in the emission of X-rays and specific elements are separated into an energy spectrum by the EDX detector (Ellingham, Thompson and Islam, 2018). The energy and intensity of the X-rays emitted by the sample were processed and recorded as a spectrum (Casuccio *et al.*, 2004).

Approximately 1 cm^2 was cut from the centre of each of the selected PCTE filters containing the sampled PM using a pair of scissors and mounted onto an Al stub using a double-sided adherent carbon conductive tape (Labrada-Delgado *et al.*, 2012). The mounting allows the determination of the morphology, surface structure, and elemental composition of the particles. Non-conductive samples must be coated and it is a common practice to coat all non-carbon content samples, the coating enhances the contrast of the SEM images and reduces the electrostatic charging of particles (Labrada-Delgado *et al.*, 2012; Ul-Hamid, 2018). The PCTE filters are non-conductive, therefore, the samples were sputter-coated with a thin layer of carbon (<10 nm) using an Agar Turbo Carbon coater (Agar Scientific, Stansted, UK).

After coating, the stubs containing the carbon-coated samples were loaded into an SEM-EDX vacuum chamber for analyses. The particle morphology was analysed using the back-scattered electron detector at a 20 kV accelerating voltage, using an electron beam intensity of ~3 nA at a working distance of 15 mm from the detector (Pallarés *et al.*, 2020). Using 20 kV improves imaging of the surface and internal structure of the particles relative to lower accelerating voltages (Ul-Hamid, 2018). All the particles analysed in the field of view were photographed, the output images were acquired with 1024 × 768 pixels and 256 greyscale levels.

Similar to Kutchko and Kim (2006), the elemental composition was analysed in a spot mode where the beam was localised on a single area that was manually chosen within the viewed sample, with the EDX focused at 15 mm. The different peaks were identified and the oxford software Aztec (version 3.3 SPI) was used to obtain the peak intensities. However, EDX is not without limitations. The results from the EDX are semi-quantitative and EDX tends to be inaccurate, particularly if the concentration of elements in the sample is low (Li *et al.*, 2017). Nonetheless, Kutchko and Kim (2006) stated that conclusions can be made from the semi-quantitative information from EDX.

SEM-EDX has its strengths and limitations, there is scientific evidence suggesting that the samples observed under SEM are susceptible to mass loss of adsorbed water or volatiles due to the vacuum operation (Khan, Oh and Kim, 2020). Furthermore, there is a possibility of damage by electron beam heating or electrostatic disruption (McDonald and Biswas, 2004). The quality of the images depends on the input parameters determined by the operator (Ul-Hamid, 2018). Elements in small concentrations are unlikely not to be detected because the resolution of the EDX is approximately 0.5% (Carvalho, 2018).

2.2.5 Preparation of samples and analyses using inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma-mass spectroscopy plays a vital role in research, thus it has become the preferred method for elemental analysis (Ammann, 2007). Elemental analysis is commonly done to understand the overall spectrum of the elements contained within the PM (Pröfrock and Prange, 2012; Gross, 2017). Such information can be useful for tracing the source(s) of the PM and to determine the harmful human health effects (Galvão *et al.*, 2018). Literature indicates that ICP-MS is a widely used technique for the elemental analysis of PM and the number of studies using this technique has increased by two folds in the past decades (Galvão *et al.*, 2018).

Similarly, in this study, ICP-MS was used to determine the elemental composition of indoor and outdoor $PM_{2.5}$ to trace the emitting source. Three indoor and outdoor samples were analysed at the University of Johannesburg Spectrum Laboratory, Auckland Park campus using a Perkin Elmer NexION 300 ICP-MS (Perkin Elmer, Waltham, MA, USA). The sample filters were folded and placed inside pre-cleaned microwave digestion vessels. A 9 mL supra pure (Merc) nitric acid (HNO_3), and 1 mL supra pure (Merc) hydrogen peroxide (H_2O_2) was added to each vessel. A reagent blank was included with the batch as a control. The vessels were closed and placed in a Mars 6 microwave (Zhang *et al.*, 2019).

The samples were then transferred to a 50 mL volumetric flask and made up to the mark using 18.2 MΩ/cm^2 ultrapure water. Calibration standards of 0 µg/L, 0.1 µg/L, 0.5 µg/L, 1.0 µg/L, 5.0 µg/L and 10 ug/L were prepared from 100 mg/L NIST traceable stock standards (Masekameni *et al.*, 2020). The samples were then filtered using a 0.45 µm syringe filter and diluted ten times (1 mL diluted to 10 mL) before analysis. ICP-MS technique and procedure were conducted for the blank filter (Masekameni *et al.*, 2020). The elements analysed using the ICP-MS included Mn, Magnesium (Mg), Silicon (Si), (Lead) Pb, Vanadium (V),

Cadmium (Cd), Sodium (Na), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), Chromium (Cr), and Zinc (Zn).

2.3 Data analysis

2.3.1 Indoor and outdoor $PM_{2.5}$ mass concentration

The gravimetric weighing was done to get the post mass of the filter using the same electronic microbalance (model-CPA225D, Sartorius, AG, Göttingen, Germany). To obtain the mass of $PM_{2.5}$. Each filter was weighed three times and the average mass was used. The final corrected mass was calculated using equation (1).

$$Final\ mass = field\ filter(post - pre) + (post - pre)blank\ filter \quad (1)$$

Where the field filter post mass is the mass collected on the filter after sampling, the field pre-mass is the mass recorded in the laboratory before sampling. The field blank post and pre are the mass recorded after transportation and before transportation of filters, respectively. The mass concentration was calculated using equation (2).

$$Concentration = \frac{m}{v} \quad (2)$$

Where (m) is the final mass calculated using equation 1, and (v) is the volume obtained by dividing the volume of sampled air provided by the pump by a thousand. The atmospheric mass concentration of particles is commonly measured in nanogram (ng/m³), microgram (µg/m³), gram (g/m³), or milligram (mg/m³) per cubic metre (Moreno *et al.*, 2011). In this study, the mass concentration was reported in µg/m³.

The I/O ratio was calculated to determine the difference between the indoor and outdoor mass concentration and to determine if there is any contribution of the outdoor PM to the indoor environment. The I/O ratio was obtained using equation (3).

$$C_i = \frac{C_{in}}{C_{out}} \quad (3)$$

Where C_i is the indoor-outdoor ratio, C_{in} is the indoor $PM_{2.5}$ mass concentration and C_{out} is the outdoor $PM_{2.5}$ mass concentration.

2.3.2 Comparison of indoor and outdoor $PM_{2.5}$ mass concentrations

Indoor and outdoor $PM_{2.5}$ mass concentrations were compared statistically using an F-test and a Student t-test. The data were entered into a Microsoft Excel 2019 spreadsheet (Redmond, Washington, USA) and the F-test was first used to determine if there is an equal or unequal variance between the standard deviation between and outdoor $PM_{2.5}$ concentrations. The null hypothesis for the F-test was that there is an equal variance between the standard deviations of indoor and outdoor $PM_{2.5}$ concentrations. The alternate hypothesis was that there was an unequal variance between the standard deviation of indoor and outdoor $PM_{2.5}$ concentrations.

The F-test also helped determine the type of t-test to employ (i.e. t-test (i): two samples assuming equal variances or t-test (ii): two samples assuming unequal variances) (Chen *et al.*, 2018). A *p*-value equal to or less than 0.05 indicated a significant difference and the null hypothesis was rejected. A *p*-value greater than 0.05 indicated a non-significant difference and the null hypothesis was accepted.

A Student t-test was based on the outcome of the F-test. The Student t-test was used to check for a statistically significant difference between the means of the indoor and outdoor $PM_{2.5}$ mass concentrations. The Student t-test was performed at a 95% confidence level and a *p*-value greater than 0.05 indicated a non-statistically significant difference while a *p*-value equal to or less than 0.05 indicated a statistically significant difference (Figueiredo Filho *et al.*, 2013).

2.3.3 Scanning electron microscopy and energy-dispersive X-ray (SEM-EDX)

The size of the particles was determined using version 1.46r of ImageJ (NIH, Maryland, USA), an open-source software. The representative indoor and outdoor SEM images were loaded on the ImageJ software which counted the number of particles and their sizes automatically. The SEM images were threshold before analysis to obtain the best results. The ImageJ software has been used in several studies (Satsangi and Yadav, 2014; Stebounova *et al.*, 2018; Makonese, Meyer and von Solms, 2019) to determine the number and size distribution of particles.

2.3.4 Inductively coupled plasma mass spectrometry (ICP-MS)

Indoor and outdoor concentrations of the elements distributed on the sampled $PM_{2.5}$ were calculated using equation (4) (Arı, Arı and Gaga, 2020).

$$C_{element} = \frac{M_e - field\ blank}{V} \quad (4)$$

Where (C_e) is the concentration of the element in µg, (M_e) is the mass of the element from the ICP-MS, and (V) is the volume in cubic metres (m^3).

2.4 Quality control

All the standard operating procedures were followed when weighing, transporting, and connecting the equipment to prevent the risk of interference that can lead to errors. Standard pendulums weighing 100 and 200 g were weighed on the microbalance before and after sampling to calibrate the scale and to validate the results. All the filters were prepared in a dust-free laboratory with controlled conditions. Forceps were used to load and unload the filters while wearing dust-free surgical gloves to avoid cross-contamination. Each filter was weighed three times before and after sampling and the average mass was used.

A blank filter was prepared for each sampling campaign and it was transported with the filed filters, the blank filter was also placed next to the sampling field filters. The blank filters were used to account for any change in any moisture content due to environmental conditions and to account for cross-contamination during transportation. One blank filter was analysed using SEM-EDX for morphology and elemental composition to ensure that the filters were not contaminated and to get the background of the filters and another was analysed using ICP-MS to check if the filter was not contaminated. The mass concentration of the elements on the blanks was subtracted from the field filters used to sample the $PM_{2.5}$.

The flow rate of the pump was checked before and after sampling using a rotameter. The flow rate was also verified using a bubble flow metre Gilibrator (Sensidyne, St Petersburg FL, USA) for quality control and the fluctuation was within the 5% deviation.

CHAPTER 3: RESULTS

This chapter begins with the descriptive results of indoor and outdoor $PM_{2.5}$ mass concentrations obtained using gravimetric techniques. $PM_{2.5}$ I/O ratios and inferential results between indoor and outdoor $PM_{2.5}$ mass concentrations are also presented. The chapter further provides results on the physical properties of indoor and outdoor $PM_{2.5}$ obtained using SEM and the semi-quantitative elemental composition of the $PM_{2.5}$ obtained using EDX. The chapter ends with the results on the elemental composition of indoor and outdoor $PM_{2.5}$ obtained using ICP-MS.

3.1 Indoor and outdoor $PM_{2.5}$ mass concentrations obtained gravimetrically

As shown in Table 2, it can be noted that outdoor $PM_{2.5}$ mass concentration was higher than indoor. The average indoor $PM_{2.5}$ mass concentration was 10.99 ± 5.10 µg/m^3 while the outdoor average concentration was 24.97 ± 6.77 µg/m^3. The I/O ratio was less than 1 suggesting that indoor $PM_{2.5}$ mass concentration was influenced by outdoor $PM_{2.5}$.

Table 2: Descriptive statistics for indoor and outdoor $PM_{2.5}$ mass concentrations (µg/m^3) levels and indoor-outdoor ratio in Meyerton

	N	Min	Mean	Max	SD	Lower quartile	Upper quartile	I/O
Indoor	30	2.88	10.99	19.19	5.10	9.08	12.89	0.44
Outdoor	30	11.68	24.97	40.44	6.77	22.44	27.49	

Min: minimum, Max: maximum, SD: standard deviation, I/O: indoor-outdoor ratio

In Figure 2, the variation between indoor and outdoor $PM_{2.5}$ mass concentrations for the three residential areas is shown. It can also be noted that outdoor $PM_{2.5}$ mass concentrations were higher than indoor. Old Sicelo presented the highest average indoor $PM_{2.5}$ mass concentration of 2.62 µg/m^3 while Noldick presented the highest average outdoor $PM_{2.5}$ mass concentration of 21.66 µg/m^3.

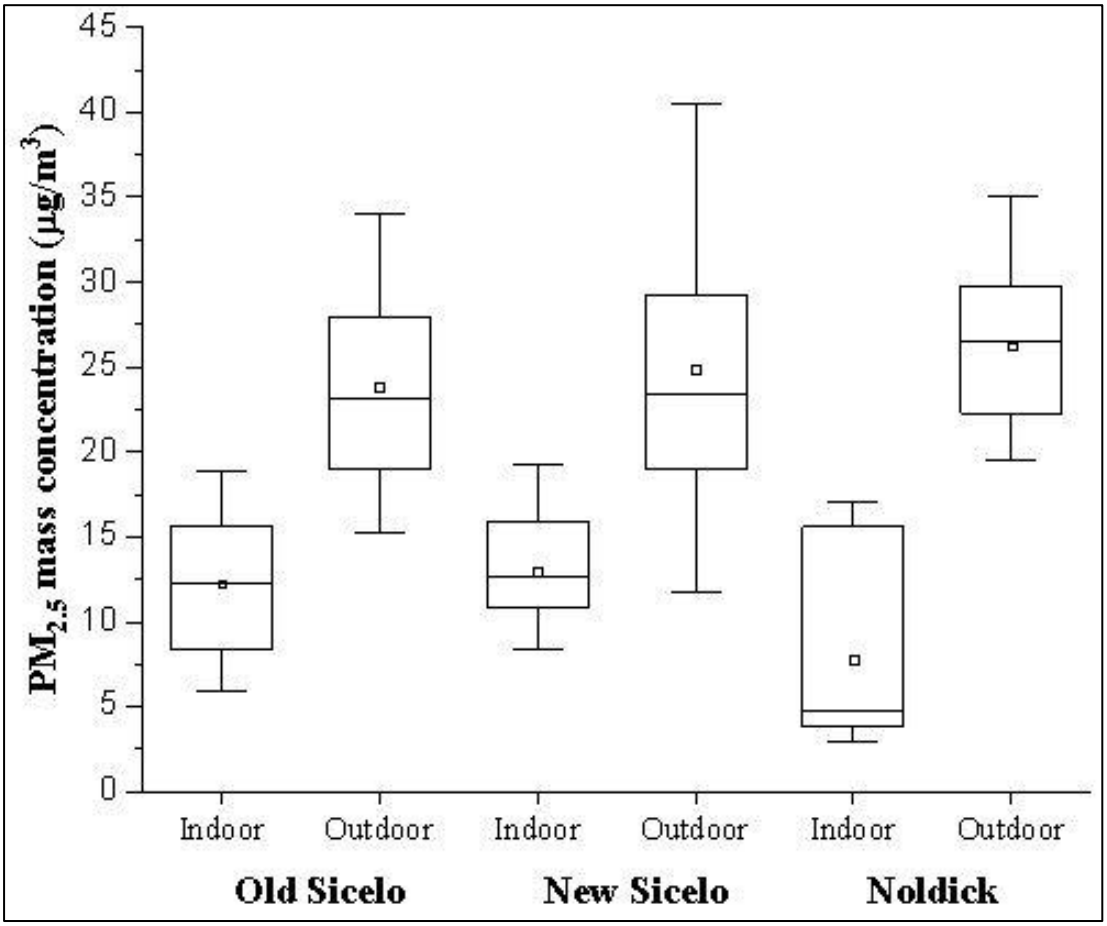


Figure 2: Box and whisker plots comparing indoor and outdoor $PM_{2.5}$ mass concentrations ($\mu g/m^3$) across the three residential areas

Table 3 shows a summary of the I/O ratios of the three residential areas. It can be noted that the average I/O ratios at Old Sicelo, New Sicelo, and Noldick were 0.50 ± 0.07, 0.54 ± 0.10, and 0.27 ± 0.17, respectively. Similar to the overall I/O ratio (Table 2), the I/O ratios across the three residential areas were less than 1, indicating that indoor $PM_{2.5}$ mass concentrations were less than the outdoor.

Table 3: Descriptive statistics of indoor-outdoor ratios across the three residential areas

Parameter	Old Sicelo	New Sicelo	Noldick
Minimum	0.39	0.39	0.14
Maximum	0.60	0.71	0.54
Mean	0.50	0.54	0.27
Standard deviation	0.07	0.10	0.17

3.2 Inferential statistics of indoor and outdoor $PM_{2.5}$ mass concentrations

Table 4 shows the inferential statistics for indoor and outdoor $PM_{2.5}$ mass concentrations in Meyerton. It can be noted that there was a significant percentage mean difference (55.99%)

between indoor and outdoor $PM_{2.5}$ mass concentrations. Furthermore, a statistically significant difference was found (P<0.05) between indoor and outdoor $PM_{2.5}$ mass concentrations.

Table 4: Statistical analysis of indoor and outdoor $PM_{2.5}$ mass concentration ($\mu g/m^3$) in Meyerton

	N	Mean	% Difference	F-Value	P-Value	Sig @ 95%
Indoor	**30**	24.97				
vs			55.99	1.76	5.8×10^{-13}	Yes
Outdoor	**30**	10.99				

sig@ 95%: statistically significant at 95% confidence interval

In Table 5, inferential statistics of indoor and outdoor $PM_{2.5}$ mass concentrations for the three residential areas are presented. Similarly, there was a significant percentage mean difference between indoor and outdoor $PM_{2.5}$ mass concentrations across the three residential areas. The mean percentage difference between indoor and outdoor $PM_{2.5}$ mass concentrations at Old Sicelo, New Sicelo, and Noldick were 48.51%, 48.02%, and 70.32%, respectively. A statistically significant difference was found (P<0.05) between indoor and outdoor $PM_{2.5}$ mass concentrations for the three pairings.

Table 5: Statistical analysis of indoor and outdoor $PM_{2.5}$ mass concentration ($\mu g/m^3$) across the three residential areas.

Pairings	N	Mean	% Difference	F-Value	P-Value	Sig @ 95%
Old Sicelo						
Indoor	10	12.25				
vs			48.51	2.02	6.5×10^{-5}	Yes
Outdoor	10	23.79				
New Sicelo						
Indoor	10	12.93				
vs			48.02	7.49	1.2×10^{-3}	Yes
Outdoor	10	24.87				
Noldick						
Indoor	10	7.78				
vs			70.32	1.47	3.7×10^{-7}	Yes
Outdoor	10	26.23				

sig@ 95%: statistically significant at 95% confidence interval

3.3 Morphology of indoor and outdoor $PM_{2.5}$ obtained using SEM-EDX

In this section, the intention was to check the similarities in the morphology of indoor and outdoor PM_{25}. Figure 3, shows representative SEM images and EDX spectrum for the blank filter. It can be noted that no particles were detected implying that the filters were not

contaminated. The micro-structure shown in the images indicates the material used to construct the PCTE filters. Since no particles were detected, it implies that the filters were suitable for field use.

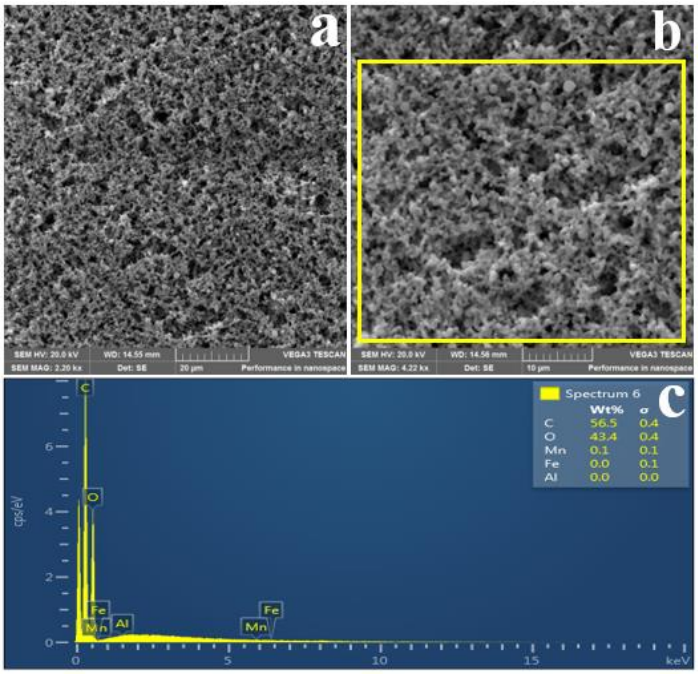


Figure 3: SEM images of the blank filter; (**a**) image captured at 20 µm (**b**) image captured at 10 µm, (**c**) EDX spectrum of the portion highlighted in yellow

As shown in Figure 4, indoor and outdoor representative SEM images of $PM_{2.5}$ sampled at Old Sicelo are shown together with the EDX spectrums. It can be noted that indoor $PM_{2.5}$ consisted of irregular and single spherical particles enriched with elements in decreasing order of Si > Al > Fe >S. It can also be noted that outdoor $PM_{2.5}$ consisted of irregular agglomerated particles enriched with Si > Al > Fe > Ca > S.

Old Sicelo

Indoor **Outdoor**

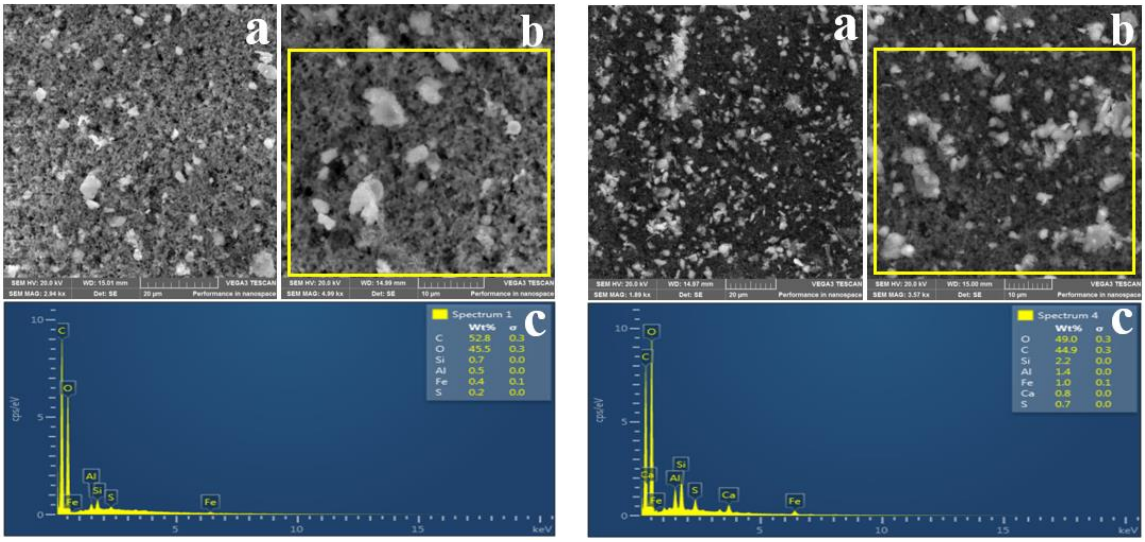


Figure 4: SEM images of indoor and outdoor $PM_{2.5}$ sampled at Old Sicelo; (**a**) image captured at 20 µm (**b**) image captured at 10 µm, (**c**) EDX spectrum of the portion highlighted in yellow

In Figure 5, indoor and outdoor representative SEM images of $PM_{2.5}$ sampled at New Sicelo are shown together with the EDX spectrums. It can be noted that indoor $PM_{2.5}$ consisted of irregular and single spherical particles enriched with Si > Al > Mn. It can also be noted that outdoor $PM_{2.5}$ consisted of irregular agglomerated particles enriched with Si > Al > Fe > Ca >S > Mn.

New Sicelo

Indoor **Outdoor**

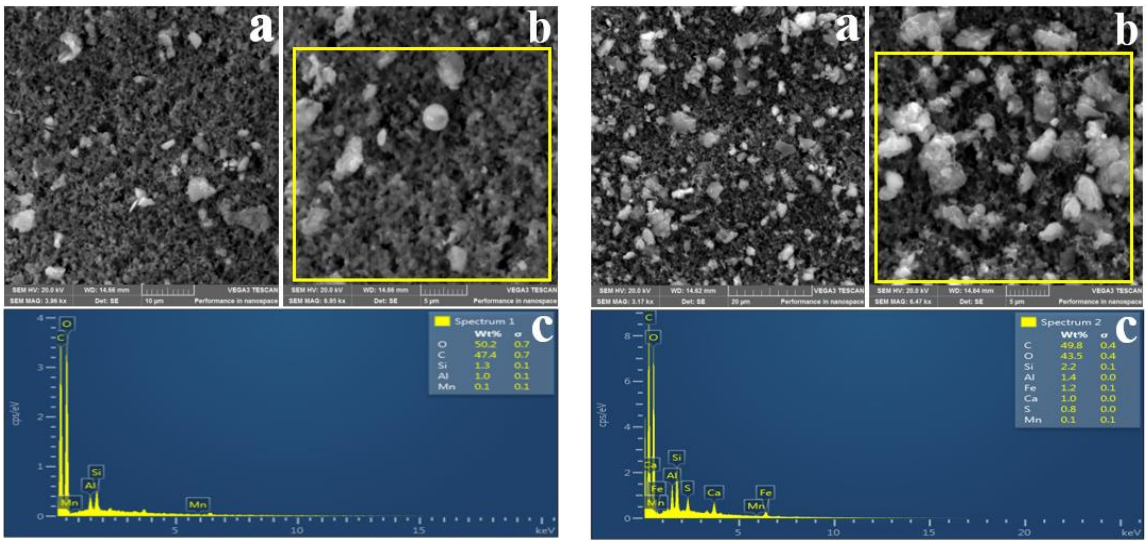


Figure 5: SEM images of indoor and outdoor $PM_{2.5}$ sampled at New Sicelo; ((**a)** indoor) image captured at 10 µm, ((**a)** outdoor) image captured at 20 µm (**b**) image captured at 5 µm, (**c**) EDX spectrum of the portion highlighted in yellow

In Figure 6, indoor and outdoor representative SEM images of $PM_{2.5}$ sampled at Noldick are shown together with the EDX spectrums. It can be noted that indoor $PM_{2.5}$ consisted of irregular particles enriched with Si > Al > Fe > Ca >S. It can also be noted that outdoor $PM_{2.5}$ consisted of irregular and agglomerated particles enriched with Si > Al > Fe > S > K> Ca >.

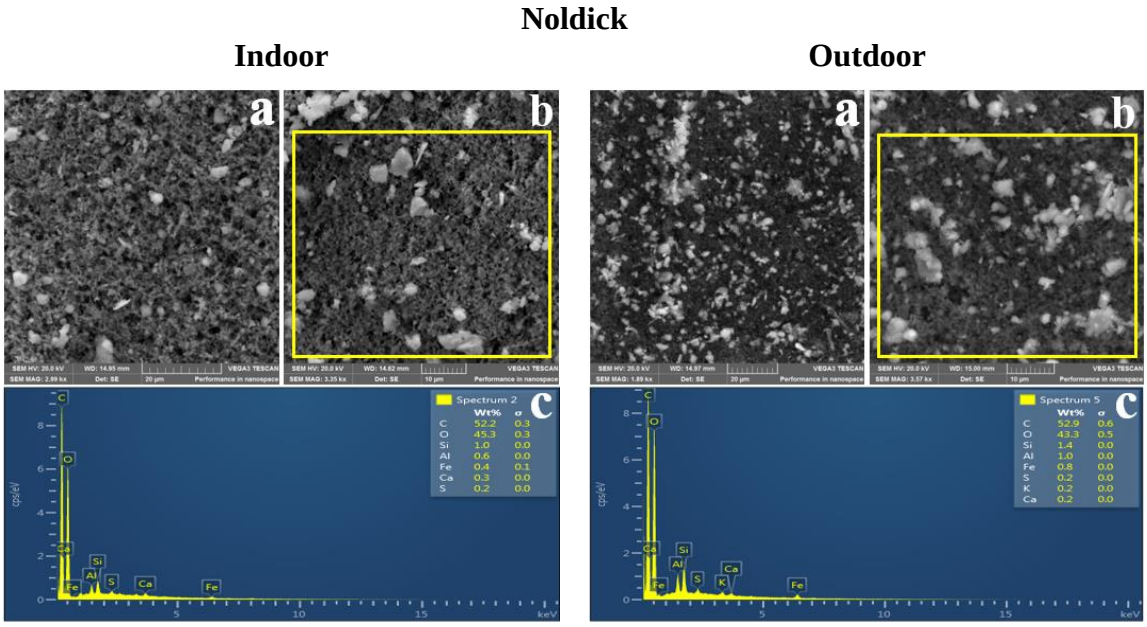


Figure 6: SEM images of indoor and outdoor $PM_{2.5}$ sampled at Noldick; (**a**) image captured at 20 µm (**b**) image captured at 10 µm, (**c**) EDX spectrum of the portion highlighted in yellow

Table 6, the elemental composition of indoor and outdoor $PM_{2.5}$ sampled across the three residential obtained using EDX is presented. Although most of the selected elements were not detected by the EDX, it can be noted that the outdoor $PM_{2.5}$ had the highest concentration of elements relative to indoor. The limit of detection for the EDX was 0.1 weight percent (Wt%).

Table 6: A summary of the elements (Wt%) detected using EDX

elements	Old Sicelo		New Sicelo		Noldick	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
Mn	<LoD	<LoD	0.10	0.10	<LoD	<LoD
Al	0.50	1.40	1.00	1.40	0.60	1.00
Si	0.70	2.20	1.30	2.20	1.00	1.40
K	<LoD	<LoD	<LoD	<LoD	<LoD	0.20
Ca	<LoD	0.80	<LoD	1.00	0.30	0.20
Fe	0.40	1.00	<LoD	1.20	0.40	0.80
S	0.20	0.70	<LoD	0.80	0.20	0.20

<LoD: below limit of detection

In Figure 7, the size distributions of indoor and outdoor $PM_{2.5}$ across the three residential areas are shown. It can be noted that indoor particles ranged between 0.1–0.7 µm in diameter

and were dominated by particles of 0.1 µm. However, most particles were found in the 0.1 µm size bin. Outdoor particles ranged between a diameter of 0.1 and 1.3 µm and were also dominated by particles of 0.1 µm.

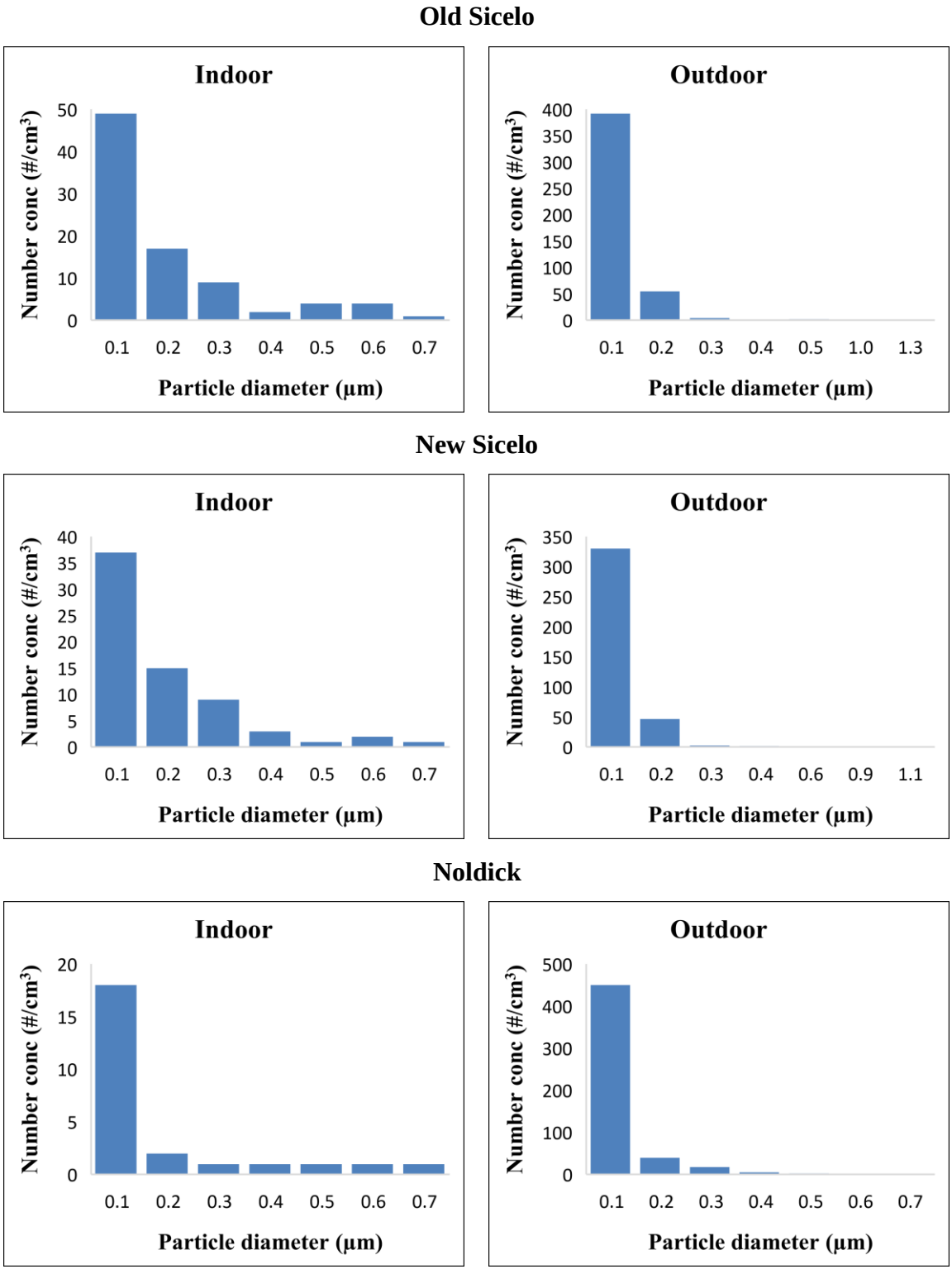


Figure 7: Size distribution of indoor and outdoor $PM_{2.5}$ sampled across the three residential areas

In Figure 8, the average concentrations of elements found on indoor and outdoor $PM_{2.5}$ in Meyerton are presented. It can be noted that outdoor elemental concentrations were higher than indoor. The highest average concentrations of elements were SI > Fe > Mn > Na > Mg > Zn. The average indoor and outdoor Mn concentrations were 1.30 µg/m^3 and 5.36 µg/m^3, respectively.

3.4 Elemental composition of indoor and outdoor $PM_{2.5}$ obtained using ICP-MS

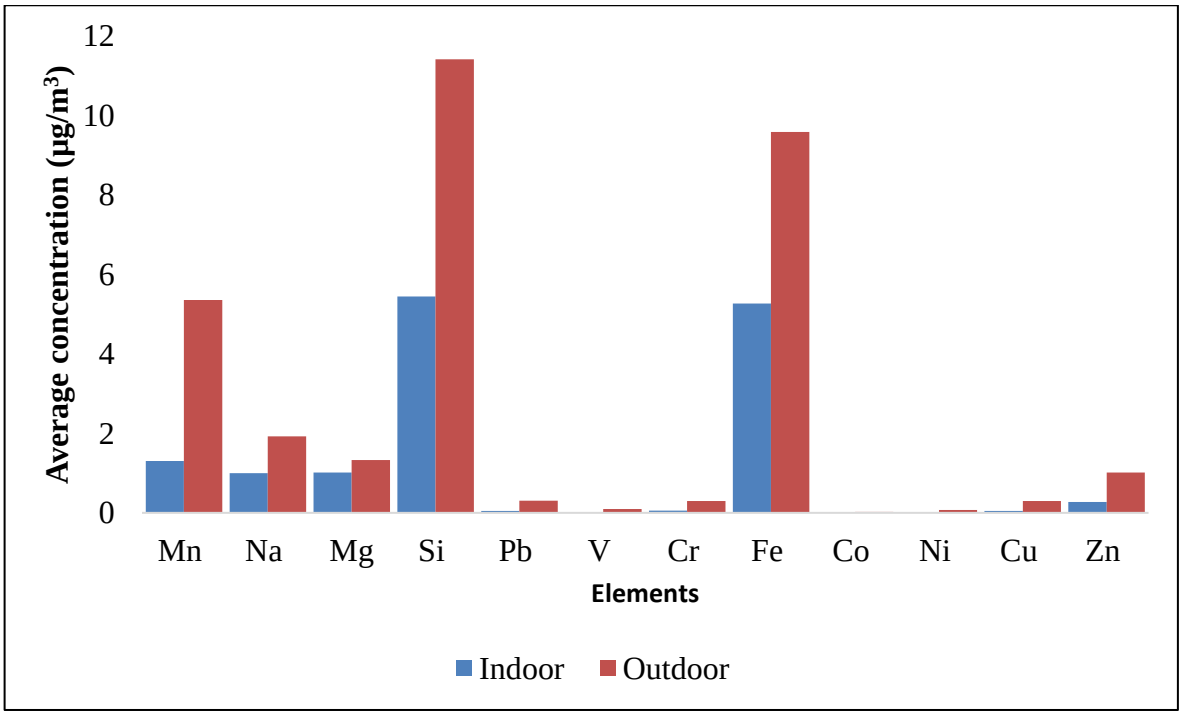


Figure 8: Average indoor and outdoor elemental concentrations (µg/m^3) distributed on the sampled $PM_{2.5}$ in Meyerton

In Table 7, the concentrations of elements found on indoor and outdoor $PM_{2.5}$ across the three residential areas are presented. It can be noted that outdoor concentrations of elements were higher than indoor. Noldick had the highest indoor and outdoor Mn concentrations. The limit of quantification for K and Cd were <10.67 and <0.033, respectively.

Table 7: Indoor and outdoor elemental concentration (µg/m^3) distributed on the sampled $PM_{2.5}$ across the three residential areas

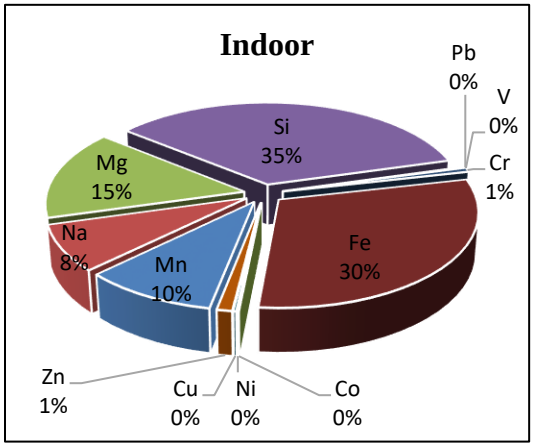
Elements	Old Sicelo		New Sicelo		Noldick	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
Mn	1.2045	3.9739	1.0346	5.5495	1.6712	6.5604
Na	0.9193	2.9715	1.1837	2.0935	0.8950	0.7115
Mg	1.5450	1.9122	0.6943	1.1227	0.8178	0.9574
Si	4.7417	11.3543	6.2718	15.3786	5.3376	7.5356
K	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Pb	0.0258	0.2958	0.0656	0.1037	0.0494	0.5098

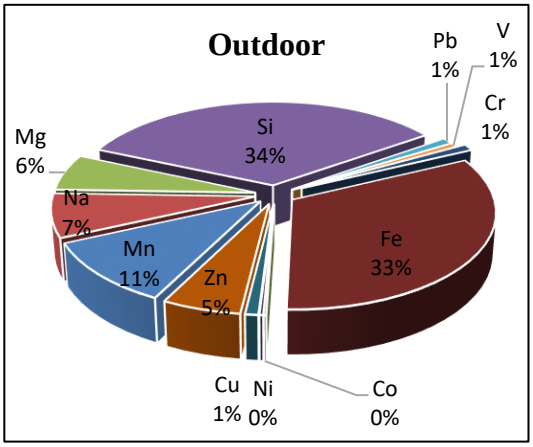
V	0.0024	0.2045	0.0225	0.0268	0.0225	0.0544
Al	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Cr	0.0586	0.3284	0.0540	0.0631	0.0610	0.5136
Fe	3.8665	10.5339	7.0881	12.0622	4.8544	6.1707
Co	0.0046	0.0667	0.0073	0.0091	0.0074	0.0080
Ni	0.0123	0.0882	0.0074	0.0510	0.0222	0.0800
Cd	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ	<LoQ
Cu	0.0241	0.3270	0.0317	0.2742	0.0866	0.2819
Zn	0.1422	1.7705	0.3307	0.7567	0.3446	0.5178

<LoQ: below limit of quantification

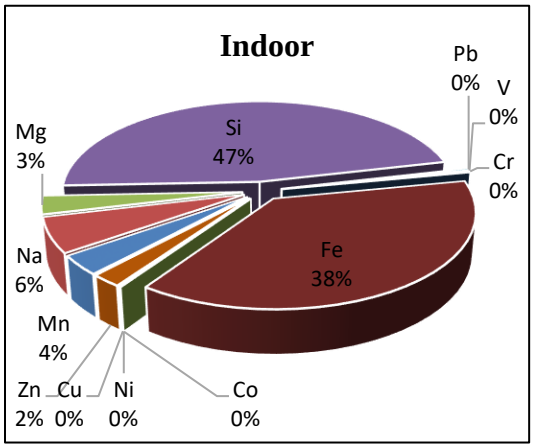
In Figure 9, the contribution of the elements on the sampled indoor and outdoor $PM_{2.5}$ is presented in percentages. It can be noted that Si > Fe > Mn >Mg contributed most on indoor $PM_{2.5}$. It can also be noted that Si > Fe > Mn >Na contributed more to outdoor $PM_{2.5}$.

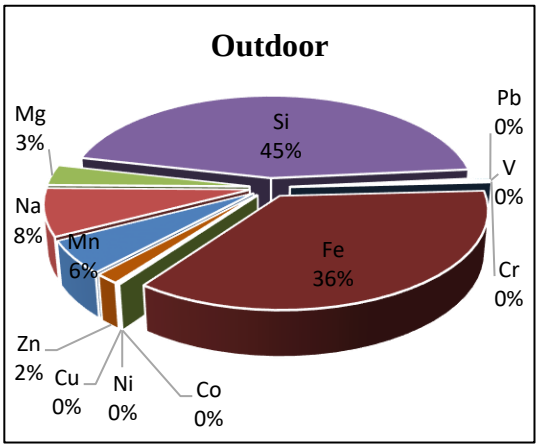
Old Sicelo





New Sicelo





Noldick

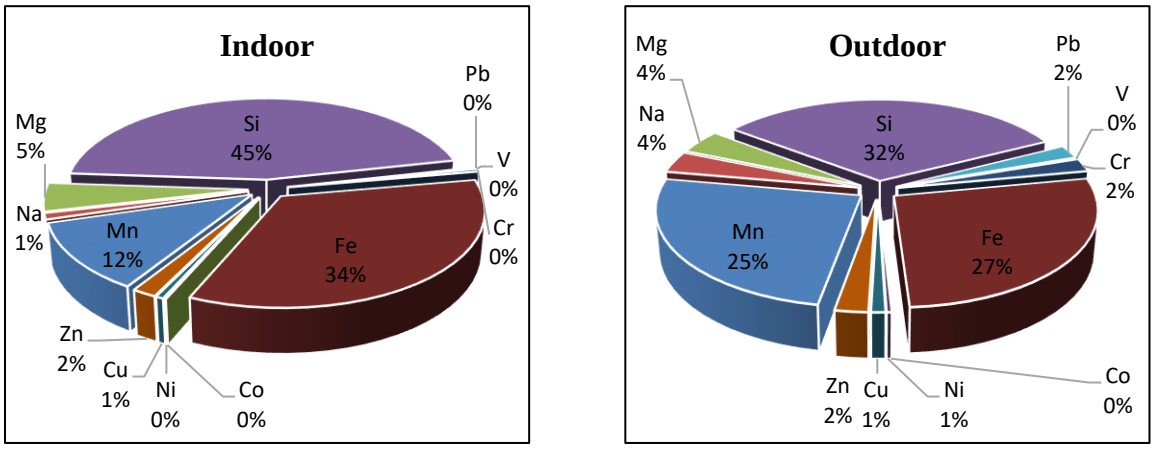


Figure 9: Percentage contribution of elements on indoor and outdoor $PM_{2.5}$ sampled across the three residential areas.

CHAPTER 4: DISCUSSION

This chapter discusses the study results which were then compared to existing literature. The results discussed below include the indoor and outdoor $PM_{2.5}$ mass concentrations obtained gravimetrically and I/O ratios. The descriptive and inferential statistical results are discussed in this chapter. The physical properties of indoor and outdoor $PM_{2.5}$ obtained from SEM and semi-quantitative elemental composition obtained from EDX are also discussed in this chapter. This chapter further discusses the elemental composition of indoor and outdoor $PM_{2.5}$ obtained from ICP-MS. The chapter ends by discussing the limitations and strengths of the study.

4.1 Synopsis of study findings

This study provides data about the physicochemical properties of indoor and outdoor $PM_{2.5}$ sampled in selected households at Meyerton. The study aimed to systematically characterise the similarities between indoor and outdoor Mn-bearing $PM_{2.5}$ in three residential areas near a ferromanganese smelter. Outdoor $PM_{2.5}$ mass concentrations were greater than the indoor across the three residential areas. Furthermore, outdoor $PM_{2.5}$ mass concentration was 2.27 fold greater than indoor which agreed with the study's hypothesis. The I/O ratio of 0.44 further indicated that indoor $PM_{2.5}$ mass concentrations were influenced by $PM_{2.5}$ from the outdoor environment. A statistically significant difference was found (P=5.8×10^{-13}) between indoor and outdoor $PM_{2.5}$ mass concentrations. Indoor $PM_{2.5}$ consisted of irregular and single spherical particles ranging from 0.1 to 0.7 µm in diameter, while outdoor consisted of irregular and agglomerated particles ranging from 0.1 to 1.3 µm in diameter. ICP-MS results indicated that both indoor and outdoor $PM_{2.5}$ were dominated by elements in decreasing order of Si > Fe > Mn > Na > Mg > Zn. However, outdoor $PM_{2.5}$ had the highest concentration of elements.

4.2 Indoor and outdoor $PM_{2.5}$ mass concentrations

Table 2 presents a summary of indoor and outdoor $PM_{2.5}$ mass concentrations in Meyerton and it can be observed that outdoor $PM_{2.5}$ mass concentration was greater than indoor. Outdoor $PM_{2.5}$ mass concentration was 2.27 fold greater than indoor. New Sicelo presented the highest average indoor $PM_{2.5}$ mass concentration (12.93 ± 3.29 µg/m^3), followed by Old Sicelo (12.25 ± 4.33 µg/m^3) and Noldick (7.78 ± 6.08 µg/m^3) as shown in Figure 2. Figure 2 also shows that Noldick had the highest average outdoor $PM_{2.5}$ mass concentration (26.23

± 5.02 µg/m^3), followed by New Sicelo (24.87 ± 9 µg/m^3), and Old Sicelo (18.74 ± 8.86 µg/m^3). The indoor and outdoor $PM_{2.5}$ mass concentration findings also support the study hypothesis that outdoor Mn-bearing $PM_{2.5}$ mass concentration would be higher than indoor.

Indoor and outdoor $PM_{2.5}$ mass concentration findings in this study complement those of Hasheminassab *et al.* (2014), Gao *et al.* (2020) and Zhao *et al.* (2020) who found that outdoor $PM_{2.5}$ mass concentrations were significantly higher than the indoor. The high indoor $PM_{2.5}$ mass concentrations at New and Old Sicelo can be attributed to stationary and mobile sources such as the ferromanganese smelter and vehicular emissions. The high indoor $PM_{2.5}$ mass concentrations can also be attributed to the re-suspension of particles through human movements. For instance, re-suspension through walking has been identified as a significant source of indoor PM (Butler, Madhavan and Alper, 2016). The indoor $PM_{2.5}$ could have also been due to dust re-suspended by wind, human activities, and vehicular movement which then enters the indoor environment.

The high indoor $PM_{2.5}$ mass concentration at New and Old Sicelo suggests that the sampled households had many or larger openings whereby the $PM_{2.5}$ infiltrated at a faster rate. Another plausible explanation is that the $PM_{2.5}$ did not only enter through openings but could also be due to foot tracking, cooking, smoking, re-suspension during walking and cleaning activities, and the use of detergents, sprays, and cosmetic products.

Studies by Urso *et al.* (2015) and Kim *et al.* (2018) affirmed that activities such as cooking, incense burning, smoking, and cleaning contribute significantly to the indoor $PM_{2.5}$ mass concentration. The higher indoor $PM_{2.5}$ mass concentration further suggests that the households at New and Old Sicelo had higher room occupancy and human activities (Butler, Madhavan and Alper, 2016). This is further supported by Perrino *et al.* (2016), who found that indoor $PM_{2.5}$ mass concentrations increased significantly when the rooms were occupied, particularly on weekends when the occupants were home.

The lower indoor $PM_{2.5}$ mass concentrations at Noldick suggest that outdoor $PM_{2.5}$ infiltrated at a lower rate. The results are not surprising since most of the sampled households in Noldick were made of brick and cement and had ceilings. The findings support the work of Abdel-Salam (2015) and Delgado-Saborit (2019) who reported that the infiltration of outdoor PM into the indoor environment depends on the characteristics of the structure. Therefore, the different housing structures in New and Old Sicelo and Noldick can explain the variation in indoor $PM_{2.5}$ mass concentrations.

Noldick had the highest outdoor $PM_{2.5}$ mass concentrations relative to Old and New Sicelo, despite that New Sicelo is nearest to the ferromanganese smelter. This finding can be explained by the height of the ferromanganese smelter stack and meteorological conditions. Studies have proven that an emission source with a high stack tends to affect areas that are further away from the source. The outdoor $PM_{2.5}$ mass concentrations at Noldick are also an indication that the ferromanganese smelter is not the only potential emitting source. Therefore, the higher outdoor $PM_{2.5}$ mass concentrations at Noldick can be attributed to vehicular exhaust emissions since the area is next to the smelter and R59 freeway.

The R551 and M61 roads pass through Noldick, Therefore, the higher outdoor $PM_{2.5}$ concentrations can also be attributed to, tyre, and brake PM. Since most of the Noldick area is paved and vegetated, the higher outdoor $PM_{2.5}$ can also be attributed to dust suspended and re-suspended at New and Old Sicelo which is blown by the wind and settles at Noldick. The variation of outdoor $PM_{2.5}$ mass concentrations across the three residential areas could be due to variation in the source, source strength, and different meteorological conditions.

The indoor and outdoor $PM_{2.5}$ mass concentration findings are an indication that indoor $PM_{2.5}$ was influenced by the outdoor. This is supported by the overall I/O ratio of less than 1 as presented in Table 2, which means that indoor was less than the outdoor $PM_{2.5}$ mass concentration. Table 3 shows the I/O ratios of the three residential areas the average I/O ratios at Old Sicelo, New Sicelo, and Noldick were 0.50 ± 0.07, 0.54 ± 0.10, and 0.27 ± 0.17, respectively. From Table 3, it can also be noted that the I/O ratios across the three residential areas are less than 1 which further suggests that indoor was influenced by $PM_{2.5}$ from the outdoor environment (Morawska *et al.*, 2017; Niu *et al.*, 2019; Madureira *et al.*, 2020).

4.3 Statistical analysis of indoor and outdoor $PM_{2.5}$ mass concentration

A summary of the statistical results for indoor and outdoor $PM_{2.5}$ mass concentrations in Meyerton is presented in Table 4. A statistically significant difference was found ($P=5.8\times10^{-13}$) between indoor and outdoor $PM_{2.5}$ mass concentrations in Meyerton. This implies that there was a significant difference between the means of indoor and outdoor $PM_{2.5}$ mass concentrations. Table 5 presents a summary of the statistical results between indoor and outdoor $PM_{2.5}$ mass concentrations for the three residential areas. Similarly, a statistically significant difference was found ($P<0.05$) between indoor and outdoor $PM_{2.5}$ mass concentrations across the three residential areas. This also implies that there was a significant

difference between the means of indoor and outdoor $PM_{2.5}$ mass concentrations across the three residential areas.

4.4 Morphology of indoor and outdoor $PM_{2.5}$

Figure 3 presents the SEM-EDX for the blank filter and it can be observed that no particles were detected on the filter. Semi-quantitative elemental results from EDX indicated the presence of carbon (56.5%), oxygen (43.4%), and Mn (0.1%), which are the common constituents of PCTE filters. This implies that the filters were not contaminated, thus suitable for sampling.

The representative SEM images of indoor and outdoor $PM_{2.5}$ sampled in the three residential areas are presented in Figure 4 to Figure 6. It can be observed that the particles had different sizes and shapes. SEM revealed that indoor $PM_{2.5}$ at Old Sicelo, New Sicelo, and Noldick consisted of irregular and spherical particles, while outdoor $PM_{2.5}$ consisted of agglomerated and irregular particles. The two microenvironments reported the same or similar morphologies, suggesting that the source of emission is the same for indoor and outdoor $PM_{2.5}$.

In a study conducted near a ferromanganese alloy plant in Cantabria, north of Spain, Hernández-Pellón *et al.* (2017) reported Irregular Mn enriched PM_{10} particles. In their study, Jiang *et al.* (2018) also reported irregular agglomerated particles and concluded that they are due to vehicular emissions and re-suspended dust particles. Therefore, the irregular shape of the indoor and outdoor particles reported in the current study suggests that they are from combustion sources such as motor vehicle engines or the ferromanganese smelter.

The outdoor agglomerated particles are an indication that the particles were of submicron size and agglomerated to form larger particles. These results are consistent with those of Gupta *et al.* (2020), who reported spherical, agglomerated, and irregular particles enriched with elements associated with anthropogenic sources such as industrial activities and vehicular emissions.

It has been well established that spherical particles commonly originate from natural processes such as pollen or anthropogenic sources such as high-temperature combustion processes (Smichowski and Gómez, 2012; Ahmed, Guo and Zhao, 2017). The spherical particles can either exist as single or agglomerated particles (Ahmed, Guo and Zhao, 2017). A study by Gjønnes *et al.* (2011), reported spherical submicron Mn oxide particles that agglomerated to form larger particles which were also observed in the current study.

Although the study by Gjønnes *et al.* (2011) was conducted inside a Mn smelter during various processes it can still be concluded that the indoor spherical particles are from a high combustion source such as the Mn-smelter or motor vehicles (Labrada-Delgado *et al.*, 2012).

A summary of the elemental composition of indoor and outdoor $PM_{2.5}$ for the three residential areas obtained using EDX is presented in Table 6. EDX results indicated that indoor $PM_{2.5}$ sampled at Old Sicelo was dominated by elements in a decreasing order of Si > Al > Fe > S. New Sicelo was dominated by Si > Al > Mn, while indoor $PM_{2.5}$ sampled at Noldick had an abundance of Si > Al > Fe > Ca > S. EDX results also indicated that outdoor $PM_{2.5}$ sampled at Old Sicelo was dominated by Si > Al > Fe > Ca > S. New Sicelo was dominated by Si > Al > Fe > Ca > S > Mn, while the outdoor $PM_{2.5}$ at Noldick was dominated by Si > Al > Fe > S > K > Ca. From Table 6, it can be noted that outdoor $PM_{2.5}$ had the highest concentration of elements.

Potassium is associated with the combustion of solid fuels such as wood and coal, while the other elements are associated with ferromanganese smelters and vehicular emissions (Gholampour *et al.*, 2016). However, elements such as Si, Ca, and Mg are naturally occurring and abundant in the soil. These results are similar to those reported by Hernández-Pellón *et al.* (2017), who used EDX to analyse the elemental composition of PM_{10} particles and reported spherical Mn and Fe enriched particles. However, the elemental concentrations from the EDX are semi-quantitative and small conclusions can be made from such results. Hence in this study, ICP-MS was used to overcome this limitation.

Figure 7 shows the size distribution of indoor and outdoor $PM_{2.5}$ sampled across the three residential areas. The size of indoor particles at Old Sicelo ranged between 0.1 and 1.3 µm while the outdoor particles ranged between 0.1 and 0.7 µm diameter. At New Sicelo indoor particles ranged between 0.1 and 0.7 µm while outdoor particles ranged between 0.1 and 1.1 µm diameter. Indoor particles at Noldick ranged from 0.1 to 0.7 µm while outdoor particles ranged between 0.1 and 0.7 µm in diameter.

Indoor $PM_{2.5}$ across the three residential areas was dominated by particles ranging from a diameter of 0.1 and 0.7 µm while outdoor $PM_{2.5}$ was dominated by particles of 0.1 and 1.3 µm. The particle size findings in this study complement that of Ali *et al.* (2020) who conducted a study in residential areas near a heavily industrialised site in Pakistan. The study reported indoor and outdoor particles ranging from 0.1 to 1.02 µm and 0.1 to 1.6 µm, respectively.

4.5 Elemental composition of indoor and outdoor $PM_{2.5}$

The average concentrations of the elements distributed on the sampled indoor and outdoor $PM_{2.5}$ are presented in Figure 8. The average indoor and outdoor Mn concentration was 1.18 µg/m^3 and 3.07 µg/m^3, respectively. Apart from Mn, other elements selected for the ICP-MS analysis were also detected, however, K and Cd were below the limit of quantification. Surprisingly, the EDX detected Al, however, it was below the limit of quantification of the ICP-MS. Si > Fe > Na > Mg > Zn were the most abundant elements on the indoor and outdoor sampled $PM_{2.5}$. Although both indoor and outdoor $PM_{2.5}$ had an abundance of these elements, outdoor $PM_{2.5}$ had the highest concentration of elements. Similar results have been reported by Wang *et al.* (2019) in dormitories in Nanjing, China. The authors found that the outdoor concentration of elements on $PM_{2.5}$ was higher than the indoor.

The elements reported in the current study have been confirmed to be commonly emitted from ferromanganese smelters (Kero *et al.*, 2019). Studies by Hernández-Pellón *et al.* (2017) and Hernández-Pellón *et al.* (2019) conducted near a ferromanganese alloy plant in Spain also reported an abundance of these elements on ambient PM_{10} samples. Specifically, the authors found an abundance of Mn and Fe enriched PM_{10}. The fact that the elemental concentration findings of this study agree with previous studies suggests that the ferromanganese smelter in Meyerton is a major contributing source to ambient air pollution in the three nearby residential areas.

Table 7 presents the elemental composition of indoor and outdoor $PM_{2.5}$ for the three residential areas. Noldick had the highest indoor Mn concentration (1.67 µg/m^3), followed by Old Sicelo (1.20 µg/m^3), while New Sicelo had the least concentration (1.03 µg/m^3). Noldick also had the highest outdoor Mn concentration (6.56 µg/m^3), followed by New Sicelo (5.55 µg/m^3) and Old Sicelo (3.97 µg/m^3). The percentage contribution of the elements on the sampled indoor and outdoor $PM_{2.5}$ across the three residential areas is presented in Figure 9. Similar to the results reported by Jeong *et al.* (2019), outdoor Mn concentration is higher than indoor. The findings also agreed with the study hypothesis that outdoor Mn-bearing $PM_{2.5}$ concentrations would be higher than indoor.

Although Noldick is located furthest from the ferromanganese smelter relative to New Sicelo, it had the highest concentration of elements. The high concentration of Mn at Noldick can be explained by the meteorological conditions during the sampling period. These results are not surprising and agree with previous studies. Studies by Ledoux *et al.* (2006) and Hernández-Pellón *et al.* (2019) conducted around a ferromanganese alloy plant found that

the concentration of elements increased as the distance away from the source increased. Therefore, there is a possibility that the pollutants can be transported further and even change from the air compartment to water and soil.

The increase in the concentration of elements is an indication that the ferromanganese smelter is not the only contributing source. Motor vehicles are also a potential source, this is plausible given that Pb was replaced with Mn as an anti-knock in fuel. Subsequently, motor vehicular emissions are enriched with Mn-bearing and Fe-enriched PM. Moreover, Noldick is nearer the R59 freeway and the M59 which busy roads used by light and heavy motor vehicles.

Iron was detected both in indoor and outdoor $PM_{2.5}$ across the three residential areas and contributed significantly. The high Fe concentrations can be attributed to the ferromanganese smelter, metallurgy industries, and vehicular emissions (Lu *et al.*, 2015; Hernández-Pellón *et al.*, 2017). A study by Sanderson *et al.* (2016) reported that engine blocks can contribute significantly to the ambient Fe concentration and therefore, some of the Fe can be attributed to motor vehicles. However, the Fe can also be attributed to the corrugated Fe used for roofing.

Silicon is a naturally occurring element that is abundant on the earth and the presence of high Si content on the indoor and outdoor $PM_{2.5}$ could be due to the suspension of soil dust by vehicles, wind, and other human activities and release from industrial combustion (Hasheminassab *et al.*, 2014; Gholampour *et al.*, 2016; Zeb *et al.*, 2018). The presence of Cu in indoor and outdoor $PM_{2.5}$ could be due to the combustion of fossil fuels since Cu is an indicator of combustion sources such as coal-burning (Gholampour *et al.*, 2016).

4.6 Study limitations

Due to limited funds, only two indoor and outdoor filters per residential area were analysed using ICP-MS. The study did not use a weather monitoring station to obtain meteorological data which are important for the transportation and dispersion of ambient pollutants. Due to this limitation, the $PM_{2.5}$ concentrations are not correlated with meteorological data such as wind speed, wind direction, humidity, and temperature.

Time-activity patterns were also not included in this study. The time-activity patterns would have assisted in the understating of the contribution of indoor sources to the $PM_{2.5}$ mass concentration. The data were collected during the spring period and the emissions are

unlikely to remain consistent throughout the different seasons. Information about the production rate of the smelter was also unobtainable.

The air exchange rate in the sampled household was not measured, it could have helped determine the infiltration and deposition rate of outdoor $PM_{2.5}$ into the indoor environment. Furthermore, the study did not use linear regression to determine the relationship between outdoor and indoor $PM_{2.5}$, instead, only the I/O ratio was used to determine the relationship between indoor and outdoor $PM_{2.5}$.

4.7 Study strengths

This is the first study to investigate the physicochemical properties of particulate matter in a residential area near a ferromanganese smelter in South Africa. The study investigated indoor and outdoor $PM_{2.5}$ and did not rely on data from fixed monitoring stations to represent the potential exposure at the level of the receptor. The study also managed to point out the major potential emitting sources of indoor and outdoor Mn-bearing-$PM_{2.5}$. However, additional studies are required to affirm the source or single out one emitting source of indoor and outdoor Mn-bearing $PM_{2.5}$ in Meyerton.

CHAPTER 5: CONCLUSION

This chapter begins by providing the relevance and significance of the study. Based on the study findings, future research and recommendations are provided. Conclusion and lessons drawn from this study are also provided in this chapter.

5.1 Significance of the study

This study investigated the similarities between the physicochemical properties of indoor and outdoor $PM_{2.5}$ sampled in residential areas near a ferromanganese smelter. The average indoor $PM_{2.5}$ mass concentration was 10.99 ± 5.10 µg/m^3 while the outdoor was 24.97 ± 6.77 µg/m^3. Outdoor $PM_{2.5}$ mass concentration was found to be 2.7 fold greater than indoor which agreed with the study's hypothesis. The I/O ratio was less than 1 supporting the finding that outdoor $PM_{2.5}$ was greater than indoor and that indoor was influenced by $PM_{2.5}$ from the outdoor environment.

Indoor $PM_{2.5}$ had a presence of irregular and agglomerated particles ranging from 0.1–0.7 µm in diameter while $PM_{2.5}$ outdoor also consisted of irregular but single spherical particles ranging from 0.1–1.3 µm in diameter. SEM images indicated that indoor and outdoor $PM_{2.5}$ are from the same or similar emission source. Both indoor and outdoor $PM_{2.5}$ across the three residential areas were dominated by particles of 0.1 µm in diameter.

Indoor and outdoor particles were enriched with Mn and Fe oxides suggesting that they are from a high combustion source such as the Mn smelter or vehicles. Elements commonly emitted from ferromanganese smelters were found on indoor and outdoor $PM_{2.5}$. Mn > Si > Fe > Na > Mg > Zn were the elements found both in indoor and outdoor $PM_{2.5}$, however, outdoor $PM_{2.5}$ had the highest concentration of elements. The findings from this study suggest that motor vehicles and the nearby ferromanganese smelter are major potential emitting sources of Mn-bearing $PM_{2.5}$ in Meyerton.

This is the first study in South Africa to investigate the physicochemical properties of indoor and outdoor $PM_{2.5}$ in a residential area near a ferromanganese smelter. The findings from this study contribute to the understanding of indoor and outdoor $PM_{2.5}$ in residential areas near ferromanganese smelters. The study found that most indoor $PM_{2.5}$ originated from outdoor sources, with the ferromanganese being the main contributing source. Moreover, the $PM_{2.5}$ was enriched with Mn, which can lead to chronic health outcomes amongst vulnerable

groups. The findings can be used to support epidemiological studies where ferromanganese smelters have been associated with neurodegenerative illnesses such as PD.

The findings can be essential for assessing exposure to pollutants associated with ferromanganese smelters located near residential areas. This is important given that the smallest particle size reported in this study is 0.1 µm in diameter which has a high probability of penetrating deeper into the alveolar upon uptake.

5.2 Recommendations

Future studies conducting exposure assessment in the Meyerton area are necessary because this study was focused and confined to the characterisation of $PM_{2.5}$. Future studies can investigate the impact of the ferromanganese smelter and motor vehicular emissions beyond the three residential areas studied. Furthermore, future studies can investigate the possibility of the $PM_{2.5}$ changing from the air compartment to water and soil.

Given that the findings of this study suggest the potential for exposure to the Mn-bearing $PM_{2.5}$ both in indoor and outdoor environments. Time-activity pattern studies are necessary to quantify how much time the residents spend indoors, outdoors, and outside the boundaries of their microenvironment. Time-activity pattern studies are necessary since the development of adverse health outcomes depends on the duration of exposure. Therefore, time-activity patterns can be used to collect data that will be useful for exposure assessment and modeling the intake and uptake of $PM_{2.5}$.

Exposure assessment studies can be done by collecting personal concentration in the breathing zone. Breathing zone concentration is suggested to be an accurate estimation of how much the receptor is exposed to relative to ambient and indoor concentration. Future studies should also investigate particle number concentration since this study only reported the mass concentrations of indoor and outdoor $PM_{2.5}$. The bioavailability and bio-accessibility of the Mn-bearing particle should be studied in future studies.

Findings from the current study have indicated that there is a risk of exposure to Mn-bearing $PM_{2.5}$ both in the indoor and outdoor environment. Therefore, there is a need for interventional studies to protect public health. For example, the interventional studies can investigate the type of the interventions needed and where they can be placed to effectively reduce exposure to $PM_{2.5}$ Mn-bearing particles both indoor and outdoor. Interventional studies are important given the health outcomes associated with exposure to Mn-bearing $PM_{2.5}$.

Furthermore, measures are needed to reduce or trap airborne PM in residential areas near smelters. Such measures can include landscape covering with tar, paving, or grass to improve occult deposition. A tree cultivation program can also be initiated, particularly along the road sides as part of an occult deposition programme.

Findings from this study can also be used to conduct a human health risk assessment and environmental impact assessment. The findings can also be useful to future epidemiological studies that want to associate emission from ferromanganese smelters and adverse health outcomes.

Lessons drawn from this study is that there is a need for integrated town planning and industrial development strategies aimed at protecting public health. Therefore, industries such as ferromanganese smelters should be located near residential areas. Conversely, residential areas should also not be developed near such industries, particularly downwind. Residential areas near industries are developed because people want to be closer to their workplace and want to reduce costs associated with transport. Environmental impact studies should be conducted before developing such areas and the potential air quality impacts should be assessed using dispersion models such as Calpuff and Airmod.

CHAPTER 6: REFERENCES

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Appendix A: Plagiarism declaration form



PLAGIARISM DECLARATION TO BE SIGNED BY ALL HIGHER DEGREE STUDENTS

SENATE PLAGIARISM POLICY: APPENDIX ONE

I **SETLAMORAGO JACKSON THOBEJANE** (Student number: **2281450**) am a student registered for the degree of **MASTER OF SCIENCE IN EXPOSURE SCIENCE** in the academic year **2021**.

I hereby declare the following:

- I am aware that plagiarism (the use of someone else's work without their permission and/or without acknowledging the original source) is wrong.
- I confirm that the work submitted for assessment for the above degree is my own unaided work except where I have explicitly indicated otherwise.
- I have followed the required conventions in referencing the thoughts and ideas of others.
- I understand that the University of the Witwatersrand may take disciplinary action against me if there is a belief that this is not my own unaided work or that I have failed to acknowledge the source of the ideas or words in my writing.

Signature: Thobejane SJ Date: **23 June 2021**

Appendix B: Research ethics clearance certificate

UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG

R14/49 Prof Gill Nelson et al

HUMAN RESEARCH ETHICS COMMITTEE (MEDICAL)

CLEARANCE CERTIFICATE NO. M150466

NAME: (Principal Investigator)	Prof Gill Nelson et al
DEPARTMENT:	School of Public Health Meyerton (Gauteng) and Potchefstroom (North West), South Africa
PROJECT TITLE:	Motor and Cognitive Health Outcomes in a Manganese-Exposed African Community
DATE CONSIDERED:	24/04/2015 (Initial approval 15/06/2015)
DECISION:	Approved unconditionally
CONDITIONS:	Protocol amendment (including change of study site)
SUPERVISOR:	
APPROVED BY:	Professor CB Penny, Chairperson, HREC (Medical)
DATE OF APPROVAL:	04/09/2018

This clearance certificate is valid for 5 years from date of approval. Extension may be applied for.

DECLARATION OF INVESTIGATORS

To be completed in duplicate and **ONE COPY** returned to the Research Office Secretary on the Third Floor, Faculty of Health Sciences, Phillip Tobias Building, 29 Princess of Wales Terrace, Parktown, 2193, University of the Witwatersrand. I/we fully understand the conditions under which I am/we are authorized to carry out the above-mentioned research and I/we undertake to ensure compliance with these conditions. Should any departure be contemplated, from the research protocol as approved, I/we undertake to resubmit the application to the Committee. **I agree to submit a yearly progress report**. The date for annual re-certification will be one year after the date of convened meeting where the study was initially reviewed. In this case, the study was initially reviewed in **April** and will therefore be due in the month of **April** each year. Unreported changes to the application may invalidate the clearance given by the HREC (Medical).

Principal Investigator Signature Date

PLEASE QUOTE THE PROTOCOL NUMBER IN ALL ENQUIRIES

Appendix C: Data capturing sheet

Date: _____

Sample number/ ID: _____

Time

Start time: _____ End time: _____

Weather condition

Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7

***Sunny: 1 Windy: 2 Cloudy: 3 Rainy 4**

Pump flow rate

Pre- flow rate: _____ Post flow rate: _____

Filter mass

Pre mass: _____ Post mass: _____

Additional information:

_____
_____
_____
_____
_____
_____

Details of the data collector

Name & Surname: _____ Cell number: _____

Appendix D: Standard operating procedures

Preparation of filters

- The filters were conditioned for 24 hours before and after weighing

During the preparation of filters, the conditions of the weighing room were as follows:

- Sterile environment
- The temperature ranged between 21–22˚C
- The humidity was between 35–37%
- There was no cross ventilation in the room

Quality checks

- Ensure that the working surfaces are clean and free from dust
- Switch on the microbalance scale (Sartorius, CPA 225D)
- Allow the microbalance scale to condition for 30 minutes
- Weigh the standard pendulums of 100 and 200 g on the microbalance before and after sampling to calibrate the scale and to validate the results.
- Wear powder-free latex gloves

Consumables

- Forceps
- Filter cassette
- Filters
- Ghost wipes
- Powder-free latex gloves
- Cyclone

Weighing procedure

- Ensure the microbalance doors are tightly closed
- Ensure that the reading on the microbalance scale is zero
- Use forceps to remove the PCTE filter from the filter holder
- Use the hand to open the door of the microbalance scale
- Gently place the filter onto the microbalance scale
- Gentle close the microbalance doors and ensure they are tightly closed
- View the mass of the display screen
- Allow the scale to stabilize
- Record the mass

- Remove the filter and re-weigh three times using the same procedure as described above
- If the mass does not vary significantly, calculate the average filter mass and record it on the datasheet
- Transfer the filter into the filter cassette
- Place and store the cassettes in a cooler box

Pump calibration

- The flow rate must be set at 2.75L/m

Procedure for calibrating the flow rate:

- Place the pump on a flat and stable table that is not disturbed
- Connect the tube to the inlet of the pump then connect the tube to the outlet of the cassette. Connect the tube of the inlet of the cassette, then to the outlet of the gilibrator (Figure 10).
- Use a soap dispenser for flow estimation
- Pour the soap dispenser into the inlet of the gilibrator

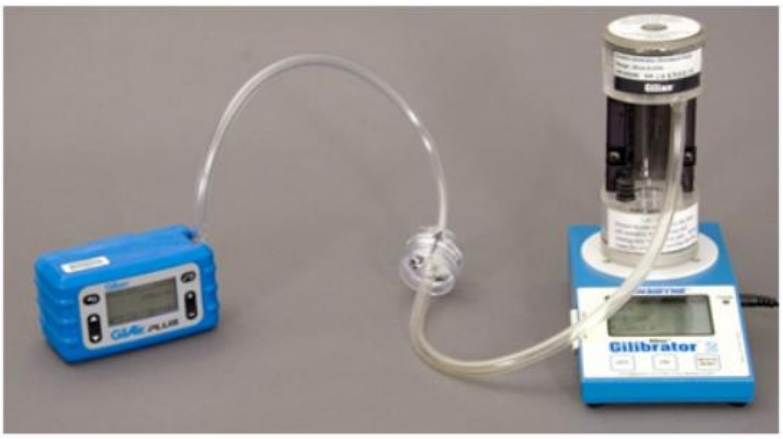


Figure 10: Calibration train

Operation

- Switch on the gilibrator
- Switch on the pump
- Press the black button on the gilibrator to generate a bubble. Repeat the process three times and record the estimated flow rate on the display screen
- Record the average flow rate and compare it with the flow rate of 2.75L/m
- Use the crew driver provided by the manufacturer to adjust the flow rate to 2.75L/m

- Record the flow rate into the datasheet pre flow rate
- Disconnect the calibration sampling train
- Pack the gilibrator

Field sampling

- Place the pump in the allocated space of the selected houses
- Connect the sampling tube of one meter in length
- Attach the $PM_{2.5}$ cyclone (Gs-3 multiple-inlet cyclone) into the inlet of the sampling cassette

Attachment of cyclone:

- Remove the third ring of the sampling cassette inlet
- Attach the $PM_{2.5}$ cyclone
- Connect the sampling tube to the outlet of the sampling cassette (Figure 11)
- Attach the cyclone coupled with the cassette to the sampling holder inside and outside the house



Figure 11: Sampling train

Selection of sampling location

- The sampling location indoor must be selected to ensure the non-disturbance of the samplers due to household movements. The sampler must be placed at a height of ~1.5 meters above the ground
- The selection of the outdoor sampling location must be at the roof height attached to the building wall
- The outdoor sampler must be towards the windward direction of the smelter.

- Record the meteorological conditions in the data collection sheet
- Connect the pump to an electric power supply
- Switch on the pump and record the starting time
- Check the pump after every second day to ensure it is still in operation
- On the 7^{th} day, switch off the pump and record the time
- Remove the sampling cassette together with the cyclone
- Remove the cyclone and fit in the inlet ring
- Use the cassette caps to close the inlet and outlet of the cassette
- Place the samples into a cooler box
- Transport the samples to the laboratory within 24 hours.