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# **Xenobiotic Particle Emission Formation in Fixed-Bed Domestic Coal Combustion**

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## Abstract

Combustion of solid fuels have been reportedly associated with several cases of cardiovascular, respiratory and neurological diseases. Furthermore, it is suggested that premature deaths and morbidity cases may be prevented by the use of clean energy technologies than coal and wood burning. In South Africa, despite 87% of households being connected to the grid, over 50% and 75% of households in urban and rural areas continue to depend on wood and coal for major household activities respectively. In 2004 the Department of Minerals and Energy advocated for the use of top-lit updraft method (TLUD) as an interim clean coal burning technology. The initiative has been associated with the reduction of visible smoke/particulate matter (~80%) and coal consumption. However, studies suggest that there might be other emissions other than PM at household or regional level from such technologies which may be detrimental to health and environmental performances, which requires further investigations.

This present study has investigated the emissions of xenobiotic pollutants emitted from small-scale combustion technology currently in use and advocated to be used in South African low-income settlements. The study focused on emission factors from small-scale coal combustion technologies, influence of coal properties on emissions, particle size distribution at different combustion phases, the physicochemical properties of emitted particles, risk assessment of BTEX emissions, toxicity and cellular uptake of particulate matter from coal combustion. All experiments were carried out in a laboratory environment in order to minimize contribution of other environmental contaminants, which were not intended for the scope of the project.

The emission factors of CO<sub>2</sub>, CO, and NO<sub>x</sub> ranged from 98–102 g MJ<sup>-1</sup>, 4.1–6.4 g MJ<sup>-1</sup>, and 75–195 mg MJ<sup>-1</sup>, respectively. Particulate matter (PM<sub>2.5</sub> and PM<sub>10</sub>) emissions were in the range 1.3–3.3 g MJ<sup>-1</sup> for the BLUD method, and 0.2–0.7 g MJ<sup>-1</sup> for the TLUD method, for both field and lab-designed stoves. When employing the TLUD method, emission factors of PM<sub>2.5</sub>/PM<sub>10</sub> reduced by up to 80% compared to the business as usual BLUD method. The fuel moisture content (from 2.4 wt.% to 8.6 wt.%) led to an 18 and 30% decrease in fire-power when using the TLUD and BLUD methods, respectively. Measured carbon monoxide (CO) emission factors (EF) increased with an increase in moisture content, while carbon dioxide (CO<sub>2</sub>) EF remained unchanged. The use of A-grade coal resulted in 49% increase in PM emissions compared with D-grade coal at high ventilation rates. Particles from the top-lit updraft (TLUD) showed an ultrafine geometric mean diameter centred at approximately 109 ± 18.4 nm for the ignition phase, 54.9 ± 5.9 nm for the pyrolysis/flaming phase, and 31.1 ± 5.1 nm for the coking phase. In studying the physical properties of smoke particles from coal burning three types of shapes were classified, viz., spherical organic particles with similar characteristics to tarballs (ignition), soot particles (flaming), and mineral particles (char-burning). Elemental composition was determined using ICP-MS and it was found that 55%, 28% and 17% of the selected elements (Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) were emitted during the char burning, flaming and ignition phase, respectively. However, during ignition most emitted element were K and Si, which may be used as markers for the simultaneous combustion of wood and coal. When using near-field breathing zone concentration of BTEX in a simulated exposure scenario applicable for a typical coal burning South African household, the cancer risk for adult males



and females, was found to be 1.1 -1.2 and 110-120 folds higher than the US EPA designated risk severity indicator [ $1E^{-6}$ ], respectively. All four TEX compounds recorded the Hazard Quotient [HQ] of less than 1, indicating a low risk of developing related non-carcinogenic health effects. Lastly, smoke particles emitted from the TLUD ignition from a high-ventilated stove were used to determine the cytotoxicity and cellular uptake. Particles from three combustion phases showed mild toxicity on the bronchial epithelial cells at highest concentration of 150  $\mu\text{g/ml}$  while lower concentrations (20  $\mu\text{g/ml}$ , 60  $\mu\text{g/ml}$  100  $\mu\text{g/ml}$ ) did not indicate significant toxicity on the cells.

The results of this study have shown that the emissions of health and environment damaging may be significantly reduced by the correct selection of stove to fuel combinations. The PM emissions are directly proportional to the stove type, fuel properties and ignition method. Stoves with higher ventilation rate ignited using fuel with low moisture content and lit with the TLUD ignition method, produces optimum performance on the reduction of  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ . However, the use of fire ignition method and coal with different moisture content did not show a convincing reduction on the gaseous emissions. Therefore, it remains important when promoting clean coal burning technologies to take cognisance on non-conclusive information of emission performance, particularly on gaseous emissions. It was further, established that particles emitted from domestic coal burning are of small diameter with an average mean of less than 100 nm. This is concerning due to the longer residence time of small particles on air spaces and higher deposition rate in the lower respiratory track of the exposed individual. The emitted particles low to medium temperature produced organic enriched spherical particle with similar characteristics to tarballs. The emissions of BTEX remains a worrying subject given the high probability of cancer under a defined exposure scenario defined under this project. Therefore, it remains important not to rule out the potential harm associated with gaseous emissions when promoting the technology (use of TLUD ignition method).

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## **Declaration**

The work contained in this thesis is my own, unless otherwise acknowledged. This thesis has not been presented for examination at any other university. The researcher designed the study, carried out all experimental work and data analysis. The author declare collaboration with other laboratories during the course of this project. However, all work carried out in collaboration was done by the author. Parts of this thesis have been presented at national and international conferences. Chapter 2 to 7 have been published or submitted in peer reviewed journals.

## **Publications**

### **Chapter 2: Publication 1**

**Masekameni M.D**, Makonese T, Annergan HJ, Forbes P. Emission factors of domestic coal-burning braziers. “*South African Journal of Science*”, 113(3–4), pp. 1–11. doi: 10.17159/sajs.2017/20160187.

**M.D** and T conceptualised the project, carryout all experiments and data analysis. D.M collected braziers from the field while T initiated the first draft of the paper. M.D edited the draft before submission to H.J and P. The project was supervised by H.J while P did grammar checks and quality control. Personal contribution to the project is 55%.

### **Chapter 3: Publication 2**

**Masekameni M.D**, Makonese T, Annergan HJ. “Influence of coal properties on the performance of fixedbed coal-burning braziers”, *Journal of Energy in Southern Africa*”, 28(2), pp. 40–51. doi: 10.17159/2413-3051/2017/v28i2a1374.

**M.D** and T conceptualised the project, conducted all experiments and data analysis. D.M collected braziers from the field while T initiated the first draft of the paper. M.D edited the draft before submission to H.J and P. The project was supervised by H.J. Personal contribution to the content of this work is 60%.



### **Chapter 4: Publication 3**

**Masekameni MD**, Brouwer D, Makonese T, Rampedi I.T, Gulumian M. “Size Distribution of Ultrafine Particles Generated from Residential Fixed-bed Coal Combustion in a Typical Brazier”, *Aerosol and Air Quality Research*, 18: 2618 - 2632, 2018. doi: 10.4209/aaqr.2018.03.0105.

**M.D.** conceptualized and prepared the manuscript. He developed the methodology and data analysis. T, M and D edited the manuscript and validated methodology and supervised the data analysis process, interpretation, and the presentation of arguments. I assisted in the editing of the manuscript. Personal contribution to the content of this work is 80%.

### **Chapter 5: Publication 4**

**Masekameni MD**, Makonese T, Rampedi I.T. “Morphology and elemental analysis of freshly emitted particles from packed-bed domestic coal combustion”. Manuscript submitted to the *Air Quality, Atmosphere & Health-Under review*

**M.D.** conceptualized and prepared the manuscript. He developed the methodology and data analysis. T edited the manuscript and validated methodology and supervised the data analysis process, interpretation, and the presentation of arguments. I assisted in the editing of the manuscript. Personal contribution to the content of this work is 80%.

### **Chapter 6: Publication 5**

**Masekameni MD**, Moolla R, Brouwer D, Gulumian M. “Risk Assessment of Benzene, Toluene, Ethyl Benzene, and Xylene Concentrations from the Combustion of Coal in a Controlled Laboratory Environment”, *International Journal of Environmental Research and Public Health*. 16, 95: 1-18, doi:10.3390/ijerph16010095.

**M.D.** conceptualized and prepared the manuscript. He also carried out the experiment and writing up of the paper. R. developed the methodology for data analysis. She further analyzed the data and assisted in the editing of the



manuscript. M. edited the manuscript and validated methodology for risk assessment. D. supervised the data analysis process, interpretation, and the presentation of arguments, and assisted in the editing of the manuscript. Personal contribution to the content of this work is 80%.

## **Chapter 7: Publication 6**

**Masekameni MD**, Gulumian M, Vetten M. Makonese T. “Toxicity and cellular uptake of smoke particles generated from residential coal burning on bronchial epithelial cells”. *Manuscript in preparation*.

**M.D.** conceptualized and prepared the manuscript. He developed the methodology and data analysis. MV edited the manuscript and validated methodology and supervised the data analysis process, interpretation, and the presentation of arguments. M assisted in the editing of the manuscript. Personal contribution to the content of this work is 80%.

### **Conference presentations:**

Kasangana KK, Makonese T, **Masekameni DM**. Knowledge and Perceptions of Hazards Associated with Traditional Cooking and Heating Fuels. Proc 26<sup>th</sup> Conf Domest Use of Energy. DUE 2018: 35-41.

**Masekameni D**, Kasangana KK, Makonese T. A comprehensive review on small-scale combustion technologies in Southern Africa, what is known, done and emergent knowledge gaps? Proc 25<sup>th</sup> Conference Domest Use of Energy, DUE 2017. 2017: 30-38.

Mbonane TP, **Masekameni D**, Mokoatle C, Kasangana KK. A review paper on traditional fuel use , indoor air pollution , and Respiratory diseases : Lessons for South Africa. Proc 26<sup>th</sup> Conference Domest Use of Energy. DUE 2018:17-23.



## **Dedication**

I would like to dedicate this Doctoral thesis to my wife Mmamokobe Jeanet Masekameni, my daughters (Paulinah and Mokgadi Masekameni) and my sons (Rampedi, Sello and Setete Masekameni) for their understanding, support, care and always being there when I need them. This journey was a very long one. Although it was difficult with the support of my family I have managed to remain positive throughout. I thank them and may the lord almighty keep, harness and protect them.







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## **Disclaimer**

This thesis might contain some repetition especially on methodology, description of concepts, use of references and presentation of arguments as contained in several publications.





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## Glossary of Terms

<b>AEC</b>	Atomic Energy Corporation of South Africa (AEC)
<b>BLUD:</b>	Bottom-lit Updraft
<b><i>BnM:</i></b>	<i>Basa njengo Magogo</i>
<b>BTEX:</b>	Benzene, Toluene, Ethyl-benzene and Xylene
<b>CDI:</b>	Chronic daily intake
<b>CO:</b>	Carbon Monoxide
<b>CO<sub>2</sub>:</b>	Carbon dioxide
<b>EPA:</b>	Environmental Protection Agency
<b>EF:</b>	Emission Factor
<b>HAP:</b>	Household Air Pollution
<b>HQ:</b>	Hazard quotient
<b>ICP-MS:</b>	Inductive Couple Plasma- Mass Spectrometry
<b>IEA:</b>	International Energy Outlook
<b>NO<sub>x</sub>:</b>	Nitrogen Oxide
<b>PM:</b>	Particulate Matter
<b>PSD:</b>	Particle Size Distribution
<b>R<sub>f</sub>C:</b>	Reference Dose
<b>SMPS:</b>	Scanning Mobility Particle Sizer
<b>TEM:</b>	: Transmission Electron Microscopy
<b>TEX:</b>	Toluene, Ethyl-benzene and Xylene
<b>TLUD:</b>	Top-lit Updraft
<b>VOC:</b>	Volatile Organic Compounds
<b>WHO:</b>	World Health Organization

# CHAPTER ONE

*This chapter introduces an overview of residential coal use globally and emphasised reference is given to South Africa and other developing countries, and presents air pollution issues, health and environmental challenges. The research problem statement is stated, the domain of the study specified, and the specific research objectives are presented. A justification of the study is presented and the scope of the study is highlighted. An overview of the thesis layout is given at the end of the Chapter.*

## 1. Introduction and Background

### 1.1 Small scale-combustion

Despite recent global transformation in increasing access to clean energy, over three billion people of the global population continue to rely on solid fuel as a primary source of energy (Bonjour *et al.*, 2013), especially for cooking and space heating purposes (IEA, UNDP and UNIDO, 2010; Panos, Densing and Volkart, 2016). Solid fuels such as coal, wood, agricultural residues and cow dung are widely used due to their inherent natural reliability characteristics and low-cost implications (Finkelman, 2004; Smith *et al.*, 2014). Although, biomass amongst other solid fuels is a sustainable and renewable energy source with the potential to replace or minimise reliance on fossil fuel for domestic activities, it is linked with high emissions of particulate matter (Boman *et al.*, 2003; Winkler, 2005, 2007).

Residential solid fuel in developed countries, particularly those with low energy output (cow dung and agricultural residue) reliance despite being in declined, wood and coal remain major fuels for space heating and cooking in low income countries (Bonjour *et al.*, 2013; International Energy Agency (IEA), 2014; Energy Information Administration, 2016). However, in developing nations over 50% of households still depend on coal, wood and animal dung to meet their daily energy requirements (IEA, UNDP and UNIDO, 2010; International Energy Agency (IEA), 2014; Makonese and Ifegbesan, 2018).

#### 1.1.1 Residential burning of solid fuel

Solid fuels occupy contribute immensely to the household energy share of energy due to their inherent multi-purpose use, especially in low income settlements or household (Smith *et al.*, 1994; Balmer, 2007; Zhang and Smith, 2007). Over half of the world population burn solid fuels daily to accomplish their household energy requirements (Ezzati and Kammen, 2002; Bonjour *et al.*, 2013; Energy Information Administration, 2016). Solid fuels are diverse in nature and they have different characteristics, composition, availability and general household use (Makonese, Masekamani and Annegarn, 2016). Solid fuel budget in terms of resources includes wood, coal, charcoal, agricultural residues and animal dung (Girard, 2002; Ludwig *et al.*, 2003; Noonan and Balmes, 2010). However,

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coal and wood are the main dominant energy sources preferred in many households (Jaramillo, Griffin and Matthews, 2007; Mohr and Evans, 2009; Forouzanfar *et al.*, 2015). In other instances, coal and wood are used interchangeably; while on the other hand only one source is used. Factors influencing household choice on energy sources vary per household characteristics (Makonese and Ifegbesan, 2018; Mgwambani *et al.*, 2018). Variables often leading to choice of individual or multiple fuels includes culture, availability, affordability, heating requirements, ease of burning, availability of devices to combust the fuel resource and governmental factors (Balmer, 2007; Zhang and Smith, 2007; Kimemia and Annegarn, 2011)(Heltberg, 2005).

### 1.1.2 Solid fuel burning in developing countries

Despite reported cases on increased pre-mature deaths, cardiovascular illnesses and respiratory infection due to inhaling gaseous and particulate matter emitted from solid fuel burning, consumption of coal and wood remains high in the domestic sector (Smith *et al.*, 2007; International Energy Agency (IEA), 2014). Over 50% and 75% of households use solid fuels for cooking and heating in urban and rural areas respectively (Bruce, Perez-Padilla and Albalak, 2002; WHO, 2008). Studies suggest that coal and wood dependence will remain a major source of domestic energy for a prolonged period of time despite introduction of energy alternatives (Chamber of Mines of South Africa, 2018). In Asia coal consumption remains high due to low temperatures which requires high heating output appliances and energy sources (Zhang *et al.*, 2000; Zhang and Tao, 2009). In China since early 1990 there is a massive economic growth which is correlated with increased urbanisation. This has put China under immense pressure to increased urbanisation leading to massive energy supply gaps (Forouzanfar *et al.*, 2015) (Peters *et al.*, 2007). Several studies attempted to quantify household emissions, however, in developing countries information on this subject it is either scarce or not accurate (Cai *et al.*, 2010). China is the leading consumer of energy at household level compared to other countries at 9.7 GJ per year per household (Finkelman *et al.*, 2002; Li *et al.*, 2006; Chafe *et al.*, 2015).

The impact of solid fuel use goes beyond health but inclusive of environmental imbalance, disruption of ecosystem and deforestation (Hand *et al.*, 2005; Tóth *et al.*, 2014a; Li *et al.*, 2015; Rainey, Vaganay and MacIntyre, 2016). Due to large consumption of wood in Asia, focus was to substitute wood with coal. It was later found that increased consumption of coal led to water pollution and poor air quality (Vejahati, Xu and Gupta, 2010; Annesi-Maesano *et al.*, 2013). In addition to pollution it was found that coal mining also deteriorated the ecosystem (Petaloti *et al.*, 2006). Furthermore, combustion of coal increased the concentrations of CO, CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub> (Sippula *et al.*, 2007; Wei *et al.*, 2008).

In countries like India the use of solid fuels remains high as a consequence of limited clean energy resources (Fine, Cass and Simoneit, 2004; Finkelman, 2004; Garg, 2011). Over 85% of Indian households continue to burn fire wood on daily basis using inefficient devices (Pachauri and Jiang, 2008; Muller and Yan, 2014). In summary, both China and India have over a billion households and faces significant challenges in accessing clean energy supply (Patil, 2011a). China is the second leading country in energy consumption globally while India is the fifth consumer of energy



(Bhattacharyya, 2006; Parikh and Ghosh, 2009). In both countries coal and wood energy sources supply 80% of their population while 20% is additional share from grid electricity (Patil, 2011b; Pereira *et al.*, 2011). Despite universal access to electricity in China for all households, there is a continued dependence on coal (Pereira *et al.*, 2011; Alghamdi *et al.*, 2014). Using this literature, lessons can be learned that coal and wood remains and will continue to be the most reliable, available and affordable energy sources for foreseeable future (Urban, 2009; Balachandra, 2011; Marć, Zabiegała and Namieśnik, 2014). Therefore, more studies are needed to understand the dynamic of solid fuel burning, potential release of pollutant, exposure pathway and health/ environmental responses.

In Africa similar to other developing countries from other continents a larger proportion of households continue to depend on fire wood and coal despite consequence of adverse health and environmental impacts (Kimemia and Annegarn, 2011). Over 80% of people in the sub-Saharan region have no access to clean energy sources (Brew-Hammond, 2010; Bazilian *et al.*, 2012; Kahsai *et al.*, 2012). This paramount of poor access is largely associated with lack of policies which enhance a better dispatch of energy sources deemed cleaner (Winkler, 2007). Similarly, to developing Asia over 80% of households have no access to electricity (Pereira *et al.*, 2011).

In the Southern African Developing Community (SADC), access to electricity remains a developmental challenge, with just 30% of the countries being able to achieve electrification rate of above 50% (International Energy Agency (IEA), 2014; Energy Information Administration, 2016). However, in the few countries with high electrification rate, over 75% of households continue to depend on solid fuels for cooking and space heating (Le Roux, Zunckel and McCormick, 2009; Scorgie, 2012); while electricity is mainly used for entertainment, illumination and refrigeration (Makonese, Masekameni and Annegarn, 2016; Kasangana, Masekameni and Saliwa, 2017; Masekameni, Kasangana and Makonese, 2017).

In South Africa, over 87% of the population is connected to the grid (Badjagbo *et al.*, 2010; Israel-akinbo, Snowball and Fraser, 2018). However, dependence on solid fuel remains high due to affordability and unreliability of the electricity supply system (Barnes *et al.*, 2009; Bohlmann and Inglesi-Lotz, 2018). Over the past five years the National Energy Regulator of South Africa has been requesting electricity tariff increases ranging from 8-16% (Abdullah *et al.*, 1929; Goliger and Mcmillan, 2018). This has led to increase in the cost of electricity relative to solid fuels (Baker, Newell and Phillips, 2014; Baker and Phillips, 2018). Continuous power outages due to cable theft and inability of the grid to withstand high electricity demands also contributed significantly on the reliability of the grid energy (Baker, Newell and Phillips, 2014; Kelly and Geyer, 2018; Kumar *et al.*, 2019).

In addition to the formal settlements in South Africa there is an increase in the illegal occupation of land leading to increase on the number of informal settlements. Over 4.7 million people reside in informal settlement without access to electricity (Chikoto, 2009; Housing Development Agency HDA, 2013). Coal, wood and paraffin remain the major sources of energy in the informal settlement



(Kimemia *et al.*, 2013). Moreover, there is inadequate access of proper and clean burning technologies leading to poor combustion of such fuels and consequently increasing the emissions of gases and particulate matter in both indoors and outdoors environment (Masekamani, Makonese and Annegarn, 2014; Makonese *et al.*, 2015a, 2017b). The multi-diversional uses of fuels in informal settlements remain a major obstacle for pollution or health risks source mapping (Balmer, 2007; Rogalsky DK, Mendola P, Metts TA, 2014). Poor source or inadequate information on pollution/health risks source mapping to date has led to several catastrophes such as increase in the number of respiratory infections, cardiovascular illnesses, carbon monoxide poisoning, shack fires and child burns (Usmani, Biddiscombe and Barnes, 2005; Naeher *et al.*, 2007; Barnes *et al.*, 2009; Forouzanfar *et al.*, 2015; Kumarathanan *et al.*, 2018). However, most of this unfortunate events occurring in typical households in South Africa are poorly documented, communicated and captured in several literatures (Ludwig *et al.*, 2003; GroundWork, 2016).

In light of goal 7 of the sustainable development goals, arguably the provision of affordable and access to clean energy is nothing new as it was previously addressed under the millennium development goals (Panos, Densing and Volkart, 2016; Bohlmann and Inglesi-Lotz, 2018). Despite vast measures being introduced to address energy inequalities in South Africa, very few studies attempted to determine the success of such initiatives (Israel-akinbo, Snowball and Fraser, 2018). Therefore, this paucity of information indicates the need for more studies in addressing energy issues, emissions of airborne pollutants, human exposure and health outcome holistically (Kauppinen and Pakkanen, 1990; Kocbach *et al.*, 2006, 2008; Jalava *et al.*, 2010).

### 1.1.3 Coal combustion emissions

Domestic coal and wood combustion is a major source of carbonaceous aerosols and several gaseous compounds (Cai *et al.*, 1996; Johansson *et al.*, 2004; Zhang *et al.*, 2018). Combustion of solid fuels is done using varied appliances, meaning there is no a standardised device often scaled up in the market to perform household energy activities (Makonese *et al.*, 2015a; Masekamani *et al.*, 2018). Unlike in the industrial sector where several proto-types and commercial devices are available to burn solid fuels. The lack of efficient cookstoves lead to poor combustion of wood and coal (SurrIDGE *et al.*, 2004; Le Roux, Zunckel and McCormick, 2009). Processes involving incomplete combustion due to the use of inefficient stoves is associated with the increase on the emissions of particulate matter and gases (Oberdörster, 2001; Cohen *et al.*, 2005; Bond *et al.*, 2007).

The burning of coal or wood is predicted to cause various forms of pollution indoors and outdoors (Smith *et al.*, 2009, 2014). Nevertheless, it is suggested that with proper combustion technology modification, an improved performance can be achieved (Madubansi and Shackleton, 2006; Kimemia and Annegarn, 2012). Therefore, it is essential to investigate combustion parameters, which can improve combustion condition in small-scale coal burning (Sippula *et al.*, 2007; Frey, 2014; Zhang *et al.*, 2018).

In rural communities and low-income urban areas, the use of solid fuel for domestic activities exposes households to copious emissions of health-damaging pollutants, including volatile organic





compounds, polycyclic aromatic hydrocarbons, fine and ultra-fine PM (Boström *et al.*, 2002; Chakrabarty *et al.*, 2010, 2014). The World Health Organisation (WHO) estimates that every year more than 7 million lives are lost due to inhaling polluted air (Lim *et al.*, 2012; Gordon *et al.*, 2014; Forouzanfar *et al.*, 2015). Smith *et al.* (2014), contends that most of these deaths occur in developing countries, where wood and coal are used as primary energy sources. In South Africa, combustion of solid fuels in low-income households is done in self-fabricated and inefficient stoves, leading to increased emissions (Balmer, 2007; Makonese *et al.*, 2012; Kimemia *et al.*, 2013; Masekameni, Makonese and Annegarn, 2014). Therefore, a need to evaluate the emission performance of existing small-scale coal-combustion devices in use is relevant in order to develop interventions which will prevent acute and chronic exposure from this sources (Ezzati and Kammen, 2002; Winkler, 2005, 2007; Le Roux, Zunckel and McCormick, 2009; Noonan and Balmes, 2010). Information from this study will be useful for predicting emission formation in the design of energy production units to meet emission regulations and to assess the environmental effects of different alternatives and also filling the knowledge gap presented in other studies (Sippula *et al.*, 2007; Sippula, 2010; Torvela *et al.*, 2014).

Coal used in domestic combustion technologies comprises of over 60% carbon, 20% volatile organic compounds, less than 10% moisture content and over 20% ash content. The amount of volatile matter in coal is low compared to wood, which is above 70% (Tissari *et al.*, 2008; Jalava *et al.*, 2010; Frey, 2014). Therefore, during ignition, coal requires a catalyst to burn; often-wood kindling is used for ignition due to the inherent higher volatiles (Wang and Luo, 2009; Lu *et al.*, 2017; Wang *et al.*, 2018).

The formation of particles is high at low-temperature conditions and during incomplete processes, where soot might be formed comprising of elementary carbon, black carbon and gas precursor to aerosols as PAHs (G. Liu *et al.*, 2008; Y. Liu *et al.*, 2008; Li *et al.*, 2015; Zhang *et al.*, 2018). Some of the aerosols present are influenced by the fly ash comprising of the inorganic compounds contained in the fuel (McGee *et al.*, 2003; Petaloti *et al.*, 2006; Tóth *et al.*, 2014b, 2014a). Previous studies reported emissions from small-scale combustion as average concentration of particles above 2.5  $\mu\text{m}$  over the entire burn cycle, with little emphasis on varied combustion phases (Masekameni, Makonese and Annegarn, 2014; Makonese, 2015; Masondo *et al.*, 2016; Makonese *et al.*, 2017b). However, combustion in fixed bed varies at various phase (ignition, pyrolysis and coking/ char-burning phase) (Jalava *et al.*, 2010; Geng *et al.*, 2014; Zhang *et al.*, 2014). It is, therefore, essential to evaluate emission/ concentrations of emitted pollutants at each combustion phase; this information may be essential for the purpose of designing an optimum performing devices capable of reducing emissions (Makonese *et al.*, 2015a).

Coal combustion at large scale involve fixed bed, fluidized bed often pulverized varied with specific combustion requirements (Frey, 2014). Residential small-scale combustion, involve fixed-bed combustion, using different fuel particle size. In contrast, fluidize bed involves spraying fuel (oil) on top of the fuel bed to aid combustion (Bond *et al.*, 2004, 2006, 2007) (Bond *et al.*, 2006). Therefore, combustion conditions will vary significantly, at each combustion technology. In order to understand emissions associated with environmental xenobiotic particles, each technology must be investigated.





#### 1.1.4 Residential coal combustion technologies in South African low income settlements

In small-scale residential burning coal is burned as lump and combustion of such fuels in a brazier/*imbaula* is done without a chimney, with varied ventilation holes and at time without fuel grate (Kimemia and Annegarn, 2011; Masekameni, Makonese and Annegarn, 2014). The conventional ignition method is the most known traditional way of lighting the stove in coal burning communities in a brazier. The most common name referenced in literature describing the classical or conventional method of ignition coal in a brazier is known as the bottom-lit updraft ignition technique (BLUD) (Le Roux, Zunckel and McCormick, 2009). The BLUD ignition method has been associated with the release of high emissions and fuel consumption. In BLUD ignition the fuel is arranged in the following order: wood as kindling at the bottom of the stove (preferably on the grate), paper and coal on top (Kimemia *et al.*, 2013; Masondo *et al.*, 2016; Makonese *et al.*, 2017b). However, the coal on top is added once the kindling flame is established. After coal is added on top of the wood kindling flame, the fire choke and high smoke emissions is observed. The fire zone migrates from the bottom of the fuel bed, as wood kindling pyrolysis the coal. Coal undergoes thermal decomposition and releases the semi-volatile organic compounds (Mobarak *et al.*, 2012; Forouzanfar *et al.*, 2015). The semi-volatile organic compounds migrate upwards passing through a cold zone at the top of the fuel bed before escaping to the atmosphere. During this process, the emitted smoke enriched with volatiles leaves the stove unburned and then after condenses in to droplets where a white to brown thick plume can be seen as in Figure 1.

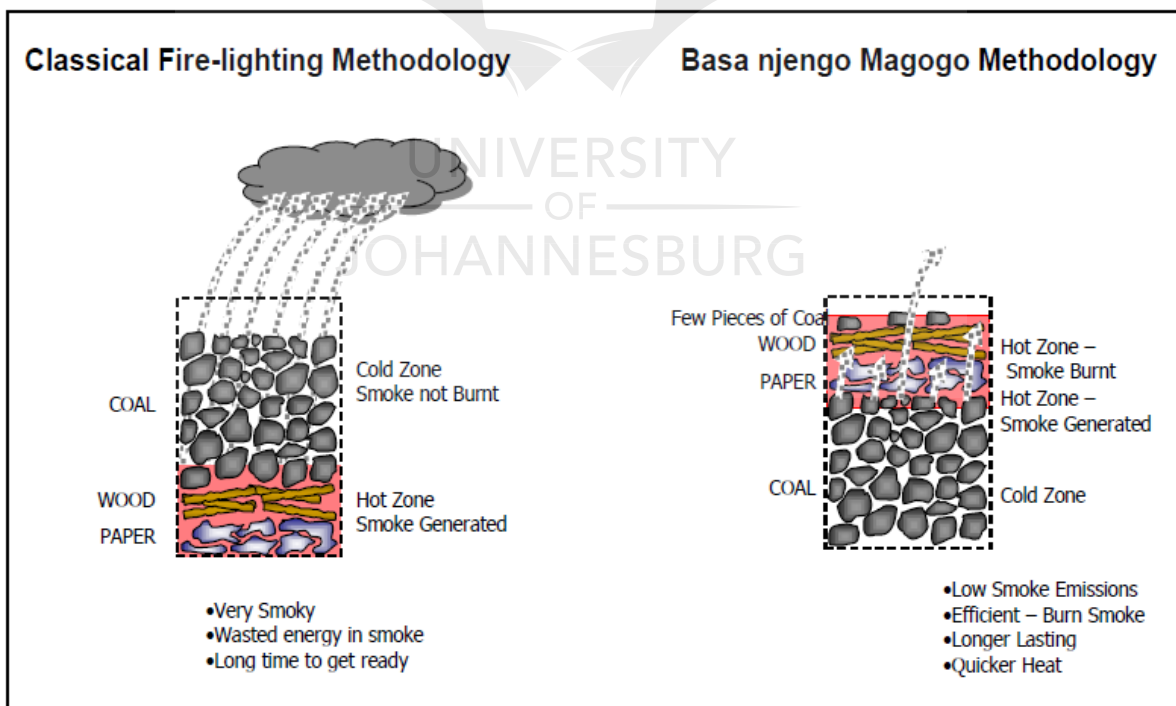


Figure 1: Demonstration of the BLUD and TLUD ignition methods applicable in South African coal burning settlements using a brazier. (Department of Minerals and Energy, 2004)

The top-lit updraft (TLUD) have been used alternatively to the BLUD ignition method (Sania, 2018). During the TLUD ignited fires the combustion process with the fuel drying due to wood kindling fire



(Makonese, 2011). Then after, as the moisture is driven out the pyrolytic zone migrates downwards from the few coal lumps ignited by the wood fire to the fuel bed (Wentzel, 2006). As the process continues semi-volatile organic compounds are released and mixed with heated air projected from outside to the top/ side air holes of the devices. Volatiles organic compounds are therefore, heated before escaping. This method in operation is similar to downwards gasifiers which used natural/ force draft to improve combustion conditions (Tryner, Volckens and Marchese, 2018). The different between the gasifier and a brazier is that a gasifier often is fitted with a chimney while braziers are without (Masekameni, Makonese and Annegarn, 2014). However, the air supply for the two designs are similar in that both uses forced draft which is based on the air coming in from the bottom of the fuel bed while the natural draft is introduced from the top of the stove.

Since, it has been illustrated that the conventional fire ignition method contributes significantly to the release of volatiles organic compounds and local visibility the Department of Minerals and Energy looked for an alternative fire ignition method (Le Roux, Zunckel and McCormick, 2009). During the year 2003, Nobelungu Mashinini of eMbalenhle township in Secunda, Mpumalanga province demonstrated that a change in fire ignition method (*Basa njengo Magogo*) can significantly reduce fuel cost and emissions (Julies *et al.*, 2005). The NOVA institute and Sasol Infrachem carried out a pilot study in eMbalenhle low income and coal dependant settlement to evaluate the efficiency of the method in 2003. The method focused on a change in fuel ordering which is different from the BLUD method (Wentzel, 2006). However, the method did not opt to alter the design parameters of the device. In the *Basa njengo Magogo* (*BnM*) ignition method the basic principle is that the pyrolytic zone migrates from the top to the bottom of the fuel bed, ensuring that the escaping volatiles passes through a hot zone phase (Makonese *et al.*, 2017b).

The DME developed an integrated household clean energy strategy emphasising on a roll-out of *BnM* in coal burning settlement. The TLUD/ *BnM* ignition method was favoured by the department since it was proven to reduces particulate matter by 80% and a total of over 50% reduction on fuel consumption (Le Roux, Zunckel and McCormick, 2009). During the TLUD ignition method the fuel to stove combination is arranged in the following order: 75% of the coal load is laid on top of the fuel support grate, wood kindling, paper and 25% of the remaining coal is evenly distributed on top (Makonese, 2011). During the flaming phase as coal undergo thermal decomposition the escaping semi-volatiles passes through a hot zone at the top of the fuel-bed where they are burned and only few escapes without being fully combusted (Makonese *et al.*, 2017b). In BLUD the smoke is usually pre-mature relative to little visible more matured smoke from the TLUD fire as in Figure 1. In addition to emission reduction and cost saving ability, the method may reduce the health burdens associated when using the BLUD ignition method without changing the fuel or the device. The TLUD method successes are deemed to be fully reliant on a change of user behaviour.

#### 1.1.5 Coal combustion emissions and health effects

Attempt to investigate human exposure to xenobiotic combustion particles centred *in-vivo* and *in-vitro* studies (Oberdörster, 2001; Sioutas, Delfino and Singh, 2005; Jafta *et al.*, 2017; Wang *et al.*, 2018). Several epidemiological studies linking association between coal combustion soot to



respiratory infections depend on human exposure assessments (Krewski *et al.*, 2005; Pope and Dockery, 2006). However, such studies are costly, time-consuming and only limited effects can be investigated due to varied additional health-related conditions, including pre-existing diseases prior exposure, genetic defects and susceptibility (Andreoli, 1997; Zhang and Smith, 2007; Hobson and Guy, 2014). Such associations may also be obtained from *in-vivo* animal studies, which are once again costly and time-consuming. To assess the hazard associated with exposure to coal particles, this study will use *in-vitro* approach (Barnes *et al.*, 2009; Kocbach Bølling *et al.*, 2009; Bølling *et al.*, 2012).

Earlier studies shown that most particulate emissions from residential coal and wood burning are below 1  $\mu\text{m}$  in diameter and are often referred to as ultra-fine particles, with the mean diameter in the Nano-region (Monn and Becker, 1999; Becker, Soukup and Gallagher, 2002; Sioutas, Delfino and Singh, 2005, 2005; Ning and Sioutas, 2010). Previous studies conducted focussed on various particle size ranges from  $\text{PM}_{2.5}$  to course particles while limited studies were conducted to quantify nanoparticle emissions from small-scale packed-bed solid fuel combustion sources (Mc Donald and Biswas, 2004; Makonese, Masekameni and Annegarn, 2017; Zhang *et al.*, 2018).

Particle size ranges from 1 000 nm to 10 nm present both environmental and public health concerns (Kumar *et al.*, 2010; Shah *et al.*, 2012; Hobson and Guy, 2014; Smith *et al.*, 2014). However, the health effects of nanoparticles on human will vary from person to person, due genetics and existing disease, as well as exposure index (Hueglin *et al.*, 1997; Sioutas, Delfino and Singh, 2005; Bruinen De Bruin *et al.*, 2008; Lim *et al.*, 2013). Correlation between increased exposure to nanoparticles lower than 1000 nm and, respiratory and cardiovascular diseases, various cancer and mortality have been shown in several epidemiological studies (Brunekreef and Forsberg, 2005; Ping, 2015; Jafta *et al.*, 2017).

The Environmental Protection Agency suggests that people are exposed 10 folds to health damaging pollutants emitted from residential solid fuel burning when they are indoor environment than when they are outdoor (USEPA, 2004; Kumar *et al.*, 2014; Zhang *et al.*, 2015). Domestic activities such as cooking, heating, and illumination are the primary producer of nanoparticles lower than 100 nanometres (Oberdörster, Oberdörster and Oberdörster, 2005; Grassian *et al.*, 2007). Outdoors activities such as vehicular, industrial and residential burning finds their way to the inside environments/ indoors, however, the contribution is often varying due to the building envelope (Sioutas, Delfino and Singh, 2005). This results in elevated indoor air pollution, given that people spend more than 80% of their time indoors (Zhang and Smith, 2007; Muller and Yan, 2014).

Small scale combustion activities release particles lower than 100 nanometres, thereafter, small particles fuse together during agglomeration stage, while other forms aggregates during accumulation mode to form particles at a range of 100 nm – 2.5  $\mu\text{m}$  (Mc Donald and Biswas, 2004; Neer and Koylu, 2006). Therefore, it remains a gap in understanding how particles are generated, aggregates and agglomerates (Ning and Sioutas, 2010). Available literature in this field reported emission data set above 1  $\mu\text{m}$ ; nevertheless, attempt to investigate particle lower than 1  $\mu\text{m}$  have been reported on



vehicle-related emissions, large-scale combustion technology and wood burning (Nussbaumer *et al.*, 2001; Jalava *et al.*, 2010).

Consequently, emissions from low-temperature household combustion activities have been associated with the infections of lower respiratory system (Pakkanen *et al.*, 2001; Bølling *et al.*, 2012). Furthermore, acute inflammatory responses in animal studies have shown that chronic exposures may lead to cases of cardiovascular, neurological and respiratory illnesses (Jalava *et al.*, 2005, 2006). Compelling literature from coal have demonstrated that coal emissions are among the leading cause of lung cancer, morbidity and liver damages (Zhang *et al.*, 2015; Lui *et al.*, 2017).

Moreover, it is reported globally that indoor exposure to residential fuel burning emissions is the cause of 4.3 million pre-mature deaths while 3.7 million pre-mature deaths (Lim *et al.*, 2013; Gordon *et al.*, 2014; Forouzanfar *et al.*, 2015). Despite, this dearth of evidence been reported on the health effects associated with coal and wood burning the mechanism as to how the diseases develop is still yet to be understood (Pope *et al.*, 2004; Cohen *et al.*, 2005; Kocbach *et al.*, 2008). Other studies, suggest that the biological effects of solid fuel emissions are based on the physicochemical properties of particles emitted (Zuberi *et al.*, 2005; Schneider *et al.*, 2006; Fitzpatrick *et al.*, 2007). Other, studies have reported that the health effects of particles emitted are influenced by particle diameter, where it is suggested that smaller particles are harmful relative to the larger particles (Hetland *et al.*, 2005; Jalava *et al.*, 2006, 2010; Schwarze *et al.*, 2006).

Studies carried out in China focused on the emissions of metals from cookstoves and associated health effects (Finkelman, 1999; Petaloti *et al.*, 2006). The emissions of Selenium from coal burning activities, was reportedly found in ash and subsequently entered through the food chain (Zheng *et al.*, 1999). Majority of Chinese who consumed food containing high quantities of selenium suffered from selenium poisoning which is an acute diseases known as Selenosis (Zheng *et al.*, 1999). In a separate study carried out in Guangzhou Province of China, found that burning of bituminous coal is a major source of inorganic Arsenic airborne exposure in indoor spaces (Finkelman, 2004; Luo, Li and Zhang, 2011). Coal fire was used for drying of chilli where additional exposure route to inhalation was through oral intake during the consumption of dried chili (Zheng *et al.*, 1999; Lu *et al.*, 2010). Arsenic poisoning was found to be prevalence at the study site. Arsenic poisoning is an early sign of lung cancer if the exposure is prolonged. Another disease found to be associated with coal burning emissions in China was fluorosis (Finkelman, 1999, 2004; Luo, Li and Zhang, 2011). Fluorosis is a diseases associated with the intake of fluoride. The study conducted in the Western Part of China in 13 provinces and municipalities found that over 10 million Chinese suffers from fluorosis. Fluorosis is known to cause dental deterioration and few cases of bladder and lung cancer have been anticipated (Finkelman, 1999, 2004; Ando *et al.*, 2001; Zhang and Smith, 2007). However, the associated cancer risks evidence is still lacking significantly (Zhang and Smith, 2007).

In South Africa, emissions from residential coal burning has be shown to cause several cases of pre-mature mortalities, respiratory disease, cardiovascular and cases of morbidity (Usmani, Biddiscombe and Barnes, 2005; Barnes *et al.*, 2009; GroundWork, 2016). Recently, several cases of carbon



monoxide poisoning have been reported in local newspapers. In 2014, a man and four children were found dead inside a shack the following morning after exposure to CO emissions from coal burnt using a brazier. During the same year, a boy age 16 and man (26) were found dead after being exposed to CO from coal fire. Similarly, in Witbank, Mpumalanga, South Africa three families were killed by CO emission from similar combustion emissions. In 2012, over 20% and 25% of respiratory related admission and childhood mortalities have been reported and associated with coal combustion emissions in Tshwane, Gauteng Province in South Africa (R Norman, D Bradshaw, M Schneider, 2007). However, it must be noted that information on health associated exposure to residential coal burning emission from small-scale combustion technologies in South Africa is still lacking (Bl *et al.*, 2007; Barnes *et al.*, 2009; GroundWork, 2016).

## 1.2 Problem statement and knowledge gaps

Epidemiological studies have associated domestic solid fuel burning with several health outcomes (Krewski *et al.*, 2005; Pope and Dockery, 2006; Jalava *et al.*, 2010; Bølling *et al.*, 2012). Exposure to toxic emissions from domestic coal and wood burning were associated with morbidity and mortalities in many developed countries (Kocbach *et al.*, 2006, 2008; Leiman *et al.*, 2007; Lim *et al.*, 2012; Gordon *et al.*, 2014). However, fewer studies have been carried out with effort to generate emission data from solid fuel burning to support epidemiological studies (Smith, 2000; Hetland *et al.*, 2005; Schwarze *et al.*, 2006; Kumar *et al.*, 2010). In China and other developing countries, domestic solid fuel burning has been associated with emissions of volatile organic compounds and submicron particulate matter (Smith *et al.*, 1994; Finkelman and Gross, 1999; Bhattacharya, Albina and Myint Khaing, 2002; Johnson *et al.*, 2011; Chafe *et al.*, 2015; Zhou *et al.*, 2016). Despite validations from epidemiological studies on the association between exposure to domestic combustion emissions and risk of cardiovascular, respiratory and systemic disease development, the mechanisms as to how diseases develops is still unclear. Previous literatures attempted to provide information which might built on the accuracy of data sets but several knowledge gaps still exist which requires further investigation (Monn and Becker, 1999; Kocbach *et al.*, 2006; Kocbach Bølling *et al.*, 2009; Jalava *et al.*, 2010). This study was triggered by existing knowledge gaps in small-scale coal combustion as follows:

There is a growing concern regarding pollutant inventories in order to understand the major sources of emissions and their impacts (Atkinson and Arey, 2003). There is an emerging body of knowledge which suggests that indoor household burning presents a major threat to public health (Azuma, Uchiyama and Ikeda, 2007; Azari *et al.*, 2012) arising from lack of access to clean energy sources, which has been identified as a major contributor to local indoor air pollution (Badjagbo *et al.*, 2010; Balakrishnan, Cohen and Smith, 2014). Gaseous and particulate matter exposure emitted during residential exposure have been already mentioned or shown to cause several cases of diseases and morbidity. However, very few studies to date have investigated the emission factors of both particulate and gaseous emissions (Bond *et al.*, 2007; Shen *et al.*, 2010). A correct determination of emission factors is essential in both health and environmental impact study models. Nevertheless, currently there is few or inconsistence emission factor data from this subject (Fernandez *et al.*, 2003; Shen *et al.*, 2010). Consequently, lack of reliable EF data will lead to incorrect determination of





emissions inventory which will later complicate the use of such data during source apportionment and epidemiological studies. It is reported, in recent literature that the inconsistency in EF data is due to several factors including, fuel properties, stove design, fire ignition method and experimental conditions (Sippula *et al.*, 2007; Tissari *et al.*, 2008; Shen *et al.*, 2010; Bølling *et al.*, 2012; Chen, Roden and Bond, 2012; Silva *et al.*, 2012). The study intends to provide EF data from small scale coal combustion from a braziers applicable in South Africa. Furthermore, the study will provide information several factors (fuel properties, stove design, and fire ignition method) on the EF from coal burning braziers.

Particles and gases are primarily emitted as a consequence of a combustion sources as primary pollutants (Cai *et al.*, 1996; Lu *et al.*, 2010; Torvela *et al.*, 2014; Zhang *et al.*, 2018). Freshly smoke produced particles account for 90% of the total number of particles, are produced during nuclei mode, and account about 20% of the total mass (Chou *et al.*, 2013) (Chou *et al.*, 2011). The accumulation stage, comprising mainly of carbonaceous agglomerates, accounts for higher particle mass, while less than 20% of the sample mass is from coarse particles (Tiwari *et al.*, 2014). The nuclei mode is highly associated with low-temperature conditions, as the temperature increases the soot particle are formed influenced by carbonaceous agglomerates (Wang and Luo, 2009). The nuclei mode is sensitive to dilution while the accumulation mode is not (Kittelson, Watts and Johnson, 2002; Ning and Sioutas, 2010). However, as particles and gases are released some undergo chemical reactions, while others experience physical transformation (Naeher *et al.*, 2007). Burning of solid fuels will result in releasing primary and secondary particulate emissions (Bond *et al.*, 2004, 2007, 2013). A change from primary to secondary emissions will depend on local meteorological conditions such as humidity, wind speed, and temperature. In order to eliminate the uncertainty linked to ultra-fine particles on human health, local visibility, acid rain and climate change effect, there is a need to deepen our understanding of the physicochemical properties of atmospheric particles (Jiang and Bell, 2008; Chafe *et al.*, 2015; Zhang *et al.*, 2018). Such understanding needs to cover a broader spectrum of particle size distribution, number concentration per surface area, and deposition potential into the atmosphere and human respiratory system (Johansson *et al.*, 2004; Sioutas, Delfino and Singh, 2005; R. Zhang *et al.*, 2008; Zhang *et al.*, 2012). It is therefore, suggested that additional studies be carried out in order to understand particle and gases evolution at different combustion zones or phases (Zhang *et al.*, 2012; Tiwari *et al.*, 2014) . Study, on particle size distribution is essential in health studies where mathematical models can further be used to estimate particle deposition (Nussbaumer *et al.*, 2001; Hobson and Guy, 2014).

Furthermore, such information is needed for the determination of the internal dose and prediction of possible health outcome (Usmani, Biddiscombe and Barnes, 2005; Grassian *et al.*, 2007). There is a growing literature suggesting lack realistic and reliable expression of exposure units. Toxicological studies suggest that expression of exposure concentration using mass concentration ( $\mu\text{g}/\text{m}^3$ ) does not provide a reliable information especially in toxicity testing (Pakkanen *et al.*, 2001; Naeher *et al.*, 2007). Expression of exposure concentration for nanoparticle as number concentration ( $\#/ \text{cm}^2$ ) is suggested to be more reliable in studying toxicity of nanoparticles (Wang and Luo, 2009; Wang *et al.*, 2018). Furthermore, it is reported in fewer studies that emissions of particles or particles precursor



gases to particle phase are of smaller diameter ranging from 30 nm to 300 nm (Zhang *et al.*, 2012; Tiwari *et al.*, 2014; Wang *et al.*, 2018). It is therefore, important to put emphasis on particle diameter and number concentration for toxicological studies (Pakkanen *et al.*, 2001; McGee *et al.*, 2003; Kocbach *et al.*, 2005; Jalava *et al.*, 2006; Kocbach Bølling *et al.*, 2009). Information on particle diameter is essential in deposition modelling and can assist in studying particle intake, uptake and clearance (Nussbaumer *et al.*, 2001; Linak *et al.*, 2002; Kumar *et al.*, 2010). In the present study, an appropriate monitoring methodology is developed to study particle size distribution from coal burning brazier in order to provide additional information on particle number concentration ( $\#/cm^2$ ) to existing data on mass concentration ( $\mu g/m^3$ ).

The correct identification and chemical characterization of domestic coal burning particles is essential not only for health studies but can be used for speciation, source apportionment and use in atmospheric modelling studies (Y. Liu *et al.*, 2008; Cai *et al.*, 2010). Moreover, it is essential to have additional studies on this subject to understand emissions characteristics from this sources (Kocbach *et al.*, 2006; Xu *et al.*, 2011). Furthermore, lack of physicochemical data from residential coal burning emissions often complicates results interpretation during toxicological studies (Monn and Becker, 1999; Becker, Soukup and Gallagher, 2002; Bølling *et al.*, 2012).

Low temperature combustion has been associated with high emissions of volatiles organic compounds which present an important class of pollutants due their inherent associated health effects (Bruce, Perez-Padilla and Albalak, 2002; Bruinen De Bruin *et al.*, 2008). VOCs at low concentration causes eye irritation, nausea, asthma attacks, fatigue and mental confusion (Crump, 1996; Paxton, 1996; Durmusoglu, Taspinar and Karademir, 2010). From the list of hazardous VOCs, the mono-aromatic volatile organic compounds (benzene, toluene, ethylbenzene, and xylenes- BTEX) are singled out as the most harmful especially is exposure is chronic even at low concentration (Dutta *et al.*, 2009; IARC, 2012; Edokpolo, Yu and Connell, 2014). Efforts to regulate exposure to BTEX globally, is based on risk assessment as tool to determine the relative associated risk and develop plans to reduce the effects (Gariazzo *et al.*, 2005; Katsoyiannis *et al.*, 2012). Currently, there is no standard in South Africa to regulate BTEX exposure of BTEX emitted from coal burning technologies and no risk assessment has been carried out before to determine the relative risk from this source. The study seeks to fill this knowledge gap by carrying out a risk assessment of exposure to BTEX concentration from residential coal in a brazier.

Since several epidemiological studies has associated exposure to fine particulate matter from residential wood and coal burning, there is a need to use other methodologies to qualify this claim (Boman *et al.*, 2003; Naeher *et al.*, 2007; Forouzanfar *et al.*, 2015). Information from epidemiological studies often lacks exposure assessment data or the data is not accurate (Pope *et al.*, 2004; Kocbach *et al.*, 2008; Bølling *et al.*, 2012). Other studies suggest that despite increasing literature from epidemiological studies there is still a paucity of information on the mechanism as to how the diseases develop (Kauppinen and Pakkanen, 1990; Jalava *et al.*, 2010). This knowledge gap lead to interest in determining mechanisms to investigate the toxicity of combustion particles. Several *in vitro* and *in vivo* studies carried elsewhere found that exposure to combustion particles lead to several toxicity including reduced cell viability, inflammatory response and oxidative stress (Andreoli, 1997; Sioutas, Delfino and Singh, 2005; Cantone *et al.*, 2011; Hobson and Guy, 2014). Nevertheless, the current



available data is not yet sufficient to understand this concept better (Smith *et al.*, 2009, 2014). In South Africa no toxicological data on this subject. Therefore, the study will carry-out an exposure assessment using particles collected from different combustion phases and assess the toxicological effects.

#### 1.2.1 Aim

The study aims to carry out a systematic investigation of gaseous and fine particle formation and size distribution at various phases of combustion (i.e. ignition, pyrolysis, coking/ char-burning phase) on solid fuel technologies. The study will investigate the physical and chemical characteristics of fine and ultra-fine particles emitted from small-scale fixed-bed coal combustion technologies. A hazard assessment of exposure to physicochemical properties of particles emitted from low to high-temperature combustion stages will be conducted using *in vitro* experiments.

#### 1.2.2 Hypothesis

It is hypothesized that the formation of xenobiotic emissions from domestic coal burning (affected by method of ignition, ventilation rate and fuel properties) lead to carcinogenic health risk.

#### 1.2.3 Objectives

In order to achieve the above aims the following objectives were set out:

- a. to determine the emission factors of field and laboratory designed domestic coal-burning;
- b. to investigate the effect of coal properties on the emissions of gaseous and particulate matter;
- c. to determine particle size distribution at three combustion phases (ignition, flaming and coking);
- d. to carry-out risk assessment of benzene, toluene, ethylbenzene, and xylenes emissions from residential coal burning using a brazier;
- e. to investigate the morphology and elemental composition of freshly emitted particles from packed-bed domestic coal combustion;
- f. to conduct toxicity and cellular uptake assays of residential coal combustion particles on the bronchial epithelial cells.

### 1.3 Relevance of Study

This study is relevant in that it builds on the work of Makonese (2015) regarding emissions from fixed-bed coal combustion technologies used in the domestic sector. Unlike the work of Makonese (2015), which focussed on developing emissions factors for dispersion modelling, this work extends the study to evaluating the particle size distribution of the particles at different combustion phases, determining the cancer risks of users of the fuel/stove combination, determination of the physicochemical properties of coal combustion emissions and carrying out the toxicity of the





particles on epithelial cells. Since inhalation is a major exposure pathway into the human system, particle size distribution is essential to predict particle deposition and translocation (Oberdörster, 2001; Oberdörster *et al.*, 2004). Moreover, the study on particle composition is instrumental in evaluating the toxicity of xenobiotic particles and can be used in longitudinal epidemiological studies (Sioutas, Delfino and Singh, 2005; Jalava *et al.*, 2006; Cantone *et al.*, 2011). Information from this study is useful for assessing the health effects of continued uses of coal even in a well air ventilated brazier using the government advocated top-lit updraft (TLUD) method (Masekamani *et al.*, 2018). Information on the toxicity of coal smoke particles and risk assessment of BTEX emitted from fixed-bed coal combustion systems is useful for the health sector and needed for intervention strategy development purposes (Winkler, 2007).

This study seeks to provide the first comprehensive study on Nano toxicology involving residential coal combustion technologies in South Africa. The information will be useful for policy formulation and in enhancing local and indoor air quality. Furthermore, this study will contribute to understanding particle formation, PSD and morphology arising from packed bed domestic coal combustion phases and how cells react to the toxicity of particulate matter (PM)- Information on the physicochemical characteristics of particles is useful for health risk assessments and needed for epidemiological disease correlation studies and partly for identifying the sources.

#### 1.4 Scope of the Study

The scope of the study is limited to investigate the emission factors from coal burning braziers, the effects of fuel properties on emissions of gaseous and particulate matter, size distribution of smoke particles, physicochemical properties of smoke particles, risk assessment of BTEX emissions during residential coal burning scenario and particle cytotoxicity and cellular uptake assays.

Toxicity of soot particles was carried out through in *vitro* laboratory exposure methods. We did not attempt to use in *vivo* studies in our work. The information generated through this method is important and can be used during longitudinal epidemiological studies. This information is the first compressive study in South African context and can be used globally were similar exposures exists such as China, Mongolia, Sierra Leone and India.

During laboratory systematic investigation on the emission factor and factors influencing the emissions, the following parameters were kept constant: coal type (D-grade bituminous coal), coal moisture content (3%) and coal particle size. We used varied ignition method (TLUD and BLUD), stove ventilation type (low, medium and high), hole type and size (since there is no standardised brazier in South African context), stove grate height and stove height. The remainder of the studies as outlined in objective 3-7 only a high ventilated stove and the TLUD ignition method were used. The use of high ventilated stove and the TLUD ignition method was found to produce optimum performance on emissions reduction (Le Roux, Zunckel and McCormick, 2009). Since, it is envisaged that in South African coal burning settlement the high ventilated stove and TLUD ignition method will be the most used combination, this study set to investigate potential risk from this combination (Sole and Wagner, 2018). Some, studies were carried out in a laboratory environment mimicking



field practices (Masekameni *et al.*, 2018). The notion of mimicking field practices was mainly to ensure that the study findings try to imitate what is actually in practice.

The study is limited to coal burning braziers because these types of devices are widely used in South African context. Although there are other coal-burning devices, which can produce different emission profiles, their distribution is limited to a few households. Therefore, they are excluded from this systematic investigation. In studying the toxicity of combustion particles, we limited our research to *in vitro*, because the technique was available, reliable, less time consuming and cost effective. However, it is acknowledged that replication of similar study using *in vivo* method is useful for future studies.

### 1.5 Limitations of the study

We do acknowledge that in South African low-income settlement there are other essential energy fuels, which are used in combination with coal. However, the study is only limited to coal burning using braziers and ignited with TLUD and BLUD. The results obtained from this study are based on laboratory experiments. No attempt was made to collect field samples. Despite this being a laboratory-based study consideration was given to several field practices, features and characteristics. Factors such as stove type, fuel characteristics, user behavior, and the organization of fire were all adopted from the field.

### 1.6 Chapter Overview

The study comprises of 8 chapters with the first chapter and the eighth chapter focuses on the introduction and summary of the study, respectively. Chapters 2-7, provide details on the objectives, findings and are presented as publications. The structure of the thesis is as follows:

**Chapter 1:** Introduces lump-coal as a domestic fuel in South Africa and other developing countries worldwide. A problem statement is formulated, the domain of the study specified, aim and objectives set out. A justification of the study is presented and the general approach to the study is outlined.

**Chapter 2:** Presents results of emission factors of domestic coal-burning braziers. The study carried out a comprehensive and systematic survey of gaseous and particulate matter (PM) emissions from the combustion of commonly used D-grade coal in typical artisanal coal-burning braziers. The information provided in this article is useful for improving emission inventories for CO, CO<sub>2</sub>, NO<sub>x</sub> and PM from domestic coal combustion.

**Chapter 3:** Following uncertainties around emission factors due to ignition method and air ventilation rates, this chapter presents a detailed critique and analysis of the effect of coal properties on the performance of fixed-bed coal-burning braziers.

**Chapter 4:** The chapter critically examines the size distribution of ultrafine particles generated from residential fixed-bed coal combustion in a typical brazier. The present study focused on the submicron particles (11 nm–365 nm) and aim to assess the number size distribution of particles emitted from fixed-bed coal combustion in typical braziers using the top-lit updraft (TLUD) method.

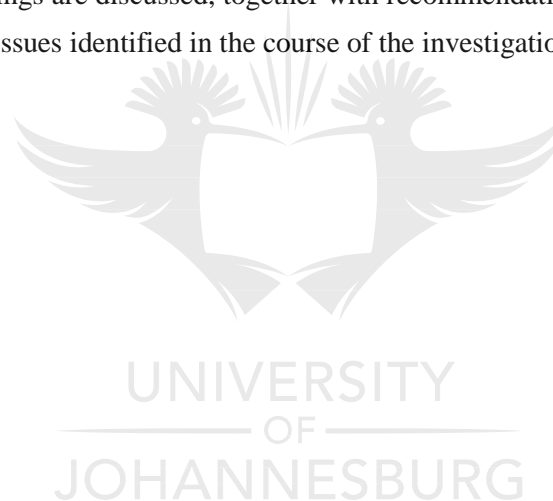


**Chapter 5:** Information on particle size distribution provided a need to deepen our understanding on the physicochemical properties of emitted particles. In this study we investigated the Physical and chemical properties of submicron particles emitted during residential small scale coal combustion.

**Chapter 6:** in this chapter we have defined a methodology for conducting risk assessment of BTEX concentration from combustion of coal in a laboratory environment, mimicking field practices. The main focus in this study was to assess the carcinogenic and non-carcinogenic effects of BTEX exposure due to emissions from coal burning in braziers.

**Chapter 7:** This chapter investigates the toxicity and cellular uptake of smoke particles generated from residential coal burning on bronchial epithelial cells. The study adopts *in vitro* methods to assess whether combustion emitted particles could lead to cell toxicity. The study further determines the contribution of exposure concentration or the combustion phase on the toxicity of particles

**Chapter 8:** This chapter provides a summary of the study main findings. A synthesis of the results is presented in a logical fashion to demonstrate the validity of the hypothesis. The originality and significance of the findings are discussed, together with recommendations for further investigations to address outstanding issues identified in the course of the investigations.





## CHAPTER TWO

*This chapter provides a systematic investigation of emission factor of three laboratory stoves and 3 field obtained stoves in a controlled laboratory environment. The chapter outline the effects of fire ignition method on the emissions of CO, CO<sub>2</sub>, NO<sub>x</sub>, PM<sub>10</sub> and PM<sub>2.5</sub>. Furthermore, the chapter provide information on the influence of the stove ventilation on the emission factor. Justifications on factors influencing emission factors are provided in this chapter for future replicates studies or the designing of future interventions.*

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## 2. Emission Factors of Domestic Coal-Burning Braziers

### 2.1 Abstract

This paper presents experimental results of emission factors from a suite of domestic coal-burning braziers (lab-fabricated and field-collected) that span the possible range of real-world uses in the Highveld region of South Africa. The conventional bottom-lit updraft (BLUD) method and the reduced smoke top-lit updraft (TLUD) method were evaluated using coal particle sizes between 20 mm and 40 mm. The emission factors of CO<sub>2</sub>, CO, and NO<sub>x</sub> ranged from 98–102 g MJ<sup>-1</sup>, 4.1–6.4 g MJ<sup>-1</sup>, and 75–195 mg MJ<sup>-1</sup>, respectively. Particulate matter (PM<sub>2.5</sub> and PM<sub>10</sub>) emissions were in the range 1.3–3.3 g MJ<sup>-1</sup> for the BLUD method, and 0.2–0.7 g MJ<sup>-1</sup> for the TLUD method, for both field and lab-designed stoves. When employing the TLUD method emission factors of PM<sub>2.5</sub>/PM<sub>10</sub> reduced by up to 80% compared to the business as usual BLUD method. Results showed the influence of ventilation rates on emission factors that reduced by ~50% from low to high ventilation rates. In the case of energy specific emission rates, the combined (3-hr) PM<sub>10</sub> emission rates were determined in the range 0.0028–0.0120 g s<sup>-1</sup> whilst the combined average CO emission rates were in the range 0.20–0.26 g s<sup>-1</sup> and the combined rates for CO<sub>2</sub> were in the range 0.54–0.64 g s<sup>-1</sup>. The reported emission factors from coal braziers provide the first comprehensive, systematic set of emission factors for this source category, and fill a major gap in the previous efforts to conduct dispersion modelling of South African Highveld air quality.

### 2.2 Introduction

Exposure to fine particulate matter (PM) from solid fuel combustion is associated with morbidity (Englert, 2004; Naeher *et al.*, 2007; Titcombe and Simcik, 2011) and mortality, (Bruce, Perez-Padilla and Albalak, 2000; Barnes *et al.*, 2009) especially in the developing world. About three billion people worldwide are exposed daily to harmful emissions from the combustion of solid fuels. Combustion of these fuels releases products of incomplete combustion such as carbon monoxide, particulate matter (PM) and volatile organic compounds. The WHO Global Health Observatory has reported



that household air pollution (HAP) caused premature deaths of ~4.3 people globally in 2012, while a further 3.7 million deaths were attributable to ambient air pollution (Gordon *et al.*, 2014; Forouzanfar *et al.*, 2015). HAP is associated with many health effects such as acute and chronic respiratory disorders, pulmonary and systemic diseases (Smith and Liu, 1994; Oberdörster, 2001; LaMorte, 2017).

Emission inventories for PM are critical in establishing how sources affect health and climate and therefore need to be continuously improved (Shen *et al.*, 2010). To date, emission factors (EF) from the literature are still adopted in the development of emission inventories. However, there is currently a lack of sufficient and reliable data, especially for emission factors (EFs) leading to uncertainties and bias in many emission inventories due to influences of a variety of parameters (Fernandez *et al.*, 2003; Shen *et al.*, 2010). For example, combustion technology and operational practice of appliances have a major influence on the physicochemical properties of the emitted particles (Tissari *et al.*, 2008; Bølling *et al.*, 2012; Makonese *et al.*, 2014; Uski, 2014). Emission factors reported in the literature often vary due to differences in the following parameters:

- fuel properties (e.g. moisture and volatile matter content),
- stove design,
- fire ignition methods (top-lit versus bottom-lit),
- fire management and ventilation (e.g. air supply amount and fuel-air mixing condition), and
- experimental methods (e.g. laboratory chamber, simulated stove/open burning, and field measurement (Shen *et al.*, 2010; Chen, Roden and Bond, 2012; Jetter *et al.*, 2012; Silva *et al.*, 2012).

In South Africa, particularly on the interior Highveld plateau, combustion of coal in informal braziers is among the largest sources of particulate matter (PM) and black carbon (BC) emissions. Coal is still used as a primary cooking and heating fuel for the majority of the population (Makonese *et al.*, 2015a). There are two ignition methods for lighting a coal fire, namely the traditional bottom-lit updraft (BLUD) method and the reduced smoke top-lit updraft (TLUD) method, locally known as the *Basa njengo Magogo (BnM)* method (SurrIDGE *et al.*, 2004; Le Roux, Zunckel and McCormick, 2009). The rapid electrification of households after 1990, now reaching over 95% of urban dwellings, did not result in the anticipated switch away from combustion of solid fuels for heating and cooking (Davis, 1998; Madubansi and Shackleton, 2006). As an interim method to reduce population exposure to domestic smoke emissions, the Department of Energy embarked on a public awareness campaign to encourage the dissemination and uptake of the *Basa njengo Magogo* method (TLUD) as a no-cost method of reducing smoke emissions (Leiman *et al.*, 2007; Makonese, 2011). The TLUD approach is a simple intervention in the manner domestic fires are lit, involving placing kindling at the top rather than at the bottom of the fuel load in a brazier or stove. In contrast, the traditional bottom-lit updraft (BLUD) method involves placing the kindling and igniting it at the bottom of the brazier or stove, with the bulk of the fuel placed on top of the burning kindling (Makonese *et al.*,



2015b; Sole and Wagner, 2018). This method is estimated to result in a 70–90% reduction in ambient particulate emissions and a 20% reduction in coal consumption at no additional cost to households (Le Roux, Zunckel and McCormick, 2009). For several years (from 2009 to 2014), the implementation of the *Basa njengo Magogo* rollout became a national priority energy intervention programme.

However, on examination, these reports showed limitations that could have profound implications on the reported emission factors. The studies did not carry out systematic evaluations of the braziers regarding fuel quality, ventilation rates, and fuel moisture content leading to substantial uncertainties in emission inventories as reported (Bhattacharya, Albina and Myint Khaing, 2002; An *et al.*, 2007; Le Roux, Zunckel and McCormick, 2009). To improve the understanding of emission characteristics and reduce emission factor estimation uncertainty, there is a need to determine the influences of fuel properties and combustion conditions on emissions from domestic coal-burning braziers (Shen *et al.*, 2010; Wei *et al.*, 2012). In 1997, the Atomic Energy Corporation of South Africa (AEC) characterised ten low-smoke fuels and one standard coal sample for physical, chemical and pollutant emission factors (Sole and Wagner, 2018). It was concluded that there are many different stoves and brazier designs in use in South Africa and that emission factors would be influenced by brazier designs. As such, it is likely that specific fuels would have altered emission profiles when combusted in different braziers.

This study aimed to carry out a comprehensive and systematic study of gaseous and particulate matter (PM) emissions from the combustion of commonly used D-grade coal in typical artisanal coal-burning braziers. The information provided in this article will be useful for improving emission inventories for CO, CO<sub>2</sub>, NO<sub>x</sub> and PM from domestic coal combustion.

## 2.3 Materials and methodology

### 2.3.1 Experimental stoves

Brazier stoves are made by hand out of metal drums with perforations of varying sizes punched around the sides, with a wire grate installed across the middle to support the fuel bed. There is no standard brazier design, as the devices vary widely regarding the number, size and distribution of the side holes (which affects ventilation rates), as well as the presence or absence of a grate and its position in the drum. Braziers are used widely in informal settlements and less affluent suburbs for heating and roadside cooking while burning wood, coal or even trash.

Three braziers (*imbaula*) procured from users in communities (referred to hereafter as field stoves) (Figure 1a–c) and three stoves designed and built at the SeTAR laboratory (hereafter referred to as lab stoves) (Figure 1d–f) were evaluated for emissions performance. The lab stoves had uniformly sized and spaced holes Figure 1. Hole densities were determined so that the total ventilation hole area approximated the artisanal field stoves, high, medium and low ventilation cases, respectively. Tests were carried out under laboratory-controlled conditions at the SeTAR Centre, University of Johannesburg, South Africa. Brazier stoves are hand-made out of metal drums with perforations of





varying sizes punched around the sides, and a wire grate installed across the middle of the container to hold the solid fuel. Although the stoves commonly have a fuel support grate made of wire or a perforated plate, some are operated without one. With a fire grate in place, the rate of burning is increased due to increased airflow through the fuel bed. There is no standard brazier design, as the devices vary widely regarding the number, size, and distribution of the side holes (i.e. affecting ventilation rates), as well as the presence or absence of a grate and its position in the metal drum. The stoves are used to burn wood, coal, or a combination of both, and often trash, which may include waste plastic.



**Figure 1: Photographs of experimental field procured braziers with (a) high ventilation, (b) medium ventilation and (c) low ventilation; and experimental lab-designed braziers with (d) high ventilation, (e) medium ventilation and (f) low ventilation.**

Three braziers (*imbaula*), part of a set of 11 procured from user communities (hereafter field stoves) (Figure 1a–c) and three stoves designed and built at the SeTAR laboratory at the University of Johannesburg (hereafter lab stoves) (Figure 1d–f) were evaluated for emissions performance. Tests were conducted under laboratory controlled conditions at the SeTAR Centre. The lab stoves had uniformly sized and spaced holes, designed so that the total ventilation hole area approximated the corresponding field stoves – high, medium and low ventilation cases, respectively. By the nature of the *imbaula* device, the irregular shape and packing density of coal pieces within a particular



combustion sequence does not allow for precise measurement or replication of air flow through the holes into the combustion zone. While the lab stove makes an attempt to replicate the ‘as found’ artisanal field stoves by reproducing the same ventilation hole area in a regularly spaced array of uniform size holes, complete congruency could not be established between the field and lab stoves.

### 2.3.2 Stove ventilation rates

Stove ventilation rates, as a function of air hole density, can affect the overall performance of a fuel/stove combination. Ventilation rates differ from one brazier model to another depending on the hole size, hole configuration (or pattern) and hole density. Ventilation rates need to be measured and specified to be able to evaluate and compare the performance of two or more braziers (Makonese *et al.*, 2014). The total hole areas, indicative of the ventilation rates of the braziers, for the field and lab stoves are given in Table 1. Lab stoves were fabricated by drilling 20-mm-diameter air holes on new, empty 20-L metal paint drums (H=360 mm, D=295 mm); different hole densities were employed for the high, medium and low ventilation cases, and holes were distributed above and below the grate. The grate was set at 120 mm from the base – a height typical of the prototype braziers collected from the informal settlement (Kimemia *et al.*, 2013). The hole sizes in the field stoves varied from 10 mm to 40 mm; a uniform hole diameter of 20 mm was used for the lab stoves.

### 2.3.3 Fire ignition method

The *BnM* fire ignition method is a local derivative of the TLUD procedure. The sequence for setting a TLUD fire is to place the major portion of the coal load on the fuel grate, and then place kindling (paper and wood chips) on top, ignite the kindling, and finally put a few coal nuggets on top of the burning kindling a few minutes after ignition. As such, about 2.0 kg of coal was added onto the fuel grate, followed by 0.4 kg of kindling (0.04 kg newspaper and 0.36 kg wood chips). After ignition, ~1.0 kg of coal is added on top of the burning kindling (Makonese *et al.*, 2014). For the BLUD, the sequence is reversed: ~1.0 kg of coal is placed onto the grate, followed by 0.4 kg of kindling. After ignition, ~2.0 kg of coal is added to the burning kindling. The BLUD method results in copious smoke emissions, as the fire is oxygen-starved during the initial stages of combustion (Makonese, 2011).

### 2.3.4 Fuel characterisation

The coal fuel used in the experiments was purchased from a local coal merchant and compared with coal sourced directly from a colliery in the Witbank Emalahleni coalfield. The initial field survey revealed that local merchants obtained a D-grade type coal fuel from Slater Coal Mine (Dundee, KwaZulu-Natal, South Africa). In light of the above, batches of D-grade coal, sufficient to conduct a range of comparative tests, were purchased from the coalfield. For each fuel batch, the fuel was first mixed for homogeneity and then three 2-kg samples were taken to an independent laboratory for analyses. Calorific value, proximate (moisture, ash, volatile organic compounds, fixed carbon) and ultimate (%C, %H, %S, %O<sub>2</sub> and mineral elements) analyses were performed (Table 2). The coal was crushed and sieved. The fraction passing through a 40- mm upper sieve and retained by a 20- mm lower sieve was used in all experiments to avoid variability from coal particle size – a variable





that was not investigated in this study. The fuel was then stored in moisture free containers. Immediately before commencing a series of combustion tests, a sample of the fuel was re-analysed for moisture content using an electric oven. The quantities of fuel used in the experiments are detailed in the section on the fire ignition method.

**Table 1:** Air hole areas of the experimental stoves

Stove Type	Air hole area above the grate (cm <sup>2</sup> )	Air hole area below the grate (cm <sup>2</sup> )	Total air hole area (cm <sup>2</sup> )
<b>Field Stoves</b>			
High ventilation	159	248	407
Medium ventilation	166	189	355
Low ventilation	91	63	154
<b>Lab Stoves</b>			
High ventilation	126	138	264
Medium ventilation	101	50	151
Low ventilation	63	38	101

**Table 2:** Fuel analysis data for the D-grade coal used in the experiments

Parameter (Air Dried Basis)	Standard Method	Slater Colliery D-Grade Coal
Moisture content (%)	ISO 5925	3.5
Volatiles (%)	ISO 562	20.3
Ash (%)	ISO 1171	24.2
Fixed carbon (%)	By difference	52.0
Calorific value (MJ kg <sup>-1</sup> )	ISO 1928	23.4
Calorific value (Kcal kg <sup>-1</sup> )	ISO 1928	5590
Total sulphur (%)	ASTM D4239	0.63
Carbon (%)	ASTM D5373	62.6
Hydrogen (%)	ASTM D5373	2.72
Nitrogen (%)	ASTM D5373	1.43
Oxygen (%)	By difference	4.96

## 2.4 Sampling procedure

### 2.4.1 Gas measurement techniques

In this study, the hood method was used for monitoring emissions from domestic coal-burning braziers (Ahuja *et al.*, 1987). Because the experimental braziers did not have a flue, the stoves were placed under a smoke collection hood attached to the SeTAR dilution system responsible for the ducting and dilution of the exhaust gas stream (Makonese *et al.*, 2014). When using an extraction fan, high extraction rates tend to influence the combustion characteristics of a stove (Bhattacharya, Albina and Myint Khaing, 2002). In light of this, an extractor fan was not used for drawing air through the hood and duct. An extractor fan may be useful in preventing flue gases escaping from the bottom of the hood (Bhattacharya, Albina and Abdul Salam, 2002). However, our system relies on the carbon mass balance method, which only requires a representative sample of the exhaust gases to quantify the emissions and not the total capture of all combustion products. An advantage of the hood method is that it can be employed for the simultaneous determination of thermal and emission



parameters in a standard and systematic manner (Zhang *et al.*, 1999). Figure 2 shows the experimental set-up.

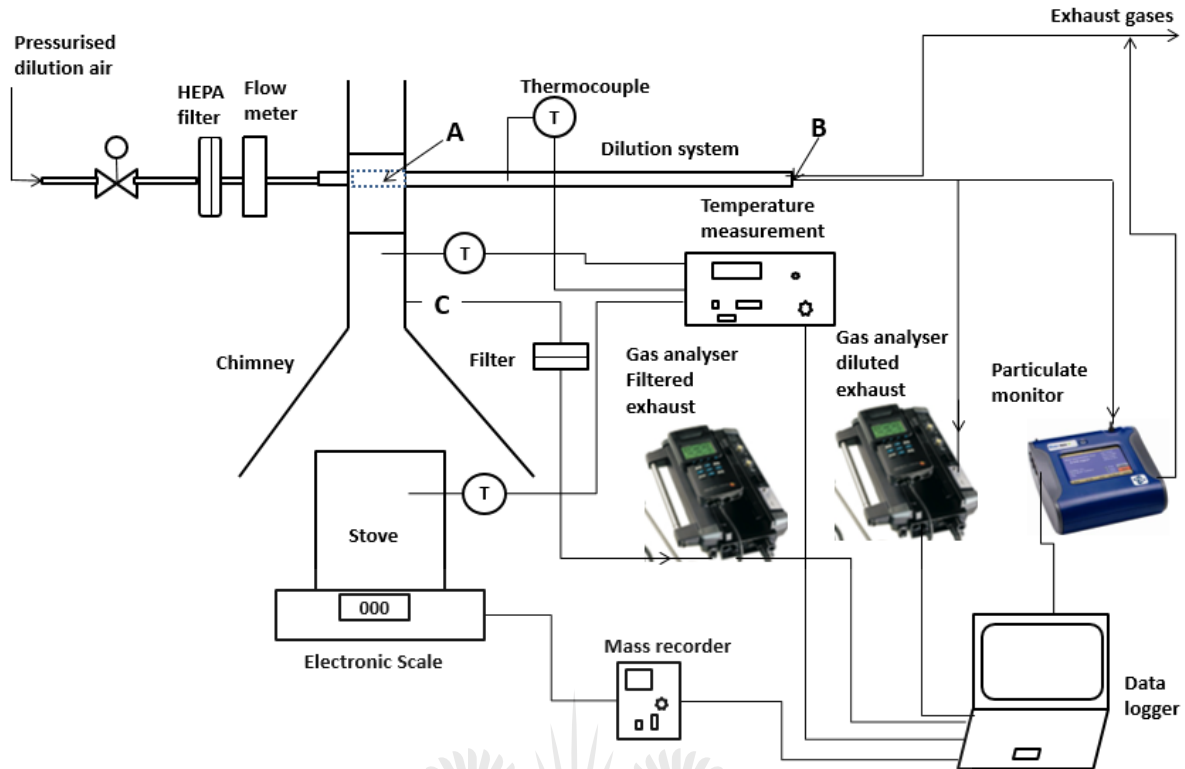
The measurement instruments (gas and particle analysers) used in this study cannot cope with the dense smoke emitted from braziers during the initial phases of combustion. This dense smoke saturates the analytical instruments, which results in underreporting of emission factors as a result of the concentrations exceeding the measurement range of the instruments, or causes the machines to clog with condensed organic deposits, resulting in erroneous readings. The SeTAR dilution system was designed with these consequences in mind. The dilution system is connected to the hood and the sampling nozzle is placed in the stack gas.

The inlet of the sampling nozzle is not equipped with a PM<sub>2.5</sub> fractionating cyclone, as the majority of the particles are condensation or Aitken particles below 1 µm in diameter. This sampling nozzle is followed by a mixing tunnel in which the hot exhaust is diluted with aerosol-free filtered air. The diluted exhaust then passes through a 0.9-m long ageing chamber (mixing chamber), and then through sampling ports for gaseous and particle emissions monitoring. The dilution level can be pre-set or changed by continuously varying the volume of dry air, depending on need. By recording diluted CO<sub>2</sub> and undiluted CO<sub>2</sub>, the dilution ratio can be calculated for each 10-s interval. As such, there is no need for flow monitoring or calibration of flow meters. The volume of dry CO<sub>2</sub>-free air supplied through the jet can be controlled by using a rotameter with a needle-valve flow controller.

The sampling configuration for the undiluted gas channel comprised Teflon tubing, a 4-µm pore diameter filter pack, and a flue gas analyser (Testo® 350XL/454) with cells for CO<sub>2</sub>, CO, NO<sub>x</sub> and O<sub>2</sub> (Masekamani, Makonese and Annegarn, 2015). For the diluted channel, the sampling configuration included the dilution system, a Teflon tube, and a flow splitter to duct gas streams to a DustTrak DRX 8533 aerosol monitor and a second Testo® analyser.

#### 2.4.2 Particle measurement techniques

The particle mass concentration is determined in the unfiltered, diluted air stream. The sampling configuration for PM included the SeTAR dilution system and the particulate monitor (DustTrak DRX 8533 aerosol monitor), connected by Teflon tubing (Figure 2). The DustTrak aerosol monitor is an optical particle counter that simultaneously measures size segregated mass fraction concentrations (PM<sub>1</sub>, PM<sub>2.5</sub>, PM<sub>4</sub>, PM<sub>10</sub> and total particle mass) in real time over a 0.001–150 mg/m<sup>3</sup> concentration range. The instrument is calibrated by the manufacturer, Raeco, annually. It is noted that the mass of the sub-micron fractions reported by optical particle counters may be overestimated in comparison with gravimetric methods (Wentzel *et al.*, 1999; Lipsky *et al.*, 2004). PM emission factors reported in this paper are based on the mass determined from the optical particle counter, and no post measurement correction factors have been applied to compensate for possible overestimations. While relevant for purposes of dispersion modelling, any discrepancies in the mass will not invalidate the comparisons made between ignition methods and ventilation rates.



**Figure 2: Schematic illustration of the SeTAR stove testing rig, showing the mixing point (A) where the exhaust is mixed with filter compressed air for dilution; and the sampling point (B) where the diluted exhaust is channelled to the monitoring instruments.**

## 2.5 Calculations

### 2.5.1 Gas emission factors

The measurement of emissions using the hood method was carried out on three field and three lab stoves that span the range of braziers used in the informal settlements of Gauteng Province. As in Bhattacharya et al. (2002), concentrations of CO, CO<sub>2</sub> and NO<sub>x</sub> were monitored, enabling calculation and estimation of emission factors for each pollutant. Emission factors presented in this study are calculated as in Bhattacharya et al. (2002), with slight modifications (methane and non-methane hydrocarbons are not reported herein), for energy-specific emission factors in units (g/MJ) of energy in the fuel. The lower heating value is used for calculations of thermal efficiency numbers and the determination of energy-specific emission factors. For each test, CO, CO<sub>2</sub> and NO<sub>x</sub> concentrations (ppmv) were recorded every 10 s for the duration of the burn sequence or the test experiment. Using the carbon mass balance method, CO and CO<sub>2</sub> emission factors were calculated using:

$$C_{\text{moles}} = (C_{\text{weight}} - C_{\text{ash}}) / M_{\text{carbon}} \quad \text{Equation 1}$$

where  $C_{\text{moles}}$  is the total moles of carbon burnt,  $C_{\text{mass}}$  is the mass of carbon in the fuel,  $C_{\text{ash}}$  is the mass of carbon in the ash and  $M_{\text{carbon}}$  is the molecular mass of carbon.

$C_{\text{moles}}$  in the flue gas can be determined by the following equation:

$$C_{\text{moles}} = \eta_{\text{CO}} + \eta_{\text{CO}_2} \quad \text{Equation 2}$$



where  $\eta_{CO}$  refers to the moles of carbon in CO in the flue exhaust, and  $\eta_{CO_2}$  to the moles of carbon in  $CO_2$  in the flue exhaust.

$$\eta_{CO_2} = (C_{moles})_{CO_2} (CO + CO_2)^{-1} \quad \text{Equation 3}$$

$$\eta_{CO} = (C_{moles})_{CO} (CO + CO_2)^{-1} \quad \text{Equation 4}$$

Mass specific emission factors for  $CO_2$  and CO in units [ $g\ kg^{-1}$ ] are given by:

$$CO_2EF = \eta_{CO_2} \times M_{CO_2} (\text{mass of fuel consumed})^{-1} \quad \text{Equation 5}$$

$$COEF = \eta_{CO} \times M_{CO} (\text{mass of fuel consumed})^{-1} \quad \text{Equation 6}$$

where  $M_{CO_2}$  and  $M_{CO}$  are the molecular weights of  $CO_2$  and CO, respectively.

Energy specific emission factors for  $CO_2$  and CO expressed in units  $g\ MJ^{-1}$  are given by:

$$CO_2EF = \eta_{CO_2} \times M_{CO_2} (\text{Net Heat Gained})^{-1} \quad \text{Equation 7}$$

$$COEF = \eta_{CO} \times M_{CO} (\text{NET Heat Gained})^{-1} \quad \text{Equation 8}$$

where the Net Heat gained HNET refers to the heat retained by a cooking vessel during the water heating experiments.

### 2.5.2 Excess air

Excess air (EA) was determined using the SeTAR data calculation sheet, which employs a chemically balanced approach ([www.setarstoves.org](http://www.setarstoves.org)). The determination of the total air demand ( $\lambda$ ) is given by the following equation:

$$\lambda = 1 + \frac{O_{2_{meas}} - O_{2_{oxid}}}{O_{2_{det}} - (O_{2_{meas}} - O_{2_{oxid}})} \quad \text{Equation 9}$$

where  $O_{2_{meas}}$  is the concentration of  $O_2$  measured in the exhaust;  $O_{2_{oxid}}$  is the amount of  $O_2$  required to oxidise completely unburned gases or products of incomplete combustion; and  $O_{2_{det}}$  is the total  $O_2$  in all detected gases.<sup>18</sup>



## 2.6 Particulate emission factors (energy specific)

Gaseous emission (ppmv) can be converted to other units including energy specific emission factors referenced to the energy content in the fuel consumed, [g MJ<sup>-1</sup>] or [mg MJ<sup>-1</sup>]. First, there is a need to determine Net Heat Gained (HNET) from the fuel, which is “the heat retained by a cooking vessel during a burn sequence and is expressed in units of mega joules [MJ]. It includes the heating of the pot and its contents plus the heat of evaporation of water, but excludes other heat flows through the pot, specifically radiative and convective losses from the pot sides and top” ([www.newdawnengineering.com](http://www.newdawnengineering.com)).

The mass of detected PM<sub>2.5</sub> or PM<sub>10</sub> is first multiplied by the dilution factor, and then multiplied by λ to obtain the actual mass emitted before dilution. ‘This approach is based on the foreknowledge that any missing fuel has been turned into combustion products of some type’.<sup>35</sup> This method can track and correctly determine the performance of the stove in real time while burning fuels in an inhomogeneous manner, as is often the case with biomass and coal fuels. The standard reporting metrics for the particle mass concentration include the mass of PM emitted per NET mega joule of energy delivered into the pot, or mass of PM emitted per NET mega joule of energy delivered from the fire.<sup>36</sup> For example, the mass of PM<sub>10</sub> in grams emitted during a burn sequence is determined and divided by the net heat gained HNET ([www.newdawnengineering.com](http://www.newdawnengineering.com)), yielding emissions per net mega joule [g MJ<sup>-1</sup> or mg MJ<sup>-1</sup>]. For example:

$$PM10_{EF} = \frac{PM10[g]}{H_{NET}[MJ]} \quad \text{Equation 10}$$

## 2.7 Emission rates

Emission rates (g/s) for PM and gaseous emissions were determined, averaged per hour for each hour of a maximum 3-h burn sequence, and also averaged over the first 3 h of the burn sequences.

### 2.7.1 Statistical analysis

An F-test was used to test whether different stove test results for the ignition method and ventilation rates had the same variance. Because the F-test is a relatively robust statistical tool, we used high alpha levels (0.05) and balanced layouts. The F-test result was then used to determine the best t-test analysis to use on the data (i.e. a two-sample t-test, assuming equal variances or a two-sample t-test, assuming unequal variances). A two-tailed Student t-test (at the 95% confidence level) was used for evaluating the thermal and emissions data between fire ignition methods and between ventilation rates. For this study, a statistically significant value was taken as a p-value less than 5% (p<0.05).



## Quality control

For each brazier model, a series of preliminary burn sequences was carried out to standardise procedures and to minimise the variability from differences in user/operator behaviour. After that, five definitive tests were conducted for each brazier model. After every test run, the gas probes and Teflon tube channels were cleaned, and the pumps and machines checked and zeroed. Continuous gas and particle monitoring instruments are routinely sent for calibration at intervals prescribed by the manufacturers, or at least once annually, and need to be periodically verified with laboratory standards.

Zero and span calibration were performed on all analysers before and after every test run to account for small variations in the dilution ratio. For example, the DustTrak DRX was zeroed with filtered air before each test run. Before conducting test experiments, the sampling dilution system components were disassembled, cleaned, air dried, assembled, and ‘tested for leaks to prevent contamination from the surrounding air’<sup>37</sup> to avoid contamination of the emissions with organic and metal compounds from previous burn sequences. High power compressed air and water were used to remove large particles from the sampling channels. The exhaust collection trains, involving stainless steel ducts, Teflon tubes, and sampling nozzles, were cleaned with soap and water and air dried with filtered compressed air.

The response time of monitoring instruments can be affected by the time the exhaust takes to travel from the inlet probe to the instrument and through the sensing volume within the instrument. The time lags were measured before and after a test. The system was first allowed to run on air for a few minutes to sample ambient air for purposes of obtaining background readings. Then an ignition torch was lit near the inlet of the sampling probe. After the ignition torch had been extinguished, the system sampled ambient air for a few more minutes to allow the instrument signals to return to background levels, after which the ignition torch was lit again. These time delays were noted and then corrected for in the spreadsheet when calculating pollutant emission factors for different fires.

## 2.8 Results and discussion

### 2.8.1 Gaseous emission factors

The general observations made during both fire ignition methods were as follows: For the BLUD method, when the kindling was lit the coal immediately began to give off sulphurous odours and dense whitish/yellowish smoke—a consequence of devolatilised organic matter that had not reached combustion temperature or had insufficient oxygen to oxidise fully. A few minutes elapsed before the coal could be considered ignited—taken as parts of the lowest lumps of coal glowing visibly red. However, the thick white smoke continued for up to thirty minutes as volatiles were evolved from the gradually heated coal above the rising combustion front. For the TLUD ignition method, there was considerably less smoke, with high flames above the coal bed resulting from ignition of the evolved devolatilised organic matter passing through the descending combustion front, with homogenous phase combustion continuing in the rising gas mixture above the coal bed.



### 2.8.2 Gas emission factors for lab-stoves using D-grade coal

Gas emission factors for the laboratory designed stoves, using D-grade coal, for top-lit and bottom-lit ignition methods are presented in Table 3, together with a statistical comparison of the differences. The emission factors are based on integration over the combustion sequence, from ignition until three hours had elapsed, or fuel burnout, whichever was the soonest.

**Table 3:** Gas emission factors for the lab-designed coal braziers using D-grade coal, for the TLUD and the BLUD ignition methods (n=5)

Pollutant	Ventilation rates	BLUD Method		TLUD Method		Statistical Analysis			
		Emission Factors [g MJ <sup>-1</sup> ]	Stdev [g MJ <sup>-1</sup> ]	Emission Factors [g MJ <sup>-1</sup> ]	Stdev [g MJ <sup>-1</sup> ]	% diff. between BLUD and TLUD	T-Stat	P-Value	Sig. @ 95%
CO	High	4.5	0.1	4.6	0.2	2%	-0.61	0.605	No
	Medium	6.2	0.3	5.0	0.4	-20%	3.3	0.081	No
	Low	6.4	0.5	5.7	0.2	-11%	2.1	0.173	No
CO <sub>2</sub>	High	98	6	99	2	-1%	0.36	0.753	No
	Medium	98	6	96	2	-2%	0.46	0.690	No
	Low	97	5	102	3	5%	-1.0	0.408	No
		[mg MJ <sup>-1</sup> ]	[mg MJ <sup>-1</sup> ]	[mg MJ <sup>-1</sup> ]	[mg MJ <sup>-1</sup> ]				
NO <sub>x</sub>	High	149	16	126	14	-16%	1.6	0.258	No
	Medium	118	11	99	6	-16%	2.2	0.164	No
	Low	87	5	75	5	-13%	2.5	0.126	No

When comparing the ignition methods, results show that there are no statistically significant differences ( $p > 0.05$ ) between CO, CO<sub>2</sub> and NO<sub>x</sub> emissions (Table 3), respectively, at any given stove ventilation rate, implying that the fire-ignition method may not affect the combustion characteristics of CO, CO<sub>2</sub> and NO<sub>x</sub> in the experimental devices tested. Results show that there are no statistically significant differences between NO<sub>x</sub> emissions when varying the ignition method, although there is an average 16% decrease in the emissions for the TLUD method. Our results for NO<sub>x</sub> are expected; as NO<sub>x</sub> emissions are a function of the combustion temperatures and the residence time of nitrogen at that temperature and are not influenced by the low temperature ignition conditions. Fuel NO<sub>x</sub> is formed mainly from nitrogen in the fuel. At high temperatures above 1200 °C and standard atmospheric pressure, molecules of nitrogen and oxygen in the combustion air disassociate into atoms that may participate in the *Zeldovich* mechanism to produce NO.

### 2.8.3 Gas emission factors for lab-stoves using D-grade coal

Gas emission factors for the field designed stoves, using D-grade coal, for TLUD and BLUD ignition methods are presented in Table 4.





**Table 4: Gas emission factors for the field- stoves using D-grade, for the TLUD and the BLUD ignition methods (n=5)**

Pollutant	Ventilation rates	BLUD Method		TLUD Method		Statistical Analysis			
		Emission Factors [g MJ <sup>-1</sup> ]	Stdev [g MJ <sup>-1</sup> ]	Emission Factors [g MJ <sup>-1</sup> ]	Stdev [g MJ <sup>-1</sup> ]	% diff. between BLUD and TLUD	T-Stat	P-Value	Sig @ 95 %
CO	High	4.1	0.3	4.0	0.2	-3%	1.0	0.568	No
	Medium	4.2	0.4	4.1	0.4	-4%	1.0	0.567	No
	Low	4.6	0.3	5.5	0.2	20%	-4.0	0.017	Yes
CO <sub>2</sub>	High	102	4	100	6	-2%	1.0	0.615	No
	Medium	102	5	99	3	-3%	1.0	0.489	No
	Low	98	6	101	5	2%	0.0	0.652	No
		[mg MJ <sup>-1</sup> ]	[mg MJ <sup>-1</sup> ]	[mg MJ <sup>-1</sup> ]	[mg MJ <sup>-1</sup> ]				
NO <sub>x</sub>	High	195	8	168	10	-14%	4.0	0.021	Yes
	Medium	188	10	163	4	-13%	4.0	0.015	Yes
	Low	187	11	161	9	-14%	3.0	0.036	Yes

Results presented in Table 4 show that there is no statistically significant difference in CO emissions between the TLUD method and the BLUD method at high and medium ventilation rates ( $p > 0.05$ ). However, there was a statistically significant difference in CO emissions between the fire-ignition methods at low ventilation rates (Table 4). At this ventilation rate, there is a 20% increase in CO when using the TLUD method. Lack of oxygen results in smouldering combustion conditions that favour the emission of products of incomplete combustion, including CO and PAHs. Further detailed explanations need to be sought to explain this anomaly.

## 2.9 Particle emission factors

### 2.9.1 PM emissions from lab-designed braziers with D-grade coal

Particle emission factors for the laboratory designed stoves, using D-grade coal, for TLUD and BLUD ignition methods are presented in Table 5, together with a statistical evaluation of the differences. The emission factors, expressed as particulate mass per MegaJoule of energy in the combusted fuel, are based on integration over the combustion sequence from ignition until three hours had elapsed, or fuel burnout, whichever was the soonest.



**Table 5: Particulate emission factors for the lab-designed coal braziers using D-grade coal for BLUD and TLUD ignition methods (n=5)**

Pollutant	Ventilation rates	BLUD Method		TLUD Method		Statistical Analysis			
		Emission Factors [g MJ <sup>-1</sup> ]	Stdev [g MJ <sup>-1</sup> ]	Emission Factors [g MJ <sup>-1</sup> ]	Stdev [g MJ <sup>-1</sup> ]	% diff. between BLUD and TLUD	T-Stat	P-Value	Sig @ 95%
PM <sub>2.5</sub>	High	1.3	0.1	0.3	0.02	-80%	22	0.002	Yes
	Medium	1.9	0.1	0.4	0.03	-76%	16	0.004	Yes
	Low	2.5	0.2	0.6	0.06	-76%	13	0.006	Yes
PM <sub>10</sub>	High	1.3	0.1	0.3	0.02	-80%	22	0.002	Yes
	Medium	1.9	0.1	0.4	0.03	-76%	16	0.004	Yes
	Low	2.5	0.2	0.6	0.06	-76%	13	0.006	Yes

Results show that PM<sub>2.5</sub> and PM<sub>10</sub> emissions are similar for any given ventilation rate for both the TLUD ignition method and the BLUD ignition method. From Table 5 it can be seen that PM<sub>2.5</sub> particles constitute more than 90% of PM<sub>10</sub> emissions. There are statistically significant differences (p<0.05) in particle emissions between the BLUD and TLUD methods, for all three ventilations rates. The TLUD approach reduces PM<sub>10</sub>/PM<sub>2.5</sub> emissions by 76% to 80% compared to the ‘business as usual’ BLUD method. This result is similar to assertions made by Le Roux<sup>26</sup> who found a reduction in particulate emissions of between 78% and 92% when using the TLUD ignition method.

### 2.9.2 PM emissions from field stoves with D-grade coal

Particle emission factors for the field procured stoves using D-grade coal, for top- and bottom ignition methods are presented in Table 6, together with a statistical comparison of the differences. The emission factors are based on integration over the combustion sequence, from ignition until three hours had elapsed, or fuel burnout, whichever was the soonest.

**Table 6: Particle emission factors for the field-designed coal braziers using D-grade coal in both the BLUD and the TLUD fires (n=5)**

Pollutant	Ventilation rate	BLUD Method		TLUD Method		Statistical Analysis			
		Emission Factors [g MJ <sup>-1</sup> ]	Stdev [g MJ <sup>-1</sup> ]	Emission Factors [g MJ <sup>-1</sup> ]	Stdev [g MJ <sup>-1</sup> ]	% diff. between BLUD and TLUD	T-Stat	P-Value	Sig @ 95%
PM <sub>2.5</sub>	High	1.3	0.1	0.2	0.02	-81%	15	0.0001	Yes
	Medium	2.9	0.3	0.6	0.05	-78%	15	0.0001	Yes
	Low	3.3	0.2	0.7	0.06	-80%	23	0.0000	Yes
PM <sub>10</sub>	High	1.3	0.1	0.2	0.02	-81%	15	0.0001	Yes
	Medium	2.9	0.2	0.6	0.05	-78%	15	0.0001	Yes
	Low	3.3	0.2	0.7	0.06	-80%	23	0.0000	Yes



Results show that there are statistically significant differences ( $p < 0.05$ ) in  $PM_{2.5}$  and  $PM_{10}$  emission factors between the fire-ignition methods. Emissions of  $PM_{2.5}$  and  $PM_{10}$  from the TLUD ignition method are five-fold lower (80% reduction) than those from the BLUD method, across all ventilation rates. These results confirm results presented in Table 5 for the lab-designed stoves.

### 2.10 Influence of stove ventilation rates

The effect of ventilation rates on the emissions of CO, and  $CO_2$  are investigated. Three stoves with different ventilation rates were used for each ignition method, with moisture content and other parameters held constant. The results of these experiments for the lab-designed braziers are presented in Table 7.

When comparing the high and medium ventilation rates, results show that there is a significant difference ( $p < 0.05$ ) in CO emissions, but not for  $CO_2$  emissions. When comparing medium and low ventilation rates, there are no significant differences ( $p > 0.05$ ) between the respective emissions of CO and  $CO_2$ . When comparing the high and low ventilation rates, there are significant differences ( $p < 0.05$ ) in CO emissions, but not in  $CO_2$  emissions. This shows that ventilation rates of the tested devices influence CO emissions, but may not influence the combustion characteristics of  $CO_2$ .

**Table 7: Emission factors of CO and  $CO_2$  as a function of ventilation rates (n=5)**

Ignition Method	Ventilation Rate	CO				CO <sub>2</sub>			
		Emission Factors [g MJ <sup>-1</sup> ]	T-Stat	P-value	Sig @ 95%	Emission Factors [g MJ <sup>-1</sup> ]	T-Stat	P-value	Sig @ 95%
BLUD	High	4.5 ± 0.1	-6.6	0.0	Yes	98 ± 6	0.2	0.9	No
	Medium	6.2 ± 0.3				98 ± 6			
	Medium	6.2 ± 0.3	-0.5	0.7	No	98 ± 6	0.1	0.9	No
	Low	6.4 ± 0.5				97 ± 5			
TLUD	High	4.5 ± 0.1	-5.5	0.0	Yes	98 ± 6	0.4	0.7	No
	Low	6.4 ± 0.5				97 ± 5			
TLUD	High	4.6 ± 0.2	-1.1	0.4	No	99 ± 2	1.0	0.4	No
	Medium	5.0 ± 0.4				96 ± 2			
	Medium	5.0 ± 0.4	-2.3	0.2	No	96 ± 2	-2.1	0.2	No
	Low	5.7 ± 0.2				102 ± 3			
TLUD	High	4.6 ± 0.2	-5.6	0.0	Yes	99 ± 2	-1.2	0.4	No
	Low	5.7 ± 0.2				102 ± 3			

Table 8 shows emission factors of  $NO_x$  as a function of ventilation rates. Results show that there are statistically significant differences ( $p < 0.05$ ) in  $NO_x$  emission factors between high and low ventilation rates for the BLUD fires. For the TLUD fires, a statistically significant difference exists between medium and low ventilation rates, and between high and low ventilation rates.



**Table 8: Emission factors of NO<sub>x</sub> [mg MJ<sup>-1</sup>] as a function of ventilation rates (n=5)**

Ignition Method	Ventilation Rate	NO <sub>x</sub> Emission Factors [g MJ <sup>-1</sup> ]	T-Stat	P-value	Sig @ 95%
BLUD	High	149 ± 16	2.3	0.15	No
	Medium	118 ± 11			
	Medium	118 ± 11	3.6	0.068	No
	Low	87 ± 5			
	High	149 ± 16	-8.3	0.014	Yes
	Low	87 ± 5			
TLUD	High	126 ± 4	2.5	0.13	No
	Medium	99 ± 6			
	Medium	99 ± 6	4.4	0.048	Yes
	Low	75 ± 5			
	High	126 ± 4	4.8	0.040	Yes
	Low	75 ± 5			

The effect of ventilation rates on PM<sub>10</sub> emissions was investigated, using three stoves with different ventilation rates, each tested with BLUD and TLUD ignition methods, with moisture content and other parameters held constant. The results of these experiments for the lab-designed braziers are presented in Table 9.

**Table 9: PM<sub>10</sub> mission factors from D-grade coal in lab-designed braziers at different ventilation rates (Mean and Stdev) (n=5)**

Ignition Method	Ventilation Rate	PM <sub>10</sub> Emission Factors [g MJ <sup>-1</sup> ]	T-Stat	P-value	Sig @ 95%
BLUD	High	1.3 ± 0.1	-5	0.03	Yes
	Medium	1.9 ± 0.1			
	Medium	1.9 ± 0.1	-4	0.06	No
	Low	2.5 ± 0.2			
	High	1.3 ± 0.1	5	0.03	Yes
	Low	2.5 ± 0.2			
TLUD	High	0.3 ± 0.02	-6	0.02	Yes
	Medium	0.4 ± 0.03			
	Medium	0.4 ± 0.03	-4	0.07	No
	Low	0.6 ± 0.06			
	High	0.3 ± 0.02	-8	0.02	Yes
	Low	0.6 ± 0.06			

When comparing the high and medium ventilation rates, results show that there are statistically significant differences ( $p < 0.05$ ) in PM<sub>10</sub> emissions for both ignition methods. However, there are no statistically significant differences ( $p > 0.05$ ) in PM<sub>10</sub> EF between medium and low ventilation rates for either ignition method. For the high and low ventilation rates, results show that there is a significant difference ( $p < 0.05$ ) in PM<sub>10</sub> emissions for both ignition methods, implying that the ventilation rates affect the combustion characteristics of PM<sub>10</sub> in all the experimental braziers. For a given device, PM<sub>2.5</sub> and PM<sub>10</sub> emission factors reduce by 50% from low to high ventilation rates. This advantage is offset by a firepower too high (about 10 kW) for convenient cooking and by increased fuel consumption.

The trends are that the more air holes (increased airflow) there are in a brazier, the less the particulate emissions. An increase in ventilation rate from low to high resulted in a 50% reduction of particulate emissions. However, this improvement due to increased ventilation is not as significant as the



decrease due to the top-lit ignition. A well-ventilated brazier, when used in conjunction with the TLUD ignition method, has the potential to have the maximum reduction of PM emissions from coal fires in informal braziers.

### 2.11 Emission rates

The emission rates of CO, CO<sub>2</sub> and PM<sub>10</sub> for selected braziers with three different ventilation rates, using D-grade coal, were calculated from measurements using the TLUD and BLUD ignition methods. Knowing the burn rate of the fuel (mass loss) and concentrations of the exhaust components, we determined the exhaust emission rates during the operation of the braziers, per hour of operation (Table 10) and for the full three-hour combustion sequence (Table 11). The emission rates are expressed in units [g s<sup>-1</sup>], as required by dispersion model input specifications. Averages of three tests are given together with the standard deviation. Highest particulate emission rates occur in the first hour of combustion (ignition and pyrolysis phases) compared to the second and third hours, associated with condensed semi-volatile compounds that are driven off from the kindling and during initial heating of the coal. Thereafter the particulate emission rates decrease considerably, reaching lowest levels during the last hour of the three-hour combustion sequence. In constructing realistic emission patterns of domestic combustion for dispersion modelling, the correct diurnal time evolution of emissions becomes an important factor in generating accurate dispersion predictions. Such hourly emission factors can be adapted to the lifestyle patterns of the modelled communities when conducting health risk assessments based on dispersion modelling and exposure assessments.

**Table 10: Hourly average emission rates [g s<sup>-1</sup>] during burn sequence (for dispersion modelling input) (n=5)**

Ignition	Stove	Ventilation rate	Hour	Energy [MJ h <sup>-1</sup> ]	Stdev [MJ]	CO <sub>2</sub> [g s <sup>-1</sup> ]	Stdev [g s <sup>-1</sup> ]	CO [g s <sup>-1</sup> ]	Stdev [g s <sup>-1</sup> ]	PM10 [g s <sup>-1</sup> ]	Stdev [g s <sup>-1</sup> ]
BLUD	Lab	Min	1	6.39	0.51	1.11	0.09	0.031	0.003	4.1E-02	5.1E-03
			2	2.27	0.18	0.36	0.03	0.010	0.001	1.5E-04	3.8E-05
			3	1.41	0.07	0.22	0.01	0.011	0.001	4.5E-07	2.6E-08
		Med	1	6.60	0.44	1.11	0.07	0.030	0.002	6.3E-02	6.1E-03
			2	2.27	0.17	0.38	0.03	0.020	0.002	1.4E-05	2.9E-06
			3	2.01	0.08	0.34	0.01	0.006	0.000	8.7E-07	3.6E-08
	Max	1	5.30	0.80	0.84	0.13	0.046	0.007	2.0E-02	2.4E-03	
		2	2.11	0.14	0.33	0.02	0.024	0.001	3.5E-04	5.6E-05	
		3	1.32	0.07	0.19	0.01	0.023	0.001	1.6E-05	8.8E-07	
	Field	Min	1	6.93	0.84	1.21	0.15	0.063	0.008	4.9E-02	5.9E-03
			2	2.27	0.11	0.38	0.02	0.010	0.001	5.5E-04	5.0E-05
			3	1.41	0.09	0.22	0.01	0.006	0.000	2.6E-05	1.4E-06
Med		1	7.00	0.70	1.34	0.13	0.043	0.007	3.4E-02	5.6E-03	
		2	2.43	0.15	0.34	0.02	0.012	0.001	1.4E-05	1.1E-06	
		3	1.95	0.16	0.24	0.02	0.012	0.001	7.1E-05	7.0E-06	
Max	1	7.27	1.01	1.28	0.18	0.021	0.005	2.4E-02	4.1E-03		
	2	2.55	0.13	0.44	0.02	0.027	0.002	2.0E-05	1.1E-06		
	3	1.93	0.13	0.33	0.02	0.029	0.002	9.2E-05	1.6E-05		
TLUD	Lab	Min	1	8.60	0.79	1.46	0.15	0.055	0.007	1.3E-02	1.1E-03
			2	1.86	0.12	0.29	0.02	0.014	0.001	1.5E-05	1.6E-06



		3	1.18	0.06	0.18	0.01	0.013	0.001	9.9E-06	6.9E-07
	Med	1	3.82	0.92	0.67	0.16	0.036	0.008	7.9E-03	1.4E-03
		2	3.60	0.17	0.62	0.03	0.021	0.001	3.4E-03	2.2E-04
		3	3.48	0.20	0.60	0.03	0.027	0.002	2.0E-04	2.2E-05
	Max	1	6.90	1.49	0.62	0.24	0.009	0.002	2.3E-03	1.0E-03
		2	2.70	0.20	0.42	0.03	0.028	0.002	7.0E-07	3.8E-08
		3	1.42	0.09	0.20	0.01	0.030	0.002	9.9E-07	6.6E-08
	Min	1	6.60	1.18	1.13	0.20	0.030	0.009	1.4E-02	2.0E-03
		2	1.93	0.13	0.32	0.02	0.014	0.001	3.1E-05	3.6E-06
		3	1.20	0.07	0.19	0.01	0.015	0.001	9.2E-05	1.3E-05
Field	Med	1	5.62	0.73	0.92	0.12	0.030	0.003	8.6E-03	8.4E-04
		2	2.51	0.16	0.39	0.03	0.025	0.002	4.1E-04	5.9E-05
		3	1.48	0.13	0.21	0.02	0.026	0.002	3.4E-05	3.0E-06
	Max	1	4.35	0.66	0.76	0.12	0.023	0.003	2.1E-03	3.4E-04
		2	2.30	0.17	0.38	0.03	0.021	0.001	5.3E-05	8.1E-06
		3	1.37	0.09	0.20	0.01	0.023	0.002	6.1E-07	3.6E-08

Table 11 presents a summary of three-hour (full burn sequence) emission rates for lab-designed and field-obtained braziers for each ventilation rate using the BLUD and the TLUD fire ignition methods and the combined average emission rate over the three ventilation rates. There are no differences in the combined average CO<sub>2</sub> emission rates for the two ignition methods and between the lab and field stoves. The combined average CO<sub>2</sub> emission rates are determined in the range 0.54 – 0.64 g s<sup>-1</sup>. There are differences in the combined average CO emission rates between the stoves and the ignition methods. The combined average CO emission rates are determined in the range 0.20 – 0.26 g s<sup>-1</sup>. The combined average PM<sub>10</sub> emission rates are determined in the range 0.0028 – 0.012 g s<sup>-1</sup> (Table 11).

The data presented in Table 10 and Table 11 are useful for short-term modelling of pollutants where one-hour average emission rates are required inputs for standard dispersion models. Source data input requirements for air dispersion modelling include specific mass emission rates; physical stack measurements e.g. diameter, stack height, exit velocity and temperature of the exhaust gases, and dry and wet deposition settling parameters for PM. For domestic sources that are too numerous to model individually, emissions are treated as area sources, requiring a knowledge of the source density [number of homes/emission points per km<sup>2</sup>] and the emission rate per source [g s<sup>-1</sup>]. The source density can be derived from remote sensing images and GIS methods, or from census data. However, up to now there has been no systematic study to characterize emissions from a range of domestic coal stoves and braziers, including variability of stove design, fuel quality, and stage of the burn or user behaviour. Emission values presented in Table 10 and Table 11 may be used to construct better area source emission estimates than have been available up to now, in the absence of reliable emission factors of individual coal combustion devices, and the time variations of these emissions.

**Table 11: Average emission factors over a three-hour combustion sequence (n=5)**

Ignition	Stove	Ventilation rate	Energy [MJ] per 3-h	Stdev [MJ]	CO <sub>2</sub> [g s <sup>-1</sup> ]	Stdev [g s <sup>-1</sup> ]	CO [g s <sup>-1</sup> ]	Stdev [g s <sup>-1</sup> ]	PM <sub>10</sub> [g s <sup>-1</sup> ]	Stdev [g s <sup>-1</sup> ]
<b>BLUD</b>	Lab	Min	3.36	0.25	0.56	0.04	0.017	0.0015	1.4E-02	1.7E-03
		Med	3.63	0.23	0.61	0.04	0.019	0.0012	2.1E-02	2.0E-03



	Max	2.91	0.34	0.45	0.05	0.031	0.0032	6.8E-03	8.2E-04
	<b>Avg</b>	<b>3.30</b>	<b>0.27</b>	<b>0.54</b>	<b>0.05</b>	<b>0.022</b>	<b>0.0020</b>	<b>1.4E-02</b>	<b>1.5E-03</b>
Field	Min	3.54	0.35	0.60	0.06	0.026	0.0029	1.7E-02	2.0E-03
	Med	3.79	0.34	0.64	0.06	0.022	0.0029	1.1E-02	1.9E-03
	Max	3.92	0.42	0.69	0.07	0.026	0.0029	7.9E-03	1.4E-03
	<b>Avg</b>	<b>3.75</b>	<b>0.37</b>	<b>0.64</b>	<b>0.06</b>	<b>0.025</b>	<b>0.0029</b>	<b>1.2E-02</b>	<b>1.7E-03</b>
	Min	3.88	0.32	0.64	0.06	0.027	0.0027	4.2E-03	3.6E-04
Lab	Med	3.63	0.43	0.63	0.07	0.028	0.0037	3.8E-03	5.5E-04
	Max	3.67	0.59	0.41	0.09	0.022	0.0020	7.8E-04	3.4E-04
	<b>Avg</b>	<b>3.73</b>	<b>0.45</b>	<b>0.56</b>	<b>0.08</b>	<b>0.026</b>	<b>0.0028</b>	<b>2.9E-03</b>	<b>4.2E-04</b>
TLUD	Min	3.24	0.46	0.55	0.08	0.020	0.0037	4.7E-03	6.6E-04
	Med	3.20	0.34	0.51	0.06	0.027	0.0021	3.0E-03	3.0E-04
	Max	2.67	0.31	0.45	0.05	0.023	0.0019	7.2E-04	1.2E-04
	<b>Avg</b>	<b>3.04</b>	<b>0.37</b>	<b>0.50</b>	<b>0.06</b>	<b>0.023</b>	<b>0.0026</b>	<b>2.8E-03</b>	<b>3.6E-04</b>

## 2.12 Conclusions and implications

This study is the most comprehensive systematic study to date of emission factors from domestic coal braziers in South Africa. The insights gained on the controlling variables go a long way to understanding the divergent results from prior studies that did not take into account or control for all these variables. This study reports emission factors regarding emissions per net MJ of energy in the fuel, for use in rating and comparison of stoves. The experimentally determined emission rates, in units [ $\text{g s}^{-1}$ ], directly applicable in standard dispersion models, represent a considerable improvement in previously reported emission factors for coal stoves. These results have implications on stove designs, laying the groundwork for improvements in the design of existing coal braziers and development of novel low-emission combustion technologies, and understanding potential health impacts of condensed matter emissions.

Future improvements could explore additional factors including the monitoring of organic carbon emissions, which are not explored in our experiments, and have the potential to influence the accuracy in the estimations of CO and CO<sub>2</sub> emission factors. Additional factors include varying the size of ventilation holes and the partitioning of ventilation openings below the grate (primary air) and above the grate or above the fuel load (secondary air), and the mean particle size of the fuel. We kept the fuel median size and size distribution constant between 20–40 mm throughout the course of this study. There is a need to investigate further the effect of hole density pattern on ventilation rates by clustering primary air holes below the fuel grate and a limited number of secondary air holes above the level of the packed fuel bed. Results presented herein show that the performance of braziers could be improved by optimising the air supply through the packed fuel bed, and to the space above the fuel bed (secondary air). An increase in the ventilation rates allows for more stable combustion and higher combustion temperatures, which in turn could lead to improved heat transfer. Increased ventilation could be achieved by using forced draft as in some wood pellet and biomass burning gasifiers. However, this option is not viable on brazier stoves as this may require design alterations





to existing braziers, which is however not an option for artisanal produced stoves. The target market for these stoves remains the low-income (energy poor) households situated in the Highveld region of South Africa.

In conclusion, particulate matter and trace gas emissions from coal braziers could be optimised by modifying the ignition procedure, the design of the braziers regarding hole distribution and diameter, and the position of the grate in the brazier. Condensed matter particulate (smoke) emissions can be reduced by allowing for thorough mixing of the volatile gasses from the fuel bed and the air supply, and by allowing a long residence time in the high-temperature zone. Thus, a brazier with high ventilation rates has a potential to reduce emissions of CO and PM. Future studies on the effect of ventilation rates on fixed-bed coal combustion systems should explore parameters such as the size of ventilation holes, the distribution pattern of the holes, and fuel size on particulate and trace gas emissions.





## CHAPTER THREE

*This chapter provides a comprehensive evaluation of the influence of fuel properties on the emissions of gases and particulate matter. The chapter provided methodology for assessing the effects of coal moisture content and fuel quality. The chapter is limited to coal burning technologies.*

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### 3. Influence of coal properties on the performance of fixed-bed coal burning braziers

#### 3.1 Abstract

Informal fixed-bed coal-burning braziers are used extensively in low-income communities of South Africa, for space heating and cooking needs. An investigation was carried out on the effects of coal moisture content and coal quality on the thermal and emissions performance of domestic coal-burning braziers in three field-procured braziers (with three different air ventilation rates), using the bottom-lit updraft (BLUD) and top-lit updraft (TLUD) ignition methods. Results showed that an increase in coal moisture content (from 2.4 wt.% to 8.6 wt.%) led to an 18 and 30% decrease in fire-power when using the TLUD and BLUD methods, respectively. The combustion efficiency increased by 25% with an increase in moisture content. Measured carbon monoxide (CO) emission factors (EF) increased with an increase in moisture content, while carbon dioxide (CO<sub>2</sub>) EF remained unchanged. The use of A-grade coal resulted in 49% increase in PM emissions compared with D-grade coal at high ventilation rates, despite no statistically significant differences ( $p > 0.05$ ) in CO and CO<sub>2</sub> EF produced between coal grades.

**Keywords:** combustion efficiency, emission factors, ignition methods, *imbaula*, moisture content

#### 3.2 Introduction

Coal still plays a major role in the energy mix in South Africa for the majority of low-income households on the Highveld plateau. It is envisaged that these communities will continue to rely on coal to meet their basic energy needs despite growing concerns over increased electricity tariffs. The fuel is burned in self-fabricated and inefficient metal braziers colloquially known as *imbaulas* (Makonese *et al.*, 2014). The stoves can burn wood, coal, or a combination of both, and often rubbish, which can include waste plastic. Small-scale coal combustion stoves and braziers are known to degrade air quality (Mathee, 2004; Scorgie *et al.*, 2003; Engelbrecht *et al.*, 2002) and are thermally inefficient (Masekameni, Makonese and Annegarn, 2014). High prices of alternative fuels and similar corresponding technologies and their unavailability in many parts of the country make rapid transitions and shifts away from traditional fuels and devices unlikely (Bhattacharya, Albina and Abdul Salam, 2002). Balmer (2007), contended that the low cost of coal fuel makes it attractive for



low-income households. Coal combustion in *imbaulas*, similar to other forms of energy such as electricity offers dual services to the user, space heating, and cooking. Coal fuel and coal braziers' applications will, therefore, potentially continue to meet the energy needs of the majority of poor households. The government and the private sector made concerted efforts to address air quality issues with respect to continued use of coal braziers in the Townships (Scorgie, 2012). Realising that rapid electrification does not result in an automatic and complete switch to cleaner fuels (Davis, 1998; Madubansi and Shackleton, 2006), the government encouraged the dissemination and uptake of a domestic coal ignition method known as the *Basa njengo Magogo* (a top-lit updraft method, hereafter referred to as TLUD). In 2003 the then Department of Minerals and Energy piloted the *Basa njengo Magogo* (TLUD) method in Orange farm as an alternative to the conventional (bottom-lit updraft, hereafter referred to as BLUD) method of lighting a coal fire in an *imbaula* (Le Roux, Zunckel and McCormick, 2009). The TLUD method is regarded as a no-cost way of reducing smoke emissions as there are no modifications needed on the combustion device except the manner in which the fire is started (Leiman *et al.*, 2007; Le Roux, Zunckel and McCormick, 2009; Makonese, 2011). The *Basa njengo Magogo* method is estimated to result in an 80% reduction in ambient particulate air pollution and a 20% reduction in coal use at no additional cost to the households (Le Roux, Zunckel and McCormick, 2009; Lim *et al.*, 2012; Rogalsky DK, Mendola P, Metts TA, 2014). There is a need to understand how the operation of the stove and fuel properties influence its performance in terms of emissions and thermal performance in addition to improvements in the ignition method. There is, up until now, a lack of information in the open literature on such evaluations in small-scale domestic fixed-bed coal stoves.

This investigation was particularly about the effects of coal moisture content and coal quality on fixed-bed coal braziers. Carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), particulate matter (PM<sub>2.5</sub> and PM<sub>10</sub>) were selected as indicator pollutants because of their prominence in health and environmental studies, as well as air quality dispersion modeling (Penney *et al.*, 2010; Makonese, Masekamani and Annegarn, 2017).

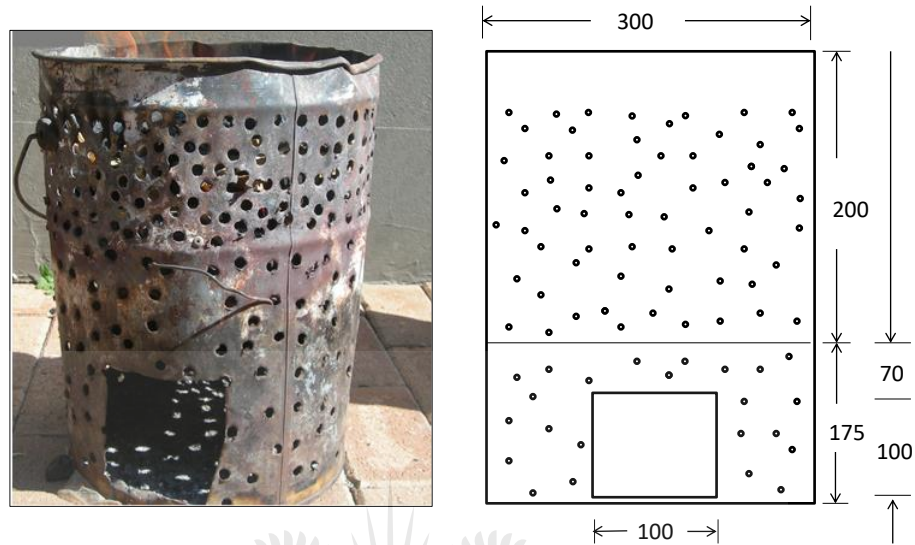
### 3.3 Material and method

#### 3.3.1 Experimental stoves and fuel analysis

Coal is a heterogeneous fuel, and the complex nature of the fuel makes it difficult to interpret results from laboratory experiments. A more homogenous coal sample would make it easier to identify the effects of coal properties on emissions and thermal performance (Jasinge, Ranjith and Choi, 2011). Three braziers procured from users in communities (referred to hereafter as field stoves) were tested for thermal performance, emissions of gases and particles. Tests were conducted under laboratory conditions at the Sustainable Energy Technology & Research Centre (SeTAR) at the University of Johannesburg. The brazier stoves or *imbaulas* are found in three normal sizes, determined by three commonly available metal drums: 20 L metal paint drums for domestic use; 70-litre metal dustbins, or sectioned 200 L oil drums for commercial purposes and typically used in street-side food vendors. Figure 3 shows a photograph and schematic diagram of a high ventilation brazier used in the



experiments. Stove ventilation rates were estimated from the number, size, and density of air holes below and above the fire grate. The devices were categorised into high, medium and low ventilation rates, depending on the total air hole area. Quantitative results of ventilation rates and other *imbaulas* used in this study are presented elsewhere (Makonese *et al.*, 2015a).



**Figure 3: A photographic and schematic representation of a high ventilation field procured optimized brazier stove used in the experiments (Not drawn to scale – dimensions are in mm).**

The braziers commonly have a fuel support grate, made of wire or a perforated plate. For example, the high ventilation brazier had a fire grate positioned about 175 mm and 200 mm from the base and the brim of the stove respectively. This fire grate increases the rate of burning. It should be noted that there is no standard *imbaula* as the devices vary widely with respect to the number and size distribution of side holes and the presence of a grate and its position in the metal drum (Kimemia *et al.*, 2011). The coal was purchased from local coal merchants and was compared with coal sourced directly from a colliery (Slater Coal Mine) in Witbank Emalahleni coalfield, South Africa. Two grades of coal fuel were consequently purchased (A-grade and D-grade) for the comparative tests, in quantities of approximately 100 kg. Because coal is a heterogeneous fuel, the coal in each batch was reasonably mixed on the floor with a shovel for homogeneity before 2 kg samples of each sample (with coal pieces in the range 40 mm < D < 60 mm) were taken to a commercial laboratory for analyses. The fuels were characterised for calorific value, proximate analysis (moisture, ash, volatile organic compounds, fixed carbon) and ultimate analysis (C, H, S, N, O and mineral elements) given in percentage weight, analysed on an air-dried basis (wt.%, adb). The coal was crushed and sieved to maintain a mean particle size diameter of 40 – 60 mm. Uniform coal size distribution was used for each fuel category to minimise errors inherent in the use of different coal sizes, especially coal being a heterogeneous material (Makonese *et al.*, 2017b). Each batch of fuel was analysed for moisture content before testing.



### 3.4 Moisture content determination

Each batch of coal was determined for moisture content (MC) before each test. The original A-grade and D-grade coals from Slater Coal Mine were stored in a moisture free environment for up to 30 days for conditioning prior to analysis. One batch of coal was stored in a container full of water, for the same duration, to increase the coal moisture content. The moist coal was then stored in a dry and moisture free environment for 48-hrs for the MC to equilibrate, assuming that the 48-hours duration is sufficient for the coal to achieve steady moisture equilibrium before combustion experiments were performed. Determining the moisture content in the coal, a small representative sample (~50 g) of the coal was weighed on a calibrated scale with a 0.1 g resolution and then dried in an oven at 100 °C for 24 hours. The sample was then taken out and re-weighed. Checking that the coal had attained dry mass, the exercise was repeated every 3 hours. Steady weight without further decrease confirmed that the coal had reached dry mass. The percentage moisture content was calculated on wet basis using Equation 11.

$$MC_{wet} = (MF_{wet} - MF_{dry} / MF_{wet}) \times 100 \quad \text{Equation 11}$$

where  $MF_{wet}$  is the mass of the wet coal and  $MF_{dry}$  is the mass of the dry coal.

### 3.5 Pot types and sizes

The pots used in this study are Hart™ aluminium 6 L capacity cooking vessels, commercially available and widely used for cooking in South Africa and regionally. Water heating experiments were carried out with 5 L for the large pots with lids from ambient temperature to the target temperature of 70 °C to prevent losses through evaporation. It is important to minimise or divert the steam from the combustion flow because it would complicate the analysis of the combustion gases. Excess water vapour has the potential to render the drier on the flue gas analyser less efficient (Makonese, 2011).

### 3.6 Fire-ignition methods

Experiments involved the TLUD method as the ignition method of choice. In the TLUD, the procedure of laying the fire was as follows: the major portion of the coal load was placed on the fire grate, followed by paper and wood kindling, with a few lumps of coal added at an appropriate time after the fire was lit. A 2 000 g of coal was added to the bottom of the brazier onto a fuel grate, followed by 36 g of paper and 360 g of kindling. After ignition of the kindling, 1 000 g of coal was added to the brazier above the kindling (Makonese *et al.*, 2014).

### 3.7 Efficiency calculations

Thermal efficiency ( $\eta$ ) of the stoves was determined, which is the ratio of work done by heating and evaporating water to the thermal energy that is generated by burning fuel, as expressed by Equation 12.



$$\eta = (C_p M_w (\Delta T) + M_e L_v) / (M_f (LHV_f) - M_c (LHV_c)) * 100 \quad \text{Equation 12}$$

where,

$M_w$  = mass of the water in the pot at the start of the test,

$C_p$  = specific heat capacity of water,

$\Delta T$  = rise in the water temperature

$M_e$  = mass of the evaporated water

$L_v$  = latent heat of vaporisation of water

$M_f$  = mass of the raw coal burned

$M_c$  = mass of the remaining char

$LHV_f$  = lower heating value of the coal

$LHV_c$  = lower heating value of the residual charcoal.

Equation 2 does not account for excess ash, which is formed in high ash containing fuels such as coal and could result in error in the evaluation of thermal performance of fuel/stove combinations (Makonese, 2011). Taylor (2009), contended that short combustion experiments with most woody biomass fuels do not pose a large source of error. When using animal waste and agricultural residues or performing long tests in stoves that are efficient in burning char, accounting for ash could, however, introduce a grave error. The ash may be accounted for by calculating the change in char mass ( $M_c$ ) as:

$$M_{c_{corrected}} = M_c - (M_f - M_c) A_{c_{fuel}} \quad \text{Equation 13}$$

where  $M_{c_{corrected}}$  is the mass of the charcoal corrected,  $M_c$  is the mass of the char,  $M_f$  is the mass of raw coal, and  $A_{c_{fuel}}$  is the ash content of the coal on a wet mass basis.

Efficiency can only be determined by separating the coal, char and ash, measuring the proportions of each, and then calculating the energy content of each. Although the method shown in Equation 13 is not recommended as a standard way of determining thermal efficiency, it has the advantage of addressing the influence of ash content in the material removed from a stove at the end of a test, thereby minimising error. There is a deduction for the mass of free ash that should be present in addition to the char. The energy accounting error (due to ash content) can be avoided and is a





significant result regarding test metrics since the error may significantly affect most other outputs of the test. As a result, thermal efficiency was calculated using Equation 14.

$$\eta = (C_p M_w \Delta T + M_e L_v) / (M_f (LHV_f) - M_{C_{corrected}} (LHV_C)) * 100 \quad \text{Equation 14}$$

The test procedure for determining the power settings used was adopted from Prasad *et al.* (1983), but with minor modifications. The burn rate can be regarded as comparable to fire-power (Bhattacharya *et al.*, 2002). The instantaneous power output of the stove is defined as the mass loss rate multiplied by the lower heating value of the coal, assuming complete combustion (i.e. products of incomplete combustion are minimal) according to Equation 15.

$$P = (LHV * \Delta m) / \Delta t \quad \text{Equation 15}$$

where  $P$  is the fire-power of the stove at a specified power setting;  $\Delta t$  is the time interval;  $\Delta m$  is the mass loss in a specified time interval; and  $LHV$  is the lower heating value of the coal.

### 3.8 Gaseous and particle matter emissions

The SeTAR dilution system, which incorporates the hood method, was used to evaluate emissions. As the experimental stoves did not have a flue gas collection system, the stoves were placed under a collection hood attached to the dilution system, which was responsible for the ducting and dilution of the exhaust gas stream. Since a high extraction rate may influence the combustion characteristics of the stove (Bhattacharya, Albina and Myint Khaing, 2002), an extractor fan was not used for drawing air through the hood and duct. The hood method could be employed simultaneously with that for the determination of thermal parameters. This has the added advantage of enabling simultaneous measurements of emissions and thermal parameters in a systematic and standard manner (Zhang *et al.*, 1999). Gaseous emissions were monitored using a Testo 350 XL flue gas analyser, while particle emissions were monitored using a DustTrak DRX 8533 aerosol monitor. The schematic of the SeTAR dilution system and experimental setup is presented in detail elsewhere (Makonese *et al.*, 2014, 2017b; Makonese, Masekameni and Annegarn, 2017). Gaseous emissions in parts per million volumes can be converted to other units, including energy specific emission factors (EF) in g/MJ, referenced to the energy content of the coal consumed. The net heat gained ( $H_{NET}$ ), in megajoules (MJ), can be determined easily. This is the heat retained by the pot during a burn sequence. It includes the energy needed to heat the pot and its contents plus the heat of evaporation of water but excludes other heat flows through the pot, specifically radiative and convective losses from the pot sides and top. The mass of detected gaseous emissions and particulate matter is first multiplied by any dilution factor applied to the equipment, then by the excess air ( $\lambda$ ) to obtain the total mass emitted. This approach is based on the foreknowledge that any missing coal was turned into combustion products of some type. This method can track and correctly determine the performance of the stove in real time while burning coal in a heterogeneous manner. For an example, the mass of carbon monoxide and particulate matter (CO and PM<sub>2.5</sub>) emitted during a burn cycle are



determined and divided by the net heat gained, yielding energy specific EF in g/MJ as shown in Equations 16 and 17.

$$CO_{EF} = CO(g) / H_{NET} (MJ) \quad \text{Equation 16}$$

$$PM_{2.5EF} = PM_{2.5} (g) / H_{NET} (MJ) \quad \text{Equation 17}$$

### 3.9 Results

#### 3.9.1 Comparative analysis of coal obtained from coal merchants and the colliery

The proximate and ultimate analyses of the result from coal used in the experiments, in wt.%, adb are presented in Table 12. Results show that the values for the same coal grade are comparable between the coal obtained from merchants and the colliery, indicating that the coal was representative of the same source. Experiments and experimental results presented herein are based solely on the A-grade, and D-grade coals obtained from the colliery, as over 100 kg of each coal grade was obtained from the colliery.

**Table 12. Proximate and ultimate analysis values for the coals (merchants and colliery) on air-dried basis.**

Parameter (air-dried basis)	Slater coal A-grade	Merchant coal A-grade	Slater coal D-grade	Merchant coal D-grade	Method of analysis
Proximate analysis results (wt.%, adb)					
Inherent moisture content (%)	3.8	3.6	3.5	3.7	SANS 5925
Volatiles (%)	25.4	26.3	20.3	19.8	ISO 562
Ash (%)	14.0	14.2	24.2	24.8	ISO 1171
Fixed carbon (%)	56.8	55.9	52.0	51.7	By difference
Ultimate analysis results (wt.%, adb)					
Total sulphur (%)	0.7	0.7	0.6	0.5	ASTM D4239
Carbon (%)	72.4	71.9	62.6	61.4	ASTM D5373
Hydrogen (%)	3.3	3.1	2.7	3.0	ASTM D5373
Nitrogen (%)	1.6	1.4	1.4	1.5	ASTM D5373
Oxygen (%)	4.4	4.0	5.0	4.6	By difference
Calorific value (MJ kg <sup>-1</sup> )	27.0	26.6	23.4	23.0	ISO 1928

#### 3.9.2 Influence of coal moisture content on emissions performance

Each batch of coal was determined for moisture content before each test. The moisture content was determined from the batches of coal as received from the field. Two distinct average moisture content values of 2.4 wt.% and 8.6 wt.% for two batches of coal were determined as in Section 3.7, equation



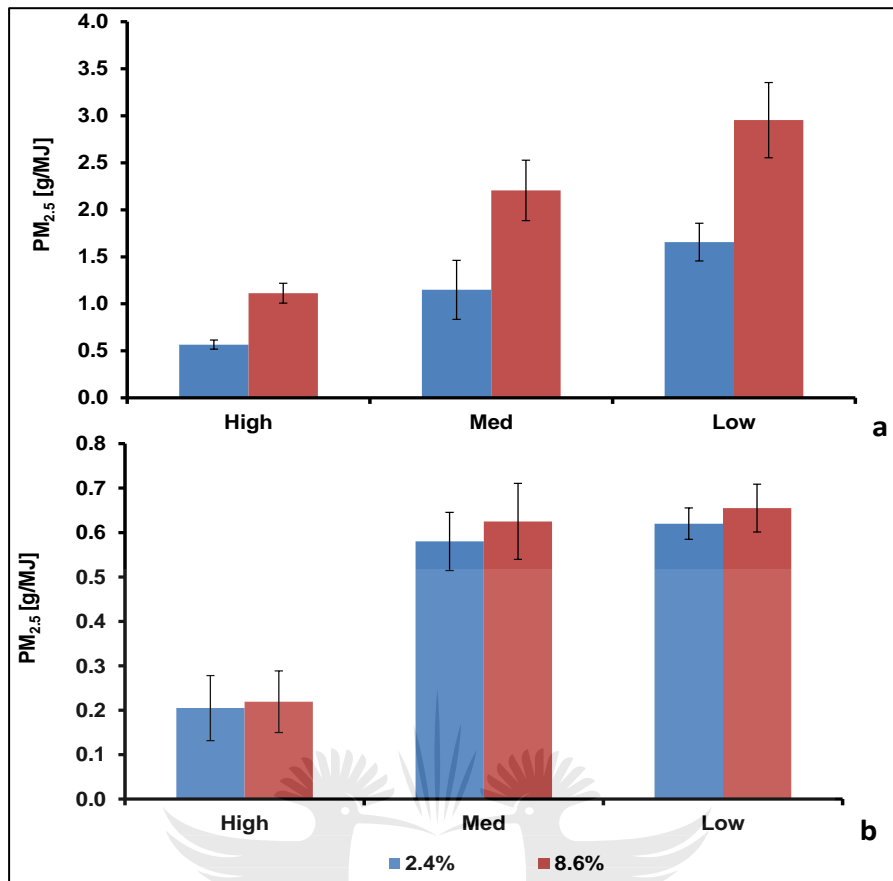
13. These values were used in the experiments to determine the influence of coal moisture level on the thermal and emissions performance of fixed-bed domestic coal-burning braziers. The emission factors of PM<sub>2.5</sub>, CO, CO<sub>2</sub> and the combustion efficiency, at different coal moisture content, are presented in Table 13. Results show that for both fire ignition methods, measured EF of PM<sub>2.5</sub> and CO increased with high coal moisture. The differences in emission factors between the moisture content levels were small but significant ( $p < 0.05$ ). The correlations were statistically significant, with the correlation coefficients of 0.97–0.99 ( $p < 0.05$ ).

**Table 13. Emission factors of stoves for different levels of moisture content of coal.**

Ignition method	MC (%)	Ventilation rates	PM <sub>2.5</sub> (g MJ <sup>-1</sup> )		CO (g MJ <sup>-1</sup> )		CO <sub>2</sub> (g MJ <sup>-1</sup> )		Combustion efficiency (%)	
			Mean	SD	Mean	SD	Mean	SD	Mean	SD
<b>BLUD</b>	2.4	High	0.6	0.05	4.5	0.3	101	7	4.4	0.4
		Medium	1.1	0.31	5.6	0.4	102	9	5.3	0.4
		Low	1.7	0.20	6.2	0.6	102	4	6.1	0.6
	8.6	High	1.1	0.11	4.5	1.3	103	7	4.5	0.6
		Medium	2.2	0.32	7.4	0.6	104	9	7.2	0.8
		Low	3.0	0.40	9.4	0.3	101	8	9.2	0.5
	2.4	High	0.2	0.02	4.1	0.3	104	4	4.0	0.6
		Medium	0.6	0.04	4.3	0.3	102	6	4.2	0.4
		Low	0.6	0.02	5.5	0.3	106	5	5.2	0.3
<b>TLUD</b>	8.6	High	0.2	0.02	6.2	2.3	101	7	6.1	0.5
		Medium	0.6	0.05	6.5	2.5	103	10	6.3	0.6
		Low	0.7	0.04	7.6	1.1	101	4	7.4	0.4

SD = standard deviation, PM<sub>2.5</sub> = particulate matter Ø 2.5 µm, CO = carbon monoxide, CO<sub>2</sub> = carbon dioxide, MC = moisture content, BLUD = bottom-lit updraft, TLUD = top-lit updraft.

Figure 4 shows the trend of PM<sub>2.5</sub> emission factors (g/MJ) as a function of different coal moisture content levels across three ventilation rates. Results indicate that, when employing the BLUD ignition technique, there was a marked increase of approximately two fold in PM<sub>2.5</sub> emission factors, with increased moisture content levels for all ventilation rates. In contrast, when employing the TLUD ignition technique, there was a slight increase in PM<sub>2.5</sub> emission factors with increased moisture content, with negligible differences at low ventilation rates.



**Figure 4: Particulate matter (PM<sub>2.5</sub>) emission factors with different coal moisture content levels across a range of ventilation rates, where (a) = bottom-lit updraft and (b) = top-lit updraft.**

### 3.10 Influence of coal moisture content on cooking efficiency and fire-power

The effect of moisture content was investigated on cooking efficiency and fire-power of the stoves with ventilation rates, ignition methods, and coal size held constant. These results are presented in Table 14 and show that, as the MC level increased from 2.4 wt.% to 8.6 wt.%, the cooking efficiency increased, while the fire-power decreased. Fire-power decreased by 18% from 8 kW (at 2.4 wt.% MC) to 6.5 kW (at 8.6 wt.% MC), and the cooking efficiency increased by 24% from 7.8% (at 2.4 wt.% MC) to 10.2% (at 8.6 wt.% MC), when employing the TLUD method in a high ventilation brazier. There was, generally, an average of 18% decrease in fire-power from 2.4 wt.% MC to 8.6 wt.% MC when using the TLUD method for all the ventilations. There was a 30% decrease in fire-power for the BLUD ignition, from 2.4 wt.% MC to 8.6 wt.% MC across the three ventilation rates (high, medium, and low). The cooking efficiency increased by an average of 25% across the three ventilations as the moisture content increased from 2.4 wt.% to 8.6 wt.%.

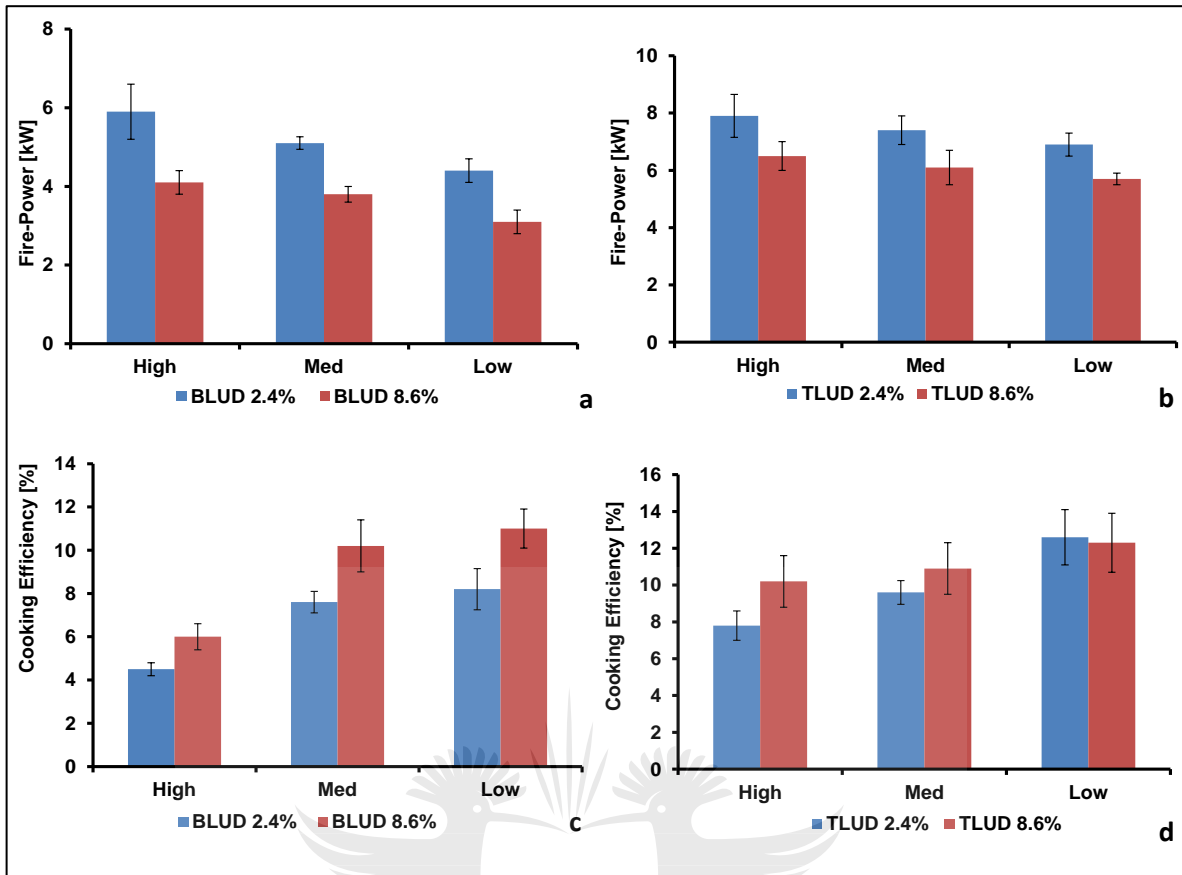


**Table 14: Comparison between top-lit updraft and bottom-lit updraft fire ignition methods with varying moisture content levels (mean  $\pm$  standard deviation) N = 3.**

Ventilation rate	Moisture content (%)	TLUD method				BLUD method			
		Fire-power (kW)		Cooking efficiency (%)		Fire power (kW)		Cooking efficiency (%)	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
<b>High</b>	2.4	7.9	0.8	7.8	0.8	5.9	0.8	4.5	0.3
	8.6	6.5	0.5	10.2	1.4	4.1	0.3	6.0	0.6
<b>Medium</b>	2.4	7.4	0.5	9.6	0.7	5.1	0.2	7.6	0.5
	8.6	6.1	0.6	10.9	1.4	3.8	0.2	10.24	1.4
<b>Low</b>	2.4	6.9	0.4	12.6	1.5	4.4	0.3	8.2	1.3
	8.6	5.7	0.2	12.3	1.6	3.1	0.3	11.0	1.2

TLUD = top-lit updraft, BLUD = bottom-lit updraft, SD = standard deviation

Figure 5 shows that when the moisture content increased fire-power decreased and cooking efficiency increased. This is because stove efficiency tends to decrease as more energy is lost to the surroundings rather than transferred to the pot. The coal in the combustion chamber was burnt gradually from the top-down (for the TLUD method) and from the bottom-up (for the BLUD method), and the existence of water in the coal slowed the combustion and reduced the temperature achieved in the combustion zone. This led to less fuel burned at any given moment resulting in reduced combustion intensity. This result is consistent with that of Mckendry (2002), which reported a reduction in combustion efficiency with an increase in moisture content.



**Figure 5: The trend of fire-power and cooking efficiency at different moisture contents across a range of ventilation rates.**

### 3.11 Influence of coal grade on emissions performance

Effect of coal type on gaseous emissions was investigated, and the results are presented in Table 15. Emissions from a grade D-grade coal were compared with emissions from a grade A-type coal, each with specifications in Section 3.9.1. Table 15 presents a comparative analysis of gaseous emission factors between D-grade and A-grade coal when employing the BLUD method. Results show that there was no statistically significant difference ( $p > 0.05$ ) in CO EF produced between coal grades at the medium and high ventilation rates. The use of the A-grade coal resulted in an 11% reduction in COEF at the medium ventilation rate, while at low ventilation rates CO EF increased by 12%. A statistically significant difference ( $p < 0.05$ ) in CO EF between coal grades at low ventilation rates was found when employing the BLUD method. This difference in CO emissions at different ventilation rates could be because of the higher volatile matter content of the A-grade coal, as shown in Table 12.

When comparing the two grades of coal across ventilation rates, results show that there was no statistically significant difference ( $p > 0.05$ ) in CO<sub>2</sub> emissions. However, the use of A-grade coal resulted in an average 4% decrease in CO<sub>2</sub> EF across the ventilation rates as shown in Table 15.



**Table 15: Comparative analysis of gaseous emission factors between D-grade and A-grade coals, for the BLUD method.**

Pollutant	Ventilation rates	BLUD method D-grade coal		BLUD method A-grade coal		Statistical Analysis			
		Emission Factors (g/MJ)	SD (g/MJ)	Emission Factors (g/MJ)	SD (g/MJ)	% diff. between D-grade & A-grade coal	T-Stat	P-Value	Sig @ 95% CI
CO	High	4.1	0.3	4.0	0.2	-1%	0.20	0.85	No
	Medium	4.2	0.4	3.8	0.3	-11%	1.68	0.17	No
	Low	4.6	0.3	5.2	0.2	12%	-2.82	0.05	No
CO <sub>2</sub>	High	102	4	98	6	-5%	1.07	0.34	No
	Medium	102	5	99	7	-3%	0.54	0.62	No
	Low	98	6	94	4	-4%	0.87	0.43	No

BLUD = bottom-lit updraft, SD = standard deviation, CO = carbon monoxide, CO<sub>2</sub> = carbon dioxide, CI = confidence interval

Table 16 compares gaseous emission factors between D-grade and A-grade coal when employing the TLUD method. Results show that gaseous pollutant emissions (CO and CO<sub>2</sub>) displayed a similar trend to BLUD fires (Table 15). The CO EF were significantly different ( $p < 0.05$ ) at high and low ventilation rates but not for the medium ventilation rate. There was, generally, a reduction in CO<sub>2</sub> EF when using A-grade coals compared to D-grade coals.

**Table 16: Comparative analysis of gaseous emission factors between D-grade and A-grade coals, for the TLUD method.**

Pollutant	Ventilation rate	TLUD Method D-grade coal		TLUD Method A-grade coal		Statistical Analysis			
		Emission Factors (g/MJ)	SD (g/MJ)	Emission Factors (g/MJ)	SD (g/MJ)	% diff. between D-grade & A-grade coal	T-Stat	P-Value	Sig @ 95% CI
CO	High	4.0	0.2	4.5	0.2	11%	-3.10	0.036	Yes
	Medium	4.1	0.4	4.0	0.1	-1%	0.19	0.862	No
	Low	5.5	0.2	6.1	0.3	10%	-2.95	0.042	Yes
CO <sub>2</sub>	High	100	6	97	6	-3%	0.58	0.595	No
	Medium	99	3	97	4	-2%	0.58	0.595	No
	Low	101	5	95	4	-5%	1.34	0.251	No

TLUD = top-lit updraft, SD = standard deviation, CO = carbon monoxide, CO<sub>2</sub> = carbon dioxide, CI = confidence interval.





The effect of coal quality (i.e. A-grade and D-grade coal) on PM emissions, when using the BLUD method (Table 17) and when employing the TLUD ignition method (Table 18) was analysed. Results show that for BLUD method there was a statistically significant difference ( $p < 0.05$ ) in  $PM_{2.5}$  and  $PM_{10}$  EF between fuel grades at high ventilation rates. There was, however, no significant difference ( $p > 0.05$ ) in  $PM_{2.5}$  and  $PM_{10}$  EF produced between the D-grade and A-grade coal at low and medium ventilation rates. The use of the A-grade coal resulted in a 49% increase in  $PM_{2.5}$  compared with D-grade coal at high ventilation rates (Table 17).

**Table 17: Comparative analysis of particle emission factors between D-grade and A-grade coals, for the BLUD method.**

Pollutant	Ventilation rates	BLUD Method D- grade coal		BLUD Method A-grade coal		Statistical Analysis			
		Emission Factors (g/MJ)	SD (g/MJ)	Emission Factors (g/MJ)	SD (g/MJ)	% diff. between D-grade & A-grade coal	T- Stat	P- Value	Sig @ 95% CI
<b>PM<sub>2.5</sub></b>	High	1.3	0.1	2.5	0.3	49%	-7.55	0.00	Yes
	Medium	2.9	0.3	3.3	0.2	12%	-2.28	0.08	No
	Low	3.3	0.2	3.6	0.2	8%	-1.75	0.15	No
<b>PM<sub>10</sub></b>	High	1.3	0.1	2.5	0.3	49%	-7.54	0.00	Yes
	Medium	2.9	0.2	3.3	0.2	12%	-2.27	0.09	No
	Low	3.3	0.2	3.6	0.2	8%	-1.73	0.16	No

BLUD = bottom-lit updraft, SD = standard deviation,  $PM_{2.5}$  = particulate matter Ø 2.5 µm,  $PM_{10}$  = particulate matter Ø 10 µm, CI = confidence interval.



**Table 18: Comparative analysis of particle emission factors between D-grade and A-grade coals, for the TLUD method**

Pollutant	Ventilation rates	TLUD Method D-grade coal		TLUD Method A-grade coal		Statistical Analysis			
		Emission Factors (g/MJ)	SD (g/MJ)	Emission Factors (g/MJ)	SD (g/MJ)	% diff. between D-grade & A-grade coal	T-Stat	P-Value	Sig @ 95% CI
PM <sub>2.5</sub>	High	0.24	0.02	0.36	0.02	33%	-7.10	0.00	Yes
	Medium	0.64	0.05	0.69	0.07	8%	-1.10	0.33	No
	Low	0.65	0.06	0.78	0.05	16%	-2.89	0.04	Yes
PM <sub>10</sub>	High	0.24	0.02	0.36	0.02	33%	-7.13	0.00	Yes
	Medium	0.64	0.05	0.69	0.07	7%	-1.09	0.34	No
	Low	0.65	0.06	0.78	0.05	16%	-2.89	0.04	Yes

**TLUD = top-lit updraft, SD = standard deviation, PM<sub>2.5</sub> = particulate matter Ø 2.5 µm, PM<sub>10</sub> = particulate matter Ø 10 µm, CI = confidence interval.**

Results in Table 18 shows that, for the TLUD method, the use of A-grade coal resulted in significant increases ( $p < 0.05$ ) in PM, 33% at high ventilation rates and 16% at low ventilation rates. At medium ventilation rates, the coal grade change did not give a significant change in PM emissions ( $p > 0.05$ ). (Zhang *et al.* (2008), reported that coals with low maturity have relatively high volatile contents, which is the precursor material for particulate matter during combustion. Therefore, emission factors of particulate matter from coal-burning braziers are expected to increase as the volatile matter content of the coal increases.

### 3.12 Discussion

The effect of moisture content on gaseous emissions is consistent with findings by Erdol (1999). The increase in CO emission factor appears to be due to lowering of gas phase reaction (oxidation) rates at reduced temperatures caused by higher moisture content (Kumar *et al.*, 2014). A positive correlation between MC in coal and CO emission factor was obtained, which was in contrast to findings in Huangfu *et al.* (2014) and Shen *et al.* (2013). Huangfu *et al.* (2014) and Shen *et al.* (2013) found that CO emission decreased with an increase in MC in the experiments with a TLUD wood stove at four moisture levels. The TLUD stove used in their investigations had secondary air supplied from the top channel ensuring mixing of burned gas with hot secondary air, which resulted in the reduction of CO emission El *et al.* (2013).

The emissions performance of the fuel/stove combination is reduced in situations where the coal is wet. Wet coal is, generally, hard to ignite and often, more starting kindling (wood and paper) is needed to get the fire going. Extra energy is required to vaporise water in the burning of high moisture



coal, resulting in reduced coal combustion efficiency and increased emissions caused by incomplete combustion (Rogge *et al.*, 1998; Pósfai *et al.*, 2003; Fine, Cass and Simoneit, 2004; Shen *et al.*, 2013). Erdol (1999), found that during combustion the surface-adsorbed superficial free water is removed most readily from the coal, while capillary condensed surface moisture and ‘absorbed’ moisture is more difficult to remove. High coal moisture content lowers the combustion and flame temperatures, leading to increased condensation of volatile matter in the post-flame region of the stove, resulting in elevated levels of PM emissions. The concentration of smoke particles tends to decrease rapidly during the pyrolysis phase of combustion when considering the entire combustion cycle (Mitchell *et al.*, 2016). This is because the water in the coal eventually evaporates and the degree of incomplete combustion is reduced.

An impact on thermal performance is attributed to condensation that normally occurs at the bottom of the pot. When the flame and combustion temperatures are low, the water evaporating from the coal tend to condense on the bottom of the pot, with a possibility to drop into the combustion chamber or coal bed, affecting the performance of the fuel/stove combination. In this study, this phenomenon was not observed.

The stove type and ignition method are the key reason why the relationships between MC and emission factors were in contrast to the results of the study conducted by Huangfu *et al.* (2014). The presence of secondary air holes in the stove plays a major role in minimising emissions of PM and CO. Results from this investigation are in agreement with reported findings of Bhattacharya *et al.* (2002) and Wei *et al.* (2012), where, in both cases, rocket type stoves were used (Jetter *et al.*, 2012), but without secondary air holes. The braziers used in this investigation did not have the ability to inject hot secondary air to the top of the combustion chamber to aid combustion of products of incomplete combustion. For example, when wood logs or firewood chips with higher moisture content are burning in the rocket-type stove, the presence of water in the wood tends to lower the combustion temperatures in the fire hopper, causing thick white smoke to escape out of the stove without being burned. Huangfu *et al.* (2014) used a semi-gasifier cookstove, which was the same type of stove used in Shen *et al.* (2010). In this type of stove, wood is batch loaded and lit from the top. The secondary air-feeding system is responsible for burning the combustion products, including CO and PM<sub>2.5</sub>. Although the presence of water in the coal affects the combustion and flame temperatures, once the wood is lit and char produced on the top, the char would keep the temperatures high enough to combust the coal. This produces combustible products, which burn in the presence of the hot air provided by the secondary air-feeding system (Huangfu *et al.*, 2014).

The significant impact of coal MC on the emission factors observed in this study substantiates the importance of MC in the performance evaluation of fuel/stove combinations. This has implications for future testing protocols that should specify or restrict the MC of the coal to be used in the performance evaluation, to avoid any bias resulting from different MC levels (Huangfu *et al.*, 2014). It can be inferred from the present results that in future studies, especially those aimed at estimating total pollutant amounts based on emission factors, there is need to include the MC of the coal in the different testing regimen and prediction models to minimize the error caused by coal MC levels.



Results of the influence of coal grade on PM emissions are ambiguous, not giving a consistent difference across fire ignition methods or ventilation rates. This aspect requires further investigation, also bearing in mind that coal is a heterogeneous fuel that behaves in a complex manner during combustion. In general, PM emissions are dependent on the volatility of the coal. Coal with high volatile matter is likely to produce high PM emission levels especially if the combustion device is poorly designed. During coal pyrolysis, the coal separates into char and volatile matter. Once the volatiles have been released, they travel up through the combustion chamber of the stove mixing and combusting with primary and secondary air. High volatile coal has the potential to release copious amounts of volatile organic matter upon pyrolysis. If the combustion device is poorly designed or the fire-ignition method not optimised, the volatile matter condenses and is released into the atmosphere as a dense plume of smoke. A-grade coal used in our experiments had high-volatile matter content compared to the D-grade coal (See Table 12). This may explain why an increase in PM was observed with the use of A-grade coal. However, PM formation is a complex process involving many elemental steps, which can be affected by many factors such as the organic content of a fuel, combustion temperature, oxygen supply rate during combustion, and the structure of stoves (Ge *et al.*, 2004).

### 3.13 Conclusions

This study investigated the influence of coal properties on the thermal and emissions performance of coal-burning braziers. The following conclusions can be drawn: Coal moisture content (MC) has an influence on particles and gaseous emissions. Higher moisture content reduces coal-bed and flame temperatures, resulting in an increase in emissions in the post-flame region of the stove. When considering the entire combustion sequence, the concentration of smoke particles tends to decrease rapidly during the pyrolysis phase of combustion. This is because the water in the coal eventually evaporates and the degree of incomplete combustion is reduced. Low coal MC reduces particle emissions by up to 50%. Moist coal produces higher pollution in conventionally ignited braziers. For the TLUD ignition, particle emissions are similar for the two moisture levels for medium and high ventilation rates; for low ventilation, the TLUD emissions for the low moisture coal are relatively small but significant.

Coal quality influences the combustion conditions and the formation of particle and gaseous emissions. The two coal batches used in this study had ash contents of 14 wt.%, adb –A-grade and 24 wt.%, adb –D-grade. Changing from A-grade to D-grade reduces particulate emissions in the top-lit braziers. For the BLUD method, particle emissions are similar with a switch from A-grade to D-grade, except at low ventilation. For the TLUD method, low ash A-grade coal increases particle emissions by up to 100% at any given ventilation rate. Emissions of CO and CO<sub>2</sub> were not influenced by the coal quality.

The significant impact of coal MC and coal quality on the emission factors observed in this study ascertains the importance of MC in the performance evaluation of fuel/stove combinations. This has implications for future testing protocols that should specify or restrict the MC and quality of the coal to be used in the performance evaluation, to avoid any bias resulting from different coal properties



## CHAPTER FOUR

*This chapter provide information on particle size distribution at three distinct combustion phases. The information provided is presented for particle size and number concentrations. The implications of particles sizes emitted in this chapter are provided and justification for further studies are provided.*

*Aerosol and Air Quality Research, 18: 2618 - 2632, 2018.*

### 4. Size Distribution of Ultrafine Particles Generated from Residential Fixed-bed Coal Combustion in a Typical Brazier

#### 4.1 Abstract

The ultrafine particles (with a small mean diameter) released from domestic coal combustion are an important parameter to consider in air pollution, as they affect air quality and human health. It has been suggested that poor combustion conditions release particles of different sizes enriched with health-damaging chemicals such as polycyclic aromatic hydrocarbons. Furthermore, both smouldering and highly efficient combustion conditions release particles, which are often carcinogenic. Information on the particle size distribution (PSD) of char or soot emitted from fixed-bed domestic coal combustion is limited, with many studies reporting on wood combustion. This study investigated the influence of coal combustion phases (ignition, flaming, and coking) on the particle number concentration and size distribution of ultrafine particles. D-grade bituminous coal was crushed to a particle diameter ( $\emptyset$ ) of 40–60 mm and combusted in a laboratory designed coal brazier (*Imbaula*) during experimental investigations of the particle size distribution normalised to the particle number concentration against the particle diameter. Experiments were carried out using the reduced smoke top-lit updraft method, colloquially known as the *Basa njengo Magogo (BnM)* method. The tests were carried out in a laboratory-controlled environment. Particulate matter was monitored using a NanoScan Scanning Mobility Particle Sizer (SMPS). Particles from the top-lit updraft (TLUD) showed an ultrafine geometric mean diameter centred at approximately  $109 \pm 18.4$  nm for the ignition phase,  $54.9 \pm 5.9$  nm for the pyrolysis/flaming phase, and  $31.1 \pm 5.1$  nm for the coking phase. The particle mode diameter rapidly increased during the ignition phase (145 nm) and gradually decreased during the flaming phase (35 nm) and the coking phase (31 nm). This study shows that during smouldering combustion conditions (ignition), the particle diameter increases, whereas it decreases as the temperature increases. This information is essential for estimating particle deposition in the lungs and the associated health risks.

#### 4.2 Introduction

Over half of the global population continue to depend on solid-fuels for domestic cooking and heating, with the majority found in developing countries (Bonjour *et al.*, 2013; International Energy Agency, 2015). Household solid-fuel burning releases copious amounts of particulates and coal-



burning are major sources of fine particulate matter leading to high levels of household air pollution (HAP). As such, studies on poor indoor air quality have received renewed interest due to associated health consequences (Dockery et al., 1993; Andreae and Merlet, 2001; Cincinelli and Martellini, 2017). Domestic solid-fuel burning using inefficient cookstoves has been identified as a significant source of poor air quality in human settlements in both developed and developing countries (Dockery et al., 1993; GACC, 2009; Smith and Peel, 2010).

Most studies have focused on large-scale solid-fuel combustion systems including power plants and large boilers as significant sources of ambient particulate matter (Gladney, 1974; Gladney, 1976; McElroy et al., 1982; Morawska et al., 2008). Efforts to separate large-scale combustion particles from residential solid-fuel burning suggested that particles from the industrial operations are more than 100 nm in diameter but can grow during the accumulation mode to 1000 nm (Kumar et al., 2011). Particulate matter (PM) emissions from residential coal burning are estimated to be at a size range of lower than 100 nm. However, the particle diameter can grow to 300 nm during the accumulation mode (Morawska et al., 2008). This differentiation based on size fraction can be used in source apportionment exercises (Naeher et al., 2007).

Extensive epidemiological studies pointed out that exposure to particulate matter (PM) below 2.5  $\mu\text{m}$  either on a short or long-term basis lead to the development of cardiovascular and respiratory diseases, which reduces life expectancy (Dockery et al., 1993). It is estimated that, globally, household air pollution is responsible for 4.3 million aggravated mortalities (Gordon et al., 2014; Forouzanfar et al., 2015). Several studies have shown that solid-fuel combustion is a significant contributor to increased premature mortalities (Smith et al., 1994; Lim et al., 2012). A study conducted by the European Environmental Agency between 2010 and 2012 revealed that inhalation of combustion particles resulted in 400,000 premature deaths throughout Europe (Rainey et al., 2016). A study carried out in Mpumalanga, South Africa, in 2012 indicated 8% hospital admissions and 9% mortalities per annum due to combustion particles. In the City of Tshwane, South Africa, 20–25% hospital admissions and respiratory-related mortalities per annum were attributed to inhaling domestic coal combustion particles (Scorgie, 2012). Furthermore, smoke emissions from combustion activities were responsible for 4.3% and 6% infant mortality rates per annum in Mpumalanga Province and the City of Tshwane, respectively (Stats SA, 2010).

Globally, it is envisaged that there is a need to introduce clean energy alternatives as a mechanism to reduce dependence on solid-fuels for domestic cooking, heating and lighting (International Energy Agency, 2015). Furthermore, other studies suggest that reducing emissions of PM will minimize incidences of air pollution health risks and premature mortalities (GACC, 2009; ISO IWA, 2012; WHO, 2014). The dissemination of improved cookstoves is seen as a viable option to reducing exposure to noxious pollutants from household energy uses (Smith et al., 2007). Towards this goal, successful cookstove dissemination programmes have been reported in Asia and Africa (Smith et al., 2004). Literature suggests that with improved combustion conditions, there is a possibility of reduced particle emissions (Le Roux et al., 2004; Zhang and Smith, 2007; Makonese et al., 2015). However,





recent studies have shown that enhanced combustion conditions release fine particles (Kumar et al., 2010; Zhang et al., 2012; Tiwari et al., 2013).

For decades, emissions of particulate matter by mass concentrations (given in unit  $\text{mg m}^{-3}$ ) were widely used to estimate the potential harm of PM to the human population (Jian and Bell, 2008). However, in a separate study conducted on emissions from diesel combustion, reporting exposure using mass-based emissions was criticized. The authors reported that particles of larger diameter presented minimum harm to human relative to ultrafine particles (Kittelson, 1998; Fernandez et al., 2003; Bølling et al., 2009). Ultrafine particles contribute less to the PM mass, but they present severe human health effects due to their large surface area and higher deposition efficiency in the small airways and alveoli of the lungs, and they can subsequently translocate to other vital organs through the bloodstream (Oberdörster et al., 2005; Tranfield and Walker, 2012). Due to the health consequences posed by solid-fuels, there has been considerable effort to characterise coal combustion products dating back to the 1970s. Submicron aerosols from coal combustion have been found to have a stronger impact on human health as they are enriched with toxic elements (Kauppinen and Pakkanen, 1990; Smith et al., 2009). In addition to the toxic substances contained in coal combustion particles, is the ability of the submicron particles to remain suspended in the air for a prolonged duration, which increases the risk of exposure (Kauppinen and Pakkanen, 1990). In light of this, fine and ultrafine particles from domestic coal combustion are receiving increased attention in South Africa, from both the scientific community and environmental management regulators.

Domestic coal combustion in South Africa is a major source of PM emissions in both ambient and indoor environments (Ezzati et al., 2000; Scorgie et al., 2003; Bruce et al., 2000; Barnes et al., 2005, 2009). During the early 1990s, over 20 million people daily combusted coal as their primary source of energy for domestic cooking, heating and water boiling (Terblanche et al., 1994; Annegarn and Sithole, 1997). The government of South Africa introduced mass electrification program aiming at delivering access to poor households to reduce dependence on coal and other solid-fuels (DME, 2004). By the end of 2006, over 73% of human settlements were connected to the electricity grid (DME, 2006). However, half of the people continued to rely on coal and wood for domestic cooking (Balmer, 2007). Other surveys indicated a sustained reduction in coal and wood dependence over the years with electricity being a significant source for cooking and heating (Statistics South Africa, 1998, 2003, 2007). To the contrary, a study conducted by Makonese et al. (2016) in Johannesburg's informal settlements found that over 90% of the surveyed households relied on coal for cooking and space heating. Moreover, Kasangana et al. (2017) found that over 80% of households in Mpumalanga depend on wood for space heating and cooking. Location and fuel availability dictate the differences in energy use patterns. In the Highveld, reliance on coal is high while in the Lowveld, wood is the dominant fuel (Balmer, 2007).

During coal combustion, the underlying mechanisms on how particles are formed and released depend on various factors. Particles from freshly emitted soot are in the fine mode, which includes the nuclei and the accumulation mode (Anastasio and Martin, 2001). During the nucleation phase, particles are formed from the condensation of a low-pressure vapour in the atmosphere or through





atmospheric chemical reactions. These particles have a diameter of less than 100 nm (Sioutas et al., 2005). After nucleation the particles undergo accumulation. In this stage, the smaller particles coagulate with other particles to form diffusion accretion chains that are 100–1000 nm long (Kumar et al., 2011). Primary particles from combustion processes, often produced as soot, remain an essential factor in understanding particle transportation and deposition. It is accepted that fine particles remain airborne in the atmosphere for a longer duration, thus increasing the exposure potential. Due to their smaller diameter, combustion particles are less susceptible to gravity increasing the resident time and can travel a longer distance (Kumar et al., 2010).

According to Hosseini et al. (2010), particle size distribution can differ as a function of the combustion phase (ignition, flaming, coking), fuel characteristics (moisture content, ash content, thermal content) and fuel types (lignite, bituminous, anthracite). Several studies have documented emissions from different coal combustion processes due to the importance of particle size on air quality, health and climate modelling (Linak et al., 2002; Yi et al., 2008; Xu et al., 2011; Zhang et al., 2015). PSDs from coal combustion have been studied for a variety of coal combustion processes including boilers (Kauppinen and Pakkanen, 1990; Linak et al., 2002), power stations (Yi et al., 2008), and drop tube furnaces (Xu et al., 2011). However, earlier studies have shown a wide variation in PSD due to differences in the combustion conditions, as well as measurement techniques and the instruments used (Kauppinen and Pakkanen, 1990). To date, there is limited information on PSD from fixed-bed domestic coal combustion processes (Zhang et al., 2015). Previous studies on residential coal combustion in South Africa have focused on the development of mass and energy specific emission factors (van Niekerk, 1997; CSIR, 2005; Makonese et al., 2014).

A suite of instruments has been employed to determine PSD from coal combustion processes. These include Nano Scanning Mobility Particle Sizer (SMPS) (Linak et al., 2002), Aerodynamic Particle Sizer (APS) (Linak et al., 2002), Low-Pressure Impaction (LPI) (Linak et al., 2002; Kauppinen and Pakkanen, 1990), Electrical Low Pressure Impactor (ELPI) (Yi et al., 2008), Dekati Low Pressure Impactor (DLPI) (Xu et al., 2011), and Wide-range Particle Spectrometer (WPS) (Zhang et al., 2015). This study makes use of the Nano Scanning Mobility Particle Sizer, since it has been widely used in similar studies and results are comparable. Zhang et al. (2012) conducted a survey of particle size distribution from burning coal under laboratory-controlled conditions using particle spectrometer (WPS, Model 1000XP, MSP Co., USA). Fine particles were emitted and had a mode of 63 nm for the flaming stage of combustion. Similar to Zhang et al. (2012), Tiwari et al. (2014) reported PSD of coal fires in the fine mode with the mean diameter of around 43 nm using a Differential Mobility Analyser (DMA) and a Condensation Particle Counter (CPC). However, in both studies, the description of the device, coal size, stove operational mode and ignition methods were not adequately provided.

It has been demonstrated in previous studies that a high air ventilation brazier ignited using top-lit updraft method (TLUD) improves the combustion condition significantly (Masekamani et al., 2014) compared to igniting a poorly ventilated brazier using the bottom-lit updraft (BLUD) (Makonese et al., 2015). Therefore, experiments in this study are limited to a high air ventilation brazier and the



TLUD ignition method. Experimental studies to compare the PSD between the TLUD and the BLUD are recommended for future work. The present study focused on the submicron particles (11 nm–365 nm) and aimed to assess the number size distribution of particles emitted from fixed-bed coal combustion in typical braziers using the TLUD method. A suite of monitoring instruments including the NanoScan Mobility Particle Sizer (SMPS) was employed to measure the evolution of PSD from the ignition phase to the coking phase of combustion. This study reports, for the first time, detailed PSD from domestic coal combustion in braziers in use in the Highveld region of South Africa.

### 4.3 Materials and methodology

#### 4.3.1 Combustion Lab

Experiments were conducted at the SeTAR Centre stove testing laboratory, situated at the University of Johannesburg, Bunting Road Campus. The combustion experiments were carried out in a galvanized iron hut that houses the measuring and monitoring equipment. The flue gases from the burning fuel were exhausted through a 4 m long chimney (located in the center of the laboratory) with a diameter of 15 cm. A detailed description of the combustion facility including the sampling trains is given in Makonese et al. (2015). Unlike in Hosseini et al. (2010), the SeTAR lab was not pressurized with preconditioned ambient air to control parameters such as temperature and humidity. This can only be done if the primary goal is to capture all the entrainment through the ducting system. The SeTAR Heterogeneous Stove Testing Protocol (HTP) uses a chemically mass balanced method to determine emission factors/rates—a representative sample of the exhaust is needed for this determination (Makonese, 2015).

#### 4.3.2 Stove Description

In the present work, PSD was investigated using high air ventilation laboratory designed braziers, where holes were punched uniformly at the same size around the device. The design parameters of the braziers are provided in Table 19 and photograph of a high ventilation brazier is shown in Figure 6.

#### 4.3.3 Fuel and Fire Preparation

It has been reported elsewhere that coal characteristics (moisture content, ash content, thermal content) and fuel type (lignite, anthracites and bituminous) produces different PSD (Hossien et al., 2010). In this study, bituminous D-grade coal commonly used in the townships of South Africa was used throughout the experiments. The coal used in this study was purchased from Slater coalmine in the Mpumalanga Province. The fuel was stored at room temperature of 21°C in sealed containers to prevent moisture loss. The coal was homogeneously mixed using a shovel before a sample was taken for external analysis. The coal was crushed and sieved to maintain a mean size diameter of 40–60 mm. Each batch of fuel was analyzed for moisture content before the test experiments commenced. For this study, a D-grade type of bituminous coal was used in a high ventilation field *Imbaula* using the top-lit updraft method (TLUD). The fuel specifications, the high ventilation brazier, and the order of laying a top-lit updraft fire are presented in detail elsewhere (Makonese et al., 2014).



The fire was set out using government advocated ignition method, but less favored top-lit updraft (TLUD) method, colloquially known as *Basa njengo Magogo* (meaning “make fire like a granny”). The stove was set using ~35 g of paper, ~400 g of wood kindling and ~4000 g of coal. The same mass of wood and paper was used for the three tests. During the TLUD ignition method, the fuel arrangement in the brazier entailed placing 2500 g of coal on the grate, followed by the paper (35 g), wood (400 g), and the remaining 1500 g of coal on top as in Figure 6. The entire stove was placed on a heat shield located on the platform of the mass balance. The use of a heat shield was to protect the mass balance from overheating and fire damage.

**Table 19: Stove ventilation rate characterisation.**

Brazier ventilation rate	Height (mm)	Dia. (mm)	Grate height (mm)	Area of holes below grate (cm <sup>2</sup> )	Area of holes above grate (cm <sup>2</sup> )	Total area of holes (cm <sup>2</sup> )
High	370	290	185 (50%)	248 (61%)	159 (39%)	407



**Figure 6: Laboratory designed high ventilation stove.**

### **Fuel Analysis and Moisture Content**

The D-grade bituminous coal used in this study was sent to a South African National Accreditation System (SANAS) accredited laboratory for analyses before the experiments commenced. The fuels were characterised for proximate analysis (moisture, ash, volatile organic compounds, fixed carbon) and ultimate analysis (C, H, S, N, O and mineral elements) given in percentage weight, analysed on an air-dried basis (wt.%, adb).

The coal moisture content (MC) was further verified before testing as different MC values can affect the combustion characteristics of the stove. A small representative sample (~100 g) was weighed on a calibrated scale with a 0.1 g resolution and then dried in an oven at 100°C for 48 hours, assuming that the 48-hour duration is sufficient for the coal to achieve steady moisture equilibrium. The sample was then taken out and reweighed. The exercise was repeated every three hours to check that the fuel had attained dry mass (Makonese et al., 2017). The percentage moisture content was calculated using Equation 18:



$$M = \frac{M_{wet} - M_{dry}}{M_{wet}} \times 100$$

Equation 18

where  $M_{wet}$  is the mass of the coal as received, and  $M_{dry}$  is the mass of the dry coal.

#### 4.3.4 Separation of Combustion Phases

In the present paper, three variables to separate combustion phases (temperature, visible smoke and CO), by observation and data interpretation. During the ignition phase, there was noticeable white to brown smoke, characterised by an increase in CO emissions (4500 ppm) and low temperature (< 200°C). During the flaming stage, the temperature increased to above 400°C, while the CO emissions decreased (~1500 ppm) and there was a significant flame protruding from the top of the stove. During the coking phase, the CO emissions (900 ppm) and temperature (~300°C) are relatively stable, with no visible flame. At this stage, the combustion conditions are homogeneous and only coke/fixed carbon is burning, and heat transfer is in the form of radiant heat. A full description of the separation of the combustion phases in coal-burning braziers is presented in Makonese et al. (2015).

#### 4.3.5 Particle Measurement

The sampling platform for monitoring PM was located at a distance of 2.5 m from the combustion hut, in a data capturing room, where all particle and gaseous measuring instruments are stationed. Figure 7 shows a schematic presentation of the measurement and sampling system.

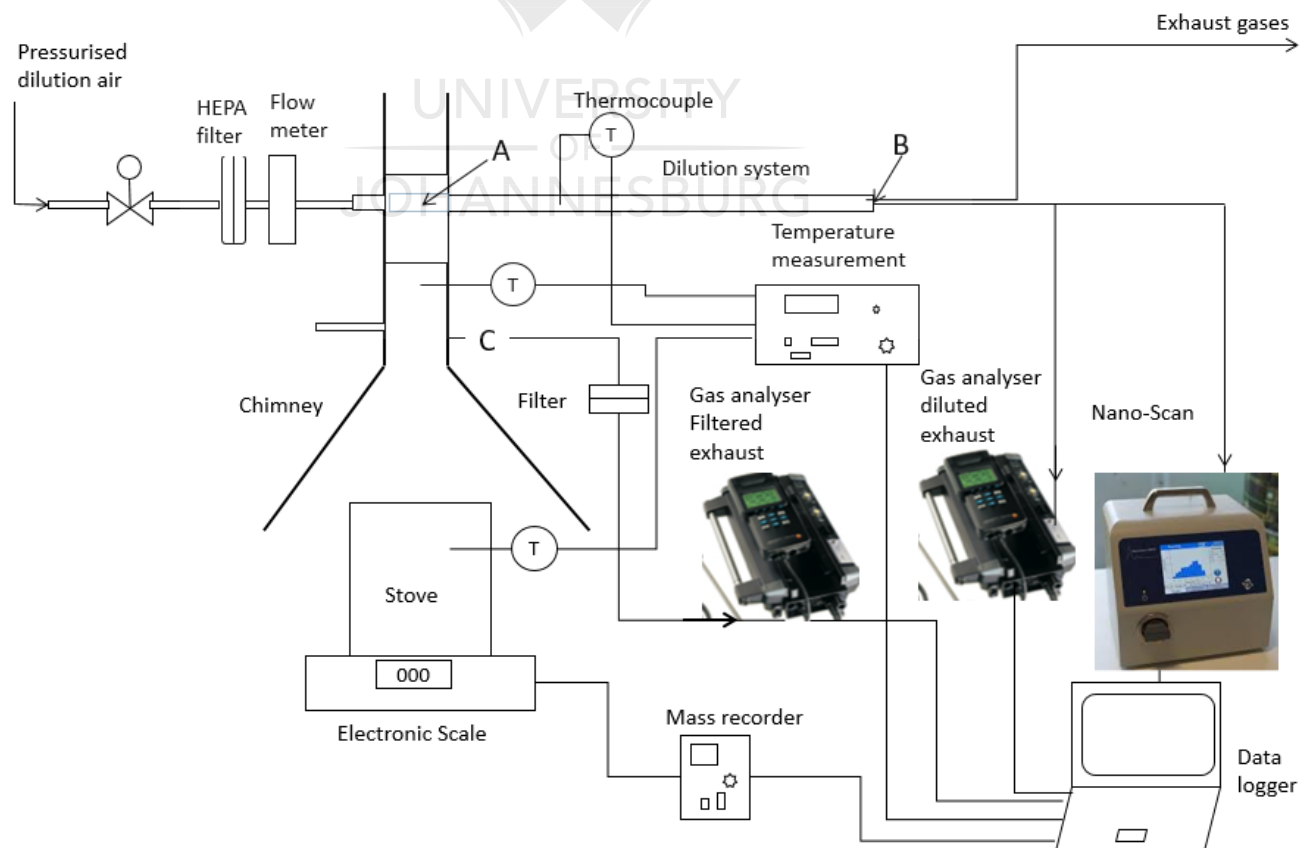


Figure 7: Schematic diagram of the SeTAR Centre testing rig.



First, a sample of the exhaust was drawn from the chimney and diluted using the SeTAR variable dilution system. The SeTAR Centre dilution system was used to dilute the exhaust to protect the NanoScan Scanning Mobility Particle Sizer from clogging. Burning coal using braziers produce high levels of emissions, especially during ignition and flaming. It is essential to dilute the particles concentration to below the upper limit of detection of  $1E6 \# \text{ cm}^{-3}$ ; this will not lead to modification of particles through either condensation or coagulation in dilution channel. The diluted sample was directed to a NanoScan Scanning Mobility Particle Sizer (SMPS) and a Testo XL 350 flue gas analyzer. The NanoScan Scanning Mobility Particle Sizer 3910 (TSI Inc., Shoreview, MN, USA) was used to study particles with a diameter ranging between 10 nm and 420 nm. The instrument response time is 3 seconds but averages size distribution over a 60 second interval (45 s up-scan, 15 s down-scan). The instrument measures particles continuously and records a maximum of  $1E+06$  particles  $\text{cm}^{-3}$ .

The undiluted sample was channeled to a Testo XL 350 flue gas analyser (Testo Inc., Sparta, USA). The Testo gas analyser is coupled with sensors that measures  $\text{CO}_2$ , CO,  $\text{NO}_x$ ,  $\text{NO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{S}$ , S,  $\text{SO}_2$  and  $\text{O}_2$ . The monitor was equipped with measurement modules for  $\text{O}_2$ , CO, NO and  $\text{NO}_2$  as standard. Also, measurement modules for CXHY,  $\text{NO}_{\text{low}}$ ,  $\text{CO}_{\text{low}}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  or  $\text{CO}_2$  by the infrared are optionally available. The monitor uses electrochemical cells for gas measurements.  $\text{CO}_2$  is determined using a non-dispersive infrared cell and is typically depicted as  $\text{CO}_2$  IR. Oxygen balance is used for the calculation of excess air.

The design of the sampling system enabled the carbon dioxide mixing ratios of the diluted and undiluted exhaust to be measured to determine the dilution ratio, using the method described in Makonese (2015). Instantaneous dilution levels across the entire burn sequence were multiplied with the instantaneous particle concentrations to convert the diluted concentrations to undiluted exhaust concentrations equation 19.

$$DR = \frac{CO_{2(i)undiluted} - CO_{2ambient}}{CO_{2(i)diluted} - CO_{2ambient}} \quad \text{Equation 19}$$

where  $\text{CO}_{2(i)undiluted}$  is the percentage of carbon dioxide in a raw sample;  $\text{CO}_2$  is the ambient carbon dioxide concentration measured, and  $\text{CO}_{2(i)}$  is the percentage of carbon dioxide in a diluted sample. Makonese (2015) reports further details of the SeTAR Centre dilution system in a study that systematically investigated smoke emissions from domestic coal combustion devices.

#### 4.3.6 Quality Control

Before sampling, the dilution system was assembled, cleaned using potable water to remove any particles and other residual materials. After that, the dilution system was re-assembled, compressed air was blown in, and leaks were checked. Both the SMPS and Testo instruments are sent for calibration and servicing according to the manufacturer's recommendations, or at least once per annum, and are



also periodically verified with laboratory standards. Zero and span calibration were performed on all analyzers before and after every test run to account for small variations in the dilution ratio. For example, the NanoScan was zeroed with filtered air before each test run. Tests were repeated three or more times to check for repeatability, due to the heterogeneous nature of coal. The same person did the fire preparation to minimize variability in setting up, which might alter the combustion performance. We further subdivided the burn cycle into three combustion phases (i.e., ignition, flaming and coking). The tests were run for equal durations of three hours, and the combustion phases were separated for the three tests. Each combustion phase was further split into two stages, early and late. The test results were averaged over the three definitive tests.

Background concentrations were accounted for because particles from outside the testing facility can infiltrate the testing laboratory and contribute to the final concentration reading. In addition, other internal activities or airflow might re-suspend particles, which could affect the results. This study employed the ARIMA model to remove the contribution of background concentration to the actual activity generating submicron particles (Klein et al., 2011) (Equation 20). The instruments were run for an hour before the three-hour testing duration and after that operated on compressed air for 10 minutes, to remove any fugitive emissions along the sampling train.

$$C_{combustion} = C_{activity} - C_{without} \quad \text{Equation 20}$$

where the  $C_{combustion}$  is the final concentration,  $C_{activity}$  is the actual sample collected after the PM generating activity was taking place + background concentration.  $C_{without}$  is the concentration of particles obtained in the absence of the activity under investigation.

#### 4.3.7 Study Limitations

The study is limited to submicron particle size diameters of 10–365 nm emitted from freshly produced coal smoke in a high air ventilation brazier, ignited using TLUD. The high air ventilation brazier and the TLUD ignition method are currently advocated as significant performance optimization parameters in fixed-bed coal combustion in braziers; hence the tests were only limited to these two variables.

#### 4.4 Results and discussion

The experiments described generate information on the particle number concentrations and size distributions corresponding to combustion phases over the entire burn sequence. In Table 20, results of the fuel analysis carried out by the SANAS accredited external laboratory are presented. The fuel composition is essential to determining the combustion emissions. The particle size distribution is influenced by several factors, including the fuel properties, testing conditions, and measuring instrument (Hosseini et al., 2010). In a separate study conducted by Chakrabarty et al. (2006), it was found that fuel with a high moisture content (wet) produced particles with a larger diameter relative to dry fuel combusted under the same conditions. In the study conducted by Makonese (2015), it was reported that high moisture content in fuel can improve or impair combustion. Combusting fuel with





a high moisture content led to increased emissions of CO. Furthermore, the same study indicated that fuel with a high calorific value emitted high concentrations of CO and PM in poorly ventilated stoves, whereas the same fuel in highly ventilated stoves emitted reduced concentrations of CO and PM. Therefore, in order to reduce the uncertainty in reported PM size distributions, fuel analysis must be incorporated.

**Table 20: Fuel analysis specification.**

Parameter (Air Dried Basis)	Standard Method	Slater Mine D-Grade Coal
Moisture content (%)	ISO 5925	1.8
Volatiles (%)	ISO 562	20.3
Ash (%)	ISO 1171	24.2
Fixed carbon (%)	By difference	52.0
Calorific value (MJ kg <sup>-1</sup> )	ISO 1928	23.4
Calorific value (Kcal kg <sup>-1</sup> )	ISO 1928	5590
Total sulphur (%)	ASTM D4239	0.63
Carbon (%)	ASTM D5373	62.6
Hydrogen (%)	ASTM D5373	2.76
Nitrogen (%)	ASTM D5373	1.0
Oxygen (%)	By difference	5.0
Total silica as SiO <sub>2</sub> (%)	ASTM D4326	58.6
Aluminium as Al <sub>2</sub> O <sub>3</sub> (%)	ASTM D4326	27.6
Total iron as Fe <sub>2</sub> O <sub>3</sub> (%)	ASTM D4326	6.63
Titanium as TiO <sub>2</sub> (%)	ASTM D4326	0.82
Phosphorous as P <sub>2</sub> O <sub>5</sub> (%)	ASTM D4326	0.55
Calcium as CaO (%)	ASTM D4326	2.30
Magnesium as MgO (%)	ASTM D4326	0.83
Sodium as Na <sub>2</sub> O (%)	ASTM D4326	0.42
Potassium as K <sub>2</sub> O (%)	ASTM D4326	0.79
Sulphur as SO <sub>3</sub> (%)	ASTM D4326	1.10
Manganese as MnO <sub>2</sub> (%)	ASTM D4326	0.12

The results presented in Table 21 indicate that particles were emitted throughout the experiments. However, the most particles were emitted during the flaming phase, followed by the coking phase, with the fewest particles emitted during the ignition phase. By contrast, in studies conducted by Makonese et al. (2014) and Masekamani (2015), it was found that the most particles were emitted during the ignition phase, followed by the flaming and the coking phases. The difference between the current study and previous studies on this subject is the use of different units in reporting data, i.e., both Makonese and Masekamani studies focused on the particle size diameter in the range of PM<sub>2.5</sub> to PM<sub>10</sub>. The limitation of the present is that it focuses on submicron particles (11–365 nm) and does not attempt to cover the entire size range (11 nm–10 μm). However, other studies using different methods reported similar findings to our studies, when using particle diameter and mass. In a recent study conducted by Chu et al. (2017) simulating particle size distribution using the fractal theory and Monte Carlo technique found that the smaller particles were most dominant compared to larger particles.

**Table 21: Particle number concentration per combustion phase relative to the entire burn sequence.**

Phase	(# cm <sup>-3</sup> ) N = 3	Duration (minutes)	GMD (nm)	GSD (nm)





Entire Combustion Sequence	1,20E+07 (100%)	180	51.9	2.1
Ignition	2,71E+03 (0.02%)	20	109.8	18.4
Flaming	6,67E+06 (55%)	60	54.9	5.9
Coking	5,34E+06 (44%)	100	34.3	5,1

Table 22 presents percentage shares of nucleation, Aitken, and accumulation modes at each combustion phase. The Aitken and the accumulation modes dominate the particle concentration during the ignition phase. At this phase, there is a limited supply of combustion air and low temperatures. The particles condense and coagulate to form larger particles. The flaming and coking phases are dominated by the nucleation mode, with a relatively small contribution in the accumulation mode. Particularly during the coking phase, the combustion conditions are favourable, with sufficient supply of oxygen. The volatile organic compounds are often driven out during flaming before the transition to the coking phase. During coking phase, only fixed carbon burns and the rate of combustion is limited by oxygen adsorption onto the carbon matrix. These results are reasonably comparable to Tiwari et al. (2014, 2015), where coal combustion particles were dominated by nucleation (47.2%) and Aitken (41.3%) modes. According to Chang et al. (2004), coal combustion particles are often in the range of 40–50 nm. The study results agree with Chang et al. (2004)—most of the particles were reported to be in nucleation mode, especially during coking and flaming. The difference between the present study and Tiwari et al. (2014) and Chang et al. (2004) is that, results are presented in this study are per combustion phase, while the results from the other two studies are given over the entire combustion sequence. Tiwari et al. (2015) further studied particle mass accumulation using three size fractions (respirable, fine and ultrafine). In the same study it was found that accumulated mass of particle > 100 nm was 1.5  $\mu\text{g m}^{-3}$  while particle in the range of > 100 nm but < 300 nm was 1  $\mu\text{g m}^{-3}$ . Although in the present study size distribution is based on number concentration, the study agrees with Tiwari et al. (2015). In the present study, particles were largely emitted during the flaming and coking phase where combustion conditions are likely to be favourable. Given that smaller particles occupy less mass but larger surface area, the results are comparable.

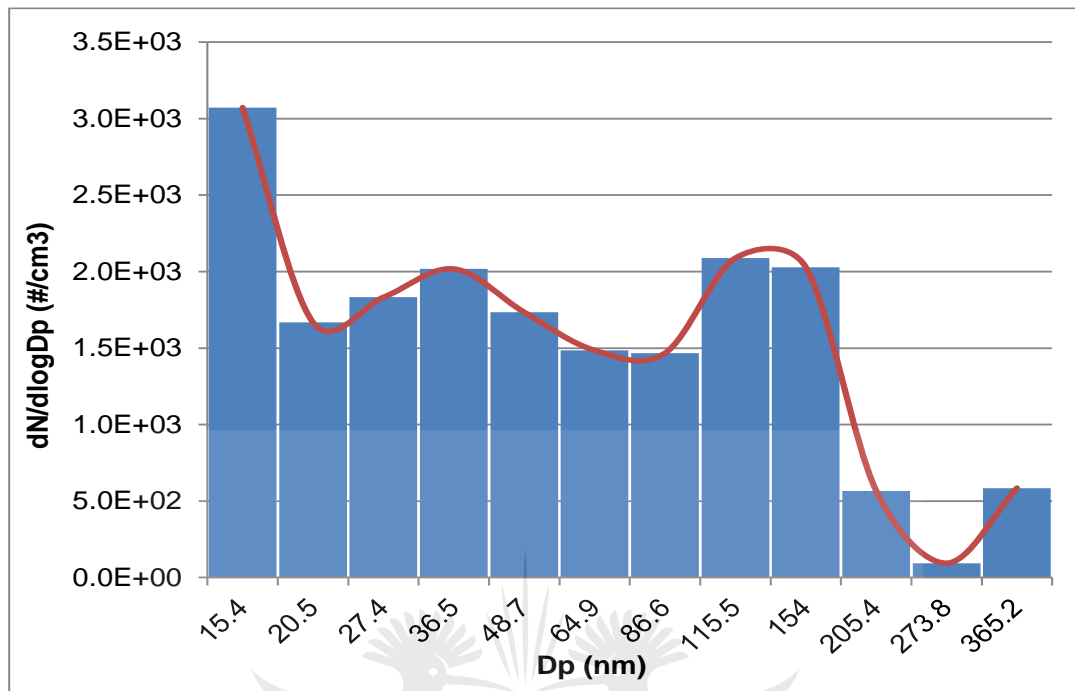
**Table 22: Contribution of combustion phase on PSD for the three modes (Nucleation, Aitken and Accumulation).**

Combustion phase	Nuclei (Dp < 50 nm) (%)	Aitken (Dp 50–100 nm) (%)	Accumulation (Dp > 100 nm) (%)
Ignition	15,3	45,5	39,2
Flaming	46,8	30,8	22,4
Coking	83,9	13,4	2,6

Before ignition, ambient particulate matter size distribution and number concentration were monitored to account for ambient PM contributions. Figure 8 shows the number size distribution for the background PM measured using the TSI NanoScan Scanning Mobility Particle Sizer. Results showed a polydispersed size distribution, and the background particle concentrations decreased sharply above 180 nm. This result is similar to findings by Hosseini et al. (2010) who noted that background particle concentration decreases significantly above 200 nm. As expected, the

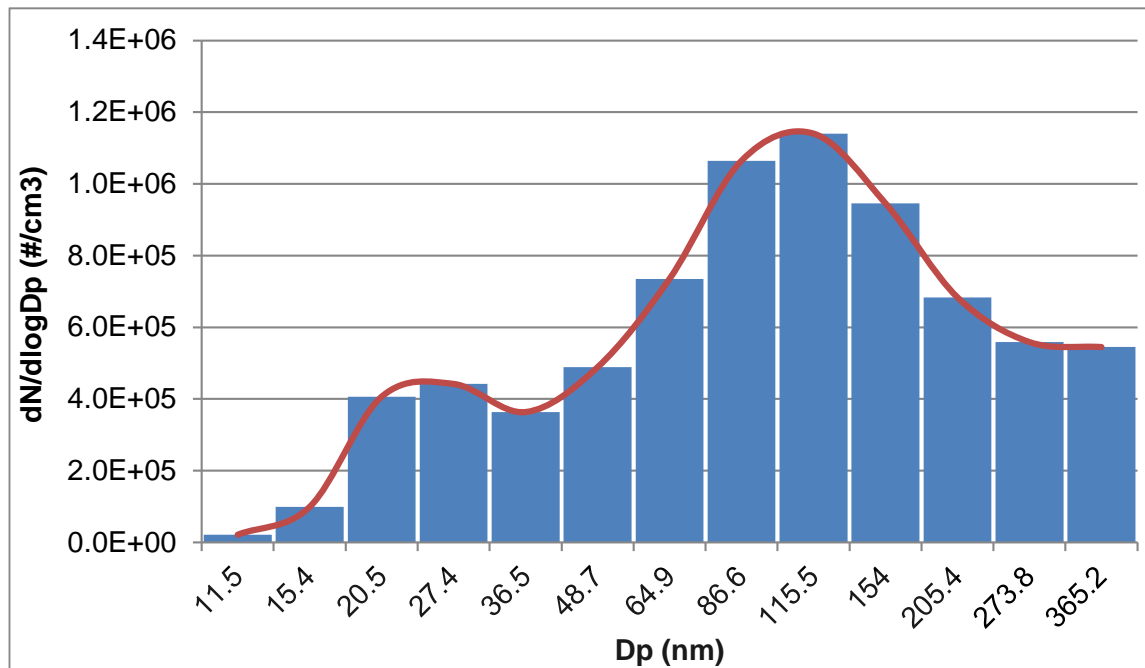


background concentrations are lower than combustion-specific concentrations measured during the different phases of the burn sequence (Figs. 9–15).



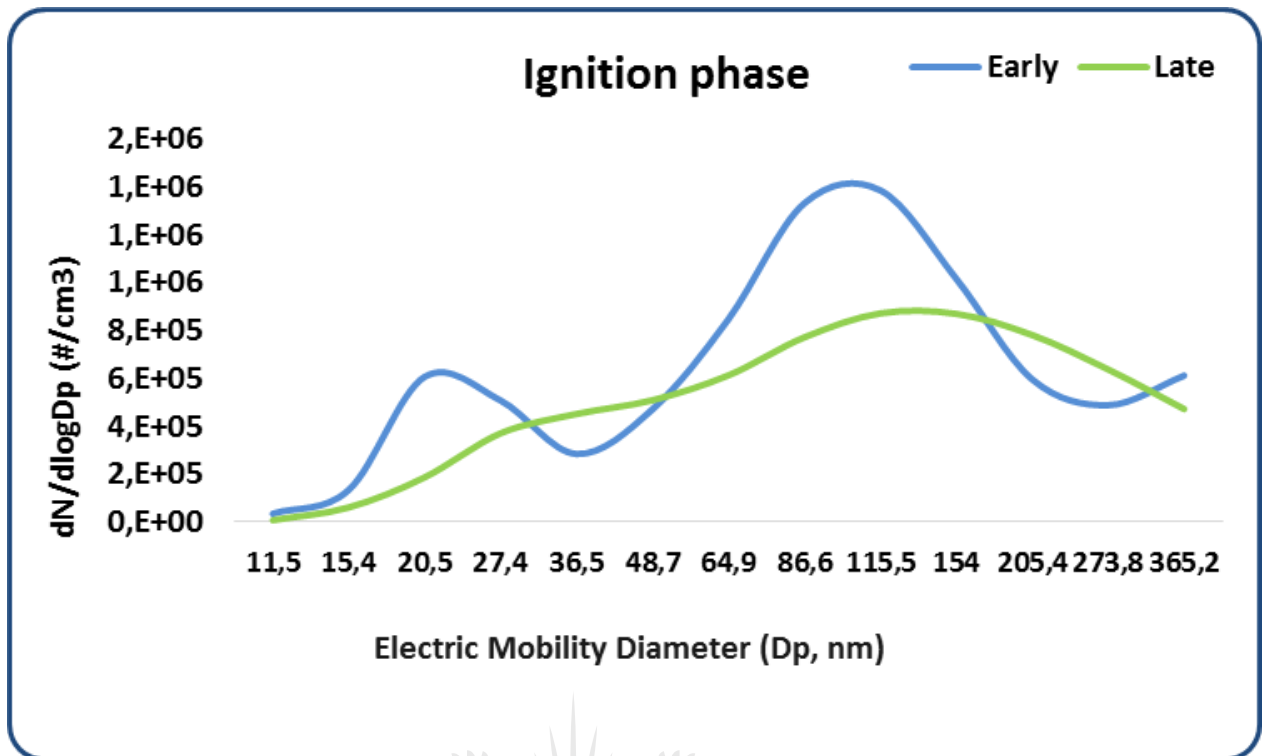
**Figure 8: Particle size distributions corresponding to the background concentrations.**

In this study, an attempt was made to separate particle emissions over the different combustion phases during each burn sequence, using the criteria presented in Makonese et al. (2015). Details of this segregation are also described in detail in Makonese (2015). Figure 9 shows a size distribution and number concentration for the ignition phase. During this phase, combustion conditions are smouldering, with limited oxygen supply and low flame temperatures. Particles emitted during this phase are often expected to be larger relative to particles emitted during the flaming and the coking phase because of incomplete combustion conditions. However, the number of particles emitted at this phase is lower compared to the other stages. The particles at this phase are more in the range of 64 nm to 365 nm. These results confirm the association between oxygen starved combustion with increasing emissions of larger particles. The ignition phase shows a bimodal distribution with a geometric mean diameter (GMD) of  $109.8 \pm 16.4$  nm and a mode that is estimated at 145.3 nm.



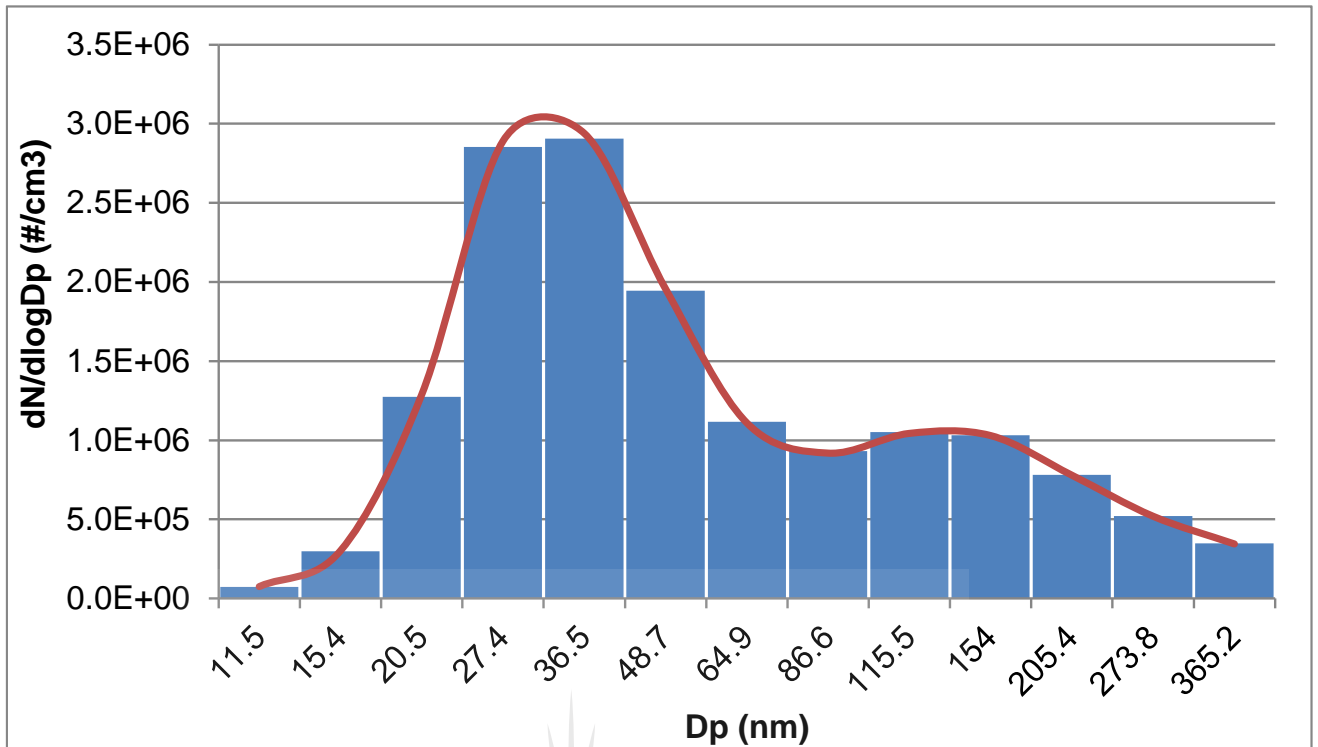
**Figure 9: Particle size distribution corresponding to the ignition phase.**

The ignition phase was further divided into the early ignition (i.e., first 10 minutes) and late ignition (i.e., last 10 minutes of ignition)—the ignition phase constituted 20 minutes of the entire burning duration. Figure 10 shows a bimodal size distribution during the early stages of combustion, with particle diameter at  $109.8 \pm 16.4$  nm, while the mode diameter was estimated at 155.1 nm. Late ignition showed a near bimodal distribution with the particle mean diameter at  $110.7 \pm 20.6$  nm, while the mode was determined at 134.6 nm. Early ignition will comprise mainly particles emitted from wood kindling, while the late ignition includes emissions from both wood kindling and coal. The mode diameter is greater during the early stage of ignition where smouldering conditions are imminent. However, the particle mean diameter was found to be similar. This finding suggests that there is no significant difference in particle diameter between the early and late ignition phases.



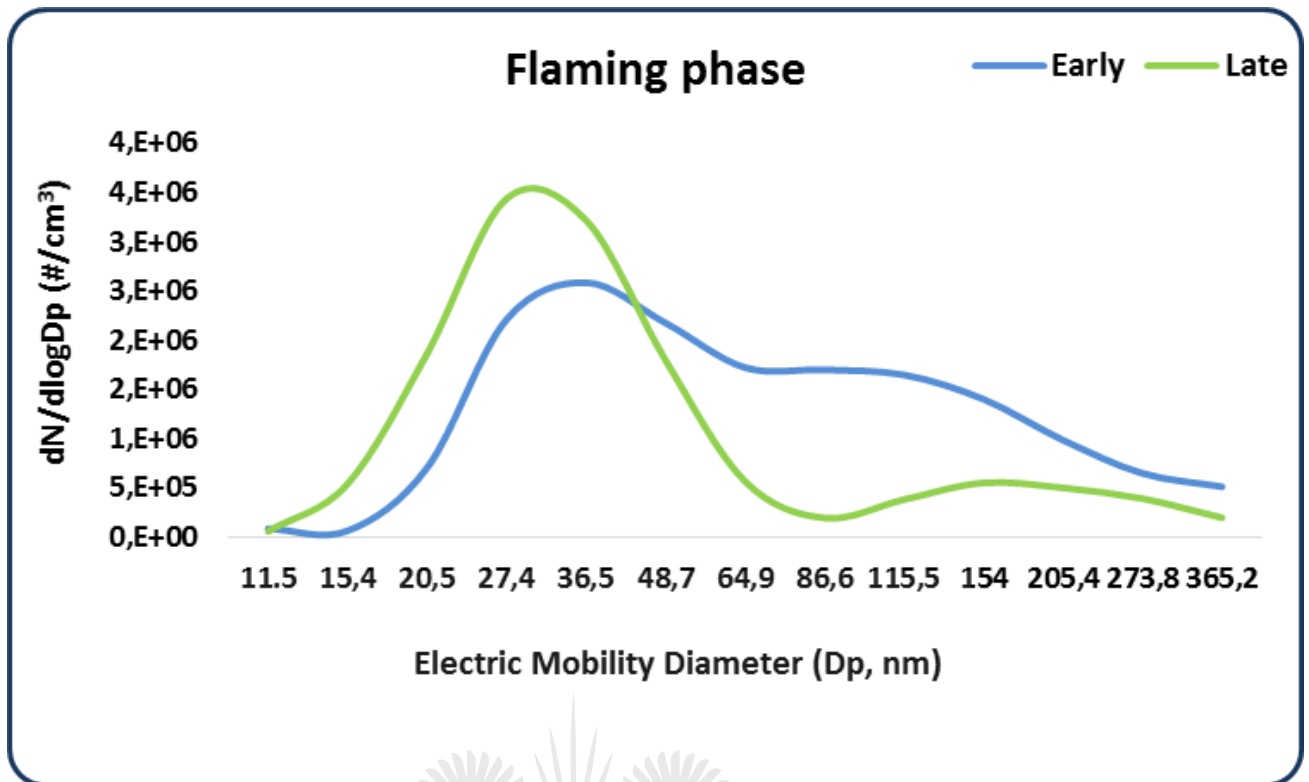
**Figure 10: Particle size distribution during early and late ignition.**

The bulk of particles emitted during a top-lit updraft coal fire were given off during the flaming stage (Figure 11). The flaming phase showed a bimodal distribution with the GMD estimated at  $54.9 \pm 5.9$  nm and the mode at 34.8 nm. Relative to ignition, number size distribution is reduced by 50%, which suggests that with improved combustion conditions more fine particles are emitted. The number size distribution of particles during this flaming phase is similar to that of the average of the entire burn sequence (Figure 15). Hosseini et al. (2010) reported similar findings when burning biomass under laboratory-controlled conditions. However, field measurements conducted by Zhang et al. (2015) reported a unimodal particle size distribution ranging from 70.3 to 75.7 nm. Furthermore, findings from the two studies, which are varied, might have been influenced by different testing conditions, i.e., field (uncontrolled) and laboratory (controlled). Also, sampling location regarding distance from the emitting source (Zhang et al., 2015) and residence time, which might allow particle coagulation or agglomeration, could be an essential factor in this regard. Results from this study are comparable with previous limited studies, which attempted to study particle size distribution from domestic coal burning (McElroy et al., 1982; Bond et al., 2002; Hosseini et al., 2010; Zhang et al., 2012; Tiwari et al., 2014).



**Figure 11: Particle size distribution corresponding to the flaming phase.**

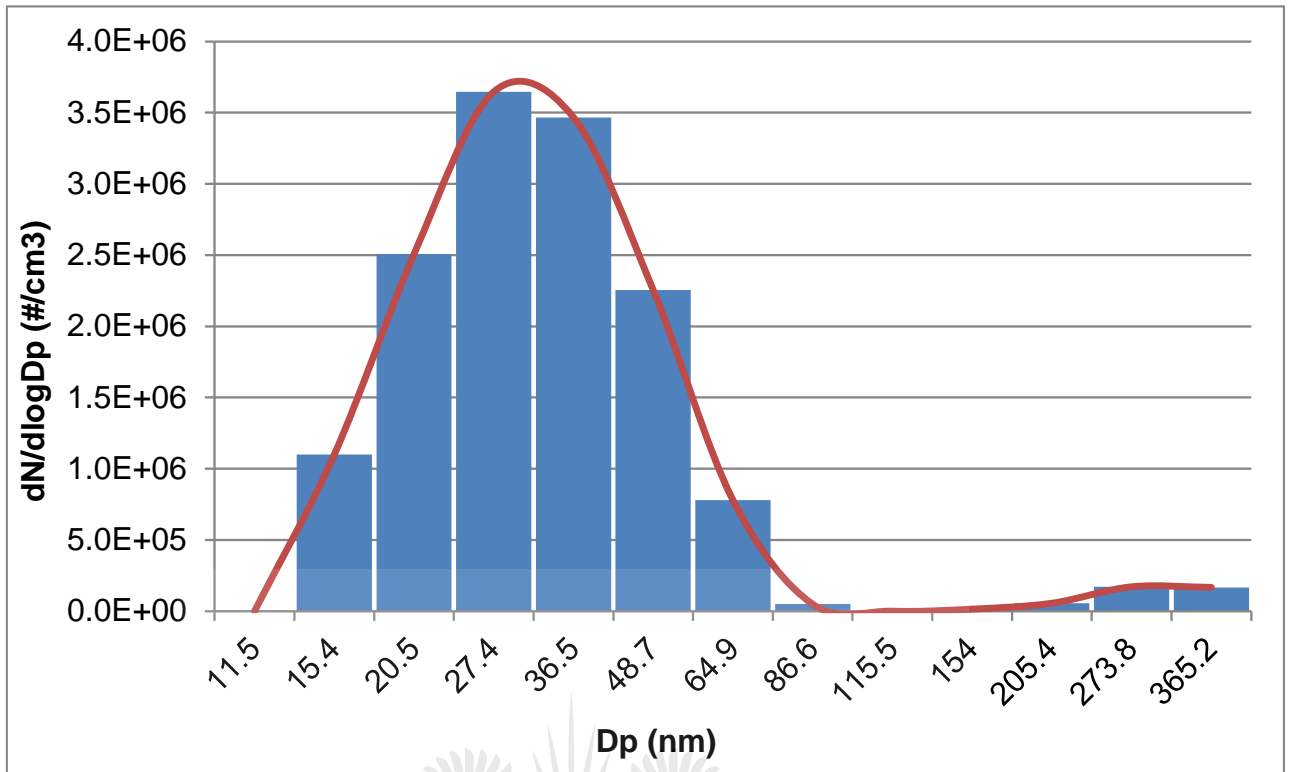
The flaming phase was separated into early and late stages to differentiate number size distribution relative to improved combustion conditions. Figure 12 shows a bimodal distribution during early flaming with a mode diameter at 39.8 nm while the mean diameter was at  $67.6 \pm 6.5$  nm. Late flaming shows a near bimodal distribution with the mode diameter of 29.9 nm and the geometric mean diameter of  $42.9 \pm 5.5$  nm. Particle GMD and mode diameter decreased by 36% and 25%, respectively, during late flaming relative to the early flaming phase. A decrease in mode diameter during this phase suggests improved combustion conditions, and particle diameter decreases with optimum combustion conditions.



**Figure 12: Particle size distribution during early and late flaming.**

During the coking phase, there were no visible flames, and the burning coal had turned into hot ambers. The period between the flaming phase and the coking phase referred to as the “mixed” phase in Hosseini et al. (2010) was not separately investigated in our study. However, Hosseini et al. (2010), separated particle distribution at the flaming phase; particle number concentration and number size distribution were reported at the start of flaming and for the mixed phase. Furthermore, the flaming and the “mixed” phases were collectively used under a single umbrella term “flaming phase”, since the flame is still visible during the “mixed” phase.

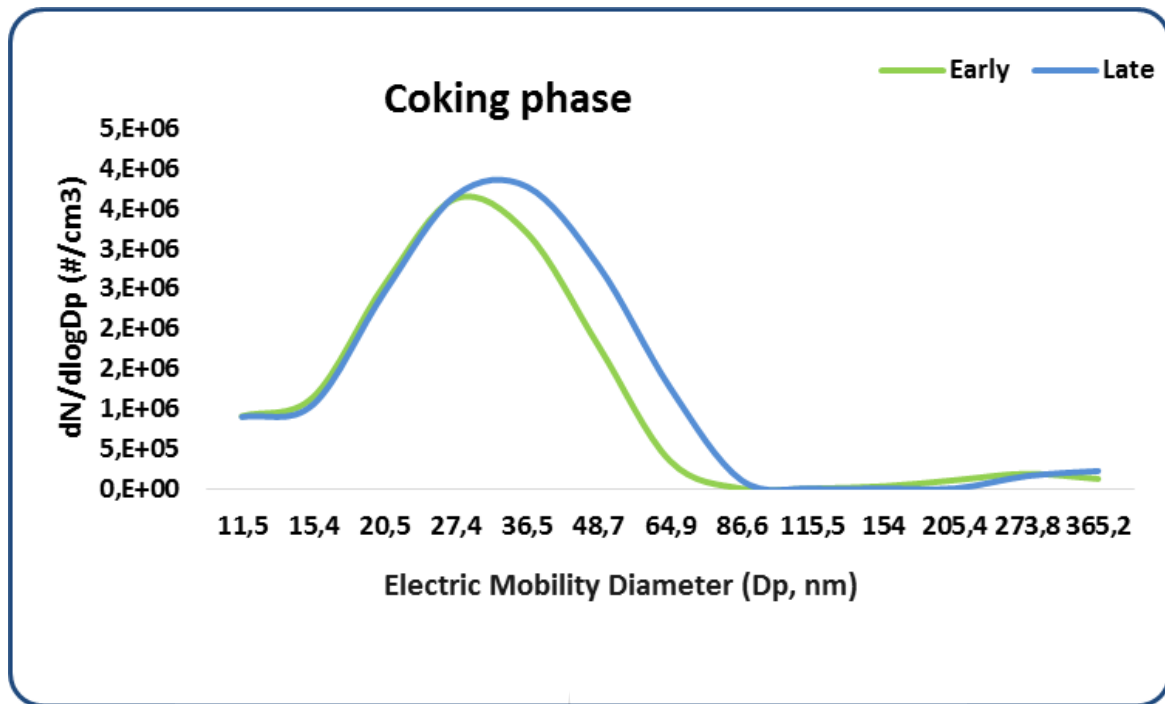
The distribution during the coking phase showed a near unimodal particle size distribution with a GMD of  $32.8 \pm 5.1$  nm and a mode of 31 nm (Figure 13). The size distribution indicates that particle number concentration gradually increases above 180 nm. Particle number concentration during this phase is comparable to particle number concentrations during the flaming phase. A possible explanation for this is that during the coking phase (at the top of the fuel bed) there will be some coal still igniting and pyrolyzing at the bottom of the fuel bed. As the particles pass through the burning red-hot combustion zone, they are burned resulting in the emission of particles with a lower GMD. The results presented under this phase are similar to the one presented by Li et al. (2017); moreover, the study focused on particle size distribution from a coal-fired power station. A unimodal distribution was found but the average particle size was above 10  $\mu\text{m}$ .



**Figure 13: Particle size distribution corresponding to the coking phase.**

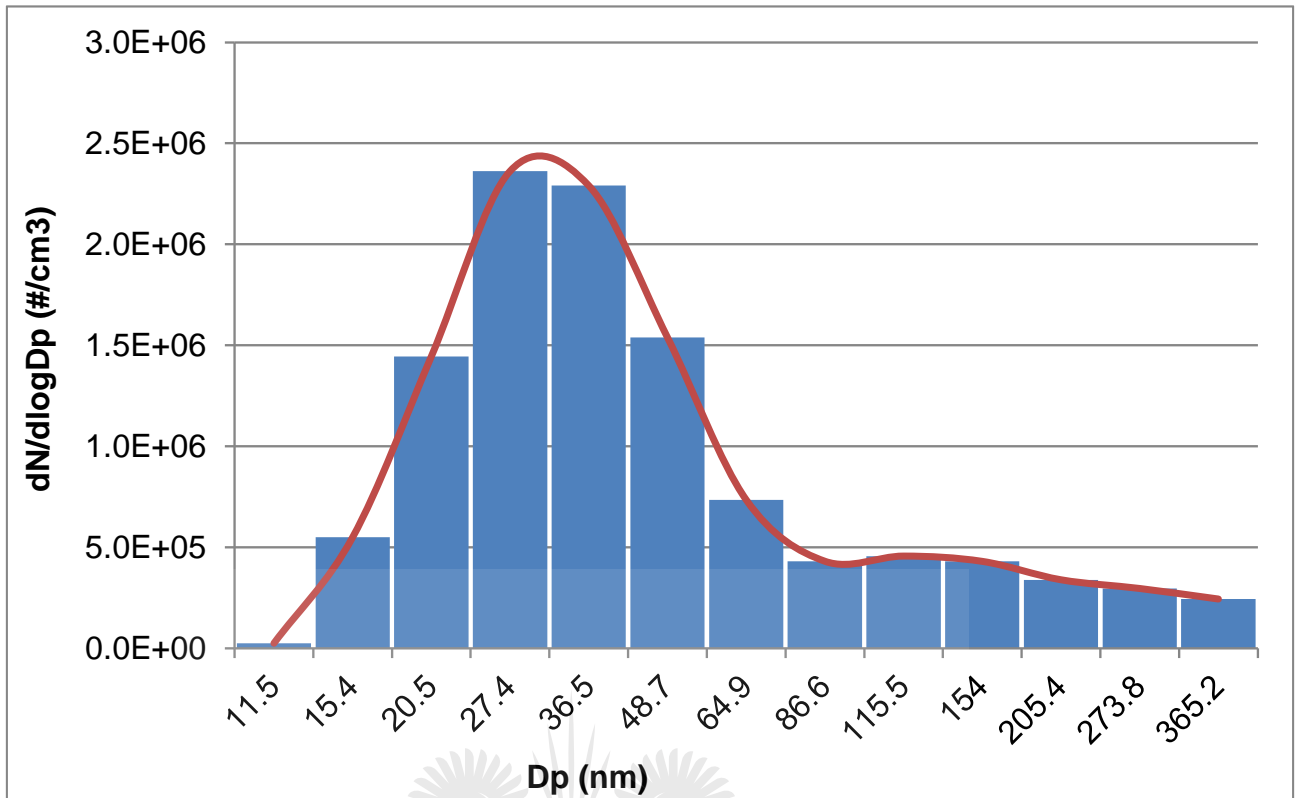
In Figure 14, the coking phase was separated into two stages (i.e., early and late coking). Separation of the combustion phase did not produce different number size distributions, with the distribution similar to the entire phase average as indicated in Figure 15. This is because the combustion conditions at this stage are homogeneous, with no visible flame nor smoke. Heat produced is in the form of radiant heat, and all volatiles have been driven out at the end of the flaming phase, and only fixed carbon burns with oxygen adsorption and temperature limiting the rate of combustion.





**Figure 14: Particle size distribution during early and late coking.**

In Figure 15, number size distribution and particle number concentration corresponding to the entire burn sequence are presented. The average number size distribution for the whole combustion sequence was found to be nearly bimodal, with a particle mode of 130 nm. After this mode, above 180 nm, particle number concentration was reduced gradually, and the GMD and mode were determined to be  $51.6 \pm 2.0$  nm and 50.6 nm, respectively. Other studies also showed PSD from all combustion phases to be bimodal with particle concentrations peaking between 30 and 150 nm (Hays et al., 2002; Hedberg et al., 2002; Hosseini et al., 2010; Zhang et al., 2011; Zhang et al., 2012). Bond et al. (2002) observed that burning coal briquettes particles are emitted in size range between 20 and 100 nm. Earlier lab-based studies have found bimodal PSD from pulverized coal combustion with fine particle mode peaking at around 100 nm (McElroy et al., 1982).



**Figure 15: Particle size distribution corresponding to the entire burn cycle.**

Results as depicted by the above figures, where PSD have been presented for each combustion phase a meaningful insight on this subject can be drawn, especially when there is a need to compare the effect of combustion conditions on PSD (Figure 15). Since the combustion conditions are not constant throughout the whole burn-sequence, it is essential to indicate number size distribution for each identical burn sequence. Looking at Figure 15 only, one can conclude that emissions of particles above 80 nm are attributable to the entire burn sequence. While the contribution of larger particles is associated with the ignition and early transitional combustion stage (i.e., ignition to flaming) phase (Figs. 8 –11), smaller particles are associated with both flaming and coking phases (Figs. 12–14). The ignition phase produced particles in the accumulation mode, which was influenced by smouldering conditions and the release of volatile organic compounds under low-temperatures. As the combustion progressed, there was a shift in particle mode from accumulation to Aitken, where particle diameter reduced during the transitional stage. During late flaming to coking, the mode changed to nucleation, where particle diameter further decreased under stable combustion conditions. This observation is similar to the distribution reported in Zhang et al. (2012).

#### 4.5 Summary and conclusions

This paper presents the number size distribution of the submicron particle fraction from combusting D-grade coal in a high air ventilation brazier using the top-lit updraft method. Particle size distributions were measured using a TSI NanoScan Scanning Mobility Particle Sizer. The monitor measured the PSD throughout the entire burn sequence (from ignition to coking). The PSD curves were separated into three combustion phases: ignition, flaming, and coking. The GMD of the particle



size distribution was estimated to be 51.6 nm for the averaged burn sequence. Particle number concentrations were high during the flaming and coking phases compared to the ignition phase. The GMD rapidly increased during the ignition phase and gradually decreased during the flaming and coking phases.

The particle size distribution was bimodal across the first two combustion phases for the D-grade coal used in our experiments but was unimodal during the coking phase. The unimodal distribution suggests homogeneous combustion conditions, when the radiant heat flow is constant and the particle emissions are identical. All volatiles are driven out during the coking phase, with only fixed carbon burning under ideal combustion conditions and with a sufficient air supply. Although the study does not attempt to investigate the particle emission composition, it is anticipated that particle emission during the coking phase is attributable to fly ash. Despite limitations due to assessing the particle size distribution only for small-scale coal combustion, important lessons were drawn from findings by other studies that focused on wood burning technologies. Studies conducted by multiple researchers reported a unimodal particle size distribution under ideal wood burning conditions (Hays et al., 2002; Hedberg et al., 2002; Hosseini et al., 2010; Zhang et al., 2011; Zhang et al., 2012), while McElroy et al. (1982) reported a bimodal PSD. Nevertheless, in all of these studies, a bimodal distribution was attributed to poor combustion conditions and the agglomeration process.

The present study has demonstrated in this study that improving combustion conditions emits particles with a smaller diameter. This finding is worrying, given the consequences, as outlined in epidemiological studies, that smaller particles are easily inhaled and have a higher potential for uptake through blood circulation. However, the toxicity of these particles must be investigated for various combustion phases in order to draw conclusions regarding the potential health effects of emitted particles with varied number size distributions.

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## CHAPTER FIVE

*This chapter present information on the morphology and elemental composition of emitted particle at each combustion phase. The study was limited to the identification of the particle from TEM with no attempt to utilise EDS to quantify the elemental composition. ICP-MS was used to provide details on the elemental composition of the selected few trace elements. Environmental and health implications of several morphologies and elements are presented in this chapter.*

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### 5. Morphology and elemental composition of coal particles emitted from domestic coal burning brazier

#### 5.1 Abstract

This study was conducted in a laboratory-controlled environment aiming at studying the physical properties and elemental composition of coal combustion smoke particles emitted from a brazier. Particles were sampled ~1 m above the stove using a partector, where particles were collected on gold TEM grids and polycarbonate filters for transmission electron microscopy (TEM) and inductively coupled mass spectrometry (ICP-MS) analysis, respectively. Particles for elemental analysis were sampled ~ 1 m above the stove using a Gillian pump where particles were collected using a 37 µm polycarbonate filters. During sampling, a 2.5 µm cyclone was attached to the sampling cassette to isolate larger particles. The results have shown that combustion particles emitted during the early stage of combustion where single spherical particles with a diameter of around 450 nm. As the combustion progresses, the particle diameter gradually decreases and the morphology changes to accretion chain and fluffy bead structure for the flaming and char burning phase, respectively. The study results imply that smouldering coal combustion condition may be a major source of atmospheric spherical organic particles (SOP), which need to be included during source inventory development. Over 50% of trace elements dominated by silicon were released during the char burning phase. Since silicon was used as a marker for coal combustion emission. We therefore, confirmed that the spherical particles with characteristics of tar balls were generated from the small-scale coal combustion.

**Keywords:** physical properties, TEM, ICP-MS, elemental composition

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#### 5.2 Introduction

For decades, solid fuel burning is highly associated with increased air pollution. Regarding the global population, over 3 billion people to date still depend on solid fuels daily (Smith *et al.*, 2007, 2009; Zhang and Smith, 2007). Particulate matter has been singled out as a form of pollutants, which



continues to pose a significant threat to the environment and human health. Suspension of particles in the atmosphere is a contribution of natural and anthropogenic sources (Mc Donald and Biswas, 2004; Chafe *et al.*, 2015). Several studies have indicated a significant increase in emissions of particles from various anthropogenic activities such as transport, mining and combustion (Smith and Liu, 1994; Kumar *et al.*, 2014; Forouzanfar *et al.*, 2015; Kumarathanan *et al.*, 2018). However, it is further illustrated that the suspension of particles is influenced by several factors such as the meteorological conditions, particle diameter and chemical property (Köylü, Xing and Rosner, 1995; Nussbaumer *et al.*, 2001; Petaloti *et al.*, 2006). Combustion sources are reported to have contributed to over 90% of the total mass of particles in the atmosphere (Smith *et al.*, 1994; Alexander, Crozier and Anderson, 2008; Zhou *et al.*, 2015). Significant progress has been made to date to evaluate the health impacts of particles on human health (Zhang *et al.*, 2000; Jalava *et al.*, 2010; Rainey, Vaganay and MacIntyre, 2016). The contribution of particles in the sub-micron size diameter was found to have a higher residence time in the atmosphere and further associated with higher deposition in the human's respiratory system (Meij and Winkel, 2007; Sippula, 2010; Silva *et al.*, 2012).

Several epidemiological studies have pointed out that particles in the nano-region are associated with the infection of the lower respiratory tract, cardiovascular system disruption and morbidity (Oberdörster, 2001; IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 2010; Kumar *et al.*, 2010; Lim *et al.*, 2012). Despite significant effort made by several authors associating nanoparticles with severe health impacts, fewer studies have been done to investigate the morphology of particles, from packed-bed domestic coal combustion (i.e. shape, size and chemical properties) (Li *et al.*, 2003; Kocbach *et al.*, 2005; Torvela *et al.*, 2014; Zhang *et al.*, 2018). In addition to the health risks, combustion particles have been associated with environmental impacts (Chakrabarty *et al.*, 2010; Chung, Ramanathan and Decremmer, 2012). Sub-micron particles are often enriched with black carbon/ brown carbon, which contributes to the physicochemical processes occurring in the troposphere. Combustion particles from low-temperature combustion can absorb solar radiation from the sun (Chakrabarty *et al.*, 2010; Liu *et al.*, 2014; Tóth *et al.*, 2014b). Furthermore, combustion particles also contribute to the light scattering effects, and provide an active site for the uptake of several chemical species and trace gases (Bond *et al.*, 2002; Hand *et al.*, 2005; Gwaze, 2007). In combustion sciences, more emphasis has been placed on the characterization of emissions of sub-micron particles in the transport sector and large-scale combustion processes such as power plants (Streets and Waldhoff, 2000; Petaloti *et al.*, 2006; Meij and Winkel, 2007). However, very few studies to date have studied the morphology of particles emitted from small scale coal combustion technologies even though significant associated risks have been reported in countries like China, India and Finland (Zhang *et al.*, 2000; He, Liang and Jiang, 2002; Niemi *et al.*, 2006; An *et al.*, 2007; Smith *et al.*, 2007; Wilkinson *et al.*, 2009; Chafe *et al.*, 2015).

Substantial characterization of the organic fractions emitted from domestic coal burning technologies has been reported globally (Nussbaumer *et al.*, 2001; Zhang *et al.*, 2012; Torvela *et al.*, 2014). However, very few studies focused on the characterization of trace elements emitted from residential coal burning (Petaloti *et al.*, 2006; Vejehati, Xu and Gupta, 2010; Silva *et al.*, 2012). Studies



conducted in China have slightly reported the possible health effects of trace elements emitted from residential coal burning (Zhang and Smith, 2007; R. Zhang *et al.*, 2008; Y. Liu *et al.*, 2008). In the province of Guizhou, over 3000 people suffered arsenic poisoning, bone deformation, human selenosis and fluorosis because of exposure from residential coal burning (Ando *et al.*, 2001; Finkelman *et al.*, 2002; Silva *et al.*, 2012; Zhou *et al.*, 2015). Furthermore, it was also established that the health effects of trace elements from coal-burning would vary according to coal properties and exposure scenarios (Chang *et al.*, 2004; Xu *et al.*, 2011; Makonese, Masekameni and Annegarn, 2017).

Coal used in domestic combustion technologies often contains a lower amount of volatile organic compounds, which influences conditions for complete combustion (Moreira Dos Santos, De Almeida Azevedo and De Aquino Neto, 2004; Tissari *et al.*, 2008; Frey, 2014; Torvela *et al.*, 2014). Consequently, during ignition, coal requires a catalyst to burn. Often, wood kindling is used for ignition due to the inherent higher volatility of this fuel (Makonese, 2015). The formation of particles is high at low-temperature conditions and during incomplete combustion conditions, where soot might be formed comprising of elementary carbon, black carbon and gas precursor to aerosols as polycyclic aromatic hydrocarbons (PAHs) (Wang and Luo, 2009; Tiwari *et al.*, 2014).

Previous studies reported emissions from small-scale combustion as average concentration of particles above 2.5  $\mu\text{m}$  over the entire burn cycle, with less emphasis on monitoring emissions at specific combustion phases (Makonese *et al.*, 2015a, 2017a). However, combustion in fixed-bed systems varies at different stages (ignition, pyrolysis and char burning) (Masekameni, Makonese and Annegarn, 2014; Daniel M. Masekameni *et al.*, 2018). During the moisture contained in the wood, kindling turn to reduces the combustion temperature leading to the release of a thick white plume comprising of condensing volatile organic compounds escaping without being burned (Braasch *et al.*, 2013). At the flaming phase, the combustion conditions improve as the moisture contained in the fuel is driven out (Wei *et al.*, 2012). The char burning phase is associated with a stable fire where char burns homogeneously in the presence of sufficient air supply (Huangfu *et al.*, 2014). However, other studies contradict what was reported, indicating that fine particles, which are said to have health consequences are mostly emitted during the char burning phase and flaming phase (Tiwari *et al.*, 2014; Masekameni *et al.*, 2018). It is, therefore, essential to evaluate the physical and elemental composition of coal particles at each combustion phase to further understand mechanisms on particle formation, distribution and identification.

In South Africa, especially in the central plateau of the Highveld region coal burning using unvented stoves continue to be a significant source of energy for domestic cooking and space heating (Wentzel *et al.*, 1999; Balmer, 2007; Makonese *et al.*, 2017a). Efforts to reduce dependence on coal at the domestic level have been commissioned before but not yet fully implemented (Winkler, 2005; Kimemia and Annegarn, 2011; Bonjour *et al.*, 2013). However, studies suggest that there is an insignificant shift from coal usage to clean energy alternatives due to the abundance of coal in this region and cost of alternative clean energy sources, hence the pollution levels indoors and outdoors remains high (Balmer, 2007; Winkler, 2007; StatsSA, 2017). From the reviewed literature, it was





noted that moisture content, coal grade, stove ventilation, fire ignition method and coal particle size affect performance profiles (Huangfu *et al.*, 2014; Makonese *et al.*, 2017b). However, in this paper, the primary dependent variables were the fire ignition method and ventilation rates. In 2004, the South African government developed and rolled-out the use of top-lit updraft (TLUD) as an interim household air pollution intervention (Le Roux, Zunckel and McCormick, 2009). It is suggested that the use of top-lit updraft reduces emissions of particles by 80% relative to the bottom lit updraft ignition (Le Roux, Zunckel and McCormick, 2009; Masekameni, Makonese and Annegarn, 2014; Makonese *et al.*, 2017b). Therefore, based on the South African government's adoption of the strategy, the use of high ventilation stoves and the TLUD method for optimum performance requires further investigation to validate such claims (Wei *et al.*, 2012; Makonese *et al.*, 2014; Makonese, 2015).

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are important tools to study the shape and morphology of aerosol particles (Schneider *et al.*, 2006; Gwaze, 2007). Equipped with energy dispersive X-ray (EDX) or electron energy loss (ELL) spectroscopy, they give information on the elemental composition of the particles of interest (Nussbaumer *et al.*, 2001). While TEM allows a higher resolution down to the Nano and atomic scale, SEM usually has better contrast (Kocbach *et al.*, 2005). For TEM, very thin grids (often copper/ gold) coated with a carbon film/ gold, are used. The quality of this film is essential to obtain a good resolution (Mathis *et al.*, 2005). If samples are used for quantitative analysis (e.g. of the size distribution), care must be taken to have defined size fractions during the sampling process (Nussbaumer *et al.*, 2001; Bond *et al.*, 2006). In addition to particle morphology, the correct identification and determination of the elemental composition rely on the use of effective analytical techniques. Inductive couple mass spectrometry (ICP-MS) has been widely used to study the elemental composition of combustion particles (Graham *et al.*, 2002; Suzuki, 2006; De Jong *et al.*, 2008; Zhang *et al.*, 2012; Forouzanfar *et al.*, 2015). In this study, we have evaluated the physical properties and selected elemental composition (Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu 63, Zn) generated during residential coal burning at three combustion phases (ignition, flaming and cooking).

The current practice in determining the state of air quality in South Africa is through monitoring of indicator pollutants such as particulate matter, NO<sub>x</sub>, O<sub>3</sub> and SO<sub>2</sub> (GroundWork, 2016; SANS, 2005; Moolla, Curtis and Knight, 2015). Part of the government's effort to assess the effectiveness of clean energy alternatives is to conduct source apportionment. Therefore, the study on the morphology and chemical analysis are needed to conclusively determine source contribution and further our understanding of pollutant source distribution. The study is limited to D-grade coal burned in a high ventilated stove and lit with a TLUD ignition method for the three combustion phases (ignition, flaming and char burning).

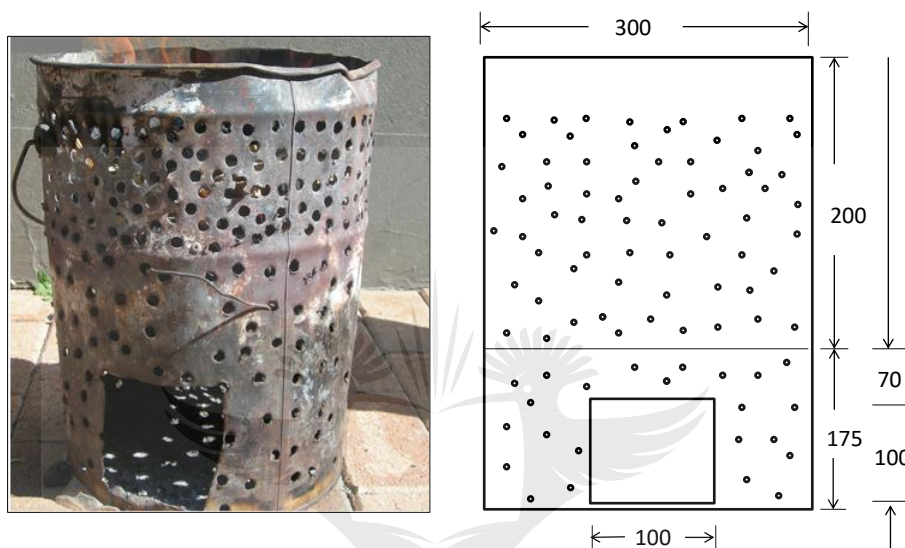




## 5.3 Materials and Methods

### 5.3.1 Experimental stove and fuel analysis

D-grade coal was burned in a high-ventilated stove lit using top-lit ignition method in a laboratory-controlled environment in three distinct combustion phases (ignition, flaming and char burning). In the present study, due to variations of field-based factors, several variables were kept constant (Ventilation rates, the height and position of the grate, size of fuel, ignition method and fuel). A high ventilation stove was used for the laboratory experiment, and the stove characteristics such as grate and stove height are shown in Figure 16.



**Figure 16: A photographic and schematic representation of a high ventilation field procured optimized brazier stove used in the experiments (Not drawn to scale – dimensions are in mm) (Makonese *et al.*, 2017b).**

Coal particle size was determined by sieving the coal to a 40 mm x 60 mm diameter mesh. Coal used in this study was analysed by an independent laboratory, using the appropriate recommended methods (Bureau Veritas Inspectorate Laboratories (Pty) Ltd). Experimental results presented in this paper have been based on the proximate and ultimate D grade coal analyses conducted on an air dried basis (Results of the coal analyses are given in the results section in Table 2). During the TLUD ignition method, the fuel ordering entailed placing 2 500 g of coal on the grate, followed by the paper (35 g), wood (400 g), and the remaining 1 500 g of coal on top. Details on the division of the combustion phases, fuel properties and ignition method are presented elsewhere (Masekameni, Makonese and Annegarn, 2014; Masondo *et al.*, 2016; Makonese *et al.*, 2017b).

### 5.3.2 Sampling

Particles were collected on TEM gold grids and polycarbonate membrane filters for TEM and ICP-MS analyses, respectively. The TEM gold grids were placed on a grid holder from the partector aerosol dosimeter TEM sampler (Naneos particle solutions, Switzerland), and the particles were deposited directly onto the grid. The sampling train included a Teflon tube connecting the partector inlet to the sampling cassette fitted with a 2.5  $\mu\text{m}$  cyclone. The partector was set at a flow rate of 2.8



L/m according to the cyclone's specification. Sampling for ICP-MS was done using polycarbonate membrane filters (37 mm). The exhaust was drawn onto the membrane filter inside a cassette by a GilAir Plus pump (Model) set at a flow rate of 2.2 L/minute. The filters were changed at each combustion phase (ignition, flaming and char burning phases).

### 5.3.3 Preparation of filters

A total of 12, 37 mm diameter polycarbonate membrane filters with a pore size of 0.08  $\mu\text{m}$  were stored in a controlled laboratory environment prior field sampling. The temperature ranged from 22 – 23  $^{\circ}\text{C}$  and the humidity was recorded at 35 %. The filters were conditioned for 24 hours and pre-weighed using a Sartorius electronic microbalance (model- CPA225D, supplied with a balance pan) with a minimum resolution of 0.001 mg (i.e., one microgram) and a precision of 0.001 mg (Figure 17). The same procedure was repeated after a three-hour burn cycle sampling of particulate matter was completed. A field blank was handled the same way with the field filter. However, the field blank was not exposed to the particulate matter. The use of field blank is to overcome or account for moisture loss due to meteorological condition particularity during transportation and contamination during filter handling. The determination of the final mass was calculated using equation 21.

$$\text{Final mass} = \text{Field filter (post - pre)} + \text{field blank (post - pre)} \quad \text{Equation 21}$$

Where the field filter post mass is the mass collected from the filter after sampling while the field pre-mass is the mass recorded before sampling. The field blank post and pre masses are the masses recorded after transportation and before transportation of filters respectively.



**Figure 17: Sartorius electronic microbalance (model- CPA225D)**

### 5.3.4 Inductively coupled mass spectrometry (ICP-MS)

The sample filters for ICP-MS analysis were folded and placed inside pre-cleaned microwave digestion vessels 9 mL supra pure (Merc) nitric acid ( $\text{HNO}_3$ ), and 1 mL supra pure (Merc) hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) 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. The digestion method made the vessels ramp to 200 for 20 minutes, and hold the temperature for another 15 minutes. The samples were then quantitatively transferred to a 50 mL volumetric flasks and made up to the mark using 18.2 M  $\Omega$ /cm ultrapure water. Calibration standards of 0  $\mu\text{g/L}$ , 0.1  $\mu\text{g/L}$ , 0.5  $\mu\text{g/L}$ , 1.0  $\mu\text{g/L}$ , 5.0  $\mu\text{g/L}$  and 10  $\mu\text{g/L}$  were prepared from 100 mg/L NIST traceable stock standards. The samples were then filtered using a 0.45  $\mu\text{m}$  syringe filter and diluted another ten times (1 ml diluted to 10 ml) before analysis by ICP-MS. The blank filter analysis using the ICP-MS technique was carried out in the same manner as the actual sample filters.

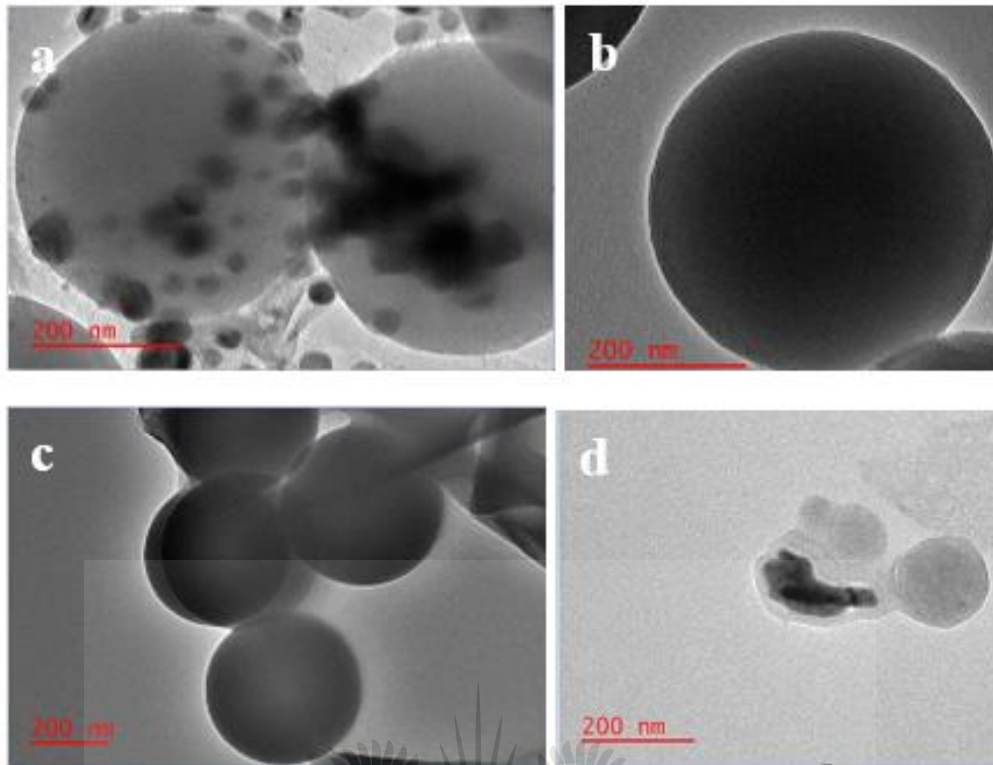
#### 5.3.5 *Transmission electron microscopy (TEM)*

Combustion smoke particles were imaged for their morphologies using JEM-2100 is a multipurpose, 200 kV analytical electron microscope at the University of Johannesburg. The instrument is manufactured by Jeol Ltd from Akishima, Tokyo, Japan. A TEM has been used to study the semi-structure especially in particles with a smaller diameter in contrast to an optical microscope, which uses light as an illumination source for imaging. The TEM uses electrons, which provide an opportunity to separate arrangements of atoms in small structure/ combustion soot aggregates (Kocbach *et al.*, 2005; Wang *et al.*, 2018). The TEM microscope combines the JEM-2100 optic system with an advanced control system for enhanced ease of operation.

### 5.4 **Results and Discussion**

#### 5.4.1 *Morphology of coal particles emitted during the ignition phase*

We have used TEM analysis to study and distinguish different smoke particle morphologies similar to previously conducted studies (Pósfai *et al.*, 2004; Chakrabarty *et al.*, 2010; Tóth *et al.*, 2014a). Figure 18, presents, the morphologies of smoke particles emitted during residential coal combustion. The morphologies presented herein are from the ignition phase.



**Figure 18: TEM images of particles emitted during the ignition phase- a) carbonaceous spherical particle, b) internal structure of spherules with evidence of aggregates, c) Onion-like structured soot particles.**

Figure 18a shows a spherical organic particle with the same characteristics of tarballs collected from low-temperature combustion during the ignition phase. This finding suggests that the spherical particles are emitted because of low-temperature combustion. Posfai *et al.* (2003) contended that these carbonaceous particles are formed in smouldering fires and that they increase in abundance in the atmosphere as the plume ages.

Furthermore, Posfai *et al.* (2004) reported similar morphologies. However, the source contribution was veld fire, which is often dominated by biomass burning. Figure 18a and b shows large organic spherical particles infused with diffusion accretion chains forming soot. It was observed that since these particles were collected at 1 m above the stove, the morphology might change with an increase in the height of sampling due to ageing.

Figure 18c shows particle growth as the spherical organic particles fuse probably due to collision. Thujadeen *et al.* (2015) contended that particle-particle collisions are the dominant particle growth mechanism during combustion even though the particles may restructure or rearrange after the collision and fail to coalesce. Similar morphologies to those presented in this paper were observed from biomass burning fires (Li *et al.*, 2003; Hand *et al.*, 2005; Cong *et al.*, 2010; Thajudeen, Jeon and Hogan, 2015). Figure 3d displayed an onion-like structure with disordered graphic layers under the high-resolution TEM image (Wang *et al.*, 2018; Zhang *et al.*, 2018).



Spherical organic particles presented in the above figures indicate a homogeneous structure (spherical) showing darker and lighter areas under the TEM. The spherical organic particles have properties similar to tarballs from biomass burning. Similar results were observed and reported in previous studies Martin *et al.* (1998), Gelencser *et al.* (2003), Gao *et al.* (2003). However, the existing literature suggests that tarballs are only released as a consequence of smouldering wood burning fires. Several scholars have indicated that tarballs are not emitted during coal or oil combustion (Katrinak *et al.*, 1992; Ramsden and Sibaoka, 1982; Parungo *et al.*, 1992; Posfai *et al.*, 2010).

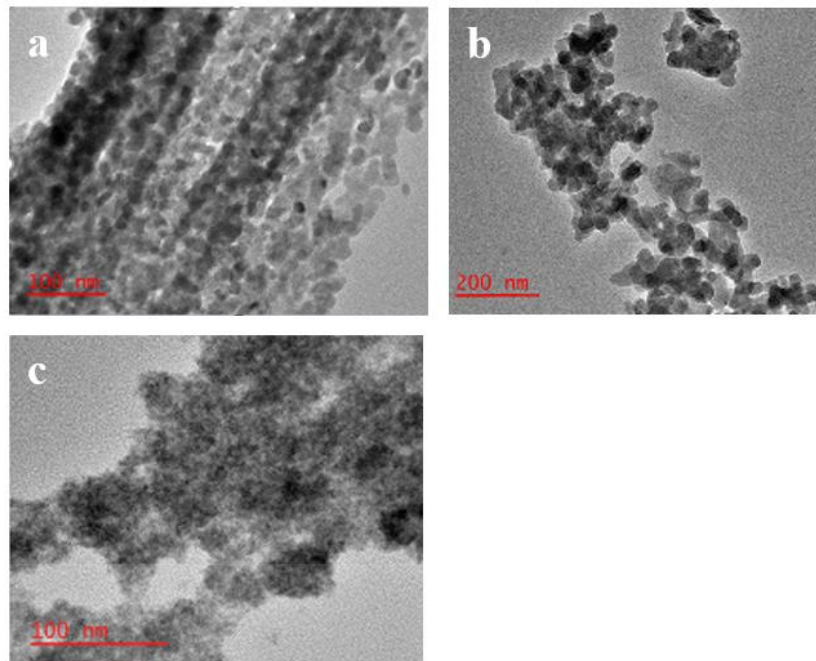
#### 5.4.2 Morphology of coal particles emitted during the flaming phase

During the flaming phase, particle diameter reduced compared to the ignition phase as in Figure 18a-d. The formation of the spherical particles during ignition is thought to be influenced by the release of polar compounds during smouldering fires. During flaming, fewer polar compounds, which affect particle growth, are emitted compared to the ignition stage. The particles observed using TEM indicate fused small particles with diffusion accretion chains with similar characteristics to soot (Figure 19a-c). Soot contains aggregates of small particles often in the diameter of less than 30 nm. A morphology similar to the present study was reported in Li *et al.* (2003). However, Li *et al.* (2003) investigated the morphology of particles in ageing smoke from the wood fire. It is important to note that in the current study the images were obtained from freshly produced particles.

A well-arranged morphology consisting of single particles can be seen in figure 19b. It was reported in previous literature that particle diameter decreases as the combustion conditions improve (Zhang *et al.*, 2012; Tiwari *et al.*, 2013; Masekamani *et al.*, 2018).

In the study by Li *et al.* (2003) and Posfai *et al.* (2004), there was an increase on the number of tar balls in samples collected far field, suggesting particle growth due to the condensation of organic gases or transformation due to collision with other organic atmospheric particles. In our study, we have established a mechanism to which particles transform as the combustion progresses. It was established that as coal heat up, it swells and cracks open. It is through the cracks that organic particles are released and depending on the ignition method and combustion condition, a brown to thick white plume is evident and may pass through a cold zone above the burning coal to the ambient (Wentzel *et al.*, 1999; Masekamani, Makonese and Annegarn, 2014; Makonese, 2015). It was demonstrated that as the combustion progresses fine particles often enriched with low volatile organic gases are emitted (Masekamani *et al.*, 2018). Furthermore, particle growth is as a result of the water injection in the coal and released as water vapour as the coal pyrolysis. Therefore, the establishment of accretion chains may be caused by coagulation of particles directly emitted from the flaming phase (Makonese, 2015; Makonese, Masekamani and Annegarn, 2017). As coal fully pyrolysis, fluffy micro-structures are formed and have the same characteristics as soot particles.





**Figure 19: TEM images of carbonaceous particles emitted during the flaming phase- a) Carbonaceous soot particle showing as aggregates, b) A more established and well-arranged accretion chain, c) fluffy micro-structure resembling the formation of soot.**

In summary, the results presented herein builds on the work by Makonese (2015) and Toth *et al.* (2014), which recommended further studies to reaffirm the existence of spherical organic particles, tarballs and related particle formation mechanisms in the domestic combustion process. We therefore, confirm that spherical organic particles with similar characteristics to tarballs are emitted as a consequence of smouldering combustion conditions. In this study, we have demonstrated that residential coal burning is a source of tarball like spherical organic particle emissions

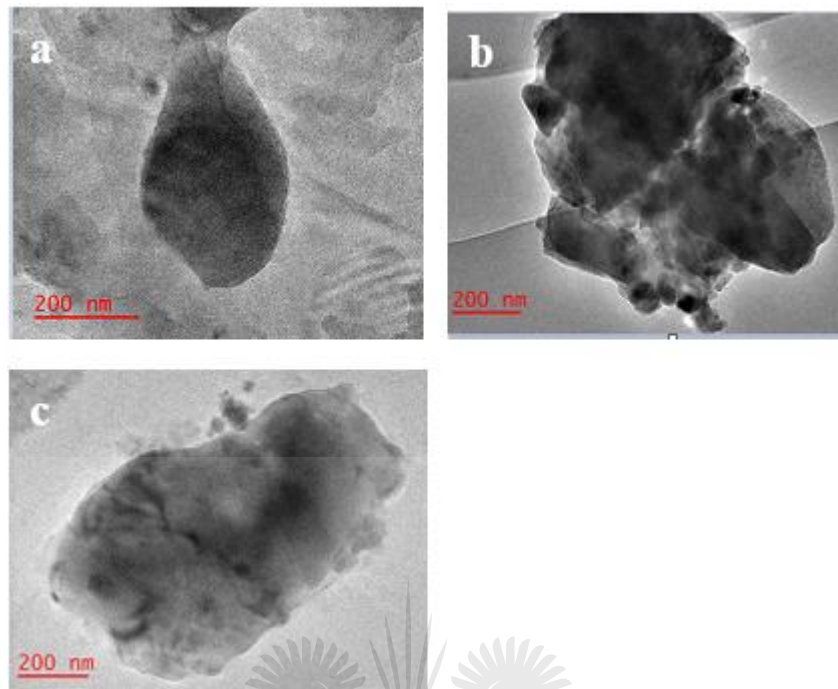
#### 5.4.3 Morphology of coal particles emitted during the coking phase

Figure 20 shows images of particles collected during the char burning stage of coal-combustion in a typical brazier. During the char-burning phase, as described in the literature, almost all volatile organic compounds have been released during the ignition and flaming phases (Masekameni *et al.*, 2014; Makonese *et al.*, 2017; Roden *et al.*, 2007). This results in the emission of non-carbonaceous matter, usually in the form of mineral particles from the burning char. In this stage, the fire burns uniformly in sufficient oxygen supply, and particles emitted during this stage are similar to ash. The mineral particles are irregular in shape and tend to be much bigger in diameter compared to soot and homogeneous spherical organic particles. According to Wang *et al.* (2009), these particles are composed of crucial mineral elements including Si, Ca, Al, Fe, Na, K, Mg, and P.

However, this study did not employ EDX to semi-quantitatively determine the composition of each mineral particle. It is recommended that further studies be carried out to determine the elemental composition of specific mineral particles emitted during the char burning stage of domestic fixed-bed coal combustion. This study has employed ICP-MS to ascertain the elemental contribution of



each combustion stage to the overall emissions of elements across the entire burn cycle (discussed in more detail in Section 5.3.4).



**Figure 20:** TEM images of particles emitted during the char burning phase- a) irregular structure of semi-spherical particles, b) evidence of mineral particles infused with small carbonaceous particles, c) A fully established macro-structure indicating the presence of non-water soluble compounds.

#### 5.4.4 Elemental analysis of coal combustion particles from three distinct combustion phases

Table 23 presents the ICP-MS results of selected trace elements collected during the three combustion phases (ignition, flaming, and char burning) and across the entire burn cycle. During the ignition phase calcium (Ca), silicon (Si), Iron (Fe), potassium (K) constituted the highest percentage released. The ICP-MS results, especially on the emission of Si and K, suggest a particle partitioning similar to previous studies (Hand *et al.*, 2005; Meij and te Winkel, 2007; Zhang *et al.*, 2018). The smoke particles with high silicon content can be used as a marker for coal combustion processes; while the smoke particles with high potassium suggest emissions from biomass burning.

**Table 23: Elemental composition results from ICP-MS analysis**

Combustion phase	Elements (µg/g)															
	Na	Mg	Al	Si	K	Ca	Ti	V	51	Cr	Mn	Fe	Co	Ni	Cu	63
Ignition	0.8	0.2	0.2	2.3	1.4	3.9	0.1	0.0	0.1	0.0	0.8	0.0	0.1	0.0	0.0	0.2
% contribution	8.3	2.3	2.0	22.5	13.8	38.4	0.7	0.0	1.4	0.2	7.5	0.1	0.5	0.1	2.2	
Flaming	0.9	0.4	2.0	3.8	3.2	1.6	0.1	0.0	0.3	0.1	2.6	0.0	0.0	0.0	1.1	





% contribution	5.3	2.7	12.5	23.3	20.0	9.9	0.9	0.0	1.6	0.4	16.0	0.1	0.1	0.2	7.0
Char burning	1.3	1.0	6.3	8.1	4.8	2.3	0.4	0.0	0.2	0.2	5.7	0.0	0.0	0.1	1.7
% contribution	4.1	3.1	19.7	25.3	14.9	7.3	1.1	0.0	0.6	0.5	17.9	0.0	0.1	0.2	5.3

During the ignition phase, both Si and K were high because wood was used as kindling to ignite the coal nuggets (Xu *et al.*, 2003). In the flaming phase, the percentage contribution of potassium is higher relative to the ignition and char burning phases. The increase of K during flaming is possibly due to the pyrolysis of the wood kindling. A noticeable decline in potassium percentage contribution can be seen during the char burning phase. For the marker of coal emissions, a relatively steady increase in Si emission confirms that the particles are from coal combustion. All trace elements emissions except Ca and K steadily increased as the combustion progressed. K and Ca emissions are thought to be associated with wood kindling, which often burns out in the second half of the flaming stage (Makonese *et al.*, 2014).

In previous studies, the elemental composition from coal-burning boilers/ furnaces was limited to fly ash, with little emphasis on the elemental composition of smoke emissions from various combustion phases (Yi *et al.*, 2008; Vejahati, Xu and Gupta, 2010; Silva *et al.*, 2012). Meij and Winkel (2009) argued that low volatile organic trace elements categorized in class one (i.e. Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, Th and Ti) are comparable in smoke and ash. During coal combustion, the minerals in the coal are deposited as bottom ash, and some are given off as fly ash (Lu *et al.*, 2017). The type of mineral elements released is related to the mineral content of the fuel (Table 24).

**Table 24: Comparing percentage contribution elemental species between smoke particles and the fuel**

ICP-MS Results		Fuel Analysis Results	
Element	% Contribution	Standard Method	% Contribution
Si	23.7	ASTM D4326	58.6
Al	11.4	ASTM D4326	27.6
Fe	13.8	ASTM D4326	6.6
Ti	0.9	ASTM D4326	0.8
Cr	1.2	ASTM D4326	0.6
Ca	18.5	ASTM D4326	2.3
Mg	2.7	ASTM D4326	0.8
Na	5.9	ASTM D4326	0.4
K	16.2	ASTM D4326	0.8



S	1.1	ASTM D4326	1.1
Mn	0.4	ASTM D4326	0.1

Results in Table 23 and Table 24 provided a comparison of the fuel burned composition and emitted trace elements. The particles emitted contained K; while there was a relatively low amount of K in the coal. This was expected as wood was used as kindling to ignite the coal. These results found traces of elements similar to those described or obtained in the ash by other studies (Meij and te Winkel, 2007; Makonese, 2015; Zhang *et al.*, 2018).

Table 25 shows the results of the percentage contributions of trace elements for the three combustion phases. With decreasing volatile matter from the burning fuel, mineral particles dominated the char burning phase. As expected, the bulk of the elements were emitted during the char burning phase relative to the flaming and ignition phases (Zhang *et al.*, 2018). This finding suggests that the majority of particles emitted during the ignition and flaming phases could be dominated by elements and volatile organic compounds (Zhou *et al.*, 2016). During the char burning phase, most non-water soluble trace elements are expected to be released.

**Table 25: percentage contribution of trace elements emitted per combustion phase**

Combustion phase	Total elements ( $\mu\text{g/g}$ )	% Contribution
Ignition	10.1	17
Flaming	16.2	28
Char burning	31.9	55
<b>Sum</b>	<b>58.2</b>	<b>100</b>

## 5.5 Conclusion

This study was conducted to examine the morphology and elemental characteristics of freshly emitted individual particles emitted at three distinct combustion phases in domestic packed-bed domestic coal combustion processes. Three types of particles were classified, viz., spherical organic particles with similar characteristics to tarballs, soot particles, and mineral particles. Spherical organic compounds were predominant in the ignition stage due to smouldering combustion conditions, while soot particles dominated the flaming stage. The identification of spherical organic particles is essential to understand how particles evolve once released into the atmosphere. Mineral particles were predominant in the char burning stage. Elemental composition analysis showed that the particles were rich in Si, K, Al, Fe, Ca, Zn, Na, Mg, and Ti depending on the combustion phase. The type of mineral elements released was related to the mineral content of the fuel.

This information is essential in updating emission inventory sources, understanding of radiation forcing potential and provide a basis for warming estimation. In addition to the morphology, the information on trace elements can play a role in source identification due to chemical signatures or emission markers. Both Si and K were high during the ignition phase indicating simultaneous combustion of wood and coal. In this case, wood was used as kindling. For the marker of coal



emissions, a relatively steady increase in Si emission confirmed across the entire combustion cycle indicated the particles were emitted from coal combustion.

### 5.6 Acknowledgement

This work was done in collaboration with several people or groups. Sincere appreciations to Mr Shalala Mgwambani and Mr Kevin Kasangana for their assistance during laboratory experiments. Mr Siyasanga Mpelane for assisting with TEM analysis. Extended appreciation to Mr. Philip Pieterse for assisting with ICP-MS analysis.





## CHAPTER SIX

*This chapter provide for the first time in South African context describe a methodology for risk assessment in coal burning areas. The section provides details on the carcinogenic and non-carcinogenic risks of exposure to BTEX concentrations emitted from residential coal burning in a defined exposure scenario. The cancer risk factor and the hazard quotient use in establishing the risk methodologies are well explained.*

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### 6. Risk assessment of BTEX concentration from the combustion of coal in a controlled laboratory environment

#### 6.1 Abstract

D-grade type coal was burned under simulated domestic practices in a controlled laboratory set-up, to characterize the emissions of volatile organic compounds (VOCs); namely, benzene, toluene, ethylbenzene, and xylenes (BTEX). Near-field concentrations were collected in a shack-like structure constructed using corrugated iron, simulating a traditional house found in informal settlements in South Africa (SA). Measurements were carried out using the Synspec Spectras GC955 real-time monitor over a three-hour burn cycle. The 3-hour average concentrations (in  $\mu\text{g}/\text{m}^3$ ) of benzene, toluene, ethylbenzene, p-xylene, and o-xylene were  $919 \pm 44$ ,  $2051 \pm 91$ ,  $3838 \pm 19$ ,  $4245 \pm 41$  and  $3576 \pm 49$ , respectively. The cancer risk for adult males and females in a typical SA household exposure scenario was found to be 1.1 and 1.2 respectively, which are 110- and 120-fold higher than the U.S. Environmental Protection Agency (EPA) designated risk severity indicator ( $1 \times 10^{-6}$ ). All four TEX (toluene, ethylbenzene, p-xylene and o-xylene) compounds recorded a Hazard Quotient (HQ) of less than 1, indicating a low risk of developing related non-carcinogenic health effects. The HQ for TEX ranged from 0.001 to 0.05, with toluene concentrations being the lowest, and ethylbenzene the highest. This study has demonstrated that domestic coal burning may be a significant source of BTEX emission exposure.

**Keywords:** coal; BTEX; hazardous air pollutants; domestic fuel burning

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#### 6.2 Introduction

The introduction of several chemicals into the atmosphere has been widely associated with increased health risks (Abbate *et al.*, 1993; Ahaghotu *et al.*, 2005). Anthropogenic sources of higher exposure to air pollutants are suggested to be attributed to industrial activities (Aksoy *et al.*, 1972; Annesi-Maesano *et al.*, 2013). Several studies have been conducted globally, investigating the emissions of



larger industrial activities such as power generation on the external environment (Atash, 2007; Atabi *et al.*, 2013). The mechanisms as to how pollutants are emitted and distributed are well understood, especially on larger stationary sources in developed countries and parts of developing Asia.

Globally, there is a growing concern regarding pollutant inventories to understand the primary sources of emissions and their impacts (Atkinson and Arey, 2003). There is an emerging body of knowledge which suggests that indoor household burning presents a significant threat to public health (Azuma, Uchiyama and Ikeda, 2007; Azari *et al.*, 2012) arising from lack of access to clean energy sources, which has been identified as a major contributor to local indoor air pollution (Badjagbo *et al.*, 2010; Balakrishnan, Cohen and Smith, 2014). The majority of households, especially in developing countries, rely on multiple energy sources combusted daily, using inefficient devices in poorly ventilated environments (Bond *et al.*, 1986; Bonjour *et al.*, 2013).

The emission of volatile organic compounds (VOCs) under these conditions may present an important class of pollutants as it has been associated with health and environmental impacts (Bruce, Perez-Padilla and Albalak, 2002; Bruinen De Bruin *et al.*, 2008; Borhani and Noorpoor, 2017). It is reported that VOCs, even at low concentrations, can produce several health effects, including nausea, eye, and throat irritation, the induction of asthma attacks, fatigue, dizziness, and mental confusion (Crump, 1996; Chikoto, 2009; Chang *et al.*, 2010; Durmusoglu, Taspinar and Karademir, 2010; Chen *et al.*, 2011). VOCs, in general, are quite numerous; however, the emphasis is given to mono-aromatic volatile organic compounds termed BTEX (benzene, toluene, ethylbenzene, and xylenes). This group of VOCs are often considered carcinogenic (Dutta *et al.*, 2009; IARC, 2012; Edokpolo, Yu and Connell, 2014; Marć, Zabiegała and Namieśnik, 2014). Mainly, benzene and ethylbenzene exposure are associated with an increased risk of leukemia and hematopoietic cancers (Edwards *et al.*, 2001; Edokpolo, Yu and Connell, 2015). Toluene and xylene are non-carcinogenic, but they may produce reproductive adverse effects; especially when exposures are chronic at low to high concentrations (Environmental Protection Agency, 2005).

Exposure inventories for BTEX is mainly in occupational environments, while less information is available for non-occupational settings (Gelman, Maszle and Alexeef, 1996; Ernstgård *et al.*, 2002; Gariazzo *et al.*, 2005; Garte *et al.*, 2008; Garg, 2011; Forouzanfar *et al.*, 2015). The sources of BTEX in residential areas are diverse, including domestic care products; lifestyle-related chemicals such as cigarette smoke; and combustion energy-related sources (Gordon *et al.*, 2014). It has also been suggested that the risk of exposure is higher in indoor environments relative to the outdoor environments (Haghighat, Lee and Ghaly, 2002; Guo *et al.*, 2003; Housing Development Agency HDA, 2013; GroundWork, 2016; Hazrati *et al.*, 2016; Hosny, Elghayish and Noweir, 2017).

Exposure to airborne pollutants is influenced by many factors, such as the emission rate at the source, air exchange rate, pollutant concentration and time spent indoors, and the meteorological conditions prevalent at the time of assessment (Haghighat, Lee and Ghaly, 2002; Gariazzo *et al.*, 2005; IARC, 2012; Gordon *et al.*, 2014). Children and the elderly are the most vulnerable groups, as they spend most of their time indoors and also due to a weaker immune system (IARC, 2012). The study conducted by



(Haghighat, Lee and Ghaly, 2002; Gariazzo *et al.*, 2005; Gordon *et al.*, 2014), have emphasized that infants and children are at greater risk than adults, due to their high metabolic and resting rate compared to adults. It was further found that children spend most of their time indoor next to their mothers. Thus, they are exposed to elevated concentrations of combustion pollutants during cooking and heating conditions (Crump, 1996).

In regulating exposure to toxic compounds on human health, many countries use risk assessments as a tool to determine the relative risk, and to develop action plans based on emissions or concentration. However, a risk assessment considers various factors in estimating the possibility of a biological response. Factors such as hazard source identification, exposed group, exposure pathway, the concentration of the contaminant, target organ, and the potential biological response dose, which might trigger a response, are investigated (Gariazzo *et al.*, 2005; IARC, 2012). Hematotoxicity and immunotoxicity have been widely used as indicators for the non-carcinogenic effects of benzene exposure (Jia, Batterman and Godwin, 2008; Katsoyiannis, Leva and Kotzias, 2008; IARC, 2012; Katsoyiannis *et al.*, 2012; Karachaliou *et al.*, 2016). Chronic exposure to benzene has been reported in several studies, and reviews indicating the risk of anemia, bone marrow hyperplasia, aplastic anemia, leukopenia, lymphocytopenia, thrombocytopenia, and pancytopenia have been shown (Katsoyiannis, Leva and Kotzias, 2008; Keretse *et al.*, 2008; Edokpolo, Yu and Connell, 2015).

Exposure to high concentrations of BTEX have been widely associated with several adverse health effect in countries such as USA, India, and China (Lee *et al.*, 2006; Katsoyiannis, Leva and Kotzias, 2008; Keretse *et al.*, 2008; Lan and Binh, 2012; Kumar *et al.*, 2014). Despite several human health effects reported elsewhere regarding exposure to BTEX, in South Africa, very few studies have been conducted to quantify indoor and environmental exposure to BTEX, especially from domestic activities where coal burning has been consistently linked to severe health effects (Lee *et al.*, 2002; Lim *et al.*, 2012). The present study aims to quantify the concentrations of BTEX from domestic coal burning process; and evaluate the potential health risks concerning with respect to cancer and non-cancer effects. The study uses experimental data on BTEX emission as proxies for near-field concentration, to estimate exposure mimicking the indoor use of coal in a brazier applicable in the South African informal settlements. Similar, studies conducted in this field mainly focused on the effect of fire ignition and ventilation on particulate matter and gaseous emissions (PM<sub>2.5</sub> and PM<sub>10</sub>) (Lin *et al.*, 2004; Bonjour *et al.*, 2013); while the study by (Makonese *et al.*, 2012; Makonese, 2015) investigated the effect of coal particle size and moisture on gaseous and particulate matter, respectively. The presentation of data as an emission factor provides little information on the concentration of the studied compounds, and further, it becomes difficult to use such information in health-related studies.

The selection of the combustion device (high-ventilation stove) and the fire ignition method (top-lit updraft) is based on the South African government air pollution reduction strategy that is applicable for informal settlements. The combustion of coal in a highly ventilated stove, ignited by using the top-lit updraft ignition method, has been reported in several studies, to reduce particulate emissions by margins by up to 80%. This is in comparison to a low-ventilated stove that is lit by using the





bottom-up draft (BLUD) ignition method (Lin *et al.*, 2004; Bonjour *et al.*, 2013; Makonese, 2015); while no significant difference in the gaseous emissions were found in studies by (Bonjour *et al.*, 2013; Makonese *et al.*, 2015a). Presently, epidemiological studies in South Africa use emission factor data to associate the exposure to health outcomes (Haghighat, Lee and Ghaly, 2002). Consequently, the use of an emission factor as a concentration has been interchangeably used as the same term in several studies in this field, which might complicate the interpretation of results (Lee *et al.*, 2002; Makonese *et al.*, 2012). However, despite such reductions reported on PM, very few studies have been carried out to investigate the emissions of gases, especially VOCs, due to their inherent health risks. Therefore, in this study, BTEX emissions are used as proxies to determine the concentration that can be used to determine the dose in different exposure scenarios.

The study hopes to assist in contributing to knowledge on domestic solid fuel burning technologies, and it might aid in supporting future epidemiological and other studies in South Africa, and in other low-to-medium income countries with domestic coal burning activities, using similar combustion technology. Also, it may be noted that this is the first study in a South African context that attempted to carry out a risk assessment on BTEX exposure that is applicable for informal settlement, according to the knowledge of the author.

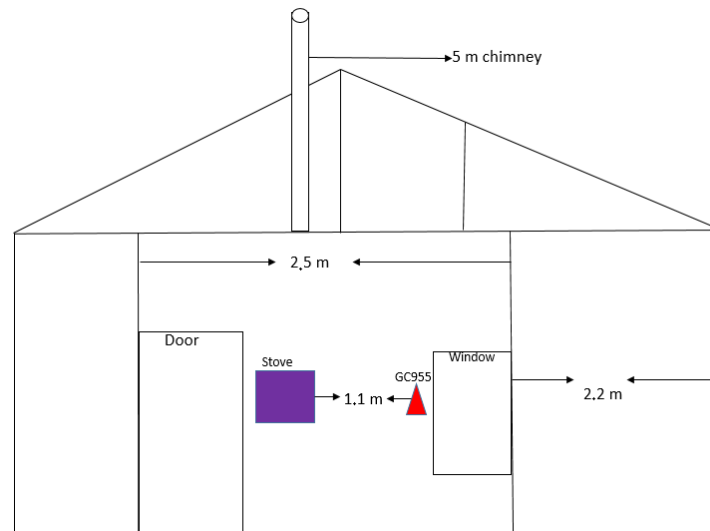
### 6.3 Materials and Methods

#### 6.3.1 BTEX Sampling Condition

BTEX compounds were sampled under laboratory conditions simulating community-based activities. The combustion laboratory was constructed from corrugated iron sheets and combustion materials included coal, wood kindling, and paper. The selection of the stove, known as brazier (*imbaula*), to fuel combination (top-lit updraft (TLUD) and high ventilated stove), was based on the government project roll-out program of the TLUD ignition method as an interim air pollution reduction strategy initiative, and the selection of high ventilated stoves was based on local studies which proved that the use of a high ventilated stove lit with TLUD leads to the reduction of emissions (Bonjour *et al.*, 2013; Makonese *et al.*, 2015a). Tests were performed over three hours, and further details on the burn sequences are provided in (Masekamani, Makonese and Annegarn, 2014; Makonese, 2015). The stove was lit by using the TLUD method in a high ventilated brazier. Further, details on the stove and fuel combination can be obtained in published literature, as contained in the references (Makonese, 2015; Makonese, Masekamani and Annegarn, 2016; Masondo *et al.*, 2016; Makonese *et al.*, 2017b).

The study was carried out at the University of Johannesburg's Sustainable Energy and Research Centre in South Africa. The stove and the GC955 sampling inlet were placed at the center of the combustion hut, respectively. The sampling location was made to mimic common practice with informal dwellers, where the stove is placed in the middle of the hut. The combustion laboratory was built to simulate a typical informal house, colloquially known as a shack, constructed using corrugated iron, with a small window (300 mm × 400 mm) and a standard door (840 mm × 1.8 m), as shown in Figure 21.





**Figure 21: Schematic diagram of a traditional corrugated iron house in a typical South African informal settlement, stove, and GC955 sampling inlet. (Not drawn to scale).**

### 6.3.2 Domestic Combustion Scenario in a South African Low-Income Settlement

Before stove ignition, all openings leading to the outside of the shack were closed/sealed, mimicking field-based practices. Nevertheless, it must be noted that air leaks could occur, since the sealing of openings were not comprehensive enough to contain all emitted pollutants, which might be similar to a typical shack. The stove was placed at the center of the combustion lab, and measurements were taken 1 m above the floor, and 1.2 m away from the stove, as shown in Figure 21. A domestic coal fire is generally associated with high heat generation, simultaneously increasing the indoor temperature significantly. Due to the sensitivity of the monitoring equipment, care was given to separate the experimental and the data capturing rooms. The detection device was placed in the analysis room next to the combustion laboratory. The sampling probe, 1.9 m in length, was used to draw the exhaust to the detection device/gas analyzer. The isolation or removal of the detection device from the hot environment was done to avoid similar challenges experienced during field monitoring in Moolla, Curtis and Knight. (2015), where the higher temperature led to the instrumentation malfunctioning, and a loss of data.

Samples were taken and averaged for each distinct time aggregate (15 minutes, 45 minutes, and two hours, to coincide with burn cycles). The first sample was taken from the time the fuel was lit until the establishment of the flame, i.e., the first 15 minutes of the combustion where the condition is smoldering (i.e., burning slowly with visible smoke but without flames) with insufficient air supply and a low fuel bed temperature; the next stage is when the fire is well-established and the combustion process is at the mixing stage and takes about 45 minutes. The last stage involved the combustion of char for ~120. The laboratory experiments were done three times per combustion time interval, where the average concentrations over three tests were used in the study.

### 6.3.3 BTEX Sampling Instruments

In the present study, five VOCs were monitored using Synspec Spectras gas chromatography (GC955, series 600, Groningen, Netherland). This instrument is widely used to monitor BTEX and



has been approved as per the service specification EN 14662-3. The samples were drawn in through the inlet feeder, operated at a flow rate of 5 mL/min, connected at the back of the instrument. A 37 mm filter was connected between the monitoring instrument and the inlet probe, to isolate or exclude foreign particles. Drawn in hydrocarbons are firstly pre-concentrated in the Tenax GR, where they were pre-heated and desorbed, and after that separated according to the columns. The instrument is coupled with a photoionizer detector (PID) that assists in increasing the sensitivity for benzene and other aromatic hydrocarbons. The running cycle can be from 15 minutes upwards, which can be adjusted and operated at a temperature of <70 °C. Helium was used as a carrier gas, and set at a pressure of 350 kPa, connected using Teflon tubing at a distance of 1.8 m (from the gas cylinder to the GC).

#### 6.4 Risk Assessment

BTEX emissions were monitored at near-field (inside the room, 1.2m away from the emitting source), and they were then used as room concentrations. In a typical coal-burning house in South Africa, coal stoves are often used indoors during the winter season between 18:00 and 21:00. This is due to the inherent heat production of the technology, while in summer, it is unlikely that the stove will be used indoors for either cooking or space heating. The winter period in South Africa is from June to August (equivalent to 92 days). During winter, all of the outlets leading to the external environment are closed, with the intention to contain all produced or radiated heat from the device. Due to the hazardous nature of coal and the associated carbon monoxide poisoning, households often extinguish the fire and remove the stove from the indoor spaces before going to bed (Makonese *et al.*, 2017b). We, therefore, used this scenario to estimate the exposure duration.

In general, we have conducted a risk assessment to estimate the potential exposure to BTEX from domestic coal burning, and similar to other studies, we used the data to assess the risk to human health (Kumar *et al.*, 2014; Marć, Zabiegała and Namieśnik, 2014; Masekameni, Makonese and Annegarn, 2014; Makonese, Masekameni and Annegarn, 2016). Risk assessment is a comprehensive process which includes hazard source identification, evaluation, characterization, and control, aiming at the prevention of possible health outcomes. Thus, this research has aimed at assessing both carcinogenic and non-carcinogenic potential risk by estimating the exposure to BTEX.

##### 6.4.1 Hazard Identification

During data collection, BTEX concentrations from the coal burning device were monitored. The focus of the monitoring was limited to BTEX emissions, due to their inherent carcinogenic and non-carcinogenic health impacts on the exposed groups. As mentioned earlier, benzene is classified as a Group A human carcinogenic, according to the U.S. Environmental Protection Agency (USEPA) (Masih *et al.*, 2016, 2017). Using the approach similar to the one described below, a lifetime exposure duration of 30 years was assumed for residential dwellers as a default value, based on the USEPA (Masih *et al.*, 2017). The common occupants in South African informal settlements are often unemployed individuals or those who fall in the low-income brackets. In the study conducted by (Mc Donald and Biswas, 2004; Masondo *et al.*, 2016), it was found that the majority of the households



live on an average income of R3500. Predominately, adult males and females reside in informal settlements, while there is only a small number of school-going children (McKenzie *et al.*, 2012). Informal settlements are often built closer to employment sites or in industrial zones (Midzenski *et al.*, 1992; Mc Donald and Biswas, 2004). The average age of dwellers was estimated to be 35 years, while the majority of shack owners are males, at 61% relative to females (McKenzie *et al.*, 2012). A small proportion of children below 18 years were recorded during a census in 2010, at 1% of the total dwellers in the informal sector (Midzenski *et al.*, 1992).

#### 6.4.2 Exposure Assessment

For the exposure assessment, we have considered an estimated dose, expressed as a chronic daily intake (mg/kg/day). Due to the inadequacy of available methodologies for determining the internal dose, we used a near-field breathing zone concentration for the exposure assessment. We assumed that the breathing zone concentration is equal to the near-field concentration, or the emission zone (Masih *et al.*, 2017). The driving factors in dose estimation were the exposure pathway (air), including the route of entry (inhalation), the frequency to which one is expected to be exposed, the duration of the exposure, and the population age group (Adults male and females). Since this was a laboratory-based study simulating the experience of residents, where information on population demographics is not present, the study adopted some of the parameters for the exposure scenario from the USEPA's risk assessment guidelines, and South African Statistics as in Table 26 (McKenzie *et al.*, 2012; Masih *et al.*, 2017).

**Table 26: Summary of the exposure scenario factors and values used in this study.**

Parameter	Description	Value	Unit
C	Room concentration	-	mg/m <sup>3</sup>
IR	Inhalation rate	20	m <sup>3</sup> /day
BW	Body weight	70 males/ 60 kg females	kg
ED	Exposure days	92 (3 hours per day)	Days/year
YE	Years of exposure	30 (Residential)	Years
AT	Years in lifetime	60 male/67 female	Years

The default inhalation rate, body weight, and residential exposure from U.S. Environmental Protection Agency (USEPA) (USEPA, 2004), while the male and female years in life were adopted from (StatsSA, 2017).

A dose-response relationship was used to estimate the potential biological response for each pollutant. Similar to (Moolla *et al.*, 2013; Moolla, Curtis and Knight, 2015), the average concentration for the entire burn cycle was used to calculate the chronic intake concentration. The chronic daily intake (CDI) (Equation 1) for both the carcinogenic and non-carcinogenic pollutants was calculated by using the values as shown in **Error! Reference source not found.** The average C DI<sub>year</sub> provides the estimated daily intake corresponding to an annual dose.

For the exposure assessment, we have considered the estimated dose, expressed as a chronic daily intake (mg/kg/day). Due to the inadequacy of available methodologies for determining the internal



dose, we used a near-field breathing zone concentration for the exposure assessment. We assumed that the breathing zone concentration is equal to the near-field concentration or emission zone (Masih *et al.*, 2017). The driving factors in dose estimation were exposure pathway (air), including the route of entry (inhalation), the frequency to which one is expected to be exposed, the duration of exposure, and the population age group (adult males and females). Since, this was a laboratory-based study simulating the experience of residents, where information on population demographics is not present, the study adopted some of the parameters for the exposure scenario from the USEPA's risk assessment guidelines and South African Statistics, as in **Error! Reference source not found.**

ADDIN CSL\_CITATION {"citationItems":[{"id":"ITEM-1","itemData":{"DOI":"10.1016/j.atmosenv.2016.09.067","ISBN":"1352-2310","ISSN":"18732844","PMID":"20614196","abstract":"BTEX are recognized for their contribution as toxic and carcinogenic human health effects, and enhancement of the global greenhouse effect. Thus, an investigation of ambient BTEX was conducted at selected locations in Gorakhpur for a span of one year in order to ascertain the contagion levels. The concentrations of BTEX were measured at four locations in the city of Gorakhpur, which covers residential, agricultural, roadside and industrial areas with the help of low volume sampler. The samples were extracted with carbon disulphide by occasional agitation and the aromatic fraction was subjected to GC-FID. The average concentration of total BTEX in all samples was 50.8 µg/m<sup>3</sup> and the total range was from 10.9 µg/m<sup>3</sup> to 208.1 µg/m<sup>3</sup> with the median of 44.8 µg/m<sup>3</sup>. The BTEX concentrations were found to be 27.8, 35.9, 65.6 and 68.6 µg/m<sup>3</sup> at residential, agricultural, roadside and industrial sites respectively. The maximum concentration of total BTEX was found to be 61.9 µg/m<sup>3</sup> in winter season, followed by 47.9 µg/m<sup>3</sup> in summer and 42.7 µg/m<sup>3</sup> in monsoon season. The industrial site (35%) had the highest BTEX contribution followed by roadside (33%), agricultural (18%) and residential site (14%). The concentration of BTEX decreased in the order toluene > benzene > ethylbenzene > xylene. The integrated lifetime cancer risk for benzene at all sites, and ethylbenzene at roadside area was found to be higher than the acceptable value and ranges between 1.0E-05 and 7.6E-06, although the non-cancer health risk was found to be within acceptable limit along all the sites. Risk assessment can be used as a tool to ascertain influence on public health and also to encourage risk preclusion approaches directed towards effectual reduction of adverse health effects."},"author":[{"dropping-particle":"","family":"Masih","given":"Amit","non-dropping-particle":"","parse-names":false,"suffix":""},{dropping-particle":"","family":"Lall","given":"Anurag S.","non-dropping-particle":"","parse-names":false,"suffix":""},{dropping-particle":"","family":"Taneja","given":"Ajay","non-dropping-particle":"","parse-names":false,"suffix":""},{dropping-particle":"","family":"Singhvi","given":"Raj","non-dropping-particle":"","parse-names":false,"suffix":""}],"container-title":"Atmospheric Environment","id":"ITEM-1","issued":{"date-parts":[["2016"]]},"page":"55-66","publisher":"Elsevier Ltd","title":"Inhalation exposure and related health risks of BTEX in ambient air at different microenvironments of a terai zone in north India","type":"article-journal","volume":"147"},"uris":["http://www.mendeley.com/documents/?uuid=6cfd9712-e589-"]



443d-aaa5-2ec117978d30"}],{"id":"ITEM-2", "itemData":{"DOI":"10.1016/j.scitotenv.2012.02.018", "ISBN":"0048-9697", "ISSN":"00489697", "PMID":"22444058", "abstract":"Background: Technological advances (e.g. directional drilling, hydraulic fracturing), have led to increases in unconventional natural gas development (NGD), raising questions about health impacts. Objectives: We estimated health risks for exposures to air emissions from a NGD project in Garfield County, Colorado with the objective of supporting risk prevention recommendations in a health impact assessment (HIA). Methods: We used EPA guidance to estimate chronic and subchronic non-cancer hazard indices and cancer risks from exposure to hydrocarbons for two populations: (1) residents living >1/2. mile from wells and (2) residents living ≤1/2. mile from wells. Results: Residents living ≤1/2. mile from wells are at greater risk for health effects from NGD than are residents living >1/2. mile from wells. Subchronic exposures to air pollutants during well completion activities present the greatest potential for health effects. The subchronic non-cancer hazard index (HI) of 5 for residents ≤1/2. mile from wells was driven primarily by exposure to trimethylbenzenes, xylenes, and aliphatic hydrocarbons. Chronic HIs were 1 and 0.4. for residents ≤1/2. mile from wells and >1/2. mile from wells, respectively. Cumulative cancer risks were 10 in a million and 6 in a million for residents living ≤1/2. mile and >1/2. mile from wells, respectively, with benzene as the major contributor to the risk. Conclusions: Risk assessment can be used in HIAs to direct health risk prevention strategies. Risk management approaches should focus on reducing exposures to emissions during well completions. These preliminary results indicate that health effects resulting from air emissions during unconventional NGD warrant further study. Prospective studies should focus on health effects associated with air pollution. © 2012 Elsevier B.V.", "author":[{"dropping-particle":"","family":"McKenzie", "given":"Lisa M.", "non-dropping-particle":"","parse-names":false, "suffix":""}, {"dropping-particle":"","family":"Witter", "given":"Roxana Z.", "non-dropping-particle":"","parse-names":false, "suffix":""}, {"dropping-particle":"","family":"Newman", "given":"Lee S.", "non-dropping-particle":"","parse-names":false, "suffix":""}, {"dropping-particle":"","family":"Adgate", "given":"John L.", "non-dropping-particle":"","parse-names":false, "suffix":""}], "container-title":"Science of the Total Environment", "id":"ITEM-2", "issued":{"date-parts":[["2012"]]}, "page":"79-87", "publisher":"Elsevier B.V.", "title":"Human health risk assessment of air emissions from development of unconventional natural gas resources", "type":"article-journal", "volume":"424"}, {"uris":["http://www.mendeley.com/documents/?uuiid=9c7f63cd-3968-438e-a32d-a7048f767d94"]}], "mendeley":{"formattedCitation":"(McKenzie *et al.*, 2012; Masih *et al.*, 2016)", "plainTextFormattedCitation":"(McKenzie et al., 2012; Masih et al., 2016)", "previouslyFormattedCitation":"(McKenzie *et al.*, 2012; Masih *et al.*, 2016)", "properties":{"noteIndex":0}, "schema":"https://github.com/citation-style-language/schema/raw/master/csl-citation.json"}(McKenzie *et al.*, 2012; Masih *et al.*, 2016):

$$CDI(\text{ averaged daily intake}) = \frac{C \times CF \times IR \times ED}{BW \times AT} \quad \text{Equation 22}$$





The chronic daily intake (CDI) determination was used as a basis for risk assessment calculation, similar to the current risk assessment studies (Midzenski *et al.*, 1992; Pandit, Srivastava and Mahan Rao, 2001; Nazaroff and Weschler, 2004; Moolla *et al.*, 2013; Moolla, Curtis and Knight, 2015), where:

CDI is the chronic (averaged) daily intake over a year (mg/kg/day);

C is the breathing zone concentration of BTEX in ( $\mu\text{g}/\text{m}^3$ ), derived from three identical experiments taken over a 3-hour burn cycle;

CF is the concentration conversion ( $\text{mg}/\mu\text{g} = 0.001$  or  $1 \mu\text{g}$ ) factor;

IR is the inhalation rate (default in adults,  $20 \text{ m}^3/\text{day}$ );

ED is the exposure duration as in Equation 23 (11.5 days);

BW is the average body weight (70 kg, 60 kg for male and female adults, respectively);

AT is the number of days per year.

However, the default values as contained in **Error! Reference source not found.** assume a daily intake of a pollutant over 24-hours are often constant, and can be extrapolated over a year. In our study, there was a variation on the exposure duration, due to the activity data available (i.e. nature of how households use the technology).

In Equation 22, we determined a procedure that was used to estimate the exposure duration in a typical winter period in South Africa. The limitation of this method was that the exposure duration seeks to be confined to the coal combustion period (3 hours), without taking into account the exposure resulting from accumulated concentrations that might take time to vent from indoor to outdoor. Since this was a laboratory study, the authors intentionally left out other variables in an ordinary house in informal settlements. Such variables may include the ventilation rate, or the building envelope, which influences the air ratio, taking into account the exchange from inside to outside. The exposure duration obtained in Equation 23 indicates a daily average exposure, given that the exposure involves a 3-hour duration over a 92 days in a year from this source (to allow for a full season).

$$ED = \frac{\text{Actual exposure duration}}{24 \text{ hours}} \times 92 \text{ days} \quad \text{Equation 23}$$

where:

ED is the exposure duration (days/year);

Actual exposure duration is the 3-hour combustion period;

24 hours is the total hours in a day; and

92 days is the number of exposure days in a year.

In Equation 22, an average annual chronic daily intake was determined. However, for the risk assessment, a cumulative lifetime exposure concentration intake needs to be completed. In Equation 24, the average 30-years chronic dose ( $\text{CDI}_{30 \text{ year}}$ ) is calculated by using the 30-year residential exposure duration, as obtained from USEPA default value:

$$\text{CDI}(30 \text{ years dose}) = \sum \frac{\text{CDI} \times 365 \times \text{YE}}{60 / 67} \quad \text{Equation 24}$$

where:

CDI is the cumulative average 30-year dose (mg/kg/day);

CDI is the chronic daily intake (mg/kg);

YE is estimated lifetime residential exposure duration, which is equivalent to 30 years;

365 is the total number of days in a year;

60 is the male life expectancy, and 67 is the female life expectancy in South Africa.



Therefore, for a risk assessment calculation, we need the adjusted lifetime chronic daily intake ( $CDI_{adj.}$ ), taking in to account the life expectancy for a female and a male South African adult resident. In Equation 4, we calculated the average  $CDI_{adj.}$ , assuming a lifetime daily dose intake.

$$CDI_{adj.} = \frac{CDI \text{ (30 years average dose)}}{\text{life expectancy in days}} \quad \text{Equation 25}$$

We assume that the average chronic daily adjusted dose over a lifetime amongst female and male adults will better simplify the risk assessment calculation, as in Equation 4.

#### 2.4.3. Toxicity Assessment and Risk Characterization

Risk characterization is the last step in the risk assessment, which provides information on the hazard status of a contaminant or pollutant (Paustenbach, Bass and Price, 1993). For both carcinogenic and non-carcinogenic effects, the use of an inhalation reference concentration (RfC) assists in determining the health risks that are associated with an exposed population. For carcinogenic pollutants (such as benzene), the use of the slope factor can be used to estimate the relative risk. Furthermore, the use of the inhalation reference concentration was based on toxicological/occupational epidemiology studies, focusing on several health outcomes, such as cellular necrosis. In summary, the inhalation reference concentration (RfC) is an estimated daily human inhalation exposure that is suggested not to cause a health effect in a lifetime (Rao *et al.*, 2007; Katsoyiannis, Leva and Kotzias, 2008; Keretsetse *et al.*, 2008).

A lifetime inhalation dose of BTEX was determined, based on the absolute lymphocyte count (ALC) at the adjusted benchmark concentration (BMCL) of  $8.2 \text{ mg/m}^3$ . The inhalation benzene lifetime exposure was therefore calculated, using the benchmark dose modeling, and it was found to be  $0.03 \text{ mg/m}^3$ . The value of  $0.03 \text{ mg/m}^3$  was thus described to be the RfC for benzene (Paxton, 1996). The non-carcinogenic effects of the TEX inhalation reference concentration for each pollutant were used to calculate the hazard quotient, as in Table 27 (Epa, 1987; U.S. Environmental Protection Agency, 2003; Environmental Protection Agency, 2005).

Since benzene is the only confirmed human carcinogenic (category A) pollutant amongst the BTEX pollutants, the slope factor was used to calculate the cancer risk. We have adopted the methodology for calculating the cancer risk, using the slope factor from previous similar studies (Schneider *et al.*, 2001; Rao *et al.*, 2007; Katsoyiannis, Leva and Kotzias, 2008; Katsoyiannis *et al.*, 2012; Karachaliou *et al.*, 2016). It must be noted that there is no threshold for carcinogenic compounds. Therefore, the use of reference levels is used as a guide, to probably support a decision. In our study, we used both designated cancer severity indicators for one case:  $1 \times 10^{-4}$  and  $1 \times 10^{-6}$  (Tunsaringkarn *et al.*, 2012; Masih *et al.*, 2016, 2017).

**Table 27: Benzene slope factor, and toluene, ethylbenzene, and xylenes (TEX) inhalation reference values.**

Chemical	Inhalation Reference Concentration (RfC)	Inhalation Slope Factor (SF)
	( $\text{mg/m}^3$ )	( $\text{mg/kg/day}$ ) <sup>-1</sup>
Benzene	0.03	0.0273
Toluene	5	N/A
Ethylbenzene	1	N/A





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O-xylene	0.1	N/A
P-xylene	0.1	N/A

---

For carcinogenic pollutants, it must be noted that there is no safe threshold. Therefore, the risk characterization followed was similar to the method that was described by the USEPA's Risk Assessment Guidance for Superfund (USEPA, 2004). We thus calculated the risk of cancer by using Equation 26 (Tunsaringkarn, *et al.*, 2012; Edokpolo, Yu and Connell, 2015).

$$CR = CDI_{adj} \times SF \quad \text{Equation 26}$$

where:

SF is the slope factor for the carcinogenic pollutant (0.0273);

CR is the carcinogenic risk; and

$CDI_{adj}$  is the cumulative lifetime adjusted dose (Equation 25) over an estimated exposure in a lifetime of 60 or 67 years for male and female adult, respectively.

Therefore, a cancer risk  $>1 \times 10^{-6}$  and  $1 \times 10^{-4}$  means that there are carcinogenic effects of concern, while a cancer risk  $<1 \times 10^{-6}$  and  $<1 \times 10^{-4}$  means that there is a designated cancer severity indicator.

For non-carcinogenic pollutants, a hazard quotient (HQ) was used to estimate the potential health risk of the dwellers. Where a HQ value is greater than one, it is regarded as a hazardous exposure; a HQ value of less than one means that there is a low probability of developing the associated health effects. In Equation 6, the procedure for calculating HQ is shown.

$$HQ = CDI_{adj} \cdot ((mg/kg)/day) / (RfC(mg/m^3) \times 20m^3 / (70 kg)) \quad \text{Equation 27}$$

where:

HQ is the hazard quotient;

$CDI_{adj}$  is the cumulative intake dose;

RfC is the reference;

$20 m^3$  is the default value for the average adult daily air volume; and

70 kg is the average body weight for a male adult, while 60 kg will be used for female adult.

## 6.5 Quality Control

All monitoring instruments were maintained and operated according to the manufacturer's instructions, and returned to the suppliers for factory calibration at prescribed intervals. Before each test, the gas probes were cleaned by means of compressed air, to remove any residue from prior tests, which might negatively affect the next results. All monitoring instruments were zero-checked, according to the manufacturer's instructions, before monitoring/sample collection.

The GC955 instrument was tested in accordance with the EMC directive 89/336/EMC, test specification EN 50081-1:1991 and EN 50082-2: 1994. The monitoring instruments were calibrated before use (calibration was done in the range of 0 to 10 ppb). Quality control checks were conducted during or after the monitoring campaign, and a correction factor of 2 ppb and 4 ppb for benzene and toluene, respectively, were used, to counter systematic under-sampling of the instrument.

Background concentrations were accounted for, as BTEX from outside the testing facility could infiltrate the testing laboratory and contribute to the final concentration readings. The instrument was run for 30 minutes before the three-hour testing duration, and the background concentrations were calculated, using Equation 28.



$$C_{combustion} = C_{activity} - C_{without} \quad \text{Equation 28}$$

where:

the  $C_{combustion}$  is the final concentration;

$C_{activity}$  is the actual sample collected while the BTEX generating activity was taking place + background concentration;

$C_{without}$  is the concentration of BTEX obtained in the absence of the activity under investigation.

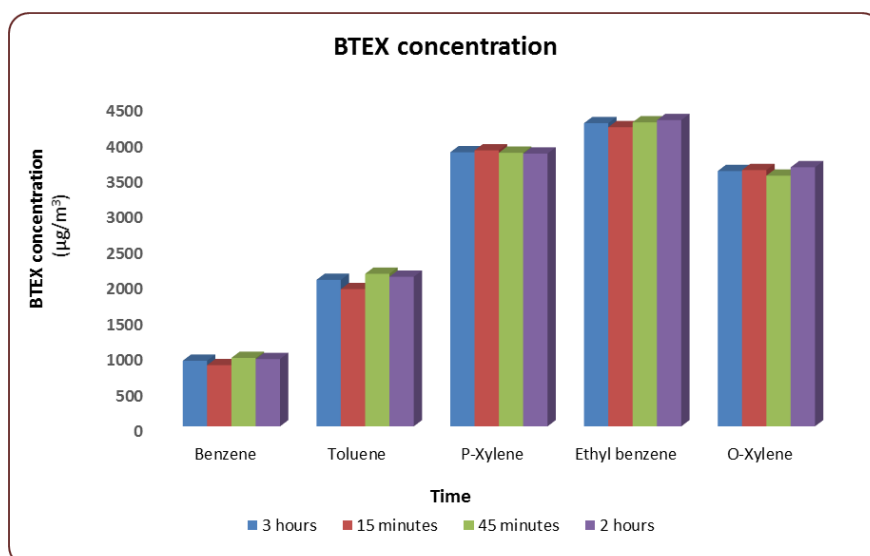
In experimental studies, the use of the equipment, which are accurately calibrated, is an important quality control feature, and it assists in the reduction of the uncertainty of the dataset. Trial runs before the actual tests might help in the identification of instruments malfunctioning, and detection signal faults.

## 6.6 Results and Discussion

### 6.6.1 BTEX Concentration under Laboratory Conditions

The results from the coal combustion brazier under a laboratory-controlled environment are presented herein. In Figure 22, the time aggregates concentration for each BTEX compound is presented as an average concentration for the specified time (15, 45, and 120 minutes). Using a 3-hour average concentration, benzene was the lowest emitted VOC, while ethylbenzene was found to be the most highly emitted pollutant throughout the combustion cycle. From the results, it was shown that the relative concentration of the BTEX species was consistent throughout the entire 3 hours burn cycle.

Benzene and ethylbenzene concentration steadily increases, as the combustion process progresses. The minimum concentration, as depicted from Figure 22, is associated with the first 15 minutes of the combustion. Contrary to benzene and ethylbenzene, the concentrations of toluene and xylene were the highest at 45 minutes and 120 minutes, respectively. The observed BTEX profile reported in our study was similar to the one presented in the study by (Ernstgård *et al.*, 2002). However, the observed differences may require additional statistical analyses, to provide more details on the concentration variation at different time intervals. Unfortunately, the differences in BTEX concentration at different time aggregates were not within the scope of the current project. The implication of this finding indicates for the first time in the South African domestic sector that the determination of domestic coal combustion as might be an important source of BTEX in indoor air spaces.



**Figure 22: Time series of benzene, toluene, ethylbenzene, and xylenes (BTEX) concentration for a 3-hour combustion cycle.**

In Table 28, BTEX near-field room concentrations are presented for replicates of three experiments as averages over a 3-hour burn cycle. Benzene concentration ranged from 857–942  $\mu\text{g}/\text{m}^3$ , with a mean of 919  $\mu\text{g}/\text{m}^3$  over a three-hour burn cycle. The benzene concentration observed in our study varied from those conducted in India, where the concentrations have ranged from 44–167  $\mu\text{g}/\text{m}^3$  (Lee *et al.*, 2006). However, in the latter study, the emissions of benzene were associated with kerosene burning, which is different from our present study. Lower values of indoor benzene concentrations were also reported in several other studies where the concentration ranged from 0.7–7.2  $\mu\text{g}/\text{m}^3$  (USEPA, 2003; USEPA, 2004; Tunsaringkarn *et al.*, 2012). In the Hong Kong Special Administrative Region of China, similar low benzene indoor levels were reported, which were mainly associated with vehicular emissions at 0.5–4.4  $\mu\text{g}/\text{m}^3$  (Guo *et al.*, 2004; Lin *et al.*, 2004). However, studies conducted in petrol refineries reported that concentrations for benzene varied between 12–17,000  $\mu\text{g}/\text{m}^3$ , with the highest exposure concentrations being mainly from refinery workers working in indoor environments (Atkinson and Arey, 2003; Lin *et al.*, 2004; Edokpolo, Yu and Connell, 2015).

Toluene, ethylbenzene, and xylenes (TEX) results are comparable with several studies conducted elsewhere; however, most of these studies were conducted in occupational settings (Gelman, Maszle and Alexeef, 1996; Keretsetse *et al.*, 2008; Moolla *et al.*, 2013; Edokpolo, Yu and Connell, 2015). The ethylbenzene concentration measured in our study was higher than the concentration reported elsewhere (Moolla, Curtis and Knight, 2015). In the study by Moolla *et al.* (2015), the focus was on an occupational setting, which is suggested to be highly contaminated, relative to the residential environment. In this light, it can be seen that the exposure in a residential environment might be higher than in occupational settings, especially where coal burning is used as a primary energy source. In summary, our toluene, ethyl-benzene, and xylenes were not the highest concentrations reported in the field. Despite the TEX results being found to be lower compared to the highest reported concentrations in other studies, it is suggested that they may present several health effects,



even at lower concentrations (Vitali *et al.*, 2006; Wang, Ang and Tade, 2007; Al Zabadi *et al.*, 2008; Wah, Yu and Kim, 2010).

**Table 28: Time-weighted average BTEX room concentrations.**

Duration	Benzene ( $\mu\text{g}/\text{m}^3$ ) <i>n</i> = 3	Toluene ( $\mu\text{g}/\text{m}^3$ ) <i>n</i> = 3	P-Xylene ( $\mu\text{g}/\text{m}^3$ ) <i>n</i> = 3	Ethylbenzene ( $\mu\text{g}/\text{m}^3$ ) <i>n</i> = 3	O-Xylene ( $\mu\text{g}/\text{m}^3$ ) <i>n</i> = 3
15 minutes	857 $\pm$ 32.40	1922 $\pm$ 127.5	3864 $\pm$ 48.33	4189 $\pm$ 87.11	3589 $\pm$ 48.74
45 minutes	958 $\pm$ 5.73	2137 $\pm$ 27.04	3831 $\pm$ 15.12	4257 $\pm$ 31.26	3510 $\pm$ 13.66
2 hours	942 $\pm$ 13.36	2095 $\pm$ 36.59	3819 $\pm$ 9.60	4288 $\pm$ 91.51	3628 $\pm$ 9.42
3 hours					
Average concentrations	919 $\pm$ 44	2051 $\pm$ 93	3838 $\pm$ 19.04	4245 $\pm$ 41.13	3576 $\pm$ 49

In Table 29, we investigated a percentage contribution of individual BTEX compounds. From the total BTEX indoor air concentration, benzene was found to have contributed less at 6%, while ethyl benzene was the highest, at 29%. Fairly comparable percentage contributions between P-xylene and O-xylene were observed at 26 and 25, respectively. However, despite benzene being the least quantified VOC, it is worrying, given its hazardous nature to human health. Toluene was found to be the lowest contributed VOC amongst the TEX, at 14%.

**Table 29: Percentage contribution of each BTEX pollutant, averaged over a 3-hour burn cycle ignited in a high ventilated stove (HIGH) and ignited using the top-lit updraft method (TLUD).**

Pollutant	Ignition Stove ventilation	Concentration ( $\mu\text{g}/\text{m}^3$ ) <i>n</i> = 3	Contribution %
Benzene	TLUD	919 $\pm$ 44	6
	HIGH		
Toluene	TLUD	2051 $\pm$ 93	14
	HIGH		
P-Xylene	TLUD	3838 $\pm$ 19.04	26
	HIGH		
Ethyl benzene	TLUD	4245 $\pm$ 41.13	29
	HIGH		
O-Xylene	TLUD	3576 $\pm$ 49	25

#### 6.6.2 Potential Health Risk Analysis of BTEX

Results presented in Table 30 and Table 31 depict the carcinogenic and non-carcinogenic risks of BTEX exposure from domestic coal burning for adult females and males, respectively. The determination of risks associated with BTEX was achieved when using the cancer risk for the carcinogenic compound (benzene), while the non-carcinogenic effects of TEX were determined by calculating the hazard quotient, as shown in Equation 26 and Equation 27, respectively. The cancer risk for adult females and males were determined to be  $1.2 \times 10^{-4}$  and  $1.1 \times 10^{-4}$ , respectively. The cancer risk for females was found to be higher than that of males. This finding suggests that women will be more vulnerable than men, even though the exposure concentration is the same. As shown in Table 30, the cancer risk for women suggests that 120 people will be at risk of cancer per million



people in the exposed population. Furthermore, in Table 31, the results show that 110 men per million people exposed will be at risk of carcinogenic health effects. In both exposure scenarios (male and female), the cancer risk was found to be higher than the acceptable risk levels of  $1 \times 10^{-6}$  and  $1 \times 10^{-4}$ .

**Table 30: Carcinogenic and non-carcinogenic risks for adult females.**

Pollutant	Average concentration	CDI <sub>year</sub>	CDI <sub>30 year</sub>	CDI <sub>adj.</sub>	CR	HQ	CR/10 <sup>6</sup>	CR/10 <sup>4</sup>
	µg/m <sup>3</sup>	mg/kg/day	mg/kg/day	mg/kg/day				
Benzene	919	0.0097	$1.06 \times 10^2$	$4.32 \times 10^{-3}$	$1.2 \times 10^{-4}$	N/A	120	1
Toluene	2051	0.0215	$2.36 \times 10^2$	$9.64 \times 10^{-3}$	N/A	0.001	N/A	N/A
P-Xylene	3838	0.0403	$4.41 \times 10^2$	$1.73 \times 10^{-2}$	N/A	0.050	N/A	N/A
Ethylbenzene	4245	0.0446	$4.88 \times 10^2$	$2.00 \times 10^{-2}$	N/A	0.006	N/A	N/A
O-Xylene	3576	0.0376	$4.11 \times 10^2$	$1.68 \times 10^{-2}$	N/A	0.049	N/A	N/A

CDI<sub>year</sub>: the estimated daily intake corresponding to an annual dose; CDI<sub>30 year</sub>: cumulative average 30-year dose; CDI<sub>adj.</sub> is the cumulative intake dose; CR: carcinogenic risk; HQ: hazard quotient.

**Table 31: Carcinogenic and non-carcinogenic risks for adult males.**

Pollutant	Average concentration	CDI <sub>year</sub>	CDI <sub>30 year</sub>	CDI <sub>adj.</sub>	CR	HQ	CR/1E <sup>6</sup>	CR/1E <sup>4</sup>
	µg/m <sup>3</sup>	mg/kg/day	mg/kg/day	mg/kg/day				
Benzene	919	0.0083	$9.06 \times 10$	$3.70 \times 10^{-3}$	$1.1E \times 10^{-4}$	N/A	110	1
Toluene	2051	0.0185	$2.02 \times 10^2$	$8.27 \times 10^{-3}$	N/A	<0.001	N/A	N/A
P-Xylene	3838	0.0345	$3.78 \times 10^2$	$1.55 \times 10^{-2}$	N/A	0.045	N/A	N/A
Ethyl benzene	4245	0.0382	$4.18 \times 10^2$	$1.71 \times 10^{-2}$	N/A	0.005	N/A	N/A
O-Xylene	3576	0.0322	$3.52 \times 10^2$	$1.44 \times 10^{-2}$	N/A	0.042	N/A	N/A

The cancer risks for adult females and males were determined with reference to the female/male body weights (default value from USEPA, 2010) and life expectancies (StatsSA, 2017), as in **Error! Reference source not found.** The cancer risks in adult females and males were found to be 120- and 110-fold higher than the designated cancer severity indicator of  $1E^{-6}$ , respectively. These findings confirm those reported by (WHO, 2018; World Bank, 2018), where 17% of premature lung cancer deaths in adults were found to be attributable to exposure to carcinogens from household air pollution caused by cooking with kerosene or solid fuels, such as wood, charcoal, or coal and the risk for women was higher, due to their role in food preparation.

For non-carcinogenic health effects, a hazard quotient was used to determine the risk. A hazard quotient of greater than one was used as a reference value; whereby, a value greater than one indicated a higher probability of contracting a related health effect. For both adult males and females, the hazard quotient was found to be below 1 for the TEX. Toluene indicated the lowest hazard quotient, while ethylbenzene was potentially found to have the highest hazard quotient, at a value of 0.05. The results presented in our study indicate that there is a lower probability of non-carcinogenic health effects as a result of exposure to domestic coal combustion technology, as described in this study.

Despite the non-carcinogenic effects rating a hazard quotient of less than one, this might change significantly, especially in households where coal burning devices are used indoors for longer durations. This includes overstretched winter periods, and prolonged exposure durations, based on



activity. For instance, in some households, especially during winter, this type of technology can be used to warm for the entire day time (06:00 to 18:00), and for some part of the night period (18:00 to 21:00). This implies that exposure to TEX from this combustion activity may significantly vary from one household to the other, depending on the case scenarios used.

### 6.7 Study Limitations

In the absence of field exposure data, the results presented herein had several limitations.

The individual information used for risk assessment is average person default values. As it is known that there are no average people in the world, this might significantly affect the accuracy of risk determination. Individuals vary based on the biological make-up, which might influence parameters such as the breathing rate, and moreover, the exposure scenario. Furthermore, we used average values to overlook the issue of individual susceptibility, which might affect the risk score. Also, we used a room concentration to assess the risk, assuming that a three-hour exposure at near-field breathing zone is the average exposure duration. The influence of pollutants leakage was not addressed, where there might be loss due to leakages. The BTEX concentration reported in this study was obtained from a laboratory environment, which might vary from field concentrations.

Despite these limitations, this study has shown that exposure to domestic coal combustion pollutants may lead to the risk of a carcinogenic effect, while non-carcinogenic effects were found to be unlikely. However, it must be noted that the results presented herein were on an experimental laboratory study, where several variables that might influence stove to fuel performance were controlled. Such performance determinants includes the stove operational method, the fire ignition method, the coal particle size, the moisture content, and the coal grade (Bonjour *et al.*, 2013; Masekameni, Makonese and Annegarn, 2014; Makonese, 2015; Masondo *et al.*, 2016).

### 6.8 Conclusions

The study attempted to quantify the BTEX concentration from domestic coal combustion in a brazier, simulating its use in South African informal settlements. Based on the results presented in this study, it can be concluded that domestic coal burning might be a significant source of BTEX in indoor spaces. The results showed a constant concentration of BTEX throughout the combustion cycle of 3 hours.

The study further attempted to utilize a breathing zone near-field BTEX concentration, as averaged over a 3-hour burning cycle in adult females and males, to estimate the carcinogenic and non-carcinogenic health effects, simulating practices in informal settlements. The cancer risks were found to be 110- to 120-fold higher than the designated cancer severity indicator of  $1 \times 10^{-6}$ .

The health risk assessment of TEX, through calculating the hazard quotient, was below the reference value of 1; indicating a potentially low exposure to these pollutants, and possibly a reduced risk of the associated health effects. The lessons drawn from this experimental laboratory study suggest the need for further studies in this field to have an improved understanding of exposure scenarios, for





informed risk characterization from this source. This study presented the first risk assessment arising from domestic coal burning activities in a laboratory environment, while mimicking field practices that are relevant to the South African situation.

Notably, risk assessment is a comprehensive and iterative process for assessing the relative risk for several exposure scenarios. It must be understood that the risk assessment has several uncertainties, the accuracy of the results depends on the correct risk identification and use of accurate exposure information. Despite all uncertainties in our experiments, we attempted to ensure that the exposure scenarios were accurately defined.

Furthermore, this study has proven that the use of a high ventilated stove and the top-lit updraft might not have a significant effect on the reduction of BTEX, relative to what the technology is reportedly capable of (i.e., the reduction of particulate matter by 80%). However, this study was not intended to carry out a comparative assessment on emissions reduction by using different technologies (stove ventilation and ignition method); such a comparison might be useful in future projects/studies.

In summary, the use of a high ventilated stove and the TLUD ignition method may not be a useful household indoor air pollution intervention, due to the inherent carcinogenic risk. Therefore, other clean energy alternatives may be exploited and be introduced in these settlements, to improve indoor air quality.

**Author Contributions:** D.M. conceptualized and prepared the manuscript. He also experimented and wrote up of the paper. R.M. developed the methodology for data analysis. She further analyzed the data and assisted in the editing of the manuscript. M.G. edited the manuscript and validated methodology for risk assessment. D.B. supervised the data analysis process, interpretation, and the presentation of arguments, and assisted in the editing of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.



## CHAPTER SEVEN

*This chapter provides information on particle toxicity and cellular uptake using in vitro studies. The methodology for particle collection, removal, cell culturing, cell preparation, cell treatment and analysis are provided in this chapter. The health implication from thesis processes are explained, and recommendations to reduce harm from similar exposures are presented.*

*Manuscript in preparation for submission in Particle and Fibre Toxicology Journal*

### 7. Toxicity and cellular uptake of smoke particles generated from residential coal burning braziers on bronchial epithelial cells

#### 7.1 Abstract

Smoke particles from residential coal burning brazier were collected on polycarbonate filters at three distinct combustion phases (i.e. ignition, flaming and char burning). The study aimed to investigate the cytotoxicity and particle cellular uptake of coal smoke combustion particles on the bronchial epithelial cells. Bronchial epithelial cells (BEAS- 2B) were cultured in aseptic conditions and incubated at 37 °C and 5% CO<sub>2</sub>. Cytotoxicity assay was performed on the xCELLigence to determine the cytotoxicity of suspended at four different concentrations (20 µg/ml, 60 µg/ml, 100 µg/ml, 150 µg/ml). Dark-field and hyperspectral imaging were employed to confirm the uptake of coal combustion smoke particles. Images confirming particle cellular uptake were captured with CytoViva on the dried up EZ-slides. Smoke particles collected at the distinct combustion stages (ignition, flaming and char-burning) induced toxicity with an increase in the concentration of suspended particles. Particles from the three phases were toxic to the cells after 48-hours of incubation/ treatment. However, particles collected from individual combustion phases did not seem to induce toxicity in the bronchial epithelial cells at low particle concentration. Results of cellular uptake using CytoViva showed that particles from the three phases were found in the cells after 2-hours of cell treatment. It can be concluded that regardless of the combustion phase, the toxicity of combustion smoke particles from residential coal burning braziers depends on particle concentration. However, further studies are needed to develop our understanding regarding particle evolution, exposure and toxicity.

**Keywords:** BEAS- 2B, cytotoxicity; coal smoke particles; xCELLigence



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## 7.2 Introduction

Residential solid fuel burning is a significant source of fine particles emissions at the domestic levels, especially in the developing world (Zhang *et al.*, 2012; Tiwari *et al.*, 2014; Masekameni *et al.*, 2018). It is reported that low-temperature combustion process emits copious amounts of health damaging pollutants such as polycyclic aromatic hydrocarbons and toxic elements (Jalava *et al.*, 2005, 2010). In South Africa, the majority of households despite being electrified, depend on either wood, coal or combination of the two for cooking and space heating (Balmer, 2007; Kimemia *et al.*, 2013).

Consequently, the combustion of coal and wood fuels is often done using poorly vented and non-chimney stoves (Wentzel *et al.*, 1999; Madubansi and Shackleton, 2006; Le Roux, Zunckel and McCormick, 2009). Also, the cooking space occupied by low-income households often lacks ventilation, leading to poor indoor to outdoor air exchange. Therefore, emissions of health damaging pollutants are expected to be higher indoors than outdoors (Muller *et al.*, 2003; Usmani, Biddiscombe and Barnes, 2005; Barnes *et al.*, 2009).

Several epidemiological studies have associated exposure to fine particulate matter (PM) from solid fuel burning with cardiovascular and respiratory illnesses, and mortality (Boman *et al.*, 2003; Naeher *et al.*, 2007; Forouzanfar *et al.*, 2015). Furthermore, studies have suggested that there is an association between fine PM exposure from combustion sources and pre-mature deaths (Gordon *et al.*, 2014; Forouzanfar *et al.*, 2015). Despite prevalence information on exposure induced health outcomes, there is a paucity of data on the mechanisms regarding exposure to combustion particles leading to the development of certain diseases (Kocbach *et al.*, 2005, 2006; Kocbach Bølling *et al.*, 2009).

Due to fewer toxicological studies being carried out on residential exposure, epidemiological studies often report the association between exposure and related diseases with a high level of uncertainty (Muller *et al.*, 2003; GroundWork, 2016). Moreover, the lack of toxicity data leads to inadequate justification of source exposure pathways and diseases development (Monn and Becker, 1999; Becker, Soukup and Gallagher, 2002; Jalava *et al.*, 2010).

Inhalation remains an important exposure route of entry when dealing with airborne contaminants. Several studies have been carried out using bronchial epithelial cells, studying the toxicity of wood smoke particles (Boman *et al.*, 2003; Naeher *et al.*, 2007). Experimental studies using in vivo methods found that exposure to transition metals from fine particles caused inflammation and interfere with the defence functioning of macrophage cells in rodents (Monn and Becker, 1999; Becker, Soukup and Gallagher, 2002; Kocbach Bølling *et al.*, 2009).

The potency of fine particles from combustion processes is suggested to be highly influenced by the physical and chemical properties of the particle, particle diameter exposure duration and human biological make-up (Kocbach *et al.*, 2008; Ghio *et al.*, 2012). The combustion condition and burning phase influence the physicochemical properties of combustion particles. Previously it has been demonstrated that the combustion process varies as the fire ages (Kocbach *et al.*, 2006). During the



early stage, often termed the ignition phase, low-temperature conditions prevail leading to the release of semi-volatile organic compounds (Makonese *et al.*, 2017a). The ignition phase is followed by the flaming stage, which is associated with visible flames. In this stage, residual volatile matter burns at sufficient temperature releasing less visible smoke particles. The coking / char-burning phase involves the burning of the carbon matrix making up the fuel (Fitzpatrick *et al.*, 2007). During the coking phase, it is suggested that particles that are emitted contain high levels of oxygenated organic compounds while particles from the ignition phase are dominated by organic emissions particularly those with levoglucosan mass spectral signatures (Schneider *et al.*, 2006; Weimer *et al.*, 2008).

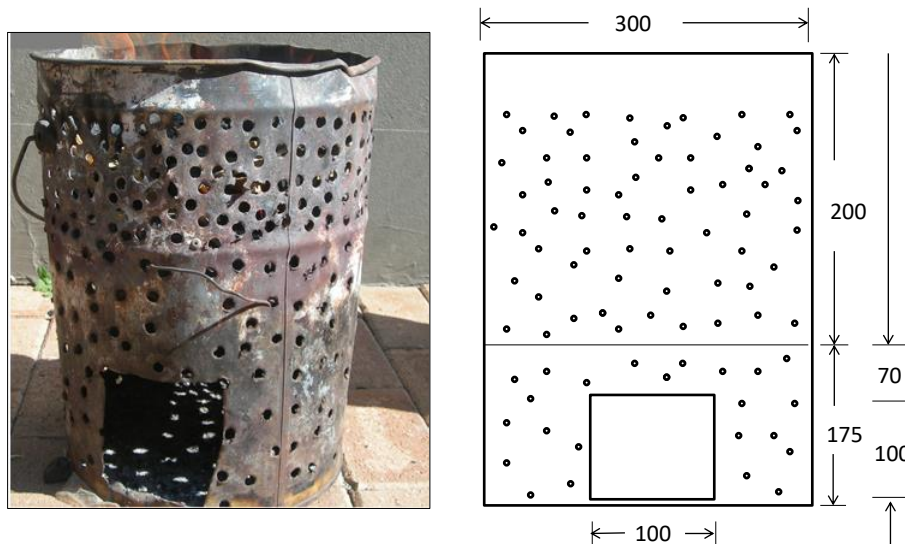
Limited toxicity studies carried out on wood particles suggest that the toxicity of fine particles largely depends on the stove type and ventilation rate but not the combustion phase (Schwartländer *et al.*, 2011; Bølling *et al.*, 2012). On the contrary, other studies have indicated that the toxicity of combustion particles is influenced by the combustion phase (Fitzpatrick *et al.*, 2007; Weimer *et al.*, 2008; Johnson *et al.*, 2011; Boman *et al.*, 2017). On the other hand, some studies focused on the effect of particle size on the biological response and found no difference in the response (Hetland *et al.*, 2005; Jalava *et al.*, 2006, 2010; Schwarze *et al.*, 2006).

To understand the toxicity of fine particles from residential coal burning, this study for the first in South African context aimed to study the biological response of bronchial epithelial cells following exposure to coal burning smoke particles emitted from three distinct combustion phases (i.e. ignition, flaming and coking/ char-burning), and across the entire burn cycle. The study intended to extend existing limited knowledge on the influence of combustion phase on particle toxicity as reported in previous studies where the focus was on biomass burning (Fitzpatrick *et al.*, 2007; Jalava *et al.*, 2010; Bølling *et al.*, 2012).

### 7.3 Materials and Methods

#### 7.3.1 Coal combustion setting and stove used during the experiment

The study was carried out in a laboratory environment where several factors could be kept constant. A high ventilation stove as shown in Figure 23, was used for the experiment. The stove is made of a 25 l, recyclable metal bucket (see Makonese, 2015 for more details). The stove was placed at the center of the combustion hut (See Masekamani *et al.*, 2018 for details regarding the hut). The combustion hut was designed in a manner which mimicked a common dwelling occupied by South African coal-burning low-income community. A D-grade coal purchased from Slater mine in Witbank, South Africa was combusted in a high ventilation stove with a top-lit updraft (TLUD).



**Figure 23: A photographic and schematic representation of a high ventilation field procured optimized brazier stove used in the experiments (Not drawn to scale – dimensions are in mm)**

### 7.3.2 Fuel used and ignition method

The type of fuel used during the laboratory evaluations had to be similar to the fuel available in the community. This was done so that the results obtained from these experiments could resemble life scenario in the targeted communities. Otherwise, it will have been pointless to test the stoves using fuel unavailable in the targeted communities.

Different factors such as the ignition method, fire preparation, stove ventilation and coal grade consistent with using solid fuel were acknowledged and accounted for during the testing procedures. The stove was set using ~35 g of paper, ~400 g of wood kindling and ~ 4 000 g of coal. The same mass of wood and paper was used for all tests for consistent operation and ease of comparison of the results. During the TLUD ignition method, the fuel ordering entailed placing 2 500 g of coal on the grate followed by the kindling (i.e. paper (35 g), wood (400 g)). The kindling was then ignited, after which the remaining 1 500 g of coal was added on top of the burning kindling. Further details on the stove to fuel combinations, including the determination of the combustion phases can be referred to in previous publications (Masekamani, Makonese and Annegarn, 2014; Makonese, 2015; Masondo *et al.*, 2016).

### 7.4 Sampling of particles

A gravimetric sampling technique was used to collect particulate matter at various combustion phases (i.e. ignition, flaming and coking/ char-burning). The ignition phase was limited to the first 20 minutes of combustion, flaming was the next 40 minutes while the coking phase was the last 2 hours of combustion (see Makonese *et al.*, 2017a; Makonese, Masekamani and Annegarn, 2017 for more details on the separation of combustion phases). Polycarbonate membrane filters (37  $\mu\text{m}$  in diameter and pore size of 0.8  $\mu\text{m}$ ) were inserted in a cassette attached to the Gillian pump to collect particles. A 2.5  $\mu\text{m}$  cutoff cyclone with a 50% efficiency was used to separate fine particles. The filters were





conditioned in a weighing room overnight before the filters were weighed for the sampling campaign. The filters with embedded particles were conditioned again overnight under similar conditions before being weighed to determine the possibility of mass loss or gain due to environmental conditions. The weighing room temperature ranged between 22 – 25 °C and humidity of 35 % (Jalava *et al.*, 2010). In order to obtain sufficient particles for toxicological study, each filter was exposed to particles 3 times for each combustion phase.

#### 7.4.1 Particle removal

Sample filters embedded with smoke particles and blank filters were transferred to a 100 ml glass beakers containing 10 ml of methanol each. The beaker was wide enough to avoid cutting or subdividing the filters. Filters were faced down in the glass beaker and suspended on methanol. Removal of particles from the filters was completed using a sonication technique in a water bath for 60 minutes (Jalava *et al.*, 2005). Particles suspended in methanol were transferred to a 50 ml centrifuge tube and then centrifuged at 5000 rpm for 45 minutes. The suspended particles in the methanol formed a pellet that settled at the bottom of the centrifuge tube. The residual methanol containing PM was evaporated IN a rotatory evaporator (Labcon, model FSI-SP08, Labex PTY, Johannesburg, South Africa), operated at 38 °C and 50 rpm. Dry particles collected per combustion phase were suspended at each sample centrifuge tube using 3 ml of Roswell Park Memorial Institute (RPMI) 1640 Medium supplemented with 1% l-glutamine, 1% penicillin streptomycin and 10% FBS (Pakkanen *et al.*, 2001). The RPMI media with the suspended particles was sonicated in a water bath for 30 minutes, to ensure that particles does not settle at the bottom of the tube (Kocbach *et al.*, 2006).

A final concentration of particles per volume was determined for each sample centrifuge tube. Four different concentrations (20, 40, 80, 150 µg/ml) of particles per combustion phase was used for cellular exposure assessment experiment. A total of three independent duplicates were completed for each combustion phase. A single negative and positive control at each plate was used in order to check for possible contaminations.

#### 7.4.2 Cell culture for cytotoxicity

Cytotoxicity assay was performed on the xCELLigence to determine the cytotoxicity of combustion particles. A cell titration experiment was carried out prior to the cytotoxicity assay to test cell proliferation. A 50 µl of cell culture media (RPMI) was added to each well of the E-plate, which comprised of 90 wells, and left in the biosafety cabinet for 30 minutes for the plate to equilibrate. A background scan was performed on the xCELLigence where no cells were present in the wells for one minute to check for possible contamination in the medium. A 100 µl of cell suspension was added to each well and left for 30 minutes in the biosafety cabinet to allow sufficient time for cells to settle uniformly on the bottom of each well. A Scan was performed on the E-Plate for each well every 15 minutes for 24-hour period.

After 24-hour cell incubation period, cells were treated with 50 µl of suspended particles collected from three combustion phases (ignition, flaming and char-burning/ coking) in each well at four different concentrations (20 µg/ml, 60 µg/ml, 100 µg/ml, 150 µg/ml). Two wells were treated with





media without cell suspension and were used as controls. An xCELLigence scan was performed for every minute for the first 2 hours and then after every 15 minutes for the remainder of the experiment. Cell cytotoxicity was performed after 48 hours of scanning, where the cell index (CI) was used as a determining factor for cytotoxicity.

#### 7.4.3 Cell culture for cellular uptake

Human bronchial epithelial cell lines BEAS-2B were cultured in a 75 cm<sup>2</sup> flask and incubated at 37 °C, and 5% CO<sub>2</sub>. At a confluence of above 80% and viability of above 90%, the cells were seeded at 2 x 10E<sup>4</sup> cells per well in an eight well EZ-slide. The culture media used for sub-culturing was RPMI 1640 supplemented with 1% l-glutamine, 1% penicillin streptomycin and 10% FBS (Jalava *et al.*, 2006). The cells were left to grow over 24 hours before the cellular uptake experiment (Vetten *et al.*, 2013).

#### 7.4.4 Cellular uptake

After treatment, the culture media was removed, and the washing process commenced. The slides were washed three times with 200 µl of RPMI media and 200µ PBS, sequentially. The Cells were then fixed with 4% formaldehyde in Tris/HCl at 4°C for 15 min on an EZ-slide, then washed and air dried. Fixing of cells on the slides prevents cells from being washed away and movements during imaging. Coverslips were immobilised onto slides with Kaiser's gelatin (10 µl per 2 blocks), and allowed to dry overnight. After the slides had dried out, images were captured with CytoViva.

#### 7.4.5 Statistical analysis

An F-Test for the null hypothesis that two normal populations have the same variance was used in the data analyses. This test can be used in practice, with care, particularly when a quick check is required, and is subject to associated diagnostic checking. The F-Test can be used to 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). A p-value >0.05 indicates that the variances are the same; a p value <0.05 indicates that the variances are unequal. A two-tailed student T-test (at 95% confidence level) was used for statistical evaluation of the cytotoxicity and cellular uptake of smoke particles for the three combustion phases. For this study, a significant number meant that the P Value was less than 5% (p<0.05); a number that was not significant meant that the p-value was higher than 5% (p>0.05).

#### 7.4.6 Quality control

The preparation of filters, cell culturing and exposure assessments were carried out in a sterile laboratory environment. A set of standard operating procedures (SOPs) were followed for each laboratory experiment. Before cell culturing, the responsible technician for the cellular exposure assessment experiment was trained by a competent medical scientist and assigned a competency signing off. Also, the work was performed under the supervision of senior laboratory personnel to ensure adherence to SOPs.

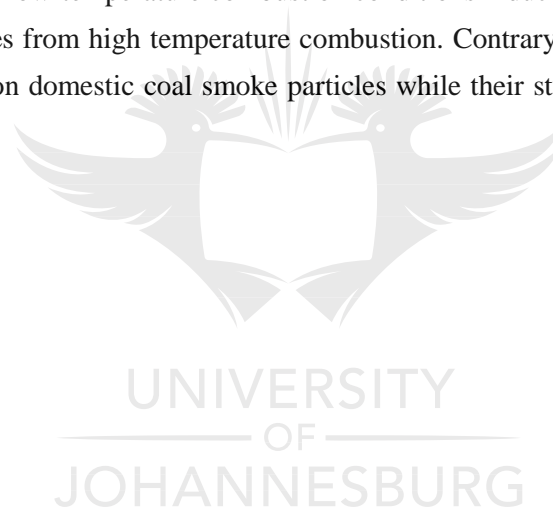


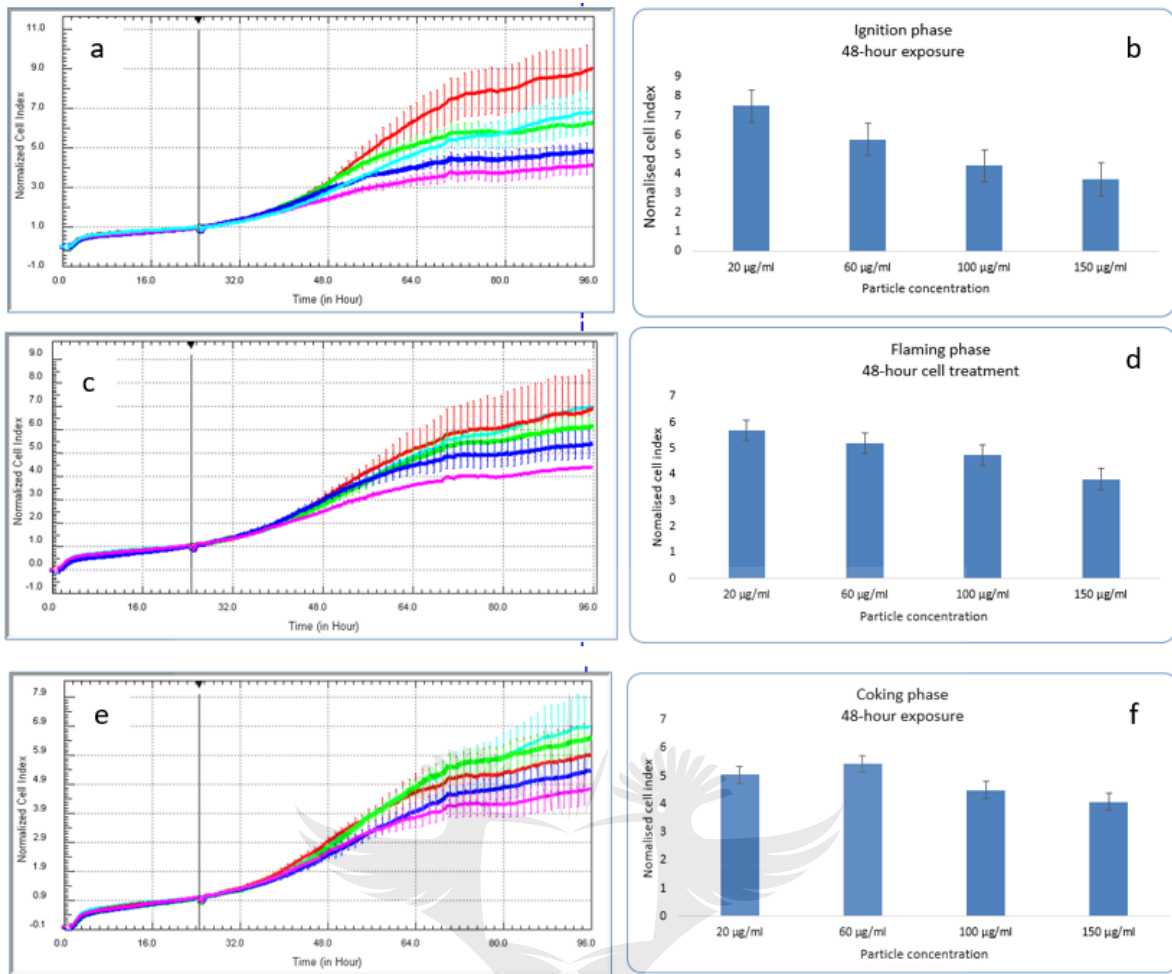
## 7.5 Results and Discussion

### 7.5.1 Cytotoxicity assay

In Figure 24, cytotoxicity results on BEAS-2B bronchial epithelial cell lines obtained from the xCELLigence analysis are presented as averages of three replicates for each concentration and combustion. In Figure 24 (a, c and e) real-time data series results indicate that the cell response to particulate matter exposure takes place after 48- hours. Before 48-hours after exposing the cells to particles from coal combustion smoke, the cells did not show any response. For the three combustion phases toxicity was highest at high concentrations (150  $\mu\text{g/ml}$ ). For both the ignition and flaming phases, an increase in particle concentration was directly proportional to an increase in cell toxicity (Figure 24b and c). However, for the coking phase, cell toxicity does not seem to vary with a change in particle concentration (Figure 24e and f)

The results presented in this study are similar to findings in Bølling *et al.* (2012) ) that cytotoxicity of particles depends on the combustion conditions. Bølling *et al.* (2012) found that after 40 hours of exposure particles from low-temperature combustion conditions induced the toxicity of the exposed cells relative to particles from high temperature combustion. Contrary to Bølling *et al.* (2012), the present study focused on domestic coal smoke particles while their study focused on wood smoke particles.





**Figure 24: Viability of bronchial epithelial cells (BEAS- 2B) exposed to particles from the ignition (a and b) = 20, 60, 100 and 150 150 µg/ml), flaming (c and d)= 20, 60, 100 and 150 150 µg/ml) and coking phase (e and f) = 20, 60, 100 and 150 µg/ml). NB\* red= untreated control, light blue= cell treatment at 20 µg/ml, green= cell treatment at 60 µg/ml, dark blue=cell treatment at 100 µg/ml and pink= cell treatment at 150 µg/ml.**

During the flaming phase, the viability of particles declined with an increase in dosage. However, the toxicity of the particles during this stage seem to be lower compared to the ignition phase. This finding was expected since during the flaming phase the combustion conditions are relatively better compared to smouldering fires (Schneider *et al.*, 2001; Weimer *et al.*, 2008). There is a need to further investigate whether particle diameter and composition induce cell toxicity across all combustion phases. Nevertheless, the results of this studies further owe to whether the toxicity might be influenced by particle diameter and the physicochemical properties, since the response seem to be dose depended for all the combustion phases (Jalava *et al.*, 2010).

#### 7.5.2 Statistical significance of particle induced toxicity as a function of concentration

The results shown in Table 32, provide statistical information on the effect of particle concentration (60, 100 and 150 µg/ml) on toxicity. From the results, during the ignition and coking phase there was a statistical significant difference in cell viability due to an increase of particle concentration from 60 µg/ml and 100 µg/ml; 60 µg/ml and 150 µg/ml. However, at the same combustion phase, there



was no statistical significant difference in the toxicity of cells when the particle concentration increases from 100 µg/ml to 150 µg/ml. Similar concentrations have been previously found to be toxic in wood burning studies (Jalava *et al.*, 2005, 2010; Kocbach *et al.*, 2008; Kocbach Bølling *et al.*, 2009).

During the flaming phase, results showed statistically significant differences in cell viability when the concentration was increased from 60 to 150 µg/ml. There were no statistically significant differences in cell toxicity between 60 and 100 µg/ml PM concentrations, and between the 100 and 150 µg/ml PM concentrations (Table 32). However, a maximum of 35% toxicity at the ignition phase (highest and lowest concentration) was established, followed by a 26% and 25% toxicity for the flaming and coking phases, respectively.

**Table 32: Toxicity of combustion smoke particles as a function of dose**

Combustion phase	Concentration µg/ml	CI N=3	F-test	T-test	Viability reduction	Sig @
					%	95%
<b>Ignition</b>	60	5,74 ± 0,09	0,07	0,01	20	Yes
	100	4,40 ± 0,48				
	60	5,74 ± 0,09	0,16	<0,01	35	Yes
	150	3,71 ± 0,30				
	100	4,40 ± 0,48	0,55	0,10	16	No
	150	3,71 ± 0,30				
<b>Flaming</b>	60	5,20 ± 0,40	0,87	0,28	8	No
	100	4,76 ± 0,46				
	60	5,20 ± 0,40	0,75	0,02	26	Yes
	150	3,85 ± 0,52				
	100	4,76 ± 0,46	0,88	0,08	19	No
	150	3,85 ± 0,52				
<b>Coking</b>	60	5,45 ± 0,40	0,89	0,04	18	Yes
	100	4,45 ± 0,44				
	60	5,45 ± 0,40	0,85	0,02	25	Yes
	150	4,07 ± 0,46				
	100	4,45 ± 0,44	0,96	0,35	9	No
	150	4,07 ± 0,46				

### 7.5.3 Statistical significance of particle induced toxicity as a function of the combustion phase

Table 33 presents, statistical analysis of the toxicity of residential coal combustion smoke as a function of the concentration of particles emitted at three distinct combustion phases (i.e. ignition, flaming and coking). From the Table, it can be seen that there were no statistically significant differences in the cell index between combustion phases. This result is in agreement with previous studies on the same theme (see Pakkanen *et al.*, 2001; Kocbach *et al.*, 2005, 2008; Bølling *et al.*, 2012). Results of this study are in disagreement to findings by Fitzpatrick *et al.* (2007), Weimer *et al.* (2008) and Boman *et al.* (2017) who found that the cell index differed as a function of the combustion phase.



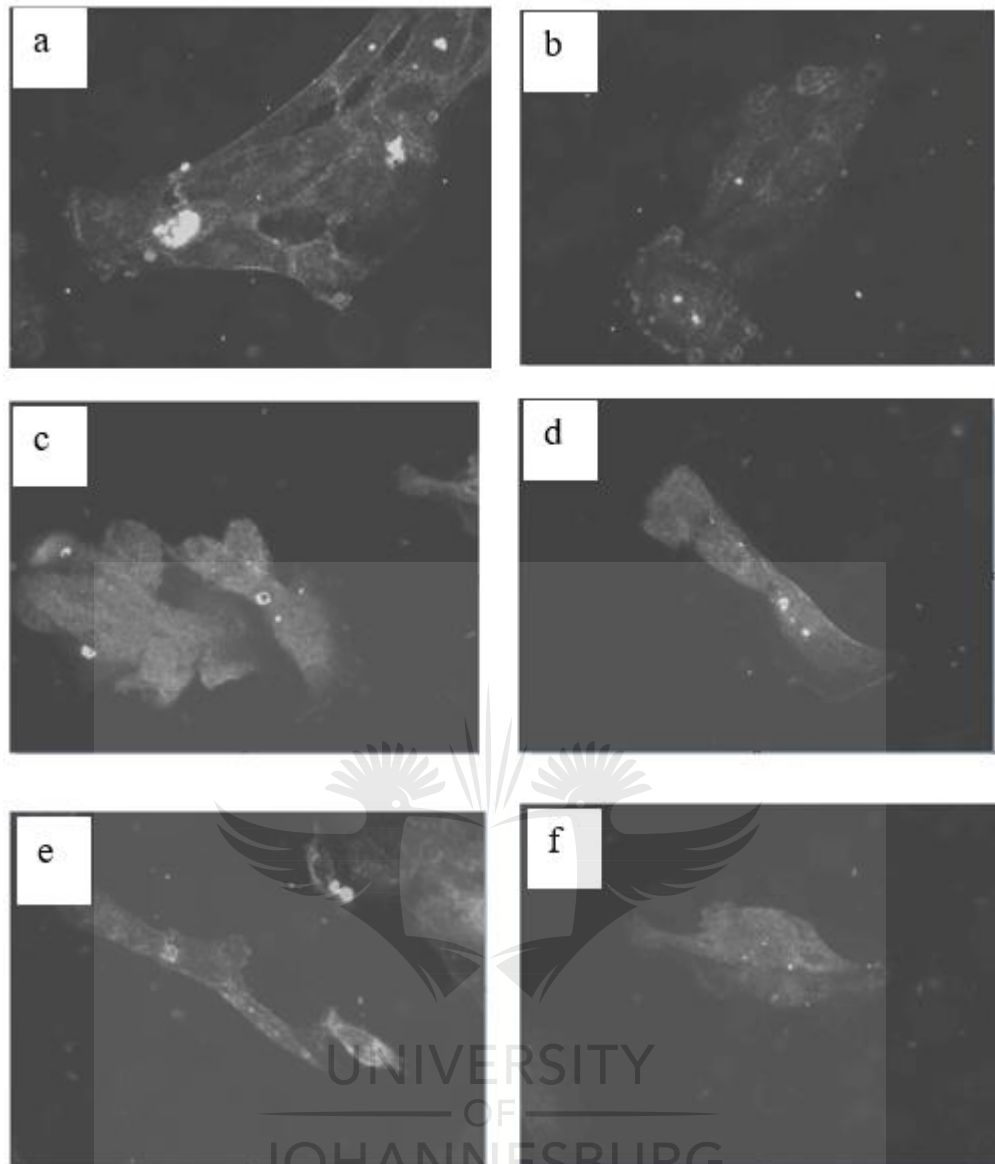
**Table 33: Toxicity of combustion smoke particles as a function of the combustion phase**

Concentration µg/ml	Combustion phase	Cell index N=3	F-test	T-test	Sig @ 95%
<b>Ignition</b>	Ignition	5,74 ± 0,09	0,09	0,09	No
	Flaming	5,20 ± 0,40			
	Ignition	5,74 ± 0,09	0,10	0,28	No
	Coking	5,45 ± 0,40			
	Flaming	5,20 ± 0,40	0,98	0,49	No
	Coking	5,45 ± 0,40			
<b>Flaming</b>	Ignition	4,40 ± 0,48	0,95	0,41	No
	Flaming	4,76 ± 0,46			
	Ignition	4,40 ± 0,48	0,91	0,90	No
	Coking	4,45 ± 0,44			
	Flaming	4,76 ± 0,46	0,96	0,45	No
	Coking	4,45 ± 0,44			
<b>Coking</b>	Ignition	3,71 ± 0,30	0,50	0,70	No
	Flaming	3,85 ± 0,52			
	Ignition	3,71 ± 0,30	0,59	0,32	No
	Coking	4,07 ± 0,46			
	Flaming	3,85 ± 0,52	0,88	0,61	No
	Coking	4,07 ± 0,46			

Our findings suggest that the combustion conditions do not have an effect on the toxicity (Kocbach Bølling *et al.*, 2009). However, since it is established that the toxicity depends on the concentration, it is therefore important to note that most organic volatile organic compounds are emitted during the ignition phase. In practice, the ignition phase is suggested to release over 50% of total PM emitted in small-scale domestic coal-burning devices (Le Roux, Zunckel and McCormick, 2009; Makonese *et al.*, 2012, 2015b). Furthermore, other studies suggest that most particles are emitted during the flaming and coking phases when using particle #/concentration (Zhang *et al.*, 2012; Tiwari *et al.*, 2014; Masekameni *et al.*, 2018).

#### 7.5.4 Cellular uptake

To understand the toxicity of the smoke particles further, we carried out cellular uptake investigation. Figure 25 shows darkfield images of cellular uptake of smoke particles collected at three distinct combustion phases (ignition, flaming and char-burning/ coking). Figure 25 (a and b) indicate cellular uptake of particles from the ignition phase. It can be seen that particles agglomerated inside the cells Figure 25a. In Figure 25b, there is evidence pointing to the existence of single particles outside the cells. In Figure 25a, it can be seen that particles agglomerated inside the cells as in Figure 25b evidence of single particles outside the cells and in the cytoplasm of the cells. Interesting to observe the cell undergoing apoptosis stage as the outer layer of the cell pearls away from the body of the cell in Figure 25b as a function of particle toxicity on cells.



**Figure 25: Dark-field images of cellular uptake of combustion smoke particles obtained using the CytoViva microscopic technique. Cells were treated over 2-hour period with particles collected from the ignition, flaming and coking phases.**

A consistent and similar uptake is shown for the flaming and coking phases (Figure 25 (c-d) and 25 (e-f)). From the dark-field images, it is evident that the majority of particles are still outside the cell. This can be different if the treatment time could be extended to 48 hours. In the current study on cellular uptake, the cells were treated for two hours, and no attempt was made to expose them for 48 hours. Nevertheless, most importantly it was possible to show is that there was an uptake of particles by cells in all combustion phases.

In summary, this study has presented cytotoxic effects of residential coal smoke particles emitted at different combustion phases on BEAS-2B epithelial cells. Cytotoxicity measurements showed that this cell line was sensitive to domestic coal smoke particles regardless of the physicochemical properties of the particles. Higher particle concentrations were more toxic with increased levels of cytotoxicity observed during the ignition phase. Intracellular localization of the smoke particles





depends on the duration of treatment of the cells, and the majority of the particles were localized in agglomerates outside the cells. Some cells showed agglomerates of the particles in the cytoplasm of the cells. With longer incubations it is expected that some of the particle agglomerates in the cytoplasm will be exocytosed.

## 7.6 Conclusion

For the first time in the South African context, particularly on residential coal burning a toxicity study was carried out to systematically assess the cytotoxicity of emitted particles in three different combustion conditions/ phases. In this study, it was found that the combustion smoke particles induce toxicity on bronchial epithelial cells, especially at high concentration of above 100 µg/ml. Over 24-hour of incubation but cells started to undergo apoptotic cell death after 48-hours of exposure. It was further, demonstrated that emitted particles from three combustion phases induced the same toxicological effect on exposed cells over 48-hours of incubation which was dose-dependent. Further studies may however need to be conducted to elucidate the mechanisms involved in this toxicity.

**Author Contributions:** D.M. conceptualized and prepared the manuscript. He also experimented and wrote up of the paper. M.V. developed the methodology for cellular uptake and toxicity. She further analyzed the data. M.G. edited the manuscript and validated methodology for risk assessment. T.M. Supervised the sampling of PM, data analysis process, interpretation, and the presentation of arguments, and assisted in the editing of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.



## CHAPTER EIGHT

### 8. Review and discussion of main findings

*In this chapter the main findings of the study are synthesised and integrated aiming at showing the link from the first objective to the last. The synthesis of the thesis is based on literature review as presented in chapter one of the study and six study objective outlined as research publications. The chapter further provide the study significance, limitations, recommendations for future projects and conclusive remarks based on the initial hypothesis testing.*

#### 8.1 Summary from searched literature, problem statement and knowledge gap

Extensive literature points out that over half of the global population to date rely on solid fuels such as coal and wood in both domestic and industrial settings. However, coal has been said to be the most dominant fuel in large industrial activities such as transportation, mining, power generation and manufacturing plants; while wood was associated with residential activities such as cooking and house heating. Nevertheless, studies carried out in developing Asia and Africa suggest that coal remains an important fuel energy source for many households activities due to its inherent dual function characteristics. Coal can be burned in a household for cooking and heating needs simultaneously. In the developed part of the world it is reported that domestic coal and wood burning at household level is minimum while in Asia and Sub-Saharan Africa residential solid fuel remains high and it is expected to rise for more decades.

Coal as a residential or industrial energy sources has been termed a “dirty” fuel due to its potential to release emissions of health damaging and environmental alteration potential. Other, studies conflict with the term “dirty” fuel on the basis of several factors which are often ignored when rating the performance of a certain technology. Studies suggest that coal can be burned cleaner if emphasis is given on fuel to stove combination. There is dearth of literature in South Africa and China, where the optimisation of coal burning devices, fuel characteristics, stove operator behaviour and the combustion conditions led to reduced emissions of particulate matter and gases. Therefore, it remains unclear as to which stove to fuel combination can be suggested to meet the need of coal users globally, due to stove design variability, total energy output requirements variability, different coal properties and socio-economic variability.

Over the past two decades several epidemiological studies have associated exposure to coal emissions to several health burdens. Exposure to coal particles has been identified as a major cause of cardiovascular diseases followed by respiratory illnesses. Other studies found a positive association between coal combustion smoke with morbidity, neurological disorder and accelerated mortalities. However, it must be noted that epidemiological studies are not conclusive since it relies on data from other disciplines which is often limited or less available. In order to support current epidemiological



studies there is a need to carry out systematic evaluation on coal burning emissions, understand factors influencing the release of pollutants, conduct source mapping including activity patterns and contextualise the use for a particular exposure scenario. Currently, several toxicological studies have been carried out in India, China, Finland and Hong Kong seeking to understand the toxicity of coal and wood smoke emissions using either *in vivo* or *in vitro* studies. From the toxicological studies conflicting results are reported depending with regard to toxicity of particles from different coal/wood combustion technologies. However, several studies found that emissions from smouldering or low temperature combustion are more toxic than emissions from high temperature combustion technologies.

Very few exposure assessment studies have been carried out at residential settings. It is common practice that despite residential solid fuel using variety of appliances to burn their fuels that most of this devices lacks optimisation parameters leading to high emissions. Especially, in the Sub-Saharan Africa there is no standardised coal burning device, unlike in developing Asia where government put larger amount of money in providing subsidy for approved coal burning devices. In South Africa coal is burned using a 20 L/ 25 L recycled metal drum with holes punched around for air supply. Consequently, the devices used for this process are often inefficient due to poor ventilation and draught regulation. The use of brazier colloquially known as *imbaula* is common in low-income settlement and in off-electricity grid connection. Burning of coal in devices is unfortunately being associated with the release of copious emissions of health damaging pollutants. Due to the fact that this stove does not have chimney is anticipated that most of the emissions will be released at a near-field berating concentration and contributes to indoor and local air pollution. Several, risks are anticipated from this combustion sources but very limited data has been reported to date especially on particle size distribution, #/concentration and the physicochemical composition.

Information on particle size distribution is essential in order to estimate or determine particle intake or potential for deposition in the respiratory system. Studies reported elsewhere suggested that particles from residential coal burning are often lower than 1 $\mu$ m in diameter, while the current literature in South Africa on similar source only report on PM<sub>2.5</sub> and PM<sub>10</sub>. This remain a knowledge gap, hence this study determined particle size distribution from this set of devices. Furthermore, since smaller particles are reported to be toxic than the coarse particles, other studies indicate that the toxicity of particles are influenced by the physicochemical properties and the emitting source. The study provided a comprehensive characterisation of the physicochemical properties of the emitted particles. Moreover, the emissions of VOC's also in other literature are said to be the causing agents of cancer, liver damage, morbidity and neurological dis-functioning. For the first time in South Africa this study defined an exposure scenario and evaluated the carcinogenic and non-carcinogenic health effects of BTEX emissions from residential coal burning. The study ended by determining the toxicity of emitted particles using bronchial epithelial cells.

In summary, the study defined an energy source and combustion technologies applicable in South African context, carryout a systematic evaluation on the emission factor, followed by the determination of factors which can improve the performance of the stove to fuel combination. Then



after an optimum performance combination which includes: the use of high ventilation stove ignited with government advocated ignition method (TLUD) were used to further the understanding on the characterisation of particle size distribution, physicochemical properties, BTEX exposure and related health effects and the toxicity of coal smoke particles.

## 8.2 Summary of main findings

In this section summary of major findings are presented based on the objectives of this study.

### *a) To determine the emission factors of field and laboratory designed domestic coal-burning;*

A total of six field and laboratory designed stoves were used to determine gaseous and particulate matter emission factors from the combustion of coal in these devices. The stoves were ignited using the bottom-lit updraft (BLUD) and the top-lit updraft (TLUD) ignition methods. Three gaseous emission factors were determined over 3-hour burn cycles. The emission factors of CO<sub>2</sub>, CO, and NO<sub>x</sub> ranged from 98–102 g MJ<sup>-1</sup>, 4.1–6.4 g MJ<sup>-1</sup>, and 75–195 mg MJ<sup>-1</sup>, respectively. We investigated the effect of stove ventilation and the fire ignition method on the gaseous emission factors. A change in stove ventilation showed no statistical difference in the gaseous emission factors. This finding suggests that the gaseous emissions are not dependent on the stove air ventilation rates (i.e. from low to high) but on the composition and characteristics of the fuel. A change in the fire ignition method from BLUD to TLUD, when using the laboratory designed stoves, did not produce a significant statistical difference for CO, CO<sub>2</sub> and NO<sub>x</sub> emission factors. On the contrary, field stoves showed a statistical significance difference in NO<sub>x</sub> emission factors between the BLUD and the TLUD method.

Particulate matter (PM<sub>2.5</sub> and PM<sub>10</sub>) emissions were in the range 1.3–3.3 g MJ<sup>-1</sup> for the BLUD method, and 0.2–0.7 g MJ<sup>-1</sup> for the TLUD method, for both the field and lab-designed stoves. When employing the TLUD method, emission factors of PM<sub>2.5</sub>/PM<sub>10</sub> reduced by up to 80% compared to the business as usual BLUD method. Results showed the influence of ventilation rates on PM emission factors that reduced by ~50% from low to high ventilation rates. In summary, the results of this study indicate that particulate emission factors can be significantly reduced by a change from low to high ventilation and from BLUD to TLUD ignition method.

This finding is significant because this piece of information is not available in the South African context and is needed for updating emission inventories, and for dispersion modelling and source apportionment studies. Furthermore, the introduction of the TLUD ignition method was believed to solve the issue of high pollutant emissions from these combustion technologies. The study demonstrated that the use of TLUD fire ignition method in a stove with high air ventilation rates does not significantly bring a reduction on the gaseous emissions, but in PM emissions.



b) *to investigate the effect of coal properties on the emissions of gaseous and particulate matter;*

In this objective D-grade and A-grade type coals with moisture contents (MC) of 2.4% and 8%, respectively were compared for emissions of CO, CO<sub>2</sub> and PM. Three stoves with different air ventilation rates (low, medium, and high) were ignited using the BLUD and TLUD methods to characterise the effect of moisture and coal grades on the emissions. The CO and PM emissions increased with high moisture content, but no change was found concerning CO<sub>2</sub> emissions. The use of A-grade on high ventilation led to the increase of PM by 49% while a change in fuel grades did not significantly change the CO and CO<sub>2</sub> emissions. Fuel with high moisture content is often difficult to ignite and requires more energy to start the fire. Hence, both gaseous and particulate emissions were higher compared to low MC coal. The use of A-grade was anticipated to reduce the emissions.

c) *to determine particle size distribution at three combustion phases (ignition, flaming and coking);*

The TLUD method was selected as an ignition method of choice in this study as it is being promoted by the South African government as a low-cost strategy to replace the traditional method in coal-burning areas. Particle size distribution (PSD) of smoke emissions from residential coal-burning technologies was carried out in a laboratory controlled environment. The coal particle size ranged from  $109 \pm 18.4$  nm for the ignition phase,  $54.9 \pm 5.9$  nm for the pyrolysis/flaming phase, and  $31.1 \pm 5.1$  nm for the coking phase. This finding is worrying given the deposition efficiency and health effects associated with this size range. Sub-micro particles are known to deposit in the lower respiratory region and translocate to other vital parts of the body and cause several cases of undesired health outcomes. Due to higher surface area submicron particles occupies in the respiratory lower regions, impacts are greater compared to larger particles. Despite the TLUD being associated with the reduction of over 80% of particulate matter, the claim was made based on mass while other studies suggest that particles emitted from small-scale coal combustion are often in the sub-micron region. Therefore, using size distribution and number concentration as proxies to evaluate PM emissions seem to be instrumental in order to understand the evolution mechanisms of PM. This study has showed that the use of the TLUD ignition method might significantly reduce emissions of larger particles, but not sub-micron particles. Therefore, this finding suggest that households using the TLU ignition method might also be at risk due to the emission of sub-micron particles.

When using the mass concentration as a unit of measurement for PM, the literature suggests that most particles are emitted during the ignition phase. However, in this research, particle #/concentration as a unit of measurement was used for PM. Since, submicron particles are light in mass, most monitoring/ sampling instrument might have limitations in terms of the detection limit. Therefore, the use of particle #concentration is essential in order to study the emissions of sub-micron particles. It was found that more particles were emitted from the coking phase, followed by the flaming, and ignition stages, in that order. This finding is important to predict particle deposition efficiency and possibilities of translocation in a human system. Furthermore, information on particle size is essential



in environmental studies due to the ability of these particles to remain suspended for a more extended period. Particles with higher suspension residence time are often associated with radiation forcing through light scattering and solar absorption. However, the radiation forcing effects of particles depend on the physicochemical properties.

*d) to investigate the morphology and elemental composition of freshly emitted particles from packed-bed domestic coal combustion;*

The chemical signature and physical properties of smoke particles are essential for source identification, mapping and characterisation for the establishment of air quality interventions. In this thesis, we used microscopic techniques to determine the morphology and elemental composition of smoke particles emitted from domestic coal combustion processes. Using the Transmission Electron Microscope (TEM), images of particles collected during the ignition phase revealed spherical organic particles with tar-ball like characteristics. However, the literature has it on record that tarballs can only be emitted during biomass burning conditions due to the lignin in the wood. Soot particles, some long with diffusion accretion chains, were observed during the flaming phase. The morphology of particles emitted during the coking/ char-burning phase indicated some semi-spherical particles with mineral element inclusion. The morphology of particles emitted during this stage is similar to morphologies from previous studies focusing on coal ash particles

Elemental composition of coal smoke particle was studied using ICP-MS. During ignition, the most emitted elements were silicon, calcium and potassium. Higher quantities of silicon and potassium can be used as markers of wood and coal combustion particles. In our experiments, wood was used as kindling to ignite the coal. Thus, the emission of silicon and potassium indicated the simultaneous or co-combustion of wood and coal. The ICP-MS results showed that over 50% of the elements were emitted during the coking phase. The morphology of mineral enriched particles during the char-burning phase can be supported by the ICP-MS results. This information is relevant in distinguishing the difference between tarballs emitted from biomass burning and spherical organic particles emitted from residential coal combustion.

*e) to carry-out risk assessment of BTEX emissions from residential coal burning using a brazier;*

Risk assessment of exposure to BTEX emitted from residential coal burning braziers was carried out in a corrugated iron sheet structure mimicking a typical one roomed “shack” dwelling in South African low-income settlements. Lifetime exposure to BTEX from coal-burning emissions was calculated, and the information was used together with the emission concentration to determine the risk. Since BTEX are reportedly associated with carcinogenic and non-carcinogenic effects among the exposed individuals, we used the USEPA cancer severity indicator and the hazard quotient to determine the risks posed by the TEX compounds. The calculated cancer risk for adult males and females in a typical South African household exposure scenario was found to be 1.1 and 1.2 respectively, which are 110- and 120-fold higher than the U.S. Environmental Protection Agency





(EPA) designated risk severity indicator of  $1 \times 10^{-6}$ . All four TEX (toluene, ethylbenzene, p-xylene and o-xylene) compounds recorded a Hazard Quotient (HQ) of less than 1, indicating a low risk of developing adverse health outcomes.

These results addressed a knowledge gap which was previously not being investigated or documented regarding the probability of cancer development among exposed groups due to residential coal burning. However, it must be noted that risk assessment is complex where exposure to the development of a particular disease depends on several confounding factors such as exposure source, intensity, exposure pathway and the biological make-up of the receptor. r.

*f) to conduct toxicity and cellular uptake assays of residential coal combustion particles on the bronchial epithelial cells.*

The study on cytotoxicity remains essential to determine the toxicity of coal smoke particles. In this study, an in vitro experiment was used to study the toxicity of emitted coal particles from different combustion phases. Particles collected across the entire burn sequence were found to be toxic to the BEAS-2B bronchial epithelial cells after 48-hours of incubation through the use of the xCELLigence assay technique. Furthermore, the toxicity of particles was found to depend on the concentration, increasing as the particle concentration increased from 20, 60, 100 to 150  $\mu\text{g/ml}$ . However, particles from different combustion phases did not show significant differences in cell toxicity. Therefore, cumulative particles collected across the entire burn sequence are likely to be harmful to human health depending on factors such as dose, the biological make-up of the exposed individual, exposure duration and frequency of exposure. Furthermore, the study sought to understand how these particles are causing toxicity by determining the cellular uptake of particles using dark field imaging from CytoViva. After 2-hours of cell treatment, results indicated that there was an uptake of particles collected from the three combustion phases. The finding suggests that to reduce the toxicity of particles emitted from these technologies, the exposure concentration need to be lower than 60  $\mu\text{g/ml}$ . This can be done through completion of the ignition phase outside an enclosed environment, and transferring the stove into the room for cooking or heating, then taking the device outdoors once the cooking or heating task is complete.

### **8.3 Synthesis and Logical Analysis of the Hypothesis**

The study hypothesized that the formation of xenobiotic emissions from domestic coal burning (affected by method of ignition, ventilation rate and fuel properties) lead to carcinogenic health risk. In order to confirm that the hypothesis is true or false, firstly we identified conditions and factors which influence the emissions and exposure to from residential coal burning. Furthermore, a laboratory experiments were carried out to (i) characterise emissions of gaseous and PM from field and laboratory manufactured stoves, (ii) investigate the effect of coal grade, moisture content and ignition method on the emissions of gases and PM, (iii) investigate PSD at different combustion stage and across the entire burn-cycle, (iv) investigate the morphology of coal smoke particles, (v) carryout a risk assessment of BTEX and (ix) carryout toxicity assessment using macrophage epithelial cells.



Results obtained from laboratory experiments shown that stove ventilation have an effect on the emissions of PM while no significant different on the gaseous emissions. The PM emissions from a high ventilation stove was 50% lower compared to low ventilation stove. The mechanism involved herein in high ventilation stove there is adequate flow of air to the combustion devices leading to the improvement of combustion conditions. In the low ventilation stove there is air restriction which leads to smouldering combustion conditions.

The ignition method has been associated with reduced emissions of particulate matter especially when switching from BLUD to TLUD. The TLUD ignition method reduced the emissions of PM by 80% relative to BLUD. During TLUD the pyrolytic zone moves down wards ensuring that emitted hydrocarbons passes through a hot fire zone before escaping to the ambient. As the hydrocarbons migrate from the bottom they pass through a well-established fire zone where they are burned and only small fraction escape unburned. Using A-grade coal resulted with an increase of emissions to 100% when compared to a D-grade coal. Furthermore, coal with moisture level of 2-3% reduced emissions by 50% when compared to coal with moisture level of 8%.

Information on the influence of stove ventilation and fuel properties assisted in the selection of stove to fuel combination which can be used to study PSD, physicochemical properties of PM, risk assessment and Toxicity. Particles emitted from a high ventilation stove ignited with TLUD method ranged from 31 nm to 109 nm in diameter with the particle diameter mode of 145 nm, 35 nm and 31 nm for the ignition, flaming and coking phase, respectively. It has been demonstrated that larger particles are associated with smouldering condition while small particle are associated with well-established combustion conditions. During the ignition method the smouldering conditions exist due to in adequate air supply and young flames. The emissions of sub-micron particles are essential in order to understand exposure to dose mechanisms. The sub-micron particles are essential for health study modelling due to their higher deposition in the lower region of the lung.

PM was collected to determine their chemical signatures which can be used to apportion the source in our study at three distinct combustion stages/ phases. particles emitted from the ignition phase where spherical enriched with organics. The PM samples contained high percentage of K and Si which can be used as markers for simultaneous combustion of wood and coal. In the present study wood was used as a catalyst to ignite coal lumps. During the flaming phase emitted PM showed a morphology which simulated soot. When combustion temperature increases in flame fire most hydrocarbons are combusted chain like aggregates with characteristics of soot are formed. At the char-burning/coking phase almost all hydrocarbons are driven out and combustion takes place in sufficient air supply. Emitted PM is enriched with organic mineral element inclusion. The implication of this finding suggest that particles are emitted throughout the combustion phases but with different physical properties and chemical signature.

BTEX emissions presented a different class of pollutants often investigated in this type of combustion activities. BTEX emissions were investigated over a three-hour burn cycle and time aggregated concentration was used as a proxy to estimate the dose. A risk assessment matrix was developed to



characterise the carcinogenic and non-carcinogenic risk of BTEX exposure. The cancer risk for adult male was found to be 110- and 120-fold higher than the U.S. Environmental Protection Agency (EPA) designated risk severity indicator, while the HQ for TEX was found to be less than the reference non-carcinogenic risk of 1.

The use of cell viability assay and cellular uptake were employed to assess the toxicity of coal smoke particles emitted from residential coal burning. Macrophage BEAS-2B were exposed to PM concentration of 20 µg/ml, 60 µg/ml, 100 µg/ml and 150 µg/ml to assess the toxicity of emitted PM on cells. The study proved that particles from three different combustion phases were toxic to the cells especially at high dosage. The toxicity of particles corresponded well with increase in exposure concentration and duration. Moreover, particles from different combustion phases induced the same toxicity on the macrophage cells.

The research hypothesis which suggest that emissions from coal smoke burning are harmful to human health is conditionally confirmed. Exposure to benzene was found to have the potential to cause cancer in adult males and females. However, exposure to TEX was found not to present a risk. Exposure to PM was found to induce toxicity to the macrophage epithelial cells especially at concentrations above 60 µg/ml.

#### 8.4 Future research avenue

Field-based studies are necessary to validate the laboratory data set and also to provide real exposure inventory where parameters are not kept constant. We have only addressed emission characterisation from domestic coal-burning scenarios while other essential energy sources may present different risks. Therefore, additional studies are recommended for various energy sources.

The study on particle size distribution was limited to coal burning using a D-grade type coal, ignited with TLUD method in a high ventilation stove. It is known that in the South African coal burning low-income settlements there are no standard braziers. Additional studies on PSD should be carried out to cover a suite of brazier models, fuel types and ignition methods available in the field.

The study on risk assessment was limited to three months of coal burning in a lifetime attempting to mimic field practices. Future studies are needed to determine the exert coal; usage period in the residential sector. It is important to carry out risk assessment evaluations in real-world situations. The activity patterns of the exposed individuals, duration of stove operation, biological make-up of the receptor/ exposed individual, building envelope (exchange of air from in and out), and the actual exposure concentration can be determined and used in the risk assessment models.

Information on chemical properties of the emitted smoke particles was limited to BTEX and trace elements. Additional studies are recommended to provide a full chemical analysis of pollutants from fixed-bed coal burning in the residential sector. Such information is needed for health studies and for designing policies and strategies for pollution prevention and health promotion.



The study on toxicity was based on *in vitro* experiments. It is recommended that future research also employ *in vivo* studies. The results from the two techniques can then be compared to determine which one is more efficient for cytotoxicity assays.

## 8.5 Conclusion and significance

This thesis has demonstrated that there are several factors which influence the emissions of health and environmentally damaging pollutants from residential coal burning. Factors such as stove ventilation, fire ignition and fuel moisture content have been demonstrated to have the ability to reduce the emissions of gaseous and particulates pollutants. The study also pointed out that residential coal burning might be a significant source of gaseous and particulate matter. Furthermore, the findings suggest that the emissions of particles are those of small particle diameter and are a significant for higher deposition in the human respiratory system. The emitted particles from these combustion technologies were of similar morphology to biomass/ wood smoke, which have been previously reported to cause severe environmental alteration through light scattering and radiative forcing.

This study further provided a comprehensive systematic study of emission factors/rates from residential coal combustion technologies at various combustion phases. In addition, in this study smoke particle formation were investigated at various combustion phases (ignition, pyrolysis, coking/ char-burning) extending to the investigation of the submicron particles. The use of the mass/number concentration in regulatory frameworks will not be adequate in understanding the mechanisms regarding disease development unless the physicochemical properties of the particles are known.

Risk assessment can also be used to estimate the probability of health-related outcome due to acute or chronic exposure to combustion pollutants. In addition to probabilistic risk assessment techniques, the use of *in vitro* techniques in estimating the cytotoxicity and cellular uptake might assist in understanding the mechanisms involved in the development of diseases. Toxicological studies can provide additional information to the current body of knowledge in the field.-Association between chemical compositions as well as other properties of the pollutants emitted, and biological endpoints would complement epidemiological studies. This has the potential to provide a sound basis for risk assessment in the field of indoor/ ambient air pollution.

This study indicated that the majority of low-income households in South Africa, especially those residing in slums, are at risk of developing diseases due to exposure to health damaging pollutants emitted from coal-burning braziers. This implies that despite government advocating for the dissemination and adoption of the TLUD ignition method as an interim air quality strategy, additional energy/ air quality interventions are required to prevent exposure. Since the phasing out of coal as a domestic energy fuel is not feasible in low-income settlements, it is encouraged that other competing cleaner energy technologies should be sought to reduce dependence on coal.



The information provided in this research will be useful for air quality dispersion modelling, climate and lung deposition models, adding to existing research on domestic fuel uses and related health effects (especially concerning residential coal combustion), improving the emissions inventory of criteria pollutants from the domestic sector in South Africa. The study may also add value to policy development, implementation and monitoring of residential energy expansion programs, through assessing the risks posed by coal combustion or competing technologies vs health and environmental benefits.





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