# LOCAL DEVELOPMENT AND CALIBRATION OF A PASSIVE SAMPLER FOR MONITORING OF PARTICULATE MATTER

BY

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This is dedicated to Winnet, my lovely and supporting wife, Marlon my son, and the Mukota family at large for their unwavering support. Their words of encouragement kept me going strong even in the most difficult of times. To the Almighty God, I give my all.

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ABSTRACT

The measurement of ambient particulate concentration ($PM_{10}$ and $PM_{2.5}$) using active monitors requires expensive or labour-intensive apparatus or both. This has precluded widespread or intensive ambient particulate monitoring networks to be set up in South Africa, except in some priority areas, although particulate matter is generally acknowledged to be an air pollutant of concern in large parts of Southern Africa. In this study, I report on the calibration of locally manufactured passive diffusive monitoring devices (samplers) for ambient PM (from $PM_{2.5}$ to $PM_{30}$ and intermediate sizes) based on a design initially published by researchers at the University of North Carolina (UNC). Modifications include the configuration of the diffusion screen and the insertion of a microscope slide to facilitate sample handling. For calibration purposes, duplicate samplers of each type (local and UNC) were co-located at eight tapered element oscillating microbalance (TEOM) and beta attenuation mass (BAM) monitoring sites in three networks (City of Tshwane, SASOL and ESKOM). Imaging of the substrate was carried out using an optical microscope. The images (10 to 49 per sample) were analysed using both proprietary (Zeiss Axiovision®) and open-source (ImageJ) software at 100X and 200X magnification. Results of the calibration show a considerable variation amongst the two co-located local and UNC samplers although the latter show lesser discrepancies when analysed using the AxioVision software. Greater agreement of the local samplers and the continuous monitors is noted at a 200X and 100X magnification using the AxioVision software with $R^2$=0.81 and $R^2$=0.79 respectively. Uncertainty has not been reported elsewhere in this format. Both Wagner and Leith (2001b) and Assael et al (2010) report close correspondence between passive samplers and reference stations.

The precision of $PM_{10-2.5}$ measured with the passive samplers was highly variable with calculated CVs ranging from a low CV of 10.4% to a high CV of 73.3%. 82% of the CVs were less than 40%. The average CV for all samplers was 34.6%. Sampler analyses using the AxioVision software recorded lesser average discrepancies of 45.3% at 100X and 37.3% at 200X magnification. Samplers analysed using ImageJ at 100X magnification exhibited the highest percentage difference from the reference values (81.2%). Using a two factor ANOVA we can show that (at 95% confidence) the analysis software and the imaging magnification have a significant effect on the calculated sampler concentration results.

Using the local samplers for indoor air quality monitoring to indicate the seasonal variation in particulate concentration and functionality of offset air quality interventions in a specific residential location showed that most indoor particulates were associated with outdoor activities such as waste incineration and carryover of dust from unpaved roads. The calculated mean indoor daily concentrations were significantly higher than the national standards in summer and winter.

Advantages of the passive sampling technology include low capital cost of the device and its small size (~20mm in diameter and 10mm thick), which makes it unobtrusive. Computer-based image analysis reduces the labour cost. A disadvantage is the low time resolution of two to seven days required to produce statistically significant values hence disqualifying it for use as a reference method. The device is, therefore, more suitable for screening-level, high spatial density sampling, but some non-regulatory applications are pointed out.

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## Acronyms

| | |
|---|---|
| **ANOVA** | Analysis of Variance |
| **BAM** | Beta attenuation monitor |
| **CEN** | European committee for standardisation |
| **CFD** | Computational Fluid dynamics |
| **CV** | Coefficient of variation |
| **CoT** | City of Tshwane |
| **DEA** | Department of environmental Affairs |
| **ESKOM** | Electricity Commission Supply (of South Africa) |
| **FRM** | Federal Reference Method |
| **ISO** | International Organisation of for Standardisation |
| **IT** | Interim target |
| **LOD** | Limit of detection |
| **LOQ** | Limit of quantification |
| **µg/m$^3$** | micrograms per cubic meter |
| **µm** | micrometre |
| **PM** | Particulate matter |
| **PM$_{2.5}$** | PM with aerodynamic diameter less than 2.5 micrometres |
| **PM$_{10}$** | PM with aerodynamic diameter less than 10 micrometres |
| **TEOM** | Tapered element oscillating microbalance |
| **TSP** | Total suspended particulates |
| **UNC** | University of North Carolina |
| **UF** | Ultra-fine particulates |
| **USEPA** | United States Environmental Protection Agency |
| **WHO** | World Health Organisation |

# 1 CHAPTER 1: INTRODUCTION

South African cities and mining towns are characterised by high concentrations of airborne particulate matter (PM) (McGranahan, 2003). Fifteen years after the National Environmental Management Act Air Quality Act (NEMAQA), air pollution in South Africa is still an issue of priority and the problems associated with air pollution are far from being solved. The observed levels of particulate matter (PM) and ozone in areas declared as hotspots (Priority Areas) in South Africa are of great concern. The main sources of particulate matter in these areas have been identified as industry, mining, motor vehicles, and biomass and domestic burning (Tshehla, 2019). PM consists of airborne particles that range in size from larger than 100 micrometres to nanometres, but because of their health impact, those with an aerodynamic diameter of less than 10 micrometres ($PM_{10}$) are considered in this study. This includes the fraction less than 2.5 micrometres ($PM_{2.5}$) which has been shown to be more harmful than the larger sizes. PM represents a complex mixture of organic and inorganic substances as well as a mixture of primary and secondary compounds. Primary compounds are emitted directly to the atmosphere from sources such as industrial activity, transportation, power generation and natural processes (e.g. windblown dust, oceanic bubble bursting and volcanic eruptions) while secondary particles emanate from gas-to-particle conversions and heterogeneous reactions within the atmosphere Keywood and Selleck, (2016). As presented by the current study, it is possible to determine the nature of particulate matter accumulating on the samplers by using polycarbonate substrates and employing analysis by scanning electron microscopy (SEM) coupled with energy dispersive X-ray microanalysis (EDX). The composition of atmospheric PM has been investigated by number analytical techniques (Singh *et al.*, 2014).

Over the last decade, much attention has been paid to the development of different types of air monitoring equipment. Such equipment or air monitoring methods can be classified into four common generic types which are passive samplers, active samplers, automatic online analysers and remote sensors (Schwela, 2010). A fifth type that is not so common is the bio-indicator. Active methods of PM monitoring usually consist of suction pumps, filters, timers, batteries and containers of chemical solutions. These active methods are standardised methods that are used for national and regional air quality monitoring in most countries. Most of these active samplers require electric power to pump the sampled air through the collection medium. The greater the volume of air sampled, the more sensitive the equipment is with regards to sampling averaging time. Active equipment for PM monitoring includes but is not limited to Tapered Element Oscillating Microbalances (TEOMs) and Beta Attenuation Monitors (BAMs).

Berlin *et al.* (1987) state that passive diffusive samplers are devices that are capable of taking samples of gas or vapour pollutants from the atmosphere at a rate controlled by a physical process such as molecular diffusion through a static air layer, or penetration through a membrane, but which does not involve the active movement of air through the sampler. Different types of passive air samplers have been developed for the measurement of PM. Their principle of operation differs as illustrated by Assael, Melas and Kakosimos, (2010). These authors state that only four methods have been reported in the international literature (Brown *et al.*, 1995; Vinzents, 1996; J. Wagner and Leith, 2001; Yamamoto, 2006). In their paper, they highlight the methods as (i) Brown's method relying on the electrostatic charge to separate PM from the air, (ii) Vinzents' method using sticky substrates for particle adhesion, (iii) Wagner, Leith and (iv) Yamamoto's methods are similar and based on the diffusion of PM through a size-selective mesh and the microscopic analysis of the collected PM. The last two methods are incorporated in this study with the use of both the UNC and a locally manufactured sampler.

The data quality objectives for any monitoring campaign are the ultimate criteria for selecting the technology. Practical considerations such as local economic constraints and the availability of skilled manpower can be pivotal in equipment selection. There tends to be a clear trade-off between instrument performance, cost, complexity, reliability and ease of use (Schwela, 2010).

Multiple indicators such as total suspended particulates, (TSP), black smoke, $PM_{10}$, and $PM_{2.5}$ are used to describe the spectrum of PM because of the importance of particle size in determining human exposure. Hinds (1999) states that the hazard caused by inhaled particles depend on the chemical composition and on the site at which they deposit within the respiratory system. The International Organisation for Standardisation (ISO) and the European Committee for Standardisation (CEN) have defined the various types of particle indicators (ISO, 1995). $PM_{10}$ denotes particles that pass through a size-selective inlet with a 50% efficiency cut-off at $10\mu$m and an upper cut-off of $30\mu$m. $PM_{10}$ roughly corresponds to the thoracic particles. Outdoor $PM_{10-2.5}$ concentrations are ordinarily determined by subtracting $PM_{2.5}$ from $PM_{10}$, where both methods are used according to Federal Reference Methods (Leith, Sommerlatt and Boundy, 2007). This requires the purchase of two sets of equipment for the relative measurement of each particle class, hence making the method expensive.

Studies in the United States have shown that an increase of 10 $\mu g/m^3$ in the concentration of $PM_{10}$ in the atmosphere could lead to an increase in mortality rate by 6-7% (Dockery *et al.*, 1993; Pope, 2007).

$PM_{2.5}$ corresponds to the respirable particles that can penetrate the bronchioles. Hinds (1999) further elaborates that the alveolar deposition of particles 0.1-1$\mu m$ is about 10-20% and is approximately independent of the particle size. These particles have detrimental effects on the respiratory system, while evidence is emerging that other organs might also be affected, specifically by the smaller particles (Katsouyanni *et al.*, 2001; Samoli *et al.*, 2008; Brook *et al.*, 2010).

Most cities use large and expensive reference monitoring stations to measure ambient air quality. In South Africa, cities and municipalities such as Johannesburg, Cape Town, Durban, Ekurhuleni and Tshwane, use such monitoring stations (Coop et al 2009; SAAQIS 2016). Reference stations play a role in air quality monitoring but owing to size, cost and operational requirements, they are sparsely located and in many instances, poorly maintained (Assael, Melas and Kakosimos, 2010; South African Instrumentation and Control, 2010). These reasons make it difficult for both the public and private sectors to do long term air quality monitoring as the cost is prohibitive. Baseline studies can also come at a prohibitive cost if such equipment is to be incorporated. Knowledge of the variability at a local scale, however, is critically important to avoid exposure misclassification and the expense of purchasing and operating a sufficient number of filter-based samplers to capture this variability is often impractical (Ott, Kumar and Peters, 2007).

Passive aerosol samplers, on the other hand, are small devices that are capable of monitoring and measuring PM in an inexpensive way over longer time periods. They can be networked to measure PM concentrations over larger geographical areas and provide reliable information on incidences. These portable and unsophisticated devices are capable of taking long term samples to investigate chronic exposures (Pope, 2007), but have not been widely used in South Africa for the measurement of PM, although gaseous pollutant concentrations are routinely measured using passive devices (Martins *et al.*, 2007). The University of North Carolina at Chapel Hill (UNC) passive aerosol sampler developed by Wagner and Leith, (2001); (Wagner and Leith, 2001b; Wagner and Macher, 2003), has been used for indoor and outdoor PM monitoring. It consists of a standard SEM stub and an annular cap with a mesh top attached to the cap. Particles pass through the annular region and collect on a substrate on top of the stub (Leith, Sommerlatt and Boundy, 2007). The rate at which particles deposit is due to gravity, convective diffusion and diffusion (Wagner and Leith. 2001). Previous studies incorporating similar samplers (Wagner and Leith, 2001a; Wagner and Macher, 2003; Ott, Cyrs and Peters, 2007; Ott, Kumar and Peters, 2007; Assael, Melas and Kakosimos, 2010; Arashiro and Leith, 2013; Sawvel, 2013; Sawvel *et al.*, 2015) have found it to be relatively accurate and in good agreement with official or reference monitoring methods.

The purpose of the present study was to calibrate locally fabricated passive samplers at various locations in South Africa's Gauteng and Mpumalanga provinces where reference and standard air quality monitoring stations exist for the monitoring of PM. As stated previously, this work utilises the UNC passive sampler design principles. Locally fabricated passive samplers utilised in this study incorporate an aluminium stub and cap with the mesh consisting of multiple non-tapered laser bored holes with an approximate diameter of 200µm. Two of the local and two UNC samplers were co-located with the reference stations and the PM concentration was measured so that the passive results could be compared to those of the reference station for the measurement period concerned. The samplers were housed using a protective shelter similar to that used by Ott and Peters (2008). Microscopic analysis was done using a Zeiss optical microscope to establish the particle count and size distribution analysis.

## 1.1 The Research Question

Hundreds of thousands of people in the SADC region are likely to be exposed to concentrations of various pollutants in the ambient air in excess of the World Health Organisation (WHO) guidelines. However, due to the lack of monitoring information, it is difficult to be specific about numbers and impacts. It is also likely that a large proportion of the population using biomass fuels indoors will be exposed to health-damaging concentrations of pollutants (Tiwary and Colls, 2013). South Africa implemented new air quality legislation in 2004 (Department of Environmental Affairs [DEA], 2004). This includes new national standards for ambient air pollutants and the monitoring thereof, with particulate matter being addressed as a “problem pollutant” under the Air Quality Management tools (Mdluli, 2010).

There is, therefore, a need for widespread monitoring of particulate matter. The current measuring stations may not be sufficient and cost-competitive to provide essential particulate matter pollution data for use in policy development and implementation. Passive aerosol samplers have been applied for particulate matter measurements successfully at wide scales across the globe but not extensively in South Africa. Concerns continue to be raised on the existence of a cost-effective particulate matter monitoring network in the country so as to establish compliance with national and WHO guidelines (Chin *et al.*, 2007; Ramanathan and Feng, 2009; Thambiran and Diab, 2010).

## 1.2 Justification for the Proposed Research

According to the 2017 national framework for air quality management in the Republic of South Africa, there is a need to prioritise the following issues (Department of Environmental Affairs, 2018);

- Development of emission factors and activity rates for specific pollution sources for input into the NAEIS;
- Consideration of new or emerging pollutants, their impact on health and the establishment of health-based objectives;
- Consideration of existing, new and/or emerging pollutants, their impact on the environment and ecosystems and the establishment of appropriate objectives;
- Development of proactive management of future potentially problematic sources (e.g. new fuels);
- Consideration of policies and strategies to address both climate change and air pollutant emissions to deliver co-benefit solutions;
- Investigation of trans-boundary air pollution sources and their impacts on South Africa;
- Development of strategies to deal with ambient concentrations of heavy metals and POPs, their impact and the establishment of suitable objectives; and,
- Development of strategies for tackling nuisance pollutants such as odours and dust and the establishment of guidelines and objectives for effective management.

Such goals are only achievable by increasing the number of monitoring stations. It is envisaged that once more networks start reporting to the South African Air Quality Information System (SAAQIS), particularly with the increase in historical observations, a better picture on the trends will emerge.

The passive aerosol sampler has presented many advantages over the traditional reference stations that have been used to measure particulate matter for decades. Ott, Kumar and Peters, (2007) give the advantages of this sampler as being cheap, applicable outdoors, correlating with the US Federal Reference methods and having the options of either using a Scanning Electron Microscopy (SEM) for particle speciation or less expensive visual light microscopy and automated analysis of images for particle size determination. Martins *et al.* (2007) highlight further advantages of the sampler as being small, lightweight, silent, not requiring electricity or field calibration, and being easily deployed by non-specialists. As a result, they can be used to obtain long term measurements at rural, regional and global scales. Wagner and Leith, (2001) elaborate that many techniques for characterizing aerosols are relatively obtrusive, expensive, maintenance intensive, and costly. These qualities stem from the air-moving and/or detection components housed within most samplers. In contrast, the aerosol sampler described by Wagner and Leith (2000a, b) is of simple, passive design; after sampling, the collected particles are analysed by microscopy (SEM-EDS or optical). Images can then be treated using image analysis software and the results calculated to obtain PM mass concentrations for aerosols over the sampling period. The passive sampler can sample unattended for hours to weeks and has potential utility as a personal sampler. It is small, lightweight (1.7g), inexpensive, and easy to operate. Such advantages make the passive sampler ideal for the monitoring of particulate matter on a wide scale practicable in the context of South Africa. However, limitations in the use of this sampler exist. Not every lab in the country's institutions is capacitated to perform such analyses on a wide and frequent scale and there is need for extensive personnel training on how to use this method.

It is also imperative to acquire air quality data in order to access compliance with national standards. The search for literature also shows a gap in the use of these samplers for the monitoring and measurement of particulate matter in the South African context hence providing the motivation to pursue this research.

## 1.3 Aim and objectives of the Study

The major goal of the study is to calibrate passive aerosol samplers manufactured in South Africa against the UNC aerosol sampler and the reference active and continuous PM monitors usually set in air quality stations, provided by SASOL, ESKOM and the City of Tshwane. In order to achieve such a goal, the objectives of the research are;

1. Determining the precision and accuracy of the locally developed sampler when compared to the UNC sampler and air monitoring station BAM and TEOM equipment,
2. Determining the microscope magnification that gives the most accurate relative particle count data,
3. Testing available image analysis software that gives good correlation with 'reference' concentration data.
4. To test the locally developed sampler for indoor exposure use.

# 2 CHAPTER 2: LITERATURE SURVEY

## 2.1 Particulate matter as an air pollutant

Atmospheric particles consist of a complex mixture of chemical components and sizes. Hence there can be no single method that is able to quantify all the properties of particles and in most cases, one or a number of properties of the particles are measured and used as authorised substitutes along with valid assumptions to quantify the particles (Keywood and Selleck, 2016).

As stated in the Global Air Pollution Forum Air Pollution Monitoring Manual (2010), air pollutants can broadly be classified according to the;

- State of matter (particulate, gaseous pollutants);
- Origin of pollutants (primary, secondary pollutants);
- Chemical composition (organic, inorganic pollutants).

Aerosols exist as either solid or liquid and are composed of inert or chemically reactive materials of size ranging from 2 nanometres (nm) to 500 micrometres ($\mu$m). Subcategories include suspended particulate matter, (SPM), dust, smoke, soot, fumes, mist, fog, and haze. Particles are distinguished as coarse, fine and ultrafine. Coarse particles are those of size between 10 and 2.5 $\mu$m ($PM_{10-2.5}$); fine particles are those with an equivalent aerodynamic diameter of 2.5 $\mu$m and less (denoted as $PM_{2.5}$) and ultrafine particles are those of size less than 0.1 $\mu$m (Schwela, 2010). Gaseous pollutants include gases and vapours such as sulphur oxides, oxidized and reduced nitrogen, oxygen, and organic compounds. Major gaseous pollutants in the urban air are $SO_2$, nitric oxide (NO), nitrogen dioxide ($NO_2$), ozone ($O_3$), carbon monoxide (CO), and the greenhouse gas carbon dioxide ($CO_2$).

Primary pollutants are those directly emitted into the atmosphere from the source; secondary pollutants are those formed due to the interaction of one or more primary pollutants or as results of a reaction with atmospheric constituents (e.g. $O_3$ formation). Organic pollutants include methane and non-methane hydrocarbons, aldehydes, volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs).

Table 1 below shows the different sources of particulate air pollution into different subcategories.

**Table 1:** Particle sources and their causal action. (Keywood and Selleck, 2016)

| Source Type | Source | Causal Action |
|---|---|---|
| **Natural** | | |
| | Volcanic Eruption | Release of solid particles, gases and heat waves |
| | Sandstorm | Dust particles spread through wind circulation around the Earth |
| | Vegetation fire | Smoke from wildfire and forestry management |
| | Plant pollen | Spread of plant pollen spread through wind motion |
| | Sea spray | Liquid droplets spread through wind near coastlines |
| **Man-made** | | |
| | Transport | Combustion of petrol/diesel and generation of particles and gases |
| | Power generation | Release of particles and gases of combustion |
| | Industry | Manufacturing and processing of steel, non-iron metals, textiles, refining of petroleum, handling of materials |
| | Construction | Particle pollution due to material handling and other associated activities |
| | Agriculture | Emissions from ploughing and use of fertilisers, pesticides and insecticides |
| | Leisure activities | Emissions from motor racing, barbeque, boats, private planes, lawnmowers, and other leisure-related appliances |
| | domestic | Burning of solid organic materials indoors such as coal, charcoal, wood, dung and agricultural residues |

Particulate matter properties of relevance to this study that can be measured include;

- Size distribution
- Concentration of particle mass
- Concentration of the number of particles

### 2.1.1 Total Suspended Particulates (TSP)

Suspended particulate matter (SPM) and total suspended particulates (TSP) both mean total airborne particles; often measured by high volume samplers without a size-selective inlet. According to the encyclopaedia of public health (2002), (TSP) is an archaic regulatory measure of the mass concentration of particulate matter (PM) in community air. It was defined by the (unintended) size-selectivity of the inlet to the filter that collected the particles. Unfortunately, the size cut varied with wind speed and direction and was from 20 to 50 µm (microns) in aerodynamic diameter. Under windy conditions the mass tended to be dominated by large wind-blown soil particles of relatively low toxicity. The smallest size range is between 0.1µm and 1.0µm. The intermediate suspended particles are secondary with size ranges between 1.5µm to 2.5µm. The rest is of coarse nature and as shown in Figure 1 below, have an aerodynamic diameter up to 100µm with the main bulk of atmospheric aerosol mass lying between 0.1µm and a few µm (Tiwary and Colls, 2013).

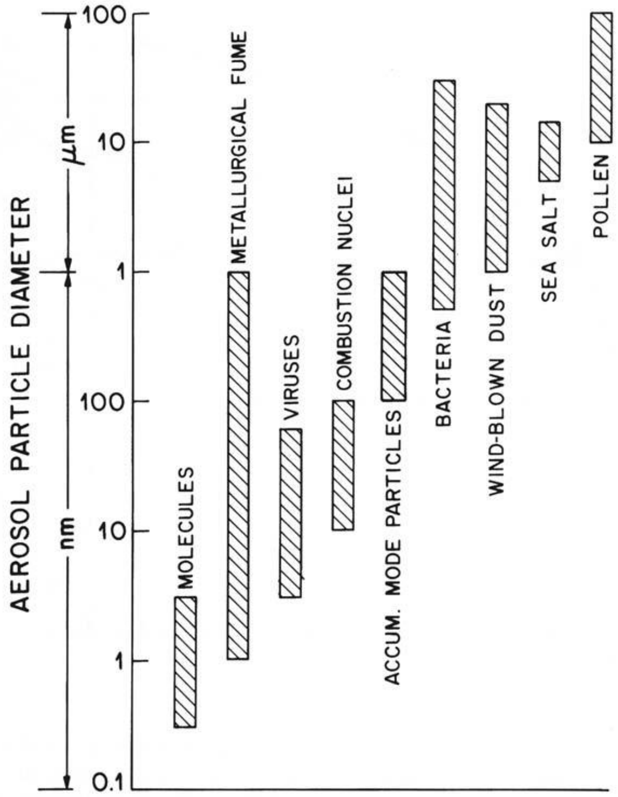

**Figure 1:** Characteristic size ranges of particles from different sources with molecular sizes shown for comparison. Source: Leygraf and Graedel (2000), in Tiwary and Colls (2013).

### 2.1.2 Respirable particulate matter (<10 µm)

$PM_{10}$ is the mass concentration of PM due to particles that pass through a size-selective inlet that has 50% efficiency at an aerodynamic diameter of 10µm. $PM_{2.5}$ is the corresponding concentration for a cut diameter of 2.5µm. (Tiwary and Colls 2013). Re-suspension of soil and road dust by wind and moving vehicles, as well as construction work, industrial emissions and agricultural activities have been attributed in the formation of coarse particles ($PM_{10}$) (Newby *et al.*, 2015). $PM_{10}$ comprises the particle mass that enters the respiratory tract and includes both the coarse ($PM_{10-2.5}$) and the fine ($PM_{2.5}$) particles considered to contribute to both the epidemiological and ecological effects observed in urban and rural environments.

### 2.1.3 Fine particles (< 2.5 µm)

Fine PM mainly consists of particulates with an aerodynamic diameter less than 2.5µm but not smaller than 0.1µm (Tiwary and Colls, 2013). Fine PM is characteristically more varied in composition when compared to coarse PM and is secondary in nature, having condensed from the vapour phase, been formed by chemical reactions from gaseous species through nucleation, condensation, and coagulation, or remained following evaporation of water from contaminated fog and cloud droplets. Sulphur and nitrogen oxides ($SO_x$ and $NO_x$) are often oxidized to their corresponding acids and neutralized with ammonium cations as particulate salts (Kuhlen *et al.*, 2008). Fine PM may also contain condensates of volatile organic compounds, volatilized metals, and products of incomplete combustion (Dos Santos *et al.*, 2009).

## 2.2 Air quality legislation regarding PM

Coarse, fine and ultrafine particulates pose health risks and as such, legislation has been implemented worldwide to reduce the health risks posed by these. In 1987, the United States Environmental Protection Agency (USEPA) changed its air quality standards from TSP to $PM_{10}$. $PM_{10}$ standards have also been adopted in, for example, Brazil, Japan, South Africa Europe and the Philippines. These fine particulates with an aerodynamic diameter less than 10µm have been proposed for adoption for ambient standards for airborne particles, in light of the emerging evidence on their health impacts (Sierra-Vargas *et al.*, 2009). There is concern regarding $PM_{10}$ and $PM_{2.5}$ due to the potential health risks that they pose to both plants and animals since these have the potential to be deposited deeper in the respiratory tract and gaseous exchange parts of the lungs. The PM limits and standards issued locally and abroad are explained in the following sections and summarised in Table 2.

### 2.2.1 WHO air quality guidelines

There is evidence of the effects of exposure to respirable particles leading to adverse health effects in both developed and developing countries. According to the World Health Organisation (WHO, 2005) air quality guidelines (AQGs) of 2005, the risk of various consequences have been shown to increase with exposure and there is little indication to suggest a threshold below which no adverse health effects would be observed.

$PM_{10}$ is proposed as an indicator with significance to the bulk of the epidemiological data and for which there is more widespread measurement data throughout the world. For example, in a major multi-city survey combining data from Europe, Canada and the United States, a $10\mu g/m^3$ increase in $PM_{10}$ was associated with 0.2-0.6% increase in all-cause mortality with similar effect sizes in the US and Europe and larger effects in Canada (Samoli *et al.*, 2008).

Nonetheless, the numerical guideline value is based on studies using $PM_{2.5}$ as an indicator and a $PM_{2.5}/PM_{10}$ ratio of 0.5 is often used to derive an appropriate $PM_{10}$ guideline value. Based on known health effects, both the short term (24 hours) and long term (annual) guidelines are needed for both the PM indicators. The WHO guidelines are given in table 2.

**Table 2:** Air Quality Guidelines and interim targets for PM: Annual and 24-hour mean.

| **Annual mean level** | **PM$_{10}$ ($\mu g/m^3$)** | **PM$_{2.5}$ ($\mu g/m^3$)** | **Basis for the selected level** |
|---|---|---|---|
| **WHO interim target 1 (IT-1)** | 70 | 35 | These levels are estimated to be associated with about 15% higher long-term mortality than at AQG levels |
| **WHO interim target 2 (IT-2)** | 50 | 25 | In addition to other health benefits, these levels lower risk of premature mortality by approximately 6% [2-11%] compared to WHO-IT1 |
| **WHO interim target 3 (IT-3)** | 30 | 15 | In addition to other health benefits, these levels reduce mortality risk by another approximately 6% [2-11%] compared to WHO-IT2 levels. |
| WHO Air quality guidelines (AQG) | **20** | **10** | These are the lowest levels at which total, cardiopulmonary and lung cancer mortality have been shown to increase with more than 95% confidence in response to PM$_{2.5}$ in the ACS study (Pope et al., 2002). The use of PM$_{2.5}$ guideline is preferred. |
| **24-hour mean level** | PM$_{10}$ ($\mu g/m^3$) | PM$_{2.5}$ ($\mu g/m^3$) | Basis for the selected level |
| **WHO interim target-1 (IT-1)** | 150 | 75 | Based on published risk coefficients from multi-centre studies and meta-analyses<br>(about 5% increase of short-term mortality over AQG) |
| **WHO interim target-2 (IT-2)** | 100 | 50 | Based on published risk coefficients from multicentre studies and meta-analyses<br>(about 2.5% increase of short-term mortality over AQG) |
| **WHO interim target-3 (IT-3)** | 75 | 37.5 | (about 1.2% increase in short-term mortality over AQG) |
| **WHO Air quality guidelines (AQG)** | **50** | **25** | Based on relation between 24-hour and annual PM levels |

Dose-response relationships for PM$_{10}$ and PM$_{2.5}$ concentrations considered in studies in the document gave a linear relationship between human exposure to particulates and various health indicators. This approach was not well accepted by policymakers and air quality specialists as it is not always the case that the dose-response relationships are linear.

As a result, the WHO Working Group on Air Quality Guidelines recommended that the updated WHO air quality guideline document define concentrations which, if achieved, would be expected to reduce the rates of adverse health effects. Such guidelines would provide air quality managers and policymakers with explicit objectives when setting national air quality standards. Given that air pollution levels in developing countries frequently far exceed the recommended WHO Air Quality Guidelines (AQGs), the working group also proposed interim targets (IT), higher than the WHO's AQG levels, to promote steady progress towards meeting the AQG objectives as shown in Table 2.

Air quality standards for $PM_{2.5}$ had (by the end of 2006) been set by various countries such as the USA, Canada, and Australia (see Table 4).

The 24-hour mean values denote the 99th percentile of the distribution of diurnal values - that is the 4th highest value of the year. The frequency distribution of daily $PM_{2.5}$ or $PM_{10}$ values is most regularly approximately log normal. Contingent to the specific characteristics of their sources and location, countries may find that either the 24-hour guidelines or interim targets were given in the document (WHO, 2005), or the mean average values are more limiting. When evaluating the WHO AQG and interim targets, the annual average is suggested to take precedence over the 24-hour average since, at low levels, there is less concern about episodic excursions. Adhering to the guideline values for 24-hour means should protect against peaks of pollution that would lead to substantial increased illness or mortality. It is suggested that countries with areas not adhering to these guideline values commence on corrective actions in their earliest convenience.

**Table 3:** Air quality standards for $PM_{2.5}$

| **Authority** | **Maximum 24-hour concentration(µg/m³)** | **Average annual concentration (µg/m³)** |
|---|---|---|
| Australia | 25[a] | 8[a] |
| US EPA | 35[b] | 15 |
| Canada | 30[c] | - |
| European Union | - | 20 |

[a] Advisory reporting standards and goal for particles as PM2.5. Measure schedule commenced in 2005 (www.deh.gov.au/atmosphere/airquality/standards.html).
[b] to attain this standard, the 3-year average of the 98th percentile of the 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 µg/m³ (www.epa.gov/air/criteria.html).
[c] Canada-Wide Standards issued by the Canadian Council of Ministers of the Environment.

In addition to $PM_{2.5}$ and $PM_{10}$, ultra-fine particles (UF) have lately captured significant scientific and medical attention. These are particulates smaller than 0.1µm and are formed by nucleation, that is, condensation of low vapour-pressure substances formed by high-temperature vaporization or by chemical reactions in the atmosphere to form new particles (nuclei) ( WHO Regional office for Europe, Copenhagen, Denmark, 2000). While there is a substantial toxicological indication of potentially damaging effects of UF particulates on human health, the existing body of epidemiological substantiation is unsatisfactory to reach a conclusion on the exposure/response relationship to UF particles. Therefore no recommendations can be provided as to guideline concentrations of UF particles at this point (WHO, 2005).

### 2.2.2 Local and international guidelines and standards

In December 2009, South Africa's Department of Environmental Affairs and Tourism gazetted new air quality standards. The gazetted $PM_{10}$ standards are given as 75 µg/m³ for highest daily (compared to the previous standard of 180 µg/m³) and 40 µg/m³ for annual averages (compared to 60 µg/m³ previously) (Department of Environmental Affairs, 2009). The PM10 limits and standards issued nationally and abroad are documented in Table 5.

**Table 4:** Air quality standard for inhalable particulates ($PM_{10}$), (Department of Environmental Affairs, 2005)

| Authority | Maximum 24-hour concentration (µg/m³) | Average annual concentration (µg/m³) |
|---|---|---|
| **SA standards (AQA)** | 120 | 40 |
| **SANS limits (SANS 1929:2005)** | 75[a]<br>50[b] | 40 |
| **Australia** | 50 | 30 |
| **European Commission (EC)** | 50 | - |
| **World bank (General Environmental Guidelines)** | 70 | 30[c]<br>20[d] |
| **World Bank (Thermal Power guidelines)** | 150 | 50 |
| **UK** | 50 | 40 |
| **US EPA** | 150 | 50 |
| **WHO** | 50 | 20 |

[a] Limit value. Permissible frequencies of exceedance, the margin of tolerance, and date by which limit value should be complied with, to be determined through a complete standard-setting process through the SABS.
[b] Target value. Permissible frequencies of exceedance, and date by which limit value should be complied with, to be determined through a complete standard-setting process through the SABS.
[c] EC First Daughter Directive, 1999/30/EC (http://europa.eu.int/comm/environment/air/ambient.htm). Compliance by 1 January 2005
[d] EC First Daughter Directive, 1999/30/EC (http://europa.eu.int/comm/environment/air/ambient.htm). Compliance by 1 January 2010.

In recognition of the negative health impacts associated with particulate matter with an aerodynamic diameter of less than 2.5 micrometres, the NAAQS was amended in 2012.The South African National Air Quality Standard for annual average $PM_{2.5}$ is currently 20µg/m³ and is effective until December 2029 (DEA, 2012).

## 2.3 Air quality monitoring equipment

Globalisation, rapid industrialisation and increased use of vehicles have seen an upward trend in pollution levels with numerous health and environmental consequences in many countries. High concentrations of criteria pollutants such as fine particulate matter (PM), sulphur dioxide ($SO_2$), nitrogen dioxide ($NO_2$), ozone ($O_3$) and lead (Pb) have been recorded in most parts of the world, posing a threat to human and animal health. Ambient air pollution can be defined as “the presence of contaminants/pollutants in the outdoor atmosphere in such concentrations and of such durations which may adversely affect human health” (Schwela, 2010). This study is limited to the use of passive aerosol samplers and active (particulate) monitors (analysers) and thus these only will be reviewed.

### 2.3.1 Passive samplers

These devices usually disc or tube-shaped, collect a target pollutant by absorption or diffusion onto a selected chemical, electronically charged or inert substrate. After exposure for a suitable sampling period, the sampler is transported to the laboratory for chemical analysis. A special type of passive sampler is the diffusive sampler. A diffusive sampler is a device which is capable of taking samples of gas or vapour pollutants from the atmosphere, at a rate controlled by a physical process such as molecular diffusion through a static air layer, or penetration through a membrane, but which does not involve the active movement of air through the sampler (Berlin *et al.*, 1987).

Given this definition, Schwela (2010), concludes that diffusive sampling is not feasible for the monitoring of dust or particulate matter, practically due to the fact that the uptake rate of the gas should be exclusively controlled by molecular diffusion and should not involve any active movement of air. However, particle deposition models have been developed e.g. Sehmel and Hodgson, (1978); Slinn and Slinn, (1980); Nazaroff and Cass, (1987); Noll, Fang and Watkins, (1988); Cooper, Peters and Miller, (1989); Pui, Ye and Liu, (1990); Schneider, Bohgard and Gudmundsson, (1994); Wagner and Leith, (2001a), which help in making diffusive samplers usable for particulate matter monitoring. The deposition velocity model consists of a theoretical component and an empirical component. The theoretical component incorporates gravitational, inertial, and diffusive mechanisms, but can be approximated by the simple terminal settling velocity in many cases (Wagner and Leith 2001).

Asseal et al (2010) and Ott, Kumar and Peters (2007) summarise the passive aerosol sampling methods that have been reported in international literature (Brown, Wake, Thorpe, Hemingway, & Roff, 1994; Noll, Fang, & Watkins, 1988; Vinzents, 1996; Wagner & Leith, 2001a; Yamamoto et al., 2006). As stated previously, all these methods have different ways in which particulates attach to the surface of the substrate.

As assessed by Wagner and Macher, (2003), the passive aerosol sampler described by Wagner and Leith (2001a,b) is a potentially useful tool for exposure and ambient air monitoring assessments. The sampler (Figure 2) does not require a pump and is capable of sampling for periods of minutes to weeks, depending on the ambient aerosol concentration. They also state that the passive sampler is silent and unobtrusive, weighs 1.7 g, and is 1.5 cm wide. Thus, it interferes minimally with human activities. The sampler consists of a standard scanning electron microscope (SEM) stub, a collection substrate, and a protective mesh cap. During sampling, particles are transported by gravity, convective diffusion, and inertia through the 157 $\mu$m-diameter holes of the mesh cap and deposit on a substrate mounted on the stub. The stub is oriented such that the substrate axis lies parallel to and is in the same plane as that of the stub, (i.e. horizontal). After sampling, the mesh cap is removed, the stub can be placed in an SEM, (if the substrate is a poly-carbonate tape), or on an optical microscope, and the particles are counted and sized to determine the particle flux. For this study, the substrate is a glass cover that is analysed using an optical microscope. A semi-empirical, particle size-dependent deposition velocity model is used in conjunction with the measured flux to obtain the ambient mass size distribution and mass concentration over the sampling period.

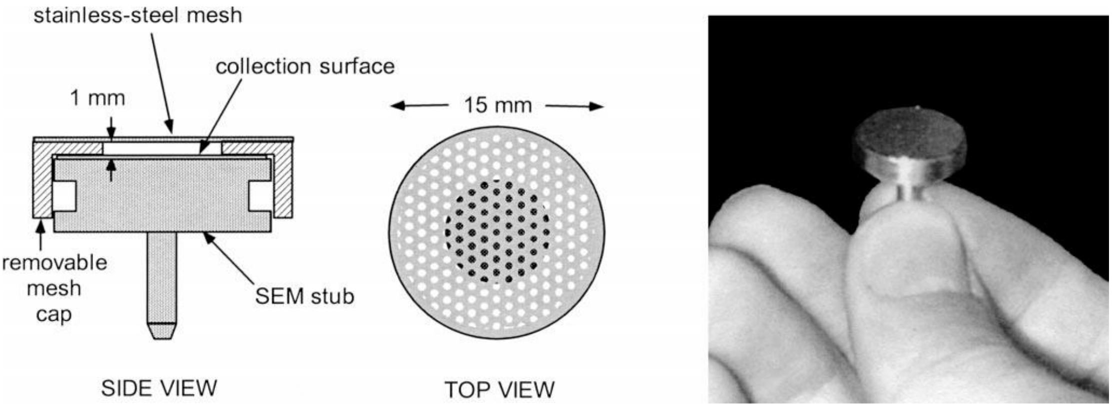

**Figure 2:** The UNC Passive Aerosol Sampler ( Wagner and Leith, 2001) **.**

The difference between the UNC aerosol sampler and that used in this study is the mesh. As stated previously, the mesh used in the UNC sampler is commercially available in the United States and has size-selective aerosol inlet holes with a diameter of approximately 157-160$\mu m$, with slightly tapered sides (see Figure 3 below). The mesh used in this study was manufactured in South Africa (Laser Technologies) and has non-tapered holes with a 190-200$\mu$m diameter. The difference in hole shape was caused by the different manufacturing techniques used. This work incorporates a shelter designed and tested by Ott and Peters, (2008) to house and protect the samplers from precipitation and the effects of wind on the deposition of particles to its collection surface. Assael, Melas and Kakosimos, (2010) conducted a computational fluid dynamics (CFD)-aided evaluation for the protective cover to protect samplers and the optimum design chosen is shown in Figure 4a. This design is quite expensive since it incorporates a data logger to measure the meteorological data. The passive sampler in a flat plates shelter offers an inexpensive means to assess ambient $PM_{10-2.5}$ without on-site measurement of wind speed, humidity, temperature, rainfall and wind direction (Ott and Peters, 2008). The flat plate shelter has been used successfully in other studies, (Willis *et al.*, 2009; Sawvel, 2013; Byeon, Willis and Peters, 2015; Sawvel *et al.*, 2015). There is need for more studies in the design and efficiency comparison of sampler shelters. All the required measurement data was recorded by equipment at the reference monitoring stations used in the study, thus eliminating the need to design and use shelter with housing for a data logger as shown in Fig 4a.

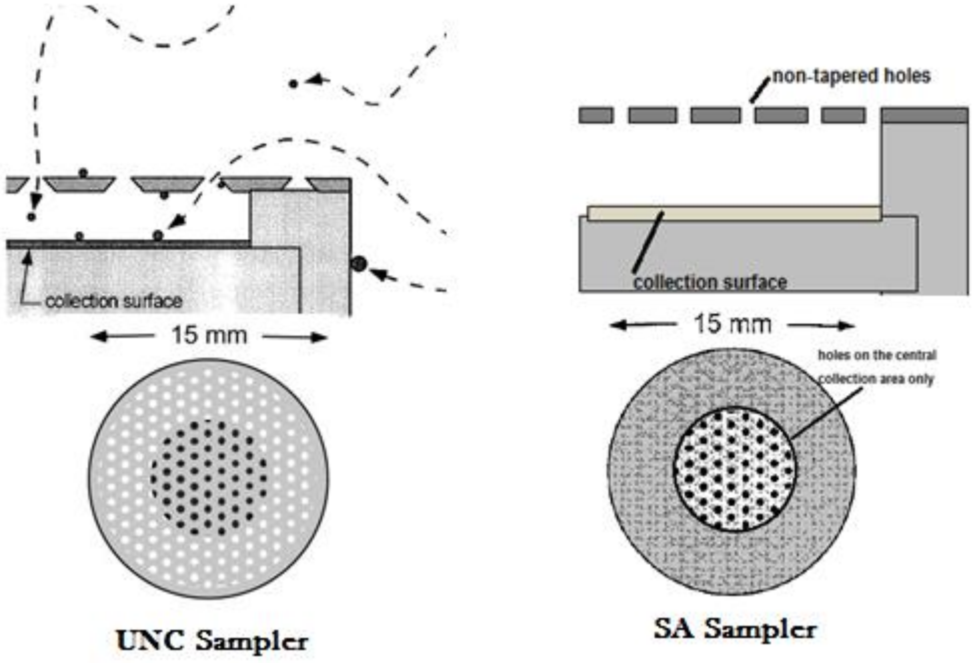

**Figure 3:** The UNC and locally designed sampler.

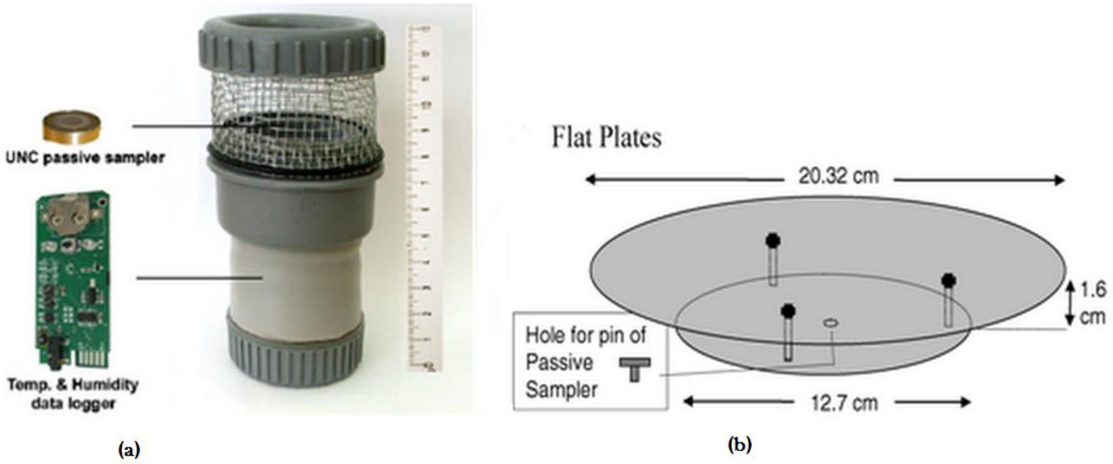

**Figure 4:** Different designs for passive sampler shelters, (a) (Assael, Melas and Kakosimos, 2010) and (b) (Ott and Peters, 2008).

The passive sampler can sample unattended for hours to weeks and has potential utility as a personal sampler. The main disadvantage of the passive sampler lies in its limited time resolution thus will only provide information on integrated average pollutant concentrations. Table 6 shows a comparison of passive and active samplers.

### 2.3.2 Active Samplers

These are devices that require electric power to pump sampled air through a chemical or physical collection medium. These devices usually have a pump attached to suck in the ambient air to be analysed. Although they are more complex and expensive than passive samplers, active samplers for PM monitoring are relatively simple to operate and have proved highly reliable. An extensive baseline of measurements from active samplers is available for much of the world, and it is important that measurement continuity with this database is maintained so that long-term trends can be deduced.

Active automatic analysers provide continuous monitoring which can be divided into techniques that measure gravimetric mass specifically and methods that measure a proxy such as the optical or chemical properties of particles. Gravimetric methods are the only type that meet the United States Environmental Protection Agency (USEPA) Federal Reference Method (FRM) requirements and can be used for the reporting of National Environmental Protection Measures for Ambient Air Quality (NEPM) $PM_{10}$ standards and $PM_{2.5}$ advisory standards (Keywood and Selleck, 2016). Despite the considerable advantages of gravimetric air pollution samplers, not least in terms of ease of use, and robustness, there are some monitoring applications, which necessitate the fine time response - of hours or less - provided by active automatic analysers. These instruments use some property of the particulates that can be continuously detected, usually by optoelectronic methods. Sampled air enters a reaction chamber where an optical property of the sample can be measured directly. A light detector produces an electrical signal that is proportional to the concentration of the pollutant being measured. Portable, even hand-held, automatic analysers have become available for particulates. These are usually based on laser detection methods. However, the stability, specificity and limited sensitivity of such devices still limit their wider application.

The advanced capabilities of automatic analysers are obtained at the expense of increased capital, running and support costs: these instruments also tend to be more susceptible to technical problems than gravimetric samplers, and require skilled manpower for routine operation. More sophisticated quality assurance methods may also be required for automatic analysers. Continuous analysers also produce large quantities of data, which usually necessitate telemetry systems for data acquisition and computers for subsequent processing and analysis. Well-proven continuous analysis techniques are available for the priority urban pollutants.

However, it should be recognised that the relatively high cost (typically over $10,000 per pollutant) and operational complexity of these devices may render them unsuitable for use in some places. Their use may be inadvisable when the necessary support infrastructure and trained manpower are not available. It is common for state-of-the-art networks using active automatic analysers to continue to coexist with active and passive sampler type surveys. In practice, these measurements can often be regarded as complementary activities. Active measurements are not necessarily intrinsically superior, and the mistake of ceasing all sampler-based activities when automatic analysers are first deployed should be avoided. Table 5 below shows a comparison of active and passive samplers used in the study design (Keywood 2016, Schwela 2010).

**Table 5:** Comparison of different air monitoring methods and equipment.

| AQM Device | Advantages | Disadvantages | Approximate Cost |
|---|---|---|---|
| **Passive Samplers** | • Collected samples can be used for chemical composition analysis and thus source apportionment.<br>• Sampling equipment is not costly.<br>• There is no power required for sampling.<br>• They are simple to set up.<br>• Can be deployed in very large numbers.<br>• Useful for screening and mapping. | • Unproven for some pollutants.<br>• They do not possess a high time resolution. In general, they only provide weekly and monthly averages.<br>• Labour intensive and need for adequately trained technical staff for analysis.<br>• Slow data throughput<br>• Not approved for use as reference methods. | R500-R2000/sample |
| **BAM** | • Meets NEPM reporting requirements<br>• South African standards exist<br>• Sampling equipment moderately priced<br>• Time resolution can be increased by the inclusion of light scattering devices in some models<br>• Provide hourly data and online information | • Complex and expensive to set up network,<br>• Hourly resolution means that only one data point is collected per hour<br>• High recurrent costs due to maintenance<br>• Cannot be used in remote places without access to electricity<br>• | Maintenance costs up to R500 000/a |
| **TEOM** | • Meets NEPM reporting requirements<br>• South African standards exist<br>• Sampling equipment moderately priced to highly priced<br>• High time resolution<br>• Provide hourly data and online information | • Complex and expensive to set up networks,<br>• Sample heated to 50°C so volatile mass lost; this can be mitigated by the use of FDMS which increases cost.<br>• High recurrent costs due to maintenance<br>• Cannot be used in remote places without access to electricity | Maintenance costs up to R800 000/a |

This study considers only two types of active samplers that are used in the air quality monitoring stations across the field in South Africa, namely the Beta Attenuation Monitor (BAM) and the Tapered Element Oscillating Microbalance (TEOM). The locally developed and the UNC passive samplers were placed at reference monitoring stations to compare them with the reference monitoring equipment. Through a method described by Wagner and Leith, (2001a, b), the ambient concentration can thus be calculated and the precision decided by statistical analysis.

### 2.3.3 Beta Attenuation Monitors

Jaklevic *et al.*, (1981) explains Beta Attenuation as the absorption of beta radiation by solid particles which is only dependent on the mass of the particle, (i.e. not density, chemical composition or optical or electrical properties). In this sampler, air is drawn through a filter at a known rate for a known period, (generally one hour) and attenuation of a beta ray signal (generated from a small source such as Carbon-14) is measured with a scintillation detector. This is then compared with a measurement of the beta attenuation of the non- exposed filter (determined before sample collection commenced) to determine the gravimetric concentration of the ambient particulate matter. In essence, this means that the more PM that settles on to the tape during the hour, the more attenuation there is of the signal (Raja *et al.*, 2016).

Beta attenuation monitors can be operated with size-selective inlets (e.g. $PM_{10}$, $PM_{2.5}$, and $PM_1$). Several BAM instruments are commercially available, and, in most instruments, the 1-hour measurements resolution can be increased to minute resolution by including a light scattering measurement (e.g. nephelometer) that is calibrated using the hourly BAM mass measure. One example of such a device is the BAM 1020 shown in Figure 5. It is low-priced when compared to other active automatic PM monitoring devices. It is a highly reliable device with a data capture reliability that is greater than 95%. It is also simple to start up and operate. It has a filter tape that has a 2-month lifespan (Envirotech Instruments, 2010).

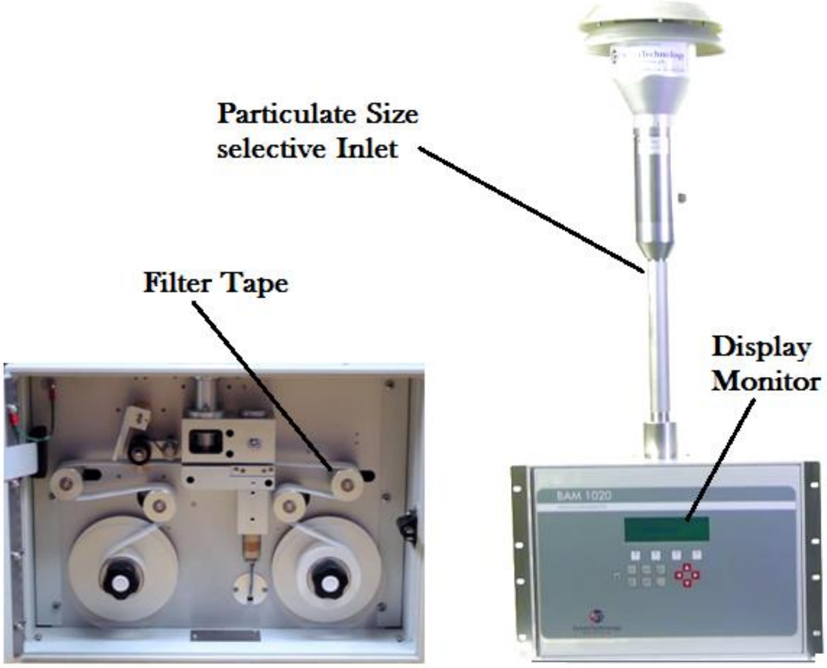

**Figure 5:** The BAM 1020 showing the interior and exterior setup.

### 2.3.4 Tapered Element Oscillating Microbalance (TEOM)

The TEOM determines particle mass by measuring the change in frequency of an oscillating microbalance as the particle mass on the microbalance changes (Allen *et al.*, 1997). This is only dependent on the mass of the particles. Air is drawn through a filter resting on a microbalance at a known flow rate and the change in frequency of the microbalance relative to the blank filter weight determines the volumetric concentration of particulate matter in ambient air. The resolution of the measurement is one data point per minute.

Solomon and Sioutas, (2006) state that aerosol mass loss due to volatilisation; (the standard TEOM operates at around 50°C can be measured by adding a Filter Dynamic Measurement System (FDMS) to the TEOM. The FDMS determines the mass lost by periodically drawing particle-free air through the oscillating microbalance and measuring the mass of aerosol lost from the filter as the particles equilibrate with surrounding air. The typical resolution of a TEOM is $0.5\mu gm^{-3}$. The TEOM can be operated with size-selective inlets (e.g. $PM_{10}$, $PM_{2.5}$, and $PM_1$)

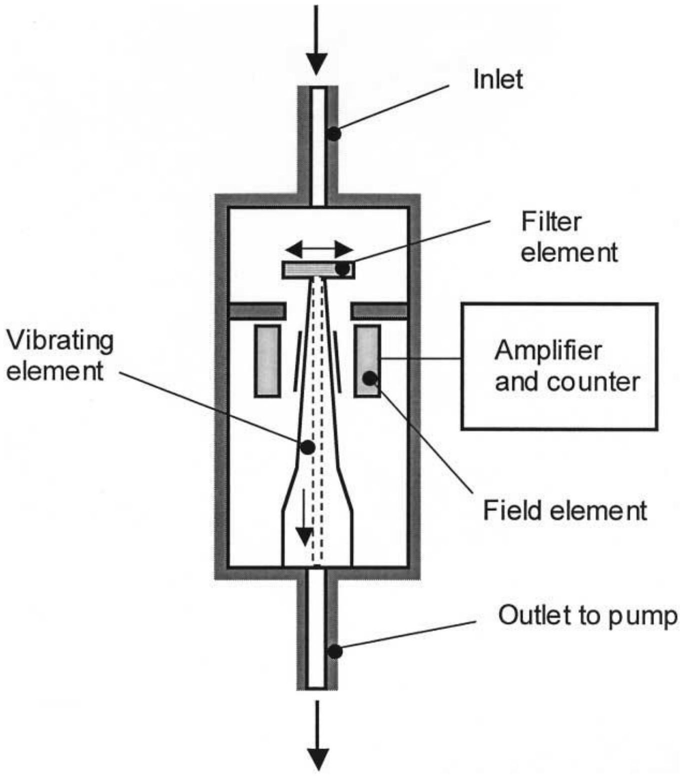

**Figure 6:** The schematic diagram of a TEOM showing the tapered-element and the frequency response with increasing PM deposition on the filter plate (https://www.researchgate.net/figure/Schematic-diagram-of-TEOM_fig9_229277099).

## 2.4 The impacts of particulate matter on the environment

Air pollutants have been known to exhibit both chronic and acute effects on flora and fauna. Numerous health effects and associations have been reported in the literature so far to ascertain the impacts and burden it causes. Particulate matter is known to cause respiratory-related illnesses and effects such as reduced lung functioning, asthma attacks, coughing and wheezing, exacerbation of diseases such as bronchitis and cardiovascular related illness. Other non-respiratory interactions include, but are not limited to, increased hospital admissions, premature death and irritation of such organs as the eyes, nose, mouth and throat. A number of different types of adverse health effects have been attributed to PM pollution in the air, although the severity of response depends greatly on the type of pollution (Coarse, fine and or ultrafine) the level of exposure, and individual susceptibility.

Ambient PM is also known to affect vegetation resulting in reduced biodiversity and the loss of ecosystem "goods and services" (Westman, 1977; Daily *et al.*, 1997). Exposure of vegetation to ambient PM can occur either on the vegetative surfaces, through the soil or both. Information available points to a greater impact occurring through the soil (Grantz, Garner and Johnson, 2003). The following text refers to the impacts and pathways of ambient PM pollution to both animal and vegetative life.

### 2.4.1 Health Impacts of PM

The effects of airborne particles on living organisms have been extremely and dynamically investigated for several decades (Dockery *et al.*, 1993; Bascom *et al.*, 1996; Pope III *et al.*, 2002; U.S. Environmental Protection Agency, 2004; Pope, 2007). Even with the presence of such studies, the specific characteristics of PM that are harmful are not entirely understood. PM has been strongly correlated to several adverse human health effects including an upsurge in hospital admissions and emergency room visits, respiratory symptoms, exacerbation of chronic respiratory and cardiovascular diseases, decreased lung function, and premature mortality e.g.,(Dockery *et al.*, 1993; Laden *et al.*, 2000; Pope III *et al.*, 2002; Samoli *et al.*, 2008).

PM undergoes augmented enrichment with certain trace and major elements under the right conditions. Kumar *et al.*, (2014), state that the effects of PM on human health include diseases such as asthma, chronic bronchitis, chronic obstructive pulmonary disease (COPD), rhinitis, irritation of lungs, pneumonia, decreased resistance to respiratory infection, chronic cough, phlegm production, allergy, headache, fatigue, lung cancer and premature death. Studies have also proven that high particle concentration is associated with substantial short-term increases in morbidity and mortality (Peters *et al.*, 2000, 2004; Zeger *et al.*, 2000; Daniels *et al.*, 2004; Brunekreef and Forsberg, 2005; Dominici *et al.*, 2005; Wang, Zhang and Li, 2008; Katsouyanni *et al.*, 2009; M.L. and K., 2012; Newby *et al.*, 2015).

Dusseldorp *et al.*, (1996) have studied the association of $PM_{10}$ and airborne iron with respiratory health of adults living near an industrial area in Wijk aan Zee, the Netherland and a statistically significant decrease in peak expiratory flow (PEF) was found to be associated with increasing $PM_{10}$ concentrations. The American Lung and Heart Associations have linked long term exposure to elevated levels of particulate matter to higher rates of lung cancer, decreased lung function among children and teenagers, overall lung damage, increased risk of cardiovascular morbidity and mortality, and decreased life expectancy(American Lung Association, 2008; Brook *et al.*, 2010).

In a study conducted by Atkinson *et al.*, (2014), the mean increase of all-cause mortality for augmentation of 10 $\mu g/m^3$ in momentary exposure to $PM_{2.5}$ was 1% with significant regional variation worldwide. An upsurge in mortality due to respiratory disease (+1.5%) and cardiovascular disease (+0.8%) was established. Multi-city studies of 29 cities in Europe (Katsouyanni *et al.*, 2001) and 20 cities in the United States (L Zeger *et al.*, 2001) stated short-term mortality effects for $PM_{10}$ of 0.62% and 0.46% per 10 µg/$m^3$ respectively.

A study (Ha *et al.*, 2001), based on air pollution and asthma admission among children has been carried out in Hong Kong, China. It was found that the ambient levels of $PM_{10}$ and $NO_2$ were associated with childhood asthma hospital admissions. Kumar *et al.*, (2008) studied the effects of airborne SPM on respiratory allergy in children of industrial areas of Delhi and found the mean level of indoor SPM was statistically and significantly high in the houses where children had asthma. Other studies have been carried out globally (in such countries as Chile, Brazil, Spain, Oman, Russia and India), and the chemical composition and deposition of PM in the human respiratory tract has been linked to toxic effects from metals such as Pb, Cd, and As, (Williamson, 2001; Quiterio *et al.*, 2004; Thakur *et al.*, 2004; Abdul-wahab, Worthing and Al-Maamari, 2005; Richter *et al.*, 2007; Srivastava and Jain, 2007).

Dockery *et al.*, (1993) have studied the association between air pollution and mortality in six cities of the United States and observed a statistically significant association between air pollution and mortality. Air pollution was positively associated with death from lung cancer and cardiopulmonary diseases but not death from other causes. The Harvard Six Cities cohort study found that for each 10 µg/m3 increase in $PM_{2.5}$ levels, the risk of all-cause mortality, cardiovascular mortality, and lung cancer mortality went up 14%, 26%, and 37% respectively (Johanna *et al.*, 2012).

As shown by the studies conducted by the US EPA, (2013), there is a decreased public health concern with PM larger than 10 microns because it is filtered out through the nose, cilia, and mucus of the respiratory tract. The US national health standards for the quality of ambient air is based on the mass concentration of “inhalable particles,” defined only by very small particles ($PM_{10}$) that can easily be inhaled into the lungs and negatively impact on human health. Fine-particulate ($PM_{2.5}$) pose a greater risk to human health because this can penetrate deep into the lungs and is more toxic than larger particles (Dockery *et al.*, 1993).

The physiological effects of a particle are determined by physical and chemical nature of the particles itself, the physics of deposition, distribution in the respiratory tract, and the biological events that occur in response to the particles (Hinds, 1999). Toxicological methods and approaches may focus the effects of a single agent or mixture of particles on the respiratory tract or alveoli of human beings with short term to long term effects initially (Bascom *et al.*, 1996).

Particulate deposition of in the respiratory system is characterised by the particle size. Models prove the deposition of inhaled particles is related to the aerodynamic diameter and the site of deposition of the particle in the respiratory system (ICRP, 1994; Berico, Luciani and Formignani, 1997; Daigle *et al.*, 2003). Particles larger than 5µm in aerodynamic diameter, (such as acid fog), settle in the upper airways or larger lower airways of the respiratory system of human beings. Smaller particles are more likely to be deposited within the lung. Hygroscopic growth, dimensions of the airways, breathing rate and respiratory secretions largely influence the sites of particle deposition in the airways. Lung diseases can alter particle deposition by changing airway dimension or airflow patterns. Exercise and increased activity escalate breathing, bypassing the nasal passages, and increases total ventilation, increasing particle velocity and inertial impaction. Both these changes result in greater particle deposition in the lower airways (Brain and Valberg, 1980).

Several mechanisms can remove particles from the respiratory system. Wiping and sneezing remove those deposited in the frontal nasal cavity, while the rest of particles deposited in the nose are cleared posteriorly to the pharynx. Swallowing and coughing remove those particles deposited in the trachea, bronchi, and bronchioles (Finch *et al.*, 1987). Particles deposited proximal to the bronchioles are largely eliminated by lung macrophages and/or dissolution. Inhalation of ultrafine particles may result in a highly increased interstitial access and acute inflammatory reaction within the lung parameters (Oberdörster, 1993).

### 2.4.2 Ecological Effects of PM.

Particulate matter typically consists of a mixture of both organic and or inorganic chemicals that include carbon, sulphates, nitrates, metals, acids and semi-volatile compounds. The effects of size-segregated rather than chemically speciated PM on ecosystem function is arbitrated by effects on dynamism, competitive practicality, and reproductive fitness of individual plants (Grantz, Garner and Johnson, 2003).

Different phytotoxic responses are associated with exposure to airborne particulates. These responses are dependent on the nature of the mixture of deposited particles. The particulate deposition and its subsequent effects on vegetation include but are not limited to; (1) nitrate and sulphate and their associations in the form of acidic and acidifying deposition and (2) trace elements and heavy metals, including lead. Despite the fact that size is associated with the mode and extent of deposition, it may be a convenient substitute for chemical composition (Whitby, 1978 in Mohapatra and Biswal (2014). Anthropogenic aerosols are generally characterised by acid-forming nitrate and sulphates particles while mineral dust are typically less soluble and less reactive (Fowler *et al.*, 1989; Grantz, Garner and Johnson, 2003). Vardaka *et al.*, (1995) state that dusts with pH values ≥ 9, may damage leaf tissue on which they are deposited or indirectly through alteration of soil pH (Hope *et al.*, 1991; Auerbach, Walker and Walker, 1997) and dust containing toxic soluble salts may pose harmful effects on plants (Prajapati and Tripathi, 2008).

Research by Monteith and Reifsnyder, (1974) has proven that plants absorb short wave radiation from the atmosphere, convert and emit it as long wave radiation. The optical properties of a leaf such as its surface reflectance and the amount of light available for photosynthesis may be altered by dust deposited on its surface (Eller, 1977; Hope *et al.*, 1991; Keller and Lamprecht, 1995). This tends to increase the surface temperatures of a snow-covered leaf by 4 to 11°C above the ambient temperatures (Spatt and Miller, 1981; Spencer and Tinnin, 1997), alters the structure and composition of plant species (Auerbach, Walker and Walker, 1997; Spencer and Tinnin, 1997), thus potentially altering the grazing patterns of animals (A Walker and R Everett, 1987).

It has been noted that the temperature of leaves may increase by 2-3°C in arid environments due to an increase in dust loads by 40 g.m$^{-2}$ (Rasoul Sharifi, C. Gibson and Rundel, 1997). Deposition of dust on the leaf surface may impede gaseous diffusion within and outside of the leaf. The upper surface of the leaf is affected more by coarse particles (Thompson *et al.*, 1984; Kim, Kalman and Larson, 2000), whilst fine and ultrafine particles have a greater impact on the lower surface (Ricks and Williams, 1975; Krajíčková and Mejstřik, 1984; Fowler *et al.*, 1989; Beckett, Freer-Smith and Taylor, 1998). In dusty environments species having stomata in grooves, or covering of wax on stomata might be affected less than species in which the stomata are located at the outer surface of the leaf (Prajapati, 2012).

Although in Europe, the concept of critical load is moving from a focus on the organism to a focus on the community and ecosystem, there is still a requirement for more molecular, plant-based markers of specific pollutant effects. At the present time, it is difficult to identify a widespread threat to ecosystem function due to un-speciated PM. Specific chemical constituents (e.g., nitrogen, H+), however, may pose a variety of threats at local to regional scales. Extensive research exists on the use of plants as biomonitoring tools. Plant response to air pollution may be used to evaluate the quality of air that may deliver early warning indications of air pollution tendencies. Biomonitoring tools can range from lichens to higher plants. Table 7 below, shows the impact of pH variations in different plants (Rai, 2016).

**Table 6: Impact of pH variations on stomatal behaviour and photosynthesis (Modified after (Taylor, El-Khatib and Freer-Smith, 2003)**

| pH range | Plants | Impact | Reference |
|---|---|---|---|
| 4.0–5.6 | Poplar *(Liriodendron tulipifera)* | Decreased photosynthesis and stomatal conductance. | Martens et al. (1989) and Freer-Smith and Taylor (1992) |
| 4.0–5.6 | Spruce (*Picea abies, two clones)* | Decreased photosynthesis and stomatal conductance in one clone. | Van Elsacker and Impens (1988) and Freer-Smith and Taylor (1992) |
| 2.5–5 | Spruce (*Picea rubens*) | Long-term depression of transpiration | Eamus et al. (1989) and Freer-Smith and Taylor (1992) |
| 3.0–5.5 | Beech *(Fagussylvatica*) | Increased stomatal conductance and inhibition of night-time closure. | Fliickinger et al. (1988) and Freer-Smith and Taylor (1992) |
| 3.5–5.5 | Spruce (*Picea abies*) | Decreased maximum and increased minimum of stomatal conductance. | Barnes et al. (1990) and Freer-Smith and Taylor (1992) |
| 5.0–6.5 | *Mangifera indica* | Affect chlorophyll and decrease photosynthesis | Thawale et al. (2011) and Chauhan (2010) |
| 5.5–6.5 | *Psidium guajava* | Decreased photosynthesis and stomatal conductance | Dwivedi and Tripathi (2007), Choudhury and Banerjee (2009) and Joshi and Bora (2011) |
| 7.0–9.0 | *Ficus religiosa* | Increases the conversion of hexosugar to ascorbic acid | Dwivedi and Tripathi (2007), Choudhury and Banerjee (2009) and Thambavani and Sabitha (2011). |

## 2.5 Application of passive samplers for monitoring of PM: Case studies.

Similar studies have been carried out in different countries,( Wagner and Leith, 2001; Leith, Sommerlatt and Boundy, 2007; Ott, Kumar and Peters, 2007; Willis *et al.*, 2009; Assael, Melas and Kakosimos, 2010; Arashiro and Leith, 2013; Nagar *et al.*, 2018). In all the studies mentioned above, use of the UNC passive aerosol sampler was utilised for the monitoring and measurement of fine and coarse PM. Other PM passive monitoring techniques shown in recent studies include filter-based methods, (Einstein *et al.*, 2012; Canha *et al.*, 2014) , and the Sigma-2 (VDI 2119, 2011) (Afshari, Matson and Ekberg, 2005), which collects ambient particles in the size ranges of 2.5-80μm which are deposited via sedimentation into a small acceptor dish (~5.5 cm in diameter).

Wagner and Leith (2000), carried out field tests to evaluate the passive aerosol sampler described by Wagner and Leith (2000a,b) in a well-ventilated occupational environment that had high concentrations of coarse aerosols. They set up an eight-stage cascade impactor onto which 3 passive samplers were also mounted adjacent the impactor. Assuming that the samplers were placed in an indoor environment, there was no need for protective shelters. One passive sampler blank was associated with each sampling event. Results on the samplers were obtained by subtracting the values obtained on the respective blanks. The passive sampler exposure times ranged from 27 minutes to 473 minutes. Using the deposition velocity model, the measured friction velocities at this site were less than 0.4m/s. They set up 5 sampling events and measured parameters such as the sampling time, temperature, relative humidity and typical wind speeds. The substrate they used was aluminium tape due to its high conductivity in SEM analysis. They carried out a qualitative analysis using XRDF for particle sizes ranging between 0, 1-10μm. They gave no information concerning image analysis method used and how the average particles count on the passive samplers were obtained. No information is stated pertaining to the exact magnification and voltage they used during microscopy. However, in their study, passive sampler results correlated well with those of the eight-stage cascade impactors, with $R^2$ =0.80 and 0.93 for $PM_{2.5}$ and $PM_{10}$ respectively. In order to quantify the precision of the passive samplers, they measured the coefficient of variation (CV) for the samplers. The average $CV_{PM10}$ for all samples was 20% and $CV_{PM2.5}$ was 16%. The US EPA 2013 recommends that alternative monitoring methods have a CV less than or equal to 10% with the Federal reference methods.

Ott, Cyrs and Peters (2007), developed a passive sampling method to measure ambient $PM_{10-2.5}$. In their study, they conducted eight 7-day field trials at three sites using UNC passive samplers (Wagner and Leith 2001a, b). At each site, three passive samplers were collocated with a dichotomous sampler and meteorological equipment to record temperature, relative humidity and the wind speed. The samplers were placed in shelters (Ott and Peters, 2008) to protect them from wind turbulence and precipitation. They prepared three blank passive samplers for this campaign. In order to calculate and quantify the uncertainty, blanks from both the field and laboratory tests were used to estimate the limit of detection (LOD) and the limit of quantification (LOQ) using a bootstrap analysis. The LOD for a 5 day was determined to be 2.3μg/m³. An elaborate description of the analysis method used is stated in this study. The magnification used, number of images taken per sample, and the analysis software is clearly stated. In their method, they use a deposition model like that used by Wagner and Leith (2001a) to calculate the aerosol concentrations but excluded the Cunningham slip correction factor. They also assume that the particle aerodynamic diameter $d_a$, is equal to the particle projected area diameter, $d_{pa}$ obtained from microscopy to eliminate the need to estimate the aerodynamic shape factor, $S_D$. In their fields tests, they used a method proposed by Wagner and Macher (2003), whereby a constant dynamic shape factor, $S_D$ =1.41 and a constant volumetric shape factor, $S_V$ =1.61 are employed. Using this method, they found out that the CV of $PM_{10-2.5}$ measured with collocated sampler was 20.1% in laboratory tests and 11.6% in field tests. They also concluded that the average $PM_{10-2.5}$ measured passively deviated from that measured with the filter-based dichotomous sampler by 29% in field tests. A strong correlation between the passive samplers and filter-based sampler for the $PM_{10-2.5}$ concentrations was derived, ($R^2$ = 0.97). A conclusion based on experimental evidence in this study suggested that at least 300 particles should be imaged to stabilise the analytical variability of the method.

Seven sampling sites were chosen in another study (Leith, Sommerlatt and Boundy, 2007) to determine the $PM_{10-2.5}$ concentrations in ambient air. In this study, the passive samplers were collocated with the Federal Reference Method (FRM) samplers and sampling periods ranged from 5-15 days. In this study, a glass substrate was employed, and imaging was carried out at 200X magnification. The analysis was carried out using ImageJ software with the values for dynamic shape factor, volume shape factor and particle density taken as 1.4, 1.6, and $2g/cm^3$ respectively. These values are similar to those used in the Wagner and Macher (2003) study. Information concerning the shelter used to protect the samplers is not furnished. The particle deposition model is used in this study to estimate the particle aerodynamic diameter from the projected area diameter using the Cunningham slip correction factor, particle projected area diameter and the particle volume shape factor. Measured concentrations were found to be within one standard deviation of the concentrations measured with the FRM samplers and ranged from $<10\mu g/m^3$ to $\sim 40\mu g/m^3$.

Another study to capture the spatial variability of airborne coarse particles ($PM_{10-2.5}$) was carried out during the same year, (Ott, Kumar and Peters, 2007). In this study, passive samplers were deployed over three 7-day periods at 33 sites in a medium-sized city (Iowa City, IA) with the approximate distance between sites being 4.4km. A real-time optical counter mounted on a mobile platform was selected to generate the overall sampling design that captured 95% of the total variance in $PM_{10-2.5.}$ The passive sampler imaging and analysis were similar to those mentioned in the study conducted by Ott, Cyrs and Peters (2007). Using these passive samplers, it was noted that $PM_{10-2.5}$ was heterogeneously dispersed throughout the study area. The weekly CV ($23\,\% \leq CV \leq 29\%$) was greater than the criterion of 20% to indicate heterogeneity and the maximum coefficient of divergence (COD) ranged between 0.21 to 0.36, which is above the criterion suggested by the USEPA to indicate heterogeneity (COD>0.2). The spatial variability coupled with the random error accounted for 29% of the total variability. They concluded that the exposure estimates made with data from centrally located filter-based methods are comparable to those made using passive samplers after resolving the spatial estimates to reduce the exposure misclassification errors in epidemiological studies.

In a study conducted in Thessaloniki in Greece, the uncertainty of the passive sampler was tested indoors and outdoors. Twenty UNC passive samplers were placed at specific locations across the greater Thessaloniki area. The indoor samplers were collocated with a Dustrak 8250 sampler and the outdoor samplers were placed close to official PM monitoring stations.  A cylindrical container was used to protect the sampler during the study period and a data logger circuit for ancillary data was attached in the inside casing of this container. The particle deposition model employed in this study is similar to that used by Leith, Sommerlatt and Boundy, (2007). They used a very high magnification, (400X) to acquire 49 images over a ~4mm substrate surface.

No statistical procedures were employed in this study to determine the exact agreement with the reference methods although the authors concluded that the results recorded using the passive samplers are in good agreement with those from the official monitoring stations.

In a study carried out in the United Arab Emirates, (Yeatts *et al.*, 2012), data were analysed and obtained in order to assess the precision of the passive sampler measurements using data from duplicate pairs that were deployed in a large field study. To ascertain their precision, 88 samplers were prepared and deployed as collocated pairs for one week – indoors in 41 residences and outdoors at three homes. The indoor samplers were protected using a metal cage while the outdoor ones were protected by an outdoor shelter. The samplers were analysed using a computer-controlled scanning electron microscope (CCSEM) at unspecified magnifications only stated as high and low magnification. Image analysis was conducted using ImageJ software. The CVs were compared between paired samplers and to the CV specified by the United States Environmental Protection Agency (U.S. EPA). Results showed that the samplers provide mass concentrations of $PM_{2.5}$ and $PM_{10-2.5}$ in the field with relative standard deviations that approach 15%, with greater precisions associated with higher concentrations ($PM_{2.5}$>5$\mu$g/m$^3$ and $PM_{10-2.5}$ >20$\mu$g/m$^3$). They also state the sources of any variability as arising from counting statistics and open spaces on the mesh screen (Arashiro and Leith, 2013).

A relatively recent study conducted in Cleveland, Ohio used passive samplers to capture the spatial variability of coarse particles by composition (Sawvel *et al.*, 2015). The samplers were deployed at 25 sites for three week-long intervals. After exposure, the samplers were analysed using CCSEM with energy-dispersive X-ray spectroscopy (EDS) for determining the concentrations of $PM_{10-2.5}$. The highest concentrations were observed at three industrial sites whereas substantially lower concentrations were observed in other areas. The work demonstrated that some components of coarse particles are considerably more spatially heterogeneous than other components. $PM_{10-2.5}$ mass in general and components associated with steel and cement production exhibited substantial heterogeneity. The mass concentration was calculated using methods derived from Wagner and Leith, (2001) and Ott et al., (2008a). Shirdel *et al.*, (2018), motivates the use of passive samplers as an alternative to the use of active samplers in occupational environments. They use the UNC passive sampler at four mine locations along with respirable cyclones, $PM_{10}$ and $PM_{2.5}$ impactors and an aerodynamic particle sizer to examine the effect of increased resolution for microscopic imaging. In their study, they concluded that the use of an area factor and a higher resolution eliminates the underestimation of $PM_{10}$ and $PM_{2.5.}$

Most of the methods incorporated in this study have been derived from the studies mentioned above to aid in the calibration of the locally manufactured passive samplers employed in this study. Sampler preparation, substrate material used, and the pattern followed during microscopy imaging are not stated in most of these studies, yet these have a huge impact on the results obtained. The present study used trial and error methods initially to determine the best methods and materials that give reliable results. This proved to be fruitful and a definite and well-defined methodology was developed.

# 3 CHAPTER 3: METHODOLOGY

## 3.1 INRODUCTION

The University of North Carolina (UNC) passive sampler developed by Wagner and Leith (2001 a,b) is a low-cost aerosol sampler that can be used to measure and determine the atmospheric particulate concentration. It consists of an SEM stub that is approximately 15mm in diameter, a substrate for collecting the dust and a stainless-steel mesh cap utilising commercially available mesh openings of the order of 200 micrometres. After exposure, the substrate can be analysed by light microscopy or electron microscopy. Both the sampler and analysis are relatively inexpensive and unobtrusive since they require no electrical power. These samplers have been applied for both indoor and outdoor studies, (Leith, Sommerlatt and Boundy 2007, Sawvel et al 2015, Ott and Peters 2007, Ott, Kumar and Peters 2007, Byeon, Willis and Peters 2007, Aseal et al 2010, Ashiro and Leith 2012).

In this study, passive samplers whose stainless-steel mesh was manufactured in South Africa were calibrated using data from different stations. These samplers (hereafter referred to as local samplers) were collocated with the UNC-type passive samplers and the conventional TEOMs and BAMs found at different sampling sites, for the measurement of $PM_{10}$ and or $PM_{2.5}$ in the atmosphere. The passive samplers collected particles by gravity, convective diffusion and convection onto a glass coverslip. This report further elaborates on the methods used during sampling and analysis.

## 3.2 Sampling

This study was conducted in four sampling campaigns. Sampling dates were selected according to the access to the monitoring stations on these dates. The sampling exposure was varied for the purposes of determining the optimum exposure time. The first sampling campaign was carried out for seven consecutive days (from 03-11-2017 to 09-11-2017) at five ambient monitoring stations operated by Eskom SOC [Chicken Farm (Buyani), Kendal, Phola] and Sasol Synfuels, (Club and eMbalenhle) respectively. The second sampling campaign had an exposure period of ten days (from 16-11-2017 to 25-11-2017) and was carried out at the sites provided by the City of Tshwane (Ekundustria, Olievenhoutbosch, Mamelodi and Bodibeng). The third sampling campaign was also carried out at the four city of Tshwane stations for a period of fifteen days (from 02-02-2018 to 17-02-2018) and the fourth and final campaign used an exposure period of five days (from 24-11-2017 to 28-11-2017). Four blank samplers were prepared for each campaign and these were placed in tightly sealed containers during the transportation and deployment of samplers. Four samplers were deployed and exposed at each station and these consisted of two local and two UNC samplers (duplicates to gather data on reproducibility) all housed under one protective shelter. The protective shelters that were used were similar in principle and design as those used by Ott (2007) and Ott and Peters (2008). The shelters were placed on the wind mast posts at the stations approximately 2m from the ground. All samplers were delivered to the sites and subsequent sampling followed with a constant start time (9 am). The station equipment was used to record the temperature, rainfall, wind speed, wind direction, relative humidity and $PM_{10-2.5}$ and the relevant data was obtained for the sampling period concerned. The blank passive samplers were also carried along in unopened containers and analysed for each period.

### 3.2.1 Description of the Sampling sites.

This study was performed with the samplers being collocated at eight existing air quality monitoring stations located in different areas. Permission was sought prior to sampling with the station operators namely ESKOM, SASOL and the City of Tshwane granting access to stations within their jurisdiction. An area map (Figure 7) and the site descriptions from the SAAQIS database appear below (http://saaqis.environment.gov.za/).

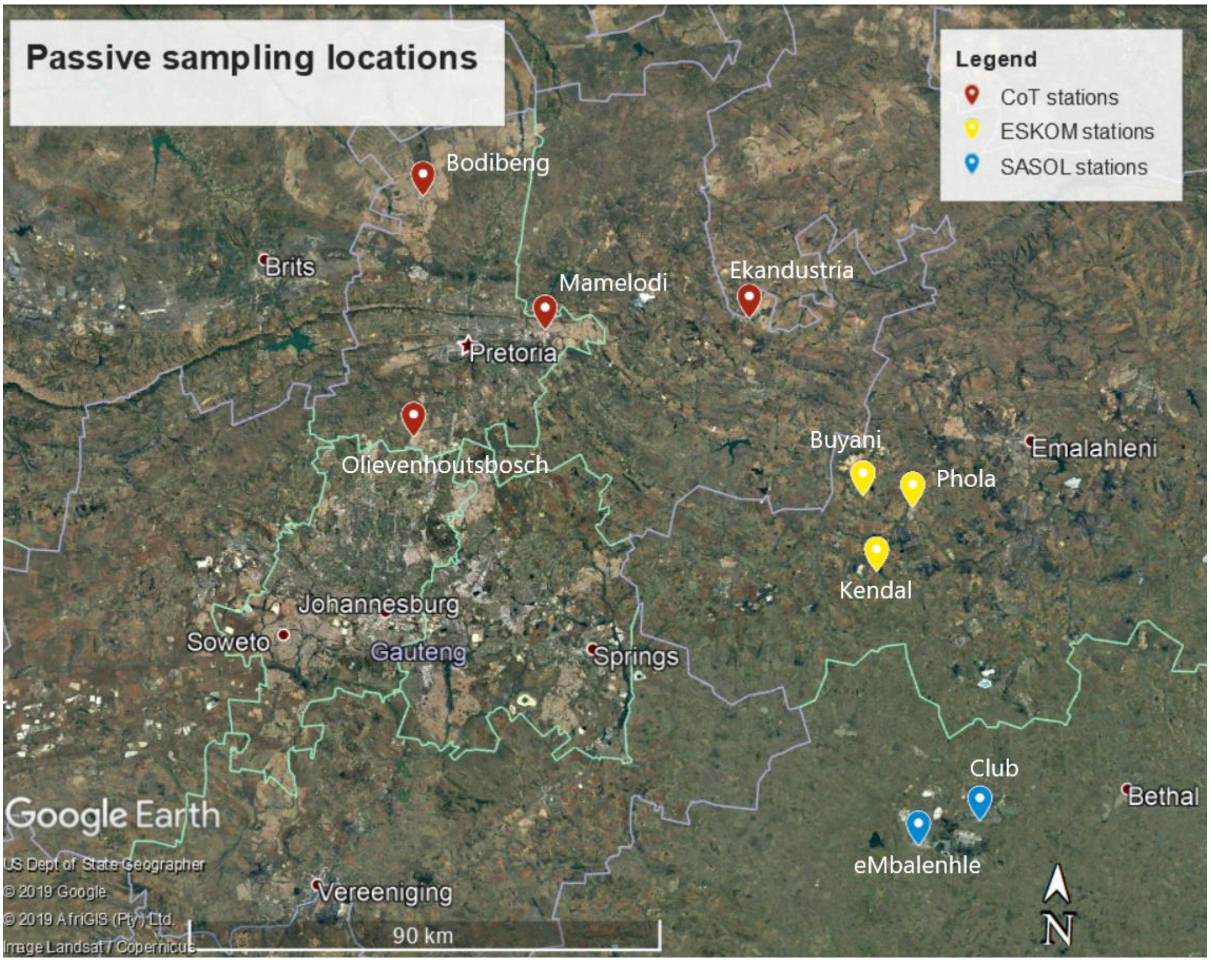

**Figure 7:** Map of the air quality monitoring stations used in the study

### 3.2.2 Olievenhoutbosch

This is a site located in an urban centre far from industrial, mining and power generation emission sources. It is located at a longitude of 28.092939 and latitude of -25.911667 while at 502m above sea level. This station is within the boundary fence of the Olievenhoutbosch clinic and is on the City of Tshwane Air monitoring network. The location is widely representative of city-wide background conditions as commercial and residential sites are located within a 5km radius. The ambient air monitoring equipment is stored in an air-conditioned unit with TEOM equipment for the measurement of PM at a data interval of ten seconds.

### 3.2.3 Mamelodi

This is a station provided by the City of Tshwane located at longitude 28.336606 and latitude -25.716567. Its site data interval is ten seconds and is 1323m above sea level. It is situated in a high population density residential area on the outskirts of the city. Commercial and residential places are situated within a 5km radius of the station. Emission sources within this station include but are not limited to a bus terminus nearby, a filling station, light industrial area, traffic, residential, schools and hospitals. The ambient air monitoring equipment is stored in an air-conditioned unit with TEOM equipment for the measurement of PM at a data interval of ten seconds.

### 3.2.4 Ekundustria

This is a station provided for by the City of Tshwane and the objectives of this station are to monitor the impacts of pollution from residential, traffic, industrial, and mining sources. This site is located at a longitude of 28.712833 and latitude of -25.69556 at 1500m height above sea level. The station is in the Bronkhorstspruit area within the borders of Gauteng. The emission sources within this site include industries within 5km, mining and farming. A low-density residential settlement lies to the north of this site and vast agricultural and industrial land to the other sides. This site uses a BAM for PM monitoring.

### 3.2.5 Bodibeng

This is a station located in Soshanguve 1121m above sea level with the longitude of 28.093733 and latitude of -25.492833. The station provider is the City of Tshwane and it is a source/target-oriented station with a mandate to monitor residential and traffic emissions. It is within the border fences of a library site and within a 1km range of a busy shopping centre. Soshanguve is a high-density suburb and much of the emissions are residential and traffic related. A BAM is used for the monitoring of PM at this station.

### 3.2.6 Chicken farm

This site is part of the ESKOM Air Quality Monitoring Network. It is located in the Nkangala Municipality in Mpumalanga and surrounded mainly by farmland. The Medupi and Kendal power stations are within a 10km radius. Mining also takes place within a 5km radius and as suggested by the name there is a commercial chicken rearing facility on the site. This site's longitude is 28.942892 and latitude is -25.978832 at 1571m above sea level. The objectives of the site are to monitor industrial emission sources. The site uses BAM equipment for PM monitoring at a data interval of five seconds.

### 3.2.7 Kendal

This is an ambient air monitoring station located at a longitude of 28.974496 and latitude of -26.107888 at a height of 1616m above sea level in the province of Mpumalanga. This site is part of the Eskom Air monitoring network and is located within 2.4 kilometres of the Kendal power station and its ash treatment and disposal facility is just 2.5km to the west. There is a paved road nearby used by coal haulage trucks.  The facility uses BAM equipment for PM monitoring at a data interval of five seconds.

### 3.2.8 Phola

This is a station located in the Emalahleni area in Mpumalanga under the Nkangala Municipality on a school site within a residential area. Its GPS coordinates are 29.038164, -25.995669 and it is located 1534m above sea level. The overseeing authority is ESKOM, and this is one of the stations on the ESKOM Air Quality Monitoring Network. The equipment is housed in a Chromadeck shelter and uses BAM for PM monitoring at a data interval of sixty seconds. Its purpose is to monitor the impact of the surrounding activities on the local communities. The emission sources include power generation, (as it within the vicinity of Kendal and Medupi power stations), petrochemical, mining, residential and farming.

### 3.2.9 Sasol Club

This is an air quality monitoring station provide by Sasol. This is a station situated on the southern outskirts of the Secunda residential area. The site is located close to the main road and may be affected by vehicular emissions. The Sasol synthetic fuels industrial site is within a 5 km radius and coal handling activities are also close by.  The station is located at 29.189667 longitude and -26.523333 latitude. The air monitoring equipment at this site uses TEOM (Thermo Scientific) technology at a data interval of five seconds.

### 3.2.10 eMbalenhle South

This station is situated ±9km to the west of the Sasol synfuels complex in the Gert Sibande municipality. It is operated by Sasol and it is located at longitude 29.1125 and latitude -26.551667. It is located on a secondary school site within the eMbalenhle residential area and its objective is to monitor industrial and residential emissions. The emission sources include fuel burning from the Sasol synfuels complex and residential coal burning for space heating in winter and for everyday cooking.  TEOM PM monitoring equipment is installed at this site and measurements are at a data interval of five seconds.

## 3.3 Passive Sampler Analysis

Prior to exposure, the samplers are thoroughly cleaned using alcohol, moist wipes and compressed air and then transported to the site in airtight polytop containers. Following its exposure to the atmosphere for a predetermined time period, each sampler was put back into an airtight polytop container and transported to the laboratory for analyses. These polytop bottles were clearly labelled with the station name and, mesh type and sampling period. After removal from the sampler the glass coverslips were taped onto a glass slide with the exposed side facing the glass side. For each glass surface, digital photos were taken using a light microscope, Zeiss Imager.A1m Microscope (Carl Zeiss, Germany), equipped with a digital camera AxioCam MRc5 (Carl Zeiss, Germany) at 100X and 200 X magnification for a ~6mm exposure diameter. The photographs were taken using a specific Cartesian plane pattern enabling the capture of the entire surface. The light intensity, hue, saturation and background were kept constant for all photos by setting the measurement parameters, so enabling a uniform histogram. Digital images were saved and stored in .tiff format in corresponding folders using the AxioVision SE64 software (Carl Zeiss, Germany)) after the creation of an image gallery database.

Particle counting and sizing was done using ImageJ (NIH, Bethesda, MD) and AxioVision SE64 software. Using ImageJ, this involved the subtraction of the image background before converting it to an 8-bit image. The image’s threshold was then set to a value that avoids bias by either erosion or dilation after having converted it to a binary image. Automated counting using a custom macro followed and the particles were grouped into 6 arbitrary size bins. The macro outputted a list of the projected area, image coordinates, and circularity for each particle detected in the images. Image edge effects were neglected because the area of the image was very large compared to the size of the particles of interest and because the imaging minimised double capturing of any particles due to the pattern used. Results from both types of particle analysis software were exported to an Excel spreadsheet for further treatment. Following the work of Noll, Fang and Watkins, (1988), the count data was converted to a number distribution by plotting the results on a log probability graph as cumulative for each group against the upper size limit of that group. Further mathematical inferences stated below were applied to acquire the particle concentration data. This study takes into consideration particles with an aerodynamic diameter greater than 2.5 micrometres since an optical microscope will not image smaller particles. SEM was not considered as an analysis method in the calibration because optical microscopy was cost effective and readily available.

### 3.3.1 Volume shape Factor

Since the particles that are observed under a light microscope are usually irregular, the particle Projected Area Diameter ($d_{PA}$) is used to describe the size of the particles and relate it to the actual aerodynamic diameter ($d_a$) of a particle. In this work, maximum Ferret's diameter, which is the furthest distance between any two parallel tangents on the particle, is used. Martin's diameter would be preferable as it allocates a more accurate equivalent but is not used as it is not included in the measurement parameters for both software types (see figure 8). Following the work of Ott, Cyrs and Peters, (2007), the deposition theory (Hughmark, 1977; Schlichting, 1979; Hinds, 1999; Wagner and Leith, 2001b, 2001a) establishes particle characteristics such as the aerodynamic diameter that were employed to calculate the PM concentrations.

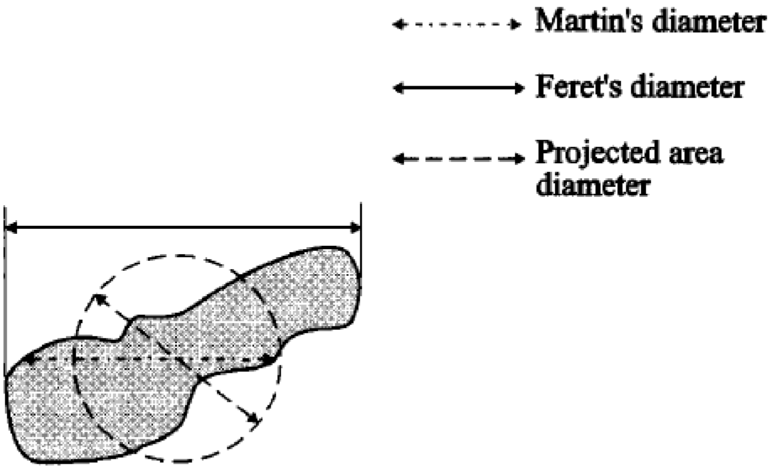

**Figure 8:** Schematic Illustration of different particle diameters based on the 2-D projected image (Whiting and Fox, 2019).

From Wagner and Leith (2001a), the aerodynamic diameter $d_a$ may be calculated from the projected area diameter of a particle, $d_{PA}$, derived from microscopic analysis as;

$$d_a = \frac{d_{PA}}{S_V\left[\frac{\rho_p}{S_D\rho_0}\right]}^{0.5} \tag{1}$$

Where $S_V$ is the volumetric shape factor, $\rho_p$ is the particle density, $S_D$ is the aerodynamic shape factor, and $\rho_0$ is unit density *(*1gcm$^{-3}$*)*. The mass of a particle, *m*$_i$, may be estimated as

$$m_i = \left(\frac{\pi}{6}\right) \rho_p \left[\frac{d_{PA}}{S_V}\right]^3 \tag{2}$$

Although it is important to accurately estimate each of the parameters in Eqn. (1) and (2), Wagner and Leith showed that $\rho_p$ and $S_D$ have a relatively minor influence on particle mass concentration compared to $S_V$. Whereas a 10% error in the estimate of $\rho_p$or $S_V$ results in a 5% error in calculated mass, the same error in the estimation of $S_V$ translates into a 21% error in calculated mass.

Researchers such as Schneider *et al.* (2002) and Vinzents (1996) have assumed mean values for density, volumetric shape factor, and dynamic shape factor when estimating ambient mass concentration from microscopic data. Particle composition consists mainly of abrasive materials and soft synthetic or naturally occurring organic materials. Due to this, Ott and Peters (2007), state that Wagner and Macher (2003) assumed a mean value of 2.0 gcm$^{-3}$ for $\rho_p$. They highlight the difficulty in assigning a mean value for $S_V$ and $S_D$ for ambient particles. The work of Davies, (1979) is often cited to justify a mean value of 1.4 for $S_D$ for ambient particles, although this value appears to be the average of the specific dusts studied, quartz, sand, talc, anthracite coal, and bituminous coal. Alternatively, Davies, (1979) and Wagner and Leith, (2001a), suggested selecting from a list of $d_a/d_{pa}$ ratios for eight dusts, including $d_a/d_{pa}$ =1.0 for sand if $S_D$ is unknown. Noll, Fang and Watkins, (1988), identified values of $S_V$ for coarse particles (>1 $\mu$m) ranging from 1.35 to 3.15 in 34 atmospheric samples. More recent studies have used shape information from scanning electron microscopy (SEM) to derive shape factors (Franck and Herbarth, 2002; Pratesi *et al.*, 2007). Pratesi et al. (2007) found substantial heterogeneity in the shape of coarse particles.

Following the work of Ott and Peters 2007, this work presents a revised method to estimate ambient PM$_{10\text{-}2.5}$ from samples collected with both the local and the passive samplers of Wagner and Leith (2001a). Particle mass concentration is estimated from surface loading with an assumed $\rho_p$ and $S_D$ but with $S_V$ derived from microscopy. In this way, the most sensitive parameter in calculating mass concentration from microscopic data, $S_V$, is based on individual characteristics of each particle.

### 3.3.2 Mass Concentration Calculation

The determination of the airborne mass concentration from the projected area diameter of the deposited particles involves the following key steps. From the work of Wagner and Leith (2001a), the deposition velocity, $V_{dep}$, was estimated for each particle, *i*, as;

$$V_{dep,i} = V_{amb,i}\gamma_{mesh,i} \tag{3}$$

Where $V_{amb,i}$ is the particle settling velocity and $\gamma_{mesh,i}$is an empirical modifier to account for the presence of the mesh cap. $V_{amb,i}$ and $\gamma_{mesh,i}$were calculated as;

$$V_{amb} = \tau g \tag{4}$$

and

$$\gamma_{mesh} = 0.00595\left(\frac{d_{PA}\tau g}{v}\right)^{-0.439} \tag{5}$$

Where $\tau$ is the relaxation time of the particle, *g* is the gravitational constant, and *v* is the kinematic viscosity of air. The relaxation time,$\tau$ was calculated as;

$$\tau = \frac{\rho_p d^2{}_a}{18\eta} \tag{6}$$

where ŋ is the dynamic viscosity of air. A Cunningham slip correction factor was not included in the calculation of $\tau$ due to its minor influence on the calculation for particles of the coarse size range. Particle aerodynamic diameter, $d_a$, was assumed equal to the projected area diameter $d_{pa}$, obtained from microscopy to eliminate the need to estimate the aerodynamic shape factor, $S_D$. This assumption is supported by Davies (1979) work that showed that $d_a/d_{pa}$ was equal to one for sand and near one for most other coarse mineral dust (Wagner and Macher, 2003). It is also supported by the fact that $S_D$ has a relatively minor influence on mass calculation (Wagner & Leith, 2001a).

The mass of a single particle, $m_i$, was then calculated using Eq. (2). For field tests, particle density was assumed to be 2.0gcm$^{-3}$ following Wagner and Macher (2003). The volume shape factor $S_V$ is a dimensionless constant that can be used to correct for the relative circularity of the particle and was determined for each particle from particle circularity, $C_p$, output by ImageJ as;

$$S_{V,i} = \frac{1}{C_{p,i}} = \frac{1}{\left[4\pi\left(\frac{A_i}{P^2{}_i}\right)\right]} \tag{7}$$

where *P* is the perimeter and *A* is the projected area of the particle. A circularity of unity indicates that the particle is a perfect sphere, while circularity progressively decreases from unity the more irregularly shaped a particle appears. The contribution of a single particle to mass concentration, *C*, was calculated as;

$$C_i = \frac{F_i}{V_{dep,i}} = \left(\frac{m_i}{A_T t}\right)\frac{1}{V_{dep,i}} \tag{8}$$

where *F* is the mass flux of the particle to the deposition surface translating to the particles collected per area time, $A_T$ is the total area of the sample that was imaged ($A_T$ is the number of images times the area of one image), and *t* is the sample time. $PM_{10\text{-}2,5}$ was calculated as;

$$PM_{10-2.5} = \sum_{i=1}^{n} C_i E_i \;\; (if\ d_a > 2.5\ \mu m) \tag{9}$$

where *E* is the $PM_{10}$ curve as defined by Hinds (1999):

$$E_i = 0.9585 - 0.00408 d_{a,i}{}^2 \;\; for\ d_{a,i} < 15\mu m \tag{10}$$

and

$$E_i = 0 \;\; for\ d_{a,i} > 15\mu m \tag{11}$$

### 3.4 Statistical and Uncertainity Analysis

Kennedy et al., (1995) in the National Institute for Occupational Safety and Health (NIOSH) handbook state that the LOD is a decision point which decides whether to report a significant analyte signal from the sample. It can be interpreted as the mass of analyte which gives a mean signal $3\delta_b$ above the mean blank signal, where $\delta_b$ is the standard deviation of the blank signal. The LOQ is the smallest amount of analyte which can be measured with precision. It is hence the lowest mass that can be reported with acceptable precision. LOQ is the larger of;

a) The mass corresponding to the mean blank signal $+10\delta_b$ (i.e., ± 30% uncertainty), or

b) The mass above which recovery is ≥ 75%.

These parameters relate to the low-concentration end of the analytical working range and do not provide information about accuracy, precision, or sensitivity at higher concentration.

The passive blanks were analysed to determine the limit of detection (LOD) and the limit of quantification (LOQ) by mass of $PM_{10\text{-}2.5}$ following the work of Leith et al. (2007). The LOD of the method was derived through the analysis of blank samples. The LOD by mass was calculated as the mean concentration ($\mu$g/m$^3$) per blank times three plus the standard deviation for each of the nine field blanks. The LOQ by mass for the samplers was determined from the mean concentration per blank plus ten times the standard deviation. The percentage of the sites with mean concentrations greater than the LOD and the LOQ were calculated over the whole sampling period.

The coefficient of determination ($R^2$), was computed as an indicator for the correlation between the performance of the local passive samplers at the same station, the UNC passive samplers at the same station, the correlation between the local and UNC samplers at the same station and that between the same substrates at 100X and 200X magnification. The correlation coefficient, p-value, estimate and standard error were computed by carrying out a regression analysis in a spreadsheet (Excel, Microsoft, Redmont, Washington for the eight site pairs. The precision of the samplers in their measurement of the mass concentrations at each site was expressed as the coefficient of variation (CV). This was determined by calculating the standard deviation divided by the sampler mean times 100%. The accuracy of measurement of $PM_{10\text{-}2.5}$ of the samplers was determined as a calculation of the ratio between the mean $PM_{10\text{-}2.5}$ measured by the samplers and that measured by the TEOM and BAM equipment at each station. The results were tabled graphically and the standard error was used as a measure for the determination of the error.

To estimate the uncertainty in the microscopic analysis and image analysis part of the method, four substrates, (two UNC and two local) were randomly selected and imaged and analysed three times. The CV was calculated for each substrate and this measure was used as an indication of the precision of each sampler. In order to find out the average agreements between the passive samplers and the TEOM and BAM equipment, the following relation was used;

$$\%\ Difference = \frac{Passive\ sampler\ result - PM\ Equipment\ result}{\frac{Passive\ sampler\ result + Equipment\ result}{2}} \times 100\% \qquad (12)$$

The results of equation 11 thus were used to allocate the discrepancies for each sampler to estimate the potential source of error.

### 3.5 Indoor monitoring using the local PM samplers.

Lebohang is a low-income settlement in the Mpumalanga Highveld whose air quality is likely affected by nearby power generation activities, indoor combustion and outdoor activities. Sasol Synfuels, through the NOVA Institute SA, has devised air emission offset interventions to counteract these possible sources. The intervention considered in this study is household-based (Increased insulation of the houses) aimed at improving the thermal performance of informal structures to facilitate a transition from solid fuels to use of cleaner alternatives.

In order to quantify and ascertain the sources of pollution passive diffusive samplers (Mukota and Kornelius, 2018), were used for both summer and winter monitoring across 20 households. Indoor sampling was particularly chosen because people spend most of their time indoors (Bo *et al*., 2017).

For the monitoring of indoor concentrations, samplers with glass substrates were used and poly-carbonate substrates were placed to find out the elementary composition of particles for source apportionment. These samplers were placed in 20 households in summer (26-03-18 to 01-04-2018) and in winter (10-07-18 to 17-07-18). Ten blank samplers were also prepared for determining the LOD and LOQ. The blank samplers were prepared just like the other samplers used indoors. However, they were never exposed but kept in poly-top bottles during the transportation and sampling periods to ensure similarity of particle deposition due to transport. Five of these blank samplers were analysed after three days and the other five after seven days. Sampling was done for three days and seven days at each of the households and another sampler was placed for SEM-EDS analysis to determine the nature of particles for source apportionment. Samplers were placed on holders (Figure 9) that were secured to the walls inside the houses, for the indoor measurement of $PM_{10-2.5}$. No weather shields were used, as these are not required for indoor sampling. Optical microscopy was used to image the glass substrates and SEM-EDS was used to analyse the poly-carbonate substrates.

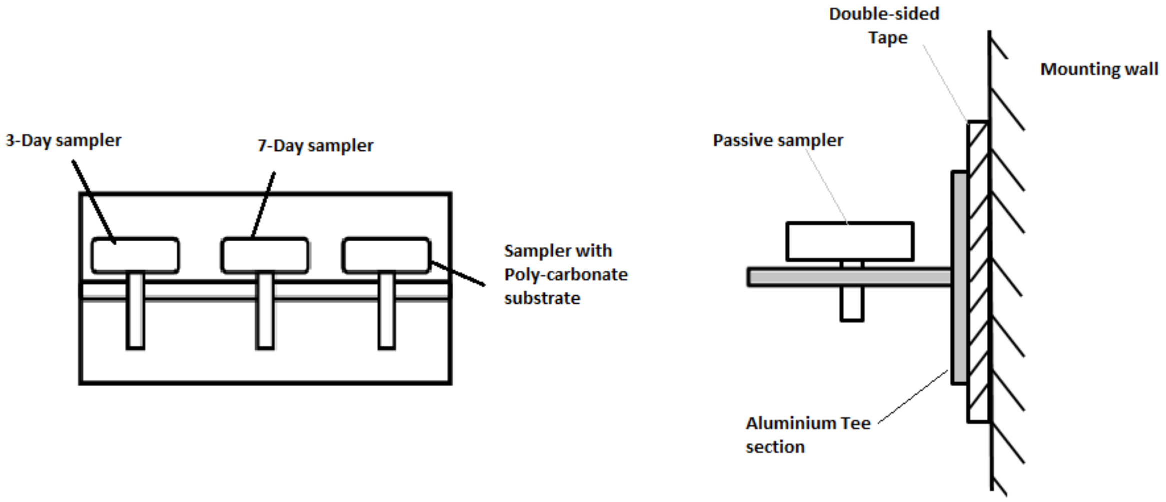

**Figure 9:** Configuration of the local passive sampler holder used for indoor monitoring.

### 3.5.1 Microscopy methods and analysis.

The analysis method used followed the calibration procedure of the locally developed aerosol samplers described above (Mukota and Kornelius, 2018). After removal from the sample holders, the samplers are transported back to the lab in airtight poly-top bottles. The cover glasses are carefully removed from each sampler and are taped to a microscope slide with the exposed side facing the slide. The slides are then imaged at a 200X magnification with a uniform hue, saturation and light intensity for all fields of view using a Zeiss Imager A1 microscope (Carl Zeiss Germany). The images for each coverslip are stored in a folder and in one tiff format. The images are then analysed using the proprietary Zeiss AxioVision software. The result is the acquisition of data such as the aerodynamic diameter, Ferret minimum and maximum diameter, circularity and perimeter of each particle which can then be used in the calculation of the particulate concentration for the entire sampling period.

Particles were collected on polycarbonate substrate which provides a flat, featureless substrate for computer controlled Scanning electron microscopy (CCSEM) analysis. The substrates were mounted on an SEM stub. Collected particles were analyzed with the Zeiss Ultra Plus with Sigma 3 flexible detection. Both instruments are equipped with secondary and backscattered electron detectors and thin-window, energy-dispersive X-ray detectors (EDX) that enable X-ray detection of carbon and heavier elements. Both instruments use proprietary software to perform CCSEM analysis of the sample and to enable off-line review and processing of CCSEM data. More details on particle analysis by CCSEM are provided in Mamane *et al.* (2001). The following SEM parameters were used: 20 kV accelerating voltage, magnification of 720X,  16 mm working distance, backscatter detection mode, and an EDX acquisition time of 2.5 sec, sufficient to acquire a robust X-ray spectrum. CCSEM was conducted in the area analysis mode, whereby the electron beam was focused over a specified area of each particle while X-rays were acquired. The total number of particles analysed per sample was 280. The analysis time per sample was about 4–5 hrs in which approximately 80% of the exposed collection area was analyzed. Samples were gold-coated prior to analysis. The particles in each sample were classified using rules based on their elemental composition into chemical classes and particle types.

### 3.5.2 Statistical and uncertainty analysis.

The passive blanks were analysed to determine the limit of detection (LOD) and the limit of quantification (LOQ) by mass of $PM_{10-2.5}$ following the work of Leith et al. (2007). The LOD for the method was derived through the analysis of blank samples. Like the previous calibration study, the LOD by mass was calculated as the mean concentration ($\mu g/m^3$) recorded per blank multiplied by 3, plus the standard deviation for each of the four blanks. The LOQ by mass for the samplers was determined as the mean concentration per blank plus ten times the standard deviation.

A student t-test was also conducted to find out if there is any significant difference between values calculated during the three day sampling period and the seven day period, and the difference between the summer and winter values. A 90% confidence interval was used.

To convert the 3 and 7-day concentrations measured here to a maximum daily value for comparison to ambient air quality standards, a proposal from Beychok (2005) was applied to the multi-day values. Beychok (2005) states that time-averaged concentrations, $C_p$ (valid for averaging time $t_p$) can be converted to an equivalent time-averaged concentration $C_x$ (valid for averaging time $t_x$) using equation 12 below.

$$\frac{C_x}{C_p} = (1/t_x)^{0.53} \tag{13}$$

Where: $t_x$ = actual sampling days

$C_p$ = equivalent highest 24- hour average concentration.

$C_x$ = actual concentration measured over $t_x$

Equation 12 was used to convert both the 3-day measurements and the 7-day measurements to equivalent the highest daily (24h) values. These values were then compared to the SA ambient air quality standards given in Table 8.

**Table 7:** SA national ambient air quality standards (NAAQS), and WHO air quality standards on PM.

| **Pollutant** | | **Mass concentration ($\mu$g/m$^3$)** | | **Frequency of Exceedance** |
|---|---|---|---|---|
| | | **NAAQS** | **WHO** | |
| $PM_{10}$ | 24 Hours | 75 | 50 | 4 |
| | Annual | 40 | 20 | 0 |
| $PM_{2.5}$ | 24 Hours | 40 | 25 | 4 |
| | Annual | 20 | 10 | 0 |

A comparison of the household's concentration over the three and seven-day campaigns and during the summer and winter periods was conducted. The household with the highest indoor PM10-2.5 concentration had its polycarbonate bearing substrate analysed using SEM-EDS as mentioned above.

# 4 CHAPTER FOUR: RESULTS

Sections 4.1 to 4.6 discuss the results of the outdoor (ambient) measurements. Section 4.7 discusses the results of the indoor measurements.

## 4.1 Introduction.

Concentration results from the stations are presented in this section, along with the calculated results from the passive samplers using the two types of software at a hundred times (100X) and two hundred times (200X) magnification, using either ImageJ or AxioVision software for particle analysis. Figures 10 and 11 show some pictures of the images taken at 100X and 200X magnification for the blanks and exposed samplers respectively. In total, 36 samplers were deployed, 18 being UNC and the other 18 using the local sampler. Only 28 were analysed because four samplers placed at Mamelodi were destroyed due to vandalism and the continuous sampler at Ekundustria was offline during the monitoring period. A simple regression analysis was conducted in order to find out the linear relationship between the calculated duplicate values and the concentration recorded at the stations. The duplicate values were averaged, and their standard deviations were used to understand how well they agree with each other. The coefficient of determination ($R^2$), measures the proportion (or percentage) of variation in the dependent variable that is explained by the independent variable. The $R^2$ value for collocated samplers is presented and through visual inspection, a comparison can be made.

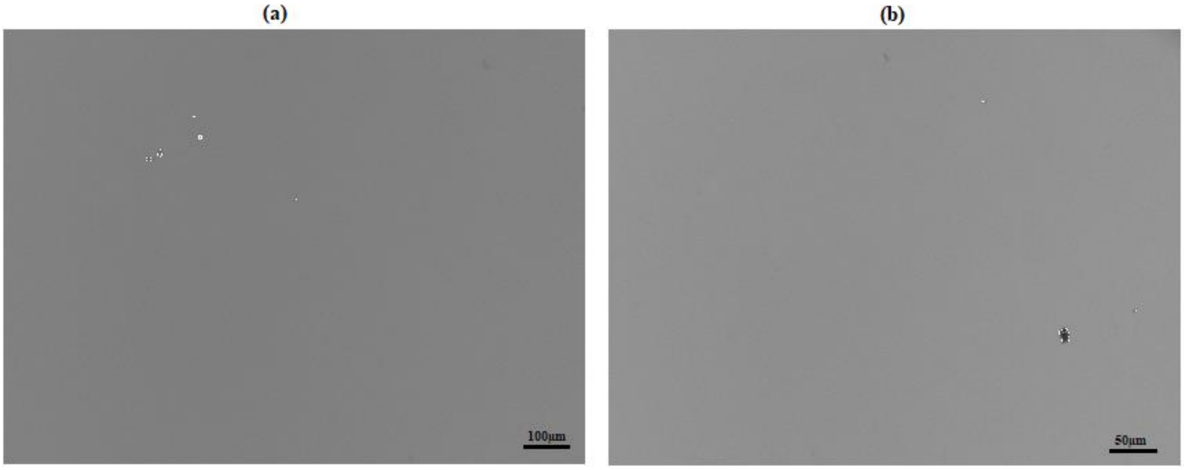

**Figure 10:** Unprocessed images taken at 100X (a), and 200X (b) magnification for a blank sampler.

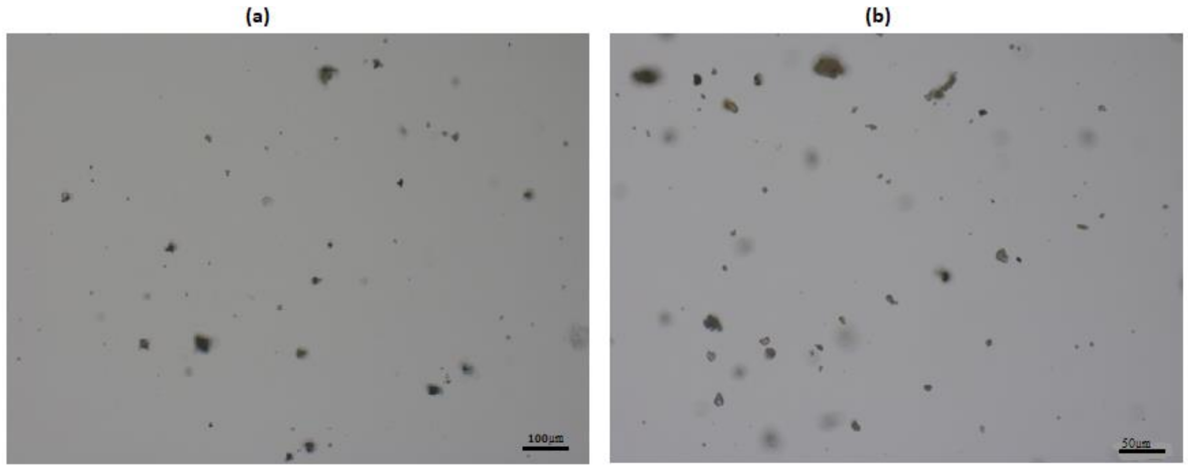

**Figure 11:** Unprocessed images taken at 100X (a), and 200X (b) magnification for a local sampler stationed at Chicken Farm.

Analysis of variance (ANOVA) is a hypothesis test approach to test for equality of means across multiple populations. To find out the effect that each treatment or factor has on the calculated concentration, an ANOVA, using two factors (without replication) was carried out between the samplers. The two factors were the magnification and the analysis tool used for the particle counts. The test was carried out at a 5% level of significance. The null hypothesis for all the tests followed as;

$H_0$: The magnification used will have no significant effect on the calculated concentration results.

$H_0$: The analysis software will have no significant effect on the concentration results.

$H_0$: The magnification used, and analysis software interaction will have no significant effect on the concentration results.

Table 14 shows the F-statistic, critical and P-values calculated for all the stations where passive sampler duplicates were placed. The sample represents the analysis tool whilst the columns are the magnification. The discrepancies between the calculated values and measured values are also presented as a percentage spanning between positive and negative values in order to represent both the magnitude and nature of difference. The Co-efficient of variation (CV) is presented last to obtain the precision as a percentage for each sampler across all stations.

The results section also consists of data gathered after the use of passive samplers in indoor environments. Results for the 21 households sampled in Lebohang Mpumalanga are tabled and the SEM-EDS analysis results for household 14 are presented.

## 4.2 LOD and LOQ

A total of 9 blank passive samplers were analysed, for different sampling durations ranging from one to fifteen days. The average number of images at 100X is 32 and 56 at 200X magnification. As shown in Table 8, this translates to a particle count of 32 (1.07 particles per image) at 100X magnification and (0.53 per image) at 200X magnification for the blanks. This is substantially less than the particles collected in the field tests and indoor samples and is as a result of handling and transportation.

**Table 8:** Particle count summary

| | Blanks | Field tests | Indoor Sampling |
|---|---|---|---|
| Mean Particle count per sample (st.dev.) | 31.74 (19.62) | 1846 (568) | 598 (304) |

If these blank particle counts were collected during a 1-day sample, they would translate to a mean $PM_{10-2.5}$ concentration of 5.7µg/m$^3$ with a standard deviation 3.9 µg/m$^3$. The 95% confidence limits on the mean were 3.9-7.5 µg/m$^3$. The LOD was 3.68µg/m$^3$ and the LOQ was 39 µg/m$^3$. To adjust these values to different sample periods in days, one simply divides by the number of days as shown in Figure 10.

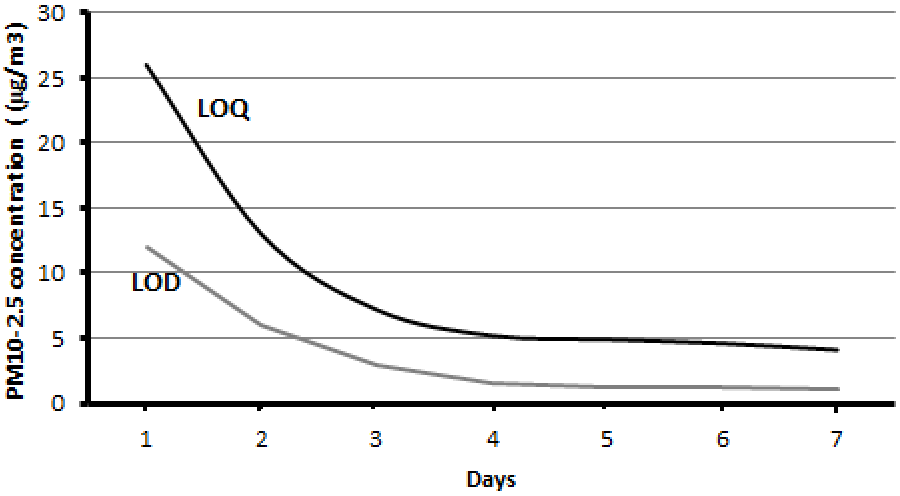

**Figure 12:** The LOQ and LOD calculated for different sampling durations.

The mean $PM_{10}$ concentrations observed at each station over the four sampling periods (03-11-2017 to 28-11-17) across Gauteng and Mpumalanga are shown in Table 9 and Table 10. The results after the analysis of each sampler using a set magnification and analysis software are also presented in the tables. As can be seen in both tables, 100% of the calculated values had a concentration greater than the LOD and the LOD.

**Table 9:** Comparison of the mean concentrations calculated at 100X magnification.

| | 100X magnification | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Image J | | | | AxioVision | | | |
| | **Station Readings $PM_{10}$ (µg/m³)** | **Local samplers** | | **UNC samplers** | | **Local samplers** | | **UNC samplers** | |
| | | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| **ESKOM STATIONS** | | | | | | | | | |
| CHICKEN FARM | 49,51 | 204,47 | 136.01 | 207.89 | 302.87 | 124,32 | 98.49 | 117.39 | 136.52 |
| KENDAL | 84.10 | 141.42 | 324.96 | 428.46 | 326.24 | 209.87 | 112.34 | 96.92 | 200.34 |
| PHOLA | 60.27 | 142.90 | 194.36 | 152.77 | 174.61 | 45.67 | 67.78 | 97.60 | 113.20 |
| **SASOL STATIONS** | | | | | | | | | |
| CLUB | 21 | 23,11 | 9.76 | 8.90 | 15.3 | 17.62 | 28.40 | 14.42 | 18.97 |
| BUYANI | 18 | 152.67 | 78.31 | 125.76 | 134.88 | 36.80 | 57.52 | 34.81 | 28.47 |
| **CoT STATIONS** | | | | | | | | | |
| BODIBENG | 47,80 | 56,81 | 38.59 | 49.31 | 86.69 | 45.78 | 56.89 | 44.7 | 49.56 |
| OLIVEN | 49.53 | 131.65 | 58.73 | 46.94 | 119.4 | 67.32 | 78.68 | 75.56 | 86.97 |

**Table 10:** Comparison of the mean concentrations calculated at 200X magnification.

| | 200X magnification | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Image J | | | | AxioVision | | | |
| | **Station Readings PM10 (µg/m³)** | **Local samplers** | | **UNC samplers** | | **Local samplers** | | **UNC samplers** | |
| | | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| **ESKOM STATIONS** | | | | | | | | | |
| CHICKEN FARM | 49,51 | 45.35 | 225.78 | 144.86 | 133.50 | 123.56 | 89.11 | 67.89 | 79.50 |
| KENDAL | 84.10 | 81.06 | 142.27 | 129.23 | 272.26 | 122.75 | 98.50 | 75.43 | 44.87 |
| PHOLA | 60.27 | 254.47 | 125.19 | 126.66 | 345.22 | 123.67 | 83.40 | 99.31 | 84.56 |
| **SASOL STATIONS** | | | | | | | | | |
| CLUB | 21 | 53.08 | 47.17 | 78.42 | 52.22 | 46.07 | 34.22 | 67.30 | 40.32 |
| BUYANI | 18 | 15.88 | 73.43 | 153.66 | 67.48 | 28.42 | 34.76 | 21.67 | 16.04 |
| **CoT STATIONS** | | | | | | | | | |
| BODIBENG | 47,80 | 56,81 | 38.59 | 49.81 | 86.69 | 88.31 | 42.36 | 29.34 | 56.43 |
| OLIVEN | 49.53 | 131.65 | 58.73 | 46.94 | 119.4 | 94.21 | 67.33 | 39.31 | 87.6 |

## 4.3 Inferences of magnification and type of analysis software for duplicate samplers.

The sections 4.3.1 to 4.3.4 are based on the results calculated for the collocated passive samplers. A bar graph of results gives a visual attestation of the concentrations measured by the passive samplers in comparison to the continuous samplers. A fixed standard deviation is shown by the error bars on each bar and represents the variation between the continuous value and the calculated value on each sampler. Furthermore, a regression analysis is carried out on all the passive measurements in collation with the continuous measurements, thus giving an indication of the $R^2$ value and the slope. The variation between duplicate samplers is represented on the same regression graph by error bars.

### 4.3.1 100X Magnification with image J

Collocated samplers were analysed using ImageJ software and an optical microscope at 100X magnification. Figure 11 shows the bar graph with a precision of 1 standard deviation. A summary of the $PM_{10-2.5}$ measured by each passive sampler compared to that measured by the active $PM_{10}$ samplers at the air monitoring stations is also presented. The station mean values are represented by the non-shaded bars with the other bars representing the calculated concentrations after analysis on both UNC and local samplers.

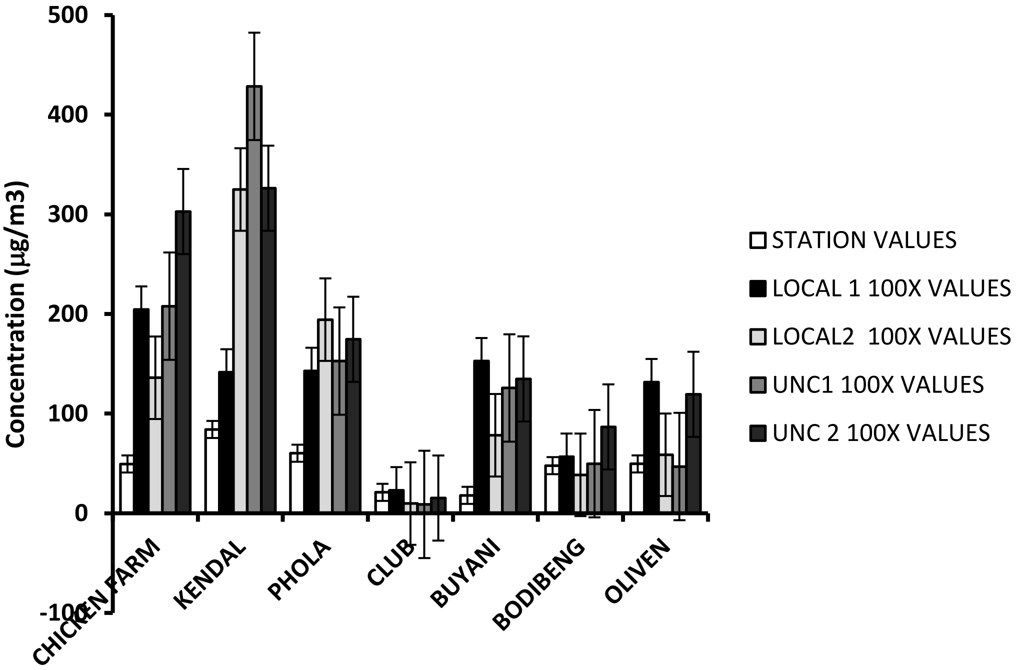

**Figure 13:** $PM_{10-2.5}$ measured at each passive sampler location by local samplers at 100X magnification using ImageJ. Error bars indicate 1 standard deviation.

A regression analysis was conducted for the set of concentrations obtained from the two local samplers that were collocated at each station and imaged at 100X magnification (Figure 12). The calculated concentrations for each sampler were presented against those measured at the station. This was done in order to visualise and understand the variability of $R^2$ values for multiple samplers undergoing the same treatment. $R^2$ is always between 0 and 100%:

- 0% represents a model that does not explain any of the variations in the response_variable around its mean. The mean of the dependent variable predicts the dependent variable as well as the regression model.

- 100% represents a model that explains all the variations in the response variable around its mean.

In the context of this study, the response variable is the average of the calculated duplicate concentrations measured by the collocated passive samplers and analysed at different parameters such as the magnification and analysis software. The mean values recorded at the stations over the sampling period are taken as the independent variable. The same was done for the UNC samplers at an imaging magnification of 100X, as presented in Figure 13. The error bars represent the custom error between each of the collocated duplicates at all the stations.

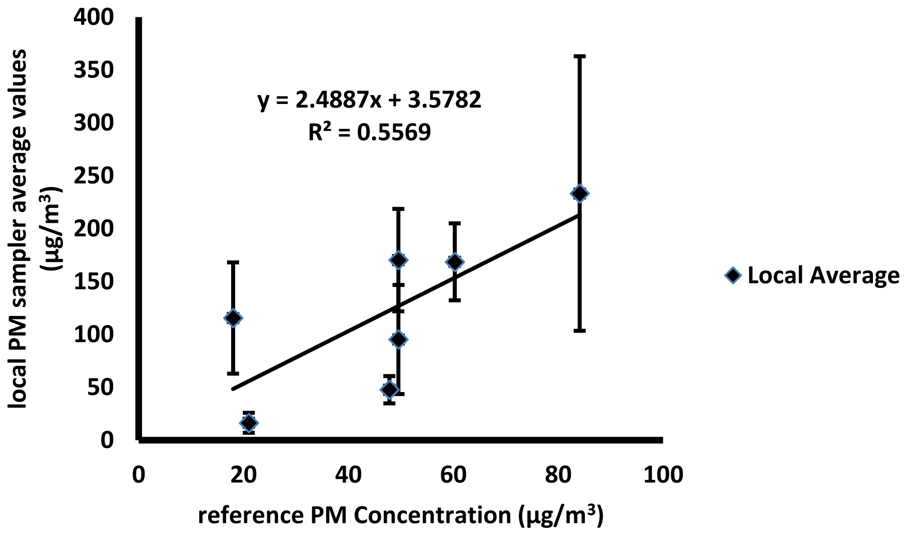

**Figure 14:** Regression analysis for the collocated local samplers imaged at 100X magnification and analysed using ImageJ.

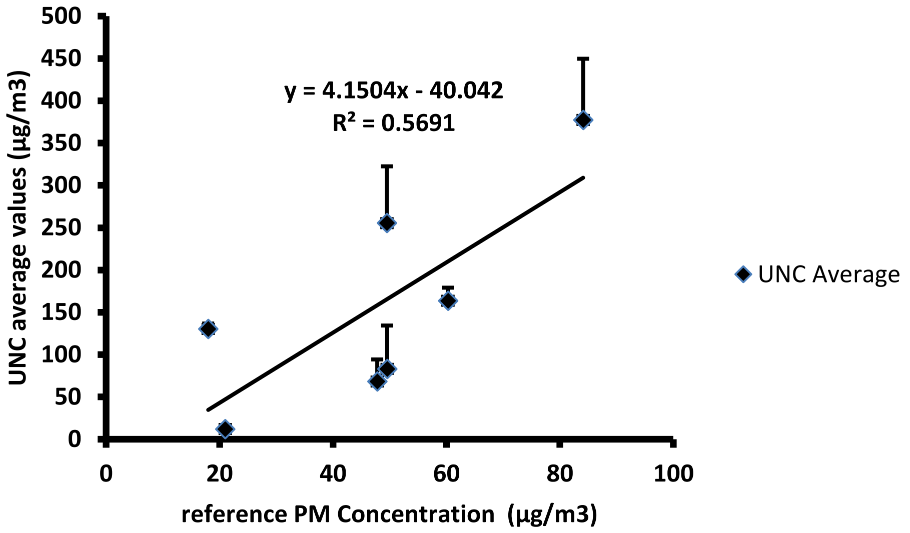

**Figure 15:** Regression analysis for the collocated UNC samplers imaged at 100X magnification and analysed using ImageJ.

The $R^2$ values provide an indication of is a statistical measure of how close the data are to the fitted regression line. As seen in figures 12 and 13, the $R^2$ values for the local and UNC samplers are 0.56. This means that 56% of the variability in calculated sampler values is explained by the model, i.e. 56% of the variation in the calculated sampler values is accounted for by its regression in the concentration values measured by the continuous samplers. Statistically, this may be viewed as a good fit. A gap in literature exists as there is no set regulation, both locally and internationally, about the acceptable values for $R^2$ for equivalent PM monitoring methods. The slope of a regression line predicts the change in the independent variable (station concentrations) when the dependent variable, (sampler concentration) increases. The slopes for the local and UNC samplers at 100X magnification are 2.5 and 4.2 respectively. This means that using these parameters, (ImageJ at 100X magnification), as station concentration increases by 1 unit, the calculated sampler values increase by 2.5 and 4.2 for the local and UNC samplers. The slope may be useful for predicting actual concentration values in the absence of continuous samplers.

### 4.3.2 100X Magnification with AxioVision

Collocated samplers were analysed using AxioVision software and optical microscopy at 100X magnification. Figure 14 shows the bar graph drawn to 1 standard deviation. A summary of the $PM_{10-2.5}$ measured by each passive sampler and the concentrations recorded across the air monitoring stations is henceforth presented. The station mean values are represented by the non-shaded bars with the other bars representing the calculated concentrations after analysis on both UNC and local samplers.

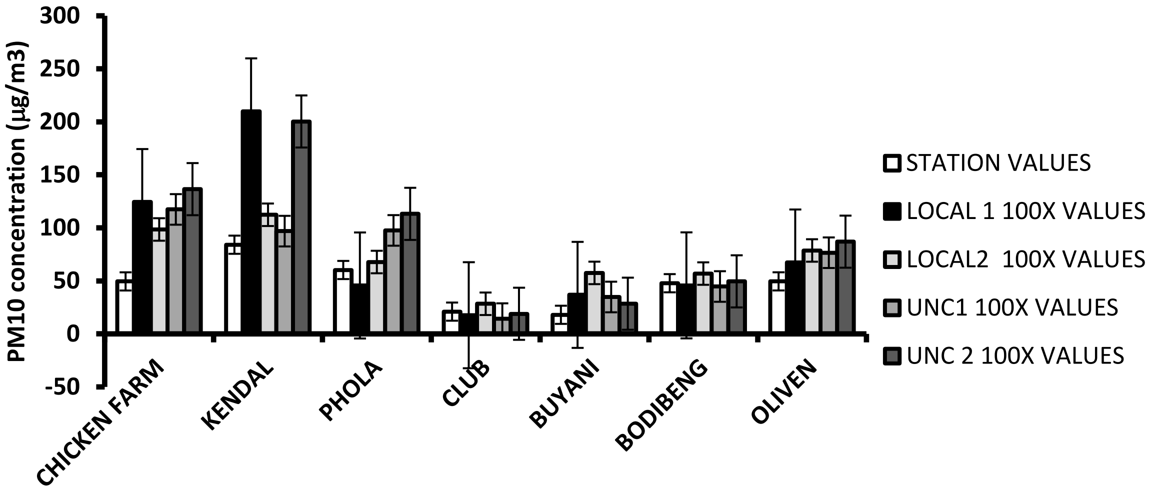

**Figure 16:** $PM_{10-2.5}$ measured at each passive sampler location using UNC samplers at 100X magnification and AxioVision. Error bars indicate 1 standard deviation.

A regression analysis carried out over the values calculated on the local samplers and UNC samplers is presented in Figure 15 and Figure 16 respectively. In Figure 15, the analysis is carried out on the two collocated passive samplers placed at each station. The two samplers were then imaged at 100X magnification and analysed using AxioVision software. The same was done for the UNC samplers and the regression analysis results are presented in Figure 16. The error bars are shown to acquire a visual understanding between the dissimilarities presented by each pair of collocated samplers.

As seen in figures 15 and 16, the $R^2$ values for the local and UNC samplers are 0.66 and 0.79 respectively. This means that 66% and 79% of the variability in calculated sampler values is explained by the model, i.e. 66% and 79% of the variation in the calculated sampler values is accounted for by its regression in the concentration values measured by the continuous samplers. Statistically, this may be viewed as a good fit and better than that observed at 100X magnification with ImageJ. The slopes for the local and UNC samplers at 100X magnification are 1.68 and 1.96 respectively. This means that using these parameters, (AxioVision at 100X magnification), as station concentration increases by 1 unit, the calculated sampler values increase by 1.68 and 1.96 times respectively for the local and UNC samplers.

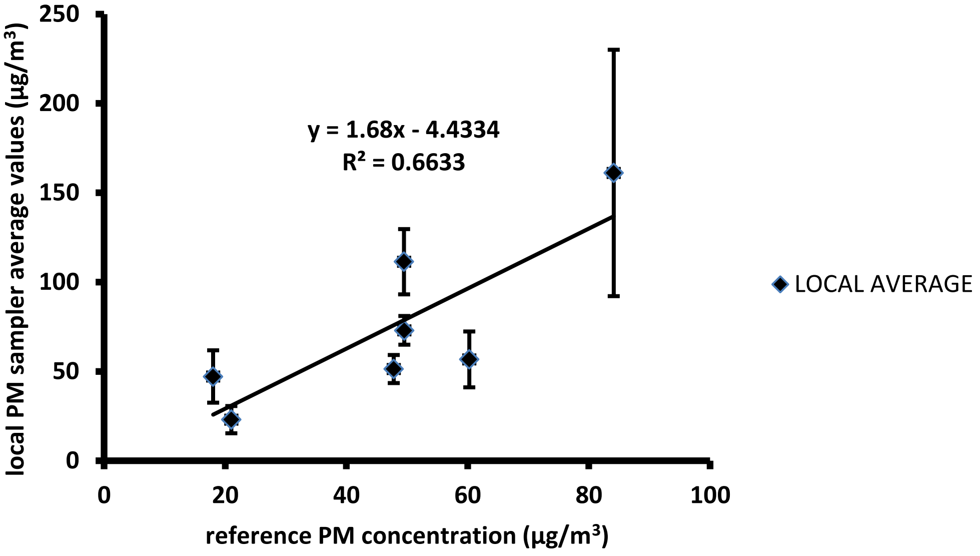

**Figure 17:** Regression analysis at 100X magnification using AxioVision as an analysis tool for the two collocated local samplers at each station.

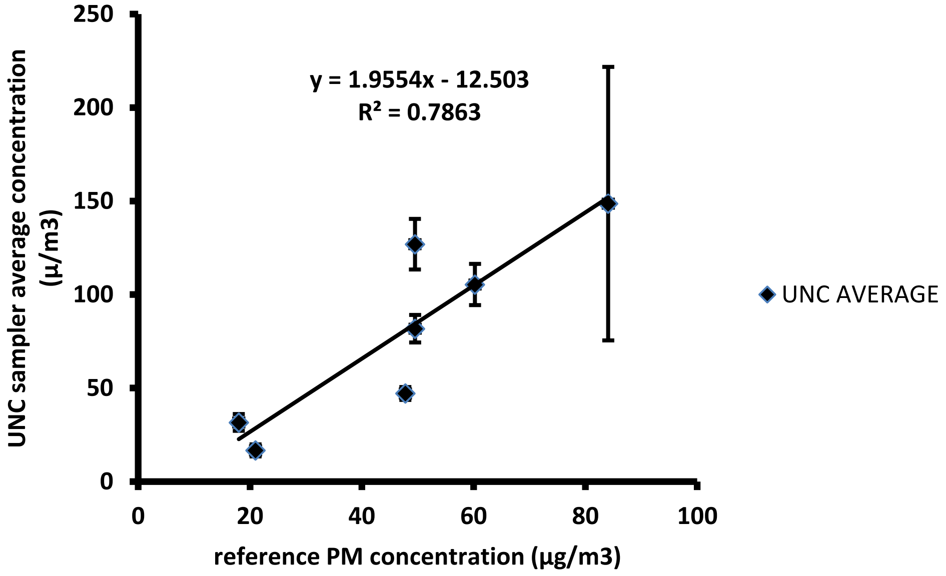

**Figure 18:** Regression analysis at 100X magnification using AxioVision as an analysis tool for the two collocated UNC samplers at each station.

### 4.3.3 200X Magnification with ImageJ

Collocated samplers were analysed using ImageJ software and optical microscopy at 200X magnification. Figure 17 shows the bar graph drawn to 1 standard deviation. A summary of the $PM_{10-2.5}$ measured by each passive sampler and the concentrations recorded across the air monitoring stations. The station mean values are represented by the non-shaded bars with the other bars representing the calculated concentrations after analysis on both UNC and local samplers.

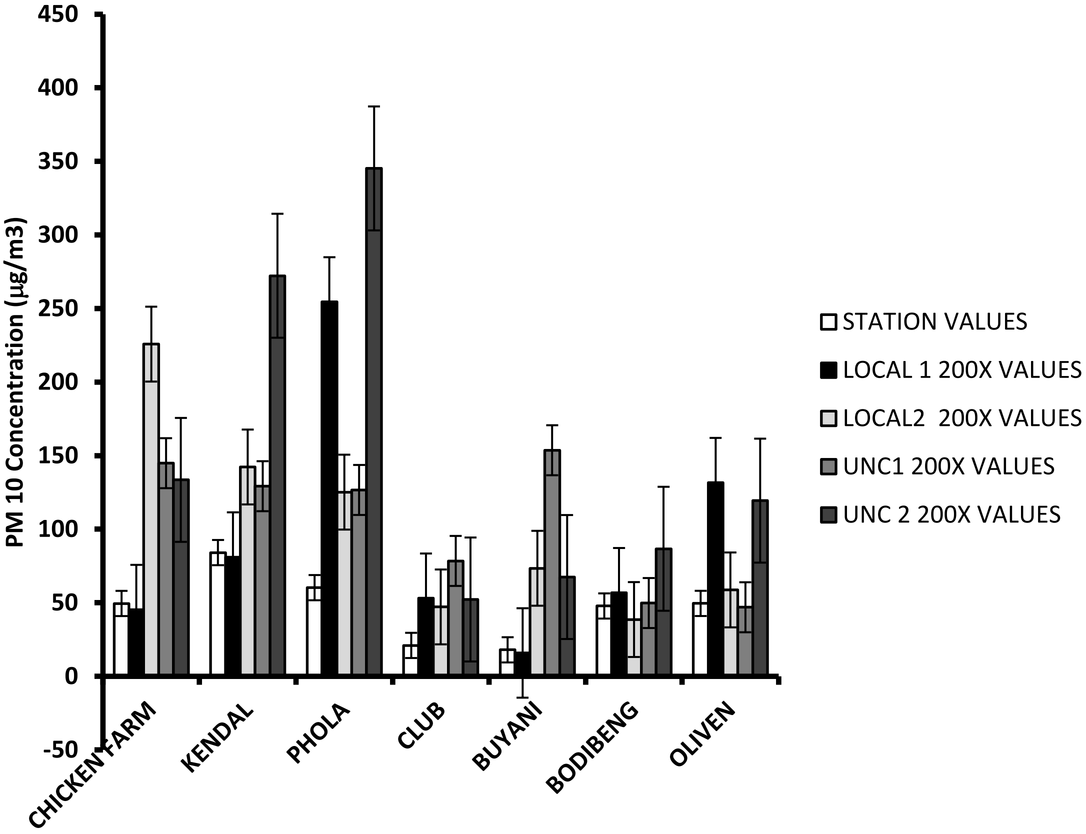

**Figure 19:** $PM_{10-2.5}$ measured with each passive for all locations. Passive samplers were analysed with ImageJ at 200X magnification. Error bars indicate 1 standard deviation.

Similarly, to the samplers analysed earlier, a regression analysis is carried out over the values calculated on the local samplers and UNC samplers is presented in Figure 18 and Figure 19 respectively. In Figure 18, the analysis is carried out on the two local collocated passive samplers placed at each station. The two samplers were then imaged at 200X magnification and analysed using Image J software. The same was done for the UNC samplers and the regression analysis results are presented in Figure 19. Like previous treatments, the error bars represent the dissimilarities presented by each pair of collocated samplers.

Observing figures 18 and 19, the $R^2$ values for the local and UNC samplers are 0.38 and 0.45 respectively. This means that 38% and 45% of the variability in calculated sampler values for the local and UNC samplers is explained by the model, i.e. 38% and 45% of the variation in the calculated sampler values is accounted for by its regression in the concentration values measured by the continuous samplers. Statistically, this may be viewed as a moderate to poor fit and lower than that observed at 100X magnification using both ImageJ and AxioVision software. The slopes for the local and UNC samplers at 200X magnification are 1.68 and 1.99 respectively. This means that using these parameters, (AxioVision at 100X magnification), as reference PM concentration increases by 1 unit, the calculated sampler values increase by 1.68 and 1.99 times respectively for the local and UNC samplers.

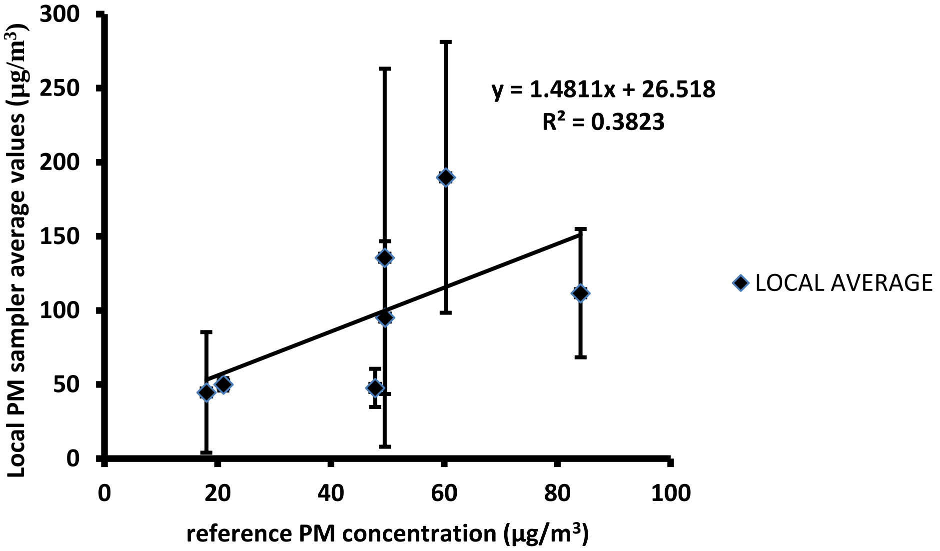

**Figure 20:** Regression analysis at 200X magnification using ImageJ as an analysis tool for the two collocated local samplers at each station.

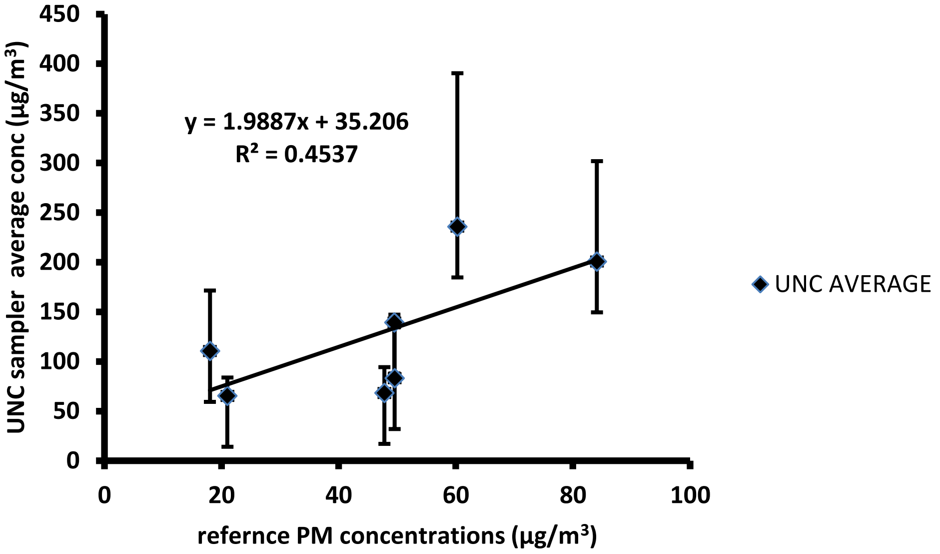

**Figure 21:** Regression analysis at 200X magnification using ImageJ as an analysis tool for the two collocated UNC samplers at each station.

### 4.3.4 200X Magnification with AxioVision

Figure 20 is a summary of results obtained after analysis by both software on all the local and UNC samplers at the seven stations. All samplers were imaged at a 200X magnification using an optical microscope.

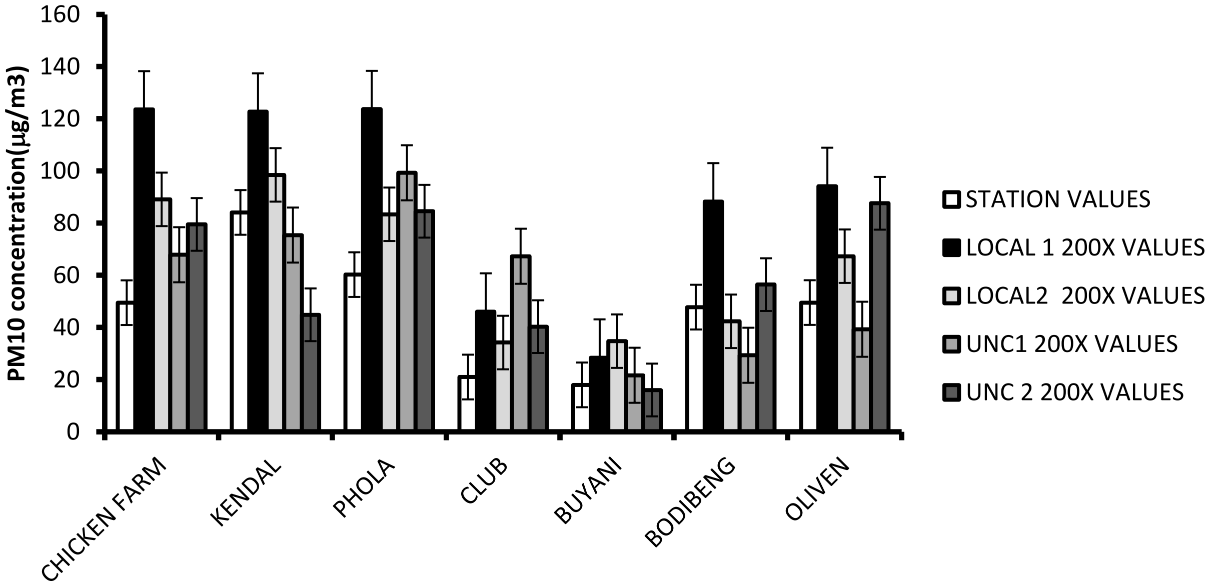

**Figure 22:** $PM_{10-2.5}$ measured with each passive for all locations. Passive samplers were analysed with AxioVision at 200X magnification. Error bars indicate 1 standard deviation.

A regression analysis conducted on the local and UNC values yields the graphs shown below for the two collocated local samplers (Figure 21) and the UNC samplers (Figure 22). Observing these figures, the $R^2$ values for the local and UNC samplers are 0.81 and 0.33 respectively. 81% and 33% of the variability in calculated sampler values is explained by the model, i.e. 81% and 33% of the variation in the calculated sampler values is accounted for by its regression in the concentration values measured by the continuous samplers. The significant difference between the values obtained for the local samplers versus the UNC samplers may be due to values of $S_v$ and $\gamma_{mesh}$ that were used that correspond better to the local samplers. Statistically, this may be viewed as a strong fit for the local samplers and a poor fit for the UNC samplers. The strong fit observed on the local samplers is an indication of the strength and closeness of the data points to the regression line. The $R^2$ value obtained by the UNC samplers is the lowest in comparison with the rest. The slopes for the local and UNC samplers at 200X using AxioVision are 1.28 and 1.59 respectively. As the concentration values recorded by the continuous samplers increase by 1 unit, the calculated sampler values increase by 1.28 and 1.59 times respectively for the local and UNC samplers imaged at 200X magnification and analysed with AxioVision software.

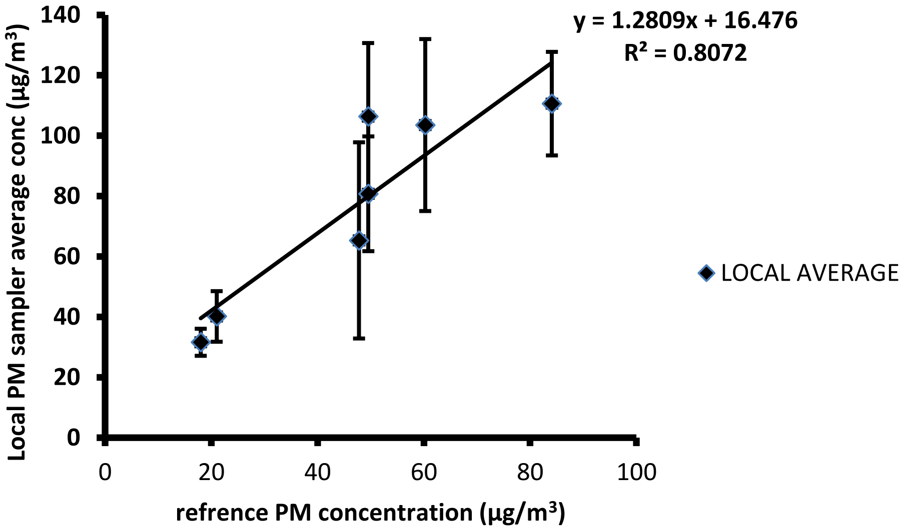

**Figure 23:** Regression analysis at 200X magnification using AxioVision as an analysis tool for the two collocated local samplers at each station.

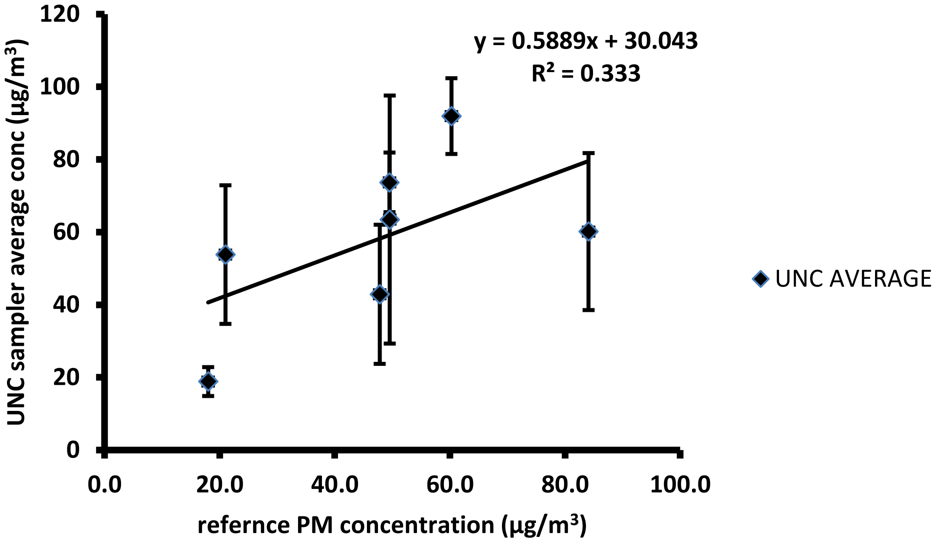

**Figure 24:** Regression analysis at 200X magnification using AxioVision as an analysis tool for the two collocated UNC samplers at each station.

As seen in the regression analysis of all the samplers, AxioVision software produced better correlations compared to the ImageJ software because AxioVision is specifically developed for particle analysis while ImageJ is a generic image analysis package. Another reason as explained in the discussion section could be that AxioVision allows the subtraction and deletion of undesirable particles through individual image selection whereas ImageJ may count shading as particles when analysing unevenly illuminated images in batch mode after setting a specific threshold value.

## 4.4 ANOVA

A two-factor ANOVA without replication was carried out with the factors considered being the magnification and the analysis software used. As stated previously, the factors to be considered are the magnification and the analysis software. A two-factor analysis without replication is conducted because there is no duplication of measurement in each sampler. Each measurement is independent and not accrued to the next analysis. Table 11 shows the results of ANOVA carried out on all the samplers at all the stations. The analysis enables us to understand the factors that will have a significant effect on the calculated values.

**Table 11:** Two-factor Analysis of variance (ANOVA), with replication for samplers at the seven stations.

ANOVA

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Sample (Analysis tool) | 13251,65 | 1 | 13251,65 | 7,240804 | 0,014938 | 4,413873 |
| Columns (Magnification) | 54464,24 | 2 | 27232,12 | 14,87984 | 0,000153 | 3,554557 |
| Interaction | 8766,969 | 2 | 4383,485 | 2,39517 | 0,11959 | 3,554557 |
| Within | 32942,43 | 18 | 1830,135 | | | |
| | | | | | | |
| Total | 109425,3 | 23 | | | | |

## 4.5 Discrepancies

Tables 12 and 13 show the percent differences between passive sampler measurements and the reference stations values at each sampling event. These values have been calculated using Equation 11. The experimental value is the calculated value (sampler results), and the theoretical value is the known value (station values). A percentage very close to zero is an indication of the closeness to the targeted value, which is good. It is always necessary to understand the cause of the error, such as whether it is due to the imprecision of the equipment, or own estimations, or a mistake in the experiment. For instance, an imprecision in 'own estimation' would regard the inaccurate range of particle size consideration in the analysis. Particles sizes considered in this study ranged from 10 $\mu m \geq d_{pa} \leq 2\mu m$. Agglomeration of particles may cause overestimation of particle size distribution and this range may be insufficient to counteract this phenomenon. Another imprecision may arise in our own estimation of particle density which is taken as $2g/cm^3$ in this study as adapted from Wagner and Macher (2003). This assumed mean value for particle density is used because particles are made up of a combination of crystal materials and less dense man-made or natural organic material (Ott et al., 2007). However, there may be slight to moderate variations in the actual density of particles considered in the study.

**Table 12:** Calculated percentage discrepancies of the collocated samplers from the mean station concentration. Samplers were imaged at 100X magnification with an optical microscope.

| | **IMAGE J** | | | | | **AXIOVISION** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **STATION READINGS PM10 (µg/m3)** | **LOCAL SAMPLERS (%)** | | **UNC SAMPLERS (%)** | | **LOCAL SAMPLERS (%)** | | **UNC SAMPLERS (%)** | |
| | | **1** | **2** | **1** | **2** | **1** | **2** | **1** | **2** |
| **ESKOM STATIONS** | | | | | | | | | |
| CHICKEN FARM | 49,509 | 122 | 93,25 | 61,53 | 143,8 | 86,07 | 66,19 | 81,34 | 93,55 |
| KENDAL | 84,099 | 50,83 | 117,76 | 134,37 | 118,01 | 85,57 | 28,75 | 14,17 | 81,73 |
| PHOLA | 60,265 | 81,35 | 105,32 | 86,844 | 97,36 | -27,55 | 11,73 | 47,3 | 61,03 |
| **SASOL STATIONS** | | | | | | | | | |
| CLUB | 21 | 9,57 | -73,08 | -80,94 | -31,4 | -17,5 | 29,96 | -37,15 | -10,16 |
| BUYANI | 18 | 157,81 | 125,24 | 149,92 | 152,63 | 68,61 | 104,66 | 63,66 | 45,06 |
| **CoT STATIONS** | | | | | | | | | |
| BODIBENG | 47,801 | 17,22 | -21,32 | 4,11 | 57,83 | -4,32 | 17,36 | -6,705 | 3,613 |
| OLIVEN | 49,55 | 90,62 | 1,7 | 5,41 | 82,69 | 30,41 | 45,43 | 42,84 | 54,84 |

**Table 13:** Calculated percentage discrepancies of the collocated samplers from the mean station concentration. Samplers were imaged at 200X magnification with an optical microscope.

| | **IMAGE J** | | | | | **AXIOVISION** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **STATION READINGS PM10 (mg/m3)** | **LOCAL SAMPLERS (%)** | | **UNC SAMPLERS (%)** | | **LOCAL SAMPLERS (%)** | | **UNC SAMPLERS (%)** | |
| | | **1** | **2** | **1** | **2** | **1** | **2** | **1** | **2** |
| **ESKOM STATIONS** | | | | | | | | | |
| CHICKEN FARM | 49,509 | -8,77 | 128,06 | 98,11 | 91,79 | 85,57 | 57,13 | 31,31 | 46,49 |
| KENDAL | 84,099 | -3,68 | 51,39 | 42,31 | 105,6 | 37,37 | 15,77 | -10,87 | -60,83 |
| PHOLA | 60,265 | 123,41 | 70,02 | 71,04 | 140,55 | 68,94 | 32,21 | 48,93 | 33,55 |
| **SASOL STATIONS** | | | | | | | | | |
| CLUB | 21 | 86,61 | 76,78 | 115,51 | 85,28 | 74,76 | 47,88 | 57,3 | 63,01 |
| BUYANI | 18 | -15,88 | 121,25 | 158,06 | 115,77 | 45,12 | 63,53 | 18,5 | -11,52 |
| **CoT STATIONS** | | | | | | | | | |
| BODIBENG | 47,801 | 17,06 | -21,32 | 4,11 | 57,83 | 59,52 | -12,06 | -47,86 | 16,56 |
| OLIVEN | 49,55 | 90,62 | 16,9 | -5,41 | 82,69 | 62,13 | 30,42 | -23,05 | 55,49 |

At 100X magnification (see Table 12), high discrepancies were noted with the local samplers analysed using ImageJ. In comparison, the percentage differences calculated for UNC samplers using the same analysis software are low. Lower discrepancies are recorded when both local and UNC samplers are analysed using AxioVision software. The highest average discrepancy recorded for all the local samplers analysed is 62% and the analysis software used was ImageJ at 100X magnification. The lowest average discrepancy calculated for all the local samplers was 37.5% and this was noted using AxioVision as an analysis tool and at 100X magnification.

At 200X magnification, the UNC samplers recorded the lowest average discrepancy (15.5%) from the continuous values and this was achieved using AxioVision as analysis software. ImageJ recorded high discrepancies at this magnification (52.3% for the local samplers and 88% for the UNC samplers.

### 4.6 Precision of co-located Field Samples (CV).

To investigate the potential source of variability, the CVs for calculated $PM_{10-2.5}$ concentrations at all stations were analysed. The coefficient of variation (CV) measures the spread of the data set, i.e. comparing scores from datasets with significantly different means. In this case, the scores are the concentration results calculated at different magnification and using different analysis software. A CV > 40% is not desirable and points to inaccuracies in measurement. Table 14 shows the CVs calculated for all the samplers (both UNC and local) using different magnifications and analysis software. The lowest CV was recorded by samplers placed at Bodibeng and were imaged at 100X magnification using AxioVision as an analysis tool. The best average CV (24.6%) is noted when using the 100X magnification and ImageJ as analysis software. Imaging at 200X magnification using ImageJ yielded an average CV > 40% with all samplers.

**Table 14:** Coefficient of Variation (CV) (%) calculated for all the collocated samplers at the seven stations.

| | Chicken Farm | Kendal | Phola | Club | Buyani | Bodibeng | Oliven | Average CV (%) |
|---|---|---|---|---|---|---|---|---|
| **100X (Image J)** | 32,218 | 39,150 | 13,842 | 45,851 | 25,842 | 35,467 | 47,699 | 34.3 |
| **100X (AxioVision)** | 13,341 | 37,761 | 37,250 | 30,260 | 31,958 | 11,120 | 10,433 | 24.6 |
| **200X (Image J)** | 53,748 | 52,320 | 50,277 | 24,328 | 73,318 | 35,467 | 47,699 | 48.2 |
| **200X (AxioVision)** | 26,648 | 38,893 | 19,179 | 30,623 | 32,220 | 46,834 | 34,222 | 32.7 |

## 4.7 Indoor Sampling: Lebohang Mpumalanga

Lebohang is a small income settlement in the Mpumalanga Highveld whose air quality is likely affected by nearby power generation activities, indoor combustion and outdoor activities. Sasol Synfuels, through NOVA institute SA, has devised air emission offset interventions to counteract these possible sources. The intervention considered in this study is household-based (increased insulation of the houses) aimed at improving the thermal performance of informal structures to facilitate a transition from solid fuels to use of cleaner alternatives. In order to quantify and ascertain the sources of pollution passive samplers (Mukota and Kornelius 2018), were used for both summer and winter monitoring across 20 households. The passive diffusive sampler is a low-cost aerosol sampler allowing for multiple measurements across large area. Indoor sampling was particularly chosen because people spend most of their time indoors (Bo et al 2017).

Sampling was done for three days and seven days and another sampler was placed for SEM-EDS analysis to determine the nature of particles for source apportionment. Samplers were placed on supports that were secured to the walls inside the houses, for the indoor measurement of $PM_{10-2.5}$. Optical microscopy was used to image the glass substrates and SEM-EDS was used to analyse the poly-carbonate substrates.

The LoQ by mass for the samplers was determined as the mean concentration per blank plus ten times the standard deviation. In this study, the LoD and LoQ were determined to be $2.8 \mu g/m^3$ and $4.7 \mu g/m^3$ respectively.

### 4.7.1 Summer sampling campaign

Table 15 is a summary showing the daily concentrations after a three day and seven-day exposure in some of the households during the summer period. There is no statistically significant difference (even at the p=0.1 level) between the averages for the houses using solid fuel and those that do not. Similarly, there is no statistically significant difference between the highest daily values converted from 3-day exposure and 7-day exposure periods. This is probably due to the extreme variation in the measured values. The suffix "s" indicates that solid fuels were used over the measuring period; "n" that no solid fuel was used. Error in handling and sampling resulted in nullification of results in some households, e.g. houses 2, 10, 13, 14, 17 and 18.

**Table 15:** Calculated maximum daily $PM_{10-2.5}$ concentration: Summer measurements.

| House number | Calculated from 3-day exposure | Calculated from 7-day exposure |
|---|---|---|
| 1s | 48.53 | 101.75 |
| 2n | | 24.50 |
| 3s | 70.67 | 64.08 |
| 4s | 55.05 | 38.06 |
| 5s | 26.62 | 80.64 |
| 6n | 36.84 | |
| 7s | 29.22 | 50.72 |
| 8s | 44.69 | |
| 9n | 34.76 | 53.17 |
| 10n | | |
| 11s | 43.15 | 24.61 |
| 12n | 59.91 | |
| 13n | | 90.92 |
| 14n | | 218.22 |
| 15n | 107.85 | 86.69 |
| 17s | | 59.22 |
| 18s | | 78.94 |
| 19n | 43.75 | 154.39 |
| 20s | 44.53 | 79.58 |
| 21n | 23.73 | 17.94 |
| **Averages** | 47.81 | 76.47 |

### 4.7.2 Winter sampling campaign

Results for the winter sampling campaign are shown in Table 16. Values were calculated using the AxioVision software and imaging at 200X magnification.

**Table 16:** Calculated maximum daily $PM_{10}$ concentration: Winter measurements.

| House number | Calculated from 3-day exposure (ug.m$^3$) | Calculated from 7-day exposure (or ug/m$^3$) |
|---|---|---|
| 1s | 231.11 | 138.53 |
| 2n | 0.00 | 36.89 |
| 3s | 137.60 | 121.94 |
| 4s | 56.75 | 35.17 |
| 5s | 104.64 | 70.36 |
| 6n | 31.00 | 44.86 |
| 7s | 27.89 | 45.31 |
| 8s | 45.80 | 34.69 |
| 9n | 41.27 | 93.53 |
| 10n | 21.82 | 18.31 |
| 11s | 32.45 | 99.08 |
| 12n | 73.69 | 137.44 |
| 13n | 331.02 | 284.92 |
| 14n | 20.15 | 13.11 |
| 15n | 89.13 | 106.03 |
| 17s | 190.65 | 124.83 |
| 18s | 28.76 | 47.03 |
| 19n | 0.00 | 0.00 |
| 20s | 58.22 | 78.00 |
| **Averages** | 89.50 | 85.00 |

Similarly, for the winter campaign, there is no statistically significant difference (even at the p=0.1 level) between the averages for the houses using solid fuel and those that do not. Similarly, there is no statistically significant difference between the highest daily values converted from 3-day exposure and 7-day exposure periods. This is probably due to the extreme variation in the measured values.

### 4.7.3 Comparison of the winter and summer data

For PM$_{10}$, the 3-day winter values recorded higher concentrations over the summer values except for house 11, 12, 15 and 19. The high summer values can be as a result of informal waste incineration, dust from unpaved roads and re-suspension of dust and are less likely from the household heating and cooking activities. Due to the lower ambient temperature, during the winter months, space heating can account for some of the coarse particulates in some households. Figure 23 below summarises the 3-day and 7-day summer and winter data for PM$_{10-2.5}$. Over the 7-day period, eight households recorded higher concentrations in winter than in summer. Four houses had summer concentrations higher than their winter counterparts. Outdoor suspended particulate also contributes to indoor pollution. During winter, it is mostly dry and less humid compared to summer; hence the coarse particles can be generated by the suspension of outdoor dust.

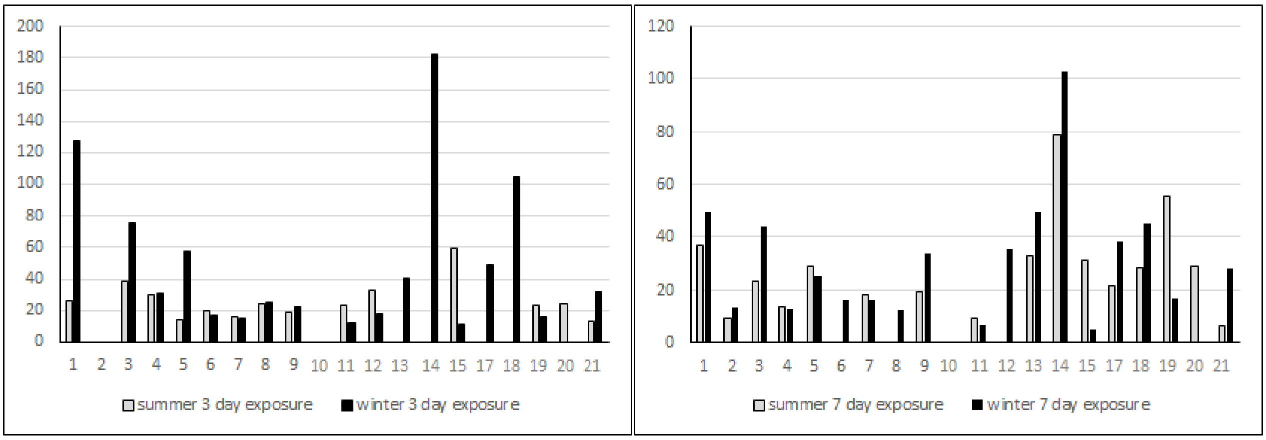

**Figure 25:** Seasonal variation for PM$_{10}$ ($\mu g/m^3$).

As shown in Table 17, summer PM$_{10-2.5}$ values over the three-day period show the least variability (lowest COV) and those recorded over seven days are the most varied. A t-test carried out at (p=0.1) shows that there is no significant difference between the calculated values in winter and summer for both the three-day and seven-day exposures. The huge variability in the data is not linked to the sampling season and neither is it connected to the exposure period involved.

**Table 17:** COV for the winter and summer concentrations for PM$_{10}$

| | **Summer 3 Days** | **Winter 3 Days** | **Summer 7 Days** | **Winter 7 Days** |
|---|---|---|---|---|
| **Std dev.** | 11.867 | 18.38 | 47.879 | 23.279 |
| **Mean** | 26.294 | 27.528 | 49.239 | 30.60 |
| **COV** | 0.451 | 0.668 | 0.972 | 0.761 |

House 14 exhibits a high $PM_{10-2.5}$ concentration exposure in both summer and winter regardless of the use of cleaner burning fuel, LPG. This suggests that combustion may not be the source of coarse particulate contamination. SEM-EDS analysis confirmed the elemental composition by atomic percentage of most of the particles. Following Jung *et al.* (2010), the chemical composition of the $PM_{10-2.5}$ samples was sorted into six major particle-type categories: soil/road dust, iron-containing, carbonaceous, aluminium, secondary nitrates/sulphates, and other. Soil/road dust included Al-Si, Al-Si-K, Al-Si-Mg, Ca/S, Ca/Si, Ca-Mg, Ca-rich, and Si-rich components. Particles in the iron-containing class had EDS spectra in which iron x-rays comprised at least 20% of the EDX spectrum. Oxygen x-rays comprised at least 50% of the EDS spectrum for the oxide class. Aluminium particles were distinguished from soil/road dust particles by their absence of silicon. Secondary nitrates/sulphates included Na/Cl, Na-rich and S-rich components.

The order of abundance of the major particle types for House 14 during summer was: oxygen-containing > aluminium > soil/road dust > Iron-containing > calcium-containing > others > secondary nitrates/sulphates. This sample was dominated by aluminium-containing particles.

Figures 24 and 25 are SEM-EDS images for for typical particles found on the substrate for the sampler placed in house 14. As seen in figure 24, singular coarse particles and agglomerates are typically Al-Si-Ca containing and are attributed to road dust. Fibrous particles typically contain Al-Si elements and are also constituents of road dust. These could have dispersed from a nearby unpaved road and settled indoors. Particles emanating from power stations due to energy generation activities usually contain fly-ash and the most abundant phase is composed of aluminum silicon oxide, the second largest is silicon oxide and the least numerous aluminum oxide in most size fractions (Stoch, 2000; Costa, Santos and Witkowski, 2016; Suárez-ruiz *et al.*, 2017).

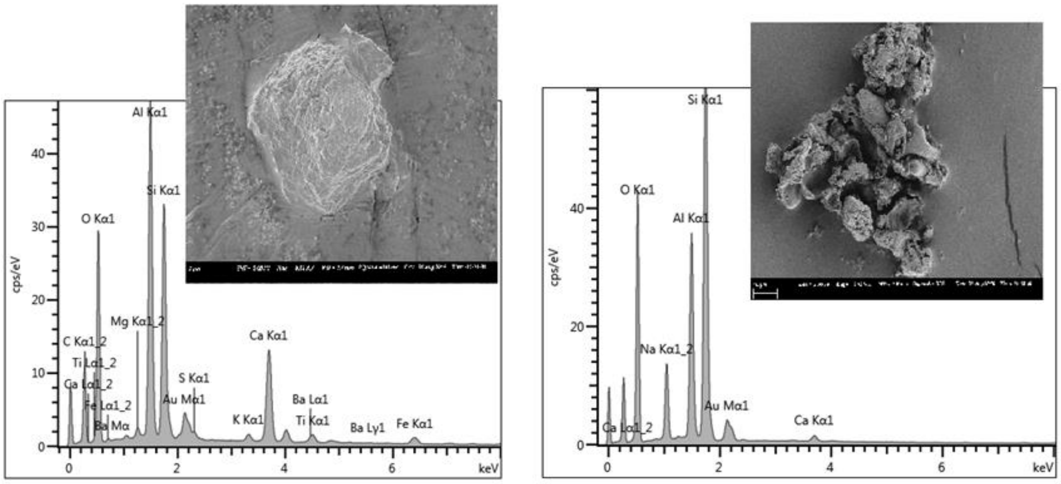

**Figure 26**: Typical Al-Si-Ca particles found in house 14 during the summer sampling campaign.

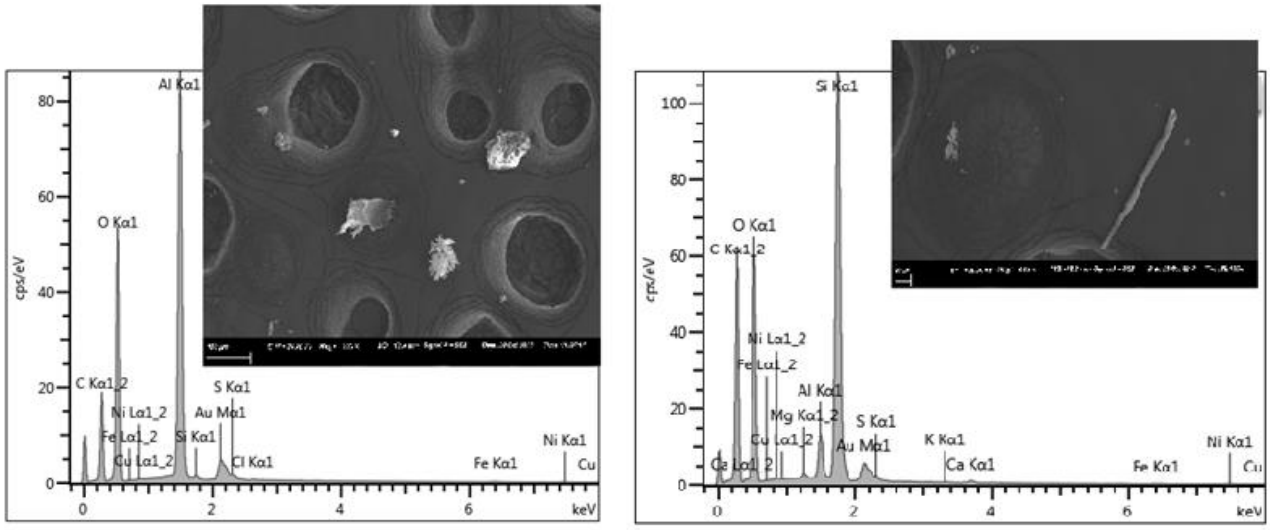

**Figure 27:** Typical Al-Si containing particles in house 14 during the winter sampling campaign.

# 5 CHAPTER 5: DISCUSSION

## 5.1 Calibration of local samplers

Limit of detection (LOD) is a decision point used to decide whether to report a significant analyte signal from the sample. LOQ is the smallest amount of analyte which can be measured with precision. The parameters relate to the low- concentration end of the analytical working range and do not provide information on about accuracy, precision, or sensitivity at higher concentrations. In the absence of interferences, it is known that with ≈ 99% confidence, that an individual sample giving a signal equal to, or greater than that of the LOD level does contain the analyte (Kennedy *et al.*, 1995).

In the analysis of the nine blanks, LOD was determined to be 13.1µg/m$^3$ for one sampling day. For a seven-day sampling period, the LOD is equivalent to 1.9 µg/m$^3$. The LOQ was calculated to be 26.7 µg/m$^3$ for a one-day sampling event and 3.8 µg/m$^3$ for a seven-day campaign. None of the calculated values was below the LOD. Typically, blank values were meant to be subtracted from the raw results in order to improve on the robustness of the method. No blank correction was carried out in the study because the blank values were below the limit of detection.

Evaluating the LOD may designate the need to sample for longer durations. The LOD in this study, (1.9 µg/m$^3$ for a seven-day sampling period) was 11.8% higher than the value obtained by Ott, Cyrs, and Peters (2008), (1.7 µg/m$^3$ after seven days). This explains why the CV calculated in their study (CV= 11.6%) is lower than any of the CV in this study. Two factors may affect the LOQ. If the sampling substrate is overloaded, individual particles will appear merged as agglomerates, subsequently under-estimating the particle count concentration and hence over-estimating the particle size. According to the (EPA 2009), a lower CV would better assess $PM_{10-2.5}$ exposure in the range of 7.4µg/m$^3$ to 13µg/m$^3$ where associations with cardiovascular hospital admissions have been observed.

Basing on a visual inspection of Figure 11, 14, 17 and 20, the passive samplers recorded higher values than the mean values recorded at the stations. A huge variation from the station mean concentrations is especially noted for the stations Chicken Farm and Kendal. These stations are located within close vicinity of power generation activities (≈ 5km radius). There is also a likelihood that these values would be higher than the mean recorded value because an unpaved road exists just along the air monitoring station at Chicken Farm and an ash treatment facility is also located near the Kendal air quality monitoring station. It would be expected for collocated samplers to record similar values after undergoing the same treatment (same magnification and analysis software), but it is evident that the contrary is true. An ocular inspection of Tables 9 and 10 confirm that none of the collocated samplers (both local and UNC) recorded similar values despite undergoing the same treatment.

Regression analysis provides an accurate way to determine and find out the relationship between the station values, local and UNC values. As observed in Figures 12, 13, 15, 16, 18, 19, 21 and 22, the calculated concentrations of the duplicate local and UNC samplers placed at all the stations differed from each other. Most of the duplicate samplers were not in agreement with each other as shown by the span in the error bars in the figures mentioned earlier. The highest recorded standard deviation within the concentration calculated with the passive samplers was > 200µg/m3. This high standard deviation was recorded when using ImageJ and using 200X magnification. The least variation (≈ 70µg/m$^3$) was recorded between UNC duplicates analysed using Image J at 100X magnification. Although there was a seemingly huge variance in the calculated concentrations of collocated samplers, Figures 12, 15 and 22 are an indication that some of the passive samplers recorded values closer to the mean station values. $R^2$ values of 0.56, 0.66, 0.79 and 0.81 depict moderate to strong relationships between the concentrations calculated on some of the local samplers and the mean station values. However, as noted previously, a lack of consistency exists amongst collocated samplers, regardless of undergoing the same treatment. This trend is notable in the local samplers that recorded a 143% difference in calculated concentrations at a 100X magnification with the use of image J and a 198% difference using the UNC samplers at a 200X magnification. Tables 18 and 19 provide a summary of the actual $R^2$ values and the percent differences in $R^2$ values for all the collocated samplers at different magnifications using either of the software.

**Table 18:** Actual $R^2$ values for passive samplers compared to the reference stations at all sites.

| | **ImageJ** | | **AxioVision** | |
|---|---|---|---|---|
| **Magnification** | Local samplers | UNC samplers | Local samplers | UNC samplers |
| 100X | 0.56 | 0.57 | 0.66 | 0.79 |
| 200X | 0.38 | 0.45 | 0.81 | 0.33 |

To find out the consistency of the collocated samplers, equation 11 was used to calculate the percentage difference between the two similar samplers placed at each location (both UNC and local

PM sampler). In this case, the calculation used the $R^2$ value of each sampler and calculation is shown below;

$$\% \, difference \ in \ R^2 = \frac{Higher \ R^2 value - Lower \ R^2 value}{(Higher \ R^2 \ value + lower \ R^2 \ value)/2} \times 100\% \tag{14}$$

A low percentage difference (<10%) shows good consistency in measurement for similar samplers undergoing the same treatment and any value greater than 10% shows variation in measurement.

**Table 19:** Percentage difference in $R^2$ values for all the calculated concentrations.

| | **ImageJ** | | **AxioVision** | |
|---|---|---|---|---|
| **Magnification** | Local samplers | UNC samplers | Local samplers | UNC samplers |
| 100X | 142.9 | 8.7 | 1.3 | 37.0 |
| 200X | 4.0 | 197.5 | 3.4 | 23.5 |

As seen in Table 19, the use of AxioVision software as an analysis tool results in a better consistency between collocated samplers. The higher percentage differences in the $R^2$ values calculated using ImageJ are probably attributed to the inconsistent thresholding in ImageJ that allows darker areas on an image to be treated as particles. This phenomenon can be confirmed as the particle count using ImageJ was significantly higher than that using AxioVision for the same images.

An ANOVA carried out on the calculated results (Table 13) can be interpreted as follows.

For the sample factor, which is the Analysis software used, P= 0.0149 <0.05, there is a 1.49% chance of getting results by random chance. Using this P-value, we fail to reject the null hypothesis that the analysis software will have no significant effect on the calculated concentration results. An alternative hypothesis can thus be formulated.

$H_1$: The analysis software used will have a significant effect on the calculated concentration results.

For the column factor, which is the magnification used, P= 0.00015 <0.05, there is a 0.015% chance of getting results by random chance. Using this P-value, we fail to reject the null hypothesis that the magnification will have no significant effect on the calculated concentration results. An alternative hypothesis can thus be formulated.

$H_1$: The magnification used will have a significant effect on the calculated concentration results.

The interaction between the analysis software and the magnification used yield a different result. The P-value is greater than 0.05 hence we fail to reject the null hypothesis.

The discrepancies shown in Tables 14 and 15 present a percentage difference in the $PM_{10-2.5}$ concentration values recorded at the stations and the calculated concentrations using a set method. Positive values indicate that the calculated values were above the values recorded at the stations whilst negative values indicate the phenomenon whereby calculated values are below the mean values recorded at the stations.

17.9% imaged at a100X magnification were below the station values whilst 16% of those imaged at 200X magnification were below the recorded station values. Most of the calculated values were above the recorded values at both magnifications owing to greater particle loading on substrates. The analyses of the samplers using the AxioVision software recorded lesser average discrepancies of 45.3% at 100X and 37.3% at 200X magnification. The samplers analysed using ImageJ at 100X magnification exhibited the highest percentage difference from the reference values (81.2%). These observations suggest that $PM_{10-2.5}$ discrepancies were due to random errors associated with high $PM_{10-2.5}$ sample mass. All samplers typically recorded a larger particle count per image than the blanks. The systematic trend in discrepancies suggests that physical mechanisms were responsible, and several mechanisms are suspected. At a lower magnification such as 100X, it is likely that agglomerated particles are imaged as single particle thus affecting the actual shape factors and particle densities. These may tend to differ from the actual parameters used in the passive sampler calculations. Also, as noted by Wagner and Leith, (2001a), local wind gradients could have caused aerosol concentrations to be different in the air spaces above the two sampler types which were typically located about 1.5m-2m apart.

A more likely source of discrepancy is the threshold limits set in ImageJ for any greyscale image that tend to interpret darker and shaded areas as particles. AxioVision software provides an option to individually select and remove such unclear shapes before any particle analysis can take place. This may be a little time consuming especially when dealing with data from multiple samplers but worth the wait.

The CV of mass concentration was calculated by dividing the standard deviation by the mass concentration for the four co-located samplers placed at each station. Differences in mass concentration were compared between the samplers and those that had poor measurement precision (CV>40%) were investigated further to identify sources of increased variability. The precision of $PM_{10-2.5}$ measured with the passive samplers was highly variable and ranged from a low CV of 10.4% to a high CV of 73.3%. 82% of the CVs were less than 40%. This is fairly comparable to similar studies (Sawvel, 2013) with 80% of the CVs being above 40% .

The average CV for all samplers was 34.6%. This is fairly high when compared to similar studies (Jeff Wagner and Leith, 2001a; Leith, Sommerlatt and Boundy, 2007; Ott, Kumar and Peters, 2007; Arashiro and Leith, 2013) whose CV were 20%, 15%, 23% and 12% respectively. Wilson et al (2005) proposed a criterion CV>20% to indicate heterogeneity. The USEPA (2006) proposed a criterion of <10% for the operational precision of $PM_{10-2.5}$ monitoring.

The lowest CV (10.4%) was recorded at Olievenhoutbosch air quality monitoring station and was imaged at 100X magnification and analysed using AxioVision. This hints that of the two factors one is being a more accurate and precise method for the analysis of passive samples in calculating mass concentrations in South Africa. Comparatively, the AxioVision software was more precise in the analysis at both magnifications when compared to ImageJ. Analysis using AxioVision gave CVs of 24.6% and 32.7% at 100X and 200X magnification respectively. Analysis using ImageJ gave CVs of 34.3% and 48.2% at 100X and 200X magnification.

## 5.2 Indoor sampling

Passive sampling can be used to obtain suspended aerosol data such as the mass concentration, particle size distribution and chemical composition of the aerosols. The limitations when using optical microscopy to analyse the collected samples should be recognised in the sense that particles smaller than 2 µm are not easily seen and the results are best indicated as $PM_{10-2.5}$.

In this study, 21 households represent the sample size. Owing to mishandling error and unavailability of occupants during the sampling period, the study is limited to 17 households. Analysis of the passive samplers follows the recommendations put forth by a precedent study in which these locally developed samplers were calibrated.

Due to the high variability in the sampled values, both during winter and summer, the confidence level of the conclusions drawn is low. The difference between the 3-day values and the 7-day values for both seasons is not statistically significant, even at the p=0.1 level. Similarly, the difference between summer and winter averages is not significant at the p=0.1 level, and the difference between the houses that use solid fuels and those that don't is not significant.

**Table 20:** Average relative abundances and standard deviations (weight %) of $PM_{10-2.5}$ composition by particle types from House 14 in both summer and winter.

| **Particle type** | | **Weight % (Standard deviation)** | |
|---|---|---|---|
| | | **Summer** | **Winter** |
| Soil/road dust | Sum of | 73 (±1) | 74 (±2) |
| | *Al-Si, Al-Si-K, Al-Si-Mg* | *55* | *52* |
| | *Ca/S, Ca/Si, Ca-Mg, Ca-rich* | *14* | *15* |
| | *Si-rich* | *5* | *6* |
| Iron-containing | | 4 (±0.8) | 5 (±1.2) |
| Carbonaceous | | 3 (±2) | 7 (±3) |
| Aluminium | | 5 (±3) | 3 (±1) |
| Secondary nitrates/sulphates | Sum of | 2 (±1) | 3 (±1) |
| | *Na/Cl, Na/s, Na-rich* | *1* | *1* |
| | *S-rich* | *1* | *2* |
| Others | | 12 (±8) | 8 (±3) |

As shown in Table 20 the order of abundance of these major particle types for the outdoor samples was: soil/road dust > others > iron-containing > aluminium > carbonaceous > secondary nitrates/sulphates. Soil/road dust particles were the greatest contributors to coarse particle mass in house 14 during both sampling seasons, accounting for 73% (summer) to 74% (winter) of $PM_{10-2.5}$. Within the soil/road dust classification, aluminium silicate particles accounted for the greatest percentage by weight followed by calcium-containing particles and finally silicon-rich particles for both summer and winter samples. Carbonaceous particles accounted for 1%–10%, secondary pollutants as nitrates and sulphates were 2%–3%, others were 4%–20%, iron-containing were 3.2%–6.2% and aluminium particles were 2%–4%.

The overall conclusion seems to be threefold:

- The combined particle concentration ($PM_{10-2.5}$ given here and $PM_{2.5}$ given in the NWU report), exceed the $PM_{10}$ daily limit value by a considerable margin; this can also be expressed as the $PM_{10-2.5}$ values given here exceeding the inferred limit for that particle size by a considerable margin both in winter and in summer.
- The origin of the particles in this size range cannot be linked directly to the energy supply activities in the households. Chemical analysis using SEM indicate that most of the coarse particles are of mineral origin.

- The inference to be drawn from the above two points is that management measures to reduce community dust exposure in residential areas should not be limited to combustion processes but should also address other fugitive dust sources such as unpaved road dust.

Passive diffusive sampling can be used to measure $PM_{10-2.5}$ when analysed with optical microscopy but can also be used to measure fine particulates when samples are analysed with an electron microscope. This process is more expensive and time-consuming since electron microscopes are less available.

# 6 CHAPTER 6: Conclusion and recommendations

This work presents a simplified method to measure and monitor $PM_{10-2.5}$ using prior knowledge developed by Wagner and Leith at the University of North Carolina. The work provides precision data and accuracy of passive diffusive samplers when compared to reference air monitoring methods.

In this work, a type of passive sampler for ambient air monitoring was calibrated and tested against recorded station values for PM10 concentrations. The passive sampler, referred to as the local sampler, was collocated with the UNC sampler and the station BAMs and TEOMs at seven ambient air monitoring stations across Tshwane area and Mpumalanga province. Two local and two UNC samplers were placed at each station. The PM collected on the glass substrate is systematically imaged using an optical microscope at 100X and 200X magnification so as to determine the optimum magnification. Particle analysis is carried out using two software suites namely the open-source Image J and the proprietary Zeiss AxioVision. The particle data is then transferred into an Excel programme where the mean PM10 concentration values are obtained as a function of the exposure time and derived from particle projected area diameter, circularity and perimeter.

To assign solutions to some of the specific objectives set earlier in the study, conclusive evidence exists to definitively answer the research questions set. Evidence exists at a 95% level of confidence that the magnification used during substrate imaging and the analysis software used has a significant effect on the calculated results. The locally developed samplers tend to be more consistent when imaged at 200X magnification and using AxioVision as analysis software. Although the precision measurements made with this simple device may be worthy of note, the passive aerosol sampler is not suggested as a reference method. For ambient PM monitoring, it would be ideal and beneficial to use the local samplers compared to the UNC samplers due to their much lower cost and their local availability of the materials used.

The method, however, has several limitations. First, the presence of background contamination complicates the analysis when particle counts are low. The second issue arises when trying to sample sub-micron particles. The method is limited to the detection of $PM_{10-2.5}$ size fraction due to the inability to detect sub-micron particles using an optical microscope. However, the method is unlikely to be biased in environments where the size range is small such as ambient, indoor and occupational spaces.

The other limitation is the time consumed in analysing a sample. If the process is not automated, many samples may prove rigorous to analyse. This may result in the establishment of a systematic error. Passive sampler precision could be improved by increasing the number of particles collected by either sampling in higher concentration areas or by increasing the collection time of each sampler past one week. An example is a study undertaken by (Lagudu *et al.*, 2011) in which the samplers were exposed for periods up to three weeks. Future work that aims to determine values of variability in these and other parameters in ambient and indoor settings would be valuable in defining the extent to which correction factors are needed.

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