

Chapter 3

Experimental procedures

This chapter describes the selected sampling site (Par 3.1), the sampling methods and data processing (Par 3.2), as well as the sampling equipment (Par 3.3) used to achieve the objectives stated in Chapter 1.

3.1. Sampling site

Measurements were conducted at Marikana (25.698476°S, 27.480588°E, 1170m AMSL), which is a small village approximately 35km east of Rustenburg, in the North West Province of South Africa. The site was situated on the property of the Marikana Municipal clinic, which provided access to electrical supply and also ensured the safe keeping of equipment. There were no mining and/or industrial activities within a 1km radius of the site. The closest surroundings included semi-formal (government-built housing developments, mostly with some form of informal housing additions by the occupants) and informal (self-erected, sometimes unauthorised, mostly without municipal services) settlements, a formal residential area with a petrol station and shops, as well as tarred and un-tarred roads serving the communities in this area. In Figure 3.1, the location of the sampling site is shown on a geographical map of South Africa together with a satellite image obtained from Google Earth.

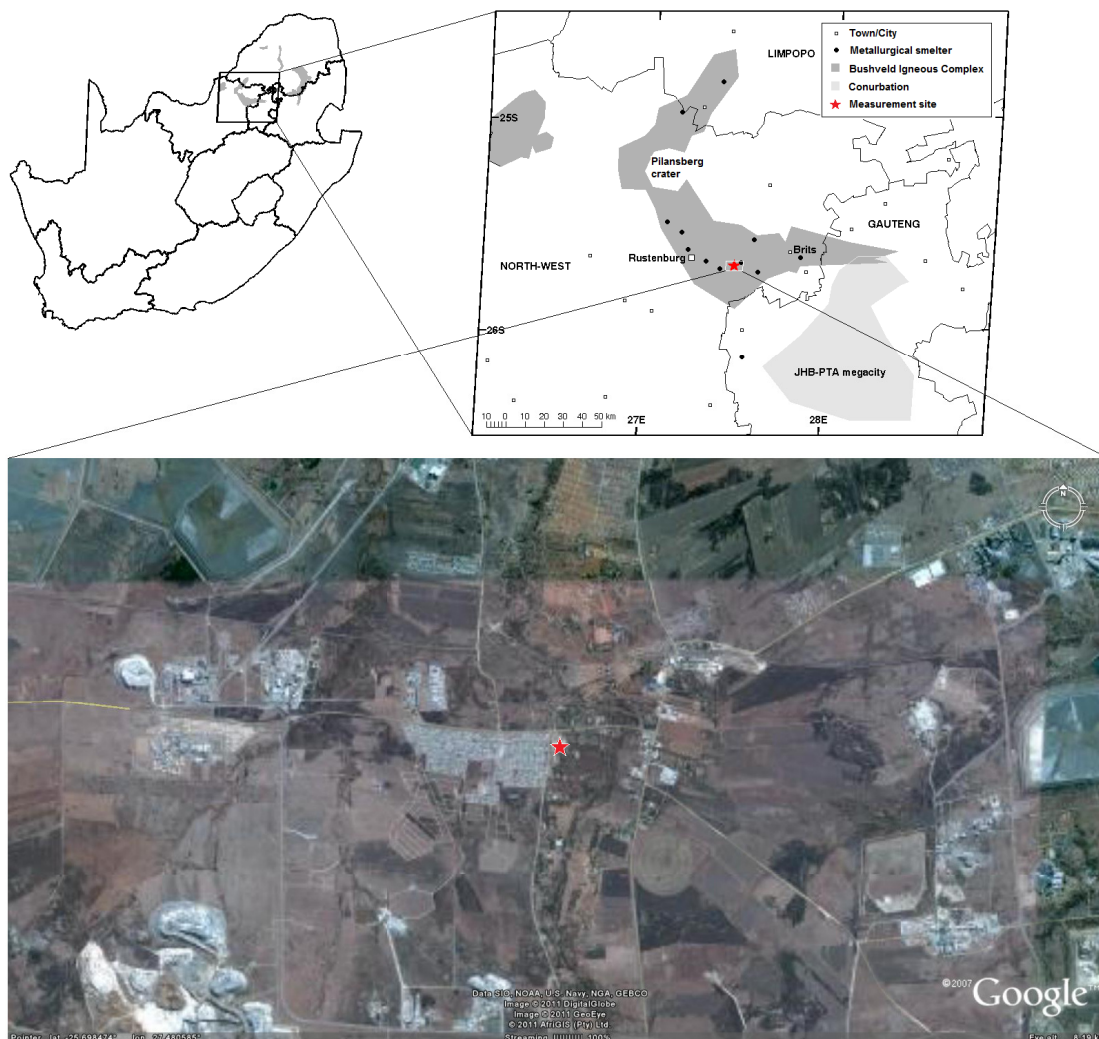


Figure 3.1: Geographical map of South Africa and a satellite image indicating the location of the measurement site ($25.698476^{\circ}\text{S}$, $27.480588^{\circ}\text{SE}$)

Geographically, Marikana is almost in the centre (east to west) of the southern section of the western BIC, south of the Pilanesberg crater. The western BIC is known as a mining and metallurgical-industrialised region. Some of these operations include platinum mining, associated base metal refineries, chromite mining and ferrochrome smelting operations, ferrovanadium and vanadium pentoxide production, as well as fertiliser production. The major point sources, i.e. pyrometallurgical smelters, are indicated in Figure 3.1. The heights of stacks emitting off-gases into the atmosphere are dependent on the specific industrial activity (Piketh *et al.*, 2005). Apart from these obvious large point

sources, other potential sources of air pollution from the mining and metallurgical industries include wind-blown dust from slimes/tailings dams, landfills, haul roads used by mining and large transport vehicles and fugitive emissions.

Due to the lure of employment in the above-mentioned sectors, the western BIC is frequented by formal (larger cities and towns, such as Rustenburg and Brits), semi-formal and informal settlements. Incomplete combustion of coal and wood in ineffective appliances for household heating and cooking is a common occurrence in the semi-formal and informal settlement sector. The Johannesburg-Pretoria mega-city conurbation (with more than 10 million people) could also influence the area since Pretoria is approximately 74km to the east and Johannesburg approximately 80km to the south-east (Figure 3.1).

Traffic volumes in the area are relatively high, due to the large amounts of raw materials being transported for mining and metallurgical operations by road. The vehicular fleet in South Africa is fairly old and public transport is not readily available, increasing private vehicle use. Various tarred and un-tarred roads cross the western BIC, and the N4 national highway between Pretoria and Rustenburg passes the measurement site approximately 7.5km to the south.

In the areas not affected by industrial activities or human settlements, farming activities are still practiced. Rainfall is relatively low and it is regarded as a semi-arid region. Most of the farming activities are associated with grazing, cash crop production (e.g. maize) or game farming. Some citrus and vegetable cultivation also takes place because the area is almost frost free during winter.

Although the site is almost completely surrounded by anthropogenic activities (e.g. mining/metallurgical operations, human settlements, traffic related emissions and farming activities), a less anthropogenically affected area occurs towards the south of the N4 highway.

The dry and cold winters (June to August) result in increased biomass burning (veld fires) and combustion for domestic space heating. The emissions from veld fires are similar to those generated by coal and wood combustion. Veld fire smoke influences the visibility and the landscape's aesthetic quality, and contributes to the degradation of regional scale air quality (Bohlweki, 2009).

3.2. *Sampling methods and data processing*

The measurement instruments were placed inside a Eurowagon 4500u (length 4.5m, width 2.1m, height 2.3m, weight 2500kg) measurement trailer. The atmospheric measurement station was operated in collaboration between the North-West University (NWU) and the University of Helsinki (UH). A more detailed description of the trailer, data analysis and calibration methods was provided by Laakso *et al.* (2008), Petäjä *et al.* (2007) and Vakkari *et al.* (2011). Measurements were conducted for the sampling period 8.2.2008 to 17.5.2010 and were only interrupted when power failures occurred, instruments were serviced or calibrated and when general maintenance was performed.

The measurement trailer was visited once a week for maintenance and basic inspections. Weekly maintenance at the trailer consisted of inspection and adjustment of instrument flows, inlet cleaning, as well as other *ad hoc* procedures as required. Monthly maintenance consisted of filter changes on the gaseous instruments, cleaning the radiation sensor and calibration of the PM₁₀ measurement equipment. Comprehensive gas calibrations were conducted quarterly. Maintenance of vacuum pumps was performed when required. An electronic diary was kept in which all actions and visits to the monitoring site were recorded.

All the instruments in the measurement trailer were connected to a master PC that was linked to a GPRS modem that sent measurement and diagnostic data to a server at the UH/NWU on a daily basis. Data collected from the various aerosol measurement instruments were transferred via serial port connections. A PICO ADC-16 (Pico Technology Ltd.) logger collected analogue signals from the gas analysers, meteorology measurement systems and instrument flow rates.

Gas and metrological data were averaged (mean) from 1 minute data to obtain 15 minute averages that were used in data analysis. Each 15 minute average was based on at least 10 minutes of measurements (66.7% data coverage required). Gas readings were calibration corrected between calibration checks assuming that the analyser response changed linearly in time. Additionally, data was filtered based on visual inspection of the data and diary notes. The span gas bottle concentration was compared with a new bottle in May 2009. The span checks before 27.5.2009 are corrected assuming that the span bottle concentration has changed linearly since the date the certificate was issued.

The NO_x calibration corrected data gave negative readings at certain periods between the calibration checks. This indicates that the zero from calibrations was not a true zero. For these periods, the calibration check offsets were corrected to give zero for the lowest NO_x readings between the calibration checks.

Global radiation [W/m²] was calculated from the photosynthetic photon flux density (PPFD) radiation sensor [μmol/m²s] by multiplying with 500.

PM₁₀ data was collected from 20.7.2006-11.2.2009 using a TEOM instrument and from 12.2.2009-17.5.2010 using a SHARP instrument. Data was also filtered based on diary notes and visual inspection of the data. The zero level of the data was corrected based on the nephelometer calibration of the SHARP (Par 3.3.8.) or HEPA filter inlet readings for TEOM (Par 3.3.7.). Between calibrations, the zero value was assumed to change linearly, which is taken into account in the correction.

3.3. *Sampling equipment*

3.3.1. *SO₂*



Figure 3.2: The pulsed fluorescence SO₂ analyser

Ambient SO₂ concentrations were measured using a model 43S SO₂ analyser from Thermo Environmental Instruments Inc. with a detection limit of 0.1ppb. A flow rate of 0.5l/min was maintained to this instrument. This instrument provides continuous, real-time measurements of ambient sulphur dioxide done by pulsed fluorescence (Figure 3.3). This technique is based on the principal of sulphur dioxide molecules absorbing fluorescent energy, producing an electronically excited SO₂ molecule with a known spectral decay rate. The fluorescence emitted by the reaction is detected by a photo multiplier tube and the signal is proportionally converted to an electronic output signal. A wavelength of 230-190nm is used, although other wavelengths also excite SO₂. This wavelength is most stable, has the lowest signal noise and is not influenced by other pollutant species (Thermo Environmental Instruments, 1989).

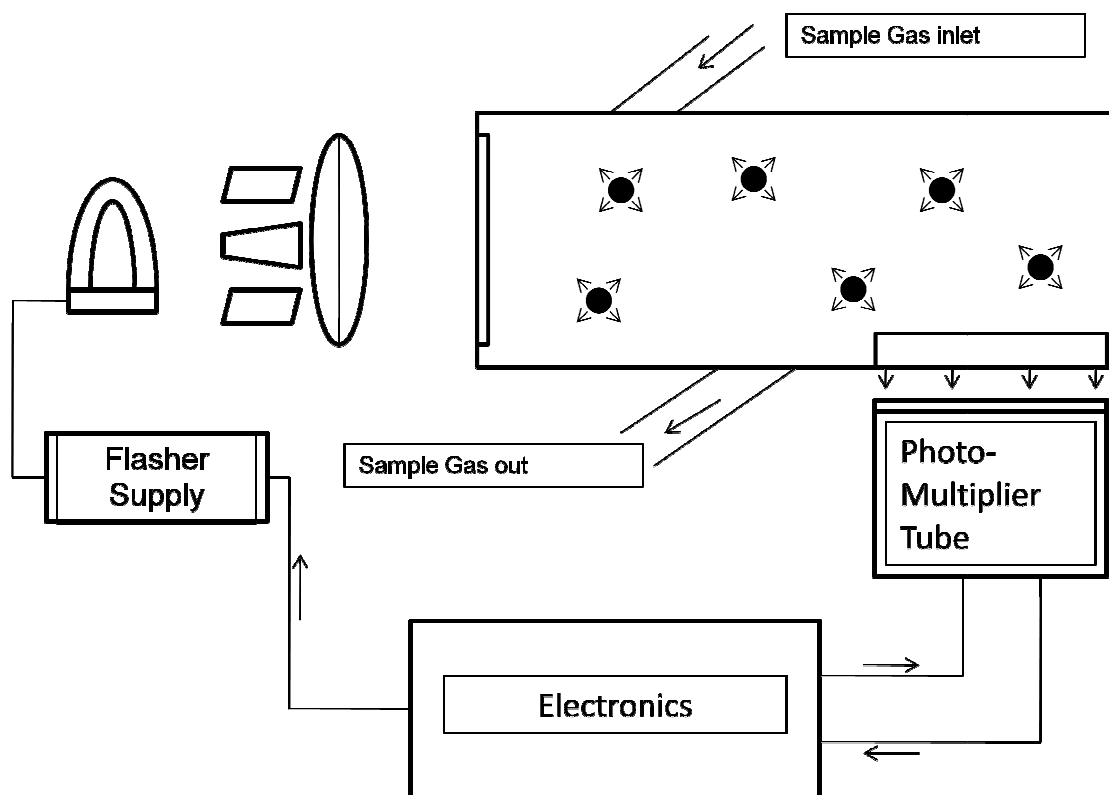


Figure 3.3: Graphic representation of sulphur dioxide measurement by pulsed fluorescence

3.3.2 NO_x

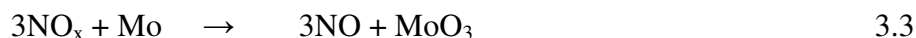


Figure 3.4: The chemiluminescent NO/NO_x analyser

Continuous, real-time NO_x measurements were performed using a Teledyne API NO/NO₂/NO_x – Model 200AU Analyser. This instrument has an upper detection limit of 2000ppb and measures at intervals of 1ppb. The Teledyne API Model 200AU Analyser is designed to measure the concentration of nitric oxide (NO), total oxides of nitrogen (NO_x) and, by calculation, nitrogen dioxide (NO₂). The instrument measures the light intensity of the chemiluminescent gas phase reaction of NO and O₃ as follows:



The reaction of NO with ozone results in electronically excited NO₂ molecules, as shown in Equation 3.1. When the excited NO₂ molecules return to the ground state, excess energy is released by emitting a photon (Equation 3.2). The light intensity produced is directly proportional to the NO concentration present. The analyser samples the gas stream and measures the NO concentration by digitising the signal from the analyser's photomultiplier tube (PMT). A valve then routes the sample stream through a converter containing heated (315°C) molybdenum to reduce any NO_x present to NO by the following reaction (API, 1999):



The analyser now measures the total NO_x concentration. The NO value is then automatically deducted from the NO_x value, yielding the NO₂ concentration. In the third measurement phase, the instrument measures sample gas that has been mixed with ozone outside of the reaction cell. This pre-reactor allows the measurement of any hydrocarbon interferences present in the sample gas stream. The three results, [NO], [NO_x], and [NO₂], are then further processed and stored by the computer yielding several instantaneous and long-term averages of all three components (API, 1999).

The software uses an adaptive filter to accommodate rapid changes in concentration. The algorithm monitors the rate of change in concentration for both the NO and NO_x channels. When a change in concentration is detected, the software changes the sample

filters to rapidly respond to the change. The filters are adjusted to minimise the errors introduced by the time delay between the NO_x and NO channel measurements; this assures accurate NO_2 measurements. When the rate of change decreases, the filters are lengthened to provide better signal/noise ratios. The parameters used to operate the adaptive filter have been tuned to match the electrical and pneumatic characteristics of the M200AU (API, 1999).

3.3.3. O_3



Figure 3.5: The O_3 analyser

The 41M Environment SA is a continuous ozone analyser. Detection is based on the absorption of ultraviolet light (253.7 nm) by ozone. The ozone concentration is directly proportional to the quantum of absorbed light. The instrument is also capable of automatic pressure and temperature compensations. This principle allows for continuous operation for long periods with little maintenance required. The 41M has a detection limit ranging from 1ppb to 10ppm with a sample flow rate of 1.6l/min (Environment, 1999).

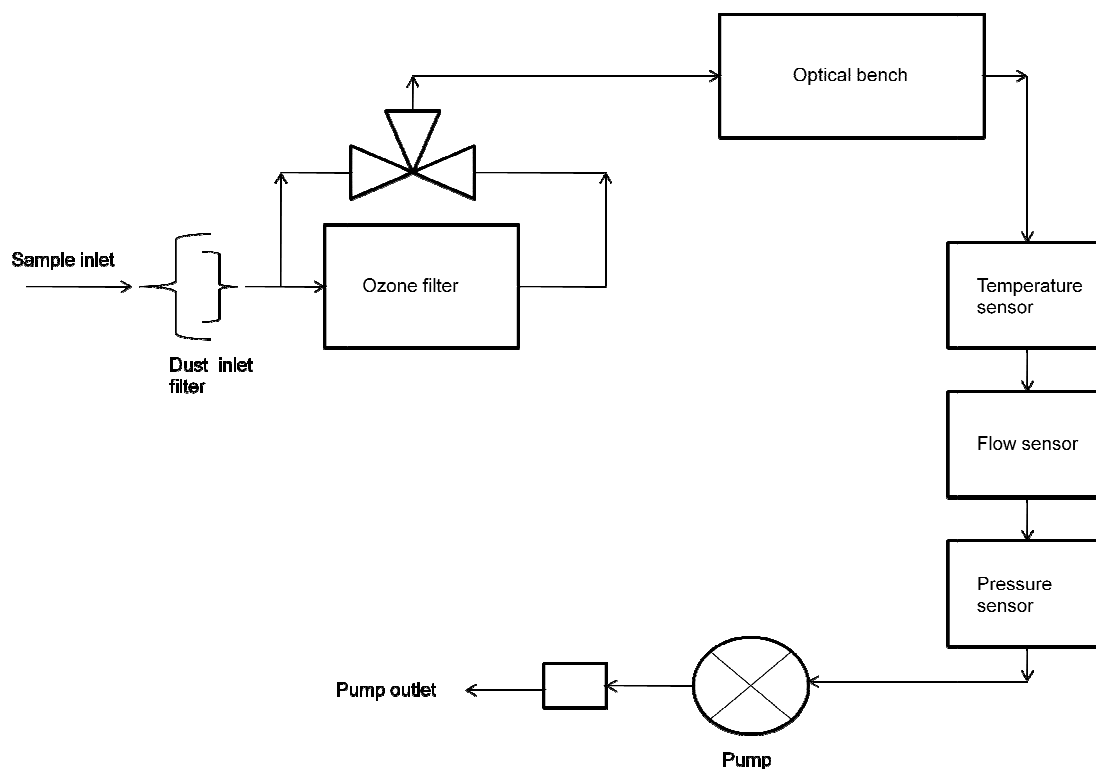


Figure 3.6: A schematic diagram depicting the main components of the ozone analyser

A full measurement cycle consists of the following: (i) Passage of gas through the O_3 selective filter. (ii) Ventilation of the measurement chamber. (iii) Measurement of UV energy through the chamber without O_3 sample. (iv) The switching of the solenoid valve allows for the passage of gas directly into the measurement chamber and the measurement of UV energy through the chamber with the O_3 sample. The amount of UV absorbed by O_3 is in proportion with the concentration (Environment, 1999).

3.3.4. CO



Figure 3.7: The ambient CO monitor

The Horiba APMA-360 uses cross-flow modulated non-dispersive infrared absorption to measure carbon monoxide that eliminates the need for optical adjustments. This ensures stable and sensitive measurements. The APMA-360 calculates the CO concentration by analysing sample air and reference air alternately and subtracting the concentrations. The reference gas is generated by oxidising the CO to CO₂ in the sample air. This eliminates the interference of other elements, resulting in extremely accurate measurements. The APMA-360 is approved by various environmental protection agencies, e.g. the US EPA (Kato & Yoneda, 1997).

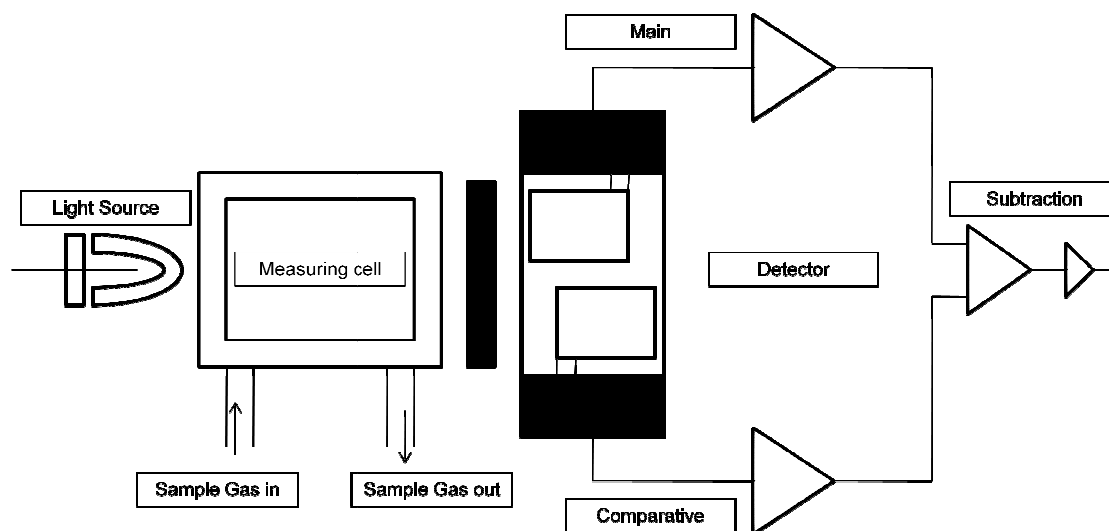


Figure 3.8: A schematic diagram depicting the main components of the CO analyser (Kato & Yoneda, 1997)

3.3.5. *TEOM*

Operating for the period 20.7.2006-11.2.2009, the tapered element oscillating microbalance (TEOM) provided a continuous direct mass measurement of particulate PM_{10} . The TEOM can provide measurements in the ranges of 0 to $5g/m^3$ with a precision of $\pm 1.5ng/m^3$ for each one-hour average, while maintaining an accuracy of $\pm 0.75\%$ for the mass measurement (Rupprecht & Patashnick, 2002).



Figure 3.9: The TEOM 1400ab used to measure PM_{10} in the period 20.7.2006-11.2.2009

3.3.6. *SHARP*

The Synchronised Hybrid Ambient Real-time Particulate Monitor (SHARP), model 5030, replaced the TEOM on 12.9.2009 and was used to determine the PM_{10} mass for the remainder of the sampling period.



Figure 3.10: The SHARP 5030 used to measure PM_{10} in the period 12.9.2009-17.5.2010

The SHARP consists of a C^{14} source, detector and a light scattering Nephelometer. The SHARP monitor utilises proprietary digital filtering to continuously mass calibrate the nephelometric measurement of PM_{10} . The intelligent moisture control system (IMR)

regulates humidity levels using a heating system that is linked to a relative humidity sensor located just upstream of the sample, providing a representative measurement of the relative humidity at the particulate measurement head ensuring that the volatile aerosol remains intact for accurate measurement (Thermo Fisher Scientific, 2010).

The SHARP has a span drift of less than 0.02 % per day with an hourly precision of $\pm 2 \mu\text{g}/\text{m}^3$ for ambient concentrations smaller than $80 \mu\text{g}/\text{m}^3$ and $\pm 5 \mu\text{g}/\text{m}^3$ for values greater than $80 \mu\text{g}/\text{m}^3$ (Thermo Environmental Instruments, 1989).

3.3.7. *Meteorology*

Basic meteorological parameters were measured using a Rotronic MP 101A for temperature and relative humidity data collection, while a Vector W200P and a Vector A101ML were used for wind speed and direction, respectively. A LiCor LI-190SB measured the Photosynthetic Photon Flux Density (PPFD) and Thies 5.4103.20.041 recorded the precipitation.

In the following chapter individual criteria pollutants will be analyzed to seek (seasonal, diurnal and daily) trends, compared to national and European standards set by government and, in the case of CO, compared against meteorological data.