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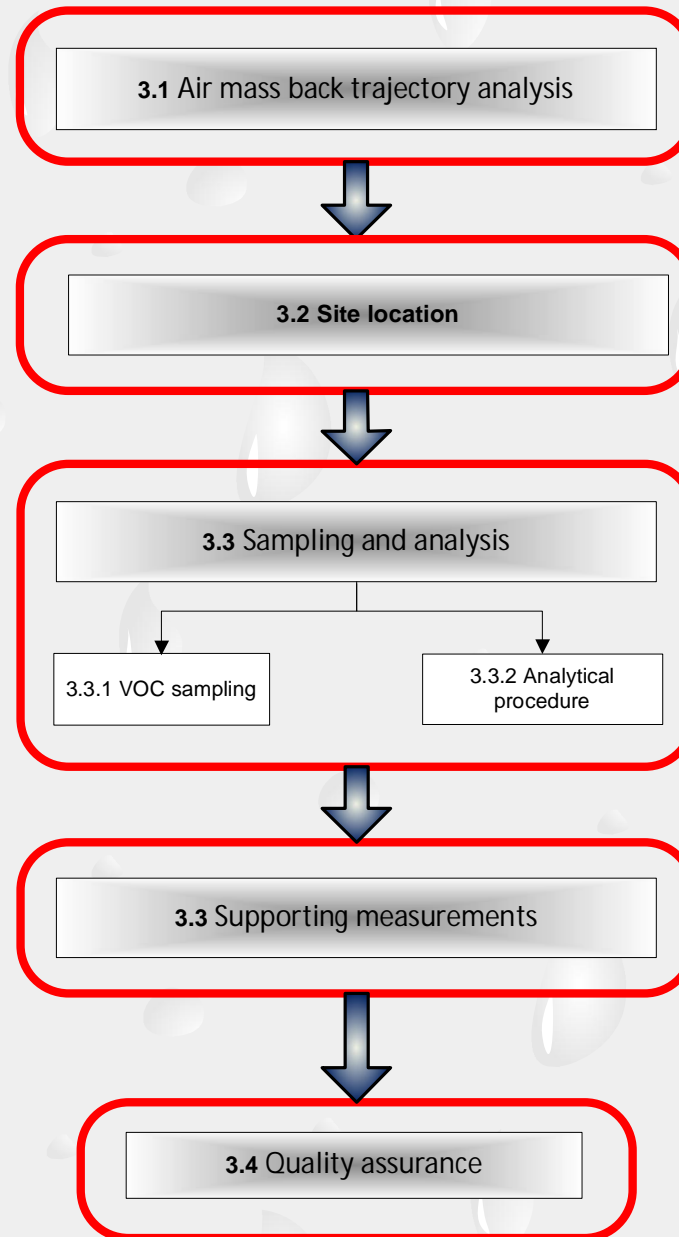
Chapter 3
Experimental procedures

3.1 Air mass back trajectory analysis

Air mass back trajectory analysis was performed as described by Beukes *et al.* (2012) and Vakkari *et al.* (2011). Individual hourly back trajectories were compiled with the HYSPLIT 4.8 model, developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler & Hess, 2004). This model was run with meteorological data of the GDAS archive of the US National Weather Service's National Centre for Environmental Prediction (NCEP) and archived by the ARL (Air Resources Laboratory, 2009). Each hourly arriving back trajectory was calculated for 96 hours (4 days) backwards. An arrival height of 100m was chosen, since VOCs are mainly emitted within the lowermost layer of the troposphere. Furthermore, the orography in HYSPLIT is not very well defined, and therefore lower arrival heights could result in larger error margins on individual trajectory calculations.

In order to link VOC measurements to back trajectories, three back trajectories for every two-hour VOC sample were calculated for the entire year of sampling. These back trajectories were obtained at the start, middle and end of daytime (11:00 to 13:00) and night-time (23:00 to 1:00) sampling periods.

3.2 Site location

The measurement site, i.e. Welgegund (latitude 26°34'11"S, longitude 26°56'21"E, 1480m AMSL), is situated approximately 100km west of Johannesburg on a commercial farm. Welgegund is considered to be a regionally representative background site with no direct impacts from pollution sources in close proximity to the site. **Figure 3.1** presents a photo of the measurement station during the rainy season. The immediate area around the measurement station is grassland savannah that is grazed by cattle and sheep. Currently, a detailed vegetation mapping is being conducted for the area surrounding the measurement station. This mapping was, however, not yet available when this thesis was written. The

dominant grass species that occurred in the vicinity of the measurement station were *Hyparrhenia hirta* and *Sporobolus pyramidalis,* as well as non-grassy forbs, which include *Acacia sieberiana*, *Rhus rehmanniana*, *Walafrida densiflora*, *Spermacoce natalensis*, *Kohautia cynanchica* and *Phyllanthus glaucophyllus* (Welgegund, 2010).

Figure 3.1: Photo of the Welgegund measurement station during the rainy season, with cattle grazing the surroundings

Notwithstanding the lack of local pollution sources, Welgegund is impacted by plumes from major anthropogenic source regions in the interior of South Africa, i.e.:

- the western and the eastern Bushveld Igneous Complexes (BIC), from which most of the world's ferrochrome and platinum group metals (PGMs) are produced. The western BIC has recently been incorporated into the newly declared Waterberg Priority Area (Government Gazette, 2012).

- the Johannesburg-Pretoria (JHB-PTA) metropolitan conurbation with more than 10 million inhabitants, which has been indicated as being relatively heavily polluted (Lourens *et al.*, 2012).

- the Vaal Triangle, which has numerous petrochemical operations, coal-fired power stations and metallurgical smelters. This area, together with part of the southern Gauteng province, was the first area to be declared a priority area, i.e. the Vaal Triangle Airshed Priority Area (Government Gazette, 2005).

- the Mpumalanga Highveld, where most of South Africa's coal-fired power stations are concentrated, together with a large petrochemical operation and several

pyrometallurgical smelters. This area, together with parts of the Gauteng province, was declared a priority area in 2007, i.e. the Highveld Priority Area (Government Gazette, 2007).

In **Figure 3.2**, the position of Welgegund (indicated with a red star), in relation to most of the major point sources occurring in the above-mentioned anthropogenic source regions, is presented.
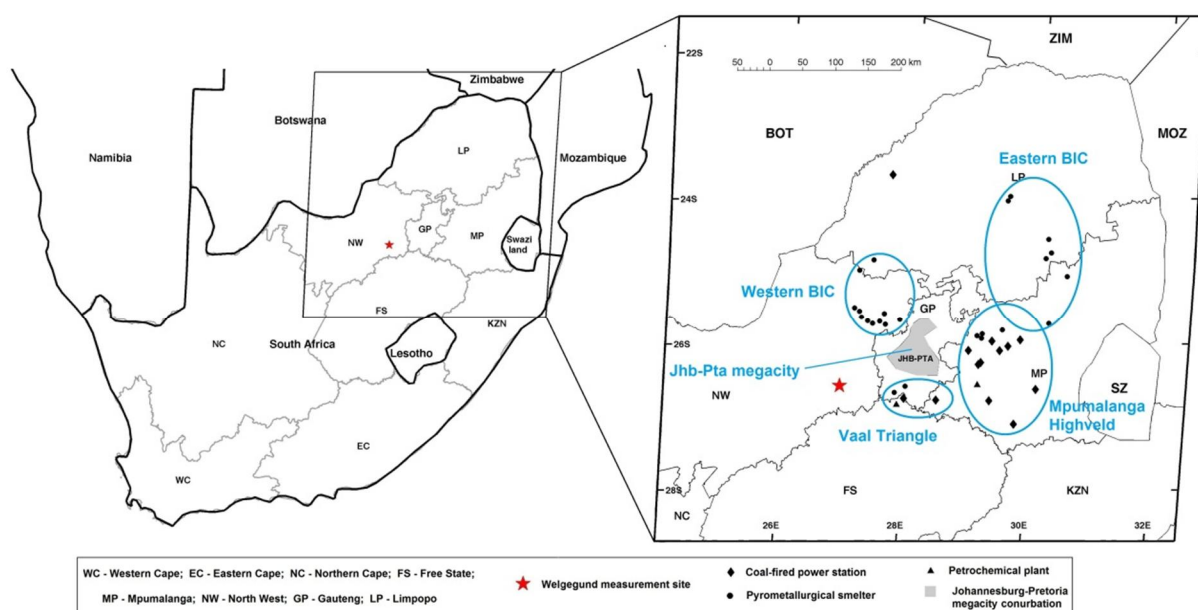

Figure 3.2: Southern African map, indicating the location of the Welgegund measurement station, large point sources in the industrial hub of South Africa and anthropogenic source regions impacting Welgegund

As mentioned earlier (**Section 2.6**), air mass circulation over the South African interior is dominated by anti-cyclonic recirculation. A relatively high percentage of air masses that arrive at Welgegund therefore follow an anti-cyclonic pattern. These air masses are usually not representative of the clean regional background, since they represent aged air masses that had passed over the industrial hub of South Africa. **Figure 3.3** indicates 96-hour back trajectories calculated to arrive hourly at an arrival height of 100m at Welgegund, over lied for a period of approximately two years. The region that constitutes the area from where most of the calculated 96-hour back trajectories arrive at Welgegund is indicated in red. As is evident, this region represents the area from where air masses mainly travel in an anti-cyclonic movement, before arrival at Welgegund. Air masses arriving from this area

therefore have to be considered as a separate source region, since the composition of these air masses is likely to differ from that of the previously discussed anthropogenic source regions.

Apart from the afore-mentioned source regions, Welgegund is also impacted by air masses originating from a relatively clean sector with very few large anthropogenic activities that lies west of the site. This area will be referred to as the Regional Background source region in this study.
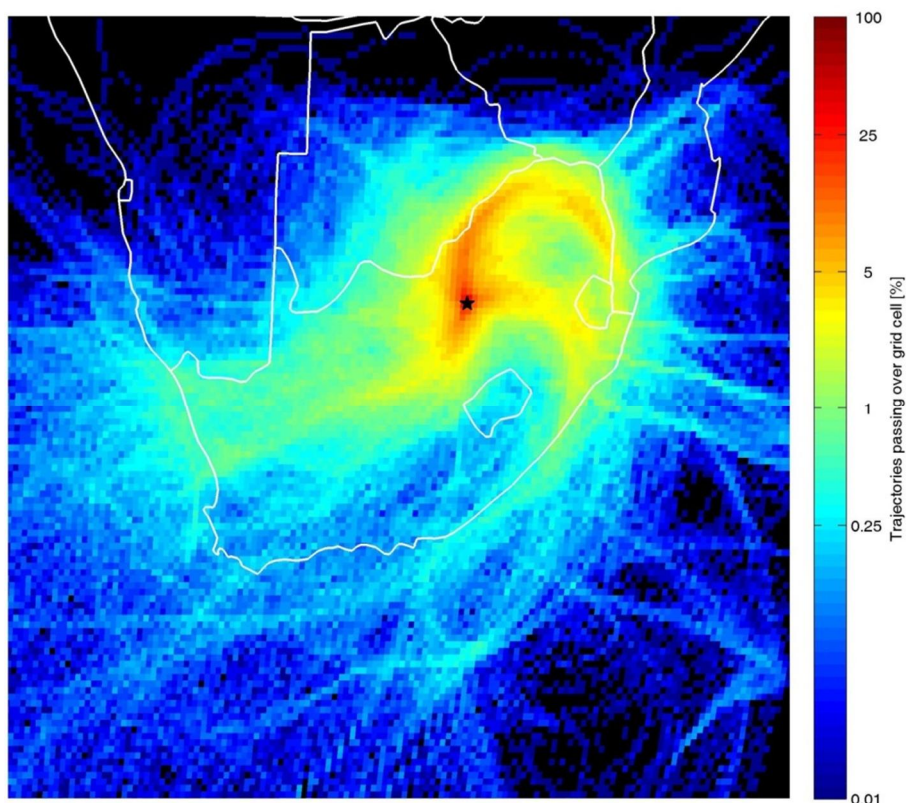

Figure 3.3:   96-hour back trajectories calculated to arrive hourly at Welgegund at 100m arrival height for the period 2007 to 2008. These trajectories were over lied with a fit for purpose MATLAB program. The map area was divided into 0.2° x 0.2° grid cells. The original background is black and each individual trajectory is represented by a dark blue line. The colour of each grid cell then depends on the frequency of trajectories passing over it, with red indicating the grid cells with the highest frequency

Beukes *et al.* (2012) recently defined these source regions more precisely, as observed from Welgegund. In an attempt to characterise air masses that had passed over the afore-mentioned source regions, Beukes *et al.* (2012) measured the straight-line distance between Welgegund and each major point source in each source region. These authors then drew

circles around each major point source, with the radius of each circle corresponding to 30% of the afore-mentioned straight line distance between Welgegund and the major point source. The outsides of these circles were then connected to give the spatial distribution of the western BIC, the Vaal Triangle and Mpumalanga Highveld source regions, as observed from Welgegund. Similarly, the spatial distribution of the JHB-PTA metropolitan conurbation was enlarged by 30% of the straight-line distance from the outer expanses of the area covered by the conurbation and Welgegund, perpendicular to the outside. This 30% straight-line distance method, as briefly described here, was used by Beukes *et al.* (2012) to compensate for the errors associated with the calculations of back trajectories. In addition to the source regions defined by the 30% straight-line distance method, Beukes *et al.* (2012) combined the eastern BIC and the area from where most of the air masses travelled in an anti-cyclonic movement pattern before arriving at Welgegund (**Figure 3.3**) into a single source region, since these two areas overlapped significantly. The afore-mentioned resulted in the definition of six source regions, i.e. i) the JHB-PTA metropolitan conurbation, ii) the Vaal Triangle, iii) the Mpumalanga Highveld, iv) the western BIC, v) the Anti-cyclonic recirculation and eastern BIC combined and vi) the Regional Background. **Figure 3.4** indicates the geographical distribution of these source regions graphically (Beukes *et al.*, 2012). The grey areas in this map indicated the areas for which it would be impossible to determine, within the error margins associated with back trajectory calculations, whether a specific back trajectory had passed over a source region or the neighbouring source region. These areas were therefore defined as shared/mixed source regions by Beukes *et al.* 2012.
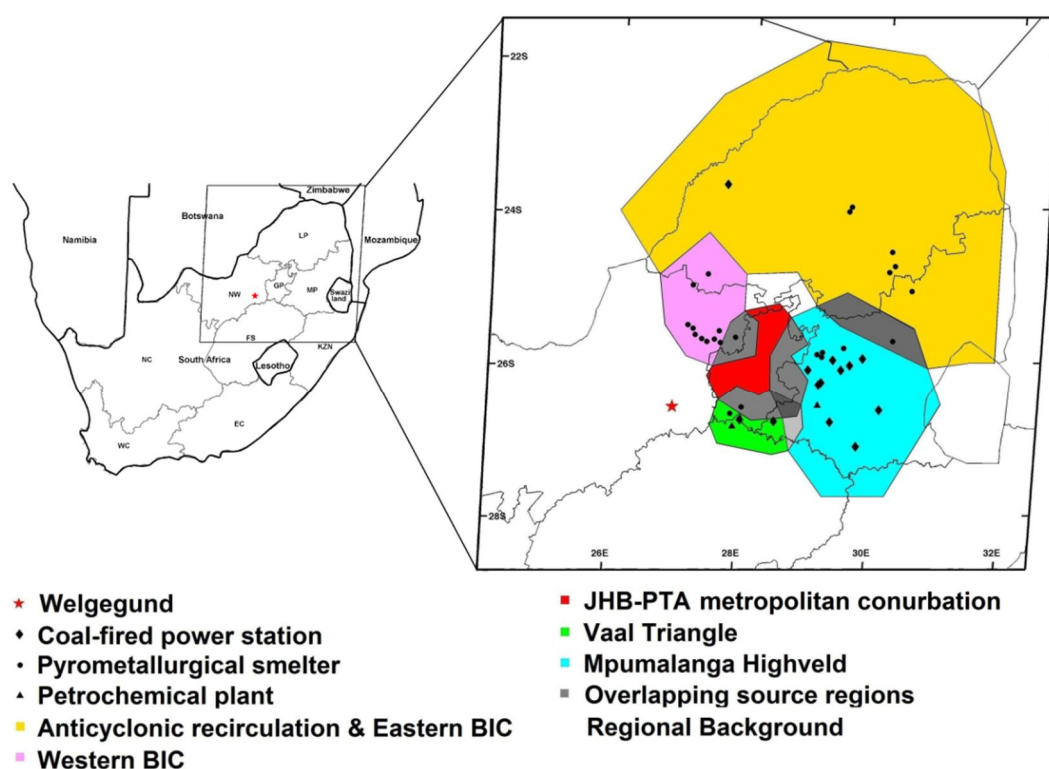
Figure 3.4: Southern African map with the north-eastern part enlarge, indicating the location of the Welgegund measurement station, large point sources in the industrial hub of South Africa and source regions defined by Beukes *et al.* (2012) for the Welgegund measurement site

In this study, VOCs were measured only four times per week, for two hours per sample over a one-year sampling period (**Section 3.2.3.3**). After data quality control (**Section 3.4**), 194 samples were deemed to be of good quality. These samples were then allocated to air masses that had passed over the afore-mentioned source regions. However, having a relatively small dataset (194 samples) resulted in a not statistically significant number of samples being allocated to each of the six source regions, as defined by Beukes *et al.* (2012). In order to improve the statistical significance of the samples that were allocated to air masses that had passed over the source regions, the JHB-PTA metropolitan conurbation, the Vaal Triangle and the Mpumalanga Highveld source regions were grouped together. These source regions were identified as the regions with the highest anthropogenic impact (Beukes *et al.*, 2012). There were also significant overlaps between the areas allocated to these source regions (**Figure 3.4**). In this study, this combined source region will be referred to as Area I. Additionally, the Western BIC, the eastern BIC and the anti-cyclonic recirculation source regions were grouped together, since all these source regions lie on the anti-cyclonic

recirculation path of air masses towards Welgegund (Beukes *et al.*, 2012). This combined source regions will be referred to as Area II in this study. Lastly, the Regional Background source region was kept as defined by Beukes *et al.* (2012). In **Figure 3.5**, the newly-defined source regions, as used in this study, are presented.
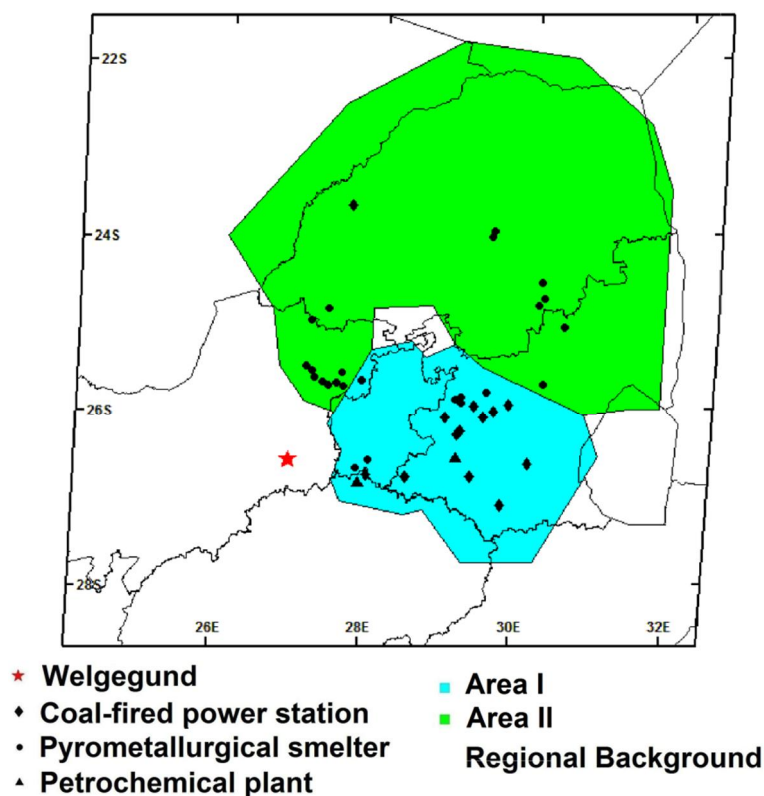

Figure 3.5: Map of South Africa with the north-eastern part enlarge, indicating the location of the Welgegund measurement station, large point sources in the industrial hub of South Africa and the newly-defined source regions for the Welgegund measurement site as used in this study

3.3   Sampling and analysis

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, which was commissioned in April 2010, was operated in collaboration between the North-West University (NWU), the University of Helsinki (UH) and the Finnish Metrological Institute (FMI). A more detailed description of the trailer, measurement instruments, operation procedures, data analysis, as well as calibration and maintenance procedures has

been presented by Laakso *et al.* (2008), Vakkari *et al.* (2011), Hirsikko *et al.* (2012) and Venter *et al.* (2012).

3.3.1 VOC sampling

VOC measurements were conducted for one year (9 February 2011 to 4 February 2012) to record any seasonal variability. Samples were collected twice a week for two hours during daytime and two hours during night-time. VOCs were sampled at a height of 2m above ground level. The first 1.25m of the inlet (made from stainless steel) was heated to 120ºC using heating cables and thermostats (Thermonic) (**Figure 3.6**) to remove O_3 that could lead to sample degradation (Hellén *et al.*, 2012), as well as to remove moisture. The O_3 removal efficiency was checked with an O_3 monitor at regular intervals.
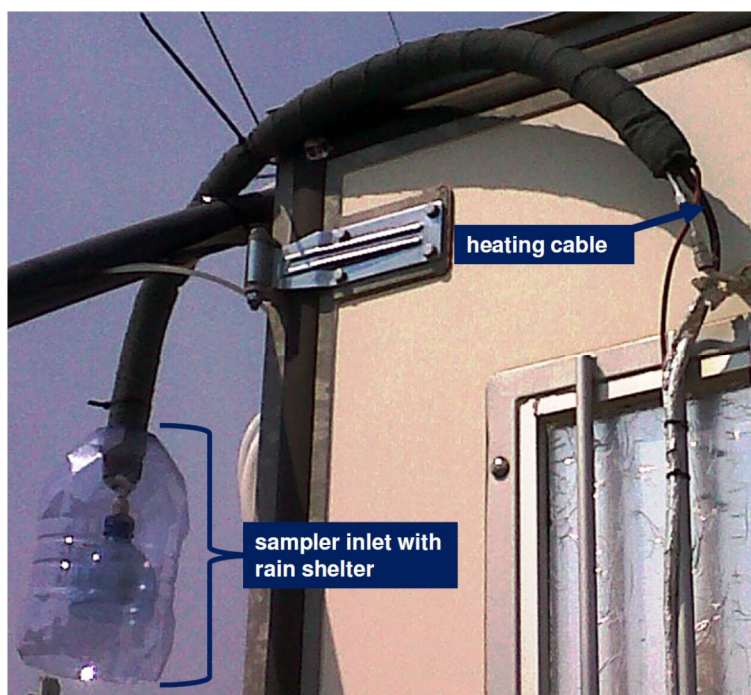

Figure 3.6:   VOC sampler inlet with rain shelter and heating cables

VOC samples were collected in Tenax-TA and Carbopack-B adsorbent tubes (**Section 2.5.2**) by using a constant flow type automated programmable sampler as shown in **Figure 3.7**. Critical orifices attached to the pump were used to keep the flow constant and a needle valve controlled which tube was sampled. After the sampling period of a specific tube was completed, the tube was automatically sealed off and the next tube was prepared for sampling. The flow of the pump was calibrated each week. A sampling flow between 100 and 110ml min $^{-1}$ was used throughout the study. Hellén *et al.* (2002) detected no

breakthrough for Tenax-TA and Carbopack-B tubes when sampling for 4 hours at a flow rate of 100ml min $^{-1}$. The two-hour samples were collected in two tubes during the day (11:00 to 13:00) and two tubes during the night (23:00 to 1:00) on Tuesdays and Saturdays. After sampling, the tubes were removed and closed with Swagelok® caps. Each tube was separately wrapped in aluminium foil and stored in a container for transport to the laboratory. Tubes were stored in the laboratory in a freezer within a clean environment to minimise pre-analysis elution and breakdown of the sampled compounds.
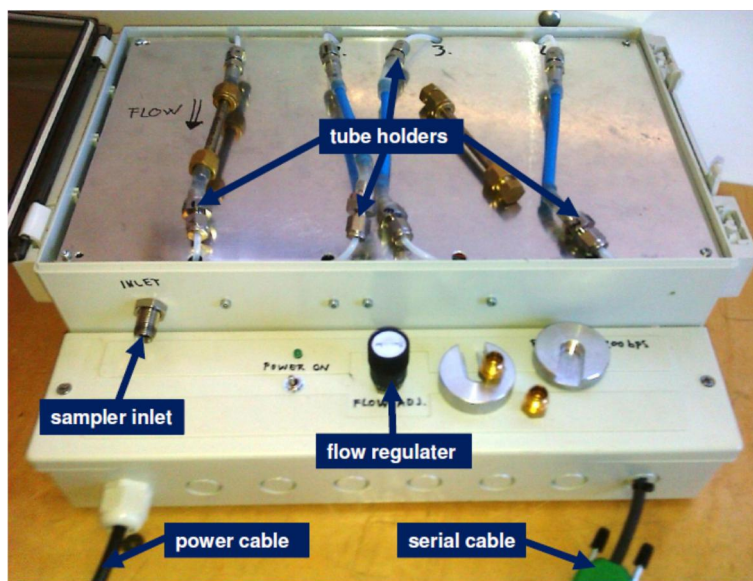

Figure 3.7:   Constant flow type automated programmable sampler used in this study

3.3.2 Analytical procedure

The analytical setup used for the preparation and analysis of adsorbent tubes is presented in **Figure 3.8**. A thermal desorption unit (Perkin-Elmer TurboMatrix^{TM} 650, Waltham, USA) was connected to a gas chromatograph (Perkin-Elmer® Clarus® 600, Waltham, USA) with a DB-5MS (60m, 0.25mm, 1µm) column and a mass detector (Perkin-Elmer® Clarus® 600T, Waltham, USA).

Figure 3.8:   Thermal desorption unit connected to a gas chromatograph with a DB-5MS column and a mass detector used in this study

The sampled tubes were desorbed at 300°C for 5 minutes, cryofocused in a Tenax cold trap (-30°C) prior to injecting the sample into the column by rapidly heating the cold trap at a heating rate of 40°C min^{-1} to 300°C. A three-point calibration curve was obtained by using liquid standards dissolved in methanol. Standard solutions were injected into adsorbent tubes and were flushed with helium or nitrogen (100 ml min^{-1}) for five to ten minutes in order to evaporate the methanol. Standard tubes were desorbed and analysed using the same method as applied to sampled tubes. The detection limits, calculated as three times the standard deviation of blanks, or from a signal-to-noise ratio of 3:1, varied from 5 to 84ng m^{-3}. In **Table 3.1**, the detection limits for the VOCs reported in this study are presented.

Table 3.1: Detection limits for the VOCs measured during this study

Biogenic	ppb	Aromatics	ppb
isoprene	0.0012	benzene	0.0263
MBO	0.0009	toluene	0.0132
α-pinene	0.0009	ethylbenzene	0.0045
camphene	0.0009	(m,p)-xylene	0.0026
β-pinene	0.0009	styrene	0.0043
3Δ-carene	0.0009	o-xylene	0.0033
ρ-cymene	0.0009	propylbenzene	0.0010
1,8-cineol	0.0008	3-ethyltoluene	0.0010
limonene	0.0009	4-ethyltoluene	0.0010
terpinolene	0.0009	1,3,5-trimethylbenzene	0.0011
4-acetyl-1-methylcyclohexene	0.0009	2-ethyltoluene	0.0010
nopinone	0.0009	1,2,4-trimethylbenzene	0.0013
bornylacetate	0.0006	1,2,3-trimethylbenzene	0.0010
longicyclene	0.0006	**Alkanes**	**ppb**
iso-longifolene	0.0006	2,2,4-trimethylpentane	0.0064
β-caryophyllene	0.0006	heptane	0.0025
aromadendrene	0.0006	hexane	0.0028
α-humulene	0.0006	2-methylpentane	0.0014
alloaromadendrene/farnesene	0.0006	octane	0.0011
4-Allylanisole	0.0008	nonane	0.0010
		decane	0.0024

3.4   Supporting measurements

Other measurements continuously conducted at Welgegund were used to help interpret the VOC results. These measurements included trace gaseous species, i.e. sulphur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO) and ozone (O_3). Trace gases were measured by utilising a Thermo-Electron 43S SO_2 analyser (Thermo Fisher Scientific Inc., Yokohama-shi, Japan), a Teledyne 200AU NO_x analyser (Advanced Pollution Instrumentation Inc., San Diego, Cam USA), an Environment SA 41M O_3 analyser (Environment SA, Poissy, France) and a Horiba APMA-360 CO analyser (Horiba, Kyoto, Japan). Furthermore, a Rotronic MP 101A was used to measure temperature and relative humidity, 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.

Although not included in this study, new particle formation was measured with an Air Ion Spectrometer (AIS) and a differential mobility particle sizer (DMPS). Particulate matter concentrations (PM_{10}), chemical composition of PM_1 particles with an aerosol chemical speciation monitor (ACSM) and aerosol trace metal content were also measured at

Welgegund. For a more detailed set of parameters monitored at Welgegund, refer to Beukes *et al.* (2012).

3.5   Quality assurance

Preconditioning of VOC adsorbent tubes

Before sampling, all adsorbent tubes were tested for leaks and preconditioned with helium for 30 minutes at 350ºC at a flow of 40ml min^{-1}. These tubes were then analysed (**Section 3.3.2**) to ensure that no target VOC species were present in the tubes. After treatment, the tubes were sealed with Swagelok® brass ¼" caps and stored in a fridge at temperatures below 18ºC before they were transported to the field for sampling.

VOC blank samples

Each month, a field blank was exposed to ensure that contamination from sample collection, transportation and storage of samples was acceptable.

O_3 removal verification

As mentioned in **Section 3.3.1**, moisture and O_3 in the air may affect the trapping ability of the sorbents in the tubes. Therefore, the inlet air stream was heated with heating cables and a thermostat (Thermonic). The purpose of the heated inlet was to mitigate the influence of O_3 on the absorption of VOCs onto the packing material and to remove the moisture content. The ozone removal efficiency was checked with the onsite ozone monitoring instrument (**Section 3.4**) at regular intervals and it was found to be acceptable. Ozone removal by a heated inlet and subsequent VOC recoveries has been tested by Hellén *et al.* (2012).

Instrument maintenance and servicing

The measurement site was maintained in a similar manner as procedures described by Venter *et al.* (2012), Laakso *et al.* (2012), Vakkari *et al.* (2011) and Laakso *et al.* (2008). All the instruments were checked and maintained weekly, and a full service was made approximately every three months. In addition to on-site checks, data was downloaded automatically every day to a server via GPRS modem and visually inspected for quality assurance. This enabled immediate corrective actions if irregularities were found. An electronic diary was also kept of all onsite activities, so that the effect of these activities could be reviewed later.

Data analysis

The trace gaseous species and meteorological measurements were visualised and corrected with a fit-for-purpose MATLAB programme set, as previously described by Venter *et al.* (2012), Hirsikko *et al.* (2012), Laakso *et al.* (2012) and Vakkari *et al.* (2011). The measurement data were averaged to correspond to the VOC data sampling time. The concentrations of the VOC compounds that were below the detection limits of the analytical procedure were taken as half of the detection limits (**Section 3.3.2** and **Table 3.3**). This is a conservative approach that applies a precautionary allocation of values, rather than assuming that values below the detection limit of the analytical procedure are equal to zero. The application of this principal is quite common (Wyngaardt, 2011).