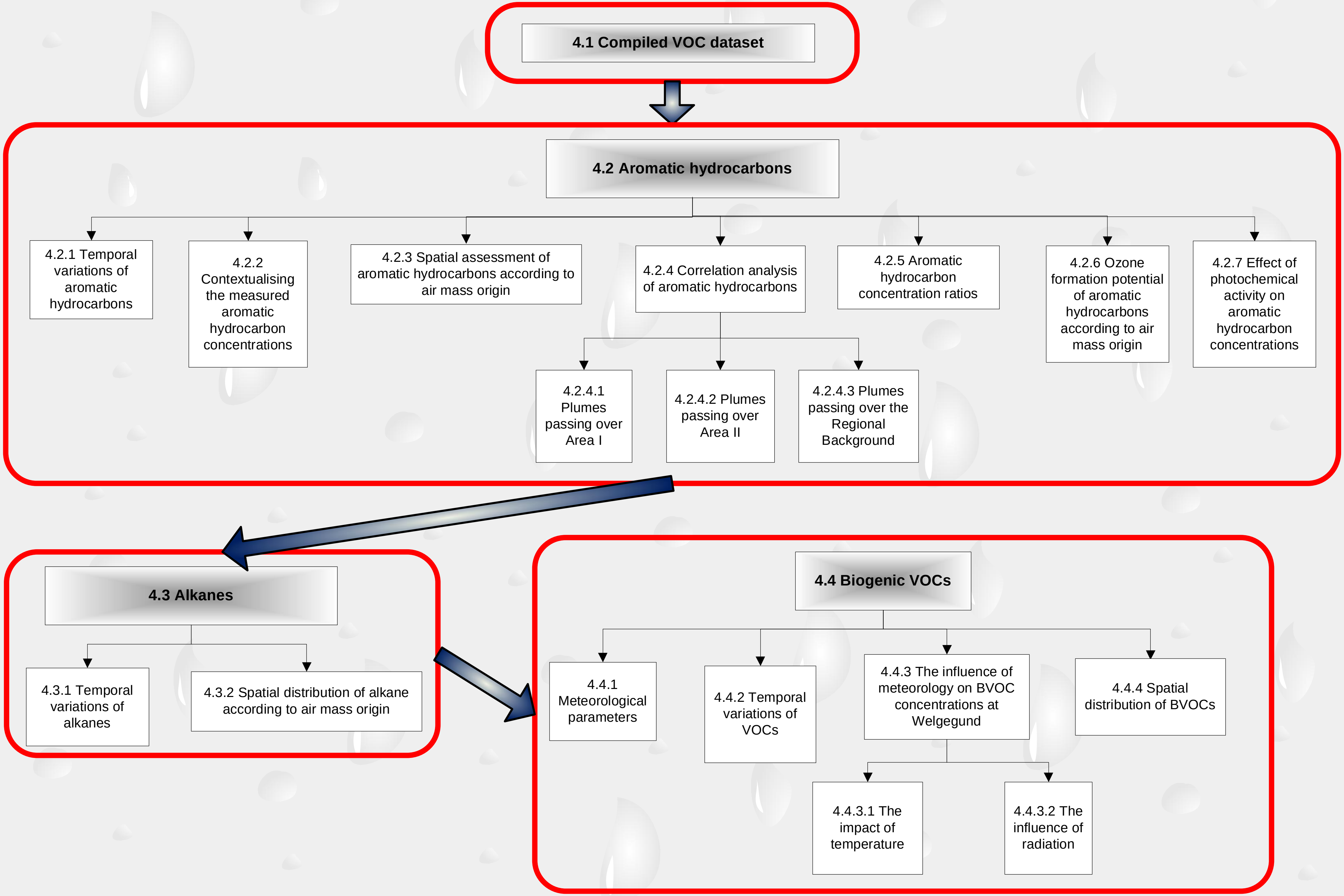
Graphical layout of Chapter 4



Chapter 4

Results and discussion

4.1 Compiled VOC dataset

A total of 40 VOCs were characterised and quantified in samples collected at the Welgegund monitoring station. These species included 20 biogenic VOCs, as well as 13 aromatic hydrocarbons and seven alkanes that are usually associated with anthropogenic emissions. The full dataset is attached in **Appendix A**.

Benzene, toluene, ethylbenzene and o,m,p-xylene (BTEX) are historically the most commonly assessed species. Benzene's concentration was only once below the detection limit of the analytical technique (**Section 3.3.2**) during the entire sampling period. Benzene's concentration ranged between 0.027 and 8.730 ppb, while toluene's concentration was between 0.138 and 6.128 ppb for the one-year sampling period. Ethylbenzene, (m,p)-xylene and o-xylene had concentrations that ranged between 0.01 and 1.837 ppb, 0.119 and 5.191 ppb and 0.007 and 1.980 ppb, respectively. The remaining aromatic hydrocarbons, which included propylbenzene, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, styrene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene, had concentrations ranging between 0.001 and 3.971 ppb.

The alkane concentrations, which included heptane, hexane, octane, decane, nonane, 2,2,4-trimethylpentane and 2-methylpenatane, ranged between 0.003 and 1.405 ppb, which were consistently lower than the aromatic hydrocarbon levels. For the first two months of sampling, nonane and decane were not detected, while 2,2,4-trimethylpentane and 2-methylpentane were not detected in the last nine months of sampling.

For the biogenic VOCs, isoprene's concentration ranged between 0.00165 and 0.442 ppb. The monoterpene (MT) concentrations, which included α-pinene, β-pinene, 3Δ-carene, camphene, p-cymene, limonene and terpinolene, ranged between 0.00109 and 89.47035 ppb. The sesquiterpene (SQT) concentrations, which included longicyclene, iso-longifolene, β-caryophyllene, aromadendrene, α-humulene and alloaromadendrene (farnesene), ranged between 0.0061 and 0.4134 ppb. Other measured biogenic VOC concentrations, which included 2-methyl-3-buten-2-ol (MBO), 1,8-cineol, 4-acetyl-1-methylcyclohexene (AMCH), nopinone, bornylacetate and 4-allylanisole, ranged between 0.0006 and 4.6113 ppb.

For the entire sampling period, aromatic hydrocarbons accounted for 66% (4.24 ppb) of the average mass of the measured VOCs, while alkanes accounted for 10% (0.64 ppb). Biogenic VOCs contributed approximately 24% (1.56 ppb) to the average composition of the quantified VOCs.

4.2 Aromatic hydrocarbons

4.2.1 Temporal variations of aromatic hydrocarbons

As described in **Section 3.3.1**, samples were collected during daytime and night-time. However, the results indicated no statistically significant differences between daytime and night-time aromatic hydrocarbon concentrations. Therefore, no distinction is made in subsequent sections based on daytime or night-time sampling for the aromatic hydrocarbons.

The monthly annual temporal variations of the measured aromatic hydrocarbon species are presented in **Figure 4.1**. These figures indicate the median, mean, 25 and 75 percentiles, as well as ±2.7 the quartile for each species (MATLAB, 2010), thereby providing a good statistical representation of the results. The number of samples per month (N) is also provided. These results indicate relatively high values in February 2011 and March 2011 for all the aromatic hydrocarbon species, with the exception of benzene. If these higher values, measured in the first two months, were linked to a seasonal cycle, one would have expected similar higher values in the corresponding months during the next year. However, no such increase was observed in February 2012. It therefore seems that no distinct seasonal cycles were observed for the aromatic hydrocarbons. No seasonal patterns for BTEX were also observed in a previous investigation conducted in the Mpumalanga Highveld and Vaal Triangle (Lourens *et al.*, 2011). The reason(s) for this apparent absence of a well-defined monthly annual temporal variation will be further explored later in this chapter.

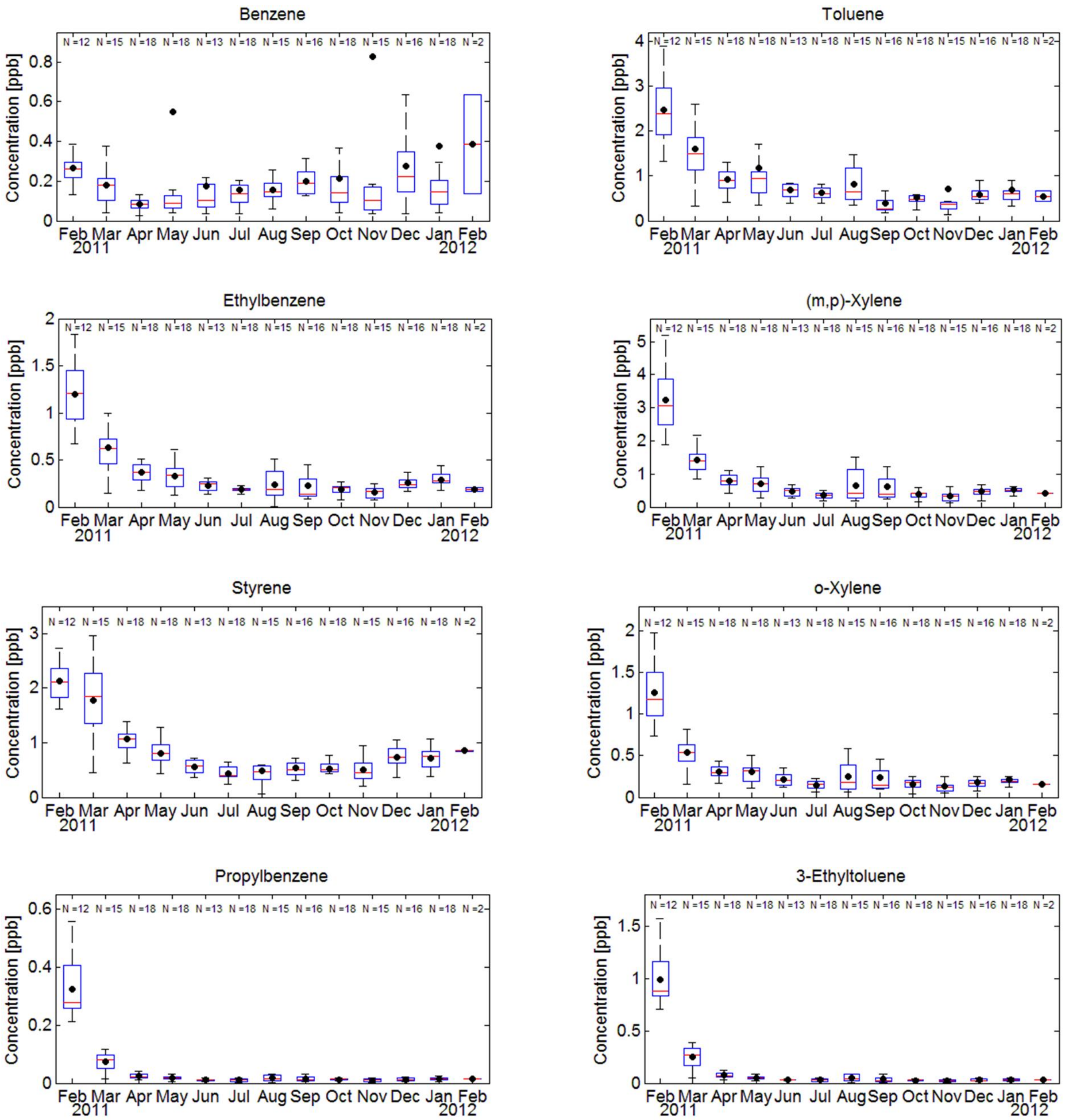


Figure 4.1: Monthly annual variation of aromatic hydrocarbon concentrations measured during the one-year sampling period. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers $\pm 2.7\sigma$ or 99.3% coverage, if the data has a normal distribution (MATLAB, 2010). The values displayed on top of each box and whisker plot for each month indicate the number of samples (N) analysed for each month

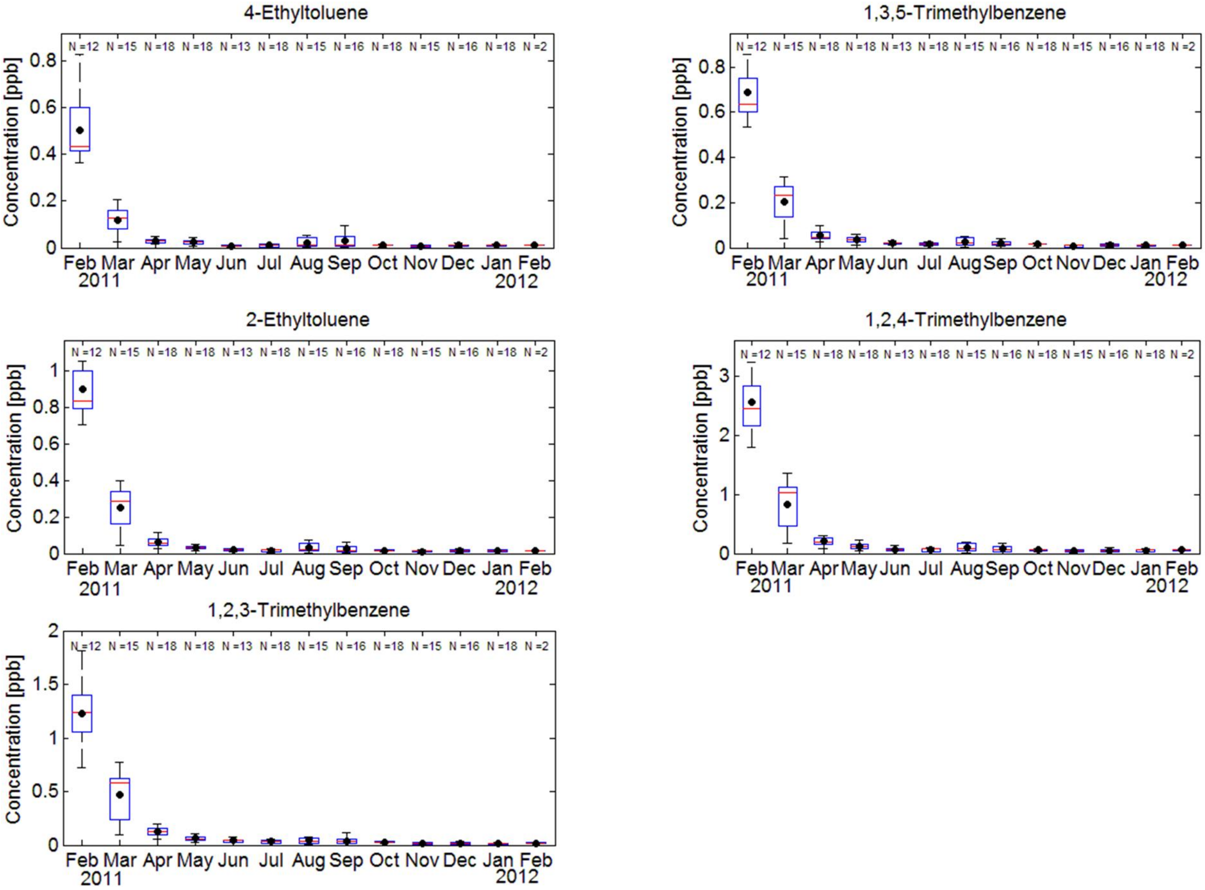


Figure 4.1: *Continued from previous page.* Monthly annual variation of aromatic hydrocarbon concentrations measured during the one-year sampling period. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ±2.7σ or 99.3% coverage, if the data has a normal distribution (MATLAB, 2010). The values displayed on top of each box and whisker plot for each month indicate the number of samples (N) analysed for each month

In **Table 4.1,** the average concentrations of the aromatic species measured at Welgegund for the four different seasons, i.e. winter (June to August), summer (December to February), spring (September to November) and autumn (March to May), are presented. These results indicate higher concentrations of aromatic hydrocarbons during summer and autumn. In various previous studies, seasonal variations in aromatic hydrocarbons were generally characterised by high concentrations during winter (Brocco *et al.*, 1997; Liu *et al.*, 2000; Na & Kim, 2001; Hellén *et al.*, 2002; Hoque *et al.*, 2008; Nguyen *et al.*, 2009). However, as indicated in **Figure 4.1**, higher concentrations were measured for most aromatic hydrocarbons during the first two months of the study. The reported seasonal averages are therefore likely to be bias, due to the general absence of seasonal cycles and the higher concentrations measured in the first months. As was stated previously, the reason(s) for the lack of well-defined temporal variations and the higher concentrations measured in the first months will be discussed later in this chapter.

Table 4.1: Average seasonal concentrations of aromatic hydrocarbons measured at Welgegund. Winter defined as June to August, summer as December to February, spring as September to November and autumn as March to May

ppb	Winter	Summer	Spring	Autumn
benzene	0.161	0.317	0.396	0.276
toluene	0.701	1.097	0.538	1.213
ethylbenzene	0.213	0.503	0.191	0.432
(m,p)-xylene	0.478	1.184	0.445	0.953
styrene	0.487	1.080	0.521	1.183
o-xylene	0.199	0.458	0.175	0.376
propylbenzene	0.013	0.091	0.012	0.037
3-ethyltoluene	0.037	0.269	0.029	0.116
4-ethyltoluene	0.013	0.134	0.015	0.055
1,3,5-trimethylbenzene	0.021	0.180	0.016	0.091
2-ethyltoluene	0.023	0.236	0.018	0.106
1,2,4-trimethylbenzene	0.079	0.678	0.062	0.358
1,2,3-trimethylbenzene	0.039	0.319	0.027	0.207

4.2.2 Contextualising the measured aromatic hydrocarbon concentrations

The monthly medians for aromatic hydrocarbon concentrations determined in this study were typically in the range of 0.01 to 3.1 ppb. Benzene is a carcinogenic compound that causes leukaemia (WHO, 2000; Hellén *et al.*, 2002). According to the World Health Organization (WHO), benzene leads to approximately six additional cases of leukaemia per million inhabitants, if the population is exposed to 0.31 ppb benzene through inhalation for a lifetime (WHO, 1999). The monthly benzene concentrations are (**Figure 4.1**), however, difficult to interpret within the South African legislative context, since no monthly standard for benzene exists in the local legislation. Benzene is currently the only VOC listed as a criteria pollutant in the South African (SA) Air Quality Act (Government Gazette, 2004; Lourens *et al.*, 2011), with an annual average limit of 1.6 ppb (2015 standard). The Welgegund annual median benzene concentration was 0.13 ppb. This was lower than the limit indicated in the SA standard. The highest daily benzene concentration exceeded 8.7 ppb, which indicated that the site is sometimes significantly impacted by sources. As previously mentioned, Lourens *et al.* (2011) measured benzene in the Mpumalanga Highveld and the Vaal Triangle. These authors reported an annual median benzene concentration of 0.91 ppb, which is higher than the value measured at Welgegund. This can probably be attributed to the measurement sites in the afore-mentioned study being closer to the large point sources in the Mpumalanga Highveld and the Vaal Triangle. Furthermore, Van der Walt (2008) measured benzene in a South African metropolitan area and reported an annual mean of 1.8 ppb. By comparing the Welgegund benzene results with the afore-mentioned references, it seems to indicate that Welgegund can be considered as a regional background site, which is on occasion impacted by major plumes from various sources.

Toluene was the most abundant aromatic hydrocarbon species, with its annual median concentrations (0.63 ppb) being nearly five times higher than that of benzene. This was not unexpected, since the concentration of toluene is typically two to four times higher than benzene (Brocco *et al.*, 1997; Na & Kim, 2001; Borbon *et al.*, 2002). Lourens *et al.* (2011) also reported toluene concentrations to be substantially higher than that of benzene in the Mpumalanga Highveld and the Vaal Triangle. Considering that toluene also has negative effects on human health, and it is a precursor for O_3 and secondary organic aerosol formation (**Section 2.4.4**), it should be considered to also include toluene in future South African air quality legislation.

The second and third most abundant aromatic hydrocarbons were styrene and (m,p)-xylene with annual median concentrations of 0.66 and 0.50 ppb, respectively. The other two BTEX species, i.e. o-xylene and ethylbenzene, had annual median concentrations of 0.20 and 0.25 ppb, respectively. The remaining aromatic hydrocarbons had annual median concentrations lower than 0.008 ppb. A possible reason for their low levels can be related to their atmospheric lifetimes, which are influenced by their photochemical reactivity leading to faster degradation (Parra *et al.*, 2006). The aromatic hydrocarbon levels observed in this study were somewhat lower than reported by Liu *et al.* (2000), who conducted a study in a relatively non-polluted area at a background site (Changchun) in the northeast of China. These authors reported average BTEX concentrations ranging between 1.7 and 9.6 ppb. The difference in BTEX concentrations measured at background sites suggests that the difference in regional climate, geographic location, as well as the influence of industrial and vehicle emission will strongly affect the aromatic hydrocarbon concentrations measured at these sites. Long-range transport can result in diluted concentrations of pollutants being advected into rural regions. Moreover, the dispersion, deposition and chemical reactions occurring during transport will lead to even more fluctuations in the concentrations of aromatic hydrocarbons at rural sites.

4.2.3 Spatial assessment of aromatic hydrocarbons according to air mass origin

Since no distinct seasonal cycles could be identified for the measured aromatic hydrocarbon species (**Section 4.2.1**), the possible influence of air mass origin on the concentration of these species was explored. In **Section 3.2** and **Figure 3.5,** the source regions considered in this study, together with the explanations of how these source regions were defined, were presented. According to the afore-mentioned definition of the source regions, source Area I consisted of the Mpumalanga Highveld, the Vaal Triangle and the Johannesburg-Pretoria metropolitan conurbation, while source Area II encompassed the western and eastern Bushveld Igneous Complexes (BIC), and the geographical region from where most of the air masses flow in an anti-cyclonic pattern towards Welgegund (**Section 3.2** and **Figure 3.5**). The regional background source region was defined as the area not covered by the afore-mentioned two source regions.

For the entire VOC measurement period, 582 back trajectories were generated (**Section 3.1**) and classified. 86% of all trajectories could be classified as passing over just one of the three source regions defined, without passing over another source region, on their way to Welgegund. The remaining 14 % of trajectories passed over multiple source regions and were therefore classified as being of mixed origin. Data collected during the periods that these mixed source region trajectories arrived at Welgegund was not included in further data analyses in this section (**Section 4.2.3**).

Figure 4.2 indicates the manner in which back trajectories arriving at Welgegund were classified as passing over the defined source regions. As indicated (**Figure 4.2**), a substantial fraction of the air masses arriving at Welgegund passed over Area II (39 %) and the Regional Background (33 %). Only 14 % of the hourly air mass back trajectories passed over Area I. The reason for the low percentage of trajectories passing over Area I may be due to the persistence of the anti-cyclonic recirculation pattern over the interior of South Africa. This circulation pattern favours the arrival of air masses at Welgegund from the north to north-eastern sector and not the east to southerly sector where source Area I is situated.

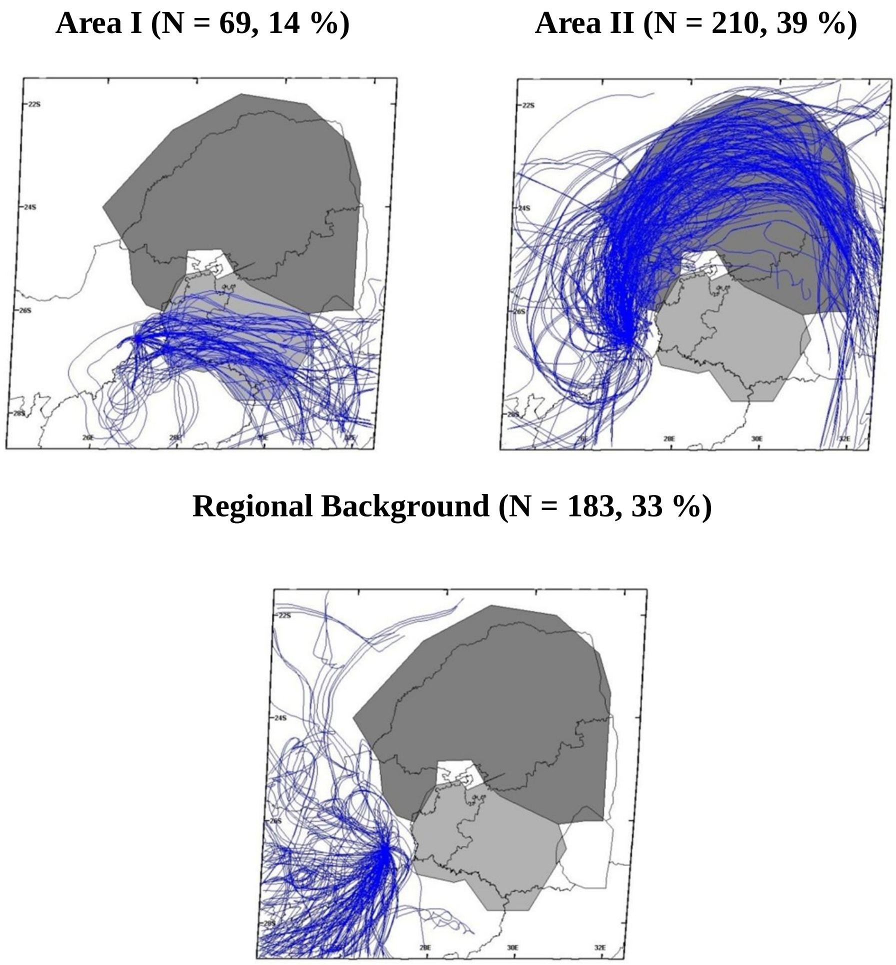


Figure 4.2: Graphical representations of back trajectories allocated as passing over the defined source regions. The percentage of the trajectories allocated as passing over a specific source region and the number of trajectories it represents are provided in brackets

In **Figure 4.3,** the monthly fractional distribution of hourly air mass back trajectories arriving at Welgegund, after passing over the various source regions, is presented. This spread of air mass history can be used to explain the lack of seasonal patterns observed for the aromatic hydrocarbon species (**Section 4.2.1** and **Figure 4.1**). During the first month of the measurements, more than 60 % of the air masses that arrived at Welgegund passed over Area I. As mentioned earlier, this source area consists of the Johannesburg-Pretoria metropolitan conurbation that is inhabited by more than 10 million people (Community Survey, 2007; Lourens *et al.*, 2012), as well as the Vaal Triangle and the Mpumalanga Highveld. Both of the afore-mentioned areas have been declared as national priority areas by the SA government (Government Gazette, 2005; Government Gazette, 2007), which indicates that these areas are relatively heavily polluted. According to Scorgie (2004), VOC emissions in the Vaal Triangle are estimated to be 46200 tonnes per annum, with industries accounting for more than 97 % of the emissions. Considering the high frequency of air masses arriving at Welgegund after passing over Area I during the initial period of the study (**Figure 4.3**), the relatively high aromatic hydrocarbon levels measured in February 2011 and March 2011 (**Figure 4.1**) can be explained. Conversely, during the rest of the study, most of the air masses that arrived at Welgegund passed only over Area II and the Regional Background, which corresponds with lower concentrations measured (**Figure 4.1**). It is therefore postulated that the monthly seasonal cycles presented for the aromatic hydrocarbon species (**Figure 4.1**) are not directly related to seasonal patterns, but rather depend on the origin of the air masses sampled.

The above-mentioned postulation is strengthened by a slight concentration increase of most of the aromatic hydrocarbon species observed during August and September 2011 (**Figure 4.1**), which correlated with an increase in frequency of the arrival of air masses that had passed over Area I (**Figure 4.3**). However, the increase in the frequency in the arrival of air masses passing over Area I during the last three months of the measurement period does not correlate perfectly with the corresponding concentrations.

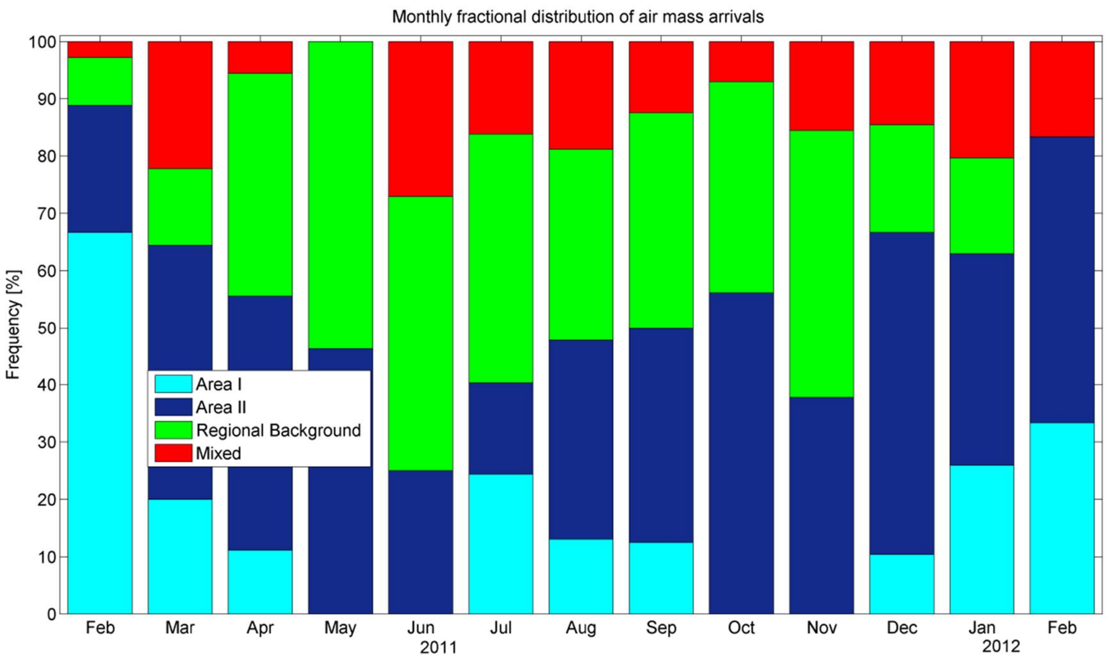


Figure 4.3: Monthly fractional distribution of air mass arrivals at Welgegund after passing over the defined source regions

The aromatic hydrocarbon concentrations for the air masses sampled, after passing over the various source regions, are summarised in **Table 4.2** and **Figure 4.4**. **Table 4.2** provides the median and mean values, as well as the 5, 25, 75 and 95 percentile values of the aromatic hydrocarbons of air masses arriving at Welgegund, after passing over the defined source regions. **Figure 4.4** provides a graphical representation of these results for the BTEX compounds.

Table 4.2: The aromatic hydrocarbon concentrations of air masses sampled at Welgegund after passing over the defined source regions

	Area I			**Area II**			**Regional Background**		
	Median	Mean	$5^{th}/25^{th}/75^{th}/95^{th}$ percentile	Median	Mean	$5^{th}/25^{th}/75^{th}/95^{th}$ percentile	Median	Mean	$5^{th}/25^{th}/75^{th}/95^{th}$ percentile
benzene	0.239	0.228	0.064/0.150/0.288/0.409	0.146	0.335	0.036/0.075/0.210/0.406	0.111	0.299	0.042/0.077/0.161/1.237
toluene	0.960	1.482	0.347/0.721/2.344/3.516	0.547	0.796	0.219/0.422/0.966/1.724	0.624	0.796	0.249/0.482/0.857/1.527
ethylbenzene	0.384	0.653	0.155/0.225/0.989/1.678	0.220	0.300	0.087/0.167/0.407/0.627	0.257	0.279	0.110/0.176/0.355/0.640
(m,p)-xylene	0.794	1.665	0.317/0.428/2.629/4.793	0.454	0.661	0.175/0.328/0.844/1.502	0.507	0.612	0.208/0.354/0.752/1.339
styrene	1.065	1.288	0.387/0.546/2.098/2.386	0.617	0.746	0.189/0.438/0.933/1.842	0.666	0.730	0.298/0.462/0.822/1.588
o-xylene	0.323	0.647	0.129/0.180/1.039/1.847	0.187	0.254	0.059/0.123/0.331/0.591	0.217	0.253	0.085/0.148/0.329/0.621
propylbenzene	0.029	0.142	0.009/0.015/0.270/0.492	0.015	0.025	0.004/0.007/0.022/0.081	0.015	0.021	0.005/0.011/0.020/0.043
3-ET	0.080	0.422	0.020/0.038/0.859/1.400	0.030	0.074	0.009/0.022/0.058/0.266	0.040	0.059	0.014/0.028/0.061/0.129
4-ET	0.030	0.211	0.007/0.013/0.419/0.709	0.013	0.035	0.003/0.008/0.025/0.131	0.015	0.026	0.003/0.009/0.028/0.069
1,3,5-TMB	0.047	0.289	0.009/0.018/0.620/0.910	0.017	0.051	0.004/0.010/0.043/0.231	0.021	0.038	0.005/0.014/0.040/0.082
2-ET	0.046	0.373	0.011/0.021/0.804/1.157	0.017	0.062	0.005/0.012/0.046/0.284	0.022	0.044	0.007/0.015/0.040/0.106
1,2,4-TMB	0.151	1.073	0.043/0.077/2.194/3.491	0.066	0.196	0.022/0.046/0.175/1.032	0.080	0.146	0.024/0.056/0.134/0.346
1,2,3-TMB	0.075	0.518	0.016/0.030/1.101/1.590	0.029	0.101	0.007/0.018/0.077/0.618	0.045	0.076	0.009/0.021/0.072/0.197

Note: TMB= trimethylbenzene and ET= ethylbenzene

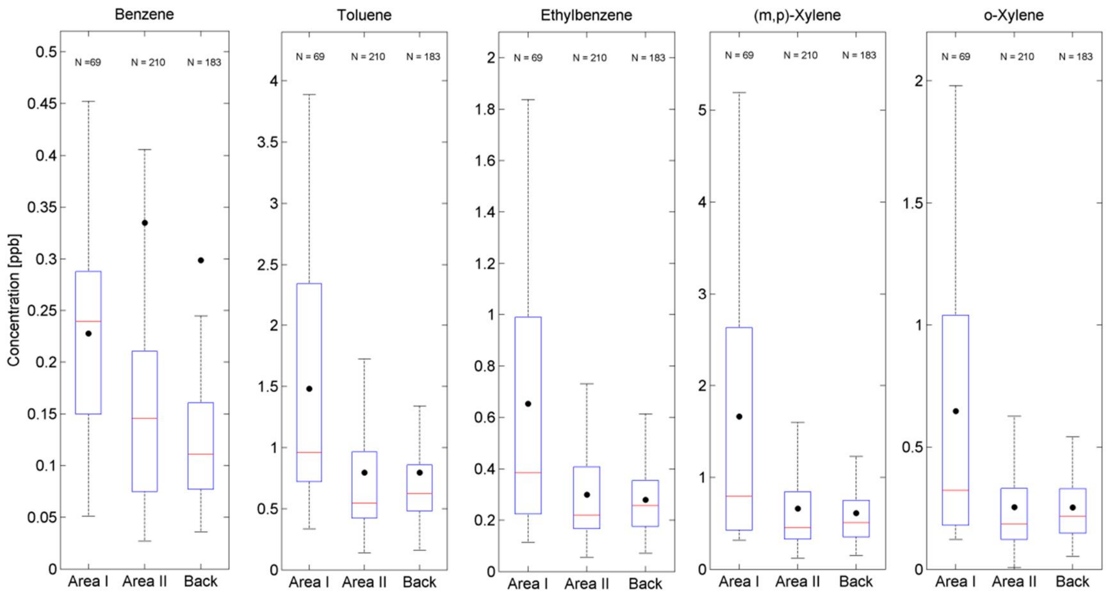


Figure 4.4: BTEX concentrations measured in air masses arriving at Welgegund, after they had passed over the defined source regions. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers $\pm 2.7\sigma$ or 99.3 % coverage, if the data has a normal distribution (MATLAB, 2010). The values displayed on top of each box and whisker plot indicate the number of samples (N) analysed for each source area.

As expected, aromatic hydrocarbon concentrations were in general substantially higher in air masses that had passed over Area I. The higher median concentrations of aromatic hydrocarbons in air masses that had passed over Area I can likely be due to the abundant number of large point sources, as well as the Johannesburg-Pretoria megacity that is relatively heavily polluted, which are present in this source region.

Air masses that had passed over Area II had much lower aromatic hydrocarbon levels than air masses that passed over Area I. This can partially be explained by the differences in the VOC pollution sources in the anthropogenic source regions. The large point sources in Area II are mainly pyrometallurgical smelters (**Section 3.1** and **Figure 3.1**) that produce metals from ores by means of reducing processes (e.g. ferrochromium, as indicated by Beukes *et al.*, 2012; 2011). VOC emissions are not usually associated with these activities. In addition, the large point sources in Area II are on average further away from Welgegund than the large point sources in Area I.

This is particularly the case for large point sources in the eastern BIC (**Figure 3.1**). This longer travelling time will result in the increased oxidation of the aromatic hydrocarbon species.

Air masses that had passed over the Regional Background source region had much lower aromatic hydrocarbon levels than air masses passing over Area I and were in the same order as concentrations measured for air masses passing over Area II. There were, however, instances of higher aromatic hydrocarbons measured in Area II compared to the Regional Background. Aromatic hydrocarbons measured in air masses from the Regional Background can possibly be attributed to smaller cities, as well as agricultural activities in this region. Studies conducted at remote background sites, e.g. Antarctica and in the Arctic, have only reported concentrations of long-lived VOC compounds, such as alkanes and alkenes, in the atmosphere (Hellén *et al.*, 2012b; Clarkson *et al.*, 1997; Gros *et al.*, 1998; Kaspers *et al.*, 2004; Read *et al.*, 2007; Bottenheim *et al.*, 2002; Swanson *et al.*, 2002; Jobson *et al.*, 1994). It is therefore impossible to compare the results in air masses emanating from the Regional Background at Welgegund to such measurements.

4.2.4 Correlation analysis of aromatic hydrocarbons

Several authors (Brocco *et al.*, 1997; Na & Kim, 2001; Hoque *et al.*, 2008; Anthwal *et al.*, 2010; Christensen *et al.*, 1999; Wang *et al.*, 1993) have performed correlation analyses to determine the possible source(s) for aromatic hydrocarbons. In this section, Pearson's correlation analyses were conducted and the aromatic hydrocarbon concentrations were correlated with each other, as well as trace gas concentrations in air masses that had passed over the defined source regions. These correlations are presented in **Table 4.3**.

Table 4.3: Correlation analysis for aromatic hydrocarbons with one another and with inorganic trace gases, from air masses that had passed over the defined source regions

Area I	benzene	toluene	ethylbenzene	(m,p)-xylene	styrene	o-xylene	propylbenzene	3-ET	4-ET	1,3,5-TMB	2-ET	1,2,4-TMB	1,2,3-TMB	SO_2	NO_x	CO	O_3
benzene	1.000																
toluene	0.725	1.000															
ethylbenzene	0.676	0.985	1.000														
(m,p)-xylene	0.668	0.973	0.994	1.000													
styrene	0.594	0.884	0.880	0.850	1.000												
o-xylene	0.669	0.972	0.994	1.000	0.848	1.000											
propylbenzene	0.633	0.926	0.955	0.978	0.787	0.979	1.000										
3-ET	0.619	0.927	0.956	0.977	0.819	0.978	0.997	1.000									
4-ET	0.631	0.926	0.950	0.971	0.812	0.972	0.996	0.998	1.000								
1,3,5-TMB	0.602	0.924	0.952	0.969	0.853	0.970	0.986	0.996	0.994	1.000							
2-ET	0.605	0.924	0.950	0.967	0.848	0.968	0.986	0.996	0.995	0.999	1.000						
1,2,4-TMB	0.624	0.901	0.906	0.918	0.841	0.919	0.943	0.956	0.969	0.965	0.973	1.000					
1,2,3-TMB	0.609	0.883	0.881	0.888	0.858	0.889	0.910	0.929	0.943	0.946	0.954	0.995	1.000				
SO_2	-0.264	-0.536	-0.551	-0.554	-0.666	-0.552	-0.544	-0.554	-0.552	-0.571	-0.564	-0.561	-0.577	1.000			
NO_x	0.211	-0.319	-0.429	-0.444	-0.426	-0.442	-0.450	-0.465	-0.456	-0.484	-0.483	-0.442	-0.441	0.578	1.000		
CO	0.612	0.067	-0.019	-0.035	0.016	-0.041	-0.083	-0.093	-0.086	-0.101	-0.102	-0.073	-0.063	0.162	0.551	1.000	
O_3	-0.046	0.300	0.364	0.380	0.258	0.392	0.400	0.412	0.397	0.411	0.407	0.326	0.297	-0.175	-0.609	-0.314	1.000

Note: TMB= trimethylbenzene and ET= ethylbenzene

Table 4.3: *Continued from previous page.* Correlation analysis for aromatic hydrocarbons with one another and with inorganic trace gasses, from air masses that had passed over the defined source regions

Area II	benzene	toluene	ethylbenzene	(m,p)-xylene	styrene	o-xylene	propylbenzene	3-ET	4-ET	1,3,5-TMB	2-ET	1,2,4-TMB	1,2,3-TMB	SO_2	NO_x	CO	O_3
benzene	1.000																
toluene	0.740	1.000															
ethylbenzene	0.013	0.657	1.000														
(m,p)-xylene	0.083	0.689	0.977	1.000													
styrene	-0.006	0.557	0.880	0.836	1.000												
o-xylene	0.088	0.690	0.974	0.994	0.842	1.000											
propylbenzene	-0.029	0.485	0.844	0.875	0.753	0.874	1.000										
3-ET	-0.036	0.490	0.851	0.880	0.753	0.879	0.998	1.000									
4-ET	-0.046	0.470	0.833	0.868	0.732	0.867	0.988	0.990	1.000								
1,3,5-TMB	-0.049	0.488	0.854	0.876	0.772	0.876	0.992	0.996	0.986	1.000							
2-ET	-0.043	0.484	0.844	0.872	0.752	0.871	0.994	0.998	0.988	0.999	1.000						
1,2,4-TMB	-0.050	0.469	0.829	0.855	0.759	0.855	0.981	0.984	0.973	0.991	0.990	1.000					
1,2,3-TMB	-0.057	0.460	0.816	0.838	0.769	0.838	0.955	0.960	0.948	0.974	0.970	0.994	1.000				
SO_2	-0.050	-0.153	-0.187	-0.170	-0.270	-0.168	-0.125	-0.120	-0.111	-0.116	-0.109	-0.108	-0.108	1.000			
NO_x	0.266	0.052	-0.166	-0.134	-0.203	-0.171	-0.103	-0.114	-0.110	-0.116	-0.106	-0.106	-0.114	0.313	1.000		
CO	0.065	-0.195	-0.283	-0.205	-0.346	-0.224	-0.178	-0.188	-0.165	-0.188	-0.178	-0.186	-0.195	0.247	0.549	1.000	
O_3	-0.077	-0.266	-0.260	-0.205	-0.385	-0.206	-0.174	-0.184	-0.169	-0.196	-0.182	-0.204	-0.233	0.410	0.174	0.715	1.000

Note: TMB= trimethylbenzene and ET= ethylbenzene

Table 4.3: *Continued from previous page.* Correlation analysis for aromatic hydrocarbons with one another and with inorganic trace gasses, from air masses that had passed over the defined source regions

Regional Background	benzene	toluene	ethylbenzene	(m,p)-xylene	styrene	o-xylene	propylbenzene	3-ET	4-ET	1,3,5-TMB	2-ET	1,2,4-TMB	1,2,3-TMB	SO_2	NO_x	CO	O_3
benzene	1.000																
toluene	0.922	1.000															
ethylbenzene	0.037	0.369	1.000														
(m,p)-xylene	0.179	0.452	0.945	1.000													
styrene	0.023	0.334	0.850	0.797	1.000												
o-xylene	0.382	0.632	0.892	0.960	0.730	1.000											
propylbenzene	0.002	0.183	0.574	0.651	0.583	0.611	1.000										
3-ET	-0.011	0.174	0.572	0.647	0.575	0.605	0.999	1.000									
4-ET	-0.018	0.168	0.588	0.664	0.583	0.619	0.997	0.998	1.000								
1,3,5-TMB	-0.016	0.173	0.555	0.620	0.584	0.579	0.993	0.996	0.993	1.000							
2-ET	-0.020	0.159	0.547	0.621	0.560	0.577	0.996	0.998	0.996	0.998	1.000						
1,2,4-TMB	-0.017	0.168	0.553	0.621	0.581	0.578	0.992	0.994	0.991	0.997	0.997	1.000					
1,2,3-TMB	-0.022	0.177	0.566	0.624	0.613	0.582	0.981	0.984	0.980	0.992	0.989	0.996	1.000				
SO_2	-0.053	-0.094	-0.149	-0.135	-0.085	-0.140	-0.051	-0.060	-0.078	-0.077	-0.076	-0.074	-0.086	1.000			
NO_x	-0.065	-0.168	-0.248	-0.217	-0.191	-0.247	-0.065	-0.078	-0.088	-0.097	-0.088	-0.085	-0.109	0.797	1.000		
CO	-0.086	-0.205	-0.241	-0.189	-0.246	-0.215	-0.111	-0.119	-0.116	-0.137	-0.126	-0.125	-0.153	0.580	0.623	1.000	
O_3	0.022	-0.068	-0.113	-0.129	-0.214	-0.077	-0.174	-0.186	-0.186	-0.207	-0.186	-0.202	-0.221	-0.030	-0.323	0.120	1.000

Note: TMB= trimethylbenzene and ET= ethylbenzene

4.2.4.1 Plumes passing over Area I

The relatively good correlation (r > 0.8) between most of the aromatic hydrocarbons, except benzene, in this source region indicates that the sources of these species could be the same (McClenny *et al.*, 1989; Cohen *et al.*, 1991; Wang *et al.*, 1993; Jose *et al.*, 1998; Baldasano *et al.*, 1998). Large coal-fired power stations, petrochemical operations and pyrometallurgical smelters in source Area I, together with vehicle emissions, might be the predominant sources of aromatic hydrocarbons in this source region. Venter *et al.* (2012) recently indicated that household combustion, which is a very common occurrence in especially semi- and informal settlements, could also contribute substantially to local and regional pollution.

Benzene, well known as a tracer species for automobile exhaust emissions (Kerbachi *et al.*, 2006), showed a relatively good correlation (r > 0.6) with other aromatic species and CO. Benzene did, however, not correlate with SO_2 and NO_x concentrations. The relatively good correlation of benzene with CO may be an indication that benzene originated from the same sources as CO. CO is likely to originate mainly from incomplete combustion sources, such as vehicle emissions, household combustion and biomass combustion. However, biomass combustion and household combustion for space heating are only prevalent from May to September (Laakso *et al.*, 2008; Venter *et al.*, 2012).

Another noteworthy observation was that benzene showed a negative correlation with ozone. A negative correlation with ozone can be used as an indicator of the photochemical degradation of VOCs (Tran *et al.*, 2000). It is therefore possible that benzene had undergone significant photochemical degradation in air masses that had passed over Area I.

4.2.4.2 Plumes passing over Area II

With the exception of benzene and toluene, the other aromatic carbons in Area II correlated well with each other. Although benzene and toluene did not correlate with the other aromatic hydrocarbons, they correlated relatively well (r = 0.74) with each other. All the aromatic hydrocarbons did not correlate well with the trace gases and most of these species had a negative correlation with ozone. This indicates that these species can be a precursor in the area for ozone formation. A strong correlation was also observed between CO and O_3, possibly because CO is a known precursor for O_3 (Haagen-Smit & Fox, 1956; Atkinson, 1994; Atkinson, 1997)

4.2.4.3 Plumes passing over the Regional Background

Similar to air masses passing over source Area II, benzene was well correlated ($r = 0.92$) with toluene; however, no such correlation was evident between the other aromatic hydrocarbons and trace gases. The results also indicate that some of the aromatic hydrocarbons, e.g. ethylbenzene, styrene, (m,p)-xylene and o-xylene, correlated well ($r > 0.8$) with each other.

4.2.5 Aromatic hydrocarbon concentration ratios

The aromatic hydrocarbon interspecies ratios are presented in **Table 4.4**. Interspecies ratios have been used by several authors as indicators of the age of the air mass and as tracers for emission sources (Hoque *et al.*, 2008; Khoder, 2007; Guo *et al.*, 2007; Kerbachi *et al.*, 2006). Since most of the aromatic hydrocarbons are more reactive than benzene, the toluene/benzene (T/B), (m,p)-xylene/benzene ((m,p)-X/B), o - xylene/benzene (o-X/B) and (m,p)-xylene/ethylbenzene ((m,p)-X/EB) ratios can provide additional information, e.g. the distance of emission sources and the estimated photochemical age of the air mass (Derwent *et al.*, 2000; Monod *et al.*, 2001). The T/B ratio increases with increasing anthropogenic emissions and decreases with an increase in distance from the sources (Lee *et al.*, 2002). A value of one is usually an indication of fresh emissions originating from traffic (Gelencser *et al.*, 1997; Simon *et al.*, 2004).

Table 4.4: The aromatic hydrocarbon ratios for the specific source regions

	Area I	Area II	Regional Background	Automotive exhaust
toluene/benzene	6.51	2.38	2.66	2.70 [a]
(m,p)-xylene/benzene	7.31	1.97	2.05	1.80 [b]
o-xylene/benzene	2.84	0.76	0.85	0.90 [c]
ethylbenzene/benzene	2.87	0.89	0.93	
1,3,5-TMB/benzene	1.27	0.15	0.13	
styrene/benzene	5.66	2.23	2.44	
propylbenzene/benzene	0.62	0.07	0.07	
m,p-xylene/ethylbenzene	2.55	2.20	2.19	
o-xylene/ethylbenzene	0.99	0.85	0.91	

(a) Brocco *et al*. (1997); Guicherit (1997). (b) Stevenson *et al*. (1997). (c) Guicherit (1997).

As indicated in **Table 4.4**, the highest aromatic hydrocarbon ratios were observed for plumes passing over Area I, whereas lower ratios were detected in plumes passing over Area II and the Regional Background.

The ratios for plumes passing over Area I were 6.51, 7.31, 2.84, 2.55 and 2.87 for (T/B), ((m,p)-X/B), (o-X/B) ((m,p)-X/EB) and (EB/B), respectively. These ratios indicate the influence of anthropogenic activities in this area. These ratios also indicate that the sources in Area I are also relatively close to the Welgegund monitoring station.

The ratios for plumes passing over Area II were 2.38, 1.97, 0.76, 2.20 and 0.89 for (T/B), ((m,p)-X/B), (o-X/B) ((m,p)-X/EB) and (EB/B), respectively. Although anthropogenic activities are also associated with this source area, the major industrial activities in this area close to Welgegund (western BIC) are not usually associated with high emissions of VOCs. The sources in Area II, especially those in the eastern BIC, are also further away from the measurement site than in Area I. The ratios therefore indicated aged air masses. Furthermore, Area II is also strongly influenced by aged air masses that are circulated by the dominant anti-cyclonic circulation pattern from the industrial hub of South Africa. Therefore, it is hypothesised that most of the hydrocarbons had undergone photochemical degradation in the Area II, thereby leading to lower ratios.

The aromatic hydrocarbon interspecies ratios were 2.66, 2.05, 0.85, 2.19 and 0.93 for (T/B), ((m,p)-X/B), (o - X/B) ((m,p)-X/EB) and (EB/B), respectively, in plumes passing over the Regional Background (**Table 4.4**). These ratios compared with the ratios calculated for Area II. These results indicate that aromatic hydrocarbons in these air masses do not come from local sources. As previously mentioned, the (T/B) ratio decreases as the distance from the pollution source increases and lower (T/B) ratios, as well as other ratios calculated, imply an aged air parcel (Hsieh & Tsai, 2003).

According to certain literature sources, the use of solvents (e.g. in paint) are also thought to be a major non-traffic sources of aromatic hydrocarbons. According to Brocco *et al.* (1997), toluene, ethylbenzene, and o,m,p-xylene (TEX) make up the largest portion in solvents. In **Figure 4.5,** the concentration ratios of TEX/total aromatics for air masses that had passed over the various sources regions for each month are illustrated. The ratios show a seasonal pattern with the maximum in summer and minimum in winter. This correlates with Rappenglϋck and Fabian (1999) who reported that the evaporation of solvents makes a greater contribution to VOCs at higher temperature, i.e. summer. It can therefore be postulated that VOCs originating from solvents make a contribution to air masses that had passed over all three source regions, including the regional background.

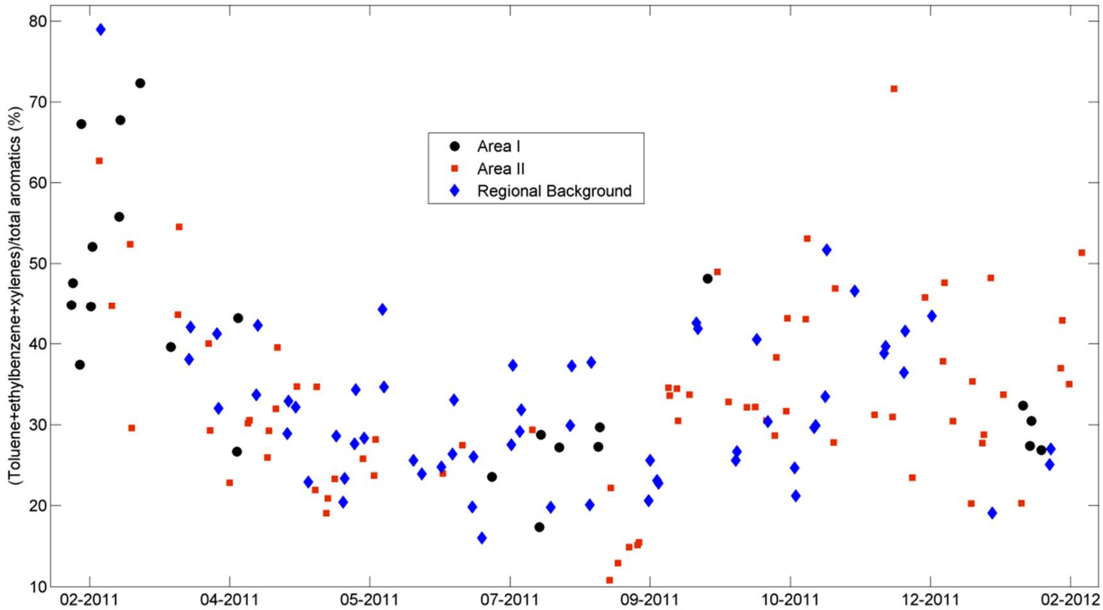


Figure 4.5: Temporal variation of the concentration ratios of the sum of toluene, ethylbenzene and xylenes to total aromatics from air masses arriving at Welgegund after passing over the defined source regions

4.2.6 Ozone formation potential of aromatic hydrocarbons according to air mass origin

While the ranking of airborne pollutants on a mass concentration (ppb) basis is of interest in order to assess human exposure to toxic compounds like benzene, it is also of interest to examine the relative importance of these pollutants for their role in production of ozone (Carter, 1994).

In this section, the relative contribution of aromatic hydrocarbons to photochemical ozone formation in air masses that have passed over the various source regions defined is examined (**Section 3.2** and **Figure 3.5**). This can be done by ranking the hydrocarbons according to their ability to produce ozone, by calculating for each compound the product of its average concentration and the compound's maximum incremental reactivity coefficient (MIR), i.e. ozone formation potential = VOC×MIR (Carter, 1994). The MIR scale indicates how much the compound may contribute to ozone formation in the air mass. As mentioned in **Section 2.4.4.1**, several reactivity scales can be used to estimate ozone formation for a given hydrocarbon. For the purpose of this study, the MIR scale was selected. The MIR scale has also been used to assess aromatic hydrocarbon reactivity in other studies (Hoque *et al.*, 2008; Singla *et al.*, 2012; Grosjean *et al.*, 1998; Na *et al.*, 2005)

The ranking of the aromatic hydrocarbon species according to air mass origin for ozone formation potential is provided in **Table 4.5**. As indicated (**Table 4.5**), the highest contribution of aromatic hydrocarbon concentrations to ozone formation potential were observed for plumes passing over Area I, with Area II and the Regional Background in the same order of magnitude. Based on the ozone formation potential values, xylenes ((m,p)-xylene plus o-xylene) are the most dominant contributor to ozone formation among aromatic hydrocarbons for air masses that have passed over Area I; 1,2,4-trimethylbenzene was the second largest contributor. The ozone formation potential of benzene was the lowest, even though it is the most hazardous species among aromatic hydrocarbons. It is clearly seen from **Table 4.5** that TEX coming from evaporative emissions contributes more to ozone formation than those from other sources. It therefore suggests that ozone abatement may be achieved by regulating the use of solvents and gasoline spills.

Table 4.5: Ozone formation potential of the aromatic hydrocarbon concentrations of air masses passing over the defined source regions

	Area I			Area II		Regional Background	
	Mean	**MIR coefficient**	**O_3 formation potential**	**Mean**	**O_3 formation potential**	**Mean**	**O_3 formation potential**
benzene	0.228	0.42	0.096	0.335	0.141	0.299	0.125
toluene	1.482	2.70	4.001	0.796	2.148	0.796	2.148
ethylbenzene	0.653	2.70	1.762	0.300	0.809	0.279	0.753
(m,p)-xylene	1.665	8.20	13.653	0.661	5.418	0.612	5.014
styrene	1.288	2.20	2.834	0.746	1.641	0.730	1.607
o-xylene	0.647	6.50	4.208	0.254	1.651	0.253	1.645
propylbenzene	0.142	2.10	0.298	0.025	0.053	0.021	0.043
1,3,5-TMB	0.289	10.10	2.916	0.051	0.512	0.038	0.381
1,2,4-TMB	1.073	8.80	9.444	0.196	1.728	0.146	1.289
1,2,3-TMB	0.518	8.90	4.608	0.101	0.900	0.076	0.674

Note: TMB= trimethylbenzene

4.2.7 Effect of photochemical activity on aromatic hydrocarbon concentrations

As was mentioned in **Section 2.4**, aromatic hydrocarbons are mainly removed by their chemical reactions with $^{\bullet}OH$ radicals, which is the predominant removal process for aromatic hydrocarbons in the atmosphere (Brocco *et al.*, 1997). The $^{\bullet}OH$ radical is generated from the photolysis of ozone in sunlight at a wavelength of 319nm (NRC, 1991). Therefore, theoretically, the photochemical removal of VOCs occurs faster in summer than in winter.

To explore the influence of photochemical activity on the concentration of aromatic hydrocarbons, the correlation graphs between the benzene and toluene for summer (December to February) and winter (June to August) were generated. These correlation graphs are presented in **Figure 4.6**. A relatively good correlation between benzene and toluene is observed during the winter (r = 0.55, slope = 0.29), while a much more scattered correlation (r = 0.34, slope = 0.22) is observed during summer. Toluene is more reactive than benzene and is removed from the atmosphere faster. This difference between the two correlations can be attributed to the higher photochemical reactivity in the summer leading to faster rates of depletion of toluene. Additionally, it also seems as if the summer data (**Figure 4.6**) could be grouped into two distinct groups that could be fitted with two separate linear trend lines. At present, this could not be explained, although it is currently being investigated further.

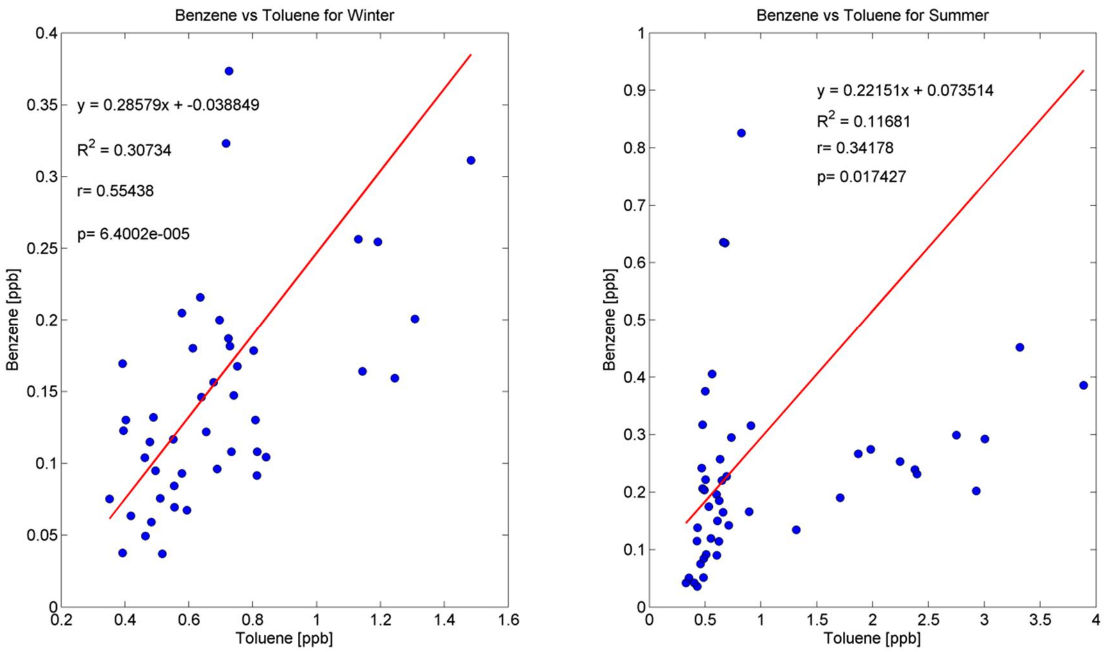


Figure 4.6: Relationship between the benzene and toluene concentrations for measurements obtained in summer (December to February) and winter (June to August)

4.3 Alkanes

4.3.1 Temporal variations of alkanes

The monthly annual temporal variations of the alkane species measured during the one-year sampling period are presented in **Figure 4.7**. It is evident from these results that alkane species seem to follow the same trend as observed for the aromatic hydrocarbons. These results also indicate relatively high values in February 2011 and March 2011 for most of the alkanes determined. There were, however, alkanes that were not detected during these two months, while hexane had higher concentrations during June 2011 and July 2011. Similar to the aromatic hydrocarbons, these higher concentrations were not observed for February 2012, which indicates that this could not be attributed to a seasonal cycle. The higher concentrations of most of the alkanes in February 2011 and March 2011 could also possibly be explained by the majority of air masses arriving at Welgegund that had passed over Area I (**Section 4.2.3** and **Figure 4.2**). This source region had more anthropogenic sources and these sources are in general closer to the site than the point sources in Area II.

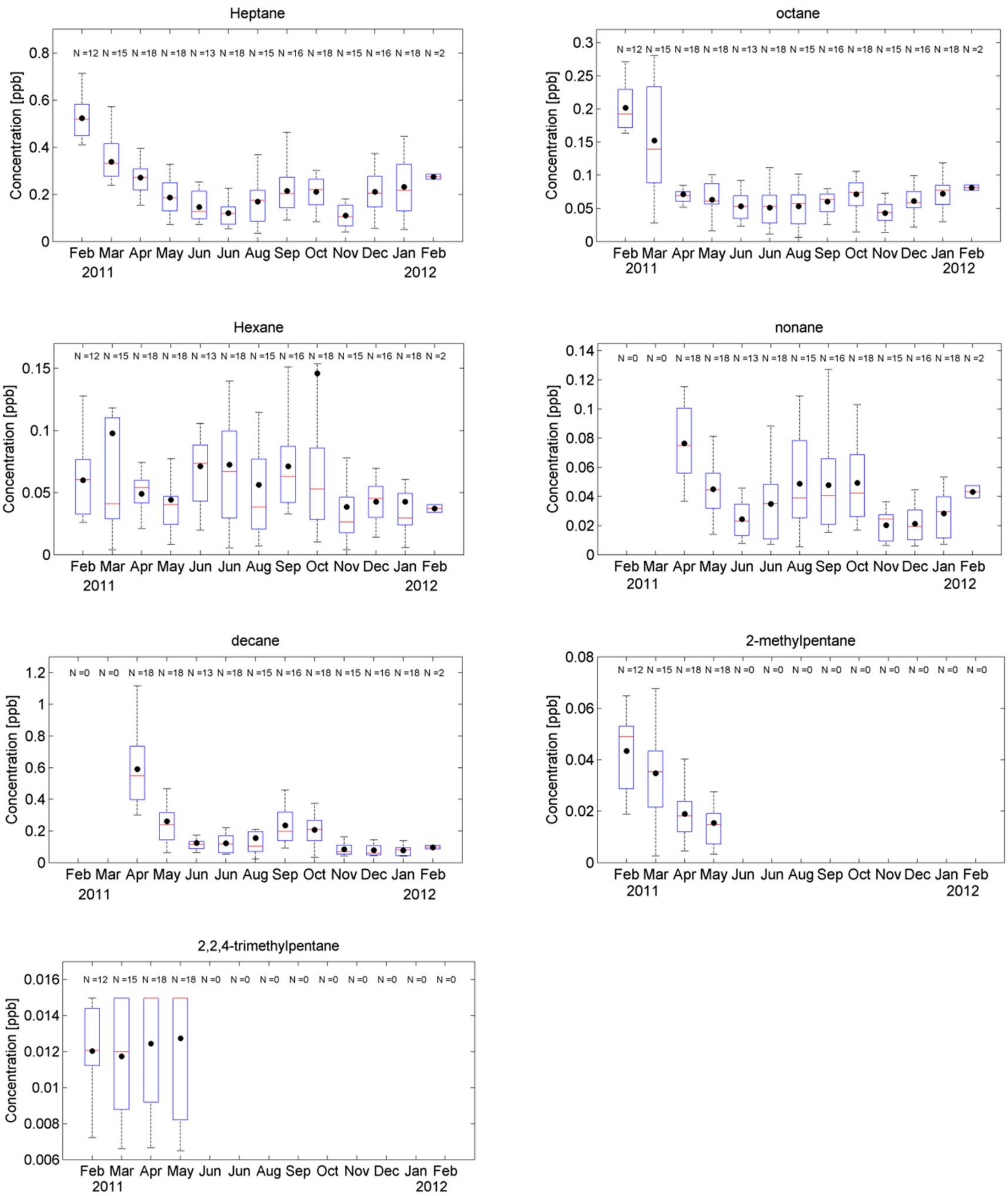


Figure 4.7: Monthly annual variation of alkanes measured during the one-year sampling period. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ±2.7σ or 99.3% coverage, if the data has a normal distribution (MATLAB, 2010). The values displayed on top of each box and whisker plot for each month indicate the number of samples (N) analysed for each month

The monthly median alkane concentrations ranged between 0.012 and 0.52 ppb. Heptane was the most abundant species, with an annual median concentration of

0.22 ppb. This was not unexpected, since heptane is synthesised by some of the large petrochemical industries occurring in the anthropogenic source regions defined (Sithole, 2012). Heptane can also be converted to toluene, which could contribute to it being the most abundant aromatic hydrocarbon measured (**Section 4.2.2**). The second most dominant alkane was decane, with an annual median concentration of 0.19 ppb.

4.3.2 Spatial distribution of alkane according to air mass origin

Since no distinct seasonal cycles could be identified for the measured alkane species (**Section 4.3.1**), the possible influence of air mass origin on the concentration of these species was explored. The alkane concentrations for the air masses sampled, after passing over the various source regions (**Section 3.2** and **Figure 3.5**), are summarised in **Table 4.6** and **Figure 4.8**. Heptane, hexane and octane concentrations were higher in plumes arriving from Area I, while the concentrations of each of the other alkanes measured were in the same order in air masses arriving from all three source areas. Concentrations measured for air masses arriving from Area II and the Regional Background of all the alkane species were comparable.

Table 4.6: The alkane concentrations in air masses that had passing over the defined source regions

	Area I			**Area II**			**Regional Background**		
	Median	Mean	$5^{th}/25^{th}/75^{th}/95^{th}$ percentile	Median	Mean	$5^{th}/25^{th}/75^{th}/95^{th}$ percentile	Median	Mean	$5^{th}/25^{th}/75^{th}/95^{th}$ percentile
2,2,4-TMP	0.0116	0.0113	0.0072/0.0092/0.0132/0.0150	0.0150	0.0130	0.0074/0.0092/0.0150/0.0150	0.0150	0.0123	0.0065/0.0078/0.0150/0.0150
heptane	0.2772	0.3228	0.072/0.1752/0.4842/0.6128	0.2198	0.2185	0.0558/0.1214/0.3017/0.3871	0.1843	0.1920	0.0637/0.1214/0.2483/0.3945
hexane	0.0741	0.0703	0.0193/0.0364/0.099/0.1369	0.0410	0.0445	0.0101/0.0259/0.0566/0.1048	0.0418	0.0711	0.0098/0.0258/0.0673/0.1287
2-MP	0.0453	0.0412	0.0124/0.0235/0.0559/0.0666	0.0188	0.0208	0.0041/0.012/0.0255/0.0456	0.0178	0.0196	0.0032/0.0097/0.027/0.0418
octane	0.0983	0.1303	0.0438/0.0661/0.1908/0.2746	0.0620	0.0678	0.0144/0.044/0.0866/0.1782	0.0648	0.0677	0.0196/0.0529/0.082/0.1135
nonane	0.0396	0.0418	0.0108/0.0301/0.043/0.1063	0.0326	0.0393	0.0069/0.0194/0.0524/0.0973	0.0398	0.0449	0.0079/0.0249/0.0537/0.1023
decane	0.1241	0.2218	0.0615/0.0871/0.1931/1.0112	0.1342	0.1913	0.0423/0.0629/0.2504/0.5888	0.1616	0.2113	0.0524/0.0856/0.2750/0.6071

Note: TMP= trimethylpentane and MP= methylpentane

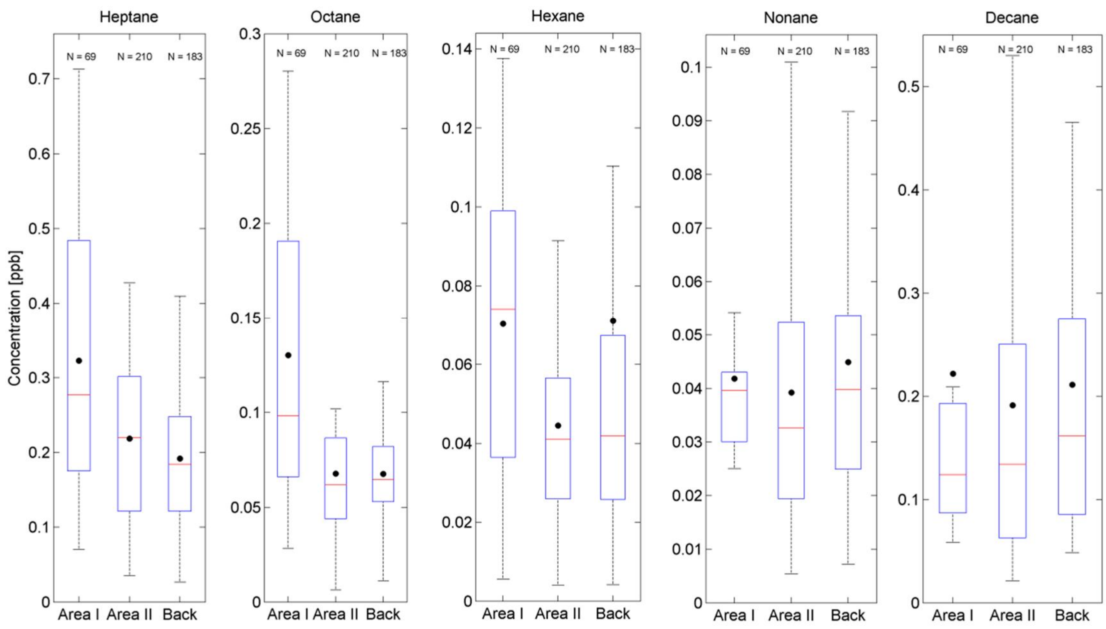


Figure 4.8: The concentrations for some of the alkane compounds in air masses that had passed over the defined source regions. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers $\pm 2.7\sigma$ or 99.3 % coverage, if the data has a normal distribution (MATLAB, 2010). The values displayed on top of each box and whisker plot for each source region indicate the number of samples (N) analysed

4.4 Biogenic VOCs

4.4.1 Meteorological parameters

Biogenic VOCs (BVOCs) are species such as isoprene, 2-methyl-3-buten-2-ol (MBO) and terpenes (monoterpenes and sequiterpenes). BVOCs have much shorter lifetimes in the atmosphere than VOCs emitted from anthropogenic activities do. The lifetimes of these species range from minutes to hours (Atkinson & Arey, 2003). Therefore, air mass movements calculated by back trajectories cannot be used to link measured BVOC concentrations to sources. Sources of BVOCs will be relatively close to the measurement site; hence, meteorological data will be more useful to determine possible sources of BVOCs. Monthly meteorological data, i.e. temperature, relative humidity, wind speed, wind direction and Photosynthetically Active Radiation (PAR) measured at Welgegund during the sampling periods, as well as rain frequency measured for the entire period, are presented in **Figure 4.9**.

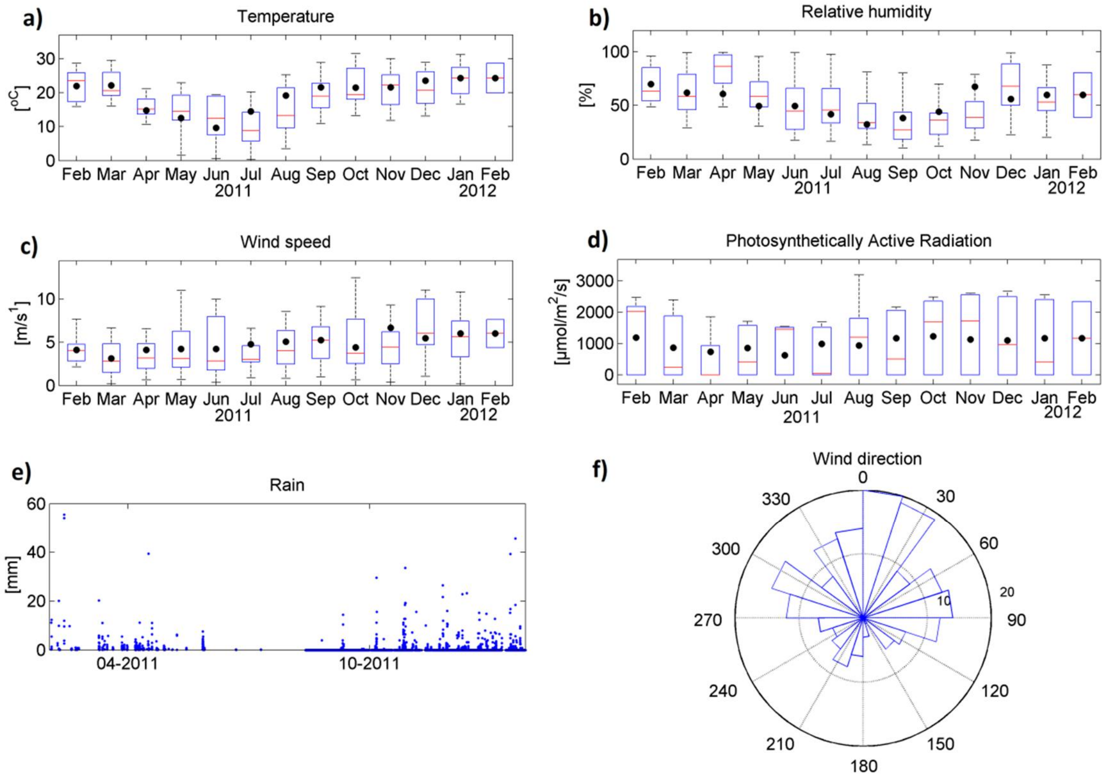


Figure 4.9: Monthly variation of **(a)** temperature **(b)** relative humidity **(c)** wind speed **(d)** Photosynthetically Active Radiation (PAR) (**e**) rain and (**f**) wind direction. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ±2.7σ or 99.3 % coverage, if the data has a normal distribution (MATLAB, 2010)

As can be seen from the presented meteorological data (**Figure 4.9**), distinct seasonal cycles can be identified. The monthly median temperature varied by approximately 15°C during the sampling periods. Due to the times when the samples were collected, i.e. during the day (11:00 to 13:00) and during the night (23:00 to 1:00) on Tuesdays and Saturdays (**Section 3.3.1**), temperatures were never below 0°C. The monthly median temperatures for the times when samples were collected varied between 8.7 and 13°C in winter and between 21 and 24°C in summer. Summertime temperatures occasionally reached values in excess of 30°C, while the coldest temperature reached in winter was 2°C. The relative humidity (RH) was low in the colder months and relatively high in warmer months. The RH ranged between

30 and 80% during the sampling period. The monthly median wind speeds were the highest during the summer months when unstable meteorological conditions are prevalent in the interior of SA (Tyson *et al.*, 1996). Welgegund is in a region of SA characterised by dry winter months and wet summer months, which was also observed in the precipitation data presented in **Figure 4.9(e)**. A seasonal pattern is also observed for the monthly median photosynthetically active radiation (PAR), which is indicative of the presence of sunlight. The mean wind rose compiled for times when samples were taken indicates that the dominant wind direction is in the sector between the north-east and north-west. This correlates with the back trajectory analysis, which showed that more than 39% of air masses also came from that direction (**Sections 4.2.3** and **Figure 4.2**).

Figure 4.10 presents micrometeorological CO_2 flux measurements at Welgegund. Unfortunately, at the time when this thesis was written, only CO_2 flux data for the period of February 2011 to August 2011 was available. However, even this limited period of data provides insight into the seasonal activity patterns of vegetation at Welgegund. This data shows typical changes in the seasonal uptake of CO_2 by vegetation. Negative values (downward CO_2 flux) indicate the net uptake of CO_2 by the vegetation, with the Gross Primary Production (GPP) exceeding the total respiration. Positive values indicate the emission of CO_2 by the vegetation. A period of dormancy is observed in winter that extends from June to September. The Net Ecosystem Exchange (NEE) at full light (maximum downward flux) increases gradually until February/March as a response to the increases of the photochemical efficiency of CO_2 assimilation in the vegetation surrounding the site and the solar elevation angle. The daily maximum NEE starts to decrease in April, when the solar elevation angle declines and ground moisture drops. Winter dormancy commences in June as a result of lower temperatures (**Figure 4.9(a)**) and the fact that most of the plants lose their leaves.

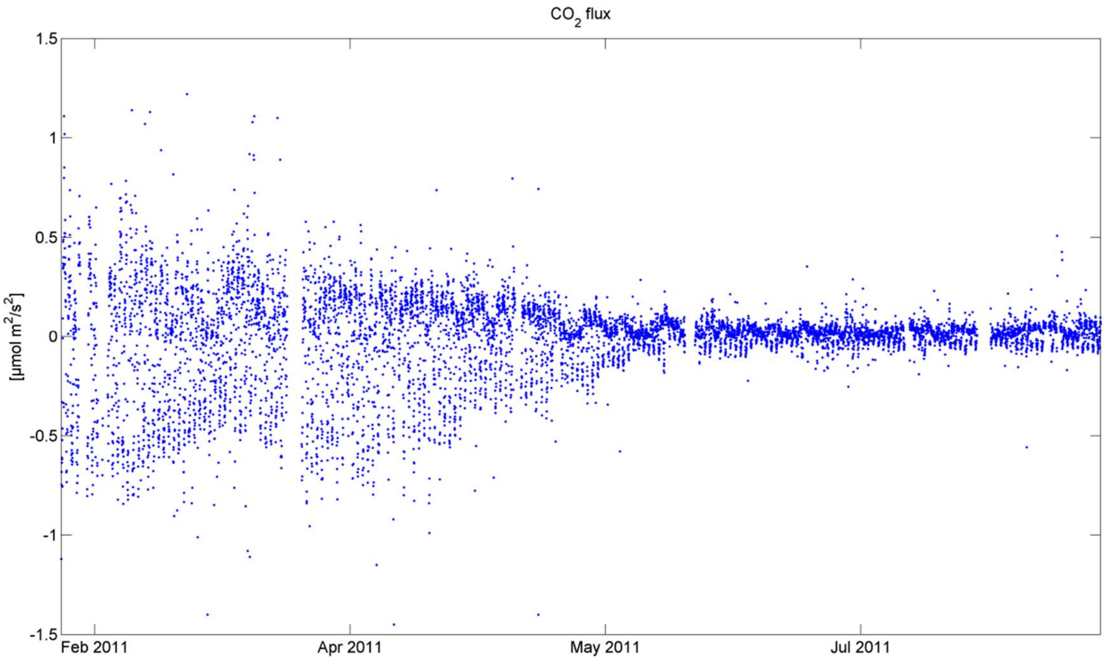


Figure 4.10: Micrometeorological CO_2 flux measurements at Welgegund (February 2011 to August 2011)

4.4.2 Temporal variations of BVOCs

The monthly annual temporal variations of the measured BVOCs are presented in **Figure 4.11**. The total concentrations of the monoterpenes (MT) and sesquiterpenes (SQT) were obtained by summing the concentrations of individual species. Considering the data presented (**Figure 4.11**), it is evident that isoprene and MBO exhibited more distinct seasonal patterns, i.e. higher values in summer and lower values in winter, than the MT and the SQT.

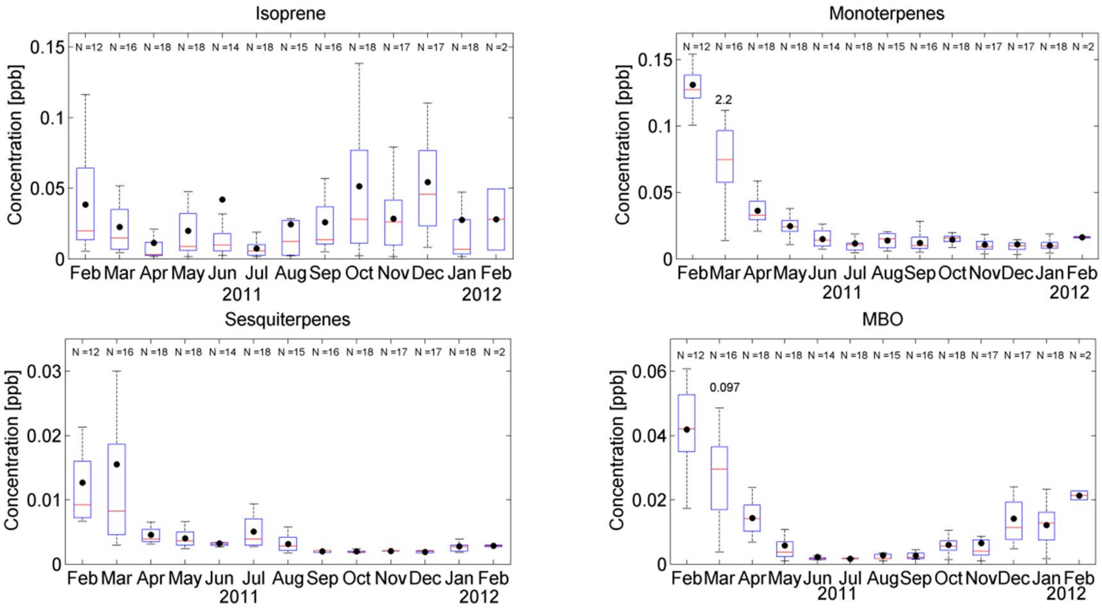


Figure 4.11: Monthly annual variation of isoprene, monoterpenes, sesquiterpenes and MBO measured during the one-year sampling period. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles and the whiskers ±2.7σ or 99.3% coverage, if the data has a normal distribution (MATLAB, 2010). The values displayed on top of each box and whisker plot for each month indicate the number samples (N) analysed for each month

Isoprene is emitted from many plant species (Hakola *et al.*, 1998; Hellén *et al.*, 2006a; Guenther, 2002) and these emissions are dependent on foliar density, temperature and PAR. Distinct differences in isoprene emissions were observed from month to month, which generally agreed with temperature and PAR trends (**Figure 4.9 (a)** and **(d)**). The monthly median isoprene concentrations varied between a maximum of 0.046 ppb in summer (December) and a winter (July) minimum of 0.006 ppb (**Figure 4.11**). During the winter months (June to August), the isoprene concentrations showed a clear minimum, which was also predicted by a model presented by Otter *et al.* (2003) and measurement by Otter *et al.* (2002) at Nylsvley. On occasion, isoprene concentrations were even below the detection limit during the winter months. Lower isoprene values in winter can be expected, since foliar density declines rapidly in winter as deciduous trees lose their leaves. However, emissions increase in spring, due to an increase in foliar density after the first rains that usually fall in October (**Figure 4.9(e)**). Monson *et al.* (1994) showed that in spring, isoprene emissions are delayed for up to a month after leaf emergence; however, these leaves could be induced to emit isoprene when exposed to warm temperatures (32ºC) (Monson *et al.*, 1994), as is usually the case in South Africa. Otter *et al.* (2002) reported that the increase of isoprene was more immediate after the first rain than the increase in MT, SQT and MBO (**Figure 4.11**). In this study, isoprene emissions peaked during the months of December to February when foliar densities were at their peak (**Figure 4.11** and **Appendix A**).

Terpene (monoterpenes, sesquiterpenes) emissions (with some exceptions) are not dependent on PAR, but are mainly influenced by foliar density and temperature, making the seasonal variation less pronounced (Otter *et al.*, 2002). MT was observed frequently throughout the study. The monthly median MT concentrations varied between a maximum (0.127 ppb) in February and a minimum (0.009 ppb) in November (**Figure 4.11**). The most abundant MT was α-pinene, with its annual median concentration equal to 0.468 ppb. The second and third highest average MT concentrations were observed for 3Δ-carene and limonene with annual medians of 0.455 ppb and 0.223 ppb, respectively. The annual median concentrations of the other MTs, i.e. camphene, β - pinene, ρ-cymene and terpinolene, ranged between 0.016 and 0.112 ppb. Similar to isoprene, most of the MTs had concentrations below the detection limit of the analytical procedure during the winter months.

SQTs are reactive species and are difficult to detect in ambient air samples. This resulted in concentrations of these species frequently being below the detection limit of the analytical procedure. The monthly median SQT concentrations varied between a maximum (0.009 ppb) in February and a minimum (0.002 ppb) in November (**Figure 4.11**). The most abundant SQT was β-caryophyllene, with its annual median concentration being equal to 0.022 ppb. The annual median concentrations of the other SQTs, i.e. longicyclene, iso-longifolene, aromadendrene, α-humulene and alloaromadendrene ranged between 0.002 and 0.004 ppb.

The other measured biogenic VOCs, which included 2-methyl-3-buten-2-ol (MBO), 1,8-cineol, 4-acetyl-1-methylcyclohexene (AMCH), nopinone, 4-allylanisole and bornylacetate, were also detected during the study. Some of these species had concentrations below the detection limit of the analytical procedure during the winter months. The most abundant of these was 1,8-cineol, with its annual median concentration being 0.034 ppb. The annual median concentrations of the other species ranged between 0.002 and 0.016 ppb.

In **Table 4.7,** the average concentrations of the BVOC species measured at Welgegund for the four different seasons, i.e. winter (June to August), summer (December to February), spring (September to November) and autumn (March to May), are presented. Isoprene concentration averages for winter, spring, summer and autumn were 0.0233, 0.0358, 0.0396 and 0.0178 ppb, respectively. The rapid rise in the early summer atmospheric isoprene concentration could be explained by the capability of trees to synthesise and emit isoprenoids, which generally develop during the early stages after leaf emergence.

MT concentration averages for winter, spring, summer and autumn were 0.013, 0.013, 0.040 and 0.710 ppb, respectively (**Table 4.7**). This autumn maximum is consistent with CO_2 fluxes (February 2011 to April 2011), which indicates the evaporation of MT pools formed during the summer (Otter *et al.*, 2002). As previously mentioned, MT might also peak in March, when foliar densities are at their peak, which was also observed by Otter *et al.* (2002).

SQT concentration averages for winter, spring, summer and autumn were 0.004, 0.002, 0.005 and 0.008 ppb, respectively (**Table 4.7**). These concentrations did not differ that much from season to season.

The other BVOCs, which included 2-methyl-3-buten-2-ol (MBO), 1,8-cineol, 4-acetyl-1-methylcyclohexene (AMCH), nopinone, bornylacetate and 4-allylanisole, had concentrations averages for winter, spring, summer and autumn that ranged between 0.0021-0.0059, 0.0023-0.0051, 0.0049-0.3194 and 0.0024-0.1014 ppb, respectively (**Table 4.7**).

As mentioned in **Section 3.2**, the dominant grass species that surround the measurement site at Welgegund are *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). These species also produce BVOCs in the beginning of the rainy season due to increased foliar density. This is, however, not the peak period for BVOC emission from vegetation. Literature indicates that emissions would increase slowly and will only peak in December or January (Scholes & Scholes, 1997).

Table 4.7: Average seasonal concentrations of BVOCs measured at Welgegund, with winter defined as June to August, summer as December to February, spring as September to November and autumn as March to May

ppb	Winter	Summer	Spring	Autumn
isoprene	0.0233	0.0396	0.0358	0.0178
MBO	0.0022	0.0205	0.0051	0.0367
α-pinene	0.0378	0.0995	0.0296	1.6347
camphene	0.0092	0.0071	0.0031	0.0438
β-pinene	0.0082	0.0275	0.0070	0.2832
carene	0.0027	0.0074	0.0034	1.7285
ρ-cymene	0.0153	0.0925	0.0165	0.3111
1,8-cineol	0.0021	0.0252	0.0035	0.1014
limonene	0.0169	0.0299	0.0243	0.7865
terpinolene	0.0030	0.0178	0.0040	0.1853
AMCH	0.0024	0.0049	0.0023	0.0200
nopinone	0.0046	0.0056	0.0103	0.0056
bornylacetate	0.0024	0.3194	0.0023	0.0024
longicyclene	0.0020	0.0062	0.0021	0.0056
iso-longifolene	0.0023	0.0033	0.0024	0.0028
β-caryophyllene	0.0129	0.0232	ND	0.0295
aromadendrene	0.0025	0.0024	0.0025	0.0025
a-humulene	0.0025	0.0024	0.0025	0.0029
farnesene	0.0024	0.0027	0.0025	0.0032
4-Allylanisole	0.0059	0.0138	ND	0.0172
monoterpenes	0.013	0.040	0.013	0.710
sesquiterpenes	0.004	0.005	0.002	0.008

ND= not detected

4.4.3 The influence of meteorology on BVOC concentrations at Welgegund

Both the BVOC concentrations and the net CO_2 uptake measured at Welgegund have a maximum in February to April 2011 and a minimum in June to August 2011 (**Figure 4.10** and **Figure 4.11**). This indicates that there is a direct link between BVOC concentrations and seasonal phenological factors (study of periodic biological phenomena). It is especially seasonal variations of temperature; PAR, rainfall (soil moisture) and CO_2 flux (**Figure 4.9** and **Figure 4.10**) that could be related to BVOC concentrations. Although soil moisture and CO_2 flux were measured at Welgegund, these datasets were not available for the entire measurement period and additional data quality issues have to be addressed before this data can be used with certainty. It was therefore decided to only explore the impact of temperature and radiation on BVOC concentrations in the subsequent sections.

4.4.3.1 The impact of temperature

The influence of temperature on biogenic emissions has been studied in several investigations (Guenther *et al.*, 1991; Sharkey & Loreto, 1993; Geron *et al.*, 2001). All these studies indicated that emissions of isoprene and MT increased with increases in temperatures up until 35 to 45^{o}C, followed by a rapid decline in emission rates as temperature was increased further. However, there is also contrasting evidence that shows that isoprene emissions do not decline at these high temperatures (Harrison *et al.*, 2001). In contrast, several investigations (Kuzma & Fall, 1993; Monson *et al*. 1992, 1994, 1995; Loreto & Sharkey, 1993) have shown that some isoprene-emitting species, maintained at cool temperatures, even fail to emit any isoprene until exposed to high temperatures. It can be expected that the emission rates will be strongly dependent on the plant species present, the area where the plants are grown and the peak activity of BVOC synthesis.

In **Figure 4.12**, the correlation between the concentrations of different BVOC species measured at Welgegund and temperature is provided. Although the correlation coefficients (r-values) calculated was low, there seems to be a general trend that higher atmospheric concentrations were measured for all the BVOCs at higher temperatures. The poor correlations are likely due to the fact that BVOC emissions are not only related to temperature, but also to other important factors, such as soil moisture and radiation. In order to determine the contribution of all such contributing factors, multi-linear regression analyses of all such factors have to be considered to determine the relative importance of each factor. However, since data on all these factors were not available, such an analysis is beyond the scope of this thesis.

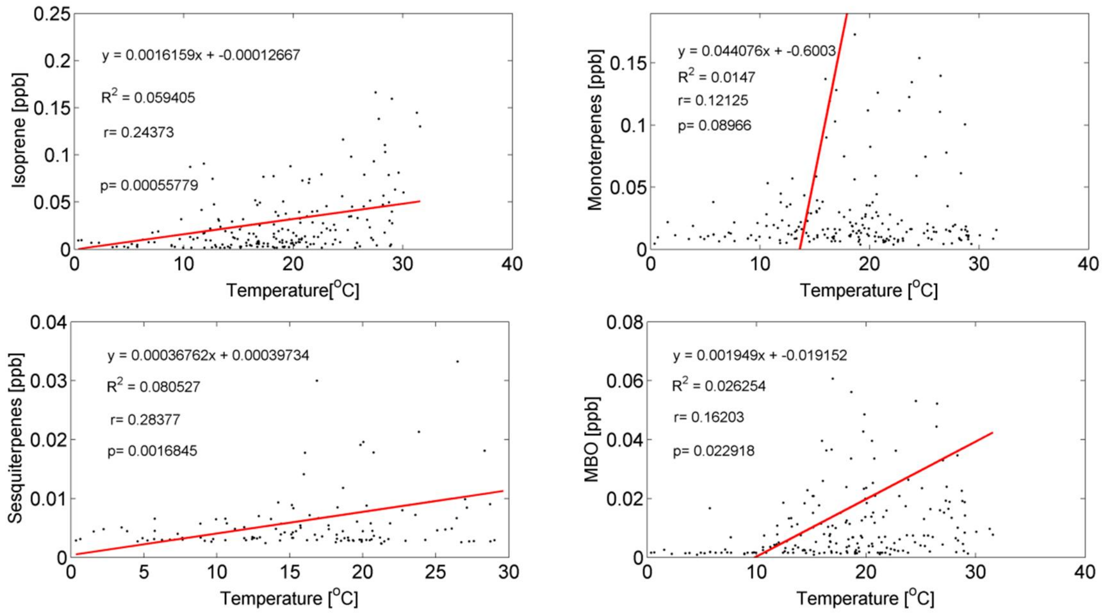


Figure 4.12: Correlations between BVOC concentrations and atmospheric temperature

4.4.3.2 The influence of radiation

In **Figure 4.13**, the monthly day and night average concentrations of the different BVOC species are presented. Isoprene showed the strongest dependence on radiation. It has previously been shown that isoprene emissions will almost immediately stop after sunset (Tingey *et al.*, 1981; Evans *et al.*, 1985; Guenther *et al.*, 1991; Sanadze, 1991). In this study, the differences in day and night-time isoprene concentrations were especially evident in the spring and summer months, when isoprene was most likely to be emitted.

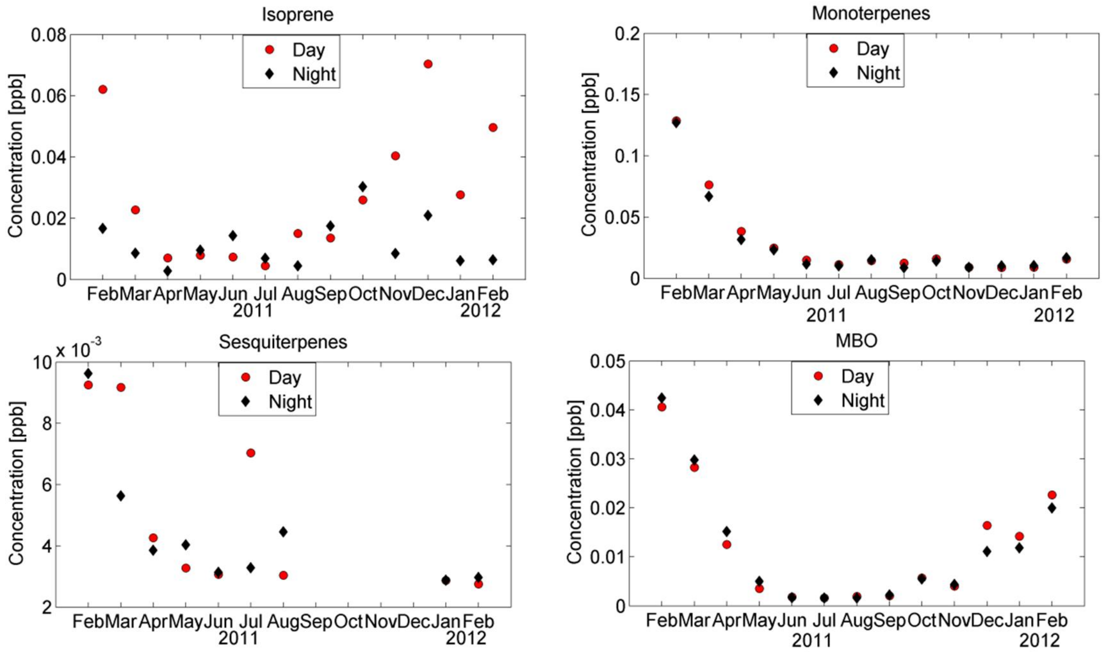


Figure 4.13: Difference between day and night concentrations of biogenic VOCs

MT concentrations showed no real difference between day- and night time. MT emissions are usually regarded as being independent of light and are mostly influenced by temperature (Monson *et al.*, 1995; Lerdau *et al.*, 1997; Guenther *et al.*, 1993). There are, however, several plant species that have been identified as light-dependent emitters of MT (Kesselmeier *et al*., 1996; Simon *et al*., 1994; Staudt & Seufert, 1995). In southern Africa, researchers such as Greenberg *et al.* (2003), Guenther *et al*. (1996) and Otter *et al.* (2002) reported that plant species such as *Colophospermum mopane, Acacia tortilis, A. mellifera* and *A. erioloba* that emit MT are highly dependent on sunlight. During the SAFARI-2000 measurement campaign, Otter *et al*. (2003) compiled a map from modelling studies, indicating the distribution of areas in southern Africa that are dependent on light for MT emissions (**Figure 4.14**). From this map, it is evident that Welgegund (indicated by the red star) is located in a region where MT emissions are not dependent on sunlight. This can partially explain the low correlation between MT and sunlight.

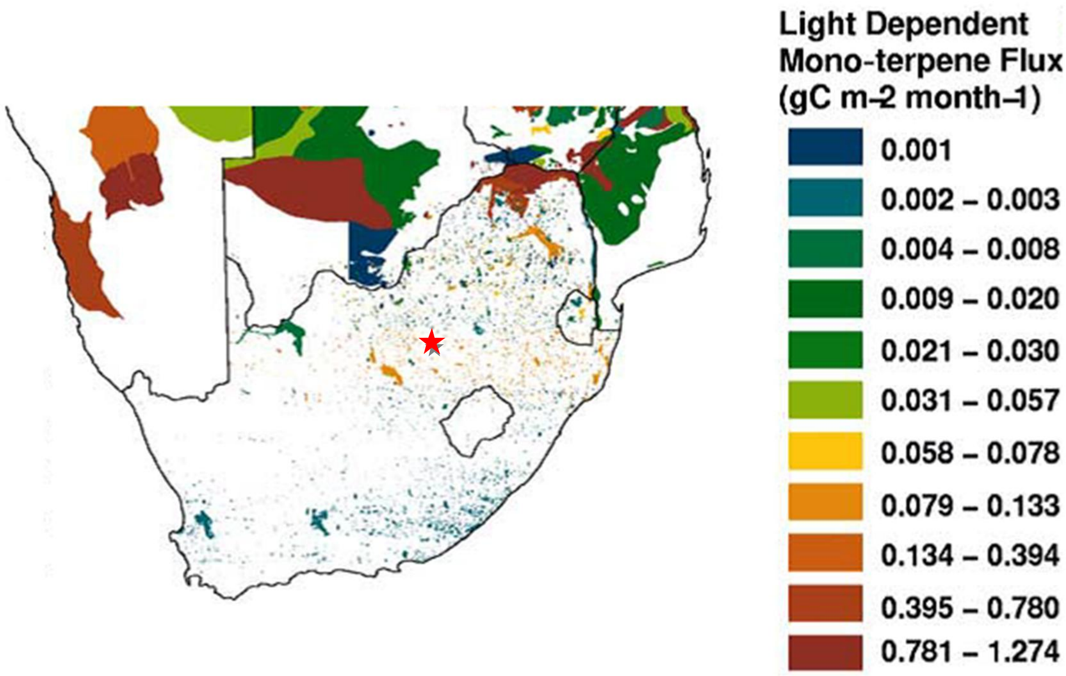


Figure 4.14: A map indicating the distribution of light-dependent MT emissions across southern Africa (compiled by Otter *et al.*, 2003); the red star indicates the approximate location of the Welgegund measurement site

Studies that have examined the light dependency of SQT emissions found that certain SQT emissions are solely controlled by temperature, while others are also influenced by radiation (Duhl *et al*., 2008). In this study, no distinct difference between day- and night-time SQT concentrations was observed. This implies that species emitting SQT at Welgegund are mostly independent of radiation. In a similar manner, no distinct difference between day- and night-time MBO and 1,8-cineol concentrations was observed.

4.4.4 Spatial distribution of BVOCs

The location of the Welgegund measurement station, within the context of vegetation type and bioregion, is presented in **Figure 4.15**. This figure indicates that the measurement site is situated within the transition between four types of vegetation, i.e. the Vaal-Vet sandy grassland vegetation type, the dry Highveld grassland bioregion, the savannah biome and the grassland biome. The immediate area surrounding the site is grazed by cattle and sheep, with crop fields (mostly maize and to a lesser extent sunflowers) covering the areas that are not grazed (Beukes *et al.*, 2012)

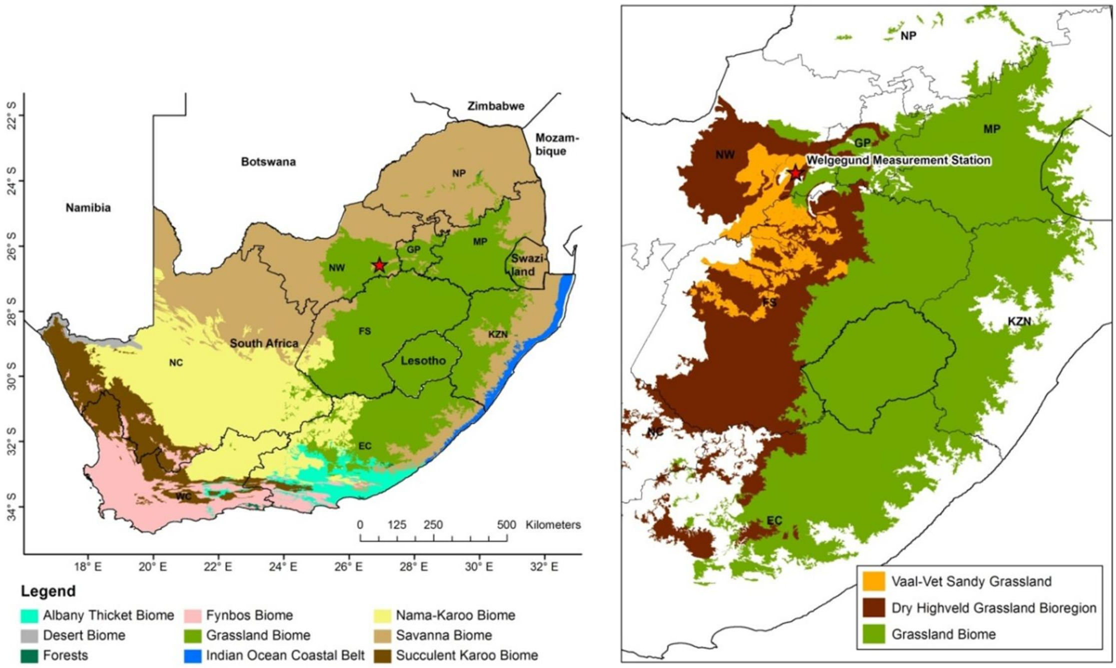


Figure 4.15: South African map indicating the location of the Welgegund measurement station within the context of vegetation type and bioregion (Beukes *et al.*, 2012)

In an effort to determine the transport of BVOCs from the vegetation surrounding the site, pollution roses for the isoprene, MT, SQT and MBO were compiled. These pollution roses are presented in **Figure 4.16** for the average (red) and median (blue) concentrations indicated.

The average isoprene pollution rose shows a dominance of sources from the north-west to the north-east, as well as the south-east. These directions correlated to areas where pockets of the savannah biome are located (**Figure 4.15**). Otter *et al.* (2002) also measured higher isoprene at Nylsvley, which is situated in a *Burkea africana* and *Acacia tortilis* savannah landscape. As mentioned in **Section 3.2**, the site is situated on the property of a commercial farm. Many researchers consider crops and grass to have low isoprene-emitting capacities or to emit no isoprene at all (Kesselmeier & Staudt, 1999; Wang *et al.*, 2003; Guenther *et al.*, 2006; Wang *et al.*, 2007; Karl *et al.*, 2009; Zheng *et al.*, 2010). It is therefore unlikely that isoprene originated from such species. Less well-defined deductions with regard to the possible origin of emissions can be made for the other species from the presented pollution roses (**Figure 4.16**).

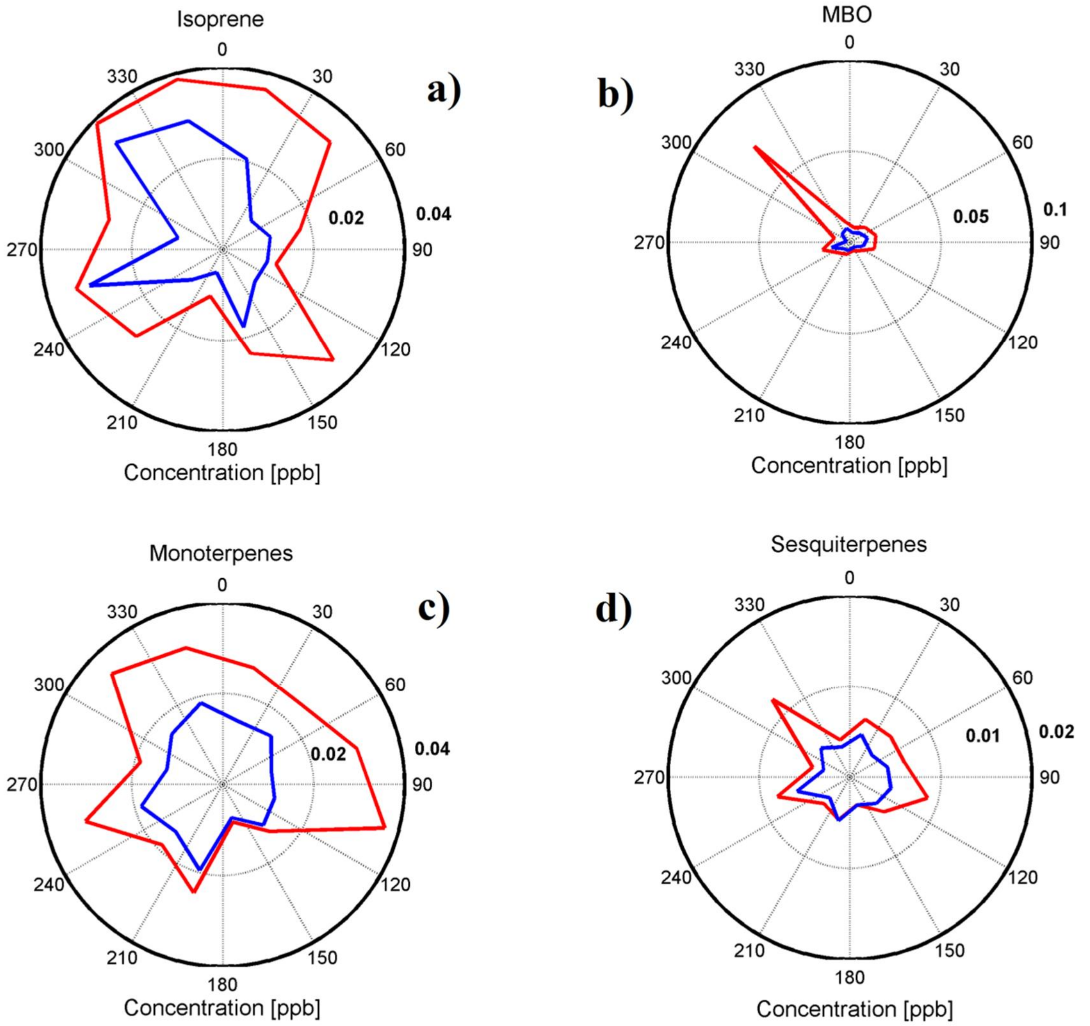


Figure 4.16: Pollution roses for BVOCs measures at Welgegund for the mean (red) and median (blue) concentrations; (**a**) isoprene, (**b**) MBO, (**c**) SQT and (**d**) MT

4.5 Conclusion

From the results presented in this chapter, it can be concluded that the monthly seasonal cycles presented for the aromatic hydrocarbon species and the alkanes are not directly related to seasonal patterns, but rather depend on the origin of the air masses sampled. However, considering the BVOC data, it is evident that isoprene and MBO exhibited more distinct seasonal patterns, i.e. higher values in summer and lower values in winter, than the MT and the SQT.

Chapter 5 will conclude this dissertation and present recommendations for future research.