# Chapter 3

# Comparison of air pollutants levels over the Highveld air pollution hotspots

> Airborne monitored levels of $O_3$, $NO_X$, $SO_2$ and $PM_{2.5}$ aerosols will be compared over the Highveld air pollution hotspots; i.e. Secunda, Witbank, Rustenburg and the Vaal Triangle in three seasons studied. The seasonal change in atmospheric loading of these air pollutants over the Highveld air pollution hotspots will be evaluated. Factors that influence the atmospheric loading of these air pollutants, like the prevailing meteorological conditions, and the temporal cycle of the photochemical processes will be considered.

**Autumn campaign**

*Autumn campaign meteorological overview*

The surface synoptic conditions over the country during the autumn campaign case study days were dominated by the presence of a surface trough (Figure 3.1). The trough was either situated over the central interior, extending to the southern interior, or centred over the southern or western interior. It brought about partly cloudy to cloudy conditions with showers and thundershowers. Rustenburg weather station on 16/03/2005 measured 0.2 mm of rain between 09h00 and 10h00 (SAST). Witbank weather station recorded daily rainfall of 1.4 mm on 16/03/2005 and 1 mm of rain on 17/03/2005 between 15h00 and 17h00 (SAST). Vereeniging weather station observed 26.2 mm of rain on 16/03/2005 between 0h00 and 10h00 (SAST). The temperatures were generally warm during the autumn campaign (Table 3.1). The winds were generally light winds on the days considered for case studies (Figure 3.3).

Figure 3.2 shows the Irene weather observation station temperature profiles which were used to characterise the vertical structure of the lower part of the troposphere. In all the three case studies the lower troposphere was characterised by a low level nocturnal inversion layer in the morning (Figure 3.2(a)), resulting in a shallow mixing layer. In the afternoon the nocturnal inversion was eroded causing a deeper mixing layer (Annegarn *et al*., 1996b). The lower troposphere was unstable in the afternoon during the three days, except on 18/03/2005 where there was an inversion at 2775 magl (Figure 3.2(b)).

The top of the morning surface inversion layer on 16/03/2005 (Figure 3.2(a)) was at 184 magl (above ground level) and at 14°C. Hourly averaged temperatures at Irene in Table 3.1 show that it was eroded at about 06:00 (SAST). The surface winds at Rustenburg on 16/03/2005 by 09:00 (SAST) where above the critical threshold value of 2 $ms^{-1}$ (Figure 3.3) for nocturnal surface inversion erosion (Hunt *et al*., 2006). Given the hourly averaged temperature was 16.1 ˚C at 09:00 (SAST), Rustenburg was likely monitored after the surface erosion was mixed out. On 17/03/2005 the surface inversion layer top on Figure 3.2(a) was at 276 magl and at 16.4°C. The Irene hourly averaged temperatures in Table 3.1 show that it was eroded between 07:00 and 08:00 (SAST). On 17/03/2005 at Witbank by 09:00 (SAST) the wind was already above the critical threshold value (Figure 3.3) for surface inversion erosion and the hourly averaged temperature was 17.2 ˚C at that time (Table 3.1). The monitoring of Witbank was likely done after the surface inversion was mixed out. On 18/03/2005 the surface inversion layer on Figure 3.2(a) was shallow with a top at 92 magl and at 18.4 °C. Irene hourly averaged temperatures in Table 3.1 show that it mixed out between 08:00 and 09:00 (SAST). The wind speeds at Ermelo and Witbank at 09:00 (SAST) on the 18/03/2005 were above the critical threshold value (Figure 3.3) for surface inversion erosion and the hourly averaged temperature were about 16.0 ˚C at that time (Table 3.1). It can be cautiously deduced that this was the case at Secunda which is close to both sites. Secunda was likely monitored after the surface inversion was mixed out.

Table 3.1: Hourly averaged surface temperature at Irene and study sites weather stations: from the morning up to the afternoon during the autumn campaign.

| Site | Date | Time(SAST) | 06:00 | 07:00 | 08:00 | 09:00 | 10:00 | 11:00 | 12:00 | 13:00 |
|---|---|---|---|---|---|---|---|---|---|---|
| Irene | 16/03/2005 | Average Temperature (°C) | 14.2 | 14.7 | 15.8 | 16.6 | 16.1 | 17.5 | 22.2 | 23.0 |
| Rustenburg | 16/03/2005 | Average Temperature (°C) | 16.1 | 16.5 | 16.7 | 16.1 | 18.1 | 20.4 | 21.2 | 22.9 |
| Irene | 17/03/2005 | Average Temperature (°C) | 13.3 | 13.8 | 16.7 | 19.2 | 21.1 | 22.0 | 23.4 | 23.6 |
| Witbank | 17/03/2005 | Average Temperature (°C) | 12.9 | 14.2 | 15.8 | 17.2 | 17.9 | 19.8 | 21.1 | 21.7 |
| Irene | 18/03/2005 | Average Temperature (°C) | 12.7 | 13.6 | 15.4 | 19.0 | 20.3 | 21.6 | 23.5 | 24.7 |
| Ermelo | 18/03/2005 | Average Temperature (°C) | 12.9 | 13.4 | 15.0 | 15.9 | 17.7 | 18.6 | 19.3 | 19.8 |
| Witbank | 18/03/2005 | Average Temperature (°C) | 12.8 | 14.0 | 14.0 | 15.8 | 18.0 | 18.9 | 20.9 | 21.7 |

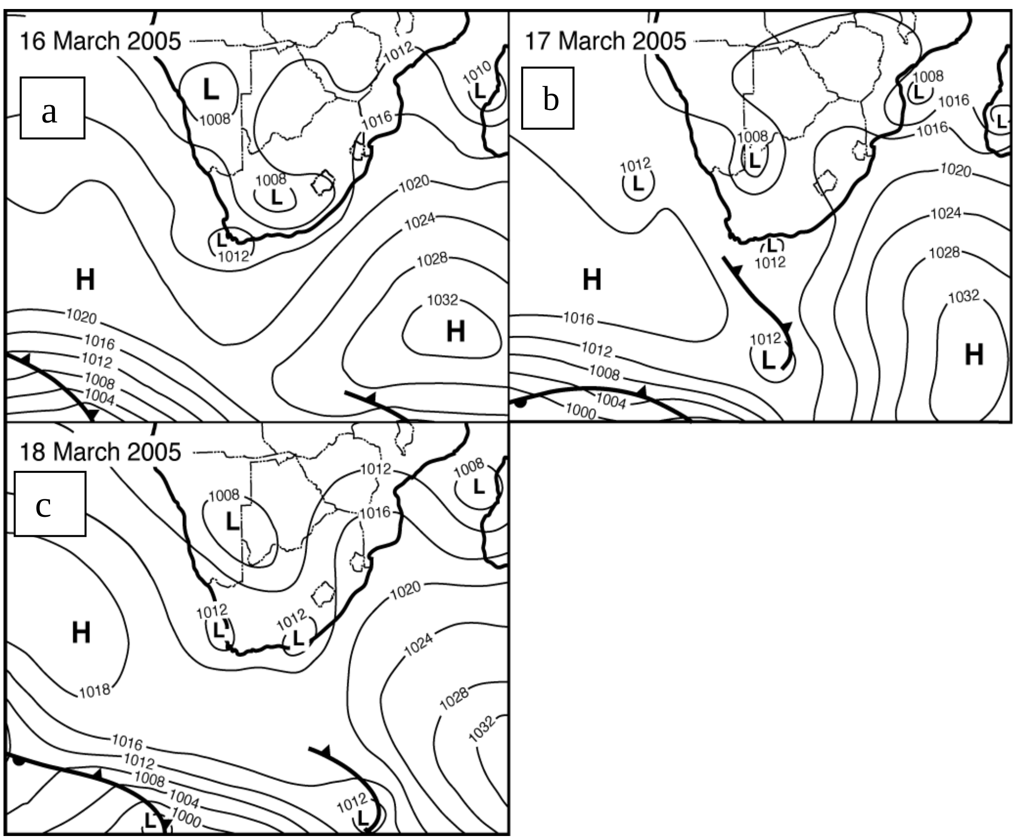


Figure 3.1: Autumn campaign 14h00 (SAST) surface synoptic charts 3.1(a), 3.1(b) and 3.1(c); 16/03/2005, 17/03/2005 and 18/03/2005 respectively.

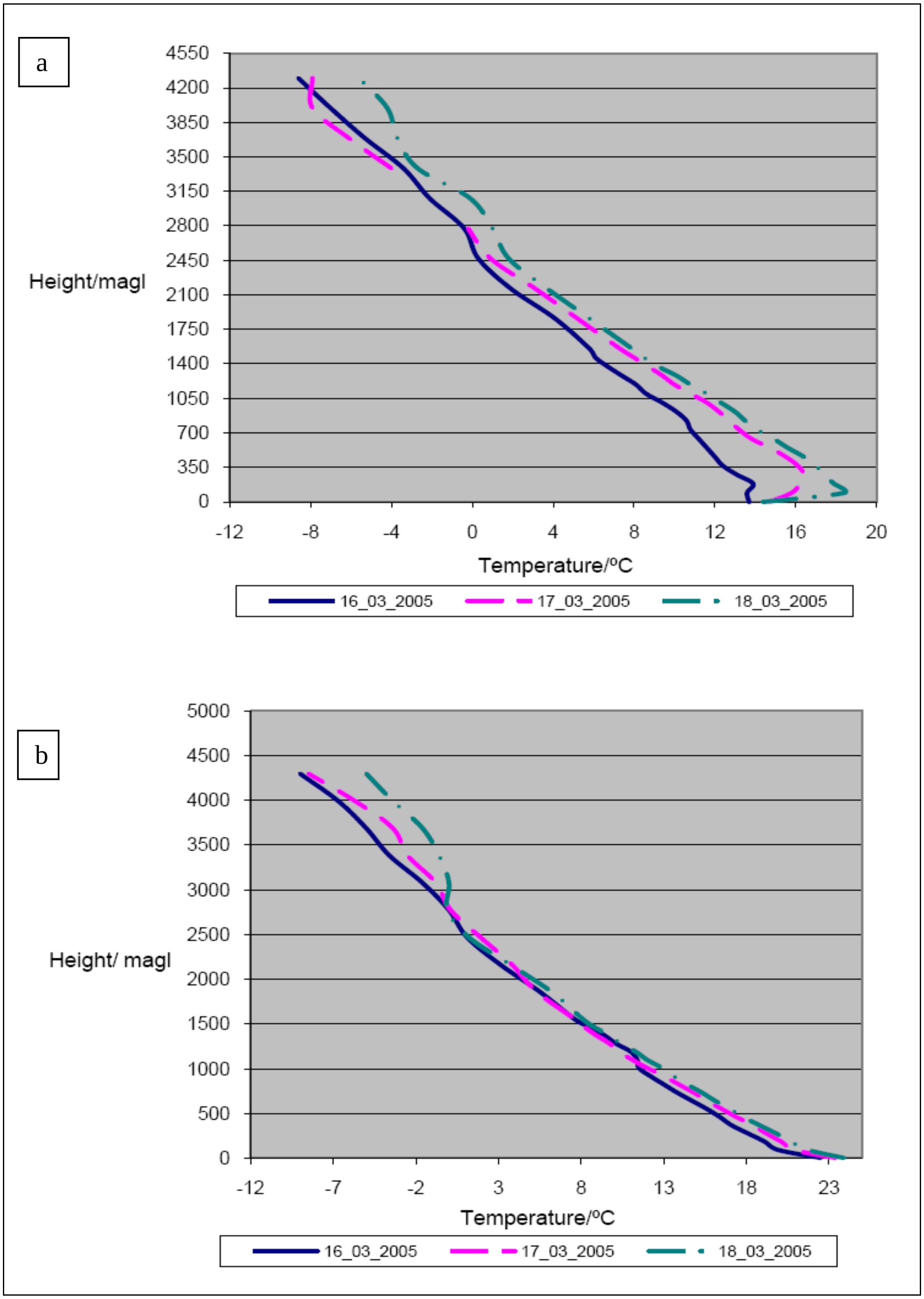


Figure 3.2: Temperature vertical profiles measurements over Irene weather observation station during the autumn campaign. Figure 3.2(a) is a midnight profile and Figure 3.2(b) is an afternoon profile.

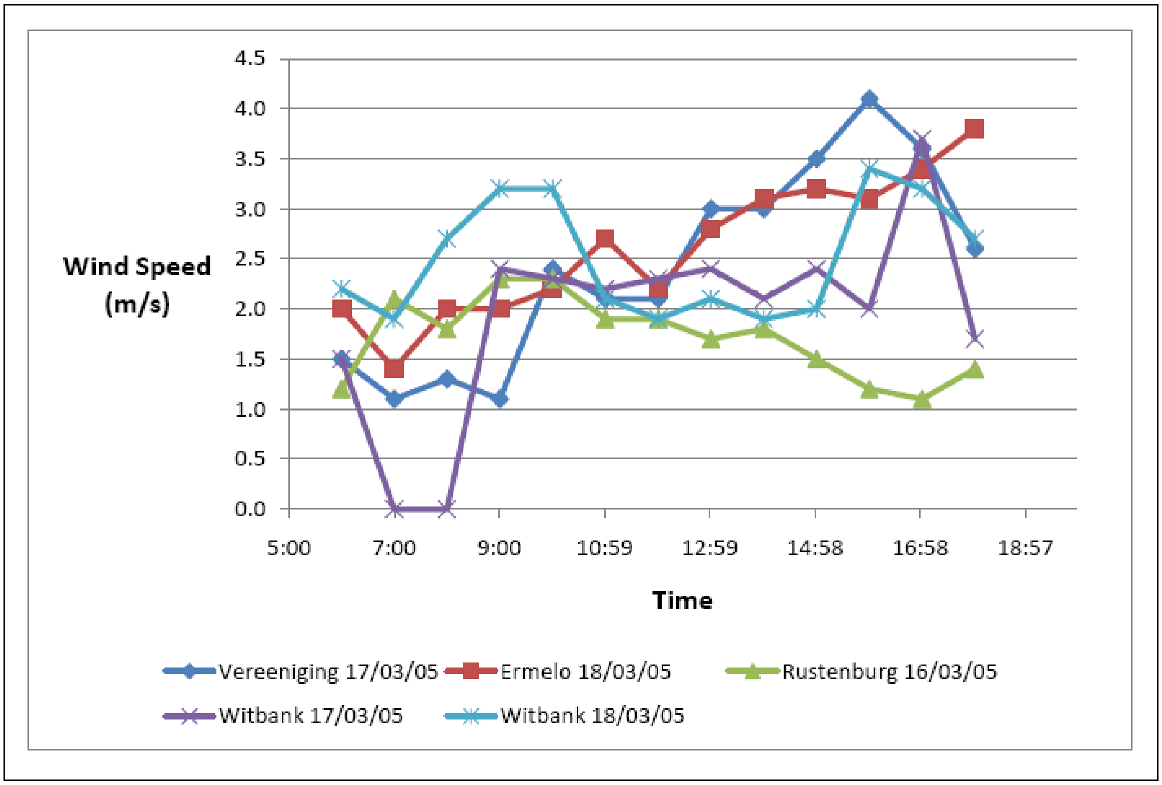


Figure 3.3: Wind speed measurements at the study sites during the autumn campaign.

*Comparison of air pollutants levels over the Highveld air pollution hotspots during the autumn campaign*

The Tables 3.2, to 3.6 show statistical analysis of the concentration distribution of $O_3$, NO, $NO_2$, $SO_2$ and $PM_{2.5}$ aerosols respectively over the four Highveld air pollution hotspots. The data were collected approximately at 167 magl during the autumn campaign. Data from apparent industrial plume penetration were eliminated for this analysis. The Rustenburg site was monitored on 16/03/2005 from 10:22:55 to 11:09:22 (SAST). Witbank and the Vaal Triangle area were monitored on 17/03/2005, Witbank from 09:42:35 to 10:21:20 (SAST) and Vaal Triangle area from 15:17:00 to 15:47:38 (SAST). Secunda was monitored on 18/03/2005 from 10:35:00 to 11:17:00 (SAST). Similar synoptic conditions allowed the comparison of the four air pollution hotspots.

*Ozone*

Table 3.2 shows $O_3$ concentration distribution data over Rustenburg, Witbank and Secunda monitored in the morning, and the Vaal Triangle monitored in the afternoon. When comparing the sites monitored in the morning, Secunda was found to have the highest $O_3$ average concentration of 30.00 ppb followed by Rustenburg with an average concentration of 28.46 ppb, then Witbank with an average concentration of 24.41 ppb. Secunda had the most variable $O_3$ concentration spatial distribution, followed by Witbank then Rustenburg, with relative standard deviations of 20.37%, 10.36% and 7.57% respectively.

The $O_3$ concentration distribution at Rustenburg was shifted toward higher $O_3$ concentration values in comparison to Secunda and Witbank. It had higher minimum and first quartile $O_3$ concentration values in comparison to Secunda and Witbank. This is due to a generally low NO concentration distribution over Rustenburg as compared to Secunda and Witbank (Table 3.3). NO destroys $O_3$ through NO and $O_3$ titration reaction (Kleinman, 1994; Kley *et al.,* 1994; Poulida *et al.,* 1994; Hobbs *et al.,* 2003; Taubman *et al.,* 2004).

The inclusion of the afternoon Vaal Triangle $O_3$ data in Table 3.2 was to show the influence of photochemistry and diurnal evolution of the mixing layer on the diurnal variation of $O_3$ concentration. The Vaal Triangle $O_3$ average concentration of 42.51 ppb and the $O_3$ concentration distribution in general is higher than all the three study areas monitored in the morning. The spatial distribution of $O_3$ concentration was relatively more uniform over the Vaal Triangle with a relative standard deviation of 5.44%. This is because of the turbulent mixing in the mixing layer which is at its peak in the afternoon (Annegarn *et al*., 1996a; Betts *et al*., 2002). The relatively stronger winds observed at Vereeniging during the monitoring period (Figure 3.3) supports the turbulent mixing (Hunt *et al*., 2007). The high $O_3$ concentration over the Vaal Triangle area is due to accumulation of $O_3$ from $O_3$ photochemical production, which reaches its peak in the afternoon (Trainer *et al*., 1987; Poulida *et al*., 1994; Annegarn *et al*., 1996b; Betts *et al*., 2002; Taubman *et al*., 2004).

Table 3.2: Autumn campaign Highveld hotspots comparison: $O_3$ concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Rustenburg | 24.45 | 26.74 | 28.25 | 30.04 | 33.24 | 28.46 | 7.57 | 2788 |
| Witbank | 16.43 | 22.91 | 24.68 | 26.14 | 28.70 | 24.41 | 10.36 | 2326 |
| Vaal Triangle | 37.87 | 40.48 | 42.31 | 43.91 | 47.93 | 42.51 | 5.44 | 1839 |
| Secunda | 16.37 | 24.39 | 31.90 | 34.24 | 47.00 | 30.00 | 20.37 | 2521 |

*Nitrogen monoxide*

Table 3.3 shows NO concentration distribution data over the study sites. For NO levels monitored during the morning flights, Secunda was found to have the highest average concentration of 1.20 ppb followed by Witbank with an average concentration of 0.65 ppb, then Rustenburg with an average concentration of 0.26 ppb. Rustenburg was found to have the most variable NO concentration spatial distribution with the relative standard deviation of 100.86%, followed by Witbank with the relative standard deviation of 90.72%, and then Secunda with a relative standard deviation of 88.45%. The high spatial variability of NO over these sites is due to its short atmospheric life-time (one day) and the uneven distribution of its sources (IPCC, 2001; QEPA, 2006; Seinfeld and Pandis, 2006; USEPA, 2006c; WMO, 2006a).

The afternoon NO concentration distribution data over the Vaal Triangle is included in Table 3.3, to show the influence of diurnal variation of the mixing layer height and photochemistry on the diurnal variation of NO concentration. Over the Vaal Triangle no NO was detected in the parts per billion (ppb) measurement scale in the afternoon. NO concentration is normally at its minimum in the afternoon. This is because of its dilution by turbulent mixing in the mixing layer of a larger volume in the afternoon (Annegarn *et al*., 1996a; Turner, 1996), and maximum photochemical oxidation to produce $NO_2$ during this time of the day (Kley *et al*., 1994; Poulida *et al*., 1994; Hobbs *et al*., 2003, Taubman *et al*., 2004). The relatively stronger winds monitored at Vereeniging during the flight monitoring period (Figure 3.3) may have enhanced NO concentration dilution through turbulent mixing (Hunt *et al*., 2007). Leading to the impact of continuous industrial emissions not detectable in ambient air.

Table 3.3: Autumn campaign Highveld hotspots comparison: NO concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Rustenburg | 0 | 0.051 | 0.21 | 0.40 | 1.15 | 0.26 | 100.86 | 2788 |
| Witbank | 0 | 0.055 | 0.59 | 0.94 | 2.89 | 0.65 | 90.72 | 2326 |
| Vaal Triangle | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1839 |
| Secunda | 0 | 0.38 | 0.87 | 1.79 | 4.33 | 1.20 | 88.45 | 2521 |

*Nitrogen dioxide*

Table 3.4 shows $NO_2$ concentration distribution data over the study sites. When comparing the sites monitored in the morning, Secunda was found to have the highest $NO_2$ average concentration of 1.48 ppb followed by Witbank with an average concentration of 0.65 ppb, then Rustenburg with an average concentration of 0.17 ppb. Witbank $NO_2$ concentration spatial distribution was most variable with the relative standard deviation of 147.35%, followed by Rustenburg with the relative standard deviation of 94.07%, and then Secunda with a relative standard deviation of 67.20%. The high spatial variability of $NO_2$ over these sites is due to its short atmospheric life-time (one day) and the uneven distribution of its sources (IPCC, 2001; QEPA, 2006; USEPA, 2006c; WMO, 2006a).

The afternoon $NO_2$ concentration distribution data over the Vaal Triangle is included in Table 3.4. Its inclusion is to show the influence of diurnal variation of the mixing layer height and photochemistry on the diurnal variation of $NO_2$ concentration. Over the Vaal Triangle no $NO_2$ was detected in the parts per billion (ppb) measurement scale in the afternoon. This is because $NO_2$ concentration is diluted by turbulent mixing in the mixing layer of a larger volume (Annegarn *et al*., 1996a; Turner, 1996), which is supported by relatively stronger winds observed at Vereeniging (Figure 3.3) and its maximum photochemical consumption in $O_3$ formation in the afternoon (Crutzen *et al*., 1999; Taubman *et al*., 2004).

Table 3.4: Autumn campaign Highveld hotspots comparison: $NO_2$ concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Rustenburg | 0 | 0.038 | 0.095 | 0.25 | 0.51 | 0.17 | 94.07 | 2788 |
| Witbank | 0.006 | 0.23 | 0.63 | 1.03 | 1.74 | 0.65 | 147.35 | 2326 |
| Vaal Triangle | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1839 |
| Secunda | 0 | 0.84 | 1.28 | 1.79 | 4.52 | 1.48 | 67.20 | 2521 |

*Sulphur dioxide*

Table 3.5 shows $SO_2$ concentration distribution data over the study sites. Secunda was found to have the highest morning $SO_2$ average concentration of 17.02 ppb followed by Witbank with an average concentration of 13.07 ppb, then Rustenburg with an average concentration comparable to that of Witbank of 12.17 ppb. Secunda was found to have the most variable $SO_2$ concentration distribution in space with a relative standard deviation of 71.33%, followed by Witbank with a relative standard deviation of 38.61%, then Rustenburg with a relative standard deviation of 30.23%. Though Rustenburg's $SO_2$ average concentration is slightly less in comparison to that over Witbank, its $SO_2$ concentration distribution is slightly shifted toward higher $SO_2$ concentrations, except for the third quartile value.

The afternoon $SO_2$ concentration distribution data over the Vaal Triangle is included in Table 3.5 for the same reasons as with the other pollutants. The average $SO_2$ concentration of 6.97 ppb over the Vaal Triangle in the afternoon was generally lower than that of all the study areas monitored in the morning. $SO_2$ concentration was less variable in space in comparison to the other study areas, with a relative standard deviation of 23.23%. Like $NO_X$ concentrations, $SO_2$ concentrations are at their minimum in the afternoon. This is because of dilution by turbulent mixing in the afternoon mixing layer of a deeper depth (Annegarn *et al*., 1996a; Turner, 1996; Hunt *et al*., 2007), supported by relatively stronger winds (Figure 3.3) during the monitoring period, and optimal photochemical oxidation of $SO_2$ to form $SO_4^{2-}$ particles (Brock *et al*., 2002; Taubman *et al*., 2004; Springston *et al*., 2005; WMO, 2006c). The favourable mixing conditions in the afternoon minimises the atmospheric loading of pollutants from continuous industrial emissions.

Table 3.5: Autumn campaign Highveld hotspots comparison: $SO_2$ concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Rustenburg | 5.85 | 9.44 | 12.07 | 14.19 | 28.11 | 12.17 | 30.23 | 2788 |
| Witbank | 4.57 | 9.20 | 11.39 | 17.85 | 27.84 | 13.07 | 38.61 | 2326 |
| Vaal Triangle | 4.91 | 5.73 | 6.60 | 7.66 | 14.05 | 6.97 | 23.23 | 1839 |
| Secunda | 2.61 | 4.40 | 17.74 | 25.54 | 44.28 | 17.02 | 71.33 | 2521 |

*$PM_{2.5}$ aerosols*

Table 3.6 shows the $PM_{2.5}$ aerosols concentration distribution data over the study areas. Witbank was found to have the highest morning average aerosols concentration of 1166.23 $cm^{-3}$, followed by Secunda with an average concentration of 1052.33 $cm^{-3}$ then Rustenburg with an average concentration of 872.52 $cm^{-3}$. The relative standard deviation of aerosols concentration over Secunda of 40.09% indicates aerosol concentrations were more variable in space over Secunda, than over Witbank with a relative standard deviation of 25.56%. The aerosols concentration spatial distribution over Rustenburg was found to be least variable with a relative standard deviation of 11.75%.

The afternoon $PM_{2.5}$ aerosols concentration distribution data over the Vaal Triangle area is included in Table 3.6 for similar reasons as with the other pollutants. The aerosols average concentration of 580.89 $cm^{-3}$ over the Vaal Triangle in the afternoon was generally lower than that of all the study areas monitored in the morning. The aerosols concentration variability in space was comparable to that found over Witbank in the morning, its relative standard deviation was 26.69%. The concentration distribution of aerosols over Vaal Triangle was generally lower than that over the other study sites, but with a minimum concentration value that was comparable to the one over Witbank, which was monitored in the morning. The general low concentrations may be the result of dilution by turbulent mixing in the afternoon mixing layer of a greater volume (Annegarn *et al*., 1996a; Turner, 1996), supported by relatively stronger winds observed at Vereeniging (Figure 3.3).

Table 3.6: Autumn campaign Highveld hotspots comparison: $PM_{2.5}$ aerosols concentration distribution at approximately 167 m above ground level.

| Site | Min (#/cm$^3$) | 25% (#/cm$^3$) | Median (#/cm$^3$) | 75% (#/cm$^3$) | Max (#/cm$^3$) | Average (#/cm$^3$) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Rustenburg | 545.00 | 815.73 | 864.56 | 914.05 | 1471.66 | 872.52 | 11.75 | 2788 |
| Witbank | 361.59 | 963.06 | 1160.54 | 1370.16 | 2487.57 | 1166.23 | 25.56 | 2326 |
| Vaal Triangle | 339.12 | 448.22 | 540.97 | 695.47 | 1252.22 | 580.89 | 26.69 | 1839 |
| Secunda | 406.01 | 664.11 | 1025.85 | 1370.87 | 2507.22 | 1052.33 | 40.09 | 2521 |

**Winter campaign**

*Winter campaign meteorological overview*

During the winter campaign case study days the synoptic conditions over the country were dominated by either a high pressure system or surface trough. Figure 3.4 shows afternoon 14h00 (SAST) surface synoptic conditions charts during the winter campaign case study days. On the 27/07/2005 and 03/08/2005 the interior was under the influence of high pressure systems, a characteristic winter circulation type (Garstang *et al*., 1996; Tyson *et al*., 1996). Ridging from the eastern part of the country on 27/07/2005 (Figure 3.4(a)) and centred over the central interior on 03/08/2007 (Figure 3.4(b)). It brought about clear conditions over the country. The temperatures were generally mild (Table 3.7) and the winds were varying from calmn to moderate winds (Figure 3.6). On 05/08/2005 and 08/08/2005 the interior was under the influence of low pressure troughs, a characteristic summer circulation type (Garstang *et al*., 1996; Tyson *et al*., 1996). On 05/08/2005 it was centred over the western interior (Figure 3.4(c)) and on 08/08/2005 it was situated over the eastern interior extending south of the country (Figure 3.4(d)). The temperatures were also mild (Table 3.7) and the winds were generally light winds (Figure 3.6).

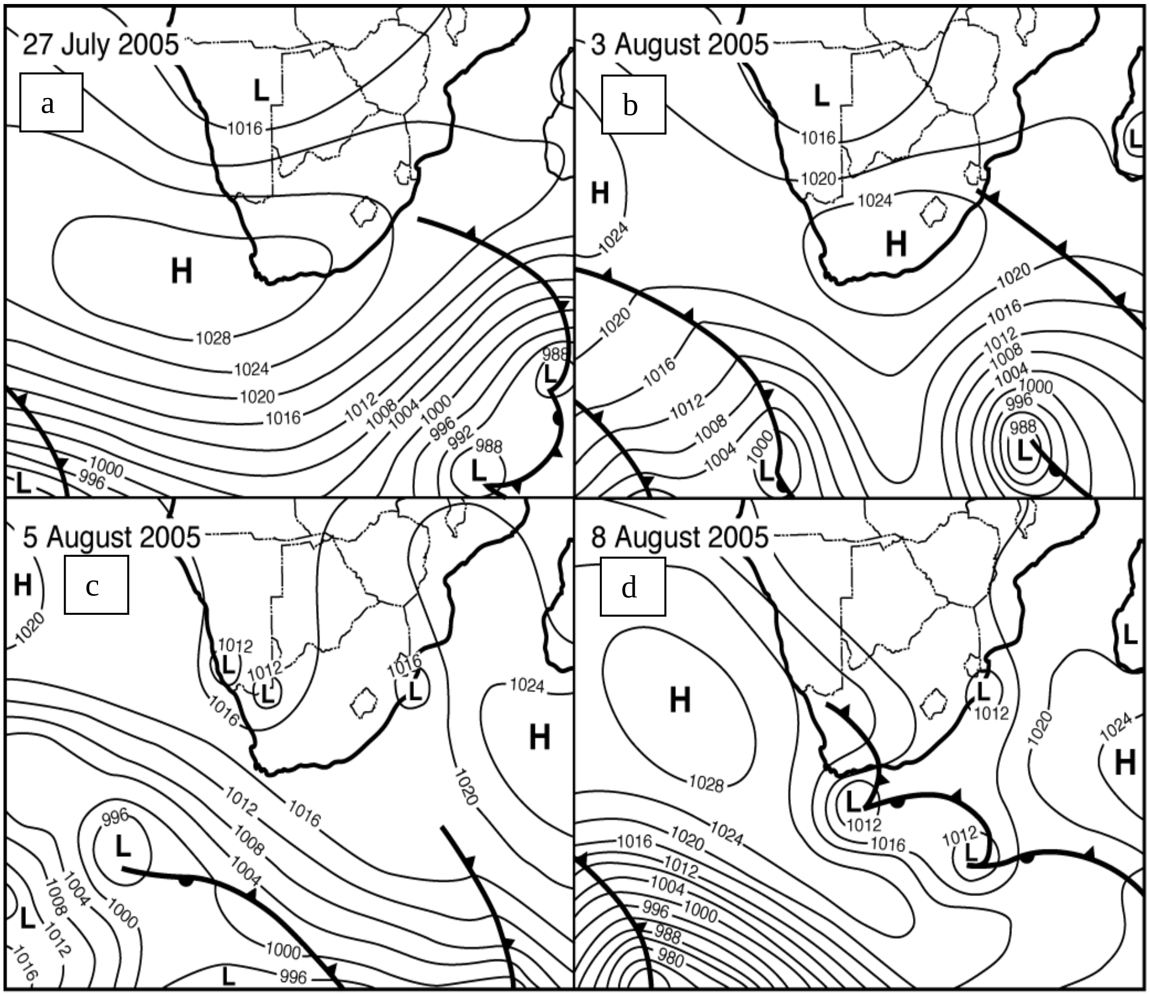


Figure 3.4: Winter campaign surface synoptic charts 3.4(a) to 3.4(d); 27/07/2005, 03/08/2005, 05/08/2005 and 08/08/2005 respectively.

Figure 3.5 shows the Irene weather station temperature profiles during the winter campaign case study days considered. The temperature profiles were used to characterise the vertical structure of the lower section of the troposphere. As it were with autumn campaign case study days, in all the four winter campaign case studies the lower troposphere was characterised by a surface nocturnal inversion layer in the morning. The temperature profiles in the morning during the winter campaign case study days were also characterised by upper level inversions varying in height from about 1000 to

1800 magl (Figure 3.5(a)). In the afternoon the surface nocturnal inversions were eroded resulting a deep mixing layer, however capped by the upper level inversions varying in their heights from 1200 to 1800 magl. It is only on the 27/07/2005 this temporal persistent stable discontinuity was not observed (Figure 3.5(b)).

The top of the morning surface inversion layer on Figure 3.5(a) on 27/07/2005 was at 183 m above ground level (magl) and at 12.2 °C. Hourly averaged temperatures at Irene in Table 3.7 show that it was eroded between 08:00 and 09:00 (SAST). Given Rustenburg was monitored in the afternoon, the site was monitored long after the erosion of the surface inversion layer. On 03/08/2005 the top of the surface nocturnal inversion layer in Figure 3.5(a) was at 184 magl and at 16.4 °C. Irene hourly averaged temperatures in Table 3.7 show that it was mixed out between 09:00 and 10:00 (SAST). Wind speeds at Ermelo and Witbank on the 03/08/2005 at 08:00 (SAST) were already above 2 $m.s^{-1}$ the critical threshold value (Figure 3.6) for surface inversion erosion (Hunt *et al*., 2007), and were averaged at 4.7 $m.s^{-1}$ and 4 $m.s^{-1}$ respectively, during the monitoring time. As Secunda is close to both sites, it can be deduced with caution that the winds at Secunda were also strong enough to erode the nocturnal surface inversion. Hence Secunda was likely monitored after the surface inversion was mixed out. On 05/08/2005 the morning surface inversion layer top in Figure 3.5(a) was at 275 magl and at 11 °C. Hourly averaged temperatures at Irene in Table 3.7 show that it was eroded between 08:00 and 09:00 (SAST). As the Vaal Triangle was monitored in the afternoon, the site was monitored long after the erosion of the nocturnal surface inversion layer. On 08/08/2005 the top of the morning surface inversion layer on Figure 3.5(a) was also at 184 magl and at 16.4 °C. Irene hourly averaged temperatures in Table 3.7 show that it was also mixed out between 09:00 and 10:00 (SAST). On 08/08/2005 at Witbank by 10:00 (SAST) the wind was already above the critical threshold value (Figure 3.5(a)) for surface inversion erosion (Hunt *et al*., 2007) and the hourly averaged temperature was 18.0 ˚C at that time. The monitoring of Witbank was likely done after the surface inversion was mixed out.

Table 3.7: Hourly averaged surface temperature at Irene weather station: from the morning up to the afternoon during the winter campaign.

| Site | Date | Time(SAST) | 06:00 | 07:00 | 08:00 | 09:00 | 10:00 | 11:00 | 12:00 | 13:00 |
|---|---|---|---|---|---|---|---|---|---|---|
| Irene | 27/07/2005 | Average Temperature (°C) | 8.7 | 8.9 | 12.5 | 17.4 | 19.7 | 20.9 | 22.3 | 24.5 |
| Rustenburg | 27/07/2005 | Average Temperature (°C) | 11.9 | 11.5 | 15.0 | 16.8 | 20.7 | 22.5 | 24.2 | 24.8 |
| Irene | 03/08/2005 | Average Temperature (°C) | 7.0 | 6.6 | 10.7 | 14.9 | 18.1 | 20.8 | 21.7 | 22.3 |
| Ermelo | 03/08/2005 | Average Temperature (°C) | 9.4 | 7.5 | 10.0 | 13.2 | 15.7 | 18.2 | 19.1 | 19.9 |
| Witbank | 03/08/2005 | Average Temperature (°C) | 8.6 | 6.3 | 12.7 | 16.4 | 18.4 | 19.7 | 20.5 | 21.6 |
| Irene | 05/08/2005 | Average Temperature (°C) | 5.1 | 5.1 | 8.2 | 12.7 | 15.5 | 16.9 | 18.6 | 19.8 |
| Vereeniging | 05/08/2005 | Average Temperature (°C) | 3.9 | 3.7 | 9.5 | 14.9 | 18.2 | 19.6 | 20.5 | 21.1 |
| Irene | 08/08/2005 | Average Temperature (°C) | 7.5 | 7.4 | 10.8 | 15.9 | 18.7 | 20.6 | 21.6 | 21.9 |
| Witbank | 08/08/2005 | Average Temperature (°C) | 7.6 | 7.1 | 12.2 | 15.4 | 18.0 | 19.3 | 20.2 | 22.0 |

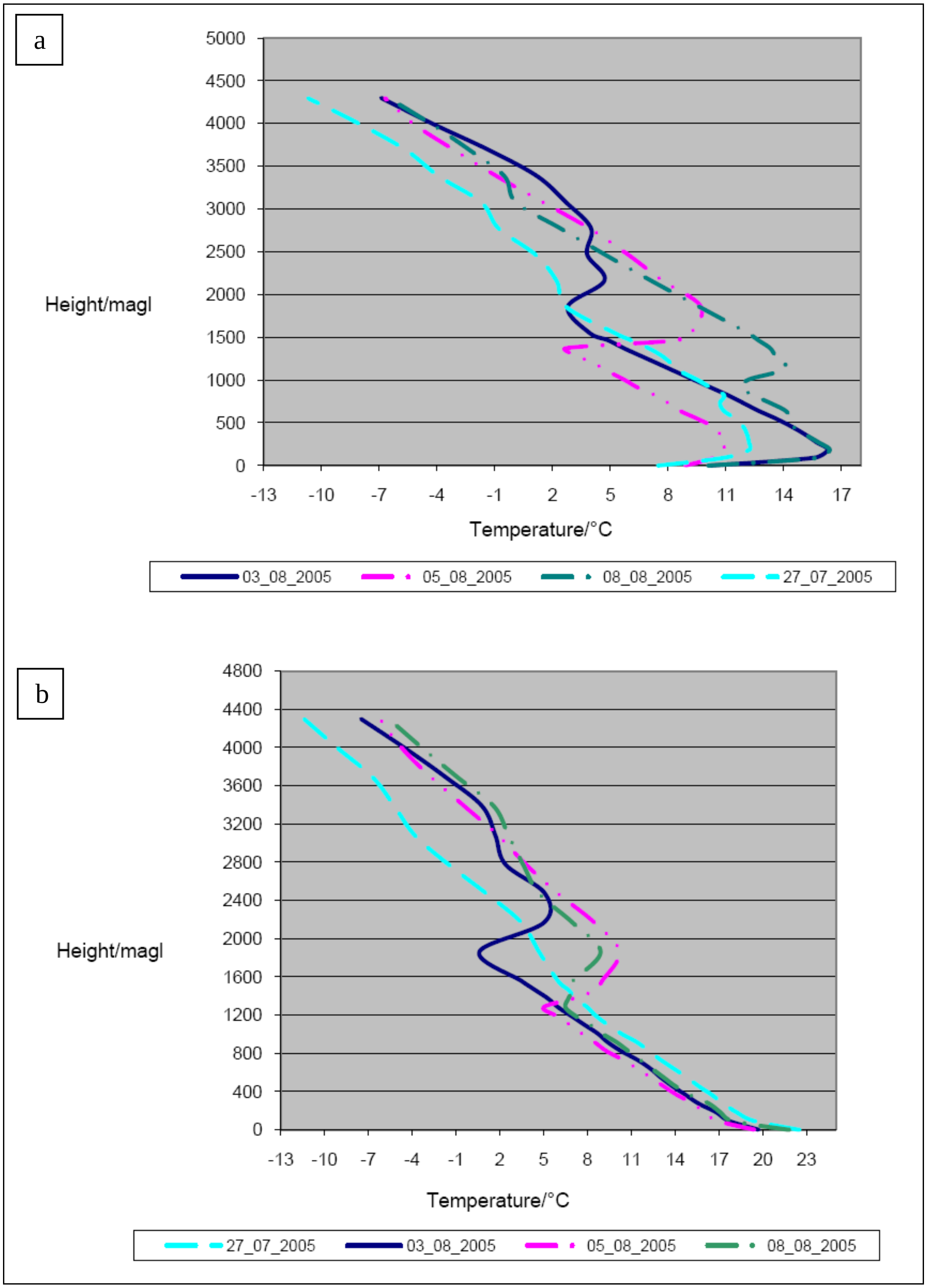


Figure 3.5: Temperature vertical profiles measurements over Irene weather observation station during the winter campaign. Figure 3.5(a) is a midnight profile and Figure 3.5(b) is an afternoon profile.

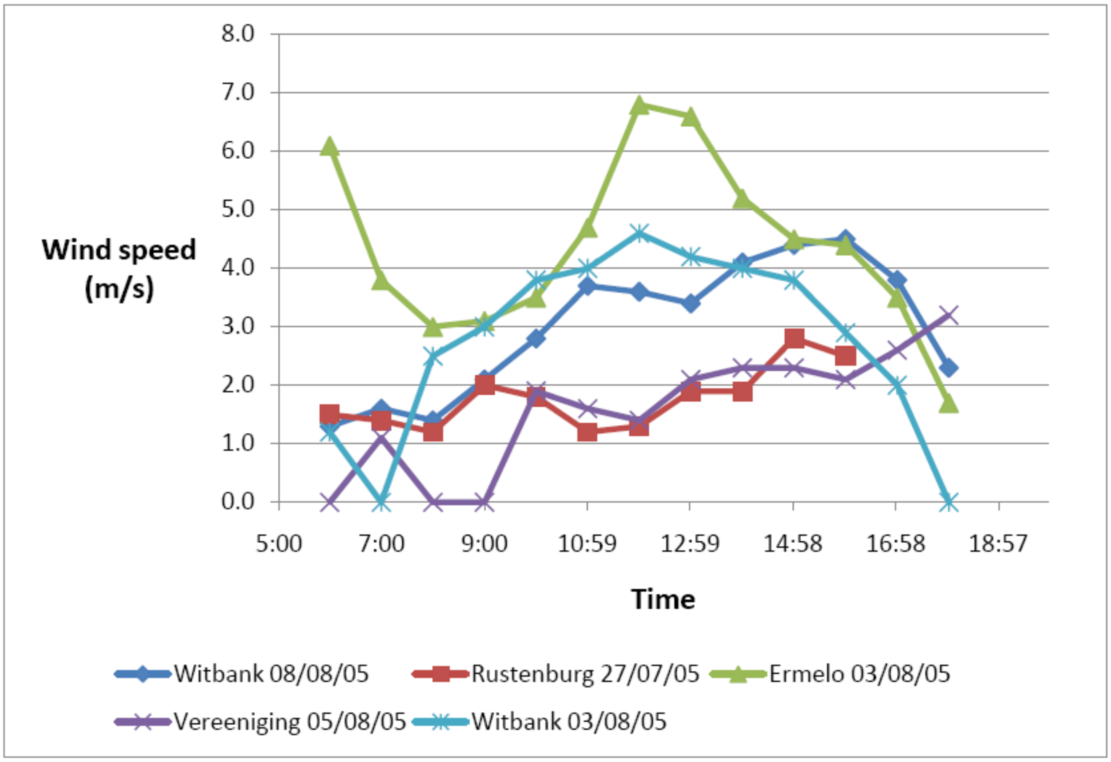


Figure 3.6: Wind speed measurements at the study sites during the winter campaign.

*Comparison of air pollutants levels over the Highveld air pollution hotspots during the winter campaign.*

The Tables 3.8 to 3.12 show statistical analysis of the concentration distribution of $O_3$, NO, $NO_2$, $SO_2$ and $PM_{2.5}$ aerosols respectively over the four Highveld air pollution hotspots. The data were collected approximately at 167 magl during the winter campaign. Data from apparent industrial plume penetration incidences were eliminated for this analysis. The Rustenburg site was monitored on 27/07/2005 from 14:43:55 to 15:27:00 (SAST). Secunda was monitored on 03/08/2005 from 10:23:20 to 11:19:10 (SAST). The Vaal Triangle area was monitored on 05/08/2005 from 12:56:22 to 13:29:16 (SAST). Witbank was monitored on 08/08/2005 from 10:59:41 to 11:28:20 (SAST). The winter campaign comparison of the four air pollution hotspots is complicated by the different circulation types prevailing on the four case study days and the different times of the day they were monitored. Both these factors influence the levels of air pollutants in the atmosphere. Sites monitored in the morning will be compared, and so will be sites monitored in the afternoon.

*Ozone*

Table 3.8 shows $O_3$ concentration distribution data over Secunda, Witbank, Rustenburg and the Vaal Triangle. When comparing the sites monitored in the morning, Secunda and Witbank were found to have comparable $O_3$ average concentrations. The Secunda average concentration was 46.55 ppb and that of Witbank was 46.03 ppb. Both sites were found to have low $O_3$ concentration spatial variation. The $O_3$ concentration relative standard deviations at Witbank and Secunda were 2.43% and 4.79% respectively. The relative uniform distribution of $O_3$ concentration in space over Witbank and Secunda is supported by the relatively strong winds which were prevailing during the monitoring of these sites (Figure 3.6).

The afternoon Vaal Triangle and Rustenburg $O_3$ average concentrations were also found to be comparable. The Vaal Triangle $O_3$ average concentration was 56.36 ppb and that of Rustenburg was 53.15 ppb. The relative standard deviations of $O_3$ concentration at Rustenburg and the Vaal Triangle were 13.82% and 8.59% respectively. This indicates that the $O_3$ concentration was more variable in space over Rustenburg than over the Vaal Triangle.

The afternoon Rustenburg and the Vaal Triangle average $O_3$ concentrations and $O_3$ concentrations distribution are generally higher than the ones over Secunda and Witbank monitored in the morning. The high afternoon $O_3$ concentration over Rustenburg and the Vaal Triangle are due to a build-up of $O_3$ from $O_3$ photochemical production, which is at its peak in the afternoon (Trainer *et al*., 1987; Poulida *et al*., 1994; Annegarn *et al*., 1996b; Betts *et al*., 2002; Taubman *et al*., 2004).

Table 3.8: Winter campaign Highveld hotspots comparison: $O_3$ concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Rustenburg | 41.22 | 46.62 | 52.29 | 57.98 | 73.39 | 53.15 | 13.82 | 2586 |
| Secunda | 32.37 | 46.03 | 46.81 | 47.54 | 58.10 | 46.55 | 4.79 | 2892 |
| Vaal Triangle | 46.2 | 53.52 | 55.39 | 59.98 | 68.70 | 56.36 | 8.59 | 1975 |
| Witbank | 40.99 | 45.17 | 46.01 | 46.86 | 48.86 | 46.03 | 2.43 | 1720 |

*Nitrogen monoxide*

Table 3.9 shows NO concentration distribution data over the study sites. When comparing the sites monitored in the morning, Witbank was found to have a slightly higher NO average concentration of 0.93 ppb than that over Secunda of 0.74 ppb. The difference in the NO average concentratons of the two sites is likely due to the difference in the height of the mixing layers during the monitoring of the two sites, on 03/08/2005 the mixing height was at 1860 magl and on 08/08/2005 it was at 1280 magl (Figure 3.5(b)). The NO concentration relative standard deviation of 125.10% over Secunda and of 72.44% over Witbank indicates that NO concentration was more variable in space over Secunda than over Witbank.

The Vaal Triangle area was found to have a higher afternoon NO average concentration of 3.14 ppb than that over Rustenburg of 0.71 ppb. This can be attributed to the limited depth of the mixing layer by an inversion at 1280 magl on 05/08/2005 and the deeper mixing layer on 27/07/2005 (Figure 3.5(b)). The Vaal Triangle was found to have the NO concentration relative standard deviation of 89.40% and Rustenburg of 77.20%. This indicates that the NO concentration distribution in space was more variable over the Vaal Triangle than over Rustenburg.

The morning Witbank NO average concentration and NO concentrations distribution in Table 3.9 are slightly higher than that over Rustenburg monitored in the afternoon. However the morning Secunda NO average concentration was comparable to that over Rustenburg and it's NO concentrations distribution was slightly lower than that over Rustenburg. It is expected that the NO loading in the morning to be higher than that in the afternoon. This is because air pollutants accumulate in the shallow morning mixing layer and they are diluted in the deeper afternoon mixing layer (Annegarn *et al*., 1996a; Turner, 1996). The low morning NO concentrations over Secunda and Witbank may be explained by relatively stronger winds which were prevailing during the monitoring of these two sites as compared to winds prevailing during Rustenburg monitoring (Figure 3.6). Though Secunda and Witbank mixing layers were capped by inversions at about 1860 magl and 1280 magl repectively during their monitoring (Figure 3.5(b)). The relatively strong winds were enhancing air pollutants concentrations dilution through turbulent mixing (Hunt *et al*., 2007).

The relatively high afternoon NO average concentration over Rustenburg, which is comparable to the morning average concentrations over Witbank and Secunda could be due to continuous emission sources, emitting throughout the day, which are likely to be industrial sources. The Vaal Triangle high afternoon NO average concentration, which is higher than the average concentrations of the other sites could also be due to continuous sources emitting throughout the day, which are also likely to be industrial sources. The 750-700 hPa persistent stable discontinuity at 1280 magl which limits vertical mixing and the light winds which were prevailing before and during the monitoring of Vaal Triangle, might have contributed to the relatively high afternoon NO levels over Vaal Triangle (Garstang *et al*., 1996: Freiman and Tyson 2000; Hunt *et al*, 2007).

Table 3.9: Winter campaign Highveld hotspots comparison: NO concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Rustenburg | 0 | 0.33 | 0.63 | 0.97 | 4.40 | 0.71 | 77.20 | 2586 |
| Secunda | 0 | 0.28 | 0.49 | 0.74 | 6.31 | 0.74 | 125.10 | 2892 |
| Vaal Triangle | 0 | 1.11 | 1.99 | 4.02 | 12.37 | 3.14 | 89.40 | 1975 |
| Witbank | 0 | 0.44 | 0.78 | 1.07 | 3.70 | 0.93 | 72.44 | 1720 |

*Nitrogen dioxide*

Table 3.10 shows $NO_2$ concentration distribution data over the study sites. Witbank was found to have a higher morning $NO_2$ average concentration of 5.08 ppb than that over Secunda of 1.65 ppb. This may be ascribed to the difference in the depth of the mixing layers during the monitoring of the two sites, on 03/08/2005 the mixing height was at 1860 magl and on 08/08/2005 it was at 1280 magl (Figure 3.5(b)). The $NO_2$ concentration relative standard deviation of 54.36% over Witbank was lower than that of 86.69% over Secunda. This implies the $NO_2$ concentration over Witbank was less variable in space than over Secunda.

The Vaal Triangle area was found to have a higher afternoon $NO_2$ average concentration of 19.51 ppb than that over Rustenburg of 6.33 ppb. As is the case with NO, this can be ascribed to the limited depth of the mixing layer by an inversion at 1280 magl on 05/08/2005 and the deeper mixing layer on 27/07/2005 (Figure 3.5(b)). The $NO_2$ concentration relative standard deviation of 79.88% over Rustenburg was higher than that of 66.38% over the Vaal Triangle. This implies the $NO_2$ concentration over the Vaal Triangle was less variable in space than over Rustenburg.

The afternoon Vaal Triangle and Rustenburg average $NO_2$ concentration and $NO_2$ concentration distribution in Table 3.10 are higher than that over Secunda and Witbank monitored in the morning. Normally it would be expected that the morning $NO_2$ concentrations over Secunda and Witbank be higher than the afternoon $NO_2$ concentrations over the Vaal Triangle and Rustenburg. This is because of limited vertical dispersion of air pollutants in the shallow morning mixing layer leading to accumulation of air pollutants, and in the afternoon air pollutants are diluted by turbulent mixing in a deeper afternoon mixing layer (Annegarn *et al*., 1996a; Turner, 1996). Photochemical processes which are optimal in the afternoon, like the oxidation of $NO_2$ by OH radicals to form nitric acid ($HNO_3$) and peroxyacetylnitrate (PAN) (Parrish *et al*., 1990; IPCC, 2001) and photolysis of $NO_2$ in the formation of $O_3$ (Crutzen *et al*., 1999; Taubman *et al*., 2004) reduces $NO_2$ concentration in the afternoon. As in the case of NO concentrations in the morning over Secunda and Witbank, low $NO_2$ concentrations in the morning over these two sites can also be explained by relatively stronger winds which were prevailing during the monitoring of these two sites as compared to winds prevailing during Rustenburg and Vaal Triangle monitoring (Figure 3.6).

The high afternoon $NO_2$ concentrations over the Vaal Triangle and Rustenburg could be due to continuous emission sources, emitting throughout the day, which are likely to be industrial sources. As is the case with NO, the occurrence of the 750-700 hPa stable discontinuity at 1280 magl (Figure 3.5(b)) and the light winds which were prevailing before and during the monitoring of Vaal Triangle might have contributed to the high afternoon Vaal Triangle $NO_2$ levels by restricting vertical and horizontal mixing of pollutants (Garstang *et al*., 1996: Freiman and Tyson 2000; Hunt *et al*., 2007).

Table 3.10: Winter campaign Highveld hotspots comparison: $NO_2$ concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Rustenburg | 0 | 2.45 | 4.94 | 9.09 | 23.04 | 6.33 | 79.88 | 2586 |
| Secunda | 0 | 0.67 | 1.26 | 2.12 | 8.16 | 1.65 | 86.69 | 2892 |
| Vaal Triangle | 4.30 | 7.27 | 17.43 | 27.80 | 49.44 | 19.51 | 66.38 | 1975 |
| Witbank | 0.57 | 3.38 | 4.43 | 5.47 | 15.10 | 5.08 | 54.36 | 1720 |

*Sulphur dioxide*

Table 3.11 shows $SO_2$ concentration distribution data over the study sites. When comparing the sites monitored in the morning, Witbank was found to have a slightly higher $SO_2$ average concentration of 7.45 ppb than that over Secunda of 6.65 ppb. As was the case with NO and $NO_2$ the difference may be attributed to the difference in mixing layer heights during the monitoring of the two sites. The relative standard deviation of $SO_2$ concentration of 37.70% over Witbank indicates that $SO_2$ concentration is more variable in space over Witbank than over Secunda with a relative standard deviation of 26.71%.

The Vaal Triangle area was found to have a higher afternoon $SO_2$ average concentration of 11.05 ppb than the one over Rustenburg of 4.62 ppb. This can be ascribed to the limited depth of the mixing layer by an inversion at 1280 magl on 05/08/2005 and the deeper mixing layer on 27/07/2005 (Figure 3.5(b)). The $SO_2$ concentration relative standard deviation over Rustenburg of 56.34% was found to be higher than the one of 48.83% over the Vaal Triangle area. This implies the $SO_2$ concentration over the Vaal Triangle was less variable in space than over Rustenburg.

The morning Secunda and Witbank $SO_2$ average concentrations and $SO_2$ concentrations distribution in Table 3.11 are generally higher than that over Rustenburg monitored in the afternoon. The morning Secunda and Witbank $SO_2$ concentrations would probably have been much higher if the winds which were prevailing during the monitoring of the two sites were not as strong (Figure 3.6), supporting dilution of pollutants through turbulent mixing (Hunt *et al.*, 2007).

The Vaal Triangle afternoon $SO_2$ concentration distribution was generally higher than of all the other study sites, including Secunda and Witbank which were monitored in the morning. This implies that $SO_2$ loading over the Vaal Triangle was generally high throughout the day, since $SO_2$ concentration is normally low in the afternoon due to dilution (Annergarn *et al*., 1996b). Its high afternoon $SO_2$ average concentration could be due to emission sources with less emitting diurnal cycle, emitting throughout the day, which are likely to be industrial sources. The presence of the 750-700 hPa stable discontinuity at 1280 magl (Figure 3.5(b)) and the light winds which were prevailing before and during the monitoring of Vaal Triangle (Figure 3.6), might also have contributed to the high afternoon $SO_2$ levels.

Table 3.11: Winter campaign Highveld hotspots comparison: $SO_2$ concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Rustenburg | 1.14 | 2.69 | 3.54 | 6.31 | 14.58 | 4.62 | 56.34 | 2586 |
| Secunda | 3.64 | 5.68 | 6.40 | 7.05 | 19.16 | 6.65 | 26.71 | 2892 |
| Vaal Triangle | 3.40 | 6.63 | 10.18 | 12.80 | 26.42 | 11.05 | 48.83 | 1975 |
| Witbank | 3.69 | 5.46 | 6.51 | 8.70 | 19.95 | 7.45 | 37.70 | 1720 |

*$PM_{2.5}$ aerosols*

Table 3.12 shows $PM_{2.5}$ aerosols concentration distribution data over the study sites. Witbank was found to have a higher morning aerosols average concentration of 709.61 $cm^{-3}$ than that over Secunda of 393.42 $cm^{-3}$. As is the case with the other pollutants, this is likely due to mixing height difference during the monitoring of these sites (Figure 3.5(b)). The relative standard deviations of aerosols concentration over Witbank of 22.02% and Secunda of 21.22% show that the aerosols concentration variability in space over the two sites was comparable.

The Vaal Triangle area was found to have an afternoon aerosols average concentration of 1010.77 $cm^{-3}$ that is more than twice the average concentration of 482.02 $cm^{-3}$ over Rustenburg. Despite the general higher concentration distribution over the Vaal Triangle compared to Rustenburg, the Vaal Triangle aerosols concentration was less variable in space than over Rustenburg, it had a relative standard deviation of 21.24% and over Rustenburg it was 63.91%.

The morning Witbank aerosols average concentration and concentration distribution in Table 3.12 was generally higher than the one over Rustenburg monitored in the afternoon. But the opposite situation occurred between Secunda monitored in the morning and Rustenburg monitored in the afternoon. The Rustenburg aerosols average concentration was higher than the Secunda average aerosols concentration. The low morning aerosols average concentrations over Secunda and Witbank can be attributed to the relative stronger winds which prevailed during the monitoring of these sites (Figure 3.6) leading to dilution of air pollutants through turbulent mixing (Annegarn *et al*., 1996a; Turner, 1996; Hunt *et al.*, 2007).

The Vaal Triangle afternoon aerosols average concentration and concentration distribution was generally higher than all the other study sites, including Witbank and Secunda which were monitored in the morning. Because aerosols concentrations are normally at their minimum in the afternoon (Annegarn *et al*., 1996b), this implies that aerosols loading over the Vaal Triangle was generally high on this particular day. The high afternoon aerosols average concentration over the Vaal Triangle must be due to emission sources, emitting throughout the day, which are likely to be industrial sources. As is the case with other pollutants, the occurrence of the 750-700 hPa stable discontinuity at 1280 magl (Figure 3.5(b)) and the light winds which were prevailing before and during the monitoring of Vaal Triangle (Figure 3.6) might have contributed to the high afternoon Vaal Triangle $PM_{2.5}$ aerosols levels.

Table 3.12: Winter campaign Highveld hotspots comparison: $PM_{2.5}$ aerosols concentration distribution at approximately 167 m above ground level.

| Site | Min (#/cm$^3$) | 25% (#/cm$^3$) | Median (#/cm$^3$) | 75% (#/cm$^3$) | Max (#/cm$^3$) | Average (#/cm$^3$) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Rustenburg | 87.05 | 202.44 | 402.99 | 668.65 | 1394.70 | 482.02 | 63.91 | 2586 |
| Secunda | 165.36 | 343.51 | 382.89 | 426.52 | 964.07 | 393.42 | 21.22 | 2892 |
| Vaal Triangle | 499.02 | 840.79 | 1006.73 | 1161.61 | 1730.36 | 1010.77 | 21.24 | 1975 |
| Witbank | 318.40 | 598.28 | 690.07 | 802.95 | 1372.15 | 709.61 | 22.02 | 1720 |

**Spring campaign**

*Spring campaign meteorological overview*

The synoptic conditions over the country during the spring campaign case study days were similar to the ones that were prevailing during the autumn campaign. They were dominated by a surface trough. Figure 3.7 shows similar or comparable afternoon 14h00 (SAST) surface synoptic charts during the spring campaign case study days. On the 20/09/2005 and 23/09/2005 the interior was under the influence of a surface trough, it was situated over the central interior and extending to the southern interior. It brought about partly cloudy to cloudy conditions. The temperatures were generally warm during the spring campaign case study days (Table 3.13), and the winds were varying between calm and fine, and fine and moderate at different stations in different days (Figure 3.8).

Figure 3.9 shows the Irene weather station temperature profiles which were used to characterise the vertical structure of the lower part of the troposphere during the spring case study days. In both days of the case studies the lower troposphere was characterised by low level nocturnal inversion layers in the morning (Figure 3.9(a)), resulting a shallow mixing layer. These inversions occurred at the surface and 184 magl on 20/09/2005. On 23/09/2005 the inversion layers occurred at the surface, 184 magl and 641 magl. In the afternoon the nocturnal inversion layers were mixed out resulting a deep mixing layer

(Annegarn *et al*., 1996a). This mixing layer was capped by upper level inversions at 3080 magl on 20/09/2009 and at 1464 magl on 23/09/2005 (Figure 3.9(b)).

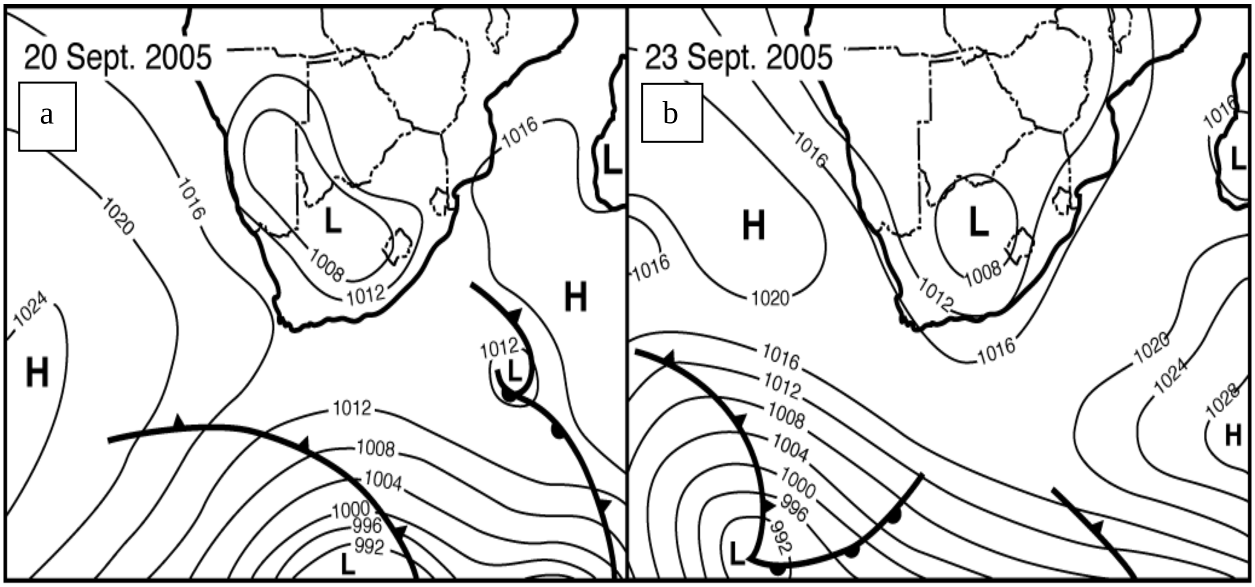


Figure 3.7: Spring campaign surface synoptic charts. Figure 3.7(a) and Figure 3.7(b) represents the charts on 20/09/2005 and 23/09/2005 respectively.

Table 3.13: Hourly averaged surface temperature at Irene and study sites weather stations: from the morning up to the afternoon during the spring campaign.

| Site | Date | Time(SAST) | 06:00 | 07:00 | 08:00 | 09:00 | 10:00 | 11:00 | 12:00 | 13:00 |
|---|---|---|---|---|---|---|---|---|---|---|
| Irene | 20/09/2005 | Average Temperature (°C) | 14.2 | 14.8 | 19.1 | 22.0 | 24.5 | 26.7 | 28.4 | 28.7 |
| Ermelo | 20/09/2005 | Average Temperature (°C) | 12.9 | 15.4 | 19.2 | 22.3 | 24.8 | 26.7 | 26.8 | 26.4 |
| Witbank | 20/09/2005 | Average Temperature (°C) | 12.0 | 14.5 | 17.8 | 21.2 | 23.1 | 25.6 | 27.7 | 28.0 |
| Irene | 23/09/2005 | Average Temperature (°C) | 15.0 | 16.7 | 19.5 | 22.1 | 23.9 | 26.1 | 27.0 | 28.9 |
| Rustenburg | 23/09/2005 | Average Temperature (°C) | 12.6 | 15.0 | 20.3 | 22.3 | 24.4 | 26.5 | 29.2 | 30.4 |

The top of the morning surface inversion layer in Figure 3.9(a) on 20/09/2005 was at 92 magl and at 19.8 °C. Hourly averaged temperatures at Irene in Table 3.13 show that it was eroded between 08:00 and 09:00 (SAST). The wind speed at Witbank at 09:00 (SAST) on the 20/09/2005 was at the critical threshold value and at Ermelo at the same time was above the critical threshold value (Figure 3.8) for surface inversion erosion (Hunt *et al.*, 2007). The hourly averaged temperatures at Witbank and Ermelo were 21.2 ˚C and 22.3 ˚C respectively at 09:00 (SAST) (Table 3.13). It can be deduced with caution that the conditions were similar at Secunda which is close to both sites. Secunda was likely monitored after the surface inversion was mixed out. On 23/09/2005 the morning surface inversion layer top in Figure 3.9(a) was also at 92 magl and at 17.7 °C. Hourly averaged temperatures at Irene in Table 3.13 show that it was mixed out between 07:00 and 08:00 (SAST). The surface winds at Rustenburg on 23/09/2005 by 09:00 (SAST) were averaged to 1.2 $m.s^{-1}$ (Figure 3.8), and the temperature was averaged at 22.3 ˚C at that time. It was likely that the Rustenburg site was monitored after the surface inversion was mixed out. As the Vaal Triangle and Witbank sites were monitored in the afternoon, both sites were monitored long after the erosion of the nocturnal surface inversion.

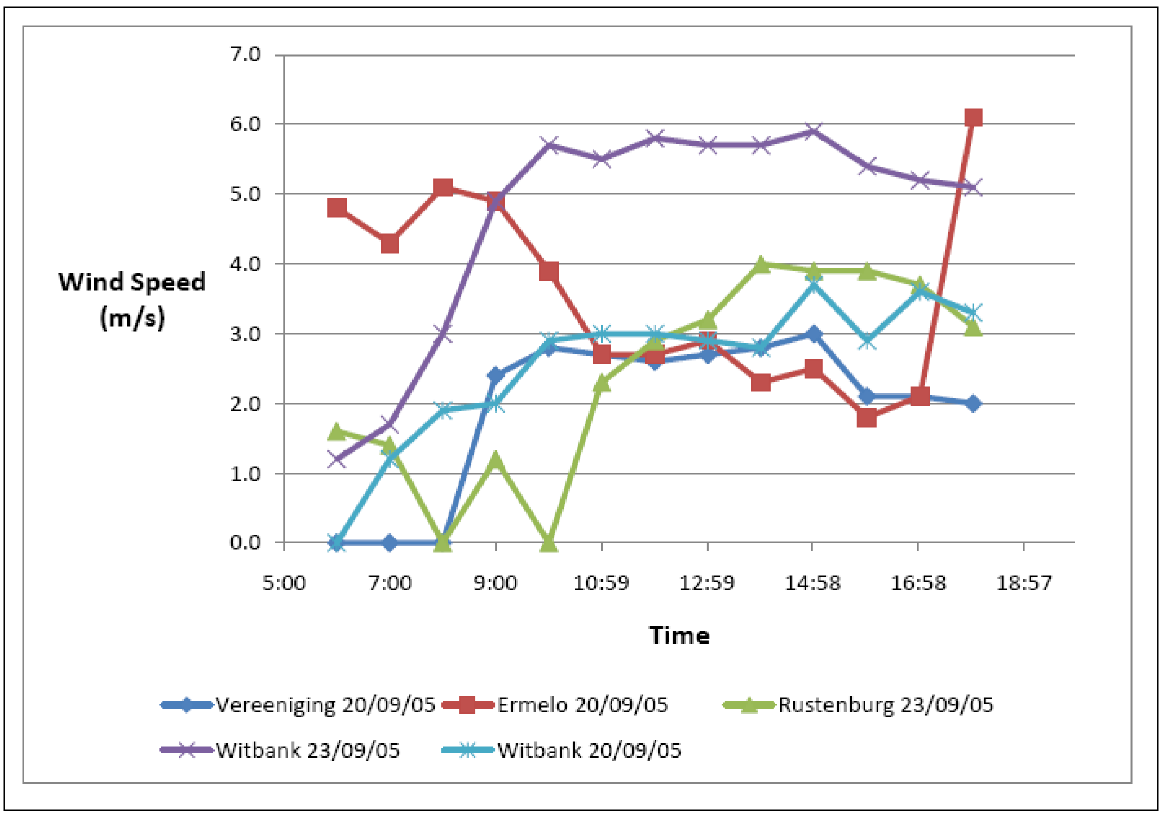

Figure 3.8: Wind speed measurements at the study sites during the spring campaign.

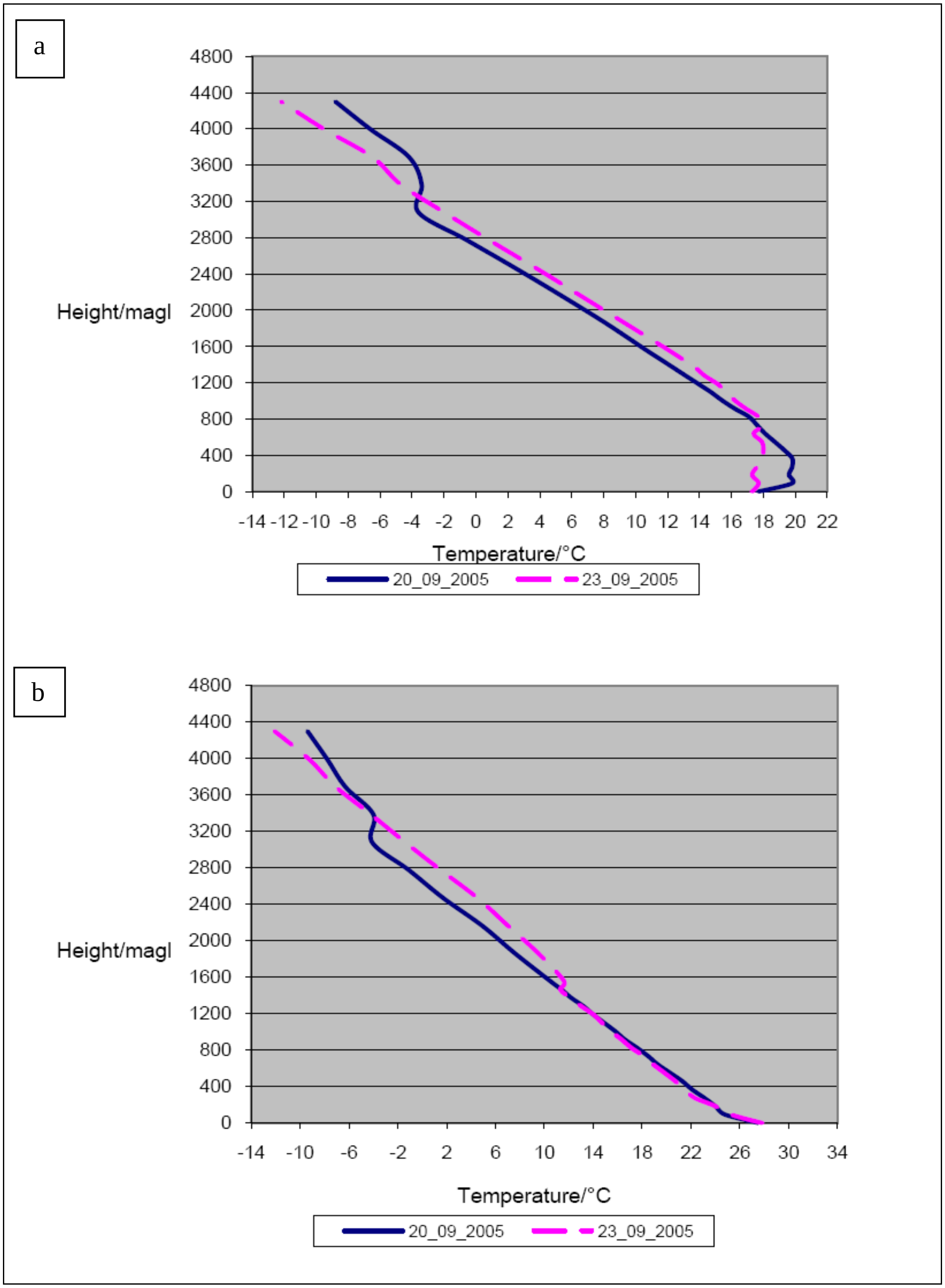

Figure 3.9: Temperature vertical profiles measurements over Irene weather observation station during the spring campaign. Figure 3.9(a) is a midnight profile and Figure 3.9(b) is an afternoon profile.

*Comparison of air pollutants levels over the Highveld air pollution hotspots during the spring campaign.*

Tables 3.14 to 3.18 show the statistical analysis of the concentration distribution of $O_3$, NO, $NO_2$, $SO_2$ and $PM_{2.5}$ aerosols respectively over the four Highveld air pollution hotspots. The data were collected approximately 167 m above ground level during the spring campaign. Data from apparent industrial plume penetration were eliminated for this analysis. Secunda and Vaal Triangle sites were monitored on 20/09/2005, the Secunda area from 09:31:56 to 10:13:51 (SAST), and the Vaal Triangle area from 14:02:36 to 14:20:07 (SAST). Rustenburg and Witbank areas were monitored on 23/09/2005, the Rustenburg area from 09:51:07 to 10:53:28 (SAST), and the Witbank area from 14:36:29 to 15:08:07 (SAST). The similar synoptic conditions during the spring campaign monitoring days allowed the comparison of the four air pollution hotspots. The only complication to the comparison is the different times of the day these sites were monitored, because that influences the levels of air pollutants in the atmosphere.

*Ozone*

Table 3.14 shows $O_3$ concentration distribution data over Secunda and Rustenburg monitored in the morning, and over Witbank and the Vaal Triangle monitored in the afternoon. Rustenburg was found to have a higher $O_3$ average concentration of 58.80 ppb than that over Secunda of 54.20 ppb. This is due to a generally less NO concentration over Rustenburg as compared to Secunda (Table 3.15), which destroys $O_3$ through NO and $O_3$ titration reaction (Kleinman, 1994; Kley *et al.,* 1994; Poulida *et al.,* 1994; Hobbs *et al.,* 2003; Taubman *et al.*, 2004). The $O_3$ concentration spatial variability was higher over Secunda than Rustenburg. Secunda had $O_3$ concentration relative standard deviation of 17.63% and Rustenburg of 7.78%.

Witbank was found to have a higher afternoon $O_3$ average concentration of 71.26 ppb than that over the Vaal Triangle of 63.46 ppb. As the wind at Witbank was stronger than at the Vaal Triangle during the times the sites were monitored (Figure 3.8) and NO concentration was higher at Witbank than at the Vaal Triangle (Table 3.15), the higher $O_3$ concentration at Witbank could be attributed to the inversion at 1464 magl (Figure 3.9(b)). The $O_3$ concentration was less variable in space over both sites, it had low relative standard deviations of 3.31% over Witbank and 1.96% over the Vaal Triangle.

Afternoon Witbank and Vaal Triangle $O_3$ average concentrations and $O_3$ concentrations distribution are generally higher than that over Secunda and Rustenburg which were monitored in the morning. The high afternoon $O_3$ concentration over Witbank and the Vaal Triangle are due to a build-up of $O_3$ from $O_3$ photochemical production, which is at its peak in the afternoon (Trainer *et al*., 1987; Poulida *et al*., 1994; Annegarn *et al*., 1996b; Betts *et al*., 2002; Taubman *et al*., 2004).

Table 3.14: Spring campaign Highveld hotspots comparison: $O_3$ concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Secunda | 20.90 | 53.05 | 56.42 | 59.07 | 70.92 | 54.20 | 17.63 | 2516 |
| Vaal Triangle | 60.97 | 62.86 | 63.62 | 63.86 | 67.36 | 63.46 | 1.96 | 1052 |
| Rustenburg | 27.68 | 56.42 | 59.40 | 61.32 | 69.36 | 58.80 | 7.78 | 3742 |
| Witbank | 63.75 | 69.50 | 71.34 | 72.76 | 76.93 | 71.26 | 3.31 | 1899 |

*Nitrogen monoxide*

Table 3.15 shows NO concentration distribution data over the study sites. When comparing the sites monitored in the morning, Secunda was found to have a higher morning NO average concentration of 0.75 ppb than that over Rustenburg of 0.22 ppb. The distribution of NO concentration in space was less variable over Secunda than over

Rustenburg. Secunda had $NO_2$ concentration relative standard deviation of 68.53% and Rustenburg of 135.82%.

Witbank was found to have a higher afternoon NO average concentration of 0.32 ppb than that over the Vaal Triangle of 0.012 ppb. The higher afternoon NO concentration over Witbank could be ascribed to the subsidence inversion that occurred at 1464 magl on 23/09/2005 (Figure 3.9(b)). The NO concentration relative standard deviation of 137.22%% over Witbank and of 132.29% over the Vaal Triangle suggest that the spatial variations of NO concentrations over the two sites were comparable and high.

The morning Secunda NO average concentration and NO concentrations distribution in Table 3.15 are generally higher than both the ones over Witbank and the Vaal Triangle monitored in the afternoon. On the other hand Rustenburg morning NO average concentration is higher than that over the Vaal Triangle but lower than that over Witbank. Normally it would be expected that the morning Rustenburg NO average concentration be higher than both the afternoon Vaal Triangle and Witbank NO average concentrations, because of dilution and photochemical consumption in the afternoon. The relatively low morning NO levels over Rustenburg could be the result of less emissions of NO over the site.

Table 3.15: Spring campaign Highveld hotspots comparison: NO concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Secunda | 0 | 0.37 | 0.67 | 0.92 | 3.2 | 0.75 | 68.53 | 2516 |
| Vaal Triangle | 0 | 0.003 | 0.006 | 0.018 | 0.03 | 0.012 | 132.29 | 1052 |
| Rustenburg | 0 | 0.074 | 0.14 | 0.22 | 1.61 | 0.22 | 135.82 | 3742 |
| Witbank | 0 | 0.065 | 0.13 | 0.35 | 1.89 | 0.32 | 137.22 | 1899 |

*Nitrogen dioxide*

Table 3.16 shows $NO_2$ concentration distribution data over the study sites. Secunda was found to have a higher morning $NO_2$ average concentration of 7.06 ppb than that over Rustenburg of 4.69 ppb. The $NO_2$ concentration relative standard deviations of 29.83% over Secunda and of 19.60% over Rustenburg suggest that the $NO_2$ concentration was more spatially variable over Secunda than over Rustenburg.

Witbank was found to have a higher afternoon $NO_2$ average concentration of 9.07 ppb than that over the Vaal Triangle of 7.45 ppb. The inversion at 1464 magl (Figure 3.9(b)) on 23/09/2005 could have contributed to the relative high $NO_2$ concentration at Witbank. The $NO_2$ concentration relative standard deviation of 16.32% over Witbank and 10.19% over the Vaal Triangle indicate that the $NO_2$ concentration was more variable in space over Witbank than over the Vaal Triangle.

The morning Secunda $NO_2$ average concentration is comparable to the Vaal Triangle afternoon $NO_2$ average concentration, but lower than the Witbank afternoon $NO_2$ average concentration. On the other hand, Rustenburg morning $NO_2$ average concentration is lower than both the Vaal Triangle and Witbank afternoon $NO_2$ average concentrations. The high afternoon $NO_2$ average concentrations over the Vaal Triangle and Witbank could be due to continuous sources emitting throughout the day, which are likely to be industrial sources. The subsidence inversion at 1464 magl on 23/09/2005 in Figure 3.9(b) could have also contributed to the relatively high afternoon $NO_2$ levels at Witbank.

Table 3.16: Spring campaign Highveld hotspots comparison: $NO_2$ concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Secunda | 3.15 | 5.26 | 7.11 | 8.09 | 12.71 | 7.06 | 29.83 | 2516 |
| Vaal Triangle | 6.27 | 6.85 | 7.15 | 7.86 | 9.38 | 7.45 | 10.19 | 1052 |
| Rustenburg | 3.30 | 4.05 | 4.44 | 5.08 | 9.92 | 4.69 | 19.60 | 3742 |
| Witbank | 3.38 | 8.46 | 8.81 | 9.28 | 17.01 | 9.07 | 16.32 | 1899 |

*Sulphur dioxide*

Table 3.17 shows the $SO_2$ concentration distribution data over the study sites. Secunda was found to have a higher morning $SO_2$ average concentration of 14.50 ppb as compared to Rustenburg with an average concentration of 3.96 ppb. The relative standard deviation of $SO_2$ concentration of 34.06% over Secunda and 55.00% over Rustenburg show that $SO_2$ concentration was more variable in space over Rustenburg than over Secunda.

The Vaal Triangle was found to have a slightly higher afternoon $SO_2$ average concentration of 8.41 ppb than that over Witbank of 7.39 ppb. The $SO_2$ concentration was more variable in space over Witbank than over the Vaal Triangle. It had a relative standard deviation of 52.45% over Witbank and 12.82% over the Vaal Triangle.

The morning Secunda $SO_2$ average concentration and $SO_2$ concentration distribution in Table 3.17 are generally higher than the ones over the Vaal Triangle and Witbank monitored in the afternoon. On the other hand, morning Rustenburg $SO_2$ average concentration and $SO_2$ concentration distribution is generally lower than the ones over the Vaal Triangle and Witbank monitored in the afternoon. The high afternoon $SO_2$ concentrations over the Vaal Triangle and Witbank as compared to Rustenburg in the morning could be due to more and stronger emission sources with small emitting diurnal cycle (emitting throughout the day), which are likely to be industrial sources. The subsidence inversion at 1464 magl on 23/09/2005 in Figure 3.9(b) could have also contributed to the relatively high afternoon $SO_2$ levels at Witbank.

Table 3.17: Spring campaign Highveld hotspots comparison: $SO_2$ concentration distribution at approximately 167 m above ground level.

| Site | Min (ppb) | 25% (ppb) | Median (ppb) | 75% (ppb) | Max (ppb) | Average (ppb) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Secunda | 7.26 | 10.74 | 13.31 | 17.21 | 29.66 | 14.50 | 34.06 | 2516 |
| Vaal Triangle | 7.03 | 7.73 | 7.87 | 8.85 | 11.29 | 8.41 | 12.82 | 1052 |
| Rustenburg | 2.40 | 2.66 | 3.13 | 3.99 | 15.53 | 3.96 | 55.00 | 3742 |
| Witbank | 4.25 | 5.36 | 5.46 | 7.27 | 23.95 | 7.39 | 52.45 | 1899 |

*$PM_{2.5}$ aerosols*

Table 3.18 shows the $PM_{2.5}$ aerosols concentration distribution data over the study sites. Rustenburg was found to have a higher morning aerosols average concentration of 1021.56 $cm^{-3}$ as compared to Secunda with an average of 822.57 $cm^{-3}$. The aerosols concentration was more variable in space over Rustenburg than over Secunda, with relative standard deviations of 24.52% and 17.40% respectively.

Witbank was found to have a higher afternoon aerosols average concentration of 785.56 $cm^{-3}$ as compared to the Vaal Triangle with an average concentration of 609.08 $cm^{-3}$. The inversion at 1464 magl (Figure 3.9(b)) on 23/09/2005 could have contributed to the relative high aerosols concentration at Witbank. The relative standard deviations of aerosols concentrations of 20.50% over Witbank and 19.30% over the Vaal Triangle, show that the aerosols concentration variability in space over the two sites was comparable.

The morning Secunda and Rustenburg aerosols average concentrations and concentrations distribution were generally higher than those over Witbank and the Vaal Triangle monitored in the afternoon. Though the morning aerosols concentrations were higher in comparison with afternoon concentrations, the difference in aerosols average concentrations between Witbank and the Vaal Triangle with Secunda is not marked. This suggests that there is some contribution to aerosols loading over the Vaal Triangle and Witbank from relatively strong and continuous sources, which are likely to be industrial sources.

Table 3.18: Spring campaign Highveld hotspots comparison: $PM_{2.5}$ aerosols concentration distribution at approximately 167 m above ground level.

| Site | Min (#/cm$^3$) | 25% (#/cm$^3$) | Median (#/cm$^3$) | 75% (#/cm$^3$) | Max (#/cm$^3$) | Average (#/cm$^3$) | StdDev % | Number |
|---|---|---|---|---|---|---|---|---|
| Secunda | 326.44 | 726.24 | 808.22 | 909.50 | 1326.15 | 822.57 | 17.40 | 2516 |
| Vaal Triangle | 218.60 | 541.80 | 600.62 | 669.78 | 1061.60 | 609.08 | 19.30 | 1052 |
| Rustenburg | 176.39 | 854.87 | 1017.99 | 1190.99 | 1933.86 | 1021.56 | 24.52 | 3742 |
| Witbank | 160.35 | 691.18 | 788.24 | 885.72 | 1394.54 | 785.56 | 20.50 | 1899 |

**Comparison of seasonal variation of air pollutants levels over the Highveld air pollution hotspots**

The Tables 3.19 to 3.23 show seasonal spatial average concentrations of $O_3$, NO, $NO_2$, $SO_2$ and $PM_{2.5}$ aerosols respectively over the four Highveld air pollution hotspots. The data is extracted from the considered seasonal case studies in Tables 3.2 to 3.6, 3.8 to 3.12, and 3.14 to 3.18. Average concentrations were determined from data collected at 167 magl over all the study sites and on the three studied seasons. The seasons that are compared are autumn, winter and spring.

*Ozone*

Surface $O_3$ loading varies seasonally. It has a broad peak in the dry season that is due to a large photochemical generation occurring in this season (Jacobs *et al*., 1995; Betts *et al*., 2002). In southern Africa it has peak concentrations in spring months from August to November (Zunckel *et al*., 2004). Emissions from wide spread biomass burning (Figure 3.10), both regional and long-range transported from countries lying north of South Africa, lightning during the inter-dry and wet season period and biogenic emissions contribute to the peak $O_3$ concentrations throughout the lower troposphere from August to November (Betts *et al*., 2002; Diab *et al*., 2004). The warm temperature around this period supports the emission of biogenic hydrocarbons and anthropogenic volatile organic compounds, both precursors of $O_3$ (Sillman and Samson, 1995). From the Southern Hemisphere Additional Ozonesondes (SHADOZ) project, Diab *et al*., (2004) established using data from 1998-2002 that the Total Tropospheric Ozone over the industrial Highveld (Irene) has changed from having a broad peak from September to November to a sharper October maximum in the recent period.

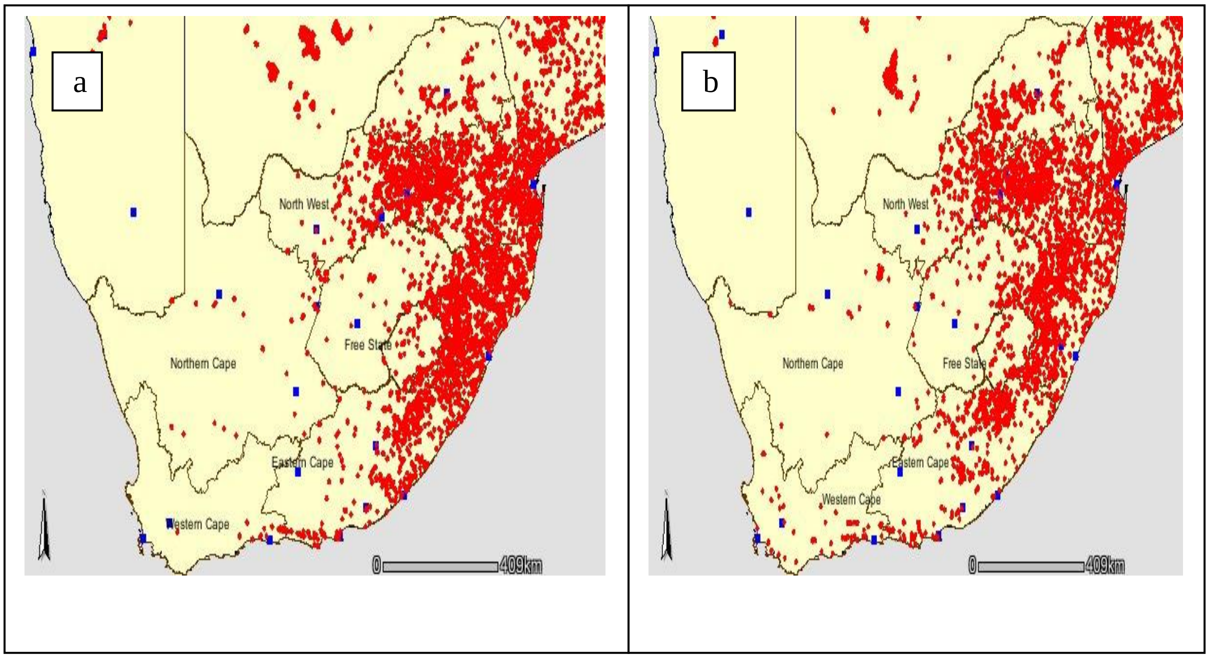


Figure 3.10: Monthly fires and their location detected by satellite over the region shown by red spots, the blue spots represents towns. Figure 3.10(a) shows the fires detected during the month of August 2005. Figure 3.10(b) shows the fires detected during the month of September 2005. (AFIS).

From the monitoring results of the three season campaigns shown in Table 3.19, all the study sites generally show a seasonal variation in $O_3$ average concentrations. The low values were observed during the autumn campaign. During the winter campaign higher values were observed and the highest values were observed during the spring campaign. Secunda and the Vaal Triangle were monitored consistently at the same time of the day, Secunda in the morning and the Vaal Triangle in the afternoon. Both these sites had seasonal change increments of +/- 10 ppb in spatial $O_3$ average concentrations. The Witbank spatial $O_3$ average concentration difference between winter and autumn was 21.62 ppb, in both cases $O_3$ was monitored in the morning. The Rustenburg spatial $O_3$ average concentration difference between spring and autumn was 30.32 ppb, in both cases $O_3$ was also monitored in the morning.

Table 3.19: Highveld hotspots seasonal spatial $O_3$ average concentrations comparison

| Seasonal $O_3$ average concentrations (ppb) | | | |
|---|---|---|---|
| Site | Autumn | Winter | Spring |
| Secunda | 30.00 | 46.55 | 54.20 |
| Witbank | 24.41 | 46.03 | 71.26* |
| Rustenburg | 28.48 | 53.15* | 58.80 |
| Vaal Triangle | 42.51* | 53.52* | 63.46* |

* $O_3$ monitored in the afternoon

*Nitrogen oxides*

Surface $NO_X$ have seasonal peak concentrations in winter (Parish *et al*., 1990; Doddridge *et al*., 1992). The peak $NO_X$ concentrations in winter over the study sites are due to stronger emissions in winter from wide spread biomass burning (GDACE, 2004), domestic fossil fuel burning and power generating plants for space heating (Annegarn *et al*., 1996b; Diab *et al*., 2004), and slower removal by less efficient photochemical processes (Parish *et al*., 1990; Doddridge *et al*., 1992).

From the monitoring results of the three season campaigns in Table 3.20, all the study sites show winter peak spatial NO average concentrations except Secunda. The Witbank winter peak would probably have been higher than the one reported, and the Secunda NO concentration winter peak would probably have been observed, if the sites did not experience relatively strong winds which were prevailing during the monitoring of these two sites. Rustenburg and the Vaal Triangle winter NO concentrations were monitored in the afternoon, which implies the concentrations could have been at their diurnal minimum (Annegarn *et al*., 1996a). The Rustenburg spatial NO average concentration derived from afternoon monitoring was higher than both autumn and spring spatial NO average concentrations derived from morning monitoring. The Vaal Triangle winter peak spatial NO average concentration was the highest.

Table 3.20: Highveld hotspots seasonal spatial NO average concentrations comparison

| Seasonal NO average concentrations (ppb) | | | |
|---|---|---|---|
| Site | Autumn | Winter | Spring |
| Secunda | 1.20 | 0.74 | 0.75 |
| Witbank | 0.65 | 0.93 | 0.32* |
| Rustenburg | 0.26 | 0.71* | 0.22 |
| Vaal Triangle | 0* | 3.14* | 0.012* |

* NO monitored in the afternoon

From the monitoring results of the three season campaigns in Table 3.21, only Rustenburg and the Vaal Triangle show peak winter spatial $NO_2$ average concentration. Both these sites were monitored in the afternoon, which implies the concentrations must have been at their diurnal minimum (Annegarn *et al*., 1996a). The Rustenburg spatial $NO_2$ average concentration derived from afternoon monitoring was higher than both the autumn and spring spatial $NO_2$ average concentrations derived from morning monitoring. The Vaal Triangle winter spatial $NO_2$ average concentration was higher than the one over Rustenburg. The winter peak $NO_2$ average concentrations were not observed for Secunda and Witbank, as a result of relatively strong winds which were prevailing during the monitoring of these two sites as mentioned in the previous passages.

Table 3.21: Highveld hotspots seasonal spatial $NO_2$ average concentrations comparison

| Seasonal $NO_2$ average concentrations (ppb) | | | |
|---|---|---|---|
| Site | Autumn | Winter | Spring |
| Secunda | 1.48 | 1.65 | 7.06 |
| Witbank | 0.65 | 5.08 | 9.07* |
| Rustenburg | 0.17 | 6.33* | 4.69 |
| Vaal Triangle | 0* | 19.51* | 7.45* |

* $NO_2$ monitored in the afternoon

*Sulphur dioxide*

Surface $SO_2$ loading also varies seasonally with peak concentrations in winter. The peak $SO_2$ concentrations in winter over the study sites are due to stronger emissions from domestic fossil fuel combustion and power generating plants for space heating (Annegarn *et al*., 1996b; van Horen *et al*., 1996; Diab *et al*., 2004). The high pressure systems which are more frequent in winter worsen the high winter $SO_2$ levels by causing subsidence, limiting vertical dispersion of air pollutants (Scheifinger, 1992; Tyson *et al*., 1996; GDACE, 2004).

From the monitoring results of the three season campaigns in Table 3.22, only the Vaal Triangle show peak winter spatial $SO_2$ average concentration. The Vaal Triangle was monitored in the afternoon in all the monitoring campaigns, this imply the $SO_2$ concentrations could have been at their background concentrations (Annegarn *et al*., 1996a). The Rustenburg winter spatial $SO_2$ average concentration monitored in the afternoon was only higher than the spring, but lower than the autumn spatial $SO_2$ average concentration, the autumn and spring $SO_2$ levels were both monitored in the morning. The winter peak $SO_2$ concentrations were not observed in Table 3.22 for Secunda and Witbank, for the same reason the winter peak of NO and $NO_2$ concentrations were not observed.

Table 3.22: Highveld hotspots seasonal spatial $SO_2$ average concentrations comparison

| Seasonal $SO_2$ average concentrations (ppb) | | | |
|---|---|---|---|
| Site | Autumn | Winter | Spring |
| Secunda | 17.02 | 6.65 | 14.50 |
| Witbank | 13.07 | 7.45 | 7.39* |
| Rustenburg | 12.17 | 4.62* | 3.96 |
| Vaal Triangle | 6.97* | 11.05* | 8.41* |

* $SO_2$ monitored in the afternoon

*$PM_{2.5}$ aerosols*

Surface atmospheric aerosols loading varies seasonally, with peak concentrations in winter. The high winter aerosols concentrations over the study sites are associated with stronger emissions from wide spread biomass burning (Butler *et al*., 2003; Eck *et al*., 2003; Hobbs et a., 2003), domestic fuel burning and power generating plants for space heating (van Horen *et al*., 1996; Annegarn *et al*., 1996b; Diab *et al*., 2004). The semi-permanent, subtropical, continental anticyclones which frequently occur in winter aggravates the high winter aerosol loading by producing subsidence temperature inversions (Scheifinger, 1992; Tyson *et al*., 1996; Hobbs *et al*., 2003; GDACE, 2004).

From the monitoring results of the three season campaigns in Table 3.23, only the Vaal Triangle show peak winter spatial aerosols average concentration. The Vaal Triangle was monitored in the afternoon in all the monitoring campaigns, this imply the aerosols concentrations might have been at their minimum diurnal concentrations (Annegarn *et al*., 1996b). The Rustenburg winter spatial aerosols average concentration monitored in the afternoon was lower than both the autumn and spring spatial aerosols average concentration, which were both monitored in the morning. The winter peak $PM_{2.5}$ aerosols concentrations were not observed in table 3.23 for Secunda and Witbank, for the same reason the winter peak for NO, $NO_2$ and $SO_2$ concentrations were not observed.

Table 3.23: Highveld hotspots seasonal spatial $PM_{2.5}$ aerosols average concentrations comparison

| Seasonal $PM_{2.5}$ aerosols average concentrations (#/cm$^3$) | | | |
|---|---|---|---|
| Site | Autumn | Winter | Spring |
| Secunda | 1052.33 | 393.42 | 822.57 |
| Witbank | 1166.23 | 709.61 | 785.56* |
| Rustenburg | 872.52 | 482.02* | 1021.56 |
| Vaal Triangle | 580.89* | 1010.77* | 609.08* |

* $PM_{2.5}$ aerosols monitored in the afternoon

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The concentration distribution of $O_3$, $NO_X$, $SO_2$ and $PM_{2.5}$ aerosols over the Highveld air pollution hotspots were compared in all monitored seasons. Seasonal change in atmospheric loading of these air pollutants over the Highveld air pollution hotspots was also assessed. In the comparisons of the Highveld air pollution hotspots, it was taken into account the prevailing meteorological conditions, and the temporal cycle of the photochemical processes, which both affect the atmospheric loading of air pollutants.