ANALYSIS OF A PERIOD OF ELEVATED OZONE CONCENTRATION REPORTED OVER THE VAAL TRIANGLE ON 2 JUNE 2013

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Abstract

A peak in the ambient ozone concentration was observed at three of the six ambient air quality monitoring stations in the Vaal Triangle Airshed Priority Area on the second of June 2013. The ozone peak was associated with elevated concentrations of particulate matter, including PM_{10}, $PM_{2.5}$ and black carbon, but not sulphur dioxide, oxides of nitrogen, carbon monoxide nor benzene. Back trajectory analysis using Hysplit showed that the air masses containing the high levels of ozone passed over areas influenced by coal fired power stations in the Waterberg, metal processing in the Bojanala region and high intensity fires 30km to 50km upwind of the stations.

1 INTRODUCTION

Tropospheric ozone is an important pollutant. It is involved in the production of photochemical smog, particularly over metropolitan areas and has a negative impact on crop productivity (Chameides et al., 1992). It plays an important role in atmospheric chemistry, influencing the production of the OH radical and thereby influences the oxidative capacity of the atmosphere. Tropospheric ozone is considered to have two major sources, firstly the incursion of ozone rich stratospheric air into the troposphere and secondly the de novo synthesis. In the presence of nitrogen oxides (NOx) ozone may be produced through the photochemical oxidation of hydrocarbons or carbon monoxide (CO) (Chameides et al., 1992; Seinfeld & Pandis, 2006). For this reaction to occur the presence of NOx, Volatile Organic Compounds (VOC) or CO and solar radiation is required (Chameides et al., 1992; Crutzen & Lelieveld, 2001).

Exposure to high concentrations of ozone has been implicated in increased premature mortality and reduced respiratory function (Silva et al., 2013; WHO, 2013). Due to the importance of ozone on human health, ozone is considered a criteria pollutant in South Africa (DEA, 2009). National Standards have been set with a limit value of 61 ppb as an eight hour running average (with 11 exceedances allowed annually). Many monitoring stations in South Africa report exceedances of the National Ambient Air Quality Standard for Ozone.

On the 2nd of June 2013 a peak in the ambient ozone concentrations which substantially exceeded the National Ambient Air Quality Standard was observed at three of the ambient air quality monitoring stations in the Vaal Triangle Ambient Air Quality Monitoring Network (Figure 1). Due to the extremely high levels of ozone that were observed it was decided that further investigation in the origins of this ozone episode was required.

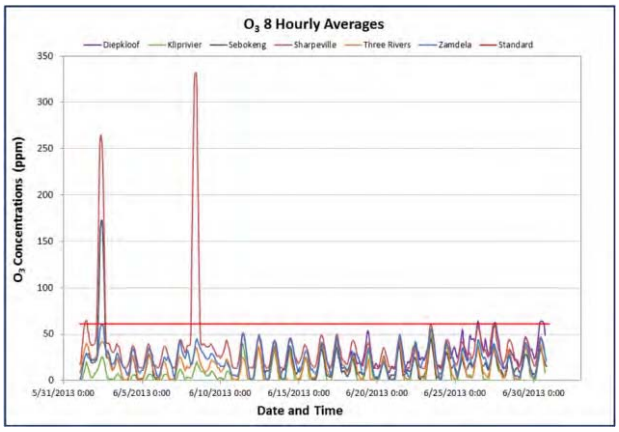

Figure 1 Time series of the 8 hour running ozone concentration for the 6 ambient air quality monitoring stations in the Vaal Triangle Priority Area Air Quality Monitoring Network

2 Methods and Materials

2.1 Ambient Air Quality Monitoring Network

The Vaal Triangle is an urban and an industrial heartland of South Africa. The combination of industrial, domestic, transport, biomass burning, agricultural and other emission sources have led to degraded air quality over the area. This in turn directly impacts on the health and well-being of people residing in the Vaal Triangle (Trade and Industry Chamber, 2004). In 2007 a network of 6 ambient air quality monitoring stations were set up in the Vaal Triangle with stations located at Diepkloof, Kliprivier, Sebokeng, Sharpeville, Three Rivers and Zamdela (Sasolburg) Figure 2. on next page.

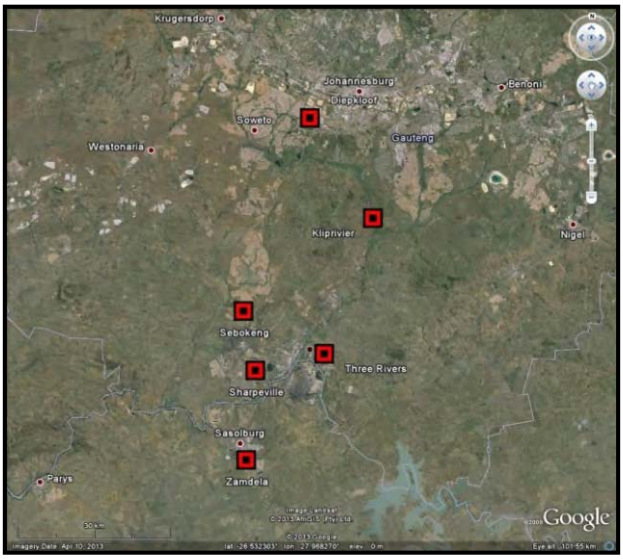

Figure 2: Google Earth image showing the location of the ambient air quality monitoring stations in the Vaal Triangle Ambient Air Quality Monitoring Network

Each of the stations is equipped with instrumentation for the measurement of meteorological parameters and for the measurement of atmospheric chemical constituents (Table 1). In addition, the Zamdela station is equipped with a Thermo Electron Multi-Angle Absorption Photometer instrument (MAAP) for the measurement of atmospheric black carbon. All instrumentation is regularly calibrated according to the SANAS TR07-03 requirements (SANAS, 2012) using certified calibration gas traceable to the national reference standard (Air Liquid) and a Thermo Electron 146i Multigas Calibrator. At the time of the period of high ozone concentration on the 2nd of June the instrument at Diepkloof was offline for repairs, therefore the Diepkloof station will not be considered in this analysis.

Table 1 Instrumentation for measurement of Atmospheric Chemical Constituents

Parameter	Model	Minimum Detection Limit	Averaging Period
PM_{10} and $PM_{2.5}$	Thermo Electron FH62 C14	1µg/m³	5 minutes
SO_2	Thermo Electron Model 43I	1ppb	5 minutes
CO	Thermo Electron Model 48I	0.04ppm	5 minutes
O_3	Thermo Electron Model 49I	0.5ppb	5 minutes
NO_x	Thermo Electron Model 42I	0.4ppb	5 minutes
BTEX	Synspec GC955 Series 600	0.1µg/m³	15 minutes

2.2 Atmospheric Conditions and Trajectory analysis

Due to the importance of atmospheric conditions, on the formation and movement of ozone and ozone precursors, an analysis of the atmospheric conditions at the time of the ozone exceedance was conducted. The synoptic charts for the central regions of South Africa were obtained from the South African Weather Service and information relating to the upper air was obtained for the balloon assent of the 2nd of June 2013 at the Irene Weather Station located approximately 100km to the north east of the Vaal Triangle.

To assess the possible source locations of ozone precursors back trajectory analysis was performed using the Hysplit model for a 24 hour back trajectory. An ending height of 100m above ground level was chosen.

2.3 Remote Sensing of fire locations

The fire map was downloaded from Advanced Fire Information System (AFIS) at http://southernafrica.afis.co.za. The system gives the near real-time and historical satellite-based fire monitoring information, covering multiple regions across the globe. The fires are detected by sensors on-board the Earth observation satellites, NASA MODIS and EUMETSAT MSG. A query was made on fires that occurred in southern Africa over a period of 24 hours on 2 June 2013, (i.e. fires that occurred during 2 June 2013 00:00 and 3 June 00:00) and the study area was zoomed into. AFIS then gives geographic location of fires and their intensity represented by different colours, yellow representing low, orange medium, red high and deep red extreme intensity(Van Rooi, 2012).

3 Results

3.1 Ozone Concentration 2 June 2013

The analysis of the 5 minute averaged ozone data from the stations at Sharpeville, Kliprivier, Sebokeng, Zamdela and Three Rivers stations (Figure 3) shows that a peak in the recorded ozone concentration occurred between ~9:00 and ~16:00 at the Sebokeng, Sharpeville and Zamdela Stations. At the Three Rivers and Kliprivier Stations this period of elevated ozone concentration was not observed. The maximum 5 minute ozone concentration recorded was 957 ppb for Sharpeville at 12:45, 784 ppb at Sebokeng at 13:05, 336 ppb at Zamdela at 12:40. Three Rivers and Kliprivier, which did not experience the period of elevated ozone concentration, had maximum concentrations of 51 ppb and 32 ppb at 14:00 and 14:30, respectively (Figure 3). The timing of the maximum ozone concentration at the stations showing the incident of high ozone is slightly earlier than at the other two stations. The ozone concentration at the Eskom owned Waterworks Station, located in the Vaal Triangle Region showed a

maximum ozone concentration of 218 ppb during the same time period. In all of the stations the concentration of ozone returned to the normal levels by approximately 16:00.

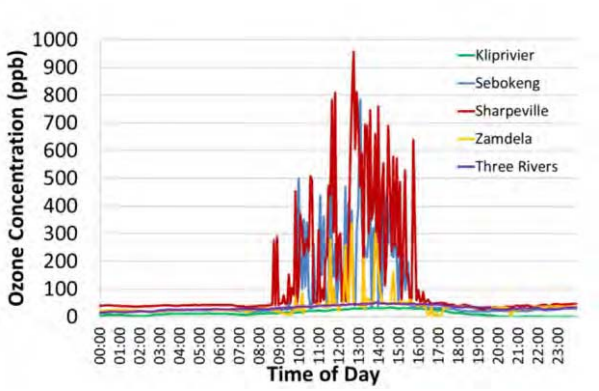

Figure 3 Time Series of ozone concentration (5 minute average) recorded on the 2 June 2013 at the Vaal Triangle Stations.

3.2 Other Chemical Parameters

The ambient concentration of PM_{10} at the three stations where the elevated ozone occurred showed an approximate 5 fold elevation during the period from 10:00 to 15:00 (Figure 4). A peak 5 minute PM_{10} concentration of 464 µg/m³ was observed at Sharpeville at 13:20, 35 minutes after the maximum recorded ozone concentration, but well within the period of elevated ozone. The elevation of the PM_{10} concentrations was much less pronounced at Three Rivers and Kliprivier which did not display the elevation in ozone concentration.

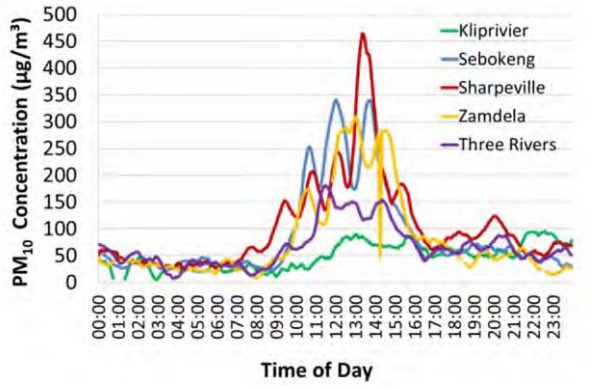

Figure 4 Time Series of PM_{10} Concentration (µg/m³) on the 2nd June 2013 for the Vaal Triangle monitoring Network.

The concentrations of $PM_{2.5}$ at Zamdela, Sharpeville and Sebokeng showed an approximate threefold increase during the hours of 10:00 to 15:00 coinciding with the period of elevated ozone concentration. This elevation in $PM_{2.5}$ was not as pronounced in the Three Rivers and Kliprivier stations.

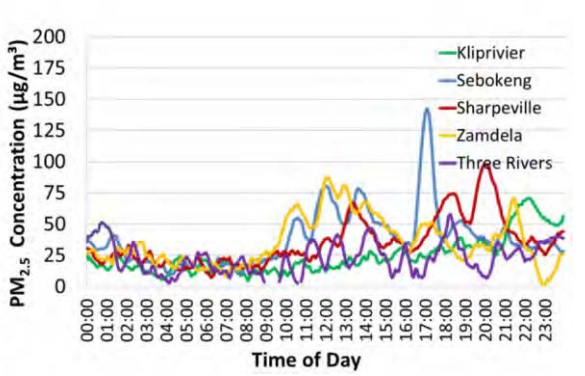

Figure 5 Time Series of $PM_{2.5}$ concentration (µg/m³) on the second of June 2013 for the Vaal Triangle Monitoring Network.

Black carbon is a strong indicator for combustion. During the period of elevated ozone, the black carbon concentration increased from approximately 1 µg/m³ to approximately 3 µg/m³, this is during the part of the day when the concentration of black carbon is expected to decrease as the atmosphere is more thoroughly mixed and localized sources of combustion such as domestic burning are not as prevalent as they would be during the evening and early morning hours. The elevation of the black carbon concentration that would typically be expected in the early evenings and that is associated with domestic burning is seen from approximately 18:00.

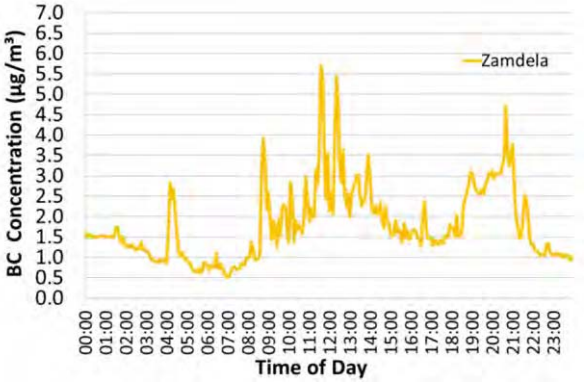

Figure 6 Time Series of Black Carbon concentration (µg/m³) on the second of June 2013 for the Zamdela Station

During the period of the peak in ozone there is a strong increase in the ratio of PM_{10} to black carbon, which is not seen for the ratio of $PM_{2.5}$ to black carbon. This implies that during this period there was a change in the composition of the particulate matter with an increase in the large size fractions (Figure 7). Figure on next page.

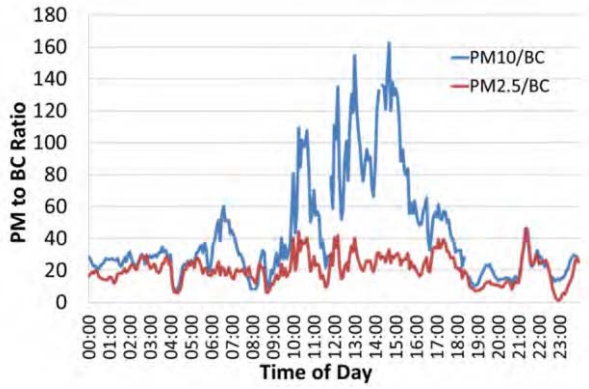

Figure 7 Time series of the ratio of particulate matter to black carbon on the second of June at the Zamdela station.

The concentration of SO_2 (Figure 8) which is often considered to be an indicator of industrial activity did not show any consistent increase during the period of elevated ozone concentration. Peaks in the SO_2 concentration were observed at Zamdela which are likely to be associated with local industrial emissions from the industrial operations to the north of the monitoring station.

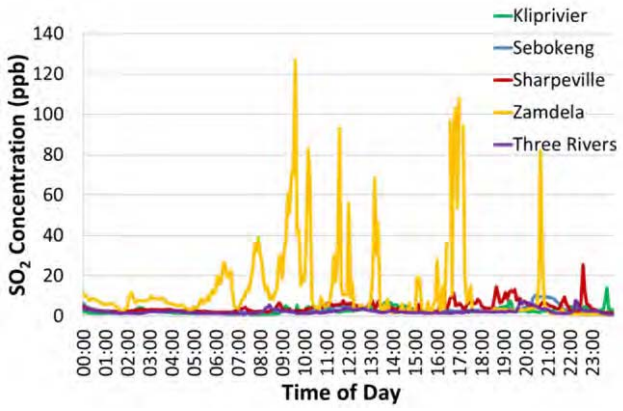

Figure 8 Time Series of SO_2 concentration (ppb) on the second of June 2013 for the Vaal Triangle Monitoring Network.

The concentrations of CO were not elevated at any of the sites during the period of elevated ozone concentration. Increases in the CO concentration in the early evening are typically associated with domestic combustion activities in the low income residential areas surrounding the stations. Figure 9 on next column.

The concentration of NO_x does not show a significant elevation during the period of high ozone concentration, while there is an increase between 12:00 and 14:00 this does not discriminate between the stations that show higher levels of ozone and those that do not. Figure 10 on next column.

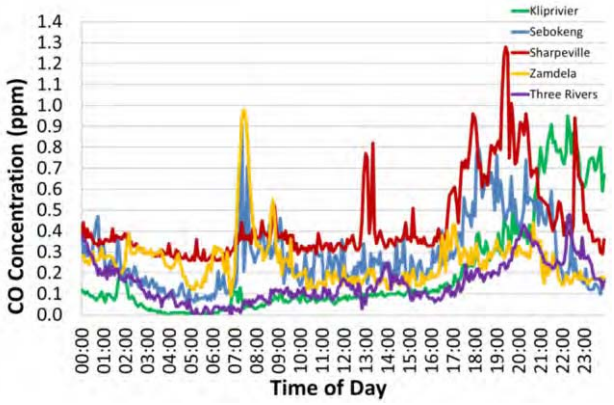

Figure 9 Time Series of CO concentration (ppb) on the second of June 2013 for the Vaal Triangle Monitoring Network.

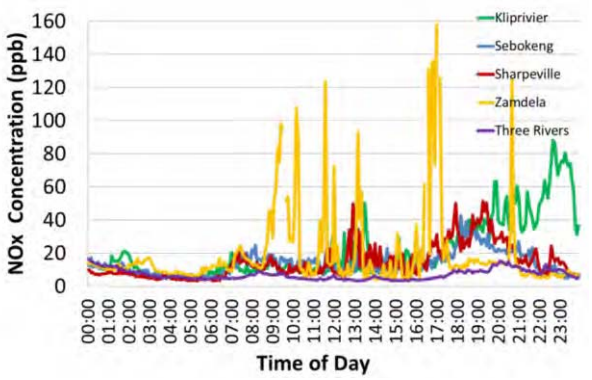

Figure 10 Time Series of NOx concentration (ppb) on the second of June 2013 for the Vaal Triangle Monitoring Network.

Analysis of the concentrations of benzene on the 2 June 2013, do not show significant changes in the benzene concentration during the period of elevated ozone concentration, a similar pattern is seen for the other VOC's measured including Xylene and Toluene.

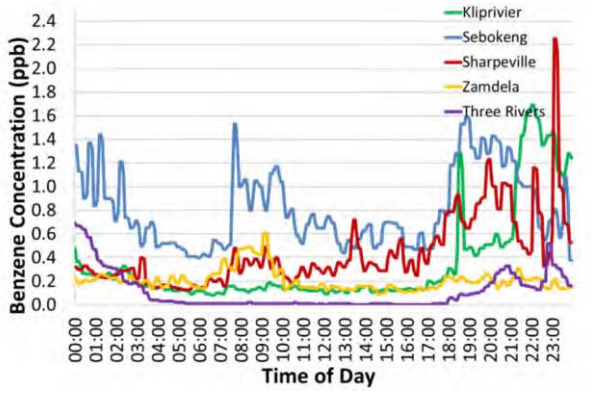

Figure 11 Time Series of Benzene concentration (ppb) on the second of June 2013 for the Vaal Triangle Monitoring Network.

3.3 Atmospheric Conditions over the Vaal Triangle on 2 June 2013

During the time of the reported period of elevated ozone the synoptic conditions in South Africa were represented by a strong frontal system that was crossing the country from the south west, preceded by a surface trough extending from the north west to the south east over the interior of the country. The area ahead of the front typically experiences stable conditions with the occurrence of dry descending air. The synoptic chart for the 2 June 2013 is presented in Figure 12.

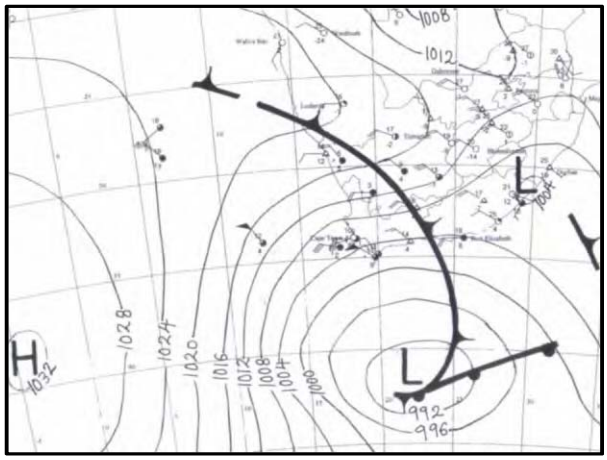

Figure 12 Synoptic chart on the 2 June 2013 14:00 SAST(SAWS, 2013)

The atmospheric profile was obtained for the upper air balloon assent on the second of June. The vertical profile taken at the Irene Station shows that there is a strong inversion layer between 2133m and 2308m above ground level (Figure 13). The tropopause is situated at 13000m above ground level. Examination of the radiosonde measurements from the previous week indicate that the inversion was in place for a number of days prior to the reported incident.

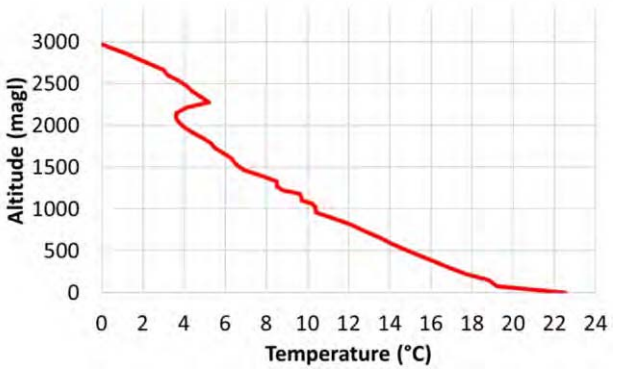

Figure 13 atmospheric temperature profile taken at the Irene weather Station

3.4 Back trajectory and wind analysis

A back trajectory analysis of the air mass carrying the elevated concentrations of ozone was conducted using Hysplit trajectory model where the back trajectory for a period of 24 hours was analysed for all stations. The back trajectory analysis (Figure 14) shows that the air mass originated in the Waterberg region directly over the town of Lephalale, which is the location of a large coal fired power station, it then moved due south, passing over the Bojanala District and the Platinum mining activities in the region before passing over the gold mining region of Randfontein, located to the west of Johannesburg. During the time of the elevated ozone concentration the wind at the monitoring stations was from the north-west and north-north-west with a wind speed of between 5.7m/s to 11m/s (Figure 15).

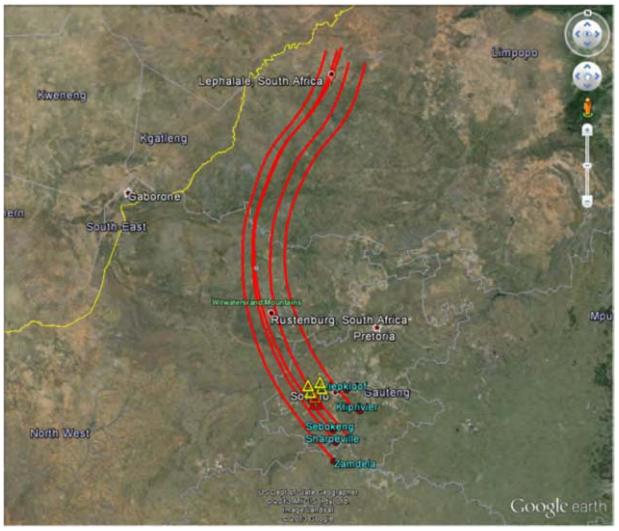

Figure 14 24 hour back trajectory analysis for the stations recording elevated ozone

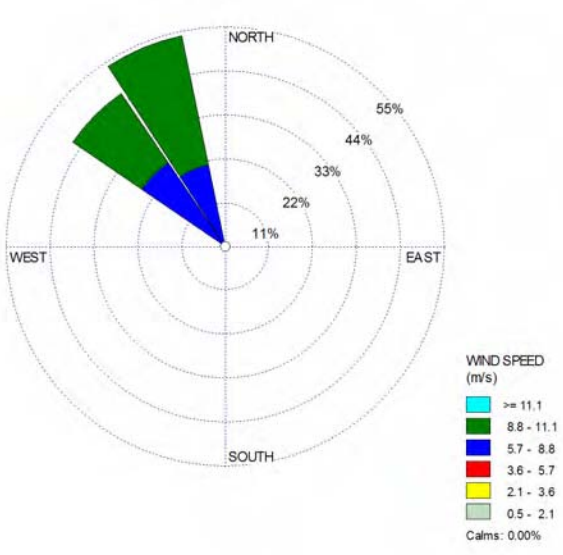

Figure 15 Wind-rose, Sebokeng station for the period 9:00 - 16:00

3.5 Fire Occurrence

Satellite Information from EUMETSAT MSG was used to identify the location and intensity of veld fires in the region which may have impacted on the production of ozone precursors and ultimately resulted in the extremely high concentrations of tropospheric ozone that were observed over some of the stations in the Vaal Triangle on the 2 June 2013. During the second of June there was considerable biomass burning in the central regions of South Africa. Figure 13 shows the EUMETSAT MSG output over the Vaal Triangle region. Of those fires, six were within the direct path of the air mass that carried the high ozone concentration those being the fires located to the north west of the stations as shown in Figure 16.

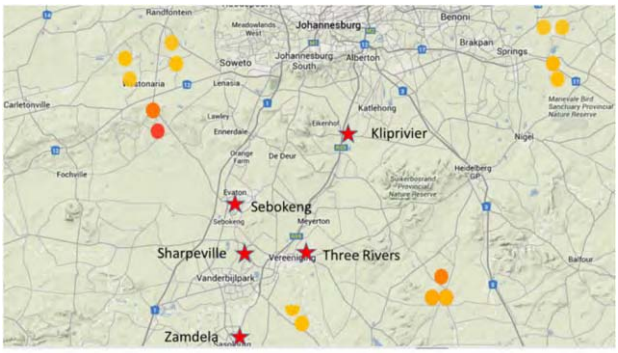

Figure 16 Occurrence of wild fires over Vaal Triangle Region on the 2nd June 2013

4 Discussion

The period of high ozone concentrations that was reported at some of the stations in the Vaal Triangle on the 2nd of June 2013 is unusual in terms of the magnitude of the increase in the ozone concentration. The peak in the ozone concentration is associated with increases in the concentrations of particulate matter, especially of the PM_{10} size classes, but also the concentration of black carbon. The concentrations of CO, SO_2, NO_x and benzene did not show significant changes associated with the elevation in ozone concentration. Back trajectory analysis indicates three potential sources for the ozone precursors that fell within the path of the air mass arriving at the monitoring stations. Those include; 6 wild fires that were active 30 km to 40 km to the north west of the monitoring stations, the mineral processing activity in the Bojanala district surrounding Rustenburg and the coal fired power station at Lephalale approximately 300km to the north of the monitoring stations where the air mass originated 24 hours previously.

Analysis of the corresponding concentrations of other pollutants provides some indication as to which of the potential sources of the precursors is responsible for the high ozone concentrations reported on the day. It is expected that if the source of the ozone precursors responsible for the formation of the ozone peak observed at the Sharpeville, Sebokeng and Zamdela stations was due to industrial activity such as the combustion of coal or the processing of sulphate rich minerals, the peak in ozone concentration would be associated with increases in the concentrations of SO_2 and NO_x. This however did not occur. It is known that the NO_x and SO_2 in power station plumes can be removed rapidly through chemical processing (Zhou et al., 2012). The SO_2 and NO_x loss is reported to be greater under cloudy conditions.

However if the production of ozone is associated with a biomass combustion source the ozone peak would associated with increases in the concentrations of PM and specifically black carbon as a product of incomplete combustion. In this case the temporal changes in the concentration of the other monitored pollutant indicate that the source of the ozone precursors is likely to be biomass burning. The wind direction and location of fires in the Vaal Triangle region strengthen this explanation. Analysis of ozone production in African biomass burning plumes, has reported elevations of the ozone concentration of up to 98ppb 18km downwind of savanna fires in South Africa (Yokelson et al., 2003).

5 Conclusion

The management of ambient air quality in complex environments such as the Vaal Triangle can be difficult; this is especially true for secondary pollutants such as ozone, which are formed through the interaction of numerous chemical precursors and the environmental conditions. This study presents an analysis of the chemical and environmental conditions during a period of extremely high ozone concentration. Evidence suggests that biomass burning played an important role in the period of elevated ozone, but other factors such as the long range transport of precursors from power generation and mineral processing activities may have played a role in allowing for such high concentrations of ozone to be formed. Further modelling to better understand the chemical processes and the precursor concentration requirements would help in understanding the processes that occurred and identify the precursor sources, thus enabling focused management interventions on the local or regional scales.

6 References

Chameides, W. L., Fehsenfeld, F., Rodgers, M. O., Cardonelino, C., Martinez, J., Parrish.D, … Wang, T. (1992). Ozone Precursor Relationships in the Ambient Atmosphere. Journal of geophysical Research, 97(91), 60376055. doi:0148-0227/92/9IJD-03014$05.00

Crutzen, P. J., & Lelieveld, J. (2001). Human impacts on atmospheric chemistry. Annual Review of Earth and Planetary Sciences, 29(1), 1745. Retrieved from http://www.annualreviews.org/doi/abs/10.1146/annu

rev.earth.29.1.17

DEA. (2009). National Ambient Air Quality Standards. Government Gazette, 4.

SANAS. (2012). Tr 07-03 Supplementary Requirements for the Accreditation of Continuous Ambient Air Quality Monitoring Stations (pp. 112).

SAWS. (2013). Daily Weather Bulletin 2 June 2013 (p. 2). Pretoria.

Seinfeld, J. H., & Pandis, S. N. (2006). Atmospheric Chemistry and Physics (2nd ed., p. 1203). Hoboken: John Wiley and Sons.

Silva, R. a, West, J. J., Zhang, Y., Anenberg, S. C., Lamarque, J.-F., Shindell, D. T., … Zeng, G. (2013). Global premature mortality due to anthropogenic outdoor air pollution and the contribution of past climate change. Environmental Research Letters, 8, 034005. doi:10.1088/1748-9326/8/3/034005

Trade and Industry Chamber. (2004). Funds for Research into Industrial Development Growth and Equity (FRIDGE) Study to examine the potential socia-economic impact of measures to reduce air pollution from combustion.

Van Rooi, W. (2012). Advanced Fire Information System. Retrieved from http://www.techtransfer.csir.co.za/2012/09/advanced-fire-information-system/

WHO. (2013). " Review of evidence on health aspects of air pollution REVIHAAP " (p. 29). Retrieved from http://www.euro.who.int/__data/assets/pdf_file/0020/182432/e96762-final.pdf

Yokelson, R. J., Bertschi, I. T., Christian, T. J., Hobbs, P. V, Ward, D. E., & Hao, W. M. (2003). Trace gas measurements in nascent , aged , and cloud-processed smoke from African savanna fires by airborne Fourier transform infrared spectroscopy (AFTIR). Journal of Geophysical Research, 108(D13), 8478. doi:10.1029/2002JD002322

Zhou, W., Cohan, D. S., Pinder, R. W., Neuman, J. a., Holloway, J. S., Peischl, J., … Zheng, W. G. (2012). Observation and modeling of the evolution of Texas power plant plumes. Atmospheric Chemistry and Physics, 12(1), 455468. doi:10.5194/acp-12-455-2012