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Keywords : *Tropospheric ozone, oxides of nitrogen, seasonal variations.*

GJSFR-B Classification : *FOR Code: 039901*

SEASONAL VARIATIONS OF TROPOSPHERIC OZONE CONCENTRATIONS

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Seasonal Variations of Tropospheric Ozone Concentrations

Nnenesi A. Kgabi [α] & Ramotsamai M. Sehloho [σ]

Abstract - This study shows strong seasonality of ground level ozone concentrations with spring (September and October) maximum and winter (May and June) minimum levels. The levels were observed in decreasing order per season as: spring>summer>autumn>winter. The Johannesburg ozone levels were much lower than Botsalano and Marikana levels. The monthly levels for the 2007 to 2008 period were determined in order of decreasing abundance as Marikana (21.07 – 50.02 ppb), Botsalano (28.17 – 37.94 ppb), Buccleuch (2.03 – 23.42 ppb), Delta (5.76 – 17.32 ppb) and Newtown (1.73 – 17.19 ppb). The precursors of ozone (NO_x, NO_2, and NO) also showed peaks in winter (May-June). Anti-correlation of ozone and its precursors (NO_x, NO_2, and NO) were also observed. The authors also conclude that the formation of ozone in Johannesburg occurs under the VOC-sensitive regime, and that the possible sources of ozone in the city are vehicular and industrial and businesses.

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I. Introduction

Ozone is considered as a pollutant at ground level and the overall effect of its exposure leads to decrease of lung capability to perform normal function. The reduction of surface ozone which is harmful to human health, animals, and plants, is an important objective of air quality policy for many governments (Reddy et al, 2011).

Ground level ozone (O_3) is a major component of smog, produced in the troposphere by the catalytic reactions of nitrogen oxides (NO_x = NO + NO_2) with carbon monoxide (CO), methane (CH_4), and non-methane volatile organic compounds (NMVOCs) in the presence of sunlight (Avnery et al, 2011). Exposure to elevated concentrations of surface ozone (O_3) causes substantial reductions in the agricultural yields of many crops. As emissions of O_3 precursors rise in many parts of the world over the next few decades, yield reductions from O_3 exposure appear likely to increase the challenges of feeding a global population projected to grow from 6 to 9 billion between 2000 and 2050 (Avnery et al, 2011). Through the absorption of infrared radiation at 9.6 mm, ozone also acts as a greenhouse gas, which has implications for the global climate. Even though the warming effect of ozone is small compared to gases such as CO_2, methane, and water vapor, at ~0.35 W m^{-2}, it is still significant (Intergovernmental Panel on Climate Change, 2007).

About 50% of all large biomass fires on earth occur in Africa (Hao et al., 1991) where burning emissions are strongest in the dry season mainly south of the equator between July and October. Of these fires, 50% is attributed to savanna burning, 24% to shifting cultivation, 10% deforestation, 11% domestic burning and 5% agricultural waste burning (Hao and Liu, 1994). These biomass sources make a 35% contribution to global photochemical ozone formation (Marufu, 1999). According to Zunckel et al. (2004), mean surface ozone concentrations exhibit strong seasonal and diurnal variations over Southern Africa. The major anthropogenic source regions of atmospheric pollutants in southern Africa are the mining and smelting activities on the Copperbelt in northern Zambia and emissions from coal in the South African Highveld (Fleming and van der Merwe, (2002).

Levine et al. (1996) indicated that biomass burning is a major source of gases and aerosols in the Southern African atmosphere. Biomass burning is seasonal and occurs almost exclusively during winter and spring, July to September. Biomass burning of the African savannas is known to produce large amounts of photochemically active aerosols and trace gases that are necessary precursors of tropospheric ozone (Crutzen and Andreae, 1990).

Biomass burning, fossil fuel combustion, and other anthropogenic activities generate CO, CH_4, VOCs, etc., which are oxidized to ozone in a NO_x-rich environment. The main sources of NO_x are fossil fuel combustion, biomass burning, soil microbial activity, and lightning. NO plays a critical role in ozone production, even in rural regions, where NO concentration is higher than 10 parts per trillion (ppt) (Lin et al., 1988). Emissions of NO_x are produced primarily when fossil fuels are burned in motor vehicle engines, power plants, and industrial boilers. Mobile sources (including on-road and others) of NO_x include emissions from aircraft, trains, ships, recreational boats, industrial and construction equipment, farm equipment, off-road recreational vehicles, and other equipment. Stationary sources include both internal and external combustion processes in industries such as manufacturing, food processing, electric utilities, and

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petroleum refining. Area-wide sources include residential fuel combustion, waste burning, and fires (Drechsler et al., 2006).

Besides the photochemical reactions affected by solar radiation and variations in anthropogenic emissions, boundary layer processes and meteorological parameters also play important roles in the process of diurnal variations in O_3 and its precursors. Ozone concentrations depend sensitively upon meteorological parameters such as temperature, sunlight, wind speeds and the mixed layer depth. Therefore, changes in these meteorological parameters due to climate change will necessarily impact surface ozone concentrations (Reddy et al, 2011). Meteorology also plays a crucial role in the formation, dispersion, transport, and dilution of ozone in the atmosphere (Elminir, 2005; Tu et al., 2007).

In this study, monthly ground level ozone concentrations were measured at Botsalano Game Reserve and Marikana in the North West province (which depends mostly on agriculture and mining activities); and Buccleuch, Delta, and Newtown in Johannesburg - Gauteng province (which is highly industrialized and is mostly urban); and the relation between ozone and NO_x, NO_2, and NO was also determined. The significance of this study is on provision of knowledge of the interactions between O_3 and its precursors, which according to Mioduszewski et al, (2011) is also crucial to understanding their atmospheric concentrations and lifetimes and the environmental impacts that can be expected with modifications to their sources and sinks. The study presents observations and analysis of the seasonal variations in tropospheric ozone (O_3) in association with its precursors, nitrogen oxides $(NO_x = NO + NO_2)$, and the meteorological conditions; thus giving a better understanding of the relationship between ozone precursors and formation of ozone in industrialized and non-industrialized environments, which is also a critical pre-requisite for development of effective O_3 control strategies.

II. Material and Methods

Environment SA 41 m UV photometric ozone analyzer was used to measure ozone concentrations in Botsalano and Marikana during the period 2007 to 2008. The ozone analyzer operates on a full scale of 0 – 500 ppb, at a temperature range of 10^oC to 35^oC, with response time setting of 11 (Automatic response time), and with or without any of the internal ozone generator, and span external control (zero/span solenoid valve) (www.epa.gov/ttn/amtic/criteria.html). The UV photometric method is not subject to interference from any of the common gaseous pollutants.

The ozone analyzer has three major systems: the optical system, the pneumatic system, and the processing electronic system. Pneumatic system consists of sample probe, sample inlet line, particulate filter which eliminates the dust particles contained in the sample to be analyzed, solenoid valves, and scrubber, internal tubing, flow meter which maintains the necessary flow in the measurement system, and pump, all used to bring ambient air samples to the analyzer inlet (McElroy and Nees, 1997).

The ozone concentrations were measured continuously and air sampled 24 hours a day by a pump which passed first through exchangeable Teflon filter. The filter was changed after every two weeks.A detector measured the light intensity in the absence of ozone and the Beer-Lambert equation was used to calculate the concentration of ozone from ratio of the light intensity (US EPA, 1996). The data logger was connected to the instruments to log the data to the computer. The data for temperature, relative humidity, rain, and wind speed and wind direction were also recorded and stored daily.

Calibration of the ozone analyzer is carried out until the preset values of reading in the analyzer match the current applied to the UV lamp. The O_3 determination is based on a commercial instrument using UV mercury absorption of 253.7 nm radiation. The O_3 analyzer is so designed that it absorbs ozone at 253.7 nm, and the UV mercury lamp used in the instrument also emits light of the same wavelength. The calibration factor is not be required in this process. The detector is employed before and after the absorption takes place in the fixed length flow path. So the variations in the intensity of the light are balanced. In order to check the zero reading of the analyzer zero air has to be admitted which is free of ozone. If the analyzer is reading a higher value for zero air, then the ozone scrubber in the analyzer needs to be changed; for which the analyzer scrubbers continually check the zero every 10 s and goes to the sample line (Reddy et al, 2008).

Temperature and relative humidity were measured using Rotronic MP 101A (Vaisala HMP50), rain intensity was measured using Thies 5.4103.20.041 Adolf Thies GmbH Co.KG, and wind direction and wind speed were measured using Vector A101ML (Vector W200P). Data on three monitoring stations (Buccleuch, Delta, and Newtown) in Johannesburg were supplied by the Johannesburg City and the South African weather Services.

Figure 1 shows the location of study sites within Gauteng (Buccleuch, Delta, and Newtown) and North West Province (Botsalano and Marikana). The Botsalano game reserve is situated 18 km east of Ramatlabama (Botswana – South Africa) border post, and 65 km north of Mafikeng. The Game Reserve is situated between longitude 25degrees 32' 30.4" south and latitude 25degrees 45' 17.8" east and is far from the central business districts and mining industries. Ozone concentrations and meteorological parameters were

also measured at Marikana municipal offices, with a community health clinic, community hall and library buildings in the same location. Marikana is a township situated between longitude 27°21'53.61" south and latitude 27°28'36.58" east, located to the east of Rustenburg, a pollution hotspot in the North West Province.

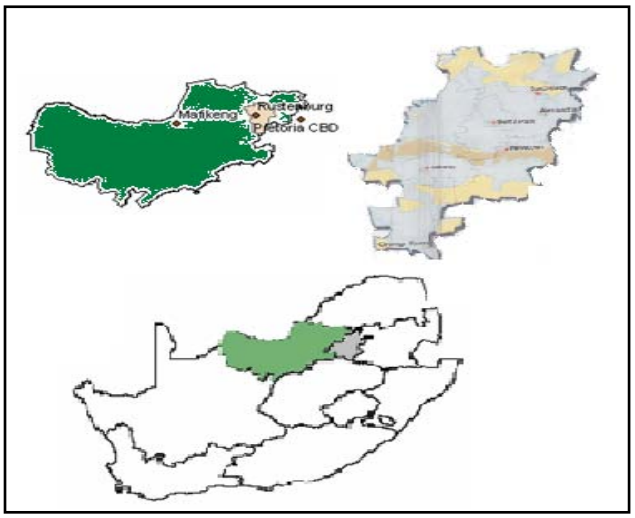

Figure 1 : Location of the study sites within North West (green shading) and Gauteng Province (grey shading) of South Africa.

The Newtown station (Latitude: -26.2052; Longitude: 28.0321) located within Johannesburg Central Business District measures urban, commercial and industrial emissions; the Buccleuch station is located at the intersection of the N1 and M_1 highways (Latitude: -28.0453; Longitude: 28.0991) within the City of Johannesburg to measure vehicle emissions; and the Delta Park (Latitude: -26.125; Longitude: 28.0086) is located with the Delta Park Environmental Centre. This station is not exposed to any direct emissions from air pollution sources. However, measured concentrations at this station compare well with the rest of the stations and it is therefore not representative of background concentrations.

III. Results and Discussion

a) Monthly Ozone Concentrations and Meteorology

i. *Monthly ozone concentrations for Botsalano Game Reserve and Johannesburg during 2007*

Ozone formation is high during summer, long hours of sunlight and high temperatures speed up the ozone forming photochemical reactions. Low wind leads to the build-up of high local pollutants concentrations and high wind speed promotes the dispersion of ozone precursors and wind direction turn to direct the precursors for the source point to the area without large sources (Goddish, 1991). An increase in relative humidity leads to the decrease in ozone levels (Li et al., 2007).

Figure 2 shows that highest monthly mean ozone concentration was observed in October (37.94 ppb), and the lowest concentration was observed in July (28.17 ppb). The results also show seasonal variations, with the maximum occurring in spring to early summer, and minimum during the autumn to winter period.

The low ozone concentrations were observed in July when temperature and wind speed were also low, and there was no precipitation. The low ozone concentration in winter months is associated with low ambient temperatures (Altshhuler, 1975).

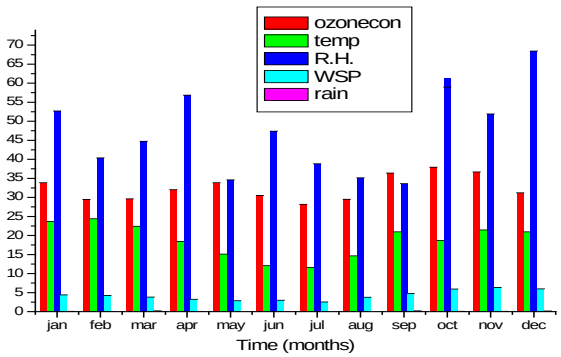

Figure 2 : Monthly mean ozone concentrations and meteorology at Botsalano in 2007.

The monthly maximum observed in October occurred at monthly average temperature of 18.66 ^{0}C and relative humidity of 61.19%. A positive correlation of ozone with temperature and wind speed was obtained as 0.30 and 0.62 respectively. A spring maximum and winter minimum was also observed from monthly concentrations at Etosha, Namibia during the period June 2000 to May 2002, were a maximum (30 ppb) was measured in October 2000 and a minimum of about 11 ppb in March 2001 (Zunckel et al, 2004).

Similar trends in ozone concentrations were also observed in the same year (2007) at three monitoring sites (Figure 3) within the heavily industrialized city of Johannesburg. The minimum levels were measured in winter (June and July) and a maximum in September.

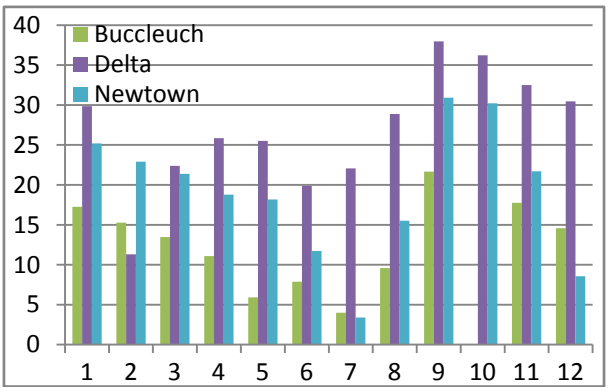

Figure 3 : Monthly mean ozone concentrations at the city of Johannesburg in 2007.

The monthly levels ranged from 3.98 to 21.66$\mu g/m^3$ (2.03 to 11.03 ppb) for Buccleuch, from 11.31 to 37.97 $\mu g/m^3$ (5.76 to 19.33 ppb) for Delta;and 3.39 to 30.92 $\mu g/m^3$ (1.73 to 15.74 ppb) for Newtown. The levels observed in the three sites were however lower than the Marikana levels for the same year.

ii. *Monthly ozone concentrations for Marikana and Johannesburg during 2008*

Minimum levels (21.07 ppb) were observed at Marikana in April 2008 and a maximum in October (50.02 ppb) as shown in Figure 4. A positive correlation between ozone and temperature, and ozone and wind speed, with correlation coefficients of 0.38 and 0.29 respectively was also observed. The observed high concentrations during spring can be attributed to the higher temperatures which promote photochemical generation of ozone. The concentration of ozone increases with the increase in the temperature (Garcia et al., 2005). Clear skies, warm temperatures have a great influence on ozone concentrations (Vecchi and Valli, 1999). Ozone concentrations increased with temperature at this site, and relative humidity was high when both temperature and ozone concentrations were low, with a moderate wind speed.

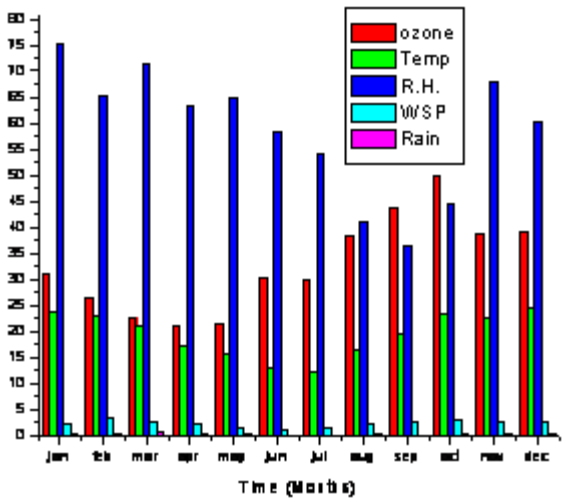

Figure 4 : Monthly average ozone and meteorology 2008.

Zunckel et al (2004) found that the seasonal maximum surface ozone in the Southern African regions generally occur in the spring months to early summer, that is from August to November. The solar radiation becomes intense in spring, causing photochemical reactions of ozone precursors that were accumulated during winter and this contribute to high ozone concentration to be observed during spring. The long lifetime of ozone in winter, which is about 200 days, also allows the anthropogenically formed ozone to accumulate in the inversion layer and then contributes to the high spring ozone concentrations (Monks, 2000). Three monitoring sites (Figure 5) within the heavily industrialized city of Johannesburg showed minimum levels from autumn to winter (April to July) and high levels from spring to early summer (September to November), with a maximum in October.

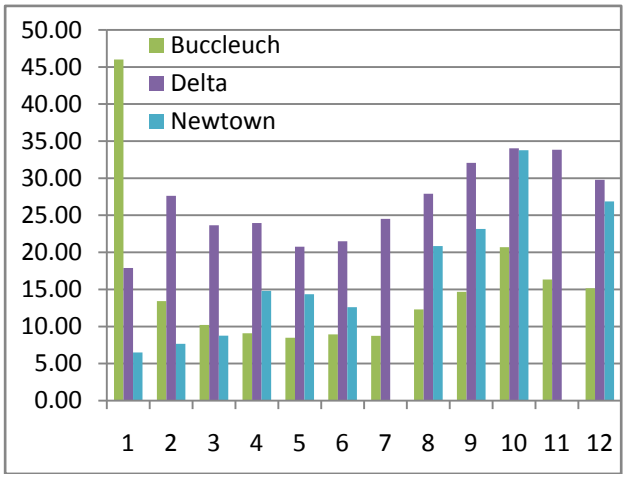

Figure 5 : Monthly mean ozone concentrations at the city of Johannesburg in 2008.

The ozone concentrations for Johannesburg sites were measured in the range of 8.48 - 46.01 $\mu g/m^3$ (4.32 - 23.42 ppb), 17.89 - 34.03 $\mu g/m^3$ (9.11 - 17.32 ppb), and 6.50 - 33.78 $\mu g/m^3$ (3.31 - 17.19 ppb), for Buccleuch, Delta, and Newtown respectively.

The City of Johannesburg has a temperate climate, experiencing over eight hours of sunlight per day in both winter and summer. Temperatures are mild with average maximum day-time temperatures of 26 °C in January, dropping to 16 °C in June. Rainfall averages about 710 mm per annum although significant inter-annual variation in total rainfall is experienced. Rainfall occurs predominantly during the summer months in late afternoon electrical storms.

Significant positive correlation coefficients were also found between O_3 and temperature by Khoder (2010) in two seasons and between O_3 and relative humidity in the summer season, indicating that high temperature and high relative humidity besides the intense solar radiation (in summer) are responsible for the formation of high O_3 concentrations.

The low levels observed in autumn can be due to the non-availability of enough solar radiation due to the cloudy skies that reflect back the solar radiation from reaching the surface, and also the washouts of air pollutants from the atmosphere by precipitation. The highest ozone concentrations occurred in Botswana and Mpumalanga, in both regions the spring time maximum was between 40 and 69 ppb, but reached an average of more than 90 ppb on October 2000. Zunckel et al. (2004) found that minimum average monthly ozone concentration occurred in December and January.

For the 2007 and 2008 period, similar seasonal variations of ozone concentrations were observed at two different environments. A general representation of the variations of ozone can be given in order of decreasing concentrations as follows: spring, summer, autumn, and winter for all the study sites. The levels were also similar to those reported by Lacaux et al. (1993) (between 30 and 40 ppb) in central Africa during 1983 and 1988. Combrink et al. (1995) also obtained surface ozone concentrations in the range between 25 and 50 ppb at two stations in South Africa.

b) Ozone and the Oxides of Nitrogen

i. *Monthly Ozone and the Oxides of Nitrogen*

Photochemical production of ozone associated with emissions of CO, hydrocarbons and NO_x from biomass burning may contribute significantly to high values of ozone, Logan and Kirchhoff (1986). The figures 6, 7 and 8 below show the monthly levels of NO_x, NO_2, and NO measured from January to December 2007 at the Buccleuch, Delta, and Newtown monitoring stations within Johannesburg. The occurrence of high NO_x concentrations in all the three stations is resultant of the sum of NO_2 and NO, and may also be caused by anthropogenic sources of NO_x that occur throughout the southern African region (Fleming and van der Merwe, 2002) and soil emissions (Levine et al., 1996).

High ozone concentrations might be registered within a city or at a distance downwind because of the high emissions of precursors in urban areas. These precursors may also be transported over long distances, resulting in ozone formation far from the sources under the influence of meteorological conditions (Hastie et al., 1999). Thus, the potential for high ozone concentrations in an area that has small amounts of local nitrogen oxides and non-methane hydrocarbons is created, as reported by Cheng (2001). A similar observation was made at the Delta station (Figure 6) throughout the 2007 monitoring period, where ozone concentrations (11.31-37.97 μg/m3) were higher than the NO (1.96 – 17.98 $\mu g/m^3$) and NO_2 (8.76 – 22.28 $\mu g/m^3$), and lower than NO_x (13.49 – 45.23 $\mu g/m^3$) levels.

High levels of NO_x, NO_2 and NO were observed in winter (May to July), and O_3 in spring (September-October).

The oxides of nitrogen, (NO_x ($NO+NO_2$) mainly emitted into the atmosphere as NO, which is subsequently transformed into NO_2 and other nitrogenous species play important roles in controlling the oxidative chemistry of the lower atmosphere, including regulation of the photochemical production of ozone, nitric acid and organic nitrates (Adon et al, 2010).

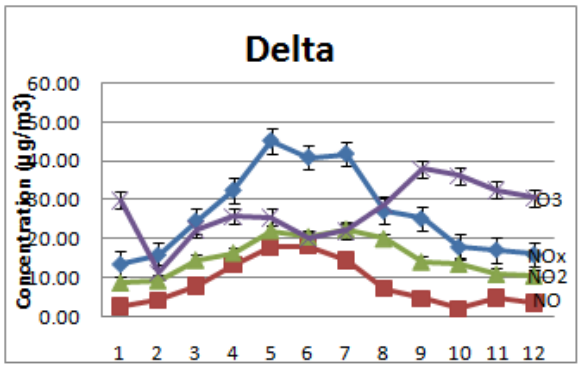

Figure 6 : Concentrations of ozone, NO_x, NO_2, and NO at the Delta station.

The Buccleuch station (Figure 7) however, reported low ozone levels (3.98 – 21.66 $\mu g/m^3$) with high NO_x (85.98 – 232.54 $\mu g/m^3$), NO_2 (17.06 – 73.56 $\mu g/m^3$), and NO (69.66 – 197.17 $\mu g/m^3$) concentrations for the same period (January to December 2007).

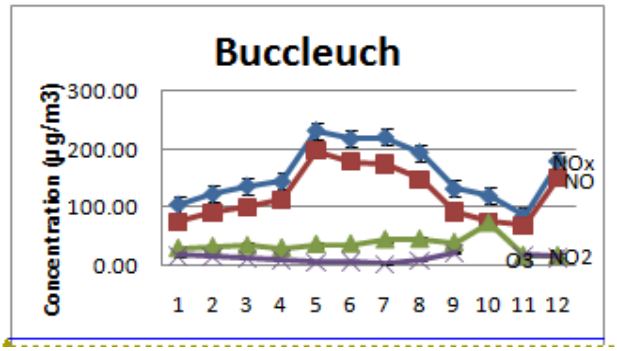

Figure 7 : Concentrations of ozone, NO_x, NO_2, and NO at the Buccleuch station.

Figure 8 shows the levels for Newtown as follows: ozone (3.39 – 30.92 $\mu g/m^3$), NO_x (33.93 – 104.44 $\mu g/m^3$), NO_2 (18.80 – 36.15 $\mu g/m^3$), and NO (16.53 – 96.09 $\mu g/m^3$), indicating the low ozone high NO_x, NO_2, and NO relation. The high levels of NO_x and NO were observed in winter (May to July), for NO_2 in spring (October), and O_3 in spring (September). An inverse relation between ozone and the oxides of nitrogen is evident in this site/station.

Favorable conditions for photochemical O_3 production are high temperature, high intensity of solar radiation, and sufficiently high concentrations of NO (Naja and Lal 2002).

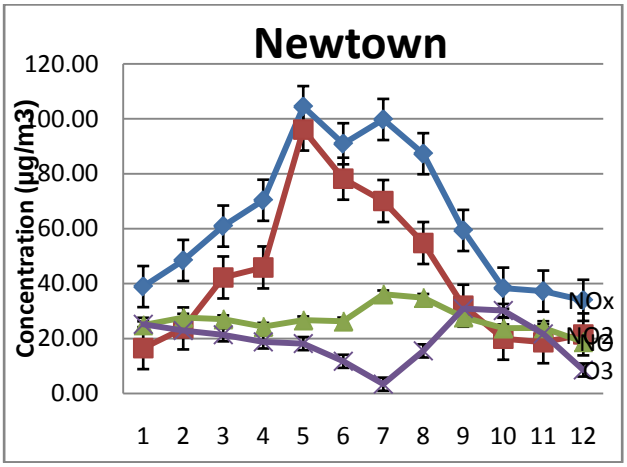

Figure 8 : Concentrations of ozone, NO_x, NO_2, and NO at the Newtown station.

Elevated NO_2 concentrations in the Newtown station are associated with the City's highways (N3, N1, M_2 and M_1) and the Central Business District (CBD) due to vehicle tailpipe emissions. Although elevated O_3 concentrations were anticipated to occur across the City, the main impact areas associated with the emission of O_3 precursors from sources within the City occur within areas to the south and south-east of the City due to the prevailing airflow patterns (ICF International, 2009).

An increase in ozone levels as NO_x, NO_2, and NO decreases is evident for the Buccleuch and Newtown sites within Johannesburg. High levels of NO_x, NO_2 were observed in winter (May and June) and for O_3 in spring (September and October). The seasonal behavior of NO_x, and NO_2 (peaks in winter) observed for the three sites may suggest fuel/biomass burning as one of the sources of ozone precursors. Excessive NO_x in urban areas is unbeneficial for the accumulation of ground-level ozone. O_3 shows a well-defined seasonal variation at these sites. The low values appear in winter, while the high values appear in early summer. This is attributed to the higher NO_x concentration from vehicular emission and also due to the fast titration of O_3. This feature of ozone variations distinguishes the urban and rural sites (Reddy et al, 2011).

Percentage contribution to the total NO_x measured in Johannesburg was determined by ICF International, (2009) as 86.9 for area sources, vehicular sources (7.9), industrial sources (5.2). The main area sources were identified as domestic cooking fuel use and emissions from small industrial facilities and businesses.

ii. *Correlation of O_3 to NO_x, NO_2, NO*

Anti-correlation between O_3 and NO_x, NO_2, and NO is evident for the three study sites as shown in Table 1.NO and NO_2 shown a negative correlation at Buccleuch, strong positive correlation at Delta, and weak positive correlation at Newtown. The NO concentrations were highly correlated to NO_x for the three sites. NO_2 levels showed high correlation to NO_x for Delta and Newtown, and a weak positive one for Buccleuch.

Table 1: Correlation matrix for the Johannesburg study sites.

	O_3	NO	NO_2
Delta			
NO	-0.43		
NO_2	-0.16	0.84	
NO_X	-0.28	0.96	0.94
Buccleuch			
NO	-0.78		
NO_2	-0.46	-0.02	
NO_X	-0.85	0.98	0.12
Newtown			
NO	-0.51		
NO_2	-0.29	0.47	
NO_X	-0.51	0.96	0.68

The observed nonlinearities may be due to the fact that ozone production potential per unit NO_x increases as NO_x concentrations decrease (Atherton et al. 1996).

The most important biogenic emission for tropospheric ozone production is the direct emission of nitric oxide (NO) from recently wetted-soils (Williams et al, 2009). For instance, Jaegle et al. (2004) investigated the spatial and seasonal variation of the release of NO from soils, and concluded that such soil emissions account for approximately 40% of surface NO_x in Africa, affecting $3X10^6$ km^2 of sub-Saharan Africa during the wet season. Once emitted, NO is oxidized to NO_2 via the reaction with HO_2, CH_3O_2 or O_3. This additional NO_2 can then be either rapidly photolysed (producing O_3) or react with reactive free-radical species such as OH, HO_2 or $CH_3C(O)O_2$ to form more stable reservoir species for reactive nitrogen, namely HNO_3, HNO_4 or PAN.

The reason for the winter anomaly is biological activity in the ground related to the availability of the water during the humid season, which increases NO emissions (Otter et al., 1999).

It may not be possible to calculate and draw conclusions on ozone formation budgets without measuring the levels of VOC's since the two (oxides of nitrogen and VOC's) play an important role in ozone formation. The anti-correlation observed between NO_x and O_3 in the three sites however, suggests that formation of ozone in Johannesburg occurs under the VOC-sensitive regime, which according to (Geng et al,

2009), is associated with a decrease in O_3 concentrations with enhancement of NO_x concentrations.

iii. *Annual Ozone and the Oxides of Nitrogen*

Annual levels for the three Johannesburg stations in Table 2 show a general decrease in annual O_3, NO_x, NO_2, and NO levels from 2007 to 2009 for the Delta study site. Annual average ozone levels also decreased during the 1984-1986 period from 0.037 ppm to 0.016 ppm, then steadily increased to 0.033 ppm in 1990, and has since decreased and leveled out around 0.028 ppm. Annual average NO_2 levels at South Hills dropped from 0.1 ppm in 1984 to 0.02 ppm in 1985, and have since mainly fluctuated around this level (GJMC, 2000).

The ozone levels at Buccleuch showed no specific trend whilst a decrease in NO_x, NO_2, and NO levels from 2007 to 2009 was observed.

Table 2 : Annual levels of O_3, NO_x, NO_2 and NO.

		2007	2008	2009
		(μg/m^3)	(μg/m^3)	(μg/m^3)
O_3	Buccleuch	12.62	17.04	11.71
	Delta	26.59	26.39	23.92
	Newtown	18.77	17.47	19.54
NO_x	Buccleuch	158.37	-	122.32
	Delta	26.91	20.15	16.17
	Newtown	64.89	52.99	59.81
NO_2	Buccleuch	37.82	-	28.08
	Delta	15.27	12.91	13.41
	Newtown	26.94	26.90	26.61
NO	Buccleuch	123.92	-	94.23
	Delta	8.51	6.65	6.83
	Newtown	45.16	34.34	37.34

No specific trends were observed for Newtown except for a decrease in NO_2 levels from 2007 to 2009. A decrease in NO_x, NO_2 and NO annual averages were observed from 1995-1996 for Newtown (GJMC Photochemical Smog Monitoring Program, 1996). The Newtown station covering the central business district (CBD) showed an increase in average annual ozone levels from 0.012 to 0.013 ppm, as well as CO levels from 2.33 to 2.51 ppm during 1995/1996. A rise in ozone levels of 2-3 ppb per annum was thus estimated in the inner city by the state of the environment report (GJMC State of Air Pollution Report, 2000).

In general, annual levels for the three sites show anti-correlation of O_3 to NO_x, NO_2, and NO, which agrees with the Northern Works (sub-rural) monitoring station at the Northern sewage works within Johannesburg, where a slight increase in annual levels of NO_x (0.015-0.024 ppm), NO_2 (0.008-0.013 ppm) (15.05 – 24.45 μg/m^3) and N_O (0.002-0.012 ppm) (2.45 – 14.7 μg/m^3) from 1985-1989, and a decrease in ozone (0.033-0.015 ppm) (64.78 – 29.45 μg/m^3) and hydrocarbons (0.329-0.283 ppm) was observed (GJMC Photochemical Smog Monitoring Program, 1996).

IV. Conclusion

The study has shown that ground level ozone concentrations exhibit strong seasonality, with a seasonal maximum occurring during spring (September and October) and minimum levels in winter (May and June) for all the sites studied. This implies that high temperature and relative humidity besides the intense solar radiation in summer are responsible for the formation of high O_3 concentrations. The levels of ozone were observed in order of decreasing abundance as follows: spring, summer, autumn, and winter. Though a similar seasonal behavior was observed for Botsalano, Marikana, and Johannesburg study sites, the Johannesburg ozone levels were much lower than Botsalano and Marikana levels throughout the study. The monthly levels of ozone for the 2007 to 2008 period can be given in order of decreasing abundance as Marikana (21.07 – 50.02 ppb), Botsalano (28.17 – 37.94 ppb), Buccleuch (2.03 – 23.42 ppb), Delta (5.76 – 17.32 ppb) and Newtown (1.73 – 17.19 ppb).

The precursors of ozone (NO_x, NO_2, and NO) also showed a general seasonality throughout the study period with peaks in winter (May-June). Elevated NO_2 concentrations were observed in the Newtown station, suggesting traffic and other industrial sources.

Delta station levels were recorded as 1.96 – 17.98 μg/m3, 8.76 – 22.28 μg/m^3, and 13.49 – 45.23 μg/m^3 for NO, NO_2 and NO_x levels respectively while the levels for Buccleuch and Newtown were recorded as NO_x (85.98 – 232.54 μg/m^3), NO_2 (17.06 – 73.56 μg/m^3), and NO (69.66 – 197.17 μg/m^3); and NO_x (33.93 – 104.44 μg/m^3), NO_2 (18.80 – 36.15 μg/m^3), and NO (16.53 – 96.09 μg/m^3) respectively.

The anti-correlation of ozone and its precursors (NO_x, NO_2, and NO) was also observed, thus suggesting that the formation of ozone in Johannesburg occurs under the VOC-sensitive regime.

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References Références Referencias

1. Adon,M, Galy-Lacaux, C, Yobou´e, V, Delon, C, Lacaux, J.P, Castera, P, Gardrat, E, Pienaar, J, Al Ourabi, H, Laouali, D, Diop, B, Sigha-Nkamdjou, L, Akpo, A, Tathy, J.P, Lavenu, F, Mougin, E. (2010), Long term measurements of sulfur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in Africa using passive samplers, Atmos. Chem. Phys., 10, 7467–7487,
2. Altshuler, A.P. (1975), SO_2 and oxidants in air, In: *Fate of Pollutants in the Air and Water Environment*, Vol. 2. Wiley-Interscience Publication, 26 – 30.
3. Atherton, C.S., Grotch, S., Parrish, D.D., Penner, J.E., & Walton, J.J (1996), The role of anthropogenic emissions of NO_x on tropospheric ozone over the North Atlantic Ocean: A three-dimensional, global model study, Atmospheric Environment, 30 (10-11), 1739-1749.
4. Avnery, S, Mauzerall, D.L, Liu, J, Horowitz, L.W, (2011), Global crop yield reductions due to surface ozone exposure: 1. Year 2000 crop production losses and economic damage, Atmospheric Environment 45, 2284 - 2296
5. Brunke, E. G. & Scheel, H. E. (1998), Surface ozone measurements at Cape Point (34^0S, 18^0E). In: Bojkov R. D. & Visconti G., (Eds), Atmospheric Ozone, *Proceedings of the XVIII Quadrennial Ozone Symposium*, L'Aquila, Italy, 12 – 21 September 1996 (1998), 331 – 396.
6. Cheng W, (2001). Synoptic weather patterns and their relationship to high ozone concentrations in the Taichung Basin, *Atmospheric Environment*, 35, 4971 – 4994.
7. Combrink, J., Diab, R.D., Sokolic, F. & Brunke, E.G. (1995), Relationship between surface, free tropospheric and total column ozone in 2 contrasting areas in South Africa, *Atmospheric Environment* 29(6), 685 – 691.
8. Crutzen, P. J. & Andreae, M. O. (1990). Biomass burning in the tropics impact on atmospheric chemistry and bio-geochemical cycle. *Science* 250, 2739 – 2750.
9. Drechsler et al., (2006), In: Public Health, www.nyserda.ny.gov/Publications/ Accessed 10 April 2008
10. Elminir, H. K. (2005), Dependence of urban air pollutants on meteorology, Sci. Total Environ., 350, 225–237, doi:10.1016/j.scitotenv.2005.01.043.
11. Fleming, G., van der Merwe M. (2002). Spatial disaggregation of greenhouse gas emissions inventory data for Africa south of the equator, http://gis.esri.com/library/userconf/proc00/professional/papers/PAP896/p896.htm. Accessed 10 April 2008
12. Garcia, M. A., Sanchez, M. L., Perez, I. A., & De Torre, B. (2005), Ground level ozone concentrations at a rural location in northern Spain, *Science of the Total Environment*, 348, 135 – 150.
13. Geng, F,, Zhang, Q, Tie, X, Huang, M, Ma, X, Deng, Z, Yu, Q, Quan, J, Zhao, C, (2009). Aircraft measurements of O_3, NO_x, CO, VOCs, and SO_2 in the Yangtze River Delta region, Atmospheric Environment 43 584–593
14. Greater Johannesburg Metropolitan Council GJMC, (1996), *Photochemical Smog Monitoring Program.* Greater Johannesburg Metropolitan Council (GJMC), (2000) http://www. ceroi. net/reports /johannesburg/csoe/html/nonjava/Pollution/Air/anualairstat.htm, Accessed 20 October 2011
15. Greater Johannesburg Metropolitan Council (GJMC), (2000), *State of Air Pollution Report*, http://www.ceroi.net/reports/johannesburg/csoe/html/nonjava/Pollution/Air/state.htm, Accessed 20 October 2011
16. Goddish, T. (1991). Indoor Air Pollution, Air Quality, Michigan, Lewis Publisher Inc. Hao et al. (1991) Estimates of annual and regional releases of CO_2 and other Trace gases to the atmosphere from fires in the tropics based on the FAO statistics for the period 1975 – 1980. In*: Fire in the tropical Biota*, ed. JG Goldammer, Springer-Verlag, Berlin, pp440 – 462.
17. Hao, W.M. & Liu, M.H., (1994). Spatial and temporal distribution of tropical biomass burning. *Global Biogeochemical Cycles* 8, 495 – 503.
18. Hastie, D.R., Narayan, J., Sciller, C., Niki, H., Hepson, P.B. & Sills, D. (1999). Observational evidence for the impact of the lake breeze circulation on ozone concentrations in Southern Ontario*, Atmospheric Environment* 33, 323 – 335.
19. ICF International (2009), Final Report Sub-Saharan Africa Refinery Project, Volume 1-A: Health Study: Volume 1A, June 2009
20. Intergovernmental Panel on Climate Change (2007), Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by S. Solomon et al., Cambridge Univ. Press, Cambridge, U. K. Jaegle at al (2004), In: J. E. Williams, M. P. Scheele, P. F. J. van Velthoven, J.-P. Cammas, V. Thouret, C. Galy-Lacaux, & A. Volz-Thomas (2009), The influence of biogenic emissions from Africa on tropical tropospheric ozone during 2006: a global modeling study, *Atmospheric Chemistry and Physics*, 9, 5729–5749.
21. Khoder, M.I. (2010), Diurnal, seasonal and weekdays–weekends variations of ground level ozone concentrations in an urban area in greater Cairo, Environmental Monitoring and Assessment, Volume 149, Numbers 1-4, 349-362, DOI: 10.1007/s10661-008-0208-7

22. Lacaux et al. (1993), In: Jonnalagadda, S.B., Bwila, J.& Kosmos, W., (2001). Surface ozone concentrations in Eastern Highlands of Zimbabwe. *Atmospheric Environment* 35(25), 4341–4346.
23. Levine, J.S., Winstead, E.L., Parsons, D.A.B., Scholes, M.C., Scholes, R.J., Cofer, W.R., Cahoon Jr D.R. & Sebacher, D.I. (1996). Biogenic Soil Emissions of nitric oxide and nitrous oxide from savannas in South Africa: The Impact of Wetting and Burning. *Journal of Geophysical Research* 101(D19), 23689 – 23697.
24. Li, W., Tu, J., Xia, Z., & Wang, H. (2007), Temporal variations in surface ozone and its precursors and meteorological effects at urban sites in China, *Atmospheric Research* 85, 310 -337.
25. Lin, X., Trainer, M, and Liu, S.C (1988), On the nonlinearity of the tropospheric ozone production, J. Geophys. Res., 93, 15,879–15,888, doi:10.1029/JD093iD12p15879.
26. Logan, J & Kirchhoff, V (1986), Seasonal variations of tropospheric ozone at Natal, Brazil, *Journal of Geophysical Research,* 91(D7), 7875-7881.
27. Marufu, T.M., (1999). Photochemistry of the African Troposphere: The influence of Biomass Burning. *PhD Thesis*, University of Utrecht. Mcelroy, F. & Nees, M. (1997). Determination of Ozone by Ultraviolet Analysis. A New Method for Volume II, Ambient Air Specific Methods, Quality Assurance *Handbook for Air Pollution Measurement*. http://mattson.creighton.edu/Ozone/OzoneEPAMethod.pdf Accessed 10 April 2008.
28. Mioduszewski, J, Yu, X-Y, Morris, V, Berkowitz, C, Flaherty, J (2011), Insitu monitoring of trace gases in a non–urban environment, Atmospheric Pollution Research 2 89-98,
29. Monks, P.S. (2000). A review of the observations and origins of the ozone maximum, *Atmospheric Environment,* 34, 3545 – 3561.
30. Naja, M., Lal, S. (2002), Surface ozone and precursor gases at Gadanki (13.5_ N, 79.2_ E), a tropical rural site in India, J. Geophys. Res, 107, 4197, doi:10.1029/2001JD000357.
31. Otter, L., Yang, W., Scholes, M. & Meixner, F. (1999), Nitric oxide emissions from a southern African savannah, *Journal of Geophysical Research* 104(D15): DOI;10.1029/1999JD900148.
32. Penkett, S. A. & Brice, K. A. (1986). The spring maximum in photooxidants 406 in the Northern Hemisphere troposphere, *Nature*, 319, 655–658.
33. Penkett, S. A., Blake, N. J., Lightmann, P., Mardr, A. R. W., Ancoyl, P. & Butcher, G. (1993), The seasonal variation of nonmethane hydrocarbons in the free troposphere over the North Atlantic Ocean: possible evidence for extensive reaction of hydrocarbons with the nitrate radical, *Journal of Geophysical Research.*, 98, 2865–2885,.
34. Reddy, B.S.K., Reddy L.S.S., Cao J, Kumar K.R., Balakrishnaiah G, Gopal K.R., Reddy R.R, Narasimhulu K, Lal S, Ahammed Y.N, (2011), Simultaneous Measurements of Surface Ozone at Two Sites over the Southern Asia: A Comparative Study, Aerosol and Air Quality Research, 11: 895–902
35. Reddy R.R, Gopal, K.R, Reddy L.S.S,, Narasimhulu K., Kumar K.R, Ahammed, Y.N,, Reddy, C.V.K (2008), Measurements of surface ozone at semi-arid site Anantapur (14.62°N, 77.65°E, 331 m asl) in India, J Atmos Chem 59:47–59
36. Tu, J., Xia, Z.-G., Wang, H, and Li, W (2007), Temporal variations in surface ozone and its precursors and meteorological effects at an urban site in China, Atmos. Res., 85, 310–337, doi:10.1016/j.atmosres.2007.02.003.
37. US Environmental Protection Agency (1996), Air Quality Criteria for Ozone and Related Photochemical Oxidants, EPA/600/P-93/004Q-CF, 3-90 – 3-102.
38. Vecchi R, Valli G. (1999). Ozone assessment in the southern part of the Alps. *Atmospheric Environment* 33(1): 97–109.
39. Williams, J.E., Scheele, M.P., van Velthoven, P.F.J., Cammas, J.P., Thouret, V., Galy-Lacaux, C. & Volz-Thomas, A. (2009), The influence of biogenic emissions from Africa on tropical tropospheric ozone during 2006: a global modeling study, *Atmospheric Chemistry and Physics*, 9, 5729–5749
40. Zunckel, M., Venjonoka, K., Pienaar, J.J., Brunke, E-G., Pretorius, O., Koosialee, A.,Raghunandan A., & Van Tienhoven, A.M. (2004). Surface Ozone Over Southern Africa: Synthesis of Monitoring Results During The Cross Border Air Pollution Impact Assessment Project, *Atmospheric Environment*, 38, 619 – 6147.