Interactive comment on "Seasonal influences on surface ozone variability in continental South Africa and implications for air quality" by Tracey Leah Laban et al. (Ref. No.: acp-2017-1115)

Anonymous Referee #1

Received and published: 4 February 2018

The paper describes observations of ozone and other relevant gas phase species made over a number of years in central South Africa and attempts to evaluate the ozone production regime. The paper describes the sites used and the methodology for assessment.

There are few reported observations of air pollution in Africa and this paper provides a useful description of the regional background conditions present in South Africa. In general, the publication is suitable for publication. However, I have a couple of suggestions which might improve the usefulness of the publication. I outline my major comments and then identify some minor issues.

We would like to thank Referee #1 for the positive review of this paper through recognition of the usefulness of this manuscript and deeming this work suitable for publication in ACP. We would also like to thank Referee #1 for the major and minor suggestions made, which were each carefully considered and addressed/implemented in the paper. Below is a point-by-point response to each of these comments/questions. In addition, a marked-up version of the revised manuscript is also provided indicating all changes made throughout the manuscript. The paper was also proofread by a professional language editor.

Source of the ozone. The authors are trying to make the case that CO plays a significant or dominant role in the production of O3 over south Africa - 'Abstract: It was indicated that the appropriate emission control strategy should be CO (and VOC) reduction associated with household combustion and regional open biomass burning to effectively reduce O3 pollution in continental South Africa.' They do this through Figure 6 which shows the that trajectories arriving with high CO are the same trajectories with high O3. They back this up with the arguments from their calculation of ozone production which is essentially ranks the local O3 production for the different VOCs / CO by their OH reactivity. The difficulty with the trajectories argument is that it provides evidence of a common source (biomass burning) but doesn't necessarily show that the CO is leading to the ozone. Biomass burning is known to emit significant quantities of VOCs and NOx into an airmass, which overall leads to O3 production. Attributing the ozone production to the CO specifically from the biomass burning is difficult and probably requires a more detailed analysis than that provided here. Similarly, the local reactivity calculation shows that CO is a significant player in the reactivity, but there are not many datapoints in Figure A2 where the CO is the dominant source of the reactivity. For much of the time it appears that the aromatics, presumably from local industrial activities would outweigh the CO.

Given this, I think that the strength of the comments about the role of CO should probably be toned down. CO is obviously playing a large role here and this is surprising as CO is generally not seen as really leading to regional O3 production. However, I think a policy of reducing both the CO and the VOCs together is likely the story here rather than an emphasis on CO alone. This would probably change the emphasis of sources from those for CO alone (domestic burning, biomass burning) to include some industrial component which would presumably be the source of the aromatic compounds.

We agree with Referee #1 that the strength of the role of CO on O_3 formation should be toned down and that policy should focus on reducing both CO and VOCs. However, the significance of CO to O_3 formation for this region where biogenic VOCs are relatively less abundant (Jaars et al., 2016) is indicated in this paper, especially through the correlation plots in Fig. 9 and 10 (now Fig. 8 and 9 in the revised manuscript). Therefore the strength of the role of CO on O_3 was toned down in the manuscript in different sections and the contribution of VOCs indicated, without compromising the significance of CO on O_3 formation shown for this region in this paper. Section where changes were made are:

Abstract:

"…emissions of NO_x in the interior of South Africa. The study indicated that the most effective emission control strategy to reduce O_3 levels in continental South Africa should be CO and VOC reduction mainly associated with household combustion and regional open biomass burning."

Section 3.3.1 (now Section 3.4.1):

"…characterise the dispersion of biomass burning emissions over southern Africa (Mafusire et al., 2016). Therefore the regional transport of CO and VOCs (and NO_x to a lesser extent) associated with biomass burning occurring from June to September in southern Africa can be considered an important source of surface O_3 in continental South Africa (Fig. A4)."

Section 3.4.1 (now Section 3.5.1):

"In Fig. 8 the correlations between O_3, NO_x and CO concentrations at Welgegund, Botsalano and Marikana are presented, which clearly indicates higher O_3 concentrations associated with increased CO levels, while

O_3 levels remain relatively constant (or decrease) with increasing NO_x. The highest O_3 concentrations occur for NO_x levels below 10 ppb, since the equilibrium between photochemical production of O_3 and chemical removal of O_3 shifts towards the former i.e. greater O_3 formation. In general there seems to exist a marginal negative correlation between O_3 and NO_x (Fig. A6) at all four sites, which is a reflection of the photochemical production of O_3 from NO_2 and the destruction of O_3 through NO_x titration. These correlations between NO_x, CO and O_3 indicate that O_3 production in continental South Africa is limited by CO (and VOCs) concentrations, i.e. VOC-limited."

Section 3.4.2 (now Section 3.5.2):

"…concentrations, which is most pronounced (highest CO/NO_x ratios) during winter and spring. This indicates that the winter and spring O_3 maximum is primarily driven by increased peroxy radical production from CO and VOCs. The seasonal maximum in O_3 concentration coincides with the maximum CO concentration at the background sites, whilst the O_3 peak occurs just after June/July when CO peaked at the polluted site Marikana (Fig. A5). This observed seasonality in O_3 production signifies the importance of precursor species emissions from open biomass burning during winter and spring in this region, while household combustion for space heating and cooking is also an important source of O_3 precursors as previously discussed."

Section 3.5.2 (now Section 3.6.2):

"As indicated above (Section 3.4 and 3.5), O_3 formation in the regions where Welgegund, Botsalano and Marikana are located can be considered VOC-limited, while the highly industrialised region with high NO_x emissions where Elandsfontein is located could also be considered VOC-limited. Rural remote regions are generally considered to be NO_x-limited due to the availability of NO_x and the impact of BVOCs (Sillman, 1999). However, Jaars et al. (2016) indicated that BVOC concentrations at a savannah-grassland were at least an order of magnitude lower compared to other regions in the world. Therefore very low BVOC concentrations together with high anthropogenic emissions of NO_x in the interior of South Africa result in VOC-limited conditions at background sites in continental South Africa.

It is evident that reducing CO and VOC concentrations associated with anthropogenic emissions e.g. household combustion, vehicular emissions and industries, would be the most efficient control strategy to reduce peak O_3 concentrations in the interior of South Africa. It is also imperative to consider the seasonal variation in the CO and VOC source strength in managing O_3 pollution in continental southern Africa. This study also revealed the significant contribution of biomass burning to O_3 precursors in this region, which should also be considered when implementing O_3 control strategies. However, since open biomass burning in southern Africa is of anthropogenic and natural origin, while O_3 concentrations in continental South Africa are also influenced by trans boundary transport of O_3 precursors from open biomass burning occurring in other countries in southern Africa (as indicated above), it is more difficult to control. Nevertheless, open biomass burning caused by anthropogenic practices (e.g. crop residue, pasture maintenance fires, opening burning of garbage) can be addressed."

Conclusions:

"The relationship between O_3, NO_x and CO at Welgegund, Botsalano and Marikana indicated a strong correlation between O_3 on CO, while O_3 levels remained relatively constant (or decreased) with increasing NO_x. Although NO_x and VOCs are usually considered to be the main precursors in ground-level O_3 formation, CO can also drive photochemical O_3 formation. The seasonal changes in the relationship between O_3 and precursors species also reflected the higher CO emissions associated with increased household combustion in winter, and open biomass burning in late winter and spring. The calculation of the $P(O_3)$ from a two-year VOC dataset at Welgegund, indicated that at least 40% of O_3 production occurred in the VOC-limited regime. These results indicated that large parts in continental South Africa can be considered VOC-limited, which can be attributed to high anthropogenic emissions of NO_x in this region. It is, however, recommended that future studies investigate more detailed relationships between NO_x, CO, VOCs and O_3 through photochemical modelling analysis, while concurrent measurement of atmospheric VOCs and $^{\bullet}OH$ would also contribute to the better understanding of surface O_3 in this region.

In this paper some new aspects on O_3 for the continental South Africa have been indicated, which must be taken in consideration when O_3 mitigation strategies are deployed. Emissions of O_3 precursor species associated with the concentrated location of industries in this area could be regulated, while CO and VOC emissions associated with household combustion and regional open biomass burning should also be targeted. However, emissions of O_3 precursor species related to factors, such as household combustion associated with poor socio-economic circumstances and long-range transport, provides a bigger challenge for regulators."

Observed concentrations. It would be useful to provide a basic time series of concentration for the key compounds measured at the 4 sites (O3, CO, NO, NO2 etc). The summary plots (Figure 3 and Figure 4) are fine in themselves but it would be useful to see the full dataset as this would show the scope of the observations and boost the confidence in the quality of the dataset and the subsequent analysis.

Basic time series of O_3, NO_x and CO were included in the Appendix in Fig. A2, A7 and A8, respectively. The following was also included in Section 3.2 (now Section 3.1) and Section 3.3.1 (now Section 3.4.1) referencing these time series plots:

"In Fig. 2 the monthly and diurnal variation for O_3 concentrations measured at the four sites in this study are presented (time series plotted in Fig. A2). Although there is some variability between the sites, monthly…"

"…open biomass burning emissions (i.e. NO_x and CO indicated in Fig. A3 and Fig. A4, respectively – time series plotted in Fig. A7 and A8), while O_3 levels at Botsalano were predominantly…"

The abstract says that much of region is above 40 ppbv of ozone, whereas the corresponding text (Page 13 lines 15) says that this is the case only in the spring time. Figure 3 would suggest that the observational sites are rarely above 40 ppbv. Can this all be clarified? The color scale on Figure 2 makes it almost impossible to define the color for 40 ppbv. Could this be improved and the color scale on Figure 2 lengthened so that the relationship between colors and concentrations is easier to understand?

We agree with Referee #1 on both aspects indicated here. Although O_3 concentrations exceeded 40 ppb on a daily basis at most of the sites throughout the year as indicated in Fig. 4 (now Fig. 2 in the revised manuscript), this is not clearly indicated in Fig. 3 (now Fig. 4 in the revised manuscript), since mean O_3 concentrations are presented in this figure. The spatial map, i.e. Fig. 2 (now Fig. 3) compiled from average spring O_3 concentrations do, however, indicate relatively high O_3 levels across the region, albeit not necessarily above 40 ppb. Therefore the text referring to the regional O_3 problem in the Abstract, Section 3.1.1 (now Section 3.2.1) and the Conclusions was changed as follows:

Abstract

"…four sites in continental South Africa was conducted. The regional O_3 problem was evident with O_3 concentrations regularly exceeding the South African air quality standard limit, while O_3 levels were higher compared to other background sites in the Southern Hemisphere. The temporal O_3 patterns observed at the four sites…"

Section 3.1.1 (now Section 3.2.1)

"…Johannesburg-Pretoria megacity, while the rural Vaalwater site in the north also has significantly higher O_3 levels. From Fig. 3 it is evident that O_3 can be considered a regional problem with O_3 concentrations being relatively high across continental South Africa during spring. Fig. 3 also clearly indicates that the four research sites…"

Conclusions

"A spatial distribution map of O_3 levels in the interior of South Africa indicated the regional O_3 problem in continental South Africa, which was signified by the regular exceedance of the South African air quality standard limit. The seasonal and diurnal O_3 patterns observed at the four sites in this study resembled typical trends for O_3 in continental…"

The colour scale in Fig. 2 (now Fig. 3) was also improved by lengthening the scale and adding more values on the scale.

Reactivity calculation The reactivity calculation is based on the measured CO and the measured VOCs. It is therefore a lower limit. This should be more explicitly explained. There are some obvious missing compounds in this calculation methane, alkanes, alkenes etc. Their concentrations could be estimated. Would they change the perspective offered on whether the site is VOC or NOx limited? Presumably not and it it would only have a slight tendency to move the data-points in figure 11 upwards but not very much? It would be better to make some comments about this head on rather than ignoring it.

We agree with Referee #1 that our VOC reactivity estimates are a lower limit. We can only speciate a fraction of the VOCs present in our grab samples. Although we are likely measuring the major contributors to VOC reactivity at Welgegund such as *o*-xylene, CO, styrene, *p*,*m*-xylene, toluene, ethylbenzene limonene, isoprene, α-pinene, β-pinene, hexane (depicted in Fig. A2), we are certainly missing methane that could also contribute to increasing the VOC reactivity. Yet, assuming a global ambient concentrations of 1.85 ppm and a rate of oxidation by OH radicals of 6.68×10^{-15} cm^3 $molec^{-1}$ s^{-1} (Srinivasan et al., 2005) would lead to a VOC reactivity of 0.3 s^{-1}. Thus, as Referee #1 mentions, a slight tendency to move the data points upwards by 0.3 s^{-1}. However, this shift would not impact the O_3 production regime inferred. Nonetheless, our VOC dataset is quite comprehensive and includes 6 trace gases, 19 biogenic VOCs and 20 anthropogenic VOCs, including 13 aromatic and 7 aliphatic compounds as presented in Jaars, et al. 2014, 2016.

To further address Referee #1 comments, we have also amended our tone in the paragraph to discuss all sources of error and estimation in detail in an attempt to be transparent with our calculations and assumptions. Consequently, the paragraph presenting the model in Section 2.4 has been entirely rewritten to address these issues as follows:

"The only speciated VOC dataset available and published in South Africa exists for Welgegund (Jaars et al., 2016; Jaars et al., 2014), which could be used to model instantaneous O_3 production at this site. The concentration of these biogenic and anthropogenic VOCs were obtained from grab samples taken between 11:00 and 13:00 LT over the course of two extensive field campaigns conducted from February 2011 to February 2012 and from December 2013 to February 2015. During this time, 6 trace gases, 19 biogenic VOCs and 20 anthropogenic VOCs, including 13 aromatic and 7 aliphatic compounds were measured. The VOC reactivity were calculated from the respective rate coefficients of each VOC with $^{\bullet}$OH radicals obtained from chemical kinetic databases such as JPL, NIST and the MCM (e.g. Jaars et al., 2014), to estimate ozone production at 11:00 LT at Welgegund. Specifically, each VOC reactivity was then summed to obtain the total VOC reactivity for each measurement, i.e. VOC reactivity = $\sum k_{1i}[\mathrm{VOC}]_I$. The major contributors to VOC reactivity are depicted in Fig. A1 and include, in approximate order of contribution, *o*-xylene, CO, styrene, *p*,*m*-xylene, toluene, ethylbenzene limonene, isoprene, α-pinene, β-pinene and hexane. Of note, key compounds such as methane are not included that could contribute to VOC reactivity, and thus this VOC reactivity can only be a lower estimate. However, if a global ambient concentration of 1.85 ppm and a rate of oxidation by $^{\bullet}$OH radicals of 6.68×10^{-15} cm^3 molec^{-1} s^{-1} is assumed (Srinivasan et al., 2005), a VOC reactivity of 0.3 s^{-1} would be obtained and would therefore account for a small increase in the VOC reactivity calculated in Fig. A1 and Fig. 10.

A mathematical box-model was applied to model O_3 production as a function of VOC reactivity and NO_2 concentrations. This model involves three steps, (1) estimation of HO_x (sum of $^{\bullet}$OH and $HO_2^{\bullet}$ radicals) production, (2) estimation of the $^{\bullet}$OH radical concentration, and (3) the calculation for O_3 production (Murphy et al., 2006; Geddes et al., 2009). The VOC concentrations are the limiting factor in the ability to model O_3 production at Welgegund, since only data for the 11:00 to 13:00 LT grab samples was available (Fig. A1). Therefore, the model approach does not coincide with peak O_3 typically observed around 14:00 to 15:00 LT, and thus likely represents a lower estimate.

The production rate of HO_x ($P(HO_x)$) depends on the photolysis rate of O_3 (J_{O3}), concentration of O_3 and vapour pressure of water (Jaegle et al., 2001). The photolysis rate proposed for the Southern Hemisphere, i.e. $J_{O3} = 3 \times 10^{-5}$ s^{-1} (Wilson, 2015) was used from which $P(HO_x)$ was calculated as follows:

$$P(HO_X) = 2J_{O3}k_{O3}[O_3][H_2O]$$

and estimated to be 6.09 × 10^6 molec cm^{-3} s^{-1} or 0.89 ppbv h^{-1} (calculated for a campaign O_3 average of 41 ppbv and a campaign RH average of 42 % at 11:00 LT each day) at STP. The $P(HO_x)$ at Welgegund is approximately a factor of two lower compared to other reported urban $P(HO_x)$ values (Geddes et al., 2009). The factors and reactions that affect [$^{\bullet}$OH] include:

- linear dependency between $^{\bullet}$OH and NO_x due to the reaction $NO + HO_2 \rightarrow {}^{\bullet}OH + NO_2$, until $^{\bullet}$OH begins to react with elevated NO_2 concentrations to form HNO_3 ($OH + NO_2 + M \rightarrow HNO_3 + M$);

- $P(HO_x)$ is affected by solar irradiance, temperature, O_3 concentrations, humidity; and

- partitioning of HO_x between RO_2, HO_2, OH.

[$^{\bullet}$OH] was calculated at 11:00 LT each day as follows:

$$A = k_{5eff}\left(\frac{VOC\ reactivity}{k_{2eff}[NO]}\right)^2$$

$$B = k_4[NO_2] + \alpha * VOC\ reactivity$$

$$C = P(HO_x)$$

$$[OH] = \frac{-B + \sqrt{B^2 + 24C * A}}{12 * A}$$

The instantaneous production rate of O_3, $P(O_3)$ could then be calculated as a function of NO_2 levels and VOC reactivity. A set of reactions used to derive the equations that describe the dependence of the $^{\bullet}$OH, peroxy radicals ($HO_2^{\bullet}+RO_2^{\bullet}$) and $P(O_3)$ on NO_x is given by Murphy et al. (2006), which present the following equation to calculate $P(O_3)$:

$$P(O_3) = k_{2eff}[HO_2 + RO_2][NO] = 2 * VOC\ Reactivity * [OH]$$

where $k_2$eff is the effective rate constant of NO oxidation by peroxy radicals (chain propagation and -termination reactions in the production of O_3). The values of the rate constants and other parameters used as input parameters to solve the equation above, can be found in Murphy et al. (2006) and Geddes et al. (2009)."

In addition Section 3.4.3 (now Section 3.5.3) was also rewritten to indicate limitations of the model as follows:

"In Fig. 10 P(O_3) as a function of VOC reactivity calculated from the available VOC dataset for Welgegund (Section 2.4) and NO_2 concentrations is presented. O_3 production at Welgegund during two field campaigns, specifically at 11:00 LT, were found to range between 0 and 10 ppbv h^{-1}. The average P(O_3) over the 2011 to 2012 and the 2014 to 2015 campaigns combined were 3.0 ± 1.9 ppbv h^{-1} and 3.2 ± 3.0 ppbv h^{-1}, respectively. The dashed black line in Fig. 10, called the ridge line, separates the NO_x- and VOC-limited regimes. To the left of the ridge line is the NO_x-limited regime, when O_3 production increases with increasing NO_x concentrations. The VOC-limited regime is to the right of the ridge line, when O_3 production decreases with increasing NO_x. According to the O_3 production plot presented, approximately 40% of the data is found in the VOC-limited regime area, which would support the regional O_3 analysis conducted for continental South Africa in this study. However, the O_3 production plot for Welgegund transitions between NO_x- and VOC-limited regimes with Welgegund being in a NO_x-limited production regime the majority of the time, especially when NO_x concentrations are very low (<1 ppb). As indicated in Section 2.4, limitations to this analysis include limited VOC speciation data, as well as a single time-of-day grab sample. The O_3 production rates can therefore only be inferred at 11:00 am LT despite O_3 concentrations peaking during the afternoon at Welgegund. Therefore, clean background air O_3 production is most-likely NO_x-limited (Tiitta et al., 2014), while large parts of the regional background of continental South Africa can be considered VOC-limited."

Minor comments.

The abstract is rather long. Could this be shortened?

We agree with Referee #1 (and Referee #2) that the abstract is too long, which was significantly shortened in the revised manuscript as follows:

"Although elevated surface ozone (O_3) concentrations are observed in many areas within southern Africa, few studies have investigated the regional atmospheric chemistry and dominant atmospheric processes driving surface O_3 formation in this region. Therefore an assessment of comprehensive continuous surface O_3 measurements performed at four sites in continental South Africa was conducted. The regional O_3 problem was evident with O_3 concentrations regularly exceeding the South African air quality standard limit, while O_3 levels were higher compared to other background sites in the Southern Hemisphere. The temporal O_3 patterns observed at the four sites resembled typical trends for O_3 in continental South Africa with O_3 concentration peaking in late winter and early spring. Increased O_3 concentrations in winter were indicative of increased emissions of O_3 precursors from household combustion and other low-level sources, while a spring maximum observed at all the sites was attributed to increased regional biomass burning.

Source area maps of O_3 and CO indicated significantly higher O_3 and CO concentrations associated with air masses passing over a region with increased seasonal open biomass burning, which indicated CO associated with open biomass burning as a major source of O_3 in continental South Africa. A strong correlation between O_3 on CO was observed, while O_3 levels remained relatively constant or decreased with increasing NO_x, which supports a VOC-limited regime. The instantaneous production rate of O_3 calculated at Welgegund indicated that ~40% of O_3 production occurred in the VOC-limited regime. The relationship between O_3 and precursor species suggests that continental South Africa can be considered VOC-limited, which can be attributed to high anthropogenic emissions of NO_x in the interior of South Africa. The study indicated that the most effective emission control strategy to reduce O_3 levels in continental South Africa should be CO and VOC reduction mainly associated with household combustion and regional open biomass burning."

The explanation of ozone production at the top of page 3 is a little confused. It starts of saying that the only way to produce ozone is through NO2 photolysis but then says that this doesn't make ozone. Can this be re-phrased to be clearer?

NO_2 photolysis is the only known way through which O_3 is produced in the troposphere. However the resultant O_3 reacts with NO to form NO_2, which will again undergo photolysis to produce O_3 and NO resulting in a null cycle, i.e. the photostationary state (PSS). This equilibrium is disturbed when peroxy radicals alter the PSS producing NO_2, which lead to the formation of O_3 in excess of the null cycle.

This entire paragraph in the Introduction was changed in accordance with a suggestion made by Referee #2 and to address the confusion indicated by Referee #1 in the above mentioned comment as follows:

"Tropospheric O_3 concentrations are regulated by three processes, i.e. chemical production/destruction, atmospheric transport and losses to surface through dry deposition (Monks et al., 2015). The photolysis of nitrogen dioxide (NO_2) in the presence of sunlight is the only known way of producing O_3 in the troposphere (Logan, 1985). O_3 can recombine with nitric oxide (NO) to regenerate NO_2, which will again undergo photolysis to regenerate O_3 and NO. This continuous process is known as the NO_x-dependent photostationary state (PSS) and results in no net production or consumption of ozone (null cycle). However, net production of O_3 in the troposphere occurs outside the PSS when peroxy radicals (HO_2 and RO_2) alter the PSS by oxidising NO to produce 'new' NO_2 (Cazorla and Brune, 2010) resulting in net O_3 production. The main source of these peroxy radicals in the atmosphere is the reaction of the hydroxyl radical ($OH^{\bullet}$) with volatile organic compounds (VOCs) or carbon monoxide (CO) (Cazorla and Brune, 2010)."

Page 4 line 30. It would be useful to explain what the South Africa AQ standard for O3 is here. It is mentioned in a couple of places in the text but it take us a bit of time to find out what these values are.

We thank Referee #1 for pointing this out. The following has been included in the Introduction:

"…provincial governments, local municipalities and industries (http://www.saaqis.org.za). High O_3 concentrations are observed in many areas within the interior of South Africa that exceed the South African standard O_3 limit, i.e. an 8-hour moving average of 61 ppb (e.g. Laakso et al., 2013). These exceedances can be attributed to high anthropogenic…"

The resolution of Figure 7 is rather low. The country names are not clear at the output resolution.

We agree with Referee #1 and have improved the resolution, text size and marker sizes. The modified figures are presented below.

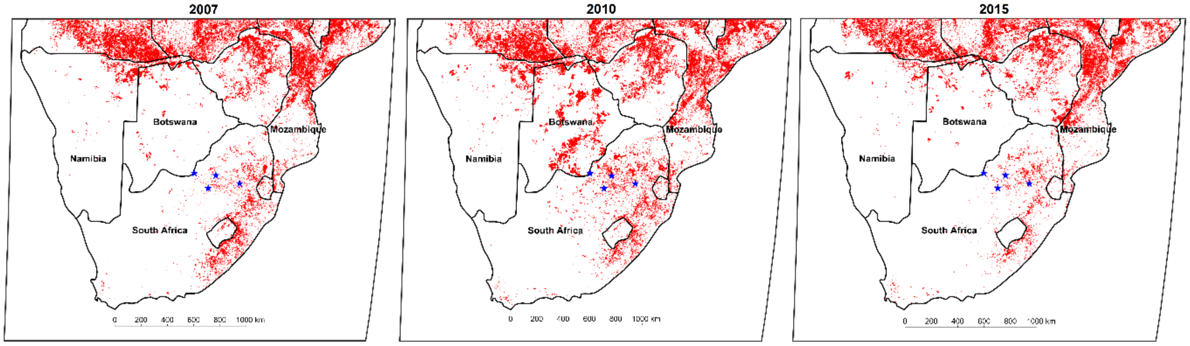

Fig. 7. Spatial distribution of fires in 2007, 2010 and 2015 from MODIS burnt area product. Blue stars indicate (from left to right) Botsalano, Welgegund, Marikana and Elandsfontein.

The text at the start of section 3.4 is a little confused. The first sentence says that there is an absence of VOC data. The next sentence talks about a two-year dataset. It's not obvious what the first sentence therefore means.

We completely agree with the confusion/inconsistence in these two sentences indicated by Referee #1. What was meant here is that no continuous measurement data existed for VOCs for any of the sites. However, there was VOC data available for Welgegund from VOC measurements conducted with adsorbent tubes during two sampling campaigns, which could be used to calculate the instantaneous production rate of O_3. Therefore the text was changed as follows to clarify the confusion:

“The relationship between O_3, NO_x and CO was used as an indicator to infer the O_3 production regime at Welgegund, Botsalano and Marikana (no CO measurements were conducted at Elandsfontein as indicated above), since no continuous VOC measurements were conducted at each of these sites. However, as indicated in Section 2.4, a two-year VOC dataset was available for Welgegund (Jaars et al., 2016; Jaars et al., 2014), which was used to calculate the instantaneous production rate of O_3 as a function of NO_2 levels and VOC reactivity (Geddes et al., 2009; Murphy et al., 2006).”

I’m not sure that Figure A1 is necessary. Its comes out of the calculation but its isn’t really needed for the calculation of P(O3) which essentially just uses the reactivity. Just stating the campaign average value and the variability is enough to show that the calculation is giving a reasonable number.

Figure A1 was removed from the Appendix as suggested by Referee #1. In response to a previous comment by Referee #1, the paragraph presenting the model in Section 2.4 was also entirely rewritten.

Interactive comment on "Seasonal influences on surface ozone variability in continental South Africa and implications for air quality" by Tracey Leah Laban et al. (Ref. No.: acp-2017-1115)

Anonymous Referee #2

Received and published: 23 February 2018

This paper reports four sets of surface ozone measurements in South Africa to explore the spatio-temporal variations as well as the major processes affecting surface ozone variability. Although the measurement data are quite valuable and can enrich the global tropospheric ozone observation database, the current manuscript cannot merit for publication at a high quality journal like ACP. The authors are encouraged to revise the manuscript and submit to another localized journal. I have the following concerns and comments for the author's reference.

We would like to thank Referee #2 for reviewing this manuscript and indicating that valuable measurement data are presented, which can enrich the global tropospheric ozone observation database. However, in view of the positive review of Referee #1 of this paper, who deemed this work suitable for publication in ACP, we do consider that the work presented in this paper does merit publication in ACP. Referee #1 also highlighted that few observations of air pollution in general are reported for Africa and that a useful description of regional background conditions are presented for South Africa. The results presented in this paper are also considered to be novel and relevant for *southern* Africa, and not only South Africa, which indicate that it is not only of local interest. The relevance and significance of atmospheric measurements conducted in South Africa are also emphasised by the solid body of papers published in ACP during the last few years on atmospheric studies conducted in South Africa. Other original aspects in this paper include: 1) the use of the Tropospheric Ozone Assessment Report data to compile a surface plot to indicate ozone spatial variations for this region; and 2) relating the ozone spring peak in this region to CO and VOCs (and co-emitted species) associated with biomass burning rather than biogenic VOCs. None of these aspects have been indicated in previous papers published for this region. Also by addressing each of the major and minor comments made by both referees, the scientific relevance of this paper was further improved.

We would also like to thank Referee #2 for major concerns raised and minor comment made, which were each carefully considered and addressed/implemented in the paper. Below is a point-by-point response to each of these comments/questions. In addition, a marked-up version of the revised manuscript is also provided indicating all changes made throughout the manuscript. The paper was also proofread by a professional language editor.

Major Concerns:

On the significance of this study: the current manuscript looks more like a report other than an academic paper. Almost all the results and findings regarding the ozone variations and processes are already well known, except for that the data are newly acquired from South Africa (actually some of the data had been reported in previous studies). The authors need shorten the general description and interpretation of the results and elaborate more about the new findings and significance of the present study.

The novelty and significance of this study are argued in the response to the general introductory comment made by Referee #2. The manuscript in general was shorten (by ~1300 words as indicated in the marked-up version of the revised manuscript) and written more concisely through addressing comments/suggestions made by Referee #1 and Referee #2.

On the writing of the paper: although the organization and writing of the paper is overall fair, the manuscript is too long and contains a lot of very basic information which I presume the readership of the journal has already known. Some discussions are redundant with each other. For example, the abstract and conclusions are very long and should be largely shortened. The second paragraph in the Introduction (Page 3) describes the ozone formation principles which are very familiar with the community. Seasonal variations of ozone were discussed in Sections 3.1.2 (Fig. 3), 3.2 (Fig. 4), and 3.3 (Fig. 5). The authors are encouraged to remove/shorten such general description and focus on the main findings, and write the paper more concisely.

We agree with Referee #2 that certain sections in the manuscript are too long and therefore these sections were shortened to exclude basic information and repetition. In addition, the Results section was also restructured in order to contribute to a more concise manuscript:

3.1 Temporal variation of O_3
3.2 Spatial distribution of O_3 in continental South Africa
3.3 Comparison with international sites
3.4 Sources contributing to surface O_3 in continental South Africa
3.4.1 Anthropogenic and open biomass burning emissions
3.4.2 Stratospheric O_3
3.5 Insights into the O_3 production regime
3.5.1 The relationship between NO_x, CO and O_3

3.5.2 Seasonal change in O_3-precursors relationship

3.5.3 O_3 production rate

3.6 Implications for air quality management

3.6.1 Ozone exceedances

3.6.2 O_3 control strategies

Shortened/re-written sections include:

Abstract:

"Although elevated surface ozone (O_3) concentrations are observed in many areas within southern Africa, few studies have investigated the regional atmospheric chemistry and dominant atmospheric processes driving surface O_3 formation in this region. Therefore an assessment of comprehensive continuous surface O_3 measurements performed at four sites in continental South Africa was conducted. The regional O_3 problem was evident with O_3 concentrations regularly exceeding the South African air quality standard limit, while O_3 levels were higher compared to other background sites in the Southern Hemisphere. The temporal O_3 patterns observed at the four sites resembled typical trends for O_3 in continental South Africa with O_3 concentration peaking in late winter and early spring. Increased O_3 concentrations in winter were indicative of increased emissions of O_3 precursors from household combustion and other low-level sources, while a spring maximum observed at all the sites was attributed to increased regional biomass burning. Source area maps of O_3 and CO indicated significantly higher O_3 and CO concentrations associated with air masses passing over a region with increased seasonal open biomass burning, which indicated CO associated with open biomass burning as a major source of O_3 in continental South Africa. A strong correlation between O_3 on CO was observed, while O_3 levels remained relatively constant or decreased with increasing NO_x, which supports a VOC-limited regime. The instantaneous production rate of O_3 calculated at Welgegund indicated that ~40% of O_3 production occurred in the VOC-limited regime. The relationship between O_3 and precursor species suggests that continental South Africa can be considered VOC-limited, which can be attributed to high anthropogenic emissions of NO_x in the interior of South Africa. The study indicated that the most effective emission control strategy to reduce O_3 levels in continental South Africa should be CO and VOC reduction mainly associated with household combustion and regional open biomass burning.

Introduction:

"High surface O_3 concentrations are a serious environmental concern, due to their detrimental impacts on human health, crops and vegetation (National Research NRC, 1991). Photochemical smog, comprising O_3

as a constituent together with other atmospheric oxidants, is a major air quality concern on urban and regional scales. Tropospheric O_3 is also a greenhouse gas that directly contributes to global warming (IPCC, 2013).

Tropospheric O_3 concentrations are regulated by three processes, i.e. chemical production/destruction, atmospheric transport and losses to surface through dry deposition (Monks et al., 2015). The photolysis of nitrogen dioxide (NO_2) in the presence of sunlight is the only known way of producing O_3 in the troposphere (Logan, 1985). O_3 can recombine with nitric oxide (NO) to regenerate NO_2, which will again undergo photolysis to regenerate O_3 and NO. This continuous process is known as the NO_x-dependent photostationary state (PSS) and results in no net production or consumption of ozone (null cycle). However, net production of O_3 in the troposphere occurs outside the PSS when peroxy radicals (HO_2 and RO_2) alter the PSS by oxidising NO to produce 'new' NO_2 (Cazorla and Brune, 2010) resulting in net O_3 production. The main source of these peroxy radicals in the atmosphere is the reaction of the hydroxyl radical ($OH^{\bullet}$) with volatile organic compounds (VOCs) or carbon monoxide (CO) (Cazorla and Brune, 2010).

O_3 precursor species can be emitted from natural and anthropogenic sources. Fossil fuel combustion is considered to be the main source of NO_x in South Africa, which include coal-fired power-generation, petrochemical operations, transportation and residential burning (Wells et al., 1996; Held et al., 1996). Satellite observations indicate a well-known NO_2 hotspot over the South African Highveld (Lourens et al., 2012) attributed to industrial activity in the region. CO is produced from three major sources, i.e. fossil fuel combustion, biomass burning, as well as the oxidation of methane (CH_4) and VOCs (Novelli et al., 1992). Anthropogenic sources of VOCs are largely due to industrial and vehicular emissions (Jaars et al., 2014), while biogenic VOCs are also naturally emitted (Jaars et al., 2016). Regional biomass burning, which includes household combustion for space heating and cooking, agricultural waste burning and open biomass burning (wild fires), is a significant source of CO, NO_x and VOCs (Macdonald et al., 2011; Crutzen and Andreae, 1990; Galanter et al., 2000; Simpson et al., 2011) in southern Africa. In addition, stratospheric intrusions of O_3-rich air to the free troposphere can also lead to elevated tropospheric O_3 concentrations (Diab et al., 1996; Diab et al, 2004). O_3 production from natural precursor sources, the long-range transport of O_3 and the injections from stratospheric O_3 contribute to background O_3 levels, which is beyond the control of regulators (Lin et al., 2012).

Since O_3 concentrations are regulated in South Africa, O_3 monitoring is carried out across South Africa through a network of air quality monitoring stations established mainly by provincial governments, local municipalities and industries (http://www.saaqis.org.za). High O_3 concentrations are observed in many areas within the interior of South Africa that exceed the South African standard O_3 limit, i.e. an 8-hour moving average of 61 ppb (e.g. Laakso et al., 2013). These exceedances can be attributed to high anthropogenic emissions of NO_x and VOCs in dense urban and industrial areas (Jaars et al., 2014), regional biomass burning (Lourens et al., 2011) and O_3 conducive meteorological conditions (e.g. sunlight). Since O_3 is a secondary pollutant, high levels of O_3 can also be found in rural areas downwind of city centres and industrial areas. In order for South Africa to develop an effective management plan to reduce O_3 concentrations through controlling NO_x and VOC emissions, it is important to determine whether a region is NO_x- or VOC-limited. However, O_3 production has a complex and non-linear dependence on precursor emissions (e.g. National Research NRC, 1991), which makes its atmospheric levels difficult to control (Holloway and Wayne, 2010). Under VOC-limited conditions, O_3 concentrations increase with increasing VOCs, while a region is considered NO_x-limited when O_3 production increases with increasing NO_x concentrations. Results from a photochemical box model study in South Africa, for instance, revealed that the Johannesburg-Pretoria megacity is within a VOC-limited regime (Lourens et al., 2016). VOC reductions would therefore be most effective in reducing O_3, while NO_x controls without VOC controls may lead to O_3 increases. In general, it is considered that O_3 formation in regions close to anthropogenic sources are VOC-limited, while rural areas distant form source regions are NO_x-limited (Sillman, 1999).

Previous assessments of tropospheric O_3 over continental South Africa focussed on surface O_3 (Venter et al., 2012; Laakso et al., 2012; Lourens et al., 2011; Josipovic et al., 2010; Zunckel et al., 2004), as well as free tropospheric O_3 based on soundings and aircraft observations (Diab et al., 1996; Thompson, 1996; Swap et al., 2003; Diab et al., 2004). Two major field campaigns (SAFARI-92 and SAFARI 2000) were conducted to improve the understanding of the effects of regional biomass burning emissions on O_3 over southern Africa. These studies indicated a late winter early spring (August and September) maximum over the region that was mainly attributed to increased regional open biomass burning during this period, while Lourens et al. (2011) also attributed higher O_3 concentrations in spring in the Mpumalanga Highveld to increased regional open biomass burning. A more recent study demonstrated that NO_x strongly affects O_3 levels in the Highveld, especially in winter and spring (Balashov et al., 2014). A regional photochemical modelling study (Zunckel et al., 2006) have attempted to explain surface O_3 variability, which found no dominant source/s on elevated O_3 levels.

The aim of the current study is to provide an up-to-date assessment of the seasonal and diurnal variations in surface O_3 concentrations over continental South Africa, as well as to identify local and regional sources of precursors contributing to surface O_3. Another objective is to use available ambient data to qualitatively assess whether O_3 formation is NO_x- or VOC-limited in different environments. An understanding of the key precursors that control surface O_3 production is critical for the development of an effective O_3 control strategy."

Section 3.1.2 (now Section 3.3 and Fig. 4):

"In an effort to contextualise the O_3 levels measured in this study, the monthly O_3 concentrations measured at Welgegund were compared to monthly O_3 levels measured at monitoring sites in other parts of the world (downloaded from the JOIN web interface https://join.fz-juelich.de (Schultz et al., 2017)) as indicated in Fig. 4. Welgegund was used in the comparison since it had the most extensive data record, while the measurement time period considered was from May 2010 to December 2014. The seasonal O_3 cycles observed at other sites in the Southern Hemisphere are comparable to the seasonal cycle at Welgegund with slight variations in the time of year when O_3 peaks as indicated in Fig. 4. Cape Grim, Australia; GoAmazon T3 Manancapuru, Brazil; Ushuaia, Argentina; and El Tololo, Chile are regional background GAW (Global Atmosphere Watch) stations with O_3 levels lower than the South African sites. However, the O_3 concentrations at El Tololo, Chile are comparable to Welgegund. Oakdale, Australia and Mutdapliiy, Australia are semi-rural and rural locations, which are influenced by urban and industrial pollution sources, which also had lower O_3 concentrations compared to Welgegund.

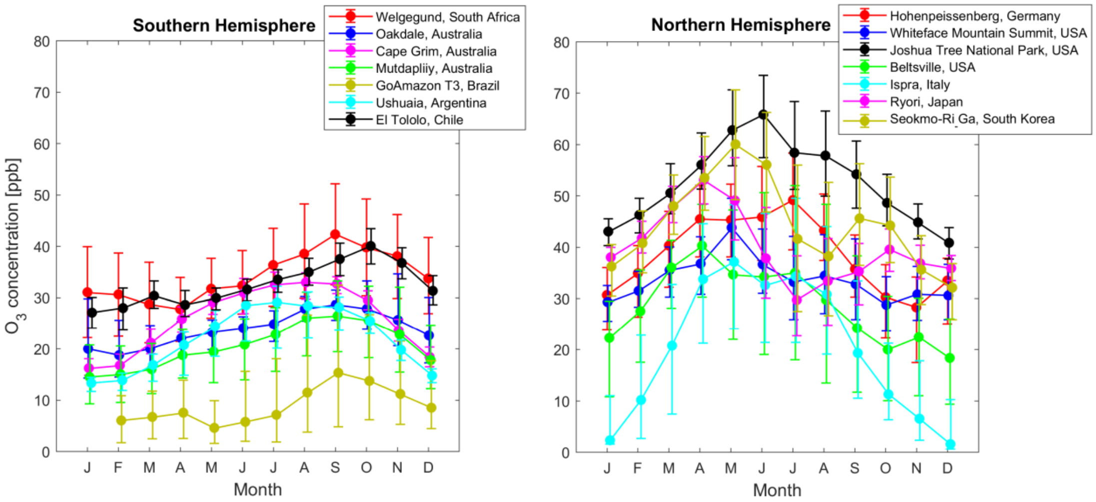

Fig. 4. Seasonal cycle of O_3 at rural sites in other parts of the world. The black dot indicate monthly median (50th percentile) and the upper and lower limits the 25th and 75th percentile, respectively for monthly O_3 concentrations. The data is averaged from May 2010 to December 2014, except in a few instances where 2014 data was not available.

The Northern Hemispheric O_3 peak over mid-latitude regions is similar to seasonal patterns in the Southern Hemisphere where a springtime O_3 maximum is observed (i.e. Whiteface Mountain Summit, Beltsville, Ispra, Ryori and Seokmo-Ri Ga). However, there are other sites in the Northern Hemisphere where a summer maximum is more evident (Vingarzan, 2004), i.e. Joshua Tree and Hohenpeissenberg. The discernible difference between the hemispheres is that the spring maximum in the Southern Hemisphere refers to maximum O_3 concentrations in late winter and early spring, whilst in the Northern Hemisphere it refers to a late spring and early summer O_3 maximum (Cooper et al., 2014). The spring maximum in the Northern Hemisphere is associated with stratospheric intrusions (Zhang et al., 2014; Parrish et al., 2013), while the summer maximum is associated with photochemical O_3 production from anthropogenic emissions of O_3 precursors being at its highest (Logan, 1985; Chevalier et al., 2007). Maximum O_3 concentrations at background sites in the United States and Europe are similar to values at Welgegund in spring with the exception of Joshua Tree National Park in the United States that had significant higher O_3 levels. This is most-likely due its high elevation and deep boundary layer (~4 km asl) during spring and summer allowing free tropospheric O_3 to be more effectively mixed down to the surface (Cooper et al., 2014). Maximum O_3 levels at the two sites in East Asia (Ryori and Seokmo-Ri Ga) were also generally higher than at Welgegund, especially at Seokmo-Ri Ga."

<u>Section 3.2 (now Section 3.1 and Fig. 2):</u>

"In Fig. 2 the monthly and diurnal variation for O_3 concentrations measured at the four sites in this study are presented (time series plotted in Fig. A2). Although there is some variability between the sites, monthly O_3 concentrations show a well-defined seasonal variation at all four sites, with maximum concentrations occurring in late winter and spring (August-November), which is expected for the South African interior as indicated above and previously reported (Zunckel et al., 2004; Diab et al., 2004). In Fig. A1 monthly averages of meteorological parameters and total monthly rainfall for Welgegund are presented to indicate typical seasonal meteorological patterns for continental South Africa. These O_3 peaks in continental South Africa, generally points to two major contributors of O_3 precursors, i.e. open biomass burning (wild fires) (Vakkari et al., 2014) and increased low-level anthropogenic emissions e.g. increased household combustion for space heating and cooking (Oltmans et al., 2013; Lourens et al., 2011). In addition to the seasonal patterns of O_3 precursor species, during the dry winter months synoptic scale recirculation is more predominant and inversion layers are more pronounced, while precipitation is minimal (e.g. Tyson and Preston-Whyte, 2000). These changes in meteorology results in the build-up of precursor species that reaches a maximum in August/September when photochemical activity starts to increase. The diurnal concentration profiles of O_3 at the four locations follow the typical photochemical cycle, i.e. increasing during daytime in response to maximum photochemical production and decreasing during the nighttime due to titration with NO. O_3 levels peaked from midday to afternoon, with a maximum at approximately 15:00 (LT, UTC+2). From Fig. 2 it is also evident that nighttime titration of O_3 at Marikana is more pronounced as indicated by the largest difference between daytime and nighttime O_3 concentrations in comparison to the other sites, especially, compared to Elandsfontein where nighttime concentrations of O_3 remain relatively high in winter."

Section 3.3.1 (now Section 3.4.1 – Fig. 5 removed from manuscript to avoid repetition):

"Comparison of the O_3 seasonal cycles at background and polluted locations is useful for source attribution. From Fig. 3 it is evident that daytime O_3 levels peaked at Elandsfontein, Marikana and Welgegund during late winter and spring (August to October), while O_3 levels at Botsalano peaked later in the year during spring (September to November). This suggests that Elandsfontein, Marikana and Welgegund were influenced by increased levels of O_3 precursors from anthropogenic and open biomass burning emissions (i.e. NO_x and CO indicated in Fig. A3 and Fig. A4, respectively – time series plotted in Fig. A6 and A7), while O_3 levels at Botsalano were predominantly influenced by regional open biomass burning (Fig. A4). Although Welgegund and Botsalano are both background sites, Botsalano is more removed from anthropogenic source regions than Welgegund (Section 2.1.3), which is therefore not directly influenced by the increased concentrations of O_3 precursor species associated with anthropogenic emissions during winter. Daytime O_3 concentrations were the highest at Marikana throughout most of the year, which indicate the influence of local and regional sources of O_3 precursors at this site (Venter et al., 2012). In addition, a larger difference between O_3 concentrations in summer and winter/spring is observed at Marikana compared to Welgegund and Botsalano, which can be attributed to local anthropogenic emissions (mainly household combustion) of O_3 precursors at Marikana.

O_3 concentrations at Elandsfontein were lower compared to the other three sites throughout the year, with the exception of the winter months (June to August). The major point sources at Elandsfontein include NO_x emissions from coal-fired power stations and are characterized by high-stack emissions, which are emitted above the low-level nighttime inversion layers. During daytime downwards mixing of these emitted species occurs, which result in daytime peaks of NO_x (as indicated in Fig. A3 and by Collett et al., 2010) and subsequent O_3 titration. In contrast, Venter et al. (2012) indicated that at Marikana low-level emissions associated with household combustion for space heating and cooking was a significant source of O_3 precursor species, i.e. NO_x and CO. The diurnal pattern of NO_x and CO (Fig. A3 and Fig. A4, respectively) at Marikana was characterised by bimodal peaks during the morning and evening, which resulted in increased O_3 concentrations during daytime and nighttime titration of O_3, especially during winter. Therefore the observed differences in nighttime titration at Marikana and Elandsfontein can be attributed different sources of O_3 precursors, i.e. mainly low-level emissions (household combustion) at Marikana (Venter et al., 2012) compared to predominant high-stack emissions at Elandsfontein (Collette et al., 2010)

The higher O_3 concentrations at Elandsfontein during winter are most-likely attributed to the regional increase in O_3 precursors."

Section 3.5.2 (now section 3.6.2):

"As indicated above (Section 3.4 and 3.5), O_3 formation in the regions where Welgegund, Botsalano and Marikana are located can be considered VOC-limited, while the highly industrialised region with high NO_x emissions where Elandsfontein is located could also be considered VOC-limited. Rural remote regions are generally considered to be NO_x-limited due to the availability of NO_x and the impact of BVOCs (Sillman, 1999). However, Jaars et al. (2016) indicated that BVOC concentrations at a savannah-grassland were at least an order of magnitude lower compared to other regions in the world. Therefore very low BVOC concentrations together with high anthropogenic emissions of NO_x in the interior of South Africa result in VOC-limited conditions at background sites in continental South Africa.

It is evident that reducing CO and VOC concentrations associated with anthropogenic emissions e.g. household combustion, vehicular emissions and industries, would be the most efficient control strategy to reduce peak O_3 concentrations in the interior of South Africa. It is also imperative to consider the seasonal variation in the CO and VOC source strength in managing O_3 pollution in continental southern Africa. This study also revealed the significant contribution of biomass burning to O_3 precursors in this region, which should also be considered when implementing O_3 control strategies. However, since open biomass burning in southern Africa is of anthropogenic and natural origin, while O_3 concentrations in continental South Africa are also influenced by trans boundary transport of O_3 precursors from open biomass burning occurring in other countries in southern Africa (as indicated above), it is more difficult to control. Nevertheless, open biomass burning caused by anthropogenic practices (e.g. crop residue, pasture maintenance fires, opening burning of garbage) can be addressed."

Conclusions:

"A spatial distribution map of O_3 levels in the interior of South Africa indicated the regional O_3 problem in continental South Africa, which was signified by the regular exceedance of the South African air quality standard limit. The seasonal and diurnal O_3 patterns observed at the four sites in this study resembled typical trends for O_3 in continental South Africa with O_3 concentration peaking in late winter and early spring (cf. Zunckel et al., 2004), while daytime O_3 corresponded to increased photochemical production. The seasonal O_3 trends observed in continental southern Africa could mainly be attributed to the seasonal changes in emissions of O_3 precursor species and local meteorological conditions. Increased O_3 concentrations in winter at Welgegund, Marikana and Elandsfontein reflected increased household combustion for space heating and the trapping of low-level pollutants near the surface. A spring maximum observed at all the sites was attributed to increased regional open biomass burning. Significantly higher O_3 concentrations, which corresponded with increased CO concentrations, were associated with air masses passing over a region in southern Africa where a large number of open biomass burning occurred from June to September. Therefore the regional transport of CO associated with open biomass burning in southern Africa was considered a significant source of surface O_3 in continental South Africa. A very small contribution from the stratospheric intrusion of O_3-rich air to surface O_3 levels at the four sites was indicated.

The relationship between O_3, NO_x and CO at Welgegund, Botsalano and Marikana indicated a strong correlation between O_3 on CO, while O_3 levels remained relatively constant (or decreased) with increasing NO_x. Although NO_x and VOCs are usually considered to be the main precursors in ground-level O_3 formation, CO can also drive photochemical O_3 formation. The seasonal changes in the relationship between O_3 and precursors species also reflected the higher CO emissions associated with increased household combustion in winter, and open biomass burning in late winter and spring. The calculation of the $P(O_3)$ from a two-year VOC dataset at Welgegund, indicated that at least 40% of O_3 production occurred in the VOC-limited regime. These results indicated that large parts in continental South Africa can be considered VOC-limited, which can be attributed to high anthropogenic emissions of NO_x in this region. It is, however, recommended that future studies investigate more detailed relationships between NO_x, CO, VOCs and O_3 through photochemical modelling analysis, while concurrent measurement of atmospheric VOCs and $^{\bullet}OH$ would also contribute to the better understanding of surface O_3 in this region.

In this paper some new aspects on O_3 for the continental South Africa have been indicated, which must be taken in consideration when O_3 mitigation strategies are deployed. Emissions of O_3 precursor species associated with the concentrated location of industries in this area could be regulated, while CO and VOC emissions associated with household combustion and regional open biomass burning should also be targeted. However, emissions of O_3 precursor species related to factors, such as household combustion associated with poor socio-economic circumstances and long-range transport, provides a bigger challenge for regulators."

On the calculation of the ozone production rate: the authors should carefully evaluate if this empirical method is applicable to the environmental conditions in the present study. From the equation in the paper, the P(O3) was calculated as the double reaction rates of VOCs with OH. This assumption may only work to some degree for the high NOx and low VOC conditions. And even under such conditions, the ozone production rate might be also largely underestimated as the contributions of the VOC oxidation products to ozone formation are ignored. Furthermore, the empirical calculation of OH concentrations should be also only applicable to rural atmospheres where ozone photolysis is the dominant OH source, and may be subject to large uncertainty in polluted areas where other radical sources such as HONO and OVOCs photolysis become more important. Therefore, the calculation of P(O3) in this study may be subject to large uncertainty that the authors have to address.

We agree with Referee #2 that the P(O3) model utilised in this study may be subject to uncertainty. However, it can only be our current best tool for estimating P(O3), and we have rewritten the paragraph on ozone production in Section 2.4 to highlight the assumptions made and the caveats of this model as follows:

"The only speciated VOC dataset available and published in South Africa exists for Welgegund (Jaars et al., 2016; Jaars et al., 2014), which could be used to model instantaneous O_3 production at this site. The concentration of these biogenic and anthropogenic VOCs were obtained from grab samples taken between 11:00 and 13:00 LT over the course of two extensive field campaigns conducted from February 2011 to February 2012 and from December 2013 to February 2015. During this time, 6 trace gases, 19 biogenic VOCs and 20 anthropogenic VOCs, including 13 aromatic and 7 aliphatic compounds were measured. The VOC reactivity were calculated from the respective rate coefficients of each VOC with $^{\bullet}OH$ radicals obtained from chemical kinetic databases such as JPL, NIST and the MCM (e.g. Jaars et al., 2014), to estimate ozone production at 11:00 LT at Welgegund. Specifically, each VOC reactivity was then summed to obtain the total VOC reactivity for each measurement, i.e. VOC reactivity = $\sum k_{1i}[VOC]_I$. The major contributors to VOC reactivity are depicted in Fig. A1 and include, in approximate order of contribution, *o*-xylene, CO, styrene, *p*,*m*-xylene, toluene, ethylbenzene limonene, isoprene, α-pinene, β-pinene and hexane. Of note, key compounds such as methane are not included that could contribute to VOC reactivity, and thus this VOC reactivity can only be a lower estimate. However, if a global ambient concentration of 1.85 ppm and a rate of oxidation by $^{\bullet}OH$ radicals of 6.68×10^{-15} cm^3 $molec^{-1}$ s^{-1} is assumed (Srinivasan et al., 2005), a VOC reactivity of 0.3 s^{-1} would be obtained and would therefore account for a small increase in the VOC reactivity calculated in Fig. A1 and Fig. 10.

A mathematical box-model was applied to model O_3 production as a function of VOC reactivity and NO_2 concentrations. This model involves three steps, (1) estimation of HO_x (sum of $^{\bullet}OH$ and $HO_2^{\bullet}$ radicals) production, (2) estimation of the $^{\bullet}OH$ radical concentration, and (3) the calculation for O_3 production (Murphy et al., 2006; Geddes et al., 2009). The VOC concentrations are the limiting factor in the ability to model O_3 production at Welgegund, since only data for the 11:00 to 13:00 LT grab samples was available (Fig. A1). Therefore, the model approach does not coincide with peak O_3 typically observed around 14:00 to 15:00 LT, and thus likely represents a lower estimate.

The production rate of HO_x ($P(HO_x)$) depends on the photolysis rate of O_3 (J_{O3}), concentration of O_3 and vapour pressure of water (Jaegle et al., 2001). The photolysis rate proposed for the Southern Hemisphere, i.e. $J_{O3} = 3 \times 10^{-5}$ s^{-1} (Wilson, 2015) was used from which $P(HO_x)$ was calculated as follows:

$$P(HO_X) = 2J_{O3}k_{O3}[O_3][H_2O]$$

and estimated to be 6.09×10^6 molec cm^{-3} s^{-1} or 0.89 ppbv h^{-1} (calculated for a campaign O_3 average of 41 ppbv and a campaign RH average of 42 % at 11:00 LT each day) at STP. The $P(HO_x)$ at Welgegund is approximately a factor of two lower compared to other reported urban $P(HO_x)$ values (Geddes et al., 2009). The factors and reactions that affect [$^{\bullet}$OH] include:

- linear dependency between $^{\bullet}OH$ and NO_x due to the reaction $NO + HO_2 \rightarrow {}^{\bullet}OH + NO_2$, until $^{\bullet}OH$ begins to react with elevated NO_2 concentrations to form HNO_3 ($OH + NO_2 + M \rightarrow HNO_3 + M$);
- $P(HO_x)$ is affected by solar irradiance, temperature, O_3 concentrations, humidity; and
- partitioning of HO_x between RO_2, HO_2, OH.

[$^{\bullet}$OH] was calculated at 11:00 LT each day as follows:

$$A = k_{5eff}\left(\frac{VOC\ reactivity}{k_{2eff}[NO]}\right)^2$$

$$B = k_4[NO_2] + \alpha * VOC\ reactivity$$

$$C = P(HO_x)$$

$$[OH] = \frac{-B + \sqrt{B^2 + 24C * A}}{12 * A}$$

The instantaneous production rate of O_3, $P(O_3)$ could then be calculated as a function of NO_2 levels and VOC reactivity. A set of reactions used to derive the equations that describe the dependence of the $^{\bullet}OH$, peroxy radicals ($HO_2^{\bullet}$+$RO_2^{\bullet}$) and $P(O_3)$ on NO_x is given by Murphy et al. (2006), which present the following equation to calculate $P(O_3)$:

$$P(O_3) = k_{2eff}[HO_2 + RO_2][NO] = 2 * VOC\ Reactivity * [OH]$$

where $k_2$eff is the effective rate constant of NO oxidation by peroxy radicals (chain propagation and -termination reactions in the production of O_3). The values of the rate constants and other parameters used as input parameters to solve the equation above, can be found in Murphy et al. (2006) and Geddes et al. (2009)."

In addition Section 3.4.3 (now Section 3.5.3) was also rewritten to indicate limitations of the model as follows:

"In Fig. 10 P(O_3) as a function of VOC reactivity calculated from the available VOC dataset for Welgegund (Section 2.4) and NO_2 concentrations is presented. O_3 production at Welgegund during two field campaigns, specifically at 11:00 LT, were found to range between 0 and 10 ppbv h^{-1}. The average P(O_3) over the 2011 to 2012 and the 2014 to 2015 campaigns combined were 3.0 ± 1.9 ppbv h^{-1} and 3.2 ± 3.0 ppbv h^{-1}, respectively. The dashed black line in Fig. 10, called the ridge line, separates the NO_x- and VOC-limited regimes. To the left of the ridge line is the NO_x-limited regime, when O_3 production increases with increasing NO_x concentrations. The VOC-limited regime is to the right of the ridge line, when O_3 production decreases with increasing NO_x. According to the O_3 production plot presented, approximately 40% of the data is found in the VOC-limited regime area, which would support the regional O_3 analysis conducted for continental South Africa in this study. However, the O_3 production plot for Welgegund transitions between NO_x- and VOC-limited regimes with Welgegund being in a NO_x-limited production regime the majority of the time, especially when NO_x concentrations are very low (<1 ppb). As indicated in Section 2.4, limitations to this analysis include limited VOC speciation data, as well as a single time-of-day grab sample. The O_3 production rates can therefore only be inferred at 11:00 am LT despite O_3 concentrations peaking during the afternoon at Welgegund. Therefore, clean background air O_3 production is most-likely NO_x-limited (Tiitta et al., 2014), while large parts of the regional background of continental South Africa can be considered VOC-limited."

On the "CO-limited ozone formation regime": the authors concluded from the O3-NOxCO relationship analysis that CO played a significant role in O3 formation in South Africa (or the so-called "CO-limited O3 formation regime"). I highly suspect that this should be not true. In general, CO is less important than VOCs for ozone formation even though it contributes to a significant fraction of OH reactivity. This is because that the contributions of VOCs can be magnified by not only the ROx radical cycle but also the further reactions of their oxidation intermediates and products. The authors are strongly encouraged to utilize the available data of VOCs, NOx, CO and O3 to perform a photochemical modeling analysis to examine the detailed O3 formation regimes.

This point was also raised by Referee #1 who suggested that the comments on the strength of the role of CO on O_3 formation should be toned down and that policy should focus on reducing both CO and VOCs. However, the significance of CO to O_3 formation for this region where biogenic VOCs are relatively less abundant (Jaars et al., 2016) is indicated in this paper, especially through the correlation plots in Fig. 9 and 10 (now Fig. 8 and 9 in the revised manuscript). In addition, Referee #1 also recognised the large role of CO on O_3 formation shown in this study. In view of the comment of Referee #1, the strength of the role of CO on O_3 was toned down in the manuscript in different sections and the contribution of VOCs indicated, without compromising the significance of CO on O_3 formation shown for this region in this paper. Section where changes were made are:

Abstract:

"…emissions of NO_x in the interior of South Africa. The study indicated that the most effective emission control strategy to reduce O_3 levels in continental South Africa should be CO and VOC reduction mainly associated with household combustion and regional open biomass burning."

Section 3.3.1 (now Section 3.4.1):

"…characterise the dispersion of biomass burning emissions over southern Africa (Mafusire et al., 2016). Therefore the regional transport of CO and VOCs (and NO_x to a lesser extent) associated with biomass burning occurring from June to September in southern Africa can be considered an important source of surface O_3 in continental South Africa (Fig. A4)."

Section 3.4.1 (now Section 3.5.1):

"In Fig. 8 the correlations between O_3, NO_x and CO concentrations at Welgegund, Botsalano and Marikana are presented, which clearly indicates higher O_3 concentrations associated with increased CO levels, while O_3 levels remain relatively constant (or decrease) with increasing NO_x. The highest O_3 concentrations occur for NO_x levels below 10 ppb, since the equilibrium between photochemical production of O_3 and chemical removal of O_3 shifts towards the former i.e. greater O_3 formation. In general there seems to exist a marginal negative correlation between O_3 and NO_x (Fig. A5) at all four sites, which is a reflection of the photochemical production of O_3 from NO_2 and the destruction of O_3 through NO_x titration. These correlations between NO_x, CO and O_3 indicate that O_3 production in continental South Africa is limited by CO (and VOCs) concentrations, i.e. VOC-limited."

Section 3.4.2 (now Section 3.5.2):

"…concentrations, which is most pronounced (highest CO/NO_x ratios) during winter and spring. This indicates that the winter and spring O_3 maximum is primarily driven by increased peroxy radical production from CO and VOCs. The seasonal maximum in O_3 concentration coincides with the maximum CO concentration at the background sites, whilst the O_3 peak occurs just after June/July when CO peaked at the polluted site Marikana (Fig. A4). This observed seasonality in O_3 production signifies the importance of precursor species emissions from open biomass burning during winter and spring in this region, while household combustion for space heating and cooking is also an important source of O_3 precursors as previously discussed."

<u>Section 3.5.2 (now Section 3.6.2):</u>

"As indicated above (Section 3.4 and 3.5), O_3 formation in the regions where Welgegund, Botsalano and Marikana are located can be considered VOC-limited, while the highly industrialised region with high NO_x emissions where Elandsfontein is located could also be considered VOC-limited. Rural remote regions are generally considered to be NO_x-limited due to the availability of NO_x and the impact of BVOCs (Sillman, 1999). However, Jaars et al. (2016) indicated that BVOC concentrations at a savannah-grassland were at least an order of magnitude lower compared to other regions in the world. Therefore very low BVOC concentrations together with high anthropogenic emissions of NO_x in the interior of South Africa result in VOC-limited conditions at background sites in continental South Africa.

It is evident that reducing CO and VOC concentrations associated with anthropogenic emissions e.g. household combustion, vehicular emissions and industries, would be the most efficient control strategy to reduce peak O_3 concentrations in the interior of South Africa. It is also imperative to consider the seasonal variation in the CO and VOC source strength in managing O_3 pollution in continental southern Africa. This study also revealed the significant contribution of biomass burning to O_3 precursors in this region, which should also be considered when implementing O_3 control strategies. However, since open biomass burning in southern Africa is of anthropogenic and natural origin, while O_3 concentrations in continental South Africa are also influenced by trans boundary transport of O_3 precursors from open biomass burning occurring in other countries in southern Africa (as indicated above), it is more difficult to control. Nevertheless, open biomass burning caused by anthropogenic practices (e.g. crop residue, pasture maintenance fires, opening burning of garbage) can be addressed."

<u>Conclusions:</u>

"The relationship between O_3, NO_x and CO at Welgegund, Botsalano and Marikana indicated a strong correlation between O_3 on CO, while O_3 levels remained relatively constant (or decreased) with increasing

NO_x. Although NO_x and VOCs are usually considered to be the main precursors in ground-level O_3 formation, CO can also drive photochemical O_3 formation. The seasonal changes in the relationship between O_3 and precursors species also reflected the higher CO emissions associated with increased household combustion in winter, and open biomass burning in late winter and spring. The calculation of the $P(O_3)$ from a two-year VOC dataset at Welgegund, indicated that at least 40% of O_3 production occurred in the VOC-limited regime. These results indicated that large parts in continental South Africa can be considered VOC-limited, which can be attributed to high anthropogenic emissions of NO_x in this region. It is, however, recommended that future studies investigate more detailed relationships between NO_x, CO, VOCs and O_3 through photochemical modelling analysis, while concurrent measurement of atmospheric VOCs and $^{\bullet}OH$ would also contribute to the better understanding of surface O_3 in this region.

In this paper some new aspects on O_3 for the continental South Africa have been indicated, which must be taken in consideration when O_3 mitigation strategies are deployed. Emissions of O_3 precursor species associated with the concentrated location of industries in this area could be regulated, while CO and VOC emissions associated with household combustion and regional open biomass burning should also be targeted. However, emissions of O_3 precursor species related to factors, such as household combustion associated with poor socio-economic circumstances and long-range transport, provides a bigger challenge for regulators."

We agree with Referee #2 that photochemical modeling would greatly assist in establishing O_3 formation regime. However, comprehensive modeling was beyond the scope of this paper (which is already long as indicated by Referee #2) since this was a measurement study. However, this is an important future recommendation that was included in the Conclusions section:

"It is, however, recommended that future studies investigate more detailed relationships between NO_x, CO, VOCs and O_3 through photochemical modelling analysis, while concurrent measurement of atmospheric VOCs and $^{\bullet}OH$ would also contribute to the better understanding of surface O_3 in this region."

Other comments:

Section 2.2: it would be better to provide the detection limit and measurement accuracy of the individual measurements. The traditional NO2 measurements may be subject to positive interference from the catalytic conversion, especially in rural and remote areas. The authors need elaborate more about their NOx measurements.

NO_2 levels determined with the Teledyne 200AU NO/NO_x analyser (used at three of sites) were compared with NO_2 concentrations measured with a quantum cascade laser used for NO_2 flux measurements at Welgegund, which indicated very good comparison between these two instruments. Therefore we have a high level of confidence in the NO_x levels measured with the chemiluminescent measurement techniques at the four sites.

In view of our effort to shorten the paper and exclude basic information as suggested by Referee #2, we do not deem it necessary to elaborate more on the NOx measurements. In addition, the NOx measurements were used to as supportive date to assist in interpreting O_3 measurements. However, a sentence on the comparison with the QCL instrument could be included if requested by Referee #2.

Figure 2: it would be better to highlight the four measurement sites in the present study in the map, and indicate the prevailing wind directions.

The author agree. We have improved the map, by including smaller overlay back trajectory maps of the 4 four study sites, which indicates the air mass movement patterns towards the afore-mentioned sites. The four measurement sites in the present study were also highlighted. This map is indicated below:

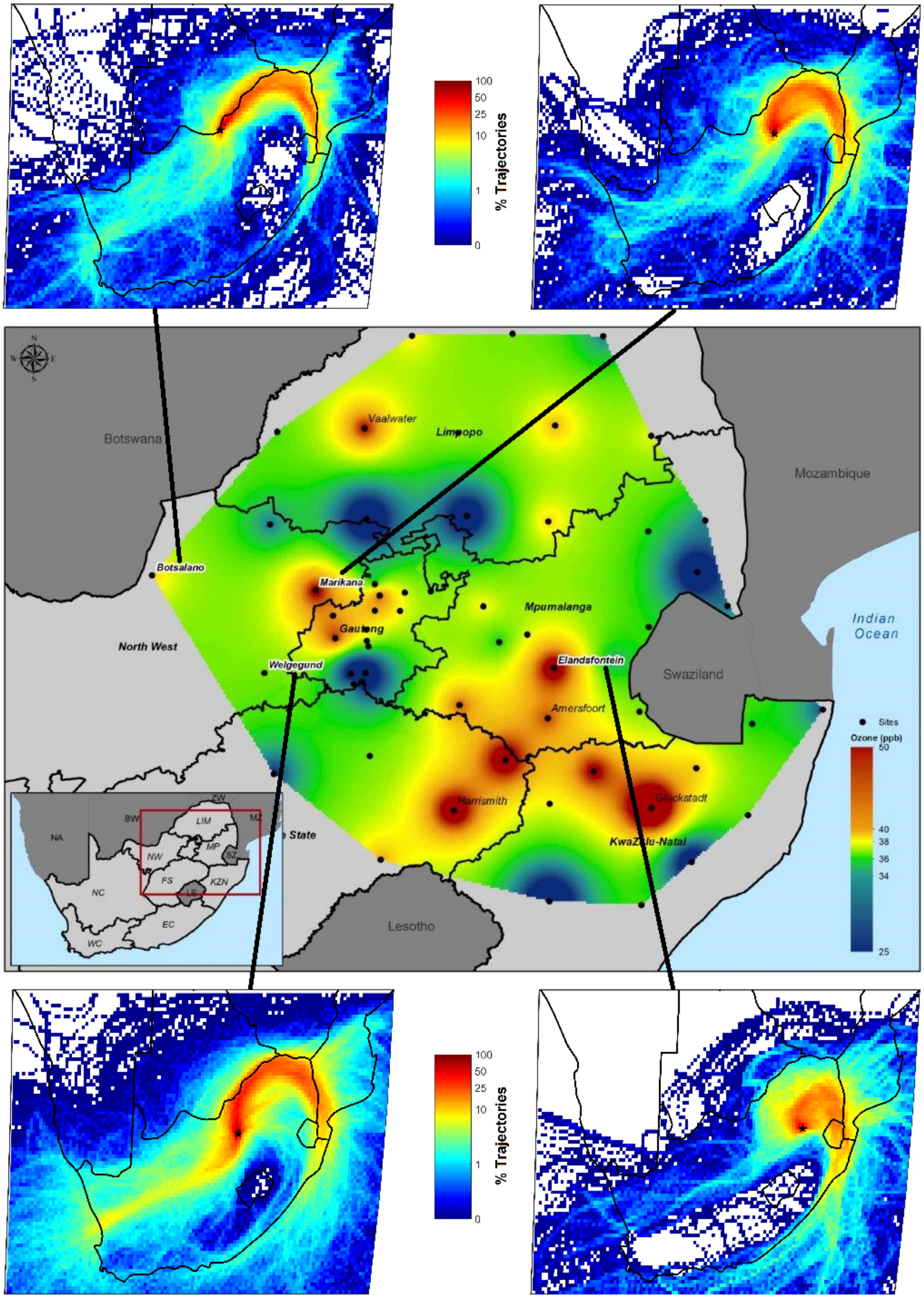
100
50
25
10
1
0
% Trajectories
Botswana
Mozambique
Vaalwater
Limpopo
Botsalano
Marikana
Gauteng
Mpumalanga
North West
Welgegund
Elandsfontein
Swaziland
Indian Ocean
Amersfoort
Harrismith
Glückstadt
KwaZulu-Natal
State
Lesotho
Sites
Ozone (ppb)
50
40
38
36
34
25
NA
BW
ZW
MZ
LIM
NW
MP
SZ
NC
FS
LS
KZN
EC
WC
N
S
E
W

Fig. 2. The main (central map) indicating spatial distribution of mean surface O_3 levels during springtime over the north-eastern interior of southern Africa ranging between 23.00 ° S and 29.03 ° S, and 25.74 ° E and 32.85 ° E. The data for all sites were averaged for years when the ENSO cycle was not present (by examining SST anomalies in the Niño 3.4 region). Black dots indicate the sampling sites. The smaller maps (top and bottom) indicate 96-hour overlay back trajectory maps for the four main study sites, over the corresponding springtime periods.

Page 13, Line 1: “Marikana” is a typo?

We thank Referee #2 for pointing out this typo, which was changed as follows:

“…during springtime (S-O-N), when O_3 is usually at a maximum as indicated above. The mean O_3 concentration over continental South Africa ranged from 20 ppb to 60 ppb during spring. From Fig. 3 it can be seen that O_3 concentrations at the industrial sites Marikana and Elandsfontein were higher than O_3 levels at Botsalano and Welgegund. As mentioned previously, Elandsfontein…”

Section 3.1.2 and Fig. 3: it would be much helpful if the measurement results in East Asia can be also compared to obtain a wider spatial coverage.

Section 3.1.2 and Fig. 3 (now Section 3.3 and Fig. 4) were improved in accordance with the above general comment on the writing of the paper. The seasonal patterns of additional South African sites were removed from Fig. 3 (now Fig. 4) and only Welgegund was used in the comparison to other Southern Hemisphere sites since it had the most extensive data record of all the sites reported on in this study. Therefore Fig. 3 (now Fig. 4) was separated into two figures presenting seasonal patterns for Southern- and Northern Hemisphere sites. In addition, two East Asian sites, i.e. Ryori, Japan and Seokmo-Ri Ga, South Korea, which could be obtained from the TOAR database, were included in the comparison.

Section 3.1.2 (now Section 3.3 and Fig. 4):

“In an effort to contextualise the O_3 levels measured in this study, the monthly O_3 concentrations measured at Welgegund were compared to monthly O_3 levels measured at monitoring sites in other parts of the world (downloaded from the JOIN web interface https://join.fz-juelich.de (Schultz et al., 2017)) as indicated in Fig. 4. Welgegund was used in the comparison since it had the most extensive data record, while the measurement time period considered was from May 2010 to December 2014. The seasonal O_3 cycles observed at other sites in the Southern Hemisphere are comparable to the seasonal cycle at Welgegund with slight variations in the time of year when O_3 peaks as indicated in Fig. 4. Cape Grim, Australia; GoAmazon T3 Manancapuru, Brazil; Ushuaia, Argentina; and El Tololo, Chile are regional background GAW (Global

Atmosphere Watch) stations with O_3 levels lower than the South African sites. However, the O_3 concentrations at El Tololo, Chile are comparable to Welgegund. Oakdale, Australia and Mutdapliiy, Australia are semi-rural and rural locations, which are influenced by urban and industrial pollution sources, which also had lower O_3 concentrations compared to Welgegund.

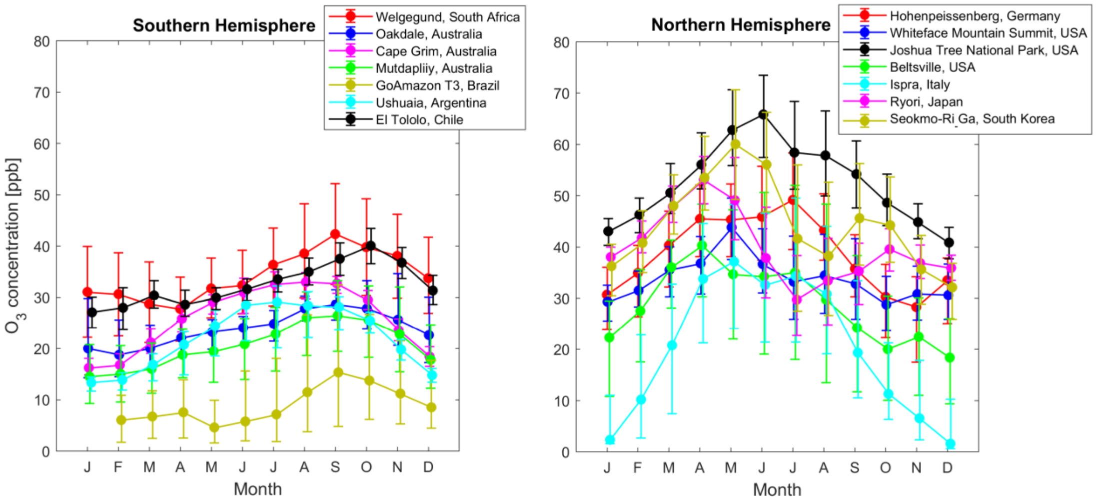

Fig. 4. Seasonal cycle of O_3 at rural sites in other parts of the world. The black dot indicate monthly median (50th percentile) and the upper and lower limits the 25th and 75th percentile, respectively for monthly O_3 concentrations. The data is averaged from May 2010 to December 2014, except in a few instances where 2014 data was not available.

The Northern Hemispheric O_3 peak over mid-latitude regions is similar to seasonal patterns in the Southern Hemisphere where a springtime O_3 maximum is observed (i.e. Whiteface Mountain Summit, Beltsville, Ispra, Ryori and Seokmo-Ri Ga). However, there are other sites in the Northern Hemisphere where a summer maximum is more evident (Vingarzan, 2004), i.e. Joshua Tree and Hohenpeissenberg. The discernible difference between the hemispheres is that the spring maximum in the Southern Hemisphere refers to maximum O_3 concentrations in late winter and early spring, whilst in the Northern Hemisphere it refers to a late spring and early summer O_3 maximum (Cooper et al., 2014). The spring maximum in the Northern Hemisphere is associated with stratospheric intrusions (Zhang et al., 2014; Parrish et al., 2013), while the summer maximum is associated with photochemical O_3 production from anthropogenic emissions of O_3 precursors being at its highest (Logan, 1985; Chevalier et al., 2007). Maximum O_3 concentrations at background sites in the United States and Europe are similar to values at Welgegund in spring with the exception of Joshua Tree National Park in the United States that had significant higher O_3 levels. This is most-likely due its high elevation and deep boundary layer (~4 km asl) during spring and summer allowing free tropospheric O_3 to be more effectively mixed down to the surface (Cooper et al., 2014). Maximum O_3

levels at the two sites in East Asia (Ryori and Seokmo-Ri Ga) were also generally higher than at Welgegund, especially at Seokmo-Ri Ga."

Section 3.2: on the interpretation of the late winter and early spring ozone maximum, what are the meteorological conditions (e.g. temperature, solar radiation, etc.) during this period?

We have included monthly averages of temperature, relative humidity, global radiation and wind speed, as well as total monthly rainfall, for the O_3 measurement period at Welgegund in the Appendix (Fig. A3) to indicate typical meteorological conditions for this part of South Africa. The following sentence was also added to Section 3.2 (now Section 3.1)

"In Fig. A3 monthly averages of meteorological parameters and total monthly rainfall for Welgegund are presented to indicate typical seasonal meteorological patterns for continental South Africa."

Page 19, Lines 1-15: the authors attributed the lower ozone concentrations at Elandsfontein to the high-stack emissions. However, the surface ozone in the industrialized areas can be also titrated by the freshly emitted NOx. It would be helpful for the authors to examine the Ox (Ox=O3+NO2) levels to exclude the effect of NO titration.

We agree with Referee #2 that low-level freshly emitted NO_x could also contribute to O_3 titration at industrial sites. This was clearly shown for Marikana, where NO_x emissions were predominantly associated with low-level emissions as indicated by the bimodal diurnal NO_x peaks (Fig. A3, now Fig. A4), as well as the nighttime titration of O_3 (Fig. 4, now Fig. 2) as discussed in this section. However, the diurnal NO_x pattern at Elandsfontein clearly shows daytime NO_x peaks (Fig. A3, now Fig. A4) resulting from downward mixing of high-stack NO_x emissions as the predominant source of NO_x at Elandsfontein, while the nighttime titration of O_3 is also less significant compared to Marikana (Fig. 4, now Fig. 2). This was also indicated in by Collett et al., 2010 for Elandsfontein. Therefore, in our view the major contributing sources to O_3 titrations at these two industrial sites are adequately indicated by the O_3 (Fig. 4, now Fig. 2) and NO_x (Fig. A3, now Fig. A4) temporal patterns presented in the manuscript.

Page 28, Lines 11-13: from Fig. 11, most the data points fall in the NOx-limited regime zone. This doesn't support the statement that large part of the regional background of continental South Africa can be considered VOC-limited.

Most of the points on the graph do indeed lie in the NOx-limited regime. Since Welgegund is the only station for which VOCs have been measured in South Africa, we cannot directly compare O_3 production with other sites. It would be likely that O_3 production at Welgegund may not be representative of regional

O_3 production conditions across the country. However, ~ 40% of the data is found in the VOC-limited regime area, which would support the regional O_3 analysis conducted for continental South Africa in this study. In addition, O_3 production is mainly in the NOx limited regime at low NOx concentrations. Therefore, clean background air O_3 production is most-likely NO_x-limited, while large parts of the regional background of continental South Africa can be considered VOC-limited. We also feel that this comparison truly highlights the need for further research to reconcile O_3 production at Welgegund and the positive correlations observed between O_3 and CO at most of our other sites that would indicate a rather VOC-limited regime. Therefore Section 3.4.3 (now Section 3.5.3) on O_3 production rate was rewritten as follows:

"In Fig. 10 $P(O_3)$ as a function of VOC reactivity calculated from the available VOC dataset for Welgegund (Section 2.4) and NO_2 concentrations is presented. O_3 production at Welgegund during two field campaigns, specifically at 11:00 LT, were found to range between 0 and 10 ppbv h^{-1}. The average $P(O_3)$ over the 2011 to 2012 and the 2014 to 2015 campaigns combined were 3.0 ± 1.9 ppbv h^{-1} and 3.2 ± 3.0 ppbv h^{-1}, respectively. The dashed black line in Fig. 10, called the ridge line, separates the NO_x- and VOC-limited regimes. To the left of the ridge line is the NO_x-limited regime, when O_3 production increases with increasing NO_x concentrations. The VOC-limited regime is to the right of the ridge line, when O_3 production decreases with increasing NO_x. According to the O_3 production plot presented, approximately 40% of the data is found in the VOC-limited regime area, which would support the regional O_3 analysis conducted for continental South Africa in this study. However, the O_3 production plot for Welgegund transitions between NO_x- and VOC-limited regimes with Welgegund being in a NO_x-limited production regime the majority of the time, especially when NO_x concentrations are very low (<1 ppb). As indicated in Section 2.4, limitations to this analysis include limited VOC speciation data, as well as a single time-of-day grab sample. The O_3 production rates can therefore only be inferred at 11:00 am LT despite O_3 concentrations peaking during the afternoon at Welgegund. Therefore, clean background air O_3 production is most-likely NO_x-limited (Tiitta et al., 2014), while large parts of the regional background of continental South Africa can be considered VOC-limited."

Seasonal influences on surface ozone variability in continental South Africa and implications for air quality

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Abstract

Although elevated surface ozone (O_3) concentrations are observed in many areas within southern Africa, few studies have investigated the regional atmospheric chemistry and dominant atmospheric processes driving surface O_3 formation in this region. Therefore, an assessment of comprehensive continuous surface O_3 measurements performed at four sites in continental South Africa was conducted. The regional O_3 problem was evident, with O_3 concentrations regularly exceeding the South African air quality standard limit, while O_3 levels were higher compared to other background sites in the Southern Hemisphere. The temporal O_3 patterns observed at the four sites resembled typical trends for O_3 in continental South Africa, with O_3 concentrations peaking in late winter and early spring. Increased O_3 concentrations in winter were indicative of increased emissions of O_3 precursors from household combustion and other low-level sources, while a spring maximum observed at all the sites was attributed to increased regional biomass burning. Source area maps of O_3 and CO indicated significantly higher O_3 and CO concentrations associated with air masses passing over a region with increased seasonal open biomass burning, which indicated CO associated with open biomass burning as a major source of O_3 in continental South Africa. A strong correlation between O_3 on CO was observed, while O_3 levels remained relatively constant or decreased with increasing NO_x, which supports a VOC-limited regime. The

instantaneous production rate of O_3 calculated at Welgegund indicated that ~40% of O_3 production occurred in the VOC-limited regime. The relationship between O_3 and precursor species suggests that continental South Africa can be considered VOC-limited, which can be attributed to high anthropogenic emissions of NO_x in the interior of South Africa. The study indicated that the most effective emission control strategy to reduce O_3 levels in continental South Africa should be CO and VOC reduction, mainly associated with household combustion and regional open biomass burning.~~Although elevated ozone (O_3) concentrations are observed in many areas within continental southern Africa, few studies have investigated the regional atmospheric chemistry and dominant atmospheric processes driving surface O_3 formation in this region. The aim of this study was to conduct an assessment of comprehensive continuous surface O_3 measurements performed at four sites located in continental South Africa. These sites were representative of regional background (Welgegund and Botsalano) and industrial regions (Marikana and Elandsfontein) in the north-eastern interior in South Africa as indicated by comparison with other sites in this region. The regional O_3 problem was also shown with O_3 concentrations being higher than 40 ppb at many sites in the north-eastern interior, while the South African air quality standard limit for O_3 was regularly exceeded at the four sites in this study. O_3 levels were generally lower at other background sites in the Southern Hemisphere compared to the South African sites, while similar seasonal patterns were observed. The temporal O_3 patterns observed at the four sites resembled typical trends for O_3 in continental South Africa, i.e. O_3 concentration peaking in late winter and early spring, and daytime O_3 peaks associated with increased photochemical production. The seasonal O_3 trends observed in continental South Africa were mainly attributed to the seasonal changes in emissions of O_3 precursor species and changes in meteorological conditions. Increased O_3 concentrations in winter were indicative of increased emissions of O_3 precursors from household combustion for space heating and the concentration of low-level pollutants near the surface. A spring maximum was observed at all the sites, which was attributed to increased regional biomass burning during this time. Source area maps of O_3 and CO indicated significantly higher O_3 and CO concentrations associated with air masses passing over a region where a large number of seasonal open biomass burning occurred in southern Africa, which indicated CO associated with open biomass burning as a major source of O_3 in continental South Africa. The relationship between O_3, NO_x and CO indicated a strong dependence of O_3 on CO, while O_3 levels remained relatively constant or decreased with increasing NO_x. The seasonal changes in the relationship between O_3 and precursors species also reflected the seasonal changes in sources of precursors. The instantaneous production rate of O_3, P(O_3), calculated at Welgegund indicated that at least 40% of O_3 production occurred in~~

~~the VOC-limited regime. These relationships between O_3 concentrations and P(O_3) with O_3 precursor species revealed that large parts of the regional background in continental South Africa can be considered CO- or VOC-limited, which can be attributed to high anthropogenic emissions of NO_x in the interior of South Africa. It was indicated that the appropriate emission control strategy should be CO (and VOC) reduction associated with household combustion and regional open biomass burning to effectively reduce O_3 pollution in continental South Africa.~~

Keywords: ozone (O_3) production, NO_x-limited, VOC-limited, biomass burning, regional O_3, air quality

1. Introduction

~~Elevated levels of surface (lower troposphere) ozone (O_3) have been globally reported for several decades, especially, in North America and Europe, and more recently in Asia, which is generally attributed to increased fossil fuel combustion contributing to increased emissions of O_3 precursors (Jaffe and Ray, 2007).~~ High surface O_3 concentrations are a serious environmental concern~~,~~ due to ~~its~~ their detrimental impacts on human health, crops and vegetation (National Research NRC, 1991). Photochemical smog, comprising O_3 as a constituent together with other atmospheric oxidants~~ (e.g. nitrogen- and sulphur oxides)~~, is a major air quality concern on ~~an~~ urban and regional scales. Tropospheric O_3 is also a greenhouse gas that directly contributes to global warming (IPCC, 2013).

Tropospheric O_3 concentrations are regulated by three processes, i.e. chemical production/destruction, atmospheric transport, and losses to surface through dry deposition (Monks et al., 2015). The photolysis of nitrogen dioxide (NO_2) in the presence of sunlight~~, followed by the addition of the O atom to O_2~~ is the only known way of producing O_3 in the troposphere (Logan, 1985). ~~:~~

~~NO_2 + hv → O + NO (1)~~

~~O_2 + O + M → O_3 + M (2)~~

O_3 can ~~and~~recombine with nitric oxide (NO) ~~recombine~~ to regenerate NO_2, which will ~~once~~ again undergo photolysis to regenerate O_3 and NO. ~~:~~

~~O_3 + NO → O_2 + NO_2 (3)~~

This continuous process is known as the NO_x-dependent photostationary state (PSS) and results in no net production or consumption of ozone (null cycle). However, ~~N~~net production of O_3 in the troposphere ~~(‘new ozone’)~~ occurs outside the PSS when ~~an atmospheric pool of~~ peroxy radicals (HO_2 and RO_2) alter~~s~~ the PSS by ~~reacting with~~oxidising NO ~~and~~ to produce~~ing~~ ‘new’ NO_2 (Cazorla and Brune, 2010), resulting in net O_3 production. The main source of these peroxy radicals in the atmosphere is the reaction of the hydroxyl radical ($OH^{\bullet}$) with volatile organic compounds (VOCs) or carbon monoxide (CO) (Cazorla and Brune, 2010).~~:~~

~~$OH^{\bullet} + RH + O_2 \longrightarrow H_2O + RO_2$ (4)~~

~~$OH^{\bullet} + CO + O_2 \longrightarrow CO_2 + HO_2$ (5)~~

~~These organic peroxy radicals or hydroperoxy radicals oxidise atmospheric NO:~~

~~$RO_2 + NO \longrightarrow RO + NO_2$ (6)~~

~~$HO_2 + NO \longrightarrow OH + NO_2$ (7)~~

~~reducing the sink for O_3 (Atkinson, 2000), since the resultant NO_2 leads to the production of O_3 through reaction (1) and (2).~~

~~These~~ O_3 precursor species can be emitted from natural and anthropogenic sources. ~~Anthropogenic f~~Fossil fuel combustion is considered to be the main source of NO_x in South Africa, which includes coal-fired power-generation, petrochemical operations, transportation and residential burning (Wells et al., 1996; Held et al., 1996~~; Held and Mphepya, 2000~~). Satellite observations indicate a well-known NO_2 hotspot over the South African Highveld (Lourens et al., 2012) attributed to industrial activity in the region. CO is produced from three major sources, i.e. fossil fuel combustion, biomass burning, as well as the oxidation of methane (CH_4) and VOCs (Novelli et al., 1992). Anthropogenic sources of VOCs are largely due to industrial and vehicular emissions (Jaars et al., 2014), while ~~emissions from vegetation provide the~~ biogenic ~~source~~ VOCs are also naturally emitted (Jaars et al., 2016). Regional biomass burning, which includes household combustion for space heating and cooking, agricultural waste burning and open biomass burning (wild fires), is a significant source of CO, NO_x and VOCs (Macdonald et al., 2011; Crutzen and Andreae, 1990; Galanter et al., 2000; Simpson et al., 2011) in southern Africa. In addition, stratospheric intrusions of O_3-rich air to the free troposphere ~~may also occur that~~ can also lead to elevated tropospheric O_3 concentrations (~~Yorks et al., 2009; Lin et al., 2012~~Diab et al., 1996; Diab et al, 2004). ~~The production of~~ O_3 production from natural precursor sources, the long-range transport of O_3 and the injections from stratospheric O_3 contribute to background O_3 levels, which is beyond the control of regulators (Lin et al., 2012).

~~Knowledge of the O_3 production regime, which is generally classified as either VOC- or NO_x-limited, is crucial in designing effective O_3 control policies for a given location. However, O_3~~

~~production has a complex and non-linear dependence on precursor emissions (e.g. National Research NRC, 1991), which makes its atmospheric levels difficult to control (Holloway and Wayne, 2010). The VOC/NO_x ratio has been widely used to categorise an environment as being either NO_x- or VOC-limited, since net O_3 production requires NO_x and VOCs to exist in specific ratios for the photochemical reaction to occur. O_3 formation is NO_x-limited when the VOC/NO_x ratio is high, while a low VOC/NO_x ratio indicates that O_3 formation is VOC-limited. In the NO_x-limited regime, O_3 concentrations increase with increasing NO_x and are insensitive to VOCs. Therefore NO_x reductions are most effective in reducing O_3 levels. Under VOC-limited conditions, O_3 concentrations increase with increasing VOCs and decrease with increasing NO_x. VOC reductions will therefore be most effective in reducing O_3, while NO_x controls may lead to O_3 increases. There exists a transitional region between the NO_x- and VOC-limited regimes where O_3 is equally sensitive to each species, and control of both VOC and NO_x might be preferred (National Research NRC, 1991). In general, it is considered that O_3 formation in urban areas, close to anthropogenic sources, is VOC-limited, while rural areas distant form source regions are NO_x-limited (Sillman, 1999).~~

Since O_3 concentrations are regulated in South Africa, O_3 monitoring is carried out across South Africa through a network of air quality monitoring stations established mainly by provincial governments, local municipalities and industries (http://www.saaqis.org.za). High O_3 concentrations are observed in many areas within the interior of South Africa, which ~~that~~ exceed the South African standard O_3 limit, i.e. an ~~8~~eight-hour moving average of 61 ppb (e.g. Laakso et al., 2013).~~,~~ ~~which~~These exceedances can be attributed to high anthropogenic emissions of NO_x and VOCs in dense urban and industrial areas (Jaars et al., 2014), regional biomass burning (Lourens et al., 2011), and O_3 conducive meteorological conditions (e.g. sunlight). ~~Furthermore,~~ ~~s~~Since O_3 is a secondary pollutant, high levels of O_3 can also be found in rural areas downwind of city centres and industrial areas. In order for South Africa to develop an effective ~~national/provincial~~ management plan to reduce O_3 concentrations ~~through~~ by controlling NO_x and VOC emissions, it is important to determine whether a region is NO_x- or VOC-limited. However, O_3 production has a complex and non-linear dependence on precursor emissions (e.g. National Research NRC, 1991), which makes its atmospheric levels difficult to control (Holloway and Wayne, 2010). Under VOC-limited conditions, O_3 concentrations increase with increasing VOCs, while a region is considered NO_x-limited when O_3 production increases with increasing NO_x concentrations. Results from a photochemical box model study in South Africa, for instance, revealed that the Johannesburg-Pretoria megacity is within a VOC-limited regime (Lourens et al., 2016). VOC reductions would, therefore, be most effective in reducing O_3, while NO_x controls without VOC controls may lead to O_3 increases. In general, it is considered that O_3 formations in regions close to anthropogenic sources are VOC-limited, while rural areas distant ~~form~~from source regions are NO_x-limited (Sillman, 1999).

Previous assessments of tropospheric O_3 over continental South Africa have focu~~s~~sed on surface O_3 (Venter et al., 2012; Laakso et al., 2012; Lourens et al., 2011; Josipovic et al., 2010;~~ Martins et al., 2007;~~ Zunckel et al., 2004), as well as free tropospheric O_3 based on soundings and aircraft observations (Diab et al., 1996; Thompson, 1996; Swap et al., 2003; Diab et al., 2004). Two major field campaigns (SAFARI-92 and SAFARI 2000) were conducted to improve the understanding of the effects of regional biomass burning emissions on O_3 over southern Africa. These studies indicated a late winter-~~-~~early spring (August and September) maximum over the region~~, which~~ that was mainly attributed to increased regional open biomass burning ~~(wild fires)~~ during this period, while~~.~~ Lourens et al. (2011) also attributed higher O_3 concentrations in spring in the Mpumalanga Highveld to increased regional open biomass burning. A more recent study demonstrated that NO_x strongly affects O_3 levels in the Highveld, especially in winter and spring (Balashov et al., 2014). A regional photochemical modelling study (Zunckel et al., 2006) ~~have~~ has attempted to explain surface O_3 variability, which found no dominant source/s on elevated O_3 levels.

The aim of ~~this~~ the current study ~~was~~ is to provide an up-to-date assessment of the seasonal and diurnal variations in surface O_3 concentrations over continental South Africa, as well as to identify local and regional sources of precursors contributing to surface O_3. Another ~~significant~~ objective ~~was~~ is to use available ambient data ~~as a means of~~ to qualitatively assess~~ing~~ whether O_3 formation is NO_x- or VOC-limited in different environments. An understanding of the key precursors that control surface O_3 production ~~will assist in establishing the O_3 production regime, which~~ is critical for the development of an effective O_3 control strategy.

2. Methodology

2.1 Study area and measurement stations

Continuous in-situ O_3 measurements obtained from four research stations in the north-eastern interior of South Africa, indicated in Fig. 1, which include Botsalano (25.54° S, 25.75° E, 1420 m a.s.l.), Marikana (25.70º S, 27.48º E, 1170 m a.s.l.), Welgegund (26.57 º S, 26.94º E, 1480 m a.s.l.) and Elandsfontein (26.25º S, 29.42º E, 1750 m a.s.l.), were analysed. This region is the largest industrial (indicated by major point sources in Fig. 1) area in South Africa, with substantial gaseous and particulate emissions from numerous industries, domestic fuel burning and vehicles (Lourens et al., 2012; Lourens et al., 2011), while the Johannesburg-Pretoria megacity is also located in this area (Fig. 1). A combination of meteorology and anthropogenic activities has amplified the pollution levels within the region. The seasons in South Africa correspond to typical austral seasons, i.e. winter from June to August, spring from September to November, summer from December to February and autumn from March to May. The climate is semi-arid with an annual average precipitation of ~~around~~ approximately 400~~-~~ to 500 mm (Klopper et al., 2006; Dyson et al., 2015), although there is considerable inter-annual variability associated with El Niño Southern Oscillation (ENSO) phenomena. Precipitation in the north-eastern interior occurs mostly during the austral summer, from October to March, whereas the region is characterised by a distinct cold and dry season from May to September, i.e. late autumn to mid-spring, during which almost no precipitation occurs. During this period, the formation of several inversion layers ~~are~~ is present in the region, which ~~that~~ limits the vertical dilution of air pollution, while more pronounced anticyclonic recirculation of air masses also occurs. This synoptic-~~–~~scale meteorological environment leads to an accumulation of pollutants in the lower troposphere in this region, which can be transported for several days (Tyson and Preston-Whyte, 2000; Garstang et al., 1996). The SAFARI-92 and SAFARI 2000 campaigns indicated that locations in southern Africa, thousands of kilometres apart, are linked through regional anticyclonic circulation (Swap et al., 2003).

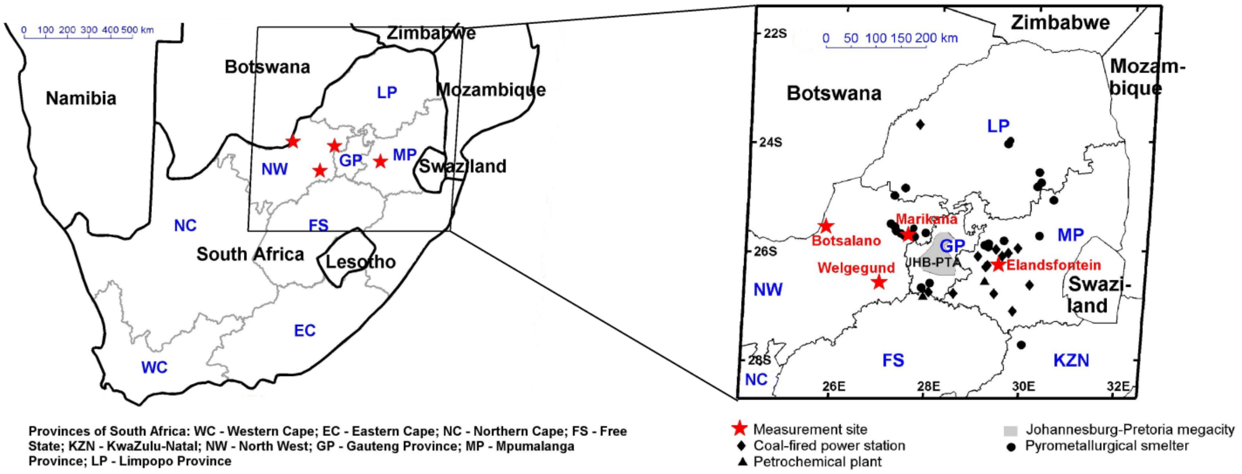


Fig. 1. Location of the four measurement sites in South Africa~~.~~

2.1.1 Botsalano

The Botsalano measurement site ~~was~~ is situated in a game reserve in the North West P~~p~~rovince of South Africa, which is considered to be representative of regional background air. The surrounding vegetation is typical of a savannah biome, consisting of grasslands with scattered shrubs and trees (Laakso et al., 2008). The area is quite sparsely populated and has no local anthropogenic pollution sources (Laakso et al., 2008; Vakkari et al., 2013). The western Bushveld Igneous Complex, where numerous platinum, base metal, vanadium and chromium mining/smelting industries are situated, is the largest regional anthropogenic pollution source, with the Rustenburg area located approximately 150 km to the east. Botsalano is also occasionally impacted by plumes passing over the industrialised Mpumalanga Highveld and the Johannesburg-Pretoria megacity (Laakso et al., 2008; Vakkari et al., 2011). In addition, the site is influenced by seasonal regional savannah wildfires during the dry period (Laakso et al., 2008; Vakkari et al., 2011; Mafusire et al., 2016). Measurements were conducted from 20 July 2006 until 5 February 2008 (Laakso et al., 2008; Vakkari et al., 2011; Vakkari et al., 2013).

2.1.2 Marikana

The Marikana measurement site ~~was~~ is located within the western Bushveld Igneous Complex, which is a densely populated and highly industrialised region, where mining and smelting are the predominant industrial activities. Marikana is a small mining town located ~~about~~ approximately 30 km east of Rustenburg and ~~about~~ approximately 100 km northwest of Johannesburg. The measurement site ~~was~~ is located in the midst of a residential area, comprising low-cost housing settlements and municipal buildings (Hirsikko et al., 2012; Venter et al., 2012). Anthropogenic emissions from household combustion, traffic and industry in the wider region have a strong influence on the measurement site (Venter et al., 2012). Data was collected ~~for a period~~ from 8 February 2008 to 16 May 2010 and has been previously used in other studies (Venter et al., 2012; Vakkari et al., 2013; Petäjä et al., 2013; Hirsikko et al., 2012; Hirsikko et al., 2013).

2.1.3 Welgegund

This measurement site is approximately 100 km west of Johannesburg and is located on a commercial arable and pastoral farm. The station is surrounded by grassland savannah (Jaars et al., 2016). The station can be considered a regionally representative background site with few local anthropogenic sources. Air masses arriving at Welgegund from the west reflect a relatively clean regional background. However, the site is, similar to the Botsalano station, at times impacted by polluted air masses that are advected over major anthropogenic source regions in the interior of South Africa, which include the western Bushveld Igneous Complex, the Johannesburg-Pretoria megacity, the Mpumalanga Highveld and the Vaal Triangle (Tiitta et al., 2014; Jaars et al., 2016; Venter et al., 2017). In addition, Welgegund is also affected by regional savannah and grassland fires that are common in the dry season (Vakkari et al., 2014). The atmospheric measurement station has been operating at Welgegund since 20 May 2010, with data measured up until 31 December 2015 utilised in this study.

2.1.4 Elandsfontein

Elandsfontein is an ambient air quality monitoring station operated by Eskom, the national electricity supply company, primarily for legislative compliance purposes. This station was upgraded and co-managed by researchers during the EUCAARI project (Laakso et al., 2012). The Elandsfontein station is located within the ~~industrialized~~ industrialised Mpumalanga Highveld at the top of a hill approximately 200 km east of Johannesburg and 45 km south-southeast of eMalahleni (previously known as Witbank), which is a coal mining area (Laakso et al., 2012). The site is influenced by several emission sources, such as coal mines, coal-fired power-generating stations, a large petrochemical plant and traffic emissions. Metallurgical smelters to the north also frequently impact the site (Laakso et al., 2012). The Elandsfontein data~~-~~set covers the period 11 February 2009 until 31 December 2010 during the EUCAARI campaign (Laakso et al., 2012).

2.2 Measurements

A comprehensive dataset of continuous measurements of surface aerosols, trace gases and meteorological parameters has been acquired through these four measurement sites (Laakso et al., 2008; Vakkari et al., 2011; Venter et al., 2012; Laakso et al., 2012; Vakkari et al., 2013; Petäjä et al., 2013). In particular, ozone (O_3, nitric oxide (NO), nitrogen dioxide (NO_2) and carbon monoxide (CO), as well as meteorological parameters, such as temperature (^{o}C) and relative humidity (%) measurements were used in this study. Note that Botsalano, Marikana and Welgegund measurements were obtained with the same mobile station (first located at Botsalano, then relocated to Marikana and thereafter permanently positioned at Welgegund), ~~whilst~~ while

Elandsfontein measurements were conducted with a routine monitoring station. O_3 concentrations at Welgegund, Botsalano and Marikana research stations were measured using the Environment SA 41M O_3 analyser, while a Monitor Europe ML9810B O_3 analyser was utilised at Elandsfontein. CO concentrations were determined at Welgegund, Botsalano and Marikana with a Horiba APMA-360 analyser, while CO was not measured at Elandsfontein. NO_x ($NO+NO_2$) concentrations were determined with a Teledyne 200AU NO/NO_x analyser at Welgegund, Botsalano and Marikana, whereas a Thermo Electron 42i NOx analyser was used at Elandsfontein. Temperature and relative humidity were measured with a Rotronic MP 101A instrument at all the sites.

Data quality at these four measurement sites ~~were~~ was ensured through regular visits to the sites, during which instrument maintenance and calibrations were performed. The data collected from these four stations ~~were~~ was subjected to detailed cleaning (e.g. excluding measurements recorded during power interruptions, electronic malfunctions, calibrations and maintenance) and the verification of data quality procedures (e.g. corrections were made to data according to in-situ calibrations and flow-checks). Therefore, the datasets collected at all four measurement sites are considered to represent high quality, high resolution measurements as indicated by other papers (Laakso et al., 2008; Petäjä et al., 2013; Venter et al., 2012; 2011; Laakso et al., 2012; Vakkari et al., 2013). Detailed descriptions of the data post-processing procedures were presented by Laakso et al. (2008) and Venter et al. (2012). The data was available as 15-minute averages and all plots using local time (LT) refer to local South African time, which is UTC+2.

In order to obtain a representative spatial coverage of continental South Africa, O_3 data from an additional 54 ambient monitoring sites was selected. These included O_3 measurements from 18 routine monitoring station~~s~~ measurements (SAAQIS) for the period January 2012 ~~–~~to December 2014 (downloaded from the JOIN web interface https://join.fz-juelich.de (Schultz et al., 2017)) and 36 passive sampling sites located in the north-eastern interior of South Africa where monthly O_3 concentrations were determined for two years from 2006 to 2007 (Josipovic, 2009). Spatial analyse~~i~~s were conducted with a geographic~~al~~ information system mapping tool (ArcGIS software), which used ordinary kriging to interpolate the O_3 concentrations measured at the 58 sites in order to build the spatial distribution. The interpolation method involved making an 80/20% split of the data (80% for model development, 20% for evaluation), where 20% ~~was~~were used to calculate the root squared mean error (RSME = 0.2804331). Optimal model parameters were selected using an iterative process and evaluated on the basis of the best performance statistics obtained (reported in the ArcGIS kriging output), with particular emphasis on minimising the

RSME. The extent of area was 23.00154974 (top), -29.03070026 (bottom), 25.74238974 (left) and 32.85246366 (right).

2.3 Air mass history

Individual hourly four-day back trajectories for air masses arriving at an arrival height of 100 m above ground-level were calculated for the entire measurement period at each monitoring site, using HYSPLIT 4.8 (Hybrid Single-Particle ~~Lagrangian~~Langrangian Integrated Trajectory model) (Stein et al., 2015; Draxler and Hess, 1998). The model was run with the GDAS meteorological archive produced by the US National Weather Service's National Centre for Environmental Prediction (NCEP) and archived by ARL (Air Resources Laboratory, 2017). Overlay back trajectory maps were generated by superimposing individual back trajectories onto a southern African map divided into 0.5° X 0.5°grid cells. In addition, source maps were compiled by assigning each grid cell with a mean measured O_3 and CO concentration associated with trajectories passing over that cell, similar~~ly~~ to ~~the simple approach applied in other papers where concentrations of species were related to individual back trajectories~~ previous methods (Vakkari et al., 2011; Vakkari et al., 2013; Tiitta et al., 2014)~~, each grid cell was assigned the mean measured O_3 concentration associated with trajectories passing over that cell~~. A minimum of ten trajectories per cell ~~was~~ were required for the statistical reliability.

2.4 Modelling instantaneous production rate of O_3

The only speciated VOC dataset available and published in South Africa exists for Welgegund (Jaars et al., 2016; Jaars et al., 2014), which could be used to model instantaneous O_3 production at this site. The concentration of these biogenic and anthropogenic VOCs ~~were~~was obtained from grab samples taken between 11:00 and 13:00 LT over the course of two extensive field campaigns conducted from February 2011 to February 2012 and from December 2013 to February 2015. During this time, ~~6~~six trace gases, 19 biogenic VOCs and 20 anthropogenic VOCs, including 13 aromatic and ~~7~~seven aliphatic compounds were measured. The VOC reactivity ~~were~~was calculated from the respective rate coefficients of each VOC with •OH radicals obtained from chemical kinetic databases such as JPL, NIST and the MCM (e.g. Jaars et al., 2014)~~,~~ to estimate ozone production at 11:00 LT at Welgegund. Specifically, each VOC reactivity was then summed to obtain the total VOC reactivity for each measurement, i.e. VOC reactivity = $\sum k_{1i}[VOC]_i$. The major contributors to VOC reactivity are depicted in Fig. A1 and include, in approximate order of contribution, *o*-xylene, CO, styrene, *p*,*m*-xylene, toluene, ethylbenzene limonene, isoprene, α-pinene, β-pinene and hexane. Of note, key compounds such as methane are not included, which ~~that~~ could contribute to VOC reactivity, and ~~thus~~therefore this VOC reactivity can only be a lower estimate. However, if a global ambient concentration of 1.85 ppm and a rate of oxidation by •OH radicals of 6.68 × 10^{-15} cm^3 $molec^{-1}$ s^{-1} ~~is~~are assumed (Srinivasan et al., 2005), a VOC reactivity of 0.3 s^{-1} would be obtained and would therefore account for a small increase in the VOC reactivity calculated in Fig. A1 and Fig. 10.

A mathematical box-model was applied to model O_3 production as a function of VOC reactivity and NO_2 concentrations. This model involves three steps, i.e. (1) the estimation of HO_x (sum of •OH and HO_2• radicals) production, (2) the estimation of the •OH radical concentration, and (3) the calculation for O_3 production (Murphy et al., 2006; Geddes et al., 2009). The VOC concentrations are the limiting factor in the ability to model O_3 production at Welgegund, since only data for the 11:00 to 13:00 LT grab samples was available (Fig. A1). Therefore, the model approach does not coincide with peak O_3 typically observed around 14:00 to 15:00 LT, and ~~thus~~therefore likely represents a lower estimate.

The production rate of HO_x ($P(HO_x)$) depends on the photolysis rate of O_3 (J_{O3}), concentration of O_3 and vapour pressure of water (Jaegle et al., 2001). The photolysis rate proposed for the Southern Hemisphere, i.e. $J_{O3} = 3 \times 10^{-5}$ s^{-1} (Wilson, 2015), was used, from which $P(HO_x)$ was calculated as follows:

$$P(HO_X) = 2J_{O3}k_{O3}[O_3][H_2O]$$

and estimated to be 6.09 × 10^6 molec cm^{-3} s^{-1} or 0.89 ppbv h^{-1} (calculated for a campaign O_3 average of 41 ppbv and a campaign RH average of 42 % at 11:00 LT each day) at STP. The $P(HO_x)$ at Welgegund is approximately a factor of two lower compared to other reported urban $P(HO_x)$ values (Geddes et al., 2009). ~~A mathematical model developed by Murphy et al. (2006) and used in Geddes et al. (2009) was applied to calculate the •OH radical concentration at a particular measurement time (Fig. A1). The production rate of HO_x ($P(HO_x)$) was required to calculate the •OH radical concentration, which was estimated to be 0.89 ppb/h (calculated for an O_3 average of 41 ppbv and RH of 42 % at 11:00 LT each day).~~ The factors and reactions that affect [•OH] include:

- linear dependency between $^{\bullet}OH$ and NO_x due to the reaction $NO + HO_2 \rightarrow {}^{\bullet}OH + NO_2$, until $^{\bullet}OH$ begins to react with elevated NO_2 concentrations to form HNO_3 ($OH + NO_2 + M \rightarrow HNO_3 + M$);
- $P(HO_x)$ is affected by solar irradiance, temperature, O_3 concentrations, humidity; and
- partitioning of HO_x between RO_2, HO_2, OH.

[$^{\bullet}$OH] was calculated at 11:00 LT each day as follows:

$$A = k_{5eff}\left(\frac{VOC\ reactivity}{k_{2eff}[NO]}\right)^2$$

$$B = k_4[NO_2] + \alpha * VOC\ reactivity$$

$$C = P(HO_x)$$

$$[OH] = \frac{-B + \sqrt{B^2 + 24C * A}}{12 * A}$$

The instantaneous production rate of O_3, $P(O_3)$ could then be calculated as a function of NO_2 levels and VOC reactivity. ~~VOC reactivity was calculated from the product of the VOC concentration and its rate constant for the reaction with a $^{\bullet}$OH radical (Seinfeld and Pandis, 2006), which were then summed to obtain the total VOC reactivity for each measurement, i.e. VOC reactivity = $\sum k_{1i}[VOC]_i$, (Fig. A2).~~ A set of reactions used to derive the equations that describe the dependence of the $^{\bullet}$OH, peroxy radicals ($HO_2^{\bullet}+RO_2^{\bullet}$) and $P(O_3)$ on NO_x is given by Murphy et al. (2006), which presents the following equation to calculate $P(O_3)$:

$$P(O_3) = k_{2eff}[HO_2 + RO_2][NO] = 2\cancel{k_1} * VOC\ Reactivity * [OH]$$

where ~~k_1 is the rate constant of VOC oxidation by $^{\bullet}$OH;~~ $k_2$eff is the effective rate constant of NO oxidation by peroxy radicals (chain propagation and -termination reactions in the production of O_3). The values of the rate constants and other parameters ~~e.g. concentrations of peroxy radicals and the hydroxyl radical~~ used as input parameters to solve the equation above~~,~~ can be found in Murphy et al. (2006) and Geddes et al. (2009).

3. Results and discussion

3.1 Temporal variation of O_3

In Fig. 2, the monthly and diurnal variations for O_3 concentrations measured at the four sites in this study are presented (time series plotted in Fig. A2). Although there is some variability between the sites, monthly O_3 concentrations show a well-defined seasonal variation at all four sites, with maximum concentrations occurring in late winter and spring (August to November), which is expected for the South African interior as indicated above and previously reported (Zunckel et al., 2004; Diab et al., 2004). In Fig., A3 monthly averages of meteorological parameters and total monthly rainfall for Welgegund are presented to indicate typical seasonal meteorological patterns for continental South Africa. These O_3 peaks in continental South Africa~~,~~ generally point~~s~~ to two major contributors of O_3 precursors, i.e. open biomass burning (wild fires) (Vakkari et al., 2014), and increased low-level anthropogenic emissions, e.g. increased household combustion for space heating and cooking (Oltmans et al., 2013; Lourens et al., 2011). In addition to the seasonal patterns of O_3 precursor species, during the dry winter months, synoptic scale recirculation is more predominant and inversion layers are more pronounced, while precipitation is minimal (e.g. Tyson and Preston-Whyte, 2000). These changes in meteorology result~~s~~ in the build-up of precursor species that reach~~es~~ a maximum in August/September when photochemical activity starts to increase. The diurnal concentration profiles of O_3 at the four locations follow the typical photochemical cycle, i.e. increasing during daytime in response to maximum photochemical production and decreasing during the night-time due to titration with NO. O_3 levels peaked from midday to afternoon, with a maximum at approximately 15:00 (LT, UTC+2). From Fig. 2, it is also evident that night-time titration of O_3 at Marikana is more pronounced as indicated by the largest difference between daytime and night-time O_3 concentrations in comparison to the other sites, especially~~,~~ compared to Elandsfontein where night-time concentrations of O_3 remain relatively high in winter.

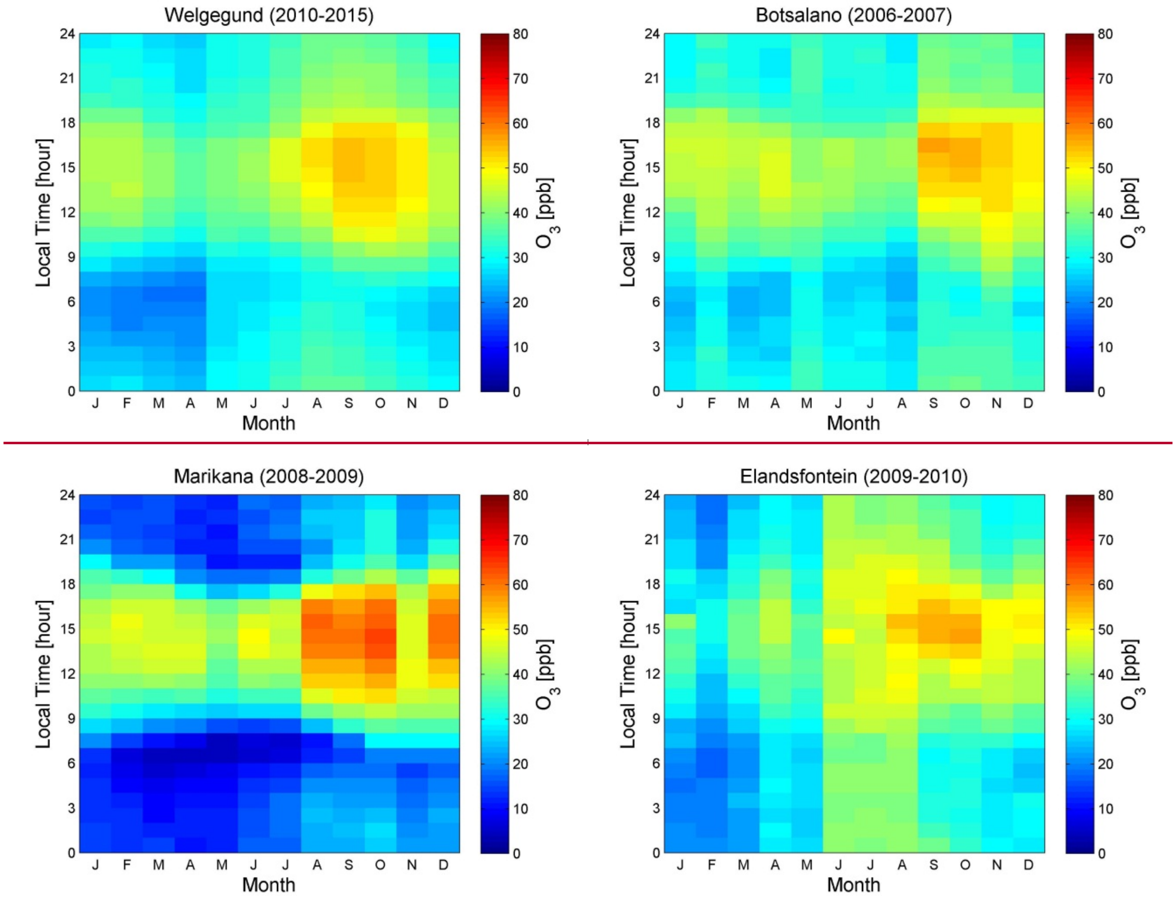


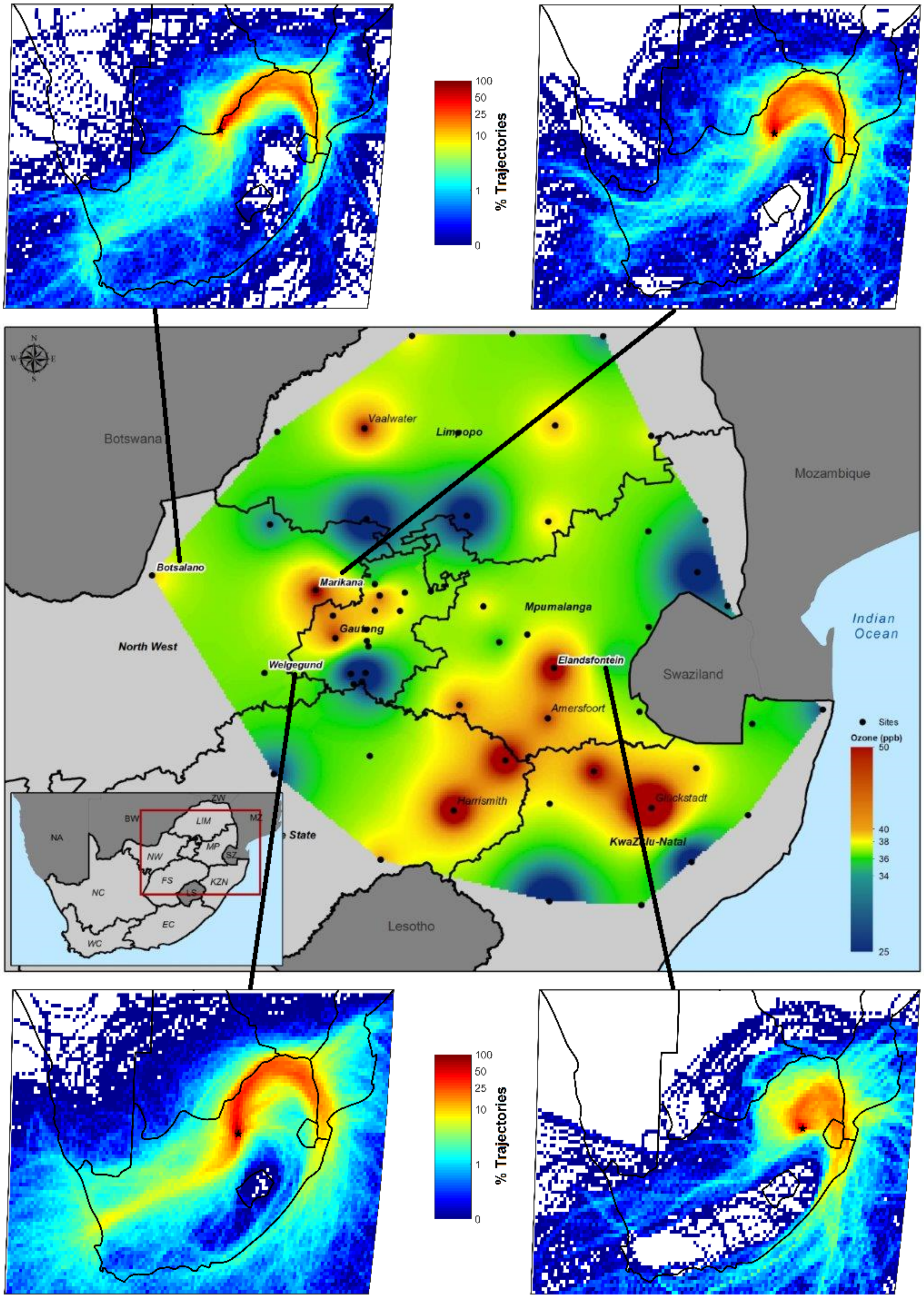
Fig. 2. Seasonal and diurnal variation of median O_3 concentrations at Welgegund, Botsalano, Marikana and Elandsfontein. The O_3 measurement periods varied among sites, which combined spanned a period from July 2006 to December 2015.

~~3.1 Contextualisation of O_3 levels~~

3.2~~1.1~~ Spatial distribution of O_3 in continental South Africa

~~In order to contextualise the O_3 concentrations measured at the four sites in this study and to obtain a representative spatial coverage of continental South Africa, O_3 data from an additional 54 ambient monitoring sites was selected. This included O_3 measurements from 18 routine monitoring stations measurements (SAAQIS) for the period Jan 2012 – Dec 2014 (downloaded from the JOIN web interface https://join.fz-juelich.de (Schultz et al., 2017)) and 36 passive~~

~~sampling sites located in the north-eastern interior of South Africa where monthly O_3 concentrations were determined for two years from 2006 to 2007 (Josipovic, 2009). Spatial analysis were conducted with a geographical information system mapping tool (ArcGIS software), which used ordinary kriging to interpolate the O_3 concentrations measured at the 58 sites in order to build the spatial distribution. The interpolation method involved making an 80/20% split of the data (80% for model development, 20% for evaluation) where 20% was used to calculate the root mean squared error (RSME = 0.2804331). Optimal model parameters were selected using an iterative process and evaluated on the basis of the best performance statistics obtained (reported in the ArcGIS kriging output), with particular emphasis on minimising the RSME. The extent of area was 23.00154974 (top), -29.03070026 (bottom), 25.74238974 (left) and 32.85246366 (right).~~ Fig.~~ure~~ ~~2~~3 depicts the spatial pattern of mean surface O_3 concentrations over continental South Africa during springtime (S-O-N), when O_3 is usually at a maximum as indicated above. Also presented in Fig. 3, are 96-hour overlay back trajectory maps for the four main study sites~~,~~ over the corresponding springtime periods. The mean O_3 concentration over continental South Africa ranged from 20 ppb to 60 ppb during spring. From Fig. 3, it can be seen that O_3 concentrations at the industrial sites Marikana and Elandsfontein were higher than O_3 levels at Botsalano and Welgegund. As mentioned previously, Elandsfontein is located within the industriali~~z~~sed Mpumalanga Highveld with numerous large point sources of O_3 precursor species. It is also evident from Fig. 3 that rural measurement sites downwind from Elandsfontein, such as Amersfoort, Harrismith and Glückstadt had significantly higher O_3 concentrations, which can be attributed to the formation of O_3 during the transport of precursor species from source regions. Lourens et al. (2011) indicated that higher O_3 concentrations were associated with sites positioned in more rural areas in the Mpumalanga Highveld. Venter et al. (2012) attributed high O_3 concentrations at Marikana, which exceeded South African standard limits on a number of occasions, to the influence of local household combustion for cooking and space heating, as well as to regional air masses with high O_3 precursor concentrations. Higher O_3 concentrations were also measured in the north-western parts of Gauteng, at sites situated within close proximity ~~of~~to the Johannesburg-Pretoria megacity, while the rural Vaalwater site in the north also has significantly higher O_3 levels. From Fig. 3, it is evident that O_3 can be considered a regional problem with O_3 concentrations being relatively high across continental South Africa during spring. Fig. 3 also clearly indicates that the four research sites where surface O_3 was assessed in this study are representative of continental South Africa.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Amersfoort
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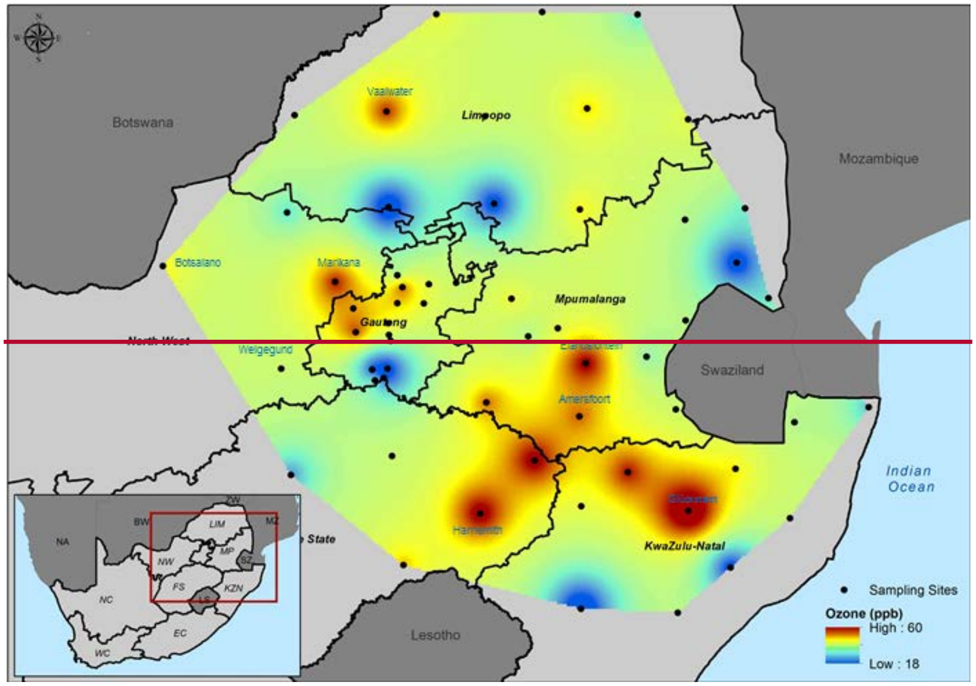
Fig. 2. The main (central) map~~)~~ indicating spatial distribution of mean surface O_3 levels during springtime over the north-eastern interior of southern Africa ranging between 23.00 º S and 29.03 º S, and 25.74 º E and 32.85 º E. The data for all sites ~~were~~was averaged for years when the ENSO cycle was not present (by examining SST anomalies in the Niño 3.4 region). Black dots indicate the sampling sites. The smaller maps (top and bottom) indicate 96-hour overlay back trajectory maps for the four main study sites, over the corresponding springtime periods.



~~**Fig. 2.** Spatial distribution map of mean surface O_3 levels during springtime over the north-eastern interior of southern Africa ranging between 23.00 º S and 29.03 º S, and 25.74 º E and 32.85 º E. The data for all sites were averaged for years when the ENSO cycle was not present (by examining SST anomalies in the Niño 3.4 region). Black dots indicate the sampling sites.~~

~~The mean O_3 concentration over continental South Africa ranged from 20 ppb to 60 ppb during spring. From Fig. 2 it can be seen that O_3 concentrations at the industrial sites Marikana and Elandsfontein were higher than O_3 levels at Botsalano and Marikana. As mentioned previously, Elandsfontein is located within the industrialized Mpumalanga Highveld with numerous large point sources of O_3 precursor species. It is also evident from Fig. 2 that rural measurement sites downwind from Elandsfontein, such as Amersfoort, Harrismith and Glückstadt had significantly higher O_3 concentrations, which can be attributed to the formation of O_3 during transport of~~

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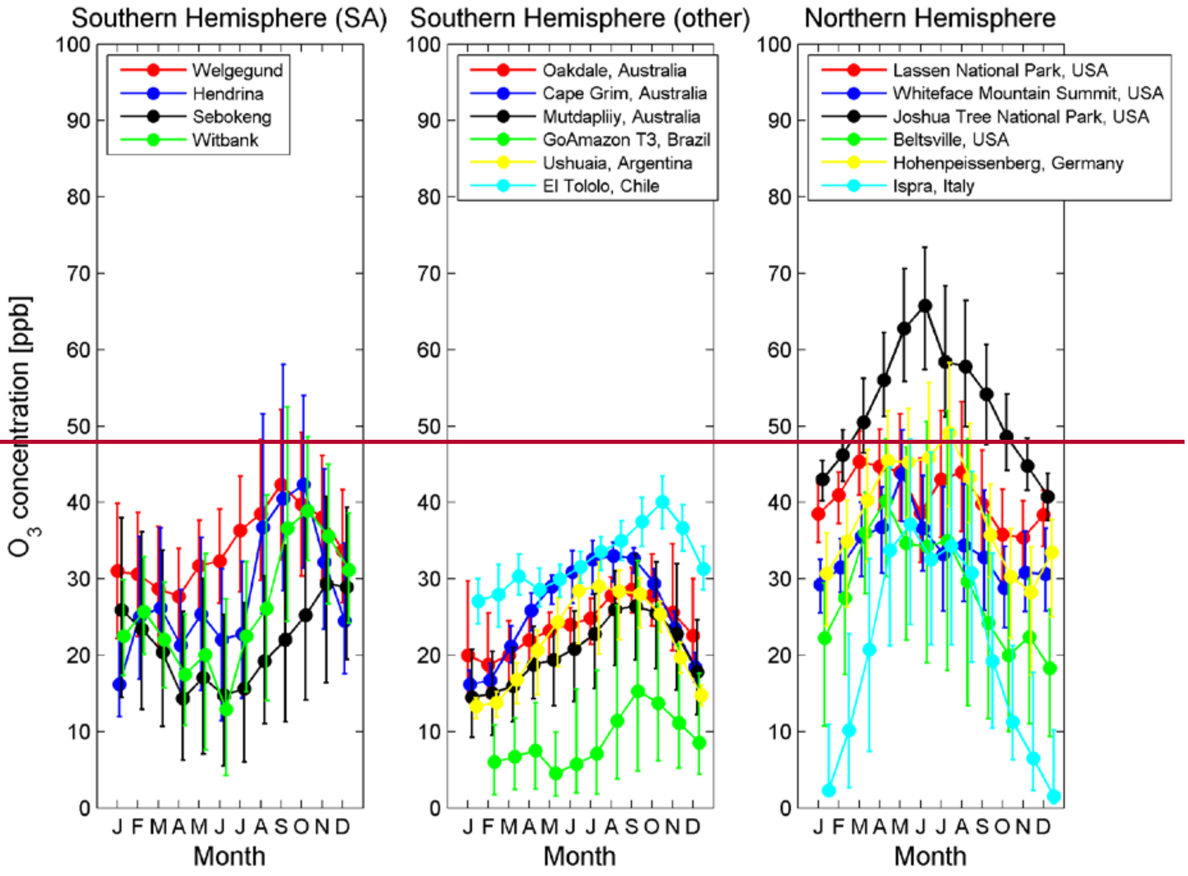
3.3~~1.2~~ Comparison with international sites

~~In an effort to contextualise O_3 concentrations measured at South African sites, t~~In an effort to contextualise the O_3 levels measured in this study, the monthly O_3 concentrations measured ~~in South Africa~~at Welgegund were compared to monthly O_3 levels measured at monitoring sites in other parts of the world (downloaded from the JOIN web interface https://join.fz-juelich.de (Schultz et al., 2017)) as indicated in Fig. 4~~3~~. Welgegund was used in the comparison since it had the most extensive data record, while~~ T~~ the measurement time period considered was from May 2010 to December 2014. ~~Of the four sites assessed in this paper, only Welgegund was used in the comparison since it had the most extensive data record, while three other South African routine monitoring stations influenced by local and regional pollution sources were included, i.e. Hendrina (rural), Sebokeng (industrial, low-income housing) and Witbank (industrial) (SAAQIS). It is evident from Fig. 3 that the rural sites with few local sources (Welgegund, Hendrina) experience higher O_3 levels than Witbank and Sebokeng, which are situated in highly industrialised and densely populated urban areas. The seasonal O_3 cycles at Hendrina, Witbank and Sebokeng are similar to that observed at Welgegund.~~ The seasonal O_3 cycles observed at other sites in the Southern Hemisphere are comparable to the seasonal cycle~~s~~ at ~~the South African sites~~Welgegund, with slight variations in the time of year when O_3 peaks as indicated in Fig. 4~~3~~. Cape Grim, Australia; GoAmazon T3 Manancapuru, Brazil; Ushuaia, Argentina; and El Tololo, Chile are regional background GAW (Global Atmosphere Watch) stations with O_3 levels lower than the South African sites. However, the O_3 concentrations at El Tololo, Chile are comparable to Welgegund. Oakdale, Australia and Mutdapliiy, Australia are semi-rural and rural locations, which are influenced by urban and industrial pollution sources, which also had lower O_3 concentrations compared to ~~the South African sites~~Welgegund.



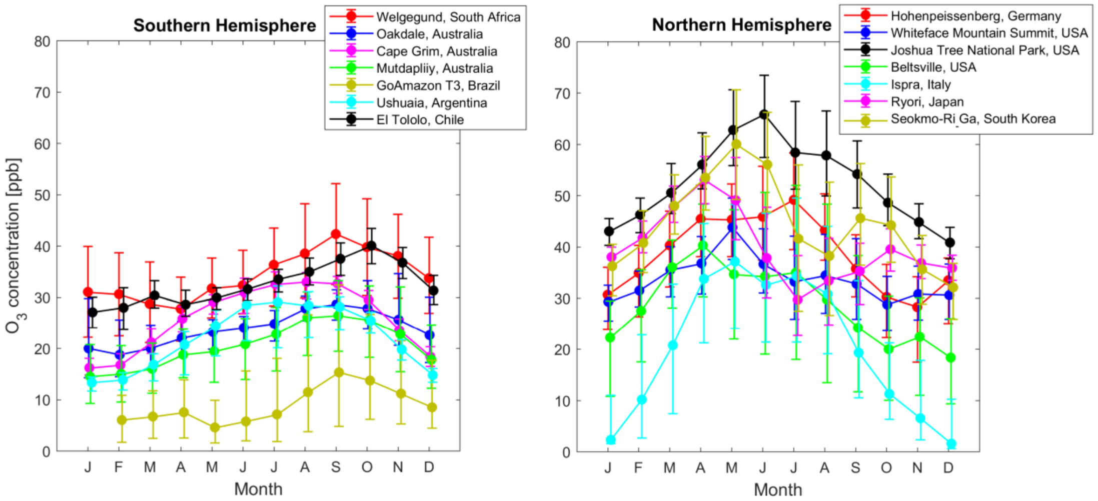


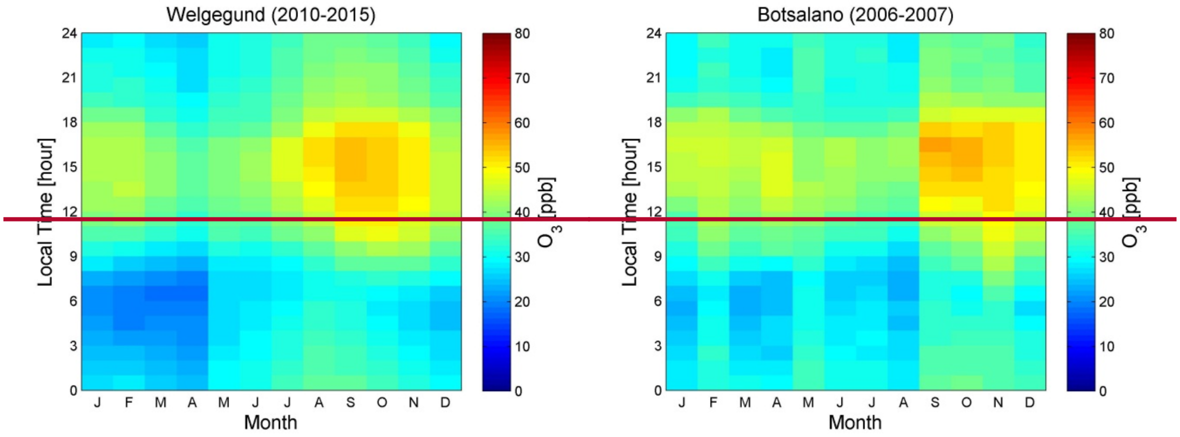
Fig. 4~~3~~. Seasonal cycle of O_3 at rural sites in other parts of the world. The ~~black~~ dots indicate monthly median (50th percentile) and the upper and lower limits the 25th and 75th percentile, respectively for monthly O_3 concentrations. The data is averaged from May 2010 to December 2014, except in a few instances where 2014 data was not available.

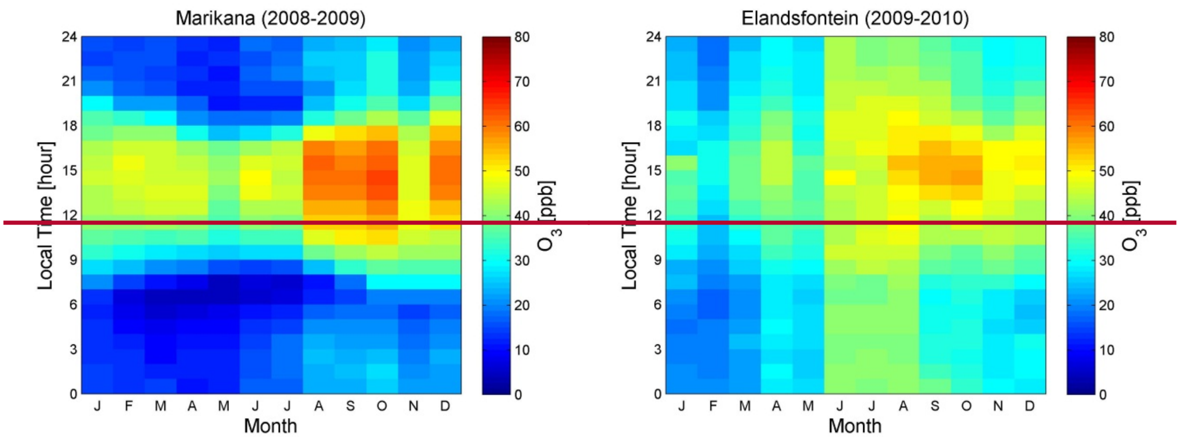
The Northern Hemispheric O_3 peak over mid-latitude regions is similar to seasonal patterns in the Southern Hemisphere where a springtime O_3 maximum is observed (~~e.g.~~i.e. Whiteface Mountain Summit, Beltsville, Ispra, Ryori and Seokmo-Ri Ga). ~~although~~However, there are other sites in the Northern Hemisphere where a summer maximum is more evident (Vingarzan, 2004), ~~such as~~i.e. Joshua Tree and ~~and Beltsville~~ Hohenpeissenberg. The discernible difference between the hemispheres is that the spring maximum in the Southern Hemisphere refers to maximum O_3 concentrations in late winter and early spring, whil~~st~~e in the Northern Hemisphere, it refers to a late spring and early summer O_3 maximum (Cooper et al., 2014). The spring maximum in the Northern Hemisphere is associated with stratospheric intrusions (Zhang et al., 2014; Parrish et al., 2013), while the summer maximum is associated with photochemical O_3 production from anthropogenic emissions of O_3 precursors being at its highest (Logan, 1985; Chevalier et al., 2007). ~~-~~Maximum O_3 concentrations at background sites in the United States and Europe are similar to values at ~~the South African sites~~Welgegund in spring~~.~~ with the exception of ~~The exceptions are Lassen National Park and~~ Joshua Tree National Park in the United States, which~~,~~ ~~which have~~ that had ~~higher values~~significantly higher O_3 levels. This is ~~than the Southern Hemispheric sites~~ most ~~-~~likely due its high elevation and deep boundary layer (~4 km asl) during spring and summer allowing free tropospheric O_3 to be more effectively mixed down to the surface (Cooper et al., 2014). ~~Note that Lassen National Park is at a slightly higher altitude than the South African sites and, generally,~~ Maximum O_3 levels at the two sites in East Asia (Ryori and Seokmo-Ri Ga) were also generally higher than at Welgegund, especially at Seokmo-Ri Ga.~~O_3 concentrations increase with increasing elevation (Jaffe and Ray, 2007; Burley and Bytnerowicz, 2011) as is evident. Joshua Tree National Park shows the highest O_3 levels from all sites, reaching monthly means between 60 and 70 ppb during summer, most likely due to its high elevation and deep boundary layer (~4 km asl) during spring and summer allowing free tropospheric O_3 to be more effectively mixed down to the surface (Cooper et al., 2014). Similarly in Europe, there is either a spring maximum as observed at Hohenpeissenberg or a summer maximum as seen at Ispra. The latter has similar O_3 levels during spring and summer as the South African sites, but decreases significantly during the rest of the year. The discernible difference between the hemispheres is that the spring maximum in the Southern Hemisphere refers to maximum O_3~~

~~concentrations in late winter and early spring, whilst in the Northern Hemisphere it refers to a late spring and early summer O_3 maximum (Cooper et al., 2014).~~

~~3.2 Seasonal and diurnal variation of O_3~~

~~In Fig. 4 the monthly and diurnal variation for O_3 concentrations measured at the four research sites in this study are presented. Although there is some variability between the sites, monthly O_3 concentrations show a well-defined seasonal variation at all four sites, with maximum concentrations occurring in late winter and spring (August-November). This observed late winter and spring O_3 peak are expected for the South African interior as previously reported (Zunckel et al., 2004; Diab et al., 2004; Combrink et al., 1995). These O_3 peaks in continental South Africa, generally points to two major contributors of O_3 precursors, i.e. open biomass burning (wild fires) (Fishman and Larsen, 1987; Vakkari et al., 2014) and increased low-level anthropogenic emissions (Oltmans et al., 2013; Lourens et al., 2011). In addition, not only are some O_3 precursor sources seasonal, but during the dry winter months synoptic scale recirculation is more predominant and inversion layers are more pronounced, while precipitation is minimal (e.g. Tyson and Preston-Whyte, 2000). O_3 concentrations increase in the dry period due to the build-up of precursor species and reach a maximum in August/September when photochemical activity starts to increase. The influences of sources of O_3 precursors will be explored in Section 3.3.~~





~~**Fig. 4.** Seasonal and diurnal variation of median O_3 concentrations at Welgegund, Botsalano, Marikana and Elandsfontein. The O_3 measurement periods varied among sites, which combined spanned a period from July 2006 to December 2015.~~

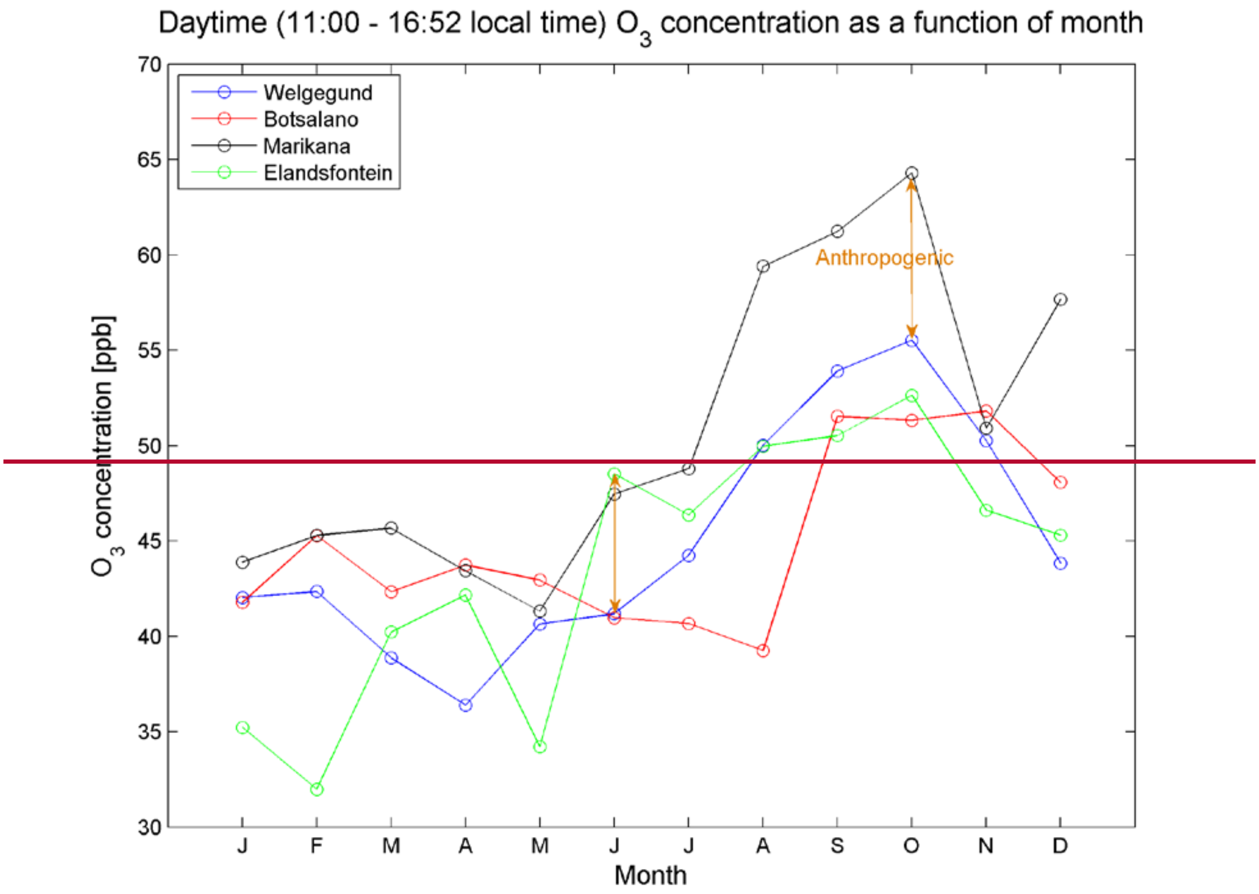
~~The diurnal concentration profiles of O_3 at the four locations follow the photochemical cycle, i.e. decreasing during the nighttime and increasing during daytime. O_3 peaked from midday to afternoon, with a maximum at approximately 15:00 (LT, UTC+2), in response to maximum photochemical production (Seinfeld and Pandis, 1998; Crutzen et al., 1999). In the absence of solar radiation during nighttime, photochemical production of O_3 ceases and titration of O_3 occurs due to reaction with NO resulting in higher NO_2 (Eq. (3)) (Dueñas et al., 2002). In addition, O_3 is also removed through dry deposition at night. The lower O_3 levels are maintained throughout the night and early morning hours with a minimum just before sunrise at approximately 6:00 LT. After sunrise, the inversion layer gradually breaks up and the O_3 concentrations steadily start to increase due to the downward mixing of the residual layer and increasing sunshine. O_3 formation starts later in the day (around 7:00 LT) in autumn and winter due to the shift in local time of sunrise. From Fig. 4 is also evident that nighttime titration of O_3 at Marikana is more pronounced as indicated by the largest difference between daytime and nighttime O_3 concentrations in comparison to the other sites, especially, compared to Elandsfontein where nighttime concentrations of O_3 remain relatively high in winter.~~

3.4~~3~~ Sources contributing to surface O_3 in continental South Africa

As indicated above (s~~S~~ection 3.1), the O_3 peaks in continental South Africa usually reflect~~s~~ increased concentrations of precursor species from anthropogenic sources during winter, as well as the occurrence of regional open biomass burning in late winter and early spring. In addition, stratospheric O_3 intrusions during ~~the~~ spring (Lefohn et al., 2014) could also partially contribute to increased surface O_3 levels.

3.~~3~~4.1 Anthropogenic and open biomass burning emissions

A c~~C~~omparison of the O_3 seasonal cycles at background and polluted locations is useful for source attribution. ~~In Fig. 5 the monthly average daytime (11:00-17:00 LT) O_3 concentrations at the four sites are compared. Daytime measurements were used, since the boundary layer height was high and well-mixed, while nighttime surface deposition did not occur (Cooper et al., 2012).~~ From Fig. 3,~~5~~ it is evident that daytime O_3 levels peaked at Elandsfontein, Marikana and Welgegund during late winter and spring (August to October), while O_3 levels at Botsalano peaked later in the year during spring (September to November). ~~Therefore~~ This suggests that Elandsfontein, Marikana and Welgegund were influenced by increased levels of O_3 precursors from anthropogenic and open biomass burning emissions (i.e. NO_x and CO indicated in Fig. A4~~3~~ and Fig. A54, respectively – time series plotted in Fig. A7 and A8), while O_3 levels at Botsalano were predominantly influenced by regional open biomass burning (Fig. A54). ~~As mentioned previously, during winter an increase in concentration atmospheric pollutants occurs in continental South Africa due to increased household combustion for space heating, as well as the prevailing meteorological conditions, i.e. more pronounced anticyclonic recirculation and inversion layers causing decreased vertical mixing. High O_3 levels in spring can also be related to increased local photochemical production of O_3 in conjunction with increased concentrations of precursors (Atlas et al., 2003; Carvalho et al., 2010).~~ Although Welgegund and Botsalano are both background sites, Botsalano is more removed from anthropogenic source regions than Welgegund is (s~~S~~ection 2.1.3), which is therefore not directly influenced by the increased concentrations of O_3 precursor species associated with anthropogenic emissions during winter. Daytime O_3 concentrations were the highest at Marikana throughout most of the year, which indicates the influence of local and regional sources of O_3 precursors at this site (Venter et al., 2012). In addition, a larger difference between O_3 concentrations in summer and winter/spring is observed at Marikana compared to Welgegund and Botsalano, which can be attributed to local anthropogenic emissions (mainly household combustion) of O_3 precursors at Marikana.



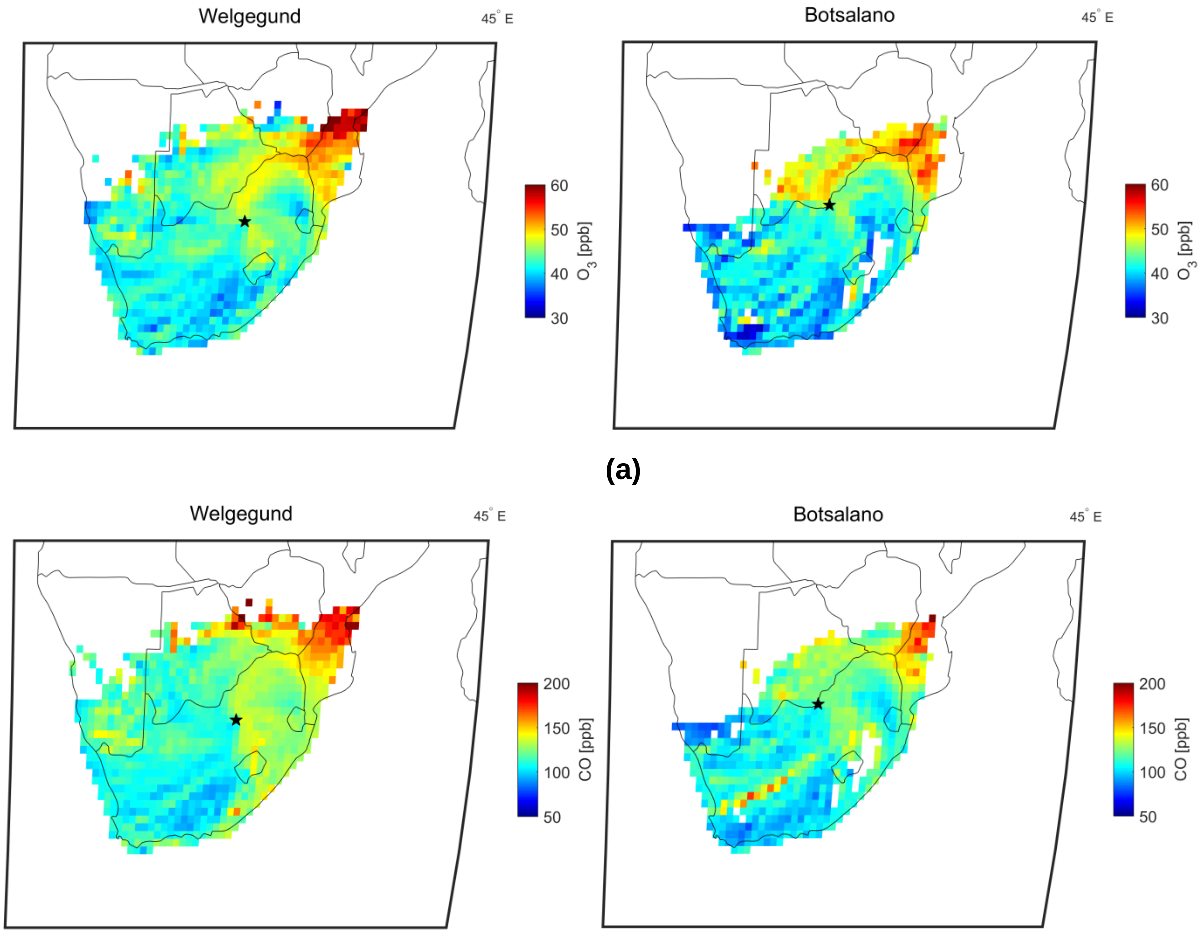
~~**Fig. 5.** Monthly mean daytime (11:00 to 17:00 LT) O_3 levels at the four continental sites in South Africa. The O_3 measurement periods varied among sites, which combined spanned a period from July 2006 to December 2015.~~

O_3 concentrations at Elandsfontein were lower compared to the other three sites throughout the year, with the exception of the winter months (June to August). ~~Although major point sources impacting Elandsfontein are important sources of O_3 precursors (e.g. NO_x emissions from coal-fired power stations), t~~These~~se~~ major point sources at Elandsfontein include NO_x emissions from coal-fired power stations and are characteris~~z~~ed by high-stack emissions, which are emitted above the low-level night-time inversion layers. During day time, downwards mixing of these emitted species occurs, which results in daytime peaks of NO_x (as indicated in Fig. A4~~5~~ and by Collett et al., 2010) and subsequent O_3 titration. In contrast, Venter et al. (2012) indicated that, at Marikana, low-level emissions ~~(below the nighttime inversion layer)~~ associated with household combustion for space heating and cooking ~~was~~ were a significant source of O_3 precursor species, i.e. NO_x and CO. The diurnal pattern of NO_x and CO (Fig. A~~3~~4 and Fig. A5~~4,~~ respectively) at

Marikana was characterised by bimodal peaks during the morning and evening, which resulted in increased O$_3$ concentrations during daytime and night-time titration of O$_3$, especially during winter. Therefore, the observed differences in night-time titration at Marikana and Elandsfontein can be attributed to different sources of O$_3$ precursors, i.e. mainly low-level emissions (household combustion) at Marikana (Venter et al., 2012) compared to predominantly high-stack emissions at Elandsfontein (Collette~~.~~ et al., 2010). The higher O$_3$ concentrations at Elandsfontein during winter are most ~~-~~likely attributed to the regional increase in O$_3$ precursors.

~~The influence of anthropogenic emissions on O$_3$ concentrations can also be illustrated by comparison of the monthly O$_3$ levels measured at the rural background and an industrial site. Comparison between O$_3$ concentrations at Welgegund and Marikana indicated small differences between the O$_3$ levels during the summer (January, February) and autumn (March to May) months. During June a ~10 ppb monthly O$_3$ concentration difference is observed, which increases to ~15 ppb during October. This baseline shift observed between Welgegund and Marikana can be attributed to local anthropogenic emissions (mainly household combustion) of O$_3$ precursors at Marikana. The baseline shift is smaller in winter due to increased O$_3$ titration associated with increased NO$_x$ emissions.~~

The spring maximum O$_3$ concentrations can be attributed to increases in widespread regional biomass burning in this region during this period (Vakkari et al., 2014; Lourens et al., 2011). Biomass burning has strong seasonality in southern Africa, extending from June to September (Galanter et al., 2000), and is an important source of O$_3$ and its precursors during the dry season. In an effort to elucidate the influence of regional biomass burning on O$_3$ concentrations in continental South Africa, source area maps of O$_3$ were compiled by relating O$_3$ concentrations measured with air mass history, which are presented in Fig. ~~6~~5 (a). Source area maps were only generated for the background sites Welgegund and Botsalano, since local sources at the industrial sites Elandsfontein and Marikana would obscure the influence of regional biomass burning. In addition, maps of spatial distribution of fires during 2007, 2010 and 2015 were compiled with the MODIS collection 5 burnt area product (Roy et al., 2008; Roy et al., 2005; Roy et al., 2002), which are presented in Fig. 6~~7~~.



(a)

(b)

Fig. 5~~6~~. Source area maps of (a) O_3 concentrations and (b) CO concentrations for the background sites Welgegund and Botsalano. The black star represents the measurement site and the colour of each pixel represents the mean concentration of the respective gas species. At least ten observations per pixel are required.

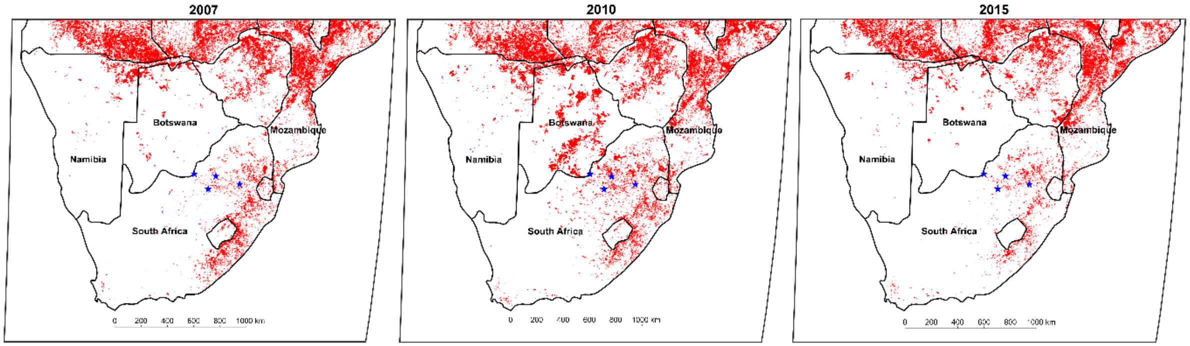
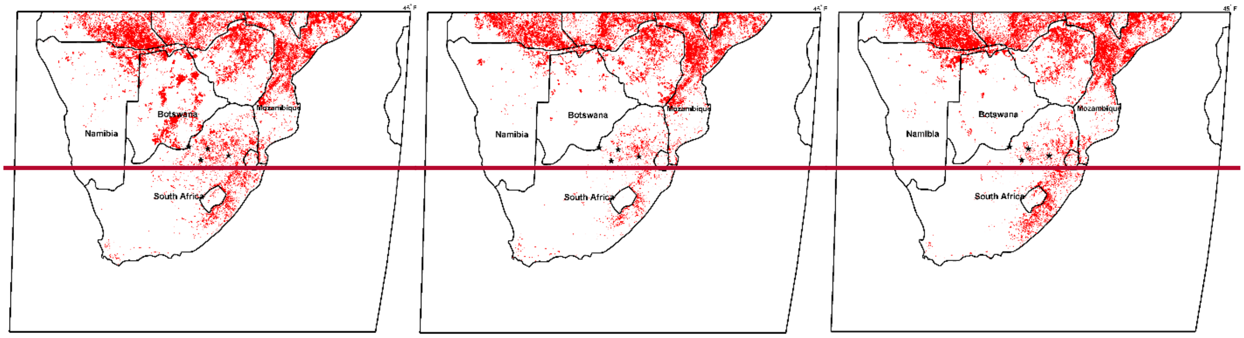


Fig. 7. Spatial distribution of fires in 2007, 2010 and 2015 from MODIS burnt area product. Blue stars indicate (from left to right) Botsalano, Welgegund, Marikana and Elandsfontein.



~~(a) 2007~~ ~~(b) 2010~~ ~~(c) 2015~~

~~**Fig. 7.** Spatial distribution of fires in 2007, 2010 and 2015 from MODIS burnt area product. Black stars indicate (from left to right) Botsalano, Welgegund, Marikana and Elandsfontein.~~

The highest O_3 concentrations measured at Welgegund and Marikana were associated with air masses passing over a sector north to north-east of these sites, i.e. southern and central Mozambique, southern Zimbabwe and south-eastern Botswana. O_3 concentrations associated with air masses passing over central and southern Mozambique were particularly high. In addition to O_3 source maps, CO source maps were also compiled for Welgegund and Botsalano, as indicated in Fig. ~~6~~5 (b). It is evident that the CO source maps indicated a similar pattern than that observed for O_3 with the highest CO concentrations corresponding with the same regions where O_3 levels are the highest. From the fire maps in Fig. 6,~~7~~ it can be observed that a large number of fires occur in the sector, associated with higher O_3 and CO concentrations, with the fire map indicating, especially, a high fire frequency occurring in central Mozambique. During 2007, more fires occurred in Botswana compared to the other two years, which is also reflected in the higher O_3 levels measured at Botsalano during that year for air masses passing over this region. Open biomass burning is known to emit more CO than NO_x, while CO also has a relatively long atmospheric lifetime (1 to 2 months, Kanakidou and Crutzen, 1999) compared to NO_x (6 to 24 hours, Beirle et al., 2003) and VOCs (few hours to a few weeks, Kanakidou and Crutzen, 1999) emitted from open biomass burning. Enhanced CO concentrations have been used previously to characterise the dispersion of biomass burning emissions over southern Africa (Mafusire et al., 2016). Therefore, the regional transport of CO and VOCs (and NO_x ~~and VOCs~~ to a lesser extent) associated with biomass burning occurring from June to September in southern Africa can be considered an important source of surface O_3 in continental South Africa (Fig. A5~~4~~).

3.~~3~~4.2 Stratospheric O_3

Elevated levels of tropospheric O_3 may also be caused by stratospheric intrusion of O_3-rich air (Zhang et al., 2014; Parrish et al., 2013; Lin et al., 2012), especially on certain days during late winter and spring when O_3 is the highest on the South African Highveld (Thompson et al., 2014). However, the importance of the stratospheric source over continental South Africa has not yet been specifically addressed. The ~~A~~assessment of meteorological fields and air quality data at high-elevation sites is required to determine the downward transport of stratospheric O_3. Alternatively, stratospheric O_3 intrusions can be estimated through concurrent in-~~—~~situ measurements of ground~~-~~-level O_3, CO and humidity, since stratospheric intrusions of O_3 into the troposphere are characterised by elevated levels of O_3, high potential vorticity, low levels of CO and low water vapour (Stauffer et al., 2017; Thompson et al., 2015; Thompson et al., 2014). Thompson et al. (2015) defined low CO as 80 to 110 ppbv, ~~whilst~~ while low relative humidity (RH) is considered <15 %. In Fig. 7,~~8~~ the 95th percentile O_3 levels (indicative of "high O_3") corresponding to low daily average CO concentrations (< 100 ppb) are presented together with the daily average RH. Only daytime data from 07:00~~-~~ to 18:00 (LT) ~~were~~ was considered in order to exclude the influence of night-time titration. From Fig. 7,~~8~~ it is evident that very few days complied with the criteria indicative of stratospheric O_3 intrusion, i.e. high O_3, low CO and low RH, which indicates a very small influence of stratospheric intrusion on surface O_3 levels. However, it must be noted that the attempt in this study to relate~~d~~ surface O_3 to stratospheric intrusions is a simplified qualitative assessment and more quantitative detection methods should be applied to understand the influence of stratospheric intrusions on surface O_3 for this region.

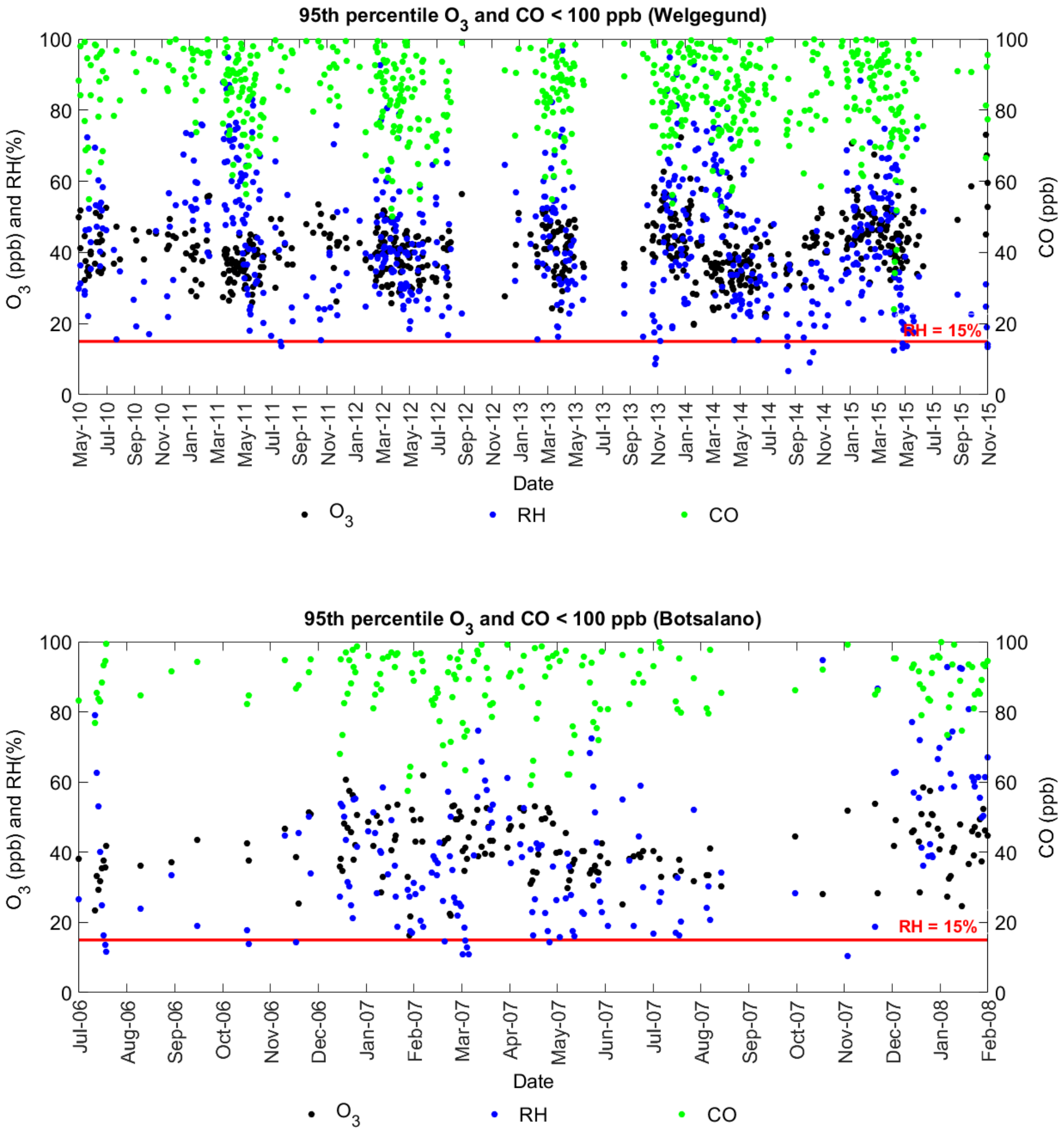


Fig. 7~~8~~. Simultaneous measurements of O_3 (daily 95th percentile), CO (daily average ppb) and RH (daily average) from 07:00 to 18:00 LT at Welgegund, Botsalano and Marikana.

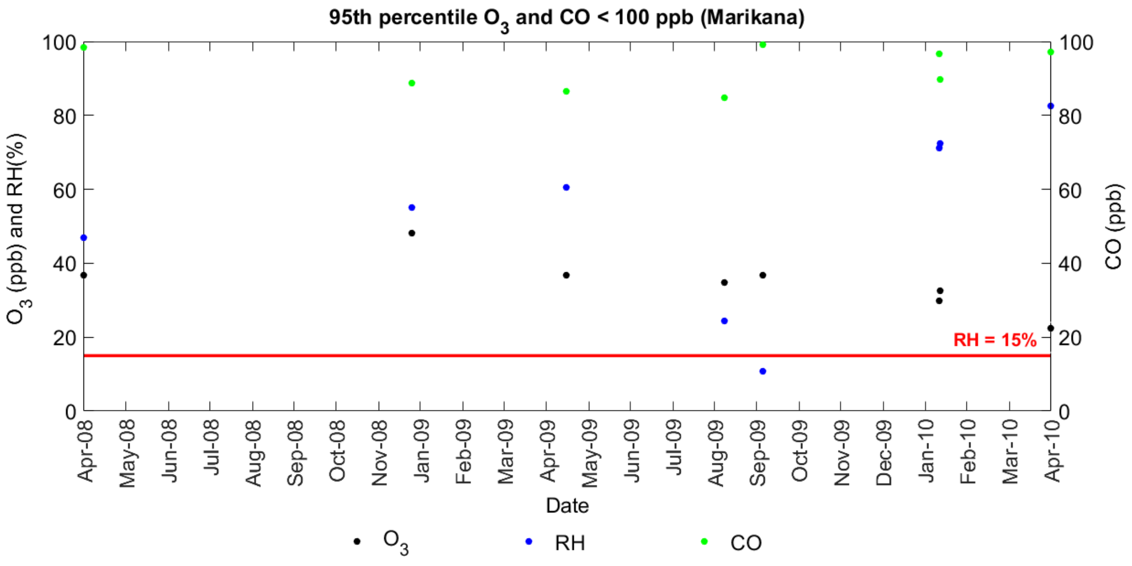


Fig. 7~~8~~. Continued.

3.5~~4~~ Insights into the O_3 production regime

~~In the absence of VOC data, t~~The relationship between O_3, NO_x and CO was used as an indicator to infer the O_3 production regime at Welgegund, Botsalano and Marikana (no CO measurements were conducted at Elandsfontein as indicated above), since no continuous VOC measurements were conducted at each of these sites. However, as indicated in Section 2.4, ~~A~~a two-year VOC dataset ~~compiled during two sampling campaigns~~ was available for Welgegund (Jaars et al., 2016; Jaars et al., 2014), which was used to calculate the instantaneous production rate of O_3 as a function of NO_2 levels and VOC reactivity (Geddes et al., 2009; Murphy et al., 2006).

3.~~4~~5.1 The relationship between NO_x, CO and O_3

In Fig. 8,~~9~~ the correlations between O_3, NO_x and CO concentrations at Welgegund, Botsalano and Marikana are presented, which clearly indicate~~s~~ higher O_3 concentrations associated with increased CO levels, while O_3 levels remain relatively constant (or decrease) with increasing NO_x. The highest O_3 concentrations occur for NO_x levels below 10 ppb, since the equilibrium between photochemical production of O_3 and chemical removal of O_3 shifts towards the former, i.e. greater O_3 formation. In general, there seems to exist a marginal negative correlation between O_3 and NO_x (Fig. A6~~5~~) at all four sites, which is a reflection of the photochemical production of O_3 from

NO_2~~ (Eq. (1) and Eq. (2))~~ and the destruction of O_3 through NO_x titration~~ (Eq. (3))~~. These correlations between NO_x, CO and O_3 indicate that O_3 production in continental South Africa is limited by CO (and VOCs) concentrations, i.e. VOC~~(CO)~~-limited.

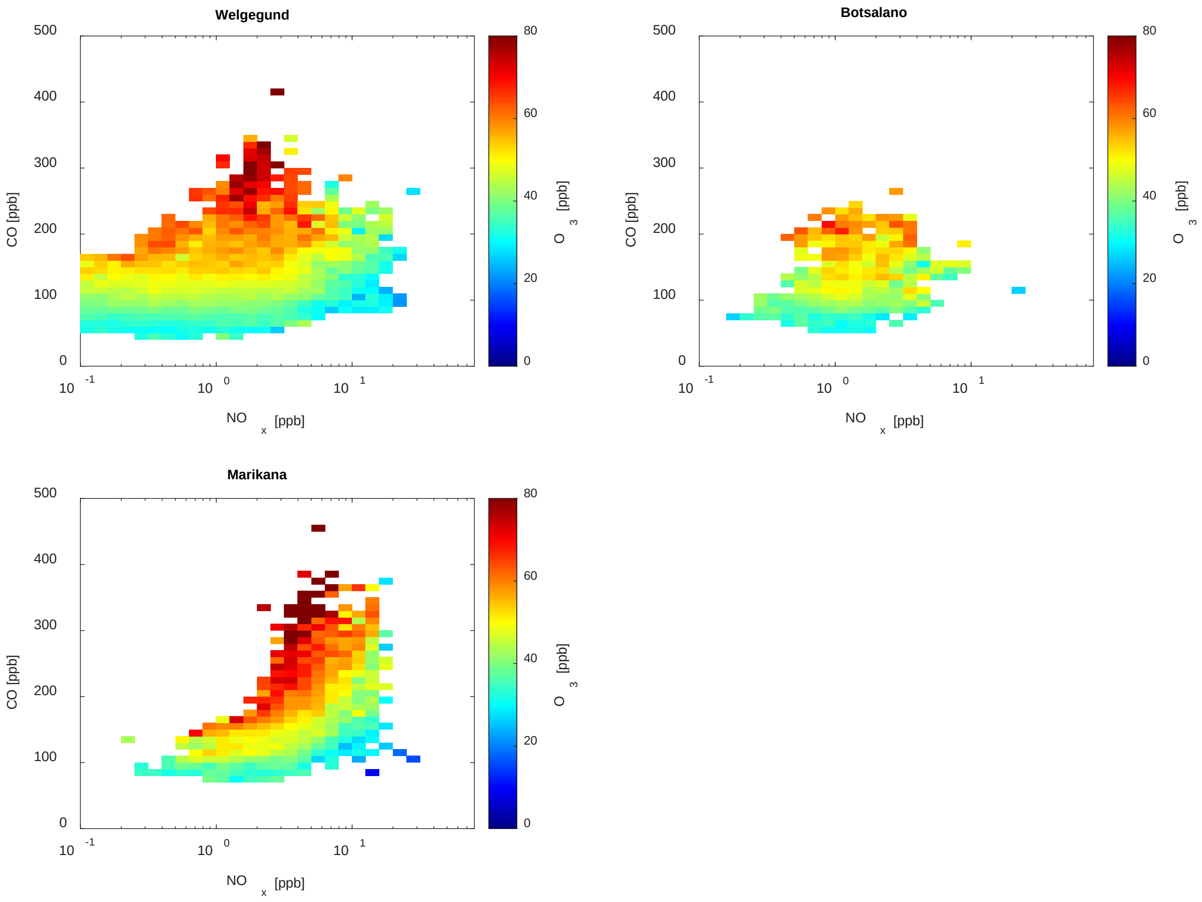


Fig. 8~~9~~. Mean O_3 concentration averaged for NO_x and CO bins. Measurements were only taken ~~during period~~from 11:00 to ~~-~~17:00 LT when photochemical production of O_3 is at a maximum.

This finding shows a strong ~~dependence of~~ correlation between O_3 on CO and suggests that high O_3 can be ~~mainly~~ attributed to the oxidation of CO in the air masses, i.e. as long as there is a sufficient amount of NO_x present in a region, CO serves to produce O_3. Although NO_x and VOCs are usually considered as the main precursors in ground-level O_3 formation, CO acts together with NO_x and VOCs in the presence of sunlight to drive photochemical O_3 formation~~ (Eq. (5))~~. According to Fig. 8~~9~~, reducing CO emissions should result in a reduction in surface O_3 and it is assumed that this response is analogous to that of VOCs. It is, however, not that simple, since the ambient NO_x and VOCs concentrations are directly related to the instantaneous rate of production of O_3 and not necessarily to the ambient O_3 concentration at a location, which is the result of chemistry, deposition and transport that ~~has~~ have occurred over several hours or a few days (Sillman, 1999). Notwithstanding the various factors contributing to increased surface O_3 levels, the correlation between ambient CO and O_3 is~~,~~ especially~~,~~ relevant given the low reactivity of CO with respect to $^•$OH radicals compared to most VOCs, which implies that the oxidation of CO probably takes place over a timescale of several days. It seems that the role of CO is of major importance in tropospheric chemistry in this region, where sufficient NO_x is present across continental South Africa and biogenic VOCs are relatively less abundant (Jaars et al., 2016), to fuel the O_3 formation process.

3.~~4~~5.2 Seasonal change in O_3-precursors relationship

Seasonal changes in the relationship between O_3 and precursor species can be indicative of different sources of precursor species during different times of the year. In Fig. ~~10~~9, the correlations between O_3 levels with NO_x and CO are presented for the different seasons, which indicate seasonal changes in the dependence of elevated O_3 concentrations on these precursors. The very high CO concentrations relative to NO_x, i.e. high CO to NO_x ratios, are associated with the highest O_3 concentrations, which ~~is~~ are most pronounced (highest CO/NO_x ratios) during winter and spring. This indicates that the winter and spring O_3 maximum is primarily driven by increased ~~$HO_2^•$~~peroxy radical production from CO and VOCs ~~(Eq. (5))~~. The seasonal maximum in O_3 concentration coincides with the maximum CO concentration at the background sites, ~~whilst~~ while the O_3 peak occurs just after June/July when CO peaked at the polluted site Marikana (Fig. A5~~4~~). This observed seasonality in O_3 production signifies the importance of ~~of CO to O_3 formation in continental South Africa, as well as that CO~~ precursor species emissions from open biomass burning during winter and spring ~~can be considered to be a major source of O_3~~ in this region, while household combustion for space heating and cooking is also an important source of ~~CO during winter~~O_3 precursors, as previously discussed. The strong diurnal CO concentration patterns observed during winter at Marikana (Fig. A5~~4~~) substantiate the influence of household combustion on CO levels as indicated by Venter et al. (2012).

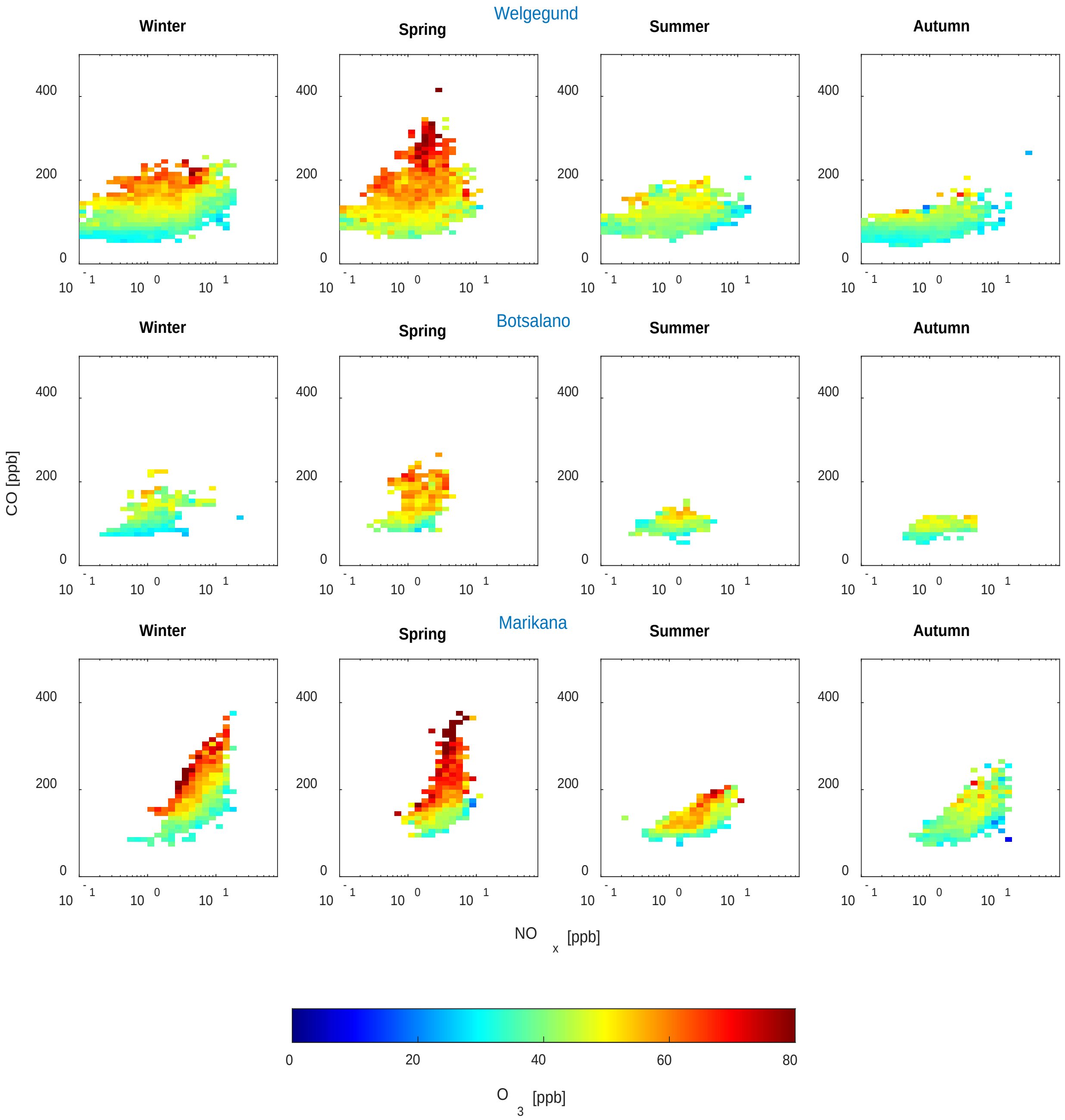


Fig. 9~~10~~. Seasonal plots of the relationship between O_3, NO_x and CO at Welgegund, Botsalano and Marikana.

3.5~~4~~.3 O_3 production rate

In Fig. 10, $P(O_3)$ as a function of VOC reactivity calculated from the available VOC dataset for Welgegund (Section 2.4) and NO_2 concentrations is presented. O_3 production at Welgegund during two field campaigns, specifically at 11:00 LT, ~~were~~was found to range between 0 and 10 ppbv h^{-1}. The average $P(O_3)$ over the 2011 to 2012 and the 2014 to 2015 campaigns combined were 3.0 ± 1.9 ppbv h^{-1} and 3.2 ± 3.0 ppbv h^{-1}, respectively. The dashed black line in Fig. 10, called the ridge line, separates the NO_x- and VOC-limited regimes. To the left of the ridge line is the NO_x-limited regime, when O_3 production increases with increasing NO_x concentrations. The VOC-limited regime is to the right of the ridge line, when O_3 production decreases with increasing NO_x. According to the O_3 production plot presented, approximately 40% of the data is found in the VOC-limited regime area, which would support the regional O_3 analysis conducted for continental South Africa in this study. However, the O_3 production plot for Welgegund transitions between NO_x- and VOC-limited regimes, with Welgegund being in a NO_x-limited production regime the majority of the time, especially when NO_x concentrations are very low (<1 ppb). As indicated in s~~S~~ection 2.4, limitations to this analysis include limited VOC speciation data, as well as a single time-of-day grab sample. The O_3 production rates can therefore only be inferred at 11:00 am LT despite O_3 concentrations peaking during the afternoon at Welgegund. Therefore, clean background air O_3 production is most-likely NO_x-limited (Tiitta et al., 2014), while large parts of the regional background of continental South Africa can be considered VOC-limited. ~~A VOC dataset was available from two sampling campaigns conducted at Welgegund from 2014 to 2016 (Jaars et al., 2016), which was used to calculate VOC reactivity and $P(O_3)$ as described in Section 2.4 at this site. The $P(O_3)$ at Welgegund as a function of VOC reactivity and NO_2 concentrations is presented in Fig. 11. The dashed black line in Fig. 11, often called the ridge line, separates the NO_x- and VOC-limited regimes. To the left of the ridge line is the NO_x-limited regime, i.e. O_3 concentrations decrease with decreasing NO_x and are insensitive to VOCs, while to the right of the ridge is the VOC-limited regime, i.e. O_3 concentrations decrease with decreasing VOCs and increase with decreasing NO_x. According to the O_3 production plot presented, at least 40% of the data is found in the VOC-limited regime area. However, the O_3 production plot for Welgegund also indicates a NO_x-limited region at very low NO_x concentrations (<1 ppb). Therefore Welgegund transitions between NO_x- and VOC-limited regimes. This can be attributed to Welgegund being impacted by the major source regions in the north-eastern interior of South Africa, as well as a relatively clean background region (Tiitta et al., 2014). Therefore, for clean background air O_3 production is most-likely NO_x-limited, while large parts of the regional background of continental South Africa can be considered VOC-limited.~~

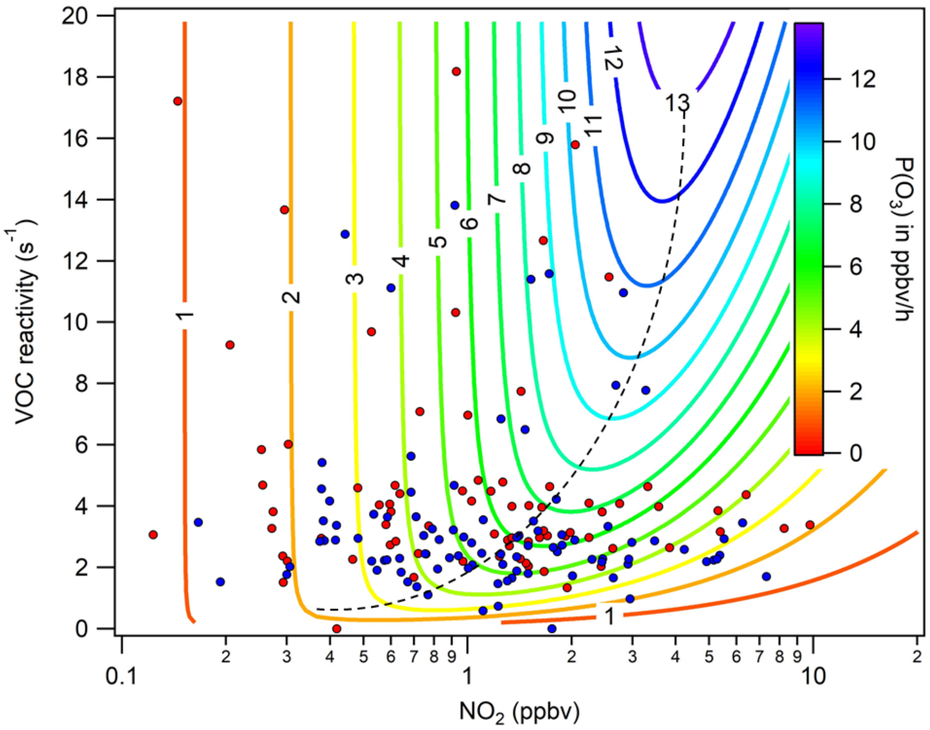


Fig. 10~~1~~. Contour plot of instantaneous O_3 production (P(O_3)) at Welgegund using daytime (11:00 LT) grab sample ~~surface~~ measurements of VOCs and NO_2 ~~based on the model developed by Murphy et al. (2006)~~. The blue dots represent the first campaign (2011-2012), and the red dots indicate the second campaign (2014-2015).

3.6~~5~~ Implications for air quality management

3.~~5~~6.1 Ozone exceedances

The South African National Ambient Air Quality Standard (NAAQS) for O_3 is an ~~8~~eight-hour moving average limit of 61 ppbv with 11 exceedances allowed annually (Government Gazette Republic of South Africa, 2009). Fig.~~ure~~ 11~~2~~ shows the average number of days per month when this O_3 standard limit was exceeded at the four measurement sites. It is evident that the daily ~~8~~eight-h-O_3-maximum concentrations regularly exceeded the NAAQS threshold for O_3 and the number of exceedances annually allowed at all the sites, including the most remote of the four sites, Botsalano. At the polluted locations of Marikana and Elandsfontein, the O_3 exceedances peak early on in the dry season (June onwards), ~~whilst~~ while at the background locations of Welgegund and Botsalano, the highest numbers of exceedances occur later in the dry season (August to November). These relatively high numbers of O_3 exceedances at all the sites (background and industrial) highlight~~s~~ the regional O_3 problem in South Africa, with background sites being impacted by the regional transport of O_3 precursors from anthropogenic and biomass burning source regions.

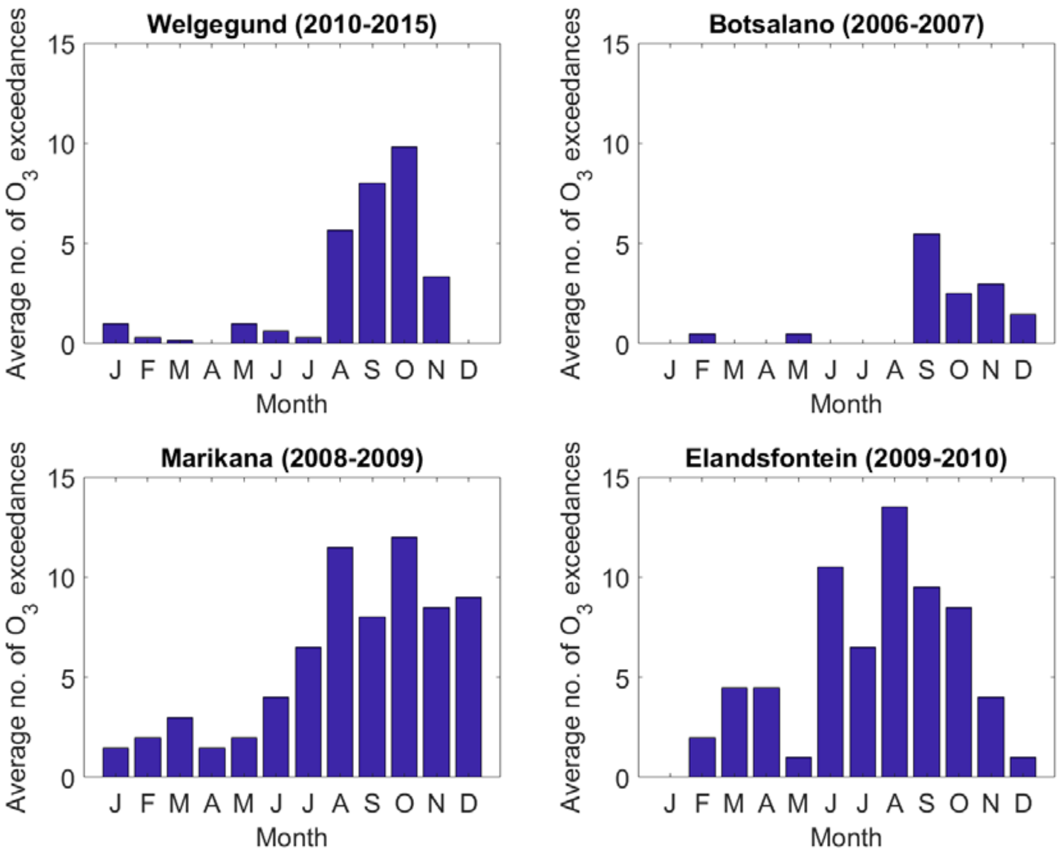


Fig. 11~~2~~. Monthly number of exceedances of the daily 8-h-O_3-max (i.e. highest value of all available 8-hour moving averages in that day) above 61 ppbv at Welgegund, Botsalano, Marikana and Elandsfontein.

3.~~5~~6.2 O_3 control strategies

~~The inverse relationship between O_3 and NO_x at all four study sites (Fig. A5) is evidence that photochemical O_3 production is inhibited by high NO_x. In addition, the colour map of O_3 concentration as a function of NO_x and CO concentrations at Welgegund, Botsalano and Marikana (Fig. 9), shows that high O_3 depends strongly on high CO, while the contour plot of $P(O_3)$ as a function of VOC reactivity and NO_x at Welgegund (Fig. 11) also indicated a relatively strong dependence on VOCs. Therefore, the~~As indicated above (s~~S~~ections 3.4 and 3.5), O_3 formation in the regions where Welgegund, Botsalano and Marikana are located can be considered VOC~~(CO)~~-limited, while the highly industrialised region with high NO_x emissions where ~~. It can even be deducted that these sites are CO-limited, although this term "CO-limited" is not commonly used when referring to O_3 production regimes (Seinfeld and Pandis, 2006). In addition, since~~ Elandsfontein ~~-~~is located~~ in a highly industrialised region with high NO_x emission, this area~~ ~~-~~could also be considered VOC-limited.~~-~~ Rural remote regions are generally considered to be NO_x-limited due to the availability of NO_x and the impact of BVOCs~~ and the availability of NO_x that limits photochemical O_3 formation~~ (Sillman, 1999). However, Jaars et al. (2016) indicated that BVOC concentrations at a savannah~~-~~ grassland were at least an order of magnitude lower compared to other regions in the world.~~,~~ Therefore, very low BVOC concentrations, ~~which~~ together with high anthropogenic emissions of NO_x in the interior of South Africa, result in VOC-limited conditions at background sites in continental South Africa~~ and not only in industrialised areas~~. ~~In addition, high CO and VOC emissions associated with biomass burning result in high O_3 production rates as indicated above.~~

~~Form the results and discussion presented above i~~It is evident that reducing CO~~-~~ and ~~(as well as anthropogenic and biomass burning~~ VOC~~s~~ concentrations associated with anthropogenic emissions, e.g. household combustion, vehicular emissions and industries,~~)~~ would be the most efficient control strategy to reduce peak O_3 concentrations in the interior of South Africa. It is also imperative to consider the seasonal variation in the CO and VOC source strength ~~-~~in managing O_3 pollution in continental southern Africa. ~~Anthropogenic emissions of CO, which include emissions from increased household combustion for space heating and cooking during winter, as well as other low-level sources contributing to increased CO levels associated with the concentration of pollutants during winter such as vehicular emissions, should be targeted to reduce CO emissions. It was also indicated in t~~This study also revealed the significant contribution of biomass burning ~~that open biomass burning is a significant source of~~to O_3 precursors in this region, which should also be considered when implementing O_3 control strategies. ~~and it should therefore also be aimed to reduce the influence of regional biomass burning, which is a major source of CO (and VOC) emissions during late winter and early spring, on increased O_3 concentrations.~~ However, ~~-~~since open biomass burning in southern Africa is of anthropogenic and natural origin, while O_3 concentrations in continental South Africa ~~is~~are also influenced by ~~the~~ trans boundary transport of O_3 precursors from open biomass burning occurring in other countries in southern Africa (as indicated above), it is more difficult to control. Nevertheless, open biomass burning caused by anthropogenic practices (e.g. crop residue, pasture maintenance fires, opening burning of garbage) can be addressed.

4. Conclusions

~~In this study continuous O_3 measurements were presented for four sites in the north-eastern interior in South Africa.~~ A spatial distribution map of O_3 levels in the interior of South Africa indicated ~~Two of these sites, i.e. Welgegund and Botsalano are considered to be regional background sites, while the other two sites were in close proximity to anthropogenic sources, i.e. Marikana and Elandsfontein. Contextualisation of these four sites with other sites in the north-eastern interior of South Africa, indicated that the sites in this study are representative of continental South African O_3 levels, while~~ the regional ~~problem of~~ O_3 problem in continental South Africa~~was also shown~~, which was ~~with O_3 concentrations being higher than 40 ppb at many of these sites. The regional problem of O_3 in continental South Africa was also~~ signified by the regular exceedance of the ~~61 ppbv 8-hour moving average~~ South African air quality standard limit ~~at the four sites in this study~~. ~~O_3 levels were generally lower at other background sites in the Southern Hemisphere compared to the South African sites, while similar seasonal patterns were observed.~~ The seasonal and diurnal O_3 patterns observed at the four sites in this study resembled typical trends for O_3 in continental South Africa,~~, i.e.~~ with O_3 concentrations peaking in late winter and early spring (cf. Zunckel et al., 2004), ~~and~~ while daytime O_3 ~~peaks associated~~ corresponded ~~with~~to increased photochemical production.

The seasonal O_3 trends observed in continental ~~South~~ southern Africa ~~can~~ could mainly be attributed to the seasonal changes in emissions of O_3 precursor species~~, as well as~~ and ~~changes in~~ local meteorological conditions~~ and synoptic scale circulation~~. Increased O_3 concentrations in winter at Welgegund, Marikana and Elandsfontein ~~were indicative of~~reflected increased ~~emissions of O_3 precursors from~~ household combustion for space heating and the ~~the concentration~~ trapping of low-level pollutants near the surface. ~~Furthermore, seasonal and diurnal patterns of O_3 concentrations at Elandsfontein also reflected high-stack emissions associated with industries in the Mpumalanga Highveld, while temporal O_3 patterns at Marikana were indicative of low-level emissions of O_3 precursors.~~ A spring maximum ~~was~~ observed at all the sites~~, which~~ was attributed to increased regional open biomass burning~~ during this time~~. ~~Source area maps of O_3 indicated s~~Significantly higher O_3 concentrations, which corresponded with increased CO concentrations, were associated with air masses passing over a region in southern Africa, where a large number of open biomass burning occurred from June to September~~, i.e. southern and central Mozambique, southern Zimbabwe and south-eastern Botswana, while CO concentrations were also considerably higher in air masses passing over this region~~. ~~These source maps indicated that the~~Therefore, the regional transport of CO associated with open biomass burning ~~occurring from June to September~~ in southern Africa ~~i~~was considered a significant source of surface O_3 in continental ~~South~~ South Africa. ~~Furthermore, a~~A very small contribution from the stratospheric intrusion of O_3-rich air to surface O_3 levels ~~measured~~ at the four sites was indicated.

~~In the absence of VOC data, t~~The relationship between O_3, NO_x and CO at Welgegund, Botsalano and Marikana ~~was investigated, which~~ indicated a strong ~~dependence of~~correlation between O_3 on CO, while O_3 levels remained relatively constant (or decreased) with increasing NO_x. Although NO_x and VOCs are usually considered ~~as~~ to be the main precursors in ground-level O_3 formation, CO can also ~~acts together with NO_x and VOCs in the presence of sunlight to~~ drive photochemical O_3 formation. ~~In addition, t~~The seasonal changes in the relationship between O_3 and precursors species also reflected the ~~seasonal changes in sources of precursors, i.e.~~ higher CO emissions associated with increased household combustion in winter, and open biomass burning in late winter and spring. The calculation of the $P(O_3)$ from a two-~~–~~year VOC dataset at Welgegund~~,~~ indicated that at least 40% of O_3 production occurred in the VOC-limited regime. These ~~relationships between O_3 concentrations and $P(O_3)$ with O_3 precursor species~~ results indicated that large parts ~~of the regional background~~ in continental South Africa can be considered ~~CO-limited or~~ VOC-limited, which can be attributed to high anthropogenic emissions of NO_x in ~~the interior of South Africa~~this region. It is, however, recommended that future studies should investigate more detailed relationships between NO_x, CO, VOCs and O_3 through photochemical modelling analysis, ~~,~~while concurrent measurement of atmospheric VOCs and •OH would also ~~increase~~ contribute to the better understanding of surface O_3 in this region.

In this paper, some new aspects on O_3 for ~~the~~ continental South Africa~~n~~ have been indicated, which must be taken into consideration when O_3 mitigation strategies are deployed. Emissions of O_3 precursor species associated with the concentrated location of industries in this area could be regulated, while~~ These results help to identify the key sources and precursor species for O_3 formation, which also highlight the regional problem of O_3 pollution in southern Africa with notably high rural O_3 concentrations in areas far removed from pollution sources. It was indicated that~~ CO and VOC emissions associated with household combustion and regional open biomass burning should also be targeted~~ to reduce O_3 concentrations in the interior of South Africa~~. ~~However, open~~

~~biomass burning can also be of natural origin, while the influence of regional transport on O_3 precursors in continental South Africa was also evident. In general, the influence of long-range transport must be considered when designing O_3 control strategies. A contributing factor to O_3 exceedances observed in the north-eastern interior in South Africa is the concentrated location of industries in this area, e.g. nine coal-fired power stations and a petrochemical plant located in this region. Emissions of O_3 precursor species could therefore be regulated in this region by enforcing mitigations strategies on these industries. However, e~~However, emissions of O_3 precursor species related to factors~~,~~ such as ~~regional biomass burning, as well as~~ household combustion associated with poor socio-economic circumstances and long-range transport~~,~~ provide~~s~~ a bigger challenge for regulators.

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Appendix A

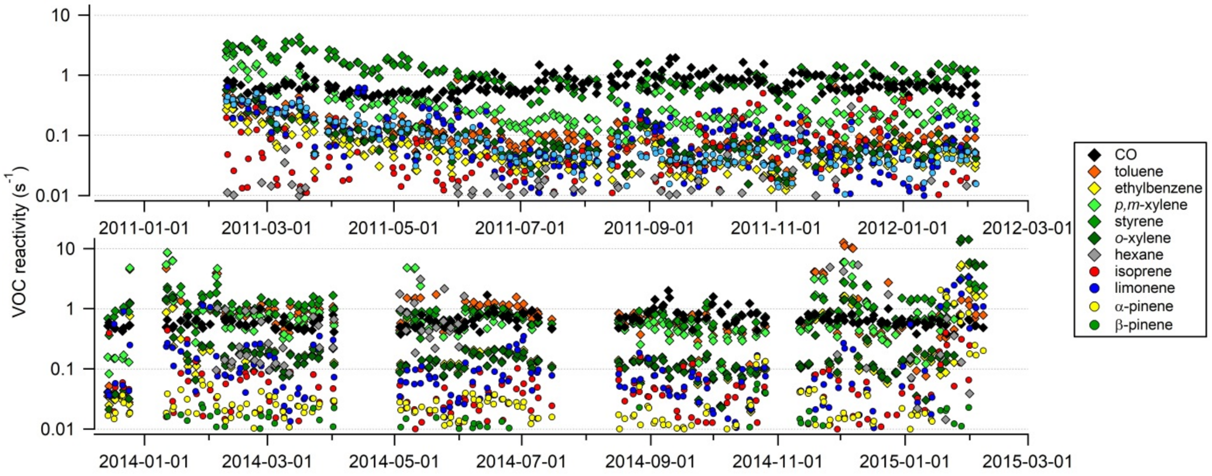

Fig. A~~2~~1. Individual VOC reactivity time series. In the calculation of instantaneous O_3 production ($P(O_3)$), CO was treated as a VOC.

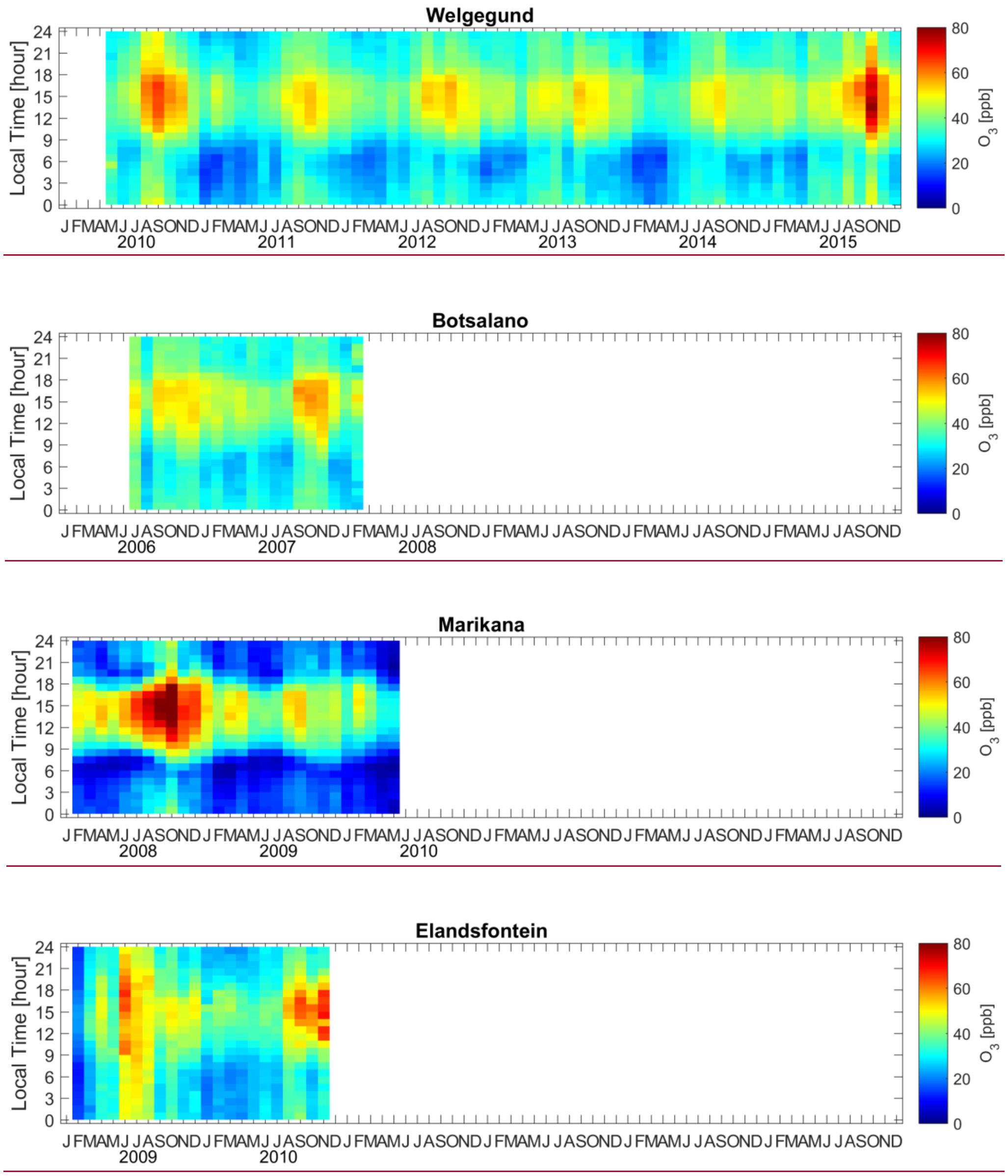

Fig. A2. Time series of monthly median O_3 concentrations for each hour of the day at the four sites

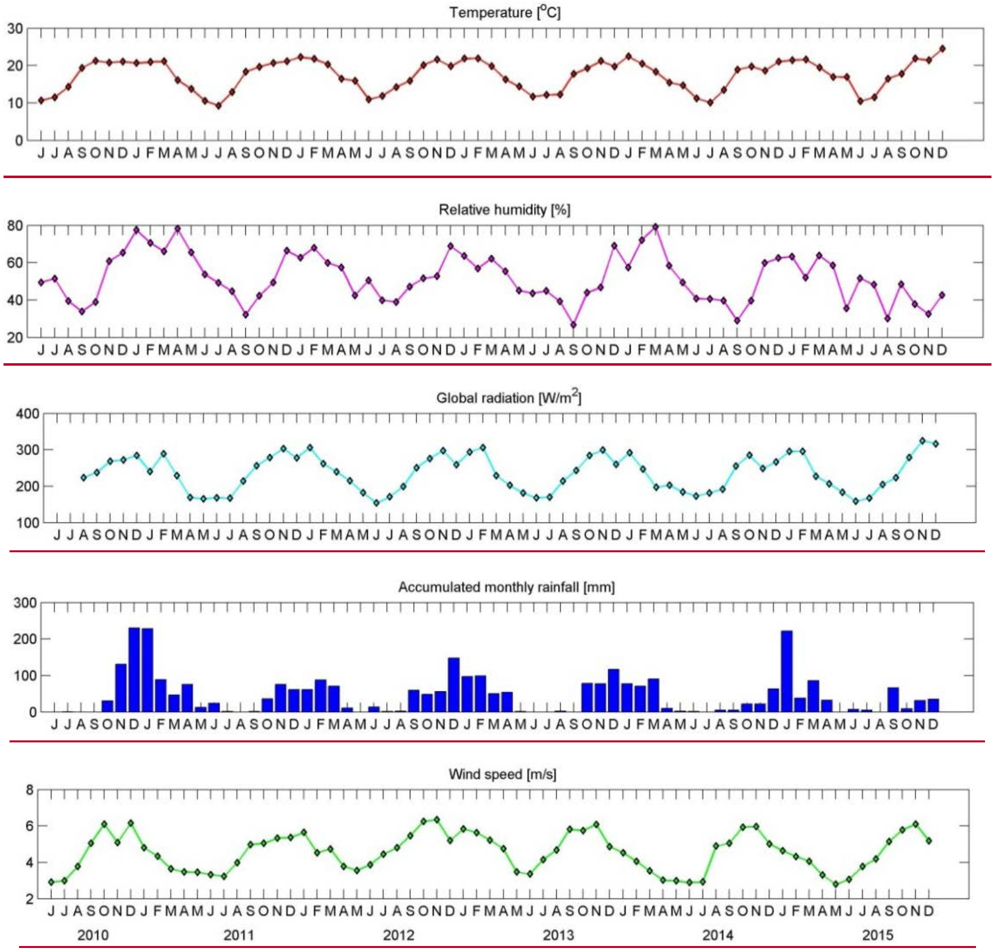

Fig. A3. Monthly averages of meteorological parameters at Welgegund to show typical seasonal patterns in continental South Africa. In the case of rainfall, the total monthly rainfall values are shown.

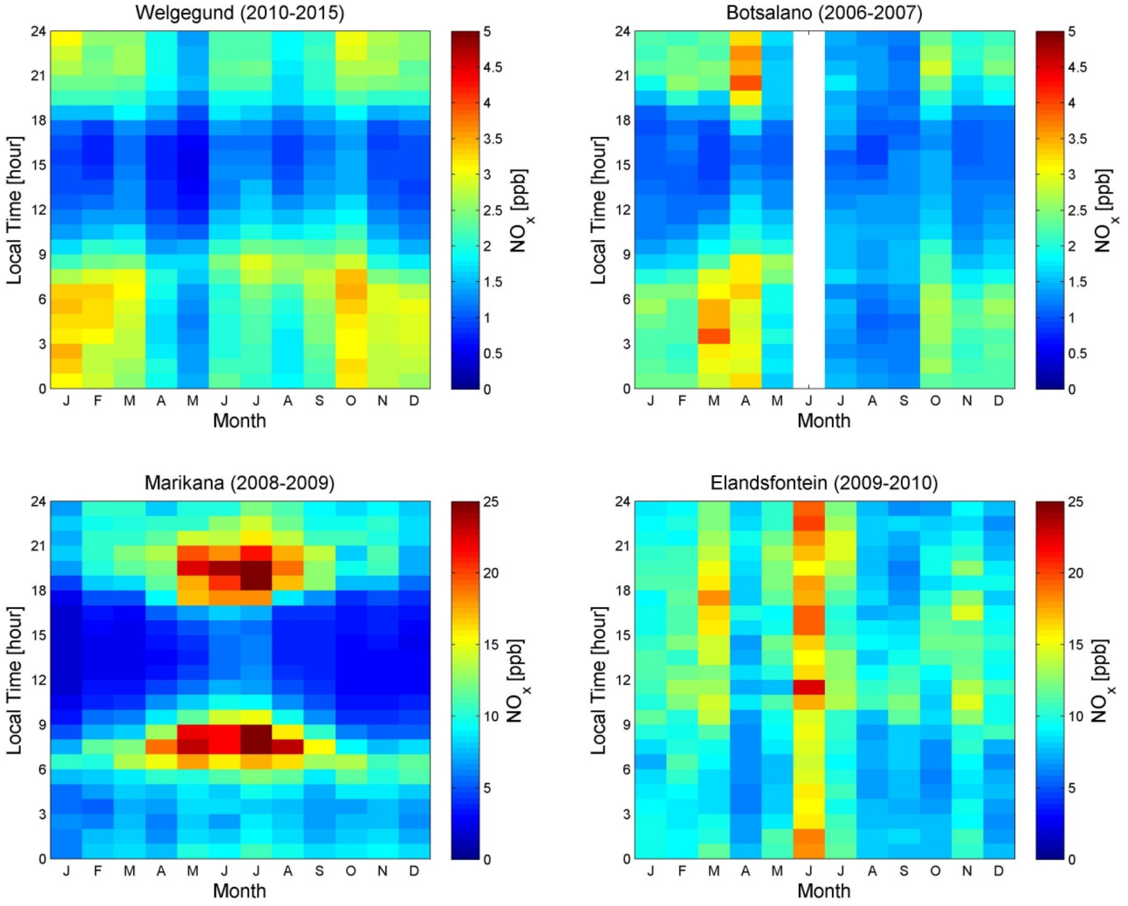

Fig. A4~~3~~. Seasonal and diurnal variation of NO$_x$ at Welgegund, Botsalano, Marikana and Elandsfontein (median values of NO$_x$ concentration were used).

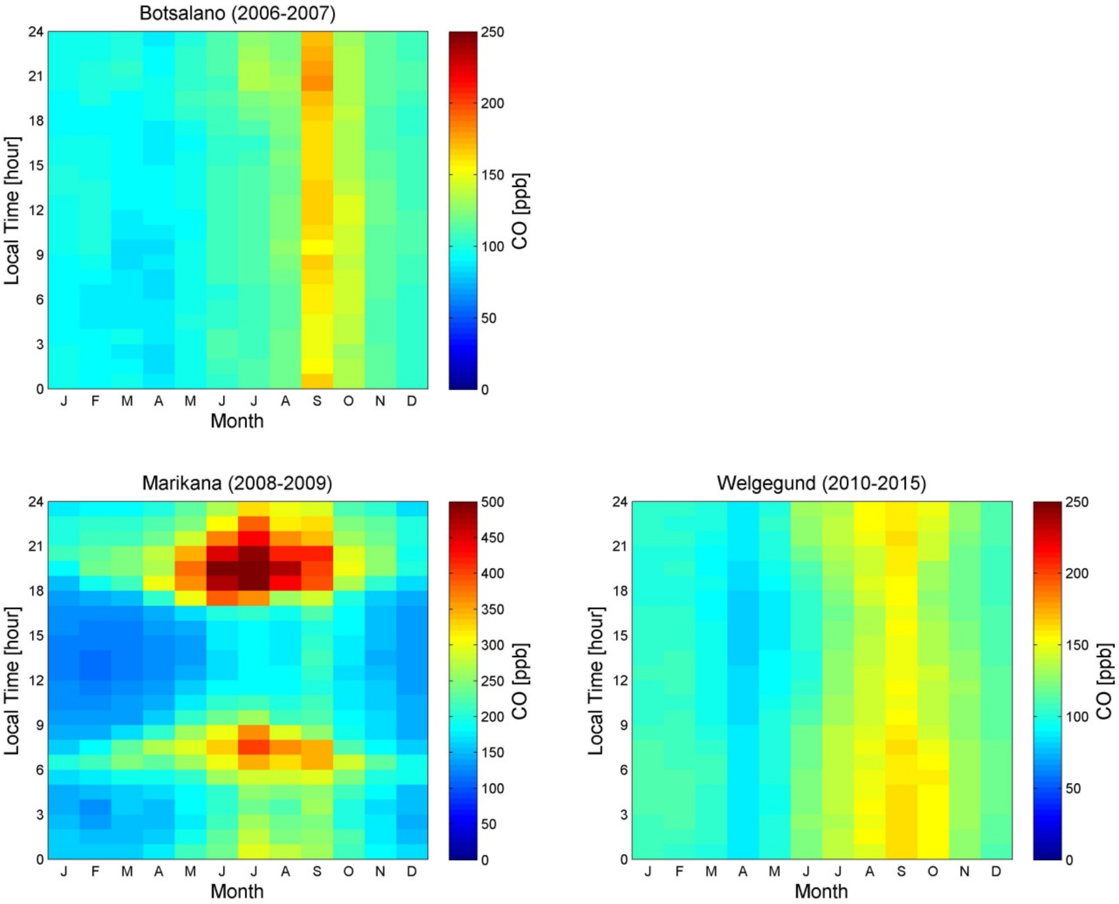

Fig. A54. Seasonal and diurnal variation of CO at Welgegund, Botsalano and Marikana (median values of CO concentration were used). Note that CO was not measured at Elandsfontein.

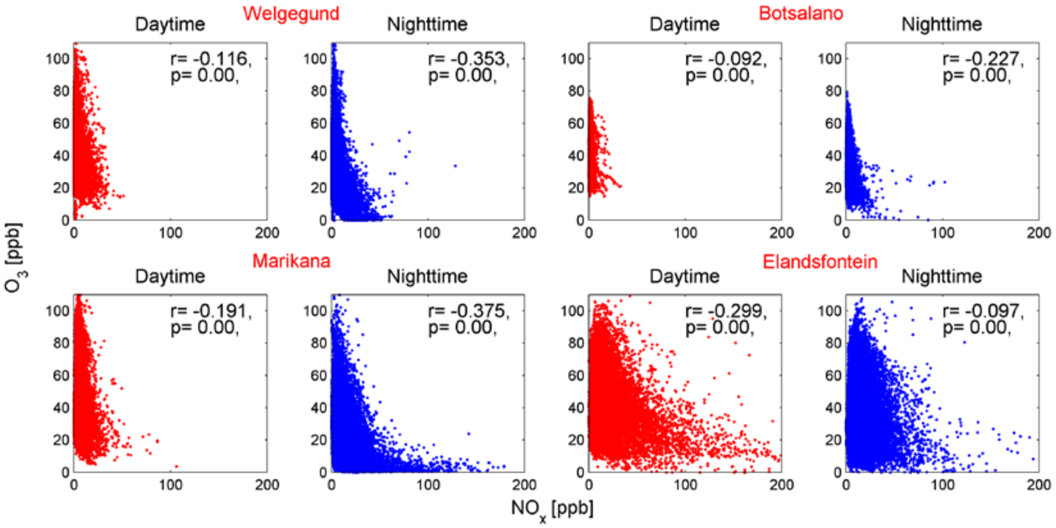

Fig. A6~~5~~. Scatter plots of O_3 vs. NO_x for daytime (9:00 a.m. to 4:52 p.m.), and night-time (5:00 p.m. to 8:52 a.m.) at Welgegund, Botsalano and Marikana and Elandsfontein. The correlation coefficient (r) has a significance level of $p < 10^{-10}$, which means that r is statistically significant ($p < 0.01$).

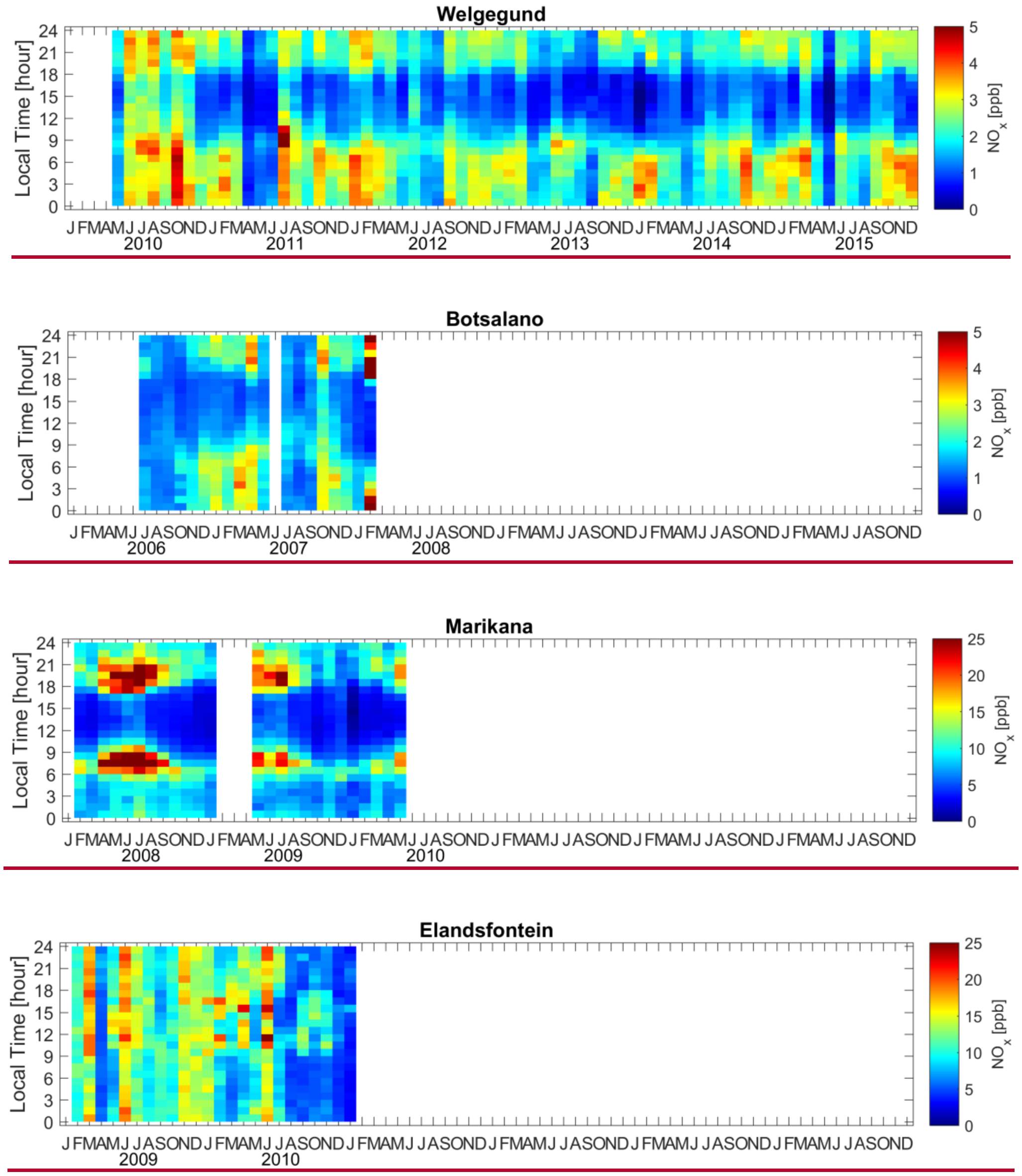

Fig. A7. Time series of monthly median NO_x concentrations for each hour of the day at the four sites

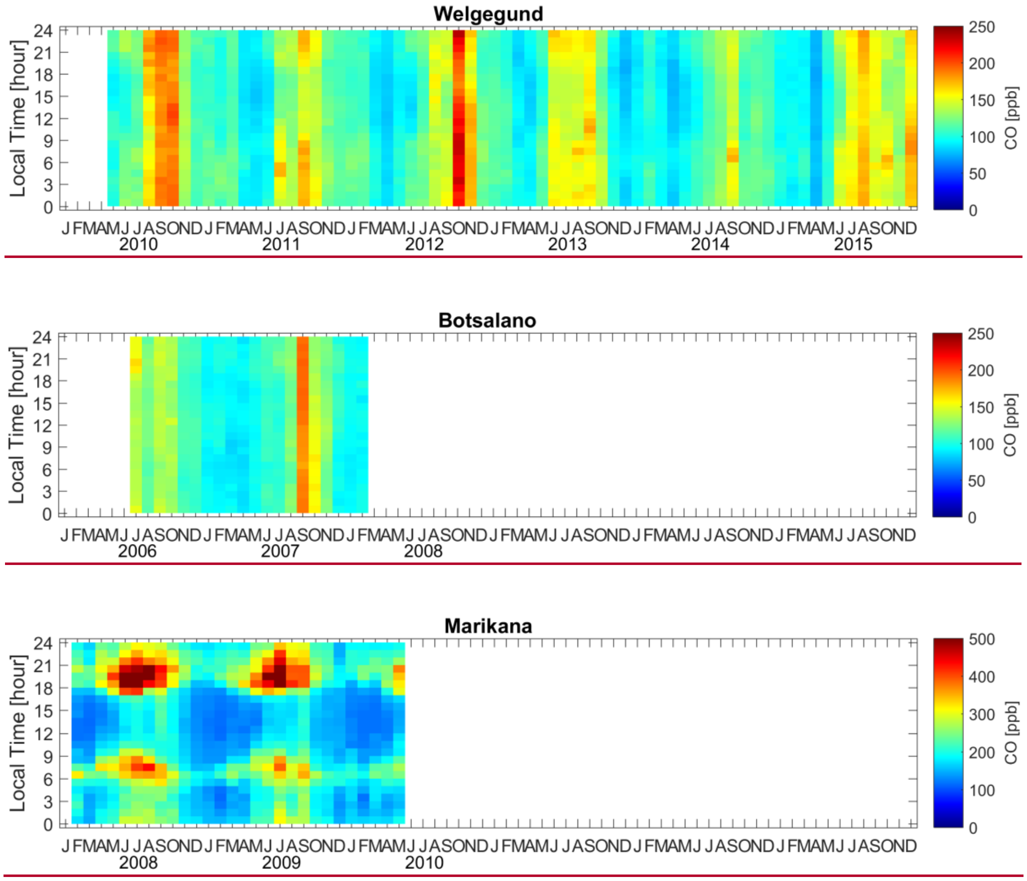

Fig. A8. Time series of monthly median CO concentrations for each hour of the day at the four sites