

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

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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 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 NO_x into an air mass, 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 O₃ formation should be toned down and that policy should focus on reducing both CO and VOCs. However, the significance of CO to O₃ 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 O₃ was toned down in the manuscript in different sections and the contribution of VOCs indicated, without compromising the significance of CO on O₃ 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 O₃ 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 O₃ in continental South Africa (Fig. A4).”

Section 3.4.1 (now Section 3.5.1):

“In Fig. 8 the correlations between O₃, NO_x and CO concentrations at Welgegund, Botsalano and Marikana are presented, which clearly indicates higher O₃ concentrations associated with increased CO levels, while O₃ levels remain relatively constant (or decrease) with increasing NO_x. The highest O₃ concentrations occur for NO_x levels below 10 ppb, since the equilibrium between photochemical production of O₃ and chemical removal of O₃ shifts towards the former i.e. greater O₃ formation. In general there seems to exist a marginal negative correlation between O₃ and NO_x (Fig. A6) at all four sites, which is a reflection of the photochemical production of O₃ from NO₂ and the destruction of O₃

through NO_x titration. These correlations between NO_x, CO and O₃ indicate that O₃ 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 O₃ maximum is primarily driven by increased peroxy radical production from CO and VOCs. The seasonal maximum in O₃ concentration coincides with the maximum CO concentration at the background sites, whilst the O₃ peak occurs just after June/July when CO peaked at the polluted site Marikana (Fig. A5). This observed seasonality in O₃ 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 O₃ precursors as previously discussed.”

Section 3.5.2 (now Section 3.6.2):

“As indicated above (Section 3.4 and 3.5), O₃ 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 O₃ 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 O₃ pollution in continental southern Africa. This study also revealed the significant contribution of biomass burning to O₃ precursors in this region, which should also be considered when implementing O₃ control strategies. However, since open biomass burning in southern Africa is of anthropogenic and natural origin, while O₃ concentrations in continental South Africa are also influenced by trans boundary transport of O₃ 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 O₃, NO_x and CO at Welgegund, Botsalano and Marikana indicated a strong correlation between O₃ on CO, while O₃ 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 O₃ formation, CO can also drive photochemical O₃ formation. The seasonal changes in the relationship between O₃ and precursor 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(O₃) from a two-year VOC dataset at Welgegund, indicated that at least 40% of O₃ 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 O₃ through photochemical modelling analysis, while concurrent measurement of atmospheric VOCs and •OH would also contribute to the better understanding of surface O₃ in this region.

In this paper some new aspects on O₃ for the continental South Africa have been indicated, which must be taken in consideration when O₃ mitigation strategies are deployed. Emissions of O₃ 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 O₃ 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 O₃, 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 O₃ 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 O₃ 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 O₃ 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 O₃ concentrations are presented in this figure. The spatial map, i.e. Fig. 2 (now Fig. 3) compiled from average spring O₃ concentrations do, however, indicate relatively high O₃ levels across the region, albeit not necessarily above 40 ppb. Therefore the text referring to the regional O₃ 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 O₃ problem was evident with O₃ concentrations regularly exceeding the South African air quality standard limit, while O₃ levels were higher compared to other background sites in the Southern Hemisphere. The temporal O₃ 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 O₃ levels. From Fig. 3 it is evident that O₃ can be considered a regional problem with O₃ 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 O₃ levels in the interior of South Africa indicated the regional O₃ problem in continental South Africa, which was signified by the regular exceedance of the South African air quality standard limit. The seasonal and diurnal O₃ patterns observed at the four sites in this study resembled typical trends for O₃ 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 NO_x limited? Presumably not and 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 Welgegend 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 $6.68 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ (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 O₃ 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 Welgegend (Jaars et al., 2016; Jaars et al., 2014), which could be used to model instantaneous O₃ 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 •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 Welgegend. Specifically, each VOC reactivity was then summed to obtain the total VOC reactivity for each measurement, i.e. $\text{VOC reactivity} = \sum k_i [\text{VOC}]_i$. 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 $\bullet\text{OH}$ radicals of $6.68 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ 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 $\bullet\text{OH}$ and $\text{HO}_2\bullet$ radicals) production, (2) estimation of the $\bullet\text{OH}$ 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 ($P(\text{HO}_x)$) depends on the photolysis rate of O_3 (J_{O_3}), concentration of O_3 and vapour pressure of water (Jaegle et al., 2001). The photolysis rate proposed for the Southern Hemisphere, i.e. $J_{\text{O}_3} = 3 \times 10^{-5} \text{ s}^{-1}$ (Wilson, 2015) was used from which $P(\text{HO}_x)$ was calculated as follows:

$$P(\text{HO}_x) = 2J_{\text{O}_3}k_{\text{O}_3}[\text{O}_3][\text{H}_2\text{O}]$$

and estimated to be $6.09 \times 10^6 \text{ molec cm}^{-3} \text{ s}^{-1}$ 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 $P(\text{HO}_x)$ at Welgegund is approximately a factor of two lower compared to other reported urban $P(\text{HO}_x)$ values (Geddes et al., 2009). The factors and reactions that affect $[\bullet\text{OH}]$ include:

- linear dependency between $\bullet\text{OH}$ and NO_x due to the reaction $\text{NO} + \text{HO}_2 \rightarrow \bullet\text{OH} + \text{NO}_2$, until $\bullet\text{OH}$ begins to react with elevated NO_2 concentrations to form HNO_3 ($\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$);
- $P(\text{HO}_x)$ is affected by solar irradiance, temperature, O_3 concentrations, humidity; and
- partitioning of HO_x between RO_2 , HO_2 , OH .

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

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

$$B = k_4[\text{NO}_2] + \alpha * \text{VOC reactivity}$$

$$C = P(HO_x)$$

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

The instantaneous production rate of O₃, P(O₃) could then be calculated as a function of NO₂ levels and VOC reactivity. A set of reactions used to derive the equations that describe the dependence of the •OH, peroxy radicals (HO₂•+RO₂•) and P(O₃) on NO_x is given by Murphy et al. (2006), which present the following equation to calculate P(O₃):

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

where k_{2eff} is the effective rate constant of NO oxidation by peroxy radicals (chain propagation and - termination reactions in the production of O₃). 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(O₃) as a function of VOC reactivity calculated from the available VOC dataset for Welgegund (Section 2.4) and NO₂ concentrations is presented. O₃ 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(O₃) 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 O₃ production increases with increasing NO_x concentrations. The VOC-limited regime is to the right of the ridge line, when O₃ production decreases with increasing NO_x. According to the O₃ production plot presented, approximately 40% of the data is found in the VOC-limited regime area, which would support the regional O₃ analysis conducted for continental South Africa in this study. However, the O₃ 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 O₃ production rates can therefore only be inferred at 11:00 am LT despite O₃ concentrations peaking during the afternoon at Welgegund. Therefore, clean background air O₃ 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 NO_2 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 O₃ 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 (NO₂) in the presence of sunlight is the only known way of producing O₃ in the troposphere (Logan, 1985). O₃ can recombine with nitric oxide (NO) to regenerate NO₂, which will again undergo photolysis to regenerate O₃ 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 O₃ in the troposphere occurs outside the PSS when peroxy radicals (HO₂ and RO₂) alter the PSS by oxidising NO to produce ‘new’ NO₂ (Cazorla and Brune, 2010) resulting in net O₃ production. The main source of these peroxy radicals in the atmosphere is the reaction of the hydroxyl radical (OH*) 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 O₃ concentrations are observed in many areas within the interior of South Africa that exceed the South African standard O₃ 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.

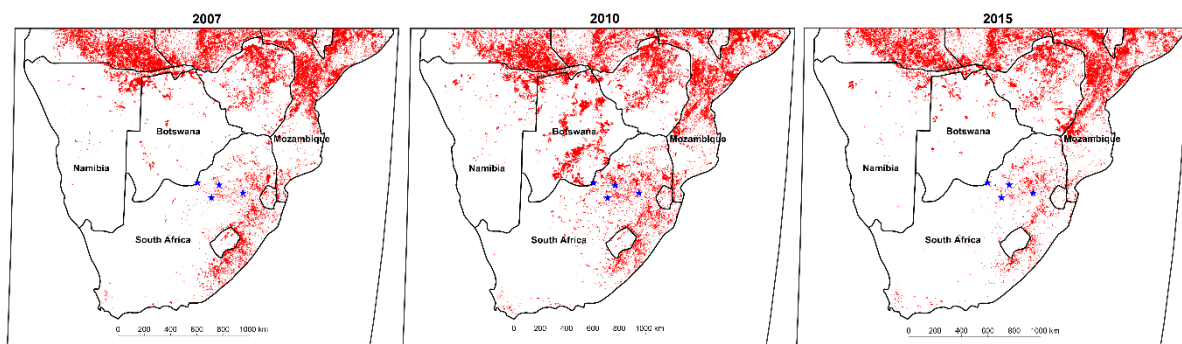


Fig. 7. Spatial distribution of fires in 2007, 2010 and 2015 from MODIS burnt area product. Blue stars indicate (from left to right) Botsalano, Welgegund, Marikana and Elandsfontein.

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 O₃. Therefore the text was changed as follows to clarify the confusion:

“The relationship between O₃, NO_x and CO was used as an indicator to infer the O₃ 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 O₃ as a function of NO₂ 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.