

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 O₃
- 3.2 Spatial distribution of O₃ in continental South Africa
- 3.3 Comparison with international sites
- 3.4 Sources contributing to surface O₃ in continental South Africa
 - 3.4.1 Anthropogenic and open biomass burning emissions
 - 3.4.2 Stratospheric O₃
- 3.5 Insights into the O₃ production regime
 - 3.5.1 The relationship between NO_x, CO and O₃
 - 3.5.2 Seasonal change in O₃-precursors relationship
 - 3.5.3 O₃ production rate
- 3.6 Implications for air quality management
 - 3.6.1 Ozone exceedances

3.6.2 O₃ control strategies

Shortened/re-written sections include:

Abstract:

“Although elevated surface ozone (O₃) concentrations are observed in many areas within southern Africa, few studies have investigated the regional atmospheric chemistry and dominant atmospheric processes driving surface O₃ formation in this region. Therefore an assessment of comprehensive continuous surface O₃ measurements performed at 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 resembled typical trends for O₃ in continental South Africa with O₃ concentration peaking in late winter and early spring. Increased O₃ concentrations in winter were indicative of increased emissions of O₃ 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 O₃ and CO indicated significantly higher O₃ 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 O₃ in continental South Africa. A strong correlation between O₃ on CO was observed, while O₃ levels remained relatively constant or decreased with increasing NO_x, which supports a VOC-limited regime. The instantaneous production rate of O₃ calculated at Welgegund indicated that ~40% of O₃ production occurred in the VOC-limited regime. The relationship between O₃ 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 O₃ levels in continental South Africa should be CO and VOC reduction mainly associated with household combustion and regional open biomass burning.

Introduction:

“High surface O₃ concentrations are a serious environmental concern, due to their detrimental impacts on human health, crops and vegetation (National Research NRC, 1991). Photochemical smog, comprising O₃ as a constituent together with other atmospheric oxidants, is a major air quality concern on urban and regional scales. Tropospheric O₃ is also a greenhouse gas that directly contributes to global warming (IPCC, 2013).

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). 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^*) 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, O₃ concentrations increase with increasing VOCs, while a region is considered NO_x-limited when O₃ 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 O₃, while NO_x controls without VOC controls may lead to O₃ increases. In general, it is considered that O₃ formation in regions close to anthropogenic sources are VOC-limited, while rural areas distant from source regions are NO_x-limited (Sillman, 1999).

Previous assessments of tropospheric O₃ over continental South Africa focussed on surface O₃ (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 O₃ 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 O₃ 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 O₃ concentrations in spring in the Mpumalanga Highveld to increased regional open biomass burning. A more recent study demonstrated that NO_x strongly affects O₃ 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 O₃ variability, which found no dominant source/s on elevated O₃ levels.

The aim of the current study is to provide an up-to-date assessment of the seasonal and diurnal variations in surface O₃ concentrations over continental South Africa, as well as to identify local and regional sources of precursors contributing to surface O₃. Another objective is to use available ambient data to qualitatively assess whether O₃ formation is NO_x- or VOC-limited in different environments. An understanding of the key precursors that control surface O₃ production is critical for the development of an effective O₃ control strategy.”

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

“In an effort to contextualise the O₃ levels measured in this study, the monthly O₃ concentrations measured at Welgegund were compared to monthly O₃ 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 O₃ 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 O₃ peaks as indicated in

Fig. 4. Cape Grim, Australia; GoAmazon T3 Manacapuru, Brazil; Ushuaia, Argentina; and El Tololo, Chile are regional background GAW (Global Atmosphere Watch) stations with O₃ levels lower than the South African sites. However, the O₃ 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 O₃ concentrations compared to Welgegund.

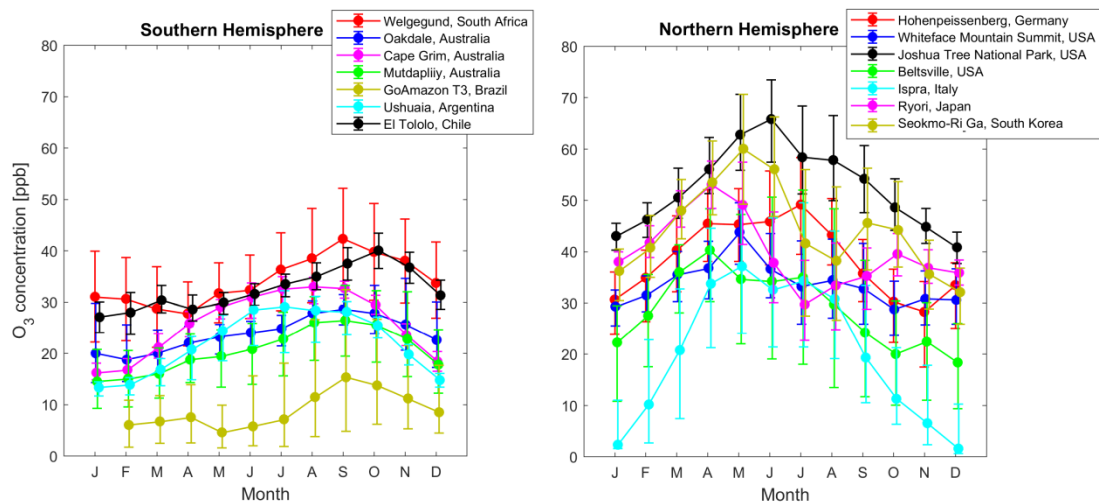


Fig. 4. Seasonal cycle of O₃ at rural sites in other parts of the world. The black dot indicate monthly median (50th percentile) and the upper and lower limits the 25th and 75th percentile, respectively for monthly O₃ concentrations. The data is averaged from May 2010 to December 2014, except in a few instances where 2014 data was not available.

The Northern Hemispheric O₃ peak over mid-latitude regions is similar to seasonal patterns in the Southern Hemisphere where a springtime O₃ 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 O₃ concentrations in late winter and early spring, whilst in the Northern Hemisphere it refers to a late spring and early summer O₃ 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 O₃ production from anthropogenic emissions of O₃ precursors being at its highest (Logan, 1985; Chevalier et al., 2007). Maximum O₃ 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 O₃ levels. This is most-likely due its high elevation and deep boundary layer (~4 km asl) during spring and summer allowing free tropospheric O₃ to be more effectively mixed down to the

surface (Cooper et al., 2014). Maximum O₃ 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 (now Section 3.1 and Fig. 2):

“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 O₃ 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 O₃ peaks in continental South Africa, generally points to two major contributors of O₃ 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 O₃ 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 O₃ 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. O₃ 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 O₃ at Marikana is more pronounced as indicated by the largest difference between daytime and nighttime O₃ concentrations in comparison to the other sites, especially, compared to Elandsfontein where nighttime concentrations of O₃ 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 O₃ seasonal cycles at background and polluted locations is useful for source attribution. From Fig. 3 it is evident that daytime O₃ levels peaked at Elandsfontein, Marikana and Welgegund during late winter and spring (August to October), while O₃ 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 O₃ 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 O₃ 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 O₃ precursor species associated with anthropogenic emissions during winter. Daytime O₃ concentrations were the highest at Marikana throughout most of the year, which indicate the influence of local and regional sources of O₃ precursors at this site (Venter et al., 2012). In addition, a larger difference between O₃ 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 O₃ precursors at Marikana.

O₃ 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 O₃ 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 O₃ 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 O₃ concentrations during daytime and nighttime titration of O₃, especially during winter. Therefore the observed differences in nighttime titration at Marikana and Elandsfontein can be attributed different sources of O₃ 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 O₃ concentrations at Elandsfontein during winter are most-likely attributed to the regional increase in O₃ precursors.”

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:

“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 South Africa with O₃ concentration peaking in late winter and early spring (cf. Zunckel et al., 2004), while daytime O₃ corresponded to increased photochemical production. The seasonal O₃ trends observed in continental southern Africa could mainly be attributed to the seasonal changes in emissions of O₃ precursor species and local meteorological conditions. Increased O₃ 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 O₃ 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 O₃ in continental South Africa. A very small contribution from the stratospheric intrusion of O₃-rich air to surface O₃ levels at the four sites was indicated.

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 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(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.”

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 NO_x 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 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 Welgegund. Specifically, each VOC reactivity

was then summed to obtain the total VOC reactivity for each measurement, i.e. VOC reactivity = $\sum k_{i,l}[\text{VOC}]_l$. 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:

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

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

$$C = P(HO_x)$$

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

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.”

On the “CO-limited ozone formation regime”: the authors concluded from the O₃-NO_x-CO 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 RO_x 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, NO_x, 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 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). In addition, Referee #1 also recognised the large role of CO on O₃ formation shown in this study. In view of the comment of Referee #1, 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 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.”

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 Welgegend, 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 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 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(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.”

We agree with Referee #2 that photochemical modeling would greatly assist in establishing O₃ 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 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.”

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 NO_x measurements.

NO₂ levels determined with the Teledyne 200AU NO/NO_x analyser (used at three of sites) were compared with NO₂ concentrations measured with a quantum cascade laser used for NO₂ 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 NO_x measurements. In addition, the NO_x measurements were used to as supportive data to assist in interpreting O₃ 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:

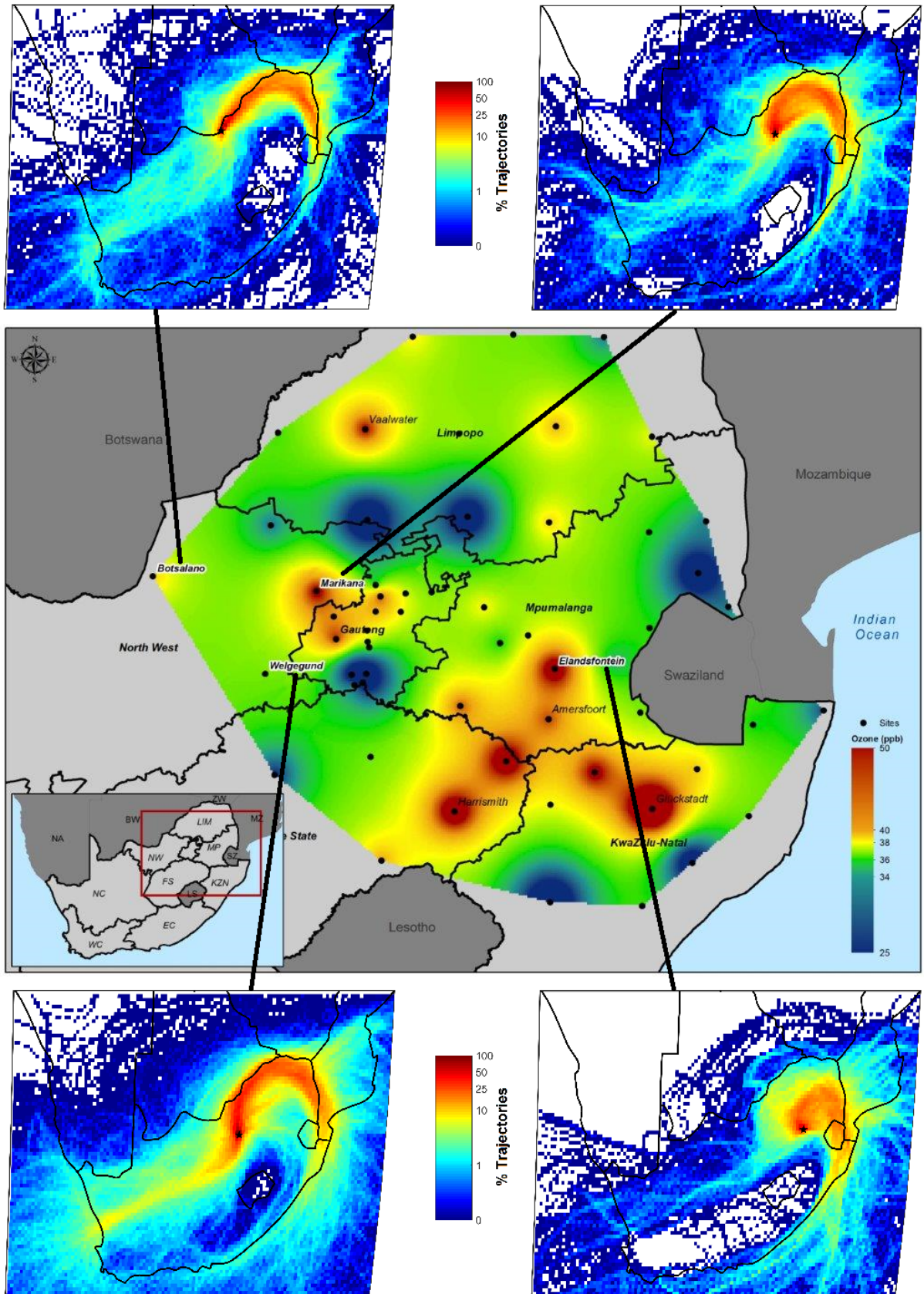


Fig. 2. The main (central map) indicating spatial distribution of mean surface O₃ levels during springtime over the north-eastern interior of southern Africa ranging between 23.00° S and 29.03° S,

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 O₃ is usually at a maximum as indicated above. The mean O₃ concentration over continental South Africa ranged from 20 ppb to 60 ppb during spring. From Fig. 3 it can be seen that O₃ concentrations at the industrial sites Marikana and Elandsfontein were higher than O₃ 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 O₃ levels measured in this study, the monthly O₃ concentrations measured at Welgegund were compared to monthly O₃ 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 O₃ 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 O₃ peaks as indicated in Fig. 4. Cape Grim, Australia; GoAmazon T3 Manacapuru, Brazil; Ushuaia, Argentina; and El Tololo, Chile are regional background GAW (Global Atmosphere Watch) stations with O₃ levels lower than the South African sites. However, the O₃ 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 O₃ concentrations compared to Welgegund.

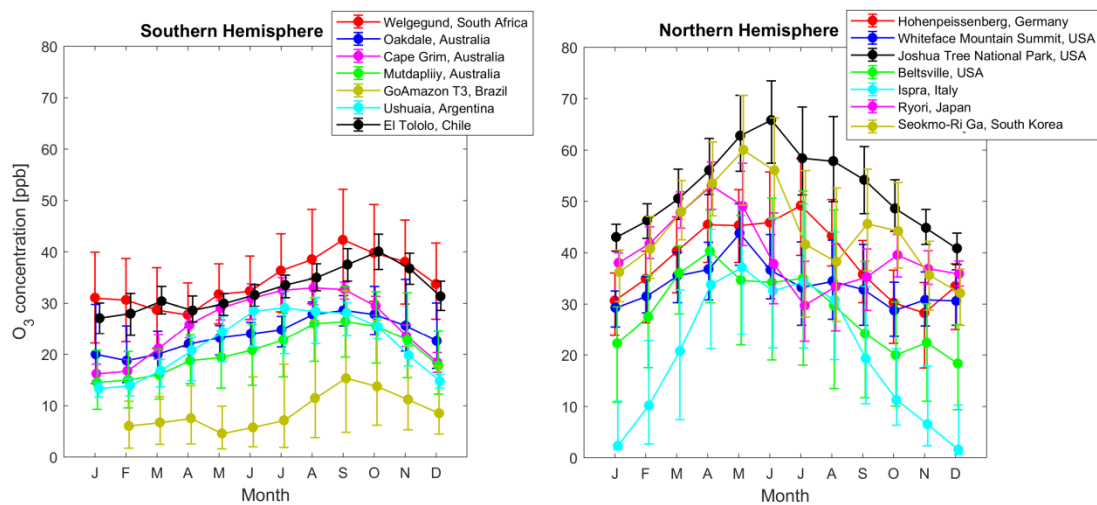


Fig. 4. Seasonal cycle of O₃ at rural sites in other parts of the world. The black dot indicate monthly median (50th percentile) and the upper and lower limits the 25th and 75th percentile, respectively for monthly O₃ concentrations. The data is averaged from May 2010 to December 2014, except in a few instances where 2014 data was not available.

The Northern Hemispheric O₃ peak over mid-latitude regions is similar to seasonal patterns in the Southern Hemisphere where a springtime O₃ 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 O₃ concentrations in late winter and early spring, whilst in the Northern Hemisphere it refers to a late spring and early summer O₃ 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 O₃ production from anthropogenic emissions of O₃ precursors being at its highest (Logan, 1985; Chevalier et al., 2007). Maximum O₃ 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 O₃ levels. This is most-likely due its high elevation and deep boundary layer (~4 km asl) during spring and summer allowing free tropospheric O₃ to be more effectively mixed down to the surface (Cooper et al., 2014). Maximum O₃ 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 O₃ 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 NO_x. It would be helpful for the authors to examine the O_x (O_x=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 O₃ 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 O₃ (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 O₃ 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 O₃ titrations at these two industrial sites are adequately indicated by the O₃ (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 NO_x-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 NO_x-limited regime. Since Welgegund is the only station for which VOCs have been measured in South Africa, we cannot directly compare O₃ production with other sites. It would be likely that O₃ production at Welgegund may not be representative of regional O₃ production conditions across the country. However, ~ 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. In addition, O₃ production is mainly in the NO_x limited regime at low NO_x concentrations. Therefore, clean background air O₃ 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 O₃ production at

Welgegund and the positive correlations observed between O₃ 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 O₃ production rate was rewritten 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.”