Interactive comment on “Measurements of biogenic volatile organic compounds at a grazed savannah-grassland-agriculture landscape in South Africa” by Kerneels Jaars et al. (Ref. No.: acp-2016-471)

Anonymous Referee #1

Received and published: 12 September 2016

Jaars et al. report interesting measurements and analysis of biogenic VOC concentrations from an African grassland savannah ecosystem. The data from these regions are extremely limited and difficult to collect but are desired by the scientific community to understand the biological processes as well as the atmospheric abundance and fate of these molecules in these unexplored ecosystems. The paper should be an important reference and could inspire more research in those regions. Overall, I enjoyed reading the paper, thank you very much for this nice contribution, and I think the collected dataset is in itself extremely interesting so it deserves acceptation in ACP. However, I still feel the story has a significant potential for a little more in-depth analysis. In the relatively minor comments/questions below I just want to inspire some additional thoughts and suggestions for further manuscript enhancement.

We would like to thank Referee #1 for the positive review of this paper and acknowledging the relevance of the work presented, as well as for indicating appreciation of the manuscript. We would also like to thank Referee #1 for the relatively minor comments/questions, which were each carefully considered in order to answer the questions raised or implement the suggestions made. Below is a point-by-point response to each of these comments/questions.

1) The paper is focused on the biogenic VOCs while the same authors described anthropogenic VOCs at Welgegund in a separate paper (Jaars et al. 2014) which maybe could be specified as a companion paper. I wonder if it could be interesting for the atmospheric chemistry context to try and look more closely at anthropogenic vs biogenic VOC interactions. For example, have you tried categorizing the data into pollution and clean periods based on high aromatics/NOx/SO2/O3 episodes to see for example if there is a difference in stress related monoterpenes or how different would be ozone and particle formation in these contrasting scenarios?

We agree with Referee #1 that this paper could be specified as a companion paper to the paper published on anthropogenic VOCs measured at Welgegund by Jaars et al., 2014. This will also contribute to enhancing the citability of these papers. We will follow this matter up with the handling editor.

We also agree that we must look at the anthropogenic vs biogenic interactions, which was recognised during preparation of the both the anthropogenic and biogenic VOC papers. Therefore a third paper was prepared (and very close to submission) where positive matrix factorisation (PMF) analysis was performed in order to pull together the anthropogenic and biogenic VOCs measurements together with other ancillary measurements conducted at Welgegund e.g. SO_2, NO_2 and O_3. The O_3 formation potential relating to each of the factors determined with PMF will be explored in this paper. The PMF analysis will also be taken further in another paper where the reactions of all the VOCs (anthropogenic and biogenic) with oxidants, e.g. OH, O_3 will be further explored with atmospheric models in order to establish, for instance, whether O_3 formation within the region is VOC- or NO_2-limited. Therefore these two papers that are currently in preparation are included as future perspectives in the "Conclusions" section as follows:

"…BVOCs measured at Welgegund. In addition, the interactions between anthropogenic and biogenic VOCs must also be further explored, together with other ancillary measurements conducted at Welgegund (e.g. SO_2, NO_2 and O_3). Future work must also include investigating the reactions of all the VOCs measured with atmospheric oxidants (e.g. $^{\bullet}OH$ and O_3) with atmospheric chemistry models in order to establish, for instance, whether O_3 formation within the region is VOC- or NO_2-limited."

In addition, as indicated in our response to Comment 5, no notable amounts of stress related monoterpenes were detected, which could therefore not be investigated.

2) The paper suggests the concentrations of the biogenics were actually quite low compared to other woody biomass regions. Indeed, it could be very interesting to contrast this type of ecosystem to forests or tree plantations in Africa and elsewhere. One general issue is that the concentrations cannot tell us everything because despite the low concentration of a molecule there could still be a substantial flux and I was wondering if the authors have tried scaling these concentrations to turbulent parameters? In addition, isoprene concentration are known to exhibit strong diurnal variation as a function of time of day so there is implication of the sampling time (always the same time of day) at least for isoprene which warrants more dicussion. What percentage of isoprene concentration maximum was captured by these measurements could be easily inferred from a MEGAN algorithm for isoprene if the data for PAR and temperature are available.

In our discussion in Section 3.2 and in Table 3 our BVOCs concentrations are compared to other BVOC measurements in Africa and other parts of the world, which include measurements at forests. We indicate that BVOC emissions were quite low, which is mainly attributed to the significant lower isoprene levels measured at Welgegund. Therefore we consider that this part of the comment is addressed in our manuscript.

We agree with Referee #1 that concentrations are influenced by factors other than fluxes and so a low concentration does not always indicate a low flux. In addition to fluxes, these VOC concentrations are also sensitive to oxidation rates and boundary layer height. Greenberg et al. (1999) have shown that isoprene concentrations at most sites are relatively constant during daytime since the strong diurnal pattern of emission is offset by the strong diurnal variation in oxidation rate and boundary layer height. As suggested by the reviewer, we used the observed temperature and PAR at the site to drive the MEGAN BVOC emission model and found that the measurement time (11:00 to 13:00 local time) captured most of the period of maximum isoprene emission (typically about 12:00 to 2:00 local time). By assuming a typical diurnal variation in VOC oxidation rate and boundary layer height, we also find that the isoprene concentration of the measurement time is representative of the daytime isoprene concentration.

In addition to our response to this comment, the median (mean) daytime to night-time concentration ratios of all the BVOCs measured during both sampling campaigns were included in Table 2, in order to indicate the light dependence of BVOC emissions. These daytime to night-time concentration ratios indicated that there were not significant differences in levels of most of the BVOCs measured during daytime and night-time at Welgegund, with the exception of isoprene measured during the first sampling campaign, as well as two monoterpenes (terpinolene, bornylacetate) and the SQT aromadendrene measured duirng the second sampling campaign. Therefore isoprene levels measured during the first sampling campaign reflected the light dependency usually associated with isoprene emissions. However, daytime to night-time concentration ratios of isoprene did not exhibited the very strong light dependency typically associated with atmospheric isoprene concentrations, which could be attributed to the characteristics of sources of these species that are discussed later in the manuscript. Therefore the light dependency associated with these small number of BVOCs measured at Welgegund was addressed in the first paragraph in Section 3.2 as follows:

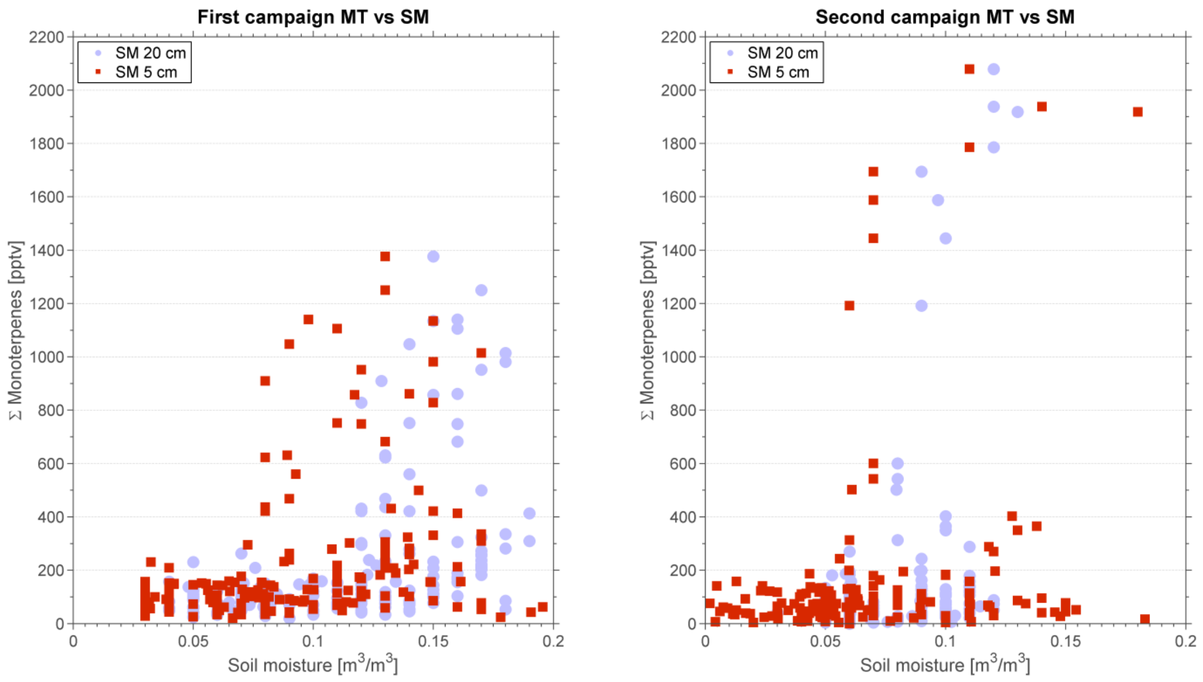
"In Table 2, the median (mean) and inter-quartile range (IQR, 25th to 75th) concentrations, as well as the median (mean) daytime to night-time concentration ratios of the BVOC species determined during the two sampling campaigns at Welgegund are presented. It is evident from the median (mean) daytime to night-time concentration ratios that there were not significant differences in levels of most of the BVOCs measured during daytime and night-time at Welgegund, with the exception of isoprene measured during the first sampling campaign, as well as the monoterpenes terpinolene and bornylacetate, and the SQT aromadendrene measured duirng the second sampling campaign. Isoprene levels during the first sampling campaign were approximately two times higher during daytime, which reflect the light dependency usually associated with isoprene emissions. However, daytime to night-time concentration ratios of isoprene did not exhibited the strong light dependency typically associated with atmospheric isoprene concentrations, which could be attributed to the characteristics of sources of these species that are discussed in subsequent sections. The temperature and photoactive radiation (PAR) measurements at Welgegund was used in the MEGAN BVOC emission model, which indicated that the measurement time (11:00 to 13:00 local time) captured most of the period of maximum isoprene emission (typically about 12:00 to 2:00 local time). In addition, by assuming a typical diurnal variation in VOC oxidation rate and boundary layer height, it was also found that the isoprene concentration of the measurement time is representative of the daytime isoprene concentration (Greenberg et al., 1999). In Table 3, the concentrations of BVOC species measured during other campaigns in South Africa and the rest of the world are presented."

Greenberg, J. P., A. Guenther, P. Zimmerman, W. Baugh, C. Geron, K. Davis, D. Helmig and L. F. Klinger (1999). "Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer." Atmospheric Environment **33**(6): 855-867.

3) The results of soil moisture relationship to monoterpene concentrations is very interesting. It would be instructive to see if the response was more like the threshold or did it exhibit a gradual dependence? It might be useful for potential modeling to see the actual scatter plots of soil moisture vs monoterpene concentration.

We agree with Referee #1 that this data could be useful for potential modelling. Therefore, scatter plots of soil moisture vs monoterpene and soil moisture vs SQT were included as supplementary material in the manuscript and are presented below:

(a)



(b)

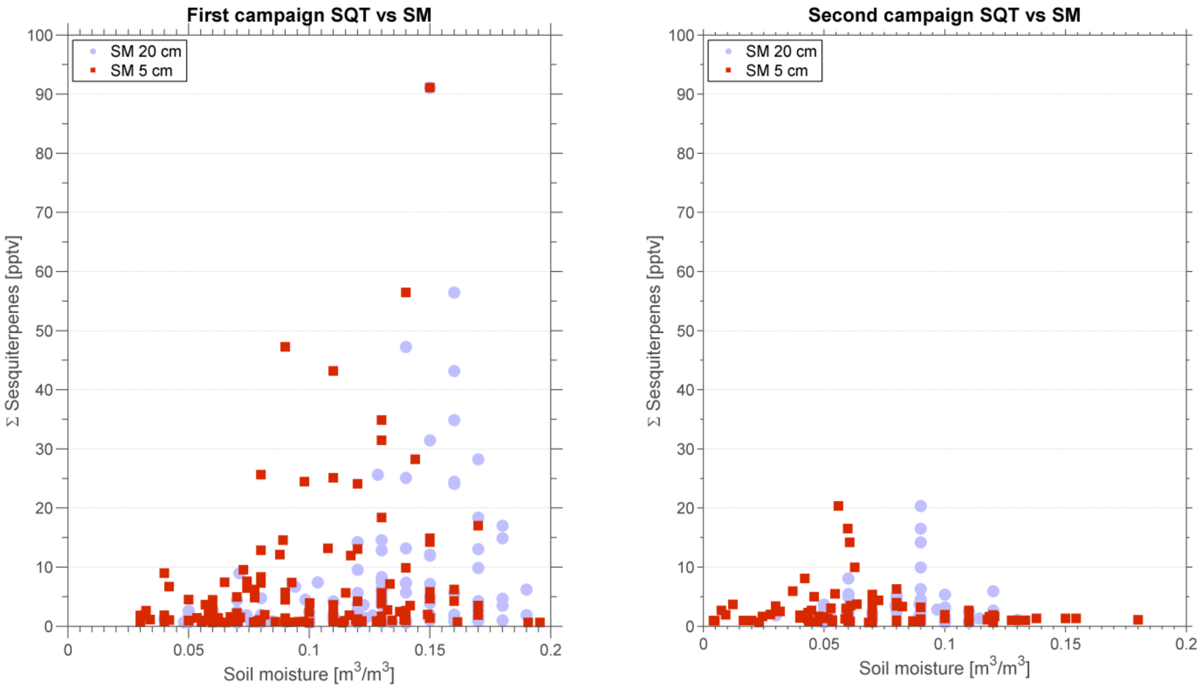


Figure S1. Correlation between soil moisture and monoterpene concentrations (a), and soil moisture and SQT (b)

These plots clearly shows higher monoterpene and SQT concentrations associated with increased soil moisture. In addition, the following sentences were added to the text in Section 3.3:

"…monoterpene and SQT concentrations measured during the first sampling campaign were generally higher compared to the second sampling campaign. In Figure S1 (a) and (b) the relationship between soil moisture and monoterpene concentrations, as well as between soil moisture and SQT are presented, respectively. It is evident that higher concentrations of monoterpene and SQT are associated with higher soil moisture measured at a depth of 5 and 20 cm. Otter et al. (2002) also reported a more pronounced seasonal pattern…"

4) I was particularly intrigued by substantial concentrations of estragole (p-allylanisole). Unfortunately, this incredibly interesting aromatic compound is only listed in the tables but I think it could be really nice to discuss this compound, in particular its likely origin (basil, anise, fennel, pines, palms?) and maybe even its behavior as a function of time/season. For example, I am wondering where it might be coming from and what its function is in this ecosystem. Could it be a pollinator attractant emitted by flowers (Misztal et al., 2010) or an insect deterrent emitted by conifers (Bouvier-Brown et al., 2009)? An additional minor suggestion would be to place p-allylanisole and p-cymene in a different category because these compounds are not strictly monoterpenes. You could consider something like "biogenic

benzenoid” or “monoterpene-related BVOCs”. AMCH is not strictly a monoterpene either but can be considered an oxygenated terpene.

The occurrence of potential sources of estragole (p-allylanisole) in this region could be confirmed by our botanist co-authors on this paper. Foeniculum vulgare (fennel) is an abundant and common weed in this study region. In addition, pine trees are common foreign tree species that are planted on farms, while numerous palm trees occurs in cities/towns surrounding Welgegund. Furthermore, and also linking to Comment 6, p-allylanisole emissions could also potentially have floral origin. Floral emissions would typically occur from October to February in this region. It is well-known that meadows in South Africa/this region have a significant number of species that flowers. South African grasslands are considered to be among the most diverse in the world, since it is primary grasslands, i.e. not man-made. In addition, these floral emissions could also be a potential source for other monoterpenes, which also could explain the relatively low isoprene concentrations compared to the relatively abundant monoterpenes. The following paragraphs have been included in Section 3.4:

“…within a 1 to 2 km radius, as indicated in Figure 2. The high monoterpene concentrations determined during the second sampling campaign may be associated with specific monoterpene emitting plants in the region.

Floral emissions could also be considered a potential source of monoterpenes in this region, which could also contribute to the relatively abundance of monoterpenes compared to the relatively low isoprene concentrations. Floral emissions in this region would typically occur with the onset of the wet season in October up until February. It is well-known that meadows, i.e. grazed grasslands in South Africa/this region have a significant number of species that flower. South African grasslands are considered to be exceptionally species rich (Siebert, 2011), since it is ancient, primary grasslands, i.e. not man-made (Bond, 2016).

Of particular interest is the potential sources of 4-allylanisole (estragole) due to its relatively substantial levels as indicated in Table 2. Bouvier-Brown et al. (2009a) and Misztal, et al., (2010) indicated that this species could potentially have a significant contribution to regional atmospheric chemistry due to relatively large estragole emissions measured from ponderosa pine trees and oil palms, respectively. As mentioned previously, pine trees are typically found on farms in this region as intruder tree species (Rouget, 2002), while numerous palm trees occurs in cities/towns surrounding Welgegund (Lubbe *et al.*, 2011). In addition, *Foeniculum vulgare* (fennel) – considered a typical source of estragole – is an abundant and common weed in this study region (Lubbe *et al.*, 2010). Furthermore, estragole emissions could also potentially have a floral origin.”

In addition, p-allylanisole, p-cymene and AMCH were classified as “monoterpene-related BVOCs” in Table 2. The text in Section 2.3.1 paragraph 3 was also changed as follows:

“…and 2-methyl-3-butene-2-ol (MBO) with MDL between 0.9 and 1.4 pptv. The monoterpenes (α-pinene, camphene, β-pinene, Δ^3-carene, limonene, 1,8-cineol, terpinolene, nopinone and bornylacetate) and monoterpene-related BVOCs (p-cymene, 4-allylanisole and 4-acetyl-1-methylcyclohexene (AMCH)) MDL was between 0.6 and 1.6 pptv. The term “monoterpene(s)” used in the discussions in subsequent sections in the manuscript refers to both the monoterpene and monoterpene-related BVOCs.”

5) Have you observed any monoterpenes (or other BVOCs) related to stress? For example _-ocimene, methyl salicylate, green leaf volatiles?

The compounds mentioned in this comment were not included in our standard, but notable amounts were not detected.

6) Could some emissions at the Welgegund site have floral origin which could further explain why isoprene is relatively low whereas monoterpenes (and potentially other compounds such as p-allylanisole) are relatively abundant? Is the flowering happening an entire year round or seasonally? It would be very interesting because floral BVOCs from meadow-like flowering ecosystems can sometimes be abundant but receive relatively little attention compared to foliar emissions.

This comment was addressed in our response to Comment 4.

7) Table 4 contains interesting correlations, in particular, that MBO correlates with monoterpenes. Are these compounds coming from a conifer-like sources? On the other hand, I wonder if the result of isoprene correlating with MBO is more unexpected and it is also not discussed. Baker et al. 2001 found that if MBO is thermally treated (as is the case in GC) it can dehydrate and be detected as isoprene. Do you think this could be the case? While this is not meant to be a criticism, and given the different wind-roses and dependence on soil moisture/temperature perhaps the issue was probably minor but I still think it is worth giving this potential issue a general thought and discuss implications for isoprene/MBO data interpretation.

As discussed in Section 3.4, wind direction did not indicate any significant differences in the concentrations of MBO, monoterpenes and SQTs. As indicated in the discussion, it is difficult to point to specific sources of these species. However, in our response to Comment 4, it is mentioned that pine trees are common foreign tree species that are planted on farms. Therefore, pine trees could be considered a possible conifer-like source of MBO and monoterpenes. The following sentence was added in Section 3.4 (paragraph 2):

"…most likely to be the main sources, which can possibly include the urban footprint indicated in this region. In addition, pine trees are common foreign tree species that are planted on farms in this region (Rouget, 2002), which could be potential sources of MBO and monoterpenes."

As discussed in Section 3.2 (paragraph 4): "Guenther (2013) indicated that MBO is emitted from most isoprene emitting vegetation at an emission rate of ~1 % of that of isoprene. However, MBO measured at Welgegund was approximately 30 % of the isoprene concentrations, which indicated that the main source of MBO at Welgegund is not from isoprene emitters, but from other MBO emitters." Furthermore, the possible dehydration of MBO to isoprene was considered to be insignificant, since when known amounts of MBO are injected into adsorbent tubes and analyzed with the analytical setup used in this study, <3% of isoprene is detected compared to MBO. Therefore as Referee#1 indicates, this correlation was unexpected and not further discussed.

8) Figure 4. This is an interesting figure. It seems that it is adopted from a different manuscript but clearly shows beautiful CO2 assimilation during the day and respired carbon during the night. If the data were available, it might be worth coloring these markers by PAR to better visualize assimilation vs respiration vs potentially anthropogenic CO2(?).

We thank Referee #1 for suggesting this improved visualisation of the figure. The markers in this figure were coloured with PPFD to better visualise assimilation vs respiration. Fig. 4 was replaced with the figure below:

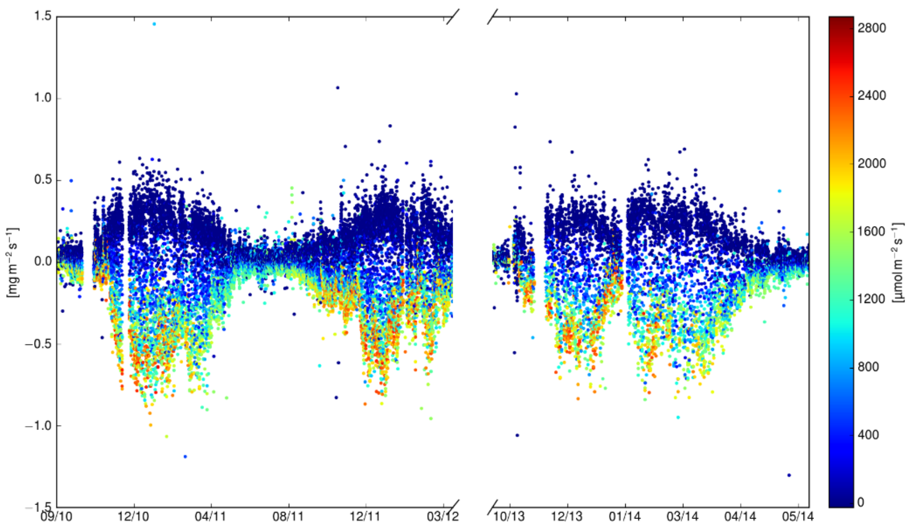


Figure 4. Micrometeorological CO_2 flux measurements at Welgegund (Räsänen et al., 2016). The colour bar indicates the Photosynthetic Photon Flux Density (PPFD).

The following sentence was added in the text in Section the 3.1:

"…uptake of CO_2 by vegetation. In addition, the Photosynthetic Photon Flux Density (PPFD) is also indiacted with a colour bar. Negative values (downward CO_2 flux) indicate…"

9) It is mentioned several times (abstract, P22 L15 and in other places) that isoprene concentrations were higher from the western direction. "western direction" is not very informative for a reader in particular in the abstract. Careful reading points to the sentence in P5 L11 that ". . .western sector contains no major point sources and can therefore be considered to be representative of a relatively clean regional background". Maybe you meant to say that this direction does not contain any *anthropogenic* point sources of isoprene? Otherwise I wonder where this isoprene is coming from? If isoprene concentrations exhibit temperature dependence, it implies biogenic source but if there is no vegetation to the west, could there be a different source (e.g. heated rubber?). My suggestion would be simply to expand more clearly on the potential sources of the western isoprene.

The term "major point sources" in Section 2.1 does refer to "major anthropogenic point sources" and we thank Referee #1 for highlighting out this small, but significant technical point that creates confusion. Although not impossible, it is unlikely that isoprene measured at Welgegund will have an anthropogenic source e.g. heated rubber. The text was changed in Section 2.1 as follows:

"…Johannesburg-Pretoria conurbation (Tiitta, et al., 2014). From Figure 1, it is also evident that the western sector contains no major anthropogenic point sources and can therefore be considered to be representative of a relatively clean regional background."

With regard to expanding more clearly on the potential sources of the western isoprene, we consider that this topic is adequately explained in the manuscript in paragraphs 2 and 3 in Section 3.3. As argued in these paragraphs, it seems that the isoprene is mainly from the savanna grassland regions. This is indicated by the differences in the seasonal patterns of isoprene during the two sampling campaigns. A relatively distinct seasonal pattern was observed during the first sampling campaign for which the concentration rose indicated higher isoprene concentrations associated with winds originating in the south-western to southern sector from the grassland region in close proximity of Welgegund (Figure 2). During the second sampling campaign isoprene was only associated with the south-western to northern sector, i.e. a region with cultivated land in close proximity of Welgegund (Figure 2). The correlation between higher wind speed and isoprene was therefore considered to reflect isoprene emissions from a more distant savanna grassland fetch region in the south-western to northern sector.

We also agree with Referee #1 that the term "western direction" is not very informative for the reader in the context of the abstract, as well as in Section 3.4 (paragraph 2) and in the "Conclusions" section. Therefore this term was replaced…

in the Abstract as follows:

"…concentrations measured at Welgegund. An analysis of concentrations by wind direction indicated that isoprene concentrations were higher from the western sector that is considered to be a relatively clean regional background region with no large anthropogenic point sources (Figure 1), while wind direction did not indicate any significant differences in the concentrations of the other BVOC species. Statistical analysis indicated that soil moisture…",

and in Section 3.4 as follows:

"…concentrations, roses were compiled, as presented in Figure 6. In general, the concentration roses indicated that isoprene concentrations were higher from the western sector (indicated by the average and highest concentrations) that is considered to be a relatively clean regional background region with no large anthropogenic point sources, while wind direction did not indicate any significant differences in the concentrations of the other BVOC species. On occasion, higher MBO, monoterpene and SQT concentrations…"

The "Conclusions" section was re-written as suggested by Referee #1 in Comment 12 and the term "western direction" was not included in the revised "Conclusions" section.

10) I understand the median is often used to represent more episode-free concentration scenario. However, isoprene is only emitted during the day, so does it still make sense to show the monthly median for isoprene? Because you were collecting data both during the day and at night, I think it could be very interesting to separate day and night concentrations. In particular because monoterpenes unlike isoprene can often accumulate during the night in a shallow boundary layer so the overall median (or mean) concentration differences between the compounds (e.g. isoprene and monoterpenes) may not reflect strictly their emission strengths or true variability. I wonder if looking at some of the episodic events of high concentrations would not be an even more interesting opportunity to understand the chemistry scenarios.

This comment was addressed as part of our response to Comment 2 where it was indicated that median (mean) daytime to night-time concentrations ratios of BVOCs were included in Table 2 in order to separate daytime and night-time concentrations. These daytime to night-time concentrations ratios revealed the expected light dependency of isoprene for isoprene levels measured during the first sampling campaign, while no significant differences were observed for the other BVOCs measured (except for two monoterpenes and one SQT). Therefore, only the isoprene seasonal pattern plotted in the left panel in Figure 5(a) was replaced with seasonal patterns measured during daytime and night-time. The following sentences was included in the first paragraph in Section 3.3:

"…wet (October to April) and dry (May to September) season concentrations of the respective compounds measured for the two campaigns. As indicated in Section 3.2, isoprene measured during the first sampling campaign had higher median (mean) daytime concentrations compared to median (mean) night-time concentrations, which reflects the light dependency expected from isoprene. All other BVOCs with the exception of two monoterpenes and one SQT did not indicate significant differences between daytime and night-time median (mean) concentrations. Therefore the seasonal plots of only isoprene were separated between daytime and night-time median concentrations."

11) Further to the point above, you are talking about ozone formation potentials from these BVOCs but maybe it would be worthwile to show some oxidant data. I am just curious how ozone (and also NOx, SO2, etc.) concentrations varied during the daytime and nighttime VOC sampling times and if it could teach us anything about the chemistry at the site.

As indicated in our response to Comment 1, a paper is currently being prepared where the reactions of all the VOCs (anthropogenic and biogenic) with oxidants, e.g. OH, O_3 will be further explored with atmospheric models in order to establish, for instance, whether O_3 formation within the region is VOC- or NO_2-limited. This paper will also incorporate the diurnal patterns of O_3 and NO_2. This work is included as future perspectives in the "Conclusions" section as indicated in our response at Comment 1.

12) It is recommended that the conclusions are made more succinct and emphasize major take-home messages which should be even more impressive than just the summary of the paper. For example, one could consider concluding about the implications for atmospheric chemistry and air quality in the region. In particular, the last two sentences of conclusions are unclear but the synopsis of future measurements is definitely needed to attract more attention and support more measurements in these almost completely unexplored regions of Africa.

We thank Referee #1 for suggesting an improved emphasised take-home message in this section. Therefore the Conclusion section was rewritten in order to be more succinct and to better emphasise the major take-home messages as follows:

"The annual median concentrations of isoprene, MBO, monoterpene and SQT determined during two sampling campaigns indicated that the sum of the concentrations of the monoterpenes was an order of magnitude higher than the concentrations of other BVOC species, with α-pinene being the most abundant species. Although monoterpene concentrations were similar to levels measured at other regions in the world and in a South Africa, very low isoprene concentrations at Welgegund led to a significantly lower total BVOC concentration compared to levels reported in most previous studies. In addition, total BVOC concentrations were an order of magnitude lower compared to the total aromatic VOC concentrations measured by Jaars et al. (2014) at Welgegund.

Distinct seasonal patterns were observed for MBO during both sampling campaigns, which coincided with wet and warmer months. Although less pronounced, a similar seasonal trend than for MBO was observed for isoprene during the first sampling campaign, while higher isoprene concentrations during the second sampling campaign were associated with higher wind speeds that indicated a distant source region of isoprene. No distinct seasonal pattern was observed for monoterpene and SQT concentrations. However, significantly higher levels of monoterpene and SQT, as well as MBO were measured from February to April 2011 during the first sampling campaign, which were attributed to the considerably higher soil moisture measured at a depth of 20 cm resulting for the wet season preceding the first campaign and is indicative of biogenic emissions from deep-rooted plants.

Woody species in the grassland region were considered to be the main sources of BVOCs measured, while sunflower and maize crops were also considered to be potential sources for BVOCs in this region. Multilinear regression analysis indicated that soil moisture had the most significant impact on atmospheric levels of MBO, monoterpene and SQT concentrations, while temperature had the greatest influence on isoprene levels.

The O_3 formation potentials of the BVOCs measured were an order of magnitude smaller than that determined for anthropogenic VOCs measured at Welgegund. Isoprene and the monoterpenes: □-pinene, p-cymene, limonene and terpinolene, had the largest contribution to O_3 formation potential. □-Pinene and limonene had the highest reaction rates with O_3, while isoprene exhibited relatively small contributions to the O_3 depletion. Limonene, □-pinene and terpinolene had the largest contributions to the OH-reactivity of BVOCs."

In addition, the last two sentences (last paragraph) were also improved as follows:

"It is important in future work that a comprehensive study on BVOC emissions from specific plant species in the area surrounding Welgegund must be performed in order to relate the emission capacities of vegetation types to the atmospheric BVOCs measured. It is also recommended that the oxidation products of BVOC species are measured in order to verify distant source regions of BVOCs measured at Welgegund."

and as indicated in our response to Comment 1, the following was also added to the synopsis of future work:

"In addition, the interactions between anthropogenic and biogenic VOCs must also be further explored, together with other ancillary measurements conducted at Welgegund (e.g. SO_2, NO_2 and O_3). Future work must also include investigating the reactions of all the VOCs measured with atmospheric oxidants (e.g. $^{\bullet}OH$ and O_3) with atmospheric chemistry models in order to establish, for instance, whether O_3 formation within the region is VOC- or NO_2-limited."

References:

Baker, B., Guenther, A., Greenberg, J., and Fall, R.: Canopy Level Fluxes of 2-Methyl-3-buten-2-ol, Acetone, and Methanol by a Portable Relaxed Eddy Accumulation System, Environ Sci Technol, 35, 1701-1708, 10.1021/es001007j, 2001.

This reference was not added in the manuscript as indicated in our response to Comment 7.

Bouvier-Brown, N. C., Goldstein, A. H., Worton, D. R., Matross, D. M., Gilman, J. B., Kuster, W. C., Welsh-Bon, D., Warneke, C., de Gouw, J. A., Cahill, T. M., and Holzinger, R.: Methyl chavicol: characterization of its biogenic emission rate, abundance, and oxidation products in the atmosphere, Atmos. Chem. Phys., 9, 2061-2074, 2009.

This reference was added in the manuscript as indicated in our response to Comment 4.

Misztal, P. K., Owen, S. M., Guenther, A. B., Rasmussen, R., Geron, C., Harley, P., Phillips, G. J., Ryan, A., Edwards, D. P., Hewitt, C. N., Nemitz, E., Siong, J., Heal, M. R., and Cape, J. N.: Large estragole fluxes from oil palms in Borneo, Atmos. Chem. Phys., 10, 4343-4358, 10.5194/acp-10-4343-2010, 2010.

This reference was added in the manuscript as indicated in our response to Comment 4.

Interactive comment on “Measurements of biogenic volatile organic compounds at a grazed savannah-grassland-agriculture landscape in South Africa” by Kerneels Jaars et al. ((Ref. No.: acp-2016-471))

Anonymous Referee #2

Received and published: 21 October 2016

Summary: The authors present two separate years of atmospheric measurements of biogenic volatile organic compounds (BVOCs) at a grazed savannah-grasslandagriculture landscape in South Africa. This long-term and chemically detailed data set allows the authors to accurately assess the seasonal variability of these reactive compounds and provides the scientific community with a valuable dataset of BVOC emissions in a rarely studied ecosystem. The author’s present a careful comparison of the observed emissions to the surrounding vegetation and other physical parameters such as soil moisture. The contributions of each species to potential ozone formation are explored. The data is of high quality and the manuscript is very well written. I suggest publication with only minor revisions.

We would like to thank Referee #2 for the positive review of this paper, as well as acknowledging the relevance of the work presented and the high quality of the dataset. We would also like to thank Referee #2 for the minor technical comments, which were each addressed. Below is a point-by-point response to each of these comments.

Technical comments (P=page number and L=line number):

P1L22 and P3L5: These are not exactly the same statements. The first infers that anthropogenic sources only contribute 10% of the global annual VOC budget. The second statement (referencing Guenther et al.) states that 90% of BVOC emissions are from vegetation/terrestrial sources (i.e., only 10% from oceanic sources). Please be sure that these distinctions are more clear in the manuscript to avoid confusion by clarifying the contribution of BVOC vs. anthropogenic VOC. Also, do the emissions refer to mass or carbon or some other unit?

We thank Referee #2 for pointing out the confusion in these statements. It was meant to be stated that 90% of BVOC emissions are from vegetation. In addition, the emissions refer to mass per annum. Therefore the sentences in the Abstract and Introduction was changed as follows:

“…one (O_3) and secondary organic aerosols (SOA). Ecosystems produce and emit a large number of BVOCs. It is estimated on a global scale that approximately 90 % of annual BVOC emissions are from terrestrial sources. In this study, measurements…”

"…with typically 0.2 to 10 % of the carbon uptake during photosynthesis being converted to BVOCs (Kesselmeier et al., 2002). It is estimated that, on a global scale, approximately 90 % of annual BVOC emissions are from vegetation/ terrestrial sources (~1000 Tg year^{-1}) (Guenther et al., 2012)."

P2L12: lower for the grassland savannah or the other landscapes?

It was lower for grassland savannah. The sentence was changed as follows in the Abstract:

"However, comparisons with measurements conducted at other landscapes in southern Africa and the rest of the world that have more woody vegetation indicated that BVOC concentrations were, in general, significantly lower for the grassland savannah."

P4L25 and P29L2: African to Africa

The correction was made as follows:

"…concentrations covering a full seasonal cycle in southern Africa and for a grassland bioregion…"

P8L3: Can you state what the efficiency of the ozone removal was?

The efficiency of the ozone removal was stated in the paper by Jaars et al., 2014. However, we agree that it will be good to also indicate it in this paper. The following was added in Section 2.3.1:

"At regular intervals, the efficiency of this O_3 removal was verified with an O_3 monitor, which indicated that O_3 concentrations decreased from median values ≥ 30 ppb to < 2 ppb (Jaars et al., 2014)."

Section 2.3.1. Please add a brief description on how the samples were stored/transported prior to analysis. How much time would elapse between collection and analysis?

Handling of the samples after sampling and prior to analysis were also discussed in detail in the paper by Jaars et al., 2014. We also agree with Referee #2 that a brief summary can be included in this paper and the following was added in Section 2.3.1:

"…helium for 30 minutes at 350 ºC at a flow of 40 ml min^{-1}. The adsorbent tubes were removed from the sampler once a week and closed off with Swagelok® caps. Each tube was stored in a container for transport to the laboratory, where the adsorbent tubes were stored in a freezer for two to four weeks prior to analysis."

Section 3.5. How much of the correlation is simply driven by the fact that MBO, MTs, and SQTs generally have higher concentrations at night while isoprene will have the largest daytime emission? It would be interesting to compare the day and night time values of the compound classes, perhaps just for the wet season when emissions were enhanced.

In our response to a comment of Referee #1, median (mean) daytime to night-time concentrations ratios of all the BVOCs measured during both sampling campaigns were included in Table 2. These daytime to night-time concentration ratios indicated that there were no significant differences in levels of most of the BVOCs measured during daytime and night-time at Welgegund, with the exception of isoprene measured during the first sampling campaign, as well as two monoterpenes (terpinolene, bornylacetate) and the SQT aromadendrene measured duirng the second sampling campaign. Therefore isoprene levels measured during the first sampling campaign reflected the light dependency usually associated with isoprene emissions. However, daytime to night-time concentration ratios of isoprene did not exhibited the very strong light dependency typically associated with atmospheric isoprene concentrations, which could be attributed to the characteristics of sources of these species. Therefore the light dependency associated with these few BVOCs measured at Welgegund was addressed in the first paragraph in Section 3.2 as follows:

"In Table 2, the median (mean) and inter-quartile range (IQR, 25th to 75th) concentrations, as well as the median (mean) daytime to night-time concentration ratios of the BVOC species determined during the two sampling campaigns at Welgegund are presented. It is evident from the median (mean) daytime to night-time concentration ratios that there were not significant differences in levels of most of the BVOCs measured during daytime and night-time at Welgegund, with the exception of isoprene measured during the first sampling campaign, as well as the monoterpenes terpinolene and bornylacetate, and the SQT aromadendrene measured duirng the second sampling campaign. Isoprene levels during the first sampling campaign were approximately two times higher during daytime, which reflect the light dependency usually associated with isoprene emissions. However, daytime to night-time concentration ratios of isoprene did not exhibited the strong light dependency typically associated with atmospheric isoprene concentrations, which could be attributed to the characteristics of sources of these species that are discussed in subsequent sections. The temperature and photoactive radiation (PAR) measurements at Welgegund was used in the MEGAN BVOC emission model, which indicated that the measurement time (11:00 to 13:00 local time) captured most of the period of maximum isoprene emission (typically about 12:00 to 2:00 local time). In addition, by assuming a typical diurnal variation in VOC oxidation rate and boundary layer height, it was also found that the isoprene concentration of the measurement time is representative of the daytime isoprene concentration (Greenberg et al., 1999). In Table 3, the concentrations of BVOC species measured during other campaigns in South Africa and the rest of the world are presented."

Furthermore, based on these daytime to night-time concentration rations, it also does not seem that the observed correlations are driven by daytime and night-time emissions.

Measurements of biogenic volatile organic compounds at a grazed savannah-grassland-agriculture landscape in South Africa

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Abstract

Biogenic volatile organic compounds (BVOCs) are important role players in the chemistry of the troposphere, especially in the formation of tropospheric ozone (O_3) and secondary organic aerosols (SOA). Ecosystems produce and emit a large number of BVOCs. It is estimated on a global scale that approximately 90 % of annual BVOC emissions are ~~BVOCs~~from terrestrial sources. In this study, measurements of BVOCs were conducted at the Welgegund measurement station (South Africa), which is considered to be a regionally representative background site situated in savannah grassland. Very few BVOC measurements exist for grassland savannah and results presented in this study are the most extensive for this type of landscape. Samples were collected twice a week for two hours during daytime and two hours during night-time through two long-term sampling campaigns from February 2011 to February

2012 and from December 2013 to February 2015. Individual BVOCs were identified and quantified using a thermal desorption instrument, connected to a gas chromatograph and a mass selective detector. The annual median concentrations of isoprene, 2-methyl-3-butene-2-ol (MBO), monoterpenes and sesquiterpenes (SQT) during the first campaign were 14, 7, 120 and 8 pptv, respectively, and 14, 4, 83 and 4 pptv, respectively, during the second campaign. The sum of the concentrations of the monoterpenes were at least an order of magnitude higher than the concentrations of other BVOC species during both sampling campaigns, with α-pinene being the most abundant species. The highest BVOC concentrations were observed during the wet season and elevated soil moisture was associated with increased BVOC concentrations. However, comparisons with measurements conducted at other landscapes in southern Africa and the rest of the world that have more woody vegetation indicated that BVOC concentrations were, in general, significantly lower for the grassland savannah. Furthermore, BVOC concentrations were an order of magnitude lower compared to total aromatic concentrations measured at Welgegund. An analysis of concentrations by wind direction indicated that isoprene concentrations were higher from the western sector that is considered to be a relatively clean regional background region with no large anthropogenic point sources~~western direction~~, while wind direction did not indicate any significant differences in the concentrations of the other BVOC species. Statistical analysis indicated that soil moisture had the most significant impact on atmospheric levels of MBO, monoterpenes and SQT concentrations, while temperature had the greatest influence on isoprene levels. The combined O_3 formation potentials of all the BVOCs measured calculated with MIR coefficients during the first and second campaign were 1162 and 1022 pptv, respectively. α-Pinene and limonene had the highest reaction rates with O_3, while isoprene exhibited relatively small contributions to O_3 depletion. Limonene, α-pinene and terpinolene had the largest contributions to the OH-reactivity of BVOCs measured at Welgegund for all of the months during both sampling campaigns.

1 Introduction

Ecosystems produce and emit a large number of biogenic volatile organic compounds (BVOCs) that are involved in plant growth and reproduction. These species also act as defensive compounds, e.g. enhancing tolerance to heat and oxidative stress (Sharkey and Yeh, 2001; Loreto and Schnitzler, 2010), preventing the colonisation of pathogens after wounding, and deterring insects or recruiting natural enemies of herbivores (Holopainen and Gershenzon, 2010). The BVOC production rate in an ecosystem depends on several physical (e.g. temperature, precipitation, moisture, solar radiation and CO_2 concentration) and biological parameters (e.g. plant species and the associated emission capacity, phenology, biotic and abiotic stresses, attraction of pollinators) (Blande et al., 2014; Fuentes et al., 2000; Kesselmeier and Staudt, 1999; Sharkey and Yeh, 2001), with typically 0.2 to 10 % of the carbon uptake during photosynthesis being converted to BVOCs (Kesselmeier et al., 2002). It is estimated that, on a global scale, approximately 90 % of annual BVOC emissions are ~~by~~from vegetation/ terrestrial sources (~1000 Tg~~ C~~ year^{-1}) (Guenther et al., 2012).

BVOCs can contribute significantly to the carbon balance in certain ecosystems (Kesselmeier et al., 2002; Malhi, 2002). BVOC concentrations in ambient air depend on several factors, which include emission rates from vegetation, atmospheric transport and mixing, as well as the chemical composition and oxidative state of the atmosphere, which determines the sink of these species. BVOCs are important in the formation of tropospheric ozone (O_3) and secondary organic aerosols (SOA). BVOCs in the troposphere react with the major oxidants in the atmosphere, which include tropospheric O_3, hydroxyl radicals ($^{\bullet}$OH, referred to, from here on, as OH for simplicity) and nitrate radicals ($NO_3^{\bullet}$, referred to, from here on, as NO_3 for simplicity) (Atkinson and Arey, 2003a). These oxidants strongly affect the concentrations of atmospheric BVOCs (Lelieveld et al., 2008; Di Carlo et al., 2004). BVOCs are also crucial in the formation of the stabilised Criegee intermediate – a carbonyl oxide with two free-radical sites – or its derivative (Mauldin III et al., 2012; Welz et al., 2012), which also contributes to atmospheric oxidation. A complex range of reaction products are formed from atmospheric BVOCs, including less volatile oxygenated compounds that condense to form aerosol particles.

Various studies have indicated the link between BVOCs and the formation of SOA (Vakkari et al., 2015; Andreae and Crutzen, 1997; Ehn et al., 2014), while the influence of BVOCs on the growth of newly formed aerosol particles has also been indicated (Kulmala et al., 2004; Tunved et al., 2006). However, there are many uncertainties associated with the exact chemical reactions and physical processes involved in SOA formation and aerosol particle growth, which largely depends on regional emissions and atmospheric processes (Kulmala et al., 2013; Ehn et al., 2014). Vakkari et al. (2015) indicated the importance of VOCs for new particle formation and growth in clean background air in South Africa. Therefore, it is essential to understand the sources, transport and transformations of these compounds for air quality management and climate change-related studies, as well as for the modelling of atmospheric chemistry at global, regional and local scales (Laothawornkitkul et al., 2009; Peñuelas and Staudt, 2010; Peñuelas and Llusià, 2003).

Long-term ambient BVOC measurements to establish seasonal cycles have been conducted extensively in several regions, which include boreal forest (Hakola et al., 2009; Hakola et al., 2000; Rinne et al., 2000; Rinne et al., 2005; Rantala et al., 2015; Räisänen et al., 2009; Eerdekens et al., 2009; Lappalainen et al., 2009), hemiboreal mixed forest (Noe et al., 2012), temperate (Spirig et al., 2005; Stroud et al., 2005; Fuentes et al., 2007; Mielke et al., 2010), Mediterranean (Davison et al., 2009; Harrison et al., 2001) and tropical (Rinne et al., 2002) ecosystems. Shorter campaigns have also been conducted in Western and Central Africa, which include several different studies in the framework of the African Monsoon Multidisciplinary Analyses (AMMA) (Grant et al., 2008; Saxton et al., 2007) and the EXPeriment for the REgional Sources and Sinks of Oxidants (EXPRESSO) (Serca et al., 2001). Zunckel et al. (2007) and references therein indicated that limited research has been conducted on BVOC emissions in southern Africa, which consisted mainly of short campaigns measuring BVOC emission rates. Considering that BVOC emissions on a global scale are considered to be significantly higher (ca. 10 times) than the emission of anthropogenic VOCs, it is very important that longer-term BVOC measurements are conducted in southern Africa. Furthermore, a large part of the land cover in South Africa consists of a grassland bioregion, as indicated in Figure 1. Although it is considered that grasslands cover approximately one quarter of the Earth's land surface, relatively few studies have been conducted on BVOC emissions from grasslands, while there are no long-term BVOC studies reported for these landscapes (Bamberger et al., 2011; Ruuskanen et al., 2011; Wang et al., 2012). Therefore, the aim of this study was to quantify the ambient BVOC concentrations over different seasons at a regional background site in South Africa. In addition, the objective was also to characterise their seasonal patterns, as well as to relate BVOC concentrations measured in southern Africa to levels in other regions in the world. According to the knowledge of the authors, this is the first record of ambient BVOC concentrations covering a full seasonal cycle in southern Africa~~n~~ and for a grassland bioregion anywhere in the world.

Insert Figure 1

2 Measurement location and methods

2.1 Site description

Measurements were conducted at the Welgegund measurement station (26.57°S, 26.94°E, 1480 m a.s.l.) (Welgegund measurement station, 2016), which is located on the property of a commercial maize and cattle farmer approximately 100 km west of Johannesburg, as indicated in Figure 1. Welgegund is a regional background station with no pollutant sources in close proximity. The distances to the nearest blacktop road and nearest town are approximately 10 and 30 km, respectively. Welgegund is, however, affected by the major anthropogenic source regions in the north-eastern interior of South Africa (as indicated by the major large point sources in Figure 1), which also include the Johannesburg-Pretoria conurbation (Tiitta, et al., 2014). From Figure 1, it is also evident that the western sector contains no major anthropogenic point sources and can therefore be considered to be representative of a relatively clean regional background.

Welgegund is geographically located within the South African Highveld, which is characterised by two distinct seasonal periods, i.e. a dry season from May to September that predominantly coincides with winter (June to August), and a wet season during the warmer months from October to April. The dry period is characterised by low relative humidity, while the wet season is associated with higher relative humidity and frequent rains that predominantly occur in the form of thunderstorms. The mean annual precipitation is approximately 500 mm with approximately >80 % of rain events occurring during the wet season. During the sampling period, the coldest temperature recorded in winter at Welgegund was -5.1 °C in June 2011, while the highest temperature recorded in summer was +35.6 °C in October 2011. The mean maximum temperature ranges between 16 and 32 °C, while the mean minimum temperature ranges between 0 and 15 °C. Winters are also characterised by frequent and severe frost days (26-37 days per year) (Mucina and Rutherford, 2006).

2.2 Vegetation

The Welgegund measurement station is located in the Grassland Biome (Figure 1), which covers 28 % of South Africa's land surface (Mucina and Rutherford, 2006). This biome has been significantly transformed, primarily as a result of cultivation, plantation forestry, urbanisation and mining (Daemane et al., 2010 and references therein). It has also been severely degraded by erosion and agricultural development. The station is situated within Vaal-Vet Sandy Grassland with Andesite Mountain Bushveld of the Savannah Biome prominent on nearby ridges. At present, only 0.3 % of the Vaal-Vet Sandy Grassland is statutorily conserved, while the rest is mostly used for grazing and crop production. In Figure 2, a land cover map within a 60 km radius from Welgegund is presented indicating the extent of cultivation in this region. The land cover survey was performed within a region that was estimated to represent the BVOC footprint at Welgegund, which was calculated from typical atmospheric lifetimes (Table 1) of the species measured and the general wind speed(s) (Figure 3) at Welgegund. The immediate area surrounding Welgegund is grazed by livestock, with the remaining area covered by crop fields (mostly maize and to a lesser degree sunflower). In the demarcated 60 km radius, a further three vegetation units of the Dry Highveld Grassland Bioregion (Grassland Biome) and another two of the Central Bushveld Bioregion (Savannah Biome) are also present. In addition, alluvial vegetation is found associated with major rivers and inland saline vegetation in scattered salt pans.

Insert Figure 2

The study area comprises a highly variable landscape with scattered hills and sloping, slightly irregular, undulating plains, which are dissected by prominent rocky ridges. Soil in the catchment area is heterogeneous and rocky, varying from sandy to clayey depending on the underlying rock types, such as andesite, chert, dolomite, mudstone, quartzite, sandstone and shale.

Land use within the surrounding area is divided into six major land cover types, i.e. cultivated land, grasslands, mountainous areas, plantations, urban areas and water bodies, as indicated in Figure 2. Mountainous areas, grassland and water bodies (riparian areas) comprised many different vegetation units. The other homogenous areas were anthropogenically altered and no longer representative of the surrounding natural vegetation. The study area is characterised by a grassland-woodland vegetation complex, dominated by various grass and woody species, and recognised by the presence of non-native species in altered environments.

The most dominant woody species of the entire study area include the trees *Celtis africana*, *Searsia pyroides*, *Vachellia karroo* and *Ziziphus mucronata*, and the thorny shrub *Asparagus* *laricinus*. Tree diversity increases where there are patches of deep sand, characterised by *Gymnosporia buxifolia* and *Vachellia erioloba*, or in mountainous areas, where *Euclea undulata*, *Grewia flava* and *Senegallia caffra* become most prominent. Woody vegetation occurs sparsely in grasslands and when present is found on isolated ridges, including the small trees *Pavetta zeyheri*, *Vangueria infausta* and *Zanthoxylum capense*. In anthropogenically altered environments, native species decrease and introduced species dominate, such as *Eucalyptus camaldulensis*, *Pinus roxburghiana* and *Populus canescens* in plantations; *Gleditsia triacanthos*, *Pyracantha coccinea* and *Salix babylonica* along rivers and water bodies; and *Celtis sinensis*, *Melia azedarach* and *Robinia pseudoacacia* in the urban footprint.

The most dominant species of the grass sward in the entire study area include *Cynodon dactylon*, *Eragrostis chloromelas*, *Heteropogon contortus*, *Setaria sphacelata* and *Themeda triandra*. The dry, western grassland (Vaal-Vet Sandy Grassland specifically) is characterised by *Anthephora pubescens*, *Cymbopogon caesius*, *Digitaria argyrograpta*, *Elionurus muticus* and *Eragrostis lehmanniana*, and the moist Rand Highveld Grassland in the south-east by *Ctenium concinnum*, *Digitaria monodactyla*, *Monocymbium ceresiforme*, *Panicum natalense* and *Trachypogon spicatus*. The north-eastern parts of the study area on dolomite are dominated by *Brachiaria serrata*, *Digitaria tricholaenoides*, *Eragrostis racemosa* and *Loudetia simplex*.

2.3 Measurement methods

2.3.1 BVOC measurements and analysis

BVOC measurements were conducted for a period of more than two years through a 13-month sampling campaign from February 2011 to February 2012 and a 15-month sampling campaign from December 2013 to February 2015. Samples were collected twice a week for two hours during daytime (11:00 to 13:00 local time, LT) and two hours during night-time (23:00 to 1:00 LT) on Tuesdays and Saturdays. Several previous studies have demonstrated that the maximum emissions of isoprene and monoterpenes from vegetation occur around midday (Fuentes et al., 2000; Kuhn et al., 2002). Understandably, the chosen sampling schedule, i.e. same days each week and same hours of the day, was prone to some bias. As mentioned by Jaars et al. (2014), considering the distance of the sampling site from the nearest town and logistical limitations during the sampling campaigns, the sampling schedule applied was the most feasible option that enabled the collection of data for more than two years. VOCs were sampled at a height of 2 m above ground level, with a 1.75 m long inlet. The first 1.25 m of the inlet was a stainless steel tube (grade 304 or 316) and the second 0.5 m was Teflon. To prevent the degradation of BVOC by O_3, the stainless steel part of the inlet was heated to 120 ºC using heating cables and thermostats (Thermonic), thereby removing ozone from the sample stream (Hellén et al., 2012a). At regular intervals, the efficiency of this O_3 removal was verified with an O_3 monitor, which indicated that O_3 concentrations decreased from median values $\geq$ 30 ppb to $<$ 2 ppb (Jaars et al., 2014).

VOCs were collected with stainless steel adsorbent tubes (6.3 mm ED x 90 mm, 5.5 mm ID) packed with Tenax-TA and Carbotrap-B by using a constant flow type automated programmable sampler. A detailed description of the sampling procedure is presented by Jaars et al. (2014). In short, the flow rate of the pump was set at between 100 and 110 ml min^{-1} throughout the campaigns and was calibrated each week. Prior to sampling, all adsorbent tubes were tested for leaks and preconditioned with helium for 30 minutes at 350 ºC at a flow of 40 ml min^{-1}. The adsorbent tubes were removed from the sampler once a week and closed off with Swagelok® caps. Each tube was stored in a container for transport to the laboratory, where the adsorbent tubes were stored in a freezer for two to four weeks prior to analysis.

Individual BVOCs were identified and quantified using a thermal desorption instrument (Perkin-Elmer TurboMatrixTM 650, Waltham, USA) connected to a gas chromatograph (Perkin-Elmer® Clarus® 600, Waltham, USA) with a DB-5MS (60 m, 0.25 mm, 1 µm) column and a mass selective detector (Perkin-Elmer® Clarus® 600T, Waltham, USA). Samples were analysed using the selected ion mode (SIM). A five-point calibration was performed by using liquid standards in methanol solutions. Standard solutions were injected onto adsorbent tubes that were flushed with helium at a flow of 100 ml min^{-1} for 10 min in order to remove methanol. BVOCs quantified for the two campaigns included isoprene with method detection limit (MDL) between 1.2 and 2.4 pptv and 2-methyl-3-butene-2-ol (MBO) with MDL between 0.9 and 1.4 pptv. The monoterpenes (α-pinene, camphene, β-pinene, Δ^3-carene, ~~p-cymene, ~~limonene, 1,8-cineol, terpinolene, ~~4-acetyl-1-methylcyclohexene (AMCH), ~~nopinone~~,~~ and bornylacetate~~ and 4-allylanisole~~) and monoterpene-related BVOCs (p-cymene, 4-allylanisole and 4-acetyl-1-methylcyclohexene (AMCH)) MDL was between 0.6 and 1.6 pptv. The term “monoterpene(s)” used in the discussions in subsequent sections in the manuscript refers to both the monoterpene and monoterpene-related BVOCs. The sesquiterpenes (SQT) (longicyclene, iso-longifolene, aromadendrene, α-humulene and alloaromadendrene) MDL was ~0.6 pptv. Since the analytical system did not separate myrcene and β-pinene, β-pinene concentrations determined were the sum of these two species. VOC concentrations were field and lab blank corrected. When monthly median BVOC concentrations were calculated, sample concentrations below the method detection limit (MDL) were replaced with ½MDL.

2.3.2 Ancillary measurements

Ancillary measurements continuously performed at the Welgegund station were used to interpret the measured BVOC concentrations. General meteorological parameters, i.e. temperature (T), relative humidity (RH), wind speed and direction, and precipitation were measured. Soil temperature and moisture at different depths (5 and 20 cm) were measured with a PT-100 and Theta probe ML2x (Delta-T), respectively. Additional soil moisture information was obtained with a 100 cm PR2 soil moisture profile probe (Delta-T). Direct photosynthetic photon flux density (PPFD) between 400 and 700 nm was measured with a Kipp & Zonen pyranometer (CMP 3 pyranometer, ISO 9060:1990 Second Class).

Trace gas measurements were performed utilising a Thermo-Electron 43S sulphur dioxide (SO_2) analyser (Thermo Fisher Scientific Inc., Yokohama-shi, Japan), a Teledyne 200AU nitrogen oxide (NO_x) analyser (Advanced Pollution Instrumentation Inc., San Diego, Cam USA), an Environment SA 41M O_3 analyser (Environment SA, Poissy, France) and a Horiba APMA-360 carbon monoxide (CO) analyser (Horiba, Kyoto, Japan). The net ecosystem exchange (NEE) of carbon dioxide (CO_2) was measured with the eddy covariance method with a Licor 7000 closed path infrared gas analyser (IRGA) and a three-dimensional Metek sonic anemometer at a height of 9 m, which is well above the average tree height of 2.5 m (Räsänen et al., 2016). A more detailed description of additional parameters monitored at Welgegund is given by Beukes et al. (2015).

2.3.3 Lifetime of BVOCs

In Table 1, the atmospheric lifetimes (τ) of BVOCs measured in this study calculated from OH- and O_3 reactivity are reported. BVOC lifetimes according to O_3 reactivity were calculated with Eq. (1):

$$\tau = \tau_{O3} = \frac{1}{k_{O3,[O_3]}} \tag{1}$$

where $[O_3]$ is the annual average O_3 concentration (ca. 36 ppbv) measured during the two campaigns at Welgegund and k_{O3} the reaction rate constant for the reaction between a specific

BVOC and O_3. Since direct OH reactivity measurements were not available, the average concentration of OH radicals ([OH]) (ca. 0.04 pptv) reported by Ciccioli et al. (2014) was used in the calculations, using Eq. (2):

$$\tau = \tau_{\mathrm{OH}} = \frac{1}{k_{\mathrm{OH},}[\mathrm{OH}]} \tag{2}$$

where k_{OH} is the reaction rate constant for the reaction between a specific BVOC and OH.

Insert Table 1

3 Results and discussion

3.1 Meteorological conditions during the measurement campaigns

Local meteorological influences on the measured BVOC concentrations are likely to be more significant than regional impacts of air masses due to the short lifetimes associated with atmospheric BVOCs (Table 1). Therefore, BVOC concentrations were only interpreted in terms of local meteorological patterns and no back trajectory analyses were employed. In Figure 3, the monthly medians of the meteorological parameters – precipitation, T, RH, wind speed and -direction, and soil moisture depth (5 and 20 cm) – measured at Welgegund during each of the two sampling campaigns are presented. From Figure 3a and b, the wet season (October to April) associated with warmer months and the dry season (May to September) associated with colder months as discussed in section 2.1 are evident. Rainfall in this region of South Africa is typically characterised by relatively large inter-annual variability (Conradie et al., 2016). The monthly median temperatures for the periods during which samples were collected ranged between 8.8 and 13 °C in winter and 19.7 and 24.9 °C in summer (Figure 3b). During the warmer months, temperatures up to 30 °C and higher were reached frequently. During the wet season, the monthly median RH ranged between 30 (with the onset of the wet season) and 80 % (at the end of the wet season), while the RH ranged between 20 and 50 % during the dry season (Figure 3c). The highest monthly median wind speeds occurred during the warmer months (Figure 3d) when unstable meteorological conditions are prevalent in the interior of South Africa (Tyson et al., 1996). The seasonal variations of wind direction during the two sampling campaigns (Figure 3e) indicated that the prevailing wind direction was from the northern to eastern sector, which agrees with the back trajectory analysis performed for the first sampling period at Welgegund by Jaars et al. (2014). Soil moisture measurements mimicked the seasonal precipitation pattern, i.e. higher soil moisture associated with the wet season (Figure 3f and 3g). The soil moisture measurements conducted from January to August at a depth of 20 cm were significantly higher during the first sampling campaign. During December 2010 and January 2011, prior to the first sampling campaign, precipitation (Figure 3a) was clearly higher than during the second campaign, i.e. December 2013 to January 2014. Subsequently, the soil moisture measured at 20 cm (Figure 3g) was clearly higher during the first sampling campaign than during the second campaign from the beginning of the campaign until the middle of the dry season.

Insert Figure 3

Figure 4 presents micrometeorological CO_2 flux measurements at Welgegund, which indicate typical changes in the seasonal uptake of CO_2 by vegetation. In addition, the Photosynthetic Photon Flux Density (PPFD) is also indiacted with a colour bar. Negative values (downward CO_2 flux) indicate the net uptake of CO_2 by vegetation, with the gross primary production (GPP) exceeding the total respiration. Positive values indicate the emission of CO_2 by the vegetation. A period of an approximately 0 (small positive) net CO_2 flux is observed in the winter months that extend until September, which can be attributed to decreased microbial activity associated with lower temperatures, low rainfall and most of the vegetation losing their leaves. The net ecosystem exchange (NEE) at full light (maximum downward flux) increases gradually until February in response to the increases of the photochemical efficiency of CO_2 assimilation in the vegetation surrounding the site and the solar elevation angle. The daily maximum NEE starts to decrease in March/April when the solar elevation angle declines and soil moisture drops.

Insert Figure 4

3.2 Contextualising BVOC concentrations measured at Welgegund

In Table 2, the median (mean) and inter-quartile range (IQR, 25th to 75th) concentrations, as well as the median (mean) daytime to night-time concentration ratios of the BVOC species determined during the two sampling campaigns at Welgegund are presented. It is evident from the median (mean) daytime to night-time concentration ratios that there were not significant differences in levels of most of the BVOCs measured during daytime and night-time at Welgegund, with the exception of isoprene measured during the first sampling campaign, as well as the monoterpenes terpinolene and bornylacetate, and the SQT aromadendrene measured duirng the second sampling campaign. Isoprene levels during the first sampling campaign were approximately two times higher during daytime, which reflect the light dependency usually associated with isoprene emissions. However, daytime to night-time concentration ratios of isoprene did not exhibited the strong light dependency typically associated with atmospheric isoprene concentrations, which could be attributed to the characteristics of sources of these species that are discussed in subsequent sections. The temperature and photoactive radiation (PAR) measurements at Welgegund was used in the MEGAN BVOC emission model, which indicated that the measurement time (11:00 to 13:00 local time) captured most of the period of maximum isoprene emission (typically about 12:00 to 2:00 local time). In addition, by assuming a typical diurnal variation in VOC oxidation rate and boundary layer height, it was also found that the isoprene concentration of the measurement time is representative of the daytime isoprene concentration (Greenberg et al., 1999). In Table 3, the concentrations of BVOC species measured during other campaigns in South Africa and the rest of the world are presented.

Insert Table 2

Insert Table 3

The most abundant species observed throughout the study was the monoterpene, α-pinene, and the total monoterpene concentration was at least an order of magnitude higher compared to the concentrations of other BVOC categories. The total annual median (IQR) monoterpene concentration was 120 (73-242) pptv during the first campaign and 83 (54-145) pptv during the second campaign. As indicated in Table 2, α-pinene, p-cymene and limonene were the predominant compounds measured during the first campaign, constituting more than 63 % of the ambient monoterpene concentrations, while during the second campaign, the dominant monoterpenes were α-pinene, limonene and terpinolene, constituting more than 70 % of the ambient monoterpene concentrations. BVOC flux measurements conducted by Greenberg et al. (2003) during SAFARI 2000 at a mopane woodland in Botswana indicated that 60 % of the monoterpene flux was attributed to α-pinene, while limonene and β-pinene contributed almost all of the rest of the monoterpenes. Various studies in other regions have also indicated that α-pinene is the dominant monoterpene in ambient air reflecting the ubiquitous nature of its emission (Hellén et al., 2012b; Hakola et al., 2012; Noe et al., 2012). During the AMMA experiment, Saxton et al. (2007) also detected several monoterpenes in ambient air at Djougou with concentrations generally higher than monoterpene concentrations recorded by Serca et al. (2001) (less than 20 pptv) during EXPRESSO at a forest in Northern Congo. Monoterpene concentrations reported for boreal forest (Hakola et al., 2009; Hakola et al., 2000; Rinne et al., 2000; Rinne et al., 2005; Rantala et al., 2015; Räisänen et al., 2009; Eerdekens et al., 2009; Lappalainen et al., 2009), hemiboreal mixed forest (Noe et al., 2012), temperate (Spirig et al., 2005; Stroud et al., 2005; Fuentes et al., 2007; Mielke et al., 2010), Mediterranean (Davison et al., 2009; Harrison et al., 2001) and tropical (Rinne et al., 2002) ecosystems ranged between 40 and 7 200 pptv (Table 3). Therefore, there is a large variation in the monoterpene concentrations measured in different ecosystems, with concentrations measured at Welgegund being in the low to mid-range. Unlike isoprene that is approximately 10 times lower than isoprene levels at other ecosystems in the world, the mean monoterpene concentration at Welgegund is comparable to the previous studies at other ecosystems summarised in Table 3.

The annual median (IQR) isoprene concentration measured during the first campaign was 14 (6-35) pptv, while the annual median (IQR) isoprene concentration measured during the second sampling campaign was 14 (7-24) pptv. The highest isoprene concentration, i.e. 202 pptv, was recorded in summer (wet season). Harley et al. (2003) reported that the maximum isoprene concentration measured during an eight-day campaign in the wet season at a *Combretum-Acacia* savannah in southern Africa was 860 pptv with a mean midday concentration of 390 pptv, which is considerably higher than isoprene levels measured at Welgegund. Ambient BVOC measurements conducted by Saxton et al. (2007) at a rural site near Djougou, Benin in June 2006 during the AMMA project indicated isoprene concentrations >3 000 pptv. Grant et al. (2008) conducted VOC measurements at a small rural Senegalese village during September 2006 that was also a sampling location for the AMMA project and reported that isoprene, which had a mean concentration of 300±100 pptv, was the only biogenic hydrocarbon present in all air samples. Serca et al. (2001) reported ambient the mean isoprene concentration for a tropical forest of Northern Congo during the EXPRESSO study to be 1820±870 pptv at the beginning of the wet season and 730±480 pptv at the end of the wet season. Nakashima et al. (2014) reported that the mean isoprene concentration at the Manitou Experimental Forest (MEF) was 68 ± 69 pptv. In general, mean isoprene concentrations measured at Welgegund were at least an order of magnitude smaller compared to other isoprene measurements in South Africa, Africa and most other parts of the world.

The annual median (IQR) MBO concentrations measured during the first and second campaign were 7 (3-16) and 4 (3-10) pptv, respectively. MBO and isoprene are both produced from dimethylallyl diphosphate (DMADP) (Gray et al., 2011). Guenther (2013) indicated that MBO is emitted from most isoprene emitting vegetation at an emission rate of ~1 % of that of isoprene. However, MBO measured at Welgegund was approximately 30 % of the isoprene concentrations, which indicated that the main source of MBO at Welgegund is not from isoprene emitters, but from other MBO emitters. MBO concentration measurements at Manitou Experimental Forest, USA were 1 346 ± 777 pptv (Nakashima et al., 2014), which is three orders of magnitude higher compared to the MBO levels measured at Welgegund. According to the knowledge of the authors, there are no previous ambient MBO concentrations measured for Africa.

Most SQTs are highly reactive species and are difficult to detect in ambient air samples, which resulted in concentrations of these species being frequently below the detection limit of the analytical procedure. This is also reflected in the concentrations of these species being an order of magnitude lower compared to the other BVOC species measured in this study. The total annual median (IQR) SQT concentration measured during the first sampling campaign was 8 (5-14) pptv and 4 (3-11) pptv during the second sampling campaign. The most abundant SQT during the first sampling campaign was longicyclene with an annual mean concentration of 4 (1-4) pptv. During the second sampling campaign, α-humulene was the most abundant SQT with an annual mean concentration of 3 (1-5) pptv.

The lower BVOC concentrations measured at Welgegund compared to other regions can mainly be attributed to the much lower isoprene concentrations measured. However, monoterpenes that are important for SOA formation are similar to levels thereof in other environments. In an effort to explain the BVOC concentrations measured at Welgegund, a comprehensive vegetation study was conducted, as described in section 2.2. The influence of the type of vegetation in the region surrounding Welgegund on ambient BVOC concentrations will be further explored.

Jaars et al. (2014) presented concentrations of aromatic VOCs measured at Welgegund during the same two sampling campaigns discussed in this paper. The total BVOC concentrations measured were at least an order of magnitude lower compared to concentrations of aromatic VOCs measured at Welgegund. The most abundant aromatic compound, toluene, had a median value of 630 pptv, while the most abundant BVOC measured, α-pinene, had a median value of 37 pptv. In addition, the median of the concentrations of the all the monoterpene species (120 and 83 pptv) was approximately six times lower compared to toluene concentrations (Jaars et al., 2014).

3.3 Seasonal variations

In Figure 5, the panels on the left show monthly median concentrations of (a) isoprene, (b) MBO, (c) monoterpenes and (d) SQT measured for the two campaigns, while the panels on the right present the wet (October to April) and dry (May to September) season concentrations of the respective compounds measured for the two campaigns. As indicated in Section 3.2, isoprene measured during the first sampling campaign had higher median (mean) daytime concentrations compared to median (mean) night-time concentrations, which reflects the light dependency expected from isoprene. All other BVOCs with the exception of two monoterpenes and one SQT did not indicate significant differences between daytime and night-time median (mean) concentrations. Therefore the seasonal plots of only isoprene were separated between daytime and night-time median concentrations. Seasonal variations in BVOC concentrations are expected due to the response of emissions to changes in environmental conditions, e.g. temperature and rainfall, as discussed in section 3.1, and the associated biogenic activity. In addition, BVOC emission is expected to be lower during the winter months (June to August), since foliar densities rapidly decrease due to deciduous trees dropping their leaves in winter (Otter et al., 2002). As expected, it is evident that the concentrations of all the BVOC species, with the exception of the isoprene (Figure 5a), and SQT values (Figure 5d) measured during the second sampling campaign, were higher in the wet season. The wet season also had more occurrences of BVOC concentrations that were higher than the range of the box and whisker plot (whiskers indicating ±2.7σ or 99.3 % coverage if the data have a normal distribution). In an isoprene and monoterpene emissions modelling study for southern Africa conducted by Otter et al. (2003), it was estimated that BVOC emissions will decrease by as much as 85 % in the dry winter season for grassland and savanna regions. BVOC concentrations measured in this study indicated much lower decreases from summer (December to February) to winter (June to August), with isoprene and monoterpene decreasing by only 37 and 29 %, respectively during the first sampling campaign, while isoprene and monoterpene decreased by only 42 and 23 %, respectively during the second sampling campaign. This can partially be attributed to the significant transformation of this biome, as discussed in section 2.2, with large areas transformed to cultivated land, as indicated in Figure 2. In addition, the study by Otter et al. (2003) was conducted for the entire southern African region.

Insert Figure 5

The monthly median isoprene concentrations (Figure 5a) measured during the first sampling campaign indicated the expected seasonal pattern with higher isoprene concentrations coinciding with the wet and warmer months, with the exception of April that had lower isoprene concentrations. Surprisingly, during the second sampling campaign, there was no distinct seasonal pattern observed. However, higher isoprene concentrations seem to coincide with higher wind speeds (Figure 3d), which are observed for both sampling campaigns. This indicates that the major sources of isoprene measured at Welgegund can be considered not to be within close proximity. However, since oxidation products of isoprene (e.g. methyl vinyl ketone, methacrolein) were not measured in this study, more distant sources of isoprene could not be verified. It is evident from Figure 2 that the region in close proximity of Welgegund in the south-western to north-eastern sector largely comprises cultivated land, while in the north-eastern to south-western sector the predominant land coverage is grassland and natural vegetation. It is expected that isoprene emissions from the cultivated land will be lower compared to savanna grassland (Otter et al., 2003). Therefore, if Welgegund is more frequently affected by winds from the south-western to north-eastern sector, higher wind speeds will coincide with higher isoprene levels, since the savanna grassland fetch region is distant from Welgegund and related to the approximately three-hour atmospheric lifetime of isoprene due to OH radicals.

In Figure 6, the wind roses for the BVOCs species measured in this study are presented. It is evident that the highest isoprene concentrations for the first sampling period were associated with winds originating from the south to south-western sector, i.e. predominantly from the grassland region in close proximity during the first sampling campaign resulting in a relatively more distinct seasonal pattern for isoprene levels. During the second sampling campaign, higher isoprene concentrations were associated with winds originating from the south-western to the northern sector, i.e. from the cultivated land area. Therefore, isoprene concentrations measured during the second sampling period coincided predominantly with stronger wind speeds from more distant fetch regions.

Insert Figure 6

Distinct seasonal patterns are observed for MBO (Figure 5b) concentrations during both sampling campaigns, i.e. higher MBO concentrations coinciding with wet warm months and lower levels corresponding with dry cold months (Figure 3). The MBO concentrations also corresponded to the seasonal CO_2 uptake (Figure 4). It is also evident from Figure 5b that MBO concentrations during the wet season in the first sampling campaign were higher compared to the second sampling campaign, especially from February to April 2011. As mentioned in section 3.1, the soil moisture measured at a depth of 20 cm (Figure 3g) during the first sampling campaign was significantly higher from February to August compared to the second sampling campaign. Therefore, these increased MBO levels measured during the first sampling campaign can be attributed to increased emissions from deep-rooted plants, e.g. shrubs and trees. In addition to decreased biogenic activity in the dry winter, the conversion of MBO to isoprene in the atmosphere could also lead to decreased MBO levels during this period. Jaoui et al. (2012) reported that MBO conversion to isoprene increased by an order of magnitude during dry conditions compared to humid conditions. This can also contribute to elevated isoprene concentrations measured during the dry months at Welgegund (Figure 5a).

No distinct seasonal pattern is observed for monoterpene and SQT concentrations, with the exception of significantly higher levels measured from February to April 2011 during the first sampling campaign. These increased monoterpene and SQT concentrations can also be attributed to the significantly higher soil moisture measured at a depth of 20 cm during the first sampling campaign (Figure 3g), as observed for the MBO. The monoterpene and SQT concentrations measured during the first sampling campaign were generally higher compared to the second sampling campaign. In Figure S1 (a) and (b) the relationship between soil moisture and monoterpene concentrations, as well as between soil moisture and SQT are presented, respectively. It is evident that higher concentrations of monoterpene and SQT are associated with higher soil moisture measured at a depth of 5 and 20 cm. Otter et al. (2002) also reported a more pronounced seasonal pattern for isoprene compared to monoterpene emissions at the Nylsvley Nature Reserve, which is approximately 200 km north-west from Welgegund.

3.4 BVOC emissions from surrounding vegetation

As discussed in section 2.2 and indicated in Figure 2, Welgegund is situated in a region that has been significantly transformed through cultivation. Cultivated land within the demarcated 60 km radius (Figure 2) consists mainly of maize and, to a lesser degree, sunflower production. These cultivated lands are also typically characterised by eucalyptus trees, which have a very high BVOC emission potential (Kesselmeier and Staudt, 1999), planted on their peripheries as is evident in Figure 2. The grassland region in close proximity of Welgegund (south-western to north-eastern sector) has a high diversity of grass and woody species, as mentioned in section 2.2. In general, it can be considered that the woody species in the grasslands are major sources of all the BVOCs measured in this study. Otter et al. (2003) also considered woody vegetation to be the most important in terms of BVOC emissions in southern Africa. It is generally considered that crops and grass have very low isoprene-emitting capacities (Kesselmeier and Staudt, 1999; Guenther, 2013). However, Schuh et al. (1997) indicate that sunflowers emit isoprene; the monoterpenes α-pinene, β-pinene, sabinene, 3-carene and limonene; and the sesquiterpene β-caryophyllene predominantly. In addition, Chang et al. (2014) (with references therein) also indicated that isoprene has anthropogenic sources in urban areas, which indicates that the surrounding towns can also contribute to the isoprene concentrations.

In an effort to determine possible sources of BVOC species, concentrations roses were compiled, as presented in Figure 6. In general, the concentration roses indicated that isoprene concentrations were higher fro~~r~~m the western sector~~direction~~ (indicated by the average and highest concentrations) that is considered to be a relatively clean regional background region with no large anthropogenic point sources (Figure 1), while wind direction did not indicate any significant differences in the concentrations of the other BVOC species. On occasion, higher

MBO, monoterpene and SQT concentrations were observed from the south-eastern region, which may be attributed to a large eucalyptus plantation approximately 15 km south-east from Welgegund, indicated in Figure 2. However, high isoprene emissions are also usually associated with eucalyptus trees, which are not observed in the isoprene concentration roses. Therefore, other sources of MBO, monoterpene and SQT in these regions are most likely to be the main sources, which can possibly include the urban footprint indicated in this region. In addition, pine trees are common foreign tree species that are planted on farms in this region (Rouget, 2002), which could be potential sources of MBO and monoterpenes.

The similar concentration roses determined for monoterpenes and SQT during the first sampling campaign can be attributed to similar sources of these species. However, most SQTs have short atmospheric lifetimes (< 4 min) (Atkinson and Arey, 2003a), which indicated similar sources within close proximity (~1 – 2 km radius) of Welgegund. Gouinguené and Turlings (2002) indicated the emissions of several SQT from young maize plants by testing the effects of soil humidity, air humidity, temperature, light and fertilisation rate on the emission of BVOCs from these plants. Therefore, maize production may be a source of monoterpenes and SQT. The higher SQT concentrations in the south-west and north-west can most likely be attributed to smaller eucalyptus plantations within a 1 to 2 km radius, as indicated in Figure 2. The high monoterpene concentrations determined during the second sampling campaign may be associated with specific monoterpene emitting plants in the region.

Floral emissions could also be considered a potential source of monoterpenes in this region, which could also contribute to the relatively abundance of monoterpenes compared to the relatively low isoprene concentrations. Floral emissions in this region would typically occur with the onset of the wet season in October up until February. It is well-known that meadows, i.e. grazed grasslands in South Africa/this region have a significant number of species that flower. South African grasslands are considered to be exceptionally species rich (Siebert, 2011), since it is ancient, primary grasslands, i.e. not man-made (Bond, 2016).

Of particular interest is the potential sources of 4-allylanisole (estragole) due to its relatively substantial levels as indicated in Table 2. Bouvier-Brown et al. (2009a) and Misztal, et al., (2010) indicated that this species could potentially have a significant contribution to regional atmospheric chemistry due to relatively large estragole emissions measured from ponderosa pine trees and oil palms, respectively. As mentioned previously, pine trees are typically found on farms in this region as intruder tree species (Rouget, 2002), while numerous palm trees occurs in cities/towns surrounding Welgegund (Lubbe *et al.*, 2011). In addition, *Foeniculum vulgare* (fennel) – considered a typical source of estragole – is an abundant and common weed in this study region (Lubbe *et al.*, 2010). Furthermore, estragole emissions could also potentially have a floral origin.

Although a comprehensive vegetation survey has been conducted within a 60 km radius of Welgegund, vegetation types have been identified only generally at this stage, as indicated in section 2.2. Therefore, the predominant woody species in each of the regions surrounding Welgegund associated with specific BVOC emissions have not yet been characterised.

3.5 Statistical correlations

Spearman's correlation analyses were applied to correlate the measured concentrations of isoprene, MBO, monoterpenes and SQT measured to each other in order to substantiate sources of these species. These correlations for the two sampling campaigns are presented in Table 4, with correlations in the wet seasons listed in the lower bottom (not highlighted~~ light blue~~) and correlations in the dry season presented in the top right (bold highlighted~~ light grey~~). It is evident that MBO had good correlations with monoterpenes and SQT in the wet season, as well as with monoterpenes in the dry season during the first sampling campaign. Although not as distinct as during the first sampling campaign, MBO did also correlate with monoterpenes during the wet and dry season, as well as with SQT in the dry season during the second sampling campaign. During the first sampling campaign, monoterpenes had a strong correlation with SQT in the wet season and moderate correlation during the dry season, while strong correlations between monoterpene and SQT were determined in the dry season and a moderate correlation during the wet season during the second sampling campaign. As indicated previously, concentration roses did indicate similar sources of MT and SQT, especially during the first sampling campaign, which is signified by these correlations.

Insert Table 4

Spearman correlations between BVOCs and other paramaters measured at Welgegund did not show significant correlations. However, in certain instances, good correlations were observed between soil moisture and MBO, monoterpenes and SQT concentrations. This is expected, since the monthly average concentrations of these species indicated increased levels thereof that were associated with increased soil moisture from February to April 2011. Therefore, in an effort to further statistically explore the dataset, explorative multilinear regression was performed by using all ancillary measurements as input data in order to indicate parameter interdependencies on the BVOC concentrations measured. In Figure 7, the root mean square error (RMSE) difference between the calculated and measured BVOC concentrations, as a function of the number of independent variables included in the optimum MLR solution, is presented. It is evident that interdependence between temperature, soil temperatures and PAR yielded the largest decrease in RMSE for isoprene concentrations measured. However, for MBO, monoterpenes and SQT, a much more significant contribution from soil moisture is observed to decrease the RMSE differences between calculated and measured BVOC levels. It is also evident that the interdependence between soil moisture and soil temperature at 20 cm is important to estimate MBO, monoterpene and SQT concentrations. Therefore, explorative MLR indicated that temperature had the largest influence on isoprene concentrations, while soil moisture was the most significant for MBO, monoterpenes and SQT levels.

Insert Figure 7

3.6 Reactivity of BVOCs

It is important to evaluate the significance of BVOCs on their atmospheric reactivity, since these species are important precursor species in the photochemical formation of tropospheric O_3 and SOA. This is particularly relevant for South Africa, with various recent studies indicating that O_3 is currently the most problematic pollutant in South Africa (Laakso et al., 2013; Venter et al., 2012; Beukes et al., 2013). In addition, Vakkari et al. (2015) also indicated the importance of VOCs for new particle formation and growth. Therefore, the O_3 formation potential (OFP), reaction rates with O_3 and OH reactivities of the BVOCs measured in this study were evaluated.

The OFP of BVOCs was determined by calculating the product of the average concentration and the maximum incremental reactivity (MIR) coefficient of each compound, i.e. OFP = VOC×MIR (Carter, 2009). The MIR scale has been used to assess OFP for aromatic hydrocarbons in numerous previous studies (Hoque et al., 2008; Jaars et al., 2014; Na et al., 2005). The reaction rates for reactions between O_3 and BVOCs were calculated with Eq. (3):

$$\text{reaction rates} = k_{\mathrm{X,O3}}[\mathrm{X}][\mathrm{O_3}], \quad (3)$$

where [X] is the BVOC concentration, [O_3] the ozone concentration and $k_{\mathrm{X,O3}}$ the reaction rate constant for the reaction between X and O_3. Since direct OH reactivity measurements were not available, the OH reactivities (s^{-1}) of the BVOCs were calculated, using Eq. (4):

$$\text{OH reactivity} = k_{\mathrm{X,OH}}[\mathrm{X}] \quad (4)$$

where [X] is the BVOC concentration and $k_{\mathrm{X,OH}}$ the reaction rate constant of the reaction between X and OH. In Table 5, the OFP calculated for each of the BVOCs measured in this study, as well as the reaction rate constants for the reactions of these species with O_3 and OH, are listed.

Insert Table 5

Table 5 indicates that, according to the OFP calculated with MIR coefficients, α-pinene, isoprene and p-cymene had the highest OFP in descending order during the first sampling campaign. During the second sampling campaign, α-pinene also had the highest OFP, while limonene and isoprene had the second and third highest OFPs, respectively. A comparison of the OFP calculated in this study to the OFP calculated by Jaars et al. (2014) for anthropogenic aromatic hydrocarbons measured at Welgegund (with MIR coefficients) indicates that the OFP of BVOCs is an order of magnitude smaller than the OFP of aromatic hydrocarbons at Welgegund. The combined O_3 formation potentials of all the BVOCs measured calculated with MIR coefficients during the first and second campaign were 1162 and 1022 pptv, respectively.

In Figure 8 (a), the monthly mean reaction rates for the reactions between O_3 and BVOCs measured in this study are presented. Higher reaction rates between BVOCs and O_3 contribute to increased atmospheric O_3 depletion. Significantly higher reaction rates were calculated for February 2015. It is evident from Figure 8(a) that α-pinene and limonene had the highest reaction rates with O_3, while isoprene exhibited relatively small contributions the O_3 depletion. The other BVOCs also had relatively low reaction rates for their reactions with O_3. In Figure 8(b), the relative monthly contributions of each of the BVOCs to the total OH-reactivity of

BVOCs are presented. It is evident that largest contributions to the OH-reactivity of BVOCs measured at Welgegund are from limonene, α-pinene and terpinolene for all of the months during both sampling campaigns. This is expected, since monoterpenes had the highest atmospheric concentrations compared to the other BVOCs measured in this study. It is also evident, especially during the first sampling campaign, that isoprene levels increased with the onset of spring in September.

Insert Figure 8

4 Conclusions

The annual median concentrations of isoprene, MBO, monoterpene and SQT determined during two sampling campaigns indicated that the sum of the concentrations of the monoterpenes was an order of magnitude higher than the concentrations of other BVOC species, with α-pinene being the most abundant species. Although monoterpene concentrations were similar to levels measured at other regions in the world and in a South Africa, very low isoprene concentrations at Welgegund led to a significantly lower total BVOC concentration compared to levels reported in most previous studies. In addition, total BVOC concentrations were an order of magnitude lower compared to the total aromatic VOC concentrations measured by Jaars et al. (2014) at Welgegund.

Distinct seasonal patterns were observed for MBO during both sampling campaigns, which coincided with wet and warmer months. Although less pronounced, a similar seasonal trend than for MBO was observed for isoprene during the first sampling campaign, while higher isoprene concentrations during the second sampling campaign were associated with higher wind speeds that indicated a distant source region of isoprene. No distinct seasonal pattern was observed for monoterpene and SQT concentrations. However, significantly higher levels of monoterpene and SQT, as well as MBO were measured from February to April 2011 during the first sampling campaign, which were attributed to the considerably higher soil moisture measured at a depth of 20 cm resulting for the wet season preceding the first campaign and is indicative of biogenic emissions from deep-rooted plants.

Woody species in the grassland region were considered to be the main sources of BVOCs measured, while sunflower and maize crops were also considered to be potential sources for

BVOCs in this region. Multilinear regression analysis indicated that soil moisture had the most significant impact on atmospheric levels of MBO, monoterpene and SQT concentrations, while temperature had the greatest influence on isoprene levels.

The O_3 formation potentials of the BVOCs measured were an order of magnitude smaller than that determined for anthropogenic VOCs measured at Welgegund. Isoprene and the monoterpenes: α-pinene, p-cymene, limonene and terpinolene, had the largest contribution to O_3 formation potential. α-Pinene and limonene had the highest reaction rates with O_3, while isoprene exhibited relatively small contributions to the O_3 depletion. Limonene, α-pinene and terpinolene had the largest contributions to the OH-reactivity of BVOCs.

It is important in future work that a comprehensive study on BVOC emissions from specific plant species in the area surrounding Welgegund must be performed in order to relate the emission capacities of vegetation types to the atmospheric BVOCs measured. It is also recommended that the oxidation products of BVOC species are measured in order to verify distant source regions of BVOCs measured at Welgegund. In addition, the interactions between anthropogenic and biogenic VOCs must also be further explored, together with other ancillary measurements conducted at Welgegund (e.g. SO_2, NO_2 and O_3). Future work must also include investigating the reactions of the measured VOCs with atmospheric oxidants (e.g. $^{\bullet}OH$ and O_3) with atmospheric chemistry models in order to establish, for instance, whether O_3 formation within the region is VOC- or NO_2-limited.

~~14, 7, 120 and 8 pptv, respectively, and 14, 4, 83 and 4 pptv, respectively, during the second campaign. The concentrations of BVOCs measured during the second campaign were generally lower compared to levels during the first campaign, which can be attributed to significantly higher rainfall during the wet season preceding the first campaign. The sum of the concentration of the monoterpenes was an order of magnitude higher than the concentrations of other BVOC species during both sampling campaigns, with α-pinene being the most abundant species. Very low isoprene concentrations at Welgegund led to a significantly lower total BVOC concentration compared to levels measured at other regions in the world and during the SAFARI 2000 campaign in a South African national park. However, monoterpene concentrations were similar to levels reported in most previous studies. In addition, total BVOC concentrations were an order of magnitude lower compared to the total aromatic VOC concentrations measured by Jaars et al. (2014) at Welgegund.~~

~~The monthly median MBO levels measured during both campaigns, as well as, although less pronounced, the monthly median isoprene concentrations measured during the first campaign, indicated a distinct seasonal pattern with higher MBO and isoprene concentrations coinciding with the wet and warmer months. During the second campaign, higher isoprene concentrations were associated with higher wind speeds, which were attributed to a larger distant source region. No distinct seasonal pattern was observed for monoterpene and SQT concentrations, with the exception of significantly higher levels measured from February to April 2011 during the first campaign. In addition, MBO concentrations measured during these months were also significantly higher. These increased MBO, monoterpene and SQT concentrations were attributed to the significantly higher soil moisture measured at a depth of 20 cm resulting from the wet season preceding the first campaign, which is indicative of biogenic emissions from deep-rooted plants.~~

~~Concentration roses indicated that isoprene concentrations were higher from the western direction, while wind direction did not indicate any significant differences in the concentrations of other BVOC species. Woody species in the grassland region were considered to be the main sources of BVOCs measured, while sunflower and maize crops were also considered to be potential sources for BVOCs in this region.~~

~~Multilinear regression analysis utilising all the ancillary measurements at Welgegund indicated that soil moisture had the most significant impact on atmospheric levels of MBO, monoterpenes and SQT concentrations, while temperature had the greatest influence on isoprene levels.~~

~~The combined O_3 formation potentials of all the BVOCs measured calculated with MIR coefficients during the first and second campaign were 1162 and 1022 pptv, respectively, with isoprene and the monoterpenes: α-pinene, isoprene, p-cymene, limonene and terpinolene, having the largest contribution to O_3 formation potential. α-Pinene and limonene had the highest reaction rates with O_3, while isoprene exhibited relatively small contributions to the O_3 depletion. Limonene, α-pinene and terpinolene had the largest contributions to the OH-reactivity of BVOCs measured at Welgegund for all of the months during both sampling campaigns.~~

~~A comprehensive study on BVOC emissions from important plant species must be performed future studies in order to relate the emission capacities of vegetation types in the area surrounding Welgegund to the measured atmospheric BVOCs. It is also recommended that~~

~~oxidation products of BVOC species are measured in future in order to verify distant source regions.~~

Acknowledgements

The authors would like to acknowledge the Finnish Academy (project #132640), the University of Helsinki, the Finnish Meteorological Institute, the North-West University and the National Research Foundation (NRF) for financial support. Opinions expressed and conclusions arrived at are those of the authors and are not necessarily to be attributed to the NRF. Assistance with data processing from Ms Rosa Gierens is also acknowledged.

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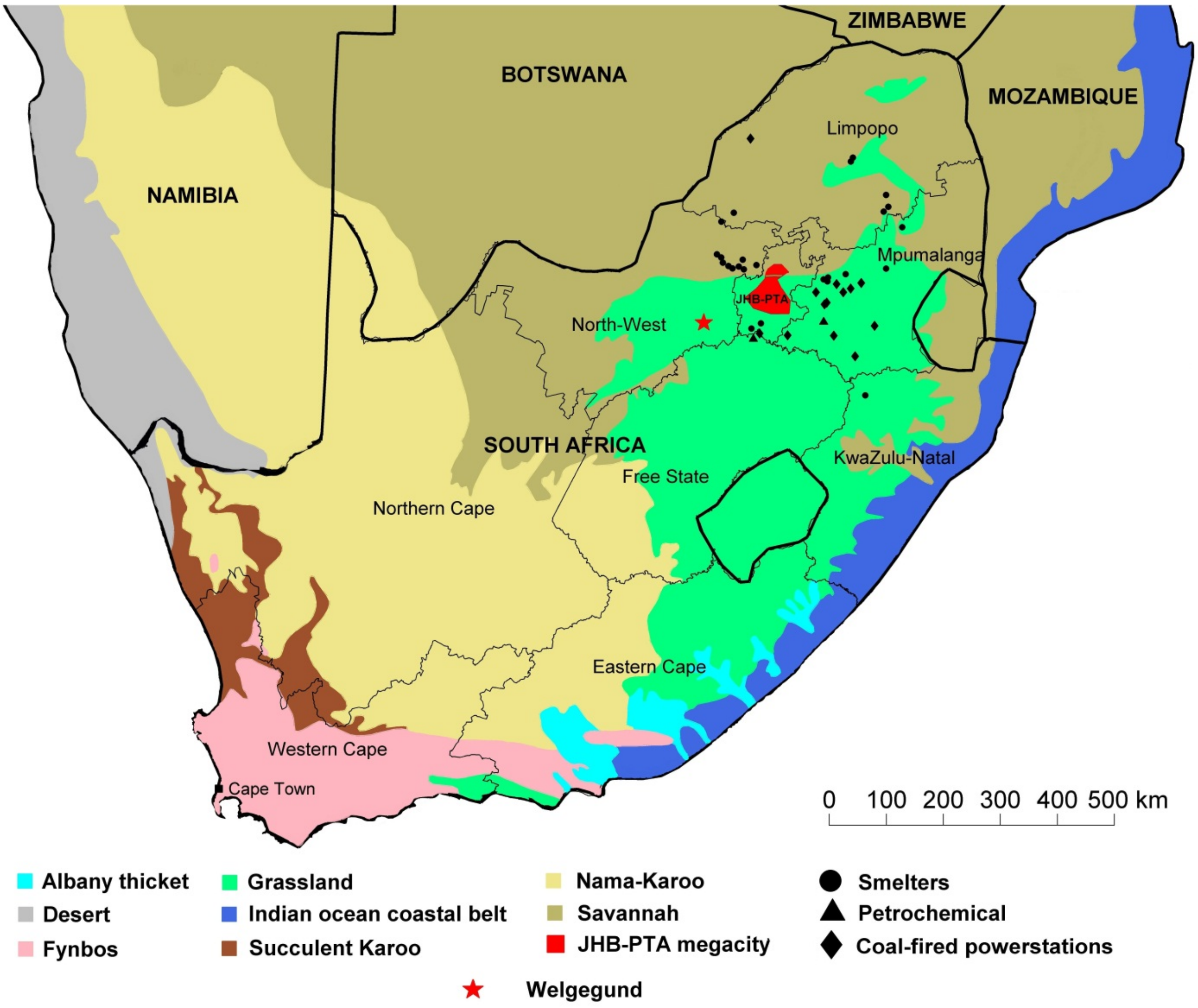


Figure 1. Map of southern African indicating the location of the Welgegund measurement station within the context of bioregion and large point sources in the industrial hub of South Africa (Mucina and Rutherford, 2006).

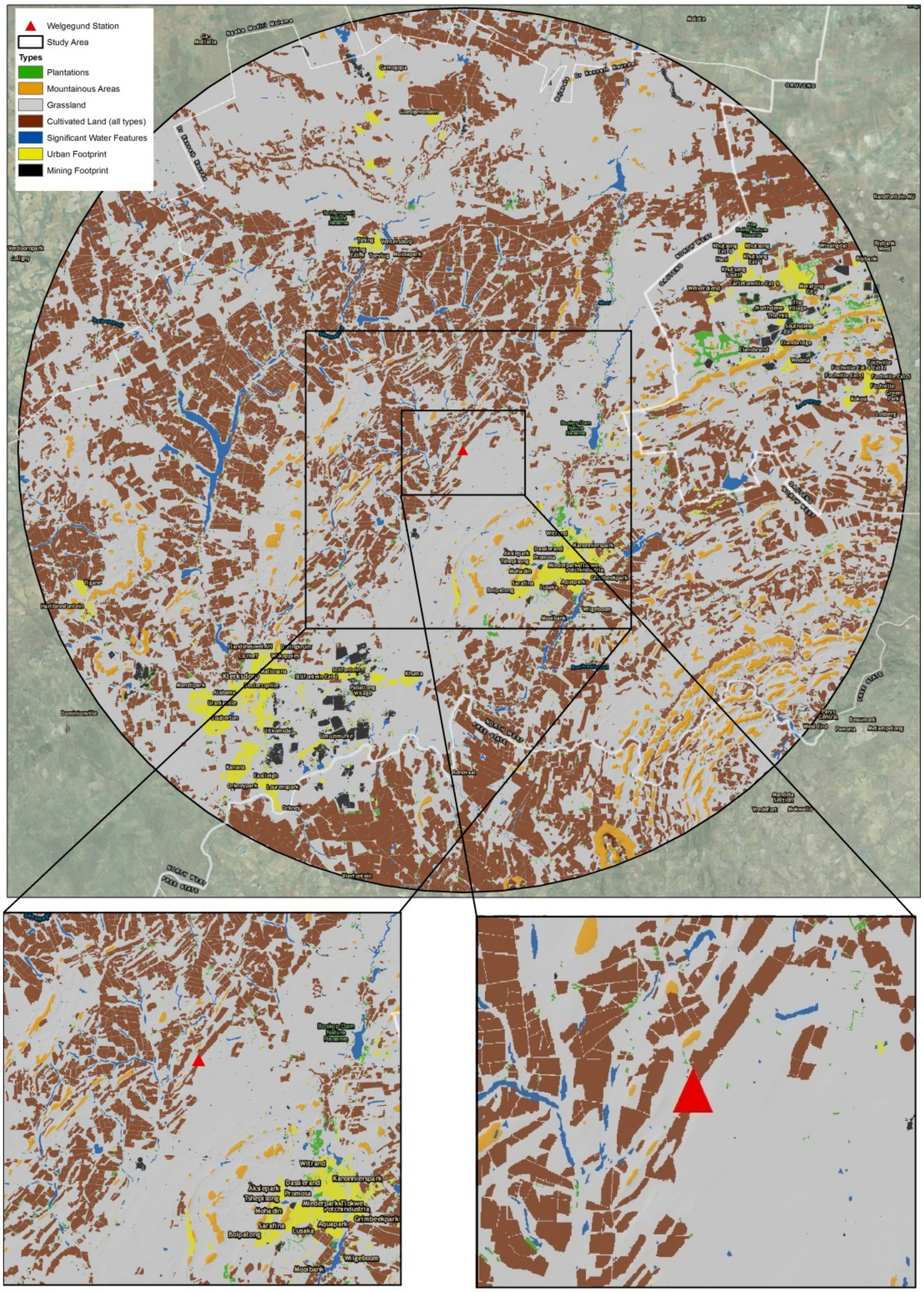


Figure 2. General vegetation map for 60 km radius of Welgegund measurement station.

Table 1. Lifetime (τ) of BVOCs calculated for the average concentration of OH radicals (ca. 0.04 pptv) as reported by Ciccioli et al. (2014) and the annual average O_3 (ca. 36 ppbv) concentration measured for the two campaigns at Welgegund.

		τ_{OH}	τ_{O3}
	Isoprene	2.8 hr	1 day
	MBO	10.3 hr	7.5 day
Monoterpenes	α-Pinene	5.3 hr	3.6 hr
	Camphene	5.3 hr	14.5 day
	β-Pinene	3.6 hr	20.9 hr
	Δ^3-Carene	3.2 hr	8.5 hr
	p-Cymene	18.8 hr	261.6 day
	1,8-Cineol	12.5 hr	-
	Limonene	1.7 hr	1.6 hr
	Terpinolene	12.6 hr	2.3 hr
	AMCH	2.9 hr	-
	Nopinene	1.4 day	-
	Bornylacetate	1.5 day	-
	4-Allylanisole	5.2 hr	1.1 day
Sesquiterpenes	Longicyclene	1.3 day	-
	iso-Longifolene	2.9 hr	1.1 day
	Aromadendrene	4.5 hr	1.1 day
	α-Humulene	1 hr	21.6 min

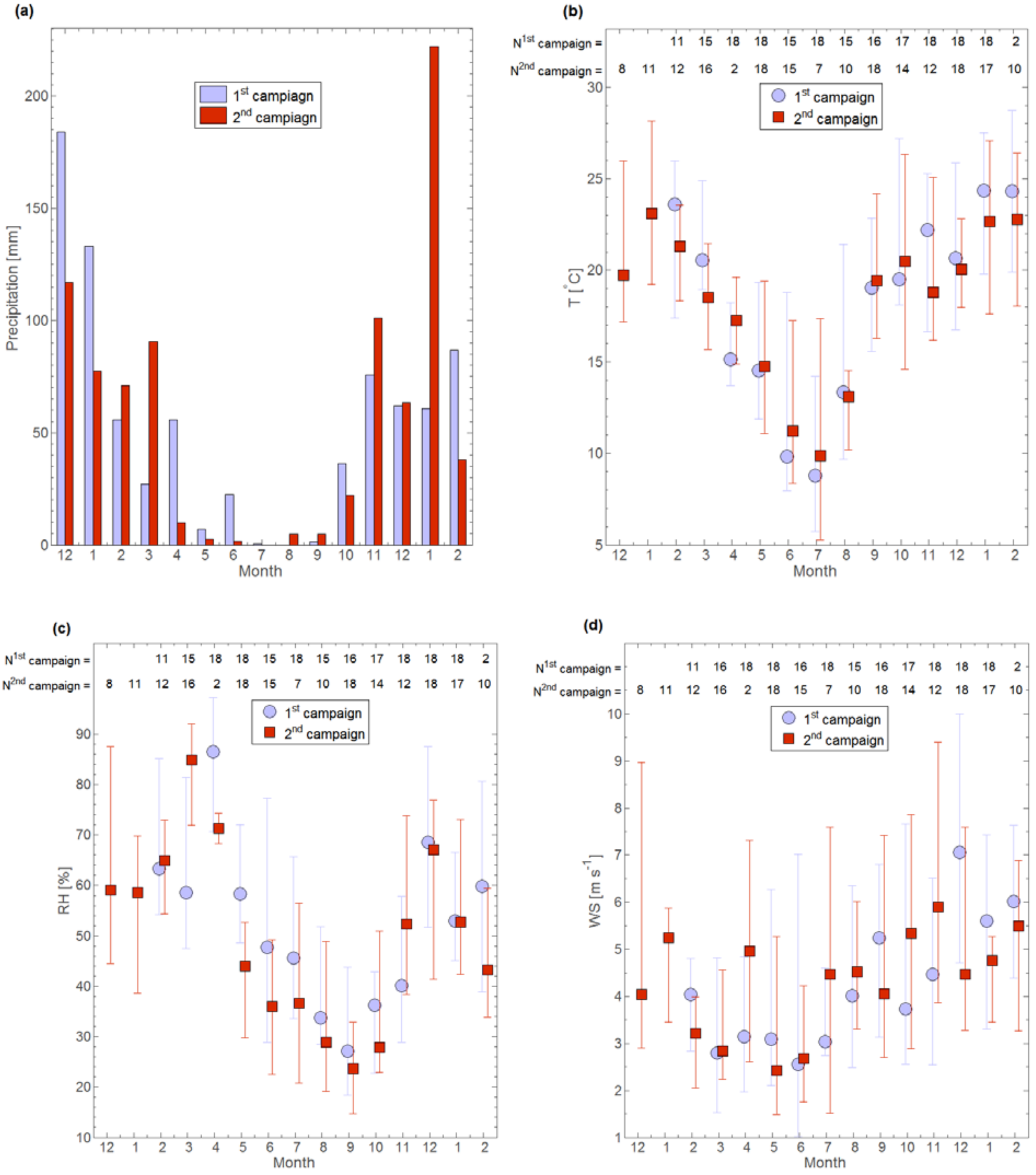


Figure 3. Monthly variation of **(a)** accumulated precipitation, **(b)** temperature, **(c)** relative humidity, **(d)** wind speed, **(e)** wind direction, and **(f)** and **(g)** soil moisture at 5 and 20 cm depth, respectively. Error bars indicate upper and lower quartiles.

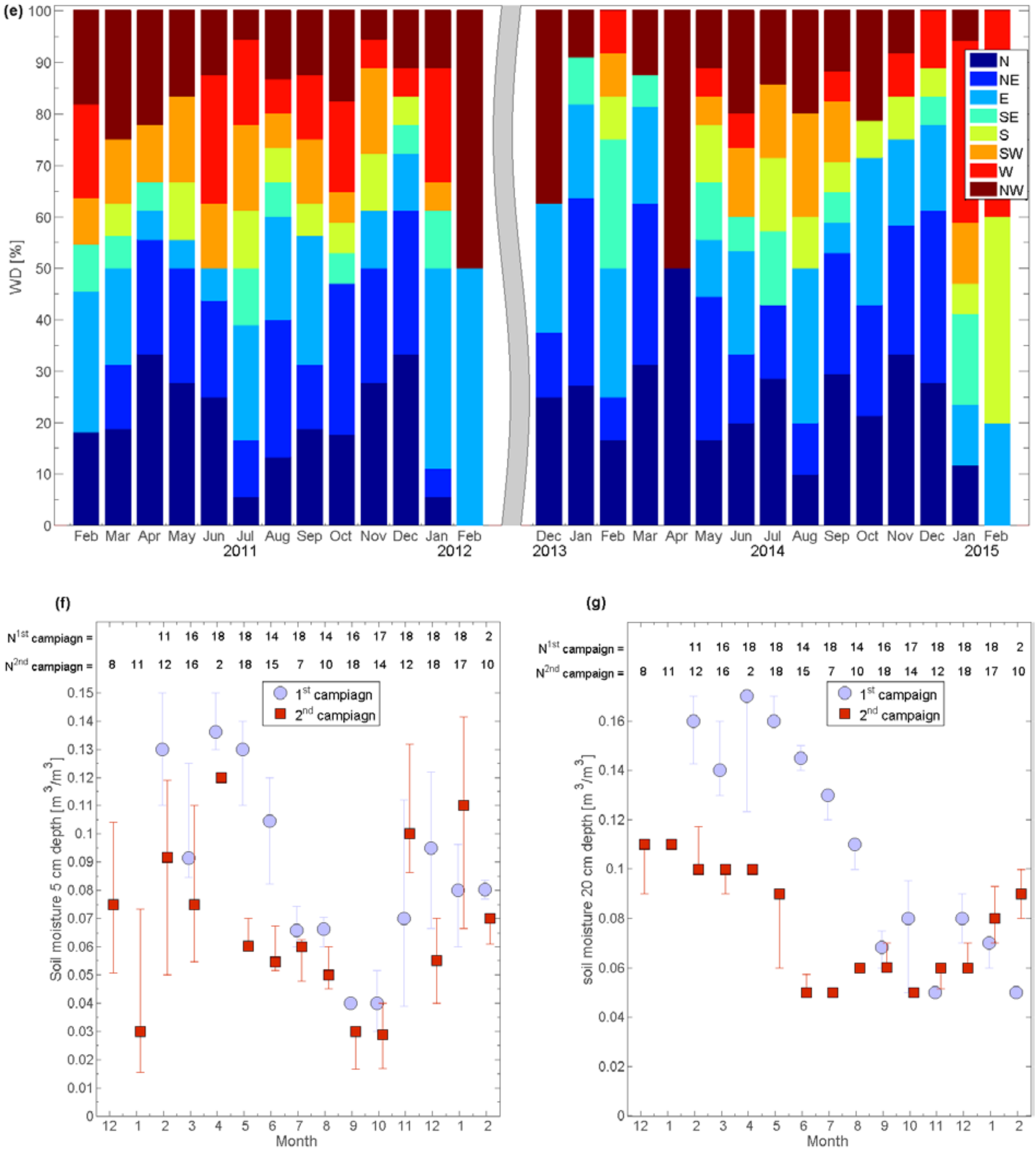


Figure 3. Continued.

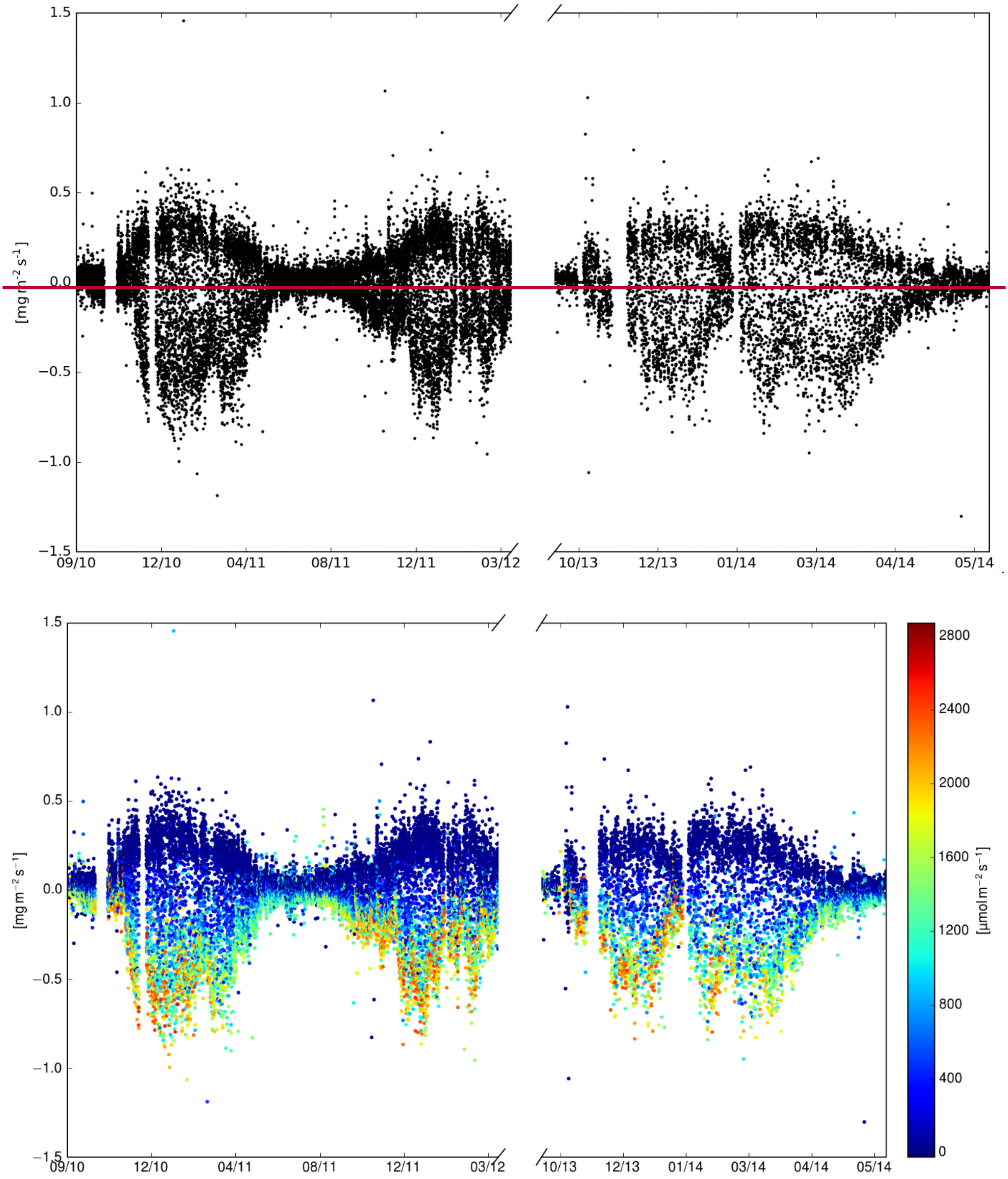


Figure 4. Micrometeorological CO$_2$ flux measurements at Welgegund (Räsänen et al., 2016). The colour bar indicates the Photosynthetic Photon Flux Density (PPFD).

Table 2. The ambient BVOC concentration for the two campaigns measured at Welgegund.

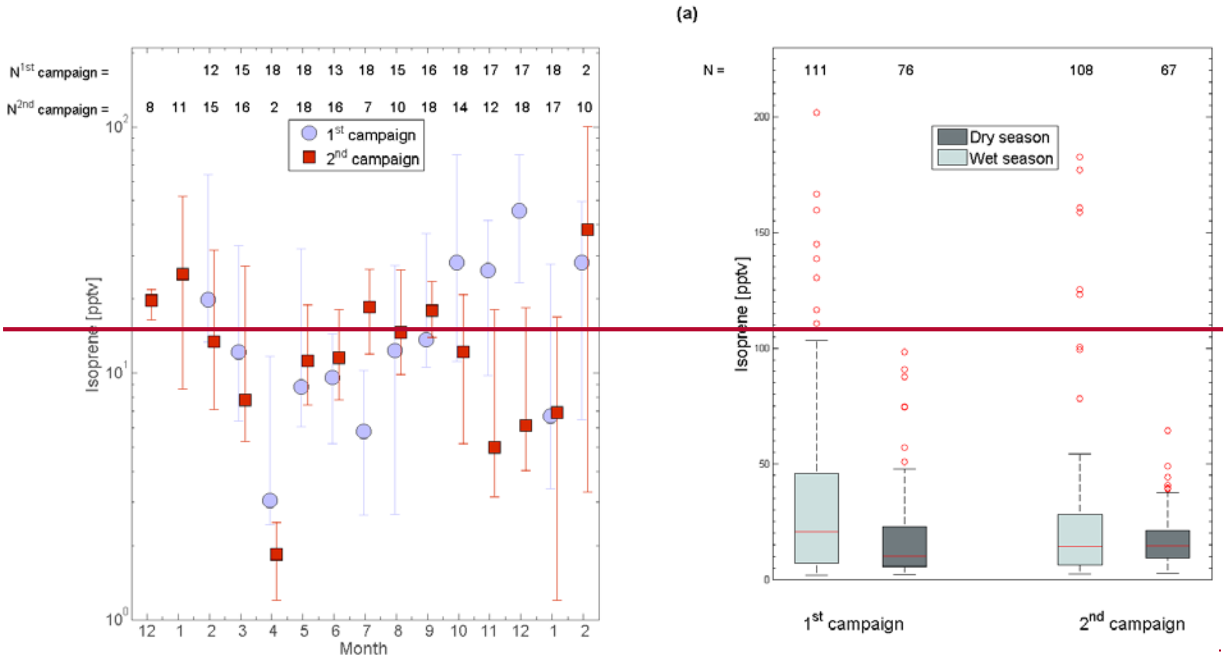
	First campaign				Second campaign			
	Median (Mean)	IQR (25th - 75th)	Median (Mean) day/night ratio	N	Median (Mean)	IQR (25th - 75th)	Median (Mean) day/night ratio	N
Isoprene	14 (28)	6-35	2.01 (1.7)	187	14 (23)	7-24	0.99 (1.31)	175
MBO	7 (12)	3-16	0.94 (0.91)	178	4 (8)	3-10	1.13 (1.20)	163
Monoterpenes								
α-Pinene	37 (71)	28-83	1.14 (0.93)	197	15 (57)	9-23	1.23 (1.09)	191
Camphene	4 (8)	2-9	1.26 (1.08)	178	2 (4)	1-3	1.20 (0.88)	113
β-Pinene	9 (19)	5-18	1.11 (0.98)	195	3 (5)	2-6	1.31 (1.23)	171
Δ^3-Carene	3 (6)	2-5	1.52 (1.13)	156	2 (4)	1-4	1.13 (0.71)	58
1,8-Cineol	3 (13)	1-7	1.04 (0.92)	162	1 (2)	1-2	0.94 (0.77)	75
Limonene	21 (30)	9-40	1.24 (1.04)	197	16 (54)	8-36	1.23 (0.96)	187
Terpinolene	4 (14)	3-11	1.35 (1.02)	141	22 (28)	16-34	1.57 (1.60)	25
Nopinene	6 (7)	4-9	1.13 (1.09)	167	8 (11)	6-13	1.31 (1.26)	176
Bornylacetate	1 (2)	1-2	1.19 (1.08)	49	2 (3)	1-3	1.40 (1.82)	101
Monoterpene-related BVOCs								
p-Cymene	20 (48)	12-33	1.08 (0.96)	197	7 (15)	4-13	1.20 (0.97)	186
4-Allylanisole	8 (11)	5-13	1.26 (0.96)	118	1 (12)	1-3	1.32 (0.59)	70
AMCH	5 (7)	1-12	0.28 (0.64)	41	3 (4)	2-5	1.33 (1.29)	24
Σ monoterpenes and monoterpene-related BVOCs	120 (235)	73-242			83 (198)	54-145		
Sesquiterpenes								
Longicyclene	2 (4)	1-4	1.32 (1.19)	152	1 (2)	1-3	0.95 (0.65)	34
iso-Longifolene	2 (3)	1-4	1.06 (0.89)	52	1 (1)	1	1.19 (1.39)	7
Aromadendrene	1 (1)	1		2	2 (2)	1-3	1.65 (1.91)	73
α-Humulene	1 (1)	1		3	1 (3)	1-5	0.86 (3.53)	4
Alloaromadendrene	2 (3)	1-4	0.96 (0.84)	31				
Σ Sesquiterpenes	8 (12)	5-14			4 (8)	3-11		

Table 3. Ambient BVOC concentrations (pptv) as reported by Noe et al. (2012) for various ecosystems and then modified. avg = mean value, med = median value, max = maximal value of the measurements reported.

Location	Isoprene	MBO	Monoterpenes	Date	References
Grassland					
Welgegund, SA	28 (avg), 202(max)	12 (avg), 61(max)	235(avg), 1744(max)	Feb 2011-Feb 2012	this study
	23(avg), 182(max)	7 (avg), 47(max)	198(avg), 3081(max)	Dec 2013-Feb 2015	this study
Savannah					
KNP, SA	390(avg),860(max)			Feb 2001	Harley et al. (2003)
Benin	>3000(max)		>5000(max)	7-13 Jun 2006	Saxton et al. (2007)
Village, Senegal	300(avg)			Sept. 2006	Grant et al. (2008)
Boreal					
Hyytiälä, Finland			900(avg), 1800(max)	2000-2007	Hakola et al. (2009)
	40–110		100–700	Apr 2005	Eerdekens et al. (2009)
	220(med),360(max)		300(med), 600(max)	Summer 2006/2007	Lappalainen et al. (2009)
	70(med), 110(max)		200(med), 300(max)	Winter 2006/2007	
	110(avg), 430(max)		100(avg), 2700(max)	Jul 2004	Rinne et al. (2005)
			40–450	37 m, Aug 1998	Rinne et al. (2000)
			140–500	19.5 m, Aug 1998	
			450–630	2 m, Aug 1998	
Huhus, Finland			900(avg), 2160(max)	Jun.–Sep 2003	Räisänen et al., (2009)
Pötsönvaara, Finland	320–1690		1700–3200	Apr.–Oct 1997, 1998	Hakola et al. (2000)
Hemiboreal					
Järvselja, Estonia	360–2520		1800–7200	Spring and Summer 2010	Noe et al. (2012)
	120–200 (med)		400–1400 (med)	Oct 2009–Sep 2010	Noe et al. (2012)
Temperate					
Michigan, USA	2520(avg), 8160(max)		310(avg), 1100(max)	Summer 2008	Mielke et al. (2010)
Jülich, Germany	1980(avg), 10790(max)		250(avg), 1470(max)	Jul 2003	Spirig et al. (2005)
Duke Forest, USA	1500–2200		310–790	Jul 2003	Stroud et al. (2005)
Oak Ridge, USA	5000–15000		500–1600	Jul 1999	Fuentes et al. (2007)
MEF, USA	70(avg)	1346(avg)	0.497(avg)	22-28 Aug. 2008	Nakashima et al. (2014)
Mediterranean					
Castelpoziano, Italy	141–250		100–200	May–Jun 2007	Davison et al. (2009)
AM, Greece	1500(avg), 7900(max)		900(avg), 5000(max)	Jul–Aug 1997	Harrison et al. (2001)

Tropical				
FNT, Brazil	2000(avg), 4000(max)	50(avg), 130(max)	Jul 2000	Rinne et al. (2002)
NNNP, NC	1820±870		16–24 Ma. 1996	Serca et al. (2001)
	730±480		21 Nov–11 Dec 1996	

SA = South Africa
WA = West Africa
KNP = Kruger National Park
MEF = Manitou Experimental Forest
AM = Agrafa Mountains
FNT = Floresta Nacional do Tapajos
NNNP = Nouabale-Ndoki National Park
NC = Northern Congo



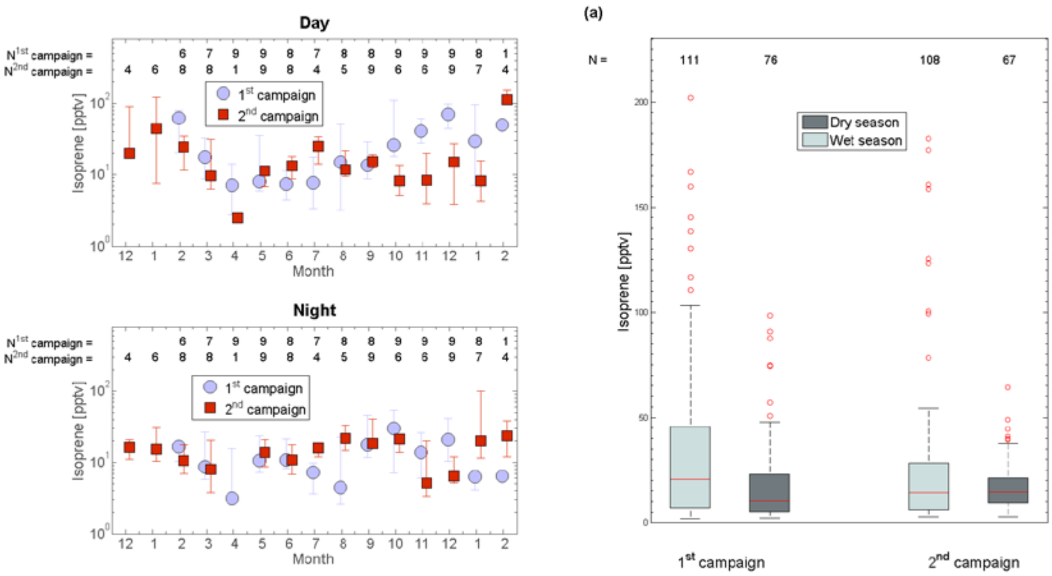


Figure 5. The panels on the left show monthly median concentrations of (a) isoprene, (b) MBO, (c) monoterpenes and (d) SQT measured for the two campaigns. Error bars indicate upper and lower quartiles. The values displayed near the top of the graphs indicate the number of samples (N^{1st} and N^{2nd} campaign) analysed for each month. The panels on the right show the wet and dry season concentrations of the respective compounds measured for the two campaigns. The red line of each box indicates the median (50th percentile), the black dot the mean, the top and bottom edges of the box the 25th and 75th percentiles, the whiskers ±2.7σ or 99.3 % coverage if the data have a normal distribution and the red circles outliers of the range of the box and

whisker plot. The values displayed near the top of the graphs indicate the number of samples (N) analysed for the wet and dry season.

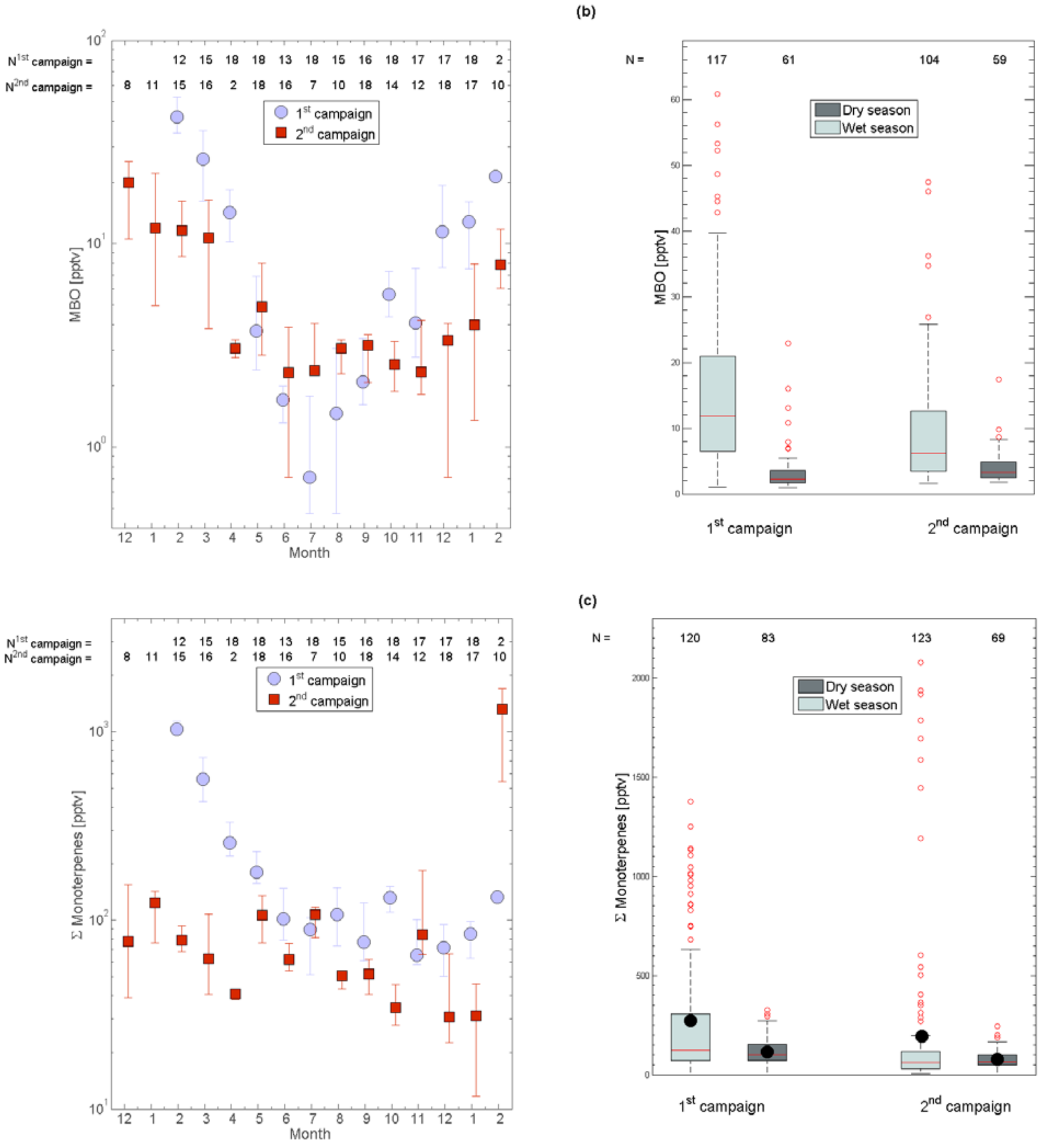
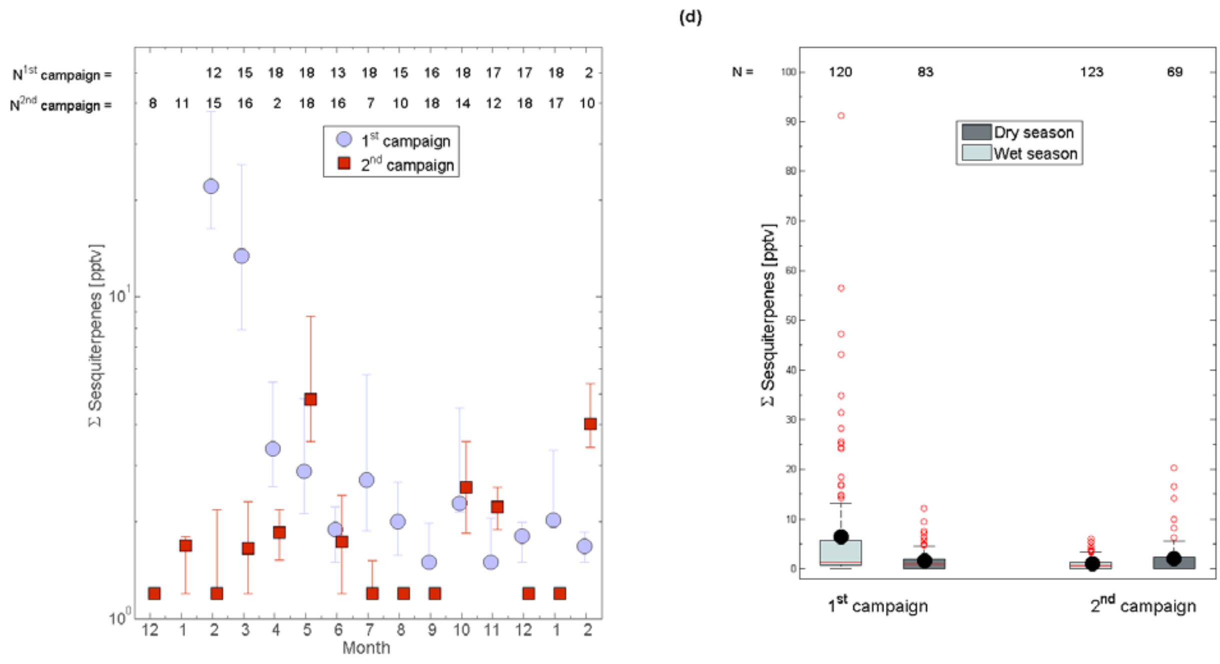


Figure 5. Continued.



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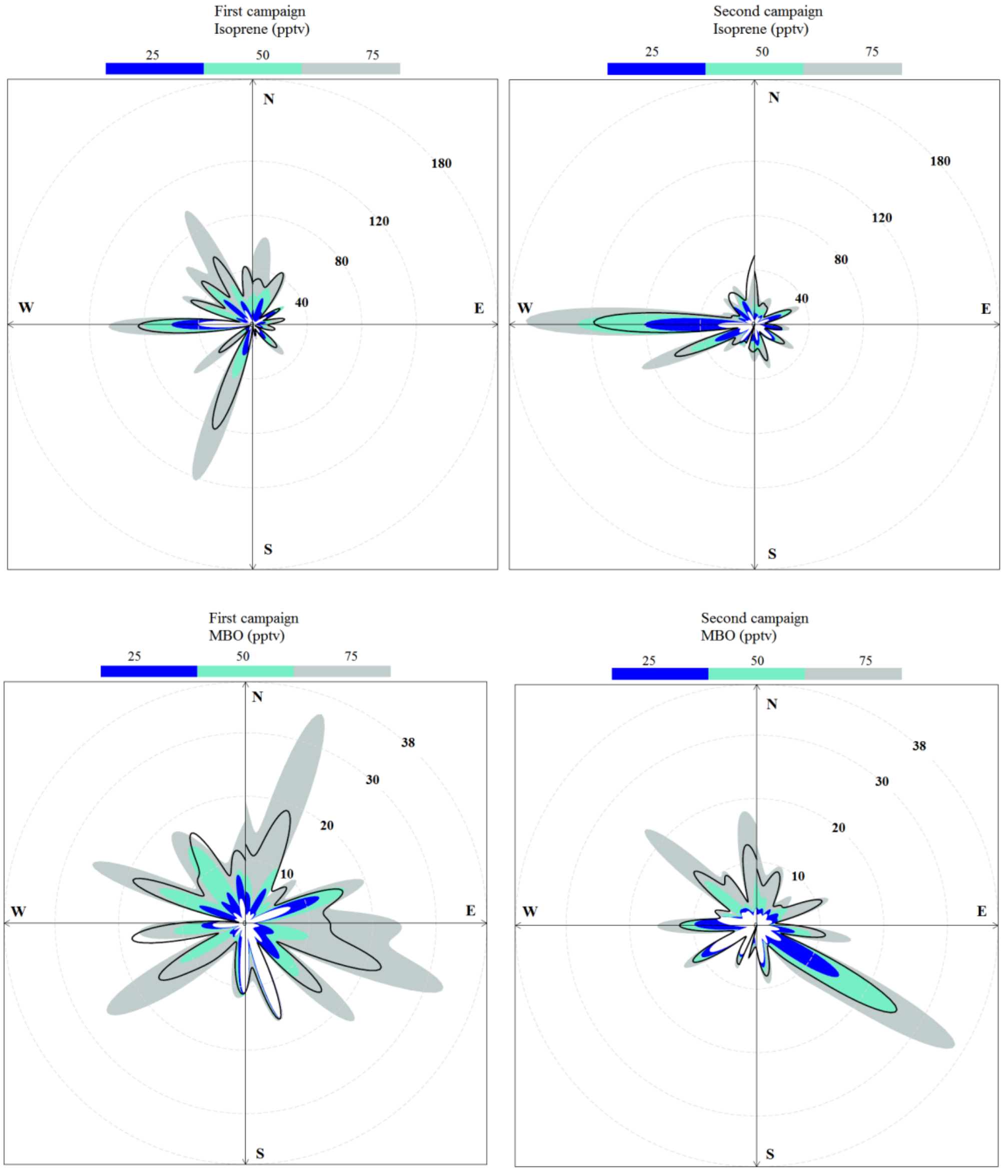


Figure 6. BVOC concentration rose at Welgegund for the two sampling campaigns. Different colours represent percentiles: blue 25 %, aquamarine 50 %, azure75 % and the black solid line the average.

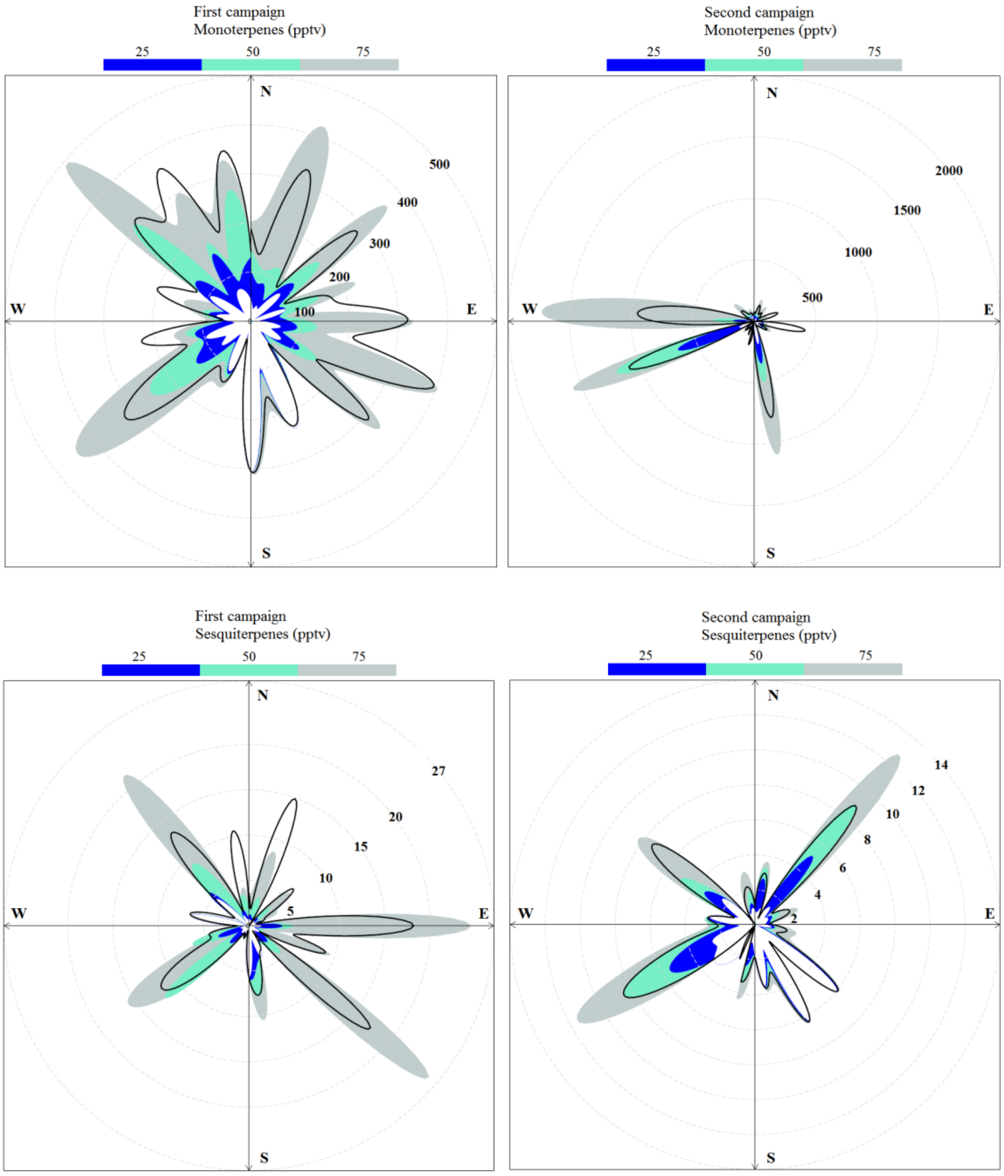


Figure 6. Continued.

Table 4. Spearman's correlation coefficients between the BVOCs during the wet and dry season of the first campaign (a) and second campaign (b).

(a)

		Dry season			
		Isoprene	MBO	MT	SQT
Wet season	Isoprene	-	**0.52**	**0.03**	**-0.10**
	MBO	0.09	-	**0.57**	**-0.10**
	MT	-0.20	0.68	-	**0.27**
	SQT	-0.04	0.56	0.80	-

(b)

		Dry season			
		Isoprene	MBO	MT	SQT
Wet season	Isoprene	-	**0.39**	**-0.11**	**0.09**
	MBO	0.50	-	**0.39**	**0.48**
	MT	0.27	0.38	-	**0.60**
	SQT	0.20	0.01	0.26	-

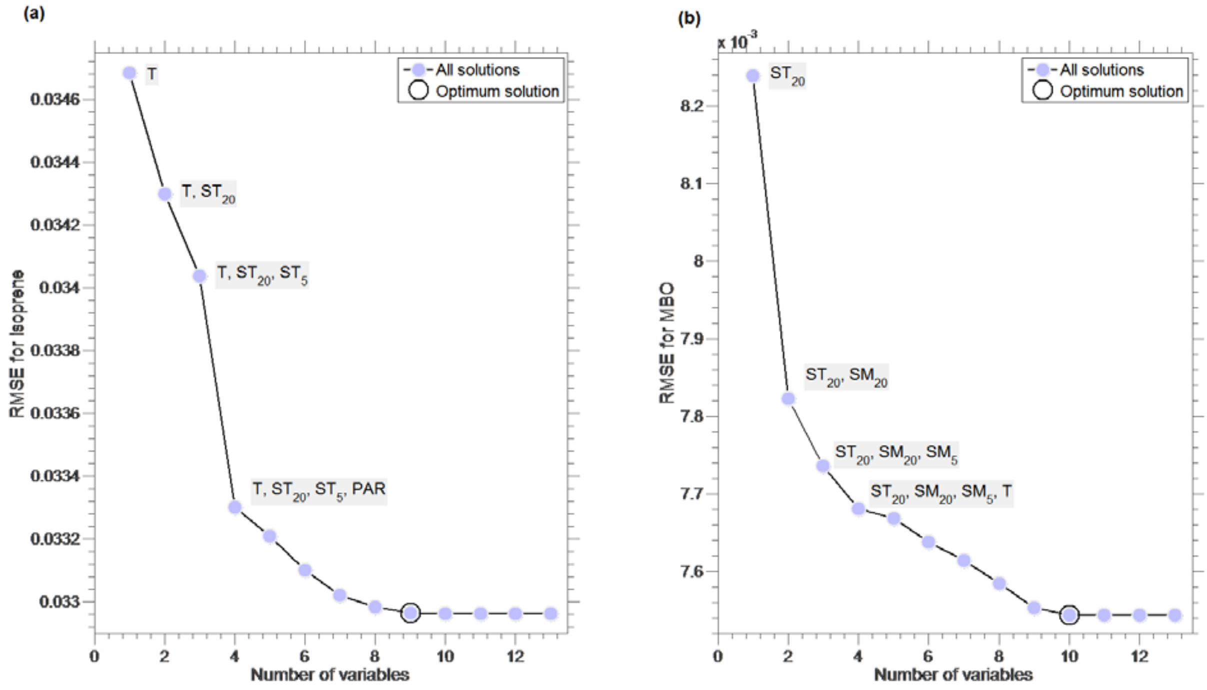


Figure 7. The optimum combination of independent variables to include in a MLR equation to calculate the dependant variable, i.e. BVOC concentrations. The root mean square error (RMSE) difference between the calculated and measured concentrations indicated that the inclusion of (a) 9 parameters for isoprene, (b) 10 parameters for MBO, (c) 7 parameters for MT, and (d) 12 parameters for SQT in the MLR solution was the optimum.

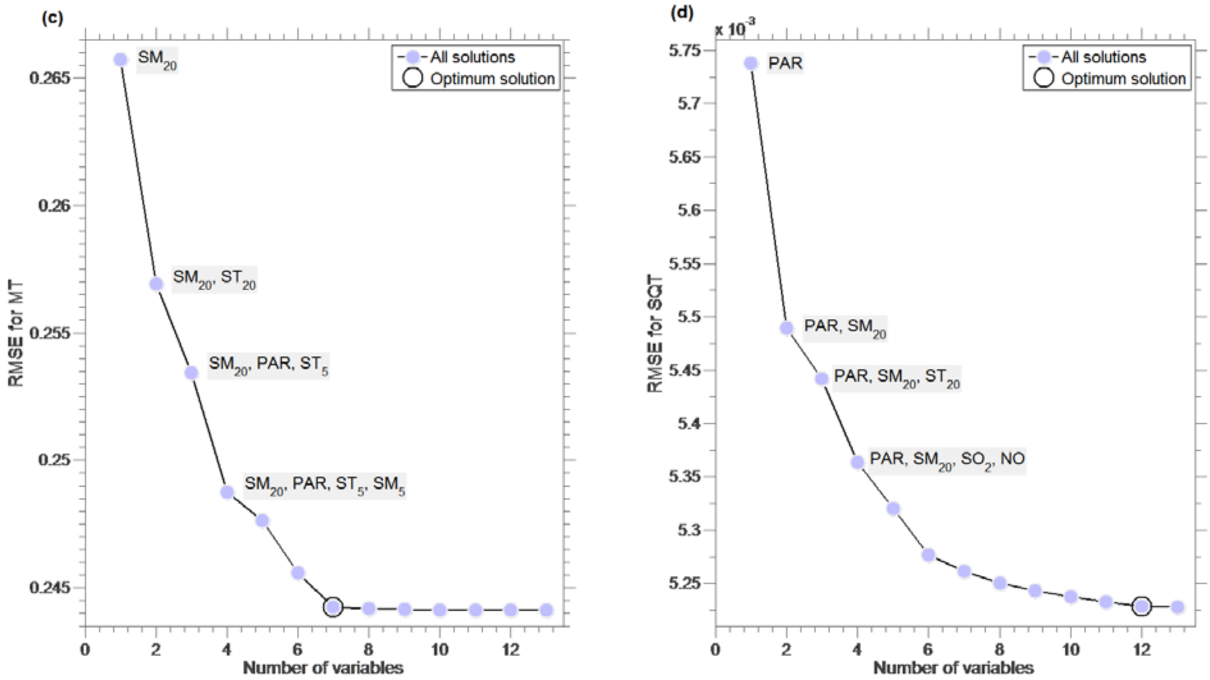


Figure 7. Continued.

Table 5. Photochemical properties of measured BVOCs during the first and second campaign at Welgegund.

			First period		Second period		[cm^3 molecule^{-1} s^{-1}]	
		MIR[a]	Avg	OFP	Avg	OFP	$k_{OH} \times 10^{12}$	$k_{O3} \times 10^{18}$
	Isoprene	10.28	28	289	23	234	101.0	13.0
	MBO	4.73	12	56	7.7	37	27.5	1.8
	α-Pinene	4.38	71	313	57	251	53.7	86.6
	Camphene		7.9		3.8		53.0	0.9
	β-Pinene	3.38	19	64	4.6	16	78.9	15.0
	Δ^3-Carene	3.13	6.1	19	4.1	13	88.0	37.0
	p-Cymene	4.32	48	206	15	66	15.0	0.05
	1,8-Cineol		13		1.9		22.6	
Monoterpenes	Limonene	4.4	30	131	54	236	171.0	200.0
	Terpinolene	6.16	14	84	28	170	22.5	138.0
	AMCH		6.7		4.2		98.6	430.0
	Nopinene		7.3		11		8.6	
	Bornylacetate		1.7		3.1		7.7	
	4-Allylanisole		11		12		54.3	12.0
	Longicyclene		4.2		1.7		9.4	
	iso-Longifolene		3.0		0.9		96.2	11.4
Sesquiterpenes	Aromadendrene		1.0		2.4		62.5	12.0
	α-Humulene		0.9		2.7		290.0	870.0
	Alloaromadendrene		3.2					

[a] MIR denotes maximum incremental reactivity (g O_3/g VOCs) (Carter, 2009).

The rate constants are from Atkinson (2000) and Atkinson and Arey (2003b) except those for α-humulene and longifolene OH reaction rates, which are from Shu and Atkinson (1995). Other sesquiterpene data is from CSID:1406720, http://www.chemspider.com/Chemical-Structure.1406720.html (last access: 2 May 2016). Predicted data is generated using the US Environmental Protection Agency's EPI Suite.

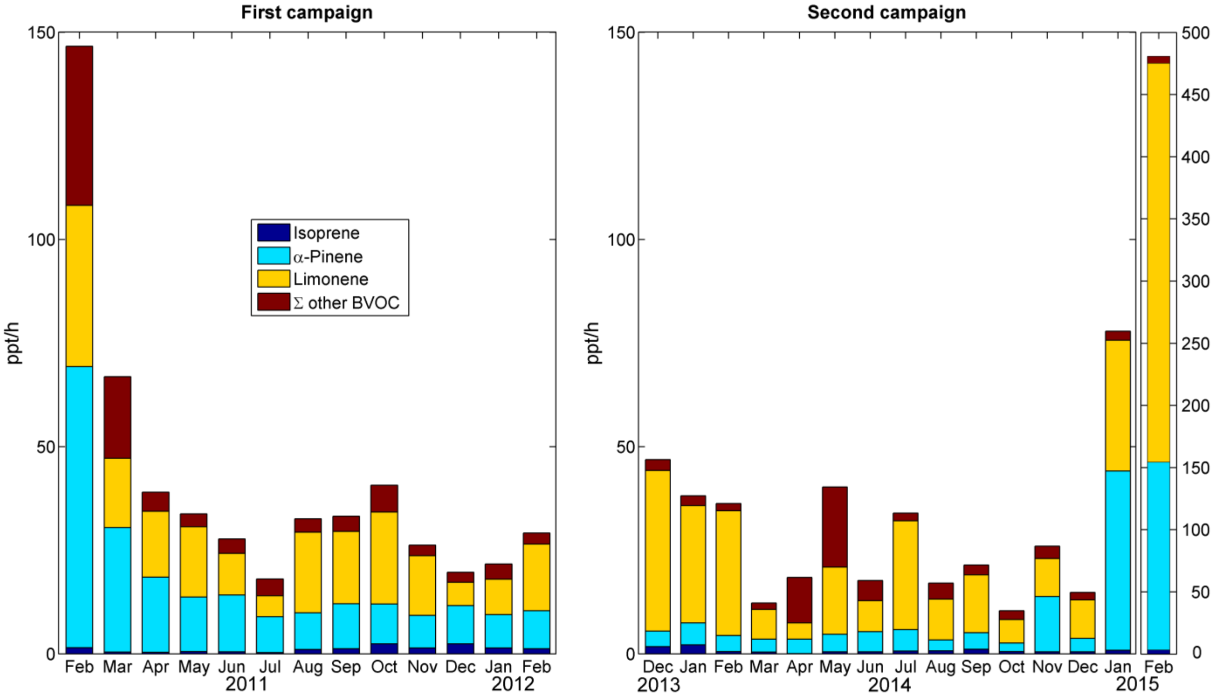


Figure 8a. Monthly means of reaction rates calculated for reactions between O_3 and BVOCs at Welgegund. A secondary axis is introduced for reaction rates calculated for February 2015 due to much higher reaction rates caluclated for this month.

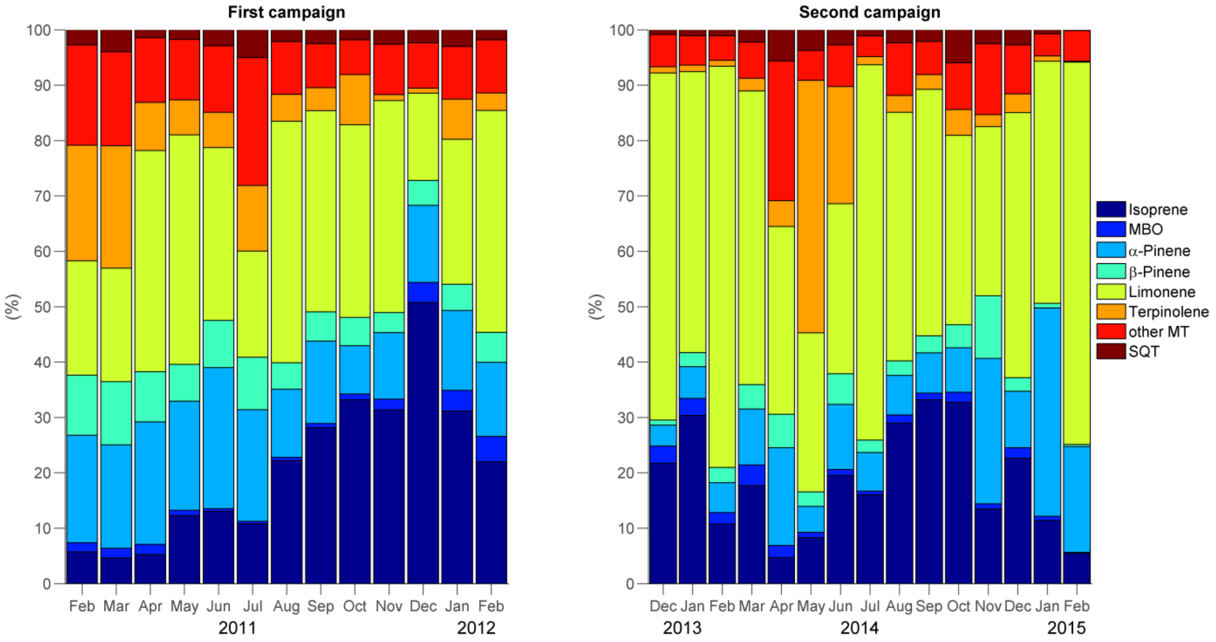
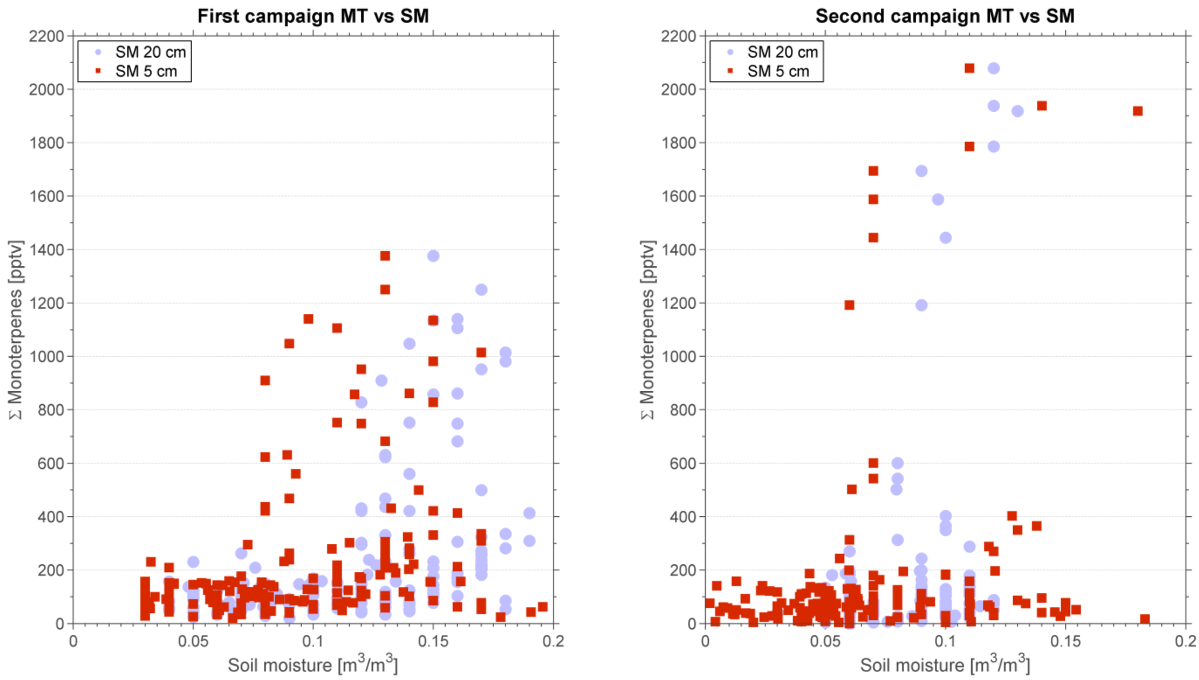


Figure 8b. The relative monthly contribution of different BVOCs to the OH-reactivity at Welgegund.

Supplement

(a)



(b)

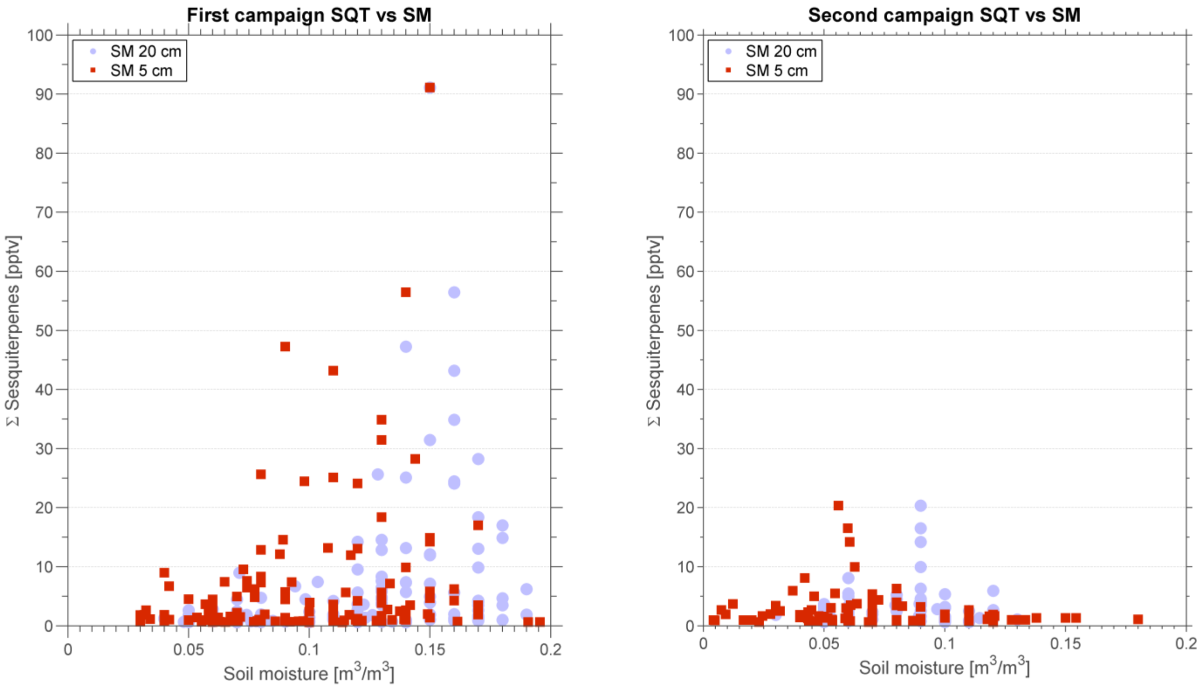


Figure S1. Correlation between soil moisture and monoterpene concentrations (a), and soil moisture and SQT (b)