

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-grassland-agriculture 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 authors 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 (O₃) 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 ($\sim 1000 \text{ Tg year}^{-1}$) (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 $\geq 30 \text{ ppb}$ to $< 2 \text{ ppb}$ (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 $350 \text{ }^\circ\text{C}$ 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 during 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 exhibit 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 during 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 exhibit 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 ratios, it also does not seem that the observed correlations are driven by daytime and night-time emissions.