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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Volatile organic compound emissions from *Larrea tridentata* (creosotebush)" *by* K. Jardine et al.

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We would like to express high gratitude to reviewer 1 for taking considerable time to provide us with helpful comments that will make our manuscript better! Our point by point responses to the comments are below.

Comment 1

The paper by Jardine et al. reports interesting measurements of VOC emissions from desert vegetation. However, the paper lacks in clarity of its results. There is a long list of Figures presenting time series of the emissions and concentrations of different compounds (eight figures, each with six to ten panels). I feel this is too much especially as the time series look quite similar and they are not discussed so much. I would suggest

to the authors to try to condense this information better. A lot of the information in the figures is already in Table 1. I would suggest including some measure of the variability to this table and moving most of the time series to supplementary material. Also I suggest the authors try to be more clear on what they think are the main messages of the paper.

Response 1

We feel that the main point of our paper is well described in our manuscript. Although desert ecosystems are generally considered unimportant sources of biogenic VOC emissions, we found that during the summer monsoon season in southern Arizona, they can be strong sources of atmospheric VOCs. Given the enormous complexity of creosotebush VOC emissions observed, in this paper we attempt to provide a broad overview of branch emission rates and ambient concentrations of the different structural classes, many of which have not been previously described from other ecosystems. If our manuscript is accepted for publication, we will attempt to present a more clear description of these results and mainly restrict our discussion to atmospheric processes.

We agree that the complete list of time series figures presented at the end of the manuscript is unnecessary given that most of the compounds display a similar diurnal emission/concentration pattern (but with different emission magnitudes). We will reduce this set to only the first three time series plots with embedded GC-PTR-MS chromatograms and move the remaining time series plots to supplementary material. In addition, Table 1 will now include a measure of variability of noontime branch VOC emission rates (standard deviation of seven branches).

Comment 2

The methods of VOC measurements and calibrations should be presented in more detail. It is especially important for the reader to understand the methodology used as the authors give recommendations on calibration in the beginning of chapter 3.1. Also more information on chamber measurements should be given (including how many

replicates were measured). I my opinion just referring to supplementary information is not enough. The paper should be understandable alone.

Response 2

We agree and will include more information on VOC measurements and calibration so that the main paper can be understandable alone. We will also include more detail regarding the chamber measurements and the number of branch replicates.

Comment 3

Page 17115, line 20: Reference to Karl et al. (2004) on VOC emissions from tropical rainforests and to Rinne et al., (2005) on boreal forests. Here one could refer rather to reviews on tropics by Kesselmeier at al. (2009) and boreal region by Rinne et al. (2009).

Response 3

These excellent review papers are now referenced at the mentioned locations.

Comment 4

Pages 17116-17117, lines 27-1: How are the emissions adjusted to 30 oC. As there is no commonly accepted formula for e.g. methanol and acetaldehyde it unclear how comparable are the normalized emissions.

Response 4

An error was made as the emissions mentioned from Geron et al., 2006 were not adjusted to 30 oC. The phrase “adjusted to 30 oC” is now removed. However, when comparing our emission measurements of monoterpene emissions from creosotebush measured at 40 oC in section 3.5 to those of Geron et al., 2006, we used the Algorithms of Guenther et al. 1993 to adjust their emissions to 40 oC.

Comment 5

Page 17120, lines 14-15: “In the case where more than one compound contributes to a given m/z value measured by PTR-MS, we estimate that they possess similar normalized sensitivities”. What is meant by normalized sensitivity? The authors should present the equation as there can be different ways to define this (are the changes is cell pressure, water cluster and zero counts taken into account).

Response 5:

The term “normalized sensitivities” is now replaced with the term “calibration factors” and calculated as described by Eq. (1). Cell pressure and drift tube voltage was not considered as they were held constant at 2.1 mbar and 600 V respectively throughout the experiment. We now include the following in section 2.3 (Ambient air VOC concentration measurements). “The raw VOC signal intensities (counts per second, cpsVOC) were normalized by the primary ion signal (cps21) and thirty minute averages were calculated. Background signals from the zero air measurements were also normalized by the primary ion single and subtracted from the ambient air measurements to obtain normalized counts per second (ncps) according to Eq. (1).

ncps = (cpsVOC/cps21)sample-(cpsVOC/cps21)zeroair (1)

VOC concentrations were calculated by multiplying a calibration factor (as discussed in section 2.5) by the ncps. Because the signals at m/z 32 (O2+) and m/z 37 (H2O-H3O+) remained below 5% and 2% of the primary ion signal respectively, reactions between VOCs and water clusters (H2O-H3O+) and oxygen (O2+) were not considered.”

In section 2.5 (PTR-MS calibration) we now include, “Calibration factors (ppbv/ncps) were calculated for both methods by dividing the mixing ratio of the compound in the calibration sample (ppbv) by the normalized background-subtracted calibration signals (ncps, see Eq. (1)).”

Comment 6

Page 17121, lines 14-16: “Because methanol production in plants is related to cell

wall expansion during growth and not recently photoassimilated carbon: : :" I believe methanol can also be emitted from decaying or drying plant matter (e.g. de Gouw et al., 1999; Warneke et al., 2002). Could this have an effect on measurements?

Response 6

We acknowledge that decaying or drying plant matter can be a source of methanol at night and contribute to our observations. We adjusted this sentence to include this possibility. "Because methanol production in plants is related to cell wall expansion during growth (Fall, 2003) and decaying/drying plant matter (de Gouw et al., 1999), continued production and emission at night is possible.

Comment 7

Page 17121, line 27: "2000–2500 PAR". PAR is not a unit but abbreviation for photosynthetically active radiation. Please insert proper units (most likely μmol m-2 s-1).

Response 7

We inserted the proper units for photosynthetically active radiation of μmol m-2 s-1.

Comment 8

Page 17123, lines 13-14: "large loss of nitrogen from these ecosystems of 8.4 ngN m-2 s-1 with a maximum loss rate of 35 ngN m-2 s-1 (normalized to leaf area)" It would make the comparison with other ecosystems easier is the normalization would be to land area. How does this compare to other N fluxes at these ecosystems?

Response 8

We included the following sentence to facilitate the comparison of observed nitrile fluxes from creosotebush to inorganic nitrogen fluxes from other ecosystems, "Assuming a creosotebush leaf area index of 0.9 (Gibson et al., 2004) and a 14 % cresotebush land cover (Kurc and Benton, 2010), this corresponds to a nitrogen loss rate of 1.1 ngN m-2 s-1 with a maximum loss rate of 4.4 ngN m-2 s-1 (normalized to ground area)."

Comment 9

Page 17124, lines 3-5: "dimethyl sulfide (DMS) and 2,4-dithiapentane measured with PTR-MS at m/z 63 (0.2 gC gdw-1 h-1) and m/z 109 (1.2 gC gdw-1 h-1), respectively" Was the identification confirmed by GC?

Response 9

The identification of the PTR-MS signal at m/z 109 (2,4-dithiapentane) was confirmed by GC (Table 1). However, the PTR-MS signal at m/z 63 (DMS) was not. However, it is widely accepted that from biogenic sources, the PTR-MS signal at m/z 63 is unique to DMS (Kameyama et al., 2009; Soukoulis et al., 2010; Jordan et al., 2009; Sinha et al., 2007; Warneke et al., 2005; Hayward et al., 2002; Warneke and de Gouw, 2001; Warneke et al., 2001; Williams et al., 2001; Taucher et al., 1996). We attributed the lack of detection of DMS by GC-MS to its highly volatile nature which prevents it from being retained on sorbent tubes under field conditions and/or is lost during dry purging. From the results and discussion section, "Except for a variety of alkanes which cannot be detected by PTR-MS (hexane, dodecane, tridecane, etc.), the PTR-MS was used to quantify the majority of the compounds identified by GC-MS from creosotebush branch enclosures. PTR-MS was also used to quantify several additional VOCs that the GC-MS did not detect well, including the highly volatile compounds methanol, acetaldehyde, ethanol, and dimethyl sulfide. These compounds are not quantitatively retained on sorbent tubes under field conditions and/or are lost during dry purging."

Comment 10

17126: Volatile isoprenoids: Here it would be interesting if the authors would look at the dynamics of the monoterpene emission more closely. Does the emission originate from synthesis or from monoterpenes stored in specific storage structures (see e.g. Grote and Niinemets, 2008; Ghirardo et al., 2010).

Response 10

In section 3.5 (volatile isoprenoids), we now include the following; Because the emission rates of isoprenoids can be tightly linked with carbon assimilation rates or unlinked by evaporation from storage pools (resins), future research could address this question by using 13CO2 labeling and PTR-MS analysis to separate de novo and pool isoprenoid emissions (Ghirardo, 2010).

Comment 11

The authors should check the order of figures. It seems that they are not referred in their numerical order.

Response 11

Figures are now referred to in numerical order.

Comment 12

Page 17116, lines 8-9: "..:contributions to regional biogenic VOC emissions could be significant. Creosotebush leaves are opposite: : :" I would start a new paragraph between these sentences as the subject changes from land-cover to finer structure id creosote bush.

Response 12

We start a new paragraph where mentioned.

Comment 13

Page 17117, lines 7-8: ": : :10 to 30 times less: : :" and ": : :3 to 8 times less: : :" This expression is not very clear. I believe the authors mean 3 – 10

Response 13

For clarity, we replaced this sentence with the following, "Modeling results from Geron et al. suggested that isoprene emissions from the Mojave are 10-30 times less than

from Eastern US forests while monoterpene emissions are 3-8 times less (normalized to land area)."

Comment 14

Page 17122, line 6: "Unlike the Geron et al. observations: : :" I would rather write "Unlike the observations by Geron et al."

Response 14

The recommended change has been made.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 17113, 2010.