

Interactive comment on “Emissions of terpenoids, benzenoids, and other biogenic gas-phase organic compounds from agricultural crops and their potential implications for air quality” by D. R. Gentner et al.

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We would like to thank the editor and the reviewers for their consideration of this manuscript and helpful comments. The manuscript has been revised to reflect many of the suggested changes. Responses to individual comments are shown following each comment.

Anonymous Referee #1

C12232

Lots of data have been presented and analyzed in the manuscript and results show the importance of biogenic VOCs on atmospheric chemistry and air quality. Earlier OH reactivity studies have shown that there are lots of unknown OH reactivity in the atmosphere which is not explained by traditional VOCs e.g. aromatics or monoterpenes. In this study they have also studied several other novel compounds and this is certainly interesting and worth publishing. Therefore I recommend publishing manuscript with minor revisions.

My main concern was that measurement methods used are well-established for aromatics and monoterpenes, but are they suitable for the all other studied compounds. I would like to see some comment on this (e.g. comment on uncertainties for them). How about losses in ozone traps? Pollmann et al. did not show the suitability of the ozone trap for all these compounds. Did you have standards for all these compounds? Reference Gentner et al. (2012) do not clearly answer for these questions and therefore a few more words about the measurement methods should be added. I think data is worth publishing even if measurement methods have not been carefully validated for all these compounds; however this should be clearly stated in the paper.

Response: We understand the reviewers concern, and have added the following passage in section 3.2: “Given the novelty of the measurements for these compounds, no previous work validates the efficacy of measurement methods or interactions with ozone removal traps at the inlet. While additional measurement uncertainty is warranted, we are confident in the methods for these compounds as we were able to accurately measure other compounds in their volatility range (C11-15) and greater in this study and Gentner et al. (2012). Also, the ozone traps used in this work were tested by Pollmann et al (2005) and shown to be acceptable for several sesquiterpenes, which are less volatile, more reactive, and albeit less functionalized than the chemical species reported here. Nevertheless, the measurements we report are potentially lower limits in the event of chemical or physical losses in our sampling/measurement system.”

Specific comments: How long time plants are averagely flowering? One week in a

C12233

year or one month? This information would give perspective for the importance of the flowering event.

Response: The orange trees flowered for about 1 month, but this varies by plant species. We have added a sentence on this in the 3.5.6 Implications section.

Page 28359, line 12: should there be 'NO₃' instead of 'NO'. OH radicals have also great impact on diurnal cycles both in spring and summer and this should also be added.

Response: Since it refers to reaction with ozone, NO is the correct compound. We have revised this section to improve clarity on this point and added a comment on OH radicals.

Fig. 1. You tell that not all sesquiterpenes could be quantified, but should it be that they were not identified as you mention in the text.

Response: The figure has been clarified to reflect this.

Anonymous Referee #2

General comments:

This work combines a large variety of measurements (greenhouse measurements as well as several field campaigns) with modeling efforts to give an important contribution to understand the impact of agricultural crops on the local air quality using a case study of an orange orchard which is the seventh most prominent crop in the studied San Joaquin Valley. The large amount of data presented led in some parts to some missing details. I recommend the manuscript for publication after some minor revisions.

Specific comments: Abstract:

P28345L9 talking about agricultural vs. anthropogenic emissions is a bit misleading as agricultural emissions should also be considered anthropogenic. Please consider rephrasing such as e.g. 'other anthropogenic emissions'.

C12234

Response: While there is no definite convention on the classification of agricultural emissions as biogenic or anthropogenic, we have tried to clarify this statement and the rest of the manuscript.

P28345L15-18 At this point it is not clear if this results (net effect of ozone) is from a measurement or from a model. Please clarify.

Response: This conclusion was a result of a combination of measurements and modeling efforts. We have revised the abstract to clarify this point.

Introduction:

P28346 When talking about VOCs you only mention emissions but later on you also talk about oxidation products. It might be worth mentioning in the introduction that some of these VOCs are not directly emitted but oxidation products.

Response: We have reviewed our manuscript and it is unclear what discussion of oxidation products this comment refers to. The scope of this manuscript is focused on primary emissions of gas-phase organics and their potential to form ozone and SOA through atmospheric oxidation. A few of the oxygenated compounds that we characterize as part of flowering, can also be formed via atmospheric oxidation of other BVOCs (e.g. linalool). In this study, given their strong correlation with other flowering compounds and the timescales for oxidation in the canopy, we are confident in our apportionment.

P28347 P19-26 You don't mention your modeling effort in this short summary which seems to be a big part on the whole paper. Please mention it here so the reader knows it is an important contribution to the paper.

Response: We agree and have added a statement.

Materials and methods:

P28348L16-18 Even though you cite Fares et al 2011 for experimental details for an

C12235

extensive collection of emission factors from different tree types I think this is too little experimental information. Mention for example sample sizes of each tree species to give the emission values presented later on more significance.

Response: Additional details have been added to the mentioned paragraph, including information on the number of individuals for each species.

P28348L26 It would be worth mentioning here what exact result you refer to, based on which you chose the orange orchard over another crop as measurement site.

Response: We have clarified the statement

P28350L18-20 You mention in line 12 above that not all the compounds are clearly emitted only by one pathway. But then based on r^2 all compounds are put into either one or the other category, right? Why is this method justified?

Response: In this manuscript, we do not intend to specify modeling methods for each compound class and plant species. Our goal in testing modeling methods is to provide future users of the provided data with information to make informed decisions as to which methods they test and use. To clarify this we have modified the mentioned text and added the following note to Table S2 where the results are presented. "Note: A better reported coefficient of determination or slope does not imply our endorsement of a particular modeling method. When testing and using the crop survey data in this paper, users of this data should consult literature on the temperature or temperature & light dependence of a species and consider the relevant uncertainties in this study (discussed in Sections 3.1 and 3.1.1)."

P28350L28-29 Please explain how the ozone formation potential is derived. And explain SAPRC acronym.

Response: The ozone formation potentials are just pulled in from a reference and not calculated in this work. We have reworded the sentence to read, "The ozone formation potential of these emissions are compared as maximum incremental reactivity (MIR)

C12236

values for each compound (or compound class) calculated by Carter (2007) using the SAPRC (Statewide Air Pollution Research Center) chemical mechanism."

Results and discussion:

P28351L14 Please clarify if this results are from enclosure measurements using flowering or non-flowering plants.

Response: We have added the following sentence to clarify the point; "With the exception of two orange trees, all plants were in a non-flowering state."

P28352L2 and table 2: Why is the sample size (N) for each crop type so variable (2-200)? And why is the sample size different for the different VOC classes (monoterpenes, sesquiterpenes and oxygenated monoterpenes). Is each sample not analyzed for all VOC's?

Response: There are several reasons why the number of samples varies between columns. First, the BEF sample size is the number of measurement samples that met the standard conditions, while the sample size in the beta column refers to the number of measurement samples where the compounds were observed and used to calculate the beta value. Second, there is variability because some crops were tested more than others some compound classes were observed above detection limits more often than others (e.g. monoterpenes vs. sesquiterpenes). We have added a similar comment to the footnote of the table.

P28353L7 Where emission peaks observed during harvesting during the 2010 summer campaign in the orange orchard?

Response: Yes, we discuss it on P28363 L15-16 and 28368 L7-10, and reference Fares et al. (2012a), which focuses more on harvesting emissions.

P28355L19 Where emission factors from flowering for other crops then citrus measured in the greenhouse?

C12237

Response: No, flowering was not a part of the study design. We are reporting the interesting results from the greenhouse since the flowering emissions were particularly important. This should be clarified by the addition responding to comment P28351L14 above.

P28357L5 Please give a citation for the 'well known' plant wounding compound

Response: We have added a reference to Fall, R., Karl, T., Hansel, A., Jordan, A., and Lindinger, W.: Volatile organic compounds emitted after leaf wounding: on-line analysis by proton-transfer-reaction mass spectrometry. *J. Geophys. Res.*, 104, 15963-15974, 1999.

P28357L28 Please give a reference that shows the suitability for sesquiterpene measurements

Response: The have added references to Bouvier-Brown et al. (2009) and Pollmann et al. (2005).

P28358L20 and table 3: It is not clear to me at this point if the VOC's not observed during summer time are due to instrument difficulties or due to the fact that they were not present. Text and table suggest different implications. Please clarify.

Response: The text is accurate; sesquiterpenes could not be measured during the summer due to chromatographic and detector difficulties. Other compounds observed during the spring, were not present during the summer. We have expanded the statement in the footnote of Table 3 to make this clear to the reader.

P28360L12-17 This method could use a little bit more description or a citation

Response: There is no citation we know of as we developed this method. We have revised this section to clarify our objectives and approach.

P28360L21 This comparison would be nice to be shown in the supplement

Response: It has been added as Figure S3

C12238

P28363L18 Did you observe a change in ozone or SOA measurements during the times of spring flowering, pruning, harvesting and fertilizer application. If so please mention here.

Response: We did not have measurements of SOA at the site, and ozone measurements at the site are too close to look at the net effects with formation, which must be assessed after processing time downwind. Year-long ozone flux measurements at the site show greater non-stomatal ozone flux into the canopy (i.e. reaction of BVOCs with ozone) during these periods of increased emissions (Fares et al., 2012b).

Tables and Figures:

Table 2: see Results and discussion

Response: Addressed above.

Table 4: Where are reaction rate constants with OH taken from?

Response: "Where available, literature values are presented for the reaction constants of newly measured biogenic compounds with atmospheric oxidants (Atkinson and Arey, 2003a; Atkinson and Arey, 2003b). Otherwise, theoretical values are estimated using the U.S. EPA's EPI Suite program (2000)." P28351 L4-7 in the ACPD version of the paper.

Figure 6: At some point in the text or the figure caption the compounds summed for anthropogenic and biogenic should be listed.

Response: I have added more detail to section 3.5.1 and the caption for figure 6.

Technical corrections:

P28347L17 You spell out the meaning for the acronym MEGAN but not for BEIGIS, why?

Response: The meaning of the BEIGIS acronym is rarely used (Biogenic Emission

C12239

Inventory Geographic Information System), but we have added it now for clarity.

P28348P21 Please introduce the GC/MS acronym here as it is used later in the text.

Response: Corrected, thank you.

Table S7: Please check the unit for PAR.

Response: Corrected, thank you.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 28343, 2013.

C12240