Dear Editor,

We received two sets of referee comments for our manuscript acp-2014-600. Anonymous Referee #1 suggested "major revisions," while Anonymous Referee #2 suggested publication "essentially as is" with "technical corrections" only. We thank the referees for their helpful suggestions. We believe the discrepancy in evaluations by the two referees may be resolved by improved clarity regarding the goals and purpose of our campaign overview paper, which we re-emphasize in the revised manuscript. Our point-by-point responses to both sets of referee comments are reproduced in italics below alongside the relevant changes to the manuscript.

All authors have read the revised manuscript and approved the suggested changes. On behalf of my co-authors,

Tran B. Nguyen

Anonymous Referee #1

Received and published: 18 September 2014

General comments

- **Referee Comment:** This manuscript describes the design of atmospheric chamber experiments aimed at better simulating the atmospheric conditions under which biogenic compounds undergo photooxidation. The simultaneous use of many different experimental approaches and synthesized standards is expected to allow for better controlled and measured conditions in the chamber experiments, as well as the opportunity to do cross-calibration experiments for instruments used in both field and chamber studies with overlapping detection capabilities.

  I was genuinely surprised, given that the various experimental conditions that are exquisitely described and tabulated (i.e., Table 2), that there are very few specific results given for these experiments in this manuscript. I can suppose that the authors thought their achievement of chamber conditions that are more representative of the atmosphere is publication worthy, but without directly demonstrating that useful results actually came out of these experiments, I'm not sure what audience will find this paper immediately useful. The "Preliminary results and atmospheric implications" section is not much more than just a teaser (for example, air quality modelers cannot do much with the qualitative information that "the high-NO isoprene hydroxy nitrate yield is closer to the high end of the spectrum," even though this is a provocative result). While the manuscript provides interesting details on the challenges of

designing the experiments, it doesn't seem appropriate as an ACP research article. Perhaps it would be appropriate as a technical note in ACP or as an article in another journal?

That being said, I look forward to a full report of the results of this study, as it does appear that many new important insights have been (or will be) gained. Therefore, rather than publishing this methods-centered article now, it might be more impactful to integrate the methods descriptions that make up this manuscript into the series of papers that seem likely to result when the full outcomes of the experiments are available.

- ***Response:*** *We appreciate the referee's comments and welcome the opportunity to clarify the justification behind the submission of this campaign overview manuscript to ACP. Indeed, the goals of this overview are to describe the specific objectives, experimental conditions, participants, instrumental methods, and preliminary results of the FIXCIT 2014 Campaign, instead of comprehensive results. The full results and impacts of FIXCIT are outside the scope of this manuscript and are left to the individual participants to describe in forthcoming publications that are focused on specific topics and datasets within the campaign.*

  This overview is written in the spirit of other overviews of collaborative field and laboratory campaigns. There are too many papers to name; thus, we list only list select examples published in ACP below that set the precedence for this work:

  1. *MILAGRO (Molina et al., 2010)*
  2. *CONCERT (Voigt et al., 2010)*
  3. *AMAZE-08 (Martin et al., 2010)*
  4. *INTEX-B (Singh et al., 2009)*
  5. *MCMA-2003 (Molina et al., 2007)*
  6. *NAMBLEX (Heard et al., 2006)*

  An overview for SOAS (the affiliated field campaign to FIXCIT) is, likewise, forthcoming from A.G. Carlton et al.

  We note that some overview manuscripts are written long after the campaign is over, and thus, may contain a summary of published results (e.g., AMAZE-08). Others seek only to provide context for papers that are co-submitted in a special issue or are forthcoming (e.g., NAMBLEX). Our manuscript belongs to the latter category. It is our understanding that a special issue of the Southeastern Atmosphere Studies (collectively called SAS) will be organized in ACP and we intend for this manuscript to serve as a central source of technical information to be cited by forthcoming related manuscripts in order to avoid excessively-long methods sections and redundancy across related works.

- ***Changes:*** *We have added a clarifying sentence to the abstract "This work provides context for forthcoming publications affiliated with FIXCIT campaign."*

  We also added a discussion of preliminary results for the low-NO cold-trapping yields of MVK and MAC (Section 3) to make the manuscript more immediately useful for the reader.

<u>Specific comment</u>

- **Referee Comment:** I very much appreciate the effort described to minimize RO_2 + RO_2 reactions in the present study, but since virtually none of the rate coefficients are known, I would contend that it is quite difficult to know whether the experimental conditions described actually minimized the influence of RO_2 + RO_2 reactions.
    - ***Response:*** *We agree with the referee's point that there is still much uncertainty surrounding rate coefficients for RO_2+RO_2 reactions. However, to say that "virtually none" of the rate coefficients for RO_2+RO_2 reactions are known is too strong of a statement. For example, the review by Lightfoot et al., 1992 contains a compilation of RO_2+RO_2 rate coefficients. We used experimentally constrained recommendations by Jenkin et al., 1998 who produced RO_2 radicals by OH reaction to 1,3-butadiene, 2,3-dimethyl-1,3-butadiene and isoprene and detected the RO_2 radicals by their UV absorption at 270 nm and 280 nm. Jenkin et al provided rate coefficients (self and cross reactions) for greater than 10 isomer-specific RO_2 radicals.*

      Our goal was to minimize (not completely eliminate) the prevalence of RO_2+RO_2 reactions in our system by using atmospherically-relevant isoprene mixing ratios of ~ 20 ppb for some low-NO experiments. We will now add information about the specific reaction conditions (in addition to Table 2) that allow us to reduce the importance of RO_2+RO_2 chemistry in the experiments.

      We state in the text that we are able to constrain the prevalence of RO_2+RO_2 reactions by tracking the RO_2+HO_2 products (ISOPOOH + IEPOX) and RO_2 + NO products within the first 15 minutes of reaction, where we measured ~ 95% of the reacted isoprene carbon goes to forming ISOPOOH+ IEPOX. Thus, the RO_2+RO_2 channel should be small in our reactions. This method is not affected by uncertainties in RO_2+RO_2 reaction kinetics, and limits the bulk RO_2+RO_2 to be < 5 %.

    - ***Changes:*** *We added the following sentences to clarify how we ensured RO_2+RO_2 reactions were minimized at the specific conditions of the experiments: "For experiments using $[H_2O_2]$ as an OH precursor, RO_2+RO_2 reactions were largely minimized by using reaction conditions that ensures $[HO_2] > [RO_2]$ (e.g., $[H_2O_2]_0/[ISOP]_0 \sim 10^5$ and $J[H_2O_2] \sim 4 - 5 \times 10^{-6}\ s^{-1}$). Thus, the peroxy radical self-reaction channels are minor compared to RO_2+RO_2 chemistry." and "The molar yield of the low-NO products ISOPOOH + IEPOX (measured within the first 15 minutes of reaction) was estimated to be 95%, supporting the dominance of RO_2 + HO_2 chemistry over other channels."*

- **Referee Comment:** I don't think the secondary photooxidation chemistry of the isoprene system is really well known enough to be sure that the observation of C_5 diols can be exclusively attributed to RO_2 + RO_2 reactions and the authors themselves mention the recent finding that ISOPN (high NO) can lead to IEPOX (low NO), which also confuses the interpretation of the dominant fate of RO_2 radicals in their experiments.
    - ***Response:*** *It is true that we cannot be sure that diols come exclusively from RO_2 +RO_2 pathways, as new mechanisms are perpetually being discovered. They can however be used as an upper limit estimate of the rate RO_2 + RO_2 chemistry. An additional established pathway to the isoprene diol formation is through hydrolysis of the isoprene*

nitrates, particularly 1-OH-2-ONO_2-ISOPN. This pathway however has a negligible impact, as the first generation isoprene nitrates are quantified to be < 2% of the ISOPOOH + IEPOX mixing ratio in the low-NO reaction, and their hydrolysis lifetime is known to be long for the conditions of the experiment. This has been clarified.

- ***Changes:*** *We now state that high-RO_2 chemistry can be tracked by diols "and other products" and added information on the quantitative method we used to deduce that RO_2+RO_2 and RO_2+NO reactions were unimportant for our low-NO experiments (see the changes immediately above).*

Anonymous Referee #2

Received and published: 23 September 2014

General Comments:

- **Referee Comment:** This paper provides a summary of the focus, experiments, measurements, and initial results from the FIXCIT laboratory study conducted at Caltech in 2014 to investigate the atmospheric chemistry of isoprene and other selected biogenic compounds. The campaign was meant to complement the field studies conducted earlier in the Southeastern US in 2013. The manuscript describes in adequate detail the experiments conducted, their justification, the facilities and instruments employed, participants, problems encountered, and results to date and their implications. The paper is well written and concise and provides a useful starting point for reading the many future publications likely to result from this large and important study. In my opinion the paper should be published in ACP essentially as is, although I have a few very minor comments.
  - ***Response:*** *We thank the referee for the helpful comments and suggestions.*

Specific Comments:

- **Referee Comment:** Page 21617, line 1: Both carbonyl and non-carbonyl products are produced from Criegee intermediates.
  - ***Response:*** *Agreed.*
  - ***Changes:*** *We have revised the relevant text to: "The subsequent reactions of sCIs produce both carbonyl products and non-carbonyl products such as hydroperoxides." We also changed "carbonyl" to refer to more-specific functional groups, such as aldehydes and ketones.*

- **Referee Comment:** Section 2.1 or elsewhere: I did not find any mention of how the chamber volume was regularly measured in the study. This depends on how full the Teflon bag is.

- ***Response:*** *Indeed, the chamber volume was regularly checked and was slightly different for every experiment. We now include this information in Section 2.1.*
- ***Changes:*** *We added the following sentences: "The chamber volume was measured regularly by quantitative transfer of highly volatile organics such as isoprene by an externally calibrated GC-FID. Quantitative transfer was checked via injections of a measured quantity of isoprene (checked by gravimetric, volumetric, and FT-IR methods) into a pillow bag with known volume by timing a calibrated mass flow of air into the pillow bag. For most experiments, the chamber volume was between 23 – 24 m^3."*

Technical Comments:

- **Referee Comment:** Page 21614, line 3: Should this be "comprised" instead of "comprising"?
  - ***Response:*** *Done as suggested.*
  - ***Changes:*** *The word "comprising" has now been changed to "comprised."*

- **Referee Comment:** Page 21619, line 22: I believe "which" should be capitalized in question 1.
  - ***Response:*** *Thank you for pointing this out. "Which" and "What" in 1 and 7, respectively, were originally capitalized in our manuscript but the typesetter did not capitalize words following a colon in adherence to Copernicus guidelines. We understand the typesetting rule but agree with the referee that the lack of capitalization is distracting.*
  - ***Changes:*** *We changed the colon following each question series to a period. Now words immediately following are capitalized.*

- **Referee Comment:** Page 21620, line 13: I believe "what" should be capitalized in question 7
  - ***Response:*** *Please see response immediately above.*
  - ***Changes:*** *Please see changes immediately above.*

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