Response to Referees for ACP-2015-508
What do Correlations tell us about anthropogenic-biogenic interactions and SOA formation in the Sacramento plume during CARES?

by L. Kleinman et al

The authors thank both reviewers for their constructive comments and suggestions. The Reviews are reproduced below in italics. Interspersed are our point by point responses. Both Reviewers asked whether we found an A-B enhancement. The answer is yes. Increased prominence is given to actual numbers in the text. Enhanced OA is noticed most prominently in data collected during a pollution episode. Any OA in excess of that predicted by a bilinear model based on lower concentration data is called an enhancement. That enhancement has the requisite property of appearing when both anthropogenic and biogenic precursors have high concentrations and is equated to an A-B interaction. These points have been made clearer in the text.

Response to Anonymous Referee #1

This paper goes through a detailed correlation and regression analysis to assess if possible synergism can be found in OA formation from mixtures of anthropogenic and biogenic emissions (i.e., A-B enhancement). The analyses are based on a unique aircraft data set collected during the DOE CARES field study. A similar, but less in-depth, analysis has already been published with the same data set in other papers. This paper is unique in that it attempts a more rigorous approach.

The paper is well written and for the most part very clear. However, after reading through it there was no clear answer given to the objective of the analyses. What is the finding regarding the fundamental question the paper seeks to answer, is there evidence for A-B enhancement in this data set, yes, no, maybe, and with what uncertainty? This should be added to the Abstract, Conclusions, etc. A clear statement on this is desperately needed.

We agree that prominent and clear statements on A-B enhancements would improve the paper.

There is already a detailed discussion of methodology for determining A-B interactions in Section 4.3. Two sets of numerical values based on Figs 8-10 and on Fig. 11 are given. In Figs 8-10 data are binned coarsely into four subsets having the different combinations of low and high anthropogenic and biogenic VOCs. In Fig. 11, enhancements are derived by doing a bilinear fit to all of the transects not in the high-high subset, then applying that fit to the high-high subset.

An estimate of variability has been added in Sec 4.3:
"Numbers in parentheses are normalized root mean square deviations, a measure of the spread in A-B enhancements extracted from the high-high subset points in Fig. 11."
A true measure of uncertainty requires more information about the A-B mechanism(s) than we have.

Text added so that the Abstract concludes with:

"After taking into account linear effects as predicted from low concentration data an A-B enhancement of OA by a factor of 1.2 to 1.5 is estimated."

Conclusion #6, given below provides now provides a more to the point presentation of A-B enhancement factors.

In the background the authors may wish to explain or discuss an observation sometimes used to support A-B enhancement, that is much higher OA in isoprene dominated but anthropogenic influenced SE compared to pristine isoprene dominated Amazon, eg, Poschl et al. (2010). How is this related to the findings of this paper (ie, maybe the authors can say, it is just the linear combination of A and B SOA in the SE US).

Some of what you suggest is already in the Introduction. Page 25383, starting at Line 13 The "first problem" of unexpectedly high concentrations of OA, most prominently noticed downwind of urban areas, is described (references include Volkamer et al; 2006). On Page 25384 Line 12-16, it is noted that models do better as the anthropogenic influence decreases. An aside: One of the references for greater model accuracy in regions dominated by biogenic emissions is Chen et al (2009) who analyze the same wet season Amazon data set as Pöschl et al (2010). Chen et al contrast their good model agreement with the order of magnitude model under-prediction determined by Volkamer et al (2006) in Mexico City.

I believe that it would be speculation on our part to explain the Southeastern US results in terms of an addition of A and B aerosol. Xu et al (2015) provide evidence that surface OA in Centerville, AL has significant contributions from NO_3 reactions with terpenes and aqueous phase reactions of IEPOX mediated by sulfate ion. Carlton and Turpin (2013) show the importance of particle phase water, determined by RH and anthropogenic inorganic aerosol constituents, in allowing soluble biogenic gas phase compounds to partition to aerosols at which point chemical reaction can lead to SOA.

Text has been added to the last paragraph of the Conclusions suggesting that caution be used in extrapolating results from CARES to other regions. Referring to the eastern US in comparison with CARES:

"...aerosols have higher relative and absolute amounts of inorganic constituents and there is a greater abundance of liquid water, perhaps enabling A-B mechanisms to a greater extent than observed in the CARES region."

Regarding the discussion: The idea that more volume provided by the upwind biogenic OA may lead to enhanced anthrop. SOA assumes the process is all gas-particle partitioning to dry particles. One needs to consider the wet size at ambient RH (ie hygroscopicity, which is a function of composition), and if even more sophistication is desired, the possibility of aqSOA.

Text added specifying that aerosol volume includes associated water, along with a reference to Carlton and Turpin, 2013. Reference to review article by Ervens et al. (2011) added for aqueous phase reactions. This is good background information, but as now mentioned at end of the Conclusion section, the aerosol composition that was observed in CARES had low concentrations of inorganic components.

The last line of the discussion, referring to CalNex results, do not seem to apply to this work. In that case there was little biogenic VOC (in a relative sense to anthropogenic VOCs) impacting SOA formation in that environment. Is the point that in CalNex there was not biogenic/anthrop interaction? This discussion could be clarified.

There was no intention to use CalNex measurements to address A-B interactions. CalNex was brought up to address a perceived inconsistency in urban locations such as Atlanta in which plume OA correlates best with CO but consists primarily of non-fossil carbon. The situation at the CalNex measurement site is similar to Atlanta but not as extreme. The average non-fossil component is 58%, with a minimum value of 42% during the day. Daytime outflow from western LA would give a correlation between OA and CO, whilst the appreciable background gives a large non-fossil signal – though not as large as that observed in the daytime in Atlanta. The last paragraph of the Discussion Section has been removed.

Typo pg 25397 line 10. … simultaneously a have high …
Typo corrected

Conclusion #5, did Zotter really find that most the OA in LA was non-fossil based on 14C analyses? I believe this statement is incorrect.

Most (58%) of the OA measured at the Pasadena site was non-fossil. You are correct that this does not equate to most of the OA in LA (or as used in Conclusion 5, in the outflow from LA) being non-fossil. At the time of the day that the Pasadena site is measuring outflow from LA, the ^{14}C fraction of OA has a minimum value of 42%. The similarity that was intended (but not correctly expressed) in Conclusion #5 was of an anthropogenic plume superimposed on a biogenic background. The phrase "a finding similar to that observed in Pasadena, CA by Zotter et al. (2014)" has been removed from Conclusion #5.

Conclusion #7, what is the conclusion, ie, is it that one cannot say, based on the unusual event, if or if not there was an A-B enhancement. Clarify.

The word "unusual" was used in the Discussion section, page 25401, line 21, in the question "What was unusual about this day?" It was not meant to imply that the event was unusual in the sense of being a climatological outlier. Text changed from "unusual" to "distinctive". Though not "unusual", the pollution event is important in that it contains the data with high concentrations of both biogenic and anthropogenic VOCs against which other data subsets are compared.

Conclusion #6 and #7 have new material addressing your question. They now read:
"6) Evidence for A-B interaction comes from comparing ΔOA between data subsets having different combinations of low and high mixing ratios of anthropogenic and biogenic tracers. We are able to reproduce the findings of Setyan et al., (2012) and Shilling et al., (2013) that high values of OA only

occur when anthropogenic and biogenic compounds both have a high mixing ratio. Differences in precursor abundance between data subsets should be taken into account to determine what portion of OA can be attributed to A-B interactions. Doing so by using residuals from a bilinear fit to the amongst transect data set, yields estimates that A-B interactions can increase OA concentration by a factor of 1.2 to 1.5 depending on the compound used as a tracer of biogenic emissions. This increase is relative to the bilinear relation describing data not in the high CO – high Bio subset. A-B interactions up to a factor of 3.6 are obtained from a fit to coarser subset-averaged data."

"7) The data subset with high values of anthropogenic and biogenic precursors is dominated by two flights on the last day of the field campaign. Temperature reached 40 ºC and wind speed was ~ 2 m s^{-1}. Concentrations of OA, O_3, and biogenic trace gases were the highest recorded, and CO was close to the highest recorded. In addition to the many mechanisms for A-B interactions described in the literature (e.g. Carlton et al., 2010; Hoyle et al., 2011; Xu et al., 2015) it is useful to consider whether additional mechanisms are enabled during a pollution episode such as occurred on 28 June. Poor ventilation and high temperatures lead to increased biogenic emissions, higher ambient amounts of biogenic and anthropogenic SOA precursors, and increased photochemical activity as evidenced by a higher O_3 mixing ratio, the latter requiring the presence of anthropogenic NO_x. Thus, the highest SOA concentrations are likely to occur coincident with elevated mixing ratios of both anthropogenic and biogenic tracers."

Text added to abstract
Highest values of ΔO_3, along with high temperatures, clear skies, and poor ventilation also occurred in the high ΔCO - high ΔBio data set. A complicated mix of A-B interactions can result.

Text added/altered in the Introduction:
"OA and its anthropogenic and biogenic precursors are expected to be mutually enhanced through a common dependence on meteorological conditions (e.g ventilation, sunlight, and temperature) occurring in pollution episodes (Goldstein et al., 2009). Such conditions promote A-B interaction and may also give rise to an altered, non-synergistic dependence of OA on precursors. Our analysis cannot distinguish between causes of enhanced OA, leading us to equate the net effect of enhanced OA above that expected from a bilinear model of low concentration data to an A-B interaction."

Fundamentally, as noted in the last line of the paper, it all comes down to a correlation analysis, which cannot prove causation. Running a high resolution chemical transport model, as suggested, will not resolve the problem as the mechanisms of SOA formation are too poorly constrained. Have the authors thought of trying to do the same regression analyses on a better know process, O3 chemistry, as way to "calibrate" the approach. That is, one might expect an O3 enhancement due to biogenic VOCs and NOx mixing within and downwind of the urban environment. Modeling would also be more informative for this chemistry.

I agree that model calculations alone are unlikely to provide quantitative mechanistic information on A-B interactions. However, I believe that much could be learned even though important processes are poorly constrained. One could calculate whether transport patterns vis a vie emission locations could account for the correlations observed. A point of interest is the determination of the fidelity to which various tracers of A and B emissions actually serve their purpose. One could determine the perturbation

upon aerosol concentrations caused by the meteorological conditions leading to a pollution/stagnation event. It would be of interest to subject model output for clean and polluted conditions to the types of analyses done in this and other studies. Sensitivity studies could be used to examine how model uncertainties effect calculated correlations.

Your suggestion about ozone production is worth pursuing. It is mentioned in the Introduction that (motivated by the work of Herndon et al, 2008 and Wood et al., 2010) the dependence of ozone production on meteorological factors and on anthropogenic and biogenic precursors could yield insights on SOA production. I had not thought about it from the point of view of "calibrating" a model. A comparison of observed and calculated ozone production efficiencies might yield insights.

That said, it is unfortunately a major undertaking and outside of the scope of the current study to add high resolution chemical transport model studies.

Finally, the findings of Xu et al., PNAS 2015 are discussed, but not tested in this study. That is, was there any evidence for a similar isoprene SOA dependence on sulfate aerosol in this data?

Xu et al, 2015 make a strong case for the importance of sulfate in A-B interactions in the Southeastern US. However, aerosol composition in the CARES region is very different than in the SE US. Sulfate levels in CARES were much lower than in the SE, both in absolute and relative terms. Average values equal 0.3 $\mu g/m^3$ and 5%, respectively. Also the weather during CARES was typically dry and sunny with low daytime RH. Thus aqueous phase processing is unlikely to be important. This is seen in the OA size distribution at T1 (Setyan et al, 2012) which shows a prominent peak at ~ 250 nm.

Text has been added to the end of the Conclusion section cautioning that the CARES campaign is not the proper venue for describing aerosol chemistry in the southeastern US, if such chemistry depends on the abundance of liquid water and inorganic constituents.

Response to Anonymous Referee #2

General:

This paper explores anthropogenic(A)-biogenic(B) interactions during the CARES field campaign and builds upon the findings of Setyan et al and Shilling et al. Using linear regression analysis, the authors explore the sources of OA observed during CARES, perturbations to OA, and synergies between A-B interactions. The paper is very well written and is recommended for publication after consideration of the following comments.

My main comment is similar to that posed by reviewer #1. The authors clearly state 2 main objectives in the paper: to determine if OA is dominantly from A or B sources, which they did. The second objective is to determine if synergies exist between biogenic and anthropogenic sources that would enhance the production of OA; this wasn't explicitly determined.

From the response to Referee #1:

We agree that prominent and clear statements on A-B enhancements would improve the paper.

There is already a detailed discussion of methodology for determining A-B interactions in Section 4.3. Two sets of numerical values based on Figs 8-10 and on Fig. 11 are given. In Figs 8-10 data are binned coarsely into four subsets having the different combinations of low and high anthropogenic and biogenic VOCs. In Fig. 11, enhancements are derived by doing a bilinear fit to all of the transects not in the high-high subset, then applying that fit to the high-high subset.

An estimate of variability has been added in Sec 4.3:
"Numbers in parentheses are normalized root mean square deviations, a measure of the spread in A-B enhancements extracted from the high-high subset points in Fig. 11."
A true measure of uncertainty requires more information about the A-B mechanism(s) than we have.

Text added so that the Abstract concludes with:
"After taking into account linear effects as predicted from low concentration data an A-B enhancement of OA by a factor of 1.2 to 1.5 is estimated."

Conclusion #6, given below provides now provides a more to the point presentation of A-B enhancement factors.

The paper would greatly benefit from a discussion both in the abstract as well in the discussion section of what their findings mean for A-B interactions. Do the authors mainly see evidence for enhanced OA due to synergies between A-B interactions or do correlations between episodes of elevated OA and tracers for anthropogenic emissions suggest a coincidental relationship or do the authors see evidence for both depending on the subset of data? Answering this question more explicitly would greatly improve the conclusions drawn from this work.

As in response to Reviewer #1,

Text added/modified in abstract:
"Highest values of ΔO_3, along with high temperatures, clear skies, and poor ventilation also occurred in the high ΔCO - high ΔBio data set. A complicated mix of A-B interactions can result. After taking into account linear effects as predicted from low concentration data, an A-B enhancement of OA by a factor of 1.2 to 1.5 is estimated."

Text added/modified in the Introduction:
"OA and its anthropogenic and biogenic precursors are expected to be mutually enhanced through a common dependence on meteorological conditions (e.g. ventilation, sunlight, and temperature) occurring in pollution episodes (Goldstein et al., 2009). Such conditions promote A-B interaction and may also give rise to an altered, non-synergistic dependence of OA on precursors. Our analysis cannot distinguish between causes of enhanced OA, leading us to equate the net effect of enhanced OA above that expected from a bilinear model of low concentration data to an A-B interaction."

Conclusions #6 and #7 have been changed to read:
"6) Evidence for A-B interaction comes from comparing ΔOA between data subsets having different combinations of low and high mixing ratios of anthropogenic and biogenic tracers. We are able to reproduce the findings of Setyan et al., (2012) and Shilling et al., (2013) that high values of OA only occur when anthropogenic and biogenic compounds both have a high mixing ratio. Differences in precursor abundance between data subsets should be taken into account to determine what portion of OA can be attributed to A-B interactions. Doing so by using residuals from a bilinear fit to the amongst transect data set, yields estimates that A-B interactions can increase OA concentration by a factor of 1.2 to 1.5 depending on the compound used as a tracer of biogenic emissions. This increase is relative to the bilinear relation describing data not in the high CO – high Bio subset. A-B interactions up to a factor of 3.6 are obtained from a fit to coarser subset-averaged data."

"7) The data subset with high values of anthropogenic and biogenic precursors is dominated by two flights on the last day of the field campaign. Temperature reached 40 ºC and wind speed was ~ 2 m s^{-1}. Concentrations of OA, O_3, and biogenic trace gases were the highest recorded, and CO was close to the highest recorded. In addition to the many mechanisms for A-B interactions described in the literature (e.g. Carlton et al., 2010; Hoyle et al., 2011; Xu et al., 2015) it is useful to consider whether additional mechanisms are enabled during a pollution episode such as occurred on 28 June. Poor ventilation and high temperatures lead to increased biogenic emissions, higher ambient amounts of biogenic and anthropogenic SOA precursors, and increased photochemical activity as evidenced by a higher O_3 mixing ratio, the latter requiring the presence of anthropogenic NO_x. Thus, the highest SOA concentrations are likely to occur coincident with elevated mixing ratios of both anthropogenic and biogenic tracers."

As noted at the end of the Conclusion section:
"By its very nature conclusions based on correlations are inferential."

The authors should also provide more interpretation for the variable and sometimes high values of A-B interaction factors. Do these provide evidence of A-B synergies?

I assume that the variable and high values that are referred to are 1.2 – 1.5 from Fig. 11 vs. 1.3 – 3.6

from Figs. 8-10. The methods used to derive these factors are described in Section 4.3. The latter values (1.5, 3.6, and 1.3 for biogenic tracer = isoprene, MVK+MACR, or CH_3OH) each are derived from four subset averaged concentrations, while the first set of enhancements (1.2, 1.5, and 1.2 for biogenic tracer = isoprene, MVK+MACR, or CH_3OH) each depend on data from 56 transects. Enhancements are defined relative to a baseline. Text added to Sec. 4.3: "Note that the choice of data subset used for the low concentration bilinear fit will effect the calculated enhancements and may contribute to differences between values determined here and published values."

As noted above, an estimate of variability has been added in Sec 4.3

There are a maximum of 9 points in the high-high data set to which the estimate of variability refers. This number is low because it refers to plume transects rather than a short sampling period. I don't see how one could extract further information. The problem with using a large number of high frequency points is that they are not independent variables (see Supplement).

Another comment is that the last paragraph of the introduction on page 25386 is one of the main conclusions of the paper, " Although there is a high anthropogenic, high biogenic, subset that stands out as having high concentrations of delta OA, most of the spatial variability of OA within a transect and delta OA amongst transect can be explained by CO or delta CO, respectively. These observation suggest a primarily anthropogenic origin for OA produced in the Sacramento plume. In contrast, the variability of background OA is much better explained by background CH3OH, which suggests a biogenic origin. As background OA is more abundant than OA formed in the Sacramento plume, the plume OA, though correlating best with CO, is expected to have a 14C signature of non-fossil, biogenic carbon." The current writing in the abstract that makes mention of this finding is vague. I recommend adding a 1-2 sentence version of this paragraph in the abstract.

We agree. One has to piece together several pieces of the abstract to arrive at the conclusion in the last sentence quoted. The relevant portion of the abstract has been changed to:

"Because background OA was ~60% of peak OA in the urban plume, peak OA should be primarily biogenic and therefore non-fossil, even though the day to day and spatial variability of OA within the plume is best described by the anthropogenic tracer, CO."

Typos:

Page 25384, Line 8: "later" should be "latter"

Corrected in two places

Page 25386, Line 28: "observation" should be plural
Corrected