Review of "Chamber investigation of the formation and transformation of secondary organic aerosol in mixtures of biogenic and anthropogenic volatile organic compounds" by Voliotis et al.

This paper reports on the initial findings of a series of laboratory experiments conducted in the Manchester Aerosol Chamber to examine the behavior of oxidation of mixed biogenic and anthropogenic VOCs to determine deviations from expectations of the yields of secondary organic aerosols, and possible reasons for such deviations. The paper presents the experimental design and selected results in a logical sequence that is generally easy to follow and understand. This reviewer found the topic interesting with cleverly designed experiments and insightful interpretation of the wide array of measurements. This paper represents a valuable contribution to our understanding of the details of oxidation of VOCs as related to production of aerosols under various conditions. The McFiggans group has led the community in the interesting area of mixed biogenic-anthropogenic VOC oxidation and production of SOA. This paper, and the ones to follow about these experiments, continues that legacy.

On the organization of the paper, after the introductory material, the figures are discussed along with aspects of the study (starting on line 375). The last figure (13) is referenced on line 650. Then in the discussion, the figures are discussed again (starting on line 674) in order. This reviewer suggests that the authors say everything to be said about the figures in the first pass, and then shorten the discussion to only the key points of the study. This is only a suggestion for the authors to consider.

General comments.

While this review found the paper overall well-written and organized, there were some instances of jargon usage and awkward wording. These are pointed out in the specific comments. In the discussion and conclusions, the interference of VOCs in the measurement of ozone was noted. Had this been recognized earlier, an alternative method of measurement could have been employed (e.g. reverse NO chemiluminescence). Perhaps this should be briefly mentioned. It is also important to note that the Thermo 42i NOx analyzer has significant interference from reactive nitrogen compounds other than NO_2 in the NOx mode due to the converter employed in this instrument. This should also be mentioned, perhaps in a footnote of Table 2.

Specific comments.

Line 60. In the first mention of VOC:NO_x ratio, indicate that it is a ratio of mixing ratios (in other words, a molar ratio). This is important because is could be a ratio by mass.

Line 61. It is not clear what is meant by "less mechanistically". Perhaps use different terminology.

Line 66. What is meant by "numerous representations of atmospheric SOA"? Consider different wording.

Line 129. Suggest "use these metrics to quantify interactions in the oxidation of VOC mixtures leading to changes in SOA formation compared to those expected based on…"

Line 132. Suggest "use a suite of online and offline measurements…and the resulting properties of potential atmospheric significance."

Line 141. Perhaps reword or add additional text to explain "…makes a comprehensive programme intractable."

Line 151-2. Suggest "…study of a random mixture is expected to yield novel, but complex results. Thus, care is required to fully interpret information from such studies." …or something similar.

Line 159-160. This reviewer is not convinced that it is established how NO_x affects SOA formation yields dramatically. While some studies have shown this, others are less convincing. It is not even obvious what the slope of the yield versus NO_x function is. Suggest softening this assertion.

Line 162. The sentence that begins "Truly low NO_x regimes do not occur widely in the ambient atmosphere…" could certainly elicit discussion. It depends on the definition of "low NO_x" and "widely", which have not been presented here. There are certainly remote regions where the NO_x is very low (10s of pptv), but it probably is hard to argue that such locations are widespread. Suggest softening this assertion. Since the use of low and moderate NO_x levels are used in the paper, perhaps somewhere consider quantifying what is meant by these descriptors.

Line 182. Suggest changing "…sort of atmosphere that…" to something else that is clearer, such as "…level and mixture of atmospheric components that are employed to approximately represent a given atmospheric situation."

Line 188. Several places in this paper use future tense, when present tense is more appropriate. This is one of those places. Suggest "…of the current approach is of considerable interest."

Line 196. The use of ammonium sulfate particles is mentioned and justified, but the reason for this particular choice is not mentioned. Perhaps include a bit more information.

Line 203. Suggest "Ammonium sulphate solutions are nebulized into…".

Line 210. Table 2 is referenced here, before Table 1. Suggest renumbering and reordering the tables. It is stated that the measurements are "state-of-the-science". While this is true for some of the instruments, it is not universally true. Suggest rewording this sentence.

Line 211. Time resolution of the measurements is mentioned. Perhaps include the time resolution or integration time in the instrument table.

Line 215. It is a little unclear what is meant by "collection of sufficient mass" in this context. Perhaps add a few words to indicate that the detection limits for aerosol components are enhanced by maximized the total mass of aerosol collected.

Line 234. It is not clear what is meant by "…throughout the photochemistry…". Suggest rewording.

Line 236. Suggest rewording "…characterization of the transformations of the oxidation products…". The oxidation products are the result of oxidant attack on the primary VOCs, perhaps in multiple generations, so oxidation products can be oxidized, but it is not clear what the point is here.

Line 237. It is unusual to use the term "payload" for instruments used in a ground based laboratory or field study. It is usually reserved for aircraft studies. Suggest using "suite" or some other term.

Line 251. Suggest "The biogenic VOCs that were chosen were α-pinene and isoprene…"

Line 256. Suggest "This means that the initial amounts are added in a α-pinene : isoprene : o-cresol ratio of 309 : 164: 400 based…".

Line 266-7. Suggest rewording this sentence. This appears to be a disjoint collection of sentence fragments. It might be easily fixed by a couple of transition words.

Line 273. Change to present tense: "non-linearity leads to changes in the…".

Line 277. Could eliminate the word "Ambient…".

Line 287. Suggest "…mimic a specific atmospheric region, but more to explore…".

Line 289. I'm not sure what is mean by "neutral seed experiments". Suggest rewording.

Line 290. Suggest "…particularly acid catalysed reactions."

Line 298. Suggest replacing "space blanket" with "Mylar film". Also suggest "…homogenise the light intensity throughout the chamber."

Line 302. Suggest "…transmit light up to 100% above 305 nm."

Line 318. Suggest "…is conducted using full illumination without the UV filter on the arc lamps and using ppm levels…"

Line 322. It is not obvious why the term "stock solution" is used and why the concentration is given, since the sentence indicates that the concentration is changed to control the seed concentration. Suggest rewording.

Line 325. Suggest rewording the phrase to read "…by irradiating the chamber mixture for the selected conditions of VOC and NO_x.

Line 327 and 329. It appears these are almost the same sentence. Suggest eliminating one of them. It is possible that all the text in lines 327-330 could be replaced by "The correction for the interference by o-cresol is determined by the ozone instrument signal measured before the experiment began and using the change in o-cresol concentration determined by the CIMS instrument."

Line 345. Suggest beginning this sentence with "The instrumentation includes: a high-resolution…"

Line 351. Suggest "…of the online instrumentation was changed after several hours of reaction to cycle…"

Line 353. Suggest "…Table 2 provides the list of instrumentation…". Also change table number as per previous suggestion.

Line 357. Suggest adding more detail about the "actinometry and off-gassing experiments". At least say what parameters were determined, and maybe briefly describe how they are done. Also include references as appropriate.

Line 362. Suggest "…in the MAC forms O_3 which rapidly establishes the photostationary state…".

Line 367. It seems that the phrase "at a given OH" could be removed. If there is isoreactivity, then it doesn't matter what the OH is, correct?

Line 369. Suggest "…concentration), in practice the loss rate of each VOC…"

Line 371-3. The formation of HONO on chamber walls and release to the gas phase is well-known and has been studied for a long time. Suggest a more recent reference and perhaps a bit more discussion for those readers that might not be familiar with this issue.

Line 379. Figure 1 x-axis label. Suggest something like "Illumination time (h)".

Lines 382-395. With the discussion of the photostationary state and the Leighton ratio, in principle you could calculate the HO_2+RO_2 concentration that explains the observed ratio. Not discussed were the instances where the ratio is observed to be less that unity. Suggest adding some text to expand this discussion, or alternatively to eliminate the topic completely.

Line 420. Suggest "…not all VOC were consumed…". This is because VOC is plural. This reviewer prefers VOC for singular and VOCs for plural, but this is not widely accepted.

Line 431. Suggest “The same colour scheme as in Figure 2 is used.”

Lines 440-1 and 443. The terms “particle mass” and “SOA particle mass” are used interchangeably in the first sentence, but this is not strictly correct. It is not really necessary to include “particle” with SOA, since SOA includes “aerosol”. “SOA mass” should suffice in this discussion. Note that “particle mass” and “SOA particle mass” are used incorrectly (meant to mean SOA mass, but strictly meaning total aerosol mass) throughout page 18 (and Figure 4 caption), and perhaps elsewhere in the paper. Please search for this term and correct its usage.

Lines 443-444. It is difficult to see that that this sentence is a list of possible alternatives for calculation of yields. Perhaps number (1, 2, 3) of add a letter (a, b, c) to the various options, or change the wording of the first part to indicate that various options are coming in the rest of the sentence, for example “…the yield is reported as a single number that could be calculated from data at various times in an experiment, including at maximum SO2 mass, …”

Line 480. The term “referenced” is used, but perhaps “compared” would be better. This applies at many places in the paper.

Line 481-481. The nomenclature for the various yield calculations can make the sentence grammar confusing. This sentence is an example. The use of “yield at maximum mass” might be better with a symbol (such as Y_{MM}) which is defined somewhere and then used in the discussion. Likewise with the other types of yield calculations (e.g. Y_{MVC}).

Line 482. Suggest “The uncertainties in SOA mass yields were calculated by…”. Also, this implies the uncertainties shown in Table 3 are 1σ, but this is not explicitly stated.

Table 3. In an earlier table, a “-“ indicated missing data. What does it mean in this table?

Line 485. In this sentence “organic mass” is used to mean “SOA mass”. Suggest being consistent in the terminology throughout the paper. Also, this sentence is confusing, because it apparently refers to equation (4), but equation (3) is shown first. Suggest reordering the text and equations to make things clearer. The symbols in both equations need to be defined. The term “additively combining” means simply that the predicted yield is the mass of SOA for each component determined from the single VOC experiments at the same amount of VOC reacted divided by the sum of the amounts of each VOC that reacted. It may be that the sentence in line 485-6 is meant to say this, but it is a bit confusing. Consider rewording.

Line 490-3. This sentence is also confusing. Are the two-product fits referred to from equation 3? Perhaps more information is needed to clarify this sentence. Also, the term “particle mass” is used again.

Line 528. It is not clear what is meant by “decremental decay” in this context.

Page 23. There are several instances of “particle mass” on this page.

Line 539. Suggest “Measured (15% error) and reconstructed decays of (a) isoprene and (b) α-pinene in…”.

Line 540. Suggest “In each case, the initial decay of the VOC due to reaction with ozone was calculated based on the initial concentrations of O_3 and the VOC along with the appropriate reaction rate coefficient.”

Line 548-549. Suggest “…yields owing to the differences in the tendencies of oxidation products from reaction with different oxidants to condense.”

Line 551. Suggest "…AMS total signal at m/z values of 44 (f_{44}) and 43 (f_{43}) to represent more or less oxygenated contributions, respectively, to the SOA mass."

Line 554. Suggest "…in all systems explored in this study."

Line 564. It is not clear what is meant by "…more oxidized and higher…". Suggest rewording.

Line 576. Suggest "A more thorough study of the aerosol composition using analysis of the high resolution AMS is data is the…". Not all readers will be familiar with what "high resolution" means in this context, so somewhere define that it is high mass resolution (as opposed to high time resolution or some other type).

Line 587. Suggest "…and mixed α-pinene / o-cresol systems…".

Line 599. Suggest defining "-ve" and "+ve" ionization modes here or elsewhere in the paper.

Line 601. Suggest "…phase reactions cannot be determined from these…".

Line 606. It may be obvious, but suggest defining the term "unique-to-mixture" compounds somewhere.

Line 616. Suggest "Panel (a): Amounts of $C_7H_7NO_4$ isomers products in o-cresol systems as measured by…of each experiment in this study; and (b) time series of total aerosol phase $C_7H_7NO_4$ (all isomers) from…". Also, do these plots indicate inconsistency between the two measurements? If so, this should be discussed in the text.

Line 625. Suggest "…found predominately in the aerosol phase (i.e. exhibiting low volatilities)."

Line 632-3. It is not clear why the data from the end of each experiment was presented in Figure 11. Would it not be better to either show time series or to show data at the peak of the SOA yield. Suggest adding some explanation in the caption or the text why this approach was taken.

Line 656. Suggest "The evolution of these properties for all the systems in this study are discussed in detail…"

Line 666. Suggest "The control of photochemical conditions in the VOC mixtures studied here is challenging."

Lines 666-673. In the discussion of the challenges with different reactivities of OH and O_3 for the various VOCs, you might want to discuss the philosophy of adding oxidant scavengers. For example, a carefully selected alkane could be used to scavenge OH and then O_3 reactions could be studied in isolation. The (as stated elsewhere in the paper) an alternative OH source that doesn't make ozone could be used to study OH reactions separately. Good understand of single oxidant systems could then be followed by those with multiple oxidants. Clearly, in a study such as this, one must be careful with such approaches, but it would be helpful for the reader if the topic is discussed.

Lines 681-2. Need to define "+ve" and "φ".

Line 690-694. In this discussion, it is clear that the chemistry of SOA formation needs to be understood over the range of oxidants studied: from pure OH to pure O_3. With such understanding, studies in specific systems of OH : O_3 can potentially be compared. It is complex, but as with other chemical systems, the detailed mechanistic understanding must be developed before results from complex systems can be interpreted. Did you consider trying to develop a detailed model (using MCM with specific additions, for example) to try and constrain the mechanism responsible for the observations?

Line 700. Suggest "…derived RO_2 must be considered."

Line 702. Suggest "…reaction with NO_2 can be quite complex."

Page 33 and 34. In the discussion of the complexity of such systems as in this study involving multiple oxidants with reactivities of VOCs toward the oxidants changing with time, it should be recognized and pointed out that oxidants can be measured. Indeed, you have direct measurements of O_3 (albeit with the o-cresol interference) and direct OH measurements are possible. Such measurements seem critical to the success of studies such as the one presented in this paper. There are alternative methods (such as decay of a VOC that only reacts with OH; VOC decay mentioned in line 719) to determine oxidant levels. Also, OH levels can be minimized by addition of compounds that do not affect aerosol yields, such as CO. Thus, it is conceivable that many of the complex issues discussed on these pages could be managed by careful design of experiments, including the addition of further experiments. Additionally, it is conceivable that compounds other than those selected might be better choices for a mixed oxidant system. For example, selection of an aromatic compound with an unsaturated side chain might be a better choice than o-cresol. Perhaps one of the other terpenes with different relative reactivities toward OH and O_3 might be more suitable.

Line 704. Suggest "…the oxidant regime is also complex."

Lines 705-6. The first part of this sentence is not clear. Why does NO_x level affect the reactivity of alkanes toward OH? Suggest rewording to make clearer.

Line 712. Suggest "…since anthropogenic VOCs seldom exist…"

Lines 713-4. It is asserted that reduced NO_x levels lead to reduced OH levels, but this is not necessarily true. It depends on the how high NO levels are in the first place. It could actually be the opposite that reduction in NO leads to an increase of OH. This argument needs to be reworded or removed. Also, remove the future tense in "This will inevitably lead…". Change to present tense.

Line 716-7. It is not clear what is meant by the last phrase that states that the VOCs were chosen for their reactivities which leads to their concentrations be of comparable magnitude for mixture reactivities that are comparable. First, "comparable magnitude" is a vague term that is not well defined. It is stated elsewhere that the ratios of VOCs at equivalent OH reactivity are 309:164:400, which implies the ratio of the highest to lowest amount is 2.4. Is this comparable? Second, what does comparable mixture reactivities mean? Does it mean that the sum of the VOC reactivities toward OH (1/k[VOC]) for the binary and ternary experiments are similar to the reactivities for the single compound ones? In any case, suggest rewording the last part of this paragraph.

Line 721. It is not clear what is meant by "…in the system practice." Suggest rewording.

Line 722. This sentence has "owing" twice. Suggest rewording. Also as stated earlier, recognize that other methods of ozone measurement exist and could be used for such studies.

Line 725. It is not clear that it has been demonstrated that the amount of OH in the chamber is adequately constrained. If true, this needs to be discussed in more detail to make the case more clearly. To begin, the term "adequately constrained" needs to be defined.

Line 730. The limitations due to the offline filter collection and analysis has been mentioned several times. It constrains how low initial VOC levels can be, for example. Are there alternative analytical techniques that could take the place of this approach? Elimination of this constraint would certainly make the experiments easier to design.

Line 727-743. It seems that employing detailed chemical models might help in the interpretation and design of the conditions and evolution of these experiments. Rather than state something "would like" be the case, specific and quantitative statements could be made. Employing such models is

still possible even in the post-analysis phase of these experiments, although they could also have been very useful in the initial design of the study.

Line 747. The word “straightforwardly” and elsewhere “straightforward” is used several times. Suggest rewording these sentences. Also, it is not clear how an equation can be easily applied but with consideration of oxidant regime. An equation has inputs and an output. How does this change with “consideration”? Suggest rewording.

Line 751. Suggest “…that the corrections accounting for the loss of particles…”.

Line 759-60. Suggest “…since there are likely significant vapour pressure differences for the products of different chamber experiments and there are also likely dependencies of wall loss rates on species vapour pressures.

Line 750-764. This discussion is interesting and important for all chamber systems. Are there references to studies that could make this issue more quantitative? Does the EUROCHAMP consortium have information about differences in SOA yields from VOCs in chambers with differing surface-to-volume ratios and wall composition? It seems that this discussion could be more than it is “unquantifiable”. Important information may exist that can be used in this study.

Line 765. Need to define “single value yields”.

Line 768. Why is “predictions” in quotes?

Line 770. Suggest “…that such predictions are valid.” (use present tense)

Line 771. Suggest “…the mixed yield depends on the question…”.

Line 775. Suggest “…initial isoprene concentration studied and hence…”.

Line 779. Suggest changing “reference” in this context (the single VOC experiments) to something else (e.g. “base case” or “constraint”). The term “reference” could be confusing since it is used for previous related published papers.

Line 780. Suggest removing the parenthesis in “…shown in Figure 5b, the…”

Line 781. Suggest coming up with a term to describe the SOA yield from α-pinene / isoprene experiments that does not include the change in isoprene concentration, since the normal approach to calculated yield is the ratio of the increase in SOA divided by the decrease in VOC. Developing terminology for this case is preferable to stating “excluding isoprene in the calculations”. One could imagine using Y (for yield) with various superscripts or subscripts to indicate the various cases, for example $Y_{pin,isop}^{pin,isop}$ and $Y_{pin}^{pin,isop}$ could (1) indicate the SOA yield from a binary α-pinene / isoprene system (superscript) using the loss of both compounds in the calculation (subscript), while (2) could indicate the SOA yield from a binary α-pinene / isoprene system (superscript) using the loss of α-pinene only in the calculation. Just a thought.

Line 813. The question of whether the inorganic aerosol mass should be somehow included in the yield is important. Has anyone done multiple experiments (say with α-pinene) under identical conditions with varying amounts and identities of inorganic seeds, perhaps also including different size distributions? This seems to be a critical part of performing such experiments in the laboratory chambers. If such work exists, suggest referring to it here and adjusting the discussion accordingly.

Lines 819-20. Suggest “…composition is an important topic for a future study.”

Line 823. Suggest “…chemical composition would provide important…”.

Line 835. It Is not clear what is meant by the phrase “from the beginning of the experiment”. Suggest removing it.

Line 840. In the discussion of which process could form the substances that are observed on the filters collected in ternary experiments, it should also be mentioned that there are known processes of oxidation of surface aerosol substances by gas-phase oxidants, and also condensed-phase chemical oxidation. Addition of one or more references here would be helpful to the reader.

Line 843. Should the term “ternary” be added to “…only found in the ternary mixed system.”?

Line 846. Remove right parenthesis on “Figure 10a”.

Line 849. Suggest “…there are confounding differences…”

Lines 851-2. Are there composition data from the FIGAERO-CIMS during the experiments (not just at the end)? If so, consider a way to present these data, too.

Line 861. Suggest “…which expresses the FIGAERO-CIMS…”.

Line 862. Suggest “…in the mixture and in the single…”.

Line 885. This reviewer does not think the word “certainly” is appropriate here. It is conceivable, possible, and even highly likely that scavengers could influence the oxidation product distribution, but it is not certain until the appropriate experiment has been performed. Suggest rewording.

Line 886. Suggest “…secondary oxidant formation occurs in the real…”. While this is a true statement, it does not necessarily justify that initial mixed VOC experiments must be conducted in mixed oxidant environments. It is better to conduct the mixed VOC experiments with single oxidants first and then graduate to mixed oxidant situations.

Line 888. It is not true that high peroxide concentrations are required in experiments that use peroxide as an OH precursor. The peroxide can be added constantly to maintain a relatively low steady-state level. This is actually preferred because OH reacts rapidly with hydrogen peroxide. Suggest rewording.

Line 892. Suggest “…may increase the OH : O_3 ratio such that the OH reaction pathways dominate…”.

Line 897. The statement “…maybe more suited to targeted laboratory studies than to chamber experiments” is confusing since chamber studies are target laboratory studies. Suggest different wording for “targeted laboratory studies” such as “flow tube kinetic studies” or something similar.

Line 904. This sentence is confusing because it uses “resolution” and “temporally resolved” together. One needs to be clear whether resolution refers to temporal or mass resolution (as in mass spectrometry). Suggest rewording.

Line 906. Suggest “…reactor experiments to study multiple steady states…”. The authors should also consider more detail in what is meant by multiple steady states, along with references.

Line 909. Suggest “…thought it should be recognized that oxidation and SOA formation occur during…”.

Line 910. It is not clear what is meant by “mixed night-time oxidation by NO_3”. Also, suggest “…should be considered” instead of “should not be forgotten.”

Line 915. Suggest “…to their interpretation, several important observations…”

Line 917. It is not clear what is meant by “photochemical trajectory”. Suggest defining somewhere with discussion to amplify its importance in the present study.

Line 925. Suggest "…existence and to quantify any interactions affecting the observed SOA mass and yield."

Lines 928-9. Here is "straightforward" used in two sentences in a row. Suggest rewording.

Line 931. This reviewer is not sure the term "reference point" is the best. Suggest rewording.

Line 939. See earlier comment about "unique-to-mixture".

Line 940. Suggest "…of the particles depends on the rates…".

Line 942. Suggest "…for our understanding of atmospheric…".

Line 943. Suggest "…the interpretation is complex, and both the experimental design and evaluation need to be…".

Figure S4 caption. Suggest "…in the single precursor α-pinene and…". Also, why is the x-axis scale of the plot logarithmic? The symbols are very similar and hard to distinguish. Suggest changing to make clearer.