In reply to referee comments on acp-2014-274 Wyche *et al.*, 2014

The authors are grateful to both referees for their excellent, thoughtful and insightful reviews, their comments were most welcome and indeed were very useful for manuscript improvements to be implemented. The following document addresses all of the points raised by both reviewers and explicitly details all of the correction made to the manuscript (revised manuscript attached separately with "track changes" documenting alterations) in accordance with both of the referee's suggestions.

Author response key:

> *Indented blue, italicised text denotes direct author response to preceding reviewer comment.*
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> Indented red text denotes author changes to the manuscript in response to requests or recommendations from the reviewer.
>
> Indented plain, black text denotes unchanged areas of the manuscript.

Anonymous Referee #1

Emissions of biogenic volatile organic compounds and subsequent photochemical production of secondary organic aerosol in mesocosm studies of temperate and tropical plant species

The authors describe experiments with emissions from real trees in a photochemical reaction chamber. Focus was put on SOA formation and characterization of the gaseous precursors and oxidation products by GC-MS, PTR-MS and a CIR-TOF-MS. Experiments were conducted with and without ammonium sulfate seeds. The authors contrast a monoterpene (& other BVOC) emitter, birch, with tropic trees fig and palm, which are isoprene emitter. The birch serves also to test the current results against previous experiments. As expected SOA mass from isoprene emitters is small and was only achieved in seeded experiments. The isoprene SOA yields are a high while the MT yields are in the ballpark of previous experiments. The authors show indirectly that the relative large yields for the isoprene emitter likely arise from other BVOC, partly below the detection limits. The study was well conceptual well designed and the manuscript presents new material, especially about emissions from tropical tree species and their oxidation products as well as their SOA formation potential. The manuscript is well written.

It should be published in ACP after the authors addressed the following major and minor points. Major remarks:

Contaminations?
Section 2.2, p. 14296f
The description of the plant chamber unit cast some doubt about contaminations: "PVC foam stripes ensured an airtight seal between chamber"; "Heavy-duty double-sided tape (RS components, UK) was used to secure the Teflon bags to the frame"

Was the plant chamber tested for contaminations? Could intrusions and emanations from tape material have affected the SOA yields for the isoprene emitter?

All non-Teflon components were on the exterior of the chamber or frame in order to prevent any contamination from these components entering the chamber (Plant Chamber Design, Methods and Materials). This is stated in section 2.2, p 14297, lines 2 and 3: "The interior of the plant chamber was only exposed to Teflon surfaces."

Irrespective of this, both the plant chamber and reaction chamber were tested for contaminants separately and when joined together by running the system with an empty plant chamber and by carrying out a blank run prior to each set of experiments. For clarity, this statement has been added to the end of section 2.3.

Section 2.5, p. 14302

"Both the pots and soil were isolated by enclosing them in PFTE sheeting; this acted to prevent VOC emissions from the plastic pots and soil NO_x emissions from entering the chamber air." Was this explicitly checked?

NO_x emissions into both the plant and reaction chamber were explicitly checked and no significant NO_x emissions from the pots or substrate were detected.

Mass balance considerations (section 4.1, p. 14315, l.26ff and section 4.2, p. 14319, l.4ff):

The authors argue that, *cum grano salis,* the mass balance is closed in the experiments (Figures 3 and 6). However, the mass should increase by addition of oxygen. The conservative quantity is the amount of carbon. Insofar the mass balance discussion is inconclusive; it should be cancelled/or weakened and or the Carbon balance should be discussed.

We thank the reviewer for pointing this out; it was clearly an oversight on our part during compilation of the text. Consequently, the following changes have been made to the manuscript to correct for this and to account for the reviewers' suggestions:

Section 4.1, p. 14315, l.26ff, paragraph altered:

"As can be seen from inspection of Fig. 3, the transfer of mass through the *Betula pendula* experiment ~~was~~ appeared roughly conservative, with a small and steady ~~the primary point of note being a small~~ loss of measured mass from the reaction matrix ~~over time (~~after ~ 220 min~~)~~. With the addition of oxygen to the starting body of hydrocarbon material during such an experiment, the total measured mass (i.e. ΣVOCs + SOA) within the system would be expected to increase with time. The absence of such a total measured mass gain (and indeed the mass deficit observed towards the end of the experiment), can most likely be accounted for by considering the various measurement uncertainties involved in producing these data (e.g. assumptions in PTR sensitivity, uncharacterised fragmentation following ionisation, instrument detection limits, etc.) and influences imposed by the chamber walls (including potential loss of more highly oxidised material from the gas phase and greater than expected loss of SOA). Indeed, there is potential for a system mass increase by the end of the experiment to lie within the uncertainty bounds of the CIR-TOF-MS/PTR-MS measurements alone, e.g. the average, single compound PTR measurement uncertainty is ~ ± 30 %, allowing the final measured value of 130 µg m^{-3} to have an upper limit of 170 µg m^{-3}, i.e. greater than the starting value. Considering these results it seems that the system studied is reasonably well characterised given the complications involved in such a task."

Section 4.2, p. 14319, l.4ff, paragraphs altered:

"~~As with the *Betula pendula* experiments,~~ As can be seen in Fig. 6 mass transfer through the *Ficus benjamina* system was ~~relatively conservative, with only~~ characterised by a slight mass decrease ~~measured during the central phase~~ just after the start of the experiment followed by a gradual increase in mass with time. As was stated in section 4.1 a mass increase is expected with time during such an experiment, owing to the addition of oxygen to the precursor hydrocarbon material. Consequently, when considering the data presented in Fig. 6 in the context of potential uncertainties involved (including difficult to characterise influences imposed by the chamber walls), it appears ~~indicating again~~ that the system being studied is reasonably well characterised.

By comparing Figs. 3 and 6 we see that the monoterpene dominated *Betula pendula* system, which produces larger and lower vapour pressure oxidation products than the isoprene dominated *Ficus* system, as well as measureable SOA, is the case which exhibits measured mass loss. From this contrast it is reasonable to assume a significant fraction of any mass deficit observed during *Betula pendula* oxidation could result from the loss of the heavier, lower volatility compounds that are present in the *Betula pendula* oxidation system but not in the *Ficus* system."

Moreover, the mass concentrations axis on the right side in Figures 3 and 6 seems strange. Did you really measured exactly 100 respectively 200 ug/m3 in the experiments?

The right axis of both Figures 3 and 6 were manually scaled to the nearest 100 µgm^{-3} for neatness of appearance and to allow the reader to best resolve the black "total mass" line against the coloured bars in the background. Altering the right axis scale in either case to values other than 200 and 100 µgm^{-3}, respectively makes the graph more difficult for the reader to view and interpret. We have however, included additional text in the legend of figures 3 and 6 to clarify the role of the axes:

"**Figure 3.** Evolution of mass through the *Betula pendula* system (7 July 2009), showing the relative contribution of precursor compounds, oxidation products and SOA mass to total measured mass, with time (coloured bars, left axis) and total measured mass (i.e. ΣVOCs + SOA) with time (black line, right axis). Note: ammonium sulphate seed mass removed from the SOA mass concentration."

> "**Figure 6.** Evolution of mass through the *Ficus benjamina* system (23 June 2009), showing the relative contribution of precursor compounds and oxidation products to total measured mass, with time (coloured bars, left axis) and total measured mass (i.e. ΣVOCs + SOA) with time (black line, right axis)."

Missing detection limits:
Section 2.4.1, p. 14299
Detection limits are not stated for PTR-MS and CIR-TOF-MS, however, these are used to argue later, e.g. sec 3.1.1, p. 14307, lines 5f, in the isoprene case (sec. 4.2, p. 14320, line 18ff).

> *As CIR-TOF-MS and PTR-MS detection limits are method, reagent, reaction, matrix and analyte specific, it is always difficult to give a simple statement detailing the "detection limit" of the technique, however a statement has been added to section 2.4.1, p. 14300 giving a range of typical values along with a reference for further information:*

> "CIR-TOF-MS and PTR-MS detection limits are reagent, reaction, analyte and sample matrix specific. However, typical CIR-TOF-MS detection limits, using PTR ionisation from hydronium, are of the order 0.4 ppbV (10 min)$^{-1}$ for more polar compounds, such as OVOCs (e.g. 2-hexanone) and as much as 10 ppbV min^{-1} for certain less polar compounds, such as smaller hydrocarbons (e.g. 1-pentene). For further details see Wyche et al., 2007."

SOA yields for birch:
Values in abstract and section 3.1.2 do not match the values given in section 4.1 (p. 14315, l. 13). This questions the comparison with Mentel et al. 2009, and the qualifying as low end yields.

> *We thank the reviewer for point this out, the values in section 4.1 are simply "typos", and the values given in the abstract and section 3.1.2 are indeed the correct values. The values of 16 and 11 % given in section 4.1 have been corrected to 39 and 26 %. Furthermore, the statement referring to Mentel et al. 2009 has been altered appropriately:*

> "~~Furthermore~~ In a comparable study to ours, Mentel et al., (2009) reported a fractional mass yield of 11 % for their *Betula pendula* experiments, i.e. slightly lower than those given here, but within the bounds of quantified experimental errors. The yield values obtained here for the *Betula pendula* mesocosm system lie ~~at~~ roughly in the middle ~~lower~~ ~~end~~ of the single precursor yield range."

Minor remarks
p. 14305, §1st : [OH] for birch and palm experiments are not given? How large were they? p. 14306, l. 25: "...only 2.0 (±1.0) ppbV isoprene was detected". The fraction of isoprene amounts to 10-15%. This is a significant contribution! Please, comment in the manuscript.

> *[OH] could not be calculated for Birch experiments because the ozone reacted preferentially with the large concentrations of monoterpenes and sesquiterpenes produced. Therefore it was not possible to use the more stable isoprene (as in the ficus experiments) to calculate the production of [OH] from the reaction of isoprene with ozone. The palm trees were only used in a mixed canopy experiment but these results were not discussed in the manuscript.*

p. 14306, l. 25f : Table 3 states the species found but not their relative abundance !

> *We are not quite sure what the reviewer is referring too here; Table 3 gives the yields of the species listed, in effect, this is the abundance.*

p. 14308, l. 14ff: The authors discuss lifetimes but they quote rate coefficients. I suggest to use a mean [OH] from the experiments and explicitly state the lifetimes.

> *As requested, lifetimes have now been given (p. 14308, 1. 14ff)*

p. 14308, l. 24ff: a-hydroxy carbonyl compounds from OH addition to double bonds have also short lifetimes.

> *This has been noted in the text on p. 14308 by inclusion of the following additions to the text:*
>
> "This relatively short lifetime gives further insight into the potential identity of the *m/z* 111 and 93 signals, perhaps indicating the presence of multiple C=C bonds in the hydrocarbon structure, as would be found in the primary C_7 aldehydes obtained from the oxidation of ocimene or myrcene for example. Other short-lived biogenic oxidation products that could exist in such mesocosm systems, include α-hydroxy carbonyls, similarly formed following OH addition to a C=C bond."

p. 14321, §2nd: This paragraph is difficult understand. A few more descriptive words about the concept and what the authors are aiming at will be helpful.

> *The paragraph has been altered as suggested:*
>
> "For 78 of the 120 measurement-and-parameter sets tested, the estimated residual SOA mass resulting solely from isoprene oxidation was negative – i.e., production of SOA from isoprene oxidation was not required to close the mass balance. Values were calculated based on the widest range of peak masses observed during the *ficus* experiments (M_p = 1.3 µg m^{-3} and 5.5 µg m^{-3}), and assume the lowest (29 %) and highest (100 %) VOC terpene yields and lowest (5 %) and highest (47 %) SOA yields from non-isoprene precursors, respectively, as observed in previous experiments conducted within this chamber. These ranges result in calculated residual SOA mass of -28.5 to +5.0 µg m^{-3} produced

solely from isoprene oxidation. Hence, there are combinations of measurements, observations and oxidation/phase-change parameters — omitting isoprene and its oxidation products — that can account for ~20 times the observed aerosol mass production, and other combinations of measurements and parameters that leave up to ~ 90 % of the condensed mass to be explained by isoprene oxidation. If, instead of using the limiting cases, the closest approximation to the *ficus cyathistipula* system is used (i.e. Y_{VOC} = 77 % and Y_{SOA} = Y_{SOA} = *a*-pinene = 15 %), non-isoprene products could have accounted for around 145 % of the SOA mass that was produced. We have no way of assigning formal likelihoods to each set of measurements and parameters in this exercise, but we note that the great preponderance of parameter combinations do not require an isoprene contribution to the SOA mass (i.e. 78/120 measurement-and-parameter sets tested) under our experimental conditions. Moreover, our experiments produce much less SOA mass than would be expected from published experiments using individual mono- and sesquiterpenes."

p. 14326/14327: Did the authors found indications for induced emissions in PTR-MS data etc. ?

No, we did not observe any evidence to suggest that exposure to ozone induced the emission of additional VOCs from the trees, over and above the ones emitted in the absence of ozone; i.e. there was no evidence of additional (i.e. induced) emissions after the onset of ozone exposure – only the formation of ozone-VOC reaction products.

The reference Hamilton et al. (2013) is missing in reference list.

The reference has been added:

Hamilton, J. F., Alfarra, M. R., Robinson, N., Ward, M. W., Lewis, A. C., McFiggans, G. B., Coe, H., and Allan, J. D.: Linking biogenic hydrocarbons to biogenic aerosol in the Borneo rainforest. Atmos. Chem. Phys., 13(22), 11295-11305, doi:10.5194/acp-13-11295-2013, 2013.

Table 2: The authors should state relative abundances, at least for the main components.

A new table 2 has been created with abundances and inserted in the manuscript.

Figure 3 and Figure 6: There are already reaction products in the first bin. I suggest plotting the VOC mix just before the oxidation starts into the first bin.

Yes, the reviewer is correct there are, and there should be, reaction products in the first bin(s), as the first bin is the 10 minute data point from lights on to + 10 minutes after lights on. Hence, as the reaction has begun, we expect products to begin to evolve. If the reader requires information on pre-lights on data, they *can simply refer to Figs. 2 and 5, which provide this information in a much clearer manner. We feel that adding more data to Figs. 3 and 6 (that is already given in the previous figures), which are already somewhat congested with data, would reduce the clarity of the information we are trying to impart. As such and as the reviewer has no major concerns regarding these figures, we would like to leave them as they are.*

Typos
p. 14295, l. 6: Jiang *Done*
p. 14 309, l. 21: Hex *e* nal ? *Done*
p. 14 310, l. 2: towards *the end of* the experiment ? *Done*
p. 14 314, l. 11: calcu *l* ation *Done*
p. 14 317, l. 6: Figure *10* ? *Done*
p. 14 323, l. 1: (Kiendler-Scharr et al., 2009 *a*) ? *Done*
p. 14 326, l. 6: (Kiendler-Scharr et al., 2009 *a*) ? *This line does not refer to this reference?*
Figure 9, captions, a blank is missing before Ficus *Done*

Anonymous Referee #2

***Interactive comment on* "Emissions of biogenic volatile organic compounds and subsequent photochemical production of secondary organic aerosol in mesocosm studies of temperate and tropical plant species" *by* K. P. Wyche et al.**

Received and published: 7 August 2014

Overall Comment and Recommendation:
This manuscript examines the emissions of BVOCs from silver birch and three South-east Asian tropical plants grown in a whole-tree chamber. These BVOCs were then transferred to an irradiation chamber for subsequent production and characterization of gas- and aerosol-phase oxidation products. I have a number of reservations about the current version of this manuscript. I list these below and strongly encourage the authors to address these carefully before acceptance of this manuscript can be considered.

I was surprised how little particle-phase data was presented and discussed from off-line filter analyses.

> *The data from the filters was intended for use to highlight the formation of SOA and to highlight some major features in what is a complex sample. A full and rigorous analysis of the filter samples that we were able to record is outside of the scope of this (what is already a somewhat large) piece of work.*

Further, the SOA yields presented and discussed have many hidden issues that have to be carefully addressed in a revised manuscript.

> *In the main, we agree with the reviewers' comments here regarding making yield estimates; they can be misleading and must be treated in context. Having said this, our methodology of yield calculation, taking into account the size dependent particle losses to the walls, is at least as rigorous as those from any other group or published work, more so than many in fact. We recognise that yields are completely dependent on the experimental conditions (e.g. T, RH, oxidant, VOC/NO_x ratio, VOC concentration, light intensity and spectrum); this clearly means that chamber SOA yields are not necessarily directly comparable between conditions, unless all others are held constant. Furthermore, we recognise that SOA yields are also dependent on the specific chamber in which the experiment is conducted (wall material, surface area to volume ratio, mixing timescale). This means that the yields are not necessarily comparable between chambers. Finally, and most importantly, the yield is dependent on the volatility of the products and the ratio of the mass transfer rate of the products to the particles and the loss rates to the walls.*
>
> *However, owing to all of these issues, we have attempted to be deliberately transparent in our discussion of our SOA yield calculation methodology. We feel that owing to the extensive use of SOA yield values in the literature, it was necessary and in the context of all of the above, informative to the reader to do so.*

Again, we fully recognise the views of the reviewer in this regard, however, we believe that as we have included all of our working methodology, and that the assumptions required are clear, any reader can understand what we have done in their own interpretation of the data/findings presented.

Overall, I recommend that this paper is not accepted until the Editor feels these specific comments below are adequately addressed.

Specific Comments:

1.) SOA yields and ELVOCs:
Based on the extra low-volatility VOCs (ELVOCs) recently discovered by Ehn et al. (Nature Letters, 2014) and isoprene-epoxydiols (IEPOX) (Paulot et al., 2009, Science), can the authors comment on the wall losses for these sticky low-volatile compounds? Specifically, how might these losses affect the interpretation of these results? This seems like a reasonable question to ask of the authors, especially considering that they report SOA yields throughout the entire text. These losses seem quite apparent, especially considering the effect of having pre-existing seed aerosol; that is, SOA was measurable and seed aerosol was typically more conducive to increasing SOA yields. My guess is as you guys increase the total surface area of your inorganic seed aerosol, you see more OA growth as a result of lower wall losses. Did the authors systematically test this? Since this is likely an issue, why focus the discussion on SOA yields?

As with every single other chamber experiment conducted so far, our yield calculations do not take into account the losses of these compounds. The text has been altered to state this explicitly:

"It should also be noted that along with previous caveats made regarding the role of the chamber walls and other measurement uncertainties, these yield values also do not take into account the potential loss of particularly "sticky" low volatility compounds (e.g. Ehn et al., 2014) to internal surfaces of the chamber."

Losses to walls will be in competition with the losses that contribute to the condensational growth. Each of these losses results from the product of two terms - i) the mass transfer rate to the available surface and ii) the available effective absorptive surface / mass. Any ELVOCs that are produced, will be produced everywhere in the chamber and the seed particles will provide their effective mass uniformly throughout the chamber. It is likely that the ELVOC molecules formed away from the walls will collide with a particle before they collide with the wall and will stick irreversibly to it. ELVOC molecules formed nearer the walls will become increasingly likely to stick to the walls. The effective wall surface so far as the molecules in the middle of the bag are concerned is negligible (or it could alternatively be viewed that the ratio of likely number of collisions with the wall : likely number of collisions with particles, is very low), increasing towards the wall. The results should therefore be interpreted that the decrease in yields attributable to ELVOCs in a smaller *bag will be higher than in a larger bag. <u>BUT</u> ELVOCs have only been seen in terpene ozonolysis and hence this argument is not true for isoprene.*

Furthermore, in addition to there being no evidence that isoprene actually yields ELVOCs, there is conflicting evidence about IEPOX. If it is assumed that reactive uptake requires acidity, then there is no reason to believe our walls are acidic and our particles are likely close to neutral (being originally ammonium sulphate). The neglect of wall effects with respect IEPOX uptake in such a case will likely be minimal. If we proceed with the findings of Nguyen et al., then the wall uptake will be in competition with the seed uptake and the same argument will apply as for ELVOCs above (and the decrease in yields attributable to IEPOX in a smaller bag will be higher than in a larger bag). But this is in apparent contradiction to the fact that the lowest yields have been observed in the largest bag (i.e. SAPHIR).

It is a naive simplification to state that more OA growth will occur with more seed. There are many other concomitant processes at play. We have not systematically tested this - the signal was very small and we were conducting very low realistic precursor concentration experiments.

2.) Page 14295, Lines 9-12:

The authors forget to mention the important effect of acidic aerosol on the reactive up- take of isoprene epoxydiols (IEPOX), which are major 2nd generation oxidation products from isoprene that yield most of the SOA from isoprene under low-NO conditions (Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T).

On the contrary, Nguyen et al., (2014) found that "The results are consistent with weak correlations between IEPOX-derived OA and particle acidity or liquid water observed in field studies, as the chemical system is nucleophile-limited and not limited in water or catalyst activity". The manuscript has been altered to reflect the work that supports the contention of the reviewer and that of Nguyen et al. to illustrate the conflicting literature evidence:

"Modelling, laboratory chamber experiments and field studies provide a range of possible yields of SOA from isoprene, typically of the order 0.4 – 3 % by mass, with some values reported as high as 5.5 % (van Donkelaar et al., 2007;Kleindienst et al., 2009, 2007;Kroll et al., 2005, 2006;Claeys et al., 2004a;Edney et al., 2005). SOA yields from the further oxidation of first and subsequent generation isoprene oxidation products, such as methacrolein, are ~~is~~ estimated to be as much as ~~up to~~ 15 % (Rollins et al., 2009;Carlton et al., 2009;Claeys et al., 2004b;Robinson et al., 2010). Recent work has highlighted that under low NO_x conditions, SOA mass formed from isoprene oxidation could be influenced by the acidity of pre-existing aerosol via the reactive uptake of certain key isoprene oxidation products, namely isoprene epoxydiols (IEPOX; Surratt et al., 2010; Lin et al., 2012). More recently, Nguyen et al. (2014) found that the "pH dependence for OA formation from IEPOX was weak for AS particles". There is further evidence from chamber studies using temperate tree species such as birch, spruce and pine that isoprene may in fact suppress SOA formation from other VOC precursors, when present when present (Kiendler-

Scharr et al., 2009a;Kanawade et al., 2011)." It should be noted however; it is unclear in most cases how wall effects have been considered in the production of such yield values and whether the treatments employed are adequate such that the yields are comparable between chambers, or indeed between experiments.

3.) Page 14296, Line 25:
Did the plywood base emit BVOCs? Could these have leaked into chamber?

It is unlikely that the plywood base emitted VOC into the plant chamber as it was covered in its entirety in foil and then Teflon sheeting. To ensure any background VOC were accounted for, blank chamber samples were taken prior to each change of experiment and then background subtracted from the biogenic samples. Following comments from reviewer #1, this has been clarified in the manuscript (see above).

4.) Page 14301-14302, Line 28 and Lines 1-2:
Why wasn't the chemical composition dependent CE calculated as recently done by Middlebrook et al. (2012, AS&T)?

The AMS data reported in this manuscript was only limited to one SOA nucleation experiment where the particles were composed of only organic material, therefore the composition dependent CE suggestion is not relevant to the reported data. In addition, we only reported the fractional contribution of m/z 44 to total organic mass, which is, being a ratio, not dependent on the applied CE value.

5.) Page 14302, Lines 3-5:
Were denuders used in front of quartz filters? I worry that gaseous absorption of ELVOCs or IEPOX could have occurred on these filters, and thus, skewing the chemical composition results due to positive artifact formation. Have the authors confirmed there are no artifacts. I have to admit the data presented from these filters is very weak and limited, and doesn't really add much to the text in terms of sources of SOA.

Aerosols were collected without the use of denuders. However, they were collected using a flow rate of 3 m^3/min over a period of around 6 minutes and were frozen within a further few minutes of collection. The procedure is much faster than traditional filter collection methods and should minimise the negative and positive artefacts. It is also important to emphasise that filters were collected at the end of the experiment, i.e. after several hours of photochemistry and therefore any ELVOCs, which were produced earlier should have had enough time to already condense onto particles. As the precursor VOCs concentrations had reached a minimum by this point, there was little source for ELVOC production when the filters were collected. It is also unlikely that any ELVOCs present would preferentially condense to the filters when the entire chamber contained more readily available particle surfaces on which to *condense to. As the filters were not acidic there is no evidence that IEPOX could condense effectively onto them.*

Minor appropriate additions to the text have been applied:

"Filter samples for offline analysis were collected (without denuders) in a specially constructed holder, positioned in the chamber vent line. Aerosol samples were collected onto 47 mm quartz fibre filters (Whatman) at a rapid flow rate of 3 m^3 min^{-1} (sample time ca. 6 mins.). After sampling, filters were immediately placed in pre-cleaned glass vials and stored below -20 °C until analysis. The filter collection procedure employed here is much faster than traditional filter collection methods, which should minimise any potential negative and positive artefacts."

6.) Page 14302, Line 7:
Why didn't the authors consider extracting the filters with a more flexible solvent (such as methanol) that can remove both polar and less polar SOA compounds? I worry that water extractions really removes only the most polar SOA constituents and from my experiences with monterpenes (and especially sesquiterpenes). I have found methanol is a better solvent for these two classes of VOCs. Thus, do the authors worry they are missing important aerosol compounds in their off-line chemical analyses?

In contrast to the reviewer, in our experience we have found very little difference between using methanol and water as the extraction solvent (see Hamilton et al., Characterization of Polar Compounds and Oligomers in Secondary Organic Aerosol Using Liquid Chromatography Coupled to Mass Spectrometry, 2008, Analytical Chemistry), with slightly higher recoveries of most species in water. Therefore, we feel it is unlikely that methanol will improve the extraction.

7.) Page 14303, Line 12-15:
What is the concentration of your atomizing solution? This should be listed.

A typical ammonium sulphate solution concentration of 2 g/l was employed. However, as the number, mass and size distribution of the seed produced was always well characterised, the solution strength was not rigorously document.

How much volume of seed aerosol was injected into your experiments? This detail should be added to the experimental section or in the Table summarizing your experiments.

The injected seed volumes information is already included in Figure 8 in the form of seed mass at time zero, i.e. before the start of photochemistry.

Did you all calculate the aerosol pH of your atomized seed aerosol? Since BVOC-derived SOA (especially isoprene-derived SOA) is so sensitive on aerosol pH, this could be an important parameter to add as well.

> *No, we did not explicitly measure the solution pH and as the solution strength was not rigorously defined, it would be somewhat meaningless in this instance to attempt to calculate the aerosol pH. Aerosol acidity was not a key driver in this study, we did not have the time of resources to enter into this complex issue, which would comprise a whole separate study on its own. However, this is something that we are considering for the next phases of our work.*

8.) Page 14303, Lines 16-28:
I would argue that for isoprene SOA formation, there is plenty of literature now that clearly shows that it forms due to REQUIRED acidity that allows for the reactive up-take and subsequent particle-phase chemistry of IEPOX (Surratt et al., 2010, PNAS; Lin et al., 2012; Nguyen et al., 2014, ACP) and MAE (Lin et al., 2013, PNAS). Without acidic particles, SOA formation from isoprene will be quite limited (e.g., Lin et al. 2012, ES&T). Thus, I wonder how relevant these experiments are for isoprene SOA formation?

> *Whilst it is recognised that there is near consensus in the literature that particle acidity is required for formation of SOA from isoprene (with the exception, for example, of Nguyen et al 2014 - who also investigated wet ammonium sulphate seed - and Brégonzio-Rozier et al., ACPD 2014), it is far from clear that ambient particles will always carry substantial acidity where isoprene photochemistry is active; for example the Amazon:*
>
> *"Sulphate levels in Borneo are around four times greater than in the Amazon. Inspection of back trajectories suggests marine and anthropogenic sources of sulphate external to Borneo (Robinson et al., 2011a). A charge balance of sulphate and ammonium ions show excess sulphate over the oceans (Robinson et al., 2011b) compared to the ground site where charge is usually balanced. As acidic sulphate had been shown to play an important role in isoprene SOA formation in previous studies, its presence may contribute to the greater significance of MF in Borneo, although chamber studies have not shown sulphate isoprene SOA mechanisms likely to yield MF (Surratt et al., 2010)" - Robinson et al. (ACP 11, 1039-1050, 2011).*
>
> *The presence of a more neutral or non-acidic, background aerosol in locations such as the Amazon (and also the lack of evidence for prolific distributions of acidic aerosol), lends support to the relevance of our work and lends a degree of justification to our use of an ammonium sulphate seed (which better approximates ambient conditions in such geographical locations). Indeed there perhaps exists a counter argument, which could debate the realism of conditions employed in some experiments that report the importance of acid-catalysed reactions, without reference to the real atmosphere.*
>
> *In summary, one has to be cautious regarding the role of acidity of the aerosol. There is no doubt that Surratt et al. have shown the importance of acidity of the*

> *aerosol, however in contrast Nguyen et al. (2014) and Brégonzio-Rozier et al., (2014) have shown SOA formation on neutral seed. As yet there appears to be no clear picture on the effect of acidity on isoprene SOA formation, we are not attempting here to make an argument for one case or another, we are simply reporting our observations and discussing them in open context.*

The seed aerosol in our experiments were always "wet",

9.) Page 14319, Lines 18-21:
I would argue that this is due to the lack of acidic sulfate aerosol. This has been repeatedly shown as a requirement to produce isoprene SOA (Edney et al., 2005; Surratt et al., 2007; Surratt et al., 2010; Lin et al., 2012; Nguyen et al. 2014).

> *We are slightly confused as to the referees' contention here, owing to the contradiction they make in the next point, where the referee then states that they "would suspect a LOT of isoprene SOA* (under near-neutral conditions) *in the aerosol phase, especially based on recent work by Nguyen et al.", i.e. in opposition to their statement here.*
>
> *However, as we stated above in our reply to point (8), there does exist some lack of consensus in the literature regarding the role of pre-existing acidic aerosol in the production of SOA from isoprene oxidation (e.g. Nguyen showed OA formation on neutral ammonium sulphate aerosol). However, this section of the manuscript is discussing nucleation of gases in the absence of a pre-existing surface. Consequently, the argument regarding the presence of a certain type of seed is not relevant here. Moreover, in the same paragraph, just prior to this statement, we do indeed acknowledge the potential role played by a lack of seed in these particular experiments:*
>
> *"A lack of SOA mass formation during our unseeded Ficus benjamina experiments could have resulted from a number of different factors, not least of which was simply the absence of a seed surface to help facilitate partitioning of the semi-volatile oxidation products to the aerosol phase and produce particles of sufficient size and measureable particle mass".*
>
> *In order to acknowledge the potential role played by a lack acid surface (specifically) here, this statement has been altered slightly in the revised manuscript:*
>
> "A lack of SOA mass formation during our unseeded Ficus benjamina experiments could have resulted from a number of different factors, not least of which was simply the absence of a seed surface (acidic or otherwise) to help facilitate partitioning of the semi-volatile oxidation products to the aerosol phase and produce particles of sufficient size and measureable particle mass".

10.) Page 14321, Lines 27-28:
Why wasn't off-line filter characterization data presented for the tropical plants to confirm that isoprene oxidation wasn't making much SOA in the seeded experiments?

Since the experiments are very humid, I would suspect a LOT of isoprene SOA in the aerosol phase, especially based on recent work by Nguyen et al. (2014) that utilized only ammonium sulfate seed aerosol.

> *Owing to the relatively low level of isoprene present in the chamber, insufficient aerosol mass was formed during these experiments to allow us to make compositional measurements using the techniques we had available e.g. see Figure 8. To clarify this point, the following statement has been added to the end of section 4.2 (page 14322), line 10:*
>
> "Unfortunately, insufficient SOA mass formed during *Ficus* experiments to allow us to conduct any form of compositional analysis."
>
> *Here we are reporting that we did not see any mass formed above background; we are simply reporting what we saw in these instances. There is some degree of split in the literature regarding this and we hope that our findings can add to the debate.*

11.) Page 14322, Lines 16-22:

Not EXACTLY. The methyl furan resulted from the decomposition of IEPOX-derived SOA, as recently shown by the Surratt group (Lin et al., 2012, ES&T; Budisulistiorini et al., 2013, ES&T).

> *This is correct. It was stated in Robinson et al. that the 3MF was a thermal decomposition product of isoprenoid SOA. However the following text and the suggested references have been added on P14322 to clarify:*
>
> "(i.e. thermal decomposition of isoprene derived SOA)"

12.) Page 14323, Lines 19-23:

Not only contrasting NOx environments, but also contrasting aerosol acidity environments (as shown by Lin et al., 2012, ES&T; Lin et al., 2013, ACP; Pye et al., 2013, ES&T).

> *As was stated in the above replies to reviewer comments, there does exist some degree of disagreement in the literature (and in the reviewers commentary) regarding the need for/role of acidic seed (c.f. Nguyen et al., 2014; Brégonzio-Rozier et al., 2014; see previous replies). Owing to the volume of work required in this area the dependence on acidity should have to be the subject of further work and was never intended to be the primary driver of this study. However, as suggested by the reviewer, the additional potential importance of acidity of the environment has been noted with the following changes to the text, P14323, L 19 – 23:*
>
> "Understanding the exact role played by isoprene in air containing many different VOCs, and being able to account for the differing isoprene SOA yields under contrasting NO_x and acidity (Lin *et al.*, 2012; Lin *et al.*, 2013; Pye *et al.*, 2013) environments, will undoubtedly help to significantly improve global

modelling estimates of total SOA loading even further (Couvidat and Seigneur, 2010)”

Minor Comments:
1.) Page 14294, Line 12: insert "have an" *Done*
2.) Page 14302, Line 9: Delete the "d" *Done*
3.) Page 14303, Line 4: insert comma between ppbv and respectively *Done*
4.)Page 14320, Line 10: Please provide acitations for this range of yields. *Done*
5.) Page 14324, Lines 1-2: Please provide supporting citations for this statement. *Done, Mentel et al., has been referenced.*

References added, following alterations as suggested by reviewer 2:

Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Marth, W. J., Baumann, K., Edgerton, E. S., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T., Gold, A. and Surratt J. D.: Real-Time Continuous Characterization of Secondary Organic Aerosol Derived from Isoprene Epoxydiols in Downtown Atlanta, Georgia, Using the Aerodyne Aerosol Chemical Speciation Monitor, Environ. Sci. Technol., 47 (11), 686–5694, doi: 10.1021/es400023n, 2013

Brégonzio-Rozier, L., Siekmann, F., Giorio, C., Pangui, E., Morales, S., B., Temime-Roussel, B., Gratien, A., Michoud, V., Ravier, S., Tapparo, A., Monod, A. and Doussin J.-F.: Gaseous products and Secondary Organic Aerosol formation during long term oxidation of isoprene and methacrolein, Atmos. Chem. Phys. Discuss., 14, 22507-22545, 2014

Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Dal Maso, M., Berndt, T., Petaja, T.,Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, Nature, 506 (7489), 476-479, doi: 10.1038/nature13032, 2014

Lin, Y. H., Zhang, Z., Docherty, K. S., Zhang, H., Budisulistiorini, S. H., Rubitschun, C. L., Shaw, S. L., Knipping, E. M., Edgerton, E. S., Kleindienst, T. E., Gold, A., and Surratt, J. D.: Isoprene Epoxydiols as Precursors to Secondary Organic Aerosol Formation: Acid-Catalyzed Reactive Uptake Studies with Authentic Compounds, Environ. Sci. Technol., 46 (1), 250–258, doi: 10.1021/es202554c, 2012

Lin, Y. H., Knipping, E. M., Edgerton, E. S., Shaw, S. L., and Surratt, J. D.: Investigating the influences of SO$_2$ and NH$_3$ levels on isoprene-derived secondary organic aerosol formation using conditional sampling approaches, Atmos. Chem. Phys., 13, 8457-8470, doi: 10.5194/acp-13-8457-2013, 2013

Pye, H. O. T., Pinder, R. W., Piletic, I. R., Xie, Y., Capps, S. L., Lin, Y. H., Surratt, J. D., Zhang, Z., Gold, A., Luecken, D. J., Hutzell, W. T., Jaoui, J., Offenberg, J. H., Kleindienst, T. E., Lewandowski, M., and Edney E. O.: Epoxide Pathways Improve Model Predictions of Isoprene Markers and Reveal Key Role of Acidity in Aerosol Formation, Environ. Sci. Technol., 47 (19), 11056–11064, doi: 10.1021/es402106h, 2013