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.
- 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\textsubscript{x} emissions from entering the chamber air.” Was this explicitly checked?

*NO\textsubscript{x} emissions into both the plant and reaction chamber were explicitly checked and no significant NO\textsubscript{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 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 \(~ \pm 30\%\), allowing the final measured value of 130 \(\mu g\) m\(^{-3}\) to have an upper limit of 170 \(\mu g\) 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 \textit{Betula pendula} experiments, As can be seen in Fig. 6 mass transfer through the \textit{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 \textit{Betula pendula} system, which produces larger and lower vapour pressure oxidation products than the isoprene dominated \textit{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 \textit{Betula pendula} oxidation could result from the loss of the heavier, lower volatility compounds that are present in the \textit{Betula pendula} oxidation system but not in the \textit{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 \(\mu g/m^3\) in the experiments?

\textit{The right axis of both Figures 3 and 6 were manually scaled to the nearest 100 \(\mu g/m^3\) 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 \(\mu g/m^3\), 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:}

“\textit{Figure 3.} Evolution of mass through the \textit{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. \(\Sigma\text{VOCs} + \text{SOA}\)) 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, l. 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 C7 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 (\(M_p = 1.3 \, \mu g \, m^{-3}\) and \(5.5 \, \mu g \, m^{-3}\)), 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 \(\mu g \, m^{-3}\) 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. \( Y_{\text{VOC}} = 77\% \) and \( Y_{\text{SOA}} = Y_{\text{SOA}} = a\text{-pinene} = 15\% \)), 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:*


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. 14309, l. 21: Hex e nal ? Done
p. 14310, l. 2: towards the end of the experiment ? Done
p. 14314, l. 11: calcu l ation Done
p. 14317, l. 6: Figure 10 ? Done
p. 14323, l. 1: (Kiendler-Scharr et al., 2009 a ) ? Done
p. 14326, 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/NOx 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. **BUT** 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 uptake 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;Kleinidendst et al., 2009, 2007;Kroll et al., 2005, 2006;Claeyss 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 estimated to be as much as up to 15 % (Rollins et al., 2009;Carlton et al., 2009;Claeyss et al., 2004b;Robinson et al., 2010). Recent work has highlighted that under low NOx 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-
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 m³/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 monoterpenes (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 uptake 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 NOx 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:


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

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Abstract: Silver birch (*Betula pendula*) and three Southeast Asian tropical plant species (*Ficus cyathistipula*, *Ficus benjamina* and *Caryota millis*) from the pantropical fig and palm genera were grown in a purpose-built and environment-controlled whole-tree chamber. The volatile organic compounds emitted from these trees were characterised and fed into a linked photochemical reaction chamber where they underwent photooxidation under a range of controlled conditions (RH ~ 65 – 89%, VOC/NO\textsubscript{x} ~ 3 – 9 and NO\textsubscript{x} ~ 2 ppbV). Both the gas phase and the aerosol phase of the reaction chamber were monitored in detail using a comprehensive suite of on-line and off-line, chemical and physical measurement techniques.

Silver birch was found to be a high monoterpene and sesquiterpene, but low isoprene emitter, and its emissions were observed to produce measurable amounts of SOA via both nucleation and condensation onto pre-existing seed aerosol (Y\textsubscript{SOA} 26 – 39%). In contrast, all three tropical species were found to be high isoprene emitters with trace emissions of monoterpenes and sesquiterpenes. In tropical plant experiments without seed aerosol there was no measurable SOA nucleation, but aerosol mass was shown to increase when seed aerosol was present. Although principally isoprene emitting, the aerosol mass produced from tropical fig was mostly consistent (i.e., in 78 out of 120 aerosol mass calculations using plausible parameter sets of various precursor specific yields) with condensation of photooxidation products of the minor VOCs co-emitted; no significant aerosol yield from condensation of isoprene oxidation products was required in the interpretations of the experimental results. This finding is in line with previous reports of organic aerosol loadings consistent with production from minor
biogenic VOCs co-emitted with isoprene in principally-isoprene emitting landscapes in Southeast Asia. Moreover, in general the amount of aerosol mass produced from the emissions of the principally-isoprene-emitting plants, was less than would be expected from published single-VOC experiments, if co-emitted species were solely responsible for the final SOA mass. Interpretation of the results obtained from the fig data sets, leaves room for a potential role for isoprene in inhibiting SOA formation under certain ambient atmospheric conditions, although instrumental and experimental constraints impose a level of caution in the interpretation of the results.

Concomitant gas and aerosol phase composition measurements also provide a detailed overview of numerous key oxidation mechanisms at work within the systems studied and their combined analysis provides insight into the nature of the SOA formed.

*Keywords: Secondary organic aerosol, biogenic volatile organic compounds, BVOC, gas-aerosol partitioning, isoprene, monoterpenes, mesocosm*
Introduction

Atmospheric aerosols change the radiative balance of the Earth through scattering and absorbing incident solar radiation (Kim and Ramanathan, 2008); they directly and indirectly affect the properties and formation of clouds, thus altering the hydrological cycle (Gunthe et al., 2009; Junkermann et al., 2009; Stevens and Feingold, 2009); and they may have an impact on the efficiency of plant photosynthesis (Mercado et al., 2009), thereby modifying the uptake of atmospheric carbon. Hence, aerosol particles affect the Earth’s climate in several ways (as reviewed in Hallquist et al., 2009; IPCC, 2007; Isaksen et al., 2009; Carslaw et al., 2010) as well as having a detrimental impact on human health (e.g., Baltensperger et al., 2008).

A large fraction of the observed atmospheric aerosol composition is organic (Zhang et al., 2007). A primary organic component is emitted directly into the atmosphere from anthropogenic activities, such as biomass burning and fossil fuel combustion, or is emitted from natural sources, such as plant abrasion and the sea surface. Secondary aerosol particles are formed within the atmosphere by gas-to-particle conversion; those formed from gas-phase organic precursors are known as secondary organic aerosol (SOA) (e.g., Riipinen et al., 2012). There is considerable uncertainty surrounding the chemical transformation of anthropogenic and biogenic volatile organic compounds (AVOC and BVOC, respectively) from the gas phase to the aerosol phase and hence, considerable uncertainty in the global source of SOA (Hallquist et al., 2009; Donahue et al., 2009; Ng et al., 2006; Virtanen et al., 2010).
On a global scale, approximately 90% of all volatile organic compound emissions originate from biogenic sources (Guenther et al. 2012), with almost half of this being emitted from tropical and subtropical forests. The ability of biogenic VOC to form SOA is therefore of particular interest and potential importance. Globally, isoprene (2-methyl-1,3-butadiene, C\textsubscript{5}H\textsubscript{8}) is the biogenic VOC with the largest mass emission rate. It is estimated to account for about 50% of BVOC emissions by mass (Guenther, et al. 2012), but it is still uncertain how much it contributes to SOA formation (Karl et al., 2009; Carlton et al., 2009).

Modelling, laboratory chamber experiments and field studies provide a range of possible yields of SOA from isoprene, typically of the order 0.1–3% 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; Brégonzio-Rozier et al., 2014). SOA yields from the further oxidation of first and subsequent generation isoprene oxidation products, such as methacrolein, are estimated to be as much as 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\textsubscript{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 epoxides (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 \cite{Kiendler-Scharr2009b,Kanawade2011}. It should be noted at this point that 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.

Here, we characterised the BVOC emissions from three south-east Asian tropical plant species (\textit{Ficus cyathistipula}, \textit{Ficus benjamina} and \textit{Caryota millis}) and in a series of coupled plant growth chamber–atmospheric reaction chamber experiments, we examined the ability of their oxidation products to contribute to SOA formation under atmospherically relevant conditions. In order to provide a geographically and chemically contrasting study, we replicated these experiments using common silver birch (\textit{Betula pendula}). Silver birch has previously been shown to contribute to the formation of secondary organic aerosol via the emissions of mono- and sesquiterpenes \cite{Kiendler-Scharr2009a,Kiendler-Scharr2009b,Mentel2009}. Seeded (ammonium sulphate) and un-seeded experiments were carried out to allow studies of both fresh nucleation and condensation onto pre-existing aerosol.

\textbf{Methods and materials}

\textit{2.1 Plant selection and pre-screening}
Three non-clonal specimens of common silver birch (*Betula pendula*), a monoterpenic and isoprene emitting tree species; two species of fig (*Ficus benjamina* and *Ficus cyathistipula*), and one species of palm (*Caryota millis*), each approximately 1.5 m in height were used. Figs and palms are abundant in all tropical rainforests. We chose three species found in abundance throughout south and southeast Asia to be consistent with our field work (Hewitt et al., 2010a; MacKenzie et al., 2011). *Ficus benjamina* (Moraceae) is native to Malaysia and has previously been found to be a high isoprene emitter (0.03 – 8.7 µg C g⁻¹ h⁻¹, potted and in soil) with emissions of the monoterpenes, limonene (0.02 µg C g⁻¹ h⁻¹) and β-ocimene (1.8 – 2.5 µg C g⁻¹ h⁻¹), and the sesquiterpenes β-caryophyllene and α-copaene (Carvalho et al., 2005; Geron et al., 2006). In addition, emissions of benzaldehyde (0.53 µg C g⁻¹ h⁻¹) and acetaldehyde (69 µg C g⁻¹ h⁻¹) from potted specimens have been detected (Carvalho et al., 2005). No previous data are available on the BVOC emissions from *Ficus cyathistipula* or *Caryota millis*. Proton transfer-reaction mass spectrometry (PTR-MS) and gas chromatography–mass spectrometry (GC-MS) screening, prior to the start of the coupled chamber experiments, confirmed that both species were high isoprene emitters with *Ficus cyathistipula* also emitting limonene, β-phellandrene, α-damascone and acetaldehyde. Analytical methods are described in detail in section 2.4.

**2.2 Plant chamber design**
A 4.7 m$^3$ plant chamber was constructed out of two rectangular Teflon bag sections and a Teflon lid (0.05 mm FEP) (Adtech Polymer Engineering, UK), which were each supported by frames built using 25 mm$^2$ box aluminium (Speed Frame, RS Components, UK). The framework stood on a raised foil and Teflon covered marine plywood base. PVC foam strips (RS Components, UK) ensured an airtight seal between chamber sections. Heavy-duty double-sided tape (RS components, UK) was used to secure the Teflon bags to the frame. The interior of the plant chamber was only exposed to Teflon surfaces.

Compressed air was constantly supplied to the plant chamber via a mass flow controller and regulator (ALICAT MCR-500 SLPM-D, Premier Control Technologies Ltd, UK) at 780 L min$^{-1}$ and 7.5 bar via a 12.7 mm (outer diameter- OD) reinforced tube. This was reduced to approx 1 bar and between 250 to 300 L min$^{-1}$ (+/- 0.8 %) dependent on the photosynthetic and transpiration rate of each plant species (equivalent to one complete air change every 15 - 20 mins). The air stream was passed through a 12.7 mm (OD) PTFE tube to three in-series filters to remove any pre-existing VOCs (activated carbon filter P3KFA14ASMN, Parker Pneumatic, UK), and submicrometer particles (HEPA CAP 75 filter capsule (FDP-780-050K, Fisher Scientific, UK), and NO$\_x$ (Purafil and activated charcoal, Purafil Inc. USA). Finally, the air was re-humidified by passing it through a 2 L Teflon barrel (Jencons, UK) filled with warmed distilled water. The plant chamber outlet air was either vented into the laboratory via a 50 mm (OD) stainless steel pipe and valve, or used to fill an 18 m$^3$ Teflon reaction chamber.
To enhance mixing, air entered the plant chamber via a perforated 12.7 mm (OD) PTFE tube that circled the base of the chamber. One 12.7 mm stainless steel bulkhead fitting (Swagelok, UK) was inserted through the frame to secure the PTFE tube to the base of the plant chamber. A 50 mm (OD) stainless steel pipe was inserted into the upper corner of the chamber and supported by a Teflon (inner surface) and Nylon (outer surface) manifold (Plastics Direct, UK). The manifold also supported an EGM probe (EGM-4, PP Systems, UK), which recorded relative humidity (RH), temperature (T), CO₂ and photosynthetically active radiation (PAR).

Plants were kept in 255 – 330 mm (height) pots depending on species, watered to pot dripping point and sprayed twice weekly. Plant chamber conditions were maintained at 31 – 33.5 °C / 22 – 24 °C (day/night), 29 – 40 % / 33 – 44 % (day/night) RH, and 335 – 385 ppmV / 390 – 404 ppmV (day/night) CO₂. Owing to structural restrictions, PAR could not be measured directly under the growth lamps in the centre of the canopy. At the top edge of the canopy it was 500 μmol m⁻² s⁻¹ with a 12 hr day / night cycle.

2.3 Reaction chamber description

The aerosol photochemical reaction chamber at the University of Manchester is composed of an 18 m³ FEP Teflon bag mounted on three rectangular extruded aluminium frames (Alfarra et al., 2012). A bank of halogen lamps and a 6 kW Xenon arc lamp are mounted on the enclosure housing the bag, which is coated with reflective “space blanket” providing an integrating sphere, maximising the irradiance
in the bag and ensuring even illumination for the production of photochemical species such as the hydroxyl radical (OH). The air introduced to the bag is dried and filtered for gaseous impurities and particles, prior to humidification with high purity deionised water. A high capacity O$_3$ generator provides controlled ambient levels of O$_3$ (used as an oxidant) and high O$_3$ concentrations (serving as a cleaning agent between experiments).

Size-dependent (diffusional and gravitational) wall-loss rate constants were calculated based on particle mobility and the surface-to-volume ratio of the chamber (Verheggen and Mozurkewich, 2006). The diffusional loss rate uses a constant of proportionality, which can only be determined empirically. A time period was selected near the end of each experiment where the wall losses were deemed to be the dominant process affecting the size distribution. The volume size distribution at the beginning of this period had the calculated wall loss rate applied to simulate the evolution of the size distribution over the selected time period. If the calculated loss rate loss rate didn't reproduce the measured volume evolution within the specified tolerance (1 – 2 % in this work), the constant of proportionality for diffusional losses was adjusted such that the simulated volume at the end of the selected period matched the measured volume within the specified tolerance. The time-integrated gravitational and (optimised) diffusional loss rate constants were then applied to the volume size distribution throughout the experiment in order to reconstruct a wall loss corrected size distribution, which was then used to calculate the wall-loss-corrected particle mass.
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.

### 2.4 Analytical techniques

#### 2.4.1 Gas phase measurements

The volatile and semi-volatile organic compounds and oxygenated volatile organic compounds in both the plant chamber and the reaction chamber were measured by soft-ionisation mass spectrometry (PTR-MS, CIR-TOF-MS, described below) and gas chromatography-mass spectrometry (GC-MS).

The proton-transfer-reaction mass spectrometry (PTR-MS) instrument employed (Ionicon, Austria) comprises two turbomolecular pumps, a heated silica steel inlet system and a 9.6 cm long stainless steel drift tube. The nominal response time is approximately 1 s. The operating parameters of the PTR-MS were held constant during measurements, except for the secondary electron multiplier voltage, which was optimised each day. The drift tube pressure, temperature and voltage were 2.2 hPa, 50 °C, and 600 V, respectively. The central reaction chamber of the drift cell was operated at an $E/N$ (i.e. electric field/gas number density) of 125 Td. The count rate of $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ ions was 1 – 2 % of the count rate of $\text{H}_3\text{O}^+$ ions. The PTR-MS sampled continuously with a flow rate of 100 – 150 ml min$^{-1}$ through 3.2 mm PTFE tubing.
The chemical-ionisation-reaction time-of-flight mass spectrometer (CIR-TOF-MS) comprises a temperature controlled (40 (±1) °C) ion-source drift cell assembly coupled to an orthogonal time-of-flight mass spectrometer equipped with a reflectron array (Kore Technology Ltd, Ely, UK). The ion-source deployed was a hollow cathode discharge type (Blake et al., 2009) and the chemical ionization technique used was proton transfer reaction from hydrated hydronium (H$_3$O$^+$.H$_2$O) (Jenkin et al., 2012). Sample air was delivered in a continuous stream directly to the drift cell via a 0.5 m long, 6.35 mm (internal diameter) Teflon sample line, heated to 40 (±1) °C, at a constant flow rate of 80 ml min$^{-1}$. The central reaction chamber of the drift cell was operated at an $E/N$ ratio of ~ 90 – 100 Td, with a tuned energy ramp at the base of the cell to remove potential water-cluster ions (e.g. RH$^+$.H$_2$O). Further information regarding the CIR-TOF-MS design and a detailed discussion regarding its operation can be found in Blake et al. (2004) and Wyche et al. (2007).

The PTR-MS and CIR-TOF-MS were calibrated using three different methods: (i) step-wise dilution of a gravimetrically prepared gas standard (BOC Special Gases, UK) containing a variety of VOCs and OVOCs; (ii) using calibration material produced in-house via the injection of liquid samples into 10 l Tedlar bags (SKC Inc., USA) containing either humidified or dry, pure nitrogen; and (iii) using gas standards derived from permeation tubes (Vici Inc., US; Ecocientific, UK), diluted, humidified and delivered by a commercial calibration unit (Kintec, model: 491). Where experimental calibration was not possible for a specific compound, either the calibration sensitivity for a structurally similar surrogate was used or calculated
concentrations were employed (Jenkin et al., 2012). For the quantification of isobaric signals, a single sensitivity value was used, e.g. α-pinene sensitivity for \( \Sigma \) (monoterpenes) and β-caryophyllene sensitivity for \( \Sigma \) (sesquiterpenes); again working on the principal that structurally similar compounds possess similar PTR and CIR sensitivities.

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.

The GC-MS system (GC-MS Turbomass Gold, Perkin Elmer, USA) comprised a thermal desorption autosampler (Perkin-Elmer ATD 400) connected via a heated (200 °C) transfer line to a Hewlett-Packard 5890 GC with a 5970 mass-selective detector. Compounds were desorbed at 280 °C for 5 min at 25 mL min\(^{-1}\) onto a Tenax-TA cold trap maintained at -30 °C. The cold trap was then heated to 300 °C for 6 min to desorb compounds onto the GC column. Chromatographic separation was achieved using an Ultra-2 column (Agilent Technologies: 50 m × 0.2 mm ID × 0.11 µm film, 5% phenylmethyl silica). An initial oven temperature of 35 °C was maintained for 2 min, and then increased at 4 °C min\(^{-1}\) to 160 °C followed by an increase of 45 °C min\(^{-1}\) to 300 °C, which was maintained for 10 min. The carrier gas was Helium.
supplied at a rate of 1 mL min$^{-1}$, with an injector temperature of 250 °C. The limit of
detection for isoprene and monoterpenes was approximately 0.25 ng on column and 2
ng on column for sesquiterpenes, corresponding to 100 pptV of isoprene, 50 pptV of
monoterpenes, and to 400 pptV of sesquiterpenes in a 1 L sample. Sampling was
conducted by drawing 8 L of the analyte air through 6.35 mm PTFE tubing onto the
GC-MS sample tubes using a handheld pocket pump (SKC Ltd, UK) at a flow rate of
150 ml min$^{-1}$ (total sample time ~ 43 mins). Sample tubes were stored at 4 °C until
analysed. VOC quantification was by comparison with commercially available liquid
standards (Aldrich, Fluka and Sigma) diluted in methanol. Isoprene quantification
was by comparison with a 700 ppbV in N$_2$ certified gas standard (BOC, UK).

NO and NO$_2$ mixing ratios were measured using a chemiluminescence gas analyser
(Model 42i, Thermo Scientific, MA, USA). Ozone was measured using a UV
photometric gas detector (Model 49C, Thermo Scientific, MA, USA).

2.4.2 Particle phase measurements

Within the main reaction chamber, a scanning mobility particle sizer (SMPS) system
was used to measure the particle size distribution and total aerosol mass concentration
(without sample drying). A particle density of 1.3 g cm$^{-3}$ was assumed for calculating
the mass of SOA particles in un-seeded experiments (Alfarra et al., 2006; Bahreini et
al., 2005). For seeded experiments, a density of 1.77 g cm$^{-3}$ was used to calculate the
ammonium sulphate seed mass and 1.3 g cm$^{-3}$ was assumed for calculating the
additional SOA mass. A water-based condensation particle counter (wCPC, TSI
3786) was used to count the total particle number concentration between 2.5 nm and
approximately 3 µm. Further instrument details can be found in Alfarra et al., 2012,
and references therein.

Real-time broad chemical characterisation of the SOA was made using a compact
Time-of-Flight Aerosol Mass Spectrometer (cToF-AMS, Aerodyne Research Inc.,
USA). A detailed description of the instrument, its operation and calibrations can be
found elsewhere (Drewnick et al., 2005; Canagaratna et al., 2007). The instrument was
operated in the standard configuration, taking both mass spectrum (MS) and particle-
time-of-flight (PToF) data and was calibrated for ionisation efficiency using 350 nm
monodisperse ammonium nitrate particles. The vapouriser was set at approximately
600 °C and data were collected at a time resolution of 2 min. A collection efficiency
value of unity was applied to these data, based on evidence from a previous chamber
study (Alfarra et al., 2006).

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 m³ 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.
The filters were extracted into high purity water, filtered, evaporated to dryness and redissolved in 1 ml 50 % MeOH : 50 % H₂O. The water-soluble compounds were analysed using liquid chromatography-ion trap mass spectrometry (LC-MS/MS).

Reverse phase LC separation was achieved using an HP 1100 LC system equipped with an Eclipse ODS-C₁₈ column with 5 µm particle size (Agilent, 4.6 mm x 150 mm). Samples (60 µl) were injected then eluted by gradient elution with solvents A: 0.1% v/v formic acid water (Optima grade, Fisher) and B: methanol (Optima grade, Fisher) and a gradient program of 3 % B at time 0 min to 100 % B at 60 minutes with a flow rate of 0.6 ml min⁻¹. Mass spectrometry analysis was performed in negative ionisation mode using an HCT-Plus ion trap mass spectrometer with electrospray ionisation (Bruker Daltonics GmbH). Electrospray ionisation (ESI) was carried out at 350 °C with a nebuliser pressure of 4.82 bar and a nitrogen drying gas flow of 12 l min⁻¹. Further details can be found in Hamilton et al., 2013.

2.5 Experimental protocol

Three plants were placed in the plant chamber a minimum of 48 hours prior to the start of the experiment. 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 NOₓ emissions from entering the chamber air. Three experiments were carried out on each species over a one-week period, after which the plants were removed and replaced with three plants of the next species, and the experiment cycle repeated.
Prior to each experiment, ozone was added to the chamber to give a mixing ratio of approximately 2 ppmV and was left overnight. The chamber was then filled and flushed several times using clean air from the facility’s main inlet system (including Purafil, charcoal and HEPA filters as described above), until the total particle count (as measured by a water based condensation particle counter) was below 10 cm$^{-3}$ and the O$_3$ and NO$_x$ levels were less than 1 and 2 ppbV, respectively. At this point, the reaction chamber was flushed and then connected to the plant chamber for filling with the plant VOC emissions. Aerosol and gas phase composition and concentrations were continuously monitored throughout. At the end of the filling process, the plant chamber was disconnected from the reaction chamber, and within the space of roughly one minute, both the chamber lights were turned on and pure O$_3$ was injected to provide an initial concentration of around 20 or 70 ppbV (experiment dependent). The switching on of the chamber lights marked the start of each experiment, which typically lasted 6 hours from this point. For experiments using pre-existing seed, polydisperse ammonium sulphate particles (diameter between 40 – 60 nm) were generated from an aqueous solution using an aerosol nebuliser (Topas, ATM 230) and injected without drying into the reaction chamber at the end of the filling from the plant chamber.

In our experiments we chose to use ammonium sulphate for the aerosol seeds, rather than acidic particles that could otherwise promote isoprenoid particulate mass formation. Whilst it is recognised that isoprenoid SOA mass can be enhanced by the presence of acidic aerosol seed as originally reported by Jang et al. (2002) and
subsequently by Limbeck et al. (2003), Edney et al. (2005), Kleindienst et al. (2007),
Limbeck et al. (2007) and Surratt et al. (2007), we have limited our study to SOA
formation in the mixed precursor systems without deliberate enhancement of particle
mass by condensed phase reaction. There is clear evidence that isoprene oxidation can
contribute to atmospheric SOA formation (e.g. Claeys et al., 2004, Edney et al., 2005)
and we have previously found that enhancement in SOA from isoprene oxidation
above the Bornean rainforest compared with the Amazon may result from an
enhanced marine acidic sulphate contribution to sub-micron aerosol (Robinson et al.,
2011). Intermediates in SOA formation from isoprene have been identified (e.g. Lin
et al., 2012, 2013) and mechanisms for the acid catalysed formation proposed (Surratt
et al., 2010). Whilst out of the scope of the current study, this should be the focus of
future work.

Air samples were taken from three separate locations: 1) immediately before the plant
chamber (pre-PC) for blank subtraction, 2) immediately after the plant chamber (post-
PC) during the reaction chamber filling period for directly emitted BVOC and 3) from
the reaction chamber (RC) during the experiment. RC air was monitored continuously
using PTR-MS and CIR-TOF-MS for VOC decay and formation of reaction products.
Air samples from the pre-PC and post-PC position, as well as RC air samples
immediately at the start of each experiment and 1, 2, 4 and 6 hours after the lights
were switched on, were collected on Tenax TA and Carbotrap filled stainless steel
tubes (Supelco Inc, PA, USA) for GC-MS analysis.
Relative humidity (%), CO₂ (ppmV), PAR (µmol m⁻² s⁻¹), and temperature (°C) in the plant chamber were recorded every 5 or 10 mins during reaction chamber filling, and every 15 or 20 mins overnight. System blanks were taken at the start and end of the experimental period. The reaction chamber background was checked and characterised through the performance of regular blank experiments (one in every five experiments). NOₓ (NO, NO₂ and NO₃) and O₃ were continuously monitored in the reaction chamber. A list of all experiments and their general parameters is given in Table 1.

2.6 Calculated OH concentrations

Since isoprene losses are controlled by reaction with ozone and the hydroxyl radical (OH), the concentration of OH available to react with isoprene in the reaction chamber for each experiment was calculated based on the measured concentrations of O₃ and isoprene in each experiment, the rate of change in isoprene concentration, and the rate constants for the reactions of isoprene with OH and O₃, using equation (1):

\[
\frac{d[\text{Isoprene}]}{dt} = k_{O_3}[O_3][\text{Isoprene}] - k_{\text{OH}}[\text{Isoprene}] = [OH]
\]

Eq. (1)

Hourly averaged concentrations of O₃ and isoprene were calculated for five of the experiments using the tropical fig. Using these data along with equation (1) a range of OH concentrations were obtained. For the first hour after lights on, [OH] was estimated to be 1.9 x 10⁵ – 9.5 x 10⁵ molecules cm⁻³, whereas, towards the end of the
experiment after roughly five hours, values of $8.1 \times 10^5 - 1.9 \times 10^6$ molecules cm$^{-3}$ were obtained. In general, during the tropical fig experiments, [OH] estimated from isoprene and ozone was observed to steadily increase over the duration of the experiment from 0 – 5 hours after lights on.

### 2.7 VOC/NO$_x$ Conditions

Figure 1 shows the time-dependent mixing ratios of ozone and oxides of nitrogen for each experiment set. Although every effort was made to keep the concentrations of oxides of nitrogen low, measurable amounts were present, giving initial VOC/NO$_x$ ratios of the order 2 – 6 and 3 – 9 (see Table 1), for the birch and fig experiments, respectively (where here, the VOC concentration is equal to the sum of all potential precursor concentrations). In terms of a “Sillman plot” (Sillman, 1999), the experiments were carried out in the “VOC sensitive regime”.

The absolute concentration of VOCs in the reaction chamber was roughly ten times greater than those measured over the rainforest during our field experiments (Mackenzie et al., 2011) and the VOC/NO$_x$ ratios employed here were as much as ten times lower (i.e. typical ratio of 20:1, isoprene:NO$_x$ over the rainforest) (Hewitt et al., 2010b). The source of the NO$_x$ in the reaction chamber (initially ~ 2 – 6 ppbV NO$_x$, but increasing to ~ 5 – 9 ppbV after ~ 5 hours) is attributed to a small amount of diffusion of outside ambient air across the porous Teflon membrane into the reaction chamber. The production of certain reactive intermediates in the oxidation of VOCs
(e.g., hydroxyl hydroperoxides from isoprene oxidation) is very sensitive to NOx concentrations in the reaction mixture.

**Results**

3.1 Experiments with *Betula pendula*

3.1.1 Gas phase

Continuous gas phase monitoring with the CIR-TOF-MS and PTR-MS throughout the experiments, indicated successful transfer of VOC precursor material from the plant chamber to the reaction chamber prior to lights on. The data indicated that there was negligible loss of precursor compounds during the chamber transfer process (Fig. 2a).

Immediately after initiation of the photochemistry, the VOC precursor concentrations were observed to decay and product ions began to appear in the CIR and PTR mass spectra. Approximately sixty product-ion peaks were observed by the CIR-TOF-MS and the PTR-MS in the organic gas phase during a typical *Betula pendula* experiment.

The temporal profiles of a number of the most abundant (O)VOCs measured are shown in Fig. 2. From a combination of the CIR-TOF-MS, PTR-MS and GC-MS observations (and from those observations discussed below for the tropical plant experiments), over fifty different hemi-, mono- and sesqui-terpene oxidation products were tentatively identified (Fig. 3 and Tables S1 – S5 in the supplementary information).
From initial inspection of the data, it is clear that monoterpenes dominate during the *Betula pendula* experiments (Fig. 2a and b), with strong signals observed in the CIR-TOF-MS and PTR-MS mass spectra at \( m/z \) 137 (protonated parent ion) and 81 (hydrocarbon fragment). A small amount of isoprene was also detected during *Betula pendula* experiments; however this was always significantly lower in magnitude than that of the sum of monoterpenes; for example, during the experiment on 07/07/09, 12.6 (± 3.8) ppbV monoterpenes were measured in the reaction chamber prior to lights on (c.f. 11.4 ppbV total monoterpenes measured at the post-PC position by the GC-MS), whereas only 2.0 (± 1.0) ppbV isoprene was detected. Speciation of the monoterpenes by GC-MS indicated that the most dominantly emitted C\(_{10}\) compounds from *Betula pendula* were α- and β-pinene (Table 2).

C\(_{15}\) sesquiterpenes (parent ion \( m/z \) 205) were detected in the plant and reaction chambers during each *Betula pendula* experiment, with the most abundant species identified by GC-MS being β-caryophyllene (Table 2). Sesquiterpenes were also measured in the reaction chamber by CIR-TOF-MS (Fig. 2c), however for the majority of the experiments they were present at concentrations either close to or below the detection limit, hence they could not always be monitored as a function of reaction time. For the experiment on 07/07/09, 1.7 (± 0.9) ppbV sesquiterpenes were measured by the CIR-TOF-MS prior to lights on (c.f. 2.2 ppbV total sesquiterpenes measured at the post-PC position by the GC-MS). An ion of \( m/z \) 153 was also observed in the PTR and CIR mass spectra of the plant chamber emissions and
subsequently in the reaction chamber air, tentatively assigned (and here after referred to) as camphore.

During the reaction phase of the Betula pendula experiments the CIR-TOF-MS mass spectra were dominated by ions of relatively high mass (i.e. \( m/z > 100 \)) pertaining to products of both monoterpene and sesquiterpene oxidation. The ions of highest mass (i.e. \( m/z 170 – 290 \)) are characteristic of sesquiterpene oxidation, and have been observed recently during a similar chamber study investigating \( \beta \)-caryophyllene photo-oxidation (Jenkin et al., 2012). Drawing a comparison between these data and the detailed \( \beta \)-caryophyllene study conducted by Jenkin et al. (2012), a number of tentative assignments have been made for \( \beta \)-caryophyllene products, with the assumption that other precursor specific structural isomers may also occupy the same mass channels. A full list of example tentative assignments is given in the supplementary information (Table S2). In total the sum of all sesquiterpene products measured in the chamber was estimated to be ~ 1.5 ppbV (assuming an average PTR sensitivity for such high mass, oxygenated, compounds).

In contrast to the small amounts of sesquiterpene products observed in the reaction chamber, the products observed in greatest abundance were those derived from monoterpene decay. The largest (combined) product signal measured by the CIR-TOF-MS was that of \( \Sigma (I_{111}, I_{93}) \), where \( I_x \) is the intensity of the mass spectrum at \( m/z = x \) (Fig. 2d). Previously, the \( m/z 111 \) and 93 signals have been shown to correspond to various primary \( C_7 \) unsaturated aldehydes formed during the oxidation of
unsaturated acyclic monoterpenes, such as myrcene, ocimene and linalool (Lee et al., 2006a; Lee et al., 2006b; Ng et al., 2006; Wyche et al., In Preparation). In the case of myrcene and ocimene, the m/z 111 and 93 signals correspond to the parent ion (MH+) and the dehydrated daughter fragment, respectively (MH+-H2O), and in the case of linalool m/z 111 corresponds to the dehydrated daughter ion and m/z 93 is a further fragment. The concomitant m/z 111 and 93 signals have also been reported to result from a C7 cyclic ketone formed during the oxidation of terpinolene (not found in the Ficus emission profile and < 1 ppbV found in the Betula profile). The m/z 111 and 93 ions have previously been observed to be significant contributors to total ion signal in the PTR mass spectra during single precursor chamber experiments with concomitant SOA formation (Lee et al., 2006a; Lee et al., 2006b; Ng et al., 2006; Wyche et al., In Preparation), and the m/z 111 ion has also been observed in ambient air measurements over a forested region (Holtzinger et al., 2005).

As can be seen from observation of Fig. 2(d), the Σ(l111, l93) signal rises rapidly during the initial stages of the experiment, much more so than other monoterpene oxidation products (c.f. Fig. 2e), suggesting that the precursor has a much shorter lifetime with respect to OH and O3. Of those monoterpenes speciated by the GC-MS, ocimene and linalool have the shortest lifetimes, with kOH = 3.04 and 1.6 × 10^-10 cm^3 molecule^-1 s^-1 (average lifetimes with respect to OH ~ 44 and 55 mins.), respectively, compared to kOH = 7.4 × 10^-11 cm^3 molecule^-1 s^-1 for β-pinene (average lifetime with respect to OH ~ 1458 mins.) (Atkinson and Arey, 2003; Kim et al., 2011). The Σ(l111,
Signal peaks at around 60 – 100 mins at 3.0 (± 0.7) ppbV (concentration estimated using pinonaldehyde sensitivity), before decaying at a greater rate than that of the precursor monoterpenes and the other monoterpene products. 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 C7 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.

Other dominant signals observed by the PTR-MS and CIR-TOF-MS during oxidation of the Betula pendula air matrix, include the sum of m/z 169 + 151 + 107, which respectively correspond to the parent ion and two daughter fragments of a number of primary monoterpene keto-aldehydes (which, from the speciated monoterpene plant chamber data, are most likely to be pinonaldehyde, caronaldehyde and α/γ-terpinaldehyde); and m/z 139, corresponding to the parent ion of a number of primary monoterpene ketones (most likely to be nopinone and caronone, again when considering the monoterpenes speciated by the GC-MS). As shown in Fig. 2(e) the primary keto-aldehyde and ketone signals had similar temporal profiles to one another, growing at a slower rate than that of Σ(I93, I93), to peak concentrations of around 0.9 (± 0.3) and 1.2 (± 0.3) ppbV, respectively, as the monoterpene trace tended towards zero. The temporal profile for the sum of all other “monoterpene like” product ions (i.e. ions of m/z > 90) was very similar to those of the primary keto-
aldehyde(s) and ketone(s), peaking at a combined mixing ratio of approximately 3.5 ppbV (assuming an average PTR sensitivity for such high mass, oxygenated, compounds).

During the oxidation of compounds emitted by *Betula pendula*, the primary isoprene products, methyl vinyl ketone (MVK) and methacrolein (MACR) (measured together at \( m/z \) 71) were observed to evolve in the same manner as the primary monoterpene keto-aldehyde(s) and ketone(s), peaking at an approximate mixing ratio of 0.4 (± 0.1) ppbV (Fig. 2e). A series of lower \( m/z \) ions were also observed to evolve within the reaction chamber, including \( m/z \) 61 (acetic acid), 59 (acetone), 47 (formic acid), 45 (acetaldehyde), 33 (methanol) and 31 (formaldehyde). Each of these compounds has previously been associated with monoterpene oxidation and/or with off-gassing from illuminated chamber walls. Methanol, acetone and \( m/z \) 99 (potentially cis-3-hexenal) were also observed within the reaction chamber prior to lights on, with a combined mixing ratio of approximately 20 ppbV.

### 3.1.2 Particle phase

From inspection of the CPC and SMPS data we see that SOA mass formed during oxidation of the *Betula pendula* air matrix. As can be seen from Fig. 4, during unseeded experiments nucleation occurred immediately after lights on, with no induction period prior to mass formation. After nucleation, SOA mass increased rapidly to ~11 µg m\(^{-3}\) by ~40 minutes (experiment 06/07/09), followed by a relatively stable plateau (after the application of wall loss corrections) and a slight increase...
towards the end of the experiment. In order to suppress nucleation, seed particles were introduced in some experiments, as has been used previously (Dommen et al., 2009; Meyer et al., 2009; Surratt et al., 2007; Kleindienst et al., 2006; Carlton et al., 2009). This more closely represents the conditions encountered in the ambient atmosphere where there is pre-existing aerosol. Consistent with the nucleation experiments described above, SOA mass was observed to increase as soon as the photochemistry was initiated when an ammonium sulphate seed was present (Fig. 4, experiment 07/07/09).

Using the wall-loss-corrected mass data, along with the corresponding quantity of the sum of precursor species reacted and equation (2), SOA yields were obtained for the Betula pendula oxidation system:

$$Y_{SOA} = \frac{M_p}{\Delta(\Sigma V O C)} \quad \text{Eq}(2)$$

In this instance, $Y_{SOA} =$ SOA mass yield, $M_p =$ peak SOA mass (µg m$^{-3}$) and $\Delta(\Sigma V O C)$ = the sum of gas phase precursors reacted by the time $M_p$ is reached (µg m$^{-3}$) (Odum et al., 1997). In order to determine $\Delta(\Sigma V O C)$, the time-dependent VOC mixing ratios for total sesquiterpenes, total monoterpenes, camphore and isoprene were independently converted to their corresponding mass concentrations (µg m$^{-3}$) and the four data sets were combined to give a “total” VOC precursor decay profile. From the total VOC profile, $\Delta(\Sigma V O C)$ was calculated, using the starting mass of $\Sigma V O C$ at time = 0 and the mass of $\Sigma V O C$ at the time of $M_p$. The uncertainty in $\Delta(\Sigma V O C)$ is
estimated to be ± 41 %. Using equation (2) for the two Betula pendula experiments for which both gas phase mixing ratio and wall-loss-corrected aerosol data were available, SOA yield values of 39 and 26 % were obtained (Fig. 4). 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.

It should be noted in the above yield calculations that the partitioning of material between the vapour phase and chamber walls has not been taken into account. Matsunaga and Ziemann (2010) showed that semi-volatile organic compounds move towards equilibrium between the walls and the vapour phase and that the equilibration timescale and equivalent absorptive mass of the walls was dependent on the molecular properties of the partitioning species. Kokkola et al. (2013) demonstrated in their model study that OVOC wall losses will have significant implications on their partitioning between the gas and particle phase, such that the mass components of very low volatility will almost completely be depleted to the chamber walls during the experiment while the depletion of OVOCs of higher volatilities is less efficient. The implications of such partitioning to chamber walls are such that comparison between any yields determined experimentally in different chambers should be conducted with caution. Even when calculated from experiments in the same chamber, yields should be interpreted qualitatively and relatively and not extrapolated to the atmosphere.
3.2 Experiments with tropical species

3.2.1 Gas phase

In order to study the contrast between species that primarily emit monoterpenes and those that primarily emit isoprene, and hence to better understand the isoprene-SOA system, the coupled plant chamber-reaction chamber system was employed to study several tropical species. Two species of fig and one species of palm were selected during the pre-experiment screening process. Those experiments using the figs, *Ficus cyathistipula* and *Ficus benjamina* gave the most complete data set; hence their results are used as a focus for discussion.

Fig. 5 shows the temporal evolution of a number isoprenoids detected in both the plant and reaction chambers (a and b) and the concomitant evolution of a selection of isoprenoid oxidation products (c and d), during a typical *Ficus benjamina* experiment (23/06/09). During a typical *Ficus benjamina* experiment, approximately thirty precursor and product-ion peaks were observed by the CIR-TOF-MS and PTR-MS in the gas phase. Tentative product identification is reported in the supplementary information (Fig. 6, Tables S1 – S5). A similar set of ions was observed during a typical *Ficus cyathistipula* experiment.

From inspection of Fig. 5(a) and (b), the dominance of isoprene in the *Ficus benjamina* system is clear, with 12.3 (± 4.1) ppbV isoprene detected in the reaction chamber at lights on, compared to 0.8 (± 0.4) ppbV monoterpenes, 0.5 (± 0.9) ppbV
sesquiterpenes and an estimated 2.7 (± 0.6) ppbV camphore. Speciation of the
monoterpenes by GC-MS indicated that the most dominantly emitted C10 compounds
for Ficus benjamina were α-pinene, limonene, sabinene and linalool and for Ficus
cyathistipula were α-pinene, β-pinene and limonene (Table 2). The sequiterpenes, β-
caryophyllene and α-cubebene were also identified.

Products of isoprene were observed to dominate the evolving Ficus benjamina and
Ficus cyathistipula oxidation systems, with the isobaric primary species MACR and
MVK comprising the strongest signals (measured together at m/z 71). For example,
during the Ficus benjamina experiment of 23/06/09, a combined peak MACR + MVK
mixing ratio of 2.9 (± 0.7) ppbV was observed (Fig. 5c).

Along with MACR and MVK, a series of other ions also associated with isoprene
oxidation were detected during Ficus benjamina oxidation, including m/z 117 and 99
(4-hydroxy-2-methyl-but-2-enoic acid), 103 (C5-alkenediols, C4-hydroxydialdehydes
and MPAN), 87 (C4-hydroxycarboxyls and methacrylic acid), 83 (3-methyl furan), 75
(hydroxy acetone) and 31 (formaldehyde). Additionally, a signal of m/z 101 was also
measured, possibly corresponding to the sum of a series of C5-hydroxycarboxyls and
C5-hydroxy hydroperoxides (Tuazon and Atkinson, 1990; Paulson and Seinfeld,
1992; Jenkin et al., 1997; Benkelberg et al., 2000; Sprengnether et al., 2002,
Benkelberg et al., 2000; Zhao et al., 2004; Surratt et al., 2006;
http://mcm.leeds.ac.uk/MCM, v3.1). Of the signals observed, those of m/z 83 and 87
(tentatively assigned to be 3-methyl furan and C4-hydroxycarboxyls/methacrylic
acid), were the greatest in magnitude after MACR + MVK (Fig. 6). The temporal evolution of the sum of all of these products suggests that they are predominantly secondary in nature, forming in the chamber after MACR and MVK. They continued to increase in magnitude as the isoprene signal decreased and as the MACR + MVK signal began to fall (Figs. 5 and 6). During a typical Ficus benjamina experiment, the sum of these isoprene products was estimated to reach a peak mixing ratio of ~ 1.7 ppbV.

A series of lower molecular weight ions were also observed to evolve within the reaction chamber, including m/z 61 (acetic acid), 47 (formic acid), 45 (acetaldehyde), 33 (methanol) and 31 (formaldehyde). Each of these compounds has previously been associated with isoprene oxidation and/or with off-gassing from illuminated chamber walls. The m/z 43 and 46 signals, indicative of carbonyls and nitrates, respectively, were also observed to increase significantly during photo-oxidation, indicating the formation and evolution of such species with increasing experiment duration.

Besides ions pertaining to the oxidation products of isoprene, a number of spectral features typically derived from monoterpane oxidation products were also observed to form and evolve in the reaction chamber, including, m/z 151, 125, 109, 107, 93 and 91. To a first order approximation, the total peak quantity of oxidation products not believed to result from isoprene decay was estimated to be of the order 2 ppbV. However, it should be noted that the presence of isobaric interference in such a complex system, uncharacterised fragmentation, detection limits and the use of
pseudo and averaged calibration sensitivities, impose a certain level of unknown
uncertainty upon this final value.

3.2.2 Particle phase

Contrary to the immediate and abundant formation of new particles in the un-seeded
Betula pendula experiments, the total number of particles and total aerosol mass did
not increase above background levels after lights were turned on in the un-seeded
tropical Ficus benjamina experiments. Figure 7 shows the observed and wall-loss-
corrected particle mass concentration during two typical Ficus benjamina experiments
(22/06/09 and 23/06/09) along with a chamber background experiment. Owing to a
lack of particle nucleation in those experiments, the total particle number
concentration was too low for the wall loss correction (described in section 2.3) to be
implemented. Instead, the average of the wall loss constants determined for the
seeded experiments was used to calculate the wall loss corrected mass concentrations
reported in Figure 7.

Figure 8 shows the observed and wall-loss-corrected particle mass concentration for
ammonium sulphate seeded experiments using VOC emissions of Ficus benjamina
and Ficus cyathistipula, as well as a seeded background experiment. The mass at the
start of the experiment represents the initial ammonium sulphate mass. In order to
quantify the formation of SOA mass during these experiments, the mass increase
relative to the starting seed mass was determined in Figure 9 by subtracting the initial
ammonium sulphate seed mass from the total wall loss corrected mass. The same
calculation was also performed for the Betula pendula seeded experiment (07/07/09).

In contrast to the unseeded Ficus benjamina and Ficus Cyathistipula experiments, SOA mass was observed to form when a seed was present in the reaction chamber. The calculated SOA traces in Figure 9 illustrate a slower build-up of mass during the isoprene dominated Ficus benjamina (15/07/09) and Ficus Cyathistipula (30/06/09 and 02/07/09) experiments compared to the much faster SOA mass formation in the monoterpene dominated Betula pendula experiment. Peak masses of the order 1.3 – 5.5 µg m\(^{-3}\) were observed, which when employed with the methodology described in section 3.1.2, produce SOA yields of 10 and 14 % for each of the two Ficus Cyathistipula experiments for which both gas and wall-loss-corrected aerosol data were available, i.e. 30/06/09 and 02/07/09, respectively (Fig. 9). Uncertainty in \(\Delta(\Sigma VOC)\) is estimated to be ± 47 % and in the size distribution measurements used in the wall loss calculations, of the order of ± 2 %. The uncertainties in the wall-loss correction will likely be substantially greater, but remain unquantified at present.

**Discussion and Conclusions**

**4.1 Betula pendula**

In this study we coupled a plant chamber to a photochemical reaction chamber in order to investigate secondary organic aerosol production from a biogenically consistent mixture of biogenic volatile organic compounds. We studied silver birch...
(Betula pendula), which emits predominantly monoterpenes, with some sesquiterpenes and oxygenated VOCs but only trace isoprene (Table 2, Fig 3).

Our Betula pendula experiments showed significant SOA formation (Fig. 4) both in the presence and absence of an ammonium sulphate seed, and reproduced the rate of production and growth of SOA observed in earlier published studies (Mentel et al., 2009; Carlton et al., 2009; e.g. VanReken et al., 2006; Hallquist et al., 2009; Kiendler-Scharr et al., 2009a; Kiendler-Scharr et al., 2009b).

The SOA yield values of 39 and 26 % obtained here for Betula pendula compare reasonably well with those reported within the literature for single precursor work conducted under similar conditions. For instance, for the two most abundant monoterpenes emitted by Betula pendula, i.e. α-pinene and β-pinene, single precursors yields of the order 1 – 43 (16) and 3 – 30 %, respectively, have been observed (values given in parenthesis were obtained from the Manchester aerosol chamber). Similarly for other common monoterpenes such as limonene, myrcene, Δ3-carene and α-terpinene, SOA yields of 9 – 34, 6 – 43 (15), 2 – 38 and 8 – 25 %, respectively, have been reported and for β-caryophyllene, 37 – 79 (50) % (Lee at al., 2006a and references therein; Alfarra at al., 2012). 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 roughly in the middle of the single precursor yield range.
As can be seen from inspection of Fig. 3, the transfer of mass through the *Betula pendula* experiment appeared roughly conservative, with a small and steady loss of measured mass from the reaction matrix 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.

Certain insights into the mechanisms of SOA formation and growth during the *Betula pendula* experiments can be obtained through a combined examination of the VOC
The data in Fig. 10 demonstrates that during oxidation of the *Betula pendula* emissions and in absence of a seed, SOA mass evolution can be roughly split into two phases. In the early stages of the experiment after nucleation, SOA mass growth increased somewhat rapidly with respect to the amount of precursors reacted; however, after roughly 30% of the initial precursor mass had been consumed, the rate of mass growth with respect to VOC precursor consumption was observed to reach an approximate steady state. When ammonium sulphate seed was present within the chamber, there was a similarly rapid initial growth with respect to VOC consumption, however this time subsequent aerosol evolution was characterised by a roughly linear mass increase to a much higher final mass by the end of the experiment. Considering the various species of precursor VOCs detected in the *Betula pendula* plant chamber air, and the relative lifetimes of these VOCs, it would seem possible that initially the shorter-lived sesquiterpenes react to form a significant proportion of the high mass, nucleating/condensing species, before being removed from the system (e.g. Jenkin et al., 2012). Subsequent aerosol mass formation as the air in the reaction chamber ages towards the central phase of the experiment, is then likely to result from the partitioning of relatively more volatile products formed from slower reacting monoterpenes, e.g. products such as pinic and pinonic acid from α-pinene oxidation (e.g. Jenkin, 2004; Camredon et al., 2010), and products such as the primary acyclic unsaturated aldehydes, (m/z 111 + 93); the temporal profile of which demonstrates
gas-phase loss concomitant with wall-loss-corrected aerosol growth reaching a steady state.

Further understanding of the composition and evolution of SOA typical of temperate plant environs comes from investigation of Figure 11, which shows the evolution of the fraction of the ratio of more/less oxygenated material present in the aerosol during the initial stages of a typical unseeded *Betula pendula* experiment (06/07/09). Figure 11 was constructed using the ratio of m/z 44 to 43 obtained from the AMS (i.e. f44/43, where m/z 44 is derived from “more” oxidised material and m/z 43 from “less” oxidised material, Ng et al., 2010). In this instance, the f44/43 ratio exhibits linear growth with time, from a value of ~ 0.8 to ~ 1.1, suggesting an increase in the oxygenated content of the aerosol as the experiment ages. Such an increase in oxygenated content is generally observed when precursor species contain multiple C=C bonds (e.g. ocimene and myrcene), offering significant potential for higher aerosol O:C composition (e.g. perhaps species such as acyclic unsaturated aldehydes and their subsequent generations of products). Indeed, the evolution of the f44/43 ratio observed here is consistent with those results obtained from single precursor experiments investigating the acyclic monoterpene, myrcene and the sesquiterpene, β-caryophyllene (Alfarra et al., 2012; Alfarra et al., 2013).

Off-line compositional analysis of the SOA collected at the end of the *Betula pendula* experiments supports the findings obtained from the on-line gas phase and bulk aerosol composition data. The LC-MS² analysis produced chromatograms with peaks
matching those seen in comparable single precursor BVOC experiments, with tracer compounds of both sesquiterpene and monoterpene SOA, detected (Fig. 12). Amongst the compounds observed were those of molecular weight (MW) 238, 242, 254 and 256, corresponding to 4-(3,3-dimethyl-2-(3-oxopropyl)cyclobutyl)pent-4-enoic acid, 3-(3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)-3-hydroxypropanoic acid, β-nocaryophyllumic acid/β-caryophyllinic acid and β-nocaryophyllinic acid, respectively, produced during β-caryophyllene oxidation (e.g. Alfarra et al., 2013) and MW 184, corresponding to cis-pinonic acid, produced during α-pinene oxidation. Many other terpene oxidation tracers were detected, including compounds of molecular weight 118 and 200, which are also prevalent in SOA obtained from single precursor myrcene experiments. This observation is in line with findings obtained from the gas phase data, which suggest a relatively significant presence of gaseous acyclic unsaturated aldehydes that would originate from acyclic unsaturated terpenes, such as myrcene.

4.2 Tropical species

In addition to Betula pendula, we studied three tropical plant species: two figs (Ficus benjamina and Ficus cyathistipula) and one palm (Caryota millis); in this work, we focus on results obtained from the fig plants. All three tropical species were found to be strong isoprene emitters, with very much smaller emissions of monoterpenes, sesquiterpenes, and oxygenated VOCs (Table 2, Fig. 6).
During the tropical plant experiments, the primary gas-phase isoprene oxidation products MACR, MVK, formaldehyde, isoprene hydroxy hydroperoxides and the secondary product hydroxyacetone were all observed (e.g. Figs. 5 and 6 and Tables S4 and S5 in the supplementary information). MACR, the isoprene hydroxy hydroperoxides (isoprene epoxide (IEPOX) and isoprene hydroperoxide (ISOPOOH)) and hydroxyacetone are all believed to be precursors to SOA formation (Jaoui et al., 2010; Carlton et al., 2009; Kleindienst et al., 2009; Paulot et al., 2009; Kleindienst et al., 2007; Lee et al., 2006; Kroll et al., 2006; Surratt et al., 2006; Claeys et al., 2004b; Rollins et al., 2009; Robinson et al., 2010). In this study, with the exception of MACR and MVK, these products all formed at yields lower than those previously reported (Table 3), with MACR + MVK, hydroperoxides, hydroxy acetone and formaldehyde being observed to form in yields of 17 – 36, 1 – 3, 0 – 2 and 2 – 7 %, respectively during our work. This disagreement may result from differences in OH concentrations and NOx concentrations in each of the experimental studies. Other isoprene products tentatively identified from the CIR-TOF-MS and PTR-MS data include, C5-alkenediols, C4-hydroxycarbonyls/methacrylic acid and 3-methyl furan (Table S4), which have also previously been associated with SOA formation (e.g. Claeys et al., 2004; Surratt et al., 2006; Robinson et al., 2010). For a typical Ficus benjamina experiment (23/06/09) the sum of these and other potential isoprene products, excluding MACR + MVK, was estimated to have a combined gas phase yield of the order 18 % (Fig. 5).
As can be seen in Fig. 6 mass transfer through the *Ficus benjamina* system was characterised by a slight mass decrease 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 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.

Despite the detection of a number of first- and second-generation gas phase products that have previously been directly linked with isoprene SOA composition (Claeys et al., 2004; Wang et al., 2004; Edney et al., 2005; Surratt et al., 2006; Healy et al., 2008), there was no accompanying evidence of SOA formation from the isoprene-emitting tropical plants during unseeded, nucleation style experiments (Fig. 7). 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 (e.g. Kroll et al., 2006). Another potentially significant contributing factor in suppressing SOA formation during these experiments was our relatively low VOC/NO\textsubscript{x} ratio and the resultant gas phase chemistry. In the presence of high (i.e. ppbV-level) NO\textsubscript{x} mixing ratios, RO\textsubscript{2} radicals react with NO to produce mainly alkoxy (RO) radicals. For low molecular mass VOCs such as isoprene, these RO radicals generally fragment into smaller, more volatile products that do not easily partition from the gas phase to the aerosol phase, resulting in a low SOA yield (Surratt et al., 2010). Conversely, under low NO\textsubscript{x} conditions, RO\textsubscript{2} radicals are known to undergo self- and cross-reactions to produce organic peroxides and hydroperoxides of relatively low volatility. For example, Surratt et al. (2010) showed that under high NO\textsubscript{x} conditions the yield of the potentially SOA forming gas phase IEPOX was reduced with respect to the equivalent value under low NO\textsubscript{x} conditions, where IEPOX formed in substantial yields (upward of 75 \%) from the further oxidation of ISOPOOH by OH.

In contrast to our unseeded Ficus experiments, when an ammonium sulphate seed was present (and following wall loss correction), SOA mass was observed to form and evolve within the reaction chamber (Fig. 9). From estimates of the total concentrations of precursor VOCs within the reaction chamber matrix (primarily isoprene, e.g. Fig. 5), an SOA mass yield of the order 10 – 14 \% was obtained for the *Ficus Cyathistpula* system. If it were to be assumed that the SOA were solely formed
from oxidation products of isoprene as the major emitted VOC, this yield would appear excessive in comparison with those obtained previously from single precursor isoprene studies, i.e. ~ 0.4 – 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; van Donkelaar et al., 2007; Kleindienst et al., 2009, 2007; Kroll et al., 2005, 2006; Claeys et al., 2004a; Edney et al., 2005; Brégonzio-Rozier et al., 2014). However, we must consider that the mesocosm system is in fact an ensemble of precursors, albeit an ensemble dominated by isoprene, analogous to ambient air above a tropical forested region (Hewitt et al., 2010; MacKenzie et al., 2011).

For the experiments of 30/06/09 and 02/07/09, for which SOA yields were obtained for the *Ficus Cyathistipula* system, a fraction of camphore was also observed in the air entering the reaction chamber (presumably for these two particular experiments, sesquiterpenes and monoterpenes were present at concentrations below the detection limits of the PTR-MS and CIR-TOF-MS). The concentration of camphore at lights on was estimated to be ~ 0.5 – 0.9 ppbV for the *Ficus cyathistipula* system and ~ 1.4 – 2.7 ppbV for *Ficus benjamina*, and the sum of all non-precursor ions in the CIR-TOF-MS mass spectrum > m/z 100 (indicative of non-isoprene-like oxidation products; excluding m/z 103 and 117) was estimated to be of the order 2 ppbV by the end of the experiments. This calculation approximates the m/z > 100 summation as one large, multifunctional analyte with a PTR sensitivity similar to pinonaldehyde (a typical, multifunctional, high MW molecule resulting from terpene oxidation).

Continuing this assumption and taking a range of known VOC terpene product yields
\( Y^p_{VOC} \) obtained from previous work at the Manchester chamber (i.e. \( Y^p_{VOC} = 100 \% \) the limiting case; 77 \% from \textit{Ficus Benjamina} oxidation; 55 \% from \textit{Betula Pendula} oxidation; and 29 \% for pinonaldehyde and \( \Sigma(I_{111}, I_{63}) \), a non-isoprene \( VOC_{\text{precursor}} \) concentration may be estimated. Taking a range of known SOA yields obtained from the same reaction chamber (i.e. \( \alpha \)-pinene, myrcene, linalool and \( \beta \)-caryophyllene; Alfarra et al., 2013), the SOA yield obtained here for the \textit{Betula pendula} system and the estimate of \( [VOC_{\text{precursor}}] \), Eqn. (2) may be solved to provide a crude estimate of the mass of SOA formed from non-isoprene precursors. Consequently, an estimate of the residual SOA mass derived from isoprene oxidation within the \textit{Ficus} system can be inferred for each of the experiments shown in Fig. 9.

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 \textit{ficus} experiments \( (M_p = 1.3 \ \mu g \ m^{-3} \text{ and } 5.5 \ \mu g \ m^{-3}) \), 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 \ \mu g \ 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 $Y_{SOA} = Y_{SOA} = \alpha$-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.

There are three principal reasons why the estimates of aerosol production from isoprene in the tropical plant experiments span such a large range. Firstly, the plants in the mesocosm emit a complicated mixture of biogenic VOCs, some of which are known to oxidise much more rapidly than isoprene and which will produce condensable compounds when oxidised. Secondly, these minor compounds co-emitted from principally-isoprene emitting tropical trees are imperfectly quantified because of the sensitivity of the chemical ionisation (PTR and CIR) instruments. Thirdly, these minor co-emissions are imperfectly characterised because many higher molecular weight compounds, such as the mono- and sesquiterpenes, are isobaric in the PTR and CIR instruments and so precise chemical structures cannot easily be assigned. Without better instrument detection sensitivity and high time resolution

Kevin Wyche 1/9/14 16:52

**Deleted:** For the majority (i.e. 78/120) of measurements and parameter sets (i.e. variables, $Y_{VOC}$ and $Y_{SOA}$) tested, the estimated residual SOA mass resulting solely from isoprene oxidation was negative, with values ranging from -28.5 $\mu$g m$^{-3}$ (30/06/09, $M_p = 1.3$ $\mu$g m$^{-3}$, assuming $Y_{VOC} = 29\%$ and $Y_{SOA}$ for non-isoprene precursors $Y_{SOA} = 47\%$) to -5.0 $\mu$g m$^{-3}$ (15/07/09, $M_p = 5.5$ $\mu$g m$^{-3}$, assuming $Y_{VOC} = 100\%$ and $Y_{SOA}$ for non-isoprene precursors $Y_{SOA} = 5\%$). That is, there are combinations of measurements and oxidation/phase-change parameters — omitting isoprene and its oxidation products — that can account for roughly 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. Taking $Y_{VOC} = 77\%$ and $Y_{SOA}$ = $Y_{SOA}$ for $\alpha$-pinene = 15\% as the closest approximation to the *Ficus cyathistipula* system, for the experiment of 30/06/09 for example, 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 but we note the great preponderance of combinations that do not require an isoprene contribution to the secondary organic aerosol mass (78 out of 120 measurement and parameter sets) under our experimental conditions and which produce much less SOA mass than would be expected from published experiments using individual mono- and sesquiterpenes.
chemical identification for the reactive compounds co-emitted with isoprene, it is not
possible to constrain further the aerosol yield from the tropical plants. Unfortunately,
insufficient SOA mass formed during *Ficus* experiments to allow us to conduct any
form of compositional analysis.

4.3 Atmospheric significance

Our results are specific to VOC/NO$_x$ ratios of 3 - 9 and NO$_x$ mixing ratios of ~
2 ppbV. Note, however, that the three reasons given above for the uncertainty in the
aerosol production ascribed to isoprene in our experiments will also pertain to field
measurements, often being exacerbated by variability and the difficulties of operating
in the field. A contribution of isoprene to SOA is supported by recent observations of
isoprene related SOA formation above the tropical forest of Danum Valley, Borneo, a
high isoprene, low NO$_x$ region (typical ratio of 20:1, isoprene/NO$_x$) (Hewitt et al.,
2010b). Robinson *et al* (2010) observed that up to 15 % by mass of atmospheric sub-
micron organic aerosol above the tropical forest of Danum Valley was comprised of
methyl furan, the most likely source of which is the oxidation of isoprene (*i.e.* thermal
decomposition of isoprene derived SOA) (Ruppert and Becker, 2000; Robinson *et al*.,
2010; Lin *et al*., 2012; Budisulistiorini *et al*., 2013). Although much smaller in
magnitude, the monoterpene emissions measured at Danum Valley were more than
adequate to account for the remaining sub-micron organic aerosol (MacKenzie *et al*.,
2011), just as in the majority of aerosol mass calculations for principally-isoprene-
emitting tropical trees, described above.
It has recently been proposed that isoprene can inhibit aerosol formation when present in air containing other potential SOA precursors, such as mono- and sesquiterpenes (Kiendler-Scharr et al., 2009a). Kiendler-Scharr et al. propose that isoprene could effectively act as an OH scavenger, suppressing new particle formation by slowing the oxidation of available monoterpenes (and presumably sesquiterpenes). In line with this thesis, interpretation of the results obtained from our seeded experiments with *Ficus* species leaves room for a potential role for isoprene in inhibiting SOA formation under certain atmospheric conditions, i.e. our results imply that isoprene may impact negatively on the overall SOA forming potential of air containing other biogenic SOA precursors. However, owing to the constraints laid upon our experiments by the instrumentation and apparatus employed, it is difficult to assign a given certainty level to the role played by isoprene in the ambient atmosphere and caution should be taken when interpreting such findings.

The fact that isoprene accounts for approximately 50% of the total global burden of non-methane VOC, (Guenther et al., 2006), would make it a significant contributor to global SOA. It has been estimated that, even if the secondary organic aerosol yield from isoprene is small (e.g. 1%), the overall contribution to total atmospheric aerosol could be up to 6 Tg yr\(^{-1}\) (Carlton et al., 2009). Van Donkelaar et al. (2007) found that using an isoprene SOA yield of 2% improved the relationship between model simulations and organic aerosol measurements, and contributed 10 – 50% of the total organic aerosol loading over the United States during the summer. 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 NOx 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).

Further to any such potential impacts imposed by isoprene, it has recently been shown that a range of other BVOC emissions, released in response to a range of environmental stress factors, can also have significant impacts on biogenic SOA formation and yield (Mentel et al., 2013). It has been shown that the emissions of sesquiterpenes, methyl salicylate and C17 BVOCs, released as a result of certain environmental stress factors have a net positive impact on SOA yield; whereas certain stress induced green leaf volatiles ((Z)-3-hexenol and (Z)-3-hexenylacetate) behave similarly to isoprene, suppressing SOA formation (Mentel et al., 2013).

Given the highly differing reported yields of isoprene SOA under various oxidant schemes, the uncertainty in the exact role played by isoprene and its oxidation products in realistic mixtures of VOCs (in particular in the context of SOA nucleation rates; Kiendler-Scharr et al., 2009) and the lack of knowledge regarding stress induced BVOCs, their atmospheric oxidation and their roles in biogenic SOA formation (and impact on chemical and physical properties), we suggest that there is a pressing requirement for additional, atmosphere-relevant laboratory and field studies to give us the necessary insight to successfully control biogenic SOA (Carlton et al., 2010).
Acknowledgements

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5 References


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Wang, W., G. Vas, R. Domnisses, K. Loones and M. Claeys (2004). "Fragmentation study of diastereoisomeric 2-methyltetrols, oxidation products of isoprene, as their


### Table 1: List of experiments conducted and their general parameters

<table>
<thead>
<tr>
<th>Date</th>
<th>Tree Species</th>
<th>Initial NOx/NOy ppbV</th>
<th>VOC/NOy x</th>
<th>Relative Humidity / %</th>
<th>Pre-existing Seed</th>
</tr>
</thead>
<tbody>
<tr>
<td>22/06/09</td>
<td>Ficus benjamina</td>
<td>3</td>
<td>4.2</td>
<td>79</td>
<td>None</td>
</tr>
<tr>
<td>23/06/09</td>
<td>Ficus benjamina</td>
<td>6</td>
<td>2.7</td>
<td>75</td>
<td>None</td>
</tr>
<tr>
<td>25/06/09</td>
<td>Ficus benjamina</td>
<td>2</td>
<td>6.3</td>
<td>65</td>
<td>Sulphate</td>
</tr>
<tr>
<td>29/06/09</td>
<td>Ficus cyanistipula</td>
<td>2</td>
<td>9.4</td>
<td>71</td>
<td>None</td>
</tr>
<tr>
<td>30/06/09</td>
<td>Ficus cyanistipula</td>
<td>2</td>
<td>7.8</td>
<td>75</td>
<td>Sulphate</td>
</tr>
<tr>
<td>02/07/09</td>
<td>Ficus cyanistipula</td>
<td>3</td>
<td>5.6</td>
<td>78</td>
<td>Sulphate</td>
</tr>
<tr>
<td>06/07/09</td>
<td>Betula pendula</td>
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</tr>
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<td>5.5</td>
<td>73</td>
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</tr>
<tr>
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<td>1.5</td>
<td>70</td>
<td>Sulphate</td>
</tr>
<tr>
<td>10/07/09</td>
<td>Betula pendula +</td>
<td>2</td>
<td>5.5</td>
<td>70</td>
<td>Sulphate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>36 ppbV isoprene</td>
</tr>
<tr>
<td>13/07/09</td>
<td>Ficus benjamina</td>
<td>2</td>
<td>7⁻¹</td>
<td>87</td>
<td>Sulphate</td>
</tr>
<tr>
<td>15/07/09</td>
<td>Ficus benjamina</td>
<td>3</td>
<td>7⁻¹</td>
<td>89</td>
<td>Sulphate</td>
</tr>
<tr>
<td>Date</td>
<td>Plant</td>
<td>Species</td>
<td>Concentration</td>
<td>Amount</td>
<td>Notes</td>
</tr>
<tr>
<td>---------</td>
<td>------------------</td>
<td>------------------</td>
<td>---------------</td>
<td>--------</td>
<td>------------------------</td>
</tr>
<tr>
<td>16/07/09</td>
<td>Ficus benjamina</td>
<td>+</td>
<td>4.5 ppbV</td>
<td>2</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>limonene</td>
<td></td>
<td>85</td>
<td>None</td>
</tr>
</tbody>
</table>

Notes:

1. No quantified VOC data available
Table 2: GC-MS identification of the biogenic VOC present in the plant chamber air immediately before RC filling began. Quantification of isoprene, total monoterpenes and total sesquiterpenes was carried out using PTR-MS and CIRMS (see Figures 2 and 5).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Compounds detected by GC-MS (abundance ppbV) (trace = &lt;0.1 ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Isoprene</td>
</tr>
<tr>
<td>B. Pendula</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.25-1.19)</td>
</tr>
<tr>
<td></td>
<td>ocimene (trace – 1.22)</td>
</tr>
<tr>
<td></td>
<td>Δ3-carene (1.89 – 4.94)</td>
</tr>
<tr>
<td></td>
<td>γ-terpinene (trace)</td>
</tr>
<tr>
<td></td>
<td>2, 4, 6-octatriene,2,6-dimethyl (trace)</td>
</tr>
<tr>
<td></td>
<td>4,7-methano-1H-indene,octahydro (trace)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Species</td>
<td>Presence</td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
</tr>
<tr>
<td><em>F. Benjamina</em></td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><em>F. Cyathistipula</em></td>
<td>Yes (75.08)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Mixed canopy</em></td>
<td>Yes</td>
</tr>
<tr>
<td></td>
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<tr>
<td><em>F. Benjamina</em></td>
<td></td>
</tr>
<tr>
<td><em>F. Cyathistipula</em></td>
<td></td>
</tr>
<tr>
<td><em>C. Millis</em></td>
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</table>
Table 3: Yields of isoprene oxidation products compared to literature values. Yields are an average from all *Ficus* experiments (seeded and unseeded) (n = 4) calculated at 4 hours after lights on (HALO). Yield is based on the calculated relationship between the amount of isoprene reacted and the oxidation product in question.

<table>
<thead>
<tr>
<th>Isoprene Hydroperoxides$^1$, MVK + MACR, Hydroxyacetone, Formaldehyde</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.33</td>
</tr>
<tr>
<td>1</td>
<td>0.05</td>
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<tr>
<td>1</td>
<td>0.33</td>
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<tr>
<td>1</td>
<td>0.46 – 0.60</td>
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<td>1</td>
<td>0.18</td>
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<td></td>
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<tr>
<td>1</td>
<td>0.27</td>
</tr>
<tr>
<td>1</td>
<td>0.01 – 0.17</td>
</tr>
<tr>
<td>Isoprene Hydroperoxides(^1)</td>
<td>MVK +MACR</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
</tr>
</tbody>
</table>

Notes:

1. Sum of isoprene epoxide (IEPOX) and isoprene hydroperoxide (ISOPOOH)
**Figure Captions**

Figure 1: Temporal evolution of NO, NO₂, NOₓ and O₃ during typical *Ficus Cyathistipula* (a) and *Betula pendula* (b) experiments (25/06/09 and 07/07/09, respectively).

Figure 2: Temporal evolution of a series of isoprenoid “precursor” compounds and their oxidation products, as observed in the main reaction chamber during an example *Betula pendula* experiment (07/07/09). The top panel (a) shows the entire experiment process in terms of monoterpene evolution, from background (BG) and plant chamber (PC) measurements, to reaction chamber (RC) fill and the main photooxidation experiment within the reaction chamber. Figure (b) shows monoterpene evolution, (c) shows sequiterpenes (red circles and lines) and camphore (black triangles and lines), (d) Σ(I₁₁₁, I₉₃) and (e) the primary ketone (m/z 139) (red circles and lines), primary keto-aldehyde (m/z 107 + 151 + 169) (black triangles and lines) and MVK + MACR (m/z 71) (grey diamonds and dashed line).
Figure 3: Evolution of measured 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. $\Sigma$VOCs + SOA) with time (black line, right axis). Note: ammonium sulphate seed mass removed from the SOA mass concentration.

Figure 4: Particle number and mass concentrations measured during nucleation (06/07/09) and ammonium sulphate seeded (07/07/09) *Betula pendula* experiments (a). In the bottom panel (b), both the measured (dashed lines) and the wall loss corrected (solid lines) mass concentrations are shown.

Figure 5: Temporal evolution of a series of isoprenoid “precursor” compounds and their oxidation products, as observed in the main reaction chamber during an example *Ficus benjamina* experiment (23/06/09). Panel (a) shows isoprene (red circles and lines) and camphore (black triangles and lines) evolution, (b) shows monoterpenes (red circles and lines) and sesquiterpenes (black triangles and lines), (c) MVK + MACR ($m/z$ 71) and (d) $\Sigma$(monoterpene products) (black triangles and lines) and $\Sigma$(non MVK+MACR isoprene products) (red circles and lines)

Figure 6: Evolution of measured mass through the *Ficus benjamina* system (23 June 2009), showing the relative contribution of precursor compounds and oxidation products.
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).

Figure 7: Observed and wall loss corrected particle mass concentrations during unseeded Ficus benjamina (22/06/09, 23/06/09) and chamber background (26/06/09) experiments. The reaction chamber was filled with plant chamber air over a period of 1 – 1.5 hours. Chamber filling was carried out in the dark. Ozone was added immediately prior to lights on. Time begins at the point at which the reaction chamber was illuminated, then increments in hours after lights on.

Figure 8: Observed and wall loss corrected particle mass concentrations during ammonium sulphate seeded Ficus benjamina (15/07/09), Ficus cyathistipula (30/06/09, 02/07/09) and chamber background (03/07/09) experiments. Ozone and ammonium sulphate seed were added immediately prior to lights on.

Figure 9: Calculated SOA mass concentrations during ammonium sulphate seeded experiments for Betula pendula (07/07/09), Ficus benjamina (15/07/09) and Ficus cyathistipula (30/06/09, 02/07/09). See text for details.
Figure 10: Time dependent growth curves for two typical *Betula pendula* experiments (red circles- nucleation experiment on 06/07/09 and black triangles- ammonium sulphate seeded experiment on 07/07/09), showing SOA growth behaviour with respect to consumption of the VOC precursors.

Figure 11: Temporal evolution of the *m/z* 44/43 ratio (red circles) during a typical *Betula pendula* experiment (06/07/09) and wall loss corrected SOA mass (black line); demonstrating the increase in oxygenated content of the SOA as the air matrix begins to age.

Figure 12: LC-MS$^2$ selected ion chromatograms derived from the off-line analysis of SOA collected on filters at the conclusion of a typical *Betula pendula* experiment (07/07/2009). Notes: Upper; *m/z* 183 = MW 184, 1 = cis-pinonic acid. Middle; *m/z* 253 = MW 254, 2 = β-nocaryophyllonic acid, 3 = β-caryophyllinic acid, 4 = similar to sesquiterpene SOA. Lower; *m/z* 257 = MW 118 [2*[M-H] + Na]$^-$, also seen in myrcene SOA, with same MS$^2$ spectra.