Linking biogenic hydrocarbons to biogenic aerosol in the Borneo rainforest

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Abstract. Emissions of biogenic volatile organic compounds are thought to contribute significantly to secondary organic aerosol formation in the tropics, but understanding these transformation processes has proved difficult, due to the complexity of the chemistry involved and very low concentrations. Aerosols from above a Southeast Asian tropical rainforest in Borneo were characterised using liquid chromatography–ion trap mass spectrometry, high-resolution aerosol mass spectrometry and Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) techniques. Oxygenated compounds were identified in ambient organic aerosol that could be directly traced back to isoprene, monoterpenes and sesquiterpene emissions, by combining field data on chemical structures with mass spectral data generated from synthetically produced products created in a simulation chamber. Eighteen oxygenated species of biogenic origin were identified in the rainforest aerosol from the precursors isoprene, α-pinene, limonene, α-terpinene and β-caryophyllene. The observations provide the unambiguous field detection of monoterpene and sesquiterpene oxidation products in SOA above a pristine tropical rainforest. The presence of 2-methyl tetrod organosulfates and an associated sulfated dimer provides direct evidence that isoprene in the presence of sulfate aerosol can make a contribution to biogenic organic aerosol above tropical forests. High-resolution mass spectrometry indicates that sulfur can also be incorporated into oxidation products arising from monoterpene precursors in tropical aerosol.

1 Introduction

Tropical and equatorial forests account for over half of the world’s forests and play a crucial role in climate regulation, through their interaction with solar radiation and hydrological cycle, and as a source of precursors of cloud condensation nuclei. Globally, tropical forests are estimated to emit ~500 Tg C yr⁻¹ as biogenic volatile organic compounds (BVOC) to the atmosphere, half of the global BVOC emission (Guenther et al., 1995, 2006: global total 1150 Tg C yr⁻¹). Atmospheric oxidation of BVOCs by the hydroxyl radical, ozone and nitrate radical leads to the formation of more oxidised compounds, which can lead to the formation of secondary organic aerosol (SOA). The majority of studies of organic aerosol composition in forested regions have taken place in boreal (Kristensen and Glasius, 2011; Kallio et al., 2006) and temperate forests (Gomez-Gonzalez et al., 2012; Surratt et al., 2007; Wang et al., 2008) of the Northern Hemisphere. The tree species found in tropical rainforests are very different, being dominated by lowland evergreen broadleaf rainforest. There are relatively limited reported studies of the interaction between tropical forests and atmospheric chemistry, with the majority of these studies taking place in Amazonia (Martin et al., 2010; Andreade...
et al., 2002), a small number in Africa (Capes et al., 2009; Redelsperger et al., 2006) and very little in Southeast Asia. The rainforest of Amazonia is a large inland forest, whereas SE Asia is a complex series of islands, with rainforests that are in much closer proximity to the maritime environment. Predictably the architecture and taxonomy of trees are also different, with SE Asian forest being dominated by the family Dipterocarpaceae (Whitmore, 1984).

The multinational OP3 (Oxidant and Particle Photochemical Processes above a south-east Asian tropical rainforest) project and the ACES (Aerosol Coupling in the Earths System) project had the aim of better understanding the complex links between the biosphere, atmospheric composition and climate (Hewitt et al., 2010). Two highly instrumented, intensive measurement campaigns were carried out at the Global Atmospheric Watch station, in Danum Valley, Sabah, Borneo. This is situated within a region that was selectively timber harvested in 1988 (Tangki and Chappell, 2008) and is around 5 km from the protected forest area known as the Danum Valley Conservation Area (DVCA). Measurements of BVOCs taken as part of the OP3 project indicated that the dominant BVOC species observed was isoprene, with an average ground level mixing ratio of around 1 ppb and a maximum value of 2.5 ppb (Jones et al., 2011). Speciated monoterpenes and sesquiterpenes present that were not analysed using the GC-FID technique of Jones et al. (2011).

Even when aerosol measurements have been made, surprisingly little is known about the composition of BSOA in tropical forests due to the generally low levels of OA encountered and the highly complex chemical nature of the OA matrix. During the OP3 study presented here, Robinson et al. (2011a) used positive matrix factorization on high-resolution aerosol mass spectrometer (HR-AMS) data and identified an AMS factor, 82Fac, that was linked to isoprene oxidation products and which corresponded to an average of 23 % (0.18 µg m$^{-3}$) and reaching as much as 53 % (0.50 µg m$^{-3}$) of the total organic loading. This AMS factor provided some insight into an active role for isoprene but without chemical structures made it impossible to determine the chemistry involved. Isoprene SOA tracer compounds 2-methyl tetrols have been measured in aerosol collected in a tropical rainforest, although they constituted a very small fraction of the total aerosol mass (Claeys et al., 2004). There remains rather limited knowledge of the mechanisms by which monoterpenes contribute to BSOA formation in tropical forests in contrast to a number of studies published on boreal locations; although monoterpenes may be present in much lower gas phase abundance here compared to isoprene, they may have significantly higher aerosol yields. During the day monoterpenes react with hydroxyl radicals and ozone and during the night with ozone and NO$_3$ radicals to form oxidised reaction products. There have been many lab-based studies of these reactions and a large amount of information on their oxidation products is available in the published literature, but there is only very limited evidence of the occurrence of these in real-world ambient aerosol. Additionally in a tropical rainforest there are likely to be emissions of sesquiterpenes, which have also been implicated in new particle formation (Bonn and Moortgat, 2003).

This paper reports our investigation of the links between BSOA and a range of BVOC precursors, with the aim of better understanding organic aerosol formation in tropical rainforests. Using photochemical reaction chamber experiments, synthetic BSOA was initially produced from a series of biogenic precursors believed to be present in Danum Valley, based on previous taxonomic studies. These proxy-aerosols were used to generate representative organic chemical tracers and associated mass spectra of BSOA that could be linked to specific BVOCs precursors. The synthetic step has been essential, since most biogenic oxidation products are not commercially available. Aerosol samples were collected at the WMO Bukit Atur Global Atmospheric Watch station (GAW), Sabah, in Malaysian Borneo (4.981° N, 117.844° E) during June and July 2008 and analysed using off-line techniques, including liquid chromatography coupled to electrospray ionisation ion trap mass spectrometry (LC-MS$^2$) and Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS).

2 Experimental

2.1 Offline aerosol analysis

Particles less than 2.5 µm were collected onto pre-fired 47 mm quartz filters using a Partisol Plus 2025 (Thermo) with a PM$_{2.5}$ impactor. Twenty-four hour samples were collected at two locations from midnight to midnight local time. Eleven samples were collected between 28 June 2008 and 9 July 2008 at 10 m on a hill surrounded by forest, effectively at canopy top height at the Bukit Atur GAW station. An additional eleven samples were collected between the 12 July 2008 and 23 July 2008, at a site within the forest canopy at a height of 2 m. Full details on the site locations can be found in (Hewitt et al., 2010). Filters were transported at sub zero temperatures and stored in a freezer at –20 °C until analysis. Approximately an area of 7/8th of the filter sample was extracted into high purity water, filtered and reduced to 1 mL using a vacuum solvent evaporator (Biotage, Sweden) and the remaining portion retained for other analysis. The water soluble compounds were analysed initially using liquid chromatography–ion trap mass spectrometry (LC-MS/MS). Reversed phase LC separation was achieved using
Fig. 1. Total ion chromatograms for LC-MS analysis in negative ionisation mode. Black: OP3_all extract from filters collected at the Bukit Atur, Borneo, site. Red: blank control sample. Many of the peaks after 45 minutes are contaminants from the methanol used in the LC analysis.

an HP 1100 LC system equipped with an Eclipse ODS-C \(_{18}\) column with 5 µm particle size (Agilent, 4.6 mm × 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 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\(^{-1}\). Two different separations were carried out for each sample, one with positive MS ionisation and one in negative ionisation, scanning from \(m/z\) 50–600 and with automatic selection of the three most abundant ions for MS\(^2\) by collision induced dissociation (CID). Negative ionisation has been used as the primary means of identification of tracers since the positive ionisation mode resulted in the formation of sodium adducts, which generally produced few diagnostic ions when subjected to CID.

The detection limit of the LC-MS\(^2\) method was found to be rather high for the daily ambient samples and it was difficult to obtain product ion mass spectra. The instrument was thoroughly cleaned and subsequently optimised using a \(cis\)-pinonic acid standard (20 ppb) to improve the sensitivity. The remaining pieces of each filter left over from the other analysis were combined to give one high concentration extract for the entire campaign, labelled here as rainforest OA extract. This extract was redissolved in 200 µl of solvent only, which was sufficient to carry out a LC-MS\(^2\) analysis in positive and negative ionisation mode and a direct infusion on the FTICRMS. The extract now shows many peaks and an increased baseline over the blank chromatogram, a result of the co-elution of many low concentration species, as shown in Fig. 1.

Samples were also analysed at high mass resolution using a Bruker APEX 9.4 T Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Extracts were sprayed at a flow rate of 2 µL min\(^{-1}\), into an Apollo II electrospray interface with ion funnelling technology. Spectra were acquired in both positive and negative ion mode over the scan range \(m/z\) 100–3000 using the following MS parameters: nebulising gas flow: 0.9 L min\(^{-1}\); drying gas flow: 5 L min\(^{-1}\); drying temperature: 190 °C; collision cell accumulation: 0.05–0.5 s; and data acquisition size: 2 Mb (yielding a target resolution of 130 000 at \(m/z\) 400). Data were analysed using DataAnalysis 4.0 software (Bruker Daltonics, Bremen, Germany). The instrument was calibrated using protonated
(positive ion mode) or deprotonated (negative ion mode) arginine clusters. The mass spectra were internally recalibrated with a series of prominent peaks. Background contaminants also seen in pure water and blank extracted filters were identified.

The MS software uses a user defined set of conditions to determine the molecular formulae. In this case the following molecular configurations were allowed; unlimited numbers of C, H and O, 0–3 nitrogen and 0–1 sulfur. Chemical formulae were assigned to the masses of singly charged ions 100 < m/z < 600 after internal recalibration using fatty acid signals and a maximum error of 10 ppm for ions with a relative intensity of greater than 0.01 %. Isotopic ratios were used for further confirmation of the formulae. Background contaminant peaks also seen in pure water and blank extracted filters were manually removed from the analysis.

2.2 Simulation chamber experiments

Simulation chamber experiments were used to generate aerosols that could subsequently be used to aid in the identification of biogenic SOA tracer compounds. The Manchester aerosol chamber used for these experiments is a 18 m$^3$ (3 m (H) × 3 m (L) × 2 m (W)) FEP Teflon bag mounted on three rectangular aluminum frames. The air charge in the bag was dried and filtered for gaseous impurities and particles using a combination of Purafil, charcoal and HEPA filters, prior to humidification with ultrapure deionised water. Precursor VOCs were introduced into the chamber through injection into a heated gas bulb fed with a flow of high purity nitrogen. NO$_x$ levels were controlled by injection from a cylinder into the charge line and a high capacity O$_3$ generator was employed to control initial O$_3$ concentrations as well as serving as a cleaning agent during flushing between experiments. A series of halogen lamps and a 6 kW Xenon arc lamp were used to irradiate the chamber and initiate OH chemistry. Full details can be found in (Hamilton et al., 2011). Experiments were carried out at 25°C and nominal relative humidity of 50–70 %. A complete list of chamber experiments used to determine tracer compounds is shown in Table 1. For example, pinonic acid is seen in our field samples, despite the difference in NO$_x$ regimes. The chamber filters were extracted into water and analysed using the same LC-MS$^2$ method as the field filters. A large number of peaks were seen in each SOA sample. The addition of LC allows monoterpene oxidation product isomers, with the same m/z but different structures to be separated. An example of this are the isomers with MW = 168 Da, where pinonaldehyde (from α-pinene), limonalddehyde (from limonene) and α-terpininaldehyde (from α-terpinene) have different retention times and product ion mass spectra, allowing them to be differentiated. For each single precursor, there are often over a hundred isolated species and a structural analysis of the SOA components is very time consuming. Rather than attempt a structural characterisation of each compound, instead, an SOA library has been constructed (ACES library), containing the basic mass spectrum of each isolated SOA component.

A series of scripts were designed for use with the Bruker Compass Automation Engine Software. The first script plots extracted ion chromatograms for a user defined range of m/z values, then carries out peak finding and integration. The peaks are labelled with their retention time and the associated product ion mass spectrum of the peak (MS$^3$). The second script exports each peak into the ACES library, labelled by its retention time and precursor. For example, pinonic acid is found in the library under the label “26.5 apine”. Using this biogenic VOCs. The BVOCs chosen for synthetic production in the chamber were based on knowledge gained from leaf cuvette measurements of the dominant tree species in a 300 m$^2$ footprint of the GAW tower (S. Owen, personal communication, 2010) and represented a range of reactivities and functionalities. Seven chemical species were chosen, including isoprene, monoterpenes (α-pinene, limonene, myrcene, α-terpinene), oxygenated monoterpene (linalool) and a sesquiterpene (β-caryophyllene). Photo-oxidation experiments using approximately 50 and 250 ppb initial BVOC precursor concentrations were carried out at the Manchester Aerosol Chamber for each species as shown in Table 1. For limonene and β-caryophyllene, filters were also collected at 2, 4 and 6 h to investigate the effect of ageing (Alfarra et al., 2012). Experiments were carried out at relatively high NO$_x$ levels (VOC:NO$_x$ ∼2) and so a direct comparison of the overall composition distribution between the chamber samples and the field samples (VOC: NO$_x$ ∼100) is not possible. The higher NO$_x$ levels in the chamber will inevitably lead to some differences in the reaction mechanism. This has been seen in the case of isoprene where at low NO$_x$, RO$_2$ + RO$_2$ and RO$_2$ + HO$_2$ reactions dominate and at high NO$_x$, RO$_2$ + NO reactions dominate. However, towards the end of the experiment, when all NO has been converted to NO$_2$/NO$_y$, any remaining BVOC will react with ozone and OH under more relevant conditions. Therefore, oxidation products formed under low NO$_x$ conditions should also be present and thus can act as tracers for a specific BSOA precursor in our field samples, despite the difference in NO$_x$ regimes.
system, all peaks are inserted into the library, rather than just the structurally identified species. The library also includes peaks from control samples, including water, methanol and blank filters extracted in the same way as the samples, to allow any background contaminants to be removed. Finally, a third script compares the field samples to the library and identifies any matches based on a series of user defined conditions.

The field samples were compared to the chamber samples using the library and the retention time and MS² of each identified species was also manually compared to the chamber samples to ensure the library was functioning properly. Peaks also found in the blank samples have been ignored. Additional SOA tracer species, such as organosulfates, identified in previous literature as constituents of OA in forest locations, but not found in our chamber SOA, have also been investigated by manually studying the LC-MS² data using extracted ion chromatograms. In total, eighteen SOA tracer compounds were found in the Borneo rainforest OA extract. A list of the molecular weight, retention time (tR), MS² product ions observed and the suggested hydrocarbon precursor of the BSOA tracer compounds are shown in Table 2. The similarity of each BSOA tracer mass spectrum to the corresponding library spectrum are given in Table 1 as the Fit and Reverse Fit (Rfit) parameters out of 1000 (where 1000 is a perfect match both in terms of m/z present and their intensities, further details in SI Appendix). The majority of identified species have Fit and RFit values greater than 900 indicating the BSOA tracer has a very good fit to the library spectrum and visa versa. Retention time matching was also applied, with a maximum deviation of 1 min allowed, although the compounds identified here have a maximum deviation of only 0.2 min from the associated chamber peak.

In order to structurally identify the common oxygenated tracer compounds, commercially available standards and literature product ion mass spectra were used where available. In addition, some compounds were tentatively identified based on their MS² product ions. Single ion chromatograms for the BSOA tracer ions found in the Borneo OA sample are shown in the Supplement Fig. 1. The Borneo OA chromatograms are complex, indicating that there may be additional BSOA tracers from other monoterpenes and sesquiterpenes that have not been identified. The product ion mass spectra for all eighteen compounds are given in the Supplement Figs. S2–18. Where compounds have been identified based on MS² patterns, the high resolution FTICRMS data was used to determine if a matching component of the correct molecular formula was present. Molecular formulae matching all of the identified BSOA tracers were found with calculated mass accuracies below 0.7 ppm, well within acceptable errors, and are given in Table 2 along with the measured m/z and error (ppm).

Table 1. Experimental details of chamber experiments used to build the mass spectral library.

| Exp Date       | Exp # | SOA Precursor | [VOC]³ | [NO₃]₀ | RH² (± sd) (%) | Temp²(± sd) (°C) | Duration (h) | Peak mass concentration³ | Peak number concentration⁴ |
|----------------|-------|---------------|--------|--------|---------------|------------------|--------------|--------------------------|-----------------------------|
| 12.03.2008     | 1     | β-caryophyllene | 50     | 34     | 53.9 ± 0.6    | 25.3 ± 0.2       | 04:04        | > 21.6                   | 2.63 × 10⁴                   |
| 13.03.2008     | 2     | β-caryophyllene | 250    | 117    | 49.4 ± 0.6    | 24.9 ± 0.3       | 04:03        | > 130.3                  | 3.39 × 10⁴                   |
| 19.03.2008     | 3     | Limonene      | 250    | ~40    | 51.2 ± 0.2    | 25.0 ± 0.1       | 06:00        | > 33.4                   | 1.45 × 10⁴                   |
| 28.03.2008     | 4     | Limonene      | 250    | 124    | 53.7 ± 0.3    | 25.1 ± 0.1       | 04:02        | > 140.1                  | 3.45 × 10⁴                   |
| 08.04.2008     | 5     | Limonene      | 250    | 136    | 53.5 ± 0.3    | 25.3 ± 0.1       | 02:02        | > 128.2                  | 3.65 × 10⁴                   |
| 10.04.2008     | 6     | β-caryophyllene | 250    | 130    | 49.2 ± 0.2    | 24.7 ± 0.1       | 02:00        | > 125.3                  | 2.97 × 10⁴                   |
| 16.04.2008     | 7     | β-caryophyllene | 250    | 128    | 44.4 ± 0.7    | 26.1 ± 0.3       | 06:02        | < 220.0                  | 3.56 × 10⁴                   |
| 17.04.2008     | 8     | Limonene      | 250    | 142    | 49.1 ± 0.8    | 26.3 ± 0.3       | 06:02        | < 382.4                  | 3.26 × 10⁴                   |
| 22.04.2008     | 9     | Limonene      | 50     | 54     | 54.3 ± 0.2    | 25.2 ± 0.1       | 02:00        | < 52.2                   | 1.51 × 10⁴                   |
| 23.04.2008     | 10    | β-caryophyllene | 50     | 31     | 53.4 ± 0.7    | 25.4 ± 0.3       | 02:00        | < 50.1                   | 2.94 × 10⁴                   |
| 24.04.2008     | 11    | β-caryophyllene | 50     | 28     | 47.9 ± 0.9    | 25.4 ± 0.4       | 05:58        | < 65.6                   | 2.48 × 10⁴                   |
| 28.04.2008     | 12    | Limonene      | 50     | 32     | 53.6 ± 0.6    | 25.3 ± 0.2       | 04:01        | < 31.1                   | 1.67 × 10⁴                   |
| 16.06.2008     | 13    | Myrcene       | 50     | 31     | 53.6 ± 2.4    | 25.8 ± 1.1       | 03:03        | 18.5                     | 5.47 × 10⁴                   |
| 17.06.2008     | 14    | Myrcene       | 250    | 137    | 51.3 ± 2.7    | 26.0 ± 1.3       | 06:00        | < 134.8                  | 1.62 × 10⁵                   |
| 20.06.2008     | 15    | Linalool      | 50     | 29     | 48.9 ± 0.4    | 25.4 ± 0.2       | 06:00        | < 7.4                    | 6.54 × 10⁴                   |
| 23.06.2008     | 16    | Linalool      | 250    | 122    | 52.7 ± 1.6    | 24.6 ± 0.7       | 06:03        | < 53.2                   | 1.8 × 10⁵                    |
| 07.07.2008     | 17    | Isoprene⁵     | 300    | 36     | 68.5 ± 1.3    | 26.9 ± 0.3       | 04:00        | < 15.66                  | 2.38 × 10⁴ ⁶                   |
| 10.07.2008     | 18    | Limonene⁶     | 50     | 75     | 71.9 ± 1.0    | 25.6 ± 0.3       | 07:30        | < 44.88                   | 4.44 × 10⁴ ⁸                   |
| 11.07.2008     | 19    | α-Pinene      | 50     | 34     | 71.4 ± 1.5    | 25.6 ± 0.5       | 06:00        | < 11.9                   | 3.92 × 10⁴                   |
| 25.04.2008     | 20    | Background    | Nil    | 82.7    | 52.2 ± 0.7    | 25.5 ± 0.3       | 06:00        | < 0.3                    | 1.04 × 10³                   |

¹ Nominal concentration values estimated based on the amount introduced into the chamber without accounting for losses.
² Average value for the experiment duration.
³ Measured by a differential mobility particle sizer (DMPS) and assuming a particle density value of 1.3 g cm⁻³.
⁴ Measured by a water based condensation particle counter (wCPC 3785, TSI Inc., USA).
⁵ On ammonium sulfate seed particles.
⁶ Peak values for the seed particles, not for isoprene SOA.
⁷ On β-caryophyllene SOA seed particles.
⁸ Peak values for the total seed and SOA particles.
3.1 Isoprene SOA

The first isoprene SOA tracer compound in the Danum samples with MW = 216 Da and \( t_R = 2.9 \) min has been identified as 2-methyl tetrolic organosulfate based on the reference product ion spectrum in (Gomez-Gonzalez et al., 2008), showing a major fragment ion at \( m/z = 97 \) (HSO\(^-\)). A matching molecular formula (\([M-H]^- = C_5H_11O_7S\)) was seen in the FTICRMS analysis, with an error of \(-0.07 \) ppm. A compound with MW = 334 Da and \( t_R = 3.6 \) min, showed fragment ions of 315, 215, 97 and 97 Da and is identified as a C5-epoxydiol dimer organosulfate based on comparison to a reference spectrum in Yasmeen et al. (2011). No matching formula was updated in Surratt et al. (2010). No matching formula was found in the FTICRMS data.

3.2 \( \alpha \)-pinene SOA

A total of 6 \( \alpha \)-pinene SOA tracer compounds were found in the ambient samples. One compound had a MW 158 and \( t_R = 12.0 \) min. This has been assigned as terbic acid using the reference product ion spectrum in Yasmeen et al. (2011). This is also an oxidation product of \( \Delta 3 \)-carene. The chamber mass spectrum of this peak shows the expected non-

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### Table 2. BSOA tracer compounds identified using LC-MS\(^2\) in ambient aerosol collected at Danum Valley, Borneo in order of retention on the LC column. Accurate masses were obtained using syringe pump infusion ESI-FTICRMS in negative ionisation mode. Numbers in bold are the base peak in the MS\(^2\) mass spectra.

| MW  | [M-H]\(^-\) | \( t_R \) (mins) | Fragment ions | Suggested precursor | Library fit (out of 1000) | Reverse library fit (out of 1000) | Proposed identity | Matching peaks in FTICR-MS | Measured \( m/z \) | error (ppm) |
|-----|-------------|-----------------|---------------|---------------------|---------------------|---------------------|---------------------|---------------------|-----------------|-----------|
| 216 | 215         | 2.9             | 97            | isoprene            | a                   | a                   | 2-methyl tetrolic OS | C\(_2\)H\(_{11}\)O\(_7\)S | 215.02311      | \(-0.07\)  |
| 334 | 333         | 3.6             | 315, 197, 97  | isoprene            | a                   | a                   | C\(_5\)-epoxydiol dimer OS | none              |                 |           |
| 188 | 187         | 4.2             | 171, 115      | limonene            | 1000               | 1000                | n.i.                |                    |                 |           |
| 204 | 203         | 4.7             | 185, 141, 111 | limonene            | 901                | 953                 | n.i.                |                    |                 |           |
| 170 | 169         | 10.8            | 151           | \( \alpha \)-terpinene | b                   | b                   | \( \alpha \)-terpinalic acid | C\(_6\)H\(_{15}\)O\(_3\) | 169.08703      | \(-0.05\)  |
| 188 | 187         | 8               | 169, 143, 125, 111 | limonene            | 962                | 994                 | n.i.                |                    |                 |           |
| 188 | 187         | 9.5             | 169, 125      | \( \alpha \)-pinene | 1000               | 997                 | n.i.                |                    |                 |           |
| 158 | 157         | 12              | 113           | \( \alpha \)-pinene | 1000               | 1000                | caryophyllene acid | C\(_6\)H\(_{15}\)O\(_3\) | 187.06117      | 0.14      |
| 172 | 171         | 14.1            | 153, 127      | \( \alpha \)-pinene | 997                | 1000                | terpenyl acid       | C\(_6\)H\(_{11}\)O\(_3\) | 171.0671       | 0.3       |
| 204 | 203         | 15.8            | 185           | \( \alpha \)-pinene | 994                | 994                 | MBTCA               | C\(_6\)H\(_{15}\)O\(_6\) | 203.05609      | 0.09      |
| 186 | 185         | 15.8            | 141.97, 71    | \( \alpha \)-pinene | 888                | 922                 | fragment of MBTCA  |                    |                 |           |
| 216 | 215         | 16.1            | 197, 171, 153 | \( \beta \)-caryophyllene | 603                | 841                 | n.i.                |                    |                 |           |
| 216 | 215         | 22.8            | 197, 153      | \( \alpha \)-pinene | 912                | 983                 | n.i.                | C\(_{10}\)H\(_{15}\)O\(_3\) | 215.09251      | \(-0.07\)  |
| 172 | 171         | 26.4            | 127           | limonene            | 1000               | 991                 | ketolimononic acid | C\(_6\)H\(_{15}\)O\(_3\) | 171.06628      | 0.3       |
| 184 | 183         | 26.5            | 139           | \( \alpha \)-pinene | 993                | 975                 | cis-pinonic acid    | C\(_{10}\)H\(_{15}\)O\(_3\) | 183.10263      | 0.18      |
| 254 | 253         | 35.4            | 235, 211, 191 | \( \beta \)-caryophyllene | 953                | 993                 | nocaryophyllonic acid |                    | 253.1447       | \(-0.68\) |

*No MS\(^2\) spectrum in library.

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covalently bonded dimer formation at \( m/z \) 337. This was not seen in the ambient mass spectrum, which may be a consequence of lower concentrations or an ion suppression effect. A compound with MW 172 and \( t_R = 14.1 \) min was identified as terpenyl acid using the reference product ion spectrum in Yasmeen et al. (2010) although no MS\(^3\) has been carried out for confirmation. The compound with MW 184 and \( t_R = 26.5 \) min was identified as cis-pinonic acid using a commercially available standard. The retention time matched but no MS\(^2\) data was available from the rainforest OA sample for confirmation due to very low ion intensity and overlapping signals. The compound with MW 188 and a \( t_R = 9.5 \) min was seen in both the \( \alpha \)-pinene SOA and the ambient samples. It has not been possible to identify this compound. The product ion mass spectrum is very similar to an unidentified compound found by Yasmeen et al. (2011) in K-puszta aerosol (Fig. A4b in Yasmeen et al., 2011). The compound with MW 204 and \( t_R = 15.7 \) min was identified as 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) using the reference product ion spectrum in Yasmeen et al., (Yasmeen et al., 2011) with the MS\(^3\) product ion mass spectrum of \( m/z \) 185 being a very close match in terms of fragments and intensities. The unidentified \( \alpha \)-pinene tracer with MW 216 and
component in the library (Fit 953, RFit 993) but the retention time did not match. It is hypothesized that this represents SOA from a different sesquiterpene and is not identified at present.

### 3.6 Molecular composition

The rainforest OA extract was also analysed using FTICRMS to obtain information on the elemental composition. Just under 1000 monoisotopic compounds were found in the filter extracts. Compounds were screened to remove unlikely molecular formulae. Compounds were removed from the list if they contained any of the following; H: C < 0.5, O : C > 3 and a double bond equivalent (DBE) > 20. Around 200 peaks were removed using this screening process. The list still includes a number of formulae that are difficult to explain, such as C_{10}H_{15}O_{5}, but these have been kept in the analysis. Molecular formulae showed the presence of compounds containing C, H and O (CHO), containing C, H, O, N (CHON), containing C, H, O and S (CHOS), containing C, H, O, N and S (CHONS) and non-oxygen containing (CHN, CHS and CHNS) (LeClair et al., 2012). In total, 554 CHO, 203 CHON, 109 CHOS, 104 CHONS, and 23 CHN/CHS/CHNS formulae were identified and a full list is given in the Supplement Tables S1–S5. The CHO compounds are by far the most abundant group, representing 71 % of the total ion count of all identified species as shown in the Supplement Table S6.

In addition to the BSOA tracers identified in the LC-MS analysis, a number of other molecular formulae were obtained that may correspond to BSOA tracers and these are given in Table 3. These formulae correspond to organosulfates from isoprene and monoterpenes, which have been previously detected in chamber and in ambient aerosol. Five formulae match isoprene OS including the MW 216 identified previously (Surratt et al., 2008). In addition there is C_{14}H_{24}NO_{10}S, which matches an isoprene nitroxy organosulfate identified in isoprene SOA (Surratt et al., 2008) and ambient aerosol at K-puszta in Hungary, a mixed deciduous/coniferous forested site (Gomez-Gonzalez et al., 2008). Six formulae were found that match monoterpenoid OS compounds, seen in chamber generated limonene or α-pinene SOA (Surratt et al., 2008). However, these compounds were either below the threshold for MS² analysis or were below the limit of detection of the LC-MS analysis and without standards or product ion mass spectra it is impossible to confirm the identity of these species. There are other sources that may contribute to these OS species (Shalamzari et al., 2013; Surratt et al., 2008), for example the MW 214 species may be related to 2- or 4-pentenal SOA (Gomez-Gonzalez et al., 2008). The formation pathways of organosulfates remains unclear with epoxides from isoprene and methacrylic acid oxidation (Lin et al., 2013) and sulfate radical chemistry (Nozière et al., 2010; Schindelka et al., 2013) both potential routes.
Table 3. Isoprene and monoterpene organosulfates identified using FTICRMS in ambient aerosol collected at Danum Valley, Borneo.

| Observed m/z | Error (ppm) | Proposed Formula [M-H]^- | O : C | H : C | Isoprene or Monoterpene |
|--------------|-------------|--------------------------|-------|-------|-------------------------|
| 152.986326   | -0.05       | C_3H_2O_4S               | 1.67  | 1.67  | isoprene                |
| 198.992003   | -1.03       | C_4H_2O_7S               | 1.75  | 1.75  | isoprene                |
| 210.991775   | 0.10        | C_5H_2O_7S               | 1.40  | 1.40  | isoprene                |
| 213.007602   | -0.73       | C_6H_2O_7S               | 1.40  | 1.80  | isoprene                |
| 215.023112   | -0.07       | C_5H_11O_7S              | 1.40  | 2.20  | isoprene                |
| 223.028166   | 0.07        | C_7H_11O_8S              | 0.86  | 1.57  | monoterpene             |
| 226.986808   | -0.42       | C_8H_11O_8S              | 1.60  | 1.40  | monoterpene             |
| 251.059918   | -1.74       | C_9H_15O_9S              | 0.67  | 1.67  | monoterpene             |
| 260.008391   | -0.83       | C_5H_{10}NO_9S           | 1.80  | 2.00  | isoprene                |
| 265.07574    | -2.29       | C_{10}H_{17}O_8S         | 0.60  | 1.70  | monoterpene             |
| 279.055453   | -3.79       | C_{10}H_{15}O_7S         | 0.70  | 1.50  | monoterpene             |
| 297.066003   | -3.50       | C_{10}H_{17}O_8S         | 0.80  | 1.70  | monoterpene             |

The average O : C and H : C ratios fit with the emerging pattern of bulk OA composition and would sit very close to the line of −1 slope on a Van Krevelen plot as seen for ambient data from other locations (Heald et al., 2010). The elemental ratios of the sub micron organic aerosol were determined using a HR-AMS and the 10 min averaged data for the OP3 measurement campaign are shown in Fig. 3. The majority of the points have O : C ratios within the range 0.25 to 0.75, with an average value of 0.49. There is a good correlation present with $R^2 = 0.80$, and a line of best fit through all the points has a gradient of −0.8 and an intercept of 1.75. During a period of biomass burning influence at the start of the campaign (blue stars), the O : C ratio is higher with an mean value and standard deviation of 0.56 ± 0.06, compared to the remainder of the campaign (red crosses) which had a mean value of 0.47 ± 0.07, although care should be taken in this interpretation due to the overlap of uncertainties. During AMAZE-08, Chen et al. (2009) observed a O : C ratio of 0.42 from organic aerosol during periods of in-basin sources in Amazonia compared to 0.49 for periods of out of basin influence. Trajectory analysis indicates that the Borneo site is strongly influenced by aged regional background from off island sources and that although the rainforest and adjacent oil palm plantations are sources of BSOA, there are no periods where BSOA dominates as in the case of the AMAZE-08 project (Robinson et al., 2011b). Thus the averaged O : C ratio for OP3 is consistent with the out of basin values obtained from the Amazon.

3.7 Comparison of O : C ratios

The O : C value obtained by FTICRMS (0.37) is lower than the average AMS value but they are remarkably close considering the different instrumentation and size fractions collected. The AMS analyses the sub micron non-refractory composition, whereas the FTICR-MS analyses the water-soluble extract of PM$_{2.5}$. There are significant amounts of primary biological aerosol particles (PBAP) between 1 and
They have also been identified above a tropical forest, where diols (Lin et al., 2012). The 2-methyl tetrol organosulfates isoprene epoxides (IEPOX) to 3-methyltetrahydrofuran-3,4-diol specific SOA tracers. In this study, chamber simulations of important BVOCs given off from tree species in a tropical rainforest in Borneo were used to identify BSOA tracers of a range of biogenic precursors. In total 18 precursor specific BSOA tracer compounds were identified using LC-MS. It is clear that the OA at Danum Valley in Borneo contains products from the oxidation of isoprene, monoterpene emissions often dominate over isoprene.. How- however, this study provides the first unambiguous identification of monoterpene and sesquiterpene SOA in a tropical rainforest.

4 Discussion

BVOCs are predicted to make a significant contribution to SOA formation in tropical regions, but it is difficult to really understand their role without the identification of compound specific SOA tracers. In this study, chamber simulations of important BVOCs given off from tree species in a tropical rainforest in Borneo were used to identify BSOA tracers of a range of biogenic precursors. In total 18 precursor specific BSOA tracer compounds were identified using LC-MS. It is clear that the OA at Danum Valley in Borneo contains products from the oxidation of isoprene, monoterpene emissions often dominate over isoprene.. How- ever, this study provides the first unambiguous identification of monoterpene and sesquiterpene SOA in a tropical rainforest. pollution levels are generally much lower, using a single particle mass spectrometer (PALMS) on an aircraft platform (Froyd). The current study confirms the presence of IEPOX organosulfates and indicates that they can also be present close to the top of the canopy in a tropical forest. AMS measurements carried out during OP3 indicated that the sub micron aerosol over Borneo had a much higher sulfate : organic ratio than that seen in Amazonia, which has been attributed to marine sulfate sources, and that Borneo is often influenced by significant off island sources such as biomass burning. Oxidation of dimethylsulfide emitted from the surrounding maritime source may provide an acidic aerosol surface, which may catalyse organosulfate formation from IEPOX. Other possible pathways are that the interaction of more polluted air from biomass burning with the pristine forest environment may enhance the formation of organosulfates over the forest or it may be that the organosulfates are transported onto the island through long-range transport. Further work is needed to understand the formation of these compounds in regions such as Borneo where tropical forests are subject to periods of anthropogenic pollution.

Isoprene was the most abundant VOC measured during OP3, with a mean daytime maximum mixing ratio of around 2 ppb. Other VOCs observed directly in Danum include a small range of monoterpenes, however this speciation is unlikely to represent all monoterpenes present. Sesquiterpenes were not observed in the gas phase but were believed to be present given leaf cuvette observations. A number of tracers, particularly those from α-pinene have been identified in ambient aerosol in boreal and temperate forests, where monoterpane emissions often dominate over isoprene.. However, this study provides the first unambiguous identification of monoterpene and sesquiterpene SOA in a tropical rainforest.

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Fig. 3. Van Krevelen plot of 10 minute average O:C and H:C ratios determined using HR-AMS. Blue crosses indicate ratios measured during a period of increased biomass burning influence (POI1). Red crosses indicate the measurements taken after POI when lower pollution levels were seen.
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