

# Evidence for a significant proportion of Secondary Organic Aerosol from isoprene above a maritime tropical forest

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**Abstract.** Isoprene is the most abundant non-methane biogenic volatile organic compound (BVOC), but the processes governing secondary organic aerosol (SOA) formation from isoprene oxidation are only beginning to become understood and selective quantification of the atmospheric particulate burden remains difficult. Organic aerosol above a tropical rainforest located in Danum Valley, Borneo, Malaysia, a high isoprene emission region, was studied during Summer 2008 using Aerosol Mass Spectrometry and offline detailed characterisation using comprehensive two dimensional gas chromatography. Observations indicate that a substantial fraction (up to 15% by mass) of atmospheric sub-micron organic aerosol was observed as methylfuran (MF) after thermal desorption. This observation was associated with the simultaneous measurements of established gas-phase isoprene oxidation products methylvinylketone (MVK) and methacrolein (MACR). Observations of MF were also made during experimental chamber oxidation of isoprene. Positive matrix factorisation of the AMS organic mass spectral time series produced a robust factor which accounts for an average of 23% ( $0.18 \mu\text{g m}^{-3}$ ), reaching as much as 53% ( $0.50 \mu\text{g m}^{-3}$ ) of the total organic loading, identified by (and highly corre-

lated with) a strong MF signal. Assuming that this factor is generally representative of isoprene SOA, isoprene derived aerosol plays a significant role in the region. Comparisons with measurements from other studies suggest this type of isoprene SOA plays a role in other isoprene dominated environments, albeit with varying significance.

## 1 Introduction

In order to assess the regional and global impacts of anthropogenic aerosols, it is necessary to quantify the contribution of the natural background. Aerosols can interact directly with incoming radiation by scattering or absorption, or indirectly through their effect on cloud formation and lifetime. A large fraction of the background particulate matter in the atmosphere is composed of organics thought to be formed by secondary processes from biogenic precursors (Kanakidou et al., 2005). Isoprene (2-methyl-1,3-butadiene) is potentially a major source of secondary organic aerosol (SOA) (Henze and Seinfeld, 2006), but highly time resolved atmospheric identification of isoprene derived SOA have so far proven elusive (Hallquist et al., 2009). In Amazonia, 2-methyltetrols identified on ambient filter samples were hypothesised to arise from isoprene oxidation (Claeys et al., 2004), and subsequently found to be present



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in chamber photo-oxidation of isoprene under low  $\text{NO}_x$  conditions ( $<1$  ppb of  $\text{NO}_x$  with isoprene: $\text{NO}_x \sim 500:1$ ; Surratt et al., 2006). Low  $\text{NO}_x$  isoprene chamber studies have identified reactive photo-oxidation products in the gaseous and particulate phases such as epoxides (Paulot et al., 2009; Surratt et al., 2010), tetrols (Surratt et al., 2006, 2010; Kleindienst et al., 2009) and organosulphates (Surratt et al., 2008). These isoprene derived SOA species have also been measured offline in field studies (Chan et al., 2010; Surratt et al., 2008).

While previous work has identified a number of potentially important mechanisms (Chan et al., 2010; Paulot et al., 2009), the ambient measurements are largely based on offline analysis of bulk samples. These measurements are limited by low time-resolution, which prevents detailed photochemical analysis and comparison to rapidly changing parameters, such as photolysis rates and oxidant concentrations. However, one recent study has measured isoprene SOA online, with IEPOX-derived organosulphates being detected using Particle Analysis by Laser Mass Spectrometry (PALMS; Froyd et al., 2010).

The Aerodyne Aerosol Mass Spectrometer (AMS; Canagaratna et al., 2007) allows for online measurements of organic aerosols with a high time resolution and has been used previously for studies concerning isoprene oxidation (e.g. Capes et al., 2009). While the AMS reports bulk organic matter, the identification of specific chemical markers is required for more comprehensive biogenic source apportionment.

Here we present results from intensive measurements in an isoprene-dominated tropical forest environment and attempt to interpret a previously unreported chemical marker within the measurements. Factor analysis and comparisons with other datasets are used to estimate its importance both locally and in a global context.

## 2 Measurements

Measurements were made above a South East Asian Rainforest at the Danum Valley Conservation Area Global Atmospheric Watch (GAW) station, Sabah, in Malaysian Borneo ( $4.981^\circ$  N,  $117.844^\circ$  E) as part of both the Oxidant and Particulate Photochemical Processes Above a South East Asian Rainforest project (OP3) (Hewitt et al., 2009, 2010) and the Aerosol Coupling in the Earth's System (ACES) project, during June and July 2008. A wide suite of aerosol, gas, radical and meteorological instruments were deployed in order to study the local atmospheric chemical processes as comprehensively as possible. In addition to the ground-based measurements, airborne measurements were made using instruments aboard the Facility for Airborne Atmospheric Measurements (FAAM) BAe 146 aircraft.

At the ground site, air was sampled from a height of 33 m above ground level on the top of a ridge surrounded by rain-

forest. The inlet sampled at a rate of  $1500\text{ l min}^{-1}$  through a 30 m long, 15 cm i.d. diameter polypropylene tube insulated against solar heating. Air was then sub-sampled isokinetically from the centre of this flow at  $35\text{ l min}^{-1}$ . To avoid condensation in the lines, sampled air was dried using a 780 tube Nafion drier using a dry air counter flow, where the air was decelerated to the laminar flow regime. After drying the air was decelerated further before being sampled by the suite of online instruments. Comparison of size distributions at the top and bottom of the inlet show that the aerosol transmission efficiency is approximately 70% in the size range  $0.3\text{--}1\text{ }\mu\text{m}$  and comparison of total number series show a transmission efficiency of  $>96\%$  for the smaller particles that dominate the number mode (Whitehead et al., 2010). The aircraft missions consisted of two separate sets of stacked straight and level runs (at 100–250, 1500, 3000 and 6000 m) over regions of rainforest (centred around the ground site) and homogeneous agro-industrial region of oil palm agriculture (centred around  $5.25^\circ$  N,  $118.25^\circ$  E). Aerosol was sampled on board the FAAM through a Rosemount inlet (Foltescu et al., 1995) and approximately 0.7 m of stainless steel tubing with a total residence time of  $\sim 4$  s in the inlet system.

Filter samples (Thermo Scientific Partisol) were collected at the ground site from a height of 10 m. Particles less than  $2.5\text{ }\mu\text{m}$  were collected onto pre-fired quartz filters which were transported and stored at  $-20^\circ\text{C}$  until analysis. Organic aerosol material was thermally desorbed from the filter for off-line analysis by comprehensive two dimensional gas chromatography with detection by Time-of-Flight Mass Spectrometry ( $\text{GC} \times \text{GC}/\text{ToF-MS}$ ) (Phillips and Beens, 1999; Hamilton et al., 2004). A dual stage commercial thermal desorption injector was used incorporating a thermal desorption unit (TDU) connected to a programmable-temperature vaporisation (PTV) injector, CIS-4 plus (Gerstel, Mulheim an der Ruhr, Germany), using a heated transfer line. 10–20 mg of filter paper containing each different sample was loaded into cleaned thermodesorption tubes using tweezers to ensure no contamination of the sample. The  $\text{GC} \times \text{GC}/\text{ToF-MS}$  system consisted of an Agilent 6890 (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph and a Pegasus III TOF-MS (LECO, St. Joseph, MI, USA). The first column was a non-polar DB5 ( $29\text{ m} \times 0.32\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$  film thickness) and the second column a DB17 ( $1.5\text{ m} \times 0.10\text{ mm i.d.} \times 0.10\text{ }\mu\text{m}$  film thickness).

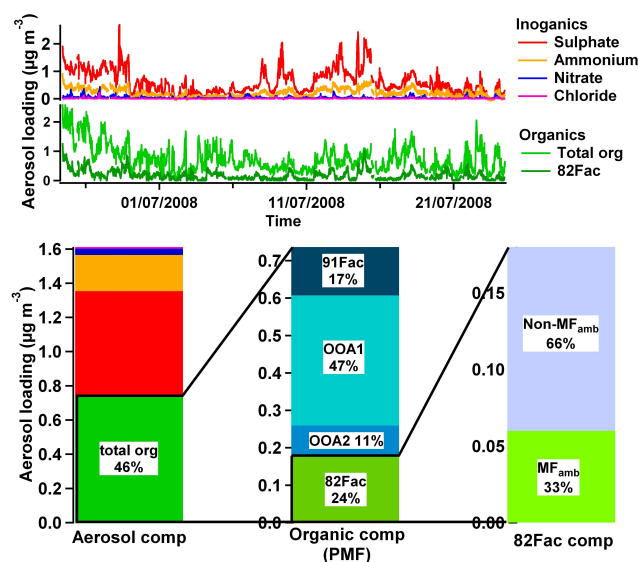
Ground and airborne VOC measurements were made using Proton Transfer Reaction Mass Spectrometry (PTRMS) (Lindinger et al., 1998). Ground VOC measurements were made using an inlet separate to the one described above and further details can be found in Langford et al. (2010) and Murphy et al. (2010). The PTRMS can measure methylvinylketone (MVK) and methacrolein (MACR), both first generation isoprene oxidation products. These species have the same molecular mass and cannot be separated using this technique, so are reported as the sum of the two, referred to as  $\text{MVK} + \text{MACR}$ .

Online aerosol composition was measured using two Aerodyne time of flight Aerosol Mass Spectrometers; a high mass resolution version (HR-AMS) (DeCarlo et al., 2006) for measurements at the 33 m level of the ground site measurement tower, and a compact version (C-AMS) (Drewnick et al., 2005) for airborne measurements on the FAAM. The AMS provides quantitative online measurements of sub-micron non-refractory aerosol composition and size. Despite extensive fragmentation of particulate matter species, compositional information can be gained from inspection of ions in the mass spectra. For example, the ratio of  $m/z$  44 (mainly  $\text{CO}_2^+$ ) to  $m/z$  43 (mainly  $\text{C}_2\text{H}_3\text{O}^+$ ) can be used as a proxy for the oxidation of organic aerosols (Morgan et al., 2010; Ng et al., 2010) and  $m/z$  60 can be used as a marker for fresh biomass burning (Alfarra et al., 2007; Capes et al., 2008). The high resolution mode of the HR-AMS can resolve ion mass at a higher resolution ( $\sim 4300$ ) than the C-AMS, allowing separation of ions with different elemental composition detected at the same  $m/z$ .

Positive matrix factorisation (PMF) analysis was also performed on the organic HR-AMS unit mass resolution data. This multivariate technique attempts to explain the AMS ensemble organic mass spectral time series as the sum of time series of differing amounts of static “factor” spectra which can then be linked to distinct contributions to the total organic mass (Paatero and Tapper U., 1994; Paatero, 1997; Ulbrich et al., 2009). Details of this analysis are included in the Supplement. In short, a variety of solutions were calculated exploring different starting parameters and rotational ambiguities, and the most satisfactory solution was obtained when four factors were used. A detailed discussion of the results of PMF analysis will be included in Robinson et al. (2011a).

### 3 Results

Total sub-micron non-refractory organic aerosol mass was less in Borneo than typical measurements in the Northern mid latitudes, which have an average of  $2.8 \mu\text{g m}^{-3}$  for remote sites (Zhang et al., 2007). A mean organic matter loading of  $0.74 \mu\text{g m}^{-3}$  was measured from the ground site, which is comparable to a mean loading of  $0.64 \mu\text{g m}^{-3}$  measured in Amazonia (Chen et al., 2009). A time series of organic and inorganic sub-micron non-refractory aerosol loading is shown in Fig. 1. The ambient organic spectra from both AMS instruments shows a distinctive peak at  $m/z$  82 (Fig. 2a and b), a feature not seen in the mid-latitude environments that make up the majority of ambient AMS observations to date. Furthermore, the high mass resolution capability of the HR-AMS was able to attribute the majority of the  $m/z$  82 peak of the AMS mass spectrum to the  $\text{C}_5\text{H}_6\text{O}^+$  ion (Fig. 2b and c). One of the PMF factors exhibited strong signals at  $m/z$  82 and 53, henceforth called 82Fac, which was found to be very robust when subjected to variations in the starting conditions

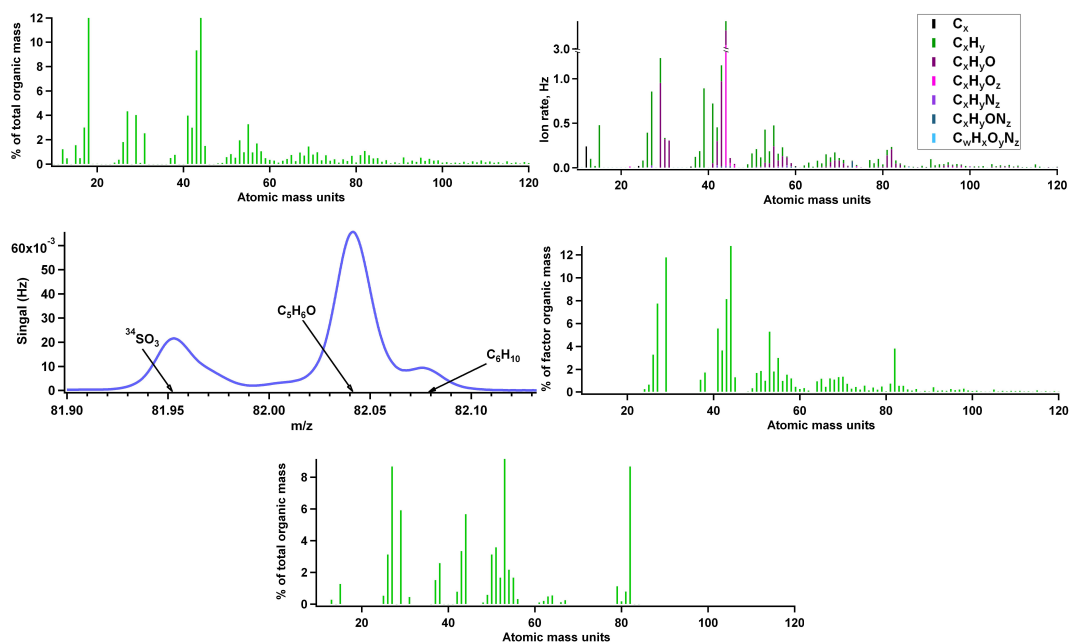


**Fig. 1.** Top, time series of inorganic and, below that, organic aerosol loading as measured by the AMS. The organic time series also details the  $m/z$  82 containing PMF factor (82Fac). On the bottom are bars showing: the mean aerosol composition (with same colour scheme as in the time series legend); an expansion of the organic component to show the individual PMF factors; and an expansion of the 82Fac to show the contribution from MF which is calculated from the  $\text{C}_5\text{H}_6\text{O}^+$  signal using Eq. (1).

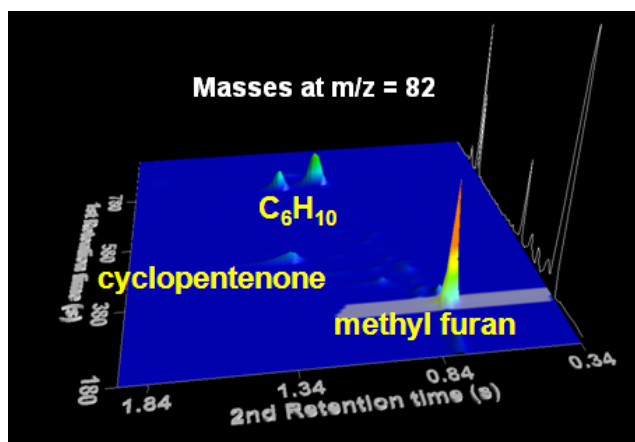
(starting seed) or when rotational ambiguity in the solutions was explored (fpeak; see Supplement and Fig. 1). It was closely correlated with the  $m/z$  82 peak with an  $r^2$  of 0.86. Also, the other factors contained largely insignificant contributions from this  $m/z$ .

GC  $\times$  GC chromatography was used to investigate the source of the  $m/z$  82 ion, as shown in Fig. 3. The dominant peak was identified as methylfuran (MF) based on a standard solution retention time and electron ionisation mass spectrum, although under this column set, the 2- and 3-methylfuran isomers cannot be separated. It is clear that there are no other substantial contributions to  $\text{C}_5\text{H}_6\text{O}^+$ . The AMS  $m/z$  82 peak was found to occur in conjunction with a prominent  $m/z$  53 peak (Pearson’s  $r^2$  of 0.96) corresponding to  $\text{C}_4\text{H}_5^+$ , the most abundant electron ionisation fragment ion of MF (NIST mass spec database, Stein, 2009). Combined with the GC  $\times$  GC/ToF-MS results, this suggests that the  $m/z$  82 fragment in the AMS can be attributed to the MF molecular ion, and confirms that the filter-identified MF was particulate and was not attributable to a gaseous artifact.

An AMS spectrum of pure 3-methylfuran (3MF) (Fig. 2e) was obtained by nebulising commercially available 3MF (Fisher Scientific, UK; 98% pure) suspended in deionized water in the laboratory. A background spectrum of deionized water measured using the same equipment was subtracted to remove any influences from contamination sources. The measured sample spectrum compared well to the 3MF



**Fig. 2.** Various AMS mass spectra showing a MF peak at  $m/z$  82, including (a) a C-AMS mass spectrum measured aboard the FAAM aircraft during a period of high  $m/z$  82 signal, (b) a high resolution mass spectrum measured from the ground site during a period of high MF signal, (c) detail of the  $m/z$  82 peaks during the same period of high MF signal, (d) the 82Fac organic aerosol factor from PMF analysis of the ground site mass spectra and (e) a mass spectrum of 3MF suspended in water and measured in the laboratory.

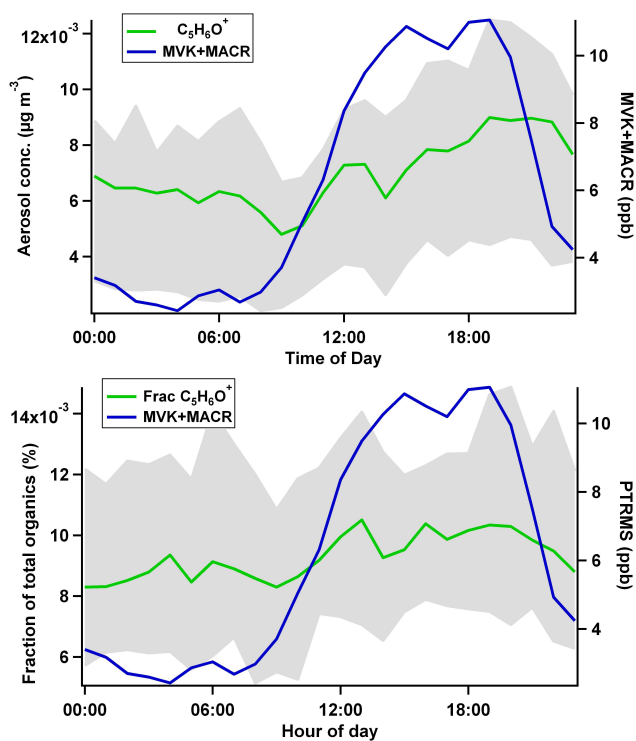


**Fig. 3.** GC  $\times$  GC chromatogram of  $m/z$  82. The first and second retention times (s) are plotted against the  $y$ - and  $x$ -axis respectively. The dominant peak is based on methylfuran.

reference spectrum (NIST mass spec database, Stein, 2009) and the unusual features of the ambient organic spectrum, such as the prominent  $m/z$  82 and 53 peaks. Inspection of the high resolution  $m/z$  82 peak of the pure 3MF mass spectrum showed only  $C_5H_6O^+$  ions to be present, comprising 13% of the total organic mass.

The average diurnal profile of the  $C_5H_6O^+$  signal shows an increase throughout the day with a maximum in the early evening (Fig. 4a). This is also the case for the diurnal profile of the fraction of organic aerosol at  $C_5H_6O^+$  (Fig. 4b). These elevated levels in the evening may be caused by partitioning of semi-volatile aerosol as the ambient temperature drops. They may also be transported from the isoprene rich oil palm plantations (Hewitt et al., 2009) close to the site (around 30 km), causing a time lag between production and measurement. The first-generation isoprene oxidation products MVK+MACR, also show a strong diurnal cycle linked to the peak in the emission of isoprene at midday with the delay caused by the photochemical reaction rate. If it is assumed that the  $C_5H_6O^+$  signal has a similar precursor, the fact it peaks later in the day could imply that it is produced by a longer or slower sequence of reactions.

Airborne PTRMS measurements of MVK+MACR, and AMS measurements of  $m/z$  82 were also compared (Fig. 5). The median of the AMS  $m/z$  82 and  $m/z$  53 peaks measured in the boundary layer over each of eight individual flights correlated well with gas phase MVK+MACR, with respective Pearson's  $r^2$  values of 0.92 and 0.87. This shows that both measurements exhibited systematically similar daily increases, which would be expected if they shared a common precursor. A substantial  $m/z$  82 signal was observed throughout the surface mixed layer to a height of 3000 m, with little signal observed in the lower free troposphere above (Fig. 6a). That MF was measured throughout the boundary layer shows

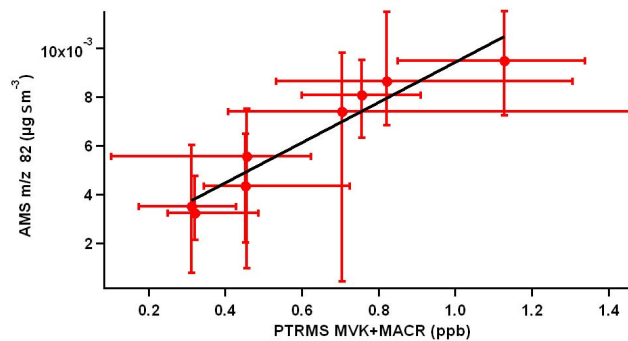


**Fig. 4.** Diurnal averages of (a)  $C_5H_6O^+$  signal and MVK+MACR and (b) fraction of organic signal at  $C_5H_6O^+$  and MVK+MACR.  $C_5H_6O^+$  interquartile ranges are shown by shaded regions.

that it is of regional importance. Altitude profiles show the AMS aerosol signal at  $m/z$  82 increases throughout the day, at all altitudes in the boundary layer, which is consistent with production from photochemical processing of precursors rather than direct emission from the surface. This increase in the afternoon is also observed in the altitude profile of gas phase MVK+MACR (Fig. 6b), although this increase is mostly below 2000 m. The averaged values of organic mass and  $m/z$  82 at the lowest altitudes are similar to those measured at the ground site at the same time of day. The altitude profiles are consistent with semi-volatile aerosol partitioning at the top of the boundary layer where it is cooler, with a change of temperature of 298 K at  $\sim 500$  m to 283 K at  $\sim 3000$  m. This may also explain the disparity between the MVK+MACR profile and the  $m/z$  82 profile at the top of the boundary layer.

#### 4 Possible sources of MF

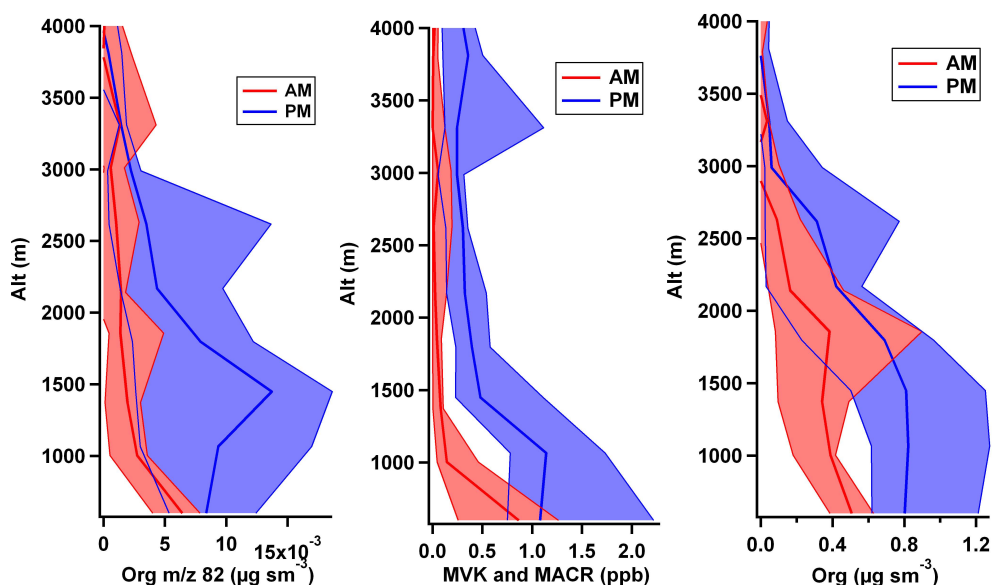
Previous studies have presented evidence of gas-phase methylfuran formation through oxidation of isoprene by OH radicals: MF has been measured in simulation chamber studies of isoprene oxidation (Atkinson et al., 1989; Ruppert and Becker, 2000; Sprengnether et al., 2002) and, in a study of a rural US forest, ambient measurements of gaseous MF were



**Fig. 5.** AMS  $m/z$  82 aerosol loading (in  $\mu\text{g sm}^{-3}$ , defined as  $\mu\text{g m}^{-3}$  at 273 K and 1013 hPa with no condensation or evaporation) vs. PTRMS gas phase MVK+MACR as measured in the boundary layer from the FAAM research aircraft. Each data point represents the median of all boundary layer data collected during a single flight. Bars are 25th and 75th percentiles.

found to correlate with isoprene (Montzka et al., 1995). The likelihood of MF being present in the condensed phase was investigated using methods to estimate first the normal boiling point (Nannoolal et al., 2004), and then the vapour pressure (Nannoolal et al., 2008), evaluated as being the best available for atmospheric purposes (Barley and McFiggans, 2010). A literature boiling point was used (Burness, 1956) (338.65 K) with the above vapour pressure method to give an estimated value of 0.217 atm at 298.15 K. This value was then used to estimate the abundance of MF that would be expected to be present in secondary organic aerosol under equilibrium conditions at 298.15 K. Using a partitioning model (Barley et al., 2009) with a reasonable and representative set of assumptions ( $2 \mu\text{g m}^{-3}$  of completely involatile, perfectly organic core of molar mass  $320 \text{ g mol}^{-1}$  with total concentration of the considered molecule set to  $2 \mu\text{g m}^{-3}$ ), it was estimated that MF contributed  $1.41 \times 10^{-9} \mu\text{g m}^{-3}$  to the condensed mass ( $7.05 \times 10^{-8}\%$  by mass). Based upon an equilibrium partitioning consideration, MF should not be present in the condensed phase in detectable quantities under reasonable atmospheric conditions.

That MF is measured from condensed material may be explained if it is directly incorporated into the particles by some means other than absorptive partitioning, such as reversible reactive uptake. However, no such mechanism is known. Instead, we hypothesise that MF measurements are a result of decomposition of some condensed phase isoprene photo-oxidation product upon the thermal vapourisation used in the GC  $\times$  GC and AMS analyses reported here. This is supported by the association of detected MF with the gas-phase isoprene photo-oxidation products MVK + MACR. The diurnal profiles shown in Fig. 4 also support this, being consistent with comparisons of day and night filter samples from previous studies which show greater levels of isoprene SOA markers during the day when isoprene emissions and photochemistry are greatest (Kourtchev et al., 2008; Ion et al.,



**Fig. 6.** Average altitude profiles of (a)  $m/z$  82 signal, (b) gas phase MVK+MACR and (c) organic aerosol loading as measured from the FAAM research aircraft. Red lines from data before midday and blue lines from data after midday, local time. Thick lines are median values and shaded areas (outlined with thin lines) denote interquartile ranges.

2005). Known potential sources of isoprene SOA include epoxides (Paulot et al., 2009; Surratt et al., 2010), tetrols (Surratt et al., 2006, 2010; Kleindienst et al., 2009), peroxides (Surratt et al., 2006) or oligomers (Surratt et al., 2010) (formed through accretion reactions) but at present it is unclear how they would produce MF upon volatilisation. It is conceivable that this relation of MF to MVK+MACR could be caused by terpene photo-oxidation products produced at a similar rate to isoprene products. However, there is no evidence in the literature for MF formation from terpene photo-oxidation, in contrast to various isoprene mechanistic studies. This suggests that the MF could be a product of a form of isoprene SOA not previously identified.

The previously reported isoprene: $\text{NO}_x$  ratio measured during OP3 had a typical value of 20:1 (Hewitt et al., 2009) which is comparable to ratios in  $\text{NO}_x$ -limited chamber oxidation studies of isoprene (e.g. Lane et al., 2008). The formation of gas-phase 3MF during isoprene photo-oxidation studies has previously been attributed to cyclisation/dehydration of unsaturated  $\text{C}_5$  1,4-hydroxycarbonyls formed (Sprengnether et al., 2002; Dibble, 2007), in a process that would also be possible during the heating involved in the analyses reported here. A  $\text{C}_5\text{H}_8\text{O}^+$  ion has been attributed to the fragmentation of 1,4-hydroxycarbonyls in previous isoprene photo-oxidation studies (Zhao et al., 2004). This signal was present in the ambient mass spectrum in Borneo and was covariant with the molecular ion of MF with a Pearson's  $r^2$  of 0.57 but absent in the laboratory 3MF spectrum, consistent with the hypothesis that unsaturated 1,4-hydroxycarbonyls are the source of the ambient MF measurements. While these studies were performed at  $\text{NO}_x$  lev-

els higher than in Borneo, they do provide a possible candidate for a mechanism that yields MF measurements. Two unsaturated  $\text{C}_5$ -hydroxycarbonyls (4-hydroxy-2-methyl-but-2-enal and 4-hydroxy-3-methyl-but-2-enal), are known to be formed as substantial first generation products of the OH-initiated degradation of isoprene, with their collective molar yield reported to be approximately 15–20% in a number of studies performed in the presence of  $\text{NO}_x$ , albeit at higher concentrations than in the atmosphere (Kwok et al., 1995; Zhao et al., 2004; Baker et al., 2005). Hydroxycarbonyls have also been observed in  $\text{NO}_x$ -free systems with a collective yield approaching 20% (Ruppert and Becker, 2000), with the dominant contribution estimated to be attributable to the above 1,4 isomers (Jenkin et al., 1998) and substantial formation may occur under the range of conditions of the OP3 field campaign.

Similar partitioning calculations as for MF were performed for  $\text{C}_5$ -hydroxycarbonyls. They were estimated to have a boiling point of 463.06 K and a vapour pressure at 298.15 K of  $3.38 \times 10^{-5}$  atm. The  $\text{C}_5$ -hydroxycarbonyls contributed  $9.05 \times 10^{-6} \mu\text{g m}^{-3}$  to the condensed mass ( $4.5 \times 10^{-4}\%$  by mass). It is apparent from these calculations that, if either or both of the  $\text{C}_5$ -hydroxycarbonyls are degrading upon measurement to give MF, it must itself be a degradation product of another, less volatile compound. Again it is unclear how  $\text{C}_5$ -hydroxycarbonyls could be formed from established isoprene or terpene SOA species. One possibility is that some isoprene SOA could be in the form of peroxyhemiacetals which produce MF upon analysis. Hydroperoxide species (ROOH), such as isoprene derived hydroxyhydroperoxides, can be formed under (low

NO<sub>x</sub>) NO<sub>x</sub>-limited conditions where RO<sub>2</sub>+HO<sub>2</sub> reactions become important. Under such conditions peroxyhemiacetals can be formed from the (reversible) reactions of isoprene derived 1,4-hydroxycarbonyls with hydroperoxides and hydroperoxides with aldehydes. The formation of high molecular weight peroxyhemiacetals has been characterised in previous studies of condensed organic material formed from the ozonolysis of alkene and monoterpene systems (Tobias and Ziemann, 2000; Docherty et al., 2005). Future chamber studies investigating isoprene SOA should seek to identify the potential sources of C<sub>5</sub>-hydroxycarbonyls and MF in analytical measurements.

## 5 Mass estimates of MF related aerosol

The fraction of the ambient  $m/z$  82 peak present as C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> was calculated as a function of time using the high resolution AMS data. Averaged over the whole data set, these time series have a ratio of mean values of 80%, showing the C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> ion to be the major contributor to the  $m/z$  82 mass. This high resolution time series was scaled to the unit mass resolution data to ensure consistency with calibrations, and used to derive a quantitative estimate of the C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> signal (used in Fig. 1). By scaling the laboratory 3MF spectrum so its  $m/z$  82 peak is the same magnitude as the ambient C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> signal, it is possible to estimate an upper limit to the MF loading detected, MF<sub>amb</sub>, using

$$\text{MF}_{\text{amb}} = \frac{3\text{MF}_s}{\text{C}_5\text{H}_6\text{O}_s^+} \text{C}_5\text{H}_6\text{O}_{\text{amb}}^+ \quad (1)$$

where 3MF<sub>s</sub> is the total organic loading of the laboratory sample spectrum, C<sub>5</sub>H<sub>6</sub>O<sub>amb</sub><sup>+</sup> is the C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> signal in the ambient spectrum and C<sub>5</sub>H<sub>6</sub>O<sub>s</sub><sup>+</sup> is the C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> signal in the laboratory 3MF sample spectrum ( $m/z$  82 loading). This estimation method assumes that C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> is entirely from the molecular ion of a thermal fragment rather than a fragment ion produced during ionization. Given that the GC-MS retention times of the  $m/z$  82 peak from analysis of field and laboratory samples were the same, and the tendency of oxygenated organic species to generate odd  $m/z$  fragments under ionization (McLafferty and Turecek, 1993), this is considered to be a reasonable assumption. The mean ambient C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> signal measured at the ground site during OP3 was 1.0% of the mean ambient total organic aerosol loading. Accounting for fragments of the molecular MF ion, this gives a mean MF<sub>amb</sub> loading of 0.06 μg m<sup>-3</sup>, or 8% of the organic aerosol. The maximum (95th percentile) MF<sub>amb</sub> loading was 0.14 μg m<sup>-3</sup>, and the maximum fractional loading was 15% of the simultaneously measured total organic aerosol.

The mass of particulate SOA due to isoprene oxidation in the ambient will be greater than the mass of MF it produces upon analysis, meaning this approach underestimates the loading of isoprene derived SOA. An estimate of the total amount of organic aerosol due to isoprene oxidation can

be made using the 82Fac from the PMF analysis of the HR-AMS unit mass resolution spectrum (see Supplement). It should be noted that the mass spectrum of 82Fac (Fig. 2d) is more complex than the 3MF laboratory mass spectrum (Fig. 2e) implying other organic components also contribute to the 82Fac PMF factor. However, the close correlation of 82Fac with  $m/z$  82 ( $r^2 = 0.86$ ) identifies it as being derived from the same organic aerosol as MF, either directly as other components that are also formed on thermal degradation, or indirectly as isoprene SOA species that are produced simultaneously but through a different mechanism.

Note that it is conceivable that isoprene SOA produced at a different rate to the MF-precursor aerosol may also be contributing to other factors (such as OOA2), although we have no evidence to suggest this is the case. It is likely that, if MF is indeed indicative of isoprene SOA, the 82Fac PMF factor provides a good estimate of the amount of isoprene SOA in the region.

## 6 Global extent of MF

Such a prominent  $m/z$  82 signal has not been reported in previously published studies over biogenic sources of VOCs. However, analysis of HR-AMS mass spectra from a study in the Amazon Basin, previously published as part of the Amazonian Aerosol Characterization Experiment (AMAZE-08) (Chen et al., 2009), also shows evidence for C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> during periods dominated by in-Basin sources, though with a lower mean signal comprising 0.5% of the organic mass, compared to the mean C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> signal of 1% measured in Borneo. Table 1 compares  $m/z$  82 and C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> signals from projects in various locations around the World showing the fractional contribution of  $m/z$  82 to the total organic matter and its comparison with the adjacent peaks, which is an indicator of how distinct the signal is compared to other peaks in that part of the mass spectrum. Though these two metrics are useful for comparing projects, care should be taken in their interpretation as both are vulnerable to conflating circumstances: for example, the  $m/z$  82 peak will appear as a low fraction of the total mass if MF yielding aerosol is present in low levels compared to other organic aerosol, and if large amounts of a species that fragment at masses around  $m/z$  82 are measured then the  $m/z$  82 peak may be a significant fraction of the total mass without being prominent. It should also be noted that it is impossible to assess the contribution of non-MF ions to  $m/z$  82 peaks unless high mass resolution data is available.

The  $m/z$  82 peak in the rainforest environments is more prominent, implying these measurements are from stable molecular ions, rather than background fragments resultant from the breakup of non-MF-precursor organic aerosol. Higher levels of C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> yielding aerosol have been measured in these two isoprene dominated rainforest environments than in a North American temperate forest of mixed terpene and isoprene influence (BEARPEX campaign, see

**Table 1.** Comparison of % of organic aerosol signal measured at  $m/z$  82 and at  $C_5H_6O^+$ , the ratio of organic  $m/z$  82 to the mean adjacent organic peak heights, and the % of the organic  $m/z$  82 peak that is  $C_5H_6O^+$ , at different locations across the World, and in isoprene oxidation experiments (isoprene: $NO_x > 200 : 1$ ) in the Harvard Environmental Chamber. Standard errors calculated from propagation of standard deviations of time series are shown (where appropriate). The Borneo data points are from the OP3 project as reported in this paper. The Amazonia data are from the AMAZE campaign as reported by Chen et al. (2009), in-basin classification. The boreal European data were collected as part of the EUCAARI campaign (Kulmala et al., 2009). The North American temperate data (see Appendix A) were taken as part of the BEARPEX campaign.

	Borneo ensemble	Borneo PMF factor	Chen et al. Amazonia	European boreal	North American temperate	Isoprene SOA in HEC
org82:org	1.24±0.01%	3.82%	0.68±<0.01%	0.48±0.01%	0.40±<0.01%	0.44±<0.01%
$C_5H_6O^+$ :org	1.01±0.01%		0.50±0.01%	0.25±0.01%	0.40±<0.01%	0.43±<0.01%
82:avg(81,83)	2.14±0.02	5.84	1.18±0.01	0.66±0.02	0.49±<0.01	3.38±0.05
$C_5H_6O^+$ :org82	81.5±0.4%		74.0±0.6%	50±1%	98.2±0.2%	97.2±0.4%

Appendix A), which in turn has higher levels than a terpene dominated environment (Kulmala et al., 2009). This is consistent with the detection of MF being a result of isoprene derived SOA.

HR-AMS data from low  $NO_x$  isoprene photo-oxidation experiments (isoprene: $NO_x > 200 : 1$ ) in the Harvard Environmental Chamber (King et al., 2010) also show an  $m/z$  82 peak distinct from the adjacent peaks. While the  $m/z$  82 peak is responsible for less signal than in either of the tropical field studies (0.4% of total organic mass), the prominence of the  $C_5H_6O^+$  ion at  $m/z$  82 strongly suggests that the same SOA formation mechanism is taking place and could be isolated through further laboratory work. 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).

## 7 Conclusions

AMS and GC × GC measurements of organic aerosol composition in Borneo identified a MF signal at  $m/z$  82 and 53, the parent ion and major fragment respectively. This was confirmed by laboratory measurements of a 3MF sample which showed the same  $m/z$  82 and 53 peaks. The  $m/z$  82 signal was present throughout the boundary layer with the signal increasing throughout the day, associated with the isoprene oxidation products MVK + MACR through correlation of aircraft data and diurnal profiles of ground data. This is consistent with production of SOA from photochemical processing

of isoprene. Volatility modelling calculations showed MF to be too volatile to be present in the condensed phase meaning it is likely to be a product of some other molecule, produced upon the vapourisation involved in both the AMS and GC × GC analyses. One such potential condensable MF precursor could be peroxyhemiacetal oligomers, derived from gas-phase isoprene photo-oxidation products such as unsaturated 1,4-hydroxycarbonyls. However, the actual specific MF precursor (or precursors) require laboratory identification. Future work will attempt to detect the  $m/z$  82 peak in the laboratory, both from established isoprene SOA and from the compounds suggested here. Comparisons of two metrics,  $m/z$  82 fractional organic mass and peak prominence, show that isoprene dominated environments seem to have greater MF loadings than terpene dominated. The  $m/z$  82 peak was also observed in isoprene oxidation chamber experiments. PMF analysis of the HR-AMS mass spectral time series yielded a robust factor that was characterised by strong  $m/z$  82 and 53 signals.

The ubiquity of the enhanced  $m/z$  82 peak at all measurement locations influenced by isoprene suggests that the mechanism forming this SOA is important in all high isoprene/low  $NO_x$  (i.e.  $NO_x$  limited) environments, which are widespread throughout the unpolluted tropics. Given the lower fractional contribution in the Amazon, it could be speculated that other factors may decide its importance, such as the presence of acids, which have been shown to be important in other SOA studies (Lim and Ziemann, 2009; Surratt et al., 2010).

Although progress is being made, evidence from chamber studies of isoprene photo-oxidation still does not reveal a consistent picture, with greater variation in isoprene SOA yields than for systems such as  $\alpha$ -pinene (Carlton et al., 2009). Models estimating the global contribution of isoprene SOA give a wide range of values (Carlton et al., 2009). Better agreement with measurements can be reached with top-down approaches (Capes et al., 2009), however these do not account for any conflating uncertainties in processes and emissions, so are of limited use as predictive tools under future



climates, CO<sub>2</sub> concentrations and land uses. While established isoprene SOA such as IEPOX derived organosulphates may be the precursor aerosol to MF measurements, it is unclear what mechanism could produce MF from these species. It is possible therefore that MF is produced from previously unidentified isoprene product(s). As such, identification of the MF precursor aerosol may provide key insights into missing SOA, and the identification of the relationship of the AMS *m/z* 82 peak to isoprene SOA opens up the opportunity for more high time resolution isoprene SOA measurements in other projects. The PMF analysis suggests that an average of 23% (0.18 μg m<sup>-3</sup>), and as much as 53% (0.5 μg m<sup>-3</sup>) of the organic aerosol may be produced from isoprene oxidation in Borneo. The natural balance of isoprene is being affected by deforestation for oil palm agriculture (McMorrow and Talip, 2001) which emits five times as much isoprene as the natural forest (Hewitt et al., 2009), meaning isoprene SOA will only become more important with further similar land use change.

## Appendix A

### Details of unpublished data from the BEARPEX campaign

The North American temperate HR-AMS measurements presented in Table 1 of the main text, took place during the BEARPEX (Biosphere Effects on AeRosols and Photochemistry EXperiment) campaign at Blodgett Forest Ameriflux site in 2007. The site is a mid-elevation ponderosa pine plantation owned by Sierra Pacific Industries, and located ~75 km northeast of Sacramento on the western slope of California's mid-elevation Sierra Nevada mountains (38.90° N, 120.63° W, 1315 m elevation). AMS measurements were taken between 19 August and 28 September 2007, at the top of an 18 m tower. The site has been previously described in detail Dreyfus et al. (2002). Wind patterns throughout the measurement period were consistent, with westerly to south-westerly wind during the day and northeasterly to easterly winds at night Murphy et al. (2006). This results in a consistent diurnal pattern of VOCs in which a mix of terpenes and other pine-derived biogenic VOCs are observed in the morning followed by isoprene and its oxidation products at mid-day as air is transported over a lower elevation band of oak forest Dreyfus et al. (2002). In the afternoon, a mix of biogenic and anthropogenic VOCs are caused by transport of polluted air from the Sacramento area. The Blodgett forest canopy is dominated by *Pinus ponderosa* L., planted in 1990 with a mean height of 8 m, with few Douglas fir, white fir and incense cedar. The understory includes mountain whitehorn and manzanita. The data presented have been screened for the influence of biomass burning.

### Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys.net/11/1039/2011/acp-11-1039-2011-supplement.pdf>.

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