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In situ measurements of isoprene and monoterpenes within a South-East Asian tropical rainforest

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Abstract

Biogenic volatile organic compounds (BVOCs) emitted from tropical rainforests comprise a substantial fraction of global atmospheric VOC emissions, however there are only relatively limited measurements of these species in tropical rainforest regions. We present observations of isoprene, α-pinene, camphene, Δ-3-carene, γ-terpinene and limonene, and oxygenated VOCs (OVOCs) of biogenic origin such as methacrolein, in ambient air above a tropical rainforest in Malaysian Borneo. Daytime composition was dominated by isoprene, with an average mixing ratio of the order of ~1 ppb. γ-terpinene, limonene and camphene were the most abundant monoterpenes, with average daytime mixing ratios of 102, 71 and 66 ppt, respectively, and with an average monoterpene to isoprene ratio of 0.3 during sunlight hours, compared to 2.0 at night. Limonene and camphene abundances were seen to be related to both temperature and light conditions. In contrast, γ-terpinene emission occurred into the late afternoon/evening, under relatively low temperature and light conditions. We observe good agreement between surface and aircraft measurements of boundary layer isoprene and methacrolein above the natural rainforest, suggesting that the ground-level observations are broadly representative of isoprene emissions from this region.

1 Introduction

Emissions of volatile organic compounds (VOCs) affect the oxidising capacity of the atmosphere (Kesselmeier et al., 2000), radiative forcing (through formation of secondary organic aerosol, Padhy and Varshney, 2005) and the global carbon cycle (Kuhn et al., 2002; Fuentes et al., 2000). VOCs scavenge oxidants such as the hydroxyl radical (OH), ozone (O_3) and the nitrate radical (NO_3) (Atkinson and Arey, 2003), and in polluted, high NO_x (NO and NO_2) environments, VOC emissions lead to net tropospheric O_3 production through catalytic reactions between oxidised VOC derivatives (peroxy radicals) and NO (Atkinson and Arey, 2003; Lelieveld et al., 2008).

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Biogenic VOCs (BVOCs) such as isoprene, monoterpenes and sesquiterpenes are thought to provide the largest fraction (>90%) of the total global VOC source term (Greenberg et al., 1999), with a total BVOC flux of the order of $1100\,\text{Tg}\,\text{C}\,\text{yr}^{-1}$ (Guenther et al., 1995; Simpson et al., 1999), compared to $50\text{–}100\,\text{Tg}\,\text{C}\,\text{yr}^{-1}$ anthropogenic VOCs (Holzke et al., 2006). Biosynthesis of isoprene and monoterpenes occurs within plants via the precursors dimethylallyl pyrophosphate (DMAPP) and isopentenyl pyrophosphate (IPP) (Fuentes et al., 2000), and has been linked with a number of physiological processes such as temperature regulation, reducing drought-induced stress and promotion of flowering (Kesselmeier and Staudt, 1999). BVOC emissions (by mass) are often dominated by isoprene (Guenther et al., 2000), and estimates of the global isoprene flux are in line with global methane emissions (Wildermuth and Fall, 1996; Sharkey and Yeh, 2001).

BVOC emissions from the tropics are considered to have a disproportionately large impact upon the chemistry of the atmosphere (IPCC, 2001), since deep convection in this region drives rapid transport of ground level emissions to higher altitudes, such that local emissions may become distributed over a relatively broad area. In fact, more than 70% of BVOCs are thought to originate from the tropics (Karl et al., 2007), yet there have been only a limited number of BVOC measurements within this region, and very few of these datasets include in situ measurements of a comprehensive range of monoterpenes (Kesselmeier et al., 2000; Kuhn et al., 2002; Wilske et al., 2007; Saxton et al., 2007). The majority of previous tropical BVOC datasets are for Amazonia (Kesselmeier et al., 2000), whilst BVOC measurements from South-East Asia are more sparse (Hewitt et al., 2010). Since BVOC emissions from vegetation are strongly species-dependent, increasing the spatial and temporal range of measurements of these gases is fundamental to achieving improved characterisation of their local, regional and global scale impact on the chemistry of the atmosphere.

Here we present in situ measurements of isoprene and the monoterpenes α-pinene, camphene, Δ-3-carene, γ-terpinene and limonene, together with a range of other C_2–C_7 VOCs and OVOCs, in ambient air at the Bukit Atur Global Atmosphere Watch (GAW)

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station within the Danum Valley rainforest in Sabah, Borneo, as part of the Oxidant and Particle Photochemical Processes above a South-East Asian tropical rainforest (OP3) campaign. We also present measurements of selected VOCs (including isoprene) from an aircraft platform, which reveal regional variations in VOC concentrations in response to changes in land use across Malaysian Borneo.

2 Methods

Gas chromatography with flame ionization detection (GC-FID) was used to provide automated continuous hourly measurements of selected VOCs in ambient air at the Bukit Atur GAW station, located in the Danum Valley rainforest conservation area in Sabah, Borneo (4°58′49.33″ N, 117°50′39.05″ E, 426 m a.s.l.). The site was located in a clearing at the top of a hill, above most of the surrounding rainforest, and air was sampled for analysis of VOCs from ~5 m a.g.l. The ground-based component of the OP3 project consisted of three measurement phases during 2008 (Hewitt et al., 2010), and in situ measurements of VOCs at Bukit Atur were made during two of these – from 7 April to 1 May (OP3-I), and 23 June to 20 July (OP3-IIII).

Volatile trace gases were pre-concentrated from 1 l air samples by pumping several litres of ambient air per minute from 5 m a.g.l. through a ~10 m long 1/2″ i.d. manifold, and sub-sampling 100 ml min^{-1} air from this manifold through a 1/4″ i.d. ~1 m long stainless steel line to the instrument. Samples were initially passed through a glass condenser, held at –30 °C by immersion in a water ethylene glycol solution, to remove moisture before being passed onto a Peltier-cooled multi-bed carbon-based chemical adsorbent trap, held at –20 °C for 10 min periods. The trap was subsequently flushed with helium for 3.5 min to remove methane, before desorption of the volatile components into the helium carrier gas stream by heating to 325 °C. Chromatographic separation was achieved using a dual-column Agilent 6890 GC system, which facilitates simultaneous analysis of both non-methane hydrocarbons (NMHCs), which were

separated using a 50 m aluminium oxide (Al_2O_3) porous layer open tubular (PLOT) column, and oxygenated VOCs (OVOCs) and monoterpenes, which were separated using two 10 m LOWOX columns in series. Following desorption, the analytes were split between the PLOT and LOWOX columns, with each column coupled to a FID.

5 Calibration of the majority of VOCs was achieved using an Apel Reimer 54 component gas standard (serial number CC236306), however in the field the monoterpenes (which suffer from degradation in gas canisters) were calibrated based upon the relationship between the FID response to each monoterpene relative to toluene (empirically derived by liquid injection calibrations prior to field studies). Further details of the NMHC and

10 OVOC sampling and GC-FID separation, analysis and calibration using this system are given elsewhere (Hopkins et al., 2002, 2011).

The monoterpenes analysed using this system were α-pinene, camphene, Δ-3-carene, γ-terpinene, limonene and β-pinene. Analysis of pure monoterpene liquids in laboratory tests showed that in some cases a small amount of inter-conversion be-

15 tween several monoterpene isomers occurred within the system, presumably during pre-concentration on the adsorbent trap. There was no significant degradation/inter-conversion of camphene, Δ-3-carene or γ-terpinene, however ~8% of limonene injected in to the system was converted to γ-terpinene, and α-pinene experienced the most degradation, with ~10% converted to camphene and ~5% converted to limonene

20 (Hopkins et al., 2011). Since these in-system isomerizations were repeatable, the reported monoterpene mixing ratios in ambient air samples have been corrected accordingly. It should be noted that although β-pinene was detected in standards, it was not detected in ambient air samples in the Danum Valley rainforest. A summary of the VOCs and OVOCs routinely monitored during this study is given in Table 1.

25 During the third phase of the OP3 experiment (OP3-IIII), an almost identical Perkin Elmer dual channel GC-FID instrument was used to analyse whole air samples collected aboard the Facility for Airborne Atmospheric Measurements (FAAM) BAe146 research aircraft. During the first phase of the OP3 project (OP3-I) the system was briefly deployed at the Bukit Atur GAW station alongside the ground-based Agilent

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instrument. The excellent agreement in atmospheric isoprene mixing ratios determined by the two instruments when co-located at the GAW station (see Fig. 1) has enabled direct comparisons between data collected at the ground and those collected during flights in the region. Air samples taken on board the aircraft were not analysed for monoterpenes, as their stability in canisters has not been tested, and the instrument was not optimised for monoterpene analysis.

3 Results and discussion

3.1 Summary of ground-based and aircraft-based VOC measurements

Table 1 summarises the VOC atmospheric mixing ratios in air at ground-level at the Bukit Atur rainforest site, and in air samples collected from the aircraft platform. To enable some comparability, the daytime (06:00 a.m.–06:00 p.m.) range and mean average mixing ratios are shown in both cases (since no night-time air samples were collected on board the aircraft), and ground-based data refers to the second measurement period (concurrent with the aircraft study) only. The airborne measurements have been separated according to whether the air samples were collected above the natural rainforest, or over palm oil plantations, which now cover vast areas of Malaysian Borneo (Hewitt et al., 2009).

The average daytime mixing ratios of isoprene and one of its oxidation products, methacrolein, at ground-level were in good agreement with the levels observed in air above the natural rainforest. This suggests that the Bukit Atur site may be considered broadly representative of this natural forest region, with respect to isoprene emission and oxidation chemistry. However, significantly higher maximum daytime isoprene mixing ratios were observed in the aircraft samples (almost double the maximum mixing ratios observed at ground-level), indicating the presence of local isoprene "hotspots" within the natural rainforest, and/or suppression of ambient isoprene at ground-level as a consequence of localised pollution (see below).

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Isoprene was highly elevated in air above the oil palm plantations, with an average daytime mixing ratio approximately four times higher compared to that above the surrounding natural rainforest, demonstrating that man-made land use change may potentially have significant implications for atmospheric chemistry (Hewitt et al., 2009).

The daily maximum isoprene mixing ratio was generally higher and more variable during the first measurement period in April (OP3-I) compared to the June–July period (OP3-IIII) (see Fig. 2). A lack of any marked seasonality in the Danum Valley conservation area has been previously reported for 2008 (Hewitt et al., 2010), hence significant seasonal differences were not anticipated. Given the low wind speeds and relatively short atmospheric lifetimes for these BVOCs, their mixing ratios at Bukit Atur are considered to result predominantly from local emissions, however, there may also have been some influence from regional air masses reaching the site, and whilst the station was influenced by air from most directions during OP3-I, during OP3-IIII trajectories were consistently from the south (Hewitt et al., 2010).

A further potentially important factor in the apparent suppression of isoprene during OP3-IIII was a period of local pollution in the form of NO (median peak noon-time NO was ~ 0.08 ppb and ~ 0.14 ppb during OP3-I and OP3-III, respectively, Pike et al., 2009), which gave rise to elevated OH mixing ratios (median midday values of $\sim 1.6 \times 10^6$ molec cm^{-3} OH for OP3-I, compared to $\sim 3.4 \times 10^6$ molec cm^{-3} during OP3-III; http://badc.nerc.ac.uk/browse/badc/op3/data). At midday, we estimate that this would result in a $\sim 50\%$ decrease in the atmospheric lifetime of isoprene during OP3-III compared to OP3-I, whilst the 24 h-averaged isoprene and monoterpene lifetimes would be reduced by approximately $\sim 30\%$.

We infer therefore, that the isoprene and monoterpene mixing ratios observed during OP3-III were likely suppressed to some extent by higher OH levels during this period. Whilst this means that the ambient air BVOC mixing ratios reported from OP3-III likely represent an under-estimate of the levels that might be expected above the pristine rainforest in this region, the diurnal variability and relative contributions of primary emitted BVOCs to the carbon budget and boundary layer chemistry remain broadly

representative of the Danum Valley conservation area.

3.2 Factors controlling ground-level ambient BVOC mixing ratios within the natural rainforest

Several previous studies have demonstrated considerable diurnal variability in the release of isoprene and monoterpenes from vegetation, with maximum emissions occurring around midday (Fuentes et al., 2000; Kuhn et al., 2002). The diurnal variation in boundary layer isoprene is generally attributed to an emission pathway dependent upon both light and temperature (Kuhn et al., 2002). Monoterpene release from broad-leaved species is thought to be controlled by a similar dual light and temperature dependence, whilst there is evidence to suggest that some monoterpenes may be stored within coniferous plants, with release from these reservoirs regulated exclusively by temperature, and independent of light levels (Kuhn et al., 2002; Noe et al., 2006; Wilske et al., 2007).

A strong diurnal signature was observed in the isoprene and monoterpene mixing ratios at Bukit Atur (see Figs. 2 and 3), and whilst daytime BVOC emissions were dominated by isoprene, the monoterpenes were found to persist at night, when, in the absence of sunlight, isoprene mixing ratios dropped to as low as ~0.05 pptv (Fig. 3). In fact, the average monoterpene to isoprene ratio increased from ~0.3 during the day (06:00 a.m.–06:00 p.m.) to ~2.0 at night (06:00 p.m.–06:00 a.m.). The daytime monoterpene to isoprene ratio is in fairly good agreement with the average {total monoterpene}/isoprene emission ratio derived from flux measurements made during the same period at Bukit Atur (0.23±0.3, Langford et al., 2010), as well as with emission ratios from other studies (Guenther et al., 2008). The marked increase in the ambient monoterpene/isoprene ratio at night was not reflected in the relative emission rates measured at Bukit Atur, however the flux measurements were made at a height of 75 m a.g.l. (compared to 5 m for the "ground-level" measurements reported here), and there is evidence to suggest that at night the 75 m platform was de-coupled from the boundary layer (Pearson et al., 2010; Hewitt et al., 2010).

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Figure 3 shows the hourly averaged concentrations of isoprene, methacrolein and the three most abundant monoterpenes (camphene, limonene and γ-terpinene), to give diurnal profiles derived from all measurements between 23 June–20 July 2008, together with the average daily photosynthetically active radiation (PAR) and temperature profiles. Figure 4 shows the correlations of isoprene and the monoterpenes with temperature and PAR. The concentration profiles and correlation plots (Figs. 3 and 4) indicate that isoprene, limonene and camphene were well correlated with both temperature and PAR, whilst γ-terpinene showed a more moderate dependence upon both factors. Notably, the γ-terpinene mixing ratio remained significantly elevated during the late afternoon/evening, well after PAR and temperature had started to decrease, and remained above 80 ppt (on average) for 1–2 h after PAR had dropped to zero (Fig. 3). Since γ-terpinene is one of the shorter-lived monoterpenes (typical lifetime $\sim$45 min, Atkinson and Arey, 2003), persistence into the late afternoon/evening suggests that leaf emissions were still occurring at this time, even under very low light levels. Although the γ-terpinene mixing ratio did eventually decrease at night, the difference between day and night time concentrations was not as extreme as for isoprene and the other monoterpenes. Table 2 summarises the Spearman's rank correlation coefficients, which quantify the extent of correlation between each of the BVOCs with air temperature and PAR (where a correlation coefficient of $+1$ or -1 indicates a perfect correlation, and a coefficient of 0 indicates no correlation).

Isoprene was found to be strongly correlated with temperature, whilst the statistical test on all measurements indicates a comparatively weaker correlation with PAR. This slightly weaker relationship with PAR may be a consequence of competing light-dependent isoprene emission and destruction pathways, which ultimately determine the net mixing ratio. The isoprene mixing ratio peaked just after midday, slightly later than the maximum PAR; concurrent OH observations at Bukit Atur (Whalley et al., 2011) show that OH peaked at local noon, suggesting that although maximum isoprene emission may have occurred around midday inline with maximum PAR, rapid removal of isoprene by OH suppressed ambient concentrations during this time. Suppression of

ambient isoprene in the late morning–midday period by OH reduces the strength of the apparent correlation between isoprene levels and PAR in the midnight–midday period, whilst in contrast, measurements made between midday and midnight demonstrate a much stronger correlation between isoprene and PAR, comparable to the correlation

5 between isoprene with temperature (Table 2). Figure 5 shows the isoprene-PAR correlations separated into the midnight–midday and post midday–midnight periods, and demonstrates that the isoprene mixing ratios measured in the morning were generally reduced compared to values in the afternoon, for equivalent PAR. In contrast, the equivalent plot of isoprene vs. temperature (Fig. 5b) shows no significant difference

10 between the pre-midday and post-midday correlations. Since ozone concentrations were very low (typically $\sim$5 ppb), scavenging of BVOCs by ozone was presumed to be insignificant compared to loss by reaction with OH.

With the exception of limonene, the monoterpene correlation plots and Spearman's rank coefficients derived from all measurements are generally more consistent with

15 a temperature-controlled emission pathway, and suggest a relatively weaker dependence upon light levels (Fig. 4 and Table 2). The correlation coefficients derived solely from the post-midday measurements suggest that emissions of limonene and camphene, in particular, may also be influenced to some extent by light levels (Table 2). This is consistent with changes in the relative atmospheric monoterpene composition

20 according to the time of day (Fig. 6) and with the treatment of monoterpenes in the model study of Pugh et al. (2010), which assumes a light-dependent emission pathway. However, caution must be exercised in the interpretation of these statistical tests, since temperature and PAR were themselves reasonably well-correlated (ρ=0.58 for all measurements, see Table 2), particularly in the midday–midnight period (ρ=0.70).

25 As such, the stronger correlations between both limonene and camphene with PAR after midday may be, at least in part, simply an artefact of the PAR vs. temperature correlation.

Figure 6 shows the diurnal variability in the relative abundance of each monoterpene. At night, monoterpene emissions were dominated by γ-terpinene ($\sim$46%), however

during sunlit hours, although γ-terpinene was still the most abundant monoterpene, its relative contribution was reduced (∼36%), whilst the relative amount of camphene, and to a lesser extent limonene, increased. Between 06:00 a.m. and 06:00 p.m., camphene contributed on average ∼24% of the monoterpene emissions, but supplied only ∼14% at night. Likewise, limonene contributed an average of ∼26% of the total monoterpenes during the day, compared to ∼22% at night. In absolute terms, α-pinene and Δ-3-carene were present in much lower levels compared to the other monoterpenes, however, like γ-terpinene, the fraction supplied by Δ-3-carene did decrease during the day (from ∼10% at night to ∼7% during daytime). The average contribution from α-pinene of ∼8% was approximately constant over a 24 period.

Table 3 summarises Spearman's rank correlation coefficients to quantify the extent of correlation between the atmospheric mixing ratios of selected VOCs. The strong correlations between certain BVOCs are indicative of a common source, and/or similar atmospheric removal rates. Camphene and limonene demonstrated the strongest correlation (ρ=0.95), whilst both were also well correlated with α-pinene (ρ=0.81 and 0.77 for camphene and limonene, respectively). In addition, α-pinene, camphene and limonene all showed significant correlations with isoprene. Since the particularly strong correlation between camphene and limonene cannot be explained by comparable loss rates (as limonene has a shorter atmospheric lifetime with respect to reaction with OH compared to camphene, Atkinson and Arey, 2003), we assume that in this case the apparent similarities in their atmospheric mixing ratios are most likely driven by a substantial common (local) emission source.

Li et al. (2008) also observed strong correlations between limonene, camphene and α-pinene, in emissions from Chinese pine (*Pinus tabulaeformis)*, and inferred that biosynthesis of these monoterpenes may be controlled by a common metabolic pathway. However, in contrast to our measurements, they did not find that these monoterpenes were also strongly correlated with isoprene.

Methacrolein was most strongly correlated with its atmospheric precursor isoprene, although the relatively weak correlation (compared to those between the primary

BVOCs) is most likely a result of a slight time-delay between primary emission of isoprene, and its gas phase oxidation to produce methacrolein (apparent in the respective diurnal average mixing ratio profiles, Fig. 3). The non-biogenic VOCs (e.g. ethane) showed no significant correlation with temperature or PAR (Table 2), or with any BVOC (Table 3).

3.3 VOC carbon budget and OH reactivity within the natural rainforest

The relative contributions of each VOC to the atmospheric carbon mass budget and to boundary layer OH removal have been assessed for the tropical boundary layer at Bukit Atur (Fig. 7). As there was strong diurnal variability in many BVOC mixing ratios, these analyses have been separated for daytime (06:00 a.m.–06:00 p.m.) and night time (06:00 p.m.–06:00 a.m.) observations. These analyses are based upon data from OP3-III only, since this was the period with the most comprehensive VOC measurements.

The average daytime total VOC carbon concentration during OP3-III was 6150 ng C m^{-3} – approximately double the average night time value (3130 ng C m^{-3}). Figure 7 shows that during sunlit hours, isoprene provided the largest single source of volatile organic carbon, with an average contribution of 36%, compared to a 14% average daytime source from the monoterpenes and 27% from OVOCs (sum of methacrolein, methanol, acetone and acetaldehyde). Around midday, isoprene supplied up to 70% of boundary layer volatile organic carbon, while within an hour after sunrise and before sunset, the contribution from isoprene was as little as 5%. During the night, the absolute concentrations of isoprene, monoterpenes and OVOCs were reduced relative to the daytime, and the fraction of volatile organic carbon supplied as OVOCs and monoterpenes increased, to 35% and 20%, respectively, while the isoprene contribution decreased, to 13%.

The reactivity of each VOC with respect to OH was calculated from each instantaneous measured mixing ratio and the relevant published rate constant (Atkinson et al., 1986; Atkinson, 1997; Atkinson and Arey, 2003). Figure 7 shows the average day

and night resolved distribution of the total OH reactivity with respect to VOCs, based upon all measurements from OP3-III. Night time reactivities have been determined in addition to the daytime values since OH was intermittently above instrument detection limits during the night at Bukit Atur (Whalley et al., 2011). During the day, isoprene contributed on average ~64% of OH removal by VOCs, while the total combined contribution from the monoterpenes was ~27%. The OVOCs, alkanes and alkenes all made smaller contributions (~5, ~0.5 and ~3.5%, respectively). During the night, however, the potential removal of OH was dominated by the monoterpenes, with a total OH reactivity of ~48%, compared to ~34% from isoprene. The total average daytime OH reactivity based upon the VOCs reported here was $3.6\,\mathrm{s}^{-1}$. The contribution to OH reactivity from the individual monoterpenes increased in the order α-pinene<Δ-3-carene<camphene<limonene<γ-terpinene.

3.4 Regional differences in VOC composition and OH reactivity

Strong regional differences were apparent in the isoprene and methacrolein mixing ratios over Borneo; the area to the north-east of the Danum Valley conservation area is predominantly oil palm, and is characterised by regionally higher levels of isoprene and methacrolein, compared to the natural forest (Fig. 8) (Misztal et al., 2010). Conversely acetylene, used as a tracer of anthropogenic pollution, was more uniform across both the plantation and natural forest regions (Fig. 9). The total VOC OH reactivity in the palm region was greater than that in the natural rainforest, with total reactivities of 4.3 and $14.4\,\mathrm{s}^{-1}$ over the Bukit Atur site and palm regions, respectively. A more detailed description of the regional variations observed in boundary layer isoprene over Borneo during OP3 is given elsewhere (Hewitt et al., 2009, 2010).

4 Summary

VOC observations in the atmosphere above Borneo's Danum Valley rainforest demonstrate that isoprene provides the single largest volatile carbon source in this region, whilst monoterpenes were found to contribute a comparatively smaller, yet still significant fraction. During sunlit hours, the atmospheric isoprene mixing ratio was, on average, almost four times larger than the combined monoterpene mixing ratio, however monoterpenes were found to make a substantial contribution both to the carbon mass budget (comprising a daytime average of ~14% of carbon by mass supplied to the atmosphere as VOCs) and in the removal of the atmospheric oxidant OH (contributing ~27% of VOC initiated OH destruction). In the absence of sunlight, however, monoterpenes were the most abundant class of VOCs, with an average night time combined mixing ratio double that of isoprene, and accounting for, on average, 48% of the total nocturnal OH reactivity.

Since the individual monoterpenes have differing OH reaction rate constants, speciated monoterpene observations are preferable over some techniques which report only the total monoterpene signal, in order to achieve the most accurate interpretation of their significance as an atmospheric carbon source, as well as determining their impact upon OH reactivity. The relative abundance of the individual monoterpenes generally increased in the order α-pinene$\sim\Delta$-3-carene$<$camphene$<$limonene$<\gamma$-terpinene, and as a result of their abundance and relatively high OH reactivities, limonene and γ-terpinene accounted for, on average, 86% of day time monoterpene removal of OH from this rainforest region. Despite their comparable atmospheric lifetimes, the fraction of the total monoterpenes comprised of γ-terpinene was reduced during the day, whilst the relative fraction of limonene increased. Further investigation is required to clarify whether there is some level of light-controlled release of limonene and camphene in the vicinity of Bukit Atur, or whether their apparently strong correlations with PAR are merely an artefact of the correlation between PAR and ambient air temperature. Overall, the monoterpene mixing ratios in the Danum Valley conservation area

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were generally more consistent with a temperature-controlled emission pathway, whilst isoprene mixing ratios also demonstrated strong light dependence.

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Table 1. Mean average daytime VOC mixing ratios observed within the natural rainforest at Bukit Atur, and in air samples collected above the natural rainforest and oil palm plantations. In each case the range of observed daytime mixing ratios in ppt are given in brackets (5th and 95th percentiles).

VOC	Mixing ratios (ppt)		
	Bukit Atur – natural rainforest (ground level)	Aircraft natural rainforest	Aircraft oil palm
Isoprene	1058 (50–2474)	1219 (252–4664)	4215 (414–10 522)
α-pinene	24 (9–40)	–	–
Camphene	66 (14–129)	–	–
Δ-3-carene	22 (9–41)	–	–
γ-terpinene	102 (53–166)	–	–
Limonene	71 (26–127)	–	–
Methacrolein	106 (42–234)	105 (23–268)	221 (42–517)
Methanol	1798 (933–2807)	3450 (1131–6593)	2907 (681–5278)
Acetone	426 (212–666)	1332 (694–2486)	1130 (588–2494)
Ethene	77 (36–132)	147 (83–237)	186 (80–411)
Propene	47 (19–56)	23 (14–38)	34 (13–90)
Iso-butene	111 (63–175)	12 (6–20)	12 (7–17)
Acetylene	121 (71–182)	152 (84–222)	181 (112–299)
Ethane	368 (222–560)	320 (250–420)	325 (253–456)
Propane	173 (24–378)	94 (46–144)	93 (65–128)
n-pentane	26 (13–45)	15 (4–28)	14 (7–24)
Iso-pentane	33 (9–71)	17 (5–30)	20 (9–37)
Cyclo-pentane	9 (5–14)	6 (5–8)	7 (5–8)

Table 2. Spearman's rank correlation coefficients to demonstrate the degree of correlation between VOC mixing ratios with air temperature (°C) and PAR (μmol m^{-2} s^{-1}).

	Air temperature	PAR (all data)	PAR (00:00–12:00)	PAR (12:00–00:00)
Isoprene	0.78	0.71	0.64	0.79
α-pinene	0.70	0.67	0.53	0.68
Camphene	0.71	0.68	0.61	0.78
Δ-3-carene	0.53	0.34	0.28	0.43
γ-terpinene	0.67	0.61	0.55	0.69
Limonene	0.70	0.72	0.63	0.79
Methacrolein	0.43	0.05	−0.09	0.19
Acetylene	−0.10	−0.24	−0.19	−0.27
Ethane	−0.17	−0.05	−0.05	−0.05
Air temperature	–	0.58	0.52	0.70

Table 3. Spearman's rank correlation coefficients to illustrate the extent of correlation between monoterpenes, isoprene, methacrolein and ethane. The most significant correlations are highlighted in bold.

	α-pinene	Camphene	Δ-3-carene	γ-terpinene	Limonene	Metha-crolein	Ethane
Isoprene	**0.78**	**0.76**	0.61	0.61	**0.79**	0.52	−0.16
α-pinene		**0.81**	0.49	0.60	**0.77**	0.32	−0.07
Camphene			0.49	0.62	**0.95**	0.20	0.21
Δ-3-carene				0.33	0.58	0.48	−0.07
γ-terpinene					**0.77**	0.27	0.20
Limonene						0.22	0.0
Methacrolein							−0.23

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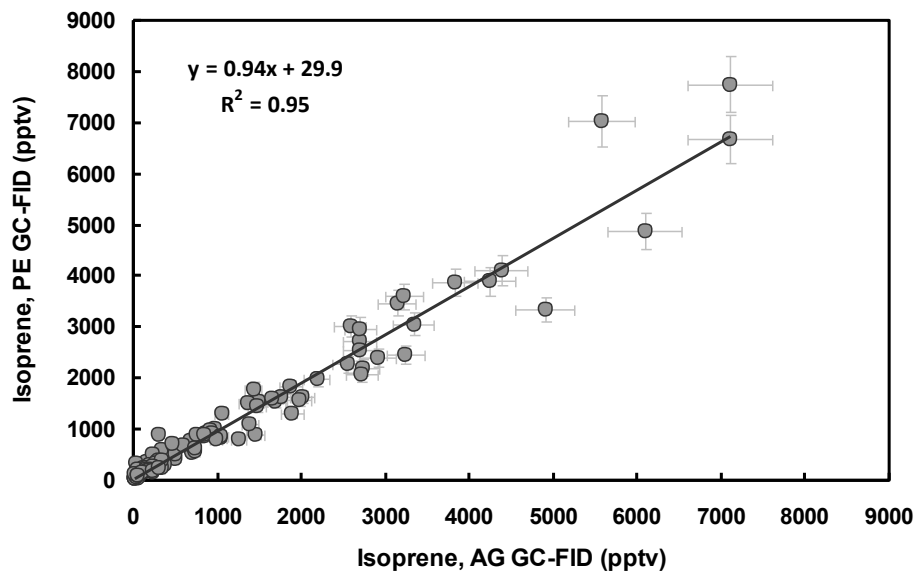
Fig. 1. Correlation between isoprene mixing ratios in ambient air quantified by the independent Agilent and Perkin Elmer GC-FID instruments at the Bukit Atur GAW station in April 2008. Note only mixing ratios derived from simultaneous measurements (sampling periods within ±5 min) were used for this comparison.
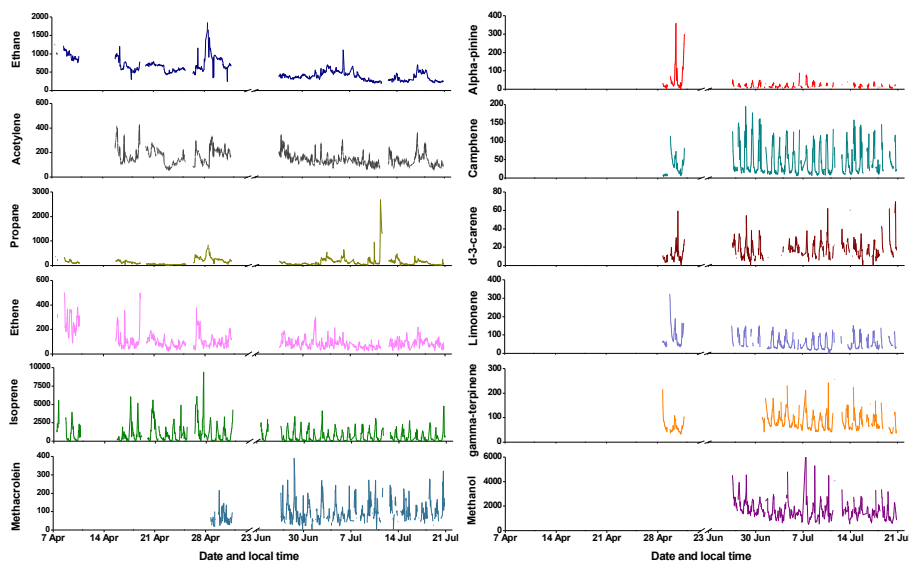
Fig. 2. Time-resolved measurements of isoprene and its oxidation product methacrolein, the monoterpenes α-pinene, camphene, Δ-3-carene, limonene and γ-terpinene, methanol, and selected other VOC thought to be of primarily anthropogenic origin (ethane, acetylene and propane) at the ground-based site at Bukit Atur during the two OP3 field measurement campaigns. Only limited monoterpene and OVOC data is shown from the first measurement period, due to instrument failures.
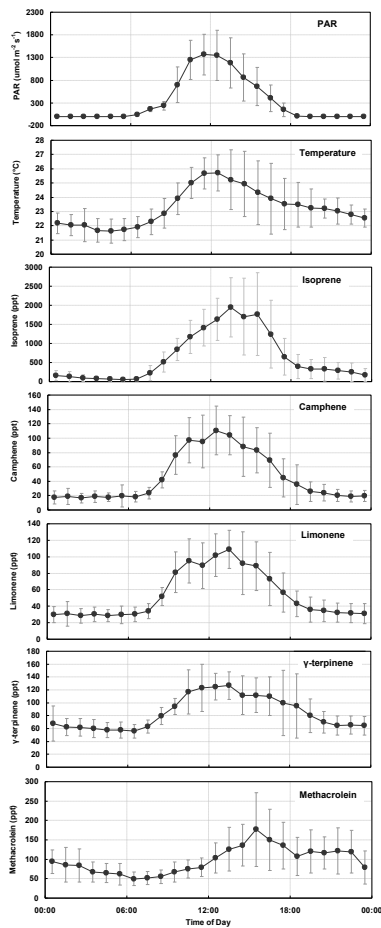
Fig. 3. Diurnal average PAR and temperature profiles and mixing ratios of isoprene, the three most abundant monoterpenes (limonene, γ-terpinene and camphene) and methacrolein.
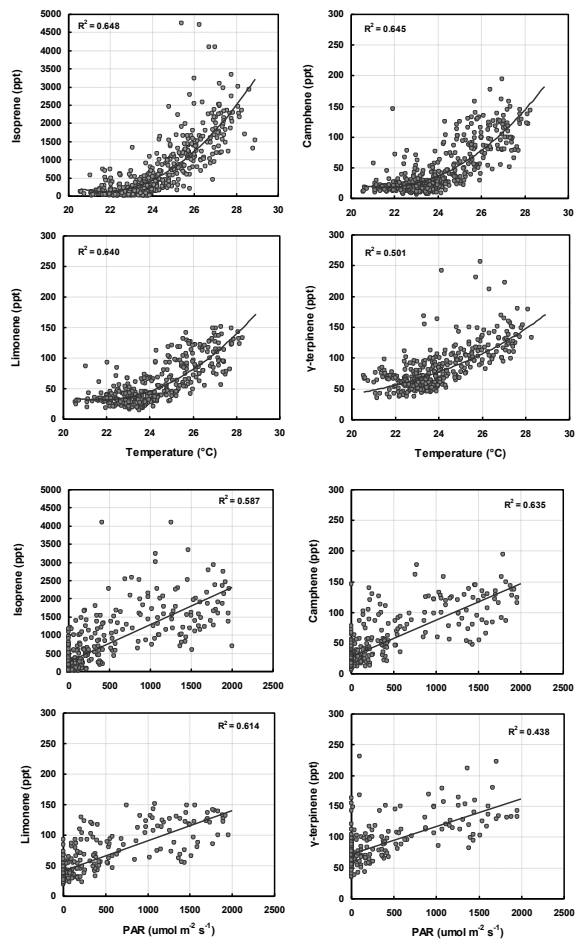
Fig. 4. Plots to show the correlations between isoprene, limonene, camphene and γ-terpinene vs. ambient air temperature and vs. PAR.

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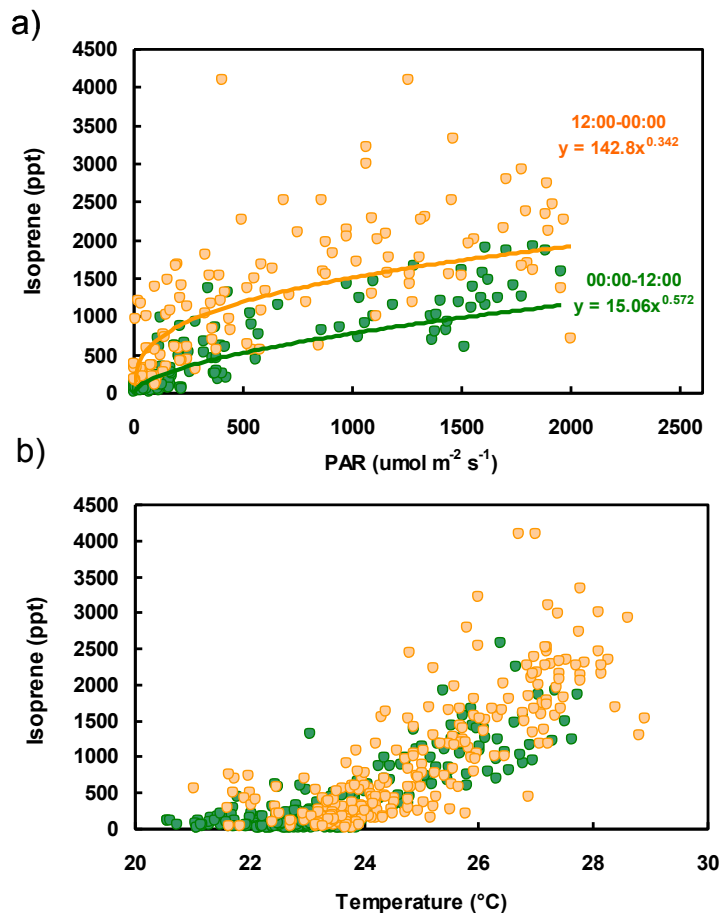
Fig. 5. Correlations between the ambient isoprene mixing ratio with, **(a)** PAR and **(b)** temperature, in the morning (between midnight and midday – green circles) and in the afternoon (between midday and midnight – orange circles).

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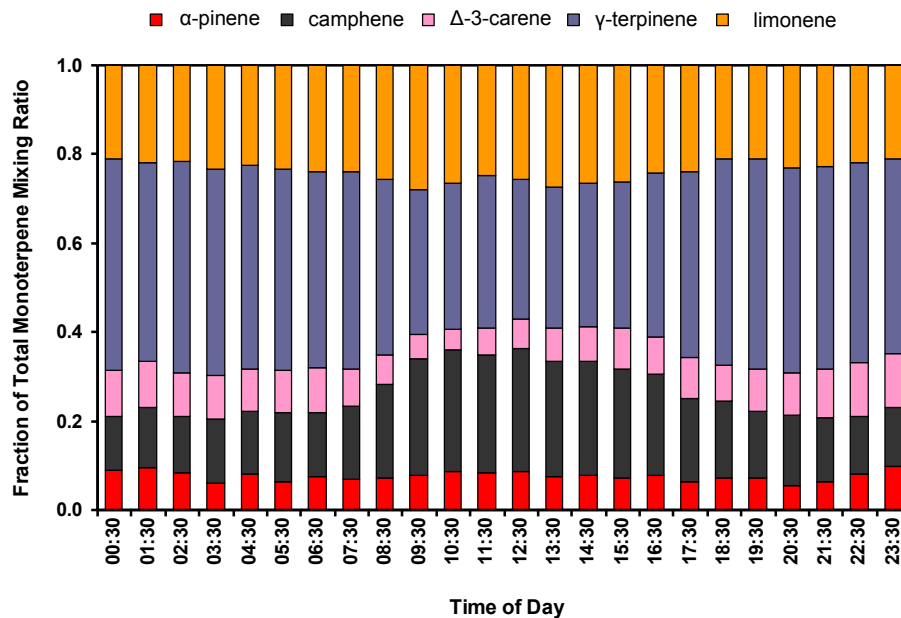
Fig. 6. Average diurnal variation in the relative fractions of the individual monoterpenes α-pinene (red), camphene (grey), Δ-3-carene (pink), γ-terpinene (blue) and limonene (orange), based upon measurements between 23 June–20 July.
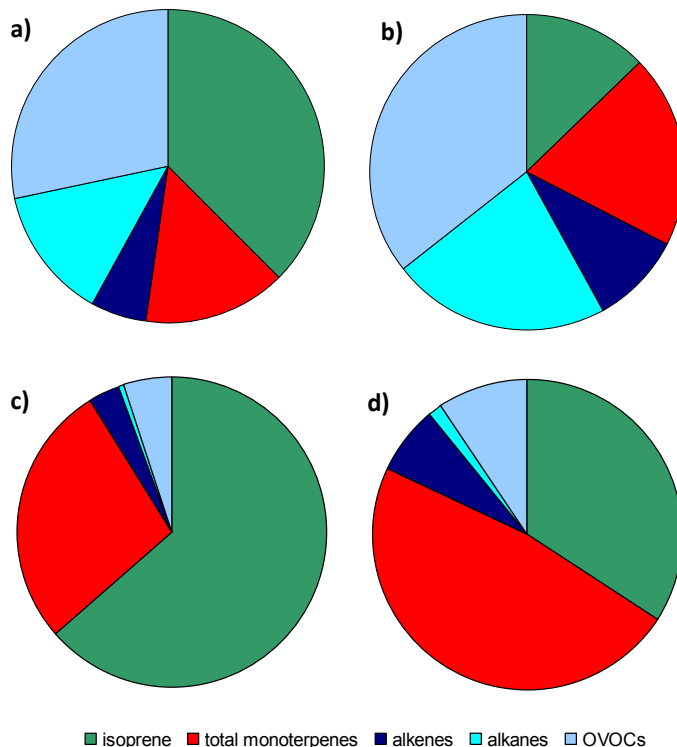
isoprene ■ total monoterpenes ■ alkenes ■ alkanes ☐ OVOCs

Fig. 7. Plots **(a)** and **(b)** represent the average instantaneous fraction of the total volatile organic carbon comprised of isoprene, monoterpenes, alkenes, alkanes and OVOCs in ground-level air at Bukit Atur, during the day (06:00 a.m.–06:00 p.m.; **a**) and night time (06:00 p.m.–06:00 a.m.; **b**). Plots **(c)** and **(d)** demonstrate the relative VOC reactivity with respect to OH for each VOC class during day time **(c)** and at night **(d)**, based upon the rate constants from Atkinson et al. (1986); Atkinson (1997); Atkinson and Arey (2003).

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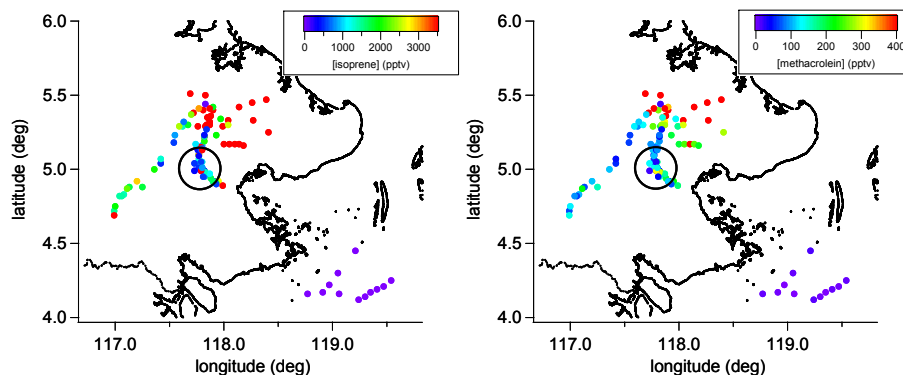Printer-friendly Version

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Fig. 8. Regional variations in isoprene and methacrolein mixing ratios across Borneo (circle highlights the Danum Valley conservation area), for all samples collected on board the aircraft, below 500 ft. (VOC analysis was carried out by GC-FID analysis of whole air samples).
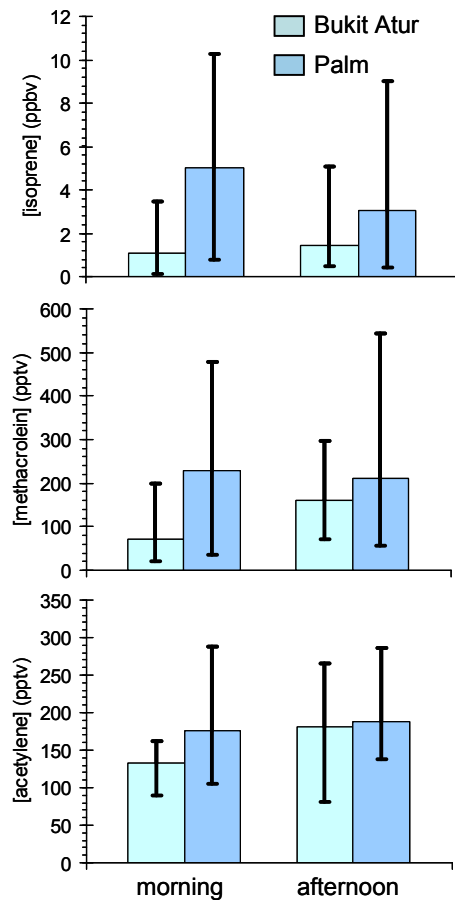
Fig. 9. Mean mixing ratios of isoprene, methacrolein and acetylene observed within the boundary layer (<500 ft) above the natural rainforest in the vicinity of the Bukit Atur site, and over the oil palm plantations.