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Fluxes and concentrations of volatile organic compounds from a South-East Asian tropical rainforest

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Abstract

As part of the OP3 field study of rainforest atmospheric chemistry, above-canopy fluxes of isoprene, monoterpenes and oxygenated volatile organic compounds were made by virtual disjunct eddy covariance from a South-East Asian tropical rainforest in Malaysia. Approximately 500 hours of flux data were collected over 48 days in April–May and June–July 2008. Isoprene was the dominant non-methane hydrocarbon emitted from the forest, accounting for 80% (as carbon) of the measured emission of reactive carbon fluxes. Total monoterpene emissions accounted for 18% of the measured reactive carbon flux. Monoterpenes were not emitted at night, and during the day their flux rate was dependent on both light and temperature. The oxygenated compounds, including methanol, acetone and acetaldehyde, contributed less than 2% of the total measured reactive carbon flux. The sum of the VOC fluxes measured represents a 0.4% loss of daytime assimilated carbon by the canopy, but atmospheric chemistry box modelling suggests that most (90%) of this reactive carbon is returned back to the canopy by wet and dry deposition following chemical transformation. The emission rates of isoprene and monoterpenes, normalised to 30 °C and 1000 μmol m^{-2} s^{-1} PAR, were 1.6 mg m^{-2} h^{-1} and 0.46 mg m^{-2} h^{-1} respectively, which was 4 and 1.7 times lower respectively than the default value for tropical forests in the widely-used MEGAN model of biogenic VOC emissions. This highlights the need for more direct canopy-scale flux measurements of VOCs from the world's tropical forests.

1 Introduction

It is currently estimated that tropical forests sequester up to 1.3 Pg of carbon annually (Lewis et al., 2009). Some of this is released back into the atmosphere in the form of reactive volatile organic compounds such as isoprene and monoterpenes (Laothawornkitkul et al., 2009). Emissions of biogenic volatile organic compounds (BVOC) therefore contribute to the global carbon cycle. They can influence both atmospheric composition and global climate in several key ways. First, due to their high reactivity with respect to the hydroxyl radical (OH), BVOC emissions mediate the oxidative capacity of the Earth's atmosphere, possibly amplifying the persistence of important greenhouse gases such as methane and HCFCs (Granier et al., 2000; Lelieveld et al., 2002). Secondly, monoterpenes and sesquiterpenes are known to be precursors for biogenic secondary organic aerosol (BSOA) (e.g., Hallquist et al., 2009), which are radiatively active and hence important in the global climate system. There is evidence that isoprene also contributes to BSOA formation (Claeys et al., 2004; Paulot et al., 2009). Although the aerosol yield from isoprene is small or negligible in chamber studies (Kroll et al., 2005, 2006; Kleindienst et al., 2006; Ng et al., 2008), the globally high emission rates of isoprene (500–750 Tg yr^{-1}; Guenther et al., 2006) indicate that its contribution to organic aerosol may be significant (Zhang et al., 2007), perhaps through the formation of water soluble compounds such as hydroxyhydroperoxides and epoxides (Paulot et al., 2009). Finally, VOCs mediate in the formation of photochemical pollutants such as tropospheric ozone and peroxyacetyl nitrate (PAN) (e.g., Sillman, 1999; Hewitt et al., 2009). At high concentrations, ozone can be directly toxic with detrimental impacts on human health, crops and forests (Fowler, 2008).

Despite the important roles played by VOCs in mediating atmospheric composition and climate, relatively little is known about their emission rates from tropical forests. Current estimates suggest that these regions may account for up to half of all global BVOC emissions (Guenther et al., 2006), yet this estimate is based on a limited number of field studies. To date, the majority of these field observations have focused on tropical forests in Amazonia (Zimmerman et al., 1998; Helmig et al., 1998; Stefani et al., 2000; Rinne et al., 2002; Kuhn et al., 2007; Karl et al., 2007, 2009) and, to a lesser extent, regions of Africa (Klinger et al., 1998; Greenberg et al., 1999; Serca et al., 2001).

In current global biogenic VOC emission models such as the Model of Emissions of Gases and Aerosols from Nature (MEGAN G06) (Guenther et al., 2006), emissions of isoprene from the world's tropical forests are, in part, based on standardised emission rates calculated using measurements conducted in Amazonia. This assumes a degree of uniformity across all tropical forests, which has yet to be confirmed by independent observations and which would be surprising, considering the variety of tree species in rainforests (Pitman et al., 1999), and the very substantial interspecies differences in BVOC emission rates amongst those species that have been measured (Guenther, 1997). The influence of seasonality, which has been shown to be significant in Amazonia (Kuhn et al., 2002; Barkley et al., 2009), but less marked in SE Asia, may also require model emission algorithms to be more region-specific. As well as providing improved estimates of natural BVOC emissions, region-specific measurements alsobenchmark the BVOC chemical climatology from which land-use change is causing deviations (Misztal et al., 2010), with potentially serious implications for regional air quality (Hewitt et al., 2009). There is, therefore, an obvious need for more landscape-scale flux measurements, especially in SE Asia where to date no direct micrometeorological flux observations have been made.

Here we present both direct canopy-scale concentration and flux measurements of a range of BVOCs (but not methane) above a tropical rainforest in SE Asia and compare the results to observations made in Amazonia and Africa (Sect. 3.2.1). Our findings are discussed in relation to the meteorology and then used to optimise the light and temperature algorithms of the MEGAN model for the tropical forests of SE Asia (Sect. 3.2.2). Finally, the measured VOC fluxes are related to co-located measurements of CO_2 exchange and a canopy carbon budget is calculated.

2 Methods

2.1 Site description and setup

Measurements were made as part of the OP3 (Oxidant and Particle Photochemical Processes above a South-East Asian Rainforest) project (Hewitt et al., 2010a) at the Bukit Atur global atmosphere watch (GAW) station in the Danum Valley region of

Sabah, Malaysia (4°C 58′49.33″ N, 117°C 50′39.05″ E, 426 m above mean sea level). The aims and objectives of the OP3 project are summarised by Hewitt et al. (2010a), who also give a detailed site description and overview of the measurements located at the GAW station. The flux footprint of the tower encompassed areas of both primary and selectively logged forest, with regions of both clear-felled-forest and oil palm plantations found some distance beyond, well outside the flux footprint. The selectively logged forest in the flux footprint was logged in 1988 and has since been rehabilitated by enrichment planting. Measurements were carried out over two separate four week periods with phase 1 (OP3-I) taking place during the months of April and May 2008 and phase 2 (OP3-III) occurring between June and July 2008. OP3-II consisted of measurements at a nearby oil palm plantation (Misztal et al., 2010).

For analysis of VOC concentrations and fluxes, a high-sensitivity proton transfer reaction mass spectrometer (PTR-MS) (Ionicon Analytik GmbH: Lindinger et al., 1998) equipped with three Varian turbo molecular pumps and heated Silcosteel inlet was used in conjunction with an ultrasonic anemometer (Windmaster Pro, Gill Instruments, UK). The anemometer and main gas sample line (PTFE 1/2″ OD) were fixed to a 2 m boom mounted on the north east edge of the tower at a height above ground level of 75 m. As the GAW tower is a 100 m tall open pylon-type tower located on a hill, the effective measurement height was estimated to be between 100–150 m above the forest canopy below (Helfter et al., 2010). The PTR-MS was housed inside an air-conditioned laboratory located at the base of the tower and sub-sampled from a low pressure (60 kPa) 1/2″ OD inlet line at a rate of 0.3 l min^{-1} via a short length of PTFE tubing (1/8″ OD). All tubing in the air conditioned room was heated to 40°C to prevent condensation. Visual inspection and good agreement between CO_2 and H_2O fluxes measured with open and closed path sensors (sharing the same line) (Siong et al., 2010) confirmed that no condensation occurred in the main inlet. Data from each sensor were logged onto a single laptop computer in combination with meteorological observations using a program written in LabVIEW 8.5 (National Instruments, Austin, Texas, USA).

Throughout the measurement period the PTR-MS operating conditions were held constant to maintain an *E/N* ratio of approximately 140 Td, which represented the best compromise between the optimal detection limit for VOCs and the minimisation of the impact of high relative humidity (Hayward et al., 2002; Hewitt et al., 2003; Tani et al., 2004). Drift-tube pressure, temperature and voltage were typically maintained at 0.165 kPa, 45°C and 500 V respectively, which gave a primary ion count in the range 6 to 8×10^6 ion counts per second (cps). The sensitivity (S_{norm}) of the PTR-MS for each atomic mass unit (amu, *m/z*) was calculated at regular intervals using a gas standard (Apel-Riemer Environmental Inc.), which contained methanol, acetonitrile, acetaldehyde, acetone and isoprene at a nominal concentration of 1.0 ppmv each as well as limonene at 0.18 ppmv. Volume mixing ratios were calculated adopting the approach of Taipale et al. (2008), where the operating conditions of the PTR-MS are first standardised by normalizing the primary ion count to 1×10^6 cps and accounting for the first water cluster:

$$\mathrm{VMR} = \left(\frac{I(\mathrm{RH}^+)_{\mathrm{norm}}}{S_{\mathrm{norm}}}\right) \tag{1}$$

In this equation $I(\mathrm{RH}^+)_{\mathrm{norm}}$ is the normalised count rate (ncps) of an individual *m/z* which is calculated using Eq. (2):

$$I(\mathrm{RH}^+)_{\mathrm{norm}} = 10^6\left(\frac{\mathrm{RH}_i}{M21+M37} - \frac{\mathrm{RH}_{\mathrm{zero}}}{M21_{\mathrm{zero}}+M37_{\mathrm{zero}}}\right) \tag{2}$$

Here RH_i represents the ion count signal at mass M_i (cps), $\mathrm{RH}_{\mathrm{zero}}$ is the signal of the mass measured from the zero air source, *M21* and *M37* are the counts of the primary ($\mathrm{H}_3^{18}\mathrm{O}^+$) and reagent cluster ions $\mathrm{H}_3^{16}\mathrm{O}^+$ $\mathrm{H}_2^{16}\mathrm{O}^+$, respectively, while $\mathrm{M21}_{\mathrm{zero}}$ and $\mathrm{M37}_{\mathrm{zero}}$ are the primary and reagent cluster ions when measuring from the zero air source.

For those compounds not contained in the gas mixture, empirical sensitivities were calculated based on the instrument-specific transmission characteristics (Taipale et al., 2008; Davison et al., 2009). During OP3-I the multi-component gas standard was not available. Consequently only isoprene could be calibrated directly, using a low mixing ratio gas standard (4.52 ppbv±5%) (see Lee et al., 2006, for details). Subsequent analysis of the two isoprene standards by GC-FID showed less than 2% difference. Calibration for all other compounds measured during the first campaign was based on the instrument specific transmission curve, relative to isoprene.

2.2 PTR-MS operation and flux calculations

Fluxes of individual VOC species were calculated using the virtual disjunct eddy covariance technique (vDEC) (Karl et al., 2002) as implemented previously (Langford et al., 2009, 2010; Davison et al., 2009). In order to provide both flux data and information on the full VOC composition, the PTR-MS was programmed to operate in two modes, flux and scan. During the flux mode, 13 protonated masses were targeted with a dwell time of 0.5 s per mass, as well as the primary ion count (quantified indirectly from $H_3^{18}O^+$ at *m/z* 21) and the first water cluster ion count (detected directly as $H_3^{16}O^+\ H_2^{16}O^+$ at *m/z* 37) which were both measured with a 0.1 s dwell time. This resulted in a total scan cycle time of 6.7 s and the acquisition of ~224 data points (*N*) per 25-min flux averaging period. The remaining 10 min of each hour were used to obtain basic concentration information across the mass spectrum (21–206 amu, *m/z* resolution=1 amu) (5 min), and to monitor the instrument background (5 minutes), which was subtracted during post processing. The instrument background was monitored by sampling ambient air that had passed through a zero air generator, which comprised a glass tube packed with platinum catalyst powder heated to 2°C. A summary of the masses targeted and their likely contributing compounds, formulas, dwell times, instrument sensitivities and detection limits are all summarised in Table 1.

In order to account for the sampling delay induced by the distance between inlet and instrument, and so synchronise the PTR-MS data with that collected by the ultrasonic anemometer, a cross-correlation function of vertical wind velocity (w') and scalar con-

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centration (χ') was used with the peak value over a 25 s time window. Following this synchronisation, each 25-min flux file was then subject to a quality assessment, as described by Langford et al. (2010). Briefly, a two dimensional coordinate rotation was applied. Data were rejected where the friction velocity (u_*) fell below 0.15 m s^{-1} or non-stationary conditions were apparent. Data that passed these criteria were ranked as either high- or low-quality, based on the exact outcome of the stationarity test, and the precision of each individual flux measurement was calculated at the 99.7% confidence interval following the procedure outlined by Spirig et al. (2005). This value was then used as a proxy for the limit of detection of the flux system.

2.3 Validity of flux measurements and potential losses

In order to assess the validity of measurements made, several analyses were undertaken. Firstly, the integral turbulent statistics of the vertical wind velocity were evaluated by comparison of the measured ratio of the standard deviation of vertical wind component to friction velocity (σ_w/u_*) with values obtained using the model of Foken et al. (2004), which predicts σ_w/u_* for a set of ideal conditions.

Following the assessment criteria used in the FLUXNET program (Foken et al., 2004), over 90% of the collected data were rated category 6 or better (i.e., suitable for general use) and less than 1% of the data qualified for rejection with a rank of class 9. This suggests that the turbulence encountered at this site, although light, was sufficiently well developed for the precise and accurate determination of fluxes and that flux measurements at this high measurement height were not adversely influenced by the effects of wake turbulence generated by the tower or surrounding topography Helfter et al. (2010).

The vDEC flux system was evaluated to establish flux losses due to bandwidth limitation. High frequency flux losses encountered due to the response time of the PTR-MS, which cannot resolve fluctuations in the sub ~0.2 s range, were estimated from Horst (1997) and found to be negligible, ranging between 1 and 2%. In contrast, the low frequency flux losses, arising from insufficient averaging periods, were more significant, as shown by Fig. 1. For a detailed description of the method, see Langford et al. (2010). Eddies with a time period of between 30 and 90 min increase the flux of sensible heat (H) by ~15%, while eddies with a period of 150 min carried a further 6% of the flux. Assuming similarity and identical frequency behaviour between sensible heat and VOC fluxes, it is probable that VOC fluxes measured at the GAW site using 25-min averaging periods will underestimate the true surface exchange by 15–20%. In contrast, an investigation into the daytime energy budget closure at this site suggests closure within 5% based on 30 min flux values (Helfter et al., 2010). However, since the footprint of the net radiation measurements was not ideal, this closure may be slightly fortuitous.

Additional flux losses may be encountered due to the high relative humidity encountered (60–90%), which can cause condensation in sample lines, attenuating the signal of water soluble compounds such as methanol. In order to evaluate these losses, latent-heat fluxes (λE) were calculated using the PTR-MS, which was first calibrated using data recorded by a closed path infrared gas analyser (IRGA) (LI-COR LI-7000, Biosciences, Nebraska, US.) in a method similar to that of Ammann et al. (2006). The IRGA sub-sampled directly after the PTR-MS from the same sample tube. PTR-MS λE was then compared against the measurement of an open-path IRGA (LI-COR LI-7500, Biosciences, Nebraska, US.) which was mounted directly below the 75 m sonic anemometer during the OP3-III campaign (June–July 2008). As the open-path instrument provides an in situ measurement of water vapour concentrations, fluxes calculated using this sensor are not subject to signal damping and therefore a direct comparison with PTR-MS fluxes can provide an estimate of flux losses along the sample line. For a detailed description of the IRGA setup and results, see Siong et al. (2010).

Figure 2 shows λE measured by PTR-MS and open-path IRGA over an 11-day period. Measured fluxes agree reasonably well (R^2=0.54, p=<0.0001), but on average PTR-MS fluxes are lower, suggesting a typical flux loss of around <30%. This flux loss is much larger than direct comparisons between open and closed path IRGA λE fluxes, which showed just a 1% underestimation, again resulting from the long sample line (R^2=0.93, p=<0.0001, y=0.9916 x–0.9632). It should be noted that the PTR-MS λE fluxes are in fact sampled disjunctly, which, when coupled with (i) the indirect calibration against the closed-path IRGA and (ii) the greater uncertainty associated with lag time analyses of disjunctly sampled data (Taipale et al., 2010), may account for the larger disparity between the measurement systems.

These analyses suggest that VOC fluxes measured at this site are underestimated due to both insufficient averaging periods and some signal attenuation along the ~75 m sampling line, but the flux loss is unlikely to exceed 30% for any compound. No corrections for these flux losses were applied to the data presented in this study. The estimated losses are small compared to the differences between measured and estimated emissions (Sect. 3.2.2, below).

3 Results and discussion

3.1 Ambient BVOC mixing ratios

Figure 3 shows the average diurnal mixing ratios of the nine VOCs measured during the OP3 campaign and the results are summarised in Table 2a. During the daytime, mixing ratios for each compound were always above the calculated limit of detection, with the exception of methanol and *m/z* 83 and 85, which we tentatively ascribe to hexanal and/or cis-3-hexenol, and ethyl vinyl ketone (EVK), respectively. For methanol, instrument background counts were unusually high, resulting in a very high detection limit of 1.2 ppbv. Although our measurements of methanol were always close to or below the detection limit, they are of a similar magnitude to measurements made by GC-FID during the campaign (Jones et al., 2010), hence their inclusion here.

Isoprene was the second most abundant compound observed after methanol, accounting for approximately 30% of the total measured species. Mixing ratios ranged between 0.17 and 3.4 ppbv with an average of 1.3 ppbv. Methacrolein (MACR) and methyl vinyl ketone (MVK), which are measured at the same atomic mass unit (amu) by the PTR-MS and consequently presented as the sum of the two (MACR+MVK), ranged between 0.05 and 0.67 ppbv, with an average value of 0.25 ppbv. Isoprene oxidation is the only known source of MACR and MVK; hence, the ratio of (MACR+MVK) to isoprene can provide an indication of the extent of isoprene oxidation. Average ratios of 0.16 and 0.22 were observed for the first and second campaigns, respectively. These findings are similar to observations by Kesselmeier et al. (2002) who reported above-canopy ratios in Amazonia of 0.23 and 0.3 during the wet and dry seasons respectively. Similarly, Kuhn et al. (2007) reported a ratio of 0.3 for dry season measurements above the Amazon. Following the method of Karl et al. (2004), the time taken between isoprene emission and detection by our system was estimated at 8 min (based on the average [isoprene]/[MVK+MACR] ratio and an assumed atmospheric lifetime for isoprene of 40 min). Accordingly, isoprene mixing ratios were estimated to have originated from within a footprint length of 1.4 km (based on an average wind speed of 3 m s^{-1}). This is consistent with approximate footprint calculations reported by Helfter et al. (2010) for OP3 under unstable daytime conditions.

Over the course of a typical day, the (MVK+MACR)-to-isoprene ratio shows a distinct pattern, with a sharp decline observable at dawn as the nocturnal ratio decreased from 0.36 to 0.1 in the early morning. This relates to the response of the canopy to the increasing light and temperature which drives the isoprene emissions and a decrease in the transport time between canopy and the measurement height. As the isoprene emissions are transported away from the canopy they react to form more MVK+MACR and thus the ratio increases steadily throughout the day before reaching a stable nocturnal maximum, when the isoprene emission and photochemistry shut off.

Monoterpene mixing ratios were relatively low, ranging between 0.02 and 0.47 ppbv with an average of 0.17 ppbv, which is approximately 50% lower than the average of measurements made above Amazonia (Karl et al., 2007). Due to limitations of the PTR-MS approach, the measurement can only measure total monoterpene concentrations as this concentration is derived from a fragment that is common to the different compounds. Gas chromatography measurements reported elsewhere indicate that the

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monoterpene emissions at this site were dominated by γ-terpinene and camphene (Jones et al., 2010).

Acetone mixing ratios ranged between 0.46–1.10 ppbv, with an afternoon maximum which typically occurred 1 to 3 h after the maximum in isoprene mixing ratios. Our measured values were similar to those reported above a tropical rainforest in Costa Rica (Karl et al., 2004) and approximately half of those reported above regions of Amazonia (Karl et al., 2007; Williams et al., 2001). Mixing ratios of acetone were slightly higher during OP3-I than OP-III which was also the case for acetic acid. Acetic acid mixing ratios ranged between 0.22–0.5 ppbv, but in contrast to the trend in acetone, peak values occurred in the early afternoon, closely following the diurnal pattern in ambient air temperature. This close relationship with temperature is typical for this compound, particularly in remote locations (Martin et al., 1991; Khare et al., 1999), but the observed values are slightly lower than those reported elsewhere (Kuhn et al., 2002; Karl et al., 2004).

3.2 Surface-layer VOC fluxes

3.2.1 Isoprene and monoterpene surface-layer fluxes

Figures 4 and 4 show measured isoprene and total monoterpene fluxes relative to the meteorological drivers light, temperature, wind speed/direction, frictional velocity and sensible heat flux, for both measurement phases and their statistics are summarised in Table 2B. During these periods, midday (10:00–14:00) temperature (at 30 m above ground) ranged between 23 – 28°C, and photosynthetically active radiation (PAR) between 336–2027 $\mu\text{mol m}^{-2}\ \text{s}^{-1}$, whereas at night, temperatures fell to 22 – 24°C. Sensible heat fluxes were positive during the day, ranging between 200 and 400 W m^{-2}, with occasional troughs associated with convective cloud cover and rain events, as clearly seen on both 30 June and 5 July. Wind speed and friction velocities varied between 0.6–4.7 m s^{-1} and 0.06–0.52 m s^{-1} (5th–95th percentiles), with particularly low values of both recorded at night. Accordingly, VOC fluxes were generally only observed between 09:00 and 17:00 and not at night.

During the night the measurement platform became de-coupled from the canopy below, as observed from nocturnal cloud formation at the canopy top, below the measurement height, and validated through LIDAR measurements of the mixed layer height (Pearson et al., 2010). Subsequently, any nocturnal emissions such as nocturnal monoterpene fluxes from temperature-dependent plant emitters could not be captured by our measurement system. In contrast, early morning emissions of both isoprene and monoterpenes that accumulated in the shallow nocturnal boundary layer were occasionally observed as large spikes at around 08:00–09:00 during the break up of this stable air. However, in-canopy gradient measurements of these compounds during OP3-III showed that both compounds did not build up inside the canopy during the night and that dark emissions were negligable (Ryder et al., 2010). The LIDAR measurements confirm that after sunrise the boundary layer quickly expanded. Therefore little of the daytime fluxes were lost due to de-coupling from the canopy.

Emissions of isoprene were the largest of all the measured VOCs, with an average midday flux (10:00–14:00 LT) of 1.85 mg m^{-2} h^{-1} for the entire 48-day period. This value represented approximately 80% (as carbon) of all measured non-methane BVOC emissions from the forest canopy, with the remaining 20% accounted for by emissions of total monoterpenes (18% as carbon) and oxygenated VOCs (OVOC) (2% as carbon), including methanol, acetone and acetaldehyde – see Sect. 3.2.3. The mean integrated daily flux of isoprene was 6.0 mg m^{-2} d^{-1} and 12.9 mg m^{-2} d^{-1} respectively, for the OP3-I and OP3-III campaigns with an average of 10.5 mg m^{-2} d^{-1} for all collected data (approximately 500 hours of data collected over 48 days). Here, missing night-time data were gap-filled with zero fluxes, consistent with the light-sensitivity of the isoprene emissions. The mean integrated daily fluxes for each phase are statistically different at the 95% level (two-tailed t-test). The observed increase in emission rates between the two campaigns was consistent with a difference in integrated ambient air temperature (0.3°C) and PAR (3549 µmol m^{-2} s^{-1} PAR) for the average day, and normalising these emissions to standard conditions (30°C and 1000 µmol m^{-2} s^{-1} PAR), using the algorithms of Guenther et al. (2006) described in the next section, reduced the difference in standard emission rates between the two campaigns to within 6%. A recent study has suggested that isoprene-emitting vegetation in Amazonia experiences a wide-scale leaf flushing which promotes new growth in preparation for the coming dry season, resulting in an annual shutdown of isoprene emissions (Barkley et al., 2009). Seasonality in Borneo is much less marked than in Amazonia; and our measurements showed no evidence of a similar process occurring at this site.

The average daytime ratio of monoterpene to isoprene fluxes was 0.23±0.3 (standard deviation) and remained relatively constant throughout the day, including the early morning when nocturnal emissions were vented from the shallow nocturnal boundary layer. This relative constancy suggests that nocturnal, light-independent emissions of monoterpenes are negligible at this site, which is consistent with Owen et al. (2002) and with the in-canopy profile measurements made by Ryder et al. (2010) who did not detect monoterpene emissions from the darker under storey during the day or night-time build-ups inside the canopy. Guenther et al. (2008) summarise the monoterpene: isoprene emission rates observed in other tropical forests, with values typically found to be ∼0.15.

Polar plots of isoprene and monoterpene fluxes shown in Fig. 5 (top two panels), indicate that canopy emissions were spatially very heterogeneous, with observed fluxes strongly skewed towards the south-east. Analysis of polar plots for temperature and PAR shows a similar south-east skew. This direction-dependent temperature effect was accounted for by normalising measured fluxes to give the base emission rate (BER; 30°C (canopy temperature) and 1000 µmol m^{-2} s^{-1} PAR). The resulting polar plots of BER (Fig. 5, bottom two panels) were less pronounced in the south east, but still showed considerable variability in emission rates between wind sectors, with values ranging between 0.8 and 2.9 mg m^{-2} h^{-1} for isoprene and between 0.21 and 0.70 mg m^{-2} h^{-1} for monoterpenes. Average BERs during the OP3 campaigns were 1.6 and 0.46 mg m^{-2} h^{-1} for isoprene and monoterpenes, respectively, which was in close agreement with up-scaled leaf level measurements made by Owen et al. (2010)

for isoprene (2.1 mg m^{-2} h^{-1}) and monoterpenes (0.47 mg m^{-2} h^{-1}) within the flux footprint of the GAW tower.

Although the extrapolated leaf level measurements are on average ~13% larger than measured fluxes they are still well within the range of emission rates observed between wind sectors. The close agreement between canopy-scale fluxes and leaf level measurements suggests that, although the tree species composition of the flux footprint is spatially heterogeneous, up-scaling of leaf level measurements can still yield representative results for this area.

Table 3 summarises the isoprene and monoterpene fluxes measured during the OP3 campaigns relative to previous findings from Amazonia, Africa and South East Asia. Our measurements of isoprene compared very closely to leaf-level estimates made from a dipterocarp forest on mainland Malaysia (Saito et al., 2008) and to observations above regions of the Congo, but were at the extreme lower end of observations from Amazonia. In contrast, our measurements of total monoterpene fluxes are somewhat larger than those previously reported for other tropical forests.

3.2.2 Comparison of isoprene and monoterpene fluxes with modelled fluxes

Emissions of isoprene from the flux footprint were simulated using the light and temperature algorithm from the G06 emission model of Guenther et al. (2006). In the original G06 algorithm the fitting coefficients (Eqs. 5–9 of Guenther et al., 2006) are based on observations reported from five independent studies (Monson et al., 1994; Sharkey et al., 1999; Geron et al., 2000; Hanson and Sharkey, 2001; Petron et al., 2001), all of which report measurements from temperate plant species. In light of this, the coefficients used in the G06 algorithm were optimised for the emissions data reported in this paper by minimising the normalised mean square error (M) between observed and modelled data using a quasi-Newton Raphson iterative method (Microsoft Excel 2003, Microsoft Corporation, Redmond, WA, USA):

$$M = \frac{\left(\overline{E_0 - E_p}\right)^2}{\overline{E_0} \times \overline{E_p}} \tag{3}$$

Here E_o is the observed emission, E_p is the predicted emission and over bars denote mean values. The performance of the model is rated by the M score, which is a function of bias magnitude, bias variance and intensity of association (Guenther et al., 1993) and decreases with increasing model performance. In order to constrain the optimisation to environmentally realistic conditions, each coefficient was given a tolerance of ±50%, with the exception of the temperature maximum (T_{max}) which was restricted to ±1%. Table 4 lists the standard coefficients presented by Guenther et al. (2006) and the new optimised coefficients based on the results of this study.

Model variables such as PAR and temperature (past and present) were supplied from the in situ measurements made at the GAW station. Before use, the ambient air temperature measurements were first converted to give the canopy leaf temperatures required by the model using the resistance analogy described by Nemitz et al. (2009). Leaf temperatures during the afternoon were up to 2°C higher than air temperature. Base emission rates describing isoprene and monoterpene emissions under constant (standard) conditions of temperature and PAR were inferred from the measured fluxes as described above. Our analysis assumes, as do all previous such analyses, that the BER is constant throughout the day. However, there are indications that BER varies throughout the day and this finding is explored more fully elsewhere (Hewitt et al., 2010b). Figure 6 shows the simulated fluxes of isoprene (panel a) and monoterpenes (panel b) relative to the observed emissions over a 19-day period (2–21 July 2008).

Model estimates using the standard coefficients compare reasonably well with measured values, confirming temperature and light to be the primary drivers of observed emissions. On occasion, peak fluxes do not agree temporally between measured and modelled values. On 9–10 July, measured VOC fluxes peak in the morning, 2–3 h earlier than the modelled output. This is most likely the result of venting of the nocturnal boundary layer, described in Sect. 3.2.1. On other days (12–13 July), the peaks match temporally but are underestimated by the model. As the measured fluxes are integrated across the whole flux footprint, which covers an area of several square kilometres (Helfter et al., 2010) emissions respond to fluctuations in light and temperature across that footprint, which are not fully captured by our point measurements of PAR and temperature. In addition, the tree species composition in the footprint around the tower is very variable. Lowering the point of flux measurement closer to the canopy and thus reducing the flux footprint might improve model performance and result in a closer fit to the data, as demonstrated by measurements above an oil palm plantation reported by Misztal et al. (2010), but at the cost of spatial representativeness.

Optimisation of the standard G06 coefficients resulted in new light and temperature curves, which are shown in Fig. 7. For isoprene, the temperature response (γ_T), shown in panel A, doubles the normalised emission rates at peak values compared with the standard G06 response. The shape, higher T_{max} and increased emission rate of the fitted response is consistent with laboratory measurements of tropical plant species (*Ficus virgata* and *Ficus microcarpa*) made by Oku et al. (2008). In contrast, optimisation of the temperature response based on monoterpene fluxes showed no deviation from the standard G06 response. This is not unexpected due to the light dependent nature of the monoterpene emissions reported at this site (Ryder et al., 2010). Panel B shows the light response (γ_P) of the fitted coefficients alongside the standard G06 light response. The fitted response of isoprene and monoterpenes are very similar, with emission rates following a steeper gradient at lower PAR values and saturating from 500 µmol m^{-2} s^{-1} of PAR onwards. This light response curve is very similar to those derived from laboratory measurements of oil palm (Wilkinson, 2006), a biofuel crop very common to the region, but not present within the GAW tower flux footprint.

Implementation of the optimised light and temperature response curves described above resulted in only a slight improvement in model performance, which suggests that the standard response curves of the G06 algorithm to perform adequately for both temperate and tropical vegetation, if the BER is adjusted. The BER appears to be the most important parameter, and failure to accurately characterise this can result in very large under- or over-estimations of canopy emission rates. For example, applying the default isoprene BER for tropical forests contained within MEGAN (6.6 mg m^{-2} h^{-1}; value modified by the appropriate land cover type for the Danum valley region, see Hewitt et al. (2010a), Sect. 2.4), a parameter based on measurements made over the Amazonian rainforest, to regions of Borneo would result in a >4 times overestimation of the emission rate. Similarly, applying the default total monoterpene emission rate (0.8 mg m^{-2} h^{-1}) would result in an overestimation of >70%. This highlights the need for more direct canopy-scale flux measurements of VOCs above the world's tropical forests to allow for further evaluation and constraint of models such as MEGAN.

3.2.3 Fluxes of other BVOCs

Fluxes of seven other BVOCs including methanol, acetone, acetaldehyde and acetic acid were measured during the two phases of the OP3 campaign; their average diurnal profiles are plotted alongside those of isoprene and monoterpenes in Fig. 8 with the results summarised in Table 2b. In addition to the canopy emissions of isoprene and monoterpenes discussed above, positive fluxes of acetaldehyde, acetone, hexanal and/or cis-3-hexenol, and EVK, were also observed. Average emission fluxes of acetaldehyde and acetone were of a similar magnitude and range, but emissions of acetone were larger during June and July relative to April and May, whereas acetaldehyde fluxes were slightly larger during April and May. Fluxes of hexanal and EVK were approximately half that of acetone and acetaldehyde, averaging 20 µg m^{-2} h^{-1}, but mixing ratios of these two compounds were either very close to or below the limit of detection and therefore the fluxes of these compounds are not discussed further.

Previous studies over tropical forests have shown the bidirectional exchange of organic acids between canopy and atmosphere (Kuhn et al., 2002; Karl et al., 2004). Our measurements are consistent with these findings, with deposition fluxes observed for acetic acid during morning and early afternoon as well as small emission fluxes at certain times. Deposition velocities were in the range of 1–3 mm s^{-1}, which is similar to those reported over the Amazonian rainforest by Kuhn et al. (2002) during the wet season. Correlations between instantaneous measurements of fluxes and ambient mixing ratios did not clearly show a compensation point as has been previously reported in leaf-level studies. However, it is likely that other sinks exist in the canopy (such as adsorption to leaf surfaces), which would affect the relationship between fluxes and concentrations. These findings should be treated with some caution as measurements of acetic acid by PTR-MS can be affected by memory effects in the inlet system and drift tube (de Gouw and Warneke, 2007).

Canopy profile measurements of methanol mixing ratios made by Ryder et al. (2010) showed elevated values close to the forest floor, which is suggestive of methanol emissions from decomposing leaf material (Fall, 2003). However, our canopy scale flux measurements showed periods of both emission and deposition, with small net deposition. Previous studies in Amazonia have also shown both positive and negative fluxes of methanol, but the net exchange has always been reported as positive (Karl et al., 2004). The net deposition of methanol at this site, combined with its small deposition velocity, suggests that photo-oxidation is its primary source.

The net exchange of MACR+MVK was negligible, with both positive and negative fluxes observed during each campaign. Positive fluxes were more common in the morning, whereas negative fluxes tended to be observed in the afternoon. This flux pattern may relate to the interplay between chemical sources/sinks and boundary layer dynamics. The net flux is the balance between the chemical production above and below the measurement height. During the first half of the day the boundary layer is shallower and most of the chemical formation happens below the measurement height, while in the afternoon most of the formation occurs above the canopy. Again, from the analysis of in-canopy gradients, Ryder et al. (2010) derived top-of-the-canopy emissions of MVK+MACR of ~0.2 mg m^{-2} h^{-1} which was on average 15% of the isoprene emissions derived by the same technique. This fraction is consistent with the canopy conversion factors that were derived in other studies (e.g., Makar et al., 1999; Stroud et al., 2005). There is increasing evidence that MVK/MACR are deposited efficiently to vegetation (e.g., Karl et al., 2004; Misztal et al., 2010).

3.3 Net ecosystem exchange of carbon

Tropical forests currently act as a net carbon sink (Grace and Rayment, 2000). However, the sink strength is offset somewhat by the emission of VOCs from both the forest canopy and forest floor. We estimated this offset by analysing total VOC emissions (all VOC measured during OP3; see table 2B for list) with respect to concurrently measured CO_2 fluxes obtained during the OP3-III campaign (20 June–20 July 2008). Figure 9 shows the average diurnal profile of CO_2 fluxes and total VOC exchange occurring above the forest canopy. Integrated CO_2 fluxes yield a daytime (08:00–18:00) net carbon sink strength of 3120 mg C m^{-2} d^{-1}. Total VOC emissions, which had an integrated flux of 13.2 mg C m^{-2} d^{-1} represented 0.4% of this (as carbon). The carbon offset from VOC fluxes above this SE Asian rainforest is lower than values reported above an Amazonian forest (1.2–3.7 %; Kuhn et al., 2007; Karl et al., 2004), but this may be attributable to the limitations of the measurement system, which was de-coupled from the canopy at night (see above) and unable to resolve nocturnal CO_2 emissions due to respiration. Consequently our estimates of net ecosystem exchange (NEE) are for daytime only and guaranteed to be an overestimate. For a more detailed discussion of CO_2 fluxes recorded during this campaign see Siong et al. (2010).

VOC emissions represent a loss of reactive carbon from the canopy, which after emission, will be photochemically processed and some of this carbon may therefore be deposited back to the canopy and hence the amount of carbon escaping the ecosystem is less than the measured VOC flux. In order to trace the fate of carbon emitted as VOCs we ran the CiTTyCAT box model of atmospheric chemistry (Wild et al., 1996; Evans et al., 2000; Donovan et al., 2005; Hewitt et al., 2009; Pugh et al., 2010), including detailed isoprene chemistry (Taraborrelli et al., 2009), in the boundary layer above the flux footprint. The model also includes detailed monoterpene chemistry (Jenkin, 1996; Stockwell et al., 1997), however the lumping of species within these schemes leads to a carbon loss of around 10% in the model. Therefore monoterpene emissions were neglected in these calculations to conserve carbon. For details on the CiTTyCAT model set-up see Pugh et al. (2010).

Isoprene was emitted following the diurnal cycle defined by the MEGAN algorithm (Guenther et al., 2006). The 24 h average emission rate was 6.88×10^{10} molecules cm^{-2} s^{-1} (0.28 mg m^{-2} h^{-1}). The only other emitted species was NO, at a constant rate of 6.53×10^{9} molecules cm^{-2} s^{-1} (5.5 µg m^{-2} h^{-1}). A deposition velocity of 1.5 cm s^{-1} for MACR and MVK was adopted, following the findings of Pugh et al. (2010). Wet deposition (after Real et al., 2008, S-WET2 scheme) was also employed. A carbon budget was calculated over the final four days of an eight-day model run, tracing the ultimate destination of the carbon emitted as isoprene. The model run indicated the bulk of the reactive carbon emitted from the canopy that is rapidly returned to the canopy in the near vicinity of the point of emission through both wet (60%) and dry (27%) deposition processes. A small fraction (<4 %) of the aldehydes, acids, nitrates and peroxides formed through photochemical reactions persist to be either further oxidised or deposited on a longer timescale, but ultimately only 9% (0.04% of daytime NEE) of the emitted reactive carbon escapes the landscape in the form of CO_2.

4 Summary and conclusions

Direct canopy-scale measurements of VOC fluxes above a SE Asian tropical rainforest showed that isoprene was the dominant compound emitted, accounting for 80% (as carbon) of the total measured reactive carbon fluxes. Typical daytime fluxes ranged between 0.2 and 4.4 mg m^{-2} h^{-1} (10:00–14:00; 5th and 95th percentiles), which, when normalised to standard conditions (30°C; 1000 µmol m^{-2} s^{-1} PAR), gave an average base emission rate of 1.6 mg m^{-2} h^{-1}. This value was found to be 4.1 times smaller than the default standard emission rate used in the MEGAN model for tropical forests. With the exception of BER, optimisation of the empirical coefficients describing the temperature and PAR response used within MEGAN did not significantly improve the fit between measured and modelled data, lending confidence to the global application of these coefficients.

Total monoterpenes accounted for 18% of the reactive carbon fluxes, ranging between –0.1 and 1.0 mg m^{-2} h^{-1} (10:00–14:00; 5th and 95th percentiles) with an average base emission rate of 0.46 mg m^{-2} h^{-1}. This value was 70% lower than the standard emission rate for monoterpenes used in the MEGAN model for tropical forests. Combined with the evidence from in-canopy measurements, these data demonstrate that monoterpenes were not emitted at night and during the day they were found to be dependent on both light and temperature.

The fluxes of other VOCs including the OVOCs, methanol, acetaldehyde and acetone, accounted for <2% of the total reactive carbon flux. In total, the sum of the measured reactive carbon fluxes offset the daytime net carbon sink strength of the forest canopy by 0.4%, but atmospheric box modelling suggests that most (90%) of this reactive carbon is returned back to the canopy by wet and dry deposition following chemical transformation.

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Table 1. List of compounds measured during the OP3 campaigns, including their formula, dwell time, average sensitivity and detection limit. Detection limits were calculated based on the signal to noise ratio of measured ion counts following Karl et al. (2003) ($\mathrm{LOD}=2\times\sigma_{\mathrm{background}}/\mathrm{sensitivity}$).

m/z [amu]	Contributing compound(s)	Formula	Dwell time [s]	Average sensitivity [ncps ppbv^{-1}]	Limit of Detection [ppbv]
21	water isotope	$H_2^{18}O$	0.1 s	–	–
33	methanol	CH_4O	0.5 s	11.6	1.2
37	water cluster	$(H_2O)_2$	0.1 s	–	–
42	acetonitrile	C_2H_3N	0.5 s	19.6	–
45	acetaldehyde	C_2H_4O	0.5 s	22.8	0.1
59	acetone propanal	C_3H_6O	0.5 s	25.2	0.1
61	acetic acid	$C_2H_4O_2$	0.5 s	26.5	0.09
69	isoprene furan methyl butenol fragment	C_5H_8	0.5 s	1.6	0.2
71	methyl vinyl ketone methacrolein	C_4H_6O	0.5 s	27.1	0.07
81	monoterpene fragment	–	0.5 s	4.0	0.04
83	hexanal fragment *cis*–3–hexenol fragment	–	0.5 s	30.3	0.04
85	ethyl vinyl ketone	C_5H_8O	0.5 s	30.3	0.06
137	monoterpenes	$C_{10}H_{16}$	0.5 s	3.7	0.04
149	estragole	$C_{10}H_{12}O$	0.5 s	–	–
205	sesquiterpenes	$C_{15}H_{24}$	0.5 s	–	–

Table 2a. Summary of VOC mixing ratios (ppbv) measured during the two intensive OP3 campaigns.

	Isoprene	Σ Monoterpene	Methanol	Acetaldehyde	Acetone	MVK+MACR	Acetic acid	Hexanal	EVK
OP3 I (Wet)									
Mean	1.14	0.24	1.15	0.36	0.91	0.23	0.40	0.05	0.05
Median	0.95	0.22	1.19	0.34	0.90	0.18	0.38	0.05	0.05
Percentiles									
−95th	2.84	0.55	1.88	0.64	1.29	0.67	0.58	0.09	0.07
−5th	0.28	0.06	0.42	0.16	0.50	0.04	0.28	0.02	0.04
σ	0.80	0.15	0.46	0.14	0.22	0.20	0.09	0.02	0.01
n	746	744	746	751	704	745	755	703	751
OP3 III (Early Dry)									
Mean	1.39	0.14	1.48	0.54	0.70	0.26	0.31	0.06	0.06
Median	1.05	0.10	1.38	0.52	0.68	0.19	0.30	0.06	0.06
Percentiles									
−95th	3.57	0.44	2.67	0.84	0.99	0.67	0.43	0.09	0.10
−5th	0.12	0.05	0.48	0.31	0.45	0.05	0.20	0.03	0.03
σ	1.19	0.15	0.67	0.16	0.16	0.20	0.07	0.02	0.02
n	1269	1290	1252	1369	1364	1374	1372	1382	1378
OP3 All data									
Mean	1.30	0.18	1.36	0.48	0.77	0.25	0.34	0.06	0.06
Median	1.00	0.15	1.28	0.47	0.75	0.19	0.33	0.06	0.05
Percentiles									
−95th	3.36	0.48	2.54	0.78	1.10	0.67	0.50	0.09	0.09
−5th	0.17	0.02	0.46	0.22	0.46	0.05	0.22	0.03	0.03
σ	1.07	0.16	0.62	0.18	0.21	0.20	0.09	0.02	0.02
n	2015	2034	1999	2120	2068	2119	2127	2085	2129

Table 2b. Summary of VOC fluxes (mg m^{-2} h^{-1}) measured during the two intensive OP3 campaigns.

	Isoprene	Σ Monoterpene	Methanol	Acetaldehyde	Acetone	MVK+MACR	Acetic acid	Hexanal	EVK
OP3 I (Wet)									
Mean	0.54	0.15	−0.02	0.01	0.007	−0.0024	−0.005	0.004	0.004
Median	0.22	0.11	−0.05	0.02	0.009	−0.005	−0.006	0.006	0.005
Percentiles									
−95th	2.23	0.62	0.30	0.11	0.115	0.079	0.052	0.053	0.047
−5th	−0.12	−0.10	−0.34	−0.08	−0.091	−0.098	−0.061	−0.447	−0.035
σ	0.82	0.22	0.21	0.06	0.065	0.055	0.036	0.032	0.025
n	373	329	421	416	417	461	421	406	406
OP3 III (Early Dry)									
Mean	1.18	0.29	−0.04	0.004	0.002	−0.002	−0.003	0.003	0.002
Median	0.76	0.21	−0.08	0.006	0.019	0.003	−0.010	0.005	0.004
Percentiles									
−95th	4.02	0.92	0.51	0.127	0.119	0.091	0.058	0.034	0.032
−5th	−0.38	−0.10	−0.60	−0.116	−0.081	−0.109	−0.059	−0.027	−0.03
σ	1.42	0.37	0.35	0.084	0.065	0.072	0.004	0.021	0.021
n	578	550	622	667	702	739	672	644	647
OP3 All data									
Mean	0.93	0.241	−0.033	0.007	0.012	−0.002	−0.038	0.003	0.003
Median	0.46	0.164	−0.063	0.014	0.014	−0.002	−0.008	0.005	0.004
Percentiles									
−95th	3.67	0.835	0.457	0.120	0.116	0.083	0.058	0.042	0.04
−5th	−0.28	−0.109	−0.537	−0.108	−0.084	−0.107	−0.06	−0.035	−0.033
σ	1.25	0.329	0.299	0.073	0.065	0.066	0.037	0.026	0.023
n	951	879	1043	1083	1119	1200	1093	1050	1053

Table 3. Isoprene and monoterpene flux measurements from the world's tropical forests and their typical ratios (monoterpene/isoprene). All values are in units of mg C m^{-2} h^{-1}. Where available, errors show ±1 standard deviation.

Location	Season	Method	Isoprene	Σ Monoterpene	Ratio	Reference
Borneo, SE Asia	L Wet	EC	0.48 ± 0.72	0.13 ± 0.19	0.27	Langford et al., this study
Borneo, SE Asia	E Dry	EC	1.04 ± 1.25	0.25 ± 0.33	0.24	Langford et al., this study
Malaysia, SE Asia	Dry	LL	1.05	–	–	Saito et al. (2008)
Amazon, Brazil	E Dry	MB	2.73	0.24	0.23	Zimmerman et al. (1998)
Amazon, Peru	E Dry	MLG	7.2	0.45	0.06	Helmig et al. (1998)
Amazon, Brazil	L Wet	EC, REA	2.1	0.23	0.11	Rinne et al. (2002)
Amazon, Brazil	L Dry	EC	7.3 ± 2.7	1.5 ± 1.1	0.21	Karl et al. (2007)
Amazon, Brazil	L Dry	MLG	10.2 ± 3.5	2.2 ± 0.7	0.22	Karl et al. (2007)
Amazon, Brazil	L Dry	MLV	11.0 ± 0.9	3.9 ±1.1	0.35	Karl et al. (2007)
Amazon, Brazil	E Dry	REA	2.1 ± 1.6	0.39 ± 0.43	0.19	Kuhn et al. (2007)
Amazon, Brazil	E Dry	SLG	3.4 ± 3.6	0.38 ± 0.58	0.11	Kuhn et al. (2007)
Amazon, Brazil	–	REA	1.1	0.2	0.18	Stefani et al. (2000)
Amazon, Brazil	–	BM	1.9	0.16	0.08	Greenberg et al. (2004)
Amazon, Brazil	–	BM	4.7	0.20	0.04	Greenberg et al. (2004)
Amazon, Brazil	–	BM	8.6	0.54	0.06	Greenberg et al. (2004)
French Guyana, Suriname	Dry	CBL	6.1	–	–	Eerdekens et al. (2009)
Costa Rica	Wet	REA	2.2	–	–	Geron et al. (2002)
Costa Rica	Dry	DEC	2.2	0.29	0.13	Karl et al. (2004)
Congo, Africa	–	A–REA	0.9	–	–	Greenberg et al. (1999)
Congo, Africa	–	LL	0.8 – 1	–	–	Klinger et al. (1998)
Congo, Africa	–	REA	0.46 – 1.4	–	–	Serca et al. (2001)

EC = Eddy covariance; (A)-REA = (Airborne) Relaxed eddy accumulation; SLG = Surface layer gradient; MB = Mass Budget; MLG = Mixed layer gradient; MLV = Mixed layer variance; LL = leaf level extrapolation; BM box = modelling; CBL = Convective boundary layer budgeting.

Table 4. Summary of the coefficients used to drive the MEGAN model. Standard coefficients are based upon studies of temperate plant species, whereas fitted coefficients relate to the measured flux data obtained during OP3-III over a tropical rainforest.

		G06 Standard Coefficients		G06 Fitted Coefficients	
Coefficients		Isoprene	Σ Monoterpenes	Isoprene	Σ Monoterpenes
CT_1	(Eq. 5)	95	95	142	95
CT_2	(Eq. 5)	230	230	232	230
p_o	(Eq. 7)	200	200	200	200
$T_{\max}$	(Eq. 8)	313	313	316.1	312.9
x^1	(Eq. 6)	0.004	0.004	0.006	0.006
x^2	(Eq. 6)	0.0005	0.0005	0.0004	0.00025
x^3	(Eq. 7)	0.0468	0.0468	0.0702	0.0702
x^4	(Eq. 9)	2.034	2.034	3.051	2.058
x^5	(Eq. 8)	0.6	0.6	0.52	0.47
BER		1.65	0.4	2.5	0.5
R^2		0.47	0.44	0.50	0.45
M		0.56	0.51	0.43	0.37

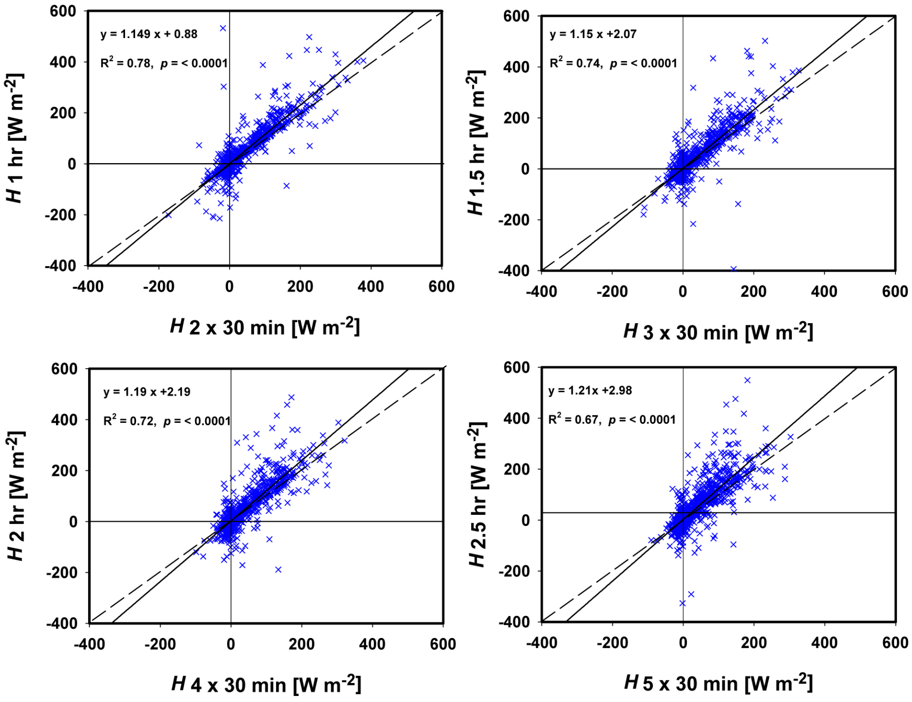

Fig. 1. An analysis of low frequency flux losses for sensible heat flux data *(H)* collected at the GAW site during the OP3 campaign. Solid line shows the best linear fit and dashed line represents the 1:1 line.

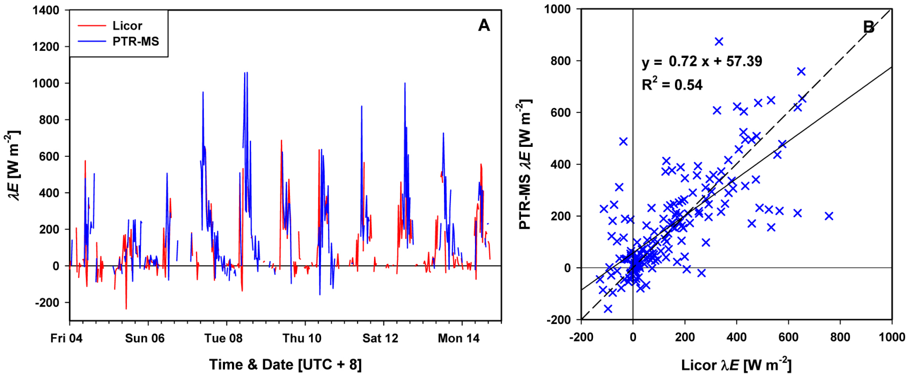

Fig. 2. Latent heat fluxes measured at the GAW site during the period of 4–14 July by open path IRGA (LICOR – 7500) and PTR-MS. PTR-MS water vapour measurements recorded as *m/z* 37 were calibrated against a closed path IRGA (LICOR – 7000) which sampled from the same 70 m sample line as the PTR-MS. **(B)** indicates the amount of flux lost due to dampening of water vapour which can be used to estimate a worst case scenario of VOC flux losses.

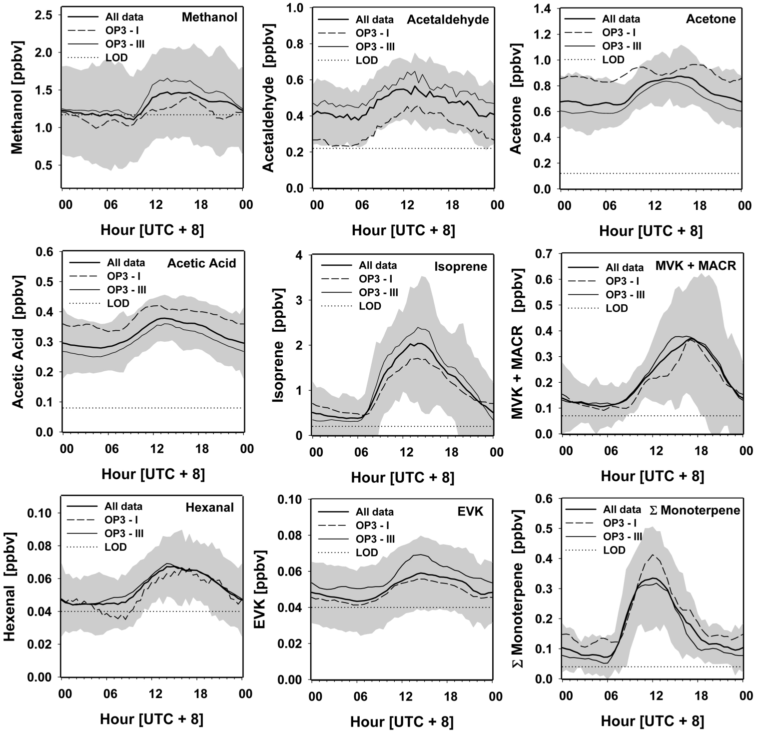

Fig. 3. Average diurnal profiles of VOC mixing ratios measured during the two intensive OP3 field campaigns which took place between 20 April–7 May (OP3-I) and 20 June and 20 July (OP3-III), 2008. Grey error bands show ±1 standard deviation of averaged hourly values and dotted lines show the limit of detection (LOD=$2\times\sigma_{\mathrm{background}}$/sensitivity).

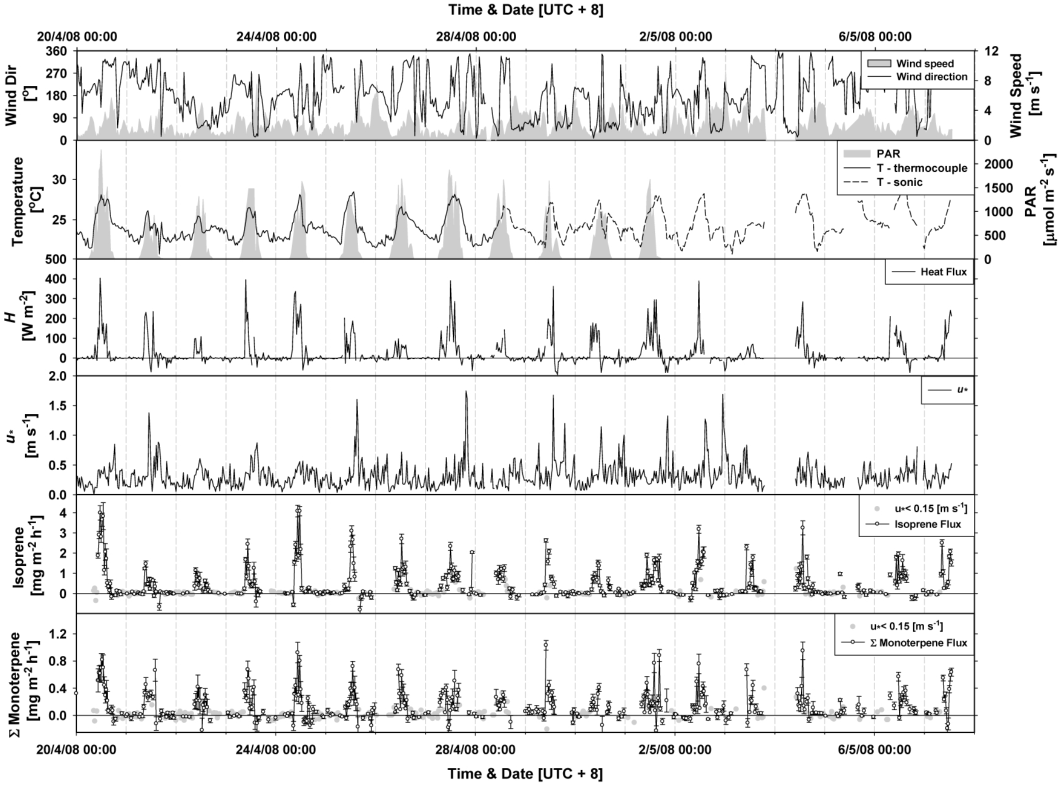

Fig. 4a. Summary of the meteorology and main VOC fluxes during the first intensive OP3 field campaign (OP3 – I) which took place during April and May, 2008. Wind speed and wind direction measurements were recorded by a senor (WXT-510 Weather Transmitter, Vaisala) situated at 75 m on the GAW tower. Temperature was recorded at 30 m by an aspirated thermocouple and sonic anemometer, PAR was measured from the roof of the GAW laboratory and sensible heat, friction velocity and VOC fluxes were all measured from the 75 m platform of the GAW tower. VOC flux data recorded during periods of low turbulence ($u_* < 0.15\,\mathrm{m\,s^{-1}}$) were rejected from the final analysis, but are shown here as grey circles.

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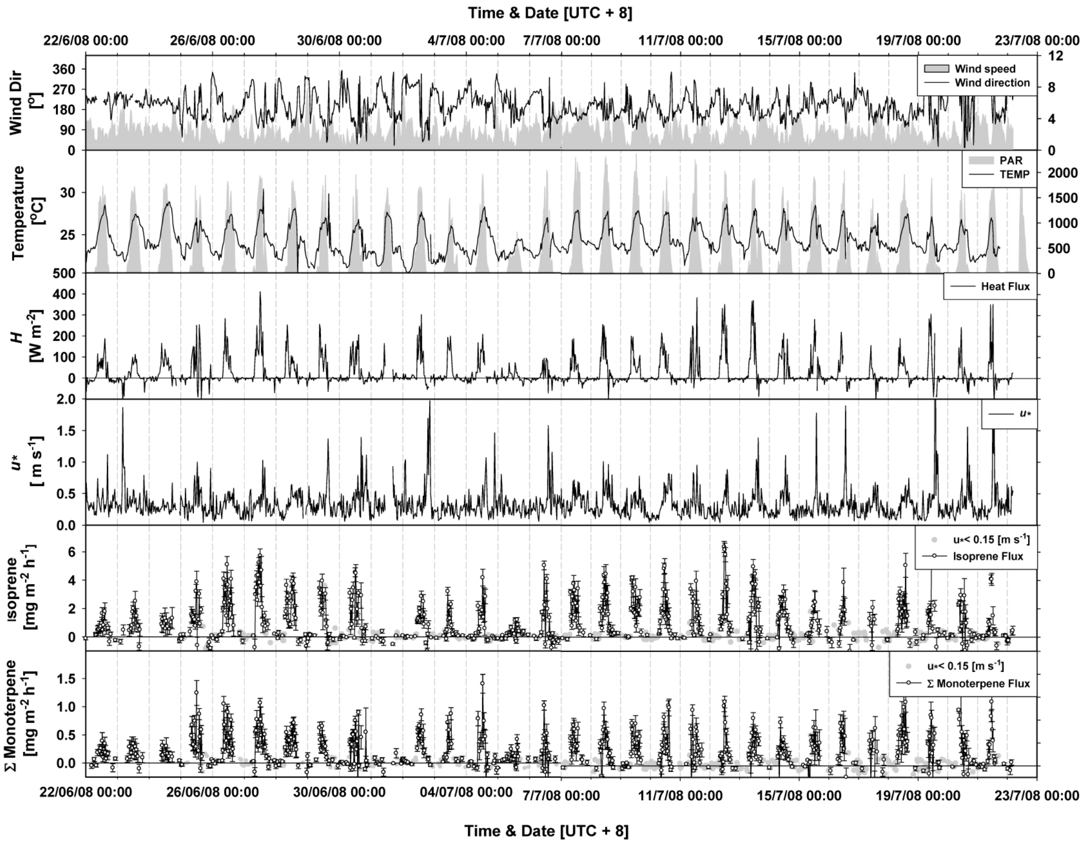

Fig. 4b. Summary of the meteorology and main VOC fluxes during the second intensive OP3 field campaign (OP3 – III) which took place during June and July, 2008. Measurement instrumentation as above. VOC flux data recorded during periods of low turbulence ($u_* < 0.15\,\mathrm{m\,s^{-1}}$) were rejected from the final analysis, but are shown here as grey circles.

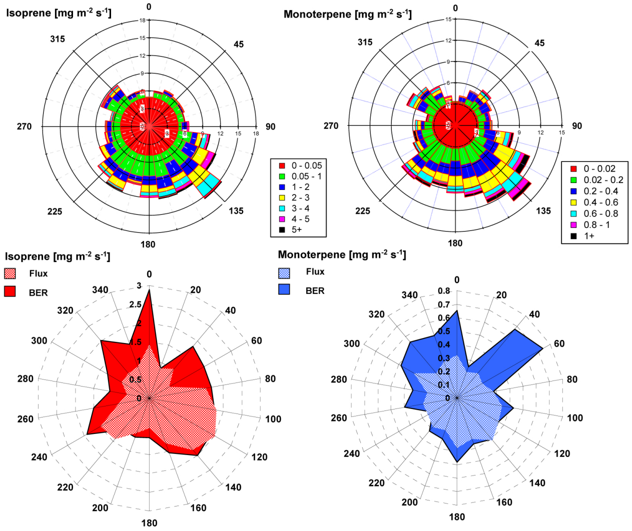

Fig. 5. Wind roses of isoprene and monoterpene fluxes (top) measured during the two OP3 campaigns. The bottom plots show the same flux data normalised to standard conditions (30 °C (Canopy temperature), 1000 µmol m^{-2} s^{-1}) using the light and temperature algorithms from the MEGAN model (Guenther et al., 2006).

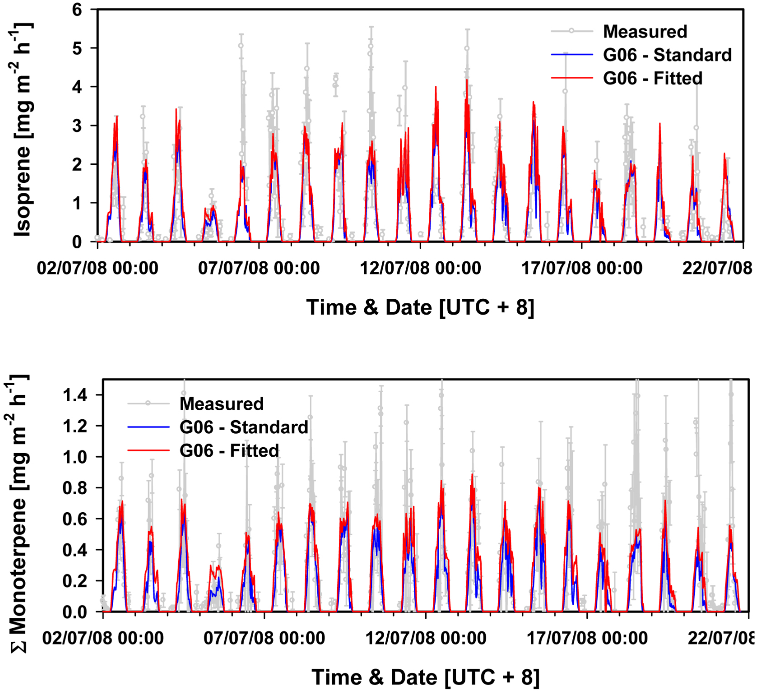

Fig. 6. Isoprene and monoterpene fluxes (grey line) measured by the continuous flow disjunct eddy covariance technique during the OP3-III field campaign. The blue line shows the model output when configured using the standard G06 coefficients and the red line shows the same output generated with empirically fitted parameters. Both sets of parameters, including basal emission rates normalised to 30°C and 1000 µmol m^{-2} s^{-1} are listed in Table 3.

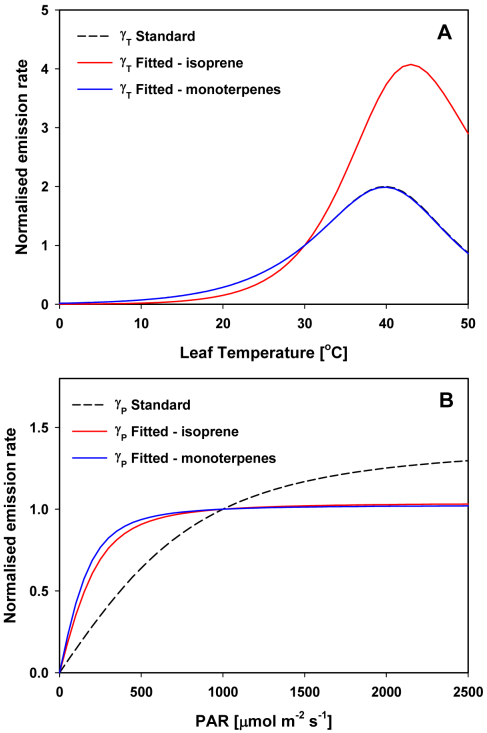

Fig. 7. The temperature **(a)** and light **(b)** response of the G06 algorithm. Dashed lines show the G06 response using standard coefficients which are based on temperate species only (in (a), the dashed line is directly below the blue line). Solid lines show the G06 response for isoprene (red) and monoterpenes (blue) using new coefficients which were obtained by fitting the algorithm response to measured fluxes above a tropical rainforest in Malaysian Borneo. In each response, past light and temperature values were set to: T24=297, T240=297, PAR24=360, PAR 240=375.

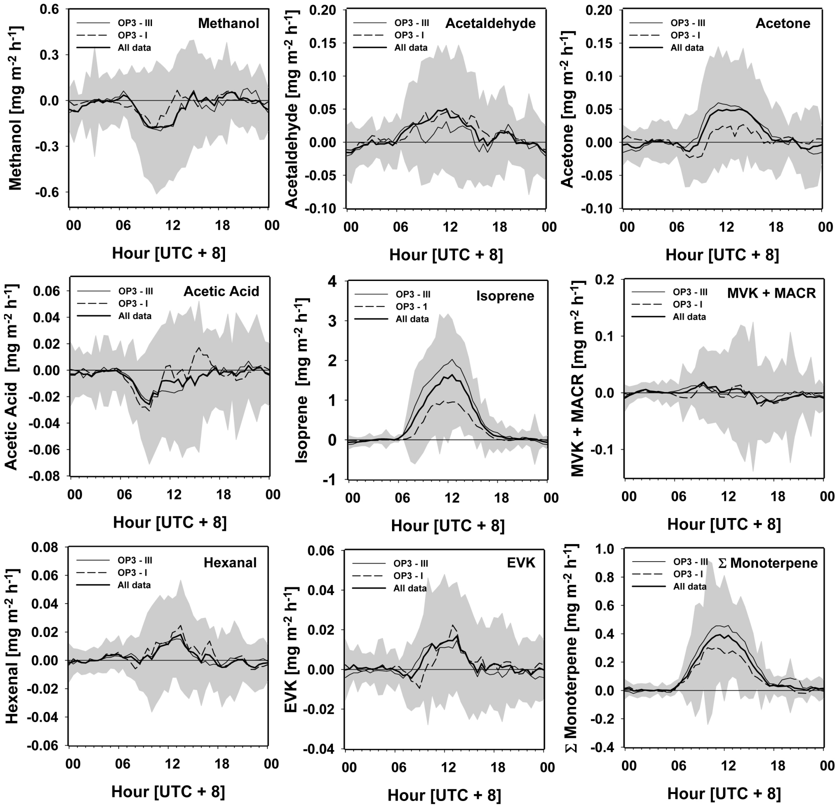

Fig. 8. Average diurnal profiles of VOC fluxes measured during the two intensive OP3 field campaigns which took place between 20 April–7 May (OP3-I) and 20 June and 20 July (OP3-III), 2008. Greyed bands show ±1 standard deviation of averaged hourly values.

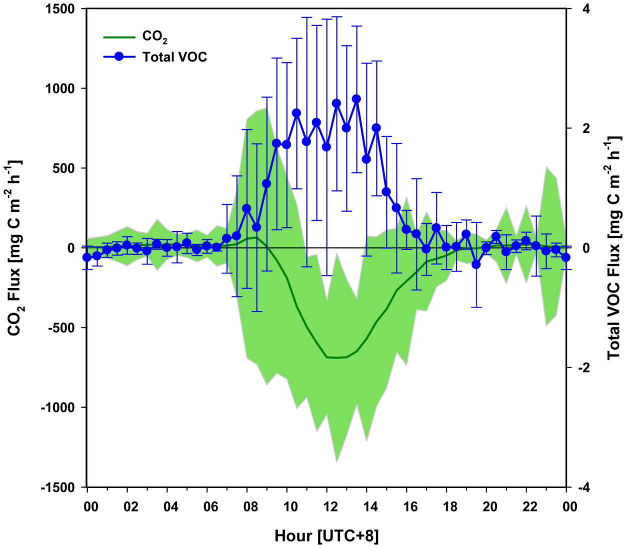

Fig. 9. Averaged diurnal profiles of CO_2 and total VOC (sum of isoprene, monoterpenes, methanol, acetaldehyde, acetone, acetic acid, MVK+MACR, hexanal and EVK fluxes) fluxes measured above a SE Asian tropical rainforest during the period of 20 June–20 July 2008. Error bars and greyed bands show ±1 standard deviation of mean averaged values.