Supplementary Material for "Direct ecosystem fluxes of volatile organic compounds from oil palms in South-East Asia"

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15 SI-1 Ambient and canopy temperature

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- 17 Figure S1 shows diurnal patterns of measured ambient temperature and the average canopy
- 18 temperature estimated from extrapolation of the ambient temperature to the surface, using the
- 19 sensible heat flux and the resistance approach (Nemitz et al., 2009).



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Figure S1. Comparison between the ambient ($T_a(15 \text{ m})$) and canopy (T_c) temperature estimated from

22 resistance approach. Inset showing regression and higher variability in the upper range.

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2 SI-2 Proton Transfer Reaction Mass Spectrometry (PTR-MS)

3 The concentrations and eddy fluxes of biogenic volatile organic compounds (BVOCs) were 4 measured by a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) operated in 5 continuous flow disjunct eddy covariance (cfDEC) mode, also referred to as the virtual 6 disjunct eddy covariance (vDEC) mode, described in the next section. The instrument was the 7 high-sensitivity model (Ionicon, Austria, s/n 04-03) which was equipped with an additional 8 turbomolecular pump for the detection chamber and incorporated Teflon®, instead of Viton®, 9 gaskets in the drift tube. Since the characteristics of instrument design and operation have 10 been thoroughly described in the literature (Blake et al., 2009; de Gouw, 2007; Hansel et al., 1995; Lindinger et al., 1998; Warneke et al., 2001), only a general overview specific to 11 12 running at high humidity will be given here.

13 The principle of PTR-MS is the soft ionisation of VOCs by hydronium ions formed in a 14 hollow cathode ion-source from pure water vapour; these effectively transfer protons to all 15 molecules with proton affinities (PA) greater than that of water. Most VOCs have sufficiently 16 large PA for effective ion transfer, but a few low-weight molecular compounds, with PA only 17 slightly higher than water (e.g. formaldehyde), may require specific optimisation to minimise the impact on sensitivity of humidity dependent back-reactions. The conditions inside the 18 19 reaction chamber are dependent on both electric field (E) and the number density of the buffer 20 gas (N) and the ratio of these (E/N) determines the degree of fragmentation and clustering. At typical ambient conditions this ratio is kept in the range 120 - 140 Td (1 Td = 10^{-17} V cm²). 21 22 However, for a constant E/N ratio the sensitivity is proportional to N and thus operation at 2 23 mbar or larger is recommended (Warneke et al., 2001). The protonated ions are filtered through a quadrupole mass filter (QMA 400) and counted with a Secondary Electron 24 25 Multiplier (Pfeiffer SEM-217) coupled to an ion-count preamplifier (Pfeiffer CP-400). The radio frequency and direct current are generated by an RF box (Pfeiffer QMH 400). Since the 26 27 sampled VOCs undergo protonation, they are detected at a mass to charge (m/z) ratio equal to 28 one unit greater than their molecular weight. The soft ionisation method means that most 29 compounds can be detected as their parent ion. For heavier compounds (m/z > 100) the 30 protonated masses reflecting two or more fragments may need to be taken into account. This 31 is the case, for example, for monoterpenes (m/z 137, 81) (e.g. Tani et al., 2003) and sesquiterpenes (m/z 205, 149) (Kim et al., 2009). Because some compounds fragment more 32

than others, appropriate calibration and calculation approaches have to be applied (sections
 SI-3 and SI-5).

3 The optimisation of the PTR-MS and the sampling system sought a compromise between 4 reliable measurements at very high humidity and sensitivity for VOCs. Tani et al. (2004) showed that sample humidity has a significant impact on fragmentation patterns at normal 5 6 E/N ratios, but has no influence if E/N is kept around 140 Td. The water vapour pressures 7 tested by these authors ranged from 0.59 to 2.4 kPa. However, the vapour pressures 8 encountered at the oil palm site were much higher, ranging from 2.5 to 3.2 kPa (2.75 kPa on 9 average) due to high relative humidity (88% on average) accompanied by high temperatures 10 (22 – 31 °C). Humidity effects on PTR-MS measurements were also studied by Warneke et 11 al. (2001), who noted decreasing sensitivities at higher humidities, although again the levels of specific humidity encountered in Borneo were not tested by these authors. Although the 12 13 sensitivity could be enhanced by increasing the drift tube pressure to 2 - 3 mbar this approach 14 was not possible for the conditions here, because the high flow in the sampling line and the 15 high specific humidity would have required operation at a detection pressure close to or above 16 the set points of the instrument. In addition, higher drift tube pressure would have increased 17 the likelihood of internal condensation.

18 Therefore, the optimal operating conditions were determined experimentally to be a drift tube 19 pressure of 1.6 mbar, inlet and drift-tube temperatures of 45 °C and drift voltage of 485 V, giving an E/N value of 140 Td. This was maintained constant throughout the experiment. Our 20 21 subsequent measurements in the laboratory revealed less than 5% reduction in sensitivity when operating at 1.6 mbar drift tube pressure, compared to 2.2 mbar at the same E/N ratio. 22 23 However, high ambient water vapour pressure had an additional impact on the sensitivities, 24 and normalisation for the presence of water clusters was required (Davison et al., 2009; Tani 25 et al., 2004). The overall reduction in sensitivity was estimated at 20% with respect to operation at temperate humidities. 26

The system was automated to run continuously in 3 modes: (1) m/z 21-206 scan of ambient air; (2) multiple ion detection (MID) of 11 pre-selected VOCs at 0.5 s dwell time each (0.2 s for additional m/z 21 and 37 corresponding to $H_3^{18}O^+$ and $H_3^{16}O(H_2^{16}O)^+$, respectively; and (3) m/z 21-206 background measurement of humid VOC-free air. Mode 1 was set to run for the first 5 minutes of each hour, then 25 min was devoted to mode 2, then mode 3 for 5 min and again mode 2 for the remaining 25 min. The switching between modes was automated through a solenoid valve system operated from the 12 V DC power port of the PTR-MS power supply unit and managed through a QS422 sequence. The online preview and logging of volume mixing ratios and fluxes was done using the DDE feature of the Balzer sequencer communicating with a LabVIEW program which logged the sonic anemometer data together with the PTR-MS data to one file, so that each 25-min file contained 30000 rows of wind data, 210 of which also contained PTR-MS data which were synchronised in time, but not yet corrected for the lag-time associated with the residence time in the tubing (see Sect. SI-5).

8 Direct calibration used a VOC gas mixture supplied by Apel-Riemer Environmental Inc., 9 USA, which contained methanol, acetaldehyde, acetone, isoprene, acetonitrile and 10 formaldehyde, each at 1 ppmv, and d-limonene at 0.18 ppmv. This standard was checked after the campaign by reference to a GC-MS calibrated with a different isoprene standard (BOC 11 gases, UK) and a d-limonene standard prepared from a diluted (with methanol) liquid 12 13 standard (Sigma Aldrich, UK) injected directly onto the column. Agreement for isoprene and monoterpenes was within 4% and 10%, respectively. The other VOCs were compared with 14 15 another gas standard delivered by Apel-Riemer (at 0.5 ppm concentration per VOC) which was 2 years older and contained the same VOCs plus MVK, and other organics. The 16 17 agreement was within 18%; the older standard showed 8-18% smaller concentrations for all VOCs except for acetaldehyde, which was 8% higher possibly through contributions of 18 fragments from other organic species (e.g. MVK) that were not present in the other mixture. It 19 has been assumed that the calibration standard was within the certified 5% standard precision 20 for isoprene and other VOCs at the time of calibration. A larger uncertainty of 20% has been 21 22 attributed to MVK sensitivity, which was not present in the calibration standard in the field, 23 but which was inferred from the comparison of the sensitivity curves in the laboratory derived from the MVK containing standard. It was also assumed that the sensitivity for the sum of 24 25 MVK+MACR is the same as for MVK only.

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27 SI-3 Derivation of volume mixing ratios (VMRs)

The signal intensities measured as counts per second I_{mz} (cps) for each of the monitored m/zchannels were first converted to normalised counts per second I_{mz} (ncps) (Davison et al., 2009) in order to compensate for fluctuations in the primary ion, water vapour and drift-tube pressure.

$$I_{mz}(ncps) = \frac{I_{mz}(cps) \times 10^{6}}{I_{21}(cps) \times 500 + I_{37}(cps) + I_{55}(cps)} \times \frac{p_{dnorm}}{p_{d}},$$
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(S1)

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where I_{21} , I_{37} and I_{55} are the instantaneous counts (cps) of H₃¹⁸O⁺ (approximately a factor of 3 500 lower than $H_3^{16}O^+$, $H_3^{16}O(H_2^{16}O)^+$, and $H_3^{16}O(H_2^{16}O)_2^+$, respectively. The *m/z* 21 4 channel instead of m/z 19 was selected for monitoring the primary ions in order to prevent 5 detector saturation. Generally a natural ${}^{16}O/{}^{18}O$ isotope ratio of 500 is used in the calculation 6 7 (Kuhn et al., 2007; Langford et al., 2009a) although the use of a slightly lower precise ratio of 8 487 was proposed (Taipale et al., 2008). In fact, the true ratio might differ slightly depending 9 on the location (e.g. close to oceanic waters) and one of the purposes of normalisation is to 10 make the results uniform for comparisons with other results, where the level of primary ions used was different. In our case the level of primary ion counts was $6.5-7.5 \times 10^6$ cps. The 11 12 volume mixing ratios (χ) were obtained for each VOC as:

$$\chi_{VOC} = \frac{I_{mz} (\text{ncps}) - I_{mz(zero)} (\text{ncps})}{S_{mz} (\text{ncps/ppbv})}$$

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(S2)

Here, $I_{mz(zero)}(ncps)$ is the background normalised count rate for the given m/z channel, and the S_{mz} (ncps/ppbv) is the normalised sensitivity for a given compound. The S_{mz} for compounds present in the gas standard was obtained from the slope of a 6-point calibration line in the range 0 to 500 ppbv (0 to 90 ppbv for monoterpenes) corrected for background I_{mz} (ncps).

19 The standard was appropriately diluted in clean Tedlar bags using VOC-free air, generated by 20 purging ambient air through a Pt/Al₂O₃ catalyst heated to 200 °C. This catalyst removed most 21 VOCs effectively, but did not significantly affect water vapour concentrations, thereby 22 avoiding problems arising from using dry calibration gas. However, normalisation for water 23 clusters was always performed (Eq. S1). For compounds not present in the standard, the 24 empirical sensitivity S'_{mz} was approximated from the relative transmission curve (RTC) 25 (Davison et al., 2009; Taipale et al., 2008). Only the sensitivities of non-fragmenting 26 compounds which are known not to deviate significantly from the RTC (e.g. methanol, 27 acetaldehyde, acetone, acetonitrile) were used to derive the relationship between the 28 sensitivities and the transmission coefficients from using the reaction rate coefficients for the 29 proton transfer reaction taken from Zhao and Zhang (2004). Since no large m/z compounds were used in calibration, the RTC approach was limited to the 21-71 range, and was extended later after comparison to the classical transmission coefficients using higher MW compounds such as xylene and camphor. The calibration error using the standard is assumed to be less than 5% while that from using reaction rate constants can be up to 100% (Steinbacher et al., 2004). However, the relative transmission approach used here can offer less than 30% relative error (Taipale et al., 2008).

7 SI-4 Graphical method for LODs, standard deviations and means

8 For the data which had lognormal distribution, common for environmental datasets, the 9 exponent of the slope of the lognormal line on a log-probability plot corresponds to the geometrical standard deviation (and the exponential of the intercept corresponds to the 10 geometrical mean). The geometrical LOD can be found from the exponential of the intercept 11 12 (Helsel, 1990). Similarly, for normally-distributed data, the slope of the line of nonlogarithmic VMR values versus normal cumulative distributions corresponds to the arithmetic 13 14 standard deviation and the intercept to the arithmetic mean. For compounds whose 15 distributions turned out to be multimodal (e.g. isoprene, MVK) the graphical methods were 16 not applicable.

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19 Figure S2. An example of the graphical estimation of the limit of detection and other statistical

20 parameters from lognormal data values (a) and normal data values (b) plotted against normal

21 cumulative distributions.

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2 SI-5 Flux derivation and validation

3 PTR-MS, with its relatively high sampling rate, is a perfect tool for application in direct, eddy 4 covariance, but when more than one m/z are monitored sequentially the timeseries are not 5 continuous any more, but disjunct. As typically several compounds are selected, the 6 instrument can serve as a disjunct sampler, such that the quadrupole analyses one m/z after 7 another during continuous flow. Its use in this manner has been termed 'virtual disjunct eddy 8 covariance' (vDEC) (Karl, 2002) or 'continuous flow disjunct eddy covariance' (cfDEC) 9 (Rinne et al., 2008; Rinne et al., 2002); both names denote the same approach. Files containing 25-min arrays of wind and PTR-MS data were validated for periods of breakdown 10 or other disturbances according to the log file. After a careful examination, no raw data files 11 12 have been marked for despiking or detrending. Double coordinate rotation has been applied to 13 the wind speed vectors in order to account for tilts of the anemometer. Each data row 14 corresponding to a given VOC was converted to ppbv (as described in Sect. SI-3) and subsequently to $\mu g \ m^{-3}$ using instantaneous pressure values from the Vaisala sensor attached 15 16 close to the sonic anemometer. For PTR-MS and wind data, the gaps between PTR-MS rows 17 were filled with "NaN"s in order to align the frequency of the two time series, and the 18 covariance function was then obtained by computing separately for each VOC the covariance 19 between the instantaneous deviation in mixing ratio (χ') and the instantaneous deviation in 20 vertical wind velocity (w') (i.e., $cov < w' \chi >$) for each time lag step (0.05 s) expressed as a 21 shift in the wind row versus concentration row. If a clear maximum in the covariance was 22 found within the time lag window, which was defined as at least twice the theoretical lag time 23 and not less than twice the cycle length, then the time lag was recorded for this 25 min period and applied in the final computation of the flux as below: 24

$$F_{VOC} = \sum (w_i - \overline{w}) \times (\chi_{i+\tau} - \overline{\chi})$$

$$(S3)$$

where w_i and \overline{w} are the instantaneous value and mean over an integration period, respectively, for vertical wind velocity, $\chi_{i+\tau}$ is the lag-time adjusted instantaneous value for the mixing ratio and $\overline{\chi}$ is the mean mixing ratio over the same integration period.

The optimum time lag was found automatically from the maximum covariance using a 1 2 LabVIEW program. If no acceptable maximum was found, or if the flux value was below the 3 detection limit (defined as 3 times the standard deviation of the covariance for lag times well 4 outside the possible window (Spirig et al., 2005), then the data point was marked as invalid 5 and was not included in further analysis. Finally, the accepted lag times were manually examined in terms of their variability. If the lag time exceeded the theoretical lag time (based 6 7 on sample flow rates) by more than the length of a measurement cycle, or if the lag time 8 found from the covariance functions of shorter integration time sub-periods (e.g. 5 min) was 9 found variable within the 25 min period, then any peak in the covariance found by the program was marked unreal (pseudopeak). However, the lag time value was allowed to be 10 11 variable by not more than 30% within a 25-min period (as found on 5-min integration times).

12 In addition, the data were labelled according to routine tests commonly used in eddy covariance for filtering purposes (Clement et al., 2009; Foken and Wichura, 1996; Langford 13 et al., 2009a; Moncrieff et al., 1997): the lower limit for the friction velocity was normally set 14 to 0.15 m s⁻¹ and points below this threshold were not included in analyses unless for specific 15 tests. According to the FLUXNET criteria for ideal conditions described by Foken et al. 16 (2004) the turbulence was quite well developed at the site, with 90 % of data in the first 3 17 classes and no data ranked in 8th or 9th category. However, at night, friction velocities were 18 typically below the threshold of 0.15 m s⁻¹. According to the recommendations of Foken and 19 Wichura (1996), data were not included in further analysis if the deviation from the ideal 20 integral similarity characteristics was higher than 60%, and were labelled lower quality if they 21 22 were within 30-60% of the ideal. A stationarity test (the value for the flux integrated over 25 23 min compared with the average of 5 values of fluxes integrated over 5 min segments of the 24 same averaging period) was used to exclude non-stationary data when the difference was 25 above 60% and to label as low quality periods with differences between 30 and 60%. These tests were done on the sensible heat data and the affected periods were also removed from the 26 27 VOC flux datasets.

Flux losses associated with signal damping due to residence time in the tubing were assessed by comparing latent heat fluxes derived from m/z 37, calibrated using specific humidity converted from relative humidity (Vaisala WXT Weather Transmitter), with latent heat fluxes from the an open path gas analyser (LI-COR 7500 Infrared Gas Analyser; (Skiba et al.,





Figure S3. Comparison of latent heat fluxes derived by PTR-MS and open-path infrared gas analyser:
a) time series b) linear regression.

Finally, low frequency losses were examined by comparison with fluxes with longer averaging periods (Langford et al., 2009a) and the error introduced by disjunct sampling was estimated by comparing disjunct series for sensible heat flux (corresponding to times when PTR-MS data were available) with continuous data for sensible heat flux (Langford et al., 2009b). The overall flux losses were found to be below 10% and no corrections have been made. Taking all above into account an average 35 % precision for the flux was estimated.

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15 SI-6 Distributions of mixing ratios

Figure S4 shows the frequency distributions of the mixing ratios for the individual VOCsobserved over the oil palm plantation.



Figure S4. Distributions of the volume mixing ratio values of the compounds measured in the flux
mode. Green areas correspond to detection limits.

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5 SI-7 Possible isoprene hydroxyhydroperoxides and epoxides

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Figure S5 shows the aproximate mixing ratio of the sum of isoprene peroxides and epoxides as derived from m/z 101.



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2 Figure S5. Possible isoprene peroxides and epoxides coinciding at 101 m/z ion channel.

4 SI-8 Comparisons between parameterised and original G06 model

The Guenther et al. (2006) model (G06) is the most advanced empirical model for terpene 5 6 emission, which is a significant advancement from previous Guenther et al. models (e.g. 7 Guenther et al., 1995) in that the parameters which used to assume constant values (i.e., α , Cp, 8 Topt and Eopt) were extended to simulate variations in enzymatic kinetics and isoprene 9 substrate availability, caused by previous history of temperature and PAR, as tested in a range of field studies (Geron et al., 2000; Hanson and Sharkey, 2001; Monson et al., 1994; Petron et 10 11 al., 2001; Sharkey et al., 1999). Ten empirical parameters have been chosen and labelled 12 analogously to those in equations presented for estragole emission parameterisation by Misztal et al. (2010). These equations for the temperature and PAR dependent activity factors 13 14 $(\gamma T \text{ and } \gamma P)$ were merged together into one equation so the parameterised flux is represented 15 as below (S4) with the 10 parameters marked as b1-b6, Tb, P0, CT1 and CT2 to be optimised 16 to fit the experimental data from oil palms. The dependent variables were the photosynthetically active radiation (PAR) and the canopy temperature (T) estimated from an 17 18 ambient temperature using the resistance approach. The P24 and T24 are the 24 h averages of 19 previous PAR and T, respectively; and P240 and T240 are the previous 10-day averages.

$$F_{G06} = \text{BER} \cdot b_{3} \cdot \exp[b_{2} \cdot (P_{24} - P_{0})] \cdot (P_{240})^{0.6} \cdot \frac{[b_{1} - b_{2} \ln(P_{240})] \cdot PAR}{\sqrt{1 + [b_{1} - b_{2} \ln(P_{240})]^{2} \cdot PAR^{2}}} \cdot b_{5} \cdot \exp[b_{6} \cdot (T_{24} - 297)] \cdot \exp[b_{6} \cdot (T_{240} - 297)] \cdot \frac{C_{T2} \cdot \exp[C_{T1} \cdot (\frac{1}{T_{opt}} - \frac{1}{T}) \cdot \frac{1}{0.00831}]}{C_{T2} - C_{T1} \cdot [1 - \exp[C_{T2} \cdot (\frac{1}{T_{opt}} - \frac{1}{T}) \cdot \frac{1}{0.00831}]}$$

2 Comparison between the original G06 model using $T_a(15 \text{ m})$, measured 3 m above the 3 canopy, and the measurement is presented in Figure S6a, and the analogous comparison using 4 the canopy temperature (T_c) in the G06 model in Figure S6b. By optimising the G06 parameters based on the measured canopy flux, the model fit improves significantly from 5 originally $r^2 = 0.75$ to 0.91, if a constant basal emission rate (BER) and $T_a(15 \text{ m})$ are used (not 6 7 shown). Replacing $T_a(15 \text{ m})$ for T_c in the original model increases the coefficient of 8 determination to 0.83 (Figure S6b) which after parameter adjustment improves further to 0.93 9 (Figure S6c). The corresponding time series are almost identical. The comparison of the 10 original and the parameterised G06 model outputs for oil palms has a quadratic relationship 11 (Figure S6d), which suggests that the original model underestimates the emission at moderate 12 temperatures and light levels. For the adjusted BER, the original G06 has a tendency to 13 overestimate the small flux region (morning, afternoon) while underestimating the high fluxes 14 (noon) in comparison with the 1:1 slope with measurement.

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(S4)



Figure S6 Comparison of measured fluxes with the original G06 using ambient temperature at a
constant BER of 12.8 mg m⁻² h⁻¹ (a), with the original G06 using canopy temperature at a constant
BER of 12.8 mg m⁻² h⁻¹ (b), and the parameterised G06 optimised for oil palm plantation using canopy
temperature at a constant BER of 22.8 mg m⁻² h⁻¹ (c). The relationship between original and optimised
G06 model is shown in (d).

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Figure S7 shows isoprene emission in response to PAR derived from canopy measurements.
The curve is getting much steeper after 1000 μmol m-2 s-1. The relation ship with

10 temperature was presented in the main text.





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