Ground-level ozone influenced by circadian control of isoprene emissions

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Correction to Supplementary Information

A typographical error was made in Eq. S7 of the Supplementary Information. This equation describes the response of the observed circadian control at the oil palm plantation and should read as follows:

$$f(t) = -54.2t^6 + 141.5t^5 - 118.0t^4 + 25.8t^3 + 4.1t^2 + 1.2t$$

Ground-level ozone influenced by circadian control of isoprene emissions: Supplementary information

Supplementary methods

1. Canopy scale flux measurements

Measurements of isoprene (and other volatile organic compounds (VOCs)) were made above both tropical rainforest and oil palm plantation canopies in Sabah, Malaysia in 2008. The measurements made above the rainforest were done as part of the UK-NERC funded consortium project “Oxidant and particle photochemical processes above a South-East Asian tropical rainforest” (OP3), while the measurements at the oil palm plantation were made as part of the OP3 sister project “Aerosol coupling in the Earth’s system” (ACES). The overall aims and objectives of these projects, site descriptions and significant findings are described in detail by Hewitt *et al.* (2010)¹. The broad impacts of land use change in SE Asia on surface – atmosphere exchange² and atmospheric composition^{3,4} are discussed elsewhere.

At the rainforest, micrometeorological measurements were made from the 100 m tall Bukit Atur Global Atmosphere Watch (GAW) tower (4° 58′ 49.33″ N, 117° 50′ 39.05″ E). The GAW tower is located within the Permanent Forest Estate (PFE) Production Forest of the Ulu Segama – Malua Forest Reserve, and is 5 km east of the 438 km² area of PFE Protection Forest known as the Danum Valley Conservation Area. The Ulu Segama – Malua Forest Reserve is 2411 km² in area and is divided into annual timber harvesting coupes. The GAW tower lies at the centre of the 22.6 km² ‘Coupe 88’ which was subjected to selective timber harvesting in 1988. An average of 96 m³ of timber ha⁻¹ was cut by both tractor and high-lead harvesting⁵. The central area of this coupe was subsequently rehabilitated by enrichment planting⁶. As part of a study covering a 225 km² area, Tangki and Chappell⁵ calculated an average tree biomass of 172 t ha⁻¹ for Coupe 88 in 1997. Tangki (2008)⁷ demonstrated that *Dipterocarpaceae* were the most abundant tree family recorded for the 225 km² area as a whole (comprising of only lowland evergreen broadleaf rainforest), but *Euphobiaceae* had become more abundant in Coupe 88 following timber harvesting and enrichment planting.

The GAW tower was instrumented with an ultrasonic anemometer (Wind Master Pro, Gill Instruments, U.K.) affixed to the north-west facing corner at a height of 70 m. As the GAW tower is located on a hill, the effective measurement height was ~ 100 m above the forest canopy below, giving a measurement height of ~5h (where h is the canopy height of ~25 m above ground). A high sensitivity proton transfer reaction mass spectrometer (PTR-MS; Ionicon Analytik GmbH, Innsbruck, Austria) was installed in an air-conditioned laboratory at the base of the tower for the online analysis of volatile organic compound mixing ratios. Air for analysis was sub-sampled by the PTR-MS along a short heated length of 1/8″ (OD) PFA tubing at 300 ml min⁻¹ from the main 1/2″ (OD) PFA sample tube, which brought air from directly below the sonic anemometer at a flow rate of 60 l min⁻¹. The PTR-MS was optimised to run at an E/N ratio of 140 Td, with drift tube

voltage, temperature and pressure set to 500 V, 45 C and 1.65 mbar respectively, giving a primary ion count in the range of $(6 - 8) \times 10^6$ ion counts per second. In total 13 compounds were targeted with a dwell time of 0.5 s per m/z , resulting in scan cycles of ~ 7 seconds.

The ambient air temperature was measured by aspirated thermocouples at heights of 30 m, 45 m, 60 m and 70 m and photosynthetic activation radiation (PAR) was recorded by a sensor located on the laboratory roof at the base of the tower. This positioning was sub-optimal and led to some shading of the sensor by the lattice structure of the GAW tower between sunrise and 10:00 local time.

The Sabahmas oil palm plantation measurement site ($5^{\circ}14'58.69''$ N, $118^{\circ}27'15.76''$ E) was located in a 33 ha flat area of oil palm (*Elaeis guineensis* $\times$ *Elaeis oleifera* hybrid, progeny "Guthrie") trees. The trees were of uniform age (12 years) and height ($h = 12$ m). The site comprised a 15 m tower and an 8 m canopy access platform. The effective measurement height was 1.3h. Instruments were housed in a hut at the base of the platform. The analytical methods used were the same as at Bukit Atur.

During both sets of field measurements the PTR-MS was calibrated every few days using a gas standard (Appel-Reimer, Boulder CO, USA) containing, methanol, acetonitrile, acetaldehyde, acetone and isoprene at volume mixing ratios of 1 ppmv and limonene at 0.1 ppmv. The sensitivity for isoprene was of the order 1.6 cps/ppbv, normalised to 10^6 cps primary ion signal.

Isoprene fluxes were derived using the continuous flow disjunct eddy covariance technique, which has been described in detail by Langford et al. (2010)⁸ Briefly, VOC mixing ratios were paired with the corresponding vertical wind velocities, using a cross-correlation function to account for the delay between anemometer and PTR-MS measurements. Flux measurements were block averaged over 25 minute periods, with 10 minutes of each hour used to monitor the instrument background (by sampling air that had first passed through a custom-built platinum catalyst) and atmospheric bulk composition. Flux data from the rainforest site and from the oil palm plantation are described elsewhere^{1, 9, 10}.

Data from the two sites underwent identical quality assessments. Fluxes measured during periods of non-stationarity and low turbulence (based on friction velocities, u_*) were rejected⁸. Increasingly stringent thresholds of u_* (<0.15 ; 0.2 ; 0.25 m s⁻¹) were applied to the data, with no significant change to the outcome of our analysis. Therefore we applied the lower threshold of 0.15 m s⁻¹ in order to maximise the data available. In addition, flux data below the calculated limit of detection, which was estimated as 1.96 times the standard deviation of the cross-correlation function at a distance far from the true lag time (between 160 – 180 s), were also discarded. Finally, an analysis of the integral turbulent statistics of the vertical wind velocity (σ_w/u_* = standard deviation of the vertical wind velocity normalised by the friction velocity) was carried out at each site to assess the validity of the flux measurements. Overall, the above quality checks resulted in the rejection of 46% and 32% of daytime measurements (08:00-18:00) at the rainforest and oil palm sites respectively. The higher data rejection rate at the rainforest reflects the lower levels of turbulence and smaller fluxes encountered at this site relative to the oil palm plantation.

2. Calculating base emission rates (BERs) and modelled fluxes

The Guenther *et al.* (2006) algorithm¹², hereafter termed G06, is most commonly used to estimate canopy or landscape-scale fluxes of isoprene (F_x) by multiplying a given base emission rate, BER, by an activity factor, γ and a canopy production and loss term, ρ :

$$F_x = [\text{BER}] [\gamma] [\rho] \quad (1)$$

The activity factor describes variations in isoprene emission due to fluctuations in both the ambient and past (24 - 240 h) light (γ_P) and temperature (γ_T) conditions, while the base emission rate (BER) describes the rate at which the plant emits isoprene at a set of standard light and temperature conditions (30 °C and 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ PAR). Until the work of Wilkinson *et al.* (2006)¹³, it was assumed that BER is a constant and does not vary with time of day. The BER is usually measured at leaf, branch or whole plant level using leaf cuvettes or plant chambers and it is assumed that this constant value can be applied to the canopy- or ecosystem scales and be used to obtain canopy- or ecosystem-scale emission rates under varying value of T and PAR at any time of the day. However, where the isoprene flux has been measured directly at the canopy scale using micrometeorological techniques, Eq. (1) may be re-arranged to normalise the measured flux to standard conditions and provide a more direct canopy-scale BER, which avoids errors associated with extrapolation or representativeness.

We applied this procedure to 12 days of isoprene fluxes measured above the oil palm plantation and to 19 days of isoprene fluxes measured above the tropical rainforest at Bukit Atur. In each instance, BERs were calculated using the most basic form of the G06 algorithm (where $\gamma = \gamma_P \times \gamma_T$ and $\rho = 1$), only driving the model with light and air temperature data for the period of measurements and for the preceding 240 hours. The resulting time series of BERs, which should show a constant BER if fluctuations in past and present light and temperature conditions account for all the variation in isoprene emission, were averaged to give a typical diurnal profile in BER.

The resultant data were used in two ways. First, the peak BER value, which occurred around 11:00 LT (local time), was fed back into Eq. (1) to derive a flux for the original measurement period – i.e. a constant BER was used. Secondly, the diurnal profile of BER was used in Eq. (1) - i.e. a variable BER was used, varying with time of day. It is obvious that the agreement between measured and modelled fluxes is strongly dependent on the time of day that the BERs were derived. We estimated the optimal time of day to estimate constant BERs from measurements on oil palm by re-running the G06 algorithm. The results showed the closest agreement between integrated fluxes when deriving constant BERs from measurements made between 10:00 and 11:00 local time (LT) or between 13:00 and 14:00 LT. However, by using these values, the goodness-of-fit (intensity of association and bias magnitude of the daily cycle between measured and modelled fluxes was severely compromised. The results of this analysis are shown in Figure S1.

2a. Eliminating abiotic controls as a cause of varying base emission rates

We have identified two diurnally varying abiotic factors that could confound our determination of the circadian control of BER: rapid removal of isoprene by chemical oxidation occurring during turbulent transport from the canopy source to the measurement point; and the difference between leaf and air temperatures.

At the rainforest site, fluxes of isoprene were measured from a height of $\sim 5h$ (where h is the canopy height of ~ 25 m above ground), introducing the potential for flux divergence, caused by changes in both convective mixing and isoprene chemistry across the day. In order to confirm that the diurnal pattern we see in BERs at the rainforest is attributable to circadian control and not just a consequence of other abiotic processes, we investigated the role of isoprene chemistry and transport at this site.

In order to estimate the effect of chemistry on our flux measurement, we estimated the mixing time scale between the canopy top to our sensors using the convective velocity timescale (τ_{conv}), calculated as a function of time of day⁹:

$$\tau_{conv} = \frac{z_m}{w_*} \quad (2)$$

where z_m is the measurement height (this was the estimated average distance between the canopy height and measurement sensor) and w_* is equal to

$$w_* = \left[\frac{g \times z_i}{T_v} F_H \right]^{1/3} \quad (3)$$

where, g is acceleration due to gravity (9.81 m s^{-2}), z_i is the boundary layer height (obtained from Lidar measurements), T_v is potential temperature, and F_H is the kinematic heat flux. Recognising that τ_{conv} does not reflect all transport time-scales involved in the transport between emission and detection at z_m , the overall transport time is still expected to scale with τ_{conv} .

The diurnal pattern in isoprene lifetime was calculated by first adjusting the isoprene rate constant to the ambient air temperature and then accounting for the changing OH concentration, which was directly measured at a height of 5 m at the base of the GAW tower¹. Figure S2 shows the isoprene lifetime (blue line) and convective mixing time scales (red line) which follow a similar pattern, with shorter mixing times and isoprene lifetimes occurring in the late morning and increasing steadily throughout the afternoon. The net effect of these two processes on our measurements of isoprene was calculated using the Damköhler number (black line),

$$Da = \frac{\tau_{mix}}{\tau_{chem}} \quad (4)$$

where we equate the mixing timescale (τ_{mix}) with τ_{conv} and the chemical time-scale (τ_{chem}) with the chemical lifetime. A Da number of 1 or greater would indicate

reactions time to be fast compared with transport, resulting in a significant loss of isoprene between the canopy top and the measurement height.

Figure S2 shows the Da number to follow a distinct diurnal pattern, with the largest isoprene losses occurring in the late morning (1.5 – 2%). As part of a theoretical exercise, we incorporated these results into our analysis of BERs at the rainforest site by increasing the measured flux by the Da number by time of day. Dividing this by the activity factor (γ) gives us the “corrected” BER which we then compare back to our original BER, shown here in Figure S3. The results show the corrected BER to have an increased amplitude, implying that the “uncorrected” diurnal profile of varying BER presented in this manuscript is very slightly dampened due to the effects of isoprene chemistry and transport. A similar result is obtained, if the mixing time-scale is based on the friction velocity (u^*) that describes transport in the lowest part of the boundary-layer due to surface friction. On the basis of this we also conclude that isoprene chemistry will not influence the analysis made at the oil palm plantation as measurements were made much closer (3 m) to the canopy top. This time-scale analysis is further supported by the observation of only small net emissions of the first-order isoprene oxidation products (methylvinylketone and methacrolein) at the forest site⁹ and net deposition of these compounds to the oilpalm plantation¹⁰.

The diurnal pattern we see in BERs at the oil palm and rainforest is also influenced through our choice of temperature measurements used in the analysis. The ambient air temperature differs significantly from the canopy temperature, particularly during the daytime. We use air temperature because (i) we have direct measurements of air temperature, but not of the distribution of leaf temperature through the canopy and (ii) air temperature is commonly used to drive biogenic VOC emissions models.

In order to assess the importance of the temperature metric used we converted the ambient air temperature measurements to give the “big leaf” canopy temperature using a resistance analogy as described by Nemitz *et al.* (2009)¹⁴. This conversion increased the temperature by as much as 2 °C during the daytime, but only very slightly at night. Figure S4 duplicates Figure S1 using canopy temperatures instead of the ambient air temperature. Using leaf temperature rather than air temperature reduces the mean BER, but the diurnal pattern in BER persists at both the rainforest and oil palm plantation.

2b. *Circadian control of emissions of other compounds*

In addition to isoprene, we also observed circadian control of the emissions of the C10 family of monoterpenes from the rainforest (individual monoterpenes are not distinguishable from one another with proton transfer reaction mass spectrometry, hence we calculated fluxes for the entire family of compounds). However, we did not include the circadian control of these compounds in our model analyses of atmospheric chemistry.

3. *Modelling the impact of circadian control on global isoprene emissions*

Global isoprene emission rates were modelled using the MEGAN PCEEA algorithms¹². The activity factors, γ_P and γ_T , were calculated using hourly air

temperature and PAR data from the Meteorological Office's Unified Model of global climate for current climate conditions within (re-sized) 0.5° x 0.5° grid cells. The activity factors relating to leaf age and leaf area index were derived from leaf area index data (file LAI20) provided by the National Center for Atmospheric Research (NCAR). The normalized constant base emission rate was calculated for each grid cell by summing the contribution of the plant functional types (PFTs) within each cell, such that:

$$\text{BER} = \sum_{\text{PFT}=1}^n \text{BER}_{\text{PFT}} \times f_{\text{PFT}} \quad (5)$$

where BER_{PFT} is the base emission rate for each of n PFTs in the grid cell and f_{PFT} is the fraction of the grid cell covered by that PFT. For all of the model runs, f_{PFT} was taken from the PFT distribution map (PFT20) supplied by NCAR for use with their community version of the MEGAN PCEEA model¹². BER_{PFT} was based on the emission factor map for isoprene (EF20), again from NCAR, but was modified to mimic the circadian control-variable BERs described here. The methodology for this modification is outlined below in the description of the model runs. All the model runs were performed for the same five-day period in July, which represents the middle of the continuous period of flux measurement at both sites. For each model run the hourly emissions of isoprene ($\text{mg m}^{-2} \text{h}^{-1}$) were calculated for each grid cell and these results used to generate hourly emissions for an average day.

The first model run was a baseline case, which used the constant emission factors (BER_{PFT}) from NCAR's emission factor map. We then performed two experiments in which we modified the emission factors (BER_{PFT}) for all trees and shrubs. The first experiment assumed that woody plant species everywhere would also be under the same strong circadian control as that displayed by the oil palm. The second case used the more moderate circadian variation in BER detected above the rainforest. For each of these two cases, BER_{PFT} was modified to mimic circadian control so that it varied with the local time of day for each grid cell, such that:

$$\text{BER}_{\text{PFT}} = \text{EF}_{\text{PFT}} \times f(t) \quad (6)$$

where EF_{PFT} is NCAR's (constant) emission factor or BER and $f(t)$ is a function of time, where time is the fraction of daylight hours that have elapsed since dawn. The multiplier $f(t)$ was determined by fitting a polynomial function to the data, such that the value of $f(t)$ was set to 1 for a pre-determined standard BER. The standard BER for the oil palm was taken as $10.3 \text{ mg m}^{-2} \text{h}^{-1}$, which is the emission factor assigned by NCAR to broadleaved trees in the grid cell containing the Sabahmas oil palm plantation where our flux measurements were made. This corresponded to the observed BER at 11:00 LT at the measurement site. Thus the BER at 11:00 LT at the rainforest site was taken as the standard BER for these data as the diversity of species at this site made it impossible to ascertain it in any other way. The modifying factor $f(t)$ for the oil palm circadian control is shown below in Eq. 7, and that for the rainforest in Eq. 8:

$$f(t) = -54.2t^6 + 141.5t^5 - 118.0t^4 + 25.8t^3 + 4.1t^2 + 1.2t \quad (7)$$

$$f(t) = -3.4t^2 + 3.8t \quad (8)$$

where t is the fraction of daylight hours elapsed.

In each of the circadian simulations the BER_{PFT} for all trees and shrubs was calculated using Eq. 6 and Eq. 7 or Eq. 8 as appropriate, while BER_{PFT} for all other (herbaceous) PFTs were assumed to have a constant BER throughout the day.

4. Boundary layer box modelling

The CiTTyCAT box model of atmospheric chemistry¹⁵⁻¹⁹, incorporating MIM2 isoprene chemistry²⁰, was run in the planetary boundary layer, centred over the Bukit Atur Global Atmosphere Watch station and the Sabahmas oil palm plantation. Runs were carried out for 8-day periods to allow concentrations to approach steady-state. Average diurnal temperature, PAR and mixed layer height profiles measured at the Bukit Atur site²¹ were used for all runs, as diurnal mixed layer height measurements, which are strongly linked to surface temperature, were not available at the oil palm plantation. However aircraft vertical profiles of potential temperature suggest mixed layer heights are similar at both sites. Wet deposition was enabled in the model and the dry deposition velocity for the isoprene oxidation products methacrolein and methylvinyl ketone was set to 1.5 cm s^{-1} following the results of Pugh *et al.*¹⁸. A complete description of the model setup can be found in Pugh *et al.*¹⁸. For the purposes of this numerical experiment, isoprene is the only non-methane VOC emitted into the box.

Use of the variable BER leads to lower modelled isoprene concentrations, primarily due to the decreased total isoprene emission. For the Bukit Atur scenario, peak mixing ratios of isoprene fall from 5.7 ppbv to 3.6 ppbv. In both cases the isoprene concentration is stable at these concentrations for several days in the model output. Figure 1(c) shows the percentage change in ozone concentration caused by using a variable BER, as calculated for the rainforest, instead of a constant BER, for a range of isoprene and NO emission rates. Hence the change in boundary-layer ozone concentration for a range of conditions found across the globe is illustrated. The position of the rainforest measured during OP3 is marked by the black dot, with a small increase in ozone concentration being simulated under these low $[\text{NO}_x]$ conditions. However, as NO emission increases, a decrease in ozone concentration is simulated using the variable BER. For the OP3 rainforest landscape, this turnover occurs when NO emission is sufficient to take ambient NO_x mixing ratios beyond $\sim 0.3 \text{ ppbv}$. At a NO_x mixing ratio of 10 ppbv , the OP3 rainforest landscape is simulated to experience a 12% decrease in ozone concentration (NO_x mixing ratios of $\sim 10 \text{ ppbv}$ are typical of rural northern Europe or N. America²²). As isoprene emissions increase, for instance in a region such as Amazonia, where the emission rate is typically larger, the turnover point in Figure 1(c) from an increase to a decrease in $[\text{O}_3]$ occurs under a higher NO emission rate. This is principally because the resulting decrease in isoprene concentrations when using the variable BER results in less ozone being lost as a result of its direct reaction with isoprene.

Several studies have demonstrated difficulties in modelling OH concentrations in the presence of isoprene under low [NO_x] conditions^{18,22-30}. However recent studies have shown that the ability of box models to accurately predict ozone concentrations in these regions does not appear to be affected^{18,31}. It has been postulated²⁴ that OH might be regenerated in the isoprene oxidation scheme by an as yet unverified mechanism (so called OH 'recycling'). Several suggestions for appropriate mechanisms have been proposed^{24,32-35}, yielding varying success in comparisons against observations^{18,25,26,28,29}. In addition, an alternative hypothesis that HO₂ is cycled back to OH via an unknown NO-like substance has also been proposed^{26,29}. However, the principal implication of any of these methods for the modelling presented in this paper is to result in an increased OH production rate. In the absence of a consensus on this OH 'recycling' method, we have tested the effects on our results of an increased OH production in the presence of isoprene using the simple reaction following Kubistin *et al.* (2010)³¹:

In this experiment the comparison of constant and variable BER scenarios was repeated using an OH recycling of $m = 1.0$. This results in a significant reduction in the magnitude of the difference in peak isoprene mixing ratios (1.8 ppbv for a constant BER and 1.2 ppbv for a variable BER for the OP3 rainforest landscape) but does not significantly change the ozone mixing ratios. For example, using the OP3 isoprene emission rates, the change in ozone mixing ratio is less than 5 ppbv across the range of NO flux rates where OH recycling may be an important contributor. Furthermore the magnitude and behaviour of $\Delta[\text{O}_3]$, due to changing from a constant to a variable BER, remains unaltered.

As moderate to high NO_x concentrations are unlikely to be present without significant concentrations of anthropogenic VOCs, the runs above were also repeated using an anthropogenic VOC emission rate typical of the eastern USA (total VOC emission 6.24×10^{12} molecules cm⁻² s⁻¹)³⁶. This gives rise to an increase of ~10% in the peak ground-level ozone concentration; however the cross-over point from NO_x-limited to VOC-limited conditions and the relative behaviour of the constant and variable BER scenarios are almost unchanged.

Runs carried out for the oil palm landscape display the same general behaviour as the rainforest. However, due to the much higher isoprene emission rates from the plantation compared to the rainforest, a considerably higher NO emission flux is required in order to cause a decrease, rather than an increase, in ozone concentration using the variable BER. This turn-over point occurs at 1.3 ppbv NO_x (c.f. 0.3 ppbv NO_x modelled for the rainforest conditions measured during OP3). The maximum potential mixing ratios of ozone attained are also much higher in the oil palm landscape than in the rainforest landscape, as we have previously discussed³⁷.

The above changes in ozone are primarily caused by the decreased daily flux of isoprene using the variable (circadian-controlled) BER. To test the effect on chemistry of the different timing of the circadian-controlled isoprene emissions, two further sensitivity studies were carried out with only the NO emission rates varying, for the oil palm landscape, using the emission profiles of the constant and

variable BERs respectively, but with the same daily integrated isoprene emission. The oil palm landscape was selected for these experiments because the difference between isoprene emission profiles using constant and variable BERs is more pronounced there than in the rainforest landscape.

At moderate $[\text{NO}_x]$ (~ 1 ppbv) the isoprene concentration is suppressed using the variable BER. This is because less isoprene emission occurs in the morning when the concentration of O_3 is low, and more occurs later in the day when $[\text{O}_3]$ is high. This leads to a greater proportion of the isoprene being oxidized by O_3 rather than by OH. The direct result of this is a 9% increase in daytime mean boundary layer [OH] when using the variable BER. However at higher NO_x mixing ratios (2 - 30 ppbv), concentrations of OH during the day are considerably higher, due to greater cycling of HO_2 to OH, via the reaction of $\text{NO} + \text{HO}_2$. In this regime, the dominance of OH as the main sink of isoprene is increased, hence the greater midday flux of isoprene calculated using the variable BER more strongly depletes the midday OH concentration, dominating over the aforementioned early-morning effect seen at lower $[\text{NO}_x]$. The result is a decrease in daytime mean boundary layer [OH] of up to 10%, compared to when a constant BER is used. Regimes with NO_x mixing ratios < 1 ppbv are ignored due to the aforementioned problems with modelling OH and isoprene oxidation at low $[\text{NO}_x]$. Therefore, in addition to the effects of a lower integrated daily flux of isoprene, the timing of the isoprene emission can have important effects on the oxidation capacity of the boundary layer, with potentially significant repercussions for the lifetime of trace gases.

5. *Regional scale modelling*

Regional scale simulations were performed using the regional chemistry transport model WRF-Chem, version 3.2. WRF-Chem is the Weather Research and Forecasting (WRF) model³⁸ coupled with Chemistry³⁹. The model configuration includes online biogenic emissions, dry deposition⁴⁰, and radiation and photolysis rates⁴¹⁻⁴³. The MYJ boundary layer scheme^{44,45} and the RUC land surface model⁴⁶ were used.

The simulations were performed hourly from July 1 to 10, 2008 over the south-eastern USA with a horizontal resolution of 24 km x 24 km and 51 vertical levels from the surface up to 10 hPa. The gas-phase chemistry is represented in the model by the MOZART-4 (Model for Ozone and Related chemical Tracers, version 4) gas-phase chemical mechanism⁴⁷, which is coupled to the aerosol scheme GOCART (Goddard Chemistry Aerosol Radiation and Transport model)⁴⁸. The meteorological initial and boundary conditions were obtained from the National Center for Environmental Prediction's (NCEP) Global Forecast System (GFS) analyses. The chemical initial and boundary conditions were constrained by global chemical transport simulations from MOZART-4 with $0.7^\circ \times 0.7^\circ$ horizontal resolution⁴⁹.

The anthropogenic emissions used for the WRF-Chem model are based on the US EPA's 2005 U.S. National Emissions Inventory (NEI-2005). Biomass burning emissions are estimated from the Fire INventory from NCAR (FINN V1)⁵⁰ and are distributed vertically in the model using an online plume-rise module⁵¹. Biogenic emissions are calculated online from the Model of Emissions of Gases and Aerosols

from Nature (MEGAN)¹². Two model simulations were run: a reference run with the standard MEGAN configuration and a sensitivity run that included the algorithm describing the circadian control of isoprene emissions as observed in the oil palm plantation flux data. Figure S5 shows the resultant difference in surface isoprene concentrations between the two runs for the period 5 – 9 July 2008 (average of hourly data between 12 UTC and 22 UTC).

As an example of regional scale model results, Figure S6 shows the average simulated change in hourly surface ozone concentrations associated with the addition of the isoprene circadian emission algorithm in the WRF-Chem simulation for the south-eastern USA for 12 – 22 UTC for the period 5 - 9 July 2008. The circadian emission activity factor results in a 17% decrease in isoprene emissions for the 14UT period and a 5% increase for the 16UT period. The general pattern of ozone changes for 14UT and 16UT are similar, with some regions having up to 8 ppb higher simulated ozone, while other regions have up to 14 ppb lower ozone associated with the circadian factor. The similarities in ozone response in those hours that include a period of isoprene decrease (14UT) and a period of isoprene increase (16UT) may be due to the transport of relatively long-lived isoprene oxidation products including formaldehyde and organic nitrogen. Large decreases in ozone concentrations are simulated for Florida and a zone running from southern Mississippi to northern Georgia and the Carolinas. Considerable ozone increases are simulated for the Ozarks and a zone running from northern Mississippi to Tennessee and West Virginia. WRF-Chem simulations for other periods had a similar range in ozone increase and decrease but the spatial distributions are different.

6. Calculation of improvement in the fit of modelled to observed ozone

The equation used to calculate the improvement in the fit of modelled to observed ground-level ozone shown in Figure 2 is:

$$\%improvement = \frac{([O_3]_{WRF-Chem} - [O_3]_{obs})_{circadian} - ([O_3]_{WRF-Chem} - [O_3]_{obs})_{base}}{([O_3]_{WRF-Chem} - [O_3]_{obs})_{base}} \times 100 \quad (10)$$

7. Global scale chemistry-transport modelling

Global impacts on surface ozone were evaluated using the FRSGC/UCI chemical transport model (CTM). This offline CTM is run at T42 resolution (approximately 2.8° × 2.8° degrees horizontal resolution) with 37 levels in the vertical extending from the surface to 2 hPa (45 km). The model is driven here with meteorological data from the ECMWF IFS model for 2001 at 3-hourly resolution using the configuration described in Wild *et al.*⁵². Anthropogenic emissions are based on scenarios for the year 2000 constructed by the International Institute for Applied Systems Analysis (IIASA) for an earlier model intercomparison⁵³. Monthly-mean biomass burning emissions from the Global Fire Emissions Database⁵⁴ were averaged over the 1997-2003 period. Results from the

model using these emissions have been evaluated against observations of surface ozone in previous studies^{55,56}.

Hourly global isoprene emissions generated off-line with MEGAN for 5 days in July under each of the circadian control scenarios described in Section 3 above were averaged to generate a single diurnal cycle of emissions to minimise the effect of day-to-day differences in meteorology. The resulting hourly emissions for each scenario were then applied in the CTM. The model was initialised at the start of July and run for one month for each scenario. Hourly surface ozone data from these runs were then compared with data from a control assuming no circadian control of emissions. Results for the first 5 days of each run were discarded as spin-up.

There is a strong geographical pattern to the surface ozone changes that reflects the key isoprene emission regions and highlights the relatively short lifetime of isoprene and its immediate oxidation products. However, small ozone changes are shown over a wide region reflecting the transport of ozone, which may have a lifetime of several weeks in the lower troposphere under cleaner conditions. These results provide a good indication of the effects on surface ozone in summer, but do not represent the full steady-state response of ozone, which would require that the long-term effects of changes in methane and oxidised nitrogen carriers such as peroxyacetyl nitrate (PAN) are fully accounted for. The results presented are diurnal-mean changes; while high surface ozone levels in summer generally occur in the early afternoon period local time, we find that changes at this time of day are only marginally (about 10%) larger than diurnal-mean changes over the eastern USA.

Significant uncertainties remain in our understanding of isoprene chemistry and its representation in models. Global and regional model studies typically overestimate surface ozone over the south-eastern USA⁵⁵ where both natural isoprene emissions and anthropogenic industrial emissions of ozone precursors are high. Uncertainties in the fate of isoprene nitrates may contribute to this overestimation^{56,57}, but poor representation of the separation of natural and anthropogenic emissions and of boundary layer mixing processes at the coarse resolution of current models are also likely to contribute. More detailed analysis of the factors controlling surface ozone in this region with nested or high-resolution models containing a more detailed treatment of isoprene oxidation processes will be necessary to resolve these issues fully.

Supplementary references

1. C.N. Hewitt *et al.* Overview: oxidation and particle photochemical processes above a south-east Asian tropical rainforest (the OP3 project): introduction, rationale, location characteristics and tools. *Atmos. Chem. Phys.* **10**, 169-199 (2010).
2. D. Fowler *et al.* Effects of land use on trace gas emissions and deposition in Borneo: comparing atmosphere-surface exchange over oil palm plantations with a rainforest. *Philosophical Transactions of the Royal Society of London* (in press) (2011).

3. A. R. MacKenzie *et al.* The atmospheric chemistry of trace gases and particulate matter emitted by different land uses in Borneo. *Philosophical Transactions of the Royal Society of London* (in press) (2011).
4. J. A. Pyle *et al.* The impact of local surface processes in Borneo on atmospheric composition at wider spatial scales: coastal processes, land use change and air quality. *Philosophical Transactions of the Royal Society of London* (in press) (2011).
5. H. Tangki, N. A. Chappell. Biomass variation across selectively logged forest within a 225 km² region of Borneo and its prediction by Landsat TM. *Forest Ecol. Man* **256**, 1960-1970 (2008).
6. P. Moura-Costa *et al.* Large scale enrichment planting with dipterocarps as an alternative for carbon offset – methods and preliminary results. In *Proceedings of the Fifth Round Table Conference on Dipterocarps*. J. Trop. For. Sci (Eds S. Appanah, K. C. Khoo, Thailand) (1996).
7. H. Tangki. Biomass variation across selectively logged forest in Borneo and its prediction by Landsat TM data. (*MPhil Thesis*. Lancaster University, UK) (2008).
8. B. Langford *et al.* Fluxes and concentrations of volatile organic compounds above central London, UK. *Atmos. Chem. Phys* **10**, 627-645 (2010).
9. B. Langford *et al.* Fluxes and concentrations of volatile organic compounds from a south-east Asian tropical rainforest. *Atmos Chem Phys*, **10**, 8391 - 8412 (2010).
10. P. K. Misztal *et al.* Direct ecosystem fluxes of volatile organic compounds from oil palms in South-East Asia. *Atmos. Chem. Phys Disc* **11**, 12671-12724 (2011).
11. T. Foken *et al.* Post-field data quality control in Handbook of Micrometeorology: A guide for surface flux measurement and analysis. W. M. X. Lee, B. Law. Dordrecht, Kluwer Academic Publishers. **29**, 181-203 (2004).
12. A. Guenther *et al.* Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys* **6**, 3181-3210 (2006).
13. M. J. Wilkinson *et al.* Circadian control of isoprene emission from oil palm (*Elaeis guineensis*). *Plant Journal* **47**, 960 (2006).
14. E. Nemitz *et al.* Intercomparison and assessment of turbulent and physiological exchange parameters of grassland. *Biogeosciences* **6**, 1445-1466 (2009).
15. M. J. Evans *et al.* Evaluation of a Lagrangian box model using field measurements from EASE (Eastern Atlantic Summer Experiment) 1996. *Atmos. Environ* **34**, 3843-3863 (2000).
16. K. M. Emmerson *et al.* A Lagrangian model with simple primary and secondary aerosol scheme 1: comparison with UK PM10 data. *Atmos. Chem. Phys* **4**, 2161-2170 (2004).
17. R.G. Donovan *et al.* Development and application of an urban tree air quality score for photochemical pollution episodes using the Birmingham, United Kingdom, area as a case study. *Environ. Sci. Technol* **39**, 6730-6738 (2005).
18. T. A. M. Pugh *et al.* Simulating atmospheric composition over a south-east Asian tropical rainforest: performance of a chemistry box model. *Atmos. Chem. Phys* **10**, 279-298 (2010).

19. T.A.M. Pugh *et al.* Modelling chemistry in the nocturnal boundary layer above tropical rainforest and a generalised effective nocturnal ozone deposition velocity for sub-ppbv NO_x conditions, *J. Atmos. Chem* **65**, 89–110 (2011).
20. D. Taraborrelli *et al.* Mainz Isoprene Mechanism 2 (MIM2): an isoprene oxidation mechanism for regional and global atmospheric modelling. *Atmos. Chem. Phys.* **9**, 2751–2777 (2009).
21. G. Pearson *et al.* Remote sensing of the tropical rain forest boundary layer using pulsed Doppler lidar, *Atmos. Chem. Phys.* **10**, 5891–5901 (2010).
22. D. Tan *et al.* HO_x budgets in a deciduous forest: Results from the PROPHET summer 1998 campaign. *J. Geophys. Res. Atmos* **106**, 24407–24427 (2001).
23. J. A. Thornton *et al.* Ozone production rates as a function of NO_x abundances and HO_x production rates in the Nashville urban plume. *J. Geophys. Res* **107**, D12, doi:10.1029/2001JD000932 (2002).
24. J. Lelieveld *et al.* Atmospheric oxidation capacity sustained by a tropical forest. *Nature* **452**, 737–740, (2008).
25. T. Butler *et al.* Improved simulation of isoprene oxidation chemistry with the ECHAM5/MESSy chemistry-climate model: lessons from the GABRIEL airborne field campaign. *Atmos. Chem. Phys* **8**, 4529–4546 (2008).
26. A. Hofzumahaus *et al.* Amplified trace gas removal in the troposphere. *Science*, **324**, 1702–1704, doi:10.1126/science.1164566 (2009).
27. T. A. M. Pugh *et al.* The influence of small-scale variations in isoprene concentrations on atmospheric chemistry over a tropical rainforest. *Atmos. Chem. Phys.* **11**, 4121–4134 (2011).
28. T. Stavrou, *et al.* Improved global modelling of HO_x recycling in isoprene oxidation: evaluation against the GABRIEL and INTEx-A aircraft campaign measurements. *Atmos. Chem. Phys.* **10**, 9863–9878 (2010).
29. L. K. Whalley *et al.* Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest. *Atmos. Chem. Phys. Discuss.* **11**, 5785–5809 (2011).
30. R. C. Pike *et al.* NO_x and O₃ above a tropical rainforest: an analysis with a global and box model. *Atmos. Chem. Phys.* **10**, 10607–10620 (2010).
31. D. Kubistin *et al.* Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA. *Atmos. Chem. Phys.* **10**, 9705–9728 (2011).
32. J. Peeters, Nguyen, T. L., and Vereecken, L. HO_x radical regeneration in the oxidation of isoprene. *Phys. Chem. Chem. Phys.* **11**, 5935–5939, doi:10.1039/b908511d (2009).
33. F. Paulot *et al.* Unexpected epoxide formation in the gas-phase photooxidation of isoprene. *Science*, **325**, 730–733 (2009).
34. T.L. Nguyen, Vereecken, L., and Peeters, J. HO_x Regeneration in the oxidation of isoprene III: Theoretical study of the key isomerisation of the Z-delta-hydroxy-peroxy isoprene radicals. *Chem. Phys. Chem.* **11**, 3996–4001 (2010).
35. G. Da Silva, Graham, C., and Wang, Z.-F. Unimolecular beta-hydroxyperoxy radical decomposition with OH recycling in the photochemical oxidation of isoprene. *Environ. Sci. Technol.* **44**, 250–256 (2010).
36. J. G. Olivier *et al.* Recent trends in global greenhouse gas emissions: regional trends and spatial distribution of key sources. In: *Non-CO₂ Greenhouse Gases*

- (*NCGG-4*), A. van Amstel (coord.) (Millpress, Rotterdam, ISBN 90 5966 043 9, 325-330 (2005).
37. C.N. Hewitt *et al.* Nitrogen management is essential to prevent tropical oil palm plantations from causing ground-level ozone pollution. *PNAS* **106**, 18447 – 18451 (2009).
 38. W.C. Skamarock, Klemp, J. B. Dudhia, J., Gill, D. O., Barker, D. M., Duda, M. Huang, X.-Y., Wang, W., and Powers, J. G.: A Description of the Advanced Research WRF Version 3, NCAR Technical Note (2008).
 39. Grell, G. A., *et al.* Fully coupled online chemistry within the WRF model. *Atmos. Environ* **39**, 6957-6975 (2005).
 40. Wesely, M. L.: Parameterization of surface resistance to gaseous dry deposition in regional-scale numerical models. *Atmos. Environ* **23**, 1293–1304 (1989).
 41. Mlawer, E. J., *et al.* Radiative transfer for inhomogeneous atmosphere: RRTM, a validated correlated-k model for longwave. *J. Geophys. Res* **102**, 16663–16682 (1997).
 42. Chou, M.-D. and Suarez, M. J. An efficient thermal infrared radiation parameterization for use in general circulation models. NASA Tech. Memo. 104606, 85 pp. (1994).
 43. Madronich, S. Photodissociation in the atmosphere, 1, actinic flux and the effects of ground reflections and clouds. *J. Geophys. Res* **92**, 9740–9752 (1987).
 44. Mellor, G. L. and Yamada, T. Development of a turbulence closure model for geophysical fluid problems. *Rev. Geophys. Space Phys* **20**, 851–875 (1982).
 45. Janjic, Z. I. Nonsingular Implementation of the Mellor-Yamada Level 2.5 Scheme in the NCEP Meso Model, NCEP Office Note, No. 437, 61 pp. (2002).
 46. Smirnova, T. G., *et al.* Parameterization of cold-season processes in the MAPS land- surface scheme. *J. Geophys. Res* **105**, 4077–4086 (2000).
 47. Emmons, L. K., *et al.* Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4). *Geosci. Model Dev* **3**, 43–67 (2010).
 48. Chin, M., *et al.* Tropospheric aerosol optical thickness from the GOCART model and comparisons with satellite and sun photometer measurements. *J. Atmos. Sci* **59**, 461-483 (2002).
 49. Pfister, G. G., *et al.* Characterizing summertime chemical boundary conditions for airmasses entering the US West Coast. *Atmos. Chem. Phys* **11**, 1769-1790 (2011).
 50. C. Wiedinmyer *et al.* The Fire INventory from NCAR (FINN) – a high resolution global model to estimate the emissions from open burning. *Geosci. Model Dev. Discuss* **3**, 2439-2476 (2010).
 51. S. R. Freitas *et al.* Including the sub-grid scale plume rise of vegetation fires in low resolution atmospheric transport models. *Atmos. Chem. Phys* **7**, 3385–3398 (2007).
 52. O. Wild *et al.* Chemical transport model ozone simulations for spring 2001 over the western Pacific: Comparisons with TRACE-P lidar, ozonesondes, and Total Ozone Mapping Spectrometer columns. *J. Geophys. Res* **108**, doi:10.1029/2002JD003283 (2003).
 53. D.S. Stevenson *et al.* Multimodel ensemble simulations of present-day and near-future tropospheric ozone. *J. Geophys. Res* **111**, D08301, doi: 10.1029/2005JD006338 (2006).

54. G. R. van der Werf *et al.* Carbon emissions from fires in tropical and subtropical ecosystems. *Global Change Biol* **9**, 547-562 (2003).
55. A.M. Fiore *et al.* Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States. *J. Geophys. Res* **110**, D12303, doi:10.1029/2004JD005485 (2005).
56. A.M. Fiore *et al.* Multimodel estimates of intercontinental source-receptor relationships for ozone pollution. *J. Geophys. Res.* **114**, D04301, doi:10.1029/2008JD010816 (2009).
57. O. Wild *et al.* Photochemical trajectory modelling studies of the North Atlantic region during August 1993. *J. Geophys. Res.* **101**, 29269-29288 (1996).

Figure S1. Analysis of landscape scale isoprene emission rates. Panel A shows the diurnal variation in base emission rates (BERs) of isoprene from oil palm (*Elaeis guineensis* × *Elaeis oleifera*), observed at both leaf and canopy scales. Green circles show the results of a laboratory study by Wilkinson *et al.* (10) where isoprene emissions were measured using a leaf cuvette at standard conditions (PAR and leaf temperature held constant at $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ and 30°C respectively). Blue circles show BERs calculated from direct eddy covariance flux measurements above the Sabahmas oil palm plantation. Algorithms describing the dependence of isoprene emission rates on ambient light and air temperature (9) have been used to normalise flux rates measured at varying ambient values of PAR and air temperature to the standard conditions of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ and 30°C . The shaded area shows ± 1 standard deviation of averaged BERs. The red line shows an idealised square wave function in which BER is independent of time of day (daytime only). Panel D shows similar, but less pronounced diurnal variations in base emission rates of isoprene derived from measurements made above a rainforest canopy. Panel B shows the averaged measured (black line) and modelled isoprene fluxes (between 29/05/2008 and 11/06/2008) at the Sabahmas oil palm plantation and Panel E shows the measured (black line) and modelled isoprene fluxes (between 02/07/2008 and 21/07/2008) at the Bukit Atur Global Atmosphere Watch rainforest site, Sabah, Malaysia. The red lines show the G06 modelled fluxes using the idealised square-wave function for BER (panels A and D) in which BER remains constant during

the daytime. The blue lines show the G06 modelled fluxes obtained using the measured diurnal profiles of BER (panels A and D) as a variable and the green line in Panel B shows the same modelled output using the laboratory-derived diurnally-varying BER profile. The red lines in Panels C and F show the percentage differences between modelled and measured isoprene fluxes as a function of time of day, without consideration of circadian control of base emission rates (note the change of scales in panels C and F). The blue lines show the percentage differences between modelled and measured isoprene fluxes as a function of time of day using the varying (circadian-controlled) BER.

Figure S2. The average boundary layer convective mixing velocity (t_*) and isoprene lifetimes for the period 02 - 21 July 2008 above a tropical rainforest. The Damköhler number (black line) indicates the amount of isoprene that would be lost to chemical reaction before detection by our measurement system, which was located at ~ 100 m above the forest canopy top. Because the Bukit Atur GAW tower is located on a hill it is not possible to be more precise about this height.

Figure S3. Theoretical study showing the changes in isoprene BER that could be expected if the effects of isoprene chemistry (i.e. flux divergence) are considered for the rainforest scenario.

Figure S4. Analysis of landscape scale isoprene emission rates. Duplication of Figure S1, using leaf level temperature calculated from resistance analogy¹⁴ instead of the ambient air temperature.

Figure S5. Difference in surface isoprene concentrations estimated by WRF-Chem between emissions calculated by MEGAN on-line with and without the “oil palm” circadian function in isoprene base emission rate. The plots show the average difference of the hourly values (12 – 22 UTC) for the period 5 – 9 July 2008.

Figure S6 Difference in surface ozone concentrations estimated by WRF-Chem using isoprene emissions calculated with and without the “oil palm” circadian function in base emission rate, as shown in Figure S5. The plots show the average difference of the hourly values (12 – 22 UTC) for the period 5 – 9 July 2008.