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Ground-level ozone influenced by circadian control of isoprene emissions

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The volatile organic compound isoprene is produced by many plant species, and provides protection against biotic and abiotic stresses[1]. Globally, isoprene emissions from plants are estimated to far exceed anthropogenic emissions of volatile organic compounds[2]. Once in the atmosphere, isoprene reacts rapidly with hydroxyl radicals[3] to form peroxy radicals, which can react with nitrogen oxides to form ground-level ozone[4]. Here, we use canopy-scale measurements of isoprene fluxes from two tropical ecosystems in Malaysia—a rainforest and an oil palm plantation—and three models of atmospheric chemistry to explore the effects of isoprene fluxes on ground-level ozone. We show that isoprene emissions in these ecosystems are under circadian control on the canopy scale, particularly in the oil palm plantation. As a result, these ecosystems emit less isoprene than present emissions models predict. Using local-, regional- and global-scale models of atmospheric chemistry and transport, we show that accounting for circadian control of isoprene emissions brings model predictions of ground-level ozone into better agreement with measurements, especially in isoprene-sensitive regions of the world.

Circadian rhythms are common in nature, controlling such processes as body temperature and sleep patterns in animals and leaf movement and stomatal aperture in plants. Circadian clocks have been shown to confer a competitive advantage in plants: those with a circadian clock period matched to the external light–dark cycle contain more chlorophyll, fix more carbon, grow faster, have stronger defences and survive better than plants with circadian periods differing from their environment[5,6]. Despite the importance of circadian rhythms to plant physiology, circadian control has not previously been observed at the forest-canopy or landscape scales and so has not yet been built into our understanding of land–atmosphere interactions. On the basis of our own laboratory studies[7], in which we observed, at the leaf level, that emissions of isoprene from oil palm (*Elaeis guineensis*) are under circadian control, we reasoned that nature (and, inadvertently, agronomy) selects strongly for circadian resonance in plants, and that circadian rhythms should be visible on the landscape scale.

We made canopy-scale eddy-covariance measurements of isoprene fluxes from two tropical landscapes in Sabah, Malaysia, 70 km apart[8,9]. To establish the effects of rapidly expanding palm-oil production, we measured fluxes above a monoculture plantation of oil palm trees of uniform age and height[10]. To study fluxes from a natural lowland dipterocarp tropical rainforest we used the Bukit Atur Global Atmosphere Watch station[11]. The rainforest flux footprint contains more than 20 different fully grown tree species and more than 40 different sapling species per hectare, plus an unknown number of smaller plant species. Measurements were made in April–July 2008. The measurement methods and data analysis techniques used are described elsewhere[8] and in the Supplementary Information.

The rate at which plants emit isoprene under a set of standard conditions (air temperature: 30 °C; photosynthetically active radiation flux, PAR: 1,000 μmol m^{-2} s^{-1}) is termed the base emission rate (BER) and is a fundamental parameter in the algorithms used to model regional- and global-scale isoprene emissions[2,12,13]. Until now it has been assumed that BER is constant throughout the day and that actual emission rates depend on this value being modified by recent-past and instantaneous leaf temperatures, received PAR and some long-term environmental effects, including water availability. However, analysis of our canopy-scale flux data reveals that BER does not remain constant throughout the day (see Supplementary Information for details of this analysis).

Figure 1a shows how isoprene BER varies during the day and deviates significantly from the flat line of non-circadian-controlled BER at both sites. Circadian control of BER is more evident at the oil palm plantation than at the rainforest. We attribute this to the diversity of plant species within the rainforest isoprene flux footprint, each emitting species having a different amplitude, and possibly phase, of circadian control. Therefore, there is a smoothing in the overall canopy-scale response to time of day in the rainforest, compared with the monoculture oil palm plantation, where isoprene emissions from that particular tree species are under strong circadian control[7].

We used the Model of Emissions of Gases and Aerosols from Nature (MEGAN; ref. 2) to estimate global isoprene emissions for a five-day period in July. A reference case was first run using the standard constant BERs of the MEGAN model and driven by hourly air temperature and PAR data from the UK Meteorological Office's Unified Model of global climate for present climate conditions. Two further simulations were then carried out, using the same meteorology, but modifying isoprene emissions to reflect the circadian control observed over the rainforest and over the oil palm plantation in Malaysia (see Supplementary Information for details of these modifications).

Figure 1b shows the percentage differences in isoprene emission rates between the reference and circadian-controlled runs. The use of a constant BER causes significant over-estimation relative to the

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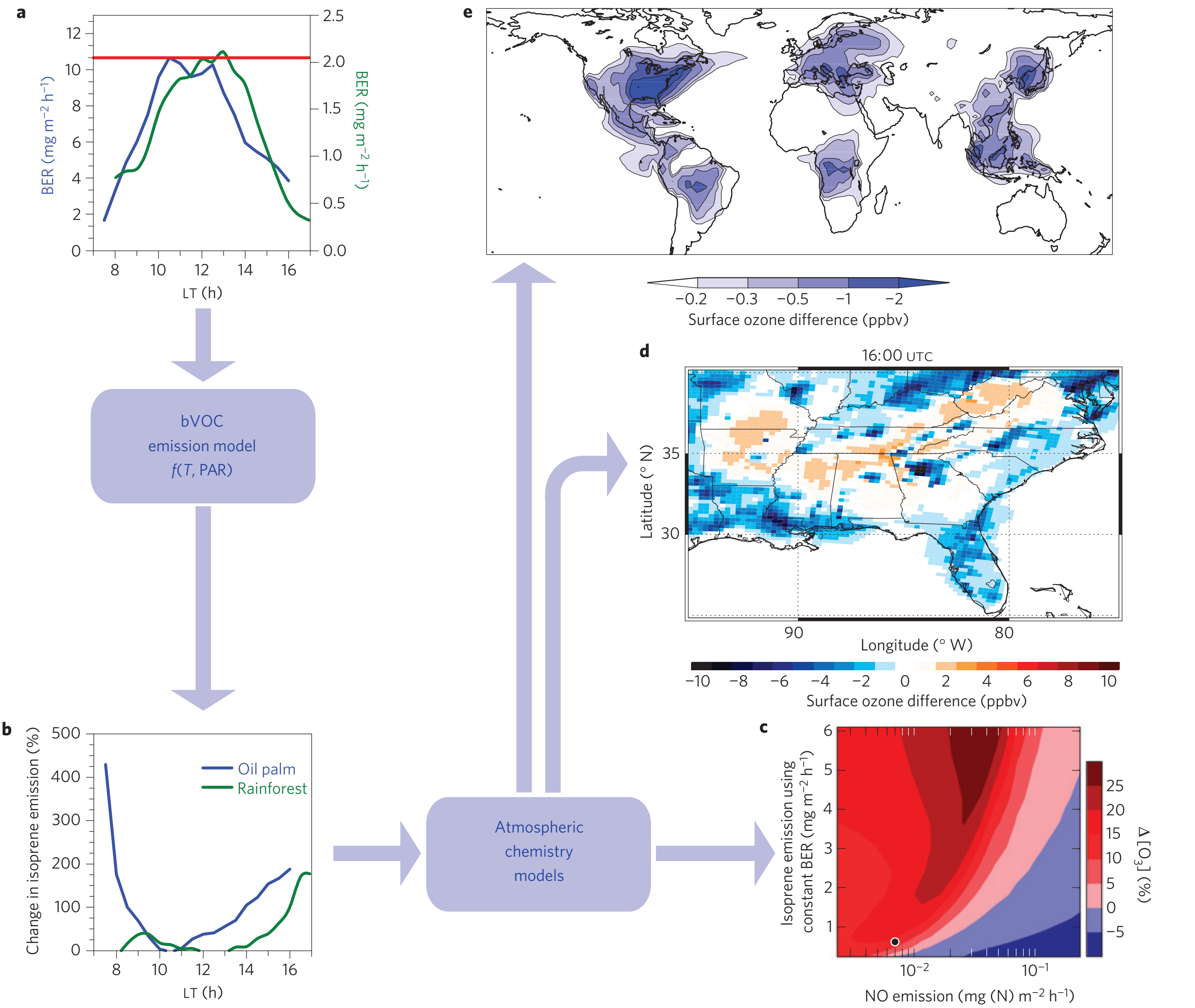

Figure 1 | The circadian control of isoprene emissions on the landscape scale mediates ground-level ozone concentrations on all scales. a, The oil palm plantation (blue) and rainforest (green) BERs of isoprene compared with a constant BER (red). **b**, The differences in isoprene emission rates between constant (red line in **a**) and circadian-controlled BERs (oil palm: blue; rainforest: green) as estimated by MEGAN (ref. 2). **c**, Changes in ground-level ozone resulting from changing isoprene and nitrogen oxide emission rates using CiTTyCAT (ref. 16). The dot represents the present position of the rainforest. **d**, Changes in regional-scale WRF-Chem (ref. 20)-modelled ground-level ozone for 11:00 LT using an 'oil palm' circadian-controlled BER compared with a constant BER. **e**, Changes in global-scale FRSGC/UCI (ref. 21)-modelled ground-level ozone for July using the same scenario as **d**.

observed flux during both the morning and afternoon, strongly so in the case of oil palm (blue line) and less so in the case of the rainforest (green line). On a global basis, daily emissions of isoprene (averaged over the five days of the simulations) are decreased by 21% if all tree species exhibit the same degree of circadian control as the oil palm and by 5% if all trees exhibit the more muted degree of circadian control of the rainforest.

We now model the effects of the circadian control of isoprene emissions on atmospheric chemistry and ground-level ozone concentrations on scales from the local to the global, using chemical schemes that reflect present practice. Isoprene photochemistry is still uncertain[14,15] but the impact of these uncertainties on modelled ground-level ozone is small (~25%; refs 16,17). We ran the CiTTyCAT box model of atmospheric chemistry[16] to investigate the impacts of these decreases in isoprene emission rates, resulting from circadian control, on the formation of ground-level ozone. The model was run with both constant and time-dependent BERs for two different land-use scenarios—remote rainforest and oil palm plantation—and using NO_x emission rates ranging from those appropriate for remote rainforest to those appropriate for rural areas in Europe or North America[9]. The range of NO_x emissions also tests the model in scenarios where ozone production is NO_x- and volatile organic compound (VOC)-limited. Figure 1c shows, for strongly NO_x-limited conditions, use of the variable (circadian-controlled) BER resulted in increases in middle-of-the-day (10:00–16:00 local time, LT) ground-level ozone concentrations of up to 10% for the rainforest and 25% for the oil palm emissions scenarios, respectively. In contrast, when NO_x mixing ratios exceed 0.3 ppbv for the rainforest scenario and 1.3 ppbv for the oil palm scenario, decreases in the middle-of-the-day mean ozone concentration of up to 20% are estimated. Hence, the decreased biogenic isoprene emissions—due to the use of circadian-controlled variable BERs—lead to simulations with increased ground-level ozone concentrations in remote regions of the world and decreased ground-level ozone concentrations in more polluted regions.

The most significant changes in simulated ground-level ozone occur where the circadian-controlled decrease in isoprene emissions moves the chemistry away from the [VOC]/[NO_x] ratio optimal for photochemical ozone production. In the classic 'Sillman plot'[18], the region of greatest impact of decreased isoprene emissions is just on the NO_x-saturated, or VOC-limited, side of the ozone ridge ([VOC]/[NO_x] $\leq \sim 6$), for those situations where biogenic isoprene makes up a large part of the VOC: that is, during sunny periods in polluted rural environments such as the southeastern USA[19].

We then use the regional-scale air-quality model WRF-Chem (ref. 20) to confirm our interpretation of the box-model runs for the southeastern USA. Some polluted areas of the region show hourly average decreases in ozone of more than 10 ppbv when the same degree of circadian control of isoprene emissions as seen in the oil palm plantation data is included in WRF-Chem. In other, less-polluted, areas of the southeastern USA, the model predicts increases of more than 3 ppbv in ground-level ozone concentrations (see Fig. 1d and Supplementary Information).

We now extend our study on the impacts of using a variable rather than constant BER for isoprene emissions from the box and landscape (regional) scales to the global scale using the FRSGC/UCI chemistry–transport model[21]. In the scenario based on the observed circadian behaviour of oil palm there is a decrease in daily mean continental (background) ground-level ozone concentrations between 20° S and 45° N in July of about 0.8 ppbv (3%). In the scenario based on the more moderate circadian control of the rainforest, the decrease in (background) continental ozone averages 0.3 ppbv (1%). These global responses are smaller than those found in the box-model and regional-scale modelling studies, and ozone concentrations only decrease, because, at the resolution of the global model, regions of high and low NO_x emissions are averaged, such that decreasing isoprene emissions always produces a decrease in ozone. Figure 1e shows the distribution of these ground-level ozone concentration changes using the same degree of circadian control as observed for the oil palm plantation compared with a control run in which isoprene emissions are assumed not to be under any degree of circadian control. The largest decreases in ground-level ozone concentrations in the global model are seen over the southeastern USA, where they average 2 ppbv (or ~4%). The model also shows that other regions where circadian control of isoprene emissions matters for ground-level ozone are the Mediterranean, southeastern Asia and Japan.

Both regional- and global-scale chemical transport models typically over-estimate summertime ground-level ozone over the southeastern USA[19,22]. We compared our WRF-Chem simulations of hourly average ground-level ozone with and without circadian control of isoprene emissions with observed hourly average ground-level ozone concentrations at 290 US Environmental Protection Agency (EPA) monitoring sites in the southeastern USA[23] (Fig. 2). Accounting for circadian control brings the simulations into better agreement with the observations for local times between 07:00 and 12:00 (three-quarters of sites show an improvement in model–observation fit, with a median improvement of 9% across all sites). The spread of values in Fig. 2 indicates that other processes are also important in the model–observation discrepancy for ground-level ozone in the southeastern USA.

Our findings show that the emissions of isoprene from tropical tree canopies are under circadian control, both in a monoculture oil palm plantation and in a natural rainforest. This confirms that the circadian control on isoprene emission observed in the laboratory[7] is also observable on the landscape scale. This has significant implications for the modelling of isoprene emissions on both landscape (regional) and global scales.

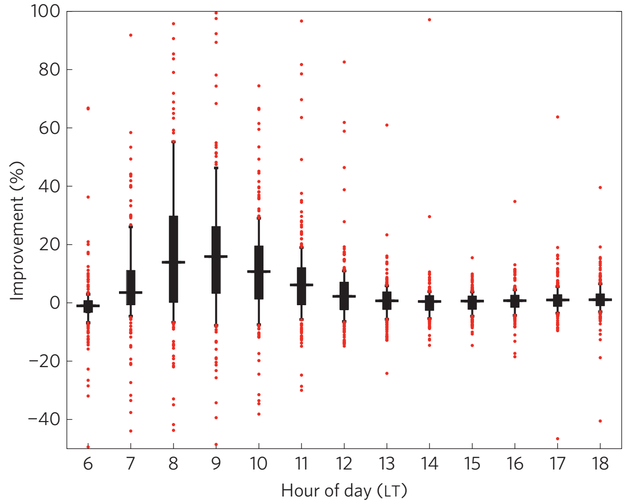

Figure 2 | Effect of including circadian control of isoprene emissions on model–observation fit for ozone in the southeastern USA. Percentage of the discrepancy between the original WRF-Chem model and observed ground-level ozone concentrations in the southeastern USA that can be resolved through inclusion of circadian control of isoprene emissions. The hourly data shown are from all 290 US EPA monitoring stations within the domain shown in Fig. 1d. A value of +100% would indicate complete agreement between the revised model and observations. The box and whisker plots show the median, quartiles and 5th and 95th percentiles. Details of this are given in the Supplementary Information.

The application of typical emissions routines without accounting for circadian control causes models to over-estimate total daily isoprene emission rates and to give an inaccurate daily cycle of emissions. Accounting for the observed circadian control on isoprene emission rates can increase or decrease predicted ground-level ozone concentrations, depending on the prevailing landscape-scale [VOC]/[NO_x] ratios. Our three models all show decreases in ground-level ozone concentrations in warm, sunny summertime conditions in polluted rural environments, such as the southeastern USA, where isoprene makes a significant contribution to ground-level ozone[19,22,24–26], bringing modelled ozone concentrations into closer agreement with observations.

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References

1. Laothawornkitkul, J. *et al.* Biogenic volatile organic compounds in the Earth system: A Tansley Review. *New Phytol.* **183,** 27–51 (2009).
2. Guenther, A. *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).
3. Pugh, T. A. M. *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).
4. Fehsenfeld, F. C. *et al.* Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry. *Glob. Biogeochem. Cycles* **6,** 389–430 (1992).
5. McClung, C. R. Circadian rhythms in plants. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **52,** 139–162 (2001).
6. Wang, W. *et al.* Timing of plant immune responses by a central circadian regulator. *Nature* **470,** 110–114 (2011).
7. Wilkinson, M. J. *et al.* Circadian control of isoprene emission from oil palm (*Elaeis guineensis*). *Plant J.* **47,** 960–968 (2006).
8. Hewitt, C. N. *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).
9. Hewitt, C. N. *et al.* Nitrogen management is essential to prevent tropical oil palm plantations from causing ground-level ozone pollution. *Proc. Natl Acad. Sci. USA* **106,** 18447–18451 (2009).

10. Misztal, P. K. *et al*. Direct ecosystem fluxes of volatile organic compounds from oil palms in South-East Asia. *Atmos. Chem. Phys.* **11,** 8995–9017 (2011).
11. Langford, B. *et al*. Fluxes and concentrations of volatile organic compounds from a south-east Asian tropical rainforest. *Atmos. Chem. Phys.* **10,** 8391–8412 (2010).
12. Guenther, A. *et al*. A global model of natural volatile organic compound emissions. *J. Geophys. Res. Atmos.* **100,** 8873–8892 (1995).
13. US EPA Biogenic Emissions Inventory System model, available at ftp://ftp.epa.gov/amd/asmd/beis3v12.
14. Lelieveld, J. *et al*. Atmospheric oxidation capacity sustained by a forest. *Nature* **452,** 737–740 (2008).
15. Ito, A. *et al*. Global chemical transport model study of ozone responses to changes in chemical kinetics and biogenic volatile organic compounds emissions due to increasing temperatures: Sensitivities to isoprene nitrate chemistry and grid resolution. *J. Geophys. Res.* **114,** D09301 (2009).
16. Pugh, T. A. M. *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).
17. Archibald, A. T. *et al*. An isoprene mechanism intercomparison. *Atmos. Environ.* **44,** 5356–5364 (2010).
18. Sillman, S. The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. *Atmos. Environ.* **33,** 1821–1845 (1999).
19. Reidmiller, D. R. *et al*. The influence of foreign vs. North American emissions on surface ozone in the US. *Atmos. Chem. Phys.* **9,** 5027–5042 (2009).
20. Grell, G. A. *et al*. Fully coupled online chemistry within the WRF model. *Atmos. Environ.* **39,** 6957–6975 (2005).
21. Wild, O. *et al*. Chemical transport model ozone simulations for spring 2001 over the western Pacific: Comparisons with TRACE-P Lidar, ozone sondes, and Total Ozone Mapping Spectrometer columns. *J. Geophys. Res.* **108,** 8826–8838 (2003).
22. Ryerson, T. B. *et al*. Observations of ozone formation in power plant plumes and implications for ozone control strategies. *Science* **292,** 719–723 (2001).
23. US Environmental Protection Agency. Air Quality System Data Mart, available at http://www.epa.gov/ttn/airs/aqsdatamart. Accessed July 9 (2010).
24. Fiore, A. M. *et al*. Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States. *J. Geophys. Res.* **110,** D12303 (2005).
25. Chameides, W. L. *et al*. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science* **241,** 1473–1475 (1988).
26. Cardelino, C. A. & Chameides, W. L. The application of data from photochemical assessment monitoring stations to the observation-based model. *Atmos. Environ.* **34,** 2325–2332 (2000).

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Author contributions

C.N.H. led the project; C.N.H. and A.R.M. devised the research, obtained financial support and wrote the paper; K.A., A.B., A.G., B.L., P.K.M., E.N., T.A.M.P., A.C.R. and O.W. carried out research; all authors discussed results, analysed data and commented on the paper.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to C.N.H.