Vol 452|10 April 2008|doi:10.1038/nature06870 nature

LETTERS

Atmospheric oxidation capacity sustained by a tropical forest

J. Lelieveld[1], T. M. Butler[1], J. N. Crowley[1], T. J. Dillon[1], H. Fischer[1], L. Ganzeveld[1], H. Harder[1], M. G. Lawrence[1], M. Martinez[1], D. Taraborrelli[1] & J. Williams[1]

Terrestrial vegetation, especially tropical rain forest, releases vast quantities of volatile organic compounds (VOCs) to the atmosphere[1–3], which are removed by oxidation reactions and deposition of reaction products[4–6]. The oxidation is mainly initiated by hydroxyl radicals (OH), primarily formed through the photodissociation of ozone[4]. Previously it was thought that, in unpolluted air, biogenic VOCs deplete OH and reduce the atmospheric oxidation capacity[5–10]. Conversely, in polluted air VOC oxidation leads to noxious oxidant build-up by the catalytic action of nitrogen oxides[5–10] ($NO_x = NO + NO_2$). Here we report aircraft measurements of atmospheric trace gases performed over the pristine Amazon forest. Our data reveal unexpectedly high OH concentrations. We propose that natural VOC oxidation, notably of isoprene, recycles OH efficiently in low-NO_x air through reactions of organic peroxy radicals. Computations with an atmospheric chemistry model and the results of laboratory experiments suggest that an OH recycling efficiency of 40–80 per cent in isoprene oxidation may be able to explain the high OH levels we observed in the field. Although further laboratory studies are necessary to explore the chemical mechanism responsible for OH recycling in more detail, our results demonstrate that the biosphere maintains a remarkable balance with the atmospheric environment.

Since forests appeared and proliferated during the Devonian period (approximately 400 million years ago), terrestrial vegetation has been a major contributor to biomass production. At present, terrestrial ecosystems supply more than half the primary production of carbon, dominated by tropical forests and savannahs[11]. The carbon throughput directly affects the atmosphere through the exchange of carbon dioxide, and forests are a major source of volatile organic compounds (VOCs). The main class of compounds comprises the C_5 hydrocarbon isoprene (2-methyl-1,3-butadiene) and polymeric derivates such as C_{10} monoterpenes and C_{15} sesquiterpenes. Annually, plants and trees emit more than a gigatonne of VOC (equivalent to 10^{15} g of carbon), of which isoprene contributes about 40%, several times more than anthropogenic sources[1–3].

The natural VOC emissions serve important biological functions, for example by attracting pollinators and repelling herbivores. The biosphere uses the ambient air as a communication and transport medium, and oxidation of these compounds brings about the concentration gradients sensed by insects. The functionality of isoprene is not fully resolved, although it is known that the molecule sustains the thermal stability of plant cells, counters drought stress and promotes flowering, and that its emission into the atmosphere is strongly dependent on light and temperature[12–15]. After release into the air, isoprene is oxidized within hours by the reaction with OH, the 'detergent' of the atmosphere.

The primary formation of OH results from the photodissociation of ozone by solar ultraviolet radiation in the presence of water vapour[4]. Formation rates are highest in the tropics, where irradiation is intense and the air often humid[6]. After the initial reaction of isoprene with OH, peroxy radicals are formed that either recycle OH by reactions with nitrogen oxide (NO) (pathway I) or recombine into peroxides (pathway II). This is illustrated in Fig. 1, where the peroxides are represented by hydrogen peroxide. The peroxides from pathway II are removed by deposition processes, so that radicals are lost, whereas the recycling through pathway I comes with ozone formation.

However, both pathways have disadvantages for the forest. In the absence of NO in pathway II, the OH radicals and thus the atmospheric oxidation capacity can be depleted. Alternatively, if NO is present in abundance, pathway I generates photochemical smog in which ozone and other toxic oxidants become abundant. Because tropospheric ozone is a powerful greenhouse gas, excess ozone also contributes to climate change. Obviously, the optimum condition for the vegetation is a balance between pathways I and II, but on the basis of the traditional understanding of atmospheric chemistry it is

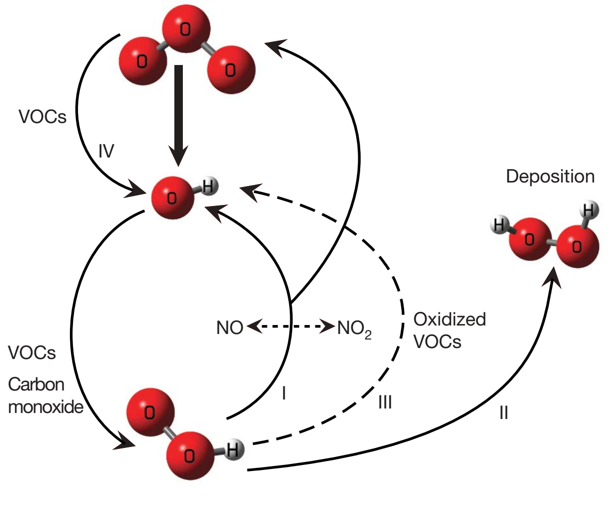

Figure 1 | OH recycling. Photodissociation of ozone leads to primary OH formation (straight arrow). Subsequent OH reactions with carbon monoxide and VOCs produce peroxy radicals. In high-NO conditions OH is recycled and ozone smog builds up through the catalytic conversion between NO and NO_2 (pathway I). In low-NO conditions the deposition of peroxides (pathway II) causes a net loss of OH. We propose that pathway III with oxidized VOCs—in particular organic peroxy radicals—is important in low-NO conditions (dashed arrow). Pathway IV with unsaturated VOCs also occurs, although our results suggest that it has little influence on atmospheric OH.

---

[1] Max Planck Institute for Chemistry, 27 Becherweg, 55128 Mainz, Germany.

©2008 Nature Publishing Group

Table 1 | Measured changes in atmospheric chemistry

	Tropical Atlantic		Tropical forest	
	Boundary layer	Free troposphere	Boundary layer	Free troposphere
Isoprene (p.p.b.v.)	0.20 (0.20)	—	2.00 (0.76)	0.07 (0.12)
α-pinene and β-pinene (p.p.b.v.)	—	—	0.42 (0.11)	0.21 (0.08)
CO (p.p.b.v.)	89.2 (10.7)	100.7 (12.8)	113.9 (13.9)	100.8 (21.7)
O_3 (p.p.b.v.)	14.7 (3.3)	33.3 (11.0)	18.5 (4.6)	36.9 (9.9)
NO (p.p.b.v.)	0.01 (0.01)	0.01 (0.01)	0.02 (0.02)	0.02 (0.01)
CH_2O (p.p.b.v.)	0.52 (0.62)	0.34 (0.44)	1.15 (0.86)	0.36 (0.54)
H_2O_2 (p.p.b.v.)	2.43 (0.95)	3.59 (1.09)	2.41 (1.43)	2.76 (1.37)
Organic peroxides (p.p.b.v.)	0.70 (0.27)	0.85 (0.36)	0.96 (0.28)	0.81 (0.25)
CH_3COCH_3 (p.p.b.v.)	0.47 (0.16)	0.54 (0.25)	0.81 (0.24)	0.59 (0.20)
CH_3OH (p.p.b.v.)	1.27 (0.69)	1.82 (0.98)	1.89 (0.78)	1.80 (0.70)
OH (10^6 molecules cm^{-3})	9.0 (4.0)	10.1 (3.1)	5.6 (1.9)	8.2 (3.0)
HO_2 (10^8 molecules cm^{-3})	6.7 (2.3)	5.5 (2.2)	10.5 (2.7)	4.9 (2.0)

The results stated are the mean measurements during daytime, with standard deviations in parentheses. The approximate boundary layer height was 1 km over the ocean and 1.5 km over land. The mixing ratios in the free troposphere are given up to an altitude of 7 km.

difficult to imagine how the atmospheric oxidation capacity could be supported without excess ozone.

Here we propose that the forest makes use of a third, previously overlooked, pathway that combines benefits and circumvents drawbacks (Fig. 1). It appears that in unpolluted low-NO environments isoprene chemistry can directly recycle radicals (pathway III), and the degradation products yield OH more efficiently than was assumed in atmospheric chemistry models. Our hypothesis is based on aircraft measurements of OH radicals and related species in unpolluted air over the Amazon rainforest, laboratory measurements and numerical modelling.

The aircraft measurements were performed in October 2005 between 3–6° N and 50–60° W over the tropical Atlantic Ocean and the pristine forests of Suriname, Guyana and Guyane (French Guiana). Once the coast had been crossed westbound, from the ocean to the forest, the observed boundary layer changes in atmospheric chemistry differed greatly from those expected. The concentration of HO_x ($OH + HO_2$) increased by more than 50%, and that of formaldehyde increased by a factor of two (Table 1). The concentration of hydrogen peroxide remained nearly constant, probably because the higher production rate is compensated by dry deposition, and the concentrations of organic peroxides were enhanced by nearly 40%, probably owing to increasing amounts of peroxides of isoprene. The concentration of methanol increased by about 50%, because of forest emissions, and that of CO by more than 25%, owing to VOC oxidation.

Perhaps most impressively, from about 10 km inland the mean HO_x levels and the diel HO_x cycle were relatively constant, that is, over a distance of at least 1,000 km downwind over the forest, even though local variability can be large. It appears that biosphere–atmosphere interactions quickly reach a steady state, independent of topographical heterogeneity and large biodiversity. Our main finding was that the concentration of OH radicals changed much less than expected. In the tropical marine boundary layer we typically measured 9×10^6 molecules cm^{-3} during daytime, and this decreased by less than 40% over the forest, despite large increases in the concentrations of isoprene and other hydrocarbons. Between the marine and terrestrial free troposphere, the measured differences in concentrations were small.

These measurements are at odds with the results of global atmospheric chemistry models in which the strong biogenic VOC emissions unrealistically deplete OH and isoprene consequently accumulates in the atmospheric boundary layer[5–10]. To circumvent this problem, atmospheric chemistry modellers typically reduce the strength of the isoprene source by a factor of two or more. Such model manipulations hamper the understanding of atmospheric composition changes associated with deforestation and air pollution. Furthermore, it is difficult to imagine how the oxidation capacity was maintained during geological warm epochs when vegetation was copious and VOC emissions probably much stronger than they are today.

To help interpret our results we employed an atmospheric chemistry model with the Mainz isoprene mechanism (MIM)[9,16,17]. Although the primary OH production pathway was accurately reproduced, OH concentrations were strongly underestimated. By testing the MIM against the comprehensive master chemical mechanism[18] we discovered that simplifications commonly applied in atmospheric chemistry models, including the lumping of carbonyls, peroxy radicals and peroxides, caused discrepancies for low-NO environments. By using a new, extended, version of our mechanism,

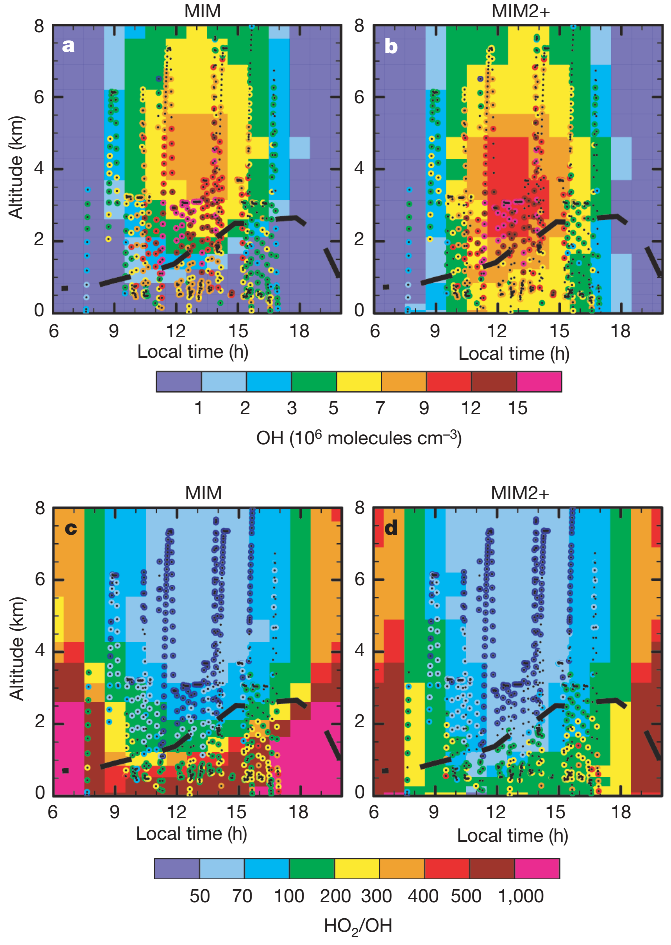

Figure 2 | Model calculations (background) and measurements (circles) of HO_x radicals over Suriname (4° N, 56° W) in October 2005. Daytime OH concentrations (**a**, **b**) and ratios of HO_2 to OH (**c**, **d**). The black dashed lines delineate the upper bound of convective mixing. In **a** and **c** model results are based on the MIM without enhanced OH recycling, and in **b** and **d** on the MIM2+ with 80% OH recycling.

©2008 Nature Publishing Group

the MIM2, we reached close agreement with the master chemical mechanism, but the total OH formation rate remained too low to explain the observations.

An important improvement was achieved by including recycling of OH by reactions of HO_2 with organic peroxy radicals (RO_2) through pathway III, in accordance with indirect laboratory and field measurements[19–21]. The MIM2 scheme does not include this class of reactions, because they are not present in the master chemical mechanism. We performed laboratory experiments, and by direct detection of OH confirmed a high OH yield of up to ~50% (see Supplementary Information). Although additional experiments will be needed to better characterize isoprene degradation, it seems that several similar reactions may produce OH. Earlier analyses of field data involving isoprene chemistry also pointed to important discrepancies between measured and modelled radical production[21–24].

To test the importance of isoprene-derived peroxy radical reactions we assumed a total OH recycling efficiency of 40–80% in an extended mechanism, the MIM2+. The results in Fig. 2 show that the agreement between the modified model and measurements is good, in contrast with that found using the original MIM (Fig. 2a). Figures 2b and 3b show that the MIM2+ realistically simulates the diel OH cycle. Importantly, the ratio of HO_2 to OH, which is a critical constraint on the chemistry mechanism and greatly overestimated in the boundary layer using the original MIM, was improved dramatically by applying the MIM2+ (Fig. 2c,d). To illustrate the environmental impact, in Fig. 3c we present the global OH changes in the boundary layer.

In addition to isoprene, the forest releases highly reactive terpenes[25]. These contain unsaturated carbon bonds that react with ozone more efficiently than does isoprene and produce OH, shown by pathway IV in Fig. 1. We performed sensitivity studies by implementing terpene–ozone reactions in the model. Although the OH yield of several of these VOCs, such as limonene, myrcene and terpinolene, is close to 100%, their emissions are far too low to increase the concentration of OH in the boundary layer substantially. We also added α-pinene, which is the most abundant monoterpene and reactive towards ozone, to the model. This resulted in a small OH decrease because α-pinene also rapidly reacts with OH.

Although it is conceivable that the forest releases substantial amounts of as-yet-unidentified VOCs[26,27], we believe that their chemical impact is largely limited to the canopy[28] and to the formation of aerosol particles[3]. This is substantiated by the modest concentrations of reaction intermediates such as formaldehyde and organic peroxides in the boundary layer and the presence of a haze layer over the forest. Furthermore, compared to that in the marine boundary layer, the concentration of ozone even increased by a few parts per billion by volume (p.p.b.v.) during transport over the forest (see Table 1), owing to convective mixing with the more ozone-rich free troposphere, which precludes a strong ozone sink by reactions with unsaturated VOCs.

Our research thus points to efficient OH recycling in isoprene chemistry of the order of 40–80%. Nevertheless, additional pathways to OH cannot be ruled out and it seems likely that a combination of factors work in the same direction. For example, it is plausible that multifunctional peroxides, expected products of $RO_2 + HO_2$, photodissociate more efficiently than is currently assumed, because the solar radiation absorption of organic peroxides may be spectrally shifted towards visible irradiances and may thus regenerate OH. This would allow stronger VOC emissions[26,27], without creating a discrepancy between the modelled and measured oxidation products, especially if they condense into aerosol particles.

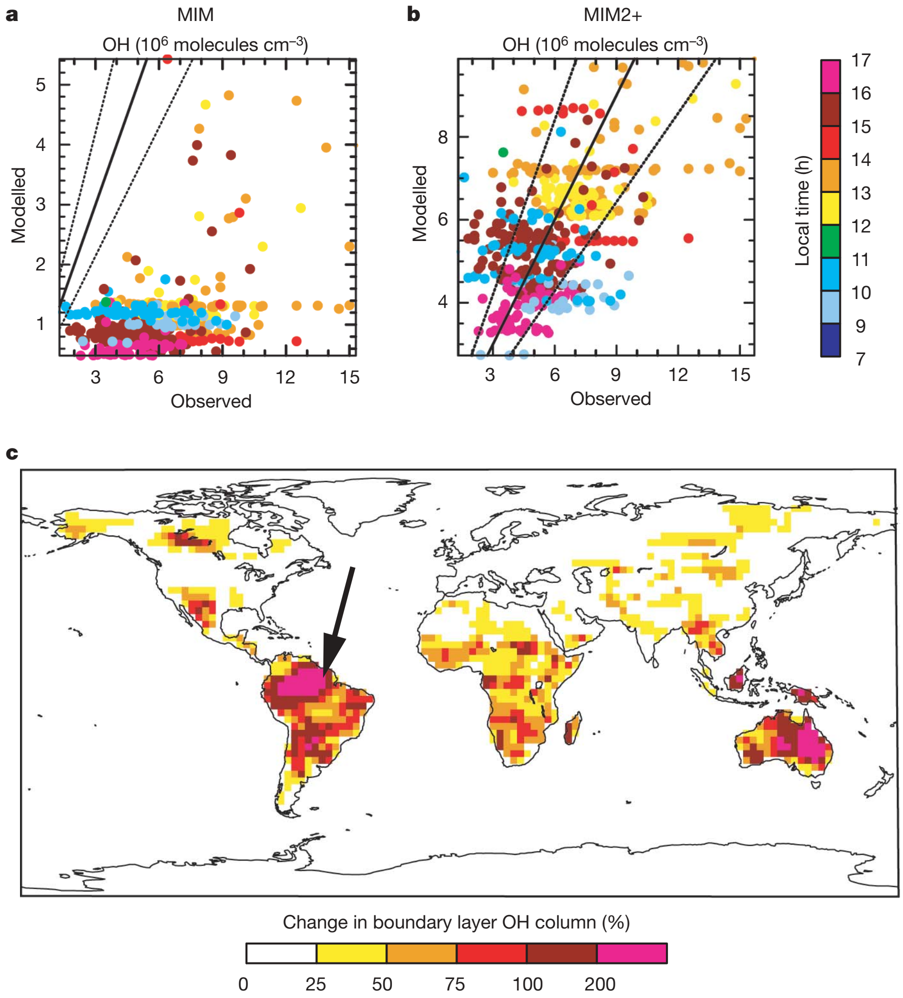

Figure 3 | Difference in OH in the boundary layer, calculated by including enhanced OH recycling in the model. **c**, Percentage difference in the annual mean OH, as calculated using the MIM2+ and the MIM (the arrow indicates the location of Suriname). **a**, **b**, scatter plots between the amounts of OH respectively observed and modelled in the boundary layer over Suriname in October 2005, comparing the MIM (**a**) and the MIM2+ (**b**). The solid lines indicate ideal agreement and the dashed lines the ±40% range, based on the measurement accuracy. Although the global model cannot reproduce the observed small-scale variability over Suriname, the MIM2+ accurately simulates the mean OH and its diel cycle.

©2008 Nature Publishing Group

We conclude that the biosphere–atmosphere interactions of tropical forest ecosystems maintain a subtle balance. The forest uses the ambient air to transport VOCs for communication and defence, and to dispose of metabolic products while sustaining an auspicious atmospheric environment without the build-up of toxic compounds. Rather than depleting the atmospheric oxidation capacity, as was believed previously, the photochemistry of VOCs over the forest recycles OH in a manner that does not contribute to photochemical smog, in contrast to the anthropogenically influenced atmosphere. Our results show only modest changes in atmospheric oxidation capacity between the marine and terrestrial boundary layers, and differences in the free troposphere are minor. The rapid oxidation by OH of biogenic VOCs that carry sulphur, nitrogen or halogens prevents the loss of nutrients from the ecosystem, because they are locally preserved through the deposition of reaction products. The efficient OH recycling may also explain how the atmospheric oxidation capacity could be sustained in geological warm periods with abundant vegetation.

It is clear that replacing rainforest by agricultural, urban or industrial areas will be associated with enhanced emissions of carbon dioxide, carbon monoxide and NO. In the tropical troposphere the efficient HO_x cycling by NO will strongly enhance photochemical air pollution, posing an additional threat to the remaining biosphere. The resultant excess ozone will also contribute to climate change because ozone is a particularly effective radiative forcing agent in the tropical troposphere. However, in the absence of external influence the forest appears to manage its atmospheric sustainability remarkably well.

METHODS

Field measurement campaign. Our aircraft measurements included OH and HO_2 radicals, NO, ozone, speciated VOCs and oxidation products including ketones, aldehydes and peroxides (see Supplementary Information). The project took place in October 2005, with the operational base in Suriname (5° N, 55° W). There October is relatively dry, with rainfall rates of about 100 mm per month (about half the annual mean), and the regular southeasterly trade winds transport Atlantic air over Guyane, Suriname and Guyana. The region is largely covered by pristine rainforest and local anthropogenic emissions are insignificant, although the free troposphere is occasionally influenced by long-distance transport of biomass-burning emissions. Local perturbations from villages along the coast, small fires or cumulonimbus convection can easily be avoided. This environment was selected to contrast the background marine atmosphere with air that travels over the pristine forest for several days under constant meteorological conditions.

Modelling. We used an atmospheric chemistry and climate model[10] together with a high-resolution single-column model[29] and a chemical box model[17] (see Supplementary Information). Biosphere–atmosphere interactions were computed on-line and the NO and isoprene emission fluxes shown to be realistic for, for example, a rainforest site in the central Amazon[22,29]. Isoprene oxidation reactions in the standard model were described using the MIM[9,16,17], which recycles $\sim$5% of the OH radicals (relative to those consumed in the first isoprene oxidation step). The MIM was first extended to the MIM2, to closely reproduce the master chemical mechanism[18]; the MIM2 recycles $\sim$10% of the OH. An extended version, the MIM2+, was forced to recycle 40–80% by prescribing OH yields from reactions between HO_2 and organic peroxy radicals.

Received 10 October 2007; accepted 22 February 2008.

1. 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).
2. Kesselmeier, J. & Staudt, M. Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. *J. Atmos. Chem.* **33,** 23–88 (1999).
3. Goldstein, A. H. & Galbally, I. E. Known and unexplored organic constituents in the Earth's atmosphere. *Environ. Sci. Technol.* **41,** 1515–1521 (2007).
4. Levy, H. II. Normal atmosphere: large radical and formaldehyde concentrations predicted. *Science* **173,** 141–143 (1971).
5. Wang, Y., Jacob, D. J. & Logan, J. A. Global simulation of tropospheric O_3-NO_x-hydrocarbon chemistry, 3. Origin of tropospheric ozone and effects of non-methane hydrocarbons. *J. Geophys. Res.* **103,** 10757–10767 (1998).
6. Lelieveld, J., Peters, W., Dentener, F. J. & Krol, M. Stability of tropospheric hydroxyl chemistry. *J. Geophys. Res.* **107,** doi:10.1029/2002JD002272 (2002).
7. Lawrence, M. G. *et al.* A model for studies of tropospheric photochemistry: description, global distribution and evaluation. *J. Geophys. Res.* **104,** 26245–26278 (1999).
8. Granier, C., Petron, G., Müller, J.-F. & Brasseur, G. The impact of natural and anthropogenic hydrocarbons on the tropospheric budget of carbon monoxide. *Atmos. Environ.* **34,** 5255–5270 (2000).
9. von Kuhlmann, R., Lawrence, M. G., Pöschl, U. & Crutzen, P. J. Sensitivities in global scale modelling of isoprene. *Atmos. Chem. Phys.* **4,** 1–17 (2004).
10. Jöckel, P. *et al.* The atmospheric chemistry general circulation model ECHAM5/MESSy: Consistent simulation of ozone from the surface to the mesosphere. *Atmos. Chem. Phys.* **6,** 5067–5104 (2006).
11. Field, C. B., Behrenfeld, M. J., Randerson, J. T. & Falkowski, P. Primary production of the biosphere: Integrating terrestrial and oceanic components. *Science* **281,** 237–240 (1998).
12. Terry, G. M., Stokes, N. J., Hewitt, C. N. & Mansfield, T. A. Exposure to isoprene promotes flowering in plants. *J. Exp. Bot.* **46,** 1629–1631 (1995).
13. Wildermuth, M. C. & Fall, R. Light-dependent isoprene emission. *Plant Physiol.* **112,** 171–182 (1996).
14. Singsaas, E. L., Lerdau, M., Winter, K. & Sharkey, T. D. Isoprene increases thermotolerance of isoprene emitting species. *Plant Physiol.* **115,** 1413–1420 (1997).
15. Penuelas, J., Lluisa, J., Asensio, D. & Munne-Bosch, S. Linking isoprene with plant thermotolerance, antioxidants and monoterpene emissions. *Plant Cell Environ.* **28,** 278–286 (2005).
16. Pöschl, U., von Kuhlmann, R., Poisson, N. & Crutzen, P. J. Development and intercomparison of condensed isoprene oxidation mechanisms for global atmospheric modelling. *J. Atmos. Chem.* **37,** 29–52 (2000).
17. Sander, R., Kerkweg, A., Jöckel, P. & Lelieveld, J. Technical note: The new comprehensive atmospheric chemistry module MECCA. *Atmos. Chem. Phys.* **5,** 445–450 (2005).
18. Saunders, S. M., Jenkin, M. E., Derwent, R. G. & Pilling, M. J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. *Atmos. Chem. Phys.* **3,** 161–180 (2003).
19. Hasson, A. S., Tyndall, G. S. & Orlando, J. J. A product yield study of the reaction of HO_2 radicals with ethyl peroxy ($C_2H_5O_2$), acetyl peroxy ($CH_3C(O)O_2$), and acetonyl peroxy ($CH_3C(O)CH_2O_2$) radicals. *J. Phys. Chem.* **108,** 5979–5989 (2004).
20. Jenkin, M. E., Hurley, M. D. & Wallington, T. J. Investigation of the radical product channel of the $CH_3COO_2 + HO_2$ reaction in the gas phase. *Phys. Chem. Chem. Phys.* **9,** 3149–3162 (2007).
21. Thornton, J. A. *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,** doi:10.1029/2001JD000932 (2002).
22. Kuhn, U. *et al.* Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower-based and airborne measurements, and implications on the atmospheric chemistry and the carbon budget. *Atmos. Chem. Phys.* **7,** 2855–2879 (2007).
23. Tan, D. *et al.* HO_x budgets in a deciduous forest: Results from the PROPHET summer 1998 campaign. *J. Geophys. Res.* **106,** 24407–24427 (2001).
24. Karl, T. *et al.* The tropical forest and fire emissions experiment: Emission, chemistry and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia. *J. Geophys. Res.* **112,** doi:10.1029/2007JD008539 (2007).
25. Williams, J., Yassaa, N., Bartenbach, S. & Lelieveld, J. Mirror image hydrocarbons from tropical and boreal forests. *Atmos. Chem. Phys.* **7,** 973–980 (2007).
26. Di Carlo, P. *et al.* Missing OH reactivity in a forest: Evidence for unknown reactive biogenic VOCs. *Science* **304,** 722–725 (2004).
27. Goldstein, A. H. *et al.* Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs. *Geophys. Res. Lett.* **31,** doi:10.1029/2004GL021259 (2004).
28. Ciccioli, P. *et al.* Emission of reactive terpene compounds from orange orchards and their removal by within-canopy processes. *J. Geophys. Res.* **104,** 8077–8094 (1999).
29. Ganzeveld, L. N. *et al.* Global soil-biogenic NO_x emissions and the role of canopy processes. *J. Geophys. Res.* **107,** doi:10.1029/2001JD001289 (2002).

Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgements We are grateful to the GABRIEL campaign team: S. Bartenbach, C. Becker, H. Bozem, S. Engemann, H. Franke, S. Gebhardt, C. Gurk, H. Hoeseni, R. Hofmann, T. Klüpfel, R. Königstedt, D. Kubistin, R. Maser, D. Noorden, U. Parchatka, D. Rodrigues, M. Rudolf, B. Scheeren, C. Schiller, V. Sinha, A. Stickler, B. Tan, P. van Velthoven, T. Warsodikromo and G. Wesenhagen. We thank the Modular Earth Submodel System (MESSy) team for model support, in particular P. Jöckel and H. Tost, and P. J. Crutzen for comments on the manuscript.

Author Information Reprints and permissions information is available at www.nature.com/reprints. Correspondence and requests for materials should be addressed to J.L. (lelieveld@mpch-mainz.mpg.de).

©2008 Nature Publishing Group