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The fluxes and air chemistry of isoprene above a deciduous hardwood forest

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Isoprene is a non-methane hydrocarbon that is emitted by certain plant species. This compound affects the chemistry of the troposphere because it is oxidized by the hydroxyl radical and its oxidation products are precursors for the photochemical production of ozone.

In 1992, we conducted a study on the controls of isoprene emission from a temperate deciduous forest. We draw upon data from this field experiment, and the literature, to describe the biological, chemical and physical processes that control the synthesis, emission and atmospheric lifetime of isoprene. Isoprene biosynthesis is associated with photosynthesis. Once produced, isoprene molecules diffuse through the stomata and laminar boundary layer of leaves to reach the atmosphere. Then isoprene molecules are transported by turbulence through the plant canopy and into the atmosphere's boundary layer. The ultimate fate of isoprene is controlled primarily by chemical oxidation and deposition to the surface. Emission rates of isoprene from leaves can be predicted by an algorithm that is a function of light energy and leaf temperature. Scaling of isoprene fluxes from the leaf to canopy scale is accomplished by linking the leaf algorithm to a canopy micrometeorological model. Field tests of the scaling model indicate that it can successfully estimate canopy-scale isoprene flux densities, as long as the biomass of isoprene emitting plants is used as a driving variable.

1. Introduction

Isoprene (C_5H_8) is a non-methane-hydrocarbon compound produced by selected plants (Rasmussen 1970; Evans *et al.* 1982). Isoprene is of particular interest to atmospheric chemists because it participates in a suite of tropospheric reactions that produce ozone (Trainer *et al.* 1987; Jacob & Wofsy 1988) and its oxidation by the hydroxyl radical (OH) reduces the oxidative capacity of the atmosphere (Ehhalt *et al.* 1991).

The rate isoprene enters the atmosphere and its duration there depend upon an ensemble of biological, physical and chemical processes that control its pro-

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duction, transport and destruction. In brief, isoprene biosynthesis is associated with photosynthesis (Sharkey *et al.* 1991; Monson *et al.* 1991). Once produced, isoprene molecules travel a tortuous path to reach the atmosphere. This trip initiates with diffusion through the stomata and laminar boundary layer of leaves (Tingey *et al.* 1981). Then isoprene molecules are transported through the plant canopy and into the atmosphere's boundary layer by turbulence. The ultimate fate of isoprene is controlled by chemical oxidation and deposition to plant and soil surfaces (Gao *et al.* 1993; Jacob & Wofsy 1988).

Our ability to predict isoprene emission rates and concentrations over vegetated surfaces is imperfect. Difficulties arise because the processes contributing to the synthesis, transport and chemical destruction of isoprene are complicated in the vicinity of vegetation (Jacob & Bakwin 1990; Gao *et al.* 1993). Since comprehensive studies on isoprene emission and chemistry over broadleaf forest canopies are rare (Lamb *et al.* 1986; Martin *et al.* 1991), we conducted a multidisciplinary study on isoprene emission from a deciduous forest during the summer of 1992. Our experimental design involved participation from analytical chemists (to measure isoprene concentrations), plant physiologists (to characterize leaf emission rates), ecologists (to inventory the amount of isoprene emitting species and biomass), meteorologists (to characterize turbulent transfer and to measure governing environmental variables) and mathematical modelers (to synthesize and scale the flux information from leaf to canopy and landscape dimensions). The objective of this paper is to draw from our experiment and on data in the literature to describe the biological, chemical and meteorological processes that affect the biogenic emission of isoprene and its lifetime in the atmosphere.

2. Framework

(*a*) *Experiment*

The field experiment was performed near Oak Ridge, TN (lat. 35° 57′ 30″; long. 84° 17′ 15″). The forest was vegetated with a mixed stand of oak, hickory, maple and pine (spp *Quercus alba*, *Q. prinus*, *Carya glabra*, *Acer rubrum*, *Liriodendron tulipifera*, *Pinus taeda*, *Pinus virginiana*). The stand was 50 years old, its mean height was 24 m and its leaf area index was 4.9 (Hutchison *et al.* 1986).

A 44 m tower in the forest canopy allowed access and support for micrometeorological and physiological instrumentation. Flux densities of isoprene between the canopy and the atmosphere were determined by using flux-gradient and relaxed eddy accumulation methods (see § 5 *b*). Rates of isoprene emission from leaves were determined with a cuvette-based gas exchange system (Harley *et al.* 1994). The isoprene concentration of air was measured with a gas chromatograph equipped with a flame ionization detector.

(*b*) *Theory*

The interactive roles of biology, chemistry and meteorology on isoprene transfer and its atmospheric lifetime are best examined in light of the conservation budget for a reactive scalar. The conservation equation for a horizontally homogeneous surface is

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -\frac{\partial F}{\partial z} + Q_{\mathrm{biol}} + Q_{\mathrm{chem}}. \tag{2.1}$$

Equation (2.1) states that the temporal change of isoprene's mixing ratio (dc/dt) equals the summation of its vertical flux divergence ($\partial F/\partial z$), its volumetric rate of biological production (Q_{biol}) and its volumetric rate of chemical destruction (Q_{chem}). In the following sections we describe the relative roles of biology, chemistry and meteorology on the conservation budget of isoprene in detail.

3. Biology

Biology influences the emission of isoprene from vegetation in many ways. First, biochemical processes synthesize organic compounds that form isoprene. Second, biological factors regulate barriers that may restrict the diffusion of isoprene between the biosphere and atmosphere. Finally, biology defines the form and structure of the plant canopy. This last factor governs the amount of plant surface area that potentially emits isoprene.

The purpose and benefits of isoprene emission by plants are subjects of debate. Some scientists argue that terpenoids, derived from isoprene, defend plants against pathogens and insects (Langeheim 1990). Others counter-argue that this function has not been directly attributed to isoprene (Fall 1991). Fehsenfield *et al.* (1992) mention that plants evolved in a low NO environment, where non-methane hydrocarbons act as ozonocides – quenchers of free radicals. Finally, it is possible that isoprene emission from plants has no function, but is an inefficient product that evolution has not selected to remove.

The loss of isoprene from a plant has important biogeochemical implications because it constitutes a sizable loss of carbon from a plant. Carbon losses, associated with isoprene, typically range between 0.5 and 3% of photosynthetic carbon gains (Sharkey *et al.* 1991; Monson & Fall 1989). Extreme values exceed 8% of carbon fixed (Monson & Fall 1989).

(*a*) *Isoprene biosynthesis*

Descriptions of the pathways of isoprene biosynthesis have evolved over the last two decades. Early investigators (Jones & Rasmussen 1975) believed that intermediates in the photorespiratory pathway were involved in isoprene biosynthesis. Recent experiments, using photorespiratory inhibitors and variations of CO_2 and oxygen (Hewitt *et al.* 1990), have conclusively disproved any role that photorespiration may have on isoprene synthesis. It is now clear that isoprene production is closely associated with photosynthetic processes. Experiments using $^{13}CO_2$ (Sharkey *et al.* 1991) demonstrate that isoprene synthesis is very closely linked to precursors generated in the photosynthetic carbon reduction pathway (probably 3-phosphoglyceric acid, 3-PGA) and its energy requirement is supplied by adenosine tri-phosphate (ATP) generated via photophosphorylation. For example, isoprene synthesis is limited when the rate of 3-PGA generation in the carbon reduction cycle is reduced, as when CO_2 and O_2 concentrations are low (Loreto & Sharkey 1990) or during the photosynthetic induction following a dark–light transition (Sharkey *et al.* 1991). Under other conditions, isoprene synthesis rates are strongly correlated with measured levels of ATP (Loreto & Sharkey 1990). Control by ATP best explains a number of observed phenomena. These observations include the parallel responses of photosynthesis and isoprene emission to varying light (Monson *et al.* 1989), the rapid decline in isoprene synthesis during a light–dark transition (Loreto & Sharkey 1990) and the decrease in isoprene emission often reported at elevated CO_2 (Loreto & Sharkey 1990; Monson & Fall 1989). In addition to these controls on ATP generation, the possibility that the activity of isoprene synthase is regulated by light cannot be discounted.

The metabolic pathway leading to isoprene production is still being explored. However, Sharkey *et al.* (1991) hypothesize that pyruvate (which is formed by the carbon fixing enzyme-RUBISCO) is converted to acetyl CoA. This substrate is then used by the mevalonic pathway to produce dimethylallyl pyrophosphate (DMAPP). The final, and circumstantial step, involves enzymatic elimination of pyrophosphate from DMAPP to produce isoprene.

(*b*) *Leaf-level emission rates and responses to environmental and plant variables*

(i) *Measurements*

Under reference conditions (leaf temperature equalling 30 °C and photon flux density equalling 1000 $\mu mol\ m^{-2}\ s^{-1}$) isoprene emission rates of white oak leaves (Quercus alba) growing near Oak Ridge, TN were 30 and 51 $nmol\ m^{-2}$ (leaf area) s^{-1} on shade and sun leaves, respectively, (Harley *et al.* 1994). On a dry weight basis, isoprene emission rates on sun and shade leaves were not significantly different (isoprene efflux densities equaled 89 and 99 $\mu g\ C\ g^{-1}\ h^{-1}$, respectively). For comparison, Guenther *et al.* (1994*b*) surveyed the literature and concluded that a reference rate for emission rates from oaks was 70 $\mu g\ C\ g^{-1}\ h^{-1}$.

Theory derived from ecological cost-benefit analysis may explain why isoprene fluxes differed on a leaf area basis but were similar on a leaf weight basis. Photosynthesis requires ribulose bisphosphate carboxylase/oxygenase (RUBISCO), an enzyme rich in nitrogen, to fix carbon. Numerous studies, thereby, show that photosynthetic capacity is correlated with leaf nitrogen (or its surrogate specific leaf weight) (Field & Mooney 1986). In nature, it is expensive and unnecessary for plants to allocate equal amounts of nitrogen to all leaves because lower, shade leaves are exposed to much less light energy than are upper shade leaves. Consequently, plants allocate nitrogen according to a leaf's vertical position (Chen *et al.* 1993). Since isoprene emissions are linked to photosynthesis (which in turn scale with specific leaf weight), it is logical to expect isoprene emission rates to scale with specific leaf weight too.

(ii) *Light energy*

The rate that isoprene is emitted from leaves is a nonlinear function of photon flux density (Q_p) (Harley *et al.* 1994; figure 1*a*). Initially, isoprene flux densities increase linearly with additional light energy. At higher photon flux densities (e.g. 500–1000 $\mu mol\ m^{-2}\ s^{-1}$) isoprene emission rates reach an asymptote. The isoprene–light relationship resembles the association observed between leaf photosynthesis and photon flux density at ambient CO_2 concentrations (Loreto & Sharkey 1990; Monson & Fall 1989; Harley *et al.* 1994).

(iii) *Temperature*

Isoprene emission rates are very sensitive to changes in leaf temperature (Loreto & Sharkey 1990; Monson *et al.* 1992; Harley*et al.* 1994). Qualitatively, isoprene emission rates increase exponentially with temperature until an optimum (figure 1*b*). At temperatures exceeding the optimum isoprene emission rates collapse. For the *Quercus alba* leaves, isoprene emission rates increased threefold as leaf

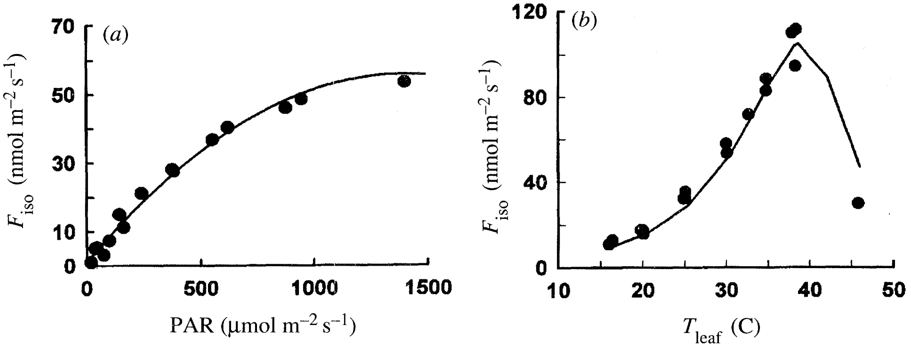

Figure 1. (*a*) The response of isoprene emission rates to photon flux density. Measurements were made on sunlit *Quercus alba* leaves (after Harley 1994). The mean leaf temperature was 30 °C. (*b*) The response of isoprene emission rates to leaf temperature. Measurements were made on sunlit *Quercus alba* leaves (after Harley *et al.* 1994). Photon flux density was 1000 μmol m^{-2} s^{-1}.

temperature increased from 20 to 30 °C. The temperature optimum occurred at 41 °C.

The temperature dependency of isoprene emission rate is not due to an increased volatility of this essential oil, as is the case for terpenes, because the pool of carbon substrate is small (Sharkey *et al.* 1991*a*). Neither can the temperature dependence of isoprene emission rates be attributed to temperature dependencies of electron transport and carbon assimilation; both carbon assimilation processes exhibit optimal rates at temperatures 5–10 °C less than the optimum temperature for isoprene emission (Monson *et al.* 1992). Instead the temperature dependency of isoprene emission rates stems from changes in the temperature kinetics of the enzyme isoprene synthase. Evidence for this conclusion comes from the observation that isoprene efflux rates and enzyme activity parallel one another as temperature changes (Sharkey *et al.* 1991*a*; Monson *et al.* 1992). The reader should also recognize that temperature and light energy do not impact isoprene emission rates independently. Monson *et al.* (1992) and Harley *et al.* (1994) observed that the quantum yield of isoprene emission rates increases with temperature.

(iv) *Stomatal regulation*

There is ample evidence that isoprene enters the atmosphere by diffusion through stomata (Tingey *et al.* 1981; Fall & Monson 1992). Despite this route of travel, stomatal closure does not restrict isoprene diffusion rates. As stomata close the isoprene concentration in the leaf increases and maintains a concentration potential that offsets any reduction in stomatal conductance (Fall & Monson 1992). Based on this evidence, Fall & Monson (1992) argue that it is unnecessary to consider stomatal diffusion as a limiting step when modelling isoprene emission rates.

In the field, stomatal closure may have an indirect influence on isoprene emission rates. Stomatal closure reduces transpiration rates and increases leaf temperature. Since isoprene efflux densities possess a strong dependence on leaf temperature (figure 1*b*), an indirect increase in isoprene emission rates may be experienced via stomatal closure.

(v) *Species dependence*

Surveys reveal that only certain plants emit isoprene (Rasmussen 1970; Evans *et al.* 1982; Guenther *et al.* 1994*b*). In general, highest isoprene emission rates come from tree and shrub species, while crop and herbaceous species have low to non-detectable emissions. On the other hand, it is not possible to attribute isoprene emissions to particular families. Within selected groups (such as *Pinaceae* and *Leguminosae*) high to non-detectable rates of isoprene emission are possible (Evans *et al.* 1982). Among popular plant genera, aspen, poplar (*Populus*), oak and eucalyptus are high emitters (greater than 35 $\mu g\, g^{-1}\, h^{-1}$), sycamore, willow and spruce are medium emitters (2–35 $\mu g\, g^{-1}\, h^{-1}$), soybeans are poor emitters and maples, many pines and potatoes do not emit isoprene (Rasmussen 1970; Evans *et al.* 1982; Guenther *et al.* 1994*b*). Strong isoprene emission rates are associated with shade intolerant species, while low and negligible emissions are associated with shade tolerant species (Chris Geron, personal communication).

Surveying North American forests, Guenther *et al.* (1994*b*) report that 13 out of 49 major tree genera in the North America emitted isoprene. Focusing down to the Oak Ridge, TN forest, we observed that oaks (*Quercus alba*, *Q. prinus*, *Q. velutina*) and black gum (*Nyssa sylvatica*) are strong isoprene emitters and sweetgum (*Liquidambar styraciflua*) is a weak emitter (Dilts *et al.* 1994). Others show that maple (*Acer rubrum*) and beech (*Fagus* spp), which also inhabit this forest, are non-emitters (Evans *et al.* 1982; Guenther *et al.* 1994*b*).

(vi) *Biomass*

When studying the transfer of water and CO_2 between the surface and the atmosphere, it is sufficient to relate flux densities to biomass indices of the entire canopy. For studies on isoprene emission from a mixed forest stand, broad indicators of canopy architecture are insufficient. In mixed forest stands, the quantity of biomass that emits isoprene changes markedly within spatial scales that define the flux footprint. At the forest near Oak Ridge, TN, the biomass of isoprene emitting trees exceeded 200 $g\, m^{-2}$ within 50 m of the measurement tower, equalled about 150 $g\, m^{-2}$ between 50 and 250 m upwind of the tower and dropped to less than 25 $g\, m^{-2}$ between 250 and 500 m upwind (figure 2). These biomass figures differ significantly from the total biomass of the Oak Ridge forest, which, on average, was 364 $g\, m^{-2}$ (Hutchison *et al.* 1986).

(vii) *Seasonality*

Photosynthesis and isoprene emission rates both show a dependency on leaf age. However, new data by Dilts *et al.* (1994) and Monson *et al.* (1994) suggest that isoprene emission rates do not initiate with the onset of photosynthesis, after leaf emergence. Instead, isoprene emission rates commence after a given amount of thermal units are accumulated (number of growing degee days above 5 °C). After synthesis initiation, flux densities of isoprene from aspen, eucalyptus, bean, sweetgum and cowpea increase with age until the leaves are about 20 days old – afterwards, rates of isoprene emission decrease with additional age (Fehsenfield *et al.* 1992).

(*c*) *Isoprene emission model: leaf scale*

Isoprene is not sequestered, but is emitted immediately upon synthesis. Consequently, an environmentally driven algorithm, derived by Guenther *et al.* (1991,

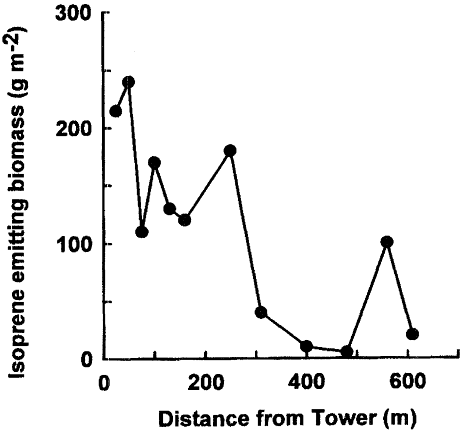

Figure 2. The horizontal transect of isoprene emitting biomass at the Oak Ridge, TN field site. The data are adapted from Lamb *et al.* (1994).

1993), calculates isoprene emission rates from leaves well,

$$F_{\text{isoprene}} = S_I f(Q_{\text{p}}) f(T_{\text{l}}), \tag{3.1}$$

where S_I is a standard emission factor at a specified leaf temperature and photon flux density, and $f(Q_{\text{p}})$ and $f(T_{\text{l}})$ are adjustments factors to the standard emission rate, due to variations in photon flux density and temperature, respectively. The adjustment factor for photon flux density is

$$f(Q_{\text{p}}) = \alpha C_{\text{L}} Q_{\text{p}} / \sqrt{(1 + \alpha^2 Q_{\text{p}}^2)}, \tag{3.2}$$

where α and C_{L} are empirical constants. For *Quercus alba*, α equals 0.00276 for shade leaves and 0.00165 for sun leaves. For comparison, Guenther *et al.*'s (1991) standard model uses equal to 0.0027; this value is an average derived from measurements on eucalyptus, sweet gum, aspen and velvet bean.

Guenther *et al.* (1991) derived the temperature adjustment factor for isoprene efflux densities using a function that defines the temperature dependency of enzyme activity:

$$f(T) = \frac{\exp[C_{T1}(T_k - 303)/303RT_k]}{1 + \exp[C_{T2}(T_k - T_{\text{opt}})/303RT_k]}. \tag{3.3}$$

R is the universal gas constant, C_{T1} and C_{T2} are coefficients and T_{opt} is the optimum temperature. The scaling factor equals one when temperature equals 303 K. For *Quercus alba*, typical values for C_{T1}, C_{T2} and T_{opt} are 78 000 J mol^{-1}, 380 000 J mol^{-1} and 314 K, respectively (Harley *et al.* 1994).

Although equation (3.1) is empirical and simple, it is a robust and accurate model. Tests indicate that the model can account for 90% of observed variability of isoprene flux densities during the day and it can predict emission rates within 35% (Guenther *et al.* 1993).

4. Chemistry

Plants modify their chemical environment by emitting isoprene (and other non-methane hydrocarbons) and by removing a plethora of oxidizing and acidifying compounds. Specifically, the concentrations of ozone, hydroxyl (OH) and peroxy radicals (RO_2, HO_2), and NO within and above a plant canopy affect the rate by which isoprene is oxidized and ozone is subsequently produced. In this section we discuss the salient chemical reactions involving isoprene.

(*a*) *The fate of isoprene*

During the day 95% of isoprene that is oxidized is destroyed by the hydroxyl radical (OH) and the remainder is destroyed by reactions with ozone (Zimmerman *et al.* 1988). The primary oxidation reaction produces an organic peroxy radical (RO_2):

$$C_5H_8 + OH \overset{O_2}{\rightarrow} RO_2. \tag{R1}$$

The oxidation of isoprene by OH has three ramifications on the chemistry of the troposphere. One is a reduction of the atmosphere's oxidative capacity (Fehsenfield *et al.* 1992). Another ramification is the initiation of steps leading to the formation of ozone (Lloyd *et al.* 1983; Trainer *et al.* 1987; Chameides *et al.* 1992). Finally, the product of isoprene oxidation (RO_2) reacts with NO to form peroxy radicals, oxygenated hydrocarbons (ketones and aldehydes), organic peroxides, organic acids and organic nitrates (Lloyd *et al.* 1983; Trainer *et al.* 1987, 1991; Jacob & Wofsy 1988; Chameides *et al.* 1992; Martin *et al.* 1991; Fehsenfield *et al.* 1992).

To better understand ısoprene's role on the chemistry of atmosphere let's start with the hydroxyl radical (OH), the atmosphere's vacuum cleaner (Ehhalt *et al.* 1991). OH is formed when ozone is photolysed by ultraviolet radiation ($\lambda <$ 320 nm) and the resulting singlet oxygen molecule reacts with water vapour:

$$O_3 + h\nu \rightarrow O_2 + O(^1D), \tag{R2}$$

$$O(^1D) + H_2O \rightarrow OH + OH. \tag{R3}$$

In classical chemistry, OH is consumed by reactions with CO or CH_4 (Ehhalt *et al.* 1991):

$$OH + CH_4 \overset{O_2}{\rightarrow} RO_2 + H_2O, \tag{R4}$$

$$OH + CO \overset{O_2}{\rightarrow} HO_2 + H_2O. \tag{R5}$$

Reactions (R4) and (R5) are noteworthy because they form organic peroxy radicals (RO_2) or hydroperoxyl radicals (HO_2), which in turn, react with NO to form NO_2:

$$HO_2 + NO \rightarrow OH + NO_2, \tag{R6}$$

$$RO_2 + NO \rightarrow RO + NO_2. \tag{R7}$$

Ozone is ultimately produced when NO_2 is photolysed by ultraviolet radiation:

$$NO_2 + h\nu \rightarrow NO + O, \tag{R8}$$

$$O + O_2 \rightarrow O_3. \tag{R9}$$

Isoprene oxidization is important because it provides another route for producing RO_2 and HO_2 in the atmosphere (Jacob & Wofsy 1988; Trainer *et al.* 1991; Fehsenfield *et al.* 1992). It, thereby, accelerates reactions (R6) through (R9) because OH reacts faster with isoprene than with CO or methane. For instance, Rasmussen & Khalil (1988) report that isoprene is 5 to 10 times more reactive with OH than is CO in the clean air over an Amazonian forest.

The sequence of reactions, initiated with isoprene oxidation can also be a net source of OH radicals; isoprene oxidation consumes one OH molecule (R1), but products of this reaction (in the presence of NO) form one ozone molecule which can be photolysed to form two OH molecules (R3).

Reactions involving the production of nitric acid and peroxides ultimately limit the production of ozone because they are sinks for OH and HO_2:

$$OH + NO_2 \rightarrow HNO_3, \tag{R10}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \tag{R11}$$

$$HO_2 + RO_2 \rightarrow ROOH, \tag{R12}$$

and these products deposit rapidly from the atmosphere.

In the absence of isoprene (and other hydrocarbons), peroxy radicals become scarce, allowing the photostationary state to exist. Consequently, ozone production is balanced by ozone consumption, via reactions (R8), (R9) and (R13):

$$NO + O_3 \rightarrow NO_2 + O_2. \tag{R13}$$

In remote regions, where NO levels are below 5–10 ppt, the oxidation of isoprene by OH leads to ozone destruction. Peroxy radicals (RO_2) react with one another (R11) to form hydrogen peroxide. Then HO_2 consumes ozone to recycle OH (Jacob & Wofsy 1988; Ehhalt *et al.* 1991).

During the night OH is rapidly depleted and ozone is deposited to the surface (Zimmerman *et al.* 1988). The key chemical pathways for nocturnal isoprene removal involves reactions with the NO_3 radical (Fehsenfield *et al.* 1991) and deposition to the surface (Guenther *et al.* 1994*a*).

5. Meteorology

Meteorological processes are responsible for the physical transport of material (atmospheric turbulence and molecular diffusion) and the transfer of photons and energy that affects chemical kinetics and drive photolytic reactions. Micrometeorological theory can also be exploited to measure flux densities of isoprene over plant canopies. In this section we describe the behaviour of relevant meteorological variables within and above a deciduous forest and outline several meteorological methods that have been used to measure isoprene flux densities.

(*a*) *Flux divergence*

Flux divergence can be visualized, mathematically, using the flux gradient relationship for vertical flux density of a trace gas ($F = -K\partial c/\partial z$):

$$\frac{\partial F}{\partial z} = -\frac{\partial K \partial c/\partial z}{\partial z} = -\left(\frac{\partial K}{\partial z}\frac{\partial c}{\partial z} + K\frac{\partial^2 c}{\partial z^2}\right). \tag{5.1}$$

Flux divergence occurs when turbulent mixing coefficients (K) and concentration gradients varying in the vertical dimension. For a passive scalar, this effect is most prominant inside a plant canopy where turbulence is heterogeneous and near field diffusion causes curvature of the scalar concentration gradient (Raupach 1988; Baldocchi 1991).

(*b*) *Microclimate*

The state of meteorological variables, which control isoprene emission from leaves, are a function of turbulent mixing, the physiological status of the vegetation and the fate of the incoming and outgoing streams of photons (Norman 1979; Baldocchi 1991). In practice, the micrometeorological conditions within and above a plant canopy are described using models derived from the equations describing the conservation of energy, mass, momentum and turbulent kinetic energy (Raupach 1988) and the short and long wave radiation balance (Norman 1979). Leaf temperature and the vapour concentration inside the leaf are assessed by evaluating the leaf energy balance. The associated flux densities of sensible and latent heat are functions of the leaves' boundary layer and stomatal conductances.

The microclimate within a deciduous forest is unique because of the way its foliage is distributed in space. About 75% of the foliage is positioned in the upper quarter of the canopy and the leaves are congregated in clumps (Hutchison *et al.* 1986). This architecture alters the length, time and velocity scales of turbulence throughout the canopy and affects how photons are propagated through the foliar space (Baldocchi 1989).

Why should turbulence properties be of concern to someone studying isoprene in a forest? The relative difference between turbulence and chemical timescales affect how we treat the scalar conservation equation (equation (2.1)). If the time scale of turbulence exceeds the timescale of chemical reactions, material in a fluid parcel may be destroyed before turbulence can transport the parcel between adjacent reference levels. Gao *et al.* (1993), for example, show that hydroxyl oxidation of isoprene perturbs the isoprene concentration profile inside a forest canopy as compared to a case without chemistry. Furthermore, NO released from the soil is not always vented through a forest canopy because it is destroyed via reaction (R13) faster than it is transported out of the canopy (Jacob & Bakwin 1988; Gao *et al.* 1991, 1993).

Vegetation intercepts and absorbs photons. This process causes the photon flux density to diminish with depth in the canopy. Photon absorption by vegetation is consequential because it perturbs the photochemical synthesis of isoprene and affects the photolysis of NO_2, O_3, H_2O_2, and HNO_3 inside the canopy. The absorption of photons also alters the energy balance of leaves and the underlying soil – the surface energy balance determines its temperature and thereby affects chemical kinetics of isoprene synthesis. Clumping of foliage enhances the probability of beam penetration, as compared to transport through a randomly spaced turbid medium. Consequently, a radiative transfer model that accounts for clumping should be used to evaluate the canopy microclimate and isoprene emission algorithms within a deciduous forest.

(*c*) *Measurement methods*

The flux-gradient method, the relaxed eddy accumulation method and dual tracer method offer the most potential for measuring isoprene flux densities over vegetation. The flux-gradient method infers flux densities of isoprene as the product of an eddy diffusivity (K) and the vertical gradient of isoprene concentration in the internal boundary layer of the canopy. Direct measurements of K involve measuring the ratio of flux density and vertical gradient of a tracer (e.g. heat, moisture or CO_2). Indirect estimates of K can be obtained by aerodynamic, en-

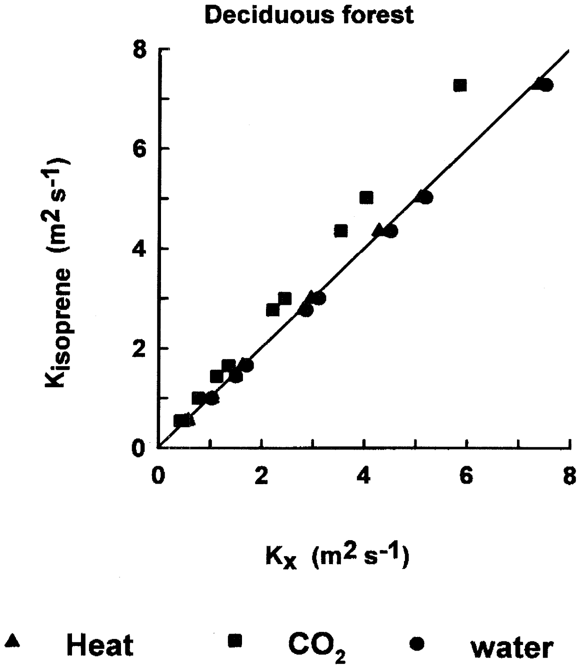

Figure 3. Theoretical calculations of eddy exchange coefficients over a deciduous forest. Eddy exchange coefficients for isoprene are compared against those for water vapour (●), sensible heat (▲) and CO_2 (■).

ergy balance methods (Baldocchi *et al.* 1988) or by invoking Monin–Obhukov similarity theory (Cellier & Brunet 1992). Indirect methods must be used with caution over tall canopies because Ks will underestimate directly measured values by factors of 2 to 3 (Cellier & Brunet 1992).

One restriction associated with flux-gradient theory is the requirement that K for the tracer must equal that for isoprene. This restriction will be violated when sources and sinks of the tracer and the scalar under investigation are not co-located. Theoretical calculations (figure 3) suggest that eddy exchange coefficients for isoprene can be approximated from eddy exchange coefficients for water vapour or heat. Eddy exchange coefficients of isoprene and CO_2, on the other hand, differ because CO_2 transfer is bidirectional (foliar uptake and soil loss) while isoprene transfer is generally unidirectional.

The relaxed eddy accumulation method estimates flux densities using an equation defined by Businger & Oncley (1990),

$$F = b(C_u - C_d)\sigma_w, \tag{5.2}$$

where b is a coefficient (about 0.60), C_u and C_d are the mean concentrations sampled in bags associated with updrafts and downdrafts, respectively, σ_w and is the standard deviation of vertical wind velocity. The measurement system relies on a fast solenoid valve to switch and direct air into the relevant bags as up and down drafts are detected by the anenometer. Guenther *et al.* (1994*a*) are the first experimenters to apply this method for isoprene. They report a 20% difference between REA and flux gradient measurements, with the latter method yielding smaller values.

Allwine *et al.* (1985) and Lamb *et al.* (1986) applied the tracer diffusion method to evaluate isoprene flux densities over a forest canopy. This method involves the known release of a passive tracer (e.g. SF_6) and the measurement of crosswind integrated isoprene and tracer concentrations at some downwind location. Lamb *et al.* (1986) conclude that the method has merit by its ability to yield flux densities which agreed with measurements from branch enclosure studies.

The flux measurement methods, surveyed above, depend on accurate measurements of isoprene concentration. Concentration measurement methods have been reviewed by Fehsenfield *et al.* (1992). Isoprene concentrations are most often measured using gas chromatography. Detection is commonly accomplished with a flame ionization detector. In other instances photoionizaton detectors, mass spectrometers, tunable diode lasers and chemiluminescence methods have been used.

Flux densities of passive scalars are constant with height in the surface boundary layer when the scalar concentration is steady with time and no chemical reactions are occurring. In the vicinity of plant canopies, turbulent transfer is associated with large scale coherent structures, whose timescales range between 40 and 200 s (Paw *et al.* 1993). In comparison, the atmospheric lifetime of isoprene is defined from

$$\tau = 1/[\mathrm{OH}]k_{ab}. \tag{5.3}$$

As [OH] increases from 5×10^5 to 5×10^6 molecules per cm^{-3} the lifetime of isoprene decreases from over 5 h to less than 1 h. From a 'back of the envelope' calculation, one may conclude that isoprene acts as a passive scalar because the chemical timescale (equation (5.3)) far exceeds typical turbulence timescale. On the other hand, Gao *et al.* (1993) show that chemical reactions between isoprene and OH theoretically perturb the concentration and flux density profile of isoprene within and above a forest canopy. Micrometeorologists may draw two conclusions from these data. First, chemical reactions will impose a finite (though small) error on direct measurements of isoprene flux density. Second, flux densities inferred from concentration gradients may be subject to larger errors because the interpretation of the flux densities from the concentration gradient is confounded by chemical kinetics.

6. Isoprene concentrations and emission rates

(*a*) *Field measurements*

(i) *Concentration measurements*

Figure 4 shows the diurnal pattern of isoprene concentrations measured over the deciduous forest on day 218 (August 5). Isoprene concentrations experienced a distinct diurnal variation. Concentrations were near zero at sunrise and increased with time through the morning and early afternoon. Peak concentrations occurred during midafternoon and then decreased as evening approached Through midday, greater isoprene concentrations were associated with updrafts. On day 218, concentrations as high as 12 and 5 ppbv were observed for updrafts and downdrafts, respectively. The maximum isoprene concentrations, measured on day 218, were also the highest values observed during our three week study. The observation of greater isoprene concentrations in the updrafts is indicative that the canopy was a source of isoprene.

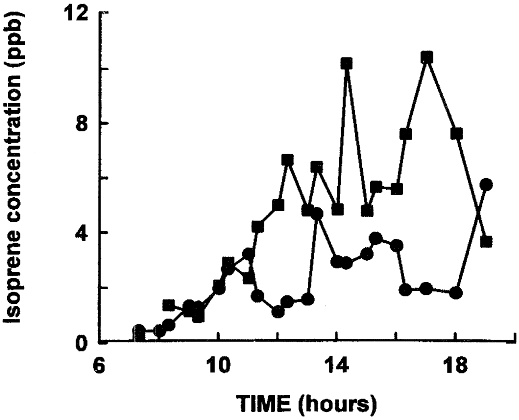

Figure 4. Diurnal variation of isoprene concentration over a deciduous forest on 5 August 1992. Air was sampled with the relaxed eddy accumulation system (Westberg, Guenther and Zimmerman, unpublished) ●, Downdrafts; ■, updrafts.

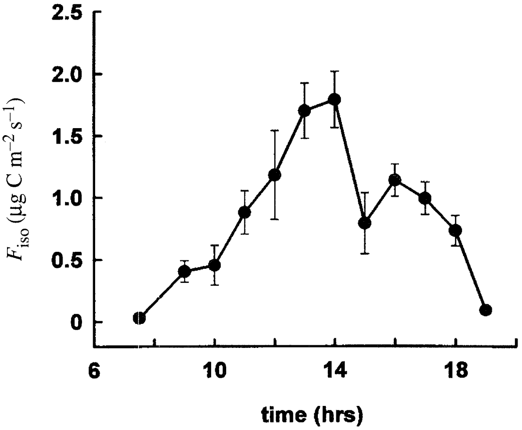

Figure 5. The mean diurnal variation of isoprene flux density measured over a deciduous forest. These data were obtained with the flux gradient and relaxed eddy accumulation methods during the period between 20 July and 5 August 1992 (adapted from Guenther *et al.* 1994*a*).

The diurnal behaviour of isoprene concentrations is consistent with measurements from over a mixed forest in Pennsylvania (Martin *et al.* 1991; Fehsenfield *et al.* 1992) and an Amazonian forest (Zimmerman *et al.* 1988; Rasmussen & Khalil 1988). During the Pennsylvania study mean daytime peak isoprene concentrations were about 15 ppbv and extreme values exceeded 30 ppbv (Martin *et al.* 1991). In addition, isoprene comprised 26% of the non-methane hydrocarbons measured in the air. Over the Amazon, isoprene concentrations ranged between 1 and 3 ppbv in the atmosphere's mixed layer and exceeded 8 ppbv near the forest canopy (Zimmerman *et al.* 1988; Rasmussen & Khalil 1988).

(ii) *Flux density measurements*

Figure 5 shows the average diurnal pattern of isoprene flux densities measured over the deciduous forest. On most days, isoprene flux densities were positive, but near zero in the early morning; occassionally isoprene deposition was detected. As the day progressed, isoprene flux densities increased with time until about 14 h.

At this time, peak values exceeded 1.5 μg C m^{-2} s^{-1} (90 nmol m^{-2} s^{-1}). During the afternoon, isoprene flux densities diminished due to the presence of convective clouds and a reduction of incident solar energy. As sunset approached, isoprene flux densities diminished to near zero again.

Lamb *et al.* (1994) summarized these data in the form of a probability distribution. They report that isoprene emission rates rarely exceeded 3 μg C m^{-2} s^{-1} and the mean value during the experiment was 1.06 ± 0.80 μg C m^{-2} s^{-1}. In comparison, Lamb *et al.* (1986) report that the typical flux density of isoprene from an oak grove in Washington was about 6.9 μg C m^{-2} s^{-1}. In this later case the biomass scaling factor was 804 g m^{-2} while in the present study the biomass factor ranged between 100 and 300 g m^{-2} (figure 2). The values shown in figure 5 are in closer agreement with data from the Amazon forest, where Zimmerman *et al.* (1988) reported a canopy emission rate of 0.86 g m^{-2} s^{-1}.

At the continental scale, 3.93 Tg of C are emitted per year from deciduous and pine forests in the US (Lamb *et al.* 1993) and isoprene accounts for 14% of the non-methane hydrocarbon emissions in the US. Globally, isoprene emissions range between 250 and 450 Tg per year (Zimmerman *et al.* 1988; Fehsenfield *et al.* 1992) and constitute 40% of global NMHC emissions.

(*b*) *Integrated model calculations*

Integrating isoprene flux densities from the leaf to the canopy scale requires the computation of controlling abiotic and biotic variables as they vary with depth through the canopy and as they differ on sunlit and shaded leaf fractions (Norman 1979; Baldocchi 1991). This additional level of complexity is advised because the isoprene emission algorithms are nonlinear functions of their independent variables. The CANOAK model links micrometeorological and physiological theory to scale isoprene emissions from leaf to canopy dimensions of a deciduous forest. The model is described and tested in another work (Baldocchi & Harley 1995). In this section, we examine the capability of the CANOAK model to scale isoprene fluxes from leaves to canopy dimensions and explore the role of environmental variables on the isoprene emission rates of the whole canopy.

Figure 6 compares calculations and measurements of isoprene flux density. Model calculations are shown for two representative biomass factors. The lower biomass factor (110 g m^{-2}) is the average value for the 600 m transect and the higher biomass factor (220 g m^{-2}) is representative of a distance weighted average (figure 2). Measurements of isoprene fluxes envelope calculations derived from the lower biomass factor, while calculations based on the higher biomass factor significantly overestimate measurements.

Considering a larger body of data, Lamb *et al.* (1994) report that the ensemble mean of isoprene flux calculations were not significantly different from measured values (0.99 ± 0.55 versus 1.06 ± 0.80 μg C m^{-2} s^{-1}) when the biomass factor of 110 g m^{-2} was used. These data illustrate the importance of obtaining the appropriate index of isoprene emitting biomass when performing model calculations. Use of total forest biomass (364 g m^{-2}) may be appropriate to scale fluxes of water and CO_2 from leaf to canopy dimensions (Baldocchi & Harley 1995), but it is inappropriate to scale isoprene fluxes.

Among the modelling community there is a debate on the merits or demerits of executing leaf energy balance calculations in regional isoprene emission models (Lamb *et al.* 1994; Guenther *et al.* 1993). Detailed micrometeorological models can

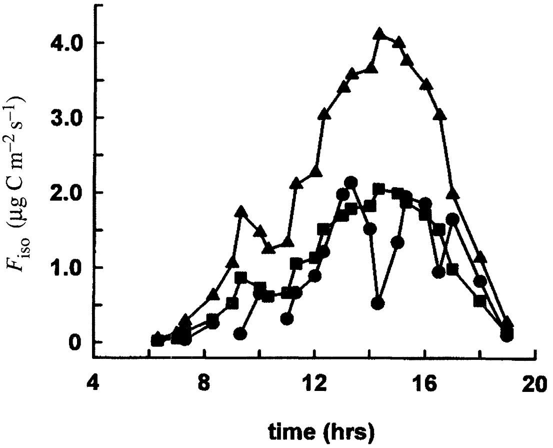

Figure 6. Comparison between measured and calculated isoprene flux densities. The lower biomass value (110 g m^{-2}, ■) is representative of vegetation several hundred metres upwind of the tower. The higher value (220 g m^{-2}, ▲) is representative of vegetation with 100 m of the tower. Measurements (●) were based on the relaxed eddy accumulation method and were obtained on 5 August (D218). This figure is adapted from Lamb *et al.* (1994).

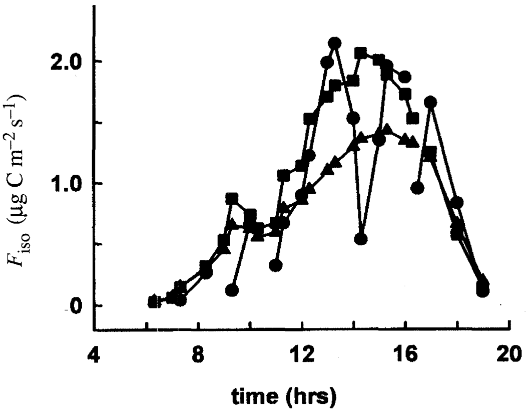

Figure 7. Comparison between measured and calculated isoprene flux densities. Two model versions were used. One assumed that leaf temperature equalled air temperature ($F_{\rm iso} = f(T_{\rm a})$, ▲). The other model version computed leaf temperature via leaf energy balance calculations ($F_{\rm iso} = f(T_{\rm leaf})$, ■). Measurements (●) were based on the relaxed eddy accumulation method and were obtained on 5 August (D218).

serve as guides for such debates. Figure 7 compares two calculations of isoprene flux densities. One version executed the leaf energy balance module of CANOAK and the other version assumed that leaf temperatures equaled air temperatures. Figure 7 shows that the simpler model ($F_{\rm iso} = f(T_{\rm a})$) yielded lower estimates of isoprene flux density than the version that considered the energy balance of leaves. Furthermore, the leaf energy balance model yielded results that more closely fit peak, midday flux measurements.

Figure 8 summarizes the theoretical dependency of canopy isoprene flux density on air temperature and photosynthetically active radiation (PAR). In all cases, isoprene flux densities increase with available PAR. The sensitivity, however, is strongly modified by air temperature. Warm air temperature (35 °C) enable flux

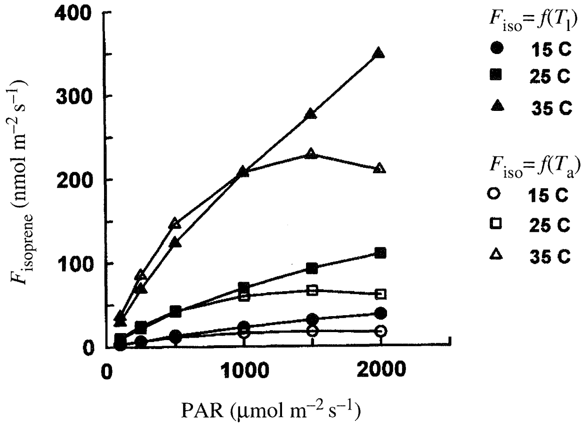

Figure 8. Calculations of isoprene emission flux densities as a function of incoming photon flux density and air temperature. Wind speed was assumed to equal 3.0 m s^{-1} and humidity was 15 mg m^{-3}. The canopy biomass was assumed to equal 360 g m^{-2}.

densities to exceed 300 nmol m^{-2} s^{-1}. Furthermore these emission rates are nearly triple those calculated for air temperature ten degrees cooler. Another point to be drawn from figure 8 is the role of modelling leaf temperature. Under low PAR inputs (e.g. PAR less than 500 μmol m^{-2} s^{-1}) estimates of isoprene flux density are relatively insentive to whether leaf temperature is a function of air temperature or its surface energy balance. At higher PAR levels and air temperatures equal to and under 25 °C, smaller flux densities are calculated with the model that assumes leaf temperature equals air temperature. Under this circumstance leaf temperatures exceeds air temperatures. The converse result holds when air temperature is extreme ($T_{\mathrm{a}} = 35$ °C) and PAR levels are weak.

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