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Leaf, branch, stand and landscape scale measurements of volatile organic compound fluxes from U.S. woodlands

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Summary Natural volatile organic compound (VOC) fluxes were measured in three U.S. woodlands in summer 1993. Fluxes from individual leaves and branches were estimated with enclosure techniques and used to initialize and evaluate VOC emission model estimates. Ambient measurements were used to estimate above canopy fluxes for entire stands and landscapes.

The branch enclosure experiments revealed 78 VOCs. Hexenol derivatives were the most commonly observed oxygenated compounds. The branch measurements also revealed high rates of isoprene emission from three genera of plants (*Albizia, Chusqua* and *Mahonia)* and high rates of monoterpene emission from three genera (*Atriplex, Chrysthamnus* and *Sorbus)* for which VOC emission rates have not been reported. Measurements on an additional 34 species confirmed previous results. Leaf enclosure measurements of isoprene emission rates from *Quercus* were substantially higher than the rates used in existing emission models.

Model predictions of diurnal variations in isoprene fluxes were generally within ± 35% of observed flux variations. Measurements with a fast response analyzer demonstrated that 60 min is a reasonable time resolution for biogenic emission models. Average daytime stand scale (hundreds of m) flux measurements ranged from about 1.3 mg C m^{-2} h^{-1} for a shrub oak stand to 1.5–2.5 mg C m^{-2} h^{-1} for a mixed forest stand. Morning, evening and nighttime fluxes were less than 0.1 mg C m^{-2} h^{-1}. Average daytime landscape scale (tens of km) flux measurements ranged from about 3 mg C m^{-2} h^{-1} for a shrub oak–aspen and rangeland landscape to about 7 mg C m^{-2} h^{-1} for a deciduous forest landscape. Fluxes predicted by recent versions (BEIS2, BEIS2.1) of a biogenic emission model were within 10 to 50% of observed fluxes and about 300% higher than those predicted by a previous version of the model (BEIS).

Keywords: biogenic emission model, diurnal variation, hexenol derivatives, isoprene, monoterpenes, sesquiterpenes, spatial variation.

Introduction

The chemical composition of the atmosphere is strongly influenced by surface fluxes of volatile organic compounds (VOCs). Guenther et al. (1995) estimate that vegetation emits over 90% of global VOC emissions. Quantitative investigations of atmospheric chemistry require estimates of surface fluxes of natural VOC fluxes. The first estimates of VOC fluxes, which were based on measurements made by enclosing tree branches in chambers, demonstrated that large quantities of VOCs were emitted by some, but not all, plant species. Total VOC emissions from oak trees, for example, are more than two orders of magnitude greater than from elm trees. The measurements reported in this paper include branch enclosure measurements as well as smaller (leaf) and larger (stand, landscape) scale studies. Leaf measurements represent a spatial scale of a few cm so it is possible to generate uniform environmental conditions (e.g., light and temperature) that are not possible at larger scales. Stand and landscape scale measurements have spatial scales of hundreds of m and tens of km, respectively, and can provide estimates of above-canopy fluxes that are not compromised by the artificial disturbances introduced by enclosures.

The accuracy of regional and global natural VOC emission models (e.g., Geron et al. 1994, Guenther et al. 1995) is limited by the relatively few data for initializing and evaluating VOC flux estimates. Model initialization requires measurements of VOC emission rates for the dominant plant species in a landscape, estimates of total biomass and species composition, and climatological data. Model evaluation requires above-canopy measurements of ambient VOC concentrations. Therefore, to evaluate the ability of models to simulate observed fluxes, we investigated summertime VOC emission rates at four sites including an urban mixed forest preserve, a deciduous forest, a shrub oak woodland and a mixed conifer–hardwood site. Detailed leaf-level measurements at the urban forest site and measurements at the mixed conifer–hardwood site are reported in companion papers (Harley et al. 1996, Isebrands et al. 1996). The specific objectives of this study were to determine: (1) whether existing databases accurately reflect isoprene and monoterpene emission rates for individual plant species, (2) if

sesquiterpenes and oxygenated VOCs are emitted from the dominant plants, (3) if models simulate diurnal variations in isoprene fluxes, and (4) if models predict spatial variations in above-canopy isoprene fluxes.

Field site descriptions

Fluxes of VOCs were measured in an urban forest preserve in Atlanta, Georgia, in June 1993 (Fernbank Forest, 33°24′ N, 84°14′ W), in mixed forests in the Appalachian mountains of western North Carolina in June and July 1993 (Coweeta, 35°4′ N, 83°26′ W), and a shrub oak woodland in western Colorado in August 1993 (Temple Ridge, 40°25′ N, 107°14′ W).

The Fernbank Forest site is within a 25-ha mixed hardwood and conifer woodland located in Atlanta, Georgia. Fernbank Forest has been preserved since the early 1800s and thus represents a mature remnant stand of natural Georgia Piedmont forest (Skeen 1974). Mean canopy height at the tower was 30 m, and mean leaf area index (LAI) was 4.8. Dominant tree species in the forest include two species known to emit isoprene, *Quercus alba* L. (white oak) and *Liquidambar styraciflua* L. (sweet gum), and two species that do not emit isoprene, *Liriodendron tulipifera* L. (tulip poplar) and *Pinus taeda* L. (loblolly pine). Major understory plants include *Hedera helix* L. (English ivy), wisteria (*Wisteria* spp.) and miscellaneous pteridophytes.

The Coweeta site is located within the Coweeta Basin of Coweeta Hydrologic Laboratory of western North Carolina. Coweeta Hydrologic Laboratory is comprised of two basins, encompassing 2185 ha in the southern Appalachian Mountains. The Coweeta Basin was extensively logged at the turn of the century and has been strictly managed since 1934 as a site for various watershed studies (USDA 1984). As a result of this management, numerous vegetation community types surround the site including a hardwood forest, a monotypic *Pinus strobus* L. (white pine) stand, and a river bottom ecosystem dominated by *Rhododendron maximum* L. The mixed deciduous and conifer forests surrounding this site cover about 80% of the surface area within a 30 km radius extending from this site. Trees representing 25 genera are found within this region. Oaks (*Quercus*) and pines (*Pinus*) together contribute about half of the total tree foliar density, whereas *Oxydendron*, *Carya*, *Liriodendron*, *Cornus*, *Acer*, *Betula*, *Robinia*, *Nyssa*, *Tsuga* and *Fagus* each contribute between 1 and 7%, and an additional 13 genera each contribute about 0.5% of the total foliar density.

Vegetation on Temple Ridge is dominated by open *Quercus gambelii* Nutt. (Gambel oak) and *Amelanchier alnifolia* Nutt. (serviceberry) shrubland. Ground cover includes *Artemisia tridentata* Nutt. (big sagebrush) and *Symphoricarpos occidentalis* Hook. (snowberry). The open canopy within 100 m of the tower had a mean canopy height of about 2 m and a mean LAI of 0.92. Landscapes within 30 km of the site are dominated by cropland and rangeland (85% of the surface area) and scrub woodland (15%). In addition to Gambel oak, aspen (*Populus tremuloides* Michx.) and spruce (*Picea* spp.) are common tree species within this region.

Methods

Thirty-min average climatological data were measured with tower-mounted sensors at each site. Quantum sensors (LI-190SA, Li-Cor, Inc., Lincoln, NE) were used to measure photosynthetically active radiation (PAR) above and within the canopy. Above-canopy wind direction and wind speed were measured with prop-vane anemometers (Model 05305-5, R.M. Young, Traverse City, MI). Mean temperature and humidity were measured with Vaisala sensors (HMP35C, Vaisala, Woburn, MA).

Belt transects were used to characterize the composition, successional status and environmental setting of vegetation communities at each site. Biological data included tree species identification, tree diameter at breast height (DBH), canopy LAI and absolute understory cover. At each site, LAI was radiometrically derived with an LI-2000 (Li-Cor, Inc.). Specific leaf density was determined for all dominant tree species from leaf area and leaf dry weight measurements on representative leaves. Canopy foliar density was estimated from LAI and specific leaf density measurements. Environmental data included measurements of terrain slope, aspect, location and elevation.

At the Fernbank Forest site, eight belt transects 10 m in width and between 80 and 340 m in length radiated from the 40-m tower at 45° intervals. Five belt transects 10 m wide by 100 m long extended from the 10-m tower at the Temple Ridge site in N, NW, W, SW and S directions which corresponded with a relatively gentle slope. Three belt transects 10 m wide and between 100 and 300 m long were used to characterize the three dominant vegetation communities at the Coweeta site. Foliar mass, crown cover and species composition were also estimated for regions with a radius extending 30 km from the center of the Temple Ridge and Coweeta sites based on data compiled by Hansen et al. (1992) and the model of Geron et al. (1994).

Rates of VOC emission from individual leaves and branches were estimated with portable, open-flow, rigid enclosures. Isoprene emission rates from individual leaves and entire branches were measured with a 0.5-l leaf enclosure and a 50-l enclosure, respectively. Hydrocarbon-free air with a CO_2 concentration of about 350 ppm was passed over the enclosed foliage at a constant rate. In most cases, both foliar area and dry weight were determined after sampling so that emissions could be expressed on both a foliar area and an oven-dried foliar mass basis. Leaf temperature, enclosure temperature, relative humidity, PAR and general sampling conditions were recorded for each enclosure measurement.

Leaves were enclosed in the cuvette of a modified gas exchange measurement system with environmental control (MPH1000, Campbell Scientific, Logan, UT) that is described in detail by Harley et al. (1996). Isoprene was analyzed by gas chromatography (GC) with a reduction gas detector (Harley et al. 1996) at Fernbank and with a fast response (< 10 s) chemiluminescence detector (Hills and Zimmerman 1990) at Temple Ridge.

Two independent methods were used to analyze VOCs in the branch enclosure samples. Samples were collected in electro-

polished stainless steel canisters by means of a metal bellows pump that generated a pressure of about 0.3 MPa. The canister samples were analyzed by GC. Sample aliquots were cryogenically preconcentrated, injected onto a DB-1 column and separated by temperature-programed GC (Model 5890, Hewlett Packard, Palo Alto, CA). Isoprene and selected monoterpenes were quantified by flame ionization detection, FID (Greenberg and Zimmerman 1984).

A second sample was collected by drawing 1 liter of the enclosure air through a multistage solid adsorbent cartridge. The adsorbents selected allowed the analysis of VOCs in the volatility range of approximately C_3 to C_{15}. After sample collection, the adsorbent cartridges were stored in an ice chest and transported to the laboratory for analysis. The trapped VOCs were released from the adsorbent cartridge by temperature-controlled thermal desorption, purged into a cryogenic freeze-out trap, and then injected onto a DB-1 GC column by flash heating. After temperature-programed GC, individual VOCs were identified by mass spectrometry (MS) in the scan mode (MSD 5970, Hewlett Packard). Semi-quantitative results were derived from the integrated total ion signals and scaled to an added internal standard. This analytical method enabled the analysis of a wide range of VOCs, including isoprene, monoterpenes, sesquiterpenes and more polar compounds such as alcohols, acids and esters.

A 40-m tower at Fernbank and a 10-m tower at Temple Ridge provided access to the atmospheric surface-layer above the canopies at these sites. Above-canopy isoprene fluxes, F (mg C m^{-2} h^{-1}), were estimated from surface-layer measurements using a vertical gradient profile method:

$$F = -K\Delta C/\Delta z, \tag{1}$$

where Δz is the vertical height difference between two sampling points (m), ΔC (mg C m^{-3}) is the difference in isoprene concentration, and K is eddy diffusivity (m^{-2} h^{-1}). Fluxes estimated from surface-layer measurements are representative of an entire forest stand (hundreds of m upwind). Daytime estimates of eddy diffusivity were calculated using the Bowen ratio, energy-balance technique (Fritschen and Simpson 1989). Nighttime estimates of K were computed using similarity theory (Kaimal and Finnigan 1994). The Bowen ratio, energy-balance estimates of K were based on measurements made with net radiometers (Model Q6, REBS, Seattle WA) and temperature and humidity sensors (Model HMP35C, Vaisala) positioned at the same heights as the air sampling systems. In addition, soil heat flux at the Temple Ridge site was estimated with heat flow transducers (Model HFT-3, REBS) and soil thermocouples (Model 107B, Campbell Scientific) positioned at soil depths between 5 and 10 cm.

Estimates of ΔC (see Equation 1) for the Temple Ridge site were obtained from ambient air samples collected in Teflon bags by means of a whole-air sampling unit similar to the system described by Zimmerman et al. (1988). Thirty-min average samples were collected simultaneously at two heights within the surface-layer using automatic timers on the pumps. Samples were analyzed for isoprene by the GC–FID method.

At Temple Ridge, fluxes were only measured during daytime periods when wind conditions (flow along the gradually sloping ridge) minimized errors caused by the terrain. At the Fernbank site, 30-min average air samples were collected by pulling air through 40-m Teflon lines into sampling loops of an automated GC–FID system deployed at the base of the tower.

Lamb et al. (1985) provide a detailed sensitivity analysis of their gradient profile measurements of isoprene fluxes in the surface-layer and estimate a total uncertainty of about ± 55%. We estimated that our daytime surface-layer flux estimates have a similar level of uncertainty, equivalent to about ± 0.7 mg C m^{-2} h^{-1} for most sampling periods. Nighttime estimates of K were more uncertain; however, the low fluxes observed during these periods resulted in uncertainties of less than ± 0.05 mg C m^{-2} h^{-1}.

Above-canopy isoprene fluxes were estimated from mixed-layer measurements by a mass balance technique:

$$F = z_iC/\tau, \tag{2}$$

where z_i is the height (m) of the mixed-layer, C is the mixed-layer average isoprene concentration (mg C m^{-3}), and τ is the lifetime (h) of isoprene due to oxidation by OH and ozone. Fluxes estimated from mixed-layer measurements are representative of an entire landscape (tens of km upwind). To develop Equation 2, we begin with a mixed-layer scalar conservation equation and assume that turbulent horizontal fluxes and mean vertical advection are negligible, the vertical flux profile is linear, the mean concentration has reached steady state and is homogeneous in space, entrainment flux is negligible, and isoprene is oxidized primarily by OH and O$_3$. These assumptions result in an estimated uncertainty of about ± 50% (cf. Guenther et al. 1996).

Estimates of z_i were made with a cross-chain LORAN atmospheric sounding system, CLASS (Lauritsen et al. 1987). The CLASS airsondes measured temperature and humidity profiles up to heights of 5 km above ground level (AGL). The mixed-layer height was identified by an inversion layer that appears as a region of increasing potential temperature with height. To estimate the lifetime of isoprene, τ, we used the OH and ozone reaction rate coefficients reported by Atkinson (1990), an estimated ozone concentration of 40 ppb (variations in O$_3$ concentration result in relatively small changes in τ), a maximum OH concentration of 4×10^6 mol cm^{-3} and the OH diurnal variation described by Lu and Khalil (1991).

Our estimate of the mean isoprene concentration, C, was determined from ambient air samples collected in Teflon bags by means of the whole-air sampling unit described above. The samplers were attached to the tether line of a helium-filled balloon, and samples were collected simultaneously for a 30-min period at two to four heights between 150 m and 1 km AGL. Samples were transferred to stainless steel canisters for transport to the laboratory and analyzed by GC–FID.

Emission model estimates of isoprene fluxes were calculated as:

$$F = \varepsilon D\gamma, \tag{3}$$

where ε is a landscape average emission potential (μg g^{-1} h^{-1}), D is total foliar density (g dry weight m^{-2}), and γ is an emission activity factor that accounts for variations in temperature and PAR. An emission potential is the emission rate expected for a particular plant species at a temperature of 30 °C and PAR of 1000 μmol m^{-2} s^{-1}. The landscape average isoprene emission potential is the weighted average ($\Sigma\varepsilon_i D_i$) of isoprene emission potentials representative of various plant types, ε_i, where D_i is the fraction of the total foliar density composed of each plant type (i).

Three models were used to estimate ε, γ and D including BEIS (Pierce et al. 1990), BEIS2 (Geron et al. 1994) and a modified form of the BEIS2 model referred to here as BEIS2.1. The field measurements were used to calculate D and D_i for the BEIS2.1 model. An additional modification for BEIS2.1 is that the *Quercus* and *Populus* genera are assigned isoprene emission potentials of 100 μg C m^{-2} h^{-1} rather than the value of 70 μg C m^{-2} h^{-1} used by BEIS2. The value of $\varepsilon = 100$ μg C m^{-2} h^{-1} reflects recent leaf-level measurements (Monson et al. 1994, Isebrands et al. 1996). Significant uncertainties are associated with each of the terms in Equation 3. Estimates calculated with the three models differed by about 25% for D and γ, and 300% for ε.

Results and discussion

Twenty-one of the plant genera found at the three field sites are not included in the extensive database of isoprene and monoterpene emission rates compiled by Guenther et al. (1994). The branch enclosure measurements identified four genera with medium or high isoprene emission rates: *Albizia, Chusqua, Mahonia* and *Pueraria* (Table 1). High monoterpene emission rates were observed for three genera: *Atriplex, Chrysthamnus* and *Sorbus*. The 34 plant species listed in Table 2 represent genera included in the database compiled by Guenther et al. (1994). Measurements for 25 of the 34 species agreed reasonably well with the emission rates reported by Guenther et al. (1994). It is not known why the emission rates measured for the other species, including *Nyssa sylvatica* Marsh. and *Carya* species, deviated considerably from the emission rates reported by Guenther et al. (1994).

A wide variety of VOCs were identified by the branch enclosure measurements at the Fernbank site (Table 3). Fifty-three terpenoid compounds were observed including isoprene, monoterpenes and sesquiterpenes. Twenty-five oxygenated compounds were found including alcohol, ether, ketone, aldehyde and acid/ester compounds. Hexenol derivatives were the most commonly observed oxygenated compounds.

Isoprene emission rates of *Q. gambelii* and *L. styraciflua* trees were measured with leaf enclosure systems that set leaf temperature at 25 °C and PAR at 1000 μmol m^{-2} s^{-1}. The algorithms of Guenther et al. (1993) were then used to estimate emission potentials (ε_i) at 30 °C of 121 $\pm$ 4 μg C m^{-2} h^{-1} ($n = 39$) for *Q. gambelii* and 70 $\pm$ 5 μg C m^{-2} h^{-1} ($n = 32$) for *L. styraciflua*. Our estimate of ε_i for *L. styraciflua* agrees with the range (70 $\pm$ 35 μg C m^{-2} h^{-1}) reported by Guenther et al. (1994), whereas our estimate of ε_i for *Q. gambelii* is at the high

Table 1. Rates of VOC emission for plant species in genera that are not included in the database complied by Guenther et al. (1994). Emission rates were categorized as: high (> 40 μg g^{-1} h^{-1}, H), medium (10–40 μg g^{-1} h^{-1}, M), low (1–10 μg g^{-1} h^{-1}, L) and negligible (< 1 μg g^{-1} h^{-1}, N) for isoprene, and high (> 3 μg g^{-1} h^{-1}, H), medium (1–2 μg g^{-1} h^{-1}, M), low (0.2–1 μg g^{-1} h^{-1}, L) and negligible (< 0.2 μg g^{-1} h^{-1}, N) for monoterpenes. Sample size, n, and location (Temple Ridge, CO, Fernbank Forest, GA, and Coweeta, NC) are indicated (n.a. = not analyzed).

Species	Isoprene	Terpenes	n	Site
Aesculus flava	N	N	2	NC
Albizia julibrissin	M	N	1	GA
Amelanchier alnifolia	N	N	1	CO
Artemisia tridentata	N	N	1	CO
Atriplex canescens	N	H	1	CO
Castanea dentata	N	N	2	NC
Catalpa spp.	N	N	1	NC
Cercocarpus montanus	N	N	1	CO
Chrysothamnus nauseosus	N	H	1	CO
Chusqua spp.	H	N	1	GA
Crataegus spp.	N	N	1	GA
Ginkgo biloba	N	(n.a.)	1	GA
Hamamelis virginiana	N	N	1	NC
Kalmia latifolia	N	N	1	NC
Mahonia spp.	M	N	1	GA
Malus domestica	N	L	1	CO
Metasequoia spp.	L	(n.a.)	1	GA
Pueraria lobata	M	L	1	NC
Sorbus scopulina	N	H	1	CO
Symphoricarpos occidentalis	N	N	1	CO
Tilia americana	L	(n.a.)	1	GA

end of the range (70 $\pm$ 35 μg C m^{-2} h^{-1}) reported by Guenther et al. (1994) for a wide variety of oak species, but agrees with the value (112 $\pm$ 7 μg C m^{-2} h^{-1}) reported by Isebrands et al. (1996) for *Quercus rubra* L. Compared to leaves growing within the canopy (i.e., shade leaves), isoprene emission potentials for leaves exposed to full sun (i.e., sun leaves) were 10 and 72% higher for *Q. gambelii* and *L. styraciflua*, respectively, indicating the importance of distinguishing between shade and sun leaves at the time of measurement (cf. Harley et al. 1996).

The fast response time of the analyzer used at Temple Ridge provided a nearly continuous record of variations in isoprene emission rate from a *Q. gambelii* leaf during a 10-h period (Figure 1). These data demonstrate that isoprene emission rate responds quickly to the fluctuations in PAR and leaf temperature that occur on cloudy days. Figure 1 also shows that the variations in isoprene emission rate observed throughout the day can be simulated by the temperature- and PAR-dependent algorithms developed by Guenther et al. (1993). The predicted and observed variations were closely correlated ($r^2 = 0.88$), and about a third of the predicted variation in emission rates was within 15% of the observed and two thirds were within 35% of the observed. Because the equations used to simulate the isoprene emission response to light and temperature are strongly nonlinear (Guenther 1993), we postulated that the

Table 2. Comparison of isoprene and monoterpene emission rates with those reported by Guenther et al. (1994). In each case, we note if measured emissions fell within the same category as the database (≈), were one category lower (↓), one category higher (↑), two or more categories lower (⇓), or two or more categories higher (⇑). Sample sizes, n, are given for both isoprene and monoterpene measurements. Study sites are the same as in Table 1.

Species	Isoprene	n	Monoterpenes	n	Site
Abies lasiocarpa	≈	1	≈	1	CO
Acer pennsylvanicum	≈	1	⇓	1	NC
Betula allegheniensis	≈	1	↓	1	CO
Carpinus caroliniana	↑	1	⇓	1	GA
Carya spp.	↑	3	⇓	2	GA, NC
Cornus florida	↑	1	⇓	1	GA
Fagus grandifolia	≈	1	⇑	1	GA
Juglans nigra	≈	1	≈	1	NC
Liquidambar styraciflua	↓	2	≈	1	GA
Liriodendron tulipifera	↑	1		0	GA
Magnolia acuminata	≈	1	⇓	1	NC
Morus alba	≈	2		0	GA
Nyssa sylvatica	↓	5	⇓	4	GA, NC
Oxydendrum arboreum	↑	3	↓	2	GA, NC
Picea engelmannii	↑	1	↓	1	CO
Pinus contorta	≈	1	≈	1	CO
Pinus strobus	≈	1	≈	1	NC
Pinus taeda	↑	1		0	GA
Plantanus occidentalis	≈	1	≈	1	NC
Populus angustifolia	≈	1	⇑	1	CO
Populus tremuloides	↓	1	⇑	1	CO
Prunus virginiana	≈	1	≈	1	CO
Quercus alba	≈	2	↓	1	GA, NC
Quercus falcata	≈	2	↓	1	GA, NC
Quercus gambelii	≈	5	↓	5	CO
Quercus prinus	↓	2	↓	2	NC
Quercus rubra	↓	2	↓	2	GA, NC
Quercus stellata	≈	1		0	GA
Quercus velutina	≈	2	≈	2	GA, NC
Robinia pseudoacacia	↑	1	↓	1	NC
Salix spp.	≈	2	↑	2	CO, NC
Sassafras albidium	≈	1	≈	1	NC
Tsuga canadensis	↑	2	↓	1	GA, NC
Ulmus rubra	↑	1	≈	1	GA

Table 3. Volatile organic compounds identified in branch enclosure emission measurements at Fernbank Forest, Atlanta, GA.

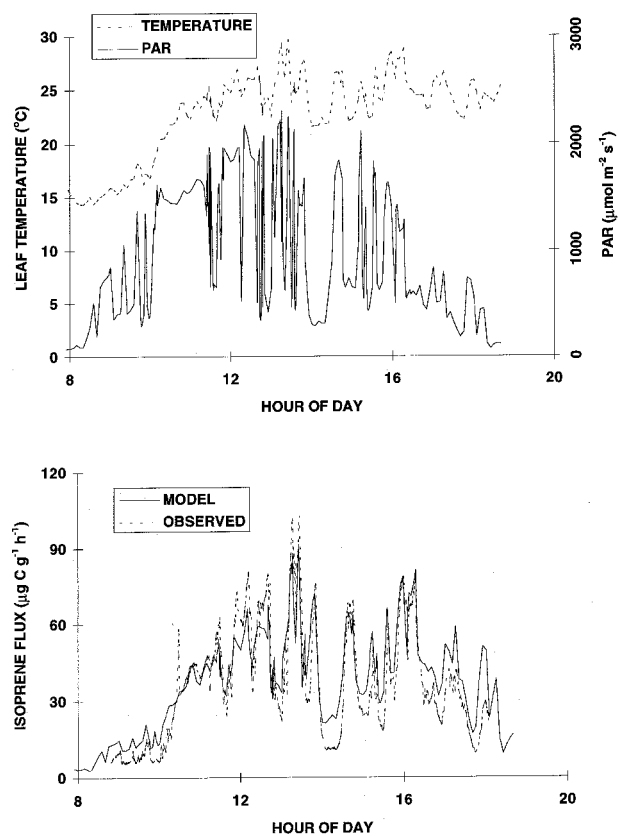| Compound class	Number identified	Examples
Hemiterpene	1	Isoprene
Monoterpene	25	α-Pinene, α-Fenchene, Camphene, β-Pinene, β-Myrcene, α-Phellandrene, 3-Carene, α-Terpine, *p*-Cymene, *d*-Limonene, *c*-Ocimene, *t*-Ocimene, *g*-Terpinene, *p*-Cymenene, Terpinolene
Sesquiterpene	27	
Alcohol	7	Ethanol, 1-Hexen-1-ol, 3-Hexen-1-ol, 1-Heptanol, 1-Octanol
Ether	2	Anisole, 2-Methylfuran
Ketone	4	Acetone
Aldehyde	7	Hexanal, 2-Hexenal
Acid/ester	5	Acetic acid, 3-Hexen-1-ol-acetate

Figure 1. Diurnal variation in 30-s average isoprene flux from a single *Quercus gambelii* leaf observed with a leaf enclosure and a fast-response sensor, and the 30-s average fluxes predicted using the leaf temperature- and PAR-dependent model of Guenther et al. (1993).

hourly average PAR and leaf temperature used for most regional or global emission models will introduce significant errors. Figure 2 demonstrates that the use of hourly average PAR and leaf temperature data resulted in a predicted isoprene flux for the 10-h period that was only 3% greater than that estimated using 30-s average PAR and leaf temperature data. Estimates for five 1-h periods were within ± 10%, and all estimates for ten 1-h periods differed by less than ± 20%. We conclude, therefore, that 1 h is a reasonable time step for regional biogenic VOC emission models.

Model evaluations

Surface-layer measurements were used to evaluate stand-scale (hundreds of m) isoprene fluxes predicted by the BEIS2.1 model at the Fernbank and Temple Ridge sites. The BEIS and

BEIS2 models predict fluxes on larger spatial scales and so cannot be compared directly with stand-scale fluxes. The landscape at Temple Ridge is representative of an open shrub canopy. The mean flux of 1.95 mg C m^{-2} h^{-1} predicted by the BEIS2.1 model is about 50% higher than the flux based on
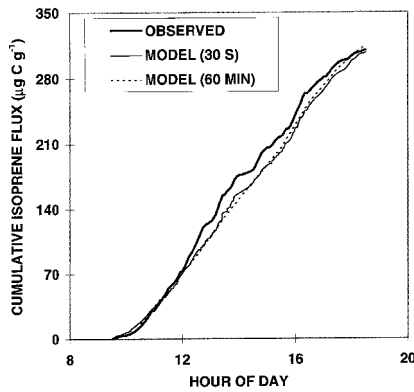
Figure 2. Cumulative isoprene flux from a single *Quercus gambelii* leaf predicted using the model of Guenther et al. (1993) and the temperature and PAR shown in Figure 1 with 30-s and 1-h averaging times.

surface-layer measurements (Equation 1), which is within the uncertainty associated with the surface-layer flux estimates.

Fluxes were measured at Fernbank up to 12 times daily over a period of 2 weeks to provide a stand-level record of diurnal variation in isoprene fluxes (Figure 3). Observed variation in fluxes generally followed that predicted by the algorithms developed by Guenther et al. (1993). Table 4 shows that the mean flux for morning, evening and nighttime periods is 0.07 mg C m^{-2} h^{-1} which is 5% or less of daytime fluxes. The heterogeneity of species composition and total foliar mass within the forest stand at the Fernbank site resulted in significant differences in the fluxes predicted by the BEIS2.1 model for different wind directions (i.e., different source regions). Transect average estimates of total foliar mass, D, varied from 189 to 323 g m^{-2}, and the fraction of isoprene emitting foliage, the sum of D_i estimated for *Quercus, Liquidambar* and *Nyssa*
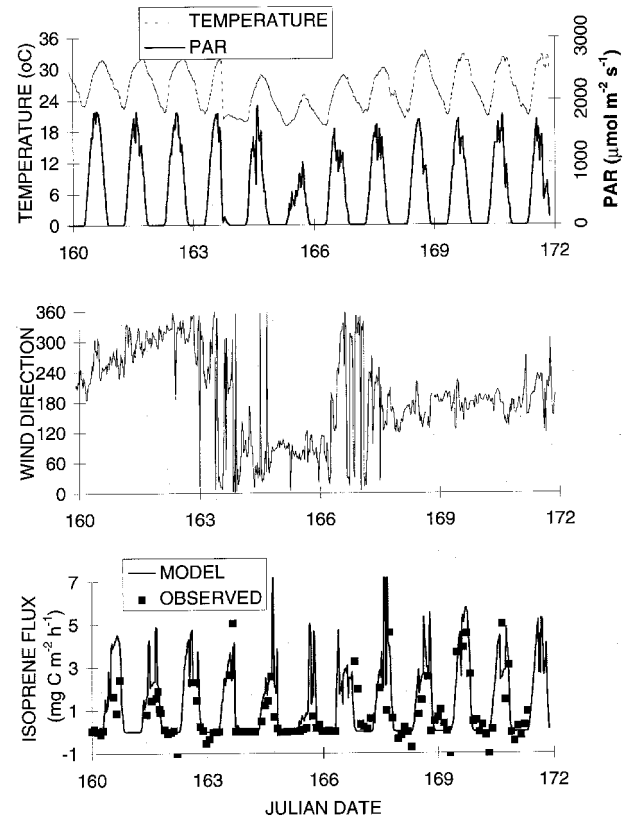

Figure 3. Diurnal variation in 30-min average isoprene fluxes observed with surface-layer measurements at the Fernbank forest site and predicted by the BEIS2.1 model.

species, ranged from 0.19 to 0.48 for the eight transects radiating from the Fernbank tower. These variations in D and D_i resulted in a mean flux of 3.34 mg C m^{-2} h^{-1} predicted for sampling periods with northwest, southeast, south and south-

Table 4. Evaluation of the BEIS2.1 emission model with stand-scale (hundreds of m) fluxes estimated from surface-layer measurements (Equation 1).

Location	Temple Ridge, CO	Fernbank, GA	Fernbank, GA	Fernbank, GA
Conditions	All	Night, evening, morning	Daytime, W, N, NE winds	Daytime, NW, SE, S, SW winds
Vegetation community	Oak scrub	Mixed forest	Mixed forest	Mixed forest
Number of sampling periods	9	72	17	21
Mean tree foliar density, D (g m^{-2})	92	237	211	253
Mean tree species composition (D_i)				
Liquidambar	0.0	0.06	0.03	0.08
Nyssa	0.0	0.01	0.03	0.01
Quercus	0.56	0.20	0.12	0.18
Nonisoprene spp.	0.0	0.73	0.82	0.73
Ambient conditions (mean and range)				
PAR (μmol m^{-2} s^{-1})	1500 (950 to 1700)	29 (0 to 286)	1100 (380 to 1780)	990 (400 to 1700)
Temperature (°C)	22.0 (15.9 to 24.4)	24.0 (19 to 30.5)	28.1 (20.2 to 32.1)	29.1 (22.3 to 32.7)
Isoprene flux estimates (mg C m^{-2} h^{-1})				
Surface-layer measurements	1.29 ± 0.21	0.07 ± 0.08	1.45 ± 0.29	2.48 ± 0.55
BEIS2.1 Model	1.95 ± 0.20	0.05 ± 0.02	1.92 ± 0.22	3.34 ± 0.27

west winds that was 73% higher than the mean flux of 1.92 mg C m^{-2} h^{-1} predicted for sampling periods with west, north and northeast winds. The observed flux for sampling periods with northwest, southeast, south and southwest winds was 71% higher than the observed flux for other wind directions. These data demonstrate that variations in species composition and foliar mass can result in significant spatial variations in isoprene emission within a forest stand. The mean predicted daytime flux was about 30% higher than the observed flux and was within the uncertainty limits (55%) associated with these measurements.

Regional and global models require fluxes on scales of tens of km. These landscape scale fluxes can be estimated from mixed-layer measurements (Equation 2) (Table 5). The observed mean landscape scale flux at Coweeta was more than twofold higher than the observed mean flux at Temple Ridge. Mean temperatures were about 5 °C higher at Coweeta than at Temple Ridge, but PAR values were similar at the two sites. The mean observed flux at Temple Ridge was an order of magnitude higher than the flux predicted by the BEIS model. Fluxes predicted by the BEIS2.1 model were 44% higher than fluxes predicted by the BEIS2 model but were still 20% lower than the mean observed isoprene flux of 3.0 ± 2.1 mg C m^{-2} h^{-1} ($n = 8$). The mean observed isoprene flux of 6.7 ± 4.4 mg C m^{-2} h^{-1} ($n = 12$) for the Coweeta site was fivefold higher than the mean flux predicted by the BEIS model. The BEIS2 and BEIS2.1 model predictions are both within about ± 20% of the observed flux. These results show that the BEIS model substantially underestimates observed fluxes and that the BEIS2 and BEIS2.1 model predictions are within the uncer-

tainty limits (50%) associated with observed fluxes.

We conclude that existing databases can provide isoprene and monoterpene emission rate potentials, with a range of about ± 50%, for the dominant plant species at these three woodland sites. A factor of three or more difference was found for a few plant species. These species contribute only a small portion of the total foliar mass at these sites but may be important in other landscapes. Sesquiterpenes and oxygenated VOCs were emitted from many plant species including some of the dominant trees at each site. Existing models can simulate diurnal variations in isoprene emissions from an individual leaf and from an entire forest stand. BEIS2 and BEIS2.1 model predictions agree reasonably well with observed area-average fluxes at all sites, but the BEIS model underestimates fluxes by a factor of five or more.

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Table 5. Evaluation of isoprene emission models with landscape-scale (tens of km) fluxes estimated from mixed-layer measurements (Equation 2).

Site	Temple Ridge, CO	Coweeta, NC
Landscape	Shrub oak–aspen rangeland	Mixed deciduous forest
Number of sampling periods	8	12
Tree foliar density, D (g m^{-2})	63	335
Species composition (D_i)		
Nyssa spp.	0.0	0.017
Picea spp.	0.038	0.0
Populus spp.	0.366	0.0
Quercus spp.	0.514	0.370
Robinia spp.	0.0	0.022
Nonisoprene spp.	0.082	0.591
Ambient conditions (mean and range)		
PAR (μmol m^{-2} s^{-1})	1160 (800 to 1410)	1230 (440 to 1700)
Temperature (°C)	22.8 (17 to 27)	27.7 (25 to 30)
Isoprene flux estimates (mg C m^{-2} h^{-1})		
Mixed-layer measurements	3.01 ± 1.90	6.74 ± 4.36
BEIS Model	0.34	1.31
BEIS2 Model	1.70	5.38
BEIS2.1 Model	2.44	7.65

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