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BIOGENIC VOLATILE ORGANIC COMPOUND EMISSIONS (BVOCs)

II. LANDSCAPE FLUX POTENTIALS FROM THREE CONTINENTAL SITES IN THE U.S.

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ABSTRACT

Landscape flux potentials for biogenic volatile organic compounds (BVOCs) were derived for three ecosystems in the continental U.S. (Fernbank Forest, Atlanta, GA; Willow Creek, Rhinelander, WI; Temple Ridge, CO). Analytical data from branch enclosure measurements were combined with ecological survey data for plant species composition and biomass. Other quantitative flux measurements at the leaf and landscape level were incorporated to scale the results from the enclosure measurements to the landscape level. Flux estimates were derived by using a one week ambient temperature and light record (30 min time resolution) and adjusting all emission rates to these conditions with temperature and light correction algorithms. © 1999 Elsevier Science Ltd. All rights reserved

Although uncertainties due to the branch enclosure technique limit the conclusions, tentative data which is valuable to define future research attention and needs is derived. Scaled to the landscape level, this technique allowed identification of those plant species that are responsible for the major fraction of the total BVOC landscape flux and to identify the major compounds emitted. It was found that for each of the sites investigated, a very few selected plant species contribute to the major fraction of the total emissions. Northern red oak, post oak, white oak and American beech accounted for 71% of the total BVOC emissions at the Atlanta site. Quaking aspen and

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Northern red oak were the dominating species at the Wisconsin site with 68% of the total emissions. At the Colorado site, Gambel oak and service berry made up 86% of the BVOC emissions. Total daily average BVOC landscape fluxes determined by this method were 2.0, 4.5 and 2.4 mgC $m^{-2}h^{-1}$ for the Atlanta, Wisconsin and Colorado sites, respectively. The contribution of isoprene to this overall BVOC flux was calculated to be 45, 38 and 54% at the three sites, respectively.

The branch enclosure technique combined with ecological surveying and landscape-scale isoprene flux measurements proved to be a valuable tool for screening a high number of plant species and for identifying the major and most important emitters for a more thorough investigation. The obtained data, the suitability of this approach and its limitation to derive BVOC fluxes on the ecosystem level are critically evaluated and factors introducing experimental errors are identified.

1. INTRODUCTION

The role of emissions of biogenic volatile organic compounds (BVOCs) in atmospheric processes and the formation of tropospheric ozone have been extensively discussed (Fehsenfeld et al., 1992; Helmig et al., 1998). In the summer of 1993, BVOC emissions from vegetation were measured by a variety of different analytical approaches in three ecosystems in the continental US: (1) Fernbank Forest, an urban forest preserve in Atlanta, GA, (2) Willow Springs, a mixed deciduous and coniferous forest in the Chequamegon National Forest in Northern Wisconsin and (3) Temple Ridge, a mixed shrub oak woodland in western Colorado. Studies performed included cuvette experiments for the measurement of light and temperature response of emissions, branch enclosure experiments, tower gradient measurements, and profiling of the mixed boundary layer from a tethered balloon sampling platform. Selected results from these studies have been reported (Greenberg et al., 1994; Guenther et al., 1996a; Isebrands et al., 1998). Here, we use data from the branch enclosure experiments reported by Helmig et al. (1998) to derive landscape scale flux potentials at three sites using the results of extensive biomass surveys, ambient temperature and light data series, and scaling to measured landscape-level isoprene fluxes. This approach relies on the current knowledge of temperature and light dependence of isoprene and other BVOC emission rates and developed algorithms to scale the data from the experimental conditions to normalized standard values.

2. EXPERIMENTAL

At each of the three sites investigated transects were used to characterize the composition, successional status, and environmental setting of vegetation communities. Biological data included tree species identification, tree diameter at breast height (DBH) (~1.5 m), canopy leaf area index (LAI), and understory cover. 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.

Site Description

Fernbank Forest. The Fernbank Forest site is within a 25 ha mixed hardwood and conifer woodland located in suburban East Atlanta, GA (latitude 33° 24'N, longitude 84° 14'W) and is managed by the DeKalb County School System. Fernbank Forest has been preserved since the early 1800s and represents a mature remnant stand of natural Georgia Piedmont forest (Skeen, 1974). Mean canopy height is 30 m and mean overstory LAI is 4.8 m^2 m^{-2} (integrated leaf area/ground area). Dominant tree species include *Quercus alba* (white oak), *Liquidambar styraciflua* (sweet gum), *Liriodendron tulipifera* (tulip poplar) and *Pinus taeda* (loblolly pine). Major understory plants include *Hedera helix* (English ivy), *Wisteria sp.* (Wisteria), and several pteridophytes. Field measurements at this site were performed during June 1993. Ambient air and landscape flux measurements were also made during this experiment and are described by Guenther et al. (1996).

Willow Springs. The Willow Springs site near Lac du Flambeau is located in the Chequamegon National Forest in Northern Wisconsin (45° 48' N; 90° 04'W). The site is surrounded by a mosaic of forest and bog forest, and bog communities. The forests are comprised mainly of aspen (*Populus tremuloides*), red maple (*Acer rubrum*), and eastern hemlock (*Tsuga canadensis*) with overstory LAIs ranging from 3.1 to 5.5. Mean canopy height is about 20 m in the forests and 4 m in the bog forests. Bog forests overstory is dominated by black spruce (*Picea mariana*) and tamarack (*Larix laricina*) with overstory LAIs of 0.3 to 0.4. The majority of the living biomass in the bogs and bog forests is in the understory vegetation, primarily *Sphagnum* mosses and sedges (*Eriophorum* spp.). Measurements at this site were performed during July 1993 (Isebrands et al., 1998).

Temple Ridge. The Temple Ridge site is located at a Federal Aviation Administration (FAA) communication relay tower site (40° 25' N, 107° 14' W). Overstory vegetation on Temple Ridge is characterized by open *Quercus gambelii* (Gambel oak) and *Amelanchier alnifolia* (serviceberry) shrubland. Ground cover includes *Artemisia tridentata* (big sagebrush) and *Symphoricarpos occidentalis* (snowberry). The open canopy has a mean height of about 2 m and a mean overstory LAI of 0.92. Landscapes within 30 km of the site are dominated by cropland and range land (≈ 50% of the surface area) and scrub woodland (≈ 15%). In addition to Gambel oak, aspen (*Populus tremuloides*) and spruce (*Picea spp.*) are common tree species in this region. This experiment was conducted during August 1993. Other flux measurements performed at the landscape level are described by Guenther et al. (1996).

Ecological Characterization

Representative vegetation communities at each site were identified, gridded, then sampled in 10 m x 10 m contiguous plots along 100-200 m transects. In each plot, all trees were identified, and the stem DBH and stem height was recorded. Trees were defined as living individuals ≥ 4 cm DBH and ≥ 1.5 m tall. Smaller individuals (saplings) were identified and counted. Tree layer LAI, understory layer LAI, shrub and non-woody understory species cover, slope, and elevation were also recorded for each plot. Slope and tree height were measured using a clinometer, elevation was measured using an altimeter. LAI of green foliage was determined using two (above and below canopy) LAI-2000 meters (LICOR, Lincoln NE). Four LAI measurements were taken per plot, two at 1.5 m height to determine tree layer LAI and two on the ground to determine understory LAI. Conifer LAI measurements were adjusted according to LICOR manual procedures.

Branches of each tree species occurring in the transects were collected and measured in the laboratory for leaf area, using a leaf area meter (CID, Moscow, ID) and leaf dry weight, by drying leaves for 24 h at 50°C and weighing. Data were averaged to determine the conversion ratio (CR [cm^2g^{-1}]) of leaf area to leaf biomass for each species.

Basal area for an individual tree ($BA_i[cm^2]$) was calculated as

$$BA_i = \pi\,(DBH/2)^2 \qquad (1)$$

Leaf area index for a given tree species (LAI_{spl}) in each plot was calculated as

$$LAI_{spl} = LAI_{tl}\,(BA_{spl}/\Sigma BA_i) \qquad (2)$$

where LAI_{tl} is the measured tree layer LAI and BA_{spl} is the sum of BA_i for that species in the plot. It is recognized that this method may underestimate (by ≈ 25%) the LAI of broad-crowned trees such as oaks and overestimate (by ≈ 35%) the LAI of narrow-crowned trees such as sweetgum and tulip poplar (Geron et al., 1994).

Green foliage dry biomass for a given species ($FB_{spl}[g]$) was calculated as

$$FB_{spl} = LAI_{spl} \bullet CR_{spl} \qquad (3)$$

where CR_{spl} is the empirically derived leaf area to leaf biomass conversion ratio for that species.

For the Willow Springs site, Landsat Multi-Spectral Scanner (MSS) images acquired on May 11, 1989 and October 8, 1991 were used in concert with transect data for an overall areal estimation of species composition. The Landsat data was analyzed using the ENvironment for Visualizing Images (ENVI version 1.1; RSI, Boulder, CO) software package to classify ground cover types within a 14 km radius of the site. The two images were corrected prior to quantitative analysis to minimize atmospheric effects on the radiometric signal. In addition, the two images were co-registered with the use of ground control points and USGS topographic quadrangle maps to enable multi-temporal pixel-to-pixel comparisons. This co-registration procedure provided eight data points at each pixel (2 samples with 4 spectral channels each) for spectral analysis and classification. The multi-temporal nature of these data aided classification by inherently incorporating changes in vegetation phenology (Wolter et al., 1995).

Seven ground training areas (open water, mixed conifers, black spruce bog forest, open bog, aspen-dominated hardwoods, mixed hardwoods, and grassy fields) were selected for image classification purposes using a USFS vegetation survey map as a digital overlay (USFS, Park Falls, WI). The average radiometric signal from each training area was used to classify the remainder of the image pixels based on a spectral angle mapper (SAM) classification procedure. The SAM classification assigns classes based on the highest similarity between an individual pixel's spectrum and each training class average spectrum (Kruse et al., 1993).

At this site, the seven subjectively located 100 m^2 belt transects used for quantifying species composition and biomass of various forest types on the ground all fell within four of the seven cover classes. Three transects were classified as aspen-dominated hardwoods, two transects were classified as mixed hardwoods, and one transect each fell into the mixed conifer and black spruce bog classes, respectively. To estimate the overall biomass of each tree species within the sample area, transect data within each class were averaged and multiplied by the respective absolute class percentage cover. In total, these four classes comprised 78% of the ground cover types within the sample area, with open water, open bog, and grassy fields covering the remainder of the area. For comparison, a forest inventory database of the region that contains the study area estimates that these four forest classes comprise 85% of the ground cover (Hansen et al., 1992). Within a 14 km radius of the study site, the aerial coverage of all seven ground classes were (in %) grassy fields (1), open bog (6), mixed conifers (7), mixed hardwoods (11), open water (12), black spruce bog (21) and aspen-dominated hardwoods (39).

3. RESULTS

Table 1 lists all plant species sampled and their percentage leaf biomass at the three sites as determined from the transect and remote sensing analyses. A number of the plant species that were growing at the sites were not present in any of the transects. These species are listed with the biomass < 0.01% to indicate that they were present and sampled in the respective area. The majority of these species were exotics (i.e. they were planted, such as Gingko at Fernbank). The reason these species were sampled was purely for inventory purposes. The total percentage of the overall tree/shrub leaf biomass in the transect area that was covered by the branch enclosure measurements was 92.8%, 92.3%, and 100% for Fernbank Forest, Willow Springs and Temple Ridge, respectively.

Cumulative relative landscape fluxes (CLF) were derived by multiplying the normalized (30°C/1000 μmol $m^{-2}s^{-1}$) BVOC/species emission rates (ER) from the branch enclosure experiments (Tables 2 - 4 in Helmig et al. (1998)) by the biomass contribution (%BM) of each plant species (i) (Table 1) and summarizing for each site:

Table 1

Vegetation species sampled at each field site and their absolute and relative biomass abundances.

Species		**Fernbank***		**Willow Springs****		**Temple Ridge***	
Common name	Latin name	Total Biomass (g/m2)	Rel. Biomass (%)	Total Biomass (g/m2)	Rel. Biomass (%)	Total Biomass (g/m2)	Rel. Biomass (%)
Alternate-leaved dogwood	*Cornus alternifolia*	0.09	0.03	<0.01	<0.01		
American beech	*Fagus grandifolia*	7.7	3.0				
American hornbeam; Ironwood	*Carpinus caroliniana*	7.4	2.9				
Apple	*Malus sp.*					<0.01	<0.01
Ash	*Fraxinus sp.*			12	7.1		
Balsam fir	*Abies balsamea*			4.3	2.5		
Bamboo	*Chusqua sp.*	3.9	1.5				
Basswood	*Tilia americana*	3.6	1.4	3.7	2.2		
Beaked hazelnut	*Corylus cornuta*			3.3	2.0		
Big sagebrush	*Artemesia tridentata*					12	9.2
Big-toothed aspen	*Populus grandidentata*			<0.01	<0.01		
Black ash	*Fraxinus nigra*			1.7	1.0		
Black cherry	*Prunus serotina*	1.2	0.45	0.07	0.04		
Black gum	*Nyssa sylvatica*	2.2	0.87				
Black oak	*Quercus velutina*	2.9	1.2				
Black spruce	*Picea mariana*			15	8.6		
Bog heather	*Chamaedaphne calyculata*			<0.01	<0.01		
Box elder	*Acer negundo*	0.80	0.31				
Chinese Spruce	*Picea asperata*			<0.01	<0.01		
Choke cherry	*Prunus virginiana*			0.08	0.05	1.3	0.98
Cottongrass	*Eriophorum Sp.*			<0.01	<0.01		
Dawn redwood	*Metasequoia sp.*	4.6	1.8				
Downy serviceberry	*Amelanchier arborea*			0.29	0.17		
Eastern hemlock	*Tsuga canadensis*	0.01	<0.01	21	12		
Elm	*Ulmus sp.*			0.02	0.01		
Engelmann spruce	*Picea engelmannii*					<0.01	<0.01
Flowering dogwood	*Cornus florida*	1.5	0.58				
Four-winged saltbush	*Atriplex canescens*					3.8	2.9
Gambel's oak	*Quercus gambelii*					73	56
Gingko	*Ginkgo biloba*	<0.01	<0.01				
Green ash	*Fraxinus pennsylvanica*			0.40	0.24		
Hawthorn	*Crataegus flava*	0.01	<0.01				
Hickory	*Carya sp.*	10	4.1				
Hop hornbeam	*Ostrya virginiana*			0.33	0.20		
Labrador tea	*Ledum groenlandicum*			<0.01	<0.01		
Loblolly pine	*Pinus taeda*	40	16				
Lodgepole pine	*Pinus contorta*					<0.01	<0.01
Magnolia	*Magnolia sp.*	0.01	0.01				
Mimosa	*Albizia julibrissin*	3.4	1.3				
Mountain mahogany	*Cercocarpus montanus*					4.2	3.2
Northern red oak	*Quercus rubra*	18	7.1	6.8	4.0		
Northern white cedar	*Thuja occidentalis*			1.7	1.0		
Paper birch	*Betula papyrifera*			5.8	3.4		
Persimmon	*Diospyros virginiana*	<0.01	<0.01				
Pin cherry	*Prunus pensylvanica*			0.05	0.03		
Post oak	*Quercus stellata*	14	5.4				
Quaking aspen	*Populus tremuloides*			32	19		
Rabbitbrush	*Chrysothamnus nauseosus*					<0.01	<0.01
Raspberry	*Rubus sp.*			<0.01	<0.01		
Red maple	*Acer rubrum*	2.6	1.0	35	21		
Red mulberry	*Morus rubra*	3.5	1.4				
Red pine	*Pinus resinosa*			<0.01	<0.01		
Red-osier dogwood	*Cornus stolonifera*			0.01	<0.01		
Redbud	*Cercis canadensis*	4.3	1.7				
Sassafras	*Sassafras albidium*	<0.01	<0.01				
Serviceberry	*Amelanchier alnifolia*					27	21
Slippery elm	*Ulmus rubra*	0.15	0.06				
Snowberry	*Symphoricarpos occidentalis*					8.7	6.7
Sourwood	*Oxydendrum arboreum*	4.2	1.6				
Southern magnolia	*Magnolia grandiflora*	2.3	0.90				
Southern red oak	*Quercus falcata*	<0.01	<0.01				
Speckled alder	*Alnus rugosa*			<0.01	<0.01		
Sphagnum moss	*Sphagnum sp.*			(unknown)	(unknown)		
Subalpine fir	*Abies lasiocarpa*					<0.01	<0.01
Sugar maple	*Acer saccharum*	<0.01	<0.01	16	9.4		
Sweet gum	*Liquidambar styraciflua*	14	5.6				
Tamarack	*Larix laricina*			0.04	0.02		
Tulip poplar	*Liriodendron tulipifera*	79	31				
Umbrella magnolia	*Magnolia tripetala*	0.07	0.03				
Water oak	*Quercus nigra*	1.8	0.73				
White ash	*Fraxinus americana*			0.71	0.42		
White mulberry	*Morus alba*	0.14	0.06				
White oak	*Quercus alba*	20	7.9				
White pine	*Pinus strobus*			<0.01	<0.01		
White spruce	*Picea glauca*			0.01	0.01		
Willow	*Salix sp.*			<0.01	<0.01	<0.01	<0.01
Yellow birch	*Betula allaghenienses*			8.5	5.0		
Unknown	Unknown			1.1	0.63		
	All Species	250	100	170	100	130	100

* Denotes sites where biomass estimates were based solely on ecological transect data.

** Denotes site where biomass estimates were based on transect data weighted by a remote sensing classification (see text).

$$CLF = \Sigma\,(ER_{BVOCi} * \%BM_i) \qquad (4)$$

The respective data for isoprene were then normalized to the estimated and normalized (30°C/1000 μmol $m^{-2}s^{-1}$) landscape flux (LF) for isoprene:

$$LF_{isoprene} = \Sigma\,(ER_{Isoprene,i} * \%BM_i) \qquad (5)$$

Absolute landscape fluxes of other BVOCs were then calculated by scaling to the respective isoprene data:

$$LF_{BVOC} = \frac{\Sigma\,(ER_{BVOCi} * \%BM_i)}{\Sigma\,(ER_{isopene,i} * \%BM_i)} * LF_{isoprene} \qquad (6)$$

Different techniques were used at the three sites to measure isoprene landscape fluxes (Isebrands et al., 1998; Guenther et al., 1996). At Fernbank Forest, tower gradient flux measurements of isoprene (Greenberg et al., 1994) gave a normalized isoprene flux of approximately 2.3 mg C $m^{-2}h^{-1}$ (mean value for all wind directions). This method covers emissions from the direct tower environment with a footprint area of approximately 300 m radius around the tower base. For the Willow Springs site, we used landscape scale isoprene flux measurements from sampling with a tethered balloon sampling platform. The balloon measurements cover a much larger footprint area than tower measurements. Footprint areas with a radius of approximately 10 km can be achieved. More detailed descriptions of these measurements are given by Guenther et al. (1996) and Isebrands et al. (1998). The normalized mean isoprene flux determined here was 4.4 mg C $m^{-2}h^{-1}$. For the Temple Ridge site isoprene gradient measurements from a 10 m high radio tower were used, resulting in a mean and normalized isoprene flux of 3.3 mg C $m^{-2}h^{-1}$.

The calculated landscape emission rates for all compounds at the three sites are tabulated in Table 2. The data listed in the first column for each site is normalized for the environmental conditions of 30°C and 1000 μmol $m^{-2}s^{-1}$. Actual BVOC emissions will vary because of changes in ambient temperature and light. While most BVOC emissions respond primarily to temperature, isoprene has been shown to respond to light; isoprene emissions subside during the night. Over a given diurnal scenario of light and temperature conditions, non-isoprene BVOC emissions will therefore have a significant higher contribution to the total BVOC flux than at standard conditions of 30°C and 1000 μmol $m^{-2}s^{-1}$. In order to demonstrate the magnitude of this effect and to derive correction factors from standard conditions to actual ambient conditions, estimates of total and percentage BVOC fluxes under real-ambient conditions were derived by the approach detailed in the following.

Figure 1 shows a one-week record of PAR and temperature recorded at 30 min intervals at the Fernbank Forest site during the experimental week in June 1993. These parameters were measured on the tower at 40 m above

Table 2
Landscape flux potentials for all VOCs identified (in ugC/(m2h)) at the three sites for 30oC/1000 umol/(m2s) and adjusted for a one-week record of ambient temperature and light conditions.

Compound	Fernbank Forest				Willow Springs				Temple Ridge			
	30/1000		ambient		30/1000		ambient		30/1000		ambient	
	total	% of total	total	% of total	total	% of total	total	% of total	total	% of total	total	% of total
Ethanol	3	0.1	2	0.1					20	0.4	15	0.6
Acetone	8	0.2	6	0.3	5	0.1	04	0.1	19	0.4	14	0.6
Pentane	4	0.1	3	0.1								
Isoprene	2300	61	890	45	4400	53	1700	38	3300	69	1300	54
Methacrolein	0.7	0.0	0.5	0.0					7	0.1	5	0.2
Methylvinylketone	0.7	0.0	0.5	0.0								
2-Methylfuran	1.4	0.0	1	0.1	2	0.0	1	0.0				
Acetic Acid	5.2	0.1	4	0.2					2	0.0	1	0.1
2-Ethylfuran	12	0.3	9	0.4	26	0.3	19	0.4				
n.i. (710.5)	3	0.1	2	0.1								
n.i. (732.7)									6	0.1	4	0.2
n.i. (757.5)									0.1	0.0	0.1	0.0
2-Methyl-butanoic acid methyl ester (t)	7	0.2	5	0.3								
n.i. (768.8)									0.1	0.0	0.1	0.0
2-Methyl-4-pentenal (t)					9	0.1	7	0.1	0.1	0.0	0.1	0.0
Hexanal	13	0.3	10	0.5	15	0.2	11	0.2	6	0.1	4	0.2
1-Octene									2	0.0	1	0.1
C7H10O isomer (t)	0.6	0.0	0.4	0.0								
C7H10O isomer (t)	0.5	0.0	0.4	0.0								
2-Hexyn-1-ol (t)	41	1.1	30	1.5								
2-Hexenal					250	3.0	190	4.2				
n.i. (835.0)	0.4	0.0	0.3	0.0								
cis-3-Hexene-1-ol	47	1.2	34	1.7	1700	20	1200	27	260	5.4	190	7.9
trans-3-Hexene-1-ol (t)	7	0.2	5	0.3	27	0.3	20	0.4				
1-Hexanol	0.2	0.0	0.1	0.0					0.1	0.0	0.1	0.0
C10H16	0.1	0.0	0.1	0.0								
1-Nonene									4	0.1	3	0.1
Methoxybenzene (Anisole)	0.5	0.0	0.4	0.0								
cis-3-Hexene-1-ol-formate					17	0.2	12	0.3				
Santolina Triene									3	0.1	2	0.1
MT (907.3)					3	0.0	2	0.0				
Dimethyl-3(5H)-furanone isomer (t)									12	0.3	9	0.4
Dimethyl-3(5H)-furanone isomer (t)									23	0.5	17	0.7
5-Ethyl-2(5H)-furanone (t)					20	0.2	15	0.3	20	0.4	15	0.6
Tricyclene					7	0.1	5	0.1	45	0.9	33	1.4
a-Thujene	2	0.1	1	0.1	8	0.1	6	0.1	6	0.1	4	0.2
MT (931.0)	1.3	0.0	1	0.0								
Benzaldehyde	0.7	0.0	0.5	0.0	8	0.1	6	0.1	0.1	0.0	0.1	0.0
a-Pinene	77	2.0	57	2.8	200	2.4	150	3.3	53	1.1	39	1.6
MT (940.6)					3	0.0	2	0.0				
1-Heptanol	0.2	0.0	0.1	0.0								
a-Fenchene	3.4	0.1	2	0.1	14	0.2	10	0.2	0.3	0.0	0.2	0.0
Camphene	43	1.1	32	1.6	180	2.2	130	2.9	17	0.4	12	0.5
Phenol	0.2	0.0	0.1	0.0					0.1	0.0	0.1	0.0
6-Methyl-5-heptene-2-one					0.1	0.0	0.1	0.0				
MT (967.1)	3	0.1	2	0.1								

Table 2 (continued)

Artemiseole									5.9	0.1	4	0.2
Sabinene	4	0.1	3	0.1					0.4	0.0	0.3	0.0
n.i. (973.5)	3	0.1	2	0.1	1	0.0	1	0.0				
b-Pinene	12	0.3	9	0.4	75	0.9	55	1.2	3.9	0.1	3	0.1
1-Methylethenylbenzene	0.2	0.0	0.1	0.0								
MT (983.1)									0.7	0.0	0.5	0.0
Octanal	10	0.3	7	0.4	6	0.1	4	0.1	14	0.3	10	0.4
b-Myrcene	19	0.5	14	0.7	19	0.2	14	0.3	0.6	0.0	0.4	0.0
cis-3-Hexene-1-ol-acetate	68	1.8	50	2.5	740	8.9	540	12	610	13	440	18
trans-3-Hexene-1-ol-acetate	12	0.3	9	0.4	8	0.1	6	0.1				
a-Phellandrene	22	0.6	16	0.8	16	0.2	12	0.3	2.3	0.0	2	0.1
3-Carene	1	0.0	0.7	0.0	35	0.4	26	0.6				
n.i. (1012.7)	0.7	0.0	0.5	0.0	7	0.1	5	0.1				
a-Terpinene	80	2.1	59	2.9	22	0.3	16	0.4	2.2	0.0	2	0.1
p-Cymene	120	3.2	88	4.4	74	0.9	54	1.2	11	0.2	8	0.3
1,8-Cineole									6.2	0.1	5	0.2
n.i. (1031.1)	0.3	0.0	0.2	0.0								
d-Limonene	97	2.6	71	3.6	160	1.9	120	2.7	20	0.4	15	0.6
c-Ocimene	66	1.7	48	2.4								
Acetophenone	0.1	0.0	0.1	0.0								
t-Ocimene	100	2.6	73	3.7					45	0.9	33	1.4
g-Terpinene	59	1.6	43	2.2	12	0.1	09	0.2	2	0.0	1	0.1
1-*Octanol*	0.2	0.0	0.1	0.0								
MT (1067.0)	2	0.1	1	0.1								
Artemisia Alcohol									12	0.3	9	0.4
Fenchone					3	0.0	2	0.0				
p-Cymenene	29	0.8	21	1.1	29	0.3	21	0.5	1	0.0	1	0.0
MT (1083.7)	0.4	0.0	0.3	0.0								
Terpinolene	7	0.2	5	0.3	20	0.2	15	0.3	3	0.1	2	0.1
MT (1087.2)	23	0.6	17	0.8								
Nonanal	21	0.6	15	0.8	45	0.5	33	0.7	28	0.6	21	0.9
a-Thujone					2	0.0	1	0.0				
b-Fenchol					2	0.0	1	0.0				
n.i. (1110.0)	0.3	0.0	0.2	0.0								
n.i. (1113.3)									15	0.3	11	0.5
C10H14									0.4	0.0	0.3	0.0
Camphor					1	0.0	1	0.0	10	0.2	7	0.3
n.i. (1154.0)									36	0.8	26	1.1
Borneol					1	0.0	1	0.0	1	0.0	1	0.0
cis-3-Hexene-1-ol-n-butyrate	15	0.4	11	0.6	18	0.2	13	0.3	8	0.2	6	0.2
4-Terpineol									4.0	0.1	3	0.1
Methyl *salicylate*	2	0.1	1	0.1	4	0.0	3	0.1				
Decanal	1	0.0	0.7	0.0								
cis-3-Hexene-1-ol-iso-valerate					10	0.1	7	0.2	3.0	0.1	2	0.1
Thymol					1	0.0	1	0.0				
Isobornyl acetate					40	0.5	29	0.7				
Dodeceneol isomer (t)	0.9	0.0	0.7	0.0								
Hexene-ol-hexanoate isomer									2.0	0.0	1	0.1
n.i. (>1300)	5	0.1	4	0.2								
Total Sesquiterpenes	440	12	320	16	5	0.1	4	0.1	140	3	103	4
Total:	3800	100	2000	100	8300	99	4500	100	4800	100	2400	99

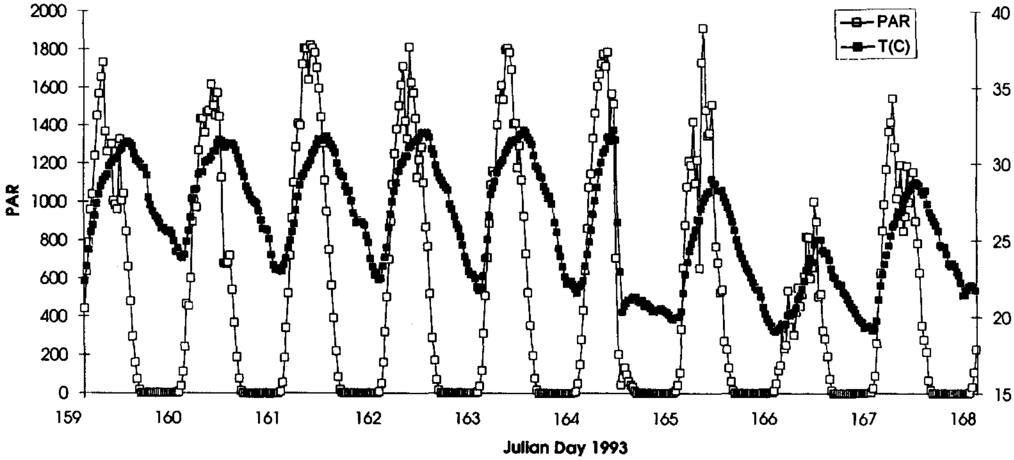

Figure 1:
Meteorological parameters (ambient temperature in °C) and photosynthetically active radiation ([PAR] in μmol m^{-2} s^{-1}) during a one week study period in Fernbank Forest, Atlanta, GA during June 1993.

ground level using a Vaisala sensor (HMP35C, Woburn, MA) for temperature and a quantum sensor (LI-COR LI-190SA, Lincoln, NE) for PAR. Light and temperature response factors were calculated from these meteorological data in the same manner as described for the correction of the branch enclosure conditions (Helmig et al., 1998). Isoprene was corrected for temperature and light effects. All other compounds were corrected for temperature only. The normalized emission rates were then multiplied by these canopy-level factors at 30 min time intervals to give the emission-time profile shown for Fernbank Forest in Figure 2. Except for isoprene, individual compounds were grouped into the compound classes monoterpenes, sesquiterpenes, hexenol derivatives and others. Compounds that were included in the hexenol derivatives group were all C_6 aldehydes, alcohols and esters that were identified. A distinct diurnal cycle is observed for all compounds. However, while isoprene emissions drop to zero at night, all other compound fluxes drop to about half of their daytime maxima. The total BVOC flux from the summation of all individual compounds shows variations of a factor of approximately 4 to 5, with daytime maxima reaching 4.5 mg C m^{-2}h^{-1} and nighttime minima around 1 mg C m^{-2}h^{-1}.

Temperature and light conditions at the two other sites during the study period were quite similar to the record from Fernbank Forest. Therefore, the average correction factor for the meteorological conditions encountered during the one week period at Fernbank Forest was used to adjust the normalized emission rates for the Willow Springs and Temple Ridge sites to model the change of compound class emission patterns under real ambient conditions. Time-averaged emission potentials for all sites were calculated by integrating over the one-week period and are included in Table 2. Pie graph diagrams depicting the time-averaged percentage and total VOC fluxes of the major BVOCs and BVOC compound classes are illustrated in Figure 3 for Fernbank Forest, Willow Springs and Temple Ridge, respectively. The data sets can also be broken up by plant species. The derived landscape level

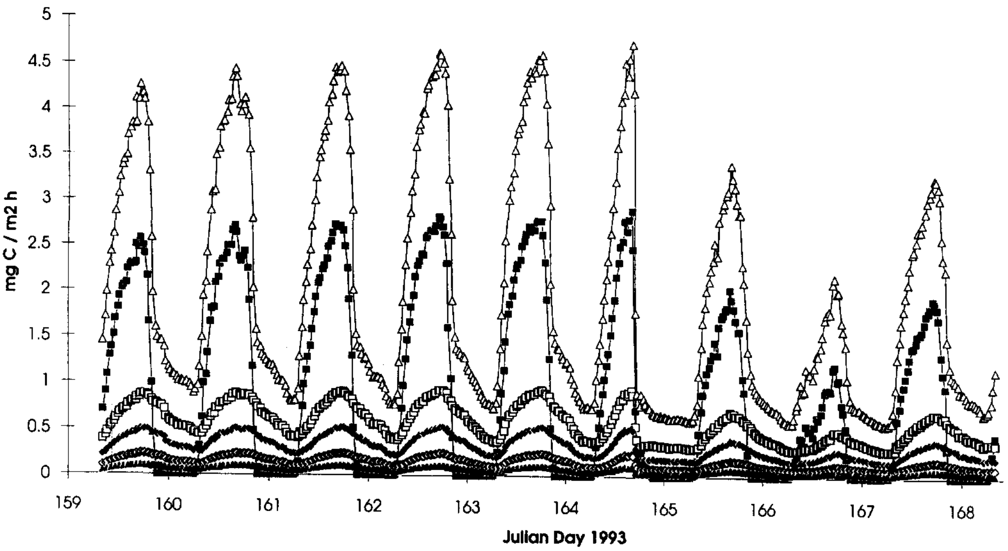

Figure 2:
Compound and compound class fluxes at Fernbank Forest adjusted to the meteorological parameters depicted in Figure 1. Plotted traces are: Total VOC (open triangles), isoprene (filled squares), monoterpenes (open squares), sesquiterpenes (filled diamonds) hexenol derivatives (open diamonds) and others (filled triangles).

emission rates for each shrub and tree species at the three sites are given in Table 3.

4. DISCUSSION

Isoprene is the predominant BVOC emission at the Fernbank Forest site (Table 2, Figure 3). The time-averaged isoprene flux is 890 μgC $m^{-2}h^{-1}$, contributing to 45% of the total BVOC flux. Other individual BVOC fluxes are less than a tenth of the isoprene flux. However, total sesquiterpenes and monoterpenes account for 560 μgC $m^{-2}h^{-1}$ (28%) and 320 μgC $m^{-2}h^{-1}$ (16%), respectively. Individual monoterpenes (μgC $m^{-2}h^{-1}$) with the highest fluxes are *p*-cymene (87), *t*-ocimene (73) and limonene (71). All oak trees combined make up 64% of the total BVOC emissions (time-averaged, Table 3).

A surprising result is found for the Willow Springs site. Isoprene emissions are ranked second, exceeded by emissions of hexenol (incl. hexanal) derivative compounds. Hexenol derivative emissions were observed from 18 different plant species growing at this site. The major plant contributor to this landscape flux is quaking aspen. With a normalized total BVOC emission rate of 105 μg C $h^{-1}gdw^{-1}$ and a biomass of 32 g m^{-2} this tree species alone contributes to 57% of the overall BVOC flux, with the significant fraction in the form of hexenol compounds. Unfortunately, the data were derived from just one individual measurement and the inclusion of literature reference data (Helmig et al., 1998). Because of these reasons, there is a likely possibility that this sample may have been artificially contaminated from disturbances to the plant. The degree of this possible error can not be assessed at this time. It is also striking that the overall landscape BVOC flux (time-averaged 4.5 mg C $m^{-2}h^{-1}$) is about a factor of

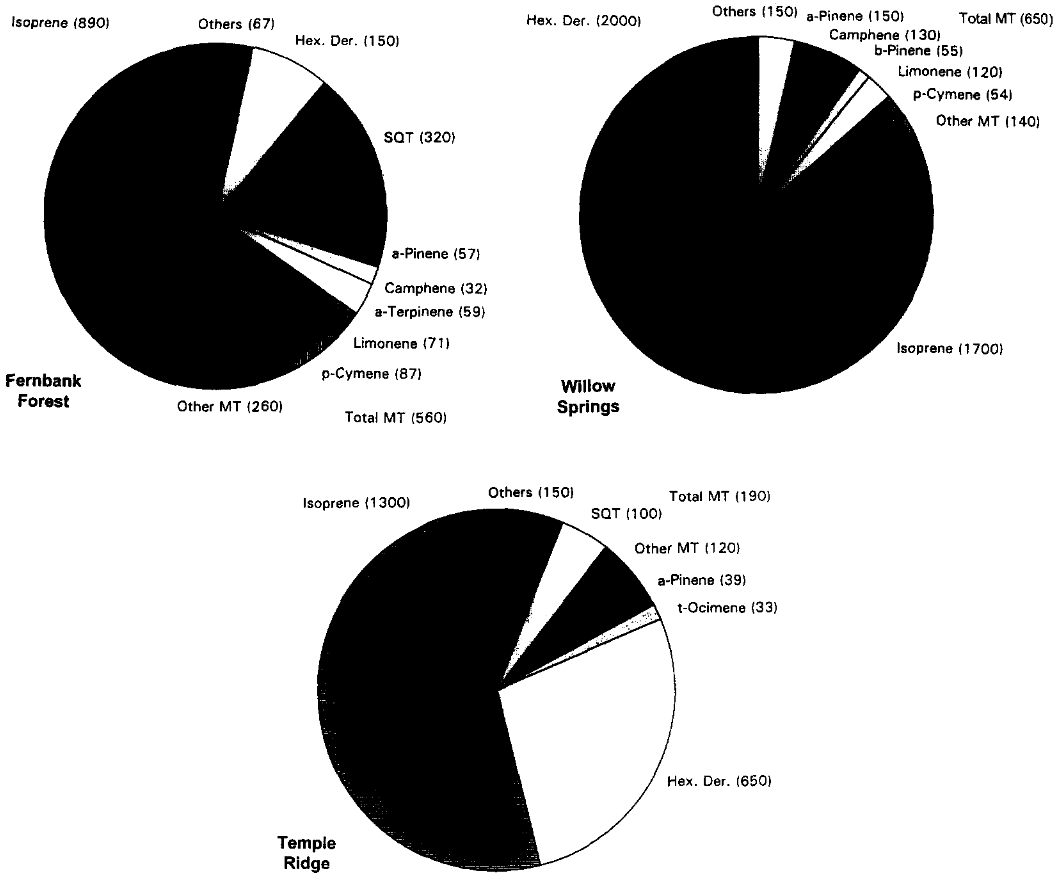

Figure 3:
Contribution of individual BVOCs and VOC compound classes to the overall BVOC flux at Fernbank Forest, Atlanta, GA; Willow Springs, near Rhinelander WI; and Temple Ridge, CO. This data is the average flux for the meteorological record shown in Figure 1. Fluxes are given in $\mu gC\ m^{-2}h^{-1}$. The total BVOC flux accounts to 2000, 4500 and 2400 $\mu gC\ m^{-2}h^{-1}$ for the three sites, respectively.

two higher than for the other two sites. Besides the discussed *cis*-3-hexene-1-ol/aspen contribution, several other factors may lead to this high flux. Emissions were scaled to the ambient isoprene flux measurement results from tethered balloon sampling at Willow Springs (4.4 mg C $m^{-2}h^{-1}$ at normalized conditions) and to the percentage biomass contribution of isoprene emitting plants from the remote sensing results. The transect/remote sensing results gave fairly low biomass percentages for all oak trees in this region (4% total biomass) which are expected to be a major isoprene emitter. It is possible, however, that the biomass of isoprene emitting species within the footprint area of the tethered balloon sampling was higher than the result from the remote sensing studies on the survey area or that some major isoprene emitting species were not measured by the branch enclosure experiment. Also, the isoprene emission rate and percentage biomass of sphagnum moss are uncertain. Our sampling of sphagnum moss showed some isoprene emissions, however, it could not be determined if these emissions were from the moss or from

Table 3

Total VOC flux from vegetation species at the three sites at standard conditions (30oC and 1000 umol/(s m2)) and under an ambient scenario of light and temperature conditions. Fluxes are given in microgram carbon per square meter and hour (ug C m-2h-1).

Species		**Fernbank Forest**				**Willow Springs**				**Temple Ridge**			
		30/1000		ambient		30/1000		ambient		30/1000		ambient	
Common name	Latin name	ug C	total %	ug C	total %	ug C	total %	ug C	total %	ug C	total %	ug C	total %
Alternate-leaved dogwood	*Cornus alternifolia*					1	0.0	0	0.0				
American beech	*Fagus grandifolia*	360	9.5	260	13.0								
American hornbeam; Ironwd	*Carpinus caroliniana*	15	0.4	10	0.5								
Apple	*Malus sp.*									0	0.0	0	0.0
Balsam fir	*Abies bàlsamea*					340	4.3	250	5.8				
Bamboo	*Chusqua sp.*												
Basswood	*Tilia americana*	17	0.4	12	0.6	59	0.7	43	1.0				
Beaked hazelnut	*Corylus cornuta*					33	0.4	24	0.6				
Big sagebrush	*Artemesia tridentata*									290	6.0	210	8.9
Big-toothed aspen	*Populus grandidentata*					5	0.1	2	0.0				
Black ash	*Fraxinus nigra*					95	1.2	70	1.6				
Black cherry	*Prunus serotina*					3	0.0	3	0.1				
Black gum	*Nyssa sylvatica*	5	0.1	2	0.1								
Black oak	*Quercus velutina*	85	2.2	36	1.8								
Black spruce	*Picea mariana*					410	5.2	180	4.2				
Bog heather	*hamaedaphne calyculata*					2	0.0	1	0.0				
Chinese Spruce	*Picea asperata*					4	0.1	3	0.1				
Choke cherry	*Prunus virginiana*									16	0.3	12	0.5
Cottongrass	*Eriophorum Sp.*					1	0.0	0	0.0				
Dawn redwood	*Metasequoia sp.*	36	0.9	24	1.2								
Downy serviceberry	*Amelanchier arborea*					0	0.0	0	0.0				
Eastern hemlock	*Tsuga canadensis*	0	0.0	0	0.0	330	4.2	240	5.6				
Engelmann spruce	*Picea engelmannii*									0	0.0	0	0.0
Four-winged saltbush	*Atriplex canescens*									140	2.9	100	4.2
Gambel's oak	*Quercus gambelii*									3800	79	1600	68
Gingko	*Ginkgo biloba*	0	0.0	0	0.0								
Hop hornbeam	*Ostrya virginiana*					4	0.1	3	0.1				
Labrador tea	*Ledum groenlandicum*					2	0.0	1	0.0				
Loblolly pine	*Pinus taeda*	90	2.4	63	3.2								
Lodgepole pine	*Pinus contorta*									0	0.0	0	0.0
Northern red oak	*Quercus rubra*	1000	26	430	22	970	12	470	11				
Northern white cedar	*Thuja occidentalis*					25	0.3	18	0.4				
Paper birch	*Betula papyrifera*					110	1.4	80	1.9				
Post oak	*Quercus stellata*	820	22	460	23								
Quaking aspen	*Populus tremuloides*					4900	62	2500	58	0	0.0	0	0.0
Rabbitbrush	*hrysothamnus nauseosus*									11	0.2	8	0.3
Raspberry	*Rubus sp.*					5	0.1	4	0.1				
Red maple	*Acer rubrum*					310	3.9	210	4.9				
Red mulberry	*Morus rubra*	1	0.0	1	0.1								
Red pine	*Pinus resinosa*					1	0.0	1	0.0				
Serviceberry	*Amelanchier alnifolia*					0	0.0	0	0.0	550	11	410	17
Slippery elm	*Ulmus rubra*	0	0.0	0	0.0								
Snowberry	*mphoricarpos occidentalis*									14	0.3	10	0.4
Southern red oak	*Quercus falcata*	210	5.5	86	4.3								
Speckled alder	*Alnus rugosa*					0	0.0	0	0.0				
Sphagnum moss	*Sphagnum sp.*												
Subalpine fir	*Abies lasiocarpa*									0	0.0	0	0.0
Sugar maple	*Acer saccharum*					120	1.5	91	2.1				
Sweet gum	*Liquidambar styraciflua*	250	6.6	170	8.5								
Tamarack	*Larix laricina*					2	0.0	1	0.0				
Tulip poplar	*Liriodendron tulipifera*	260	6.8	190	9.5	1	0.0	0	0.0				
White ash	*Fraxinus americana*					3	0.0	3	0.1				
White mulberry	*Morus alba*	0	0.0	0	0.0								
White oak	*Quercus alba*	630	17	260	13.0								
White pine	*Pinus strobus*					0	0.0	0	0.0				
White spruce	*Picea glauca*					2	0.0	1	0.0				
Willow	*Salix sp.*									0	0.0	0	0.0
Yellow birch	*Betula allaghenensis*					180	2.3	130	3.0				
	Total:	3800	99	2000	100	7900	100	4300	101	4800	100	2400	99

embedded other plants or microbiological processes in litter within the moss. An accurate biomass estimation of mosses in this area was not available.

BVOC fluxes at the Temple Ridge site are clearly dominated by isoprene emissions from Gambel oak (Figure 3, Table 3). This site was the most homogenous of the sites studied with 56% of the biomass from Gambel oak. The total time-averaged contribution of isoprene to the overall BVOC flux is 54% with 68% of the total BVOC flux being from Gambel oak. The isoprene flux (1300 μgC $m^{-2}h^{-1}$) is followed by *cis*-3-hexenyl acetate (440), *cis*-3-hexene-1-ol (190) and α-pinene (39).

5. METHOD UNCERTAINTIES AND IMPROVEMENTS

Uncertainties and errors arising from the branch enclosure technique and the chemical analysis methods were discussed in detail by Helmig et al. (1998). The major sources of error identified were the temperature and light control during the branch enclosure, sample collection, water management during analysis, chromatography and mass spectrometric detection, and the sample representativeness and plant disturbance. However, it was also concluded that random errors partially cancel out and that scaling of the bag enclosure results to emission rates obtained from cuvette experiments improves the data quality. Additional factors that impact the accuracy of the data reported here are mainly from the biomass survey, from canopy effects and errors in the landscape isoprene flux measurements.

Biomass Survey Methods of species composition and biomass estimation varied between sites: at Willow Springs, a more regional sampling procedure was used, transects to sample representative species assemblages were distributed over a large area and the isoprene flux measurements were made using a tethered balloon technique. A rigorous accuracy assessment of the remote sensing classification has not been completed and thus the percentages of biomass determined from this analysis must be treated as preliminary in nature. In contrast, at the other two sites, transects radiated out from a central tower from which flux estimates were derived. This discrepancy in methodology may contribute to the variation between the Wisconsin site and the two other sites. The accuracy of the biomass survey is estimated to be on the order of ± 50%.

Canopy Effects Harley et al. (1996) showed that emission rates from leaves can be significantly different depending on where a leaf is growing within a canopy environment. Differences in the emission rates are related to the changing light and temperature conditions as a result of vertical attenuation of PAR through the canopy. For the calculations reported here, the use of reference isoprene fluxes determined on the landscape level partially corrects for these effects. This approach assumes, however, that all vegetation species investigated experience the same degree of shading, which is an inaccurate approximation. Likewise, this method assumes that all species considered are experiencing the same ambient temperatures, which, again, within a diverse forest stand, is only a rough approximation. We estimate that the fluxes reported here are closest to the actual flux for the Temple Ridge site, due to a lower biomass density that allows more of the total canopy leaf area to be exposed to the same levels of PAR and temperature. We estimate errors from canopy effects to be on the order of ± 30%.

6. CONCLUSIONS

Despite the remaining large margins of error the developed technique and data presented allow to identify future research needs for improvements in the experimental setup and data analysis and to identify focus areas for BVOC measurements. The overall error for this method is difficult to assess. It is estimated that data for individual plant species are accurate to within a factor of ≈ 2-3. Since all branch enclosure experiments were performed using the same experimental technique and under similar experimental conditions statistically systematic errors are to some extent corrected for by treating data for all species relative to each other and then scaling the cumulative data to the absolute landscape level results for isoprene. The BVOC emission potentials on the landscape level are therefore estimated to be within an overall error margin of a factor ≈ 2.

The branch enclosure method in combination with a detailed biomass survey is a valid approach to identify the major emitting plant species in a given ecosystem. By thoroughly investigating a few selected plants, the bulk fraction of the total BVOC emissions can be assessed. Since reliable methods for the measurement of BVOC fluxes (other than for isoprene) at the ambient level are scarce, more attention should be given to refining the branch enclosure technique. This method currently appears to be the best experimental approach to screen a large number of vegetation species.

Within the discussed margins of error, the results of this study indicate that at the three sites investigated, non-isoprene BVOC emissions can be significant and contribute to as much as 46 to 63% of the overall BVOC flux. Therefore, BVOC emission studies need to include the investigation of these compounds and not focus on isoprene fluxes only. The consideration of this portion of the BVOC emission is also important for atmospheric chemistry models.

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