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NATURAL VOLATILE ORGANIC COMPOUND EMISSION RATE ESTIMATES FOR U.S. WOODLAND LANDSCAPES

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Abstract—Volatile organic compound (VOC) emission rate factors are estimated for 49 tree genera based on a review of foliar emission rate measurements. Foliar VOC emissions are grouped into three categories: isoprene, monoterpenes and other VOCs. Typical emission rates at a leaf temperature of 30°C and a light intensity of 1000 $\mu mol\ m^{-2}\ s^{-1}$ range from <0.1 to 70 $\mu g\ C\ g^{-1}\ h^{-1}$ for isoprene, <0.1 to 3 $\mu g\ C\ g^{-1}\ h^{-1}$ for monoterpenes, and <0.5 to 5 $\mu g\ C\ g^{-1}\ h^{-1}$ for other VOCs. Isoprene emission factors are given for biogenic emission models that incorporate canopy shading effects and thus require leaf-level emission rates and for emission models that do not include a canopy model and therefore require branch-level isoprene emission factors which already account for some shading.

Landscape-level emission rates are estimated by combining emission rate factors determined for tree genera with species composition and foliar mass data. Landscape emission rate factors are determined for each of the 91 woodland landscapes in the high resolution (1.1 km) gridded land-cover database compiled by the EROS Data Center (EDC) from satellite and ancillary data. This database covers the entire contiguous United States of America. Landscape emission rates are also be determined using gridded tree distribution data, based on aerial photographs and ground measurements, such as that available in the U.S. Forest Service (USFS) Eastwide Forest Inventory Database (EFID). Emission rates are reported for 41 of the 65 tree genera in the EFID including all of the most common genera.

Total VOC emission rate factors for the 91 EDC woodland-cover types range from 0.8 to 11 $mg\ C\ m^{-2}\ h^{-1}$ at a standard condition of 30°C and 1000 $\mu mol\ m^{-2}\ s^{-1}$. These landscape factors are based on branch-level emission factors and thus already incorporate canopy shading effects. The estimated fluxes of isoprene and monoterpenes are in relatively good agreement with field measurements of area-averaged fluxes if accurate species composition data (e.g. from the EFID) are available. Total VOC emission rate estimates range from 0.8 to 4.3 $mg\ C\ m^{-2}\ h^{-1}$ for scrub woodlands and 2.2 to 11 $mg\ C\ m^{-2}\ h^{-1}$ for mixed deciduous/coniferous woodlands. The chemical composition of the VOC flux ranges from 8 to 91% isoprene, 1 to 56% for monoterpenes and 8 to 73% for other VOC. On an area-weighted basis, the U.S. average total VOC emission rate factor of 5.1 $mg\ m^{-2}\ h^{-1}$ for all woodlands is comprised of 58% isoprene, 18% monoterpenes and 24% other VOC. In comparison to previous estimates, these emission rates are generally higher for isoprene and lower for monoterpenes.

Key word index: Volatile organic compound, isoprene, terpene, biogenic, natural emissions.

1. INTRODUCTION

Volatile organic compounds are present in all living organisms. The emission of these compounds from plant foliage to the atmosphere accounts for about half of the estimated total VOC emissions in the United States of America (Lamb *et al.*, 1987) and two-thirds of global VOC emissions (Müller, 1992). Numerical atmospheric chemistry models have demonstrated that concentrations of ozone and other oxidants in the troposphere are sensitive to both biogenic and anthropogenic VOC concentrations (Chameides *et al.*, 1988). Accurate estimates of both biogenic and anthropogenic VOC emission rates are important components of the numerical studies that provide the basis of global change scenarios and regulatory emission control strategies.

The characterization of biogenic VOC sources is complex due to the large variety of chemical and plant species. The composition and quantities of the more than 40,000 volatile organic compounds found within plant cells (Harborne, 1991) vary greatly among the hundreds of thousands of plant species. Investigations of foliar VOC emissions have focused on the dominant hydrocarbon compounds emitted, the hemiterpene (C_5) isoprene and several monoterpenes (C_{10}), and on the dominant trees (e.g. oak and pine) of temperate forests.

Zimmerman (1979) provided the first extensive database of quantitative estimates of biogenic VOC emission rates. These emissions data are branch enclosure measurements of vegetation at field sites throughout the United States of America. Lamb *et al.* (1987) used a subset of these data to estimate VOC emission rates from woodlands, shrublands, grasslands, and urban areas within the United States of America. The contiguous United States surface area was categorized by Lamb *et al.* (1987) as 31% woodlands, 20% scrublands, 16% pasture and grasslands, 27% crop and miscellaneous lands, 3% urban areas

and 2% water using a county level database (Olson, 1980). Woodlands were divided into three categories: oak (29%), non-oak deciduous (33%), and coniferous (38%).

Foliar emission rates of different tree species vary considerably. The dominant tree species in a category such as a non-oak deciduous woodland have VOC emission rates that differ by more than an order of magnitude. Variations in biomass density can also result in large differences in estimated emission rates. The relatively detailed VOC emission rate measurements (e.g. Zimmerman, 1979; Lamb *et al.*, 1985) and land-cover data (e.g. Loveland *et al.*, 1991; Hansen *et al.*, 1992) available for U.S. woodlands allow a more detailed characterization of emission rates than is currently possible for other landscapes. In this paper, we provide a detailed description of emission rates for U.S. tree genera and describe an extrapolation scheme based on remote sensing and ground measurements. This methodology for assigning base emission rates represents a significant improvement over existing VOC emission modeling approaches and will improve attempts to estimate biogenic VOC emissions in the United States of America and elsewhere.

2. EMISSION RATE MEASUREMENTS

Members of a plant genus tend to have similar foliar VOC emission rates (e.g. Zimmerman; 1979). By assigning VOC emission rates at the genera level, we have a scheme that is general enough to extrapolate emissions to continental scales but is specific enough to account for the large differences observed within more general categories such as the oak, non-oak deciduous, and coniferous woodland classifications of Lamb *et al.* (1987). Representative species of the dominant plant genera in U.S. woodlands have been surveyed but there are relatively few measurements reported for the dominant plant genera of other landscapes (e.g. grasslands and shrublands).

In this section, VOC emissions from tree genera are described. VOC emissions are grouped into three categories: isoprene, monoterpenes, and other VOC. Isoprene is reported separately because the algorithms used to simulate isoprene emission rate variations are different than those used for other VOCs (Guenther *et al.*, 1991, 1993). We have used the arithmetic mean emission rates from the one laboratory and seven field databases (described below) to develop a set of representative emission rates that includes values for all of the tree genera that are commonly observed in the United States of America and Canada. As foliar VOC emission rates can be temperature and light dependent (e.g. Tingey, 1981), emissions were normalized to a leaf temperature of 30°C and a photosynthetically active radiation (PAR) flux of 1000 μmol m^{-2} s^{-1}. The algorithms developed by Guenther *et al.* (1993) were used to normalize the individual emission rates in three field data sets: Lamb *et al.* (1984, 1985), Zimmerman (1979) and Guenther *et al.* (1994). Guenther *et al.* (1993) recommend the use of these algorithms based on their evaluation of nine hydrocarbon emission algorithms. The Guenther *et al.* (1993) algorithms were also used to normalize the arithmetic mean emission rates reported by Evans *et al.* (1982) at 28°C and 1000 μmol m^{-2} s^{-1} and the mean emission rates described by Arey *et al.* (1991a) and Winer *et al.* (1992) for the reported mean temperatures. Two of the data sets used in this analysis, Lamb *et al.* (1984, 1985) and Winer *et al.* (1983) contain reported mean emission rates that were normalized using the algorithms developed by Tingey (1981). Guenther *et al.* (1993) have shown that using different environmental adjustment algorithms results in small differences (less than 15%) when normalizing emission rate measurements made at temperature and light conditions within 10°C and 500 μmol m^{-2} s^{-1} of the standard conditions.

The database described by Zimmerman (1979) contains the results of one of the most extensive field campaigns to focus on plant VOC emissions and has been used as the basis for numerous estimates of regional and global biogenic VOC emissions (e.g. Lamb *et al.*, 1987; Müller, 1992). For these reasons, we have re-analysed the data reported by Zimmerman (1979) to (1) include only isoprene emissions measured in full sunlight, (2) exclude samples with negative values, (3) classify "unknown" major peaks based on comparison with recent GC–FID and GC–MS analyses, and (4) evaluate the procedures used to estimate non-terpenoid emissions.

Isoprene emissions from plants are strongly dependent upon light intensity up to approximately half full sun light intensity where the emissions reach a saturation regime (Guenther *et al.*, 1993). Therefore, only samples collected during daytime, clear skies (saturated light conditions) were included for isoprene emission estimates. Negative monoterpene emission rates were sometimes observed in the measurements of a few individuals of a given plant species in the Zimmerman database. Likely causes are physical disturbances resulting in high background concentrations or uncertainties in estimating enclosure volumes. In order to obtain a representative emission rate for a species, the few samples with negative values were excluded.

In the Zimmerman database, 6 of the 24 overstory tree species sampled had an unknown as a dominant emission. These unknowns were labeled as numbers 21, 22, 26A, 27, 29 and 29A. Each of these unknowns was eluted within the terpene region for the chromatographic column used by Zimmerman (1979) and was a dominant emission in only a few species. Recent measurements of emissions from these same tree species have identified and quantified all major VOC compounds (Guenther *et al.*, 1994). Comparison of the Zimmerman (1979) chromatograms with these recent GC–FID and GC–MS analyses of the same tree species has tentatively identified some of these compounds and has confirmed that the unknowns listed

above are most likely terpenes. For example, Zimmerman (1979) found that one compound, which was labeled unknown 21, comprised over 80% of the total monoterpene emission from red maple. Guenther *et al.* (1994) found that the terpene, sabinene, accounted for over 80% of total monoterpene emissions from red maple. This observation, in addition to the similarity in retention times (relative to known monoterpenes on the columns used in these studies), suggests that unknown 21 is sabinene. This analysis resulted in classifying these unknowns as terpenes instead of others. For a few test cases in the Zimmerman (1979) database, the original chromatogram, data sheets and emission rate calculations were reviewed. The total areas of the dominant peaks and the summed areas for paraffins, olefins, and aromatics agreed with the total areas previously calculated and reported by Zimmerman (1979).

The process of estimating representative emission rates from data reported in a variety of different studies is not straightforward. The mean emission rates have considerably different uncertainties due to different sampling techniques and sample sizes. At constant temperature and light intensity, Guenther *et al.* (1991) observed leaf-to-leaf and plant-to-plant variations (ratio of the standard deviation to the mean) of about $\pm 50\%$ for both isoprene and monoterpene emissions from eucalyptus. The 28 tree species measured in the field by Zimmerman (1979) tended to have even larger within-species variation. Therefore, instead of assigning one emission rate for each genera, we defined discrete emission categories with a representative rate and a range of $\pm 50\%$.

Emission categories were defined based on the tendency of normalized tree genera emission rates to fall within certain ranges (e.g. negligible, low, moderate, high). We defined four isoprene emission rate categories and five categories for monoterpene emission rates. The species average emission rates from the various studies fell within a single category for a majority (greater than 75%) of the 49 tree genera. When reported rates fell within more than one category, the tree genus was assigned to the category where most rates occurred. In most of these cases, differences in the reported means can be attributed to extremely small sample sizes. For isoprene emissions, the low normalized emission rate estimates reported for some studies may be due to errors in estimating light intensity since quantitative estimates were sometimes not available.

2.7. *Isoprene emissions*

The function of isoprene in plants and the mechanisms controlling foliar isoprene emissions are not well understood (Fall, 1991). However, some environmental and developmental effects such as light intensity, leaf temperature, humidity, and leaf age have been characterized. Isoprene emissions are strongly dependent on photosynthetically active radiation (PAR) at low light levels but become saturated at less than one-half of full sunlight (Guenther *et al.*, 1993). Isoprene emissions increase exponentially with increasing leaf temperatures below approximately 30°C and decrease with increasing temperatures above approximately 40°C (Guenther *et al.*, 1993). Variations in relative humidity between 30 and 100% have only a minor effect on isoprene emission rates but the use of dehumidified air in a flow-through enclosure system may reduce isoprene emission rates by as much as 20% (Guenther *et al.*, 1991). In addition, isoprene emissions have been shown to follow a developmental pattern with young leaves emitting isoprene at levels as much as an order of magnitude lower than mature leaves (Kuzma and Fall, 1993).

Isoprene emission from trees appears to be relatively insensitive to the physical disturbances that occur when enclosure methods are used to measure biogenic emission rates (Zimmerman, 1979). Greater errors can occur when isoprene emissions are normalized to account for variations due to environmental conditions. As discussed above, we have used the algorithms developed by Guenther *et al.* (1993) to normalize isoprene emission rates to a leaf temperature of 30°C and a PAR flux of 1000 μmol m^{-2} s^{-1}. Emissions measured at temperatures between 25 and 35°C and at PAR levels above 150 μmol m^{-2} s^{-1} can be normalized to 30°C and 1000 μmol m^{-2} s^{-1} with an error of less than 35% (Guenther *et al.*, 1993). Difficulties arise when attempting to normalize field measurements that are not accompanied by quantitative estimates of PAR. As mentioned previously, this problem has been minimized by including only emission rates measured under clear sky, daytime conditions.

The isoprene emission rates reported in seven of the eight databases described above represent branch-level enclosure measurements. The data described by Guenther *et al.* (1994) include both leaf-level and branch-level measurements. These data demonstrate that leaf-level measurements produce results that are about 75% higher than branch-level measurements. This is to be expected since light extinction models predict that the lower light on the shaded portion of a branch will result in lower emissions. For a branch with a leaf area index of around 3 m^2 m^{-2}, this can result in emissions from leaves at the top of the branch that are 75% higher than the average for the entire branch. We have associated both a leaf-level and a branch-level isoprene emission rate with each isoprene emission category.

The species average isoprene emission rates shown in Table 1, normalized to 30°C and 1000 μmol m^{-2} s^{-1}, range from less than 0.1 to 70 μg C g^{-1} h^{-1}. Isoprene emission rates greater than 1 μg C g^{-1} h^{-1} have been reported for over 30 indigenous U.S. tree species. Thirteen of the 49 genera listed in Table 1 have significant isoprene emission rates. These include nine angiosperm, three monocot and one gymnosperm (*Picea*) genera. We have devised a classification system for normalized leaf-level iso-

Table 1. Isoprene and monoterpene emission rates of U.S. trees. Code corresponds to Table 4. N is the number of emission rate measurements and N_{sp} is the number of species represented by these measurements. Area is the percent of the total 3.8×10^6 km^2 of U.S. woodlands where the genus is a dominant component of the landscape (based on Loveland *et al.*, 1991). Emission rates ($\mu g\,C\,g^{-1}\,h^{-1}$) are representative of a leaf temperature of 30°C and a leaf-level PAR flux of 1000 $\mu mol\,m^{-2}\,s^{-1}$. Isoprene emission rates for a branch-level PAR flux of 1000 $\mu mol\,m^{-2}\,s^{-1}$ are given in parenthesis. References include A (Arey *et al.*, 1991a), E (Evans *et al.*, 1982), G (Guenther *et al.*, 1994), L (Lamb *et al.*, 1985, 1986), W (Winer *et al.*, 1983), and Z (Zimmerman, 1979). A–Z refers to all references while E–Z refers to all references except Arey and coworkers

Family	Genus	Code	Example	N	N_{sp}	Area	Isoprene	Terpene	Reference
Pinaceae	*Abies*	abi	Fir	2	1	1.4%	<0.1	3	Z
Leguminosae	*Acacia*	aca	Acacia	4	2	<1%	<0.1	3	Z
Aceraceae	*Acer*	ace	Maple	89	2	25%	<0.1	1.6	E–Z
Verbenaceae	*Avicennia*	avi	Black mangrove	3	1	<1%	<0.1	<0.1	Z
Betulaceae	*Betula*	bet	Birch	1	1	22%	<0.1	0.2	L
Betulaceae	*Carpinus*	cap	Hornbeam	2	1	<1%	<0.1	1.6	L, Z
Juglandaceae	*Carya*	car	Hickory	12	4	11%	<0.1	1.6	G, L, Z
Casuarinaceae	*Casuarina*	cas	Ironwood	1	1	<1%	70 (40)	<0.1	Z
Pinaceae	*Cedrus*	ced	Deodar-cedar	10	1	<1%	<0.1	1.6	W
Ulmaceae	*Celtis*	cel	Sugarberry	2	2	<1%	<0.1	0.2	G, Z
Leguminosae	*Cercis*	cer	Redbud	4	1	<1%	<0.1	<0.1	E
Cupressaceae	*Chamaecyparis*	cha	Port-Orford Cedar	1	1	<1%	<0.1	0.2	Z
Rutaceare	*Citrus*	cit	Orange	31	2	<1%	<0.1	1.6	A, Z
Cornaceae	*Cornus*	cor	Dogwood	4	2	<1%	<0.1	1.6	G, L, Z
Ebenaceae	*Diospyros*	dio	Persimmon	1	1	<1%	<0.1	<0.1	Z
Myrtaceae	*Eucalyptus*	euc	Eucalyptus	8	1	<1%	70 (40)	3	E
Fagaceae	*Fagus*	fag	Beech	2	1	16%	<0.1	0.6	L, Z
Oleaceae	*Fraxinus*	fra	Ash	146	1	4%	<0.1	<0.1	W, Z
Aquifoliaceae	*Ilex*	ile	Holly	3	2	<1%	<0.1	0.2	Z
Juglandaceae	*Juglans*	jug	Walnut	5	1	5%	<0.1	3	A
Pinaceae	*Juniperus*	jun	Juniper	947	2	7%	<0.1	0.6	G, W, Z
Combretaceae	*Laguncularia*	lag	White mangrove	14	1	<1%	<0.1	<0.1	Z
Hamamelidaceae	*Liquidambar*	liq	Sweetgum	110	1	10%	70 (40)	3	E, G, Z
Magnoliaceae	*Liriodendron*	lir	Tulip-tree	4	1	10%	<0.1	0.2	L, G, Z
Magnoliaceae	*Magnolia*	mag	Magnolia	81	2	<1%	<0.1	3	W, Z
Meliaceae	*Melia*	mel	Chinaberry	1	1	<1%	<0.1	<0.1	G
Moraceae	*Morus*	mor	Mulberry	4	1	<1%	<0.1	0.2	Z
Nyssaceae	*Nyssa*	nys	Gum	4	2	1%	14 (8)	0.6	L, G
Ericaceae	*Oxydendrum*	oxy	Sourwood	1	1	<1%	<0.1	0.6	Z
Lauraceae	*Persea*	per	Bay	3	1	<1%	<0.1	0.6	Z
Pinaceae	*Picea*	pic	Spruce	27	2	4%	14 (8)	3	E, Z
Pinaceae	*Pinus*	pin	Pine	359	10	62%	<0.1	3	E–Z
Platanaceae	*Platanus*	pla	Sycamore	112	2	<1%	35 (20)	<0.1	E, L, W
Salicaceae	*Populus*	pop	Poplar	38	3	3%	70 (40)	<0.1	E, Z
Rosaceae	*Prunus*	pru	Cherry	6	3	<1%	<0.1	<0.1	A, G, L
Pinaceae	*Pseudotsuga*	pse	Douglas-fir	13	1	10%	<0.1	1.6	L, Z
Fagaceae	*Quercus*	que	Oak	220	17	64%	70 (40)	0.2	A–Z
Rhizophoaceae	*Rhizophora*	rhi	Red mangrove	16	1	<1%	<0.1	<0.1	Z
Leguminosae	*Robinia*	rob	Locust	42	1	<1%	14 (8)	0.2	L, W
Palmae	*Sabal*	sab	Cabbage palmetto	11	1	<1%	14 (8)	<0.1	Z
Salicaceae	*Salix*	sal	Willow	16	1	<1%	35 (20)	<0.1	E, Z
Lauraceae	*Sassafras*	sas	Sassafras	2	1	<1%	<0.1	<0.1	L, G
Palmae	*Serenoa*	ser	Saw-palmetto	32	1	<1%	35 (20)	<0.1	Z
Taxodiaceae	*Taxodium*	tax	Bald-cypress	19	2	<1%	<0.1	3	G, Z
Cupressaceae	*Thuja*	thu	Western redcedar	2	1	2.4%	<0.1	0.6	L
Pinaceae	*Tsuga*	tsu	Hemlock	1	1	3%	<0.1	0.2	L
Ulmaceae	*Ulmus*	ulm	Elm	177	1	<1%	<0.1	<0.1	G, W, Z
Ericaceae	*Vaccinium*	vac	Blueberry	1	1	<1%	<0.1	<0.1	G
Palmae	*Washingtonia*	was	Fan palm	82	1	<1%	14 (8)	<0.1	W

prene emission rates that consists of the four emission ranges ($\mu g\,C\,g^{-1}\,h^{-1}$); (1) negligible: <0.1, (2) low: 14 ± 7, (3) moderate: 35 ± 17.5, and (4) high: 70 ± 35. Branch-level emission rates of <0.1, 8, 20 and 40 $\mu g\,C\,g^{-1}\,h^{-1}$ are associated with these four categories. The highest isoprene emission rates, greater than 70 $\mu g\,C\,g^{-1}\,h^{-1}$, have been reported for species in the *Quercus* (oak), *Eucalyptus* and *Populus* (aspen) genera.

2.2. *Monoterpene emissions*

A number of ecological roles have been suggested for monoterpenes including defense against herbivory, attraction of pollinating insects, pheromonal production, and plant–plant allelopathy (Harborne, 1991). The precise mechanisms controlling monoterpene production and emission are not well understood. In contrast to isoprene, monoterpenes are stored in specialized tissues. However, the relative composition

Table 2. Examples of monoterpenes emitted by vegetation into the atmosphere (Zimmerman, 1979; Isidorov, 1985)

Major	Frequent	Occasional
Δ^3-Carene	α-Thujene	α-Fenchene
d-Limonene	Tricyclene	β-Fenchene
Myrcene	Terpinolene	δ-Fenchene
α-Pinene	α-Terpinene	ε-Fenchene
β-Pinene	β-Terpinene	Bornylene
Sabinene	γ-Terpinene	Alloocimene
Camphene	*p*-Cymene	Methyl chavicol
1,8-Cineole	α-Phellandrene	*p*-Cymen-8-ol
β-Phellandrene	*trans*-Ocimene	Linalool
	cis-Ocimene	2-Methyl-6-methylene-1, 7-octadiene-3-one
	2-Carene	Pinocarvone
		Verbenone
		Fenchone
		Thujone
		Camphor

of stored leaf monoterpenes is not sufficient to predict emission rates (Schindler and Kotzias, 1989). Tingey *et al.* (1991) suggest that long-term variations in monoterpene emissions are a function of ambient humidity, monoterpene vapor pressure and solubility, leaf temperature, morphology and resin content. Short-term variations in monoterpene emission appear to be controlled by leaf temperature (Guenther *et al.*, 1993).

Individual tree species may emit 10 or more monoterpene compounds but there are typically no more than three dominant monoterpenes for a given tree species (Zimmerman, 1979). Table 2 lists 35 monoterpenes which have been identified in foliar emissions from trees. We have categorized these monoterpenes into three groups based on the relative frequency with which they are emitted: (1) compounds that are major emission components for at least some trees species, (2) compounds that are frequently found in the emissions of at least some trees, and (3) compounds that have only occasionally been reported in the emissions of trees.

Guenther *et al.* (1993) have shown that monoterpene emissions measured at leaf temperatures between 20 and 40°C can be normalized to 30°C with an error of about 25%. Investigators (e.g. Zimmerman, 1979) have noted that monoterpene emission rates are very sensitive to the mechanical disturbances which can occur when enclosure methods are used to measure biogenic emission rates. These disturbances may introduce the greatest errors in monoterpene emission rate measurement datasets.

Monoterpene emission rates greater than 0.1 $\mu g\ C\ g^{-1}\ h^{-1}$ were observed for 30 of the 49 genera listed in Table 1. Our classification system for normalized monoterpene emission rates consists of five emission ranges ($\mu g\ C\ g^{-1}\ h^{-1}$), (1) negligible: <0.1, (2) very low: 0.2 ± 0.1, (3) low: 0.6 ± 0.3, (4) moderate: 1.6 ± 0.8, and (5) high: 3 ± 1.5. As shown in Table 1, 9 of the 49 genera are considered high monoterpene emitters, while 28 are negligible or very low emitters. In general, most (6 of 10) gymnosperms are moderate or high monoterpene emitters while most (22 of 36) angiosperms are very low or negligible monoterpene emitters. However, examples of high and low emitters can be found among both gymnosperms (e.g. pines are high emitters while hemlock are very low emitters) and angiosperms (e.g. sweetgum are high emitters while ash are negligible emitters). The three monocot genera listed in Table 1 have negligible monoterpene emissions.

2.3. *Emissions of other VOC*

In addition to isoprene and monoterpenes, there are a number of other volatile organic compounds emitted from vegetation. In this paper, the term other volatile organic compounds (OVOC) refers to volatile organic compounds other than methane, isoprene and monoterpenes. Examples of these compounds are given in Table 3. They are classified into three groups according to their predicted atmospheric reactivity with the OH radical and thus their ability to influence tropospheric chemistry. The three classes include compounds with low (e.g. acetone), moderate (e.g. methanol), and high (e.g. Z-3-hexen-1-ol) reactivity.

Isoprene and monoterpenes contribute less than 20% of the total VOC emission from many agricultural crops (Winer *et al.*, 1992) and a few trees (Zimmerman, 1979; Arey *et al.*, 1991b). The amount and type of OVOC emitted vary significantly between tree species. For example, many plants emit Z-3-hexen-1-ol and Z-3-hexenylacetate as their major OVOC emission (Arey, 1991b; Ohta, 1984). However, the emission of these compounds varies from <0.05 (not detected) to 1.3 $\mu g\ g^{-1}\ h^{-1}$ for Z-3-hexen-1-ol and from <0.05 (not detected) to 3.4 $\mu g\ g^{-1}\ h^{-1}$ for Z-3-hexenylacetate. The majority of OVOCs have no known functional role. The environmental and physiological controls over the emission of most OVOCs are not known.

Table 3. Examples of other volatile organic compounds emitted by vegetation into the atmosphere (Winer *et al.*, 1992; Arey *et al.*, 1991b; Isidorov *et al.*, 1985) and their reactivity with respect to OH radical attack (Atkinson, 1990)

Class	Compound	Reactivity (d)		
		High (< 1)	Moderate (1–100)	Low (> 100)
n-Alkanes	Ethane			×
	Propane		×	
	n-Hexane		×	
	n-Heptane		×	
	n-Nonane		×	
	n-Decane	×		
	C_{11}–C_{17}	×		
Alkenes	Ethylene	×		
	Propene	×		
	Butene	×		
	1-Decene	×		
	1-Dodecene	×		
	1-Hexadecene	×		
	p-Mentha-1, 3, 8-triene	×		
	1-Pentadecene	×		
	1-Tetradecene	×		
Alcohols	Methanol		×	
	Ethanol		×	
	cis-3-Hexen-1-ol	×		
Aldehydes	Acetaldehyde	×		
	n-Hexanal	×		
	trans-2-Hexenal	×		
Acetates	Butylacetate		×	
	Bornylacetate	×		
	cis-3-Hexenylacetate	×		
Ketones	Acetone			×
	3-Hexanone		×	
	2-Heptanone		×	
Ethers	*p*-Dimethoxybenzene		×	
	p-Methylanisole		×	
	Estragole	×		
Esters	Methylsalicylate		×	
Sesquiterpenes	B-Caryophyllene	×		
	Cyperene	×		
	a-Humulene	×		

Reported OVOC emission rates typically range from around 0.5 to 5 $\mu g\, g^{-1}\, h^{-1}$ (see Zimmerman, 1979; Winer, *et al.*, 1992). It is not known whether these values represent all major OVOC since many of these compounds may require specific sampling, storage, and quantitation techniques to adequately represent their true values. As a result, there are large uncertainties associated with any foliar OVOC emission factor.

Zimmerman (1979) identified and quantified emissions of OVOCs from more than 24 tree species under normal field conditions. This database is currently the largest set of OVOC measurements of the major tree genera in the United States of America. Zimmerman used separate columns for the quantitation of ethylene, ethane, acetylene and methane; the light hydrocarbons, C_2–C_6; the heavy hydrocarbons, C_4–C_{12} and the heavy hydrocarbons and oxygenates, C_4–C_{12}. Generally, these OVOC were observed in very small quantities. Rather than individually identifying each compound, they were summed into three categories: paraffins, olefins, and aromatics. Identifications were based upon their retention time for a given column. In addition, there were a number of major peaks that could not be positively identified; these were designated as numbered unknowns and were included as OVOC by Zimmerman (1979). Zimmerman's results suggest that, though extremely variable, OVOC may account for 30% (on average) of the total VOC emissions.

Pierce and Waldruff (1991) used the Zimmerman (1979) data to assign individual estimates to oak trees (1.8 $\mu g\, g^{-1}\, h^{-1}$), other deciduous trees (1.5 $\mu g\, g^{-1}\, h^{-1}$), and coniferous trees (1.3 $\mu g\, g^{-1}\, h^{-1}$). Using the data of Zimmerman (1979), re-analysed as described above, we find that there is no significant difference between the OVOC emission rates determined for different U.S. tree species. These emissions were not normalized as the influence of environmental factors upon these emissions is not yet known. We

recommend that the geometric mean OVOC emission rate of 1.5 $\mu g\, g^{-1}\, h^{-1}$ determined for typical U.S. trees (e.g. oaks, pines, maples and hickories) be used to represent OVOC foliar emissions for all trees in the United States of America. An accompanying 10-fold range, 0.5–5 $\mu g\, g^{-1}\, h^{-1}$, is representative of the current uncertainties in this estimated rate. This estimate does not include the potentially large emission ($> 1\ \mu g\, g^{-1}\, h^{-1}$) of methanol which MacDonald and Fall (1993) have recently reported for a variety of tree species. Future work focusing on the identification and quantitation of all OVOC emissions is needed to accurately define these emissions, develop mechanistic algorithms to predict their variation, and assess and narrow uncertainties in OVOC emission estimates.

3. AREA-AVERAGE EMISSION RATES

The emission rates associated with individual plant species or genera listed in Table 1 must be combined with estimates of biomass densities and species composition to provide the area-averaged rates needed for numerical models. Zimmerman (1979) provided an initial attempt to assign VOC emission rates to different land-cover types. This simple classification scheme divided the U.S. into seven major biotic regions including three woodland biomes: temperate rain forest, deciduous forest, and coniferous forest. Lamb *et al.* (1987) refined this scheme by using a much higher spatial resolution (the U.S. was divided into 3070 counties rather than 4 latitudinal bands) and land-cover data which partially accounted for human influences (Olson, 1980). Woodlands were again divided into only three categories: oak, non-oak deciduous, and coniferous forest.

Recent advances in applying remotely sensed data, such as that provided by the Advanced Very High Resolution Radiometer (AVHRR) satellite, to the characterization of regional land-cover provide an improved method of estimating natural emissions. This data provides high resolution (which can be updated regularly), detailed landscape classifications, and current land-cover conditions. In addition, the data can be assembled for a uniform grid and can potentially be extended to provide global coverage. The 1.1-km resolution land-cover database developed by Loveland and coworkers (1991) at the EDC covers the entire contiguous U.S.A. and contains a total of 167 land-cover types. Of these land-cover types, 91 contain woodlands. These include 5 deciduous forest, 19 conifer forest, 26 mixed deciduous/coniferous forest, 5 wetland forest, 17 scrub woods and 19 mixed woodland/cropland landscapes (Loveland *et al.*, 1991). We have assigned area-averaged VOC emission rate estimates to each of the woodland landscapes in the EDC database by combining emission rates associated with the dominant genera in a landscape with rates representative of ground-cover and non-dominant species.

The EDC database contains a description of the dominant plants associated with each land-cover class. For example, one land-cover class is characterized by birch, oak, hickory, walnut and tulip-trees while several others are characterized by pine trees. We have estimated the isoprene and monoterpene emissions contributed by the dominant trees in each EDC land-cover class using the normalized emission rates compiled in Table 1. As discussed earlier, all leaf biomass is assigned an emission rate of 1.5 $\mu g\, g^{-1}\, h^{-1}$ of other VOC. Emission rate measurements have been reported for each of the 22 different genera of tree species listed as dominant vegetation in at least one EDC class. The leaf biomass density associated with the dominant genera is assumed to be 85% of the total leaf biomass in forests, 50% in scrub woodlands and 42% in mixed woodland/croplands based on estimates reported by Leith and Whittaker (1975). In most cases, we have assumed that the biomass associated with the dominant genera is evenly divided between each tree genera. The remaining biomass (15–38%) represents grass, shrubs, non-dominant trees and crops. These sources are estimated to have low isoprene ($8\ \mu g\, g^{-1}\, h^{-1}$) and moderate monoterpene ($1.5\ \mu g\, g^{-1}\, h^{-1}$) emission rates (see Zimmerman, 1979). The apportionment of leaf biomass among the dominant vegetation and the remaining biomass, and the isoprene and monoterpene emission rates of the non-dominant biomass are somewhat arbitrary but provide a means of obtaining a first order approximation. The continuous gradient of biomass densities and species composition in natural landscapes makes accurate assignments difficult unless ground-based measurements are available. For example, if a landscape is characterized by oaks, pines and douglas-fir trees, then one-third of the biomass attributed to dominant vegetation is assigned to each of these genera. If oak/pine/douglas-fir woodlands vary between 10% oak and 50% oak, we expect as much as a factor of four variation in total VOC emissions from this landscape type.

A leaf biomass density has been estimated for each woodland landscape in the EDC data set based on the growing season integrated vegetation index (IVI) reported by Loveland *et al.* (1991). Running and Nemani (1988) have demonstrated that annual IVI is linearly proportional to annual net primary production in forests ranging from Alaska to Florida. The IVI estimates associated with each land-cover category were used to interpolate between upper and lower bound estimates of leaf biomass density reported by Box (1981) for general forest categories. For example, forest biomass density ranges from 400 to 800 $g\, m^{-2}$ and IVI ranges from 134 to 159 for the 19 conifer forest landscapes. Therefore, a conifer landscape with an IVI of 145.5 (the minimum IVI plus 44% of the difference between the minimum and maximum values) is assigned a biomass density of 586 $g\, m^{-2}$ (the minimum biomass density plus 44% of the difference between the minimum and maximum).

Leaf biomass densities and landscape average emission rates for selected individual landscapes are listed in Table 4. All 91 landscapes are grouped into six broad categories to facilitate comparison with other studies and are summarized in Table 5. These 91 woodland landscapes cover about half (3.87 $\times 10^6$ km^2) of the entire surface area of the contiguous United States of America. An area-weighted average normalized TVOC emission of 5.1 mg C m^{-2} h^{-1} is estimated for all U.S. woodland landscapes with a range of more than an order of magnitude (0.8 to 11 mg C m^{-2} h^{-1}) for individual landscapes. The

Table 4. Total volatile organic compound (TVOC) emission rate factors (mg C m^{-2} h^{-1}) for selected EDC woodland landscapes. Dominant tree genera within each landscape are indicated by codes which correspond with Table 1. Surface areas were estimated by Loveland *et al.* (1991). Emission factors are normalized to a temperature of 30°C, an above canopy PAR flux of 1000 μmol m^{-2} s^{-1} and the indicated foliar mass. Isoprene, monoterpenes, and OVOC are shown as a percent of TVOC

Landscape	Code	Area (10^3 km^2)	Foliage (g m^{-2})	TVOC	Isoprene	Monoterpene	OVOC
Northwest conifers	abi, pse, tsu	2.9	400	1.7	27	37	36
Pine/juniper	jun, pin	44.8	430	1.9	27	37	36
Western pine	pin	45.8	510	2.8	21	50	29
Douglas-fir/fir	abi, pse	2.1	590	2.9	24	44	32
Douglas-fir/pine	pin, pse	54.2	610	3.2	23	48	29
Southern pine	pin	150	640	3.5	21	50	29
Northwest conifers	thu, pic, pse, tsu	70.4	750	4.3	50	23	27
Aspen	pop	6.3	300	4.3	87	1	12
Mixed deciduous	bet, que, car, jug, lir	201	500	6.7	81	7	12
Northern deciduous	ace, bet, que, fag	122	420	5.0	82	5	17
Southern mixed	pin, que	188	650	8.7	72	16	12
Western mixed	pin, pse, que	0.8	300	3.9	74	14	12
Northern mixed	pin, ace, bet, fag	4.4	550	2.2	29	33	38
Northern mixed	pic, pin, ace, que, fag	34.8	570	7.0	75	12	13
Northeast mixed	abi, pic, ace, bet, fag	24.4	570	3.3	44	28	28
Northern mixed	pin, ace, que, fag	101	610	6.8	75	14	11
Southeast mixed	pin, que, liq, lir	184	670	11	78	12	10
Northwest mixed	thu, pse, tsu, que	23.8	700	8.4	81	6	13
Southern wetland	pin, sab, ser, que, avi	7.9	490	5.9	77	10	13
Northern wetland	pic, pin, ace, bet, que, fag	5.4	600	6.2	68	16	16
Coastal wetland	tax, avi	7.4	440	1.7	31	29	40
Pine/juniper scrub	jun, pin	31.9	270	0.8	33	27	40
Alpine scrub	pin	14.5	200	1.09	31	33	36
Oak scrub	que	51.2	330	4.3	86	2	12
Pine/oak scrub	pin, que	49.6	350	3.6	77	7	16
Oak/sum woods/crops	que, nys	29.5	170	4.4	80	4	16
Hardwoods/crops	bet, pop	17.4	170	4.7	75	3	22
Oak/pine woods/crops	pin, que	57.1	200	5.1	68	8	24
Pine woods/crops	pin	126	220	2.2	7	33	60
Hardwoods/crops	ace, bet, fag	181	220	1.8	9	17	74

Table 5. VOC emission rate factors (mg C m^{-2} h^{-1}) for six broad woodland categories. The number of EDC landscapes (N) in each general category and the relative contribution of each category to the total 3.8 $\times$ 10^6 km^2 of tree-covered surface area in the contiguous U.S.A. are based on Loveland *et al.* (1991). Total VOC (TVOC) emissions are normalized to a temperature of 30°C, an above canopy PAR flux of 1000 μmol m^{-2} s^{-1} and a foliar mass (g m^{-2}) that is representative of the landcover type. Isoprene, monoterpenes and other VOC emissions are shown as a percent of TVOC. Mean emissions are area-weighted estimates

Other VOC Category	N	Area (%)	Foliar mass Range	TVOC Mean	TVOC Range	Isoprene Mean (%)	Isoprene Range (%)	Monoterpenes Mean (%)	Monoterpenes Range (%)	OVOC Mean (%)	OVOC Range (%)
Decid. forest	4	11	300–500	5.5	4.2–7.3	80	79–91	7	1–8	13	8–15
Conifer. forest	19	15	400–800	3.0	1.7–4.3	26	25–50	46	22–51	28	26–35
Mixed forest	27	29	300–700	7.7	2.2–11	75	30–81	13	6–33	12	9–37
Wetland forest	5	1	350–600	3.7	1.4–6.2	52	31–77	22	11–30	27	17–39
Scrub woods	17	12	200–350	2.2	0.8–4.3	62	31–87	14	2–33	24	11–49
Mixed woods/crop	19	32	600–1000	4.5	1.7–8.0	50	8–75	13	3–33	37	19–73
All	91	100	200–1000	5.1	0.8–11	58	8–91	18	1–51	24	8–73

landscape average emission factors reported in this paper are normalized to 30°C and 1000 μmol $m^{-2} s^{-1}$. When these factors are adjusted to account for actual light and temperature conditions, including the effect of canopy shading, the actual magnitudes and relative compositions may be very different. Isoprene will typically comprise a smaller fraction of the total emission due to its light dependence. The area-weighted average TVOC emission factor for all U.S. woodland areas is estimated to be predominately isoprene (58%) with significant contributions of monoterpenes (18%) and other VOC (24%). There are extremely large variations in the estimated contribution of isoprene (8–91%) and monoterpenes (1–51%) from individual landscapes. The highest area-weighted TVOC emission rates are estimated for mixed (7.7 mg C $m^{-2} h^{-1}$) and deciduous (5.5 mg C $m^{-2} h^{-1}$) forests followed by woodland/cropland landscapes (4.5 mg C $m^{-2} h^{-1}$), wetland (3.7 mg C $m^{-2} h^{-1}$) and coniferous (3.0 mg C $m^{-2} h^{-1}$) forests and scrub woodlands (2.2 mg C $m^{-2} h^{-1}$).

Total VOC emission rate estimates for the four deciduous forest categories range from 4.2 to 7.3 mg C $m^{-2} h^{-1}$. These forests comprise about 14% of all U.S. woodland areas. Isoprene is estimated to contribute from 79% of daytime emissions in northern hardwood forests, dominated by maple, birch, oak and beech, to 87% in western deciduous forests dominated by aspen. At least some isoprene emitters, e.g. aspen, oak or sweetgum, occur in each of the four deciduous forest landscapes.

The EDC land-cover database contains 19 coniferous forest categories covering 15% of forested areas. TVOC emissions estimated for coniferous forests range from 1.7 to 4.3 mg C $m^{-2} h^{-1}$. Higher emissions are associated with southern and northwestern forests that have the highest estimated leaf biomass densities. The lower monoterpene rates assumed for some conifers (e.g. western redcedar, hemlock, juniper) result in only slightly lower estimated total VOC emission rates in coniferous forests dominated by these species. Monoterpene emissions are estimated to account for about half of all emissions in most coniferous forests. Coniferous forests which have a significant spruce component have higher isoprene emissions (about 50% of the daytime TVOC emission factor).

TVOC emission estimates vary by about a factor of 5 in the 27 mixed forests (2.2–11 mg C $m^{-2} h^{-1}$) and 5 wetland forests (1.4–6.2 mg C $m^{-2} h^{-1}$). Mixed forests account for 29% of all woodlands, while wetland forests represent only 1%. Estimated daytime TVOC emissions tend to be dominated by isoprene in both mixed (75%) and wetland (52%) forests. The contribution of isoprene in individual landscapes ranges from 30 to 81% in mixed forests and 31 to 77% in wetland forests.

Scrub woods cover an estimated 12% of U.S. woodland surfaces while mixed woodland/cropland landscapes account for 32%. The latter category includes landscapes that contain a mix of woods and croplands within a 1 km^2 area. TVOC emissions are estimated to range from 0.8 mg $m^{-2} h^{-1}$ for sub-alpine/tundra (pine) scrub woods and 1.8 mg $m^{-2} h^{-1}$ for northern hardwoods/cropland (maple, beech, birch, soybeans, corn) to 4.3 mg $m^{-2} h^{-1}$ for oak scrub woods and southern mixed forest/cropland (pine, oak, sweetgum, soybean, corn, cotton). Isoprene tends to dominate (50–62%) in these landscapes although the estimated contribution ranges from 31 to 87% in scrub woods and 8 to 75% in woodland/cropland landscapes.

The spatial distribution of landscape average isoprene and terpene emission factors for U.S. woodlands are shown in Fig. 1. High isoprene emission factors are associated with mixed forests containing oaks (west coast, southeast, Appalachian mountains) and aspen (Rocky Mountains). Moderate isoprene and high monoterpene emission is estimated for spruce forests in the northcentral and northeast United States of America. Low isoprene and high monoterpene emission is estimated for woodlands dominated by pines in the western United States of America.

Extensive effort has been directed at developing inventories of timber volume in the United States of America. The Forest Inventory and Assessment program, coordinated by the Regional Experiment Stations of the USDA Forest Service, has resulted in detailed inventories of tree populations which are available as the Eastwide Forest Inventory Database (EFID) for the eastern U.S.A. (Hansen *et al.*, 1992). The EFID data contain tree diameter measurements for individual tree species and are based on ground measurements and aerial photography. Inventories developed for the eastern U.S.A. contain population estimates of over 200 types of trees in 65 genera. The emission rates listed in Table 1 cover 41 of these genera. The 14 genera for which emission rates are not reported are limited in range within the U.S.A. or do not make a significant contribution to total biomass in any part of their range.

The tree diameter measurements compiled in the USDA forest inventory can be used to estimate dry weight leaf biomass using relationships developed for conifer (Baldwin, 1989) and hardwood trees (Clark *et al.*, 1985). We have used these relationships to estimate leaf biomass density estimates for the 40 genera of trees included in the EFID for 16 counties in eastern Georgia surrounding the SOS-ROME field site in George Smith State Park and the three counties in western Alabama surrounding the SOS-ROSE field site in Kinterbish Wildlife Refuge. The emission rates listed in Table 1 for 31 of these tree genera have been combined with these leaf biomass estimates. The resulting TVOC flux estimates are 4.8 mg $m^{-2} h^{-1}$ (73% isoprene, 15% monoterpenes) for eastern Georgia and 7.0 mg $m^{-2} h^{-1}$ for western Alabama (75% isoprene, 14% monoterpenes). The contribution of each tree genus is shown in Table 6. Over 99% of all isoprene emissions from either region are from oaks, gum, and

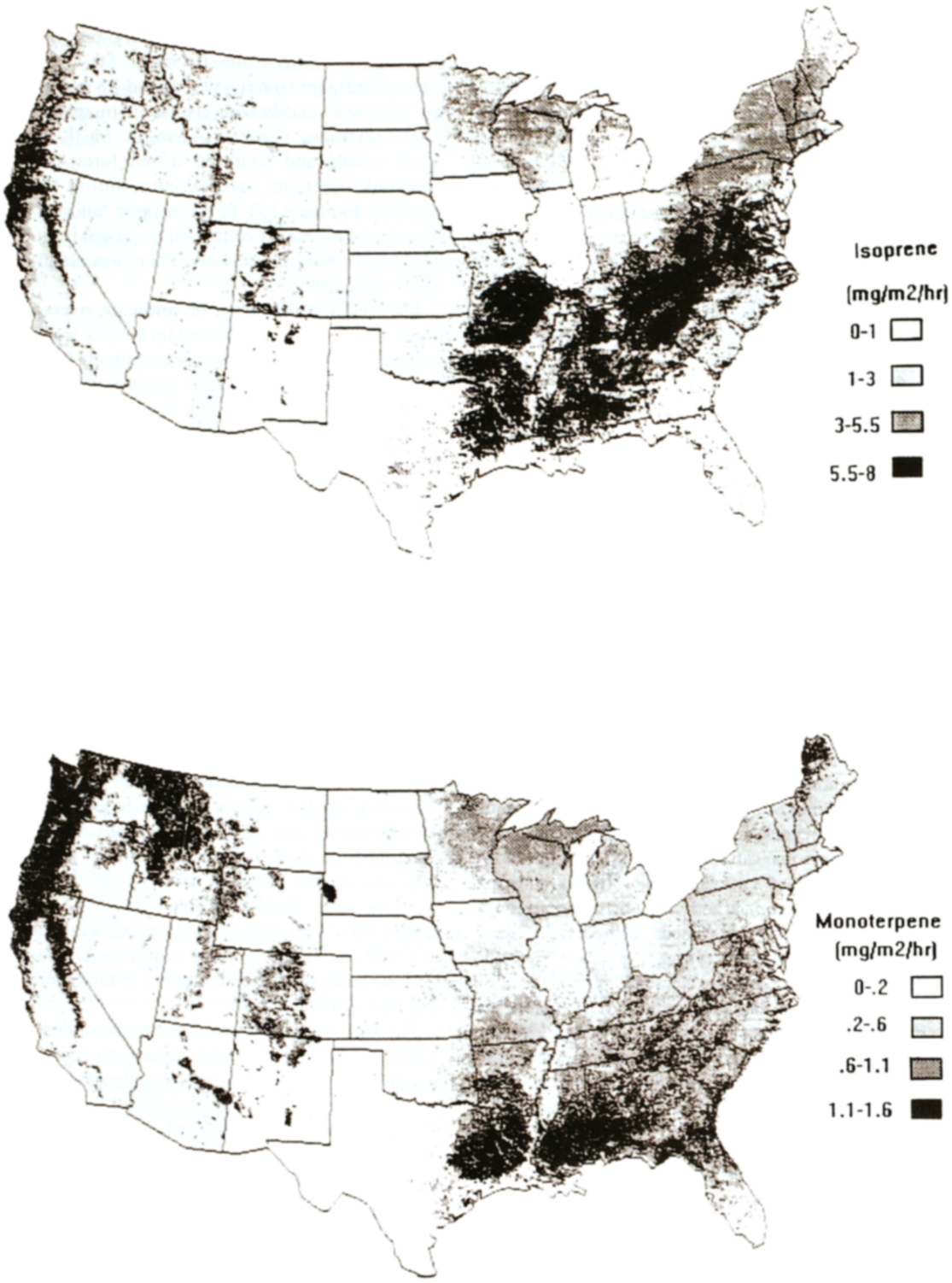

Fig. 1. Landscape average isoprene and monoterpene emission rate factors (mg C $m^{-2} h^{-1}$ at 30°C and an above canopy PAR flux of 1000 μmol $m^{-2} s^{-1}$) for U.S. woodlands.

sweetgum. Pines contributed about 70% of the monoterpene flux from both of these regions. Sweetgum, gum, maple and cypress trees together contributed an additional 20% of the monoterpene flux from these areas. The leaf biomass from the nine tree genera for which emission factors are not listed in Table 1 represents only 1% in the Alabama forest and 0.2% in the Georgia forest. This small contribution to the total

Table 6. Average foliar mass ($g\,m^{-2}$) and percent contribution to landscape total isoprene and terpene emissions based on EFID tree density estimates

		Eastern Georgia			Western Alabama		
Genus	Example	Foliar mass	Isoprene (%)	Terpene (%)	Foliar mass	Isoprene (%)	Terpene (%)
Acer	Maple	21.79	0	5.5	11.30	0	3.4
Betula	Birch	0.22	0	0	1.32	0	0.1
Carpinus	Hornbeam	0.00	0	0	5.66	0	0.9
Carya	Hickory	3.84	0	0.8	12.85	0	2.1
Celtis	Hackberry	0.43	0	0	7.96	0	0.2
Cercis	Redbud	0.02	0	0	0.41	0	0
Cornus	Dogwood	0.76	0	0.1	7.27	0	1.2
Diospyros	Persimmon	0.49	0	0	2.29	0	0
Fagus	Beech	1.94	0	0.1	2.92	0	0.2
Fraxinus	Ash	3.19	0	0	6.69	0	0.1
Ilex	Holly	0.92	0	0	1.46	0	0
Juglans	Walnut	0.00	0	0	0.14	0	0
Juniperus	Redcedar	0.05	0	0	6.13	0	0.1
Liquidambar	Sweetgum	24.23	27.5	10.1	52.20	40	16
Liriodendron	Tulip-tree	10.25	0	0.2	5.41	0	0.1
Magnolia	Magnolia	4.82	0	1.9	3.03	0	0.9
Melia	Chinaberry	0.15	0	0	0.24	0	0
Morus	Mulberry	0.25	0	0	1.30	0	0
Nyssa	Gum	54.49	12.5	4.6	7.46	1.1	0.1
Oxydendron	Sourwood	0.00	0	0	2.38	0	0.1
Persea	Redbay	1.40	0	0.1	0.00	0	0
Pinus	Pine	171.40	0	70.6	243.52	0	73
Platanus	Sycamore	0.32	0.1	0	2.38	0.9	0
Populus	Cottonwood	0.13	0.1	0	0.36	0.3	0
Prunus	Cherry	2.34	0	0	0.86	0	0
Quercus	Oak	52.16	59.6	1.4	74.70	57	0.2
Salix	Willow	0.30	0.1	0	0.29	0.2	0
Sassafras	Sassafras	0.12	0	0	0.41	0	0
Taxodium	Cypress	11.80	0	4.8	3.00	0	0.9
Ulmus	Elm	2.66	0	0	9.42	0	0.1
Vaccinium	Sparkleberry	0.00	0	0	0.17	0	0
Other		0.73	<1	<1	5.36	<1	<1

biomass was dominated by species in the *Ostrya* and *Tilia* genera but also included *Catalpa*, *Aesculus*, *Crataegus* and *Maclura* in Alabama and *Gleditsia*, *Gledenia* and *Planera* in Georgia. Even if we assume that these species have high isoprene ($8\ \mu g\,g^{-1}\,h^{-1}$) and monoterpene ($1.5\ \mu g\,g^{-1}\,h^{-1}$) emission rates their contribution to the total emission is much less than 1%. The isoprene and monoterpene emissions associated with ground cover in forests is not well known but probably results in a very small contribution since the leaf biomass associated with forest ground cover is only a small fraction of tree leaf biomass (Leith and Whittaker, 1975).

The high spatial resolution of the EDC land-cover data can be combined with the detailed source estimates available from the EFID forest inventory data and the USDA 1987 Agricultural Census crop data. Our analysis of these databases, for the counties in Georgia and Alabama described above, indicate that the crops and trees which are dominant components of the EDC landscapes are the same as those reported in EFID forest inventory and the 1987 USDA Agricultural Census. The relative contribution of individual crops and trees, however, varies considerably. Databases such as the EFID and Agricultural Census inventories should be used, when available, to apportion the total foliar mass among individual crops and trees.

4. COMPARISON WITH OTHER ESTIMATES

The area average emission rates summarized in Tables 4 and 5 are compared with previous estimates of biogenic emission rate factors in Table 7. Each of these studies (Zimmerman, 1979; Lamb *et al.*, 1987; Pierce and Waldruff, 1991; Lamb *et al.*, 1993) used similar techniques to estimate rates for a few general forest types (e.g. coniferous, oak deciduous, deciduous). It is difficult to directly compare these emission factors because many of the more detailed landscape categories do not fall within only one of these broad categories. In particular, many landscapes previously classified as deciduous or coniferous forests are now classified as mixed forests, woodlands or other categories.

Normalized TVOC emission rates ranging from $3.1\ mg\,m^{-2}\,h^{-1}$ to $6.5\ mg\,m^{-2}\,h^{-1}$ were previously

Table 7. Comparison of total VOC emission rate factors, mg C $m^{-2} h^{-1}$ at 30°C and 1000 μmol $m^{-2} s^{-1}$, and percent contribution of isoprene for U.S. woodlands

Reference	Conifer forests	Southern U.S. mixed forest	All U.S. woodlands
Zimmerman (1979)	6.5 (15%)	6.5–6.7 (15–59%)	6.5–6.7 (15–59%)
Lamb *et al.* (1987)	6.4 (17%)	6.2–6.4 (17–77%)	5.2–6.4 (17–77%)
Pierce *et al.* (1991)	3.1 (24%)	3.1–4.3 (24–73%)	3.1–4.3 (24–73%)
Lamb *et al.* (1993)	3.3 (21%)	3.3–3.8 (21–76%)	3.1–3.8 (21–76%)
This study			
Average	3.0 (26%)	9.8 (75%)	5.1 (58%)
Range	1.7–4.3 (25–50%)	8.7–11 (72–78%)	0.8–11 (8–91%)

estimated for coniferous forests. Isoprene was estimated to contribute between 15 and 24% of the total daytime VOC emission. In comparison, we estimate normalized TVOC emission rates ranging from 1.7 to 4.3 mg $m^{-2} h^{-1}$ for U.S. coniferous forests with isoprene contributing 25–50%. The area-weighted mean TVOC emission estimated for coniferous forests in this study, 3.0 mg $m^{-2} h^{-1}$, is on the lower end of previous estimates.

Previous studies estimated daytime TVOC emissions of 3.1–6.7 mg C $m^{-2} h^{-1}$ for the mixed forests for the southeastern U.S.A., which were classified as either coniferous or oak forests. Isoprene was estimated to contribute from 17 to 77% of TVOC. Our TVOC emission rate estimates for the southeastern mixed forests in the EDC database range from 8.7 to 11 mg C $m^{-2} h^{-1}$ with 72–78% as isoprene. These fluxes are somewhat higher than previous estimates. The area-weighted average TVOC flux for all U.S.A. woodlands, 5.1 mg C $m^{-2} h^{-1}$ (58% isoprene), is within the range of the fluxes previously estimated for general forest types.

The methodology we describe in this paper differs from previous techniques in four areas: (1) the VOC emission rate measurements used in the analyses, (2) the schemes used to assign representative emission rates to plant types, (3) the landscape categories used, and (4) the schemes used to assign species composition to landscape categories. Each of the four previous studies listed in Table 7 used only the data reported by Zimmerman (1979) to determine emission factors for woodlands. In this study, we have revised the Zimmerman data set and supplemented it with a number of other emission rate measurement data sets. Previous investigators have assumed that a given vegetation category consists of various amounts of four plant types: high isoprene, low isoprene, no isoprene deciduous, and coniferous. The Tampa Bay enclosure measurements were grouped into these four categories and averaged to generate representative VOC emission rate estimates. We have assigned emission rates at the genera level for trees and used an additional flux to represent emissions from all other plants.

The impact of using the emission factors described in this paper was evaluated by calculating emissions from forests in three states using the temperature and vegetation data employed by Lamb *et al.* (1987) and three sets of emission factors. The estimates compiled in Table 8 demonstrate that this can result in significant differences (as much as a factor of two) in estimated regional emissions. It should be noted, however, that the differences in estimates based on Lamb *et al.* (1987, 1993) are also about a factor of two. Our estimated relative contribution of isoprene is greater in each case.

The landscape average emission rates described above can be evaluated by comparison to field measurements of area-average fluxes. Knoerr and Mowry (1981) used a micrometeorological technique to estimate α-pinene (the dominant monoterpene) fluxes of 1.2–5 mg C $m^{-2} h^{-1}$ at temperatures between 28 and 34 C from a loblolly pine forest in North Carolina. The 1.8 mg C $m^{-2} h^{-1}$ total monoterpene emission rate we have estimated for southern pine woodlands at a temperature of 30°C falls within the lower end of this range.

Lamb *et al.* (1984, 1985) used micrometeorological methods to estimate an isoprene emission rate of 7.6 mg C $m^{-2} h^{-1}$ at 30°C for a deciduous forest in Pennsylvania. Using the procedures described above, we assign this landscape a total leaf biomass of 420 g m^{-2} of which 21% are isoprene emitters (oaks). This results in an isoprene emission factor of 4.1 mg C $m^{-2} h^{-1}$ at 30°C, which is 46% lower than the field measurements reported by Lamb *et al.* (1984, 1985). This estimate is based on a branch-level isoprene emission factor (40 μg C $g^{-1} h^{-1}$) for oaks so that shading effects are accounted for.

Data reported by Lamb *et al.* (1984) indicate that oaks constitute about 65% of the foliar mass at the Pennsylvania deciduous forest site. Using this site-specific data, we estimate an isoprene emission rate of 11.4 mg C $m^{-2} h^{-1}$ at 30°C and 1000 μmol $m^{-2} s^{-1}$ which is 50% higher than the flux measured by Lamb *et al.* (1984). The three-fold difference in estimated emissions due to differences in estimated species composition illustrates the importance of using accurate tree distribution data such as that in the USDA EFID inventory.

Lamb *et al.* (1984, 1985) used the gradient flux procedure to estimate a mean α-pinene (the dominant monoterpene) flux of 0.84 mg $m^{-2} h^{-1}$ at temper-

Table 8. Estimates of July total natural VOC emissions (10^9 g C) and percent contribution of isoprene from woodlands in three U.S. states using three different sets of emission factors

	Predominant woodlands	Lamb *et al.* (1987)	Lamb *et al.* (1993)	This study
Number of emission factors		3	3	56
Georgia	Deciduous and mixed	160 (58%)	96 (59%)	210 (68%)
Colorado	Conifer and scrub	76 (12%)	37 (15%)	40 (31%)
Washington	Conifer	86 (8%)	43 (11%)	32 (19%)

atures between 9 and 24°C in a douglas-fir forest in Washington State. The 1.5 mg m^{-2} h^{-1} monoterpene emission rate estimated for 30°C is equivalent to 0.66 mg m^{-2} h^{-1} at a temperature of 20°C when adjusted with the algorithm described by Guenther *et al.* (1993). This estimate is about 20% lower than the flux reported by Lamb *et al.* (1984).

Our estimates of isoprene and terpene emissions are within 50% of the estimated fluxes reported for each of the three field sites described above. Estimates of the uncertainty associated with these field flux measurements, ±50% (see Lamb *et al.*, 1984, 1985), suggest that the emission factors estimated by the techniques described above are in reasonable agreement with field measurements.

5. SUMMARY AND CONCLUSIONS

Emission rate measurements have been reported in the literature for many of the tree species in the United States of America including representatives of all of the major U.S. tree genera. Typical rates at 30°C and 1000 μmol m^{-2} s^{-1} range from <0.1 to 40 $\mu g\, g^{-1}\, h^{-1}$ for branch-level isoprene emissions and <0.1 to 70 $\mu g\, g^{-1}\, h^{-1}$ for leaf-level isoprene emissions. Monoterpene emissions range from <0.1 to 3 $\mu g\, g^{-1}\, h^{-1}$, while a range of <0.3–3 $\mu g\, g^{-1}\, h^{-1}$ has been observed for other volatile organic compounds. The genera-level emission factor scheme described in this paper results in area-averaged emission estimates that are considerably different from previous estimates. Higher emissions are estimated for most deciduous and mixed woodlands while lower emissions are estimated for conifer woodlands. The relative contribution of isoprene is estimated to be higher in almost every case. On an area-weighted basis, our estimated normalized total VOC emission rate factor of 5.1 $\mu g\, g^{-1}\, h^{-1}$ for U.S. woodlands is comprised of 58% isoprene, 18% monoterpenes and 24% other VOC. Monoterpenes and other VOC will typically contribute over half of the daily total flux, however, since isoprene emissions are negligible at night.

The EDC database developed by Loveland *et al.* (1991) can be used to simulate significant landscape-level variations which are not represented by more general schemes. The biomass density and species composition estimates that we have assigned using the EDC land-cover data set are a first approximation and should be used only if more detailed estimates, e.g. Hansen *et al.* (1992), are not available.

Field measurement programs have focused considerable attention on emissions from pines and oaks, each of which cover over 60% of all U.S. tree-covered surfaces. A more detailed emission rate classification scheme may be required for these two genera due to the large variety and distribution of species. Additional measurements are needed to reduce uncertainties in the rates assigned to other trees listed in Table 1 which have a widespread distribution but few reported emission rates (e.g. birch, beech, tulip-tree, douglas-fir and hickory). Future field measurement programs should include the quantification of a wider array of volatile organic compounds in order to reduce the large uncertainties associated with non-terpenoid compounds.

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