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SEASONAL AND SPATIAL VARIATIONS IN NATURAL VOLATILE ORGANIC COMPOUND EMISSIONS

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Abstract. Atmospheric concentrations of ozone and other air pollutants, in some regions, are sensitive to surface fluxes of volatile organic compounds (VOCs). Plant foliage is the source of at least half of all VOC emissions in the United States and more than two-thirds of global VOC emissions. Observed spatial and seasonal variations in foliar VOC emissions range over several orders of magnitude. Land characteristics data are an important component of the modeling techniques used to estimate VOC emission rate variations due to seasonal and spatial changes in species composition, foliar density, and other factors. Model techniques and land characteristics databases are compared and evaluated in this paper. Significant differences in VOC fluxes are predicted depending on spatial resolution, procedures used to develop land characteristics databases, and foliar density models. Satellite and ground observations can be combined to generate the accurate estimates of the species composition and foliar density required for natural VOC emission models.

Key words: biogenic; hydrocarbons; isoprene; landscape; model; monoterpene; volatile organic compounds (VOC).

INTRODUCTION

The chemistry of the atmosphere is strongly influenced by ecological processes that control the emission of water and trace gases from plants. Went (1960) recognized that foliar emissions of volatile organic compounds (VOCs) could have a significant impact on tropospheric chemistry by influencing the processes that control the formation of atmospheric haze. Rasmussen (1972) made the first U.S. estimate of isoprene and monoterpene emissions. Isoprene and monoterpenes are typically regarded as the predominant VOCs emitted by plants. Rasmussen placed a mix of oak and pine foliage in a 1-L flask under field conditions and expressed an emission rate as a concentration per 10 cm of foliage per hour. This rate was multiplied by 1800 h (180 10-h days) and a canopy depth that was assumed to range from 10 to 200 cm. The resulting estimated range of 2.3–46.4 Tg/yr demonstrated that natural fluxes were a significant component of the total U.S. VOC flux. Zimmerman (1979) measured emission rates from 69 vegetation species in 10 broad categories, assigned emission rates and foliar densities to seven natural vegetation biomes, accounted for the influence of seasonal temperature and foliar density variations, and estimated an annual U.S. isoprene and monoterpene flux of 65 Tg. Flux estimates based on the Zimmerman data were incorporated into regional photochemical chemistry and transport models (CTMs) and demonstrated that natural VOC can have a significant impact on ozone mixing ratios in the southeastern U.S. (Chameides et al. 1988).

The short lifetimes (minutes to hours) of natural VOC in the daytime troposphere result in large spatial and temporal variations in natural VOC mixing ratios. Accurate simulation of these mixing ratio variations requires highly resolved and accurate flux estimates. Lamb et al. (1987) developed procedures for estimating VOC emissions on scales appropriate for regional CTMs using a detailed land cover database of natural, urban, and agricultural areas as well as monthly temperature, day length, and foliar density estimates. Pierce and Waldruff (1991) implemented the Lamb et al. procedures as the Biogenic Emissions Inventory System (BEIS) designed to calculate hourly VOC emissions for regional regulatory models. A review of regional ozone pollution by the National Research Council (1991) emphasized the need for more accurate biogenic VOC emission estimates. Geron et al. (1994) responded by developing a revised model (BEIS2) that includes improved emission rate data (Guenther et al. 1994), relationships between emissions and environmental conditions (Guenther et al. 1991, 1993), and species composition and foliar density estimates (Geron et al. 1994). VOC emissions estimated by BEIS2 differ from BEIS by as much as a factor of five for some U.S. locations (Geron et al. 1995). Future improvements require a better understanding of the eco-

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logical processes controlling emissions. This paper reviews past and current natural VOC emission modeling procedures, addresses the uncertainties associated with each model component, and considers how future improvements can be made.

Model Descriptions

There are four major factors controlling natural VOC emissions: landscape average emission potential (ε, in micrograms per gram per hour), foliar density (D, in grams dry mass per square meter), an emission activity factor to account for instantaneous light and temperature conditions (γ, nondimensional), and an emission activity factor to account for longer term (>1 h) controls over emission variations (δ, nondimensional). Emission fluxes (F, in micrograms per square meter per hour) can be estimated with a model that includes each of these components,

$$F = \varepsilon D \gamma \delta. \qquad (1)$$

The complexity of each model component can range from simply assigning a constant value to simulating the processes controlling emissions. Methods for determining each model component are described in this section.

Emission potential

Emission potentials represent the emission rate per unit foliar mass expected for a plant species under a given set of conditions. This factor accounts for genetic controls over VOC emissions. The task of estimating VOC emissions would be greatly simplified if plants had similar emission potentials. Instead, VOC emission potentials for different plant species vary by more than three orders of magnitude. There are two approaches that can be used to estimate landscape average emission potentials. The first approach requires an estimate of species composition for each location in a model domain and a database of emission potentials for each plant species. Emission potentials for individual plant species are determined from leaf and branch enclosure measurement techniques. A landscape average emission potential can then be calculated as the weighted average of all plant species at each location. The second approach assigns a landscape type to each location within the model domain. An emission potential, determined from micrometeorological measurement techniques or from general assumptions of species distributions, is associated with each landscape type. Both approaches require land cover and emission potential databases.

Estimates of isoprene and monoterpene emission potentials for 49 tree genera including all of the dominant trees in the U.S. (Guenther et al. 1994) and tree species composition estimates for each county in the eastern U.S. (Geron et al. 1994) provide the data required to quantify species distributions and apply individual emission potential for each location in the model domain. All other regional models described in the literature use the second approach where each location in the model domain is assigned one of a number of landscape types.

The accuracy of regional VOC emission models is limited by a lack of emission rate measurements and appropriate land cover databases. VOC emissions tend to be higher in woodlands, requiring that, at a minimum, land cover databases correctly distinguish woodlands from other areas (Zimmerman 1979). Most regional emission models classify landscapes into three or four woodland categories and several nonwoodland landscapes (Zimmerman 1979, Lamb et al. 1987, 1993, Pierce and Waldruff 1991). A significant improvement should be expected if landscapes are classified according to species composition, e.g., oak–hickory forest landscape. Guenther et al. (1994) note that even this level of detail can result in large uncertainties. For example, if oak trees have an isoprene emission potential of 70 μg C·g^{-1}·h^{-1} and hickory trees have an emission potential of 0.1 μg C·g^{-1}·h^{-1}, then an oak–hickory forest with a foliar density of 400 g/m^2 consisting of 20% oak and 80% hickory has a landscape average emission potential of ≈ 6.4 mg C·g^{-1}·h^{-1} which is a factor of 4 lower than the weighted average emission potential of a forest with 80% oak and 20% hickory foliage.

Foliar density

Foliar density varies with location and time and can be calculated as the product of the annual peak foliar density (D_p) at a specified location and the fraction present (D_f) at a specified time of year. Zimmerman (1979) noted that peak foliar density tends to be uniform throughout vegetation associations and assigned literature values to each of seven land cover types. This approach was followed in many subsequent VOC emission model efforts (e.g., Lamb et al. 1987, 1993, Pierce and Waldruff 1991). While this is a reasonable first approach it should be recognized that peak foliar densities can vary significantly within a land cover type. Peak foliar densities for a woodland landscape can vary from <150 to ≈1500 g/m^2 depending on tree species composition and the fraction of the landscape that is tree covered (see Geron et al. 1994). Spatial variations in peak foliar densities can be estimated with net primary productivity models (Guenther et al. 1995) or from vegetation indices derived from satellite measurements of light reflectance in specific spectral bands (Guenther et al. 1994).

Significant variations in the fraction of peak foliar density present at a particular time of year, D_f, occur on time scales of weeks to months. Estimates of D_f range from a maximum of 1 to <0.1 in landscapes dominated by deciduous vegetation. Monthly variations in foliar mass or leaf area have been estimated by Lamb et al. (1987) using climatological data (first and last frost-free dates) and by Sellers et al. (1994) and Guenther et al. (1995) using satellite measurements. Lamb et al. (1987) assigned D_f a value of 1 during the growing season and 0 at other times in deciduous forests and grasslands. Evergreen forests were assigned a constant value of $D_f = 1$, while croplands were assumed to have a linear increase in foliar mass with periodic harvests.

Light and temperature

Diurnal variations in isoprene and monoterpene emissions are almost entirely due to variations in light intensity and leaf temperature. The emission activity factor that accounts for these variations, γ in Eq. 1, can increase by more than an order of magnitude from early morning to midday. Zimmerman (1979) and Lamb et al. (1987) used numerical algorithms to calculate the influence of temperature on isoprene and monoterpene emissions and considered isoprene to be emitted only during daylight hours. Pierce and Waldruff (1991) and Lamb et al. (1993) included methods for calculating hourly light intensity based on solar elevation angles and cloud cover and a canopy environment model to calculate leaf temperature and light variations with canopy depth. Guenther et al. (1991, 1993) developed numerical algorithms that simulate continuous variations in γ for isoprene and monoterpenes from a variety of vegetation types. Light and temperature controls over VOC emissions fall into two categories: VOC emissions controlled by volatilization of stored compounds and VOC emissions controlled by VOC production. Variations controlled by VOC production are calculated using the algorithms developed by Guenther et al. (1991, 1993)

$$\gamma = \left[\frac{\alpha C_{L1} L}{\sqrt{1 + \alpha^2 L^2}}\right]\left[\frac{\exp\left(\dfrac{C_{T1}(T - T_s)}{R T_s T}\right)}{C_{T3} + \exp\left(\dfrac{C_{T2}(T - T_M)}{R T_s T}\right)}\right] \qquad (2)$$

where L (in micromoles photons per square meter per second) is photosynthetically active radiation (PAR), T (kelvin) is leaf temperature, T_s (kelvin) is the leaf temperature at standard conditions, R is a constant ($=8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$) and α ($=0.0027$), C_{L1} ($=1.066$), C_{T1} ($=95\,000$ J/mol), C_{T2} ($=230\,000$ J/mol), and T_M ($=314$ K) are empirical coefficients. The value of the coefficient C_{T3} should be set equal to 0.961 rather than the value of 1 reported by Guenther et al. (1993) in order to force γ to be equal to 1 at standard light and temperature conditions. VOC production controls emission variations of isoprene from most plants (Guenther et al. 1993) and monoterpenes from at least some plants (Staudt and Seufert 1995). When VOC emissions are controlled by volatilization of stored compounds, then Guenther et al. (1993) recommend using

$$\gamma = \exp(\beta[T - T_s]) \qquad (2b)$$

where β is an empirical coefficient equal to $0.09°\mathrm{C}^{-1}$. Monoterpene emissions from a large variety of plants are controlled by volatilization of stored VOC (Guenther et al. 1993).

Other factors

Other factors that influence emission activity, δ, include growth environment (e.g., temperature, light, and CO_2 mixing ratio), leaf age, phenological events (e.g., bud break and blooming), leaf VOC concentrations, leaf nitrogen content, water status, insect herbivory, disease, physical injury, and other stresses (see Guenther et al. 1995). These processes play a role in determining day-to-day and longer variations in emissions. Investigations of these processes have provided some insights but have not yet resulted in reliable numerical algorithms that can be incorporated into regional emission models. Several studies have shown that there is a strong seasonal variation in isoprene emission (Goldstein 1994, Monson et al. 1994, Kempf et al. 1996). Emissions follow a general pattern of a winter period of negligible emissions followed by a rapid rise to a growing season maximum followed by a rapid decrease. This general behavior can be described numerically as

$$\delta = 0 \qquad J < J_0 \text{ or } J > J_0 + J_d \qquad (3a)$$

$$\delta = \sin([J - J_0]/J_d) \qquad J_0 < J < J_0 + J_d \qquad (3b)$$

where J is the current Day of Year, J_0 is the date of the annual onset of isoprene emission, and J_d is the duration of isoprene emission in days. The observed seasonal variation in isoprene emission from oak and aspen trees, observed by Goldstein (1994) and Monson et al. (1994), is at least partly due to changes in leaf age. Monson et al. (1994), however, show that the onset of isoprene emission is also related to exposure to a minimum temperature level. A combination of leaf age, derived from the estimates of D_f described above, and seasonal temperature data could provide an approach for estimating J_0 and J_d. Eq. 3 may not be appropriate

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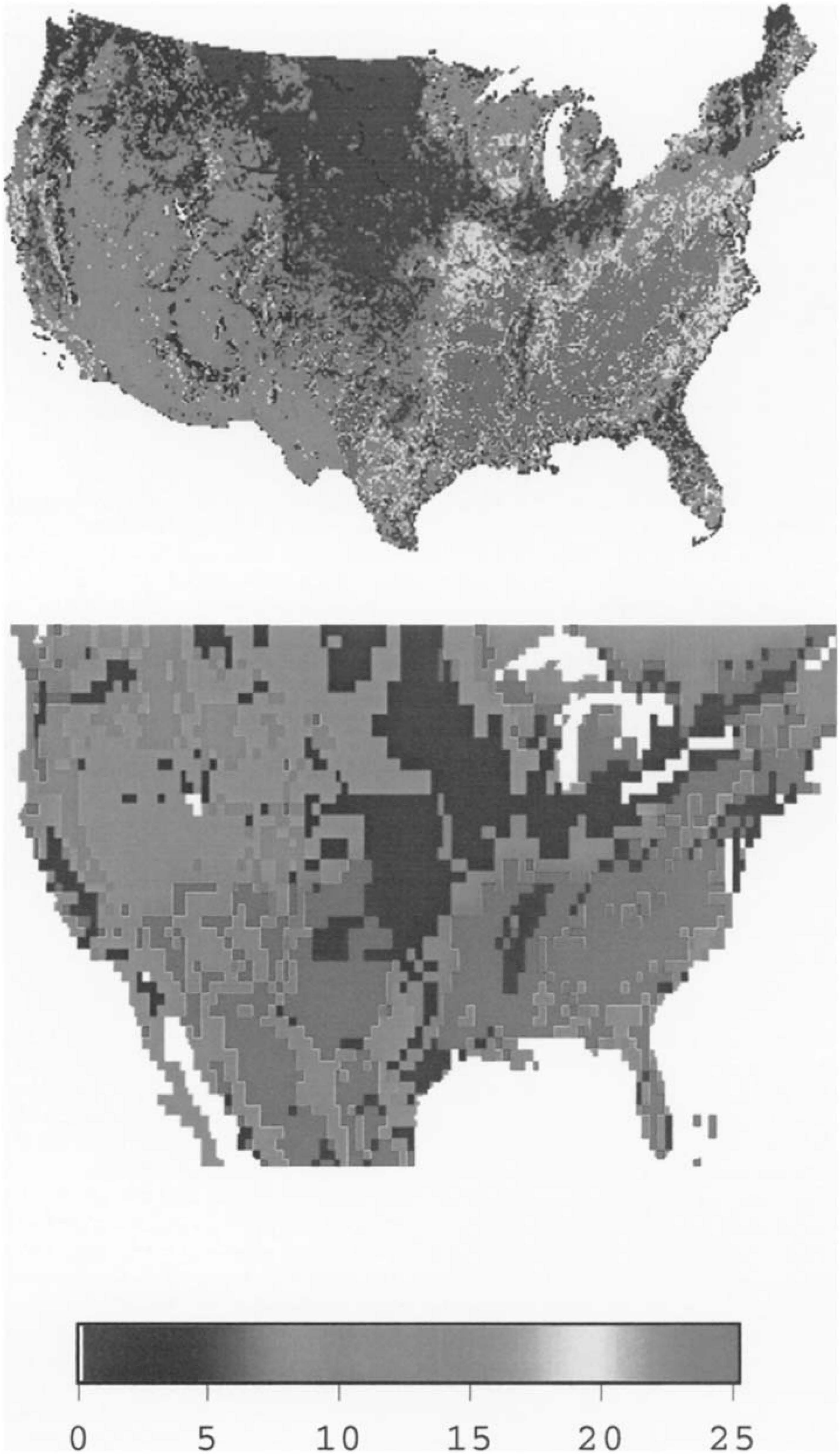
PLATE 1. Spatial distribution of U.S. isoprene emission potentials (μg $\mathrm{C \cdot g^{-1} \cdot h^{-1}}$ at a leaf temperature of 30°C and photosynthetically active radiation on 1000 μmol $\mathrm{photons \cdot m^{-2} \cdot s^{-1}}$) based on the 1.1 km LCC-AVHRR (Land Cover Characteristics-Advanced Very High Resolution Radiometer) land characteristics data and Guenther et al. (1994) emissions data (top) and the 0.5° latitude × 0.5° longitude WED (World Ecosystems Database) land characteristics data and Guenther et al. (1995) emissions data (bottom).



ISOPRENE EMISSION POTENTIALS ($\mu g \cdot g^{-1} \cdot h^{-1}$)

TABLE 1. Land cover databases used to estimate natural VOC emissions in the contiguous United States.

	LCC-MSS	EWDB	LCC-AVHRR	WED	Biome	Geoecology
Emission database	G96	Ge94	G94	G95	Z79	L87
Emission potentials	5	2237	91	59	7	6
Land database	G96	H92	L91	O92	Z79	O80
Landscape types	5	2237	167	59	7	132
Spatial resolution	0.0064 km^2	$\approx$2500 km^2	1.2 km^2	$\approx$3000 km^2	$\approx 3 \times 10^5$ km^2	$\approx$2500 km^2
Grid shape	uniform	irregular	uniform	uniform	irregular	irregular
Spatial extent	8000 km^2	eastern U.S.	U.S.	global	U.S.	U.S.
Coverage	all landscapes	woodlands	all landscapes	all landscapes	all landscapes	all landscapes
Ground data	Yes	Yes	No	No	No	No
Satellite data	Yes	No	Yes	No	No	No

Notes: Emission and landcover database references include Geron et al. 1994 (Ge94), Guenther et al. 1994 (G94), Guenther et al. 1995 (G95), Guenther et al. 1996 (G96), Hansen et al. 1992 (H92), Lamb et al. 1987 (L87), Loveland et al. 1991 (L91), Olson 1980 (O80), Olson 1992 (O92), and Zimmerman 1979 (Z79). The numbers of emission potentials and landscape types in each database are shown. Entries for ground and satellite data indicate if landcover characterization is based on field or satellite measurements, respectively. LCC-MSS = Land Cover Characteristics-Multi Spectral Scanner; EWDB = Eastwide Database; LCC-AVHRR = Land Cover Characteristics-Advanced Very High Resolution Radiometer; WED = World Ecosystems Database.

for all landscapes, e.g., tropical evergreen forests. Kempf et al. (1996) found that factors other than leaf age can play an important role in determining seasonal variations in isoprene emissions from evergreen spruce trees. Reliable algorithms for estimating δ will require a better understanding of the processes controlling these variations as well as appropriate land characteristics and climatic data.

MODEL EVALUATIONS

Natural VOC emission models are evaluated in this section by an intercomparison of model emission estimates and by comparing model estimates with field measurements. Spatial and seasonal variations predicted by VOC emission models are compared and evaluated directly below. The section *Comparison with field measurements* discusses the use of ambient measurements to evaluate natural VOC emission models.

Spatial variations

Each of the six land characteristics databases described in Table 1 have been used to estimate natural VOC emissions. A comparison of the number of landscape types, emission potentials, the size and shape of the model grids, the extent of coverage, and the accuracy of each database is summarized in Table 1 and discussed in this section. The procedures used by Guenther et al. (1994) to estimate emissions for the 91 forest landscapes in the LCC-AVHRR (Land Cover Characteristics-Advanced Very High Resolution Radiometer) database are expanded in this manuscript to cover all 167 landscapes in the LCC-AVHRR database.

Only one of the databases (WED, World Ecosystems Database) listed in Table 1 has global coverage. An additional three databases (LCC-AVHRR, Geoecology, Biome) cover the entire contiguous U.S. The EWDB (Eastwide Database) data are based on tree statistics and cover only woodland regions of the eastern U.S. Three databases contain general descriptions of landscape types (WED, Biome, Geoecology) based on potential vegetation maps. The WED and Geoecology databases have been adjusted to account for agriculture and urbanization. One database was derived from satellite measurements (LCC-AVHRR), one based on ground measurements of species composition (EWDB), and one based on both (LCC-MSS, Land Cover Characteristics-Multi Spectral Spanner).

The LCC-MSS, Biome, and WED databases use relatively few (5–59) landscape types. The number of landscape types required to accurately estimate VOC emissions depends on the size of the region covered by the database and the landscape diversity within the region. The Geoecology and LCC-AVHRR databases each contain >130 landscape types and only begin to approach the number of landscapes required to represent spatial variations in U.S. VOC emission potentials. The best characterization is provided by the EWDB database that defines a unique landscape type for each of the 2237 locations in the database.

Three of the databases (LCC-MSS, WED, and LCC-AVHRR) listed in Table 1 have uniform grids that can easily be incorporated into atmospheric chemistry models. The other databases have grid boundaries that represent political units (EWDB and Geoecology) or vegetation distributions (Biome).

Estimates of total land area for the contiguous U.S. compiled in Table 2 range from 7.58 to 7.73 10^6 km^2. Estimates of scrubland areas agree within ± 15% and forests within about ± 20%. Grassland estimates range from 0.03 to 2.16×10^6 km^2. WED classifies most grasslands as agricultural lands, resulting in a much lower grassland area. The databases that include agricultural landscape types have cropland area estimates that agree within ± 10%. The Biome database is based solely on potential vegetation and does not have an agricultural land category. This results in large overestimates of grassland and forest areas. The Geoecology database greatly overestimates the proportion of

TABLE 2. Comparison of contiguous U.S. surface areas (10^6 km^2). Databases are described in Table 1.†

Land cover	Biome	Geo-ecology	LCC-AVHRR	WED
Total woods	3.86	2.49	3.19	2.67
Conifer forest	1.17	0.96	0.61	0.93
Decid. forest	2.69	1.52	0.42	0.06
Mixed forest	···	···	1.10	0.39
Woods and crops	···	···	1.22	1.70
All grasslands	2.16	1.26	0.62	0.03
Alpine	0.03	···	0.01	0.05
Other grasslands	2.26	···	0.61	0.01
All scrublands	1.68	1.57	2.04	2.14
Scrub woods	···	···	0.46	0.43
Desert scrub	1.43	···	0.18	0.63
Other scrub	0.25	···	1.40	1.51
All croplands	···	1.83	1.62	1.84
All other lands	···	0.54	0.10	0.02
All landscapes	7.71	7.68	7.73	7.58

† Ellipses indicate categories that do not occur in given database.

deciduous forests by not considering the conversion of deciduous forests to pine plantations in the southeastern U.S.

VOC emission potentials from five different databases (Zimmerman 1979, Lamb et al. 1987, 1993, Guenther et al. 1994, 1995) are compared in Table 3. Area-weighted average monoterpene emission potentials for the entire U.S. agree within ± 5% for the Lamb et al. and Guenther et al. databases, but average emission potentials for general landscapes vary by a factor of 2 or more. The Zimmerman database results in an average U.S. monoterpene emission potential of 4.7 μg C·g^{-1}·h^{-1}. This is approximately a factor of 5 higher than the other estimates. This is due to high estimates of monoterpene emission rates for individual plant species, as discussed by Guenther et al. (1994), and due to the underestimation of total cropland area. Area-weighted average isoprene emission potentials range from 2.4 μg C·g^{-1}·h^{-1} (Lamb et al. 1993) to 15.5 μg C·g^{-1}·h^{-1} (Guenther et al. 1995). As discussed by Guenther et al. (1994), the Guenther databases contain leaf level emission potentials that are expected to be 75% higher than the branch level emission potentials in the Zimmerman and Lamb databases.

The spatial resolution of the Biome database is ≈3 × 10^5 km^2, which is sufficient only for a low-resolution global CTM. The average spatial resolution of the WED, EWDB, and Geoecology databases (≈2500 km^2) is similar to that used in many regional CTMs. The LCC-AVHRR and LCC-MSS databases have spatial resolutions of 1.2 and 0.0064 km^2, respectively, which greatly exceeds the resolution used in regional CTMs. The satellite imagery used to develop these two databases results in very high-resolution databases.

Trace gases with long lifetimes have mixing ratios that are relatively uniformly distributed throughout the troposphere. CTM results are therefore insensitive to the spatial resolution of emissions of gases with long lifetimes. Isoprene, monoterpenes, and many other natural VOCs have lifetimes of minutes to hours (Atkinson 1990). Ambient mixing ratios near the surface can vary significantly over horizontal spatial scales of ≤100 km^2. CTM results may be sensitive to the spatial resolution of emissions of these highly reactive VOC. The LCC-AVHRR database was used to investigate the sensitivity of emission estimates to landscape heterogeneity. The Guenther et al. (1994) emission potentials were assigned to nine 480-km^2 regions using two different methods. In the first case, referred to as the high spatial resolution (HSR) estimate, emission factors were assigned according to the land cover type at each

TABLE 3. Comparison of contiguous U.S. emission potential estimates (μg C·g^{-1}·h^{-1} at 30°C and 1000 μmol photons·m^{-2}·h^{-1}). Emission databases are described in Table 1.†

	Isoprene					Monoterpenes			
	Z79	L87	L93	G94	G95	Z79	L93	G94	G95
All forests	6.6	6.6	4.1	8.4	18.2	5.0	2.1	1.5	1.3
Conifer	1.5	1.7	1.1	2.3	18.1	7.9	3.4	2.3	2.3
Deciduous	8.8	9.6	6.0	19.0	45.0	3.8	1.2	1.0	0.8
Oak forests	···	12.6	7.7			···	1.4		
Mixed forests	···	···	···	20.3	18.9	···	···	2.0	0.9
Wetland forests	···	···	···	7.2	···	···	···	1.7	···
Forest and crops	···	···	···	4.9	18.9	···	···	0.7	0.9
Rain forest	1.2	···	···			8.2			
All grasslands	3.2	5.9	3.8	8.8	11.6	4.5	1.7	0.2	0.6
Alpine	2.0	···	···	···	16	6.1	···	···	0.8
Other grasslands	3.2	···	···	···	5	4.5	···	···	0.2
All scrublands	5.4	3.6	2.2	8.8	18.1	4.1	0.6	1.1	1.1
Scrub woods	···	···	···	···	16	···	···	···	2.1
Desert scrub	5.8	···	···	···	16	4.2	···	···	0.8
Other scrub	3.2	···	···	···	19.5	3.8	···	···	1.0
All croplands	···	0	0.03	5	5	···	0.1	0.2	0.2
All other lands	···	7.8	0.1	8	16	···	0.3	0.8	0.8
All landscapes	5.4	4.4	2.4	7.9	15.5	4.7	1.1	1.0	1.0

† Ellipses indicate categories that do not occur in given database.

1.1-km grid location and then averaged over the 400 locations within each region. The moderate spatial resolution (MSR) estimate was obtained by first determining the two most dominant land cover classes within a region and then assigning the average emission potential of those two land cover types. The results shown in Table 4 indicate that the MSR data resulted in isoprene emission estimates that were 26% lower to 73% higher, while monoterpene emission estimates were only slightly different, 15% lower to 16% higher. The average MSR estimate for the eight locations, however, is only 12% higher for isoprene and 5% lower for monoterpenes and the total range in estimates is similar. These results suggest that landscape heterogeneity can significantly influence predicted VOC emissions at a particular location, but there is no apparent overall bias. In the case of shrublands, model resolution had little impact because a lack of emission potential data for these land cover types resulted in the assignment of the same emission potential to most shrublands.

The spatial distributions of U.S. isoprene and monoterpene emission potential estimates are illustrated in Plates 1 and 2. As described above, the HSR emission potentials have a 1.1-km spatial resolution (Plates 1 and 2, top). The WED data (Olson 1992) and the emission potentials described by Guenther et al. (1995) were used to generate a map with a low (0.5° latitude × 0.5° longitude) spatial resolution (LSR, Plates 1 and 2, bottom). The spatial distributions of the high- and low-resolution isoprene data shown in Plate 1 have the same general features. Isoprene emission potentials are highest in the Appalachian mountains and southeastern U.S. There are a number of areas in Florida, the Great Lakes region, and the northeastern and the southwestern U.S. that are assigned high isoprene emission potentials by the LSR database and low emissions by the HSR database. Plate 2 demonstrates that estimates of monoterpene emission potentials are highest in the southeastern U.S. and parts of the Rocky mountain, Sierra, and coastal ranges of the western U.S. The lowest isoprene and monoterpene emission potentials are estimated for the north-central U.S. region, which corresponds to agricultural and rangeland areas. The small-scale heterogeneity apparent with the HSR data cannot be duplicated by the LSR data. This could significantly impact regional CTM results in areas where landscapes with high and low emission potentials occur within the same region.

Four of the six databases listed in Table 1 simply assign literature values of peak foliar densities to each land cover type. The other two databases simulate spatial variations in foliar density within a land cover type. Guenther et al. (1994) accomplish this using the satellite data of Loveland et al. (1991). A net primary productivity model was used by Guenther et al. (1995) to estimate spatial variations in foliar densities within the WED global database. The estimated U.S. average peak foliar densities listed in Table 5 range from 360 g/m^2 (Zimmerman 1979) to 705 g/m^2 (Guenther et al. 1995). Lamb et al. (1987) and Guenther et al. (1994) each estimate average foliar densities of ≈500 g/m^2. Zimmerman (1979) estimated an average scrubland foliar density (130 g/m^2) that is a factor of 2–3 lower than the other scrubland estimates (275–375 g/m^2). The grassland foliar density of 150 g/m^2 assigned by Lamb et al. (1987) is a factor of 2–3 lower than the other grassland estimates (250–365 g/m^2). The average woodland foliar density (910 g/m^2) estimated by Guenther et al. (1995) is ≈70% higher than the other estimates.

Net primary productivity models can be driven by factors such as annual average temperature, cumulative annual precipitation, CO_2 mixing ratio, and nitrogen deposition. These models can be used to evaluate the response of peak foliar densities to global changes and the resulting changes in VOC emissions. Satellite measurements can also be used for this purpose and have the advantage of being able to estimate changes in foliar density due to land use change.

Seasonal variations

Three methods of estimating seasonal foliar density variations are compared in Fig. 1 for three sites: Harvard Forest (temperate deciduous and mixed forests near Petersham, Massachusetts), Niwot Ridge (alpine mixed forest and grassland near Boulder, Colorado), and Boulder, Colorado (conifer forests, grassland and urban areas near Boulder, Colorado). Two methods based on satellite measurements (Sellers et al. 1994, Guenther et al. 1995) tend to agree within ± 10% and predict the same general pattern at each of the three sites. Some differences are expected since these data represent different years (1988 and 1990). The Sellers et al. (1994) data predict higher values of D_f outside of the growing season. The major disagreements occur for months at the beginning and the end of the growing season. The climatological model of Lamb et al. (1987) performs reasonably well for the Harvard Forest and Niwot Ridge sites, which are classified as deciduous, but performs poorly for the Boulder, Colorado site, which is classified as evergreen. The Lamb et al. model could be improved by assuming that landscapes are a

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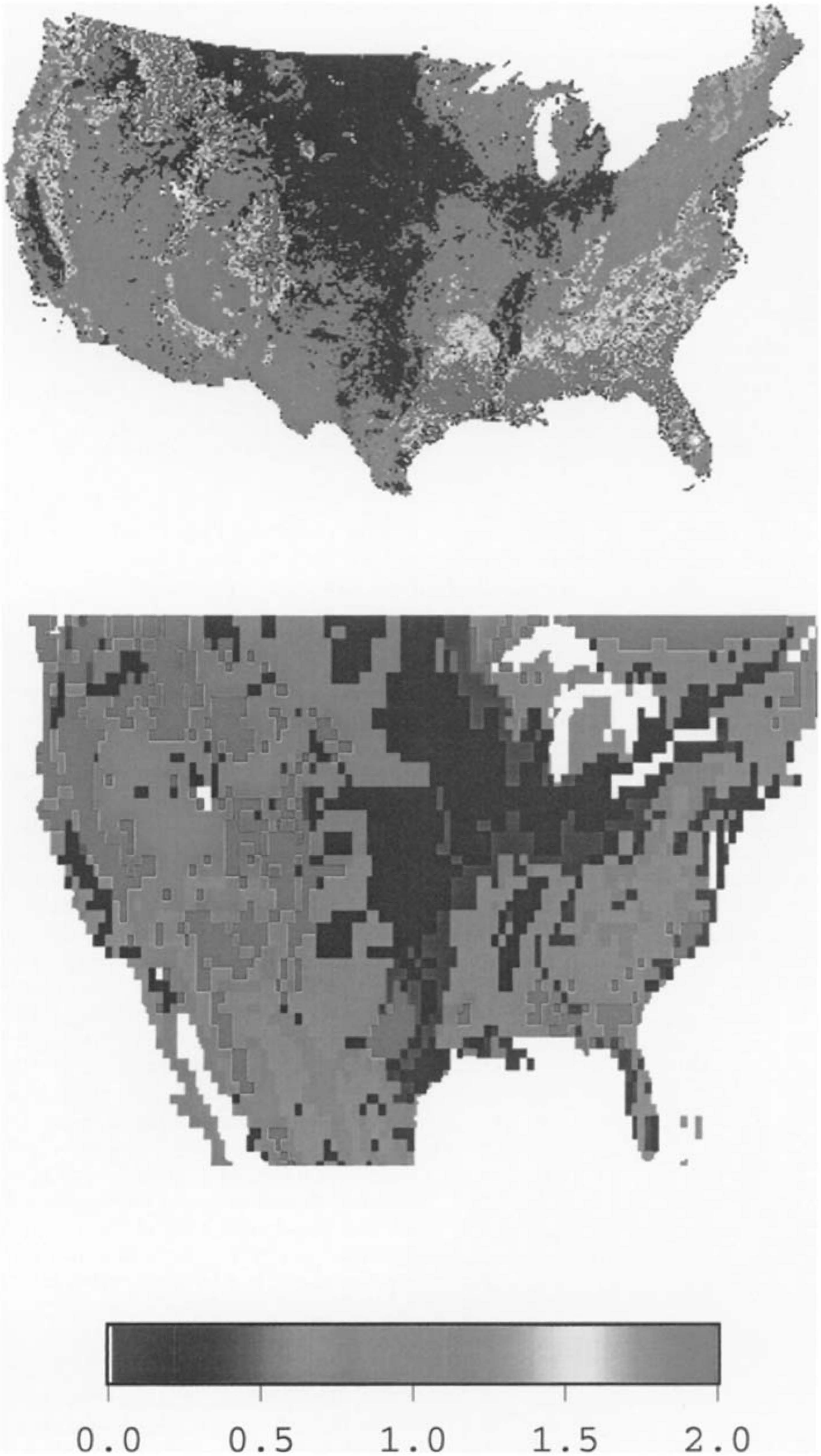
PLATE 2. Spatial distribution of U.S. monoterpene emission potentials (μg C·g^{-1}·h^{-1} at a leaf temperature of 30°C and photosynthetically active radiation of 1000 μmol photons·m^{-2}·s^{-1}) based on the 1.1 km LCC-AVHRR land characteristics data and Guenther et al. (1994) emissions data (top) and the 0.5° latitude × 0.5° longitude WED land characteristics data and Guenther et al. (1995) emissions data (bottom).



MONOTERPENE EMISSION POTENTIALS ($\mu g \cdot g^{-1} \cdot h^{-1}$)

TABLE 4. Comparison of isoprene and monoterpene emission potentials estimated using high-resolution and moderate-resolution land cover data.

		Isoprene		Monoterpene	
Location	Dominant vegetation	HSR	MSR	HSR	MSR
Northwest	mixed forest	8.33	10.4	1.39	1.17
North	crops/deciduous forest	7.52	13.0	0.8	0.78
Northeast	crops/deciduous forest	10.7	8.09	1.23	1.1
Central	crops/mixed forest	12.5	17.0	1.20	1.40
Eastern	crops/deciduous forest	23.1	22.3	1.2	1.2
Southwest	shrubland	8.1	8	0.82	0.8
South	crops/woods/savanna	17.4	20.4	1.31	1.25
Southeast	crops/mixed woods	13.0	12.2	1.34	1.17
Average		12.1	13.5	1.16	1.10
Range		7.5–23	8–22	0.8–1.39	0.78–1.4

Note: Isoprene and monoterpene emission potentials, ε (mg $C \cdot m^{-2} \cdot h^{-1}$ at a temperature of 30°C and PAR of 1000 μmol photons$\cdot m^{-2} \cdot s^{-1}$), are estimated as the mean of 400 individual 1-km^2 grids (high spatial resolution, HSR) or as the mean emission potential factor of the two most dominant landscapes in the 400 km^2 region (moderate spatial resolution, MSR) using the LCC-AVHRR (Land Cover Characteristics-Advanced Very High Resolution Radiometer) database.

mix of conifer and deciduous plants and assigning a value of D_f that is between 0 and 1 to the period outside of the growing season. An additional disadvantage of the Lamb et al. scheme is that it is difficult to extend to areas where factors other than temperature, such as precipitation, control seasonal foliar density variations.

Three of the model components described in the section *Model descriptions* contribute to monthly variations in VOC emission rates. Together they can be expected to result in monthly VOC emission rates that differ by as much as an order of magnitude. Fig. 2 shows estimates of seasonal variations in foliar density (D_f) and isoprene emission activity factors (γ and δ) for the three sites discussed above. It should be noted that the estimates of D_f, γ, and δ shown in Fig. 2 do not represent the same year and that interannual differences may be significant. Estimates of D_f are based on satellite measurements (Guenther et al. 1995), while γ is based on the light and temperature algorithms of Guenther et al. (1993). Estimates of δ are based on Eq. 3 and the isoprene measurements reported by Goldstein (1994) for Harvard Forest and Monson et al. (1994) for Niwot Ridge and Boulder, Colorado. Each of the variables makes a significant contribution to seasonal variations in VOC emission rates at each of the three sites. The three variables display the same general seasonal behavior with high values in summer and low values in winter. Isoprene emission rates from November through April are predicted to be very low at each of these sites. Natural emissions make a negligible contribution to total, natural plus anthropogenic, VOC during this time of year, so that even though the uncertainties on these rates may be very high, it may not have a major impact on CTM results. Each variable predicts that emissions agree within ≈20% of peak rates during the middle portion of the growing season. Uncertainties in emission rates are greatest during the beginning and end of the growing season. Natural emissions have a significant impact on CTM results during this time of year in at least some regions. Estimates of δ appear to have the greatest impact on predicted emissions and are by far the most uncertain. This result emphasizes the need for improving estimates of this factor.

TABLE 5. Comparison of contiguous U.S. foliar density (g dry mass C/m^2) estimates.†

Land cover	Zimmerman 1979	Lamb et al. 1993	Guenther et al. 1994	Guenther et al. 1995
All woods	527	508	580	910
Conifer forest	650	650	600	1100
Deciduous forest	450	470	400	560
Oak forest	···	375	···	···
Mixed forest	···	···	500	710
Wetland forest	···	···	475	770
Woods and crops	···	···	800	880
Temperate rain forest	1100	···	···	···
All grasslands	250	150	300	365
Alpine	180	···	275	300
Other grasslands	250	···	300	460
All scrublands	130	300	275	375
Scrub woods	···	···	325	570
Desert scrub	100	···	150	195
Other scrub	300	···	275	400
All croplands	···	900	800	825
All other lands	···	190	500	1060
All landscapes	360	480	520	705

† Ellipses indicate categories that do not occur in given database.

Comparison with field measurements

Flux measurement techniques have been developed for evaluating VOC fluxes over landscapes ranging from a few hundred meters to >10 kilometers. Large-scale flux measurement techniques include the mass balance technique and the mixed-layer gradient tech-

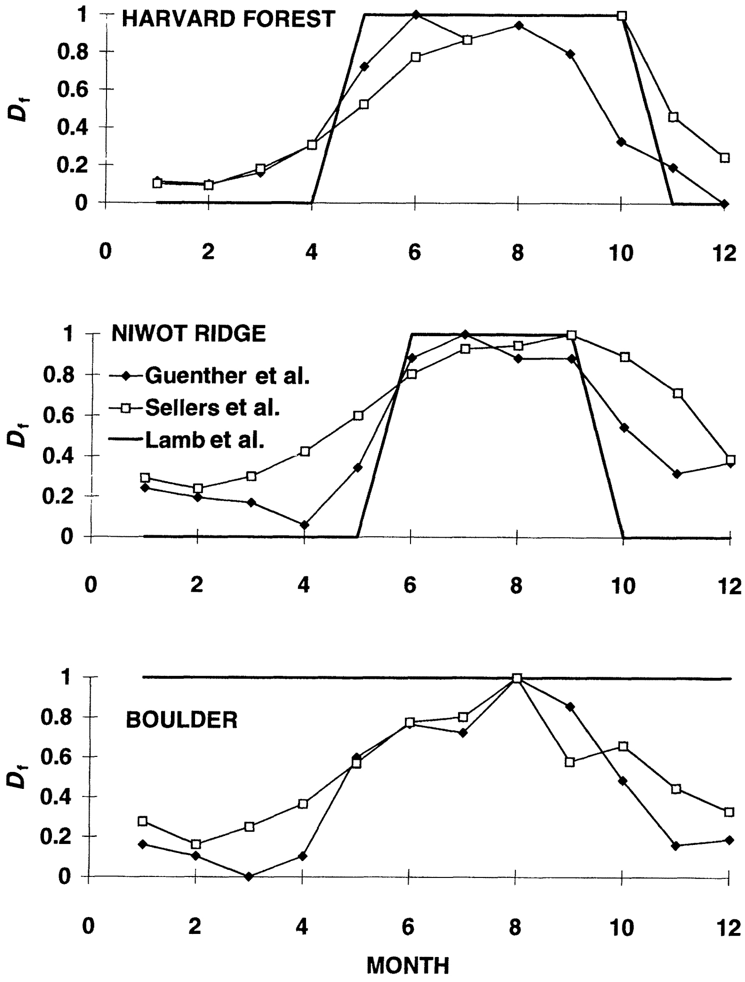


FIG. 1. Seasonal variations in foliar density (D_f) at three U.S. sites (Harvard Forest, Massachusetts; Niwot Ridge, Colorado; and Boulder, Colorado) estimated using the techniques described by Guenther et al. (1995), Sellers et al. (1994), and Lamb et al. (1987).

nique. The mass balance technique assumes that VOC fluxes are equal to the product of the mixed-layer height, the VOC loss rate, and the average VOC mixing ratio, while the mixed-layer gradient technique assumes fluxes are proportional to the observed vertical gradient of VOC in the mixed layer (Guenther et al. 1996). Guenther et al. (1996) used these two field measurement techniques to estimate fluxes at two field sites in the southeastern U.S. The total forest area at these sites was estimated with the LCC-MSS, LCC-AVHRR, EWDB, and Geoecology land cover databases and agreed within a few percent. However, when forests are grouped into three general categories (conifer, oak, and other deciduous), the four databases were not in agreement. The Geoecology database greatly underpredicts coniferous forest area because it does not account for the conversion of native deciduous forests into pine plantations. Leaf biomass estimates for some tree genera differ by more than an order of magnitude. Estimates of some of the dominant trees (pines, gum, and sweetgum) differ by a factor of 5 or more. Estimates of oak foliar mass, the major source of isoprene emission in these forests, are fairly consistent (± 15%) among the four methods. When combined with the emission potentials reported by Guenther et al. (1996), the landscape average emission potentials determined with the LCC-MSS and EWDB databases agree within 20% for isoprene and 30% for monoterpenes. The largest difference is due to disagreement in the amount of sweetgum, an important isoprene and monoterpene emitter, present at one of the sites. The isoprene fluxes calculated from the LCC-AVHRR data are 40–50% lower than the fluxes based on the EWDB and LCC-MSS data. This is primarily due to the absence of sweetgum in the list of dominant species for the LCC-AVHRR land cover types at these two sites. The Geoecology data result in 33 and 71% lower monoterpene emission potentials, relative to the EWDB data, at the two field sites by not considering the conversion of deciduous forests to pine plantations. The Geoecology data also underestimate the isoprene emission potential for one site by ≈50% by neglecting the presence of sweetgum trees.

Guenther et al. (1996) found that fluxes predicted

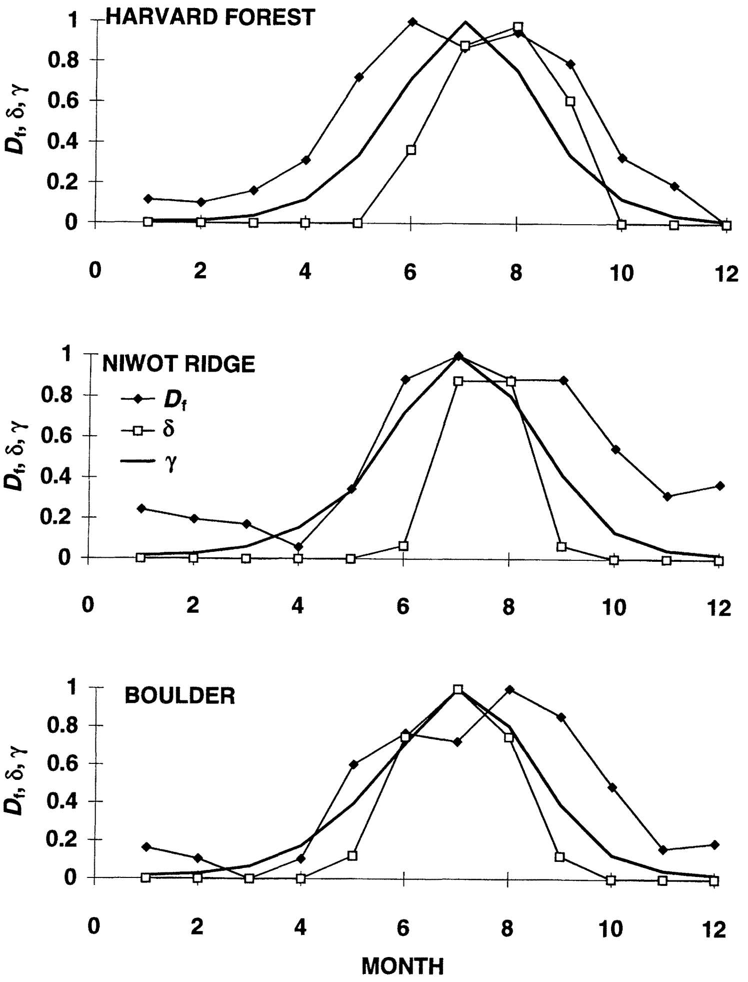


FIG. 2. Estimates of seasonal variations in isoprene emission rates due to variations in foliar density (D_f), light and temperature (γ), and other factors (δ) at three U.S. sites (Harvard Forest, Massachusetts; Niwot Ridge, Colorado; and Boulder, Colorado).

using the LCC-MSS, LCC-AVHRR, and EWDB land cover databases are in reasonable agreement (±50%) with field measurements. Our ability to evaluate the relative accuracy of the various land cover databases is limited by the uncertainties associated with the emission model results and the field flux measurements and by the small field measurement database. Recent studies have resulted in improved land cover data and emission modeling techniques and may provide a better indication of the relative accuracy of various land cover data and emission modeling techniques.

CONCLUSIONS AND RECOMMENDATIONS

The magnitude and distribution of natural VOC emission rate estimates are sensitive to land cover characteristics data. Improved emission estimates require additional emission potential measurements, as well as a better understanding of the processes that control emission rate variations.

The minimum land characteristics data required for existing natural VOC models are available on a global scale. The land cover data contained in the EWDB are recommended for woodland landscapes in the eastern U.S. The LCC-AVHRR database is recommended for the western U.S. and landscapes other than woodlands in the eastern U.S. Efforts to model emissions from regions outside of the U.S. must currently use low-resolution (>50 km) databases, e.g., the WED database, with general land cover descriptions. Global coverage of databases such as LCC-AVHRR could significantly enhance emission modeling efforts. General improvements in land cover databases, especially relating to species composition and total foliar mass, could also improve emission estimates. An important feature of remotely sensed variables is the ability to simulate actual conditions, including interannual variations. Remotely sensed data will likely play an important role in improved land cover data for emission models, due to the ability to provide a uniform grid, detailed classifications, global coverage, and time series information.

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