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A global model of natural volatile organic compound emissions

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Abstract. Numerical assessments of global air quality and potential changes in atmospheric chemical constituents require estimates of the surface fluxes of a variety of trace gas species. We have developed a global model to estimate emissions of volatile organic compounds from natural sources (NVOC). Methane is not considered here and has been reviewed in detail elsewhere. The model has a highly resolved spatial grid ($0.5^\circ \times 0.5^\circ$ latitude/longitude) and generates hourly average emission estimates. Chemical species are grouped into four categories: isoprene, monoterpenes, other reactive VOC (ORVOC), and other VOC (OVOC). NVOC emissions from oceans are estimated as a function of geophysical variables from a general circulation model and ocean color satellite data. Emissions from plant foliage are estimated from ecosystem specific biomass and emission factors and algorithms describing light and temperature dependence of NVOC emissions. Foliar density estimates are based on climatic variables and satellite data. Temporal variations in the model are driven by monthly estimates of biomass and temperature and hourly light estimates. The annual global VOC flux is estimated to be 1150 Tg C, composed of 44% isoprene, 11% monoterpenes, 22.5% other reactive VOC, and 22.5% other VOC. Large uncertainties exist for each of these estimates and particularly for compounds other than isoprene and monoterpenes. Tropical woodlands (rain forest, seasonal, drought-deciduous, and savanna) contribute about half of all global natural VOC emissions. Croplands, shrublands and other woodlands contribute 10–20% apiece. Isoprene emissions calculated for temperate regions are as much as a factor of 5 higher than previous estimates.

1. Introduction

Volatile organic compounds (VOC) are emitted into the atmosphere from natural sources in marine and terrestrial environments. Surface fluxes of these compounds are of interest because of their role in tropospheric chemistry and the global carbon cycle [see *Fehsenfeld et al.*, 1992]. The development of three-dimensional (3-D) computer models of global climate,

chemistry, surface emissions, and ecology is progressing to the point where these models can be coupled and used to investigate interactions between the processes simulated by each model. Three-dimensional climate models respond to forcings such as sea surface temperatures, planetary orientation with the sun, and the concentration of chemical species such as CO₂, CH₄, and sulfur compounds. Since VOC emission rates are critical in controlling the OH concentration of much of the troposphere, VOC emissions may play a major role in determining the growth rate of atmospheric CH₄ and CO concentrations. Since compounds such as CH₄ influence the radiative balance of the atmosphere, which in turn is related to global temperature and precipitation patterns, there is a clear link between VOC emissions and Earth climate. If global patterns and magnitudes of VOC emissions change as a function of climate-related alterations in precipitation, temperature, and radiation, these altered VOC emissions would feed back upon climate via changes in the atmospheric accumulation rates of greenhouse gases.

Several inventories of natural VOC (NVOC) on regional and global scales have been published (e.g., *Zimmerman*, 1979; *Lamb et al.*, 1987; *Mueller*, 1992), with a focus on isoprene and monoterpene emissions. These inventories indicate that annual natural emissions of these two classes of VOC exceed anthropogenic VOC emissions on a global scale. On regional scales, summer NVOC emission rate estimates range from about 3 times higher than anthropogenic emissions in the United States [*Lamb et al.*, 1987] to about 3 times lower in Germany [*Luebker and Schoepp*, 1989].

Although these existing inventories represent significant

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efforts in estimating large-scale NVOC emissions, they all contain weaknesses in the data or model algorithms. A more reliable emissions estimate for NVOC should rely on (1) accurate estimates of source types and densities, (2) accurate VOC emission factors for each source type, (3) an understanding of how changes in drivers such as temperature, light intensity, and moisture influence emissions of NVOC, and (4) estimates of driving variables for each grid and time step. This study attempts to make some progress in implementing each of these tasks. Furthermore, this effort addresses the need to develop an interactive model for investigating interactions with global changes in climate, land use, and atmospheric chemistry.

Several of the past uncertainties relating to NVOC emissions have now been constrained by new information. Recent mechanistic studies have been validated by field measurements that have also provided additional information relating emissions to specific ecosystem types. As a consequence, and because atmospheric computer models are rapidly surpassing previously available NVOC inventories in spatial resolution and geographical coverage, a new global NVOC emission modeling effort was critically needed.

We have realized that goal as part of the activities of the Global Emissions Inventories Activity (GEIA), a component of the International Global Atmospheric Chemistry Project (IGAC). GEIA's task is to develop global emissions inventories that are regarded by atmospheric scientists as authoritative and reliable and that are readily available to prospective users. In a recent review of available emission inventories [Graedel *et al.*, 1993], NVOC was recognized as one of the necessary components of the GEIA program. We thus formed an international working group to develop a global NVOC emission model that generates best estimates of emissions on a global gridded basis, as reported in this paper. Since we anticipate periodic updating of this emission model, we invite those with information that can improve these emissions estimates to communicate the details to us.

Each component of the global NVOC emission model is described in section 2. Model results for the base year of 1990, which are available in digital format, are described in section 3. The 1990 results are compared with previous estimates in section 4. The uncertainties associated with each model component and areas of potential improvement are discussed in section 5. Chemical model sensitivity to NVOC is reviewed in section 6. Section 7 contains the major conclusions of this paper.

2. Model Description

Natural sources of VOC emissions to the atmosphere include marine and fresh water, soil and sediments, microbial decomposition of organic material, geological hydrocarbon reservoirs, plant foliage and woody material. In addition, there are human influenced natural sources from harvesting or burning plant material. We have estimated emissions of VOC only from oceans and plant foliage. VOC emissions from other sources are very uncertain but probably represent less than a few percent of total global emissions [Zimmerman, 1979; Lamb *et al.*, 1987; Janson, 1992; Eichstaedter *et al.*, 1992]. Further investigation is needed to verify our assumption that these sources are negligible. Section 2.1 describes the methods used to estimate ocean emissions of VOC. The procedures used to estimate foliar emissions are outlined in section 2.2.

We have grouped natural VOC into four categories: isoprene,

monoterpenes, other reactive VOC (ORVOC), and other VOC (OVOC). Examples are given for each category in Figure 1. ORVOC are herein defined as compounds with a lifetime, under typical tropospheric conditions, of less than 1 day, while OVOC have lifetimes greater than 1 day. All data sets have been merged into a common grid system with a resolution of $0.5^\circ \times 0.5^\circ$ latitude/longitude. Hourly emission rates are estimated for one 24-hour period during each month. The daily total emission estimated from the 24-hour data is extrapolated to a monthly emission estimate. The model allows a great deal of flexibility and modularity so that improved data sets and algorithms can easily be incorporated into future versions of the model.

2.1. Ocean Emission of Volatile Organic Compounds

The ocean is supersaturated with VOC with respect to the atmosphere [Frank *et al.*, 1970; Lamontagne *et al.*, 1974]. Because of this imbalance, the ocean is considered a source of these highly reactive compounds to the atmosphere [Broadgate *et al.*, 1994; Plass-Duelmer *et al.*, 1994]. There is experimental evidence that VOC arise from the "photochemical lability" of dissolved organic matter (DOM) in the surface ocean [Ratte *et al.*, 1994], and there appears to be a relationship between the presence of chlorophyll and the lability of DOM in a parcel of surface ocean water [Plass-Duelmer *et al.*, 1993]. Satellite-derived ocean color data sets are interpreted as being a proxy for the amount of photochemically labile organic matter, in the form of dissolved organic carbon (DOC), in surface ocean waters containing varying amounts of biological activity. Recent efforts at modeling the air-sea fluxes of trace gases on global grids using general circulation models and Coastal Zone Color Scanner, CZCS, satellite data appear to be promising and these techniques are used here to refine estimates of the global marine source of VOC.

The basic concept of photochemical lability is that higher chlorophyll content of a parcel of water, as sensed by the satellite, is related to a higher production of VOC per unit photon impinging upon the surface ocean. The high spatial variability, or "patchiness," of the chlorophyll in the surface ocean may also explain the high variability of the observations of VOC in the surface ocean. Ratte *et al.* [1994] found a linear relationship between ethene concentration and DOC per unit photon in seawater. To the extent that photochemical lability covaries with DOC, this finding supports our approach. We compute the global surface ocean concentration of VOC, the global transfer velocity field for VOC, and the global flux field for VOC via a technique similar to that described by Erickson and Eaton [1993]. It should be noted that this is a first attempt at creating a global, high-resolution oceanic source term for the emission of VOC to the atmosphere and our estimated errors are at least a factor of 3. We have attempted to constrain the computed surface ocean VOC concentration with the sparse available data and appeal for further measurements.

The air-sea exchange of trace gases is modeled using the standard formula [Liss and Merlivat, 1986]. We calculate the flux as

$$F = k_w [C_{so} - C_{eq}] \quad (1)$$

where k_w is the transfer velocity for VOC, C_{so} is the surface ocean VOC concentration, and C_{eq} is the equilibrium surface ocean VOC concentration expected from equilibrium with the atmospheric concentration.

Note that C_{eq} is typically at least an order of magnitude

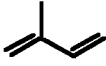

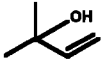

Name	Lifetime	Formula	Example	Structure
Isoprene	1 - 2 hrs	C ₅ H ₈	Isoprene	
Monoterpenes	0.5 - 3 hrs	C ₁₀ H _x	α-pinene	
Other Reactive Volatile Organic Compounds (ORVOCs)	< 1 day	C _x H _y O _z	2-methyl-3-buten-2-ol	
Other Volatile Organic Compounds (OVOCs)	> 1 day	C _x H _y O _z	methanol	

Figure 1. Categories of nonmethane volatile organic compounds (VOC).

smaller than C_{so} for most oceanic regions [Lamontagne *et al.*, 1974; Bonsang *et al.*, 1988; Donahue and Prinn, 1990]. We have selected a transfer velocity formulation based on a stability dependent theory of air-sea gas exchange [Erickson, 1993]. This method of calculating k_w gives a global area-weighted transfer velocity for CO₂ of ~20 cm h⁻¹, consistent with the ¹⁴C inventory estimates [Broecker and Peng, 1974]. Because of a lack of experimental data on the diffusivity of various VOC, we base our estimate of k_w for VOC on the diffusivity determined for CO₂. This assumption introduces at least a 50% uncertainty into the calculation.

The theoretical potential of a water parcel to produce VOC is assumed to increase with the amount of fresh, labile organic matter associated with biological activity in the surface ocean as sensed by the satellite. We compute the C_{max} term via the simple relationship

$$C_{max} = 100 [CZCS] + 300 \quad (2)$$

which is based on the oceanic data of Lamontagne *et al.* [1974] and Bonsang *et al.* [1988]. We assume that this theoretical quantity C_{max} is at the higher range of the measured values of VOC in the surface ocean. We derived equation (2) by pooling the available data and acknowledge the possible errors in using such a small database.

Winter hemisphere areas have substantially smaller supplies of radiation reaching the surface ocean than summer hemispheres, and per unit chlorophyll should result in less photochemical production of VOC [Ratte *et al.*, 1994]. We compute the surface ocean VOC concentration by scaling the maximum VOC concentration, C_{max} by the relative supply of surface radiation,

$$C_{so} = [F_{i,j,t} / F_{max}] C_{max} \quad (3)$$

where $F_{i,j,t}$ is the local value of the surface radiation flux computed by the National Center for Atmospheric Research (NCAR) general circulation model (GCM) on a 2.8° × 2.8° latitude/longitude area and F_{max} is the maximum amount of surface radiation computed by the GCM ~ 375 W m⁻².

This allows us to estimate the concentration of VOC in the surface ocean on a global scale, taking into account the

photochemical lability of the dissolved organic matter (DOM) and the supply of solar radiation. The test of the procedure lies in the comparison of modeled surface ocean concentrations to the data. As discussed in section 3, the range of modeled values compares reasonably well with the observational data sets. For example, Bonsang *et al.* [1988] found VOC concentrations of C₂-C₄ alkenes and C₂-C₃ alkanes ranging from ~40 pmol L⁻¹ to 1200 pmol L⁻¹. Lamontagne *et al.* [1974] found similar minimum concentrations but somewhat smaller maximum concentrations. From Bonsang *et al.* [1988] we assume an average molecular weight of 40 g C mol⁻¹ for ocean VOC. VOC concentrations on the global maps used for this flux model range from 0.8 ng C L⁻¹ to 48 ng C L⁻¹ with the highest concentrations in regions with an appreciable amount of biological activity and high surface radiation. Lamontagne *et al.* [1974] found highest oceanic VOC concentrations in the region 10°N and 10°S in the Pacific. This is also a general feature of our model results and is consistent with recent experimental results of Ratte *et al.* [1994] that show higher VOC concentrations per unit photon when the seawater has the higher DOC concentrations that accompany higher biological activity. It is important to note that our approach uses observational VOC data that are specific for only a fraction of all VOC in the ocean. Clearly, expanding the approach to the many individual species will be required to assess the actual impact of ocean VOC emissions on the marine boundary layer OH [Donahue and Prinn, 1990]. The measurements reported by Bonsang *et al.* [1988] suggest that the total ocean VOC flux is about 60% ORVOC and 40% OVOC. An even greater portion of the total flux may be ORVOC [Plass-Duelmer *et al.*, 1993] but given the large uncertainties, we have simply divided the total flux evenly between the ORVOC and OVOC categories. The flux estimates presented here represent a subset of all VOC emitted from the oceans and should be considered a lower limit that may be refined as more experimental data become available.

2.2. Foliar Emissions

The foliar emissions model uses the five geographically based input data sets that are described in section 2.2.1. VOC fluxes are calculated as

$$F = D \epsilon \gamma \quad (4)$$

where D is foliar density ($\text{kg dry matter m}^{-2}$), ϵ is an ecosystem dependent emission factor ($\mu\text{g C m}^{-2} \text{h}^{-1}$ at a photosynthetically active radiation (PAR) flux of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ and leaf temperature of 303.15 K), and γ is a non-dimensional activity adjustment factor that accounts for the influence of PAR and leaf temperature. The methods used to calculate each of these variables are described in this section.

2.2.1. Geographically based input data. Global gridded data sets of ecosystem type, global vegetation indices (GVI), precipitation, temperature, and cloudiness provide the inputs needed to estimate foliar emissions. We have used the data compiled by Olson [1992] to classify ecosystem types. Olson [1992] assigns each area of the Earth's land surface to one of 57 different ecosystem types with a resolution of $0.5^\circ \times 0.5^\circ$ latitude/longitude. Estimates of GVI calculated by EDC-NESDIS [1992] from the visible and near-infrared advanced very high resolution radiometer (AVHRR) channel data of the NOAA-11 satellite provide an index of plant physiological activity for the base year of 1990. The high-resolution (weekly, 1-km) satellite data were aggregated to provide monthly estimates on a $0.5^\circ \times 0.5^\circ$ grid. The monthly average estimates of temperature, cloud cover, and monthly cumulative precipitation compiled by Leemans and Cramer [1992] on a $0.5^\circ \times 0.5^\circ$ grid were also used in our analysis.

2.2.2. Foliar density. Foliar density and leaf area index (LAI, m^2 leaf area m^{-2} ground area) are estimated for each month and grid cell. Foliar density is required for equation (4) while LAI is used in the radiative transfer model described in section 2.2.5. Annual peak foliar density is determined for each $0.5^\circ \times 0.5^\circ$ surface by first estimating net primary production (NPP). Lieth [1975] developed empirical algorithms that relate NPP ($\text{g dry matter m}^{-2} \text{yr}^{-1}$) to annual average temperature, T ($^\circ\text{C}$), as

$$NPP = \frac{3000}{1 + \exp(1.315 - 0.119T)} \quad (5a)$$

and NPP to cumulative annual precipitation, P (mm), as

$$NPP = 3000(1 - \exp(-0.000664P)) \quad (5b)$$

Equations (5a) and (5b) are used to calculate temperature and precipitation limited NPP for each grid cell, and the minimum value is selected as the actual NPP, reflecting the fact that one factor, precipitation or temperature, is the limiting factor in the grid cell. Using the temperature and precipitation data of Leemans and Cramer [1992], we estimate an annual NPP of 122 Gt (10^{15} g) dry matter, which is equivalent [Lieth, 1975] to 48.8 Gt C. This estimate is similar to the estimates (mean, 53.1 Gt C, $N = 13$; range, 40.5 Gt C to 78.0 Gt C; s.d. 9.3 Gt C) reviewed by Melillo et al. [1993]. Ecosystem average NPP estimates are shown in Table 1. Temperature and precipitation data from a nearby grid cell were used for the 481 terrestrial grids in the Leemans and Cramer database that are missing temperature and precipitation data.

The peak foliar density is the maximum monthly average foliar density that occurs during the year and is estimated as

$$D_p = D_r NPP \quad (6)$$

where D_r is an ecosystem dependent empirical coefficient which we estimated using the data reported by Box [1981]. Estimates of D_r listed in Table 1 are greater than 1.0 for ecosystems dominated by plants that retain their foliage for more than one year.

Foliar densities and LAI can vary significantly with season and from year to year [Burton et al., 1991]. Running and Nemani [1988] presented experimental evidence that seasonal variations in LAI and foliar density can be estimated from satellite-derived normalized difference vegetation index (NDVI). The vegetation index, GVI, used in our analysis is directly related to NDVI as $GVI = 100(1 + NDVI)$. We estimate monthly average foliar density (D_m) in each grid cell using equations similar to those used by Fung et al. [1987] to model global photosynthetic activity. We assume that D_m is negligible when the monthly average GVI (G) is less than a set amount (G_2),

$$D_m = 0 \quad G < G_2 \quad (7a),$$

and increases exponentially with higher GVI,

$$D_m = D_p \left[\exp \left\{ \ln(2) \left(\frac{G - G_2}{G_{max} - G_2} \right) \right\} - 1 \right] \quad G > G_2 \quad (7b)$$

where G_{max} is the maximum monthly average GVI estimate during the year. In the case of missing GVI data in the EDC-NESDIS [1992] database, we set D_m equal to $0.5D_p$. On the basis of the analysis of Fung et al. [1987], we have set G_2 , the GVI at which foliage is negligible, to 110 for wooded areas and 102 for all other ecosystem types (see Table 1).

2.2.3. Emission factors. Foliar emissions of individual VOC range from undetectable to more than $100 \mu\text{g C g}^{-1} \text{h}^{-1}$ for different plant species [Guenther et al., 1994]. A few general rules of foliar VOC emission can be stated (e.g., conifer trees tend to emit monoterpenes), and emissions from a number of plant species have been characterized, but the assignment of emission factors to most ecosystems is limited by a lack of emission rate measurements.

There are two approaches to assigning emission factors to ecosystems. One approach is to quantify the species composition within an ecosystem type, assign an emission rate to each species, and aggregate the resulting emissions from each species. The second approach is to assign an emission rate directly to the ecosystem type and bypass the need for estimates of species composition. The first approach is particularly effective for an area with a low species diversity (e.g., cultivated land), whereas the second approach is best for areas with high species diversity (e.g., tropical forests). Enclosure measurement techniques provide the information needed to define emission rates for individual plant species, while area-averaged flux measurements can provide the information needed to directly assign emission rates to an ecosystem type. Field investigations that use both approaches provide a check on estimates of emission factors.

We have reviewed 22 field studies of NVOC emission. These studies were conducted in 12 nations at sites that represent 26 of the Olson [1992] ecosystem types. From the fluxes reported in these studies, we assigned the isoprene and monoterpene emission rate factors, ϵ , shown in Table 1. As discussed in section 5, actual values of ϵ for landscapes within an ecosystem category may vary widely. Estimates of ϵ are assigned to five ecosystems on the basis of fluxes estimated from ambient concentrations. Tropical rain forests are assigned a value of ϵ that agrees with fluxes estimated from the ambient isoprene and monoterpene concentrations observed by

Table 1. Isoprene, Monoterpene, and ORVOC Emission Estimates for the Ecosystems Defined by Olson [1992]

Olson Code	Description	Base Emissions, ($\mu\text{g C g}^{-1} \text{h}^{-1}$)		Global Totals, (Tg C yr^{-1})		Area	NPP	G_2	D_r	S_{LW}	T_a	Measurements	Reference*
		Iso.	Mon.	Iso.	Mon.								
		ORVOC	ORVOC										
0	ocean	0	0	0	0	362.69	Atlantic	2
20	snow/rain conifers	8	2.4	0.1	0.2	0.16	876	110	1.3	150	2.5	Spruce, hemlock	5
21	boreal conifers	8	2.4	2.3	4.6	5.24	410	110	1.7	150	-5.3	Sweden, Canada	9,10
22	snowy conifer	8	2.4	1.8	4.6	2.83	643	110	1.6	150	0.2	United States, Norway, Germany	11,15,20
23	snowy mixed	8	1.2	0.8	0.7	1.53	801	110	0.6	125	2.4	Russia, Japan	8,17
24	temperate mixed	24	0.8	8.4	1.8	1.95	1360	110	0.5	100	12.2	United States	11, 18
25	snowy deciduous	45	0.8	1.1	0.2	0.74	789	110	0.45	100	2.7	United States	11
26	temperate deciduous	45	0.8	2.9	0.3	0.5	1160	110	0.35	100	9.6	United States, Japan	11, 13
27	warm conifer	16	2.4	1.4	1.4	0.38	1320	110	0.55	150	13.2	United States	6,16,18
28	tropical montane	16	0.8	8.1	3.2	6.1	1830	110	0.7	125	19.4		
29	tropical seasonal forest	16	0.8	65.2	22.3	42.0	2050	110	0.6	125	23.8		
30	farm/city -cool	5	0.2	1.5	0.4	2.7	844	102	0.75	125	4.5		
31	farm/city -warm	5	0.2	15.2	3.7	28.0	1260	102	0.75	125	16		
32	drought deciduous	45	1.2	60.5	6.5	8.1	1510	110	0.3	125	23.3	United States	11,16,18
33	tropical rain forest	24	0.4	84.4	10.5	39.3	2310	110	0.6	125	25.1	Australia	1
36	paddy rice	5	0.2	5.7	1.6	12.1	1890	102	0.75	125	20.9	Brazil, Malaysia	3, 19
37	irrigation crop-warm	5	0.2	1.3	0.3	2.2	574	102	1	125	19.2	United States	16
40	grass/shrub-cool	16	0.8	4.2	1.0	1.8	581	102	0.7	125	2.3		
41	grass/shrub-hot	24	1.2	87.5	21.7	27.2	890	102	0.5	125	17.1	United States	16, 18
43	savanna	16	0.8	48.3	13.0	24.3	1610	110	0.5	125	24.8		
44	bog	8	0.8	0.4	0.3	0.4	520	110	0.8	150	-2.5	Canada	10
45	marsh/swamp	8	0.4	8.5	2.1	7.9	1648	110	0.5	150	23.3	United States	18
46	mediterranean	16	1.2	1.5	0.6	0.7	820	110	0.8	150	14.0	United States	16
47	dry highland	16	2.4	3.1	2.4	1.5	525	110	0.9	125	17.5	Republic of Georgia	14
48	dry evergreen	45	2.4	7.6	1.6	1	923	110	0.45	150	22.2	Australia	1
50	sand desert	16	0.8	4.0	0.5	1.0	237	102	0.3	150	21.2		
51	semidesert	16	0.8	4.8	0.7	1.3	250	102	0.3	150	20.5		
52	shrub/steppe	16	0.8	1.0	0.2	0.4	405	102	0.5	125	4.7		
53	tundra	16	0.8	1.2	0.4	0.7	267	102	0.5	125	-11.0		
55	crop/woods-cool	16	0.4	1.9	0.3	1.0	741	110	0.8	125	2.1	United States	11,12
56	regrowing woods	24	1.2	27.5	7.6	9.4	1670	110	0.5	125	18.0	United States	6,12,18
57	woods-cool	24	1.2	4.6	1.3	1.6	887	110	0.65	125	4.1	United States, Germany, Japan	4, 11, 17
58	crop/woods-warm	8	0.4	9.3	3.4	12.6	1520	110	0.75	125	17.9	United States, Malaysia	3, 6, 18
59	thorn woods	16	0.8	14.9	3.0	5.6	956	110	0.5	150	23.2		

Zimmerman *et al.* [1988] in the Amazon basin and the estimate of ϵ assigned to dry evergreen and drought-deciduous woods agrees with fluxes estimated from the ambient concentrations reported by Ayers and Gillett [1988]. Fluxes estimated from the ambient concentration data of A. Guenther *et al.* [Estimates of regional natural volatile organic compound fluxes from enclosure and ambient concentration measurements, submitted to *Journal of Geophysical Research*, 1995; hereinafter A. Guenther *et al.*, 1995] are used to assign ϵ to the warm conifer, regrowing woods, and warm crop/woods categories. Estimates of ϵ were assigned to an additional twenty-eight ecosystems on the basis of enclosure measurements of vegetation conducted in the ecosystem and general estimates of species composition. The number of plant species sampled within each ecosystem often represents only a very small portion of all plants present in the ecosystem. Default values of ϵ are assigned to the twenty-three ecosystem types where no measurements have been reported. There are no measurements reported for tropical seasonal forests and savannas and very few measurements for tropical rain forest, drought-deciduous woods, and hot grass/shrublands, which together contribute most of the total global flux of VOC.

All terrestrial ecosystems are assigned one of five values of ϵ for isoprene: 5, 8, 16, 24, and 45 $\mu\text{g C g}^{-1} \text{h}^{-1}$. The five monoterpene ϵ categories are 0.2, 0.4, 0.8, 1.2, and 2.4 $\mu\text{g C g}^{-1} \text{h}^{-1}$. Default values of ϵ are 5 $\mu\text{g C g}^{-1} \text{h}^{-1}$ isoprene and 0.2 $\mu\text{g C g}^{-1} \text{h}^{-1}$ monoterpenes for all croplands and grasslands (seven categories) and 16 $\mu\text{g C g}^{-1} \text{h}^{-1}$ isoprene and 0.8 $\mu\text{g C g}^{-1} \text{h}^{-1}$ monoterpenes for all other ecosystem types where no measurements have been reported. All ecosystems are assigned an emission factor of 1.5 $\mu\text{g C g}^{-1} \text{h}^{-1}$ of ORVOC based on the recommendations of Guenther *et al.* [1994]. This rate is also assigned for OVOC. The large uncertainties in OVOC and ORVOC emission factors are discussed in section 5.4.

2.2.4. Influence of light and temperature. There are two general models that can be used to simulate VOC emission rate variations due to changes in light and leaf temperature. The first model is temperature and light dependent while the second is dependent only on temperature. We use the first model to simulate isoprene emission rate variations and the second model to predict variations of all other compounds. Following the recommendations of Guenther *et al.* [1993], we estimate the influence of light and temperature on isoprene emission as

$$\gamma = C_L C_T$$

where light dependence is defined by

$$C_L = \frac{\alpha c_{L1} Q}{\sqrt{1 + \alpha^2 Q^2}} \quad (9)$$

where Q is the flux of PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$) and $\alpha = 0.0027$ and $c_{L1} = 1.066$ are empirical coefficients. Temperature dependence is described by

$$C_T = \frac{\exp \frac{c_{T1}(T - T_s)}{RT_s T}}{1 + \exp \frac{c_{T2}(T - T_M)}{RT_s T}} \quad (10)$$

where T is leaf temperature (K), T_s is leaf temperature at a standard condition (e.g., 303 K), R is a constant ($= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and c_{T1} ($= 95,000 \text{ J mol}^{-1}$), c_{T2} ($= 230,000 \text{ J mol}^{-1}$), and T_M ($= 314 \text{ K}$) are empirical coefficients. Guenther *et al.* [1993]

Table 1. (continued)

Olson Code	Description	Base Emissions, ($\mu\text{g C g}^{-1} \text{h}^{-1}$)		Global Totals, (Tg C yr^{-1})		Area	NPP	G_2	F_r	L_w	T_a	Measurements	Reference*
		Iso.	Mon.	Iso.	Mon.								
60	dry taiga	4.5	1.2	3.6	0.6	0.8	467	110	1.7	150	-3.3	Aspen, birch, spruce	5
62	maritime taiga	8	2.4	1.0	2.1	1.3	280	110	1.7	125	-10.0	Sweden, Canada	9,10
64	heath/moorland	5	0.2	0.06	0.01	0.1	914	102	0.5	125	8.2	United Kingdom	7
72	African swamp	5	0.2	0.3	0.07	0.5	1940	110	0.4	125	25.2	Mangrove	5
	Other crops/grass	5	0.2	0.1	0.02	0.2	479	102	0.75	125	1.4		
	Other Woods	16	0.8	1.3	0.5	1.0	516	110	1.7	150	-3.6		
	Other Desert	16	0.8	1.2	0.2	0.3	219	102	0.3	150	4.6		
	Ice	16	0.8	0.03	0.02	0.04	<1	102	1	125	-23.0		
	Other landscapes	16	0.8	2.9	0.9	1.7	1010	102	0.75	125	11.1		

Model parameters for each ecosystem include emission factors (ϵ) for isoprene (Iso.) and monoterpenes (Mon.), the ratio between peak foliar mass and NPP (D_r), the vegetation index at which foliar density is negligible (G_2), and specific leaf weight, S_{LW} , in grams per square meter. Global ecosystem areas (10^6 km^2), average ambient temperature, T_a , in degrees Celsius, and locations of representative emission rate measurements are also shown.

*¹Ayers and Gillett [1988]; ²Bonsang *et al.* [1988]; ³Cronn and Nutmagal [1982]; ⁴Eichstaedter *et al.* [1992]; ⁵Guenther *et al.* [1994]; ⁶A. Guenther *et al.* (1995); ⁷Hewitt and Street [1992]; ⁸Isidorov *et al.* [1985]; ⁹Janson [1992]; ¹⁰Klinger *et al.* [1993]; ¹¹Lamb *et al.* [1985]; ¹²Lamb *et al.* [1986]; ¹³Ohta [1986]; ¹⁴Shaw *et al.* [1983]; ¹⁵Steinbrecher [1989]; ¹⁶Arej *et al.* [1991c]; ¹⁷Yokouchi and Ambe [1988]; ¹⁸Zimmerman [1979]; ¹⁹Zimmerman *et al.* [1988]; ²⁰Hov *et al.* [1983].

found that equations (8)–(10) can describe isoprene emission rate variations for a number of different plants (aspen, oak, sweetgum, eucalyptus, velvet bean), indicating that the relationship may be valid in a variety of ecosystems.

We describe the relationship between temperature and monoterpene emission rate as

$$\gamma = \exp[\beta(T - T_s)] \quad (11)$$

where β (K^{-1}) is an empirical coefficient. We have used the value of β ($=0.09 K^{-1}$) which *Guenther et al.* [1993] recommend on the basis of an extensive review of reported measurements. This relationship appears to be valid for a variety of monoterpene compounds and plant species [*Guenther et al.*, 1993]. There is evidence that monoterpene emission rates from some plants are sensitive to light intensity [*Steinbrecher*, 1989] but this process has not been described by a numerical model. The light and temperature dependencies of ORVOC and OVOC emission rates are currently unknown.

2.2.5. Canopy radiative transfer model. We have simulated the variability in solar radiation fluxes across the Earth's surface and within a vegetation canopy using simple models that account for a majority of observed variation. The astronomical routines described by *Iqbal* [1983] are used to compute hourly solar elevation angles and above canopy direct and diffuse PAR. The incoming solar radiation is modified for the effects of monthly average cloud cover [*Hostlag and Van Ulden*, 1983].

The effects of canopy shading are determined with the canopy radiative transfer model described by *Norman* [1982]. The total leaf area in the plant canopy is divided into sunlit and shaded fractions. The sunlit portion is calculated as

$$f_{sun} = f [1 - \exp(-\frac{0.5f}{\sin(B)})] \frac{\sin(B)}{\cos(A)} \quad (12)$$

where f is LAI, A is the mean leaf-Sun angle (which we assume to be 60° , representing a canopy with a spherical leaf angle distribution), and B is solar elevation angle. Monthly average estimates of f are computed as

$$f = D_m / S_{LW} \quad (13)$$

where S_{LW} is an average specific leaf weight ($g m^{-2}$) that is specified for each ecosystem based on data reported by *Box* [1981]. The shaded fraction is equal to

$$f_{shade} = f - f_{sun} \quad (14)$$

The flux density of PAR on a sunlit leaf is estimated as

$$Q_{sun} = Q_{dir} \frac{\cos(A)}{\sin(B)} + Q_{shade} \quad (15)$$

where Q_{dir} is the flux of direct PAR above the canopy, and Q_{shade} is equal to

$$Q_{shade} = Q_{diff} \exp(-0.5 f^{0.7}) + Q_I \quad (16a)$$

where Q_I arises from multiple scattering of direct beam radiation and is given by

$$Q_I = 0.07 Q_{dir} (1.1 - 0.1f) \exp[-\sin(B)] \quad f < 11 \quad (16b)$$

$$Q_I = 0.0 \quad f > 11 \quad (16c)$$

and Q_{diff} is the flux of diffuse PAR above the canopy. The canopy can be divided into any number of vertical layers, and equations (12)–(16) evaluated for each layer. NVOC emissions, however, are relatively insensitive to the number of layers used in the model. There is a less than 5% difference in global annual isoprene emission estimated with one or five layers and no change in the estimated emissions of other VOC. Figure 2 illustrates the influence of canopy structure on light interception by leaves. In this example, an above-cloud PAR of $2500 \mu mol m^{-2} s^{-1}$ is reduced to about $1940 \mu mol m^{-2} s^{-1}$ at the top of the canopy. Leaves in direct sunlight at the top of the canopy receive an average PAR of only $1240 \mu mol m^{-2} s^{-1}$ due to the 60° mean orientation between leaves and PAR flux. The PAR flux to leaves in direct sunlight at the bottom of the canopy is about $1060 \mu mol m^{-2} s^{-1}$ owing to a lower contribution of diffuse PAR. Shaded leaves receive only diffuse PAR that ranges from about 85 to $275 \mu mol m^{-2} s^{-1}$ through the canopy.

3. VOC Emission Estimates for 1990

An annual global VOC flux of $1150 Tg C$ ($1 Tg = 10^{12}g$) is estimated for the year 1990 using the model procedures described in section 2. The contribution of each source and class of compound is shown in Table 2. Compounds with a lifetime, at typical tropospheric conditions, greater than 1 day (OVOC) contribute $260 Tg C$, which is 22.5% of the total flux. The annual estimated flux of $890 Tg C$ of reactive VOC consists of $503 Tg C$ (57%) of isoprene, $127 Tg C$ (14%) of monoterpenes, and $260 Tg C$ (29%) of ORVOC.

Woodland landscapes cover 48% of all land surfaces, according to the *Olson* [1992] classification scheme. Table 2 shows that woodland landscapes are estimated to contribute about three fourths of global isoprene and monoterpene emissions and two thirds of the emissions of other VOC. Global NVOC emissions are dominated by fluxes from tropical rain forest, tropical seasonal, drought-deciduous, and savanna woods that together cover about 15% of global land surfaces but are estimated to contribute almost half the total flux from all sources. These four woodland types occur primarily in the tropics between $20^\circ S$ and $20^\circ N$ latitude. Shrublands represent 31% of land surfaces and contribute about 20% of isoprene and monoterpene emissions. Croplands cover 10.5% of land surface (mixed cropland and woodland areas are included under

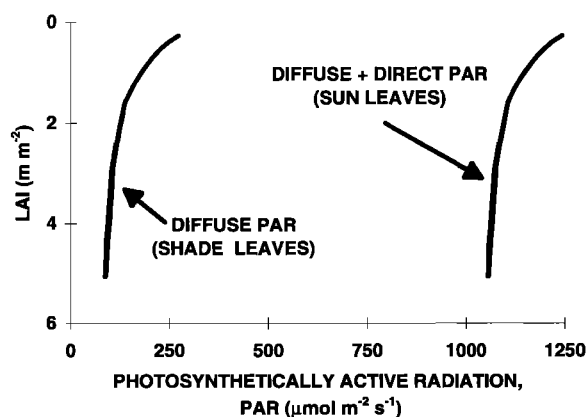


Figure 2. Model estimates of photosynthetically active radiation (PAR) for a solar elevation of 90° , a cloud cover of 70% and a canopy leaf area index (LAI) of $5 m m^{-2}$.

Table 2. Global VOC Emission Rate Estimates by Source and Class of Compound

Source	Isoprene	Monoterpene	ORVOC	OVOC	Total VOC
Woods	372	95	177	177	821
Crops	24	6	45	45	120
Shrub	103	25	33	33	194
Ocean	0	0	2.5	2.5	5
Other	4	1	2	2	9
All	503	127	260	260	1150

Estimates are in Tg C yr^{-1} .

woodlands) and are estimated to be responsible for about 17% of other VOC emissions.

Emissions have been summed for each of the ecosystem types in the Olson database and are shown in Table 1. Most isoprene (77%) and monoterpene (67%) emissions are predicted to originate from just seven of the fifty-seven ecosystems: tropical evergreen seasonal forest (class 29), drought-deciduous (class 32), tropical rainforest (class 33), warm grass and shrub (class 41), tallgrass bush and woodland savanna (class 43), regrowing woods with crops and pasture (class 56), and succulent and thorn woods (class 59). About 82% of the total other VOC are from 11 categories including marine (class 0), warm farm and settlements (class 31), paddy rice (class 36), warm crops and pasture (class 58) and the seven listed above.

Annual area-averaged VOC emissions range from less than 0.1 g C m^{-2} to greater than 40 g C m^{-2} . The highest rates are estimated for the tropics and the lowest rates for polar regions. Annual total VOC carbon fluxes range from less than 0.1% to over 4% of annual *NPP*. The estimated total VOC flux of 1150 Tg C is 2.4% of the 48.8 Gt C we estimate for global *NPP*. VOC emissions can represent a much higher proportion of a given ecosystem carbon flux over shorter time periods.

Monthly variations in VOC emissions are determined by foliar mass, solar angle, cloudiness, and temperature patterns. Figure 3 illustrates simulated variations in isoprene emission from three ecosystems. Monthly average emissions in tropical forests vary by less than $\pm 10\%$. Monthly emissions in all boreal and many temperate regions vary by several orders of magnitude. This variation is driven primarily by temperature and results in peak emissions during the hottest months.

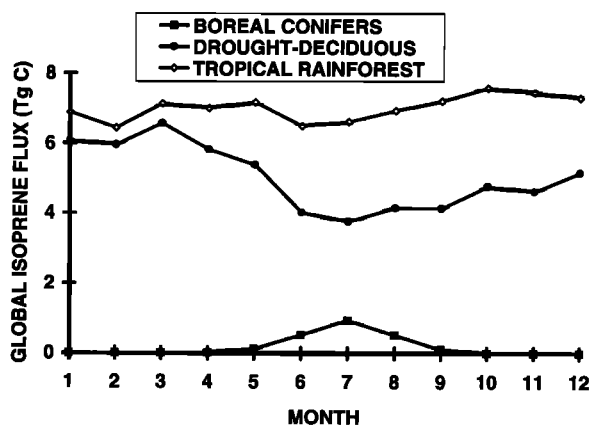


Figure 3. Estimated monthly variations in global total isoprene emissions from three ecosystems.

Seasonal variations in drought-deciduous woods are influenced by variations in foliar densities which peak after the rainy season. Wet and dry seasons do not occur at the same time in all regions of the Earth. As a result, the global average estimates given in Figure 3 predict emissions from drought-deciduous woods at all times of the year.

Estimated total global VOC emissions are evenly divided between the northern (51%) and southern (49%) hemispheres. Although the northern hemisphere has more land area, much of it is at high latitudes where emissions are minimal. Figure 4 illustrates the latitudinal variation in relative contribution to the total global emissions of reactive VOC. Most emissions (90%) in the southern hemisphere occur between the equator and 25°S latitude. Emissions are more evenly distributed in the northern hemisphere with 65% between the equator and 25°N , 27% between 25°N and 50°N , and 8% between 50°N and 80°N . Emissions of isoprene, terpenes, and other VOC follow similar latitudinal patterns that are driven by variations in biomass and temperature. There are some differences, however, which are due primarily to species composition. Higher contributions are observed from about 12° to 24°S latitude for isoprene, 8°S to 4°N for OVOC and 36°N to 68°N for monoterpenes.

Estimates of VOC concentrations in the surface ocean range from 4 ng C L^{-1} to $\sim 88 \text{ ng C L}^{-1}$ in January. Biologically productive areas that receive a reasonable amount of light have the highest predicted VOC concentrations in the surface ocean. Coastal areas off Africa and South America are characterized by relatively high biological production and have elevated VOC concentrations. The North Atlantic region has surface ocean VOC concentrations greater than 20 ng C L^{-1} over large regions and up to 48 ng C L^{-1} over limited areas in July. There is considerable spatial variability in the concentrations imparted by the variability in the *CZCS* satellite data. This spatial

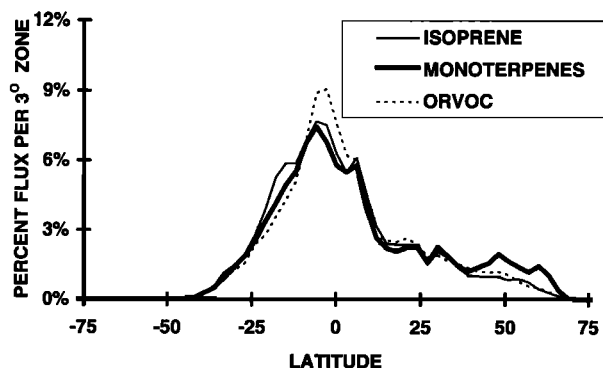


Figure 4. Estimated zonally averaged variation in natural volatile organic compounds (NVOC).

“patchiness” is typical of many biologically related variables in the observational record.

As seen in equation (1), once we have computed the C_{so} terms, we may calculate the flux by coupling the transfer velocity term with C_{so} . We do not show the global maps of the VOC transfer velocity, but they are essentially those of *Erickson* [1993]. Winter hemisphere regions experience higher transfer velocities due to high wind speeds, and there is a global range of 4-70 cm h^{-1} . As seen in Table 3, the area weighted mean k_w is $\sim 20 \text{ cm h}^{-1}$, consistent with the approach of *Donahue and Prinn* [1990]. Coupling the transfer velocity estimates with the global maps of surface ocean VOC concentration, we are able to compute the global oceanic source terms for VOC fluxes from the ocean to the atmosphere. The most striking feature of Plate 1 is that there is at least 2 orders of magnitude range between the local VOC flux estimates. For example, in oligotrophic waters that are in the winter hemisphere a flux of less than $0.25 \mu\text{g C m}^{-2} \text{ month}^{-1}$ is typical, whereas in biologically productive regions that receive a strong supply of solar radiation the fluxes are as high as $25 \mu\text{g C m}^{-2} \text{ month}^{-1}$. The high fluxes in the monsoonal regions of the Indian ocean in Plate 1 (bottom) clearly demonstrate the influence of elevated transfer velocities. The estimated annual ocean VOC flux is about 5 Tg C yr^{-1} . This is an order of magnitude less than the earlier estimate of *Bonsang et al.* [1988] which is at the low end of estimates [e.g., *Donahue and Prinn*, 1990] based on tropospheric VOC concentrations and removal rates. Our estimated flux is consistent with other recent values that are based on oceanic VOC concentrations and an air-sea exchange model [*Plass-Duelmer et al.*, 1993].

Plate 2 shows the global distribution of isoprene emission calculated by the methods described in section 2 for January (bottom) and July (top). Estimates range from less than 0.001 to about $7 \text{ g C m}^{-2} \text{ month}^{-1}$. Tropical woodlands in South America, Africa, and southeast Asia have high ($>1 \text{ g C m}^{-2} \text{ month}^{-1}$) fluxes throughout the year. High summertime fluxes are also predicted for some temperate regions including the southeastern United States, eastern China, and southern Brazil. Some boreal regions at latitudes between 50° and 60°N also have high summertime isoprene emission rate estimates. Isoprene emission rates at latitudes above 30° are estimated to be very low ($<0.1 \text{ g C m}^{-2} \text{ month}^{-1}$) during winter.

Plate 3 illustrates the estimated global distribution of monoterpene emission rates, and the distribution of ORVOC emission rates are shown in Plate 4. Estimates of both monoterpene and ORVOC emission rates range from less than 0.001 to about $5 \text{ g C m}^{-2} \text{ month}^{-1}$. The highest monoterpene emission rates for July are predicted for the western United States, eastern Canada, central Europe, and parts of the Amazon basin. The highest predicted July emission rates of ORVOC are

in the central and eastern United States, western China, southeast Asia, and tropical woods of South America and Africa. January maximum monoterpene and ORVOC emissions are predicted for tropical woods in South America and Africa.

As expected, emissions of all NVOC compounds are relatively higher in woodland areas. This result is due to higher foliar densities and base emission rate factors. In addition, higher emissions are associated with areas of higher temperatures. Differences in the spatial distributions predicted for isoprene, monoterpenes, and other VOC are primarily due to differences in the emission factors assigned to various ecosystems (Table 1).

4. Emission Rate Comparisons

Estimates of global NVOC emissions are compiled in Table 4. The range of reported rates estimated by several different methods provides some insight into the uncertainty associated with these emission rates. Early attempts to quantify total global VOC emissions resulted in estimates of about $450 \text{ Tg C per year}$ [*Rasmussen and Went*, 1965; *Robinson and Robbins*, 1968]. *Zimmerman* [1979] measured emission rates from a wide variety of trees in the southeastern United States and estimated that global emissions of isoprene and monoterpenes were 830 Tg C yr^{-1} . Recent studies [*Dignon and Logan*, 1990; *Taylor et al.*, 1991; *Turner et al.*, 1991; *Mueller*, 1992] used higher resolution climate and land use databases (monthly to seasonal and 1- to 5- degree grid cells). Our estimated isoprene emission rate of 503 Tg C yr^{-1} is slightly higher than the highest previous estimates, which range from 175 to 450 Tg C yr^{-1} . The estimated monoterpene emission rate of 127 Tg C yr^{-1} falls just below the lower end of previously reported values (143 to 480 Tg C yr^{-1}). Several previous global isoprene and monoterpene emission rate estimates were based entirely or primarily on the field measurements reported by *Zimmerman* [1979]. The higher isoprene and lower monoterpene emission rates reported by the present study are due primarily to differences in base emission factors that are based on the results of the 21 studies listed in Table 1. The isoprene emission factors for temperate regions in our model are as much as a factor of 5 higher than previous estimates. Emission rate factors for tropical areas are higher than those used in previous efforts, but this is offset by our use of a canopy light extinction model. The global totals are similar because tropical regions dominate total emissions.

Emissions of NVOC estimated with our global model are compared with estimates for individual countries in Table 5. Our isoprene estimate for northern Australia is 80% of the value reported by *Ayers and Gillett* [1988]. We used the flux estimates reported by *Ayers and Gillett* [1988] to assign emissions to several landscapes in northern Australia (see Table

Table 3. Global Area-Weighted Mean Ocean VOC Flux Equation Values

	January	July
Mean surface ocean concentration, pmol L^{-1}	135	170
Mean transfer velocity, cm h^{-1}	18.2	19.4
Mean molecular weight, g C mol^{-1}	40	40
Mean ocean to atmosphere flux, $(\text{pg C cm}^{-2} \text{ h}^{-1})$	100	124

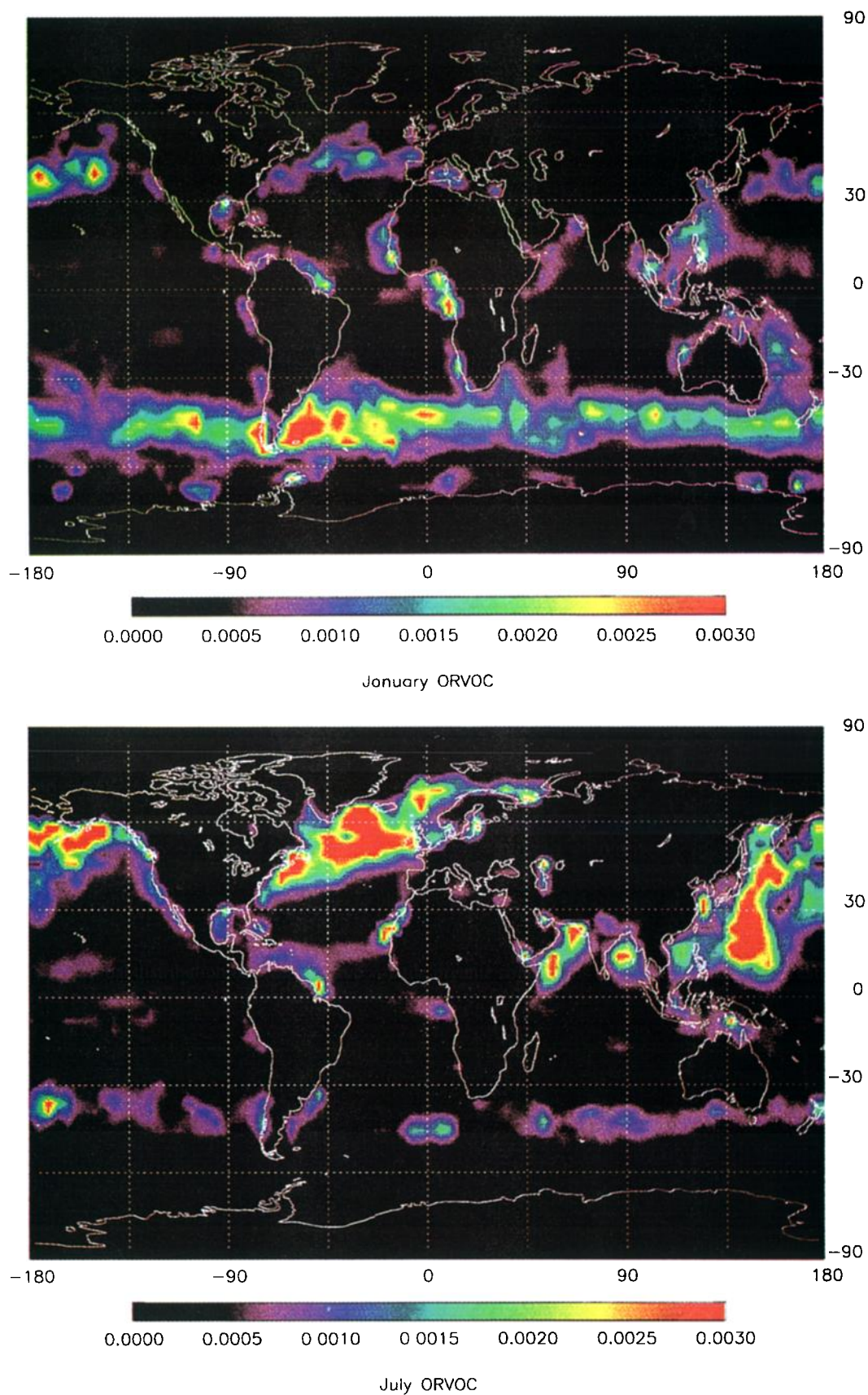


Plate 1. Global distribution of other reactive volatile organic compounds (ORVOC) emission rate estimates ($\text{g C m}^{-2} \text{ month}^{-1}$) for (top) January and (bottom) July.

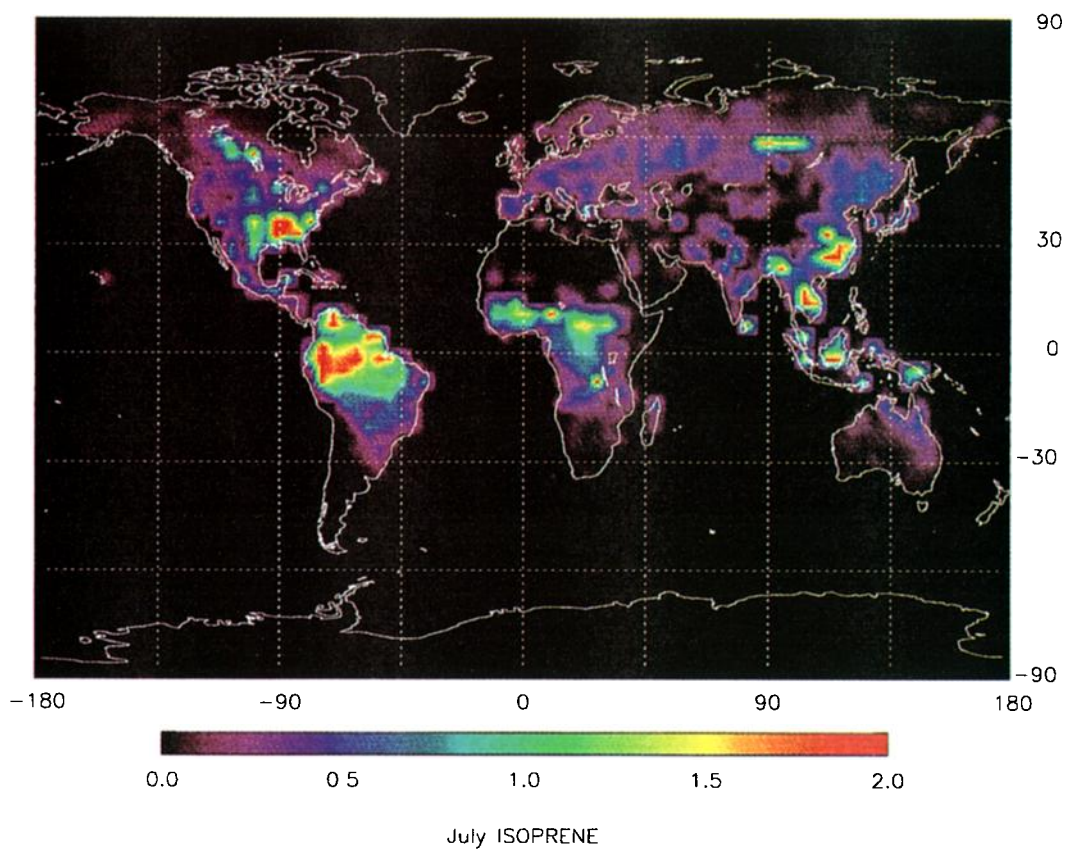
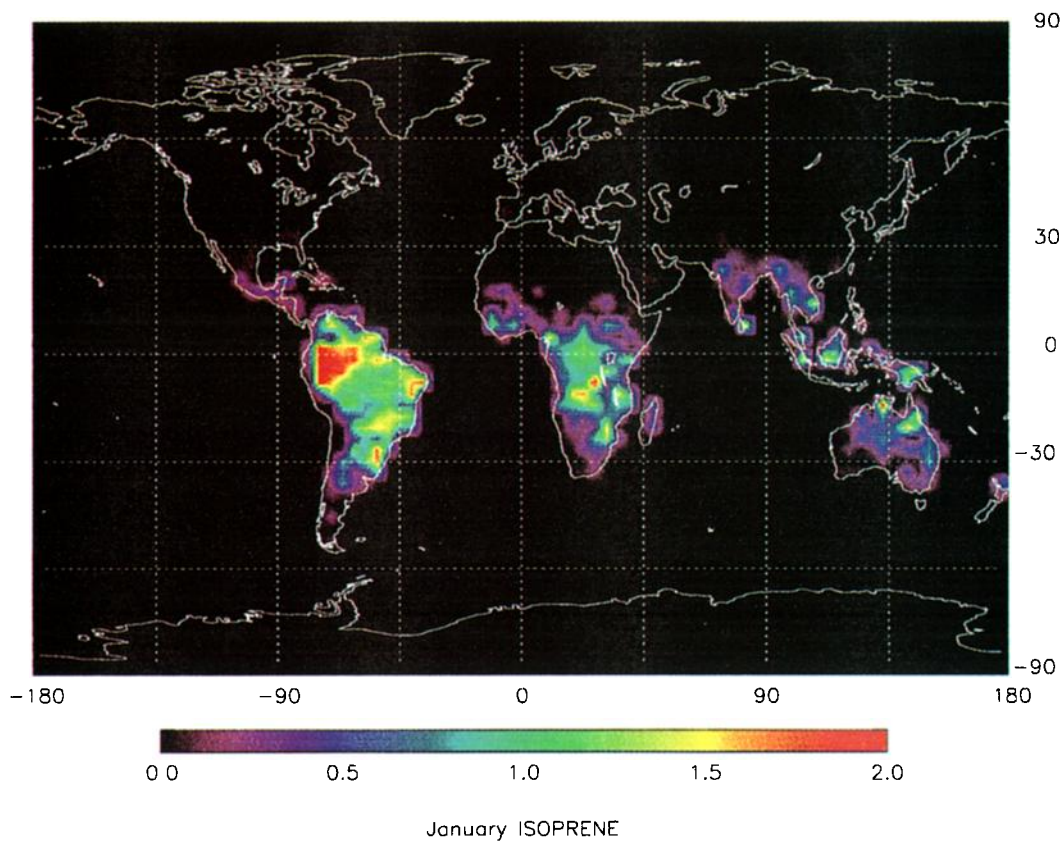


Plate 2. Global distribution of isoprene emission rate estimates ($\text{g C m}^{-2} \text{ month}^{-1}$) for (top) January and (bottom) July.

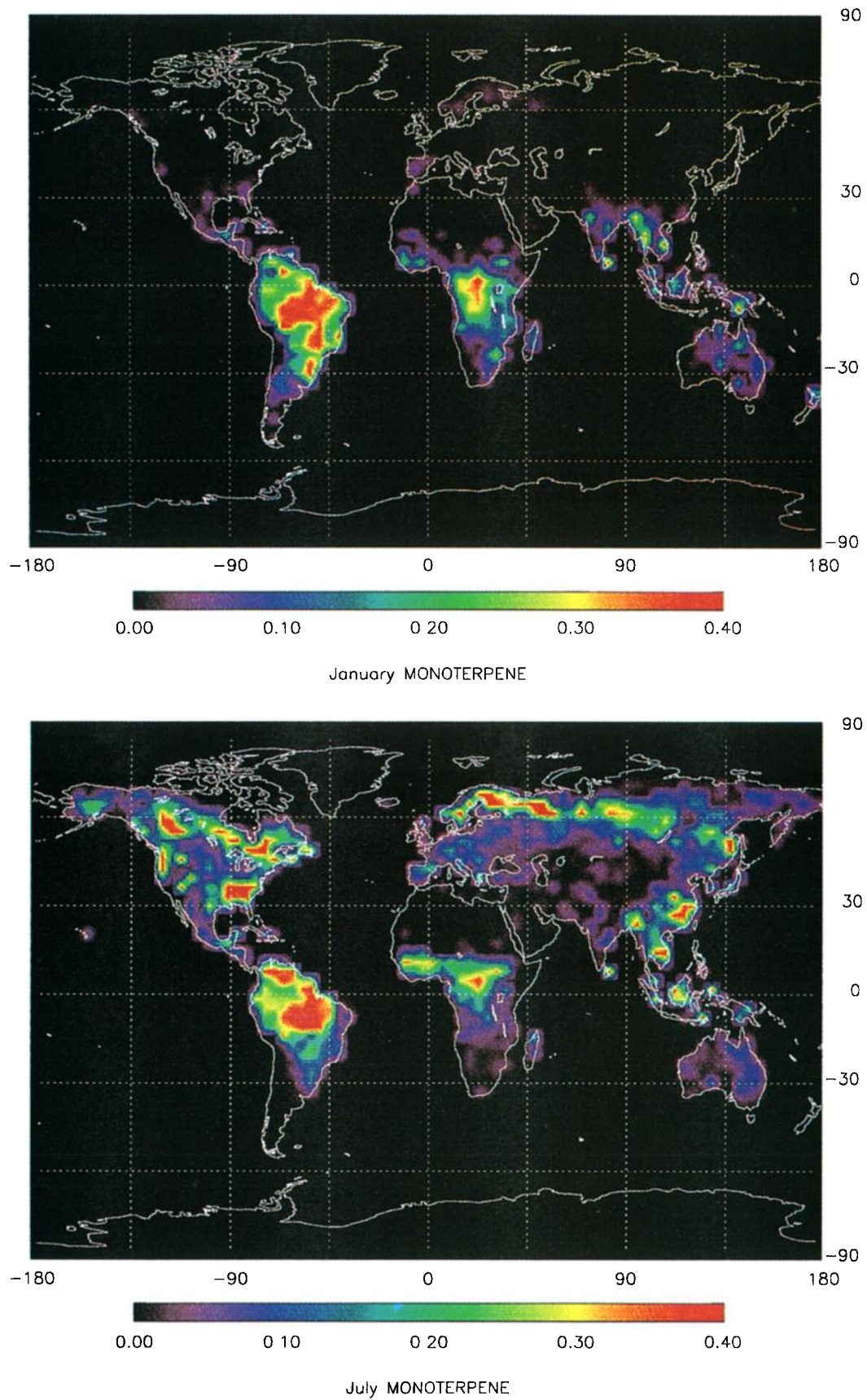


Plate 3. Global distribution of monoterpane emission rate estimates ($\text{g C m}^{-2} \text{ month}^{-1}$) for January (top) and July (bottom).

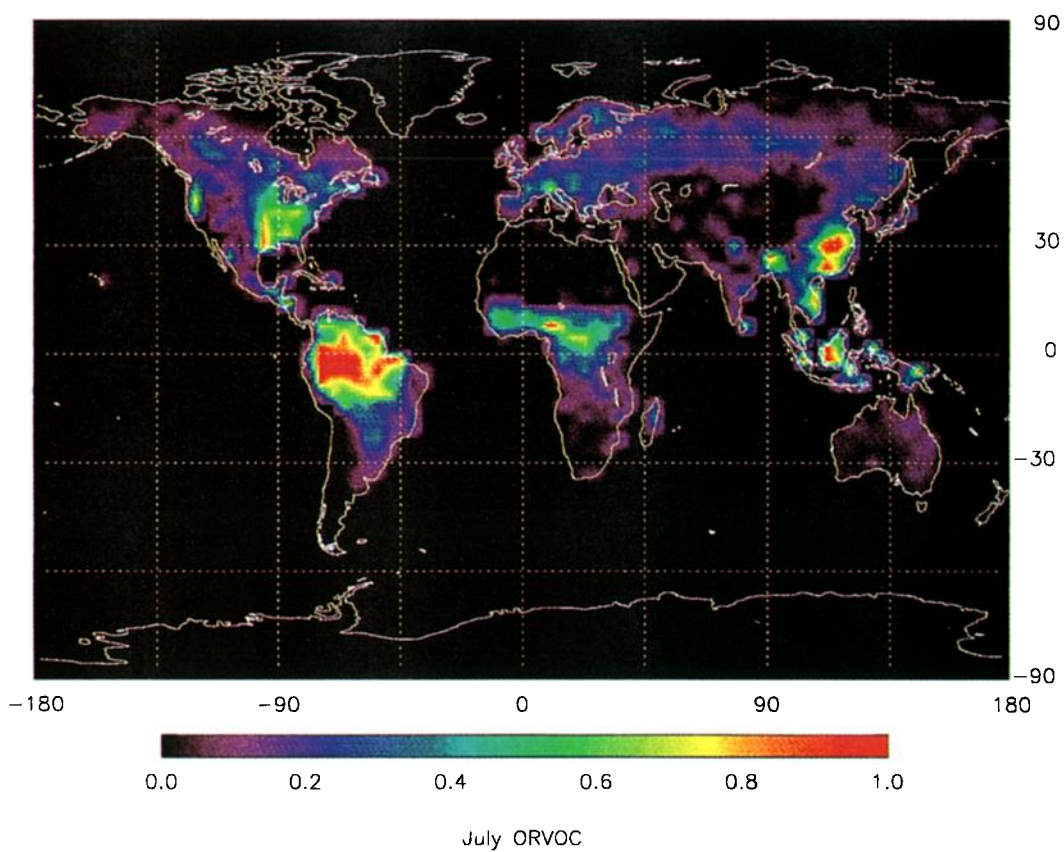
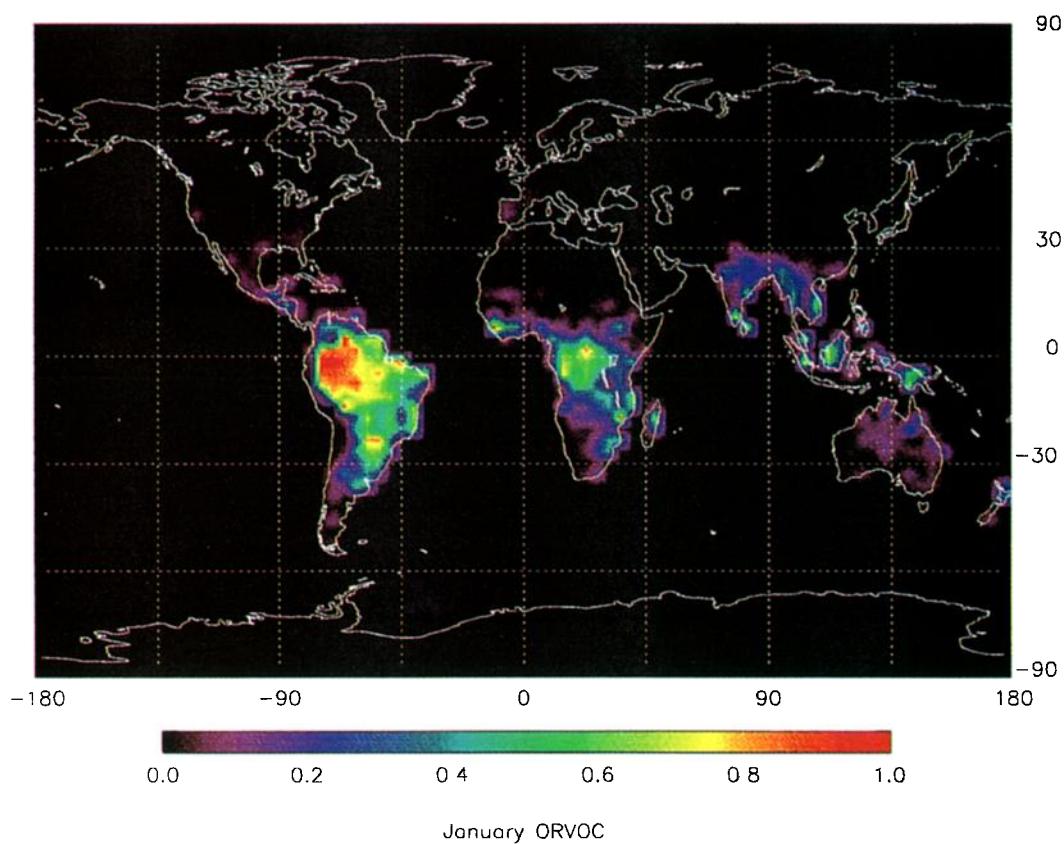


Plate 4. Global distribution of other reactive volatile organic compounds (ORVOC) rate estimates ($\text{g C m}^{-2} \text{ month}^{-1}$) for (top) January and (bottom) July.

Table 4. Comparison of Global Natural VOC Emission Rate Estimates

	Isoprene	Monoterpenes	ORVOC	OVOC	Total
<i>Rasmussen and Went</i> [1965]					432
<i>Robinson and Robbins</i> [1968]					480
<i>Zimmerman</i> [1979]	350	480			
<i>Rasmussen and Khalil</i> [1988]	452				
<i>Dignon and Logan</i> [1990]	450				
<i>Taylor et al.</i> [1990]	175	143			
<i>Turner et al.</i> [1991]	285				
<i>Mueller</i> [1992]	250	147			491
This study	503	127	260	260	1150

Estimates are in Tg C yr⁻¹.

1) but assumed that some Northern Australia landscapes, e.g., croplands and barren desert, had lower rates. Table 5 indicates agreement between regional and global model estimates when similar emission factors are used, e.g., for monoterpene emissions from Sweden and isoprene emissions from northern Australia. Our isoprene emission estimates are higher than previous estimates for the United States and for European countries. Our isoprene estimates for the United States are 50% higher than the estimate of *Zimmerman* [1979] and the highest estimates reported by *Lamb et al.* [1993] and are almost a factor of 5 higher than those of *Lamb et al.* [1987]. Monoterpene emissions estimated with the global model are a factor of 6 lower than the estimates of *Zimmerman* [1979] and fall at the low end of the range of estimates reported by *Lamb et al.*

[1993]. The differences between the global model results and those of *Lamb et al.* [1987] result primarily from the use of different base emission factors. D. Simpson et al. [Biogenic VOC emissions in Europe: emissions and uncertainties, submitted to *Journal of Geophysical Research*; hereinafter D. Simpson et al., 1995] compared a variety of emission model techniques and calculated fluxes for individual countries in Europe that have a range of about a factor of four. Our estimates for Europe tend to be about a factor of two higher than the highest estimates of D. Simpson et al. [1995]. These estimates use similar base emission factors and differences can be attributed primarily to differences in land cover estimates. Most of the other regional emission rate estimates listed in Table 5 [*Luebker and Schoepp*, 1989; *Adryukov and Timofeev*, 1989;

Table 5. Comparison of Natural VOC Emission Rates Predicted by the Global Model and by Regional Models

Country	Compounds	Global	Regional	Reference
Australia	Isoprene	19,600	25,000	<i>Ayers and Gillett</i> [1988]
Germany	Isoprene	370	40-149	D. Simpson et al. [1995]
	RVOC	1,030	349	<i>Luebker and Schoepp</i> [1989]
Hungary	RVOC	1,030	970	<i>Adryukov and Timofeev</i> [1989]
	Isoprene	120	25-113	D. Simpson et al. [1995]
	RVOC	260	22	<i>Luebker and Schoepp</i> [1989]
	RVOC	260	70	<i>Adryukov and Timofeev</i> [1989]
Spain	RVOC	260	156	<i>Molnar</i> [1990]
	Isoprene	820	138-371	D. Simpson et al. [1995]
	RVOC	1,580	1,132	<i>Luebker and Schoepp</i> [1989]
Sweden	RVOC	1,580	6,600	<i>Adryukov and Timofeev</i> [1989]
	Isoprene	370	25-108	D. Simpson et al. [1995]
	Monoterpenes	370	370	<i>Janson</i> [1992]
United Kingdom	RVOC	1,040	930	<i>Luebker and Schoepp</i> [1989]
	RVOC	1,040	600	<i>Adryukov and Timofeev</i> [1989]
	Isoprene	110	2-55	D. Simpson et al. [1995]
United States	Terpenoids	145	167	<i>Anastasi et al.</i> [1991]
	RVOC	320	38	<i>Luebker and Schoepp</i> [1989]
	RVOC	320	50	<i>Adryukov and Timofeev</i> [1989]
	RVOC	320	211	<i>Anastasi et al.</i> [1991]
United States	Isoprene	24,000	3,000-14,700	<i>Lamb et al.</i> [1993]
	Isoprene	24,000	4,900	<i>Lamb et al.</i> [1987]
	Isoprene	24,000	15,000	<i>Zimmerman</i> [1979]
	Monoterpenes	8,000	50,000	<i>Zimmerman</i> [1979]
	Monoterpenes	8,000	8,300-33,300	<i>Lamb et al.</i> [1993]
	RVOC	45,000	22,800-80,100	<i>Lamb et al.</i> [1993]
	RVOC	45,000	30,700	<i>Lamb et al.</i> [1987]

Estimates are in 10⁹ g C yr⁻¹. RVOC includes isoprene, monoterpenes and other VOC with a lifetime of less than 1 day (ORVOC).

Molnar, 1990] are based on the Lamb *et al.* [1987] analysis of the field measurements reported by Zimmerman [1979]. A review of recent measurements and a revision of the Zimmerman [1979] data by Guenther *et al.* [1994] suggests that the previous isoprene emission rate factors may be as much as a factor of 5 too low for U.S. woodlands.

Although there is a considerable range in estimates of NVOC emission, there is general agreement that the global emission rate is at least 400 Tg C yr⁻¹. Our NVOC flux estimate of 1150 Tg C yr⁻¹ is more than a factor of 7 greater than estimated global anthropogenic VOC emissions [Mueller, 1992] and is more than a factor of 2 greater than estimated annual methane emissions [Taylor *et al.*, 1991]. This flux is a significant component of the carbon flux in many terrestrial landscapes and should be considered in field investigations of carbon cycling. Eddy covariance measurements of CO₂ fluxes can be used to estimate the net ecosystem exchange of CO₂ [Wofsy *et al.*, 1993]. These measurements can potentially be extrapolated to larger scales and used to estimate global carbon sinks or sources for various ecosystems. If the annual VOC flux is of the same magnitude as the annual net CO₂ flux then VOC fluxes must be taken into account. For example, a measured annual net CO₂ sink of 75 g C m⁻² in a tropical forest could be extrapolated to estimate a global carbon sink of about 0.3 Gt C. This is a significant overestimate of the net carbon sink since estimates of annual VOC fluxes from tropical forests are as high as 75 g C m⁻².

5. Model Uncertainties and Areas of Potential Improvement

There are large uncertainties associated with any estimate of NVOC emission rates. Qualitative assessments of errors in isoprene and monoterpene emission estimates place uncertainty levels at a factor of 3 or higher [e.g., Lamb *et al.*, 1987; Hewitt and Street, 1992]. In ecosystems where emission factors are not well known, we can only assume that emissions will probably fall somewhere within the range of observed values for all other ecosystems. Recent reviews have summarized our understanding of the mechanisms controlling isoprene [Fall, 1991; Fehsenfeld *et al.*, 1992] and monoterpene [Tingey *et al.*, 1991; Fehsenfeld *et al.*, 1992] emissions. Emissions of VOC from plants are governed by a variety of physical and biological factors, the most important of which are genetic variation, light, and temperature, but which include humidity, CO₂ concentration, stomatal conductance, leaf development, time of day, season, and environmental stresses. The relative importance of these factors has been investigated for monoterpene and isoprene emission in a few plant species but is not well understood. The importance of many of these factors is not known at all for many NVOC. Some factors, e.g., the relationship between CO₂ concentration and NVOC emission, may have a negligible impact on current estimates of natural VOC emissions but may be important for estimating future emission scenarios. The sensitivity of photochemical models to natural VOC emission rate estimates, reviewed in section 6, indicates a need for further reductions in natural VOC emission rate uncertainties. In this section, factors contributing to current uncertainties are discussed, and future research priorities are outlined.

5.1. Ocean VOC Emissions

The surface ocean VOC concentrations used in our model are within the range of the existing observations, but these data are

sparse. Since fluxes are always calculated, either with modeled or observed C_{so} values, the observed fluxes have considerable uncertainty.

Improved estimates of VOC emissions from oceans may be limited by our understanding of the sources of these compounds. VOC in oceanic waters are thought to be produced by phytoplankton and abiotically by the oxidation of planktonically derived polyunsaturated lipids. Wilson *et al.* [1970] found in laboratory experiments that dissolved organic matter produced by diatoms, a common marine phytoplankton in temperate neritic waters, could produce ethene and propene if illuminated. They also found that if living cells were present, production was enhanced, and ethane and propane were also found, though in lesser amounts than the alkenes. Clearly, more observations of VOC in the surface ocean are needed to adequately constrain the computed values presented here.

5.2. Canopy Deposition

Tropospheric chemistry and transport models require estimates of surface emission and deposition fluxes. Most terrestrial surfaces are covered by a vegetation canopy, and flux estimates should represent the flux across the boundary between the top of the canopy and the bottom of the atmospheric boundary layer. Since many of our emission factors are based on leaf and branch enclosure measurements, emissions into the atmospheric boundary layer will be overestimated if chemical and deposition losses within the canopy are significant and unaccounted for. Flux estimates based on above-canopy concentration gradients agree reasonably well with enclosure measurements, indicating that most VOC escape into the atmosphere above the canopy [Lamb *et al.*, 1986]. The amount of VOC deposited on ground and canopy surfaces is not well known but could be significant. Reactions with OH could produce compounds that are quickly deposited on canopy surfaces. This probably has a small impact on daytime fluxes, since the time scale for turbulent diffusion in the canopy, <100 s [LeClerc and Shaw, 1988], is much less than the typical tropospheric lifetime, >1000 s [Atkinson, 1990], of most VOC. Under stable nighttime conditions, the time scale for diffusion in the canopy could be much larger. Field estimates of within-canopy deposition factors are needed so that this loss can be accounted for in VOC surface emission models.

5.3. Ecological Modeling

Uncertainties in foliar density and species composition estimates are a significant component of the overall uncertainties in emissions from land surfaces. VOC emission estimates for the United States and Europe have been improved by using the detailed foliar density and species composition estimates described by Geron *et al.* [1994] and D. Simpson *et al.* [1995]. Detailed vegetation inventories for many regions are currently unavailable. Existing global ecosystem distribution estimates include static databases [e.g., Olson, 1992] and estimates based on dynamic models [e.g., Bergengren and Thompson, 1994]. The estimates of Olson [1992] are based on a great deal of effort to validate individual grids and appear to provide the best means for estimating 1990 emissions. The incorporation of an accurate dynamic model of ecosystem distributions would be a significant improvement to our global VOC modeling procedures, because it provides a capability for investigating potential changes in emissions due to climate, succession,

disturbance, and land use related changes in ecosystem distributions.

Foliar VOC emission rate modeling efforts could also be improved by coupling the existing model with process-based models of global carbon and nitrogen dynamics. Ecosystem models of carbon and nitrogen fluxes and pool sizes have recently been extended to global scales by *Melillo et al.* [1993]. Some of these monthly variables (e.g., gross primary productivity, carbon, and nitrogen pool sizes) may be closely related to VOC fluxes although these relationships have not yet been quantified.

5.4. Other VOC

Investigations of natural VOC sources have focused on emissions of isoprene and monoterpenes from foliage. Emissions of other VOC sources can only be crudely estimated owing to the lack of data, but initial observations indicate that these sources may be of major importance. Emissions of methanol [*MacDonald and Fall*, 1993a], formaldehyde and acetaldehyde [*Steinbrecher et al.*, 1992], formic, acetic, and pyruvic acids [*Talbot et al.*, 1990], and (Z)-3-hexen-1-ol and (Z)-3-hexenyl-acetate [*Arey et al.*, 1991a] may contribute significantly to atmospheric concentrations of VOC. For example, recent measurements of methanol emission from leaves of 14 diverse plant species revealed an average flux of $5.4 \mu\text{g C g}^{-1} \text{h}^{-1}$ with a range of 0.2 to $18.4 \mu\text{g C g}^{-1} \text{h}^{-1}$ [*MacDonald and Fall*, 1993a]. If these measurements are confirmed, the global emission of this compound alone could be more than 100 Tg C. In addition, a wide variety of alkane, alkene, aromatic, sesquiterpene, alcohol, aldehyde, ester, ketone, and ether compounds are emitted from plants in at least trace amounts [*Zimmerman*, 1979; *Winer et al.*, 1992]. Further field measurements of ORVOC and OVOC in a variety of ecosystems are needed to establish these flux rates. Earlier reports of emissions of oxygenated VOC from plants are summarized by *Fehsenfeld et al.* [1992]. The biochemical and physiological mechanisms controlling the emission of these compounds is almost completely unknown at present.

5.5. Isoprene and Monoterpenes

Uncertainties in isoprene and monoterpene emission factors and the influence of light, temperature, and humidity are discussed in sections 5.5.1 and 5.5.2. Factors which may play an important role in regulating isoprene and monoterpene emissions but are not addressed in our current modeling procedures are discussed in the rest of this section.

5.5.1. Ecosystem-average emission factors. The major difference between the annual isoprene and monoterpene emission rates estimated by this study and the results of previous efforts are the emission factors assigned to various ecosystem types. Many of the emission factors compiled in Table 1 are based on enclosure measurements of individual plants that occur within a given ecosystem. The uncertainty in these estimates is a function of the accuracy of the emission factor for each plant that is a dominant component of an ecosystem. Variability in the species composition within each of the global ecosystems defined by *Olson* [1992] can result in variability in the ecosystem emission factor. Isoprene and monoterpene emissions reported for different plant species under identical environmental conditions range over several orders of magnitude [*Evans et al.*, 1982]. *Guenther et al.* [1994] assigned isoprene and monoterpene emission rates to all common tree

genera in the United States. Emission factors for the 91 woodland landscapes defined for the United States were estimated by summing the contribution of emissions from 49 genera of plants. *Guenther et al.* [1994] use a landcover classification scheme that is much more detailed than that developed by *Olson* [1992]. Emission factors estimated by *Guenther et al.* [1994] vary by as much as a factor of 5 for various landscapes within an ecosystem defined by *Olson* [1992]. Improved estimates for specific regions are needed for many modeling applications and require additional data than that provided by the *Olson* ecosystem database and the current emission measurement databases. The development of a database of emission factors for dominant plants is an achievable goal for some global ecosystems, such as temperate forests, but may not be practical for all regions.

Area-averaged natural VOC emissions have been measured by using various micrometeorological techniques [e.g., *Lamb et al.*, 1985; *Zimmerman et al.*, 1988]. Area-averaged isoprene and terpene emission factors for a variety of *Olson* [1992] ecosystem types, including snowy conifer (class 22), warm conifer (class 27), tropical rain forest (class 33), dry evergreen (class 48), regrowing woods (class 56), and warm crops and woods (class 58) have been estimated by using ambient measurements [*Ayers and Gillett*, 1988; *Lamb et al.*, 1985; *Zimmerman et al.*, 1988; *Hov et al.*, 1983; *A. Guenther et al.*, 1995]. Surprisingly, given the wide range in emission factors for individual plants, the landscape-average emission factors for these sites are within a factor of 5.

5.5.2 Light, temperature and humidity. Light and temperature account for most of the observed diurnal variations in isoprene and monoterpene emission rates. The algorithms developed by *Guenther et al.* [1993] adequately simulate the influence of light and temperature on isoprene and monoterpene emissions from a variety of plants. The wide applicability of these algorithms is probably due to the light and temperature dependence of isoprene emission being primarily controlled by isoprene synthase activity [see *Monson et al.*, 1992], whereas monoterpene emissions are primarily controlled by monoterpene vapor pressure [see *Tingey et al.*, 1991]. As described by *Fall and Monson* [1992], although isoprene emission occurs via stomatal pores in leaves, the emission rate is generally a function of isoprene synthesis rate and not stomatal conductance. Modeling of isoprene emission from leaves can be simplified by ignoring stomatal conductance except that this is an important parameter in determining leaf temperature. One area of uncertainty is the light dependence of monoterpene emission. Monoterpene emissions are light dependent for some plants [*Steinbrecher*, 1989] but not for others [*Guenther et al.*, 1991]. *Lerdau*, [1994] found that first-year needles of douglas fir (*Pseudotsuga menziesii*) have light-dependent monoterpene emission rates, whereas older needles do not. It may be that light has an effect only when plants are actively synthesizing monoterpenes.

Diurnal variations in humidity may cause significant variations in monoterpene emission [*Dement et al.*, 1975]. Correlations between monoterpene emission and foliar moisture have also been reported [*Lamb et al.*, 1985].

5.5.3 Plant development and growth environment. Plant developmental processes influence isoprene and monoterpene emissions in a variety of ways. *Yokouchi and Ambe* [1984] report that monoterpene emission rates vary with season but the mechanism responsible was not identified. A number of studies have found that young leaves tend to have much lower or no

isoprene emissions [Guenther *et al.*, 1991; Grinspoon *et al.*, 1991]. Kuzma and Fall [1993] have shown that this is due to a lack of isoprene synthase activity, and that increased isoprene emission in older leaves is associated with increased levels of this enzyme. Growth environment also plays an important role in determining how quickly new foliage will begin to emit isoprene at significant levels. Monson *et al.* [1994] found that aspen leaves began to emit isoprene after cumulative daily maximum temperatures above 0°C reach approximately 400 degree-days. Sharkey and Loreto [1993] found that isoprene emission could be turned off by transferring plants to low temperatures.

Isoprene emissions, expressed on a leaf area basis, decrease when plants are grown in a low light environment. This is in agreement with an observed decline in isoprene emission with depth in oak and sweetgum canopies, P. Harley *et al.* [Effects of light, temperature and canopy position on net photosynthesis and isoprene emission from leaves of sweetgum (*Liquidambar styraciflua* L.), submitted to *Tree Physiology*, 1995], which also leads to a change in leaf morphology. When expressed on a leaf weight basis, this effect is much reduced.

The CO₂ concentration during growth may influence VOC emission rates. Oak leaves from trees grown 45 days at high CO₂ (65 Pa) had twice the rate of isoprene emission as leaves grown at normal CO₂ (40 Pa), while aspen tree leaves grown similarly had 60-70% the isoprene emission rate of trees at normal conditions [Sharkey *et al.*, 1991]. The mechanism(s) of these contrasting effects are unknown but of importance in the face of rising global atmospheric CO₂ concentrations.

Phenological events may significantly alter the emission patterns of some plants. Emission of linalool, an oxygenated monoterpene, from orange trees increases by about a factor of 10 when the trees are blooming [Arey *et al.*, 1991b]. Emission of acetone from conifers occurs from bud surfaces, and the emission declines markedly at bud break [MacDonald and Fall, 1993b]. These types of events could significantly alter VOC emission rates on regional scales and should be further investigated.

5.5.4. Nutrient, water, and injury status. Lerdau *et al.* [1994] have shown that monoterpene emissions from ponderosa pine are correlated with needle monoterpene concentrations. Since needle monoterpene concentrations are influenced by nitrogen availability, this may be an important control over monoterpene emissions. Steinbrecher [1989] observed significant differences in the pattern of emitted monoterpenes and the needle monoterpene concentrations for Norway spruce, suggesting that this relationship may not be straightforward. Harley *et al.* [1994] observed increased isoprene emissions with increased nitrogen availability.

Sharkey and Loreto [1993] found dramatically increased isoprene emissions from plants subjected to water stress. This could have a significant impact on regions undergoing drought. Ayers and Gillett [1988] found that isoprene emission was much higher during the wet season in tropical Australia. This may have been due to the increased biomass during this period rather than the increased plant water status. Long-term water stress leads to increased monoterpene emission from cypress trees [Yani *et al.*, 1993].

Physical injury can trigger large increases in monoterpene synthesis [Lewinsohn *et al.*, 1991] and decreases in isoprene emissions from certain vines [Loreto and Sharkey, 1993]. The effects of wounding on monoterpene emission rates have not been quantified, but it is well known that physical leaf

disturbance and wounds in monoterpene emitters lead to a large short-term increase in emissions [Zimmerman, 1979]. Effects on isoprene emission after wounding are related to transmissible wound signals [Loreto and Sharkey, 1993].

6. Photochemical Model Sensitivity to VOC Emissions

Tropospheric photochemical model results are sensitive to VOC emission estimates and indicate that current uncertainties in NVOC estimates should be reduced. In addition, global chemical and transport models provide a means of testing VOC flux estimates by comparing modeled and observed concentrations of chemical species, such as carbon monoxide, that are dependent on VOC fluxes.

Concentrations of ozone and its precursors over North America were investigated by Jacob *et al.* [1993], using a three-dimensional, continental-scale photochemical model. They found that a doubling of isoprene emissions resulted in less than a 4-ppb increase in mean O₃ concentration anywhere in their model domain. This is to be expected for any region where O₃ production is NO_x limited. Shutting off isoprene emissions completely in the model resulted in 5 to 15 ppb decreases of O₃ over most of the eastern United States. With a relatively low isoprene emission rate, less than half of the amount estimated by our global model, Jacob *et al.* [1993] found that isoprene contributed 27% of the total source of CO over North America.

Hough and Johnson [1991] examined the budgets of photochemical oxidants on a global scale, using a zonally averaged two-dimensional chemistry and transport model. They found that a 20% reduction in annual isoprene emissions, from 450 to 360 Tg, resulted in changes in global average concentrations of +3.6% for OH, 0% for O₃, -3.0% for peroxyacetyl nitrate (PAN), -2.2% for H₂O₂, and -9.3% for CH₃COO₂H. A 20% reduction in annual monoterpene emissions, from 550 to 440 Tg, resulted in changes in global average concentrations of +0.5% for OH, 0% for O₃, -0.6% for PAN, -0.4% for H₂O₂, and -0.4% for CH₃COO₂H. The strong seasonality and distinct spatial distribution of natural VOC should result in detectable changes in the atmospheric CO signal attributable to this source. A combination of global atmospheric modeling and satellite data could provide a means for validating VOC emission estimates. Accurate estimates of CO emissions from global biomass burning would also be needed for this analysis.

7. Conclusions

The NVOC emission rate estimates described in this paper are our current best estimates for use in 3-D global computer models. Estimated isoprene emissions in temperate regions are considerably higher than previous estimates, but the global totals are similar, since they are dominated by emissions in the tropics. Isoprene and monoterpene emissions are estimated to contribute 57% and 14%, respectively, of the total reactive VOC flux and are primarily emitted from woodlands. About half the total global VOC flux is estimated to be from compounds other than isoprene and monoterpenes. Ocean emission estimates are considerably lower than most previous estimates but can still play an important role in the remote marine boundary layer.

The model described here has been used to generate an inventory of estimates for 1990. These data are available in digital format from the IGAC-GEIA archive. In addition to the

IGAC-GEIA inventory, the emission model components have been incorporated into regional and global 3-D chemistry and transport models and are being used to investigate the interactions between global change and trace gas biogeochemistry.

One of the most critical aspects of creating these high-resolution, global estimates of trace gas fluxes is to emphasize the errors and need for an enlarged observational database to check these model results. Uncertainties associated with isoprene and monoterpene emissions in some temperate regions are at least a factor of 3. Fluxes of isoprene and monoterpenes in tropical regions and fluxes of other VOC in all regions have even higher uncertainties. Field measurements of regional VOC fluxes from surfaces and vegetation types where few or no data exist will provide some sorely needed constraints on calculations such as this. A better understanding of the processes controlling NVOC emission will also lead to improvements in existing model algorithms.

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