Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America

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Abstract

The magnitudes, distributions, controlling processes and uncertainties associated with North American natural emissions of oxidant precursors are reviewed. Natural emissions are responsible for a major portion of the compounds, including non-methane volatile organic compounds (NMVOC), carbon monoxide (CO) and nitric oxide (NO), that determine tropospheric oxidant concentrations. Natural sources include soil microbes, vegetation, biomass burning, and lightning. These sources are strongly influenced by human activities that have led to significant changes in the magnitude and distribution of natural emissions in the past two centuries. The total NMVOC flux of about 84×10^{12} g of carbon (Tg C) is comprised primarily of isoprene (35%), 19 other terpenoid compounds (25%) and 17 non-terpenoid compounds (40%). Vegetation is predicted to contribute about 98% of the total annual natural NMVOC emission. The estimated annual natural NO emission of 2.1×10^{12} g of nitrogen (Tg N) from North America is primarily due to soils and lightning, while the estimated 10 Tg C of CO arises from biomass burning and vegetation. Field measurements of ambient concentrations and above canopy fluxes have validated emission estimates for a few compounds from some important landscapes. The uncertainty associated with natural emission estimates ranges from less than 50% for midday summer isoprene emission from some locations to about a factor of 10 for some compounds and landscapes. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Natural emissions of volatile compounds are an important component of the earth system responsible for

determining the composition of the atmosphere. On a global scale, natural emissions of nitric oxide (NO), carbon monoxide (CO), and non-methane volatile organic compounds (NMVOC) equal or exceed anthropogenic emissions, although anthropogenic sources usually dominate within urban areas. Biogenic NMVOC influence ozone chemistry in several ways. Isoprene, for example, can act as a direct sink of oxidants, competing with ozone as a sink for NO, can contribute to sequestration of nitrogen (allowing long distance transport), and through oxidation products (ketones, aldehydes, carbon monoxide) can have an impact on ozone chemistry (Fehsenfeld et al., 1992). Pierce et al. (1998) conclude that

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the appropriate regulatory control strategy (i.e. VOC or NO_x control) indicated by a regional oxidant model is sensitive to whether or not isoprene emissions are included and, at some locations, depends on which emission model is used to predict isoprene emission. This result emphasizes that accurate estimates of isoprene emissions are needed to determine oxidant control strategies.

Although this paper focuses on natural sources, i.e., trace gas emissions present at a significant level, even in the absence of humans, most of these natural sources are now strongly influenced by human activities. Natural sources include biological emissions (e.g., vegetation and soil microbes) and abiotic processes (e.g., geogenic, lightning, and biomass burning). NMVOC from foliage of living vegetation is the only natural emission that has been shown to influence North American oxidant control strategies (e.g., Pierce et al., 1998) and a large proportion of this review is devoted to this topic. We describe current best estimates of natural emissions and associated uncertainties and discuss recent advances in our ability to predict and assess these emissions. This review focuses on research reported since 1991, and we refer readers elsewhere (NRC, 1991; Singh and Zimmerman, 1992; Fehsenfeld et al., 1992) for details on earlier research.

2. Emission measurements and models

2.1. Vegetation

Tens of thousands of organic compounds have been identified in plant tissues and more are discovered every year. Many of these compounds have very low volatility or they are stored in plant structures that present substantial barriers to emission. As a result, there are probably less than 40 that are emitted at rates that significantly influence the chemical composition of the atmosphere. These compounds include terpenoids (isoprene, 2-methyl-3-buten-2-ol, referred to here as MBO, and monoterpenes), other reactive compounds (hexenal family compounds, alkenes, aldehydes, and organic acids), and less reactive compounds (alcohols, ketones and alkanes).

2.1.1. Measurements

Our ability to assess the impact of natural emissions on tropospheric oxidant levels is very dependent on the quality and quantity of available measurements. Measurements of natural emissions from vegetation have improved considerably during the past decade as a result of advances in analytical methods, which are reviewed by Parrish and Fehsenfeld (submitted to this issue), and flux measurement techniques which are discussed below.

2.1.1.1. Enclosure flux measurements. Table 1 summarizes enclosure methods that have been used to investigate biogenic emissions. Early studies used static enclosures, which resulted in considerable perturbations from ambient conditions, and most investigators now use dynamic (flow-through) enclosures, which cause less perturbation. Enclosures allow investigators to isolate individual emission sources and manipulate environmental conditions and have been extremely useful for developing emission capacity databases and algorithms that are used in regional emission models.

Controlled-environment enclosures, combined with towers and vehicles with extended booms to access all parts of a mature forest canopy (Harley et al., 1997; Geron et al., 1997), have greatly enhanced the measurement database available for developing models. Another useful tool is the combination of a simple enclosure with a commercial hand-held NMVOC analyzer (an industrial leak detector) for inexpensive and rapid screening a large number of plant species (Guenther et al., 1996d). This in situ screening tool does not replace the need for quantitative enclosure flux measurements but is useful for prioritizing measurements, particularly for regions with a large number of plant species.

2.1.1.2. Above-canopy flux measurements. Tower flux systems are used to evaluate diurnal, seasonal and year-to-year emission variations while aircraft and balloon flux measurements are used to evaluate emission model predictions on scales of tens to hundreds of kilometers. Eight above-canopy flux measurement techniques have been used for the North American biogenic NMVOC field studies listed in Tables 2 and 3. Methods used prior to 1992 include the surface layer gradient, tracer, mixed layer mass balance and mixed layer gradient estimation methods. Since then, more direct flux measurement methods have been employed, including the flux gradient, relaxed eddy accumulation, eddy accumulation, and eddy covariance methods. These techniques are potentially more accurate than the earlier methods and so can better constrain flux model predictions. In addition, more robust and less expensive equipment (e.g., sonic anemometers) have greatly extended the application of these methods. The most accurate flux measurement method, eddy covariance, requires selective, sensitive and fast response sensors. An appropriate sensor is currently available only for isoprene (Guenther and Hills, 1998), although eddy covariance systems for other NMVOC may be possible using analytical systems that are now available (e.g., Lindinger et al., 1998).

Tower-based flux measurements are particularly useful for evaluating model predictions of diurnal (e.g., Guenther and Hills, 1998) and seasonal (e.g., Geron et al., 1997; Goldstein et al., 1998) emission variations. Table 2 summarizes studies conducted at 18 North American sites

Table 1
Summary of selected North American enclosure studies of biogenic NMVOC fluxes

Location[a]	Study focus[b]	No. Plant species	Enclosure method[c]	Ancillary data[d]	No. of VOC	Reference
Potted	EF	1	SB		Total	Went (1960)
NC, VA, MO, CO	EF	> 4	SB		> 2	Rasmussen and Went (1965)
Potted	EA	1	DBC	T, S	1	Dement et al. (1975)
NC, WA, TX, CA	EF	> 50	SB	T	> 15	Zimmerman (1979)
Potted	EA	2	DWC	T, Q, P, S	6	Tingey (1981)
WA	EF, EA	> 20	SB	T	> 5	Lamb et al. (1985)
Potted	EA	1	DLC	T, Q, P, S	1	Hewitt et al. (1989)
CO, Potted	EA	1	DLC	T, Q, P, S, B	1	Monson et al. (1994)
CA	EA	1	DB	T, B	4	Arey et al. (1991a)
CA	EF	> 25	DB	T	> 20	Arey et al. (1991b)
Potted	EA	1	DLC	T, Q, P, S, B	1	Sharkey and Loreto (1993)
AL, CO, Potted	EA, EF	> 10	DLC	T, Q, P, S, B	2	MacDonald and Fall, 1993a,b
Potted	EA	4	DLC	T, Q, P, S, B	4	Guenther et al., 1991,1993
AL	EF, EA	1	DW	T, Q, B	1	Pier (1995)
CA, Potted	EF	10	DB	T, Q	> 20	Arey et al. (1995)
Potted	EA	1	DLC	T, Q, P, S, B	11	Lerdau et al. (1995)
TN, GA, AL	EF	> 40	DB,DLC	T, Q	> 10	Guenther et al., 1996a,c
GA, NC, CO	EF, EA	> 50	DB,DLC	T, Q	> 20	Guenther et al. (1996b)
GA, TN	EA	5	DL	T, Q, P, S, B, G	1	Harley et al., 1996,1997
NC	EF, EA	3	DLC	T, Q, P, S	1	Geron et al. (1997)
NY	EE	0	SG	T	1	Cleveland and Yavitt (1997)
TX	EF	> 40	IL	T, Q	Total	Guenther et al. (1999a)

[a] Locations are abbreviations for US states. Potted indicates that plants were grown in pots and are not necessarily representative of a particular location.

[b] EF indicates measurements of emission factors, EA indicates investigation of emission activity algorithms, EE indicates study of escape efficiency (by measuring deposition fluxes).

[c] Enclosure methods include static branch chamber (SB), dynamic-flow branch chamber with (DBC) or without (DB) environmental control, dynamic whole plant chamber with (DWC) or without (DW) environmental control, dynamic leaf cuvette with (DLC) or without (DL) environmental control, static ground enclosure (SG), and leaf cuvette with in-situ analysis by a hand-held analyzer (IL).

[d] Ancillary measurements include temperature (T), PAR (Q), photosynthesis (P), stomatal conductance, humidity and transpiration (S), Phenological status of blooms, buds, leaf age, etc. (B), and growth conditions (G).

ranging from southern Texas (27.7 N) to northern Canada (54 N). At five of these sites, measurements have been made during more than one year.

Field measurements of landscape scale (> 10 km^2) fluxes using aircraft and tethered balloon systems are summarized in Table 3. These observations can be used to evaluate emissions estimated at scales similar to those used by regional chemistry and transport models (about 25–400 km^2). The 13 sites listed in Table 3 are representative of many of the major North American landcover types. Tethered balloon systems are a relatively inexpensive alternative for investigating regional fluxes and have already provided a substantial database of regional flux estimates. Aircraft flux systems have seen only limited use but the results indicate that these systems are a potentially valuable tool for characterizing biogenic emissions across large regions.

2.1.1.3. Isotopic and near-surface concentration measurements. Global average concentrations of CO, acetone, ethane, and propane can be combined with global estimates of loss rates to place bounds on annual global emissions (Singh and Zimmerman, 1992; Singh et al., 1994; Rudolph, 1995). If the anthropogenic emissions of these compounds are reasonably well known, and the sources are relatively uniformly distributed among the different continents, then the natural emissions from North America can be estimated. Although there are large uncertainties associated with these estimates, they serve to constrain model predictions.

In recent years, scientists have begun exploring the use of radiocarbon isotopes as a way of establishing the biogenic versus anthropogenic fraction of NMVOC in ambient air. Contemporary sources of carbon (including biogenic emissions) contain elevated ^{14}C, while ancient

Table 2
Summary of North American tower-based studies of above-canopy biogenic NMVOC fluxes

Study site	Location	Year	Landscape	Duration[a]	Method[b]	Compounds[c]	References[d]
Saxapahaw	NC (35.9N, 79.3W)	76	Plantation (pine)	Short	SLG	α-p	Ar78, Kn81
Lancaster	PA (40.0N, 76.6W)	79	Deciduous forest (oak)	Short	SLG	iso	La85
Hertford	NC (36.3N, 77.0W)	80	Plantation (pine)	Short	TM	α-p	Ar82
Seattle	WA (47.3N, 122.5W)	80	Conifer forest (douglas fir)	Short	SLG	α-p	La85
Goldendale	WA (46.0N,120.7W)	82, 83	Deciduous forest (oak)	Short	TM	iso	La86
Scotia	PA (40.7N, 77.9W)	88	Deciduous forest (oak)	Short	SLG	iso	La85
Oak Ridge, SOS	TN (36.0N, 84.3W)	92, 95, 96	Deciduous forest (oak)	Short	REA, FG, EC	iso	G96b, Ha97
Harvard Forest	MA (42.5N, 72.2W)	92, 93, 95	Mixed forest (oak)	Long	FG	iso, < C5	Go96, Go98
SOS- Metter	GA (33.4N, 84.2W)	93	Urban forest (oak)	Short	FG	iso	G96c
Temple Ridge	CO (44.4N, 107.2W)	93	Scrubland (oak)	Short	FG	iso	G96c
Rhinelander	WI (45.7N, 90.1W)	93	Bog (spruce)	Short	FG	iso	Is99
Borden	Ont. (44.3N, 81.0W)	93	Forest (maple, aspen)	Short	SLG	iso	Fu96
BOREAS	Man. (53.6N, 106.3W)	94	Boreal forest (aspen)	Short	FG	iso	Fu97
BOREAS	Sask. (54.0N, 105.1W)	94	Boreal forest (spruce)	Short	REA, FG	iso	Pa97
La Copita	TX (27.7N, 98.2W)	94	Subtropical shrubland	Short	FG	iso	G99a
Duke	NC (36.0N, 79.1W)	94, 95, 96	Deciduous forest (oak)	Long	REA, EC	iso	Ge97, G98
Gainesville	FL (29N, 82W)	95	Plantation (pine)	Long	REA	iso, α-p	Lo97
Boardman	OR (45.7N, 119.6W)	95, 96	Plantation (poplar)	Long	REA, EC	iso	La99

[a] Study duration is considered long if over 30 days and short if less than 30 days.

[b] Tower flux methods include surface layer gradient (SLG), flux gradient (FG), tracer (TM), relaxed eddy accumulation (REA), and eddy covariance (EC).

[c] Compounds include isoprene (iso), α-pinene (α-p), and ethene, propene, and butene (< C5).

[d] References include Arnts et al., 1978,1982 (Ar78, Ar82), Fuentes et al., 1996,1997 (Fu96, Fu97), Geron et al. (1997) (Ge97), Goldstein et al., 1996, 1998 (Go96, Go98), Guenther et al., 1996b,c, 1999a (G96b, G96c, G99a), Guenther and Hills (1998) (G98), Hall et al. (1997) (Ha97), Isebrands et al. (1999) (Is99), Knoerr and Mowry (1981) (Kn81), Lamb et al., 1985, 1986, (La85, La86, B. Lamb, personal communication (La99), Loescher et al. (1997) (Lo97), and Pattey et al. (1997) (Pa97).

Table 3
Summary of North American tethered balloon and aircraft based studies of above-canopy biogenic NMVOC fluxes

Location	Year	Landscape	Platform[a]	Method[b]	Compounds[c]	References
PA (40.7N, 77.9W)	88	Eastern deciduous forest	TB	MLMB	iso	Greenberg et al. (1999)
AL (32.3N 88.2W)	90	Southern mixed forest/crops	TB	MLMB, MLG	iso, α-p, β-p	Guenther et al. (1996a)
GA (32.5N 82.1W)	91	Southern mixed forest/crops	TB	MLMB, MLG	iso, α-p, β-p	Guenther et al. (1996a)
TN (36.0N, 84.3W)	92, 95	Appalachian mixed forest	TB	MLMB, MLG	iso	Greenberg et al. (1999)
CO (44.4N, 107.2W)	93	Western scrub, range/crops	TB	MLMB	iso	Guenther et al. (1996a)
NC (35.1N, 83.4W)	93	Deciduous forest	TB	MLMB	iso	Guenther et al. (1996b)
WI (45.8N, 90.0W)	93	Northern mixed forest	TB	MLMB	iso	Isebrands et al. (1999)
TX (27.7N, 98.2W)	94	Subtropical shrub, range/crops	TB	MLMB	iso	Guenther et al. (1999a)
Canada (54-56N,99-106W)	94	Boreal forest	Aircraft	EA	iso	Davis et al. (1996)
Canada (54-56N,99-106W)	96	Boreal forest	Aircraft	REA	iso	Zhu et al. (1997)
NC (35.8N, 79.2W)	96	Southern mixed forest/crops	TB	MLMB, MLG	iso	Greenberg et al. (1999)
MA (42-43N, 71-72W)	96	Eastern mixed forest	Aircraft	MLMB	iso	Gao and Doskey (1997)
WA (47.2N, 122.5W)	96	Western mixed forest	TB	MLMB	iso	Lamb et al. (1997)

[a] Platforms include tethered balloon (TB) and aircraft.
[b] Flux methods include mixed layer mass balance (MLMB), mixed layer gradient profile (MLG), and eddy accumulation (EA).
[c] Compounds include isoprene (iso), α-pinene (α-p), and β-pinene (β-p).

sources of carbon (such as fossil fuels) are depleted of ^{14}C. Lewis et al. (1998) estimated that the biogenic contribution to total NMVOC at a site near Los Angeles ranged from 13% in the morning to about 34% in the afternoon and evening. In other ^{14}C studies, the biogenic fraction of carbonyls (e.g., formaldehyde) in rural areas was estimated to be 50% (Larsen et al., 1998) to 80% (Tanner et al., 1996). These studies could not distinguish between primary and secondary (i.e., atmospheric oxidation of biogenic hydrocarbons) biogenic sources. Rudolph et al. (1997) have used δ^{13}C to characterize different sources of ambient NMVOC. This method could potentially be used to identify sources of individual compounds, even distinguishing among different biogenic sources, assuming that the δ^{13}C values of the sources are significantly different.

Isoprene emission estimates have also been evaluated using 3-D chemistry and transport models and near-surface isoprene concentration measurements (e.g., Chang et al., 1996). While inverse methods are reasonable for investigating sources of long-lived gases, it is not clear that they can produce reliable results for biogenic NMVOC since most landscapes are fairly heterogeneous with respect to isoprene emission and because there are few databases that have sufficiently accurate measurements of biogenic VOC (Parrish and Fehsenfeld, this issue). In addition, photochemical oxidant models may not be suitable for evaluating emissions by inverse modeling due to the large uncertainties in the other processes that influence concentrations (e.g., mixed layer height, vertical transport, OH concentrations).

The use of ambient concentration measurements to evaluate oxygenated NMVOC emission estimates is difficult, due to anthropogenic sources and production from the tropospheric oxidation of hydrocarbons, but it may be possible to identify biogenic sources from diurnal patterns and vertical profiles. For example, Goldan et al. (1995) observed high concentrations of methanol in ambient air at two rural locations in the southeastern United States and noted that the diurnal variation suggested a biogenic source (either direct emission or via the oxidation of another biogenic compound). Andreae et al. (1988) observed a significant decrease of formic acid with height in the boundary layer above the Amazon basin and concluded that direct emission from vegetation was an important source of these compounds.

2.1.2. Modeling

Trace gas emissions from vegetation are estimated as

$$\text{Emission} = [\varepsilon][D_\text{p} D_\text{f}][\gamma_\text{P} \gamma_\text{T} \gamma_\text{A}][\rho], \qquad (1)$$

where ε is a landscape average emission capacity, D_p is the annual peak foliar density, D_f is the fraction of foliage present at a particular time of year, the emission activity factors γ_P, γ_T, and γ_A account for the influence of photosynthetic photon flux density (PPFD), temperature, and leaf age, respectively, and ρ is an escape efficiency that represents the fraction emitted by the canopy that is released into the above-canopy atmosphere.

Table 4
Categories of NMVOC emission from vegetation. Emission type corresponds with the codes given in Table 5

Emission type	Description	Role	Compounds (examples)	Mechanism that limits emission	Occurrence in plants
CHL	Chloroplast	Uncertain	Isoprene, MBO α-pinene	Light-dependent enzyme	Limited
DST	Defense (specialized tissues)	Defense	α-pinene, myrcene	Release from stored pool	Limited
DUT	Defense (unspecialized tissues)	Defense	Hexenal	Fatty acid peroxidation	Widespread
PGH	Plant growth hormone	Growth regulation	Ethene	Enzyme	Widespread
CDV	Cut and drying vegetation	Uncertain	Methanol, acetone	Uncertain	Widespread
FS	Floral scents	Attractants	Linalool, xylene	Flower development	Limited
OTH	Other	Uncertain	Acetic acid	Uncertain	Uncertain

2.1.2.1. Emission activity. Seven different processes that result in trace gas emission from vegetation are summarized in Table 4. We have numeric descriptions of emission activity behavior for only two of these processes: CHL (chloroplasts) and DST (defense: specialized tissues). The emission activity algorithm used for DST emissions is an exponential increase with temperature using the coefficients recommended by Guenther et al. (1993). Since we expect that other emissions will also increase with temperature, this algorithm is used as the default for all other processes (except CHL) in Table 4.

The CHL emission activity algorithm is used for modeling emissions from chloroplasts, including emissions of isoprene (Guenther et al., 1993), MBO (Harley et al., 1998) and some monoterpenes (Kesselmeier et al., 1996; Ciccioli et al., 1997). Guenther et al. (1993) assumed that this type of emission activity could be described as the product of two factors: one accounting for temperature (γ_T) and another accounting for light, or photosynthetic photon flux density, PPFD (γ_P). Guenther et al. (1999b) modified the algorithms for calculating these two factors and added a third (γ_A) to account for leaf age and phenology. The Guenther et al. (1993) algorithm accounts only for the environmental conditions that the leaf has been exposed to in the past hour, whereas the modified algorithm also accounts for the influence of the environmental conditions that a leaf has been exposed to in the past several weeks. Fig. 1 illustrates the predicted strong influence of both current and past leaf temperature and current and past PPFD levels on estimated CHL emission activity.

Young and old leaves emit isoprene at reduced rates (Guenther et al., 1991; Monson et al., 1994). At present, we use the general approach of Guenther et al. (1999b) to estimate leaf age emission activity, γ_A, as a function of the amount of foliage present during the current and previous months. The variations in γ_A shown in Fig. 2 capture the major features expected for various North American landscapes.
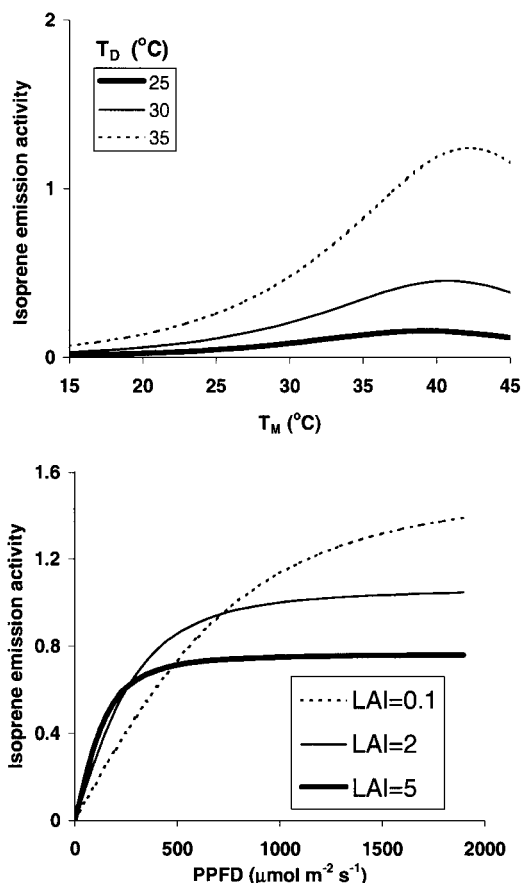

Fig. 1. Predicted influence of temperature (top) and photosynthetic photon flux density (PPFD) (bottom) on isoprene emission activity factors. T_D is the mean leaf temperature of the past 15 days and T_M is the mean leaf temperature of the past 15 minutes. LAI is leaf area index.

2.1.2.2. Emission capacity. We define foliar emission capacity as the emission rate expected from a leaf under specified environmental conditions, phenological status and growth conditions. Table 5 summarizes the emission
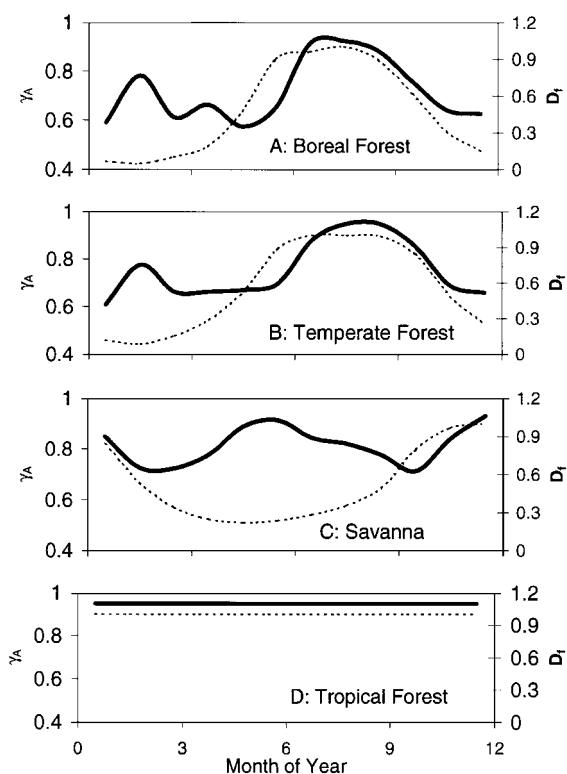
Fig. 2. Predicted seasonal variations in the ratio of current to peak foliar density, D_f (dashed line), and leaf age emission activity factor, γ_A (solid line), for landscapes in Canada (Boreal Forest), Texas (Savanna), Massachusetts (Temperate Forest), and Mexico (Tropical Forest).

capacities assigned to the different emission types described in Table 4. As is the case for emission activity, there are many more measurements characterizing CHL and DST type emissions than other processes. CHL emission capacities can be much higher than those for other processes but only about 30% of all plants have a non-zero CHL emission capacity (Guenther et al., 1994). The DST emission capacities are considerably lower but two-thirds of all plants have a non-zero DST emission capacity (Guenther et al., 1994).

There are so few data currently available for characterizing emission capacities for other emission processes that we are forced to assign the same emission capacities to all plant species. Each compound is assigned one of five emission capacities: 0.02, 0.04, 0.09, 0.16 or 0.6 μg-C g^{-1} h^{-1}. These emission capacities are based on measurements reported in the literature (Talbot et al., 1990; Servant et al., 1991; Arey et al., 1991a,b; MacDonald and Fall, 1993a,b; Nemecek-Marshall et al., 1995; Konig et al., 1995; Goldstein et al., 1996; Kesselmeier et al., 1997; Kirstine et al., 1998; Helmig et al., 1999). The emission capacities for each compound

emitted by processes other than DST and CHL are shown in Table 5 and sum to a total of 2 μg-C g^{-1} h^{-1} which is 33% lower than the value assigned by Guenther et al. (1994).

2.1.2.3. Plant species composition and foliar density. We characterized North American landcover distributions using a combination of satellite derived databases and vegetation inventories. Landcover characteristics were estimated using plant species composition data compiled on a county scale for the contiguous U.S. (US EPA BELD3, ftp://monsoon.rtpnc.epa.gov), a province scale for Canada (Lowe et al., 1994, http://nrcan.gc.ca/cfs/proj/iepb/nfdp/nfdpe.htm), and a regional scale for Mexico (based on Rzedowski, 1957) and then distributed spatially with a 1 km resolution using the Global Landcover Characteristics (GLCC) database (http://edcwww.cr.usgs.gov/landdaac/glcc/glcc.html). The temporal and spatial patterns observed by a satellite sensor (Advanced Very High Resolution Radiometer) were used to define GLCC land cover associations with fairly distinctive phenology (that is, onset, peak, and seasonal duration of greenness) and primary production.

The ratio of the foliage present at a specific time of year to the peak foliage during the year was estimated by using the average monthly leaf area index (LAI) for the years 1987 and 1988 in the ISCLCP LAI database. Fig. 2 illustrates typical results for four North American landscapes. The ISCLCP database has a resolution of 1° latitude by 1° longitude and is described by Sellers et al. (1994). The LAI estimates were derived from satellite measurements of an index (simple ratio) that is related to LAI due to the very different optical properties of green leaves in the red (high absorption) and infrared (high reflection) bands. Sellers et al. (1994) used the simple ratio to interpolate between minimum and maximum LAI values assigned to different global vegetation types.

2.1.2.4. Escape efficiency. The model described by Jacob and Bakwin (1991) can be used to calculate the fraction of a trace gas emission that enters the atmosphere. We implement this model using the methods described by Guenther et al. (1999b). Our average estimate of ρ is scaled so that it agrees with observations of microbial consumption of isoprene in soils (about 5% of that emitted by the canopy) reported by Cleveland and Yavitt (1997).

2.1.2.5. Environmental conditions. Leaf temperature and PPFD are primary driving forces for vegetation emissions. Above-canopy ambient temperature, direct PPFD, diffuse PPFD, wind speed, and humidity are used as a starting point for estimating the canopy microclimate. Hourly average estimates of each of these above-canopy environmental conditions for all of North America can be obtained from the four-times daily values

Table 5
Emission factors and annual North American emission rates. Emission type corresponds with the codes given in Table 4

Emission type	Emission capacity ($\mu g\ g^{-1}\ h^{-1}$)	Annual emission (Tg C)	Compounds
CHL	0–100	29.3	Isoprene
CHL	0–60	3.2	MBO
DST	0–2	4.5	α-Pinene
DST	0–1.5	3.2	β-Pinene
DST	0–1	2.0	$\Delta^3 -$ Carene
DST	0–0.6	0.4 to 1.1	Sabinene, d-limonene, β-phellandrene, ρ-cymene, myrcene
DST	0–1.5	0.1 to 0.4	Camphene, camphor, bornyl acetate α-thujene, terpinolene, α-terpinene, γ-terpinene, ocimene, 1,8-cineole, Piperitone, α-phellandrene, tricyclene, Other terpenoids
DUT, CDV or OTH	0.6	8.4	Methanol
OTH	0.3	4	Carbon monoxide
DUT, CDV or OTH	0.16	2.6	Hexenyl-acetate, hexenol Other reactive NMVOC, Other NMVOC
PGH	0.09	1.5	Ethene
DUT, CDV or OTH	0.09	1.5	Propene, ethanol, acetone, hexenal,
DUT, CDV or OTH	0.04	0.6	Acetaldehyde, formaldehyde, Butene, hexanal
DUT, CDV or OTH	0.02	0.2	Butanone, ethane, acetic acid, formic acid

provided by the NCEP/NCAR reanalysis (http://www.scd.ucar.edu/dss/pub/reanalysis) of the NCEP global model data. The simple scaling functions of Lamb et al. (1993) can be used to relate the vertical profiles of ambient temperature, relative humidity, and wind speed in the canopy to the existing above-canopy conditions. The distribution of PPFD within the canopy is estimated using the model described by Guenther et al. (1995) with the following modifications. First, specific leaf mass ($g\ m^{-2}$) is assumed to increase with height in the manner proposed by Geron et al. (1994) resulting in a larger mass of leaves in the upper portion of the canopy. Secondly, we first calculate the average diffuse PPFD on all leaves in the canopy (Eq. (16a) in Guenther et al., 1995) and then attenuate it through the canopy as an exponential function of LAI. Leaf temperature is estimated by solving the energy balance equation described by Lamb et al. (1993) except that leaf stomatal resistance is estimated using the analytical functions developed by Goudriaan and van Laar (1994). In addition, an improved iterative method is used to solve for leaf temperature.

2.2. Soil organisms

CO and various NMVOC (methane, ethane, ethene, propane, propene, isoprene, methanol and formaldehyde) are produced by soil microorganisms (Isidorov 1990;

Neue and Roger, 1993; Kuzma et al., 1995) but other microorganisms can metabolize these compounds (e.g., Fall and Benson, 1996) and, in many cases, soils are net sinks for these compounds (e.g., Morsdorf et al., 1992; Cleveland and Yavitt, 1997). These studies suggest that soils make a minor contribution to the total net flux of CO and NMVOC to the atmosphere and we therefore assume the net flux for North America is negligible.

The primary means for developing NO emission factors from soils has been through measurements with static or dynamic chambers (Williams et al., 1992). Although the amount of data from these types of chambers continues to increase, as evidenced by the thousands of measurements reported for the southeastern US by Thornton et al. (1997), concerns persist as to whether the chambers represent a true NO_x ($NO + NO_2$) flux between the soil and the atmosphere (Parrish et al., 1987). After observing bi-directional fluxes of NO_x over grass in the midwestern United States, Wesely et al. (1989) suggested that soil NO emissions might react rapidly with ozone near the surface. Advances in measuring and parameterizing NO_x fluxes have been reported by Lenschow and Delany (1987) and Jacob and Bakwin (1991). These efforts, however, are complicated by the demands for high frequency measurements of NO, NO_2, and O_3, the vertical divergence of NO flux as a function of height caused by rapid (~ 1 min) chemical transformations,

and the influence of vegetation canopies that tend to efficiently remove NO_2 (after NO is converted in the presence of O_3). Field studies addressing these issues may improve our understanding of these processes (Aneja, 1994). Meanwhile, concerns remain about the legitimacy of extrapolating chamber-based emission measurements to regional-scale fluxes.

Soil NO emission factors from about 50 North American landscapes are summarized by Williams et al. (1992), Yienger and Levy (1995) and Davidson and Kingerlee (1997). The reported emission factors range over two orders of magnitude. In general, wetlands and tundra have very low emissions, forests have moderate emissions, while agricultural and grasslands have the highest emission rates. Emission activity factors for soil NO emissions depend on long-term and short-term effects. Long-term effects include soil texture, organic matter content, soil pH, and nitrate levels, while short-term effects are primarily soil temperature and water-filled pore space (Potter et al., 1996). Soil NO emissions generally increase with soil nitrate levels (which are easily perturbed by the application of nitrogen-based fertilizers), soil temperature, and optimum soil moisture conditions.

2.3. Biomass burning

Biomass burning described in this assessment includes wildfires, which are often caused by lightning or unintentional human activities, and prescribed fires. The use of wood for fuel is considered an anthropogenic emission source and is not included here. Prescribed fire is used to remove logging debris, reduce competition in young stands, and minimize catastrophic wildfire hazard (by fuel reduction). Prescribed burning activity in North America tends to occur at times (e.g., March to May and nighttime or early morning) that would be unlikely to produce high tropospheric O_3 levels in most areas. However, wildfires in western North America often occur during hot, dry conditions conducive to high O_3 levels. For example, Cheng et al. (1998) estimated that a forest wildfire 300 km from Edmonton (Canada) significantly enhanced NO_2 and ozone levels in both rural and urban areas.

Biomass burning emissions are estimated as a function of an emission factor, the area burned, the organic matter density, the fraction of above ground biomass to total, and the combustion efficiency of the above ground biomass (Taylor and Zimmerman, 1991). Radke et al. (1991) note that the emission factors from various regions, fuel, and fire types are remarkably consistent. However, there are considerable differences between the initial flaming stage, with high ratios of oxidized species such as CO_2 and NO_x, and the longer smoldering stage, when more reduced compounds (CH_4 and other VOC) and fine particulate matter are emitted. Emission factors

for CO_2 are typically 450 g-C kg^{-1}, CO is approximately 45 g-C kg^{-1}, NO_x about 0.2–10 g kg^{-1}, while CH_4 and total NMVOC are each estimated to be roughly 4.5 g-C kg^{-1}. The predominant NMVOC (Radke et al., 1991), include ethane, propane, propene, and acetylene. Fuel loads tend to vary between 1 and 200 metric tons per hectare with fuel consumption efficiency varying from as low as 20 to as high as 80%.

The sporadic nature and large interannual variability of biomass burning, especially for wildfires, complicate emission estimation. North American biomass burning is primarily in coniferous and chaparral vegetation types and the area burned varies from roughly 30 to 100 million hectares per year. Wildfires are largely confined to western Canada and the US, with some in seasonally dry areas of Mexico. Prescribed fire is an important forest management activity in the southeastern ($\sim$ 2,000,000 ha burned yr^{-1}) and northwestern US ($\sim$ 150,000 ha burned yr^{-1}), and in parts of Canada ($\sim$ 200,000 ha burned yr^{-1}). Estimation of the area burned requires use of historical extent data (e.g., Vose et al., 1997), or by using fire return frequency (number of years between fires) for susceptible biomes.

We have estimated annual North American biomass burning emissions using estimates for prescribed and wildfires respectively of 2×10^6 and 4×10^6 ha yr^{-1} burned, fuel loads of 50 and 125 MT ha^{-1}, and fuel consumption of 30 and 20% (Sandberg, 1988; Stocks, 1991; Vose et al., 1997). Sandberg (1988) noted that 1% of US commercial forests are prescription burned annually, while Seiler and Crutzen (1980) estimated that approximately 0.1% of boreal coniferous forests were consumed in wildfires. We assume that total NMVOC is typically about 30% C_2–C_4 alkenes, 40% C_2–C_4 alkanes, and 10% acetylene. Emissions are estimated for a 180-day burning season from April through September.

2.4. Lightning

Globally, lightning strikes occur about 100 times per second (Borucki and Chameides, 1984). Each lightning strike is characterized by a highly ionized and high temperature channel, in which molecular nitrogen is dissociated and reacts with oxygen to form NO. While lightning is often considered to be a direct O_3 source, Sisterson and Liaw (1990) note that almost all O_3 produced by lightning will be titrated by NO to form NO_2. Temperate regions of North America, which tend to be NO_x-limited for ozone production during the warmer months, have a relatively high frequency of lightning. Lightning NO could be a significant precursor to tropospheric ozone production in these regions but investigations with photochemical grid models and ambient measurements are needed to determine if this is the case.

We use the estimates of Price et al. (1997) for lightning NO production in regions outside of the United States.

Estimates for the United States are based on cloud-to-ground (CG) observations from the National Lightning Detection Network (NLDN) and methods similar to those used by Biazar and McNider (1995). Their approach has been modified with the following assumptions: (1) approximately 15 million flashes per year are observed by the NLDN, and the NLDN has a detection efficiency of about 70% (Orville, 1994), (2) each CG strike yields 1100 mol of NO (Price et al., 1997), (3) cloud-to-cloud (CC) strikes are 2.7 times more frequent than CG strikes (Price and Rind, 1993), (4) CC strikes are 10 times less energetic than CG strikes, and therefore yield 10 times less NO per strike (Price et al., 1997).

2.5. Geogenic

Geogenic sources of ethane, propane and other NMVOC include volcanism and seepage from underground reservoirs of natural gas. Volcanoes are a source of a large number of NMVOC but at very low rates (Isidorov, 1990). We do not consider the emission of NMVOC that occurs during the production and distribution of natural gas since it is an anthropogenic source. However, natural gas can migrate through soils and enter the atmosphere in the absence of human activities. Lamb et al. (1987a) estimate that the flux of NMVOC from natural seepage ranges from 0.06 to 2.6 $\mu g\ m^{-2}\ h^{-1}$. From this estimate, we conclude that natural emissions from geogenic sources in North America are very low and do not play a significant role in tropospheric photochemistry.

3. Emission estimates

3.1. Annual North American totals

The annual North American emission rates shown in Table 6 were estimated using the procedures described in

Section 2. These estimates include Central America, Greenland and the Caribbean but 93–99% of the total is from the United States, Canada and Mexico. Soils and lightning each contribute just under half of the total annual NO emission of about 2 Tg N. Biomass burning contributes the remaining 15%. Post-burn soil NO_x fluxes are not included in these estimates. About 60% of the total CO flux of about 10 Tg C is estimated to be from biomass burning and the remaining 40% from vegetation. Prescribed burns are predicted to contribute 83% of the total biomass burning source with the remainder associated with wildfires.

About 98% of the estimated total natural NMVOC emission of 84 Tg C is from vegetation. Vegetation dominates the emission of each of the major NMVOC categories (terpenoid, other reactive, and less reactive) although the emission of a few NMVOC (e.g., ethane and propane) is primarily from soils and biomass burning. The predicted contributions of individual NMVOC to the total flux are shown in Table 5. Isoprene and methanol contribute 35 and 12%, respectively, and five other compounds (MBO, α-pinene, β-pinene, hexenol and hexenyl acetate) each comprise between 3 and 5% of the total predicted flux. The remaining 29 NMVOC each comprise between 0.3 and 2% of the total flux and together contribute about 25% of the total. The total terpenoid (e.g. isoprene, MBO, α-pinene, β-pinene) emission is about 50 Tg, which is about 60% of the total.

3.2. Regional, diurnal and seasonal distributions

There are large regional and seasonal variations in natural emission rates, particularly on small scales: e.g., a diurnal time scale or a spatial scale of a few km^2. Accurate prediction of these variations is not needed for long-lived compounds but may be necessary for short-lived compounds. Isoprene, for example, typically has a lifetime of a few hours or less and observed ambient

Table 6
Annual above canopy fluxes of NO (Tg-N), NMVOC (Tg-C) and CO (Tg-C) from natural sources in North America. Terpenoid NMVOC include hemiterpenes (isoprene and MBO), monoterpenes (e.g. α-pinene), and sesquiterpenes. Other reactive NMVOC are primarily ethene, propene, hexenol, hexenyl-acetate, hexenal, acetaldehyde and formaldehyde. Other NMVOC are primarily methanol and acetone

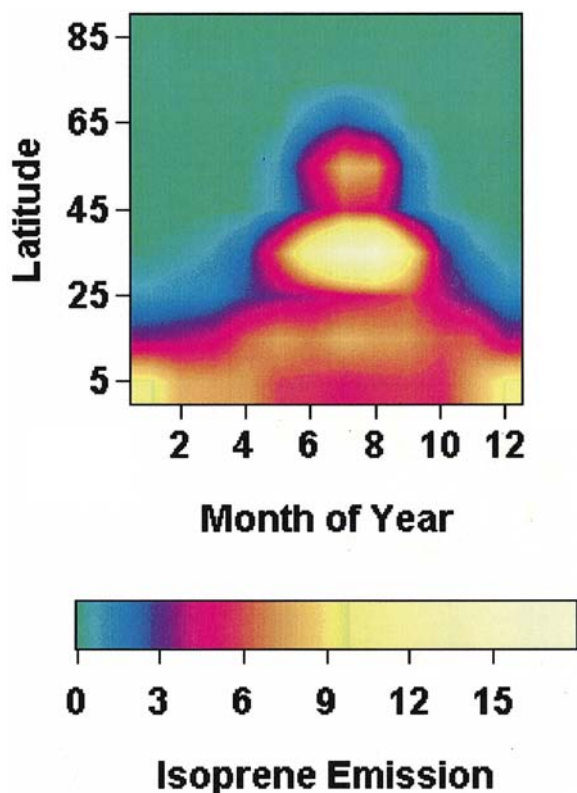| Compounds	Vegetation	Soils	Lightning	Biomass Burning	Total
NO	0	0.9	0.9	0.3	2.1
CO	4	0.0	0	6	10
Total NMVOC	82.2	1.1	0	0.6	83.9
Isoprene	29.3	0	0	0	29.3
MBO	3.2	0	0	0	3.2
Monoterpenes	17.9	0	0	0	17.9
Other reactive NMVOC	15.9	0.2	0	0.2	16.3
Other NMVOC	15.9	0.9	0	0.4	17.2

Fig. 3. Monthly variations in latitudinal distribution (averaged over 3°) of daily isoprene emission rate (mg C m^{-2} d^{-1}) averaged over all of North America.

concentrations can change by more than a factor of three within a few hours (Guenther et al., 1996a).

Biogenic NMVOC emissions increase with temperature and foliar density and, in some cases, with light intensity. As a result, emissions are much higher in summer and at lower latitudes due to higher temperatures, PPFD and, in many cases, biological productivity. As an example, Fig. 3 illustrates the large seasonal and latitudinal changes in predicted isoprene flux. Differences in landcover also result in spatial variations in NMVOC rates across North America. July daily isoprene emission rates, shown in Fig. 4, range from less than 1 to over 100 mg C m^{-2} d^{-1}. Plant species with non-zero isoprene emission factors comprise 10–50% of most North American woodlands but are less than 10% in most grassland and agricultural landscapes. Plants with high MBO emission factors are primarily limited to western North American conifer forests resulting in a much more limited area of high MBO emission.

The contributions of different regions of North America to the total NMVOC flux are shown in Table 7. The contiguous United States is estimated to emit about half the total NMVOC flux. Most of the remainder is associated with emissions from Canada (23%) and Mexico (17%). There are regional differences in the relative contribution of different compounds. For example, MBO makes a higher contribution to total NMVOC emissions in the contiguous U.S. while the contribution of monoterpenes is higher in Alaska and Canada.

Both soil and lightning production of NO vary considerably with season, the majority being produced in summer months for most of North America. Areas with intensive agriculture, such as the Midwestern US, are estimated to have the highest fluxes of soil NO. About half of the estimated North American NO emission is from the contiguous United States. Predicted emissions from Mexico and Canada are 31% and 13%, respectively.

3.3. Model comparisons

Predictions of isoprene emissions for locations in the southeastern and northwestern United States, estimated by three sets of modeling procedures, are shown in Table 8. The modeling procedures are referred to here as B1, B2, and B3. B1 and B2 are similar to the procedures used for BEIS (Pierce and Waldruff, 1991) and BEIS2 (Geron et al., 1994; Pierce et al., 1998), respectively, while B3 uses the procedures described in Section 2. All calculations were made using a flexible modeling framework, called GLOBEIS (GLObal Biogenic Emissions and Interactions System), which allows us to substitute individual model components and can easily be used to calculate emissions for various grids and timescales. B1, B2 and B3 predictions of NMVOC emission rates for a specific time, locale and compound can vary by more than a factor of 5, but the total annual U.S. flux is within 15% for all three models. The B3 and B2 annual average U.S. estimates are similar but there are significant differences for specific locations. Both B3 and B2 tend to be higher than B1 for isoprene and lower for monoterpenes and other NMVOC. The maximum predicted emission rates follow the same patterns. The emission activity factors predicted by the three models differ by as much as a factor of 2 for isoprene but are within 25% for other NMVOC in most locations and seasons. The total foliar densities predicted by the three models are within 35% for most regions and within 20% in many cases. In general, the largest contribution to differences in the emissions predicted by the three models is associated with the different landscape average emission capacities, which can vary by more than a factor of 5. For most landscapes, the differences in species compositions or landcover estimates contribute about 10–30% of the difference in predicted flux, with the remainder due to differences in species or landcover emission capacities. There are, however, regions where over 80% of the difference is due to the species or landcover estimates.
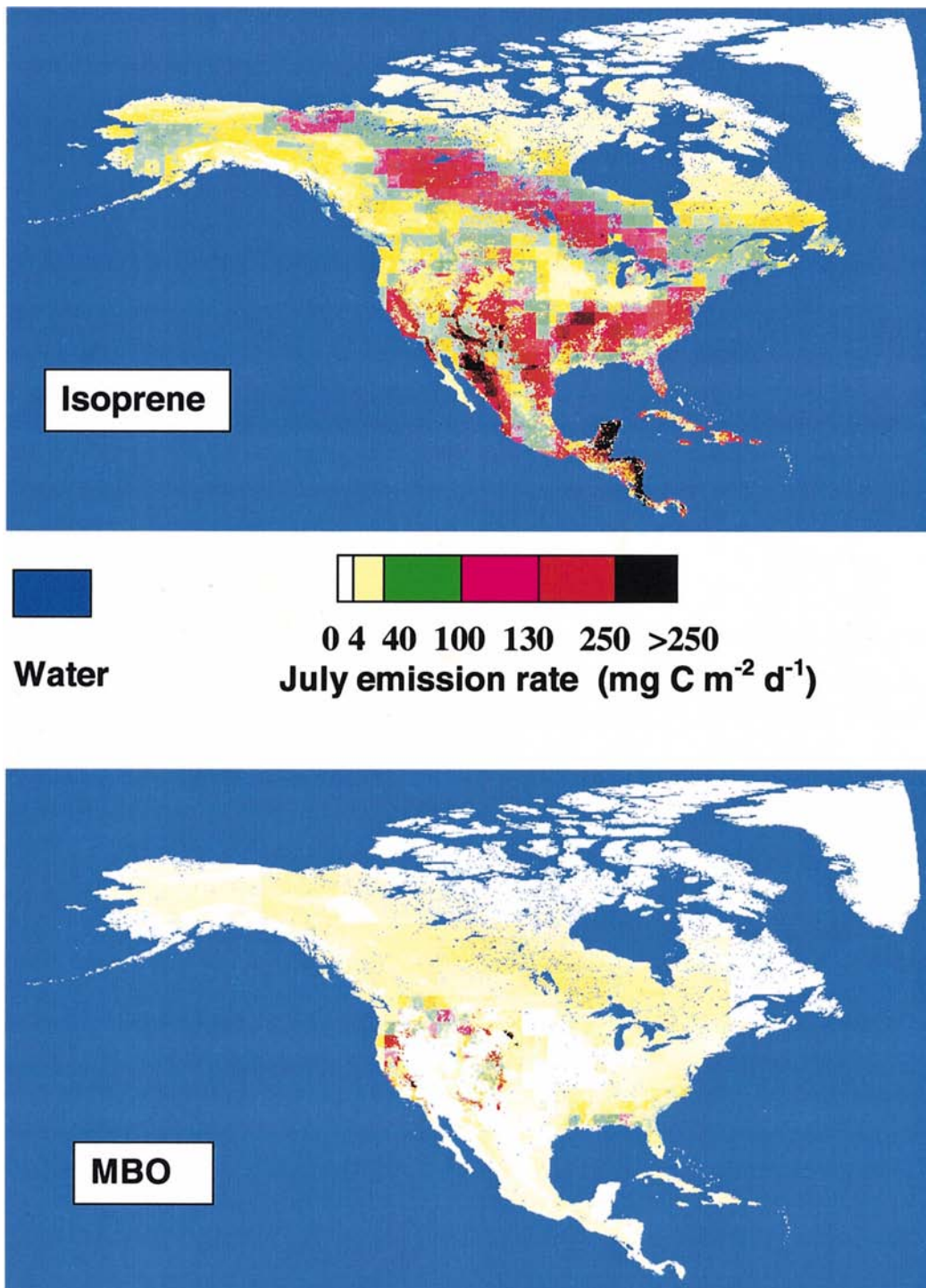
Fig. 4. Spatial distribution of North American July average isoprene and MBO emissions.

Table 7
Relative land area and contributions to total North American natural emissions

	Contiguous US	Alaska	Canada	Mexico	Other
Land Area					
	36.7%	6.7%	44.6%	9.1%	2.9%
Compounds					
NO	49%	2%	31%	13%	4%
CO	50%	3%	26%	14%	6%
Total NMVOC	51%	2%	23%	17%	7%
Isoprene	53%	1%	17%	24%	5%
MBO	89%	< 1%	6%	4%	< 1%
Monoterpenes	42%	3%	40%	11%	4%

The reaction rates and product yields of different biogenic NMVOC vary substantially (Fehsenfeld et al., 1992). Earlier emission models did not speciate individual monoterpenes or non-terpenoid VOC. Most photochemistry models cannot fully take advantage of the improved speciation shown in Table 5, since they do not include specific reactions schemes for each of these compounds, but the relative contribution to each of the chemical categories used can be estimated. For example, Table 9 contains predicted contributions of monoterpenes and non-terpenoid compounds to each category of the carbon bond IV (CBIV) scheme, which is a chemical reaction mechanism that is frequently used in regulatory oxidant modeling, e.g. Pierce et al. (1998). The improved speciation results in significant differences in the contributions to a number of the CBIV categories.

Logan (1983) modeled global soil NO emissions and reported a range of 4–16 Tg N per year. Other global estimates fall within this range, including estimates of 6 Tg N (Yienger and Levy, 1995), 10 Tg N (Potter et al., 1996), and 13 Tg N (Davidson and Kingerlee, 1997). These global model estimates for North America are all within a factor of 2 of our estimates in Table 6. Our estimate of annual soil NO emissions from the contiguous US (0.5 Tg N) is within the range (0.4 to 0.7 Tg N) of previous estimates (Logan, 1983; Potter et al., 1996). Thornton et al. (1997) used an independent emission factor database to model soil NO emissions and their results for the eastern US are within a factor of 2 of our estimates for this region. The reasonably good agreement of these models does not mean that uncertainties are low since these models are generally based on similar assumptions.

Annual global estimates of lightning NO production include 2–20 Tg N (Logan, 1983), 3–5 Tg N (Levy et al., 1996) and 12 Tg N (Price et al., 1997). Of the total North American estimate of 0.9 Tg N of lightning NO (Table 6), 0.3 Tg N is formed over the US, based on NLDN lightning observations. This estimate is within 30% of the values for the US predicted by the global models of Logan (1983) and Price et al. (1997).

4. Uncertainties and research priorities

An uncertainty factor of about three is often associated with estimates of biogenic NMVOC emission rates (e.g., NRC, 1991) but these are not based on a quantitative evaluation. While the uncertainty associated with specific

Table 8
Comparison of emission estimates for two US counties using modelling procedures B1, B2 and B3

		Burke County, GA			King County, WA		
		B1	B2	B3	B1	B2	B3
Annual emission rate (g-C m^{-2} yr^{-1})	Isoprene	2.46	4.57	5.43	0.37	0.55	0.42
	Total monoterpenes	0.57	0.68	0.71	1.08	0.48	0.65
	Non-terpenoid NMVOC	1.58	0.66	2.11	0.77	0.61	1.61
	Total NMVOC	4.61	5.91	5.43	2.22	1.64	2.48
Maximum emission rate (mg-C m^{-2} h^{-1})	Isoprene	2.23	6.39	7.45	0.13	1.28	0.26
	Total monoterpenes	0.21	0.40	0.56	0.52	0.44	0.61
	Non-terpenoid NMVOC	0.61	0.39	1.27	0.38	0.56	1.45
	Total NMVOC	3.04	4.57	9.28	1.03	1.60	2.32
Maximum hourly emission activity	Isoprene	1.38	1.20	0.91	0.21	0.38	0.19
	Total monoterpenes	1.09	1.13	1.13	0.58	0.50	0.50
	Non-terpenoid NMVOC	1.10	1.13	1.09	0.56	0.50	0.41
Emission capacity (µg-C g^{-1} h^{-1})	Isoprene	3.40	13.5	17.0	1.09	5.49	0.46
	Total monoterpenes	0.40	0.89	0.82	1.62	1.45	0.81
	Non-terpenoid NMVOC	1.15	0.87	2.00	1.23	1.85	2.00
Escape efficiency		1.0	1.0	0.95	1.0	1.0	0.95
Foliar density (g m^{-2})		476	394	507	555	610	733

Table 9
Comparison of factors used by the three models (B1, B2 and B3) described in the text to convert monoterpenes or non-terpenoid VOC into the categories used by the CBIV model

CBIV category	Total monoterpenes		Total non-terpenoids	
	B1,B2 (mol kg^{-1})	B3 (mol kg^{-1})	B1,B2 (mol kg − 1)	B3 (mol kg^{-1})
OLE	3.7	7	3.4	6.4
PAR	44	53	57	19.5
XYL	0	0.33	0	0
FORM	0	0	0	4.5
ALD2	11	6.2	0	2.1
ETH	0	0	0	2.2
MEOH	0	0	0	30
ETOH	0	0	0	2.2
NR	0	0.31	3.4	3.8

model procedures can be evaluated for particular circumstances (e.g., Lamb et al., 1987a; Guenther et al., 1993) it is extremely difficult to assign a valid uncertainty level to biogenic emission estimates due to the limited data. A factor of three is probably a reasonable estimate of the uncertainty associated with annual total NMVOC estimates for the contiguous US but predictions for specific times, locales and compounds can be much more uncertain.

Although we calculate emission estimates for approximately 40 different compounds, this does not imply that we have a good understanding of the emissions of all of these compounds. In many cases, there is very little information about the magnitude of the emission or the controls over the flux of a compound, and the model defaults to a crude estimate that may be extremely uncertain but will hopefully stimulate future research. Our current understanding of those factors responsible for the largest uncertainties are discussed below.

4.1. Driving variables

4.1.1. Environmental conditions

The above-canopy environmental conditions used to estimate biogenic emissions include temperature, direct and diffuse total solar radiation and PPFD, relative humidity, and wind speed. Relative humidity, wind speed, ambient temperature, direct and diffuse PPFD are used to determine leaf temperature, which has a strong influence on the biogenic NMVOC emissions. Emission predictions that are not based on reasonable estimates of these driving variables can have large errors (> 50%). They can be accurately measured at specific locations but regional estimates must rely on networks that report data that are representative of the region but may deviate significantly from conditions at a specific locale. These

errors probably have a small impact on seasonal and annual estimates but could be important for investigations of specific scenarios. Benjamin et al. (1997) found that the elevation gradients in the California south coast basin result in ambient temperature differences of over 20°C within this region. Solar radiation fluxes can also vary considerably on this spatial scale due to the presence of clouds. Either of these factors could result in a factor of five or more error in the isoprene emission predicted for a specific hour and location. Regional and global meteorological models that synthesize available surface and satellite data are generally the best source of estimates of above-canopy environmental conditions.

The leaves within a canopy and soils beneath the canopy can have substantially modified environmental conditions. For example, leaf temperatures can exceed air temperature by 2–8°C in the upper canopy and can be as much as 2°C below ambient in the lower canopy (Geron et al., 1997). Lamb et al. (1996) compared simple and complex canopy environment models and concluded that a simple model is sufficient for modeling regional biogenic NMVOC emissions, but that the use of an energy balance algorithm for estimating leaf temperature is an important component.

4.1.2. Landcover

Biogenic NMVOC emission models require accurate estimates of plant leaf biomass and species composition. It is not clear whether it is preferable to express biogenic NMVOC emission capacities per unit dry weight foliar mass or per unit leaf area. One deciding factor should be whether future satellite-derived foliage distribution databases will contain foliar mass or leaf area data. Although past studies have focused on the use of optical techniques to derive leaf area, these data are limited since the optical methods saturate at high LAI. Other

methods, such as lidar and radar, can penetrate the canopy and provide canopy height and vertical distributions of biomass (e.g., Lefsky et al., 1999). However, additional development is needed in order to provide foliar rather than total biomass.

Remote-sensing measurements can also be used to characterize landcover and species distributions and seasonal variations in foliage (e.g., Sellers et al., 1994), and to identify key phenological stages (e.g., Duchemin et al., 1999) for use in characterizing emission activity patterns. However, these satellite databases need to be calibrated using ground measurements. Detailed vegetation statistics are available for the United States and Canadian forests but not for all of North America. Suitable landcover data are also lacking in most urban areas. Improved urban landcover characterization requires a significant effort focusing on a specific location (e.g., Benjamin et al., 1997). The potential for high NMVOC from grasses, particularly mown lawns (De Gouw et al., 1999), indicates that urban vegetation surveys, which sometimes include only woody plants, should be expanded.

New satellite sensors are being developed specifically for the purpose of land cover classification. Advancements are likely to result both from new sensors and from new analytical methods that combine data from different spectral domains (e.g. radar, lidar, optical and thermal) and make use of time series. Efforts to apply these tools to biogenic emission modeling, including ground measurements for calibrating these data, may significantly reduce emission rate uncertainties associated with landcover data.

4.1.3. Regional landcover and climate change

Guenther et al. (1999a) investigated isoprene and monoterpene emissions from a southern Texas savanna and concluded that changes in climate and land use can result in significant changes in isoprene emission rates on a time scale of one century. A 2-fold increase in isoprene emissions was predicted for projected future increases in ambient temperature (3–6°C) and a 3-fold increase in isoprene emission was predicted for the encroachment of woody vegetation during the past century. A similar magnitude of change is expected in other regions. For example, we expect decreasing MBO emissions with reduced abundance of longleaf pine in the southeastern US and increased isoprene and decreased monoterpenes as aspen have replaced conifers in the Great Lakes region of North America.

Land-use practices in agricultural and urban landscapes can result in significant changes in emissions on time scales of a few years to a decade. For example, an agricultural landscape could alternatively be planted with wheat (low isoprene and monoterpene emissions), sunflowers (low isoprene and high monoterpene emissions), or a short-rotation (< 8 yr) poplar plantation

(high isoprene and low monoterpene emissions). Some urban areas may consider ranking trees by their biogenic NMVOC emission potential in order to reduce NMVOC emissions by altering urban tree planting strategies (see Corchnoy et al., 1992; Benjamin et al., 1996). Urban landscapes in the central US and Canada often result in increased emissions of isoprene and monoterpenes when trees are planted on native grasslands, particularly in parks and suburban areas. In other areas, urbanization is expected to lower emissions of these compounds as buildings replace native woodlands.

Emissions of NO and oxygenated VOC from North America may also be significantly influenced by changing land-use practices. Increased nitrogen inputs to soils, both from agricultural practices and nitrogen deposition, could impact soil NO emissions. Since emissions of some VOC are influenced by wounding and by the amount of organic material that is drying or decomposing, we expect that grazing, harvesting and lawn mowing could have a significant impact on emissions of these compounds (De Gouw et al., 1999). Increased use of prescribed fire is another potential landuse change that is being considered in many regions in North America in order to mitigate catastrophic wildfires. These landuse practices should be considered in future air quality planning and emission modeling efforts.

4.2. NMVOC

Zimmerman (1979) analyzed vegetation emission samples by GC-FID and reported a large number of different NMVOC that were mostly unidentified but were tentatively labeled as alkanes, alkenes and aromatics. The "alkanes" were typically about 30%, the "alkenes" about 45%, and the "aromatics" about 25% of the total emission. This database has been used to conclude that alkanes and aromatics are a significant component of volatile emissions from plants (e.g., NRC, 1991). Subsequent studies have found that aromatic and alkane compounds appear to be a very minor component of total NMVOC emissions. In addition to the compounds included in Table 5, VOC that have been reported as vegetation emissions include alkanes (C_3 to C_9), alkenes (C_6 to C_9), ketones (pentanone, octanone, methyl heptanone), alcohols (methyl propanol, butanol, octanol), aldehydes (propanal, butanal and butenal), organic acids (pyruvic and propionic acid) and organic sulfur compounds (dimethyl sulfide, dimethyl disulfide, dipropenyldisulfide and methylpropenyldisulfide) (Isidorov et al., 1985; Lamb et al., 1987b; Talbot et al., 1990; Servant et al., 1991; Winer et al., 1992; Harbourne, 1993; Konig et al., 1995; Guenther et al., 1996b; Puxbaum and Konig, 1997). The pathways for biosynthesis of some of these compounds, e.g., pentane (Pattee et al., 1974) and heptane (Savage et al., 1996), have been described, but the processes leading to the emission of many of these

compounds are unknown. Emission inventories of biogenic dimethyl sulfide and dimethyl disulfide (Guenther et al., 1989) have been produced due to their potential role in acid precipitation but the emissions of these compounds are too low (< 10 pg g^{-1} h^{-1} at 30°C) to be significant for tropospheric photochemistry. Although there is no evidence that emissions of any of these other compounds play a significant role in photochemistry, the limited data do not rule out the possibility that some are important, particularly at specific times and locations.

4.2.1. Chloroplast NMVOCs

Chloroplast emissions dominate the global NMVOC flux. Even though only about 30% of all plant species exhibit this type of emission, the emission rates are typically much higher than those of other emission processes. Isoprene is the dominant emission from most North American woodland landscapes, but there have been relatively few investigations of chloroplast emissions of MBO and monoterpenes so they could be more prevalent than is currently predicted.

Our understanding of isoprene emission from plants is not complete but it has improved considerably in the past decade (Fall, 1999). We now know that isoprene is produced in chloroplasts by a unique enzyme, isoprene synthase (Silver and Fall, 1995), and depends on the availability of photosynthetic carbon (Wildermuth and Fall, 1996), but is distinct from photorespiration (Hewitt et al., 1990). Potential roles for isoprene emission from plants have been suggested (e.g., Sharkey and Singsaas, 1995) but there is no clear understanding of why plants emit isoprene.

The light and temperature algorithm of Guenther et al. (1991,1993) can simulate diurnal variations in isoprene emission to within about 15% (Guenther et al., 1996b; Harley et al., 1997) for most plants, probably either because it describes the behavior of isoprene synthase or because it fits light-dependent channeling of recent photosynthate into the precursor of isoprene (Fall and Wildermuth, 1998). Temperature and light conditions that a leaf has been exposed to during the previous hours to days appear to significantly influence emissions but this has not been well characterized. The leaf age and phenology model described in Section 2 probably captures the gross features of seasonal change but further research is needed. Other factors, including water stress, may significantly influence isoprene emission (Sharkey and Loreto, 1993) but it is not yet clear if these factors need to be included in regional models.

Investigations of North American plant species, including those described in Table 1, have produced thousands of isoprene emission rate measurements. Synthesizing the results of these studies and assigning emission capacities is a challenging task due to difficulties in characterizing measurement errors and emission activity levels, which strongly influence the estimated emission capacity. Analytical difficulties and other measurement uncertainties call into question the accuracy of some reported emission enclosure measurements. Equally important is the lack of a suitable characterization of emission activity levels. In some cases, there is no characterization of environmental conditions during the measurement period. More often, emission rate estimates are accompanied by measurements of temperature and PPFD but there is no indication of past environmental conditions (PPFD and leaf temperature) or plant physiological status (e.g., photosynthesis, leaf age).

Guenther et al. (1994) summarized the results of eight emission measurement studies and found that most leaf-level emission capacities for oaks (*Quercus*) fell within the range 70 µg g^{-1} h^{-1} $\pm$ 50%, but there were several studies that reported much lower rates for at least some oak species. If growth environment and leaf age are nearly constant, then leaf-to-leaf variability is about 5% for a single tree (Harley et al., 1997), 10% for different trees of the same clone (Isebrands et al., 1999), and about 25% for different clones of the same genus (Isebrands et al., 1999).

Benjamin et al. (1996,1997) assigned different isoprene emission capacities to a large number of plant species. Some oaks were assigned moderately high isoprene emission capacities, e.g., 59.2 µg g^{-1} h^{-1} for *Q. garryana* and 76.6 µg g^{-1} h^{-1} for *Q. robur*, while other oaks were assigned much lower rates, e.g., 3.4 µg g^{-1} h^{-1} for *Q. lobata* and 8.7 µg g^{-1} h^{-1} for *Q. douglasii*. However, recent measurements have shown that both *Q. lobata* and *Q. douglasii* have emission capacities exceeding 80 µg g^{-1} h^{-1}. While we expect differences in isoprene emission capacities between different species, many data are inadequate for assigning unique values to individual species. Most emission measurements are only a semi-quantitative indicator of emission capacity, either because of measurement errors or insufficient characterization of emission activity, and so should be used primarily to indicate if a plant species has non-negligible isoprene emission. Guenther et al. (1994) assigned non-negligible isoprene emission capacities to 13 of 49 plant (mostly tree) genera. Five genera were assigned a high (70 µg g^{-1} h^{-1}) isoprene emission capacity and a low or moderate (14 or 35 µg g^{-1} h^{-1}) value was assigned to eight genera. Recent measurements indicate that all North American broadleaf isoprene-emitters on the Guenther et al. (1994) list can have isoprene emission capacities that exceed 80 µg g^{-1} h^{-1} (e.g., Harley et al., 1997; Isebrands et al., 1999). Plants with a leaf structure that contains fewer chloroplasts per foliar mass are expected to have a lower capacity for NMVOC emissions from chloroplasts. This may be the case for conifers (with needles) and palms (with fronds), although the reported emission capacity for at least some palms (Cronn and Nutmagul, 1982) exceeds 80 µg g^{-1} h^{-1}. Additional efforts are needed to improve our ability to characterize isoprene emission capacities.

Since relatively few genera dominate most North American woodlands, we have probably identified the plant species that make the largest contributions to the total North American isoprene flux. Although no emission measurement studies have been conducted in Mexico, the dominant plant genera in some areas, including Mexico City, have been investigated in the United States. There are few emission measurements reported for non-woody plants even though some have a high biomass density and could be important sources of isoprene in some landscapes (e.g., sphagnum moss). Few studies have investigated emissions from subtropical North American landscapes but the limited data suggest that both subtropical savannas (Guenther et al., 1999a) and forests (Lerdau and Keller, 1997) have substantial isoprene emission rates.

Other compounds that appear to be produced inside chloroplasts and in a light-dependent fashion include MBO and some monoterpenes. MBO has only recently been identified as a locally important tropospheric constituent (Goldan et al., 1993) and there have been few investigations to date. Significant MBO emissions have been observed only from certain pine species (Harley et al., 1998). Light dependent monoterpenes have been observed for some North American plants, including *Acer saccharinum* (Keiser, 1997) as well as some exotics planted in North America (Kesselmeier et al., 1996). The light and temperature dependence of MBO and these monoterpenes are similar to those of isoprene and the use of the same emission activity equations is a reasonable approximation (Kesselmeier et al., 1996; Ciccioli et al., 1997; Harley et al., 1998). Other evidence of similarities between these compounds includes the observation by Loreto et al. (1996) that the ^{13}C labeling pattern of isoprene and light-dependent α-pinene emissions is similar, indicating that they share a common carbon source. Further study is needed, however, to determine if the emissions of these compounds respond in the same way as isoprene to other environmental conditions.

The above-canopy isoprene fluxes summarized in Tables 2 and 3 can be used to evaluate our ability to predict isoprene fluxes. In most cases, the model described in Section 2 can predict the isoprene fluxes at these sites within a factor of 2 and in some cases within 25%. These studies also demonstrate that BEIS2 (Pierce et al., 1998) is more accurate than BEIS (Pierce and Waldruff, 1991). Unfortunately, most of these studies are limited to midday summer fluxes.

Differences between modeled and observed emissions may be due to errors in emission capacities, emission activity, foliar density, escape efficiency, or errors in the observations. Therefore, it is difficult to assign errors to individual model components. The observed diurnal and seasonal patterns, however, can be evaluated independently of the absolute magnitude of emissions. These evaluations suggest that emission activity algorithms capture the major features of diurnal and seasonal isoprene emission variations but there is considerable room for improvement (Geron et al., 1997; Guenther and Hills, 1998; Goldstein et al., 1998). For example, observations from temperate forests (Monson et al., 1994; Geron et al., 1997) indicate that the onset and peak isoprene emission occur at 650 and 1050 heating degree days (the cumulative daily mean temperature above $0°C$ since the last frost), respectively.

4.2.2. Defense: NMVOC from specialized tissues

Many plants produce and store terpenoid compounds within specialized tissues that act as a physical barrier to insects and pathogens and/or as a feeding deterrent if consumed. These compounds are primarily monoterpenes (C_{10}) and diterpenoids (C_{20}) with a large number, but small quantity, of sesquiterpenes (C_{15}). Recent studies have characterized monoterpene metabolism (McGarvey and Croteau, 1995) and some of the genetic, biochemical and ecological controls (Langenheim, 1994) that determine monoterpene levels and composition in plants.

Although there are thousands of terpenoids, the total emission from stored terpenoid pools is dominated by contributions from the 18 compounds listed in Table 5. It is difficult to characterize the large variability in monoterpene composition within and among plant species, but it is important due to differences in reaction rates, atmospheric oxidation pathways and aerosol yields (Hoffmann et al., 1997).

The temperature dependence of these emissions is described by an exponential increase in emission with increasing temperature, with a rate of increase (about 9% per K) based on a review of monoterpene emission rate measurements by Guenther et al. (1993). The increase with temperature is at least partially related to the vapor pressure of the compound but the increase is greater than expected and other factors are probably involved. Tingey et al. (1991) concluded that the temperature dependence should vary with vegetation species and the monoterpene being emitted. There are also indications that relative humidity (Dement et al., 1975), foliar moisture (Lamb et al., 1985) and precipitation (Helmig et al., 1998) influence the emission of monoterpenes from stored pools, but there are currently no quantitative descriptions of these relationships. Seasonal variations in emissions from stored pools may also be significant (Yokouchi and Ambe, 1984) and could be related to variation in resin cell terpene content (Tingey et al., 1991; Lerdau et al., 1995). Monoterpene production rates may be related to the level of wounding or disturbance experienced by the plant (Lewinsohn et al., 1991) but the contribution of wounding-related emissions from resin ducts and glands, relative to the emission from undamaged tissues, is not well characterized.

Fluxes of only two monoterpenes, α- and β-pinene, are reported in the studies summarized in Tables 2 and 3. Most of these studies have reported above-canopy flux measurements of summer, midday α- and β-pinene emissions that are within a factor of 2 of model predictions. The relatively small research effort directed at monoterpene emissions should be increased given their potential importance for aerosol production.

4.2.3. Defense: NMVOCs from unspecialized tissues

A number of VOC produced in unspecialized plant tissues also play a role in defending plants against disease and herbivory. For example, emissions of ethane, ethanol, methyl salicylate, octanone and methoxyphenol are associated with resistance of plants to herbivore infestations (Harbourne, 1993). These compounds can act by repelling pests or attracting predators. The hexenal family compounds (2-hexenal, 3-hexenol, 3-hexenal, 3-hexenyl acetate, hexanal, and hexanol) may have antibiotic properties (Croft et al., 1993) and can be emitted by damaged plants at very high rates (Arey et al., 1991b; Kirstine et al., 1998). There is a reasonably good understanding of the mechanisms controlling the production of hexenal family compounds which is triggered by membrane damage, typically from mechanical wounding, or the presence of pathogens (reviewed by Hatanaka, 1993).

Emission rates of hexenal family compounds reported by two studies (Arey et al., 1991b; Helmig et al., 1999) are in reasonable agreement. Together, these studies characterized emissions from a wide variety of North American agricultural and tree species under conditions that attempted to minimize wounding. Observed emission rates ranged from below detection limit to a maximum of 1.3 µg-C $g^{-1} h^{-1}$ for 3-hexenol and 3.3 µg-C $g^{-1} h^{-1}$ for 3-hexenyl acetate. Most plants had fairly low emissions resulting in median emission rates of < 0.1–0.2 µg-C $g^{-1} h^{-1}$ for the different compounds. Higher emission rates are associated when wounding occurs as a result of biological or physical stresses, including human activities (Kirstine et al., 1998).

Preliminary estimates suggest that members of the hexenal family of compounds are an important component of the total natural flux of reactive NMVOC from North America. The only reported connection of these emissions with ambient measurements is the observation of Helmig et al. (1998) that hexenyl acetate concentrations in a rural area increased after passage of an intense storm, which presumably caused significant mechanical damage to foliage. Research focusing on emissions of these compounds is needed and should include both mechanistic studies using enclosures and above canopy flux measurements.

4.2.4. Plant growth NMVOC

Ethene is a volatile hormone that controls numerous aspects of plant growth and development, including fruit ripening, seed germination, flowering, and senescence (Abeles et al., 1992). It also has a role in triggering plant defense and internal concentrations can be greatly increased by a variety of stresses. The biochemistry of ethene production is better understood than that of most other NMVOC (Fall, 1999), but most investigations of ethene emission have been directed at understanding its role as a plant hormone and provide little information for numerical emission modeling. Ethene production is widespread in plants and is likely a significant emission from most landscapes (Goldstein et al., 1996). Ethene is a significant biogenic NMVOC and further study is warranted, particularly the potential for increased ethene emissions due to increased ecosystem stress.

4.2.5. NMVOC from cut and drying vegetation

Emissions of monoterpenes and oxygenated NMVOC can increase 100-fold when some plant tissues are damaged. This is due both to increased production and the release of stored compounds (Fall, 1999). The dominant oxygenated NMVOC emissions include both reactive (e.g., acetaldehyde and hexenal family) and less reactive (e.g., methanol, acetone and butanone) compounds (Kirstine et al., 1998). Recent studies with grass and clover indicate that the major NMVOC emissions occur as cut vegetation dries (De Gouw et al., 1999). This may be especially relevant to NMVOC emissions in agricultural areas, particularly where hay is grown. Warneke et al. (1999) report that oxygenated VOC are also emitted in significant quantities when dried foliage is hydrated. Thus, the initial cutting of live vegetation as well as longer-term emissions from drying and dead vegetation may produce significant emissions. Human activities, including crop and timber harvesting, lawn mowing and rangeland management practices, have a significant impact on these emissions and need to be characterized in order to accurately simulate this emission source. More studies are needed to determine the significance of NMVOC emissions from cut and drying vegetation for tropospheric chemistry.

4.2.6. Floral scent NMVOC

Floral scents are composed of a large variety of NMVOC including alkanes, alcohols, esters, aromatics, nitrogen compounds, monoterpenes and sesquiterpenes (Borg-Karlson et al., 1994). Flowers are likely to be the dominant biogenic source of some of these compounds. Arey et al. (1991a,b) found high concentrations (17 µg m^{-3}) of linalool in ambient air, attributable to floral emissions from an orange grove. Although flowers are expected to be a minor component of annual global NMVOC emissions (Guenther, 1999), the observations of Arey et al. (1991a,b) demonstrate that flowering could play a role in photochemical processes in at least some locations at certain times.

4.2.7. Other vegetation NMVOC emissions

At least some portion of the total emission of a number of NMVOC (e.g., methanol, formaldehyde, acetone, propene, butene, formic and acetic acid) appears to be emitted by processes other than those described above. These emissions may simply represent the leakage of plant metabolites. Of these processes, only the biochemical mechanisms for ethanol and acetaldehyde production are reasonably well understood (Fall, 1999). Production of these two compounds by plants is expected under anaerobic conditions such as those experienced by roots in flooded soils, wet crevices of damaged trees (Harbourne, 1993) and by leaves under certain stressed conditions (MacDonald et al., 1989). Production pathways for acetic acid, acetone, methanol, formaldehyde and formic acid in plant cells have been proposed but need to be confirmed (Fall, 1999).

Reported emission rates for acetaldehyde, formaldehyde, acetic and formic acid, acetone, ethanol and butanone from apparently undamaged plant tissues range from less than 0.01 to about $0.5\,\mu g C\,g^{-1}\,h^{-1}$ (Talbot et al., 1990; Servant et al., 1991; MacDonald and Fall, 1993a; Konig et al., 1995; Kesselmeier et al., 1997; Kirstine et al., 1998). Considerably higher emissions, 0.1 to $> 10\,\mu g C\,g^{-1}\,h^{-1}$ have been reported for methanol (MacDonald and Fall, 1993b; Nemecek-Marshall et al., 1995; Kirstine et al., 1998). Temperature influences most of the processes related to the production, transport, and release of biogenic trace gases. Although the mechanisms are not understood, a strong temperature dependence has been reported for emission of acetone (MacDonald and Fall, 1993a), methanol (MacDonald and Fall, 1993b), formaldehyde, acetaldehyde, acetic and formic acid (Kesselmeier et al., 1997). The temperature dependence we use for these compounds is a reasonable default method, but accurate simulation will likely require further investigation. There are indications that some of these compounds are correlated with stomatal conductance (Nemecek-Marshall et al., 1995; Kesselmeier et al., 1997), possibly because these compounds are transported out of the plant through the transpiration stream. These results suggest that a model of stomatal conductance is needed, at least for predicting diurnal variations of these compounds. This can easily be incorporated into our modeling procedure, since stomatal conductance is calculated in order to estimate leaf temperature. Another factor to be considered is that the ambient and cellular concentrations of some of these compounds may be of a similar magnitude and the magnitude and direction of flux may be dependent on ambient concentrations (Servant et al., 1991; Kesselmeier et al., 1997). This may require an emission activity algorithm that includes a compensation point where emission and deposition are in equilibrium.

4.2.8. Non-vegetation NMVOC sources

Biomass burning, geogenic, and soil microbial sources of NMVOC are a minor component of the total natural NMVOC flux. Of these sources, biomass burning and soil emissions of ethane and propane are the most important. There are other sources of NMVOC, including landfills and sewage treatment plants, that we do not include as natural sources but may not be included in anthropogenic inventories. Due to the dominance of vegetation emissions of NMVOC, more accurate estimates of these emissions are generally not a priority for understanding regional photochemical oxidant production but may be important in a few local areas.

4.3. NO

Our model estimates suggest that soil emissions are an important source of NO, at least in some of the agriculturally intensive areas of North America. Agricultural lands tend to have the highest soil NO emissions and should be the focus of efforts to improve estimates. The quantity of NO emitted from these lands appears to be directly related to the amount of nitrogen-based fertilizer applied to the soils and the subsequent processing by soil bacteria (Williams et al., 1992). Other agricultural practices including burning (Levine, 1990) and tilling (Civerolo and Dickerson, 1998) can increase NO emissions by a factor of 5 or more. Soil NO emissions are also sensitive to soil temperature and soil moisture which can be reasonably simulated using relatively simple algorithms (Yienger and Levy, 1995; Williams et al., 1992).

The uncertainties associated with estimates of the canopy escape efficiency factor are even greater than those related to the primary drivers of soil NO emissions. Since NO_2 is deposited much more rapidly than NO, chemical reactions within the canopy influence above-canopy NO_x fluxes (Jacob and Bakwin, 1991) although Gao et al. (1993) predict that the impact is relatively small. Jacob and Bakwin (1991) conclude that the escape efficiency of tropical forest soil NO emissions is higher during the daytime, when canopy ventilation rates are higher, than at night, even though the leaf level deposition rates are higher during the day due to the opening of plant stomata. A better characterization of escape efficiency is an important research priority for improving estimates of above canopy NO fluxes. Since regional photochemical models also include trace gas deposition algorithms (e.g., Wesely, 1989), a careful integration of emission and deposition models is needed so that the deposition accounted for by an escape efficiency is not duplicated.

Several investigators (Hall et al., 1996; Aneja et al., 1997; Thornton et al., 1997) have postulated that soil NO is important to regional ozone formation, but the degree to which these emissions affect North American

oxidant photochemistry has remained largely unquantified. Chameides et al. (1994) performed some simple calculations for "metro-agro" complexes around the world and concluded that soil NO from agricultural activity may enhance seasonal ozone concentrations by 5 ppb. Because soil NO may comprise as much as 10% of the NO_x emissions burden in North America and because these emissions occur in areas that are generally NO_x-limited for ozone formation, more in-depth measurements and rigorous modeling studies are justified.

Despite efforts to estimate lightning NO production from theoretical, laboratory, and direct observational means, considerable uncertainty remains. The close agreement of different models is probably fortuitous and the factor of 3.5 uncertainty suggested by Logan (1983) is a reasonable estimate of the uncertainty in annual emissions. Biomass burning NO emissions have a similar level of uncertainty (Taylor and Zimmerman, 1991).

4.4. CO

The estimates shown in Table 6 predict that vegetation and biomass burning are a small but significant source of CO. Although some soils may be a significant source, others are a net sink (Scharffe et al., 1990) and we assume that the net soil flux for North America is negligible.

The formation and emission of CO on or in live plant foliage is the result of direct photochemical transformation and occurs inside the leaf (Tarr et al., 1995). The factors controlling these emissions are not well known and there are therefore considerable uncertainties in current estimates. Biomass burning emission factors for CO are reasonably well known but there are considerable uncertainties related to the other components of the emission calculation procedures (Taylor and Zimmerman, 1991).

Estimates of annual global CO budgets are constrained somewhat (e.g., Tarr et al., 1995) and North American estimates of CO emission from natural sources have an uncertainty of about a factor of three. Isotopic analysis of CO is beginning to distinguish among individual sources and may soon be able to significantly improve estimates of natural CO emissions.

4.5. Organic particles

Direct natural sources of organic particles include vegetation and biomass burning. Under natural conditions, crystalline-like leaf surface waxes are dislodged by the wind and/or by the rubbing motions of leaves against each other. While these compounds are thought to be a significant source of fine aerosol organic carbon in some regions, there are no quantitative flux estimates (Rogge et al., 1996; Mazurek et al., 1997).

5. Conclusions

5.1. General

- Improved flux measurement techniques and multidisciplinary collaborations have greatly enhanced our ability to develop and evaluate high quality natural emission models.
- Landcover and climate changes in many parts of North America are expected to result in significant changes in natural emissions.
- Longer-term, and lower concentration, regulatory standards for ozone will increase the importance of natural emissions in general and will require a stronger research focus on characterizing natural emissions throughout the day and year.

5.2. NMVOC

- Over 98% of the total annual NMVOC (84 Tg C) emission is from vegetation, primarily foliage, and isoprene is the dominant compound of the 37 NMVOC.
- Natural emissions of alkane and aromatic compounds are very low and are greatly overestimated by some earlier inventories.
- The biochemistry of some NMVOC is well known, e.g., isoprene and ethene, but there is a very limited understanding for many other compounds.
- Model estimates of total NMVOC emissions can differ by more than a factor of 5 for a specific time and location but annual US totals are within a factor of two.
- Sources of NMVOC emission from vegetation include chloroplasts, defense (specialized tissues), defense (unspecialized tissues), growth hormones, floral scents, cut and drying vegetation, and other. The total North American NMVOC flux is dominated by emissions from chloroplasts.
- The influence of mowing, harvesting and grazing practices on NMVOC emissions may be significant and needs to be better understood.
- Our understanding of C_1–C_3 emissions is rudimentary but emissions of these compounds appear to be significant and should be better characterized.
- Canopy shading and leaf energy balance models are necessary for accurate biogenic NMVOC emission estimates, but relatively simple models are recommended since there is no clear advantage to greater complexity.
- Emission models can predict midday, summer isoprene fluxes from a variety of landscapes but few attempts have been made to validate other biogenic fluxes. Estimated uncertainties range from about 50% for summer isoprene emission from some landscapes to about a factor of 10 for some compounds and landscapes.

5.3. NO and CO

- Soils and lightning each contribute about half of the annual natural NO flux of 2.1 Tg-N from North America. Biomass burning and vegetation are each responsible for about half of the natural CO emissions from North America.
- The degree to which natural NO and CO emissions affect North American oxidants is largely unquantified and more rigorous modeling studies are needed. Soil NO emissions and canopy escape efficiency need to be better understood.

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