### Title

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### Journal

Atmospheric Environment, 34(11)

### ISSN

1352-2310

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### Publication Date

2000

### DOI

10.1016/s1352-2310(99)00364-7

PERGAMON

Atmospheric Environment 34 (2000) 1761–1781

ATMOSPHERIC
ENVIRONMENT

www.elsevier.com/locate/atmosenv

# A review and synthesis of monoterpene speciation from forests in the United States

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Received 20 April 1999; accepted 4 August 1999

## Abstract

The monoterpene composition (emission and tissue internal concentration) of major forest tree species in the United States is discussed. Of the 14 most commonly occurring compounds ($\alpha$-pinene, $\beta$-pinene, $\Delta^3$-carene, *d*-limonene, camphene, myrcene, $\alpha$-terpinene, $\beta$-phellandrene, sabinene, $\rho$-cymene, ocimene, $\alpha$-thujene, terpinolene, and $\gamma$-terpinene), the first six are usually found to be most abundant. Expected regional variability based on the monoterpene composition fingerprints and corresponding tree species distribution and abundance is examined. In the southeast, $\alpha$-pinene and $\beta$-pinene seem to dominate monoterpene emissions, while in the northern forests emissions are distributed more evenly among the six major compounds. In some parts of western forests, $\beta$-pinene and $\Delta^3$-carene can be more abundant than $\alpha$-pinene. Among the other eight compounds, $\beta$-phellandrene and sabinene occasionally are significant percentages of expected local monoterpene emissions. Ocimene and $\rho$-cymene are estimated to be more common in regions dominated by deciduous broadleaf forests, although total emission rates are generally lower for these forests relative to those dominated by conifers. These percentages are compared with monoterpene composition measured in ambient air at various sites. Estimated monoterpene emission composition based on local forest species composition agrees fairly well with ambient measurements for the six major compounds. The past assumption that $\alpha$-pinene composes approximately 50% of total monoterpene emissions appears reasonable for many areas, except for possibly the northern coniferous forests and some areas in the west dominated by true firs, spruce, and western pines (lodgepole and ponderosa pines). The oxygenated monoterpenes such as camphor, bornyl acetate, and cineole often compose high percentages of the monoterpenes within plant tissues, but are much less abundant in emission samples. Even after adjusting for lower vapor pressures of these compounds, emission rates relative to the hydrocarbon monoterpenes are often lower than would be expected from their internal concentrations. More study is warranted on monoterpene emission rates and composition, especially from the spruces, true firs, hemlocks, cedars, and some deciduous species such as the maples. Non-invasive canopy level and whole ecosystem flux studies are also needed to establish uncertainty estimates for monoterpene emission models. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* $\alpha$-pinene; Conifers; Emission model; Biogenic volatile organic compounds; Essential oil

## 1. Introduction

Much of the recent work on emissions of biogenic volatile organic compounds (BVOCs) has focused on isoprene. However, in regions dominated by coniferous or non-isoprene emitting deciduous tree species, monoterpenes may dominate BVOC emissions. Current BVOC emission and air quality models aggregate all

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PII: S1352-2310(99)00364-7

monoterpene ($C_{10}H_{16}$) compounds, assuming that their fate in the atmosphere is similar. However, studies have shown that individual monoterpene compounds may react quite differently (Hoffmann et al., 1997; Atkinson et al., 1992; Atkinson, 1990; Yokouchi and Ambe, 1985). Reaction rates with $O_3$, OH, and $NO_3$ radicals can vary by an order of magnitude between these compounds. Aerosol yields can likewise vary significantly. Monoterpenes with exocyclic double bonds, such as $\beta$-pinene and sabinene, tend to form more aerosols following ozonolysis compared to those with endocyclic double bonds, such as $\alpha$-pinene and $\Delta^3$-carene (Hatakeyama et al., 1989). Those with two double bonds can react to produce even higher aerosol yields, depending on the vapor pressure of the reaction products. Open-chain monoterpenes, such as myrcene, linalool, and ocimene (Hoffmann et al., 1997), tend to produce lower aerosol yields under most circumstances. It was recently concluded that it is not possible to use generalized descriptions of terpene chemistry in models (Hallquist et al., 1999). Aerosol forming potentials of terpenes discussed here could be partially explained by their structural characteristics (Griffin et al., 1999). It was concluded that most biogenic hydrocarbons would have to be accounted for individually when modeling atmospheric aerosol formation.

Here, we examine monoterpene composition (MC) of plant and foliage enclosure emission samples, leaf oil, and extracts from woody and cortical tissues previously reported to identify patterns among dominant tree species and geographic regions in the USA. We suggest that these data be used to help speciate the monoterpene emissions estimated from future versions of Biogenic Emissions Inventory Systems (for example BEIS2, Geron et al., 1994) to support future North American tropospheric ozone and aerosol modeling efforts.

## 2. Background

Some 5000 structurally determined terpenes have been identified including monoterpenes ($C_{10}$), sesquiterpenes ($C_{15}$), diterpenes ($C_{20}$), and higher molecular weight species. However, it is the monoterpenes and possibly some sesquiterpenes that have sufficient vapor pressure and are released by plants in sufficient quantities to play a significant role in oxidant photochemistry. Our discussions will henceforth focus on monoterpenes except where noted. The monoterpenes were first isolated from plants by extraction and distillation procedures. Individual monoterpenes are usually identified in these essential oils by the traditional techniques of physical constants (boiling point, melting point, index of refraction, optical activity, density), elemental analysis, solubility, chemical reaction tests and spectral data [mass spectroscopy, infrared absorption, and nuclear magnetic resonance (NMR) spectroscopy] of the isolated (pure) compound. Today, most essential oils extracted from plants are analyzed by combined gas chromatography-mass spectrometry (GC-MS) and sometimes gas chromatography-Fourier transform infrared (IR) spectroscopy. The combined information of gas chromatographic retention time, mass spectra, and IR absorption spectra of compounds for which reference spectra or standards are available is usually sufficient to identify compounds with a reasonable degree of confidence. When this information does not match known structures, compounds may be identified only by their empirical formula, e.g., $C_{10}H_{16}$.

Techniques for identifying vapor-phase concentrations of volatile organics are increasingly less rigorous and therefore more susceptible to misidentification. The techniques of NMR and IR spectroscopy, determination of physical constants, and chemical derivatization are not generally applicable to vapor-phase concentrations because of the small quantities available. However, GC-MS can be applied to detection of vapor analytes if a preconcentration step is used. Usually this involves stripping the volatile organics from the air matrix by cryo-focusing or adsorption onto a solid substrate followed by the application of heat to volatilize or release the concentrate from the trapping media. Some of the monoterpenes are easily isomerized in stainless-steel cans, excessively heated metal transfer lines, and during storage or thermal desorption from adsorbent sampling traps. Therefore measured ratios of monoterpene emissions may be altered from their actual emission ratio (Larsen et al., 1997). For instance, $\alpha$-pinene and $\beta$-pinene can be isomerized during analysis, forming camphene and possibly other monoterpenes in the process. The potential impact of these problems on the emission rates cited in this review is difficult to evaluate. Sufficient experimental detail is usually not reported to determine whether such problems were evaluated.

However, in general, studies where sample-to-analysis times were short and whole air sampling techniques were employed (e.g., direct injection from cans, bags, or syringes onto columns or cryotraps), these problems are likely to be minimal compared with studies where samples were stored for days before analysis. We advocate standard additions to air samples under realistic measurement conditions to quantify accuracy.

Due to natural variability and analytical difficulties, monoterpene emission rates and composition are subject to considerable uncertainty. For instance, in one study 20 monoterpenes were identified using vegetation enclosures, but only eight were found in ambient air in the proximity of similar vegetation (Khalil and Rasmussen, 1992). Rough handling of vegetation during enclosure sampling has been suspected to result in artificially high emission rates (Juuti et al., 1990; Guenther et al., 1994). Summertime *Pinus taeda* monoterpene emissions were found to be 5–20 times higher following "grabbing" of foliage compared to normal experiments when rough handling was minimized (Kim et al., 1995). However, there was no effect of rough handling in the late fall. It was concluded that a film of monoterpene compounds was present on the outer surface of the foliage during summer months, but not at other times of the year. Sampling of monoterpenes from *Picea marianna* seed cones in situ versus ex situ was found to drastically affect both the emission rate as well as the monoterpene composition (Turgeon et al., 1998). Temporal and spatial factors can affect MC of a given tree species. Emissions and needle oil concentrations of $\Delta^3$-carene were lower relative to other monoterpenes in the summer but were substantially higher in the spring and fall (Janson, 1993; Lerdau et al., 1995). It was concluded that the high springtime emissions of $\Delta^3$-carene from *Pinus ponderosa* were due to the MC of the oleoresin in that species (Flyckt, 1979). *Picea sitchensis* (Bong.) basal emission rate (in μg carbon $g^{-1}$ $h^{-1}$ at leaf temperature = 30°C, referred to as emission factor or EF) and MC were found to change somewhat with the season (Street et al., 1996). Conversely, the oil composition of *Picea glauca* leaves and twigs remained nearly constant from summer through winter, while the oil composition of buds changed significantly during fall and winter (von Rudloff, 1972). However, it seems more typical that foliage MC remains fairly stable during most of the growing season (Hall and Langenheim, 1986; Maarse and Kepner, 1970; Winer et al., 1992; Street et al., 1997b; Bertin et al., 1997). This is confirmed by measurements in ambient air (Roberts et al., 1985,1983). Diurnal variation has not been examined extensively, but was found to be negligible in *Juniperus scopulorum* (Adams and Hagerman, 1976). Likewise, little diurnal variation was found in the MC of ambient (near canopy) air near forests in Colorado (Roberts et al., 1985), where nighttime versus daytime relative abundance of β-pinene, α-pinene, $\Delta^3$-carene, camphene, and *d*-limonene changed by 0–4%, although nighttime total monoterpene concentration was over a factor of 2 greater due to lower dispersion. Greater seasonal and diurnal variability in light-dependent emissions of ocimene, linalool, and 1,8-cineole was found relative to the more temperature-dependent emissions of α-pinene and *d*-limonene, which varied little temporally from *Pinus pinea* (Staudt et al., 1997). Tree age effects have also been found for MC within this species (Adams and Hagerman, 1976) as well as for *Eucalyptus* (Street et al., 1997a) and *Picea sitchensis* (Street et al., 1996). Basal EFs were also found to decrease with tree age in these latter three studies and in *Pinus elliotti* (Kim et al., 1995). An increase in basal EFs and changes in MC of emissions following wetting of foliage have been noted (Janson, 1993; Lamb et al., 1984). Humidity has also been found to increase monoterpene emission rates at the leaf (Guenther et al., 1991) and canopy (Schade et al., 1999) levels.

Regional variability in monoterpene composition within a species can also be important. Indeed, monoterpene contents of cortical resins have been used as "chemotaxonomic fingerprints" in identifying the geographic origin of genotypes of many species (Bridgen et al., 1979; Gerhold and Plank, 1970; Hanover and Furniss, 1966; Lester, 1974; Smith et al., 1988; Tosolski and Hanover, 1971; von Rudloff and Lapp, 1987; von Rudloff, 1977,1966,1967a,b,1961,1962; Hanover, 1974). *Pinus ponderosa* (Mirov, 1961) exhibits variation in MC of oleoresin samples from various geographic locations. Coastal *Pseudotsuga menziesii* samples had greater β-pinene than α-pinene concentrations in leaf oil (Maarse and Kepner, 1970), while the reverse was true for the inland variety of the species in Idaho (Hanover and Furniss, 1966). Needle oil MC was found to be less variable than cortical resin MC (Tosolski and Hanover, 1971), suggesting that growing season foliage emission MC may not vary as much regionally as that of the cortical resins. Geographic variability is typically characterized by shifts in relative amounts of terpenes present, and usually does not appear to be associated with qualitative changes in the types of compounds found in the MC fingerprint for a given species. Exceptions to this are found in limited emission samples from *Tsuga canadensis*, where α-pinene, β-pinene, *d*-limonene, camphene, and α-thujene dominated emissions from an enclosed branch in Wisconsin, USA, while ρ-cymene, camphene, and *d*-limonene were the major components from an enclosed branch in Georgia, USA (Helmig et al., 1999). *Pinus strobus* branch enclosure emission MC in the northeastern US (Lamb et al., 1984) was found to contain mostly myrcene, α-pinene, β-pinene, and lesser amounts of β-phellandrene and camphene, while the same species in Wisconsin (Helmig et al., 1999) emitted much more camphene and α-thujene instead. *Picea sitchensis* in the United Kingdom emits substantial amounts of β-phellandrene (Street et al., 1996), whereas the same species in western North America apparently does not (Evans et al., 1982,1985), although it was found to be a small constituent in a North American leaf oil sample (von Rudloff, 1977). Tissue type (foliage vs. wood, buds, etc.) and position within a tree may also affect MC, although apparently not as much as genetic controls (Flyckt, 1979; Franklin, 1976; Hanover, 1966; Moore and Hanover, 1987; Schindler and Kotzias, 1989; Wilkinson and Hanover, 1992). In these studies, a few monoterpenes, such as β-phellandrene and α-pinene, were found to vary with crown position, while others, such as β-pinene, did not. In *Quercus ilex*, habitat type, branch position, and tree age were suspected to cause changes in basal EFs, but not in MC, which was also constant between trees (Street et al., 1997b; Bertin et al., 1997).

Most of the emphasis on monoterpene composition has focused on coniferous tree species. Essential oils in temperate deciduous hardwood forest species are said to be limited to *Sassafras*, *Liquidambar* (Tattje et al., 1980), and genera in the *Magnoliaceae* family, namely

*Liriodendron* and *Magnolia* (Smith et al., 1988). However, genera in the *Juglandaceae* family (*Juglans* and *Carya*) have abundant surface peltate glands and are classified as high monoterpene emitters (Guenther et al., 1994). Terpene emissions from species such as *Acer rubrum* (Khalil and Rasmussen, 1992; Helmig et al., 1999; Guenther et al., 1996; Lamb et al., 1985; Zimmerman, 1979a), *A. saccharinum* (Lamb et al., 1985), and *Quercus ilex* (Street et al., 1997b; Bertin et al., 1997), which have no resin glands or canals, suggest that terpenes are synthesized in and emitted from leaf tissue rapidly instead of being stored. Ocimene composed 96% of the monoterpene emission from the bottomland hardwoods willow (*Salix* spp. ) and hackberry (*Celtis occidentalis*) (Khalil and Rasmussen, 1992). It was also the dominant component in the essential oil of *Liriodendron tulipifera* (Smith et al., 1988). Although EFs for these tree species are currently low (0.2 μg C $g^{-1}$ $h^{-1}$ compared to 3.0 μg C $g^{-1}$ $h^{-1}$ for high monoterpene emitters, Guenther et al., 1994), these estimates are based on limited data focusing on relatively few compounds. Actual rates may be higher for some of these tree species. Ocimene is an open-chain terpene with three C=C double bonds which reacts rapidly with $O_3$. This may partially account for its absence or low levels in enclosure or rural air measurements (Larsen et al., 1997). The sesquiterpene $\beta$-caryophyllene is often undetected unless $O_3$ is scrubbed from enclosure purge air (Helmig, 1997). This could be the case for other highly reactive $C_{10}$ compounds as well.

Monoterpene EFs from major crop species tend to be very low. It is estimated that 50% of crop BVOC emissions are monoterpenes, 50% of which is $\alpha$-pinene (Lamb et al., 1993). However, for some important crop species such as cotton and alfalfa, ocimene and myrcene have been found to be the dominant monoterpenes (Winer et al., 1983). Desert shrubs such as *Artemisia* may also be significant sources of camphene and camphor (Buttkus et al., 1977). Although these shrubs are widely distributed across the western US, their foliar biomass density is very low (roughly 10%) compared to that of forests (Guenther et al., 1995). It is estimated that forests account for 75% of global monoterpene emissions, while crops and shrublands account for 5 and 20%, respectively (Guenther et al., 1995). Similarly, monoterpene emissions from crops were estimated to account for less than 3% of total NMHC emissions in the contiguous US (Lamb et al., 1987). We therefore focus primarily on forest tree monoterpene sources in this paper, recognizing that other sources may be more important in other ecosystems.

Most studies of emission and essential oil composition focus on hydrocarbon terpenes, and typically these species compose the majority of compounds stored and emitted. The oxygenated terpenoids are occasionally dominant compounds in the leaf oil of some tree species. In *Pinus banksiana* (Lapp and von Rudloff, 1982) and *Artemisia tridentata* (Buttkus et al., 1977), at least 50% of essential oil was found to be camphor, while *Tsuga canadensis* (Shaw, 1950) and *Umbellularia californica* (Kepner et al., 1974) contained mostly bornyl acetate. *Thuja occidentalis* (von Rudloff, 1961) contained 50–60% thujone. However, these compounds are often undetected or found in low quantities in actual emission samples (Schindler and Kotzias, 1989). Their lower vapor pressures, polarity, and greater water solubility relative to the hydrocarbon terpenes may prevent them from being emitted at rates proportional to their concentrations within plant tissues. *Picea glauca* (von Rudloff, 1972) leaf oil contained over 50% camphor, while other spruces (*P. marianna, pungens, rubens*) contained mostly bornyl acetate (von Rudloff, 1977,1966,1967b,1962). In contrast, foliage emission data indicated that these compounds accounted for only 4% of the monoterpenes emitted from *Picea glauca* and less than 1% from *Picea abies* and *P. pungens* (Kempf et al., 1996). Oxygenated terpenoids do compose a large fraction of actual emissions from California black sage (*Salvia mellifera*), which was found to emit 50% camphor and 25% 1,8-cineole (Tyson et al., 1974; Dement et al., 1975). *Eucalyptus globulus* (Street et al., 1997a; Guenther et al., 1991) emitted primarily cineole, and linalool composed 50–70% of essential oils and emissions (Ortiz et al., 1978) from *Citrus*. Other oxygenated monoterpenes such as $\alpha$-terpineol and thujone were often noted as constituents in emissions or essential oils, but were typically less than 1% of MC.

## 3. Approach

We examined the literature which provided quantitative MC estimates for dominant forest tree species. Samples could be generally classified as whole plant, branch, or leaf enclosure emission samples, leaf essential oil, branch or twig essential oil, cortical (e.g., buds) resin, and xylem resin analyses. We attempted to consider only data collected during the growing season to limit seasonality effects, and we also tried to limit resin samples to those from upper crown position to limit within-tree tissue variability effects, based on the assumption that the MC of oils from these tissues would more closely resemble that of actual foliage emissions. However, information concerning sampling position and season was occasionally lacking. Past comparisons have yielded reasonable agreement between essential oil composition and hydrocarbon monoterpene emission (Lerdau et al., 1995,1994) composition derived from enclosure studies, although discrepancies have been found (von Rudloff, 1977; Lerdau et al., 1994). We focus primarily on the hydrocarbon ($C_{10}H_{16}$) terpenoid compounds in this analysis. For tree species with no known enclosure emission MC data, resin and leaf oil MC was adjusted as a function of the relative saturation vapor pressures of the individual compounds to more closely approximate the MC which should theoretically be emitted to the atmosphere. Since most of the emission data compiled here was collected with enclosure air (and presumably foliage) temperature within a few degrees of 30°C, vapor pressure differences between individual compounds should have little impact here. Furthermore, a comparison of exponential temperature coefficients (Guenther et al., 1993) for eight different terpenes indicated that 21 of 28 values fell within the range of $0.09 \pm 0.025°\mathrm{C}^{-1}$. Among the six dominant compounds in this study, $\alpha$-pinene has a vapor pressure approximately 40% higher at 30°C than $\Delta^3$-carene. However, little difference was found in the temperature dependence coefficients for emissions of these compounds from *Pinus ponderosa* (Lerdau et al., 1994). Our goals are to (1) examine emission and tissue MC of US tree species, (2) briefly discuss MC of other vegetation types in non-forest ecosystems, (3) present expected regional emission patterns of individual monoterpenes based on MC and corresponding tree species distribution and abundance, (4) present regional flux estimates and discuss which monoterpene compounds are important in various parts of the US, and (5) compare results from the above with corresponding relative monoterpene concentrations observed at various forested sites.

## 4. Results and discussion

### 4.1. Monoterpene composition analysis of US tree species

We compiled 1369 MC profiles (843 from tree species found within the US) from over 160 tree species within 43 genera. Fourteen dominant or frequently occurring hydrocarbon monoterpene compounds were identified: $\Delta^3$-carene, *d*-limonene, myrcene, $\alpha$-pinene, $\beta$-pinene, sabinene, camphene, $\beta$-phellandrene, $\alpha$-thujene, terpinolene, $\alpha$-terpinene, $\gamma$-terpinene, $\rho$-cymene, and ocimene (primarily trans-ocimene). This list is in excellent agreement with a previously published list of frequently occurring monoterpenes (Guenther et al., 1994). Table 1 summarizes estimated relative abundance of these 14 compounds emitted by major tree species in North America. Relative emission potential (REP) provides a means of ranking the importance of each tree species as a monoterpene emitter. This is calculated as the product of the basal monoterpene EF, estimated fraction of the total crown coverage within the US, and foliar density for each species. The REP indicates that species such as *Pinus taeda, P. elliottii, P. contorta, P. ponderosa, Picea glauca, Picea marianna, Pseudotsuga menziesii, Liquidambar styraciflua, and Abies balsamea* are very important as monoterpene emitters nationally, and even more so regionally. REP does not account for regional variation in temperatures. Of the 324 tree species in the US forest cover database (Geron et al., 1994), MC data was found for 139, including emission data for 130 of these. Despite the lack of data for the majority of tree species, there were MC data for species composing 96% of the monoterpene REP in the US. It is possible that some tree species of significant localized abundance and high emission rates have not yet been examined for monoterpene emission.

Significant species with no MC data we are aware of include many western fir (*Abies*) species, including *Abies amabilis*, and *A. magnifica.* In addition, *Abies concolor* and *A. procera* have but one emission sample included here. These firs compose much of the missing REP. Other significant species with no MC data but high basal monoterpene emission factors include *Pinus monophylla, Thuja plicata, Tsuga heterophylla, Juniperus osteosperma*, and many species in the *Juglans* and *Magnolia* genera. In addition, several regionally abundant tree species have very little reported MC data (less than three measurements), including *Pinus albicaulis, coulteri*, *jeffreyi, resinosa, rigida*, and many of the spruces (*Picea spp.*). It is possible that basal emission factors for these species are quite uncertain as well.

The relative proportions of the hydrocarbon monoterpenes themselves can sometimes vary considerably between emission samples and internal oil concentrations. Examples from some important tree species are illustrated in Fig. 1. Typically, the relative proportion of $\beta$-pinene is greater in leaf oil extracts than in emission samples, while the reverse is often true for $\alpha$-pinene. This may be due to the higher vapor pressure of $\alpha$-pinene and the tendency of $\beta$-pinene to isomerize or to react with $O_3$ during the course of emission sampling and analysis. In general, however, there were no consistent or statistically significant differences between internal MC and that of emission samples for the hydrocarbon terpenes examined here. Agreement appears reasonable, with emission means usually being within a standard deviation of the leaf oil means. We tested to see if adjusting MC of internal plant tissues by respective vapor pressures of the individual compounds reduced the difference between MC in emission versus internal tissue samples for tree species where both were reported. The Euclidean distances between the MC of emission samples and internal MC before and after adjusting for vapor pressure indicated that the adjustment made a very small ($< 0.1\%$) and statistically insignificant improvement in emission versus internal MC. However, this simple test was likely confounded by the different techniques, genetic variability, and individual goals of the studies cited here.

Fig. 2 shows the MC (emission and internal leaf oil data combined) of some important (regionally abundant and with a basal EF of $1.6\,\mu\mathrm{g\ C\ g^{-1}\,h^{-1}}$ or greater) monoterpene emitters in North America. In the major southern yellow pine group (*Pinus echinata, elliotti, palustris, taeda,* and several minor species) of the southeastern

Table 1

Estimated monoterpene composition for emissions from tree species in North America. Spp indicates mean values for the genus. αPin = α-pinene, βPin = β-pinene, $\Delta^3$ Car = $\Delta^3$-carene, *d*-Lim = *d*-limonene, Camp = camphene, Myrc = myrcene, αTer = α-terpinene, βPhe = βPhellandrene, Sabi = sabinene, pCym = pcymene, Ocim = ocimene, Thuj = α-thujene, Tero = terpinolene, and γTer = γ-terpinene. REP is relative emission potential for monoterpenes, and is calculated as the product of the basal monoterpene EF, estimated percentage of the total crown coverage within the US, and foliar density. (R. Rasmussen, unpublished data using published methods; Khalil and Rasmussen, 1992)

| Genus species | N | αPin | βPin | $\Delta^3$Car | dLim | Camp | Myrc | αTer | βPhe | Sabi | pCym | Ocim | Thuj | Tero | γTer | REP | Citation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Abies balsamea | 27 | 20.7 | 35.8 | 1.2 | 20.3 | 9.2 | 1.7 | 2 | 5.7 | 0 | 3.4 | 0 | 0 | 0 | 0 | 5.046 | [a] |
| Abies fraseri | 6 | 71.9 | 17 | 8.6 | 1.1 | 0 | 0.2 | 0 | 1.3 | 0 | 0 | 0 | 0 | 0 | 0 | 0.000 | [b] |
| Abies concolor | 1 | 33.3 | 35.0 | 0 | 6.2 | 6.0 | 4.2 | 0 | 2.0 | 10.0 | 0 | 0 | 0 | 2.9 | 0.4 | 3.850 | [c] |
| Abies grandis | 2 | 56.7 | 17.9 | 0.7 | 4.1 | 10.0 | 5.1 | 0 | 3.6 | 1.3 | 0 | 0 | 0 | 0.6 | 0 | 4.204 | [d] |
| Abies procera | 1 | 9.2 | 13.3 | 0 | 30.5 | 2.4 | 10.0 | 0 | 30.0 | 0 | 8.5 | 0 | 0 | 1.8 | 2.7 | 0.300 | [d] |
| Abies lasiocarpa | 2 | 22.1 | 13.9 | 1 | 29.5 | 10 | 1.5 | 12.5 | 0 | 0 | 8.5 | 0 | 1 | 0 | 0 | 3.546 | [e] |
| Acacia spp | 4 | 87.6 | 7.1 | 0 | 3.4 | 0 | 1.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.003 | [f] |
| Acer spp | 23 | 21.1 | 4.3 | 25 | 13 | 5.1 | 7.9 | 0.5 | 0 | 21.5 | 0 | 0 | 0.8 | 0 | 0.7 | 3.790 | [g] |
| Alnus spp | 1 | 12 | 44 | 0 | 21 | 0 | 0 | 0 | 0 | 0 | 2 | 19 | 2 | 0 | 0 | 0.000 | [h] |
| Amelanchier arborea | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.008 | [h] |
| Betula alleghaniensis | 1 | 28.3 | 4 | 0 | 23.2 | 26.3 | 0 | 4 | 0 | 0 | 14.1 | 0 | 0 | 0 | 0 | 0.035 | [h] |
| Betula papyrifera | 1 | 29 | 0 | 0 | 29 | 21 | 0 | 0 | 0 | 0 | 21 | 0 | 0 | 0 | 0 | 0.108 | [h] |
| Carpinus caroliniana | 2 | 28.1 | 23 | 21.7 | 9.1 | 9.1 | 0 | 0 | 0 | 0 | 9.1 | 0 | 0 | 0 | 0 | 0.175 | [h] |
| Carya spp | 13 | 24.1 | 7.2 | 33.4 | 19.2 | 0.3 | 6.9 | 0 | 0 | 3.0 | 0 | 0 | 0.2 | 5.7 | 0.1 | 1.592 | [i] |
| Celtis occidentalis | 1 | 2 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 96 | 0 | 0 | 0 | 0.018 | [j] |
| Cercocarpus montanus | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.000 | [h] |
| Chamaecyparis lawsoni | 1 | 16 | 64.3 | 0 | 19.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.002 | [k] |
| Cornus florida | 5 | 20.3 | 0.5 | 38.7 | 26.8 | 7.7 | 0 | 0 | 0 | 0 | 4.7 | 0 | 0 | 1.4 | 0 | 1.023 | [l] |
| Cupressus spp | 4 | 42.5 | 1.2 | 0 | 31.2 | 0.5 | 23.0 | 0 | 0.3 | 0.5 | 0 | 0.3 | 0.5 | 0 | 0 | 0.000 | [m] |
| Diospyros virginiana | 17 | 50.7 | 49.3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.005 | [f] |
| Eucalyptus spp | 2 | 35.4 | 18.8 | 0 | 20.8 | 0 | 0 | 0 | 0 | 0 | 0 | 25 | 0 | 0 | 0 | 0.003 | [n] |
| Fagus grandifolia | 3 | 31.5 | 12 | 6.2 | 24.3 | 4 | 1.5 | 8 | 0 | 0.3 | 12 | 0 | 0.3 | 0 | 0 | 0.418 | [o] |
| Fraxinus spp | 4 | 20.9 | 8.4 | 2.7 | 0.7 | 0.7 | 22.2 | 0 | 44.4 | 0 | 0 | 0 | 0 | 0 | 0 | 0.050 | [p] |
| Ilex opaca | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.021 | [f] |
| Juglans spp | 1 | 29 | 51.6 | 0 | 12.9 | 0 | 6.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.001 | [q] |
| Juniperus monosperma | 2 | 24.2 | 0 | 25.8 | 48 | 0 | 1.2 | 0.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.087 | [r] |
| Juniperus occidentalis | 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.025 | [k] |
| Juniperus scopulorum | 2 | 2.6 | 0 | 0 | 1.4 | 0 | 1.8 | 1 | 0.2 | 87.5 | 0 | 0 | 2.7 | 0 | 2.9 | 0.055 | [s] |
| Juniperus virginiana | 1 | 33.3 | 0 | 66.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.180 | [k] |
| Larix occidentalis | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.012 | [k] |
| Liquidambar styraciflua | 28 | 45.4 | 6.8 | 16.3 | 16.1 | 0.6 | 3.7 | 1.5 | 3.1 | 4.4 | 1.8 | 0 | 0.1 | 0 | 0 | 2.506 | [t] |
| Liriodendron tulipifera | 19 | 4.6 | 6.5 | 0.4 | 40.1 | 1.3 | 26.8 | 0 | 0.9 | 0 | 0 | 9.9 | 0 | 8.9 | 0.4 | 0.085 | [u] |
| Magnolia grandiflora | 4 | 60.6 | 26.5 | 1.6 | 5.6 | 0.6 | 5.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.072 | [v] |
| Malus spp | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.006 | [h] |
| Melia azedarach | 1 | 35.7 | 14.3 | 0 | 17.9 | 0 | 32.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.000 | [w] |
| Morus spp | 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.008 | [h] |
| Nyssa spp | 4 | 21.5 | 17.4 | 8.9 | 31.5 | 6.6 | 14.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.196 | [x] |
| Ostrya virginiana | 1 | 20 | 0 | 0 | 20 | 40 | 0 | 0 | 0 | 0 | 20 | 0 | 0 | 0 | 0 | 0.027 | [h] |
| Oxydendrum arboretum | 1 | 39.2 | 16.4 | 12.9 | 31.4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.137 | [y] |
| Persea borbonia | 3 | 61 | 39 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.017 | [f] |
| Picea abies | 14 | 45.3 | 12.4 | 8.6 | 10.1 | 8.6 | 6.6 | 0 | 4.1 | 3.3 | 0.9 | 0 | 0 | 0.1 | 0.1 | 0.094 | [z] |
| Picea engelmannii | 5 | 36.7 | 13.4 | 5.8 | 8.1 | 12.3 | 8.7 | 3 | 5.2 | 0 | 6.7 | 0 | 0 | 0.1 | 0 | 2.271 | [aa] |
| Picea glauca | 25 | 24 | 11.3 | 5.4 | 26.5 | 18.1 | 8.4 | 0.1 | 5.5 | 0.4 | 0 | 0 | 0 | 0.2 | 0.1 | 7.260 | [bb] |
| Picea marianna | 10 | 24.2 | 2.9 | 28.1 | 15.3 | 23.1 | 2.1 | 0.1 | 0.3 | 0.1 | 3.4 | 0 | 0 | 0.2 | 0.2 | 9.832 | [cc] |
| Picea pungens | 16 | 33.9 | 27.6 | 8.8 | 19.6 | 5.7 | 2.7 | 0.1 | 0.8 | 0.6 | 0.1 | 0 | 0 | 0.1 | 0.1 | 0.079 | [dd] |
| Picea rubens | 3 | 20 | 8.1 | 26.2 | 5.6 | 28.8 | 5.8 | 0 | 3 | 0 | 1.7 | 0 | 0 | 0.4 | 0.3 | 1.782 | [ee] |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Picea sitchensis | 14 | 17.3 | 10 | 0 | 0.1 | 2.2 | 51.6 | 0 | 18.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0.678 [ff] |
| Pinus albicaulis | 2 | 38.3 | 26.4 | 2.2 | 10.4 | 2.9 | 13.2 | 0 | 5.2 | 0.9 | 0.1 | 0 | 0 | 0.5 | 0 | 0.188 [gg] |
| Pinus aristata | 1 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.026 [hh] |
| Pinus attenuata | 3 | 37.9 | 21.4 | 3.7 | 15.7 | 1.3 | 10.7 | 0 | 7.8 | 0.3 | 0 | 1.1 | 0 | 0.2 | 0 | 0.021 [gg] |
| Pinus balfouriana | 2 | 98.7 | 0.8 | 0 | 0.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.003 [hh] |
| Pinus banksiana | 19 | 30.4 | 25.0 | 10.4 | 6.0 | 7.3 | 12.6 | 0.1 | 1.7 | 4.3 | 0.1 | 0.1 | 0 | 1.8 | 0 | 0.579 [ii] |
| Pinus clausa | 8 | 45.4 | 54 | 0 | 0.1 | 0.3 | 0 | 0 | 0.1 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0.192 [jj] |
| Pinus contorta | 21 | 22.0 | 19.8 | 5.0 | 18.1 | 5.4 | 9.7 | 4.4 | 10.5 | 1.4 | 1.6 | 0.2 | 0 | 1.6 | 0.3 | 3.146 [kk] |
| Pinus coulteri | 2 | 29.0 | 15.2 | 2.7 | 19.4 | 2.0 | 7.6 | 0 | 9.6 | 12.5 | 0.9 | 0.2 | 0 | 0.9 | 0.2 | 0.008 [gg] |
| Pinus discolor | 1 | 98.2 | 0 | 0 | 1.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.001 [hh] |
| Pinus echinata | 5 | 55 | 14.1 | 5 | 22.8 | 0.5 | 2.3 | 0.1 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0 | 2.474 [ll] |
| Pinus edulis | 2 | 90.7 | 4.1 | 0.5 | 0 | 0.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.630 [hh] |
| Pinus elliottii | 29 | 47.3 | 37.7 | 7.5 | 5.7 | 0.1 | 0.5 | 0 | 1.1 | 0 | 0 | 0 | 0 | 0 | 0 | 3.332 [mm] |
| Pinus engelmannii | 3 | 69.0 | 17.7 | 0 | 0.1 | 3.4 | 5.9 | 0 | 2.9 | 0.1 | 0.1 | 0 | 0 | 0.2 | 0.1 | 0.000 [nn] |
| Pinus flexilis | 1 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.160 [hh] |
| Pinus glabra | 1 | 50 | 50 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.059 [hh] |
| Pinus jeffreyi | 2 | 44.6 | 6.6 | 0 | 23.2 | 6.8 | 16.2 | 0 | 1.5 | 0.3 | 0.5 | 0.3 | 0 | 0.2 | 0 | 0.418 [c] |
| Pinus lambertiana | 1 | 83 | 17 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.185 [hh] |
| Pinus leiophylla | 1 | 94.2 | 0 | 5.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.002 [hh] |
| Pinus monticola | 8 | 29.7 | 26.1 | 32.5 | 3.4 | 0 | 8.2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.183 [oo] |
| Pinus nigra | 1 | 97.2 | 0 | 0 | 2.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.006 [hh] |
| Pinus palustris | 34 | 42 | 53.7 | 2.7 | 1.4 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.025 [pp] |
| Pinus ponderosa | 27 | 21.7 | 33.3 | 41.3 | 1.4 | 0 | 1.8 | 0.1 | 0 | 0.4 | 0 | 0 | 0 | 0 | 0 | 4.937 [qq] |
| Pinus pungens | 1 | 75.3 | 17.1 | 7.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.030 [hh] |
| Pinus radiata | 8 | 38.7 | 41.7 | 0.1 | 10.7 | 0.1 | 8.1 | 0 | 0.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0.001 [rr] |
| Pinus resinosa | 2 | 9.8 | 0.2 | 1.8 | 34.9 | 19.3 | 7.3 | 4.6 | 0 | 0 | 22 | 0 | 0 | 0 | 0 | 0.727 [ss] |
| Pinus rigida | 2 | 73.5 | 18 | 8.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.243 [tt] |
| Pinus sabiniana | 1 | 60.3 | 39.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.021 [hh] |
| Pinus serotina | 2 | 16.8 | 20.9 | 0 | 61.4 | 0.5 | 0 | 0 | 0.4 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0.311 [uu] |
| Pinus strobus | 12 | 25.3 | 19.7 | 0.1 | 0.1 | 14.2 | 29.1 | 0 | 6.8 | 0.8 | 0 | 0 | 3.9 | 0 | 0 | 1.771 [vv] |
| Pinus sylvestris | 50 | 20.7 | 21.4 | 30.5 | 7.8 | 0.4 | 9.4 | 1.9 | 7.6 | 0.2 | 0 | 0 | 0 | 0.1 | 0 | 0.095 [ww] |
| Pinus taeda | 36 | 58 | 24.1 | 1 | 6.9 | 0.8 | 8.4 | 0.2 | 0 | 0 | 0.5 | 0 | 0 | 0.1 | 0 | 11.77 [xx] |
| Pinus virginiana | 7 | 33.1 | 12.8 | 34.2 | 12.3 | 4.5 | 3 | 0 | 0 | 0.1 | 0 | 0 | 0 | 0 | 0 | 1.212 [yy] |
| Populus spp. | 7 | 32.1 | 7.5 | 0.9 | 27.1 | 16.9 | 2.7 | 0.9 | 0 | 0 | 12.0 | 0 | 0 | 0 | 0 | 0.115 [x] |
| Prunus spp | 5 | 37.6 | 15.7 | 1.2 | 9.7 | 12.0 | 9 | 0 | 0 | 0 | 0.4 | 25 | 0 | 0 | 0 | 0.038 [zz] |
| Pseudotsuga menziesii | 37 | 64.2 | 21.2 | 2.7 | 5.3 | 1 | 2.5 | 0 | 0.1 | 3 | 0 | 0 | 0 | 0 | 0 | 9.909 [aaa] |
| Quercus spp | 86 | 34.8 | 6.1 | 0.4 | 13.4 | 6.8 | 0.4 | 0 | 0 | 0.7 | 10.9 | 14.7 | 0 | 11.7 | 0 | 1.176 [bbb] |
| Robinia pseudoacacia | 2 | 0 | 0 | 0 | 0 | 0 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.032 [y] |
| Salix spp | 12 | 10.9 | 0 | 0 | 21.4 | 0 | 0 | 0 | 0 | 0 | 19.6 | 48 | 0 | 0 | 0 | 0.006 [ccc] |
| Sassafras albidum | 2 | 0 | 10.4 | 0 | 0 | 9.6 | 0 | 0 | 0 | 9.6 | 43 | 0 | 0 | 27.4 | 0 | 0.030 [r] |
| Sequoia sempervirens | 33 | 25.7 | 0.9 | 0 | 12.3 | 0.3 | 5.7 | 0.6 | 4.4 | 28.5 | 1 | 0.8 | 0.1 | 0.8 | 19.1 | 0.016 [ddd] |
| Sequoiadendron giganteum | 14 | 98.5 | 0 | 0 | 1.2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.2 | 0 | 0.000 [eee] |
| Taxodium distichum | 23 | 51.8 | 0.4 | 4.3 | 2.4 | 0 | 2.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.250 [fff] |
| Taxodium mucronatum | 1 | 86.3 | 1 | 0 | 8.8 | 0.9 | 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.242 [w] |
| Thuja occidentalis | 4 | 35.7 | 6.8 | 1.4 | 13 | 16.4 | 1.3 | 0 | 0 | 6.8 | 8.5 | 0 | 9.5 | 0 | 0.5 | 0.615 [ggg] |
| Tilia americana | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.014 [h] |
| Tsuga canadensis | 5 | 14.5 | 5.9 | 0.7 | 15.8 | 27.8 | 1.3 | 0.4 | 0 | 0 | 21.5 | 0 | 12 | 0 | 0 | 0.087 [hhh] |
| Ulmus spp | 5 | 8.7 | 31.8 | 0 | 11 | 0 | 1.4 | 0 | 0 | 42 | 0 | 0 | 5.1 | 0 | 0 | 0.010 [iii] |
| Umbellularia californica | 12 | 26 | 13.5 | 0 | 1.3 | 0.3 | 5.5 | 4.2 | 0 | 35.1 | 2.2 | 0 | 0 | 0.6 | 11.1 | 0.065 [jjj] |

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[a] Lester (1974), Helmig et al. (1999) and Zavarin and Snajberk (1972).

[b] Zavarin and Snajberk (1972).

[c] Rasmussen, unpublished data, using methods of Khalil and Rasmussen (1992).

[d] Zimmerman (1979b) and Rasmussen, unpublished data, using methods of Khalil and Rasmussen (1992).

[e] Helmig et al. (1999).

Table 1. (*Footnotes continued*)

[f] Zimmerman (1979a).

[g] Khalil and Rasmussen (1992), Helmig et al. (1999), Evans et al. (1982), Guenther et al. (1996), Zimmerman (1979a) and Helmig and Arey (1992).

[h] Helmig et al. (1999).

[i] Khalil and Rasmussen (1992), Guenther et al. (1996) and Zimmerman (1979a).

[j] Khalil and Rasmussen (1992).

[k] Zimmerman (1979b).

[l] Helmig et al. (1999), Guenther et al. (1996) and Zimmerman (1979a).

[m] Khalil and Rasmussen (1992) and Winer et al. (1983).

[n] Evans et al. (1982) and Street et al. (1997a).

[o] Helmig et al. (1999) and Lamb et al. (1985).

[p] Khalil and Rasmussen (1992) and Helmig et al. (1999).

[q] Arey et al. (1991).

[r] Guenther et al. (1996) and Lamb et al. (1985).

[s] Adams and Hagerman (1976).

[t] Khalil and Rasmussen (1992), Helmig et al. (1999), Evans et al. (1982), Guenther et al. (1996), Zimmerman (1979b), Corchnoy et al. (1992) and Wyllie and Brophy (1989).

[u] Smith et al. (1988), Helmig et al. (1999), Guenther et al. (1996) and Zimmerman (1979b).

[v] Guenther et al. (1996) and Winer et al. (1983).

[w] Guenther et al. (1996).

[x] Helmig et al. (1999) and Guenther et al. (1996).

[y] Lamb et al. (1985).

[z] Janson (1993), Helmig et al. (1999), Schindler and Kotzias (1989), Kempf et al. (1996) and Rasmussen, unpublished data, using methods of Khalil and Rasmussen (1992).

[aa] von Rudloff (1967a,1961), Lerdau et al. (1994) and Zimmerman (1979b).

[bb] von Rudloff (1972,1967a,b,1962), Kempf et al. (1996), Ogilvie and von Rudloff (1968) and Wilkinson et al. (1971).

[cc] von Rudloff (1967b,1962), Helmig et al. (1999), Wilkinson and Hanover (1992) and Fulton et al. (1998).

[dd] von Rudloff (1962), Hanover (1974), Moore and Hanover (1987), Kempf et al. (1996), Zimmerman (1979b) and Schaefer and Hanover (1986).

[ee] von Rudloff (1966,1962).

[ff] Street et al. (1996), von Rudloff (1977) and Evans et al. (1982,1985).

[gg] Mirov (1961) and Rasmussen, unpublished data, using methods of Khalil and Rasmussen (1992).

[hh] Mirov (1961).

[ii] von Rudloff and Lapp (1987), Mirov (1961), Lapp and von Rudloff (1982) and Rasmussen, unpublished data, using methods of Khalil and Rasmussen (1992).

[jj] Mirov (1961), Zimmerman (1979a,b) and Joye et al. (1972).

[kk] von Rudloff and Lapp (1987), Mirov (1961), Helmig et al. (1999) and Rasmussen, unpublished data, using methods of Khalil and Rasmussen (1992).

[ll] Khalil and Rasmussen (1992), Mirov (1961), Guenther et al. (1996), Lamb et al. (1985) and Zimmerman (1979b).

[mm] Evans et al. (1982), Franklin (1976), Guenther et al. (1996), Zimmerman (1979a), Joye et al. (1972), Tingey et al. (1980) and Roberts (1970).

[nn] Mirov (1961), Evans et al. (1982) and Rasmussen, unpublished data, using methods of Khalil and Rasmussen (1992).

[oo] Mirov (1961) and Moore and Hanover (1987).

[pp] Mirov (1961), Guenther et al. (1996) and Zimmerman (1979a,b).

[qq] Mirov (1961), Lerdau et al. (1994), Zimmerman (1979b) and Zavarin et al. (1971).

[rr] Mirov (1961), Winer et al. (1983) and Corchnoy et al. (1992).

[ss] Mirov (1961) and Helmig et al. (1999).

[tt] Mirov (1961) and Lamb et al. (1985).

[uu] Mirov (1961) and Joye et al. (1972).

[vv] Lamb et al. (1984,1985), Gerhold and Plank (1970), Mirov (1961) and Helmig et al. (1999).

[ww] Janson (1993), Bridgen et al. (1979), Tosolski and Hanover (1971)Hanover (1974) and Mirov (1961).

[xx] Khalil and Rasmussen (1992), Mirov (1961), Helmig et al. (1999), Guenther et al. (1996), Zimmerman (1979b), Joye et al. (1972) and Seila et al. (1982).

[yy] Lamb et al. (1984,1985), Mirov (1961) and Zimmerman (1979b).

[zz] Helmig et al. (1999), Guenther et al. (1996), Lamb et al. (1985) and Arey et al. (1991).

[aaa] Lerdau et al. (1995), Maarse and Kepner (1970), Hanover and Furniss (1966), Schindler and Kotzias (1989), Guenther et al. (1996) and Zimmerman (1979b).

[bbb] Helmig et al. (1999), Guenther et al. (1996) and Zimmerman (1979a,b).

[ccc] Khalil and Rasmussen (1992), Helmig et al. (1999) and Zimmerman (1979a,b).

[ddd] Hall and Langenheim (1986) and Okamoto et al. (1981).

[eee] Levinson et al. (1971).

[fff] Guenther et al. (1996) and Zimmerman (1979a,b).

[ggg] von Rudloff (1961) and Helmig et al. (1999).

[hhh] Helmig et al. (1999), Lamb et al. (1985) and Shaw (1950).

[iii] Khalil and Rasmussen (1992), Helmig et al. (1999) and Guenther et al. (1996).

[jjj] Kepner et al. (1974).

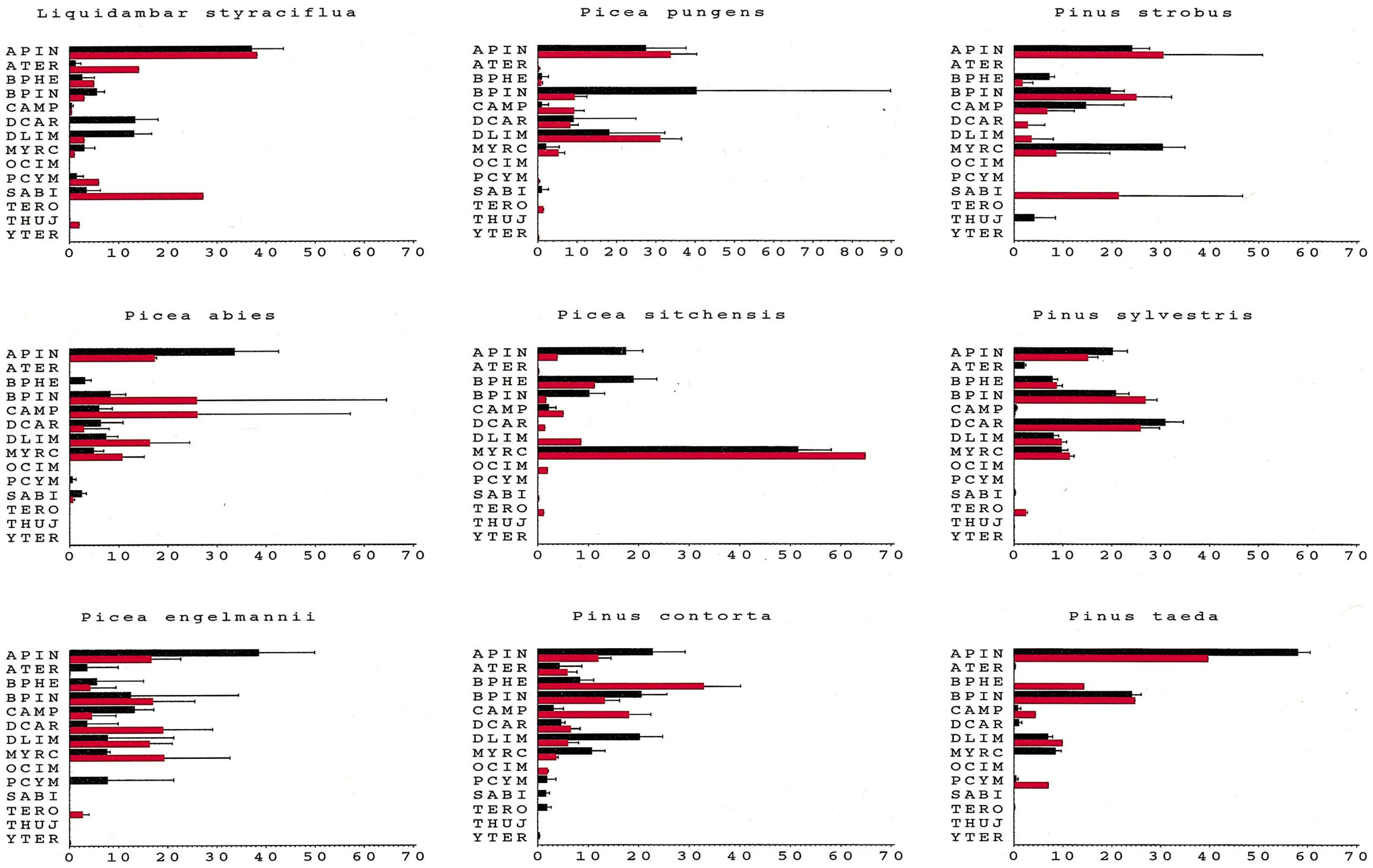


Fig. 1. Percentage of monoterpene compounds found in leaf extracts (red bars) and foliage emissions (black bars) for some important monoterpene emitting tree species in North America where both are reported. Uncertainty bars denote 1 standard deviation. Compounds are denoted as APIN = α-pinene, ATER = α-terpinene, BPHE = β-phellandrene, BPIN = β-pinene, CAMP = camphene, DCAR = $\Delta^3$-carene, DLIM = *d*-limonene, MYRC = myrcene, OCIM = ocimene, PCYM = ρ-cymene, SABI = sabinene, TERO = terpinolene, THUJ = α-thujene, and YTER = γ-terpinene.

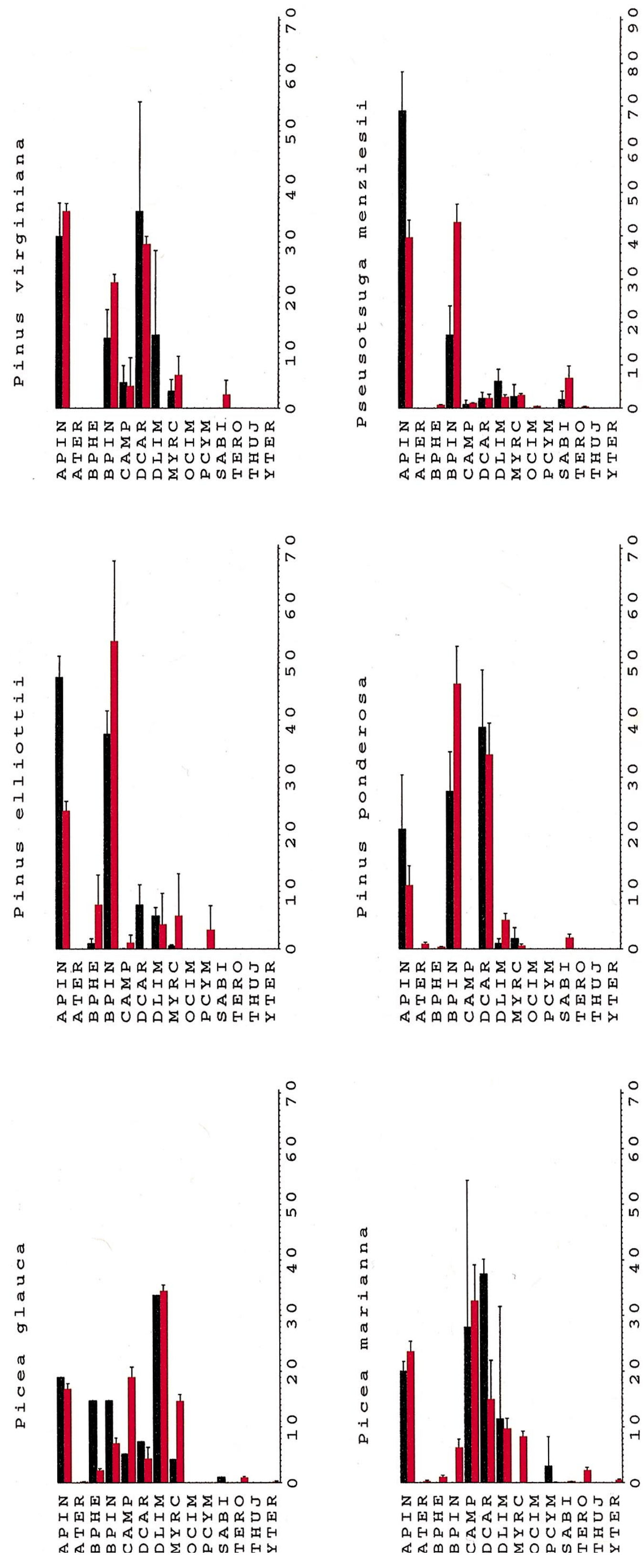


Fig. 1. (*Continued*)

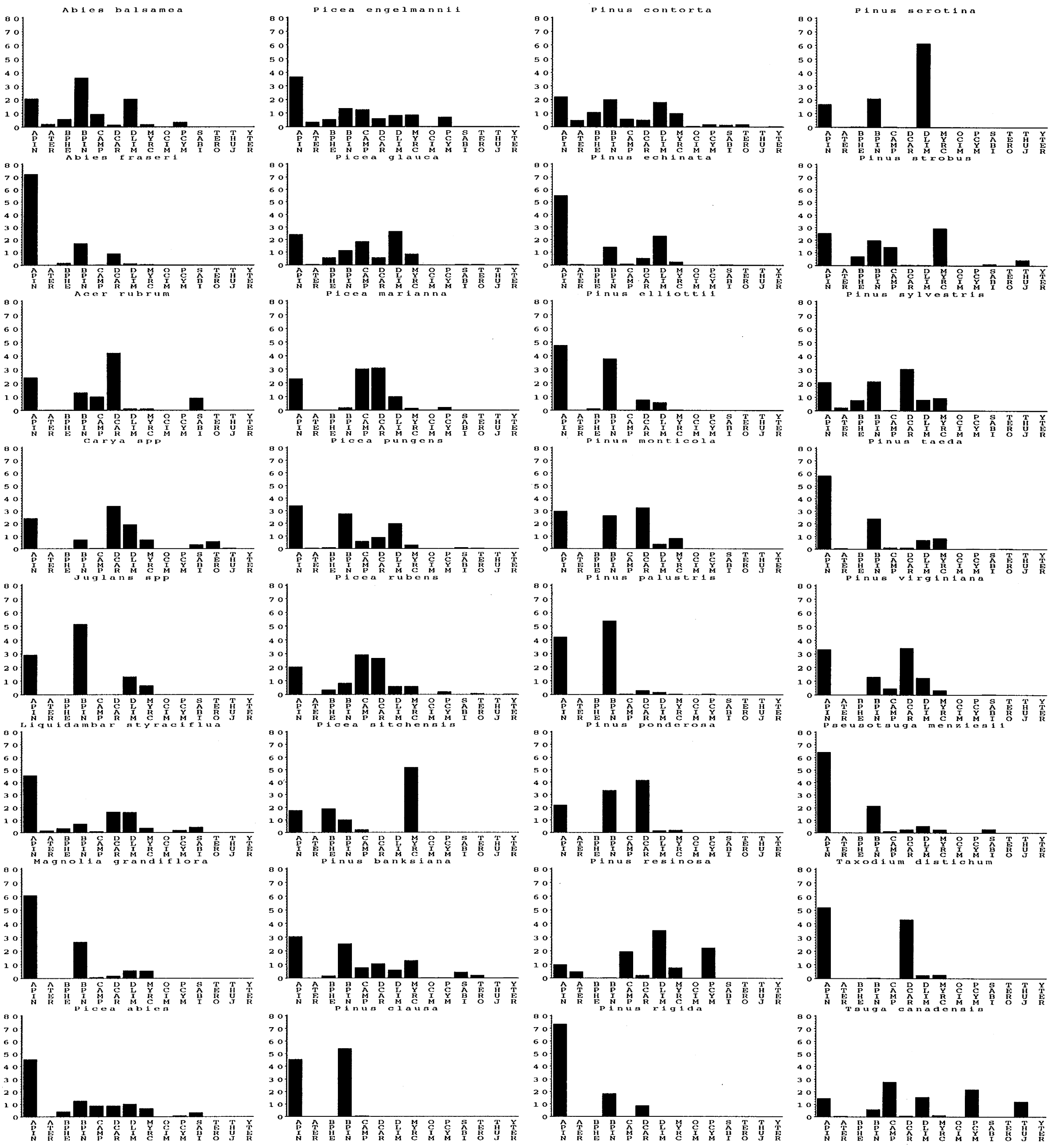


Fig. 2. Estimated monoterpene composition for some important monoterpene-emitting tree species in North America. Abbreviations for individual compounds are the same as in Fig. 1.

US, α-pinene is consistently the dominant compound, with β-pinene being second in abundance. These two compounds consistently make up greater than 75% of the MC in this group. Lesser quantities of $\Delta^3$-carene, myrcene, camphene, and *d*-limonene are also reported.

*Pinus virginiana* appears to be unique among southern pines in that $\Delta^3$-carene composes 30–40% of monoterpenes in emission samples (Lamb et al., 1984, 1985; Zimmerman, 1979a) and oil (Mirov, 1961) and is as abundant as α-pinene from this species. This is a widespread and fairly abundant pine throughout the interior southeast. *Pinus virginiana* is a member of the *Pinus* subgenus *diploxylon*, group *Insignes,* while the other major southern pines fall into the *Australes* subgroup in the *Pinus* phylogeny (Mirov, 1961). Two other less abundant pines (*P. clausa* and *P. serotina*) in this same subgroup (*Insignes*) also exhibit differing MC. In *Pinus serotina*, *d*-limonene is the most abundant compound, while $\beta$-pinene often appears to be emitted in quantities similar to $\alpha$-pinene from both *Pinus clausa* and *P. serotina*.

Some of the major western conifers (*Pinus contorta, monticola, and ponderosa* and *pseudotsuga menziesii*) present an interesting contrast to eastern conifers in that $\beta$-pinene and/or $\Delta^3$-carene are often the dominant component of the monoterpenes (Mirov, 1961; Hanover, 1966; Schindler and Kotzias, 1989; Lerdau et al., 1994). Camphene and $\beta$-phellandrene are also major components of *Pinus contorta* MC. The compound $\Delta^3$-carene was not emitted in proportion to the leaf oil MC (Schindler and Kotzias, 1989; Lerdau et al., 1994) in *pseudotsuga meziesii* and *Pinus ponderosa*, even after correcting for differences in vapor pressure. However, on average, this discrepancy does not seem to hold across all studies of this species (Fig. 1), where the proportion of $\Delta^3$-carene in the emission is somewhat greater than that found in the plant tissues, and $\beta$-pinene is second in abundance in the MC overall. *Pinus ponderosa* was placed in the *Pinus* subgenus *diploxylon*, group *Australes* (Mirov, 1961). Other members of this group are found to contain less than 5% $\Delta^3$-carene in their MC. This pine species was later placed in a separate subsection (*Ponderosae*) of the subgenus *Pinus* due to structural traits (Little and Critchfield, 1969). The leaf oil of *Pinus monticola* (subgenus *Haploxylon*, group *Strobi)* was also found to be dominated by $\Delta^3$-carene (Hanover, 1966) in many cases.

The three dominant Lake States pines (*Pinus banksiana, P. resinosa, and P. strobus*) are genetically diverse, falling into the subgenus *Diploxylon*, group *Insignes*, subgenus *Diploxylon*, group *Lariciones*, and subgenus *Haploxylon*, group *Strobi*, respectively (Little and Critchfield, 1969). $\alpha$-pinene and $\beta$-pinene are most abundant in *Pinus banksiana* and *P. strobus,* while *d*-limonene dominates *Pinus resinosa* MC. These species also emit 10–30% $\beta$-myrcene, 10–20% camphene, 10% or less $\Delta^3$-carene.

The spruces (*Picea abies, P. engelmanii, P. glauca, P. marianna, P. pungens, P. rubens, and P. sitchensis*) in northern North America also show profiles distinct from other conifers. As with the eastern conifers, $\alpha$-pinene levels are at least twice those of $\beta$-pinene, with the exception of *P. pungens*. However, camphene, $\Delta^3$-carene, *d*-limonene, and/or myrcene are often as abundant as the pinenes, and individually compose up to 50% of the MC from each *Picea* species. In addition $\beta$-phellandrene and terpinolene (in small quantities) usually are found. *Picea sitchensis* shows no $\Delta^3$-carene or *d*-limonene in MC from the data compiled here, and myrcene is the dominant compound stored and emitted (Street et al., 1996; Gerhold and Plank, 1970; von Rudloff, 1977; Evans et al., 1985). This species is primarily restricted to Alaska, the coastal areas of Pacific northwestern North America, and European areas on the Atlantic coast. However, it is often the dominant species in forests where it occurs. In comparison to leaf oil data, there are few studies reporting terpene emission rate or composition for most major North American spruces.

In contrast to the spruces, true fir *(Abies*) MC is reported to be composed almost entirely of hydrocarbon terpenes (Zavarin and Snajberk, 1972). *Abies balsamea* exhibited a much different MC than *Abies fraserii*, with the major components of the former being 35% $\beta$-pinene and 20% of both $\alpha$-pinene and *d*-limonene, while the latter was dominated by $\alpha$-pinene ( $\sim$ 70%). *Abies balsamea*, an abundant and widespread species in boreal forests, was also found to contain significant amounts of $\beta$-phellandrene. There is apparently little MC data available for the western true firs, and little information on emissions from the genus *Abies* in general. This may be a significant gap in current North American BVOC emission models, since the western true firs (*Abies amabilis, A. concolor, A. grandis, A. lasiocarpa, A. magnifica, and A. procera*) account for over 12% of the basal area of western US forests. In addition, this genus is classified as a high monoterpene emitter (Guenther et al., 1994) and carries high levels of foliage mass (Geron et al., 1994).

## *4.2. Regional monoterpene emission distribution*

The MC profile data were assigned to canopy cover of corresponding tree species in a forest landcover database (Geron et al., 1994). This database has since been expanded from the eastern 37 states to all 48 contiguous United States and Alaska. To species without reported MC data, the mean MC of other species within its genus was assigned. This primarily affected deciduous species with low monoterpene basal emission factors, but also a few of the western *Abies* species. As mentioned earlier, most major forest tree genera in North America have at least some published quantitative MC data. All of the major pine and spruce species have been examined. Using the methods of BEIS2 (Geron et al., 1994), hourly monoterpene emissions were estimated for the US at an ambient temperature of 30°C. Total monoterpene emissions were multiplied by the MC at the species level and aggregated to county and regional levels. Only emissions from live foliage were considered here. A comparatively small percentage (less than 10% of crown emissions) of monoterpenes can be emitted from detrital tissue (Zimmerman, 1979b). It is not known if MC changes as tissue dies from a given species. Forest floor emissions from a Scandinavian pine stand were thought to be primarily from roots. These emissions ranged from 20–40% of crown emissions and showed some quantitative, but not qualitative, changes in MC (Janson, 1993).

The estimated relative emission distribution of the six major compounds is shown in Fig. 3. The regional estimates of MC reflect that of the regionally dominant tree species with high basal monoterpene EFs. In the southeastern US, estimated monoterpene emissions are dominated by α-pinene (35–70% of total) and β-pinene (15–40%). Secondary compounds of significance are *d*-limonene (5–20%) and β-myrcene (2–20%). Monoterpene emissions in this region are largely controlled by *Liquidambar styraciflua*, the southern pine group which includes *Pinus taeda, echinata, elliotti, palustris, virginiana*, and to a lesser extent species in the *Acer* (maple), *Magnolia, and Carya* (hickory) genera. The Pacific Coast forests and sparse coniferous forests of the Nevada Great Basin also emit primarily α-pinene. However, in eastern Montana, the western Dakotas, the Rocky Mountain Front Range of Colorado and Wyoming, the Columbia Plateau of Eastern Oregon and Washington, the Sierra Nevada Range of California, and parts of the western Great Basin, β-pinene and $\Delta^3$-carene emissions equal or exceed those of α-pinene, due to the abundance of *Pinus contorta, monticola, ponderosa*, and their subspecies.

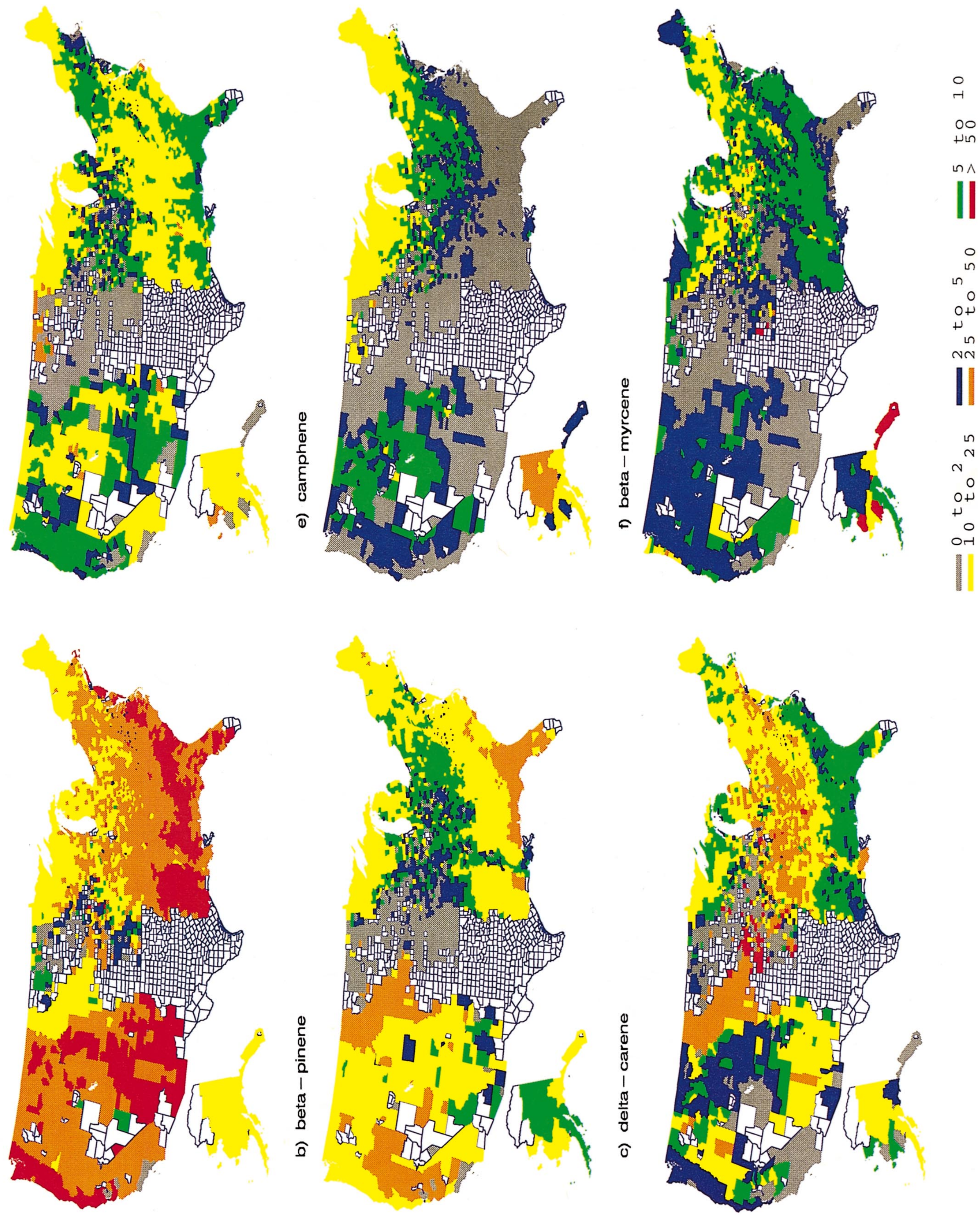
Forests in the northeast, midwest, and Appalachian regions have a much larger deciduous broadleaf component than most southern or western forests. Monoterpene composition there is more variable and, averaged spatially, is characterized by several compounds of similar abundance. The MC is composed of α-pinene (20–40%), $\Delta^3$-carene (10–40%), β–pinene (10–20%), *d*-limonene (5–20%), sabinene (10–25%), β-phellandrene (5–10%), ρ-cymene (5–10%), myrcene (0–5%), ocimene (0–5%), and terpinoline (0–5%). Most of the deciduous species MC profiles include significant amounts of ρ-cymene, and many include ocimene, sabinene, and β-phellandrene as well. In addition to its abundance in the interior western regions, $\Delta^3$-carene is estimated to be a substantial portion of the monoterpenes emitted in the midwest and Mississippi River Basin (Fig. 3c). This is largely due to its dominance in the MC of the *Acer* genus. *Acer rubrum* is a dominant species in these regions and is becoming increasingly so as a result of selective removal of more commercially valuable timber species such as the oaks. This allows shade tolerant and less commercially valuable species such as the maples to assume a greater abundance and dominant crown classes in eastern forest landscapes. It should be noted that EFs and MC of *Acer rubrum* are based on but a few branch enclosure measurements (Helmig et al., 1999; Zimmerman, 1979a).

Spruces (*Picea*) and balsam fir (*Abies balsamea*) are major forest components in the Northern US and Canada, and due to their desirable wood and pulp characteristics, their importance is increasing. Based on their dominance, the MC in much of the northern boreal forest region is expected to be a fairly even mix of the six major compounds [α-pinene (15–40%), β-pinene (10–20%), *d*-limonene (5–20%), $\Delta^3$-carene (5–15%), myrcene (5–10%) and camphene (10–20%)] in addition to β-phellandrene (5–10%) and terpinolene (1–5%).

*D*-limonene typically composes 1–10% of most *Pinus* species MC. In *Pinus echinata* and *P. resinosa*, estimates are on the order of 20% in limited sampling. It is more important in *Abies, Liquidambar, Picea,* and *Tsuga* genera where it is 10 to over 30% of MC. Consequently, it is estimated that *d*-limonene occurs in the greatest relative abundance in the northeastern US, Lake States region, Rocky Mountains, and Alaska, where it composes from 10–20% of total terpene emissions. Although basal EFs are low for *Quercus* and *Liriodendron* species, these species are dominant where they occur, and their MC appears to contain a high proportion of *d*-limonene, which accounts for its abundance in the large region extending from the Piedmont southern US to the Ozark region and the Ohio River Basin in the lower Midwest (Fig. 3d).

Camphene is present in the MC of many species in small proportions, but is more important in *Picea*, *Tsuga*, and *Acer* genera. It is estimated that camphene occurs in the greatest relative abundance in the northeastern US, Lake States region, and Central Alaska, where it may exceed 10% of total terpene emissions. It is estimated to be from 5 to 10% of MC in the Rocky Mountains and portions of the Midwest. Camphene is consistently very low ( < 2%) in the MC of the southern pines. It is a greater proportion of the MC (5–15%) of the genetically diverse Lake States Pines (*Pinus banksiana*, *resinosa*, and *strobus*). These proportions are reflected in the occurrence of camphene in Fig. 3e. This compound is also important in the leaf oil (Winer et al., 1992; Buttkus et al., 1977) and emission (Helmig et al., 1999) from the genus *Artemesia* (the sages) and may be important in the arid ecosystems featuring these shrubland species.

Myrcene typically composes less than 10% of the MC of most pine species, the notable exceptions being the white pines *Pinus strobus* and *P. monticola* and its relatives in the group *Strobi* of the *Pinus* subgenus *Haploxylon*, which have MC consisting of up 20% myrcene. It has not been reported in significant quantities from any major deciduous tree species, and is consistently found to compose 2% or less of their MC. *Picea* species contain 5–20% myrcene in their MC, and *Picea sitchensis* has been found to contain over 50% myrcene in both its leaf oil and emission samples. This is reflected in Fig. 3f, where the high proportion of myrcene in Alaska and the coastal Pacific Northwest is largely due to an abundance of this tree species and other spruces. Myrcene also reaches 10–20% of total monoterpene emissions in a band extending from the central Lake States to the lower northeastern US and Appalachians, largely due to the presence of *Pinus strobus* and *P. banksiana.*


a) alpha – pinene
b) beta – pinene
c) delta – carene
d) d – limonene
e) camphene
f) beta – myrcene
0 to 2
2 to 5
5 to 10
10 to 25
25 to 50
> 50

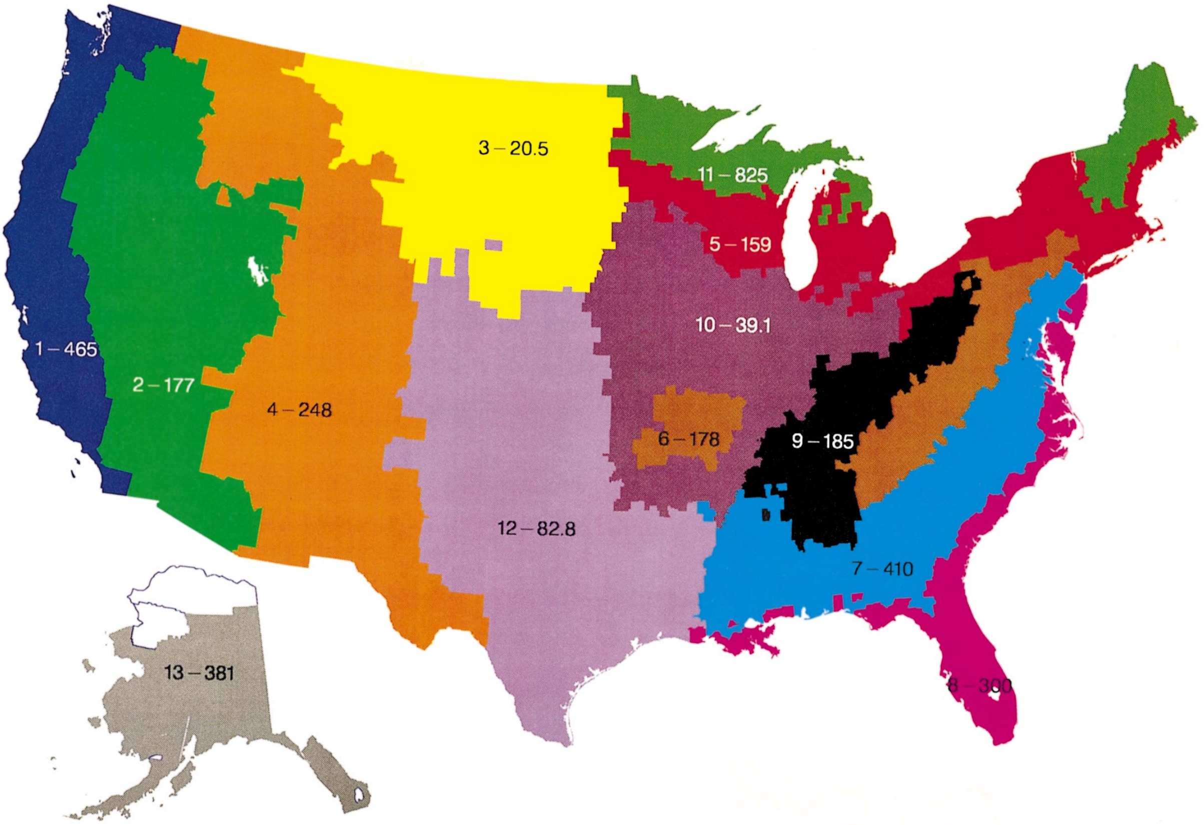


Fig. 4. Regions and regional average total monoterpene flux (μg carbon $m^{-2}$ $h^{-1}$) corresponding to the regions of Table 2. The numbers indicate region number follow by the average regional flux at 30°C.

The remaining eight monoterpene compounds are estimated to occur in less relative abundance, individually composing less than 5% of the estimated monoterpene emissions in most regions of the US. Exceptions are α-terpinene, which can account for up to 10% of monoterpene emissions in the Rocky Mountains and scattered woodlands of the upper Great Plains, since it is abundant in the leaf oil and emission of *Abies lasiocarpa* and *Pinus contorta* (von Rudloff and Lapp, 1987; Helmig et al., 1999). The most significant of these compounds could be β-phellandrene, as it has been found in abundance in the emission and leaf oil of the *Picea* genus, *Abies balsamea*, and several *Pinus* species. It is estimated to compose 5–20% of monoterpene emissions in portions of the Lake States, Northeast, Rocky Mountains, Coastal Pacific Northwest, and Alaska. This compound has been only tentatively identified in some foliage emission and ambient air samples (Janson, 1993; Street et al., 1996; Roberts et al., 1985,1983), and could be under-represented in some regions. It has been found to co-elute with *d*-limonene (Street et al., 1996; Arey et al., 1991) where DB-1 or similar type wax columns were used. β-phellandrene has been found in significant quantities in only one *Liquidambar styraciflua* (Zimmerman, 1979a) emission sample, and thus far does not appear in significant quantities in deciduous broadleaf tree species.

Ocimene emissions are very uncertain, but could compose a significant fraction ( > 20%) of monoterpene emissions in woodlands and riparian corridors in the Great Plains. However, total monoterpene emissions are expected to be low in these regions (Fig. 4, Table 2). It has been found in emission oil samples in recent studies of *Quercus, Liriodendron, Salix* species, and in *Citrus* trees as well. Emissions of ocimene from *Pinus pinea* have been

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Fig. 3. Maps showing the percentage of estimated total monoterpene emission composed by each of the six major monoterpene compounds (α-pinene, β-pinene, $\Delta^3$-carene, *d*-limonene, camphene, and myrcene) during summertime conditions.

Table 2
Estimated summertime hourly monoterpene flux (μg C $m^{-2}$ $h^{-1}$) by region and compound in the United States at leaf temperature of 30°C

| Region | αPin | βPin | $\Delta^3$Car | dLim | Camp | Myrc | αTer | βPhe | Sahi | pCym | Ocim | Thuj | Tero | γTer | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. West Coast | 225 | 105 | 23.7 | 29.3 | 14.4 | 19.1 | 5.0 | 9.0 | 15.9 | 2.8 | 0.3 | 0.20 | 2.5 | 0.5 | 465 |
| 2. Great Basin/E. WA-OR | 64.3 | 39.8 | 20.9 | 11.9 | 9.9 | 5.3 | 5.3 | 4.4 | 4.4 | 0.7 | 0.2 | 0.1 | 0.9 | 0.1 | 177 |
| 3. Northern Great Plains | 5.20 | 6.0 | 7.0 | 0.6 | 0.3 | 0.4 | 0.29 | 0.2 | 0.5 | 0.18 | 0.02 | 0.01 | 0.01 | 0.017 | 20.5 |
| 4. Interior West | 109 | 41.6 | 17.4 | 26.0 | 16.7 | 7.6 | 11.8 | 6.3 | 3.5 | 7.5 | 0.4 | 0.5 | 0.3 | 0.089 | 248 |
| 5. Northern Mixed Forest | 39.1 | 23.9 | 19.1 | 16.0 | 21.4 | 16.4 | 1.50 | 4.8 | 8.2 | 6.2 | 0.1 | 1.9 | 0.3 | 0.16 | 159 |
| 6. Appalachia / Ozarks | 58.4 | 20.2 | 37.4 | 20.6 | 11.1 | 13.2 | 0.6 | 1.6 | 7.2 | 3.7 | 0.2 | 1.1 | 2.7 | 0.097 | 178 |
| 7. Piedmont Southeast | 203 | 89.2 | 36.4 | 41.6 | 5.9 | 22.0 | 1.2 | 2.1 | 3.7 | 3.0 | 0.2 | 0.2 | 1.6 | 0.074 | 410 |
| 8. Coastal Southeast | 148 | 86.9 | 21.2 | 26.9 | 2.5 | 9.0 | 0.4 | 1.9 | 1.7 | 0.9 | 0.05 | 0.04 | 0.3 | 0.021 | 300 |
| 9. Forested MidAtlantic/ Midwest | 71.6 | 24.2 | 34.4 | 23.4 | 6.3 | 11.5 | 0.6 | 0.7 | 6.0 | 3.0 | 0.5 | 0.3 | 2.6 | 0.09 | 185 |
| 10. Agricultural Midwest | 18.1 | 5.0 | 5.1 | 5.8 | 0.8 | 0.8 | 0.1 | 0.1 | 0.8 | 0.5 | 0.2 | 0.032 | 0.7 | 0.04 | 39.1 |
| 11. Northern Coniferous Forest | 192 | 152 | 91.0 | 118 | 136 | 42.9 | 8.3 | 28.1 | 20.3 | 28.4 | 0.2 | 6.0 | 0.8 | 0.80 | 825 |
| 12. Southern Great Plains | 43.7 | 17.5 | 5.6 | 7.9 | 0.9 | 4.9 | 0.3 | 0.4 | 0.7 | 0.6 | 0.1 | 0.02 | 0.4 | 0.016 | 82.8 |
| 13. Southern/Coastal Alaska | 88.8 | 27.0 | 61.6 | 69.0 | 86.4 | 27.4 | 0.3 | 14.2 | 0.8 | 4.0 | 0.01 | 0 | 0.6 | 0.50 | 381 |

found to be light-dependent in recent European studies (Staudt et al., 1997). Similarly, ρ-cymene is also frequently found in deciduous broadleaf genera (*Betula, Carpinus, Cornus, Fagus, Ostrya, Quercus, and Salix*), as well as in a few conifers, notably *Pinus resinosa* and *Tsuga canadensis*. Its geographical distribution is similar to ocimene, and can compose 5–25% of monoterpenes in regions with low total monoterpene emission (Table 2, Fig. 4).

Sabinene composes about 5% of the MC of *Pseudotsuga menziesii, Thuja occidentalis, Pinus ponderosa*, and *P. strobus* and some deciduous genera, including some *Liquidambar* and *Quercus* species. It has been found to compose over 30% of *Acer rubrum* and *A. saccharum* MC, and is the most abundant compound in the leaf oil of *Sequoia sempervirens* and *Umbellularia californica*. It was found to be the only compound identified in the xylem resin of *Pinu s coulteri* (Mirov, 1961). It is estimated to compose 5–10% (occasionally greater) of emissions from forests on the west coast, lower Mississippi River Basin, the interior southwest, and a large region extending from the western Great Plains through the midwest and into southern New England.

Terpinolene is found in significant quantities ( > 5%) in *Liriodendron tulipifera, Carya* species, and *Cornus florida* and in small ( < 2%) fractions in the leaf oil and resin MC of all North American *Picea* species, *Pseudotsuga menziesii*, and a few *Pinus* species (*Pinus banksiana* and *P. sylvestris*). It is estimated to make up a few percent of emissions in scattered forests of the upper Great Plains and in deciduous forests of the lower midwest.

The compound α-thujene composes 1–10% of several regionally abundant conifers such as *Pinus strobus*, *Tsuga canadensis, Thuja occidentalis*, and *Juniperus* species. It composes about 5% of emissions in woodlands in the northwestern Great Plains and the central coast of California. Northeastern and Lake States forests with significant *Pinus strobus* and *Tsuga canadensis* are estimated to emit monoterpenes composed of 1–5% α-thujene. The compound γ-terpinene is very similar to α-thujene in its distribution within the western US. It composes 10–20% of the MC from the west coast species *Sequoia sempervirens* and *Umbellularia californica.* It is also found in *Juniperus scopulorum*, a common cedar of the midwestern states. We estimate that γ-terpinene makes up perhaps 5% of the monoterpene emissions from parts of the upper midwest and forests of central California.

Table 2 shows flux estimates of the individual compounds for 13 regions in the US. These regions and hourly summer total monoterpene flux from forests at 30°C are illustrated in Fig. 4. The regions dominated by coniferous forests have the highest monoterpene flux estimates. The northern coniferous and Alaskan forests are interesting in that less than 25% of estimated monoterpene emissions are accounted for by α-pinene. The west coast, interior west, and the southern pine regions

Table 3
Comparison of daytime ambient measurements of monoterpene composition (percentage with standard deviation in parentheses) with estimated monoterpene emission composition for the corresponding location proposed for BEIS3. References are Eastern GA (Guenther et al., 1996), Northern CO (Roberts et al., 1983,1985), Northern Idaho (Holdren et al., 1979), Western Alabama (Guenther et al., 1996), North Central Florida (Kim et al., 1995), eastern Tennessee (Holdren et al., 1979), and eastern California Sierra Nevada Mountains (Helmig and Arey , 1992). Trace amounts (t) represent less than 0.5% of total monoterpenes. Unquantified (but detected) or tentatively identified compounds are denoted by ∗. NA indicates that data are not available

| | Eastern GA | | Northern CO | | Northern ID | | Western AL | | Central FL | | Eastern TN | | Eastern CA | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cmpd | Observ. | BEIS3 | Observ. | BEIS3 | Observ. | BEIS3 | Observ. | BEIS3 | Observ. | BEIS3 | Observ. | BEIS3 | Observ. | BEIS3 |
| αPin | 36 (21) | 47 | 20 (2.4) | 12 | 41 (NA) | 48 | 49 (16) | 53 | 53 (NA) | 50 | 53 (11) | 38 | 48 (8.1) | 36 |
| βPin | 14 (6.0) | 32 | 36 (3.8) | 33 | 32 (NA) | 21 | 25 (11) | 20 | 27 (NA) | 33 | 26 (10) | 10 | 47 (7.4) | 31 |
| $\Delta^3$-car | 6.0 (4.1) | 9.1 | 19 (2.2) | 4.3 | 23 (NA) | 4.6 | | 5.3 | | 7.2 | ∗ | 24 | ∗ | 7.5 |
| d-lim | 17 (6.1) | 6.3 | 11 (3.9) | 7.8 | 4.0 (NA) | 4.1 | 26 (25) | 10 | 10 (NA) | 6.5 | 21 (16) | 11 | 1.9 (1.4) | 6.7 |
| camp | 3.0 (1.3) | 1.0 | 14 (3.7) | 12 | | 6.6 | | 1.3 | | 5.8 | ∗ | 4.1 | 3.1 (1.6) | 4.4 |
| myrc | 24 (15) | 2.1 | t | 2.6 | | 7.2 | | 6.1 | | 1.8 | | 5.1 | ∗ | 4.7 |
| sabi | | 0.9 | | t | | 1.8 | | 1.2 | | t | ∗ | 5.3 | ∗ | 6.2 |
| β-Phe | | 0.9 | ∗ | 19 | | 4.8 | | 0.7 | | 0.9 | | t | ∗ | 1.8 |
| α-Thuj | | 0 | ∗ | t | | 0 | | t | | 0 | | t | ∗ | 0 |
| tero | | t | | 0 | | t | | t | | t | | t | | 1.9 |
| α-Terp | | t | | 6.1 | | t | | t | | t | | t | | t |
| γ-Terp | | 0 | | 0 | | 0 | | t | | 0 | ∗ | 0 | | t |
| ρ-Cym | | t | | 1.6 | | t | | 1.0 | 10 | t | ∗ | 0.8 | ∗ | t |
| ocim | | t | | 1.1 | | t | | t | | 0 | ∗ | 0.6 | | t |

of the Piedmont and coastal southeast also have estimated fluxes which exceed 200 μg carbon $m^{-2}\,h^{-1}$. α-pinene composes over half of the emissions from these regions except for parts of the western US (Fig. 3). Northern mixed, midwestern, Appalachian, and Ozarks forests have a higher hardwood component and have emission rates of approximately 150 μg carbon $m^{-2}\,h^{-1}$. The great plains and agricultural midwest have sparsely scattered woodlands and low emission rates ( < 100 μg carbon $m^{-2}\,h^{-1}$). These rates are rather low in comparison to those of isoprene which can exceed 10,000 μg carbon $m^{-2}\,h^{-1}$ from oak forests under these conditions (Geron et al., 1994; Guenther et al., 1994). Uncertainties for fluxes of these individual terpenes are difficult to estimate given analytical difficulties and gaps in knowledge of basal EFs and environmental/physiological controls. Current models (Guenther et al., 1994) assume ± 50% uncertainty in basal EFs and roughly ± 40% uncertainty in biomass and landuse accuracy (Lamb et al., 1987). An assessment of the uncertainty in MC (e.g., Fig. 1) indicates that ± 30–50% is a reasonable estimate for the six major compounds, and likely more for the eight minor compounds. This results in estimates of roughly ± 150–200% for uncertainty in fluxes of individual compounds at 30°C. Canopy environment models and temperature correction algorithms can add 50–100% uncertainty to model estimates. The estimates shown here can be adjusted to ambient temperature using the exponential equations previously published (Guenther et al., 1993). However, the trees species composition and resulting flux estimates can vary significantly within these regions.

### 4.3. *Comparison of estimates with ambient measurements*

To assess how realistic these MC estimates might be, we compare estimated MC for regions where speciated monoterpenes have been measured in ambient air. The sites are located in eastern Georgia (Guenther et al., 1996), eastern California (Helmig and Arey, 1992) (Sierra Nevada Mountains), northern Colorado (Roberts et al., 1985,1983), northern Idaho (Holdren et al., 1979), western Alabama (Guenther et al., 1996), north central Florida (Kim et al., 1995), and eastern Tennessee (Helmig et al., 1998). The BEIS3 estimates were determined by applying the MC derived from the enclosure data (Table 1) for each tree species to the foliage quantities estimated for those corresponding species within approximately 50 km of the measurement site. Table 3 shows the relative proportions of the monoterpene compounds measured at each location versus that predicted from BEIS3. Note that reactivity of individual compounds is not taken into account in these comparisons. This could especially affect comparisons at the Alabama and Georgia sites where measurements were made in the convectively mixed layer (since the monoterpenes have more time to react with $O_3$ and OH) as opposed to surface measurements made at the other sites. The model estimates of the six major monoterpenes capture the relative abundance measured at each location reasonably well. At all sites except northern Colorado, α-pinene is the most abundant compound, typically followed by β-pinene and then other four major compounds. The Colorado site features abundant *Picea* species and *Pinus ponderosa,* which likely accounts for the high relative concentrations of β-pinene and $\Delta^3$-carene at this site. The BEIS3 estimates indicate that a significant proportion of β-phellandrene might be expected at the Colorado site. This compound was tentatively identified but not quantified there (Roberts et al., 1983). At the Alabama site, *d*-limonene levels were quite variable, sometimes reaching levels as high as 6 to 9 ppbv. The majority of the time, *d*-limonene levels were at relative concentrations expected from BEIS3. The ratios between α- and β-pinene are in general agreement with fluxes estimated in Alabama and Georgia (Guenther et al., 1996) and with relative concentrations at the other sites listed below. The compound $\Delta^3$-carene is not mentioned at three of the four eastern sites, but is predicted to be present, especially at the eastern Tennessee site, where it is predicted to compose 24% of the MC. It also should be noted that significant amounts of ρ-cymene, camphene, tricyclene, sabinene, and γ-terpinene were also identified but not quantified at this site (Helmig et al., 1998). Tricyclene sometimes appears in significant quantities in ambient and enclosure air samples. It often co-elutes with o-xylene or α-thujene (Winer et al., 1992) and may warrant more attention in future studies. Myrcene was also found to be a greater component in the emission MC than is estimated at the eastern Georgia site. With the exception of ρ-cymene at the Florida site, the minor compounds were not identified, quantified, or reported by the authors at the other field sites, and typically they were estimated to individually compose less than 2% of the MC at each site. It should be mentioned that, especially for the locations where concentrations were measured near the canopy surface, MC would be heavily impacted by vegetation more local than assumed here. Upon closer examination, this partially explains low predicted $\Delta^3$-carene proportions relative to ambient values at the Colorado and Idaho sites. *Pinus monticola* and *P. ponderosa* seem to be more abundant surrounding the measurement sites than in the larger modeling domain. Conversely, *P. ponderosa* is the only $\Delta^3$-carene emitting species among five locally abundant conifers at the California site. This likely explains the low concentrations reported here relative to model estimates. The high model estimates for α-pinene at the Colorado site could be partly due to the abundance of fir at this site, for which little data are available.

Although agreement appears reasonable for the comparisons of Table 3, data are limited, and measurements in midwestern, northeastern, and boreal regions are lacking. Mean MC estimated from *Pinus sylvestris* branch enclosure emission data also agree very well with an independent Scandinavian study (Peterson, 1988) where ambient monoterpenes were quantified over a *Pinus sylvestris* plantation. Ambient measurements/predicted MC % were: α-pinene 48/49, $\Delta^3$-carene 41/37, β-pinene 2/5.6, camphene 3/1.4, *d*-limonene 5/3, and myrcene 1/0.8. Trace amounts of β-phellandrene, ρ-cymene, sabinene, terpinolene, α-thujene, and γ-terpinene were also measured in the air above the forest, and likewise the branch enclosure data indicate that trace amounts of ρ-cymene and sabinene are emitted.

In the US, mixed layer (Guenther et al., 1996) and surface layer (Geron et al., 1994) flux estimates have shown reasonable agreement with emission estimates from BEIS2 ( ± 50%), while others (Geron et al., 1994; Arnts et al., 1982) have noted monoterpene emission rates much lower than would be predicted from BEIS2 under similar environmental conditions. Janson (1993) also stated that inventory methods used for Scandinavia at that time were likely to overestimate natural monoterpene emissions. Further research is needed to understand emission controls such as humidity (Schade et al., 1999), monoterpene pool size (Lerdau et al., 1995), and the relative significance of those compounds that do not seem to be stored in long-term pools and are emitted as a function of other factors such as photosynthetically active radiation (PAR). Forests are thought to control monoterpene emissions throughout most of North America. However, in some agricultural areas of the south, midwest, and western regions, croplands may contribute significant amounts of monoterpenes. Arid lands with significant amounts of sage (*Artemisia spp.*) and mesquite (*Prosopis spp.*) may be sources of camphor and other compounds. Non-invasive canopy to landscape scale flux studies are needed to place bounds on emission model estimates for forest, shrubland, and agricultural ecosystems. Additional data on water soluble compounds and oxygenates such as ocimene 1,8 cineole, camphor, bornyl acetate, and piperitone may be warranted.

Although we recognize the current uncertainty in these estimates of MC for the 14 compounds discussed here, we feel that this scheme represents a step forward in the BEIS system, and may prove helpful to modelers needing compound-specific estimates for the monoterpenes, such as those involved in studying rural aerosol formation. The importance of monoterpenes in aerosol formation has been stressed in several recent studies (Kavouras et al., 1998; Jang and Kamens, 1999). We encourage further examination of both the flux estimates and compound identification for forest and other landscape types.

## Acknowledgements

We are grateful to Pat Meredith, who provided excellent database management and editorial support for this study. Detlev Helmig provided data from the 1995 VOC study in Oak Ridge, TN. Nancy Adams, Frank Binkowski, and Allen Goldstein provided constructive reviews.

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