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The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions

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Abstract

The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1) is a modeling framework for estimating fluxes of 147 biogenic compounds between terrestrial ecosystems and the atmosphere using simple mechanistic algorithms to account for the major known processes controlling biogenic emissions. It is available as an offline code and has also been coupled into land surface models and atmospheric chemistry models. MEGAN2.1 is an update from the previous versions including MEGAN2.0 for isoprene emissions and MEGAN2.04, which estimates emissions of 138 compounds. Isoprene comprises about half of the estimated total global biogenic volatile organic compound (BVOC) emission of 1 Pg (1000 Tg or 10^{15} g). Another 10 compounds including methanol, ethanol, acetaldehyde, acetone, α-pinene, β-pinene, t-β-ocimene, limonene, ethene, and propene together contribute another 30 % of the estimated emission. An additional 20 compounds (mostly terpenoids) are associated with another 17 % of the total emission with the remaining 3 % distributed among 125 compounds. Emissions of 41 monoterpenes and 32 sesquiterpenes together comprise about 15 % and 3 %, respectively, of the total global BVOC emission. Tropical trees cover about 18 % of the global land surface and are estimated to be responsible for 60 % of terpenoid emissions and 48 % of other VOC emissions. Other trees cover about the same area but are estimated to contribute only about 10 % of total emissions. The magnitude of the emissions estimated with MEGAN2.1 are within the range of estimates reported using other approaches and much of the differences between reported values can be attributed to landcover and meteorological driving variables. The offline version of MEGAN2.1 source code and driving variables is available from http://acd.ucar.edu/~guenther/MEGAN/MEGAN.htm and the version integrated into the Community Land Model version 4 (CLM4) can be downloaded from http://www.cesm.ucar.edu/.

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1 Introduction

Terrestrial ecosystems produce a diverse array of chemicals including many volatile and semi-volatile compounds that are emitted into the atmosphere. Some of these have an important role in atmospheric chemistry including reactive Volatile Organic Compounds (VOC) for which terrestrial ecosystems are by far the biggest contributors to the global annual flux. It is now widely recognized that these chemicals can influence atmospheric composition and quantitative estimates of their emissions into the atmosphere are needed for numerical assessments of past, present and future air quality and climate. A few biogenic compounds are now routinely included in air quality and earth system numerical models but the magnitude and variability of these emissions are not well known. Many other compounds are simply omitted from these models because they are thought to be unimportant or because their contribution is assumed to be accounted for by increasing the emission of the compounds that are included in the models or because so little is known about the emission of these compounds.

The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1) is used to estimate emissions of compounds from urban, rural and agricultural ecosystems that can influence the atmosphere. MEGAN2.1 has been updated from MEGAN2.0 (Guenther et al., 2006) and MEGAN2.02 (Sakulyanontvittaya et al., 2008) to include additional compounds, emission types, and controlling processes. MEGAN has simple mechanistic algorithms that account for the major known processes controlling biogenic emissions. Emissions of 147 chemical species are included (see Table 1) and the model can output individual compounds or categories associated with various atmospheric chemistry mechanisms. MEGAN is a global model with 1 km (or less) spatial resolution that can be used for both regional air quality modeling and global earth system modeling studies. Emissions can be estimated using any weather and landcover data and the model results are very sensitive to these driving variables.

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2 MEGAN compounds and sources

There are thousands of chemical species that are emitted into the atmosphere from terrestrial landscapes but only a small fraction of these compounds are known to have a measurable impact on the atmosphere. Most of the atmospherically relevant compounds are organics including compounds containing oxygen, nitrogen, sulfur or halogens. Inorganic compounds emitted from terrestrial ecosystems include two of the most important for the atmosphere, carbon dioxide and water. These compounds are the focus of many other models and their emission is not included in MEGAN although the response of other emissions to carbon dioxide and water is included. Earlier biogenic emission models (e.g. Lamb et al., 1987; Guenther et al., 1995) identified a few major compounds, such as isoprene and α-pinene, and grouped the rest into an undefined "other" category. Although we are no doubt missing some unknown compounds that are important for the atmosphere, MEGAN estimates only emissions of known compounds and includes additional compounds whenever they are identified as being of potential interest for the atmosphere. MEGAN2.1 calculates emissions of carbon monoxide (CO) and 146 organic compounds. These 147 compounds are lumped into the 19 categories shown in Table 1 based on how emissions vary in response to changes in environmental conditions including temperature, light, and stress. Emission variations are estimated for the 19 categories and then emissions are calculated for each of the 147 individual compounds or can be output in chemical categories associated with common atmospheric chemistry schemes (e.g. CB05, MOZART). The 19 emission categories are described in the following sections and include terpenoid, stress compounds (including some terpenoids), bidirectional exchange compounds and other compounds.

MEGAN includes all major terrestrial ecosystem emission sources except for biomass burning which is the focus of a companion model, FINN (Wiedinmyer et al., 2011). The major emission sources in terrestrial ecosystems are plants and soil microbes. Humans, wild and domestic animals, insects, fungal and abiotic sources

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also emit chemicals into the atmosphere but are generally considered to be of less importance. Exceptions include emissions from animal feedlots which are not considered in MEGAN. Foliage is thought to be the dominant vegetation source but emissions from woody tissues, roots, fruits and flowers may make important contributions for some compounds and more research is needed to quantify these sources. The MEGAN emission factors represent the sum of all emission sources in an ecosystem and so all of these sources are included but may be highly uncertain.

A single compound, e.g. α-pinene, can be emitted by different sources controlled by a variety of processes while emissions of other compounds are dominated by a single source. Some compounds are stored in tissues that are isolated from the atmosphere and are emitted only if these tissues are damaged. Other compounds are stored in structures that are open to the atmosphere and continuously emitted. Compounds can also be not stored but released immediately after production. In addition, each of these sources can be constitutive or induced. Constitutive compounds are always present in an organism while induced compounds are produced in response to some external stress factor such as extreme weather or herbivory. This array of sources and controlling processes complicate efforts to identify and characterize biogenic emissions. The MEGAN approach of assigning a whole canopy emission rate, which can be based on whole canopy flux measurements, enables the model to account for all ecosystem emission sources even if they have not been identified. However, an accurate understanding of the contributions of each ecosystem component, and the controlling processes, is needed in order to correctly extrapolate emissions to entire regions and predict future changes in emissions.

2.1 Terpenoid compounds

Terpenoid compounds have long been considered the dominant global biogenic volatile organic compound (BVOC) (Guenther et al., 1995). This incredibly diverse group includes thousands of chemical species that can be classified as hemiterpenoids (C_5), monoterpenoids (C_{10}), sesquiterpenoids (C_{15}), homoterpenes (C_{11} and C_{16}),

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diterpenoids (C_{20}) and larger compounds with such low volatility that it is unlikely that they are emitted into the atmosphere in a gaseous form. Terpenoids include oxygenated terpenes such as the hemiterpenoid methyl-butenol (MBO), the monoterpenoid linalool, and the sesquiterpenoid cedrol although they tend to be a small portion of the total terpenoid emission. About half of the 147 chemical species included in MEGAN2.1 are terpenoid compounds including some that are major contributors to global BVOC emissions (e.g. isoprene, α-pinene) and others that are minor components of the global flux.

2.1.1 Monoterpenoids

Investigations of BVOC began centuries ago with interest in commercial applications of monoterpenes in the flavor and fragrance industry. These activities led to the development of diverse analytical techniques and a considerable body of literature describing terpenoid production and distribution in the oleoresins stored within plant tissues. Very little of this information has been incorporated into BVOC emission models because the production of monoterpenes by plants and their release into the atmosphere are not always well correlated and only a small fraction of the hundreds of monoterpene compounds identified in essential oils have been observed as significant atmospheric BVOC emissions. Seven monoterpenes are represented in MEGAN2.1 as individual categories and 34 are included in the "other monoterpene" category (Table 1). Many of the species in the "other monoterpene" category are oxygenated compounds including some multifunctional oxygenates and acetylated compounds that may make a disproportionate contribution to secondary aerosol production. Some of these compounds (e.g. β-ionone, ipsenol and estragole) are not produced through the monoterpene biochemical pathway but are included here because of their similar chemical structure.

Six of the seven monoterpenes included as specific MEGAN2.1 categories (α-pinene β-pinene, limonene, sabinene, 3-carene, and myrcene) were identified as dominant components of monoterpene emissions into the atmosphere more than thirty years ago (summarized by Guenther et al., 1994). However, few literature studies report all of the

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compounds that were detected and some compounds may have been reported more frequently in the past two decades simply because these compounds were targeted based on reports in previous studies. The seventh MEGAN2.1 monoterpene category, trans-β-ocimene (referred to here as ocimene) was observed in earlier reports but not generally considered a major contributor. Because ocimene emission is associated with stress-induced, light-dependent emission, it is not always emitted by plants but when it is observed the rates are typically much higher than most monoterpene emission rates. The large variability and limited knowledge of stress controlling factors leads to more uncertainty associated with ocimene emission estimates but ocimene emission appears to be widespread in both needleleaf and broadleaf plants and has been observed as a component of above-canopy fluxes.

Characterizing monoterpene emissions with enclosure measurements is challenging due to the presence of storage structures which can be disturbed resulting in emissions at rates much higher than for undisturbed conditions. It was initially thought that all monoterpenes emanated from these storage pools and were controlled only by leaf temperature but the discovery of high emission rates of light-dependent monoterpene emissions, produced from recently synthesized carbon in a manner similar to isoprene, from European and African savanna trees (Kesselmeier et al., 1996; Greenberg et al., 2003), tropical forest landscapes (Karl et al., 2007) and common boreal conifers (Ghirardo et al., 2010) required the introduction of multiple emission processes for chemical species in MEGAN.

Above-canopy flux measurements integrate over the entire landscape without disturbing monoterpene emission rates (e.g. Karl et al., 2005). Capabilities for quantifying biogenic VOC fluxes have been steadily improving over the past decade including recent analytical advances such as the Time-of-Flight Proton Transfer Reaction Mass Spectrometer (TOF-PTRMS) that enables accurate and reliable measurement of total monoterpene fluxes. Speciation into individual monoterpene fluxes can be accomplished by collecting samples using gradient or relaxed eddy accumulation systems and analyzing with Gas Chromatographic (GC) techniques. Aircraft flux systems have

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footprints of a few km and can characterize fluxes over entire domains of regional models (Karl et al., 2007). Tower-based flux systems typically have a footprint of hundreds of meters and are well suited for quantifying diurnal, seasonal, and inter-annual variations. Biogenic VOC fluxes have been measured at more than 45 tower locations (Guenther et al., 2000; Kesselmeier et al., 2009) but most of these studies only characterized emissions for a short period of time. The existence of a global network of more than 500 flux towers constructed for water, carbon and energy flux studies provides an opportunity to add biogenic VOC measurements without the cost of basic site development (Guenther et al., 2011). Measurements at a large number of sites can be accomplished with low-cost and low-power measurements systems (e.g. relaxed eddy accumulation).

The starting point for the monoterpene emission measurements used to parameterize MEGAN2.1 is the global database of Guenther et al. (1995). These observations have been supplemented with summaries for North America (Guenther et al., 2000; Geron et al., 2000; Sakulyanontvittaya et al., 2008), South America (Greenberg et al., 2004; Karl et al., 2007), Europe (Karl et al., 2009), Africa (Guenther et al., 1999; Otter et al., 2003) and Asia (Klinger et al., 2002; Tie et al., 2006).

2.1.2 Isoprene

Organic chemists investigating monoterpenes in the late 1800s identified the hemiterpene, isoprene (2-methyl-1,3-butadiene), as the biochemical precursor of monoterpenes but it was thought to exist only within plant tissues. The discovery of substantial isoprene emissions from plants into the atmosphere was discovered more than 50 yr ago and was initially controversial (Rasmussen and Went, 1965) but for the past several decades isoprene has been recognized as the dominant global BVOC emission (Guenther et al., 1995). Isoprene contributes about half of the total global BVOC flux and so it is not surprising that it has been investigated more extensively than any other atmospheric BVOC. MEGAN isoprene emissions are based on a simple mechanistic model that considers the major processes driving variations in isoprene emissions. This

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includes a light response that is based on electron transport (Guenther et al., 1991), a temperature response based on enzymatic activity (Guenther et al., 1991), and a CO_2 response based on changes in metabolite pools, enzyme activity and gene expression (Wilkinson et al., 2009). Other studies have characterized the response of isoprene emissions to factors including leaf age (Petron et al., 2001), nutrient availability (Litvak et al., 1996), weather of the past 1 to 10 days (Sharkey et al., 1999; Geron et al., 2000; Hanson and Sharkey, 2001) and the chemical composition of the atmosphere (Loreto et al., 2004; Rosenstiel et al., 2003). Since many emission measurements are reported without these accompanying ancillary information, these observations are useful only for assigning vegetation into emitting and non-emitting categories.

The isoprene measurements used to develop the MEGAN2.1 emission factors and emission algorithm parameterizations are described by Guenther et al. (2006) and Heald et al. (2009). Most of the dominant tree genera and species in temperate and boreal forests have been characterized at least to the level of emitter or non-emitter and this information was combined with tree inventories to estimate ecoregion average isoprene emission capacities for individual Plant Functional Types (PFTs). Tropical forest isoprene emission factors are based primarily on above-canopy measurements due to the high species diversity.

2.1.3 Sesquiterpenoids

Sesquiterpenes (SQT) are a major component of essential oils stored by some plants, especially broadleaf trees, and can also be directly emitted without being stored. While some sesquiterpenes, such as longifolene, have atmospheric oxidation lifetimes (hours) that are similar to the dominant monoterpenes, such as α-pinene, the most dominant sesquiterpenes emitted into the atmosphere (β-caryophyllene and farnesene, each included as separate categories in MEGAN2.1) are much more reactive. The high reactivity and low volatility of these sesquiterpenes makes them considerably more difficult to detect and quantify and few earlier studies included sesquiterpene emission measurements since they were generally thought to be a

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minor contribution in comparison to monoterpenes. Efforts to quantify sesquiterpene emissions increased in the past decade with the growing interest in atmospheric secondary organic aerosol (SOA). Although sesquiterpenes are only a minor fraction of total BVOC, they have been recognized as important for atmospheric SOA due to their relatively high yields (Sakulyanontvittaya et al., 2008).

SQT emissions have been detected from numerous plant species including conifer and broadleaf trees, shrubs and agricultural crops. Duhl et al. (2008) reviewed laboratory and field studies of leaf age, light and temperature controls over SQT emissions and recommended emission factors for major vegetation types although they also noted a large variability within each type. The SQT emission factors and emission algorithm parameterizations used for MEGAN2.1 are based on the measurements summarized by Duhl et al. (2008).

2.1.4 2-Methyl-3-buten-2-ol

The production and emission of the hemiterpene alcohols, methylbutenols, by insects and flowers has been known for many years. Two of these compounds, 3-methyl-2-buten-1-ol and 3-methyl-3-buten-1-ol, have been observed as minor components of ecosystem BVOC emissions and are grouped with the minor BVOC in Sect. 2.6. A third compound, 2-methyl-3-buten-2-ol (referred to here as MBO) is of greater importance. It was identified as an important atmospheric BVOC in a Rocky Mountain subalpine forest by Goldan et al. (1993). It is a major emission for some, but not all, *Pinus* (pine tree) species (Harley et al., 1998) and so is a dominant BVOC emission in many western North American forests but is only a minor component of global emissions. Interestingly, MBO is emitted by both European bark beetles and North American pine trees but is not emitted in substantial amounts by either European pines or North American bark beetles. The MEGAN2.1 emission factors and response to light and temperature are based on enclosure and above-canopy flux measurements (Harley et al., 1998; Schade et al., 2000; Baker et al., 2001; Karl et al., 2002; Gray et al., 2005; Kim et al., 2010).

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2.2 Methanol, acetone and carbon monoxide

Methanol and acetone are among the most abundant VOC in the global atmosphere. High concentrations of atmospheric methanol and acetone reported by investigators beginning in the 1960s were attributed primarily to the atmospheric oxidation of VOC with minor contributions from bacteria, biomass burning and anthropogenic sources (Snider and Dawson, 1985). In the early 1990s, MacDonald and Fall (1993a) discovered high rates of methanol emissions from vegetation foliage, especially young expanding leaves. Lower rates of acetone emissions were observed from conifer buds (MacDonald and Fall, 1993b). A few years later, Warneke et al. (1999) found a smaller but significant abiotic source of methanol and acetone from decaying leaf litter.

Jacob et al. (2005) estimated that terrestrial ecosystems (biotic and abiotic) dominate the global methanol emissions with 78 % of the global annual production and the remainder being from atmospheric oxidation of VOC (15 %), biomass burning (5 %), and urban (2 %) sources. Millet et al. (2008) concluded that oceans were responsible for 35 % of the global methanol emission and assigned a contribution of 42 % to terrestrial ecosystems. The MEGAN2.1 methanol emission factors and algorithms, and the observations they are based on, have been described and evaluated with comparison to satellite and aircraft observations by Stavrakou et al. (2011).

An analysis of the global acetone budget by Jacob et al. (2002) included contributions to total emissions from terrestrial ecosystems (37 %), atmospheric oxidation of VOC (29 %), ocean (28 %), biomass burning (5 %) and anthropogenic emissions (1 %). A more recent analysis by Fischer et al. (2012) concluded that terrestrial ecosystems were responsible for only 22 % and oceans contributed 55 %. Enclosure (MacDonald and Fall 1993b; Janson et al., 1999) and above canopy eddy flux (Karl et al., 2002, 2004; Baker et al., 1999; Schade et al., 2001) studies have been used to establish the MEGAN2.1 acetone emission factors and response to light and temperature.

CO is a major constituent of the global atmosphere and has many different sources. The formation of CO in vegetation is the result of direct photochemical transformation

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and occurs inside the leaf (Tarr et al., 1995). The factors controlling these emissions are not well known and biogenic CO emission estimates are very uncertain. The MEGAN2.1 emission factors and algorithms are based on the Guenther et al. (2000) recommendation of an emission factor of 0.3 $\mu g\, C\, g^{-1}\, h^{-1}$. The resulting CO emission is about 3 % of the global total CO emissions estimated by Granier et al. (2000), which is dominated by anthropogenic CO emissions.

2.3 Bidirectional exchange compounds

Kesselmeier (2001) described both the atmospheric importance of short chained oxygenated VOCs (e.g. acetaldehyde, formaldehyde, acetic acid, formic acid) and the challenge of quantifying their atmospheric budgets. This includes the following challenges: (1) there are both natural and anthropogenic sources of these compounds, (2) there are both primary and secondary (atmospheric oxidation) sources, (3) these compounds are difficult to measure, and (4) vegetation is both a source and a sink of these compounds. The strong bidirectional exchange exhibited by these compounds requires their inclusion in a separate MEGAN2.1 category. Accurate simulation of land-atmosphere fluxes of these compounds requires estimates of their atmospheric concentrations and the compensation point for each compound. As an intermediate step, MEGAN2.1 includes a simple approach described by Millet et al. (2010).

2.3.1 Acetaldehyde and ethanol

Alcoholic fermentation in the leaves and roots of plants produces ethanol which is converted to acetaldehyde in a pathway leading to acetate consumption (Millet et al., 2010). The major sources of atmospheric acetaldehyde are oxidation of VOC (60 %), ocean (27 %) and terrestrial ecosystems (11 %). Biomass burning and anthropogenic emissions contribute to the remaining 2 % (Millet et al., 2010). The introduction of the PTRMS technique has provided an increasing number of measurements of acetaldehyde emissions from vegetation, including whole-canopy flux measurements, while

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there remain relatively few data for ethanol. The MEGAN2.1 acetaldehyde and ethanol emission factors and algorithms, and the measurements used to develop them, are described by Millet et al. (2010).

2.3.2 Formic acid, acetic acid, and formaldehyde

Substantial emissions of formaldehyde, and lesser amounts of formic and acetic acid, have been reported from studies using enclosure measurements to investigate various tree species (Kesselmeier et al., 1997; Kreuzwieser et al., 1999; Martin et al., 1999; Kesselmeier, 2001). While emissions can be considerable, there is also the potential for a strong uptake of these compounds. The MEGAN2.1 emissions are based on these enclosure measurements, which suggest that emissions of these three compounds are small, although with a large uncertainty. Recent studies using above-canopy measurements have provided evidence that formaldehyde and formic acid emissions could be much larger. Stavrakou et al.'s (2012) analysis of satellite data suggests that formic acid emissions are two to three times higher than estimated from known sources. They show that 90 % of formic acid has a biogenic origin which includes direct emission and production from terpenoids. The first whole canopy fluxes of formaldehyde measured by eddy covariance have recently been reported by DiGangi et al. (2011). The above canopy flux, a net emission, is much higher than predicted from enclosure measurements, but this may be because the flux includes both primary emissions and within-canopy production. Measurements to better constrain formic acid and formaldehyde fluxes should be a priority for future studies.

2.4 Stress compounds

Niinemets (2010) recently reviewed the environmental and biotic stresses that can substantially modify emission rates of biogenic VOC and concluded that a quantitative understanding of stress effects was needed in order to accurately represent these emissions in numerical models. Stress tolerance, timing, duration, and severity were

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identified as the key factors controlling emissions variations in response to stress. In order to highlight BVOC that are especially sensitive to stress, MEGAN2.1 includes fifteen compounds in a stress emission category (Table 1). In addition, a monoterpene (ocimene) and a sesquiterpene (farnesene) that are highly sensitive to induced stress are assigned their own categories. The current limited knowledge precludes a quantitative treatment of emission variations due to stress and so the current estimates of these compounds are highly uncertain. The resulting estimates provide a first step towards assessing the importance of these BVOC emissions and the need for additional measurements. The observations used to assign MEGAN2.1 emission factors for the fifteen stress compounds listed in Table 2 are described in this section.

Ethene is an important phytohormone and its emission rate from plants has been used as an indicator of stress (Wellburn and Wellburn, 1996). The global ethene estimate of Sawada and Totsuka (1986) was the first global estimate for a non-terpenoid BVOC. They extrapolated enclosure measurements showing widespread ethene production by plants in most landscapes. Rudolph (1997) reported a much smaller global emission estimate based on atmospheric concentration distributions. Canopy scale fluxes measured by Goldstein et al. (1996) above a temperate deciduous forest confirmed that substantial amounts of ethene were released into the atmosphere from this landscape. The Goldstein et al. (1996) canopy scale fluxes agree reasonably well with the Sawada and Totsuka enclosure measurements and are used as the basis for the MEGAN2.1 parameterization of ethene emissions.

Elevated emissions of green leaf volatiles (e.g. cis-3-hexenal, trans-2-hexenal, hexanal, 1-hexanol and cis-3-hexenol), monoterpenes (e.g. ocimene), sesquiterpenes (e.g. farnesene), homoterpenes including dimethyl-nonatriene (DMNT) and trimethyltridecatetraene (TMTT), aromatics (e.g. toluene, indole, methyl salicylate), and jasmonates (methyl jasmonate and jasmine) are among the most important compounds observed in response to plant stress (Poulton, 1990; Heiden et al., 1999; Engelberth et al., 2004; Turlings and Ton, 2006; Niinemets, 2010). Due to the importance of these emissions for plant-herbivore and plant-pathogen interactions, there have been many

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investigations of the biochemical pathways and the roles of these emissions in plant defense (Kant et al., 2009). In comparison, there are few observations suitable for incorporating into emission models.

Warneke et al. (2002) quantified above-canopy fluxes of methanol and cis-3-hexenal from an undisturbed alfalfa field in Colorado. Emissions of the two compounds were greatly increased during harvesting and continued to emit at high rates as the alfalfa was drying. In addition, fluxes of hexenylacetate, 1-hexenol, hexanal, and butanone were observed during harvesting. Similar results have been observed with lawn mowing and hay harvesting resulting in emissions that dominate total fluxes from some regions during periods of harvesting (Karl et al., 2001). In addition to the Warneke et al. (2002) and Karl et al. (2001) eddy flux studies, the MEGAN2.1 parameters for these compounds are based on the enclosure measurements of König et al. (1995) and Kirstine et al. (1998). Karl et al. (2008) used the eddy covariance technique to quantify canopy-scale fluxes of methyl salicylate from a walnut plantation and observed a strong correlation with both temperature and water stresses. Heiden et al. (1999) used enclosure techniques to characterize toluene emissions from stressed and unstressed plants. Shim et al. (2007) used inverse modeling to estimate global average biogenic emissions of hydrogen cyanide which is emitted from thousands of plant species, including many economically important food plants, when they are wounded.

2.5 Other compounds

An additional 49 compounds are included in the MEGAN2.1 "other compound" category (Table 1). This includes leaf surface compounds, organic halides, sulfur compounds, alkanes, alkenes and benzenoids. The observations used to assign MEGAN2.1 emission factors for the "other" compounds listed in Table 2 are described in this section.

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2.5.1 Semi-volatile leaf surface compounds

Leaf surfaces are covered by a waxy material that serves as a barrier for keeping water in and keeping pathogens out. Straight-chain hydrocarbons ranging from C_{16} to C_{36} are the dominant components of epicuticular leaf waxes but there are a variety of other constituents (Baker, 1982). This includes semi-volatile compounds that can be found in gas phase, especially with the high leaf temperatures (>40 °C) that occur in hot deserts. Matsunaga et al. (2008) observed significant emissions of the "sunscreen" compounds, homosalate ($C_{16}H_{22}O_3$) and 2-ethylhexyl salicylate (also known as octyl salate) ($C_{15}H_{22}O_3$), from Mojave desert plants and much lower emissions from temperate forest tree species. They were the major BVOC emission observed from mesquite (*Prosopis* spp.) which dominates large areas in the southwestern US. These photoprotective plant wax components are used in commercial sunscreens and protect plant tissues by absorbing harmful UV solar radiation.

The oxidation of plant waxes by ozone and other atmospheric oxidants produces volatile and semi-volatile products that are emitted into the atmosphere. For example, Fruekilde et al. (1998) observed significant emissions of geranyl acetone ($C_{13}H_{22}O$), 4-oxopentanal ($C_5H_8O_2$) and methyl heptenone when leaf surfaces were exposed to high levels of ozone.

2.5.2 Organic halides

MEGAN2.1 organic halides emissions include methyl bromide, methyl chloride and methyl iodide. These compounds are emitted into the atmosphere at relatively low rates but they are a significant source of halogens in the stratosphere where they are of interest because of their potential to cause ozone depletion. Quantifying the impact of terrestrial ecosystems on atmospheric organic halides is complicated by the presence of both sources and sinks but they are thought to be a net global source (Rhew et al., 2000; Yoshida et al., 2006; Sive et al., 2007). Known methyl chloride and methyl bromide sources are lower than known sinks and terrestrial ecosystems are thought to

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be contributors to the missing source, especially in the case of methyl chloride (Cox et al., 2005; Yoshida et al., 2006). Terrestrial emissions of these compounds follow diurnal and seasonal variations similar to those observed for other trace gases with higher emissions during the growing season (Rhew et al., 2000).

2.5.3 Sulfur compounds

Sulfur compounds are produced in both soils and vegetation in terrestrial ecosystems and emitted into the atmosphere at rates that are low compared to anthropogenic sulfur emissions but can be significant in pristine regions. Enclosure and micrometeorological measurements of biogenic sulfur emissions have been summarized by Bates et al. (1992). MEGAN2.1 emission factors and parameterizations for carbon disulfide, carbonyl sulfide, hydrogen sulfide, methyl mercapten, dimethyl sulfide and dimethyl disulfide are based on the values recommended by Bates et al. (1992). Measurements of diallyl disulfide, methyl propenyl disulfide, propenylpropyldisulfide reported by Puxbaum et al. (1997) are the basis of the MEGAN2.1 values for these compounds.

2.5.4 Alkenes

MEGAN2.1 includes contributions from other alkenes including propene and butene emissions which were quantified with above canopy flux measurements by Goldstein et al. (1996). Emissions of larger alkenes (1-dodecene, 1-tetradecene) have been quantified using enclosure measurements (Arey et al., 1991). In addition to the 232-methylbutenol discussed in Sect. 2.1.3, other methylbutenols include prenol, (321-MBO) an important flavour and fragrance compound, and 331-MBO, an aggregation pheromone of bark beetles e.g. *Ips cembrae*, (Stoakley et al., 1978).

1,3-octenol provides the characteristic odor of mushrooms and has been quantified in emissions from Fescue (Tava et al., 1995). Neryl acetone (Helmig et al., 2006) terpinyl acetate (Yani et al., 1993) and nonenal (Helmig et al., 1999) have also been observed using enclosure measurement techniques.

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2.5.5 Alkanes

Non-methane alkanes emitted from terrestrial ecosystems include ethane (Burr et al., 1991; Kirstine et al., 1998), propane (Janson et al., 1999), pentane (Isidorov 1985), hexane (Owen et al., 1997) and heptane (Savage et al., 1996). Although the rates reported by these investigators are typically negligible in urban areas in comparison to anthropogenic emissions of these compounds, they are included in MEGAN2.1 in recognition of the presence of biogenic sources. The MEGAN2.1 parameters for saturated aldehydes (hexanal, heptanal, octanal, nonanal, and decanal) are based on the measurements reported by Wildt et al. (2003). Other MEGAN2.1 unsaturated oxygenated VOC include octanol (Tava et al., 1995), heptanone (Connick et al., 1989), 2-butanone (Kirstine et al., 1998; Warneke et al., 2002) and pyruvic acid (Talbot et al., 1990).

2.5.6 Benzenoids

A variety of benzenoid compounds (aromatics) are produced by plants for signaling (e.g. attract pollinators with floral scents) and defense (Dudareva et al., 2006). These include compounds such as toluene and methyl salicylate that are included with the stress compounds described in Sect. 2.4. Many others are well known as components of floral scents and selected compounds have been included in MEGAN2.1 to represent this large class of compounds. These benzenoid compounds may also have a role in plant response to stress. Emission rate estimates of benzaldehyde, methyl benzoate, 2-phenylacetaldehyde, eugenol, benzyl acetate, benzyl alcohol, and naphthalene have been reported (Tava et al., 1995; Kirstine et al., 1998; Turlings et al., 1998; Kolosova et al., 2001; Krauss et al., 2005; Knudsen et al., 2006; Baghi et al., 2012) and these data have been used to assign the MEGAN2.1 parameters.

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2.6 Atmospheric biogenic compounds not included in MEGAN

Chemical species continue to be added to the list of known atmospheric biogenic compounds and it is likely that there are additional important compounds that have not yet been identified. Some compounds have escaped detection because they cannot be observed with the standard measurement techniques which previously was limited to preconcentration, thermal desorption and gas chromatography with flame ionization detection. Additional compounds were identified when gas chromatography with detection by mass spectrometry became widely available. The development and application of Proton Transfer Reaction Mass Spectrometry provided an important tool for identifying additional BVOC and their oxidation products (Karl et al., 2008). The continued development and application of analytical techniques for additional BVOC, especially semi-volatile compounds, is needed to identify more compounds.

In addition to requiring appropriate analytical tools, the detection of some BVOC requires extensive spatial and seasonal emission surveys. For example, methyl butenol is a regionally dominant emission in western North America but has negligible emissions in other regions. Significant emissions of some compounds occur only in response to specific stresses while others are associated with phenological events. These compounds would likely be missed by the short-term measurements characteristic of most BVOC studies.

Atmospheric BVOC are of interest primarily because of their impact on important atmospheric constituents including oxidants and particles. The importance of undetected BVOC can be constrained by measuring the loss or growth rate of oxidants and particles and comparing these observations with expected rates based on measurements of compounds that can be detected. Evidence for the existence of undetected compounds have been reported based on loss rates of hydroxyl radical (OH) and ozone and growth rates of aerosols.

Di Carlo et al. (2004) were unable to account for the observed OH reactivity above a forest canopy in northern Michigan and concluded that unidentified BVOC were the

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most likely candidates for this “missing OH reactivity”. This was based primarily on the observation that the amount of missing reactivity responded to temperature in a manner that closely follows the expected behavior of BVOC emissions. It was also noted that this was a rural area with few local air pollution sources. The missing OH reactivity was about equal to the known OH reactivity which was dominated by isoprene. Subsequent studies measured a more comprehensive suite of OH-reactive gases and particles but still found that the missing OH reactivity is about half of the total at rural sites and considerably less at urban sites (Lou et al., 2010). Kim et al. (2011) revisited the same Michigan site studied by Di Carlo et al. (2004) and used enclosure measurements to quantify the missing OH reactivity of the BVOC emissions of individual plant species. They concluded that primary biogenic emissions may not be responsible for the missing OH reactivity and that BVOC oxidation products were the most likely source.

Kurpius and Goldstein (2003) estimated individual components of the ozone flux to a pine plantation and suggest that a large flux of unknown BVOC (an order of magnitude higher than the known VOC) was needed to explain the observed ozone depletion near the surface. They also reviewed other reported ozone flux measurements and found that the existence of a large flux of unknown BVOC is not inconsistent with observations at other sites. However, the missing ozone-reactivity flux estimate is highly dependent on estimates of the other components and additional measurements, such as vertical divergence of ozone flux, are needed to constrain these estimates. Holzinger et al. (2005) report measurements of unidentified compounds at the same site which could represent a large flux, if they are reaction products with a low yield, or a small flux, if they are primary emissions. Additional studies are needed to identify and determine the importance of any unknown primary BVOC emissions. This should include enclosure measurements of total ozone reactivity of individual plant species.

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3 Model description

MEGAN2.1 is available as an offline code and as an integrated component of land surface and atmospheric chemistry models. The offline code is referred to here as the WRF-AQ version and is available, along with driving variables and a test case, to be downloaded from http://acd.ucar.edu/~guenther/MEGAN/MEGAN.htm. The WRF-AQ version uses WRF (or MM5) meteorological data and provides emissions in a format suitable for input to some regional air quality models (e.g. CMAQ and CAMx). MEGAN2.1 has also been embedded into the Community Land Model, (CLM4.0; Lawrence et al., 2011), which can run offline or as an on-line component of the Community Earth System Model (CESM; Gent et al., 2011). Emissions of select species following the MEGAN2.1 approach have also been integrated into global atmospheric chemistry models including GEOS-Chem v9 (Millet et al., 2010), IMAGES2 (Stavrakou et al., 2011), and ECHAM5-HAM (Makkonen et al., 2012).

A schematic of the MEGAN model algorithms and driving variables is shown in Fig. 1. Model inputs include gridded maps of driving variables for each location in a model grid. These include meteorology (e.g. hourly temperature, solar radiation, humidity, wind speed and soil moisture), and landcover data including Leaf Area Index (LAI) and Plant Functional Type (PFT) fractions. Emission factors (see Table 2) and CO_2 concentrations can be input from a coupled atmospheric model (e.g. CESM) or from a table. The main modules are leaf age, soil moisture and CO_2 algorithms (accounting for emission response to leaf age, soil moisture and CO_2, respectively) and a canopy environment model.

The two major components required for modeling biogenic emissions from terrestrial landscapes are (1) defining emission types with a representative emission factor and (2) simulating the processes controlling variations in emissions from a landscape. MEGAN2.1 estimates emissions (F_i) of chemical species i from terrestrial landscapes as the product of these two components in units of ($\mu g\, m^{-2}\, h^{-1}$) for 19 compound classes (i) according to:

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$$F_i = \gamma_i \sum \varepsilon_{i,j} \chi_j$$

where $\varepsilon_{i,j}$ is the emission factor at standard conditions for vegetation type j with fractional grid box areal coverage χ_j. The emission activity factor (γ_i) accounts for the processes controlling emission responses to environmental and phenological conditions. The 19 categories can be decomposed into 147 individual compounds which can then be lumped into the categories used for atmospheric chemistry schemes.

3.1 Emission factors

MEGAN2.0 (Guenther et al., 2006) provided multiple options for defining emission types in recognition of the different needs for local (i.e. site specific), regional (which may include detailed vegetation species composition data) and global modeling. This enabled users to customize vegetation emission type schemes ranging from very detailed (e.g. individual plant species or even sub species) to very generic (e.g. a few broad vegetation categories). For MEGAN2.1, we have adopted the PFT scheme shown in Table 3, which is used by CLM4 (Lawrence et al., 2011). The emission factors for each compound are specified based on PFT types. An option is also available to directly use input maps for individual emission categories which enables a better characterization of the regional variability in emission factors.

The previous version, MEGAN2.0 defined emission factors as the net flux of a compound into the atmosphere. This was intended to account for losses of primary emissions on their way into the above canopy atmosphere. For example, some of the isoprene emitted from leaves into the canopy airspace does not escape into the above canopy atmosphere but is consumed on canopy and soil surfaces or reacts within the canopy airspace. The MEGAN2.1 emission factor represents the net primary emission that escapes into the atmosphere but is not the net flux because it does not include the deposition flux of above-canopy chemicals into the canopy. The net primary emission used for the MEGAN2.1 emission factor can be estimated from the net flux measured

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above a canopy by subtracting an estimate of the canopy deposition flux. For example, for a typical net methanol flux measured above a forest canopy of 800 $\mu g\, m^{-2}\, h^{-1}$ and an estimate of methanol dry deposition flux of 100 $\mu g\, m^{-2}\, h^{-1}$ the net primary emission used for the MEGAN2.1 emission factor would be 900 $\mu g\, m^{-2}\, h^{-1}$. For isoprene and other terpenoid compounds, this adjustment is a few percent or less.

The ability of plants to emit a specific chemical species can be widespread, occurring in all or most plants, or limited, occurring in a select group of plants. Isoprene and MBO are examples of compounds with a limited distribution in the plant kingdom while many other VOC are emitted from most plants. A vegetation emission type scheme for a compound with a limited distribution in the plant kingdom, such as isoprene, should ideally distinguish between emitters and non-emitters. In addition, isoprene emitting plants do not all have the same emission factor which has led to the compilation of lists assigning specific emission factors to individual plant species (Benjamin et al., 1996). While it is clear that one isoprene emission factor is not sufficient for all isoprene emitters, studies have shown that much of the previously observed isoprene variability among plant species (e.g. *Quercus, Liquidambar, Nyssa, Populus, Salix*, and *Robinia* species) can be attributed to weather, plant physiology and the location of a leaf within the canopy rather than genetics (Geron et al., 2000). This suggests that it may be possible to define a limited number of isoprene emission types that have a similar isoprene emission factor. The 16 CLM4 PFTs are similar, or even more detailed, to other global land surface models but are not sufficient for describing the observed variability in isoprene emission factors. For example, the "Broadleaf Deciduous Temperate Tree" category includes maple (*Acer*) trees that have negligible isoprene emissions and oak (*Quercus*) trees that emit at high rates. For other PFTs, such as "Needleleaf Deciduous Boreal Tree" with only negligible isoprene emitters, the CLM4 scheme is sufficient. To account for this variability, the base MEGAN2.1 landcover includes more than 2000 ecoregions which allows the PFT emission factors to differ in each region. The PFT emission factors for ecoregions in the US, Europe, Australia and some other regions are based on the combination of species composition data and species-specific emission factors

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while the PFT emission factors for ecoregions in tropical forests and some other regions are directly based on above-canopy flux measurements. The global average PFT emission factors shown in Table 2 are the area-weighted average of all ecoregions.

3.2 Processes controlling emission variations

The activity factor (γ) accounts for emission response to light (γ_P), temperature (γ_T), leaf age (γ_A), soil moisture (γ_{SM}), leaf area index (LAI) and CO_2 inhibition (γ_C) as

$$\gamma = C_{CE} \mathrm{LAI} \gamma_P \gamma_T \gamma_A \gamma_{SM} \gamma_C$$

The canopy environment constant (C_{CE}) is assigned a value that results in $\gamma = 1$ for the standard conditions and is dependent on the canopy environment model being used. A value of 0.30 is used for CLM4 and a value of 0.57 for the MEGAN canopy environment model described in Sect. 3.3. The activity factor for leaf age is calculated as in Eqs. (16) and (17) of Guenther et al. (2006), with variable age class factors for each compound class as given in Table 4. Soil moisture activity factors can be calculated as Eq. (20) in Guenther et al. (2006). The activity factor associated with the CO_2 inhibition of isoprene emission follows Heald et al. (2009).

Emissions of each compound class include a light-dependent fraction (LDF) with the remaining light independent fraction (LIF = 1-LDF) that is not influenced by light. The emission activity factor accounting for the light response of emissions is estimated as:

$$\gamma_{P,i} = (1 - \mathrm{LDF}_i) + \mathrm{LDF}_i \gamma_{P\_LDF}$$

where γ_{P_LDF} follows the light-dependent activity factor described for isoprene in Eqs. (6) and (7) of Guenther et al. (2006). The light response is applied separately for the sunlit and shaded leaves in the forest canopy environment.

The temperature activity factor is similarly separated into a light-dependent and light-independent fraction (LDF, LIF). The light-dependent fraction response is calculated following the isoprene response described in Eqs. (8) and (9) of Guenther et al. (2006).

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The response of the light-independent fraction follows the monoterpene exponential temperature response function of Guenther et al. (1993). The constants used for this exponential (β_i) factor as well as the constant in the light-dependent formulation ($C_{T1,i}$) vary with compound class and are given in Table 4. The temperature activity factor is therefore calculated as:

$$\gamma_{T,i} = (1 - \mathrm{LDF}_i)\gamma_{T\_LIF,i} + \mathrm{LDF}_i\gamma_{T\_LDF,i}$$

3.3 Driving variables

3.3.1 Solar radiation and temperature

Solar radiation directly influences emissions of some BVOC and indirectly influences emissions of other BVOC through leaf temperature. The algorithms used for calculating solar radiation at the top of a canopy and for solar decomposition (direct and diffuse light components, visible and near-infrared components) vary considerably and there is a substantial range in the reported values of these variables. Another important issue is the conversion of solar radiation in $\mathrm{W\,m^{-2}}$ to Photosynthetic Photon Flux Density (PPFD) in units of $\mu\mathrm{mol\,photons\,m^{-2}\,s^{-1}}$. PPFD is the flux of photons in the 400 to 700 nm spectral range of solar radiation that photosynthetic organisms are able to use in the process of photosynthesis. Reported values for different sites and conditions range from less than 4 to greater than 5 µmol photons per Joule and the conversion factor for diffuse PPFD is considerably less than what is observed for direct PPFD (Lizaso et al., 2005; Jacovides et al., 2007). MEGAN results are also sensitive to uncertainties in the approaches used to decompose solar radiation into direct visible, diffuse visible, direct infrared, and diffuse infrared components. Algorithms for estimating diffuse visible fraction are uncertain by as much as a factor of two which can have a substantial impact on isoprene emission estimates. This is because direct light only influences sun leaves, which tend to already be light saturated, while diffuse light is important for shade leaves that often have a nearly linear increase in isoprene emission with light. The WRF-AQ version of MEGAN2.1 calculates direct visible, diffuse

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visible, direct infrared, and diffuse infrared as a function of atmospheric transmission and uses different conversion factors for direct (4.0 µmol photons per Joule) and diffuse light (4.5 µmol photons per Joule) based on observations reported by Lizaso et al. (2005) and Jacovides et al. (2007). Substituting alternative approaches for decomposing solar radiation and converting solar radiation to PPFD to drive the MEGAN2.1 algorithms results in ±30 % differences in isoprene emissions.

Wang et al. (2011) assessed the solar radiation data used to drive WRF-AQ/MEGAN2.1 emissions in the Pearl River Delta and found that the downward shortwave radiation simulated by MM5 was considerably higher than observations with a maximum bias of about 150 $W m^{-2}$. They attributed this to the lack of aerosol impacts on solar radiation in MM5. A larger problem may be inability of models to correctly simulate clouds on small scales. Solar radiation fields for air quality models, e.g. CMAQ and CAMx, are calculated from WRF output using the Meteorology-Chemistry Interface Processor (MCIP). A comparison of isoprene emission estimated using both satellite and WRF/MCIP estimated solar radiation illustrated in Figure 2 shows that using WRF/MCIP solar radiation results in North American isoprene emissions that are overestimated by 37 %. The overestimation is much higher in specific regions and during hours of peak emission. A comparison of isoprene emission estimates for clear sky conditions was conducted to avoid complications of different cloud distributions in the two datasets. The results show isoprene emissions based on WRF/MCIP solar radiation estimates are higher across the region. This indicates that the difference in solar radiation is not due to variable cloud fraction estimates but is because WRF did not capture the thin high-level baroclinic shield of cirrostratus or altostratus occurring at 6 to 9 km above sea level. The cloud thickness (approximately 300 m) is considered thin when it is compared to 1 to 2 km layer depth at this altitude and cannot be resolved in the meteorological model. This may be minimized by model simulations that accurately incorporate cloud observations. Even if models can correctly simulate average cloud cover there may be errors due to the non-linear response of emissions under conditions of scattered clouds.

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An alternative is using satellite based estimates of photosynthetically active radiation (PAR, http://www.atmos.umd.edu/~srb/par/03satellite.htm). The satellite PAR is based on actual cloud cover that avoids bias from predicted solar radiation. Using satellite PAR also eliminates uncertainty in conversion from solar radiation to PAR using a constant factor.

BVOC emissions are highly sensitive to variations in temperature. Larger errors may result from the temperature data used to drive MEGAN emissions. Wang et al. (2011) assessed the temperature data that they used to simulate biogenic VOC emissions in the Pearl River Delta and found a bias that varied from about 0.1 to 1 °C. Guenther et al. (2006) found larger differences in temperature data compiled in global datasets.

3.3.2 Canopy environment

Light and temperature vary dramatically within a vegetation canopy resulting in much lower emissions of biogenic VOC in shaded portions of a canopy, especially light dependent compounds such as isoprene. MEGAN2.1 calculates leaf temperature instead of assuming that leaf temperature is equal to ambient temperature, which typically results in small underestimates in emissions. MEGAN2.1 emission factors will by definition, result in the same emission at standard conditions even for different canopy models, which is an advantage of using landscape scale emission factors. Keenan et al. (2011) show that different canopy environment models would otherwise result in very different emissions, even at the standard conditions. However, they also show that the different canopy environment models have considerably different isoprene emission responses to changes in environmental conditions. A better understanding of canopy environment processes that is needed to improve biogenic emission estimates requires observations of emissions, light and temperature variations throughout canopies.

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3.3.3 Soil moisture

The shutdown of a plant's physiological processes in response to drought leads to a decrease and then termination of isoprene emission. MEGAN2.1 simulates this behavior with a simple algorithm, based on the observations of Pegoraro et al. (2004), that relates emission activity to soil moisture and wilting point (the soil moisture below which plants cannot extract water from soil). The Chen and Dudhia (2001) global wilting point dataset was recommended as a model input for driving this algorithm. While this provides reasonable results when used with NCEP and WRF model soil moisture estimates, Muller et al. (2008) found that when using ECMWF soil moisture data it was necessary to use ECMWF wilting point values. This finding demonstrates the need to use wilting point values that are appropriate for the soil moisture model used to drive MEGAN2.1.

3.3.4 Plant Functional Type and Leaf Area Index

Variations in BVOC emission types are accounted for in MEGAN2.1 either by inputting geogridded emission maps or by using PFT data and the PFT emission factors compiled in Table 2. The choice of PFT scheme is also used to determine parameters to use in canopy environment models. MEGAN2.1 uses the CLM4 PFT scheme. A global database of CLM4 PFT fraction distributions is available for use with the CLM4 model but can also be used to drive WRF-AQ/MEGAN2.1 simulations. The global CLM4 PFT database is available with 10′ (about 20 km) resolution which is suitable for many regional modeling studies.

Higher resolution data is desirable for some regional modeling studies. A high resolution (60 m) PFT database using the CLM4 scheme was generated for the US for the year 2008 and is available with the MEGAN2.1 input data. The database was created by combining the National Land Cover Dataset (NLCD, Homer et al., 2004) and the Cropland Data Layer (see http://nassgeodata.gmu.edu/CropScape/), which are based on 30-m LANDSAT-TM satellite data, with vegetation species composition data from

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the Forest Inventory and Analysis (see www.fia.fs.fed.us) and the soil database of the Natural Resources Conservation Services (see http://sdmdataaccess.nrcs.usda.gov/). The processing included adjusting the NLCD tree cover estimates in urban areas to account for the substantial underestimation of the LANDSAT-TM data (Duhl et al., 2011). This was accomplished using the regionally-specific adjustment factors for urban NLCD developed by Greenfield et al. (2009) using high resolution imagery.

3.3.5 Leaf Area Index

MEGAN uses LAI to quantify the amount of foliage at a given location and uses changes in LAI to estimate the age of the foliage. LAI data for driving MEGAN can be obtained from dynamic vegetation models or from satellite datasets. Some models, including CLM4, have LAI estimates separately for each PFT which can improve MEGAN simulations in regions (e.g. an oak-pine forest) with co-located high isoprene-emitting PFT (temperate broadleaf deciduous tree) and low isoprene-emitting PFT (temperate needleleaf evergreen tree) that have very different LAI seasonal patterns. Satellite LAI data that have been used to drive MEGAN include the NASA MODIS data and the European SPOT/VEGETATION data. Garrigues et al. (2008) compared these two products with ground observations and found that each product performed better in some ways (e.g. SPOT generally agreed better with observations but MODIS was better at getting the high LAI values in forests). It should be noted that the NASA MODIS team has an active effort to improve the MODIS LAI product and different versions of the MODIS data can result in substantially different emission estimates. A comparison of MODIS version 5 LAI to that based on an earlier version used for MEGAN2.0 indicates that average LAI values ranged from about 20 % higher in June, July and August to 1 % lower in March. The differences varied considerably among regions. The increase was greatest in the conifer dominated forests of the Rocky Mountains and Pacific Northwest and less in grasslands and shrublands. The new cropland LAI was about a factor of 2 lower outside the growing season in some croplands and slightly higher during the growing season. The new LAI is considerably (20 to 40 %) lower in some, but not all,

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California oak woodlands resulting in a 20 % or more decrease in isoprene emission estimated with MEGAN2.1.

The WRF-AQ/MEGAN2.1 allows the use of 8-day average satellite observations while the previous version (MEGAN2.04) was driven by monthly LAI data. Although the 8-day LAI can provide a more detailed representation of seasonal LAI variations, monthly data tends to capture the major features. The 8-day product is expected to be most useful during periods of rapid LAI change.

4 MEGAN2.1 emission estimates

The MEGAN2.1 algorithms have been incorporated into CLM4 (Lawrence et al., 2011) so that all driving variables are determined by the land model at each model timestep. CLM4 can be run as a stand-alone model, or coupled to the Community Atmosphere Model with chemistry (CAM-chem; Lamarque et al., 2012) or the full CESM. CLM4 can also be run either with a dynamic carbon-nitrogen cycle which calculates LAI (CLM-CN), or in a mode using specified LAI from MODIS satellite observations (CLM-SP). When running CAM-chem, there is also an option to have a free-running climate, or to use specified meteorology as is used in offline chemical transport models. These various options (calculated or prescribed LAI, free-running or specified meteorology) will result in significant differences in MEGAN-calculated biogenic emissions.

CLM-SP was used to calculate MEGAN2.1 global annual emission totals for all 19 compound classes for the year 2000, shown in Table 5, using PFT average emission factors, specified LAI, Qian et al. (2006) atmospheric forcing, and CO_2 concentrations fixed at 367 ppm. Because these emissions are constrained by observed land-cover (CLM-SP) and meteorology (Qian et al., 2006), we expect these estimates to have lower uncertainties. The annual global isoprene emission of 534 Tg is slightly less than the 570 Tg (equivalent to 503 Tg carbon) of isoprene estimated by Guenther et al. (1995) and is within the range of 310 to 750 Tg calculated with MEGAN2.0 using different driving variable databases (Guenther et al., 2006; Pfister et al., 2008;

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Arneth et al., 2011). Guenther et al. (2006) report substantial differences in MEGAN2.0 annual isoprene emissions when changing PFT (24 %), LAI (29 %) and meteorology (15 %) input data. Pfister et al. (2008) used three different PFT and LAI databases to drive MEGAN2.0 and found global differences of about 30 % and regional differences exceeding 60 %. Arneth et al. (2011) compared MEGAN2.0 with two other global isoprene emission models and found that the models broadly agree when driven with the same input data and that differences of more than 30 % were associated with changes in driving variables. Differences in model algorithms made a relatively small difference in global emission totals. An interesting finding from the Arneth et al. (2011) model comparison is that changing model algorithms, driving variables and emission factors had considerably different impacts in the three different models including cases where a change caused an increase in one model and a decrease in another. This result demonstrates the need for a better understanding of model sensitivities to model components and driving variables.

Formaldehyde columns based on satellite observations have been used with global atmospheric chemistry models to provide a top-down model estimate of global annual isoprene emissions. Shim et al. (2005) provided a first estimate of 641 Tg yr^{-1} using one year of GOME satellite data. Stavrakou et al. (2009) provided a much more detailed analysis of a decade of space-based formaldehyde columns including data from both the GOME and SCIAMACHY satellites. Comparisons of top-down and bottom-up emission magnitude and temporal variations indicated MEGAN2.0 was an improvement over the Guenther et al. (1995) estimates. However, they found that the calculated emissions are highly dependent on the satellite product, the retrieval methods, and details of the model used to relate formaldehyde concentration to isoprene emission. Both top-down and bottom-up model approaches have similar levels of uncertainty and so one cannot be used to validate the other but comparisons are valuable for identifying regions of disagreement that can be targeted in regional field studies.

The global annual monoterpene emission of 157 Tg estimated with CLM4 is a little higher than the 144 Tg (127 Tg carbon) estimated by Guenther et al. (1995). The

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MEGAN2.1 emissions are somewhat higher in the tropics and somewhat lower in temperate and boreal regions in comparison to Guenther et al. (1995). A CLM4 model simulation with the CLM-CN option, which provides model-calculated LAI that are generally higher than the standard CLM-SP prescribed LAI (Lawrence et al., 2011), resulted in global total monoterpenes that are 19 % higher than with CLM-SP. In contrast, the CLM-CN resulted in isoprene emissions that are 6 % lower than with CLM-SP. This indicates that CLM-CN tends to produce higher LAI in monoterpene-dominated regions and lower LAI in isoprene-dominated regions.

Schurgers et al. (2009) compared two monoterpene emission algorithms, the simple temperature dependence of Guenther et al. (1993) and the more detailed model of Ninemets et al. (2002), in a global model and found only a small (7 %) difference. The global annual monoterpene emission reported by Schurgers et al. (2009) is a factor of 5 lower than the MEGAN2.1 estimate using CLM4. Given the small difference attributed to the change in emission algorithm, differences in driving variables and emission factors are expected to be responsible for these very different estimates of total monoterpene emissions.

The CLM4 annual global estimate of methanol is within 10 % of the values reported by Stavrakou et al. (2010) for MEGAN2.1 embedded in the IMAGES2 global atmospheric chemistry model. Similarly, the acetaldehyde estimated by CLM4 is within 1 % of the estimate of Millet et al. (2010) when running MEGAN2.1 embedded in the GEOS-Chem global atmospheric chemistry model. The small differences in simulated emissions can be attributed to differences in driving variables and canopy environment models.

The CLM4 annual global estimate of about $4\,\mathrm{Tg\,yr^{-1}}$ of formic acid and $5\,\mathrm{Tg\,yr^{-1}}$ of formaldehyde are considerably lower than the biogenic source estimated from the analysis of satellite observations by Stavrakou et al. (2012). This might be accounted for by the atmospheric oxidation of terpenoid compounds but a much higher direct emission source cannot be ruled out. Recent direct eddy covariance measurements by DiGangi et al. (2012) suggest a more substantial emission of formaldehyde from

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the top of a forest canopy than what is currently estimated by MEGAN2.1. This could be a result of oxidation within the forest canopy but even in that case the input of total reactive organics to the above canopy atmosphere would be underestimated. The CLM4 estimate of about 40 Tg yr^{-1} of acetone is 14 % (compared to Jacob et al., 2002) to 25 % (compared to Fischer et al., 2012) higher than the values derived using global model inversions.

Figure 3 shows the January and July global distributions of isoprene, α-pinene, acetone, ethene, and β-caryophyllene. The results are similar to earlier studies with emissions that are generally higher in regions of high biomass density during periods of warm and sunny weather. Differences between the various compounds are also due to PFT-specific emission behavior. For example, Australia is a relatively high source of isoprene, α-pinene and β-caryophyllene. Figure 4 illustrates regional differences in annual emissions and shows that, in comparison to the Southern Hemisphere, the Northern Hemisphere has several orders of magnitude higher MBO emission, slightly more ethene emission, the same acetone emission, and about 20 % to 25 % lower isoprene, α-pinene and β-caryophyllene emission.

A comparison of MEGAN2.1 estimates calculated using CLM4 and WRF-AQ is shown in Fig. 5. The WRF-AQ simulation uses an emission factor map that accounts for species composition variability within PFTs (e.g. distinguishing between low emitting maple trees and high emitting oak trees that are both broadleaf deciduous temperate trees) while the CLM4 simulation has a constant emission factor for each PFT. The higher resolution (36 × 36 km) WRF-AQ and lower resolution CLM4 (1.9 × 2.5 deg, ~200 km) model simulations demonstrate the expected finer details for the WRF-AQ results due to higher spatial resolution. The CLM4 has higher maximum monoterpene emissions and lower maximum isoprene emissions, probably due to the difference between using emission factor maps and using PFT average emission factors.

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5 Conclusions

MEGAN2.1 provides a flexible scheme for estimating emissions of many individual BVOC from terrestrial ecosystems. The global total BVOC flux of about 1000 Tg and the chemical speciation (~50 % isoprene, ~15 % monoterpenes) is similar to results from previous models although emissions for specific locations and days may be very different. Most of the 147 compounds included in MEGAN2.1 contribute very little to the total BVOC flux but are included in a manner that results in a minimal computational expense. The relatively small number of compounds associated with most of the flux have more detailed and specific parameterizations including unique emission factors for each of 16 PFTs. Most of the dozen compounds that have annual global emissions exceeding 10 Tg yr^{-1} (>1 % of the global total), and together comprise 80 % of the total flux, have been studied in a variety of landscapes with a range of emission measurement techniques including canopy-scale direct eddy flux measurements. The exceptions include CO, ethene, propene and ethanol emissions for which there are only one or two studies that can be used to parameterize emission models. Although there are considerably more emission measurements of the other dominant compounds (isoprene, several monoterpenes, acetone, methanol, and acetaldehyde), the uncertainties associated with these emission estimates are considerable and a lack of suitable measurements makes it difficult to even quantify these uncertainties. It is clear that isoprene is the globally dominant BVOC and should continue to be the focus of BVOC emissions research although other compounds with a greater capacity for producing aerosol matter (e.g. monoterpenes and sesquiterpenes) or impacting the upper atmosphere (e.g. methyl halides) may be equally or more important for specific earth system issues.

The uncertainties associated with assigning emission factors to different landscape types are the largest contributor to the overall biogenic VOC emission estimate uncertainty. Uncertainties in landcover and meteorological driving variables are of a similar magnitude as uncertainties associated with model algorithms. The algorithms used

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to account for the major drivers of emission variability (e.g. temperature, PPFD and CO_2) provide a reasonable approximation of emission response but the lack of quantitative algorithms for describing stress response is a significant limitation for predicting emissions of some BVOC. A systematic effort to conduct leaf- and canopy-scale measurements, including both tower-based flux measurements of temporal variations and airborne-based flux measurements of spatial variations, is required to improve these estimates and to quantify uncertainties.

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Table 1. MEGAN2.1 nineteen emission categories and 147 compounds.

Emission Categories	Compound names
Categories representing individual compounds (14 compounds)	hemiterpenes (isoprene and 232-MBO), monoterpenes (α-pinene, β-pinene, limonene, sabinene, 3-carene, myrcene, t-β-ocimene), sesquiterpenes (β-caryophyllene and α-farnesene), methanol, acetone and CO
Other Monoterpenes category (34 compounds)	aromatic monoterpenes (dimethyl styrene, meta-cymenene, p-cymene, and o-cymene), monoterpenes (α-phellandrene, α-thujene, α-terpinene, γ-terpinene, terpinolene, β-phellandrene, camphene, bornene, α-fenchene, allo-ocimene, cis-β-ocimene, verbenene and tricyclene), oxygenated monoterpenes (camphor, fenchone, piperitone, myrtenal, α-thujone, β-thujone, 1,8-cineole, borneol, linalool, 4-terpineol, α-terpineol, cis-linalool oxide, trans-linaool oxide and bornyl acetate) and monoterpenoid-related compounds (β-ionone, ipsenol and estragole).
Other Sesquiterpenes category (30 compounds)	sesquiterpenes (α-bergamotene, β-bisabolene, β-farnesene, α-humulene, acoradiene, aromadendrene, β-bergamotene, α-bisabolene, β-bourbonene, δ-cadinene, δ-cadinene, α-cedrene, α-copaene, α-cubebene, β-cubebene, β-elemene, germacrene B, germacrene D, β-gurjunene, γ-humulene, isolongifolene, longifolene, longipinene, α-muurolene, γ-muurolene, β-selinene, and δ-selinene), oxygenated sesquiterpenes (cis-nerolidol, trans-nerolidol and cedrol).
Bidirectional exchange category (5 compounds)	ethanol, acetaldehyde, formaldehyde, acetic acid, formic acid
Other compound category (49 compounds)	leaf surface compounds (homosalate, 2-ethylhexyl salicylate, geranyl acetone, oxopentanal, and methyl heptenone), organic halides (methyl bromide, methyl chloride and methyl iodide), sulfur compounds (diallyl disulfide, methyl propenyl disulfide, propenylpropyldisulfide, carbon disulfide, carbonyl sulfide, hydrogen sulfide, methyl mercapten, dimethyl sulfide and dimethyl disulfide), alkanes (methane, ethane, propane, pentane, hexane, heptane), alkenes (butene, propene, 1-dodecene, 1-tetradecene), benzenoids (benzaldehyde, methyl benzoate, 2-phenylacetaldehyde, eugenol, anisole, benzyl acetate, benzyl alcohol, and naphthalene), oxygenated VOC (pentanal, hexanal, heptanal, octanal, nonanal, decanal, octanol, octenol, heptanone, 2-butanone, pyruvic acid, 331-methylbutenol, 321- methylbutenol, neryl acetone, α-terpinyl acetate, phenylacetaldehyde and nonenal)

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Table 2. MEGAN2.1 biogenic emission classes and emission factors ($\mu g\,m^{-2}\,h^{-1}$) for each of the Plant Functional Types described in Table 3.

Compound Class	EF_1	EF_2	EF_3	EF_4	EF_5	EF_6	EF_7	EF_8	EF_9	EF_{10}	EF_{11}	EF_{12}	EF_{13}	EF_{14}	EF_{15}
Isoprene	600	3000	1	7000	10 000	7000	10 000	11 000	2000	4000	4000	1600	800	200	1
Myrcene	70	70	60	80	30	80	30	30	30	50	30	0.3	0.3	0.3	0.3
Sabinene	70	70	40	80	50	80	50	50	50	70	50	0.7	0.7	0.7	0.7
Limonene	100	100	130	80	80	80	80	80	60	100	60	0.7	0.7	0.7	0.7
3-Carene	160	160	80	40	30	40	30	30	30	100	30	0.3	0.3	0.3	0.3
t-β-Ocimene	70	70	60	150	120	150	120	120	90	150	90	2	2	2	2
β-Pinene	300	300	200	120	130	120	130	130	100	150	100	1.5	1.5	1.5	1.5
α-Pinene	500	500	510	600	400	600	400	400	200	300	200	2	2	2	2
Other Monoterpenes	180	180	170	150	150	150	150	150	110	200	110	5	5	5	5
α-Farnesene	40	40	40	60	40	60	40	40	40	40	40	3	3	3	4
β-Caryophyllene	80	80	80	60	40	60	40	40	50	50	50	1	1	1	4
Other Sesquiterpenes	200	200	200	200	150	200	150	150	150	150	150	2	2	2	2
232-MBO	200	10	0.01	0.01	0.01	0.01	0.01	2	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Methanol	900	900	900	500	900	500	900	900	900	900	900	500	500	500	900
Acetone	240	240	240	240	240	240	240	240	240	240	240	80	80	80	80
CO	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600
Bidirectional VOC	500	500	500	500	500	500	500	500	500	500	500	80	80	80	80
Stress VOC	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300
Other VOC	140	140	140	140	140	140	140	140	140	140	140	140	140	140	140

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Table 3. CLM4 global land area (10^{12} km^2) and isoprene, monoterpene (MT) and other (VOC and CO) emissions for individual Plant Functional Types estimated using MEGAN2.1 algorithms in CLM4 for year 2000.

CLM PFT Number	Description	Land Area	Isoprene Tg yr^{-1}	MT Tg yr^{-1}	Other Tg yr^{-1}
	Bare	40.7			
1	Needleleaf Evergreen Temperate Tree	5.46	1.61	7.38	11.6
2	Needleleaf Evergreen Boreal Tree	10.6	5.9	6.63	9.42
3	Needleleaf Deciduous Boreal Tree	1.46	0.0002	0.52	0.89
4	Broadleaf Evergreen Tropical Tree	15.6	244	82.9	127
5	Broadleaf Evergreen Temperate Tree	2.64	21.9	4.0	8.71
6	Broadleaf Deciduous Tropical Tree	12.9	178	45.0	74.3
7	Broadleaf Deciduous Temperate Tree	5.33	35.4	5.86	13.1
8	Broadleaf Deciduous Boreal Tree	2.14	4.79	0.99	2.02
9	Broadleaf Evergreen Temperate Shrub	0.18	0.23	0.08	0.33
10	Broadleaf Deciduous Temperate Shrub	4.15	21.8	6.77	16.4
11	Broadleaf Deciduous Boreal Shrub	9.33	2.93	1.07	3.3
12	Arctic C3 Grass	4.94	0.97	0.02	1.45
13	Cool C3 Grass	14.3	11.2	0.25	26.1
14	Warm C4 Grass	13.2	5.93	0.49	51.3
15	Crop1	16.3	0.02	0.36	44.5
	Total (all PFTs)	159	535	162	390

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Table 4. MEGAN2.1 model parameters.

Compound Class	β	LDF	C_{t1}	Ceo	A_{new}	A_{gro}	A_{mat}	A_{old}
Isoprene	0.13	1	95	2	0.05	0.6	1	0.9
Myrcene	0.1	0.6	80	1.83	2	1.8	1	1.05
Sabinene	0.1	0.6	80	1.83	2	1.8	1	1.05
Limonene	0.1	0.2	80	1.83	2	1.8	1	1.05
3-Carene	0.1	0.2	80	1.83	2	1.8	1	1.05
t-β-Ocimene	0.1	0.8	80	1.83	2	1.8	1	1.05
β-Pinene	0.1	0.2	80	1.83	2	1.8	1	1.05
α-Pinene	0.1	0.6	80	1.83	2	1.8	1	1.05
Other Monoterpenes	0.1	0.4	80	1.83	2	1.8	1	1.05
α-Farnesene	0.17	0.5	130	2.37	0.4	0.6	1	0.95
β-Caryophyllene	0.17	0.5	130	2.37	0.4	0.6	1	0.95
Other Sesquiterpenes	0.17	0.5	130	2.37	0.4	0.6	1	0.95
232-MBO	0.13	1	95	2	0.05	0.6	1	0.9
Methanol	0.08	0.8	60	1.6	3.5	3	1	1.2
Acetone	0.1	0.2	80	1.83	1	1	1	1
CO	0.08	1	60	1.6	1	1	1	1
Bidirectional VOC	0.13	0.8	95	2	1	1	1	1
Stress VOC	0.1	0.8	80	1.83	1	1	1	1
Other VOC	0.1	0.2	80	1.83	1	1	1	1

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Table 5. Global annual total emissions simulated for the year 2000 using MEGAN2.1 algorithms in CLM4.

Compound Class	Compounds	Emissions ($Tg\,yr^{-1}$)
Isoprene	Isoprene	535
α-Pinene	α-Pinene	66.1
t-β-Ocimene	t-β-Ocimene	19.4
β-Pinene	β-Pinene	18.9
Limonene	Limonene	11.4
Sabinene	Sabinene	9.0
Myrcene	Myrcene	8.7
3-Carene	3-Carene	7.1
Other Monoterpenes	Camphene	4.0
	β-phellandrene	1.5
	Terpinolene	1.3
Sum of the 31 other monoterpenes		14.9
α-Farnesene	αFarnesene	7.1
β-Caryophyllene	βcaryophyllene	7.4
Other Sesquiterpenes	βFarnesene	4.0
	αHumulene	2.1
	αBergamotene	1.3
Sum of the 27 other sesquiterpenes		7.1
232-MBO	232-MBO	0.6
Methanol	Methanol	996
Acetone	Acetone	43.7
Bidirectional VOC	Ethanol	20.7
	Acetaldehyde	20.7
	Formaldehyde	5.0
	Acetic acid	3.7
	Formic acid	3.7
Stress VOC	Ethene	284
	C3-hexenal	4.9
	DMNT	4.9
	C3-hexenol	2.9
Sum of the 11 other stress VOC		7.8
Other VOC	Propene	15.8
	Butene	8.0
	Homosalate	2.0
	Geranyl acetone	0.8
Sum of the 45 other VOC		5.5
Total VOC	Sum of 146 VOC	1005
CO	CO	81.6
Total	VOC and CO	1087

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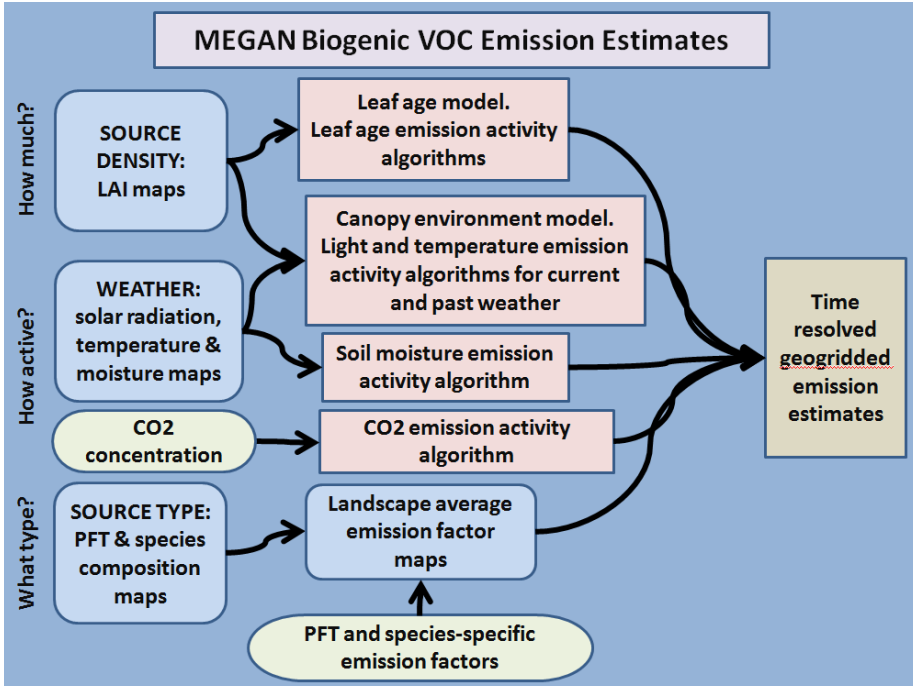

Fig. 1. Schematic of MEGAN2.1 model components and driving variables.

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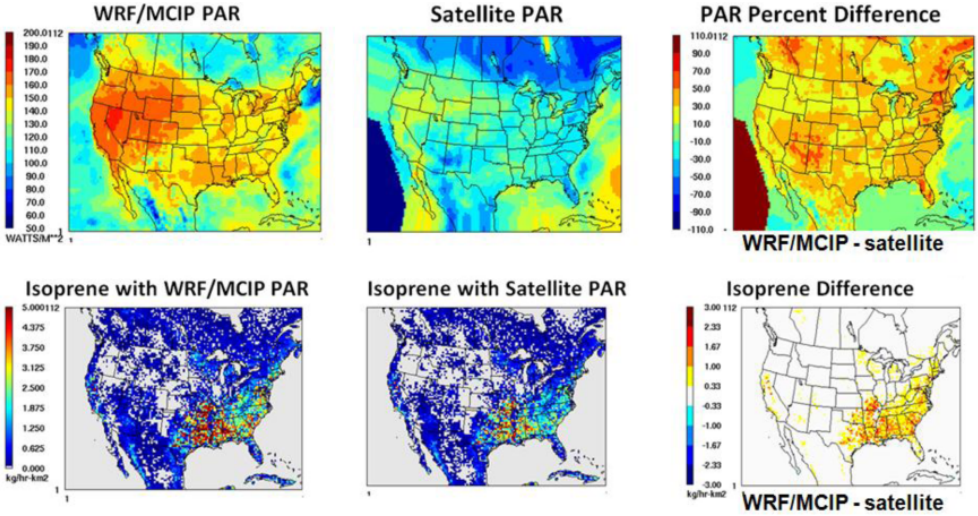

Fig. 2. 3–18 July 2008, period average estimates of PAR ($W\,m^{-2}$) from WRF/MCIP (top left) and satellite (top middle) and percent difference for WRF/MCIP – Satellite (top right) and associated isoprene emissions ($kg\,h^{-1}\,km^{-2}$) using MEGAN2.1 in WRF-AQ driven by WRF/MCIP PAR (bottom left) and satellite PAR (bottom middle) and difference (bottom right).

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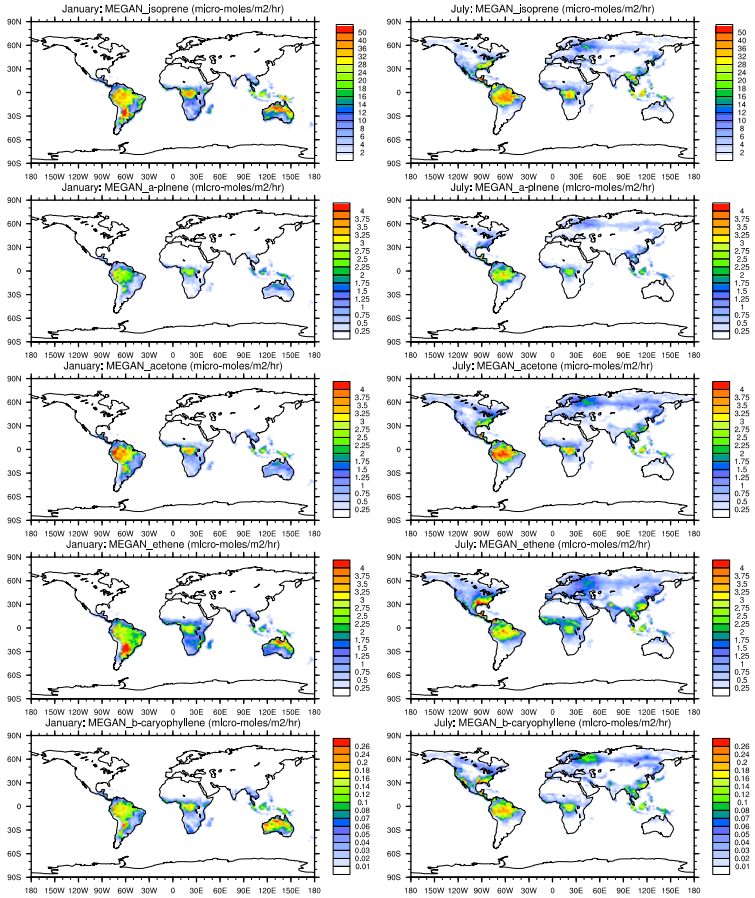

Fig. 3. January and July 2000 global emissions of isoprene, α-pinene, acetone, ethene and β-caryophyllene simulated with MEGAN 2.1 algorithms using CLM4.

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MEGAN2.1 framework for modeling biogenic emissions

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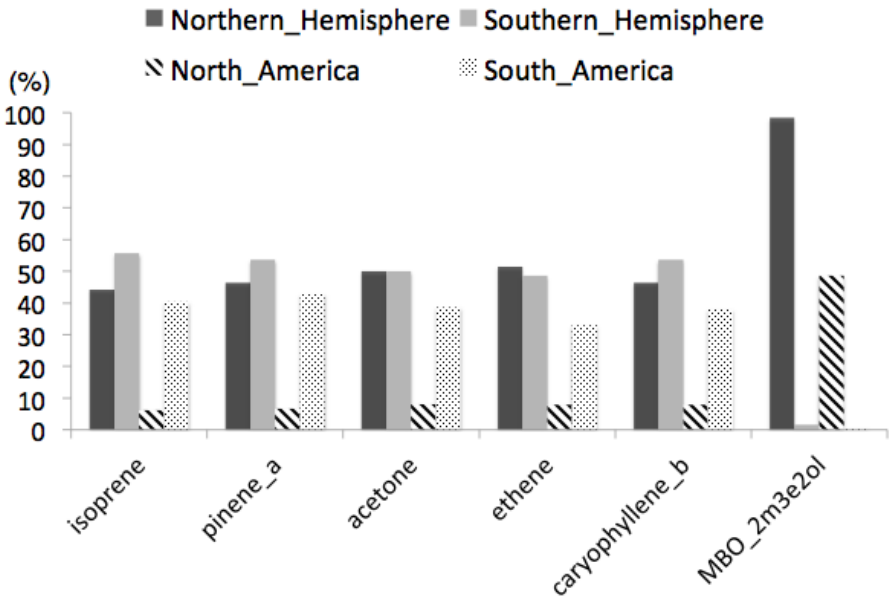

Fig. 4. Regional contributions to global total emissions of selected compounds.

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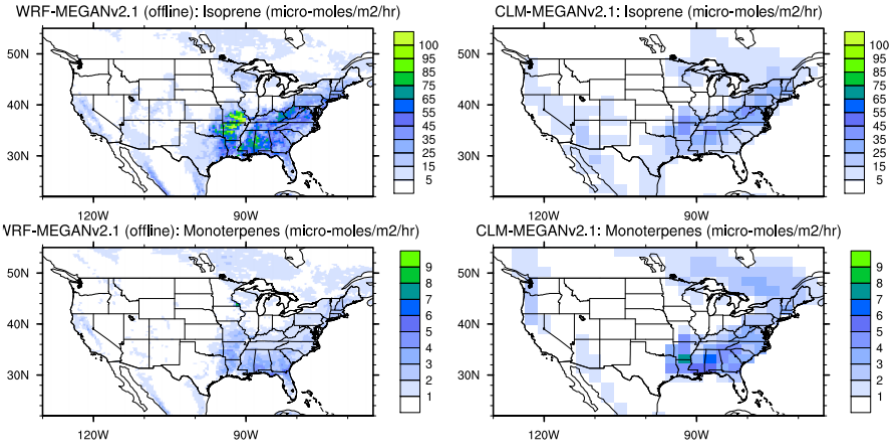

Fig. 5. MEGAN2.1 estimates of US isoprene and monoterpene emissions calculated using WRF-AQ and CLM4.

GMDD
5, 1503–1560, 2012