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Production of Secondary Organic Aerosol from Multiphase Monoterpenes

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<http://dx.doi.org/10.5772/48135>

1. Introduction

Nonmethane volatile organic compounds (NMOCs) represent a key class of chemical species governing global tropospheric chemistry and the global carbon cycle (Fehsenfeld et al. 1992; Singh and Zimmerman 1992). The most important anthropogenic sources of hydrocarbons include fossil fuel combustion, direct release from industry, industrial processing of chemicals, and waste. The global estimated anthropogenic hydrocarbon flux is 1.0×10^{14} gC per year (Singh and Zimmerman 1992). Biological processes in both marine and terrestrial environments contribute to biogenic hydrocarbon sources. For the terrestrial biosphere, the principal hydrocarbon sources come from vegetation. In regions such as eastern North America, biogenic hydrocarbon emission rate estimates exceed anthropogenic emissions (Guenther et al. 1994). At the global scale it is estimated that vegetation emits 1.2×10^{15} gC per year, an amount equivalent to global methane emissions (Guenther et al. 1995).

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. Monoterpenes comprise a significant portion of BVOC emissions (Guenther et al., 1995; Pio and Valente, 1998), and it is important to understand the atmospheric fates of monoterpenes and their oxidation products. The emission patterns of the various monoterpenes strongly depend on the type of vegetation and on the environmental conditions, however d-limonene makes up the majority of monoterpene emissions over orange groves, while α -pinene and β -pinene dominate over most other kinds of forests, especially those composed of oaks and conifers (Pio and Valente, 1998; Christensen et al., 2000). In recent years, the number of relevant studies has increased substantially, necessitating the review of this topic, including emission fluxes of monoterpenes, the effects of species and nutrient limitation on emissions, secondary organic aerosol yields via condensation and nucleation.

2. Emission fluxes of monoterpenes

2.1. Chemical structure of terpenes

Monoterpenes are organic compounds of biogenic origin whose structure may be divided into isoprene units. The more volatile mono- (C_{10}) and sesquiterpenes (C_{15}) are emitted in large quantities from the vegetation. The chemists always regard terpenes as alkenes (e.g. β -pinene, camphene), cycloalkenes (e.g. α -pinene, Δ^3 -carene), and dienes (e.g. β -phellandrene, α -terpinene) or as a combination of these classes (e.g. limonene, ocimene). Figure 1 shows the chemical structure of monoterpenes. Of the 14 most commonly occurring monoterpenes (α -pinene, β -pinene, Δ^3 -carene, d-limonene, camphene, myrcene, α -terpinene, β -phellandrene, sabinene, p -cymene, ocimene, α -thujene, terpinolene, and γ -terpinene), the first six are usually found to be most abundant.

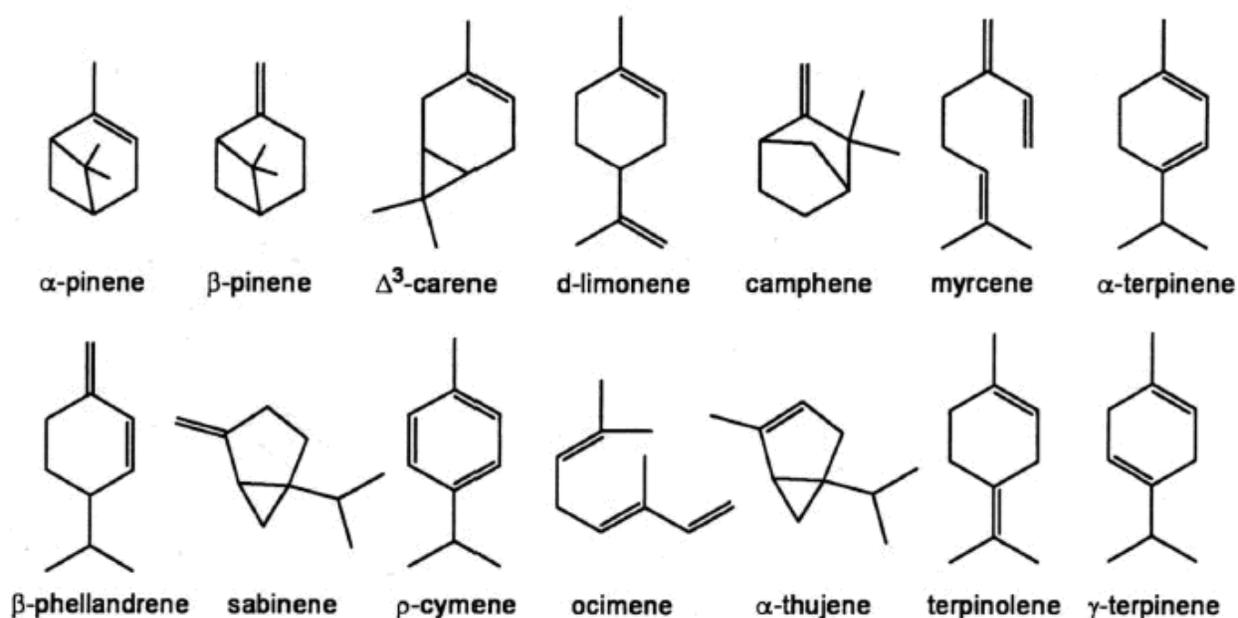


Figure 1. The chemical structures and names of monoterpenes

2.2. Biogenic sources

The biogenic volatile organic compounds (BVOCs) emitted from plants are a myriad of hydrocarbons and oxygenated and other organic compounds. These emissions occur during various stages of plant growth, plant injury and plant decay, and they are a significant source of volatile organic compounds (VOCs) in the atmosphere. Globally, emissions from BVOCs account for approximately 86% of the total of VOCs emitted while anthropogenic VOCs make up the rest (Guenther et al., 1995). BVOC emissions from trees and woody shrubs have been extensively studied (Scholes et al., 2003). The dominant compounds emitted under unperturbed conditions are isoprene, monoterpenes, sesquiterpenes and methanol. There are episodic emissions of C_6 aldehydes, esters and alcohols associated with plant injuries, and episodic emissions of ethanol and acetaldehyde associated with waterlogging (Scholes et al., 2003).

Natural sources of VOC emissions to the atmosphere also include marine and fresh water, soil and sediments, microbial decomposition of organic material, geological hydrocarbon reservoirs, plant foliage and woody material. In addition, there are human influenced natural sources from harvesting or burning plant material. We have estimated emissions of VOC only from oceans and plant foliage. VOC emissions from other sources are very uncertain but probably represent less than a few percent of total global emissions (Zimmerman, 1979; Lamb et al., 1987; Janson, 1992; Eichstaedter et al., 1992).

2.3. Emission fluxes

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 Δ^3 -carene emissions equal or exceed those of α -pinene, due to the abundance of *Pinus contorta*, *monticola*, *ponderosa*, and their subspecies. These regions and hourly summer total monoterpene flux from forests at 30°C are illustrated in Figure 2. 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 of the Piedmont and coastal southeast also have estimated fluxes which exceed 200 $\mu\text{g carbon m}^{-2} \text{ h}^{-1}$. α -pinene composes over half of the emissions from these regions except for parts of the western US. Northern mixed, midwestern, Appalachian, and Ozarks forests have a higher hardwood component and have emission rates of approximately 150 $\mu\text{g carbon m}^{-2} \text{ h}^{-1}$. The great plains and agricultural midwest have sparsely scattered woodlands and low emission rates (100 $\mu\text{g carbon m}^{-2} \text{ h}^{-1}$). These rates are rather low in comparison to those of isoprene which can exceed 10,000 $\mu\text{g carbon m}^{-2} \text{ h}^{-1}$ 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 emission factors (EFs) and environmental/physiological controls. Current models (Guenther et al., 1994) assume $\pm 50\%$ uncertainty in basal EFs and roughly $\pm 40\%$ uncertainty in biomass and landuse accuracy (Lamb et al., 1987). An assessment of the uncertainty in monoterpene composition (MC) indicates that $\pm 30\text{-}50\%$ is a reasonable estimate for the six major compounds, and likely more for the eight minor compounds. This results in estimates of roughly $\pm 150\text{-}200\%$ 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.

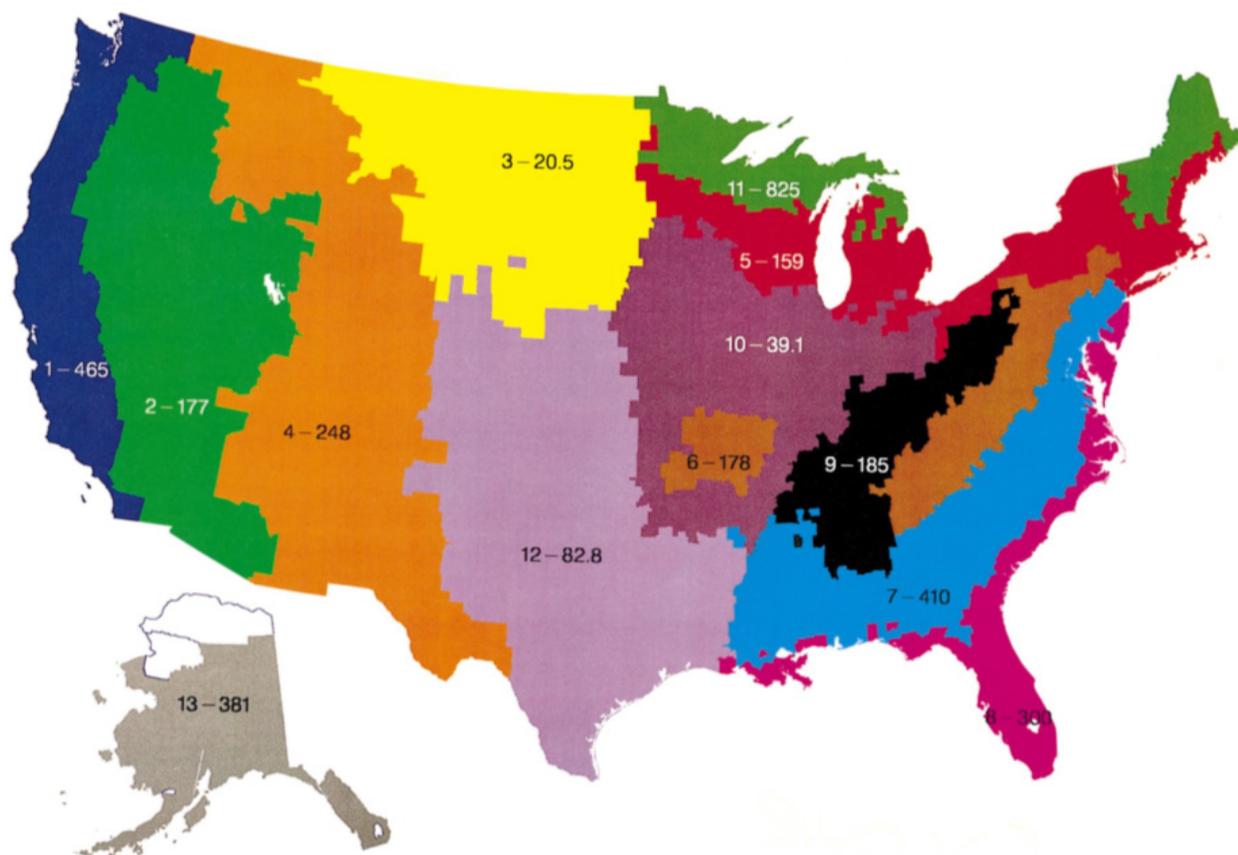


Figure 2. Regions and regional average total monoterpene flux ($\mu\text{g carbon m}^{-2} \text{h}^{-1}$). The numbers indicate region number follow by the average regional flux at 30°C.

2.4. Emission factors

The best-known environmental control on biogenic hydrocarbon emissions is temperature. For compounds such as monoterpenes that are released from resin ducts or glands, temperature is the dominant control factor (Figure 3). The increasing vapor pressure of these compounds with temperature explains the temperature response of emissions. In contrast, isoprene and some plant monoterpene emissions do not come from preexisting pools. In these cases the temperature response of emission is caused by the impact of temperature on the underlying metabolism (Monson et al. 1994). This effect can be described by calculating an activation energy.

Some monoterpene emissions are also dependent upon light. The light dependence is often similar to that of photosynthesis. Water and nitrogen content affect hydrocarbon emission primarily through their influences on enzyme activity of leaves. Another critical factor controlling hydrocarbon fluxes from leaves is the leaf developmental state. Monoterpene-emitting foliage shows its highest emission rates when the leaves are youngest (Lerdau 1993). This high emission rate from young leaves results from the role monoterpenes serve

as defensive compounds; young leaves are most at risk from pests and pathogens so they have the highest concentrations of defensive compounds (Lerdau et al. 1994). The manner in which monoterpenes and several of the oxygenated hydrocarbons (e.g., methyl chavicol) are stored within leaves and wood leads to a large effect of tissue damage upon flux rate. These compounds are stored in specialized ducts, canals, or cavities. When herbivores partially consume tissue and expose these cavities to the atmosphere, flux rates increase by several orders of magnitude. This increase stems from the change in the resistance term in Fick's law of diffusion describing the gas flux (Lerdau 1991).

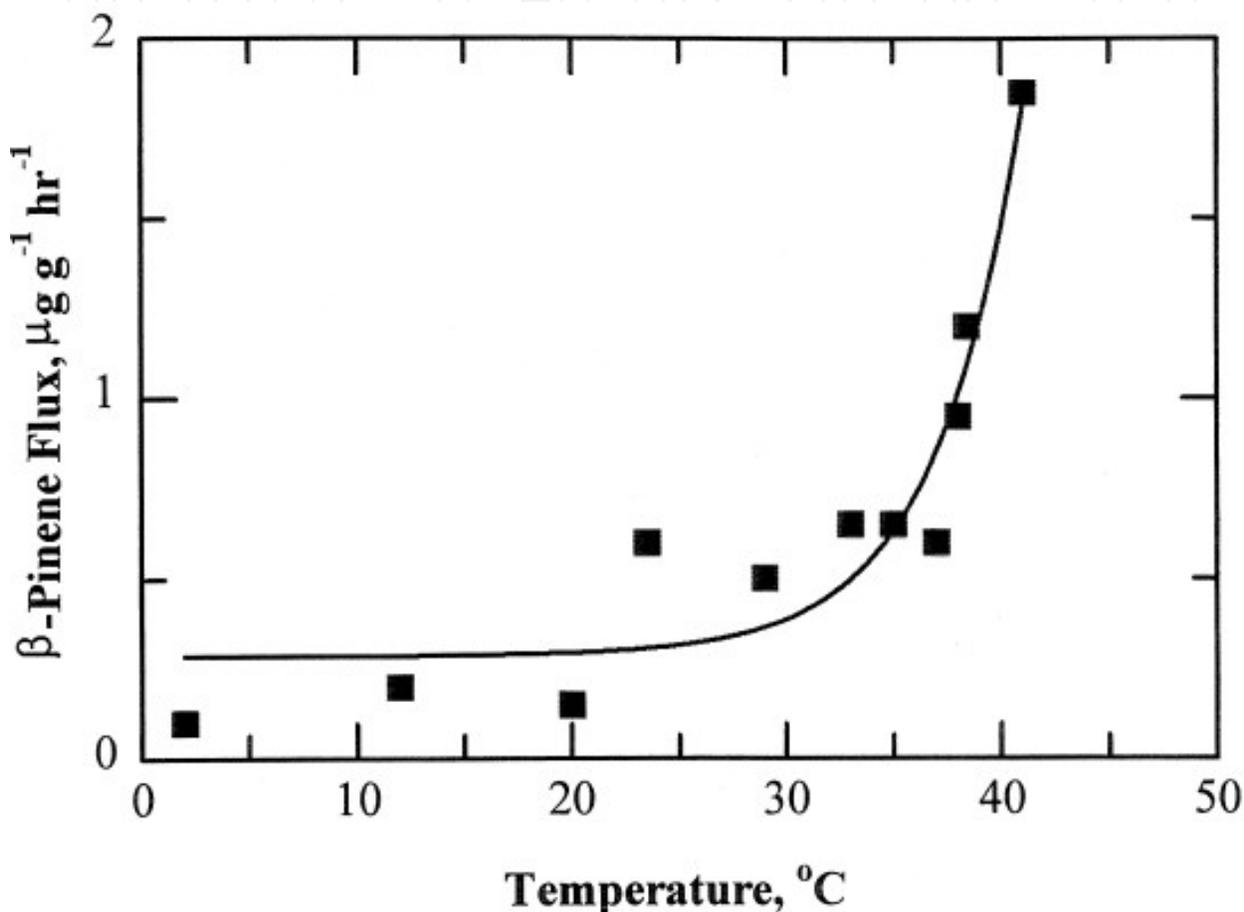


Figure 3. Variation of monoterpene emissions as function of temperature. The line represents the best fit to the data points. The emission rates are expressed per unit dry biomass weight.

2.5. Temporal and spatial distribution

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 Δ^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 Δ^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 $\mu\text{g carbon g}^{-1} \text{h}^{-1}$ at leaf temperature $\approx 30^\circ\text{C}$, 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; Winer et al., 1992; Street et al., 1997b; Bertin et al., 1997). This is confirmed by measurements in ambient air (Roberts et al., 1985). 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 monoterpene composition of ambient (near canopy) air near forests in Colorado (Roberts et al., 1985), where nighttime versus daytime relative abundance of β -pinene, α -pinene, Δ^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 ellioti* (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.

3. Secondary organic aerosol formation

Most of monoterpenes are photochemically reactive in the atmosphere because of their alkenyl bonds and other properties of their structure (Seinfeld and Pandis, 1998). Two key products of the photochemical reactions of these compounds in the atmosphere are gas-phase oxidants (including ozone) and secondary organic aerosols. These gas-phase oxidants and secondary organic aerosol can have significant effects on human health when

present in high concentrations in near surface air and are climatically active in the global atmosphere.

Gas-phase monoterpenes readily react with the major atmospheric oxidants such as ozone (O_3), hydroxyl radical (OH), and nitrate radical (NO_3). During the day, their concentrations are controlled by OH and O_3 , and at night they are controlled by NO_3 , with monoterpene lifetimes on the order of a few hours in both cases. Regardless of the initial oxidant, gas-phase oxidation of monoterpenes results in a wide variety of polyfunctional carboxylic acids, ketones, aldehydes, peroxides, and alcohols (Kavouras et al., 1998; Yu et al., 1999; Claeys et al., 2007; Presto et al., 2005; Gao et al., 2004; Dalton et al., 2005; Glasius et al., 1999; Hakola et al., 1994; Jaoui et al., 2005; Leungsakul et al., 2005). Many of these species have sufficiently low vapor pressure to partition into pre-existing particulate matter. In addition, monoterpenes can partition into aqueous particles or cloud droplets by wet deposition and undergo oxidation via aqueous chemistry, with droplets subsequently drying out into organic particles.

SOAs are formed by chemical reactions from the condensation and gas/particle partitioning of semivolatile products of hydrocarbon oxidation by OH, O_3 and NO_3 . It is currently believed that approximately 85-90% of SOAs are produced by oxidation of biogenic emissions, which corresponds to 12.2 Tg SOA/yr and 1150 TgC/yr (Kanakidou et al., 2005; Stavrakou et al., 2009; Tsigaridis et al., 2007). Some authors suggest that 91% of SOAs are considered to be caused by O_3 and OH oxidation (Chung et al., 2002), while others consider that ozonolysis dominates in SOA production compared to OH and NO_x oxidation (Kanakidou et al., 2005). 78% of SOAs are specifically products of monoterpene oxidation (Chung et al., 2002). Monoterpenes α -pinene and β -pinene are expected to be the major sources of SOAs (Kleindienst et al., 2007; Yu et al., 1999).

3.1. Chamber experiments

A number of laboratory experiments have been carried out to study SOA formation by oxidation of monoterpenes (e.g. α -pinene, β -pinene, d-limonene, Δ^3 -carene, sabinene) with NO_x , O_3 and OH (Lee et al., 2004; Jonsson et al., 2008; Northcross and Jang, 2007; Czoschke et al., 2003; Spittler et al., 2003; Colville et al., 2004; Seinfeld et al., 2001). The formation of SOA in the presence of NO_x has been studied for several monoterpenes: α -pinene, β -pinene, limonene, Δ^3 -carene, myrcene, β -ocimene, sabinene, α -terpinene, α -terpinolene (Pandis et al., 1991; Hoffmann et al., 1997; Griffin et al., 1999; Klinedienst and Currie, 1999; Presto et al., 2005; Lee et al., 2006; Zhang et al., 2006). The complexity of the dependence of NO_x concentration on monoterpene SOA yields was first noted by Pandis et al. (1991) who found that the SOA yield from the photooxidation of α -pinene increased with increasing VOC/ NO_x ratio and maximized at 8% for 10–20 ppbC:ppb NO_x . The SOA yield was found to decrease for VOC/ NO_x ratios greater than 20. More recently, Presto et al. (2005) showed that SOA yields from ozonolysis of α -pinene are lower under high- NO_x (<15 ppbC:ppb NO_x) than low- NO_x conditions. The reduction of the SOA yields was attributed to the formation of higher volatility products under high NO_x , including evidence of nitrate-

containing organic species. The NO_x dependence becomes increasingly complex when the monoterpene consists of two double bonds with differing reactivity, as is the case for limonene. Zhang et al. (2006) indicated that two competing effects contribute to the NO_x dependence of the SOA yield: reactive uptake by the aerosol and gas-phase oxidation. In the presence of ozone and at low NO_x, heterogeneous ozonolysis of the exo double bond generates condensed-phase secondary generation oxidation products. However, at high NO_x, gas-phase oxidation of the double bond becomes the dominant process for aerosol product generation. The yield dependence on NO_x is complicated when oxidation by ozone or hydroxyl radicals takes place in the presence of NO_x. The primary reason is thought to be that under high NO_x conditions, organo-peroxy radicals (RO₂) react with NO and NO₂ instead of with peroxy radicals (RO₂ or HO₂). A number of different critical values (VOC/NO_x) have been suggested (e.g. 10–15:1, Pandis et al., 1991, 8:1, Presto et al., 2005, 3–10:1, Lane et al., 2008) for the point of 50:50 branching between the two reaction paths. As the OH/O₃ ratio also depends on the VOC/NO_x ratio, it is difficult to separate changes in yield due to changes in concentrations of OH and O₃ from changes in product distribution due to the presence of NO_x (Presto et al., 2005). However, the approach adopted by Lane et al. (2008) is to identify product yields for each fundamental pathway (i.e., high-NO_x dominated by RO₂ + NO, low-NO_x by RO₂ + HO₂) and then to assume that SOA yields can be calculated by a linear combination of the “pure” mass yields scaled by the strength of each reaction pathway. Clearly, anthropogenic processes that perturb these branching ratios from their background values will influence overall SOA formation.

3.2. Field studies

The high abundant vegetation in Amazonia make this region a global hotspot for the emission of various biogenic volatile organic compounds (e.g. Keller et al., 2009). Previously it was thought that the vast emissions of VOC in the Amazon area would deplete the oxidative potential of the atmosphere (Lelieveld et al., 2002) and thus constrain the BSOA production. However, there have been strong indications that HO_x chemistry remains substantially more vigorous under low-NO_x conditions than standard mechanisms predict (Thornton et al., 2002). This was confirmed by a more recent study by Lelieveld et al. (2008) showing that the oxidative potential in the pristine rainforest is maintained through the recycling of OH via organic peroxy radical reactions under low NO_x conditions. Most attempts to estimate Amazonian BSOA production (e.g. Penner et al., 2001; Kanakidou et al., 2005) with global models have considered only monoterpenes as precursors. More recent efforts (e.g. Heald et al., 2008) have included isoprene, which has been shown to be a significant SOA precursor (Claeys et al., 2004), but still omit some potentially significant precursors such as the highly reactive sesquiterpenes which have very high BSOA yields. Both observational and modelling studies have concluded that 80% of the aerosol mass in the Amazon forest is of biogenic origin (Artaxo et al., 1990; Artaxo and Hansson, 1995; Heald et al., 2008; Chen et al., 2009) either due to primary or secondary sources (Kanakidou et al., 2005), however there is a large uncertainty in this number. One has to keep in mind that unless we have an accurate knowledge of the emissions of

primary aerosols, it will be difficult to assess the relative importance of the SOA. Measurements made during the Amazonian Aerosol Characterization Experiment 2008 (AMAZE-08), under near pristine conditions, show that the submicrometer aerosol is mostly composed of BSOA, while supermicron particles consist mainly of primary organic matter (Pöschl et al., 2010). While the submicrometer fraction was found to account for more than 99% of the ca. 200 cm^{-3} particles observed, approximately 70% of the ca. $2 \mu\text{g m}^{-3}$ total particle mass was made up by the supermicron particles. The ongoing development of the Amazon is resulting in an enhanced anthropogenic influence on regional atmospheric composition. Changes in anthropogenic pollutants (particularly NO_x and SO_2) can alter the SOA formation potential (Kroll et al., 2005; Ng et al., 2007) and the relative roles of different oxidation pathways. It is typically assumed that more SOA is formed from monoterpenes under low- NO_x conditions, such as prevail in the Amazon. Therefore a change in the amount of NO_x due to anthropogenic emissions would lead to a change in the amount of SOA. The magnitude and the sign of this change depend on the predominant VOC species.

3.3. Modeling

Current BVOC emission and air quality models aggregate all monoterpene ($\text{C}_{10}\text{H}_{16}$) 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 β -pinene and sabinene, tend to form more aerosols following ozonolysis compared to those with endocyclic double bonds, such as α -pinene and Δ^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.

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