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Plant Production and Emission of Volatile Organic Compounds

Plant-produced hydrocarbons influence not only the plant itself but the atmosphere as well

Manuel Lerdau, Alex Guenther, and Russ Monson

When asked to discuss the ways in which plant processes influence the atmosphere, most biologists first think of photosynthetic oxygen production and carbon dioxide uptake. Given a few more minutes, many will also point out that plant transpiration of water plays a role in the chemistry of the troposphere (the lower 10 km of the atmosphere). Few, however, are aware that plant processes play key roles in ozone production, methane oxidation, and the global carbon monoxide budget. Several biologists and atmospheric chemists have recognized the effects of plants on the atmosphere (Rasmussen 1972, Tyson et al. 1974, Went 1960), but only recently has research into chemical emissions from plants advanced beyond a curiosity of interest to only a handful of environmental scientists. The topic of plant chemical emissions and their role in atmospheric chemistry was thrust into the public consciousness in 1981 when Ronald Reagan stated that trees were more important causes of air pollution than were automobiles—a statement that contained an element of truth (trees *do* emit hydrocarbons) and much error (trees do *not* cause air pollution).

Isoprene and other biogenic hydrocarbons play key roles in several aspects of tropospheric chemistry, including ozone dynamics, carbon monoxide production, and methane oxidation

Aside from oxygen, hydrocarbons are the most abundant reactive chemicals that are produced by and emitted from plants, although certain plants also emit oxygenated organic compounds. Together, these compounds are referred to as volatile organic compounds (VOCs; Fehsenfeld et al. 1992). Plants emit 400–800 Tg C/yr (1 Tg = 10^{12} g) as hydrocarbons, an amount equivalent to the sum of biogenic and anthropogenic methane emissions (Guenther et al. 1995). Unlike methane, which is well mixed in the atmosphere because of its long atmospheric lifetime (8–11 years), plant-produced VOCs are extremely reactive in the troposphere, with lifetimes ranging from minutes to hours (NRC 1991). This high reactivity means that although their direct climatic influence is small, plant-produced hydrocarbons have tremendous effects on the redox balance of the atmosphere, in many cases swamping out the effects of all other reduced compounds in the troposphere (Singh and Zimmerman 1992).

Physiological and ecological controls over hydrocarbon emissions have been studied intensively during the last 15 years, with work in the last 5 years yielding some significant advances. Biologists now understand the major environmental control factors over hydrocarbon flux from any one plant at any one time. Biologists are also beginning to be able to place VOC emissions within the context of ecological theory, taking advantage of recent work on the controls over whole-plant carbon balance. In this article, we briefly summarize the history of research on biogenic hydrocarbons, describe some of the physiology and ecology underlying emissions, discuss the functions of emissions in atmospheric processes, and suggest future directions for research efforts.

History of research on biogenic VOC emissions

The first studies on the emission of organic compounds from plants were conducted in the Soviet Union in the 1920s and 1930s (Nilov 1928 as cited in Isidorov 1994). In the 1950s, Haagen-Smit et al. (1952) suggested that large quantities of monoterpenes, $C_{10}H_{16}$, came from the leaves of chaparral vegetation, and Sanadze (1957;

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as cited in Sanadze 1991), while working under a Soviet directive to study plant production of defensive compounds, found that certain plant species produce large amounts of isoprene, C_5H_8. Rasmussen and Went (1965) argued that these compounds could play significant roles in the chemistry of the lower atmosphere, but for the next 15 years, only a few scientists pursued the biological bases of these emissions.

Rei Rasmussen and his coworkers concentrated on the mechanisms of isoprene production and emission, recognizing that this compound is the single most important reduced hydrocarbon in the troposphere (in terms of impacts on photochemical oxidants). They conducted a detailed physiological study providing evidence that isoprene emission was a byproduct of photorespiration (Jones and Rasmussen 1975). Not until almost 25 years later were the critical experiments done to test (and refute) this hypothesis. The mechanisms of monoterpene emissions were identified in the 1970s by workers at NASA Ames Research Center in Moffett Field, California, and Stanford University. Working with *Salvia mellifera*, they showed that monoterpene volatilization varied exponentially with temperature and was independent of current photosynthetic rates and light levels (Dement et al. 1975, Tyson et al. 1974). These results suggested that monoterpene emissions result simply from the volatilization of monoterpenes stored within plant tissues.

The US Environmental Protection Agency recognized the potential influence of biogenic hydrocarbon emissions on regional air quality, and in the late 1970s and early 1980s it supported research programs to develop initial estimates of biogenic emissions. The first studies used enclosures to survey hydrocarbon emissions from greenhouse-grown plants. Enclosure studies were also conducted at field sites throughout the United States, with particular emphasis on sites near Tampa Bay, Florida, and Houston, Texas (EPA 1979). Laboratory studies (Tingey et al. 1979, 1981) were also conducted to relate emissions to light and temperature. Field measurements, using micrometeorological instruments mounted on towers above the canopy, confirmed that biogenic VOC emissions are transported out of the canopy and into the troposphere.

Interest in biogenic emissions increased markedly in the late 1980s, when more sophisticated biogenic hydrocarbon oxidation schemes were incorporated into models of atmospheric photochemistry. Isoprene emissions significantly influenced model predictions of ozone and carbon monoxide production in both rural and urban regions (Trainer et al. 1987). In particular, the models demonstrated that high rates of biogenic VOC emissions in some regions of the southeastern United States were an impediment to achieving compliance with national air quality standards for ozone through reductions in automotive hydrocarbon emissions (Chameides et al. 1988).

Biology of emissions

The two most abundant and best-studied VOCs are isoprene and the monoterpenes, both of which are produced by the mevalonic acid pathway (Figure 1) and are known collectively as isoprenoids. Emission of isoprenoid VOCs is a simple diffusion process that can be modeled according to Fick's first law: the flux of an isoprenoid compound from a leaf to the atmosphere is

$$\text{flux} = k(VP_{\text{leaf}} - VP_{\text{atmosphere}})/r$$

where k is a diffusion coefficient of the compound in question, VP_{leaf} is the vapor pressure of the compound within the leaf, $VP_{\text{atmosphere}}$ is the vapor pressure of the compound in the atmosphere, and r is the resistance to flux of the compound from the leaf to the atmosphere. Within this simple equation, however, is the complexity of a wealth of physiological processes, ecological patterns, and phylogenetic constraints. Resistance to flux is a function of both the physical property of the compound itself (k) and the properties of the leaf through which the compound diffuses (r).

The most straightforward term in the above equation is $VP_{\text{atmosphere}}$. Because of the high reactivity and brief lifetime of isoprenoids, this term is effectively zero in comparison with the vapor pressures found within leaves. The low atmospheric vapor pressures of the hydrocarbons can therefore be neglected, and the equation thus reduces to

$$\text{flux} = kVP_{\text{leaf}}/r$$

and our attention can then be directed to the controls over VP_{leaf} and r.

The first step in understanding the controls over flux is to consider the production and storage sites of the various VOCs. Isoprene is produced within chloroplasts and is not stored. As soon as it is produced, isoprene diffuses through the leaf and out the stomata. Monoterpenes, by contrast, are produced in specialized cells and secreted into specialized structures, such as ducts or canals, that minimize diffusional loss into the leaf and out to the atmosphere. The actual storage structures vary with the plant taxon but tend to remain constant within a taxonomic unit.

Resistance to monoterpene flux appears to be constant within a plant species, so long as one controls for morphological changes that occur during leaf ontogeny. That is, resistance depends primarily on leaf anatomy parameters that do not respond to physiologically induced changes in leaf chemistry or morphology. As with water or carbon dioxide flux across a leaf, VOC flux can be thought of as a pathway composed of resistors in series, so that r in the first equation is really composed of a series of resistances whose effects are additive:

$$r_t = r_a + r_b + r_c + \ldots + r_n$$

In the case of isoprene, the important resistances are: r_a, the resistance from the chloroplast into the cell; r_b, the resistance across the cell membrane; r_c, the resistance through the intercellular air space; and r_d, the stomatal resistance from the leaf to the atmosphere. For monoterpenes that are stored within foliage in specialized ducts, cavities, or canals (e.g., those that are found in conifers and *Eucalyptus*; Fahn 1979), the critical terms are r_a, the resistance from the monoterpene storage site within the leaves to the intercellular air spaces;

r_b, the resistance to transport through the intercellular air spaces; and r_c, the resistance in moving through the stomata to the atmosphere.

Early on, it was noted that, unlike the case of water flux from leaves, variations in stomatal resistance have no effect on emission rates of either isoprene or monoterpenes (Tingey et al. 1979). There are two possible explanations for this phenomenon: either these compounds do not pass out of leaves through the stomata, or stomatal resistance is positively correlated with the flux driving force. Guenther et al. (1991) demonstrated that monoterpenes exit both sides of hypostomatous leaves (leaves with stomata on only one side), and they suggested that these compounds are able to diffuse through leaf cuticles. The same study, however, showed that isoprene exits only through the stomatal side of hypostomatous leaves, a strong indication that it passes through the stomata.

These findings raise the question of how isoprene could be exiting through stomata when its emission rates are not controlled by stomatal resistance. Through quick-freeze analyses and other experiments on leaves that had been treated with abscisic acid to close the stomata, Fall and Monson (1992) demonstrated that as stomata close, the vapor pressure of isoprene rises linearly. This change in VP_{leaf} means that the driving force of the first equation increases in proportion to the increase in stomatal resistance. Thus, so long as VP_{leaf} remains below the saturation point and there is no feedback between VOC flux rate and VOC production rate, changes in stomatal resistance will not affect the flux rate.

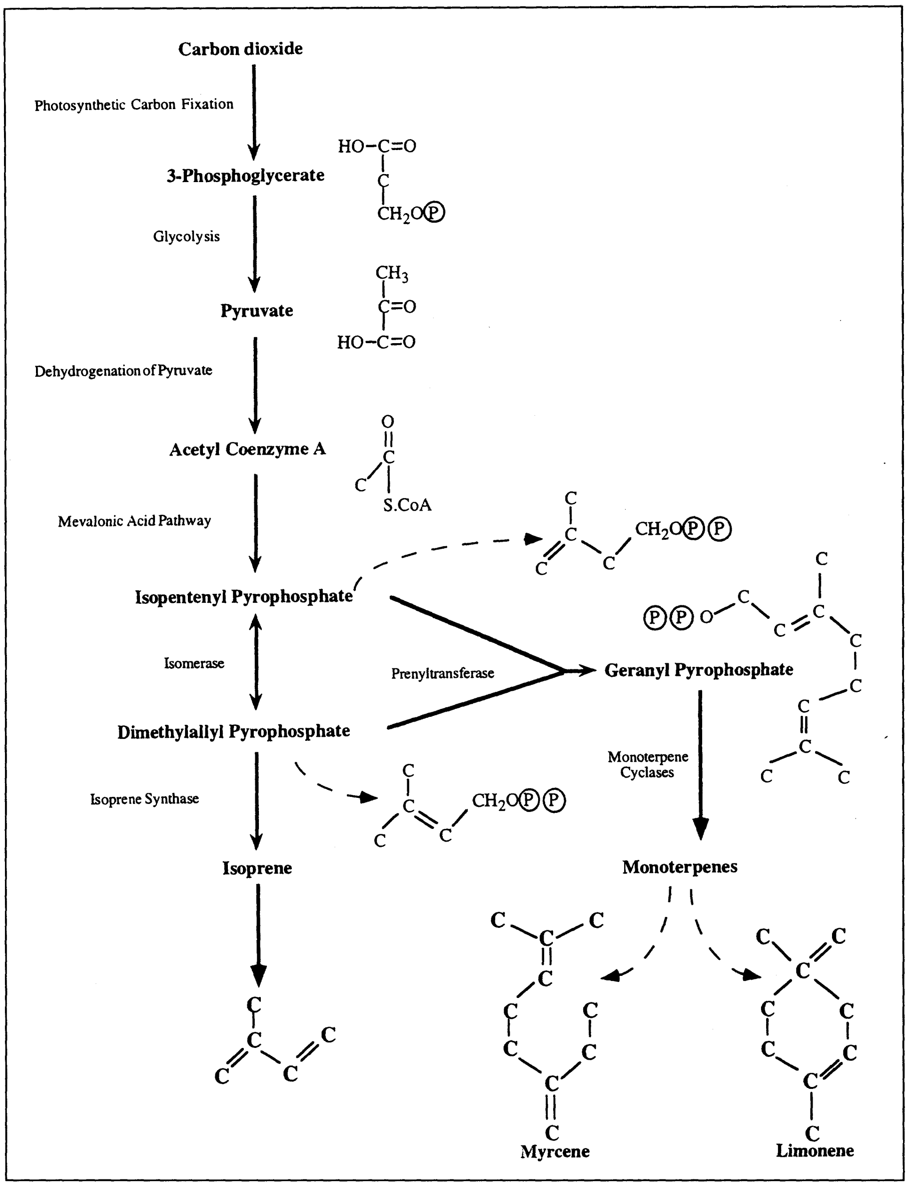

Figure 1. Biosynthetic pathway for isoprene and monoterpene production in plants. Note that pyruvate can also come directly from the breakdown of other reduced carbon sources. Synthetic pathway diagram is derived from the work of Sharkey et al. (1991), Silver and Fall (1991), Loreto and Sharkey (1993), and Gershenzon and Croteau (1993).

Isoprene production and emission. The last five years have seen substantial advances in our understanding of isoprene production and emission. The basic biochemical pathway has been identified (Sharkey et al. 1991), the protein responsible for the final step of isoprene synthesis has been purified (Silver and Fall 1991), and initial steps have been taken toward the cloning of the *isoprene synthase* gene.[1] In addition, recent evidence from physiological studies suggests that isoprene helps to protect plants against sudden increases in thermal radiation (Sharkey and Singsaas 1995). Isoprene is produced as an early step of the mevalonic acid pathway in chloroplasts, which converts two molecules of acetyl CoA into isopentenyl pyrophosphate (IPP) and its isomer dimethylallyl pyrophosphate (DMAPP). Isoprene is produced by the elimination of pyrophosphate from DMAPP (Figure 1). Because no mechanism exists to store isoprene within leaves and the isoprene vapor pressure within the leaf remains below saturation, the rate of isoprene emission equals the biosynthetic rate.

The rate of isoprene biosynthesis depends strongly on light, temperature, plant taxon, growth history and ontogeny, and resource availability. Isoprene biosynthesis depends on light in two ways. First, recently fixed carbon is the preferential carbon source for isoprene synthesis; therefore, emissions decrease when photosynthetic metabo-

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[1] R. Fall, 1996, personal communication. University of Colorado, Boulder, CO.

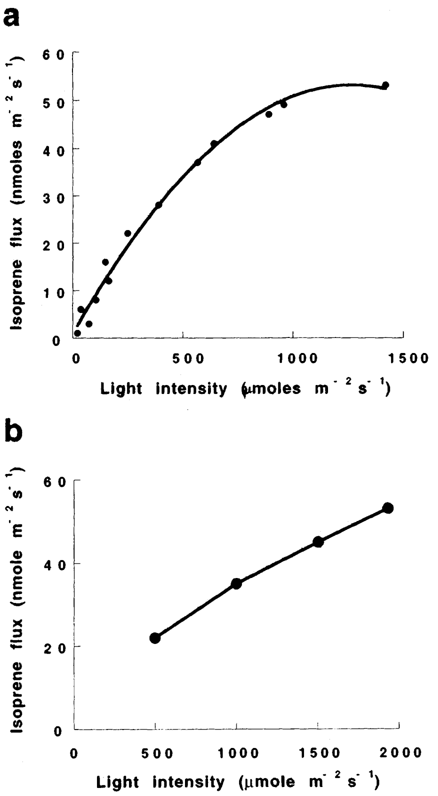


Figure 2. Light response of isoprene emission in temperate and tropical plants. (**a**) Light saturation of isoprene emission typical of temperate plants. Data are for white oak, *Quercus alba*, and are from Baldocchi et al. (1995). (**b**) Linear relationship between light intensity and isoprene emission typical of plants in tropical deciduous forests; data are for *Eugenia xerophytica* and are from Lerdau and Keller (in press).

lites are depleted during a light-to-dark transition (Loreto and Sharkey 1993). However, isoprene production can continue even in the absence of carbon fixation because plants can draw on carbon reserves to serve as the substrate for isoprene production. For example, during long-term drought stress, when photosynthesis is blocked for several days because of stomatal closure, isoprene continues to be produced (Sharkey and Loreto 1993). The second light requirement arises from the fact that isoprene synthase, which catalyzes the conversion of DMAPP to isoprene, appears to be light activated, possibly through light-driven changes in pH and Mg^{2+} ion concentrations in the stroma (Silver and Fall 1991). The relationship between isoprene biosynthesis and light intensity is fairly constant across taxa and environmental conditions, suggesting that the control mechanisms that have been studied in detail for a few species apply to many other species as well. At low light intensities, slight increases in intensity produce large increases in isoprene biosynthesis, but at higher light intensities, isoprene biosynthesis is less affected by increases in light (Figure 2a). For some species, however, isoprene emission does not plateau with increasing light intensity but instead continues to rise linearly (Figure 2b).

Isoprene emission also shows a strong temperature dependency, which suggests that it is enzymatically controlled (Guenther et al. 1991, Monson et al. 1992). The dependence on temperature is consistent across plant taxa, although there is a certain degree of species-specific variability. Most temperate and tropical plants studied have emissions maxima at approximately 40 °C (Figure 3). At very high temperatures, isoprene emission drops rapidly, confirming that the biosynthetic enzymes are becoming denatured.

Much of the taxonomic variability in isoprene emission occurs at the level of genera. For example, within the Fagaceae, most members of the genus *Quercus* (oaks) are isoprene emitters, whereas the genera *Fagus* (beeches) and *Castanea* (sweet chestnuts) appear not to emit isoprene (Evans et al. 1982, Guenther et al. 1996a). Similarly, in the Pinaceae, most members of the genus *Picea* (spruce) are isoprene emitters, whereas species in other genera do not emit isoprene (Guenther et al. 1994, Lerdau et al. 1995). This variability suggests that either isoprene production has evolved multiple times in plants or isoprene emission has been lost repeatedly.

The developmental stage of leaves also has a strong influence on the isoprene emission rate. Young leaves, which are still net sinks for carbon, generally emit low levels of isoprene. Isoprene emission rates increase when the leaves reach full expansion. This effect of leaf developmental stage appears to reflect isoprene synthase activity levels during the development of a leaf (Kuzma and Fall 1993). In addition to developmental effects, the basal level of isoprene emission (i.e., emission at a standard set of light and temperature conditions) has been tied to the exposure of plants to high temperature (32 °C or above) for short periods (approximately 24 hours; Sharkey et al. 1991). The induction of isoprene biosynthesis has been investigated in only a few species, and it is not known whether or not the induction temperature for isoprene production varies among species.

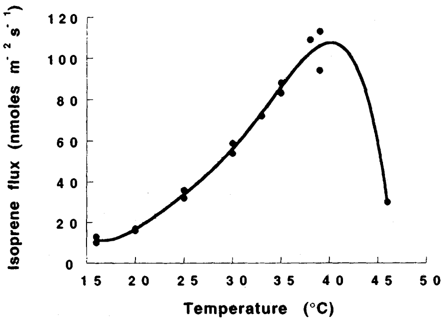


Figure 3. Relationship between temperature and isoprene emission typical of both temperate and tropical plants (after Guenther et al. 1993, Lerdau and Keller in press). Emissions are maximal at approximately 40 °C. Data are for white oak, *Quercus alba*, and are from Baldocchi et al. (1995).

The basal level of isoprene emission is also related to plant nitrogen content. There is a positive correlation between nitrogen availability and the production of isoprene at a given light and temperature (Figure 4; Harley et al. 1994). It is not known if this relationship results from higher photosynthetic rate stimulated by nitrogen and consequent greater availability of carbon for isoprene production, from nitrogen stimulation of the activity of the enzymes responsible for isoprene production, or from a combination of both effects. There is also evidence that isoprene emission is related to leaf carbon balance and is correlated with leaf starch levels (Monson et al. 1995); however, whether starch levels control isoprene production by increasing substrate availability or enzyme activity is not known.

Despite all that is known about the controls over isoprene emission rates, the function of isoprene is still under debate. One possibility is that isoprene emission is involved with high-temperature tolerance in leaves (Sharkey 1996). Placing leaves of isoprene-emitting species, such as kudzu (*Puereria alba*) or red oak (*Quercus rubra*) in a pure nitrogen atmosphere, which prevents them from producing isoprene, decreases the temperature at which irreversible damage to photosynthesis (as determined by changes in steady-state fluorescence) occurs; when isoprene is added back exogenously to the atmosphere, then the temperature threshold for damage increases (Figure 5; Sharkey and Singsass 1995). This is the first functional explanation for isoprene emission from plants, and it opens the door for field studies on the adaptive role of isoprene emission from vegetation.

Monoterpene production and emission. Monoterpene production in plants has been recognized since Neolithic chefs discovered the use of mint, sage, and rosemary as herbs. Monoterpenes are C_{10} hydrocarbons that, like isoprene, are produced by the mevalonic acid pathway (Figure 1). Unlike isoprene, however, monoterpenes are stored in specialized structures, as mentioned above. These storage structures vary with plant taxon, but some better-known examples are the glandular hairs on mints, the resin canals found in the needles of *Pinus*, the resin blisters found in *Abies*, the glandular dots of the Rutaceae, and the storage cavities in *Eucalyptus* leaves (Fahn 1979).

The monoterpene biosynthetic pathway was first formulated as the biogenetic isoprenoid rule, involving the head-to-tail addition of DMAPP and IPP to form geranyl pyrophophate (GPP; Figure 1; Ruzika 1953). Work during the 1960s and 1970s confirmed the validity of this pathway, and further research has taken our understanding of monoterpene synthesis to the molecular level. Several genes for monoterpene biosynthesis have been identified and cloned in mint, and similar research has been undertaken on conifers (McGarvey and Croteau 1995). Much of the genetic variation in absolute monoterpene concentrations is at the familial level. In some taxa, such as the Coniferae and Labiatae, most of the members have high levels of monoterpenes. In other taxa, such as Fagaceae, only a few species show significant levels of monoterpene emission. Because all plants contain the mevalonic acid pathway and produce the monoterpene precursor, GPP, it is not surprising that monoterpene production has arisen multiple times across plant families.

By contrast to the strict light dependency of isoprene emissions, monoterpene emissions are usually independent of light. A few species of oaks, however, do not emit isoprene and show light-dependent monoterpene emission. In addition, young needles on conifers can have both light-dependent and light-independent monoterpene emission (Seufort et al. 1995). In most monoterpene emitters, cells that produce monoterpenes are next to the storage structures, which minimizes transport distances. The existence of these storage structures and the fact that monoterpene emission is not light dependent indicate that monoterpene volatilization comes from stored pools and is independent of ongoing physiological processes.

Early research on the mechanism of monoterpene volatilization showed that temperature is the dominant factor controlling emission rate from any one plant at any one time (Dement et al. 1975). These workers found that the effect of temperature on emission rates matches closely what would be predicted from the relationship between vapor pressure and temperature. The vapor pressure of a particular monoterpene depends on both its volatility and its concentration in the foliage. In addition, recent studies have shown that the monoterpene concentrations within plant tissues also affect their own emission rates according to a Henry's Law relationship; that is, monoterpene emissions increase linearly with their concentrations (Lerdau et al. 1994, 1995).

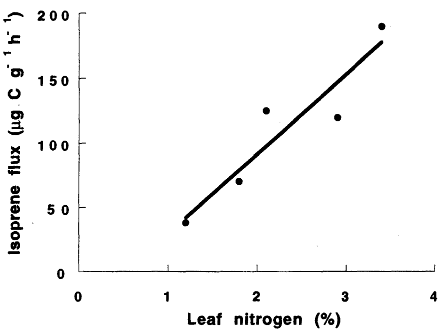
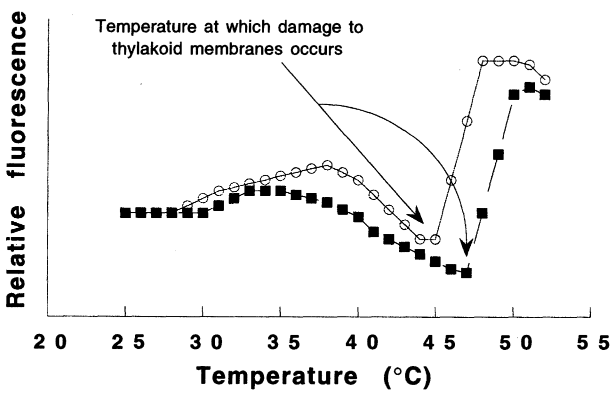


Figure 4. Relationship between leaf nitrogen concentration and isoprene emission rate at constant light and temperature. $r^2 = 0.9$. Data are for velvet bean, *Mucuna* sp., and are taken from Harley et al. (1994).

Unlike isoprene, whose ecological function is still not entirely clear, the ecological roles of monoterpenes—as feeding deterrents against generalist herbivores and toxins against fungal pathogens—have been well known for many years (see recent reviews by Langenheim 1994 and Snyder 1992). Monoterpenes are

Figure 5. Impact of isoprene on the temperature at which irreversible thermal damage, as indicated by a jump in steady-state fluorescence, occurs. Data were collected by M. Lerdau, E. Singsass, and T. Sharkey (unpublished) on red oak, *Quercus rubra*, according to the methods of Sharkey and Singsass (1995). Fully expanded leaves were placed in an environmentally controlled cuvette with a pure N_2 atmosphere to block isoprene production. Temperatures within the cuvette were then raised gradually and the steady-state fluorescence monitored. A jump in fluorescence indicates that thylakoid membranes have been damaged. The open circles represent control leaves, and the solid squares represent leaves to which isoprene was added exogenously via the airstream. Adding isoprene raised the temperature at which thylakoid membrane damage occurred by 2 °C.



not particularly toxic to herbivores (Hobson et al. 1993), but they provide trees with physical protection against herbivore attack. For example, monoterpene resin flow protects conifers against attacks by scolytid bark beetles (Lorio et al. 1995). The sheer volume of monoterpenes exuded by the attacked trees can clog the mouthparts and overwhelm the beetles. Monoterpenes also appear to act as the solvent for higher molecular weight terpenoid compounds, such as diterpenes and resin acids, that may be toxic to herbivores but are solids at ambient temperatures. Thus, monoterpenes serve as part of a plant's toxin delivery system. Although they have minimal direct effect on herbivores, monoterpenes often can be toxic to fungal pathogens. Several of the more deleterious pathogenic fungi are inhibited severely in their growth when monoterpenes are added to the growth medium (Himejima et al. 1992).

The relative concentrations of different monoterpenes is under genetic control, varying among species and sometimes even among populations within a species; these characteristic concentrations have been used as chemosystematic markers for many years (Sturgeon 1979). However, the absolute quantity of monoterpenes in a plant depends on resource availability (see Herms and Mattson 1992 for a comprehensive review of this topic) and genetic background. The confounding effect of plant damage to measurements of monoterpene concentrations led Croteau and Loomis (1972) to conclude erroneously from experiments with cut mints that monoterpenes are model "mobile defense compounds" (compounds that are produced and catabolized quickly). Recently, however, this mobility has been shown to be an artifact of cutting during the experiment. When similar studies were conducted with undamaged plants, little monoterpene metabolism was observed (Mihaliak et al. 1991).

Monoterpenes have been considered ideal examples of carbon-based defense compounds, that is, compounds whose concentrations are expected to vary inversely with the availability of soil resources (Lorio 1993). This expectation is based on the carbon/nutrient and growth/differentiation balance theories of plant chemical defense, which postulate that a tradeoff exists between allocation of resources to growth and to defense. The theories are built on the assumption that plant growth is more sensitive to nutrient availability than is photosynthesis. When nutrients limit growth but not photosynthesis, then an excess of carbon can accumulate and be used in the production of monoterpenes and other carbon-based defensive compounds (Lorio 1993).

Many plant taxa have been tested to see whether or not they fulfill the predictions of these theories. As a general rule, annual plants that produce monoterpenes adhere to the prediction of the theories quite well, whereas perennials show either no relationship or a positive relationship between monoterpene concentration and nitrogen availability (Lerdau et al. 1995). These results indicate that annual plants, which spend most of their lives growing, show a tradeoff between growth and defense, whereas those plants, such as conifers, that grow only for a short period each year show little or no tradeoff.

An alternative explanation for the poor fit that monoterpene concentrations in conifers show with respect to these theories is that the main cost of monoterpene production lies not in the substrate and cofactor costs of monoterpene synthesis itself but in the costs of making the storage structures needed to contain the monoterpenes (Bjorkman et al. 1991). Storage structures account for more than 50% of the total costs of monoterpene production and storage in conifers (Lerdau and Gershenzon in press). These storage structures contain large quantities of nitrogen and are entirely immobile—that is, they consist of fully differentiated cells that represent a permanent investment of resources (Fahn 1979). For taxa in which a large portion of the cost of monoterpenes is associated with storage, rather than substrate use, one would predict that monoterpene allocation patterns would not fit those predicted by the models for carbon-based defenses. However, for those monoterpene-producing plants in which the primary cost is in producing the monoterpene itself, then the monoterpene may behave as a carbon-based mobile defense.

Despite their role as deterrents to herbivory, monoterpenes do not confer complete protection from herbivore damage to most plants that produce them. The resulting damage to monoterpene-laden tissues can have noticeable consequences on fluxes to the atmosphere. Disruption of monoterpene storage structures exposes the reservoirs directly to the atmosphere. As a consequence of this compromising of the diffusive resistances normally imposed by the storage structures, monoterpene fluxes to the atmosphere will be driven solely by their diffusivity and the differences between tissue and atmospheric vapor pressures.

Damage by herbivores can also activate monoterpene cyclases, enzymes that are responsible for monterpene production from GPP, the precursor to monoterpenes (Figure 1). Research on bark tissues has demonstrated a severalfold increase in the activity of monoterpene cyclases following simulated herbivory (Lewinsohn et al. 1993). Similar processes in the needle tissue of several conifer species result in a fourfold increase in monoterpene production upon damage by tiger moth herbivory.[2] When combined with reductions in resistance to monoterpene diffusion, these increases in monoterpene production rates lead to a twentyfold increase in monoterpene flux to the atmosphere per unit of foliage left on a damaged plant.

Other emitted compounds. All plants studied to date emit substantial quantities of methanol when their leaves are expanding (Nemecek-Marshall et al. 1995). The mechanism for this emission is not known, but MacDonald and Fall (1993a) suggest that when cell walls expand, pectin is demethylated, producing methanol. Certain taxa emit large amounts of acetone, particularly from their buds (MacDonald and Fall 1993b). In addition, plants emit many oxygenated VOCs, but

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[2] M. Litvak and R. Monson, unpublished results.

little is known about the biology underlying their production or emission (Isidorov 1994). Two low molecular weight compounds that are emitted by plants in response to injury and whose biosynthesis has been studied are methyl jasmonate and ethylene (Farmer and Ryan 1990). Both compounds induce defensive reactions in the plants that produce them, and they also may function as signals to other plants (Farmer and Ryan 1990). However, the emission rates of these compounds are so low that they play almost no role in the chemistry of the atmosphere.

Since the 1960s, it has been known that several conifers, including ponderosa and lodgepole pines, emit methyl chavicol [1-methoxy-4-2 (2-propenyl) benzene] (reviewed by Salom and Hobson 1995). This compound elicits the strongest response of any VOC in terms of provoking avoidance behavior by bark beetles. Adding methyl chavicol to a tree (by painting on bark) can confer protection from bark beetle attack (Hobson 1995). In addition, trees that are resistant to bark beetle attack have consistently higher levels of methyl chavicol than susceptible trees (Nebeker et al. 1995). This compound may be the single most important VOC in terms of plant–herbivore interactions in conifers, but its possible impacts on atmospheric chemistry have yet to be examined. Indeed, no estimates yet exist for its emission rates from whole forests.

Large quantities of another VOC, methyl butenol [2-methyl-3-buten-2-ol], have been detected in air samples from the Colorado Rockies, but the source of this compound was not identified (Goldan et al. 1993). At the time, methyl butenol was not known to be emitted by plants, and its structure precludes it being an oxidation product of isoprene. Recent studies on loblolly pine (*Pinus taeda*) have demonstrated that methyl butenol is emitted directly from foliage (Guenther et al. 1996b). This compound has recently been shown to be extremely reactive with hydroxyl radicals, although not with ozone (Rudich et al. 1995). The high reactivity with hydroxyl radicals suggests that methyl butenol may play an important role in atmospheric chemistry by decreasing hydroxyl radical concentrations.

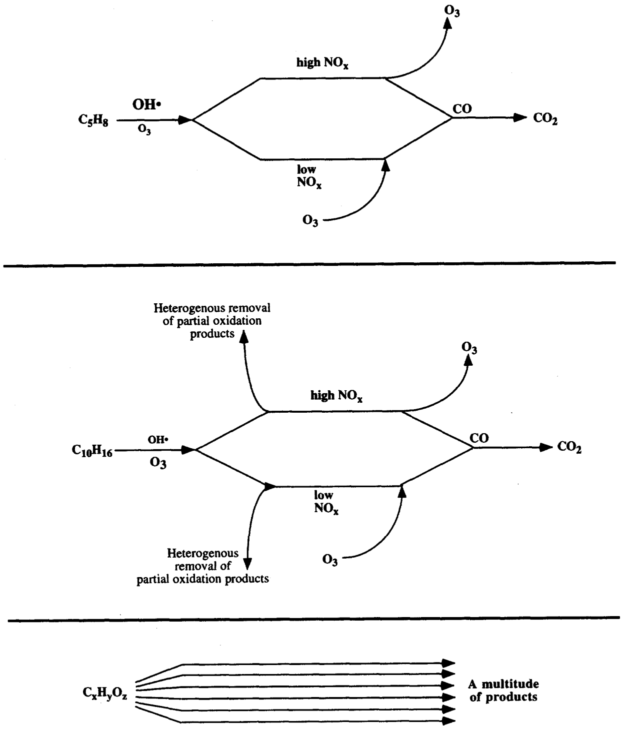

Figure 6. Simplified scheme showing the main light-dependent transformations of isoprene (top), monoterpenes (middle), and oxygenated compounds (bottom). The primary oxidants of all three types of compounds are the hydroxyl radical and ozone. The primary nighttime oxidant is the nitrate radical. The reaction schemes are from Fehsenfeld et al. (1992), Logan et al. (1981), and NRC (1991).

Two additional classes of organic compound for which there is evidence of plant production and emission are the carboxylic acids and organic sulfur compounds. Talbot et al. (1988, 1990) measured the emission of organic acids from enclosed branches of temperate and Amazonian trees, but they were unable to determine whether the compounds were produced by plants or by epiphyllous bacteria. Using measurements of ambient sulfur concentrations and soil sulfur compound flux rates to derive estimates of canopy emissions, Andreae et al. (1988, 1990) found that emissions of sulfur compounds from soils are small in comparison to those from vegetation. Most plant emission of sulfur compounds is a byproduct of catabolic processes (Rennenberg 1991). A comparison of terrestrial and aquatic sources of sulfur compounds (Kesselmeir 1991) demonstrated that fluxes from aquatic systems are one to two orders of magnitude higher than fluxes from terrestrial ones.

Atmospheric impacts of VOC emissions

Isoprene and other biogenic hydrocarbons play key roles in several aspects of tropospheric chemistry, including ozone dynamics, carbon monoxide production, and methane oxidation (reviewed in Baldocchi et al. 1995, Crutzen 1979, Fehsenfeld et al. 1992, Logan et al. 1981). These roles stem from the high reactivity of the isoprenoid hydrocarbons. Whereas methane (CH_4) is chemically saturated (i.e., its carbon atom is bonded to four hydrogen atoms, with no C=C double bonds) and has an atmospheric lifetime of 8–11 years, isoprenoids do contain C=C bonds (Figure 1), which give these compounds much shorter lifetimes, often just hours in sunlight. The main pathways of isoprenoid oxidation are outlined in Figure 6.

The key elements of isoprene oxidation in the light involve attack by one of two oxidizing sources: the hydroxyl radical (OH·) or ozone (O_3). The reaction with hydroxyl radical proceeds approximately an order of magnitude faster than the reaction with ozone and is the dominant daytime isoprene sink. During the nighttime, isoprene reacts with the nitrate radical NO_3· with a reaction rate that is approximately one-fifth that of light-dependent hydroxyl radical oxidation. Furthermore, atmospheric nitrate radical concentrations are typically so low that reaction of isoprene with hydroxyl radicals is the most important pathway of isoprene oxidation. The oxidation pathways of the monoterpenes are similar to those of isoprene but follow different rate constants.

One of the most important products of the oxidation of isoprenoids is carbon monoxide. Oxidation of hydrocarbons other than methane contributes as much as 35% of the atmospheric carbon monoxide, an amount comparable to that released by fossil fuel combustion (Brasseur and Chatfield 1991). Carbon monoxide influences the oxidizing capacity of the atmosphere in a manner similar to isoprene by acting as a sink for hydroxyl radicals and participating in photochemical reactions that can result in increased ozone concentrations (Logan et al. 1981). With a lifetime of several hours, isoprenoid compounds usually travel within the lower troposphere to a downwind distance of approximately 10 km (Fehsenfeld et al. 1992). The immediate oxidation products, such as methyl-vinyl-ketone and methacrolein, have somewhat longer lifetimes but still can persist only within approximately 100 km of the point where the primary compound was emitted. The relatively long lifetime of carbon monoxide (several months) allows biogenic isoprene emissions to influence the global atmosphere because carbon monoxide is transported far from the sites of production. Organic nitrogen compounds produced as a result of isoprenoid oxidation can similarly influence the global atmosphere by generating a relatively long-lived reservoir of reactive nitrogen.

When isoprene is oxidized in the presence of significant concentrations (greater than 10 parts per trillion by volume) of nitric oxide, large quantities of ozone are produced. High concentrations of nitric oxide are present when there is substantial combustion of fossil fuels or biomass. As a result of the isoprene–nitric oxide interaction, urban areas that have large amounts of isoprene-emitting vegetation nearby, such as Atlanta, Georgia, show substantial ozone production, even if automobile emissions of hydrocarbons are reduced through the use of catalytic converters (Chameides et al. 1988). When isoprene is oxidized in air with low amounts of nitric oxide—that is, air with little in the way of anthropogenic pollutants—ozone is consumed and isoprene oxidation reduces the concentration of this important pollutant.

Isoprene's high reactivity and lack of absorption in the infrared portion of the spectrum preclude any direct role for this compound in Earth's radiative balance. However, isoprene can have a profound indirect influence on global temperature through its impact on methane's atmospheric lifetime (Wuebbles et al. 1989). Both methane and isoprene require attack by a hydroxyl radical as the first step in their oxidation pathways. Isoprene, however, is approximately four orders of magnitude more reactive than methane and thus can serve to reduce hydroxyl radical availability and increase methane's lifetime (Jacob and Wofsy 1988). A longer atmospheric lifetime means that methane concentrations will rise (assuming no feedback to sources, which is a sound assumption for methane) and contribute more to greenhouse warming. Isoprene emission is temperature dependent, so the possibility exists for positive feedback—that is, isoprene emission influences global warming through its effect on methane lifetime, and higher temperatures cause higher isoprene emissions (Monson et al. 1991).

The atmospheric reactions and fates of monoterpenes and other biogenic VOCs are even less well understood. Some monoterpenes are highly reactive with ozone, and many monoterpenes may be removed through gas–liquid interactions between the monoterpene vapor and water (Crutzen 1979). Such heterogeneous removal of partially oxidized compounds creates the possibility for deposition of partially oxidized compounds into ecosystems and could help to explain the low pH of rainfall in certain rural areas, such as the Amazon Basin.

Global change and the ecology of emissions

Three related aspects of global change have the potential to dramatically affect biogenic hydrocarbon emissions: increases in atmospheric levels of carbon dioxide; increases in greenhouse gases, which lead to higher surface temperatures and changes in precipitation patterns; and landscape-scale alterations in vegetation type. Increases in carbon dioxide concentration may favor C_3 over C_4 plants and alter community composition in areas currently dominated by C_4 plants because C_3 plants show a larger increase in photosynthetic rates in response to an increase in ambient carbon dioxide concentration than do C_4 plants (Bazzaz 1990). Increases in greenhouse gas concentrations are predicted to lead to both temperature increases in the lower troposphere and drying in midcontinent regions (Schneider 1993). These climatic responses, in conjunction with direct human impacts on land use and vegetation, will alter biome distribution on a global scale. Each of these changes will therefore affect both the amount of hydrocarbon-emitting tissue present in ecosystems and the emissions per unit of biomass. Despite the taxonomic variability in VOC emissions, one constant is that no C_4 species has been found to emit as much isoprene or monoterpene as some C_3 species. Invasion by C_3 plants of regions now dominated by C_4 plants, such as tropical grasslands, may increase total isoprene and monoterpene emissions because some of the invading species are likely to be hydrocarbon emitters.

Because monoterpene and isoprene emissions are strongly temperature dependent, they will respond quickly to changes in global temperature. Monoterpene emissions are likely to increase exponentially with temperature because of the effect of temperature on vapor pressure. Isoprene emissions show typical Arrhenius temperature kinetics with temperature optima that range from 36 °C to 40 °C, depending on the species (Guenther et al. 1993, Lerdau and Keller in press). These temperature optima are well above the ecosystem temperatures predicted by general circulation models (reviewed in Schneider 1993), so the general effect of global warming should be an increase in both isoprene and monoterpene emissions.

Reduced precipitation over mid-continent regions could have complex effects on hydrocarbon emissions. Monoterpene concentrations in pines have been shown to increase in response to drought (Lorio et al. 1995). However, drought will also reduce the leaf area that a stand of trees can support. Consequently, there is no way to predict whether total hydrocarbon emissions will increase or decrease. Chronically water stressed plants show reduced isoprene emissions per unit leaf area (Figure 7). How much of this reduction is a direct effect of water stress and how much is an indirect effect of reduced nitrogen concentration in the leaves is not yet known, but this decrease in emissions per unit biomass, combined with the decrease in total biomass predicted by decreased water availability, means that drought is likely to cause a large decrease in ecosystem-level isoprene emissions.

In addition to the direct effects of climatic change on hydrocarbon emissions, changes in biome type, as a result of climate change and/or human land use change, will have a profound impact on emissions. Biome type has a large effect on emissions because of the high species specificity of emissions. Whereas photosynthesis and transpiration can be predicted accurately simply with a knowledge of temperature and precipitation, hydrocarbon emissions vary widely across taxa within an ecosystem. For example, in forests of the northeastern United States, oaks are major isoprene emitters, and maples emit no isoprene whatsoever. Because it is difficult to predict precisely how a biome will change, it is difficult to determine exactly the effects of climatic changes on VOC emissions. Nevertheless, because certain biome types tend to have a greater or lower proportion of emitters than others (Monson et al. 1995), it is possible to make rough generalizations.

In addition to potential climate change–induced biome shifts, four major changes in biomes are already occurring on regional and global scales as a result of changes in human land use. First, in many tropical forest regions, both deciduous and evergreen forests are being replaced with agricultural lands and pastures. Second, in tropical grasslands, grazing and suppression of natural fires have caused shrublands to expand into areas that had been dominated by grasses. Third, in large areas of Africa, deserts have expanded into grassland and woodland regions. Fourth, in eastern North America, some agricultural lands are reverting to forest.

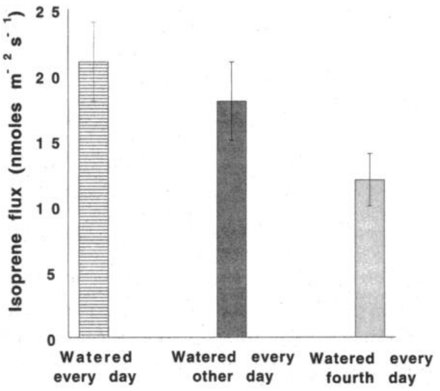

Figure 7. Impact of watering frequency on isoprene emission from velvet bean, *Mucuna* sp. Data are from A. Jasentuliyana and M. Lerdau (in preparation) and were taken from plants watered every day, every other day, or every fourth day. Isoprene emission was measured at 1000 μmoles · m^{-2} · s^{-1} of light and 30 °C.

Conversion of tropical forests to agricultural uses is, perhaps, the best-publicized of these land use changes. The effects of this conversion are usually considered in terms of biodiversity and regional water balance. However, because tropical forests are large sources of biogenic hydrocarbons, and crop species and pasture grasses are not, local photochemistry is also affected by deforestation. Likewise, desertification has probably also caused a decline of biological inputs of reduced VOCs. By contrast, in arid regions, where frequent natural fires have led to grassland systems, agricultural practices of grazing and fire suppression have allowed shrublands to spread. Many arid-region shrubs are high emitters, whereas grasses are not, and so biogenic VOC emissions have risen with the advent of agriculture in arid portions of the globe.

The forests of the eastern United States have seen two major changes since settlement by Europeans that have directly affected VOC emissions at a landscape scale. First, much of the forest land was cleared and replaced by crops. Since the turn of the century, agriculture has declined and most of this cropland has become reforested, although the trees are much smaller than those of the forests that were there before the conversion to cropland. Second, the chestnut blight of the late nineteenth and early twentieth centuries caused massive changes in forest composition. Chestnut (*Castanea dentata*), which had comprised as much as 50% of East Coast lowland forests (Braun 1950), disappeared almost completely and was replaced to a large extent by oak (Greller 1988). Unlike oak, chestnut does not emit isoprene (Guenther et al. 1996a). The chestnut blight has thus resulted in an approximate doubling of the biomass of isoprene-emitting species in the eastern United States.

It is difficult to assess the impacts of these changes in biogenic VOC emission rates on the atmosphere because the changes in VOC emissions have been accompanied by dramatic changes in emissions of other compounds, including nitrogen oxides (NO_x), which are produced during biomass burning and fossil fuel combustion. An increase in biogenic VOC emissions within a low-NO_x environment is likely to result in a decrease in the oxidizing capacity of the atmosphere. An increase in biogenic VOC emissions within a high-NO_x environment, however, will cause an increase in certain pollutant oxidants, such as ozone (Fehsenfeld et al. 1992).

Future directions in VOC research

Three aspects of biogenic VOCs are most in need of further research. The first involves the atmospheric chemical processes of hydrocarbon oxidation. These oxidation processes play important roles in the production and consumption of carbon monoxide, methane, and ozone, and possibly in the production of organic acids and nitrates. It is especially important to identify the factors governing VOC removal. That is, are VOCs removed through gas-phase reactions? Or through dissolution in water droplets? Oxidation pathways for most biogenic VOCs are unknown. Theoretical reaction schemes have been developed for isoprene but have not been confirmed with field measurements. In principle, a completely oxidized isoprene molecule could produce five carbon monoxide molecules. However, if one of the products of partial oxidation is dissolved in an aerosol and removed through precipitation, then the amount of carbon monoxide produced may be lowered. Field investigations to evaluate the fates of isoprene and other biogenic VOCs are needed to determine the impact of these compounds on the global atmosphere.

The second area that is poised for additional research concerns the impacts of herbivores and pathogens on VOC production and emission. As discussed above, monoterpene fluxes to the atmosphere from a single plant can be stimulated severalfold by insect damage. In assessing the ecosystem-level impacts of widespread herbivore damage, increases in monoterpene flux caused by induction of monoterpene cyclases and by reduction of the diffusive resistances at the needle surface must be balanced against the decreases in monoterpene flux caused by losses of foliage due to herbivore consumption. In other words, to what extent does stimulation of flux from tissues left behind compensate for the loss of flux from tissues that are consumed? An answer to this question is essential if we are to determine the potential impacts of forest herbivory on ecosystem-level controls over atmospheric chemistry.

The third major unknown in biogenic VOCs concerns emissions from tropical regions. So far, only one emissions study has been carried out in tropical forests (Lerdau and Keller in press). Modeling studies and ambient level measurements suggest that the tropics are responsible for at least 80% of the global emissions of biogenic VOCs. There is an urgent need for studies ranging from broad surveys in evergreen and deciduous forests to more mechanistic studies of emission responses to environmental parameters. Biogenic VOC emissions are one of the most important ways in which plants affect tropospheric chemistry and air quality. These emissions are also one of the least understood aspects of plant physiology and ecology.

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