Plant Production and Emission of Volatile Organic Compounds

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

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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).

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 = 10¹² 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 that 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 monoterpines, C₁₀H₁₆, came from the leaves of chaparral vegetation, and Sanadze (1957;
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_{5}H_{8}, Rasmussen and Went (1963) 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

\[
\text{flux} = k(\text{VP}_{\text{leaf}} - \text{VP}_{\text{atmosphere}})/r
\]

where \(k\) is a diffusion coefficient of the compound in question, \(\text{VP}_{\text{leaf}}\) is the vapor pressure of the compound within the leaf, \(\text{VP}_{\text{atmosphere}}\) 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 \(\text{VP}_{\text{atmosphere}}\). 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

\[
\text{flux} = k\text{VP}_{\text{leaf}}/r
\]

and our attention can then be directed to the controls over \(\text{VP}_{\text{leaf}}\) 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 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:

\[
r = r_1 + r_2 + r_3 + \ldots + r_n
\]

In the case of isoprene, the important resistances are: \(r_3\), the resistance from the chloroplast into the cell; \(r_4\), the resistance across the cell membrane; \(r_5\), the resistance through the intercellular air space; and \(r_6\), 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 \(r_3\), the resistance from the monoterpene storage site within the leaves to the intercellular air spaces;
$r_s$, the resistance to transport through the intercellular air spaces; and $r_r$, 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 hypostomatus 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 hypostomatus 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 $V_{PI}$ means that the driving force of the first equation increases in proportion to the increase in stomatal resistance. Thus, as long as $V_{PI}$ 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.

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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1R. Fall, 1986, personal communication. University of Colorado, Boulder, CO.
...centrations in the stroma (Silver and
changes in pH and Mg²⁺ catalyzes the conversion of DMAPP
to isoprene, appears to be light acti­
ond light requiremen t arises from
long-term
plants can draw on carbon reserves
for isoprene production. For example, during
drought stress, when
...evolved multiple times in plants or isoprene emission
...isoprene photosynthesis has been in­
...emitters, whereas the genera Fagus
(beeches) and Castanea (sweet chest­
...member of the genus Quercus (oaks) are isoprene
emitters, whereas the genera Fagus
(beeches) and Castanea (sweet chest­
...are from Baldocchi et al. (1995).
(b) Linear relationship between light intensity and isoprene emission
...isoprene production, from nitro­
...induction temperature for isoprene
...environmental effects, the basal level of
isoprene emission (i.e., emission at a
standard set of light and tempera­
ture conditions) has been tied to the
exposure of plants to high tempera­
ture (32 °C or above) for short peri­
ods (approximately 24 hours; Shar­
key et al. 1991). The induction of
isoprene biosynthesis has been in­
vestigated in only a few species, and
...isoprene emission during a light-to­
dark transition (Loreto and Sharkey
1993). However, isoprene produc­
tion can continue even in the ab­
sence 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 pho­
tosynthesis is blocked for several
days because of stomatal closure,
isoprene continues to be produced
(Sharkey and Loreto 1993). The sec­
ond light requirement arises from
the fact that isoprene synthase, which
...isoprene synthase activity levels during the
development of a leaf (Kuzma and
Fall 1993). In addition to develop­
ment, the basal level of
isoprene emission is also related to
plant nitrogen content. There is a positive corre­
rlation 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 conse­
quent 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 rel­
ated to leaf carbon balance and is
correlated with leaf starch levels
(Monson et al. 1995); however,
whether starch levels control iso­
prene production by increasing sub­
strate availability or enzyme activ­
ity is not known.

Despite all that is known about
the controls over isoprene emission
rates, the function of isoprene is still

![Figure 2](image_url)

**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).
Monoterpene production and emission. Monoterpene production and emission have been recognized since Neolithic chefs discovered the use of mint, sage, and rosemary as herbs. Monoterpene are C₁₀ hydrocarbons that, like isoprene, are produced by the mevalonic acid pathway (Figure 1). Unlike isoprene, however, monoterpene 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 pyrophosphate (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 monoterpene. 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 (Seufert et al. 1995). In most monoterpene emitters, cells that produce monoterpene 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).

Unlike isoprene, whose ecological function is still not entirely clear, the ecological roles of monoterpenes—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). Monoterpene emissions 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 (Pueraria 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.

Figure 4. Relationship between leaf nitrogen concentration and isoprene emission rate at constant light and temperature. r² = 0.9. Data are for velvet bean, Mucuna sp., and are taken from Harley et al. (1994).

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 N₂ 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, monoterpenes secreted by fungi protect 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 monoterpenes 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 monoterpeno 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 monoterpeno concentrations in conifers show with respect to these theories is that the main cost of monoterpeno production lies not in the substrate and cofactor costs of monoterpeno 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 monoterpeno 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 monoterpeno-producing plants in which the primary cost is in producing the monoterpeno itself, then the monoterpeno 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 monoterpeno-laden tissues can have noticeable consequences on fluxes to the atmosphere. Disruption of monoterpeno 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, monoterpeno 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 monoterpeno cyclases, enzymes that are responsible for monoterpeno production from GPP, the precursor to monoterpenes (Figure 1). Research on bark tissues has demonstrated a severalfold increase in the activity of monoterpeno cyclases following simulated herbivory (Lewinsohn et al. 1993). Similar processes in the needle tissue of several conifer species result in a fourfold increase in monoterpeno production upon damage by tiger moth herbivory.2 When combined with reductions in resistance to monoterpeno diffusion, these increases in monoterpeno production rates lead to a twentyfold increase in monoterpeno 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. 1993). 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

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.

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 carbon metabolic 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, Feinseifeld et al. 1992, Logan et al. 1981), and NRC (1991). One of the main pathways of isoprenoid oxidation is the hydroxyl radical (OH·) or ozone (O₃). 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 NO₃, 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

![Figure 6. Simplified scheme showing the main light-dependent transformation 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).](https://academic.oup.com/bioscience/article-abstract/47/6/373/290460)
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 (Feinseifeld et al. 1992). The immediate oxidation products, such as methyl-vinylketone 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 understood. Some monoterpenes are highly reactive with ozone, and many monoterpenes may be removed through gas–liquid interactions between the monoterpane vapor and water (Cruzen 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 C₄ over C₃ plants and alter community composition in areas currently dominated by C₄ plants because C₃ plants show a larger increase in photosynthetic rates in response to an increase in ambient carbon dioxide concentration than do C₄ plants (Bazzaz 1990). Increases in greenhouse gas concentrations are predicted to lead to both temperature increases in the lower stratosphere 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 C₃ species has been found to emit as much isoprene or monoterpenes as some C₄ species. Invasion by C₄ plants of regions now dominated by C₃ 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 monoterpenes and isoprene emissions are strongly temperature dependent, they will respond quickly to changes in global temperature. Monoterpane 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 midcontinent 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 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.

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), which are produced during biomass burning and fossil fuel combustion. An increase in biogenic VOC emissions within a low-NO 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 environment, however, will cause an increase in certain pollutants, 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 drop-
eters. Biogenie VOC emissions are one of the most important ways in which plants affect tropospheric chemistry and air quality. These emissions also one of the least understood aspects of plant physiology and ecology.

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June 1997

383