Role of Global Warming and Plant Signaling in BVOC Emissions

5

Saurabh Sonwani, Pallavi Saxena,
and Umesh Kulshrestha

Abstract

Plants emit a substantial amount of biogenic volatile organic compounds (BVOCs) into the atmosphere having significant effects on atmospheric chemistry, physics, and the organisms. In this chapter, important facts about BVOCs' production mechanism, storage, and emissions due to various abiotic and biotic factors have been discussed. The role of BVOCs in defense system through plant signaling has also been discussed. The chapter continues with the discussions about the importance of BVOCs in the formation of tropospheric ozone and secondary organic aerosols and ultimately strengthens our understanding about global change research.

Keywords

BVOCs • Abiotic • Biotic • Plant signalling • Defense systems • Tropospheric ozone • Secondary organic aerosol

5.1 Introduction

Generally, any organic compound having vapor pressure high enough under normal conditions to be vaporized into the atmosphere is termed as a volatile organic compound (VOC). VOCs emitted by plants are widely known as biogenic volatile organic compounds (BVOCs). BVOCs are classified according to their structure and biosynthetic origin (Pichersky et al. 2006). BVOCs represent a group of organic trace gases (except carbon dioxide and monoxide) released into the atmosphere from the plants and soils. Biogenic VOCs include isoprenoids (isoprene and monoterpenes) as well as alkanes, alkenes, carbonyls, esters, ethers, alcohols, and acids. The lifetime of BVOCs in the atmosphere varies from minutes to several days (Kesselmeier and Staudt 1999).

Isoprene (C_5H_8) is the most widely studied single BVOC which accounts for >90 % of the total BVOC emissions of a particular plant species (Blande et al. 2007). The total annual isoprene emissions account for 440–660 TgC (Guenther et al. 2006), which is a large fraction of annual global BVOC emissions (700–1000

S. Sonwani (✉) • P. Saxena • U. Kulshrestha
School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110067, India
e-mail: sonwani.s19@gmail.com

U. Kulshrestha, P. Saxena (eds.), *Plant Responses to Air Pollution*,
DOI 10.1007/978-981-10-1201-3_5

TgC) (Laothawornkitkul et al. 2009). Isoprene belongs to the biochemical class of terpenoids; other BVOCs under the same class are monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$). BVOCs produced by plants are involved in plant reproduction (by attracting pollinator), growth, wound healing, development, and defense against herbivores. They are also involved in a communication process between plants and insects, within plants, and within plant communities (Pichersky and Gershenzon 2002; Peñuelas et al. 1995; Shulaev et al. 1997) (Fig. 5.1). BVOCs can also protect plants against high temperatures. But, on the other hand, BVOC emissions increase with warming and might produce both negative and positive feedback on global warming through aerosol formation as well as direct and indirect greenhouse effects (Fig. 5.2).

Several authors have reported that plants re-emit a substantial fraction of their assimilated carbon into the atmosphere as BVOCs that can affect chemical and physical properties of the atmosphere (Peñuelas and Llusià 2001; Kesselmeier and Staudt 1999).

A large fraction of carbon can be lost during BVOC emission and it was estimated to be around ~10 % of the total carbon stored by plants through photosynthesis (Peñuelas Llusià 2003). Apart from abovementioned functions, there is another function of BVOCs that has dragged scientist attention given global warming. Recently, it is found that production and emission of certain BVOCs such as isoprene and monoterpenes, which contribute a large fraction of total BVOCs, confer protection against high temperature. There are various factors responsible for BVOC emissions and biological and physicochemical processes (Figs. 5.1 and 5.2). Several internal (biochemical and genetic) and external factors control emission rates of different BVOCs by altering their synthesis, diffusion, or vapor pressure to the atmosphere. The external factor includes abiotic (light, wind, water availability, temperature, and ozone) and biotic (animal, plant, and microorganism interactions) factors

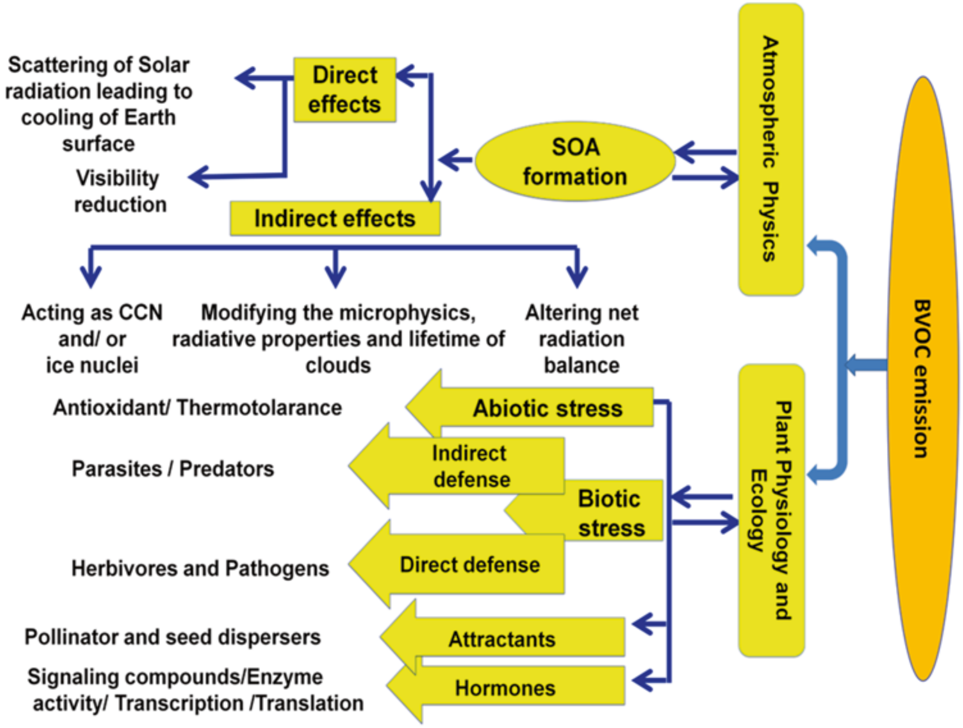

Fig. 5.1 Role of BVOCs in atmospheric physics and plant physiology

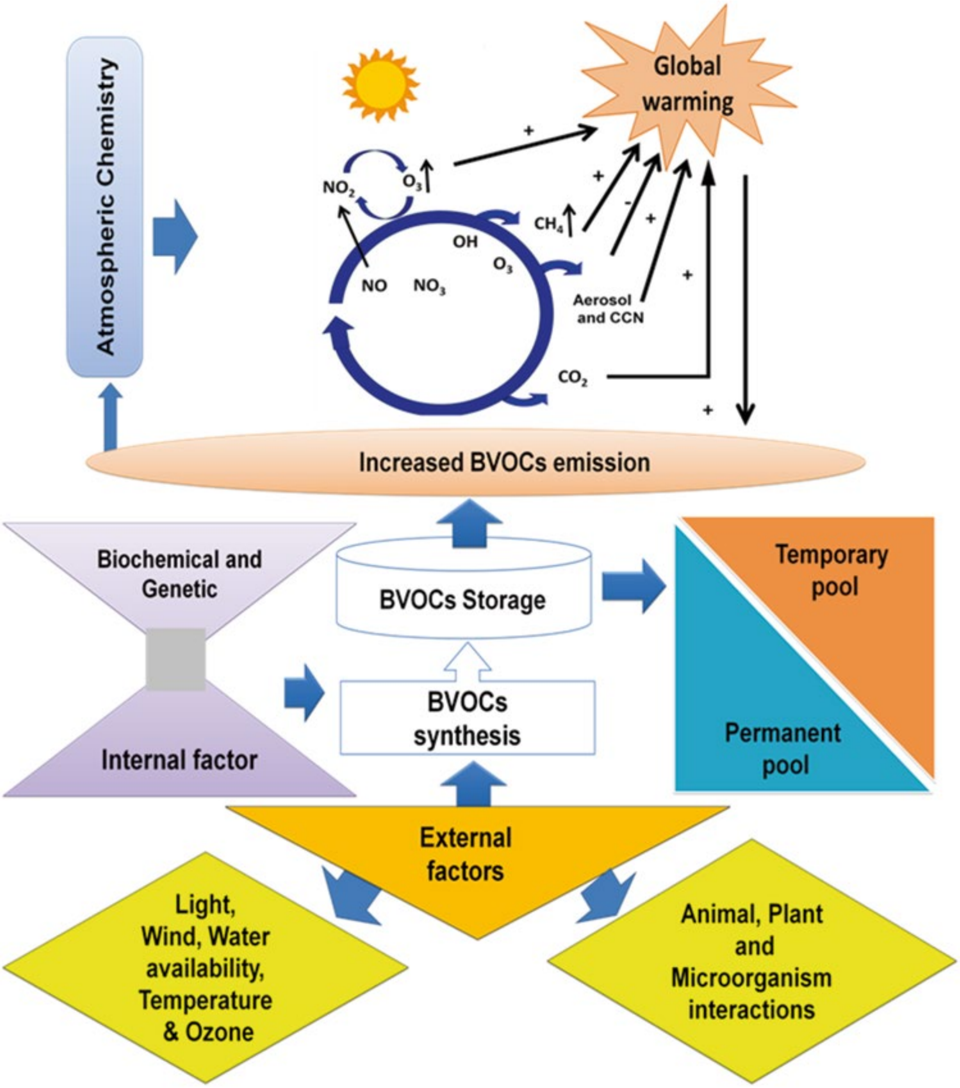

Fig. 5.2 BVOCs' synthesis, storage, and role in atmospheric chemistry

(Fig. 5.2). The complex net of these factors and their interactions and the different responses of the different BVOCs produce large qualitative and quantitative and spatial and temporal variability of emissions and frequent deviations from current standard emission models, mostly based on temperature and light response (Peñuelas and Llusià 2001). Plant emissions of BVOCs have strong relevance for plant physiology and plant ecology, atmospheric chemistry, and climate.

5.2 BVOC Emissions: Why and How

It is now well reported by several authors that a wide variety of volatile non-methane organic compounds (referred to hereafter as biogenic volatile organic compounds (BVOCs)) are emitted into the atmosphere from vegetation (Fall et al. 1999; Geron et al. 2000; Guenther et al. 1995, 2000; Fuentes et al. 2000). BVOCs are stored in specialized structures like glandular trichomes, glands, and resin ducts/resin canals (Turner et al. 2000; Franceschi et al. 2005) and are tightly separated by the surrounding cells by an impermeable layer, generally cuticular cells (Gershenzon et al. 2000). On the other hand, if plants have no storage structures for BVOCs, they have some temporary pools/nonspecific storage (observed in both conifers and broad-leaved trees) in mesophyll that freely diffuse out of the leaf along their concentration gradient. The only determining factor for this process of gas diffusion is stomatal conductance.

5.2.1 Mechanism of BVOC Emission

The mevalonic acid (MVA) pathway and the 2-deoxyxylulose 5-phosphate/2-methylerythritol 4-phosphate (MEP) pathway (Fig. 5.3) are the two metabolic routs responsible for DMAPP formation. Leucine metabolism is another pathway which works as a source of isoprenoids. The source of DMAPP within the chloroplast is the MEP pathway (Rohmer et al. 1993). The MEP pathway begins with pyruvate and glyceraldehyde 3-phosphate (Rohmer et al. 1993) and involves skeletal rearrangement to make the branched chain and finally ends with isoprene (Arigoni et al. 1997). In the MEP pathway, each carbon in the starting intermediate costs three ATPs plus two NADPH if at the redox level of a triose phosphate with CTP equivalent to ATP. According to Lichtenthaler and coworkers, this pathway is responsible for most of the isoprenoids made in plastids (Lichtenthaler et al. 1997). It is proved that this pathway is responsible for isoprene synthesis (Schwender et al. 1997; Zeidler et al. 1997). The MEP pathway is more efficient (cost is only six carbon atoms, 20 ATPs, and 14 NADPH) as compared to the MVA pathway (cost is nine carbon atoms, 24 ATPs, and 14 NADPH).

5.2.2 Role of Isoprene Synthase

Plants emit isoprene produced from DMAPP by isoprene synthase (enzyme) (Silver and Fall 1991) which works at a relatively high pH and needs Mg^{2+} (Schnitzler et al. 1996; Silver and Fall 1995) which is present inside chloroplasts (Mgaloblishvili et al. 1979; Wildermuth and Fall 1996, 1998). Wildermuth and Fall (1998) also found some isoprene synthase activity bound to thylakoid membranes. Isoprene synthase activity is found to be soluble (Wildermuth and Fall 1996, 1998). The membrane-bound form of isoprene synthase activity appeared to have the same kinetics as the soluble form. Whether the soluble

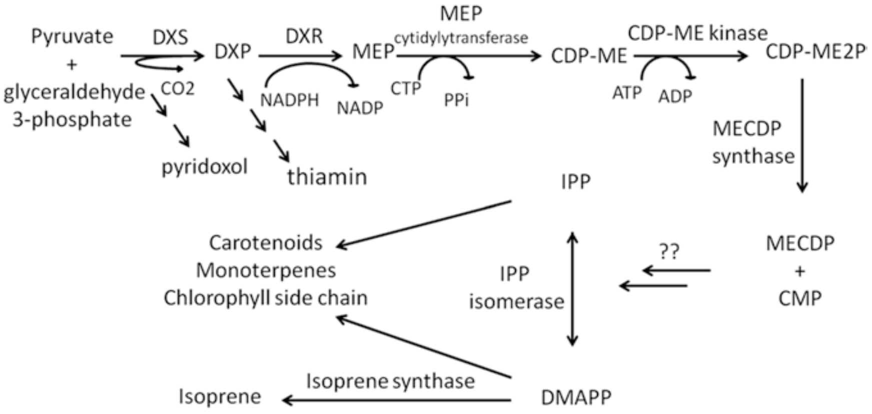

Fig. 5.3 BVOC synthesis; MEP pathway. Note: *CDP-ME2P*2-phospho-4-(cytidine50-diphospho)-2-C-methyl-D-erythritol, *CDP-ME* 4-(cytidine 50-diphospho)-2-C-methyl-D-erythritol, *DXR* deoxyxylulose-5-phosphate reductoisomerase, *DXS* deoxyxylulose-5-phosphate synthase, *MECDP* 2-C-methyl-D-erythritol 2,4-cyclodiphosphate, *IPP* isopentenyl pyrophosphate, *DMAPP* dimethylallyl pyrophosphate

form is converted to the bound form or vice versa and what effect this might have on the activity of isoprene synthase is not known. Thylakoid-bound isoprene synthase activity could be stimulated threefold by the addition of GTP and palmitoyl CoA (Wildermuth 1997). The conversion of DMAPP to isoprene is catalyzed by isoprene synthase. Perhaps isoprene is a product of the breakdown of higher isoprenoids in *E. coli*. In bacteria (*Bacillus subtilis*), isoprene emission occurs during different phases of growth (Wagner et al. 1999).

5.3 Atmospheric Chemistry and Physics of BVOCs

5.3.1 Production of Tropospheric Ozone

According to Fehsenfeld et al. (1992) and Thompson (1992), isoprene emission from plants plays a significant role in atmospheric chemistry (Fig. 5.2). BVOCs such as isoprene can alter atmospheric chemistry affecting the residence times of gases that contribute to the greenhouse effect. Isoprene oxidation in the atmosphere can give rise to ozone and smog if nitrogen oxides are present in the atmosphere (Daum et al. 2000; Haagen-Smit 1952). In the high-isoprene emission zone, like a zone with extensive tropical forest, isoprene oxidation can account for up to 71 % of the reduction in OH (compared to only 11 % for CO oxidation and 5 % for CH_4 oxidation) (Grosjean 1995). Hence, it is very important to understand the role of BVOCs in atmospheric chemistry (Thompson et al. 1992; Fehsenfeld et al. 1992). BVOC emissions can indirectly increase the concentrations of other important greenhouse gases such as methane resulting in reduced atmospheric oxidation capacity due to depletion of OH radicals (Lelieveld et al. 2008). Hydroxyl radicals are very reactive oxidants and act as the atmospheric detergent (Lelieveld et al. 2008). After the study of chemistry and transport model by Wang et al. (1998), it is clear that global emissions of BVOCs, particularly isoprene, can cause a 15 % increase in the background levels of O_3 and a 20 % decrease in the mean OH concentrations (Wang et al. 1998). Another study suggested that global VOC emissions (isoprene as a large fraction) cause an 18 % increase in the global tropospheric O_3 concentration, a 16 % decrease in the global OH concentrations, and a 20 % increase in the tropospheric lifetime of CH_4 (Poisson et al. 2000). Even the NOx spatial distribution and deposition are affected by BVOC interactions.

The oxidation of BVOCs by OH in the presence of sufficient NOx leads to the formation of O_3 in the troposphere by disruption of the photochemical steady state of O_3 (i.e., allows the oxidation of NO to NO_2 without removal of an O_3 molecule) and so causes elevated O_3 concentrations. NOx emissions may result from fossil fuel combustion, fertilizer application, and biomass burning, as well as natural production by lightning. As tropospheric photochemistry is highly nonlinear with respect to the emissions of O_3 precursors, modeling is required to determine the effects of BVOC emissions on O_3 concentrations in the troposphere (Fowler et al. 2008).

At night, NOx is present in the atmosphere as NO_2. According to Monson and Holland (2001), sunlight photolyzes NO_2 which leads to the formula of one molecule of ozone per one molecule of NO_2. In the absence of hydrocarbons, the total NOx level determines the amount of ozone in the atmosphere.

$$RH_2 + OH + O_2 \rightarrow RO_2 + H_2O \tag{5.1}$$

$$RO_2 + NO \rightarrow RO + NO_2 \tag{5.2}$$

$$RO + O_2 \rightarrow R`CHO + HO_2 \tag{5.3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{5.4}$$

$$2\left(NO_2 + O_2 \rightarrow NO + O_3\right) \tag{5.5}$$

$$NET: RH + 4O_2 \rightarrow R`HCO + 2O_3 + H_2O \tag{5.6}$$

This cycle is continued as long as there are C–H bonds available which enable the formation of ozone. At a very high NOx level, one isoprene molecule can result in multiple molecules of ozone. But at a low NOx level, isoprene emission can reduce ozone level via different set of reactions (Trainer et al. 1987). Isoprene also plays a role in the growth of aerosols in the atmosphere. Though aerosol's yield per molecule in the atmosphere is much lower than for monoterpenes, due to its large emission, isoprene became a significant source of secondary organic aerosol (Claeys et al. 2004; Edney et al. 2005; Kroll et al. 2005, 2006; Ng et al. 2006; Olcese et al. 2007). The resulting changes in climate may affect BVOC emission rates, providing a positive feedback in the climate system. The oxidation of BVOCs also contributes atmospheric CO (Hatakeyama et al. 1991; Fehsenfeld et al. 1992; Bergamaschi et al. 2000; Griffin et al. 2007) which impacts the oxidative capacity of the atmosphere similar to isoprene through acting as a sink for OH (Logan et al. 1981). Thereby, the oxidation of CO is a source or sink of O_3, depending on the NOx availability. Atmospheric oxidation of BVOCs can also result in the formation of peroxyacetyl nitrates (PANs) (Fehsenfeld et al. 1992). PANs have longer residence time and can be transported to a larger distance. PANs are a source of NOx when they are thermally decomposed in warmer air (Fehsenfeld et al. 1992; Poisson et al. 2000), contributing a high level of NOx in the regime without local NOx emissions which ultimately lead to higher O_3 levels in remote areas.

5.3.2 Secondary Aerosol Formation

According to various laboratory and field studies, BVOCs are a significant source of secondary organic aerosol (SOA) (Fig. 5.1) (Leaitch et al. 1999; Joutsensaari et al. 2005). Through the mechanism SOA formation via BVOC oxidation is still not fully explained (Kulmala 2003), but it is understood that BVOC oxidation results in lower vapor pressure compounds which triggers their condensation on preexisting atmospheric molecules (Joutsensaari et al. 2005). Terpenes and sesquiterpenes contribute more significant amounts of SOA as compared to isoprene (Claeys et al. 2004; Leaitch et al. 1999; Meskhidze and Nenes 2006). Atmospheric aerosols are considered to have direct effects on climate as they scatter solar radiation. Secondarily they also have indirect effects such as cloud condensation nuclei, changing cloud albedo, and the degree of cloud cover. The possibility that SOA formation from BVOC emissions cools the Earth and so a moderate temperature is dependent on BVOC emission from plants – and other similar feedbacks in Earth's system – is the focus of much current research. Hence, there is the potential for feedback between BVOC emissions, SOA, and climate.

5.4 Factors Affecting BVOC Emission

5.4.1 Taxonomic Characteristics

Trees are traditionally considered to be the key BVOC emitters. Isoprene, monoterpenes, and sesquiterpenes are emitted from many plants and they appear to have an adaptive role in protecting plants from abiotic stress. However, only some plant species emit isoprene. For example, taxonomic groups as distinct as mosses and oak trees emit isoprene, but in groups as closely allied as mosses and hornworts or oak and maple trees, both are emitters (mosses and oaks) and non-emitters (hornworts and maples) (Lerdau and Gray 2003; Hanson et al. 1999). Monson et al. (2013) studied various isoprene-emitting genera with high taxonomic diversity, such as the Fabaceae (old name: Leguminosae). Mosses (Hanson et al. 1999), ferns (Tingey et al. 1987), gymnosperms, and angiosperms (http:www.es.lancs.ac.uk/cnhgroup/iso-emissions.pdf for comprehensive list) consist of members emitting BVOCs and not emitting BVOCs. Isoprene synthases (IspSs) are the enzyme which catalyzes the conversion of DMAPP to isoprene. IspSs have been sequenced from several plant species such as the *Populus* species (Sasaki et al. 2005; Miller et al. 2001) and kudzu (*Pueraria lobata*) (Sharkey et al. 2005). According to Bohlmann et al. (1998), IspSs belong to the TSP-b family of terpene synthases, also code for monoterpene and sesquiterpene synthases in angiosperms. But these are absent in gymnosperms. Isoprene synthase genes analyzed so far have been found to have high-sequence homology with certain monoterpene synthase genes (Miller et al. 2001; Sharkey et al. 2005) and even a bifunctional acyclic monoterpene synthase/isoprene synthase gene (Sharkey et al. 2013). A small change in the gene sequences can easily alter both substrate and product specificity of IspS genes (El Tamer et al. 2003; Tholl 2006; Kampranis et al. 2007). North American oaks all emit isoprene, but many European oaks do not. Instead, among European oaks a variety of behaviors is found. Some clades emit isoprene, some emit monoterpenes in a light dependent manner, and some emit very little terpene (Loreto et al. 1998a, b; Csiky and Seufert 1999; Kesselmeier and Staudt 1999).

5.4.2 Temperature

BVOC emissions are highly temperature dependent because higher temperature increases the rate of chemical reaction and cellular diffusion and increases the vapor pressure of volatile compounds (Lerdau et al. 1994; Tingey et al. 1991; Sharkey and Yeh 2001; Fuentes et al. 1999). The emission rates of BVOCs are analyzed by their synthesis rates and physicochemical parameters like solubility, volatility, and diffusivity (Niinemets et al. 2004; Kesselmeier and Staudt 1999; Laothawornkitkul et al. 2009). BVOC emission rates are highly controlled by both external and internal factors. Although there are large uncertainties in the magnitude of emission rates of BVOCs, a recent estimate for North America (Guenther et al. 2000) suggests that of an estimated 84 $TgCyear^{-1}$ of BVOC emissions, 30 % are isoprene, 25 % are terpenoid compounds, and 40 % are non-terpenoid compounds including methanol, hexene derivatives, and 2-methyl-3-buten-2-ol.

BVOCs follow the Henry's law constant (K_H) and they partition between gas and liquid phases in the plants. Leng et al. (2013) reported that the measured K_H values for isoprene, limonene, α-pinene, and linalool at 298 K were 0.036, 0.048, 0.029, and 21.20 mol L^{-1} atm^{-1}, respectively. They also reported that diffusion of these BVOCs follow the first-order kinetics for rate of loss and diffusion coefficients of all the species as a function of temperature. Temperature affects the evaporation and release of a minimal part of the pools of BVOCs that leaks out the impermeable cell layer. Herbivory, strong winds, and forest fires are the other strong factors responsible for BVOC emissions (Litvak and Monson 1998). High humidity also plays a significant role in BVOC emission from the structures of plants containing BVOC pools.

The enzymes which are responsible to catalyze the synthesis of BVOCs can be easily controlled or influenced by temperature. Emissions of volatile terpenes have a $Q_{10} = 2–4$ at temperatures variable between 20 and 40 °C (Monson et al. 1992). Thus the elevation in atmospheric temperature is a direct effect of terpenes formed through enzymatic action.

5.4.2.1 Thermotolerance

Sharkey and Singsaas (1995) were the first researchers who reported that isoprene plays a significant role in thermotolerance function. Singsaas et al. (1997) showed that adding isoprene to an air stream (or nitrogen gas) that passed over these leaves could increase the temperature at which damage occurred from as low as 35 °C to as high as 45 °C. Thermotolerance was also mentioned with special reference to monoterpene emissions from *Quercus ilex* (oak species) by Loreto et al. (1998a, b). Several studies have reported the positive link between isoprene and photorespiration (Peñuelas and Llusià 2002). According to one study, "Thermotolerance of leaf discs from four isoprene-emitting species is not enhanced by exposure to exogenous isoprene" (Logan and Monson 1999) and was of substantial concern. They found that leaf disks' chlorophyll fluorescence held in darkness or light plus nitrogen did not increase until 45 °C, irrespective of whether isoprene was in the air stream. In their experiments the control leaf pieces did not exhibit photosynthetic damage below 45 °C. Measurements of the temperature where CO_2 uptake fell to zero were not reported in the study.

Two advancements were added in definitive experiments. First was the refinement of the thermotolerance hypothesis and the second was the use of fosmidomycin, the inhibitor that eliminates isoprene production without affecting photosynthesis. With these improvements, much stronger evidence for the thermotolerance hypothesis has been obtained (Sharkey et al. 2001). The study reported that the isoprene synthesis provides tolerance of short high-temperature episodes. The molecules similar to isoprene were also tested to find out the basic requirements for thermotolerance. One rule was apparent in the results. The compounds taken into consideration were alkenes (1,3-butadiene, 1-butene, and *cis* 2-butene) that provided thermotolerance though alkanes (n-butane, *iso*-butane, and 2-methyl-butan) did not; they even increased the damage caused by heat (Sharkey et al. 2001).

5.4.3 Soil Moisture

Soil moisture is one of the important factors responsible for BVOC emission from plants. Soil moisture is significantly correlated with BVOC (isoprene and monoterpene) emission (Gray et al. 2014). Several authors studied the global BVOC emission model with soil moisture. Guenther et al. (2006) estimated a 7 % decrease in isoprene emission due to soil moisture's effect, while Muller et al. (2008) calculated a 20 % decrease. The lower soil moisture can induce stomatal closure, which can reduce the production and emission of BVOCs coming directly from temporary storage pools inside the leaves (McBean et al. 2005).

5.5 BVOC Emission and Global Warming

Climate models suggest that, during the twenty-first century, the mean global temperature will increase by 1–6 °C (with a best estimate of 2–3 °C) (IPCC 2007). BVOC emissions are altered by varying their temperature; their emissions increase with temperature to a certain limit, beyond which enzyme degradation and physiological responses to heat stress affect the emission pattern (Guenther et al. 1993).

Emissions of BVOCs are always run along a vapor pressure gradient from the cellular level (containing relatively high concentrations) to the surrounding air of leaves (containing relatively low concentrations) due to transport. Temperature increases the emission rates of most BVOCs exponentially by enhancing the enzymatic activities of synthesis, by elevating the BVOC vapor pressure, and by decreasing the resistance of the diffusion pathway (Tingey et al. 1991). Penuelas and Llusia (2003) have suggested that increasing mean global temperatures by 2–3 °C could enhance global BVOC emissions by 25–45 %. The dependency of BVOC emission rates on temperature can be further explained with G93 algorithm, given by Guenther et al. (1993), where the emission rate of monoterpene can be expressed as:

$$E = E_{\mathrm{s}} \exp\left\{\beta\left(T - T_{\mathrm{s}}\right)\right\}, \tag{5.7}$$

where E and E_{s} are measured emission rates and basal emission rates at a standard temperature, i.e., 30 °C, respectively. T and T_{s} are measured and standard temperatures, respectively. β is an empirical coefficient (depends on species of vegetation and compounds emitted. With the similar model at a local temperature regime (4 °C) for Douglas fir trees, Constable et al. (1999) found a predicted increase in emission of 52 %, 46 %, and 41 % for α-pinene, β- pinene, and Δ-3 carene, respectively. Whereas isoprene emission is modeled as:

$$E = E_{\mathrm{S}} \times C_{\mathrm{T}} \times C_{\mathrm{L}}, \tag{5.8}$$

where E is the isoprene emission rate at temperature T and PAR flux L, E_{S} is the emission rate measured at standard temperature $\mathrm{T_S}$ and PAR (1000 mmol $\mathrm{m^{-2}\ s^{-1}}$), and the scaling factors $\mathrm{C_T}$ and $\mathrm{C_L}$ are defined by:

$$C_{\mathrm{T}} = \frac{\exp\left[C_{\mathrm{T1}} \times \left(T - T_{\mathrm{s}}\right)\right] / \left(R \times T \times T_{\mathrm{s}}\right)}{1 + \exp\left[C_{\mathrm{T2}} \times \left(T - T_{\mathrm{m}}\right)\right] / \left(R \times T \times T_{\mathrm{s}}\right)} \tag{5.9}$$

$$C_{\mathrm{L}} = \frac{\alpha \times C_{\mathrm{L1}} \times \mathrm{PAR}}{\sqrt{1 + \alpha^2 \times \mathrm{PAR}^2}}, \qquad (5.10)$$

where, C_{T1} (95,000 J mol^{-1}), C_{T2} (230,000 J mol^{-1}), T_{m} (41 °C), α (0·0027), and C_{L1} (1·066) are parameters calculated from experiments made on some BVOC-emitting plant species (Guenther et al. 1993). R is the gas constant (8·134 J K^{-1} mol^{-1}).

Applying the algorithms of emission response to temperature (Llusià and Peñuelas 2000; Tingey et al. 1991; Peñuelas and Llusia 2003) calculated global warming over the past 30 years and found that BVOCs increased global emissions by 10 % and a further 2–3 °C rise in the mean global temperature, which is predicted to occur this century (Houghton et al. 2001), could increase BVOC global emissions by an additional 30–45 %.

At a very high temperature, isoprene emission declines dramatically. It is possible that extreme temperature rises will eventually cause a decrease in isoprene emissions, irrespective of other changes to ecosystems.

Global warming can also indirectly influence global- and regional-scale BVOC emissions by altering vegetation species composition and vegetation characteristics (Wilmking et al. 2004; Starfield and Chapin 1996). Simulation model studies predict forest dieback at a lower latitude such as Amazonia (Cox et al. 2004). However, the models predicted that boreal forests will be exposed northward in a global warming scenario (Chapin et al. 2000; Kittel et al. 2000). The increase in boreal forests may increase BVOC emissions for species such as *Populus* sp. and *Picea* sp. (Lerdau and Slobodkin 2002). However, forests at lower altitudes may reduce BVOC emission, probably having no impact on global budgets.

5.6 BVOCs and Plant Signaling (Plant–Plant and Plant–Insect Herbivory)

Several authors discussed about the BVOC emissions and their role in many abiotic stress tolerance, including thermotolerance of photosynthesis and reduced oxidative stress (Sun et al. 2013; Singsaas et al. 1997; Loreto et al. 1998; Sharkey and Singsaas 1995; Possell and Loreto 2013; Llusià et al. 2005).

As per the authors of the recent twenty-first century, BVOCs are essential components for communication within a plant, between plants, and between a plant and an insect (Trowbridge and Stoy 2013; Dicke and Baldwin 2010; Duhl 2008; Baldwin et al. 2002). In plant–herbivore interactions, the volatiles can act as attractants or repellents to herbivores (Laothawornkitkul et al. 2008). For instance the α-pinene (monoterpene) released by wounded *Pinus sylvestris* L. (Scotch pine) acts as an attractant to *Hylobius abietis* (large pine weevil), and thus, previous damage of a conifer can increase herbivory damage. However, by repelling limonene attraction of *H. abietis* can be reduced (Nordlander 1991). According to Mithen (2001), heat-stressed *Brassica nigra* (black mustard) plants may become attractive to specialized feeders of Brassicaceae (older name, Cruciferae) due to the increasing emissions of allyl isothiocyanate (organosulfur compound and responsible for the pungent taste of the Cruciferae family). Arimura et al. (2001) found that BVOCs emitted from *Tetranychus* (spider mite)-infested lima bean/butter bean (*Phaseolus lunatus* L.) can activate genes encoding pathogenesis-related proteins and phenylalanine ammonia-lyase in leaves of noninfested neighboring plants, and GLVs can serve as signal compounds in plant–plant communication (Arimura et al. 2001). Later on it was found that such kind of sharing of information (between plants) depends on the diffusion and convection of the BVOC information between a sender and a receiver plant (Baldwin et al. 2002).

5.7 Conclusion

BVOCs played an important role in atmospheric chemistry and were also involved in the several mechanisms of plant physiology like plant signaling. Any biotic or abiotic stress is responsible for BVOC emission from plants. The overall effect of increasing BVOC emissions will depend on the positive and negative feedback mechanism. These emissions are released in support of defense mechanisms from plant species. This chapter signifies about the important component of atmospheric sciences as well as plant physiology, i.e., BVOCs which are still under progress; very less attention has been put toward this mechanism. The important environmental issue of global warming is also influenced by BVOCs. BVOCs also played an important role in the production of tropospheric ozone, aerosol formation, and ultimately SOA. In short, this chapter concludes with the fact that precursors play an important role in the production of secondary pollutants and these precursors like BVOCs take part in climate change issues.

References

Arigoni D, Sagner S, Latzel C, Eisenreich W, Bacher A, Zenk MH (1997) Terpenoid biosynthesis from 1-deoxy-D-xylulose in higher plants by intramolecular skeletal rearrangement. Proc Natl Acad Sci U S A 94:10600–10605

Arimura G, Ozawa R, Horiuchi J, Nishioka T, Takabayashi J (2001) Plant–plant interactions mediated by volatiles emitted from plants infested by spider mites. Biochem Syst Ecol 29(10):1049–1061

Baldwin IT, Kessler A, Halitschke R (2002) Volatile signaling in plant–plant–herbivore interactions: what is real? Curr Opin Plant Biol 5(4):351–354

Bergamaschi P, Hein R, Heimann M, Crutzen PJ (2000) Inverse modeling of the global CO cycle 1. Inversion of CO mixing ratios. J Geophys Res-Atmos 105:1909–1927

Blande JD, Tiiva P, Oksanen E, Holopainen JK (2007) Emission of herbivore-induced volatile terpenoids from two hybrid aspen (Populus tremula x tremuloides) clones under ambient and elevated ozone concentrations in the field. Glob Chang Biol 13:2538–2550

Bohlmann J, Meyer-Gauen G, Croteau R (1998) Plant terpenoid synthases: molecular biology and phylogenetic analysis. Proc Natl Acad Sci U S A 95:4126–4133

Chapin FS, McGuire AD, Randerson J, Pielke R, Baldocchi D, Hobbie SE, … Zimov SA (2000) Arctic and boreal ecosystems of western North America as components of the climate system. Glob Chang Biol 6(S1):211–223

Claeys M, Graham B, Vas G, Wang W, Vermeylen R, Pashynska V, Cafmeyer J, Guyon P, Andreae MO, Artaxo P et al (2004) Formation of secondary organic aerosols through photooxidation of isoprene. Science 303:1173–1176

Constable J, Litvak ME, Greenberg JP, Monson RK (1999) Monoterpene emission from coniferous trees in response to elevated CO2 concentration and climate warming. Glob Chang Biol 5(3):252–267

Cox PM, Betts RA, Collins M, Harris PP, Huntingford C, Jones CD (2004) Amazonian forest dieback under climate-carbon cycle projections for the 21st century. Theor Appl Climatol 78(1–3):137–156

Csiky O, Seufert G (1999) Terpenoid emissions of Mediterranean oaks and their relation to taxonomy. Ecol Appl 9:1138–1146

Daum PH, Kleinman L, Imre DG, Nunnermacker LJ, Lee Y-N, Springston SR, Newman L (2000) Analysis of the processing of Nashville urban emissions on July 3 and July 18, 1995. J Geophys Res 105:9107–9119

Dicke M, Baldwin IT (2010) The evolutionary context for herbivore-induced plant volatiles: beyond the ‘cry for help’. Trends Plant Sci 15(3):167–175

Duhl AB (2008) Sesquiterpene emissions from vegetation: a review. Biogeosciences 5:761–777

Edney EO, Kleindienst TE, Jaoui M, Lewandowski M, Offenberg JH, Wang W et al (2005) Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NOX/SO2/air mixtures and their detection in ambient PM2_5 samples collected in the eastern United States. Atmos Environ 39:5281–5289

El Tamer MK, Lucker J, Bosch D, Verhoeven HA, Verstappen FWA, Schwab W et al (2003) Domain swapping of Citrus lemon monoterpene synthases: impact on enzymatic activity and product specificity. Arch Biochem Biophys 411:196–203

Fall R, Karl T, Hansel A, Jordan A, Lindinger W (1999) Volatile organic compounds emitted after leaf wounding: on-line analysis by proton-transfer- reaction mass spectrometry. J Geophys Res-Atmos 104:15963–15974

Fehsenfeld F, Calvert J, Fall R, Goldan P, Guenther AB, Hewitt CN, Lamb B, Liu S, Trainer M, Westberg H et al (1992) Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry. Global Biogeochem Cycles 6:389–430

Fowler D, Amann M, Anderson R, Ashmore M, Depledge MH, Derwent D, Grennfelt P, Hewitt CN, Hov O, Jenkin M et al (2008) Ground-level ozone in the 21st century: future trends, impacts and policy implications. Policy Document 15/08. Royal Society, London

Franceschi VR, Krokene P, Christiansen E, Krekling T (2005) Anatomical and chemical defenses of conifer bark against bark beetles and other pests. New Phytol 162:353–375

Fuentes JD, Wang D, Gu L (1999) Seasonal variations in isoprene emissions from a boreal aspen forest. J Appl Meteorol 38:855–869

Fuentes JD, Lerdau M, Atkinson R, Baldocchi D, Bottenheim JW, Ciccioli P, Lamb B, Geron C, Gu L, Guenther A et al (2000) Biogenic hydrocarbons in the atmospheric boundary layer: a review. Bull Am Meteorol Soc 81:1537–1575

Geron C, Rasmussen R, Arnts RR, Guenther A (2000) A review and synthesis of monoterpene speciation from forests in the United States. Atmos Environ 34(11):1761–1781

Gershenzon J, McConkey M, Croteau R (2000) Regulation of monoterpene accumulation in leaves of Peppermint. Plant Physiol 122:205–213. 274

Gray CM, Monson RK, Fierer N (2014) Biotic and abiotic controls on biogenic volatile organic compound fluxes from a subalpine forest floor. J Geophys Res Biogeosci 119(4):547–556

Griffin RJ, Chen JJ, Carmody K, Vutukuru S, Dabdub D (2007) Contribution of gas phase oxidation of volatile organic compounds to atmospheric carbon monoxide levels in two areas of the United States. J Geophys Res Biogeosci 112:D10S17

Grosjean D (1995) Atmospheric chemistry of biogenic hydrocarbons—relevance to the Amazon. Quim Nova 18:184–201

Guenther A, Hewitt CN, Erickson D, Fall R, Geron C, Graedel T, Harley P, Klinger L, Lerdau M, McKay WA et al (1995) A global-model of natural volatile organic-compound emissions. J Geophys Res Atmos 100:8873–8892

Guenther AB, Geron C, Pierce T et al (2000) Natural emissions of non-methane volatile organic compounds; carbon monoxide, and oxides of nitrogen from North America. Atmos Environ 34:2205–2230

Guenther A, Karl T, Harley P, Wiedinmyer C, Palmer PI, Geron C (2006) Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmos Chem Phys 6:3181–3210

Haagen-Smit AJ (1952) Chemistry and physiology of Los Angeles smog. Ind Eng Chem 44(6):1342–1346

Hanson DT, Swanson S, Graham LE, Sharkey TD (1999) Evolutionary significance of isoprene emission from mosses. Am J Bot 86:634–639

Hatakeyama S, Izumi K, Fukuyama T, Akimoto H, Washida N (1991) Reactions of OH with alpha-pinene and beta-pinene in air – estimate of global CO production from the atmospheric oxidation of terpenes. J Geophys Res Atmos 96:947–958

Houghton JT et al (2001) IPCC climate change 2001: the scientific basis. Contribution of working group I in the third assessment report of Intergovernmental Panel on Climate Change. Cambridge University Press

IPCC (2007) The physical science basis. Contribution of working group I. In: Solomon S et al (eds) Fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, pp 1–996

Joutsensaari J, Loivamaki M, Vuorinen T, Miettinen P, Nerg AM, Holopainen JK, Laaksonen A (2005) Nanoparticle formation by ozonolysis of inducible plant volatiles. Atmos Chem Phys 5:1489–1495

Kampranis SC, Ioannidis D, Purvis A, Mahrez W, Ninga E, Katerelos NA et al (2007) Rational conversion of substrate and product specificity in a Salvia monoterpene synthase: structural insights into the evolution of terpene synthase function. Plant Cell 19:1994–2005

Kesselmeier J, Staudt M (1999) Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. J Atmos Chem 33:23–88

Kittel TGF, Steffen WL, Chapin FS (2000) Global and regional modelling of Arctic–boreal vegetation distribution and its sensitivity to altered forcing. Glob Chang Biol 6(S1):1–18

Kroll JH, Ng NL, Murphy SL, Flagen RC, Seinfeld JH (2005) Secondary organic aerosol formation from isoprene photooxidation under high-NOx conditions. Geophys Res Lett 32:L18808

Kroll JH, Ng NL, Murphy SM, Flagan RC, Seinfeld JH (2006) Secondary organic aerosol formation from isoprene photooxidation. Environ Sci Tech 40:1869–1877

Kulmala M (2003) How particles nucleate and grow. Science 302:1000–1001

Laothawornkitkul J, Paul ND, Vickers CE, Possell M, Mullineaux PM, Hewitt CN, Taylor JE (2008) The role of isoprene in insect herbivory. Plant Signal Behav 3(12):1141–1142

Laothawornkitkul J, Taylor JE, Paul ND, Hewitt CN (2009) Biogenic volatile organic compounds in the Earth system. New Phytol 183:27–51

Leaitch WR, Bottenheim JW, Biesenthal TA, Li SM, Liu PSK, Asalian K, Dryfhout-Clark H, Hopper F, Brechtel F (1999) A case study of gas-to-particle conversion in an eastern Canadian forest. J Geophys Res Atmos 104:8095–8111

Lelieveld J, Butler TM, Crowley JN, Dillon TJ, Fischer H, Ganzeveld L, Harder H, Lawrence MG, Martinez M, Taraborrelli D et al (2008) Atmospheric oxidation capacity sustained by a tropical forest. Nature 452:737–740

Leng C, Kish JD, Kelley J, Mach M, Hiltner J, Zhang Y, Liu Y (2013) Temperature-dependent Henry's law constants of atmospheric organics of biogenic origin. J Phys Chem A 117(40):10359–10367

Lerdau M, Gray D (2003) Ecology and evolution of light-dependent and light independent phytogenic volatile organic carbon. New Phytol 157:199–211

Lerdau M, Slobodkin L (2002) Trace gas emissions and species-dependent ecosystem services. Trends Ecol Evol 17(7):309–312

Lerdau MT, Dilts SB, Westberg H, Lamb BK, Allwine EJ (1994) Monoterpene emission from Ponderosa pine. J Geophys Res 99:16609–16615

Lichtenthaler HK, Schwender J, Disch A, Rohmer M (1997) Biosynthesis of isoprenoids in higher plant chloroplasts proceeds via amevalonate-independent pathway. FEBS Lett 400:271–274

Litvak ME, Monson RK (1998) Patterns of induced and constitutive monoterpene production in conifer needles in relation to insect herbivory. Oecologia 114(4):531–540

Llusià J, Peñuelas J (2000) Seasonal patterns of terpene content and emission from seven Mediterranean woody species in field conditions. Am J Bot 87:133–140

Llusià J, Peñuelas J, Munné-Bosch S (2005) Sustained accumulation of methyl salicylate alters antioxidant protection and reduces tolerance of holm oak to heat stress. Physiol Plant 124(3):353–361

Logan BA, Monson RK (1999) Thermotolerance of leaf discs from four isoprene-emitting species is not enhanced by exposure to exogenous isoprene. Plant Physiol 120:821–825

Logan JA, Prather MJ, Wofsy SC, McElroy MB (1981) Tropospheric chemistry – a global perspective. J Geophys Res C Oceans Atmos 86:7210–7254

Loreto F, Ciccioli P, Brancaleoni E, Valentini R, De Lillis M, Csiky O et al (1998a) A hypothesis on the evolution of isoprenoid emission by oaks based on the correlation between emission type and Quercus taxonomy. Oecologia 115:302–305

Loreto F, Fo¨rster A, Du¨rr M, Csiky O, Seufert G (1998b) On them onoterpene emission under heat stress and on the increased thermotolerance of leaves of Quercus ilex L. fumigated with selected monoterpenes. Plant Cell Environ 21:101–107

McBean G, Alekseev G, Chen D, Førland E, Fyfe J, Groisman PY et al (2005) Arctic climate: past and present. Arctic climate impact assessment scientific report

Meskhidze N, Nenes A (2006) Phytoplankton and cloudiness in the Southern Ocean. Science 314:1419–1423

Mgaloblishvili MP, Khetsuriana ND, Kalandaze AN, Sanadze GA (1979) Localization of isoprene biosynthesis in poplar leaf chloroplasts. Sov Plant Physiol 26:837–842

Miller B, Oschinski C, Zimmer W (2001) First isolation of an isoprene synthase gene from poplar and successful expression of the gene in Escherichia coli. Planta 213:483–487

Mithen RF (2001) Glucosinolates and their degradation products. Adv Bot Res 35:213–232

Monson RK, Holland EA (2001) Biospheric trace gas fluxes and their control over tropospheric chemistry. Annu Rev Ecol Evol Syst 32:547–576

Monson RK, Jaeger CH, Adams WW, Driggers EM, Silver GM, Fall R (1992) Relationships among isoprene emission rate, photosynthesis, and isoprene synthase activity as influenced by temperature. Plant Physiol 98:1175–1180

Monson RK, Jones RT, Rosenstiel TN, SCHNITZLER JP (2013) Why only some plants emit isoprene. Plant Cell Environ 36(3):503–516

Müller J-F, Stavrakou T, Wallens S, De Smedt I, Van Roozendael M, Potosnak MJ, Rinne J, Munger B, Goldstein A, Guenther AB (2008) Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model. Atmos Chem Phys 8:1329–1341

Ng NL, Kroll JH, Keywood MD, Bahreini R, Varutbangkul V, Flagan RC et al (2006) Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons. Environ Sci Tech 40:2283–2297

Niinemets U et al (2004) Physiological and physicochemical controls on foliar volatile organic compound emissions. Trends Plant Sci 9:180–186

Nordlander G (1991) Host finding in the pine weevil Hylobius abietis: effects of conifer volatiles and added limonene. Entomol Exp Appl 59(3):229–237

Olcese LE, Penner JE, Sillman S (2007) Development of a secondary organic aerosol formation mechanism: comparison with smog chamber experiments and atmospheric measurements. Atmos Chem Phys Discuss 7:8361–8393

Peñuelas J, Llusià J (2001) The complexity of factors driving volatile organic compound emissions by plants. Biol Plant 44:481–487

Peñuelas J, Llusià J (2002) Linking photorespiration, monoterpenes and thermotolerance in Quercus. New Phytol 155:227–237

Penuelas J, Llusia J (2003) BVOCs: plant defense against climate warming? Trends Plant Sci 8:105–109

Penuelas J, Filella I, Gamon JA (1995) Assessment of photosynthetic radiation-use efficiency with spectral reflectance. New Phytol 131(3):291–296

Pichersky E, Gershenzon J (2002) The formation and function of plant volatiles: perfumes for pollinator attraction and defense. Curr Opin Plant Biol 5(3):237–243

Pichersky E, Noel JP, Dudareva N (2006) Biosynthesis of plant volatiles: nature's diversity and ingenuity. Science 311:808–811

Poisson N, Kanakidou M, Crutzen PJ (2000) Impact of non-methane hydrocarbons on tropospheric chemistry and the oxidizing power of the global troposphere: three-dimensional modelling results. J Atmos Chem 36:157–230

Possell M, Loreto F (2013) The role of volatile organic compounds in plant resistance to abiotic stresses: responses and mechanisms. In: Biology, controls and models of tree volatile organic compound emissions. Springer, Dordrecht, pp 209–235

Rohmer M, Knani M, Simonin P, Sutter B, Sahm H (1993) Isoprenoid biosynthesis in bacteria: a novel pathway for the early steps leading to isopentenyl diphosphate. Biochem J 295:517–524

Sasaki K, Ohara K, Yazaki K (2005) Gene expression and characterization of isoprene synthase from Populus alba. FEBS Lett 579:2514–2518

Schnitzler J-P, Arenz R, Steinbrecher R, Lehning A (1996) Characterization of an isoprene synthase from leaves of Quercus petraea (Mattuschka) Liebl. Bot Acta 109:216–221

Schwender J, Zeidler J, Gr¨oner R, M¨uller C, Focke M et al (1997) Incorporation of 1-deoxy-D-xylulose into isoprene and phytol by higher plants and algae. FEBS Lett 414:129–134

Sharkey TS (2013) Is it useful to ask why plants emit isoprene? Plant Cell Environ 36:517–520

Sharkey TD, Singsaas EL (1995) Why plants emit isoprene. Nature 374:769

Sharkey TD, Yeh S (2001) Isoprene emission from plants. Annu Rev Plant Physiol Plant Mol Biol 52:407–436

Sharkey TD, Yeh S, Wiberley AE, Falbel TG, Gong D, Fernandez DE (2005) Evolution of the isoprene biosynthetic pathway in kudzu. Plant Physiol 137:700–712

Sharkey TD, Gray DW, Pell HK, Breneman SR, Topper L (2013) Isoprene synthase genes form a monophyletic clade of acyclic terpene synthases in the tps-b terpene synthase family. Evolution 67(4):1026–1040

Shulaev V, Silverman P, Raskin I (1997) Airborne signalling by methyl salicylate in plant pathogen resistance. Nature 385:718–721

Silver GM, Fall R (1991) Enzymatic synthesis of isoprene from dimethylallyl diphosphate in aspen leaf extracts. Plant Physiol 97:1588–1591

Silver GM, Fall R (1995) Characterization of aspen isoprene synthase, an enzyme responsible for leaf isoprene emission to the atmosphere. J Biol Chem 270:13010–13016

Singsaas EL, Lerdau M, Winter K, Sharkey TD (1997) Isoprene increases thermotolerance of isoprene-emitting species. Plant Physiol 115:1413–1420

Sun Z, Hüve K, Vislap V, Niinemets Ü (2013) Elevated [CO_2] magnifies isoprene emissions under heat and improves thermal resistance in hybrid aspen. J Exp Bot 64:5509–5523, ert318

Tholl D (2006) Terpene synthases and the regulation, diversity and biological roles of terpene metabolism. Curr Opin Plant Biol 9:297–304

Thompson AM (1992) The oxidizing capacity of the Earth's atmosphere: probable past and future changes. Science 256:1157–1165

Thompson AM, Hogan KB, Hoffman JS (1992) Methane reductions: implications for global warming and atmospheric chemical change. Atmos Environ Part A 26(14):2665–2668

Tingey DT, Evans R, Bates EH, Gumpertz M (1987) Isoprene emissions and photosynthesis in three ferns – the influence of light and temperature. Physiol Plant 69:609–616

Tingey DT, Turner DP, Weber JA (1991) Factors controlling the emissions of monoterpenes and other volatile organic compounds. In: Sharkey TD, Holland EA, Mooney HA (eds) Trace gas emissions from plants. Academic, San Diego, pp 93–119

Trainer M, Williams EJ, Parrish DD, Buhr MP, Allwine EJ, Westberg HH, Fehsenfeld FC, Liu SC (1987) Models and observation of the impact of natural hydrocarbons on rural ozone. Nature 329:705–707

Trowbridge AM, Stoy PC (2013) BVOC-mediated plant-herbivore interactions. In: Biology, controls and models of tree volatile organic compound emissions. Springer, Dordrecht, pp 21–46

Turner GW, Gershenzon J, Croteau RB (2000) Development of peltate glandular trichomes of peppermint. Plant Physiol 124:665–679. 274

Wagner WP, Nemecek-Marshall M, Fall R (1999) Three distinct phases of isoprene formation during growth and sporulation of Bacillus subtilis. J Bacteriol 181:4700–4703

Wang YH, Jacob DJ, Logan JA (1998) Global simulation of tropospheric O_3-NOxhydrocarbon chemistry. 3. Origin of tropospheric ozone and effects of non-methane hydrocarbons. J Geophys Res 103(10):757–767

Wildermuth MC (1997) Subcellular location and biophysical regulation of foliar isoprene production (chloroplasts). PhD thesis. University of Colorado Boulder, 307 pp

Wildermuth MC, Fall R (1996) Light-dependent isoprene emission – characterization of a thylakoid-bound isoprene synthase in Salix discolor chloroplasts. Plant Physiol 112:171–182

Wildermuth MC, Fall R (1998) Biochemical characterization of stromal and thylakoid-bound isoforms of isoprene synthase in willow leaves. Plant Physiol 116:1111–1123

Wilmking M, Juday GP, Barber VA, Zald HS (2004) Recent climate warming forces contrasting growth responses of white spruce at treeline in Alaska through temperature thresholds. Glob Chang Biol 10(10): 1724–1736

Zeidler JG, Lichtenthaler HK, May HU, Lichtenthaler FW (1997) Is isoprene emitted by plants synthesized via the novel isopentenyl pyrophosphate pathway? Z Naturforsch Teil C 52:15–23