Chapter 2
Biogenic Volatile Organic Compounds in Amazonian Forest Ecosystems

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2.1 Introduction

Biogenic volatile organic compounds (BVOCs) are produced directly within plants via biochemical pathways associated with primary and secondary metabolic processes. Although non-volatile metabolites are typically bound within specific cellular organelles in lipids or aqueous phases, BVOC volatile metabolites can readily partition between these phases and the intracellular airspace (Fall 2003). Thus, many BVOCs may freely exchange among cellular organelles, cells, and tissues, contributing to an integration of whole organism carbon and energy metabolism. Moreover, exchange of the intracellular airspace with the atmosphere may help coordinate the metabolisms of different plants within an ecosystem in response to environmental and biological factors (Yan and Wang 2006). In addition, land–atmosphere exchange of VOCs integrates local and regional atmospheric chemistry with plant metabolism (Jardine et al. 2011a).

The emerging field of volatile ecosystem metabolomics integrates the volatile component into the chemical, physical, and biological processes involved in the processing of metabolites within the land–atmosphere interface including potential perturbations of the system by anthropogenic activities (e.g. VOC emissions from

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biomass and fossil fuel burning). The power of volatile metabolomics comes from the fact that many cellular processes leave unique chemical fingerprints (biomarkers) behind in the atmosphere (e.g. BVOCs, such as volatile isoprenoids, organic acids, alcohols, esters, aldehydes, ketones, aromatics, sulphides, nitriles). Therefore, volatile metabolomics provides non-invasive techniques to study plant metabolism from a variety of spatial and temporal scales. The application of these methods in the tropics may improve our mechanistic understanding of how environmental and biological variables associated with climate and land use change affect the carbon and energy metabolism of natural and managed forests.

Tropical ecosystems cycle more carbon than any other biome (~1.4 versus 0.5 Pg C $year^{-1}$ for temperate ecosystems (Sarmiento et al. 2010)) and are estimated to account for nearly 80 % of global BVOC emissions (Levis et al. 2003). The Amazon basin is a major tropical source of BVOCs to the global atmosphere (Greenberg et al. 2004), yet less is known about BVOCs from its vegetation than from that in other regions of the world (Guenther 2013). This is due to a number of factors, among which are the extremely high tree species diversity (ter Steege et al. 2013; Macarthur 1965) and difficulties in conducting and sustaining remote field studies with highly sensitive analytical chemistry instrumentation for even short periods of time. What we do know about Amazonian BVOCs primarily results from a few important short-term plant enclosure studies, above-canopy measurements, and aircraft observations (Kesselmeier et al. 2002; Karl et al. 2007; Jardine et al. 2011b).

Historically, BVOCs have been studied with respect to their significant impacts on the chemistry and physics of the atmosphere, which remains an active area of research (e.g. Artaxo et al. 2009). The focus of this chapter is towards developing a mechanistic understanding of BVOC dynamics within plants and ecosystems. First is a brief overview of BVOC production within plants followed by an introduction to the field of volatile metabolomics. Next, examples of Amazonian plant and ecosystem functional roles of several BVOCs are discussed. The chapter ends with suggested directions for Amazonian BVOC research including detailed plant VOC emission surveys, the identification of new BVOCs, and the characterisation of potential BVOC ecosystem–atmosphere bidirectional exchange (i.e. emission and consumption by vegetation).

2.2 BVOC Biosynthesis in Plants

During photosynthesis, plants assimilate atmospheric carbon dioxide (CO_2) into primary metabolites which are essential components required for growth and development. Primary metabolites can be used as substrate for the biosynthesis of new biomass including proteins, nucleic acids, carbohydrates, and lipids or can be used as a carbon and energy source during respiration (Bourgaud et al. 2001; Tegeder and Weber 2008). Secondary metabolites are a diverse set of compounds which are intricately involved in many physiological and ecological processes

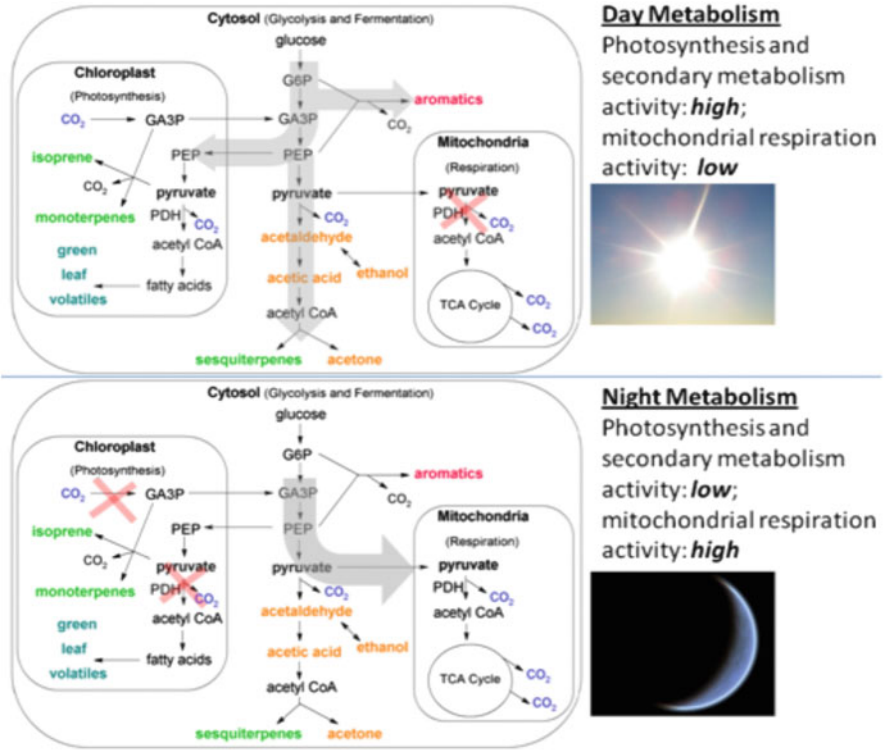

Fig. 2.1 A simplified representation of the flow of carbon in the cytosol, chloroplast, and mitochondria, which produce classes of biogenic volatile organic compounds (BVOCs) in photosynthetic cells during primary and secondary metabolism

within plants (Weng et al. 2012). For example, secondary metabolites have been identified as plant defences against abiotic and biotic stresses and chemical communication within and between species (Weng et al. 2012; Jardine et al. 2008; Karl et al. 2008; Pophof et al. 2005). Both primary and secondary metabolic pathways within plants create intermediates with sufficient vapour pressures to be directly emitted into the atmosphere in the gas phase as BVOCs.

Plant metabolic pathways involved in BVOC biosynthesis occur in and across a number of cellular organelles including the cytosol, chloroplast, mitochondria, and peroxisome (Fig. 2.1). Some BVOCs, such as isoprene, are strictly light dependent with a strong connection to recently assimilated carbon (Jones and Rasmussen 1975). In contrast, instantaneous emissions of other BVOCs, such as methanol, are much less light dependent and can be produced at night (Fall and Benson 1996; Harley et al. 2007).

Key substrates (i.e. glyceraldehyde-3-phosphate, phosphoenol pyruvate, pyruvate, and acetyl-CoA) can be produced independently within plant compartments or can be transported across compartmental boundaries. For example, pyruvate is a

central substrate in the biosynthesis of BVOC classes such as volatile isoprenoids (isoprene, monoterpenes, sesquiterpenes), oxygenated VOCs (acetaldehyde, ethanol, acetic acid, acetone, volatile acetate esters), and fatty acid oxidation products (green leaf volatiles, e.g. Z-3-hexenol, Z-3-hexenal). Pyruvate is also a product of glycolysis and photosynthesis and a key substrate in photorespiration and mitochondrial respiration.

Acetyl CoA is another central substrate, which integrates primary and secondary metabolic processes as well as signalling and regulatory mechanisms. It is used as the primary substrate of mitochondrial respiration for the biosynthesis of lipids including fatty acids and isoprenoids and can be produced through a fermentation-like process involving the activation of acetic acid (Jardine et al. 2013). In addition to many non-volatile organic compounds (e.g. fatty acids, some amino acids, flavonoids, phenolics) (Oliver et al. 2009), acetyl CoA provides substrate for a large array of BVOCs including volatile isoprenoids, oxygenated VOCs, fatty acid oxidation products, and volatile acetate esters (e.g. methyl acetate, ethyl acetate).

2.3 Volatile Metabolomics

The emerging field of volatile metabolomics is the study of the gas phase component of the chemical, physical, and biological processes involved in the production of metabolites within an ecosystem, allowing for a molecular understanding of biogeochemical cycles. This field aims to combine traditional biochemical pathway studies involving destructive tissue sampling and metabolite extraction and analysis with non-invasive atmospheric analytical chemistry techniques used for the identification and quantification of BVOCs within and above forest canopies to gain new insights into within-plant carbon and energy allocation to primary and secondary metabolic processes. For example, plant BVOC exchange fluxes using enclosures and ambient BVOC concentrations and fluxes within and above forest canopies can be made in situ in real time and used as biomarkers of carbon allocation processes such as photosynthesis, photorespiration, respiration, and fermentation (Jardine et al. 2010b; Loreto et al. 2007; Kesselmeier et al. 1997; Bracho-Nunez et al. 2012), cell wall expansion and growth (Harley et al. 2007), acetyl-CoA and fatty acid biosynthesis and degradation (Fall et al. 1999; Jardine et al. 2012b), and signalling and defence against abiotic and biotic stresses (Niinemets 2010; Karl et al. 2008; Jardine et al. 2014).

For example, Jardine et al. (2010b) used positional ^{13}C-labelled pyruvate to trace the metabolic pathways responsible for the biosynthesis of volatile isoprenoids and oxygenated VOCs in real time for individual mango leaves (*Mangifera indica*). While the metabolic pathways leading to isoprenoid biosynthesis are well documented, those leading to the production of oxygenated VOCs are still uncertain. In their study, leaves fed with the pyruvate-2-^{13}C solution resulted in large enrichments (^{13}C/^{12}C) of both ^{13}C-labelled isoprenoids and oxygenated VOCs (up to 266 % for sesquiterpenes and 154 % for acetaldehyde for example).

However, when mango leaves were fed with pyruvate-1-^{13}C, ^{13}C labelling of BVOCs was greatly reduced. Positional pyruvate labelling was then used to demonstrate that the $C_{2,3}$ atoms of pyruvate are directly utilised for the biosynthesis of volatile and non-volatile metabolites and biopolymers. However, the C_1 of pyruvate has a completely different fate and is decarboxylated to CO_2, representing a new source of CO_2 not previously considered in studies of plant CO_2 sources and sinks (Jardine et al. 2013). Thus, BVOCs can be used to track cellular processes that imprint a unique chemical fingerprint on the atmosphere surrounding individual plants. When applied at the ecosystem level, volatile metabolomics has the potential to advance mechanistic understanding of BVOC biosynthesis as a function of changing environmental conditions.

2.4 BVOCs as Biomarkers of Lipid Peroxidation Under Oxidative Stress

Lipids serve numerous critical functions in plant biology including providing membrane structure and participating in the light reactions of photosynthesis, antioxidant, and signalling processes. Saturated lipids are extremely resistant to oxidation within plants and the environment, where plant alkanes with ages greater than one billion years have been detected in lake sediments (Oro et al. 1965). In contrast, unsaturated lipids including isoprenoids and fatty acids are highly susceptible to oxidisation with their pools rapidly turned over in oxidising conditions. Moreover, the oxidative power of the lower atmosphere is strongly influenced by the emission of unsaturated volatile lipids from vegetation, especially isoprenoids and reactive volatile lipids which can be emitted at high rates from many plants fuelling atmospheric chemistry through photo-oxidation reactions (Monson 2002).

Reactive oxygen species (ROS) including singlet oxygen ($^1O_2$), superoxide anion (O_2^-), hydrogen peroxide (H_2O_2), and the hydroxyl radical (OH) are continuously generated in plants by the incomplete reduction of oxygen (O_2). While ROS concentrations within plants are generally kept low by ROS quenching and scavenging systems, excessive ROS accumulation can result in extensive oxidation of plant lipids (Apel and Hirt 2004; Jardine et al. 2010a). While traditionally described as the 'Oxygen Paradox' where ROS are a toxic by-product of aerobic metabolism, ROS-lipid signalling is now recognised as an integral component of plant response to abiotic and biotic stress as well as regulation of growth, development, and programmed cell death (Suzuki et al. 2011; Mittler et al. 2011).

In a changing global climate with increasing air pollution and rapid land use changes, plants are exposed to a wide variety of biotic (e.g. microbes, insects) and abiotic (e.g. thermal, radiative, drought) stressors. In plant tissues, these stressors can cause the accumulation of ROS, which if left unchecked can overwhelm cellular antioxidant defences including enzyme-mediated ROS quenching reactions, internal systems for ROS scavenging, and defence gene activation (Møller

2001). This can lead to extensive ROS-mediated oxidation of important components, such as nucleic acids, proteins, and lipids leading to cell death (Apel and Hirt 2004). Therefore, plants with a diverse suite of antioxidant defences may better tolerate stressful environmental conditions occurring in response to local and global changes in climate.

The oxidation of plant fatty acids via non-enzymatic (Durand et al. 2009; Mene-Saffrane et al. 2009) and enzymatic (Andreou and Feussner 2009; Gigot et al. 2010; Heiden et al. 2003) mechanisms produces a broad range of oxidation product biomarkers termed oxylipins. The accumulation of ROS in plant tissues initiates fatty acid (e.g. α-linolenic acid) peroxidation, yielding a large array of 'oxidative stress' biomarkers. Lipid peroxidation generates a number of products, which have been extensively used as quantitative indicators of oxidative damage in plants (Gutteridge 1995; Shulaev and Oliver 2006). For example, 4-hydroxy-2-nonenal (HNE), 4-hydroxy-2-hexenal (HHE), and malondialdehyde are widely used as biomarkers of non-enzymatic lipid peroxidation (Hartley et al. 1999; Halliwell and Gutteridge 1999; Long and Picklo 2010). However, the extraction from plant tissues, derivatisation, and compound-specific analysis (GC-MS or HPLC) of these reactive carbonyl compounds remains a challenge due to their trace abundances, high reactivity, water solubility, and volatility (Shibamoto 2006). Nonetheless, a number of classes of lipid peroxidation products have been identified including hydrocarbons, ketones, furans, alkanals, 2-alkenals, 2,4-alkadienals, 2-hydroxyalkanals, 4-hydroxy-2-alkenals, and dicarbonyls (Kawai et al. 2007; Steeghs et al. 2006; Frankel et al. 1989; Mark et al. 1997; Moseley et al. 2003; Nielsen et al. 1997).

Given the volatile nature of many of these biomarkers, it is interesting to speculate on the potential of detecting them in atmospheric samples as non-invasive indicators of oxidative stress at a variety of temporal and spatial scales. Numerous volatile oxylipins have been recently observed as direct emissions from plants under oxidative stress generated by freeze–thaw treatment of tropical leaves (Table 2.1). These include alkanals (e.g. propanal, butanal, pentanal,

Table 2.1 Example of isoprene (bold) and fatty acid peroxidation biomarkers from plants under oxidative stress

Parent lipid	Class	Oxidation Biomarkers
isoprene	**isoprene**	**methacrolein, methyl vinyl ketone**
isoprene	**isoprene**	**3-methyl furan, 2-methyl-3-buten-2-ol**
fatty acids	GLVs	3-hexenal, 3-hexen-1-ol, 3-hexen-1-yl acetate
fatty acids	furans and furanones	tetrahydrofuran, 2-ethyl furan, 5-ethyl 2(5H)-furanone
fatty acids	alkanes	propane, butane, pentane…undecane
fatty acids	2-alkenes	2-propene, 2-butene, 2-pentene…2-undecene
fatty acids	alkanals	propanal, butanal, pentanal…undecanal
fatty acids	2-alkenals	2-propenal, 2-butenal, 2-pentenal…2-undecenal
fatty acids	2,4-alkadienals	2,4-hexadienal, 2,4-heptadienal, 2,4-octadienal
fatty acids	2-ketones	2-butanone, 2-pentanone... 2-undecanone
fatty acids	alkenones	1-hexen-3-one, 1-penten-3-one, 1-octen-3-one, 6-methyl-5-hepten-2-one
fatty acids	4-hydroxy 2-alkenals	4-hydroxy-2-hexenal, 4-hydroxy-2-nonenal
fatty acids	dicarbonyls	malondialdehyde, gyloxal, methyl glyoxal, diacetyl

hexanal), 2-alkenals (e.g. 2-propenal, 2-butenal, 2-pentenal, 2-hexenal), 2-alkenes (e.g. 2-propene, 2-butene, 2-pentene, 2-hexene), 2,4-alkadienals (e.g. 2,4-hexadienal), furans and furanones (e.g., tetrahydrofuran, 2-ethyl furan), and dicarbonyls (e.g. malondialdehyde, gyloxal, methyl glyoxal, and diacetyl). In addition, the enzymatic peroxidation of plant fatty acids by lipoxygenase enzymes can lead to the formation and emission of characteristic oxidation products known as green leaf volatiles (GLVs) via the lipoxygenase pathway (Loreto and Schnitzler 2010; Hatanaka 1993; Fall et al. 1999). In this pathway, the formation of the classic 6-carbon (C6) GLVs in plants is initiated by the ubiquitous type 2 lipoxygenase enzymes (13-LOX) in chloroplasts which catalyse the oxygenation of α-linolenic acid (the dominant fatty acid in the aerial tissues of most plants) to form 13-hydroperoxy linolenic acid (HPLA) (Andreou and Feussner 2009). HPLA can be degraded (catalysed by hydroperoxide lyase) to form the primary GLV (Z)-3-hexenal which is then reduced and acetylated to form the corresponding alcohol (Z)-3-hexen-1-ol and acetate ester (Z)-3-hexen-1-yl acetate, respectively (D'Auria et al. 2007).

The emissions of GLVs from plants have been documented during processes known to be associated with ROS accumulation including programmed cell death during senescence (Holopainen et al. 2010) and a wide variety of biotic and abiotic stresses including pathogen attack (Jansen et al. 2009), high ambient ozone concentrations (Heiden et al. 2003; Beauchamp et al. 2005), herbivory (Arimura et al. 2009), desiccation (De Gouw et al. 2000), high light and temperature (Loreto et al. 2006), mechanical wounding (Fall et al. 1999), and freeze–thaw events (Fall et al. 2001). Thus, both enzymatic and non-enzymatic lipid peroxidation mechanisms lead to the formation of characteristic fatty acid peroxidation biomarkers that may be detectable as gas-phase emissions from plant tissue under stress at the ecosystem scale. Although not yet reported from Amazonian ecosystems, these and other lipid peroxidation biomarkers may be emitted under environmental extremes associated with changes in land use and climate and are therefore prime candidates for ecosystem scale volatile metabolomics studies (Kawai et al. 2007; Steeghs et al. 2006; Frankel et al. 1989; Mark et al. 1997; Moseley et al. 2003; Nielsen et al. 1997).

The five-carbon molecule, isoprene, is estimated to be the most abundant and well-studied BVOC emitted from terrestrial ecosystems (Rasmussen and Khalil 1988). Isoprene is a biomarker of photosynthesis and concentrations are known to positively correlate with light and temperature (Fig. 2.2) (Monson and Fall 1989). As reviewed by Vickers et al. (2009), a rich literature exists demonstrating the role of isoprene as a photosynthesis protector from oxidative stress caused by high temperature and light. Isoprene has also been shown to quench ozone and hydrogen peroxide (Loreto and Velikova 2001), singlet oxygen (Velikova et al. 2004), and nitric oxide (Velikova et al. 2005), suggesting an antioxidant role for isoprene. Recently, investigations using mango leaves and branches (*Mangifera indica*) as well as ambient air samples from an enclosed tropical mesocosm and a central Amazon forest support the role of antioxidant properties of isoprene (Jardine et al. 2012a, 2013). Observations of temperature-stressed leaves from isoprene-

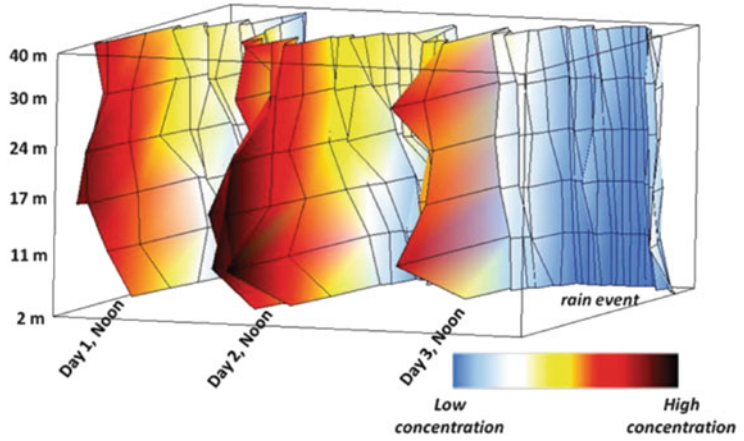

Fig. 2.2 A snapshot of the diurnal patterns of isoprene concentration variations over a 3-day period measured from a tower in a central Amazon forest. The *x*-axis represents time, while the *y*-axis shows measurement heights from 2 m above the ground to 10 m above the canopy. The *colour scale* ranges from minimum (*blue*) to maximum (*black*) concentrations. The vertical gradients show clear sources within the under-canopy (10–17 m) and canopy (30 m) layers corresponding with maximum temperature and light at midday and minimum concentrations at night. A sudden drop in concentration at all heights occurring during a rain event which decreased temperatures and light and likely diminished ecosystem photosynthesis is also observable

emitting plants showed production of first-generation oxidation products of isoprene: methyl vinyl ketone (MVK), methacrolein (MAC), and 3-methyl furan (3-MF). The authors suggested that the emissions of isoprene oxidation products increased with temperature stress due to direct chemical reactions with ROS or, in other words, in-plant oxidation of isoprene (Fig. 2.3).

To a large extent, the oxidative power of the lower atmosphere is controlled by ecosystem emissions of biogenic VOCs, especially those that contain carbon–carbon double bonds, such as volatile isoprenoids, which are readily available for oxidation through reaction with hydroxyl radicals, ozone, and nitrate radicals (Monson 2002). However, current models cannot adequately describe atmospheric oxidant levels in biogenically dominated areas like the Amazon basin (Lelieveld et al. 2008). The discovery of significant primary emissions of isoprene oxidation products in the central Brazilian Amazon (Jardine et al. 2012a) may reduce previous estimates of the effect of VOCs on the oxidising power of the troposphere and increase the role of leaves as a source for at least the first-generation products of VOC oxidation to the atmosphere. These findings may have important implications for characterising the oxidising capacity of the atmosphere and its impacts on atmospheric chemistry and climate. Understanding lipid production and oxidation dynamics within plants may be critical for predicting ecosystem response to the increasing temperature and light as a result of a changing climate. Investigating these mechanistic processes is complex, because of the very broad scale over which lipid production is influenced and over which they react. For example, isoprene

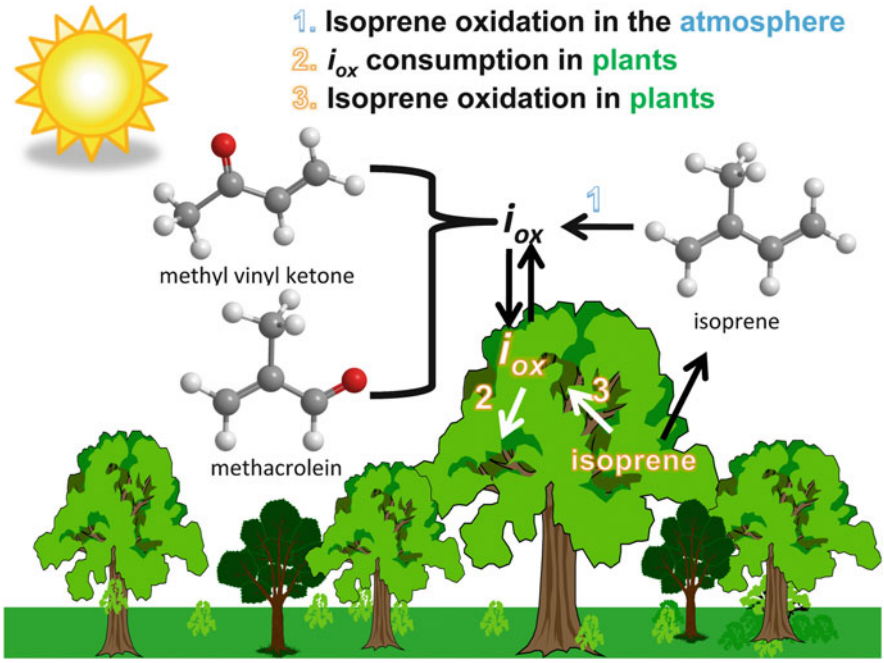

Fig. 2.3 A simplified schematic showing the production of isoprene and its oxidation products methyl vinyl ketone and methacrolein in plants as well as their emission to the atmosphere

starts at the subcellular level in chloroplasts and ultimately impacts key atmospheric processes, which in turn modify global climate, which in turn influences isoprene production in the biosphere. Investigation therefore requires a mixture of expertise and collaborating disciplines.

2.5 BVOC Bidirectional Biosphere–Atmosphere Exchange

There is a growing consensus that a large number of oxygenated compounds are both emitted and consumed by plants and that bidirectional exchange occurs between tropical forests and the atmosphere (Jardine et al. 2008, 2011a; Karl et al. 2005; Ganzeveld et al. 2008; Andreae et al. 1988). The compensation point is the point at which the ambient air mixing ratio of a BVOC results in a net zero flux, where consumption and emission are balanced.

A recent study focused on methanol and acetone Ganzeveld et al. (2008) showed that a commonly applied algorithm to simulate global acetone and methanol biogenic exchanges substantially overestimates ambient concentrations and emission strengths (compared with observations). In contrast, the use of a compensation point approach simulated ambient concentrations and exchange dynamics that were

much more comparable to observations. Another example comes from studies focused on gas-phase formic acid (FA) and acetic acid (AA) (Kesselmeier 2001; Gabriel et al. 1999; Andreae et al. 1988; Talbot et al. 1990), which are found ubiquitously in the atmosphere (Paulot et al. 2011). Jardine et al. (2011a) conducted a study in a central Amazon forest ecosystem comparing ratios of FA to AA (FA: AA) providing the first ecosystem scale evidence for the bidirectional FA and AA exchange between the forest canopy and the atmosphere and further estimated an ecosystem compensation point for each acid. While traditionally viewed strictly as emission sources to the atmosphere, these recent works demonstrate that plants can act as both a source and sink for BVOCs, especially those that are intermediates in metabolic pathways. Thus, in order to improve simulations of biosphere–atmosphere fluxes and atmospheric concentrations of oxygenated VOCs in Earth System Models, development of modelling approaches that embrace the bidirectional exchange of BVOCs warrants further investigation.

2.6 Conclusions

Studies of biogenic volatile organic compounds within the Amazon have been conducted for nearly 30 years (Rasmussen and Khalil 1988; Andreae et al. 1988); however, we are still at the forefront of our understanding of what BVOCs are emitted from vegetation, the metabolic pathways that produce them within plants, their functional roles in terrestrial ecosystems, and how these roles may change under a changing climate. Some of the basic yet extremely important questions to address with respect to BVOCs in the Amazon are: (i) What are the identities, concentrations, and fluxes of BVOC emissions from individual tree species and whole ecosystems? (ii) What are the functional biological roles of BVOCs and what roles will they play under future land use and climate change? (iii) What controls the amount of assimilated carbon allocated to the production and emission of BVOCs in relation to non-volatile metabolites and respiratory processes?

Addressing these questions requires intensive observations at both the plant species and ecosystem scales within the Amazon basin. As highly sensitive analytical chemistry tools become available, the identification and quantification of novel BVOCs is also emerging. The promising area of research, volatile metabolomics, is beginning to provide non-invasive methodologies to develop a mechanistic understanding of BVOC metabolism and therefore may lead to new understanding of the functional roles of BVOCs at the plant and ecosystem scales. In turn, improvements in Earth System Models can further our ability to predict changes in BVOC impacts on atmospheric chemistry and climate.

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