Lawrence Berkeley National Laboratory
Climate & Ecosystems

Title
Biogenic Volatile Organic Compounds in Amazonian Forest Ecosystems

Permalink
https://escholarship.org/uc/item/5nt939ff

ISBN
978-3-662-49900-9

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Publication Date
2016

DOI
10.1007/978-3-662-49902-3_2

Peer reviewed

1   **4 Biogenic volatile organic compounds in Amazonian forest ecosystems**

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9

10   *Abstract (150 words, for web purposes only)*

11   Plants produce and emit a large array of volatile metabolites termed biogenic volatile organic

12   compounds (BVOCs) as an integral part of primary and secondary metabolism. Although well

13   studied for their impacts on atmospheric processes, there is much to learn about their biological

14   functions. It is now recognized that many cellular processes leave unique volatile fingerprints

15   behind that can be studied through the acquisition of BVOC profiles in the headspace

16   atmospheres of plants across a wide range of spatial and temporal scales from leaves, whole

17   organisms, ecosystems, and regions and from seconds to seasons. In this chapter, in-plant BVOC

18   production and potential functional roles in the Amazon Basin are discussed. The chapter closes

19   with some suggested future research on Amazonian BVOCs, specifically - detailed studies on the

20   identities, fluxes, and environmental dependencies of BVOC emissions including the

21   characterization of potential bi-directional exchange.

22

23 **4.1 Introduction**

24 Biogenic volatile organic compounds (BVOCs) are produced directly within plants via

25 biochemical pathways associated with primary and secondary metabolic processes. Although

26 non-volatile metabolites are typically bound within specific cellular organelles in lipids or

27 aqueous phases, BVOC volatile metabolites can readily partition between these phases and the

28 intracellular airspace (Fall 2003). Thus, many BVOCs may freely exchange among cellular

29 organelles, cells, and tissues, contributing to an integration of whole organism carbon and energy

30 metabolism. Moreover, exchange of the intracellular airspace with the atmosphere may help

31 coordinate the metabolisms of different plants within an ecosystem in response to environmental

32 and biological factors (Yan and Wang 2006). In addition, land-atmosphere exchange of VOCs

33 integrates local and regional atmospheric chemistry with plant metabolism (Jardine et al. 2011a).

34

35 The emerging field of volatile ecosystem metabolomics integrates the volatile component into the

36 chemical, physical, and biological processes involved in the processing of metabolites within the

37 land-atmosphere interface including potential perturbations of the system by anthropogenic

38 activities (e.g. VOC emissions from biomass and fossil fuel burning). The power of volatile

39 metabolomics comes from the fact that many cellular processes leave unique chemical

40 fingerprints (biomarkers) behind in the atmosphere (e.g. BVOCs such as volatile isoprenoids,

41 organic acids, alcohols, esters, aldehydes, ketones, aromatics, sulfides, nitriles, etc.). Therefore,

42 volatile metabolomics provides noninvasive techniques to study plant metabolism from a variety

43 of spatial and temporal scales. The application of these methods in the tropics may improve our

44 mechanistic understanding of how environmental and biological variables associated with climate

45 and land use change affects the carbon and energy metabolism of natural and managed forests.

46

47 Tropical ecosystems cycle more carbon than any other biome (~ 1.4 PgC/yr versus 0.5 PgC/yr for

48 temperate ecosystems, (Sarmiento et al. 2010) and are estimated to account for nearly 80% of the

49 global BVOC emissions (Levis et al. 2003). The Amazon Basin is a major tropical source of

50 BVOCs to the global atmosphere (Greenberg et al. 2004), yet less is known about BVOCs from

51 its vegetation than other regions of the world (Guenther 2013). This is due to a number of factors,

52 among which are the extremely high tree species diversity (ter Steege et al. 2013; Macarthur

53 1965) and difficulties in conducting and sustaining remote field studies with highly sensitive

54 analytical chemistry instrumentation for even short periods of time. What we do know about

55 Amazonian BVOCs primarily results from a few important short-term plant enclosure studies,

56   above-canopy measurements, and aircraft observations (Kesselmeier et al. 2002; Karl et al. 2007;

57   Jardine et al. 2011b).

58

59   Historically, BVOCs have been studied with respect to their significant impacts on the chemistry

60   and physics of the atmosphere, which remains an active area of research (see chapter x, Artaxo).

61   The focus of this chapter is towards developing a mechanistic understanding of BVOC dynamics

62   within plants and ecosystems. First is a brief overview of BVOC production within plants

63   followed by an introduction to the field of volatile metabolomics. Next, examples of Amazonian

64   plant and ecosystem functional roles of several BVOCs are discussed. The chapter ends with

65   suggested directions for Amazonian BVOC research including detailed plant VOC emission

66   surveys, the identification of new BVOCs, and the characterization of potential BVOC

67   ecosystem-atmosphere bidirectional exchange (i.e. emission and consumption by vegetation).

68   **4.2 BVOC biosynthesis in plants**

69   During photosynthesis, plants assimilate atmospheric carbon dioxide (CO_2) into primary

70   metabolites which are essential components required for growth and development. Primary

71   metabolites can be used as substrate for the biosynthesis of new biomass including proteins,

72   nucleic acids, carbohydrates and lipids, or can be used as a carbon and energy source during

73   respiration (Bourgaud et al. 2001; Tegeder and Weber 2008). Secondary metabolites are a diverse

74   set of compounds which are intricately involved in many physiological and ecological processes

75   within plants (Weng et al. 2012). For example, secondary metabolites have been identified as

76   plant defenses against abiotic and biotic stresses and chemical communication within and

77   between species (Weng et al. 2012; Jardine et al. 2008; Karl et al. 2008; Pophof et al. 2005). Both

78   primary and secondary metabolic pathways within plants create intermediates with sufficient

79   vapor pressures to be directly emitted into the atmosphere in the gas phase as BVOCs.

80

81   Plant metabolic pathways involved in BVOC biosynthesis occur in and across a number of

82   cellular organelles including the cytosol, chloroplast, mitochondria, and peroxisome **(Figure 4.1)**.

83   Some BVOCs like isoprene are strictly light dependent with a strong connection to recently

84   assimilated carbon (Jones and Rasmussen 1975). In contrast, instantaneous emissions of other

85   BVOCs like methanol are much less light dependent and can be produced at night (Fall and

86   Benson 1996; Harley et al. 2007).

87

88   Key substrates (i.e. glyceraldehyde-3-phosphate, phosphoenol pyruvate, pyruvate, and acetyl-
89   CoA) can be produced independently within plant compartments or can be transported across
90   compartmental boundaries. For example, pyruvate is a central substrate in the biosynthesis of
91   BVOC classes such as volatile isoprenoids (isoprene, monoterpenes, sesquiterpenes), oxygenated
92   VOCs (acetaldehyde, ethanol, acetic acid, acetone, volatile acetate esters), and fatty acid
93   oxidation products (green leaf volatiles, e.g. Z-3-hexenol, Z-3-hexenal). Pyruvate is also a
94   product of glycolysis and photosynthesis, and a key substrate in photorespiration and
95   mitochondrial respiration.

96

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

105

106   **[Figure 4.1-Metabolic pathways]**

107

108   **4.3 Volatile Metabolomics**
109   The emerging field of volatile metabolomics is the study of the gas phase component of the
110   chemical, physical, and biological processes involved in the production of metabolites within an
111   ecosystem, allowing for a molecular understanding of biogeochemical cycles. This field aims to
112   combine traditional biochemical pathway studies involving destructive tissue sampling and
113   metabolite extraction and analysis with non-invasive atmospheric analytical chemistry techniques
114   used for identification and quantification of BVOCs within and above forest canopies to gain new
115   insights on within-plant carbon and energy allocation to primary and secondary metabolic
116   processes. For example, plant BVOC exchange fluxes using enclosures and ambient BVOC
117   concentrations and fluxes within and above forest canopies can be made in-situ in real-time and
118   used as biomarkers of carbon allocation processes such as photosynthesis, photorespiration,
119   respiration, and fermentation (Jardine et al. 2010b; Loreto et al. 2007; Kesselmeier et al. 1997;

120   Bracho-Nunez et al. 2012), cell wall expansion and growth (Harley et al. 2007), acetyl-CoA and

121   fatty acid biosynthesis and degradation (Fall et al. 1999; Jardine et al. 2012b), and signaling and

122   defense against abiotic and biotic stresses (Niinemets 2010; Karl et al. 2008; Jardine et al. 2013c).

123

124   For example, Jardine et al. (2010b) used positional ^{13}C labeled pyruvate to trace the metabolic

125   pathways responsible for the biosynthesis of volatile isoprenoids and oxygenated VOCs in real

126   time for individual mango leaves (*Mangifera indica*). While the metabolic pathways leading to

127   isoprenoid biosynthesis are well documented, those leading to the production of oxygenated

128   VOCs are still uncertain. In their study, leaves fed with the pyruvate-2-^{13}C solution resulted in

129   large enrichments (^{13}C/^{12}C) of both ^{13}C-labeled isoprenoids and oxygenated VOCs (up to 266%

130   for sesquiterpenes and 154% for acetaldehyde for example). However, when mango leaves were

131   fed with pyruvate-1-^{13}C, ^{13}C-labeling of BVOCs was greatly reduced. Positional pyruvate labeling

132   was then used to demonstrate that the $C_{2,3}$ atoms of pyruvate are directly utilized for the

133   biosynthesis of volatile and non-volatile metabolites and biopolymers. However, the C_1 of

134   pyruvate has a completely different fate and is decarboxylated to CO_2, representing a new source

135   of CO_2 not previously considered in studies of plant CO_2 sources and sinks (Jardine et al. 2013a).

136   Thus, BVOCs can be used to track cellular processes that imprint a unique chemical fingerprint

137   on the atmosphere surrounding individual plants. When applied at the ecosystem level, volatile

138   metabolomics has the potential to advance mechanistic understanding of BVOC biosynthesis as a

139   function of changing environmental conditions.

140   **4.3 BVOCs as biomarkers of lipid peroxidation under oxidative stress**

141   Lipids serve numerous critical functions in plant biology including providing membrane

142   structure, participating in the light reactions of photosynthesis, antioxidant, and signaling

143   processes. Saturated lipids are extremely resistant to oxidation within plants and the environment,

144   with plant alkanes with ages greater than one billion years have been detected in lake sediments

145   (Oro et al. 1965). In contrast, unsaturated lipids including isoprenoids and fatty acids are highly

146   susceptible to oxidization with their pools rapidly turned over under oxidizing conditions.

147   Moreover, the oxidative power of the lower atmosphere is strongly influenced by the emission of

148   unsaturated volatile lipids from vegetation, especially isoprenoids and reactive volatile lipids

149   which can be emitted at high rates from many plants fueling atmospheric chemistry through

150   photo-oxidation reactions (Monson 2002a).

151

152   Reactive oxygen species (ROS) including singlet oxygen ($^1O_2$), superoxide anion (O_2^-), hydrogen

153   peroxide (H_2O_2), and the hydroxyl radical (OH) are continuously generated in plants by the

154   incomplete reduction of oxygen (O_2). While, ROS concentrations within plants are generally kept

155   low by ROS quenching and scavenging systems, excessive ROS accumulation can result in

156   extensive oxidation of plant lipids (Apel and Hirt 2004; Jardine et al. 2010a). While traditionally

157   described as the "Oxygen Paradox" where ROS are a toxic byproduct of aerobic metabolism,

158   ROS-lipid signaling is now recognized as an integral component of plant response to abiotic and

159   biotic stress as well as regulation of growth, development, and programmed cell death (Suzuki et

160   al. 2011; Mittler et al. 2011).

161

162   In a changing global climate with increasing air pollution and rapid land use changes, plants are

163   exposed to a wide variety of biotic (e.g. microbes, insects) and abiotic (e.g. thermal, radiative,

164   drought) stressors. In plant tissues, these stressors can cause the accumulation of reactive oxygen

165   species (ROS), which if left unchecked, can overwhelm cellular antioxidant defenses including

166   enzyme-mediated ROS quenching reactions, internal systems for ROS scavenging, and defense

167   gene activation (Møller 2001). This can lead to extensive ROS-mediated oxidation of important

168   components, such as nucleic acids, proteins and lipids leading to cell death (Apel and Hirt 2004).

169   Therefore, plants with a diverse suite of antioxidant defenses may better tolerate stressful

170   environmental conditions occurring in response to local and global changes in climate.

171

172   The oxidation of plant fatty acids via non-enzymatic (Durand et al. 2009; Mene-Saffrane et al.

173   2009) and enzymatic (Andreou and Feussner 2009; Gigot et al. 2010; Heiden et al. 2003)

174   mechanisms produces a broad range of oxidation product biomarkers termed oxylipins. The

175   accumulation of ROS in plant tissues initiates fatty acid (e.g. α-linolenic acid) peroxidation,

176   yielding a large array of 'oxidative stress' biomarkers. Lipid peroxidation generates a number of

177   products, which have been extensively used as quantitative indicators of oxidative damage in

178   plants (Gutteridge 1995; Shulaev and Oliver 2006). For example, 4-hydroxy-2-nonenal (HNE), 4-

179   hydroxy-2-hexenal (HHE), and maliondialdehyde are widely used as biomarkers of non-

180   enzymatic lipid peroxidation (Hartley et al. 1999; Halliwell and Gutteridge 1999; Long and

181   Picklo 2010). However, the extraction from plant tissues, derivatization, and compound specific

182   analysis (GC-MS or HPLC) of these reactive carbonyl compounds remains a challenge due to

183   their trace abundances, high reactivity, water solubility, and volatility (Shibamoto 2006).

184   Nonetheless, a number of classes of lipid peroxidation products have been identified including

185   hydrocarbons, ketones, furans, alkanals, 2-alkenals, 2,4-alkadienals, 2-hydroxyalkanals, 4-

186   hydroxy-2-alkenals, and dicarbonyls (Kawai et al. 2007; Steeghs et al. 2006; Frankel et al. 1989;

187   Mark et al. 1997; Moseley et al. 2003; Nielsen et al. 1997).

188

189   Given the volatile nature of many of these biomarkers, it is interesting to speculate on the

190   potential of detecting them in atmospheric samples as non-invasive indicators of oxidative stress

191   at a variety of temporal and spatial scales. Numerous volatile oxylipins have been recently

192   observed as direct emissions from plants under oxidative stress generated by freeze-thaw

193   treatment of tropical leaves (**Table 1**). These include alkanals (e.g. propanal, butanal, pentanal,

194   hexanal), 2-alkenals (e.g. 2-propenal, 2-butenal, 2-pentenal, 2-hexenal), 2-alkenes (e.g. 2-

195   propene, 2-butene, 2-pentene, 2-hexene), 2,4-alkadienals (e.g. 2,4-hexadienal), furans and

196   furanones (e.g. tetrahydrofuran, 2-ethyl furan), and dicarbonyls (e.g. malondialdehyde, gyloxal,

197   methyl glyoxal, and diacetyl). In addition, the enzymatic peroxidation of plant fatty acids by

198   lipoxygenase enzymes can lead to the formation and emission of characteristic oxidation products

199   known as green leaf volatiles (GLVs) via the lipoxygenase pathway (Loreto and Schnitzler 2010;

200   Hatanaka 1993; Fall et al. 1999). In this pathway, the formation of the classic 6 carbon (C6)

201   GLVs in plants is initiated by the ubiquitous type 2 lipoxygenase enzymes (13-LOX) in

202   chloroplasts which catalyze the oxygenation of α-linolenic acid (the dominant fatty acid in the

203   aerial tissues of most plants) to form 13-hydroperoxy linolenic acid (HPLA) (Andreou and

204   Feussner 2009). HPLA can be degraded (catalyzed by hydroperoxide lyase) to form the primary

205   GLV (Z)-3-hexenal which is then reduced and acetylated to form the corresponding alcohol (Z)-

206   3-hexen-1-ol and acetate ester (Z)-3-hexen-1-yl acetate respectively (D'Auria et al. 2007).

207

208   The emissions of GLVs from plants have been documented during processes known to be

209   associated with ROS accumulation including programmed cell death during senescence

210   (Holopainen et al. 2010) and a wide variety of biotic and abiotic stresses including pathogen

211   attack (Jansen et al. 2009), high ambient ozone concentrations (Heiden et al. 2003; Beauchamp et

212   al. 2005), herbivory (Arimura et al. 2009), desiccation (De Gouw et al. 2000), high light and

213   temperature (Loreto et al. 2006), mechanical wounding (Fall et al. 1999), and freeze-thaw events

214   (Fall et al. 2001). Thus, both enzymatic and non-enzymatic lipid peroxidation mechanisms lead to

215   the formation of characteristic fatty acid peroxidation biomarkers that may be detectable as gas-

216   phase emissions from plant tissue under stress at the ecosystem scale. Although not yet reported

217   from Amazonian ecosystems, these and other lipid peroxidation biomarkers may be emitted under

218   environmental extremes associated with changes in land use and climate and are therefore prime

219   candidates for ecosystem scale volatile metabolomics studies (Kawai et al. 2007; Steeghs et al.

220   2006; Frankel et al. 1989; Mark et al. 1997; Moseley et al. 2003; Nielsen et al. 1997).

221

222   **[Table 1: volatile oxylipin lipid peroxidaotion biomarkers]**

223

224   The 5 carbon molecule, isoprene, is estimated to be the most abundant and well-studied BVOC

225   emitted from terrestrial ecosystems (Rasmussen and Khalil 1988). Isoprene is a biomarker of

226   photosynthesis and concentrations are known to positively correlate with light and temperature

227   (**Figure 4.2**) (Monson and Fall 1989). As reviewed by Vickers et al. (2009), a rich literature

228   exists demonstrating the role of isoprene as a photosynthesis protector from oxidative stress

229   caused by high temperature and light. Isoprene has also been shown to quench ozone and

230   hydrogen peroxide (Loreto and Velikova 2001), singlet oxygen (Velikova et al. 2004) and nitric

231   oxide (Velikova et al. 2005), suggesting an antioxidant role for isoprene. Recently, investigations

232   using mango leaves and branches (*Mangifera indica*) as well as ambient air samples from an

233   enclosed tropical mesocosm and a central Amazon forest support the role of antioxidant

234   properties of isoprene (Jardine et al. 2012a; Jardine et al. 2013b). Observations of temperature-

235   stressed leaves from isoprene emitting plants showed production of first generation oxidation

236   products of isoprene; methyl vinyl ketone (MVK), methacrolein (MAC), and 3-methyl furan (3-

237   MF). The authors suggested that the emissions of isoprene oxidation products increased with

238   temperature stress due to direct chemical reactions with ROS, or in other words, in-plant

239   oxidation of isoprene (**Figure 4.3**).

240

241   **[Figure 4.2: isoprene molecule + 3-D tracks light, temp]**

242

243   **[Figure 4.3: isoprene oxidation schematic]**

244

245   To a large extent, the oxidative power of the lower atmosphere is controlled by ecosystem

246   emission of biogenic VOCs, especially those that contain carbon-carbon double bonds, such as

247   volatile isoprenoids, which are readily available for oxidation through reaction with hydroxyl

248   radicals, ozone and nitrate radicals (Monson 2002b). However, current models cannot adequately

249   describe atmospheric oxidant levels in biogenically dominated areas like the Amazon Basin

250   (Lelieveld et al. 2008). The discovery of significant primary emissions of isoprene oxidation

251   products in the central Amazon (Jardine et al. 2012c) may reduce previous estimates of the effect

252   of VOCs on the oxidizing power of the troposphere, and increase the role of leaves as a source for

253   at least the first generation products of VOC oxidation to the atmosphere. These findings may

254   have important implications for characterizing the oxidizing capacity of the atmosphere and its

255   impacts on atmospheric chemistry and climate. Understanding lipid production and oxidation

256   dynamics within plants may be critical for predicting ecosystem response to the increasing

257   temperature and light as a result of a changing climate. Investigating these mechanistic processes

258   is complex, because of the very broad scale over which lipid production is influenced and over

259   which they react. For example isoprene starts at the sub-cellular level in chloroplasts and

260   ultimately impacts key atmospheric processes, which in turn modify global climate, which in turn

261   influences isoprene production in the biosphere. Investigation therefore requires a mixture of

262   expertise and collaborating disciplines.

263   **4.4 BVOC bidirectional biosphere-atmosphere exchange**

264   There is a growing consensus that a large number of oxygenated compounds are both emitted and

265   consumed by plants and that bidirectional exchange occurs between tropical forests and the

266   atmosphere (Jardine et al. 2011c; Karl et al. 2005; Jardine et al. 2008; Ganzeveld et al. 2008;

267   Andreae et al. 1988). The compensation point is the point at which the ambient air mixing ratio of

268   a BVOC results in a net zero flux, where consumption and emission are balanced.

269   A recent study focused on methanol and acetone Ganzeveld et al. (2008), showed that a

270   commonly applied algorithm to simulate global acetone and methanol biogenic exchanges

271   substantially overestimates ambient concentrations and emission strengths (compared with

272   observations). In contrast, the use of a compensation point approach simulated ambient

273   concentrations and exchange dynamics that were much more comparable to observations.

274   Another example comes from studies focused on gas phase formic acid (FA) and acetic acid (AA)

275   (Kesselmeier 2001; Gabriel et al. 1999; Andreae et al. 1988; Talbot et al. 1990), which are found

276 ubiquitously in the atmosphere (Paulot et al. 2011). Jardine et al. (2011c) conducted a study in a

277 central Amazon ecosystem comparing ratios of FA to AA (FA/AA) providing the first ecosystem

278 scale evidence for the bidirectional FA and AA exchange between the forest canopy and the

279 atmosphere and further estimated an ecosystem compensation point for each acid. While

280 traditionally viewed strictly as emission sources to the atmosphere, these recent works

281 demonstrate that plants can act as both a source and sink for BVOCs, especially those that are

282 intermediates in metabolic pathways. Thus, in order to improve simulations of biosphere-

283 atmosphere fluxes and atmospheric concentrations of oxygenated VOCs in Earth System Models,

284 development of modeling approaches that embrace the bidirectional exchange of BVOCs

285 warrants further investigation.

286 **4.5 Conclusions**

287 Studies of biogenic volatile organic compounds within the Amazon have been conducted for

288 nearly 30 years (Rasmussen and Khalil 1988; Andreae et al. 1988), however, we are still at the

289 forefront of our understanding of what BVOCs are emitted from vegetation, the metabolic

290 pathways that produce them within plants, their functional roles in terrestrial ecosystems, and

291 how these roles may change under a changing climate. Some of the basic yet extremely important

292 questions to address with respect to BVOCs in the Amazon are: (i) What are the identities,

293 concentrations and fluxes of BVOC emissions from individual tree species and whole

294 ecosystems? (ii) What are the functional biological roles of BVOCs and what roles will they play

295 under future land use and climate change? and (iii) What controls the amount of assimilated

296 carbon allocated to the production and emission of BVOCs in relation to non volatile metabolites

297 and respiratory processes?

298

299 Addressing these questions requires intensive observations at both the plant species and

300 ecosystem scales within the Amazon Basin. As highly sensitive analytical chemistry tools

301 become available, the identification and quantification of novel BVOCs is also emerging. The

302 promising area of research, volatile metabolomics, is beginning to provide noninvasive

303 methodologies to develop a mechanistic understanding of BVOC metabolism and therefore may

304 lead to new understanding of the functional roles of BVOCs at the plant and ecosystem scales. In

305 turn, improvements in Earth System Models can further our ability to predict changes in BVOC

306 impacts on atmospheric chemistry and climate.

307

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579   **Figure and Table Captions**

580

581   **Figure 4.1.** A simplified representation of the flow of carbon in the cytosol, chloroplast
582   and mitochondria, which produce classes of biogenic volatile organic compounds
583   (BVOCs) in photosynthetic cells during primary and secondary metabolism.

584

585   **Figure 4.2.** A snapshot of the diurnal patterns of isoprene concentration variations over a

586   three-day period measured from a tower in a central Amazon forest. The x-axis represents

587   time, while the y-axis shows measurement heights from 2 meters above the ground to 10

588   meters above the canopy. The color scale ranges from minimum (blue) to maximum

589   (black) concentrations. The vertical gradients show clear sources within the under canopy

590   (10 - 17 m) and canopy (30 m) layers corresponding with maximum temperature and

591   light at midday and minimum concentrations at night. A sudden drop in concentration at

592   all heights occurring during a rain event which decreased temperatures and light and

593   likely diminished ecosystem photosynthesis is also observable.

594   **Figure 4.3.** A simplified schematic showing the production of isoprene and its oxidation

595   products methyl vinyl keytone and methacrolein in plants as well as their emission to the

596   atmosphere.

597
598   **Table 1:** Example of isoprene (red text) and fatty acid (black text) peroxidation
599   biomarkers from plants under oxidative stress.