

1 **Effect of land-use change and management on BVOC emissions – selecting climate-smart cultivars**

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4 **Running title:**

5 **Climate-smart BVOC emissions**

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21 **ABSTRACT**

22
23 Land-use change (LUC) has fundamentally altered the form and function of the terrestrial biosphere.
24 Increasing human population, the drive for higher living standards, and the potential challenges of
25 mitigating and adapting to global environmental change, mean that further changes in LUC are
26 unavoidable. LUC has direct consequences on climate, via emissions of greenhouse gases and
27 changing the surface energy balance, but also by affecting the emission of biogenic volatile organic
28 compounds (BVOCs). Isoprenoids, which dominate global BVOC emissions, are highly reactive and
29 strongly modify atmospheric composition. The effects of LUC on BVOC emissions and related
30 atmospheric chemistry have been largely ignored so far. However, compared to natural ecosystems,
31 most tree species used in bioenergy plantations are strong BVOC emitters, whereas intensively
32 cultivated crops typically emit less BVOCs. Here we summarize the current knowledge on LUC-driven
33 BVOC emissions and how these might affect atmospheric composition and climate. We further
34 discuss land-management and plant-breeding strategies which could be taken to move towards
35 climate-friendly BVOC emissions, whilst simultaneously maintaining or improving key ecosystem
36 functions such as crop yield under a changing environment.

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40 **KEYWORDS**

41

42 **Land-use change, biogenic organic volatile compounds, BVOCs, climate mitigation, climate**
43 **adaptation, land management, cultivar selection, genetic manipulation, priming, isoprene,**
44 **monoterpenes**

45

46 1 INTRODUCTION

47
48 Between 30 and 50% of the land surface today has been transformed as a result of human activities
49 (Ellis *et al.* 2010). The need to sustain the world's human population with food, fibre, building
50 material and energy was the main driver for converting natural vegetation into arable cropland and
51 pastures (Ellis *et al.* 2010). This coincided with a global population increase from an estimated less
52 than 30 million around 8000 years before present (B.P., Kaplan *et al.* 2011) to approximately 7 billion
53 today. Most of this increase has happened over the last 400 years, preceded by a slower, and
54 (averaged over time) more linear increase starting from around 1000 years B.P. (Kaplan *et al.* 2011).
55 At the beginning of the 21st century, the rate of global net land-use change is estimated to have
56 totalled $2 \times 10^5 \text{ km}^2 \text{ yr}^{-1}$ (Hurt *et al.* 2011). However, the important driving factors of human-induced
57 land cover changes go well beyond mere population dynamics, including technology (Kaplan *et al.*
58 2011), and changes in economics and social values. Present land-use changes differ widely in
59 character, from the conversion of tropical rainforest into pastures and oil palm plantations, to the
60 reforestation of abandoned croplands in North America and Eastern Europe. Despite possibilities of
61 using marginal or abandoned land for crop production, or closing yield gaps in developing nations, it
62 will likely be necessary to convert natural grasslands and forests to new agricultural land by 2050
63 (Hardacre *et al.* 2013). This need to provide food and fodder will be difficult to reconcile with the
64 supply of other ecosystem services (Naidoo *et al.* 2008), for instance climate regulation via the
65 inclusion of terrestrial ecosystems as part of international efforts to mitigate greenhouse gas
66 emissions (e.g. UN-REDD; United Nations, 2009; Azar *et al.* 2010).
67 Other than via long-lived greenhouse gases and altered surface radiation and energy balance, the
68 atmospheric and climate effects of land-use and land-cover change (LUC) have not yet shifted fully
69 into the focus of the climate change community. But with the increasing consideration of climate
70 effects of atmospherically short-lived pollutants alongside of air quality concerns (Andrea 2007;

71 Arneeth *et al.* 2009; Schindell *et al.* 2012) this is beginning to change. Biogenic volatile organic
72 compounds (BVOCs) are among the compounds receiving increasing attention in this context.
73 Because of the large mass emitted globally from terrestrial vegetation, and in particular the high
74 atmospheric reactivity of the volatile isoprenoids (i.e., isoprene and monoterpenes), it is well
75 established that these compounds exert a strong control on the burdens of tropospheric ozone,
76 methane and secondary aerosols (Atkinson and Arey 2003; Arneeth *et al.* 2010). Longer-lived
77 compounds such as methanol or acetone tend to be dispersed on a continental scale and throughout
78 the troposphere before oxidation (Tie *et al.* 2003; Arnold *et al.* 2005), thereby diluting their impact.
79 Conversion of natural vegetation into cropland and pastures is expected to decrease isoprene and
80 monoterpene emissions substantially, especially if this conversion is through deforestation (Figure 1).
81 Irrespective of the exact vegetation type, woody vegetation has much larger emission potential
82 (defined as BVOC emissions under a set of standard environmental conditions (see e.g., Niinemets *et*
83 *al.* 2010a)) than herbaceous or crop vegetation (see e.g. Kesselmeier *et al.* 2002). Reforestation,
84 however, will have the opposite effect. Further, some species, like oil palm and fast growing tree
85 species (poplar and willow) used in short-rotation coppice (SRC), have very high BVOC emissions,
86 exceeding those of natural forests (Hewitt *et al.* 2009; Ashworth *et al.* 2012).
87 BVOC emissions can be controlled and/or manipulated by the selection of specific cultivars as well as
88 by field management, so that the next generations of crop and bioenergy cultivars could also be
89 optimized during the breeding process for specific features of constitutive and inducible BVOC
90 emissions. One aim could be to favour and/or create cultivars that impact less on atmospheric
91 processes with low BVOC emission potential while at the same time selecting for BVOCs that could
92 increase plant resistance against herbivores and pests, or the tolerance against abiotic stresses
93 (Mumm and Dicke 2000; Loreto and Schnitzler 2010). Several novel biological and biotechnological
94 tools are available to alter the BVOC emission potentials of cultivars/ecotypes, including genetic
95 manipulation, priming by co-culturing or by using chemical elicitors. Cultivars with altered BVOC

96 emission potentials might better tolerate, resist and overcome combined stressful conditions in
97 future.

98

99 **2 The interplay between land-use change, climate change and BVOC emissions from vegetation**

100

101 **2.1 The role of land-use change in the climate system**

102

103 Historical LUC have contributed notably to climate warming (Le Quere *et al.* 2009; Kaplan *et al.*

104 2011), as carbon (C) emissions arising from past LUC activities to the atmosphere exceeded LUC-

105 related land C sinks. Conversion of natural ecosystems into cropland and pastures, mostly through

106 deforestation, has contributed an estimated release of more than 150 Pg C into the atmosphere, one

107 third of the approximate total anthropogenic C emissions since 1850 (Le Quere *et al.* 2009;

108 Houghton *et al.* 2012). Large uncertainties are associated with these estimates, due to absence of

109 observational constraints and methodological differences in the various model-studies that seek to

110 assess LUC effects (Houghton *et al.* 2012; Pugh *et al.* 2014). In addition, approximately 50% of the

111 observed increase in atmospheric nitric oxide (N₂O) over the same time period has been attributed to

112 agricultural fertilizer use (Zaehle *et al.* 2011), whilst anthropogenic methane (CH₄) emissions are

113 dominated by agriculture, particularly from ruminants, rice paddies and manure management

114 (Environmental Protection Agency 2012; Kirschke *et al.* 2013). CO₂, CH₄ and N₂O are potent

115 greenhouse gases and recent policy (Pittel and Rubbelke 2008; Jones *et al.* 2013; Mackey *et al.* 2013)

116 has considered land-management measures to mitigate global climate impacts, since afforestation or

117 avoided deforestation can either increase the terrestrial C sink strength, or prevent additional C

118 emissions to the atmosphere.

119 Climate change arising from changes in the sources and sinks of C- and N-containing GHGs continue

120 to operate over centuries because these gases are long-lived in the atmosphere, and also because

121 changes in vegetation and soil C and N pools operate over decades to centuries. In addition, a LUC-
122 climate response arises from changes in the land surface that alter biophysical processes controlling
123 the surface energy balance. For instance, conversion of forest into crop vegetation decreases surface
124 roughness and mixing of the near-surface air, increases the fraction of radiation reflected back into
125 the atmosphere, and changes the partitioning of the net radiation received at the surface into
126 evapotranspiration (latent heat flux) and sensible heat flux (Pitman *et al.* 2009; Arora and
127 Montenegro 2011). Compared to the greenhouse-gas climate impacts, the biophysical climate effects
128 from LUC are thus stronger regionally, and realised over a period of a few months to several decades
129 following a LUC event (Pitman *et al.* 2009; Arora and Montenegro 2011), since it is the initial changes
130 in land cover that tend to have the strongest effects on the surface radiation and energy balances.

131

132 **2.2 The role of BVOCs in the climate system**

133

134 Like the biophysical LUC climate impacts, climate effects of BVOCs are regionally heterogeneous.
135 Their climate importance is well acknowledged, operating via their effects on the burdens of CH₄,
136 tropospheric O₃, and secondary organic aerosol (SOA) (Atkinson and Arey 2003; Arneth *et al.* 2010,
137 Carslaw *et al.* 2013). However, the oxidation pathways of BVOCs are highly complex (e.g. Jenkin *et*
138 *al.*, 2003; 2012), and even for the most studied compounds such as isoprene, important aspects
139 remain unclear (Di Carlo *et al.* 2004; Lelieveld *et al.* 2008; Crouse *et al.* 2011). In a number of field
140 experiments in remote forests, detailed measurements of the hydroxyl radical (OH), the principal
141 atmospheric oxidant, could not be reconciled with isoprene mixing ratios based on state-of-the art
142 air chemistry (Lelieveld *et al.* 2008; Hofzumahaus *et al.* 2009; Pugh *et al.* 2010; 2011). Correct
143 simulation of the impact of BVOCs on OH is crucial for determining the lifetime of CH₄ in the
144 atmosphere, for which the influence of isoprene alone is of the order of 10% (Young *et al.* 2009).
145 Recent work indicates strong evidence of hitherto unknown HO_x (OH + HO₂) regeneration under the

146 low NO_x (NO+NO₂) mixing ratio typical of remote areas (Archibald *et al.* 2011; Taraborrelli *et al.*
147 2012), although the mechanism remains uncertain (e.g. Warwick *et al.* 2013). A strongly non-linear
148 behaviour in relation to NO_x-mixing ratios is typical of BVOCs chemistry (Stevenson *et al.* 2006;
149 Collins *et al.* 2010; Lamarque *et al.* 2010) and BVOCs can either increase or decrease tropospheric O₃
150 mixing ratios depending on the local ratio of BVOCs to NO_x concentrations. Typically, increased BVOC
151 emissions would suppress O₃ formation in remote locations where NO_x mixing ratio is low (known as
152 NO_x-limited conditions) and increase it in polluted ones (known as VOC-limited) (Pyle *et al.* 2011).
153 Besides their importance for gas-phase chemistry, isoprene (C₅), monoterpenes (C₁₀), and
154 sesquiterpenes (C₁₅) are crucial isoprenoid precursors for formation and/or growth of SOA (Bonn
155 and Moortgart 2003; Claeys *et al.* 2004; Tunved *et al.* 2006; Laaksonen *et al.* 2008; Carslaw *et al.*
156 2010). Conversely, under some circumstances isoprene emissions have been shown to suppress new
157 particle formation from other isoprenoids (Kiehl-Scharr *et al.* 2009; 2012). As for O₃, the level of
158 NO_x can be crucial for organic aerosol formation. Increasing NO_x tends to reduce biogenic SOA
159 formation from isoprene and monoterpenes, whilst increasing it for some sesquiterpenes (Kroll *et al.*
160 2005; 2006; Ng *et al.* 2007; Wildt *et al.* 2014).

161 Improved understanding of BVOC emission patterns is crucial in the air chemistry-climate system:
162 First, for many of the short-lived climate pollutants (SLCPs) no observations of their pre-industrial
163 baseline exist, calculations of the pre-industrial to present-day radiative forcing thus has to rely on
164 simulations of pre-industrial conditions which introduces large uncertainties in the derived values
165 (Mickey *et al.* 2001; Carslaw *et al.* 2013). Second, future changes in atmospheric BVOCs loading have
166 the potential to counteract some pollution and climate effects of anthropogenic emissions control.
167 For instance, a synthesis of field data identified potentially very strong regional climate cooling
168 feedbacks from SOA formation by BVOCs (Paasonen *et al.* 2013), while other direct and indirect
169 climate feedbacks can also be induced for isoprene-ozone interactions (Stich *et al.* 2007; Arneth *et al.*
170 2010).

171 Future (and past) responses of isoprenoid BVOC emissions to climate and atmospheric CO₂ mixing
172 ratio, in isolation and combined, are still under debate (Arneth *et al.* 2007a, b; Monson *et al.* 2007;
173 Niinemets *et al.* 2010a). Briefly, warmer temperatures and higher light intensity stimulate leaf BVOC
174 emissions – at least in short term directly by enhanced cellular production rates. Moreover, warmer
175 environment can foster higher leaf area index and hence larger emitting leaf area. The response to
176 enhanced CO₂ is more contentious for isoprene studies show declining emissions at leaf-scale in
177 enhanced CO₂ environment (for a summary of studies see Arneth *et al.* (2011). How these effects
178 emerge on the canopy scale is less clear. Sun *et al.* (2013) combined observations under controlled-
179 environment grown aspen with a simple growth model. While their study confirmed reduced leaf-
180 level isoprene emissions for plants grown under above-ambient CO₂ mixing ratios, the
181 simultaneously strongly enhanced canopy leaf dry mass, and leaf area index, counteracted the
182 results obtained at single-leaves. A number of older studies have pointed to similar interactions
183 between measured leaf-based emissions and canopy structural changes (Centritto *et al.* 2004; Possell
184 *et al.* 2005). These studies indicate that for projections of future isoprene and monoterpene
185 emissions, plant growth dynamics are equally important as leaf-scale physiology, and that BVOC
186 emission scenarios must be combined with dynamic global vegetation models (DGVMs) responding
187 to environmental changes. Moreover, it remains to be shown, whether simple CO₂-multipliers
188 (Arneth *et al.* 2007b; Heald *et al.* 2009; Niinemets *et al.* 2010a), as currently used in BVOC emission
189 modules combined with DGVMs are sufficient, or whether a stronger process-based representation
190 could be parameterised that internalises BVOC emissions by linking them more strongly to
191 photosynthesis (Morfopoulos *et al.* 2013). In addition it is unclear how different variables (leaf
192 physiology, canopy effects, climate change, LUC) simultaneously with atmospheric CO₂ mixing ratio
193 affect BVOC emissions. Sharkey and Monson (2014) showed, e.g., that the CO₂ effect on isoprene
194 emission can be tempered by increasing temperature or heat waves.

195

196 **2.3 Interactions of LUC and BVOCs**

197
198 Simulation experiments have demonstrated up to 40% reductions in global isoprene emission under
199 future LUC (Heald *et al.* 2009; Ganzeveld *et al.* 2010; Squire *et al.* 2014), with much larger reductions
200 regionally where the deforestation occurs (Lathière *et al.* 2006; 2010; Wu *et al.* 2012). One study
201 projected a 7% reduction in global tropospheric O₃ from a 45% reduction in isoprene emissions
202 (Squire *et al.* 2014), which would be consistent with an increase in CH₄ lifetime of several percent
203 (Young *et al.* 2009). However, the demonstrable effects of LUC on BVOC emissions do not necessarily
204 lead to substantial global-scale changes in burdens of associated SLCPs, especially in model exercises
205 that also account for the simultaneously occurring changes in climate and/or atmospheric CO₂ levels
206 (Wiedinmyer *et al.* 2006; Wu *et al.* 2012; Tai *et al.* 2013; Hardacre *et al.* 2013). This arises because of
207 the large spatial variability in both the influence of LUC on BVOC emissions and in the atmospheric
208 chemistry. In a changing environment, the additional accounting of LUC-induced changes in BVOCs
209 can result both in strong decreases and increases of e.g., tropospheric O₃ or SOA, and resulting
210 regional radiative forcing. In analogy to the biophysical climate effects of LUC, assessing radiative
211 forcing impacts associated with BVOC-LUC interplay is misleading when solely a global total value is
212 calculated, as warming or cooling forcing in different regions can cancel. Thus regional-scale analyses
213 are fundamental when analysing effects of altered BVOC emissions on pollution levels and climate
214 change (Young *et al.* 2009; Wu *et al.* 2012; Tai *et al.* 2013; Hardacre *et al.* 2013).

215

216 **2.4 Regional aspect of LUC-AQ-climate interactions**

217
218 The strong, and non-linear temperature- and (in the case of isoprenoids) light-dependence of many
219 BVOC emissions means that the absolute influence exerted by a given form of LUC will be enhanced
220 in warm regions with limited cloud cover. For instance, an isoprene emission rate increase of 1 mg

221 (isoprene) $\text{m}^{-2} \text{h}^{-1}$ at 20°C might become an emission of $4 \text{ mg m}^{-2} \text{ h}^{-1}$ at 30°C (e.g. Guenther *et al.*
222 2006). Likewise, because of the highly non-linear nature of the atmospheric chemistry, effects of
223 BVOCs depend strongly on local atmospheric conditions, and thus a given BVOC emission can
224 generate a wildly different response in different regions. In addition to the local NO_x mixing ratio (see
225 previous section), shortwave radiation flux density also strongly affects O_3 formation, with higher O_3
226 formation potential during summer or at lower latitudes. Here, a selection of real and hypothetical
227 examples is used to illustrate the effects of some of the most common types of land conversion on
228 BVOC emissions and atmospheric chemistry. The effects of these conversions on isoprene emissions,
229 O_3 mixing ratios and SOA concentration are summarised in Figure 2.

230

231 **2.4.1 Forest-to-cropland conversion**

232

233 Large-scale conversion of forested land to cropland has not only been a historical phenomenon (Klein
234 Goldewijk *et al.* 2011; Kaplan *et al.* 2011), but still continues today, especially in tropical areas
235 (Houghton *et al.* 2012). Conventional agricultural crops such as wheat (*Triticum* spp), maize (*Zea*
236 *mays*) and rice (*Oryza* spp), that often replace the forested land, are regarded as being low emitting
237 species (Copeland *et al.* 2012, Table 1), as are sugarcane and soybean (Kesselmeier and Staudt 1999;
238 Wiedinmyer *et al.* 2004; Winter and Rostás 2008; Moraes *et al.* 2009), the cultivation of which is
239 expanding in the tropics due to demand for biofuel and livestock feedstuff (Hardacre *et al.* 2013). In
240 contrast, forests often contain strong isoprene- and monoterpene-emitting species, particularly in
241 the tropics (Kuhn *et al.* 2004; 2007; Karl *et al.* 2007; 2009; Langford *et al.* 2010). Thus a large-scale
242 conversion of forest to crops leads to a strongly reduced emission of reactive BVOCs.

243

244 Using a future land-use scenario (IPCC A1B), Wu *et al.* (2012) simulated a decrease in surface
245 isoprene mixing ratio over the Amazon region resulting from forest-to-cropland conversions. Due to

246 the low NO_x mixing ratios over much of this region, they calculated increases in the June-August
247 mean O₃ mixing ratio of up to 7 ppbv in 2100, as compared to 2000. Squire *et al.* (2014) reported
248 similar results based on the same scenario, but using a different suite of models. On a more
249 immediate timescale, Hardacre *et al.* (2013) used a land-use model to project a range of plausible
250 cropland scenarios for tropical South America for 2030, and reported a strong reduction in isoprene
251 emissions, leading to a 0.4 – 1 ppbv increase in tropospheric O₃.

252
253 Substantial variations in the size of modelled O₃ mixing ratio changes result from (i) differences in
254 LUC scenario, (ii) model grid size (Ito *et al.* 2009; Pugh *et al.* 2013) and (iii) chosen emission factors
255 for plant species (Niinemets *et al.* 2010a; b), but (iv) also the treatment of organic nitrates which are
256 formed during BVOC oxidation. NO_x loss due to organic nitrate formation can substantially reduce O₃
257 formation in low-NO_x regions, but the details remain poorly understood (Ito *et al.* 2009; Wu *et al.*
258 2012). A decrease in nitrate formation following forest-to-cropland conversion, and associated lower
259 isoprenoid BVOC emissions may be counteracted to some extent by a decrease in uptake of NO_x in
260 the lower crop canopies (e.g. Ganzeveld *et al.* 2010) or increased emissions of oxidized nitrogen due
261 to fertilizer use.

262 Considering present-day O₃ mixing ratios in the remote Amazon of *ca.* 20 ppbv (e.g. Lelieveld *et al.*
263 2008), an additional 7 ppbv O₃ represents a very large change. However, the level remains too low to
264 bring about a substantial O₃ toxicity effect on plants and thus to indirectly influence climate through
265 reducing the biospheric C uptake (Sitch *et al.* 2007), whilst the direct radiative forcing from this
266 increase would be of the order of 0.02 W m⁻². Wu *et al.* (2012) also simulated a relatively substantial
267 reduction in biogenic SOA concentration of up to 0.5 µg m⁻³, compared with typical tropical forest
268 aerosol concentrations (e.g. 1.5-1.6 µg m⁻³; Hewitt *et al.* 2010; Huffman *et al.* 2012). Organics can

² Assumes that the 7 ppbv increase is valid across a 1000 m depth of the atmosphere which has an average density of 2.3×10^{19} molecules cm⁻³. Radiative forcing is taken as $0.042 \text{ W m}^{-2} \text{ DU}^{-1}$, where DU is Dobson Unit, a measure of integrated atmospheric O₃ column density equivalent to 2.69×10^{16} molecules O₃ cm⁻² (Ramaswamy *et al.*, 2001, section 6.5.2.2),

269 modify aerosol reflectivity, as well as their potential to act as cloud condensation nuclei, so the
270 ultimate climatic effect of SOA changes is not well understood, although recent work suggests that
271 such aerosol may have a substantial cooling effect (Boucher *et al.* 2013; Paasonen *et al.* 2013).

272

273 In contrast to forest-to-crop conversion in a low-NO_x environment, similar LUC under high NO_x mixing
274 ratios are likely to yield a decrease in local tropospheric O₃ mixing ratio. Unlike the remote tropics, in
275 the northern mid-latitudes, especially North America, Europe and Eastern China, the background
276 atmosphere is often in a state of VOC-limitation, or on the boundary between the two limitation
277 regimes. Conversion of large forest areas to cropland would tend to decrease O₃ mixing ratios and
278 organic aerosol concentrations in these regions (e.g. Chen *et al.* 2009; Wu *et al.* 2012). However, the
279 current tendency for LUC in these regions is more towards afforestation or cropland abandonment
280 (Alcantara *et al.* 2013; Erb *et al.* 2013), which has the opposite effect (analogous to the biofuel
281 example in section 2.4.2).

282

283 While these examples should be broadly representative for conversions of forest to agriculture
284 globally, at least as regards isoprene, there is considerable variation in the literature over the
285 appropriate isoprene emission factors for generic grasses and crops. Lathière *et al.* (2006) and
286 Ashworth *et al.* (2012) used isoprene emission factors for crops of the same order of magnitude as
287 for broadleaf forests (5 µg g DM⁻¹ h⁻¹ and 16 µg g DM⁻¹ h⁻¹ as, respectively). Conversely, simulations
288 based on more recent experimental data tend to use much lower crop emission factors, e.g. Karl *et al.*
289 *et al.* (2009) and Beltman *et al.* (2013) use 0 - 0.5 µg gDM⁻¹ h⁻¹, and Guenther *et al.* (2006) give canopy
290 emission factors for crops two orders of magnitude smaller than those for broadleaf trees. This
291 variation reflects to a large degree the limited measurements available at the time of formulation of
292 the widely used Guenther algorithm (Guenther *et al.* 1995). For generic crops, the balance of
293 evidence seems to support low isoprene emission factors; however, the choice will have profound

294 impacts on results of LUC studies and must be taken into account when assessing past studies. For
295 monoterpenes, there is a very wide spread in the measurements, but the typical monoterpene
296 emission factors for crops and broadleaf trees seem to be similar (Ashworth *et al.* 2012, see also
297 Table 1), although both are less than for typical needle-leaf species (Guenther *et al.* 1995; Karl *et al.*
298 2009). Clearly species-specific emission factors should be used wherever possible in assessing the
299 outcomes of LUC.

300

301 **2.4.2 Conversion for biofuels**

302

303 Although agricultural crops typically have low BVOC emissions relative to the forest species they
304 replace, there are many woody “crop” species that emit much higher levels of BVOCs than the typical
305 natural vegetation (Table 1). Key examples are oil palm (*Elaeis guineensis*) and fast growing tree
306 species like poplar (*Populus spp*), willow (*Salix spp*) or eucalyptus (*Eucalyptus spp*). These species are
307 often used in plantation systems for cellulose production or more recently in short rotation coppice
308 (SRC) for bioenergy generation.

309

310 **2.4.2.1 Oil palm**

311 Oil palm is a highly important commercial crop, grown in large monoculture plantations throughout
312 the tropics, but especially in South-East Asia. In Malaysia, 13% of land area was covered by oil palm
313 plantations in 2009 (Hewitt *et al.* 2009). In Indonesian Borneo, the figure is currently 6%, but allowed
314 leases cover 23%, and the potential maximum plantable area is 90% (Carlson *et al.* 2012; Warwick *et*
315 *al.* 2013). The majority of these plantations replace tropical rainforest. Unlike rainforest, oil palm
316 emits almost no monoterpenes, but its isoprene emission potential is approximately five times higher
317 (Hewitt *et al.* 2009; Table 1). In a field study measuring isoprene fluxes above rainforest and oil palm
318 canopies located within 60 km of each other, isoprene emissions above oil palm were on average ten

319 times higher than those over the rainforest (Langford *et al.* 2010; Misztal *et al.* 2011), reflecting also
320 the higher temperatures and lower cloudiness over the oil palm plantation (Fowler *et al.* 2011).

321
322 Despite the huge increase in isoprene fluxes, the measured O₃ mixing ratio over both oil palm and
323 rainforest landscapes was virtually identical (Hewitt *et al.* 2009; 2010). This is consistent with
324 landscape-scale model simulations that showed a strongly NO_x-limited O₃ formation regime in
325 Borneo (Hewitt *et al.* 2009). Increased NO_x emissions resulting from fertilization and processing
326 plants only proved sufficient to balance the O₃ loss due to the additional BVOC. Yet the simulations
327 also showed that an increase in NO_x mixing ratio to *ca.* 3-5 ppbv, typical of rural Western Europe,
328 would result in O₃ mixing ratios exceeding 100 ppbv. Such an increase would have a substantial direct
329 radiative forcing effect (of the order 0.3 W m⁻² following the calculations above) and notably reduce
330 the C sink potential of most plants (Sitch *et al.* 2007), as well as having considerable immediate
331 implications for crop yields and human health.

332
333 Similarly, notwithstanding the much reduced monoterpene emissions, a small increase in organic
334 aerosol concentrations was found over the oil palm relative to the rainforest (0.67 vs. 0.48 µg m⁻³;
335 Hewitt *et al.* 2010). This at least partially reflects a higher contribution from isoprene to biogenic SOA
336 (MacKenzie *et al.* 2011). Semi-volatile sesquiterpenes and phenylpropanoids may also be emitted
337 from either/both landscapes, and likely have a very high aerosol yield (Ng *et al.* 2007). Unfortunately,
338 difficulties in their measurement have limited their assessment in the field thus far. However,
339 emission of estragole, a volatile phenylpropanoid, which is important for attracting pollinators and
340 for which a very high aerosol yield has been reported (Lee *et al.* 2006), was of comparable magnitude
341 to monoterpene emissions from the rainforest (Misztal *et al.* 2010), and quite likely contributes
342 notably to the aerosol mass. An assessment of the implications of changing land-use that only

343 includes isoprene and monoterpenes, the most commonly considered reactive BVOCs, could
344 therefore predict the wrong sign for aerosol concentration change.

345

346 Larger-scale chemistry-transport model studies considering the effect of a widespread expansion of
347 oil palm plantations and associated NO_x emissions on the whole of Borneo found O₃ and biogenic
348 SOA increases of up to 15 ppbv (70%) and 0.5 µg m⁻³ (12%) respectively in some areas, with smaller,
349 but notable effects stretching 1000s km downwind (Pyle *et al.* 2011; Ashworth *et al.* 2012; Warwick
350 *et al.* 2013). However, Hardacre *et al.* (2013) calculated a non-significant impact on surface isoprene-
351 mixing ratios and chemistry when spreading oil palm production more globally, rather than
352 concentrating in South-East-Asia, although the coarse scale of this analysis (4° x 5°) precludes the
353 analysis of local effects. From the standpoint of atmospheric composition, the planting of oil palms
354 and similar high isoprene emitting crops in the tropics should have a minimal influence so long as
355 background NO_x mixing ratios are kept low and the BVOC emissions are not advected over a high NO_x
356 region before becoming oxidised and dispersed.

357

358 **2.4.2.2 Short rotation coppice plantations and alternatives**

359 Quite a different scenario can be drawn for SRC plantations in Europe where the high background
360 NO_x mixing ratios facilitate increases in O₃ formation. Isoprene emissions from typical SRC species are
361 two to six times above typical deciduous forest emission rates (Simpson *et al.* 1999). Ashworth *et al.*
362 (2013) simulated the effect of converting all excess crop, pasture and wasteland in Europe to SRC,
363 and found an increase in continental isoprene emissions from 11.5 to 16 Tg C a⁻¹, sufficient to give
364 monthly mean O₃ increases of up to greater than 12 ppbv over heavily planted regions, and 6 ppbv
365 over Eastern Europe as a whole, where the planting in the model exercise was concentrated. Using
366 more conservative SRC planting scenarios, Beltman *et al.* (2013) and Hardacre *et al.* (2013) found
367 comparable results. Ashworth *et al.* (2012) calculated an increase in monthly mean biogenic SOA

368 concentration of up to $0.6 \mu\text{g m}^{-3}$ in Eastern Europe due to SRC planting. Similar effects on O_3 and
369 aerosol have been simulated for North America for both SRC and the growth of the giant cane
370 *Arundo donax* (Wiedinmyer *et al.* 2006; Ashworth *et al.* 2012; Porter *et al.* 2012; Hardacre *et al.*
371 2013).

372

373 Several low-BVOC emitting crop species can function as a bioenergy source (Sims *et al.* 2006; Karl *et*
374 *al.* 2009; Eller *et al.* 2011; Crespo *et al.* 2013), and may offer advantages over SRC in the polluted
375 middle latitudes in terms of their influence on atmospheric composition. However, many of the
376 traditional crops have less favorable biomass yield, as compared to woody bioenergy species (Aylott
377 *et al.* 2008). Moreover, in the case of maize, the high emission of N_2O and nitrate leakage in
378 cultivation must be weighed against the effect of low BVOC emissions (Crutzen *et al.* 2007).

379 Switchgrass and elephant grass (*Miscanthus x giganteus*) are both low BVOC emitters, with an
380 isoprene emission potential being below $0.01 \mu\text{g g dry weight (DW)}^{-1} \text{h}^{-1}$ (Eller *et al.* 2011; Copeland
381 *et al.* 2012; Crespo *et al.* 2013; Table 1). Both crops are good candidates for use in second-generation
382 biofuel production, as their emission rates are much lower than those expected from eucalyptus or
383 poplar plantations (Table 1; Eller *et al.* 2011) and the annual energy yields under a temperate climate
384 are comparable to those of woody biomass species (McKendry 2002). Another perennial grass with
385 potential as a biofuel source is Black bamboo (*Phyllostachys nigra*), however, the species is a strong
386 isoprene emitter, with emission potentials ($28.5 \mu\text{g g DW}^{-1} \text{h}^{-1}$) of similar magnitude to oil palm
387 (Crespo *et al.* 2013; Table 1).

388

389 **2.5 Influence of land management processes on BVOC emissions**

390

391 In addition to the effects of abiotic factors like light intensity, temperature, atmospheric CO_2 mixing
392 ratio and nutrition, there are a range of processes related to LUC and other human activities that are

393 capable of altering BVOC emissions. By contrast to our understanding of environmental stresses and
394 the possible future climate change on BVOC emissions (Loreto and Schnitzler 2010; Holopainen and
395 Gershenson 2010), how land management will influence the atmosphere through changes in BVOC
396 emissions is largely unknown. Land management e.g. by harvesting, irrigation, and fertilisation
397 influence BVOC emission rates and pattern both directly and indirectly (Ibrahim *et al.* 2008; Fares *et*
398 *al.* 2008; Ormeno *et al.* 2009; Malkina *et al.* 2011; Davis *et al.* 2013; Crespo *et al.* 2013).

399

400 **2.5.1 Harvesting and post-harvesting**

401

402 BVOC emissions can be induced through direct rupture of storage organs i.e. mechanical wounding
403 which can occur through land clearing, harvest and management. BVOC emissions from cutting can
404 be particularly high for conifers; Haapanala *et al.* (2012) measured monoterpene emissions from a
405 clear-felled pine forest in Finland that were more than eight times higher over the growing season
406 than typical emissions from an intact forest. Scaled-up estimates suggested cutting of Scots pine
407 (*Pinus sylvestris*) in Finland increased the annual monoterpene emission from those forests by 10%.
408 Given a typical monoterpene emission factor for Scots pine of $1.2 \text{ mg m}^{-2} \text{ h}^{-1}$, the direct flux from
409 harvesting is substantial, with potential to affect both biogenic SOA and O_3 loading over clear-cut
410 areas. Although most of these emissions were believed to come from storage, Haapanala and
411 colleagues (2012) also speculated whether microorganisms might produce additional monoterpenes
412 from litter decay. This degradation process of plant materials might also result in substantial BVOC
413 emissions from cut trees even when they lack a large monoterpene storage capacity.

414

415 Large relative increases in sesquiterpene emissions following cutting have been observed in
416 heathland ecosystems (Rinnan *et al.* 2013). However, the total sesquiterpene fluxes were relatively
417 small, peaking at around $0.1 \text{ mg m}^{-2} \text{ h}^{-1}$ on the day of cutting, and declining rapidly thereafter. In the

418 Eastern US, harvesting of forests was shown to increase isoprene but decrease monoterpene
419 emissions (Purves *et al.* 2004). Other examples from Europe showed that hay harvesting in the alps
420 could influence the local air quality on a short-term basis (Karl *et al.*, 2001) with short-term total
421 BVOC fluxes up to 8.7 mg C m⁻² h⁻¹ (Ruuskanen *et al.* 2011). In general it appears, however, that
422 harvesting of non-woody ecosystems is not a major, long-term source of reactive BVOCs.

423
424 In addition to the impact of harvesting itself, different post-harvesting procedures can influence
425 BVOC emissions. Emissions from freshly cut and shredded leaves and wood of eucalypts, for
426 example, were approx. 2.35 mg C g DW⁻¹ from leaf mulch and wood chips integrated over 48 h with
427 the highest emission rate occurring directly after cutting (Kim *et al.* 2011). Ghirardo and colleagues
428 (personal communication) measured a total BVOC-released C loss from poplar wood chips of
429 approximately 0.028 % (of DW C) during six weeks of storage. Lower temperatures decreased BVOC
430 emissions by almost one third, but did not impair the drying process, suggesting that proper
431 management can optimize the drying for minimal BVOC release. Post-harvesting processes of cereals
432 also release BVOCs; Malkina *et al.* (2011) reported 80 different volatile compounds, predominantly
433 short-chain alcohols, released from maize, alfalfa (*Medicago sativa*), wheat and oat (*Avena sativa*)
434 grain silages. Beside the post harvesting treatment itself, the seasonal stage at the time of harvesting
435 can affect the release of BVOCs (Crespo *et al.* 2013).

436

437

438 **2.5.2 Fertilization**

439

440 Nitrogen fertilization can in general be expected to increase isoprenoid emissions by increasing leaf
441 photosynthetic capacity, and thus enabling higher isoprenoid biosynthesis (Ormeno *et al.* 2009;
442 Blanch *et al.* 2007). In maize, BVOC emissions from unfertilized or little-fertilized maize were minimal

443 in comparison to heavily fertilized plants (Gouinguene and Turlings, 2002). Isoprenoid production in
444 pine trees also increases due to higher N availability (McCullough and Kulman 1991; Ormeno *et al.*
445 2009), although opposite results also exist (Blanch *et al.* 2007). But such interactions with N are
446 complex, since N fertilization might be expected to affect the oxidation of BVOCs in the lower
447 atmosphere by increasing NO_x emission from the soil (see also sections 2.2 and 2.4).

448 Phosphorus levels can also influence isoprene emission rates. Fares *et al.* (2008) showed lower
449 isoprene emission under higher concentrations of phosphorus in the soil. Interestingly, and so far
450 unexplained, isoprene emission was uncoupled from photosynthetic rate under high phosphorus
451 concentrations (Fares *et al.* 2008).

452 Beside constitutive emissions, the plant nutritional status also influences pest-induced BVOC
453 emissions (Ibrahim *et al.* 2008). Oilseed rape plants grown at high soil nutrient levels showed higher
454 emissions of several different BVOCs in comparison with infested plants at a low soil nutrient level.
455 Moreover, compared to wild cultivars, sesquiterpene (α -farnesene) and homoterpene ((E)-4,8-
456 dimethyl-1,3,7-nonatriene (DMNT)) emissions from infested transgenic *Bt*-oilseed rape (expressing
457 the cry1Ac endotoxin gene from *Bacillus thuringiensis*) were more sensitive to the fertilization level
458 (Ibrahim *et al.* 2008). This may have complex implications as DMNT and α -farnesene are important
459 cues in plant-herbivore interactions (Kappers *et al.* 2005; Ghirardo *et al.* 2012).

460

461 **2.5.3 Irrigation**

462

463 Irrigation *per se* is a little studied topic in the context of BVOCs, and at present no clear answer can
464 be given in which direction land management by irrigation alters BVOC emissions. A few observations
465 have shown that monoterpene and isoprene emissions in oaks and isoprene emission in poplar are
466 diminished by severe drought stress (Brüggemann and Schnitzler 2002; Fortunati *et al.* 2008;
467 Peñuelas *et al.* 2009) and that emission levels recovered by re-irrigation (Fortunati *et al.* 2008;

468 Peñuelas *et al.* 2009). Generally it seems that isoprene and monoterpene emission potentials of trees
469 become impaired only under severe, long term drought conditions, whilst moderate water
470 limitations have no influence on emission potentials (Loreto and Schnitzler 2010).

471

472 **3 BVOC, LUC and climate change mitigation and adaptation**

473

474 **3.1 Breeding and phenotyping to decrease constitutive and induced BVOC emissions**

475

476 Awareness that BVOC emissions from different species and cultivars can vary greatly is maybe the
477 simplest starting point for species selection to manage BVOCs, and hence their air quality and climate
478 impacts. For several species and hybrids of *Populus* spp. a large number of genotypes have been
479 analysed to allow the cultivation of appropriate plants under different climatic conditions
480 (Calfapietra *et al.*, 2010). Biomass production rates from poplar are highly variable according to the
481 clone, climate and other environmental constrains, with woody biomass production often around 8–
482 12 Mg of dry matter ha⁻¹ year⁻¹ (Monclus *et al.* 2006; Calfapietra *et al.* 2010). *Populus* and *Salix* are
483 relatively easy systems to breed and the BVOC emission potentials of poplar genotypes are very
484 different (Isebrands *et al.* 1999). Eller *et al.* (2012) quantified the differences in isoprene, methanol,
485 and monoterpene emissions from 30 hybrid poplar genotypes. They were able to explain about 40-
486 to-50% of the variation in isoprene emission potential across these genotypes by a combination of
487 instantaneous photosynthesis rate and seasonal aboveground growth. Both genotype and parental
488 cross were significant predictors of isoprene and monoterpene emissions (Eller *et al.* 2012). The
489 authors of that study observed a threefold range in isoprene emission rates across all 30 genotypes,
490 with a positive trend between isoprene emission and plant productivity. This trade-off between
491 growth and isoprene emission potential may make it challenging to mitigate the BVOC emissions of
492 poplar plantations through selection (Eller *et al.* 2012). However, Guidolotti *et al.* (2011) showed no

493 clear association between isoprene emission and photosynthesis within different poplar genotypes
494 grown in a common garden experiment. The photosynthetic C lost as isoprene and isoprene emission
495 showed a linear correlation, suggesting a constant proportion of photosynthetic C directed to
496 isoprene emission (Guidolotti *et al.* 2011). According to these results isoprene emission rate might be
497 related to the final plant productivity but not to photosynthetic capacity of poplar.

498 Before phenotyping for choosing future cultivars with specifically altered BVOC emissions can be
499 realised, the plant performance under various climate scenarios and co-occurring biotic stresses
500 must be understood. In general, BVOC emissions by stressed plants are higher than by healthy,
501 undamaged plants (Degenhardt *et al.* 2003; Loreto and Schnitzler 2010; Holopainen 2011). In
502 addition to pests and pathogens (Mumm and Dicke 2010; Pichersky and Gershenzon 2002), high
503 temperature (Monson *et al.* 1992; Loreto *et al.* 2006; Behnke *et al.* 2007), limited water availability
504 (Sharkey and Loreto 1993; Brüggemann and Schnitzler 2002; Gouinguene and Turlings 2002;
505 Fortunati *et al.* 2008; Blanch *et al.* 2009), O₃ (Loreto and Velikova 2001; Loreto *et al.* 2004; Velikova
506 *et al.* 2005; Vickers *et al.* 2009), UV-B radiation (Tiiva *et al.* 2007) or physical stresses such as wind or
507 forest fires (Maleknia *et al.* 2009, Kivimäenpää *et al.* 2012, Haapanala *et al.* 2012) affect plant VOC
508 emissions in contrasting ways.

509
510 This complicates the characterization of BVOC emission potentials from field observations. For
511 example, while untreated soybean do not release high amount of BVOCs, in plants attacked by insect
512 pests large emissions of individual compounds (100-200 ng g fresh weight⁻¹ h⁻¹ α-farnesene and
513 indole) were reported (Winter and Rostás 2008). Similarly, even if healthy wheat shows almost no
514 BVOC emissions, under environmental stress emission rates up to 20 – 400 ng plant FW⁻¹ h⁻¹ (Piesik *et*
515 *al.* 2010) were reported. The large variety in the possible induced combinations of BVOCs, and in the
516 emission quantities, makes it difficult to accurately characterize BVOC emissions from stressed
517 plants. For example, when wheat, oat, and barley plants were either mechanically injured, attacked

518 by two different beetle species (*Oulema* spp.) or infected by three different fungal species (*Fusarium*
519 spp.), the result in all cases was a plant and pest-specific induction of BVOC emissions (Piesik *et al.*
520 2011). Moreover, combination of abiotic and biotic stresses is likely to further modify the emission
521 potential. Like for crops, environmental stress-conditions modify BVOC emissions from trees to a
522 large degree. Even a small temperature increase (1°C) leads to notable changes in monoterpene and
523 green leaf volatile (GLV) emission of poplar cultivars (Hartikainen *et al.* 2009). Pollution by O₃ has also
524 been shown to induce BVOC emissions. Isoprene and monoterpene emissions, e.g., can be induced
525 by very high O₃ doses (for review see Loreto and Schnitzler 2010). Further, O₃ air pollution can
526 stimulate the emission of stress-inducible low-volatility BVOCs, which may result in additional SOA
527 formation. Such aerosols may change volatile BVOC emissions by modifying PAR incident on the
528 canopy, and consequently feedback on O₃ mixing ratios.

529

530 At the moment, available data on plant ability to cope with stressful factors elicited by various
531 environmental conditions is still rather scarce (Monclus *et al.* 2006; Bidart-Bouzat and Imeh-
532 Nathaniel 2008; Long and Ort 2010). Moreover, climate change will significantly change production
533 conditions in the forthcoming years (White Paper of the European Commission: (COM(2009) 147);
534 changes in temperature and precipitation will clearly alter land suitability for agricultural use as well
535 as yield (Schmidhuber and Tubiello 2007; Long and Ort 2010). Abiotic stresses generally inhibit
536 photosynthesis (Flexas *et al.* 2006; Wahid *et al.* 2007), and plant defence against various
537 environmental stressors has direct consequences on plant biomass production. For example it has
538 been shown (Brilli *et al.* 2007; Teuber *et al.* 2008) that under abiotic (e.g. drought and salinity) stress
539 the percentage of photosynthetically fixed C emitted as VOCs increases dramatically. To be able to
540 characterise the yields and BVOC emissions for breeding purposes under future conditions, more
541 information on plant performance under multiple stresses must be collected (Holopainen and
542 Gershenzon 2010).

543

544 **3.4 Modifying and utilizing BVOC profiles for climate friendly cultivars**

545

546 **3.4.1 Genetic modification of BVOCs emission**

547

548 In order to identify the best-suited cultivars for different conditions, molecular biological tools are a
549 useful addition to silvicultural, biochemical and ecophysiological methods (Neale and Kremer 2011).
550 Genetic engineering enables the transfer of desired characteristics into plants, or the knockout of
551 specific traits, when it is not possible through conventional plant breeding. The first results using
552 genetically modified organisms (GMOs) to assess the role of individual BVOCs in different stresses are
553 very promising (Kappers *et al.* 2005; Behnke *et al.* 2007; Laothawornkitkul *et al.* 2008; Vickers *et al.*
554 2009). Plants with either silenced or up-regulated isoprenoid synthesis are not only excellent tools to
555 dissect the functional role of individual plant VOCs but also offers the opportunity to create “VOC-
556 silent plantations” or, alternatively, introduce effective volatile defence compounds helping plants to
557 mitigate abiotic and biotic stresses (Chang and Keasling 2006; Bouwmeester 2006). From the
558 perspective of air quality in areas with high NO_x mixing ratios, low or non-isoprene emitting biomass
559 plants are desirable. Several studies exist in which isoprenoid emission has been induced or brought
560 into a non-emitting plant (Kappers *et al.* 2005; Loivamäki *et al.* 2007, Vickers *et al.* 2009; Lee *et al.*
561 2010) but only a few studies have tried to create non-emitting plants. The bioenergy species poplar
562 and willow display several characteristics (rapid growth and seed development, simple clonal
563 propagation, established transformation and *in vitro* propagation protocols) that make the
564 integration of modern genomic tools with conventional techniques possible (Neale and Kremer,
565 2011). Behnke *et al.* (2007) used these characteristics to create GM poplars with almost fully
566 repressed isoprene biosynthesis. It was hypothesized that losing the trait of isoprene emission causes
567 negative effects on plant productivity, fitness and pest resistance (Loreto and Schnitzler 2010). Such

568 disadvantages were, however, not observed in semi-natural conditions (Behnke *et al.* 2012). More
569 detailed analyses of these lines proved that poplars are able to replace the benefits of isoprene
570 production by other biochemical means under certain conditions (Way *et al.* 2013; Kaling *et al.*
571 2014). However, more long-term field trials are needed (and already started (Schnitzler *et al.*,
572 unpublished)) to clarify whether non isoprene emitting bioenergy plants can prevent negative
573 atmospheric impacts of large-scale plantations under various environmental conditions.

574 Moreover, even if volatile isoprenoids are associated with plant defence properties, the down-
575 regulation of emission may sometimes also reduce the susceptibility to pests, as seen for poplar
576 where the isoprene non-emitting lines are less susceptible against a typical fungal pest (Behnke *et al.*
577 2012). Similarly, in orange trees the down regulation of D-limonene increased the resistance against
578 the fungus *Penicillium digitatum* (Rodriguez *et al.* 2014). Thus, in some cases not only fewer
579 isoprenoids are released into the atmosphere but also higher resistance may be achieved. Hewitt *et*
580 *al.* (2009) suggested that the biotechnological down regulation of isoprene emission in oil palm,
581 similarly to that done for poplar, would be essential to extinguish isoprene emissions and thus avoid
582 the potential implications discussed in section 2.4.2.

583
584 Some pesticide co-formulants are volatile and can contribute to ground-level O₃ formation. In a study
585 by Zeinali and colleagues (2011) the O₃ forming potential of pesticides ranged from 0.1 to 3.1 g O₃ g⁻¹
586 product. Thus, and due to other disadvantages pesticides have, not only non-emitting plants but also
587 plants with specific inducible BVOC emissions will be effective tools to pave the way for more
588 sustainable agriculture. Plants under herbivore attack synthesise defensive volatile compounds that
589 directly or indirectly affect herbivore performance and mediate other interactions with the
590 community (Penafior and Bento 2013). The attraction of herbivore enemies by herbivore-induced
591 plant volatiles (HIPVs) is well documented (Loreto *et al.* (2014); and articles within this special issue
592 of Plant, Cell and Environment). The discovery of the BVOCs-driven network of ecological

593 relationships has motivated further interest into BVOCs, particularly aiming at their possible
594 exploitation for bio-control of pests and pathogens in agriculture and forestry. Several examples
595 demonstrate that introduction of a specific terpene synthase gene led to higher resistance against
596 herbivores or fungal pathogens (Schnee *et al.* 2006; Dixit *et al.* 2013; Brillada *et al.* 2013). In maize a
597 single gene (*tps10*) was sufficient to mediate the indirect defence against herbivore attack (Schnee *et*
598 *al.* 2006). Also linalool-emitting GM rice was more resistant to its enemy, rice bacterial blight
599 (*Xanthomonas oryzae*) (Taniguchi *et al.* 2014). Sometimes however, it seems to be difficult to
600 manipulate isoprenoid emissions due to the very tight regulation of the biosynthetic pathways. In
601 such cases multiple manipulation acts might be necessary to override the plants' own regulation (Wu
602 *et al.* 2006; Rosenkranz and Schnitzler 2013).

603 Some other biotechnological approaches directed to decrease herbivore damage by non-volatile
604 compounds, were shown to indirectly reduce BVOC emissions. For example, maize which synthesizes
605 *Bt* (*Bacillus thuringensis*) toxins is less sensitive to herbivore feeding, and consequently emits less
606 HIPVs (Dean and De Moraes 2006). Some GM plants might even be useful for "atmospheric
607 phytoremediation" by directly removing air pollutants; Doty *et al.* (2007) have developed GM poplars
608 with greatly increased rates of metabolism which remove small pollutants through the
609 overexpression of cytochrome P450 2E1. These plants are able to successfully remove chloroform
610 and benzene from the air.

611

612 **3.4.1 Innovative, non-GM techniques to use BVOC emissions in smart agriculture**

613

614 In addition to genetic manipulation, application of priming agents, so-called elicitors, or use of plant
615 varieties that emit volatiles attractive to natural enemies are possible (Penaflor and Bento 2013;
616 Figure 3). In future it is likely that BVOCs can be induced e.g. by application of natural elicitors or
617 hormone-like substances, like cis-jasmonate, to switch on defence pathways (Pickett *et al.* 2007) and

618 to directly reduce the development of pests, diseases and weeds (Moraes *et al.* 2008). Cis-jasmonate
619 is shown to induce defence by the up-regulation of secondary metabolites in wheat (Moraes *et al.*
620 2008), maize (Oluwafemi *et al.* 2013) and barley (Delaney 2013). Methyl jasmonate (MeJA) is another
621 potential priming agent; in rape seed MeJA spraying increased BVOC emissions (Loivamäki *et al.*
622 2004) and MeJA-treated (E)- β -caryophyllene over-expressing rice plants attracted more parasitoid
623 wasps than the wild type (Cheng *et al.* 2007).

624
625 Creating co-cultures of different species and different emitter types can also be a strategy in
626 sustainable agriculture (Ninkovic *et al.* 2013). Plant-to-plant signalling by volatiles is a general
627 mechanism priming indirect defence in densely-populated plant communities, such as an agricultural
628 field (Heil and Silva Bueno 2007). Plants are able to decipher the odour profile of the neighbouring
629 plants and thus optimize their own fitness in advance of biogenic stress. For example, diverse
630 mixtures of wheat genotypes supported lower aphid populations compared to monocultures.
631 Moreover the mixtures were equally or, in the absence of aphids, more productive than
632 monocultures (Shoffner and Tooker 2013). Similarly, Ninkovic and colleagues (2013) demonstrated
633 that potato plants exposed to the odour profile of undamaged onion plants in their neighbourhood
634 were less attractive to their herbivores. Thus, mixed cultures with different BVOC emission potentials
635 might be interesting to achieve the best possible natural degree of plant protection (Ninkovic *et al.*
636 2013; Figure 3). In the study of Shoffner and Tooker (2013), however, hetero-cultures also emitted
637 higher amounts of BVOCs to the atmosphere.

638
639 The increase in the understanding of the roles of BVOC in direct and indirect defence (Dicke and
640 Loreto 2010; Loreto *et al.* 2014) allows the development of new techniques, e.g. to use BVOCs for
641 monitoring the early stages of plant diseases or microbial infection. BVOC-based profiling of plant
642 diseases could provide early information on crop health and disease propagation, and thus facilitate

643 pest control through proper management strategies (Sankaran *et al.* 2010). Jansen and colleagues
644 (2010) recommended focusing on the detection of methyl salicylate to indicate *Botrytis cinerea*
645 infections in large-scale tomato production. Some methods to detect *Fusarium* spp. by BVOC profiles
646 from wheat plantations are also very promising (Girrotti *et al.* 2010).

647

648 **4 Concluding Remarks**

649

650 From a system's perspective, BVOCs emissions *per se* are not necessarily only negative and
651 something to avoid in agricultural systems. Rather the challenge will be to reduce potentially
652 negative (health or climate) atmospheric effects, whilst enhancing the potential for stress protection.
653 To maintain sustainable agriculture and biomass production in future, it may be possible to make use
654 of the differences in BVOC emissions both of different cultivars/species and under different
655 environmental conditions, depending on local requirements. Modern biological and chemical
656 techniques can be used to lower isoprene emission in large-scale biomass plantations, stimulate
657 plant-innate immunity and trigger plant-plant or plant-herbivore communications for applications in
658 weed control or biological pest control. Further, they can be of use in early diagnosis of abiotic or
659 biotic stresses, or even as additives for functional food preparations. All these applications can be
660 envisioned based on current knowledge (Figure 3). However, large efforts are still needed to transfer
661 these examples into practice, e.g. in breeding and phenotyping programs of crops and bioenergy
662 plants, bio-control procedures, or novel co-cultivation systems of species or cultivars. Similarly,
663 simulation experiments of BVOC effects on the atmosphere under a changing environment need to
664 place much more focus not only on effects of land cover change, but also land management. For
665 once, modellers do not yet "race ahead" (Monson *et al.* 2007) of observational evidence and
666 knowledge. In particular in view of stress-responses there is still a lot of "catching up" with respects
667 to implementing emerging understanding into model analyses.

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Accepted Article

1292 **Table 1.** Biogenic volatile organic compound emission potentials of different crop and forestry
 1293 species.
 1294 The emission potentials are for standard conditions (30°C and photosynthetically active radiation
 1295 (PAR) 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$) unless otherwise noted.

	Species		isoprene		monoterpenes (or estragol when noted)	
	Latin	Common	Leaf scale	Canopy	Leaf scale	Canopy
			$\mu\text{g g DW}^{-1} \text{h}^{-1}$	$\mu\text{g m}^{-2} \text{h}^{-1}$	$\mu\text{g g DW}^{-1} \text{h}^{-1}$	$\mu\text{g m}^{-2} \text{h}^{-1}$
Crops	<i>Triticum spp</i>	Wheat	0.01 ¹		n.d. ²	
	<i>Zea mays</i>	Maize	0 ¹	0 ³	0.5 ¹	
	<i>Oryza spp.</i>	Rice	n.d. ⁴	3.7 ⁵	0.4 ⁴ ; 0.5 ¹	0.15 ⁵
Oil Palm	<i>Elaeis guineensis</i>	Oil palm	0-20 ⁶	12480 ^{a,7} 8850 ^{a,8}	1 ^{9,estragol}	102 ^{a,8} ; 113 ^{a,7} 1234 ^{a,7,estragol} ; 440 ^{9,estragol}
Woody biomass plants	<i>Populus spp</i>	Poplar	0-50 ¹⁰ 60 ¹¹ >87 ^{a,12}	6580- 9410 ^{a,13}	0.01-8 ¹⁰	
	<i>Salix spp</i>	Willow	20 ¹⁴ 34 ¹¹ 0.2-76 ¹⁰ >61 ^{a, 12}	1000 ¹⁴	0.1-10 ¹⁰ ; 0.8 ¹	
	<i>Eucalyptus spp</i>	Eucalyptus	20 ¹¹ , 15-49 ¹⁵	4000- 5000 ¹⁵	3 ¹¹ 5.4 ¹ 0.7-5.2 ¹⁵	200-600 ¹⁵
Perennial biomass plants	<i>Miscanthus x giganteus</i>	Elephant grass	0.005 ^{b,16}	n.d. ¹⁴		
	<i>Panicum virgatum</i>	Switch grass	0.018 ^{b,17}		0.038 ¹⁷	
	<i>Arundo donax</i>	Giant cane	34 ¹⁸ , 142 ¹⁹			

1296 a; converted from $\mu\text{g g carbon DW}^{-1} \text{h}^{-1}$ to $\mu\text{g g matter DW}^{-1} \text{h}^{-1}$

1297 b; includes isoprene and other C5 compounds

1298 1. Karl *et al.* 2009; 2. Piesik *et al.* 2010, 22°C, ambient light; 3. Hardacre *et al.* 2013, 4. Bao *et al.* 2008; 5.
 1299 Redeker *et al.* 2003; 6. Wilkinson *et al.* 2006; 7. Fowler *et al.* 2011, ambient conditions; 8. Hewitt *et al.* 2009,
 1300 27,9 °C and ambient light; 9. Misztal *et al.* 2010; 10. Hakola *et al.* 1998, ambient conditions; 11. Simpson *et al.*
 1301 1999; 12. Isebrands *et al.* 1999; 13. Westberg *et al.* 2000; 14. Copeland *et al.* 2012; 15. Street *et al.* 1997; 16.

1302 Crespo *et al.* 2013; 17. Eller *et al.* 2011, 30°C and PAR 500 $\mu\text{mol m}^{-2} \text{s}^{-1}$; 18. Hewitt *et al.* 90, measurements in
1303 25°C and PAR 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$; 19. Owen *et al.* 2001.
1304

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1305 **Figure Legends**

1306

1307 **Figure 1:** Present-day (average 1971-2000) isoprene (above) and monoterpene (below) emissions (g
1308 C a⁻¹) expressed as the difference with-without human land cover change. The shown examples are
1309 using the Dynamic Global Vegetation Model (DGVM) LPJ-GUESS, using land cover estimates as in
1310 Hurtt *et al.*, (2011) and climate based on the General Circulation Model MPI-ESM (for more details on
1311 see Ahlström *et al.* 2012). Figure is from Hantson, Knorr, Arneth *et al.* (manuscript in prep.)

1312

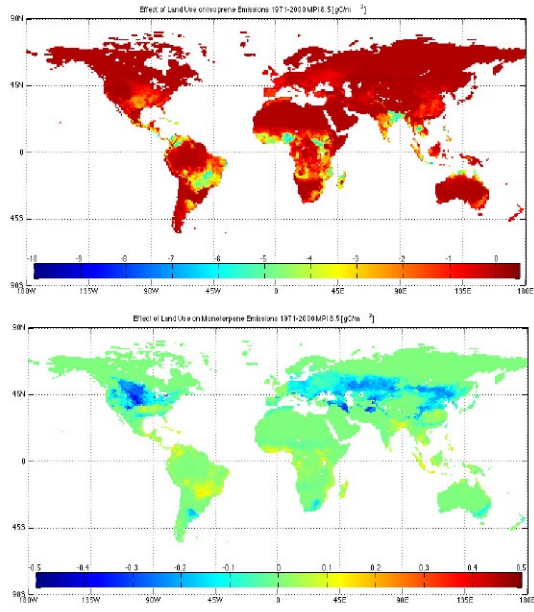
1313 **Figure 2:** Range of changes in basal emission rate of isoprene, mean ozone mixing ratios, and mean
1314 biogenic SOA (bSOA) concentration for four different land-use change scenarios, as reported by
1315 published studies. Ozone and aerosol changes are presented at the highest spatial and temporal
1316 resolution reported by the study (*ca.* 10-100 km, and either 8 hour, daily or monthly). Underlying
1317 studies are indicated by numbers: [1] Ashworth *et al.* (2012), [2] Ashworth *et al.* (2013), [3] Porter *et*
1318 *al.* (2012), [4] Chen *et al.* (2009), [5] Hewitt *et al.* (2009), [6] Hewitt *et al.* (2010), [7] Pyle *et al.* (2011),
1319 [8] Warwick *et al.* (2013), [9] Hardacre *et al.* (2013), [10] Wu *et al.* (2012), [11] Squire *et al.* (2014),
1320 [12] Guenther *et al.* (2006).

1321

1322

1323 **Figure 3:** Schematic summary of possible applications of BVOCs in smart agriculture. SQT:
1324 sesquiterpenes; GLV: green leaf volatiles; MeJA: methyljasmonate; JA: jasmonates; GM: gene
1325 modified.

1326



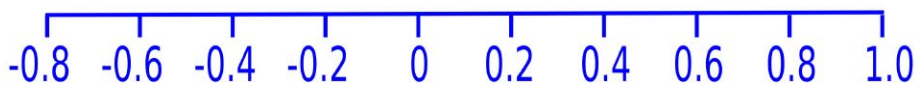
Isoprene emission
($\text{mg m}^{-2} \text{h}^{-1}$)



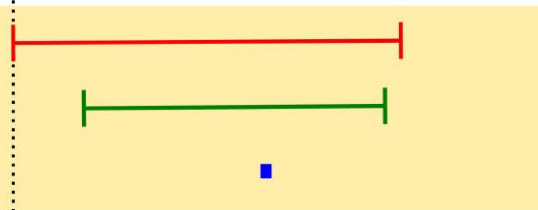
Ozone (ppbv)



bSOA ($\mu\text{g m}^{-3}$)



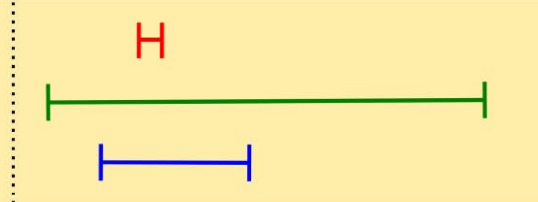
Cropland/grassland
to SRC,
Eastern Europe
[1],[2]



Cropland/grassland
to SRC,
North America
[1],[3],[4]



Forest to Oil Palm,
South East Asia
[1],[5],[6],[7],[8]

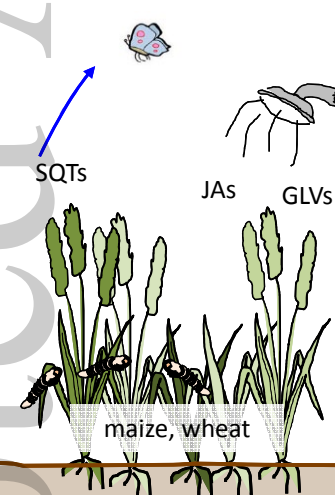
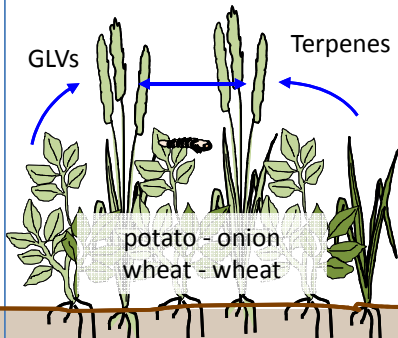
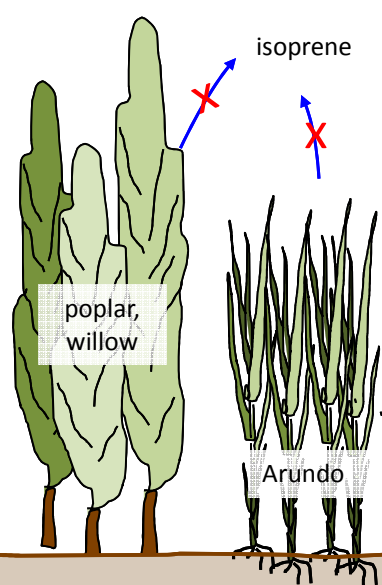


Forest to Crops,
Amazon



H

Applications of BVOCs in smart agriculture

	Monocultures	Co-cultivation systems	Bioenergy plantations
Aim of treatment	Direct priming; Plant-to-plant signalling; attraction of beneficials	Plant-to-plant signalling; attraction of beneficials	Removal/ downregulation of constitutive BVOCs
Examples	 <p>maize, wheat</p>	 <p>potato - onion wheat - wheat</p>	 <p>poplar, willow</p> <p>Arundo</p> <p>isoprene</p>
Methods	<ul style="list-style-type: none"> •VOC elicitor spraying (e.g. MeJA, GLVs) •GM crops (e.g. SQTs over-expression) 	<ul style="list-style-type: none"> •Selection of emitter types (e.g. volatile terpenoids) 	<ul style="list-style-type: none"> •Phenotyping for low emitters (e.g. isoprene) •GM plants (e.g. isoprene knockouts)