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1 **Solar UV irradiation-induced production of greenhouse gases from plant** 2 **surfaces: From leaf to Earth**

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10

11 **Abstract**

12 During the past few decades it has been documented that the ultra-violet (UV) component of natural
13 sunlight alone or in combination with visible light can instantaneously stimulate aerobic plant production of
14 a range of important trace gases: CH₄, CO₂, CO, short-chain hydrocarbons/ non-methane volatile organic
15 compounds (NMVOC), NO_x and N₂O. This gas production, near or at the plant surface, is a new discovery
16 and is normally not included in emission budgets (e.g. by the Intergovernmental Panel on Climate Change,
17 IPCC) due to a lack of information with respect to validation and upscaling. For CH₄ it is known that the light
18 dose controls emission under ambient and artificial light conditions, but the atmospheric gas composition
19 and other environmental factors can influence gas production as well. Several plant components, including
20 pectin and leaf wax, have been suggested as a precursor for CH₄ production, but underlying mechanisms
21 are not fully known. For other gases such generating processes have not been established yet and
22 mechanisms remain hypothetical. Field measurements of UV-induced emissions of the gases under natural
23 light conditions are scarce. Therefore, realistic upscaling to the ecosystem level is uncertain for all gases.
24 Nevertheless, based on empirical response curves, we propose the first global upscaling of UV induced N₂O
25 and CO to illustrate emission ranges from a global perspective and as a contribution to an ongoing
26 quantification process. When scaled to the global level, the UV-induced emission of CO by vegetation
27 surfaces amounts to up to 22 Tg yr⁻¹, which equals 11-44% of all the natural terrestrial plant sources
28 accounted for so far. The total light-driven N₂O emissions amount to 0.65-0.78 Tg yr⁻¹, which equals 7-24%
29 of the natural terrestrial source strength accounted for (range 3.3 - 9 Tg N yr⁻¹). In this review, we
30 summarize current knowledge, based on experimental work with sunlight and artificial light, and estimate

31 potential emission ranges and uncertainties, placing the available data into perspective. We discuss the
32 state of the art in proposed mechanisms, precursors, and environmental relationships, we consider the
33 relevance of measured emission rates, and we also suggest a range of future research topics. Furthermore
34 we propose and describe methods and techniques that can be used for future research.

35 *Keywords: Atmospheric chemistry, air pollution, UV-A, UV-B, stable isotopes techniques, N₂O, CH₄, NO_x,*
36 *NO_y, CO, CO₂, short-chain hydrocarbons, NMVOC, upscaling, vegetation, plants*

37

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65

66

67

68 **1 Introduction**

69 For decades it has been recognized that sunlight plays significant roles in atmospheric chemistry and that
70 the UV component is the driving force for tropospheric photochemical processes. For instance, UV-
71 photolysis of ozone generates excited state oxygen atoms, which react with water vapour to constitute the
72 primary source of hydroxyl radical (OH). OH is the major component for the overall oxidising capacity of the
73 troposphere (Isaksen et al. 2009). Lately, a number of trace gases are reported to be released by plants in
74 instantaneous responses to UV-radiation, such as methane (CH₄) (Bruhn et al. 2007, 2009, 2012, 2014a;
75 Röckmann et al. 2007; Vigano et al. 2007, 2008, 2009; McLeod et al. 2008; McLeod and Keppler, 2010;
76 Messenger et al. 2009; Fraser et al. 2015), carbon monoxide (CO) (Derendorp et al. 2011a; Bruhn et al.
77 2013), short-chain hydrocarbons (Derendorp et al. 2011b; Fraser et al. 2015), mono-nitrogen oxides (NO_x
78 and NO_y) (Hari et al. 2003; Raivonen et al. 2006, 2009) and nitrous oxide (N₂O) (Bruhn et al. 2014b).

79 These UV-driven gas productions are in principle newly revealed terrestrial sources that remain to be
80 considered in greenhouse gas accounting. Production of all gases stimulated by UV involves emissions at
81 relatively low rates, and the group of gases are diverse and have different impacts and interactions with the
82 atmosphere. However, several of the gases are potent greenhouse gases or interact with the turnover of
83 atmospheric greenhouse gases.

84 We describe current knowledge of methods and techniques for measuring these gases, with a particular
85 focus on the special requirements needed to accomplish flux measurements under controlled UV-
86 exposures and at generally very low rates. The distinction between laboratory and field measurements is
87 addressed with respect to techniques and deductions. We also report on current understanding of the
88 possible mechanisms and sources behind these gas productions, comment on current upscaling attempts,
89 and present the first upscaling and quantification of UV stimulated CO and N₂O emissions. Finally, we
90 highlight the perspectives of the newly discovered UV stimulated gas sources with respect to research
91 needs and impact on current research.

92

93 **2 Light induced gases at the plant surface**

94 Here we summarize the important features of most of the gases that are known to be formed at the plant
95 surface during exposure to UV light. The gases can be divided into two groups: i) well-mixed greenhouse
96 gases (CO₂, CH₄ and N₂O), and ii) short-lived gases (CO, NO_x, non-methane volatile organic compounds
97 (NMVOC)).

98 **2.1 Well-mixed greenhouse gases (CO₂, CH₄ and N₂O)**

99 The atmospheric concentrations of the greenhouse gases carbon dioxide (CO₂), methane (CH₄), and nitrous
100 oxide (N₂O) have all increased since 1750 due to human activity. In 2011 the concentrations of these
101 greenhouse gases were 391 ppm, 1803 ppb, and 324 ppb, and exceeded pre-industrial levels by about 40%,
102 150%, and 20%, respectively (Table 2.1). Concentrations of CO₂, CH₄, and N₂O now substantially exceed the
103 highest concentrations recorded in ice cores during the past 800,000 years (Masson-Delmotte et al. 2013).
104 The mean rates of increase in atmospheric concentrations over the past century are unprecedented in the
105 last 22,000 years (IPCC, 2013). In Table 2.1 we present the Global Warming Potential (GWP) that integrates
106 radiative forcing (RF) out to a particular time horizon, in this case 100 years. The GWP can be interpreted as
107 an index of the total energy added to the climate system by a component in question relative to that added
108 by CO₂ (Myhre et al. 2013). There are multiple sources of all three gases, which can be divided into two
109 main groups, anthropogenic and natural (Table 2.1). Quantification of the various source strengths from
110 both groups remain uncertain and global budgets remain unclear (Ciais et al. 2013).

111 The main anthropogenic CO₂ sources are burning of fossil fuels (coal, oil and gas), deforestation and
112 production of cement (Ciais et al. 2013). The removal of anthropogenic CO₂ from the atmosphere by
113 natural processes will take a few hundred thousand years (Ciais et al. 2013). The natural CO₂ sources are
114 autotrophic and heterotrophic respiration, decomposition of plant tissues (litter and soil carbon that is
115 released back into the atmosphere) and additional disturbance processes (e.g., natural fires). The natural
116 source strength is 20 times higher than the anthropogenic emission, but is counterbalanced by natural CO₂
117 uptake from the atmosphere by plant photosynthesis (Beer et al. 2010).

118 Massive increases in the number of domestic ruminants, natural gas extraction and use, expansion of rice
119 paddy agriculture and establishment of urban landfills and waste dumps represent the dominant
120 anthropogenic CH₄ sources (Stocker et al. 2013). Wetlands are the dominant natural source of atmospheric
121 CH₄ (EPA 2010). During the last two decades, natural sources of CH₄ have accounted for 35 to 50% of the
122 decadal mean global emissions (Ciais et al. 2013).

123 The anthropogenic N₂O sources are primarily agricultural, and the anthropogenic part accounts for
124 approximately 40% of the total emission (Ciais et al. 2013). Natural sources are constituted by upland soils
125 and riparian areas together with oceans, estuaries, and rivers (EPA 2010). Human-induced perturbations of
126 the nitrogen cycle, in addition to interactions with CO₂ sources and sinks, affect emissions of N₂O both on
127 land and from the ocean (Stocker et al. 2013). It is likely that N₂O emissions from soils will increase due to

128 the increased demand for feed/food and the reliance of agriculture on nitrogen fertilizers. Climate warming
 129 will likely amplify agricultural and natural terrestrial N₂O sources (Ciais et al. 2013).

130 **Table 2.1. Important features of gases that are known to be formed at the plant surface during exposure**
 131 **to UV light**

GAS	Atm. Conc.	Ref	Lifetime (years)	Ref	GWP 100 year	Ref	Source		Ref	Units	
							Antropogenic	Natural			
CH ₄	1803 ppb	3	9.1	3	28	5	354±45	1	202±35	1	Tg CH ₄ yr ⁻¹
CO ₂	391 ppm	3	n.a.	-	1	5	8.3 ± 0.7	1	n.a.	1	PgC yr ⁻¹
N ₂ O	324 ppb	3	131	3	265	5	6.9 (2.7–11.1)	1	11.0 (5.4–19.6)	1	TgN yr ⁻¹
CO	80 ppb	4	months	5	5.3** ± 2.3	7	608	1	50-200***	8	TgC yr ⁻¹
NO _x	5-999 ppt	4	hours	3	-159** ± 79	7	37.5	2	11.3	2	TgN yr ⁻¹
NMVOC	n.a.	-	hours - months	3	n.a.	-	126.9	6	440-720*	6	TgC yr ⁻¹

132
 133 **) Only isoprene and monoterpenes, **) direct and indirect aerosol effects included, ***) only from plants.*

134 References: 1) Ciais, et al. 2013; 2) Dentener et al. 2006; 3) Hartmann et al. 2013; 4) IPCC, 2001; 5) Myhre
 135 et al. 2013; 6) Boucher et al. 2013, 7) Shindell et al. 2009; 8) Tarr et al. 1995

136

137 **2.2 Short lived gases (CO, NO_x, NMVOC)**

138 Emissions of CO, NMVOCs and NO_x (NO + NO₂) do not have a direct effect on RF, but affect climate
 139 indirectly as precursors to tropospheric O₃ and aerosol formation, and their impacts on hydroxyl-
 140 concentrations and CH₄ lifetime. NMVOCs include aliphatic, aromatic and oxygenated hydrocarbons (e.g.,
 141 aldehydes, alcohols and organic acids), and have atmospheric lifetimes ranging from hours to months.
 142 Global coverage of NMVOC measurements is poor, except for a few compounds (Hartmann et al. 2013).
 143 Emissions of CO and NMVOC are virtually certain to have induced a positive RF via production of the
 144 climatic drivers CO₂, CH₄ and O₃, while emissions of NO_x are likely to have induced a net negative RF.
 145 (Table2.1; IPCC, 2013). With its lifetime of 2 to 3 months, the effect of CO emission is less dependent on
 146 location than is the case for NO_x (Myhre et al, 2013). Due to their short atmospheric lifetime (hours), NO_x
 147 concentrations are highly variable in time and space. Solomon et al. (2007) described the potential of
 148 satellite observations of NO₂ to verify and improve NO_x emission inventories and their trends, and reported
 149 NO₂ increases of 50% over the industrial areas of China from 1996 to 2004. An extension of this analysis
 150 reveals increases between of 1.7x and 3.2x over parts of China, while over Europe and the USA NO₂ has
 151 decreased by 30 to 50% between 1996 and 2010 (Hilboll et al. 2013).

152 The major sources of atmospheric CO are in situ production by oxidation of hydrocarbons (mostly CH₄ and
153 isoprene) and direct emission resulting from incomplete combustion of biomass and fossil fuels. The
154 anthropogenic CO emission is estimated to be 608 TgC yr⁻¹ (Table 2.1); natural sources have been
155 estimated to account for up to half of the global CO emissions (Khalil and Rasmussen, 1990), and direct
156 emissions from plants are estimated to be 50-200 TgC yr⁻¹ (Tarr et al. 1995). An analysis of MOPITT
157 (Measurements of Pollutants in the Troposphere) and AIRS (Atmospheric Infrared Sounder) satellite data
158 suggest a clear and consistent decline of CO columns for 2002–2010 over a number of polluted regions in
159 Europe, North America and Asia, with a global trend of about –1% yr⁻¹ (Yurganov et al. 2010; Fortems-
160 Cheiney et al. 2011; Worden et al. 2013; Hartmann et al. 2013).

161 Reports on trends in a range of NMVOCs generally indicate a decline over urban and rural regions of North
162 America and Europe, on the order of a few percent to more than 10% yr⁻¹ (Hartmann et al. 2013). The
163 anthropogenic emission is between 15 and 22% of the total NMVOC emissions (Table 2.1)

164

165 **3 Methods & techniques**

166 UV-induced gaseous emissions from specific substances, plant organs, whole plants or whole ecosystems
167 have classically been studied under controlled environmental conditions by employment of sealed
168 enclosures ranging in complexity from simple commercial test tubes to highly advanced plant cuvettes
169 (plant parts) or whole chamber enclosures (plants or plant and soil communities).

170 Generally the studied gas components are emitted at very low rates from plant surfaces, and in order to
171 achieve detectable levels of gas accumulation the use of enclosures is required. A static enclosure that is
172 operated by manual sampling or connected in a closed gas sampling loop to the analyzer (e.g. Bruhn et al.
173 2009; 2014b) provides high analytical sensitivity for determining changes in gas mixing ratios, but may
174 require appropriate meticulous techniques to control undesired changes in other gas components, e.g.
175 moisture, CO₂ and O₃. Alternatively an open flow-through design may be used whereby the enclosure is
176 continuously purged with ambient- or zero-air (e.g. Vigano et al. 2008). Meanwhile, deployment of
177 enclosures is associated with multiple challenges that may affect the experimental conditions in
178 uncontrolled and undesired directions, leading to experimental flaws and artefacts.

179 Environmental controls of temperature, humidity and air composition are crucial for work with biological
180 materials in enclosures and to reveal important abiotic controllers for the investigated processes.

181 Complications by uncontrolled changes in the environment may further be augmented by the fact that

182 relatively long enclosure times are needed in order to uncover low reaction constants. It is beyond the
183 scope of this article to provide a detailed protocol of principles and methodologies for the use of sealed
184 enclosures to study gas exchange from surfaces. Instead, the reader is referred to literature providing
185 detailed descriptions on flux-chamber design and applications (e.g. de Klein and Harvey, 2015; Altimir et al.
186 2002; Skiba et al. 1992). In appendix A, we expand methods & techniques with respect to temperature,
187 chamber material, surface reactions and reactive species, analysis of gas mixing ratios and light sources.

188

189 **4 Mechanisms, sources and emissions**

190 Sunlight can induce trace gas emission from plants by several mechanisms from different precursors. Here
191 we focus on direct effects of UV radiation on trace gas emission from terrestrial plant surfaces as these are
192 largely ignored in global budgets. Indirect effects of UV on trace gas emission and other physiological
193 functions are reviewed elsewhere (Caldwell et al. 1995, 1999; Björn et al. 1996; Rozema et al. 1997; Bruhn
194 et al. 2012).

195

196 **4.1 UV-Radiation penetration through the canopy**

197

198 Leaves throughout a canopy are affected not only by the PAR and IR-spectrum of solar radiation but also by
199 UV radiation. Leaves do not transmit UV radiation but reflect some (up to ca. 6%) UV radiation (Grant
200 1997), and the high energy light still penetrates the canopy. Canopy structure, leaf area index (LAI), the
201 extent of direct and diffuse radiation all influence UV penetration through the canopy (Brown et al. 1994;
202 Shulski et al. 2004) and leaves. The penetration by UV-B varies less than that of PAR with leaf inclination
203 due to the higher diffuse component of UV light than PAR (Caldwell 1981; Deckmyn et al 2001). For
204 example, canopy UV-B transmittance (τ) may vary with LAI between $\tau = \exp(-1.01 \text{ LAI})$ and $\tau = \exp(-$
205 $0.17(\text{LAI}-1))$ depending on species and degree of clear sky (Shulski et al. 2004).

206

207 **4.2 UV-Radiation penetration through the leaf**

208

209 UV-B absorption of adaxial leaf cuticles caused by pigments (chromophores, e.g. flavonoids and other
210 phenolic compounds covalently bound to cutin) ranges from very high in some species with <3%
211 transmittance to >64% transmittance in other species (Bauer et al. 1998). The highest absorption is typically
212 in evergreen species (Baur et al. 1998). Some evergreen species also contain fluorophores in the cuticular
213 wax, which may convert solar UV irradiation into blue light that can be harnessed for photosynthesis.

214 However, the epicuticular wax *per se* (fatty acyl chains) can also absorb significant amounts of UV-B and
215 thus protect against UV-B (Long et al. 2003). Further, trichome layers also protect against UV-B
216 (Karabourniotis & Bornman 1999). UV-A radiation penetrates deeper into the mesophyll than UV-B in all
217 examined species (Liakoura et al. 2003). Whereas pigment changes in leaves during seasonal changes result
218 in varying degrees of reflectance and transmittance of PAR and IR, there appear to be no seasonal changes
219 in degrees of reflectance and transmittance in the UV region (Yoshimura et al. 2010), despite strong
220 seasonal fluctuations in the leaf concentration of UV-absorbing compounds (Liakoura et al. 2001).

221

222 **4.3 UV-Photochemistry mechanism in and on plant surfaces**

223

224 Photochemical reactions are typically complex. UV radiation can excite various molecules and this may
225 result in a change in molecular orbital occupancy, an increase in energy, and changes in local bonding and
226 charge distribution. Upon return to a lower energy state of the molecules, the released energy or the
227 energy transfer to a neighbouring molecule triggers reactions almost instantaneously. The radiation energy
228 is inversely proportional to the wavelength. Thus, UV-B radiation causes the cleavage of more chemical
229 bonds than does for instance UV-A and PAR. Following this, a multitude of radical reactions may take place
230 and thus greatly increase the quantum yield.

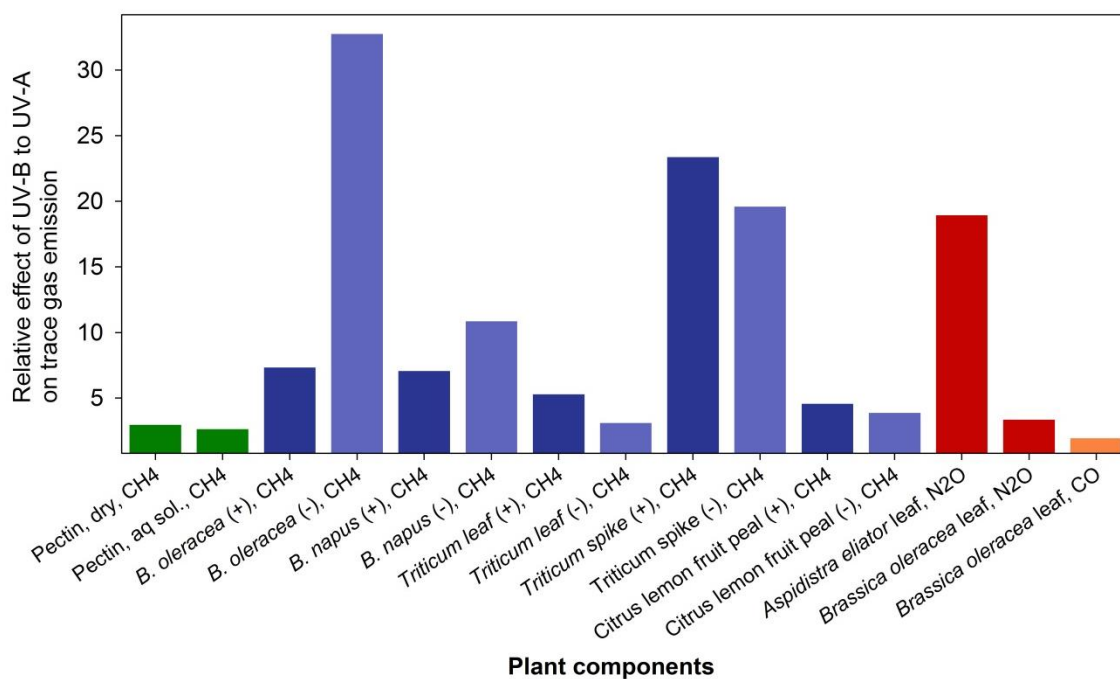
231 From the lab there is plenty of evidence that artificial UV radiation induces an almost instantaneous, i.e.
232 photochemically induced, trace gas emission from plants or plant components, such as carbon-based
233 molecules including CH₄ (McLeod et al. 2008; Keppler et al. 2008; Vigano et al. 2008, 2009; Bruhn et al.
234 2009, 2014; Messenger et al. 2009; Fraser et al. 2015), CO (Tarr et al. 1995; Schade et al. 1999; Brandt et al.
235 2009; Derendorp et al. 2011a; Bruhn et al. 2013), CO₂ (McLeod et al. 2008), and hydrocarbons (McLeod et
236 al. 2008; Derendorp et al. 2011b; Fraser et al. 2015) and nitrogen-based molecules including N₂O (Bruhn et
237 al. 2014b) and NO_x/NO_y (Hari et al. 2003; Raivonen et al. 2006, 2009). Conversely, from the field distinct
238 evidence that natural UV radiation induces an almost instantaneous, i.e. photochemically induced, trace
239 gas emission from plants is far less common, but is documented for CO (Bruhn et al. 2013), N₂O (Bruhn et
240 al. 2014b) and NO_x/NO_y (Hari et al. 2003; Raivonen et al. 2006, 2009). With respect to CH₄ and isoprene,
241 however, there are only indirect indications that natural UV radiation induces an almost instantaneous
242 emission (Keppler et al. 2006; Tiiva et al. 2007).

243

244 **4.3.1 Action spectra**

245 Additional evidence pointing towards direct UV-induced trace gas emission from plants or plant
246 components being an abiotic rather than a biotic process is that in most cases the higher energy UV-B

247 results in higher emission rates than does UV-A at a given irradiance intensity. This is observed in the lab for
 248 plant emission of CH₄ (McLeod et al. 2008; Bruhn et al. 2009), CO (Tarr et al. 1995; Schade et al. 1999;
 249 Bruhn et al. 2013) and N₂O (Bruhn et al. 2014b). Only McLeod et al. (2008) have conducted a detailed
 250 analysis of the action spectrum of direct UV-induced trace gas emission, finding the CH₄ efflux rate from
 251 citrus pectin-impregnated glass fibre sheets to scale linearly with an idealized spectral UV weighting
 252 function. The function weighted CH₄ efflux is an order of magnitude lower for each 80 nm increase in
 253 wavelength. This spectral weighting function differs from other processes where metabolic activity
 254 intrinsically is involved, such as the erythema function (see further discussion in McLeod et al. 2008).
 255



256
 257

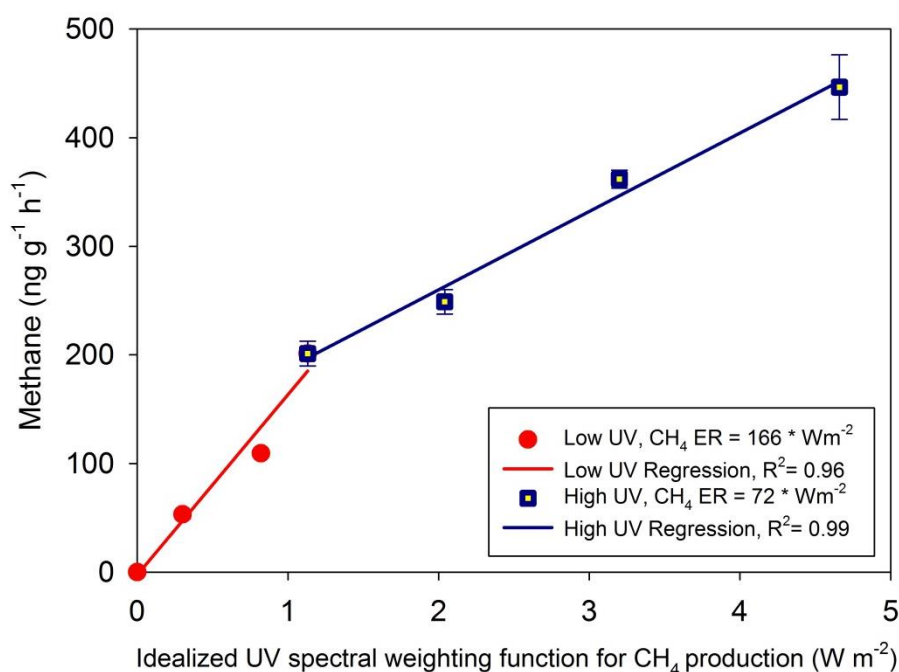
258 **Figure 4.1. Relative effect of UV-B to UV-A on trace gas emission from different plant components**
 259 **and surfaces.** The relative effect of UV-B to UV-A is here defined as emission rate in response to UV-B
 260 (312nm) relative to that in response to UV-A (375nm) when adjusted according to irradiance intensity. CH₄:
 261 Pectin, dry (McLeod et al. 2008), Pectin, aq. sol. (Bruhn et al. 2009), *Brassica oleracea* leaves, *Brassica*
 262 *napus* leaves, *Triticum* leaves, *Triticum ears*, and *citrus lemon* fruit peel (Rolsted MMM, Bruhn D, Mikkelsen
 263 TN, Ambus P unpublished); N₂O: Bruhn et al. (2014b); CO: Bruhn et al. (2013). (+) designates that natural
 264 surface wax is present, (-) designates that natural surface wax is either removed mechanically or not present
 265 at all (in the case of *Triticum* spikes). Green = CH₄ from pectin, Dark blue = CH₄ from leaf with nat. wax. Light
 266 blue = CH₄ from leaf without nat. wax, Red = N₂O, Orange=CO.
 267

268 The crude indication of an action spectrum of CH₄ emission from pectin in aqueous solution (Fig 4.1)
 269 resembles the detailed action spectrum of citrus pectin-impregnated glass fibre sheets (Fig 4.1).
 270 Importantly, though, the crude indication of action spectra of trace gas emission appear to be highly
 271 dependent on the precursor as well as the condition of that precursor (Fig 4.1). For example leaves of two
 272 *Brassica* species appear to emit relatively far more CH₄ in response to UV-B than to UV-A, as would be
 273 expected from the results of a single component such as pectin. Furthermore, in the case of the leaves of
 274 the two *Brassica* species, it appears that the removal of leaf surface wax results in a relatively higher effect
 275 of UV-B to that of UV-A in terms of CH₄ emission. This may reflect a combination of UV-A radiation
 276 penetrating deeper into the mesophyll than UV-B in all examined species (Liakoura et al. 2003) when the
 277 wax is intact. However this depends on species (Baur et al. 1998) and perhaps several plant components
 278 (incl. surface wax *per se*) are potential precursors to UV induced trace gas emission (Table 4.1).

279

280 4.3.2 UV-response functions

281 UV induced trace gas emission is commonly reported to exhibit a near linear response function from both
 282 intact organs/tissues as well as from single plant components (McLeod et al. 2008; Bruhn et al. 2009, 2013,
 283 2014a; Derendorp et al. 2011). This, together with the fact that direct UV induced trace gas emission often
 284 occurs at constant rates over long periods (Bruhn et al. 2009), strongly indicates photochemical reactions
 285 from plentiful precursors.



286

287 **Fig. 4.2.** Pectin CH₄ production (ng g⁻¹ h⁻¹) as a function of spectrally weighted UV-intensity (W m⁻²). The CH₄
 288 production decays one decade when the spectrum increases 80 nm, e.g. the CH₄ emission is 1 at 300 nm

289 and 0.1 at 380 nm: spectral weighting function from Fig. 1a and data from Table 1 in McLeod et al. (2008).
290 Data is from the UV313 lamp filtered with 125- μm cellulose diacetate which filters UV wavelengths < 290
291 nm. ER = Emission Rate. Linear regressions functions shown in box. Values are means of three replicates
292 and standard errors are less than symbol size except where visible.

293

294 However, further examination (Fig. 4.2) of the only published dataset on UV-induced pectin-based CH_4
295 productions at very low UV intensities indicates release to be more responsive (by a factor of two) than
296 under higher intensities. The role of self-shading in this context remains to be fully investigated. Thus, even
297 for simple linear responses in UV-induced trace gas emission, there is reason to believe that the underlying
298 photochemical mechanisms are complex. Only Raivonen et al. (2009) have reported on an analysis of the
299 potential linearity of the direct response function of any trace gas (NO_x) emission to natural temporal
300 variation in UV intensity (UV-A).

301

302 **4.3.3 Temperature interactions**

303 In most cases trace gas emission from plant material is also observed in darkness (PAR and UV absent) and
304 with a positive response to temperature increases, although with sensitivities too low to infer underlying
305 abiotic processes (Derendorp et al. 2011a). However, reliable indications are lacking of interactions
306 between the photochemical reactions and temperature with respect to trace gas emission from plant
307 material.

308

309 **4.3.4 $[\text{O}_2]$ or O-radicals dependency**

310 It caused quite a surprise (Kirschbaum et al. 2006, 2007) when Keppler et al. (2006) first reported an
311 aerobic plant CH_4 emission in response to solar radiation. In all examined cases of UV induced trace gas
312 emission from plant materials, there is a positive dependency on $[\text{O}_2]$ or O-radicals (Table 4.1). Further, this
313 confirms a combination of instantaneous photochemical reactions and subsequent radical reactions in
314 most cases. UV radiation can therefore in theory act as a stimulus via an increased reactive oxygen species
315 (ROS) reaction, and consequently the actual precursor of the emitted gas does not itself need to be a good
316 absorber of UV radiation for the process to occur. However, Lee et al. (2012) provide evidence that photo-
317 oxidation may only be one of several photo degradation processes, as they observed the process occurring
318 in the absence of O_2 . They speculated that the direct breakdown of chemical groups such as carboxyl,
319 carbonyl, and methoxyl groups may result in CO_2 , CO, and CH_4 release.

320

321 **4.4 Precursors**

322

323 In Table 4.1 we have compiled current knowledge on the potential precursors for trace gas formation in
 324 *direct* response to UV radiation examined and/or suggested in the literature. For the C-based trace gases
 325 there are many structural components, which may act as precursors. In contrast, for the N-based trace
 326 gases the potential precursors appear to be more dependent on surface deposited molecules (Table 4.1).

327

328 **Table 4.1 Potential precursors for trace gas formation in direct response to UV radiation examined**
 329 **and/or suggested in the literature.**

Gas	Suggested source (plant or surface deposit)	Ref	Positive [O ₂] or O-radicals-dependence	Ref
CH₄	Pectin (methyl groups)	1, 2, 3, 4, 5, 6, 7	Yes	2, 7
	Wax	8	Yes	8
	(15-nonacosanone & 2-hexadecanone)			
	Cellulose	3, 4	??	
	Lignin	3, 4	??	
	Methionine	9	??	
	Ascorbic acid	10	Yes	10
CO	Cellulose	11	Yes	12, 13, 14
CO₂	Lignin	15, 16		
C2–C5 hydrocarbons	??	11, 17	Yes	11
N₂O	Wax,	18		
	Mesophyll	18		
	Surface bound N ₂ O	19		
	NO ₃ ⁻	20		
	NH ₄ NO ₃	18, 21	Yes	20, 22, 23
NO_{x,y}	needle surfaces, HNO ₃ or NO ₃ ⁻	24, 25, 26		

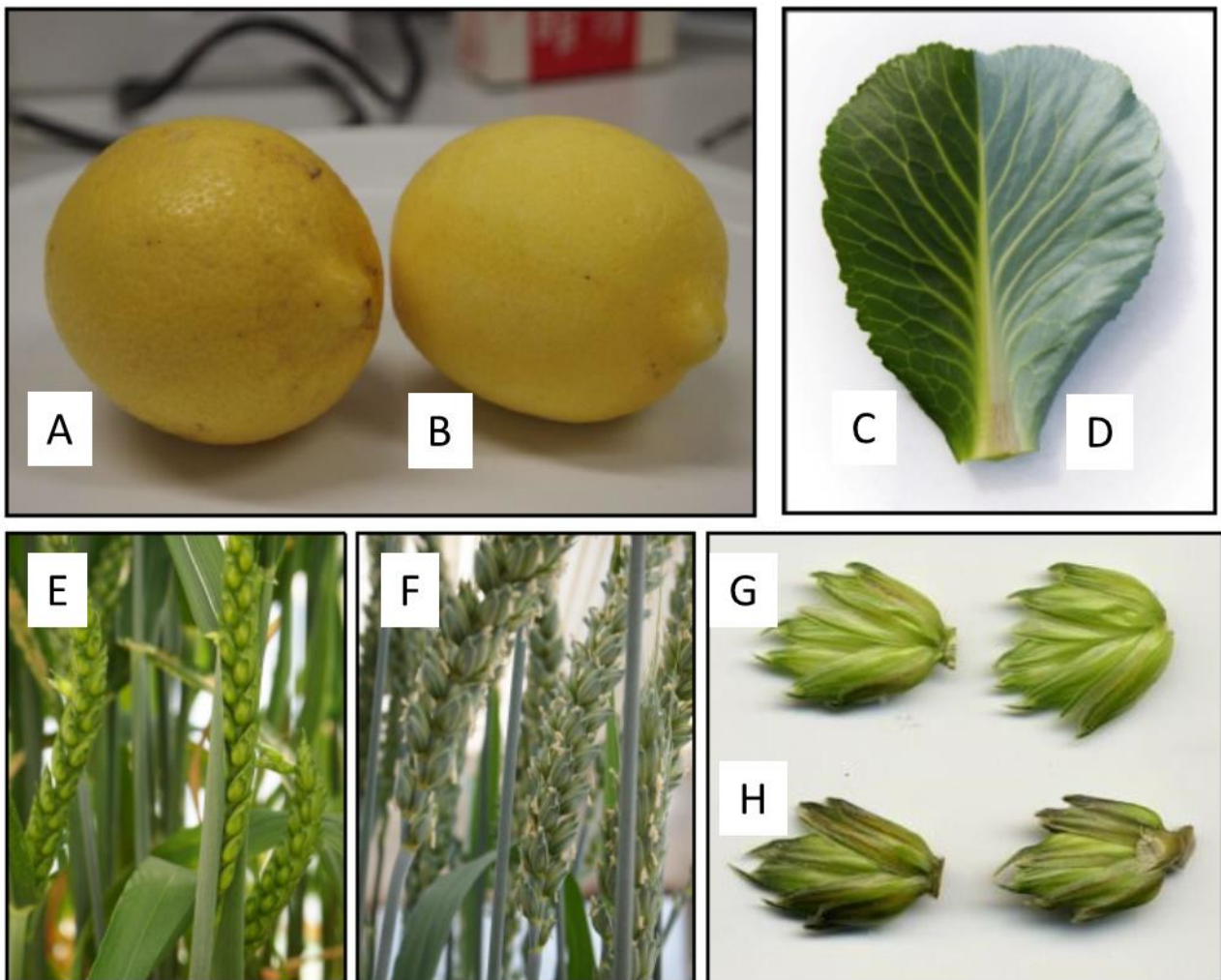
330

331 References: 1) Keppler et al. 2006; 2) Keppler et al. 2008; 3) Vigano et al. 2008; 4) Vigano et al. 2009; 5)
 332 McLeod et al. 2008; 6) Bruhn et al. 2009; 7) Messenger et al. 2009; 8) Bruhn et al. 2014a; 9) Bruhn et al.
 333 2012; 10) Althoff et al. 2014; 11) Schade and Crutzen 1999; 12) Tarr et al. 1995; 13) Yonemura et al. 1999;
 334 14) Derendorp et al. 2011; 15) Rozema et al. 1997; 16) Day et al. 2007; 17) Fraser et al. 2015; 18) Bruhn et al.
 335 et al. 2014b; 19) Kim et al. 2010; 20) Rubasinghege & Grassian, 2009; 21) Rubasinghege et al. 2011; 22)
 336 Prasad, 2002; 23) Prasad and Zipf, 2008; 24) Hari et al. 2003; 25) Raivonen et al. 2006; 26) Raivonen et al.
 337 2009. ?? equals unknown.

338

339 It seems to be the consensus that the polysaccharide pectin is the most important precursor for UV induced
340 plant CH₄ emission due to its content of methyl groups (Keppler et al. 2006, Keppler et al. 2008; Vigano et
341 al. 2008, 2009; McLeod et al. 2008; Bruhn et al. 2009; Messenger et al. 2009; Bloom et al. 2010; Fraser et al.
342 2015). Whereas we agree that pectin is one of the potential precursors, we are currently not convinced that
343 it necessarily is the most important one. Pectin is laid down in primary plant cell walls. For pectin to be
344 reached by UV irradiation in nature, UV irradiation has to first penetrate the outer surface wax layer
345 naturally occurring on plant organs. In Figure 4.3 we show different pairs of plant organs with natural
346 surface wax or without surface wax, respectively.

347



348

349 **Figure 4.3. Different pairs of plant material with different amounts of surface wax.** A+B) Organically
350 grown *Citrus limon* fruit with natural surface wax (A) or with wax mechanically removed (B) by gentle
351 scrubbing with a kitchen sponge. C+D) *Brassica oleracea capitata f. alba* leaf with surface wax removed (C)
352 or intact (D). E+F) *Triticum aestivum* "Tähti" (E, with almost no surface wax) and *Triticum aestivum* "Vinjett"

353 (F, with normal surface wax) ears. G+H) Detailed parts of *Triticum aestivum* "Tähti" (G) and *Triticum*
354 *aestivum* "Vinjett" (H) ears. Rolsted MMM, Bruhn D, Mikkelsen TN, Ambus P unpublished. Photos: Rolsted
355 MMM.

356
357 As described in Section 4.2, UV irradiation is to some degree screened at the surface of plant tissues and
358 organs. Thus, an approach to illustrate whether pectin is the most important precursor for CH₄ formation is
359 to measure and compare the UV induced CH₄ production from material of pairs of plant organs with more
360 or less natural UV-screening surface wax (Figure 4.3) as well as in samples of plant leaves with or without
361 the natural wax removed. We did this and found that UV-B induced CH₄ formation in both *citrus limon*
362 peels and *Cydonia oblonga* peels as well as in *Brassica oleracea capitata f. alba* leaves was halved upon
363 removal of the surface wax. This evidently contradicts the notion that in nature pectin is the most
364 important precursor for UV induced CH₄ formation, especially because both *citrus limon* peels and *Cydonia*
365 *oblonga* peels are chosen for industrial pectin extraction due to the high pectin content. Conversely, there
366 was no difference in UV-B induced CH₄ formation between *Triticum aestivum* "Tähti" (with almost no
367 surface wax) ears and *Triticum aestivum* "Vinjett" (with normal surface wax) ears, or between leaves of
368 *Triticum aestivum* when irradiated from either adaxial side (with almost no wax) or from the abaxial side
369 (with much natural surface wax). Removal of surface wax should, in theory, increase UV exposure of the
370 pectin, but in no case did wax removal result in a higher rate of CH₄ formation. Furthermore, we recently
371 demonstrated that the surface wax *per se* is resulting in CH₄ formation upon UV irradiation (Bruhn et al.
372 2014a). In conclusion, we are still far from having a clear understanding of the relative contribution of
373 different precursors in any UV induced trace gas formation and emission. Additionally, given that UV
374 radiation of different wave-lengths reaches different depths in the plant tissue (Liakoura et al. 2003) in a
375 species- dependent manner (Bauer et al. 1998), it seems most likely that each of the different precursors
376 (Table 4.1) are affected differently with respect to wave-lengths of UV irradiation. Consequently, we
377 cannot with any certainty extrapolate an action spectrum for one precursor to that of an entire tissue or
378 organ (Fig. 4.1).

379

380

381

382 **5 Upscaling**

383 When an unaccounted natural source is discovered there is an urgent demand for extrapolating observed
384 rates to a global scale, so the magnitude of the new source can be put into perspective. However, if

385 mechanisms are unknown, there is a high risk in an upscaling exercise, because driving forces and
386 controlling factors unintentionally might be ignored, leading to the wrong outcome. On the other hand, if
387 some factors are known, response curves can be constructed and upscaling can be conducted under
388 defined premises, even though there are still unknown factors. Results can then be treated as a platform
389 for understanding and as a contribution to an ongoing knowledge improvement process. Based on current
390 knowledge, we suggest a simple global upscaling and source strength for sunlight-induced emission of the
391 gases CH₄, CO, and N₂O at the plant surface.

392

393 **5.1 Upscaling of methane, CH₄**

394 The discovery of aerobic CH₄ emissions from plants became breaking news in 2006 (Kepler et al. 2006),
395 mainly because their global upscaling suggested a source strength of 62-236 Tg yr⁻¹, which represented
396 approximately 10–40% of the annual total of methane entering the modern atmosphere, and
397 approximately 30–100% of annual methane entering the preindustrial (0 to 1700 AD) atmosphere (Ferretti
398 et al. 2007). Four independent research groups subsequently revised the global magnitude of this potential
399 CH₄ source by different approaches, and jointly suggested emissions in the lower end compared to the
400 pioneering study by Kepler et al. (2006). Based on carbon stable isotope analysis (Ferretti et al. 2007),
401 standing leaf biomass (Parsons et al. 2006), leaf-mass-based estimation and photosynthesis-based
402 estimation (Kirschbaum et al. 2006), and extrapolation from initially reported chamber measurements
403 (Butenhoff and Khalil 2007), aerobic CH₄ emissions from vegetation were respectively estimated at 0 – 176
404 Tg yr⁻¹, 42 Tg yr⁻¹, 10 – 60 Tg yr⁻¹ and 20 - 69 Tg yr⁻¹. None of the studies revealed underlying mechanisms
405 for aerobic CH₄ emission.

406 At the American Geophysical Union (AGU) fall meeting in 2007, three groups presented a major driving
407 factor, UV-radiation, for the aerobic CH₄ emission (Bruhn et al. 2007; Röckmann et al. 2007; Vigano et al.
408 2007), and in the following years UV generated CH₄ emission was confirmed in several publications (Vigano
409 et al. (2008, 2009); McLeod et al. 2008; Kepler et al. 2008; Bruhn et al 2009; Messenger et al. 2009).
410 McLeod and Kepler (2010) concluded in a review that the proposed formation of CH₄ under aerobic
411 conditions in plants is robust, but the magnitude and significance for the global CH₄ budget remained
412 unresolved.

413 After the discovery of UV as a driving factor, only one group has tried to upscale aerobic plant generated
414 CH₄; Bloom et al. (2010) provided a putatively low global estimate of 0.2–1.0 Tg y⁻¹ plant-produced CH₄. The
415 upscaling was only based on UV-induced CH₄ emission measured from purified pectin. Bloom et al. (2010)

416 assumed that UV-induced CH₄ emission measured in purified pectin is representative of UV-induced leaf
417 CH₄ emission when taking leaf pectin content into account. However, we believe that there is good
418 evidence in the literature to indicate that this is not the case, since Vigano et al. (2008) for example showed
419 that, at a certain UV irradiation, the CH₄ emission by commercially purified pectin was ca. 80 ng CH₄ g⁻¹ DW
420 h⁻¹, whereas that of dried perennial ryegrass leaf was almost three-fold higher at ca. 200 ng CH₄ g⁻¹ DW h⁻¹
421 – see Bruhn et al (2012) for further discussions. Therefore, the current upscaling by Bloom et al. (2010)
422 must be seen as a preliminary attempt to evaluate global significance from the basis of limited information,
423 and it is important to gain more knowledge for modelling of the UV driven CH₄ from plants at a global level.
424 We suggest that future modelling of the UV driven CH₄ from plants must include data obtained under field
425 conditions with respect to plant growth and development, and exposure to natural sunlight. Such data are
426 currently not available, and therefore methane upscaling is not included in this review.

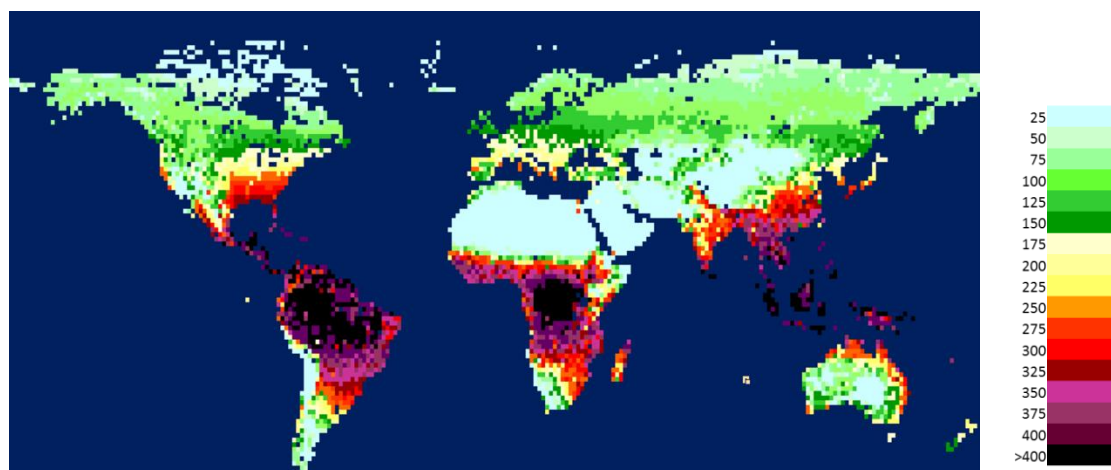
427

428 **5.2. Upscaling of carbon monoxide, CO**

429 All natural terrestrial direct CO emissions, in the range of 50–200 Tg CO yr⁻¹, have hitherto been ascribed by
430 the IPCC (1995, 2001) to photo-induced CO emission by living plants (cf. Tarr et al. 1995). However, in
431 studies on underlying photo-induced CO emission by living plants (Seiler and Giehl 1977; Seiler et al. 1978),
432 which were incorporated into global CO budgets in the early IPCC assessment reports (IPCC 1995, 2001),
433 the UV component of (sun)light was not considered (Bruhn et al. 2013). Therefore, we still await a proper
434 global estimate of UV radiance induced CO emission by living vegetation. Bruhn et al. (2013) provides the
435 first in situ measurements of ecosystem CO emission by living plants in response to natural solar UV
436 irradiation. Importantly, Bruhn et al. (2013) find that in the studied natural grass field the photo-induced
437 CO emission due to natural solar UV radiation is more than half of the value of that due to total solar
438 spectrum at the Earth's surface. This may imply that the previous global estimate of photo-induced CO
439 emission from living plants of 50–200 Tg CO yr⁻¹ (cf. Tarr et al. 1995) should perhaps be doubled. Thus,
440 future global budgets need to include CO emission caused by natural UV irradiance.

441 Here, we use the results from Bruhn et al. (2013), and estimate the global UV driven CO emissions. The
442 upscaling is based on in situ ecosystem-atmosphere CO exchange measurements from natural vegetation
443 and under ambient UV-B conditions in September and October of 2011 at DTU Risø campus (55°41'12"N,
444 12°05'52"E) in combination with laboratory experiments with artificial UV (Figure 5.1.). For materials and
445 methods see Bruhn et al. (2013), and for the upscaling procedure, see appendices B and C. There is
446 substantial geographical variation in source strength (Fig. 5.1), which is mostly caused by the geographical

447 variation in surface UV radiation intensity, similar to the responsiveness of N₂O (Fig. 5.2). The emission of
448 CO in response to the UV-component of natural solar radiation was also evident at the ecosystem scale.
449 When scaled to the global level, the UV-induced emission of CO by vegetation surfaces amounts up to 22 Tg
450 yr⁻¹, which equals 11-44% of all the natural terrestrial living plant sources hitherto accounted for, which
451 range between 50 and 200 Tg CO yr⁻¹ (IPCC, 1995, 2001; Tarr et al. 1995).



452

453 **Figure. 5.1** Estimated annual global CO emissions (mg CO m⁻²) from terrestrial vegetation surfaces induced
454 by temperature and natural UV-radiation.

455

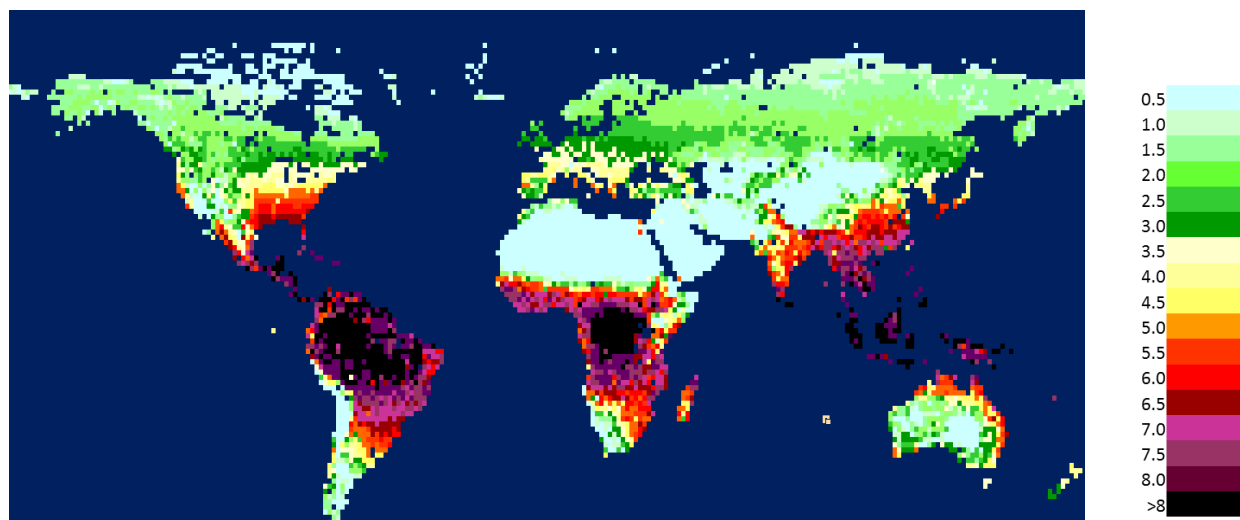
456 5.3 Upscaling of Nitrous oxide, N₂O

457 In order to evaluate the global significance of our new discovery of a terrestrial UV-driven N₂O source, we
458 attempted to scale the processes of temperature- and UV-induced N₂O emission rates by vegetation to the
459 global level (Fig. 5.2) - for materials and methods see Bruhn et al (2014) and upscaling procedure see
460 appendices B and C. The upscaling was feasible because the magnitude of measured N₂O emission rates in
461 response to natural sunlight, including low intensities of UV-radiation ranging from 280-400 nm, was similar
462 to the magnitude of measured N₂O emission rates in response to high intensities of artificial UV-radiation
463 within the 309-314 nm narrow range (Bruhn et al. 2014b). The total of these radiation-driven N₂O sources
464 amounts to 0.65-0.78 Tg yr⁻¹, which equals 7-24% of all the natural terrestrial N₂O sources hitherto
465 accounted for, which range between 3.3 and 9 Tg N yr⁻¹ (Solomon et al. 2007). There is substantial
466 geographical variation in the source strength (Fig. 5.2), which is mostly caused by the geographical variation
467 in surface UV radiation intensity – similar to the responsiveness of CO (Fig. 5.1). Importantly, the irradiance
468 responses of N₂O emissions across all examined wave length ranges (UV-B, UV-A, PAR) is steepest at low
469 irradiance intensities (Bruhn et al. 2014b). This intensity-dependent sensitivity is not taken into account in

470 our linear scaling of the UV-induced N₂O emission rates to the global level, and it is therefore likely that we
471 underestimate the N₂O source strength.

472

473



474

475 **Figure 5.2.** Estimated annual global N₂O emissions (mg N₂O m⁻²) from terrestrial vegetation surfaces,
476 induced by temperature and natural UV-radiation.

477 6 Perspectives and Conclusions

478 6.1 Realistic emission rates

479 Despite the many reports on directly UV induced trace gas emission (CH₄, CO, CO₂, C2-C5
480 hydrocarbons/NMVOC, N₂O and NO_x) from plant materials, there are very few studies with replicated
481 measurements of plant trace gas emission in response to natural solar radiation including UV (NO_y,
482 Raivonen et al. 2009; CO, Bruhn et al. 2013; N₂O, Bruhn et al. 2014b). In all three examples there were
483 indications that measured realistic emission rates were substantial compared to those of other
484 emission/uptake processes at the ecosystem level. At this stage it is unfortunately not possible to say
485 anything in general about realistic emission rates from a wider perspective.

486

487 6.2 Future studies

488 From the evidence listed above it becomes apparent that much research is necessary for a more
489 comprehensive understanding of mechanism, precursors and indeed *in situ* emission rates. Therefore we
490 suggest that future experiments include tests of:

- 491 • Action spectra and linearity in response function at low UV levels at intact tissues in many more
492 species
- 493 • Responses to natural variation in UV intensities in the field
- 494 • Effect of deposition of especially N-precursors
- 495 • Direct responses to UV after the plants previously have been exposed to variable UV exposures
496 during growth
- 497 • Investigation if stomatal conductance has any effects on the UV induced gas emission
498

499 **6.3 Known gas emission stimulated by UV**

500 It is well established that sunlight and UV in particular stimulate the production of several gases at the
501 surface or near the surface of living plants. Currently there is documented evidence for production of the
502 following gas species: CH₄, CO, CO₂, NMVOCs, NO_x and N₂O. The number of gases produced by UV
503 stimulation is probably greater, but further gas screening studies are needed to assess this. Independent of
504 gas species, the UV-induced gas emission rates documented until now are very low, and as a consequence
505 it is very challenging with respect to equipment and experimental setup to investigate these processes.
506 Most records concern CH₄ production, but there are still many unanswered questions for this gas with
507 regards to dose responses and production under natural conditions. For the other mentioned gases there
508 are even more unanswered questions, nevertheless we have enough information to provide the first
509 attempt at a global budget of UV-induced CO and N₂O emissions based on measurements from natural
510 vegetation under field conditions. The result indicates that UV driven CO production may contribute as
511 much as 11-44% of all the natural terrestrial plant sources. The UV-induced N₂O source equals 7-24% of the
512 natural terrestrial source strength. These global estimates should be regarded as a contribution to an
513 ongoing quantification process, but this high global share emphasizes the urgent need for more work. In
514 order to establish reliable global estimates and enable future predictions, it is apparent that much research
515 is necessary to elucidate mechanisms, precursors, environmental relationships and establishment of
516 relevant and realistic emission rates.

517

518 **6.4. Perspectives**

519 This newly discovered light-associated aspect of trace gas emission from living vegetation may have
520 significant consequences for our understanding of exchange processes between the global biosphere and
521 atmosphere. It is very likely a global phenomenon occurring on all leaf surfaces exposed to sunlight in both

522 managed and natural ecosystems. Our global estimates for CO and N₂O under the current environmental
523 conditions evidently show that radiation-driven processes are significant natural sources, and this could
524 also be true for the other gases. An important feature is that the gas production is occurring at or just
525 under the leaf surface, resulting in periodic high gas concentration within the boundary layer surrounding
526 the leaves. This could for instance reduce the gas uptake of ozone in leaves since CO accelerates the
527 reaction of O₃ with ethylene (Horie and Moortgat, 1998), a process that has so far not been considered in
528 ozone effect research. Through geological eras, the radiation-driven greenhouse gas (direct: CO₂, CH₄, N₂O
529 and indirect: CO) impact must have fluctuated with UV radiation and other processes producing or
530 consuming greenhouse gases (e.g. soil respiration, denitrification and methanogens in wetlands, and
531 methane oxidation in upland soils), and therefore the development of climate on Earth.

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534 for the experiments. This work was supported by the FP7 EU Eclair project.

535

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772

773

774 **Appendix A**

775 ***Methods & techniques***

776 This appendix expands 3 methods & techniques in the text with respect to environmental factors and other
777 important issues related to measurements of UV induced gases.

778

779 **Temperature**

780 Particularly challenging is temperature control inside confinements made of transparent materials and at
781 the same time exposed to intense irradiation by lamps or natural sunlight that may lead to severe scorching
782 of plants. Under laboratory conditions, experiments may be run in well vented and temperature controlled
783 growth cabinets (Bruhn et al. 2009) or enclosures equipped with heating tape (Vigano et al. 2008) to
784 maintain stable temperature conditions. Direct temperature control of enclosures may include simple and
785 inexpensive means such as ice blocks (M. Drösler, pers. comm.) or more advanced applications in the form
786 of Peltier cooling technology (Mikkelsen and Ro-Poulsen, 2002; Bruhn et al. 2014; Sundqvist et al. 2012).
787 Temperature can be determined directly at the leaf surface with a micro-thermocouple attached to the
788 material (Keppler et al. 2006) or air temperature detected by thermocouples or conventional
789 thermometers situated in the enclosure. Exterior surface temperature of enclosures can be measured by
790 using a heat conducting steel probe connected to a high precision temperature meter (Bruhn et al. 2014).

791

792 **Chamber material**

793 Chambers should be made of materials that allow transmittance of UV-radiation without filtering.
794 Commonly used materials in transparent chamber or plant cuvettes include UV-transparent synthetic
795 quartz-glass, tradename Suprasil®, that offers optimal UV-transmissions (Vigano et al. 2008; Rosenqvist et
796 al. 2012; Bruhn et al. 2014), alternatively UV-transparent acrylic materials (Rosenqvist et al. 2012; Bruhn et
797 al. 2014) can be used. Controlled transmittance of UV in experimental setups can be achieved by the
798 application of filters to reduce or filter out specific UV-wavelengths reaching surfaces being investigated.
799 Many commercial acrylic materials, with trade names such as e.g. Plexiglas or Perspex, will attenuate UV
800 penetration and can be deployed to manipulate UV intensity (Bruhn et al. 2014). For specific and controlled
801 filtering of UV radiation, various filters can be applied either at the light source or covering the enclosure
802 windows; a comprehensive review of UV manipulation is given by Aphalo et al. (2012).



803 **Figure A1.** Plant leaves inserted in UV-B transparent vials. Note vials without leaves are used as blank
804 controls.

805 **Surface reactions and reactive species**

806 Synthetic soft plastic and rubber materials used in growth cabinets such as hoses, tubes, pots, sealants and
807 wire insulators, provide potential complications if exposed in experimental setups to study UV-induced gas
808 emissions. Firstly, these materials may release phytotoxic compounds, leading to plant growth problems or
809 plant death; for a review see Rosenqvist et al. (2012). Secondly, photochemical reactions on the surface of
810 synthetic materials when exposed to UV-radiation can produce gases like methane (D. Bruhn, unpublished)
811 or N₂O (Bruhn et al. 2014) that may confound experimental results. For this reason, it is strongly
812 recommended to include empty/blank controls in the experimental protocol (Bruhn et al. 2014; Sundqvist
813 et al. 2012; Figure A1). Presence of synthetic materials in the experimental units should be minimized, and
814 materials shielded with (e.g.) PTFE replaced with inert materials (glass, metal) where appropriate or pre-
815 conditioned by heating (Sundqvist et al. 2012).

816

817 **Analysis of gas mixing ratios**

818 Analysis of mixing ratios of target gases in the enclosures can be achieved principally by two different
819 approaches. These are *i*) manual grab sampling by syringe where a subsample of enclosure headspace is
820 transferred to the analyzer or a storage vial for subsequent analysis; incubation may also take place in vials
821 that can be mounted directly in the analytical unit such as a GC-autosampler, avoiding the need for manual
822 sample transfer (Bruhn et al, 2014). Alternatively, *ii*) the headspace gas concentrations can be observed in

823 real-time where the test unit is connected to an appropriate gas analyzer in a sealed gas loop for
824 continuous or cyclic analysis (Sundqvist et al. 2012).

825

826 Gas-chromatography: Conventional GC-instrumentation equipped with Flame-Ionization-Detection [FID] for
827 CH₄ (e.g. Vigano et al. 2008), methanizer-FID for CO and CO₂ (Ueta et al. 2013) and Electron-Capture-
828 Detection [ECD] for N₂O (e.g. Bruhn et al. 2014) are applicable for grab sample analysis in order to cross-
829 check the optical techniques, and where experiments with small vials prevent measurements with optical
830 systems that require additional sample volume. The reproducibility with GC-analysis is typically ±10 ppb
831 although the micro-GC system tested by Ueta et al. (2013) for combined CO and CO₂ analysis exhibited
832 detection limits of 3 to 5 ppm. Trace-gas GC analysis at ambient concentrations require sample volumes of
833 typically 0.5-1 ml.

834

835 Laser spectroscopy: During the last couple of decades laser spectrometers for sensitive, accurate and fast
836 analysis of air trace gas constituents have become available at affordable pricing. In their work with UV-
837 induced CH₄ dynamics, Vigano et al. (2008) and Sundqvist et al. (2102) used an off-axis integrated cavity
838 output spectrometer (Los Gatos Inc.) for real-time monitoring of CH₄ mixing ratios. With use of laser
839 spectroscopy, it is necessary to pay attention to cross-interference from other gas species; Vigano et al.
840 (2008) verified this for plant emission of abundant methanol (CH₃OH). For studies on UV-induced emissions
841 of carbon monoxide (Bruhn et al. 2013) and nitrous oxide (Bruhn et al. 2014), a Los Gatos laser N₂O/CO
842 spectrometer was applied following proper correction for cross-sensitivity with water and direct cross-
843 interference between CO and N₂O. The sensitivity of laser spectrometers is several fold higher compared
844 with GC analysis, and allows reproducibility in the range of ±1 ppb.

845 Stable isotope analysis: GC combined with stable isotope (SI) analysis provides a powerful tool to study
846 source partitioning and reaction pathways of trace gases emitted from surfaces. Isotope-ratio-mass-
847 spectrometry (IRMS) in combination with proper pre-concentration (e.g. cryo-trapping) and
848 chromatographic separation of analytical compounds has been used for studying carbon (¹³C), hydrogen
849 (deuterium; D) in CH₄ (Keppler et al. 2006; 2008) and nitrogen (¹⁵N) in N₂O (Bruhn et al. 2014). The
850 reproducibility of gas mixing ratios by GC-IRMS is diminished (±20-30 ppb at ambient concentrations)
851 compared with conventional GC analysis and the sample amount required for proper analysis is in the
852 range of tens of milliliters. Dueck et al. (2007) analyzed the concentration of ¹³C-methane in CH₄ emitted
853 from fully ¹³C-labeled plant material using photo-acoustic spectroscopy in combination with a continuous-

854 wave, optical parametric oscillator (OPO) and reported a detection limit of 3 ppb. Whereas the work by
855 Dueck et al. (2007) demonstrated only negligible emissions of CH₄ based on the spectrometric method,
856 later work by Vigano et al. (2008) with the same plant material showed a contrasting result with significant
857 emissions of ¹³C-CH₄, supposedly due to different analytical sensitivities (Vigano et al. 2008).

858 SI analysis encompasses recognition of the isotopic composition in gases emitted from materials with
859 isotopic abundances at natural levels (e.g. Keppler et al. 2006) as well as from isotopically enriched
860 materials (e.g. Bruhn et al. 2014). Isotopic variations arise from mass-dependent isotope fractionation in
861 biological and chemical processes, and natural abundance analysis of the trace gases, may add information
862 about the nature and origin of precursors. Application of the rare (heavy) isotope is valuable not only for
863 revealing information on specific precursor substances but also for providing a tool to study consumption
864 processes.

865 The recent development of isotopic laser spectrometers (e.g. instruments offered by Picarro, Aerodyne, Los
866 Gatos) provides new opportunities to investigate mechanisms and processes in UV-induced trace gas
867 emissions. However, so far no work taking advantage of these instruments has been reported in literature.

868 **Light sources**

869 Work on UV-induced trace gas emissions inevitably requires selection of a proper light source and
870 establishment of associated irradiation intensities, wavelengths and action spectra. The selection of a light
871 source is application driven and depends on the requirements imposed by the study. The main
872 requirements concern the intensity and spectral distribution of radiant output of the lamp. The geometry
873 of the setup, including the source-target-distance and area of exposure, sets certain limits not only on the
874 light source but also on characteristics of the monochromator if this is applied (Aphalo et al. 2012).

875 In this context, it is important to stress that the current review addresses works investigating the direct
876 photolytic effect of UV-light exposure for plant-derived trace gas emissions. In this sense, translocation
877 studies where plants are grown under natural or controlled conditions with attenuated or enhanced UV-
878 exposure and subsequently examined for historical UV effects are not considered.

879 It is beyond the limits of this manuscript to present a detailed review and recommendation on selection of
880 proper light source equipment for UV studies. Instead, the reader is referred to comprehensive reviews on
881 usage of artificial light sources in UV photobiology given by Aphalo et al. (2012), and UV quantification
882 reviewed by Björn et al. (2012). A number of potential light sources can be selected for UV work, either as

883 single light sources, or more often in combination to achieve desired optical conditions. A brief list is shown
884 below; for a detailed discussion we refer to Aphalo et al. (2012).

885 Fluorescent lamps and tubes are low pressure mercury vapor lamps that emit radiation at specific spectral
886 lines, mostly in the UV region of the spectrum

887 Xenon arc lamps are specialized light sources that produce intense visible and UV radiation. High intensity
888 water-cooled deuterium lamps (150 W) have a fairly flat radiant intensity curve in the UV-B region that is
889 appropriate for mechanistic plant UV photobiology studies.

890 Spectrographs composed of a light source and a monochromator may be used in applications requiring
891 spectrally-resolved UV radiation exposure of biological specimens. Lasers usually produce very narrow and
892 intense beams of monochromatic light. For the purpose of UV photobiology, tuneable optical parametric
893 oscillator (OPO) pump lasers (pump wavelength 355 nm) are especially useful.

894 Specific experimental setups for studying UV-effects on plant gas emissions are described in detail in
895 literature cited above, and illustrate the complexity and experimental precautions associated with such
896 studies. As an example, Vigano et al. (2008) used 6 types of lamps, one PAR lamp, four UV-A and UV-B
897 lamps, and one UV-C lamp. The UV content (UV-A and UV-B separately) was determined with a Waldmann
898 UV meter calibrated for each individual UV lamp, except for the UV-C lamp. These authors did not report on
899 the action spectrum for CH₄ release from biomass upon UV irradiation, and the UV strength was reported
900 as the non-weighted integral over the UV-A range (400–320 nm), UV-B range (320–280 nm) or total UV
901 range (400–280 nm). By choosing this approach (using unfiltered, non-weighted UV radiation) the authors
902 neglected a possible wavelength dependence of the biologically effective dose (Vigano et al. 2008). Bruhn
903 et al. (2009), in addition to PAR lamps, used four different lighting sources to obtain desired UV-B and UV-A
904 irradiance; the UV sources were placed at varying distances to yield the reported irradiances. The irradiance
905 spectra of the experimental tubes and the transmission spectra of the glass vials used were further
906 established in order to reveal wavelength dependent responses in the experiments.

907

908

909 **Appendix B**

910 **Global drivers for CO and N₂O contribution**

911 Global CO and N₂O up-scaling was based on the parameterized response equations to UV-irradiation and
912 temperature (see Bruhn et al. 2013, 2014b; Appendix C).

913 The drivers were driven by geospatial satellite information on UV-B temperature and land surface
914 classifications derived from normalized difference vegetation index (NDVI) and snow cover (SC). The
915 UV310nm data was obtained from the Giovanni OMI/Aura Online Visualization and Analysis Daily Level 3
916 Global Gridded Products (<http://giovanni.sci.gsfc.nasa.gov/giovanni/>), the temperature data from MODIS
917 (Moderate Resolution Imaging Spectroradiometer, NASA Earth Observations, <http://neo.sci.gsfc.nasa.gov>)
918 and NDVI, LAI, and SC data from NASA Earth Observations (<http://neo.sci.gsfc.nasa.gov/>) and handled in a
919 global longitude/latitude grid (250×150). The effect of UV was scaled with the global UV Irradiance at 310
920 nm at surface level (averaged across the years 2005, 2007, 2009, Local Noon Time). Temperature
921 dependence was scaled based on daytime land surface temperatures averaged per month (over the ten
922 years 2001–2010) of available data. The temperature response parameterization did not include
923 temperatures below 0°C, while the CO/N₂O emission from grids with a temperature below 0°C were set to
924 zero in the up-scaling. Land surface area was determined from satellite land dataset information and the
925 area was calculated from longitude/latitude information. Snow cover (SC) was averaged per month (2009)
926 and we excluded areas covered by snow. The remaining land surface area was classified as being vegetation
927 covered or vegetation free based on the NDVI. The up-scaling approach was conservative in the way that
928 the surface area did not include topography. Further, most of the UV-radiation received by leaf surfaces are
929 indeed screened (absorbed or reflected) by the surface wax (Cen and Bornman, 1993; Liakoura et al. 2003;
930 Jacobs et al. 2007). Therefore, for the global estimate of the UV-effect on CO/N₂O emission by vegetation,
931 we assumed an effective Leaf Area Index (LAI) of unity. The proportions of vegetation and sand area were
932 determined by NDVI classification. Response functions for plants were applied to surface covered by
933 vegetation. The NDVI were averaged per month (2009). Correlations between LAI satellite measurement
934 and NDVI from 2009 showed that for instance NDVI around 0.3, 0.5, 0.7 and 0.75 reflects vegetation with
935 0.4, 0.9, 2.0 and 4.0 layers of leaves per ground area (LAI) respectively (data not shown). This information
936 was used to construct four groups with different distributions among vegetation and vegetation free
937 surfaces. The groups are: (1) NDVI<0.2, 100% sand; (2) 0.2<NDVI<0.4, 60% sand and 40% vegetation; 3)
938 0.4<NDVI<0.6, 20% sand and 80% vegetation; and (4) NDVI>0.6, 100% vegetation. These vegetation cover
939 values are lower than a derivation from the NDVI LAI relationship would indicate, but since vegetation
940 cover is clustered by nature with LAI values up to over 5, this must result in more vegetation free areas
941 than an average estimate would produce. For up-scaling, any LAI above 1 would give the same values. This
942 division into group categories decides the percentage area of vegetation and vegetation-free combination
943 in each of the 250×150 grid cells.

944

945 **Appendix C**

946 **Response functions for global CO and N2O contribution**

947 For each of 250×150 grid cells (Appendix B) we estimated the CO or N₂O emission rate (*ER*) on a monthly
948 basis as

$$ER = \alpha \times e^{\beta \overline{T_{day}}} \times \frac{\overline{UV}}{50} \overline{days \times DL} \times area \times \left(1 - \frac{area_{sc}}{area}\right) \times prop_{cat}$$

949 where α is a base *ER* of ecosystem CO or N₂O emission (nmol m⁻² h⁻¹) measured at 21.4 °C and 50 mW UV-B
950 (see Bruhn et al. 2013, 2014b). We assumed a response to temperature, $(T) = \alpha \times e^{\beta T}$, as measured at
951 leaf level (Bruhn et al. 2013, 2014b) when exposed to UV-B. In the up-scaling we substituted T with a mean
952 daytime temperature for the respective grid cell, $\overline{T_{day}}$. As we have demonstrated near-linear relationships
953 between irradiance of both UV-B and UV-A and CO and N₂O emissions, respectively (Bruhn et al. 2013,
954 2014b), we scaled the base *ER* of ecosystem CO or N₂O emission with the mean UV Irradiance (mW) at 310
955 nm at surface level for the grid cell. Further, *ER* for grid cell was adjusted according to the monthly average
956 day length per month, \overline{DL} , number of days per month, area and category of land vegetation.

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