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1 Differences in isoprene and monoterpene emissions from 2 cold-tolerant eucalypt species grown in the UK

3 Gemma Purser*^{1,2}, Mathew R. Heal², Stella White¹, James I.L. Morison³, Julia Drewer¹

4 ¹ UK Centre for Ecology & Hydrology, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK

5 ² School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster
6 Road, Edinburgh, EH9 3FJ, UK

7 ³ Forest Research, Alice Holt Lodge, Farnham, Surrey, GU10 4TT, UK

8 *Corresponding author

9

10 **Keywords**

11 eucalyptus, biogenic VOCs (BVOC), pinene, eucalyptol, bioenergy, short-rotation coppice,
12 air quality, ozone, SOA.

13

14 **Abstract**

15 The UK may be required to expand its bioenergy production in order to make a significant
16 contribution towards the delivery of its 'net zero' greenhouse gas emissions target by 2050.
17 However, some trees grown for bioenergy are emitters of volatile organic compounds
18 (VOCs), including isoprene and terpenes, precursors in the formation of tropospheric ozone,
19 an atmospheric pollutant, which require assessment to understand any consequent impacts
20 on air quality. In this initial scoping study, VOC emission rates were quantified under UK
21 climate conditions for the first time from four species of eucalypts suitable for growing as
22 short-rotation forest for bioenergy. An additional previously characterised eucalypt species
23 was included for comparison. Measurements were undertaken using a dynamic chamber
24 sampling system on 2-3 year-old trees grown under ambient conditions. Average emission
25 rates for isoprene, normalised to 30 °C and 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ PAR, ranged between 1.3 μg
26 $\text{C g}_{\text{dw}}^{-1} \text{h}^{-1}$ to 10 $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$. All the eucalypt species measured were categorised as
27 'medium' isoprene emitters (1–10 $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$). Total normalised monoterpene emission

28 rates were of similar order of magnitude to isoprene or approximately one order of
29 magnitude lower. The composition of the monoterpene emissions differed between the
30 species and major components included eucalyptol, α -pinene, limonene and β -cis-ocimene.
31 The emission rates presented here contribute the first data for further studies to quantify the
32 potential impact on UK atmospheric composition if there were widespread planting of
33 eucalypts in the UK for bioenergy purposes.

34

35 **1. Introduction**

36 A number of volatile organic compounds (VOCs), particularly isoprene, monoterpenes and
37 monoterpenoids, classified collectively here as terpenes, are trace gas secondary
38 metabolites that can be emitted from vegetation. It has been suggested that these biogenic
39 VOCs may provide a form of regulation against heat stress (Sharkey et al., 2008),
40 communication and can act as a defence mechanism against disease and predation
41 (Niinemets and Monson, 2013). Terpenes are highly reactive compounds whose oxidation in
42 the lower atmosphere can lead to the formation of secondary organic aerosols (SOA) and, in
43 the presence of nitrogen monoxide (NO), to the production of ozone (O_3). Terpene
44 composition has been found to be an important factor in the magnitude of ozone production
45 (Bonn et al., 2017). Both SOA and O_3 have climate impacts: SOA acts as cloud
46 condensation nuclei (Wang et al., 2016) and tropospheric O_3 is a greenhouse gas
47 (UNEP/WMO, 2011). They both also have detrimental effects on human health, the SOA risk
48 arising because it is a component of fine particulate matter ($PM_{2.5}$) (WHO, 2013). In addition,
49 O_3 causes plant damage (Felzer et al., 2007) leading to reduced agricultural crop yields
50 (Wilkinson et al., 2012). In regions of high NO emissions relative to VOC emissions, such as
51 the UK, VOCs are normally the limiting factor in O_3 formation (Finlayson-Pitts and Pitts,
52 1993). Experimentally-derived VOC emission rates from different types of vegetation are
53 important for the estimation of tropospheric O_3 concentration in regional air quality models.

54

55 Eucalyptus, a tree genus native to predominately mainland Australia and Tasmania, is a
56 known emitter of VOCs. Some eucalypt species, mainly from Tasmania (and some
57 mountainous regions of south-east Australia), are able to tolerate and grow well in colder
58 climates (Williams and Potts, 1996). These species have been the recent focus of
59 assessment and development for bioenergy trials within the UK (Leslie et al., 2019, 2012;
60 Purse and Leslie, 2016; Purse and Richardson, 2001; Stokes, 2015). The UK is required to
61 increase its bioenergy contribution to renewable resources of energy in the future in order to
62 meet the 2050 net zero greenhouse gas emissions target (Committee on Climate Change,
63 2019) which has now been adopted in UK law. Solutions to increase bioenergy production
64 could include planting of short-rotation forest (SRF) and short-rotation coppice (SRC)
65 eucalypts.

66
67 SRF uses single stem trees, as in a conventional forest plantation, but planted at a higher
68 density with a 10 – 20 year rotation (the age at which the trees will be harvested). SRC are
69 usually multi-stem trees; the above ground biomass is harvested on a rotation of 2-5 years
70 and new biomass grows from the rootstock which remains in the ground. The plantation only
71 needs replanting after 20-30 years (Drewer et al., 2018). Both SRF and SRC produce a fast-
72 growing supply of biomass for technologies such as bioenergy with carbon capture and
73 storage (BECCS) but their expansion could lead to changes in VOC emissions across the
74 UK and subsequent changes in air quality, dependant on the species grown. Eucalypts, can
75 be grown as SRF or SRC depending on the growth habit of individual species, with likely
76 rotation of <10 years (Purse and Richardson, 2001). Height growth rates for *E. gunnii* in the
77 UK have been shown to be between 1-2 m per year (Leslie et al., 2018).

78
79 However, there is still substantial uncertainty regarding the magnitude and variability of VOC
80 emissions across eucalypt species, including the profile of compounds emitted. Only a few of
81 the approximately 800 species of eucalypts (Coppen, 2002) have had their natural VOC
82 emissions to the atmosphere investigated. In addition, the majority of studies have been

83 conducted with trees acclimatised to warmer and sunnier climates than found in the UK
84 (Emmerson et al., 2020; Evans et al., 1982; He et al., 2000a; Sørensen et al., 2020; Street et
85 al., 1997; Winters et al., 2009); VOC emission rates for cold tolerant eucalypt species
86 suitable for growing in the UK have not been measured. Hence more data are needed to
87 subsequently determine whether extensive planting of SRF eucalypts will contribute
88 significantly to VOC emissions across the UK and to consequent changes in air quality
89 (Drewer et al., 2018).

90

91 VOCs reported as being emitted from eucalypts include isoprene and a range of
92 monoterpenes and functionalised monoterpenes (i.e. monoterpenoids), for example: α -
93 pinene, β -pinene, eucalyptol, limonene, cis-ocimene, terpineol, p-cymene, α -phellandrene
94 and β - phellandrene (Aylott et al., 2008; Franich, 1985; Guenther et al., 1991; He et al.,
95 2000a; King et al., 2006; Owen and Peñuelas, 2013; Rasmussen, 1972; Street et al., 1997;
96 Winters et al., 2009). Both light and temperature can affect the emission rates of isoprene
97 and monoterpenes from leaves of eucalypts (Guenther et al., 1991). The production of
98 terpenes is linked to the activity of isoprene synthase and terpene synthase enzymes which
99 are themselves linked to primary metabolic processes such as photosynthesis (Niinemets,
100 2015). However, previous studies have found variation in the total emission rates of isoprene
101 and monoterpenes between different species of eucalypt and the relative percentages of the
102 types of monoterpenes emitted (He et al., 2000a, 2000b; Owen and Peñuelas, 2013; Winters
103 et al., 2009). Ratios of monoterpenes in the leaf may be influenced by environmental factors
104 such as temperature, seasonality and herbivory, in addition to genetic variation (Keszei et
105 al., 2008). Therefore, individual measurements of each species under specific growth
106 conditions representative of a particular region are required to determine appropriate VOC
107 emission rates for country specific assessments. In addition, although within-leaf
108 monoterpene concentrations from whole leaf extractions of oil glands reported previously (Li
109 et al., 1996) may be used to provide a qualitative assessment of the types of monoterpenes

110 emitted by different eucalypt species they may not be able to give an indication of the natural
111 emission rates for some terpenes due to the plant generating “de novo” terpenes, that are
112 emitted directly into the atmosphere shortly after the point of synthesis (Ghirardo et al.,
113 2010). It is well known that emissions of VOCs can vary by orders of magnitude between
114 species, so the intention here was to investigate these relative magnitudes. This scoping
115 study aimed to quantify VOC emission rates of four previously unmeasured eucalypt species
116 potentially suitable for UK bioenergy SRF or SRC and categorise them according to previous
117 literature (Evans et al., 1982; He et al., 2000a) as “low”, “medium” or “high” emitters for
118 isoprene and monoterpenes to help focus future assessment of the impact of any of eucalypt
119 planting on UK air quality.

120

121 **2. Materials and Methods**

122 2.1 Plant specimens and growing conditions

123 Two trees of five different species of immature pot-grown eucalypts (aged 2-3 years) were
124 sourced from a specialist UK-based eucalypt grower (hardy-eucalyptus.com, Grafton
125 Nursery, Worcester, UK). The selected species were *E. pauciflora subsp. debeuzevillei*, *E.*
126 *johnstonii*, *E. cordata subsp. quadrangulosa*, *E. subcrenulata* and *E. globulus subsp.*
127 *bicostata*. Additionally, emissions from individual trees of a further four UK climate tolerant
128 eucalypt species were also measured during this study. These data are available in the
129 Supplementary Information (SI) but do not form part of the discussion presented here (Table
130 S1).

131

132 The trees were initially grown from seed in specialist air-pots® (Caledonian Tree Co. Ltd,
133 Scotland) to promote continued growth of the roots. The 5 L pots were watered daily, and
134 the trees fed weekly with chempak number 4®, high potash feed in accordance to the
135 grower’s recommendations. The trees were acclimatised outdoors for one year at the UK
136 Centre for Ecology & Hydrology (UKCEH), near Penicuik, Scotland (55° 49’ 33.6’ N, 3° 13’

137 12' W) prior to conducting the measurements. Trees were sampled for either 4 or 5 dry days
138 between June and August 2019 typically during the afternoons between 12 am and 6 pm.
139 Sampling days are given in the SI Table S2. Based on long-term hourly site monitoring data
140 collected at UK CEH the average midday air temperature in June, July and August 2019 was
141 11.8, 16.0 and 14.5 °C, respectively. Average midday photosynthetically-active radiation
142 (PAR) was 413, 364 and 346 $\mu\text{mol m}^{-2} \text{s}^{-1}$, for June, July and August. The majority (70%) of
143 the samples were collected in August. Table 1 shows the range of air temperature and PAR
144 during sample collection. Given that both air temperature and PAR are highest during June
145 to August (see SI Figure S1) it is reasonable to assume that VOC emission rates are likely to
146 peak at this time of year for this locality.

147

148 2.2 Chamber sampling method

149 A polyethylene terephthalate (PET) bag (Roast-in-oven bags, Lakeland, Windermere, UK)
150 with a transmissivity of 90% and dimensions 33 x 43 cm (approximately 6 L volume) was
151 gently attached around the stem of a small branch of similar aged leaves along with a
152 temperature and relative humidity probe (CS215, Campbell scientific, Shepshed, UK) and
153 two PTFE tubing lines, one for the inflow of ambient air and one for chamber air sampling
154 (Ortega et al., 2008; Stewart-Jones and Poppy, 2006; Vedel-Petersen et al., 2015). Only
155 leaves fully exposed to the sun were sampled. Temperature and relative humidity were
156 sampled inside the bag every minute. An opening was made at one corner of the bag to
157 allow a steady flow of ambient air through the bag and was smaller in diameter than the
158 inflow line (Sørensen et al., 2020). The air flow was delivered from an oil-free double-ended
159 diaphragm pump (Capex V2, Charles Austen pumps Ltd, Surrey, UK) (Morrison et al., 2016)
160 through PTFE tubing at a flow rate between 2-5 L min^{-1} . The air volume was therefore
161 replaced approximately every 1.2-3 min, comparable to previous studies (He et al., 2000a;
162 Winters et al., 2009). The bag was flushed for up to 15 min prior to sample collection. A
163 slight over-pressure of ambient air allowed the sample bags to become inflated, preventing

164 the foliage from rubbing against the sides of the bag (Ortega et al., 2008; Sørensen et al.,
165 2020). No filter was used on the ambient air supply during sample collection, so information
166 for local average ozone concentrations monitored nearby are provided in SI Table S3 to
167 indicate the conditions under which the branch chamber measurements were conducted.
168 The hourly ozone concentration from the nearby monitoring station ranged from 48-117 μg
169 m^{-3} across the sample days. Whilst it is possible that some ozone entering the chamber may
170 have been lost to the chamber walls (Janson, 1993), it is also possible that the ozone
171 reacted with VOCs emitted from the eucalyptus branches prior to sample collection thereby
172 reducing measured emission rates. As such these emission rates should be considered to
173 be lower estimates of emission rates for eucalyptus species grown and measured under
174 typical UK field conditions.

175

176 The PTFE sample line exiting the bag was attached to a hand pump (210-1003MTX, SKC
177 Ltd, Blandford Forum, UK) drawing air from inside the bag at a flow rate of 200 mL min^{-1}
178 through a 6 mm OD stainless steel automated thermal desorption (ATD) tube (PerkinElmer,
179 Waltham, MA, USA) packed with 200 mg Tenax TA 60/80 (11982 SUPELCO, Sigma-Aldrich,
180 St Louis, MO, USA) and 100 mg Carbotrap 20/40 (20273 SUPELCO, Sigma-Aldrich).

181 Ambient air outside the bag and air from inside the bag were sampled concurrently for about
182 30 min resulting in a 6 L sample. Three sequential samples were collected over a 1.5 h
183 period per sampling day. The sample tubes were stored in a fridge at $4 \text{ }^{\circ}\text{C}$ prior to analysis.

184

185 Measurements of PAR (SKP 215 PAR Quantum Sensor, Skye instruments, Llandrindod
186 Wells, UK) were made at 1-min intervals adjacent to the trees during the sampling but was
187 also separately archived hourly, along with ambient temperature, by a meteorological station
188 at UKCEH. PAR measurements taking outside of the chamber were corrected for a 90%
189 transmissivity of the chamber material to give PAR values appropriate to internal chamber
190 conditions.

191

192 2.3 Analytical method

193 The VOCs collected on the sorbent were analysed using gas chromatography-mass
194 spectrometry (GC-MS) with a two-stage automatic thermal desorption unit (ATD 400, Perkin-
195 Elmer, Wellesley, MA, USA). The samples were desorbed at 280 °C for 6 min under a flow
196 of helium and were subsequently trapped onto a Tenax TA cold trap at 30 °C. The second
197 stage of desorption was achieved by flash heating the cold trap to 300 °C for 6 min to flush
198 the sample through a heated transfer line (200 °C) onto the GC column (Ultra-2 column, 100
199 m length, 0.2 mm I.D., 5% phenylmethyl silica, Agilent, Palo Alto, CA, USA). The oven was
200 held at 35 °C for 2 min, ramped to 160 °C at 3 °C min⁻¹ and then to 280 °C at 45 °C min⁻¹
201 before being held at 280 °C for 10 min (as used in Morrison et al., 2016). Eluting compounds
202 were detected using a tuned Perkin Elmer mass spectrometer (Clarus 500, Perkin Elmer,
203 Wellesley, MA, USA) operating in total ion count mode.

204

205

206 2.4 Calibration

207 Standards were measured at the start and end of each GC-MS sample run. Isoprene
208 standards were prepared by direct sampling onto a sorbent tube from a certified 700 ppbv
209 gas standard (BOC, UK) for 10, 30, 45 and 60 s using a sample pump (210-1003MTX, SKC
210 Ltd, Blandford Forum, UK) producing standards of 65, 198, 296 and 395 ng. Standards (from
211 Sigma-Aldrich, Gillingham, UK) of the monoterpenes α -pinene, β -pinene, limonene, α -
212 phellandrene, β -phellandrene, 3-carene, camphene, γ -terpinene and β -myrcene, and the
213 monoterpenoids (monoterpene-based compounds with, for example, additional oxygen or
214 missing a methyl group) eucalyptol and linalool were prepared as a mixed stock solution of 3
215 ng μL^{-1} in methanol. (The term monoterpene is used henceforth in this paper to refer to all
216 measured compounds based on the C₁₀ monoterpene formula.)

217

218 Aliquots of 1, 2, 3 and 4 μL of the mixed monoterpene stock solution were pipetted directly
219 onto sample tubes under a flow of helium to produce a range of mixed monoterpene
220 standards of 3, 6, 9 and 12 ng. Note that mass loadings of isoprene and monoterpene
221 calibration standards were prepared to greater precision than quoted above but are shown
222 here as nominal values for ease of discussion. Unknown peaks in sample chromatograms
223 were identified by comparison to the internal library of the GC-MS (National Institute of
224 Standards and Technology) and by comparison with the retention time of the standard. Peak
225 areas were used in analyte quantification calculations. No calibration standard was available
226 for β -cis-ocimene, so this was analysed semi-quantitatively using the peak area ratio for the
227 identified β -cis ocimene peak against α -pinene and then multiplied by the mass of α -pinene
228 to give an estimate of the mass of β -cis ocimene collected on the sample tube.

229

230 The limit of detection (LoD) for each analyte was calculated using repeated blank
231 measurements to initially calculate the limit of the blank (LoB) for each analyte and then
232 using this with the standard deviation of repeats of the lowest standard concentration for
233 each analyte (isoprene nominal 65 ng and monoterpenes nominal 3 ng) to give an LoD for
234 the analytical method as a mass (ng) (Armbruster and Pry, 2008). Calculated LoDs were as
235 follows: isoprene (21 ng), α -pinene (0.78 ng), β -pinene (0.90 ng), β -phellandrene (0.91 ng),
236 β -myrcene (1.00 ng), α -phellandrene (1.06 ng), limonene (0.60 ng), γ -terpiene (103 ng), 3-
237 carene (0.94 ng), eucalyptol (1.76 ng), camphene (0.92 ng) and linalool (113 ng). In some
238 instances, very low emission rates of a VOC from the eucalypt branch may have resulted in
239 the mass (ng) of VOC collected being less than the respective LoD. During this study, 75%
240 of the samples measured for isoprene were greater than the LoD, although only 4% of those
241 measured for camphene. An example of an emission rate LoD based on the analytical LoD
242 (ng) is $0.16 \mu\text{g C gdw}^{-1} \text{h}^{-1}$ ($16 \mu\text{g C m}^{-2} \text{h}^{-1}$) for isoprene and for monoterpenes (limonene
243 and eucalyptol respectively) in the range of $0.0045\text{-}0.013 \mu\text{g C gdw}^{-1} \text{h}^{-1}$ ($0.45\text{-}1.3 \mu\text{g C m}^{-2}$
244 h^{-1}) assuming the following parameters: 30 min subsample at a flow rate of 200 mL min^{-1}

245 from a chamber containing a nominal total leaf mass of 4 g or total leaf area of 0.04 m² with
246 a chamber flow rate of 3 L min⁻¹.

247

248 2.5 Calculation of VOC emission rates

249 Subsequent to VOC sampling, the leaves of each branch were collected and scanned using
250 a LI-3100c area meter (LI-Cor Inc, Lincoln, NE, USA) to give single-sided leaf surface area
251 (m²). The leaves were then weighed prior to and after drying to constant mass in an oven at
252 70 °C for 48 h. This permitted VOC net foliage emission rate (ER) to be expressed on either
253 a leaf area, *A*, basis (µg C m⁻² h⁻¹), or a leaf dry mass, *m_{dry}*, basis (µg C g_{dw}⁻¹ h⁻¹), according
254 to Equations 1 and 2.

255 Equation 1 $Leaf\ mass\ ER = \frac{[C_{out} - C_{in}] \times Q}{m_{dry}}$

256 Equation 2 $Leaf\ area\ ER = \frac{[C_{out} - C_{in}] \times Q}{A}$

257 In these equations, *Q* is the flow rate of ambient air through the chamber and *C_{out}* and *C_{in}*
258 are the concentrations of VOC (µg L⁻¹) collected on the sorbent tubes for the ambient air
259 and chamber samples, respectively, with VOC mass scaled to per hour equivalent and
260 expressed as the VOC carbon content.

261

262 Average chamber temperature and PAR were measured for the duration of each individual
263 30 min sample. Both PAR and temperature are known to influence the emission rates of
264 isoprene (Guenther et al., 1993) and so all isoprene measurements were normalised to 1000
265 µmol m⁻² s⁻¹ PAR and 30 °C. It is acknowledged that emissions of some monoterpenes, such
266 as, α-pinene, may also be produced during de novo synthesis with their emission rates
267 changing in response to fluctuations in PAR (Ghirardo et al., 2010). However, eucalypt
268 leaves contain numerous sub-dermal secretory cavities, referred to here as oil storage
269 glands, which have been shown to contain largely monoterpenes and are likely the dominant
270 source of monoterpene emissions. Therefore, emissions of all monoterpene compounds are
271 in this instance only normalised for temperature (30 °C) in accordance with the algorithm

272 developed by Guenther et al. (1993). The normalised emission rates for each sample were
273 then averaged (including instances of samples with no apparent emission rate or only trace
274 emission rate) to produce a single emission rate per species (Table 1). The average
275 uncertainties for a calculated emission rate was 16% for isoprene and 17% for monoterpene
276 emissions which were derived from the uncertainty in the following measured and calculated
277 parameters: interpolation from the relevant calibration regression fit; sample time; chamber
278 volume; chamber flow rate; sample pump flow rate, foliage dry mass or leaf area;
279 temperature; PAR. The error propagation equation and the error assigned to each parameter
280 is described in Supplementary Information Section S1.

281

282 **3. Results and discussion**

283 3.1 Isoprene emissions

284 Isoprene was emitted by all five eucalypt species and the average normalised emission rate
285 for each species measured in this study is shown in Figure 1. The number and ranges of
286 emission rates, together with the ranges of PAR, chamber temperature and humidity across
287 the sampling periods, are presented in Table 1.

288

289 The species with the largest isoprene emission based on leaf mass was *E. globulus subsp.*
290 *Bicostata*, averaging $10.1 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ($704 \mu\text{g C m}^{-2} \text{h}^{-1}$), and based on leaf area was
291 *E.subcrenulata*, averaging $1136 \mu\text{g C m}^{-2} \text{h}^{-1}$ ($6.16 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$). The lowest average
292 emission rate was about an order of magnitude less, from *E. pauciflora subsp. debeuzevillei*
293 at $1.31 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ($183 \mu\text{g C m}^{-2} \text{h}^{-1}$). Eucalypts have been generically categorised as
294 high emitters of isoprene (i.e. $\text{ER} > 10 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$), with previous reported measurements
295 being in the range $10\text{-}33 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ (Evans et al., 1982).

296 However, in this study all the eucalypt species studied are categorised as medium emitters,
297 with emission rates between $1\text{-}10 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$. Although *E. globulus* gave an emission rate

298 of 10.1 $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ this is not deemed significantly greater than 10 to classify it in the high
299 emitter category.

300

301

302 PAR fluctuated across the sampling campaign depending on the time of day, day of the year
303 and local cloud cover, and, consistent with previous literature (Guenther et al., 1991; He et
304 al., 2000a; Winters et al., 2009), isoprene emission rates were generally observed to
305 increase with increasing PAR although the relationship between isoprene emissions and
306 PAR for some species was less clear. Figure 2 shows an example for *E. subcrenulata*. It is
307 noted that two measurement for PAR between 400 - 700 $\mu\text{mol m}^{-2} \text{s}^{-1}$ measured on the same
308 day seem to be outliers, the reasons for which are unclear. The remaining data exhibit a
309 significant relationship between isoprene and PAR ($R^2 = 0.47$, $P = 0.01$).

310

311 3.3 Isoprene emission comparisons with other studies

312 This study reports the first investigation into the isoprene emission rates for *E. pauciflora*
313 *subsp. debeuzevillei*, *E. johnstonii*, *E. cordata subsp. quadrangulosa*, and *E. subcrenulata*,
314 so no direct comparisons to literature values are possible. However, emission rates from *E.*
315 *globulus* have been reported previously, as summarised in Table 2, so can serve as a guide
316 on the validity of the measurements in this study for the previously untested species. It is
317 worth noting, however, that the subspecies of *E. globulus* measured in previous studies is
318 not documented and different subspecies may well have different emission rates. The *E.*
319 *globulus subsp. bicostata* subspecies investigated here is a more cold-tolerant subspecies
320 and the seed provenance from which they are grown will reflect this, which in turn could
321 produce genetic compositions that yield differing VOCs. This has been noted for
322 monoterpene composition (Boland et al., 1982).

323

324 The average emission rate for *E. globulus subsp. bicostata* measured in this study was lower
325 than those reported by Evans et al. (1982) and He et al. (2000a) when compared on a dry
326 leaf mass basis (Table 2). These earlier studies were conducted on trees that likely
327 experienced much warmer growing conditions. However, the emission rates reported here
328 are of the same order of magnitude as those from measurements conducted on mature
329 foliage during a field campaign in Australia in which cool and cloudy weather was reported
330 (Winters et al., 2009). These latter sampling conditions would be closer to those
331 encountered in Scotland when the measurements in the present study were made. The
332 temperature at which plants develop, in addition to the temperature and light conditions in
333 the days prior to leaf sampling, have been found to influence emission rates of isoprene due
334 to the regulation of the enzyme, isoprene synthase and the production of dimethylallyl
335 diphosphate (DMADP), the substrate required for isoprene production (Monson et al., 1992;
336 Sharkey et al., 2008). This may explain to some degree the lower isoprene emission rates
337 for *E. globulus subsp. bicostata* measured during the present study. In direct sunlight on hot
338 days the temperatures inside the chamber during sample collections were higher than
339 ambient temperatures (by between 2 and 9 °C) which is a common effect of using this type
340 of methodology to collect VOC emissions (He et al., 2000a; Ortega and Helmig, 2008) and
341 low flow rates for chamber flushing – but on no occasion did chamber temperature exceed
342 the critical threshold of 38 °C, above which enzyme deactivation occurs and a decline in
343 isoprene emission from *E. globulus* has been reported (Guenther et al., 1991). It is also
344 worth noting that the isoprene emissions from *E. globulus subsp. bicostata* measured in this
345 study were within the range of isoprene emission rates reported for a UK-based greenhouse
346 study (with artificially enhanced light conditions) (Owen and Peñuelas, 2013) (Table 2).

347

348 It has been suggested that levels of the isoprene synthase enzyme that regulates isoprene
349 emissions can be lower in immature leaves of some species (Vickers et al., 2010). In this
350 regard, the emissions from the new immature foliage of *E. globulus subsp. bicostata* on a
351 leaf area basis compared very well with similar immature foliage (<15 days old) at standard

352 conditions reported by Guenther et al. (1991) and on a leaf mass basis with the young
353 leaves of reported by Street et al (1997) (Table 2). This type of immature, young and rapidly
354 expanding foliage is highly representative of the first few years of eucalypt plantations that
355 are managed as short-rotation coppice. In these situations, the multi stemmed trees can
356 grow up to 2 m per year (Leslie et al., 2018).

357

358 3.4 Total monoterpene emissions

359 Average total normalised monoterpene emission rates were generally low across all five
360 eucalypt species (Figure 1 and Table 1). Total monoterpene emission rates varied from
361 $0.304 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ($52.6 \mu\text{g C m}^{-2} \text{h}^{-1}$) for *E. jonstonii* to $1.73 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ($302 \mu\text{g C m}^{-2} \text{h}^{-1}$)
362 for *E. cordata subsp. quadrangulosa*, except for *E. globulus bicostata* which had an almost
363 10-fold higher emission rate of $14.1 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ($949 \mu\text{g C m}^{-2} \text{h}^{-1}$). It was noted that the
364 highest emitting monoterpene species, *E. globulus subsp. bicostata* and *E. cordata subsp.*
365 *quadrangulosa*, had much softer new-growth foliage and waxier leaves than the other
366 species which often produced thicker sturdier leaves. Total normalised monoterpene
367 emission rates are generally the same or one order of magnitude lower than normalised
368 emission rates measured for isoprene (Table 1), which has been reported in previous
369 eucalypt studies (Emmerson et al., 2016; He et al., 2000a).

370

371 Emission rates of monoterpenes from leaves are known to be driven by the monoterpene
372 vapour pressure, which is dependent on compound volatility, oil gland concentration and air
373 temperature (Lerdau et al., 1997). In addition, it is well known that monoterpene emission
374 rates increase with temperature (Emmerson et al., 2020; Guenther et al., 1991; He et al.,
375 2000a; Nunes and Pio, 2001; Street et al., 1997; Tingey et al., 1980). During this study,
376 temperature associations with monoterpene emissions were observed for some of the
377 species such as *E. pauciflora subsp. debeuzevillei* (Figure 3), although given the similar
378 temperatures at which daily measurements were conducted this was not always obvious in

379 all species. Temperature can also act to regulate the productivity of the terpene synthase
380 enzymes and so alter the concentration of monoterpene found in the leaf glands, which will
381 have an impact upon leaf emissions. Some monoterpenes such as α -pinene may also be
382 light sensitive and their production via de novo synthesis can be correlated to the level of
383 PAR. During this study however, no clear correlation was observed between monoterpene
384 emissions and PAR which suggests that the monoterpenes may have been directly emitted
385 from the storage glands. It is worth noting that emission rates from any previous field-based
386 studies used as a species comparison here are likely also to be influenced by a range of
387 other environmental factors such as limited availability of water (Bonn et al., 2019) in
388 contrast to the well-watered trees used in the present work.

389

390 3.5 Total monoterpene emission comparisons with other studies

391 This study reports the initial assessment of monoterpene emission rates to the atmosphere
392 for *E. pauciflora subsp. debeuzevillei*, *E. johnstonii*, *E. cordata subsp. quadrangulosa*, and *E.*
393 *subcrenulata* so no direct comparisons to literature values are possible. A comparison of the
394 emission rates from *E. globulus subsp. bicostata* from this study with previous literature is
395 presented in Table 2.

396

397 The monoterpene emissions from *E. globulus subsp. bicostata* reported in this study are
398 comparable to those reported by He et al. (2000a) but are three times lower than those
399 reported for the same species by Winters et al. (2009). The monoterpene emissions
400 measured from *E. globulus subsp. bicostata* in this study were also within the range reported
401 by one other UK study (Owen and Peñuelas, 2013), though these latter emission rates were
402 not normalised to standard conditions. It has been suggested that monoterpene emissions
403 from experiments on eucalypts may arise initially via a process of leaf damage to the
404 subcuticular glands rather than an active release process (Guidolotti et al., 2019). However,
405 this suggestion does not fully explain the similar monoterpene emission rates (for a given

406 species) observed across studies, including this one, that have been measured in different
407 locations and under a range of experimental conditions.

408

409 3.6 Monoterpene composition

410 All five eucalypt species emitted similar monoterpenes but the relative proportions of these
411 compounds varied across species as is evident in Figure 4. The major monoterpenes
412 emitted from all five eucalypts were eucalyptol, β -cis-ocimene, α -pinene and limonene
413 (Table 1 and Figure 4). The compounds β -pinene, β -myrcene, α -phellandrene, β -
414 phellandrene and 3-carene were also quantified (Table 1). Small amounts of other
415 monoterpenes were found in the samples but were not positively identified or quantified as
416 they were not part of the calibration and proportionally not important.

417

418 Monoterpene emissions from *E. globulus subsp. bicostata* were dominated by eucalyptol,
419 accounting for 60% of the total monoterpene emissions. Other species such as *E.*
420 *debeuzevillei* and *E. cordata subsp. quadrangulosa* are both high emitters of β -cis-ocimene
421 while *E. subcrenulata* and *E. johnstonii* emitted roughly similar proportions of eucalyptol, α -
422 pinene and limonene or eucalyptol and α -pinene respectively.

423

424 Monoterpene emissions from *E. globulus* are well represented in literature (Evans et al.,
425 1982; Guenther et al., 1991; He et al., 2000a; Kanagendran et al., 2018; Nunes and Pio,
426 2001; Owen and Peñuelas, 2013; Rasmussen, 1972; Street et al., 1997; Winters et al.,
427 2009). The emissions of eucalyptol, the predominant emitted monoterpene found for *E.*
428 *globulus* in this study, compared well with those from new foliage (<15 days old) reported by
429 Guenther et al. (1991). However, *E. globulus* has previously been reported to be a major α -
430 pinene emitter (Guenther et al., 1991), whereas here it was observed to be a predominantly
431 eucalyptol emitter. Intrinsic natural variation between individuals of the same species is a
432 possible explanation. The chemical variation of monoterpenes found in the oil-bearing

433 glands of some eucalypt species has been linked to the genetic variation within the genus
434 (Borzak et al., 2015; Keszei et al., 2010; Külheim et al., 2015; Padovan et al., 2017, 2012;
435 Shepherd et al., 1999). In some instances, different chemotypes of a species may arise, with
436 some individuals of the same species having emissions dominant in different percentages of
437 monoterpenes (Bäck et al., 2012; Brophy and Boland, 1990; Kännaste et al., 2013).

438

439 For the other four species in this study it is not possible to compare the natural monoterpene
440 emission proportions with any previous study although data for the range of compounds
441 extracted from the glandular cells in the leaves have been reported for *E. subcrenulata*, *E.*
442 *cordata*, *E. johnstonii* and *E. globulus* (Bignell et al., 1998; Li et al., 1996, 1995). No data on
443 the composition of the oils from *E. pauciflora* subsp. *deubuzevelli* could be found in the
444 literature. The leaf gland extractions were dominated by eucalyptol for all four species of
445 eucalypt, followed by α -pinene, limonene and then γ -terpinene. In this study, all species
446 were found to have major emissions of eucalyptol, α -pinene and limonene but γ -terpinene
447 was only found in trace amounts. Only *E. globulus* was found to be a major eucalyptol emitter
448 which is comparable to the findings of Li et al (1996). The other emitted species were
449 dominated by α -pinene, limonene or β -cis-ocimene, all compounds which can be produced
450 by de novo synthesis and so could explain to some degree the lack of these compounds
451 found in the storage glands of the previous study. It is worth noting that the emissions
452 composition data in the present study is only comparable qualitatively to the previous oil
453 gland composition data. Different species chemotypes may also exist and would require
454 further investigation with many more tree replicates grown from a range of seed
455 provenances. However, a study by Sørensen et al. (2020) in which atmospheric emissions of
456 monoterpenes from eucalypts were compared directly to their extracted leaf oil monoterpene
457 concentrations from the storage glands also reported that no such correlation could be
458 inferred.

459

460

461 3.7 Natural variation of emission measurements

462 VOC emission rates varied widely between individual trees, as reflected by the standard
463 deviation, minimum and maximum values in Table 1. Using the example of *E. subcrenulata*,
464 the variability (expressed as standard deviation) of isoprene and total monoterpenes for
465 sequential measurements collected on the same day on the same branch were 33% and
466 35% respectively. Emission rate variability for samples collected between two individuals of
467 the same species on the same day was slightly higher, isoprene (43%) and monoterpenes
468 (38%), compared to the within day variability. The variability for monoterpene emissions
469 between two individuals of the same species, collected using different branches across
470 different sample days was similar (31%) compared to the within day and between species
471 measured on the same day. Isoprene emission variability, however, was slightly higher at
472 53%. The variability observed in the present branch study is similar in some cases to that of
473 leaf variability reported by Guenther et al. (1991), where the day-to-day emission variability
474 of isoprene (14%) and monoterpenes (>50%) were much lower than the leaf-to-leaf emission
475 rate of isoprene (62%) and monoterpenes (80%). The higher variability for isoprene found
476 during this branch study compared to the previously reported leaf study (Guenther et al.,
477 1991) for the same within day serial sampling could be due to the unavoidable shading of
478 some leaves within the branch chamber. Other studies have also reported similar large
479 variability in emission rates up to 80% for isoprene and 60% for total monoterpenes (He et
480 al., 2000a).

481

482 4. Trends in eucalypts for bioenergy

483 Knowledge of the suitability of certain eucalypt species for bioenergy plantations in the UK is
484 evolving. Sales figures for eucalypt seedlings and saplings in the UK show that *E.*
485 *glaucescens* accounted for 40% of the 220,000 cell-grown plants sold during the 5-year
486 period 2011-2015 (Purse and Leslie, 2016). However, a more recent poll of species
487 produced and sold as plugs in 2019 could suggest that other species such as *E. rodwayi* and

488 *E. dalrympleana* are also gaining popularity (personal comment from the eucalypt seedling
489 growers).

490

491 The choice of species is dictated by soil type and local climate conditions, in particular
492 rainfall, minimum temperatures and number of frost days (Leslie et al., 2012; Purse and
493 Leslie, 2016) therefore, different species may be grown as bioenergy plantations in different
494 regions of the UK. With climate warming the geographical ranges over which species may
495 be planted is likely to change. In 2018, 94,000 hectares of land in the UK were used to grow
496 bioenergy crops (Defra, 2019). Bioenergy in the UK has to date focused mostly on two main
497 crops, willow, grown as short-rotation coppice and *Miscanthus*, a perennial grass, harvested
498 annually. Eucalypts produce higher yields of biomass per hectare than willow or *Miscanthus*,
499 making them potentially more desirable as a future crop for bioenergy (Scottish Forestry,
500 2020).

501

502 The measurements on eucalypt species relevant for UK climate conditions presented in this
503 paper are the initial steps required to assess the impacts of VOC emissions from bioenergy
504 plantations. The data reported here only account for emissions from young living leaves on
505 trees; other sources of VOC emissions from a bioenergy plantations may exist such as those
506 from leaf litter, stems and harvesting practices. Further work on plantation scale emissions is
507 needed to fully understand the contribution of VOCs from a range of sources within SRF and
508 SRC plantations. Also, the eucalypt species measured here produced isoprene and
509 monoterpene emissions of varying amounts. In some cases isoprene and monoterpene
510 emissions were equal and in others there was at least an order of magnitude difference in
511 these emission rates. Given the complex air chemistry that may arise under such
512 circumstances, such as the formation of ozone and SOA (Bonn et al., 2017), it is important
513 that atmospheric models are used to assess the potential changes that VOC emissions from
514 eucalypt bioenergy forests grown for the purposes of reducing CO₂ emissions may have on
515 air quality in the UK.

516

517 **5. Conclusions**

518 Isoprene and monoterpene emission rates were quantified for the first time under UK climate
519 conditions from four species of eucalypt suitable for growing as short-rotation forest or
520 coppice for bioenergy, and from a previously measured eucalypt species as a point of
521 reference. All eucalypt species could be classified as 'medium' isoprene emitters with a
522 normalised emission rate between 1-10 $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$. Total monoterpene emissions rates
523 were approximately one order of magnitude lower or similar to those of isoprene. A natural
524 variation in emission rates between different eucalypt saplings and different branches was
525 noted. The composition of the total monoterpene emissions differed between the species of
526 eucalypt, but all included eucalyptol, α -pinene, β -cis-ocimene and limonene as their major
527 monoterpenes. *E. globulus subsp. bicostata* was a major eucalyptol emitter, accounting for
528 around 60% of quantified total monoterpene. Emissions from two eucalypt species *E.*
529 *cordata subsp. quadrangulosa* and *E. pauciflora subsp. debeuzevillei* were dominated by β -
530 cis-ocimene (38-44% of total quantified monoterpenes) whilst *E. johnstonii* emitted similar
531 proportions of α -pinene (38%) and eucalyptol (37%). The UK requires future expansion of
532 bioenergy plantations in order to fulfil net zero greenhouse gas emissions targets. The
533 emission rates for VOCs measured here are essential first data for future assessments of
534 biosphere-atmosphere interactions arising from any expansion of eucalypt bioenergy
535 plantations and of their potential impact on UK air quality.

536

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739 Table 1 – Summary of the range of emission rates of isoprene and selected monoterpenes on a leaf area and leaf dry weight basis for five UK
 740 eucalypt species grown and measured under a UK climate. The ranges in values of *T*, PAR and RH across the sampling occasions for each
 741 species are also presented.

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Eucalypt species	<i>N</i>	<i>d</i>	<i>T</i> / °C	PAR / μmol m ⁻² s ⁻¹	RH / %	Compound	Emission rate / μg C g _{dw} ⁻¹ h ⁻¹					Emission rate / μg C m ⁻² h ⁻¹				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
<i>E. subcrenulata</i>	14	4	21.5 - 29.3	477 - 1458	72.4 - 81.1	Isoprene	6.16	2.53	2.19	12.3	6.03	1130	523	253	2180	1110
						γ-terpinene	0.00	0.01	0.00	0.02	0.00	0.73	1.06	0.00	0.31	0.27
						Linalool	0.01	0.01	0.00	0.03	0.00	1.59	2.25	0.00	6.65	0.47
						α-pinene	0.06	0.06	0.02	0.22	0.04	11	10.2	2.03	38.7	7.91
						Camphene	0.00	0.00	0.00	0.01	0.00	0.11	0.27	0.00	0.82	0.00
						β-phellandrene	0.03	0.04	0.00	0.12	0.01	5.06	7.16	0.00	20.4	1.19
						β-pinene	0.01	0.01	0.00	0.03	0.00	1.00	1.35	0.06	4.69	0.31
						β-myrcene	0.01	0.01	0.00	0.02	0.00	1.02	1.39	0.00	3.75	0.50
						α-phellandrene	0.00	0.01	0.00	0.02	0.00	0.56	0.97	0.00	2.75	0.00
						3-carene	0.01	0.03	0.00	0.12	0.00	2.44	5.98	0.00	21.3	0.03
						d-limonene	0.09	0.12	0.02	0.42	0.04	15.5	21	1.89	74.4	8.14
						Eucalyptol	0.06	0.06	0.01	0.18	0.03	11.5	11.7	0.98	32.1	6.39
						β-cis-ocimene	0.08	0.07	0.00	0.21	0.08	12.1	9.26	0.47	24.1	12.2
						Total MT	0.35	0.32	0.08	1.26	0.28	62.6	57.8	15.5	223	47.1

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744 *N* = Total number of measurements; *d* = Total number of sampling days, *T* = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard
 745 deviation

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749 (Table 1 continued)

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Eucalypt species	N	d	T / °C	PAR / $\mu\text{mol m}^{-2} \text{s}^{-1}$	RH / %	Compound	Emission rate / $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$					Emission rate / $\mu\text{g C m}^{-2} \text{h}^{-1}$				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
<i>E. johnstonii</i>	9	4	30.0 - 36.6	1249 - 1107	60.3 - 70.4	<i>Isoprene</i>	2.86	2.33	0.05	6.99	2.18	471	359	5.88	1140	369
						<i>γ-terpinene</i>	0.00	0.00	0.00	0.00	0.00	0.12	0.18	0.00	0.42	0.00
						<i>Linalool</i>	0.01	0.01	0.00	0.02	0.00	0.88	1.05	0.00	2.46	0.06
						<i>α-pinene</i>	0.11	0.10	0.00	0.35	0.10	20.0	18.3	0.45	63.7	16.9
						<i>Camphene</i>	0.00	0.00	0.00	0.00	0.00	0.09	0.10	0.00	0.22	0.06
						<i>β-phellandrene</i>	0.01	0.00	0.00	0.01	0.01	0.88	0.83	0.00	2.07	1.08
						<i>β-pinene</i>	0.01	0.01	0.00	0.01	0.00	1.06	1.02	0.04	2.60	0.59
						<i>β-myrcene</i>	0.01	0.01	0.00	0.02	0.00	0.75	0.97	0.00	2.76	0.12
						<i>α-phellandrene</i>	0.00	0.00	0.00	0.01	0.00	0.17	0.45	0.00	1.36	0.00
						<i>3-carene</i>	0.00	0.00	0.00	0.01	0.00	0.44	0.43	0.00	1.20	0.25
						<i>d-limonene</i>	0.04	0.02	0.00	0.07	0.04	7.02	3.91	0.00	13.0	7.22
						<i>Eucalyptol</i>	0.11	0.08	0.00	0.26	0.14	19.2	14.8	0.00	46.8	24.0
						<i>β-cis-ocimene</i>	0.01	0.02	0.00	0.07	0.01	2.06	2.66	0.00	8.26	2.24
						<i>Total MT</i>	0.30	0.19	0.01	0.69	0.32	52.6	33.9	0.89	124	54.5

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752 N = Total number of measurements; d = Total number of sampling days, T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard
753 deviation

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759 (Table 1 continued)

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Eucalypt species	N	d	T / °C	PAR / $\mu\text{mol m}^{-2} \text{s}^{-1}$	RH / %	Compound	Emission rate / $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$					Emission rate / $\mu\text{g C m}^{-2} \text{h}^{-1}$				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
<i>E. globulus subsp. bicostata</i>	14	4	24.5 - 36.6	848 - 1064	60.3 - 75.5	<i>Isoprene</i>	10.1	6.75	2.36	28.2	9.57	704	487	133	2100	713
						<i>γ-terpinene</i>	0.03	0.04	0.00	0.12	0.02	2.06	2.70	0.00	8.13	0.90
						<i>Linalool</i>	0.24	0.28	0.00	0.86	0.15	16.1	18.7	0.00	57.0	10.3
						<i>α-pinene</i>	2.47	3.17	0.02	10.1	1.59	171	223	1.34	674	102
						<i>Camphene</i>	0.01	0.01	0.00	0.02	0.00	0.40	0.53	0.00	1.61	0.15
						<i>β-phellandrene</i>	0.03	0.03	0.00	0.10	0.02	1.67	1.59	0.00	5.10	1.59
						<i>β-pinene</i>	0.06	0.08	0.00	0.32	0.04	4.34	5.69	0.00	21.2	2.85
						<i>β-myrcene</i>	0.16	0.16	0.00	0.59	0.13	10.9	12.0	0.00	43.9	7.38
						<i>α-phellandrene</i>	0.01	0.02	0.00	0.06	0.01	0.91	1.23	0.00	4.12	0.39
						<i>3-carene</i>	0.01	0.01	0.00	0.02	0.00	0.39	0.45	0.00	1.59	0.23
						<i>d-limonene</i>	1.34	1.87	0.00	6.57	0.66	90.9	129	0.25	437	34.2
						<i>Eucalyptol</i>	8.56	13.6	0.02	52.3	5.29	572	907	1.56	3480	394
						<i>β-cis-ocimene</i>	1.17	1.57	0.00	4.70	0.64	78.7	104	0.12	313	42.0
<i>Total MT</i>	14.1	19.7	0.04	75.4	7.41	949	1320	3.32	5010	552						

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762 N = Total number of measurements; d = Total number of sampling days, T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard
763 deviation

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770 (Table 1 continued)

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Eucalypt species	N	d	T / °C	PAR / $\mu\text{mol m}^{-2} \text{s}^{-1}$	RH / %	Compound	Emission rate / $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$					Emission rate / $\mu\text{g C m}^{-2} \text{h}^{-1}$				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
<i>E. pauciflora</i> subsp. <i>debeuzevillei</i>	23	5	29.6 - 32.3	745- 1336	74.5 - 81.4	<i>Isoprene</i>	1.31	1.45	0.06	4.71	0.56	183	190	8.38	671	105
						<i>γ-terpinene</i>	0.01	0.02	0.00	0.06	0.00	1.92	2.59	0.00	7.61	0.67
						<i>Linalool</i>	0.14	0.26	0.00	0.93	0.01	18.0	33.9	0.00	122	1.67
						<i>α-pinene</i>	0.05	0.05	0.00	0.18	0.02	6.36	6.79	0.00	24.0	3.57
						<i>Camphene</i>	0.00	0.00	0.00	0.01	0.00	0.09	0.19	0.00	0.79	0.00
						<i>β-phellandrene</i>	0.03	0.04	0.00	0.15	0.01	3.59	6.08	0.00	20.9	1.19
						<i>β-pinene</i>	0.01	0.01	0.00	0.04	0.00	1.12	1.81	0.00	6.29	0.44
						<i>β-myrcene</i>	0.02	0.02	0.00	0.06	0.01	2.16	2.56	0.00	7.63	1.03
						<i>α-phellandrene</i>	0.01	0.01	0.00	0.02	0.00	0.82	0.75	0.00	2.87	0.59
						<i>3-carene</i>	0.01	0.01	0.00	0.02	0.00	0.96	1.01	0.00	3.24	0.60
						<i>d-limonene</i>	0.06	0.08	0.00	0.30	0.02	7.80	10.1	0.00	39.4	3.83
						<i>Eucalyptol</i>	0.17	0.19	0.00	0.78	0.15	23.2	25.0	0.00	102	18.3
<i>β-cis-ocimene</i>	0.40	0.79	0.00	2.86	0.02	52.3	102	0.06	376	3.57						
<i>Total MT</i>	0.90	1.36	0.02	4.81	0.28	118	176	3.10	631	42.1						

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773 N = Total number of measurements; d = Total number of sampling days, T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity SD = Standard
774 deviation

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780 (Table 1 continued)

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Eucalypt species	N	d	T / °C	PAR / $\mu\text{mol m}^{-2} \text{s}^{-1}$	RH / %	Compound	Emission rate / $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$					Emission rate / $\mu\text{g C m}^{-2} \text{h}^{-1}$				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
<i>E. cordata</i> subsp. <i>quadrangulosa</i>	14	4	19.9 - 31.4	731 - 1867	74.5 - 90.4	<i>Isoprene</i>	2.43	1.62	0.17	5.37	1.79	391	239	32.0	791	330
						<i>γ-terpinene</i>	0.01	0.02	0.00	0.06	0.00	1.11	2.39	0.00	9.24	0.57
						<i>Linalool</i>	0.01	0.02	0.00	0.08	0.01	2.50	3.86	0.00	14.4	1.06
						<i>α-pinene</i>	0.36	0.74	0.00	2.80	0.06	62.8	137	0.00	515	10.2
						<i>Camphene</i>	0.00	0.00	0.00	0.01	0.00	0.14	0.33	0.00	1.16	0.00
						<i>β-phellandrene</i>	0.02	0.02	0.00	0.05	0.01	2.74	2.75	0.00	7.42	1.57
						<i>β-pinene</i>	0.01	0.01	0.00	0.02	0.00	0.87	1.09	0.00	3.04	0.26
						<i>β-myrcene</i>	0.01	0.01	0.00	0.03	0.01	2.11	1.54	0.00	6.09	2.03
						<i>α-phellandrene</i>	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.00	0.11	0.00
						<i>3-carene</i>	0.02	0.03	0.00	0.09	0.00	2.61	4.83	0.00	13.1	0.00
						<i>d-limonene</i>	0.15	0.16	0.00	0.41	0.06	23.7	25.2	0.00	76.1	10.7
						<i>Eucalyptol</i>	0.50	0.91	0.00	3.33	0.16	88.2	168	0.00	612	25.9
						<i>β-cis-ocimene</i>	0.66	1.11	0.00	4.13	0.36	115	196	0.00	726	59.6
<i>Total MT</i>	1.73	2.02	0.00	6.96	0.90	302	370	0.00	1270	144						

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783 N = Total number of measurements; d = Total number of sampling days, T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard
784 deviation

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790 Table 2 – Comparison of isoprene and monoterpene emission rates from *E. globulus* with
 791 previous literature values.

species	Emission rate per leaf area / $\mu\text{g C m}^{-2} \text{ h}^{-1}$				Emission rate per dry leaf mass / $\mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$				Ref	Comment
	isoprene	total MT	eucalyptol	α -pinene	isoprene	total MT	eucalyptol	α -pinene		
<i>E. globulus</i> subsp. <i>bicostata</i>	696	949	572	171	10.0	14.1	8.56	2.47		This study
<i>E. globulus</i>					38.5		3.53	1.14	1	A
	562		1250	6430					2	B
	2590		648	2980					2	C
	3750		475	2720					2	D
	7410	871	380	152	68.5	5.41	2.37	0.89	3	E
	443	3310			1.76	13.2			4	E
					3.84	17.1	11.5	2.49	5	A,F
					37.0	185	133	27.3	5	A,G
					14.9	5.30	1.67	1.17	6	E, H
					48.7	0.700	0.00400	0.0890	6	E, I

792 MT = monoterpene. Ref = Literature reference: 1. (Evans et al., 1982) (not normalised); 2. (Guenther et al.,
 793 1991); 3. (He et al., 2000a) (normalised to 30 °C and 1000 $\mu\text{mol m}^{-2} \text{ s}^{-1}$ PAR); 4. (Winters et al., 2009)
 794 (normalised to 30 °C and 1000 $\mu\text{mol m}^{-2} \text{ s}^{-1}$ PAR); 5. (Owen and Peñuelas, 2013) (not normalised); 6. (Street et
 795 al. 1997).

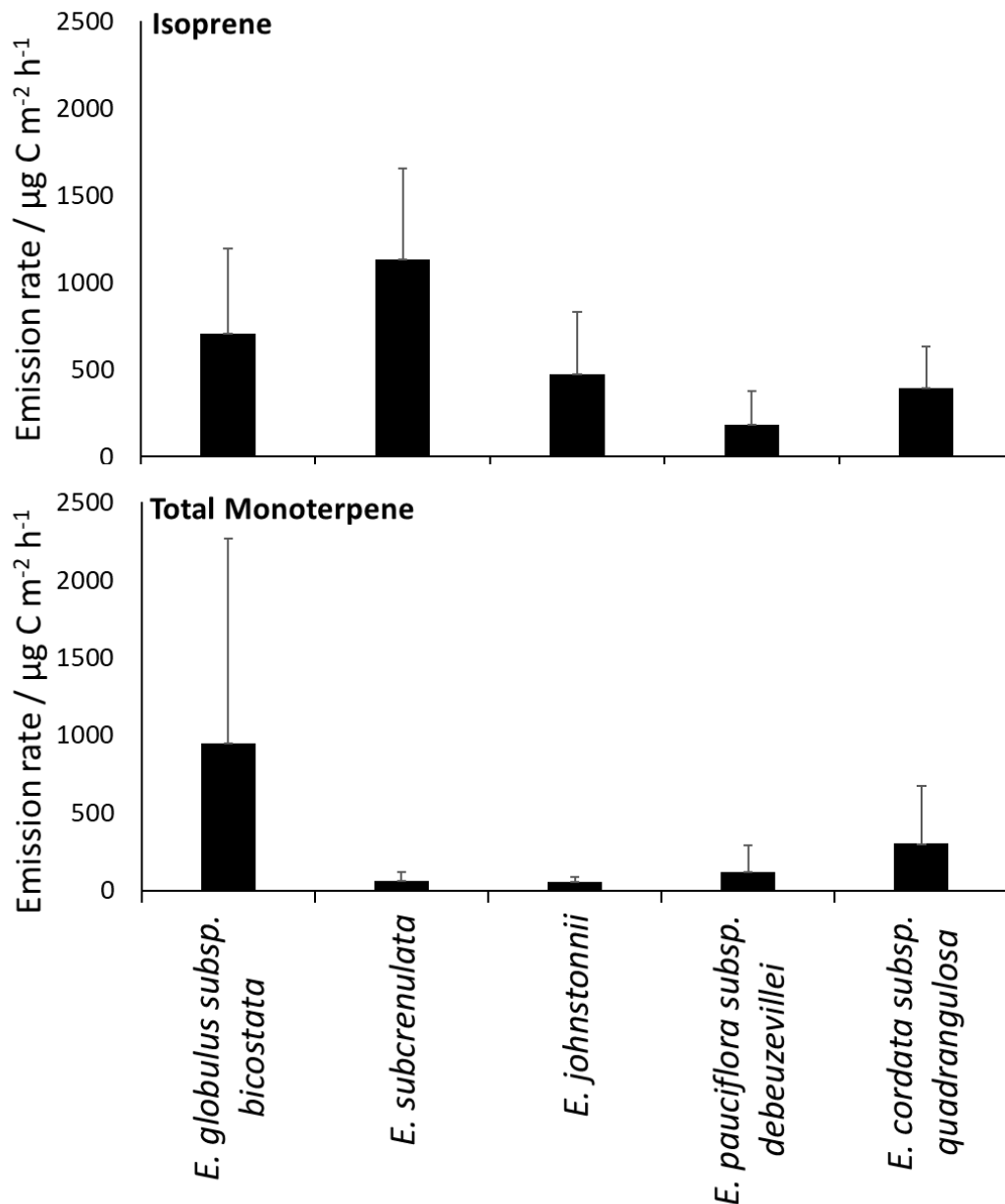
796 A. not normalised; B. 28 °C and 1000 $\mu\text{mol m}^{-2} \text{ s}^{-1}$ PAR, leaf age <15 days converted to $\mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$; C. 28 °C
 797 and 1000 $\mu\text{mol m}^{-2} \text{ s}^{-1}$ PAR, leaf age 15 - 40 days converted to $\mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$; D. 28 °C and 1000 $\mu\text{mol m}^{-2} \text{ s}^{-1}$ PAR,
 798 leaf age 40 + days converted to $\mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$; E. 30 °C and 1000 $\mu\text{mol m}^{-2} \text{ s}^{-1}$ PAR; F. Minimum reported value
 799 converted to $\mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$; G. maximum reported value converted to $\mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$; H. Young leaves; I. Old leaves

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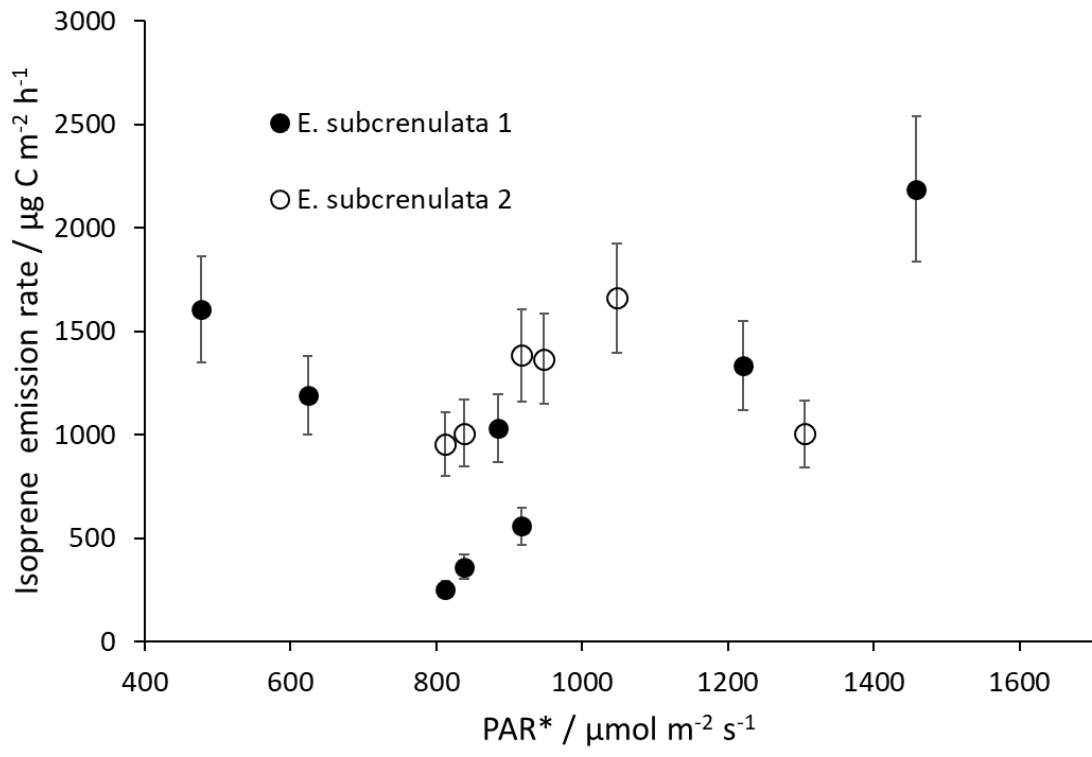


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807 Figure 1 – Average isoprene and total monoterpene emission rates for 5 eucalypt species
 808 grown and measured under a UK climate. Emission rates are expressed on a per leaf area
 809 basis and are normalised to 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ PAR and 30 °C for isoprene and to 30 °C for
 810 monoterpenes using the algorithm of Guenther et al. (1993). The error bars show the
 811 standard deviation for the total measurements for each species and the numbers of
 812 measurements contributing to each average emission rate are given in parentheses. The
 813 isoprene and total monoterpene data are presented on the same scale to illustrate their
 814 relative emission rates.

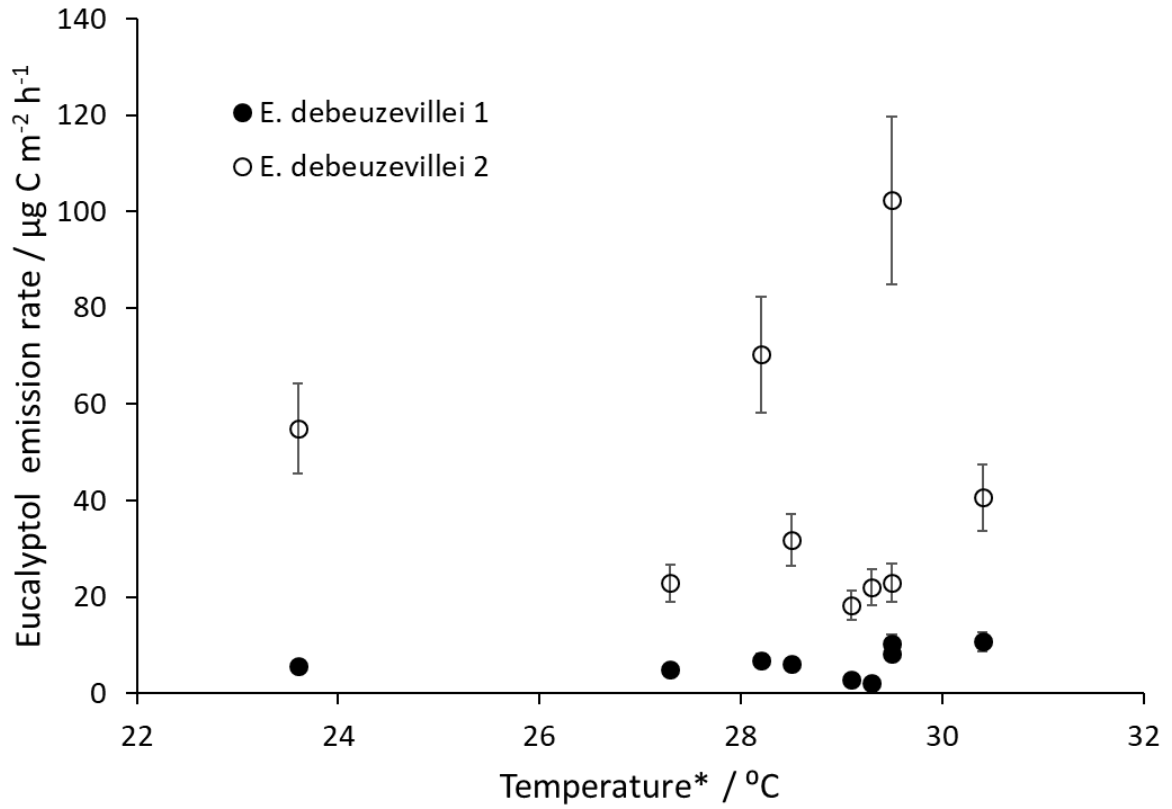
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Figure 2 – Isoprene emission rate as a function of photosynthetic active radiation (PAR) for two individual trees of *E. subcrenulata*. *Represents average value recorded for PAR during each 30 min sample collection period.



831

832 Figure 3 – Eucalyptol emission rates as a function of chamber temperature for two individual
 833 trees of *E. debeuzevillei*. *Represents average value recorded for chamber temperature during
 834 each 30 min sample collection period.

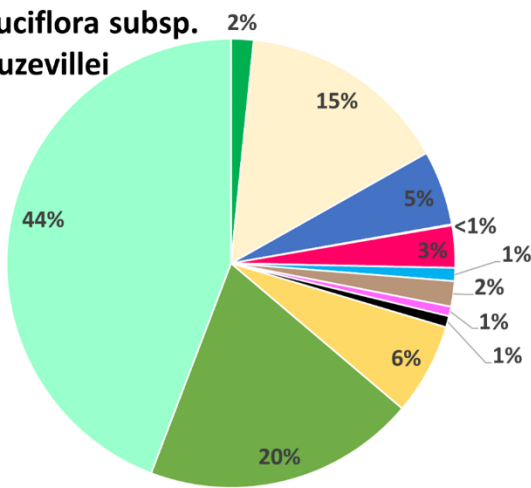
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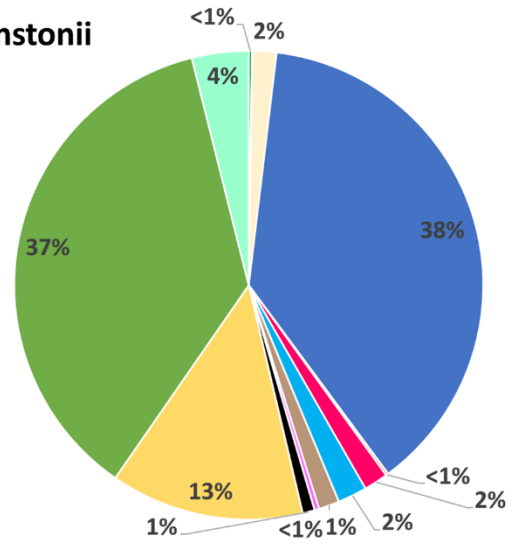
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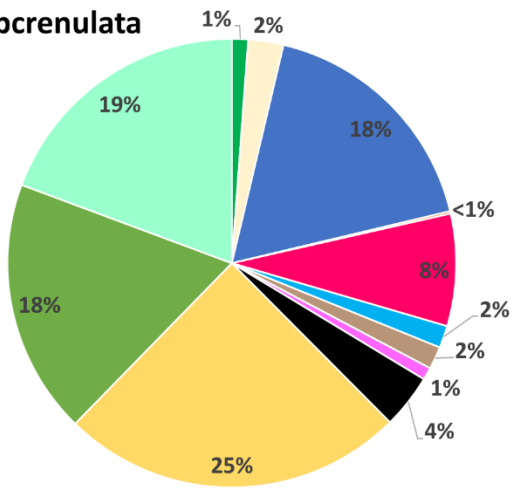
E. pauciflora subsp. debeuzevillei



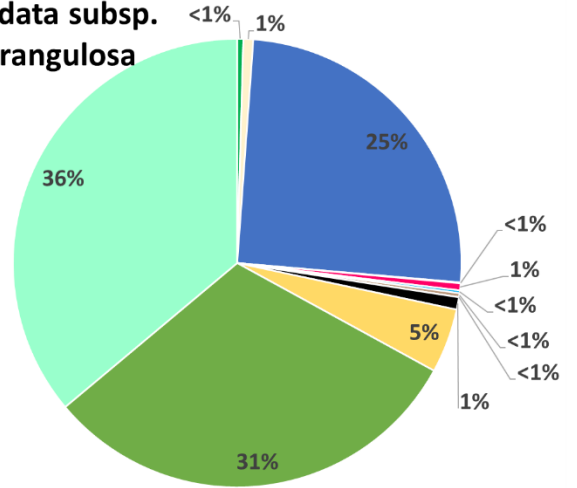
E. jonstonii



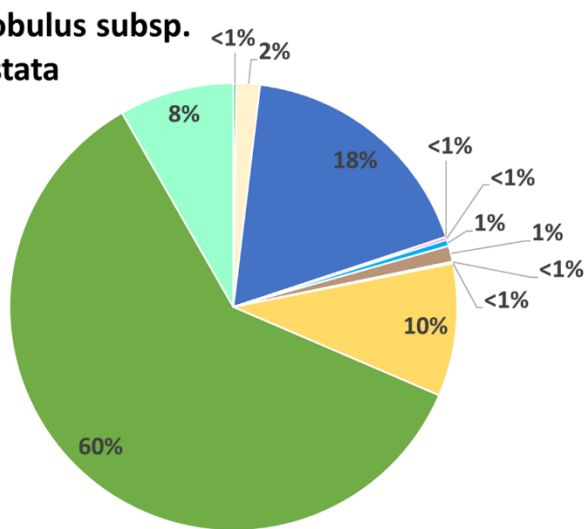
E. subcrenulata



E. cordata subsp. quadrangulosa



E. globulus subsp. bicostata



- γ-terpinene
- linalool
- α-pinene
- camphene
- β-phellandrene
- β-pinene
- β-myrcene
- α-phellandrene
- 3-carene
- limonene
- eucalyptol
- β-cis-ocimene

839

840

841 Figure 4 – Average percentage contribution of individual monoterpenes relative to total
842 quantified monoterpene emissions.

843 **Supplementary Information**

844

845 **Differences in isoprene and monoterpene emissions**
846 **from cold-tolerant eucalypt species grown in the UK**

847 Gemma Purser^{*1,2}, Mathew R. Heal², Stella White¹, James I.L. Morison³, Julia Drewer¹

848 ¹ UK Centre for Ecology & Hydrology, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK

849 ² School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster
850 Road, Edinburgh, EH9 3FJ, UK

851 ³ Forest Research, Alice Holt Lodge, Farnham, Surrey, GU10 4TT

852 *Corresponding author

853

854

855 **Content**

856

857 Table S1. Summary of the range of emission rates of isoprene and selected monoterpenes
858 from single trees of eucalypt species grown and measured under a UK climate. Where N
859 represents the number of samples measured and d is the number of days. The ranges in
860 values of T, PAR and RH across the sampling occasions for each species are also
861 presented.

862

863 Table S2 - Number of sampling days per month, average number of leaves measured, leaf
864 dry mass and leaf area for 9 species of eucalypt measured during this study.

865

866 Table S3 – Ambient air temperature and concentrations of ozone, nitric oxide and nitrogen
867 dioxide from the long term monitoring station (Bush cabin) at the UK Centre for Ecology &
868 Hydrology, Penicuik, Edinburgh on the days that VOC were sampled from 9 different species
869 of eucalypt.

870

871 Figure S1 – Daily midday (12:00) measurements of air temperature and photosynthetic
872 active radiation (PAR) for January to December 2019, recorded at the UK Centre for Ecology
873 & Hydrology, Penicuik, Easter Bush, as part of a long-term monitoring station.

874

875 Section S1– A description of the equations used to calculate the measurement uncertainties
876 for isoprene and monoterpene emission rates.

877

878 Table S1. Summary of the range of emission rates of isoprene and selected monoterpenes from single trees of eucalypt species grown and
 879 measured under a UK climate. N represents the number of samples measured and d is the number of days. The ranges in values of T, PAR
 880 and RH across the sampling occasions for each species are also presented.

Eucalypt species	N	d	T / °C	PAR / $\mu\text{mol m}^{-2} \text{s}^{-1}$	RH / %	Compound	Emission rate / $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$					Emission rate / $\mu\text{g C m}^{-2} \text{h}^{-1}$				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
<i>E. pauciflora</i> subsp. <i>pauciflora</i>	9	2	21.9–30.5	411-1108	73.0 - 79.5	<i>isoprene</i>	2.03	1.38	0.58	4.61	1.61	325	220	75.2	704	296
						<i>γ-terpinene</i>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
						<i>linalool</i>	0.01	0.01	0.00	0.03	0.01	1.36	1.52	0.00	3.78	0.81
						<i>α-pinene</i>	0.05	0.05	0.00	0.17	0.03	7.74	9.98	0.00	30.7	4.24
						<i>camphene</i>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
						<i>β-phellandrene</i>	0.01	0.01	0.00	0.03	0.01	1.71	1.35	0.00	3.31	1.77
						<i>β-pinene</i>	0.00	0.00	0.00	0.01	0.00	0.40	0.45	0.00	1.41	0.28
						<i>β-myrcene</i>	0.01	0.01	0.00	0.04	0.01	1.62	1.81	0.26	5.10	0.81
						<i>α-phellandrene</i>	0.01	0.01	0.00	0.03	0.00	1.31	1.50	0.00	4.30	0.74
						<i>3-carene</i>	0.04	0.07	0.00	0.19	0.01	7.76	12.3	0.00	35.0	0.70
						<i>d-limonene</i>	0.05	0.06	0.00	0.18	0.03	8.43	8.75	0.00	22.6	4.43
						<i>eucalyptol</i>	0.04	0.05	0.00	0.15	0.02	5.96	8.74	0.16	27.9	2.77
						<i>β-cis-ocimene</i>	0.00	0.00	0.00	0.01	0.00	0.49	0.53	0.00	1.32	0.20
<i>Total MT</i>	0.23	0.20	0.05	0.64	0.20	36.8	34.8	7.16	117	30.6						

881

882 N = Number of measurements; T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard deviation

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888 (Table S1 continued)

Eucalypt species	N	d	T / °C	PAR / $\mu\text{mol m}^{-2} \text{s}^{-1}$	RH / %	Compound	Emission rate / $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$					Emission rate / $\mu\text{g C m}^{-2} \text{h}^{-1}$				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
<i>E. gunnii</i> subsp. <i>gunnii</i>	12	4	21.9 – 35.4	267 – 1108	73.0 – 86.7	<i>isoprene</i>	6.04	5.44	0.76	18.2	5.53	933	844	123	2790	6.04
						<i>γ-terpinene</i>	0.01	0.01	0.00	0.04	0.01	2.01	2.03	0.00	6.00	1.75
						<i>linalool</i>	0.04	0.06	0.00	0.16	0.01	6.40	8.97	0.00	24.3	1.63
						<i>α-pinene</i>	0.21	0.15	0.00	0.51	0.19	31.4	24.7	0.00	84.3	28.6
						<i>camphene</i>	0.00	0.00	0.00	0.01	0.00	0.41	0.72	0.00	1.74	0.00
						<i>β-phellandrene</i>	0.08	0.07	0.00	0.22	0.05	11.8	10.4	0.00	33.8	7.58
						<i>β-pinene</i>	0.02	0.01	0.00	0.03	0.02	3.01	1.64	0.00	5.12	3.56
						<i>β-myrcene</i>	0.08	0.08	0.00	0.23	0.05	11.4	12.1	0.00	35.3	6.68
						<i>α-phellandrene</i>	0.03	0.02	0.00	0.07	0.03	4.75	3.29	0.00	10.4	4.74
						<i>3-carene</i>	0.02	0.02	0.00	0.04	0.01	2.27	2.37	0.00	6.19	1.11
						<i>d-limonene</i>	0.14	0.12	0.00	0.39	0.11	21.3	18.6	0.00	59.5	15.7
						<i>eucalyptol</i>	0.11	0.12	0.00	0.36	0.07	16.7	18.3	0.00	55.5	10.4
						<i>β-cis-ocimene</i>	1.13	1.78	0.00	5.01	0.43	158	235	0.00	665	66.4
<i>Total MT</i>	1.87	1.87	0.00	5.73	1.07	269	246	0.73	761	167						

889

890 N = Number of measurements; T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard deviation

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898 (Table S1 continued)

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Eucalypt species	N	d	T / °C	PAR / $\mu\text{mol m}^{-2} \text{s}^{-1}$	RH / %	Compound	Emission rate / $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$					Emission rate / $\mu\text{g C m}^{-2} \text{h}^{-1}$				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
<i>E. gunnii</i> subsp. <i>divaricata</i>	9	3	27.3 – 30.5	267 – 1323	75.1 – 86.7	<i>isoprene</i>	10.5	2.32	6.04	13.2	10.6	1650	375	1050	2300	1680
						<i>γ-terpinene</i>	0.00	0.00	0.00	0.01	0.00	0.31	0.51	0.00	1.43	0.10
						<i>linalool</i>	0.01	0.01	0.00	0.03	0.00	1.23	1.87	0.00	4.07	0.00
						<i>α-pinene</i>	0.06	0.04	0.02	0.12	0.04	10.1	7.49	3.56	21.1	5.74
						<i>camphene</i>	0.00	0.00	0.00	0.00	0.00	0.06	0.07	0.00	0.18	0.06
						<i>β-phellandrene</i>	0.01	0.00	0.01	0.01	0.01	1.39	0.40	0.89	2.16	1.53
						<i>β-pinene</i>	0.01	0.01	0.00	0.02	0.00	1.13	0.94	0.31	2.63	0.57
						<i>β-myrcene</i>	0.00	0.00	0.00	0.01	0.00	0.65	0.43	0.17	1.33	0.51
						<i>α-phellandrene</i>	0.00	0.00	0.00	0.01	0.00	0.43	0.45	0.00	1.09	0.28
						<i>3-carene</i>	0.00	0.00	0.00	0.02	0.01	1.61	0.92	0.70	3.75	1.46
						<i>d-limonene</i>	0.04	0.03	0.01	0.10	0.02	6.46	5.11	1.99	17.4	3.85
						<i>eucalyptol</i>	0.02	0.02	0.00	0.05	0.02	2.51	2.55	0.00	7.93	2.31
						<i>β-cis-ocimene</i>	0.02	0.01	0.00	0.03	0.02	2.15	1.78	0.00	4.90	2.54
<i>Total MT</i>	0.18	0.05	0.08	0.25	0.17	28.0	9.46	13.1	42.8	24.9						

900

901 N = Number of measurements; T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard deviation

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908 (Table S1 continued)

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Eucalypt species	N	d	T / °C	PAR / $\mu\text{mol m}^{-2} \text{s}^{-1}$	RH / %	Compound	Emission rate / $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$					Emission rate / $\mu\text{g C m}^{-2} \text{h}^{-1}$				
							Mean	SD	Min	Max	Median	Mean	SD	Min	Max	Median
<i>E. coccifera</i>	10	5	18.1 – 31.8	324 - 1719	65.5 - 90.4	<i>isoprene</i>	2.11	3.27	0.01	9.53	0.32	453	723	1.21	2050	58.8
						<i>γ-terpinene</i>	0.02	0.04	0.00	0.15	0.00	3.36	9.94	0.00	34.7	0.05
						<i>linalool</i>	0.01	0.02	0.00	0.08	0.00	1.71	5.24	0.00	18.3	0.02
						<i>α-pinene</i>	0.13	0.21	0.00	0.73	0.05	28.7	47.9	0.00	163	9.99
						<i>camphene</i>	0.00	0.00	0.00	0.00	0.00	0.20	0.33	0.00	0.96	0.00
						<i>β-phellandrene</i>	0.11	0.24	0.00	0.84	0.01	23.8	54.0	0.00	187	1.34
						<i>β-pinene</i>	0.02	0.04	0.00	0.13	0.01	4.44	8.48	0.00	29.4	1.56
						<i>β-myrcene</i>	0.02	0.04	0.00	0.13	0.00	3.69	8.28	0.00	29.0	0.28
						<i>α-phellandrene</i>	0.00	0.00	0.00	0.01	0.00	0.39	0.90	0.00	2.40	0.00
						<i>3-carene</i>	0.01	0.02	0.00	0.08	0.00	2.72	5.23	0.00	17.0	0.00
						<i>d-limonene</i>	0.11	0.15	0.00	0.38	0.03	21.9	32.5	0.00	84.2	5.25
						<i>eucalyptol</i>	0.03	0.06	0.00	0.17	0.00	7.41	13.7	0.00	37.6	0.00
						<i>β-cis-ocimene</i>	0.12	0.32	0.00	1.12	0.00	26.9	72.5	0.00	252	0.84
<i>Total MT</i>	0.58	1.09	0.00	3.77	0.11	125	247	0.00	848	20.6						

910

911 N = Number of measurements; T = Temperature; PAR = Photosynthetic active radiation; RH = Relative humidity; SD = Standard deviation

912

913

914 Table S2 - Number of sampling days per month, average number of leaves measured, leaf
 915 dry mass and leaf area for 9 species of eucalypt measured during this study.

Species	Number of sample days			number of leaves	Average	
	June	July	August		Leaf mass (dry weight) / g	Leaf area / m ²
<i>E. coccifera</i>	1	1	4	38	3.4	0.018
<i>E. cordata</i> subsp. <i>quadrangulosa</i>	1	1	2	22	5.5	0.032
<i>E. globulus</i> subsp. <i>Bicostata</i>	1	0	3	18	2.9	0.043
<i>E. gunnii</i> subsp. <i>Divaricata</i>	1	0	2	46	4.1	0.026
<i>E. gunnii</i> subsp. <i>Gunnii</i>	1	1	2	38	3.6	0.024
<i>E. johnstonii</i>	1	0	3	27	3.9	0.023
<i>E. pauciflora</i> subsp. <i>pauciflora</i>	1	0	1	11	6.4	0.041
<i>E. pauciflora</i> subsp. <i>Debeuzevillei</i>	1	1	3	11	3.8	0.025
<i>E. Subcrenulata</i>	0	1	3	23	3.6	0.022

916

917 Table S3 – Ambient air temperature and concentrations of ozone from the long-term
 918 monitoring station (Bush cabin) at the UK Centre for Ecology & Hydrology, Penicuik,
 919 Edinburgh on the days that VOC were sampled from 9 different species of eucalypt.

920

Sampling date	Air temperature / °C	Average ozone / µg m ⁻³
19/06/2019	18.0	No data
28/06/2019	20.9	No data
14/07/2019	No data	60.2
25/07/2019	26.6	117
13/08/2019	15.6	70.6
15/08/2019	17.1	70.9
23/08/2019	20.8	47.6
24/08/2019	25.1	93.7
25/08/2019	25.6	82.2
26/08/2019	22.1	67.7

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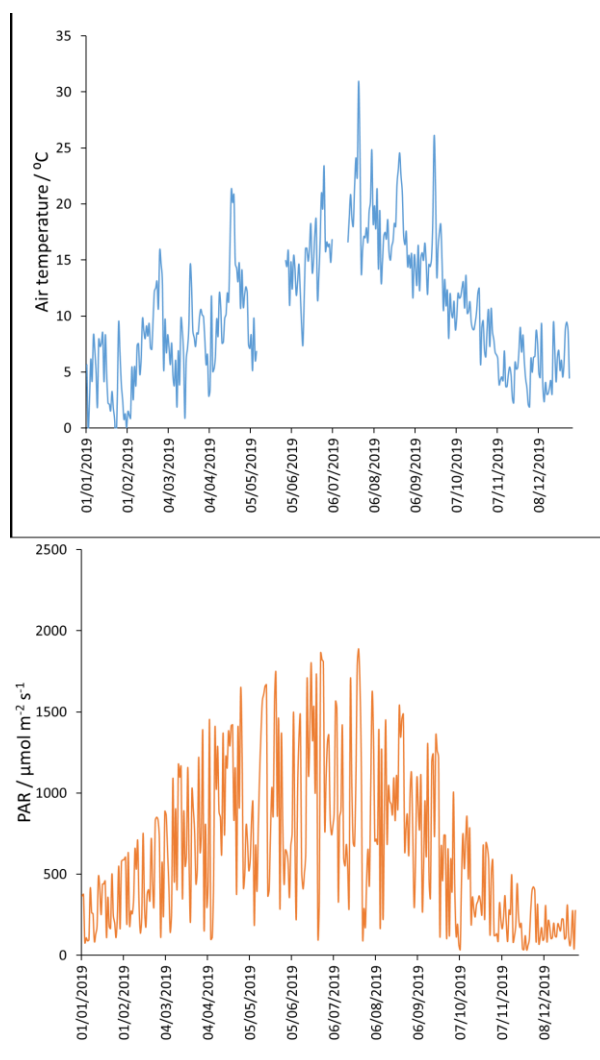
922 DEFRA Air information resource <https://uk-air.defra.gov.uk/data/>

923 Accessed 28/5/2020

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 925 [Licence](#) (OGL).

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928

929 Figure S1 – Daily midday (12:00) measurements of air temperature and photosynthetic
 930 active radiation (PAR) for January to December 2019, recorded at the UK Centre for Ecology
 931 & Hydrology, Penicuik, Easter Bush.

932

933

934 Section S1

935 Several sources of uncertainties may influence the final emission rate for a given time point
 936 and include the uncertainties on the following: ambient and chamber samples measured on
 937 the GC-MS instrument; sample time; sample pump volume; chamber flow rate; leaf mass or
 938 leaf area; chamber temperature; PAR measurement.

939 Given that net emission rates are derived from the difference between ambient and sample
 940 measurements collected in parallel then some factors cancel out such as the error of the
 941 certified standards, dilution of the certified standards (for monoterpenes) and the integration
 942 of the peaks in the chromatogram. Given this, the uncertainty in an individual concentration
 943 can therefore be determined by the interpolations for a given calibration regression fit.
 944 Therefore the standard error in the interpolated concentration was determined using
 945 Equation 1.

946

947

948

949 Equation 1

950

951
$$S_{x0} = \frac{S_{y/x}}{b} \sqrt{1 + \left(\frac{1}{n}\right) + \frac{(y_0 - \bar{y})^2}{b^2 \sum_i (x_i - \bar{x})^2}}$$

952

953 S_{x0} is the standard error in the interpolated concentration. $S_{y/x}$ is the standard error in the
954 regression line and b is the slope of the regression line calculated using the regression
955 function in Excel. n is the number of standards in the calibration line including the blank,
956 which in this instance is equal to 5. y_0 is the experimental value of y which is the peak area
957 of the compound measured in the chromatogram, \bar{y} is the mean peak area, x_i is the a
958 standard concentration and \bar{x} is the mean standard concentration.

959 The standard error in the interpolated concentration, $S_{\Delta c}$, was calculated for both the
960 ambient sample $S_{ambient}$ and chamber sample $S_{chamber}$ was then calculated using Equation 2.

961 Equation 2

962

963
$$S_{\Delta c} = \sqrt{S_{chamber}^2 + S_{ambient}^2}$$

964

965 The final error propagation, $S_{measurement}$, ($\mu\text{g g}_{dw}^{-1} \text{h}^{-1}$) for an individual emission measurement,
966 $ER_{measurement}$, ($\mu\text{g g}_{dw}^{-1} \text{h}^{-1}$) is then be calculated using Equation 3.

967 Equation 3

968
$$S_{measurement} = ER_{measurement} \times \sqrt{\left(\frac{S_{\Delta c}}{\Delta c}\right)^2 + \left(\frac{S_t}{t}\right)^2 + \left(\frac{S_{hp}}{hp}\right)^2 + \left(\frac{S_{leaf}}{leaf}\right)^2 + \left(\frac{S_{Flow}}{Flow}\right)^2 + \left(\frac{S_T}{T}\right)^2 + \left(\frac{S_L}{L}\right)^2 + \left(\frac{S_V}{V}\right)^2}$$

969 S_t is the error in the sampling time, t , estimated to be 30 seconds (0.01 h) for a 30 minute
970 (0.5 h) sample time.

971 S_{hp} is the error in the hand held sampling pump (210-1003MTX, SKC Ltd, Blandford Forum,
972 UK) flow rate, hp , where the manufacturer quotes an uncertainty of 5%. S_{hp} is therefore 0.01
973 L min^{-1} for a flow rate 0.2 L min^{-1} .

974 S_{leaf} is the error in estimating the dry leaf weight, $leaf$, using the balance or leaf area using
975 the Licor LI-3100C leaf area scanner. The errors quoted by the instrument manufacturers
976 are 1% and 6% respectively, and so we attributed 6% to this measurement. S_{leaf} would be
977 0.24 g for a sample weight of 4 g and 0.024 m^2 for a leaf area of 0.4 m^2 .

978 S_{Flow} is the uncertainty in the flow rate, $Flow$, of the chamber determined by the uncertainty
979 as measured by the rotameter (Colepalmer, St. Neots, UK) given by the manufacturer to be
980 5%. For the flow rate 120 L h^{-1} (2 L min^{-1}) the S_{Flow} would be 6 L h^{-1} .

981 S_T is the uncertainty in the temperature, T , for the sample probe CS215 (Campbell scientific,
982 Shepshed, UK) was estimated to be 4%. For a temperature of 30 °C this would be 1.2 °C.

983 S_L is the uncertainty in the measurement of PAR, L , using the SKP 215 PAR Quantum
984 Sensor (Skye instruments, Llandrindod Wells, UK) which was suggested to be between 3-
985 5%. For 5% this would be 50 $\mu\text{mol m}^{-2} \text{s}^{-1}$ for a measurement of 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$.

986 S_V is the uncertainty in the chamber volume estimated to be 1% of the total volume, V . This
987 would be 0.06 L for the 6 L chamber.

988