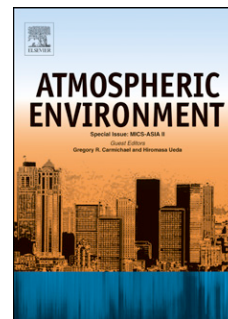


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Volatile organic compound emissions from *Miscanthus* and short rotation coppice willow bioenergy crops

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1     **Volatile organic compound emissions from *Miscanthus* and short rotation**  
2                                   **coppice willow bioenergy crops**

3

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18

19 **Abstract**

20

21 *Miscanthus x giganteus* and short rotation coppice (SRC) willow (*Salix spp.*) are increasingly  
22 important bioenergy crops. Above-canopy fluxes and mixing ratios of volatile organic  
23 compounds (VOCs) were measured in summer for the two crops at a site near Lincoln, UK, by  
24 proton transfer reaction mass spectrometry (PTR-MS) and virtual disjunct eddy covariance.  
25 The isoprene emission rate above willow peaked around midday at  $\sim 1 \text{ mg m}^{-2} \text{ h}^{-1}$ , equivalent  
26 to  $20 \mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$  normalised to  $30^\circ\text{C}$  and  $1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$  PAR, much greater than for  
27 conventional arable crops. Average midday peak isoprene mixing ratio was  $\sim 1.4$  ppbv.  
28 Acetone and acetic acid also showed small positive daytime fluxes. No measurable fluxes of  
29 VOCs were detected above the *Miscanthus* canopy. Differing isoprene emission rates between  
30 different bioenergy crops, and the crops or vegetation cover they may replace, means the  
31 impact on regional air quality should be taken into consideration in bioenergy crop selection.

32

33 **Keywords:** VOC, isoprene, bioenergy, *Miscanthus*, willow, eddy covariance

## 34 **1 Introduction**

35

36 Bioenergy crops are those grown specifically for energy production rather than food, as a  
37 means of mitigating two problems associated with the use of traditional fossil fuels:  
38 anthropogenic climate forcing and energy security (McKay, 2006). Such crops contribute to  
39 carbon neutrality since CO<sub>2</sub> produced during the combustion of the crop is offset by the CO<sub>2</sub>  
40 sequestered during growth. There is also potential for long-term storage of carbon via uptake  
41 by soil through plant roots (Grogan and Matthews, 2002). Consequently, cultivation of  
42 bioenergy crops is increasing rapidly. For example, power generators in the UK are required to  
43 increase to 15.4% by 2015/16 the energy derived from renewable sources (DTI, 2005), with  
44 biomass being acknowledged as a key resource in achieving this target.

45

46 Although bioenergy crops are perceived to be carbon neutral, full life-cycle analysis needs  
47 also to take account of changes in emissions of other potent greenhouse gases such as CH<sub>4</sub> or  
48 N<sub>2</sub>O. Also, few studies have investigated volatile organic compound (VOC) emissions from  
49 bioenergy crops. Biogenic VOC emissions from vegetation (Steiner and Goldstein, 2007) are  
50 estimated as about 10 times greater globally than VOC emissions from anthropogenic sources  
51 (Guenther et al., 1995). The dominant BVOC is isoprene (Guenther et al., 2006), but other  
52 important compounds include oxygenated VOCs and terpenoids.

53

54 Emissions of VOCs are important for several reasons. Their rapid oxidation chemistry,  
55 particularly in the presence of NO<sub>x</sub>, affects the oxidative capacity of the atmosphere, the  
56 generation of tropospheric ozone (Atkinson, 2000), of concern for human and plant health  
57 (Ashmore, 2005) and as a radiative forcing gas, and on formation of secondary organic

58 particles, which likewise affect human health (Dockery et al., 1993) and radiative forcing  
59 (Kulmala et al., 2004).

60

61 The potential for BVOC emissions from crops to have a significant impact on atmospheric  
62 composition has been demonstrated in the tropics (Hewitt et al., 2009). The aim of this study  
63 was to determine fluxes of BVOCs for two bioenergy crops grown in the UK and elsewhere:  
64 short rotation coppice (SRC) willow (*Salix spp.*), a woody crop grown in dense plantations of  
65 multi-stemmed plants and harvested every 3 years; and *Miscanthus x giganteus*, a perennial  
66 grass native to Asia, of the same taxonomic group as sugarcane, sorghum and maize (Naidu et  
67 al., 2003) but more resilient to lower temperature whilst maintaining high CO<sub>2</sub> assimilation  
68 and biomass conversion efficiency. The crop grows up to 3.5 m per year (Rowe et al., 2009),  
69 and is harvested annually between January and March. The chipped and dried biomass of both  
70 crops is used to fuel biomass burners or to co-fire existing coal-fired power stations.

71

72 Fluxes from this work are compared with those for conventional UK arable crops to assess the  
73 potential impact of this land-use change on atmospheric chemistry.

74

75

## 76 **2 Methods**

77

### 78 *2.1 Sampling site*

79 The field measurements were carried out from mid July to mid August 2010 near Lincoln, UK  
80 (53° 19' N, 0° 35' W). Figure 1 shows the layout of the site, which consisted of several fields  
81 of *Miscanthus*, willow and wheat, located within an area of predominantly flat arable fields  
82 separated by hedgerows and isolated areas of mixed deciduous woodland. Mean annual

83 rainfall at the site was 600 mm and the soil was a fine loam, overlying Charnmouth mudstone.  
84 The nearest settlement (population: 113), which had a relatively busy through-road, was ~0.7  
85 km to the southeast. A minor road running east-west was situated 0.3 km to the south.

86

87 The *Miscanthus* plot (~11 ha, planted in spring 2006) was surrounded by the following  
88 vegetation types: hedgerow and wheat to the north; willow to the east; deciduous trees to the  
89 west; willow and wheat to the south. Crop height was typically 2.5 m. Sampling was carried  
90 out from 16<sup>th</sup> July to 2<sup>nd</sup> August 2010, near the NE corner of the plot, downwind of the  
91 prevailing wind direction, at an inlet height of approximately 4 m.

92

93 The willow plot (~6.5 ha, planted in 2001 with five different genotypes) was bounded as  
94 follows: a row of deciduous trees and a ploughed field to the north; *Miscanthus* to the west;  
95 mixed deciduous woodland to the south; wheat to the east. Typical canopy height was 4 m.  
96 Sampling was carried out from 5<sup>th</sup> to 13<sup>th</sup> August 2010 at an inlet height of 6.7 m on the north  
97 edge of the field. Trees were planted in pairs of rows 1.3 m apart, with 0.6 m spacing within  
98 each pair.

99

100 Flux footprints for both sampling sites were predicted using a simple parameterisation model  
101 (Kljun et al., 2004). Model results are shown in Supplementary Information Figure S1. For the  
102 *Miscanthus* measurements, the largest distance for 80% flux contribution over the range of  
103 friction velocities encountered (122 m) was within the area of the *Miscanthus* field throughout  
104 the south-westerly sector (180 – 270°). For the willow measurements, the largest distance for  
105 80% flux contribution (185 m) meant there may have been some small flux contributions from  
106 outside the willow field when wind was from the west. Flux contribution was otherwise within  
107 the willow field for the whole southerly wind sector (90 – 270°). These sectors were used for

108 directional filtering of data prior to deriving diurnal averages. Directionally-filtered data  
109 comprised 23% and 71% of all data for *Miscanthus* and willow, respectively.

110

111 Harvesting activities in surrounding farms during this study may have affected results,  
112 particularly during *Miscanthus* measurements, and are discussed later.

113

#### 114 2.2 Proton transfer reaction mass spectrometer (PTR-MS)

115 BVOC mixing ratios and fluxes above both crop canopies were measured using proton transfer  
116 reaction mass spectrometry (PTR-MS) (Blake et al., 2009) coupled with virtual disjunct eddy  
117 covariance (vDEC) (Karl et al., 2002; Rinne et al., 2001). PTR-MS is a ‘soft’ chemical  
118 ionisation method in which hydronium ions ( $\text{H}_3\text{O}^+$ ) formed in a hollow cathode ion source  
119 pass into a drift tube subject to an electric field ( $E$ ) into which the ambient air is also  
120 introduced. As most VOC molecules have a proton affinity greater than water, they react with  
121  $\text{H}_3\text{O}^+$  ions to form protonated products, predominantly the protonated molecular ion, but also  
122 fragments or clusters. The extent of fragmentation/clustering can be controlled by tuning the  
123  $E/N$  ratio ( $N$  is the  $\text{H}_3\text{O}^+$  ion density).

124

125 The PTR-MS used in this study (Ionicon Analytik, Innsbruck, Austria) was fitted with an extra  
126 turbopump connected to the detection chamber, and Teflon instead of Viton rings in the drift  
127 tube (Davison et al., 2009; Misztal et al., 2010). Pfeiffer turbopumps replaced the Varian  
128 equivalents. The drift tube conditions were held constant throughout (pressure 2 mbar,  
129 temperature 40 °C, voltage 572 V) to maintain an  $E/N$  ratio of  $\sim 130$  Td ( $1 \text{ Td} = 10^{-17} \text{ V cm}^2$ ).

130

131 The sampling inlet and 20 Hz sonic anemometer (WindmasterPro, Gill Instruments) were  
132 positioned above the canopy using a telescopic mast. Air was sampled at  $30 \text{ L min}^{-1}$  through a

133 20 m PTFE inlet line (1/4" OD, 3/16" ID) with a T-piece for sub-sampling into the PTR-MS  
134 inlet at a rate of 100 mL min<sup>-1</sup>. Condensation of water vapour in the inlet line was prevented  
135 by wrapping with self-regulating heating tape (Omega, UK type SRF3-2C). Data were logged  
136 using a program written in LabVIEW (Version 8.5, National Instruments).

137

### 138 2.3 Determination of VOC mixing ratios and fluxes

139 The PTR-MS signal was calibrated explicitly for several VOCs using a mixed gas calibration  
140 cylinder (Apel-Riemer Environmental Inc., USA) containing 1 ppmv each of formaldehyde,  
141 methanol, acetonitrile, acetone, acetaldehyde, isoprene and 0.18 ppmv d-limonene. The  
142 calibration gas was diluted with VOC-scrubbed air to produce 6 samples with concentrations  
143 of 0.5, 1.0, 10, 20, 30 and 50% of the pure calibration gas standard. A relative transmission  
144 curve was then constructed to determine empirical calibration coefficients for other VOCs  
145 under study not present in the standard (Taipale et al., 2008). Calibrations were carried out in  
146 the lab before commencement of the field campaign, and on 22<sup>nd</sup> July during the campaign.  
147 Concentrations of gases in the calibration cylinder were verified using GC-MS calibrated with  
148 its own independent standards (details given in Section 2.4).

149

150 The PTR-MS was run in multiple ion detection (MID) mode for two 25 min sampling periods  
151 per hour. During these periods only the targeted VOC ions listed in Table 1 were measured,  
152 with dwell times of 0.5 s, in addition to the primary ion H<sub>3</sub>O<sup>+</sup>, and water cluster (H<sub>2</sub>O)H<sub>3</sub>O<sup>+</sup>,  
153 which had dwell times of 0.2 s. The sensitivities (ncps ppbv<sup>-1</sup>) and limits of detection (ppbv)  
154 for the target ions for the *Miscanthus* and willow campaigns are also included in Table 1.  
155 LODs were calculated as the ratio of twice the standard deviation of the background ion  
156 counts for a particular *m/z* throughout the campaign divided by the sensitivity (Karl et al.,  
157 2003).



158

159 The remaining 10 min per hour were used for full mass scans in the range 21 – 206 amu at a  
160 dwell time of 1 s per amu. For one 5 min period, ambient air was scanned to allow information  
161 about the full VOC composition to be acquired. For a further 5 min per hour, ‘zero air’ was  
162 scanned to determine the instrument background. Zero air was achieved by sampling ambient  
163 air through a custom-made zero-air generator comprising a glass tube packed with platinum  
164 wool and a 50:50 mixture of platinum mesh and activated charcoal heated to 200°C. The  
165 background spectrum was subtracted in subsequent processing of data.

166

167 As the PTR-MS was run in MID mode, fewer data points were generated than required for  
168 direct eddy covariance due to the non-continuous manner in which the quadrupole mass  
169 analyser measures each  $m/z$ . The set-up resulted in 30,000 wind speed measurements and up to  
170 441 VOC measurements in each 25 min sampling period (depending on how many VOCs  
171 were being measured). The total lag time between PTR-MS and wind speed data was  
172 determined by examining the cross-correlation between vertical wind speed and VOC mixing  
173 ratio as a function of lag time (with 15 s window). Total lag includes residence time in the  
174 sampling inlet line but also lag associated with collection and data writing of a full cycle of  
175 analysis by disjunct sampling and the response of the PTR-MS. The median of the lag times  
176 for each 5 min sub-period was used to calculate the flux in that 25 min period (Misztal, 2010).  
177 For example, the average lag-time for isoprene above the willow was 9.58 s, with a standard  
178 deviation between 25 min periods of 1.41 s. This method produced less variable lag times than  
179 those derived using the prevalent MAX method in cross-correlation function (~72% lower sd),  
180 and has been shown to be a practical alternative (Taipale et al., 2010).

181

182 Quality controls were used to filter data for periods of low friction velocity ( $u^* < 0.15 \text{ m s}^{-1}$ ),  
183 non-stationarity, large spikes in vertical wind speed or VOC concentration, and where  $< 20000$   
184 data points were acquired in a 25 min sampling period. Most discarded data occurred during  
185 night when turbulence was low. High frequency flux losses due to the relatively slow disjunct  
186 VOC sampling frequency (0.25 Hz, compared to 20 Hz sonic data capture) were estimated  
187 using empirical ogive analysis (Ammann et al., 2006) for each 25 min period. At least 78% of  
188 flux was captured for all individual 25 min data periods, and values were corrected  
189 accordingly. Standard rotations of the coordinate frame were applied to correct for sonic  
190 anemometer tilt for each 25 min period separately.

191

#### 192 *2.4 Chromatographic analysis of ambient air samples*

193 Ambient air samples were collected for chromatographic analysis, to confirm the identity of  
194 the VOC components measured by the PTR-MS, approximately hourly from 06:53 to 16:20 on  
195 23 September 2010 above *Miscanthus* and from 06:32 to 17:30 on 11 August 2010 above  
196 willow (at ~1 m above the canopies). Sampling above *Miscanthus* was carried out at a later  
197 date because initial samples taken during the intensive campaign were lost due to GC-MS  
198 instrument failure. A mass-flow controlled Pocket Pump (210-1000 Series, SKC Inc.) was  
199 used to pump air at  $100 \text{ mL min}^{-1}$  for 15 min through stainless steel adsorbent tubes (6 mm  
200 OD) packed with 200 mg Tenax TA and 100 mg CarboTrap (Markes International Ltd., UK).  
201 Prior to sampling, packed tubes were conditioned at  $300 \text{ }^\circ\text{C}$  for 15 min with a flow of helium.

202

203 Analyses were carried out using a Hewlett-Packard 5890/5970 GC-MS with an automated  
204 thermal desorption unit (ATD 400, Perkin Elmer) connected via a  $200 \text{ }^\circ\text{C}$  heated transfer line.  
205 Transfer of samples from the adsorbent tubes was performed in two steps: heat to  $280 \text{ }^\circ\text{C}$  for 5  
206 min at  $25 \text{ mL min}^{-1}$  to desorb samples onto a Tenax-TA cold trap at  $-30 \text{ }^\circ\text{C}$ , followed by

207 transfer to the GC column at 300 °C for 6 min. Chromatographic separation utilised an Ultra-2  
208 column (Agilent Technologies, 50 m × 0.2 mm ID × 0.11 µm film, 5% phenylmethyl silica)  
209 and a temperature program of 35 °C for 2 min, heat at 5 °C min<sup>-1</sup> to 160 °C, heat at 10 °C  
210 min<sup>-1</sup> to 280 °C, and hold for 5 min.

211

212 Calibration was carried out using a mixed monoterpene in methanol standard (10 ng µL<sup>-1</sup> α-  
213 pinene, β-pinene, α-phellandrene, 3-carene and limonene (Sigma Aldrich, UK)) and an  
214 isoprene in nitrogen gas standard (700 ppbv, BOC Gases, UK). Aliquots of the monoterpene  
215 standard (0, 1, 3 and 5 µL) were injected onto 4 adsorbent tubes with helium carrier gas. Tubes  
216 continued to be purged with helium for 2 min after the standard injection. Isoprene calibration  
217 tubes were prepared by slowly (over a period of about 2 min) injecting 0, 10, 30 and 50 mL of  
218 the gas standard onto 4 adsorbent tubes, while purging with helium. The limits of detection for  
219 isoprene, α-pinene and limonene were 0.16, 0.23 and 0.30 ng on column, corresponding to  
220 mixing ratios of 38, 27 and 35 pptv, respectively, for a 1.5 L sample.

221

### 222 *2.5 Meteorological measurements*

223 Photosynthetically active radiation (PAR), rainfall, temperature and relative humidity were  
224 available as part of long-term measurements at the site.

225

226

## 227 **3 Results**

228

### 229 *3.1 Miscanthus*

230 The time series of VOC fluxes above *Miscanthus* are shown in Figure 2 along with  $u^*$  and  
231 sensible heat flux. Two periods of missing data 21<sup>st</sup> – 22<sup>nd</sup> and 25<sup>th</sup> – 27<sup>th</sup> July were due to

232 failure of the sampling pump. Data in the first few days were relatively noisy, showing no  
233 particular diurnal trend up to 20<sup>th</sup> July. This was likely due to elevated O<sub>2</sub><sup>+</sup> impurities during  
234 transport of the instrument resulting in less reliable primary ion counts or higher LOD.  
235 Additionally, episodes of rainfall on 17<sup>th</sup>, 18<sup>th</sup>, 20<sup>th</sup> and 22<sup>nd</sup> July may have resulted in a  
236 reduction in mixing ratio of VOCs where emission is proportional to PAR.

237

238 Small net emissions of isoprene and MEK from *Miscanthus* during daytime were just  
239 discernible, most noticeable on 18<sup>th</sup> July when sensible heat flux was also at its maximum.  
240 However, in general, flux data were somewhat noisy for all VOCs measured, and mostly not  
241 significantly different from zero. The directionally-filtered diurnal averages of VOC fluxes are  
242 shown in Supplementary Information Figure S2. As described earlier, the relevant sector for  
243 the *Miscanthus* measurements was south-west (180 – 270°). The mixing ratios of  
244 MVK+MACR (the first-generation oxidation products of isoprene) showed no diurnal pattern  
245 and were below LOD, so no data for these species are shown.

246

247 The time series of VOC mixing ratios above *Miscanthus* are shown in Supplementary  
248 Information Figure S3. For the period 27<sup>th</sup> July to 2<sup>nd</sup> August, mixing ratios of all measured  
249 VOCs had maxima at night except for isoprene whose mixing ratios were elevated in late  
250 afternoon. The average diurnal VOC mixing ratios above *Miscanthus* are shown in Figure S4.  
251 Methanol, acetaldehyde, acetone, acetic acid and MEK had similar diurnal profiles in mixing  
252 ratio. All showed a minimum mixing ratio around midday. The isoprene mixing ratio peaked  
253 around midday consistent with observation of a possible small isoprene flux above *Miscanthus*  
254 (Figure S2). No isoprene or monoterpenes were detected in the GC-MS analysis of adsorption  
255 tube sampling above the *Miscanthus* canopy.

256

257 *3.2 Short rotation coppice willow*

258 The time series of VOC fluxes, and  $u^*$  and sensible heat, measured above willow are shown in  
259 Figure 3. Missing data on 10<sup>th</sup> and 12-13<sup>th</sup> August were due to failure of the mobile power  
260 supply. Data were directionally filtered to include only those from over the willow field (90 –  
261 270°) before diurnally averaging (Figure 4). Willow showed a distinct diurnal pattern of  
262 isoprene flux, peaking at  $\sim 1 \text{ mg m}^{-2} \text{ h}^{-1}$  around midday and decreasing to zero overnight,  
263 driven by the strong dependence of isoprene emissions on temperature and PAR. All other  
264 VOC measured showed positive and negative fluxes throughout the day, with no significant  
265 net positive or negative daily flux overall.

266

267 Supplementary Information Figure S5 shows the time series of VOC mixing ratios and  
268 temperature above SRC willow. The time series showed clear diurnality in mixing ratios of all  
269 VOCs measured, except for methanol. The directionally-filtered diurnal averages of mixing  
270 ratio over the willow are shown in Figure 5.

271

272 Isoprene had a dominant maximum mixing ratio in early afternoon ( $\sim 1$  ppbv), temporally  
273 coincident with the temperature profile, and low mixing ratios at night. Figure 5 also plots the  
274 isoprene mixing ratios determined by adsorption tube sampling and GC-MS analysis. There  
275 was good agreement. Small quantities of the monoterpenes  $\alpha$ -pinene and limonene were also  
276 detected by GC-MS, but no diurnal patterns were discernable in these data.

277

278 Acetic acid, acetaldehyde and MVK+MACR also showed diurnal profiles with maxima in the  
279 afternoon and minima around 6 am, closely mirroring daily temperature variation. The  
280 amplitude of the daytime maximum of MEK mixing ratio was considerably less. Acetone

281 exhibited low diurnal variability but with the small maximum in early morning similar to the  
282 observation of *Miscanthus*.

283

284 As isoprene oxidation is the only known source of MVK and MACR, the ratio of  
285 MVK+MACR to isoprene mixing ratios can be used to examine the degree of isoprene  
286 oxidation (Figure 6). The [MVK+MACR]:[isoprene] ratio peaked around midnight with an  
287 average value of about 0.8 when isoprene was not being emitted and MVK+MACR were not  
288 undergoing photochemical loss or dispersion. At dawn there was a rapid decline in the ratio as  
289 the canopy responded to increasing PAR and temperature hence isoprene emissions increased,  
290 and the boundary layer depth also increased. The minimum ratio of ~0.1 occurred for several  
291 hours around midday. The ratio rose in late afternoon as isoprene emissions declined but  
292 isoprene oxidation continued.

293

294 The average measured daytime [MVK+MACR]:[isoprene] ratio of 0.24 is comparable with  
295 those from other northern latitude studies. A daytime ratio of 0.23 was measured in a rural  
296 Canadian forest clearing (Biesenthal et al., 1998), 0.12 was reported for a mixed forest in  
297 Michigan, USA (Apel et al., 2002) and 0.4 – 0.8 in a deciduous forest in Pennsylvania, USA  
298 (Martin et al., 1991).

299

### 300 *3.3 Standardised isoprene emission*

301 As isoprene emission from plants is strongly influenced by light and leaf temperature, the  
302 canopy-level emission,  $F$ , was recalculated as a standard emission factor ( $\epsilon$ ) normalised to a  
303 standard leaf temperature of 303 K and PAR flux of  $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ , as described by the  
304 G95 algorithm (Guenther et al., 1995),

$$\varepsilon = \frac{F}{D \gamma} \quad (1)$$

305

306 where  $D$  is foliar density ( $\text{g dry weight m}^{-2}$ ) and  $\gamma$  is a non-dimensional activity adjustment  
307 factor to account for the effect of light and temperature:

$$\gamma = C_L C_T \quad (2)$$

308

309 The light dependence,  $C_L$ , is defined by

$$C_L = \frac{\alpha c_{L1} Q}{\sqrt{1 + \alpha^2 Q^2}} \quad (3)$$

310

311 where  $\alpha$  (0.0027) and  $c_{L1}$  (1.066) are empirical coefficients and  $Q$  is PAR flux ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ).

312 The temperature dependence  $C_T$ , is defined by

$$C_T = \frac{\exp\left(\frac{c_{T1}(T - T_s)}{R T_s T}\right)}{1 + \frac{\exp(c_{T2}(T - T_M))}{R T_s T}} \quad (4)$$

313

314 where  $T$  is leaf temperature (K),  $T_s$  is leaf temperature at standard conditions (303 K),  $R$  is the  
315 universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and  $c_{T1}$  ( $95000 \text{ J mol}^{-1}$ ),  $c_{T2}$  ( $230000 \text{ J mol}^{-1}$ ) and  $T_M$   
316 (314 K) are empirical coefficients.

317

318 Values of above-canopy PAR and temperature, and of isoprene flux (from Figure 4), at hourly  
319 intervals during the willow campaign were used for the calculation of  $\gamma$  and  $F$  respectively.

320 Foliar density  $D$  was estimated at  $150 \text{ g}_{\text{dw}} \text{ m}^{-2}$  for *Salix spp.* (Karl et al., 2009). Hourly  
321 emission factors  $\varepsilon$  were then determined for isoprene from willow, and were found to have a  
322 peak value of  $25 \mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$  at 10:00. A mean midday value of  $20 \mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$  for  $12:00 \pm 2 \text{ h}$   
323 was determined to allow comparison, in Table 2, with mean values from other studies.

324

325 Table 2 shows that the emission factor from this study was within the range of values derived  
326 previously for *Salix spp.* The slightly lower measurements derived in this work and in the

327 other above-canopy study (Olofsson et al., 2005) were canopy-averaged emissions factors  
328 which included leaves which were in shade as well as those in direct sunlight. It was therefore  
329 expected that these measurements would result in lower standard emission factors than from  
330 individual branch or leaf-level experiments.

331

332

#### 333 **4 Discussion**

334

335 In the context of SRC willow as a bioenergy crop, the significant isoprene emission factor  
336 could potentially impact local and regional air quality by affecting tropospheric ozone  
337 production and SOA formation. Conventional agricultural crops are regarded as being low  
338 emitting species. For example, wheat and oats are estimated as having isoprene emission  
339 factors in the range 0 - 0.5  $\mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$  (Karl et al., 2009; Konig et al., 1995), while those for  
340 rapeseed, rye and barley are zero (Karl et al., 2009; Kesselmeier and Staudt, 1999).  
341 Replacement of conventional crops with SRC willow would therefore result in increased  
342 isoprene emission. A recent study examined the impact of SRC crop cultivation in Europe  
343 (Ashworth et al., 2012). It was concluded that monthly mean increases in ozone and BSOA  
344 (+1% and +5% respectively) from low level planting scenarios were significant enough to  
345 affect regional air quality and therefore warrant consideration in short term local impact  
346 assessments, as well as life cycle analysis of bioenergy crops.

347

348 At the end of 2009, total UK plantings of *Miscanthus* and SRC willow were 12,700 and 6,400  
349 ha respectively (DEFRA, 2009). A government report stated that there is potential in the UK  
350 to increase bioenergy crop cultivation substantially by a further 350,000 ha by 2020,  
351 accounting for ~6% of total UK arable land (DEFRA, 2007), with the assumption that 70%



352 would be *Miscanthus* and SRC willow (Rowe et al., 2009). In the case of 70% being converted  
353 solely to SRC willow, then a UK-wide increase of up to  $7.35 \text{ t h}^{-1}$  in emissions of isoprene  
354 would result (assuming zero isoprene emissions from the land prior to conversion to willow,  
355  $150 \text{ g}_{\text{dw}} \text{ m}^{-2}$  willow, and an isoprene standard emission rate of  $20 \mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$  determined here).  
356 The annual increase in isoprene would require calculation using PAR and temperature data  
357 across the likely planting sites in the UK, and a whole-canopy model.

358

359 The standard emission factor for isoprene from SRC willow measured in this study was  $26.5 \text{ g}$   
360  $\text{C ha}^{-1} \text{ h}^{-1}$ . This is an order of magnitude higher than was determined for total emission of  
361 VOCs from the biofuel crop switchgrass (Eller et al., 2011), where emissions were dominated  
362 by oxygenated VOCs and isoprene contributed less than 8%.

363

364 For *Miscanthus*, the near-zero values of flux at night were in contrast to the increase in mixing  
365 ratios of oxygenated VOCs (Figure S3 & S4). Since reliability of the eddy covariance  
366 technique depends on friction velocity, the greater boundary layer stability at night (hence low  
367 friction velocity) resulted in unreliable night time flux measurements. It may therefore be  
368 possible that night time fluxes were non-zero. A more likely scenario is that increasing VOC  
369 mixing ratios at night were affected by sources in the wider area. Towards the start of the  
370 measurement period, several of the surrounding fields were subject to harvesting and  
371 subsequent ploughing activities, which are known to be a source of oxygenated VOCs (Karl et  
372 al., 2001). Mixing ratios of methanol, acetaldehyde and acetone were comparable to those  
373 measured in previous field experiments of crop cutting (Warneke et al., 2002). The enhanced  
374 mixing ratios towards dusk, and at night can be explained by reduced radical sink chemistry,  
375 together with accumulation within a shallower nocturnal boundary layer from reduced vertical  
376 transport and mixing, as demonstrated by the lower wind speed and  $u^*$  at night (Figure 2).

377 During willow measurements, atypical increases in mixing ratios of methanol, acetone and  
378 acetic acid on 8<sup>th</sup> August may also have been caused by further harvesting activity in the wider  
379 area.

380

381

## 382 **5 Conclusions**

383

384 Measurements of above-canopy fluxes and mixing ratios of VOCs revealed significant  
385 emissions of isoprene from short rotation coppice willow, with a standard emission factor of  
386  $20 \mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$ . No significant emissions were measured from *Miscanthus*. This is the first  
387 field study of bioenergy crops in the UK and shows that a change in land use from  
388 conventional to bioenergy crops could result in increased isoprene emissions. Bioenergy crop  
389 species choice should therefore include consideration of their impact on regional air quality.  
390 Further work could include measurement of VOC emissions from *Miscanthus* and SRC  
391 willow during senescence and harvesting.

392

393

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533

*Miscanthus* and coppice willow are increasingly important bioenergy crops.

Above-canopy fluxes were measured using PTR-MS and virtual disjunct eddy covariance.

Willow isoprene emission peaked at  $\sim 1 \text{ mg m}^{-2} \text{ h}^{-1}$ ,  $\equiv 20 \text{ } \mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$  standardised.

Bioenergy crop species choice should include their impact on regional air quality.

Table 1: Compounds measured during the field campaign including dwell times, sensitivities and limits of detection.

$m/z$ [amu]	Contributing compound(s)	Formula	Dwell time [s]	Sensitivity [ncps ppbv <sup>-1</sup> ]	Limit of detection [ppbv]	
					<i>Miscanthus</i>	Willow
21	water isotope	H <sub>2</sub> <sup>18</sup> O	0.2	-	-	-
33	methanol	CH <sub>4</sub> O	0.5	4.1	1.41	2.03
37	water cluster	(H <sub>2</sub> O) <sub>2</sub>	0.2	-	-	-
45	acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	0.5	12	0.44	0.21
59	acetone propanal	C <sub>3</sub> H <sub>6</sub> O	0.5	11	0.41	0.06
61	acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	0.5	10	0.08	0.06
69	isoprene furan methyl butenol fragment	C <sub>5</sub> H <sub>8</sub>	0.5	3.5	0.13	0.12
71	methyl vinyl ketone (MVK) methacrolein (MACR)	C <sub>4</sub> H <sub>6</sub> O	0.5	6.2	0.06	0.07
73	methyl ethyl ketone (MEK)	C <sub>4</sub> H <sub>8</sub> O	0.5	6.0	0.11	0.08



Table 2: Comparison of standardised emission rates of isoprene from willow. REA = relaxed eddy accumulation

Species	Standard emission rate / $\mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$	Measurement type	Reference
<i>Salix</i> spp.	20	Canopy-scale, PTR-MS	This study
<i>Salix</i> spp.	28	Branch enclosure	(Owen and Hewitt, 2000)
<i>Salix alba</i>	18	Branch enclosure, lab conditions	(Pio et al., 1993)
<i>Salix alba</i>	37.2	-	(Karl et al., 2009)
<i>Salix babylonica</i>	115	-	(Winer et al., 1983)
<i>Salix caprea</i>	18.9	Branch enclosure	(Karl et al., 2009)
<i>Salix caroliniana</i>	12.5	Air-exchange branch enclosure	(Zimmerman, 1979)
<i>Salix nigra</i>	25.2	Whole plant, air-exchange chamber	(Evans et al., 1982)
<i>Salix phylicifolia</i>	32	Branch enclosure	(Hakola et al., 1998)
<i>Salix viminalis</i>	12	Canopy-scale, REA	(Olofsson et al., 2005)

**Figure captions**

Figure 1: Aerial view of the Miscanthus and willow plantations. The white dots denote the measurement locations at the NE corner of the Miscanthus field and the N edge of the SRC willow field. (Map attributable to: ©2001 DigitalGlobe, GeoEye, Getmapping plc, Infoterra Ltd & Bluesky, TerraMetrics. Map data ©2011 Google).

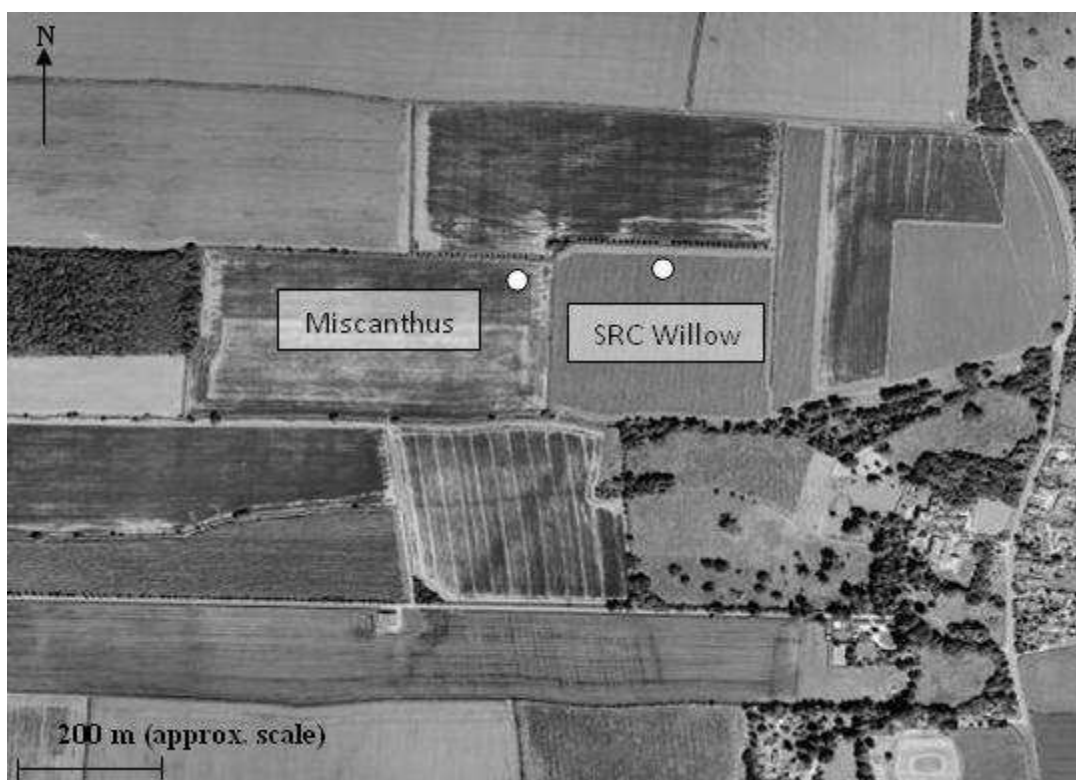
Figure 2: Time series of VOC fluxes measured above Miscanthus. Dashed gridlines denote midnight. Note the variable flux scales.

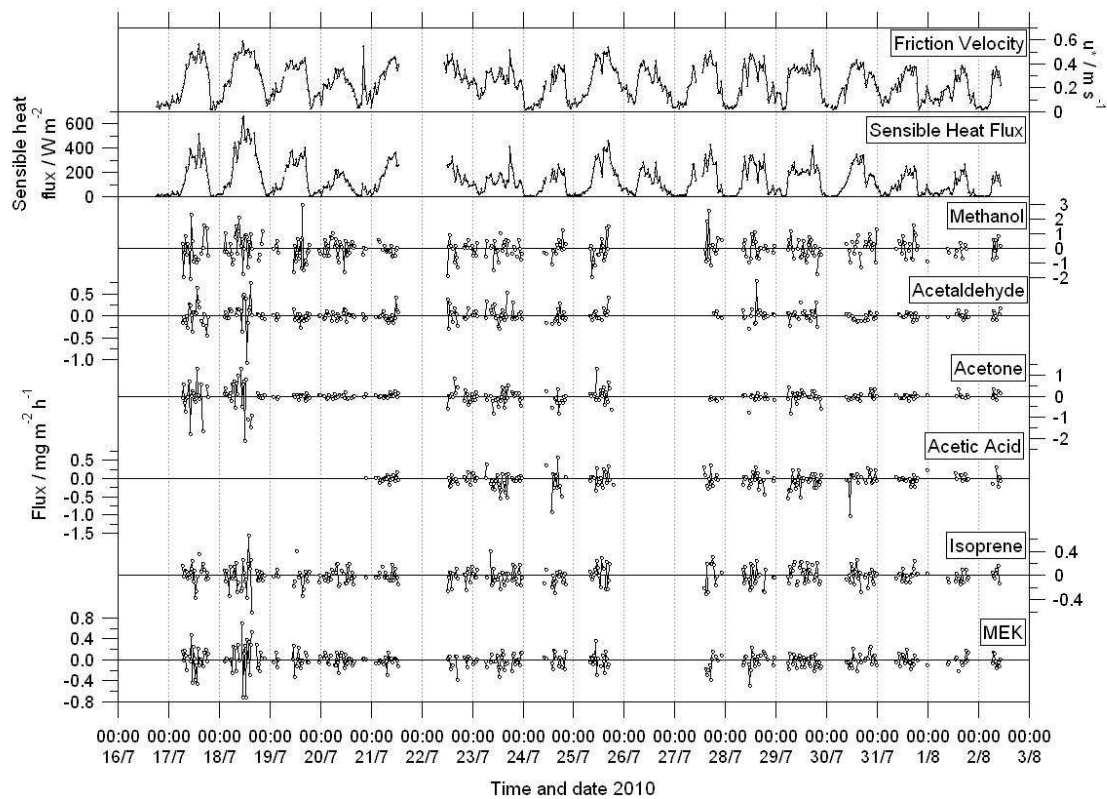
Figure 3: Time series of VOC fluxes measured above willow canopy. Dashed gridlines denote midnight. Note the variable scales.

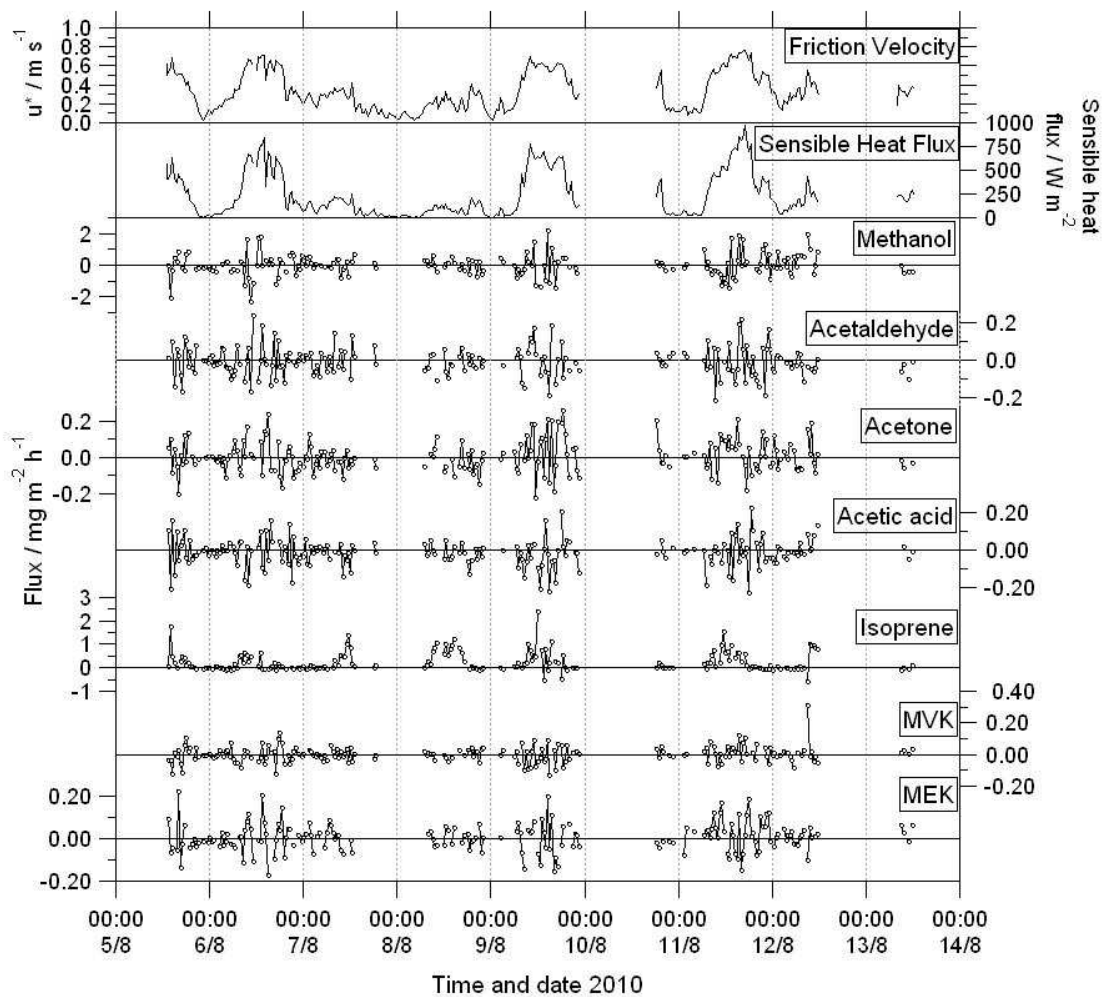
Figure 4: Average diurnal profiles of VOC fluxes above willow, and of sensible heat flux, when wind direction was between 90 and 270° (i.e. from over the willow field). Note the variable scales. Grey areas show variability calculated as  $\pm 1$  sd of the averaged half-hourly values of all measurements.

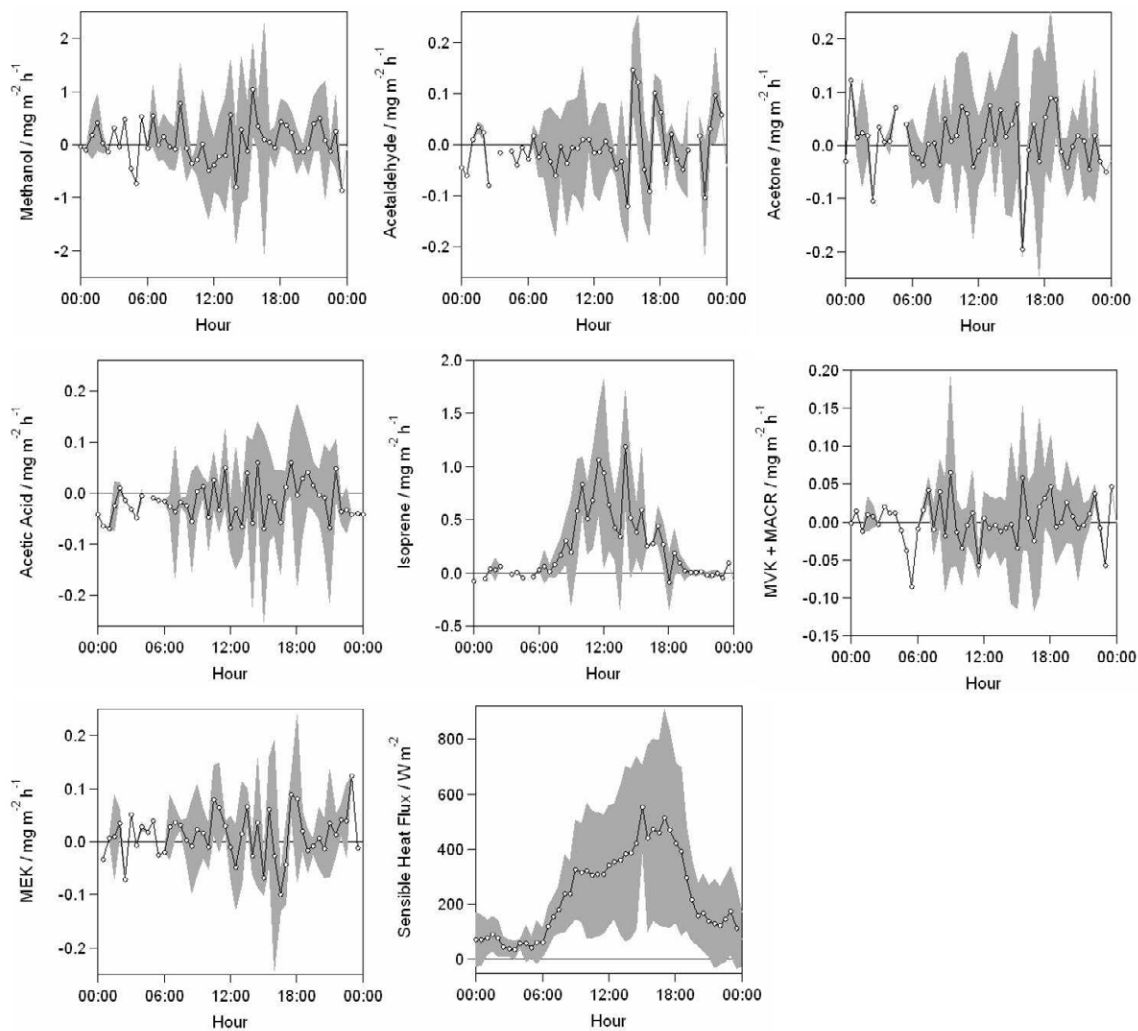
Figure 5: Average diurnal profiles of VOC mixing ratios above willow, and of temperature, when wind direction was between 90 and 270° (i.e. from over the willow field). Note the variable scales. Dashed lines denote LOD. Grey areas represent variability calculated as  $\pm 1$  sd of the averaged half-hourly values of all measurements.

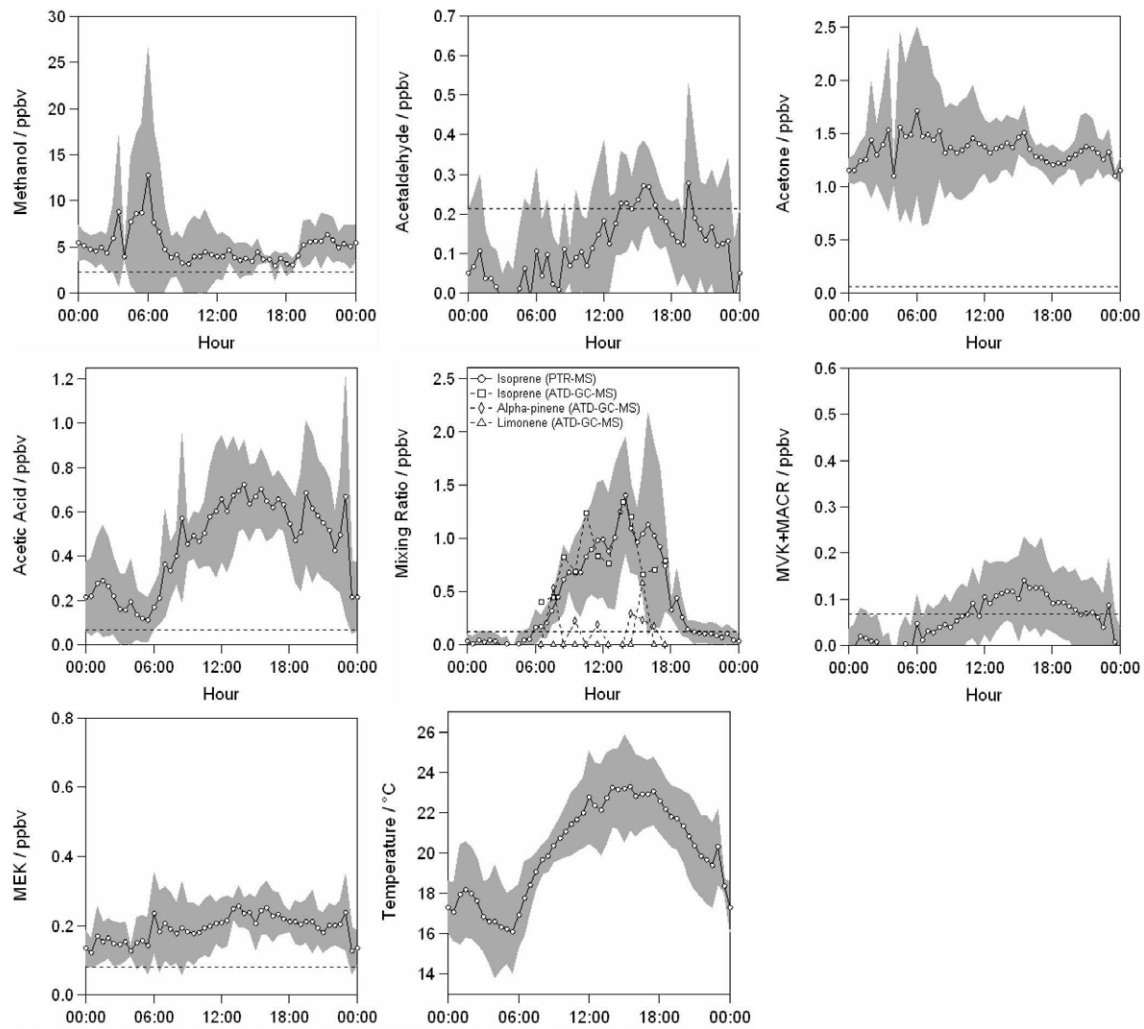
Figure 6: Average diurnal profile of [MVK+MACR]:[isoprene] ratio above the willow canopy. Grey areas represent variability calculated as  $\pm 1$  sd of the averaged half-hourly values of all measurements.

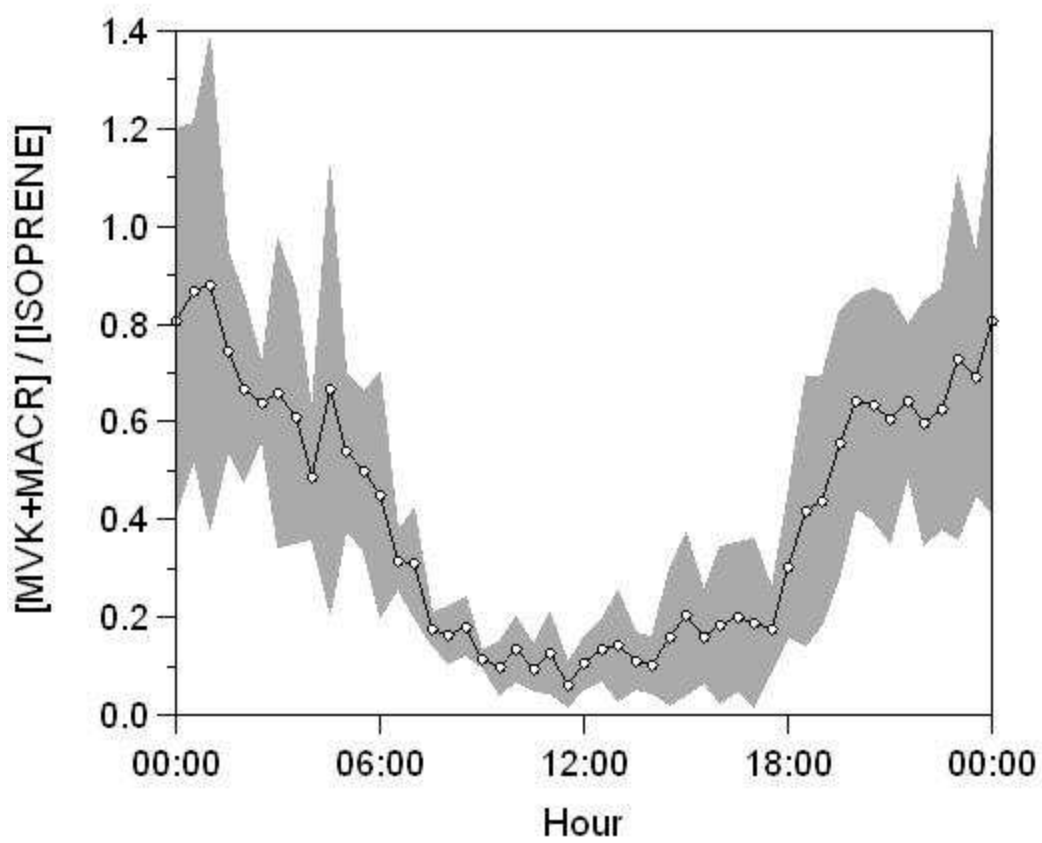














## **Supplementary Information**

### **Volatile Organic Compound Emissions from *Miscanthus* and Short Rotation Coppice Willow Bioenergy Crops**

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The main paper reports on field measurements of VOC concentrations and fluxes above *Miscanthus* and short rotation crop (SRC) willow crops.

Average diurnal profiles were derived from the time series of measurements using data filtered to examine only those times when the wind direction and flux footprint was over the relevant crop field. The flux footprint for the range of friction velocities encountered was estimated as described in the main text, and the model output is shown here in Supplementary Information Figure S1. For measurements over *Miscanthus* and willow, directional filtering was undertaken for the sectors 180 – 270° and 90 – 270°, respectively. (See also the layout of the field site shown in Figure 1.)

Time series and directionally-filtered diurnal averages of both fluxes and mixing ratios of VOCs above both *Miscanthus* and SRC willow comprise too many figures to present in the main text. The most salient are presented in the main paper, and are mainly concerned with the measurements above SRC willow since measurements above *Miscanthus* showed essentially no significant VOC fluxes. For completion, the directionally-filtered diurnal averages of fluxes above *Miscanthus* are presented here in Figure S2, and the time series and directionally-filtered diurnal averages of the VOC mixing ratios above *Miscanthus* are presented in Figures S3 and S4, respectively. The time series of VOC mixing ratios above willow are shown in Figure S5.

Figure S1: Modelled flux footprints for *Miscanthus* and SRC willow measurements. The following parameters were used. *Miscanthus*: measurement height  $z_m$  4 m; roughness length  $z_0$  0.25 m (estimated as 1/10th of the canopy height, 2.5 m); boundary layer height  $h$  1000 m. SRC willow:  $z_m$  6.7 m;  $z_0$  0.4m;  $h$  1000 m. Footprints were calculated for 90<sup>th</sup> percentile (P90), median and minimum values of  $u^*$  (1 sd of the vertical wind speed,  $\sigma_w$ , shown in brackets) as indicated on the graphs. The distance at which maximum contribution can be expected, and at which 80% of the flux is contained, are given as  $X_{max}$  and  $X_r$ , respectively.

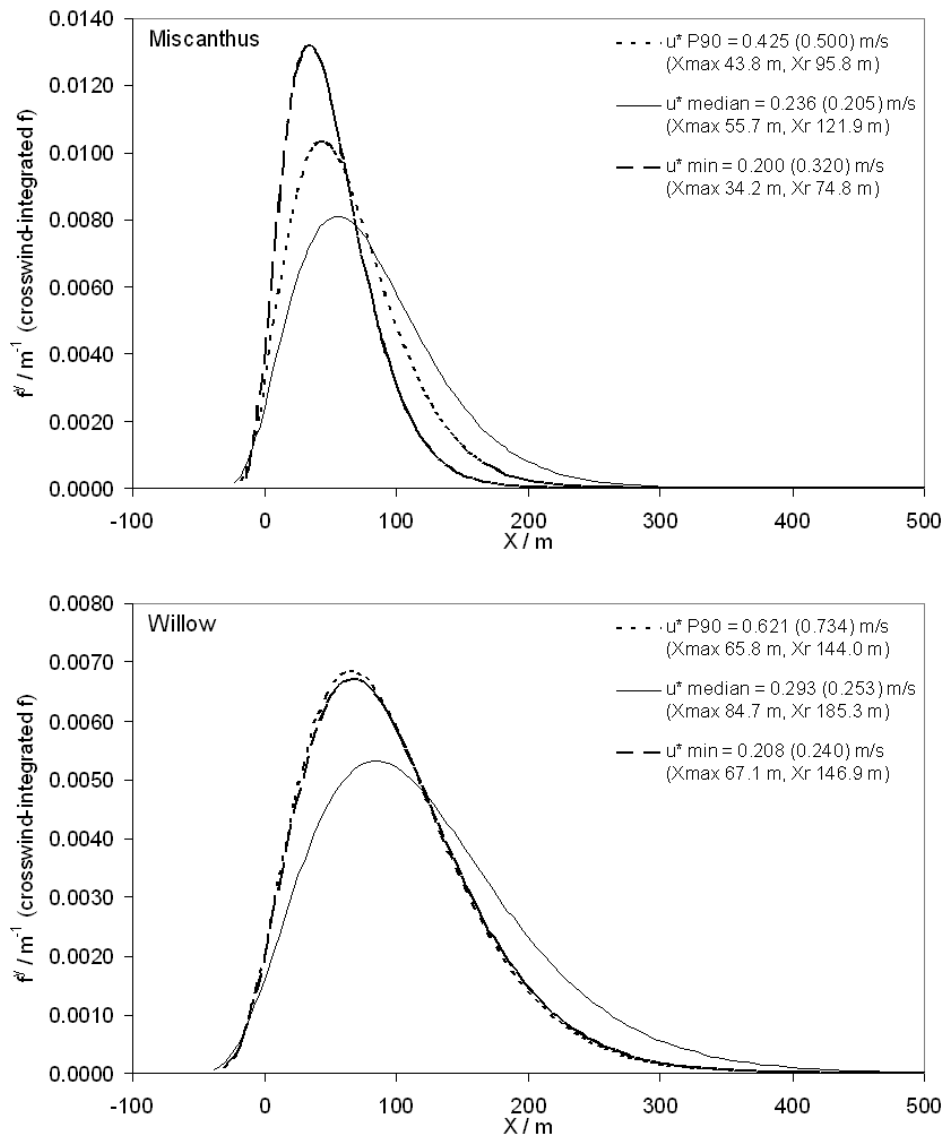


Figure S2: Average diurnal profiles of VOC fluxes above *Miscanthus* when wind direction was between 180 and 270° (i.e. from over the *Miscanthus* field). Note the variable scales. Grey areas represent variability calculated as  $\pm 1$  sd of the averaged half-hourly values of all measurements. A profile for MVK+MACR is not included due to insufficient data.

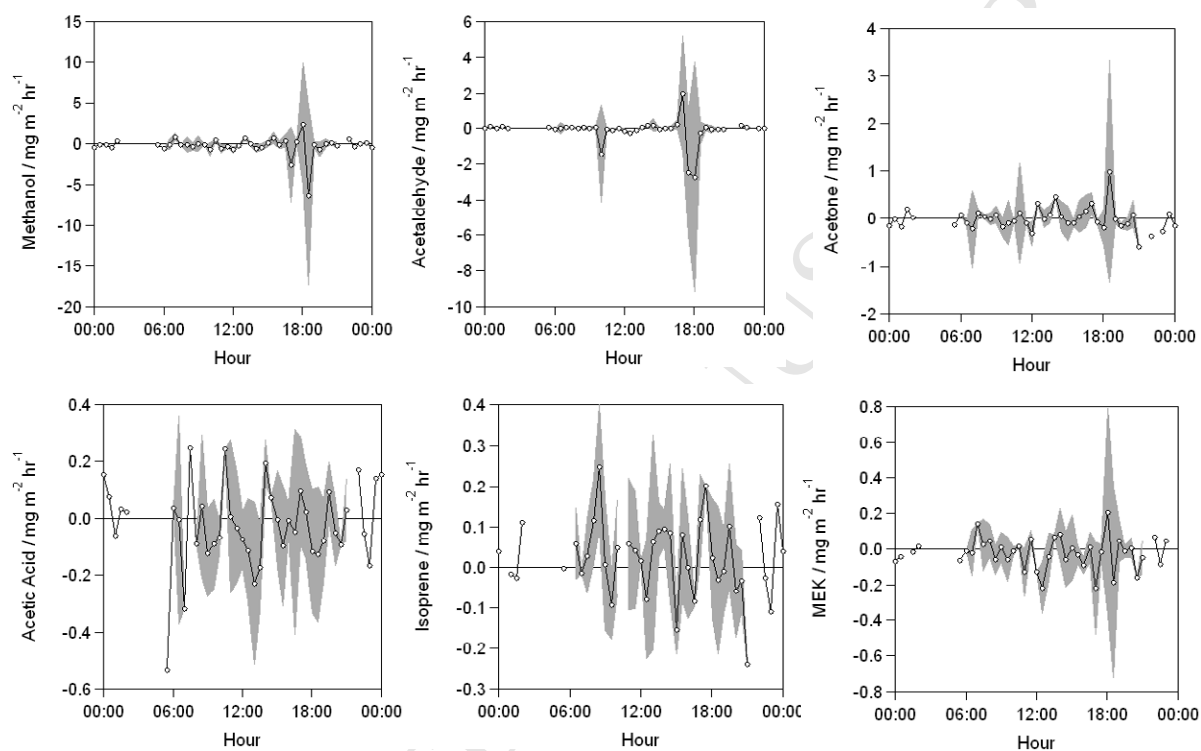


Figure S3: Time series of VOC mixing ratios, and of temperature, measured above *Miscanthus*. Dashed gridlines denote midnight. Note the variable mixing ratio scales.

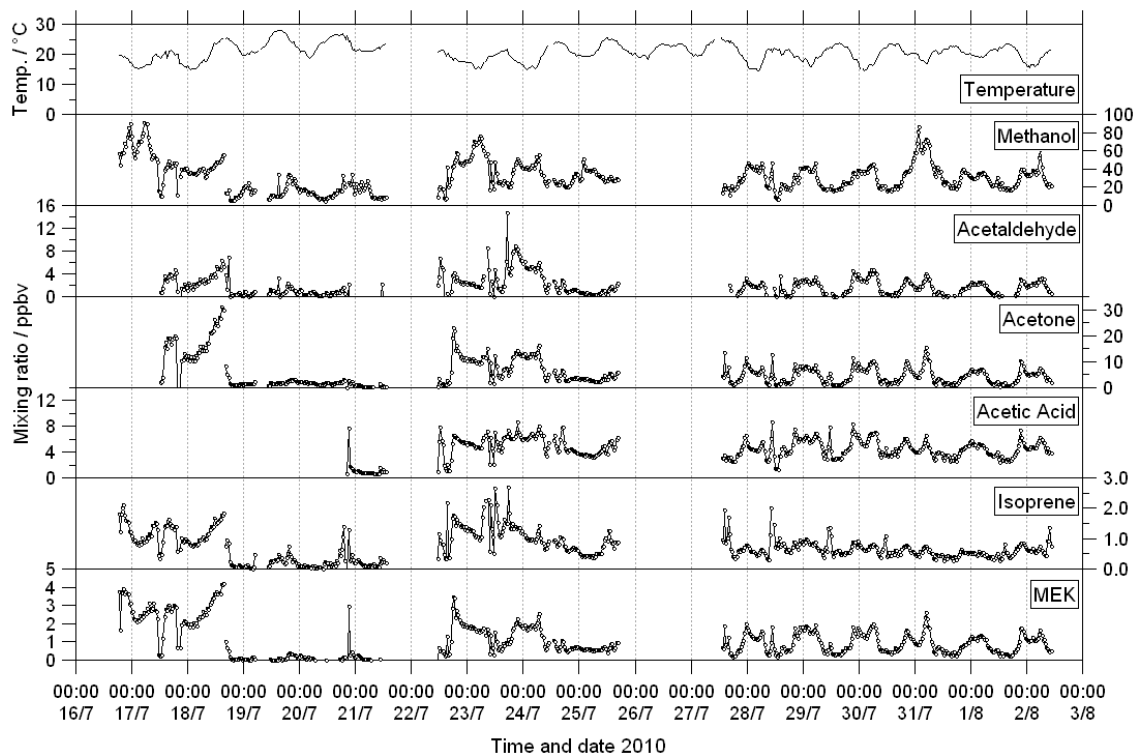


Figure S4: Average diurnal profiles of VOC mixing ratios above *Miscanthus*, and of temperature, when wind direction was between 180 and 270° (i.e. from over the *Miscanthus* field). Note the variable scales. Dashed lines denote LOD. Grey areas represent variability calculated as  $\pm 1$  sd of the averaged half-hourly values of all measurements.

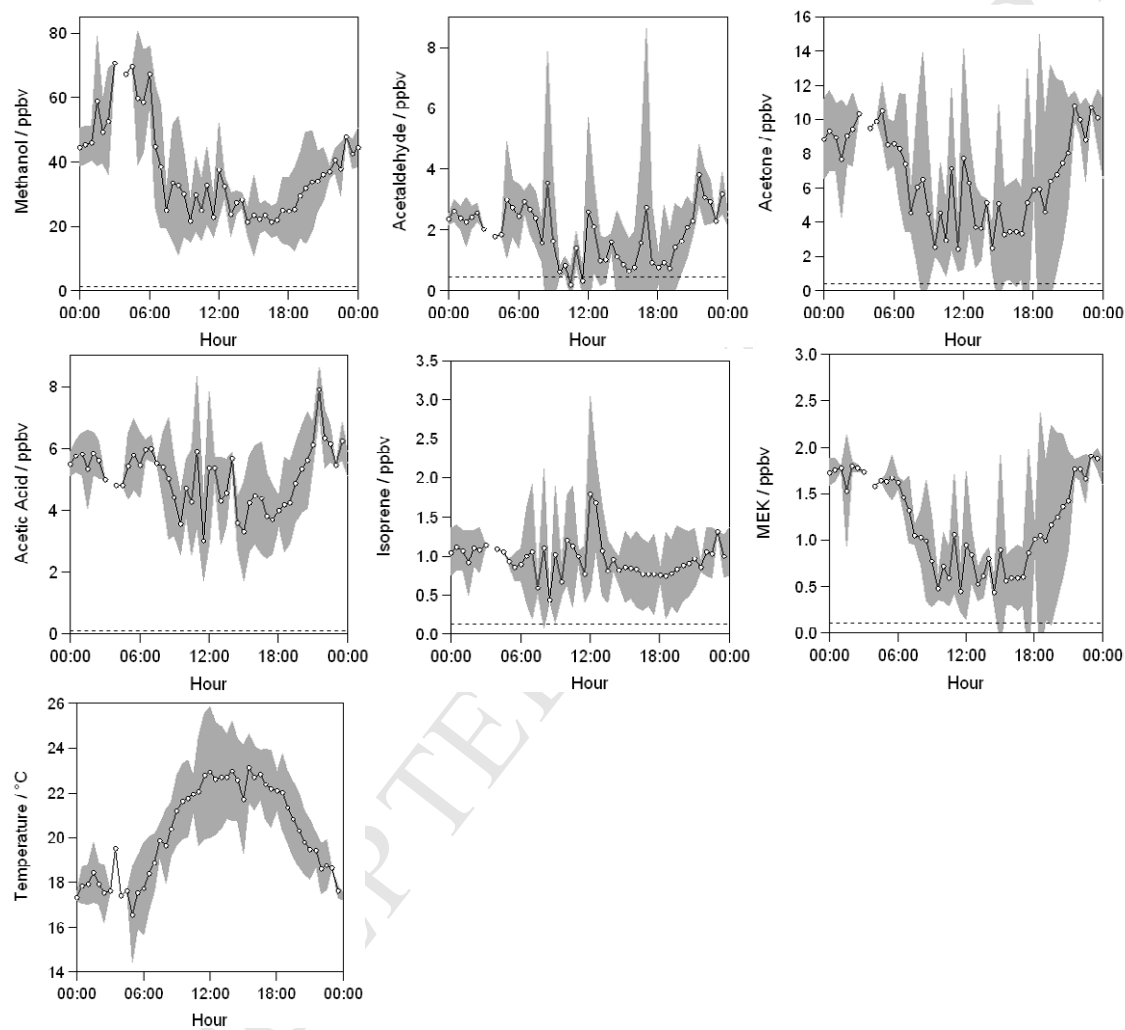


Figure S5: Time series of VOC mixing ratios, and of temperature, measured above willow. Dashed gridlines denote midnight. Note the variable mixing ratio scales.

