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Citation for published version:
Morrison, EC, Drewer, J & Heal, MR 2016, 'A comparison of isoprene and monoterpene emission rates from the perennial bioenergy crops short-rotation coppice willow and Miscanthus and the annual arable crops wheat and oilseed rape', *GCB Bioenergy*, vol. 8, no. 1, pp. 211-225. https://doi.org/10.1111/gcbb.12257

Digital Object Identifier (DOI):
10.1111/gcbb.12257

Published In:
GCB Bioenergy

GLOBAL CHANGE BIOLOGY
BIOENERGY

GCB Bioenergy (2016) **8**, 211–225, doi: 10.1111/gcbb.12257

A comparison of isoprene and monoterpene emission rates from the perennial bioenergy crops short-rotation coppice willow and *Miscanthus* and the annual arable crops wheat and oilseed rape

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Abstract

Biogenic volatile organic compounds (BVOC) emissions from bioenergy crops may differ from those of conventional crops. We compared emission rates of isoprene and a number of monoterpenes from the lignocellulosic bioenergy crops short-rotation coppice (SRC) willow and *Miscanthus*, with the conventional crops wheat and oilseed rape. BVOC emission rates were measured via dynamic vegetation enclosure and GC-MS analysis approximately monthly between April 2010 and August 2012 at a location in England and from SRC willow at two locations in Scotland. The largest BVOC emission rates were measured from willow in England and varied between years. Isoprene emission rates varied between <lod and 1960 $\mu g\ g^{-1}\ h^{-1}$. Of the monoterpenes detected from willow, α-pinene emission rates were highest (<lod to 803 $\mu g\ g^{-1}\ h^{-1}$), followed by <lod to 268 $\mu g\ g^{-1}\ h^{-1}$ for δ-3-carene, <lod to 125 $\mu g\ g^{-1}\ h^{-1}$ for β-pinene and <lod to 80.4 $\mu g\ g^{-1}\ h^{-1}$ for limonene. BVOC emission rates measured in Scotland were much lower. Low emission rates of isoprene and α-pinene were measured from *Miscanthus* in 2010 (<lod to 6.42 $\mu g\ g^{-1}\ h^{-1}$ and <lod to 20.8 $\mu g\ g^{-1}\ h^{-1}$, respectively) but were not detected in subsequent years. Emission rates from wheat of isoprene were negligible but relatively high for monoterpenes (<lod to 422 $\mu g\ g^{-1}\ h^{-1}$ and <lod to 104 $\mu g\ g^{-1}\ h^{-1}$ for α-pinene and limonene, respectively). No significant emission rates of BVOCs were measured from oilseed rape. The measured emission rates followed a clear seasonal trend. Crude extrapolations based solely on data gathered here indicate that isoprene emissions from willow could correspond to 0.004–0.03% (UK) and 0.76–5.5% (Europe) of current global isoprene if 50% of all land potentially available for bioenergy crops is planted with willow.

Keywords: bioenergy, biogenic volatile organic compounds, *Miscanthus*, oilseed rape, short-rotation coppice, willow

Received 11 June 2014; revised version received 13 February 2015 and accepted 14 February 2015

Introduction

The depletion of fossil fuel resources, pollution concerns and the challenge of energy security are driving the search for renewable energy sources. The use of lignocellulosic plant biomass as an energy source is increasing in the United Kingdom (UK) and worldwide. In the United Kingdom, up to 6% of the total arable land may be planted with perennial bioenergy crops by 2020 in order to meet renewable energy and CO_2 reduction targets (DEFRA, 2007). Several plant species that produce high biomass from low inputs have been identified. The most promising for the UK climate are the genus *Miscanthus*, a perennial rhizomatous C4 grass which can grow up to 3.5 m in a year (Rowe *et al.*, 2009), and short-rotation coppice (SRC) willow (*Salix* spp.), plantations of which can remain viable for up to 30 years. The dried biomass of these crops is used to fuel biomass burners or to cofire existing coal-fired power stations.

Although bioenergy crops are perceived as 'carbon neutral', changes in land use can have a wider impact on atmospheric composition than through CO_2 alone. Globally, emissions of biogenic volatile organic compounds (BVOC) from vegetation are estimated to be 10 times greater than VOC emissions from anthropogenic sources (Guenther *et al.*, 1995). The dominant BVOC is isoprene (Guenther *et al.*, 2006), but other important compounds include terpenes, terpenoids and oxygenated VOCs. Although terrestrial vegetation is an important source of these trace gases, with the exception of a short field campaign reported by Copeland *et al.* (2012) and experimental pot studies by Crespo *et al.* (2013), there are very few previous measurements of any of these reactive gases, except isoprene, from these bioenergy crops. Some studies have measured VOC

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emissions from other bioenergy crop such as switchgrass (Eller *et al.*, 2011; Graus *et al.*, 2013) and poplar (Eller *et al.*, 2012).

BVOC emissions are important as they directly and indirectly influence the concentrations and lifetimes of air pollutants and greenhouse gases. For example, oxidation of BVOCs generate tropospheric ozone (Fehsenfeld *et al.*, 1992; Pierce *et al.*, 1998) and secondary organic aerosols (SOA) (Bonn & Moortgat, 2003; Bonn *et al.*, 2004; Claeys *et al.*, 2004; Lim *et al.*, 2005; Singh *et al.*, 1995; VanReken *et al.*, 2006; Volkamer *et al.*, 2006) both of which have adverse human and plant health impacts and affect the Earth's radiative balance.

The individual BVOCs emitted, and their rates of emissions, are specific to each plant species. For example, standard isoprene emission rates of between 12 and 115 μg g^{-1} dry weight h^{-1} have been reported for different species of willow (Copeland *et al.*, 2012; Evans *et al.*, 1982; Hakola *et al.*, 1998; Isebrands *et al.*, 1999; Karl *et al.*, 2009; Niinemets *et al.*, 2010; Olofsson *et al.*, 2005; Owen & Hewitt, 2000; Owen *et al.*, 2003; Pio *et al.*, 1993; Winer *et al.*, 1992; Zimmerman, 1979) with a calculated standardized emission rate of between 18 and 41 μg g^{-1} dry weight h^{-1} reported for one species of willow (*Salix alba*) (Karl *et al.*, 2009; Niinemets *et al.*, 2010; Pio *et al.*, 1993). Emissions of monoterpenes have been shown to vary widely between species and also over time with one study reporting α-pinene emissions to vary between 3% and 40% of the total monoterpenes emitted from tea-leafed willow over a 5-month period (Hakola *et al.*, 1998).

These variations mean it is important to characterize emissions from bioenergy plant species directly. There are few long-term studies on BVOC emissions, with the exception of Pressley *et al.* (2005), who measured isoprene emissions from above a northern hardwood forest (containing aspen, beech, birch, maple, pine and oak) over several consecutive growing seasons. Although emissions of BVOCs from various willow species are well documented, again these studies focus on measurements taken during one month in summer (Copeland *et al.*, 2012; Isebrands *et al.*, 1999; Niinemets *et al.*, 2010) or for slightly longer periods of two to three months during the growing season (Hakola *et al.*, 1998; Olofsson *et al.*, 2005).

This study assesses the comparative contributions to the emissions of a subset of these trace gases between bioenergy crops and annual arable crops in the United Kingdom, specifically isoprene, α-pinene and β-pinene, δ-3-carene, limonene and α-phellandrene, although no emissions of the latter were ever detected. Measurements by vegetation enclosure and dynamic sampling onto adsorbent cartridges were undertaken at three SRC willow locations, one in England and two in Scotland, with measurements at the location in England also including adjacent *Miscanthus* and annual arable crops. A particular feature of this study is the long time series of measurements, up to 28 months for the site in England, in order to fully characterize the annual cycle.

Materials and methods

Field locations

All field locations were commercial farms, not crops planted specifically for research, and information on species distribution in individual fields was not available. On the other hand, these field locations reflect the variability in actual conditions on commercially operated farmland.

Lincolnshire

The longest time series of measurements of BVOC emission rates were carried out between April 2010 and August 2012 at a farm in Lincolnshire, England (53°19′N, 0°35′W). Long-term (1963–2004) mean annual rainfall at this site is 605 mm. Details of the soil composition and management of the site are described in Drewer *et al.* (2012).

The site comprised adjacent fields planted with the perennial bioenergy crops SRC willow (*Salix spp.*) and *Miscanthus x giganteus*, and the annual arable crops wheat and oilseed rape (*Brassica napus*) on rotation. The latter rotated from wheat to oilseed rape to wheat during 2010–2012. Sampling was undertaken at ten points in each crop with the uppermost section of the vegetation enclosed, typically around 0.5–0.8 m depending on the height of the vegetation. As terrain was homogeneous, accessibility of the sampling point was the main consideration. Other than the need for space for the chamber on its tripod alongside the plants, the choice of sampling point was arbitrary. The sampling points in the *Miscanthus* and arable crop fields included plants within (>10 m from the field edge) and along the edge of (within 3 m of the field margin) the plantings, with half the sampling points within the field and half along the edge. In the willow field, sampled points were sited on the edge because of space constraints. The same foliage was sampled on each visit, unless leaves had been removed for dry mass estimation, in which case it would be the closest branch.

The willow crop comprised 6.5 ha of ca. 1.5 trees m^{-2} of five different varieties planted in 2002 which is managed on a 3-year cropping cycle with harvest taking place in the autumn. It was first harvested in October 2007. The willow trees were coppiced again in winter 2010 so measurements taken in 2011 were from younger trees compared to measurements taken from trees with three year's growth in 2010 and at least a year's growth in 2012. After coppicing, branches began to develop in April followed by bud break and leaf development in May. These stages occurred slightly earlier if the willow had not been recently coppiced, with bud break occurring in early March and full leaf development by the start of April. The willow reached full biomass in August–September. Senescence

began in October, with loss of foliage during November and dormancy over winter.

The 11 ha of *Miscanthus* was established in 2005 with a planting density of ca. 1 rhizome m^{-2}. It was harvested in spring which occurred for the first time in 2007. The crop was harvested again in March 2010, 2011 and 2012, and the emergence of new shoots from the rhizomes occurred in May when average temperatures were between 3 and 6 °C. Leaf growth occurred in June, at temperatures of between 5 and 10 °C (Clifton-Brown & Jones, 1997; Hastings *et al*., 2009). Biomass rapidly accumulated throughout the summer, peaking around September (Heaton *et al*., 2010). Senescence occurred in November and the crop was harvested in March after dry down over the winter period.

Instrumentation in the *Miscanthus* field provided continuous data on rainfall and air temperature, and on soil temperature and soil water content at 5 cm depth. The climate in Lincolnshire differed between the three years of measurement. In 2010, a warm summer was followed by a cold winter with temperatures remaining below freezing on some days. Another warmer summer with low rainfall led to drought conditions in the first half of 2011 and early 2012. Spring and summer of 2012 were very wet with some flooding occurring in the fields.

Perthshire

Additional measurements from SRC willow were taken between September 2011 and August 2012 at a farm situated on the south side of the Lomond Hills Regional Park in Perth and Kinross, Scotland (56°20′N, 3°27′W), near Glenrothes. The long-term mean annual rainfall (from 1981 to 2010) is 1056 mm. The 10 ha site contained three adjacent fields, one with a slope of ~10°, planted in June 2007 with five different varieties of SRC willow at a density of ~3 trees m^{-2} (distribution of varieties unknown). Plants were cut back after one year but had yet to be harvested. Sampling was undertaken at 10 points in each field, revisited each time and included plants on the edge and within the plantation.

The soils differed slightly between the three fields, with soil pH varying between 7.02 ± 0.20 (standard deviation (SD) of three replicates collected in March 2012), 6.82 ± 0.04 and 7.29 ± 0.04, soil carbon content varying between 3.19 ± 0.05%, 3.02 ± 0.03% and 3.64 ± 0.07% and soil nitrogen content varying between 0.29 ± 0.006%, 0.28 ± 0.006% and 0.34 ± 0.01%. Soil bulk density was similar across all fields at around 0.90 g cm^{-3}. Soil moisture was determined on each visit and was similar across all fields, ranging between 23% and 33% between September 2011 and August 2012.

Continuous weather data were obtained from a meteorological station at Kinross, 4 km from the site. The climate was relatively stable over the measurement period. Summer temperatures were relatively cool and the winter was relatively warm, with an average annual temperature of 16.5 °C.

Fife

A shorter time series of measurements (March to August 2012) was taken at an SRC willow site in the south of Fife, close to Dunfermline (56°05′N, 3°62′W). Four varieties of willow (distribution unknown) were planted in May 2009 on around 35 ha with a planting density of 3 trees m^{-2}. The willow was cut back in spring 2010 but had not been coppiced before sampling. The mean annual rainfall was approximately 1080 mm based on measurements taken during the sampling period. Sampling was undertaken at 10 points at the edge of and within the plantation, revisited on each occasion.

Continuous weather data were obtained from a meteorological station at Grangemouth, 6 km from the site. The climate was relatively stable over the measurement period with an average temperature of 17.8 °C.

Vegetation enclosure system

Two cylindrical enclosure chambers were used, one of polycarbonate of 1 mm thickness (26 l) and one of polyethylene terephthalate (PET) of 1 mm thickness (66 l). Both materials were >90% transparent to photosynthetically active radiation (PAR) (400–700 nm), and both enclosures incorporated a fan to ensure mixing and separate openings for headspace flow through and to monitor internal air temperature.

During each enclosure, the PAR, total solar radiation and internal chamber temperature were recorded (sampling rate between 2 and 30 s) via a small weather station (H21-002 Hobo Micro Station Data Logger, Onset Computer Corporation, Bourne, MA, USA). Soil temperature and moisture were also measured on each sampling occasion. To determine the latter, three replicates of 10 g of soil material from 10 cm depth were freed of any large and obvious root or plant material and dried in an oven at 105 °C to constant mass.

After mounting the chamber on a tripod, the vegetation was carefully placed inside and the chamber enclosed around the branch/stem. To create a dynamic enclosure system, ambient air was drawn through the chamber at 12 l min^{-1} [as used in Crespo *et al*. (2013) and recommended by Ortega & Helmig (2008)] through Teflon tubing connected to a Charles Austen Capex V2 oil-free double-ended diaphragm pump. Chambers were flushed for at least 10 min prior to sample collection. Samples were collected by pumping air from the enclosure through Teflon tubing onto adsorbent tubes at 200 ml min^{-1} for 10 min to give a sample volume of 2 l (with corresponding analyte concentration C_{out}). During the same period, a parallel sample was collected next to the chamber using the same tubing as for the sample to yield the comparative concentration in ambient air (C_{in}). Mass-flow control Pocket Pumps (210-1000 Series, SKC Inc., Eighty Four, PA, USA) were used to collect the two samples concurrently on commercial 6 mm OD stainless steel automated thermal desorber (ATD) tubes (L4270123, PerkinElmer, Waltham, MA, USA) packed with 200 mg poly (2,6-diphenylphenylene oxide) (Tenax® TA 60/80) (11982 SUPELCO, Sigma-Aldrich, St Louis, MO, USA) and 100 mg Carbotrap® 20/40 (20273 SUPELCO, Sigma-Aldrich). Prior to sampling, the packed tubes were conditioned at 300 °C for 15 min with a flow of helium.

At the end of each sampling period, the number of enclosed leaves on the branch was counted and a subset of the foliage removed and dried in an oven at 70 °C until constant mass to estimate the total enclosed biomass. The mass of leaves on a

branch was calculated by multiplying the average mass of the subset of leaves by the total number of leaves on the branch. A number of full, destructive analyses were also carried out on enclosed branches, from which an uncertainty of ±10% was derived for this subsampling method of estimating the enclosed biomass. Only leaves were considered as biomass that yielded the BVOC measured (Guenther, 1997; Laothawornkitkul *et al.*, 2009; Owen *et al.*, 2001). A Leaf Area Index (LAI) meter (LI-3100C Area Meter, LI-COR, Lincoln, NE, USA) was used to provide data to estimate foliar area density for calculation of standard isoprene emission rates.

Determination of BVOC emission rates

Samples were analysed for BVOCs by GC-MS (5890HP GC with a 5970HP mass-selective detector, Hewlett Packard, Palo Alto, CA, USA). The automated thermal desorber (ATD 400, Perkin-Elmer, Wellesley, MA, USA) used a flow of helium at 280 °C for 6 min to desorb the sample from the tube onto a Tenax TA cold trap at −30 °C. Transfer into the GC (Ultra-2 column, 100 m length, 0.2 mm I.D., 5% phenylmethyl silica, Agilent, Palo Alto, CA, USA) was achieved by flash heating the cold trap to 300 °C for 6 min to flush the sample through a heated transfer line (200 °C). The GC was held at 35 °C for 2 min, ramped to 160 °C at 3 °C min^{-1} then ramped to 280 °C at 45 °C min^{-1} before being held at 280 °C for 10 min.

Calibration was carried out using a mixed monoterpene in methanol standard [10 ng μl^{-1} α-pinene, β-pinene, α-phellandrene, limonene and δ-3-carene (Sigma-Aldrich, Irvine, UK)] and an isoprene in nitrogen gas standard (700 ppbv, BOC Gases, Guildford, UK). Aliquots of the monoterpene standard (0, 1, 3 and 5 μl) were injected onto 4 adsorbent tubes with helium carrier gas. Tubes continued to be purged with helium for 2 min after the standard injection. Isoprene calibration tubes were prepared by slowly (over a period of about 2 min) injecting 0, 10, 30 and 50 ml of the gas standard onto four adsorbent tubes, while purging with helium. Limit of detection (LOD) was derived from twice the standard deviation of the LOD of the GC signal near the retention times of each analyte in a blank standard. The average LODs for isoprene, α-pinene, β-pinene, limonene and δ-3-carene are given in Table 1.

The net emission rate, ER, from the enclosed biomass (in $\mu g\ g^{-1}\ h^{-1}$) was calculated using

$$ER = \frac{[C_{out} - C_{in}] \times Q}{m_{dry}}$$

where C_{out} and C_{in} are the enclosure outlet and inlet concentrations of the compound of interest (g l^{-1}), Q is the flow rate of the purge air (l h^{-1}) and m_{dry} is the dried mass (g) of leaves enclosed. Net BVOC emission rates were derived from the difference between the concentrations at the chamber outlet and inlet so some sources of potential inaccuracy cancel out, for example in primary standard concentrations and their dilutions in an individual calibration curve. The major uncertainty in an individual concentration arises from the statistical uncertainty in the interpolation from a given calibration regression fit. As both the parallel blank and enclosure samples were stored and

Table 1 Summary of isoprene, α-pinene, β-pinene, limonene and δ-3-carene fluxes ($\mu g\ g^{-1}\ h^{-1}$) from willow at the Lincolnshire, Perthshire and Fife field locations. <lod = below the limit of detection

	Lincolnshire						Perthshire						Fife					
	Growing season			Non-growing season			Growing season			Non-growing season			Growing season					
	Range ($\mu g\ g^{-1}\ h^{-1}$)	n	% <lod	Range ($\mu g\ g^{-1}\ h^{-1}$)	n	% <lod	Range ($\mu g\ g^{-1}\ h^{-1}$)	n	% <lod	Range ($\mu g\ g^{-1}\ h^{-1}$)	n	% <lod	Range ($\mu g\ g^{-1}\ h^{-1}$)	n	% <lod	Average LOD (ng)
Isoprene	<lod - 1960	104	13	<lod	29	100	<lod - 269	69	17	<lod	25	100	<lod - 4.63	50	33	2.31
α-pinene	<lod - 803	104	50	<lod - 0.56	29	83	<lod - 99.9	69	7	<lod	25	100	<lod - 19.6	50	24	3.56
β-pinene	<lod - 125	104	79	<lod	29	100	<lod	69	100	<lod	25	100	<lod	50	100	1.64
Limonene	<lod - 80.4	104	66	<lod	29	100	<lod - 33.0	69	1	<lod	25	100	<lod - 0.42	50	42	1.84
δ-3-carene	<lod - 268	104	70	<lod	29	100	<lod - 13.0	69	23	<lod	25	100	<lod	50	100	1.54

analysed in identical conditions such uncertainties are minimized by the experimental design of quantification by difference. A description of the propagated error analysis is given in Morrison (2013).

Results

Willow

No emission of α-phellandrene was measured from any crop at any point. Variations in isoprene, α-pinene, β-pinene, limonene and δ-3-carene emission rates from willow in Lincolnshire and environmental variables throughout the study period are shown in Figs 1–4 (note the scales change between years) and from willow in Perthshire in Fig. 5. The largest emission rates measured in this study were for isoprene from willow where the maximum emission rate measured (1960 $\mu g\ g^{-1}\ h^{-1}$) was over twice the maximum monoterpene emission rate measured (α-pinene, 803 $\mu g\ g^{-1}\ h^{-1}$) (Table 1).

A range of isoprene emission rates between <lod and 1960 $\mu g\ g^{-1}\ h^{-1}$ were measured from willow across the three locations, as summarized in Table 1. The highest isoprene emission rates were measured in Lincolnshire, where the maximum emission rate measured was more than 7 times the maximum emission rate measured in Perthshire (269 $\mu g\ g^{-1}\ h^{-1}$) and greatly in excess of the maximum measured in Fife (4.63 $\mu g\ g^{-1}\ h^{-1}$).

As isoprene emission from plants is strongly influenced by light and leaf temperature, it is often expressed as a standard emission factor (Ɛ) normalized to a leaf temperature of 303 K and PAR flux of 1000 $\mu mol\ m^{-2}\ s^{-1}$, as described by the G95 algorithm (Guenther *et al.*, 1995). Using the measurements of isoprene emission rates from willow during the growing seasons in 2010 to 2012, standard emission rates of 16 $\mu g\ g^{-1}\ h^{-1}$, 1.9 $\mu g\ g^{-1}\ h^{-1}$ and 0.1 $\mu g\ g^{-1}\ h^{-1}$ were calculated for the Lincolnshire, Perthshire and Fife locations, respectively. Calculation of the standard emission rate used a foliar density of 150 $g_{dw}\ m^{-2}$ for *Salix* spp. based on LAI measurements taken in this study, which is similar to that of Karl *et al.* (2009). Mean specific leaf area for the crops in this study is presented in Table 2.

Emissions of α-pinene, β-pinene, limonene and δ-3-carene were quantified from willow in Lincolnshire; however β-pinene was <lod in Perthshire and Fife and δ-3-carene was <lod in Fife (Table 1). The highest α-pinene emission rates were measured in Lincolnshire, where the maximum measured emission rate (803 $\mu g\ g^{-1}\ h^{-1}$) was >8 times the maximum emission rate measured in Perthshire (99.9 $\mu g\ g^{-1}\ h^{-1}$) and 40 times the maximum measured in Fife (19.6 $\mu g\ g^{-1}\ h^{-1}$). Limonene and δ-3-carene emission rates followed the same trend (Lincolnshire > Perthshire > Fife).

Table 2 Mean specific leaf area (SLA) ($cm^2\ g^{-1}$ dry mass) and the associated one standard deviation values

Crop type	Mean specific leaf area ($cm^2\ g^{-1}$ dry weight)	Standard deviation
Willow	12.8	8.95
Miscanthus	105	32.0
Wheat	8.60	2.46

In Lincolnshire, higher emission rates of isoprene from willow were measured in 2010 (up to 1960 $\mu g\ g^{-1}\ h^{-1}$) (Fig. 1) compared with 2011 (up to 49.2 $\mu g\ g^{-1}\ h^{-1}$) (Fig. 2) and 2012 (up to 278 $\mu g\ g^{-1}\ h^{-1}$) (Fig. 3). Higher emission rates of α-pinene, β-pinene and δ-3-carene were also measured from willow in 2010. Low or <lod monoterpene emission rates were measured in 2011 but emission rates increased in 2012. The maximum emission rate of α-pinene measured in 2010 was an order of magnitude larger than that measured in 2012 (803 $\mu g\ g^{-1}\ h^{-1}$ compared with up to 83 $\mu g\ g^{-1}\ h^{-1}$, respectively). The same trend was observed for the maximum emission rate of β-pinene (125 $\mu g\ g^{-1}\ h^{-1}$ in 2010 and 4.96 $\mu g\ g^{-1}\ h^{-1}$ in 2012) and δ-3-carene (268 $\mu g\ g^{-1}\ h^{-1}$ in 2010 and 21.7 $\mu g\ g^{-1}\ h^{-1}$ in 2012). However, for limonene, a higher maximum emission rate was measured in 2012 than in 2010 (30.7 $\mu g\ g^{-1}\ h^{-1}$ in 2010 and 80.4 $\mu g\ g^{-1}\ h^{-1}$ in 2012).

The measured environmental variables in Lincolnshire are shown in Fig. 4. At each individual site, highest emissions of isoprene emissions corresponded to highest local air temperatures. The emission rates from willow at the Lincolnshire and Perthshire location followed a seasonal trend, highest in spring/summer and lowest between September and March. Measurements were not taken for sufficient duration at the Fife location to investigate seasonality.

Emission rates of isoprene, α-pinene, β-pinene, limonene and δ-3-carene from willow at the Lincolnshire location were categorized as growing season (beginning of April to end of September) and non-growing season (November to March) based on observation of plant growth and senescence. The significance of growing season and sampling point within the field as factors associated with the variation in individual BVOC emission rate was tested using the Kruskal–Wallis function in the R v2.15.1 software package (R Core Team, 2012). Emission rates of each BVOC varied significantly with season ($P < 0.01$) (with larger emission rates in the growing season), but not with sampling point.

To provide insight into potential drivers of variation in emission rates, Spearman correlation coefficients were calculated between emission rates, PAR, air temperature, soil temperature and soil moisture, also using

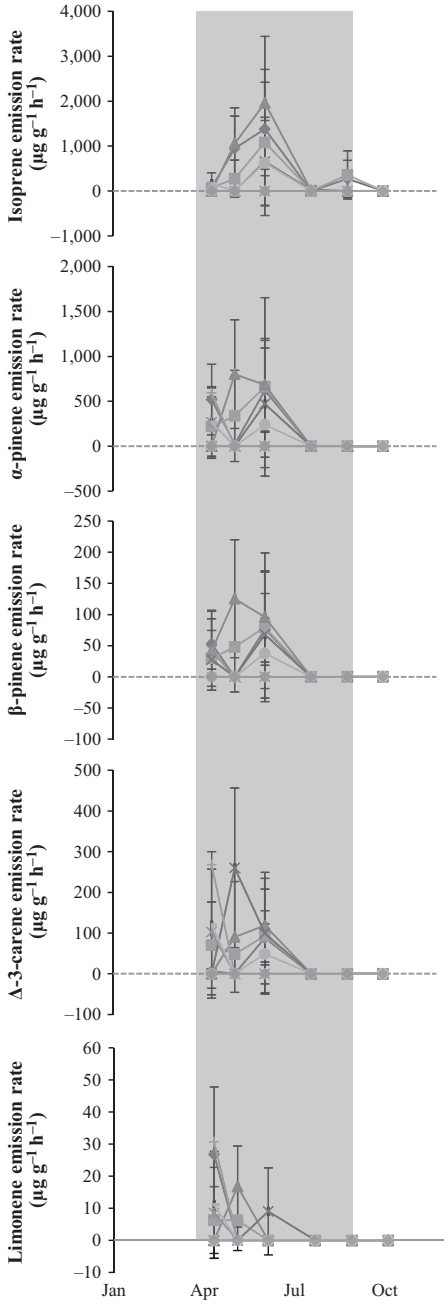

Fig. 1 Emission rates of isoprene, α-pinene, β-pinene, δ-3-carene and limonene from each of the ten individual sampling sites in short-rotation coppice willow at the Lincolnshire location in 2010. (Individual sampling sites were revisited – see main text.) The shaded area demarcates the growing season. Error bars are uncertainties calculated using propagation of error and take into account uncertainty in determination of biogenic volatile organic compounds concentration, volume, temperature, enclosure time and dried leaf mass enclosed.

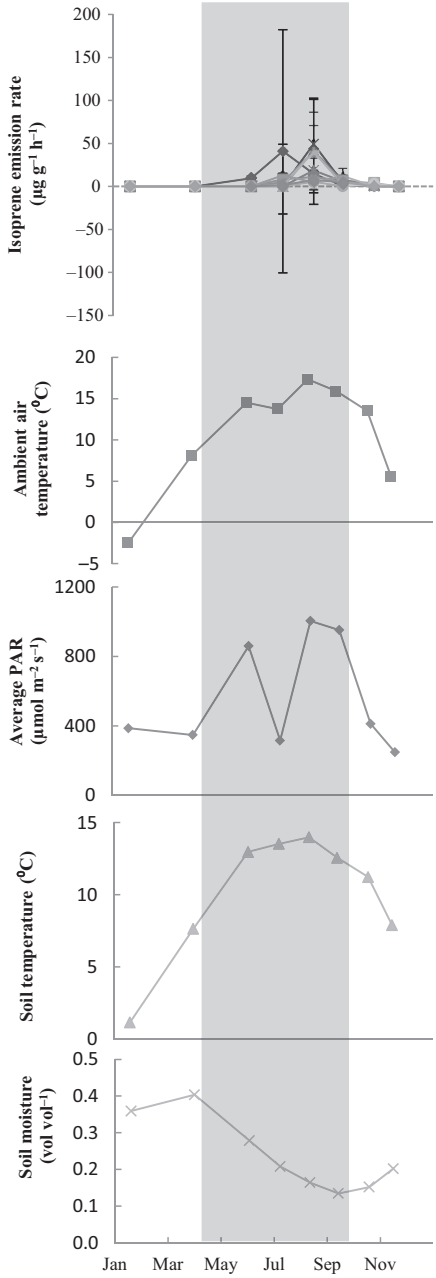

Fig. 2 Emission rates of isoprene from each of the ten individual sampling sites in short-rotation coppice willow at the Lincolnshire location in 2011 together with mean photosynthetically active radiation intensity, ambient air temperature, soil temperature and soil moisture. The shaded area demarcates the growing season. Error bars are uncertainties calculated using propagation of error and take into account uncertainty in determination of biogenic volatile organic compounds concentration, volume, temperature, enclosure time and dried leaf mass enclosed.

the R 2.15.1 software package (Table 3). Significant correlations ($P < 0.05$) were identified between isoprene, α-pinene and δ-3-carene emission rates and PAR and air temperature. There were also significant correlations between isoprene, α-pinene, β-pinene and limonene emission rates and soil temperature and soil moisture,

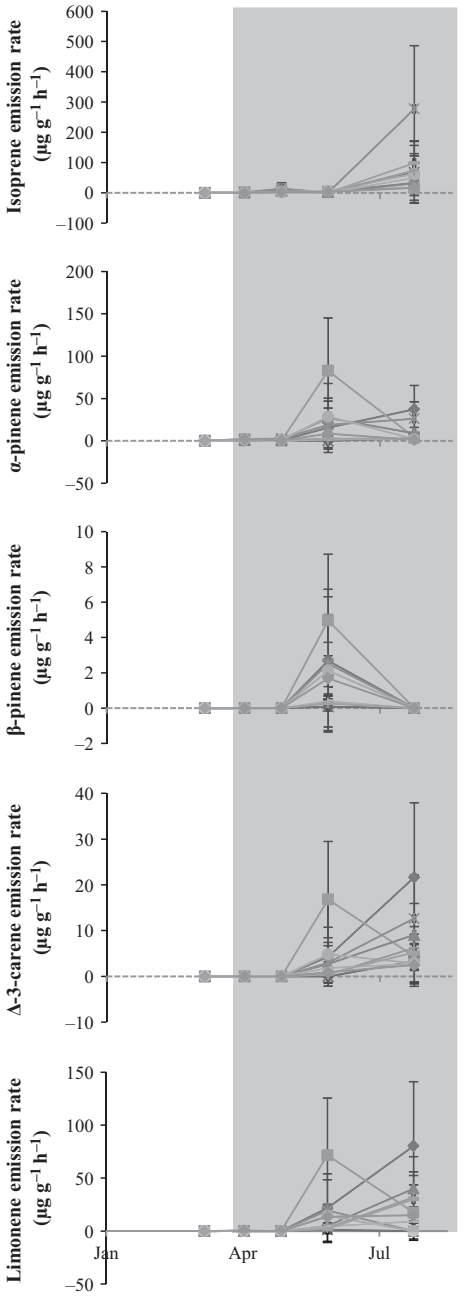

Fig. 3 Emission rates of isoprene, α-pinene, β-pinene, δ-3-carene and limonene from each of the ten individual sampling sites in short-rotation coppice willow at the Lincolnshire location in 2012. The shaded area demarcates the growing season. Error bars are uncertainties calculated using propagation of error and take into account uncertainty in determination of biogenic volatile organic compounds concentration, volume, temperature, enclosure time and dried leaf mass enclosed.

although isoprene emissions were inversely correlated with soil moisture, in contrast to the emission rates of the other compounds.

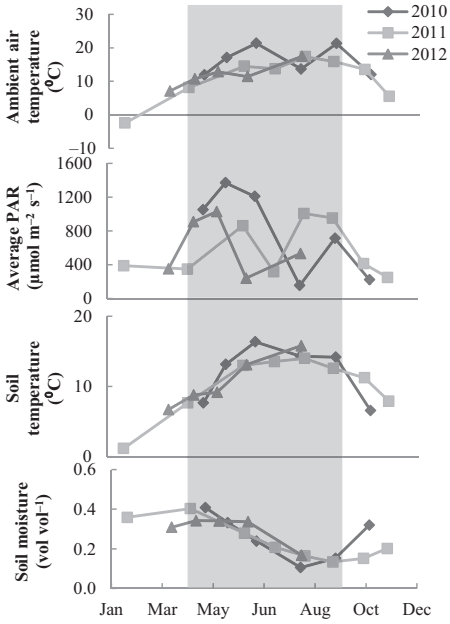

Fig. 4 Mean ambient air temperature, photosynthetically active radiation intensity, soil temperature and soil moisture in short-rotation coppice willow at the Lincolnshire location in 2010, 2011 and 2012. The shaded area demarcates the growing season.

Miscanthus

Emissions of isoprene and α-pinene were observed from *Miscanthus* in Lincolnshire (Table 4). Isoprene emission rates from *Miscanthus* were much lower than those measured from willow (between <lod and 6.42 μg g^{-1} h^{-1}). During August in 2011 and 2012, maximum emission rates of 6 and 2 μg g^{-1} h^{-1}, respectively, were measured. Over the three calendar years of sampling, maximum emissions of <1.5 μg g^{-1} h^{-1} were measured at 6 of the 10 sampling points. Emission rates of α-pinene were comparable with those measured from willow in Fife, the location with the lowest emission rates, and varied between <lod and 20.8 μg g^{-1} h^{-1}. There were no measurable emissions of β-pinene, limonene and δ-3-carene. A seasonal trend was observed with highest emissions during the growing season and undetectable emissions during winter.

Using the isoprene emission rate, measurements from *Miscanthus* measured in this study gave a standard emission rate of 0.01 μg g^{-1} h^{-1}, assuming a foliar density of 120 g_{dw} m^{-2} derived from LAI measurements taken in this study.

Wheat and oilseed rape

Low to nondetectable emissions of isoprene were measured from the two annual arable crops, wheat

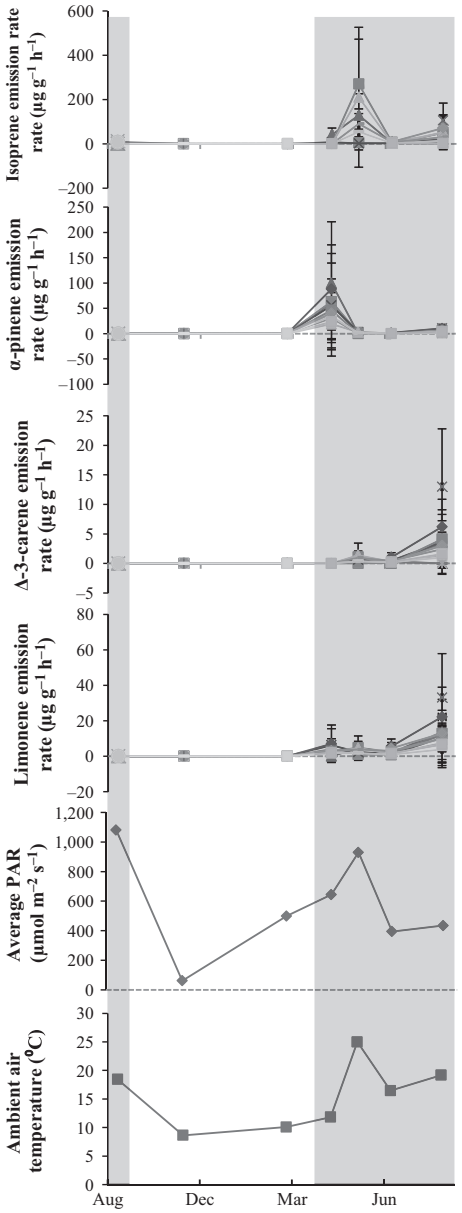

Fig. 5 Emission rates of isoprene, α-pinene, δ-3-carene and limonene from each of the thirty individual sampling sites in short-rotation coppice willow at the Perthshire location in 2011 and 2012 together with measured photosynthetically active radiation intensity, ambient air temperature, soil temperature and soil moisture. The shaded area demarcates the growing season. Error bars are uncertainties calculated using propagation of error and take into account uncertainty in determination of biogenic volatile organic compounds concentration, volume, temperature, enclosure time and dried leaf mass enclosed.

(maximum emission rate of 6 μg g^{-1} h^{-1}) and oilseed rape (maximum emission rate of 0.35 μg g^{-1} h^{-1}) (Table 5). A standard isoprene emission rate from wheat of 0.16 μg g^{-1} h^{-1} was calculated using these data and a foliar density of 30 g_{dw} m^{-2} derived from measurements taken in this study.

Emissions of α-pinene, β-pinene, limonene and δ-3-carene were measured from wheat but not oilseed rape (Table 5). Emission rates of α-pinene were highest, followed by δ-3-carene, limonene and β-pinene. No seasonal trend could be determined for emissions from wheat as it was only sampled during the summer.

Discussion

Crop type

The highest emission rates measured in this study were for isoprene from willow. The highest isoprene emission rates from willow were around 300 times greater than the maximum isoprene emission rates from *Miscanthus*. Willow also emitted considerably more isoprene than the annual arable crops wheat and oilseed rape.

The standard isoprene emission rates calculated from measurements in willow, wheat and oilseed rape in this study, summarized in Table 6, were of the same order of magnitude as those in the published literature, summarized in Table 7. Monoterpene emissions from willow, wheat and oilseed rape in this study were slightly different from those previously reported (summarized in Table 8).

The data for willow from this work are consistent with previous field measurements at leaf, branch, canopy and landscape-scale which collectively indicate that willow trees are an important source of isoprene (Table 7), as also summarized in the Introduction. Using measurements taken in Lincolnshire during the growing season (beginning of April to end of September), a standard isoprene emission rate of 16 μg g^{-1} h^{-1} was calculated which is at the lower end of the range of standard isoprene emission rates previously reported (Table 7). This difference may be due to functional differences in leaves between different climates, in a similar manner to the differences between shaded and sun-exposed leaves reported by, for example, Sharkey *et al.* (1991). For instance, the emission rates of adult spruces and pines grown in five different regions of central and northern Europe differ up to a factor of 50 (Janson, 1993). The emission rate derived here is very similar to that reported by Olofsson *et al.* (2005) for similar climatic conditions to this study, although they do not state the age of their plantation.

The monoterpene compounds identified in measurements from willow were in good agreement with other studies. A study of 160 tree species in 43 genera in the United States reported fourteen dominant or frequently occurring monoterpene compounds, of which α-pinene, β-pinene, limonene and δ-3-carene (together with

Table 3 Spearman rank correlation coefficients between isoprene, α-pinene, β-pinene, limonene and δ-3-carene emission rates and potential environmental drivers, for willow at Lincolnshire. Significant correlations ($\rho \leq 0.05$) are highlighted in bold

Factor	Isoprene	α-pinene	β-pinene	Limonene	δ-3-carene
PAR	**0.42**	**0.20**	0.14	0.03	**0.17**
$T_{\text{ambient air}}$	**0.71**	**0.21**	0.10	0.01	**0.31**
T_{soil}	**0.64**	**0.29**	**0.18**	**0.20**	0.40
Soil moisture	**−0.29**	**0.25**	**0.26**	**0.26**	0.11

Table 4 Summary of isoprene, α-pinene, β-pinene, limonene and δ-3-carene emission rates (μg g-1 h-1) from *Miscanthus* at the Lincolnshire location. <lod = below the limit of detection

	Miscanthus					
	Growing season			Non-growing season		
	Range (μg g^{-1} h^{-1})	*n*	% <lod	Range (μg g^{-1} h^{-1})	*n*	% <lod
Isoprene	<lod - 6.42	79	70	<lod	52	100
α-pinene	<lod - 20.8	79	73	<lod - 0.12	52	94
β-pinene	<lod	79	100	<lod	52	100
Limonene	<lod	79	100	<lod	52	100
δ-3-carene	<lod	79	100	<lod	52	100

Table 5 Summary of isoprene, α-pinene, β-pinene, limonene and δ-3-carene fluxes (μg g^{-1} h^{-1}) from wheat and oilseed rape at the Lincolnshire location. <lod = below the limit of detection

	Wheat			Oilseed rape		
	Range (μg g^{-1} h^{-1})	*n*	% <lod	Range (μg g^{-1} h^{-1})	*n*	% <lod
Isoprene	<lod - 5.99	35	94	<lod - 0.35	35	94
α-pinene	<lod - 422	35	26	<lod	35	100
β-pinene	<lod - 71.1	35	83	<lod	35	100
Limonene	<lod - 104	35	29	<lod	35	100
δ-3-carene	<lod - 186	35	91	<lod	35	100

Table 6 Comparison between standard isoprene emission rates in μg g^{-1} h^{-1} derived from measurements in all crop types in this study and standard emission rates from other studies

Species	Standard isoprene emission rate (μg g^{-1} h^{-1})	Measurement type	Reference
Salix spp.	0.1–15.9	Branch enclosure	This study
	12–115	Various	See Table 6
Miscanthus	0.01	Branch enclosure	This study
	0	Canopy-scale, PTR-MS	Copeland *et al.* (2012)
Wheat	0.16	Branch enclosure	This study
	0–0.5	Branch enclosure	(Karl *et al.*, 2009; König *et al.*, 1995)
Oilseed rape	0	Branch enclosure	This study
	0	–	(Karl *et al.*, 2009; Kesselmeier & Staudt, 1999)

camphene and myrcene) were usually the most abundant (Geron *et al.*, 2000a), as noted also by Guenther *et al.* (1994).

The range of α-pinene, β-pinene, limonene and δ-3-carene emission rates from willow in Lincolnshire were slightly higher than that of previously reported measurements. This may partly be due to differences in the age of vegetation sampled in comparison to other reported measurements. For example, the willow trees sampled in the study by Hakola *et al.* (1998) were young and around 1–1.5 m in height. Likewise, for the study by Evans *et al.* (1982) where the plants were grown in a

Table 7 Comparison of literature values for standardized isoprene emission rates from different willow species using different methods of measurement

Species	Standard emission rate ($\mu g\ g_{dw}^{-1}\ h^{-1}$)	Location	Measurement type	Reference
Salix spp.	20	East Midlands, UK	Canopy-scale, PTR-MS	Copeland *et al.* (2012)
Salix spp.	28	NW Mediterranean	Branch enclosure	Owen & Hewitt (2000)
Salix spp.	54.7	Wisconsin, USA	Leaf, branch, canopy & landscape	Isebrands *et al.* (1999)
Salix spp.	22.7	West Midlands, UK	Leaf, branch, canopy & landscape	Owen *et al.* (2003)
Salix alba	41	Tartu, Estonia	Branch enclosure	Niinemets *et al.* (2010)
Salix alba	37.2	–	–	Karl *et al.* (2009)
Salix alba	18	Portugal	Branch enclosure, lab conditions	Pio *et al.* (1993)
Salix babylonica	115	California, USA	–	Winer *et al.* (1992)
Salix caprea	36	Tartu, Estonia	Leaf cuvette, canopy-scale	Niinemets *et al.* (2010)
Salix caprea	18.9	–	Branch enclosure	Karl *et al.* (2009)
Salix caroliniana	12.5	Florida, USA	Air-exchange branch enclosure	Zimmerman (1979)
Salix discolor	90.7	Wisconsin, USA	Leaf, branch, canopy & landscape	Isebrands *et al.* (1999)
Salix humulis	40.5	Wisconsin, USA	Leaf, branch, canopy & landscape	Isebrands *et al.* (1999)
Salix nigra	25.2	Greenhouse	Whole plant, air-exchange chamber	Evans *et al.* (1982)
Salix petiolaris	101.5	Wisconsin, USA	Leaf, branch, canopy & landscape	Isebrands *et al.* (1999)
Salix phylicifolia	32	Vantaa, Finland	Branch enclosure	Hakola *et al.* (1998)
Salix subsericea	56.8	Wisconsin, USA	Leaf, branch, canopy & landscape	Isebrands *et al.* (1999)
Salix viminalis	12	Västergötland, Sweden	Canopy-scale, REA	Olofsson *et al.* (2005)
Salix spp.	0.1–15.9	Various, UK	Branch enclosure	This study

REA, relaxed eddy accumulation.

Table 8 Comparison of literature values for range of monoterpene emission rates in $\mu g\ g^{-1}\ h^{-1}$ from willow, *Miscanthus*, wheat and oilseed rape using different methods of measurement

Species	Range of monoterpene emission rates/$\mu g\ g_{dw}^{-1}\ h^{-1}$	Location	Measurement type	Reference
Salix spp.	0.5%	Wisconsin, USA	Leaf, branch, canopy & landscape	Helmig *et al.* (1999)
	1.2			
Salix spp.	1	West Midlands, UK	Leaf, branch, canopy & landscape	Owen *et al.* (2003)
Salix alba	1.1	–	–	Karl *et al.* (2009)
Salix caprea	0.8	–	Branch enclosure	Karl *et al.* (2009)
Salix nigra	0	Greenhouse	Whole plant, air-exchange chamber	Evans *et al.* (1982)
Salix phylicifolia	2.8–10	Vantaa, Finland	Branch enclosure	Hakola *et al.* (1998)
Salix spp.	0–803	Various, UK	Branch enclosure	This study
Miscanthus	0	Midlands, UK	Canopy-scale, PTR-MS	Copeland *et al.* (2012)
	0–20.8	Midlands, UK	Branch enclosure	
Wheat	0.041	USA	–	Lamb *et al.* (1993)
	0	Austria	Branch enclosure	König *et al.* (1995)
	0	California, USA	Branch enclosure	Winer *et al.* (1992)
	0–422	Midlands, UK	Branch enclosure	This study
Oilseed rape	0.034–0.037	Austria	Branch enclosure	König *et al.* (1995)
	0.03–0.06	Germany	Leaf	Muller *et al.* (2002)
	0.8	California, USA	Branch enclosure	Winer *et al.* (1992)
	0–0.35	Midlands, UK	Branch enclosure	This study

greenhouse and measurements taken when the plants were 3–24 months old. Both Owen *et al.* (2003) and Karl *et al.* (2009) describe the inherent difficulty in determining emission factors due to the high variability of BVOC emission rates. Variation in meteorological conditions, plantation age and plant coppice stage likely underlie the differences in emission rates from willow observed here.

The measurements presented here indicate that *Miscanthus* was not a significant emitter of the BVOCs investigated in this study. Copeland *et al.* (2012) likewise found no measurable BVOC emission rates from

Miscanthus under field conditions in Lincolnshire using a disjunct eddy covariance and PTR-MS technique. Also in agreement with this study, Copeland *et al.* (2012) reported only small concentrations of the monoterpenes α-pinene and limonene above *Miscanthus* using a GC-MS technique. Crespo *et al.* (2013) found that methanol, acetaldehyde and acetone formed the main constituents of the emissions measurements from four pots of *Miscanthus* plants in an experimental rather than a field study.

Low emission rates of α-pinene, β-pinene, limonene and δ-3-carene were measured from wheat in contrast with previous studies by König *et al.* (1995) and Winer *et al.* (1992) who reported no measurable monoterpene emissions and determined that oxygenated BVOCs accounted for around 100% of total emissions. Both of these studies also found that oilseed rape did not emit significant quantities of monoterpenes, which is in agreement with the findings of this work.

Sampling plantation

The standard isoprene emission rates calculated for Perthshire (1.9 $\mu g\ g^{-1}\ h^{-1}$) and Fife (0.1 $\mu g\ g^{-1}\ h^{-1}$) are lower than that calculated for Lincolnshire and lower than the other rates reported in the literature. Similarly, emissions of α-pinene, β-pinene, limonene and δ-3-carene were lower in Perthshire and Fife than in Lincolnshire. This is potentially linked to the younger age of the willow plants at these locations, as well as to generally cooler and more overcast days.

The willow plantation in Lincolnshire was established in 2002, whereas the plantations in Perthshire and Fife were established in 2007 and 2009, respectively. As a result, the rate of isoprene emission in the two younger plantations might have been limited by the seasonal development of isoprene synthase expression and activity (Mayrhofer *et al.*, 2005). The isoprene emission might have been further limited by growth under conditions of generally lower temperature which could have delayed the capacity of the willow plantation to achieve maximum isoprene emission rates (Wiberley *et al.*, 2005).

Differences in the meteorological conditions between the sampling locations were observed. Emission rates of isoprene and monoterpenes are known to vary with light and temperature (Guenther *et al.*, 1993) and water availability (Faubert *et al.*, 2011). Isoprene emission rates are controlled by both the capacity of the leaf to emit isoprene and the prevailing environmental conditions (Geron *et al.*, 2000b; Monson *et al.*, 1994). The temperature dependence of monoterpene emission rates varies among monoterpenes, vegetation species and other factors and is related to monoterpene vapour pressure, increasing exponentially with increasing temperature (Guenther *et al.*, 1993).

As a general observation, there were strong positive associations of emission rates with season as well as temperature, soil moisture and PAR. Emissions appeared to be related to variables that have long seasonal time constants through their range of variability as well as to variables which have shorter, subdiurnal variability such as PAR intensity. However, it is intrinsically difficult to isolate the effect of individual parameters. Different parameters may affect different BVOCs and different processes differently, as well as being inherently confounded. For example, a sunny summer day is also likely to be warm. Further confounding may also arise from plants emitting variable amounts of isoprene or monoterpenes at different stages of their growth cycles such as flowering and seeding.

Sampling year

The largest emission rates of isoprene, α-pinene, β-pinene and δ-3-carene were measured in Lincolnshire in 2010 when the trees were older. Interestingly, limonene was an exception, with higher emissions measured from younger plants. Similarly to the variation in emission rates shown between willow of different ages, this is likely related to the variation in the age of the willow plants in Lincolnshire during the period of measurement and potentially also to climate conditions.

The magnitude of BVOC emissions has been shown previously to vary with plant age; for example, Street *et al.* (1996, 1997) reported significant variation in emission rates both across the growing season and between different ages of vegetation, although the variation they observed could not be attributed to any particular factors. Studies on *Pinus* and *Camellia* species have also noted variation in the composition of BVOC emissions with plant age, with younger plants emitting a wider range of monoterpenes (Kim *et al.*, 2005; Nuñes & Pio, 2001), although another study of conifers of different ages found no variation in BVOC composition with age (Lim *et al.*, 2008). Overall, it is possible that emission rate variation seen in this study could be linked to different plant age, but any such link is not well understood.

Annual cycle

Season has been shown to greatly influence BVOC emissions. For example, Guenther (1997) reported spatial and seasonal variations in BVOC emissions ranging over several orders of magnitude. The measured emission rates from willow in Lincolnshire and Perthshire followed a seasonal trend of high emission rates in spring/summer and low emission rates between September and March. This is coincident with both the climate and the different stages of willow growth.

Emission rates often dropped below detectable levels at the start and end of the year. Willow enters dormancy around November and is harvested during the winter; the drop in emission rates to below detectable levels appears to correspond to the period immediately after harvesting when no leaf biomass is present.

Hakola *et al.* (1998) reported seasonal variation in the type of BVOC emitted, demonstrating that the isoprene emitter tea-leafed willow released significant amounts of monoterpenes during bud break and early leaf development in spring before switching over to significant isoprene emission when leaves become mature in summer. This trend is consistent with the 2010 measurements in this study, where isoprene emission rates tended to be highest in July to August and α-pinene, β-pinene, limonene and δ-3-carene emission rates tended to be highest in April to May. Interestingly, in 2012, the appearance of the expected growing season increase in all measured BVOC emission rates appeared to be delayed in comparison to the 2010 measurements. Furthermore, only isoprene emissions were detectable in 2011 and also appeared to be delayed in comparison to 2010. This is likely to be related to the coppicing of the willow plants, or perhaps to missing a major burst of emissions, for example at bud break, because of the sampling frequency, although the variance in the onset of emissions is also potentially linked to stress events such as drought and flooding.

Climate conditions

There were occasions when the fields in Lincolnshire experienced stressful climatic events including frost in winter 2010, drought in early 2011 and 2012, and waterlogged soils in spring and early summer 2012. It is acknowledged that isoprene emissions may be modified by different stresses such as drought (Laothawornkitkul *et al.*, 2009). In the willow field, isoprene emission rates were highest in June in 2010, but peak emission rates were not reached until August in the following two years. The onset of peak monoterpene emission rates was similarly delayed in 2012. The rate of BVOC emission was also lower in 2011 and 2012.

Soil moisture was lower on average in 2011 (20 ± 8 vol%) than in 2010 and 2012 (30 ± 7 vol%), a reduction of approximately 33%, and was significantly positively correlated with α-pinene, β-pinene and limonene emission rates. However, isoprene emissions were significantly inversely correlated with soil moisture, suggesting that these moderate drought conditions did not suppress isoprene emissions. This suggests that, using soil moisture as a proxy for drought conditions, emission rates were impacted by the drought, although other studies have suggested that drought and soil moisture content are not necessarily correlated (Pegoraro *et al.*, 2004). As this was an observational study, it was not designed in a controlled manner to test for drought, so it is not possible to derive directly from this data set the extent to which low soil moisture affects the BVOC emissions.

Recent experiments have demonstrated that isoprene emission is suppressed after severe prolonged drought events (Fortunati *et al.*, 2008; Sharkey & Loreto, 1993; Tani & Kawawata, 2008). Monoterpene emission has also been found to be suppressed under severe but not moderate drought conditions (Bertin & Staudt, 1996; Staudt *et al.*, 1997; Yani *et al.*, 1993). However, these studies were on young potted plants, and field investigations on emission changes due to natural drought events are lacking. Rather than suppressing emissions, changes in the plant metabolism induced by stress can sometimes involve additional production or higher losses of volatiles. Ebel *et al.* (1995) observed a significant increase in several BVOC compounds in the emissions from drought-stressed apple leaves. The varying responses of BVOC emissions to moderate drought may be a result of differences in leaf physiology, BVOC biochemistry and experimental protocol.

The effects of these climate conditions are difficult to separate from the effects of coppicing. It is also inherently difficult to study these effects independently in field experiments. Furthermore, frost, heat, nutrient deficiencies, wounding and air pollution can all constitute potential triggers for physiological changes as well as changes in trace gas emission (Kesselmeier & Staudt, 1999). It is likely that the lower emission rates measured here are associated with younger plant growth as well as climate conditions. However, the late onset of peak emission rates is most likely to be related to these stress events rather than coppicing. However, as this was an observational study, it was not designed to investigate these stress factors in a controlled manner.

The emission rates of isoprene and α-pinene measured from *Miscanthus* are low so it is difficult to discern variation between measurement years, although emissions appear to follow a similar pattern to measurements in willow. As noted above, there is almost no prior work on BVOC emissions from *Miscanthus* with the exception of Copeland *et al.* (2012) and Crespo *et al.* (2013).

An assessment of the potential significance of the emissions

Currently, total UK plantings of *Miscanthus* and willow are minor in comparison with annual arable crops such

as oilseed rape and wheat (DEFRA, 2009). However, due to concerns about climate change and energy security, the government is seeking to increase the amount of perennial energy crops produced in the United Kingdom, with the potential to use up to around 6% of UK total arable land by 2020 (DEFRA, 2007). In Europe, it is anticipated that food crop yields will continue to increase, releasing substantial areas of agricultural land for the expansion in area of bioenergy crops.

Using the results reported in this study, a rudimentary estimate of UK- and Europe-wide net BVOC emissions from the perennial bioenergy crop willow is made for current and potential future land-cover areas. This scale-up assumes that the only process occurring is the production of BVOCs from plant material and that no other processes are occurring which may affect the figures generated. In the United Kingdom, the most recent available land-use data show there were 6400 ha of willow at the end of 2009 (DEFRA, 2009). The total land cover of bioenergy crops is projected to increase to up to 350 000 ha in the next 10 years. In Europe in 2009/2010, the area of willow was around 24 000 ha (Don *et al.*, 2012). Total bioenergy crop land cover in Europe is projected to increase to up to 72 Mha in the future (Ashworth *et al.*, 2013). Rowe *et al.* (2009) suggest that 70% of this will be *Miscanthus* and willow. The hypothetical scenario considered here is that 50% of the bioenergy crops planted in future will be willow trees, as *Miscanthus* is more difficult to grow in some areas of the United Kingdom and Europe.

Using only the isoprene emission rates measured in this study, a mean value (33 ± 25 μg g^{-1} h^{-1}) was calculated using the measurements taken in willow at three locations during almost three years. This mean value encapsulates some of the variability in emission rates due to different growth stages of the plant and to interannual climate variability, as well as variability due to location in the United Kingdom. However, it is likely subject to positive bias because measurements in this study were taken only during daylight hours and because of an implicit assumption of constant foliar density through the year in the conversion from mass emission rate to area emission rate. Scaling up using this mean value, emissions of isoprene at current land cover in the United Kingdom (6.4 kha) are estimated to be between 0.001 and 0.005 Tg yr^{-1}. This may increase to between 0.018 and 0.133 Tg yr^{-1} if 50% of all potential land resources in the United Kingdom are planted with SRC willow in the future (175 kha) (Table 9). In Europe, isoprene emissions are estimated to be between 3.78 and 27.4 Tg yr^{-1}, if 50% of all land available for perennial bioenergy crops in Europe is planted with willow in the future (36 Mha).

Using literature values for the standard emission rate of isoprene from various willow species (described in Table 7), scaled-up annual emissions calculated using this method were estimated to be between 0.03 and 0.25 Tg yr^{-1} in the United Kingdom and between 5.7 and 55 Tg yr^{-1} in Europe using the range between minimum and maximum emission estimates for the 50% SRC willow future planting scenario. As these standard emission rates are based on growing season emission rates only, the range is higher than the estimates calculated here which used annual net mean emission rates to estimate comparable emissions for Europe.

These estimated emissions of isoprene from willow are expressed in Table 9 relative to the current estimated annual global turnover of around 500 Tg yr^{-1} for isoprene (Guenther *et al.*, 1995). Emissions from current land cover of willow in the United Kingdom are of the order 0.0001–0.001% (this study) and 0.002% (Winer *et al.* (1992)) of current global isoprene emissions. In

Table 9 Comparison of measurements from this study and literature values for isoprene emission rates in Tg yr^{-1} from willow for current land area coverage in the UK and estimates for potential future bioenergy crop land-cover area (50% of available land) in the UK and Europe. Also given are the relative contributions to the global turnover of isoprene emission (Guenther *et al.*, 1995)

			Isoprene emission (Tg yr^{-1})			Isoprene emission as a % of global turnover (500 Tg)		
		Isoprene emission rate (μg g^{-1} h^{-1})	Current UK land cover	Potential future UK land cover	Potential future Europe land cover	Current UK land cover	Potential future UK land cover	Potential future Europe land cover
Low	This study	8	0.001	0.018	3.78	0.0001	0.004	0.76
	Olofsson *et al.* (2005)	12	0.001	0.028	5.68	0.0002	0.006	1.14
High	This study	58	0.005	0.133	27.4	0.0010	0.027	5.49
	Winer *et al.* (1992)	115	0.010	0.264	54.4	0.0019	0.053	10.9

future, this could rise to between 0.004–0.027% (this study) and 0.05% Winer *et al.* (1992) of current global isoprene if 50% of all potentially available land in the United Kingdom is planted with willow. In Europe, isoprene emissions of between 0.76–5.5% (this study) and 10.9% (Winer *et al.*, 1992) of the current global budget could be expected. As emphasized already, this is a very rough estimation of local and global emission budgets and does not include any potential emissions from soil processes. Due to the very rudimentary nature of the scale-up method, and the potential for positive bias, the estimates presented here should be considered as semiquantitative and preliminary in nature. A more thorough assessment of the impact on BVOC budgets would take greater account of seasonal and diurnal variation and would require PAR and temperature data across the likely planting sites in the United Kingdom and Europe to be incorporated into a whole-canopy model. However, the use of several large long-term data sets provides some representation of emission rates from willow from which to extrapolate to wider areas.

The estimates of current and potential future BVOC emissions give an indication of the potential impact of continued expansion of bioenergy crops on the atmospheric budget of BVOCs. Willow emits vastly greater quantities of isoprene than the low BVOC-emitting annual arable crops that it may replace. For example, wheat and oats have estimated isoprene emission factors in the range 0–0.5 $\mu g\ g^{-1}\ h^{-1}$ (Karl *et al.*, 2009; König *et al.*, 1995), while those for oilseed rape, rye and barley are zero (Karl *et al.*, 2009; Kesselmeier & Staudt, 1999). This has the potential to impact local and regional air quality by contributing to tropospheric ozone production and SOA formation. For example, a recent study estimated that cultivation of 72 Mha of willow in Europe would lead to a 2 ppbv increase in summertime mean ground-level ozone, impacting on human mortality and crop yields (Ashworth *et al.*, 2013).

Overall, the findings from this work reinforce the importance of considering more than just the carbon budget when assessing bioenergy crops for climate change mitigation.

Acknowledgements

E. Morrison acknowledges PhD studentship funding from EaStChem School of Chemistry and NERC CEH Edinburgh. The authors thank Jonathan Wright and Frank Wilson for site access, and Nichola Copeland, Jon Finch, Alice Meehan, Susan Owen and Jocelyn Timperley for their assistance.

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