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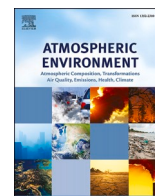
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## A first assessment of the sources of isoprene and monoterpene emissions from a short-rotation coppice *Eucalyptus gunnii* bioenergy plantation in the United Kingdom

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### HIGHLIGHTS

- First data for emissions of speciated BVOC from a UK eucalypt bioenergy plantation
- Isoprene emission from juvenile foliage six times greater than monoterpene emission
- cis-β-Ocimene and α-phellandrene major monoterpenes from juvenile foliage
- Forest floor monoterpene emissions smaller than branches and vary with lifecycle
- α-Pinene and d-limonene dominate forest floor emissions; eucalyptol from woodchip

### ARTICLE INFO

#### Keywords:

Eucalyptus  
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Atmospheric chemistry

### ABSTRACT

*Eucalyptus gunnii* is a fast-growing, cold-tolerant tree species endemic to Tasmania that is suitable for growing as short-rotation coppice (SRC) plantations in the UK. Fast growing eucalypts such as *E. gunnii* could potentially deliver higher biomass yields with a superior calorific value for the domestic bioenergy market than other SRC plantation species such as willow or poplar. However, eucalypts are known emitters of biogenic volatile organic compounds (BVOC) like isoprene and monoterpenes. These compounds contribute to the formation of atmospheric pollutants such as ozone and secondary organic aerosols. An assessment of the sources of BVOCs during the lifecycle of a UK *E. gunnii* SRC plantation found the mean standardised emissions of isoprene and total monoterpenes from branches of juvenile foliage to be  $7.50 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$  and  $1.30 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ , respectively. The predominant monoterpene emitted was cis-β-ocimene. Isoprene emissions from the forest floor were extremely low but monoterpene emissions peaked at  $50 \mu\text{g C m}^{-2} \text{h}^{-1}$ . α-Pinene and d-limonene were the major components of the monoterpene emissions, with higher emissions correlated to the abundance of leaf litter. Both the magnitude and composition of monoterpene emissions from the forest floor varied during the SRC plantation life cycle, with the coppiced and regrowth stands of eucalyptus producing less emissions. The woodchip produced at harvesting emitted only trace levels of isoprene but substantial monoterpene emissions, up to  $90 \mu\text{g C m}^{-2} \text{h}^{-1}$ , predominately eucalyptol. Harvesting and resulting biomass chips may provide a short-lived concentrated source of BVOCs in winter at SRC plantations. Modelled annual emissions using MEGAN 2.1 (canopy emissions only) suggest that BVOC emissions from a UK *E. gunnii* SRC plantation are most abundant in summer, and that modelled annual isoprene and total monoterpenes emissions could be around  $6.9 \text{ kg C ha}^{-1}$  and  $2.4 \text{ kg C ha}^{-1}$  respectively, for a young plantation. Based on the very limited data, the per-hectare *E. gunnii* isoprene emissions are smaller than estimates for other SRC/SRF plantation species in the UK; the per-hectare monoterpene emissions are in the span of estimates for other plantation species.

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## 1. Introduction

Eucalypt plantations have seen renewed interest as a potential source of biomass for the production of bioenergy in the UK and Ireland (Leslie et al., 2020; Leslie and Purse, 2016; Purse and Leslie, 2016). Eucalyptus is a genus of over 800 species of plant in the Myrtaceae family. The term eucalypt encompasses a wider range of species that are closely related and from other genera and categorised under the Eucalyptae Tribe (Coppin, 2002). Several eucalypt species that originate from south-east Australia and Tasmania have been identified as the most appropriate for planting in the relatively cold and wet UK climate (Evans, 1980). Planting trials for several eucalypt species were established in the UK for this purpose (Evans, 1980; Harrison, 2010; Leslie and Purse, 2016; Purse and Leslie, 2016; Tobin et al., 2016) and commercial eucalypt plantations grown for floristry or biomass are now gaining interest (Capurro, 2019; Elliott, 2018; Vergnault, 2019). Probably the most widely planted species of eucalypt across the UK is *Eucalyptus gunnii*, which, as well as being planted in parks and private gardens, has been grown in short-rotation forest (SRF) trials across Great Britain (Harrison, 2010) and as a commercial biomass plantation.

Eucalypt species are a favourable bioenergy crop due to their rapid growth and ability to produce higher yields per hectare (given suitable matching of planting location and eucalypt species) and for their higher calorific value ( $12.5 \text{ GJ m}^{-3}$ ) than current bioenergy crops such as willow ( $7.7 \text{ GJ m}^{-3}$ ) and other proposed rapid-growing species such as aspen ( $8.6 \text{ GJ m}^{-3}$ ) and alder ( $9.2 \text{ GJ m}^{-3}$ ) (Leslie et al., 2012, 2020, 2020; Scottish Forestry, 2020).

Bioenergy crops remove carbon dioxide ( $\text{CO}_2$ ) from the atmosphere during growth and are largely seen as carbon neutral or carbon negative when combined with carbon capture and storage (BECCS). It has been suggested that to reach net zero greenhouse gas (GHG) emissions by 2050 up to a fifth of UK agricultural land may be given over to the production of bioenergy crops (Committee on Climate Change, 2019). Therefore it will be important to optimize the productivity of future land used for growing bioenergy crops with consideration of potential environmental impacts.

Bioenergy plantations can be sources of biogenic volatile organic compound (BVOC) emissions, in particular terpenoid compounds such as isoprene and monoterpenes. Individual species of the genus *Eucalyptus* have been shown to vary widely in their emission rates and composition of isoprene and monoterpenoids (latter hereafter referred to as monoterpenes) (Emmerson et al., 2020; He et al., 2000; Kim et al., 2011; Nunes and Pio, 2001; Pio et al., 2001; Purser et al., 2021; Street et al., 1997) and may also emit other compounds such as sesquiterpenoids, benzenoids and oxygenated VOCs including carbonyls, alcohols and organic acids (Sørensen et al., 2020; Winters et al., 2009). Isoprene and monoterpenes are produced as a result of secondary metabolic processes, with emissions largely driven by photosynthetic active radiation (PAR) and temperature (Guenther et al., 1991; Sharkey et al., 1996; Tingey et al., 1980, 1981). The reasons why trees produce such a variety of compounds are still widely debated but the emissions are thought to be largely in response to stress, such as herbivory and extreme environmental conditions (e.g. drought, flooding); they may also act as a potential source of communication (Niinemets and Monson, 2013; Sharkey and Monson, 2017). On release to the atmosphere, BVOCs are oxidized by hydroxyl radicals and contribute to the production of air pollutants in the troposphere, in particular ozone and secondary organic aerosols (Finlayson-Pitts and Pitts, 1993). These two pollutants have adverse effects on human health, damage vegetation (natural ecosystems and crops) (Emmerson, 2020) and affect Earth's radiative balance. It is therefore important to quantify sources of BVOCs during biomass production in order to assess their likely impact on regional air quality.

BVOC emissions from bioenergy crops have been investigated for species such as willow (Morrison et al., 2016), *Miscanthus* (Copeland et al., 2012) and poplar (Ashworth et al., 2015; Eller et al., 2012;

Monson et al., 2020; Purser et al., 2021; Zenone et al., 2016). BVOC emissions from eucalypts have been reported but are limited to natural mixed forests (Emmerson et al., 2016; Ramirez-Gamboa et al., 2021) or *Eucalyptus globulus* plantations (Nunes and Pio, 2001; Street et al., 1997), often in much warmer climates than the UK. BVOC emissions under greenhouse conditions have previously been reported for *Eucalyptus gunnii*, which was found to be both an isoprene and monoterpene emitter, in particular of cis- $\beta$ -ocimene,  $\alpha$ -pinene, eucalyptol and d-limonene (Owen and Peñuelas, 2013; Purser et al., 2020).

Some eucalypt species can be grown as short-rotation forests (SRF), which are harvested after  $>10$  years (rotation length), and others can be grown as short-rotation coppice (SRC) in which trees are grown for  $<10$  years (rotation length) and the biomass above ground is harvested more frequently. The below-ground root system remains and new growth starts from the tree stumps. However, bioenergy plantations, particularly those managed as SRC are dynamic systems in which the mosaic of tree stands may vary in age. It is therefore important to assess the BVOC emissions that may arise from the different SRC stages illustrated in Fig. 1. In addition, there is currently no information on the contribution of the forest-floor BVOC emissions to the total emissions from a plantation of *Eucalyptus gunnii*.

This scoping case study aims to quantify for the first time the isoprene and monoterpene emissions from a range of potential BVOC sources (Fig. 1) in an operational *Eucalyptus gunnii* plantation grown for bioenergy in the UK and their relative contributions to the total plantation BVOC emissions.

## 2. Methods

### 2.1. Field site

The field site at Daneshill, Nottinghamshire, England, is a former munitions site that was redeveloped as a 24.2 ha bioenergy plantation in 2005. It contains extensive stands of *Eucalyptus gunnii* subsp. *gunnii*, referred to from here as *E. gunnii*, and *Eucalyptus nitens*, as well as a stand of other eucalypts as part of a small trial. The area used in this study was initially planted with 55,500 *E. gunnii* saplings to form a large plantation (Fig. 2, zones labelled 1, 2 and 3). The seed source was an *E. gunnii* stand in Dipton, South Island, New Zealand.

Measurements reported here were made in 2018, 2019 and 2020. The following brief history of the site provides context to the SRC areas sampled in this work and are illustrated in Figs. 2 and 3. In 2005, the saplings were planted through a plastic sheeting, which is still intact in some places on the site. During the 2010/2011 winter, prolonged cold weather caused all the trees to die back to the root collar and so they were subsequently coppiced in 2011. The majority of the above-ground biomass was removed, leaving only the stumps. The biomass was chipped and sent to a local biomass power station. Many trees survived and the stumps produced new growth to produce a plantation of multi-stemmed trees which were approximately 7 years younger than the below-ground roots. The term plantation used here describes the remaining 15 ha site at Daneshill.

*Eucalyptus gunnii* foliage changes as it develops from stemless round leaves in the juvenile form to a stemmed elongated adult form. The juvenile/adult terminology is used to distinguish foliage type in this study. Coppicing is defined here as the action of cutting back the trees to ground level in order to harvest the above-ground biomass. In 2017 (Fig. 2a), zones 1–3 contained the 7-year old regrown trees, referred to in this study as the “old stand” (Fig. 3a) containing both juvenile and adult foliage. The understorey in the old stand was largely grasses, mosses and some perennial broad-leaved weeds. During December 2017, zone 2 was again coppiced to just above ground level (Fig. 2b). In May 2018, new growth appeared on the stumps in zone 2 and by the end of 2018 the trees in this area were taller than 1 m. In October 2018, zone 1 was coppiced, subsequently referred to as the “coppiced” stand (Fig. 2c). The above-ground biomass was removed and the ground was

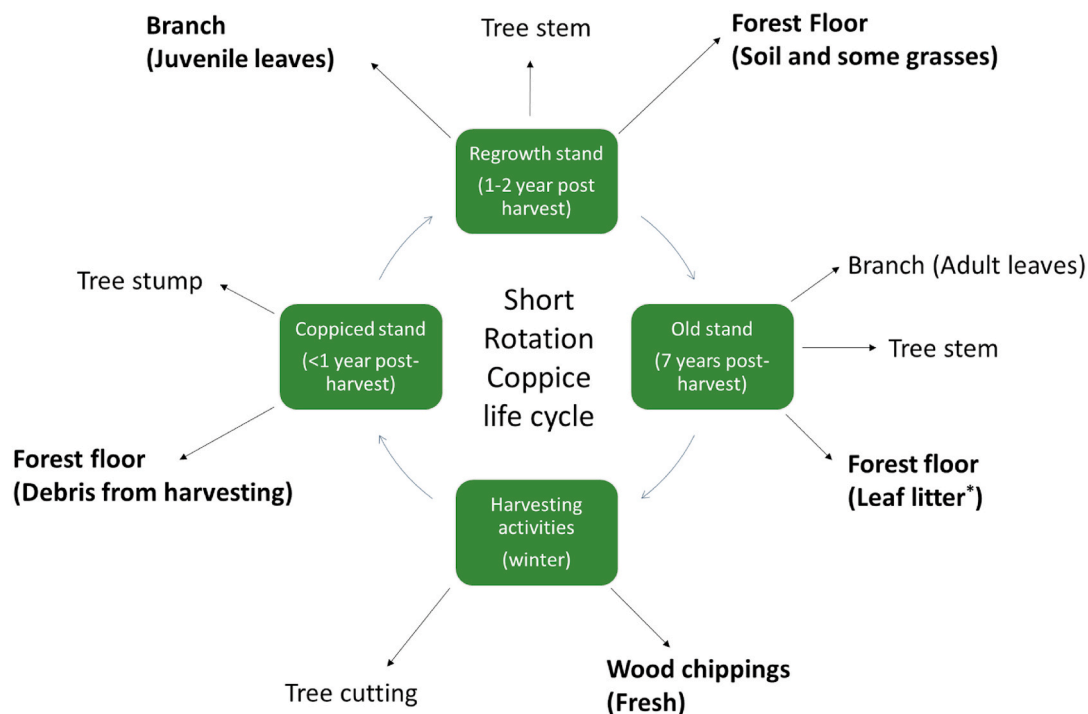


Fig. 1. Life cycle of a short-rotation coppice eucalypt plantation indicating the potential sources of BVOC emissions. The sources in bold font were investigated in this study. \*Includes bark, twigs and gumnuts.

disturbed with remnants of woody debris (Fig. 3b). By spring 2019 zone 1 was still bare, with some grasses and other perennial vegetation growing. Zone 2 was now a vigorously growing stand containing branches of juvenile foliage approximately 2–3 m in height and is referred to as the “regrowth” stand (Fig. 3c). In 2020, zones 1 and 2 were both stands of juvenile foliage with heights of 2–3 m and 3–5 m respectively, similar in appearance to Fig. 3c and still categorised as “regrowth” stand (Fig. 2d).

Measurements of BVOC emissions from both the branches and the forest floor during the described SRC activities were used as an opportunity to understand the changes that may occur during the life-cycle of a SRC plantation. Table 1 lists the samples taken during the different years.

The soil at Daneshill has a texture of sand with very little clay, silt and organic matter, and a low water-holding capacity. Analyses in July 2004 suggested only the top few cm contained organic matter and only at low levels, 0.5–2% (FBS (U.K.) Ltd, 2004). In addition, this analysis indicated the site was very low in nitrogen (1–3 ppm), low in phosphorus (25–33 ppm), marginally sufficient in potassium (63–86 ppm), and abundant in calcium and magnesium (194–269 ppm) with a pH of 7.1–7.2 (FBS (U.K.) Ltd, 2004).

Based on the closest Met Office weather station, Sheffield, approximately 38 km west of Daneshill, the maximum hourly temperatures recorded in July 2018, 2019 and 2020 were 25.4 °C, 22.7 °C and 19.7 °C respectively. Aggregated summer (Jun–Aug) rainfall in 2018 (83 mm) was less than one third that in summer 2019 (300 mm) and half that in summer 2020 (176 mm). Associated with this, total sunshine hours in summer 2018 (729 h) were much higher than in 2019 (452 h) and 2020 (507 h). A summary of local meteorological data is given in Supplementary Information S1.

## 2.2. Branch chambers

BVOC emissions from *E. gunnii* branches, with juvenile foliage, were collected using two methods. In 2018 and 2019, sampling was conducted using a removable flow-through acrylic chamber (53 L) attached

to permanent sample posts, as described in Purser et al. (2021). Flow rate through the chamber was 10 L min<sup>-1</sup> and an internal fan ensured mixing inside the chamber. In 2020, to facilitate sampling of multiple trees within a short timeframe, a flexible polyethylene terephthalate (PET) bag chamber (Roast-in-oven bags, Lakeland, Windermere, UK) of 6 L volume was used with the push-pull technique (Effah et al., 2020; Sørensen et al., 2020; Stewart-Jones and Poppy, 2006) described in Purser et al. (2020). The branch stem at the bag attachment point was prewrapped 24 h prior to sampling in PTFE tape for protection. During sampling the bag was gently sealed against the inlet line and stem. A new bag was used for each sample. The flow rate through the chamber was 2 L min<sup>-1</sup>.

In both branch sampling approaches the ambient air passed through a charcoal filter before entering the chambers and sampling was conducted after an initial equilibration period of 20 min. Samples were also taken from blank chambers. Samples of BVOCs were collected by using a handheld pump (210-1003MTX, SKC Ltd, Blandford Forum, UK) to draw chamber air directly through cartridges containing 200 mg Tenax TA 60/80 (11982 SUPELCO, Sigma-Aldrich, St Louis, MO, USA) and 100 mg Carbotrap 20/40 (20273 SUPELCO, Sigma-Aldrich).

The internal temperature and humidity (CS215, Campbell Scientific, Shepshed, UK) was measured every minute during sampling. In 2018 and 2019, photosynthetic active radiation (PAR) was sampled outside the chamber every minute and corrected for the 85% transmissivity of the chamber material. In 2020, the PAR sensor was placed inside the PET bag close to the branches being sampled and no correction was necessary.

In 2018, the same branch underwent repeat measurements so the number of leaves were counted and a sub-sample of leaves was taken from a nearby branch to estimate the plant material inside the chamber. In 2019 and 2020, the whole branch used during the measurement was removed from the plant for measurements of leaf mass. Foliage was dried in an oven at 70 °C for 48 h until constant weight.



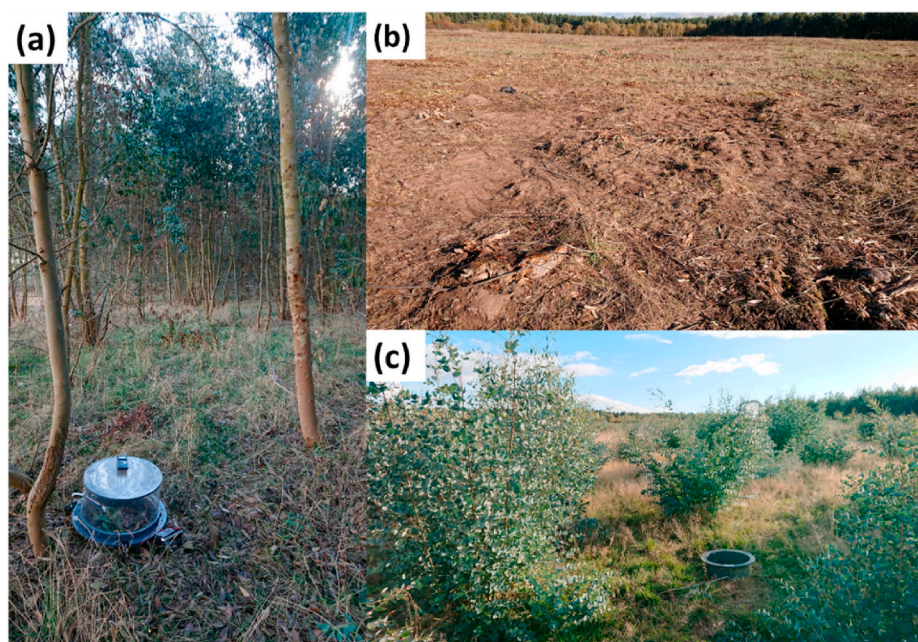
**Fig. 2.** Satellite images and associated schematic plans illustrating the changes in vegetation consequent on the management of the *E. gunnii* SRC plantation at Daneshill, Nottinghamshire, England. (a) Plantation in 2017 showing 7-year old stands of eucalypt mostly with adult foliage in zones 1, 2 and 3 (map data ©2015 Google, Google basemap). (b) Plantation in 2018 after zone 2 coppiced during December 2017 (map: Bing satellite basemap). (c) Plantation in 2019 showing an area coppiced in October 2018 (zone 1) and a 1-year old regrowth coppice stand containing juvenile foliage (zone 2) (map: ESRI satellite basemap). (d) Plantation in 2020 with 1-year old regrowth (zone 1) and 2-year old regrowth (zone 2) stands containing juvenile foliage (map: ESRI satellite basemap). All satellite images prepared in QGIS.

### 2.3. Forest-floor chambers

A static chamber method was used to sample the forest floor. Forest floor as defined here includes soils, leaf litter, fallen small twigs/branches and ground vegetation.

In 2018, four polyvinylchloride plastic soil collars 40 cm diameter x 18 cm high were installed in the old stand (7 years old) approximately 1 month before sampling commenced (Asensio et al., 2007a, 2007b, 2007a; Greenberg et al., 2012; Janson, 1993). Leaf litter and understorey vegetation were not removed from the collars prior to sampling to ensure the measurements reflected actual changes in the forest-floor composition and associated BVOC emissions. Due to the harvesting activities at the end of 2018, the soil collars were repositioned. In 2019,

three soil collars were installed in the same manner in three separate locations of the plantation: old stand (8 year old), coppiced area and regrowth stand (Fig. 3). During the sampling period no forest floor litter was removed from inside the chambers allowing an undisturbed assessment of the forest floor BVOC emissions. Therefore, the subsequent emission rates for the forest floor chambers are reported on a per m<sup>2</sup> basis. Samples of BVOC emissions were collected by placing a removable acrylic lid over the collar and drawing the internal chamber air for 30 min directly through cartridges as described in Section 2.2. Ambient air was sampled concurrently in the same way. Chamber air temperature (Electronic Temperature Instruments Ltd, Worthing, UK) and humidity (Fisherbrand™ Traceable™ Humidity Meter, Fisher Scientific, Loughborough, UK) were measured at the end of the 30 min



**Fig. 3.** The forest floor and canopy vegetation in (a) an old stand containing mostly adult foliage (forest-floor chamber visible in the foreground), (b) a coppiced area and (c) a regrowth stand of the *E. gunnii* SRC plantation at Daneshill, Nottinghamshire, England.

**Table 1**

Details of sampling zones and sample types measured in 2018–2020 at the *E. gunnii* SRC plantation, Daneshill, Nottinghamshire. For explanation of zones see text description and Fig. 2.

Year	Branch sample	Foliage type (no. of branches sampled)	Forest floor sample	Stand type (no. of chambers installed)
2018	zone 1	juvenile (1)	zone 1	old (4)
2019	zone 2	juvenile (4)	zone 1	coppiced (3)
			zone 2	regrowth (3)
			zone 3	old (3)
2020	zone 1	juvenile (18)		

sample collection period. Volumetric soil moisture (ML3 ThetaProbe Soil Moisture, Delta T, Cambridge, UK) was measured at three locations around each chamber and soil temperature was measured at a single location at 7 cm depth close to, but outside, the soil collar to avoid disturbance of the forest floor. Both measurements were carried out after sample collection to prevent perturbation of the ambient air sample.

#### 2.4. Green woodchip samples

A single sample of emissions from recently chipped *E. gunnii* trees (stem, branches and foliage) were sampled on the 29th October 2018 and the same woodpile was then resampled, collecting three samples, on the 9th February 2019. A forest-floor chamber was placed over the woodchip pile prior to sampling and samples collected using the method described in Section 2.3 for the forest-floor chambers.

#### 2.5. Forest-floor litter composition

The composition of the forest-floor litter in an old eucalypt stand (zone 1) was assessed to give an indication of the changes in litter inputs to the forest floor during the campaign and were separate to the BVOC emission measurements detailed in Section 2.3. Forest-floor litter amount and composition were assessed on two occasions in 2018. On 14th March, 1 m<sup>2</sup> quadrats were used to mark out 18 areas of the forest floor across a linear transect. A second survey was conducted on 23rd September with 10 areas marked out close to the forest-floor chambers.

The collected litter was sorted into 5 fractions comprising old decomposing leaf material, fresh green leaves, small branches, bark material and gumnuts. The dry mass fraction of each litter type was calculated after drying for 48 h in an oven at 70 °C.

#### 2.6. LAI analysis

A leaf area index (LAI) meter (LAI-2000 plant canopy analyser, LICOR, Inc., Lincoln, NE, USA) was used to provide data to estimate the foliage density,  $m^2_{\text{leaf}} m^{-2}_{\text{ground}}$ , for the old stand. In 2019, measurements were made in two locations in zone 3 on 19th January (Fig. 2). One above-canopy measurement was taken for every five below-canopy measurements and repeated to give 5 sets of data. A mixture of within and between-row measurements was included. The data from the two locations gave LAI values of 1.8 m<sup>2</sup> m<sup>-2</sup> and 2.1 m<sup>2</sup> m<sup>-2</sup> to give a mean old stand LAI of 2.0 m<sup>2</sup> m<sup>-2</sup>.

#### 2.7. BVOC quantification

Samples were analysed using gas chromatography-mass spectrometry (GC-MS) with a two-stage automatic thermal desorption unit (ATD 400, Perkin-Elmer, Wellesley, MA, USA) using the method described in Purser et al. (2020, 2021). Standards of the monoterpenes (from Sigma-Aldrich, Gillingham, UK)  $\alpha$ -pinene,  $\beta$ -pinene, d-limonene,  $\alpha$ -phellandrene,  $\beta$ -phellandrene, 3-carene, camphene,  $\gamma$ -terpinene and  $\beta$ -myrcene, and the monoterpenoids (monoterpene-based compounds with, for example, additional oxygen or missing a methyl group) eucalyptol and linalool, were prepared as a mixed stock solution of 3 ng  $\mu\text{L}^{-1}$  in methanol. The stock solution was pipetted directly onto sample tubes under a flow of helium to produce a range of mixed monoterpene standards of 3, 6, 9 and 12 ng. Isoprene standards were prepared by direct sampling onto a sorbent tube from a certified 700 ppbv gas standard (BOC, UK) using a sample pump (210-1003MTX, SKC Ltd, Blandford Forum, UK) producing standards of 65, 198, 296 and 395 ng. Note that mass loadings of isoprene and monoterpene calibration standards were prepared to greater precision than quoted above but are shown here as nominal values for ease of discussion. cis- $\beta$ -Ocimene was not included in the monoterpene stock solution but was identified in the samples using the internal library of the GC-MS (National Institute of

Standards and Technology). The concentration of cis- $\beta$ -ocimene was calculated using peak area ratio and concentration of  $\alpha$ -pinene.

The limit of detection (LOD) of the calculated emissions ranged from 0.12 to 0.35  $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$  for the branch chambers and 0.47–1.4  $\mu\text{g C m}^{-2} \text{h}^{-1}$  for the forest floor chambers. Uncertainties on an individual calculated emission rate were 16% for isoprene and 17% for monoterpenes, which were derived via error propagation methods described in Purser et al. (2020).

## 2.8. Calculation of BVOC emissions and standardisation

BVOC emissions from the forest floor ( $F_{\text{floor}}$ ) ( $\mu\text{g C m}^{-2} \text{h}^{-1}$ ) were calculated using Equation (1), where  $C_{\text{sample}}$  is the concentration of a monoterpene inside the chamber ( $\mu\text{g C L}^{-1}$ ),  $C_{\text{ambient}}$  is the concentration of a monoterpene in the ambient air outside the chamber ( $\mu\text{g C L}^{-1}$ ),  $A$  is the area of forest floor inside the chamber ( $\text{m}^2$ ),  $V$  is the volume inside the chamber (L), and  $t$  is the sampling duration (min).

$$F_{\text{floor}} = \frac{[C_{\text{sample}} - C_{\text{ambient}}] \times V \times 60}{A \times t} \quad (1)$$

In some cases, the concentration in ambient air was larger than inside resulting in a negative emission, i.e. a net uptake.

Emissions from branch chambers ( $F_{\text{branch}}$ ) ( $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ) were calculated using Equation (2), where  $f$  is the flow rate through the chamber ( $\text{L min}^{-1}$ ) and  $m$  is the dry mass (g) of foliage inside the chamber.  $C_{\text{sample}}$  is the concentration of isoprene or monoterpene inside the chamber ( $\mu\text{g C L}^{-1}$ ),  $C_{\text{blank}}$  is the concentration of isoprene or monoterpene measured inside a blank chamber ( $\mu\text{g C L}^{-1}$ ),

$$F_{\text{branch}} = \frac{[C_{\text{sample}} - C_{\text{blank}}] \times f}{m} \quad (2)$$

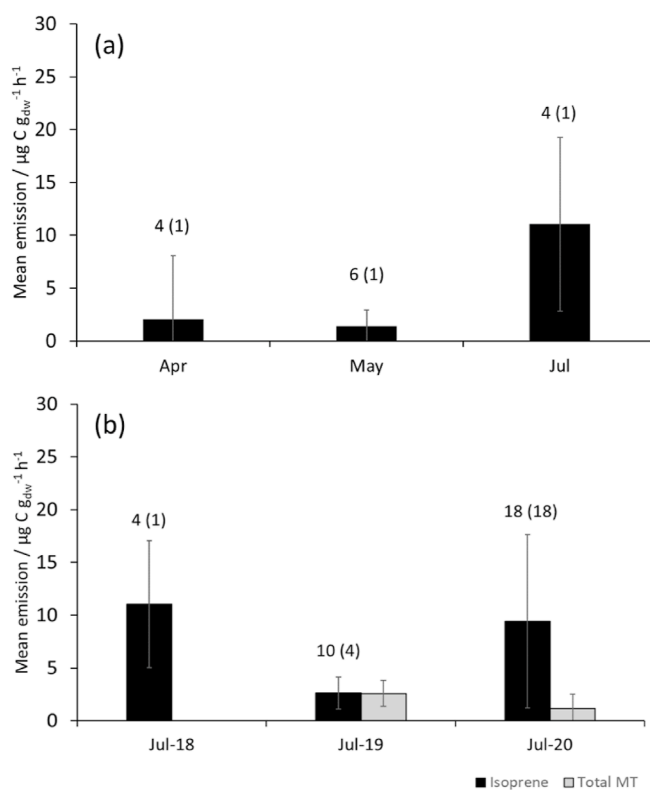
Mean chamber temperature and PAR recorded during sample collection were used to standardise branch isoprene emissions to 30 °C and 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$  and branch monoterpene emissions to 30 °C using the algorithms presented in Guenther et al. (1993). Forest-floor monoterpene emissions in previous studies have on occasion been standardised to a temperature of 30 °C (Hayward et al., 2001), based on the observations of monoterpene emissions correlated to increases in temperature in living plant specimens (Guenther et al., 1993). However, we report the data here generally as non-standardised (unless stated) given the complexity of the drivers of forest-floor BVOC emissions as discussed by Tang et al. (2019). Some of the driving factors that influenced emissions are highlighted further in Section 3.3. Where sequential samples were collected on the same branch, emissions are reported as the mean of the sequential measurements. For forest-floor chambers, the 3 or 4 chambers for a given stand type collected on the same day were pooled and reported as a mean emission for the specific stand type.

## 3. Results and discussion

### 3.1. Branch BVOC emissions

The standardised isoprene emissions measured from the same branch of juvenile *E. gunnii* foliage across the growing season in 2018 (April, May and July) increased from 2.0  $\mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$  to 11.0  $\mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$  (Fig. 4a). Although the isoprene emissions reported here have been standardised using the simplified algorithm from Guenther et al. (1993) they may still reflect the influence of PAR and temperature over the days prior to measurements on the measured emission on a given day. The more advanced algorithms from Guenther et al. (2012) could not be applied in this instance due to the lack of continuous local PAR data, in turn due to the lack of power at the site.

The standardised isoprene emissions from juvenile foliage of different branches of 18 individual trees measured across two consecutive days with similar weather in 2020 ranged between 0.6 and 24.0  $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$  (Fig. 5a). (The mean temperature and PAR during sampling on



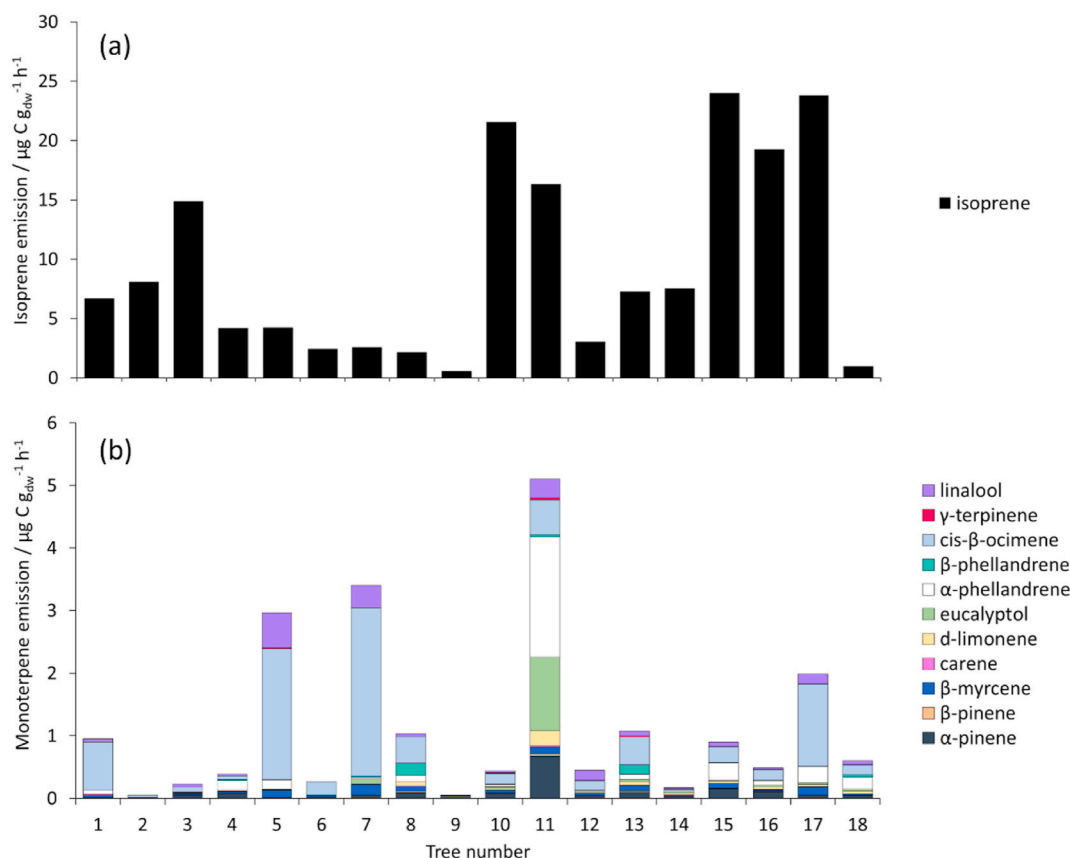
**Fig. 4.** Variability in standardised isoprene and monoterpene branch emissions from an *E. gunnii* SRC plantation in Nottinghamshire, England. (a) Mean isoprene emissions from a single juvenile branch measured during different months across the growing season in 2018. (b) Mean isoprene and total monoterpene emissions from different juvenile branches measured in July in 3 different years. The total number of measurements are stated above each column with the number of different branches given in parentheses. The error bars are the standard deviations in the mean emissions. Data for total monoterpene emissions from juvenile branches in July 2018 are missing due to instrument problems.

these two days were 24.8 °C and 27.3 °C, and 994  $\mu\text{mol m}^{-2} \text{s}^{-1}$  and 683  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , respectively.) The mean ( $\pm$  standard deviation) of the 18 individual standardised isoprene emissions is  $9.4 \pm 8.2 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ .

Fig. 4b also shows that standardised isoprene emissions measured in the same month, and on different trees and branches, had comparable magnitudes across the three years 2018–2020 (allowing for intra-year variation).

All isoprene emissions from branches of juvenile foliage measured in July (Fig. 4b) were combined to give a mean standardised isoprene emission of  $7.50 \pm 7.26 \mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$ . This value is based on 39 measurements from 23 branches across three years (2018–2020). This isoprene emission rate for *E. gunnii* is therefore less than half of that reported for other SRC species such as willow (*Salix* spp.)  $20 \mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$  ( $17.7 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ) (Copeland et al., 2012).

The standardised total monoterpene emissions ranged from 0.1 to 5.1  $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$  and were smaller than isoprene emissions for the equivalent branches (Fig. 5b). No assessment could be made of the variation of monoterpenes across different months since branch monoterpene emissions data from 2018 were lost because of instrument problems. The mean standardised total monoterpene emissions for all measurements made in July was  $1.30 \pm 1.42 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ . This is based on 30 individual measurements from 22 branches across two years (2019–2020). There was large variation in the emission of isoprene and monoterpenes between different branches measured on different trees of the same species. This variation has previously been observed in measurements taken between different individuals of the same species of



**Fig. 5.** Variability in standardised isoprene and monoterpene branch emissions from an *E. gunnii* SRC plantation in Nottinghamshire, England. (a) Isoprene emissions from a single juvenile branch of 18 different trees across two consecutive days in July 2020. (b) Monoterpene emissions from a single juvenile branch of the same 18 trees as in (a).

*E. globulus*, with emission rates varying by a factor of at least 5 (He et al., 2000).

Measurements from a previous study on young eucalypt trees grown in the UK supports the data presented here with standardised isoprene emissions in the range of 0.8–18.2  $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$  and standardised total monoterpene emissions in the range 0–5.73  $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$  (Purser et al., 2020). However, emissions from 4 to 6 month old *E. gunnii* plants (juvenile foliage) grown in pots under semi-natural conditions (an artificial light source was used) in a greenhouse in the UK and measured at 30 °C and 1000  $\mu\text{mol m}^{-2} \text{s}^{-1}$  (i.e. at standardised conditions) suggests that isoprene emissions can be much higher 19.7–40.8  $\mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$  (17.4–36  $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ) but total monoterpene emissions lower 0.04–0.97  $\mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$  (0.03–0.88  $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ) (Owen and Peñuelas, 2013). It has previously been discussed that isoprene emissions for *E. globulus* derived from greenhouse studies have been higher than when measuring the same species under field conditions (He et al., 2000). Monoterpene emissions have also been shown to vary with leaf age, with younger *E. globulus* leaves producing higher monoterpene emissions than older leaves (Pio et al., 2001; Street et al., 1997). Terpene oil yields have also been found to be higher from young leaves compared to adult leaves (Silvestre et al., 1997). It is also possible that within the field environment biotic factors such as above and below-ground herbivory, plant-plant interactions, microbial interactions and disease may induce stronger monoterpene emissions as a plant defence strategy, something which may be absent in greenhouse studies where plants are grown under controlled conditions (Arimura et al., 2010; Heil and Karban, 2010; Unsicker et al., 2009). These previous observations could account for some of the variation shown between the greenhouse-based *E. gunnii* emissions reported by Owen and Peñuelas (2013) and the field-derived *E. gunnii* emissions in our study. In addition, isoprene emissions from

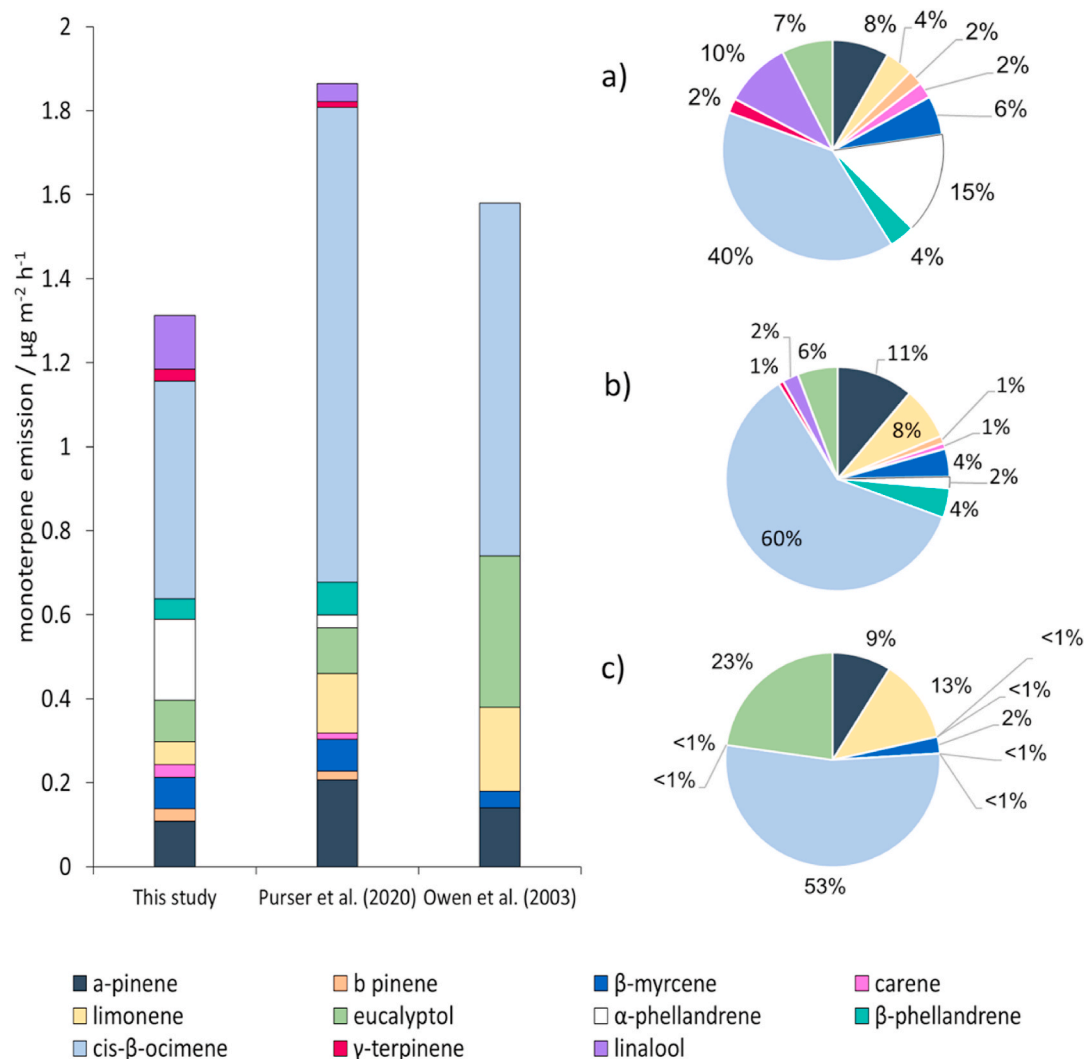
*E. gunnii* in our study are smaller than those reported from other field-based studies of bioenergy plantations grown in the UK such as SRC willow (*Salix* sp.) and SRF hybrid aspen (*Populus* sp.) where mean standardised isoprene emissions were 20  $\mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$  (17.6  $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ) and 22.8  $\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$  respectively (Copeland et al., 2012; Purser et al., 2021). Mean standardised total monoterpene emissions from *E. gunnii* in our study were at least an order of magnitude higher than from either SRC willow or SRF hybrid aspen (Copeland et al., 2012; Purser et al., 2021).

### 3.2. Branch emissions monoterpene composition

Emissions of monoterpenes were highly variable across the juvenile branches but were generally dominated by cis- $\beta$ -ocimene (Fig. 6). Owen and Peñuelas (2013) also reported that *E. gunnii* was a major cis- $\beta$ -ocimene emitter, followed by eucalyptol and  $\alpha$ -pinene (Fig. 6). However, although these authors sought to quantify the same set of monoterpenes (but not linalool) as the present study, they report data above their LOD for only five of the eleven monoterpenes. This earlier study on *E. gunnii* monoterpene emissions was performed under greenhouse conditions with additional PAR lighting. Measurements were conducted during July and August with the trees showing no signs of herbivory. The study by Purser et al. (2020) also used pot grown *E. gunnii* trees, but grown outside in the UK with a managed supply of water and nutrients.

Herbivory could be one explanation for the monoterpene difference between studies since all the juvenile growth of the *E. gunnii* trees in the coppice regrowth stand (Fig. 2d Zones 1 & 2) were infested with a psyllid species (*Ctenarytaina eucalypti*). Eucalypt psyllid species such as *Glycaspis brimblecombei* can induce an increase in the concentrations of





**Fig. 6.** The composition of the mean standardised monoterpene emissions for branches of *E. gunnii* from a) this study from an SRC plantation in Nottinghamshire, England, b) Purser et al. (2020) and c) Owen et al. (2013). Data are presented as both absolute monoterpene emissions (bar plots) and as relative percentages of the total monoterpene emissions measured (pie charts).

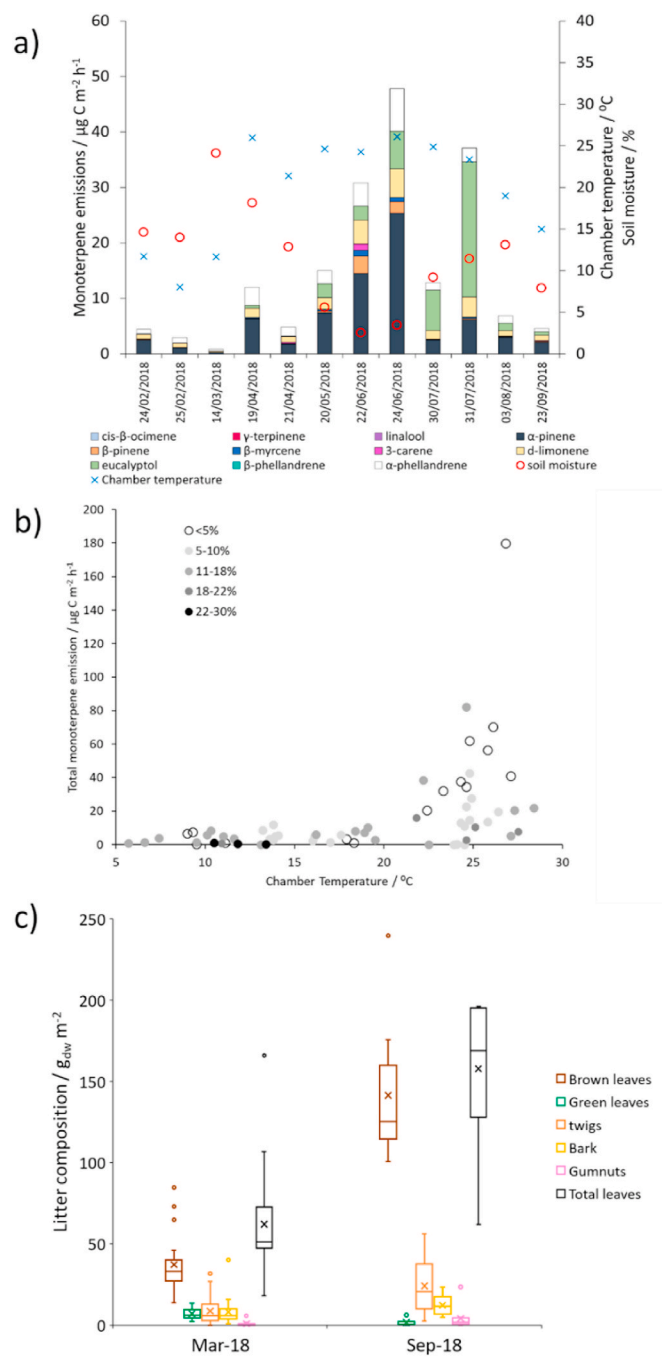
eucalyptol,  $\alpha$ -phellandrene and  $\beta$ -phellandrene in essential oils of a number of eucalypt species (Lucia et al., 2016). Fig. 6 shows that the mean composition of juvenile branch monoterpene emissions from *E. gunnii* contained both greater absolute ( $0.19 \mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$ ) and relative (15%)  $\alpha$ -phellandrene than measured in the previous studies (Owen and Peñuelas, 2013; Purser et al., 2020). Linalool emissions were also elevated from juvenile branches in the regrowth stand at the Daneshill plantation compared to previously reported data. Linalool is a terpene alcohol that is emitted by plants as a defence against herbivory (Kessler and Baldwin, 2001). Linalool emissions from the *E. gunnii* at the Daneshill plantation were  $0.13 \mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$ , accounting for 10% of the total monoterpenes reported, slightly higher than the  $0.04 \mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$  (or 2% of total monoterpenes) previously reported by Purser et al. (2020). These differences demonstrate the need for field-based plantation measurements to determine BVOC emissions data under real-world growing conditions. A study showed that the composition of monoterpene emissions from the foliage of young 3-y old *E. globulus* grown in a greenhouse differed to that from 7-y old *E. globulus* trees growing in the field (Nunes and Pio, 2001). For instance limonene and pinene were not always present in emissions from older trees, although eucalyptol was always present in both.

### 3.3. Forest-floor BVOC emissions from an old eucalypt stand

This section discusses the BVOC emissions from the forest floor of an old eucalypt stand as an example of an undisturbed SRF forest floor and the potential drivers of these emissions. Section 3.4 then discusses the changes in BVOC emissions in the disturbed forest floor after coppicing and during the regrowth phase of the plantation.

In the old *E. gunnii* stand the mean isoprene emissions from the forest floor were  $0.02 \pm 0.05 \mu\text{g C m}^{-2} \text{h}^{-1}$ . Whilst it is widely reported that the forest floor can act as a sink for isoprene (Cleveland and Yavitt, 1997), there are also sources, for example from the mosses found in this old stand (Hanson et al., 1999) or from soil microbes (Veres et al., 2014), which could collectively yield the small net isoprene emissions observed here.

Both the magnitude and composition of the mean daily monoterpene emissions from the forest floor varied in the old eucalypt stand across the sampling campaign from February 2018 to September 2018 (Fig. 7a). In general, mean daily monoterpene emissions were lower during winter and higher in the summer, with the peak emission of  $50 \mu\text{g C m}^{-2} \text{h}^{-1}$  in June 2018. The mean total monoterpene emissions for the old *E. gunnii* stand during 2018 was  $15.0 \pm 15.3 \mu\text{g C m}^{-2} \text{h}^{-1}$  (standardised  $28.6 \pm 21.5 \mu\text{g C m}^{-2} \text{h}^{-1}$ ). For context, BVOC emissions from the floor of UK Sitka spruce plantations have been reported to be  $33.6 \mu\text{g m}^{-2} \text{h}^{-1}$  (29.6



**Fig. 7.** a) Mean daily monoterpene emissions, soil moisture content and chamber temperature in an old eucalypt stand between February 2018 and September 2018. b) Relationships between total monoterpene emissions and soil moisture content or chamber temperature for all forest floor chambers sampled during 2018 and 2019 in the old eucalypt stand. c) Forest floor litter composition in the old eucalypt stand as assessed in March and September 2018. The number of  $1 \text{ m}^2$  litter plots sampled on each occasion was 18 and 10, respectively.

$\mu\text{g C m}^{-2} \text{h}^{-1}$ ) (standardised) (Hayward et al., 2001) and  $1.1\text{--}40.2 \mu\text{g C m}^{-2} \text{h}^{-1}$  (Purser et al., 2021). The similar emission rates from the forest floors of both species may reflect the presence of similar monoterpene storage areas within the leaf structure. Monoterpene emissions from the forest floor of deciduous plantations of SRF hybrid aspen and SRF Italian alder are much lower at  $0.057\text{--}3.84 \mu\text{g C m}^{-2} \text{h}^{-1}$  and  $0.11\text{--}6.51 \mu\text{g C m}^{-2} \text{h}^{-1}$  respectively (Purser et al., 2021).

Emissions of monoterpenes from the forest floor appear to be driven by a combination of temperature (inside the chamber) and soil moisture (in top 7 cm) (Fig. 7b), with the highest emissions often coinciding with days where soil moisture was low and chamber temperatures were high. It appears, however, that substantial emissions of monoterpenes were only observed at temperatures  $>22^{\circ}\text{C}$  and at soil moistures  $<18\%$ . These variables are of course not independent of each other, with higher soil temperatures tracking higher chamber temperatures and often coinciding with low soil moisture (see Supplementary Information S2).

*E. gunnii* is a broadleaf evergreen which maintains its foliage all year round. However, the input of material from the tree canopy, leaves, twigs, bark and gumnuts at different times during the year to the forest floor may also drive the mean daily monoterpene emission magnitude and composition shown in Fig. 7a. Previous literature suggests that the bulk of emissions from the forest-floor surface to the atmosphere may be as a result of understorey vegetation or litter (Mäki et al., 2019).

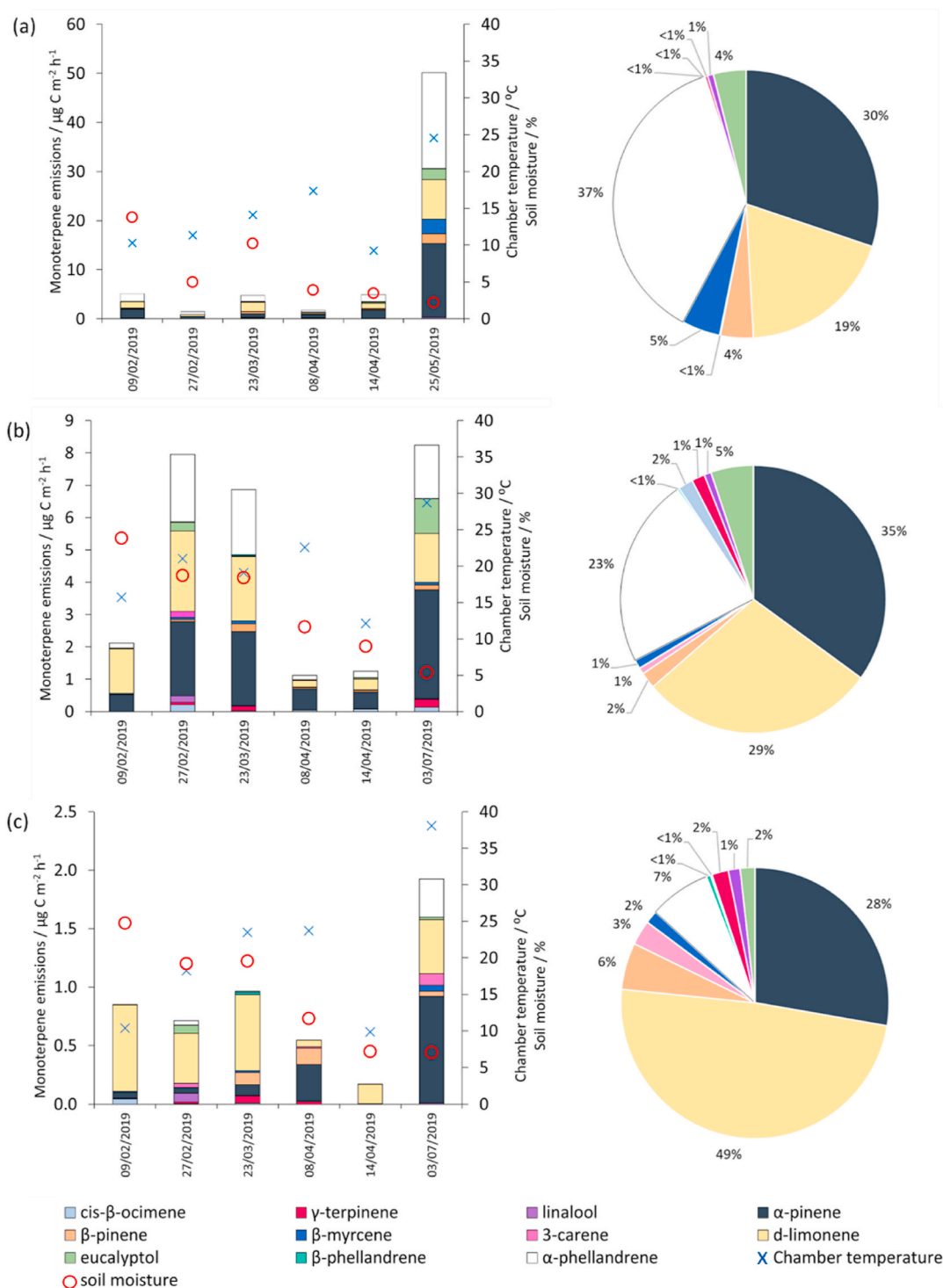
Forest-floor composition was assessed during spring (March) and autumn (September) of 2018 (Fig. 7c). Recently-fallen green leaves were notably more present on the forest floor in spring than autumn, likely due to canopy damage from strong winds and snow in early March (Met Office, 2018a). Overall, however, a larger mass of leaves were noted on the forest floor in autumn than in spring. This added input of litter to the forest floor over the summer may also contribute to the increased emissions of monoterpenes observed during the summer. It is worth noting that the canopy was visibly browner in 2018 than in the subsequent years, and that summer in 2018 in that area was  $1.5^{\circ}\text{C}$  warmer and had 50% less rainfall than the 30-y mean (Met Office, 2018b). The sand-rich and nutrient-poor soil at Daneshill may have further exacerbated leaf fall during 2018. The limited water-holding capacity of the sandy soil, in combination with its low nutrients, may have led to stress in the trees and leaf shedding. Laclau et al. (2009) have reported that a lack of nutrients shortens leaf lifespan in some eucalypt plantations. These factors are presumed to contribute to the notable increase in the mean total leaf litter (and twigs) on the forest floor in autumn.

#### 3.4. Difference in forest-floor BVOC emission with stand type

Fig. 8 shows the monoterpene emissions measured in 2019 from the forest floor of different stand types (old, coppiced and regrowth). Isoprene emissions were also measured, but are not shown as they were very low,  $\leq 0.02 \mu\text{g C m}^{-2} \text{h}^{-1}$  (as discussed in Section 3.3).

The mean ( $\pm$  standard deviation) for the total monoterpene emissions from the old stand measured in 2019 was  $11.3 \pm 19.1 \mu\text{g C m}^{-2} \text{h}^{-1}$  (standardised  $29.4 \pm 27.9 \mu\text{g C m}^{-2} \text{h}^{-1}$ ). The coppiced stand had much lower mean total monoterpene emissions of  $4.6 \pm 3.4 \mu\text{g C m}^{-2} \text{h}^{-1}$  (standardised  $16.5 \pm 10.5 \mu\text{g C m}^{-2} \text{h}^{-1}$ ) and the regrowth stand even lower still at  $0.8 \pm 0.6 \mu\text{g C m}^{-2} \text{h}^{-1}$  (standardised  $3.3 \pm 1.9 \mu\text{g C m}^{-2} \text{h}^{-1}$ ), for the same year. The old stand visibly had the highest amount of leaf litter present; the coppiced stand also still contained some traces of leaf litter and woody debris from the coppicing process. The floor of the regrowth area, which was mostly bare soil and grass with little visible sign of the original leaf litter that once covered the area (see Supplementary Information S3), had the lowest total monoterpene emissions.

The relative monoterpene composition varied between each stand type (Fig. 8). In the old eucalypt stand the forest floor emissions gave a mean monoterpene composition broadly consistent with that of the juvenile branch measurements discussed in Section 3.1, although the most abundant monoterpene was  $\alpha$ -phellandrene, with cis- $\beta$ -ocimene being noticeably absent. The explanation is assumed to be that cis- $\beta$ -ocimene is not stored in any substantial quantity in the oil glands (sub-dermal secretory cavities in eucalypt leaves) because it is produced by *de novo* synthesis (Owen et al., 2002; Staudt et al., 1997). *De-novo* synthesis is a light and temperature dependant process in living leaves and therefore would not be generated in leaf litter (Ghirardo et al., 2010). The absolute and relative abundance of  $\alpha$ -phellandrene emissions from the forest floor appears to be associated more with the amount of leaf litter present. The



**Fig. 8.** Forest-floor emissions of individual monoterpenes (bar plots) and their mean relative emission proportions (pie charts) for an *E. gunnii* SRC plantation in Nottinghamshire, England for three different managed stand types (a) a 7-year old stand (b) a recently coppiced stand, and (c) a stand where coppiced trees have 1-year regrowth.

emissions of the most abundant monoterpenes from the forest floor, d-limonene and α-pinene, could be associated with the forest soils or even roots. A study by Asensio et al. (2007a) found these compounds to be the most abundant in Mediterranean forest soil.

This difference in magnitude and composition of emissions from the floor of different phases of the SRC forest is an important consideration when assessing total BVOC emissions from the plantation. In addition, there may also be a secondary effect from changes to the forest floor

flora and microbiome due to changes in the presence of leaf litter. BVOC leachates released from eucalypt litter to the soils during decomposition has previously been shown to release compounds inhibiting growth of other plant species (He et al., 2014; Molina et al., 1991).

### 3.5. Woodchip BVOC emissions

This study shows that total monoterpene emissions could reach 90

$\mu\text{g C m}^{-2} \text{ h}^{-1}$  from fresh green woodchip (Fig. 9), although a more thorough investigation of emissions per mass of woodchip is necessary. In some eucalypt species monoterpene oils are stored in the sub-dermal layer inside oil glands contained within the leaf (King et al., 2006), whereas in pine species monoterpene compounds are stored in specific oil ducts contained within the sub-dermal mesophyll layer of the leaf (Turner et al., 2019). In addition, in some species of both pines and eucalypts monoterpenes are stored in the woody parts of the tree stem, branches and root systems (Kim et al., 2011; Latta et al., 2000; Roberts, 1970). Forest-thinning operations on ponderosa pine forests in California, USA, in which trees were removed, macerated, and the woodchips retained on site, showed a 10–30 fold increase in monoterpene emissions during this forestry activity (Schade and Goldstein, 2003). Given there are some similarities in stored monoterpenes between pines and eucalypts, the coppicing of eucalypts could lead to significant releases of BVOC to the atmosphere during coppicing operations.

In our study, the monoterpenes emitted from the fresh green whole-tree woodchip (Fig. 9) were substantially different to those from the branch foliage (Fig. 6), with much lower or <LOD abundances of cis- $\beta$ -ocimene,  $\beta$ -myrcene and linalool. These particular monoterpenes may not be stored in the foliage or woody parts of the tree in significant quantities. The dominant monoterpene from the fresh woodchip was eucalyptol, accounting for 53% of the total emissions.  $\alpha$ -Pinene, d-limonene and small amounts of  $\alpha$ -phellandrene were also present. Eucalyptol has previously been reported to be the main monoterpene in essential oils found in the leaves of *E. gunnii*, accounting for 38% (Li et al., 1996) or 68% (Bugarin et al., 2014) of total oil composition. It may be that the woodchip monoterpene emission composition reflects the stored oils in the leaf and woody parts of the tree which are only released in significant quantities from foliage upon wounding (Kim et al., 2011). In addition, eucalyptol is more soluble in water than other monoterpenes (which generally have limited solubility), and has been shown to be present in water-soluble fractions from soils and leaf litter (He et al., 2014; Molina et al., 1991; Puig et al., 2018; Weidenhamer et al., 1993). Temperatures in the top 7 cm of the fresh woodchip pile reached 54 °C and the pile produced steam. The solubility of eucalyptol may have enabled it to be disproportionately abundant in the steam arising from the fresh woodchip.

The woodchip pile remained onsite outside through the winter. In subsequent sampling after three months, the most important finding was that total monoterpene emissions had decreased dramatically, by two orders of magnitude, to  $1.06 \pm 1.13 \mu\text{g C m}^{-2} \text{ h}^{-1}$  (Fig. 9). The composition of the monoterpene emissions had also changed. The most abundant monoterpenes from the old woodchip were  $\alpha$ -pinene and d-limonene, with eucalyptol now only accounting for 3% abundance. In addition, the observation of fungal mats on the surface of the old woodchip pile means that microbial emissions from these biological

sources or the further breakdown of the wood by physical or biological processes should be further investigated in relation to the monoterpene emissions from the older woodchip pile.

Isoprene emissions from the fresh woodchip pile ( $1.98 \mu\text{g C m}^{-2} \text{ h}^{-1}$ ) were substantially lower than the total monoterpene emissions and were substantially lower again from the old woodchip pile ( $0.01 \mu\text{g C m}^{-2} \text{ h}^{-1}$ ). This is expected given that the emissions of isoprene from eucalypt foliage is associated with photosynthesis and that it is emitted directly from leaves as it is produced, with no storage in the leaf glands (Sharkey et al., 2005).

#### 4. Plantation-scale BVOC emissions

Plantation-scale estimates of isoprene and total monoterpene emissions for *E. gunnii* from our study were modelled using an Excel version of MEGAN 2.1 (Pocket MEGAN 2.1 excel 135 beta 3 calculator (Guenther et al., 2012)). The model requires standardised emission potentials. Here, mean standardised emission potentials for isoprene and monoterpenes of  $3060 \mu\text{g m}^{-2} \text{ ground h}^{-1}$  and  $530 \mu\text{g m}^{-2} \text{ ground h}^{-1}$ , respectively, were used, which in turn were based on the mean standardised emissions of isoprene ( $7.50 \mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$ ) and monoterpenes ( $1.30 \mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$ ) from branches of juvenile foliage discussed in Section 3.1. The conversion from branch emissions reported per dry mass to emissions per ground area requires the mass of foliage per  $\text{m}^2$ . This was calculated by multiplying the measured LAI data from the old stand at Daneshill,  $2.0 \text{ m}^2 \text{ m}^{-2}$ , by a leaf mass area (LMA) of  $204 \text{ g m}^{-2}$  derived from the specific leaf area for *E. gunnii* of  $4.9 \text{ m}^2 \text{ kg}^{-1}$  (Leslie et al., 2017), to give a foliar biomass of  $408 \text{ g m}^{-2}$ . It is worth noting that the measured LAI for the old stand (7-y old) of *E. gunnii* measured in this study is similar to the LAI ( $1.9 \text{ m}^2 \text{ m}^{-2}$ ) reported for an 8-y old plantation of *E. grandis*  $\times$  *E. urophylla* in Brazil (Hakamada et al., 2016). *E. globulus*, a widely studied species, was also modelled here alongside *E. gunnii* to demonstrate the potential range of isoprene and monoterpene emissions that could be emitted from different eucalypt species if used for bioenergy plantations in the UK. The isoprene and monoterpene emissions from around 30 different species of eucalypt have previously been published and vary widely in their emission rates and composition (He et al., 2000; Owen and Peñuelas, 2013; Purser et al., 2020; Sørensen et al., 2020; Winters et al., 2009). For example, *E. botryoides* has been shown to be a low emitter of isoprene ( $5.3 \pm 1.6 \mu\text{g g}_{\text{dw}}^{-1} \text{ h}^{-1}$ , equivalent to  $4.68 \pm 1.4 \mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$ ) and *E. forrestiana* was suggested to be a non-emitter of monoterpenes (He et al., 2000). In contrast, *E. globulus* has been shown to be a high emitter of both isoprene and monoterpenes, up to  $68.5 \mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$  and  $185 \mu\text{g C g}_{\text{dw}}^{-1} \text{ h}^{-1}$  respectively (He et al., 2000; Owen and Peñuelas, 2013). However, only cold-tolerant, well-adapted species may be suitable for growing in the UK as biomass for bioenergy (Leslie et al., 2012, 2020, 2020; Leslie and

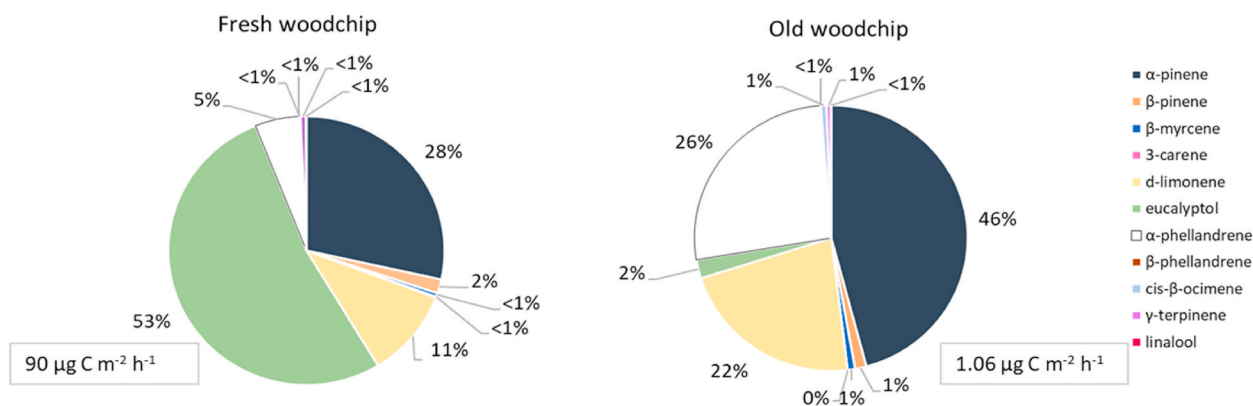


Fig. 9. Relative composition of monoterpene emissions from a eucalypt wood chip pile a) freshly chipped b) after 3-months outside. The numbers in the grey box are the mean emissions of total monoterpenes from the woodchip pile.

Purser, 2016). Additional model runs were therefore set up for *E. globulus* using the emissions potentials of  $4540 \mu\text{g C m}^{-2} \text{ground h}^{-1}$  and  $6401 \mu\text{g C m}^{-2} \text{ground h}^{-1}$  for isoprene and total monoterpenes, respectively, based on the mean standardised emissions of isoprene ( $10.0 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ) and total monoterpenes ( $14.1 \mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$ ) for UK measured from immature *E. globulus* trees (Purser et al., 2020). The LMA for *E. globulus* was  $227 \text{ g m}^{-2}$  derived from a LMA of  $4.4 \text{ m}^2 \text{ kg}^{-1}$  based on measurements taken from an unfertilised, unirrigated plantation, matching the conditions found at the unmanaged Daneshill plantation in our study (White et al., 2010). The LAI used was  $2.0 \text{ m}^2 \text{ m}^{-2}$  which is similar to previously reported values for 3-y old and 8-y old unmanaged *E. globulus* plantations (Ceulemans et al., 1996; White et al., 2010). In all cases, modelling of hourly plantation emissions was conducted using the same datasets of hourly meteorological data from east Scotland and south England for 2018 and 2019 to allow for additional comparison of estimated annual per hectare BVOC emissions from this *E. gunnii* SRC plantation with those from other species used in UK bioenergy plantations reported in Purser et al. (2021). It should be noted that apart from the different standardised isoprene and total monoterpene emissions potentials, and the assignment of a constant LAI of  $2.0 \text{ m}^2 \text{ m}^{-2}$ , all other parameters and methodology were as described in Purser et al. (2021). Hourly outputs for isoprene and total monoterpenes from the model were summed to give monthly emission totals, averaged across the two years and the two UK meteorology datasets. Modelled emissions are subject to uncertainties from a number of factors that cannot be adequately accounted for in the model. These are discussed further in Purser et al. (2021), but the main uncertainties are: the use of a single mean standardised emission factor to derive emission factors that change across seasons, the impact of weather (rainfall, high winds, snow cover), the influence of biotic factors e.g. microbial, herbivory, and the planting density of the forest and its subsequent LAI value which has an impact on the volume of emitting biomass.

In addition, the estimates discussed here for annual plantation emissions do not include the contribution of the forest floor because of the complexities associated with co-dependant variables when measuring and building models for forest-floor fluxes. However, comparison of the modelled canopy emissions with the sampled forest-floor emissions during the same season provides insight into the relative contribution of the forest floor as a source of isoprene and total monoterpenes to plantation scale emissions. For instance the mean daily modelled isoprene emissions for the canopy (based on juvenile foliage) in July was  $262 \mu\text{g C m}^{-2} \text{ground h}^{-1}$  and for total monoterpenes was  $57 \mu\text{g C m}^{-2} \text{ground h}^{-1}$ . The equivalent emissions of isoprene from the forest floor in the old stand on a per  $\text{m}^2$  basis were insignificant (as discussed in Section 3.4), whilst the mean total monoterpene emissions from the forest floor across chambers measured during July was  $31 \mu\text{g C m}^{-2} \text{ground h}^{-1}$  (about half of that of the branches) for the same month. This shows that monoterpenes from the forest floor during summer may potentially contribute up to 35% of the total plantation monoterpene emissions produced from immature foliage. However, adult foliage has been reported to produce 10-fold lower monoterpene emissions than juvenile (immature) foliage according to measurements of *E. globulus* in plantations in Portugal (Nunes and Pio, 2001; Street et al., 1997). Whilst this needs to be investigated for *E. gunnii*, if confirmed it suggests that the forest floor of an old stand of *E. gunnii* SRC plantation could contribute an even more substantial portion of the total monoterpene emissions on a per area basis.

## 5. Biomass plantations and atmospheric composition

Modelled annual emissions were determined using MEGAN 2.1 algorithms based on the calculated mean standardised emission rate of isoprene ( $3060 \mu\text{g C m}^{-2} \text{ground h}^{-1}$ ) and monoterpenes ( $530 \mu\text{g C m}^{-2} \text{ground h}^{-1}$ ) for *E. gunnii* derived from measured branch chamber emission rates and LAI during field sampling. Table 2 shows the modelled annual emissions of isoprene ( $6.9 \text{ kg C ha}^{-1}$ ) and total

**Table 2**

Modelled estimated annual and seasonal total monoterpene and isoprene emissions from a UK *E. gunnii* SRC plantation.

Modelled	Total monoterpene		Isoprene	
	/ kg C $\text{ha}^{-1}$	% of annual total	/ kg C $\text{ha}^{-1}$	% of annual total
Annual total	2.4	–	6.9	–
Winter (Dec–Feb)	0.3	13	0.1	1
Spring (Mar–May)	0.5	21	1.8	26
Summer (Jun–Aug)	1.1	44	4.2	61
Autumn (Sep–Nov)	0.6	23	0.8	12

monoterpenes ( $2.4 \text{ kg C ha}^{-1}$ ) from the canopy of this *E. gunnii* eucalypt plantation based on the branch chamber measurements in this study. For comparison, *E. globulus*, known to be a high emitter of isoprene and monoterpenes, showed much higher annual emissions at the plantation scale per hectare. In this case isoprene emissions were almost double,  $11.9 \text{ kg C ha}^{-1}$ , for *E. globulus* compared to *E. gunnii* and total monoterpene emissions 7 times larger at  $15.7 \text{ kg C ha}^{-1}$ . These annual emissions serve as a simple representation of bioenergy plantation emissions and may reflect younger eucalypt plantations in which the majority of foliage may be immature. For older stands in which the majority of foliage may be mature, the isoprene and monoterpene emission rates could be lower as suggested by studies of *E. globulus* in the field (Nunes and Pio, 2001; Street et al., 1997). The influence of foliage age on BVOC emissions at the plantation scale in stands of eucalypt at varying ages for bioenergy purposes needs further investigation.

It is worth noting that only total monoterpene emissions are modelled in this simplified way based on branch chamber emission rates from bioenergy plantations. However, the reality is that there will be a range of monoterpene compounds released at varying concentrations from the different sources from the plantation. These combined sources and their specific emission rates may give a very different composition in the atmosphere above the canopy, reflecting no single specific source. Above-canopy studies from natural eucalypt forests in Australia, for example, show eucalyptol emissions to be the dominant monoterpene (Ramirez-Gamboa et al., 2021). Based on our measurements, the assumption could be that  $\beta$ -ocimene from the canopy may be the dominant monoterpene emission from an *E. gunnii* plantation given that the forest-floor sources are smaller in magnitude and coppicing activities very short in duration by comparison. In addition, the influence of physical processes that may influence BVOC emissions from the plantation e.g. leaf and tree damage, rainfall and biological processes e.g. plant disease, browsing by herbivores, are also not possible to take into consideration in the model. There have been limited above-canopy studies focusing on BVOCs from UK plantations and none have been on eucalypt (Beverland et al., 1996; Copeland et al., 2012). Above-canopy studies may therefore provide a useful insight to how the individual BVOC sources in a plantation may contribute to the overall composition.

The modelled annual emission of isoprene ( $6.9 \text{ kg C ha}^{-1}$ ) from the *E. gunnii* plantation reported in this study is half that of the isoprene emissions previously modelled (using the same meteorology data) from Sitka spruce, *Picea sitchensis* Bong. Carr ( $13.8 \text{ kg C ha}^{-1}$ ), and hybrid aspen, *Populus tremula* ( $15.5 \text{ kg C ha}^{-1}$ ), grown as SRF (Purser et al., 2021). However the modelled monoterpene emissions from *E. gunnii* reported here are almost an order of magnitude greater than those modelled for SRF species hybrid aspen ( $0.3 \text{ kg C ha}^{-1}$ ) although 7 times smaller than those modelled for Sitka spruce ( $15.7 \text{ kg C ha}^{-1}$ ) (Purser et al., 2021).

The estimates demonstrate the large contribution of summer emissions to the calculated annual emissions from the plantation for both isoprene and total monoterpenes.

The impact of increased bioenergy planting and the seasonality of their BVOC emissions on air quality needs much more data and detailed consideration, but some general observations may be valid. Summer emissions are likely to have the highest impact on generation of ozone and secondary organic aerosol. Winter emissions contribute only minor amounts to the total annual BVOC emissions. As shown in Fig. 7a, forest-floor emissions contribute little, if at all, to the atmosphere during winter due to the colder temperatures and increases in soil moisture. However, in this case study of a commercial *E. gunnii* SRC plantation, coppicing activities have typically occurred in late autumn to early winter and the resulting woodchip is associated with large emissions of monoterpenes. It has been noted that the timing of such large emission events could have an impact on local tropospheric chemistry (Schade and Goldstein, 2003). In the UK, as elsewhere, concentrations of nitrogen oxides (NO<sub>x</sub>) are higher in the autumn and winter than in the summer. However, often it is the concentration of VOCs rather than NO<sub>x</sub> that is the limiting factor in the production of ozone. In addition, the atmospheric boundary layer height in winter is also generally lower, increasing the concentration of emitted species. Larger releases of BVOCs under these circumstances in winter could potentially lead to increases in local surface ozone concentrations, albeit that the impacts in winter from woodchip are likely to be short-lived, small in magnitude and very localised in comparison to the changes in air quality in the summer from the plantation emissions overall.

Tree planting may also have beneficial impacts on air pollution in the UK with the potential to reduce airborne particulate matter (PM<sub>10</sub>, PM<sub>2.5</sub>) and ozone through increased deposition to leaf, stem and branch surfaces (Nemitz et al., 2020; Nowak et al., 2006; Sæbø et al., 2012; Xu et al., 2019). As relevant data become available, the influence of bioenergy plantations on UK air quality needs to be assessed in more detail with regional and national scale modelling.

## 6. Conclusions

This study presents the first assessment of BVOC emissions from a short-rotation coppice (SRC) plantation of eucalypt grown in the UK as bioenergy feedstock.

Isoprene emissions from juvenile branches of *E. gunnii* in this SRC plantation were six times greater than monoterpene emissions, although emissions of isoprene were lower than previously reported for *E. gunnii*. Large variation, by a factor of 2, in both isoprene and monoterpene emissions were noted between individual trees during our study, highlighting the need for measuring multiple trees under field conditions in addition to controlled laboratory studies. This further shows the large uncertainties that may also come from assigning a single emission factor when scaling up from branch chamber to plantation-scale emissions of BVOCs. Emissions of BVOC from the forest floor of the plantation had the potential to contribute up to a third of the forest-floor plus branch emissions per unit ground area: the isoprene emissions were negligible but forest-floor monoterpene emissions were variable, with higher emissions from stands that have a more substantial covering of litter (leaves, bark, gumnut, twigs).

Coppicing management activities such as harvesting and regrowth cycles can change the magnitude and composition of monoterpene emissions. In particular, the production of wood chip may provide the most intense source of monoterpene emissions to the atmosphere (particularly of eucalyptol) although further investigation is necessary to understand the scale and duration of this BVOC source.

Chamber studies under natural field conditions offer a useful method by which to further investigate different sources of BVOCs and subsequent changes in their emissions during the lifecycle of a plantation used to produce biomass for bioenergy purposes. This in turn may lead to a better understanding of the total BVOCs emitted from potential future bioenergy plantations and lead to a better future assessment of subsequent air quality modelling.

## CRedit authorship contribution statement

**Gemma Purser:** Conceptualization, Methodology, Investigation, Writing – original draft. **Julia Drewer:** Resources, Supervision, Writing – review & editing, Funding acquisition. **James I.L. Morison:** Supervision, Writing – review & editing, Funding acquisition. **Mathew R. Heal:** Supervision, Writing – review & editing, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2021.118617>.

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