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Article type : Primary Research Articles

Modelling the effect of the 2018 summer heatwave and drought on isoprene emissions in a UK woodland

Running head: Modelling isoprene emissions during heatwave-drought

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Statement of authorship:

All authors designed the experiment and contributed to writing the manuscript. F. Otu-Larbi and K. Ashworth carried out the modelling work and analysed the output data. C. Bolas, V. Ferracci and Z. Staniaszek collected and processed the observational data from Wytham.

Conflict of interest statement: The authors declare no conflict of interest.

Abstract

Projected future climatic extremes such as heatwaves and droughts are expected to have major impacts on emissions and concentrations of biogenic volatile organic compounds (bVOCs) with potential implications for air quality, climate, and human health. While the effects of changing temperature and photosynthetically active radiation (PAR) on the synthesis and emission of isoprene, the most abundant of these bVOCs, are well-known, the role of other environmental factors such as soil moisture stress are not fully understood and are therefore poorly represented in land surface models. As part of the Wytham Isoprene iDirac Oak Tree Measurements (WIsDOM) campaign, continuous measurements of isoprene mixing ratio were made throughout the summer of 2018 in Wytham Woods, a mixed deciduous woodland in southern England. During this time, the United Kingdom experienced a prolonged heatwave and drought, and isoprene mixing ratios were observed to increase by more than 400% at Wytham Woods under these conditions. We applied the state-of-the-art FORest Canopy-Atmosphere Transfer (FORCAsT) canopy exchange model to investigate the processes leading to these elevated concentrations. We found that although current isoprene emissions algorithms reproduced observed mixing ratios in the canopy before and after the heatwave, the model underestimated observations by ~40% during the heatwave-drought period implying that models may substantially underestimate the release of isoprene to the atmosphere in future cases of mild or moderate drought. Stress-induced emissions of isoprene based on leaf temperature and soil water content were incorporated into current emissions algorithms leading to significant improvements in model output. A combination of soil water content, leaf temperature and rewetting emission bursts provided the best model-measurement fit with a 50% improvement compared to the baseline model. Our results highlight the need for more long-term ecosystem-scale observations to enable improved model representation of atmosphere-biosphere interactions in a changing global climate.

Key phrases: Isoprene emissions, Isoprene mixing ratios, Heatwave-drought, Soil Water Content, Rewetting, Canopy exchange modelling, Climate change

Introduction

The biogenic volatile organic compound (bVOC) isoprene (C_5H_8), has important impacts on atmospheric composition and chemistry due to its relative abundance and high reactivity (e.g. Fuentes et al., 2000; Laothawornkitkul, Taylor, Paul, & Hewitt, 2008). Chemical reactions involving isoprene lead to the production of secondary pollutants, e.g. ozone (O_3) and secondary organic aerosol (SOA), which are also short-lived climate forcers.

Isoprene also indirectly affects climate by reducing the oxidative capacity of the atmosphere, hence enhancing the atmospheric lifetime of climate active gases such as methane (CH_4; see e.g. Pike & Young, 2009). Increased isoprene emissions could potentially lead to up to a 50% change in surface ozone concentrations (Pike & Young, 2009) but the sign of change depends on geographical location and atmospheric composition, in particular on the concentrations of the oxides of nitrogen (NO_X=NO+NO_2). The large quantities of isoprene emitted into the atmosphere make it a major source of SOA although aerosol yield from isoprene depends on a number of factors including levels of organic aerosol loading and NO_x concentrations (Carlton, Wiedinmyer, & Kroll, 2009). SOA has an indirect impact on climate through changing cloud optical properties (Carslaw et al., 2010; Unger, 2014). Isoprene and other bVOCs have been estimated to have a net negative radiative forcing which offsets the positive radiative forcing of anthropogenic volatile organic compounds (Unger, 2014). Isoprene could therefore play an important role in future climates through its regulation of atmospheric chemistry and formation of secondary pollutants, although its overall climate impact is minor compared to greenhouse gases such as CO_2, and remains uncertain (Arneth et al., 2010).

More than 90% of global isoprene is emitted by terrestrial vegetation (Guenther et al., 2006) at a rate primarily dependent on vegetation type (with forests contributing ~80% of global annual emissions) but also on environmental conditions such as temperature, solar radiation, atmospheric CO_2 concentration and soil moisture (Guenther et al., 2006 and references therein; Laothawornkitkul et al., 2008). Several hypotheses have been proposed to explain why some plants synthesise and emit isoprene, the best supported being that it prevents cellular damage caused by heat and oxidative stress (e.g. Sharkey, 2000; Vickers, Gershenzon, Lerdau, & Loreto, 2009). Hence emissions increase under high temperature and insolation.

During periods of water stress, however, physiological processes such as stomatal conductance, photosynthesis rate and respiration are reduced, resulting in a decrease in plant productivity (Keenan, Sabate, & Gracia, 2010). Isoprene emissions are closely coupled with photosynthesis and so reductions in plant photosynthetic capacity as a result of water stress would be expected to lead to a decrease in isoprene emissions by reducing the supply of carbon available for its synthesis. Indeed, studies have observed decreases in isoprene emission rates of between 40-60% under severe drought conditions (e.g. Brüggemann & Schnitzler, 2002; Lerdau et al; 1997; Pegoraro et al., 2004a; Brilli et al., 2007).

However an increase in emissions under drought has also been reported (Brilli et al., 2007; Loreto & Schnitzler, 2010; Rennenberg et al., 2006; Sharkey & Loreto, 1993) suggesting that water stress can decouple isoprene emission from photosynthesis, possibly because isoprene emissions are unaffected by decreasing stomatal conductance (Centritto, Brilli, Fodale, & Loreto, 2011; Pegoraro et al., 2004; Tingey, Evans, & Gumpertz, 1981). Experiments using ^{13}C labelling have shown that isoprene can be produced from older pools of stored carbon when photosynthetic gas exchange is reduced by drought (e.g. Brilli et al., 2007).

The net impact of soil water stress on isoprene emissions remains uncertain due to these competing effects. It is likely that the apparently contradictory responses observed in laboratory experiments are due to differences in the severity of the applied drought and the tolerance of different plant species to water stress, with severe drought, in which the soil water content (SWC) falls below the permanent wilting point, leading to a decline in isoprene emissions and mild to moderate drought having either no impact or leading to an increase. Niinemets (2010) developed a conceptual model in which the initial increase in leaf temperature that occurs as stomata close in response to a decline in soil moisture stimulates isoprene synthesis and emissions, leading to the observed decoupling of emissions from gas exchange rates. Evidence for this model was later provided by Potosnak et al. (2014) who observed this behaviour at the onset of a prolonged drought in the Ozarks, an oak-dominated mid-latitude forest.

An additional complexity is the response of isoprene emission rates to rewetting. Sharkey & Loreto (1993) and Peñuelas, Filella, Seco, & Llusia (2009) observed a substantial increase in isoprene emissions from seedlings after rewetting but this effect has not been observed in all experiments. Pegoraro et al (2004) reported a lag of about a week between declining soil moisture and changes in isoprene emission rates most likely the result of plants having to adjust to the restoration of the photosynthetic carbon source for isoprene synthesis and emission.

The effect of temperature and solar radiation on isoprene emissions are relatively well understood and emissions estimates from land surface models have been shown to capture observed diurnal variations in fluxes and concentrations reasonably effectively across a range of ecosystems (e.g. Guenther et al., 2012; Zimmer et al., 2000). Unlike temperature and solar radiation, there is no direct impact of soil water deficit and soil rewetting on isoprene emissions and these are therefore not well represented in coupled land surface-atmosphere models although numerous studies have shown their importance to emission rates and

atmospheric composition (e.g. Emmerson, Palmer, Thatcher, Haverd, & Guenther, 2019; Guenther et al., 2006; Jiang et al., 2018; Sindelarova et al., 2014).

Rising levels of CO_2 and future changes in climate, such as increasing temperature and altered patterns of precipitation, can thus be expected to change isoprene emissions from the current estimated 450–600 Tg C y^{-1} (Arneth, Monson, Schurgers, Niinemets, & Palmer, 2008; Guenther et al. 2006; 2012). Heald et al. (2009) projected increases of as much as ~190 Tg C y^{-1} in global isoprene emissions due to a temperature increase of 2.3°C by 2100, but also showed that a decrease in isoprene emissions due to increasing CO_2 concentrations could off-set this temperature effect almost entirely.

Most studies to understand the effect of combined heatwaves and drought on isoprene emissions have been laboratory-based experiments which permit close control of environmental factors such as temperature, photosynthetic active radiation (PAR) and soil moisture but make use of saplings (e.g. Brilli et al., 2007), seedlings or young plants (e.g. Pegoraro et al., 2005) and are thus not representative of real-world forest environments. There are limited observations of isoprene emissions during drought in natural ecosystems (e.g. Emmerson et al., 2019; Potosnak et al., 2014; Seco et al., 2015) which are necessary to enable the development of robust parameterisations in emissions models.

In the summer of 2018, the United Kingdom (UK), in common with most of northern and central Europe, experienced a prolonged drought and heatwave event. The UK Met Office officially declared heatwave conditions starting on June 22nd which persisted to August 8th in southern England. Records from the UK Met Office shows that the 2018 summer mean temperature over the UK as a whole was ~2.0°C above the 1961-1990 average, making the summer of 2018 the joint warmest on record ("Regional Values", 2019). The mean temperature over southern England was 17.7°C, ~2.4°C warmer than the 1961-1990 average.

Under future climate scenarios, droughts and heatwaves that are currently thought of as anomalous (such as the one that occurred in 2018) are expected to increase in frequency (IPCC, 2013; Thornton, Ericksen, Herrero, & Challinor, 2014) with the UK Met Office predicting that the UK may experience such conditions every other year by 2050 (e.g "UK Extreme Events – Heatwaves", 2019). Given the role of isoprene and other BVOCs in the formation of short-lived climate forcers and secondary organic aerosols (SOA), the potential impacts of these changes in climate on isoprene emission rates and therefore on atmospheric composition, air quality and climate (Sanderson, Jones, Collins, Johnson, & Derwent, 2003; Pacifico, Harrison, Jones, & Sitch, 2009) must be better understood.

The combined heatwave and drought (heatwave-drought) and rewetting episodes that occurred during the Wytham Isoprene iDirac Oak Tree Measurements (WIsDOM) campaign in Wytham Woods in 2018, offered a unique opportunity to quantify the potential effect of future climate change on isoprene emissions in a natural environment. This study uses a state-of-the-art canopy model to explore the observed effects of heat and drought stress, and soil rewetting on isoprene emissions and mixing ratios in a temperate mixed deciduous woodland.

Methods

Site Description

The WIsDOM campaign took place at Wytham Woods (51°46'23.3"N 1°20'19.0"W, 160 m.a.s.l), located ~5km NW of the centre of Oxford in SW England, between May-October 2018. The forest has been owned and maintained by the University of Oxford as a site of special scientific interest since 1942 and has been part of the UK Environmental Change Network (ECN) since 1992. The forested area is made up of patches of ancient semi-natural woodland, secondary woodland, and modern plantations and is dominated by European Ash (*Fraxinus excelsior* - 26%), Sycamore (*Acer pseudoplatanus* – 18%), European Beech (*Fagus sylvatica* – 11%) and English Oak (*Quercus robur* – 7%; Kirby et al., 2014). The remainder of the forest comprises other broadleaf trees and shrubs. *Q. robur* (~95%) and *A. pseudoplatanus (~5%)* are the main contributors to the isoprene budget at Wytham Woods (Bolas, 2020). The forest has largely been undisturbed over the last 40-100 years (Morecroft, Stokes, Taylor, & Morison, 2008; Thomas et al., 2011) and as a consequence the age range of mature trees in Wytham Woods is large - from 40 to >150 years. The climate in Oxfordshire can be classified as warm temperate with rainfall occurring all year round. The 1981-2010 average summer temperature ranges between 18-20 ^{o}C and average rainfall is ~600-700 mm per year.

Measurement Campaign

Continuous measurements of isoprene mixing ratios were made approximately every 20 minutes at four heights in the forest canopy between June-October 2018 during the WIsDOM campaign. Inlets to two dual-channel iDiracs (see Bolas et al., 2019 for a full description of the instrument design and deployment) were located at 15.55m (top of canopy), 13.17 m (mid-canopy), 7.26 m (trunk height) and 0.53 m (near surface) alongside a mature *Q. robur* of ~16 m height. Measurements at the trunk and near surface levels did not start until July. The iDirac has a detection limit of ~38 ppt with an instrument precision of ±11% (Bolas et al., 2019).

Hourly measurements of temperature, PAR, relative humidity, soil moisture at a depth of 20cm, wind speed and direction, and atmospheric pressure were obtained from the Upper Seeds automatic weather station (AWS) located in a small clearing ~480 m from the site of the isoprene observations. We used 30-minute averages of the measurements made between 1st June to 30th September in our model analysis. This covers the full extent of peak growth with roughly equal periods before, during and after the heatwave-drought. For full details of the WIsDOM campaign, readers are referred to Ferracci et al. (2020).

Model Description

We applied the FORest Canopy-Atmosphere Transfer (FORCAsT) 1-D model of biosphere–atmosphere exchange to simulate the processes of biogenic emissions, chemical production and loss, vertical mixing, advection and deposition within and above the canopy at Wytham Woods. A detailed description of the FORCAsT model can be found in Ashworth et al. (2015), so here we focus only on those elements of the model configuration relevant to this study. We subdivided the 40 model levels into 10 between the ground surface and trunk height, and a further 10 within the crown space to ensure that observation heights aligned as closely as possible with the mid-point of a model level.

Vertical transport in FORCAsT is based on a modified k-theory of vertical turbulent diffusion (Blackadar, 1962; Raupach, 1989). In-canopy and above canopy mixing are simulated following Baldocchi (1988) and Gao et al. (1993) respectively. The simulated exchange of heat and trace gases are further improved by constraining the friction velocity (u^*) and the standard deviation of the vertical wind component (σ_w) following Bryan et al. (2012). As u^* and σ_w were not measured at Wytham we estimated each from the horizontal wind speed (u) following Makar et al., (2017), Eqn. 1, and Shuttleworth and Wallace (1985), Eqn. 2, respectively:

$$u^* = \frac{u \times K}{ln\left(\frac{h_c}{z_o}\right)} \quad (1)$$

$$\sigma_w\left(\frac{z}{h_c}\right) = \begin{cases} 1.25u^* & for\ \frac{z}{h_c} > 1.0 \\ u^*\left[0.75 + 0.5 \times cos\left(\pi\left(1 - \frac{z}{h_c}\right)\right)\right] & for\ \frac{z}{h_c} < 1.0 \end{cases} \quad (2)$$

where h_c is height of top of canopy (18m), Z_o is roughness length (assumed $0.1*h_c$), u is mean horizontal windspeed at height z and K is von Karman's constant (0.4).

In FORCAsT, isoprene is produced through emissions from foliage in the crown space and lost through oxidation reactions initiated by the OH and NO_3 radicals and O_3, and

through deposition to the soil (following Stroud et al., 2005). The concentration of isoprene at each level in the canopy depends on these production and loss processes as well as fluxes into and out of that layer. Previous studies (e.g. Bryan et al., 2012; Guenther et al., 2006 and references therein) have shown that for moderate height canopies such as that at Wytham Woods, canopy residence times are sufficiently short that little isoprene is lost through oxidation within the canopy. Hence, concentrations are primarily dependent on emission rates when considered over periods greater than turbulent timescales (≤ 1s to minutes). FORCAsT employs a half-hourly timestep. Our simulations therefore focused on the emissions of isoprene, which are calculated in FORCAsT by summing the contributions from 10 leaf angle classes in each crown-space model level, following the algorithms of Guenther et al. (1995):

$$ER = LAI \,.\, \varepsilon \,.\, \gamma_{iso} \quad (3)$$

where ER is the total emission rate (mg m^{-2} h^{-1}), LAI (m^2 m^{-2}) is the leaf area index and ε is a site- and species-specific emission factor (1.20 mg m^{-2} h^{-1} for *Q. robur;* Visakorpi et al., 2018) which represents the emission rate of isoprene into the canopy at standard conditions of 30 ˚C and 1000 μmol m^{-2} s^{-1}. LAI was taken as the maximum reported for the site (3.6 m^2 m^{-2}; Herbst et al., 2008) throughout this study which coincides with the period of peak growth. γ_{iso} is a dimensionless emission activity factor that accounts for changes in emission rates due to deviations from these standard conditions, with:

$$\gamma_{iso} = C_L C_T \quad (4)$$

where C_L and C_T are the light and temperature dependence of isoprene emission rates respectively and are given by:

$$C_L = \frac{\alpha C_{LI} PAR}{\sqrt{1 + \alpha^2 PAR^2}} \quad (5)$$

where α (= 0.0027) and C_{LI} (= 1.066) are empirical coefficients from Guenther et al. (1995).

$$C_T = \frac{exp^{\frac{C_{TI}(T - T_s)}{RT_sT}}}{1 + exp^{\frac{C_{T2}(T - T_m)}{RT_sT}}} \quad (6)$$

where T is leaf temperature (K), T_s is the temperature at standard conditions (i.e. 303 K), R is the ideal gas constant (= 8.314 J K^{-1} mol^{-1}), C_{TI} (= 95,000 J mol^{-1}), C_{T2} (= 230,000 J mol^{-1}) and T_M (= 314 K) are empirical coefficients determined by Guenther et al. (1995). Leaf temperature is calculated from measured air temperature in FORCAsT using a canopy energy balance.

Equations (3) to (6) describe the default model set-up (hereafter referred to as BASE). We conducted a series of experiments introducing stress-induced emissions, achieved by

further modifying the activity factor to account for extreme temperature and drought conditions. In these experiments, described below, γ_{iso} was calculated as:

$$\gamma_{iso} = C_L C_T \gamma_X \quad (7)$$

where γ_X is an additional environmental activity factor and x denotes the environmental condition affecting isoprene emission rates in each experiment- explained in detail below.

Model experiments

BASE: FORCAsT was configured using site-specific canopy parameters and isoprene emission factors and driven with meteorology measured at Wytham Woods during the WIsDOM campaign. Isoprene emission rates for each model level were calculated within the model using Eqns. 3-6. Comparison of modelled isoprene mixing ratios against observations from the iDirac instruments at four heights within the canopy showed good agreement in both diurnal profile and magnitude before and after the heatwave-drought. However, during the heatwave-drought period the model substantially underestimated isoprene mixing ratios. The results from this simulation are described in more detail later.

We therefore performed three subsequent experiments, introducing γ_X, to explore the possible environmental factors driving the sharp increase in observed isoprene concentrations that the model was unable to account for using the standard emissions algorithms. In all three experiments, model configuration and driving meteorology remained unchanged from BASE; the only difference was the change to the isoprene activity factor described below.

BASE+LFT: During periods of drought stress there is an increase in leaf temperature due to a reduction in transpiration rate as the plants attempt to conserve water (Zandalinas, Mittler, Balfagón, Arbona, & Gómez-Cadenas, 2018). Niinemets (2010) and Potosnak et al. (2014) hypothesised that this increase in leaf temperature is the cause of observed increases in isoprene emissions during mild-to-moderate drought stress. Here we test whether increases in leaf temperature explain the observed changes in isoprene mixing ratios observed during WisDOM by modifying γ_x against leaf temperature (hereafter referred to as LFT) with γ_{LFT} defined as:

$$\gamma_{LFT} = \begin{cases} 1 & T < T_{95} \\ \frac{T - Ts}{T_{95} - Ts} & T \geq T_{95} \end{cases} \quad (8)$$

where T (K) is the leaf temperature, Ts (297K) represents standard conditions for leaf temperature (Guenther et al., 2006) and T_{95} is the 95th percentile of the seasonal leaf temperature which represents the threshold temperature above which we assume heat-induced emissions occur.

BASE+SWT: Under heatwave-drought conditions it would be expected that reduced SWC and unusually high temperatures affect emissions rates simultaneously. This experiment therefore combines the effect of soil water deficit and leaf temperature on isoprene emissions into a single environmental activity factor, γ_{SWT} calculated as follows:

$$\gamma_{SWT} = \begin{cases} 1 & for\ \theta > \theta_c \\ \left[\frac{(\theta - \theta_w)}{\theta_c - \theta_w}\right]^q \times [\gamma_{LFT}] & for\ \theta_w < \theta \leq \theta_c \end{cases} \quad (9)$$

where θ ($m^3\ m^{-3}$) is the volumetric soil moisture, θ_w is the wilting point (0.15 $m^3\ m^{-3}$ following Jiang et al., 2018) , θ_c (0.22 $m^3\ m^{-3}$) is a critical soil moisture content above which we observe no effect of water stress on isoprene emissions and q is a site-specific empirical factor describing the non-linearity of the effects of soil water stress on tree physiological processes. A range q values have been tested for different plant functional types (eg. see Egea et al., 2011). Here a value of 0.40 provided the best fit to observations. γ_{LFT} is defined in Eqn 8.

BASE+RWT: This experiment investigates whether the burst of isoprene emissions observed following re-wetting after drought in laboratory studies is seen at the ecosystem scale. The environmental activity factor, γ_{RWT}, is a modification of Eqn 9 such that during periods defined as rewetting (days within the heatwave-drought period for which soil water content exceeds that of the previous 10 days), γ_{RWT} is given by:

$$\gamma_{RWT} = \gamma_{SWT} \times 1.30 \quad (10)$$

i.e. a 30% increase in isoprene emissions following soil rewetting.

Results

Here we present a comparison of continuous measurements of isoprene mixing ratios at all four iDirac inlet levels against the output from the nearest model level. For the top and middle of the canopy, we use half-hourly averages of both modelled and observed data covering the period June 1st to September 30th for this comparison; measurements are only available for the trunk and near surface levels between July 6th and September 30th. Statistical values reported in this section were restricted to isoprene mixing ratios between 0600 LT to 1900 LT coinciding with daylight hours when isoprene emissions occur, in keeping with previous studies (e.g. Potosnak et al., 2014; Seco et al., 2015). The data is presented in full as time series, and then summarised to show goodness of fit using scatter plots and a Taylor diagram (Taylor, 2001). The Taylor diagram provides a way to demonstrate the simultaneous variation of three model performance statistics: correlation coefficient (r^2), normalised standard deviation (SD), and centred root-mean-square error (RMSE). Output from an ideal

model would show the same r^2, SD and RMSE as the observations. Therefore, the closer a model's summary statistics are to that of the observations on the Taylor diagram, the better its performance. Results are first presented for the BASE simulation (i.e. the default model set-up) and then for each experiment. Model performance statistics for the top of the canopy is presented here while those for the other levels can be found in the Supplementary Information (SI). The grey shaded region on all figures indicates the heatwave-drought period as defined by the UK Met Office for southern England and the dashed white line the start of re-wetting.

Meteorological conditions

Figures 1a-c show PAR, temperature, volumetric SWC, and precipitation measured at the ECN station in Wytham Woods for the study period. Following a wet April in which rainfall was ~120% of the 1981-2010 mean ("Monthly, seasonal and annual summaries 2018"; 2019), SWC declined steadily from near field capacity (at 0.46 m^3 m^{-3}) at the start of June to 0.16 m^3 m^{-3} (just above the wilting point of 0.15 m^3 m^{-3} for this site) at the peak of the heatwave-drought in July. A few low-intensity rainfall events (total precipitation <0.2 mm) with negligible effect on SWC were recorded prior to the heatwave-drought. Rainfall during the heatwave-drought, on July 20th (3 mm) and July 27th (11.1 mm), led to increases in soil moisture and the "rewetting period" extended from 20th July to 8th August as a result. The Standardized Precipitation Index (SPI; McKee, Doesken, & Kleist, 1993), used to characterize the severity of meteorological droughts, indicates Wytham Woods experienced a moderate drought in July (https://eip.ceh.ac.uk/apps/droughts/), consistent with in-situ SWC measurements. After 8th August (the official end of the heatwave period), rainfall frequency and intensity increased with a corresponding increase in soil moisture.

The average temperature recorded at Wytham Woods was 17.5^{o}C for the entire measurement period (1st June-30th Sept), but 19.6^{o}C during the heatwave (22nd June-8th Aug). The diurnal temperature ranged from an average of 11.8^{o}C at night to 21.3^{o}C during the day for the whole season but increased sharply during the heatwave, with mean night-time and daytime temperatures of 13.5^{o}C and 25.2^{o}C respectively. For the same June to September period, climatological (1993-2015) temperature averaged 15.8^{o}C with a diurnal range of 10.2^{o}C-18.9^{o}C. Compared to the long-term average, the 2018 summer at Wytham Woods was 1.7^{o}C warmer mainly due to a 3.0^{o}C increase in temperature during the heatwave-drought. The maximum temperature recorded at Wytham Woods during the 2018 heatwave-drought (30.6^{o}C) was however lower than the climatological maximum (32.2^{o}C). Average PAR

increased from 781 W m^{-2} before the heatwave-drought to 1277 W m^{-2} during it, reflecting longer and more intense periods of sunshine associated with the underlying high pressure conditions of the heatwave period.

[FIGURE 1 GOES APPROXIMATELY HERE]

BASE model simulation

As isoprene emission rates are predominantly determined by light and temperature, BASE reliably reproduces the diurnal cycle of isoprene concentrations at each of the inlet levels (Figure 2 (a-d)). Average modelled mixing ratios outside of the heatwave-drought are in good agreement with those observed (0.44 ppb *vs.* 0.37 ppb at the top of the canopy, 0.24 ppb *vs.* 0.18 ppb at mid-canopy level, 0.17 ppb *vs.* 0.15 ppb at trunk level and 0.09 ppb *vs.* 0.11 ppb near the surface), with no apparent systematic bias, suggesting that the emission factor, ε, is appropriate for the site. However, FORCAsT underestimates concentrations at all levels during the heatwave-drought by an average of 40% leading to a total underestimation of ~25% over the entire season. During the heatwave-drought, the average isoprene mixing ratio measured at the top of the canopy was 1.97ppb (i.e. > 4 times that outside the heatwave period) but only 1.12 ppb in BASE. Similar results were obtained at the other levels for model vs observations (1.01 ppb vs 0.60 ppb at mid-canopy level, 0.84 ppb vs 0.49 ppb at trunk level and 0.58 ppb vs 0.15 ppb near the surface). Following the two rewetting episodes in July, average observed isoprene mixing ratios increased to 2.05 ppb, while modelled isoprene was nearly a factor of 2 lower at 1.12 ppb for that period. There was a 48%, 44% and 70% underestimation in the model at the mid-canopy, trunk and near surface levels respectively, following the rewetting events. These systematic discrepancies show that the emission burst observed following rewetting is unaccounted for in current emissions algorithms.

[FIGURE 2 GOES APPROXIMATELY HERE]

The time series of the difference between modelled and observed isoprene mixing ratios at the top of the canopy for BASE (Figure 3a) highlights the relatively poor skill of the standard emissions algorithms throughout the 7-week heatwave-drought (shaded region). The average diurnal profiles of isoprene mixing ratios before, during and after the heatwave-drought presented in Figure 3(b) further confirm the good performance of BASE before and after the heatwave and the substantial underestimation during the heatwave. Figures 3(c-d) explore the relationship between these differences and the possible environmental drivers: SWC and temperature. Figure 3(c) points to a soil moisture threshold with isoprene mixing ratios (and therefore emissions) independent of SWC above ~0.22 m^3 m^{-3} but increasing

rapidly as SWC drops further. This is in keeping with the concept of a critical SWC used in modelling both photosynthesis and isoprene emissions in previous work (e.g. Emmerson et al., 2019; Guenther et al., 2006; Keenan et al., 2010) although we see an increase rather than decrease as SWC declines below this threshold, similar to that reported under moderate drought stress by Potosnak et al. (2014). Figure 3(d) suggests a similar but less pronounced response to high temperatures (>20^{o}C). We found no significant relationship between PAR and the difference between modelled and measured isoprene mixing ratios and conclude that high temperature and low SWC are the key drivers of the apparent stress-induced enhancement in isoprene emissions.

[FIGURE 3 GOES APPROXIMATELY HERE]

Results of Modelling Experiments

Figures 2 and 3 show clearly that BASE underestimated isoprene concentrations during the heatwave-drought and at other times when isoprene levels in the canopy were high. In this section we present the results of our model experiments exploring the addition of stress-induced emissions and compare them to the performance of BASE over the entire season. As for BASE, model performance statistics are similar for all levels for each experiment. We therefore present only statistics for top of the canopy here; statistics for the other levels are given in Table S1 in the SI.

BASE+LFT: Modifying the isoprene activity factor when leaf temperature exceeds the 95th percentile (γ_{LFT}) reduces the net underestimation during the heatwave-drought but, as shown in Figure 4(a) and E, FORCAsT still substantially underestimates observed mixing ratios throughout this period. The average modelled isoprene mixing ratio is 1.26 ppb during the heatwave-drought (~35% lower than observed) and 0.76 ppb (25% too low) over the entire season. This tendency towards underestimation can be seen clearly in Figure 5(b) and (f) (most of the points lie below the 1:1 line) as can the improvement over the performance of BASE (shown in Figure 5(a) and €). Figure 6 further confirms that the use of a temperature-induced enhancement (γ_{LFT}) in isoprene emissions improves the overall fit to measurements. The RMSE of modelled mixing ratio is reduced (from 0.60 in BASE to 0.57 in BASE+LFT), reflecting a slightly improved accuracy during the heatwave-drought. The normalised standard deviation

(0.61 in BASE *vs* 0.66 in BASE+LFT) indicates that the model is also better able to reproduce the variability seen in the observed concentrations although still tending to

underestimate. It should be noted that the correlation between modelled and observed isoprene is very good (>0.9) for all simulations as the strong dependency of isoprene emissions on temperature and PAR is well-captured by the standard emissions algorithms (Eqns. 3-6) included in BASE. Figure 6 shows that although BASE+LFT improves model reproduction of isoprene mixing ratios, it is still unable to account for the high concentrations during the heatwave-drought and suggests that other factors are responsible for the increase in isoprene concentration during this period.

BASE+SWT: This experiment accounted for the simultaneous effect of heat and water stress. As shown in Figure 4(b) and (e), there is a clear improvement in the model's estimation of isoprene mixing ratios during the heatwave-drought period compared to both BASE and BASE+LFT and this is further confirmed by Figure 5(c) and (g), in which most points lie along or close to the 1:1 line. Fig 5(c) and (g) also show that BASE+SWT consistently underestimates when observed mixing ratios are high (>5ppb and >3ppb at the top and middle of the canopy respectively). The mean modelled isoprene mixing ratio at the top of the canopy is 1.87ppb, just ~5% lower than the observed value of 1.97ppb. There are no periods of consistent model bias, rather FORCAsT underestimates isoprene concentrations periodically through the heatwave period, resulting in the standard deviation <1.0 in Figure 6. Referring to Figure 1(b), it can be seen that these periods of underestimation correspond to rewetting periods following rainfall events. The average modelled mixing ratio during the rewetting period was 1.73ppb compared to the observed value of 2.05ppb. This constitutes ~15% underestimation compared to observed values but ~ 35% increase (improvement) over the 1.12ppb and 1.11ppb estimated in BASE and BASE+LFT respectively.

BASE+RWT: The final experiment included an additional 30% enhancement of the environmental activity factor following soil rewetting (γ_{RWT}) and, as shown in Figure 4(c) and F, further improves the model performance during the heatwave-drought. Mean isoprene mixing ratios during this period increase from 1.87 ppb in BASE+SWT to 1.98 ppb in BASE+RWT, equal to the average of observed values. Figure 5(d) and (h) indicates no systematic model bias and the use of a rewetting-enhanced soil moisture activity factor enables the model to capture the higher observed concentrations following rewetting episodes which all previous simulations failed to reproduce. The average isoprene mixing ratio during these re-wetting periods is 1.98 ppb compared to 2.05 ppb in the observations, i.e. an underestimation of only ~3%. The overall model performance statistics are depicted in Figure 6. While there is no significant difference between the overall correlation or RMSE values in

BASE+SWT and BASE+RWT, there is a clear improvement in the model's ability to match the variability shown by the observations with a normalised standard deviation of 0.97 in BASE+RWT compared to 0.89 in BASE+SWT. Compared to BASE, there is ~80% and ~50% improvement in SD (0.97 in BASE+RWT *vs* 0.61 in BASE) and RMSE (0.41 in BASE+RWT *vs* 0.60 in BASE) respectively.

[FIGURE 4 GOES APPROXIMATELY HERE]

[FIGURE 5 GOES APPROXIMATELY HERE]

[FIGURE 6 GOES APPROXIMATELY HERE]

[FIGURE 7 GOES APPROXIMATELY HERE]

Time series of Results

Figure 7 shows isoprene mixing ratios for the period July 22nd-27th 2018, selected as it falls within the heatwave-drought and includes the first of the rainfall events. These plots provide further evidence that all model configurations reproduce the observed diurnal patterns of isoprene concentrations at Wytham Woods at the top 3 levels, as expected given the strong dependency of isoprene emissions on temperature and PAR but confirm the earlier results from Figure 2 and Figure 4 that BASE and BASE+LFT models systematically and substantially underestimate isoprene mixing ratios during this period. All three experiments improve model estimations of isoprene concentrations over BASE especially during the middle of the day when observed concentrations peak. Figure 7(a-d) show clearly the effect of adding a rewetting-induced enhancement in isoprene emissions (Eqn 10). For 22nd July, when the rewetting effect is not active, the BASE+SWT and BASE+RWT lines overlap but they diverge between 23rd-27th July following rewetting. Figure 7(h) shows that all the simulations underestimate observed concentrations near the surface in the early part of the morning (before mid-day), which we ascribe to more light reaching the lower levels in the canopy than is currently accounted for in the model. Figure 7 confirms that BASE+RWT provides the overall best fit when compared to the observations at all levels.

Discussion

Wytham Woods experienced a heatwave and moderate drought (heatwave-drought) during a 7-week period in the summer of 2018 during which time the soil moisture at the site decreased from 0.46 m^3 m^{-3} (just below field capacity) to 0.16 m^3 m^{-3} (just above wilting point). Continuous measurements of isoprene mixing ratios were made at the site during the Wytham Isoprene iDirac Oak Tree Measurements (WIsDOM) campaign which was

conducted in May-October 2018. The aims of our study were to determine how well a 1-D canopy exchange model (FORCAsT) could capture the observed changes in isoprene concentrations during the heatwave-drought and to use the model to explore the environmental factors driving these changes. Modelled isoprene mixing ratios did increase substantially during the heatwave-drought in response to large increases in foliage emissions, driven by high temperature and PAR, but not to the extent observed. We conclude that the algorithms currently used in emissions models are unable to account for the actual increase in emission rate under such conditions. We hypothesise that the increase in emission rates during the heatwave-drought was most likely a mechanism to cope with abiotic stress as previously suggested by Holopainen (2004); Loreto & Velikova (2001); Peñuelas & Llusià (2002); Sharkey (1996), and in particular due to low soil moisture.

Many previous studies of the effect of soil water deficit on isoprene emissions have shown a decrease in emission rates with increasing severity of drought (e.g. Pegoraro et al., 2005; Seco et al., 2015) leading to the development of algorithms that decrease the isoprene activity factor (γ_{iso}) in response to decreasing SWC (Guenther et al., 2006). This approach has been used in emission models (e.g. Emmerson et al 2019; Guenther et al., 2006; Jiang et al., 2018) with good results for severely drought-impacted sites. However, other studies have reported that isoprene emissions are enhanced during periods of mild or moderate drought and Potosnak et al. (2014) demonstrated that the ecosystem-scale response is dependent on drought severity. Some studies have also reported an increase in isoprene after rewetting (e.g. Brilli et al. 2007; Peñuelas et al., 2009; Sharkey & Loreto 1993). The isoprene measurements made during the WIsDOM campaign (Ferracci et al., 2020 in prep) together with the findings from our model simulations support the observation that isoprene emissions can increase under moderate drought conditions and after rewetting resulting in strong enhancements in canopy concentrations. Our model results (Figure S4) also provide evidence in support of the previous observations that isoprene emissions and photosynthesis (often quantified as gross primary production, GPP, at an ecosystem-scale; e.g Brilli et al., 2007; Pegoraro et al., 2004) are uncoupled during periods of drought stress.

Emissions models have been shown to perform well in both the unstressed and severe drought phases (e.g. Guenther et al., 2012; Emmerson et al., 2019; Jiang et al., 2019) but underestimate observed concentrations during the mild-to-moderate drought phase (Potosnak et al., 2014; Seco et al., 2015). Conceptual models (Niinemets, 2010; Potosnak et al., 2014) have been developed to explain the impacts of mild droughts on isoprene emissions but these have not been tested until now. We hypothesise that drought severity is the main determinant

of changes in isoprene emission rates at the ecosystem scale as well as in the laboratory and that the previous field campaigns used to develop and verify the Guenther soil moisture activity factor (see Pegoraro et al., 2004, Seco et al., 2015) encountered soil water deficits that were more severe than those at Wytham Woods in 2018. Indeed, the Ozark site (described in Gu et al., 2006) which has been used in parameterising the Guenther soil moisture activity factor experienced two consecutive years of drought in 2011 (mild) and 2012 (severe). 2012 experienced the lowest rainfall in that decade and isoprene emissions decreased significantly (Seco et al., 2015). However, similar to Wytham Woods, isoprene fluxes were observed to increase at the Ozarks during the mild phase of the drought in 2011 (Potosnak et al., 2014).

Potosnak et al. (2014) hypothesized that an increase in leaf temperature due to reductions in transpiration during drought stress is responsible for the increase in isoprene emissions as emission rates depend on leaf rather than air temperature. We found that using a leaf temperature-based isoprene emission activity factor did improve model reproduction of observed isoprene mixing ratios but a substantial underestimation remained. We therefore incorporated a soil moisture activity factor, based on the parameterisation of Keenan et al. (2010) for changes in photosynthesis, that increases isoprene emissions under moderate drought conditions, i.e. when SWC is close to but slightly above the critical value for the soil at which the standard (severe drought) soil moisture activity factor can be applied. We found that using this new activity factor to account for soil moisture stress when estimating isoprene emission rates improved model reproduction of observed isoprene mixing ratios during the moderate drought without compromising model performance during the rest of the season. However, this was not in itself sufficient to capture the enhancement in isoprene concentrations observed after rainfall events, when soil moisture increased substantially. We found it necessary to further modify our activity factor to account for these episodes, on the hypothesis that these rewetting events were of sufficient intensity to provide near-surface roots access to water, leading to increased foliar activity and isoprene synthesis. Using this soil water and rewetting-based modifying factor that increased isoprene emission rates a further 30% improved the model fit to observations by 50% based on the root mean squared error. In comparison, Brilli et al., 2007 observed a 20-60% increase in isoprene emissions from saplings following soil rewetting. These experimental modelling results provide evidence that previous laboratory-based observations of the effect of mild-to-moderate drought stress and soil rewetting on bVOC emissions (e.g. Brilli et al., 2007; Centritto, Brilli,

562 Fodale, & Loreto, 2011; Loreto & Schnitzler, 2010; Pegoraro et al, 2004a) are also
563 observable at the ecosystem-scale.

564 Many field sites do not routinely measure either soil moisture or leaf temperature;
565 our parameterisations are therefore only appropriate for model frameworks with a detailed
566 land surface module. We performed two further experiments using air temperature and
567 vapour pressure deficit (VPD), both readily available data products, as a proxy for the effects
568 of leaf temperature and soil water content. VPD, which can be readily calculated from
569 standard meteorological measurements, increases with increasing temperatures and declining
570 soil moisture. Although VPD is not a physiologically robust metric for assessing soil and
571 foliar water availability, we found that an isoprene emission activity factor based on VPD
572 improved modelled isoprene mixing ratios compared to the base case. Our air temperature
573 and VPD parameterisation and results are shown in Eqn S1 and S4, Figures S5-8 and Table
574 S1. Although not as successful as the rewetting simulations (for example there is a ~10% and
575 ~15% improvement on BASE RMSE in BASE+T and BASE+VPD respectively compared to
576 ~50% in BASE+RWT), our results show that VPD in particular could be used to improve
577 simulated emissions at sites where soil moisture or leaf temperature measurements are not
578 available and in models without a detailed land surface parameterisation.

579 The Guenther et al., 2006; 2012 algorithms reproduce observed isoprene concentrations
580 or fluxes well in unstressed environments and in cases of severe drought. The methods
581 developed in this paper are intended to be used in cases of mild-to-moderate drought which
582 until now has remained a modelling challenge.

583 Prior to the summer of 2018, Wytham Woods experienced only infrequent moderate to
584 severe droughts (in 1976, 1995-1997 and 2003; Mihók et al., 2009). It is projected that the
585 incidence of droughts in southern England will increase in frequency, duration and severity
586 under future climate change (e.g. Milly, Dunne, & Vecchia, 2005; Schär et al., 2004; Vidale,
587 Lüthi, Wegmann, & Schär, 2007). The summer of 2018 could therefore be viewed as a
588 'natural experiment' that allowed us to investigate possible future biogenic emissions from
589 Wytham Woods and similar temperate mixed woodlands. We found that the emissions
590 algorithms currently included in global emissions and chemistry-climate models
591 underestimated total isoprene emissions during the heatwave-drought by ~40% and by ~20%
592 over the entire June to September period. While the findings of this single experiment should
593 not be extrapolated to a global scale, if these are representative of the wider picture, the
594 magnitude of the modelled change in emissions would have a major impact on local- to

regional-scale emissions and hence atmospheric chemistry and composition in many world regions.

The main advantage of our natural experiment is that we were able to observe the impacts on mature trees in a real-world (uncontrolled) environment. Such conditions are impossible to reproduce in laboratory-based experiments that investigate potential impacts of global climate change on tree physiology and bVOC emissions. Saplings and young plants, the preferred options in laboratory experiments, do provide useful information about the general behaviour of trees under various environmental stressors, but cannot replicate the combinatorial stresses and symbioses experienced by mature trees and full ecosystems. The results from WIsDOM and previous measurement campaigns carried out on mature trees (e.g. Genard-Zielinski et al., 2018; Llusia et al., 2016; Potosnak et al., 2014) show that emissions characteristics under heatwave-droughts in the natural environment differ from those observed in many laboratory experiments. However, it can be expected for the response to be dependent on tree species, with some adapted to withstand periods of water limitation, and on soil properties. It is clear therefore that more ecosystem-scale observations are required under mild, moderate and severe drought conditions if we are to understand how future changes in precipitation and ground-water levels are to affect isoprene emissions.

Acknowledgements

F. Otu-Larbi is grateful to the Faculty of Science and Technology (FST) and Lancaster Environment Centre (LEC) at Lancaster University for funding his PhD Studentship. K. Ashworth is a Royal Society Dorothy Hodgkin Fellow and thanks the Royal Society of London for their support and funding (DH150070). C. Bolas acknowledges and thanks the Natural Environmental Research Council (NERC) for the Doctoral Training Partnership studentship. The research was carried out and supported with funding from the BALI project (NE/ K016377/1). In addition, we also thank the School of Geography and the Environment, University of Oxford for help in instrument deployment and for supporting the walkway and other research facilities at Wytham Woods research forest. In particular, we thank Nigel Fisher for his day-to-day management of Wytham Woods research logistics and access. We gratefully acknowledge R. Freshwater at the University of Cambridge for his technical expertise and help. We are also grateful to the Environmental Change Network (ECN) for sharing their data from the Upper Seeds automated weather station.

Code and data availability: FORCAsT 1.0 and the data used in this study are available by request to the corresponding authors.

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FIGURE CAPTIONS

Figure 1: Meteorological data taken from the Wytham Woods Automatic ECN station: (a) Photosynthetically Active Radiation (PAR) (b) 2-m air temperature, (c) soil water content (SWC; black) and total daily rainfall (blue). The grey shaded area indicates the start and end of the heatwave-drought while the white dashed line indicates the start of the rewetting period (20th July – 8th August).

Figure 2: Observed (black) and modelled (BASE; orange) isoprene mixing ratios at the WIsDOM site at (a) the top of the canopy (~15.6 m), (b) mid canopy (~13.5 m), (c) trunk height (~7.1 m) and (d) near the surface (~0.8 m). Observations of isoprene mixing ratios at the trunk and near surface levels started on 6th July.

Figure 3: (a) Difference (in ppb) between model (BASE) and observed (OBS) isoprene mixing ratio at the top of the canopy for the BASE simulation for the entire season (1st June to 30th September 2018). Note that negative values indicate periods when the model underestimates concentrations while positive values indicate an overestimation. (b) Diurnal profiles of isoprene mixing ratios at the top of the canopy before heatwave-drought (black), during the heatwave drought (orange) and after the heatwave-drought (red). Model values are solid lines while observed values are dashed lines. Scatter plots of difference in mixing ratio

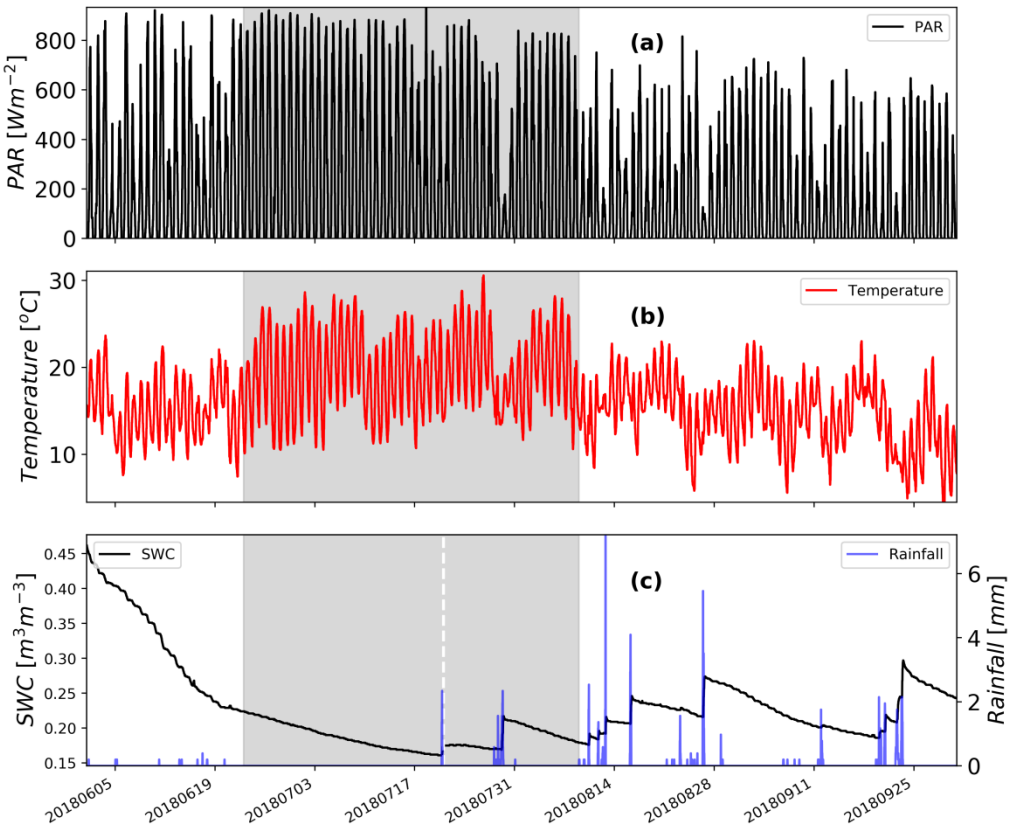
vs. (c) soil water content (SWC) coloured by temperature and (d) leaf temperature coloured by SWC.

Figure 4: Observed (OBS) and modelled (MOD) isoprene mixing ratios at the top (15.6 m; a-c) and middle (13.5 m; d-f) of the canopy. Observations are shown in black and model results in red (BASE+LFT), green (BASE+SWT), and blue (BASE+RWT). Figure S2 in the SI shows similar results for the trunk and near-surface levels.

Figure 5: Scatter plots of model (MOD) and observed (OBS) isoprene (C_5H_8) mixing ratios for (a and e) BASE coloured by SWC, (b and f) BASE+LFT coloured by SWC, (c and g) BASE+SWT coloured by temperature, (d and h) BASE+RWT coloured by temperature. Panels (a-d) show the top of the canopy (15.6 m) and panels (e-h) the middle of the canopy (13.5 m). Figure S3 in the SI reproduces these scatter plots for the trunk and near surface levels.

Figure 6: Taylor Diagram showing model output statistics from the four simulations for (a) top of canopy (15.6m), (b) middle of canopy (13.5m), (c) trunk level (7.1m) and (d) near surface (0.8m). Dashed black and brown curves and solid blue lines show normalised standard deviation, centred root mean squared error (RMS error) and correlation coefficients respectively against observations. The observed isoprene mixing ratios are summarised by the purple circle with a normalised standard deviation of 1.0, RMS error of 0.0 and correlation of 1.0. The summary statistics for the four model simulations are shown by orange (BASE), red (BASE+LFT), green (BASE+SWT), and blue (BASE+RWT) circles. Note the change in scale of standard deviation on panel (c).

Figure 7 (a-d) Time series of isoprene mixing ratios for a selected period during the heatwave-drought (22nd-27th July 2018) and (e-h) average diurnal profiles of isoprene mixing ratios for the same period. Black dashed lines are observations while the models are coloured orange (BASE), red (BASE+LFT), green (BASE+SWT) and blue (BASE+RWT). The grey shading indicates the uncertainty limits (±11%) around the observations. (a) and (e), (b) and (f), (c) and (g) and (d) and (h) are top of canopy, middle of canopy, trunk and near-surface levels respectively.



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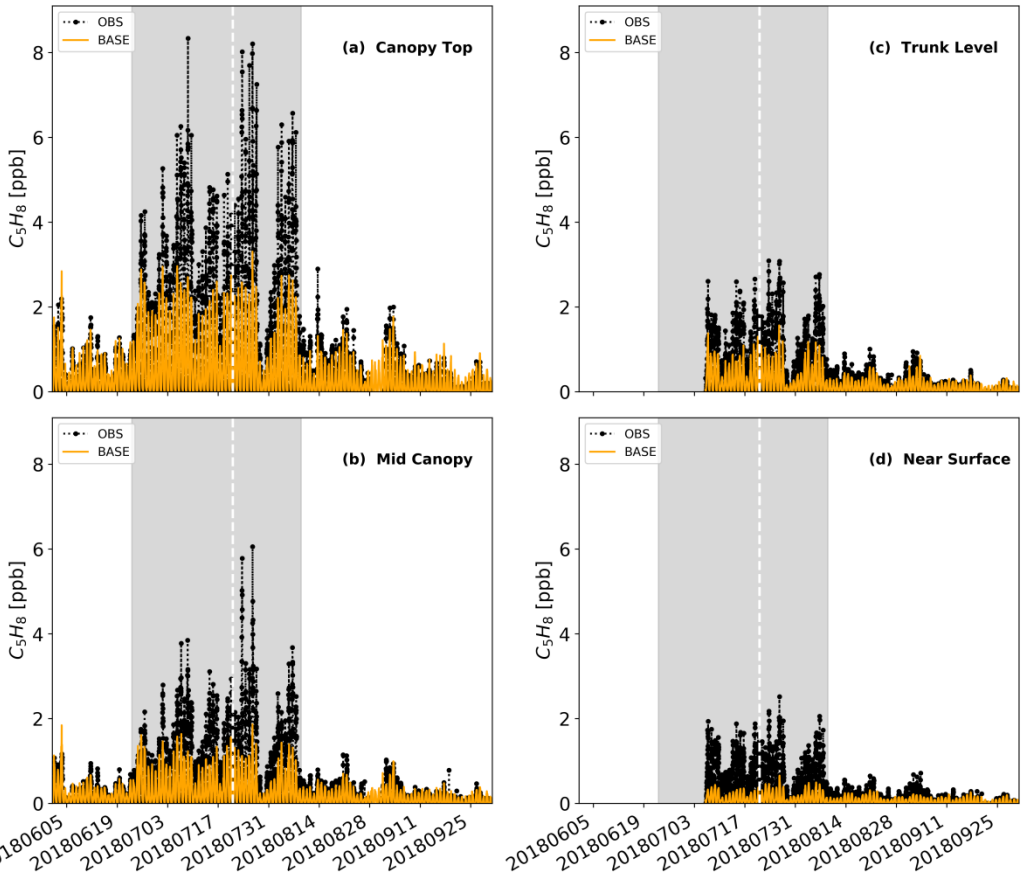

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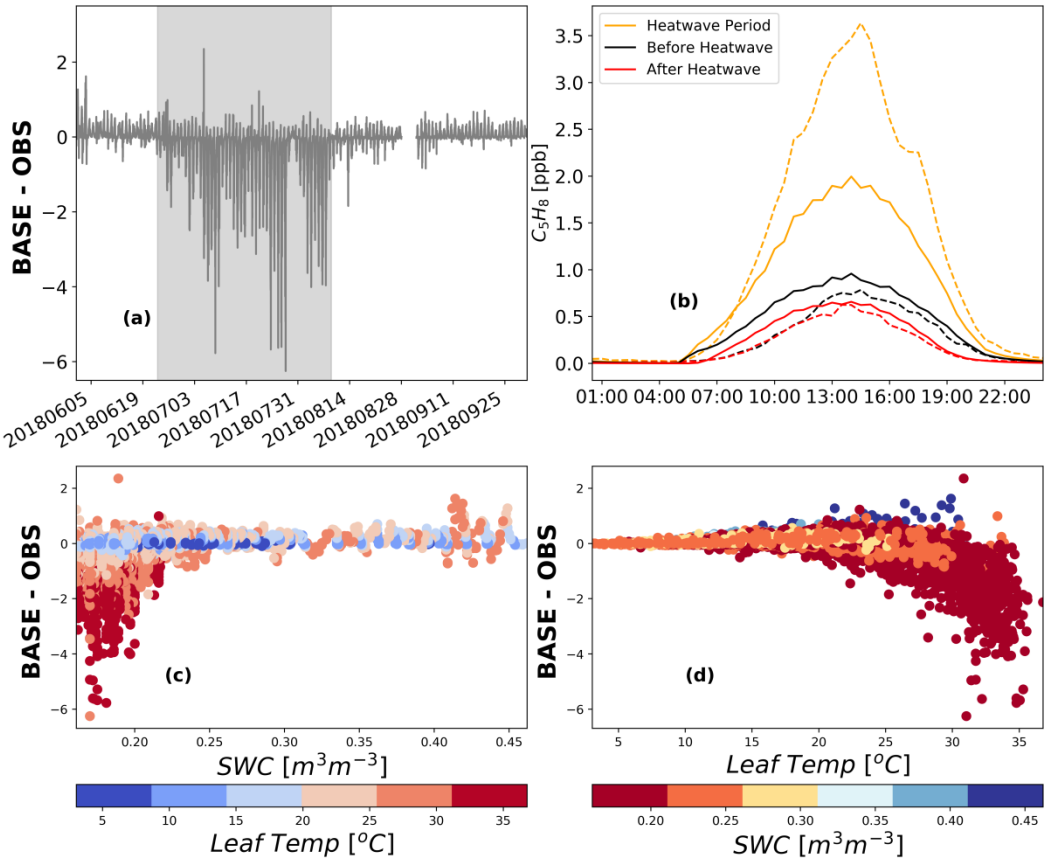

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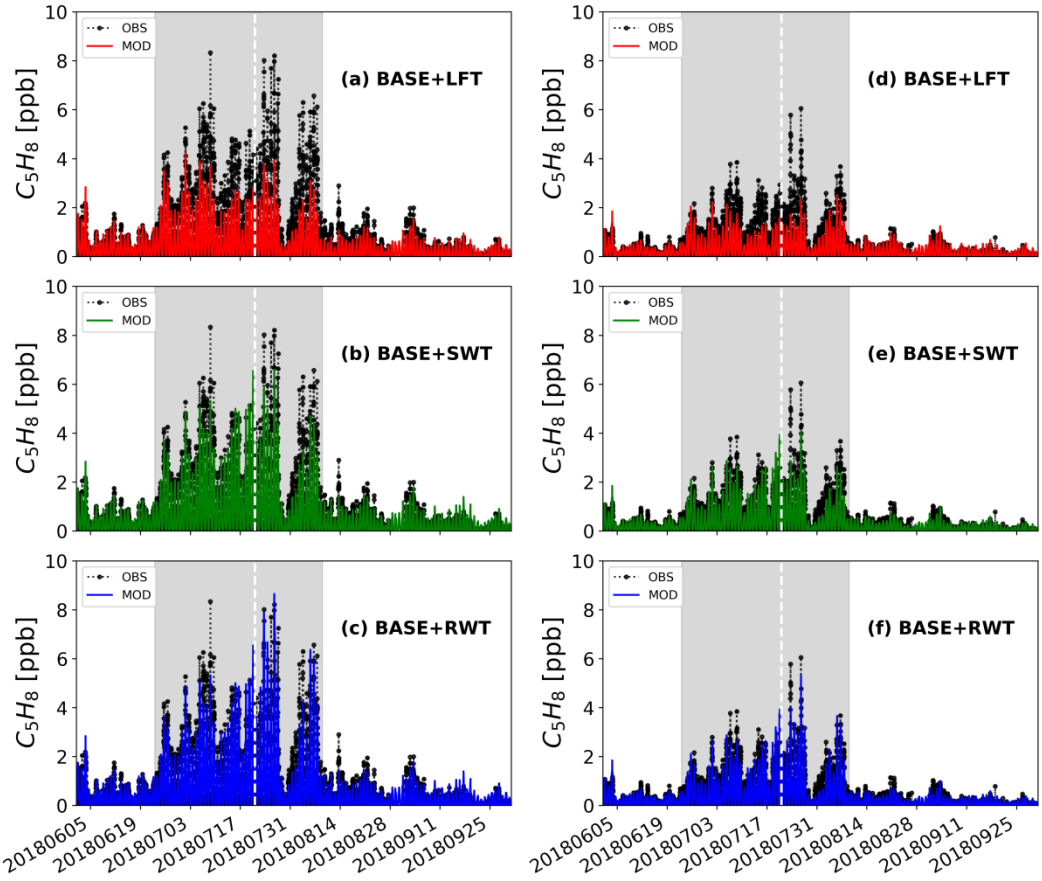

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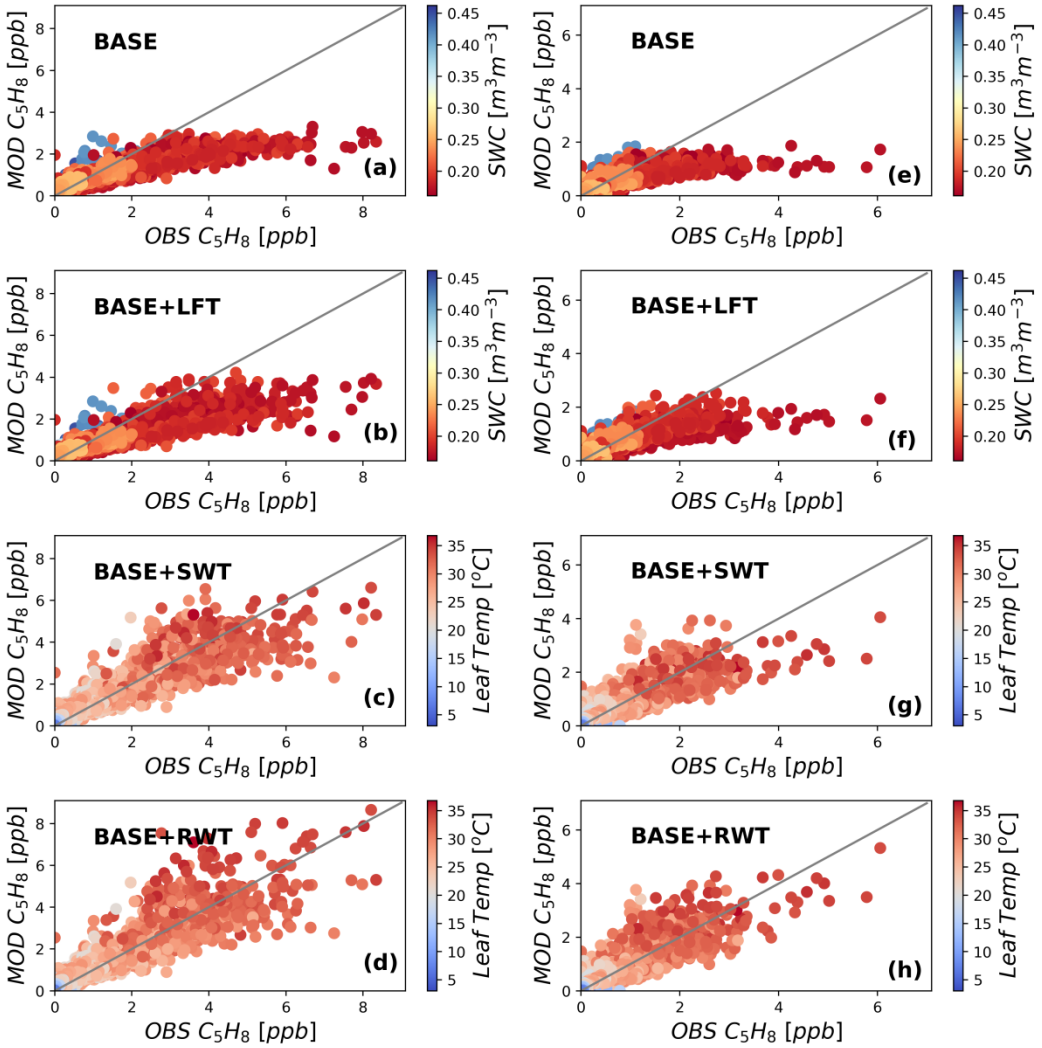

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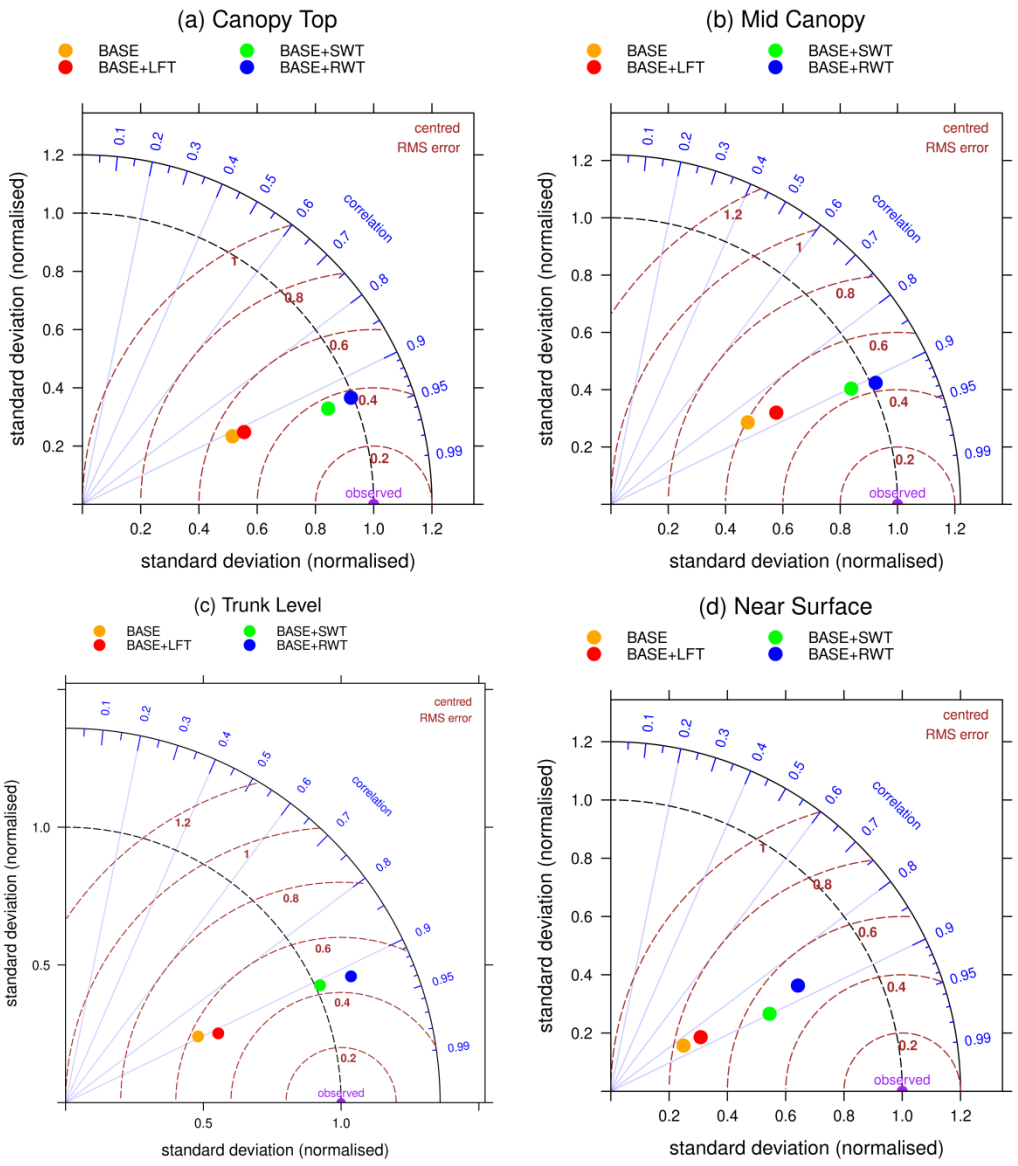

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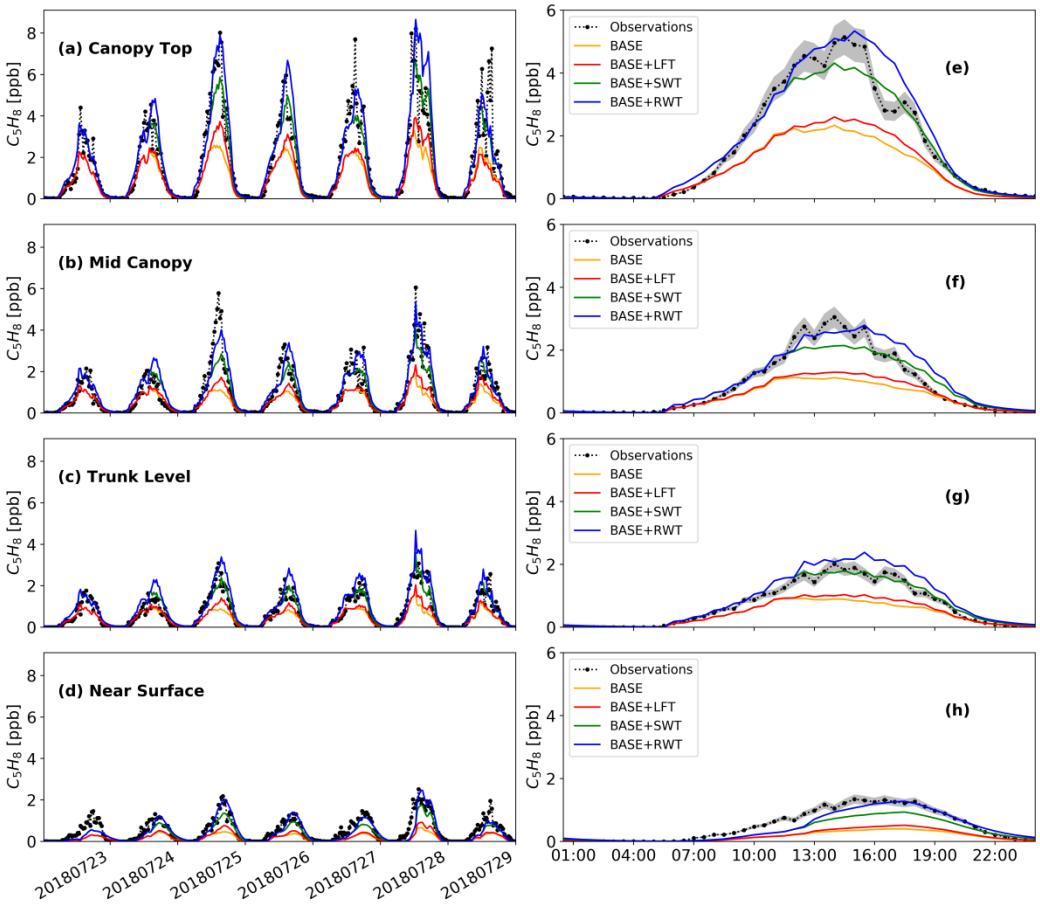

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