



1 **Developing the DO₃SE-crop model for Xiaoji, China**

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9 **Abstract**

10 A substantial body of empirical evidence exists to suggest that elevated O₃ levels are causing
11 significant impacts on wheat yields at sites representative of highly productive arable regions of ufor
12 risk assessment) to incorporate a coupled A_{net} - g_{sto} model to estimate O₃ uptake, an O₃ damage
13 module (that impacts instantaneous A_{net} and the timing and rate of senescence), and a crop
14 phenology, carbon allocation and growth model based on the JULES-Crop model. The model
15 structure allows scaling from the leaf to the canopy to allow for multiple leaf populations and
16 canopy layers. The DO₃SE-crop model is calibrated and parametrised using O₃ fumigation data from
17 Xiaoji, China for the year 2008 and for an O₃ tolerant and sensitive cultivar. The calibrated model can
18 simulate key physiological variables, crop development, and yield with a good level of accuracy
19 compared to experimental observations. DO₃SE-crop accurately depicted the difference in yield
20 reductions under ambient and elevated O₃ treatments for wheat cultivars Y16 (tolerant) and Y2
21 (sensitive) with regressions of modelled and observed absolute yields resulting in an R² of 0.99 and
22 an RMSE of 9.27 g/m². Further, when evaluated for 2007 and 2009 for all cultivars, the DO₃SE-crop
23 model simulated O₃-induced yield losses of 4-25% compared to observed yield losses of 12-34%,
24 with an R² of 0.73 and an RMSE of 58.41 g/m². Additionally, our results indicate that the variance in
25 yield reduction is primarily attributed to the premature decrease in carbon assimilation to the grains
26 under elevated O₃ exposure. This is linked to accelerated leaf senescence, which brings leaf
27 senescence forward by 7-9 days under elevated O₃ treatments.



28 Introduction

29 Ground-level ozone (O_3) is considered the most critical air pollutant causing global damage to crops.
30 Elevated O_3 concentrations are particularly problematic in Asia, where decades of rapid economic
31 growth, industrialisation, and urbanisation have seen sharp rises in pollutant emissions associated
32 with burning fossil fuels (Lin *et al.*, 2017). At the same time, climate change is considered a
33 substantial threat to arable productivity through changes in average and extreme temperature and
34 precipitation profiles across the region (IPCC, 2007 & 2014). Reductions in precipitation are
35 considered responsible for poor harvests in recent years (Liu *et al.*, 2010), and rising temperatures
36 that reduce the length of the crop growing season are thought to have caused losses in crop yield
37 (Malhi, Kaur and Kaushik, 2021). There is now substantial evidence showing that stresses from ozone
38 pollution and climate variability interact, causing either additive, synergistic, or antagonistic
39 responses in crop development, growth, and yield (Sillmann *et al.*, 2021). The threat posed by these
40 stresses is a particular cause for concern in Asia since the continent contributes approximately 43%
41 of the global wheat production, with China contributing the highest production levels at 17% (Feng
42 *et al.*, 2021). O_3 levels are rising substantially in important wheat-growing areas in China such as the
43 North China Plain and the Yangtze River Delta (Li *et al.*, 2020; Zhang *et al.*, 2023). This led to the
44 implementation in 2013 of a range of policies to try to reduce O_3 precursor emissions across China
45 e.g. a comprehensive management plan to control volatile organic compounds (VOCs) from key
46 industries, an atmospheric pollution prevention and control law of the People's Republic of China
47 and the 2020 VOCs Management Plan (Li, Zhou and Xu, 2021). As a result, nitrogen oxide (NOx)
48 emissions, an important O_3 precursor, have decreased significantly from 2013 to 2017 by 21% (Li,
49 Zhou and Xu, 2021). By contrast, VOCs have only slightly decreased by 2% over the same time
50 period. Since China has a VOC limited O_3 regime the reductions in NOx lead to rather insignificant
51 changes in O_3 concentration (Li, Zhou and Xu, 2021) though evidence suggests that reductions in O_3
52 may be higher in rural than urban areas (Lee *et al.*, 2020). This implies future policies to tackle
53 ground level O_3 pollution in China need to increase their focus on reducing VOCs along with NOx (Lee
54 *et al.*, 2020).

55 At present, methods to assess the risk to crop productivity from changes in O_3 and climate variables
56 have used a variety of different O_3 risk assessment methods. Such methods in the past relied heavily
57 on dose-response relationships, empirically derived relationships that assess changes in a response
58 variable (most commonly yield) against an ozone exposure metric (concentration or, more recently
59 flux-based indices). By contrast, methods to assess the impact of climate variables (most commonly
60 changes in temperature, precipitation, and CO_2 concentration) tend to use crop models since these
61 allow the integration of the combined effect of a number of different variables acting simultaneously
62 to affect crop development, growth, and yield (Schauburger *et al.*, 2019). There has been a growing
63 awareness of the need to integrate the ozone effect within crop models so that a holistic assessment
64 of the combined impacts resulting from these stressors can be achieved (Tao *et al.*, 2017; Emberson
65 *et al.*, 2018; Schauburger *et al.*, 2019).

66 The DO_3SE model is an ozone deposition model that can be embedded within atmospheric chemistry
67 transport models (e.g. Simpson *et al.*, 2012) and uses either a multiplicative- or coupled $A_{net}-g_{sto}$
68 model to estimate stomatal ozone flux (Pande *et al.*, sub). Accumulated stomatal ozone flux has
69 been successfully used as a damage metric (POD_y - Phytotoxic Ozone Dose over a threshold y
70 (LRTAP, 2017)) to predict ozone-induced yield loss (Pande *et al.*, sub). The ability of the DO_3SE model
71 to simulate A_{net} , and the inclusion of a process-based ozone damage module for both instantaneous
72 A_{net} and early and enhanced senescence (after (Ewert and Porter, 2000)) lends itself to the
73 development of the DO_3SE model as a process-based crop model. The inclusion of resistance
74 algorithms that can assess the transport of O_3 concentrations from a reference height above a
75 canopy down to the canopy top, mean the model can easily be embedded within existing
76 atmospheric chemistry transport schemes and hence applied for regional or global scale O_3 risk



77 assessment whilst also accurately modelling O₃ deposition. A comparison of the coupled stomatal
78 conductance-photosynthesis (A_{net} - g_{sto}) model with the multiplicative g_{sto} model within the DO₃SE
79 framework has been made in Pande et al. (sub) and showed that the A_{net} - g_{sto} model performed
80 equally well, if not better, when used to develop ozone dose-response relationships for European
81 wheat. This provides evidence of the suitability of the new photosynthetic based g_{sto} model in
82 DO₃SE.

83 In this study we describe the development of a new 'DO₃SE-Crop' model which builds on the
84 modified stomatal deposition component of the DO₃SE model (Pande et al. (sub)) so that both CO₂
85 uptake for carbon assimilation as well as ozone uptake via the stomata can be modelled consistently.
86 Further, we have incorporated the UK JULES crop model (Osborne *et al.*, 2015) to allocate assimilated
87 carbon to plant components (roots, leaves, stems and harvest organs) according to crop
88 development stage. We also take account of the modifying effect of ozone on instantaneous A_{net} as
89 well as the onset and rate of leaf senescence and timing of crop maturity through incorporation of
90 algorithms developed by (Ewert and Porter, 2000). The UK JULES crop model is used since this is the
91 UK land surface exchange scheme in the UK Earth System Model (UKESM) (Osborne *et al.*,
92 2015) which has recently been developed to include exchange and impact of trace gases (including
93 O₃) along with other biogeochemical cycling between the atmosphere and the land surface (Leung *et al.*,
94 2020). This would allow comparison of the UK JULES Crop model which are based on (Sitch *et al.*,
95 2007) with the alternative O₃ damage mechanisms used within DO₃SE-crop.

96 Here we calibrate and evaluate DO₃SE-crop model using an experimental FACE dataset collected in
97 Xiaoji, China. This allows us to investigate the ability of the model to simulate O₃ damage for a global
98 region where crop productivity is severely threatened by both ozone pollution and climate change.
99 The key objectives of the paper are to: i). assess the ability of DO₃SE-Crop to simulate key
100 physiological variables, crop development, biomass and yield; ii). the ability of DO₃SE-crop to
101 estimate the difference in O₃ induced yield loss for tolerant and sensitive cultivars caused due to
102 instantaneous versus long-term senescence effects on photosynthesis, and iii). the applicability of
103 the prescribed UK JULES crop parameters for Chinese conditions.



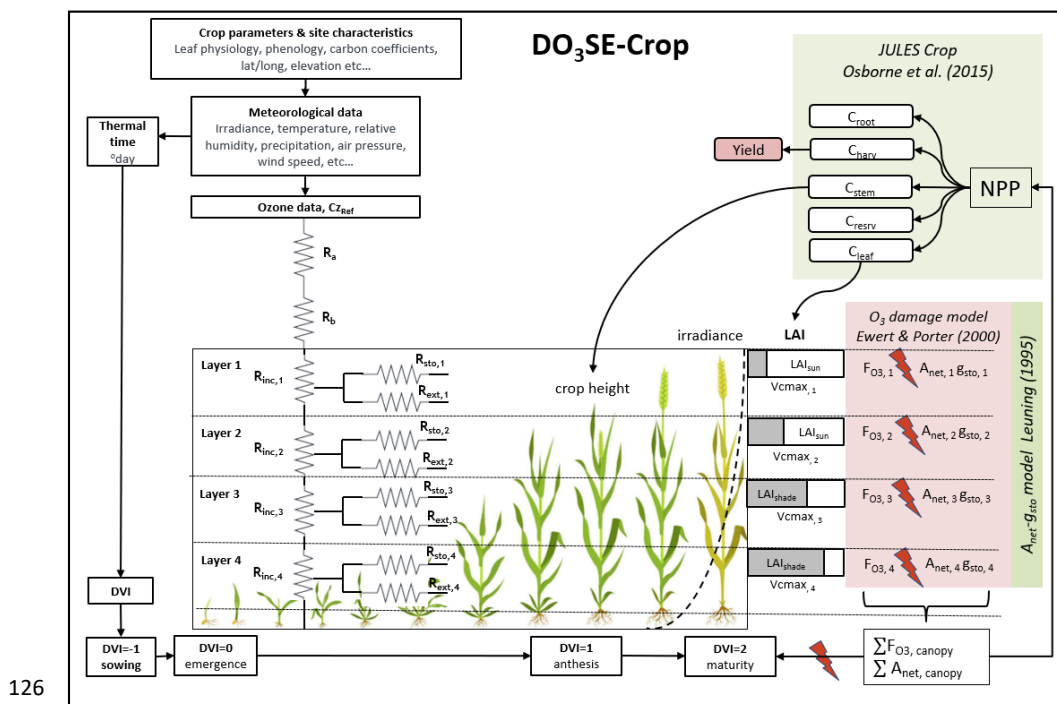
104 **Methods : DO₃SE-Crop Model development, calibration and Evaluation**

105 **1. DO₃SE-Crop Model**

106 We describe the development and calibration of ‘DO₃SE-Crop’ (version 4 (V4.39.19)), an ozone
 107 deposition model (Emberson *et al.*, 2000; Simpson *et al.*, 2012) that has been modified to simulate
 108 stomatal conductance from a coupled photosynthesis-stomatal conductance model (Leuning, 1995).
 109 Photosynthesis is simulated using a biochemical model (Farquhar, Caemmerer and Berry, 1980;
 110 Sharkey *et al.*, 2007). The DO₃SE model has also been extended to include a photosynthetic-based
 111 crop model based on the UK JULES land surface crop model (Osborne *et al.*, 2015) with ozone
 112 damage functions incorporated after (Ewert and Porter, 2000). DO₃SE-Crop is designed to simulate
 113 ozone deposition and stomatal uptake and the effects of ozone and climate related variables on crop
 114 development, biomass and yield. The DO₃SE-Crop model has been developed to simulate wheat
 115 (*Triticum aestivum*) which is widely considered to be one of the most sensitive staple crops to ozone
 116 (Feng *et al.*, 2018).

117 The key components of DO₃SE Crop are illustrated in Fig.1 and can be defined as i). crop phenology
 118 to ensure the correct length and timing of crop growth for carbon assimilation and ozone exposure;
 119 ii). leaf scale processes to ensure leaf level estimates of photosynthesis and stomatal conductance
 120 for sunlit and shaded leaves are able to accurately model carbon assimilation and stomatal ozone
 121 flux and associated damage over the leaf life span; iii). leaf-to-canopy upscaling that incorporates a
 122 within canopy irradiance and ozone concentration gradient and iv). carbon allocation processes to
 123 ensure carbon is allocated correctly to different crop compartments (roots, leaves, stem, grain)
 124 throughout the growing season.

125 Fig. 1 Schematic of DO₃SE-Crop



126



127 **1.1 DO₃SE Crop Phenology**

128 The DO₃SE-Crop model uses thermal time (TT) to define the rate of crop development in relation to
 129 the timing of three key developmental stages, TT_{emr} (the period from sowing to emergence), TT_{veg}
 130 (the period of emergence to start of grain filling) and TT_{rep} (the period from the start of grain filling
 131 to maturity) based on the method of (Osborne *et al.*, 2015). TT is calculated by estimating an
 132 effective temperature (T_{eff}) using base (T_b), optimum (T_o) and maximum (T_m) cardinal
 133 temperatures.

$$134 \quad T_{eff} = \begin{cases} 0 & \text{for } T_{air} < T_b \\ T_{air} - T_b & \text{for } T_b \leq T_{air} \leq T_o \\ (T_o - T_b) \left(1 - \frac{T_{air} - T_o}{T_m - T_o}\right) & \text{for } T_o < T_{air} < T_m \\ 0 & \text{for } T_{air} \geq T_m \end{cases} \quad [1]$$

135 Where, T_{air} is the surface air temperature in °C, T_{eff} is at a maximum when $T_{air} = T_o$, this point
 136 denotes the highest developmental rate. T_{eff} declines as the temperature falls or rises above T_o ,
 137 with a linear decrease in crop development. T_{eff} is zero, i.e. no development, when T_{air} falls below
 138 or rises above T_b and T_m respectively i.e., $T_m \leq T_{air} < T_b$. During the sowing to emergence phase,
 139 development is dependent on T_b , whereas during the vegetative and reproductive phase,
 140 development depends on T_m or T_o .

141 Winter wheat requires vernalisation (a period of exposure to low temperature during germination to
 142 accelerate flowering). Vernalisation alters the length TT_{veg} and hence flowering initiation, with
 143 subsequent effects on later growth stages such as heading. Vernalisation occurs when the minimum
 144 (VT_{min}) and maximum (VT_{max}) daily temperature is less than 15°C and 30°C respectively (Zheng
 145 *et.al.*, 2015). Accumulated vernalised days (V_{dd}) are calculated as the sum of vernalised and
 146 devernalised days from emergence to the start of anthesis (Zheng *et al.*, 2015).

$$147 \quad V_{dd} = \sum(V - V_d), \text{ where} \quad [2]$$

$$148 \quad V = \left(1.4 - 0.778 \times T_{air}, 0.5 + 13.44 \frac{T_{air}}{(T_{max} - T_{min} + 3)^2}\right) \text{ for } VT_{max} < 30^\circ\text{C and } VT_{min} < 15^\circ\text{C}$$

$$149 \quad V_d = (\min(0.5(T_{max} - 30), V_{prev})) \quad \text{for } VT_{max} > 30^\circ\text{C and } V_{dd} < 10 \text{ days}$$

150 The vernalisation factor (VF) decreases from 1 to 0 as (V_{dd}) increases. VF depends on a cultivar-
 151 specific vernalisation coefficient (PIV) as described by eq. 3.

$$152 \quad VF = 1 - (0.0054545 \times PIV + 0.0003) * (50 - V_{dd}) \quad [3]$$

153 Photoperiod (PP) or day length also affects the occurrence and timing of the flowering stage and is
 154 calculated according to latitude using standard solar geometry to estimate daylength (Jones, 1992).
 155 The photoperiod factor (PF) represents the sensitivity to PP which decreases from 1 to 0 as the
 156 photoperiod shortens and is estimated according to a cultivar-specific photoperiod coefficient (PID)
 157 after Tao *et al.* (2012) as described in eq. 4.

$$158 \quad PF = 1 - \left[\left(\frac{PID}{10000}\right) \times (20 - PP)^2\right] \quad [4]$$

159 Crop development is related to the development index (DVI) after (Osborne *et al.*, 2015) which
 160 takes values of -1 upon sowing, 0 on emergence, 1 at anthesis and 2 at crop maturity. The DO₃SE-
 161 Crop model DVI equations have been modified from (Osborne *et al.*, 2015) to take account of the
 162 photoperiod and vernalisation for winter wheat (see eq. 5); for spring wheat these factors are
 163 omitted.



$$\begin{aligned}
 164 \quad & -1 \leq DVI < 0 \quad \text{for } td < TT_{emr} \\
 165 \quad & 0 \leq DVI < 1 \quad \text{for } TT_{emr} \leq td \times VF \times PF < TT_{veg} \\
 166 \quad & 1 \leq DVI \leq 2 \quad \text{for } TT_{veg} \leq td \leq TT_{rep}
 \end{aligned} \tag{5}$$

167 DO₃SE-Crop allows for any number of representative leaf populations (*pop*) and canopy layers (*n*)
 168 to be defined over the course of the crop growing season. In this study, we used a single leaf
 169 population and 4 canopy layers (i.e. *pop* = 1; *n* = 4) for simplicity. The crop sowing is assumed to
 170 be at DVI = -1 (start of *TT_{emr}*) and emergence at DVI = 0 (start of *TT_{veg}*). The flag leaf is assumed to
 171 develop at DVI=1, at the commencement of *TT_{rep}*, marking the initiation of anthesis
 172 (*A_{start}*, flowering) and flag leaf emergence, which typically occurs 4-5 days prior to the onset and is
 173 further divided into expanding and senescing leaf periods (i.e. *tl_{ep}* and *tl_{se}*) with a default ratio of
 174 0.67 to 0.33. Maturity is assumed at DVI = 2 end of *TT_{rep}*. The model allows estimation of the *PODy*
 175 metric by accumulating stomatal ozone flux from the start of anthesis to maturity. The total leaf life
 176 span (*TT_{leaf}*) of the crop is distributed over the DVI between 0 and 2. The relationship between
 177 these different variables are described in Fig. 2).

178 1.2 DO₃SE-Crop leaf-level physiology

179 Key leaf-level physiological variables of the DO₃SE-Crop model are net photosynthesis (*A_{net}*) and
 180 stomatal conductance (*g_{sto}*). Net photosynthesis is simulated using the biochemical photosynthesis-
 181 based model initially developed by (Farquhar, G.D., von Caemmerer, S., Berry, 1980) and since
 182 modified by (Sharkey *et al.*, 2007). The coupled *A_{net}g_{sto}* model of (Leuning, 1995) is used to
 183 estimate *g_{sto}* from *A_{net}* which means that *g_{sto}* is regulated by the demand of CO₂ for *A_{net}* on
 184 consideration of environmental conditions and crop physiology. Ozone stress, causing both
 185 instantaneous effects on *A_{net}* and long-term effects on leaf senescence, is simulated based on
 186 algorithms developed by (Ewert and Porter, 2000).

187 1.2.1 Leaf net photosynthesis (*A_{net}*)

188 The *A_{net}* model assumes that photosynthesis is constrained depending on prevailing environmental
 189 conditions according to three main mechanisms: Rubisco activity (*A_c*); ribulose-1,5-bisphosphate
 190 (RuBP) regeneration, which is constrained by the speed of electron transport (*A_j*); and the low rate
 191 of transfer of photosynthetic products (most frequently triose phosphate consumption) (*A_p*)
 192 (Sharkey *et al.*, 2007a) and by soil water stress (*f_{sw}*); the algorithm for *A_c* which is based on (Medlyn
 193 *et al.*, 2002) and modified in DO₃SE-crop to include the O₃ damage functions is given in eq. 6.

$$194 \quad A_c = V_{cmax} \cdot f_{sw} \cdot \frac{(C_i - \Gamma^*) \times f_{O_{3,s}}(d) \times f_{LS}}{C_i + K_c \left(1 + \frac{O_i}{K_o}\right)} \tag{6}$$

195 where *V_{cmax}* (μmol CO₂ m⁻²s⁻¹) is the maximum carboxylation capacity at 25°C, *C_i* (μmol mol⁻¹) and
 196 *O_i* (mmol mol⁻¹) are the intercellular CO₂ and O₂ partial pressures; *K_c* (μmol mol⁻¹) and *K_o* (mmol
 197 mol⁻¹) are the Rubisco Michaelis-Menten constants for CO₂ and O₂; *Γ** (μmol mol⁻¹) is the CO₂
 198 compensation point in the absence of respiration; *f_{O_{3,s}}*(*d*) is the factor that accounts for the
 199 cumulative stomatal O₃ flux effect on *V_{cmax}* over the course of a day and; *f_{LS}* is the factor that
 200 accounts for the cumulative stomatal O₃ flux effect over the course of a leaf life span on leaf
 201 senescence. Section 1.2.1.1 gives a full description of the methods used to estimate O₃ damage. The
 202 *f_{PAW}* factor is calculated by eq. 7.

$$203 \quad f_{PAW} = \min\left\{1, \max\left\{f_{min}, f_{min} + (1 - f_{min}) \times \frac{(ASW / ASW_{fc}) \times 100 - ASW_{min}}{ASW_{max} - ASW_{min}}\right\}\right\}$$



204 Where: f_{PAW} is the plant available water factor, influencing stomatal conductance. f_{min} is the
205 minimum stomatal conductance under dry soil conditions. ASW represents the available soil water.
206 ASW_{fc} is the available soil water at field capacity, converted to a percentage. ASW_{max} is the
207 plant available soil water below which stomatal conductance will start to reduce, and ASW_{min} is the
208 plant available soil water at which stomatal conductance will equal f_{min} (Nguyen *et al.*, 2024).

209 This model scales the stomatal conductance between a minimum value and a value of unity, which
210 represents fully open stomata, based on the available soil water as a percentage of its field capacity.
211 The constraint on A_{net} due to the rate of electron transport A_j is described in eq. [8].

$$212 \quad A_j = J \times \frac{C_i - \Gamma^*}{a \times C_i + b \times \Gamma^*} \quad [8]$$

213 where J is the electron transport rate ($\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$), the parameters a and b denote the electron
214 requirements for the formation of NADPH and ATP respectively (Sharkey *et al.*, 2007)

215 Finally, the A_{net} limitation due to the low rate of transfer of photosynthetic products A_p ($\mu\text{mol CO}_2$
216 $\text{m}^{-2} \text{ s}^{-1}$) is given in eq. [9].

$$217 \quad A_p = 0.5 \times V_{cmax} \quad [9]$$

218 The net leaf photosynthetic carbon uptake (A_{net}) in $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ is calculated by eq. [10]

$$219 \quad A_{net} = (A_c, A_j, A_p) - R_d \quad [10]$$

220 Where leaf dark respiration (R_d) in $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ is calculated as $V_{cmax} \times R_{dcoeff}$ where R_{dcoeff}
221 is the leaf dark respiration coefficient initially set equal to 0.015 after Clark *et al.* (2011), a value
222 provided for C3 grasses.

223 1.2.1.1 Short- and long-term O₃ damage to A_c

224 The short-term impact of O₃ on A_c is calculated according to the $f_{O_{3,s}}(d)$ factor (between 0 and 1)
225 which allows for an instantaneous effect of O₃ on photosynthesis when stomatal O₃ flux (f_{st}), in
226 $\text{nmol O}_3 \text{ m}^{-2} \text{ s}^{-1}$ calculated as described later in section 1.2.3, overwhelms detoxification and repair
227 mechanisms (Betzberger *et al.*, 2012; Feng *et al.*, 2022), and is estimated following (Ewert and
228 Porter, 2000). Here, $f_{O_{3,s}}(h)$ represents the relationship between f_{st} and a potential decrease in A_c
229 calculated for every hour by eq. [11].

$$230 \quad f_{O_{3,s}}(h) = 1; \quad \text{for } f_{st} \leq \frac{\gamma_1}{\gamma_2}$$
$$231 \quad f_{O_{3,s}}(h) = 1 + \gamma_1 - \gamma_2 \times f_{st} \quad \text{for } \frac{\gamma_1}{\gamma_2} < f_{st} < \frac{1+\gamma_1}{\gamma_2} \quad [11]$$
$$232 \quad f_{O_{3,s}}(h) = 0; \quad \text{for } f_{st} \geq \frac{1+\gamma_1}{\gamma_2}$$

233 where γ_1 (dimensionless) and γ_2 ($\text{nmol O}_3 \text{ m}^{-2} \text{ s}^{-1}$)⁻¹ are both short-term O₃ damage coefficients,
234 with γ_1 representing the O₃ detoxification threshold below which no damage occurs to the
235 photosynthetic system and γ_2 determines the effect of f_{st} on A_c once this detoxification threshold
236 is exceeded; $f_{O_{3,s}}(d)$ and $f_{O_{3,s}}(d - 1)$ i.e. $f_{O_{3,s}}(d)$ at the end of the previous day, are calculated
237 by eq. [12].

$$238 \quad f_{O_{3,s}}(d) = f_{O_{3,s}}(h) \times r_{O_{3,s}} \quad \text{for } \text{hour} = 0;$$
$$239 \quad f_{O_{3,s}}(d) = f_{O_{3,s}}(h) \times f_{O_{3,s}}(d - 1) \quad \text{for } \text{hour} = 0 \quad [12]$$

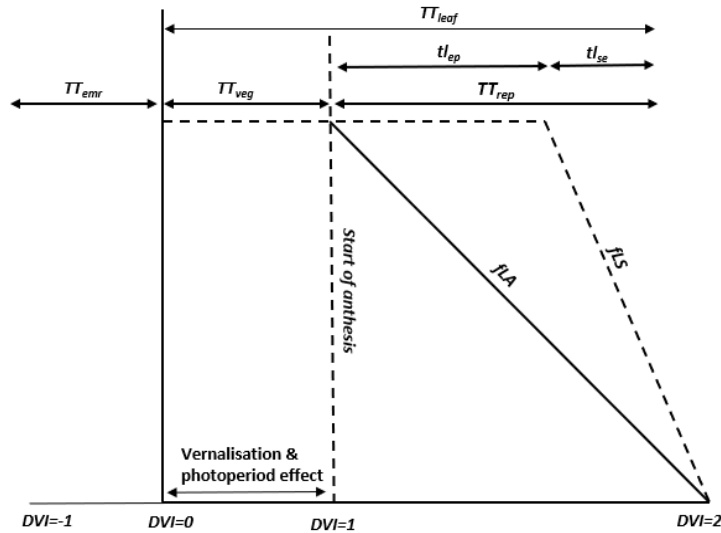


240 where $r_{O_3,s}$ (dimensionless) is incomplete recovery from O_3 overnight which depends on leaf age
 241 according to eq. [13].

$$242 \quad r_{O_3,s} = f_{O_3,s}(d - 1) + (1 - f_{O_3,s}(d - 1)) \times f_{LA} \quad [13]$$

243 The long-term impact of O_3 on V_{cmax} represented by the f_{LS} term represents the longer-term
 244 accumulation of stomatal ozone flux (acc_{fst}) causing degradation to the Rubisco enzyme which
 245 triggers early and enhanced senescence of mature leaves (Gelang *et al.*, 2000; Osborne *et al.*, 2019).
 246 The simulation of f_{LS} (and f_{LA} used in the short-term O_3 effect) are related to thermal time defined
 247 periods over the course of a leaf life span TT_{leaf} as described in Fig. 2.

248 Figure 2. The division of thermal time defined periods (TT_{emr} , TT_{veg} , TT_{rep} and TT_{leaf} and the
 249 relationship with f_{LA} and f_{LS}).



250

251 The O_3 effect on f_{LS} is first simulated by estimating a weighted accumulated fst (fO_3_l) modified
 252 from (Ewert and Porter, 2000) by eq. [14].

$$253 \quad fO_3_l = 1 - \max(\min(\gamma_3 \times (acc_{fst} - CLsO_3), 1), 0) \quad [14]$$

254 where γ_3 determines the occurrence of senescence once a critical cumulative stomatal O_3 flux
 255 $CLsO_3$ (in $mmol/m^2$) has been exceeded. The rate of senescence is determined by γ_4 , which
 256 determines the onset of senescence and γ_5 which determines maturity as described in eq. [15]

$$257 \quad tl_{epO_3} = tl_{ep} \times (1 - ((1 - fO_3_l) \times \gamma_4))$$

$$258 \quad tl_{seO_3} = tl_{se} \times (1 - ((1 - fO_3_l) \times \gamma_5)) + zc \quad [15]$$

$$259 \quad zc = tl_{ep} - tl_{epO_3}$$

260 Where tl_{ep} is the effective temperature ($teff$) accumulated by a leaf in $^{\circ}C$ days between a fully
 261 expanded leaf and the start of leaf senescence, tl_{epO_3} is tl_{ep} with an O_3 effect which may bring



262 senescence earlier, tl_{se} is the ($teff$) between the onset of senescence and maturity and tl_{seO_3} is
 263 tl_{se} with an O_3 effect which may bring maturity earlier. f_{LS} is estimated by eq. [16].
 264 $f_{LS} = 1;$ $for\ teff \leq TT_{veg} + tl_{ep}$
 265 $f_{LS} = 1 - \frac{TT_{eff} - TT_{veg} - tl_{epO_3}}{tl_{seO_3}};$ $for\ TT_{veg} + tl_{ep} < teff < TT_{leaf}$
 266 $f_{LS} = 0;$ $for\ teff \geq TT_{leaf}$ [16]

267 1.2.2 Stomatal conductance

268 The coupled photosynthesis-stomatal conductance ($A_{net}g_{sto}$) model based on (Leuning, 1995) and
 269 modified for vapour pressure deficit (VPD) is used to estimate g_{CO_2} , stomatal conductance to CO_2 in
 270 $\mu mol\ CO_2\ m^{-2}\ s^{-1}$ as described in eq. [17].

$$271\ g_{CO_2} = [f_{min} + m \times A_{net} \times f_{VPD} / (c_s - \Gamma)] \quad [17]$$

272 where f_{min} ($\mu mol\ m^{-2}\ s^{-1}$) is the minimum daytime g_{CO_2} (Leuning, 1990). The parameter m
 273 (dimensionless) is the composite sensitivity of g_{CO_2} to assimilation rate and vapour pressure deficit
 274 (VPD) with the relationship between VPD and relative stomatal conductance (f_{VPD}) estimated by
 275 eq. [18]. A_{net} ($\mu mol\ m^{-2}\ s^{-1}$) is estimated from eq [10]. f_{VPD} is calculated by eq. [18].

$$276\ f_{VPD} = \left(1 + \left(\frac{VPD}{VPD_0} \right)^8 \right)^{-1} \quad [18]$$

277 where VPD_0 is an empirical parameter, defined using boundary line analysis, describing the variation
 278 in relative stomatal conductance with VPD (Danielsson *et al.*, 2003; Pleijel *et al.*, 2007). c_s ($mmol$
 279 mol^{-1}) is the external CO_2 concentration at the leaf surface and is calculated from the external CO_2
 280 concentration at the upper surface of the leaf boundary layer c_a ($mmol\ mol^{-1}$) so that
 281 $c_s = c_a - \left(\frac{A_{net}}{g_{bCO_2}} \right)$ after (Masutomi, 2023) where g_{bCO_2} is the boundary layer conductance to CO_2 (in
 282 $mol\ m^{-2}\ s^{-1}$), conversion factors for the boundary layer are given in S1a.

283 Finally, g_{CO_2} is converted to g_{O_3} in $mmol\ O_3\ m^{-2}\ s^{-1}$ by dividing by 1000 and using the conversion
 284 factor 0.96 which assumes that the ratio of the diffusivities of gases in air are equal to the inverse of
 285 the square root of the ratio of molecular weights (as described in (Campbell, G.S., Norman, 1998),
 286 see also supplementary S1).

287 1.2.3 Stomatal ozone flux (f_{st})

288 Stomatal $[O_3]$ flux f_{st} ($nmol\ m^{-2}\ s^{-1}$) is calculated after the method described in the UNECE Mapping
 289 Manual (UNECE, 2017) described in eq. [19].

$$290\ f_{st} = C_l \times g_{O_3m/s} \times \frac{r_c}{r_{b,O_3} + r_c} \quad [19]$$

291 Where C_l is the $[O_3]$ at the upper surface of the laminar layer of a leaf ($nmol\ O_3\ m^{-3}$). Ozone
 292 concentration in ppb can be converted to $nmol\ m^{-3}$ by multiplying O_3 in ppb by $P/(R \times T_{air,k})$ where
 293 P is the atmospheric pressure in Pascal, R is the universal gas constant ($8.31447\ J/mol/K$) and $T_{air,k}$
 294 is surface air temperature in degrees Kelvin; $g_{O_3m/s}$ (m/s) is stomatal conductance to O_3 , to
 295 convert g_{O_3} ($mol\ O_3\ m^{-2}\ s^{-1}$) to $g_{O_3m/s}$ (m/s) we assume a standard temperature $T_{st}(20^\circ C)$ and air
 296 pressure P_{st} (1.013×10^5 in Pascal) and divide by 41 to give the conductance value in m/s . The
 297 $r_c/r_{b,O_3} + r_c$ term represents the O_3 deposition rate to the leaf through resistances r_b (the quasi-
 298 laminar resistance (s/m)) and r_c (the leaf surface resistance (s/m)) which allow for both stomatal and



299 non-stomatal deposition to the leaf surface. r_c is $1/(g_{O_3m/s} + g_{ext})$ where g_{ext} is $1/2500$ (s/m). r_b is
300 estimated by eq. [20].

$$301 \quad r_{b,O_3} = 1.3 \times 150 \times \sqrt{\frac{L}{u_i}} \quad [20]$$

302 Where the factor 1.3 accounts of the differences in diffusivity between heat and O_3 . and The value of
303 150 provides the equivalent conductance leaf layer for O_3 as compared to forced convection of heat
304 (Campbell, G.S., Norman, 1998), L is the cross wind leaf dimension (m) and u_i is the windspeed (m/s)
305 at the top of the leaf laminar boundary layer. The leaf boundary layer resistance to CO_2 is estimated
306 using a value of 1.24 for the difference between heat and CO_2 in place of the 1.3 value for O_3
307 (Campbell, G.S., Norman, 1998).

308 1.3 DO₃SE-Crop canopy

309 The DO₃SE crop model uses a multi-layer approach to scale from leaf to the canopy. We assume that
310 wind, irradiance, [O_3] concentration and leaf nitrogen content are the key environmental conditions
311 which change with cumulative canopy leaf area index (LAI) and influence leaf physiology and
312 therefore canopy layer estimates of A_{net} , g_{sto} and g_{ext} ; other environmental variables (e.g., $T_{air,oc}$
313 and VPD) are assumed to remain constant over the canopy.

314 1.3.1 Canopy irradiance

315 Changes in irradiance through the canopy are described as sunlit and shaded canopy fractions and
316 the associated quantity of direct and diffuse photosynthetically active radiation PAR (W/m^2), these
317 are estimated according to increasing levels of cumulative LAI using the methods of (Pury and
318 Farquhar, 1997); full details are given in the supplementary material (see section S2). Application of
319 this method requires the canopy to be divided into layers of equal LAI (including both green (LAI_G)
320 and brown (LAI_B) LAI).

321 PAR absorbed per unit leaf area is divided into PAR_{dir} , PAR_{diff} which also includes scattered (re-
322 reflected by the canopy) beam calculated by,

$$323 \quad PAR_{dir}(LAI) = (1 - \rho_{cb}(\beta)) K_b' I_b(0) \exp(-k_b' LAI) \quad [21]$$

$$324 \quad PAR_{diff}(LAI) = (1 - \rho_{cd}) K_d' I_d(0) \exp(-k_d' LAI) \quad [22]$$

325 Estimates of the LAI fractions of sunlit (LAI_{sun}) and shaded (LAI_{sh}) parts of each canopy layer (i)
326 are made by eq. 23 and 24.

$$327 \quad LAI_{sun,i} = \left[1 - \exp\left(-0.5 \times \frac{LAI_i}{\sin\beta}\right) \right] \times 2 \sin\beta \quad [23]$$

328 Where β is the solar elevation angle (see supplementary section S3)

$$329 \quad LAI_{sh,i} = LAI_i - LAI_{sun,i} \quad [24]$$

330 The DO₃SE-Crop model simulates LAI as part of the crop growth model and LAI is assumed to be
331 evenly distributed across all layers (see section 1.5.2 and eq. 43).

332 Therefore, PAR for the sunlit part of each layer can be described as

$$333 \quad \int_{LAI_i}^{LAI_{i+1}} PAR_{sun} = \int_{LAI_i}^{LAI_{i+1}} (LAI_{sun,i}) \times (PAR_{sh} + PAR_{bsun}(\beta)) dLAI$$



334 Where $\int_{LAI_i}^{LAI_n} PAR_{dir}$ can be written as $(1 - \rho cb(\beta)) \times Kb' \times Ib(0) \times [exp(-Kb'LAI_i) -$
 335 $exp(-Kb'LAI_n)]$ and $PAR_{bsun}(\beta) = (1 - \sigma)I_b(0) \frac{Cos\alpha}{Sin\beta}$

336 Similarly; PAR for the shaded part of each layer can be described as

337
$$\int_{LAI_i}^{LAI_n} PAR_{sh} = \int_{LAI_i}^{LAI_n} (LAI_{sh,i}) \times (PAR_{diff} + PAR_{bs}) dLAI$$

338 Where $\int_{LAI_i}^{LAI_n} (PAR_{diff}(LAI))$ can be written as $(1 - \rho cd) \times Kb' \times Ib(0) \times [exp(-k_d'LAI_i) -$
 339 $exp(-k_d'LAI_n)] dL$ and $\int_{LAI_i}^{LAI_n} PAR_{bs}(LAI)$ is $I_b(0) [PAR_{dir} - (1 - \sigma)k_b \times [exp(-k_bLAI_i) -$
 340 $exp(-k_bLAI_n)]$

341 **1.3.2 Canopy [O₃] concentration**

342 O₃ concentration will vary as a function of O₃ loss to the canopy (i.e. deposition via the stomates and
 343 external plant parts) and O₃ replacement from ambient air concentrations above the canopy. Limited
 344 data have been collected showing how O₃ concentrations vary with canopy depth in semi-natural
 345 communities (Jaggi *et al.*, 2006). These data suggest that a minimum, bottom canopy O₃
 346 concentration (C_{zb}), is about 0.2 times that at the top of the canopy (C_{zh}) and that the O₃
 347 concentration difference within the canopy is closely related to the LAI of the canopy layers.

348 Since each canopy layer can be assumed to be a parallel sink, the O₃ flux to a layer depends on the
 349 conductance (inverse of resistance) of that layer and the O₃ concentration at the top of the layer (C_i ;
 350 with C_0 being C_{zh} (i.e. the O₃ concentration at height C_h , the top of the canopy)); we follow and
 351 generalise the work of Waggoner.,1971 by separating the canopy into nL leaf layers. We calculate
 352 the O₃ concentration for each layer, C_i , from O₃ intake, I_i , by;

353
$$C_i = r_i I_i \tag{25}$$

354 With r_i the surface resistance for layer i . I_i is calculated as the solution to a system of linear
 355 equations. Relating r_i , I_i , and R_i , the in-canopy aerodynamic resistance for layer i . Assuming above
 356 the canopy there is a uniform O₃ concentration C_0 , we use generalised equations from Waggoner.,
 357 1971 for the difference in O₃ concentration between the exterior air and leaf interior, which for the
 358 top layer is C_0 minus 0, so C_0 and for each lower layer the difference is 0. This O₃ concentration
 359 difference is calculated by;

360
$$C_0 = R_1 \sum_{j=1}^{nL} I_j + r_1 I_1 \tag{26}$$

361 For the top canopy layer,

362
$$0 = R_i \sum_{j=i}^{nL} I_j + r_i I_i - r_{i-1} I_{i-1} \tag{27}$$

363 For each canopy layer i between the top layer and the bottom layer, and;

364
$$0 = R_{nL+1} I_{nL+1} - r_{nL} I_{nL} \tag{28}$$

365 For the bottom layer of the canopy, between the lowest leaf layer and the ground. These can also be
 366 written into the matrix form;

367
$$\begin{pmatrix} r_1 + R_1 & R_1 & R_1 & \dots & R_1 \\ -r_1 & r_2 + R_2 & R_2 & \dots & R_2 \\ 0 & -r_2 & r_3 + R_3 & \dots & R_3 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & R_{nL+1} \end{pmatrix} \begin{pmatrix} I_1 \\ I_2 \\ I_3 \\ \vdots \\ I_{nL+1} \end{pmatrix} = \begin{pmatrix} C_0 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \tag{29}$$



368 Which can be numerically solved for I_x when $r_1 \neq 0$ and $R_1 \neq 0$.

369 Resistances for each layer are calculated as described in the supplementary material (section S4)
370 using standard DO₃SE deposition modelling methods (Emberson, L.D., Ashmore, M.R., Simpson, D.,
371 Tuovinen, J.-P. and Cambridge, 2001; Simpson *et al.*, 2012).

372 1.3.3 Canopy maximum carboxylation capacity (V_{cmax})

373 We allow for an exponential decrease in leaf N with canopy depth which will influence both the
374 photosynthetic capacity (V_{cmax}) and hence dark respiration (R_d). Photosynthetic capacity at each
375 canopy layer i is calculated by eq. [30].

376

$$377 V_{cmax,i} = n_e \times n_0 \times e^{-kN \left(\frac{LAI_i}{LAI_{total}} \right)} \quad [30]$$

378 Where n_e (mol CO₂ m⁻² s⁻¹ kg C (kg N)⁻¹) is a constant relating leaf nitrogen to Rubisco carboxylation
379 capacity, n_0 (kg N[kg C]⁻¹) is the leaf N concentration at the top of the canopy and kN is a nitrogen
380 profile co-efficient initially set at 0.78 after (Clark *et al.*, 2011).

381 1.3.4 Canopy Photosynthesis ($Anet_c$)

382 Net canopy photosynthesis ($Anet_c$) determines the amount of C assimilated by the entire canopy
383 that can subsequently be allocated to different plant parts (i.e. less than the C respired for plant
384 growth and maintenance, see section 1.4.1), the amount of C assimilation will ultimately determine
385 whole plant biomass. The net photosynthesis for each canopy layer ($Anet_i$) is calculated according to
386 the LAI fraction of that layer that is sunlit ($LAI_{sun,i}$) and shaded ($LAI_{sh,i}$) within the layer (i),
387 multiplied by the net photosynthesis of the sunlit ($Anet_{sun,i,j}$) and shaded leaf ($Anet_{sh,i,j}$),
388 respectively described by eq. [31] and [32].

$$389 Anet_i = LAI_{sun,i} \times Anet_{sun,i} + LAI_{sh,i} \times Anet_{sh,i} \quad [31]$$

390 with $Anet_c$ calculated by,

$$391 Anet_c = \sum_{i=1}^n Anet_i \quad [32]$$

392 $Anet_c$ is converted from $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ to $\text{kg C m}^{-2} \text{ day}^{-1}$ by multiplying by 3600 (converting from
393 seconds to hours), multiplying by 1.2 (representing the kg of C per mol) and summing each hourly
394 $Anet_c$ over the course of a day. This $Anet_c$ is used in the equation 37.

395 1.3.5 Canopy Stomatal Conductance (g_{sto_i})

396 Similarly, canopy layer (i) stomatal conductance to O₃ ($g_{O_3,i}$), which is converted from g_{CO_2} by
397 assuming a diffusivity ratio of 0.96 to convert from CO₂ to O₃ and is calculated by eq. [33] with whole
398 canopy stomatal conductance calculated by eq. [34].

$$399 g_{sto_i} = LAI_{sun,i} \times g_{sto_{sun,i}} + LAI_{sh,i} \times g_{sto_{sh,i}} \quad [33]$$

$$400 g_{sto_c} = \sum_{i=1}^n g_{sto_i} \quad [34]$$

401 This is converted from g_{sto_i} in eq. [33] by dividing the conductance value in $\text{mmol m}^{-1} \text{ s}^{-1}$ by 41000
402 (assuming standard temperature (20°C) and air pressure (1.013×10^5 Pa)) to give conductance in
403 m/s.

404 1.4 Crop biomass, LAI, height and yield variables

405 The following section describes how to estimate crop biomass, important canopy characteristics
406 (LAI and crop height (h)) and yield variables from accumulated calculations of $Anet_c$ over the
407 course of the growing season following (Osborne *et al.*, 2015).



408 **1.4.1 Crop biomass (*NPP* and *GPP*)**

409 The simulation of crop growth requires an estimate of the net primary productivity (*NPP*) which is
 410 calculated at the end of each day and summed over the growing season. Carbon is assumed to be
 411 allocated to five key crop components: root, leaf, stem, harvest, and reserve pools (Osborne *et al.*,
 412 2015). This carbon allocation is ultimately used to simulate leaf area index (*LAI*), canopy height (*h*),
 413 biomass, harvest index, and yield at the end of each day throughout the growing season.

414 Net primary productivity *NPP* (kg C m⁻² day⁻¹) is accumulated throughout the day using the JULES-
 415 crop approach to model crop growth (Osborne *et al.*, 2015) described in eq. [35].

$$416 \quad NPP = GPP - R_p \quad [35]$$

417 where *GPP* is the gross primary productivity (kg C m⁻² day⁻¹) and *R_p* is plant respiration divided into
 418 maintenance (*R_{pm}*) and growth (*R_{pg}*) respiration (kg C m⁻² day⁻¹) (Clark *et al.*, 2011) where *R_p* =
 419 *R_{pm}* + *R_{pg}* and where *R_{pg}* is assumed to be a fixed fraction of the *NPP* as shown in eq. [36].

$$420 \quad R_{pg} = R_{gcoeff} (GPP - R_{pm}) \quad [36]$$

421 Where *R_{gcoeff}* is the growth respiration co-efficient which was initially set to 0.25 based on the
 422 value for all PFTs (i.e. forests and grasses including crops) in (Clark *et al.*, 2011). *GPP* is calculated by
 423 eq. [37].

$$424 \quad GPP = Anet_c + f_{sw}R_{dc} \quad [37]$$

425 where *Anet_c* is net canopy photosynthesis (see eq. 28) and *f_{sw}R_{dc}* is the soil-moisture modified
 426 canopy dark respiration (kg C m⁻² day⁻¹) where *R_{dc}* = *V_{cmax,i}* × *R_{dcoeff}* with *R_{dcoeff}* initially
 427 assumed to be 0.015 based on (Clark *et al.*, 2011); *V_{cmax,i}* is the maximum carboxylation efficiency
 428 for each canopy layer *i* which decreases from the top to bottom of the canopy (see eq. 30) and *f_{sw}*
 429 is calculated in eq. [7].

430 Leaf maintenance respiration (*R_{pm}*) is assumed equivalent to the soil moisture modified canopy dark
 431 respiration, while root and stem respiration are assumed to be independent of soil moisture but to
 432 have the same dependencies on C content. We assume a fixed relationship between C and N
 433 contents of these organs so that *R_{pm}* can be estimated by eq. [38].

$$434 \quad R_{pm} = R_{dc} \times (f_{sw} + (\frac{C_{root} + C_{stem}}{C_{leaf}})) \quad [38]$$

435 The C accumulating as *NPP* each day is divided into five carbon pools i.e. root (*C_{root}*), leaf (*C_{leaf}*),
 436 stem (*C_{stem}*), reserve (*C_{resv}*), and harvest (*C_{harv}*) (kg C m⁻² day⁻¹) according to partition coefficients
 437 (see eq. [39]) allowing for accumulation of C in these pools over the course of the crop growth
 438 period.

$$439 \quad \frac{dC_{root}}{dt} = p_{root}NPP,$$

$$440 \quad \frac{dC_{leaf}}{dt} = p_{leaf}NPP,$$

$$441 \quad \frac{dC_{stem}}{dt} = p_{stem}NPP(1 - \tau), \quad [39]$$

$$442 \quad \frac{dC_{harv}}{dt} = p_{harv}NPP,$$

$$443 \quad \frac{dC_{resv}}{dt} = p_{stem}NPP, \tau$$

444 where τ is the fraction of stem C that is partitioned into the reserve pool. *p_{root}*, *p_{leaf}*, *p_{stem}*,
 445 *p_{harv}* = 1. The partition coefficients are related to the crop development stage (*DVI*) and hence
 446 effective thermal time (*TT_{eff}*) since emergence. The partition coefficients are based on Osborne *et al.*
 447 *al.* (2015) and provided as a function of *DVI* using six parameters to continuously describe varying



448 partition coefficients over the duration of the crop growing season. We use the same multinomial
449 logistic as that described in (Osborne *et al.*, 2015) to define this function according to eq. [40].

$$450 \quad p_{root} = \frac{e^{\alpha_{root} + (\beta_{root} DVI)}}{e^{\alpha_{root} + (\beta_{root} DVI)} + e^{\alpha_{stem} + (\beta_{stem} DVI)} + e^{\alpha_{leaf} + (\beta_{leaf} DVI)} + 1},$$

$$451 \quad p_{stem} = \frac{e^{\alpha_{stem} + (\beta_{stem} DVI)}}{e^{\alpha_{root} + (\beta_{root} DVI)} + e^{\alpha_{stem} + (\beta_{stem} DVI)} + e^{\alpha_{leaf} + (\beta_{leaf} DVI)} + 1},$$

$$452 \quad p_{leaf} = \frac{e^{\alpha_{leaf} + (\beta_{leaf} DVI)}}{e^{\alpha_{root} + (\beta_{root} DVI)} + e^{\alpha_{stem} + (\beta_{stem} DVI)} + e^{\alpha_{leaf} + (\beta_{leaf} DVI)} + 1}, \quad [40]$$

$$453 \quad p_{harv} = \frac{1}{e^{\alpha_{root} + (\beta_{root} DVI)} + e^{\alpha_{stem} + (\beta_{stem} DVI)} + e^{\alpha_{leaf} + (\beta_{leaf} DVI)} + 1},$$

454 Where DVI is the development index; α and β partition parameters. These parameters describe the
455 shape of the thermal time varying partition coefficient for leaves, roots and stems.

456 Once C is no longer partitioned to stems, C from the stem reserve pool will mobilise to the harvest
457 pool at a rate of 10% per day following (Osborne *et al.*, 2015) described by eq. [41].

$$458 \quad C_{harv} = C_{harv} + (0.1 C_{resv}) C_{resv} = 0.9 C_{resv} \quad \text{for } p_{stem} < 0.01 \quad [41]$$

459 Total leaf C is divided between green leaf C ($C_{leaf,green}$), and brown leaf carbon ($C_{leaf,brown}$). Carbon
460 from the $C_{leaf,green}$ will mobilise to the harvest pool at the rate of 5% per day after (Osborne *et al.*,
461 2015) and to the $C_{leaf,brown}$ at a rate of 24% per day once $f_{LS} > 1$ as described in eq. [42]

$$462 \quad \{C_{harv} = C_{harv} + (0.05 C_{leaf,green}) C_{leaf,green} = 0.86 C_{leaf} \quad C_{leaf} = 0.86 C_{leaf,green} +$$

$$463 \quad 0.24 C_{leaf,brown} \} \quad \text{for } f_{LS} > 1 \quad [42]$$

464 1.4.2 Leaf area index (LAI) and stem height (h)

465 At the end of each day, the C content of the stem and leaf is used to estimate LAI by eqs. [43] and
466 [44].

$$467 \quad LAI = (C_{leaf} / f_c) \times SLA \quad [43]$$

$$468 \quad \text{where } SLA = \Upsilon (DVI + 0.06)^\delta \quad [44]$$

469 The values Υ and δ were determined by fitting the values to the paired values of DVI and specific leaf
470 area (SLA). The value of f_c is 0.5 (unitless), denotes carbon fraction of dry matter.

471 The amount of C in the stem is used to calculate the crop height h in m by eq. [45].

$$472 \quad h = k (C_{stem} / f_c)^\lambda \quad [45]$$

473 where k and λ were determined by fitting the value C_{stem} and h .

474 1.4.3 Yield variables

475 According to (Osborne *et al.*, 2015) yield can be calculated from the C allocated to the harvest pool
476 (C_{harv}) at the end of the growing season as described in eq. [46]

$$477 \quad Yield_{grain} = \frac{(C_{harv} \times (1/f_c) \times D_w \times E_g)}{1000} \quad [46]$$

478 Where harvested C is converted to total biomass (using the conversion factor $f_c=0.5$), i.e., by
479 multiplying the harvested C by $1/f_c$, and then by $1/0.84$ (D_w) to account for the grain moisture
480 content (Mulvaney and Devkota, 2020). C_{harv} includes both chaff and grain however, O_3 fumigation



481 experimentalists tend to only include grain when calculating total crop yield at the end of the
 482 growing season, so we assume 15% of the yield is chaff and include a grain to ear ratio, E_g , of 0.85.
 483 Dividing by 1000 converts yield from kg C m^{-2} to g C m^{-2} , the unit most often used to describe
 484 experimental yield results.

485 Evaluation of the DO₃SE-crop model uses a variety of growth ‘dry matter (DM)’ metrics. Some of the
 486 most important metrics and their calculations are: ‘Straw DM’ which is calculated as the sum of
 487 carbon allocated to C_{stem} , C_{leaf} , and C_{resv} ; ‘Ear DM’ is calculated from C_{harv} excluding the
 488 moisture content (D_w) conversion; ‘Grain DM’ is calculated from C_{harv} excluding both the moisture
 489 content (D_w) conversion and removing the chaff fraction conversion E_g ; ‘Above ground DM’ is the
 490 straw DM plus the Ear DM; ‘Below ground DM’ is converted from C_{root} ; and ‘Harvest index’ is
 491 the Gain DM divided by the Above ground DM. In all cases the f_c conversion factor is used to
 492 convert from e.g. g C m^{-2} to g DM m^{-2} .

493 2. DO₃SE-Crop model calibration

494 2.1 Xiaoji China experimental dataset

495 The DO₃SE-crop model was used to analyse the O₃-FACE (Free Air Concentration Enrichment)
 496 experimental data collected in Xiaoji, Jiangdu, Jiangsu Province, China. This dataset includes four
 497 modern cultivars of winter wheat (*Triticum aestivum* L.) grown under ambient and elevated [O₃] with
 498 the elevated treatment being, on average, 25% above the ambient [O₃] of 45.7 ppb for the period
 499 early March/April to end of May each year. Plants were grown in fully open-air field conditions for
 500 three consecutive growing seasons over 2007 to 2009. Table 1 describes the hourly meteorological
 501 and [O₃] data that are required to run the DO₃SE-Crop model and which are provided at the Xiaoji
 502 site.

503 Table 1. Hourly meteorological and [O₃] data measured as Xiaoji required to run the DO₃SE-Crop

| Variable | Unit | Description | Measurement height |
|---------------|----------------|---|--------------------|
| PAR_{total} | W/m^2 | Direct and diffuse PAR at the top of the canopy | - |
| T_{air} | °C | Surface air temperature in degrees Celsius | 2 m |
| VPD | kPa | Leaf to air vapour pressure deficit | 2 m |
| u_z | m/s | Wind speed at a reference height z | 2 m |
| ρ_a | Pa | Surface air pressure | 2 m |
| $O3_z$ | m/s | Ozone concentration at a reference height z | 2 m |

504 The water availability is sufficient for the wheat crop so we assume there was no soil moisture stress
 505 (Feng *et al.*, 2012). Any data gaps were filled following the AgMIP-O₃ gap filling protocol (see S4). For
 506 large [O₃] data gaps (i.e. greater than 2 weeks) which occur outside the [O₃] fumigation period we
 507 use scaled WFRChem (version 4.2) data for Xiaoji (Conibear *et al.*, 2018a) to ensure consistency in
 508 model calibration and potential applications across China. The four cultivars were Yannong 19
 509 (strong-gluten wheat, hereafter Y19), Yangmai 16 (medium-gluten wheat, hereafter Y16), Yangmai
 510 15 (weak-gluten wheat, hereafter Y15) and Yangfumai 2 (weak-gluten wheat, hereafter Y2). The
 511 dataset provides measurements of key physiological variables for the Y2 and Y16 cultivars (i.e. A_{net} ,
 512 V_{cmax} , J_{max} and g_{O3}) for the flag leaf which were used to evaluate the DO₃SE-Crop model’s
 513 simulations of these variables.

514 Additional data also provide measurements of chlorophyll content Index (CCI), which can be used to
 515 assess the level of senescence experienced by the leaf (Mariën *et al.*, 2019). The dataset also



516 provides grain yield components, including the number of ears per square meter, the number of
517 grains per ear and the grain dry matter (*Grain DM*) (the latter in g m^{-2}) (Feng *et al.*, 2011, 2016).
518 Further experimental details are provided in (Feng *et al.*, 2011, 2016).

519 2.2 DO₃SE-Crop calibration and evaluation

520 The Xiaoji experimental data were split into calibration (year 2008, Y2 and Y16 cultivars) and
521 evaluation (year 2007 & 2009, Y15 & Y19 cultivars). The calibration of DO₃SE-Crop has two main
522 steps, firstly, to calibrate for crop development and growth (i.e. phenology and C allocation). This
523 calibration was performed using the Y2 cultivar. Secondly, the calibration of the O₃ damage module,
524 this was calibrated for using the Y2 cultivar (representing a sensitive cultivar and Y16 (representing a
525 tolerant cultivar), these cultivar sensitivities followed information provided in (Feng *et al.*, 2016).

526 Calibration

527 Calibration of the DO₃SE-Crop model used a combination of automated (for phenology) and manual
528 (for leaf physiology, canopy C allocation and O₃ damage) calibration methods. Both methods require
529 defining an initial parameter value and a realistic range over which the parameter value may vary.
530 These parameter values are defined from a combination of observations from the Xiaoji
531 experimental dataset as well as values taken from the literature (see supplementary Table 2 for
532 details). The model is calibrated until certain conditions were satisfied, as explained below.

533 Calibration of the phenology module used the Xiaoji 2008 dataset for the Y2 cultivar. These data
534 were used to determine the thermal life span of the canopy from sowing to maturity (TT_{leaf}) and
535 calibrate key phenology parameters (T_b , T_0 , T_m , VT_{min} , VT_{max} , PIV , and PID , flag leaf emergence,
536 A_{start} , tl_{ep} and tl_{se}). The phenology calibration was automated by computationally applying a
537 genetic algorithm (Wang, 1997), an optimisation technique with gradient decent to find the best
538 parameters. This uses a combination of crossover strategy (selecting parameters randomly from
539 parameter pairings) and mutation strategy (which takes a parameter range and uses incremental
540 step changes) to identify the parameters which give the highest R² and lowest RMSE when compared
541 with observations of the timing (day of year) of emergence, anthesis and maturity. The calibrated
542 phenology parameters were tested for the other years (i.e. 2007 and 2009, including all the cultivars)
543 to assess their ability to represent crop development between years.

544 We applied a sensitivity analysis to identify the leaf physiology, C allocation and O₃ damage module
545 parameters that were most important to calibrate (Iwanaga *et al.*, 2022). The sensitivity analysis
546 identified the following DO₃SE-crop parameters for calibration: i). leaf photosynthesis parameters (
547 V_{cmax} , J_{max} , kN , m and VPD_0); ii). C allocation parameters (a_{root} , a_{leaf} , a_{stem} , λ , θ); iii). dark
548 respiration coefficients (R_{dcoeff} and R_{gcoeff}), and iv). O₃ damage module parameters related to
549 senescence (γ_3 , γ_4 and γ_5). Calibration for these parameters was performed manually and in steps;
550 firstly, the best parameters are found for leaf photosynthesis i.e. parameters which give a maximum
551 A_{net} value of $30 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ and g_{O_3} value of $350 \text{ mmol O}_3 \text{ m}^{-2} \text{ s}^{-1}$ (consistent with maximum
552 values observed in the Xiaoji dataset, Xhu *et al.*, 2011). Secondly, calibration is then performed for
553 the C allocation parameters, identifying the best parameters which meet each of the following
554 criteria:- a stem dry matter: leaf dry matter ratio of approx. 2:1 (after (Huang *et al.*, 2022)); relative
555 growth of different plant parts which are consistent with growth profiles found in the literature
556 ((Osborne *et al.*, 2015) and de Vries *et al.*, 1989); an R² value of above 0.90 when modelled
557 *Grain DM* is plotted against observed *Grain DM*; *Above ground DM* values are between 1200-
558 1600 g m^{-2} ; a LAI of between 4-7 $\text{m}^2 \text{ m}^{-2}$ and R_d is 30 to 60% of the assimilated A_{net} (Amthor *et al.*,
559 2019). Finally, the model is then calibrated for the O₃ parameters, while other parameters remain
560 fixed, the best calibrated parameters are those that give an R² value of above 0.90 when modelled



561 $Yield_{grain}$ difference was compared against observed $Yield_{grain}$ difference for ambient versus
562 elevated O_3 treatments.

563 Full details and description of the DO3SE-crop parameters for wheat and their associated ranges are
564 given in Table S3, S4 and S5.



565 **Results**

566 We first examine the model's ability to simulate the key phenological development stages since this
 567 is key to simulating the variation in C allocation over the course of the growing season and hence
 568 how O₃ exposure will influence growth and yield which is determined by the timing and length of the
 569 grain filling period. We also explore how DO₃SE-Crop simulates within canopy [O₃] profiles to
 570 understand which layers of the canopy are most important in determining O₃ response. We then
 571 examine the ability of the model to simulate leaf-level physiology and C allocation to the different
 572 parts of the crop. Lastly, the impact of both instantaneous and long-term O₃ damage on the crop's
 573 final grain yield is evaluated.

574 i) Crop Phenology

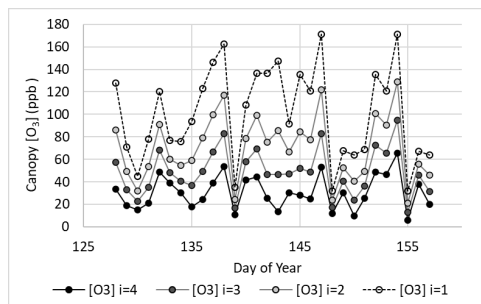
575 The Xiaoji dataset provides sowing and harvest dates for all cultivars for each year, however the date
 576 of the timing of anthesis is only provided for the year 2008 for all the cultivars. We assume that DVI
 577 = 1 is equivalent to the start of anthesis (and happens 4-5 days after the emergence of the flag leaf)
 578 as shown in Fig. 2. The model is calibrated using the 2008 Y2 data to provide the thermal times for
 579 TT_{veg} and TT_{rep} and uses the CCI data and associated breakpoint method to estimate tl_{ep} and tl_{se} .
 580 We then assume that these values are consistent across cultivars and years. Figure S1 shows the
 581 timing of crop emergence, anthesis and harvest in relation to simulated anthesis (i.e. at DVI=1).
 582 There is a variation of 4 to 10 days for anthesis in relation to days from crop emergence between
 583 years. The T_l ranges between 1325 and 1478 °C days for the three years with crop emergence
 584 occurring between day of year 37-45 and harvest occurring between day of year 135-151. The
 585 number of days from crop emergence to harvest was between 100 and 104 for the three years.

586 ii) Within canopy stomatal O₃ profile

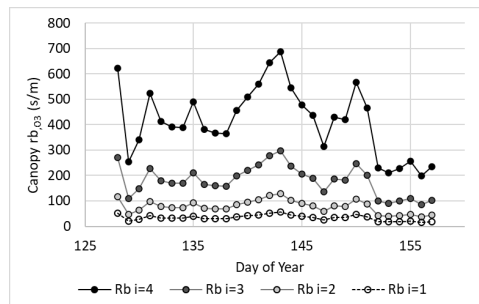
587 An important determinant of O₃ deposition and damage is stomatal O₃ deposition (or stomatal O₃
 588 uptake) which is a function of within canopy transfer of O₃ and stomatal and non-stomatal
 589 deposition. The multi-layer aspect of the DO₃SE-Crop model allows within canopy stomatal and non-
 590 stomatal O₃ deposition to be simulated. Figure 3 shows the variation in key variables that determine
 591 total and stomatal O₃ canopy deposition across 4 canopy layers as a mid-day average over the
 592 course of the tl_{ep} period of the flag leaf, for the year 2008 and the Y2 cultivar.

593 Figure 3. Plot showing variation in key O₃ deposition terms as daily maxima by canopy layer (N.B. $i =$
 594 1 is the top canopy layer, $n = 4$) a). [O₃], b). rb_{O_3} , c). PAR_{sun} and d). g_{O_3} for the duration of the
 595 flag leaf period for the Y2 cultivar E-O₃ treatment in 2008.

596 a).



b).

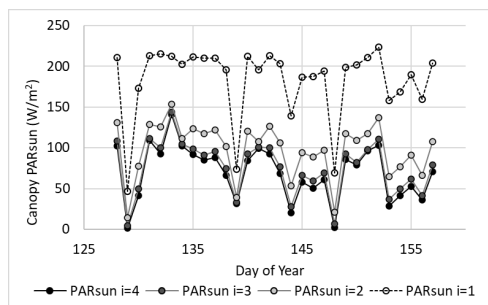


597

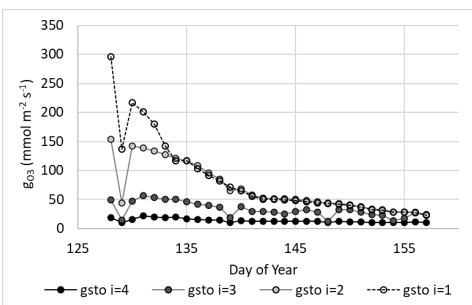
598



599 c).



d).



600

601 Figure 3a. shows a decrease of within canopy $[O_3]$ from highs of around 140ppb to values within the
 602 range of 10 to 50 ppb between the topmost and bottom canopy layer. Similarly, PAR_{sun} reduces
 603 from maximum values of around 200 W m^{-2} to values of around 100 W m^{-2} on sunny days (see Fig.
 604 3b). The leaf rb_{O_3} (Fig. 3c) also increases with canopy depth from resistances in the region of
 605 approximately 100 s m^{-1} ; and g_{O_3} (Fig. 3d) similarly reduces from around $300 \text{ nmol O}_3 \text{ m}^{-2} \text{ s}^{-1}$
 606 between canopy layers, these differences reduce with the onset of senescence.

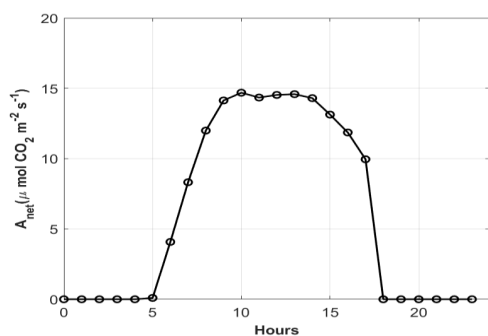
607 iii) Leaf physiology variables (A_{net} , g_{sto})

608 The DO₃SE-Crop model was able to simulate the seasonal A_{net} and g_{O_3} with values ranging from 0
 609 and 27 and 10 and 310 for A_{net} and g_{O_3} respectively over the course of the growing season (see Fig.
 610 4). The simulated daily maximum values of modelled g_{O_3} , of $310 \text{ mmol m}^{-2} \text{ s}^{-1}$ were in the range of
 611 the observed value of $340 \text{ mmol O}_3 \text{ m}^{-2} \text{ s}^{-1}$. Similarly, the modelled maximum A_{net} is $27 \mu\text{mol CO}_2 \text{ m}^{-2}$
 612 s^{-1} compared to observed value of $28 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ for the period between anthesis and 10 days
 613 before maturity for the year 2008, for both the Y2 and Y16 cultivar.

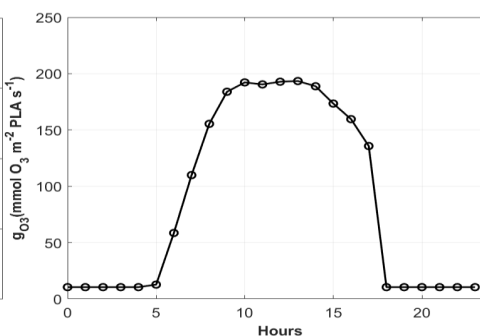
614 Fig 4. DO₃SE-Crop modelled diurnal profile of a). g_{O_3} , and b). A_{net} for a fully-expanded flag leaf prior
 615 to the start of senescence tl_{ep} for the AA and seasonal profile of daily maxima c). g_{O_3} , and d). A_{net}
 616 for the flag leaf between tl_{ep} and tl_{se} for the AA treatments. Black line showing the Start of
 617 senescence (SOS)

618

a).



b).



619

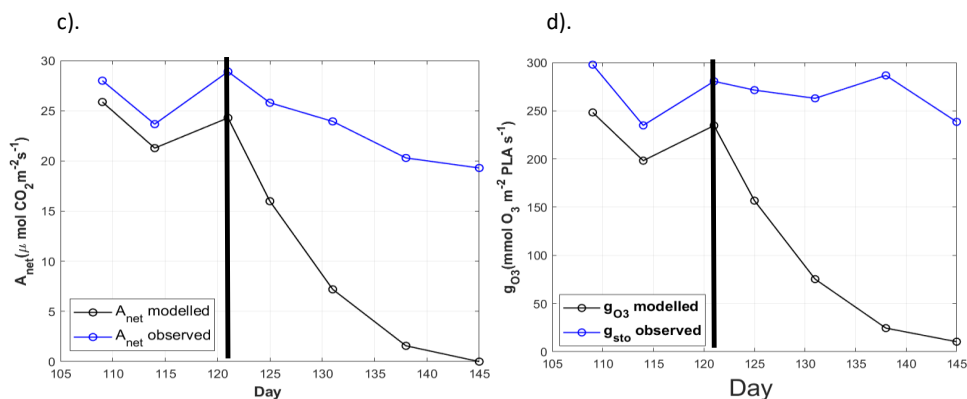
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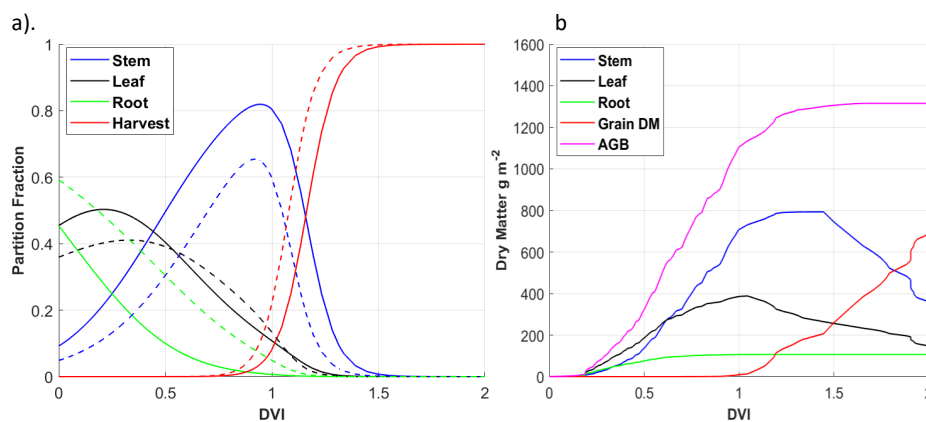
624

625 iv) Crop growth and yield.

626 The dry matter dynamics of the different parts of the crop are shown in Fig. 5. The modelled
 627 *Grain DM* value of 843 g m⁻² matched the observed value of 876 g m⁻². The stem-to-leaf ratio is
 628 2.1:1, in the range provided in the literature (Huang *et al.*, 2022). Above-ground biomass values of
 629 1510 g m⁻² also match well against the 1200-1600 g m⁻² range described in the literature (Huang *et al.*,
 630 2022; Liu *et al.*, 2022). Further, the partition fraction profiles are consistent with those of
 631 (Osborne *et al.*, 2015)(see Fig. 5); the main differences are that the modelled stem and root partition
 632 profiles are somewhat higher and lower, respectively, as compared to (Osborne *et al.*, 2015).

633 Figure 5 a). the partition fractions of the daily accumulated *NPP* partitioned to roots, stems, leaves,
 634 and grains for modelled (solid lines) vs the JULES Crop model (dashed line after (Osborne *et al.*,
 635 2015)) plotted against *DVI*, and b). the *DM* of daily accumulated *NPP* partitioned to roots, stems,
 636 leaves, and grains plotted against *DVI*.

637



638

639 v) Instantaneous and long-term O₃ impact

640

641 The *Yield_{grain}* is assumed to be damaged by both the instantaneous impact of O₃ (Farage *et al.*,
 642 1991) on photosynthesis as well as the long-term O₃ effect that can lead to enhanced senescence
 643 (Feng *et al.*, 2022). To explore which of these damage mechanisms is most important we calculated
 644 the difference between the C accumulation that would be partitioned to the grain for the AA and E-
 645 O₃ treatment as compared to a simulated very low [O₃] treatment representing pre-industrial



646 conditions for both the tolerant (Y16) and sensitive (Y2) cultivar for each of the three years (see
 647 Table 1). We found a negligible effect of O₃ (0-0.2 %) on C allocations due to the instantaneous effect
 648 of O₃ on photosynthesis compared to a highly significant (2.86-35.85 %) impact due to the long-term
 649 O₃ effect *via* the enhancement of senescence on final *Yield_{grain}*.
 650

651 Table 1. The modelled % *Yield_{grain}* loss compared to a pre-industrial O₃ scenario divided between
 652 that *Yield_{grain}* loss caused by the direct and instantaneous effect of [O₃] on photosynthesis and
 653 that due to the long-term [O₃] impact on senescence.

| Year | Tolerant: Instantaneous O ₃ effect on % <i>Yield_{grain}</i> | | Tolerant: Long-term O ₃ effect on % <i>Yield_{grain}</i> | |
|------|--|--------------------------------|--|--------------------------------|
| | Ambient versus pre-industrial | Elevated versus pre-industrial | Ambient versus pre-industrial | Elevated versus pre-industrial |
| 2007 | 0.01 | 0.01 | 2.86 | 6.6 |
| 2008 | 0 | 0 | 3.29 | 17.57 |
| 2009 | 0.03 | 0.03 | 6.40 | 25.41 |
| Year | Sensitive: Instantaneous O ₃ effect on % <i>Yield_{grain}</i> | | Sensitive: Long-term O ₃ effect on % <i>Yield_{grain}</i> | |
| | Ambient versus pre-industrial | Elevated versus pre-industrial | Ambient versus pre-industrial | Elevated versus pre-industrial |
| 2007 | 0 | 0.2 | 5.84 | 12.48 |
| 2008 | 0 | 0 | 5.21 | 26.5 |
| 2009 | 0.01 | 0.01 | 13.50 | 35.85 |

654

655 vi) Senescence

656 The breakpoint method (Mariën *et al.*, 2019) was used to determine the onset (SOS) and end (EOS)
 657 of senescence and maturity respectively using the chlorophyll content index (CCI) data which was
 658 available for the year 2008, and the Y2 and Y16 cultivars. Results showed (Fig. 6) that the E-O₃
 659 treatment for cultivars Y2 and Y16 brought forwards the SOS by 9 and 7 days respectively, and EOS
 660 by 4 and 2 days respectively.

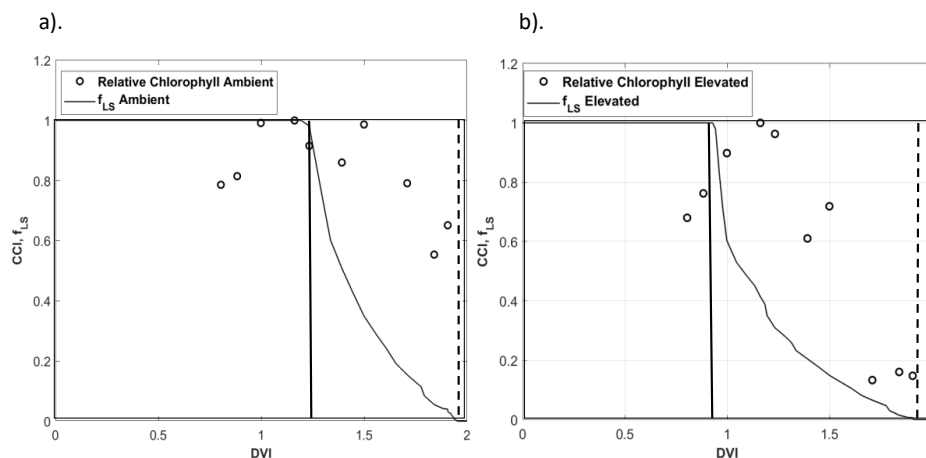
661 Figure 6. Leaf senescence profiles of O₃ induced leaf senescence for the Y2 cultivar for the
 662 a).ambient (AA) and b).elevated (E-O₃) O₃. The timing of the SOS (solid black line) and EOS (dashed
 663 black line) were determined by applying the break point method to the CCI data and are shown in
 664 relation to the *f_{LS}* simulations of senescence (grey line). The observed relative CCI data are also
 665 shown (open symbols)

666

667



668



669

670

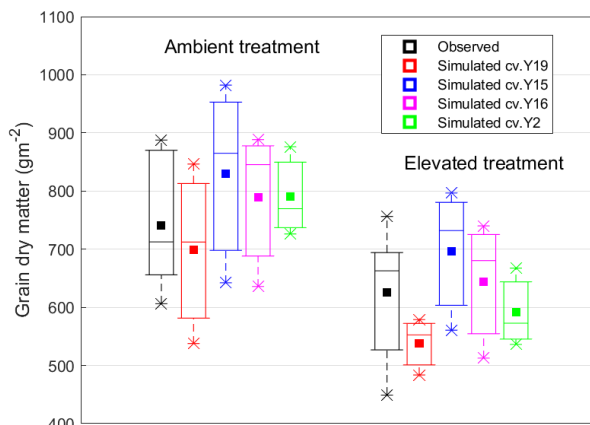
vii) Simulations across years and between cultivars

671

672 Figure 7 shows a box plot of the modelled vs observed $Yield_{grain}$ for both the sensitive (Y2) and
 673 tolerant (Y16) cultivars for each O_3 treatment (AA and E- O_3), for the years 2007, 2008 and 2009. The
 674 model simulates the difference in $Yield_{grain}$ between the AA and E- O_3 reasonably well with a
 675 simulated reduction in $Yield_{grain}$ of 29 and 131 $g\ m^{-2}$ compared with observed 81 and 165 $g\ m^{-2}$ for
 676 the tolerant and as 49 and 196 $g\ m^{-2}$ compared with observed 54 and 293 $g\ m^{-2}$ sensitive cultivars
 677 respectively. The most notable difference is that there is a larger range in the simulated $Yield_{grain}$
 678 losses of the modelled sensitive cultivar though the mean value is more conservative at 610 $g\ m^{-2}$ vs
 679 an observed value of 590 $g\ m^{-2}$.

680

681 Fig 7. Boxplots (crosses: 0.01 and 0.99 percentiles; box: 0.25 quartile, median and 0.75 quartile;
 682 square: mean) of simulated and observed wheat $Yield_{grain}$ for the tolerant (Y15 and Y16) and
 683 sensitive (Y2 and Y19) cultivars under AA and E- O_3 conditions in the years 2007, 2008 and 2009.



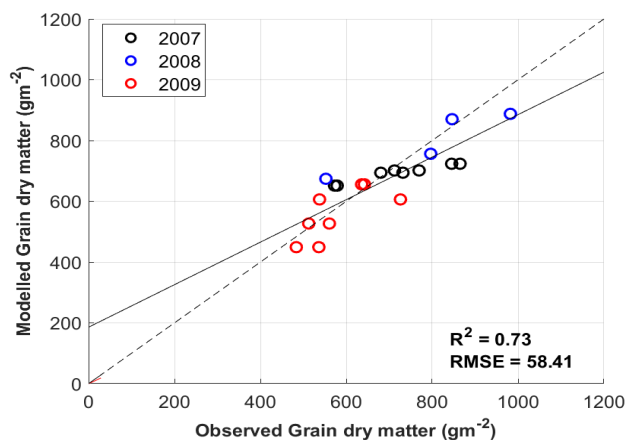
684

685 Figure 8 shows the relationship between modelled vs observed $Yield_{grain}$ (in $g\ m^{-2}$), a linear
 686 regression through these data gives an R^2 value of 0.73, showing the model is able to simulate the
 687 differences in absolute yield for different cultivars and for different years reasonably well. The data



688 points for 2007 overestimated the $Yield_{grain}$ for the E-O₃ treatments i.e. underestimating the yield
689 loss, this was due to the O₃ treatment period being substantially shorter for the year 2007 compared
690 to the other years (i.e. 2008 and 2009) by 38 days compared to 92 days.

691 Fig. 8 A scatter plot showing modelled vs observed $Yield_{grain}$ (in g m⁻²) for all 4 cultivars and 3 years
692 of the Xiaoji dataset.



693



694 Discussion

695 The DO₃SE-Crop model was found capable of simulating O₃ damage to grain yield for O₃-FACE
696 conditions at the experimental site in Xiaoji, China. Simulated yield losses between ambient and
697 elevated O₃ conditions for all years ranged between 4-19% and 7-25% for tolerant and sensitive
698 cultivars respectively, these simulated values are close to equivalent observed value ranges of
699 between 12-19% and 10-34%. However, it should be noted that the model overestimated grain dry
700 matter for the elevated O₃ treatments for the year 2007 (see Fig. 5) due to a shorter exposure
701 period. (Zhu *et al.*, 2011) argued that despite the delayed and shorter O₃ fumigation period in 2007,
702 the elevated O₃ levels were not much less than in other seasons and concluded this was the reason
703 for the same level of O₃ impact on experimental grain yield. However, the accumulated stomatal O₃
704 flux estimated by the DO₃SE-model was much higher for the elevated O₃ treatment for the years
705 2008 and 2009 (at ~ 19 mmol O₃ m⁻²) compared to 2007 (16.3 mmol O₃ m⁻²), hence the greater
706 modelled impact on the relative grain yield loss (15-18% for 2008 and 2009 versus 4-6% for 2007).

707 Overall, the DO₃SE model simulation results compare favourably to results made by the MCWLA-
708 Wheat model (Tao *et al.*, 2017) which was also calibrated for the Xiaoji experimental conditions but
709 without distinction between tolerant and sensitive varieties; MCWLA-Wheat absolute simulated
710 yield varied between ~5700 and 9000 kg/ha (compared to ~5700 to 9800 kg/ha) for ambient and
711 ~4800 to 8000 kg/ha (compared to ~5200 to 8000) for elevated O₃ treatments. A mean relative yield
712 loss of 14% was simulated by the model. For context, mean relative yield losses across East Asia
713 were estimated at 33% (with a mean range of 28-37%) by (Feng *et al.*, 2022) according to a mean
714 monitored [O₃] of 30.9 ppm h expressed as AOT40 (six-month accumulated daytime O₃
715 concentration above a threshold of 40 ppb). The mean difference in AOT40 (accumulated over only
716 75 days) between the ambient and E-O₃ treatments at Xiaoji across all years was 7.8 ppm h.

717 Crop phenology plays a crucial role in determining the entire O₃ exposure period (i.e., from crop
718 emergence to maturity), and hence O₃ damage since steady O₃ accumulation (acc_{fst}) occurring from
719 early on in the crop growth period can cause O₃ detoxification mechanisms to be overwhelmed. The
720 DO₃SE-crop model simulates the crop phenology for the three years at Xiaoji well compared to the
721 observed dataset ($R^2=0.98$, see Fig. S1). Estimating the correct timing of anthesis is crucial since the
722 period from anthesis to crop maturity is the O₃-sensitive period. During this period, accumulated
723 stomatal O₃ flux (acc_{fst}) will contribute to early and enhanced senescence once the critical
724 threshold ($CLsO_3$) is exceeded. This period also coincides with C accumulation in the grain (Kohut,
725 Amundson and Laurence, 1987; Feng, Kobayashi and Ainsworth, 2008) which may be limited by O₃-
726 induced early onset or enhanced senescence. The DO₃SE-crop model was developed to
727 accommodate the full range of effects of O₃ on senescence with revised (Ewert and Porter,
728 2000) functions able to modify both the O₃ induced onset of senescence as well as the O₃ effect on
729 maturity. This is important since experimental evidence has shown that O₃ can bring forward the
730 maturity date; for example, the flag leaf was found to have senesced 25 days earlier in a high [O₃],
731 compared to a charcoal-filtered treatment (Grandjean and Fuhrer Grandjean, 1989; Gelang *et al.*,
732 2000). O₃ was also found to cause differences in the time to maturity of the flag leaf, with Shi *et al.*
733 (2009) reporting that maturity was brought forward by eight days in an elevated O₃ (50% higher than
734 ambient) treatment. Currently, other crop models with O₃ damage functions (e.g. MLCWLA-Wheat
735 (Tao *et al.*, 2017) and LINTULLCC-22 (Feng *et al.*, 2022)) are only able to bring the O₃-induced onset of
736 senescence earlier.

737 The DO₃SE-crop model is also able to simulate differential O₃ uptake in each canopy layer. Fig. 3
738 shows that the majority of stomatal O₃ uptake occurs in the sunlit layers of the upper canopy. Similar
739 results were found in an experimental study on a productive grassland in Switzerland (Jaggi *et al.*,



740 2006) who found that different levels of O₃ exposure to canopy components predominantly located
741 in the upper and lower parts of the canopy support a multi-layer approach to modelling O₃ uptake.
742 Therefore, the focus on the upper canopy by flux-based O₃ metrics (e.g. the phytotoxic ozone dose
743 POD_y , (UNECE, 2017) seems rational in the absence of multi-layer modelling. Crop models such as
744 LINTULCC-2 (Feng *et al.*, 2022) also focus on estimating stomatal O₃ uptake at the top of the canopy
745 to estimate O₃ induced yield losses. For wheat, such an approach is further supported by the facts
746 that the upper canopy layers consist of the flag leaf, which plays a crucial role in photosynthesis and
747 grain filling (Pleijel *et al.*, 2007).

748 Our results show that the DO₃SE-crop model was able to estimate the seasonal course of A_{net} and
749 g_{O_3} daily maxima observed at the Xiaoji site (see Fig. 4a) as well as being able to produce reasonable
750 diurnal profiles for A_{net} and g_{O_3} (see Fig. 4b) when compared to other literature describing leaf
751 physiological variables (Guan *et al.*, 2015; Li *et al.*, 2022). This suggests the coupled $A_{net}g_{sto}$ model
752 is working for Chinese conditions (having previously been applied and evaluated for European O₃
753 experimental conditions – see Pande *et al.* sub). The leaf physiology parameters used in this study
754 (i.e. for Asian conditions and cultivars) are higher than parameters for European studies. For Europe,
755 V_{cmax} values of between 60 and 90 $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ were found in the literature (Feng *et al.*, 2022;
756 Pande *et al.*, sub, Van Oijen and Ewert, 1999) compared to the observed mean maximum value of
757 137 $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ at Xiaoji which was used in this study. Similarly, European J_{max} values ranged
758 from 160 to 180 $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ (Feng *et al.*, 2021, Pande *et al.* sub, Van Oijen & Ewert, 1999)
759 compared to the observed Xiaoji mean maximum value of 228 $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$.

760 Ensuring the seasonal variation in C allocation to the different components of the crop (i.e. roots,
761 stem, leaves and harvest organs) is essential for the simulation of crop growth and yield. There are
762 few data in the literature that provide these variables so we compare our results to the C allocation
763 profiles described for wheat provided in the original JULES Crop model description, recognising this
764 is intended for wheat grown globally. The DO₃SE-Crop model C allocation to the stem and roots is
765 comparatively higher than was simulated by JULES Crop ((Osborne *et al.*, 2015); see Fig. 5a).
766 However, we can justify the C allocation coefficients we used for Xiaoji since the DO₃SE-Crop model
767 was able to distribute C to different plant components to produce a well-proportioned plant over
768 the course of the growing season, this was determined by the calibration to a number of key crop
769 variables (i.e. ratios of plant respiration, LAI , stem to leaf dry matter ratios, above ground
770 components and grain dry matter. Importantly, the model, was found to simulate the grain dry
771 matter for the year 2008 and the cultivar Y16 (tolerant) & Y2 (sensitive) under the ambient and
772 elevated O₃ treatment to within 0.08- 2.19% of the observed values ($R^2 = 0.99$, 9.27 g/m² see Fig. S2).

773 The DO₃SE-Crop model, similar to other crop models with O₃ damage functions (i.e. MLCWLA-Wheat
774 (Tao *et al.*, 2017) and LINTULCC-2 (Feng *et al.*, 2022)) has the capacity to simulate both the
775 instantaneous and long-term O₃ impact on wheat grain yield. The instantaneous O₃ effect on
776 photosynthesis may cause leaf cell damage and decrease the supply of carbohydrate precursors
777 which can significantly decrease g_{O_3} , V_{cmax} and leaf chlorophyll content (Farage *et al.*, 1991).
778 Elevated O₃ also leads to generation of reactive oxygen species (ROS) in plant cells which can cause
779 oxidative damage to various cellular components. Rubisco, the enzyme responsible for C fixation in
780 the photosynthetic process, can be particularly susceptible to this damage, leading to a reduced
781 carboxylation rate (V_{cmax}). Such an ozone effect on V_{cmax} reduces net photosynthesis and can also
782 induce early senescence shortening the grain filling period (Triboi and Triboi-Blondel, 2002).
783 Results from the DO₃SE-crop model found a larger impact on yield due to the long-term O₃ impact
784 causing relative yield loss of between 2 to 36% compared to only 0 to 0.2% resulting from the
785 instantaneous O₃ impact on photosynthesis. Previous studies have also found that the long-term O₃
786 effect has a larger impact on yield compared to the instantaneous effect of O₃ on photosynthesis
787 (Emberson *et al.*, 2018; Brewster, Fenner and Hayes, 2024). Senescence is an age-dependent process



788 of degradation and degeneration that allows nutrients to be re-distributed to different plant organs
789 (Lim *et al.*, 2007). Under O₃ stress, this process is often found to occur earlier and more rapidly in
790 leaves as well as at the whole plant or crop canopy scale (Brewster, Fenner and Hayes, 2024). The
791 causes of this early and accelerated senescence are not completely understood but may be related
792 to O₃ induced enhanced expression of many genes involved in natural senescence (Miller, Arteca and
793 Pell, 1999). Elevated O₃ was also found to inhibit sugar export from leaves (Singh Yadav *et al.*, 2020;
794 Feng *et al.*, 2024) which could trigger early onset of leaf senescence.

795 The DO₃SE-crop model accounts for the impact of O₃ on the Rubisco enzyme by incorporating
796 modified (Ewert and Porter, 2000) functions for instantaneous and long-term O₃ impact on V_{cmax} as
797 an important parameter used to characterize the crop photosynthetic capacity (Ewert and Porter,
798 2000; Osborne *et al.*, 2019). The DO₃SE-crop model assumes that the O₃ will only accumulate on
799 exceedance of a stomatal O₃ flux threshold of 6 nmol O₃ m⁻² s⁻¹. The long-term O₃ impact mechanism
800 of the DO₃SE-crop model simulated the effect of senescence on V_{cmax} reasonably well as evidenced
801 by the reduction in leaf chlorophyll content. We used the breakpoint method (Yang *et al.*, no date;
802 Mariën *et al.*, 2019) to estimate the SOS and EOS using measured chlorophyll content index values
803 and. It is crucial to accurately model the timing of SOS and EOS correctly as this determines the O₃
804 effect on the duration of the grain filling period and hence the difference in yield loss due to
805 different O₃ treatments. For example, we modelled a difference of 8 and 3 and 4 and 1 days in SOS
806 & EOS respectively on average across years for the sensitive and tolerant cultivar respectively.

807 China's wheat breeding programme has seen more than 1,850 varieties used across China between
808 the 1920s to 2014 leading to increased yields from less than <1 to >5 tonnes ha⁻¹ (Qin *et al.*, 2015).
809 Here, albeit with an extremely limited dataset, we parameterise the DO₃SE-crop model for tolerant
810 and sensitive wheat crop cultivars, since many experimental studies have shown that the response
811 of different cultivars to O₃ stress differs (Biswas *et al.*, 2008). Based on the available data the model
812 seemed able to capture the difference in grain dry matter between these different cultivar groups
813 across different years reasonably well when compared against the observed dataset (R² = 0.73; see
814 Fig. 8). Such a cultivar sensitivity-based parametrisation can provide additional some information on
815 the certainty of regional yield loss estimates given the large number of wheat varieties grown across
816 China.



817 **Conclusions**

818 We have shown that the newly developed DO₃SE-Crop model can be calibrated for O₃ tolerant and
819 sensitive wheat varieties for O₃-FACE site conditions at Xioaji in China. The model is able to simulate
820 crop phenology, leaf physiology, crop growth and yield well across different years. The model is also
821 able to simulate the effect of O₃ stress on grain yield distinguishing the extent of O₃ damage
822 resulting from the same O₃ treatment on cultivars with differing O₃ sensitivities. The DO₃SE-Crop
823 model also has the advantage of simulating O₃ transfer and deposition dynamics within the wheat
824 crop canopy which could in the future improve our understanding of whole canopy O₃ effects. The
825 ability of the model to estimate relative yield losses across years also suggests the model is 'fit for
826 purpose' to assess the effects of O₃ under a variety of climate variable and [O₃] conditions.



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