Table S1: Summary of the processes employed by each crop model to simulate N. 'Indirect Env. Impacts' indicates whether water (W), CO2, or heat/ temperature are used at any stage in the model and could indirectly influence grain N through their impacts on biomass, uptake or photosynthesis, for example. 'Direct Env. Impacts' indicates which environmental variables (heat or water stress (WS) or O_3) are included as a direct influence on the grain N. The key is as follows: N demand of plant part is determined by a minimum and maximum, and/or critical N concentration = N_Dem_Part, N demand at crop/plant level is determined by a minimum and maximum, and/or critical N concentration = N_Dem_Crop, Define a N pool available to grain and set a daily rate of transfer from pool to grain = N_Grn_Rate, Define a N pool available to grain and fulfill a daily grain N demand from pool = N_Grn_Dem, N is defined on a shoot/crop basis so grain/harvest N is not distinguishable = N_Shoot, Relative C:N ratios between different plant parts = C_N. Phenology modified by N stress speeding up aging = Phen, Senescence accelerated by N stress = Sen, Biomass accumulation modified by N availability = Bio, Photosynthesis modified by N availability = Photo, Leaf area modified by N availability = L_A, O = Other, / = not simulated

** CN-Wheat calculates rate of growth, death and synthesis of proteins including protein synthesis in photosynthetic organs and the grain*

*** Leaf N is as a function of LAI and stem N is a function of degree days from sowing. Relations have been empirically determined.*

Model	**N Partitioning**	**Grain/ harvest/ storage organ N**	**Plant processes**	**Indirect Env. Impacts**	**Direct Env. Impacts**	**Source**
AFRCWheat2	N_Dem_Part	N_Grn_Dem	Phen, Sen, Bio, L_A	W, CO2, Heat	/	(Porter, 1993)
APSIM-NWheat	N_Dem_Part	N_Grn_Dem	Phen, Sen, Bio	W, CO2, Heat	Heat	(Zheng et al., 2015)
CERES-Wheat	N_Dem_Part	N_Grn_Rate	Sen, Photo, L_A	W, CO2, Heat	Heat	(Godwin and Allan Jones, 1991)
CN-Wheat	O*	O*	Photo	W, CO2, Heat	/	(Barillot et al., 2016)
CropSIM-Wheat	N_Dem_Part	N_Grn_Dem	Bio, L_A	W, CO2, Heat	Heat	(Hunt and Pararaiasingham, 1995)
CropSyst	N_Dem_Crop	N_Shoot	Bio	W, CO2, Heat	WS	(Stöckle et al., 2003)
Daisy	N_Dem_Part	N_Shoot	Photo	W, CO2, Heat	/	(Hansen et al., 1991)
DO3SE-CropN	N_Dem_Part	O (this study)	/	W, CO2, Heat	O_3	This study
EcoSys	N_Conc_Grad	N_Shoot	/	W, CO2, Heat	/	(Grant, 1998)
EPIC-Wheat	N_Dem_Crop	N_Shoot	Bio	W, Heat	/	(Williams et al., 1989)
Expert-N-Sucros	N_Dem_Part	/	?	W, CO2, Heat	?	(Kropff and Laar, 1993; Priesack et al., 2006)
FASSET	N_Dem_Part	N_Dem_Part	Bio, Photo, L_A	W, CO2, Heat	/	(Lægdsmand, 2011)
InfoCrop	N_Dem_Part	N_Grn_Dem	Phen, Bio, (Photo?), Sen	W, CO2, Heat	Heat	(Aggarwal et al., 2006)
Jules	C_N	/	Photo	W, CO2, Heat	/	(Best et al., 2011; Clark et al., 2011)
LPJmL	C_N	C_N	Photo, Bio	W, CO2, Heat	/	(Sitch et al., 2003; Von Bloh et al., 2018)
Pan et al. (2006)	O**	N_Grn_Rate	Sen	W, Heat	Heat, WS	(Pan et al., 2006)
SiriusQuality2	N_Dem_Part	N_Grn_Rate , C_N	Sen, L_A	W, CO2, Heat	/	(Martre, 2014; Martre et al., 2006)
Soltani & Sinclair	N_Dem_Part	N_Grn_Dem	Sen, L_A	W, CO2, Heat	/	(Soltani and Sinclair, 2012)
SPASS	N_Dem_Part	N_Grn_Dem	Sen, Photo, L_A	W, CO2, Heat	Heat	(Wang, 1997)
STICS	N_Dem_Part	O***	Sen, Photo, L_A	W, CO2, Heat	/	(Brisson et al., 1998; Yang et al., 2013)

**** Grain N is calculated using a N harvest index*

Summary of experimental data

Table S2: Summary of the data measured in each experiment on the Skyfall cultivar under varying levels of ozone exposure at Bangor CEH. Y=Yes data was available for this item, N=No data was not available for this item. For 2021 grain DM and grain N data was collected. However the plants did not put on any grain (Brewster, 2023) *and so the grain data for this experiment was not used*

Year	Phenology	Photosynthetic	Respiration	Straw DM	Stem & Leaf DM	Grain DM	Stem & Leaf N	Grain N
2015	Y	Y	N	Y	N	Y	N	Y
2016	Y	Y	Y	Y	N	Y	N	Y
2021	Y	N	N	Y	Y	/	Y	/

Gap filling protocol

PPFD data were obtained from NASA Power and converted to hourly PAR (NASA, 2023). All other input variables were extracted from observed meteorological data. The AgMIP Ozone gap filling protocol was followed where possible on missing experimental meteorological data (Emberson et al., 2021). Briefly, the AgMIP ozone protocol states that single hours of missing data should be filled by taking the average of neighbouring values, and several consecutive missing values should be filled by taking the average of the day before and day after. In some cases, there was not enough data available to follow the protocol. For large periods of missing temperature data, regressions from previous years between external and internal solar dome temperatures were constructed, and used to calculate internal dome temperatures. Similarly, regressions between the relative humidity (RH) of heated and ambient domes in previous years were used along with the RH of heated domes for the year of study to calculate the RH of the ambient temperature domes. All the temperature, ozone, RH and PPFD data were averaged to hourly values. Additional inputs required by DO3SE-Crop are air pressure, precipitation and wind speed which were assumed to be constant inside the solar domes and had values of 101.1818 kPa, 5 mm per hour, and 0.9 ms^{-1} respectively to account for watering and the fans inside the solar dome.

Further details of model calibration

For the purposes of this study, the focus was the calibration and evaluation of grain quality parameters and the testing of the new nitrogen module. Therefore, 100% of the available data for phenology, photosynthesis and respiration was used for calibration as these will be key determiners of the dry matter and nitrogen accumulation. For all datasets the base temperature was set as 0°C, commonly used when multiple base temperatures are not considered (Slafer and Savin, 1991). The optimum temperature was set as 21°C, which is within the range of the average optimum growth temperature over the entire growing season (Khan et al., 2021; Porter and Gawith, 1999). The maximum temperature was set as 40°C as above this temperature irreversible damage to photosynthetic organs and processes occurs (Khan et al., 2021). Following the setting of the temperature parameters, the thermal time intervals of key growth dates were calibrated so that one set of parameters was obtained for all 3 datasets.

Vcmax25 and Jmax25 were fixed at their 90th percentile values, as determined from the experimental data, to exclude outliers (148 µmol m^{-2} s^{-1} and 215 µmol m^{-2} s^{-1} respectively) for Skyfall. The dark respiration coefficient was fixed at 0.0115 by averaging the experimentally measured photosynthetic rate at 0 PAR for the ambient and elevated O3 treatments for Skyfall. D0 was fixed at 2.2. The m value was calibrated to a value of 5.641 algorithmically by maximising the R^2 between the simulated and average experimental values of gsto (535 µmol O_3 m^{-2} s^{-1}) and anet (28 µmol CO_2 m^{-2} s^{-1}).

There was a problem with the 2021 dataset in that the plants did not grow any grain (see Brewster, (2023)). Therefore, the 2021 dataset was not used to calibrate or evaluate any grain or dry matter parameters. The ratio of stem to leaf dry matter in the 2021 dataset was used to calculate a stem and leaf dry matter for the 2015 and 2016 experiments from the straw DM. These parameters ensured the splitting of straw biomass between the leaf and stem pools in the model made physiological sense. For calibration of the grain and straw (leaf + stem) dry matter the low ozone treatments from 2015 and 2016 were used. The datasets were split in half so that half of the data would be used for calibration and half for evaluation. The rationale for using a 50:50 ratio was that the Bangor 2015 dataset only had 4 recordings of dry matter; splitting any differently than 50:50 would result in only 1 data point from the 2015 experiment in either the calibration or evaluation set.

To calibrate the effect of ozone damage on grain DM, 50% of the low and very high ozone treatments from 2016 were used. The 2015 experiment was not used to calibrate ozone damage as the grain DM difference between the low and very high treatments was lower than expected for this cultivar and would result in an underestimated ozone effect on yield.

To calibrate the stem and leaf N, 50% of the low ozone treatment data from both anthesis and harvest in the 2021 dataset was used. Additionally, we used only the percentage of N in these plant parts, as the model would likely not achieve the exact correct stem and leaf DM so the absolute grams of N would likely not match the experimental data. For the leaves, the % of N was measured for flag and 2nd leaf. However, we simulate the leaf canopy as a whole. Using Barraclough et al. (2014) we understand that the flag and 2nd leaves contain more N than 3rd and 4th leaves and we expect the observations of N% in the flag and 2nd leaf to be an upper end estimate when modelling.

To calibrate grain N, 50% of the low ozone treatment data from 2016 was used. To calibrate the impact of ozone on the re-mobilisation of leaf N to the grain, 50% of the low and very high grain N % data was used from 2016.

Table S3: The parameters that were calibrated for (changed from the default parameterisation) in DO_3SE-Crop Model

Process	Parameter description	Parameter	Calibrated Value	Unit
Phenology	Base temperature	T_b	0	°C
	Optimum temperature	T_o	21	°C
	Maximum temperature	T_m	40	°C
	Plant emergence	TT_{emr}	194.7	°C days
	Flag emergence	$TT_{flag,emr}$	763.2	°C days
	Start anthesis	TT_{astart}	1271.3	°C days
	Mid-anthesis	TT_{amid}	1290.6	°C days
	Harvest	TT_{harv}	2017	°C days
Photosynthesis	Maximum carboxylation capacity at 25 °C	$V_{cmax,25}$	148	$\mu mol\ CO_2\ m^{-2} s^{-1}$
	Leaf vertical N co-efficient	kN	0	-

	Maximum rate of electron transport at 25 °C	$J_{max,25}$	215	$\mu mol\ CO_2\ m^{-2}s^{-1}$
	m	m	5.49	-
Respiration	dark respiration	R_{dcoeff}	0.0115	-
	growth respiration	R_g	0.125	-
DM parameters	Coefficient for determining DM partitioning	α_{root}	16.5	-
	Coefficient for determining DM partitioning	β_{root}	-18.61	-
	Coefficient for determining DM partitioning	α_{leaf}	18.054	-
	Coefficient for determining DM partitioning	β_{leaf}	-18.876	-
	Coefficient for determining DM partitioning	α_{stem}	17.18	-
	Coefficient for determining DM partitioning	β_{stem}	-14.384	-
	Coefficient determining specific leaf area	Ω	22.8	$m^2\ kg^{-1}$
	Fraction of stem carbon in the reserve pool	τ	0.7	-
	Fraction of DM in the harvest pool that goes to the grains (rest goes to the ear)	E_g	0.75	-
Ozone damage	O$_3$ long term damage coefficient	$\gamma 3$	9x10^{-5}	$(\mu mol\ O_3\ m^{-2})^{-1}$
	O$_3$ long term damage coefficient determining senescence onset	$\gamma 4$	4.5	-
	O$_3$ long term damage coefficient determining maturity	$\gamma 5$	1.2	-
	Critical accumulated stomatal O3 flux that determines the onset of leaf senescence	CLsO$_3$	13000	mmol O$_3$ m^{-2}

Relationship between grain DM, grain N (gm^{-2}) and grain N%

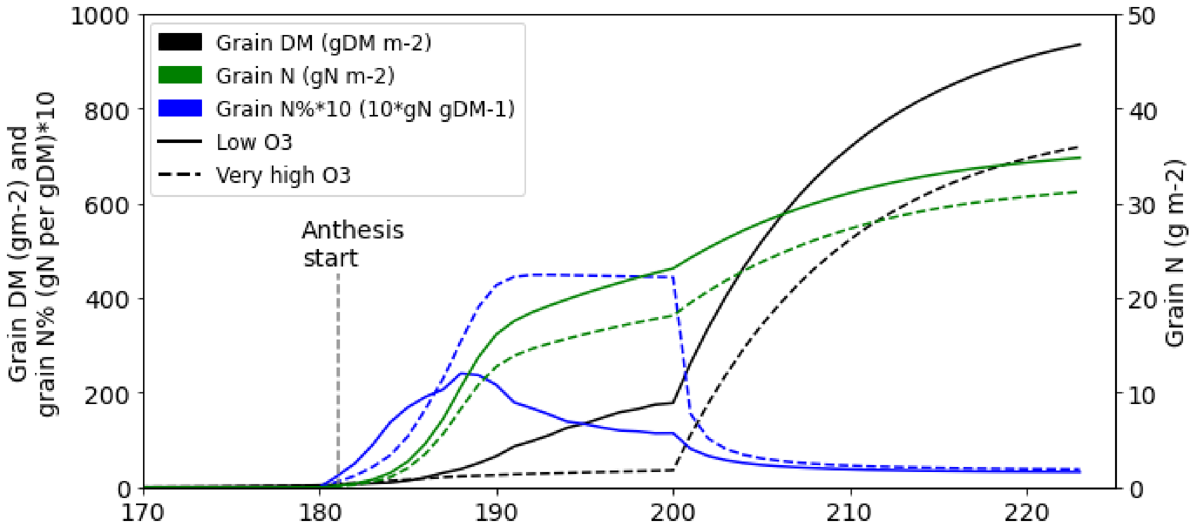

Figure S1: A conceptual figure illustrating the interdependencies between grain DM, grain N content and concentration in the newly developed DO$_3$SE-CropN model. This figure was generated using the low and very high ozone treatment data from Bangor 2015, though all years had very similar patterns. All grain N% data has been multiplied by 10 to make the figure easier to read.

Constructing N profiles from existing literature

Data was taken from all 6 field experiments of Groot (1987). For each experiment the date, Zadoks value, green leaf and dead leaf nitrogen, stem nitrogen and grain nitrogen were extracted. The nitrogen treatments were ignored at this stage. The green and dead leaf nitrogen were summed to give a total leaf nitrogen. Data were extracted for measurements in g kg^{-1} and kg ha^{-1} separately as these were measured using different methods (Groot, 1987). Additional data was extracted on leaf, stem and grain nitrogen using WebPlotDigitizer (https://automeris.io/WebPlotDigitizer/) , from Bertheloot et al. (2008) and Nagarajan et al. (1999). Bertheloot et al. (2008) and Nagarajan et al. (1999) recorded the time points of their measurements in degree days after anthesis and days after anthesis respectively. For all 3 sources, the stem, leaf and grain nitrogen measurements cover a range of soil types, cultivars, countries, nitrogen treatments and water stress; though these conditions were not taken into consideration and the data has been grouped together.

Each of the datasets had recorded the time using different metrics. Therefore, the first stage of analysis was to convert them all to the same units. Using the Groot (1987) data, a regression was fit between the number of days after sowing, and the Zadoks value for each nitrogen treatment of each experiment. Assuming a Zadoks value of 61 corresponds to anthesis, the regression was solved to calculate the number of days after sowing that anthesis occurred. Although the relation between days after sowing and the Zadoks scale is not linear, some treatments and experiments only had 2 data points so it was not possible to account for greater complexity in the relationship. Using the date of anthesis for each treatment and experiment, the number of days after anthesis was calculated for each measurement in the Groot (1987), making it the same scale as the Nagarajan et al. (1999) data. The Bertheloot et al. (2008) was measured in degree days after anthesis not days after anthesis. To calculate the time measurement in days after anthesis, the anthesis dates and final measurement dates (assumed to be harvest) were matched to calculate a conversion factor between the two.

For the leaf, stem and grain, the total nitrogen of these plant parts was summed for every time point of each treatment and experiment, and the fractional leaf, stem and grain nitrogen calculated by dividing the component nitrogen by the total. The 95% confidence intervals were calculated and smoothed using Loess smoothing in Python. The resulting plot is shown in Figure S2 and can be used to describe how the N content in the stem, leaves, and grains changes over time respective to each other.

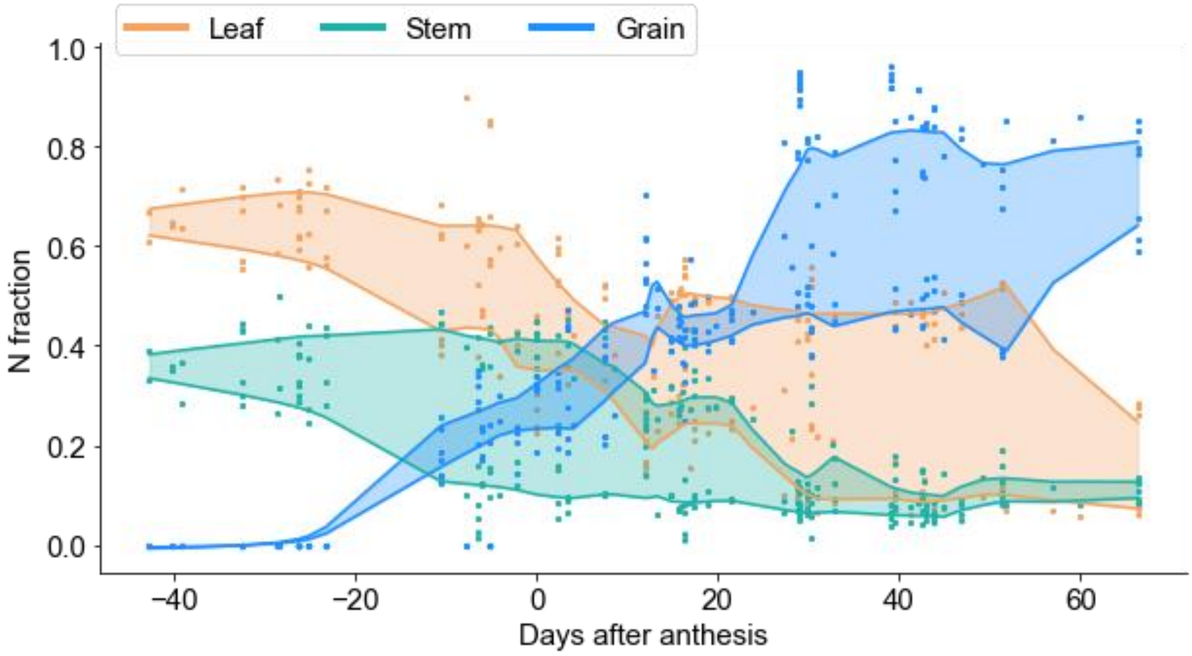

Figure S2: The proportion of total plant N stored in the leaf, stem and grain of the wheat plant using experimental data from Bertheloot et al. (2008), Groot (1987), and Nagarajan et al. (1999). The points represent the experimental data, and the solid lines indicate the upper and lower bounds of the 95% confidence interval applied using a LOESS smoothing factor of 0.2.

The grain weight (mg), and the grain N (mg per grain) were extracted from Figures 1 and 2 of Panozzo and Eagles (1999) using WebPlotDigitizer (https://automeris.io/WebPlotDigitizer/). From this the grain N% could be calculated for each treatment and timepoint. The mean of the irrigated and dry treatment data for each timepoint was calculated and the resulting profile of grain N% over time is given in Figure S3.

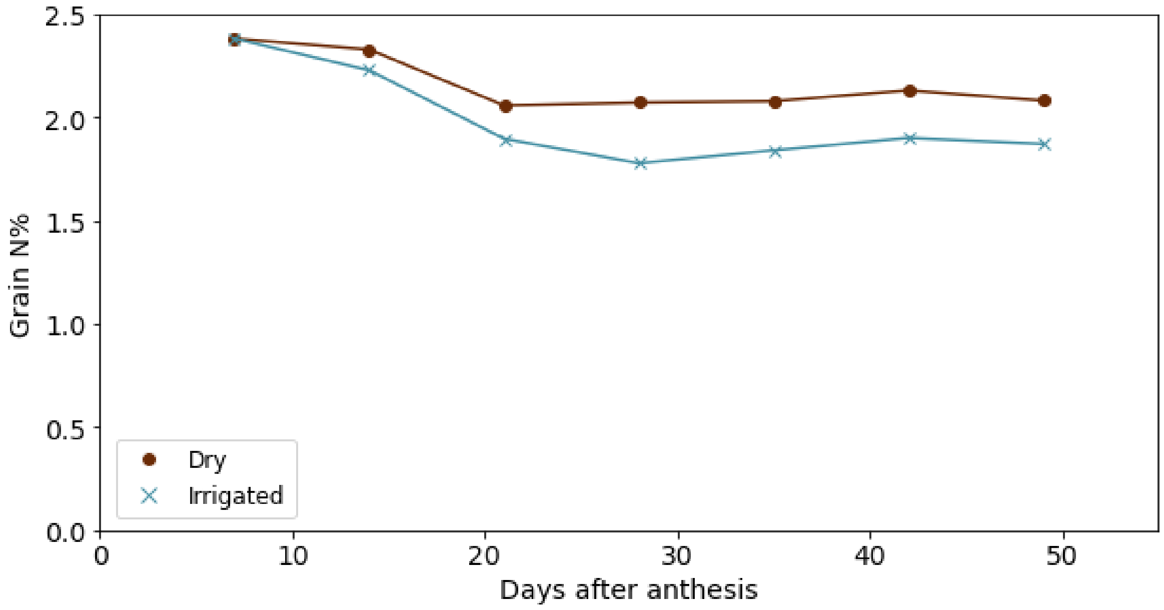

Figure S3: The dynamic profile of grain N% as calculated from available data in Panozzo and Eagles (1999) for wheat kept under dry and irrigated conditions. Figures 1 and 2 from which this data was extracted used averaged data from 4 wheat cultivars: Rosella, Hartog, Halberd and Eradu.

Profiles of grain N% were also constructed from data available in Nagarajan et al. (1999). The carbon and nitrogen content were extracted from Figures 4 and 5 in Nagarajan et al. (1999) using WebPlotDigitizer (https://automeris.io/WebPlotDigitizer/). By assuming the fraction of C in DM is 50% (Osborne et al., 2015), the existing data was used to construct the profile in Figure S4.

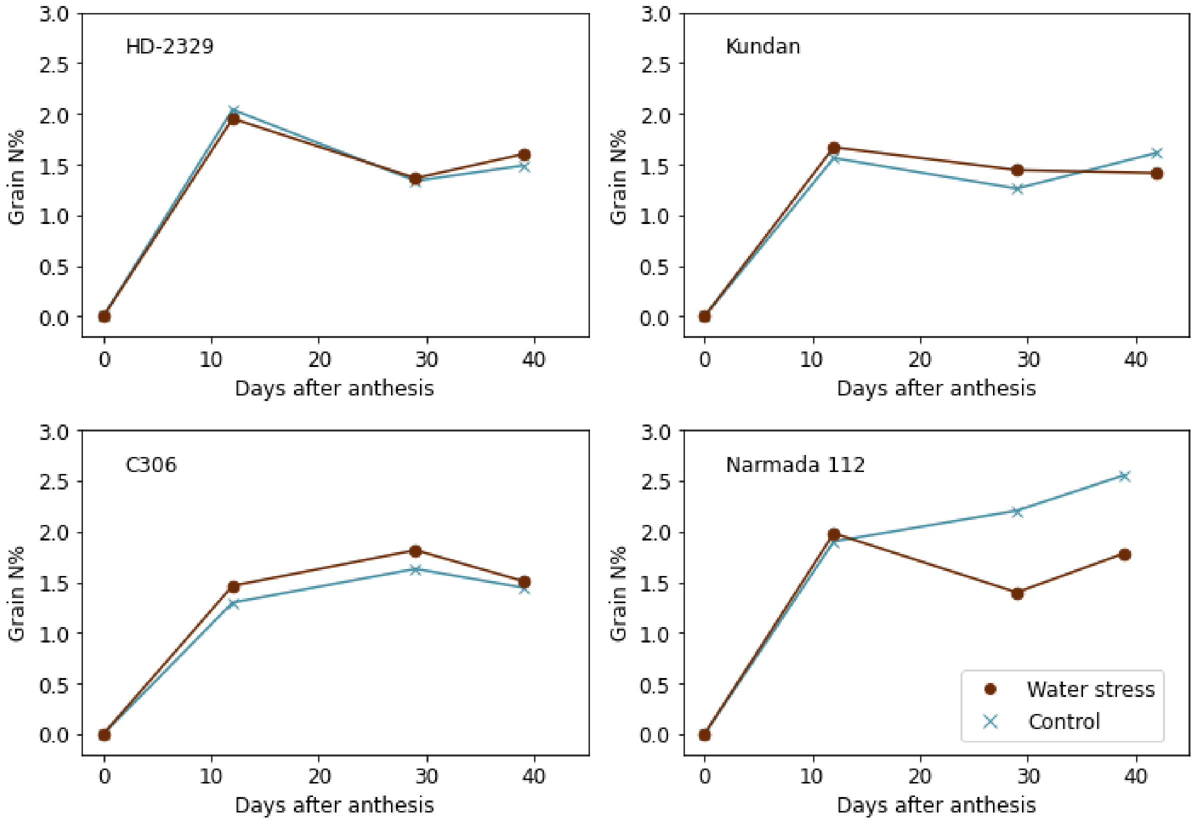

Figure S4: The temporal profile of grain N% for the 4 wheat cultivars measured by Nagarajan et al. (1999) for water stress and a control treatment.