Large but decreasing effect of ozone on the European carbon sink

Rebecca J Oliver[1], Lina M Mercado[1,2], Stephen Sitch[2], David Simpson[3,4], Belinda E Medlyn[5], Yan-Shih Lin[5], Gerd A Folberth[6]

[1] Centre for Ecology and Hydrology, Benson Lane, Wallingford, OX10 8BB, UK

[2] College of Life and Environmental Sciences, University of Exeter, EX4 4RJ, Exeter, UK

[3] EMEP MSC-W Norwegian Meteorological Institute, PB 43, NO-0313, Oslo, Norway

[4] Dept. Space, Earth & Environment, Chalmers University of Technology, Gothenburg, SE-41296 Sweden

[5] Hawkesbury Institute for the Environment, Western Sydney University, Locked Bag 1797, Penrith NSW 2751 Australia

[6] Met Office Hadley Centre, Exeter, UK.

Correspondence to: Rebecca Oliver (rfu@ceh.ac.uk)

Abstract

The capacity of the terrestrial biosphere to sequester carbon and mitigate climate change is governed by the ability of vegetation to remove emissions of CO_2 through photosynthesis. Tropospheric O_3, a globally abundant and potent greenhouse gas, is, however, known to damage plants, causing reductions in primary productivity, yet the impact of this gas on European vegetation and the land carbon sink is largely unknown. Despite emission control policies across Europe, background concentrations of tropospheric O_3 have risen significantly over the last decades due to hemispheric-scale increases in O_3 and its precursors. Therefore, plants are exposed to increasing background concentrations, at levels currently causing chronic damage. We use the JULES land-surface model recalibrated for O_3 impacts on European vegetation, with an improved stomatal conductance parameterization, to quantify the impact of tropospheric O_3, and its interaction with CO_2, on gross primary productivity (GPP) and land carbon storage across Europe. A factorial set of model experiments showed that tropospheric O_3 can ~~significantly~~ suppress terrestrial carbon uptake across Europe over the period 1901 to 2050. By 2050, simulated GPP was reduced by 4 to 9% due to plant ozone damage and land carbon storage by 3 to 7%.~~,~~ T~~However, t~~he combined physiological effects of elevated future CO_2 (acting to reduce stomatal opening) and reductions in O_3 concentrations resulted in reduced O_3 damage in the future, contrary to predictions from earlier studies. This alleviation of O_3 damage by CO_2 induced stomatal closure was around 1 to 2% for low and high sensitivity respectively (on both land carbon and GPP). Reduced land carbon storage resulted from diminished soil carbon stocks consistent with the reduction in GPP. Regional variations are identified with larger impacts shown for temperate Europe (GPP reduced by 10 to 20%) compared to boreal regions (GPP reduced by 2 to 8%). These results highlight that O_3 damage needs to be considered when predicting GPP and land carbon, and that the effects of O_3 on plant physiology need to be considered in regional ~~add to the uncertainty of future trends in the~~ land carbon cycle assessments.~~sink.~~ ~~and, as such, this should be incorporated into carbon cycle assessments.~~

Commented [ORJ1]: RC1 1):

RC1 2):

1 Introduction

The terrestrial biosphere absorbs around 30% of anthropogenic CO_2 emissions and acts to mitigate climate change (Le Quéré et al., 2015). Early estimates of the European carbon balance suggest a terrestrial carbon sink of between 135 to 205 TgC yr^{-1} (Janssens et al., 2003). Schulze et al. (2009) determined a larger carbon sink of 274 TgC yr^{-1}, and more recent estimates suggest a European terrestrial sink of between 146 to 184 TgC yr^{-1} (Luyssaert et al., 2012). The carbon sink capacity of land ecosystems is dominated by the ability of vegetation to sequester carbon through photosynthesis and release it back to the atmosphere through respiration. Therefore, any change in the balance of these fluxes will alter ecosystem source-sink behaviour.

In recent decades much attention has focussed on the effects of rising atmospheric CO_2 on vegetation productivity (Ceulemans and Mousseau, 1994;Norby et al., 2005;Norby et al., 1999;Saxe et al., 1998). The Norby et al. (2005) synthesis of Free Air CO_2 Enrichment (FACE) experiments suggests a median stimulation (23 ± 2%) of forest NPP in response to a doubling of CO_2. Similar average increases (20%) were observed for C_3 crops, although this translated into smaller gains in biomass (17%) and crop yields (13%) (Long et al., 2006). ~~The long-term effects of CO_2 fertilization on plant growth and carbon storage are nevertheless uncertain~~ (!!! INVALID CITATION !!!)~~.~~ Little attention, however, has been given to tropospheric ozone (O_3), a globally abundant ~~and increasing~~ air pollutant recognised as one of the most damaging pollutants for forests (Karlsson et al., 2007;Royal-Society, 2008;Simpson et al., 2014b). Tropospheric O_3 is a secondary air pollutant formed by photochemical reactions involving carbon monoxide (CO), volatile organic compounds (VOCs), methane (CH_4) and nitrogen oxides (NO_x) from both man-made and natural sources, as well as downward transport from the stratosphere and lightning which is a source of NO_x. The phytotoxic effects of O_3 exposure are shown to decrease vegetation productivity and biomass, with consequences for terrestrial carbon sequestration (Felzer et al., 2004;Loya et al., 2003;Mills et al., 2011b;Sitch et al., 2007). Few studies, however, consider the simultaneous effects of exposure to both gases, and few Earth-system models (ESMs) currently explicitly consider the role of tropospheric O_3 in terrestrial carbon dynamics (IPCC, 2013), both of which are key to understanding the carbon sequestration potential of the land-surface, and future carbon dynamics regionally and globally.

Commented [ORJ2]: RC2 minor comment 2.

Due to increased anthropogenic precursor emissions over the industrial period, background concentrations of ground-level O_3 have risen (Vingarzan, 2004) ~~(Parrish et al., 2012)~~. O_3 levels at the start of the 20th century are estimated to be around 10 ppb for the site Montsouris Observatory near Paris, data for Arkona on the Baltic coast increased from ca. 15 ppb in the 1950s to 20-27 ppb by the early 1980s, and the Irish coast site Mace Head shows around 40 ppb by the year 2000 (Logan et al., 2012;Parrish et al., 2012). Present day annual average background O_3 concentrations reported in the review of (Vingarzan, 2004) show O_3 concentrations range between approximately 20 and 45ppb, with the greatest increase occurring since the 1950s. Trends vary from site to site though, even on a decadal basis (Logan et al., 2012;Simpson et al., 2014b), depending, for example, on local/regional trends in precursor (especially NOx) emissions, elevation, and exposure to long-range transport. Nevertheless, there is some indication that background O_3 levels over the mid-latitudes of the Northern Hemisphere have continued to rise at a rate of approximately 0.5–2% per year, although not uniform (Vingarzan, 2004). As a result of controls on precursor emissions in Europe and North America, peak O_3 concentrations in

Commented [ORJ3]: RC2 minor comment 3.

Commented [ORJ4]: RC1 5)

these regions have decreased or stabilised over recent decades (Cooper et al., 2014;Logan et al., 2012;Parrish et al., 2012;Simpson et al., 2014b). Nevertheless, climate change may increase the frequency of weather events conducive to peak O_3 incidents in the future (e.g. summer droughts and heat-waves; e.g., (Sicard et al., 2013), and may increase biogenic emissions of the O_3-precursors isoprene and NO_x, although such impacts are subject to great uncertainty (Simpson et al., 2014b;Young et al., 2013;Young et al., 2009). I~~Furthermore, i~~ntercontinental transport of air pollution~~,~~ from regions such as Asia that currently have poor emission controls are thought to contribute substantially to rising~~means~~ background O_3 concentrations~~, have risen significantly~~ over the last decades (Cooper et al., 2010;Verstraeten et al., 2015). Northern Hemisphere background concentrations of O_3 are now close to established levels for impacts on human health and the terrestrial environment (Royal-Society, 2008). Therefore, although peak O_3 concentrations are in decline across Europe, plants are exposed to increasing background levels, at levels currently causing chronic damage (Mills et al., 2011b). Intercontinental transport means future O_3 concentrations in Europe are dependent on how O_3 precursor emissions evolve globally.~~, including regions such as Asia that currently have poor emission controls (Cooper et al., 2010;Verstraeten et al., 2015).~~

Elevated O_3 concentrations impact agricultural yields and nutritional quality of major crops (Ainsworth et al., 2012;Avnery et al., 2011), with consequences for global food security (Tai et al., 2014). As well as being a significant air pollutant, O_3 is a potent greenhouse gas (Royal-Society, 2008). High levels of O_3 are damaging to ecosystem health and reduce the global land carbon sink (Arneth et al., 2010;Sitch et al., 2007). Reduced uptake of carbon by plant photosynthesis due to O_3 damage allows more CO_2 to remain in the atmosphere. This effect of O_3 on plant physiology represents an additional climate warming to the direct radiative forcing of O_3 (Collins et al., 2010;Sitch et al., 2007), the magnitude of which, however, remains highly uncertain (IPCC, 2013).

Dry deposition of O_3 to terrestrial surfaces, primarily uptake by stomata on plant foliage and deposition on external surfaces of vegetation, is a large~~significant~~ sink for ground level O_3 (Fowler et al., 2009;Fowler et al., 2001). On entry to sub-stomatal spaces, O_3 reacts with other molecules to form reactive oxygen species (ROS). Plants can tolerate a certain level of O_3 depending on their capacity to scavenge and detoxify the ROS (Ainsworth et al., 2012). Above this critical level, long-term chronic O_3 exposure reduces plant photosynthesis and biomass accumulation (Ainsworth, 2008;Ainsworth et al., 2012;Matyssek et al., 2010a;Wittig et al., 2007;Wittig et al., 2009), either directly through effects on photosynthetic machinery such as reduced Rubisco content (Ainsworth et al., 2012;Wittig et al., 2009) and/or indirectly by reduced stomatal conductance (g_s) (Kitao et al., 2009;Wittig et al., 2007), alters carbon allocation to different pools (Grantz et al., 2006;Wittig et al., 2009), accelerates leaf senescence (Ainsworth, 2008;Nunn et al., 2005;Wittig et al., 2009) and changes plant susceptibility to biotic stress factors (Karnosky et al., 2002;Percy et al., 2002).

The response of plants to O_3 is very wide ranging as reported in the literature from different field studies. ~~We compare results from the present study to values found in literature.~~ The Wittig et al. (2007) meta-analysis of temperate and boreal tree species showed future concentrations of O_3 predicted for 2050 significantly reduced leaf level light saturated net photosynthetic uptake (-19%, range: -3% to -28%) and g_s (-10%, range: +5% to -23%) in both broadleaf and needle leaf tree species. In the Feng et al. (2008) meta-analysis of wheat, projected O_3

Commented [ORJ5]: RC2 minor comment 4.

Field Code Changed

Commented [ORJ6]: RC2 minor comment 5.

Commented [ORJ7]: RC2 minor comment 6.

Commented [ORJ8]: RC2 minor comment 7.

concentrations for the future reduced aboveground biomass (-18%) , CI -13% to -24%), photosynthetic rate (-20%) and g_s (-22%). One of few long-term field based O_3 exposure studies (AspenFACE) showed that after 11 years of exposing mature trees to elevated O_3 concentrations, O_3 decreased ecosystem carbon content (-9%), and decreased NPP (-10%), although the O_3 effect decreased through time (Talhelm et al., 2014). Zak et al. (2011) showed this was partly due to a shift in community structure as O_3-tolerant species, competitively inferior in low O_3 environments, out competed O_3-sensitivie species. Zak et al. (2011) GPP was reduced (-12% to -19%) at two Mediterranean ecosystems exposed to elevated O_3 (dominated by either *Pinus* species or *Citrus* species) studied by Fares et al. (2013). Biomass of mature beech trees was reduced (-44%) after 8 years of exposure to elevated O_3 (Matyssek et al., 2010a). After 5 years of O_3 exposure in a semi-natural grassland, annual biomass production was reduced (-23%), and in a Mediterranean annual pasture O_3 exposure significantly reduced total aboveground biomass (up to -25%) (Calvete-Sogo et al., 2014). However, these were empirical studies at individual sites, and these focus on O_3 effects on plant physiology and productivity, but do not quantify the impact on the land carbon sink. Modelling studies are needed to scale site observations to the regional and global scales. Models generally suggest that plant productivity and carbon sequestration will decrease with O_3 pollution, though the magnitudes vary. For example, based on a limited dataset to parameterise plant O_3 damage for a global set of plant functional types, Sitch et al. (2007) predicted a decline in global GPP of 14 to 23% by 2100. A second study by Lombardozzi et al. (2015) similarly predicted a 10.8% decrease of global GPP. Here we take a regional approach and take advantage of new measurements specifically for European vegetation and conduct a dedicated analysis for the European region. Results from the present study suggest projected O_3 concentrations for 2050 will reduce mean GPP for Europe (-4% to -9%), NPP (-6% to -11%), total carbon content (-3% to -7%) and g_s (-4% to -9%). Using GPP as a proxy for A_{sat} (these variables are not identical but they are related), our mean GPP and g_s estimates fall within the range given by the meta-analysis of Wittig et al. (2007). The remaining studies are not meta-analyses, so are site- and species- specific, our estimates appear to compare more conservatively with these, however these are a mean value for Europe and spatially our estimates show greater variability.

Understanding the response of plants to elevated tropospheric O_3 is challenged by the large variation in O_3 sensitivity both within and between species (Karnosky et al., 2007;Kubiske et al., 2007;Wittig et al., 2009). Additionally, other environmental stresses that affect stomatal behaviour will affect the rate of O_3 uptake and therefore the response to O_3 exposure, such as high temperature, drought and changing concentrations of atmospheric CO_2 (Mills et al., 2016;Fagnano et al., 2009;Kitao et al., 2009;Löw et al., 2006), such that the response of vegetation to O_3 is a balance between opposing drivers of stomatal behaviour. Increasing concentrations of atmospheric CO_2, for example, are suggested to provide some protection against O_3 damage by causing stomata to close (Harmens et al., 2007;Wittig et al., 2007), however the long-term effects of CO_2 fertilisation The long-term effects of CO_2 fertilization on plant growth and carbon storage remain are nevertheless uncertain (Baig et al., 2015;Ciais et al., 2013). Further, in some studies, stomata have been shown to respond sluggishly, losing their responsiveness to environmental stimuli with exposure to O_3 which can lead to higher O_3 uptake, increased water-loss and therefore greater vulnerability to environmental stresses such as drought (Mills et al., 2016;Mills et al., 2009;Paoletti and Grulke, 2010;Wilkinson and Davies, 2009). ….Mention uncertainties

Commented [ORJ9]: RC1 3/4/6)

Field Code Changed

~~around CO2 fertilisation here, nutrient cycling and stomatal sluggishness here. Maybe introduce Medlyn model here~~

Commented [ORJ10]: RC2 6)

Given the critical role g_s plays in the uptake of both CO_2 and O_3, we use an alternative~~improved~~ representation and parameterisation of g_s in JULES by implementing the Medlyn *et al.* (2011) g_s formulation. This model is b~~B~~ased on the optimal theory of stomatal behaviour, it does not currently include a representation of sluggish stomatal control, but it ~~Medlyn *et al.*, (2011)~~ has the following advantages over the current JULES g_s formulation of Jacobs (1994): i) a single parameter (g_1) which represents the marginal cost of water-use, compared to two parameters in Jacobs (1994) representing the the critical humidity deficit at the leaf surface (*dqcrit*) and the *ci*/*ca* ratio at the leaf critical humidity deficit (*f0*) (Clark et al., 2011); ii) easier~~y~~ to parameterise with leaf or canopy level observations of photosynthesis, g_s and humidity – all variables that are commonly measured, and (iii) values of g_1 are available for many different plant functional types (PFTs) derived from a global data set of ~~measured~~ leaf-level measurements ~~stomatal conductance, photosynthesis and vapour pressure deficit (VPD)~~ (Lin et al., 2015).

Commented [ORJ11]: RC2 3)

~~Here we~~The main objective of this work is to assess the impact of historical and projected (1901 to 2050) changes in tropospheric O_3 and atmospheric CO_2 concentration ~~from 1901 to 2050~~ on ~~the~~predicted GPP and the ~~European~~ land-carbon sink for Europe. These are the two greenhouse gases that directly affect plant photosynthesis and g_s. We use a factorial suite of model experiments, using the Joint UK land environment simulator (JULES) (Best et al., 2011;Clark et al., 2011), the land-surface model of the UK Earth System Model (UKESM) (Collins et al., 2011) to simulate plant O_3 uptake and damage, and to look at the interaction between O_3 and CO_2. In this work, plant O_3 damage in JULES is developed further by introducing a term for dry deposition of O_3 to external plant surfaces, an important sink for tropospheric O_3 that was previously absent from the model. Further, the model is re-calibrated using the latest observations of vegetation sensitivity to O_3, with the addition of a separate parameterisation for temperate/boreal regions versus the Mediterranean. The p~~P~~lant O_3 sensitivity of each PFT in JULES was re-calibrated for both a ~~(~~high and low plant O_3 sensitivity to account for the large variation in O_3 sensitivity within and between species.~~)~~ ~~using the latest observations for European vegetation in order to capture a range of plant sensitivities to O_3 – t~~This includes separate sensitivities for Mediterranean regions, and for agricultural crops (wheat) versus natural grassland. We make a separate distinction for the Mediterranean region where possible because the work of Büker et al. (2015) showed that different O_3 dose-response relationships are needed to describe the O_3 sensitivity of dominant Mediterranean trees. ~~We modify the representation of stomatal O_3 flux in JULES from Sitch *et al*., (2007) by including a term for non-stomatal deposition of O_3 to leaf surfaces which is recognised as an important sink for ground-level O_3.~~ In addition, we introduce an alternative g_s scheme into JULES as described above. JULES is forced with spatially varying hourly O_3 concentrations from a high resolution atmospheric chemistry model for Europe, therefore our simulations account for diurnal variations in O_3 concentration and O_3 responses allowing for more accurate estimations of O_3 uptake by vegetation. We do not attempt to make a full assessment of the carbon cycle of Europe, instead we target O_3 damage, and its interaction with CO_2, which is currently a missing component in earlier carbon cycle assessments (Le Quéré et al., 2017;Sitch et al., 2015). To this end, we prescribe changing O_3 and CO_2 concentrations from 1901 to 2050, but use a fixed pre-industrial climate. We

Commented [ORJ12]: RC2 minor comment 8.

acknowledge the use of a 'fixed' pre-industrial climate omits the additional uncertainty of the interaction between climate change and g_s which will affect the rate of O_3 uptake and therefore O_3 concentrations. To understand the impact of these complex feedback mechanisms is an important area for future work, but in the current study our aim is to isolate the physiological response of plants to both O_3 and CO_2, and determine the sensitivity of predicted GPP and the land carbon sink to this process, as the impact of O_3 on European vegetation and the land carbon sink currently remains largely unknown.

Commented [ORJ13]: RC1 2)

Commented [ORJ14]: RC2 1)

Given the critical role g_s plays in the uptake of both CO_2 and O_3, we use an improved representation and parameterisation of g_s in JULES by implementing the Medlyn *et al.* (2011) g_s formulation. Based on the optimal theory of stomatal behaviour, Medlyn *et al.*, (2011) has the following advantages over the current JULES g_s formulation: i) a single parameter (g_1) which represents the marginal cost of water-use; ii) easy to parameterise with leaf or canopy level observations, and (iii) values of g_1 are available for different plant functional types (PFTs) derived from a global data set of measured leaf stomatal conductance, photosynthesis and vapour pressure deficit (VPD) (Lin et al., 2015).

We use a factorial suite of model experiments to investigate the temporal and spatial evolution of O_3 impacts on European vegetation from 1901 to 2050. We do not attempt to make a full assessment of the carbon cycle of Europe, instead we target O_3 damage which is currently a missing component in earlier carbon cycle assessments. Accounting for the well-known differences in plant sensitivity to O_3 is complex, therefore, here we provide a sensitivity assessment by using two sets of simulations – a high and lower plant O_3 sensitivity parameterisation, with O_3 sensitivities that vary by PFT and region. We investigate the interaction between CO_2 and O_3, the two greenhouse gases that directly affect plant photosynthesis, and indirectly g_s. Our aim is to quantify the impact of these two gases on GPP and land carbon storage across Europe. We go beyond the present-day carbon budget and investigate the impact of state-of-art future scenarios up to year 2050.

2 Methods

2.1 Representation of O_3 effects in JULES

JULES calculates the land-atmosphere exchanges of heat, energy, mass, momentum and carbon on a sub-daily time step, and includes a dynamic vegetation model (Best et al., 2011;Clark et al., 2011;Cox, 2001). This work uses JULES version 3.3 (http://www.jchmr.org) at 0.5° x 0.5° spatial resolution and hourly model time step, the spatial domain is shown in Fig. S5., JULESwhich hasuses a multi-layer canopy radiation interception and photosynthesis scheme (10 layers in this instance) that accounts for direct and diffuse radiation, sun fleck penetration through the canopy, inhibition of leaf respiration in the light and change in photosynthetic capacity with depth into the canopy (Clark et al., 2011;Mercado et al., 2009). Soil water content also affects the rate of photosynthesis and g_s. It is modelled using a dimensionless soil water stress factor, β, which is related to the mean soil water concentration in the root zone, and the soil water contents at the critical and wilting point (Best *et al.*, 2011).

Commented [ORJ15]: RC2 minor comment 9.

To simulate the effects of O_3 deposition on vegetation productivity and water use, JULES uses the flux-gradient approach of Sitch *et al*., (2007), modified to include non-stomatal deposition following Tuovinen et al. (2009). JULES uses a coupled model of g_s and photosynthesis; because of the relationship between these two fluxes, the direct effect of O_3 damage on photosynthetic rate also leads to a reduction in g_s. Changes in atmospheric CO_2 concentration also affect photosynthetic rate and g_s, consequently the interaction between changing concentrations of both gases is allowed for. Specifically, the potential net photosynthetic rate (A_p, mol CO_2 m^{-2} s^{-1}) is modified by an 'O_3 uptake' factor (*F,* the fractional reduction in photosynthesis), so that the actual net photosynthesis (A_{net}, mol CO_2 m^{-2} s^{-1}) is given by equation 1 (Clark *et al.,* 2011, Sitch *et al.,* 2007).

$$A_{net} = A_P F \tag{1}$$

The O_3 uptake factor (F) is defined as:

$$F = 1 - a * max[F_{O3} - F_{O3crit}, 0.0] \tag{2}$$

F_{O3} is the instantaneous leaf uptake of O_3 (nmol m^{-2} s^{-1}), F_{O3crit} is a PFT-specific threshold for O_3 damage (nmol m^{-2} PLA s^{-1}, projected leaf area), and 'a' is a PFT-specific parameter representing the fractional reduction of photosynthesis with O_3 uptake by leaves. Following Tuovinen et al. (2009), the flux of O_3 through stomata, F_{O3}, is represented as follows:

$$F_{O3} = O_3 \left(\frac{g_b \left(\frac{g_l}{K_{O3}}\right)}{g_b + \left(\frac{g_l}{K_{O3}}\right) + g_{ext}} \right) \tag{3a}$$

O_3 is the molar concentration of O_3 at reference (canopy) level (nmol m^{-3}), g_b is the leaf-scale boundary layer conductance (m s^{-1}, eq 3b), g_l is the leaf conductance for water (m s^{-1}), K_{o3} accounts for the different diffusivity of ozone to water vapour~~is the ratio of leaf resistance for O_3 to leaf resistance for water vapour~~ and takes a value of 1.51 after Massman (1998), and g_{ext} is the leaf-scale non-stomatal deposition to external plant surfaces (m s^{-1}) which takes a constant value of 0.0004 m s^{-1} after Tuovinen et al. (2009). The leaf-level boundary layer conductance (g_b) is calculated as in Tuovinen *et al*. (2009)

Commented [ORJ16]: RC2 minor comment 10.

$$g_b = \alpha L d^{-1/2} U^{-1/2} \tag{3b}$$

α is a constant (0.0051 m $s^{-1/2}$), Ld is the cross-wind leaf dimension (m) and U is wind speed at canopy height (m s^{-1}). The rate of O_3 uptake is dependent on g_s, which is dependent on photosynthetic rate. Given g_s is a linear function of photosynthetic rate in JULES (Clark et al., 2011), from eq 1 it follows that:

$$g_s = g_l F \tag{4}$$

The O_3 flux to stomata, F_{O3}, is calculated at leaf level and then scaled to each canopy layer differentiating sunlit and shaded leaf photosynthesis, and finally summed up to the canopy level. Because the photosynthetic capacity, photosynthesis and therefore g_s decline with depth into the canopy, this in turn affects O_3 uptake, with the top leaf level contributing most to the total O_3 flux and the lowest level contributing least.

2.2 Calibration of O_3 uptake model ~~for European vegetation~~

Here we use the latest literature on O_3 dose-response relationships derived from observed field data across Europe (CLRTAP, 2017) to determine the key PFT-specific O_3 sensitivity parameters in JULES (*a* and Fo_{3crit}). Each JULES PFT (broadleaf, needle leaf, C_3 and C_4 herbaceous, and shrub) was calibrated for a high and low plant O_3 sensitivity to account for uncertainty in variation of species sensitivity to O_3, using the approach of Sitch *et al.*, (2007). For the C_3 herbaceous PFT – the dominant land cover type across Europe in this study (Fig. S1) - the O_3 sensitivity was calibrated against observations for wheat to give a representation of agricultural regions (high plant O_3 sensitivity), versus natural grassland (low plant O_3 sensitivity), with a separate function for Mediterranean grasslands (low plant O_3 sensitivity) (Table S1 and Figure S2). Broadleaf tree and shrub PFTs were calibrated against the birch/beech observed O_3 dose-response functions for the high plant O_3 sensitivity, with a separate function for Mediterranean broadleaf trees (deciduous oaks), needle leaf trees were calibrated against the function for Norway spruce, all data for dose-response functions were from CLRTAP (2017). The low plant O_3 sensitivity functions for trees/shrubs were calibrated as being 20% less sensitive based on the difference in sensitivity between high and low sensitive tree species in the Karlsson et al. (2007) study. Due to limitations in data availability, the parameterisation for C_4 herbaceous uses the observed dose-responses for C_3 herbaceous, however the fractional cover of C_4 herbs across Europe is low (Fig. S1), so this assumption affects a very small percentage of land cover.

To calibrate each JULES PFT for sensitivity to O_3, JULES was run, varying the value of parameter *a*, until model output of change in NPP with cumulative O_3 exposure matched the observed O_3 dose-response functions in CLRTAP (2017).

~~To calibrate the JULES O_3 sensitivity (parameter '*a*' in eq 2),~~ JULES was run to be as directly comparable as possible to the dose-based O_3 risk indicator used in CLRTAP (2017), using the O_3 flux per projected leaf area to top canopy sunlit leaves. ~~Hourly averaged F_{O3} in excess of F_{O3crit} were accumulated over a species specific accumulation period.~~ Values of F_{O3crit} came from the observations, the parameter '*a'* was modified until the modelled change in response variable with cumulative uptake of O_3 above the specified threshold matched the observations (see further method details in SI section S2).

Commented [ORJ17]: RC2 3)

2.3 Representation of stomatal conductance

In JULES, g_s (m s^{-1}) is represented following the closure proposed by (Jacobs, 1994):

$$g_s = 1.6RT_l \frac{A_{net}\beta}{c_a - c_i} \quad (5)$$

In this parameterisation, c_i is unknown and ~~Where~~ in the default JULES model is calculated as in equation 6, hereafter called JAC:

$$c_i = (c_a - c_*) f0 \left(1 - \frac{dq}{dqcrit}\right) + c_* \qquad (6)$$

β is a soil moisture stress factor, the factor 1.6 accounts for g_s being the conductance for water vapour rather than CO_2, R is the universal gas constant (J K^{-1} mol^{-1}), T_l is the leaf surface temperature (K), c_a and c_i (both Pa) are the leaf surface and internal CO_2 partial pressures, respectively, c_* (Pa) is the CO_2 photorespiration compensation point, dq is the humidity deficit at the leaf surface (kg kg^{-1}), dq_{crit} (kg kg^{-1}) and f_0 are PFT specific parameters representing the critical humidity deficit at the leaf surface, and the leaf internal to atmospheric CO_2 ratio (c_i/c_a) at the leaf specific humidity deficit (Best *et al.* 2011), values are shown is Table S1.

In this work, we replace equation 6 with the closure described in Medlyn et al. (2011), ~~closure~~ using the key PFT specific model parameter g_1 ($kPa^{0.5}$), and dq is expressed in kPa, shown in eq 7, hereafter called MED:

$$c_i = c_a \left(\frac{g_1}{g_1 + \sqrt{dq}}\right) \qquad (7)$$

PFT specific values of the g_1 parameter were derived for European vegetation from the data base of Lin et al. (2015) and are shown in Table S1. The g_1 parameter represents the sensitivity of ~~the~~ g_s to the assimilation rate, i.e. plant water use efficiency, and~~. It~~ was derived as in Lin et al. (2015) by~~from~~ fitting the Medlyn *et al*., (2011) model to observations of g_s, photosynthesis, and VPD, with no g_0 term ~~(Lin et al., 2015)~~. ~~The study of~~ Hoshika et al. (2013) show a significant difference in the g_1 parameter (higher in elevated O_3 compared to ambient) in Siebold's beech in June of their experiment. However, this is only at the start of the growing season, further measurements show no difference in this parameter between O_3 treatments. ~~found an effect of O_3 on g_1 for beech trees (*Fagus crenata*) only at the start of the growing season (June), but not during the following months (August and October).~~ Quantifying an O_3 effect directly on g_1 would require a detailed meta-analysis of empirical data on photosynthesis and g_s for different PFTs, which is currently lacking in the literature. As explained above, here we take an empirical approach to modelling plant O_3 damage, essentially by applying a reduction factor to the simulated plant photosynthesis based on observations of whole plant losses of biomass with O_3 exposure, for which there is a lot more available data (e.g. CLRTAP, 2017). The impact of the g_s model formulation is shown for two contrasting grid points (wet/dry) in central Europe (see SI section S3 for further details). We also carry out site level evaluation of the two g_s models compared to FLUXNET observations (see SI section S4).

2.4 Model simulations for Europe

2.4.1 Forcing datasets

We used the WATCH meteorological forcing data set (Weedon et al., 2010;Weedon et al., 2011) at 0.5° x 0.5° spatial and three hour temporal resolution for our JULES simulations. JULES interpolates this down to an hourly model time step. For this study, the climate was kept constant by recycling over the period 1901 to 1920, to allow us to fully understand the impact O_3, CO_2 and their interaction.

Commented [ORJ18]: RC2 minor comment 12.

Commented [ORJ19]: RC2 minor comment 12.

Commented [ORJ20]: RC2 minor comment 13.

Commented [ORJ21]: RC2 minor comment 19.

JULES was run with prescribed annual mean atmospheric CO_2 concentrations. Pre-industrial global CO_2 concentrations (1900 to 1960) were taken from Etheridge et al. (1996), 1960 to 2002 were from Mauna Loa (Keeling and Whorf, 2004), as calculated by the Global Carbon Project (Le Quéré et al., 2016), and 2003-2050 were based on the IPCC SRES A1B scenario and were linearly interpolated to gap fill missing years (Fig. 1).

JULES was run including dynamic vegetation with a land cover mask giving the fraction of agriculture in each 0.5° x 0.5° grid cell based on the Hurtt et al. (2011) land cover database for the year 2000. T~~Within t~~he agricultural mask means that~~,~~ only C_3/C_4 herbaceous PFTs are allowed to grow, with no competition from ~~and all~~ other PFTs, no form of land management is simulated~~are assumed absent~~. By including dynamic vegetation, grid cell PFT coverage and Leaf Area Index (LAI) is a result of resource availability and simulated competition. Following a full spin-up period (to ensure equilibrium vegetation, carbon and water states), the fractional cover of each PFT changed little over the simulation period (1901 - 2050), the land cover for 2050 is shown in Fig. S1. ~~The model experiments in this study are run for both a high and low plant O_3 sensitivity: for the high plant O_3 sensitivity, all herbaceous PFT fractional cover uses the O_3 sensitivity for wheat, and for the low plant O_3 sensitivity, all herbaceous PFT fractional cover uses the O_3 sensitivity for natural grasslands.~~

Tropospheric O_3 concentration was produced by the EMEP MSC-W model at 0.5° x 0.5° (Simpson et al., 2012), driven with meteorology from the regional climate model RCA3 (Kjellström et al., 2011;Samuelsson et al., 2011), which provides a downscaling of the ECHAM A1B-r3 (simulation 11 of Kjellström *et al.*, 2011). This setup (EMEP+RCA3) is also used by Langner et al. (2012a), Simpson et al. (2014a), Tuovinen et al. (2013), Franz et al. (2017) and Engardt et al. (2017), where further details and model evaluation can be found. Unfortunately, the 3-dimensional RCA3 data needed by the EMEP model was not available prior to 1960, but as in Engardt et al. (2017) the meteorology of 1900-1959 had to be approximated by assigning random years from 1960 to 1969. This procedure introduces some uncertainty of course, but Langner et al. (2012b) show that it is emissions change, rather than meteorological change, that drives modelled ozone concentrations. The emissions scenarios for 1900-2050 merge data from the International Institute of Applied System Analysis (IIASA) for 2005-2050 (the so-called ECLIPSE 4a scenario~~, Klimont *et al.* (2016)~~), recently revised EMEP data for 1990, and a scaling back from 1990 to 1900 using data from Lamarque et al. (2013). The EMEP model accounts for changes in BVOC emissions as a result of predicted ambient temperature changes, however as with all uncoupled modelling studies, there is no interaction between changes in leaf-level g_s, BVOCs and O_3 formation.

This study used daily mean values of tropospheric O_3 concentration from EMEP MSC-W disaggregated down to the hourly JULES model time-step. The daily mean O_3 forcing was disaggregated to follow a mean diurnal profile of O_3, this was generated from hourly O_3 output from EMEP MSC-W for the two land cover categories across the same domain as in this study. Hourly O_3 values allow for variation in the diurnal response to O_3 exposure resulting in more accurate estimation of O_3 uptake. O_3 concentrations from EMEP were calculated at canopy height for two land-cover categories: forest and grassland (Fig. S3 and Fig. S4), which are taken as surrogates for high and low vegetation, respectively. These canopy-height specific concentrations allow for the large gradients in O_3 concentration that can occur in the lowest 10s of metres, giving lower O_3 for grasslands than seen at e.g. 20 m in

Commented [ORJ22]: RC2 minor comment 16.

Commented [ORJ23]: RC2 2)

Commented [ORJ24]: RC2 minor comment 14.

a forest canopy (Simpson et al., 2012;Tuovinen et al., 2009). Figure 1 shows the regional mean annual O_3 concentration (regions are depicted in Fig. S5) along with the annual maximum. Together these clearly show the trend of increasing O_3 concentration on pre-industrial levels in all regions, although notably lower increases in the Boreal region. Around the 1990's O_3 concentrations stabilise and then start to decrease into the future.

Figure 1 shows large increases in tropospheric O_3 from pre-industrial to present day (2001), this is in line with modelling studies (Young et al., 2013) and site observations (Derwent et al., 2008;Logan et al., 2012;Parrish et al., 2012), and is predominantly a result of increasing anthropogenic emissions (Young et al., 2013). Figure's S3 and S4 show this large increase in ground-level O_3 concentrations from 1901 to 2001 occurs in all seasons. Present day O_3 concentration show a strong seasonal cycle, with a spring/summer peak in concentrations in the mid-latitudes of the Northern Hemisphere (Derwent et al., 2008;Parrish et al., 2012;Vingarzan, 2004). This is largely related to the seasonal cycle of photochemical O_3 production which is highest during periods of high radiation and temperature (Young et al., 2013), although increased stratospheric input is also thought to contribute (Vingarzan, 2004). Anthropogenic emissions, especially NO_X, contribute to the seasonal cycle of O_3 through traffic, energy production and residential heating and cooling demands (Royal-Society, 2008). Biogenic emissions are also seasonal which contributes to the seasonal change in O_3 concentrations (Pacifico et al., 2012;Young et al., 2009), and dry deposition, driven by plant productivity also has a strong seasonal component. How the seasonality of ground level O_3 changes in the future will depend on how these multiple different drivers change and interact. Modelling studies such as Dentener et al. (2006) and Young et al. (2013) suggest that anthropogenic emissions will be the main factor controlling the evolution of future O_3 concentrations, and in the recent study of Young et al., (2013) most scenarios suggest reduced O_3 burden in the future as a result predominantly of reduced precursor emissions. Seasonally, the O_3 concentrations used in the simulations in this study show increased O_3 levels in winter and in some regions in autumn and spring in 2050 compared to present day, this may be due to reduced titration of O_3 by NO as a result of reduced NO_X emissions in the future (Royal Society, 2008). Summer O_3 concentrations are lower in 2050 however, compared to 2001. Our simulations use a fixed climate, so we do not include the effect of climate change on shifting plant phenology. Therefore, our results may underestimate plant O_3 damage, since if the growing season started earlier or finished later, plants in some regions would be exposed to higher O_3 concentrations.

Commented [ORJ25]: RC2 5)

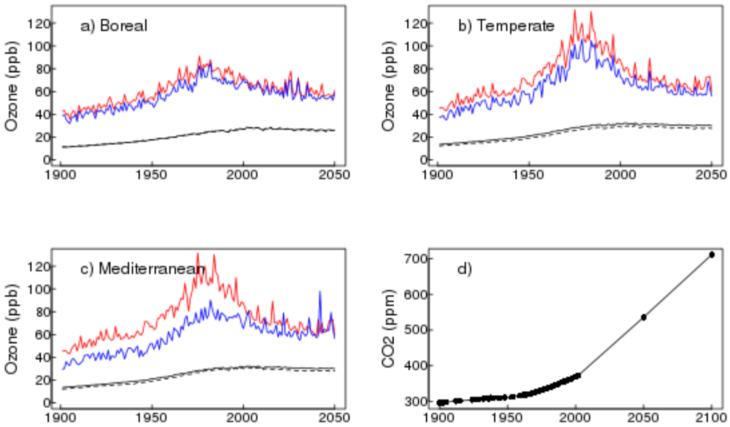

Figure 1. Regional time series of canopy height O_3 (ppb) forcing from EMEP a) to c), and d) global atmospheric CO_2 (ppm) concentration (this does not vary regionally; black dots show data points, the black line shows interpolated points). Each panel for the O_3 forcing shows the regional annual average (woody PFTs, black solid line; herbaceous PFTs, black dashed line) and the annual maximum O_3 concentration above: woody PFTs (red) and herbaceous PFTs (blue).

2.4.2 Spin up and factorial experiments

JULES was spun-up by recycling the climate from the early part of the twentieth century (1901 to 1920) using atmospheric CO_2 (296.1 ppm) and O_3 concentrations from 1901 (Fig. S3 & Fig. S4). Model spin-up was 2000 years by which point the carbon pools and fluxes were in steady state with zero mean net land – atmosphere CO_2 flux. We performed the following transient simulations for the period 1901 to 2050 with continued recycling of the climate as used in the spin-up, for both high and low plant O_3 sensitivities:

- **O3** : Fixed 1901 CO_2, Varying O_3
- **CO2** : Varying CO_2, Fixed 1901 O_3
- **CO2 + O3** : Varying CO_2, Varying O_3

We use these simulations to investigate the direct effects of changing atmospheric CO_2 and O_3 concentrations, individually and combined, on plant physiology through the twentieth century and into the future, specifically over three time periods: historical (1901-2001), future (2001-2050) and over the full time series (1901-2050). See ~~tmore details in t~~the SI section S6 for calculation of the effects due to O_3, CO_2 and O_3 + CO_2. We also use paired t-test to determine statistically significant differences between the different (high and low) plant O_3 sensitivities.

Commented [ORJ26]: RC1 13)

2.4.3 Evaluation

To evaluate our JULES simulations we compare mean GPP from 1991 to 2001 for each of the JULES scenarios and both high and low plant O_3 sensitivities against the observation based globally extrapolated Flux Network model tree ensemble (MTE) (Jung et al., 2011). We use paired t-test to determine statistically significant differences in the mean responses.

Commented [ORJ27]: RC2 3)

3 Results

3.1 Impact of g_s model formulation

The impact of g_s model on simulated g_s is shown for the wet site (Fig. 2). For the broadleaf tree and C_3 herbaceous PFT, the MED ~~edlyn g_s~~ model simulates a ~~significantly~~ larger conductance compared to the JAC ~~acobs g_s~~ model. In other words, with the MED~~edlyn g_s~~ model these two PFTs are parameterised with a less conservative water use strategy, which, for the grid point shown in Fig. 2~~used in the simulation~~, increased the annual mean leaf-level water use by 35~~22~~ % (±29%) and 45 % (±32%), respectively. In contrast, the needle leaf tree, C_4 herbaceous and shrub PFTs are parameterised with a more conservative water use strategy with the MED ~~edlyn g_s~~ model, and the mean annual g_s was decreased by 13~~6~~ % (±12%), 27~~32~~ % (±10%) and 36~~41~~ % (±13%), respectively, compared to the JAC ~~acobs g_s~~ model. This comparison was also done for a dry site, and similar results were found (Fig. S6), suggesting these results are representative across the domain. The effect of g_s formulation~~model~~ on simulated photosynthesis was much smaller because of the lower sensitivity of the limiting rates of photosynthesis to changes in c_i in the model compared to the effect of the same change in c_i on modelled g_s (Fig. S7 & S8). Changes in leaf-level g_s impact the partitioning of simulated energy fluxes. In general, increased g_s results in increased latent heat and thus decreased sensible heat flux, and vice versa where g_s is decreased (Fig. S7 & S8). Also shown is the effect of the MED ~~edlyn g_s~~ model on O_3 flux into the leaf (Fig. 2 and Fig. S6, bottom panels). For the broadleaf tree and C_3 herbaceous PFT, the MED~~edlyn~~ model simulates a larger conductance and therefore a greater flux of O_3 through stomata compared to JAC~~acobs~~, and this is indicative of the potential for greater reductions in photosynthesis (Fig. S7 & S8). The reverse is seen for the needle leaf tree, C_4 herbaceous and shrub PFTs. See SI section S4 for site level evaluation of the seasonal cycles of latent and sensible heat with both JAC and MED models compared to FLUXNET observations.

Commented [ORJ28]: RC1 10)

Commented [ORJ29]: RC1 11)

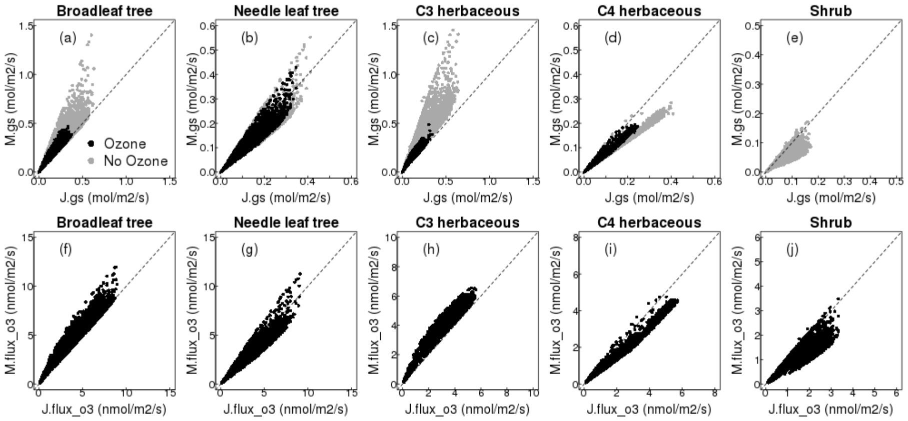

Figure 2. Comparison of simulated g_s with ~~the~~ MED~~edlyn *et al.*, (2011)~~ (y axis) versus ~~the~~ JAC~~acobs (1994) formulation~~ (x axis) ~~currently used in JULES~~ for all five JULES PFTs at one grid point (lat: 48.25; lon:, 5.25) shown are hourly values for the year 2000 (see SI section S3 for further details)., Shown are s~~ for s~~tomatal conductance (g_s, top row), and the flux of O_3 through the stomata (flux_o3, bottom row).

3.2 Evaluation of the JULES O_3 model

For all JULES scenarios similar spatial patterns of GPP are simulated compared to MTE (Fig. 3 and Fig. S10). MTE estimates a mean GPP for present day in Europe of 938 gC m^2 yr^{-1} (Fig. 3). JULES tends to under-predict GPP relative to the MTE product, estimates of GPP from JULES with both transient CO_2 and O_3 give a mean across Europe of 813 gC m^2 yr^{-1} (high plant O_3 sensitivity) to 881 gC m^2 yr^{-1} (low plant O_3 sensitivity), both of which are significantly different to the MTE product (t=27, $d.f.$=5750, p<2.2e^{-16} (high); t=4.3, $d.f.$=5750, p<1.5e^{-05} (low); Fig. 3). Forcing with CO_2 alone (fixed 1901 O_3) gives a mean GPP across Europe of 900 to 923 gC m^2 yr^{-1} (high and low plant O_3 sensitivity respectively), and O_3 alone (without the protective effect of CO_2) reduces estimated GPP to 732 to 799 gC m^2 yr^{-1} (Fig. S10). At latitudes >45^{o}N JULES has a tendency to under-predict MTE-GPP, and at latitudes <45 ^{o}N JULES tends to over-predict MTE-GPP (Fig. S11). These regional differences are highlighted in Fig. S12, where in the Mediterranean region, JULES tends to over-predict MTE-GPP, so simulations with O_3 reduce the simulated GPP bringing it closer to MTE. In the temperate region however, JULES tends to under-estimate MTE-GPP, so the addition of O_3 reduces simulated GPP further (Fig. S12). In the boreal region, JULES under-predicts GPP, but to a lesser extent than in the temperate region, and the addition of O_3 has less impact on reducing the GPP further (Fig. S12).

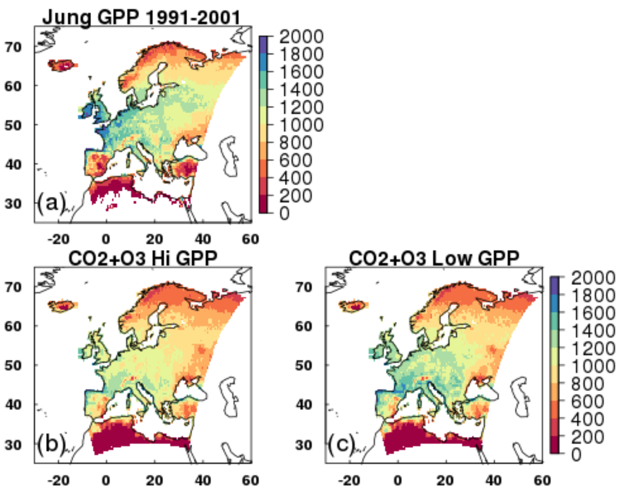

Figure 3. Mean GPP (g C m^2 yr^{-1}) from 1991 to 2001 for a) the observationally based globally extrapolated Flux Network model tree ensemble (MTE) (Jung *et al*., 2011); b, c) model simulations with transient CO_2 and transient O_3, high and low plant O_3 sensitivity respectively.

Commented [ORJ30]: RC2 3)

3.3 European simulations - Historical Period: 1901-2001

Over the historical period (1901-2001), the physiological effect of O_3 reduced GPP (-3% to -9%) for the low and high plant O_3 sensitivity parameterizations, respectively (Table 1). The difference in plant O_3 sensitivity was significant (t=102.2, $d.f.$=6270, p<2.2e^{-16}). Figure 4~~3~~ highlights regional variations, however, where simulated reductions in GPP are up to 20% across large areas of Europe, and up to 30% in some Mediterranean regions under the high plant O_3 sensitivity. Some Boreal and Mediterranean regions show small increases in~~increased~~ GPP over this period, associated with O_3 induced stomatal closure enhancing water availability in these drier regions (Fig. 5~~4~~). This allows for~~,~~ greater~~enhancing~~ stomatal conductance later in the year when soil moisture may otherwise have been limiting to growth (up to 10%, Fig. 5), and therefore higher GPP, but these regions comprise only a small area of the entire domain. Indeed, over much of the Europe, O_3-induced stomatal closure led to reduced g_s (up to 20%) across large areas of temperate Europe and the Mediterranean, and even greater reductions in some smaller regions of southern Mediterranean (Fig. 6~~5~~), and these are not associated with notable ~~significant~~ increases in soil moisture availability (Fig. 5~~4~~), resulting in depressed GPP over much of Europe as described above. Under the low plant O_3 sensitivity, similar spatial patterns occur, but the magnitude of GPP change (up to -10% across much of Europe) and g_s change (-5% to -10%) are lower compared to the high sensitivity. Over the twentieth century the land carbon sink is ~~significantly~~ suppressed (-2% to -6%, Table 1). Large regional variation is shown in Figure 4~~3~~, with temperate and Mediterranean Europe seeing a large reduction in land carbon storage, particularly under the high plant O_3 sensitivity (up to -15%). Combined, the physiological

Commented [ORJ31]: RC1 13)

Commented [ORJ32]: RC1 12)

response to changing CO_2 and O_3 concentrations results in a net loss of land carbon over the twentieth century under the high plant O_3 sensitivity (-2%, Table 1), dominated by loss of soil carbon (Table S3~~2~~). This reflects the large increases in tropospheric O_3 concentration observed over this period (Fig. 1). Under the low plant O_3 sensitivity, the land carbon sink has started to recover by 2001 (+1.5%) owing to the recovery of the soil carbon pool beyond 1901 values over this period (Table S3~~2~~).

To gain perspective on the magnitude of the O_3 induced flux of carbon from the land to the atmosphere we relate changes in total land carbon to carbon emissions from fossil fuel combustion and cement production for the EU-28-plus countries from the data of Boden et al. (2013). We recognise that our simulation domain is slightly larger than the EU28-plus as it includes a small area of western Russia so direct comparisons cannot be made, but this still provides a useful measure of the size of the carbon flux. For the period 1970 to 1979 the simulated loss of carbon from the European terrestrial biosphere due to O_3 effects on vegetation physiology was on average 1.32 Pg C (high vegetation sensitivity) and 0.71 Pg C (low vegetation sensitivity) (Table 2). This O_3 induced reduced C uptake of the land surface is equivalent to around 8% to 16% of the emissions of carbon from fossil fuel combustion and cement production over the same period for the EU28-plus countries (Table 2). Currently the emissions data availability goes up to 2011, so over the last observable decade (2002 to 2011) this land carbon loss has declined but is still equivalent to 2% to 4% of the emissions of carbon from fossil fuels and cement production for the EU28-plus countries (Table 2). Therefore, the indirect O_3 effect on the land carbon sink potentially represents a significant ~~additional~~ source of anthropogenic carbon.

3.4~~3~~ European simulations - Future Period: 2001-2050

Over the 2001 to 2050 period, region-wide GPP with O_3 only changing increased marginally (+0.1% to +0.2%, high and low plant O_3 sensitivity, Table 1, with a significant difference between the two plant O_3 sensitivities (t=57, $d.f.$=6270 $p<2.2e^{-16}$)), although with large spatial variability (Fig. 4~~3~~g & h). ~~This reflects changes in tropospheric O_3 concentration as emission control policies reduce O_3 concentrations.~~ Figures S3~~4~~ and S4~~5~~ show that despite decreased tropospheric O_3 concentrations by 2050 in summer compared to 2001 levels, all regions are exposed to an increase in O_3 over the wintertime, and some regions of Europe, particularly temperate/Mediterranean experience increases in O_3 concentration in spring and autumn. Therefore, although increased GPP (dominantly 10%, but up to 20% in some areas) on 2001 levels is simulated across large areas of Europe, decreases of up to 21% are simulated in some areas of the Mediterranean, up to 15% in some areas of the boreal region and up to 27% in the temperate zone (Fig. 4g & h). When O_3 and CO_2 effects are combined, simulated GPP increases (+15% to +18%, high/low plant O_3 sensitivities respectively, Table 1). This increase is greater than the enhancement simulated when CO_2 affects plant growth independently, because additional O_3 induced stomatal closure increases soil water availability in some regions, which enhances growth more in the O_3 and CO_2 simulations, compared to the CO_2 only run. Nevertheless, although the percentage gain is larger, the absolute value of GPP by 2050 remains lower compared to GPP with CO_2 only changing (Table S4~~3~~).

Despite small increases in GPP in the O_3-only simulation, the land carbon sink continues to decline from 2001 levels (-0.7% to -1.6%, low and high plant O_3 sensitivity respectively, Table 1). This is because the soil and

Commented [ORJ33]: RC1 13)

vegetation carbon pools continue to lose carbon as they adjust slowly to small changes in input (GPP), i.e. the soil carbon pool is not in equilibrium in 2001, and is declining in response to reduced litter input as a result of 20[th] C O_3 impacts on GPP. Nevertheless, the negative effect of O_3 on the future land sink is markedly reduced relative to the historical period. Figure 4e & f~~3~~ however highlights regional differences. Boreal regions and parts of central Europe see minimal O_3 damage, whereas some areas of southern and northern Europe see further losses of up to 8% on 2001 levels. The combined O_3 and CO_2 effects are dominated by the physiological effects of changing CO_2, with land carbon sink increases of up to 7% (Table 1).

Commented [ORJ34]: RC1 16)

3.5~~4~~ European simulations - Anthropocene: 1901-2050

Over the Anthropocene, O_3 reduces GPP (-4% to -9%, with a significant difference between the low and high plant O_3 sensitivity (t=95, $d.f.$=6270 p<2.2e^{-16})) and land carbon storage (-3% to -7%, Table 1, Fig. S13~~9~~). Regionally, O_3 damage is lowest in the boreal zone, GPP decreases are largely between 5% to 8% / 2% to 4% for the high/low plant O_3 sensitivity respectively, with large areas minimally affected by O_3 damage (Figure 7~~6~~), consistent with lower g_s of needle leaf trees that dominate this region, and so lower O_3 uptake (Fig. S14~~0~~ & S15~~1~~). In the temperate region, O_3 damage is extensive with reductions in GPP dominantly from 10% to 15% for the low and high plant O_3 sensitivity respectively. Across significant areas of this region reductions in GPP are up to 20% under high plant O_3 sensitivity (Figure 7~~6~~). In the Mediterranean region, O_3 damage reduces GPP by 5% to 15% / 3% to 6% for the high/low plant O_3 sensitivity respectively, with some areas seeing greater losses of up to 20% under the high plant O_3 sensitivity, but this is less extensive than that seen in the temperate zone (Figure 7~~6~~). In these drier regions, O_3 induced stomatal closure can increase available soil moisture (Fig. S14~~0~~ & S15~~1~~).

Commented [ORJ35]: RC1 13)

Varying CO_2 and O_3 together shows that CO_2 induced stomatal closure can help alleviate O_3 damage by reducing the uptake of O_3 (Table S6~~5~~).~~-~~In these simulations, CO_2-induced stomatal closure was found to offset O_3-suppression of GPP, such that GPP by 2050 is 3% to 7% lower due to O_3 exposure, rather than 4% to 9% lower in the absence of increasing CO_2 (Table S6~~5~~). Figure 6 shows this spatially, O_3 damage is reduced when the effect of atmospheric CO_2 on stomatal closure is accounted for, however despite this, the land carbon sink and GPP remain significantly reduced due to O_3 exposure.

Commented [ORJ36]: RC1 2)

Over the Anthropocene, changing O_3 and CO_2 in tandem results in an increase in European land carbon uptake (+5% to +9%), and an increase in GPP (+20% to +23%) by 2050 for the high and low plant O_3 sensitivity, respectively (Table 1). Nevertheless, despite this increase there remains a large negative impact of O_3 on the European land carbon sink (Fig. S13~~9~~). By 2050 the simulated enhancement of land carbon and GPP in response to elevated CO_2 alone is reduced by 3% to 6% (land carbon) and 4% to 9% (GPP) for the low and high plant O_3 sensitivity respectively, when O_3 is also accounted for (Table 1). This is a large ~~significant~~ reduction in the ability of the European terrestrial biosphere to sequester carbon.

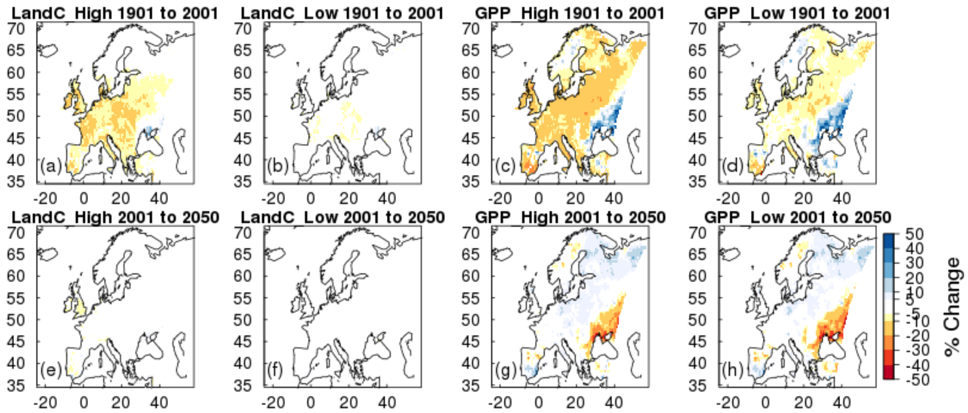

Figure 43. Simulated percentage change in total carbon stocks (Land C) and gross primary productivity (GPP) due to O_3 effects at fixed pre-industrial atmospheric CO_2 concentration. Changes are shown for the periods 1901 to 2001, and 2001 to 2050 for the high and low plant O_3 sensitivity.

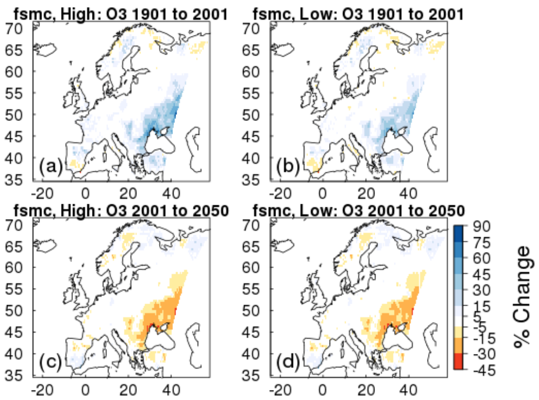

Figure 54. Simulated percentage change in plant available soil moisture (*fsmc*) due to O_3 effects at fixed pre-industrial atmospheric CO_2 concentration. Changes are shown for the periods 1901 to 2001, and 2001 to 2050 for the high and low plant O_3 sensitivity.

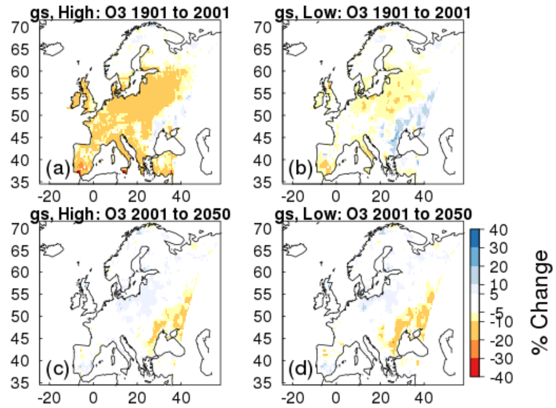

Figure 65. Simulated percentage change in stomatal conductance (g_s) due to O_3 effects at fixed pre-industrial atmospheric CO_2 concentration. Changes are shown for the periods 1901 to 2001, and 2001 to 2050 for the high and low plant O_3 sensitivity.

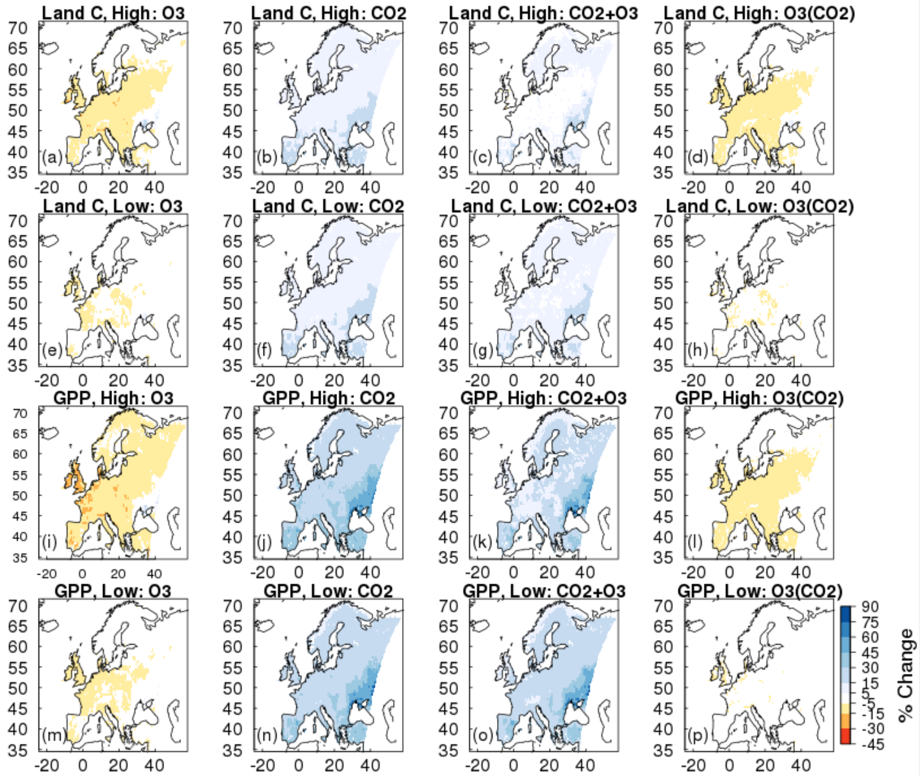

Figure 76. Simulated percentage change in total carbon stocks (Land C) and gross primary productivity (GPP) due to i) (a, e, i, m) O_3 effects at fixed pre-industrial atmospheric CO_2 concentration (O_3), ii) (b, f, j, n) CO_2 fertilisation at fixed pre-industrial O_3 concentration (CO_2), iii) (c, g, k, o) the interaction between O_3 and CO_2 effects (CO_2 + O_3) iv) (d, h, l, p) O_3 effects with changing atmospheric CO_2 concentration (i.e. O_3 damage accounting for the effect of CO_2 induced stomatal closure; $O_3(CO_2)$). Changes are depicted for the periods 1901 to 2050 for high and lower ozone plant sensitivity.

	High Plant O_3 Sensitivity					
	1901 - 2001		2001 - 2050		1901 - 2050	
	GPP (Pg C yr^{-1})	Land C (Pg C)	GPP (Pg C yr^{-1})	Land C (Pg C)	GPP (Pg C yr^{-1})	Land C (Pg C)
Value in 1901:	9.05	167	-	-	9.05	167
Absolute Change:						
O_3	-0.81	-9.21	0.01	-2.44	-0.80	-11.65
CO_2	1.16	4.24	1.42	12.98	2.58	17.22
CO_2 + O_3	0.13	-3.28	1.66	11.11	1.79	7.83
% Change:						
O_3	-8.95	-5.51	0.12	-1.55	-8.84	-6.98
CO_2	12.82	2.54	13.91	7.58	28.51	10.31
CO_2 + O_3	1.44	-1.96	18.08	6.79	19.78	4.69
	Low Plant O_3 Sensitivity					
	1901 - 2001		**2001 - 2050**		**1901 - 2050**	
	GPP (Pg C yr^{-1})	Land C (Pg C)	GPP (Pg C yr^{-1})	Land C (Pg C)	GPP (Pg C yr^{-1})	Land C (Pg C)
Value in 1901:	9.34	167.5	-	-	9.34	167.5
Absolute Change:						
O_3	-0.30	-3.59	0.02	-1.07	-0.40	-4.66
CO_2	1.15	6.43	1.35	13.14	2.50	19.57
CO_2 + O_3	0.65	2.50	1.50	12.35	2.15	14.85
% Change:						
O_3	-3.21	-2.14	0.22	-0.65	-4.28	-2.78
CO_2	12.31	3.84	12.87	7.55	26.77	11.68
CO_2 + O_3	6.96	1.49	15.02	7.26	23.02	8.87

Table 1. Simulated changes in the European land carbon cycle due to changing O_3 and CO_2 concentrations (independently and together). Shown are changes in total carbon stocks (Land C) and gross primary productivity (GPP), over three different periods (historical: 1901 to 2001, future: 2001 to 2050, and Anthropocene: 1901 to 2050). Absolute (top) and relative (bottom) differences are shown. For 2001 to 2050, please refer to Table S43 for the initial value for each run. See the SI for details of the estimation of the O_3 and CO_2 effects and their interaction.

	Mean (Pg C)				
	1970-1979	**1980-1989**	**1990-1999**	**2000-2009**	**2002-2011**
Modelled O_3 effect on land C sink :					
Higher sensitivity	-1.32	-1.01	-0.97	-0.53	-0.50
Low sensitivity	-0.71	-0.58	-0.50	-0.29	-0.26
Sum of C emissions from fossil fuel combustion and cement production (Pg C)	8.39	8.63	12.26	12.83	12.75
C lost from O_3 effect as a % of fossil fuel and cement emissions (%):					
Higher sensitivity	-15.73	-11.70	-7.91	-4.13	-3.92
Low sensitivity	-8.46	-6.72	-4.08	-2.26	-2.04

Table 2. Simulated change in total land carbon due to O_3 damage with changing atmospheric CO_2 concentration for the two vegetation sensitivities. The sum of carbon emissions for each decade from fossil fuel combustion and cement production for the EU-28 countries plus Albania, Bosnia and Herzegovina, Iceland, Belarus, Serbia, Moldova, Norway, Turkey, Ukraine, Switzerland and Macedonia (EU28-plus) are shown, the data is from Boden *et al.*, 2013. The simulated change in land carbon as a result of O_3 damage is depicted as a percentage of the EU28-plus emissions to demonstrate the magnitude of the additional source of carbon to the atmosphere from plant O_3 damage.

4 Discussion

4.1 Comparison of g_s models

Comparison of the new g_s model implemented in this study (MED~~edlyn *et al*., 2011~~) with the g_s model currently used as standard in JULES (JAC~~acobs 1994~~) revealed large differences in leaf-level g_s for each PFT, principally as a result of the data-based parameterisation of the new model. Leaf-level water use increased for the broadleaf tree and C_3 herbaceous PFTs using the MED~~edlyn gs~~ model compared to JAC~~acobs~~, but decreased for the needle leaf tree, C_4 herbaceous and shrub PFTs which displayed a more conservative water use strategy compared to the Jacobs parameterisation. These changes are in line with the work of De Kauwe et al. (2015) who found a reduction in annual transpiration for evergreen needle leaf, tundra and C_4 grass regions when implementing the Medlyn g_s model into the Australian land surface scheme CABLE. Changes in leaf-level g_s in this study resulted in differences in latent and sensible heat fluxes. Changes in the partitioning of energy fluxes at the land surface could ~~potentially~~ have consequences for the intensity of heatwaves (Cruz et al., 2010;Kala et al., 2016), runoff (Betts et al., 2007;Gedney et al., 2006) and rainfall patterns (de Arellano et al., 2012), although fully coupled simulations would be necessary to detect these effects. The differences in ~~effect of the g_s model on~~ simulated g_s ~~stomatal conductance~~ led to differences in ~~the~~ uptake of O_3 between the two ~~g_s~~ models because the leaf-level rate of g_s is the predominant determinant of the flux of O_3 through stomata. Higher O_3 uptake is indicative of greater damage. Therefore, given that C_3 herbaceous vegetation is the dominant land cover class across the European domain used in this study, this suggests a greater O_3 impact for Europe would be~~could be~~ simulated with~~ the~~ MED ~~edlyn g_s~~ model compared to JAC~~, and that studies using the Jacobs g_s formulation may underestimate the O_3 impact for Europe~~.

Commented [ORJ37]: RC2 3)

4.2 Lower than expected O_3 damage?

~~We compare results from the present study to values found in literature. The Wittig et al. (2007) meta-analysis of temperate and boreal tree species showed future concentrations of O_3 predicted for 2050 significantly reduced leaf level light saturated net photosynthetic uptake (-19%, range: -3% to -28%) and g_s (-10%, range: +5% to -23%) in both broadleaf and needle leaf tree species. In the Feng et al. (2008) meta-analysis of wheat, projected O_3 concentrations for the future reduced aboveground biomass (-18%, CI -13% to -24%), photosynthetic rate (-20%) and g_s (-22%). One of few long-term field based O_3 exposure studies (AspenFACE) showed that after 11 years of exposing mature trees to elevated O_3 concentrations, O_3 decreased ecosystem carbon content (-9%), and decreased NPP (-10%), although the O_3 effect decreased through time (Talhelm et al., 2014). GPP was reduced (-12% to -19%) at two Mediterranean ecosystems (dominated by either *Pinus* species or *Citrus* species) studied by Fares et al. (2013). Biomass of mature beech trees was reduced (-44%) after 8 years of exposure to elevated O_3 (Matyssek et al., 2010a). After 5 years of O_3 exposure in a semi-natural grassland, annual biomass production was reduced (-23%), and in a Mediterranean annual pasture O_3 exposure significantly reduced total aboveground biomass (up to -25%) (Calvete-Sogo et al., 2014). Results from the present study suggest projected O_3 concentrations for 2050 will reduce mean GPP for Europe (-4% to -9%), NPP (-6% to -11%), total carbon content (-3% to -7%) and g_s (-4% to -9%). Using GPP as a proxy for A_{sat} (these variables are not identical but they are related), our mean GPP and g_s estimates fall within the range given by the meta-analysis of Wittig et al. (2007). The remaining studies are not meta-analyses, so are site- and species- specific, our estimates appear to compare more conservatively with these, however these are a mean value for Europe and spatially our estimates show greater variability.~~

The impact of O_3 on present day European GPP simulated in this study is slightly lower compared to previous modelled estimates~~studies~~. Our estimates suggest present day O_3 reduced GPP by 3% to 9% on average across Europe and NPP by 5% to 11% (Table S3). Anav et al. (2011) simulated a 22% reduction of GPP across Europe for 2002 using the ORCHIDEE model. Present day O_3 exposure reduced GPP by 10% to 25% in Europe, and 10.8% globally in the study by Lombardozzi et al. (2015) using the Community land model (CLM). O_3 reduced NPP by 11.2% in Europe from 1989 to 1995 using the Terrestrial Ecosystem Model (TEM) (Felzer et al., 2005). Globally, concentrations of O_3 predicted for 2100 reduced GPP by 14% to 23% using a former parameterisation of O_3 sensitivity in JULES (Sitch et al., 2007). The recent study by Franz et al. (2017) showed mean GPP declined by 4.7% over the period 2001 to 2010 using the OCN model over the same European domain used in this study. These similar ~~similarly 'lower than expected'~~ results are likely the result of using the same domain, and, more importantly, O_3 forcing produced by the same model (EMEP MSC-W).

4.3 Impacts of O_3 at the land surface

In this study, O_3 has a detrimental effect on the size of the land carbon sink for Europe. This is primarily through a decrease in the size of the soil carbon pool as a result of reduced litter input to the soil, consistent with reduced GPP/NPP. Field studies show that in some regions of Europe, soil carbon stocks are decreasing (Bellamy et al., 2005;Capriel, 2013;Heikkinen et al., 2013;Sleutel et al., 2003). The study of Bellamy et al. (2005), for example, showed that carbon was lost from soils across England and Wales between 1978 to 2003 at a mean rate of 0.6% per year with little effect of land use on the rate of carbon loss, suggesting a possible link to climate change. It is understood that climate change is likely to affect soil carbon turnover. Increased temperatures increase microbial decomposition activity in the soil, and therefore increase carbon losses through higher rates of respiration (Cox et al., 2000;Friedlingstein et al., 2006;Jones et al., 2003). However, some studies have found that O_3 can decrease soil carbon content. Talhelm et al. (2014), for example, found O_3 reduced carbon content in near surface mineral soil of forest soils exposed to 11 years of O_3 fumigation. Hofmockel et al. (2011) found elevated O_3 reduced the carbon content in more stable soil organic matter pools, and Loya et al. (2003) showed that the fraction of soil carbon formed in forest soils over a 4 year experimental period when fumigated with both CO_2 and O_3 was reduced by 51% compared to the soil fumigated with CO_2 alone. It is agreed that amongst other factors that change with O_3 exposure such as litter quality and composition, reduced litter quantity also has significant detrimental consequences for soil carbon stocks (Andersen, 2003;Lindroth, 2010;Loya et al., 2003). Results from this study therefore suggest that increasing tropospheric O_3 may be a contributing factor to the declining soil carbon stocks observed across Europe as a result of reduced litter input to the soil carbon pool consistent with reduced NPP.

We acknowledge, however, that our model simulations do not include coupling of Nitrogen and Carbon cycles, or land management practices. Although we include a representation of agricultural regions through the model calibration against the wheat O_3 sensitivity function (CLRTAP, 2017), wheat is known to be one of the most O_3 sensitive crop species. As with all uncoupled modelling studies, a change in g_s and flux will impact the O_3 concentration itself. Therefore adopting the Medlyn formulation with a higher g_s and subsequently higher O_3 flux for broadleaf and C_3 PFTs (Fig 2) would lead to reduced O_3 concentration, which in turn would act to dampen the effect of higher g_s on O_3 flux. Essentially this study provides an 'upper bound' as in the high plant O_3 sensitivity scenario, all C_3/C_4 fractional cover uses the wheat O_3 sensitivity. Additionally, this version of JULES does not have a crop module; it has no land management practices such as harvesting, ploughing or crop rotation – processes which may have counteracting effects on the land carbon sink. Further, without a coupled Carbon and Nitrogen cycle, it is likely that the CO_2 fertilisation response of GPP and the land carbon sink is over estimated in some regions of our simulations since nitrogen availability limits terrestrial carbon sequestration of natural ecosystems in the temperate and boreal zone (Zaehle, 2013). This would have consequences for our modelled O_3 impact, particularly into the future where the large CO_2 fertilisation effect was responsible for partly offsetting the negative impact of O_3. Although in our simulations a high fraction of land cover is agricultural which we assume would be optimally fertilised. Nevertheless, we emphasise that this study provides a sensitivity assessment of the impact of plant O_3 damage on GPP and the land carbon sink.

Commented [ORJ38]: RC2 minor comment 16.

Another caveat we fully acknowledge is that at the leaf-level JULES is parameterised to reduce g_s with O_3 exposure. Whilst this response is commonly observed (Wittig et al., 2007;Ainsworth et al., 2012), there is evidence to suggest that O_3 impairs stomata in some species, making them non-responsive to environmental stimuli (Hayes et al., 2012;Hoshika et al., 2012a;Mills et al., 2009;Paoletti and Grulke, 2010). In drought conditions the mechanism is thought to involve O_3 stimulated ethylene production which interferes with the stomatal response to ABA signalling (Wilkinson and Davies, 2009;Wilkinson and Davies, 2010). Such stomatal sluggishness can result in higher O_3 uptake and injury, increased water-loss, and therefore greater vulnerability to environmental stresses (Mills et al., 2016). McLaughlin (2007a;2007b) and Sun et al. (2012) provide evidence of increased transpiration and reduced streamflow in forests at the regional scale in response to ambient levels of O_3, and suggest this could increase the frequency and severity of droughts. (Hoshika et al., 2012b)Hoshika et al 2012 however found that despite sluggish stomatal control in O_3 exposed trees, whole tree water use was lower in these trees because of lower gas exchange and premature leaf shedding of injured leaves. To our knowledge, the study of Hoshika et al. (2015) is the first to include an explicit representation of sluggish stomatal control in a land-atmosphere model, they show that sluggish stomatal behaviour has ~~significant~~ implications for carbon and water cycling in ecosystems. However, it is by no means a ubiquitous response, and it is not fully understood which species respond this way and under what conditions (Mills et al., 2016;Wittig et al., 2007). Nevertheless, this remains an important area of future work.

The calculation of O_3 deposition in the EMEP model uses the stomatal conductance formulation presented in Emberson et al. (2000;2001), which depends on temperature, light, humidity and soil moisture (commonly referred to as DO_3SE). Because we link two different model systems, the g_s values in the EMEP model differ from those obtained using the Medlyn formulation. We acknowledge this inconsistency as a caveat of our study, however comparison of *gmax* (maximum g_s) values from both models (EMEP and JULES) suggests the differences are small for deciduous forest (EMEP 150-200, JULES ~180, all units in mmole O_3/m^2 (PLA)/s), and C_3/C_4 crops (EMEP 270-300, JULES ~260-390 – the dominant land cover in our simulations), but are larger for coniferous forest (EMEP 140-200, JULES ~60-70) and shrubs (EMEP 60-200, JULES 360-390). The role of EMEP in this study is not to provide g_s, however, but to provide O_3 at the top of the vegetation canopy. The main driver of such O_3 levels is the regional-scale production and transport of O_3, and the main impact of g_s is in affecting the vertical O_3 gradients just above the plant canopy. Differences in g_s are known to have minimal impact on canopy-top O_3 for trees, mainly due to the efficient turbulent mixing above tall canopies, but also due to non-stomatal sink processes. For shorter vegetation, substantial O_3 gradients, driven by deposition, occur in the lowest 10s of metres of the atmosphere, and stomatal sinks (as given by g_s) can have a significant role. However, calculations of such gradients made with the EMEP model for CLRTAP (2017) showed that differences amounted to only ca. 10% when comparing O_3 concentrations at 1m height above high-g_s crops compared to moderate-g_s (*gmax* = 450 and 270 mmole O_3/m^2 (PLA)/s respectively), therefore this uncertainty is small.

Commented [ORJ39]: RC2 4)

These offline simulations show the sensitivity of GPP and the land carbon sink to tropospheric O_3, suggesting that O_3 is an important predictor of future GPP and the land carbon store across Europe. There are uncertainties in our estimates however from the use of uncoupled tropospheric chemistry, meteorology and stomatal function. For example, increased frequency of drought in the future would reduce stomatal conductance (assuming no sluggish stomatal response) and thus O_3 uptake. Since our offline simulations do not include this feedback it is possible the O_3 effect is over estimated here. Given the complexity of potential interactions and feedbacks it remains difficult to diagnose the importance of individual factors (e.g. the direct physiological response) in a fully coupled simulation. Once the importance of a process is demonstrated offline, it provides evidence of the need to incorporate such process in coupled regional and global simulations.

Commented [ORJ40]: RC1 2)

Commented [ORJ41]: RC2 1)

4.4 O_3 as a missing component of carbon cycle assessments?

Comprehensive analyses of the European carbon balance suggest a large ~~significant~~ biogenic carbon sink (Janssens et al., 2003;Luyssaert et al., 2012;Schulze et al., 2009). However, estimates are hampered by large uncertainties in key components of the land carbon balance, such as estimates of soil carbon gains and losses (Ciais et al., 2010;Janssens et al., 2003;Schulze et al., 2009;Schulze et al., 2010). We suggest that the effect of O_3 on plant physiology is a contributing factor to the decline in soil carbon stores observed across Europe, and as such this O_3 effect is a missing component of European carbon cycle assessments. Over the Anthropocene, our results show elevated O_3 concentrations reduce the amount of carbon that can be stored in the soil by 3% to 9% (low and high plant O_3 sensitivity, respectively), which almost completely offsets the beneficial effects of CO_2 fertilisation on soil carbon storage under the high plant O_3 sensitivity . This would contribute to a ~~significant~~ change in the size of a key carbon sink for Europe, and is particularly important when we consider the evolution of the land carbon sink into the future given the impact of O_3 on soil carbon sequestration and the high uncertainty of future tropospheric O_3 concentrations. Schulze et al. (2009) and Luyssaert et al. (2012) extended their analysis of the European carbon balance to include additional non-CO_2 greenhouse gases (CH_4 and N_2O). Both studies found that emissions of these offset the biogenic carbon sink, reducing the climate mitigation potential of European ecosystems. This highlights the importance of accounting for all fluxes and stores in carbon/greenhouse gas balance assessments, of which O_3 and its indirect effect on the CO_2 flux via direct effects on plant physiology is currently missing.

4.5 The interaction between O_3 and CO_2

We looked at the interaction between CO_2 and O_3 effects. Our results support the hypothesis that elevated atmospheric CO_2 provides some protection against O_3 damage because of lower g_s that reduces uptake of O_3 through stomata (Harmens et al., 2007;Wittig et al., 2007). In the present study, reductions in GPP and the land carbon store due to O_3 exposure were lower when simulated with concurrent changes in atmospheric CO_2. Despite acclimation of photosynthesis after long-term exposure to elevated atmospheric CO_2 of field grown plants (Ainsworth and Long, 2005;Medlyn et al., 1999), there is no evidence to suggest that g_s acclimates (Ainsworth et al., 2003;Medlyn et al., 2001). This suggests the protective effect of elevated atmospheric CO_2 against O_3 damage will be sustained in the long term. However, although meta-analysis suggest a general trend of reduced g_s with elevated CO_2 (Ainsworth and Long, 2005;Medlyn et al., 1999), this is not a universal response. Stomatal responses on exposure to elevated CO_2 with FACE treatment varied with genotype and growth stage in a fast-growing poplar community (Bernacchi et al., 2003;Tricker et al., 2009). In other mature forest stands, limited stomatal response to elevated CO_2 was observed after canopy closure (Ellsworth, 1999;Uddling et al., 2009). Also, some studies found that stomatal responses to CO_2 were significant only under high atmospheric humidity (Cech et al., 2003;Leuzinger and Körner, 2007;Wullschleger et al., 2002). These examples illustrate that stomatal responses to elevated atmospheric CO_2 are not universal, and as such the protective effect of CO_2 against O_3 injury cannot be assumed for all species, at all growth stages under wide ranging environmental conditions.

5 Conclusion

What is abundantly clear is that plant responses to both CO_2 and O_3 are complicated by a host of factors that are only partly understood, and it remains difficult to identify general, global patterns given that effects of both gases on plant communities and ecological interactions are highly context and species specific (Ainsworth and Long, 2005;Fuhrer et al., 2016;Matyssek et al., 2010b). This study quantifies the sensitivity of the land carbon sink for Europe and GPP to changing concentrations of atmospheric CO_2 and O_3 from 1901 to 2050. We have used a state of the art land surface model calibrated for European vegetation to give our best estimates of this sensitivity within the limits of data availability to calibrate the model for O_3 sensitivity, current knowledge and model structure. In summary, this study has shown that potential gains in terrestrial carbon sequestration over Europe resulting from elevated CO_2 can be partially offset by concurrent rises in tropospheric O_3 over 1901-2050. Specifically, we have shown that the negative effect of O_3 on the land carbon sink was greatest over the twentieth century, when O_3 concentrations increased rapidly from pre-industrial levels. Over this period soil carbon stocks were ~~significantly~~ diminished over agricultural areas, consistent with reduced NPP and litter input. This loss of soil carbon was largely responsible for the decrease in the size of the land carbon sink over Europe. The O_3 effect on the land carbon store and flux was reduced into the future as CO_2 concentration rose considerably and changes in O_3 concentration were less pronounced. However, there remained a large cumulative negative impact on the land carbon sink for Europe by 2050. The interaction between the two gases was found to reduce O_3 injury owing to reduced stomatal opening in elevated atmospheric CO_2. However, primary productivity and land carbon storage remained ~~significantly~~ suppressed by 2050 due to plant O_3 damage. Expressed as a percentage of the emissions from fossil fuel and cement production for the EU28-plus countries, the ~~additional~~ carbon emissions from O_3-induced plant injury are~~is~~ a ~~potential significant additional~~ source of anthropogenic carbon previously not accounted for in carbon cycle assessments. Our results demonstrate the sensitivity of modelled terrestrial carbon dynamics to the direct effect of tropospheric O_3 and its interaction with atmospheric CO_2 on plant physiology, demonstrating this process is an important predictor of future GPP and trends in the land-carbon sink. Nevertheless, this process remains largely unconsidered in regional and global climate model simulations that are used to model carbon sources and sinks and carbon-climate feedbacks.

Commented [ORJ42]: RC2 1)

~~, highlighting that such effects of O_3 on plant physiology significantly add to the uncertainty of future trends in the land carbon sink and climate-carbon feedbacks. Given the potential to limit the climate mitigation effect of European terrestrial ecosystems, we suggest plant O_3 damage should be incorporated into carbon cycle assessments.~~

Data availability

The JULES model can be downloaded from the Met Office Science Repository Service (https://code.metoffice.gov.uk/trac/jules - see here for a helpful how to http://jules.jchmr.org/content/getting-started). Model output data presented in this paper and the exact version of JULES with namelists are available upon request from the corresponding author.

Supplementary Information

Supplementary_Information_Oliver_et_al.docx

Competing Interests

The authors declare that they have no conflict of interest

Acknowledgements

RJO and LMM were supported by the EU FP7 (ECLAIRE, 282910) and JWCRP (UKESM, NEC05816). This work was also supported by EMEP under UNECE. SS and LMM acknowledge the support of the NERC SAMBBA project (NE/J010057/1). The UK Met Office contribution was funded by BEIS under the Hadley Centre Climate Programme (GA01101). GAF also acknowledges funding from the EU's Horizon 2020 research and innovation programme (CRESCENDO, 641816). We also thank Magnuz Engardt of SMHI for providing the RCA3 climate dataset.

References

Field Code Changed

Ainsworth, E., and Long, S.: What have we learned from 15 years of free-air CO_2 enrichment (FACE)? A meta-analytic review of the responses of photosynthesis, canopy properties and plant production to rising CO2, New Phytologist, 165, 351-372, 2005.

Ainsworth, E. A., Davey, P. A., Hymus, G. J., Osborne, C. P., Rogers, A., Blum, H., Nosberger, J., and Long, S. P.: Is stimulation of leaf photosynthesis by elevated carbon dioxide concentration maintained in the long term? A test with *Lolium perenne* grown for 10 years at two nitrogen fertilization levels under Free Air CO_2 Enrichment (FACE), Plant, Cell and Environment, 26, 705-714, 2003.

Ainsworth, E. A.: Rice production in a changing climate: a meta-analysis of responses to elevated carbon dioxide and elevated ozone concentration, Global Change Biology, 14, 1642-1650, 10.1111/j.1365-2486.2008.01594.x, 2008.

Ainsworth, E. A., Yendrek, C. R., Sitch, S., Collins, W. J., and Emberson, L. D.: The Effects of Tropospheric Ozone on Net Primary Productivity and Implications for Climate Change, Annual Review of Plant Biology, 63, 637-661, doi:10.1146/annurev-arplant-042110-103829, 2012.

Anav, A., Menut, L., Khvorostyanov, D., and Viovy, N.: Impact of tropospheric ozone on the Euro-Mediterranean vegetation, Global change biology, 17, 2342-2359, 2011.

Andersen, C. P.: Source–sink balance and carbon allocation below ground in plants exposed to ozone, New Phytologist, 157, 213-228, 10.1046/j.1469-8137.2003.00674.x, 2003.

Arneth, A., Harrison, S. P., Zaehle, S., Tsigaridis, K., Menon, S., Bartlein, P. J., Feichter, J., Korhola, A., Kulmala, M., O'Donnell, D., Schurgers, G., Sorvari, S., and Vesala, T.: Terrestrial biogeochemical feedbacks in the climate system, Nature Geosci, 3, 525-532, http://www.nature.com/ngeo/journal/v3/n8/suppinfo/ngeo905_S1.html, 2010.

Avnery, S., Mauzerall, D. L., Liu, J., and Horowitz, L. W.: Global crop yield reductions due to surface ozone exposure: 1. Year 2000 crop production losses and economic damage, Atmospheric Environment, 45, 2284-2296, https://doi.org/10.1016/j.atmosenv.2010.11.045, 2011.

Baig, S., Medlyn, B. E., Mercado, L. M., and Zaehle, S.: Does the growth response of woody plants to elevated CO2 increase with temperature? A model-oriented meta-analysis, Global Change Biology, 21, 4303-4319, 10.1111/gcb.12962, 2015.
Bellamy, P. H., Loveland, P. J., Bradley, R. I., Lark, R. M., and Kirk, G. J.: Carbon losses from all soils across England and Wales 1978–2003, Nature, 437, 245-248, 2005.
Bernacchi, C. J., Calfapietra, C., Davey, P. A., Wittig, V. E., Scarascia-Mugnozza, G. E., Raines, C. A., and Long, S. P.: Photosynthesis and stomatal conductance responses of poplars to free-air CO_2 enrichment (PopFACE) during the first growth cycle and immediately following coppice., New Phytologist, 159, 609-621, 2003.
Best, M. J., Pryor, M., Clark, D. B., Rooney, G. G., Essery, R. L. H., Menard, C. B., Edwards, J. M., Hendry, M. A., Porson, N., Gedney, N., Mercado, L. M., Sitch, S., Blyth, E., Boucher, O., Cox, P. M., Grimmond, C. S. B., and Harding, R. J.: The Joint UK Land Environment Simulator (JULES), Model description - Part 1: Energy and water fluxes, Geoscientific Model Development Discussions, 4, 595-640, 10.5194/GMDD-4-595-2011, 2011.
Betts, R. A., Boucher, O., Collins, M., Cox, P. M., Falloon, P. D., Gedney, N., Hemming, D. L., Huntingford, C., Jones, C. D., and Sexton, D. M.: Projected increase in continental runoff due to plant responses to increasing carbon dioxide, Nature, 448, 1037-1041, 2007.
Boden, T. A., Marland, G., and Andres, R. J.: Global, Regional, and National Fossil-Fuel CO2 Emissions, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., USA, 2013.
Büker, P., Feng, Z., Uddling, J., Briolat, A., Alonso, R., Braun, S., Elvira, S., Gerosa, G., Karlsson, P. E., Le Thiec, D., Marzuoli, R., Mills, G., Oksanen, E., Wieser, G., Wilkinson, M., and Emberson, L. D.: New flux based dose-response relationships for ozone for European forest tree species, Environmental Pollution, 163-174, 2015.
Calvete-Sogo, H., Elvira, S., Sanz, J., González-Fernández, I., García-Gómez, H., Sánchez-Martín, L., Alonso, R., and Bermejo-Bermejo, V.: Current ozone levels threaten gross primary production and yield of Mediterranean annual pastures and nitrogen modulates the response, Atmospheric Environment, 95, 197-206, http://dx.doi.org/10.1016/j.atmosenv.2014.05.073, 2014.
Capriel, P.: Trends in organic carbon and nitrogen contents in agricultural soils in Bavaria (south Germany) between 1986 and 2007, European Journal of Soil Science, 64, 445-454, 2013.
Cech, P. G., Pepin, S., and Korner, C.: Elevated CO_2 reduces sap flux in mature deciduous forest trees, Oecologia, 137, 258-268, 2003.
Ceulemans, R., and Mousseau, M.: Effects of elevated atmospheric CO_2 on woody plants, New Phytologist, 127, 1994.
Ciais, P., Wattenbach, M., Vuichard, N., Smith, P., Piao, S., Don, A., Luyssaert, S., Janssens, I., Bondeau, A., and Dechow, R.: The European carbon balance. Part 2: croplands, Global Change Biology, 16, 1409-1428, 2010.
Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., Chhabra, A., DeFries, R., Galloway, J., Heimann, M., Jones, C., Le Quéré, C., Myneni, R. B., Piao, S., and Thornton, P.: Carbon and Other Biogeochemical Cycles. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA., 2013.
Clark, D. B., Mercado, L. M., Sitch, S., Jones, C. D., Gedney, N., Best, M. J., Pryor, M., Rooney, G. G., Essery, R. L. H., Blyth, E., Boucher, O., Harding, R. J., and Cox, P. M.: The Joint UK Land Environment Simulator (JULES), Model description - Part 2: Carbon fluxes and vegetation, Geoscientific Model Development Discussions, 4, 641-688, 10.5194/gmdd-4-641-2011, 2011.
CLRTAP: The UNECE Convention on Long-range Transboundary Air Pollution. Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends: Chapter III Mapping Critical Levels for Vegetation, accessed via,

http://icpvegetation.ceh.ac.uk/publications/documents/Chapter3-Mappingcriticallevelsforvegetation_000.pdf, 2017.
Collins, W. J., Sitch, S., and Boucher, O.: How vegetation impacts affect climate metrics for ozone precursors, Journal of Geophysical Research: Atmospheres, 115, D23308, 10.1029/2010JD014187, 2010.
Collins, W. J., Bellouin, N., Doutriaux-Boucher, M., Gedney, N., Halloran, P., Hinton, T., Hughes, J., Jones, C. D., Joshi, M., Liddicoat, S., Martin, G., O'Connor, F., Rae, J., Senior, C., Sitch, S., Totterdell, I., Wiltshire, A., and Woodward, S.: Development and evaluation of an Earth-System model – HadGEM2, Geosci. Model Dev., 4, 1051-1075, 10.5194/gmd-4-1051-2011, 2011.
Cooper, O. R., Parrish, D. D., Stohl, A., Trainer, M., Nedelec, P., Thouret, V., Cammas, J. P., Oltmans, S. J., Johnson, B. J., Tarasick, D., Leblanc, T., McDermid, I. S., Jaffe, D., Gao, R., Stith, J., Ryerson, T., Aikin, K., Campos, T., Weinheimer, A., and Avery, M. A.: Increasing springtime ozone mixing ratios in the free troposphere over western North America, Nature, 463, 344-348, http://www.nature.com/nature/journal/v463/n7279/suppinfo/nature08708_S1.html, 2010.
Cooper, O. R., Parrish, D., Ziemke, J., Balashov, N., Cupeiro, M., Galbally, I., Gilge, S., Horowitz, L., Jensen, N., and Lamarque, J.-F.: Global distribution and trends of tropospheric ozone: An observation-based review, Elementa: Science of the Anthropocene, 2, 000029, 2014.
Cox, P. M., Betts, R. A., Jones, C. D., Spall, S. A., and Totterdell, I. J.: Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model, Nature, 408, 184-187, 2000.
Cox, P. M.: Description of the TRIFFID dynamic global vegetation model, Hadley Centre technical note 24, 2001.
Cruz, F. T., Pitman, A. J., and Wang, Y. P.: Can the stomatal response to higher atmospheric carbon dioxide explain the unusual temperatures during the 2002 Murray-Darling Basin drought?, Journal of Geophysical Research: Atmospheres, 115, 2010.
de Arellano, J. V.-G., van Heerwaarden, C. C., and Lelieveld, J.: Modelled suppression of boundary-layer clouds by plants in a CO2-rich atmosphere, Nature geoscience, 5, 701-704, 2012.
De Kauwe, M., Kala, J., Lin, Y.-S., Pitman, A., Medlyn, B., Duursma, R., Abramowitz, G., Wang, Y.-P., and Miralles, D.: A test of an optimal stomatal conductance scheme within the CABLE land surface model, 8, 431-452, 2015.
Dentener, F., Stevenson, D., Ellingsen, K., van Noije, T., Schultz, M., Amann, M., Atherton, C., Bell, N., Bergmann, D., Bey, I., Bouwman, L., Butler, T., Cofala, J., Collins, B., Drevet, J., Doherty, R., Eickhout, B., Eskes, H., Fiore, A., Gauss, M., Hauglustaine, D., Horowitz, L., Isaksen, I. S. A., Josse, B., Lawrence, M., Krol, M., Lamarque, J. F., Montanaro, V., Müller, J. F., Peuch, V. H., Pitari, G., Pyle, J., Rast, S., Rodriguez, J., Sanderson, M., Savage, N. H., Shindell, D., Strahan, S., Szopa, S., Sudo, K., Van Dingenen, R., Wild, O., and Zeng, G.: The Global Atmospheric Environment for the Next Generation, Environmental Science & Technology, 40, 3586-3594, 10.1021/es0523845, 2006.
Derwent, R. G., Stevenson, D. S., Doherty, R. M., Collins, W. J., Sanderson, M. G., and Johnson, C. E.: Radiative forcing from surface NO x emissions: spatial and seasonal variations, Climatic Change, 88, 385-401, 10.1007/s10584-007-9383-8, 2008.
Ellsworth, D. S.: CO_2 enrichment in a maturing pine forest: are CO_2 exchange and water status in the canopy affected?, Plant, Cell and Environment, 22, 461-472, 1999.
Emberson, L. D., Ashmore, M. R., Cambridge, H. M., Simpson, D., and Tuovinen, J.-P.: Modelling stomatal ozone flux across Europe, Environmental Pollution, 109, 403–413, 2000.
Emberson, L. D., Simpson, D., Tuovinen, J.-P., Ashmore, M. R., and Cambridge, H. M.: Modelling and mapping ozone deposition in Europe, Water Air Soil Pollution, 130, 577–582, 2001.
Engardt, M., Simpson, D., Schwikowski, M., and Granat, L.: Deposition of sulphur and nitrogen in Europe 1900-2050. Model calculations and comparison to historical observations, *Tellus B: Chem. Phys. Meteor.*, 69, 2017.
Etheridge, D. M., Steele, L. P., Langenfelds, R. L., Francey, R. J., M., B., and Morgan, V. I.: Natural and anthropogenic changes in atmospheric CO2 over the last 1000 years from air in Antarctic ice and firn, Journal of Geophysical Research, 101(D2), 4115–4128, doi:10.1029/95JD03410, 1996.

Fagnano, M., Maggio, A., and Fumagalli, I.: Crops' responses to ozone in Mediterranean environments, Environmental Pollution, 157, 1438-1444, 2009.

Fares, S., Vargas, R., Detto, M., Goldstein, A. H., Karlik, J., Paoletti, E., and Vitale, M.: Tropospheric ozone reduces carbon assimilation in trees: estimates from analysis of continuous flux measurements, Global change biology, 19, 2427-2443, 2013.

Felzer, B., Reilly, J., Melillo, J., Kicklighter, D., Sarofim, M., Wang, C., Prinn, R., and Zhuang, Q.: Future Effects of Ozone on Carbon Sequestration and Climate Change Policy Using a Global Biogeochemical Model, Climatic Change, 73, 345-373, 10.1007/s10584-005-6776-4, 2005.

Felzer, B. S. F., Kicklighter, D. W., Melillo, J. M., Wang, C., Zhuang, Q., and Prinn, R. G.: Ozone effects on net primary productivity and carbon sequestration in the conterminous United States using a biogeochemistry model, Tellus, 56B, 230-248, 2004.

Feng, Z., Kobayashi, K., and Ainsworth, E. A.: Impact of elevated ozone concentration on growth, physiology, and yield of wheat (Triticum aestivum L.): a meta-analysis, Global Change Biology, 14, 2696-2708, 10.1111/j.1365-2486.2008.01673.x, 2008.

Fowler, D., Flechard, C., Cape, J. N., Storeton-West, R. L., and Coyle, M.: Measurements of Ozone Deposition to Vegetation Quantifying the Flux, the Stomatal and Non-Stomatal Components, Water, Air, and Soil Pollution, 130, 63-74, 10.1023/a:1012243317471, 2001.

Fowler, D., Pilegaard, K., Sutton, M., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., and Schjørring, J. K.: Atmospheric composition change: ecosystems–atmosphere interactions, Atmospheric Environment, 43, 5193-5267, 2009.

Franz, M., Simpson, D., Arneth, A., and Zaehle, S.: Development and evaluation of an ozone deposition scheme for coupling to a terrestrial biosphere model, Biogeosciences, 14, 45-71, doi:10.5194/bg-14-45-2017, 2017.

Friedlingstein, P., Cox, P., Betts, R., Bopp, L., von Bloh, W., Brovkin, V., Cadule, P., Doney, S., Eby, M., Fung, I., Bala, G., John, J., Jones, C., Joos, F., Kato, T., Kawamiya, M., Knorr, W., Lindsay, K., Matthews, H. D., Raddatz, T., Rayner, P., Reick, C., Roeckner, E., Schnitzler, K. G., Schnur, R., Strassmann, K., Weaver, A. J., Yoshikawa, C., and Zeng, N.: Climate–Carbon Cycle Feedback Analysis: Results from the C4MIP Model Intercomparison, Journal of Climate, 19, 3337-3353, 10.1175/jcli3800.1, 2006.

Fuhrer, J., Val Martin, M., Mills, G., Heald, C. L., Harmens, H., Hayes, F., Sharps, K., Bender, J., and Ashmore, M. R.: Current and future ozone risks to global terrestrial biodiversity and ecosystem processes, Ecology and Evolution, 6, 8785-8799, 10.1002/ece3.2568, 2016.

Gedney, N., Cox, P. M., Bett, R. A., Boucher, O., Huntingford, C., and Stott, P. A.: Detection of a direct carbon dioxide effect in continental river runoff records, Nature, 439, 835-838, 2006.

Grantz, D., Gunn, S., and VU, H. B.: O_3 impacts on plant development: a meta-analysis of root/shoot allocation and growth, Plant, cell & environment, 29, 1193-1209, 2006.

Harmens, H., Mills, G., Emberson, L. D., and Ashmore, M. R.: Implications of climate change for the stomatal flux of ozone: A case study for winter wheat, Environmental Pollution, 146, 763-770, http://dx.doi.org/10.1016/j.envpol.2006.05.018, 2007.

Hayes, F., Wagg, S., Mills, G., Wilkinson, S., and Davies, W.: Ozone effects in a drier climate: implications for stomatal fluxes of reduced stomatal sensitivity to soil drying in a typical grassland species, Global Change Biology, 18, 948-959, 2012.

Heikkinen, J., Ketoja, E., Nuutinen, V., and Regina, K.: Declining trend of carbon in Finnish cropland soils in 1974–2009, Global Change Biology, 19, 1456-1469, 10.1111/gcb.12137, 2013.

Hofmockel, K. S., Zak, D. R., Moran, K. K., and Jastrow, J. D.: Changes in forest soil organic matter pools after a decade of elevated CO_2 and O_3, Soil Biology and Biochemistry, 43, 1518-1527, http://dx.doi.org/10.1016/j.soilbio.2011.03.030, 2011.

Hoshika, Y., Watanabe, M., Inada, N., and Koike, T.: Ozone-induced stomatal sluggishness develops progressively in Siebold's beech (Fagus crenata), Environmental Pollution, 166, 152-156, 2012a.

Hoshika, Y., Omasa, K., and Paoletti, E.: Whole-Tree Water Use Efficiency Is Decreased by Ambient Ozone and Not Affected by O3-Induced Stomatal Sluggishness, PLOS ONE, 7, e39270, 10.1371/journal.pone.0039270, 2012b.
Hoshika, Y., Watanabe, M., Inada, N., and Koike, T.: Model-based analysis of avoidance of ozone stress by stomatal closure in Siebold's beech (*Fagus crenata*), Annals of Botany, 112, 1149-1158, 2013.
Hoshika, Y., Katata, G., Deushi, M., Watanabe, M., Koike, T., and Paoletti, E.: Ozone-induced stomatal sluggishness changes carbon and water balance of temperate deciduous forests., Scientific Reports, doi:10.1038/srep09871, 2015.
Hurtt, G., Chini, L. P., Frolking, S., Betts, R., Feddema, J., Fischer, G., Fisk, J., Hibbard, K., Houghton, R., Janetos, A., and Jones, C. D.: Harmonization of land-use scenarios for the period 1500–2100: 600 years of global gridded annual land-use transitions, wood harvest, and resulting secondary lands, Climatic Change, 109, 117-161, 2011.
IPCC: Climate change 2013: The Physical Science Basis, IPCC Working Group I Contribution to AR5, 2013.
Jacobs, C. M. J.: Direct impact of atmospheric CO_2 enrichment on regional transpiration, Wageningen Agricultural University, 1994.
Janssens, I. A., Freibauer, A., Ciais, P., Smith, P., Nabuurs, G.-J., Folberth, G., Schlamadinger, B., Hutjes, R. W. A., Ceulemans, R., Schulze, E.-D., Valentini, R., and Dolman, A. J.: Europe's Terrestrial Biosphere Absorbs 7 to 12% of European Anthropogenic CO2 Emissions, Science, 300, 1538-1542, 10.1126/science.1083592, 2003.
Jones, C. D., Cox, P., and Huntingford, C.: Uncertainty in climate–carbon-cycle projections associated with the sensitivity of soil respiration to temperature, Tellus B, 55, 642-648, 10.1034/j.1600-0889.2003.01440.x, 2003.
Jung, M., Reichstein, M., Margolis, H. A., Cescatti, A., Richardson, A. D., Arain, M. A., Arneth, A., Bernhofer, C., Bonal, D., Chen, J., Gianelle, D., Gobron, N., Kiely, G., Kutsch, W., Lasslop, G., Law, B. E., Lindroth, A., Merbold, L., Montagnani, L., Moors, E. J., Papale, D., Sottocornola, M., Vaccari, F., and Williams, C.: Global patterns of land-atmosphere fluxes of carbon dioxide, latent heat, and sensible heat derived from eddy covariance, satellite, and meteorological observations, Journal of Geophysical Research: Biogeosciences, 116, n/a-n/a, 10.1029/2010JG001566, 2011.
Kala, J., De Kauwe, M. G., Pitman, A. J., Medlyn, B. E., Wang, Y. P., Lorenz, R., and Perkins-Kirkpatrick, S. E.: Impact of the representation of stomatal conductance on model projections of heatwave intensity., Scientific Reports, 1-7, 10.1038/srep23418, 2016.
Karlsson, P. E., Braun, S., Broadmeadow, M., Elvira, S., Emberson, L., Gimeno, B. S., Le Thiec, D., Novak, K., Oksanen, E., Schaub, M., Uddling, J., and Wilkinson, M.: Risk assessments for forest trees: The performance of the ozone flux versus the AOT concepts, Environmental Pollution, 146, 608-616, http://dx.doi.org/10.1016/j.envpol.2006.06.012, 2007.
Karnosky, D., Percy, K. E., Xiang, B., Callan, B., Noormets, A., Mankovska, B., Hopkin, A., Sober, J., Jones, W., and Dickson, R.: Interacting elevated CO2 and tropospheric O3 predisposes aspen (Populus tremuloides Michx.) to infection by rust (Melampsora medusae f. sp. tremuloidae), Global Change Biology, 8, 329-338, 2002.
Karnosky, D. F., Skelly, J. M., Percy, K. E., and Chappelka, A. H.: Perspectives regarding 50years of research on effects of tropospheric ozone air pollution on US forests, Environmental Pollution, 147, 489-506, 2007.
Keeling, C. D., and Whorf, T. P.: Atmospheric CO2 records from sites in the SIO air sampling network. In Trends: A Compendium of Data on Global Change, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A. , 2004.
Kitao, M., Löw, M., Heerdt, C., Grams, T. E., Häberle, K.-H., and Matyssek, R.: Effects of chronic elevated ozone exposure on gas exchange responses of adult beech trees (Fagus sylvatica) as related to the within-canopy light gradient, Environmental Pollution, 157, 537-544, 2009.

Kjellström, E., Nikulin, G., Hansson, U., Strandberg, G., and Ullerstig, A.: 21st century changes in the European climate: uncertainties derived from an ensemble of regional climate model simulations, Tellus A, 63, 24-40, 2011.

Kubiske, M., Quinn, V., Marquardt, P., and Karnosky, D.: Effects of Elevated Atmospheric CO2 and/or O3 on Intra-and Interspecific Competitive Ability of Aspen, Plant biology, 9, 342-355, 2007.

Lamarque, J., Shindell, D. T., Josse, B., Young, P., Cionni, I., Eyring, V., Bergmann, D., Cameron-Smith, P., Collins, W. J., and Doherty, R.: The Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP): overview and description of models, simulations and climate diagnostics, Geoscientific Model Development, 6, 179-206, 2013.

Langner, J., Engardt, M., Baklanov, A., Christensen, J. H., Gauss, M., Geels, C., Hedegaard, G. B., Nuterman, R., Simpson, D., and Soares, J.: A multi-model study of impacts of climate change on surface ozone in Europe, Atmospheric Chemistry and Physics, 12, 10423-10440, 2012a.

Langner, J., Engardt, M., and Andersson, C.: European summer surface ozone 1990–2100, Atmospheric Chemistry and Physics, 12, 10097-10105, 2012b.

Le Quéré, C., Moriarty, R., Andrew, R. M., Peters, G. P., Ciais, P., Friedlingstein, P., Jones, S. D., Sitch, S., Tans, P., Arneth, A., Boden, T. A., Bopp, L., Bozec, Y., Canadell, J. G., Chini, L. P., Chevallier, F., Cosca, C. E., Harris, I., Hoppema, M., Houghton, R. A., House, J. I., Jain, A. K., Johannessen, T., Kato, E., Keeling, R. F., Kitidis, V., Klein Goldewijk, K., Koven, C., Landa, C. S., Landschützer, P., Lenton, A., Lima, I. D., Marland, G., Mathis, J. T., Metzl, N., Nojiri, Y., Olsen, A., Ono, T., Peng, S., Peters, W., Pfeil, B., Poulter, B., Raupach, M. R., Regnier, P., Rödenbeck, C., Saito, S., Salisbury, J. E., Schuster, U., Schwinger, J., Séférian, R., Segschneider, J., Steinhoff, T., Stocker, B. D., Sutton, A. J., Takahashi, T., Tilbrook, B., van der Werf, G. R., Viovy, N., Wang, Y. P., Wanninkhof, R., Wiltshire, A., and Zeng, N.: Global carbon budget 2014, Earth Syst. Sci. Data, 7, 47-85, 10.5194/essd-7-47-2015, 2015.

Le Quéré, C., Andrew, R. M., Canadell, J. G., Sitch, S., Korsbakken, J. I., Peters, G. P., Manning, A. C., Boden, T. A., Tans, P. P., Houghton, R. A., Keeling, R. F., Alin, S., Andrews, O. D., Anthoni, P., Barbero, L., Bopp, L., Chevallier, F., Chini, L. P., Ciais, P., Currie, K., Delire, C., Doney, S. C., Friedlingstein, P., Gkritzalis, T., Harris, I., Hauck, J., Haverd, V., Hoppema, M., Klein Goldewijk, K., Jain, A. K., Kato, E., Körtzinger, A., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Lombardozzi, D., Melton, J. R., Metzl, N., Millero, F., Monteiro, P. M. S., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S. I., O'Brien, K., Olsen, A., Omar, A. M., Ono, T., Pierrot, D., Poulter, B., Rödenbeck, C., Salisbury, J., Schuster, U., Schwinger, J., Séférian, R., Skjelvan, I., Stocker, B. D., Sutton, A. J., Takahashi, T., Tian, H., Tilbrook, B., van der Laan-Luijkx, I. T., van der Werf, G. R., Viovy, N., Walker, A. P., Wiltshire, A. J., and Zaehle, S.: Global Carbon Budget 2016, Earth Syst. Sci. Data, 8, 605-649, 10.5194/essd-8-605-2016, 2016.

Le Quéré, C., Andrew, R. M., Friedlingstein, P., Sitch, S., Pongratz, J., Manning, A. C., Korsbakken, J. I., Peters, G. P., Canadell, J. G., Jackson, R. B., Boden, T. A., Tans, P. P., Andrews, O. D., Arora, V. K., Bakker, D. C. E., Barbero, L., Becker, M., Betts, R. A., Bopp, L., Chevallier, F., Chini, L. P., Ciais, P., Cosca, C. E., Cross, J., Currie, K., Gasser, T., Harris, I., Hauck, J., Haverd, V., Houghton, R. A., Hunt, C. W., Hurtt, G., Ilyina, T., Jain, A. K., Kato, E., Kautz, M., Keeling, R. F., Klein Goldewijk, K., Körtzinger, A., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Lima, I., Lombardozzi, D., Metzl, N., Millero, F., Monteiro, P. M. S., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S.-I., Nojiri, Y., Padín, X. A., Peregon, A., Pfeil, B., Pierrot, D., Poulter, B., Rehder, G., Reimer, J., Rödenbeck, C., Schwinger, J., Séférian, R., Skjelvan, I., Stocker, B. D., Tian, H., Tilbrook, B., van der Laan-Luijkx, I. T., van der Werf, G. R., van Heuven, S., Viovy, N., Vuichard, N., Walker, A. P., Watson, A. J., Wiltshire, A. J., Zaehle, S., and Zhu, D.: Global Carbon Budget 2017, Earth Syst. Sci. Data Discuss, in review, 2017.

Leuzinger, S., and Körner, C.: Water savings in mature deciduous forest trees under elevated CO_2, Global Change Biology, 13, 2498-2508, doi:10.1111/j.1365-2486.2007.01467.x, 2007.

Lin, Y.-S., Medlyn, B. E., Duursma, R. A., Prentice, I. C., Wang, H., Baig, S., Eamus, D., de Dios, V. R., Mitchell, P., and Ellsworth, D. S.: Optimal stomatal behaviour around the world, Nature Climate Change, 5, 459-464, 2015.

Lindroth, R. L.: Impacts of Elevated Atmospheric CO2 and O3 on Forests: Phytochemistry, Trophic Interactions, and Ecosystem Dynamics, Journal of Chemical Ecology, 36, 2-21, 10.1007/s10886-009-9731-4, 2010.

Logan, J. A., Staehelin, J., Megretskaia, I. A., Cammas, J. P., Thouret, V., Claude, H., De Backer, H., Steinbacher, M., Scheel, H. E., Stübi, R., Fröhlich, M., and Derwent, R.: Changes in ozone over Europe: Analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites, Journal of Geophysical Research, 117, 1-23, 2012.

Lombardozzi, D., Levis, S., Bonan, G., Hess, P. G., and Sparks, J. P.: The Influence of Chronic Ozone Exposure on Global Carbon and Water Cycles, Journal of Climate, 28, 292-305, 10.1175/jcli-d-14-00223.1, 2015.

Long, S. P., Ainsworth, E. A., Leakey, A. D. B., Nosberger, J., and Ort, D. R.: Food for Thought: Lower-Than-Expected Crop Yield Stimulation with Rising CO_2 Concentrations, Science, 312, 1918-1921, 10.1126/science.1114722, 2006.

Löw, M., Herbinger, K., Nunn, A., Häberle, K.-H., Leuchner, M., Heerdt, C., Werner, H., Wipfler, P., Pretzsch, H., and Tausz, M.: Extraordinary drought of 2003 overrules ozone impact on adult beech trees (Fagus sylvatica), Trees, 20, 539-548, 2006.

Loya, W. M., Pregitzer, K. S., Karberg, N. J., King, J. S., and Giardina, C. P.: Reduction of soil carbon formation by tropospheric ozone under increased carbon dioxide levels., Nature, 425, 705-707, 2003.

Luyssaert, S., Abril, G., Andres, R., Bastviken, D., Bellassen, V., Bergamaschi, P., Bousquet, P., Chevallier, F., Ciais, P., Corazza, M., Dechow, R., Erb, K. H., Etiope, G., Fortems-Cheiney, A., Grassi, G., Hartmann, J., Jung, M., Lathière, J., Lohila, A., Mayorga, E., Moosdorf, N., Njakou, D. S., Otto, J., Papale, D., Peters, W., Peylin, P., Raymond, P., Rödenbeck, C., Saarnio, S., Schulze, E. D., Szopa, S., Thompson, R., Verkerk, P. J., Vuichard, N., Wang, R., Wattenbach, M., and Zaehle, S.: The European land and inland water CO2, CO, CH4 and N2O balance between 2001 and 2005, Biogeosciences, 9, 3357-3380, 10.5194/bg-9-3357-2012, 2012.

Massman, W. J.: A review of the molecular diffusivities of H2O, CO2, CH4, CO, O3, SO2, NH3, N2O, NO, and NO2 in air, O2 and N2 near STP, Atmospheric Environment, 32, 1111-1127, http://dx.doi.org/10.1016/S1352-2310(97)00391-9, 1998.

Matyssek, R., Wieser, G., Ceulemans, R., Rennenberg, H., Pretzsch, H., Haberer, K., Löw, M., Nunn, A., Werner, H., and Wipfler, P.: Enhanced ozone strongly reduces carbon sink strength of adult beech (Fagus sylvatica)–Resume from the free-air fumigation study at Kranzberg Forest, Environmental Pollution, 158, 2527-2532, 2010a.

Matyssek, R., Karnosky, D., Wieser, G., Percy, K., Oksanen, E., Grams, T., Kubiske, M., Hanke, D., and Pretzsch, H.: Advances in understanding ozone impact on forest trees: messages from novel phytotron and free-air fumigation studies, Environmental Pollution, 158, 1990-2006, 2010b.

McLaughlin, S. B., Nosal, M., Wullschleger, S. D., and Sun, G.: Interactive effects of ozone and climate on tree growth and water use in a southern Appalachian forest in the USA, New Phytologist, 174, 109-124, 10.1111/j.1469-8137.2007.02018.x, 2007a.

McLaughlin, S. B., Wullschleger, S. D., Sun, G., and Nosal, M.: Interactive effects of ozone and climate on water use, soil moisture content and streamflow in a southern Appalachian forest in the USA, New Phytologist, 174, 125-136, 10.1111/j.1469-8137.2007.01970.x, 2007b.

Medlyn, B. E., Badeck, F. W., De Pury, D. G. G., Barton, C. V. M., Broadmeadow, M., Ceulemans, R., De Angelis, P., Forstreuter, M., Jach, M. E., Kellomaki, S., Laitat, E., Marek, M., Philippot, S., Rey, A., Strassemeyer, J., Laitinen, K., Liozon, R., Portier, B., Roberntz, P., Wang, K., and Jstbid, P. G.: Effects of elevated [CO_2] on photosynthesis in European forest species: a meta-analysis of model parameters, Plant, Cell & Environment, 22, 1475-1495, doi:10.1046/j.1365-3040.1999.00523.x, 1999.

Medlyn, B. E., Barton, C. V. M., Broadmeadow, M. S. J., Ceulemans, R., De Angelis, P., Forstreuter, M., Freeman, M., Jackson, S. B., Kellomaki, S., Laitat, E., Rey, A., Roberntz, P., Sigurdsson, B. D., Strassemeyer, J., Wang, K., Curtis, P. S., and Jarvis, P. G.: Stomatal conductance of forest species after long-term exposure to elevated CO_2 concentration: a synthesis, New Phytologist, 149, 247-264, 2001.

Medlyn, B. E., Duursma, R. A., Eamus, D., Ellsworth, D. S., Prentice, I. C., Barton, C. V., Crous, K. Y., de Angelis, P., Freeman, M., and Wingate, L.: Reconciling the optimal and empirical approaches to modelling stomatal conductance, Global Change Biology, 17, 2134-2144, 2011.

Mercado, L. M., Bellouin, N., Sitch, S., Boucher, O., Huntingford, C., Wild, M., and Cox, P. M.: Impact of changes in diffuse radiation on the global land carbon sink, Nature, 458, 1014-1017, http://www.nature.com/nature/journal/v458/n7241/suppinfo/nature07949_S1.html, 2009.

Mills, G., Hayes, F., Wilkinson, S., and Davies, W. J.: Chronic exposure to increasing background ozone impairs stomatal functioning in grassland species, Global Change Biology, 15, 1522-1533, 2009.

Mills, G., Hayes, F., Simpson, D., Emberson, L., Norris, D., Harmens, H., and BÜKer, P.: Evidence of widespread effects of ozone on crops and (semi-)natural vegetation in Europe (1990–2006) in relation to AOT40- and flux-based risk maps, Global Change Biology, 17, 592-613, 10.1111/j.1365-2486.2010.02217.x, 2011b.

Mills, G., Harmens, H., Wagg, S., Sharps, K., Hayes, F., Fowler, D., Sutton, M., and Davies, B.: Ozone impacts on vegetation in a nitrogen enriched and changing climate, Environmental Pollution, 208, 898-908, 2016.

Norby, R. J., Wullschleger, S. D., Gunderson, C. A., Johnson, D. W., and Ceulemans, R.: Tree responses to rising CO_2 in field experiments: implications for the future forest, Plant, Cell and Environment, 22, 683-714, 1999.

Norby, R. J., DeLucia, E. H., Gielen, B., Calfapietra, C., Giardina, C. P., King, J. S., Ledford, J., McCarthy, H. R., Moore, D. J. P., Ceulemans, R., De Angelis, P., Finzi, A. C., Karnosky, D. F., Kubiske, M. E., Lukac, M., Pregitzer, K. S., Scarascia-Mugnozza, G. E., Schlesinger, W. H., and Oren, R.: Forest response to elevated CO2 is conserved across a broad range of productivity, Proc. Natl. Acad. Sci. U. S. A., 102, 18052-18056, 10.1073/pnas.0509478102, 2005.

Nunn, A. J., Reiter, I. M., Häberle, K.-H., Langebartels, C., Bahnweg, G., Pretzsch, H., Sandermann, H., and Matyssek, R.: Response patterns in adult forest trees to chronic ozone stress: identification of variations and consistencies, Environmental Pollution, 136, 365-369, 2005.

Pacifico, F., Folberth, G. A., Jones, C. D., Harrison, S. P., and Collins, W. J.: Sensitivity of biogenic isoprene emissions to past, present, and future environmental conditions and implications for atmospheric chemistry, Journal of Geophysical Research: Atmospheres, 117, n/a-n/a, 10.1029/2012JD018276, 2012.

Paoletti, E., and Grulke, N. E.: Ozone exposure and stomatal sluggishness in different plant physiognomic classes, Environmental Pollution, 158, 2664-2671, 2010.

Parrish, D. D., Law, K. S., Staehelin, J., Derwent, R., Cooper, O. R., Tanimoto, H., Volz-Thomas, A., Gilge, S., Scheel, H. E., Steinbacher, M., and Chan, E.: Long-term changes in lower tropospheric baseline ozone concentrations at northern mid-latitudes, Atmos. Chem. Phys., 12, 11485-11504, 10.5194/acp-12-11485-2012, 2012.

Percy, K. E., Awmack, C. S., Lindroth, R. L., Kubiske, M. E., Kopper, B. J., Isebrands, J., Pregitzer, K. S., Hendrey, G. R., Dickson, R. E., and Zak, D. R.: Altered performance of forest pests under atmospheres enriched by CO2 and O3, Nature, 420, 403-407, 2002.

Royal-Society: Ground-level ozone in the 21st century: future trends, impacts and policy implications, Science Policy Report 15/08, 2008.

Samuelsson, P., Jones, C. G., Willén, U., Ullerstig, A., Gollvik, S., Hansson, U., Jansson, C., Kjellström, E., Nikulin, G., and Wyser, K.: The Rossby Centre Regional Climate model RCA3: model description and performance, Tellus A, 63, 4-23, 2011.

Saxe, H., Ellsworth, D. S., and Heath, J.: Tree and forest functioning in an enriched CO_2 atmosphere, New Phytologist, 139, 395-436, doi:10.1046/j.1469-8137.1998.00221.x, 1998.

Schulze, E.-D., Ciais, P., Luyssaert, S., Schrumpf, M., Janssens, I. A., Thiruchittampalam, B., Theloke, J., Saurat, M., Bringezu, S., and Lelieveld, J.: The European carbon balance. Part 4: integration of carbon and other trace-gas fluxes, Global Change Biology, 16, 1451-1469, 2010.

Schulze, E. D., Luyssaert, S., Ciais, P., Freibauer, A., Janssens, I. A., and et al.: Importance of methane and nitrous oxide for Europe's terrestrial greenhouse-gas balance, Nature Geosci, 2, 842-850, http://www.nature.com/ngeo/journal/v2/n12/suppinfo/ngeo686_S1.html, 2009.

Sicard, P., De Marco, A., Troussier, F., Renoua, C., Vas, N., and Paoletti, E.: Decrease in surface ozone concentrations at Mediterranean remote sites and increase in the cities, Atmospheric Environment, 79, 705-715, 2013.

Simpson, D., Benedictow, A., Berge, H., Bergström, R., Emberson, L. D., Fagerli, H., Flechard, C. R., Hayman, G. D., Gauss, M., and Jonson, J. E.: The EMEP MSC-W chemical transport model–technical description, Atmospheric Chemistry and Physics, 12, 7825-7865, 2012.

Simpson, D., Andersson, C., Christensen, J. H., Engardt, M., Geels, C., Nyiri, A., Posch, M., Soares, J., Sofiev, M., and Wind, P.: Impacts of climate and emission changes on nitrogen deposition in Europe: a multi-model study, Atmospheric Chemistry and Physics, 14, 6995-7017, 2014a.

Simpson, D., Arneth, A., Mills, G., Solberg, S., and Uddling, J.: Ozone—the persistent menace: interactions with the N cycle and climate change, Current Opinion in Environmental Sustainability, 9, 9-19, 2014b.

Sitch, S., Cox, P. M., Collins, W. J., and Huntingford, C.: Indirect radiative forcing of climate change through ozone effects on the land-carbon sink, Nature, 448, 791-794, http://www.nature.com/nature/journal/v448/n7155/suppinfo/nature06059_S1.html, 2007.

Sitch, S., Friedlingstein, P., Gruber, N., Jones, S. D., Murray-Tortarolo, G., Ahlström, A., Doney, S. C., Graven, H., Heinze, C., Huntingford, C., Levis, S., Levy, P. E., Lomas, M., Poulter, B., Viovy, N., Zaehle, S., Zeng, N., Arneth, A., Bonan, G., Bopp, L., Canadell, J. G., Chevallier, F., Ciais, P., Ellis, R., Gloor, M., Peylin, P., Piao, S. L., Le Quéré, C., Smith, B., Zhu, Z., and Myneni, R.: Recent trends and drivers of regional sources and sinks of carbon dioxide, Biogeosciences, 12, 653-679, 10.5194/bg-12-653-2015, 2015.

Sleutel, S., De Neve, S., and Hofman, G.: Estimates of carbon stock changes in Belgian cropland., Soil Use and Management, 19, 166-171, 10.1079/SUM2003187, 2003.

Sun, G. E., McLaughlin, S. B., Porter, J. H., Uddling, J., Mulholland, P. J., Adams, M. B., and Pederson, N.: Interactive influences of ozone and climate on streamflow of forested watersheds, Global Change Biology, 18, 3395-3409, 10.1111/j.1365-2486.2012.02787.x, 2012.

Tai, P. K. A., Val Martin, M., and Heald, C. L.: Threat to future global food security from climate change and ozone air pollution, Nature Climate Change, 4, 817 - 821, 2014.

Talhelm, A. F., Pregitzer, K. S., Kubiske, M. E., Zak, D. R., Campany, C. E., Burton, A. J., Dickson, R. E., Hendrey, G. R., Isebrands, J. G., Lewin, K. F., Nagy, J., and Karnosky, D. F.: Elevated carbon dioxide and ozone alter productivity and ecosystem carbon content in northern temperate forests, Global Change Biology, 20, 2492-2504, 10.1111/gcb.12564, 2014.

Tricker, P. J., Pecchiari, M., Bunn, S. M., Vaccari, F. P., Peressotti, A., Miglietta, F., and Taylor, G.: Water use of a bioenergy plantation increases in a future high CO_2 world, Biomass and Bioenergy, 33, 200-208, 2009.

Tuovinen, J.-P., Emberson, L., and Simpson, D.: Modelling ozone fluxes to forests for risk assessment: status and prospects, Annals of Forest Science, 66, 1-14, 2009.

Tuovinen, J., Hakola, H., Karlsson, P., and Simpson, D.: Air pollution risks to Northern European forests in a changing climate, Climate Change, Air Pollution and Global Challenges Understanding and Perspectives from Forest Research, 2013.

Uddling, J., Teclaw, R. M., Pregitzer, K. S., and Ellsworth, D. S.: Leaf and canopy conductance in aspen and aspen-birch forests under free-air enrichment of carbon dioxide and ozone, Tree Physiology, 29, 1367-1380, 2009.

Verstraeten, W. W., Neu, J. L., Williams, J. E., Bowman, K. W., Worden, J. R., and Boersma, K. F.: Rapid increases in tropospheric ozone production and export from China, Nature Geoscience 8, 690-695, 2015.
Vingarzan, R.: A review of surface ozone background levels and trends, Atmospheric Environment, 38, 3431-3442, https://doi.org/10.1016/j.atmosenv.2004.03.030, 2004.
Weedon, G. P., Gomes, S., Viterbo, P., Österle, H., Adam, J. C., Bellouin, N., Boucher, O., and Best, M. J.: The WATCH Forcing Data 1958-2001: a meteorological forcing dataset for land surface- and hydrological models. , WATCH Tech. Rep. 22, 41p (available at www.eu-watch.org/publications). 2010.
Weedon, G. P., Gomes, S., Viterbo, P., Shuttleworth, W. J., Blyth, E., Österle, H., Adam, J. C., Bellouin, N., Boucher, O., and Best, M.: Creation of the WATCH Forcing data and its use to assess global and regional reference crop evaporation over land during the twentieth century, Journal of Hydrometerology, 12, 823-848, doi: 10.1175/2011JHM1369.1., 2011.
Wilkinson, S., and Davies, W. J.: Ozone suppresses soil drying-and abscisic acid (ABA)-induced stomatal closure via an ethylene-dependent mechanism, Plant, Cell & Environment, 32, 949-959, 2009.
Wilkinson, S., and Davies, W. J.: Drought, ozone, ABA and ethylene: new insights from cell to plant to community, Plant, Cell & Environment, 33, 510-525, 10.1111/j.1365-3040.2009.02052.x, 2010.
Wittig, V. E., Ainsworth, E. A., and Long, S. P.: To what extent do current and projected increases in surface ozone affect photosynthesis and stomatal conductance of trees? A meta-analytic review of the last 3 decades of experiments, Plant, Cell & Environment, 30, 1150-1162, 10.1111/j.1365-3040.2007.01717.x, 2007.
Wittig, V. E., Ainsworth, E. A., Naidu, S. L., Karnosky, D. F., and Long, S. P.: Quantifying the impact of current and future tropospheric ozone on tree biomass, growth, physiology and biochemistry: a quantitative meta-analysis, Global Change Biology, 15, 396-424, 10.1111/j.1365-2486.2008.01774.x, 2009.
Wullschleger, S. D., Gunderson, C. A., Hanson, P. J., Wilson, K. B., and Norby, R. J.: Sensitivity of stomatal and canopy conductance to elevated CO_2 concentration; interacting variables and perspectives of scale, New Phytologist, 153, 485-496, doi:10.1046/j.0028-646X.2001.00333.x, 2002.
Young, P., Arneth, A., Schurgers, G., Zeng, G., and Pyle, J. A.: The CO_2 inhibition of terrestrial isoprene emission significantly affects future ozone projections, Atmospheric Chemistry and Physics, 9, 2793-2803, 2009.
Young, P., Archibald, A., Bowman, K., Lamarque, J.-F., Naik, V., Stevenson, D., Tilmes, S., Voulgarakis, A., Wild, O., and Bergmann, D.: Pre-industrial to end 21st century projections of tropospheric ozone from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), Atmospheric Chemistry and Physics, 13, 2063-2090, 2013.
Zaehle, S.: Terrestrial nitrogen–carbon cycle interactions at the global scale, Philosophical Transactions of the Royal Society B: Biological Sciences, 368, 20130125, 10.1098/rstb.2013.0125, 2013.
Zak, D. R., Pregitzer, K. S., Kubiske, M. E., and Burton, A. J.: Forest productivity under elevated CO2 and O3: positive feedbacks to soil N cycling sustain decade-long net primary productivity enhancement by CO2, Ecology Letters, 14, 1220-1226, 10.1111/j.1461-0248.2011.01692.x, 2011.

Supplementary Information

S1 Fractional cover of JULES PFTs

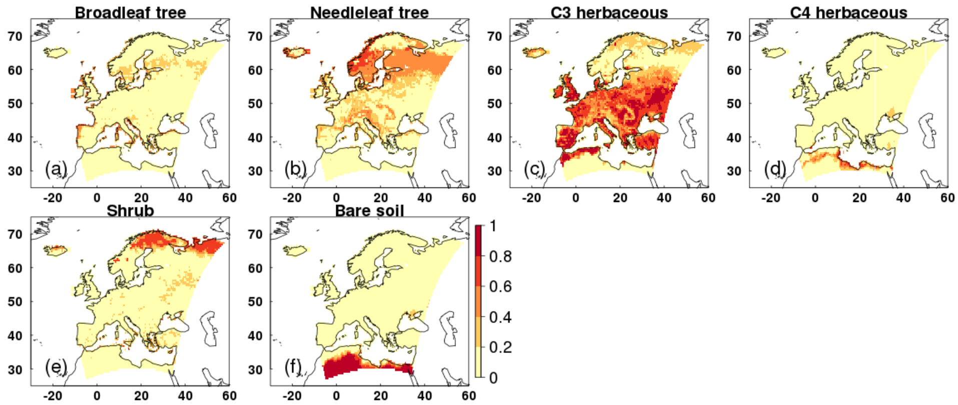

Figure S1. Fractional cover of each JULES PFT and bare soil at 0.5° x 0.5° resolution.

S2 Calibration of O_3 uptake model for European vegetation

Here we use the latest literature on O_3 dose-response relationships derived from observed field data across Europe (CLRTAP, 2017) to calculate the key PFT-specific parameters. Data comes from the UNECE CLRTAP (2017) report which is a synthesis of the latest peer reviewed literature, collated by a panel of experts and so is considered the state-of the art knowledge. Each PFT was calibrated for a high and low plant O_3 sensitivity to account for uncertainty in the sensitivity of different plant species to O_3, using the approach of Sitch *et al*., (2007). In addition, where possible owing to available data, a distinction was made for Mediterranean regions. This was because the work of Büker et al. (2015) showed that different O_3 dose-response relationships are needed to describe the O_3 sensitivity of dominant Mediterranean trees. For the C_3 herbaceous PFT – the dominant land cover type across the European domain in this study (Fig. S1) - the O_3 sensitivity was calibrated against observations for wheat to give a representation of agricultural regions (high plant O_3 sensitivity), versus natural grassland (low plant O_3 sensitivity), with a separate function for Mediterranean grasslands (low plant O_3 sensitivity), all taken from CLRTAP (2017). Tree/shrub PFTs were calibrated against observed O_3 dose-response functions for the high plant O_3 sensitivity (BT = Birch/Beech, BT-Med = deciduous oaks, NT = Norway spruce, shrub = Birch/Beech) all from CLRTAP (2017). The low plant O_3 sensitivity functions for trees/shrubs were calibrated as being 20 % less sensitive based on the difference in sensitivity between high and low sensitive tree species in the Karlsson et al. (2007) study. Due to limitations in data availability, the shrub parameterisation uses the observed dose-response functions for broadleaf trees. Similarly, the parameterisation for C_4 herbaceous uses the observed dose-responses for C_3 herbaceous, however the fractional cover of C_4 herbs across Europe is low (Fig. S1), so this assumption affects a very small percentage of land cover. See Table S1 and Figure S2.

To calibrate the O_3 uptake model for the fast carbon fluxes, e.g. net primary productivity (NPP), JULES was run across Europe forced using the WFDEI observational climate dataset (Weedon, 2013) at 0.5° X 0.5° spatial and three hour temporal resolution. JULES uses interpolation to disaggregate the forcing data down from 3 hours to an hourly model time step. The model was spun-up over the period 1979 to 1999 with a fixed atmospheric CO_2 concentration of 368.33 ppm (1999 value from Mauna Loa observations, (Tans and Keeling)). Zero tropospheric ozone concentration was assumed for the control simulation, for the simulations with O_3, spin-up used spatially explicit fields of present day O_3 concentration produced using the UK Chemistry and Aerosol (UKCA) model with standard chemistry from the run evaluated by O'Connor et al. (2014). A fixed land cover map was used based on IGBP (International Geosphere-Biosphere Programme) land cover classes (IGBP-DIS), therefore as the vegetation distribution was fixed and the calibration was not looking at carbon stores, a short spin-up was adequate to equilibrate soil temperature and soil moisture. JULES was then run for year 2000 with a corresponding CO_2 concentration of 369.52 ppm (from Mauna Loa observations, (Tans and Keeling)) and monthly fields of spatially explicit tropospheric O_3 (O'Connor et al., 2014) as necessary.

Calibration was performed using four simulations: with i) zero tropospheric O_3 concentration, this was the control simulation (NPP_control), ii) tropospheric O_3 at current ambient concentration (NPP_O3), iii) ambient +20 ppb (NPP_O3+20) and iv) ambient +40 ppb (NPP_O3+40). The different O_3 simulations (i.e. ambient, ambient + 20 and ambient + 40 ppb) were used to capture the range of O_3 conditions used in constructing the observed O_3 dose-response relationships deployed for calibration, often these had been constructed under artificially manipulated conditions of ambient + 40 ppb O_3 for example. For each simulation with O_3, JULES used the observed PFT-specific threshold value of O_3 uptake (i.e. parameter F_{O3crit}), and an initial estimate of the parameter '*a*' (equation 2). For each PFT and each simulation, hourly estimates of NPP and O_3 uptake for the top sunlit leaf in excess of F_{O3crit} were accumulated over a PFT dependent accumulation (i.e. ~6 months for broadleaf trees and shrubs, all year for needle leaf trees, and ~3 months for herbaceous species, through the growing season). Change in total NPP over the accumulation period (NPP_O3/+20/+40 divided by NPP_control) was calculated for each O_3 simulation and plotted against the cumulative uptake of O_3 over the same period. The linear regression of this relationship was calculated, and slope and intercept compared against the observed dose-response relationships. Values of the parameter 'a' were adjusted, and the procedure repeated until the linear regression through the simulation points matched that of the observations (Fig. S2). JULES is run to be as comparable as possible to the dose-based O_3 risk indicator used in CLRTAP (2017), as only the O_3 flux to top of canopy sunlit leaves is accumulated (i.e. the O_3 flux per projected leaf area). See Table S1 Figure S2.

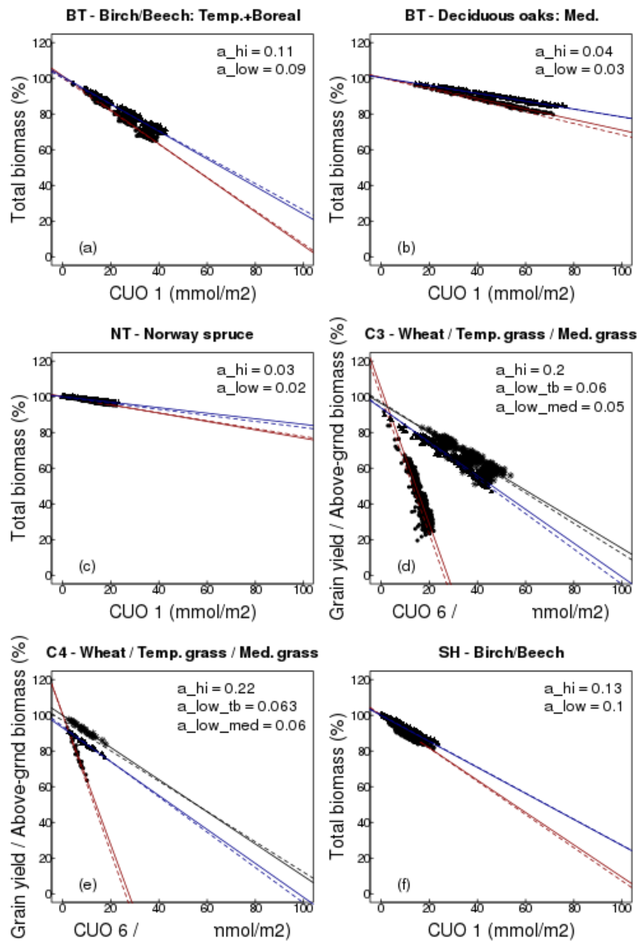

Figure S2. Calibration of JULES for O_3 impacts on plant productivity for each JULES PFT ; a) broadleaf tree – temperate/boreal, b) broadleaf tree Mediterranean, c) Needle leaf tree, d) C_3 herbaceous (split into temperate/boreal and Mediterranean for the natural grasslands), e) C_4 herbaceous (split into temperate/boreal and Mediterranean for the natural grasslands), and f) shrub. High (red) and low (blue) plant O_3 sensitivities are shown. For the herbaceous PFTs the low sensitivity calibration is separate for Mediterranean regions (black). The solid line is the regression line through the modelled points, the dashed line is the regression line from the observed dose-response relationship. The x axis is cumulative uptake of O_3 (CUO) above the critical O_3 threshold (F_{O3crit}).

Commented [ORJ43]: RC1 8)

	High Sensitivity				
	BT	**NT**	**C3**	**C4**	**SH**
F_{O3crit} (nmol/m^2/s)	1.00	1.00	1.00	1.00	1.00
a (mmol/m^2)	0.110	0.030	0.200	0.220	0.130
Function	Birch/Beech: y=100.2-0.93x	Norway spruce: y=99.8-0.22x	Wheat: y=100.3-3.85x	Wheat: y=100.3-3.85x	Birch/Beech: y=100.2-0.93x
dqcrit (kg kg^{-1})	0.09	0.06	0.1	0.075	0.1
f0	0.875	0.875	0.9	0.8	0.9
g_1 *(kPa$^{0.5}$)*	3.22	2.22	5.56	1.1	2.24
	Low Sensitivity				
	BT	**NT**	**C3**	**C4**	**SH**
F_{O3crit} (nmol/m^2/s)	1.00	1.00	1.00	1.00	1.00
a (mmol/m^2)	0.090	0.020	0.060	0.063	0.100
Function	Birch/Beech: y=100.2-0.74x	Norway spruce: y=99.8-0.17x	Temperate perennial grassland: y=93.9-0.99x	Temperate perennial grassland: y=93.9-0.99x	Birch/Beech: y=100.2-0.74x
	High Sensitivity				
	BT - Med.				
F_{O3crit} (nmol/m^2/s)	1.00				
a (mmol/m^2)	0.040				
Function	Dec. Oaks: y=100.3-0.32x				
	Low Sensitivity				
	BT - Med.	**C3 - Med.**	**C4 - Med.**		
F_{O3crit} (nmol/m^2/s)	1.00	1.00	1.00		
a (mmol/m^2)	0.030	0.050	0.060		
Function	Dec. Oaks: y=100.3-0.22x	Mediterranean annual pasture: y=97.1-0.85x	Mediterranean annual pasture: y=97.1-0.85x		

Table S1. PFT-specific parameter values used in the O_3 uptake and g_s formulation in JULES. F_{O3crit} is the critical O_3 threshold above which damage occurs, *a* determines the reduction in photosynthesis with O_3 exposure, 'function' shows the regression equation for the observed functions (x is F_{O3crit}), dq_{crit} (kg kg^{-1}) is a PFT specific parameters representing the critical humidity deficit at the leaf surface (used in the default JULES g_s model), f_0 is the leaf internal to atmospheric CO_2 ratio (c_i/c_a) at the leaf specific humidity deficit (also used in the default JULES g_s model), and g_1 is the PFT specific parameter of the Medlyn *et al*., (2011) g_s model. The parameters dq_{crit}, f_0 and g_1 vary by PFT, but not by O_3 sensitivity so are only shown once here.

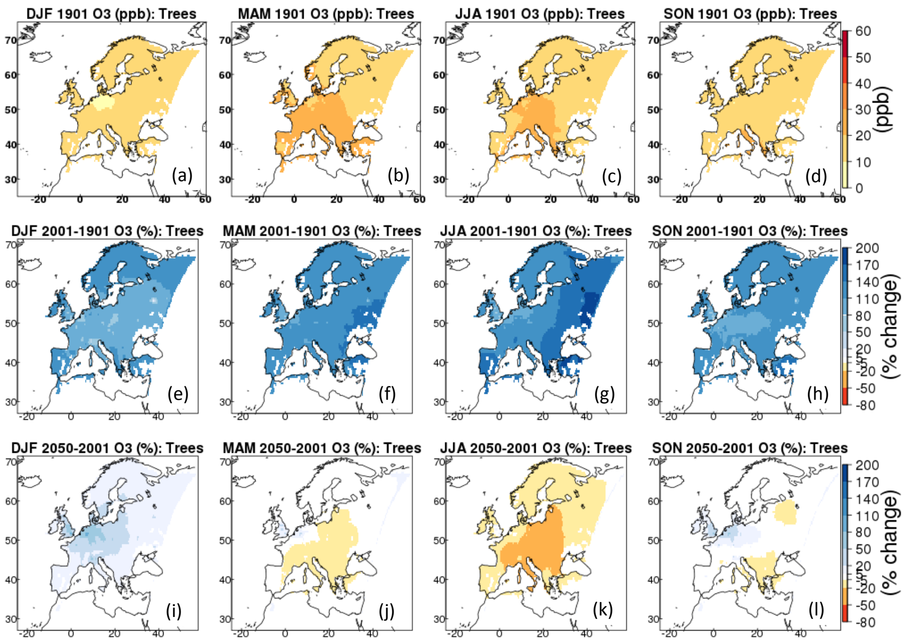

Figure S3. (a-d) 1901 seasonal mean (DJF, MAM, JJA, SON) O_3 concentration (ppb) from EMEP for woody (tree and shrub) PFTs; (e-h) change in seasonal O_3 concentration (%) from 1901 to 2001; (i-l) change in seasonal O_3 concentration (%) from 2001 to 2050.

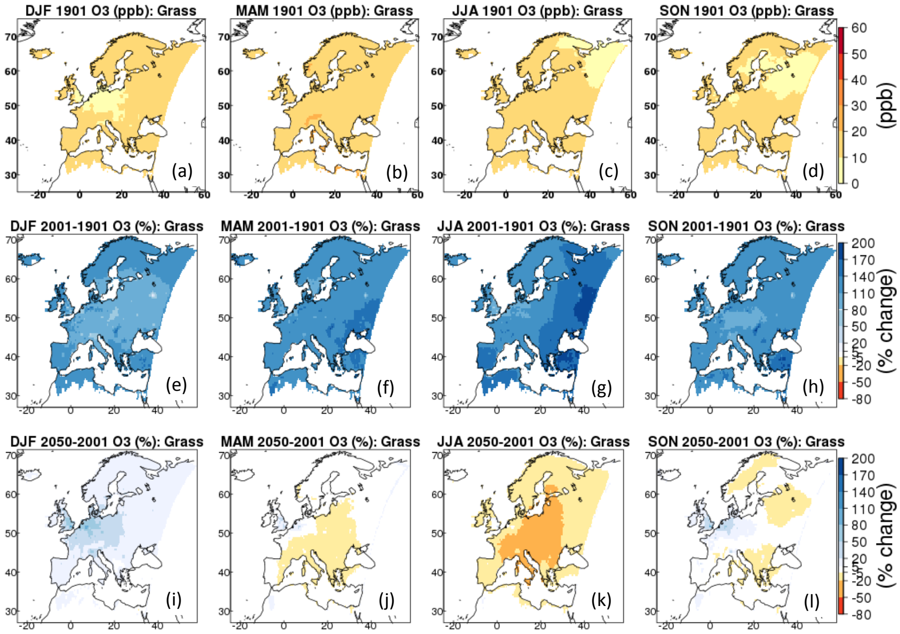

Figure S4. (a-d) 1901 seasonal mean (DJF, MAM, JJA, SON) O_3 concentration (ppb) from EMEP for herbaceous PFTs; (e-h) change in seasonal O_3 concentration (%) from 1901 to 2001; (i-l) change in seasonal O_3 concentration (%) from 2001 to 2050.

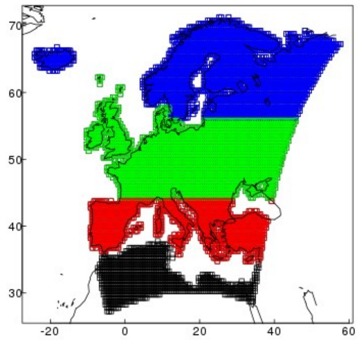

Figure S5. Regions, blue is Boreal, green is Temperate, red is Mediterranean.

S3 Assessing the difference between g_s model formulation

Here we assess the impact of g_s model formulation, comparing the standard JULES Jacobs (1994) formulation (equation 6; JAC) with the alternative Medlyn *et al*., (2011) formulation (equation 7; MED). This was done for two contrasting grid points (wet/dry) in central Europe with a fixed fractional cover of 20% for each PFT.

JULES was spun-up for 20 years (1979-1999) at two grid points in central Europe representing a wet (lat: 48.25; lon:, 5.25) and a dry site (lat: 38.25; lon:, -7.75). The modelled soil moisture stress factor (fsmc) at the wet site ranged from 0.8 to 1.0 over the year 2000 (1.0 indicates no soil moisture stress), and at the dry site fsmc steadily declined from 0.8 at the start of the year to 0.25 by the end of the summer. The WFDEI meteorological forcing dataset was used (Weedon, 2013), along with atmospheric CO_2 concentration for the year 1999 (368.33 ppm), and either no O_3 (i.e. the O_3 damage model was switched off) for the control simulations, or spatially explicit fields of present day O_3 concentration produced using the UK Chemistry and Aerosol (UKCA) model from the run evaluated by O'Connor et al. (2014) for the simulations with O_3. Following the spin-up period, JULES was run for one year (2000) with corresponding atmospheric CO_2 concentration, and tropospheric O_3 concentrations as described above. The control and ozone simulations were performed for both JAC and MED model formulations. Land cover for the spin-up and main run was fixed at 20% for each PFT. For the simulations including O_3 damage, the high plant O_3 sensitivity parameterisation was used. The difference between these simulations was used to assess the impact of *gs* model formulation on the leaf level fluxes of carbon and water.

We calculate and report in the main manuscript (results section 3.1), the difference in mean annual leaf-level water-use that results from the above simulation using the different g_s models. For each day of the simulation we calculate the percentage difference in water-use between the two simulations, we then calculate the mean and standard deviation over the year to give the annual mean leaf-level water-use.

Commented [ORJ44]: RC1 10)

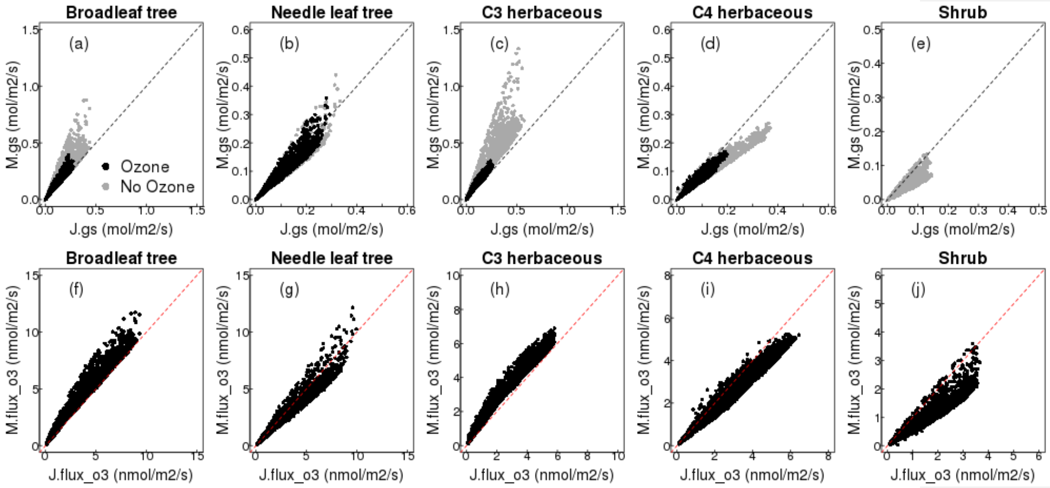

Figure S6. Comparison of the Medlyn *et al*., (2011) g_s model (y axis) versus the Jacobs (1994) g_s model (x axis) currently used in JULES for all five JULES PFTs, for stomatal conductance (*gs*, top row) and the flux of O_3 through the stomata (flux_o3, bottom row) for a dry site.

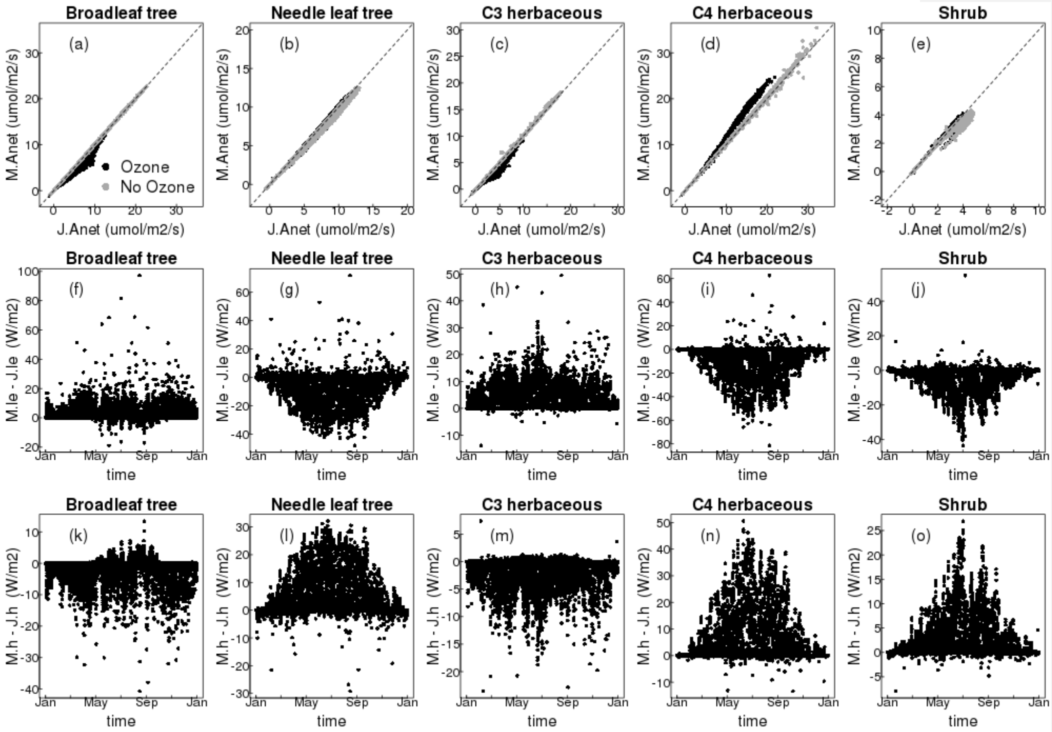

Figure S7. Comparison of the Medlyn *et al*., (2011) g_s model (y axis) versus the Jacobs (1994) g_s model (x axis) currently used in JULES for all five JULES PFTs at a wet site, for net photosynthesis (*Anet*, top row). Residual plots (Medlyn - Jacobs) show the difference between models over the year for latent heat (le, middle row) and sensible heat (h, bottom row).

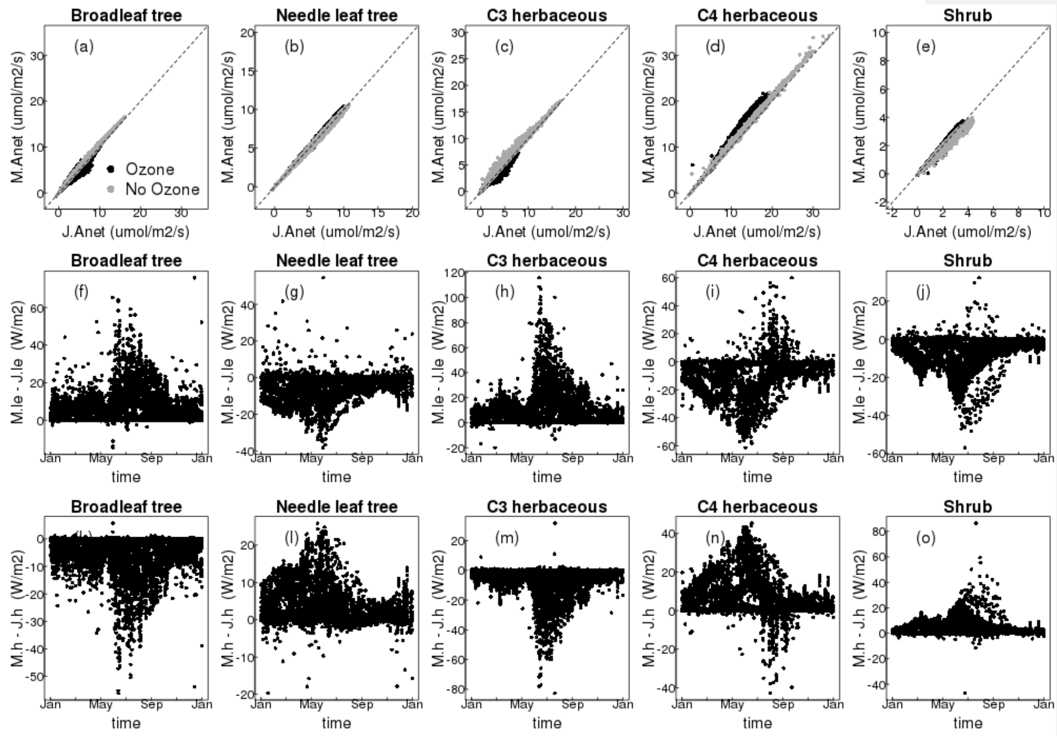

Figure S8. Comparison of the Medlyn *et al*., (2011) g_s model (y axis) versus the Jacobs (1994) g_s model (x axis) currently used in JULES for all five JULES PFTs at a dry site, for net photosynthesis (*Anet*, top row). Residual plots (Medlyn - Jacobs) show the difference between models over the year for latent heat (le, middle row) and sensible heat (h, bottom row).

S4 Site level evaluation of g_s models

We carried out site-level simulations using sites from the FLUXNET2015 dataset to evaluate the seasonal cycle of latent and sensible heat using the two g_s models JAC and MED compared to observations. Sites were selected to represent a range of land cover types (Table S2). In general, at all sites the MED model improved the seasonal cycle of both fluxes (lower RMSE), but the magnitude of this varied from site to site. At the deciduous broadleaf site US-UMB, MED resulted in large improvements of the simulated seasonal cycle particularly in the summer months for both fluxes. At the second deciduous broadleaf site IT-CA1 however, there was almost no difference between the two g_s models. Both evergreen needleleaf forest sites (FI-Hyy and DE-Tha) saw large improvements in the simulated seasonal cycles of latent and sensible heat with the MED model, primarily as a result of lower latent heat flux in the spring and summer months, and higher sensible heat flux over the same period. With the MED model the monthly mean latent heat flux was improved at the C_3 grass site (CH-Cha) as a result of increased flux in the summer months, however there was no improvement in the sensible heat flux and RMSE with MED was increased. At the C_4 grass site (US-SRG), small improvements were made in the seasonal cycle of both latent and sensible heat with the MED model. At the deciduous savannah site (CG-Tch) which included a high proportion of shrub PFT in the land cover type used in the site simulation, large improvements in the seasonal cycle of both fluxes were simulated with the MED model, as a result of a decrease in the latent heat flux and an increase in the sensible heat flux.

Site name	Country	Latitude	Longitude	Simulated years	Land cover	Dominant PFT(s)
US-UMB	USA	45.56	-84.71	2000-2014	Broadleaf forest	100% BT
IT-CA1	Italy	42.38	12.02	2011-2014	Broadleaf forest	100% BT
FI-Hyy	Finland	62	24.3	1996-2014	Needleleaf forest	100% NT
DE-Tha	Germany	51	13.57	1996-2014	Needleleaf forest	100% NT
CH_Cha	Switzerland	47.21	8.41	2006-2014	C3 grassland	80% C3, 20% bare soil
US-SRG	USA	31.8	-110.83	2008-2014	C4 grassland	80% C4, 20% bare soil
CG-Tch	Congo	-4.5	11.66	2006-2009	Deciduous savanna	50% BT, 15% C4, 25% shrub, 10% bare soil

Table S2. Sites from the FLUXNET2015 dataset used in the site simulations to evaluate *gs* models.

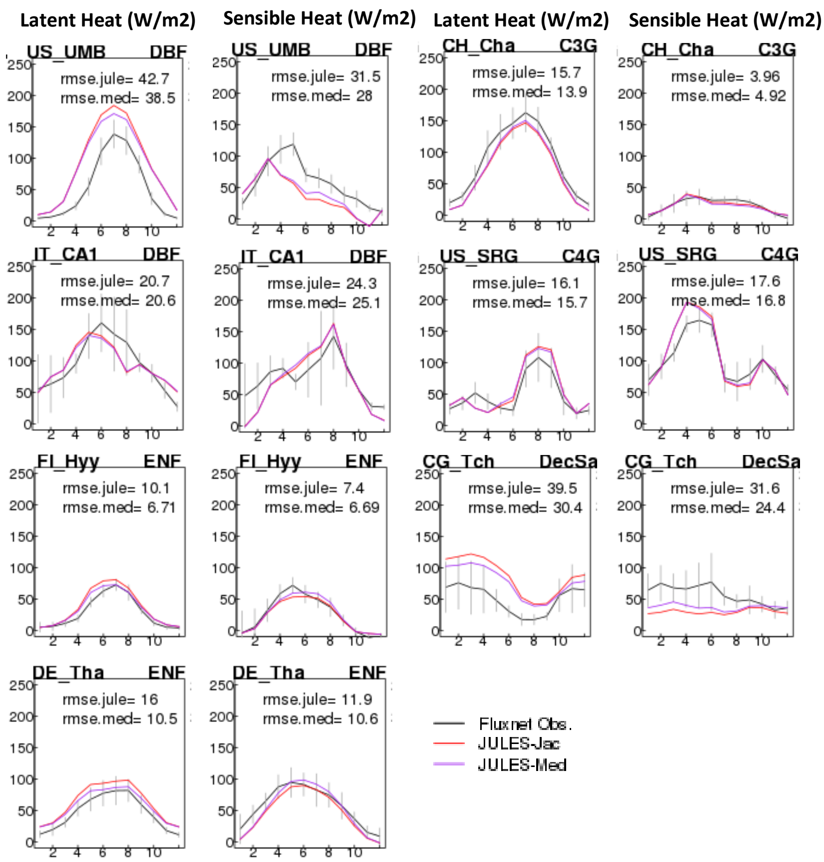

Fig. S9 Monthly mean fluxes of latent and sensible heat. Observations ± standard deviation from FLUXNET2015 sites are shown as black line with grey vertical bars, JULES with the JAC g_s model is shown in red and JULES with the MED g_s model are shown in purple. Also shown are the root mean squared error (rmse) for each simulation.

Commented [ORJ45]: RC2 3)
Site level evaluation of the gs formulations.

S5 Evaluation of JULES O_3 model

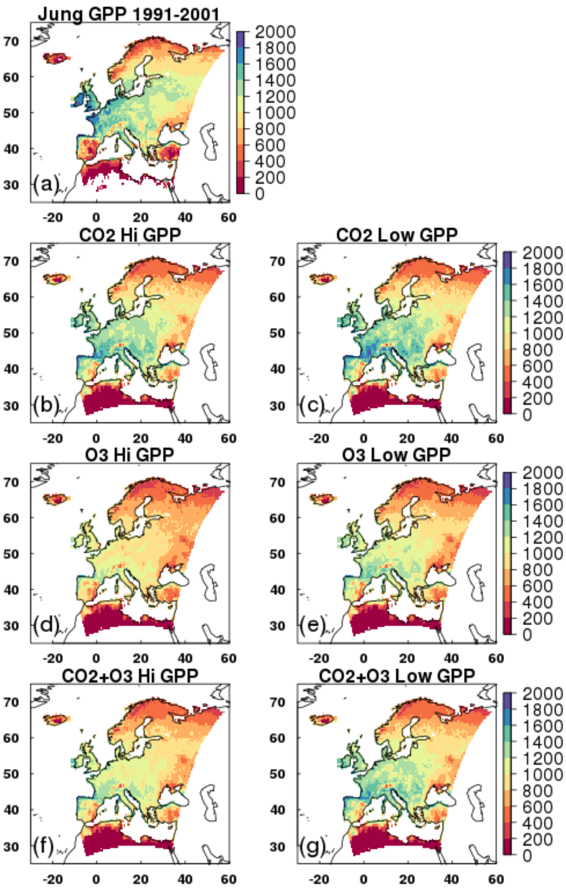

Figure S10. Mean GPP (g C m^2 yr^{-1}) from 1991 to 2001 for a) the observations based globally extrapolated Flux Network model tree ensemble (MTE) (Jung et al., 2011); b, c) model simulations with transient CO_2 and fixed O_3; d, e)model simulations with fixed CO_2 and transient O_3, and f, g) our model simulations with transient CO_2 and transient O_3. All model simulations show GPP for high and low plant O_3 sensitivity respectively.

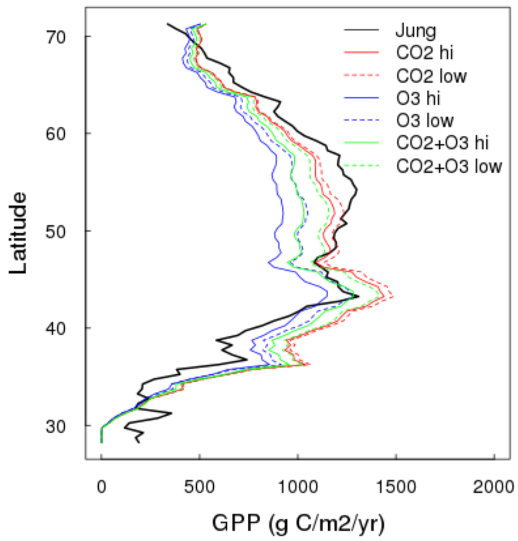

Figure S11. Zonal mean GPP from 1991 to 2001 for FLUXNET-MTE (Jung) and all JULES scenario simulations with both high (solid lines) and low (dashed lines) plant O_3 sensitivity.

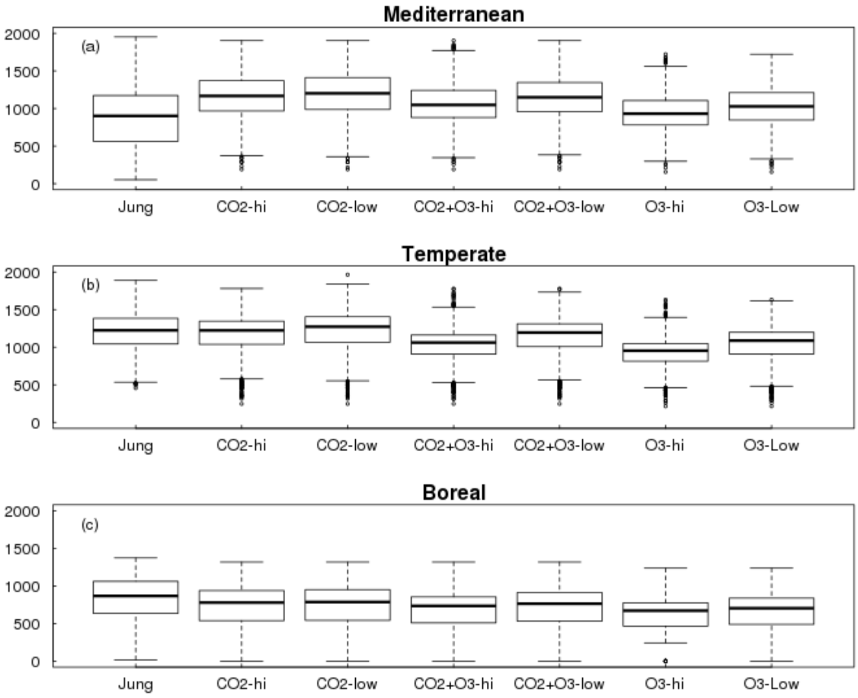

Figure S12. Mean GPP from 1991 to 2001 shown by region, comparing MTE (Jung) and all JULES scenario simulations with both high and low plant O_3 sensitivity.

Commented [ORJ46]: RC2 3)

S6 Estimation of effects due to O_3, CO_2 and O_3 with CO_2

For each variable analysed (GPP, NPP, vegetation carbon, soil carbon, total land carbon and *gs*), we use the mean over 10 years to represent each time period, e.g. the mean over 2040 to 2050 is what we call 2050, 1901 to 1910 is what we refer to as 1901. The difference between the simulations gives the effect of O_3 and CO_2 either separately or in combination over the different time periods. We look at the percentage change due to either O_3 at pre-industrial CO_2 concentration (i.e. without the additional effect of atmospheric CO_2 on stomatal behaviour), CO_2 (at fixed pre-industrial O_3 concentration) or the combined effect of both gases, which is calculated as:

$$100 * (var[y_1] - var[y_2]) / var[y_2] \quad \text{(S1)}$$

Where $var[y_x]$ represents the variable in time period y, e.g. $100 * (varO_3[2050] - varO_3[1901]) / varO_3[1901]$ gives the O_3 effect (at fixed CO_2) over the full experimental period. The meteorological forcing is prescribed in these simulations and is therefore the same between the model runs. Other climate factors, such as VPD, temperature and soil moisture availability are accounted for in our simulations, but our analysis isolates the effects of O_3, CO_2 and O_3 + CO_2.

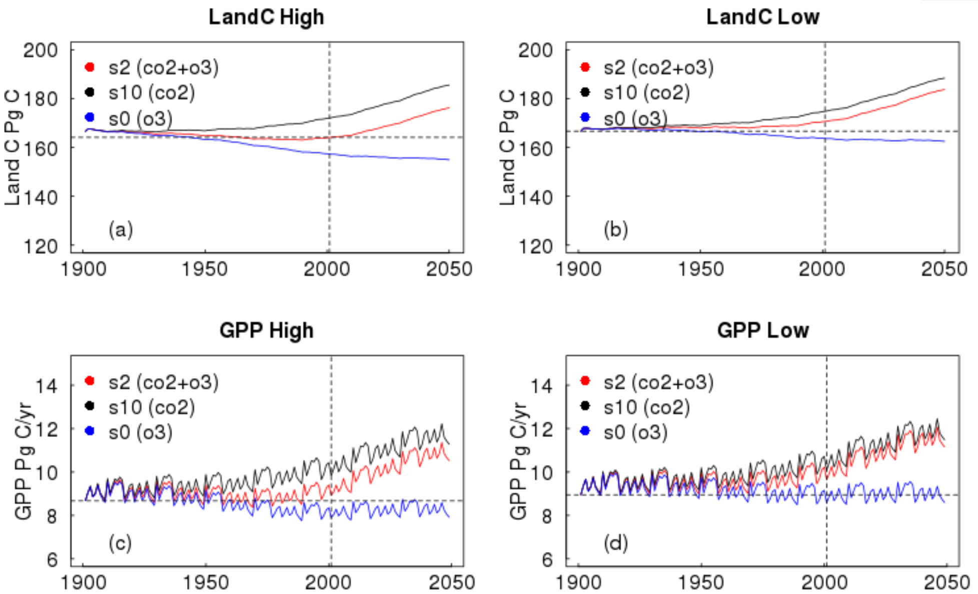

Figure S13. Times series (1901 to 2050) of changes in total carbon stocks (Land C) and gross primary productivity (GPP) due to O_3 effects at fixed pre-industrial atmospheric CO_2 concentration (O_3, blue), CO_2 effects at fixed pre-industrial O_3 concentration (CO_2, black), and effects of CO_2 and O_3 together (CO_2+O_3, red), for the higher and lower plant O_3 sensitivity. The horizontal dashed line shows the pre-industrial value, and the vertical dashed line marks the year 2001.

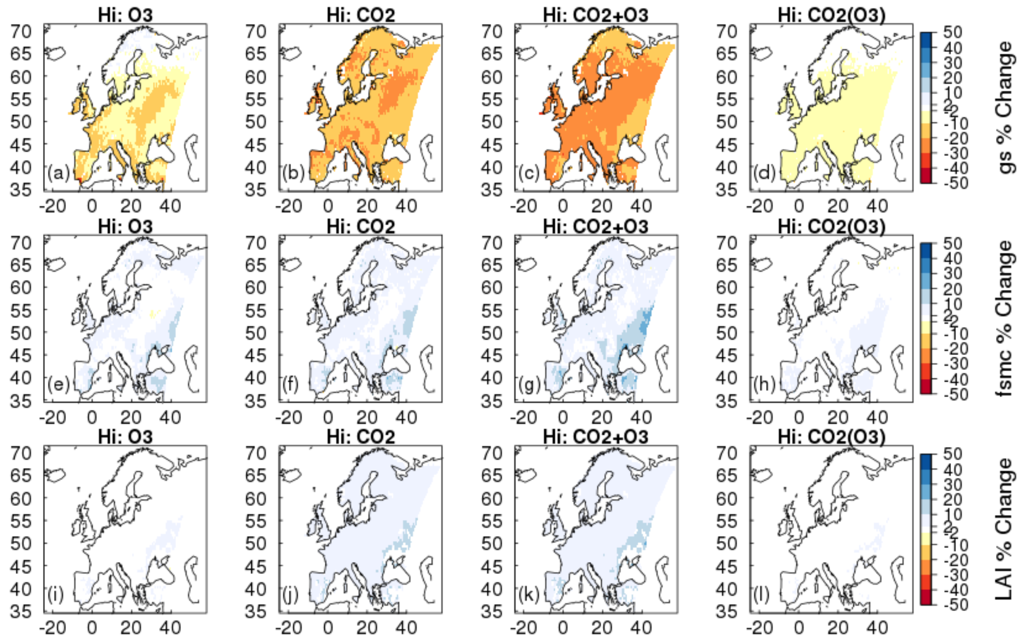

Figure S14. Simulated percentage change in stomatal conductance (gs) a-c), soil moisture availability factor (fsmc) d-e) and leaf area index (*LAI*) g-i) due to O_3 effects at fixed pre-industrial atmospheric CO_2 concentration (O3), CO_2 effects at fixed pre-industrial O_3 concentration (CO2), and effects of CO_2 and O_3 changing simultaneously (CO2+O3). Changes are shown for the periods 1901 to 2050 for the higher plant O_3 sensitivity.

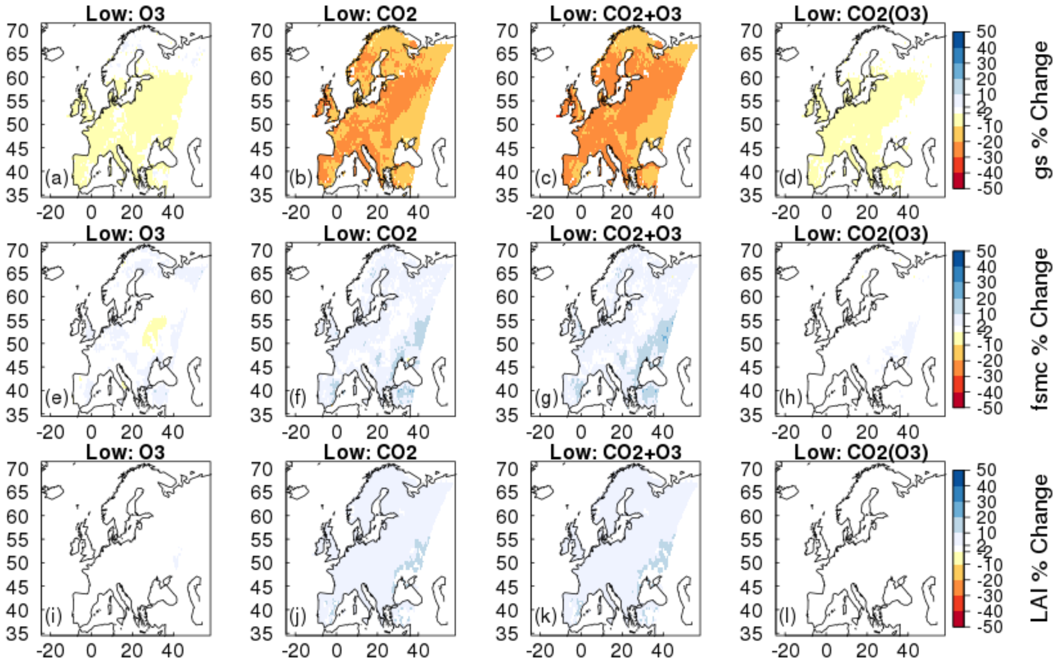

Figure S15. Simulated percentage change in stomatal conductance (gs) a-c), soil moisture availability factor (fsmc) d-e) and leaf area index (*LAI*) g-i) due to O_3 effects at fixed pre-industrial atmospheric CO_2 concentration (O3), CO_2 effects at fixed pre-industrial O_3 concentration (CO2), and effects of CO_2 and O_3 changing simultaneously (CO2+O3). Changes are shown for the periods 1901 to 2050 for the lower plant O_3 sensitivity.

	Future run, constant climate (1901 - 2001)					
	Hi Sensitivity					
	GPP (Pg C yr^{-1})	NPP (Pg C yr^{-1})	g_s (m/s)	Veg C (Pg C)	Soil C (Pg C)	Land C (Pg C)
Value in 1901:	9.05	4.46	0.03228	41.1	125.8	167
Absolute diff. (2001 - 1901):						
O_3	-0.81	-0.47	0.00	-0.02	-9.09	-9.21
CO_2	1.16	0.76	0.00	2.82	1.52	4.24
CO_2 + O_3	0.13	0.12	0.00	2.37	-5.55	-3.28
Relative diff. (%)	(%)	(%)	(%)	(%)	(%)	(%)
O_3	-8.95	-10.54	-8.55	-0.05	-7.23	-5.51
CO_2	12.82	17.04	-6.07	6.86	1.21	2.54
CO_2 + O_3	1.44	2.69	-13.66	5.77	-4.41	-1.96
	Lower Sensitivity					
	GPP (Pg C yr^{-1})	NPP (Pg C yr^{-1})	g_s (m/s)	Veg C (Pg C)	Soil C (Pg C)	Land C (Pg C)
Value in 1901:	9.34	4.65	0.03319	41.1	126.4	167.5
Absolute diff. (2001 - 1901):						
O_3	-0.30	-0.21	0.00	-0.21	-3.38	-3.59
CO_2	1.15	0.74	0.00	2.73	3.70	6.43
CO_2 + O_3	0.65	0.43	0.00	2.21	0.29	2.50
Relative diff. (%)	(%)	(%)	(%)	(%)	(%)	(%)
O_3	-3.21	-4.52	-3.31	-0.51	-2.67	-2.14
CO_2	12.31	15.91	-6.39	6.64	2.93	3.84
CO_2 + O_3	6.96	9.25	-9.88	5.38	0.23	1.49

Table S3. Simulated changes in the European land carbon cycle due to changing O_3 and CO_2 concentrations. Shown are changes in total carbon stocks (Land C), split into vegetation (Veg C) and soil (Soil C) carbon, and gross primary productivity (GPP), net primary productivity (NPP) and conductance (g_s), between 1901 and 2001.

	Future run, constant climate (2001 - 2050)					
	Hi Sensitivity					
	GPP (Pg C yr^{-1})	NPP (Pg C yr^{-1})	g_s (m/s)	Veg C (Pg C)	Soil C (Pg C)	Land C (Pg C)
Value in 2001:						
O_3	8.24	3.99	0.02952	41.08	116.71	157.79
CO_2	10.21	5.22	0.03032	43.92	127.32	171.24
$CO_2 + O_3$	9.18	4.58	0.02787	43.47	120.25	163.72
Absolute diff. (2050 - 2001):						
O_3	0.01	0.00	0.00	-0.09	-2.35	-2.44
CO_2	1.42	0.95	0.00	5.25	7.73	12.98
$CO_2 + O_3$	1.66	1.07	0.00	5.11	6.00	11.11
Relative diff. (%)	(%)	(%)	(%)	(%)	(%)	(%)
O_3	0.12	0.00	0.00	-0.22	-2.01	-1.55
CO_2	13.91	18.20	-13.89	11.95	6.07	7.58
$CO_2 + O_3$	18.08	23.36	-11.37	11.76	4.99	6.79
	Lower Sensitivity					
	GPP (Pg C yr^{-1})	NPP (Pg C yr^{-1})	g_s (m/s)	Veg C (Pg C)	Soil C (Pg C)	Land C (Pg C)
Value in 2001:						
O_3	9.04	4.44	0.03	40.89	123.02	163.91
CO_2	10.49	5.39	0.03	43.83	130.1	173.93
$CO_2 + O_3$	9.99	5.08	0.02991	43.31	126.69	170
Absolute diff. (2050 - 2001):						
O_3	0.02	-0.06	0.00	-0.13	-0.94	-1.07
CO_2	1.35	0.92	0.00	5.25	7.89	13.14
$CO_2 + O_3$	1.50	1.00	0.00	5.11	7.25	12.35
Relative diff. (%)	(%)	(%)	(%)	(%)	(%)	(%)
O_3	0.22	-1.35	-0.72	-0.32	-0.76	-0.65
CO_2	12.87	17.07	-14.64	11.98	6.06	7.55
$CO_2 + O_3$	15.02	19.69	-13.37	11.80	5.72	7.26

Table S4. Simulated changes in the European land carbon cycle due to changing O_3 and CO_2 concentrations. Shown are changes in total carbon stocks (Land C), split into vegetation (Veg C) and soil (Soil C) carbon, and gross primary productivity (GPP), net primary productivity (NPP) and conductance (g_s), between 2001 and 2050.

	Future run, constant climate (1901 - 2050)					
	Hi Sensitivity					
	GPP (Pg C yr^{-1})	NPP (Pg C yr^{-1})	g_s (m/s)	Veg C (Pg C)	Soil C (Pg C)	Land C (Pg C)
Value in 1901:	9.05	4.46	0.03228	41.1	125.8	167
Absolute diff. (2050 - 1901):						
O_3	-0.80	-0.47	0.00	-0.11	-11.44	-11.65
CO_2	2.58	1.71	-0.01	8.07	9.25	17.22
$CO_2 + O_3$	1.79	1.19	-0.01	7.48	0.45	7.83
Relative diff. (%)	(%)	(%)	(%)	(%)	(%)	(%)
O_3	-8.84	-10.54	-8.55	-0.27	-9.09	-6.98
CO_2	28.51	38.34	-19.11	19.64	7.35	10.31
$CO_2 + O_3$	19.78	26.68	-23.48	18.20	0.36	4.69
	Lower Sensitivity					
	GPP (Pg C yr^{-1})	NPP (Pg C yr^{-1})	g_s (m/s)	Veg C (Pg C)	Soil C (Pg C)	Land C (Pg C)
Value in 1901:	9.34	4.65	0.03319	41.1	126.4	167.5
Absolute diff. (2050 - 1901):						
O_3	-0.40	-0.27	0.00	-0.34	-4.32	-4.66
CO_2	2.50	1.66	-0.01	7.98	11.59	19.57
$CO_2 + O_3$	2.15	1.43	-0.01	7.32	7.54	14.85
Relative diff. (%)	(%)	(%)	(%)	(%)	(%)	(%)
O_3	-4.28	-5.81	-4.01	-0.83	-3.42	-2.78
CO_2	26.77	35.70	-20.10	19.42	9.17	11.68
$CO_2 + O_3$	23.02	30.75	-21.93	17.81	5.97	8.87

Table S5. Simulated changes in the European land carbon cycle due to changing O_3 and CO_2 concentrations. Shown are changes in total carbon stocks (Land C), split into vegetation (Veg C) and soil (Soil C) carbon, and gross primary productivity (GPP), net primary productivity (NPP) and conductance (g_s), between 1901 and 2050.

	GPP_hi (Pg C yr^{-1})	GPP_low (Pg C yr^{-1})	LandC_hi (Pg C)	LandC_low (Pg C)
Value in 1901:	9.05	9.34	167.00	167.50
Value in 2050:				
CO_2	11.63	11.84	184.22	187.07
O_3	8.25	8.94	155.35	162.84
CO_2 + O_3	10.84	11.49	174.83	182.35
† % change due to O_3 at PI CO_2	-8.84	-4.28	-6.98	-2.78
‡ % change due to O_3 at high CO_2	-6.79	-2.96	-5.10	-2.52
†† Alleviation of O_3 damage by CO_2 increase (%)	2.05	1.33	1.88	0.26

Table S6. Percentage reduction in simulated GPP and Land C by 2050 due to future O_3 effects at pre-industrial (PI) CO_2 concentration, and under increasing future CO_2 concentration. The difference between these defines the alleviation of the O_3 effect by CO_2. **O_3** = Fixed 1901 CO_2, Varying O_3 ; **CO_2** = Varying CO_2, Fixed 1901 O_3 ; **CO_2 + O_3** = Varying CO_2, Varying O_3. Calculated as: †) O_3 effect with fixed pre-industrial CO_2: 100*(fixCO_2_varO_3[2050] – value[1901])/value[1901], where value[1901] represents the hypothetical value at 2050 from a run with fixCO_2_fixO_3 which is equivalent to the initial state, i.e. the value in 1901 ; ‡) O_3 effect with increasing CO_2: 100*(varCO_2_varO_3[2050] - varCO_2_fixO_3[2050])/varCO_2_fixO_3[2050] ; ††) the alleviation of O_3 damage by CO_2 is the difference between the two runs: ‡ - †.

Commented [ORJ47]: RC1 14)

Acknowledgments

This work used eddy covariance data acquired and shared by the FLUXNET community, including these networks: AmeriFlux, AfriFlux, AsiaFlux, CarboAfrica, CarboEuropeIP, CarboItaly, CarboMont, ChinaFlux, Fluxnet-Canada, GreenGrass, ICOS, KoFlux, LBA, NECC, OzFlux-TERN, TCOS-Siberia, and USCCC. The ERA-Interim reanalysis data are provided by ECMWF and processed by LSCE. The FLUXNET eddy covariance data processing and harmonization was carried out by the European Fluxes Database Cluster, AmeriFlux Management Project, and Fluxdata project of FLUXNET, with the support of CDIAC and ICOS Ecosystem Thematic Center, and the OzFlux, ChinaFlux and AsiaFlux offices.

References

Büker, P., Feng, Z., Uddling, J., Briolat, A., Alonso, R., Braun, S., Elvira, S., Gerosa, G., Karlsson, P. E., Le Thiec, D., Marzuoli, R., Mills, G., Oksanen, E., Wieser, G., Wilkinson, M., and Emberson, L. D.: New flux based dose-response relationships for ozone for European forest tree species, Environmental Pollution, 163-174, 2015.

CLRTAP: The UNECE Convention on Long-range Transboundary Air Pollution. Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends: Chapter III Mapping Critical Levels for Vegetation, accessed via, http://icpvegetation.ceh.ac.uk/publications/documents/Chapter3-Mappingcriticallevelsforvegetation_000.pdf, 2017.

IGBP-DIS: International Geosphere-Biosphere Programme, Data and Information System, Potsdam, Germany. Available from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, TN, anailable at: http://www.daac.ornl.gov,

Jung, M., Reichstein, M., Margolis, H. A., Cescatti, A., Richardson, A. D., Arain, M. A., Arneth, A., Bernhofer, C., Bonal, D., Chen, J., Gianelle, D., Gobron, N., Kiely, G., Kutsch, W., Lasslop, G., Law, B. E., Lindroth, A., Merbold, L., Montagnani, L., Moors, E. J., Papale, D., Sottocornola, M., Vaccari, F., and Williams, C.: Global patterns of land-atmosphere fluxes of carbon dioxide, latent heat, and sensible heat derived from eddy covariance, satellite, and meteorological observations, Journal of Geophysical Research: Biogeosciences, 116, n/a-n/a, 10.1029/2010JG001566, 2011.

Karlsson, P. E., Braun, S., Broadmeadow, M., Elvira, S., Emberson, L., Gimeno, B. S., Le Thiec, D., Novak, K., Oksanen, E., Schaub, M., Uddling, J., and Wilkinson, M.: Risk assessments for forest trees: The performance of the ozone flux versus the AOT concepts, Environmental Pollution, 146, 608-616, http://dx.doi.org/10.1016/j.envpol.2006.06.012, 2007.

O'Connor, F. M., Johnson, C. E., Morgenstern, O., Abraham, N. L., Braesicke, P., Dalvi, M., Folberth, G. A., Sanderson, M. G., Telford, P. J., Voulgarakis, A., Young, P. J., Zeng, G., Collins, W. J., and Pyle, J. A.: Evaluation of the new UKCA climate-composition model – Part 2: The Troposphere, Geosci. Model Dev., 7, 41-91, 10.5194/gmd-7-41-2014, 2014.

Tans, P., and Keeling, R.: Dr. Pieter Tans, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/) and Dr. Ralph Keeling, Scripps Institution of Oceanography (scrippsco2.ucsd.edu/).

Weedon, G. P.: Readme file for the "WFDEI" dataset.available at: http://www.eu-watch.org/gfx_content/documents/README-WFDEI.pdf, 2013.

Response to RC1:

We would like to thank the reviewer for their time taken to read and comment on this manuscript. The comments have been very helpful to improve the manuscript. We hope we have addressed the comments to the full satisfaction of the reviewer. We attach the revised manuscript with track changes so it can be seen what has been changed and where. In our response below, the reviewer comments are in bold to distinguish from our responses.

This paper investigated the interaction between CO2 and O3, the two greenhouse gases that directly affect plant photosynthesis, and indirectly gs. The goal of the paper is to quantify the impact of tropospheric O3, and its interaction with CO2, on gross primary productivity and land carbon storage across Europe from 1901 to 2050 using the JULES land-surface model. In principle, the analysis is highly topical and needed.

1) Throughout the abstract, it should be more quantitative in nature. For example, line 37-38, by how much does the tropospheric O3 suppress terrestrial carbon uptake?

We have modified the abstract to make it more quantitative (lines 37 to 47).

2) Line 40-41, How much of the combined effects of elevated future CO2 (acting to reduce stomatal opening) and reductions in O3 concentrations resulted in reduced O3 damage? Moreover, elevated future CO2 will lead to climate warming simultaneously, so how do the authors remove the response of GPP and land carbon uptake to climate warming due to the increased CO2 concentration? Warming will also increase evaporation (evapotranspiration) and reduce soil water availability, is this also considered?

We have added a sentence to the abstract to show that the alleviation of O_3 damage by CO_2 induced stomatal closure was around 1 to 2% for the low and high plant O_3 sensitivities respectively (for both GPP and land C, line 42). This is discussed in more detail in the original manuscript in the Results section 3.4 pg. 18 on lines 609 to 614 and in Table S6.

This study uses a fixed climate. We cycle over the climate from 1901 to 1920 so we maintain natural climate variability, but we do not have climate change. This allows us to focus on the direct effects of changing atmospheric CO_2 and O_3 concentrations, and their complex interaction, on plant physiology through the twentieth century and into the future. We acknowledge the use of a 'fixed' pre-industrial climate omits the additional factor of the interaction between climate change and g_s which will affect the rate of O_3 uptake and therefore O_3 concentrations. Nevertheless, these simulations are an important tool to understand the direct impacts of O_3 at the land surface. This work demonstrates the sensitivity of GPP and the land carbon sink to tropospheric O_3, highlighting that it is an important predictor of future GPP. We do state in the original manuscript that we use a fixed climate (methods section 2.4.1 line 373), but we realise that we do not make it clear enough early on in the manuscript that we use a fixed climate, so we have amended this in the introduction (pg.6 , lines 214 to 223). We also add a paragraph to our discussion about potential impacts on our results (section 4.3, pg. 26, lines 808 to 816).

3) Line 43, how large are the regional variations in temperate boreal regions? Overall, some specific problems should be described in Introduction. For the O3 effect on the land C sink, what have we learned from the previous studies? What bioregions, and with what methods, have been studied?

We have added a new paragraph to the introduction to discuss the findings from previous studies from different regions (pg. 4, lines 134 to 157). Also, we have quantified the regional variations in the abstract (line 44), and in the original manuscript we discuss these spatial variations in greater detail in the results section.

4) Line 81-83, The authors mentioned few studies have considered the simultaneous effects of exposure to both O3 and CO2, so what have learned from these previous studies? Please specify previous findings.

See response to comment above. We have added a new paragraph to the introduction to discuss previous studies, both field and model-based, and what has been shown from these studies (pg. 4, lines 134 to 157).

5) Line 86-99, Please describe the O3 concentration for historical and current level in quantity. How does the O3 change over the last decades?

We have added more information about the change in O3 concentrations from historical to present day (pg.3, lines 88 to 98).

6) Line 103-104, High levels of O3 are reducing the land carbon sink. How many carbon loss was led to by O3 at regional and global scale based on previous studies?

We have added a paragraph to the introduction to discuss the findings of previous studies (pg. 4, lines 134 to 157).

7) Line 121-122, are you also going to study the effects of high temperature and drought?

This links to an earlier comment – in this study we have used a fixed pre-industrial climate. We cycle over the climate from 1901 to 1920 so we maintain natural climate variability, but we do not have climate change. This allows us to focus on the direct effects of changing atmospheric CO_2 and O_3 concentrations, and their complex interaction, on plant physiology through the twentieth century and into the future. We realise that we do not make it clear enough early on in the manuscript that we use a fixed climate, so we have amended this in the introduction (pg.6 , lines 214 to 223). We also add a paragraph to our discussion about potential impacts on our results (section 4.3, pg. 26, lines 808 to 816).

8) Please explain the CUO1 in Figure S2 caption. As shown in Table S1, the g1 parameter in NT (Needle leaf tree) is similar to that of shrub. Does it mean plant water use efficiency in NT and SH are same?

We have clarified this by adding the following to the Figure S2 caption: "The x axis is cumulative uptake of O_3 (CUO) above the critical O_3 threshold (F_{O3crit})."

The parameter values for g1 were derived from the extensive database of Lin et al., (2015). The parameter g1 is a measure of water-use efficiency. In the model, the plant water-use efficiencies of NT and SH would be similar but not identical since WUE is the ratio of carbon gain to water loss and the two PFTs have different photosynthetic rates owing to different parameter values.

9) Figure1, could you provide some O3 concentration data from observations?

This links to an earlier comment #5. Comparison of these long-term O_3 trends with observations is difficult for many reasons, not least lack of reliable data before recent decades, and limited representativity and inconsistencies in data from recent years (Logan et al., 2012;Parrish et al., 2012). For example, ozone levels at the start of the 20^{th} century are estimated to be around 10 ppb for the site

Montsouris Observatory near Paris, data for Arkona on the Baltic coast increased from ca. 15 ppb in the 1950s to 20-27 ppb by the early 1980s, and the Irish coast site Mace Head shows around 40 ppb by the year 2000 (Logan et al., 2012, Parrish et al., 2012, and refs within). Trends vary from site to site though, even on a decadal basis (Logan et al., 2012;Simpson et al., 2014), depending, for example, on local/regional trends in precursor (especially NOx) emissions, elevation, and exposure to long-range transport. As a result of this spatial variation in O_3 concentrations across Europe, comparison of the EMEP O_3 forcing in Fig. 1 (plotted as a mean across regions) with individual sites would potentially be misleading.

10) Line 342-345, what is the uncertainty (or SD) for these percentage number? It may be better if the authors mentioned how these number are calculated in methods.

These numbers were re-calculated to get the standard deviation. Previously the annual mean for each simulation was calculated, and this used to calculate the percentage difference. To get the standard deviation the daily means were calculated and the percentage difference was calculated for each day, then the mean and standard deviation were calculated, these values are now reported in the manuscript (section 3.1, pg. 14, lines 482 to 487). We explain how these numbers are calculated in the SI section S3 (lines 111 to 114). This re-calculation slightly changes the percentage differences in annual mean leaf-level stomatal conductance, but the direction of change remains the same, i.e. MED increases water-use for BT and C3, and reduced water-use for NT, C4 and SH. The standard deviations are quite large reflecting the large spread in the data, partly due to the seasonal cycle.

11) Line 352-353, For the broadleaf tree and C3 herbaceous PFT, the Medlyn model simulates a larger conductance and therefore a greater flux of O3 through stomata compared to Jacobs, but it also led to a greater flux of CO2 through stomata simultaneously, which may be helpful for increasing photosynthesis.

Figures S7 and S8 (top rows) show 1:1 plots of *Anet,* plotting MED (y axis) against JAC (x axis). These plots show that in the model, *Anet* is not as sensitive to the change in *gs* scheme as *gs* itself (Fig. 2 and Fig. S6). Although the greater conductance for BT and C3 with MED will result in high internal CO_2 concentrations, this doesn't result in a large change in modelled photosynthetic rates because in the model, the sensitivity of the limiting rates of photosynthesis to changes in *ci* is much lower that the sensitivity of g_s to the same change (see section 3.1, pg. 14, lines 488 to 490 where this is mentioned). Therefore, the WUE for BT and C3 will change, they are less WUE with MED.

12) Line 366-368, Some Boreal and Mediterranean regions show increased GPP over this period, associated with O3 induced stomatal closure enhancing water availability. But O3 induced stomatal closure also reduce the flux of CO2 through stomata simultaneously, which have a negative impact on GPP.

This is a trade-off between the opposing effects of O_3 induced stomatal closure enhancing soil water availability and also reducing GPP. The overall effect occurs seasonally, which is not shown in Figs. 4, 5, & 6. O_3 induced stomatal closure occurs during spring/early summer when O_3 concentrations are highest, at this point GPP is reduced, but in these dry regions this leads to increased soil moisture that, in the model, allows growth later in the year when conditions are still favourable but soil moisture may otherwise have been limiting. We have clarified this point in the text (section 3.3, pg. 16, lines 534-538): "Some Boreal and Mediterranean regions show small increases in GPP over this period, associated with O_3 induced stomatal closure enhancing water availability in these drier regions (Fig. 5). This allows for greater stomatal conductance later in the year when soil moisture may otherwise have been limiting to growth (up to 10%, Fig. 6), and therefore higher GPP, but these regions comprise only a small area of the entire domain."

13) Line 373-375, is the different response of GPP to low and high plant O3 sensitivity are significant?

On the advice of the reviewer, we carry out statistical testing of the different responses of GPP to the low and high plant O_3 sensitivities. We use the software R, and use paired t-tests to determine whether the O_3 effect on GPP is significantly different between the two different plant sensitivity parameterisations (section 3.3 line 531; section 3.4 line 570; section 3.5 line 597).

14) Line 437-440, CO2 induced stomatal closure can help alleviate O3 damage by reducing the uptake of O3, but it will also increase available soil moisture simultaneously.

We agree. The CO_2 induced stomatal closure is the dominant effect that helps alleviate O_3 damage. Figures S14 and S15 show that in the model the effect of CO_2 on g_s is large, whereas the effect of CO_2 on soil moisture availability (fsmc in these plots) is small in comparison. Simulated g_s declines with increasing CO_2 which may increase available soil moisture, however CO_2 enhances GPP and growth of the vegetation which can increase LAI leading to higher water-use on a leaf area basis. These responses are all captured in our simulation however with both CO_2 and O_3 changing, and in our calculation of the O_3 effect with CO_2 rising. We look at the difference in this simulation to the simulation with O_3 changing but CO_2 concentration fixed at pre-industrial concentrations, this gives us the alleviation of O_3 damage by increasing CO_2 and all associated effects, such as changes in soil moisture, but it is the effect on stomata that dominates. We have clarified the calculation of the alleviation of O_3 damage by increasing CO_2 in the legend to Table S6.

15) Contradictions are reported in Figure 4 and 5. In Figure 4a, the areas with great increasing in plant available soil moisture have less change in gs in Figure 5a. Why? In figure 4c, the areas with decreasing in plant available soil moisture have large reduction in gs.

The *fsmc* formulation (factor determining plant available soil moisture) varies with soil moisture content and is non-linear. It has a value of zero below wilting point then linearly increases to a value of 1 at field capacity, and remains at this value beyond. The wilting point and field capacity depend on soil texture. Therefore a small percentage change in soil water content in dry regions (Mediterranean) can result in a large percentage increase in *fsmc*. Likewise an increase in soil moisture in mesic areas (e.g. northern Europe) may translate into relatively small percentage changes in *fsmc*.

In Figs 5a and 6a, the areas that see a large increase in plant available soil moisture see a small increase in *gs* (up to 10%). This is looking at the change over the period 1901 to 2001 when only O_3 is changing. Over this period there is a large increase in O_3, so the O_3 induced stomatal closure is large, causing the increase in *fsmc* in this region. The changes are seasonal, these plots show the annual mean which will average out some of the change. In this region, for example, *gs* increases a lot in JJA and DJF, but there is minimal change in SON/MAM. Figures 5c and 6c are for a different time period, 2001 to 2050. Over this period the O_3 effect is reduced considerably, so by 2050 plant available water is reduced on 2001 levels because the O_3 induced stomatal closure is less. Stomatal conductance decreases in this region during this period.

16) In table 1, O3 increased GPP but decreased land carbon over the period 2001-2050. Why does land C decrease when GPP is increasing?

We refer to this in the results section (section 3.4, pg. 17, lines 585 to 589). GPP is a fast flux, whereas the land carbon store is a slower pool of carbon, it takes longer for this carbon store to adjust to changes in the flux, especially when those changes are fairly small as is the case here. This highlights the importance of using a carbon cycle model to look at the impacts of O_3 on the terrestrial biosphere.

The discussion could be improved by using subtitles more clearly.

We have amended this and added subtitles.

17) Line 525-541, the authors listed a lot of results from the literatures, but the reader is left to decide what and why is the difference between this study and previous studies? More discussion on comparing this study with previous studies in detail would be helpful.

This paragraph discusses findings from field-based studies looking at plant O_3 impacts. We have removed this paragraph and put it in the introduction as it seemed more appropriate here to place our study in context (pg. 4, lines 134 to 157).

Logan, J. A., Staehelin, J., Megretskaia, I. A., Cammas, J. P., Thouret, V., Claude, H., De Backer, H., Steinbacher, M., Scheel, H. E., Stübi, R., Fröhlich, M., and Derwent, R.: Changes in ozone over Europe: Analysis of ozone measurements from sondes, regular aircraft (MOZAIC) and alpine surface sites, Journal of Geophysical Research, 117, 1-23, 2012.

Parrish, D. D., Law, K. S., Staehelin, J., Derwent, R., Cooper, O. R., Tanimoto, H., Volz-Thomas, A., Gilge, S., Scheel, H. E., Steinbacher, M., and Chan, E.: Long-term changes in lower tropospheric baseline ozone concentrations at northern mid-latitudes, Atmos. Chem. Phys., 12, 11485-11504, 10.5194/acp-12-11485-2012, 2012.

Simpson, D., Arneth, A., Mills, G., Solberg, S., and Uddling, J.: Ozone—the persistent menace: interactions with the N cycle and climate change, Current Opinion in Environmental Sustainability, 9, 9-19, 2014.

Response to RC2:

We thank the reviewer for the time taken to read the manuscript and comment on it. The comments are very helpful and improve the manuscript. We hope we have addressed all the comments to the full satisfaction of the reviewer. We attach the revised manuscript with track changes so it can be seen what has been changed and where.

RC) Oliver et al. quantify the impact of ozone damage to European GPP and total land carbon stock on an annual basis. The authors apply a new stomatal conductance parameterization to their model, and force the model with surface ozone concentrations, meteorology and global CO2 concentration to investigate the roles of CO2 fertilization vs. O3 damage on GPP and total land carbon stock from 1901 to 2050. This new stomatal conductance parameterization simulates higher stomatal conductance than the previous, causing higher uptake of ozone through plant stomata. They find that there are spatial variations in the response of GPP and land carbon stock to CO2 fertilization vs. O3 damage. On a regional basis, CO2 fertilization dominates the response (vs ozone damage) when CO2 is allowed to evolve, but ozone does limit the land carbon sink. The impact of ozone damage from 1901 to 2050 is dominated by 1901-2001 due to increasing surface ozone concentrations during that time. Overall, it seems like there is a lot more to discuss in regards to the previous work that has been done on the leaf level to global scale on this topic (e.g., Karnosky et al., 2003) and how the Oliver et al. findings contribute substantially to knowledge. It is not really clear how these results advance Sitch et al. 2007 except examining the region-scale over Europe. A huge limitation to this study is that CO2 and meteorology are uncoupled, as well as meteorology, ozone, and stomatal conductance.

AC: This study makes significant developments to the model from that used in Sitch et al., 2007. In short these developments include:

- Re-calibration of the model for ozone impacts on vegetation using up-to-date functions published in 2017.
- A representation of ozone damage on crops and accounting for regional differences where possible (i.e. Mediterranean regions).
- A new g_s model including parameters derived from field observations which have physical meaning (i.e. measureable quantities).
- A term for non-stomatal deposition of ozone.
- A diurnal cycle of ozone forcing at a much higher spatial resolution than in Sitch *et al*., global simulations (i.e. 0.5 x0.5 vs 3.75x 2.5) from a high resolution atmospheric chemistry model for Europe.

The final paragraph of the introduction was re-arranged to highlight these advances (pg. 6, lines 193 to 214).

We also include greater discussion on previous studies in this area and move a paragraph from the discussion to the introduction (pg. 4, lines 134 to 157).

RC1) Using recycled early 20th C climate is problematic. I understand that the authors want to isolate the physiological response of plants of CO2 vs. O3 here, but ozone is high during drought and heat waves, and stomata close at that time. So if there is increasing aridity and hydrological and temperature extremes into the 21st C, then the ozone response should be much lower than the authors suggest. The authors do at some point say that their work here is an upper bound, but upper bounds have already been published.

AC: The aim of these simulations was to investigate the direct effects of changing atmospheric CO_2 and O_3 concentrations, and their complex interaction, on plant physiology through the twentieth century and into the future. These offline simulations are not coupled and therefore do not have feedbacks between climate, O_3 formation and stomatal behaviour, but nonetheless they are an important tool to understand the direct impacts of O_3 at the land surface. This work demonstrates the sensitivity of GPP and the land carbon sink to tropospheric O_3, highlighting that it is an important predictor of future GPP and the land carbon sink. We do state in the original manuscript that we use a fixed climate (methods section 2.4.1 line 373), however, we realise we do not make it clear from the beginning that we are running offline simulations, therefore we have modified the manuscript to make this point clear in the introduction (pg.6 , lines 214 to 223).

An important point that we make in the original manuscript is: "our results demonstrate the sensitivity of modelled terrestrial carbon dynamics to tropospheric O_3 and its interaction with atmospheric CO_2, highlighting that such effects of O_3 on plant physiology significantly add to the uncertainty of future trends in the land carbon sink and climate-carbon feedbacks. Given the potential to limit the climate mitigation effect of European terrestrial ecosystems, we suggest plant O_3 damage should be incorporated into carbon cycle assessments". Here the point we mean to make is that our work shows the sensitivity of modelled GPP and land carbon to the direct effect of O_3 on plant physiology, however, this process remains largely unconsidered in regional and global climate model simulations that do account for climate-carbon feedbacks and are used to model carbon sources and sinks even though it is likely contribute to the large uncertainty in future modelled carbon-climate feedbacks. We modify the text to make this point more clearly at the end of the conclusions (section 5, pg. 28, lines 879 to 883).

We add to the discussion a paragraph outlining the potential implications for our results of using uncoupled simulations (section 4.3, pg. 26, lines 808 to 816).

It is computationally expensive to run coupled simulations. Offline studies are valuable in determining the relevance of individual responses and are relatively cheap computationally. Once the importance of a process is demonstrated off line, it provides evidence of the need to incorporate such processes in coupled simulations.

RC2) Further, Langner et al. 2012 is not the appropriate work here to justify the authors' approach. Langner et al. examine the impact of climate change following the A1B scenario on surface ozone (they do not consider changes in anthropogenic precursor emissions from present to future under A1B). Langner et al. use biogenic emissions to explain some of the cross-model differences in changes from present to future in ozone due to climate. This is quite different from using the full A1B scenario which considers changes in climate & anthropogenic precursor emissions, which is what Oliver et al. do.

AC: This should be a different Langer et al., 2012 reference here, this has now been corrected:

Langner, J., Engardt, M. & Andersson, C. European summer surface ozone 1990–2100, *Atmos. Chem. Physics,* **2012b***, 12*, 10097-10105

Section 2.4.1, pg. 11, line 399.

RC3) The authors change their stomatal conductance parameterization but do not explain why. Their phrasing implies that the new gs model is truth, whereas the Jacobs 1994 model is not (e.g., "studies using the Jacobs [1994] formulation may underestimate" on line 523). I understand that parameterizations of stomatal conductance are uncertain in general, and hard

to evaluate, but it seems like there should be some reasoning and evaluation here. Further, please clarify the re-calibration (lines 130-133). This seems like a major part of your analysis and I think evaluation & inclusion of this evaluation in the main part of the paper is warranted.

AC: The main advance of the Medlyn model over Jacobs, and other empirical *gs* formulations, is the availability of observational-derived parameters for European vegetation. We discuss the advantages of the Medlyn model over the Jacobs formulation in the original text and that is our reasoning for using it in these simulations. We apologise if this is not clear, and have moved this to a separate paragraph in the introduction and expanded our reasoning (pg. 6, lines 181 to 191). We do not mean to imply that the Medlyn model is truth compared to Jacobs, and have changed the wording on line 697 (section 4.1, pg. 26) accordingly to read "studies using the Jacobs g_s formulation would simulate a lower O_3 impact for Europe".

We have included site level evaluation of the seasonal cycle of latent and sensible heat at some FLUXNET sites comparing the two g_s models against observations. This is in the supplementary information, section S4 (Fig. S9 and Table S2). We refer to this evaluation in the main text (section 2.3, pg. 10, line 365 and section 3.1, pg. 14, line 497).

We mention the calibration in the introduction, but we do not feel here is the place to expand or clarify further. We expand upon the re-calibration in the Methods (section 2.2), and have updated this section in the manuscript to clarify it further. We put additional details in the supplementary information because these are quite technical details so we feel they are not necessary in the main text.

Validation of land-surface models such as JULES for O_3 impacts is not straightforward because of small scale, site specific biotic and abiotic factors that affect the growth response of vegetation to O_3. These include competition within and between species leading to differential O_3 responses as was seen at the Aspen FACE experiment (King et al., 2005;Karnosky et al., 2007;Kubiske et al., 2007), attack by pests and diseases, nutrient limitation, drought stress. Nevertheless, we now include an evaluation of the O_3 model against the flux network model tree ensemble (MTE) product of (Jung et al., 2011). We compare mean GPP from 1991 to 2001 for each of the JULES scenarios and both high and low plant O_3 sensitivities against Jung et al., (2011). See methods section 2.4.3, results section 3.2 with new Figure 3, and section S5 in the supplementary information with new figures S10, S11 and S12.

RC4) Is Jacobs gs used in the ozone dry deposition parameterization that is used in the EMEP model used to project the ozone concentrations? Typically stomatal conductance in the dry deposition parameterizations is some form of Wesely (1989). If Wesely is used, how does the magnitude of Medlyn differs from the magnitude of stomatal conductance from Wesely? If Wesely is used, then CO2 fertilization is not in there, nonetheless ozone damage. Another caveat is that ozone damage can feedback onto ozone concentrations as demonstrated by Sadiq et al. ACP 2017.

AC: Calculations of O_3 deposition in the EMEP model are rather detailed compared to most chemical transport models. We make use of the stomatal conductance algorithm (now commonly referred to as DO_3SE) originally presented in Emberson et al. (2000;2001), which depends on temperature, light, humidity and soil moisture. Calculation of non-stomatal sinks, in conjunction with an ecosystem specific calculation of vertical O_3 profiles, is an important part of this calculation as discussed in

Tuovinen et al. (2004;2009) or Simpson et al. (2003). The methodology and robustness of the calculations of O_3 deposition and stomatal conductance have been explored in a number of publications (Emberson et al., 2007;Tuovinen et al., 2004;Tuovinen et al., 2009;Tuovinen et al., 2007).

Of course, the *gs* values used in the EMEP model differ from those obtained using a Medlyn formulation. Comparing EMEP's maximum *gs* values (*gmax*) with the 95th-100th percentiles of *gs* found in JULES simulations, we find very similar values for deciduous forest (EMEP 150-200, JULES ~180, all units in mmole O_3/m^2 (PLA)/s), and C3/C4 crops (EMEP 270-300, JULES ~260-390), but large differences for coniferous forest (EMEP 140-200, JULES ~60-70) and shrubs (EMEP 60-200, JULES 360-390). The role of EMEP in this study is not to provide *gs*, however, but to provide O_3 at the top of the vegetation canopy. The main driver of such O_3 levels is the regional-scale production and transport of ozone, and the main impact of *gs* is just in affecting the vertical O_3 gradients just above the plant canopy. Differences in *gs* are known to have minimal impact on canopy-top O_3 for trees, mainly due to the efficient turbulent mixing above tall canopies, but also due to non-stomatal sink processes. For shorter vegetation, substantial O_3 gradients, driven by deposition, occur in the lowest 10s of metres of the atmosphere, and stomatal sinks (as given by *gs*) can have a significant role. However, calculations of such gradients made with the EMEP model for CLRTAP (2017) showed that such differences amounted to ca. 10% when comparing O_3 concentrations at 1m height above high-gs crops (*gmax*=450 mmole O_3/m^2 (PLA)/s) species compared to moderate-*gs* (*gmax* 270 mmole O_3/m^2 (PLA)/s).

These inconsistencies are not ideal, but inevitable given that we link two different model systems. There are of course many uncertainties in all estimates of deposition and stomatal ozone flux (e.g. Tuovinen et al., 2009), and we believe that this particular uncertainty is an acceptable part of our procedure.

The referee's comments about CO_2 and the impacts mentioned by Sadiq are also relevant, but again there are many uncertainties associated with such effects and assessments too.

In order to keep a concise text, but mention the above points, we have added a summary of the above points to the manuscript in the discussion section 4.3, pg. 25, lines 790 to 806.

RC5) A large part of the results hinge on the seasonality of surface ozone concentrations, and how they change from PI to present. There is some discussion of this on pages 401-405 as authors examine the change in seasonality from 2001 to 2050, but there is no citation of previous work examining changes in ozone seasonality, or the implications of this for their conclusions. Also, the authors say that tropospheric ozone is increasing (e.g., line 74), but I think this is a bit misleading - due to strong changes in seasonality that are observed - please revise.

AC: We have added a paragraph to the manuscript to acknowledge and discuss the importance of the seasonality of surface ozone concentrations, citing previous work examining these changes, and the implications of this for our results (section 2.1.4, pg. 12, lines 420 to 442). Line 74 has been revised (now line 75).

RC6) In general, the paper is a bit poorly organized. Many times the authors say "see details in SI" when it's not clear what information is in there, and why it is relevant. Further it seems like some info in the SI should really be in the actual paper. In addition, the authors neglect to

mention many substantial caveats (such as the uncertainties around CO2 fertilization w.r.t. nutrient cycling, using uncoupled tropospheric chemistry & stomatal dry deposition, and stomatal sluggishness) until the very end. I think the paper would be much better if much of the discussion was moved to the introduction and used to frame the work, and motivate the authors' objectives.

AC: We apologise for the lack of clarity when referring to the supplementary information, we have amended this to make clear what section in the SI we refer to and why. In response to referee requests we have revamped the introduction to clarify the specific focus of the manuscript (i.e. carbon cycle impact of the plant physiological response to O_3 and CO_2), and therefore make it easier to understand what is and what is not included.

We discuss the caveats of the study at length in the original manuscript. These are very important, so we are sure to make clear that we are fully aware of the caveats. We also now include an additional paragraph in the discussion section 4.3 on the potential implications of uncoupled tropospheric chemistry and stomatal dry deposition for our results which was previously missing. We also introduce the issue of sluggish stomata and CO_2 fertilization in the introduction to help frame the study. However, on the whole we think that discussion of the caveats is more appropriate in the discussion.

Minor comments

RC1. The authors use the term "significant" a lot - but don't do any sort of statistical testing. Please only use the word significant when describing results that are statistically significant.

AC: We have revised our use of significant where appropriate.

RC2. Line 78: Lightning is a source of NOx, not O3 – please revise

AC: This has been amended to read "…. and lightning which is a source of NO_x". (line 79)

RC3. Lines 86-87: Parrish et al. 2012 is not really the appropriate citation here

AC: We have changed this reference for Vingarzan (2004). (line 88)

RC4. Lines 93-94: "Intercontinental transport" doesn't mean that background ozone has increased, there has always been intercontinental transport.

AC: This sentence has been changed to: "Intercontinental transport of air pollution from regions such as Asia that currently have poor emission controls are thought to contribute largely to rising background O_3 concentrations in Europe over the last decades (Cooper et al., 2010;Verstraeten et al., 2015)." (line 103)

RC5. Line 101: Citations for ozone impacts on crop yields and nutritional quality are needed

AC: We have added the following references: Ainsworth et al., (2010) and Avnery et al., (2011). (line 114)

RC6. Line 106: Do the authors mean indirect here?

AC: We mean direct – ozone has a direct effect on radiative forcing of the climate. The indirect effect is ozone damage of vegetation which reduces uptake of carbon by plant photosynthesis, allowing more CO_2 to remain in the atmosphere. (line 118)

RC7. Line 110: Fowler et al. 2009 isn't really the appropriate citation here - i.e., for saying that dry deposition is a substantial sink of tropospheric ozone

AC: We have added an additional reference: Fowler et al., (2001). (line 123)

RC8. Line 152 - as the authors mention in the discussion, ozone can directly impact gs - please revise accordingly

AC: This has been amended at line 195.

RC9. Line 160-168: please clarify the spatial domain and the resolution of this model; also, is the resolution the same as the meteorological and ozone forcing files?

AC: We added the following sentence to clarify the resolution of the model (line 247): "This work uses JULES version 3.3 (http://www.jchmr.org) at 0.5° x 0.5° spatial resolution and hourly model time step, the spatial domain is shown in Fig. S5." We also explicitly state the resolution of the all the forcing data (meteorology, CO_2, ozone and land cover) to show that they are all the same 0.5° x 0.5° resolution.

RC10. Lines 193-194: kappa_O3 is not exactly the ratio of the resistances; it's the ratio of the diffusivities

AC: This has been changed to : "K_{o3} accounts for the different diffusivity of ozone to water vapour and takes a value of 1.51 after Massman (1998)" (line 280).

RC11. Lines 220-222: What is CLRTAP (2017)? It is not in the references. Why is it being treated as the "truth"?

AC: The reference for CLRTAP (2017) is now in the reference list. It is a report on ozone impacts on vegetation, providing a synthesis of the latest peer reviewed literature, collated by a panel of experts and so is considered the state-of the art knowledge. It provides the O_3 dose response functions compiled from numerous field studies that we use to calibrate our model PFTs for sensitivity to O_3. We have expanded section 2.2 which explains this more clearly.

RC12. Section 2.3 - please clarify that Lin et al. 2015 fit g1 parameters based on the Medlyn et al. 2011 equation for stomatal conductance (except no g0 term), which is not exactly the same as putting equation 7 into equation 5; it's confusing to refer to this equation as Medlyn et al. (2011); also, I do not think that multiplying the Anet/(Ca-Ci) by R*T is the right way to convert from mol s-1 m-2 to m/s.

AC: We clarify this in the following sentence (line 352): "The g_1 parameter represents the sensitivity of g_s to the assimilation rate, i.e. plant water use efficiency, and was derived as in Lin et al. (2015) by fitting the Medlyn *et al*., (2011) model to observations of g_s, photosynthesis, and VPD, with no g_0 term." At line 346 we also say "In this work, we replace equation 6 with the closure described in Medlyn et al. (2011), ….". and then refer to it from then on as the MED model instead of the Medlyn et al (2011) model.

RC13. Lines 252-254: Please clarify "the effect" that Hoshika et al. 2013 find; does O3 increase or decrease WUE? This seems relevant to your discussion/conclusions.

AC: We clarify by adding the following (line 355): "Hoshika et al., (2013) show a significant difference in the g1 parameter (higher in elevated O_3 compared to ambient) in Siebold's beech in June of their experiment. However, this is only at the start of the growing season, further measurements show no difference in this parameter between O_3 treatments."

RC14. Lines 300-301: Clarify the "disaggregation" of ozone from the daily mean to the hourly time step. As ozone has a diurnal cycle, and stomatal conductance does as well, this could have a substantial impact on your work, and should be discussed.

AC: We have added the following sentence to clarify the disaggregation (line 408): "The daily mean O_3 forcing was disaggregated to follow a mean diurnal profile of O_3, this was generated from hourly O_3 output from EMEP MSC-W for the two land cover categories across the same domain as in this study."

RC15. Lines 305-306: Clarify the calculation of the ozone gradient from the lowest atmosphere grid box to canopy height

AC: The ozone forcing used in this study was produced by the EMEP MSC-W model, here we provide a reference to the model documentation (Simpson et al., 2012) so readers can follow up further details. It is beyond the scope of this study to document how EMEP MSC-W works.

RC16. Further details on crops in JULES should be included in Section 2.4.1 in addition to the discussion.

AC: We have amended this to the following: "The agricultural mask means that only C_3/C_4 herbaceous PFTs are allowed to grow, with no competition from other PFTs, no form of land management is simulated." We discuss the limitations of this in the discussion (lines 761).

RC17. Lines 282-283: Please specify the ozone sensitivity used for forests

AC: This has been removed as it is now explained in more detail in section 2.2.

RC18. Line 882: I don't think "in prep" studies can be cited.

AC: This has been removed.

RC19. Lines 258-259:What are the two model grid points? What does wet vs. dry refer to? This info is used later on in the paper (Figure 2), so it would be helpful for more information on this.

AC: More information to clarify this is provided in the SI section S3, but this was probably not clear because we did not make it clear which section in the SI to refer to. We have rectified this, and now state "see SI section S3 for further details" (line 364).

RC20. Please clarify in the Figure 2 caption what exactly the readers are looking at (this is just one grid cell, with each sub-tile PFT gs shown?). Why just one grid-cell? Is the data shown hourly? What is the time period?

AC: Shown are hourly values for the year 2000, from a single grid cell fixed to have 20% land cover of each PFT – therefore we are comparing g_s for each PFT under the same conditions. This information is in the SI section S3 which we hope will be clearer now as we refer to it appropriately earlier on in the manuscript.

The figure caption has been amended to: "**Figure 2.** Comparison of simulated g_s with MED (y axis) versus JAC (x axis) for all five JULES PFTs at one grid point (lat: 48.25; lon:, 5.25) shown are hourly values for the year 2000 (see SI section S3 for further details). Shown are stomatal conductance (g_s, top row), and the flux of O_3 through the stomata (flux_o3, bottom row)."

RC21. Lines 384-396: It's not clear why the authors are examining different decades for their analysis here. Second, it seems like the authors could pretty easily sample their model for an apples-to-apples comparison with Boden et al. 2013. Third, suggesting that the O3 impact on the land carbon sink is a source of carbon is not really appropriate (lines 395-396); re-phrasing would allow for the same take-away

AC: We analyse different decades because it shows how the O_3 effect has changed through time. The Boden et al data is available on a country by country basis without lat/lon information for the spatial extent of coverage. Therefore it is best to stick to our domain for comparison, but clearly acknowledge that our domain is slightly larger in extent.

RC22. Lines 401-402: Ozone precursor emission controls do not always lead to ozone reductions because formation chemistry is nonlinear; please revise.

AC: We have removed this sentence.

RC23. Line 401: Large spatial variability is not apparent to me - it would be helpful if the authors were more specific.

AC: To my eye the spatial variation is apparent in Fig. 4g & h. Nevertheless, we do describe this variation in more detail in the results section.

RC24. Lines 405-408: it's not clear what figure the authors are talking about here.

AC: This is Fig. 4g & h. This has been updated in the text.

RC25. Figure 6 - specify whether your numbers correspond to rows or columns.

AC: They refer to columns. We have amended the legend for figure 7 to make this clearer.

Refs:

CLRTAP: The UNECE Convention on Long-range Transboundary Air Pollution. Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends: Chapter III Mapping Critical Levels for Vegetation, accessed via, http://icpvegetation.ceh.ac.uk/publications/documents/Chapter3-Mappingcriticallevelsforvegetation_000.pdf, 2017.

Cooper, O. R., Parrish, D. D., Stohl, A., Trainer, M., Nedelec, P., Thouret, V., Cammas, J. P., Oltmans, S. J., Johnson, B. J., Tarasick, D., Leblanc, T., McDermid, I. S., Jaffe, D., Gao, R., Stith, J., Ryerson, T., Aikin, K., Campos, T., Weinheimer, A., and Avery, M. A.: Increasing springtime ozone mixing ratios in the free troposphere over western North America, Nature, 463, 344-348, http://www.nature.com/nature/journal/v463/n7279/suppinfo/nature08708_S1.html, 2010.

Emberson, L. D., Ashmore, M. R., Cambridge, H. M., Simpson, D., and Tuovinen, J.-P.: Modelling stomatal ozone flux across Europe, Environmental Pollution, 109, 403–413, 2000.
Emberson, L. D., Simpson, D., Tuovinen, J.-P., Ashmore, M. R., and Cambridge, H. M.: Modelling and mapping ozone deposition in Europe, Water Air Soil Pollution, 130, 577–582, 2001.
Emberson, L. D., Büker, P., and Ashmore, M. R.: Assessing the risk caused by ground level ozone to European forest trees: A case study in pine, beech and oak across different climate regions, Environmental Pollution, 147, 454–466, 2007.
Jung, M., Reichstein, M., Margolis, H. A., Cescatti, A., Richardson, A. D., Arain, M. A., Arneth, A., Bernhofer, C., Bonal, D., Chen, J., Gianelle, D., Gobron, N., Kiely, G., Kutsch, W., Lasslop, G., Law, B. E., Lindroth, A., Merbold, L., Montagnani, L., Moors, E. J., Papale, D., Sottocornola, M., Vaccari, F., and Williams, C.: Global patterns of land-atmosphere fluxes of carbon dioxide, latent heat, and sensible heat derived from eddy covariance, satellite, and meteorological observations, Journal of Geophysical Research: Biogeosciences, 116, n/a-n/a, 10.1029/2010JG001566, 2011.
Karnosky, D. F., Skelly, J. M., Percy, K. E., and Chappelka, A. H.: Perspectives regarding 50years of research on effects of tropospheric ozone air pollution on US forests, Environmental Pollution, 147, 489-506, 2007.
King, J. S., Kubiske, M. E., Pregitzer, K. S., Hendrey, G. R., McDonald, E. P., Giardina, C. P., Quinn, V. S., and Karnosky, D. F.: Tropospheric O_3 compromises net primary production in young stands of trembling aspen, paper birch and sugar maple in response to elevated atmospheric CO_2., New Phytologist, 168, 623-635, 2005.
Kubiske, M., Quinn, V., Marquardt, P., and Karnosky, D.: Effects of Elevated Atmospheric CO2 and/or O3 on Intra-and Interspecific Competitive Ability of Aspen, Plant biology, 9, 342-355, 2007.
Lin, Y.-S., Medlyn, B. E., Duursma, R. A., Prentice, I. C., Wang, H., Baig, S., Eamus, D., de Dios, V. R., Mitchell, P., and Ellsworth, D. S.: Optimal stomatal behaviour around the world, Nature Climate Change, 5, 459-464, 2015.
Massman, W. J.: A review of the molecular diffusivities of H2O, CO2, CH4, CO, O3, SO2, NH3, N2O, NO, and NO2 in air, O2 and N2 near STP, Atmospheric Environment, 32, 1111-1127, http://dx.doi.org/10.1016/S1352-2310(97)00391-9, 1998.
Medlyn, B. E., Duursma, R. A., Eamus, D., Ellsworth, D. S., Prentice, I. C., Barton, C. V., Crous, K. Y., de Angelis, P., Freeman, M., and Wingate, L.: Reconciling the optimal and empirical approaches to modelling stomatal conductance, Global Change Biology, 17, 2134-2144, 2011.
Simpson, D., Tuovinen, J.-P., Emberson, L., and Ashmore, M.: Characteristics of an ozone deposition module II: Sensitivity analysis, Water Air Soil Pollution, 143, 123–137, 2003.
Tuovinen, J.-P., Ashmore, M., Emberson, L., and Simpson, D.: Testing and improving the EMEP ozone deposition module, Atmospheric Environment, 38, 2373–2385, 2004.
Tuovinen, J.-P., Simpson, D., Emberson, L., Ashmore, M., and Gerosa, G.: Robustness of modelled ozone exposures and doses, Environmental Pollution, 146, 578–586, 2007.
Tuovinen, J.-P., Emberson, L., and Simpson, D.: Modelling ozone fluxes to forests for risk assessment: status and prospects, Annals of Forest Science, 66, 1-14, 2009.
Verstraeten, W. W., Neu, J. L., Williams, J. E., Bowman, K. W., Worden, J. R., and Boersma, K. F.: Rapid increases in tropospheric ozone production and export from China, Nature Geoscience 8, 690-695, 2015.