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A site-specific analysis of the implications of a changing ozone profile and climate for stomatal ozone fluxes in Europe

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Abstract

In this study we used eight sites from across Europe to investigate the implications of a future climate (2ºC warmer and 20% drier) and a changing ozone profile (increased background concentrations and reduced peaks) on stomatal ozone fluxes of three widely occurring plant species. A changing ozone profile with small increases in background ozone concentrations over the course of a growing season could have significant impacts on the annual accumulated stomatal ozone uptake, even if peak concentrations of ozone are reduced. Predicted increases in stomatal ozone uptake showed a strong relationship with latitude, and were larger at sites from northern and mid-Europe than those from southern Europe. At the sites from central and northern regions of Europe, including the UK and Sweden, climatic conditions were highly conducive to stomatal ozone uptake by vegetation during the summer months and therefore an increase in daily mean ozone concentration of 3 - 16% during this time of year (from increased background concentrations, reduced peaks) would have a large impact on stomatal ozone uptake. In contrast, during spring and autumn, the climatic conditions can limit ozone uptake for many species. Although small increases in ozone concentration during these seasons could cause a modest increase in ozone uptake, for those species that are active at low temperatures, a 2°C increase in temperature would increase stomatal ozone uptake even in the absence of further increases in ozone concentration. Predicted changes in climate could alter ozone uptake even with no change in ozone profile. For some southern regions of Europe, where temperatures are close to or above optimum for stomatal opening, an increase in temperature of 2°C could limit stomatal ozone uptake by enhancing stomatal closure during the summer months, whereas during the spring, when many plants are actively growing, a small increase in temperature would increase stomatal ozone uptake.

Keywords
Stomata; climate change; ozone flux; *Betula pendula; Dactylis glomerata; Leontodon hispidus*

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Introduction

Tropospheric ozone concentrations have approximately doubled across northern mid-latitudes between 1950 and 2000 (Parrish et al., 2012). More recently, there has been a reduction in emissions of ozone precursors in Europe due to a combination of legislation and modernisation of industrial sources, which has resulted in a slowed increase in ozone concentrations at some sites e.g. rural monitoring stations in the Western Mediterranean basin (Sicard et al., 2013). European annual mean surface ozone concentrations are predicted to decrease slightly based on the Representative Concentration Pathway (RCP) greenhouse gas concentration trajectory scenarios RCP 2.6, 4.5 and 6.0, but are expected to continue to rise with the RCP 8.5 scenario (Fiore et al., 2012, Wild et al., 2012). However, these annual mean projections do not show the detail of the anticipated change in the ozone concentration profiles. In particular, whilst large episodic peaks of ozone have reduced in frequency and severity across much of Europe, low- and medium-range ozone concentrations have continued to rise over the period 1990 to 2010 in Europe and the USA (Paoletti et al., 2014; Lefohn et al., 2017; Karlsson et al., 2017). This has been attributed to factors including changing meteorological conditions, background ozone and source patterns that are not always fully incorporated into models of future ozone scenarios (Akritidis et al., 2014). Further rises in mean ozone concentration in northern Europe are predicted as it is thought that reductions in precursor emissions in this region will be outweighed by increased hemispheric transport of precursors, together with reduced titration of ozone with nitric oxide (Lacressonniere et al., 2014; Wilson et al., 2012; Lefohn et al., 2017; Karlsson et al., 2017).

Current and projected future ozone concentrations are a concern for vegetation (Royal Society, 2008; Mills et al., 2011a) and detrimental effects have been reported at ambient concentrations including for trees (Braun et al., 2014; Wittig et al., 2009) and (semi-)natural vegetation (Mills et al., 2011a). Much work on effects on vegetation has focussed on the impacts of peak ozone concentrations and therefore ozone delivery within experiments has often used a pronounced diurnal profile (e.g. Calvo et al., 2007, Bender et al., 2006). Despite the continued increase in background ozone concentrations due to the predicted changes in ozone exposure profile over the coming decades, the consequence of this for vegetation remains poorly understood (Coyle et al., 2003). Some studies, however, have shown that an increase in background ozone concentration can be as deleterious to plant health as an increase in peak concentrations (Oksanen and Holopainen, 2001; Hayes et al., 2010, Harmens et al., 2018).

Ozone enters plants through stomata, which are open when climatic conditions are favourable for gas exchange. Stomatal ozone uptake can be as high in central and northern Europe, when concentrations are moderate and climatic conditions are conducive to stomatal opening, as in more southern areas where ozone concentrations are higher but conditions for uptake are less favourable (Mills et al., 2011a). Therefore, when quantifying the risk to vegetation of ozone pollution it is important to consider ozone uptake through the stomata as this has been shown to be better related to plant effects such as crop yield loss and reduced tree growth than to concentration based metrics (e.g. Pleijel et al., 2004; Mills et al., 2011a; Büker et al., 2015). Plants have some capacity to detoxify ozone that enters leaves through the stomata, with increased damage occurring when this is exceeded (Burkey et al., 2006). Using a constant threshold for stomatal ozone flux ('Y' in POD_Y (Phytotoxic Ozone Dose over a threshold flux of Y nmol m^{-2} PLA s^{-1}) is considered to act as a surrogate for an ozone detoxification threshold (Musselman et al., 2006) with different values used for different species (Mills et al., 2011b). Although this principal is sound for quantifying ozone impacts on individual plant species, there are mathematical implications when modelling fluxes close to this threshold as very small variations in value can have a large cumulative impact on POD_Y depending on whether or not the threshold has been reached.

A spring peak of ozone concentrations has been observed at many remote northern hemisphere sites. In northern Arizona this peak occurs in May and has been attributed to transport of precursor molecules from other regions (Diem, 2004). Over recent years there is some evidence of a change in seasonality of ozone, with peak concentrations occurring earlier in the year (Parrish et al., 2013), including in regions such as the north-eastern US as NOx emissions are reduced (Clifton et al., 2014). Furthermore, the start of spring has also been occurring increasingly earlier in some parts of Europe over recent decades (Peñuelas et al., 2002; Menzel et al., 2006), meaning that the timing of peak ozone concentrations now overlaps with early season plant growth (Karlsson et al., 2007, Karlsson et al., 2009, Klingberg et al., 2009). At this time, many species may be sensitive to ozone as they are fully metabolically active (Alonso et al., 2001), indicating that it is important to consider ozone concentrations and fluxes in spring. In some locations, an increased autumn ozone peak has also been observed, including Hong Kong (Lee et al., 2009) and the consequences of this for vegetation have not yet been investigated.

Alongside any changes in ozone concentration in future decades, there are likely to be changes in meteorological conditions, due to projected changes in climate. Although there is much variation in predictions of future climate, mean surface temperatures are likely to increase by at least 2°C by 2100 according to all but the most stringent mitigation scenario RCP2.6 (IPCC, 2014). Similarly, there is a spatially varying range in predictions of precipitation, however, for much of Europe a reduction in annual precipitation of 10-20% by 2100 is likely (IPCC, 2014). Both temperature and precipitation (via effects on soil moisture) affect stomatal ozone fluxes and are thus critical in determining the instantaneous and cumulative ozone uptake by plants (Klingberg et al., 2011).

In this study we investigate the possible consequences for vegetation of a combination of reduced peak and increased background ozone concentrations based on effects mediated by stomatal ozone flux for selected example sites in Europe. We use the DO_3SE model (Emberson et al., 2000a, b) which uses a multiplicative algorithm, based on that developed by Jarvis (Jarvis, 1976) to estimate leaf stomatal conductance. We use 2010 as the baseline year for climate and ozone, a typical year with relatively few ozone 'episodes' and with similar exceedances of the thresholds set to protect human health as in the previous three years (EEA, 2011). We then consider the implications of a changing ozone concentration profile by calculating stomatal ozone uptake using the DO_3SE model for a grass, a forb and a deciduous tree species widely found across much of Europe, using site-specific hourly ozone and climate data. Lastly, we calculate the ozone dose under current (2010) and future (2100) climatic conditions representative of RCP scenarios at the same sites to evaluate changes in potential risk to vegetation and test the hypothesis that predicted changes to climate will result in increased stomatal ozone uptake.

Methods

Stomatal ozone fluxes (POD_0) were calculated using the multiplicative model DO_3SE (Emberson et al., 2000a) for three species that are commonly occurring across Europe, although they may not be part of the dominant vegetation community at all of the sites used. The model was parameterised for the species *Dactylis glomerata* and *Leontodon hispidus* using stomatal conductance measurements made using a porometer (AP4, Delta-T, UK) during ozone exposure experiments in solardomes at CEH Bangor, UK. In addition, the parameterisation for *Betula pendula* used within the UNECE was also included (LRTAP Convention, 2017), using the northern Europe parameterisation. As regional-specific parameterisations were not available for all regions of Europe, the same parameterisation was used at all sites for this simulation exercise to facilitate comparison. Further details about these experiments, the method of parameterisation and the parameterisations used are included in the supplementary material (S1). The phenology function (f_{Phen}) was considered to be 1 at all times to avoid the potential, but currently unquantifiable, changes in plant phenology that may occur in future scenarios due to the influence of climatic changes. The stomatal response to ozone, f_{O3}, was not included in the model as this is not yet parameterised in LRTAP Convention (2017) for trees and grassland species. For the purposes of this modelling study, no threshold was used for the accumulation of ozone fluxes to avoid having varying species-specific influences of the threshold when assessing potential differences in calculated stomatal ozone uptake, and because small differences in ozone fluxes may appear to have a disproportionately large effect if the change moves the hourly flux across the threshold. However, due to the dependence of ozone fluxes on meteorological conditions in addition to ozone concentration, stomatal ozone flux is not directly related to ozone concentration alone.

On-site observed hourly climate and ozone data was obtained for the sites UK-Snowdon, UK-Harwell, UK-Auchencorth, UK-Strath Vaich, Germany (DE)-Linden, Italy (IT)-Arconate, Spain (ES)-Tres Cantos, Sweden (SE)-Östad for the year 2010. These sites were selected to represent a gradient of ambient climatic and ozone conditions. The monthly mean ozone concentrations and mean diurnal profile for each site are shown in Figure 1 and full details of the site locations and descriptions, and a summary of meteorological data for 2010 are shown in the supplementary material (S2). The sites are rural, but of differing altitude and distance to pollutant sources. For the UK sites, climate data was obtained from the Environmental Change Network (http://data.ecn.ac.uk/index.asp), and ozone data was obtained from the UK-AIR archive (http://uk-air.defra.gov.uk/data/). Ozone data from DE-Linden was obtained from the Hessian Air Quality Monitoring Network (http://www.hlnug.de/messwerte/luft.html), with corresponding meteorological data from the Environmental Monitoring and Climate Impact Research Station at Linden (personal communication). Data from IT-Arconate were obtained from ARPA Lombardia (Agenzia Regionale per la Protezione dell'Ambiente) air quality monitoring network of the Lombardy region (hppt://www2.arpalombardia.it/sites/QAria/). Data from ES-Tres Cantos were obtained from an experimental station run by CIEMAT (García-Gómez et al., 2016). Data from SE-Östad were obtained from local meteorological measurements on site; where needed interpolated daily values for Östad were used to fill gaps in data, obtained from official statistics on the web-site of the Swedish Meteorological and Hydrological Institute. For each of these sites, stomatal ozone fluxes for each species were calculated over the period January-December using the DO_3SE version 3.03 model (Emberson et al., 2000a; LRTAP Convention, 2017, https://www.sei-international.org/do3se) using these climate and ozone data as meteorological inputs as the 'current' scenario. We appreciate that in some parts of Europe the species will not be in leaf for the entire year. As the time window of active growth varies between sites and years and will change in a future climate, showing theoretical fluxes for the whole year provides conceptual understanding of the potential for changes during earlier springs and later autumns as climates warm.

Stomatal ozone uptake was also calculated using the same set of meteorological data, but with hourly ozone values increased by 5 ppb above ambient values when ozone was <40 ppb and decreased by 5 ppb when ambient values were >45 ppb (2100 ozone scenario). These changes are simplified, but similar to the overall model predictions for Europe for 2100 using the RCP6 emission scenario (Coleman et al., 2013), which shows decreased peak ozone concentrations of up to 8 ppb in parts of Europe in 2100 compared to current conditions. Additional model runs were also made using reduced rainfall, with hourly rainfall when it occurred decreased by 20% (-20% rain scenario), and with hourly temperature increased by 2°C (+ 2°C scenario). To compensate for the increase in VPD associated with increased temperature, in model runs where temperature was increased by 2°C, VPD was also increased by 13%. This was calculated as representing the increase in VPD that would occur within the range 20-30°C and at relative humidity of 50%, as relative humidity data was not available from all sites to allow this to be calculated directly. The ozone and climatic features of the model runs are summarised in Table 1. In all model runs, rather than DO_3SE reading in soil moisture as an input, soil moisture was modelled by DO_3SE from rainfall data, assuming a loam soil for consistency. The soil moisture module of DO_3SE is based on the Penman-Monteith model of evapotranspiration (Monteith, 1965) and uses hourly plant transpiration, soil evaporation and intercepted canopy evaporation (Büker et al., 2012).

Table 1: Summary of the ozone and climate features of the model runs performed. In each scenario '2010' indicates measured values at the sites in 2010. The 2100 ozone scenario is simulated, but based on the 2010 values at each site. Temperature, VPD and rainfall are also based on measured 2010 values, but for some scenarios each hourly value has been modified by +2°C, +13% or -20% respectively.

Scenario name (abbreviated)	**Ozone**	**Temperature**	**VPD**	**Rainfall**
Current	2010	2010	2010	2010
2100 profile	2100 simulation	2010	2010	2010
+2 °C	2010	2010 +2°C	2010 +13%	2010
-20% rain	2010	2010	2010	2010 -20%
+2 °C, -20% rain	2100 simulation	2010 +2°C	2010 +13%	2010 -20%
2100 profile +2 °C	2100 simulation	2010 +2°C	2010 +13%	2010
2100 profile -20% rain	2100 simulation	2010	2010	2010 -20%

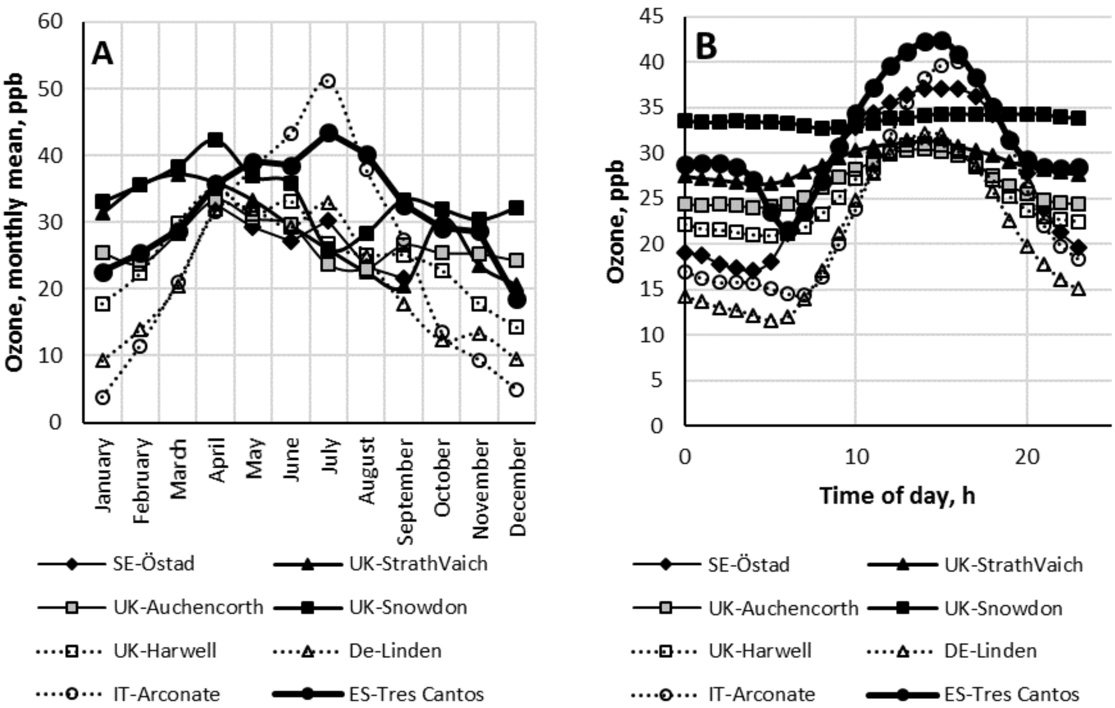

Figure 1: a) Monthly mean ozone profile and b) Mean diurnal ozone profile for the sites used in this study, based on hourly ozone data from 2010, Jan 1st – Dec 31st. Note, data for SE-Östad was available for April to September only.

Results

<u>Ozone concentrations and flux (POD_0) in 2010</u>

Almost all sites (except IT-Arconate and ES-Tres Cantos) had a 'spring peak' of ozone concentration, with the highest concentrations in March/April (Figure 1a). This pattern is common in Europe due to the seasonal variations in precursor emissions, the strength of the stratospheric source, and the balance between photochemical production and destruction of ozone (Royal Society, 2008). Diurnal ozone concentrations generally peaked in mid-afternoon, with lowest concentrations between midnight and 06:00 (Figure 1b). However, the amplitude between the minimum and maximum ozone concentration was variable with some sites having an amplitude of 25 ppb (e.g. IT-Arconate) and some showing little variation (e.g. UK- Snowdon and UK-Strath Vaich). The sites at highest altitude had higher night-time and winter-time ozone concentrations compared to those at lower altitude, which is a recognised pattern due to losses from dry-deposition being replaced from ozone-rich layers above (Royal Society, 2008). The monthly total ozone flux (POD_0) showed very different patterns between the different sites (Figure 2). The most northern sites, from the UK and Sweden, had the highest ozone fluxes in the summer months, when the ozone values were typically 5-10 ppb lower than those of the spring maxima. Interestingly, ozone fluxes calculated for *D. glomerata* between May and August were similar in SE-Östad to those of IT-Arconate despite large differences in ozone concentration and climate during this time period. For perennial grassland species such as *D. glomerata* (Figure 4) and *L. hispidus* (Figure 5), the DO3SE model predicted that stomatal ozone uptake could take place almost all year round at most sites, as meteorological conditions are conducive to stomatal opening. However, it is important to note that stomatal uptake for birch (Figure 3) would be limited to when leaves are present. Similarly, overwintering leaves of *D. glomerata* and *L. hispidus* may not be physiologically active during the winter months. Modelled total annual stomatal ozone uptake for the different climate and ozone scenarios for *B. pendula, D. glomerata* and *L. hispidus* are shown in supplementary material (S4).

Frequently at all sites, the periods of highest stomatal ozone fluxes did not coincide with the periods of highest ozone concentration, for example DE-Linden and ES-Tres Cantos had the highest ozone concentrations in summer whereas stomatal ozone fluxes were higher in spring (Supplementary material Figure S2). In many cases during the year such differences may be explained by limitations due to soil moisture availability, which are apparent when comparing model runs with and without soil moisture deficit induced reductions in stomatal ozone uptake. These show that soil moisture deficit at some sites can reduce stomatal ozone flux, with several sites showing reductions of over 50% during some months compared to fluxes under field capacity conditions (Supplementary material S3).

The majority of the total stomatal ozone flux (POD_0) occurred with ozone values between 20 and 50 ppb at all sites for both the 'current' and 2100 ozone profiles (Figure 6). The contribution to total stomatal ozone uptake from ozone concentrations above 50 ppb was comparatively low, with the exception of IT-Arconate, which had the highest ozone concentrations during the summer months and 25-50% of the total ozone flux was attributed to ozone values >50 ppb. Using the 2100 ozone scenario there was a significantly lower contribution to total stomatal ozone uptake from ozone values of 10-20 ppb for all species ($p<0.05$, $p<0.01$, $p<0.05$ for *B. pendula, D. glomerata* and *L. hispidus* respectively). There was also a significantly lower contribution from ozone values of 0-10 ppb for *D. glomerata* ($p<0.05$) and *L. hispidus* ($p<0.05$) and from ozone values of 20-30 ppb for *D. glomerata* ($p<0.01$) and *L. hispidus* ($p<0.05$). In contrast, there was a significantly higher contribution from ozone values of 40-50 ppb in the 2100 compared to the current scenario for all species ($p<0.001$). At higher ozone concentrations there was a significantly lower contribution to stomatal ozone uptake in the 2100 ozone scenario in the categories 50-60 ppb (*B. pendula,* $p<0.05$), 60-70 ppb ($p<0.05$ for all species) and 70-80 ppb (*L. hispidus,* $p<0.05$).

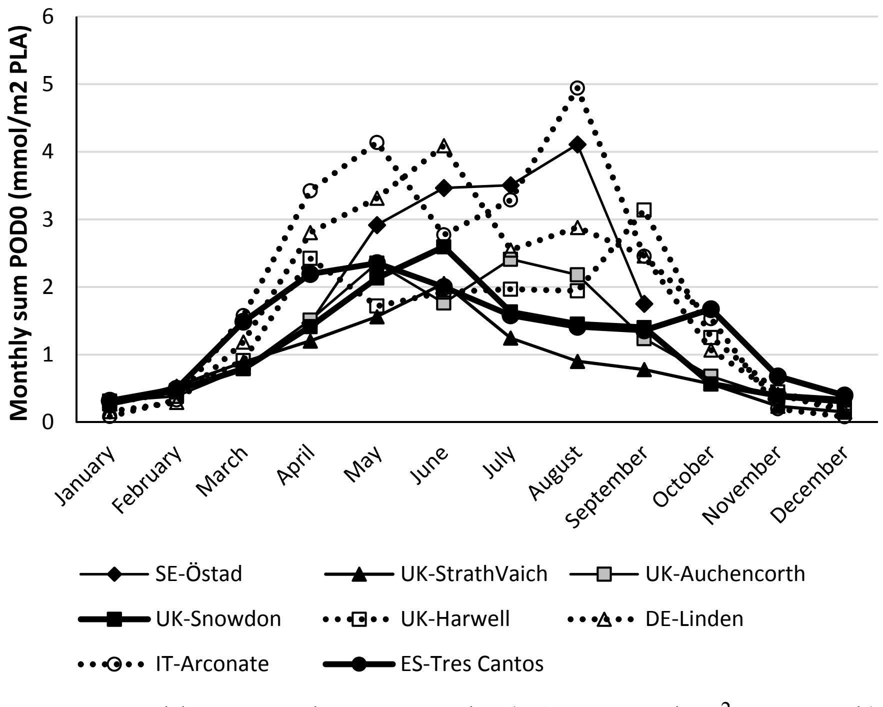

Figure 2: Monthly stomatal ozone uptake (POD_0, mmol m^{-2} per month) for *D. glomerata* in current (2010) ozone and climate conditions at all sites.

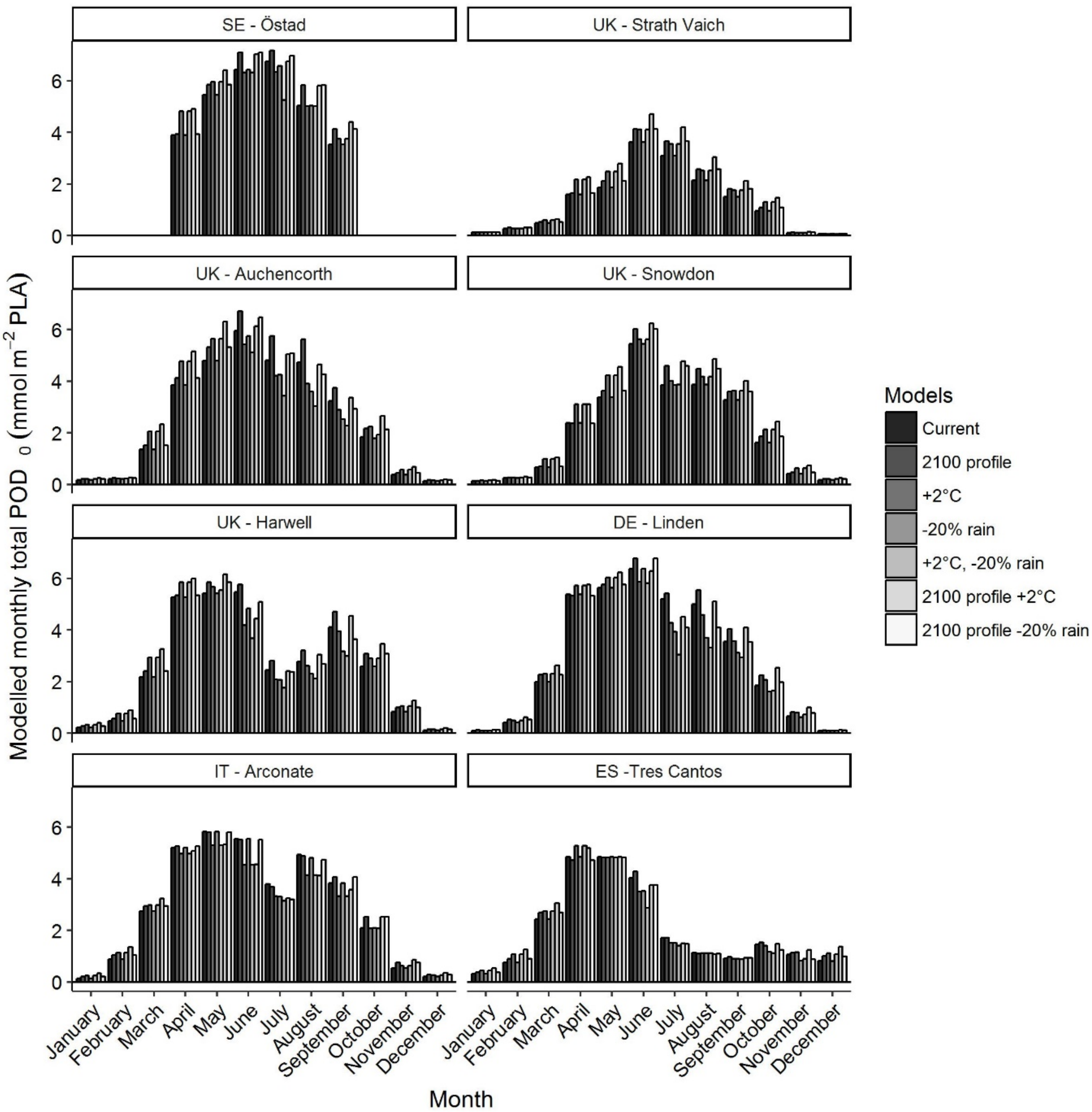

Figure 3: Modelled monthly total stomatal ozone uptake (POD_0, mmol m^{-2} per month) for *B. pendula* at selected European sites in 2010. Note: Whilst year round fluxes are provided for comparison with Figure 3 and 4, it is important to note that the leaves of *B. pendula* are shed from trees in the autumn, with bud-burst occurring in the spring with the date depending on location.

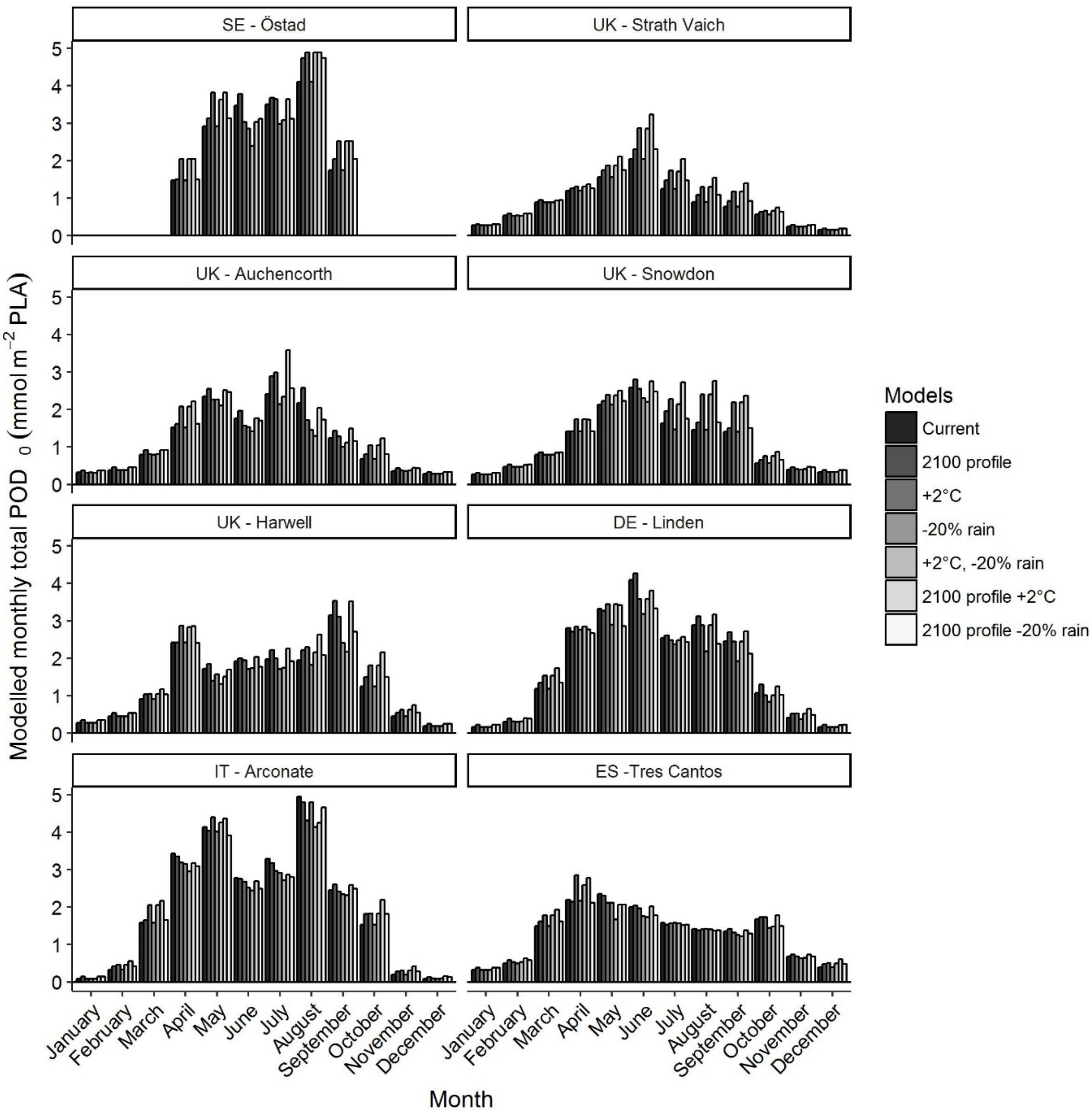

Figure 4: Modelled monthly total stomatal ozone uptake (POD_0, mmol m^{-2} per month) for *D. glomerata* at selected European sites in 2010.

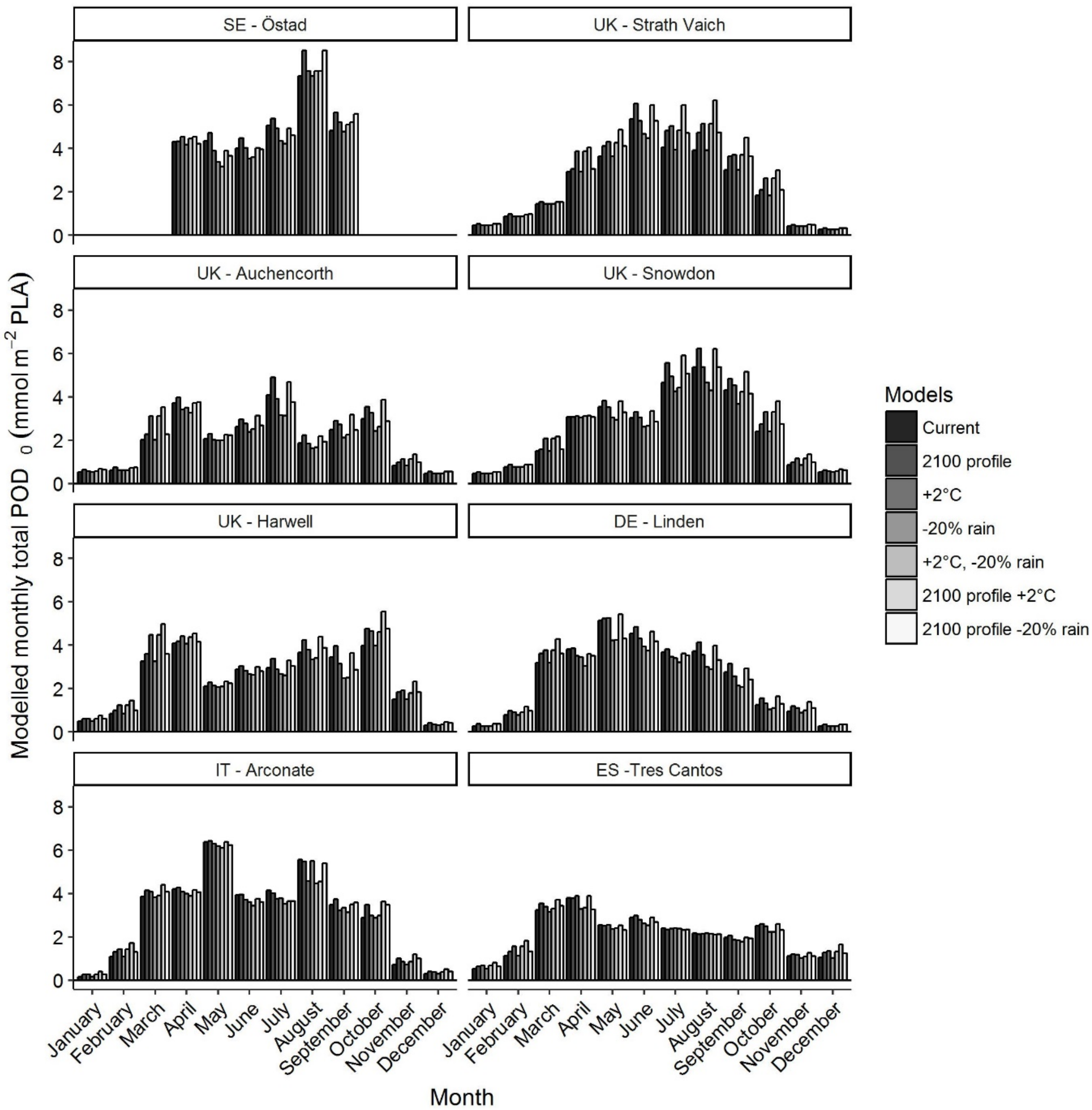

Figure 5: Modelled monthly total stomatal ozone uptake (POD_0, mmol m^{-2} per month) for *L. hispidus* at selected European sites in 2010.

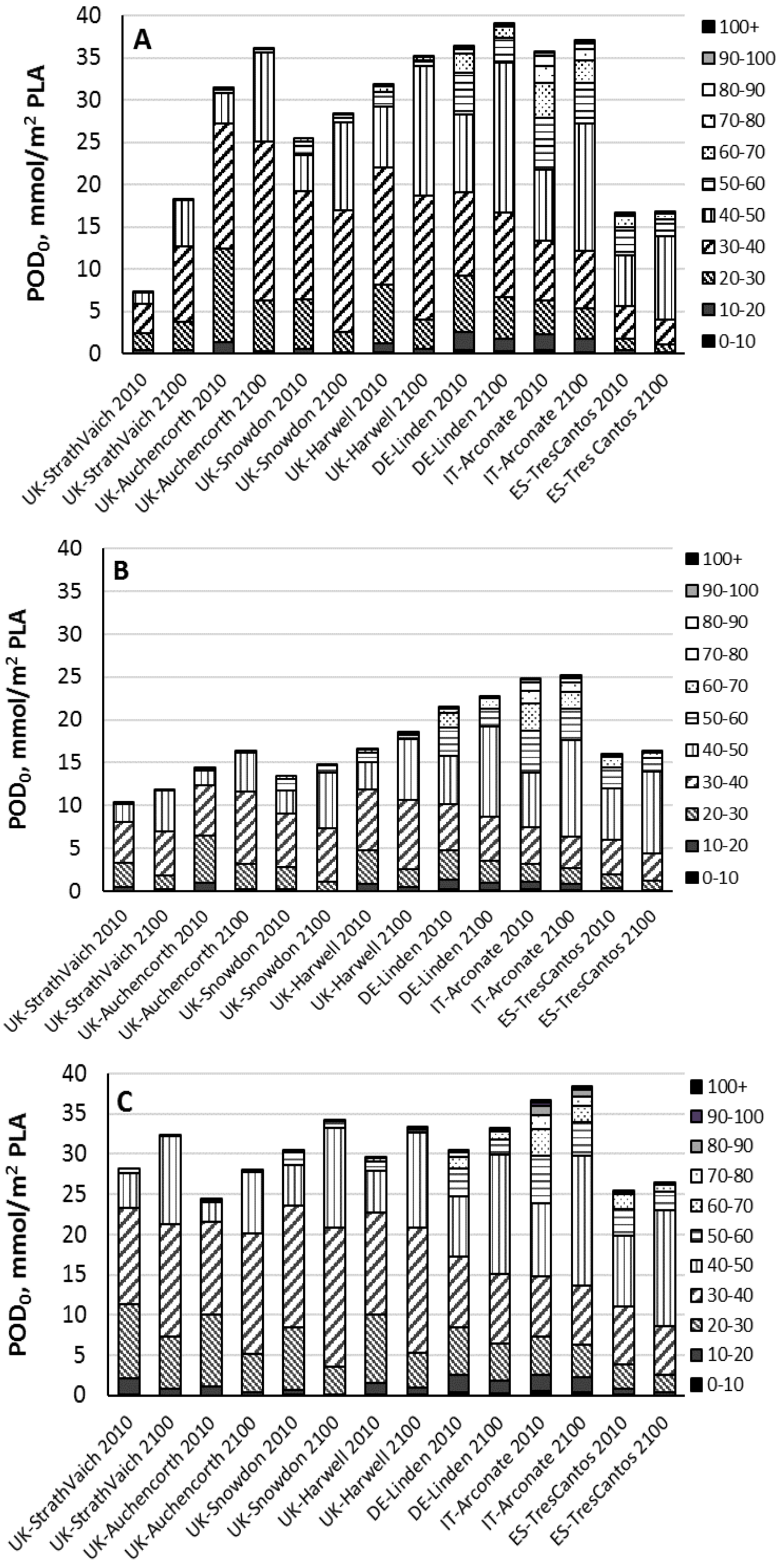

Figure 6: Total stomatal ozone flux from different categories of ozone concentration for A) *B. pendula*, B) *D. glomerata* and C) *L. hispidus* for the different sites, using the current and 2100 ozone profiles. (annual data is not available for Sweden-Östad).

Predicted ozone concentrations and POD_0 in 2100

Consequences of changes in ozone profile

The 2100 ozone profile, with increased background and decreased peaks, resulted in increased 24h mean ozone values at all sites of 1 to 4 ppb (full details are shown in Supplementary material S4). The DO_3SE model predicted that this would increase annual stomatal ozone uptake by as much as 14-18% at northern sites e.g. UK-Strath Vaich (Figure 6). In southern Europe, the increase in annual stomatal ozone uptake was lower (3% increase for *B. pendula* at IT-Arconate), partly because the higher hourly ozone concentrations of the ‘current’ dataset at these sites meant that the increase in background ozone concentrations was offset by decreases in peaks (current vs 2100 ozone profiles for all sites are shown in Supplementary material S4). The percentage increase in ozone flux using the 2100 profile compared to current was linearly related to latitude (Figure 7: r^2=0.90 for *B. pendula*, r^2=0.92 for *L. hispidus* and r^2=0.81 for *D. glomerata*), with a similar relationship with latitude for the percentage increase in ozone concentration (r^2=0.83).

The extent of additional ozone uptake due to the changing ozone profile varied throughout the year. For the majority of sites the increase in ozone flux was largest during the summer and autumn (Figures 3-5). Climate (particularly temperature) tended to limit stomatal opening in spring so that ozone fluxes were comparatively unaffected by an increase in ozone concentration, unless temperature was also increased.

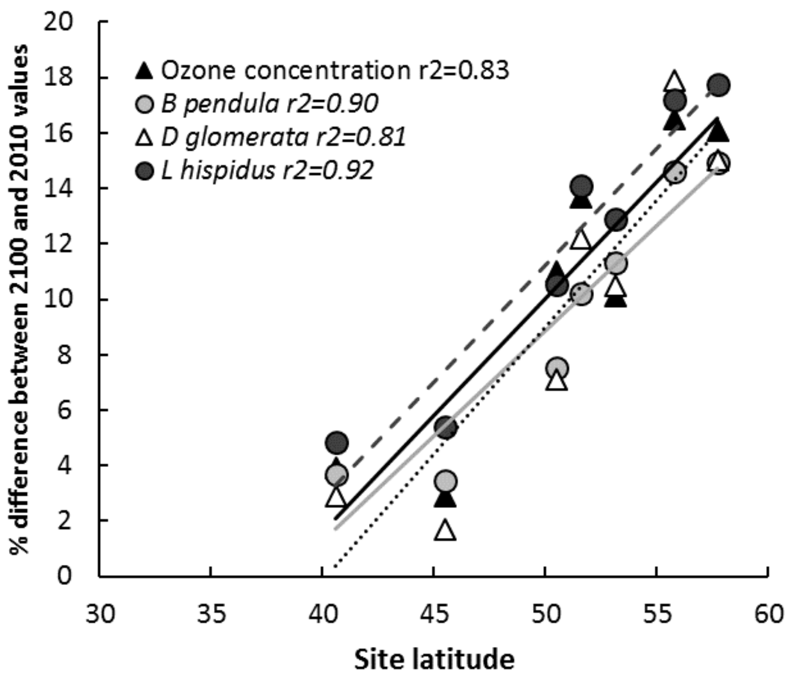

Figure 7: Percentage increase in ozone flux with the 2100 ozone profile compared to 2010 ozone for *L. hispidus*, *D. glomerata* and *B. pendula* at the different sites. The percentage increases in ozone concentration with the 2100 ozone profile compared to 2010 (based on 24h mean concentrations) are also shown. Note these do not include SE-Östad as the model runs for this site did not include the full 12 months. ▬ =ozone concentration, ▬ = *B. pendula*, -- = *L. hispidus* and ⋯ = *D. glomerata.*

Consequences of changes in climate

An increase in temperature of 2°C increased stomatal ozone uptake at all sites and had a larger impact than changing ozone profile in many cases (Figures 3-5), particularly for *B. pendula* ($p<0.01$) and *L. hispidus* ($p<0.01$). For IT-Arconate and ES-Tres Cantos there was a small increase in stomatal ozone uptake with increasing temperature, which was largest in the spring. The other sites showed increases in stomatal ozone uptake with increased temperature over a wider time-period, and although these were sometimes largest in spring (March to May), they also sometimes occurred in summer and/or autumn. *D. glomerata* has a higher T_{min} than *L. hispidus* and *B pendula* and for this species increasing temperature by 2°C in the spring was not sufficient for T_{min} to be reached, particularly in the more northern sites, and therefore there was no increase in stomatal opening. However, for *L. hispidus* and *B. pendula* the increase in temperature caused a shift from T_{min} towards T_{opt} and therefore an increase in stomatal opening.

Soil moisture limitations in the current climate were sufficient to reduce stomatal ozone uptake for *L. hispidus* and *D. glomerata* during the summer for prolonged periods at the sites IT-Arconate, ES-Tres Cantos and UK-Harwell, and for a shorter time at DE-Linden (Supplementary material S3). A reduction in rainfall by 20% reduced stomatal ozone uptake in some months at all sites, including those with high annual rainfall. For the sites IT-Arconate and ES-Tres Cantos the reduction in stomatal ozone uptake due to reduced rainfall was lower than for the other sites, because stomatal fluxes were already limited by soil moisture in 'current' conditions. Reductions in rainfall by 20% had very little impact on the stomatal ozone uptake of *B. pendula* at any of the sites used, because the stomatal conductance model parameterisation indicated that this species maintained stomatal opening at low soil water potential.

Consequences of combined changes in ozone and climate in 2100

A combination of a 2°C increase in temperature and 2100 ozone profile increased stomatal ozone uptake, although the magnitude of the increase varied. For *L. hispidus* at the sites UK-Harwell, IT-Arconate, ES-Tres Cantos and DE-Linden, the impact was largest in March and was much less in the summer, when other factors were limiting stomatal fluxes. For UK-Strath Vaich, UK-Snowdon, UK-Auchencorth and SE-Östad the combination of 2°C increase in temperature and 2100 ozone scenario corresponded with increased fluxes throughout most of the year and the impact was largest in summer and autumn. A combination of 20% decreased rainfall and 2100 ozone profile often gave monthly stomatal ozone fluxes that were intermediate between those of 2100 ozone profile and decreased rainfall, therefore, the monthly stomatal ozone uptake with this scenario were usually higher than those of the 'current' scenario.

Species-specific considerations

Calculated ozone fluxes were highest for *L. hispidus* and *B. pendula*, with *D. glomerata* fluxes generally lower at all sites. This is partly because *L hispidus* had a higher g_{max} than the other species and therefore higher stomatal conductance, but *L. hispidus* and *B. pendula* also had a lower T_{min}, enabling stomatal uptake at lower temperatures than for *D. glomerata*. This difference in response to meteorological conditions also meant that the seasonal profile of stomatal ozone flux was different for the different species, with *D. glomerata* having a more pronounced seasonal variation.

Identification of the minimum ozone concentration with a corresponding stomatal ozone uptake rate reveals that for *B. pendula*, ozone fluxes above the commonly used threshold of 1 nmol m^2 s^1 (POD_1) accumulated when ozone values were >10 ppb, if climatic conditions were optimal. Although ozone flux could be high when ozone concentrations were higher than 50 ppb, often climatic conditions were limiting. For *L. hispidus, B. pendula* and *D. glomerata,* ozone flux could be above the threshold of 1 nmol m^{-2} s^{-1} when ozone values were as low as 5 ppb, 10 ppb and 10 ppb respectively (Supplementary material S5).

Discussion

This study has shown that without any change in climate, increased background and reduced peak ozone concentrations typically predicted for Europe in 2100 as a result of increased hemispheric transport of precursors and local precursor emission reductions could result in up to a 15% increase in total stomatal ozone uptake to vegetation (POD_0) compared to 2010 ozone profiles. The north-south gradient in ozone concentration for the sites meant that the impacts of the future ozone scenario varied with latitude. In more northern sites where peak ozone concentrations were lower, a higher proportion of hourly ambient ozone values were less than 40 ppb and the applied scenario therefore increased the ozone concentration as a result of the increasing background. In contrast, the southern European sites had higher peaks of ozone in current conditions and therefore there was a larger effect of the reduction in values > 45 ppb by 5 ppb on the ozone concentrations with the 2100 scenario. Although all sites showed a net increase in mean ozone concentration and total stomatal ozone uptake with the 2100 scenario compared to current conditions, the proportionate increase was lower in the southern sites. This indicates that a changing ozone profile in Europe could have a larger impact in mid and northern regions than southern regions, especially when the increased ozone concentrations coincide with climatic conditions favourable for ozone uptake.

Changes in meteorology as a consequence of predicted climate change could also have a large influence on stomatal ozone uptake in the absence of any alterations in ozone concentration, particularly temperature, which increased modelled stomatal ozone uptake at all sites in this study. In this study only a single stomatal conductance parameterisation per species was used across Europe and it is possible that vegetation of the Mediterranean region may exhibit a reduced extent of stomatal closure with high temperature, VPD and SWP compared to that grown in more northern regions (Calvo et al., 2007, LRTAP 2017) and therefore climatic conditions may be more favourable for stomatal ozone uptake than this modelling exercise suggests. The element of climate change having the largest influence on stomatal fluxes varied according to region. This is consistent with a previous study on winter wheat and beech, where increased ozone fluxes in response to increased temperature were predicted over the period 1997-2100 in Germany (Bender et al., 2015).

This study applied a simplified 2100 scenario for ozone and meteorological conditions in the future to provide an indication of potential implications for stomatal ozone flux. However, diurnal and seasonal variations in changes in both ozone and meteorological conditions may occur in 2100 which could influence stomatal fluxes. Higher daily maxima for temperature could enhance the rate of ozone formation as well as influencing the contribution of natural sources to precursor emissions (Royal Society, 2008), increasing hourly ozone values by 1-10 ppb (Jacob and Winner, 2009). There could also be feedbacks between the vegetation and ozone and microclimatic conditions, for example, reduced stomatal ozone uptake due to increased soil moisture deficit in 2100 could lead to increased ambient ozone concentrations, (Kroeger et al. 2014; Emberson et al. 2013).

The impact of increasing temperature on stomatal ozone fluxes could be particularly important for species that have a low T_{min} and are actively growing in cooler conditions, where an increase in temperature would give conditions closer to optimum for conductance. As a consequence of predicted climate change, stomatal ozone fluxes could occur over a longer period of the year than in current conditions, including into early spring and autumn, which until recently have not been considered to be associated with a risk to vegetation from ozone pollution. It has been suggested that some species are most sensitive to ozone at or around the time of flowering (e.g. Pleijel et al., 1998, Soja et al., 2000) and ozone impacts on flowering and seed development have been shown for a wide range of species in a recent meta-analysis (Leisner and Ainsworth, 2012). Since many European species flower in March-April it is possible that these species are particularly at risk from future ozone and climate change scenarios. Spring flowering species have been poorly studied for ozone responses in northern Europe in comparison to those which flower in summer (Hayes et al., 2007). In addition, stomatal conductance model parameterisations are not available for many of these early flowering species, which may be active at lower temperatures than the species considered in this study. Further studies on spring flowering species are therefore needed to better understand the potential consequences of a changing ozone profile. In contrast, experiments in the Mediterranean region have focussed on spring flowering plants as this is the main flowering season in this region before conditions become too dry (González-Fernández et al., 2010, Calvete-Sogo et al., 2015).

Increased ozone fluxes to vegetation in autumn may also be important. It has been demonstrated that mature leaves of some tree species are more sensitive to ozone than those that are not fully-expanded in terms of both visible injury and impairment of photosynthesis (Zhang et al., 2010, Bagard et al., 2008). It is therefore possible that increased stomatal ozone uptake in autumn may damage leaves to a greater extent than a similar ozone uptake in spring if the leaves are more sensitive to ozone at this time. Ozone can also accelerate senescence (e.g. Matyssek and Sandermann, 2003), and if premature leaf loss occurs in the autumn there may be a longer period without leaves until the following spring. In addition, autumn exposure to ozone may decrease winter-hardiness of some species e.g. *Picea abies* due to changes in chloroplast shape and location within the cells (Kivimaenpaa et al., 2014). With increased background ozone concentrations these detrimental effects could be further enhanced as climatic conditions are favourable for uptake of additional ozone.

An aspect not considered in this study is that alterations in climate could also influence stomatal ozone fluxes due to changes in phenology. In Europe, a comprehensive analysis of a large phenological dataset has shown that the phenological response to climate change shows an advance in spring/summer of 2.5 days per decade (Menzel et al., 2006). Over the previous 60 years it has been demonstrated that bud-burst of beech, birch and oak is beginning increasingly earlier (Olsson, 2014), particularly at northern latitudes and it has been estimated that in Fennoscandia the growing season is extending by four days per decade (Hogda et al., 2013). This is particularly relevant for deciduous trees such as *B. pendula* because the current study has shown that climatic and ozone conditions in the early spring and late autumn months that are outside of the current growing period are also conducive to ozone uptake, should the growing season extend into these.

Ozone uptake exceeding 1 nmol m^{-2} s^{-1} (considered to be a surrogate ozone detoxification threshold for forest trees and semi-natural vegetation; Mills et al., 2011b) occurred with ozone concentrations at or below 10 ppb for the species used in this study. This demonstrates that small but frequent increases to these low concentrations could result in large impacts on total ozone fluxes over the course of a growing season. However, the ozone concentration required to reach this threshold is related to the g_{max} of the species and species with a higher

g_{max} reach this threshold at a lower ozone concentration, when climatic conditions are favourable. Due to the mis-match between high ozone concentrations and optimum climatic conditions for stomatal uptake, the species-specific minimum and optimum temperature for stomatal uptake were very influential in determining ozone fluxes, indicating that a robust parameterisation of T_{min} is essential to ensure that stomatal ozone fluxes in sub-optimal climatic conditions can be accurately assessed.

This study has used example sites from across Europe to show that a future ozone profile in Europe with increased background ozone concentrations and decreased peaks can cause a significant increase in stomatal ozone flux to vegetation. In particular at mid- to northern latitudes, large increases in ozone flux are predicted for the summer months when climatic conditions are rarely limiting. In Southern Europe, our predictions using a generalized flux model parameterisation to facilitate comparisons suggest that the changing ozone profile would have proportionately less impact on accumulated flux. Although changes in temperature, soil moisture and ozone profile can all influence accumulated flux, a combination of an altered ozone profile together with a 2°C increase in temperature gives a much larger increase in predicted stomatal ozone uptake than altered ozone profile alone. Furthermore, background ozone concentrations are also high during spring and autumn and increased impacts on vegetation during these periods may be biologically significant as some species may be more vulnerable at these times. The time window for considering vegetation at risk from ozone pollution in future scenarios should therefore be extended to include the active growing seasons in spring and autumn as significant ozone fluxes could occur during this time.

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