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Evaluating stomatal ozone fluxes in WRF-Chem: Comparing ozone uptake in Mediterranean ecosystems

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HIGHLIGHTS

- Validation of WRF-Chem estimates for stomatal uptake of ozone.
- Overestimated daytime ozone stomatal fluxes in particularly dry periods.
- Improved stomatal fluxes with VPD parameterization.
- Revision of both stomatal conductance parameterization and parameter values required.

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ABSTRACT

The development of modelling tools for estimating stomatal uptake of surface ozone in vegetation is important for the assessment of potential damage induced due to both current and future near surface ozone concentrations. In this study, we investigate the skill in estimating ozone uptake in plants by the Weather Research and Forecasting model coupled with chemistry (WRF-Chem) V3.6.1, with the Wesely dry deposition scheme. To validate the stomatal uptake of ozone, the model simulations were compared with field measurements of three types of Mediterranean vegetation, over seven different periods representing various meteorological conditions. Some systematic biases in modelled ozone fluxes are revealed; the lack of an explicit and time varying dependency on plants' water availability results in overestimated daytime ozone stomatal fluxes particularly in dry periods. The optimal temperature in the temperature response function is likely too low for the woody species tested here. Also, too low nighttime stomatal conductance leads to underestimation of ozone uptake during night. We demonstrate that modelled stomatal ozone flux is improved by accounting for vapor pressure deficit in the ambient air. Based on the results of the overall comparison to measured fluxes, we propose that additional improvements to the stomatal conductance parameterization should be implemented before applying the modelling system for estimating ozone doses and potential damage to vegetation.

1. Introduction

Near surface ozone is a toxic oxidant, which in cases of high uptake can cause substantial damage to both human health and vegetation. The near surface background concentration of ozone in the Northern Hemisphere has more than doubled since pre-industrial times, and increased concentrations have in many areas reached values at which adverse effects to vegetation can be expected (Hollaway et al., 2012; IPCC, 2013; The Royal Society, 2008). The production efficiency of tropospheric ozone is determined by the availability of precursor gases as well as climatic and meteorological conditions, and the potential for future ozone induced damage is as such dependent on both emission controls and future climatic conditions (Emberson et al., 2013; Fowler et al., 2009; Klingberg et al., 2011, 2014).

There are various metrics in use in order to estimate the risk of ozone-induced damage to vegetation. Concentration-based indexes are the most traditional ones (CLRTAP, 2015; Mills et al., 2007), however; as high ambient air concentrations do not necessarily imply high uptake, adverse effects to vegetation are more

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appropriately represented by a flux based approach, which relates risk to the actual absorbed stomatal ozone dose (e.g. CLRTAP, 2015; Gerosa et al., 2009c; Mills et al., 2011a; Pleijel et al., 2000; Simpson et al., 2007). The flux-based approach accounts for the various meteorological and environmental factors determining the stomatal flux, estimated by utilizing stomatal conductance parameterizations. Within the United Nations Economic Commission for Europe (UNECE) Convention for Long Range Transboundary Air Pollution (CLRTAP), the flux based approach is used to assess potential damage to present and future ecosystems (CLRTAP, 2015). Application of this approach also requires flux-response relationships, determining the actual damage done per absorbed dose. Such flux-based critical levels for different types of vegetation have been developed (e.g. Mills et al., 2011b). There are several modelling tools available and under constant development for estimating ozone fluxes into vegetation, e.g. the DO_3SE model (Emberson et al., 2000) which is also implemented into the The European Monitoring and Evaluation Programme (EMEP) model (D. Simpson et al., 2003; H. Fagerli et al., 2004).

The Weather Research and Forecasting model (WRF) coupled with chemistry (hereafter referred to as WRF-Chem) (Grell et al., 2005), is employed for e.g. forecasting for field campaigns, testing in relation to air pollution abatement strategies, and assimilation of satellite and in-situ chemical measurements, and could possibly prove a versatile and powerful tool for estimating stomatal flux into vegetation and help indicate both present and future high risk areas for ozone damage to vegetation.

The WRF-Chem model is equipped with a dry deposition scheme based on Wesely (1989) (hereafter referred to as the Wesely scheme), in which stomatal conductance for gaseous species is calculated. This is a widely used dry deposition scheme applied in a range of global and regional chemical transport models and climate models for the purpose of estimating dry deposition velocities for a range of chemical species. As the Wesely scheme is a versatile and widely used parameterization, several studies have been focused on validating the dry deposition velocities produced by it (Fowler et al., 2009; Hardacre et al., 2015; Park et al., 2014; Wu et al., 2011). Some limitations to particularly the surface resistance have been highlighted, related to not accounting for water stress through parameterization of vapor pressure deficit or soil moisture deficit (Fowler et al., 2009; Hardacre et al., 2015). The importance of such effects on dry deposition and particularly stomatal conductance has been demonstrated (e.g. Büker et al., 2007; Fowler et al., 2009). Although identified as a potential source of uncertainty in the Wesely dry deposition scheme, the stomatal conductance and hence the stomatal flux estimates, have to our knowledge not been as thoroughly tested.

In this study, we aim to assess whether or not the WRF-Chem modelling system, with the Wesely deposition scheme, has the potential to provide accurate dose estimates based on ozone stomatal fluxes. Although the traditional purpose of the Wesely scheme has not been to estimate stomatal conductance on a species-specific level, a special investigation into this aspect of the parameterization is required as part of the process of assessing the skill of the modelling system in estimating stomatal ozone fluxes into vegetation. As some known sources of uncertainty in the current parameterization of surface fluxes are related to the parameterization of water deficiency, we place special focus on the ability of the current model system to handle meteorological conditions characterized by limited water availability.

Building on the findings of previous studies evaluating the Wesely scheme, we compare modelled fluxes to measurements in three different Mediterranean ecosystems, during spring and summer periods representing different environmental conditions and particularly levels of water deficiency. This will give an indication of the suitability of the modelling system in estimating potentially harmful ozone doses, and more particularly, how the known weaknesses in the current parameterization potentially influence the results. Also, Mediterranean ecosystems are anticipated to be some of the highest risk areas in Europe for ozone induced damage to vegetation because of high emissions of ozone precursors close to the ecosystems combined with favorable climatic conditions for ozone production both at the present and in the future (Cieslik, 2009; Emberson et al., 2013; Gerosa et al., 2009a). The estimation of stomatal flux in high water use efficient (WUE) Mediterranean ecosystems is especially sensitive to water availability in soil and air (Büker et al., 2007; Cieslik, 2009). We also discuss to what degree the current system may be improved, based on these results and on literature.

2. Model and methodology

To validate the WRF-Chem estimates of environmental conditions, ozone concentration and ozone fluxes into various types of vegetation, we compare modelled estimates with measurements gathered during field campaigns executed at three different sites in Italy, representing different vegetation types. The selected measurement periods represent varying water stress regimes as experienced by the measured vegetation.

2.1. Model setup

WRF (Skamarock and Klemp, 2008) is a weather prediction system with a wide variety of applications, across scales ranging from large-eddy to global simulations. In WRF-Chem, a chemistry module is completely embedded in WRF, allowing it to simulate the coupling between chemistry and meteorology. Here, we use the RADM2 chemical mechanism (Middleton et al., 1990; Stockwell et al., 1990), and for the land use data we have applied the standard USGS data provided within the WRF package. A summary of the setup and choices of key physical parameterization schemes and forcing data used in this study is given in Table 1.

The model is run with 40 s time step and output is written every hour for each of the selected measurement periods. In addition, five spin-up days are added ahead of each period. The vertical resolution is 42 layers from the ground to the model top at 50 hPa. The simulations were conducted for two nested domains. The outer domain is run at a resolution of 9 km × 9 km and provides boundary conditions for the inner domains, placed to zoom in on the measurement sites in Italy at a resolution of 3 km × 3 km. The simulation domains are shown in Fig. 1, along with the locations of measurement sites.

The outer domain solutions for the temperature, air moisture and wind are nudged towards the meteorological forcing data with a nudging coefficient of 0.003 s^{-1}. For the meteorological initial and boundary conditions, we use the ECMWF ERA Interim 6 hourly reanalysis. The chemical initial and boundary conditions are gathered from the OsloCTM3 chemical transport model (Søvde et al., 2012), also at a frequency of 6 h. The NMVOC species in the OsloCTM3 model were mapped to the corresponding RADM2 components. For the anthropogenic emissions we use the TNO MACC II (Kuenen et al., 2014) gridded anthropogenic emission database. As demonstrated by Hodnebrog et al. (2011) the resolution of the emission inventory is important in accurate modelling of ozone distribution. Therefore, for the purpose of this study we have been given access to the TNO MACC II high resolution dataset (Denier van der Gon, pers. comm.), covering Europe with a resolution of 1/8° latitude by 1/16° latitude (~7 km × 7 km) (Denier van der Gon et al., 2010a; Denier van der Gon et al., 2010b). The emissions are re-gridded to fit the WRF-Chem grid and distributed in

Table 1
Key features of model setup and input datasets.

Key parameterizations	*Reference*
Land surface	Unified Noah Land Surface Model (Tewari et al., 2004)
Boundary layer	Mellor–Yamada–Janjic Scheme (MYJ) (Janjic, 1994)
Microphysics scheme	Purdue Lin Scheme (Chen and Sun, 2002)
Cumulus scheme	Grell 3D Ensemble Scheme (Grell and Devenyi, 2002)
Chemistry scheme	RADM 2 (Middleton et al., 1990)
Meteorological forcing	ERA Interim data archive (Dee et al., 2011)
Chemical initial and boundary conditions	OsloCTM3 (Søvde et al., 2012) with ECLIPSE anthropogenic emissions (Stohl et al., 2015), GFED biomass burning emissions (Randerson et al., 2013; van der Werf et al., 2006).
Anthropogenic emissions	TNO MACC II high resolution dataset (Kuenen et al., 2014), (HAC Denier van der Gon, pers. comm.)
Biogenic emissions	Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006)

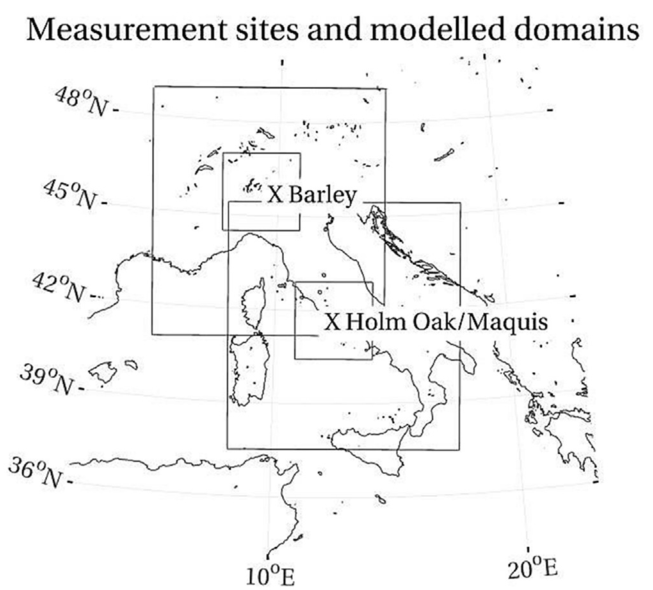

Figure 1. Location of simulation domains and measurement sites. Outer domains have resolution of 9 km × 9 km, and inner domains have a resolution of 3 km × 3 km.

time (according to day of the week and time of day) using the emissions preprocessor WRF-Emiss V3.4.1 (Hodnebrog et al., 2012). More details about the model setup and input datasets are found in the supplementary material.

2.2. Dry deposition model

The dry deposition of gaseous species and aerosols in WRF-Chem is based on the work of Wesely (1989). In the dry deposition scheme, the model's vegetation categories are grouped together to a total of 11 categories, by giving similar categories matching parameter values. The vegetation on the measurement sites was mapped by a well suited vegetation category in the model setup. For the maquis ecosystem however; we changed the vegetation category of the grid cell covering the site of measurements from "deciduous forest" to the "mixed grassland/shrub land" USGS category, for a better fit with observed vegetation at the site. The vegetation categories at the measurements sites and their corresponding Wesely-categories are given in Table 2.

In the Wesely scheme, the deposition process is considered to consist of three main phases, represented by three main resistances (which is the reciprocal of the corresponding conductance); the aerodynamical resistance (r_a), the resistance of the quasilaminar sublayer (r_b), and the bulk surface resistance (r_c), which consists of seven individual resistances, placed in four parallel pathways. The total deposition velocity can be expressed as the reciprocal of the sum of these three, and equal to the flux from the air into the vegetation (F_{O_3}), divided by the ozone concentration at canopy height (C_m) (assuming the concentration inside the soil and vegetation is zero);

$$v_d = (r_a + r_b + r_c)^{-1} = \frac{F_{O_3}}{C_m} \quad (1)$$

The main entry of gaseous species into the leaf through the stomata is parameterized here by the pathway regulated by the stomatal and mesophyll resistances. The mesophyll resistance is considered very low for ozone, it is for simplicity set to zero. The expression for stomatal resistance accounts for the surface temperature and the solar radiation;

$$r_s = r_i\left(1 + \left(200(G + 0.1)^{-1}\right)^2\right)\left(400(T_s(40 - T_s))^{-1}\right) \quad (2)$$

where G is the solar irradiation in W m^{-2}, and T_s is the surface air temperature between 0 and 40 °C. Outside this temperature range the resistance is set to a large value, assuming that the stomatal transfer has stopped. This function will give the highest stomatal conductance in day-lit conditions with temperatures around 20 °C, and completely shut the stomata at night. The parameter r_i is the minimum stomatal resistance which is vegetation type and season dependent. The non-stomatal deposition is regulated by a total of five resistances placed in three parallel pathways, representing the upper and lower canopy and the soil. The canopy resistances are adjusted for wet conditions, and the stomatal and cuticular conductances for separate gases are scaled according to their diffusivity coefficient relative to that of water vapor, reactivity factor relative to ozone, and water solubility relative to that of SO_2. A comprehensive description on the parameterization of the resistances are found in Wesely (1989).

2.2.1. VPD limitation

There are various methods in use to estimate the limiting effect of water stress on stomatal conductance. In the late afternoon air temperature often decreases, and sometimes a decrease in the vapor pressure deficit (VPD) will follow. The afternoon dehydration can in part be accounted for by applying the critical VPD function (CLRTAP, 2015; Pleijel et al., 2007; Uddling et al., 2004a). This function accumulates hourly VPD values during the day, and if the VPD sum exceeds a vegetation type specific critical VPD limit, the re-opening of the stomata in the afternoon is considered unlikely due to plant dehydration, and the conductance is forced to either stay the same as in the previous time step, or decrease.

To illustrate the effect of including such a limitation in the modelled estimates for stomatal conductance based on the accumulated VPD, we applied the critical VPD function during one period for the holm oak forest measured here. Based on the pooled

Table 2
Measurement sites and periods, and corresponding publications.

Vegetation type (Wesely category)	*Measurement site*	*Measurement period*	*Reference*
Barley field *(Agricultural land)*	Bergamo	May 10–22 2002	Gerosa et al. (2004)
Holm oak forest (*Deciduous broadleaved forest*[a])	Castelporziano	Aug. 7–20 2003	Gerosa et al. (2009b)
		Sept. 4–19 2003	Gerosa et al. (2005)
		July 1–14 2004	
		Aug. 1–16 2004	
Maquis ecosystem (*Rangeland*)	Castelporziano	May 15–29 2007	Gerosa et al. (2009a)
		July 13–26 2007	

[a] The Wesely seasonal category for this vegetation category is always summer, effectively making the category evergreen.

data from the total measurement periods from the measurement site, an analysis of the stomatal conductance in relation to the accumulated VPD, was used to obtain the critical VPD value. This was done by locating the limit of accumulated VPD above which the stomatal conductance had a clear tendency to decline, following the same procedure as described in further detail in e.g. Pleijel et al. (2007) (and illustrated in Fig. A4, supplementary material).

2.3. Measurements

In order to assess the skill of the modelling system across different ecosystems, measurements were gathered from three different field campaigns in Italy from three types of common Mediterranean ecosystems. Representative sub-periods from each field campaign were chosen based on availability and quality of data, with the aim to compare the modelled and measured surface and stomatal ozone fluxes in the various vegetation types under varying meteorological and water stress situations. An overview of measurement sites and periods along with corresponding publications is given in Table 2.

Representing the Wesely category of agricultural land, measurements were selected from a field campaign in a barley field in Comun Nuovo, Bergamo, Italy (Gerosa et al., 2004). Barley is regarded a relatively insensitive crop type with respect to ozone damage (CLRTAP, 2015; Mills et al., 2007). The selected sub-period is representative of the barley's anthesis in May. More details about the measurement site and period are found in Gerosa et al. (2004).

To represent evergreen broadleaved forest, measurements from a holm oak forest were used (Gerosa et al., 2009b; Gerosa et al., 2005). Two periods from the measurement campaign during the exceptionally hot and dry summer of 2003 were selected, along with two periods from the summer of 2004, representing more normal meteorological conditions.

Measurements from a typical Mediterranean maquis ecosystem (Gerosa et al., 2009a) were selected to represent the Wesely category of rangeland. The two selected measurement periods in May and July of 2007 represent different meteorological conditions with respect to temperature and water availability. All measurements for both the maquis ecosystem and the holm oak forest were made at the Castelporziano estate, located 20 km outside Rome, along the Latium coast. More information about the measurement sites and measurement and screening methods can be found in the supplementary material. A full analysis of the measurement data, detailed information about measurement site and meteorological conditions during campaigns is found in the publications corresponding to each campaign (Table 2), along with details about the applied eddy covariance method, in depth description of the data screening and the instrumentation used.

3. Results

Focus here is placed on the overall model performance in reproducing environmental conditions at the measurement sites for each selected time period (mainly focusing on the variables most influencing the results, namely the temperature and winds), stomatal concentrations and conductance, and hence the estimated fluxes. Results are largely presented as time-averages of the selected periods, and special emphasis is placed on the mean diurnal variations, as it is illustrative for the average response of the various vegetation types to the varying environmental conditions, and water stress in particular. It is also important in estimating correct doses of stomatal ozone uptake. All modelled results are shown as single cell output from the 3 km $\times$ 3 km grid cell covering the site of measurements. A summary of time averaged values for each measurement period and vegetation type, for ozone concentrations, temperatures and ozone fluxes is presented in Table 3.

3.1. Environmental conditions

In the following is a short description of the results for the modelled versus measured ozone mixing ratios, and a brief description of the key meteorological conditions influencing these results. The mean diurnal variations in canopy height ozone mixing ratios and temperatures for each vegetation category and period are shown in Fig. 2.

The overall performance shows that the model generally underestimates the ozone concentrations by about 5%, and an overall underestimate of temperature of 2%, across all vegetation types and measurement periods. As shown in Fig. 2, the shape of the diurnal pattern of ozone mixing ratios fit reasonably well with the measurements for most time periods (correlation coefficients range within 0.86–0.96). As mentioned, the overall model estimates of ozone mixing ratios show a slight underestimation, and as seen in Fig. 2, this is despite an overestimate of nighttime values in some periods, and resulting from a persistent modelled underestimate of mean midday values in most periods.

For the temperatures, the opposite pattern is recognized, with an overestimation of midday temperatures in most periods, and an underestimation of nighttime values. Thus, the model overestimates the diurnal variance (correlation coefficients range within 0.88–0.99).

The largest problems with the modelled ozone mixing ratios are found in the somewhat extraordinary periods during the summer of 2003 (Fig. 2, top row, middle panel). During the August period, the model underestimated the ozone mixing ratio by on average 16 ppb (mean modelled value is 39 ppb against the measured value of 55 ppb, Table 3). The ozone mixing ratios as simulated by the model are closely linked to the estimated meteorological conditions. The model does capture the high midday temperatures in this period, however it underestimates temperatures outside the midday hours, resulting in an overall underestimation of the mean temperature (Table 3). The winds during the August 2003 period are not well captured by the model, with both overestimated windspeed and for large portions of the period inaccurate wind directions. The modelled wind directions are coherent with the more normal weather conditions dominated by land sea-breeze,

Table 3
Mean (and median) values for modelled and measured results for each vegetation type. F_{tot} represents the total surface flux of ozone, while F_{st} represents the stomatal flux.

		Holm oak Aug 2004	Holm oak July 2004	Holm oak Sep 2003	Holm oak Aug 2003	Maquis July 2007	Maquis July 2007	Maquis May 2007
Mean T (°C)	*Measured*	23.7	22.7	22.7	30.7	24.1	19.4	17.9
	Modelled	24.6	23.0	21.7	27.3	23.9	19.1	17.8
Mean O_3 (ppb)	*Measured*	29.7	47.5	37.9	55.0	43.5	39.2	34.7
	Modelled	40.5	40.6	43.0	39.0	38.9	36.0	34.7
Mean F_{tot} (nmol m^{-2} s^{-1})	*Measured*	6.8	7.7	1.8	2.9	11.2	8.5	7.2
	Modelled	12.8	13.3	12.3	11.1	9.4	9.7	12.1
Mean F_{st} (nmol m^{-2} s^{-1})	*Measured*	12.8	4.7	1.8	1.8	2.8	3.7	3.2
	Modelled	5.2	6.0	4.8	3.1	3.1	3.8	8.4
Median F_{tot} (nmol m^{-2} s^{-1})	*Measured*	5.2	6.7	2.2	3.1	10.5	8.4	2.7
	Modelled	11.9	12.3	9.3	10.8	9.5	8.6	8.2
Median F_{st} (nmol m^{-2} s^{-1})	*Measured*	2.2	3.6	1.1	1.1	2.4	3.4	0.7
	Modelled	1.4	5.3	0.00	0.5	2.7	1.9	2.1

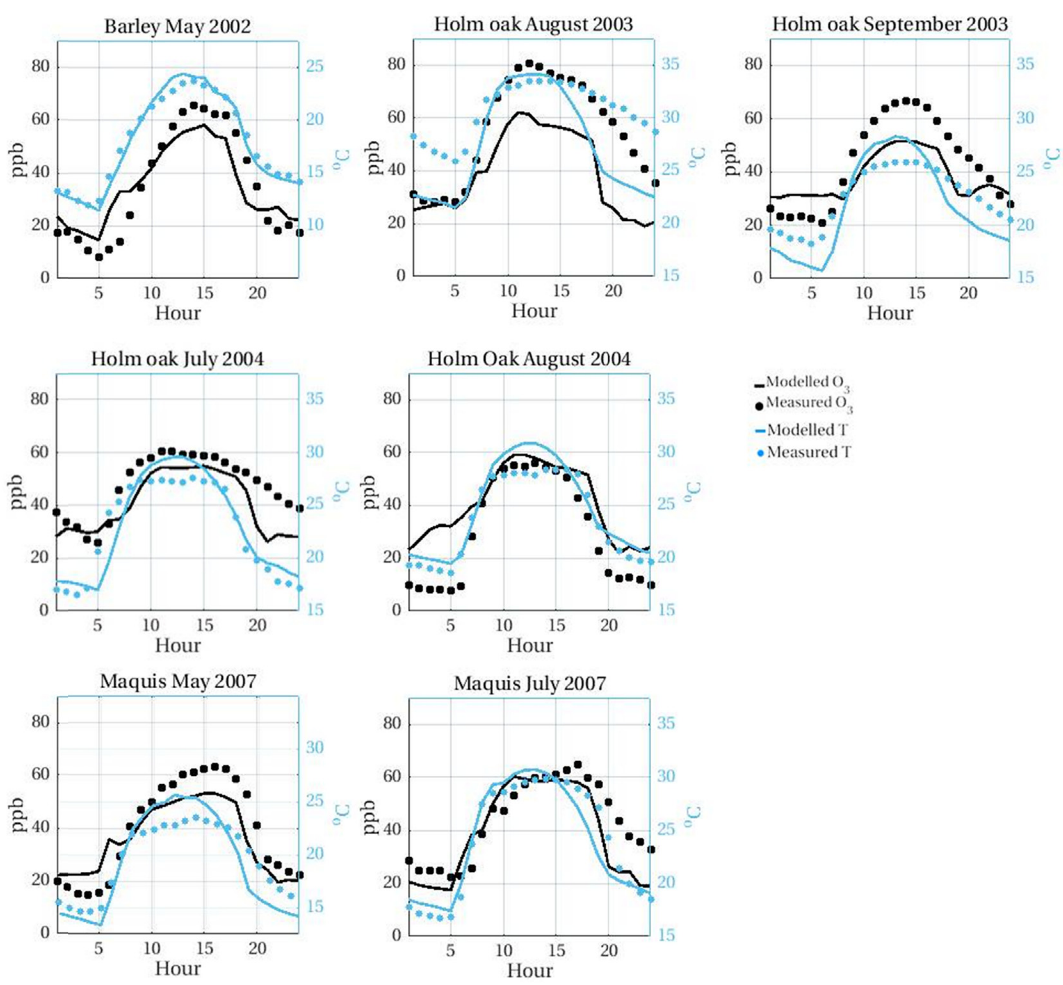

Figure 2. Mean modelled (lines) and measured (dots) diurnal variations in canopy height ozone mixing ratios (black, left axis) and temperature (blue, right axis) for each vegetation type and time period. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

however that is not recorded in the measurements for these two periods (Fig. A1, Supplementary material). This is reflected in the modelled versus measured results for the ozone mixing ratios for most of the measurement periods from this site; in periods where the wind directions were not accurately represented in the model, the mixing ratios are negatively affected. The measured and modelled wind directions are shown in Fig. A1, in the supplementary material, along with a more detailed description of meteorological conditions influencing the results for the ozone mixing ratios for each measurement period.

3.2. Stomatal conductance

The measured versus modelled stomatal conductance for each measurement period and vegetation type is presented in Fig. 3. In the model estimates, zero nighttime values are apparent across all periods and vegetation types. As seen in the Wesely parameterization of stomatal opening (Eq. (2)), the nighttime conductance is zero due to its dependence on solar radiation. According to the measurements, the plants, and particularly the woody types of vegetation, do not completely shut their stomata at night (Fig. 3, all panels, except for Barley May 2002). The modelled stomatal closure during nighttime therefore seems to represent a consistent bias compared to measurements for these ecosystems (time series of stomatal conductance are found in the supplementary material, Fig. A2).

The highest mean measured stomatal conductances are found in the barley field measurements (Table 3). The stomatal conductances for the barley field, represented by the Wesely category "agricultural land" (Fig. 3, top row, left panel), is also the vegetation type with the highest modelled conductances, and the diurnal pattern with the best match between measurements and modelled values (correlation coef. of 0.84), however on average, the daytime values are too high in the model (Table 3).

Due to the high summer time radiation in all periods, the limiting factor in the modelled stomatal day time conductance (besides the minimum resistance) is the temperature function (Eq. (2)). This is apparent in the diurnal patterns in the warm periods. By comparing the values for the maquis May and July periods, with generally higher temperatures during the July period (Table 3), the modelled vegetation response to higher temperatures is reflected through the sharp midday dip in conductance caused by the temperature function. Also for the holm oak forest, the higher the midday (modelled) temperatures, the deeper the midday dip in conductance. This pattern is not recognized in the measured conductances. Although most severe for the exceptionally dry and warm periods from the 2003 summer, all periods show a general modelled overestimation of the stomatal conductance as compared to the measurements, except during the warm midday hours, in which the (excessively) high modelled temperatures cause a sharp dip in conductance. The measured low conductance values in these periods are not limited to midday hours, but rather a more consistent level caused by high temperature and water stress (Gerosa et al., 2009b). The measurements for most of the periods show a pattern of highest conductance in the early morning hours, with a consistent decline towards the afternoon. The modelled diurnal pattern for the woody vegetation thus represents a consistent bias as compared to the measurements.

3.3. Ozone fluxes

The median diurnal variations of total and stomatal ozone fluxes are presented in Fig. 4 (median values are shown as they are more robust towards measurement outliers as compared to the mean). The site-period overall mean ratio of stomatal to total flux is slightly underestimated by the model, with a ratio of 0.43 to the measured 0.47. The warmest measurement period was the August 2003 period, which is also the period with the lowest measured stomatal ozone fluxes.

For the barley field, the average value for the modelled total ozone flux to the surface over the period is overestimated compared to the measured flux (Table 3) on all days except for the days with underestimated ozone values (time series of the fluxes are shown in Fig. A3, supplementary material). This is due to an overestimation of the surface conductance (Fig. 3). It is clear form Fig. 4 that the modelled ratio of stomatal to total flux is too high as compared to the measurements, resulting in a stomatal to total flux ratio of 0.69, compared to the measured value of 0.44. This period represents the largest overestimate of stomatal flux as compared to the measurements.

For the holm oak August 2003 period, the total flux of ozone throughout the period is overestimated by the model as compared

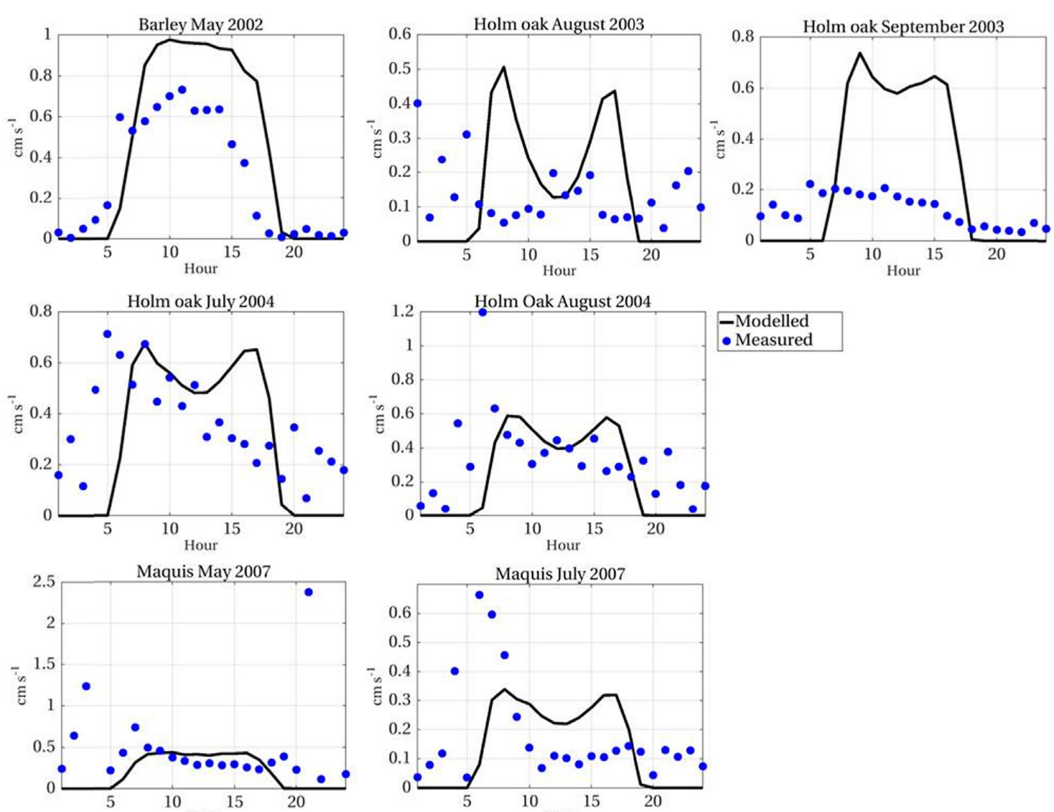

Figure 3. Mean measured (dots) and modelled (lines) stomatal conductance for each period and vegetation type. The figures are based on hourly values for both modelled and measured conductance. Note the differences in scale between panels.

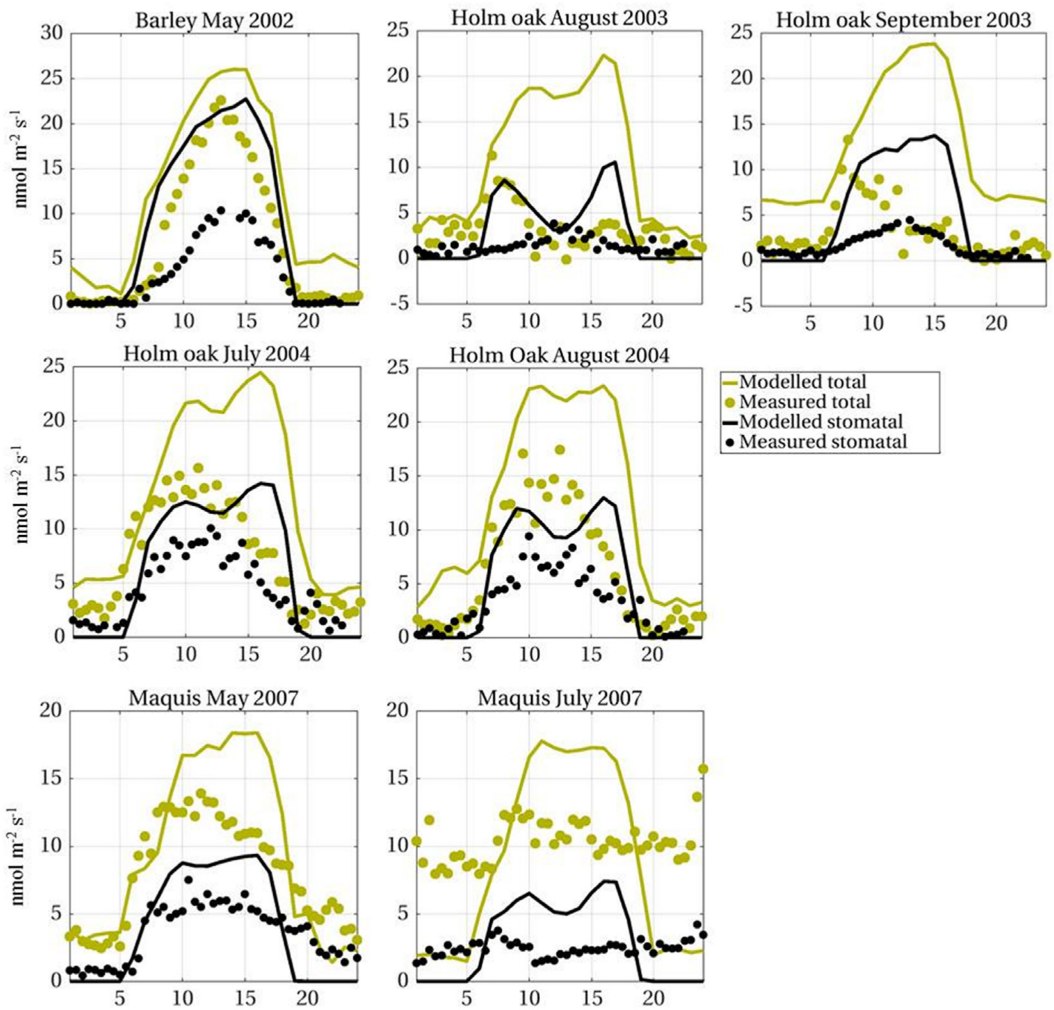

Figure 4. Median daily variations in total (green lines/dots) and stomatal (black lines/dots) measured ozone fluxes (dots) and modelled fluxes (lines) for each selected time period and vegetation type. Note the differences in scale between panels. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to the highly fluctuating measurements, despite the clear underestimation of ozone mixing ratios (Fig. 2).

The measured fluxes are very small throughout, reflecting the exceptionally warm and dry conditions experienced by the vegetation on site (Gerosa et al., 2005), and no particular diurnal pattern is recognizeable. This is not at all reflected in the modelled fluxes, which are all severely overestimated at daytime, except for in the midday hours due to the dip in stomatal conductance, and too low at nighttime. During the September period, the total and stomatal flux is overestimated to an even higher degree, partly enhanced by the fact that the ozone mixing ratios are less underestimated. The average overestimate for the stomatal flux is worse, as lower midday temperatures no longer act to limit stomatal conductance in the midday hours. Nighttime stomatal fluxes are still underestimated.

For the July 2004 period, the results for the stomatal fluxes show improvements compared to the results for the previous year, though stomatal fluxes are still overestimated particularly in the afternoon hours. The higher measured stomatal and total fluxes reflect the increased water availability and less heat stress imposed on the vegetation as compared to the previous year (Gerosa et al., 2009b). The overestimation of the modelled total flux despite the underestimation of ozone mixing ratio for the period reflects a too high surface conductance, both for the stomatal and especially the non-stomatal surface conductance. Nighttime stomatal fluxes are still underestimated by the model. For the August 2004 period (Fig. 3, middle panel) the results for the ozone fluxes follow the pattern seen from the other periods for the holm oak forest, with an overestimation of the total flux, and mismatch in the diurnal pattern of the stomatal flux caused by the midday dip in conductance, in addition to underestimated nighttime stomatal flux.

For the maquis ecosystem during the relatively cooler (Table 3) and moist May 2007 period (bottom, left panel, Fig. 4), the total ozone flux is overestimated on most days. The flux is well represented on days where the ozone mixing ratio is underestimated, which points to the overestimation of surface conductance throughout the period (Fig. 3). Nighttime levels of total fluxes are reasonably well estimated. The average value for the stomatal component of the flux fits well with the measured results (Table 3), however; as seen in Fig. 4 this is resulting from overestimated daytime (particularly afternoon) fluxes, and underestimated nighttime stomatal fluxes. For the warmer (Table 3) and drier 2007 July period, the measured total fluxes of ozone over the period are highly fluctuating and reduced as compared to the May period. The higher measured total flux for this period is reflecting the increased ozone mixing ratio, while the measured stomatal fluxes are influenced by drier conditions at the measurement site, acting to limit the stomatal conductance. The modelled stomatal fluxes are reduced despite the fact that the modelled ozone mixing ratios are increased compared to the May period, reflecting the lowered stomatal conductance caused by (excessively) high modelled temperatures (Fig. 3).

3.4. Critical VPD function

As seen in the modelled results for the stomatal conductances (Fig. 3), the afternoon drop in temperature will, according to the temperature limiting function, result in an increase in modelled stomatal conductance in the afternoon. As compared to the measurements, this causes a persistent overestimation by the Wesely scheme of particularly afternoon conductance during dry and warm periods. In our results, the most pronounced overestimation of afternoon conductances are found in the holm oak and maquis ecosystems, as they are measured in especially warm and dry periods. To illustrate the effect of including a limitation in the modelled estimates for stomatal conductance, we applied the critical VPD function during one period for the holm oak forest. As the 2003 summer periods both represent abnormal meteorological and chemical conditions, the 2004 summer period was chosen for this experiment as it is more representative of model performance under normal conditions. The analysis of the measured data resulted in a critical value of 20 kPa h for the holm oak forest (see Fig. A4, supplementary material). The accumulated VPD was based on hourly accumulated values over the sun lit hours only. For the rest of the grid, the same value was applied to similar vegetation categories, a somewhat arbitrary value of 12 kPa applied to mixed grassland/ shrub land and the value of 10 kPa h was applied to agricultural land, while dry deposition rates in non-vegetated land categories was not limited by this function. As seen in Fig. 5 the reduced afternoon peak in stomatal conductance during this period does lead to an improvement in the pattern of diurnal variation, as compared to the measurements. However; the conductance is not sufficiently limited by the application of the VPD function to match the measured values.

These changes in surface fluxes are not substantial enough to influence the mean ambient air ozone values to any significant degree. For the July 2004 period, the mean modelled ozone with VPD limitation to the stomatal conductance and uptake, stays nearly the same at 41 ppb, and is reduced by 0.4% for the domain as a total over the period.

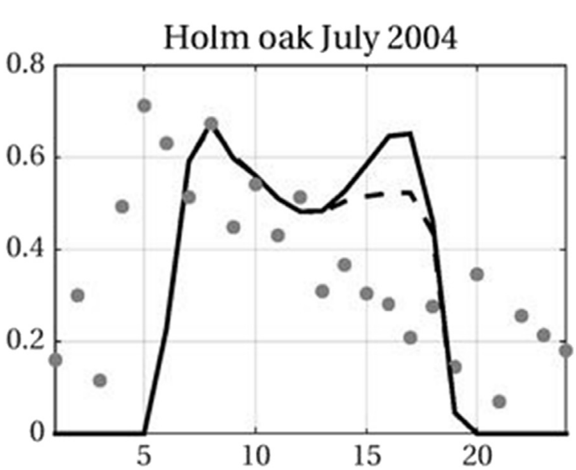

Figure 5. Mean diurnal modelled (lines) and measured (dots) stomatal conductance (cm s^{-1}) for the July 2004 Holm oak forests. Stippled line indicate modelled values limited by the accumulated VPD function.

4. Discussion

As demonstrated by the above results, the performance of the WRF-Chem system with the Wesely dry deposition scheme varies across vegetation categories and meteorological conditions. The WRF-Chem system generally underestimated both the ozone mixing ratios (by 5%) and temperatures (by 2%) as averaged across all measurement periods, although the latter is overestimated during the midday hours in several periods. Both of these variables are sensitive to wind direction. The two measurement sites in Castelporziano (holm oak and maquis) are particularly sensitive due to the placement close to both the coastline and to major cities with emission sources (Fig. 1). The chemical and meteorological conditions are alternating between marine air masses with high ozone concentrations, and plumes of low ozone concentrations caused by chemical reactions in the nearby city areas with very high anthropogenic emissions (Gerosa et al., 2009a; Gerosa et al., 2005), resulting in NOx titration. Although a further examination is beyond the scope of this study, we notice that the wind speed has also been found to influence ozone surface fluxes through its influence on the aerodynamical resistance (e.g. Zona et al., 2014).

The most severe underestimation of ozone mixing ratios occurs under the August 2003 period, for holm oak forest. The European heatwaves of the summer 2003 contributed to unusually high ozone values across central and south Europe, as documented by several studies (Fischer et al., 2007; Gerosa et al., 2009b; Hodnebrog et al., 2011; Vautard et al., 2005; Vieno et al., 2010; Zaitchik et al., 2006). Measurements from this extraordinary period were included to represent extreme conditions under which to test the model performance. The model did reflect the severe conditions by estimating the highest temperatures and lowest conductance and fluxes of all periods (Table 3). However; it severely underestimated the high ozone mixing ratios found in the measurements. The ozone levels were heavily influenced by the fail to reproduce wind speeds and direction during the same period (Fig. A1, supplementary material). The ozone values are also influenced by the chemical boundary conditions (Schurmann et al., 2009) on account of the limited size of the modelling domain. The chemical boundary conditions in this study were given by the Oslo CTM 3 chemical transport model (Table 1, and supplementary material) and this model did not fully capture the extraordinarily high surface ozone values observed for this particular period, partly on account of the coarse resolution. This also contributes to explain why the model underestimates the midday values for these periods, in addition to the inaccurately modelled meteorological conditions. Also, part of the overestimation of ozone nighttime values for some periods might be explained by the coastal placement of the measurement site, which especially during nighttime might be influenced by marine air masses with higher ozone mixing ratios, as examined by e.g. Pleijel et al. (2013).

For the woody vegetation, there is a mismatch in diurnal pattern for the stomatal conductance for all periods, which is caused partly by the temperature response function. A pronounced midday dip is seen in particularly the warm and dry periods, partly enhanced by overestimated midday temperatures. This pattern points to low optimal temperature for particularly the woody vegetation (maquis and holm oak forest). As a generic optimal temperature for Mediterranean woody species, a temperature of 23°C has been suggested (CLRTAP, 2015), which is higher than the current optimal temperature in the Wesely response function for temperature, at 20 °C. In the Wesely scheme, the same optimal temperature is used across all vegetation types. This study is based on only three vegetation categories. Based on these results, it is likely that an optimal temperature dependent on vegetation category would improve the diurnal pattern of stomatal conductance for these vegetation types.

The modelled diurnal pattern for the stomatal conductance was better in the barley field, as compared to the woody ecosystems. However; the overall stomatal conductance level was too high, particularly in the daytime, causing an overestimated stomatal flux of ozone. As the vegetation did not experience any particular water or heat stress during this measurement period (Gerosa et al., 2004), this overestimate suggests an underestimate of the minimum stomatal resistance in the model for this vegetation type.

Compared to the CLRTAP (2015) suggestion for the generic crop value for Mediterranean areas, which is 95 s m^{-1}, the corresponding Wesely scheme minimum value for this season and the broad category of “Agricultural land”, is significantly lower at 60 s m^{-1}. The CLRTAP (2015) value is based on extensive data for wheat, and as such should be more representative for barley. Our results suggest that the Wesely scheme's value for “Agricultural land” is too low for this particular crop.

However; both of these values for minimum stomatal resistance are chosen to represent very broad vegetation categories, and can as such not be expected to perfectly represent a single crop species such as barley. Although beyond the scope of this study, a more thorough review including various types of crops are necessary before any conclusions about the suitability of the value chosen to represent the broad category of “Agricultural land” in the Wesely scheme can be made. Based on our results for the other vegetation categories tested here, no conclusions can be made regarding their minimum stomatal resistance value, however; it should be noted that Wu et al. (2011) concluded that there were large uncertainties associated with the minimum stomatal resistance values applied in the Wesely scheme in WRF-Chem.

The total surface flux is overestimated for all the vegetation types and all time periods, despite underestimated midday ozone concentrations in most periods. The overestimations are higher in dry and warm periods, suggesting a particular bias in the surface conductance in these periods, thereby supporting the findings of previous studies (Hardacre et al., 2015; Vautard et al., 2005). One exception is nighttime fluxes for the maquis ecosystem, during which the surface flux is severely underestimated, in the dry July 2007 period. For the stomatal fluxes on the other hand, the causes for biases in the modelled fluxes seem to vary between vegetation types.

For the maquis and particularly the holm oak ecosystems, the zero nighttime stomatal flux seen in the model results, seems to fail to recognize the vegetation's ability to open their stomata during the nighttime. The measurements do indicate that nighttime values for conductance are not zero. Mereu et al. (2009) found that nighttime stomatal uptake of ozone was substantial in Mediterranean woody species, especially in drought situations. The parameterization of zero stomatal conductance during nighttime is inaccurate for most plants (Caird et al., 2007). The underestimation of modelled nighttime stomatal ozone uptake could enhance underestimation of night time deposition rates, and thus too high modelled estimates of ozone concentration in the stable nighttime planetary boundary layer as found by Wu et al. (2011).

For the barley field on the other hand, the total surface flux is only slightly overestimated while the stomatal flux is heavily overestimated. The meteorological variables for the period do not represent any particular biases, and the ozone levels are underestimated. As such, the overestimated stomatal fluxes points to the aforementioned uncertainties related to the value used for the minimum stomatal resistance for the ‘Agricultural land’ vegetation category used in the Wesely scheme.

A second and expected bias in the parameterization is the lack of an explicit limitation of conductance dependent on plants water availability. As plants will optimize their WUE by limiting water loss through the stomata if dehydrated, the water availability naturally plays a crucial role in determining the stomatal conductance, especially in dry and arid areas with high WUE vegetation, such as the Mediterranean (Büker et al., 2012; Gerosa et al., 2009b). In drought and water stress situations, while the vegetation closes the stomata to prevent water loss, they are preventing ozone from entering the plant and thus lowering the risk of ozone-induced damage. Therefore, models used in estimating potential risk of ozone induced damage to Mediterranean ecosystems may be particularly sensitive to such parameterizations (e.g. CLRTAP, 2015; Gerosa et al., 2009a; Gerosa et al., 2004). Such dependencies are included in most stomatal conductance parametrizations (Damour et al., 2010), however; in the Wesely scheme, the water status of plants is only taken into account in an indirect way through dependence on vegetation type and season (Wesely, 1989).

For the dry periods, both for the maquis ecosystem and the holm oak forest, the overestimation of stomatal fluxes during daytime is more severe than in wetter conditions, and particularly during the afternoon. In the modelled results, the conductance recovers from the temperature-induced midday dip, while in the measurements, the highest conductance is seen in the early morning hours, and then steadily decreases towards the evening. This behavior is explained by the accumulated water deficiency experienced by the plants during the day (Gerosa et al., 2009a; Gerosa et al., 2005). As explained in Gerosa et al. (2009a), the lowered stomatal conductance in maquis ecosystem in the July 2007 period as compared to the wetter May period, is caused by the increased water deficiency, which is also confirmed by sap-flow measurements preformed on site by Mereu et al. (2009). Similarly, by comparing the stomatal flux measurements during the summers of 2004 versus the exceptionally dry and warm 2003 summer, Gerosa et al. (2009b) conclude that the main environmental factor limiting the stomatal flux in this vegetation is the water supply, and that prolonged periods of drought severely impacts the stomatal flux and ozone uptake, even up to two months after the water supply has been replenished. The lack of such dependencies in the modelled conductance results in overestimation of daytime (especially afternoon) conductance in dry and warm periods, with high midday ozone concentrations and cause overestimations of ozone uptake and deposition rates.

Similar problems were also documented by Fares et al. (2013), who experienced overestimation of afternoon conductance estimates, using both the Jarvis and Ball-Berry conductance algorithms to calculate stomatal conductance in Castelporziano, Italy. They found discrepancies between modelled and estimated conductances especially during warm days and reduced correlation between observed and calculated conductances due to modelled recovery of midday depression in conductance, not recognized in observations. Also, Turnipseed et al. (2009) found VPD to be one of the main environmental drivers controlling stomatal conductance in their measurements. Other studies have also confirmed that closing the stomata in the afternoon in order to preserve water is common in high water use efficient vegetation, and suggested improvements by taking into account the VPD on stomatal conductance calculations parameterizations (Pleijel et al., 2007; Uddling et al., 2004b). Our results show that implementing a VPD-dependent limitation on the afternoon conductance improves the diurnal variation of the ozone flux, however it did not sufficiently limit the flux to reproduce the measured fluxes in dry and warm periods. Also, it had little effect on the ambient ozone mixing ratios. Similarly, using the CHIMERE chemistry-transport model Vautard et al. (2005) found overestimation of the Wesely scheme surface conductance while simulating ozone concentrations during the 2003 European summer drought, yielding too high deposition rates and underestimated ozone concentrations. They found that they had to double the bulk surface resistance to ozone uptake to improve simulated ozone concentrations as compared to observations.

The long-time effect of prolonged water deficiency, which dominated the measured fluxes for particularly the 2003 September period (Gerosa et al., 2009b; Gerosa et al., 2005), is not captured in the modelled results, either. Alonso et al. (2008) demonstrated that including a soil water potential limiting function in the DO_3SE model parameterization of stomatal flux in a holm oak forest greatly improved the estimates for dry and warm periods. The soil type plays a crucial role in determining soil properties and resulting estimates of soil moisture, the mapping of such is a major concern in modelling soil water limitations to the stomatal conductance. As demonstrated by Büker et al. (2012), a good representation of soil properties in the model is necessary in order to improve the results, rather than increasing uncertainty in estimates. As the low fluxes in the measurements are explained by the lack of water available to the vegetation over the dry and warm periods (Gerosa et al., 2009a, 2009b, 2005), it is likely that the modelled overestimation of total and stomatal fluxes would be improved by adding a water dependency in the stomatal conductance parameterization. Although the implementation of a soil moisture deficit dependent function to limit the stomatal conductance has obvious potential to improve these modelled results, it requires further investigation into these complex aspects of the model performance.

5. Conclusions

Here, we assess the skill of the WRF-Chem modelling system in estimating stomatal fluxes of ozone into vegetation, using the widely known Wesely dry deposition scheme. Based on previous studies evaluating the dry deposition velocities estimated by the Wesely scheme, we have put special emphasis on known issues related to the lack of a water stress parameterization, and assessed the potential effect of this on the stomatal flux estimates. Measurements from different sites in Italy representing various meteorological conditions have been chosen in order to test the model's performance with regard to particularly variations in water availability.

We find that the WRF-Chem model struggles to capture wind speeds and directions in some periods, which in turn affects temperatures and ozone mixing ratios particularly at coastal locations and sites close to major emission sources. Both of these variables influence the modelled results for the stomatal conductance and contribute to biases in the stomatal flux estimates.

Some systematic biases in the model parameterization of stomatal ozone fluxes are discovered. Compared to measurements, the parameterized assumption of zero nighttime conductances due to lack of sunlight seems to be inaccurate in particularly the woody ecosystems. Also, the temperature response function applied for all vegetation types in the Wesely parametrization applies an optimal temperature is likely too low for the woody species tested here, which results in discrepancies in the diurnal pattern of the stomatal conductance during warm periods. The adverse effect is enhanced by overestimated midday temperatures by the modelling system.

Comparing with the measurements, the minimum stomatal resistance for the crop vegetation category is too low in the case of the barley field. However; our results for the barley field are insufficient in order to establish whether the general crop value chosen to represent the category of "agricultural land" in the Wesely scheme should be revised.

The model fails to reproduce the lowered stomatal conductance in dry periods found in measurements, causing a more severe modelled overestimation of daytime stomatal fluxes in dry periods. This results from the lack of explicitly taking into account water availability in estimating stomatal conductance. In this study we find that including a dependence on the evaporative power of the atmosphere on conductance improves modelled conductance estimates for dry and warm periods, although it is not sufficient in limiting the conductance for long-term dry conditions. Based on literature, the water availability through soil moisture would likely improve model accuracy, provided the soil type and properties are accurately resolved.

The limited environmental conditions accounted for in the Wesely conductance calculations do cause specific and substantial biases compared to measurements. We found that estimating ozone doses and subsequent damage to vegetation using WRF-Chem and the Wesely deposition scheme, requires some improvements to the current parameterization for the stomatal conductance and a revision of the current parameter values for minimum stomatal resistance. These improvements would not only yield more accurate stomatal flux estimates, but also improve dry deposition rates and hence estimated mixing ratios of ozone (and potentially other gases) in the near surface atmosphere.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.08.057.

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