Dear Editor,

We are pleased to resubmit the revised version of our manuscript “No impact of tropospheric ozone on the gross primary productivity of a Belgian pine forest”. We have addressed each of the concerns of both referees as outlined below.

Referee #2

The referee’s comment: 1. I think that the ultimate sentence about ozone implication in altering the NPP/GPP ratio (lines 410-415) needs to further work to be well ascertained.

The authors’ answer:

We agree with the referee that further research is needed to investigate the effect of O_3 on growth, NPP, NPP/GPP ratios and other processes in the Scots pine stand. We have slightly reformulated the last paragraph.

The referee’s comment: 2. Some minor comments:
- Paragraph 2.2.4 Gross Primary Production (lines 131-132). Authors wrote “Gross primary productivity was derived by subtracting the modelled total (autotrophic and heterotrophic) ecosystem respiration from the measured NEE”. I think that:

NEE = NPP-Rh = GPP-(Ra + Rh) = GPP-Reco

thus GPP = NEE + Reco

where NEE: net ecosystem exchange (measured), NPP: Net Primary Production, Ra: Autotrophic respiration; Rh: Heterotrophic respiration, Reco: ecosystem respiration (total respiration).

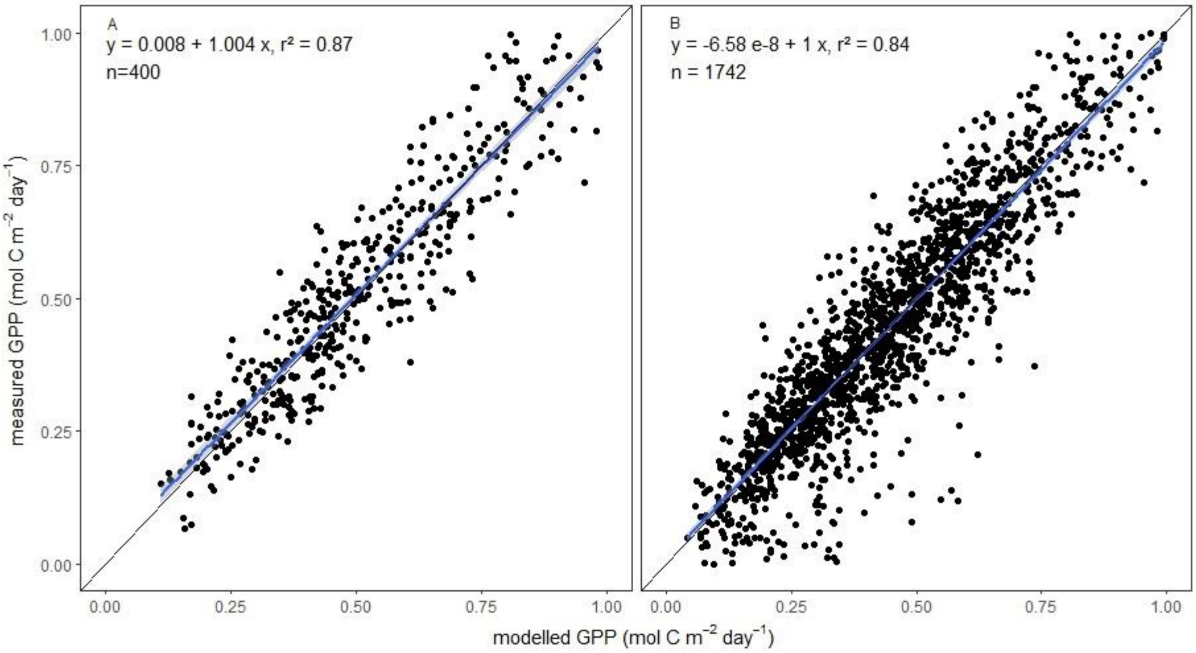
The authors’ response:

In this study GPP was always positive, and we made thus use of the convention stating that a downward flux is a positive flux. Therefore, we agree with the referee that GPP = NEE + Reco. We adapted this in the manuscript (Appendix A).

- Figure 7. Please, check regression equation of data concerning the panel (A): intercept is set at 7779 whereas in panel (B) is set at -0.0658 with similar angular coefficients (slopes) and determination coefficients.

The authors’ response:

The regression equations on both panels are correct. We adapted the scale of this figure in accordance with figure 8 and added this new figure to the manuscript.



- Please check all corresponded references between text and bibliographic list.

The authors' response:

We thank the referee for this remark. Due to a problem with endnote, some references did not show up in the reference list or were misspelled. We solved this problem.

Referee #5

The referee's comment: 1. GPP is the key parameter of this paper and should be introduced in more detail. Why did the authors choose GPP as the effect parameter, how is it linked to tree/forest growth, timber production, C sequestration etc.? Why is the effect of ozone on GPP of (ecological/economic) interest? Is there evidence in the literature that ozone affects (tree) GPP?

The authors' response:

The study of O_3 effects on GPP is relevant because GPP represents the first step in the process of C assimilation and with GPP we quantify the rate at which C substrate is provided for growth, wood production, et cetera. There is evidence in literature that O_3 affects GPP. Fares et al. (2013) investigated the effect of O_3 on C assimilation in trees. They found that O_3 has a direct negative effect on C assimilation by plants, and that this negative effect of O_3 on GPP mainly occurred within a day of exposure/uptake.

The referee's comment: 2. Due to the importance of GPP in this study, the measurement of NEE in this forest stand and the derivation of GPP from measured NEE have to be described in much more detail, at least in the appendix (the sentence "…(NEE) measured with the eddy covariance technique with the instrumentation and following the standard data quality procedures as explained in (Carrara et al., 2003;Carrara et al., 2004;Gielen et al., 2013)." is not sufficient and too vague (e.g., which instrumentation?)). Also, for which time period was NEE measured/GPP derived? For the entire growing season of all 14 years? If so, why don't the authors show in the results section scatterplots of GPP (as derived from measured NEE) against Fst or POD1?

The authors' response:

We have added a more detailed description of the NEE measurements and the GPP derivation in an Appendix (Appendix A).

Measurements of NEE started in 1998 (and thus GPP derived). Data from 1999 and 2003 were removed from the dataset due to poor data quality or coverage. It is now clearly mentioned in paragraph 2.2.4 for what period GPP values were derived and integrated.

The figure below (Figure 1) on the left shows the scatter plots of measured growing season GPP versus F_{st}, AOT40 and POD1. We have considered including these scatter plots in an earlier version of the manuscript, but found it more relevant to show GPP residuals. We think that plotting GPP versus O_3 doses is not very meaningful, because GPP variation between growing seasons is determined more by climatic variability or LAI variability than by O_3 loads. If the referee deems it necessary, we are nevertheless willing to include the scatter plots in the manuscript, e.g. as part of Figure 9.

Remark: The scatter plots show a negative relationship between GPP and O_3 dose, most notably between GPP and F_{st} (upper panel). These trends suggest a strong effect of O_3 on GPP - in the upper panel in the lower range of F_{st} (but then strangely no further effect at higher F_{st} values). The figure below on the right shows the time series of GPP and AOT40. On these time series it can be seen that there is a period of steadily increasing GPP, from 2006 until 2013, which happens to coincide with a decreasing trend of O_3 concentrations (AOT40). The increasing GPP involves forest recovery from acidification (Neirynck et al., 2008). The negative relation between GPP and O_3 dose for this period might wrongly be interpreted as an O_3 effect.

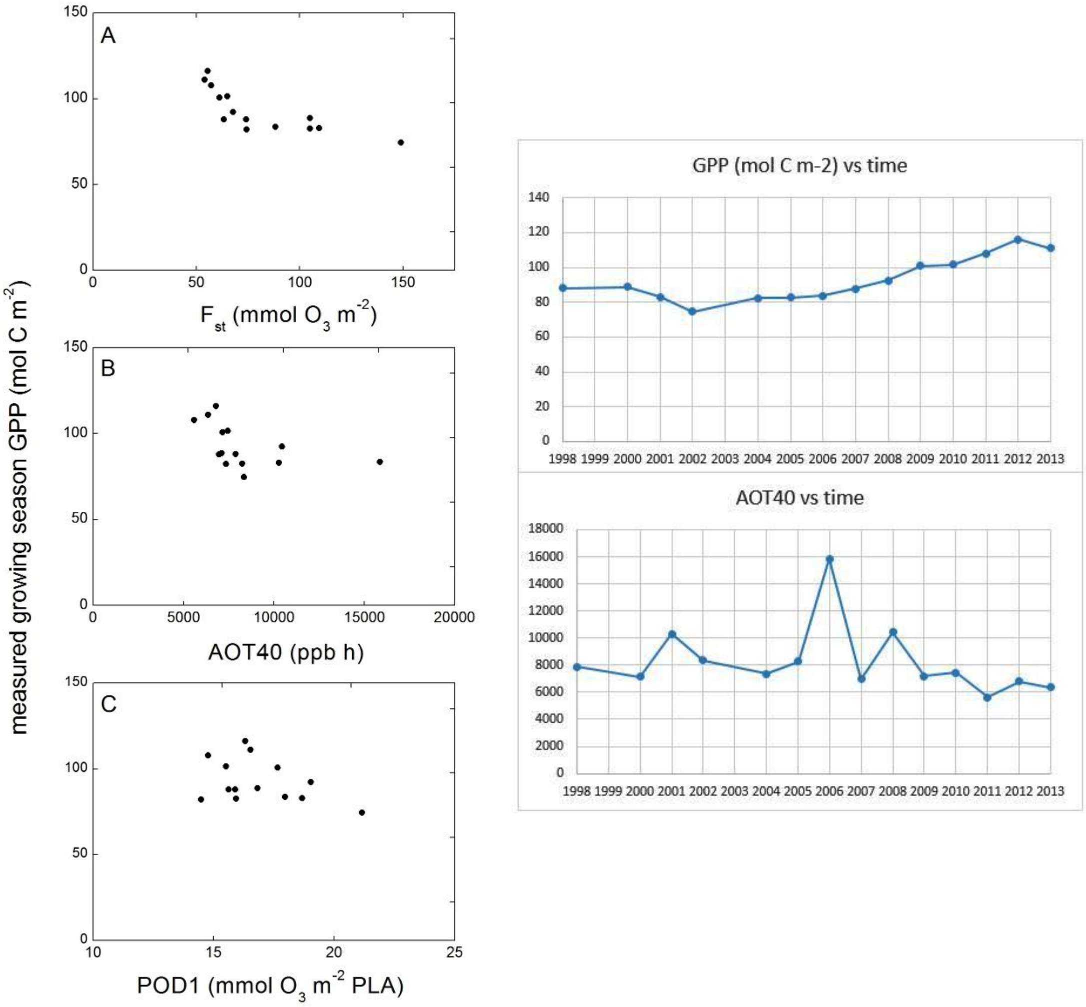


Figure 1. (left) The measured growing season GPP in function of Fst, AOT40 and POD1, (right) GPP and AOT40 in function of the years of the measuring period of this study.

The referee's comment: 3. For the derivation of LAImax across all years, measurements were also taken from the year 2003 (weather-wise an extreme year that unfortunately had to be excluded from this study – it would have been very interesting to see if it had created an outlier in figures 8 (E,F) and 9): How sure are the authors that this 2003 measurement was representative, given that European forests suffered immensely during that year from heat and drought, which might have had an effect on LAI?

The authors' response:

The LAImax of 2013 was 1.67 m² m^{-2}, which is higher than the other years after the thinning. We assume this value was representative because the dry period in 2003 reached its peak in August, after the seasonal LAI maximum had been reached and was measured (half July). The interannual variability after the thinning in 1999 was rather small, thus LAI is no big driver in stomatal uptake differences between years.

The referee's comment: 4. It would have been interesting to do a year-to-year comparison of ozone effects on GPP to analyse whether the timing/onset/length of ozone episodes (e.g. late/mid/end of season) had any effect on GPP; the authors could for example add the year to data points in Fig. 9 and relate outlier years in these figures to ozone concentration anomalies in these years?

The authors' response:

In the first version of this manuscript we included a figure showing the GPP residuals of the growing season against Fst, POD1 and AOT40 for the different years (Figure 2). We replaced this figure by Figure 9 in our manuscript to improve the readability, as the initial figure with different colours for each year did not gave any extra information and could confuse readers.

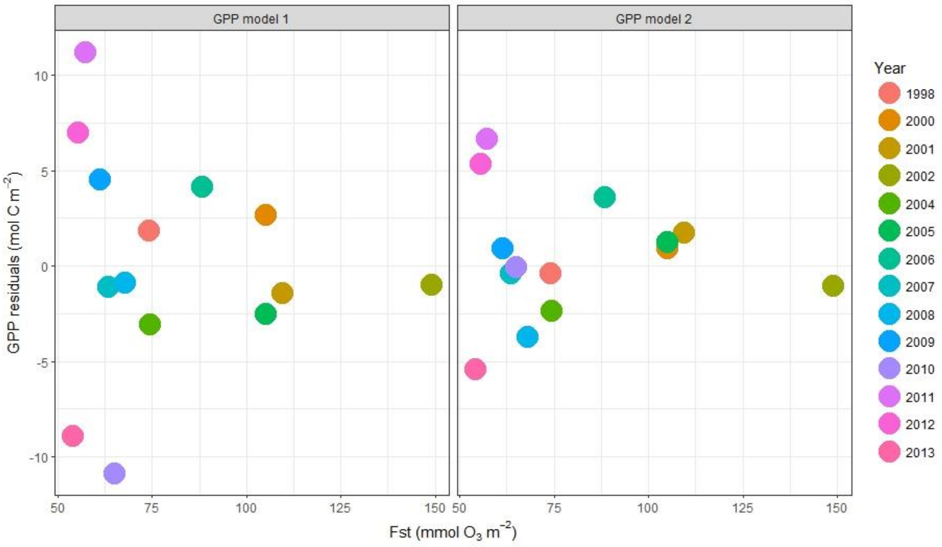


Figure 2. GPP residuals in relation to the stomatal O_3 uptake (Fst). The different colours represent the different years over the study periods.

Here we show the total stomatal O_3 uptake for each week for the positive anomaly, neutral and negative anomaly in Figure 9 of the manuscript (Figure 3). The highest positive anomaly in GPP residuals was reached in 2011 and 2012, whereas the most negative anomaly was in 2010 and 2013. In 1998, 2004, 2007, 2008 and 2009 the Fst values are comparable to 2010-2013, but no anomaly was found. In 2002 the GPP residuals are close to zero, but a high Fst was reached. In the weekly Fst data we don't see any clear differences between the four panels.

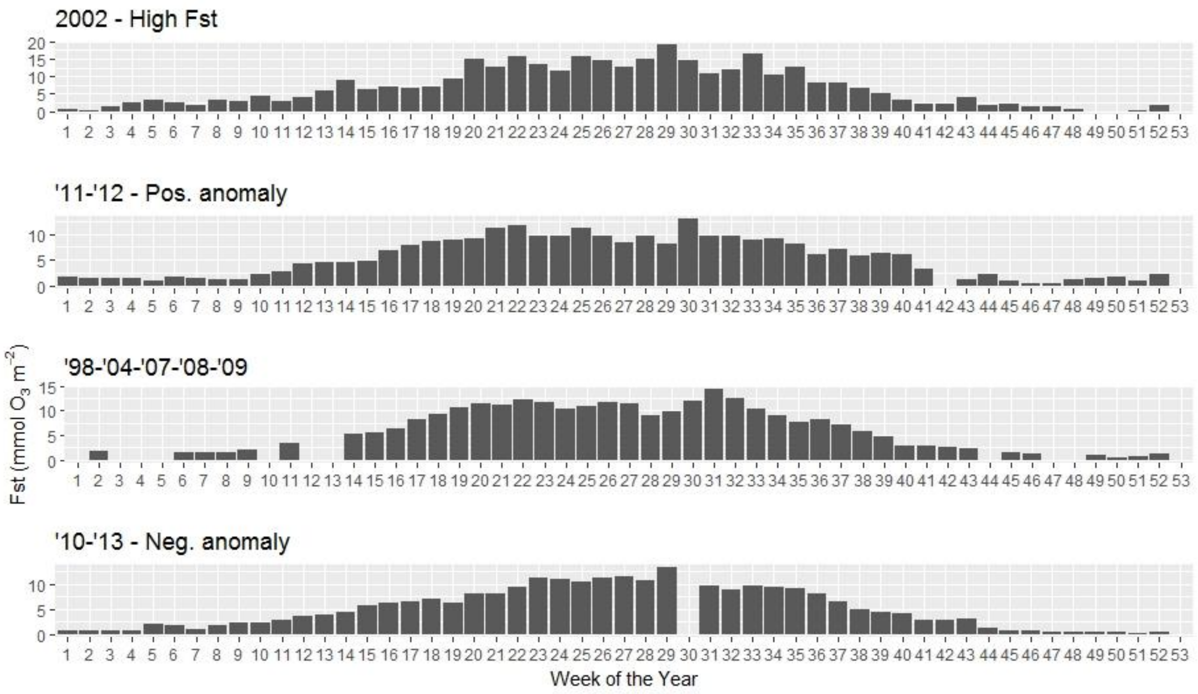


Figure 3. The stomatal O_3 uptake (Fst) for each year, for 2002 (no anomaly in Fig. 9 of the manuscript, but reaching high Fst values), 2011-2012 (positive anomaly in Fig. 9), 1998-2004-2007-2008-2009 (no anomaly in Fig. 9), 2010-2013 (negative anomaly in Fig. 9).

The referee's comment: 5. The description of the used ANN is very short, please add detail how the final model was derived. Is there any particular reason why the authors used ANNs for the analysis (could the authors maybe justify with reference to other biological studies that also used ANNs?)? One main strength of ANNs is their power to disentangle strong and weak input-output relationships, so one would have expected to at least see a ranking of parameters that define GPP. For ANN model runs with the full dataset (i.e. no exclusion of high ozone GPP days), the authors should have also included ozone as input to see whether it has any explanatory power on GPP.

The authors' response:

ANN's are a power tool to process multidimensional data in which complex nonlinear interrelationships between the parameters can be expected. In this manuscript we don't know the exact relationships between the meteorological parameters and GPP. It would lead us too far to determine these exact relations and the ANN offers us a great tool to overcome this problem. ANN's are used in terrestrial and aquatic ecosystems, remote sensing and evolutionary ecology (Lek and Guegan, 1999; Akhand et al., 2016; Liu et al., 2016), and specifically to model GPP (Rochelle-Newall et al., 2007).

We ranked all the input parameters of our model by replacing each input variable with a random permutation of its values (Table 1; Table 3 in the manuscript). Global radiation (Rg) contributed most to GPP, followed by year and day of year. Soil water content (SWC) contributed the least.

When we included O_3 as input variable to this model and calculated its contribution to GPP by ranking the parameters, O_3 has the lowest MSE. We concluded that O_3 does not contribute to the prediction of GPP in our model.

This information was added in the manuscript at the appropriate text locations in Introduction, in M&M paragraph 2.5 Detecting O_3 effects on GPP), the Results in paragraph 3.3 Ozone effects on GPP, and in Discussion in paragraph 4.3 Ozone effects on GPP.

Table 1. Ranking of the parameters that define GPP in the ANN by replacing each input variable with a random permutation of its values. (A) The parameters with their mean squared error (MSE, mol m^{-2} day^{-1}) for the model without O_3 (B) The parameters with their MSE for the model with O_3. The overall model MSE without any random permutation is also shown.

Ranking Nr.	**A**	**B**
1	Rg – 37500.81	Rg – 41358.93
2	doy – 30240.61	year – 33978.09
3	year – 27486.63	doy – 31127.90
4	VPD – 15380.68	Tsoil – 24893.78
5	Tmax – 15323.22	Tmax – 23567.45
6	Tsoil – 15076.75	Tmean - 21354.76
7	Tmean – 13858.91	VPD – 16395.14
8	WV – 13369.01	Tmin – 15418.16
9	Tmin – 12732.96	WV – 14685.97
10	SWC – 12402.04	SWC – 12831.19
11		O_3 – 11885.73
Overall model MSE	11360.85	10019.30

The referee's comment: 6. Line 204f.: "Under the assumption that O3-induced 205 GPP reduction is most likely to occur during and shortly after days of high stomatal O3 fluxes, ..", Line 239ff. "now not only excluding the days with the highest stomatal O3 fluxes from the dataset for model training but also the two following days." And Line 255f. "we excluded the days with a peak of stomatal O3 flux plus the six following days". The reasoning behind these timeframes is rather vague and these are big assumptions that need scientific discussion: Is there experimental/statistical evidence that high ozone episodes only have an effect on GPP for up to two days after the episode? Why exactly six days to look at carry-over effects? Surely timing will depend on the intensity and length of the ozone episode? How do the authors distinguish between "high" and low ozone episode? Where did they draw the line (please show how many high and low ozone episodes there were in each year)? The authors call the latter episodes "supposedly O3-damage free", which is a very bold statement. This is one of the weakest point of the methodology that should be thoroughly addressed in the revision!

The authors' response:

Firstly, we have added a few lines in paragraph 2.5 to explain the physiological mechanism on which our assumption is based: above a certain O_3 load, the tree's defensive mechanisms cannot scavenge all O_3 entering the needles and damage to the photosynthetic apparatus occurs. This leads to decreased gross photosynthetic rates and GPP. The damage is repaired afterwards when the O_3 load decreases.

Because we lack information on the defensive capacity of the trees and on the rate at which trees are able to repair O_3 damage to the photosynthetic apparatus, we performed and repeated our analysis (1) with three different peak percentages of fluxes to define the days at which an O_3 effect might occur and (2) with three different delay-periods after a peak flux that an O_3 effect can sustain. The latter was not mentioned in the manuscript, but we have done the tests with a 1-day, 2-day and 6-day delay period. Because the outcome of the analysis was similar amongst the three delay periods, only the results for the 2-day period are shown in the manuscript. We are willing to show the other results to the referee if he acts this to be necessary.

The three peak percentages and the three delay-periods have both been selected rather arbitrarily as a sample from a whole range of thresholds and delay-period lengths that could have been tested in the rather empirical approach we apply in this study to identify days with and without O_3-affected GPP.

To respond to the last part of the referee's comment: we made a distinction between high and low O_3 episode applying a stomatal O_3 flux treshold of 0.18 mmol O_3 m^{-2} day^{-1}. This is a 10 % cut-off. To make an O_3-damage free GPP model this cut-off value was the maximum value we tested for the days on which we expected a possible O_3 effect. In the table below we show per year the amounts of days which were above this value.

Table 2. The amount of days which have an Fst value > 0.18 mmol m^{-2} day^{-1} shown per year. These were considered as 'high O_3 episode'.

Year	Amount of days with high Fst
1998	41
2000	13
2001	31
2002	51
2004	15
2005	18
2006	33
2007	17
2008	23
2009	16
2010	8
2011	1
2012	7
2013	13

The referee's comment: 7. It is surprising that the authors chose the Jarvis-type stomatal conductance model rather than the Ball-Berry photosynthesis-based stomatal conductance model, which would have offered a more direct link between ozone uptake and photosynthesis/GPP. Please add a few sentences on this type of model to discussion section.

The authors' response:

We have considered using a Ball-Berry-type stomatal model coupled with Farquhar's biochemical photosynthesis model. As the referee correctly states, we could with this model simulate photosynthesis rates/GPP in addition to the stomatal O_3 fluxes. However, if dose-response relations are investigated as we do in our study (the response = GPP or GPP residual), it is crucial that the response is measured or quantified entirely independently from the dose. This is not the case if we involve the photosynthesis rates/GPP simulated with the coupled photosynthesis-Ball-Berry-type model in the calculation of the response. In this regard, the photosynthetic rates/GPP that we could obtain with that model are of little use in our study.

We then preferred the Jarvis-type stomatal model over the Ball-Berry-type model because we want to publish and provide to the ozone risk assessment community a full site-specific parameterisation of the model for Scots pine. As the referee probably knows, the Jarvis type model is embedded in the DO_3SE algorithm that is currently used to calculate ozone doses for European forests (Mapping

Manual).Scots pine is the representative species for coniferous forests in Atlantic Central Europe and the parameterisation of the stomatal model for Scots pine is based on a compilation of primary and secondary data. We like to publish a full parameterisation of the model for a specific Scots pine stand in the region, with which the DO_3SE parameterisation can be compared and which may possibly contribute to an improved parameterisation. In paragraph 4.1 we added some lines in which we compare the two parameterisations.

The referee's comment: 8. The authors should discuss long-term effects of ozone on forest/tree productivity (e.g. over the entire length of the 14 year study period), which presumably can't be captured by the approach chosen?

The authors' response:

In this study we focus on short term effects of O_3 on GPP. Tree ring growth data and wood density data are available for this forest. It will be interesting to test if O_3 has a long term effect on the biomass, but this is beyond the scope of this research. These data will be analysed in a follow-up paper.

The referee's comment: 9. Related to 8: Please more clearly summarise the limitations of your study/approach.

The authors' response:

We have added some lines to the last section of the Discussion where we summarize the limitations of the method we apply, in particular the distinction between days with and without an O_3 effect on GPP.

The referee's comment: 10. In Appendix A the authors introduce the stomatal model, including fphen, which is then set to 1 in the model runs, right? So maybe remove detail in appendix? Also, how was the start and end of growing season identified? Given the change in weather, one would have expected a variation of these two parameters from year-to-year.

The authors' response:

The function f_{phen} was not set to 1 in the model runs. The function was set to 1 only for the parameterisation of the model against the in situ g_{st} measurements, because these measurements had all been collected on fully matured needles. We rephrased this in paragraph 2.4 so that this is clear to the reader.

The start and end of the growing season were for all years fixed to doy 115 and doy 300, respectively. These values were derived from the LAI course measured in 2007 and taken as the start of LAI increase in spring and the end of the LAI decrease in autumn. There is no doubt that the start and end of the season vary from year to year and this, probably, within a two-week range. The effect of the uncertainty in the start and end of the growing season has only a small effect on the modelled stomatal conductance and stomatal O_3 fluxes, though. This is because the phenology function is set to start from and end at a value of 0.8, not a value of 0 or 0.2 or so. Being a canopy parameter, this value of 0.8 makes sense: at the start of the growing season the pine canopy bears mostly fully grown one-year-old needles and at the end of the growing it bears a mixture of fully-grown current-year needles and partly senescing one-year-old needles. A value of 0.8 is thus meaningful for our pine forest (this in contrast with a deciduous forest, for which f_{phen} should start and end at a very low value, if not 0).

The referee's comment: 11-14.
Line 340f.: Please add reference for other Scots pine forests
Some of the references seem to be rather outdated, e.g. line 25 (IPCC, 2001). Please check manuscript for more recent ones.
Please check reference list: some references mentioned in main text are missing (e.g. CLRTAP, 2015; Mills et al., 2011), some authors misspelled (e.g. Büker rather than Buker)
Please check paragraphs starting on line 48 and 204 for spelling. Also, check entire manuscript for BG criteria for correct referencing, e.g. line 124 "explained in (Carrara et al., 2003;Carrara et al., 2004;Gielen et al., 2013)" should be "explained in Carrara et al. (2003, 2004) and Gielen et al. (2013)". Make sure to leave space after ";" when listing references.

The authors' response:

We thank the referee for remarking the mistakes with the references. Due to a problem with endnote, some references did not show up in the reference list or were misspelled. We solved this problem.
At line '340' we added two references for other Scots pine forests (Altimir et al., 2004; Emberson et al., 2007). In that paragraph we have also expanded a bit on the differences between our parameterization of the Jarvis model and the parameterization used in the DO_3SE model to simulate stomatal O_3 doses for Scots pine in the Atlantic Central Europe, as explained in the mapping manual of CLRTAP.
The following references were replaced by more recent ones:

- (IPCC, 2001)
- (Middleton, 1956)
- (Darall, 1989)
- (Noble and Jensen, 1980)
- (Chappelka and Samuelson, 1998)
- (Andersen et al., 1997)

The following references were added to this manuscript:

- (Subramanian et al., 2015)
- (Young et al., 2013)
- (Ashmore, 2005)
- (Wittig et al., 2009)
- (Li et al., 2016)
- (Ainsworth et al., 2012)
- (Huttunen and Manninen, 2013)

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No impact of tropospheric ozone on the gross primary productivity of a Belgian pine forest

Lore T. Verryckt[1], Maarten Op de Beeck[1], Johan Neirynck[2], Bert Gielen[1], Marilyn Roland[1], and Ivan A. Janssens[1]

[1]Department of Biology, University of Antwerp, Wilrijk, 2610, Belgium

[2]Research Institute for Nature and Forest, Geraardsbergen, 9500, Belgium

Correspondence to: L. Verryckt (lore.verryckt@uantwerpen.be)

Abstract High stomatal ozone (O_3) uptake has been shown to negatively affect crop yields and the growth of tree seedlings. However, little is known about the effect of O_3 on the carbon uptake by mature forest trees. This study investigated the effect of high O_3 events on gross primary productivity (GPP) for a Scots pine stand near Antwerp, Belgium over the period 1998-2013. Stomatal O_3 fluxes were modelled using in situ O_3 mixing ratio measurements and a multiplicative stomatal model, which was parameterised and validated for this Scots pine stand. Ozone-induced GPP reduction is most likely to occur during or shortly after days with high stomatal O_3 uptake. Therefore, a GPP model, an artificial neural network, parameterised for days with low stomatal O_3 uptake rates was used to simulate GPP during periods of high stomatal O_3 uptake. Possible negative effects of high stomatal O_3 uptake on GPP would then result in an overestimation of GPP by the model during or after high stomatal O_3 uptake events. The O_3 effects on GPP were linked to AOT40 and POD_1. Although the critical levels for both indices were exceeded in every single year, no significant negative effects of O_3 on GPP were found and no correlations between GPP residuals and AOT40 and POD_1 were found. Overall, we conclude that no O_3 effects were detected on the carbon uptake by this Scots pine stand.

1 Introduction

Tropospheric ozone (O_3) is a secondary air pollutant that has the potential to negatively affect vegetation, leading to reduced growth and carbon sequestration potential (ICP Vegetation, 2012; Subramanian et al., 2015). Background concentrations of tropospheric O_3 have increased with 30 % since pre-industrial times (Young et al., 2013) and are projected to further increase considerably until about 2050 (IPCC, 2007). Depending on the scenarios, background O_3 levels might either increase or decrease after 2050 (IPCC, 2007).

In recent years, many studies have been conducted to investigate the mechanisms underlying the O_3 impacts on vegetation. Ozone reduces plant growth by altering photosynthetic rates, carbohydrate production, carbon sequestration, carbon allocation, and carbon translocation (Beedlow et al., 2004; Ashmore, 2005; Wittig et al., 2009). Once O_3 enters the leaves through the stomata, it can affect plant growth by direct cellular damage (Mauzerall and Wang, 2001), leading to visible leaf injury and reduced leaf longevity (Li et al., 2016). In response to O_3, respiratory processes increase, which will also affect the tree's carbon balance (Ainsworth et al., 2012). Skärby et al. (1987) proved that dark respiration of Scots pine shoots increased after long-term exposure to a low level of O_3. Protective responses, such as compensation (e. g. repair of injured tissue), avoidance (e. g. stomatal closure), and tolerance (e. g. alteration of metabolic pathways), all consume carbon and, hence, resistance to O_3 damage costs energy. The size of this cost affects the amount of carbon remaining to support growth (Skärby et al., 1998).

To assess the impact of O_3, several indices have been created, e. g. AOT40 (ppb h), the cumulated O_3 mixing ratio in excess of a threshold of 40 ppb, and POD_y, the accumulated O_3 flux above a flux threshold y (nmol m^{-2} s^{-1}). Critical levels, quantitative estimates of exposure to O_3 above which direct adverse effects may occur (CLRTAP, 2015), have been determined for these indices based on O_3 dose-response relationships from fumigation experiments with enhanced O_3 mixing ratios (Karlsson et al., 2004). The magnitude of the O_3 impact on plants depends on the intensity of O_3 exposure, environmental factors influencing both plant photosynthesis and the O_3 flux to plant surfaces, and plant species-specific defensive mechanisms (Musselman and Massman, 1999). Because of the variable plant responses to similar O_3 mixing ratios, the question arises whether widely applicable tolerable limits of O_3 mixing ratio exist (Skärby et al., 1998).

While high stomatal O_3 fluxes have been shown to affect the yield of crops and the growth of tree seedlings and saplings (e.g. (Büker et al., 2015)), little is known about the effect on mature forest trees. When scaling up the results from seedlings to mature trees the resulting data should be viewed with caution, due to differences in energy budgets, canopy:root balances and architecture and carbon allocation patterns (McLaughlin et al., 2007; Huttunen and Manninen, 2013). In addition to the uncertainties related with the up-scaling from seedlings to mature trees, data from controlled experiments should also be used with caution, because trees can react differently in field conditions (Skärby et al., 1998). The effect of O_3 uptake on carbon uptake under ambient O_3 mixing ratios by trees has hardly been studied in situ. Some studies showed reductions in plant growth due to stomatal O_3 uptake (Zapletal et al., 2011; Fares et al., 2013; Yue and Unger, 2013), while other studies did not show any effect (Samuelson, 1994; Zona et al., 2014). Whether or not an effect of stomatal O_3 uptake was found was species- and site- specific, and there is a clear need for more studies investigating the effect of O_3 on carbon uptake by mature trees in the field (Huttunen and Manninen, 2013).

In this study we investigated the effect of O_3 at ambient levels on the gross primary productivity (GPP) of a mature Scots pine stand in Flanders, Belgium over a period of 14 growing seasons between 1998 and 2013. The investigation of O_3 effects on GPP is relevant because GPP represents the first step in the process of C assimilation and quantifies the rate at which C substrate is provided for growth, wood production, et cetera. Critical levels of AOT40 and POD_1 are being exceeded for this stand (Neirynck et al., 2012), indicating a potential effect of O_3 on tree productivity already at current ambient levels. To detect O_3 effects on GPP, we adopted a modelling approach that involved simulating GPP with a model with an O_3-damage free parameterisation and evaluating model overestimations of GPP. We used an artificial neural network (ANN) to model GPP. ANN's are a power tool to process multidimensional data in which complex nonlinear interrelationships between the parameters can be expected. ANN's are successfully used in remote sensing, evolutionary ecology, et cetera, and have previously been used to model GPP (Lek and Guegan, 1999; Rochelle-Newall et al., 2007; Akhand et al., 2016; Liu et al., 2016). In this study we used ANN's since they don't employ predefined model conditions compared to conventional statistical models.

2 Materials and methods

2.1 Study area

The study area consisted of a 2-ha Scots pine stand in a 150-ha coniferous/deciduous forest named ‘De Inslag’, situated in Brasschaat (+51° 18’ 33’’ N, +04° 31’ 14’’ E), northeast of the Antwerp agglomeration and east-northeast of the Antwerp harbour (Neirynck et al., 2008). The site has a temperate maritime climate with a mean annual temperature of 11 °C and a mean annual precipitation of 830 mm (Neirynck et al., 2008). The soil has been classified as Albic Hypoluvic Arenosol (Gielen et al., 2011), a moderately wet sandy soil with a distinct humus and/or iron B-horizon (Janssens et al., 1999). The sandy layer overlays a clay layer which is situated at a depth of 0.7 - 2 m. As a result of the poor drainage groundwater depth is typically high, fluctuating between 0.5 and 2 m (Carrara et al., 2003).

The pine stand was planted in 1929 (Neirynck et al., 2008). Until the autumn of 1999, when the forest was thinned, tree density amounted to 542 trees ha^{-1}. The thinning decreased tree density to 376 trees ha^{-1}. Average canopy height is 21.4 m (Op de Beeck et al., 2010). With a peak in leaf area index (LAI) of 1.3 $\pm$ 0.5 m^2 m^{-2} in 2007 (Op de Beeck et al., 2010) and an average LAI of 1.2 $\pm$ 0.5 m^2 m^{-2} in the period 1998-2007, the stand canopy is very sparse. Only two needle-age classes are present: current-year needles and one-year-old needles (Op de Beeck et al., 2010).

The stand is part of the ICP Forests level II and Fluxnet/CarboEurope-IP networks, and is equipped with a 41 m tall instrumentation tower. Measurements of ecosystem CO_2 exchange with the eddy covariance technique and meteorological measurements are being conducted at the site on a continuous basis since 1996 (Gielen et al., 2013).

2.2 Measurements

The period of study covered the period 1998 - 2013, with the years 1999 and 2003 excluded due to poor data quality or coverage.

2.2.1 Meteorology

Air temperature (T_{air}; °C) and humidity (RH; %) were measured with a PT100 and a HMP 230 dew point transmitter (both Vaisala, Finland) in aspirated radiation shields mounted on the tower at 2, 24 and 40 m height. Wind speed (WS, m s^{-1}) was measured with a cup anemometer (LISA, Siggelkow GMBH, Germany) at 24, 32 and 40 m height. Ingoing and outgoing short-wave and long-wave radiation were measured at the top of the tower with a CNR1-radiometer and a CMP6-pyranometer (Kipp and Zonen, the Netherlands). Rainfall was registered by a tipping bucket rain gauge (NINA precipitation pulse transmitter, Siggelkow GMBH, Germany). Both T_{air} and RH were used to calculate vapour pressure deficit (VPD; kPa). Soil temperature (T_{soil}; °C) was measured at 9 cm below the soil surface with temperature probes (Didcot DPS-404, UK). Soil water content (SWC; m^3 m^{-3}) was measured at 25 cm below the soil surface with Time Domain Reflectometers (CS616, Campbell Scientific, UK). Instant SWC was read manually from the Reflectometers every three to 14 days and values were interpolated to obtain daily estimates, taking into account water inputs via precipitation (Gielen et al., 2010). Soil water potential (SWP;

MPa) was derived from the SWC measurements with the model of van Genuchten (van Genuchten, 1980). All meteorological variables (except SWC and rainfall) were measured every 10 seconds and half hourly means were calculated. Data gaps were filled with data from nearby weather stations.

2.2.2 O_3 mixing ratio

The O_3 mixing ratio ([O_3]; ppb) was measured at a 10 s resolution above the canopy at 24 m height with an UV Photometric Analyzer (model TEI 49I, Thermo Environmental Instruments) and converted to half hourly averages. Data gaps were filled with [O_3] measurements done at 40 m height. If these were not available, gaps were filled with [O_3] measurements from a nearby weather station from the Flemish Environmental Agency (VMM) at Luchtbal, which is less than 10 km from the site.

2.2.3 Leaf Area Index

A continuous time series with daily LAI values was reconstructed for the pine stand based on the historical data. The general approach was to keep the seasonal pattern measured in 2009 by Op de Beeck et al. (2010) fixed for each year and to scale it year per year to the seasonal maximum LAI (LAI_{max}). LAI_{max} had been measured with the LAI-2050 (LI-COR, Lincoln, Nebraska, USA) in 1997 and 2003 by Gond et al. ((1999) and Konôpka et al. (2005), respectively, and with digital hemispherical photography in 2007 by Op de Beeck et al. (2010). To assure consistency across the time series, measurements were corrected for clumping using a factor 0.83 (Jonckheere et al., 2005). The three measurements of LAI_{max} were interpolated linearly to derive LAI_{max} values for the missing years. The thinning event in 1999 was accounted for by subtracting the removed leaf biomass, determined with allometric relations from Yuste et al. (2005) and specific leaf area measurements from Op de Beeck et al. (2010).

2.2.4 Gross Primary Productivity

Gross primary productivity (μmol C m^{-2} s^{-1}) was derived from net ecosystem exchange (NEE) measured with the eddy covariance technique and following the standard data quality procedures as explained in Appendix A ~~Gielen et al. (2013); Carrara et al. (2003); Carrara et al. (2004)~~. ~~Gross primary productivity was derived by subtracting the modelled total (autotrophic and heterotrophic) ecosystem respiration from the measured NEE. The ecosystem respiration or total carbon loss was modelled with standardised algorithms as presented in Falge et al.~~ (2001b)~~.~~ ~~Instant~~ Half-hourly averaged values of GPP were derived for the 14 entire growing seasons of the study period, and integrated to daily and ~~yearly~~ growing season totals.

2.2.5 Stomatal conductance

Measurements of stomatal conductance to H_2O ($g_{st,\ H2O}$) were done at needle level during the summers of 2007 (Op de Beeck et al., 2010) and 2013 to obtain data for parameterisation of the multiplicative stomatal model used in the calculation of stomatal O_3 fluxes (see sections 2.3 and 2.4). The two summers were marked by quite different environmental conditions: cold and wet in 2007 and warm and dry in 2013. Measurements were carried out with the LI-6400 Gas Exchange System (LI-COR, Lincoln, Nebraska, USA) and included diurnal stomatal courses as well as stomatal responses to PAR, T_{air}, and VPD. Measurements were carried out on sets of three or four live fascicles, i.e. six to eight needles, which were enclosed in the LI-6400's leaf chamber while attached to the tree. Twenty-six needle sets were measured in total, equally divided between current-year and one-year-old needles. Each needle set was harvested after being measured and hemi-surface needle area was determined in order to express $g_{st,\ H2O}$ on the correct needle area basis. Needle area was derived from needle dimensions (length and width at top, middle, and base), assuming a hemi-circular cross-sectional needle area. Measurements of $g_{st,H2O}$ were converted to stomatal conductance to O_3 (g_{st}) by multiplying $g_{st,H2O}$ with the ratio of the molecular diffusivities of water vapour and O_3 in the air (= 0.61).

2.3 Calculation of stomatal O_3 fluxes

Stomatal O_3 fluxes were calculated at a half-hourly resolution from continuous series of half-hourly [O_3] and meteorology and daily LAI with an electric analog model built from three resistances in series:

$$R_{tot} = R_{aero} + R_{bl} + R_{can} \tag{1}$$

where R_{tot} is the total resistance to O_3, R_{aero} is the aerodynamic resistance to O_3, R_{bl} is the quasi-laminar boundary layer resistance to O_3, and R_{can} is the canopy resistance to O_3 (all expressed in s m^{-1}).

The aerodynamic resistance was calculated following (Grünhage, 2002) with:

$$R_{aero} = \frac{1}{\kappa u^*} \left[\ln\left(\frac{z-d}{z_0}\right) - \Psi_h\left(\frac{z-d}{L}\right) + \Psi_h\left(\frac{z_0}{L}\right)\right] \tag{2}$$

where κ is the von Karman constant (0.43), u* (m s^{-1}) is the friction velocity, L is the Obukhov length, z is the [O_3] measurement height (24 m), d is the zero plane displacement (= 0.1 h), z_0 is the momentum roughness parameter (= 0.65 h), h is the canopy height, and Ψ_h is the atmospheric stability function. This function is calculated using the set of coefficients published by Dyer (1974):

- for unstable atmospheric stratification (L < 0m)

$$\Psi_h = 2 * \ln\left[\frac{1}{\varphi_h(\zeta)} + 1\right] \tag{3}$$

$$\varphi_h = (1 - 16 * \zeta)^{-0.5} \tag{4}$$

$$\zeta = \frac{z-d}{L} \text{ with } z = z_2 = z_{ref,T} \text{ and } z = z_1 = d + z_0 \tag{5}$$

- for stable atmospheric stratification (L > 0m):

$$\Psi_h = -5 * \zeta \tag{6}$$

$$\zeta = \frac{z-d}{L} \text{ with } z = z_2 = z_{ref,T} \text{ and } z = z_1 = d + z_0 \tag{7}$$

- for neutral atmospheric stratification (|L| → ∞):

$$\Psi_h = 0 \tag{8}$$

The quasi-laminar boundary layer resistance was calculated following (Baldocchi et al., 1987) with:

$$R_{bl} = \frac{2}{\kappa * u^*}\left(\frac{Sc}{Pr}\right)^{2/3} \tag{9}$$

where κ is the von Karman constant (0.43), u* (m s^{-1}) is the friction velocity, which is derived from the measured momentum fluxes, Sc is the Schmidt number (1.07 for O_3), and Pr is the Prandtl number (0.72 for O_3).

The canopy resistance was calculated from a stomatal resistance (R_{st}) and a non-stomatal resistance (R_{nst}), mounted in parallel:

$$R_{can} = \left(\frac{1}{R_{st}} + \frac{1}{R_{nst}}\right)^{-1} \quad (10)$$

The stomatal resistance R_{st} was calculated with an algorithm that divides the pine canopy into eight horizontal leaf layers, with LAI being divided equally between the layers, and that simulates the transfer of radiation through the layered canopy. The algorithm then calculates the stomatal resistance for the sunlit and shaded area fraction of each leaf layer with the multiplicative stomatal model described by Jarvis (1976) and reformulated by (Emberson et al., 2000). Resistance values are then integrated over all layers to obtain canopy level R_{st}. The algorithm is explained in more detail in Op de Beeck et al. (2010). The version of the multiplicative stomatal model used in this study is described in detail in Appendix B. This model was given a site-specific parameterisation as explained in section 2.4.

The non-stomatal resistance R_{nst} was assumed to be constant in time and set to 279 s m^{-1}. This value was derived from long-term O_3 flux measurements in Brasschaat (Neirynck et al., 2012).

Total and stomatal O_3 fluxes (F_{tot} and F_{st}; nmol m^{-2} s^{-1}) were calculated on a halfhourly basis with:

$$F_{tot} = 44.64\,\frac{[O_3]}{R_{tot}} \quad (11)$$

$$F_{st} = F_{tot}\,\frac{R_{can}}{R_{st}} \quad (12)$$

where 44.64 is the molar density of air in mol m^{-3} at an air pressure of 101.3 kPa and an air temperature of 0°C, used here to convert flux units from m s^{-1} to mol m^{-2} s^{-1}. Half-hourly fluxes were aggregated to daily and yearly values.

2.4 Parameterisation and validation of the multiplicative stomatal model

The multiplicative stomatal model was parameterised and validated against the data set of g_{st} measurements collected at the site. This data set included besides measured g_{st} also PAR, T_{air}, VPD, and SWP, and was split into a parameterisation set and a validation set by grouping the odd and even rows of data after being ranked by PAR. Parameterisation was done by optimising model parameters with the function ‘lsqcurvefit’ in Matlab (Matlab and Statistics Toolbox Release 2013a), which finds the best parameter values starting from an initial values and which can be used to fit nonlinear functions with more than two independent variables. The parameters of the boundary functions f_{PAR}, f_{Tair}, f_{VPD}, and f_{SWP} were optimised separately, starting from initial values that were estimated visually from plots of g_{st} versus each of the input variables (PAR, T_{air}, VPD, and SWP). The phenology function f_{phen} was set to 1 for parameterisation of f_{PAR}, f_{Tair}, f_{VPD}, and f_{SWP}~~,~~ since g_{st} had been measured on mature needles only. We included f_{phen} in the final model to estimate the stomatal O_3 fluxes over the growing season (Appendix B).~~.~~

The parameterised model was then tested against the validation data set. Model performance was evaluated with the linear regression $y = ax + b$ fitted to the plot of measured versus modelled g_{st}, and with the following set of performance statistics: the coefficient of determination (R^2), mean bias (MB), relative mean error (RME), Willmott's index of agreement (d), model efficiency (ME), and root mean squared error (RMSE) and its systematic ($RMSE_s$) and unsystematic component ($RMSE_u$). These statistics are explained briefly in Appendix C. To evaluate visually the goodness-of-fit of each boundary function, modelled g_{st} was plotted versus each of the input variables and the corresponding boundary function added to the scatter plot.

2.5 Detecting O_3 effects on GPP

We adopted a modelling approach to detect possible O_3 effects on GPP. Under the assumption that O_3-induced GPP reduction is most likely to occur during and shortly after days of high stomatal O_3 fluxes, we parameterised a GPP model against a data set from which such days where removed and then simulated daily and growing season GPP with this supposedly O_3-damage free model. A reduction of GPP due to O_3 would become apparent as a model overestimation of daily GPP for the days on which an O_3 effect was assumed, and possibly also as an overestimation of growing season GPP. The physiological mechanism beyond the assumption made hereabove is that at high stomatal O_3 fluxes the trees' defensive mechanisms cannot detoxify all O_3 entering the needles and damage is caused to the photosynthetic apparatus (Dizengremel, 2001; Matyssek and Sandermann, 2003). This leads to decreased gross photosynthetic rates and GPP. The damage is repaired afterwards when the stomatal O_3 load decreases.

We used as GPP model a feed-forward back propagation Artificial Neural Network (ANN) in Matlab (Matlab and Statistics Toolbox Release 2013a). The ANN contained 10 nodes organised in 1 layer, which came out as the best performing network after comparing networks containing different number of nodes and/or layers (data not shown). The default settings of the Matlab Neural Network Toolbox were used. A normalisation process was applied for training and testing the data: data were scaled to [-1 1] based on the lowest and highest value in the dataset. We used the Levenberg-Marquardt algorithm to train the ANN for 1000 iterations (Marquardt, 1963). Progress of training procedure was monitored using the mean squared error (MSE) of the network. The daily GPP data were used as dependent target variable in the ANN. The input variables were year, day of year, T_{min}, T_{max}, T_{mean}, average VPD, SWC, R_g, average T_{soil}, and average WS. Daily totals of the variables were used, with the exception of VPD, T_{soil}, and WS for which daily averaged values were used. The individual weights of these parameters on our model were estimated by replacing each input variable with a random permutation of its values. This was done for the GPP model as described above, and a GPP model containing O_3 as input variable to test if O_3 had any explanatory power on GPP.

To obtain an O_3-damage free GPP model, the days for which an O_3 effect on GPP was expected were removed from the dataset. We assumed that if an O_3 effect occurs, it would occur at the days with the highest stomatal O_3 fluxes. Because the defensive capacity of the pine trees was not quantified and, hence, the O_3 load above which

O_3 would affect GPP not known, we repeated the analysis trice by removing the days~~These were taken as the days~~ with the 2 %, 5 % ~~or~~ and 10 % highest stomatal O_3 fluxes. Because the results for a 2 % and 10 % cut-off were equal to those for a 5 % cut-off, we report only results for a 5 % cut-off. The model was trained with 2/3 of the remaining dataset, while the other 1/3 was used to test the model. This O_3-damage free model was then run with the full dataset.

Model overestimation of daily GPP was evaluated (1) from the linear regression on the data of measured versus modelled GPP for the days on which an O_3 effect was assumed, testing whether the regression slope and intercept were different from 1 and 0, and (2) by comparing measured and modelled daily GPP for these days by means of a paired-samples t-test or a Wilcoxon signed-rank test if differences were not normally distributed (Shapiro-Wilk test). A significant outcome of this test in combination with a regression slope significantly lower than 1 (and an intercept not different from 0) would together point to a significant overestimation of GPP. Furthermore, (3) the regression slope and intercept were compared with the slope and intercept of the regression fitted to the dataset used to train and test the GPP model. This was done to evaluate whether GPP estimations for the days on which we assumed an O_3 effect were, in relative terms, significantly higher than GPP estimations for the days used for model training and testing. This would become apparent as a significantly lower slope (with an intercept no different from 0). Model overestimation of growing season GPP was evaluated with the first two tests above on the growing season data. Additionally, the residuals of growing season GPP (model - measurement) were plotted against AOT40, POD_1, and total growing season stomatal O_3 uptake, and linear regression lines fitted. It was tested whether regression slope and intercept were significantly different from 0 to assess the presence of a statistically significant O_3 dose response relationship.

Since it may take some time to repair damage to the photosynthetic apparatus induced by O_3, O_3 effects might last several days after a peak of O_3 exposure. They might thus ~~, they might~~ not be detected with the model parameterised as explained above. To account for such a sustained O_3 effect, the modelling was repeated, now not only excluding the days with the highest stomatal O_3 fluxes from the dataset for model training but also the ~~two~~ following days. The modelling was repeated with three different such delay periods, being the first, the first two, and the first six days following each flux peak. The results were evaluated with the same statistical tests as mentioned above. Because the result were similar for the three delay periods, only the results for the two-day period are shown.

High O_3 events are often coupled with specific meteorological conditions, i.e. high radiation and air temperatures. Since the dataset for model training had been compiled by removing the days with the highest stomatal O_3 fluxes, it was not unlikely that these conditions were underrepresented in the training dataset. If so, this could induce a bias in the model response to radiation and temperature and possibly result in overestimations of GPP for the days on which an O_3 effect was expected, which we then might wrongly attribute to O_3. To evaluate the risk for such model bias, we compared the frequency distribution and range of radiation, T_{min}, T_{max}, T_{mean}, and also VPD between the training dataset and the dataset with the days on which we expected an O_3 effect.

One of the assumptions in our approach is that O_3 effects on GPP only last on the short term, i.e. just a few days, and are hence not carried over. The presence of a carry-over effect would compromise the validity of our approach. We can rule out a carry-over effect by testing whether trees exposed to low stomatal O_3 fluxes late in the growing season behave in the same way as when exposed to similar low O_3 fluxes early in the growing season. To test this, we compiled a dataset that contained per growing season only the days after the first major peak of stomatal O_3 flux in the growing season. From this period, we further selected only the days with low stomatal O_3 fluxes for which moreover no short-term O_3 effect was expected. In other words, we excluded the days with a peak of stomatal O_3 flux plus the six following days. We trained the GPP model with these data and then predicted GPP for the days before the first major O_3 peak in each growing season. If a carry-over effect would be present, at least an effect induced during the first major O_3 flux peak, it would be somehow included in the trained model. This would then underestimate GPP for the days before each first major O_3 peak, where a carry-over effect has assumptively not yet occurred. Model underestimation of GPP was evaluated from a linear regression on the data of measured versus modelled GPP, testing whether the regression slope and intercept were different from 1 and 0. This slope and intercept were also compared with the slope and intercept of the regression line fitted to the training data. Also, measured and modelled GPP were compared with a paired-samples t-test or a Wilcoxon signed-rank test if differences were not normally distributed (Shapiro-Wilk test).

All statistics were performed with R 3.2.3 (R Core Team, 2015) at a significance level of $p = 0.05$.

3 Results

3.1 Measurements: meteorology, GPP, and LAI

Figure 1 shows a fingerprint of the multi-annual average diel and seasonal patterns of the main meteorological variables, being T_{air}, incoming global radiation (R_g) and VPD, and measured GPP. This figure gives a good overview of how meteorology and GPP typically changed over time in this forest; interannual anomalies from the average patterns can be found in Fig. S1. Distinct daily and seasonal patterns can be observed for, reaching highest values in summer, in the afternoon. Similar patterns can also be observed in GPP, which basically follows the pattern of R_g. As seen in Fig. 1, the photosynthetic period extends, on average, from day of year 115 (end of April) till day of year 300 (end of October). The time series of precipitation and SWP are provided in Fig. 2, while the seasonal LAI courses are shown for each year in Fig. 3. The yearly maximum LAI ranged from 1.4 to 1.9 $m^2\ m^{-2}$. The thinning of the forest in 1999 can clearly be observed in the LAI pattern. After the thinning, the canopy never fully closed.

3.2 Multiplicative stomatal model and simulated O_3 fluxes

The optimized parameter values of the model are presented in Table 1. The different statistics to evaluate the model performance are presented in Table 2 and this for both the parameterisation and validation dataset. For the parameterisation dataset, the measured data were plotted against modelled g_{st} and plotted in Fig. 4A. The slope of the linear fit was not significantly different from 1 ($p = 0.87$) and the intercept was not significantly different from 0 ($p = 0.81$). Model evaluation for the validation dataset was equally good as for the parameterisation dataset (Table 2). Also in the linear fit for the validation set (Fig. 4, B), the slope was not significantly different from 1 ($p = 0.98$) and the intercept was not significantly different from 0 ($p = 0.70$).

Figure 5 shows the scatter plots of measured g_{st} versus each of the model input variables: PAR, T_{air}, VPD, and SWP, and for each plot the fitted boundary function.

The average daily O_3 fluxes for the different years are presented in Fig. S2. Daily F_{st} ranges from 1.12 to 1.52 nmol O_3 m^{-2} day^{-1}. In 2011 the daily F_{st} was the lowest, while the highest values were observed in 2002. The annual average ratio F_{st}/F_{tot} varied between 24-28 % (Fig. S2). We observed the lowest ratios in the beginning and at the end of the growing season. Above-average ratios were observed at the peak of the growing season.

3.3 Ozone effects on GPP

Figure 6 shows the frequency distributions of R_g, T_{min}, T_{max}, T_{mean}, and VPD for the training data set and the dataset with days on which we assumed an O_3 effect. Days in the latter data set are generally more concentrated in the upper half of each variable's range. The training data set includes more days in the lower half, but conditions of high radiation, temperature or VPD do not seem to be underrepresented as the data set also included a substantial number of days in the higher part. For all variables, the variable range of the data set with days for we assumed an O_3 effect is fully contained range of the training data set.

All parameters in the GPP model were ranked according to their contribution to GPP prediction (Table 3). Global radiation is the most important parameter in defining GPP with a mean squared error (MSE) of 37500.81 mol m^{-2} s^{-1}, followed by doy (30240.61 mol m^{-2} s^{-1}) and year (27486.63 mol m^{-2} s^{-1}). The maximum air temperature and VPD contribute equally to the model with a MSE of about 15300 mol m^{-2} s^{-1}. Wind velocity, Tmin and SWC contribute the least to GPP. Ozone as input variable had a MSE of 11885.73 mol m^{-2} s^{-1} (Table 3, B) and contributed the least with a MSE similar to the overall model (10019.30 mol m^{-2} s^{-1}).

To test for carry-over O_3 effects, we evaluated and compared the linear regressions of measured versus modelled GPP of a dataset with low O_3 fluxes after the first major O_3 flux peak in the growing season and a dataset before this peak (Fig. 7). For both regressions, intercept and slope were not significantly different from 0 and 1 respectively (training: $p_{slope} = 1$, $p_{intercept} = 1$, testing: $p_{slope} = 0.83$, $p_{intercept} = 0.44$). The slopes were also not significantly different from each other ($p = 0.86$) and neither were the intercepts ($p = 0.53$).

Figure 8 shows measured versus modelled daily GPP for the model trained without the days with the highest stomatal O_3 fluxes (GPP model 1) and the model trained to test also for lag effects (GPP model 2). Both models reproduced daily GPP well for the dataset against which they were trained and tested, as indicated by the high R^2 values and the fitted regression lines falling on the 1:1 line (Fig. 8 A, B). For both models, the regression slope for the data set with the days on which we assumed an O_3 effect was significantly lower than 1 and the intercept significantly higher than 0 (Fig. 8 C, D). For GPP model 1, the regression slopes were not significantly different between the two data sets ($p = 0.46$), but the intercepts were ($p < 0.05$). For GPP model 2, both the regression slopes and intercepts differed significantly ($p < 0.001$) and $p < 0.001$). However, a Wilcoxon signed-rank test showed for both models that modelled daily GPP was not significantly higher than measured daily GPP for the days on which an O_3 effect was assumed ($p = 0.83$ and $p = 0.64$, respectively). Also, a paired samples t-test showed for both models that modelled growing season GPP was not significantly higher than measured growing season

GPP ($p = 0.93$ and $p = 0.55$, respectively). The slope and intercept of the linear regression line were not significantly different from 1 and 0 (Fig. 8 e, f).

No statistically significant correlations were found between the model residuals of growing season GPP and total stomatal O_3 uptake (F_{st}), AOT40, and POD1 (Fig. 9).

4 Discussion

4.1 Multiplicative stomatal model

All statistics shown in Table 2 clearly indicated that the fitted multiplicative stomatal model performed well. For both parameterisation and validation datasets, the model explained 72 % of the variance in g_{st}. For both datasets, slope and intercept of the linear regression lines of measured versus modelled g_{st} were not significantly different from 1 and 0, respectively (Fig. 4). Moreover, the model efficiency (ME in Table 2) of 0.72 and the Wilmott's index (d) close to 1 both indicate that the modelled values matched the measured values well. A good model provides low root-mean-square error (RMSE), while the systematic component ($RMSE_s$) should approach zero and the unsystematic component ($RMSE_u$) should approach RMSE (Willmott et al., 1985), which was the case for this model. Low mean bias (MB) and low mean relative error (MRE) further indicated very good performance. The good performance of the model can also be observed in Fig. 5, in which the boundary lines represented the response of g_{st} to the independent variables when other variables were not limiting. The boundary lines fitted close to the data points, which is an indication of a good model, because the multiplicative stomatal model is based on the assumption that the variables act more or less multiplicatively and independently from each other (Grüters et al., 1995).

As explained in the mapping manual of the Convention on Longe-Range Transboundary Air Pollution (CLRTAP), Scots pine is the representative species to assess the risk of O_3 damage to coniferous forests in Atlantic Central Europe (CLRTAP, 2015). This risk is assessed on the basis of O_3 doses calculated with the DO_3SE algorithm, which employs a Jarvis type stomatal model that has been parameterised for Scots pine based on a compilation of primary and secondary data (Emberson et al., 2007; Büker et al., 2015; CLRTAP, 2015). The parameterisation for our Scots pine stand differs in some numbers from the one used in the DO_3SE algorithm. The most remarkable difference is that g_{max} of the Scots pines in Brasschaat is much lower (0.14 vs 0.18 mol O_3 m^{-2} s^{-1}). This low g_{max} may imply that during episodes of high O_3 mixing ratio, the Brasschaat site is unlikely to take up very high amounts of O_3 (Altimir et al., 2004; Emberson et al., 2007). This may have contributed to the absence of a clear O_3 response at our site. A second difference is that the stomata of the pine trees remain opened at night (g_{min} = 0.02 mol O_3 m^{-2} s^{-1}), while the DO_3SE model simulates full stomatal closure. Furthermore, the response to temperature is for our Scots pine stand shifted to a slightly higher temperature (T_{opt} = 25 vs 20 °C) and the response to soil drought is much stronger (SWC_{max} = -0.19 vs -0.7 MPa and SWC_{min} = -1.18 vs -1.5 MPa). From these differences it can be inferred that stomatal O_3 uptake rates at the Brasschaat site are considerably lower than would be simulated with the DO_3SE model for generic Scots pine. This highlights the importance of a site-specific parameterisation when aiming to assess stomatal O_3 loads at site level.

~~Multiplicative stomatal models based on Jarvis (1976) have been parameterised earlier for generic Scots pine forests in Europe (Mills et al., 2011; Büker et al., 2015) and used to estimate critical levels for this species. However, the empirical dose-response relationship for Scots pine is based on only one two-year fumigation study on small seedlings and, therefore, high uncertainty exists in the modelled O_3 impact on Scots pine growth.~~

~~The parameterisation of Mills et al. (2011) and Büker et al. (2015) differ from that of this study in a number of parameters. First, the needles of the Scots pine stand in Brasschaat had a higher night-time g_{st} (g_{min}) and will therefore take up more O_3 at night. Maximal g_{st}, in contrast, is lower in Brasschaat than estimated for other Scots pine forests, implying that during episodes of high O_3 mixing ratio, the Brasschaat site is unlikely to take up very high amounts of O_3 (Altimir et al., 2004; Emberson et al., 2007). This may have contributed to the absence of a clear O_3 response at our study site. Also the Scots pine stand in Brasschaat is less sensitive to drought stress than the generic model, due to a higher VPD_{max} and a wider SWP range. The wider SWP range is mainly due to a clearly lower SWP_{max}. These differences between the parameter values and, hence, in g_{st} for generic Scots pine forests and for the Scots pine stand in Brasschaat will lead to different critical levels and under- or overestimation of possible O_3 damage. Species-specific parameterisation is important, but site-specific parameterisation is clearly important as well.~~

4.2 Stomatal O_3 fluxes

The stomatal O_3 flux contributed on average for 26 % to the total O_3 flux over the study period (Fig. S2). This fraction is similar to the 21 % stomatal O_3 flux in a Danish Norway spruce stand (Mikkelsen et al., 2004) and the 30 % stomatal O_3 flux in *Quercus ilex* in Italy (Vitale et al., 2005; Gerosa et al., 2005). Cieslik (2004) showed that in Southern Europe stomatal O_3 flux of different vegetation types, such as pine forest and Mediterranean shrubs, is typically less than 50 % of the total O_3 flux. A five-year study on a Mediterranean *Pinus ponderosa* stand showed a stomatal O_3 flux contribution of 57 % (Fares et al., 2010). Clearly, species- and site-specific differences such as tree age or micro-climate are introducing large variability in stomatal O_3 uptake (Neirynck et al., 2012).

The low relative stomatal O_3 flux in the Scots pine stand in Brasschaat could be the result of the sparse canopy with low LAI. Although no relation between stomatal O_3 flux and LAI was found in a previous site study on this site (Neirynck et al., 2012), interannual and seasonal variation in LAI is very small, rendering such a correlation analysis very difficult.

4.3 Ozone effects on GPP

A comparison of the frequency distributions of radiation, temperature, and VPD between the training dataset and the dataset with the days on which we expected an O_3 effect showed that the meteorological conditions in the latter data set were fully represented in the training dataset. From the full overlap we can rather safely assume that the GPP model did not to include a biased response to these variables that could result in a GPP overestimation that we might wrongly interpret as an effect of O_3. Also, O_3 as input variable in the ANN did not have any explanatory power on GPP as it had the lowest MSE value close to the overall model MSE. Furthermore, a GPP model parameterised to include a carry-over effect of O_3 on GPP did not overestimate GPP at a statistically detectable level for days on which such an effect was not assumed to occur. From these results, we infer that carry-over effects of O_3 were unlikely to have occurred and that the assumption on the absence of (detectable) carry-over effects was valid.

The statistical tests ran on the data sets of measured and modelled GPP did not reveal a statistically significant model overestimation of daily GPP for the days on which we assumed an O_3 effect, nor an overestimation of growing season GPP. Also no significant correlations between growing season GPP residuals and stomatal O_3 flux, AOT40, and POD_1 were found, even though critical levels for AOT40 and POD_1 were exceeded in every single year of our study period. From these results and within the limits of the modelling approach applied in this study, we can infer that no significant effect of O_3 on GPP occurred.

Some earlier studies have investigated the effect of O_3 on forest carbon uptake. Cumulative stomatal uptake of 27 mmol m^{-2} over the growing season did not result in any visible damage or a reduction in NEE of a poplar plantation in Belgium (Zona et al., 2014). Zapletal et al. (2011), on the other hand, reported that CO_2 uptake of a Norway spruce forest in the Czech Republic increased with increasing stomatal O_3 flux, followed by a sudden decrease in CO_2 uptake, suggesting that an O_3 flux threshold exists. Fares et al. (2013) showed a negative correlation between GPP and O_3 uptake at two Mediterranean ecosystems (a forest dominated by *Pinus ponderosa* in California, USA and an orchard site of *Citrus sinensis* cultivated in California, USA). A GPP reduction of 1-16 % in response to O_3 uptake under ambient O_3 mixing ratio of 30-50 ppb was determined across vegetation types and environmental conditions in the United States by Yue and Unger (2013). The magnitude of reduction depended on the sensitivity to O_3 of the species and on the biome types.

AOT40 is, at present, the European standard for forest protection (EEA, 2014), with a critical level of 5000 ppb h, equivalent to a growth reduction of 5 % (Mills et al., 2011). In this study on Scots pine in Brasschaat, this value was far exceeded in all years (Fig. 9), yet no negative effect on GPP was observed in years with higher AOT40 values.

POD_1 is considered a more appropriate index for potential O_3 damage because it considers O_3 flux. The critical level of POD_1 is species-specific; a critical level of 8 mmol m^{-2} with 2 % growth reduction is used for Norway spruce and a critical level of 4 mmol m^{-2} with 4 % growth reduction is used for birch and beech (Mills et al., 2011). A critical level for Scots pine has not yet been determined and therefore the value of 8 mmol m^{-2} for Norway spruce is often adopted as critical level for Scots pine. During this study, this critical level was exceeded every single year, and again no significantly negative correlation between total GPP residuals and POD_1 was observed. In comparison to the AOT40 level, 2006 was not the year with the highest POD_1. This difference between AOT40 and POD_1 during 2006 was due to stomatal closure; during high O_3 mixing ratio events, g_{st} was rather low (Fig. S3). POD_1 was highest in the year 2002, when O_3 mixing ratios were relatively low, but g_{st} was high. The low O_3 mixing ratios explain the lower AOT40 for 2002.

Notwithstanding the absence of a statistically significant positive correlation between GPP residuals and both AOT40 and POD_1, critical levels for both AOT40 and POD_1 were exceeded every single year. AOT40 is based on O_3 mixing ratio and these concentration-based indices have been shown to be weaker indicators for O_3 damage than flux-based indices (Karlsson et al., 2007; Simpson et al., 2007). The critical level of POD_1 for Scots pine was adopted from the critical level for Norway spruce (Mills et al., 2011). Possibly this critical level is too low for Scots pine. As shown by Reich (1987), pines are less sensitive to O_3 compared to hardwoods and crops. This supports the idea of a too low critical level.

Overall, no significant O_3 effects on daily and growing season GPP ~~accumulated over the growing season~~ were found. It can thus be concluded that O_3 did not affect GPP of the pine forest, at least if the assumptions we made in our approach to detect O_3 effects are valid. The most crucial assumption involves the distinction between days at which a GPP effect did and did not occur. It was not possible to identify these days with great precision, due to lack of knowledge on the defensive capacity of the trees and their ability to repair O_3 damage. To overcome this, we repeated our analysis with three different peak thresholds for daily stomatal O_3 uptake rates above which an effect would occur and with three different delay periods over which an induced O_3 effect would last. The fact that all nine analyses produced the same outcome provides validity to our conclusions, despite the uncertainty involved in the identification of days with O_3 effects.

The lack of a detected~~Although no significant~~ O_3 effects on GPP ~~were found in this study, it is still possible~~ does not mean that O_3 didn’t negatively affect~~ed~~ this Scots pine stand in Brasschaat. Stomatal O_3 uptake ~~was~~ has here been linked to reductions in GPP only. As already stated in the introduction, protective responses such as compensation and enhanced tolerance occur in trees (Skärby et al., 1998). It is likely that trees at our study site were able to fully detoxify the ~~incorporated~~ O_3 taken up. ~~As a result, no O_3 effects on carbon uptake were detectable. However, this protection may have come at a~~ The respiratory cost involved might have come at the expense of biomass production and growth, while gross C uptake remained unaffected. Future analyses, such as tree ring analysis, may provide an answer to whether this is the case.~~, which may have reduced the NPP/GPP ratio of this forest. The NPP/GPP ratio of our study site was very low (Nagy et al., 2006). In addition to the poor nutrient status (limitation by P and Mg, extremely high N deposition; (Neirynck et al., 2008)), O_3 uptake may partly be responsible. This can, however, not be tested because pine forest NPP data were not available at annual timescale.~~

5 Summary

We parameterised a multiplicative stomatal model for a Scots pine stand in Brasschaat. This species- and site-specific parameterised model performed very well. With this model embedded in a resistance scheme, stomatal O_3 fluxes were calculated and used to test for O_3 effects on GPP. Only very small reductions in growing season GPP were calculated. Although critical levels for AOT40 and POD_1 were exceeded in every single year, no significant correlations between total GPP residuals and stomatal O_3 flux, AOT40, and POD_1 were found. Within the limitations of the approach used in this study,~~In general,~~ we can thus conclude that ~~no~~ O_3 ~~effects were detected~~ did not affect~~on~~ the gross carbon uptake by the Scots pine stand in Brasschaat.

Appendix A Gross Primary Productivity measurements

This study investigates O_3 effects on GPP. Below is briefly explained how GPP was measured.

Gross primary productivity (µmol C m^{-2} s^{-1}) was derived from net ecosystem exchange (NEE) measured with the eddy covariance technique (Baldocchi and Meyers, 1998). The eddy covariance system was set up in august 1996. It consists of a sonic anemometer (Model Solent 1012R2, Gill Instruments, Lymington, UK) to measure turbulence and an infrared gas analyser (IRGA) (Model LI-6262, LI-COR Inc., Lincoln, NE, USA) to measure the CO_2 concentration. The measurements were conducted at the top of the tower at a height of 41 m, about 19 m above the canopy. Half-hourly NEE fluxes were calculated following the guidelines of the standard EUROFLUX methodology (Aubinet et al., 1999) as described in detail by Carrara et al. (2003; 2004). All half-hourly fluxes originating from outside the footprint were removed according to the criteria described by Nagy et al. (2006). A detailed description of the composition of the footprint can be found in the same paper. After filtering for non-forest fluxes, the remaining data have been filtered for not optimal turbulence conditions using the u* approach (Aubinet et al., 1999); the method described in Reichstein et al. (2005) has been used as basis, including the bootstrapping to estimate 100 thresholds per year. After all the filtering on average about 55 % of the half hourly fluxes were discarded. The remaining data were used to gapfill the missing data following the non-linear regressions method (NLR; (Falge et al., 2001a)) and the Marginal Distribution Sampling method (MDS; (Reichstein et al., 2005)). Gross primary productivity was derived from NEE by adding the modelled total ecosystem respiration (autotrophic plus heterotrophic) to NEE. The ecosystem respiration was modelled with standardised algorithms as presented in Falge et al. (2001b).

Appendix B The multiplicative stomatal model

In this work the multiplicative stomatal model described by Jarvis (1976) is modified specifically for the Scots pine stand in Brasschaat. The basic model is explained below.

Stomatal conductance to O_3 at needle level (g_{st}) was modelled with the multiplicative stomatal model first described by Jarvis (1976) and later reformulated by (Emberson et al., 2000). In this study we used a modified version of the model (Eq. 1).

$$g_{st} = g_{max} * f_{phen} * (f_{min} + (1 - f_{min}) * (f_{PAR} * f_T * f_{VPD} * f_{SWP})) \qquad \text{(A1)}$$

Here g_{st} is the stomatal conductance to O_3 and g_{max} is the maximal stomatal conductance to O_3. The functions f_{PHEN}, f_{PAR}, f_T, f_{VPD}, and f_{SWP} represent the modification of g_{max} by, respectively, phenology, PAR, T_{air}, VPD, and SWP. The function f_{min} is the ratio of g_{min} and g_{max} where g_{min} is the minimal stomatal conductance to O_3 Impaired stomatal aperture mechanisms (stomatal sluggishness) due to O_3 exposure (Paoletti and Grulke, 2010) were not included in this model. In this modified version PAR, T_{air}, VPD, and SWP influence the range between g_{max} and g_{min} instead of g_{max} and zero. This modification was needed to allow for a constand g_{st} during night time (= g_{min}) that increases as soon as PAR > 0 µmol m^{-2} s^{-1}, in accordance with our observations (Op de Beeck et al., 2010).

Phenology modifies g_{max} because of the variation in g_{st} due to differences in needle age. The function f_{PHEN} is modelled as follows: (A2)

if $SGS \le doy \le (SGS + c)$, then $f_{PHEN} = f_{min} + (1 - f_{min}) * (1 - b) * \left(\frac{doy - SGS}{c}\right) + b$

if $SGS + c \le doy \le EGS - d$, then $f_{PHEN} = f_{min} + (1 - f_{min}) * 1$

if $EGS - d \le doy \le EGS$, then $f_{PHEN} = f_{min} + (1 - f_{min}) * (1 - b) * \left(\frac{EGS - doy}{d}\right) + b$

where SGS is the start of the growing season (doy = 115), EGS is the end of the growing season (doy = 300), and b (= 0.8), c (= 20), and d (= 20) are species-specific parameters representing the minimum of f_{PHEN}, the number of days for f_{PHEN} to reach its maximum and the number of days during the decline of f_{PHEN} for the minimum to reach again, assuming linear increase and decrease at the start and end of the growing season.

The stomatal response to PAR is described by a rectangular hyperbola, where a_{PAR} is a species-specific parameter determining the shape of the hyperbola (Emberson et al., 2000);

$$f_{PAR} = 1 - \exp(-a_{PAR} * PAR) \qquad \text{(A3)}$$

The stomatal response to T_{air} is given by a parabolic function, where T_{min} is the minimum temperature at which stomatal opening occurs, and T_{opt} is the optimum temperature of stomatal opening (Emberson et al., 2000);

$$f_T = \max(0; 1 - \frac{(T - T_{opt})^2}{(T_{opt} - T_{min})^2}) \quad \text{(A4)}$$

The stomatal response to VPD is described by the following relationship, where VPD$_{min}$ is a threshold for minimal stomatal opening, and VPD$_{max}$ is a threshold for full stomatal opening (Emberson et al., 2000);

$$f_{VPD} = \min(1; \max\left(0; \frac{VPD_{min} - VPD}{VPD_{min} - VPD_{max}}\right)) \quad \text{(A5)}$$

The stomatal response to SWP is described by the following relationship, where SWP$_{min}$ is a threshold for minimal stomatal opening, and SWP$_{max}$ is a threshold for full stomatal opening (Emberson et al., 2000);

$$f_{SWP} = \min(1; \max\left(0; \frac{SWP_{min} - SWP}{SWP_{min} - SWP_{max}}\right)) \quad \text{(A6)}$$

Appendix C Statistics of model performance

In order to test how well the modified stomatal model performed, several model statistics were calculated. These model statistics are explained below.

The mean bias (MB) is the mean difference between the simulations (S_i) and the observations (O_i), with n being the number of data points (Stone, 1993);

$$MB = n^{-1} \sum_{i=1}^{n} (S_i - O_i) \qquad \text{(B1)}$$

The mean relative error (MRE) is the mean relative difference between the simulations and the observations (Peierls, 1935);

$$MRE = n^{-1} \sum_{i=1}^{n} \frac{|S_i - O_i|}{O_i} \qquad \text{(B2)}$$

Willmott's index of agreement (d) is a dimensionless goodness-of-fit coefficient, with $\bar{O}$ being the mean observation (Willmott, 1981); The index can vary between 0 and 1, with d equals 1 for a perfect agreement between simulations and observations.

$$d = 1 - \frac{\sum_{i=1}^{n} (S_i - O_i)^2}{\sum_{i=1}^{n} (|S_i - \bar{O}| + |O_i - \bar{O}|)} \qquad \text{(B3)}$$

The model efficiency (ME) gives an indication of how well the observations match the simulations (Nash and Sutcliffe, 1970); Model efficiency can range from -∞ to 1 and is 1 when simulations and observations match perfectly. An efficiency of 0 indicates that the simulations are as accurate as the mean observation and an efficiency of less than zero indicates that the mean observation is a better predictor than the model.

$$ME = 1 - \frac{\sum_{i=1}^{n} (S_i - O_i)^2}{\sum_{i=1}^{n} (O_i - \bar{O})^2} \qquad \text{(B4)}$$

The root-mean-squared error (RMSE) is a measure of the mean absolute difference between the simulations and the observations, weighting large differences heavily (Willmott et al., 1985); The systematic component ($RMSE_s$) estimates the model's linear or systematic error, hence, the better the regression between simulations and observations, the smaller the systematic component (Willmott et al., 1985). The unsystematic component is a measure of how much of the discrepancy between simulations and observations is due to random processes (Willmott et al., 1985). A good model will provide low values of RMSE, with $RMSE_s$ close to zero and $RMSE_u$ close to RMSE (Willmott et al., 1985).

$$RMSE = \sqrt{n^{-1} \sum_{i=1}^{n} (S_i - O_i)^2} \qquad \text{(B5)}$$

$$RMSE_s = \sqrt{n^{-1} \sum_{i=1}^{n} (S'_i - O_i)^2} \qquad \text{(B6)}$$

$$RMSE_u = \sqrt{n^{-1} \sum_{i=1}^{n} (S_i - S'_i)^2} \qquad \text{(B7)}$$

$S'_i = a * O_i + b$, where ‘a’ and ‘b’ are slope and intercept, respectively, of the linear regression of the simulations versus the observations.

Author contribution L. T. Verryckt, M. Op de Beeck, B. Gielen, M. Roland and I.A. Janssens designed the study. J. Neirynck provided the O_3 mixing ratio measurements, B. Gielen provided the EC and LAI data, B. Gielen, M. Op de Beeck and L.T. Verryckt measured g_{st} in situ, and M. Op de Beeck and L.T. Verryckt conducted the modelling. All authors contributed to the writing.

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Table 1. Optimised parameter values of the multiplicative stomatal model.

g_{max} (mol O_3 m^{-2} s^{-1})	0.14
g_{min} (mol O_3 m^{-2} s^{-1})	0.02
a_{PAR}	0.0057
T_{opt} (°C)	25.61
T_{min} (°C)	5.47
VPD_{min} (kPa)	3.16
VPD_{max} (kPa)	0.51
SWP_{min} (MPa)	-1.18
SWP_{max} (MPa)	-0.19

Table 2. Performance statistics for the multiplicative stomatal model: mean bias (MB), relative mean error (RME), systematic and unsystematic root mean squared error ($RMSE_{s/u}$), Willmott's index of agreement (d), model efficiency (ME), coefficient of determination (R^2).

Statistics	**Parameterisation**	**Validation**
MB	0.002	0.002
RME	0.34	0.33
RMSE	0.019	0.019
$RMSE_s$	0.006	0.006
$RMSE_u$	0.017	0.017
d	0.99	0.99
ME	0.72	0.72
R^2	0.72	0.72

Table 3: Ranking of the parameters defining GPP in the ANN by replacing each input variable with a random permutation of its values. (A) The parameters with their mean squared error (MSE, mol m^{-2} day^{-1}) for the model without O_3 (B) The parameters with their MSE for the model with O_3. The overall model MSE without any random permutation is also shown.

Ranking Nr.	**A**	**B**
1	R_g – 37500.81	R_g – 41358.93
2	doy – 30240.61	year – 33978.09
3	year – 27486.63	doy – 31127.90
4	VPD – 15380.68	T_{soil} – 24893.78
5	T_{max} – 15323.22	T_{max} – 23567.45
6	T_{soil} – 15076.75	T_{mean} - 21354.76
7	T_{mean} – 13858.91	VPD – 16395.14
8	WV – 13369.01	T_{min} – 15418.16
9	T_{min} – 12732.96	WV – 14685.97
10	SWC – 12402.04	SWC – 12831.19
11		O_3 – 11885.73
Overall model MSE	11360.85	10019.30

Fig. 1. Fingerprint of air temperature (T_{air}), incoming global radiation (R_g), vapour pressure deficit (VPD), and measured gross primary productivity (GPP), averaged over the period 1998-2013. Day of year is plotted on the y-axis and hour of day on the x-axis.

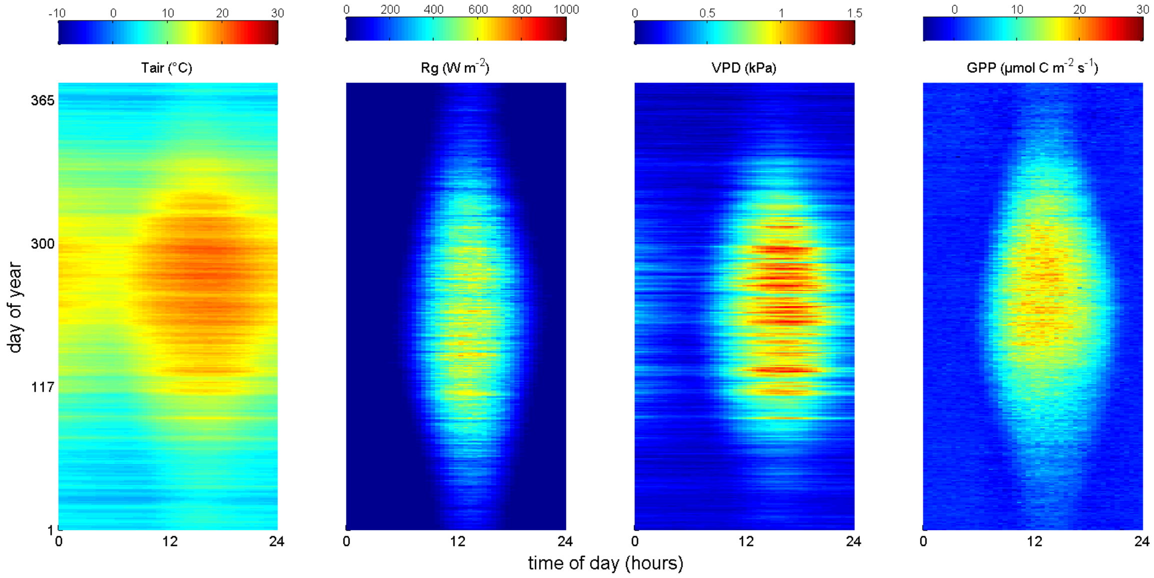


Fig. 2.Time series of the weekly total precipitation and mean soil water potential (SWP). The precipitation and SWP data are averaged over the period 1998-2013. Error bars represent the 95 % confidence intervals.

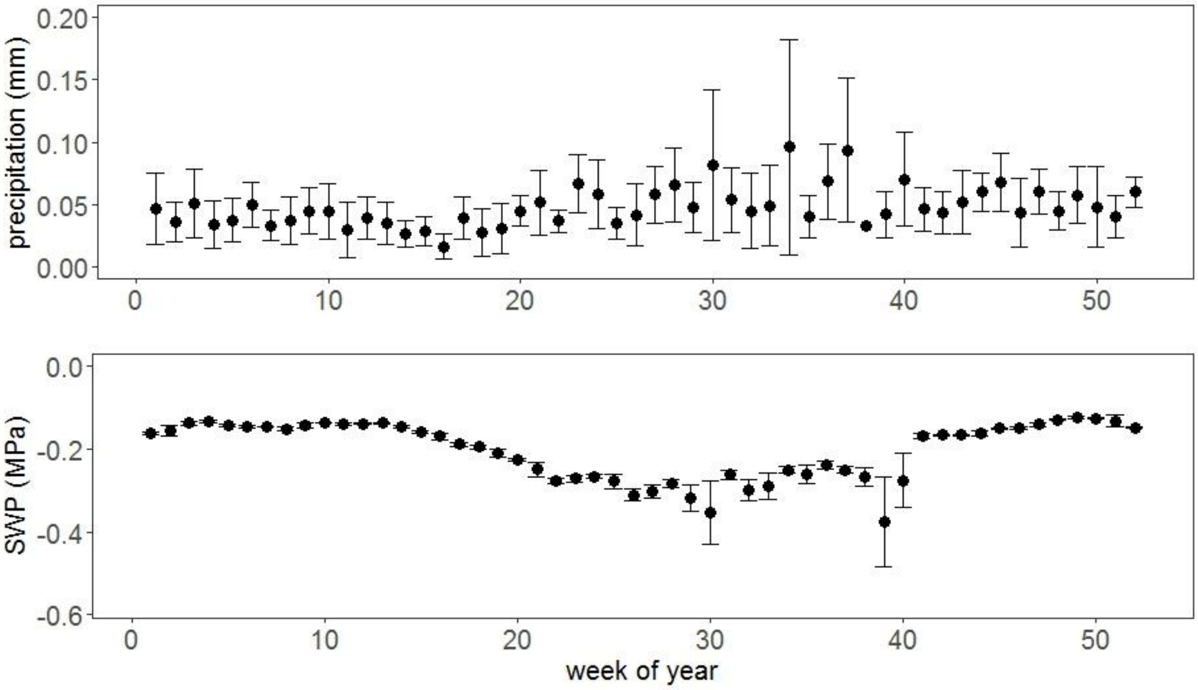


Fig. 3. Seasonal course of LAI for each of the 14 growing seasons used in this study.

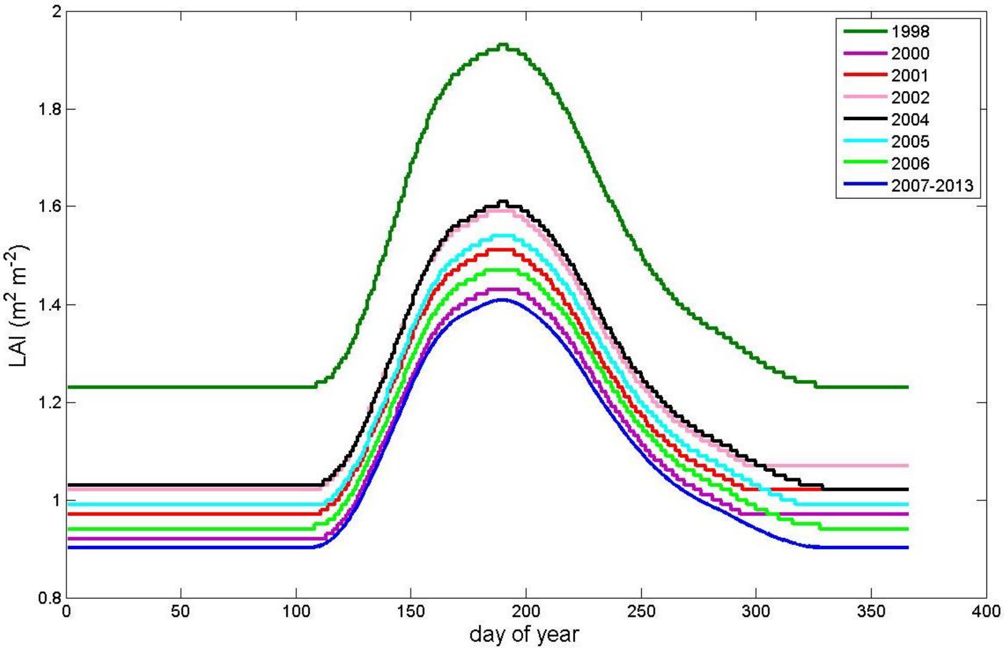


Fig. 4. Measured versus modelled stomatal conductance (g_{st}) for the parameterisation dataset (A) (n = 205) and the validation dataset (B) (n = 205). The black line is the 1:1 line. The red line is the linear fit for which the equation is given in the figure. Also shown are the p-values of test for the slope being different from 1 (p_a) and the intercept different from 0 (p_b).

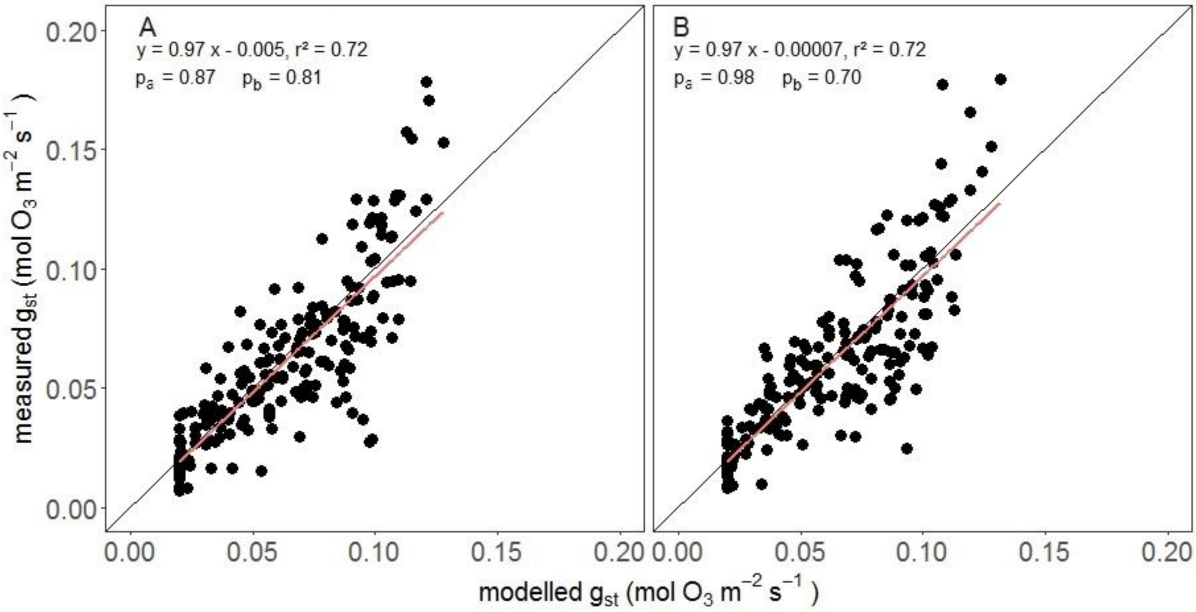


Fig. 5. Measured stomatal conductance (g_{st}) in function of the different variables used in the multiplicative model: photosynthetically active radiation (PAR), air temperature (T_{air}), vapour pressure deficit (VPD), and soil water potential (SWP). The red line represents the boundary line for which the functions are given in Appendix B (A3-A6). (n = 205)

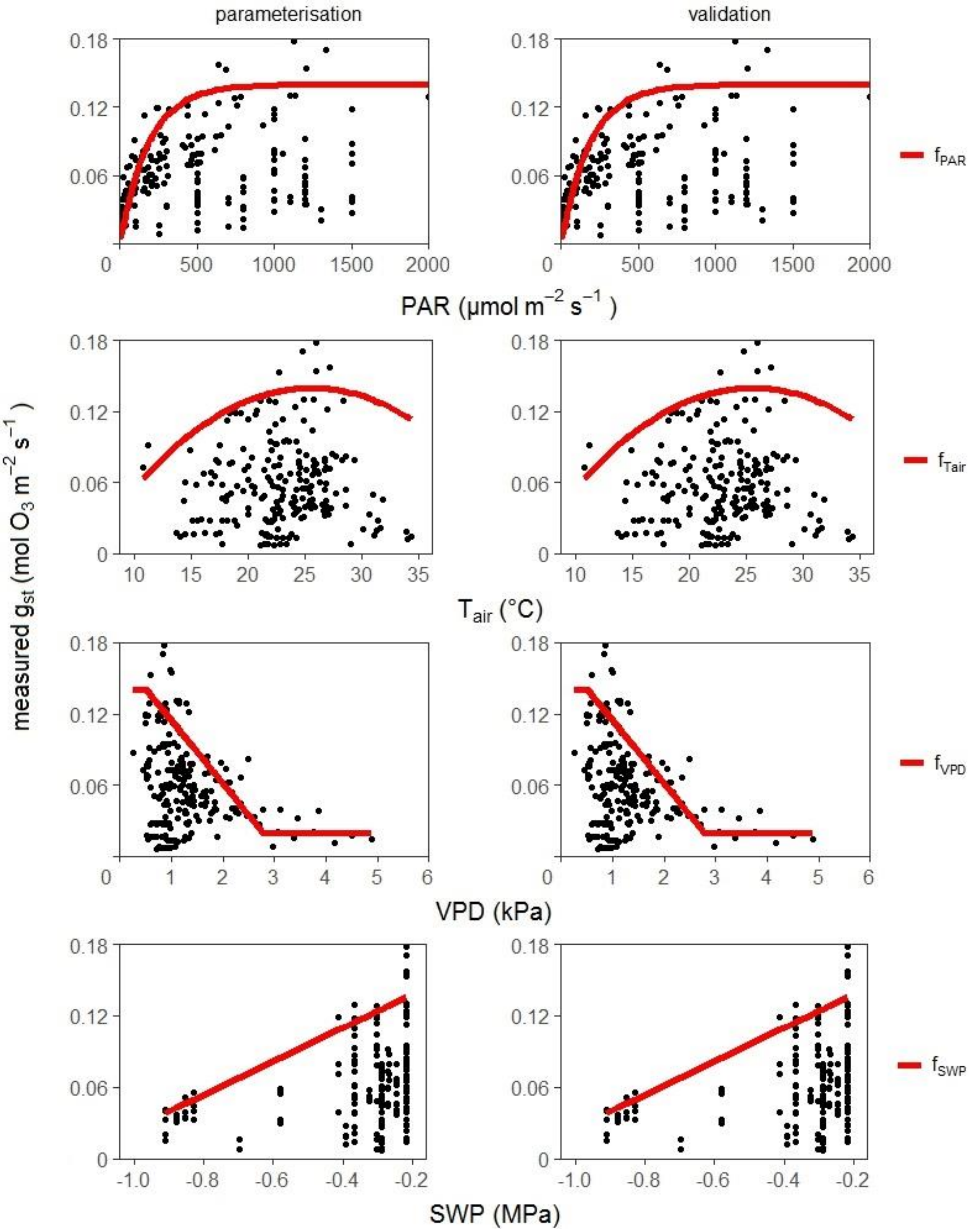


Fig. 6. Histograms of meteorological variabels for the training dataset (red) and the high O3 uptake dataset (blue). The subplots represent global radiation R_g (A), minimum temperature T_{min} (B), maximum temperature T_{max} (C), mean temperature T_{mean} (D) and vapour pressure deficit VPD (E).

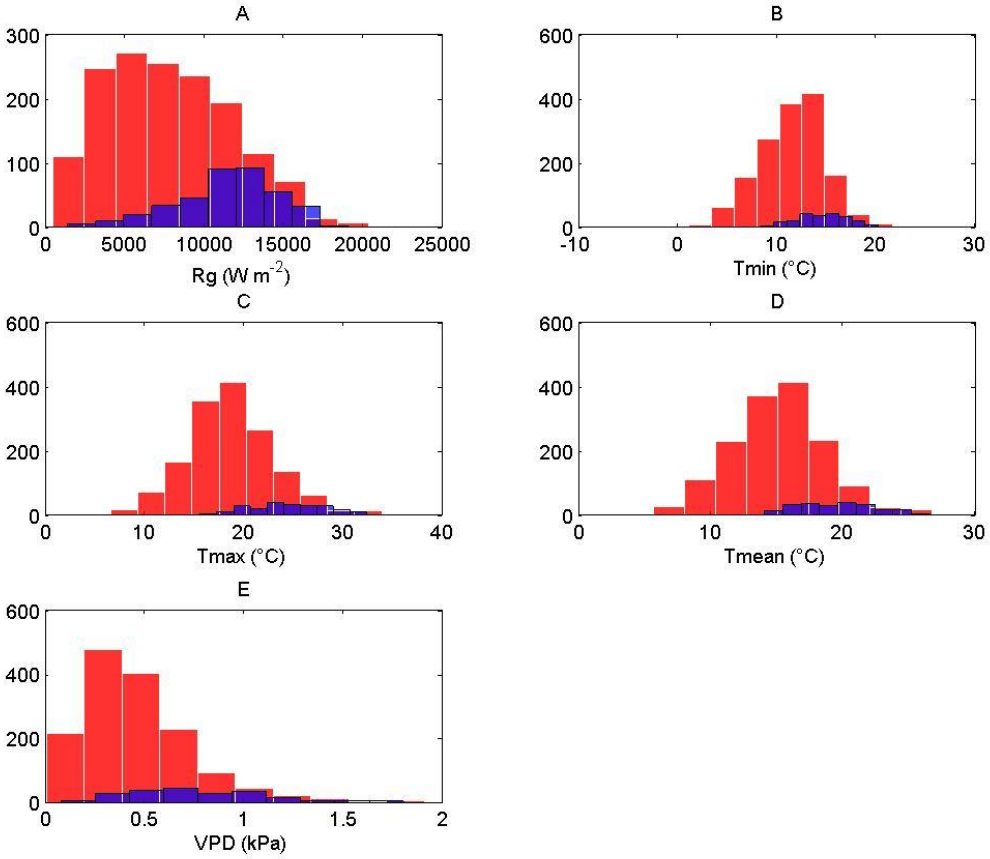
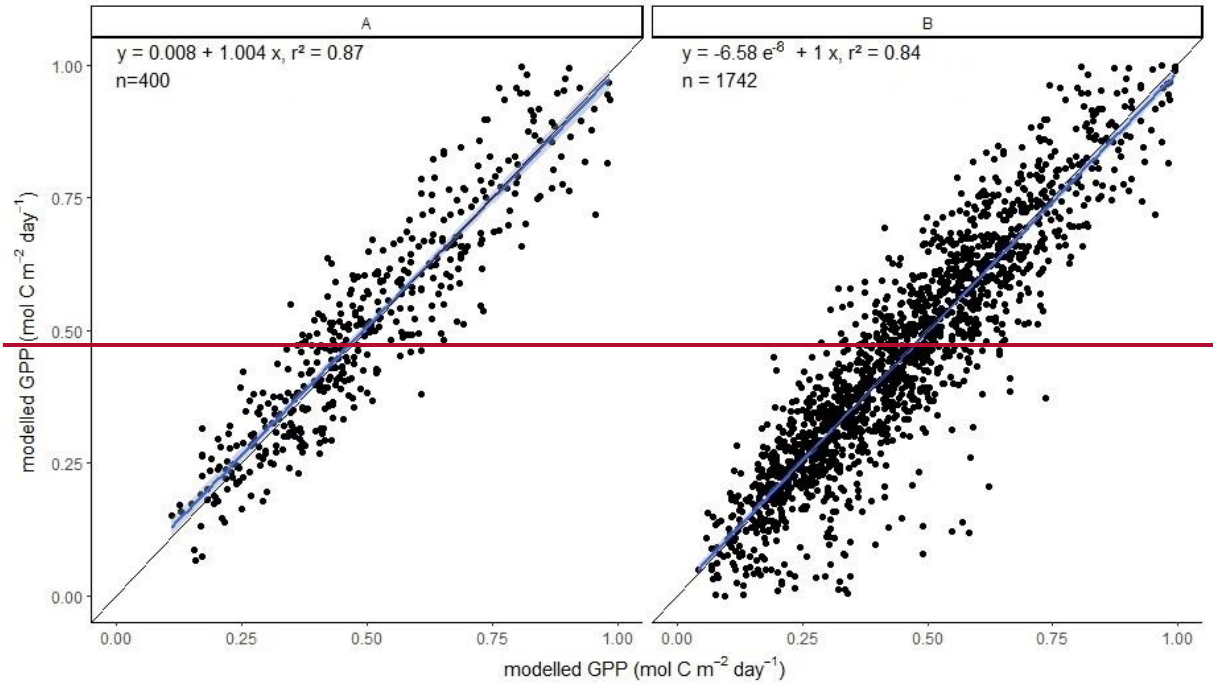


Fig. 7. Measured GPP is plotted as function of modelled GPP for two different datasets: (a) only the days before the first major O_3 peak in every year, (b) the training dataset with the days after the first major O_3 peak in every year, excluding those with high O_3 fluxes + six following days to train the network. The black line is the 1:1 line. The blue line is the regression fit including 95 % confidence intervals (in grey).



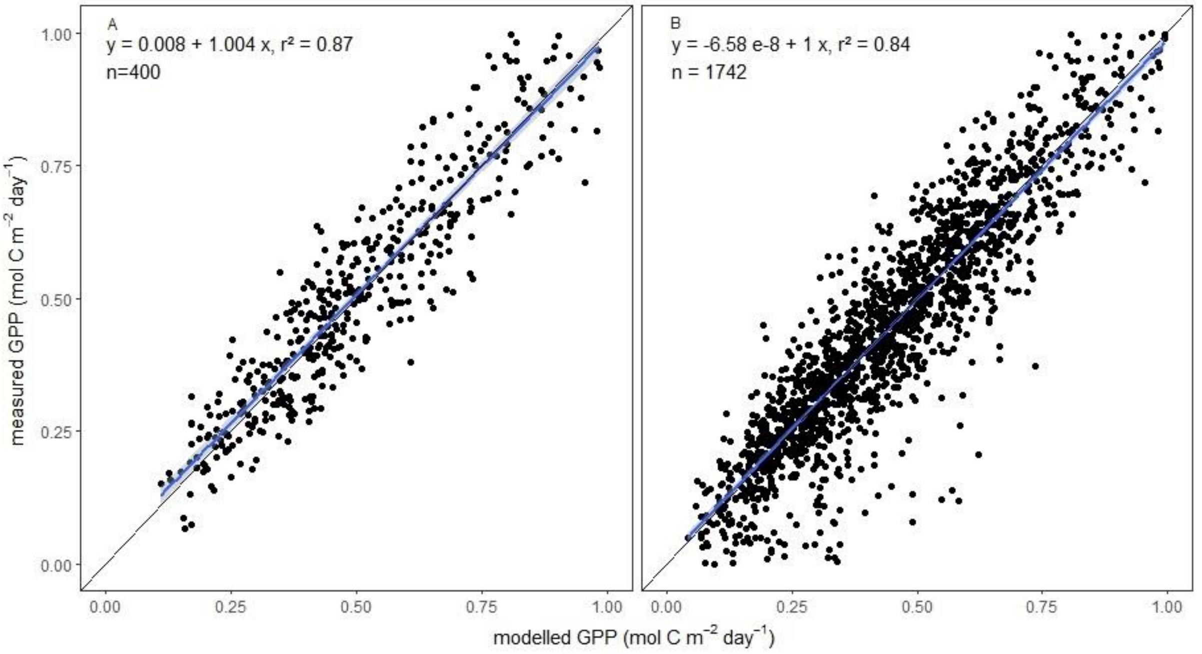


Fig. 8: Measured versus modelled gross primary productivity (GPP) for days used for model training and testing (A, B), for days on which an O_3 effect was assumed (C, D), and for the entire growing season (E, F). GPP model 1 was trained without days with the highest stomatal O_3 uptake, whereas GPP model 2 was trained to test for possible lag effects of O_3 on GPP. Black lines are fitted linear regression lines and grey lines mark the 95 % confidence bands. Also shown are p-values for the tests of slope and intercept from the regression y = a x + b being different from 1 and 0, respectively. Black lines are the fitted linear regression lines and grey lines are the 95 % confidence bands.

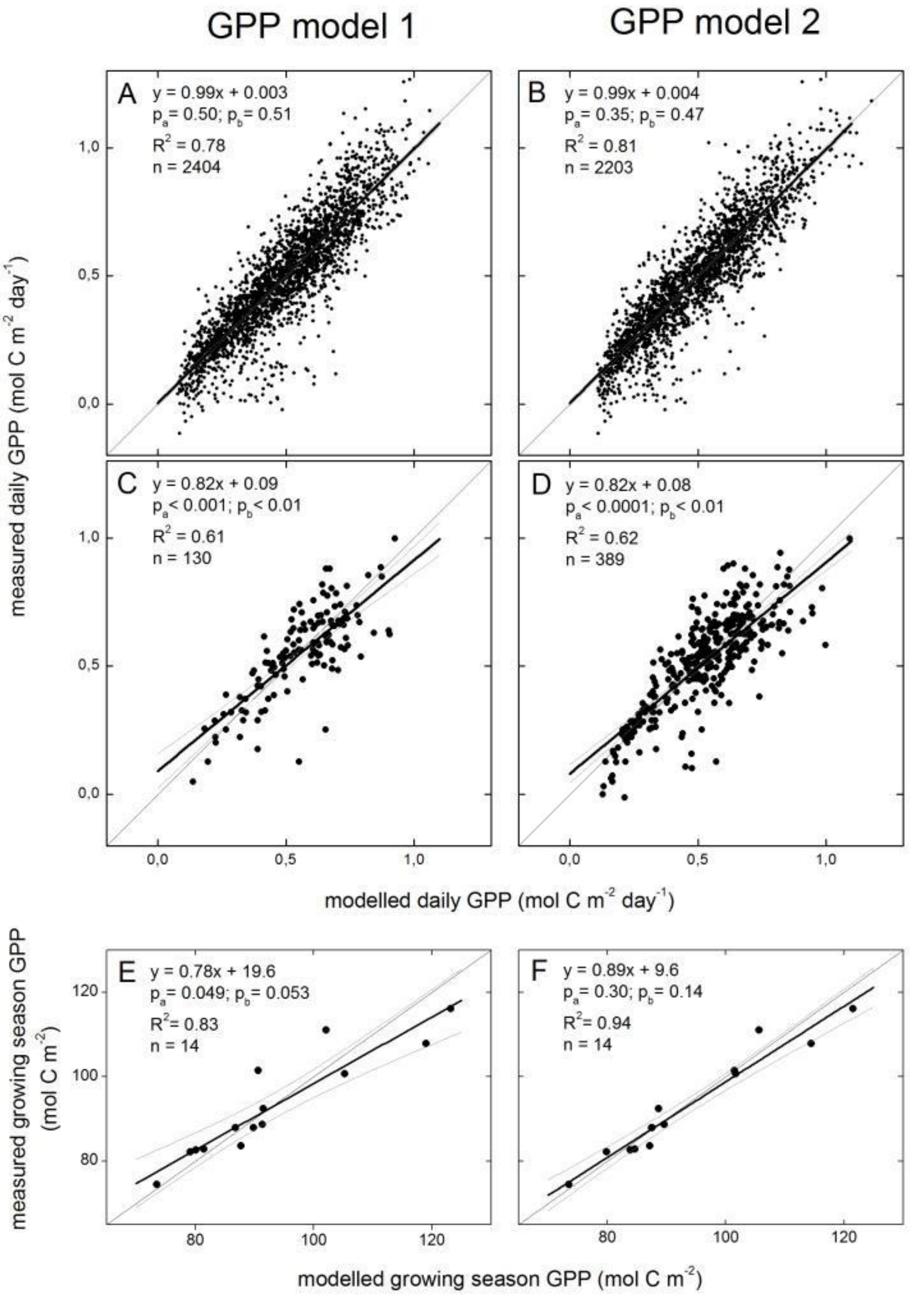


Fig. 9. Residuals of growing season gross primary productivity (GPP) in function of (A, B) total stomatal O_3 flux over the growing season (F_{st}), (C, D) AOT40, and (E, F) POD_1. PLA = projected leaf area. Negative residuals 845 indicate model overestimation of GPP. GPP model 1 was trained without days with the highest stomatal O_3 uptake, whereas GPP model 2 was trained to test for possible lag effects of O_3 on GPP. Black lines are fitted linear regression lines and grey lines mark the 95 % confidence bands. Also shown are p-values for the test of the slope and intercept from the regression y = a x + b being different from 0. (n = 14).