The development, evaluation and application of O\textsubscript{3} flux and flux-response models for additional agricultural crops.

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1. Introduction
Currently, stomatal O\textsubscript{3} flux and flux-response models only exist for wheat and potato (LRTAP Convention, 2004), as such there is a need to extend these models to include additional crop types. The possibility of establishing robust stomatal flux models for five agricultural crops (tomato, grapevine, sugar beet, maize and sunflower) was investigated. These crops were selected on consideration of their distribution across Europe, sensitivity to ozone and economic value. The stomatal flux models would be based on the DO\textsubscript{3}SE\textsuperscript{1} stomatal conductance \((g_s)\) multiplicative algorithm (MM \(g_s\)) as described in the revised UNECE Mapping Manual, (LRTAP Convention, 2004) and hence require a number of different \(g_s\) parameters and \(g_s\) relationships with environmental variables to be identified. To establish the availability of parameterisation data, a comprehensive literature search was conducted for each species. In addition, authors of scientific papers that presented \(g_s\) data in their publications were contacted in an attempt to obtain the original datasets for inclusion in parameter setting boundary line analysis. On the basis of this work, it was deemed possible to develop MM \(g_s\) models for three of the five crops selected for investigation, namely grapevine, sunflower and tomato. For the other species the current data availability was considered too limited for the definition of robust models.

The DO\textsubscript{3}SE model has been developed for application within the EMEP photo-oxidant model (Simpson et al, 2003) and is able to estimate O\textsubscript{3} dry deposition to both stomatal and non-stomatal components of vegetated surfaces. The stomatal component of this DO\textsubscript{3}SE model is that upon which the MM \(g_s\) models for wheat and potato are based. Canopy stomatal deposition is an important driver of total deposition, especially during the period of greatest physiological activity of the surface vegetation. As such, comparisons of modelled with observed total O\textsubscript{3} flux/deposition to homogenous vegetation-covered surfaces provides a useful tool to both evaluate the DO\textsubscript{3}SE model’s predictive capacity, but also to infer the role of the stomatal component of deposition and assess the importance of parameterisation of this model component. Environmental, stomatal and O\textsubscript{3} flux data collected during a campaign conducted in California (referred to here as the CODE91 campaign) are used to evaluate the DO\textsubscript{3}SE model for grapevine, and specifically the revised multiplicative \(g_s\) model parameterisation presented here. This field campaign recorded observations of total O\textsubscript{3} deposition (e.g. Massman & Grantz, 1995), enabling us to compare estimates of O\textsubscript{3} deposition with observed values.

However, the ability to faithfully simulate total deposition and O\textsubscript{3} stomatal flux is not an end in itself; to understand the impacts of absorbed O\textsubscript{3} dose requires some means of translating O\textsubscript{3} dose into effects. For wheat and potato, flux-reponse relationships have been established by relating absorbed O\textsubscript{3} doses estimated using the MM \(g_s\) model to observed effects (yield losses in grain and tuber for wheat and potato respectively). In a similar manner, the \(g_s\) models established for the three crops presented here could, in theory, also be used to derive flux-response relationships for these crops were suitable datasets identified (i.e. that provide hourly records of key environmental data and O\textsubscript{3} fumigation regimes). The possible establishment of such a relationship is discussed here in relation to an open top chamber O\textsubscript{3} fumigation study conducted by Soja et al. (2004) which provides three years worth of environmental and O\textsubscript{3} concentration
data. Re-analysis of this dataset using the updated DO\textsubscript{SE} gs multiplicative model parameterisation could provide the opportunity to establish a flux-response model for grapevine.

2. Development of stomatal flux models.

The stomatal conductance model described in the UNECE Mapping Manual (LRTAP Convention, 2004) (MM gs) is shown in Eq. 1.

\[
g_s = g_{\text{max}} \cdot \left[ \min(f_{\text{phen}}, f_{O3}) \right] \cdot f_{\text{light}} \cdot \max\left\{ f_{\text{min}}, (f_{\text{temp}} \cdot f_{\text{VPD}} \cdot f_{\text{SWP}}) \right\}
\]  

where \( g_s \) is the actual stomatal conductance (mmol \( O_3 \) m\(^{-2}\) sunlit projected leaf area (PLA) s\(^{-1}\)) and \( g_{\text{max}} \) is the species-specific maximum stomatal conductance (mmol \( O_3 \) m\(^{-2}\) PLA s\(^{-1}\)). The parameters \( f_{\text{phen}} \), \( f_{O3} \), \( f_{\text{light}} \), \( f_{\text{temp}} \), \( f_{\text{VPD}} \) and \( f_{\text{SWP}} \) are all expressed in relative terms (i.e. they take values between 0 and 1) as a proportion of \( g_{\text{max}} \). These parameters allow for the modifying influence of phenology and ozone, and four environmental variables (irradiance, temperature, water vapour pressure deficit and soil water potential) on \( g_s \) to be estimated. The fO\textsubscript{3} function is not considered further here since its parameterisation would require an extensive \( g_s \) dataset collated under O\textsubscript{3} fumigation conditions. Results of the literature search to identify data necessary for parameterisation of the MM \( g_s \) model for the five agricultural crop species (tomato, grapevine, sugar beet, maize and sunflower) are shown in Table 1.

On the basis of this work it has been possible to develop reasonably robust flux models for grapevine, sunflower and tomato, however, it should be noted that it has not been possible to find an \( f_{\text{temp}} \) relationship for sunflower (a suitable surrogate would need to be identified to apply the sunflower \( g_s \) model) and it has not been possible to establish an \( f_{\text{phen}} \) relationship for either tomato or sunflower. Maize and sugar beet are missing key parameters due to a lack of suitable data describing \( g_s \) relationships with phenology and important environmental variables. Table 1 also shows that it is not possible to parameterise the MM \( g_s \) model for any of the crop species for thermal time determined phenology (indicated by \( f_{\text{phen,e}} \) and \( f_{\text{phen,f}} \)).

### Table 1. Parameterisation of the multiplicative \( g_s \) model for five agricultural crop species based on a comprehensive literature search. The numbers in brackets refer to the published papers upon which the parameterisations are based. The grey shading indicates parameterisation founded on data with large variability.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Grapevine (\textit{Vitis vinifera})</th>
<th>Tomato (\textit{Lycopersicum esculentum})</th>
<th>Sunflower (\textit{Helianthus annuus})</th>
<th>Maize (\textit{Zea mays})</th>
<th>Sugar beet (\textit{Beta vulgaris})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g_{\text{max}} )</td>
<td>mmol ( O_3 ) m(^{-2}) PLA s(^{-1})</td>
<td>215 (16)</td>
<td>285 (8)</td>
<td>370 (15)</td>
<td>320 (3)</td>
<td>270 (10)</td>
</tr>
<tr>
<td>( f_{\text{min}} )</td>
<td>(fraction)</td>
<td>0.01 (1)</td>
<td>0.01 (1)</td>
<td>0.05 (1)</td>
<td>0.06 (2)</td>
<td>0.05</td>
</tr>
<tr>
<td>( f_{\text{phen,a}} )</td>
<td>(fraction)</td>
<td>0.2 (2)</td>
<td>-</td>
<td>0.62 (4)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( f_{\text{phen,b}} )</td>
<td>(fraction)</td>
<td>0.5 (2)</td>
<td>-</td>
<td>0.41 (4)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( f_{\text{phen,c}} )</td>
<td>days</td>
<td>60 (2)</td>
<td>-</td>
<td>34 (4)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( f_{\text{phen,d}} )</td>
<td>days</td>
<td>45 (2)</td>
<td>-</td>
<td>34 (4)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( f_{\text{phen,e}} )</td>
<td>°C days</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( f_{\text{phen,f}} )</td>
<td>°C days</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( f_{\text{light,a}} )</td>
<td>(constant)</td>
<td>0.0076 (5)</td>
<td>0.0175 (4)</td>
<td>0.002 (2)</td>
<td>0.0035</td>
<td>0.0025 (3)</td>
</tr>
<tr>
<td>( T_{\text{min}} )</td>
<td>°C</td>
<td>9 (6)</td>
<td>0 (2)</td>
<td>-</td>
<td>2 (2)</td>
<td>-</td>
</tr>
<tr>
<td>( T_{\text{opt}} )</td>
<td>°C</td>
<td>30 (6)</td>
<td>21 (2)</td>
<td>-</td>
<td>25 (2)</td>
<td>-</td>
</tr>
<tr>
<td>( T_{\text{max}} )</td>
<td>°C</td>
<td>43 (6)</td>
<td>35 (2)</td>
<td>-</td>
<td>48 (2)</td>
<td>-</td>
</tr>
<tr>
<td>( VPD_{\text{max}} )</td>
<td>kPa</td>
<td>1.6 (4)</td>
<td>1 (3)</td>
<td>1.2 (5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( VPD_{\text{min}} )</td>
<td>kPa</td>
<td>6.2 (4)</td>
<td>2.7 (3)</td>
<td>4.0 (5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( SWP_{\text{crit}} )</td>
<td>kPa</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( SWP_{\text{max}} )</td>
<td>MPa</td>
<td>-1.2 (5)</td>
<td>-0.3 (3)</td>
<td>-0.25 (8)</td>
<td>-0.12</td>
<td>-</td>
</tr>
<tr>
<td>( SWP_{\text{min}} )</td>
<td>MPa</td>
<td>-0.35 (5)</td>
<td>-1.0 (3)</td>
<td>-1.65 (8)</td>
<td>-0.8</td>
<td>-</td>
</tr>
</tbody>
</table>
since the data needed to parameterise such relationships are unavailable in the literature; only analysis of
datasets that have recorded gs over entire growing seasons in conjunction with associated mean daily
temperatures would offer the possibility of deriving these coefficients. Similarly, it has not been possible
from the literature to identify the SVPD since derivation of this parameter requires sufficient diurnal gs
measurements and associated VPD values. As such, these parameters are only presented in grey font in Table
1. For tomato, it should also be noted that there was some inconsistency in the data that have been used to
derive the f_light and f_VPD relationships.

Previous evaluations of the multiplicative gs models have found the identification of an appropriate value for
gmax to be crucial in determining the predictive abilities of the model. In view of this we present the data
describing gmax for grapevine, sunflower and tomato in Figure 1 to indicate how robust these values are. gmax
is assumed the median gmax value of all observations. In general, the lack of information describing gmax for
tomato (based only on 8 studies) is not related to problems in identifying maximum gs in papers but in the lack
of clarification of two essential pieces of information: i) the gas for which the conductance data were
recorded and ii) the leaf surface area (projected or total) on which the measurements were based. Without
this information it is not possible to use the gs data to identify gmax since values could be mis-represented by
as much as 100%. For sunflower, it is evident that there is rather large uncertainty in the derivation of gmax
with values taken from the literature ranging from 150 to over 1000 mmol O3 m2 PLA s1. The use of the
median value in effect assumes the extremely high values to be outliers.

For grapevine, further details of the gs model parameterisation are provided since a complete gs dataset was
made available (described in Jacobs et al. 1996) which allowed more robust boundary line relationships for
this species to be defined. As such, the parameterisation of the flux model for grapevine is considered the
most robust of all species investigated since the use of both published data and gs measurement datasets
provides more certainty in the fitting of the boundary lines. Figure 2 shows the data and the DO3SE model
parameterisation for the f function relationships with irradiance (PPFD, µmol m-2 s-1), air temperature (°C)
and air vapour pressure deficit (VPD, kPa) and soil water potential (inferred from measurements of pre-dawn
leaf water). The main change to the grapevine parameterisation shown here compared to that described in
Emberson et al. (2000) is in the f_VPD relationship which is now far less sensitive. This likely reflects the more
southerly distribution of grapevines and their acclimation to high atmospheric water deficits. These data
have also been used in a comparison of multiplicative and photosynthesis based gs models by Büker et al.
(this volume) to identify the most appropriate gs algorithm for use in DO3SE.

3. Evaluation of grapevine DO3SE model
The DO3SE model has been evaluated against observations of total O3 flux and gs for a number of different
ecosystem types representative of central and northern European locations (e.g. Tuovinen et al., 2001). These
have generally shown that the model performs well, although improvements in the model predications could
be achieved through “tuning” the model parameterisation for local conditions. However, the module has not
been extensively tested under Mediterranean conditions with only one comparative study (Tuovinen et al.,
2004) having been conducted to date for wheat growing in Italy. It is imperative that further evaluations
should be performed, firstly since the model should be tested under all European climate types and secondly,
since these regions are prone to co-occurring elevated ozone concentrations and high soil and atmospheric
water deficits. As such, these conditions may lead to large differences in the accumulation of exposure versus
flux-based indices that may be especially relevant to European emission abatement formulation.
Figure 1. Data used to establish $g_{\text{max}}$ for three agricultural crop species. The mean and standard deviation by species are grapevine (mean=229, S.D.=50.98); tomato (mean=284, S.D.=73.83); sunflower (mean=436, S.D.=229.07).

Figure 2. The grapevine DO$_3$SE $f$ function relationships for irradiance (PPFD, $\mu$mol m$^{-2}$ s$^{-1}$), air temperature ($^\circ$C) and air vapour pressure deficit (VPD, kPa) shown in relation to the data, collated from the literature and $g_{\text{max}}$ datasets, used in their establishment.
A Californian vineyard dataset (Massman & Grantz, 1995) collected as part of the California Ozone Deposition Experiment (CODE) during July and August of 1991, provides an opportunity to i) infer an evaluation of the DO$_3$SE grapevine $g_s$ model parameterisation through a comparison of observed and modelled total O$_3$ deposition and ii) extend the number of DO$_3$SE model evaluation studies conducted under “Mediterranean style” conditions. Measurements were taken at a grape vineyard site (Vitis vinifera L. cv. Thompson seedless) located in the San Joaquin Valley in California (36°51′36″N,120°6′7″W). There was no precipitation during the study period, but the plants had been irrigated before the start of the experiment. The sky remained virtually cloud free for the duration of the investigation. There was almost no growth in the vineyard plants, since they had reached their maximum vegetative state (LAI = 3.4, vegetation height = 1.7m). Flux data for O$_3$, heat, H$_2$O, CO$_2$ and momentum were measured half hourly using eddy covariance; corresponding measurements of meteorological variables were also made. Further details of the site measurement and data descriptions for the CODE 91 experiment are given in Massman et al. (1994).

The DO$_3$SE model as described in Emberson et al. (2000) was applied using observed reference height O$_3$ concentration and meteorological data, with the exception that the grapevine parameterisation described in Table 1 was used in place of that described in Emberson et al. (2000). Figure 3 shows a scatter plot and seasonal course of total ozone flux values modelled (using the “new” grapevine DO$_3$SE model parameterisation) in comparison with the corresponding measured O$_3$ flux data available throughout the study period. It is clear from the $R^2$ values and seasonal profile that the DO$_3$SE model is able to reproduce the seasonal diurnal profile but that the model consistently overestimates total deposition (the slope of the linear regression is approximately 0.6). The use of local parameterisation for $g_{\text{max}}$ (i.e. alteration of the value from 215 mmol O$_3$ m$^{-2}$ s$^{-1}$ to 165 mmol O$_3$ m$^{-2}$ s$^{-1}$ (i.e. within the range of $g_{\text{max}}$ extracted from the published literature) improves the prediction of the seasonal amplitude in total O$_3$ flux, although the highest modelled O$_3$ fluxes are still overestimated by approximately 20% (data not shown). The overestimation could be due to soil moisture deficit limiting actual $g_s$; this could not be introduced into the modelling since the necessary integrated root depth SWP data were not available. It may also be that the canopy $g_s$ is overestimated as all canopy leaves are assumed to be of the same age and hence have the same $f_{\text{phen}}$ relationship. In reality older leaves with lower $g_s$ may occur within the canopy, a situation that could be modelled by dividing the canopy into different leaf populations with specific $f_{\text{phen}}$ functions (as in Tuovinen et al. 2004 for wheat).

Figure 3 Scatter plot and seasonal course showing observed versus modelled total ozone flux/deposition (nmol O$_3$ m$^{-2}$ PLA s$^{-1}$) for grapevine data collected as part of the California Ozone Deposition Experiment (CODE) during July and August of 1991.

4. Development of flux-response models
The establishment of robust flux models for grapevine, tomato and sunflower identify these species for targeted future development of flux-response models. However, the establishment of such models ordinarily requires the identification of suitable O$_3$ fumigation datasets. An appropriate dataset has been obtained for
grapevines, full details of this dataset are provided in Soja et al. (2004). In summary, the data describe experiments conducted on grapevines (Vitis vinifera L.; cv. Welschriesling) that had been pre-cultivated for two years under field conditions in Eastern Austria, 30 km south of Vienna. The plants were transplanted into containers and moved to open top chambers (OTCs), ozone fumigation was started in 1994 and was continued during the growth periods until 1996. Four fumigation regimes were compared: charcoal filtered air, non-filtered air, non-filtered air + 25 nmol mol⁻¹, non-filtered air + 50 nmol mol⁻¹. Response parameters investigated were grape yield and sugar yield, the latter being defined on chemical analysis of grape juice for soluble carbohydrates. As such this dataset provides an excellent opportunity to develop flux based response relationships and re-analysis of this dataset with the revised grapevine DO₃SE gs model described in this paper will be conducted. To date, no datasets that may be appropriate for the derivation of flux-response relationships for either tomato or sunflower have been identified.

5. Conclusions
This paper has described the development of stomatal O₃ flux models for additional crop species (grapevine, tomato and sunflower) to those for which flux, and flux-response models already exist (namely, wheat and potato as described in the UNECE Mapping Manual (LRTAP Convention, 2004). The paper has highlighted the importance of the stomatal component of deposition on application of the revised grapevine DO₃SE gs model parameterisation in a study to compare modelled and measured total O₃ deposition values. This comparison suggests that the gₘₐₓ is an important driver of deposition, particularly when deposition is high during the middle of the day; as such, its parameterisation is crucial both to total deposition for O₃ mass balance modelling but also for stomatal deposition for effects modelling. In terms of effects modelling, the development of additional flux-response models should be a future priority. To this end, an O₃ fumigation dataset has been identified for grapevine that may be used with the revised grapevine DO₃SE gs model parameterisation to establish flux-effect relationships for this species. The issue of identifying an appropriate gₘₐₓ for use in this re-analysis can be dealt with by using the gs dataset collected during the fumigation study.

References