Derivation of critical absorbed doses for ozone using ozone sensitive clover clones

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Introduction

The exchange of ozone (O_3) between the atmosphere near the ground and the phytosphere is controlled by complex interactions of meteorological and biological processes. The European *critical levels* for ozone to protect vegetation have been deduced mainly from fumigation experiments in open-top chambers. As reported by several authors the application of these values in ambient air reflects the exchange process and ozone uptake insufficiently. Therefore, there is a strong need for flux-orientated concepts, which leads to a derivation of critical absorbed doses for ozone, $PAD(O_3)$, to protect vegetation.

This paper describes the derivation of such a critical absorbed dose for the onset of visible injury on the O_3 sensitive clover clone NC-S (cf Heagle et al. 1995). The study was performed in 1996 – 1999 at the Environmental Monitoring and Climate Impact Research Station Linden near Giessen, Germany (cf Grünhage et al. 1996). A standard protocol developed by the ICP Vegetation Coordination Centre was followed for the establishment of the plants (cf UNECE 2001). They were exposed in pots (∅ = 31.5 cm) at canopy height within the semi-natural grassland in Linden.

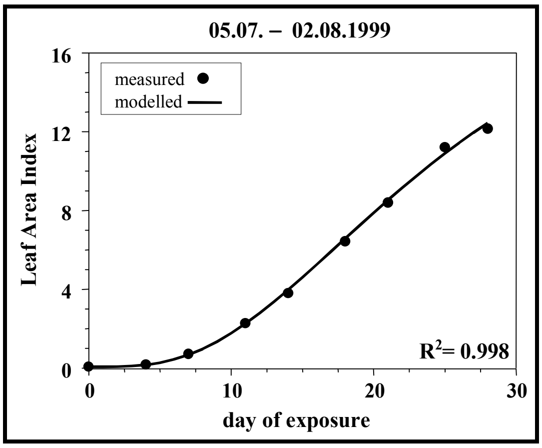

Fig. 1: Development of leaf area index (*LAI*)

Clover canopy development

Gas exchange between the clover canopies and the atmosphere is simulated using the PLant-ATmosphere INteraction model (PLATIN; cf Grünhage & Haenel 1997). Together with leaf area index and canopy height, O_3 concentration measured at a reference height above the canopy as well as horizontal wind velocity, global radiation, air temperature, air humidity, air pressure and precipitation are needed as input parameters.

The leaf area of the clover plants and canopy height (*h*) were measured every 4 days during the exposure periods in 1997 – 1999. Fig. 1 gives an example of the development of the leaf area index (*LAI*). Development of *LAI* and canopy height *h* can be described by

$$LAI = a\left(1 - \mathrm{e}^{b\,\mathrm{x}}\right)^{c} \quad \text{and} \quad h = h_0 + d\,\mathrm{x}$$

with x the running number of the days of each 28-day exposure period and h_0 the canopy height at the beginning of the exposure period. According to the protocol the exposition periods 2 – 4 of each year were analysed only. The four coefficients are summarised in Tab. 1.

Stomatal conductance

In the soil-vegetation-atmosphere-transfer (SVAT) model PLATIN the dependence of stomatal conductance (well-watered plants) on radiation, temperature and the water status of the atmosphere is described by the Jarvis-Stewart approach (Jarvis 1976, Stewart 1988). For the functions used see Grünhage and Haenel (1997).

Tab. 1: Coefficients describing development of leaf area index and canopy height

time of exposure	*leaf area index*				*canopy height* (cm)		
	a	*b*	*c*	R^2	h_0	*d*	R^2
1997							
25.06. – 21.07.	821.819	–0.00524	2.252	0.987	7.002	0.820	0.999
21.07. – 18.08.	783.149	–0.00248	1.516	0.971	6.552	0.990	0.956
18.08. – 15.09.	43.036	–0.00252	0.722	0.919	6.986	0.781	0.999
1998							
15.06. – 13.07.	1593.610	–0.00339	1.919	0.998	5.443	0.884	0.955
13.07. – 10.08.	2577.070	–0.00447	2.429	0.998	7.751	0.781	0.978
10.08. – 07.09.	184.453	–0.01021	1.987	0.999	7.740	0.644	0.980
1999							
07.06. – 05.07.	467.347	–0.00781	2.167	0.995	7.504	0.776	0.976
05.07. – 02.08.	19.391	–0.08138	4.154	0.998	5.350	0.900	0.969
02.08. – 30.08.	205.873	–0.00533	1.524	0.986	7.943	0.504	0.830

Stomatal conductance measurements for deriving the appropriate coefficients for the Jarvis-Stewart functions were performed in 1997 at leaf no. 3, 4 and 5 and in 1998 at leaf no. 3 (youngest, full developed leaf = no. 1). By means of quality controlled porometry data (n = 261) we determined for water vapour a $g_{\text{stom-leaf, max}}$ of 0.01878 m·s^{-1} (= 765 mmol·m^{-2}·s^{-1}; $R_{\text{stom-leaf, min}}$ = 53.2 s·m^{-1}). The parameterisation of the Jarvis-Stewart functions was achieved using the boundary-line analysis technique. The results are illustrated in Fig. 2a-c. The comparison of modelled vs. measured stomatal conductance $g_{\text{stom-leaf}}$ (Fig. 2d) demonstrate that the performance of the $g_{\text{stom-leaf}}$ model looks promising.

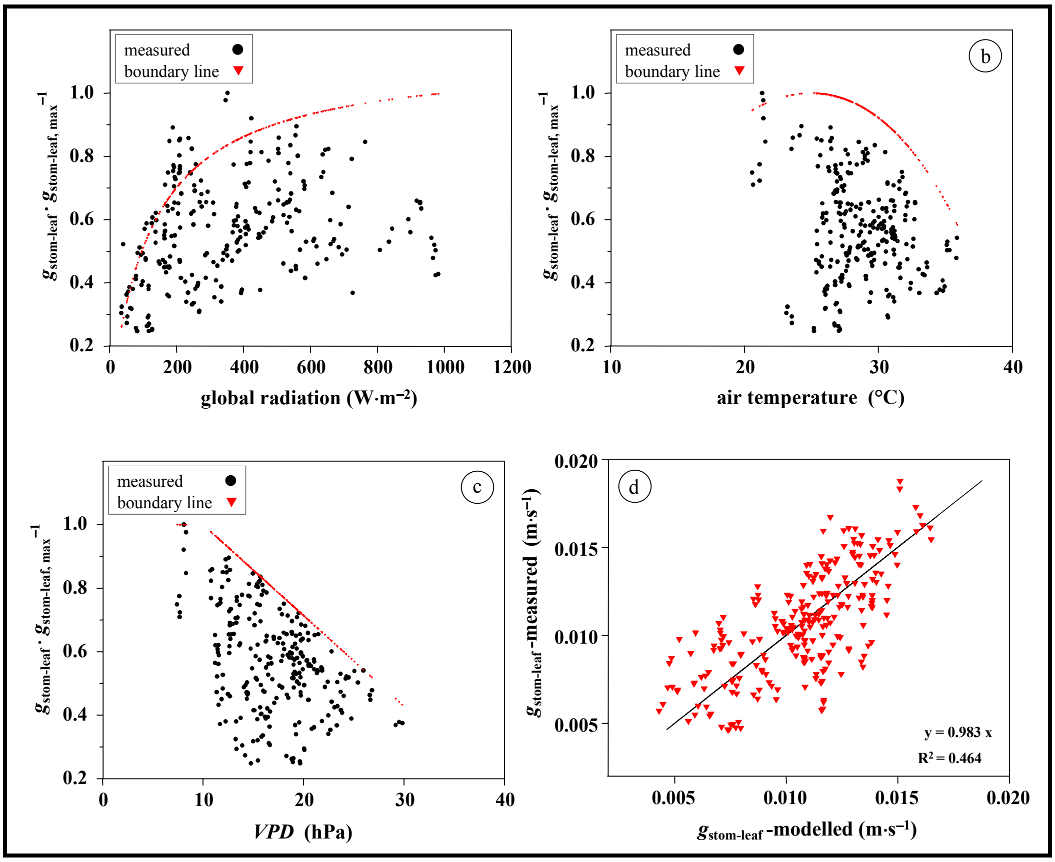

Fig. 2: Dependence of stomatal conductance $g_{\text{stom-leaf}}$ on solar radiation (a), leaf temperature (b) and *VPD* (water vapour deficit of the atmosphere) and modelled vs. measured $g_{\text{stom-leaf}}$ (d)

Because the PLATIN model follows a top-down approach, the approximation of the bulk stomatal resistance for water vapour $R_{\text{c, stom, H2O}}$ requires an up-scaling of $R_{\text{stom-leaf, H2O}}$ to canopy level. This is achieved by scaling according to leaf area index

$$R_{\text{c, stom, H2O}} = \frac{R_{\text{stom-leaf, H2O}}}{LAI},$$

resulting in a $R_{\text{c, stom, H2O, min}}$ of 8.2 s·m^{-1} for a leaf area index of 6.5 $\text{m}^2\text{·m}^{-2}$, which represents a well developed clover pot-canopy. *LAI* above 6 - 7 $\text{m}^2\text{·m}^{-2}$ indicate stages of clover canopy development, where the leaves hang over the pot rim, i.e. a situation which can not be described by the big-leaf approach. Bulk stomatal resistance for O_3 is given by

$$R_{\text{c, stom, O3}} = R_{\text{c, stom, H2O}} \cdot \frac{D_{\text{H2O}}}{D_{\text{O3}}}$$

taking into account the differences between the molecular diffusivity for water vapour D_{H2O} and ozone D_{O3}.

Applying the aforementioned Jarvis-Stewart functions, the bulk stomatal resistance $R_{\text{c, stom, H2O, min}}$ was additionally approximated by comparison of measured and modelled evapotranspiration rates of the clover pots taking into account the so-called oasis effect (cf van Eimern & Häckel 1984, Brutsaert 1984: the evapotranspiration of a small wet area embedded in a dryer environment is higher than that of an extended wet area. Thereby, the rate of increase is inversely proportional to the extension of the wet area). The adjustment leads to a $R_{\text{c, stom, H2O, min}}$ of 7.5 s·m^{-1} which is in good agreement with the up-scaled value and can be seen as an independent validation.

Validation of the big-leaf model

The PLATIN model was adjusted for pots with bare soil as well as for pots with clover using the measured 1997 and 1998 evapotranspiration rates (Fig. 3a, 4a, b). Applying the adjusted model for the 1999 data sets shows a good agreement between measured and modelled rates (Fig. 3b, 4c).

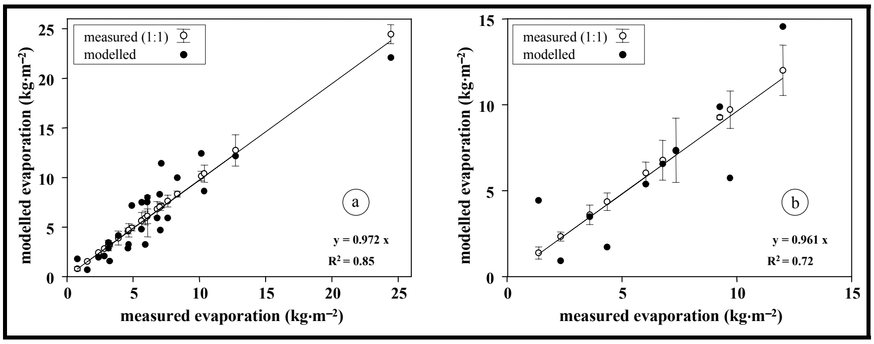

Fig. 3: Simulated vs. measured cumulative evaporation from pots with bare soil for 1997 and 1998 (a) and 1999 (b)

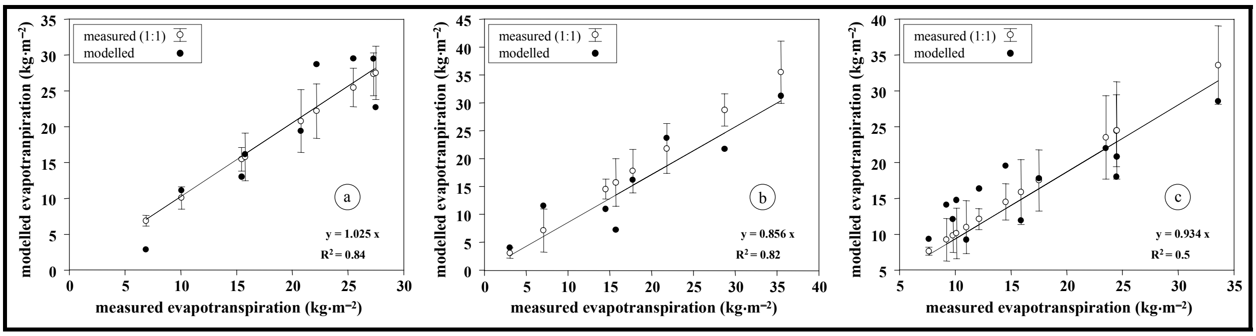

Fig. 4: Simulated vs. measured cumulative evapotranspiration of clover pots for 1997 (a), 1998 (b) and 1999 (c)

Calculation of cumulative O_3 stomatal uptake, *PAD*(O_3)

The exchange of O_3 between the phytosphere and the atmosphere near the ground, $F_{total}(O_3)$ [$\mu g \cdot m^{-2} \cdot s^{-1}$], can be modelled by:

$$F_{total}(O_3) = - \frac{\rho_{O3}(z_{ref})}{R_{ah}(d + z_{0m}, z_{ref,O3}) + R_{b,O3} + R_{c,O3}}$$

with $\rho_{O3}(z_{ref})$ the O_3 concentration measured at reference height z_{ref} [$\mu g \cdot m^{-3}$], $R_{ah}(d{+}z_{0m}, z_{ref,O3})$ the turbulent atmospheric resistance [$s \cdot m^{-1}$] describing the atmospheric transport properties between a reference height $z_{ref,O3}$ above the canopy and the conceptual height $z = d + z_{0m}$ which represents the sink for momentum (d = displacement height, z_{0m} = roughness length for momentum), $R_{b,O3}$ the quasi-laminar layer resistance [$s \cdot m^{-1}$] between momentum sink height $z = d + z_{0m}$ and the O_3 sink height $z = d + z_{0,O3}$, $R_{c,O3}$ the bulk canopy or surface resistance [$s \cdot m^{-1}$] describing the influences of the plant/soil system on the vertical exchange of O_3.

The resistance circuit allows to partition the total atmosphere-canopy flux $F_{total}(O_3)$ into the fluxes reaching the stomatal caves ($F_{absorbed}$), the external plant surfaces ($F_{external\ plant\ surfaces}$) and the soil beneath the canopy (F_{soil})

$$F_{total}(O_3) = F_{absorbed} + F_{external\,plant\,surfaces} + F_{soil}$$

The integral of $F_{absorbed}$ over time t is the ***p**ollutant **a**bsorbed **d**ose*, *PAD*(O_3) [$\mu g \cdot m^{-2}$], (Fowler & Cape 1982):

$$PAD(O_3) = \int_{t_1}^{t_2} \left| F_{absorbed}(O_3) \right| \cdot \mathrm{d}t$$

The amount of O_3 absorbed by the clover plants is calculated taking into account Kirchhoff's Current Law (cf Grünhage et al. 2002):

$$F_{absorbed}(O_3) =$$

$$- \frac{\rho_{O3}(z_{ref})}{R_{ah} + R_{b,O3} + \dfrac{R_{c,absorbed,O3}}{1-\beta^*} + \left([R_{ah} + R_{b,O3}] \cdot \dfrac{R_{c,absorbed,O3}}{1-\beta^*} \cdot \left[\dfrac{1-\beta}{R_{c,ext,O3}} + \dfrac{\beta}{R_{soil,O3}} \right] \right)}$$

with $$\frac{1}{R_{c,absorbed,O3}} = \frac{1}{R_{c,stom,O3} + R_{c,mes,O3}} + \frac{1}{R_{c,cut,O3}} \cong \frac{1}{R_{c,stom,O3} + R_{c,mes,O3}}$$

and $R_{c,mes}$ the canopy mesophyll resistance, $R_{c,cut}$ the canopy cuticle resistance, $R_{c,ext}$ the external plant surface resistance for a fully developed canopy and R_{soil} the soil resistance. β^* and β are weighting functions taking into account the actual canopy development stage (cf Grünhage & Haenel 1997).

While the simulated evapotranspiration could be validated by measured values, such a validation of the O_3 total fluxes and their partitioning could not be performed. It must be noticed that stomatal uptake calculations as proposed by e.g. Bermejo et al. (2002), Grulke et al. (2002) or Mills et al. (2002) lead to an overestimation of O_3 uptake and violate micrometeorological/physical rules.

Derivation of a *critical load* for the onset of visible injury

For the derivation of a critical absorbed dose (*critical load*) for the onset of visible injury on the NC-S clone O_3 uptake was modelled on an effective *LAI* unit according to Grünhage et al. (1999). The development of visible injury on the NC-S clover clone was monitored every 3 – 4 days, i.e. n = 89 in the four experimental years. The simulated *PAD*(O_3) accumulated over five consecutive days during daylight hours explains best for the first and the following unequivocally observed occurrence of visible injuries (n = 29). The results of four years of investigation are given in Fig. 5. It is obvious, that visible injuries appeared during periods with low to moderate (circles) as well as during periods with moderate to high (triangles) O_3 loads.

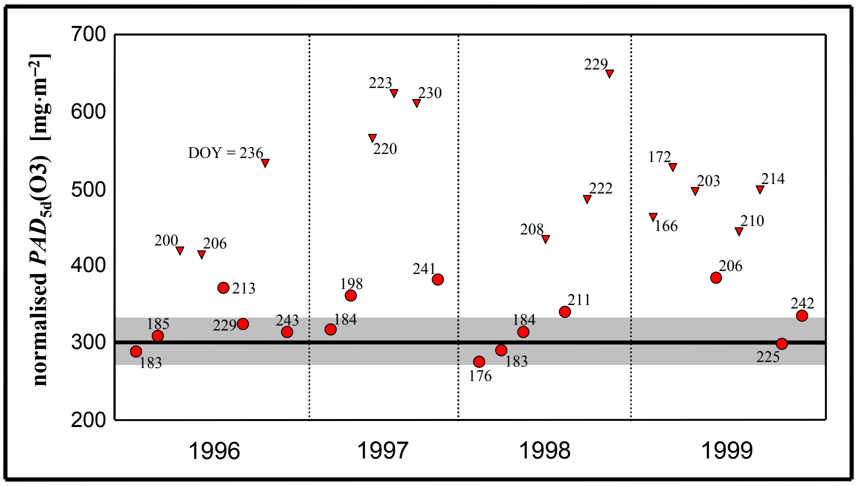

Fig. 5: O_3 stomatal uptake (*PAD*) normalised on an effective *LAI* unit and accumulated over five consecutive days during daylight hours vs. day of the year (DOY) with unequivocal records of visible injuries on the NC-S clover clone in 1996 − 1999 (visible injury was monitored every 3 − 4 days)
circles: periods with low to moderate O_3 load; triangles: periods with moderate to high O_3 load

Taking into account uncertainties due to the fact that the clover could not be monitored every day, a *critical O_3 load* of 300 ± 30 mg·m^{-2} normalised on an effective *LAI* unit and accumulated over five consecutive days during daylight hours can be deduced.

Conclusions

The approach described demonstrates the practicability of derivations of *critical loads* (cumulative stomatal uptake) for O_3 from chamber-less experiments in principle. As mentioned by Grünhage et al. (2002), the precise calculation of toxicologically effective stomatal uptake depends on the accuracy of non-stomatal deposition estimates. Therefore, it must be noticed, that an appropriate validation of O_3 flux from the atmosphere to the clover pots and the partitioning into stomatal and non-stomatal portion presupposes micrometeorological flux measurements above a white clover field.

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