Ambient flux-based critical values of ozone for protecting vegetation: differing spatial scales and uncertainties in risk assessment

L. Grünhage [1)], S.V. Krupa [2)], A.H. Legge [3)] & H.-J. Jäger [1)]

[1)] Institute for Plant Ecology, University of Giessen, Heinrich-Buff-Ring 26-32, D-35392 Giessen, Germany

[2)] Department of Plant Pathology, University of Minnesota, 495 Borlaug Hall, 1991 Buford Circle, St. Paul, Minnesota 55108, USA

[3)] Biosphere Solutions, 1601 – 11th Avenue N.W., Calgary, Alberta T2N 1H1, Canada

Abstract

The current European critical levels for ozone (O_3) to protect crops, natural and semi-natural vegetation and forest trees (Level I) are based on exposure-response relationships using the AOT40 exposure index. In the context of the revision of the 1999 UNECE multi-pollutant/multi-effect protocol that is expected in 2004 ("... no later than one year after the present Protocol enters into force"; UNECE, 1999, Article 10), a transition to a flux-based limiting value is currently under discussion. In principle, there are three alternatives for replacing the Level I approach based on European literature and scientific discussions. One alternative is a modified AOT40 index. Because of several uncertainties discussed in the literature during the recent years that approach appears questionable. The second alternative is the German VDI's MPOC (Maximum Permissible O_3 Concentration at the canopy top) concept. In contrast to the current European critical AOT40 levels, MPOC values are based on a significantly higher number of experiments, with more than 30 species for crops and wild plants and 9 species for forest trees. In principle, the MPOC concept can be applied from local, up to the European scale and fulfil the demand for the UNECE abatement strategies. The third alternative under discussion is the flux approach. Here, critical levels will have to be replaced by critical cumulative stomatal uptake (critical absorbed dose). The main problems with that approach can be attributed to uncertainties due to, (1) parameterisation of stomatal conductance (e.g. how representative are they of different geographic regions in Europe in up-scaling from leaf estimates to canopy level, (2) parameterisation of non-stomatal deposition, and (3) the representativeness of species used in flux-effect studies. Nevertheless, establishing realistic flux-effect relationships clearly requires chamber-less experiments, especially for species rich ecosystems, but will have to be based on flux estimates at the canopy level. Compared to Europe, the situation is quite different in North America. Although in general, the flux approach is well accepted by plant effects scientists there, concerted research efforts have not taken place in that direction due to a distinct lack of funding. Furthermore, because of the differences in the approach to setting ambient air quality standards in N. America, it appears very doubtful that policy makers and air quality regulators in the US and Canada will readily accept the overall philosophy.

Introduction

Tropospheric ozone (O_3) poses a critical threat and a challenging problem to present and future world food, fiber and timber production and conservation of natural plant communities, including their species diversity (Krupa et al. 2001). Some 50 years of research has taken place in the US on the adverse effects of O_3 on terrestrial vegetation. Based on the numerous studies published and the world literature, a secondary National Ambient Air Quality Standard (NAAQS) is used in the US to protect vegetation against the negative effects of O_3, while a primary standard is designed to protect human health. The current secondary standard in the US is the same as its primary 8-hour standard. That 8-hour standard is considered to be met at an ambient air quality monitoring site, when during a 3-year period, the average of the 4th highest daily maximum 8-hour mean O_3 concentration is $\leq$ 0.080 ppm (Federal Register, 1997). The Canada-Wide Standard (CWS) for O_3 is similar to the US, with the exception that the 8-hour average is 0.065 ppm (CCME, 2000).

In comparison to the long history of O_3-vegetation effects research in the US, in Europe, particularly within the UN-ECE (United Nations Economic Commission for Europe) and the European Union, as a consequence of the so-called forest die-back, since the mid 1980s, tropospheric O_3 and its impacts on human health and vegetation has received increasing attention. Although initially *critical levels* for O_3 were defined as 7-hour means over the growing period (25 ppb, 0900-1600 hrs) to protect vegetation (UN-ECE, 1988), through subsequent discussions, it was changed to an **A**ccumulated exposure index **O**ver a certain **T**hreshold, AOTx, (Fuhrer and Achermann, 1999a; EU, 2002).

However, currently there is a widespread agreement among plant effects scientists that simple air or exposure concentrations measured at some height above the surface are not very useful in relating to the corresponding plant responses, since the true underlying mechanism is the dose taken up or absorbed by the plant canopy (Krupa and Kickert, 1997). The exchange of gases between the atmosphere and the phytosphere (flux) is governed by the ambient O_3 concentration, the turbulent conductivity of the lower atmosphere, and the sink properties of the plants (Grünhage *et al.*, 1997).

Based on that principle, there is a very strong and concerted movement among the scientists within the UN-EU to arrive at a flux-based ambient O_3 air quality critical level(s) to protect vegetation. Although that represents the most desirable strategy, this paper describes some of the scientific concerns and uncertainties in applying such an approach for risk assessments at different spatial scales.

Risk assessments in the US

It is well accepted that ambient O_3 is the most important phytotoxic air pollutant in the US (Krupa *et al.*, 2001). However, at the present time, vegetation related risk assessment in the US is solely based on various exposure statistics derived from the measurements of air concentrations (US-EPA, 1996). A number of statistical yield loss functions were developed for many crops in a variety of locations using open-top chambers (OTCs). The results clearly indicated production losses due to O_3 (US-EPA, 1996). However, considerable variability was observed between and within species, between years, irrigation regimes, and environments. Combining data from 38 species in the U.S. and applying a statistical function to 7 hour mean O_3 concentration data, suggested that 11% of species would exhibit 10% yield loss when exposed to an average of 0.035 ppm and 50% of the cases at 0.050 ppm (US-EPA, 1996). Those levels of O_3 are observed during the growth season at many locations in the US (http://www.epa.gov/castnet/data.html). Extrapolation of those limited data from domesticated species grown in OTCs to the plant kingdom in general, and to the ambient environment, is subject to considerable uncertainty. However, it was estimated that O_3-induced economic damage on 8 major US crops was $1.89-3.3 billion annually (see Mauzerall and Wang, 2001). Similarly, studies have been conducted on the responses of tree seedlings and saplings to O_3 in OTCs showing adverse effects when exposed to a 7 hour average of >0.080 ppm. An analysis of ambient O_3 data for the contiguous US for the 1980-1998 period showed that the average number of summer days per year in which O_3 concentrations exceeded 0.08 ppm (level of the current secondary NAAQS) is in the range of 8-24 in the northeast and Texas and 12-73 in southern California (Lin et al. 2001). However, as with crops, a great deal of uncertainty remains regarding the extrapolation of results from seedling/sapling studies to mature trees, their populations, ambient environments, ecosystems and landscapes (US-EPA, 1996). Because of those considerations economic loss estimates are not currently available for forests and native vegetation. Nevertheless, in its final analysis**,** EPA's Clean Air Science Advisory Committee concluded that plants are more sensitive and respond more rapidly than humans to O_3 stress and therefore, the secondary NAAQS must be more stringent than the primary. However, "agreement on the level and form of such a standard is still elusive" because of "… important limitations to our understanding of the extent of the responses of vegetation to O_3 under field conditions" (Federal Register, 1997).

Risk assessments in Europe

Spatial Scales

Within the UN-ECE, it is well accepted that risk assessments should be performed at different geographic scales (Fig. 1). The development of protocols on the control of O_3 precursor emissions under the 1979 UN-ECE Convention on Long-Range Transboundary Air Pollution (LRTAP; UN-ECE, 1979) assumes that models will accurately predict the impacts of precursor pollutant control strategies on ambient O_3 concentrations and deposition across Europe. Thus, for use within the EMEP (Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe) photochemical model, a new big-leaf module was developed to estimate O_3 deposition or fluxes on to major vegetation types (Emberson *et al*., 2000a, b). Using that approach, estimates of the O_3 fluxes were based on large-scale modelled meteorology and concentration fields. Together with cumulative flux-effect relationships, outputs of the EMEP models allowed economic assessments of, for example, O_3-induced crop losses in Europe.

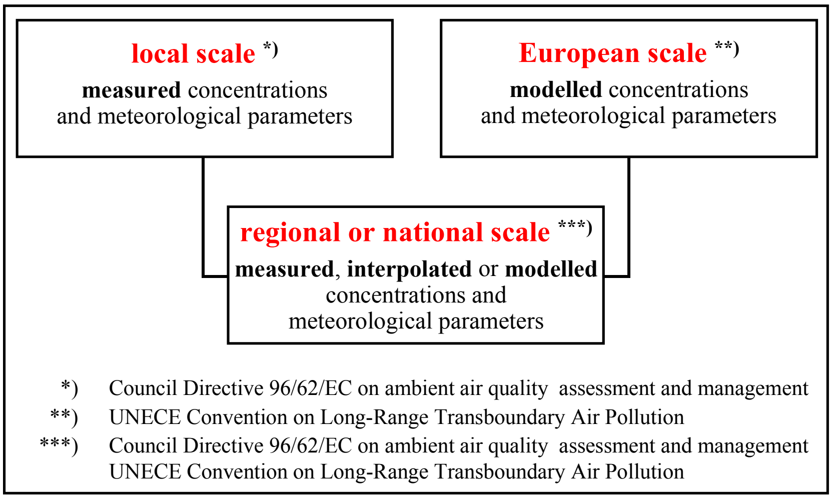

Fig. 1. Levels of risk assessments, data used and legal basis

Within the UN-ECE Mapping Programme, National Focal Centers are responsible for risk assessments at the national scale using small-scale models and data from monitoring networks (UBA, 1996). EMEP outputs can be used as boundary conditions for such national models. On the other hand, the Council Directives 96/62/EC (EU, 1996) and 2002/3/EC (EU, 2002) require risk assessment on the basis of "fixed continuous measurements" (Article 9 of EU, 2002). Such measurements for pollutant concentrations and meteorological parameters will have to be performed at local as well as on regional or national scales. That implies a network of air quality monitoring stations representative of the different geographic extents (urban, suburban, rural, rural background, and perhaps pristine air, Annex IV of EU, 2002).

Uncertainties in Critical Levels

Critical levels based on the AOT40 Level I approach are subject to several uncertainties:

- They are based on a relatively small number of experiments (17 for crops and 3 for trees; Fuhrer *et al*., 1997; Kärenlampi and Skärby, 1996);

- Only a very limited number of plant species are considered (wheat as representative of crops and semi-natural vegetation, young (0-3 yr) beech as representative of forest trees), although O_3 response data are available for other species (Grünhage *et al.*, 2001);
- Sometimes the sensitivity of the AOT40 index to variations in the input data appear to be unacceptably high (Tuovinen, 2000; Sofiev and Tuovinen, 2001).

Nonetheless, the UN-ECE Level I approach is simple and therefore attractive, however, it does not consider that the *critical levels* are related to the O_3 concentrations at the top of the canopy and not at some measurement height above the surface. It also does not consider biotic or abiotic factors that influence vegetation response to O_3. Therefore, to address these shortcomings, at the 1999 workshop on "Critical Levels for Ozone – Level II" (Gerzensee, Switzerland), three different options were identified (Fuhrer and Achermann, 1999b):

- A revision of the Level I values using factors that modify cause-effect relationships;
- A revision of the AOT40 values calculated to identify exceedances of the Level I values, using the modifying factors; and
- The development of a flux-based approach that addresses the O_3 uptake and the toxicity of the absorbed dose.

The approach of using modifying factors (cf Posch and Fuhrer, 1999) may be considered as being empirical. Similarly, based on the aforementioned uncertainties, the flux-based $AOT40_{effective}$ previously proposed by Grünhage *et al.* (1999) and Tuovinen (2000) may be considered in principle as biased.

Derivation of Flux-based Limiting Values

Any flux-based limiting value would require the application of micrometeorological Soil-Vegetation-Atmosphere-Transfer (SVAT) models, the simplest of which follows the big-leaf approach (cf Grünhage *et al.*, 2000). This SVAT model parameterises O_3 exchange $F_{total}(O_3)$ between the atmosphere near the ground and the phytosphere applying a relatively simple resistance scheme taking into account that there are sinks in the plant canopy reducing the O_3 concentration ρ_{O3} to zero (cf Laisk *et al.*, 1989; Wang *et al.*, 1995):

$$F_{\mathrm{total}}(\mathrm{O_3}) = -\frac{\rho_{\mathrm{O3}}(z_{\mathrm{ref}})}{R_{\mathrm{ah}} + R_{\mathrm{b}}(\mathrm{O_3}) + R_{\mathrm{c}}(\mathrm{O_3})} \tag{1}$$

The parameterisation of the turbulent atmospheric resistance R_{ah} describing the transport properties for O_3 between a reference height ($z_{ref,\,O3}$) above the canopy and the conceptual height ($z = d + z_{0m}$), the sink for momentum (d = displacement height, z_{0m} = roughness length for momentum) and the quasi-laminar layer resistance $R_b(O_3)$ between momentum sink height ($z = d + z_{0m}$) and the O_3 sink height ($z = d + z_{0,\,O3}$) are well accepted (Grünhage *et al.*, 2000). However, higher uncertainties exist for the parameterisation of the bulk canopy resistance $R_c(O_3)$ describing the influences of the plant-soil system on the vertical exchange of O_3.

Total O_3 flux can be partitioned into the flux absorbed by the plant through the stomata and the cuticle and the flux on the external plant surface and the soil (combined non-stomatal deposition). Investigations of cuticular permeability of O_3 and other trace gases show that penetration through the cuticle can be neglected in comparison to stomatal uptake (Kerstiens and Lendzian, 1989a, b; Lendzian and Kerstiens, 1991; Kerstiens *et al.*, 1992), thus:

$$F_{\mathrm{total}}(\mathrm{O_3}) \cong F_{\mathrm{stomatal}}(\mathrm{O_3}) + F_{\mathrm{non\text{-}stomatal}}(\mathrm{O_3}) \tag{2}$$

Because stomatal uptake $F_{stomatal}(O_3)$ is the toxicologically effective part of $F_{total}(O_3)$, flux-effect relationships should be based on that component, expressed by:

$$F_{\mathrm{stomatal}}(\mathrm{O_3}) = -\frac{\rho_{\mathrm{O3}}(z_{\mathrm{ref}})}{R_{\mathrm{ah}} + R_{\mathrm{b}}(\mathrm{O_3}) + R_{\mathrm{c,\,stomatal}}(\mathrm{O_3}) + \left[[R_{\mathrm{ah}} + R_{\mathrm{b}}(\mathrm{O_3})] \cdot R_{\mathrm{c,\,stomatal}}(\mathrm{O_3}) \cdot \dfrac{1}{R_{\mathrm{c,\,non\text{-}stomatal}}(\mathrm{O_3})} \right]} \tag{3}$$

In comparison, stomatal uptake calculations proposed for example, by Bermejo et al. (2002), Grulke et al. (2002) and Mills et al. (2002) deviate from known rules of micrometeorology or physics. Calculation of stomatal uptake by multiplying stomatal conductance with O_3 concentrations measured at some height above the canopy, neglects the influence of R_{ah}, $R_b(O_3)$ and $R_{non\text{-}stomatal}(O_3)$ on O_3 flux, resulting in an overestimation of O_3 uptake (cf Fig. 3 in Grünhage *et al.*, 2002). Therefore, any partitioning of total O_3 deposition into stomatal uptake and non-stomatal deposition has to take into account Kirchhoff's Current Law which states that the current into a node equals the current out of a node (Kirchhoff, 1845), in other words $F_{total} = F_{stomatal} + F_{non\text{-}stomatal}$.

Bulk stomatal resistance $R_{c,\,stomatal}(O_3)$ is parameterised via resistance to water vapour taking into account the differences between the molecular diffusivity for water vapour and ozone. In many SVAT models as in the EMEP big-leaf module, the dependence of bulk stomatal resistance for H_2O, on radiation, temperature and the water budgets of the atmosphere and the soil is described by the Jarvis-Stewart approach (Jarvis, 1976; Stewart, 1988). There, $R_{c,\,stomatal}(H_2O)_{min}$ represents the minimum value of the bulk stomatal resistance for water vapour and functions $f_1(S_t)$, $f_2(T)$, $f_3(VPD)$, $f_4(S_M)$ and $f_n(...)$ account for the effects of solar radiation S_t, temperature T, atmospheric water vapour deficit VPD, soil moisture SM and other factors such as the influence of plant development stage or the time of day on stomatal aperture ($0 \leq f_i \leq 1$; cf Körner *et al.*, 1995; Legge *et al.*, 1995).

$R_{c,\,stomatal}(H_2O)_{min}$ can be determined directly via micrometeorological water vapour flux measurements at the canopy level or can be estimated by an up-scaling procedure from leaf-level estimates using the leaf area index LAI (cf

Baldochi *et al.*, 1987; Kelliher *et al.*, 1995; Grünhage *et al.*, 2000). Such up-scaling procedures from leaf or twig-branch to whole canopy as applied in the EMEP big-leaf module, assume that all leaves or classes of leaves at a given time have the same potential for gas exchange and do not consider possible systematic variations in the driving forces at the leaf surface, from leaf to leaf (Jarvis, 1995). While these bottom-up approaches might be suitable for monocultures (e.g. crops), they are not appropriate for multi-species systems such as semi-natural grasslands. In addition to the uncertainties in flux estimates due to the up-scaling procedure, in principle the flux estimates can be biased if the value for the minimum stomatal resistance chosen is not appropriate or the leaf stomatal conductance model is not well calibrated. The coefficients of determination for the three sets of data in Figure 2 illustrate the difficulty with model adequacy. In that case, all measurements were performed using the same clover clone (NC-S; Heagle *et al.*, 1995) that was established following a standard protocol developed by the ICP Vegetation Coordination Centre (UN-ECE, 2001). The results show the basic necessity of validating any parameterisation of stomatal resistance via measurements of canopy level water vapour exchange.

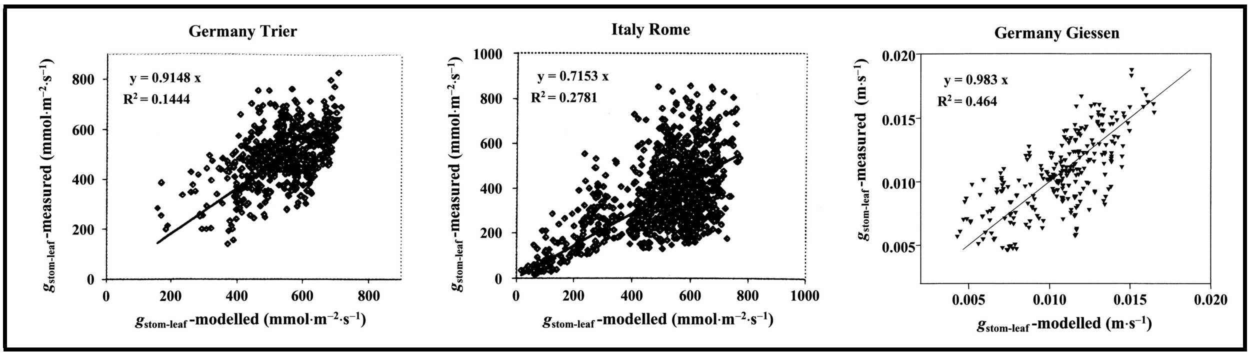

Fig. 2. Comparison between modelled and measured leaf-level stomatal conductance for a white clover clone established at three different sites in Europe (Trier, Germany [n = 775] and Rome, Italy [n = 1063]: Mills *et al.*, 2002; Linden near Giessen, Germany [n = 261]: Gavriilidou *et al.*, 2002)

Even greater uncertainty can be noticed with respect to the parameterisation of $R_{c,\ non\text{-}stomatal}(O_3)$ controlling non-stomatal deposition. $R_{c,\ non\text{-}stomatal}(O_3)$ can be estimated as the residual term in the canopy resistance if bulk stomatal resistance is known (Fowler *et al.*, 2001).

As in the EMEP big-leaf module, respectively $R_{c,\ non\text{-}stomatal}(O_3)$ components are often parameterised by constant values neglecting for example, the influence of surface wetness on the sink properties for O_3. Rondón *et al.* (1993), Coe *et al.* (1995), Fowler *et al.* (2001) and Gerosa *et al.* (2002) observed enhanced O_3 deposition to external surfaces of wheat, moorland and conifer species. Measurements by Fowler *et al.* over moorland at Auchencorth Moss in Southern Scotland showed that during a 2-year period, at a seasonal time scale, non-stomatal deposition dominated (65 %) the overall flux. The reduction of $R_{c,\ non\text{-}stomatal}(O_3)$ with increasing radiation (Fig. 3) and temperature is regarded as evidence of thermal decomposition of O_3 at the leaf surface.

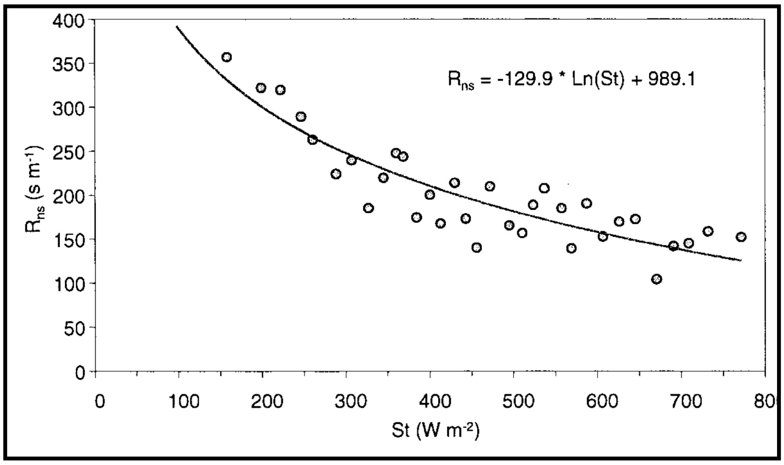

Fig. 3. The relationship between canopy resistance for non-stomatal O_3 deposition (R_{ns}) and global radiation (S_t), Auchencorth Moss daytime data. Stomatal canopy resistances ($R_{c,\ stomatal}$) for dry surfaces were estimated from water flux measurements (Fowler *et al.*, 2001)

Figure 4 illustrates the problem arising from relatively similar dial patterns of $R_{c,\ stomatal}(O_3)$ and $R_{c,\ non\text{-}stomatal}(O_3)$. Deviations can be expected only if there is a strong influence of *VPD* on stomatal aperture. Comparisons of the three flux patterns in Figure 4 show that the increase in O_3 deposition due to reduced $R_{c,\ non\text{-}stomatal}(O_3)$ during daylight hours (y = 1.144 x) can be compensated by a higher $R_{c,\ stomatal}(H_2O)_{min}$ (y = 1.003 x). This example demonstrates the need for appropriate validation procedures. Nevertheless, after validation of the parameterisation of stomatal behaviour via water vapour flux measurements, it is logical to validate parameterisation of non-stomatal deposition by micrometeorological measurements of O_3 exchange at the canopy level.

Further, modelled O_3 fluxes can be biased if air chemistry is not considered. In the first few meters above the canopy O_3 flux densities can be influenced by reaction with NO emitted from the soil and hydrocarbons emitted by the vegetation (cf Grünhage *et al*., 2000). While reaction of O_3 with NO can be important in fertilised agriculture, reactions with hydrocarbons may be significant for forest ecosystems.

Uncertainties in Flux-based Limiting Values

The application of the AOT40 *critical level* (according to its present definition), as well as the German Maximum Permissible O_3 Concentrations (MPOC; Grünhage *et al*., 2001; VDI 2310 part 6, 2002) requires the determination of O_3 concentrations at the top of the canopy, i.e. at the upper boundary of the quasi-laminar layer ($z = d + z_{0m}$), if the big-leaf approach is applied. Taking into account the aforementioned resistance parameterisations, these concentrations [$\rho_{O3}(d+z_{0m})$] can be recalculated by:

$$\rho_{O3}(d+z_{0m}) = \rho_{O3}(z_{ref}) + \left[F_{total}(O_3) \cdot R_{ah}\right] \qquad (4)$$

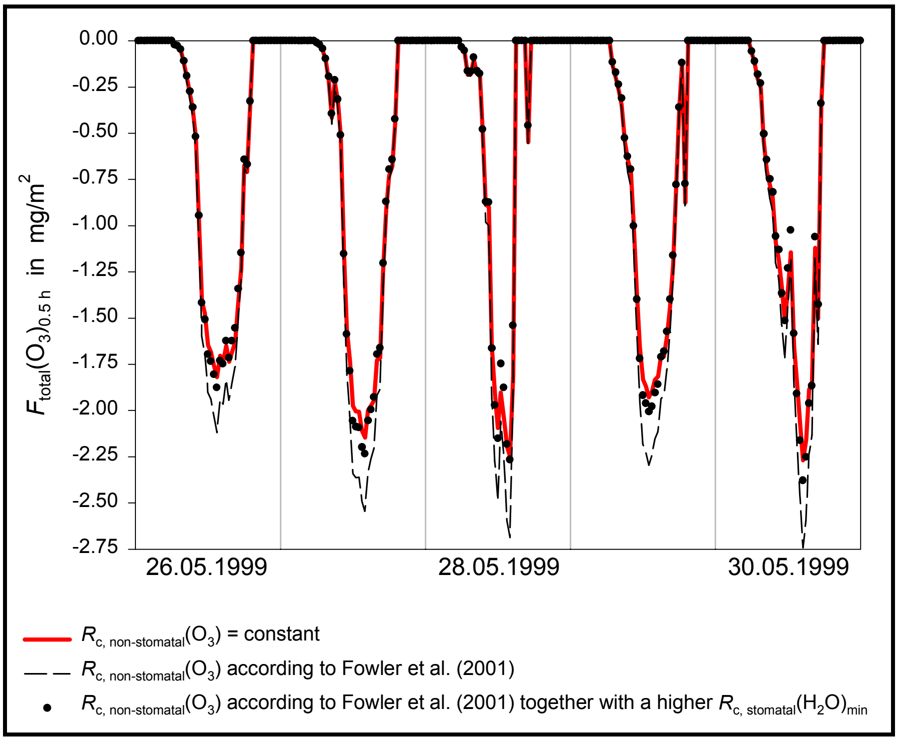

Fig. 4. Dial variation of total O_3 deposition during daylight hours (S_t > 100 W·m^{-2}) applying different parameterisations for $R_{c,\ non\text{-}stomatal}(O_3)$ and $R_{c,\ non\text{-}stomatal}(H_2O)_{min}$

It should be noted that during conditions that limit stomatal O_3 uptake such as low radiation or high water vapour pressure deficit in the atmosphere, high O_3 concentrations can occur at the top of the canopy without a significant toxicological risk. In other words, O_3 concentrations at the upper boundary of the quasi-laminar layer are not readily coupled to stomatal uptake. Thus, a correction is needed to provide toxicologically effective O_3 concentrations, by taking into account the stomatal opening. Thus, O_3 concentrations at the upper boundary of the quasi-laminar layer should be weighted with the Jarvis-Stewart factors for radiation, temperature, atmospheric water vapour pressure deficit and soil moisture.

The simplest flux-based approach is the German VDI's Maximum Permissible O_3 Concentrations (MPOC) at the canopy top (the conceptual height $z = d+z_{0m}$), rather than at some measurement height above the surface (Grünhage *et al*., 2001; VDI 2310 part 6, 2002). The MPOC values for crops, semi-natural and natural vegetation and forest trees were derived from a reanalysis, by applying a micrometeorological flux model to the 1989-1999 published data on the effects of O_3 on European plant species (see http://www.uni-giessen.de/~gf1034/ENGLISH/WINDEP.htm).

For characterising the risk to vegetation at a specific site, different types of average O_3 concentrations were calculated based on a ranking in a descending order of all half-hourly or hourly O_3 concentrations at $z = d+z_{0m}$ during the growing season of the year under consideration. Because the MPOC approach does not consider the toxicological effectiveness of the O_3 concentrations at $z = d+z_{0m}$, applying that concept can be interpreted as a 'worst-case' assessment. MPOC-risk evaluation for forests is presented in Krause *et al.* (2002) and for semi-natural vegetation discussed in Bender *et al.* (2002).

At present, the database for the derivation of critical cumulative O_3 fluxes (*critical loads*) is extremely inadequate. For spring wheat, a flux (stomatal uptake by the flag leaf) - response (relative yield) relationship was calculated from 5 open-top chamber experiments, with two "old" wheat varieties (Pleijel *et al*., 2000). Additional data on such relationships are available from open-top chamber studies with potato and the grass *Phleum pratense* (Pleijel *et al*., 2002). Because the relationships are based on leaf flux estimates, it can be argued whether they are representative of the whole canopy. For example, at the beginning of the grain filling period, the leaf area of the flag leaf represents only a fraction (20 - 25 %) of the non-senescent leaf area of the whole canopy (Pleijel *et al*., 2000). Furthermore, from an economic viewpoint, it is essential that the selected agricultural species be representative of the geographic area. In Germany for example, spring wheat represents approximately 1.6 % of the total area under wheat cultivation. Therefore, spring wheat does not appear to be the appropriate species for evaluating the risk of O_3-induced crop yield loss in that region of Europe.

Constant flux thresholds for O_3 uptake as supposed by Pleijel *et al*. (2002), appears questionable from a toxicology view point. At first, the threshold depends on the biological response parameter considered. Secondly, the threshold depends on the capacity of detoxification at the respective growth stage. The relationship between stomatal uptake and effect does not obey the law of reciprocity, according to which equal doses generate equal effects. The same cumulated stomatal O_3 uptake (pollutant absorbed dose *PAD*; Fowler and Cape, 1982)

$$PAD(\mathrm{O_3}) = \int_{t_1}^{t_2} \left| F_{\mathrm{stomatal}}(\mathrm{O_3}) \right| \cdot \mathrm{d}t \tag{5}$$

can cause more injury, shorter the time in which the dose is absorbed. In particular, high $F_{\mathrm{stomatal}}(O_3)$ can be a greater hazard if it is in sink with high O_3 concentrations and more so if that temporal relationship is repetitive. Overall, both situations lead to a premature depletion of the detoxification capacity. Consequentially, O_3 fluxes must be weighted and the frequency of the occurrences of sequentially high fluxes must be taken into account (Grünhage and Jäger, 1996, 2001).

Because until now predominant descriptions of exposure/flux-response relationships are based on chamber experiments, in principle they may be considered as biased (Jetten, 1992). Generally, O_3 exposure-response relationships derived from chamber experiments show linear or non-linear relationships between exposure and plant response. This is in contrast to the observations under ambient conditions where biological responses to O_3 exposures do not always increase with increasing exposures (Bugter and Tonneijck, 1990; Krupa *et al*., 1995). Furthermore, without any changes in the pollution climate, modifications of species composition can take place in species rich ecosystems such as the grasslands, due to the differences in radiation, air temperature and humidity between the chamber and ambient microclimates (cf Grünhage *et al*., 1990). Equally importantly, responses of a given species in isolation (monocultures) would appear to be quite different than in the presence of a competitor for resources, as in mixed plant communities and ecosystems (Andersen *et al*., 2001). Therefore it should be emphasized that realistic flux-effect relationships require chamber-less experiments (Grünhage *et al*., 2002), especially for species rich ecosystems and will have to be based on flux estimates at the canopy level.

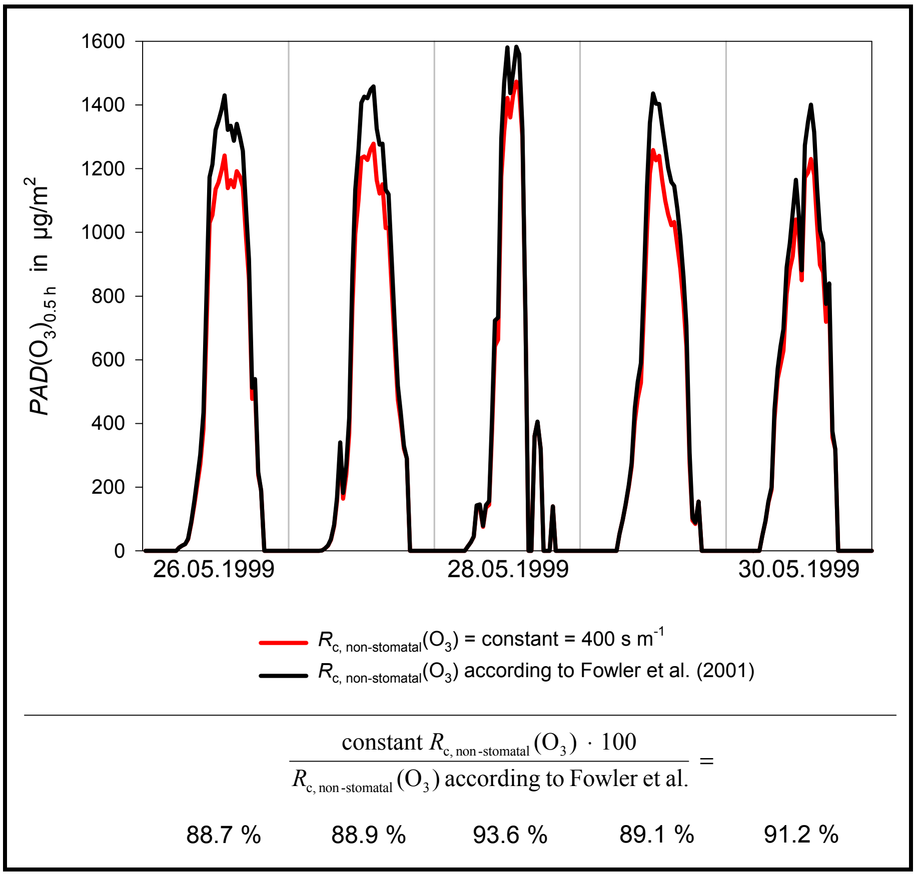

Fig. 5. Variations in absorbed O_3 doses applying different parameterisations for $R_{\mathrm{non\text{-}stomatal}}(O_3)$

The UN-ECE ICP Vegetation clover programme provided an opportunity to derive *critical O_3 loads* under chamber-less, ambient conditions. The provisional *critical absorbed O_3 dose* for the onset of visible injury on the NC-S clover clone derived by Gavriilidou *et al*. (2002) shows that the demand for validation of stomatal parameterisation via water vapour fluxes can also be achieved in pot experiments, if the so-called "oasis effect" (cf Brutsaert, 1984; van Eimern and Häckel, 1984) is taken into account. The oasis effect occurs when hot dry air blows across the edge of an oasis resulting in rapid evapo-transpiration that is governed by the sensible heat from the air and the radiant energy. Accordingly, the evapo-transpiration of a small wet area (well-watered pot of clover) embedded in a dryer environment (semi-natural grassland without irrigation) will be higher than that of an extended wet area. As illustrated in Figure 5, the pollutant-absorbed dose depends strongly on the parameterisation of non-stomatal O_3 deposition. Therefore, all of the aforementioned limiting values for O_3 to protect vegetation may not be realistic, since the values were not verified by independent experiments and by micrometeorological flux measurements.

Conceptual degrees of uncertainty for differing limiting values of O_3 to protect vegetation are illustrated in Figure 6.

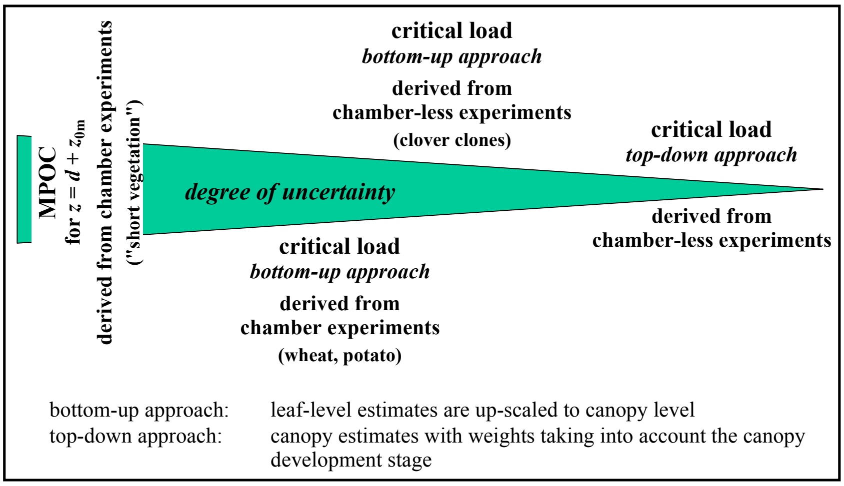

Fig. 6. Conceptual degree of uncertainty in flux-based limiting values for crops and semi-natural vegetation

Uncertainties in flux-based risk assessments

While the European O_3 risk assessments under the convention of LRTAP have a spatial grid scale of 50 km x 50 km, they have to be based on relatively generalised concepts. Site-specific meteorological conditions and pollutant climate are replaced by modelled meteorological and concentration fields, and site-specific ecosystems properties are replaced by those of a vegetation type. It is clear that such a generalised approach must be carefully calibrated by well validated models for site level risk assessments and not *vice versa*. Beside the aforementioned issues, the degree of uncertainty of the EMEP model outputs depends largely on the quality of the land use data and on the prediction of the water balance (soil moisture, atmospheric water vapour pressure deficit) of the respective vegetation types in a specific model grid.

Because the results of risk evaluations on smaller geographic scales require a higher degree of precision, they can be verified directly by for example, the farmers. In Figure 7 flux-based approaches for local scale risk evaluations for crops and natural and semi-natural vegetation are ranked by the degree of their uncertainty.

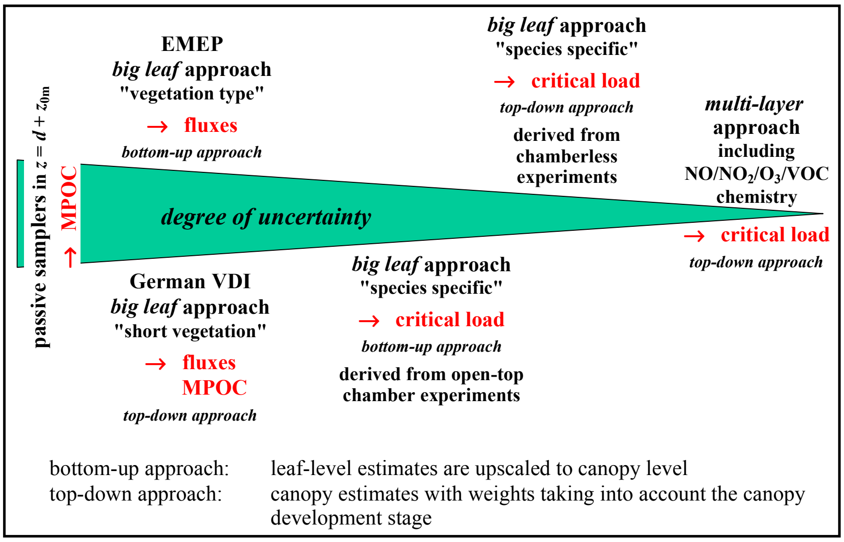

Fig. 7. Conceptual degree of uncertainty in flux-based O_3 risk assessments for crops, natural and semi-natural vegetation using measured data

There is a rapid increase in the use of passive O_3 samplers both in N. America and in Europe providing weekly or biweekly mean ambient concentrations (Krupa and Legge, 2000). Although that technology is evolving to allow the measurements of dial or diurnal concentrations, such an effort while desirable can be labour intensive and in many cases cost limiting when applied to a regional scale. While there are large uncertainties with the application of MPOC, passive samplers allow an inexpensive approach to the first order MPOC risk assessments on a local to regional scale at time scales of ≥ week (cf Krause *et al.*, 2002). Where a greater time resolution is deemed warranted, as in specific flux calculations, the preliminary studies of Krupa *et al.* (2001, 2002) that use either a Weibull probability generator or a multi-variate meteorological model represent the beginning of our efforts to simulate passive sampler data to mimic the continuously monitored frequency distributions of hourly O_3 concentrations. Overall, results from such efforts can be incorporated into the EMEP or the German VDI big-leaf model to achieve a greater utility in understanding cause-effect relationships under ambient conditions.

Conclusions

In Europe, all flux-based risk evaluations have to be based on validated models for the different climate zones, considering specific plant species, their cultivars, varieties or genotypes. Taking into account the up-scaling problems, species-specific big-leaf models based on a bottom-up approach are less precise than models based on a top-down approach. Especially for forests or highly fertilised agricultural systems, local risk evaluations based on multi-layer, Soil-Vegetation-Atmosphere-Transfer (SVAT) models, including air chemistry are more appropriate. Such extended models applied at representative sites distributed over Europe can serve as an additional fine tuning instrument for big-leaf models with a one-layered resolution of the vegetation.

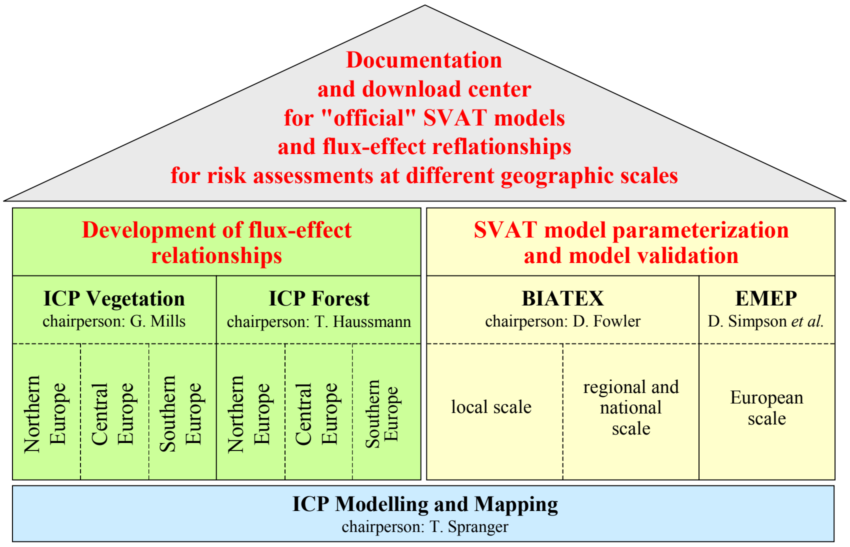

Fig. 8. Organisational chart for the establishment of *critical O_3 loads* and O_3 risk evaluation

Therefore, a network of O_3 flux monitoring sites will have to be established throughout Europe. Because on a relative scale, the existing flux-effect relationships are yet to be validated, future work will have to be directed to establishing cause-effect relationships based on chamber-less experiments at micrometeorological flux measurements sites. Progress in developing realistic risk evaluation procedures can be guaranteed only, if the existing scientific communities can come together. For Europe, integration as illustrated in Figure 8 might be reasonable. While the development of flux-effect relationships can be performed under the leadership of ICP Vegetation and ICP Forest, SVAT model parameterisation and model validation may be achieved by the BIATEX (**BI**osphere/**AT**mosphere **EX**change of Pollutants) community for local to national scales and by EMEP for the European scale. The work of those groups may be consolidated in close co-operation with the ICP Modelling and Mapping Program. It might be desirable to establish a virtual documentation group for "official" SVAT models and flux-effect relationships for risk evaluation at different geographic scales.

However, such an approach if applied to the US and Canada will have to be substantially modified based among others on the differences in the research effort and the technical organisational structure, human health considerations, on the geographic scale-climatic extent and diversity of cultivated species (crops), native vegetation and forest ecosystems. The approach to setting an air quality standard (NAAQS) in the US is very different from the EU (e.g., Federal Register, 1997). Nevertheless, some US scientists from 14 major institutions participating in an ambient O_3 – vegetation effects research project (USDA Multi-State Project # 1013) suggest as an example, that if an ambient flux-based secondary NAAQS were to be identified, although the EU might consider a time-integrated threshold or "critical level", such an approach would not capture the stochasticity of plant compensation and repair of stress that is governed by uptake beyond a point of the plant's resources and ability to cope. An alternative could be to capture the dynamics of maximal deposition and uptake. That can be accomplished by examining the time-integrated frequency distributions of the atmospheric flux and plant uptake using their percentile statistics such as the 90th or the 95th values. That is feasible to administer from a regulatory perspective, since one can develop a "Vegetation Injury Index" based on the conditions for increased O_3 synthesis/transport and period of the day and generalised climatic conditions that likely will produce maximal flux and uptake. However, for validation, such a definition must be coupled to measured plant responses. Nevertheless, it appears very doubtful that policy makers and air quality regulators in the US and Canada will readily accept such an overall philosophy.

References

Andersen, C.P., Hogsett, W.E., Plocher, M., Rodecap, K., Lee, E.H., 2001. Blue wild-rye grass competition increases the effect of ozone on pine seedlings. Tree Physiology 21, 319-327.

Baldocchi, D.D., Hicks, B.B. & Camara, P. (1987): A canopy stomatal resistance model for gaseous deposition to vegetated surfaces. Atmospheric Environment 21, 91-101.

Bender, J., Bergmann, E., Weigel, H.J., 2002. Multi-year experiments on ozone effects on semi-natural vegetation: implications for the development of critical levels. In: Background Document. Workshop on Establishing Ozone Critical Levels II under the UNECE Convention on Long-range Transboundary Air Pollution. Göteborg, Sweden, 19-22 November, 2002.

Bermejo, V., Gimeno, B.S., Granados, I., Santamaría, J., Irigoyen, J.J., Bermejo, R., Porcuna, J.L., Mills, G., 2002. Investigating indices to explain the impacts of ozone on the biomass of white clover (Trifolium repens L. cv. Regal) at inland and coastal sites in Spain. New Phytologist 156, 43-55.

Brutsaert, W., 1984. Evaporation into the atmosphere. 2nd edition. Reidel, Dordrecht.

Bugter, R.J.F., Tonneijck, A.E.G., 1990. Zichtbare beschadiging bij indicatorplanten in relatie tot ozon en zwaveldioxide. Rapport nr. R-89-10. Wageningen: Centre for Agrobiological Research, Institute for Plant Protection.

CCME – Canadian Council of Ministers of the Environment, 2000. Canada-Wide Standards for Particulate Matter (PM) and Ozone. June 5-6, 2000, Quebec City.

Coe, H., Gallagher, M.W., Choularton, T.W., Dore, C., 1995. Canopy scale measurements of stomatal and cuticular O_3 uptake by Sitka spruce. Atmospheric Environment 29, 1413-1423.

Emberson, L.D., Ashmore, M.R., Cambridge, H.M., Simpson, D., Tuovinen, J.-P., 2000a. Modelling stomatal ozone flux across Europe. Environmental Pollution 109, 403-413.
Emberson, L.D., Simpson, D., Tuovinen, J.-P., Ashmore, M.R., Cambridge, H.M., 2000b. Towards a model of ozone deposition and stomatal uptake. EMEP MSC-W Note 6/00. Oslo: Norwegian Meteorological Institute.
EU, 1996. Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management. Official Journal L 296, 21/11/1996, 55-63.
EU, 2002. Directive 2002/3/EC of the European Parliament and of the Council of 12 February 2002 relating to ozone in ambient air. Official Journal L 067, 09/03/2002, 14-30.
Federal Register, 1997. Part V. Environmental Protection Agency, 40 CFR Part 50, National Ambient Air Quality Standards for Ozone; Final Rule. Rules and Regulations. Federal Register (July 18) 62 (138), 38856-38896.
Fowler, D., Cape, J.N., 1982. Air pollutants in agriculture and horticulture. In: Unsworth, M.H., Ormrod, D.P. (Eds.), Effects of gaseous air pollution in agriculture and horticulture. Butterworth Scientific, London, pp. 3-26.
Fowler, D., Flechard, C., Cape, J.N., Storeton-West, R.L., Coyle, M., 2001. Measurements of ozone deposition to vegetation quantifying the flux, the stomatal and non-stomatal components. Water, Air, and Soil Pollution 130, 63-74.
Fuhrer, J., Achermann, B., 1999a. Critical Levels for Ozone - Level II. Environmental Documentation 115. Bern, Switzerland: Swiss Agency for the Environment, Forests and Landscape.
Fuhrer, J., Achermann, B., 1999b. Workshop summary. In: Fuhrer, J., Achermann, B. (Eds.), Critical Levels for Ozone - Level II. Environmental Documentation 115. Bern, Switzerland: Swiss Agency for the Environment, Forests and Landscape, pp. 13-15.
Fuhrer, J., Skärby, L., Ashmore, M.R., 1997. Critical levels for ozone effects on vegetation in Europe. Environmental Pollution 97, 91-106.
Gavriilidou, M., Grünhage, L., Jäger, H.-J., 2002. Derivation of critical absorbed doses for ozone using ozone sensitive clover clones. In: Background Document. Workshop on Establishing Ozone Critical Levels II under the UNECE Convention on Long-range Transboundary Air Pollution. Göteborg, Sweden, 19-22 November, 2002 (http://www.uni-giessen.de/~gf1034/pdf/Clover.pdf).
Gerosa, G., Cieslik, S., Ballarin-Denti, A., 2002. Partitioning of ozone fluxes between stomatal and other pathways over a wheat field in the Po River Plain during the growing season. In: Midgley, P.M., Reuther, M. (Eds.), Proceedings from the EUROTRAC-2 Symposium 2002. Margraf Verlag, Weikersheim, in press.
Grulke, N.E., Preisler, H.K., Fan, C.C., Retzlaff, W.A., 2002. A statistical approach to estimate O_3 uptake of ponderosa pine in a mediterranean climate. Environmental Pollution 119, 163-175.
Grünhage, L., Jäger, H.-J., 1996. Critical levels for ozone, ozone exposure potentials of the atmosphere or critical absorbed doses for ozone: a general discussion. In: Kärenlampi, L., Skärby, L. (Eds.), Critical levels for ozone in Europe: testing and finalizing the concepts. UN-ECE workshop report. University of Kuopio, Department of Ecology and Environmental Science, Kuopio, Finland, pp. 151-168.
Grünhage, L., Jäger, H.-J., 2001. Austausch von Stoffen zwischen Atmosphäre und Biosphäre. In: Guderian, R. (Ed.): Handbuch der Umweltveränderungen und Ökotoxikologie. Band 2a: Terrestrische Ökosysteme: Immissionsökologische Grundlagen - Wirkungen auf Boden - Wirkungen auf Pflanzen. Springer, Berlin, pp. 227-271.
Grünhage, L., Bender, J., Schaaf, S., Dämmgen, U., Weigel, H.J., Jäger, H.-J, 2002. A chamber-less approach to derive flux-effect relationships for crops and semi-natural vegetation. In: Background Document. Workshop on Establishing Ozone Critical Levels II under the UNECE Convention on Long-range Transboundary Air Pollution. Göteborg, Sweden, 19-22 November, 2002 (http://www.uni-giessen.de/~gf1034/pdf/SPIDER.pdf).
Grünhage, L., Haenel, H.-D., Jäger, H.-J., 2000. The exchange of ozone between vegetation and atmosphere: micrometeorological measurement techniques and models. Environmental Pollution 109, 373-392.
Grünhage, L., Hertstein, U., Schlecht-Pietsch, S., Jäger, H.-J., 1990. Auswirkungen von Luftverunreinigungen auf die ober- und unterirdische Biomasse eines Grünlandökosystems. In: Verein Deutscher Ingenieure (Ed.), Wirkungen von Luftverunreinigungen auf Böden. Einträge, Bewertung, Regelungen. VDI Berichte 837, Düsseldorf, pp. 633-652.
Grünhage, L., Jäger, H.-J., Haenel, H.-D., Hanewald, K., Krupa, S., 1997. PLATIN (PLant-ATmosphere INteraction) II: co-occurrence of high ambient ozone concentrations and factors limiting plant absorbed dose. Environmental Pollution 98, 51-60.
Grünhage, L., Jäger, H.-J., Haenel, H.-D., Löpmeier, F.-J., Hanewald, K., 1999. The European critical levels for ozone: improving their usage. Environmental Pollution 105, 163-173.
Grünhage, L., Krause, G.H.M., Köllner, B., Bender, J., Weigel, H.-J., Jäger, H.-J., Guderian, R., 2001. A new flux-orientated concept to derive critical levels for ozone to protect vegetation. Environmental Pollution 111, 355-362.
Heagle, A.S., Miller, J.E., Chevone, B.I., Dreschel, T.W., Manning, W.J., Mc Cool, P.M., Morrison, C.L., Neely, G.E., Rebbeck, J., 1995, Response of a white clover indicator system to tropospheric ozone at eight locations in the United States. Water, Air, and Soil Pollution 85, 1373-1378.
Jarvis, P.G., 1976. The interpretation of the variations in leaf water potential and stomatal conductance found in canopies in the field. Philosophical Transactions of the Royal Society of London Series B - Biological Sciences 273, 593-610.
Jarvis, P.G., 1995. Scaling processes and problems. Plant, Cell and Environment 18, 1079-1089.
Jetten, T.H., 1992. Physical description of transport processes inside an open-top chamber in relation to field conditions. Ph.D. dissertation. Agricultural University, Wageningen, The Netherlands.
Kärenlampi, L., Skärby, L., 1996. Critical levels for ozone in Europe: testing and finalizing the concepts. UN-ECE workshop report. Kuopio: University of Kuopio, Department of Ecology and Environmental Science, Kuopio, Finland.
Kelliher, F.M., Leuning, R., Raupach, M.R., Schulze, E.-D., 1995. Maximum conductances for evaporation from global vegetation types. Agricultural and Forest Meteorology 73, 1-16.
Kerstiens, G., Lendzian, K.J., 1989a. Interactions between ozone and plant cuticles. I. Ozone deposition and permeability. New Phytologist 112, 13-19.
Kerstiens, G., Lendzian, K.J., 1989b. Interactions between ozone and plant cuticles. II. Water permeability. New Phytologist 112, 21-27.
Kerstiens, G., Federholzner, R., Lendzian, K.J., 1992. Dry deposition and cuticular uptake of pollutant gases. Agriculture, Ecosystems and Environment 42, 239-253.
Kirchhoff, G., 1845. Ueber den Durchgang eines elektrischen Stromes durch eine Ebene, insbesondere durch eine kreisförmige. Annalen der Physik und Chemie - Poggendorffs Annalen 64, 497-514.
Körner, Ch., Perterer, J., Altrichter, C., Meusburger, A., Slovik, S., Zöschg, M., 1995. Ein einfaches empirisches Modell zur Berechnung der jährlichen Schadgasaufnahme von Fichten- und Kiefernadeln. Allgemeine Forst- und Jagdzeitung 166, 1-9.
Krause, G.H.M., Köllner, B., Grünhage, L., 2002. Effects of ozone on European forest tree species – a concept of local risk evaluation within ICP-Forest. In: Background Document. Workshop on Establishing Ozone Critical Levels II under the UNECE Convention on Long-range Transboundary Air Pollution. Göteborg, Sweden, 19-22 November, 2002 (http://www.uni-giessen.de/~gf1034/pdf/Forest.pdf).
Krupa, S., McGrath, M.T., Andersen, C.P., Booker, F.L., Burkey, K.O., Chappelka, A.H., Chevone, B.I., Pell, E.J., Zilinskas, B.A., 2001. Ambient ozone and plant health. Plant Disease 85,4-12.
Krupa, S., Nosal, M., Peterson, D.L., 2001. Use of passive ozone (O_3) samplers in vegetation effects assessment. Environmental Pollution 112, 303-309.
Krupa, S., Nosal, M., Ferdinand, J.A., Stevenson, R.E., Skelly, J.M., 2002. A multi-variate statistical model integrating passive sampler and meteorology data to predict the frequency distributions of hourly ambient ozone (O_3) concentrations. Environmental Pollution, in press.
Krupa, S.V., Kickert, R.N., 1997. Considerations for establishing relationships between ambient ozone (O_3) and adverse crop response. Environmental Review 5, 55-77.

Krupa, S.V., Legge, A.H., 2000. Passive sampling of ambient, gaseous air pollutants: an assessment from an ecological perspective. Environmental Pollution 107, 31-45.

Krupa, S.V., Grünhage, L., Jäger, H.-J., Nosal, M., Manning, W.J., Legge, A.H., Hanewald, K., 1995. Ambient ozone (O_3) and adverse crop response: a unified view of cause and effect. Environmental Pollution 87, 119-126.

Laisk, A., Kull, O., Moldau, H., 1989. Ozone concentration in leaf intercellular air spaces is close to zero. Plant Physiology 90, 1163-1167.

Legge, A.H., Grünhage, L., Nosal, M., Jäger, H.-J., Krupa, S.V., 1995. Ambient ozone and adverse crop response: an evaluation of North American and European data as they relate to exposure indices and critical levels. Journal of Applied Botany 69, 192-205.

Lendzian, K.J., Kerstiens, G., 1991. Sorption and transport of gases and vapors in plant cuticles. Reviews of Environmental Contamination and Toxicology 121, 65-128.

Lin, C.-Y.C., Jacob. J., Fiore, A.M., 2001. Trends in exceedances of ozone air quality standard in the continental United States, 1980-1998. Atmospheric Environment 35, 3217-3228.

Mauzerall, D.L., Wang, X., 2001. Protecting agricultural crops from the effects of tropospheric ozone exposure: reconciling science and standard setting in the United States, Europe, and Asia. Annual Review of Energy and the Environment 26, 237-268.

Mills, G., Hayes, F., Emberson, L., 2002. Modelling stomatal conductance and ozone flux for NC-S and NC-R white clover (Trifolium repens) biotypes: statistical and multiplicative flux modelling. In: Background Document. Joint ICP Vegetation/EMEP Ad-hoc Expert Panel Meeting on Modelling and Mapping of Ozone Flux and Deposition to Vegetation to be held under the UN/ECE Convention on Long-range Transboundary Air Pollution. Harrogate, U.K., 16-19 June.

Pleijel, H., Danielsson, H., Karlsson, G.P., Gelang, J., Karlsson, P.E., Selldén, G., 2000. An ozone flux-response relationship for wheat. Environmental Pollution 109, 453-462.

Pleijel, H., Danielsson, H., Karlsson, P.G., Persson, K., Karlsson, P.E., 2002. Linking modelled flux to impacts on vegetation. In: Background Document. Joint ICP Vegetation/EMEP Ad-hoc Expert Panel Meeting on Modelling and Mapping of Ozone Flux and Deposition to Vegetation to be held under the UN/ECE Convention on Long-range Transboundary Air Pollution. Harrogate, U.K., 16-19 June.

Posch, M., Fuhrer, J., 1999. Mapping Level-II exceedance of ozone critical levels for crops on a European scale: The use of correction factors. In: Fuhrer, J., Achermann, B. (Eds.), Critical Levels for Ozone - Level II. Environmental Documentation 115. Bern, Switzerland: Swiss Agency for the Environment, Forests and Landscape, pp. 49-53.

Rondón, A., Johansson, C., Granat, L., 1993. Dry deposition of nitrogen dioxide and ozone to coniferous forests. Journal of Geophysical Research 98 (D3), 5159-5172.

Sofiev, M., Tuovinen, J.-P., 2001. Factors determining the robustness of AOT40 and other ozone exposure indices. Atmosheric Environment 35, 3521-3528.

Stewart, J.B., 1988. Modelling surface conductance of pine forest. Agricultural and Forest Meteorology 43, 19-35.

Tuovinen, J.-P., 2000. Assessing vegetation exposure to ozone: properties of the AOT40 index and modifications by deposition modelling. Environmental Pollution 109, 361-372.

UBA – Umweltbundesamt, 1996. Manual on methodologies and criteria for mapping critical levels/loads and geographical areas where they are exceeded. Texte 71/96. Umweltbundesamt, Berlin.

UN-ECE, 1979, Convention on Long-Range Transboundary Air Pollution of 13 November 1979. http://www.unece.org/lrtap/conv/lrtap_c.htm.

UN-ECE, 1988, ECE critical levels workshop report. Bad Harzburg, Germany, 14-18 March 1988. Final draft report. United Nations - Economic Commission for Europe.

UNECE, 1999, Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution to Abate Acidification, Eutrophication and Ground-Level Ozone. Gothenburg, thirthieth day of November.

UNECE, 2001, ICP Vegetation experimental Protocol for 2001. ICP Vegetation Coordination Centre, CEH Bangor, UK.

US-EPA, 1996, Air quality criteria for ozone and related photochemical oxidants. Vol. II. EPA/600/P-93/004bF. Research Triangle Park, NC: US Environmental Protection Agency, National Center for Environmental Assessment.

van Eimern, J., Häckel, H., 1984. Wetter- und Klimakunde. Stuttgart: Ulmer.

VDI 2310 part 6, 2002. Maximum immission values to protect vegetation. Maximum immission concentrations for ozone. Beuth, Berlin.

Wang, D., Hinckley, M., Cumming, A.B., Braatne, J., 1995. A comparison of measured and modeled ozone uptake into plant leaves. Environmental Pollution 89, 247-254.