

# Preliminary results of modeled ozone uptake for *Fagus sylvatica* L. trees at selected EU/UN-ECE intensive monitoring plots

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*Data sets of the EU and UN-ECE/ICP-Forests monitoring network are examined regarding their suitability for the modeling of ozone uptake in trees in the view of risk assessment.*

## Abstract

The objective of this study was to establish whether EU and UN-ECE/ICP-Forests monitoring data (i) provide the variables necessary to apply the flux-based modeling methods and (ii) meet the quality criteria necessary to apply the flux-based critical level concept. Application of this model has been possible using environmental data collected from the EU and UN-ECE/ICP-Forests monitoring network in Switzerland and Italy for 2000–2002. The test for data completeness and plausibility resulted in 6 out of a possible total of 20 *Fagus sylvatica* L. plots being identified as suitable from Switzerland, Italy, Spain, and France. The results show that the collected data allow the identification of different spatial and temporal areas and periods as having higher risk to ozone than those identified using the AOT40 approach. However, it was also apparent that the quality and completeness of the available data may severely limit a complete risk assessment across Europe.  
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## 1. Introduction

Current levels of tropospheric ozone ( $O_3$ ) have been shown to cause damage to forest trees (Novak et al., 2005; Schaub et al., 2005; Matyssek and Sandermann, 2003; Innes et al., 2001), agricultural crops (Fuhrer and Booker, 2003; Mills et al., 2003) and semi-natural vegetation (Fuhrer et al., 2003). A rise in  $O_3$  concentrations has occurred on a large scale over the past decades (Collins et al., 2000) and further increases must be expected in many parts of the world either as a result of the continuing rise in the anthropogenic emissions of precursor substances (Bytnerowicz et al., 2004) or due to a continuing increase in background  $O_3$  concentration as emissions from Asia continue to increase (Solberg et al., 2005; SAEFL, 2004).

A key and as yet only partly answered question is what threat does ground level  $O_3$  pose to forest ecosystems across Europe? In order to address this, the United Nations Economic Commission for Europe (UN-ECE) has adopted an effects-based approach, using the critical loads/levels concept (Fuhrer and Achermann, 1999; Kärenlampi and Skärby, 1996).

However, there is a general agreement that cumulative  $O_3$  uptake, the instantaneous rate at which  $O_3$  is absorbed via the stomatal opening, would lead to a biologically relevant estimate of  $O_3$  risk as compared to external exposure indices such as AOT40, SUM0, and mean ambient  $O_3$  concentrations (Matyssek et al., 2004; Kolb and Matyssek, 2001). As such, there was the objective to develop a modeling approach, which could be applied to estimate and map stomatal  $O_3$  flux to major vegetation types across Europe. This move resulted in the establishment of a provisional flux and flux–response model (UN-ECE, 2004). To date, variations on this flux-based modeling approach for forest trees have been applied either on a European scale using modeled meteorological and  $O_3$

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concentration data (e.g. Emberson et al., 2000a, 2001) or on a site-specific scale using data obtained from local observations (e.g. Tuovinen et al., 2001; Baumgarten et al., 2000; Emberson et al., 2000b; Hole et al., 2004). The model evaluations offered by these site-specific studies have provided valuable information by which to improve the model formulation and parameterization for a range of forest species and cover types. However, since ultimately the model has been specifically developed for European-wide application, there is an urgent need to evaluate how well the model is able to capture the variability in flux that occurs across broader spatial scales and investigate how such information can be used to inform regional scale risk assessments for scientists as well as for policy makers.

An obvious route to achieving such an aim may be the utilization of the extensive data set that has been collected by the EU and UN-ECE/ICP-Forests monitoring programs and launched in 1985 under the Convention on Long-Range Transboundary Air Pollution of the UN-ECE. An objective of this program is to collate information that can be used to inform both current condition and trends in forest health in relation to air pollution across Europe. To achieve this aim the program has been collecting a wealth of data that may be suitable to fulfill the data requirements of the cumulative stomatal flux-based models for O<sub>3</sub>. Thus, it is our aim to (i) evaluate the feasibility and suitability to perform O<sub>3</sub> flux modeling using data obtained at beech (*Fagus sylvatica* L.) plots using the routine procedures of the EU and UN-ECE/ICP-Forests monitoring program and (ii) provisionally estimate O<sub>3</sub> uptake to representative leaves of the upper canopy of beech using the provisional cumulative stomatal flux-based model (UN-ECE, 2004).

This study investigates the suitability of field data collected from 4 different European countries in accordance with the standard routine procedures of the EU and UN-ECE/ICP-Forests monitoring program and is part of the cooperative project “Ozone at the intensive monitoring plots in South-Western European forests: levels, risks, actual and potential effects”. More detailed information about the connected working packages is described within this volume by Sanz et al. (2007). To understand how the concentration (i.e. AOT40) and flux-based indices differ in their assessments of risk, we compared the O<sub>3</sub> flux estimates with the corresponding AOT40 values (see Gerosa et al., 2007) for those stands where data are found to be suitable and appropriate for flux modeling. In addition, the collation of response data (e.g. in the form of visible injury, crown condition, growth parameters) at the EU and UN-ECE/ICP-Forests monitoring sites may also provide a means of relating flux to flux response, given the scarcity of data upon which to base O<sub>3</sub> flux–response functions (see Ferretti et al., 2007). These data coupled with the capability to model flux may prove extremely valuable to the continuing development of flux-based risk assessment methodologies.

## 2. Materials and methods

Stomatal O<sub>3</sub> flux ( $F_{st}$ ) to representative upper canopy leaves was modeled using the provisional flux-based methods developed for forest trees as

described in the recent revision of the UN-ECE mapping manual (UN-ECE, 2004). These methods provide a way to estimate the accumulated stomatal O<sub>3</sub> flux ( $AF_{st}$ ) into a single leaf, representative for the upper canopy. The modeling was performed for selected beech plots within the EU and UN-ECE/ICP-Forests monitoring network. The model requires input O<sub>3</sub> concentration and meteorological data, ideally provided at an hourly temporal resolution: these requirements were met using O<sub>3</sub> concentrations obtained from passive monitoring and observations of environmental variables recorded at the intensive monitoring network using standard protocols described by Ferretti et al. (2007) and Sanz et al. (2007). The input data for 2000, 2001, and 2002 were provided by the National Focal Centers of Switzerland, Italy, Spain, and France.

### 2.1. Flux model

The internal O<sub>3</sub> dose, i.e. cumulative O<sub>3</sub> uptake, is calculated over the course of the growing season by multiplying the ambient O<sub>3</sub> concentration by the corresponding stomatal conductance ( $g_s$ ) to water vapour.  $g_s$  was calculated using a multiplicative stomatal conductance model as a function of species-specific maximum  $g_s$  (expressed on a single leaf-area basis), phenology, and prevailing environmental conditions (photosynthetic photon flux density (PPFD), air temperature, vapour pressure deficit (VPD), and soil moisture deficit (SMD)) (see Emberson et al., 2000a).

The O<sub>3</sub> concentration at 2 m reference height is likely to be significantly lower than at the top of the beech canopy (some 20 m above the ground surface). Since the O<sub>3</sub> flux model requires the estimation of O<sub>3</sub> concentration at the top of the canopy, the concentration needs to be corrected for height. The difference between reference height ( $z_{R-O_3}$ ) (height at which O<sub>3</sub> concentration was measured; 2 m) and canopy height ( $z_1$ ) is a function of several factors, including wind speed and other meteorological factors, canopy height, and total O<sub>3</sub> deposition. The neutral stability methods described in the UN-ECE mapping manual (2004) are used to estimate the concentration difference. Using these methods, the O<sub>3</sub> concentration at the top of the canopy ( $C_{(z_1)}$ ) is estimated according to Eq. (1)

$$C_{(z_1)} = C_{(z_{R-O_3})} / [1 - (R_{a(z_{R-O_3}, z_1)} \times V_{g(z_{R-O_3})})] \quad (1)$$

where  $R_{a(z_{R-O_3}, z_1)}$  is the aerodynamic resistance between reference height and canopy height ( $\text{m}^{-1}$ ) and  $V_{g(z_{R-O_3})}$  is the deposition velocity ( $\text{m s}^{-1}$ ) at reference height  $z_{R-O_3}$  (position of O<sub>3</sub> passive samplers in the open field;  $z_{R-O_3} = 2$  m).

In neutral stability, friction velocity ( $u^*$ ) and  $R_a$  are obtained according to Eqs. (2) and (3), respectively

$$u^* = \frac{u_{(z_{R-W})} \times k}{\ln\left(\frac{z_{R-W} - d}{z_0}\right)} \quad (2)$$

$$R_{a(z_{R-O_3}, z_1)} = \frac{1}{ku^*} \ln\left(\frac{z_1 - d}{z_{R-O_3} - d}\right) \quad (3)$$

where  $u_{(z_{R-W})}$  is the horizontal wind speed measured at reference height  $z_{R-W}$  (position of wind speed device;  $z_{R-W} = 4.6$  m),  $k$  is the von Kármán constant ( $k = 0.4$ ),  $d$  is the displacement height, and  $z_0$  is the roughness length, for the grassland vegetation underneath the measurement pole located in the open field. Accordingly,  $d$  and  $z_0$  are assumed to be 0.21 m and 0.03 m, respectively.

The deposition velocity ( $V_g$ ) is estimated according to Eq. (4)

$$V_{g(z_R)} = \frac{1}{R_{a(z_{R-O_3}, z_0)} + R_b + R_c} \quad (4)$$

where  $R_a$  is the aerodynamic resistance from  $z_{R-O_3}$  to  $z_0$  (i.e. the level where  $R_a$  becomes zero).  $R_b$  is the boundary resistance, representing the limitation to O<sub>3</sub> transfer resulting from quasi-laminar boundary layer found adjacent to the leaf surface, and was set as  $R_b = 6.85/u^*$ . For these calculations we assumed an average daytime and a canopy resistance ( $R_c$ ) of 800 s/m.

Stomatal flux of O<sub>3</sub> ( $F_{st}$ ) is estimated assuming the O<sub>3</sub> concentration at the top of the canopy and represents a reasonable estimate of the concentration at the upper surface of the laminar layer of the sunlit upper canopy beech leaves. If  $C_{(z_1)}$  is the concentration of O<sub>3</sub> at canopy height ( $z_1$ ) in  $\text{nmol m}^{-3}$ , then  $F_{st}$

( $\text{nmol m}^{-2} \text{PLA s}^{-1}$ ) is calculated according to Eq. (5) where PLA is per unit projected leaf area

$$F_{\text{st}} = C_{(z_1)} \times g_{\text{sto}} \times \frac{r_c}{r_b + r_c} \quad (5)$$

where  $r_b$  and  $r_c$  are the quasi-laminar and leaf surface resistances to  $\text{O}_3$ , respectively, and  $g_{\text{sto}}$  is the stomatal conductance to  $\text{O}_3$ . The  $r_c = 1/(g_{\text{sto}} + g_{\text{ext}})$  where  $g_{\text{ext}}$  is the external leaf or cuticular conductance equal to  $1/2500$  (in  $\text{m/s}$ ).  $r_b$  is estimated using a leaf-level  $r_b$  term as a function of cross-wind leaf dimension ( $L$ , in m) and wind speed at canopy height ( $u_{(z_1)}$ ) according to Eq. (6)

$$r_b = 1.3 \times 150 \times \sqrt{\frac{L}{u_{(z_1)}}} \quad (6)$$

where the factor 1.3 accounts for the differences in diffusivity between heat and  $\text{O}_3$ . The potential value of 0.05 m provided in the mapping manual for beech is used for  $L$ .  $u_{(z_1)}$  is based on the same micrometeorological principles as the  $\text{O}_3$  concentration profile outlined in Eqs. (2) and (3) and calculated according to Eq. (7):

$$u_{(z_1)} = \frac{u^*}{k} \times \ln\left(\frac{z_1 - d}{z_0}\right) \quad (7)$$

The stomatal response to VPD between the thresholds for minimum and full stomatal opening (represented by  $\text{VPD}_{\text{min}}$  and  $\text{VPD}_{\text{max}}$ , respectively, in kPa) is described by Eq. (8):

$$g_{\text{VPD}} = \min\{1, ((1 - g_{\text{min}}) \times (\text{VPD}_{\text{min}} - \text{VPD}) / (\text{VPD}_{\text{min}} - \text{VPD}_{\text{max}})) + g_{\text{min}}\} \quad (8)$$

The stomatal response to SMD between thresholds for minimum stomatal opening and full stomatal opening (represented by  $\text{SWP}_{\text{min}}$  and  $\text{SWP}_{\text{max}}$ , respectively) is described by Eq. (9):

$$g_{\text{SWP}} = \min\{1, ((1 - g_{\text{min}}) \times (\text{SWP}_{\text{min}} - \text{SWP}) / (\text{SWP}_{\text{min}} - \text{SWP}_{\text{max}})) + g_{\text{min}}\} \quad (9)$$

Finally, the stomatal conductance term, which is central to the leaf  $\text{O}_3$  flux model, is calculated using the multiplicative algorithm in Eq. (10)

$$g_{\text{sto}} = g_{\text{max}} \times [\min(f_{\text{phen}}, f_{\text{O}_3})] \times f_{\text{light}} \times \max\{f_{\text{min}}, (f_{\text{temp}} \times f_{\text{VPD}} \times f_{\text{SWP}})\} \quad (10)$$

where  $g_{\text{sto}}$  is the actual stomatal conductance for  $\text{O}_3$  and  $g_{\text{max}}$  is the receptor-specific maximum stomatal conductance (both in  $\text{mmol O}_3 \text{ m}^{-2} \text{PLA s}^{-1}$ ). According to the Mapping Manual (UN-ECE, 2004) and Jones (1992),  $g_{\text{sto}}$  is converted to the units required in Eq. (5) by dividing the conductance expressed in  $\text{mmol m}^{-2} \text{s}^{-1}$  by 41 000 to give conductance in  $\text{m s}^{-1}$ , assuming normal temperature ( $20^\circ \text{C}$ ) and air pressure (100 kPa). The parameters  $f_{\text{phen}}$ ,  $f_{\text{light}}$ ,  $f_{\text{temp}}$ ,  $f_{\text{VPD}}$  and  $f_{\text{SWP}}$  are all expressed in relative terms (i.e. they take values between 0 and 1) as a proportion of  $g_{\text{max}}$  (Table 1).

These parameters allow for the modifying influence of phenology and 4 environmental variables (irradiance, temperature, vapour pressure deficit, and soil water potential) on maximum stomatal conductance to be estimated. Further details of the  $g_{\text{sto}}$  parameterization for beech used in this study are provided in Table 1 and the UN/ECE Mapping Manual (UN-ECE, 2004).

The required input parameters, as they are monitored by the routine EU and UN-ECE/ICP-Forests monitoring procedures, are shown in Table 2. These parameters necessary to run the  $\text{O}_3$  flux model were derived using standard techniques from meteorological data collected according to the EU and UN-ECE/ICP-Forests monitoring guidelines (EU/UN-ECE, 1998). Soil water deficit was estimated as a function of precipitation and daily mean surface temperature according to the principles of the water budget model of Mintz and Walker (1993). The soil physical characteristics necessary to translate volumetric soil moisture deficit into soil water potential were based on functions given by Milthorpe and Moorby (1974). Root depths were estimated according to Canadell et al. (1996).

## 2.2. Input data and plots

The required meteorological (i.e. wind speed, photosynthetic photon flux density, surface air temperature, relative humidity, and precipitation) and  $\text{O}_3$

Table 1

Parameterization for the  $\text{O}_3$  flux model (Emberson et al., 2000a) for *Fagus sylvatica* L. at selected Swiss and Italian EU and UN-ECE/ICP-Forests plots

Parameters	Values
$g_{\text{O}_3-s \text{ max}}$ ( $\text{mmol O}_3 \text{ m}^{-2} \text{PLA s}^{-1}$ )	134
$g_{\text{min}}$ (% $g_{\text{O}_3-s \text{ max}}$ )	13
SGS (day of year)	Calculated
EGS (day of year)	Calculated
$f_{\text{phen}_a}$	0.3
$f_{\text{phen}_b}$ (days)	50
$f_{\text{phen}_c}$ (days)	50
$f_{\text{light}_a}$	0.006
$T_{\text{min}}$ ( $^\circ \text{C}$ )	-5
$T_{\text{opt}}$ ( $^\circ \text{C}$ )	22
$T_{\text{max}}$ ( $^\circ \text{C}$ )	35
$\text{VPD}_{\text{max}}$ (kPa)	0.93
$\text{VPD}_{\text{min}}$ (kPa)	3.4
$\text{SWP}_{\text{max}}$ (kPa)	-0.05
$\text{SWP}_{\text{min}}$ (kPa)	-1.5

$g_{\text{O}_3-s \text{ max}}$ : maximum stomatal conductance for ozone;  $g_{\text{min}}$ : minimum stomatal conductance for ozone; SGS: start of growing season; EGS: end of growing season;  $f_{\text{phen}_a}$ – $f_{\text{phen}_c}$ : parameters describing the phenological responses of  $g_s$ ;  $f_{\text{phen}_a}$ : starting point for  $f_{\text{phen}}$  as proportion between 0 and 1;  $f_{\text{phen}_b}$ : days after SGS but prior to full stomatal capacity;  $f_{\text{phen}_c}$ : days after EGS but after full stomatal capacity;  $f_{\text{light}_a}$ : factor describing exponential light response of stomatal conductance;  $T_{\text{min}}$ ,  $T_{\text{opt}}$ ,  $T_{\text{max}}$ : minimum, optimum and maximum temperature of  $g_s$  response to air temperature;  $\text{VPD}_{\text{max}}$ ,  $\text{VPD}_{\text{min}}$ : maximum, minimum vapour pressure deficit determining  $g_s$ ;  $\text{SWP}_{\text{max}}$ ,  $\text{SWP}_{\text{min}}$ : maximum, minimum soil water potential for stomatal conductance.

input data (Table 2) were collected at the meteorological monitoring stations located in the open field, closest to the EU and UN-ECE/ICP-Forests monitoring plots. Hourly  $\text{O}_3$  concentrations (ppb) were derived from weekly and bi-weekly mean  $\text{O}_3$  concentrations measured with passive samplers at 2 m above ground level in an open field, closest to the respective forest stand (EU/UN-ECE, 1998) throughout the 2000–2002 growing seasons. The measurement, data and quality assurance methods used in connection with these samplers are reported by Sanz et al. (2007). Hourly  $\text{O}_3$  data were derived based on the function of Loibl and Smidt (1996), which describes the  $\text{O}_3$  daily profile as a function of relative altitude. The modeled daily  $\text{O}_3$  profile was then used as the basis for the estimate of the AOT40 values for each site where only the hours were considered with a global radiation  $>50 \text{ W m}^{-2}$ . The detailed modeling methods for the hourly  $\text{O}_3$  concentrations are described by Gerosa et al. (2007).

The input data were tested for completeness and plausibility. In order to demonstrate the data completeness and quality as they are collected in their original and available form within the EU and UN-ECE/ICP-Forests monitoring network, no data interpolation was conducted within the continuous data series for each parameter, plot, and year. To avoid any interpolation, data sets and years where more than 3% of the data were missing were

Table 2

Input parameters required for stomatal  $\text{O}_3$  flux modeling according to the UN-ECE Mapping Manual (UN-ECE, 2004)

Input parameters	Units
Hourly $\text{O}_3$ concentration ( $\text{O}_3$ )	ppb
Hourly wind speed (WS)	$\text{m s}^{-1}$
Hourly photosynthetic photon flux density (PPFD)	$(\mu\text{mol m}^{-2} \text{s}^{-1})$
Hourly and daily air temperature ( $\text{temp}_{\text{air}}$ )	$^\circ \text{C}$
Hourly relative humidity (RH)	%
Daily precipitation ( $P$ )	mm

omitted. Dubious data were checked for plausibility and eliminated if necessary.

Within the EU and UN-ECE/ICP-Forests monitoring network of the participating countries, there are 6 beech stands in Switzerland (BET(CH3), OTH(CH13), SCH(CH16), ISO(CH6), NEU(CH11), LAU(CH8)), 10 beech stands in Italy (ABR1, CAL1, CAM1, EMI2, PIE1, PUG1, VEN1, TOS3, LOM3 and LIG1), 1 beech stand in Spain (E15), and 3 beech stands in France (F57, F59 and F63) possibly available to provide the required input data and to be considered for a European-wide O<sub>3</sub> risk assessment for beech stands.

### 3. Results

The procedures of data acquisition and controls for data completeness resulted in the identification of 5 Swiss plots (Bettlachstock (CH3), Isonne (CH6), Lausanne (CH8), Othmarsingen (CH13) and Schänis (CH16)) and 1 Italian plot (Calabria 1 (IT4)) (Table 3) as providing data appropriate for O<sub>3</sub> flux modeling. Each of these plots was represented by data sets with a completeness of  $\geq 97\%$  for at least one of the years between 2000 and 2002. For most of the data sets that did not meet the criteria, irradiance (PAR) or wind speed was the limiting factor, i.e. not monitored. Most data sets were only available for 2002 and the more complete input data set of the Italian plot Calabria 1 provided data from 1 May to 30 September, allowing a comparison of all 3 seasons (2000–2002).

In order to enable a comparison with former flux estimates for beech (e.g. Emberson et al., 2000a), the monthly means for  $F_{st}$  were calculated for the month of June for 2000, 2001 and 2002 (Fig. 1). Values for the monthly means of  $F_{st}$  ranged from 1.00 (Isonne, June 2002) to 2.71 nmol O<sub>3</sub> m<sup>-2</sup> PLA s<sup>-1</sup> (Lausanne, June 2002). For all 3 seasons the monthly mean of  $F_{st}$  for the plot Calabria 1 was 2.15 in 2000, 2.47 in 2001, and 2.10 nmol O<sub>3</sub> m<sup>-2</sup> PLA s<sup>-1</sup> in 2002.

When comparing AF<sub>st</sub> from 1 May to 30 September with the AOT40 for the Italian plot Calabria 1 (Fig. 2), the AOT40 as well as the AF<sub>st</sub> were highest during the 2001 season. However, the ratio of AOT40 and cumulative seasonal O<sub>3</sub> flux was not consistent over the 3 years and varied between 2000, 2001 and 2002. The values for O<sub>3</sub> flux and AOT40 cumulated over the entire growing season correlated relatively well (Fig. 2). The amplitude between years, however, was smaller for AF<sub>st</sub> than for AOT40.

The most southern intensive monitoring plot in Switzerland, Isonne, showed the highest monthly mean O<sub>3</sub> concentration of

66.5 ppb but the lowest monthly mean of 16.3 mmol O<sub>3</sub> m<sup>-2</sup> s<sup>-1</sup> for  $g_{O_3}$  resulting in the lowest monthly AF<sub>st</sub> of 0.8 mmol O<sub>3</sub> m<sup>-2</sup> PLA for June 2002 (Fig. 3, Table 3). For the same month, the highest monthly mean for  $g_{O_3}$  and an average O<sub>3</sub> concentration of 51.6 ppb were measured at Lausanne resulting in the highest monthly AF<sub>st</sub> of 2.0 mmol O<sub>3</sub> m<sup>-2</sup> PLA among the selected plots. The annual curve for precipitation and soil moisture deficit for Isonne and Lausanne indicated hotter and drier conditions for Isonne as compared to Lausanne.

### 4. Discussion

It was the objective of this study to evaluate the feasibility of applying the flux approach in combination with the monitoring data routinely collected by the standardized procedures of the EU and UN-ECE/ICP-Forests monitoring programs for beech stands at selected EU and UN-ECE/ICP-Forests monitoring plots.

The results are comparable with the mean  $F_{st}$  values estimated for beech by Emberson et al. (2000a) who calculated values between 1.00 and 1.75 nmol O<sub>3</sub> m<sup>-2</sup> PLA s<sup>-1</sup> for June 1994. Matyssek et al. (2004) compared AOT40 values with modeled  $F_{st}$  data, also applying the O<sub>3</sub> flux model by Emberson et al. (2000a). Our seasonal AF<sub>st</sub> values fall within the same range as the modeled O<sub>3</sub> flux data, described by Matyssek et al. (2004) from sun leaves of mature beech trees at Kranzberg Forest, during 2000. Nunn et al. (2005), however, refined the parameterization of the O<sub>3</sub> flux model for  $f_{temp}$ ,  $f_{soil}$ ,  $g_{night}$  by adapting the response curve of  $g_s$  to stand conditions as they occur at Kranzberg Forest and taking night-time stomatal conductance into account. In general, they found that the original parameterization, as it is suggested in the Mapping Manual (UN-ECE, 2004), results in an overestimation of AF<sub>st</sub> compared to their model output and to field measurements on beech branches. Among others, Nunn et al. (2005) conclude, that low light conditions and reduced O<sub>3</sub> levels within the lower parts of the crown as well as increased soil drought may lead to morphological and physiological plant responses and, hence, influence O<sub>3</sub> uptake, which the O<sub>3</sub> flux model is not able to reproduce in its original parameterization.

The present data show that risk assessments based on AOT40 and O<sub>3</sub> flux seem to correspond well with each other under non-limiting conditions for stomatal conductance. Under drier conditions, where VPD and SMD may limit

Table 3

Plot name, plot-ID, country, coordinates, AOT40 (1 April–30 September), and accumulated seasonal flux of O<sub>3</sub> (AF<sub>st</sub>) for 2000, 2001 and 2002 at selected beech plots within the EU and UN-ECE/ICP-Forests monitoring network

Plot name	Plot-ID	Country	Long.	Lat.	AOT40 (ppm h)			AF <sub>st</sub> (mmol O <sub>3</sub> m <sup>-2</sup> )		
					2000	2001	2002	2000	2001	2002
Bettlachstock	BET(CH3)	CH	4 71 335	0 72 503			23.2		6.6 (1.8)	7.3 (1.7)
Isonne	ISO(CH6)	CH	4 60 734	0 90 033			39.1			-(0.8)
Lausanne	LAU(CH8)	CH	4 63 506	0 63 932			28.9			8.6 (2.0)
Othmarsingen	OTH(CH13)	CH	4 72 403	0 81 340	10.4		2.6	5.5 (1.8)		
Schänis	SCH(CH16)	CH	4 70 959	0 90 405		30.6	9.3		7.0 (1.9)	4.8 (1.0)
Calabria 1	CAL1(IT4)	IT	3 82 538	1 61 047	16.9	31.8	14.2	7.9 (1.6)	10.2 (1.8)	8.1 (1.5)

AF<sub>st</sub> values in ( ) are monthly values for June 2000–2002.

<sup>a</sup> Data from Gerosa et al., 2007.

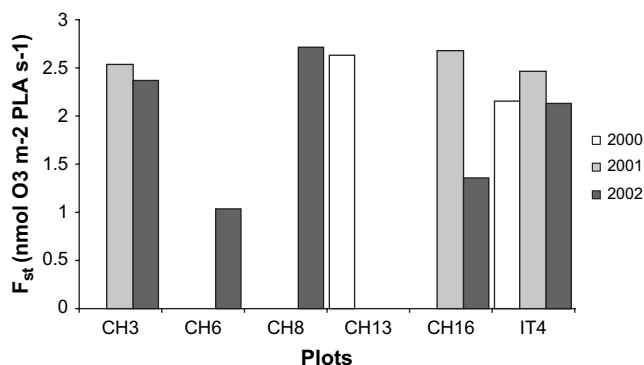


Fig. 1. Monthly means for stomatal flux of O<sub>3</sub> ( $F_{st}$ ) at 5 Swiss (CH) and 1 Italian (IT) plot for June 2000, 2001 and 2002.

physiological activity and hence influence  $g_s$ , O<sub>3</sub> flux is also limited, causing a divergence of the AOT40 and O<sub>3</sub> flux indices. For example, in June 2002, concentration and flux-based indices correlated best where the average VPD was lowest (Lausanne; VPD = 1.3 kPa). In contrast, the most southern Swiss plot of Isonne where the highest VPD (1.6 kPa) and the highest O<sub>3</sub> concentrations were recorded showed the lowest  $F_{st}$ . The annual curve for precipitation and soil moisture deficit indicated that the hot and dry conditions may have reduced the  $g_s$  and O<sub>3</sub> uptake for the beech stands at Isonne (Fig. 4A and B). In contrast, the SMD at Lausanne exceeded 80 mm only twice and only during a short period of time, suggesting that the stomatal O<sub>3</sub> uptake was not reduced by dry soil moisture conditions at this site. However, this comparison indicates clearly that an O<sub>3</sub> risk assessment under drier climatic conditions may differ significantly depending on the applied approach. In conclusion, under hotter and drier conditions (e.g. Mediterranean climate), reduced soil moisture may have a stronger effect in controlling  $g_s$ , not only compared to the concentration based AOT40 approach, but also, according to Nunn et al. (2005), compared to the currently used parameterization as suggested in the Mapping Manual (UN/ECE, 2004).

As expected, there was a distinct variation between the monthly  $F_{st}$  for all 3 seasons of 2000–2002 (Fig. 1). For all

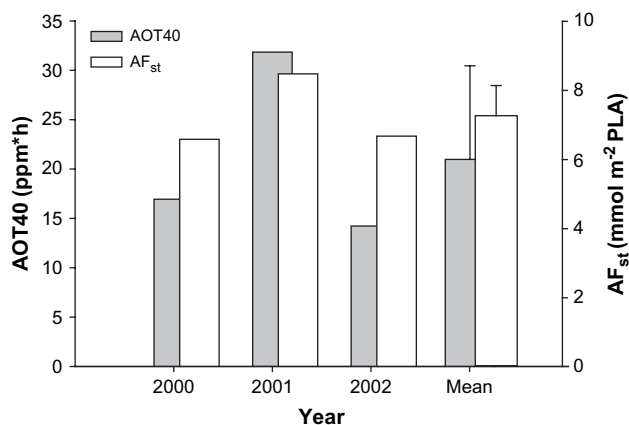


Fig. 2. AOT40 and accumulated stomatal flux of O<sub>3</sub> (AF<sub>st</sub>) from 1 May to 30 September for the Italian plot IT4 in 2000, 2001 and 2002.

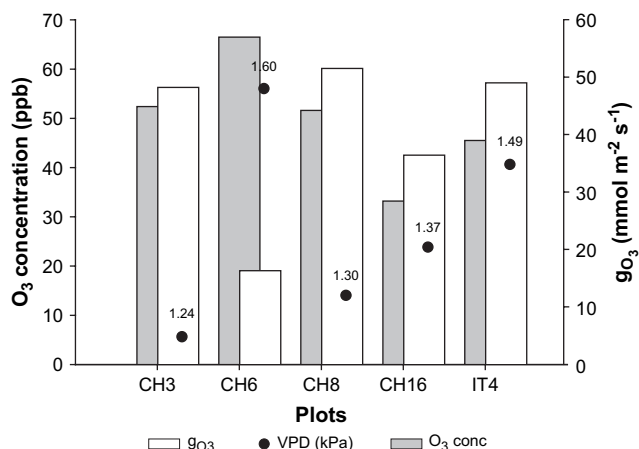


Fig. 3. Monthly means for stomatal conductance of O<sub>3</sub> ( $g_{O_3}$ ), vapour pressure deficit (VPD) and O<sub>3</sub> concentration (ppb) at 4 Swiss and 1 Italian ICP-Forests monitoring plot for June 2002.

plots, the environmental conditions in combination with the O<sub>3</sub> concentrations as they occurred in June seemed to be most favorable for a high  $F_{st}$  during the 2001 season. Indeed, the AOT40 values suggested that O<sub>3</sub> concentrations were highest in 2001 (Table 3, Fig. 1). This trend was even stronger when comparing AF<sub>st</sub> from 1 May to 30 September with the AOT40 for the Italian plot, Calabria 1 (Fig. 2). There, the AOT40 as well as the seasonal AF<sub>st</sub> was significantly higher during the 2001 season. However, the ratio of AOT40 and cumulative seasonal O<sub>3</sub> flux was not consistent over the 3 years and changed between 2000, 2001 and 2002. Also, the amplitude between years was somewhat smaller for AF<sub>st</sub> compared to the AOT40. Recognizing that the AOT40 values may not be directly comparable to the AF<sub>st</sub>, this inconsistency demonstrates that no general statement can be made about AOT40 over or underestimating the O<sub>3</sub> risk.

Massman et al. (2000) stated that developing a realistic model that provides for a relationship between ambient concentration measured routinely at monitoring sites and pollutant uptake has several benefits such as providing insight into the process of vegetation responses to pollution, to suggest possible improvements in the monitoring network. With this modeling exercise, we took advantage of the extended database of the EU and UN/ECE ICP-Forests monitoring network. Due to data gaps ( $\geq 3\%$ ) and non-existing data for certain parameters such as PAR and wind speed, our test for data completeness and plausibility resulted in 30% of the possible beech plots being identified as suitable from Switzerland, Italy, Spain, and France. Percy and Ferretti (2004) conclude that a true risk assessment remains problematic due to scientific uncertainty around the magnitude of O<sub>3</sub> flux into the plant. We applied the criteria of 97% data completeness in order to avoid any interpolation of input data, which would further increase the scientific uncertainty of the model output. Tuovinen (2000) concluded that the comparison of a European-scale uptake/deposition module against field data from a boreal pine forest illustrates the reasonably good accuracy that can be achieved, if local input parameters are used.

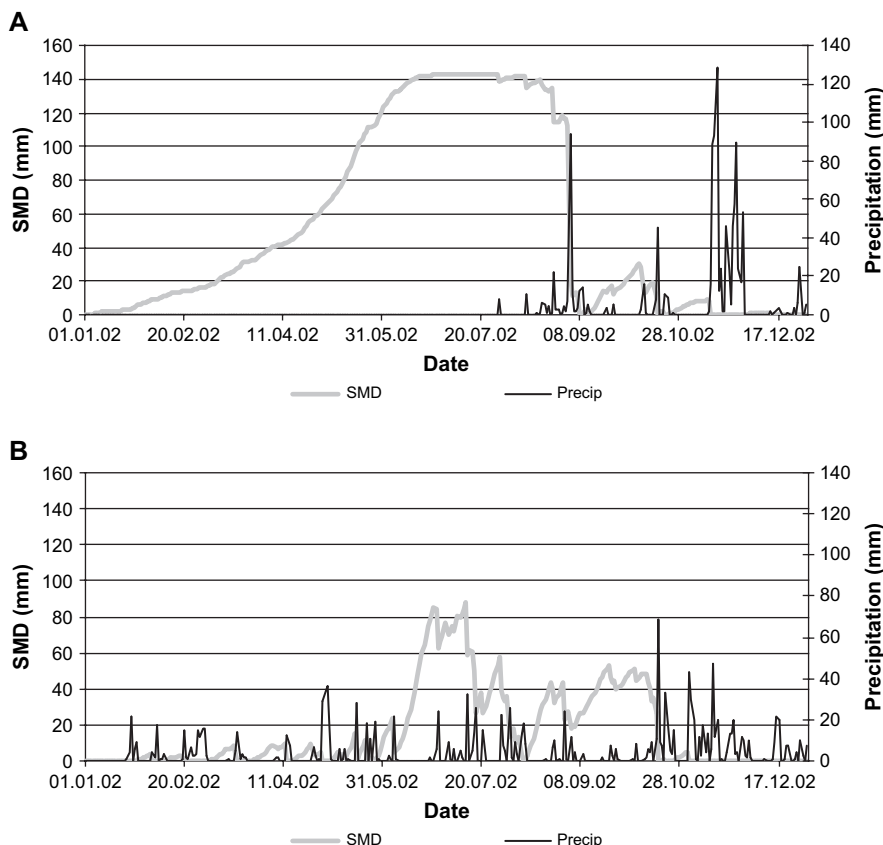


Fig. 4. Soil moisture deficit (SMD) and precipitation in 2002 at ISO(CH6) (A) and LAU(CH8) (B).

Also Wieser and Emberson (2004) emphasized the importance of local input data, which will allow regional estimates of absorbed  $O_3$  dose for use in the policy making process on European emission reductions.

On the other hand, several studies have identified those factors to be important in controlling  $g_s$  and hence the stomatal component of  $O_3$  deposition. They suggest that a more complex parameterization of the current  $O_3$  flux model is needed to take the influence of parameters such as crown light conditions, night time  $g_s$  (Musselman and Massman, 1999; Matyssek et al., 2004; Nunn et al., 2005), defense, avoidance, detoxification mechanisms (Musselman et al., 2006; Massman et al., 2000; Massman, 2004), pre-dawn leaf/needle and soil water potential, and seasonal phenology (Wieser and Emberson, 2004) into account. Without adequate effective-flux based models that integrate the detoxification capacity of the plant, the  $O_3$  flux may be overestimated (Musselman et al., 2006). While it is recognized that the limitation to such future modeling is the availability of such data, it is evident that the quality and completeness of the locally available data requires special attention. In this study, it was apparent that the quality and completeness of the locally available EU and UN/ECE ICP-Forests network data may severely limit a complete risk assessment, and hence, the use for the policy making process across Europe, in particular when considering a more complex model parameterization as well as additional tree species and/or pollutants for future risk assessments.

## 5. Conclusions

To our knowledge, this is one of the few studies that investigated the flux approach in combination with EU and UN-ECE/ICP-Forests monitoring routine procedures for intensive monitoring in respect to practical and conceptual considerations.

A risk assessment based on  $O_3$  flux to receptor sites within the leaf, rather than  $O_3$  exposure, could provide an improved estimate of the relative degree of risk of  $O_3$  damage to vegetation on a local as well as European scale. A comparison of the estimated accumulated flux with plant effect such as visible  $O_3$  injury or reduced growth is very much needed to confirm this hypothesis and further apply this approach. As the risk assessment is only driven in part by  $O_3$  uptake, but also determined by the biochemical/physiological capacity in  $O_3$  defense and repair, practical estimates on defense capacity are needed for a realistic risk assessment of  $O_3$  injury.

The estimated  $O_3$  flux values lack any validation with real-time field measurements due to the suitable evaluation data not being available (e.g. observations of  $g_s$ ,  $O_3$  concentration, light conditions, and wind speeds at varying heights within the canopy). However, for quality assurance and in order to refine the model parameterization for different climatic regions, the validation of the model output should be a priority for the future.

This study did not only assess the suitability of the data collected by the EU and UN-ECE/ICP-Forests monitoring program

for making flux-based risk assessments but, through these initial attempts to apply the flux-based methods, it identified and may initiate development of methods to derive the necessary input data that are not directly available from observations made at the monitoring sites. This will provide information on the necessary procedures for data acquisition, data processing, and quality assurance that European countries will need to implement in order to perform flux-based O<sub>3</sub> risk assessments in the future and help to identify data requirements and recommendations as how to proceed with the data collection in the future.

As such, the establishment of methods to utilize EU and UN-ECE/ICP-Forests monitoring data for O<sub>3</sub> flux modeling may be useful for those countries that intend to undertake O<sub>3</sub> risk assessments using the flux-based approach in combination with the EU and UN-ECE/ICP-Forests monitoring procedures, i.e. with O<sub>3</sub> passive samplers, for future analyses at remote sites and wider geographical scales.

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