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# Ozone Flux Data Used to Assess Damage Risk to Vegetation

By

S. CIESLIK<sup>1)</sup> & G. GEROSA<sup>2)</sup>

K e y w o r d s : Ozone surface fluxes, stomatal ozone uptake, ozone risk to vegetation.

#### Summary

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A new parameterisation of ozone uptake by vegetation, based on the observational determination of functional dependence of stomala ozone conductances on environmental parameters such as temperature, wind speed, top-of-canopy ozone concentrations, water vapour pressure deficit, and soil water content, is proposed. Measurements of ozone fluxes and related parameters have been made using micrometeorological methods over wheat in the Po river plain, Northern Italy. The results show the discrepancy between the AOT40 index, based on the ozone concentration cumulated function over the season, and the cumulated stomatal ozone flux. The new parameterisation proposes a corrected AOT index, which takes environmental and plant physiological effects into account. The corrected AOT is in agreement with the cumulated stomatal ozone uptake flux.

# Introduction

Ozone risk to vegetation in Europe is currently expressed by a quantitative exposure index, called AOT40 KÄRENLAMPI & SKARBY 1996, and defined as the sum of the differences between hourly ozone concentration and 40 ppb for each hour when the concentration exceeds 40 ppb during a relevant growing season, e.g. for forest and crops. Its use is recommended in the frame of the Convention on Long-range Transboundary Air Pollution (LRTAP) and by the European Commission (EC). This index is easy to obtain as it only needs routine ozone concentration records. Regional maps of AOT40 are readily obtained, both from these records and through the use of regional transport and chemistry models.

<sup>1)</sup> Joint Research Center, I-21020 Ispra (VA), Italy, e-mail: stanislaw.cieslik@jrc.it

<sup>&</sup>lt;sup>2)</sup> Catholic University of Brescia, v. Trieste 17, I-25121 Brescia, Italy.

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There is general agreement that ozone penetrates the plant tissues mostly through the stomatal pathway, as the deposition on cuticles is negligible (KERSTIENS & LENDZIAN 1989, VAN HOVE & al. 1999), such that the relevant parameter for assessing plant damage is the stomatal flux, i.e. the quantity of ozone entering the stomata per unit time and area. The stomatal flux is more difficult to obtain than the concentration; the eddy-correlation micrometeorological technique. combined with resistance analysis (GEROSA & al. 2003), lead to reliable stomatal flux data. A phyisiologically relevant ozone risk indicator for vegetation could be obtained by integrating the stomatal fluxes over time during a growing season, but an important information is lacking as far as the loss of biomass dure to ozone damage is not known as a function of integrated stomatal flux. For this sake, a new research programme using Open Top Chambers (OTC) with simultaneous flux determination, would be needed. The results of such a programme cannot be available in the short term. In the meantime, intermadiate solutions can be proposed. such as the development of a correction algorithm which would lead to a modified AOT40 index taking stomatal fluxes into account.

This is the main goal of the work presented. A new AOTx index is developed, in which the ozone concentrations used are not those obtained directly by measurement or model calculation. An "effective" ozone concentration  $C_{eff}$  is defined and calculated starting from the measured one  $(C_m)$  and using empirical functions of environmental parameters (soil water content, vapour pressure deficit, temperature,...) which are related to stomatal flux and conductance. The derivation of these empirical functions is makes use of observed flux data. For this sake, we measured ozone fluxes and related parameters over a barley field in Northern Italy during a growing season, and determined the stomatal fluxes. The values of  $C_{eff}$ obtained by this procedure were then used to calculate time-dependent AOTx (with variable concentration thresholds) and compared with the time-dependent intergrated stomatal fluxes (or doses).

#### Material and Methods

The measurements were made in April - June 2002 over a barley field (*Hordeum vulgare*) located in Comun Nuovo in Northern Italy (44°30'N; 9°30'E). Ozone fluxes were determined by means of the eddy-correlation method, which makes use of fast-response measurement techniques. Turbulent variables such as temperature, humidity and ozone concentrations, as well as the three components of the wind vector, were recorded at a height of 2.8 m above ground level (a.g.l.) by a sonic anemometer, a krypton-lamp hygrometer and a chemiluminescent ozone sensor making use of a reaction between ozone and an organic dye, as described by GÜSTEN & al. 1992. Turbulent variables used for the flux determination were recorded at a frequency of 10 Hz, such as to cover the whole frequency domain contributing to the total covariances. Calculation of the ogive functions ( cumulated cospectra) showed no contribution for frequencies higher than 10 Hz. Other variables were recorded by slow sensors: solar radiation, soil water content, temperature and heat flux, atmospheric pressure, and rainfall.

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#### Results and Analysis

The total ozone fluxes obtained are shown on Fig. 1. They show an increase of the daily maximum of the ozone flux, roughly proportional to the height of plants. After having reached a maximum, fluxes decrease gradually as the crop undergoes senescence. This aspect is a clear indication that plant physiology influences ozone fluxes. The fraction of ozone fluxes penetrating the leaves through the stomata, or stomatal ozone fluxes, were then obtained by combining total ozone fluxes, ozone concentrations, and water vapour fluxes as a quantifier of stomatal aperture. All these variables were included in a resistance analysis procedure, in which fluxes are expressed as currents, and concentration differences are represented as tensions, and both are related with resistances as in the Ohm's law. This leads to the calculation of stomatal resistances and their reciprocal, conductances, both quantities referringing to the stomatal pathway. The total ozone dose was calculated from

$$D_{ah} = \sum F_{st} \Delta t \tag{1}$$

where the summation is made from anthesis to harvest (*ah*), and  $\Delta t$  is a 1-hour interval. By making the upper limit of the summation variable, one obtains cumulative curves which are an indication of the evolution of accumulated stomatal flux during the season.

In parallel, the conventional AOT40 was calculated using its definition

$$AOT40_{ah} = \sum \left[ (C_m - 40) \right] \Delta t \tag{2}$$

Again, by making the upper limit of the summation variable, one obtains cumulative curves. The ozone concentration the plants are exposed to is not  $C_m$ , which was measured above the canopy, i.e. at 2.8 m height. The downward ozone flux generates a gradient, and the ozone concentration at the level of the plants is thus lower. This concentration,  $C_c$  can be calculated through

$$C_{c} = C_{m} (1 - R_{a} / R_{Tot})$$
(3)

(TUOVINEN 2000) where  $R_a$  and  $R_{Tot}$  are the aerodynamic and total resistances, respectively, to ozone fluxes. Here it is assumed that the ozone concentration vanishes at leaf level, which is a reasonable hypothesis since ozone is destroyed when it reaches the cells by oxidising some of its components. The total resistances were calculated using the Monin-Obukhov surface layer theory (MONIN & OBUKHOV 1954). The next step consisted in calculating the effective ozone concentrations  $C_{eff}$ . The procedure is based on the Jarvis multiplicative model (JARVIS 1976), which expresses the stomatal conductance as

$$G_{st} = (G_{st})_{max} \cdot \min[f_{Rad}, f_T, f_{VPD}, f_{SWC}, f_{wind}]$$
(4)

where  $(G_{st})_{max}$  is the 95<sup>th</sup> percentile of all values of the ozone stomatal conductance obtained during the campaign. The empirical functions f appearing in

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equation (4) depend on net radiation (*Rad*), temperature (*T*), water vapour pressure deficit (*VPD*), or difference between the water vapour saturation pressure at temperature *T* and the actual partial water vapour pressure, soil water content (*SWC*), and wind speed. They are species-specific and were derived graphically by means of a border-line analysis carried out on the scatter plots of  $G_{st}$  ( $G_{st}$ )<sub>max</sub> versus the various variables listed above and appearing in equation (4). The border-line analysis is illustrated on Fig. 2. and its results are :

$F_T = \max[0.1; -0.0078 \cdot T^2 + 0.2882 \cdot T - 1.6706]$	$(T \text{ in } ^{\circ}\text{C})$	(5)
$F_{VPD} = \min[1; -0.4368 \cdot VPD + 1.4705)]$	(VPD in kPa)	
$F_{SWC} = \min[1; 0.875 \cdot SWC/0.35 + 0.3]$	$(SWC \text{ in } \text{m}^3/\text{m}^3)$	

The stomatal flux is equal to the product of stomatal conductance and the ozone concentration at canopy level :

$$F_{st} = G_{st} C_c = C_c \cdot (G_{st})_{max} \cdot \min[f_{Rad}, f_T, f_{VPD}, f_{SWC}, f_{wind}] = C_{eff} (G_{st})_{max}$$
(6)

using the definition of Ceff

$$C_{eff} = C_c \cdot \min[f_{Rad}, f_T, f_{VPD}, f_{SWC}, f_{wind}]$$
(7)

The values of  $C_{eff}$  were then recalculated for the whole campaign as well as the corresponding AOTx (with different thresholds) cumulative curves. The results of this procedure are shown on Fig. 3. and compared with the cumulated AOT40 and the cumulated dose. Whereas the conventional AOT40 shows a very different behaviour compared with the cumulated dose, the corrected AOTx showed a much better agreement with the cumulated dose curve.



Fig. 1. Total ozone fluxes over barley, as measured from April to June 2002 at Comun Nuovo.



Fig. 2. Border-line analysis for the stmatal conductance (upper left frame) and the ratio Gst/Gst(max)(other frames) as functions of ozone concentration, temperature, vapour pressure deficit, and soil water content.



Fig. 3. Phytotoxicologically effective time-dependent cumulated exposures (AOT<sub>eff</sub>) calculated for different ozone concentration thresholds and cumulated ozone stomatal flux for barley. All variables have been normalised by dividing them by their maximum values.

#### Discussion

The differences between AOT40 and dose are readily explained by the difference between the processes involved: the former is concentration-dependent and

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thus related to photochemical ozone production, in turn enhanced by strong solar radiation; the latter depends on plant physiology and mainly on water supply. These two factors are often antagonistic: when the solar radiation is high, there is no rain and thus water supply is correspondingly weak. Consequently, ozone concentrations may be high while the ozone stomatal fluxes are low. The use of the corrected AOTx, where stomatal fluxes are an implicit variable, improves the ability of this index as a risk indicator.

We used different concentration thresholds for AOTx because 40 ppb seems rather arbitrary. It appears from the results that a threshold of 20 ppb is reasonable. Lower threshold values do not improve the results. Further, by using thresholds less than 20 ppb, we include nighttime situations, when the stomata are closed and thus no ozone uptake occurs.

#### Conclusions

A new concept of ozone risk index for vegetation was developed, where the measured ozone concentration is replaced by an effective concentration depending on various environmental parameters, thus implicitly on stomatal fluxes. To apply the method, one needs a time series of observations of temperature, humidity, soil water supply, wind speed and solar radiation, as well as ozone concentration. The functions f are species-specific and must be derived from previous flux measurements.

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