Science of the Total Environment 572 (2016) 56–67

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Testing approaches for calculating stomatal ozone fluxes from passive samplers☆

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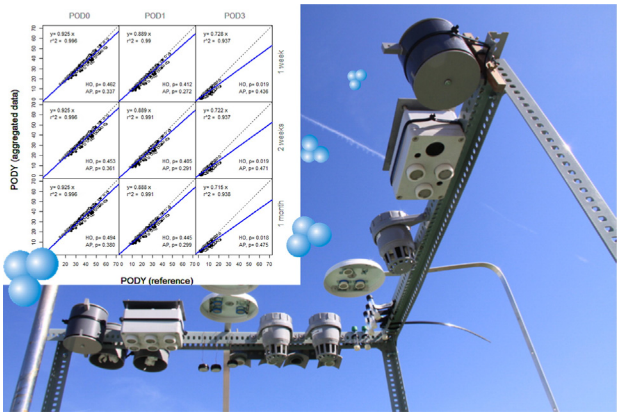
HIGHLIGHTS

- Suitability of passive sampler measurements to estimate O_3 fluxes were tested.
- Five approaches and 3 parameterizations were used to calculate PODY.
- Hourly O_3 data from active monitors and meteorological data were aggregated.
- Errors due to the use aggregated instead of hourly data were quantified.
- Calculations based on O_3 averages from 1 week to 1 month yielded similar errors.

GRAPHICAL ABSTRACT



Errors calculating accumulated O_3 fluxes from aggregated data were lower when ozone-averaged values in combination with hourly meteorological were used.

ARTICLE INFO

Article history:
Received 19 April 2016
Received in revised form 22 July 2016
Accepted 22 July 2016
Available online xxxx

ABSTRACT

Current ozone (O_3) levels are high enough to negatively affect vegetation and may become worse in the future. Ozone risk assessments have recently shifted from exposure-based to flux-based metrics. Modeling stomatal O_3 fluxes requires hourly O_3 and meteorological data, which are not always available. Large datasets of O_3 concentrations measured with passive samplers exist worldwide, and usually provide weekly to monthly means. We tested the suitability of using aggregated data instead of hourly data for O_3 flux calculations with 3-year time series of O_3 data from 24 Spanish air quality stations. Five different approaches and three different

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Abbreviations: AP, Aleppo pine (*Pinus halepensis*) parameterization; BE, Beech (*Fagus sylvatica*) parameterization; c., circa; CLef, flux-based critical level; DOY, day of year; EGS, end of the growing season (DOY); f_{light}, function for light; f_{min}, minimum g_{sto} (fraction of g_{max}); f_{phen}, function for phenology; f_{phen_1}, period from f_{phen_a} to f_{phen_b} (days); f_{phen_2}, period from f_{phen_b} to f_{phen_c} (days); f_{phen_3}, period from f_{phen_c} to f_{phen_d} (days); f_{phen_4}, period from f_{phen_d} to f_{phen_e} (days); f_{phen_a}, f_{phen} at SGS (fraction of g_{max}); f_{phen_b}, first mid-season f_{phen} (fraction of g_{max}); f_{phen_c}, second mid-season f_{phen} (fraction of g_{max}); f_{phen_d}, third mid-season f_{phen} (fraction of g_{max}); f_{phen_e}, f_{phen} at EGS (fraction of g_{max}); f_{phen_limA}, start of SWP limitation (DOY); f_{phen_limB}, end of SWP limitation (DOY); f_{temp}, function for temperature; f_{VPD}, function for VPD; g_{max}, species-specific maximum stomatal conductance for O_3; g_s, stomatal conductance for H_2O; g_{sto}, stomatal conductance for O_3; HO, Holm Oak (*Quercus ilex*) parameterization; h_r, relative altitude within a 5 km radius; $light_a$, coefficient for f_{light} function; L, cross-wind leaf dimension; MPE, median(s) of percent error(s); MAPE, median(s) of absolute percent error(s); P75APE, 75th percentile of absolute percent errors; P100APE, 100th percentile of absolute percent errors; R_g, global radiation; RH, relative humidity; SAE, sum(s) of absolute error(s); SGS, start of the growing season; SWP, soil water potential; T, temperature; T_{max}, maximum temperature at which stomatal closure occurs to f_{min}; T_{min}, minimum temperature at which stomatal closure occurs to f_{min}; T_{opt}, optimum temperature; VPD, vapor pressure deficit; VPD_{max}, VPD for max g_{sto} (fraction of g_{max}); VPD_{min}, VPD for max g_{sto} (fraction of g_{max}); Y, flux threshold.

☆ Capsule: Stomatal ozone fluxes can be calculated from passive sampler measurements.

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http://dx.doi.org/10.1016/j.scitotenv.2016.07.155

Editor: D. Barcelo

Keywords:
Ozone fluxes
Phytotoxic Ozone Dose
Passive samplers
Risk assessment

parameterizations were tested. Ozone-averaged values in combination with hourly meteorological data provided the most robust estimates of accumulated O_3 fluxes (Phytotoxic Ozone Dose with no threshold, POD0), and the median of the absolute percent error (MAPE) due to aggregation came close to 5%. Aggregations from 1 week to 1 month yielded similar errors, which is important in the cost-efficiency terms of the chosen passive sampler exposure periodicity. One major limitation of these approaches is that they are not suitable for high POD thresholds, and that accuracy of the measurements with passive samplers has to be strictly assured in order to finally obtain acceptable errors. A combination of meteorological data and O_3 passive sampler measurements may be used to estimate O_3 fluxes at remote forest sites as a valuable risk assessment tool.

1. Introduction

Tropospheric ozone (O_3) is an air pollutant of major concern due to adverse effects on vegetation (Paoletti, 2006; Karlsson et al., 2007; Matyssek et al., 2007; The Royal Society, 2008; Sicard et al., 2016). Furthermore, it is the third most important anthropogenic greenhouse gas that contributes to radiative forcing (IPCC, 2013). Despite the fact that O_3 precursor emissions have lowered in Europe over the last 20 years, climate change might reduce the benefits of the European O_3 control strategies by increasing background O_3 levels in the future (Wilson et al., 2012; Sicard et al., 2013). Long-range transport of O_3 and precursors also contributes to the exceedance of air quality standards in Europe (Derwent et al., 2010). In plants, O_3 exposure impairs CO_2 assimilation by altering carbon allocation, causes visible leaf injury, decreases photosynthesis, growth and production, alters biomass partitioning, reduces yields and changes food nutrient properties which affect, *in fine*, food security (e.g. Feng and Kobayashi, 2009; Calatayud et al., 2011; Mills et al., 2011; Fares et al., 2013; Braun et al., 2014; Feng et al., 2014, 2015; Sicard et al., 2016). Ozone may also change the species composition of natural plant communities and reduce resilience to pest attack and diseases (Krupa et al., 2000).

To protect plants from adverse O_3 effects, different impact metrics and critical levels (CL) have been established. Critical levels are defined as the "concentration, cumulative exposure or cumulative stomatal flux of atmospheric pollutants above which direct adverse effects on sensitive vegetation may occur according to present knowledge" (CLRTAP, 2015). O_3 exposure index AOT40 (Accumulated ozone exposure Over a Threshold of 40 ppb) is widely applied in Europe (CLRTAP, 2015). However, as O_3 effects on vegetation depend not only on atmospheric concentrations, but also on O_3 uptake through the stomata (Matyssek et al., 2007), the Long-Range Transboundary Air Pollution Convention has introduced stomatal flux-based metrics and critical levels (CLef) for protecting vegetation against O_3 effects (e.g., CLRTAP, 2015; Mills et al., 2011; Anav et al., 2016). These metrics take into account the varying influences of air temperature, air-to-leaf water vapor pressure deficit (VPD), light (irradiance), soil water potential (SWP) or plant available water (PAW), O_3 concentrations and phenology on the stomatal O_3 flux. This approach has been applied by the DO$_3$SE model, developed for calculating O_3 fluxes, and is encompassed in the EMEP (Co-operative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe) photochemical model, used to estimate total O_3 deposition and O_3 risk for Europe (e.g. Emberson et al., 2000a; Tuovinen et al., 2004). In combination with response-functions, on the local or regional scale, accumulated O_3 fluxes can be used to assess and quantify O_3 impacts on roundwood supply for the forest sector industry, loss of carbon storage capacity in the living biomass of trees, and for other beneficial ecosystem services provided by trees, such as reduction in soil erosion, avalanches and flooding (CLRTAP, 2015).

In order to calculate accumulated O_3 fluxes (Phytotoxic Ozone Dose above a threshold Y, PODY), hourly O_3 and meteorological data are needed. However, monitoring stations capable of providing hourly data at forest sites are limited, and their distribution is heterogeneous due to high instrumental and maintenance costs and technical challenges, such as access to electric power supply. Passive samplers are effectively used to measure the surface air pollutants levels at these sites (Sanz et al., 2007a, 2007b; Calatayud and Schaub, 2013). Yet these devices typically provide mean O_3 concentrations over 1 week to 1 month, while hourly data are required for O_3 flux calculation. Whereas several methods have been developed to estimate AOT40 from passive sampler measurements (Gerosa et al., 2007; Ferretti et al., 2012; De Marco et al., 2014), the calculation of O_3 fluxes using data from passive sampler measurements is challenging and has only been carried out at five ICP-Forests (the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests, CLRTAP) sites in Switzerland and one in Italy (Schaub et al., 2007) for beech. Hourly O_3 estimates for these calculations were obtained from passive samplers based on an O_3 daily site-specific profile that depends on the plot relative elevation within a 5 km radius (Gerosa et al., 2007). Passive O_3 concentration measurements are available from 240 ICP-Forests intensive monitoring sites located in 21 countries, with a database that contains 37,215 records and started in 2000 (Schaub et al., 2015). This demonstrates the great potential of passive ozone samplers for calculating O_3 fluxes. Furthermore, meteorological data and a wide range of parameters from soil to tree conditions have also been regularly recorded at almost all the plots for $>$25 years (Lorenz and Fisher, 2013).

As O_3 is an important driver that affects tree vitality and productivity, estimates of O_3 fluxes from passive samplers is a central issue for this international program. Although meteorological data are now available for ICP-Forests on an hourly basis, for many years data have been submitted to the central database only on a daily basis, which challenges this objective. Besides developing methods at ICP-Forests sites for calculating O_3 fluxes from passive samplers, this may be important for many other networks and areas in the world. In USA and Spanish national parks, where the impact of O_3 on vegetation is an important issue, passive samplers have been used (e.g., Ray, 2001; Sanz et al., 2007b). Extensive studies with passive samplers have been carried out in, for example, the Sierra Nevada Mountains (USA) (Lee, 2003) and the Carpatian Mountains in Europe, which took these measurements to spatially interpolate O_3 distribution (Bytnerowicz et al., 2002). Recently, there has also been growing interest in using green infrastructures to improve the air quality of cities and to quantify the pollutant removal capacity of different trees (Nowak et al., 2006). As stomatal fluxes contribute to this removal capacity, the methods investigated in the present paper can also be applied to networks of passive samplers in these types of studies on the local scale.

To overcome the above-indicated difficulties and to elucidate the feasibility to obtain consistent estimates of accumulated O_3 fluxes from passive samplers, a data aggregation method was performed and tested in this study. To this end, O_3 and meteorological data from 24 rural air quality monitoring stations in Spain were computed. By aggregating hourly O_3 data from active analyzers and simulating 1 week to 1 month passive sampler measurements, errors due to the use of aggregated rather than measured hourly data for O_3 flux calculations were assessed. The effect of using daily meteorological means instead of hourly data for O_3 flux calculations was also estimated. This study focused on tree species as receptors since passive sampler measurements