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Diel trend in plant sensitivity to ozone: Implications for exposure- and flux-based ozone metrics

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HIGHLIGHTS

- The practical significance of plant sensitivity to ozone is evaluated.
- Stomatal flux and dose of ozone are not well predicted by ambient ozone concentration.
- Flux or dose is likely to be better related to ozone impacts than is concentration.
- Effective ozone flux (incorporating plant sensitivity) is well predicted by flux.
- Flux may be more cost effective than effective flux in predicting ozone-induced injury.

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ABSTRACT

Plant sensitivity to ozone (O_3) is critical to modeling impacts of air pollution on vegetation. A diel timecourse of sensitivity (*S*) was recently determined in Pima cotton (Grantz et al., 2013). The sensitivity parameter serves as a weighting factor for stomatal uptake (ozone flux, *F*), or cumulative *F* (dose, *D*). Previous approaches used various weighting schemes to modify ozone concentration ($[O_3]$) or cumulative $[O_3]$ (exposure, *E*). Use of the S parameter allows calculation of effective flux (F_{eff}) and effective dose (D_{eff}). Though theoretically sound, the practical significance of *S* has not been evaluated due to the previous lack of available data. Here, the newly available *S* parameter is used to explore the relationships between exposure- and flux-based O_3 metrics in response to scenarios of contrasting stomatal conductance (g_s) and ambient $[O_3]$.

The O_3 scenarios were similar but differed in timing of peak $[O_3]$. *E* varied by up to 13.7%, *D* by up to 15.4%, and D_{eff}, which factors in sensitivity, by up to 19.0%. The g_s scenarios differed in midday magnitude and nocturnal closure. Cumulative g_s varied by 65.2%, which was attenuated in *D* to 49.2% and in D_{eff} to 51.1%. A simulation of hourly $[O_3]$, *F*, and F_{eff} was run using Monte Carlo techniques with a full month of ambient $[O_3]$ data. Resulting diel timecourses of $[O_3]$, *F*, and F_{eff} were realistic, with the principal sources of uncertainty in the physiological parameters, g_s and *S*.

Analysis of hourly values from the scenarios and the simulation output demonstrated significant correlation among the O_3 metrics. However, the uncertainty in both F and F_{eff} predicted from $[O_3]$ was large and proportional to $[O_3]$, yielding greatest uncertainty under conditions of high $[O_3]$ and potential phytotoxicity. In contrast, F_{eff} was significantly correlated with *F*, with low variability that was not proportional to *F*. As a result, uncertainty was low and prediction potentially useful under conditions of likely injury.

These results suggest that F, which incorporates g_s, represents a substantial improvement over ambient $[O_3]$, which does not. F_{eff}, which incorporates S, was closely related to *F*, which does not use S. The substantial effort required to measure or model *S* and F_{eff} may not be justified under some conditions. Further research to obtain additional timecourses of S and to explore additional $[O_3]$ and g_s scenarios is urgently required.

List of variables: g_s, stomatal conductance; *F*, stomatal ozone flux; F_{eff}, effective stomatal ozone flux; *D*, ozone dose; D_{eff}, effective ozone dose; *S*, plant sensitivity to ozone; $[O_3]$, ozone concentration.

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1. Introduction

1.1. Ambient ozone

The concentration of tropospheric ozone [O_3] has increased considerably since pre-industrial times (The Royal Society, 2008; USEPA 2013). Projections of future trends are uncertain (Vingarzan, 2004), depending on implementation of existing policy and assumptions regarding historical patterns of global economic growth (Avnery et al., 2011a,b). Although increasing in some locations and decreasing in others, current [O_3] in many areas causes injury to agricultural and unmanaged ecosystems (Ashmore, 2005; Booker et al., 2009). Model simulation of O_3-induced crop loss, visual degradation, and other plant injury has remained challenging. More predictive O_3 metrics are required.

1.2. Ozone exposure and flux

Ozone concentration ([O_3]) and its cumulative value, exposure (*E*), have been the most common metrics for predicting injury to vegetation. They provide regulatory stability, and in North America remain the basis for ambient air quality standards (Musselman et al., 2006; USEPA, 2013). Limitations to these metrics have long been recognized (Fuhrer et al., 1997; Grunhage et al., 2004; Heath et al., 2009). [O_3] and *E* may overestimate injury because critical physiological factors that limit stomatal uptake and determine rates of detoxification are not considered. In some cases, peaks of [O_3] may exert disproportionate impacts (Lefohn et al., 1988). In other cases (Grunhage et al., 1997), such as a vineyard in California (Grantz et al., 1995; Massman and Grantz, 1995; Massman et al., 2000), diurnal phase differences between stomatal conductance (g_s) and [O_3] may lead to asynchronicity between periods of high [O_3] and high g_s. This reduces the impact of peak [O_3] in favor of mid-range concentrations (Grunhage and Jager, 2003; Krupa et al., 1998).

This variability has been addressed with a large number of empirical thresholds and weighting factors such as AOT40, SUM06; and W126 (USEPA, 2013; Lefohn et al., 1988) based on [O_3], and weighting factors determined by plant functional group (Sitch et al., 2007; Zhang et al., 2007) or physiological status (Krupa and Teng, 1982; Lee, 1988; Soja et al., 2000). All modify [O_3] or *E* to better capture O_3-induced injury.

1.3. Flux and effective flux

Improved prediction of plant injury may be achieved using stomatal uptake of O_3 (flux; F) or its cumulative value, dose (*D*) as a metric. Use of flux-based metrics potentially addresses both the asynchronicity of g_s and [O_3] and the impact of peak [O_3]. F is likely to be more closely related than *E* to the contact of O_3 and its breakdown products with sensitive bioreceptors that leads to injury (Mills et al., 2011b; Uddling et al., 2004; Emberson et al., 2000). A series of critical levels based on a flux-based metric has been adopted in Europe (Mills et al., 2011b).

Exposure- and flux-based metrics that assume an invariant rate of O_3 detoxification, and resulting level of plant sensitivity (S), ignore the more likely diel and seasonal changes in metabolic and structural characteristics that determine *S* (Dizengremel et al., 2008; Heath et al., 2009). Because the phase differences in g_s and [O_3] may attenuate diel changes in *F* (the product of these independently varying inputs), inherent sensitivity to O_3, and the resulting effective flux (F_{eff}), may control impacts of O_3 on vegetation (Amiro et al., 1984; Musselman et al., 2006). Adding complexity, O_3 sensitivity may be out of phase with any or all of g_s, [O_3], or *F* (Heck et al., 1966; Musselman et al., 2006; Heath et al., 2009; Dizengremel et al., 2008). In other environments, sensitivity and *F* may exhibit greater temporal coherence (Massman, 2004), thus contributing to injury.

A cumulative flux-based metric, with a sensitivity-related weighting factor applied to *F* or *D* rather than to [O_3], has been shown to be effective in predicting O_3-induced plant injury (Massman et al., 2000; Karlsson et al., 2007; Mills et al., 2011a; Danielsson et al., 2013; Fares et al., 2010; Matyssek et al., 2004; Uddling et al., 2004; Wieser and Matyssek, 2007). In other cases the exposure-based metrics performed as well (Feng et al., 2012; Gonzalez-Fernandez et al., 2010; Karlsson et al., 2004). An empirically determined timecourse of a sensitivity factor, S, was recently obtained in Pima cotton (*Gossypium barbadense*; Grantz et al., 2013), allowing further investigation of the relationships among candidate O_3 metrics in contrasting environments.

1.4. Present study

While flux-based metrics have received considerable attention, there has been little ability to evaluate effective flux-based metrics, due to inadequate data. The recent availability of empirical values of *S*, albeit for a single environment and genotype, now allows preliminary evaluation of these concepts. Refinement of [O_3] or *E* to yield *F* or *D* requires empirical or modeled values of g_s. Further modification of *F* or *D* to yield F_{eff} or D_{eff} requires knowledge of *S*. Each of these potential advances may improve prediction of plant injury, but at the cost of increased experimental and computational complexity, data requirements, and uncertainty. The current analysis uses a series of real-world scenarios, involving contrasting diel patterns of directly measured [O_3], g_s, and *S*, to explore relationships between [O_3], *F* and F_{eff}. The objective is to identify cost effective approaches to scaling of O_3 impacts to the landscape.

2. Experimental methods

2.1. Plant growth and ozone exposure

Plants of Pima cotton, cv. S-6 (*G. barbadense*) were grown from germination through harvest in Teflon ozone exposure chambers (continuously stirred tank reactors, CSTRs; Heck et al., 1978). Growth temperature was 15–30 °C and illumination was with natural sunlight. Air containing O_3 with a 12 h mean concentration of 0.059 ppm was introduced at one complete air exchange per minute into each of 3 CSTRs.

O_3 was produced by corona discharge (Model SGC-11, Pacific O_3 Technology, Brentwood, CA) from a feedstock of purified oxygen (Series ATF-15, Model 1242, SeQual Technologies Inc., San Diego CA). O_3 concentration followed a half-sine wave during daylight hours, 7 days week^{-1}. Voltage to the O_3 generator was regulated by feedback from the exit stream of a master CSTR (Model 41C; Thermo Electron Corp.; Franklin MA, USA), calibrated against an O_3 calibration unit (Model 306; 2B Technologies, Boulder, CO, USA). The remaining CSTRs were controlled proportionally and monitored with a separate analyzer (Model 41C) (Grantz et al., 2010).

2.2. Ozone metrics

Concentration of ozone [O_3] is taken as the mole fraction ([O_3]; ppm) and Exposure (*E*) as the cumulative rather than mean value of [O_3] over time. O_3 flux was determined as $F = g_s \times [O_3]$ where [O_3] is mean O_3 concentration during each 2 h period. Daily O_3 dose was calculated over 07:00–21:00, approximately the daylight period, as $D = \sum F$. To facilitate calculations, measurements were aligned to the nearest quarter hour.