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Toward an ozone standard to protect vegetation based on effective dose: a review of deposition resistances and a possible metric

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Abstract

Present air quality standards to protect vegetation from ozone are based on measured concentrations (i.e., exposure) rather than on plant uptake rates (or dose). Some familiar cumulative exposure-based indices include SUM06, AOT40, and W126. However, plant injury is more closely related to dose, or more appropriately to effective dose, than to exposure. This study develops and applies a simple model for estimating effective ozone dose that combines the plant canopy's rate of stomatal ozone uptake with the plant's defense to ozone uptake. Here the plant defense is explicitly parameterized as a function of gross photosynthesis and the model is applied using eddy covariance (ozone and CO_2) flux data obtained at a vineyard site in the San Joaquin Valley during the California Ozone Deposition Experiment (CODE91). With the ultimate intention of applying these concepts using prognostic models and remotely sensed data, the pathways for ozone deposition are parameterized (as much as possible) in terms of canopy LAI and the surface friction velocity. Results indicate that (1) the daily maximum potential for plant injury (based on effective dose) tends to coincide with the daily peak in ozone mixing ratio (ppbV), (2) potentially there are some significant differences between ozone metrics based on dose (no plant defense) and effective dose, and (3) nocturnal conductance can contribute significantly to the potential for plant ozone injury.
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Keywords: Air quality standards; Effective dose; Dry deposition resistances; Ozone

1. Introduction

Ozone in the lower troposphere is a common, phytotoxic air pollutant which can cause injury to internal plant tissue and subsequent reductions in photosynthesis, plant growth, and productivity (US EPA, 1996a; Tingey et al., 2001; Panek et al., 2002). Because the primary pathway for ozone to contact plant tissue is through plant stomata (Fowler and Cape, 1982), ozone effects on vegetation are related to the effective rate of ozone uptake (effective flux) and/or to the effective cumulative uptake amount (i.e., effective dose = effective flux × time) (US EPA, 1996a; Musselman and Massman, 1999; Massman et al., 2000). In this study the term effective dose is used to distinguish between dose (= stomatal flux × time) and that component of the dose which causes plant injury (i.e., the effective dose). The main distinction is that the effective dose includes some aspect of plant defense, whereas, dose (or stomatal uptake) alone does not. This distinction is made clearer in Section 2.5. Nevertheless, whether the metric for expressing ozone effects on vegetation is based on dose or effective dose, it has always been easier to measure ozone concentration than ozone flux. Consequently, ozone effects on vegetation have primarily been related to near surface ozone concentration and current ozone exposure is usually expressed in terms of

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concentration-based metrics, such as SUM00, SUM06, AOT40, W126, etc. (Lefohn, 1992; US EPA, 1996a; Fuhrer et al., 1997). However, ozone flux measurements are becoming more common (e.g., Massman et al., 2000) and technological advances have made ozone flux sensors much less expensive (Delany et al., 1997), suggesting that there is a continuing need to develop concepts and hypotheses for relating ozone effects on vegetation to both ozone flux and effective dose.

In addition to measurement difficulties, developing a useful flux-based standard to protect vegetation is further complicated by the need for a mathematical or numerical model to partition ozone fluxes into stomatal and nonstomatal pathways. Several different ozone deposition models have been developed for this purpose (e.g., Baldocchi et al., 1987; Wesely, 1989; Padro and Edwards, 1991; Amthor et al., 1994; Erisman et al., 1994; Gao and Wesely, 1995; Grünhage and Haenel, 1997). The motivation for many of the earlier models was to better describe the dynamics of atmospheric ozone by improving the simulation of the deposition process. However, later models have begun to focus more on protecting vegetation by combining ozone exposure metrics with ozone fluxes. Along side the development of ozone deposition models has come the coupling of such models and remote sensing technology to monitor and estimate ozone dry deposition fluxes (and other fluxes) over large areas of the earth's surface (e.g., Gao et al., 1992; Gao, 1995; Hasagar and Thykier-Nielsen, 2001), suggesting it may now be possible to consider developing a flux-based standard to protect vegetation by utilizing modeling and remotely sensed data. The broad purpose of this study is to explore some aspects of this possibility. The narrower purpose is to use a diagnostic model of ozone deposition with measured eddy covariance flux data to define an ozone metric based on effective dose and to examine some implications of this approach to quantifying the potential for plant injury from ozone.

Consequently, it should also be understood that this study does not propose to replace the current EPA exposure-based standard with a flux-based standard. Rather it outlines a plant injury model with the intention of further developing concepts related to flux-based standards for dry deposition of ozone. Another distinction between the present study and current EPA exposure-based standards is that this study expresses all flux-based concepts in terms of plant injury, whereas the EPA's focus has been based on plant damage (US EPA, 1996a). This study differentiates between ozone-induced plant injury and damage according to the definitions of Guderian (1977). Injury is any biological response, such as changes in metabolism, photosynthesis, leaf necrosis, premature leaf drop, or chlorosis. Therefore, in the present context, the word injury refers to any injury, even that which is not visible. Damage, on the other hand, is the reduction in the intended use or value, such as economic production, ecological structure and function, aesthetic value, or biological or genetic diversity. In general, because plant injury precedes plant damage, the difference between injury and damage is mostly a matter of degree. Consequently, the flux-based concepts developed in this study can apply to either injury or damage.

The remainder of this study is divided into three sections. Section 2 describes the model of effective dose and the parameterizations of resistances to ozone deposition developed for simulating ozone uptake by vegetated surfaces. Because canopy Leaf Area Index (LAI) is central to estimating stomatal ozone fluxes and is an important variable for remote sensing applications the ozone deposition model is, as much as possible, specifically parameterized in terms of LAI. Section 3 details model estimations of effective dose and stomatal O_3 fluxes for eddy covariance data from a vineyard site in the San Joaquin Valley of California (CODE91: Pederson et al., 1995; Massman et al., 1994). The last section summarizes the conclusions of this study.

2. Model description

The ozone deposition model is composed of two pathways, a stomatal pathway and nonstomatal pathway. Fig. 1 shows these pathways in more detail. Each of these resistances is modeled separately from the others. This approach differs most significantly from many other bulk formulations of dry deposition by treating the boundary layer resistances of the soil and plant canopy as separate resistances. For this reason and because the nonstomatal pathway, an empirically based model explicitly parameterized (as much as possible) in terms of LAI, is also formulated in a new way, some discussion and review of the transfer processes represented by these various resistances is included in this section.

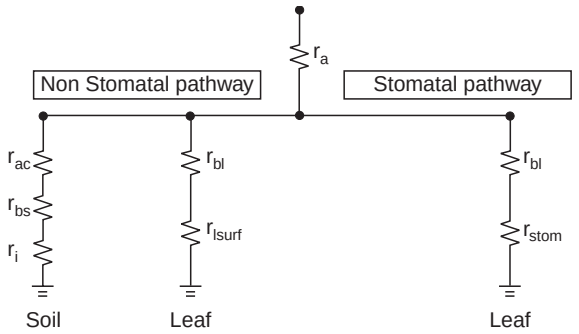

Fig. 1. Ozone deposition resistance network used in this study. Resistances are denoted with an '*r*' and are discussed in the text.

2.1. Above-canopy aerodynamic resistance, r_a

The aerodynamic resistance, r_a, is not explicitly used here because the model synthesized for this study is used to partition measured fluxes, which requires parameterizing only the surface resistances and does not explicitly require r_a or the measured ozone mixing ratio (ppbV). However, it is assumed that the fluxes are measured within the constant flux layer.

2.2. Plant stomatal pathway, r_{bl} and r_{stom}

In this study the plant stomatal pathway is comprised of two independent resistances, the canopy (bulk leaf) boundary layer resistance, r_{bl}, and the canopy (bulk leaf) stomatal resistance, r_{stom}. Although this approach allows significant simplification, it does not necessarily reflect the true relationship between these two resistances. In general, these resistances are quite strongly coupled to one another at the leaf level, to the leaf energy balance, and to leaf photosynthesis (e.g., Collatz et al., 1991; Nikolov et al., 1995; Wu et al., 2003). However, the intentions of the present study do now warrant this additional complexity.

2.2.1. The canopy boundary layer resistance, r_{bl}

The parameterization for the canopy boundary layer resistance, r_{bl}, is a combination of the models of Massman (1997) and Choudhury and Monteith (1988), as discussed in Massman (1999). For the present study, however, r_{bl} will be adjusted to ozone (mass transfer) rather than heat transfer as originally formulated. Following Massman's (1999) notation, r_{bl} is given specifically as

$$r_{bl} = \frac{B^{-1}}{u_*} = \frac{C_d}{4C_t[u_*/u(h)][1 - e^{-n/2}]u_*}, \quad (1)$$

where B^{-1} is the inverse of the Stanton number for ozone rather than heat, C_d is the leaf drag coefficient ($= 0.2$ for this study), u_* [m s^{-1}] is the friction velocity (a measured quantity during CODE91), C_t is the leaf mass or transfer coefficient and is a function of the within-canopy wind speed and leaf size (Massman, 1997), the ratio $u_*/u(h) = 0.32 - 0.264e^{-15.1C_d LAI}$ (Massman, 1997), and $n = C_d LAI/2u_*^2/u(h)^2$ is the within-canopy wind speed extinction coefficient (Massman, 1997). Expanding C_t and assuming that the typical vineyard leaf size for CODE91 is between 0.1 and 0.2 m yields

$$r_{bl} = \frac{1.75}{[u_*/u(h)]^{3/2}[1 - e^{-n/2}]\sqrt{u_*}}, \quad (2)$$

where r_{bl} is expressed in [s m^{-1}].

Because the CODE91 data includes eddy covariance measurements of the momentum flux (related to u_* as $-u_*^2$) this study uses u_*, rather than the measured wind speed, to parameterize any appropriate resistance. This avoids the need to introduce the traditional logarithmic wind profile and its attendant atmospheric stability functions and surface parameters: z_0, the surface roughness length, and d, the displacement height. Consequently, to use the present resistance model for other studies would require additional relationships to estimate u_* from other information.

2.2.2. The canopy stomatal resistance, r_{stom}

The vineyard canopy stomatal conductance, $g_{stom} = 1/r_{stom}$, is taken from Massman and Grantz (1995), who use the CODE91 vineyard leaf stomatal conductance data and water vapor eddy covariance flux data independently to estimate g_{stom}. Adapting their results to the present study yields:

$$g_{stom} = [g_x S + g_n]LAI, \quad (3)$$

where S is solar radiation [W m^{-2}], $g_x = 1.7(10^{-6})$ m s^{-1} m^2 W^{-1}, $g_n = 2.0(10^{-4})$ m s^{-1}, g_{stom} is expressed in m s^{-1}, and the vineyard LAI is 3.4 during CODE91. The fact that $g_n \neq 0$ indicates that the plant stomata are not completely closed at night, a result that is supported by the vapor eddy covariance flux data, but is less certain with the leaf conductance data (Massman and Grantz, 1995). Nevertheless, one intention of the present study is to explore the consequences and characteristics of nighttime stomatal uptake of ozone to the ozone injury metric proposed in this study. Consequently, there are some potential (scientific) benefits to the present formulation of g_{stom}. Another benefit to Eq. (3) is its simplicity. However, it is likely to be site specific.

2.3. Soil and nonstomatal plant pathways

The total nonstomatal surface pathway is composed of two components in parallel (see Fig. 1): a soil pathway and a nonstomatal leaf pathway. The soil pathway is defined by three resistances in series: the within-canopy aerodynamic resistance r_{ac}, the soil boundary layer resistance, r_{bs}, and the soil intrinsic resistance, r_i. The leaf nonstomatal pathway is comprised of two resistances in series: the canopy boundary layer resistance, r_{bl}, and the leaf surface resistance, r_{lsurf}. Here the leaf cuticular resistance is included as part of the leaf surface resistance as discussed below. Because r_{bl} was discussed in the previous section it is not discussed in this section. Because an empirical approach was chosen to develop the (four) remaining nonstomatal surface resistances, each is reviewed and synthesized, in turn, from available data.

2.3.1. The within-canopy aerodynamic resistance, r_{ac}

The turbulence that controls the exchange within the canopy and between the lower portions of the canopy and the atmosphere above the canopy are largely driven

by gusts of air penetrating into the lower canopy from above the canopy (Denmead and Bradley, 1985) and the degree to which the canopy air flow is coupled or decoupled to the air flow above the canopy (Jacobs et al., 1994; Jacobs et al., 1996). Consequently, describing this transfer in terms of a resistance will, to some extent, misrepresent the nature of the transfer. Nevertheless, many observational and modeling studies have attempted to define or quantify r_{ac}. Several of these studies are summarized in Fig. 2.

Mindful of the caveat above concerning r_{ac}, the following general statements can be made about r_{ac}. First, 'measurements' suggest that $20\ \mathrm{s\ m^{-1}} \leqslant r_{ac} \leqslant 400\ \mathrm{s\ m^{-1}}$ (Fig. 2). Furthermore, r_{ac} is likely to be dependent upon atmospheric stability (van Pul and Jacobs 1994). Second, the results of Massman and Grantz (1995) are highly uncertain and may not be statistically significantly different from the other estimates shown in Fig. 2. Nevertheless, the CODE91 estimates agree more closely with the r_{ac} values that Zhang et al. (2002) developed than with the other values shown in this figure. Zhang's et al. (2002) r_{ac} values are not included in Fig. 2 because they do not separate the soil boundary layer resistance from the surface (canopy plus soil) boundary layer resistance. Therefore, the empirically based approach they use to infer r_{ac} may also include the effects of the soil boundary layer resistance. Furthermore, their r_{ac} values, which were also developed by regression, display a large range of variability and must also be taken as very uncertain. Third, the data shown in Fig. 2 are consistent with two rather different models of r_{ac}. That is r_{ac} could be considered (i) a constant, $r_{ac} \approx 200\ \mathrm{s\ m^{-1}}$, or (ii) r_{ac} is approximately linearly dependent upon LAI and inversely dependent upon the above canopy friction velocity, u_*, although the proportionality constant would have a large range of possible values. The preferred choice is (ii) because it captures more of the true nature of the within-canopy transfer processes than (i) (e.g., McNaughton and van den Hurk, 1995). Fourth, r_{ac} may also be directly proportional to canopy height (van Pul and Jacobs, 1994, but not explicitly shown in Fig. 2). For simplicity in modeling and mindful of the potential application to remotely sensed data, r_{ac} is not modeled as a function of plant height in the present study. From the synthesis of the data shown in Fig. 2 and the above considerations r_{ac} is modeled as

$$r_{ac} = A_{ac}\,\mathrm{LAI}/u_*, \tag{4}$$

where $A_{ac} = 25$, r_{ac} is expressed in $\mathrm{s\ m^{-1}}$. Although we have specified A_{ac}, it must be recognized that A_{ac} is likely

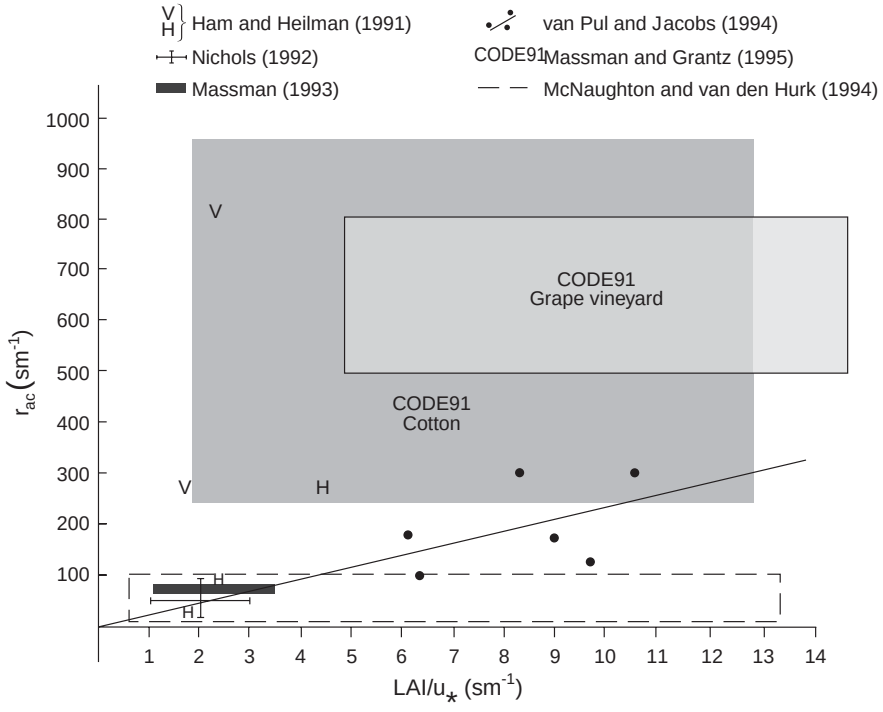

Fig. 2. Summary of observationally based inferences for the within-canopy resistance, r_{ac} (see also Ham and Heilman, 1991; Nichols, 1992; Massman, 1993; van Pul and Jacobs, 1994; Massman and Grantz, 1995; McNaughton and van den Hurk, 1994).

to be uncertain by at least a factor of 2 and probably varies with atmospheric stability.

2.3.2. The soil boundary layer resistance, r_{bs}

No direct measurements of the soil boundary layer resistance to ozone deposition have ever been made. However, there have been several studies of ozone deposition that have attempted to estimate the magnitude of r_{bs} either using models or by inferences from flux data. Table 1 summarizes several of these studies. Again within a factor of about 2, Table 1 suggests that

$$r_{bs} = 40[\mathrm{s\ m^{-1}}]. \quad (5)$$

However, this relationship is not the only possible model of r_{bs}. It is also possible to adapt results from studies of heat and water vapor transfer coefficients at the soil surface (e.g., McInnes et al., 1995; Sauer et al., 1995; Sauer and Norman, 1995; McInnes et al., 1996). In order to keep the model as simple as possible, the results of McInnes et al. (1995, 1996) are scaled by $(Sc/Pr)^{2/3}$ to account for the difference in molecular diffusivity of ozone and the thermal conductivity of air to yield the following alternative model of r_{bs}:

$$r_{bs} = A_{bs} u_*^{-1/2}, \quad (6)$$

where $10 \leqslant A_{bs} \leqslant 70\ \mathrm{s^{1/2}\ m^{-1/2}}$. The large range of variation in A_{bs} is likely associated with different soil surface roughness, different wind directions, different turbulent intensities, canopy structure, and natural variations in the observations (Sauer and Norman, 1995; McInnes et al., 1995, 1996; Massman, 1999). Because typical values for u_* range between 0.2 and 0.8 m s^{-1} for most surfaces, Eq. (6) can predict values for r_{bs} that exceed those summarized by Table 1 and Eq. (5); however, there is also a great deal of overlap and any specific value for A_{bs} is quite uncertain. In general, Eq. (5) is consistent with the results of Ham and Heilman (1991) and Massman (1992, 1993) who concluded that r_{bs} is not sensitive to the above canopy wind speed, while Eq. (6) is consistent with Sauer et al. (1995) and McInnes et al. (1995, 1996) who observe significant wind speed dependence. For this study Eq. (6) is used to model r_{bs} with $A_{bs} = 40\ \mathrm{s^{1/2}\ m^{-1/2}}$ because it is based on more direct studies of r_{bs} than the more empirically based Eq. (5).

2.3.3. The intrinsic soil resistance, r_i

Observed and inferred values for the soil intrinsic resistance to ozone deposition are summarized in Fig. 3 for both wet and dry soils. Not included in this figure are the results of Sánchez et al. (1997) or Zhang et al. (2002). In the case of the first study Sánchez et al. (1997) combine r_i and r_{ac} for a semi-arid steppe to produce a single resistance, R_{soil}, which is in general agreement with the present results. In second study Zhang et al. (2002) combine r_i and r_{bs} into a single soil resistance, R_{g0}, applicable to several sites. In general their results support the present parameterization for r_{bs} and r_i (for dry soils). Fig. 3 clearly suggests that wet soils are associated with relatively greater resistances than dry soils. The only possible exceptions to this are the desert data of Güsten et al. (1996) for a dry soil and the wet soil observations of Garland (1976). This discrepancy can be accounted for if either (or both) the soil organic content or the soil porosity are greater at the wet soil site than at the desert site because r_i decreases with increasing soil organic content (Garland, 1976) and increasing porosity (Turner et al., 1974). In general, Fig. 3 suggests that $10 \leqslant r_i(\mathrm{dry}) \leqslant 180\ \mathrm{s\ m^{-1}}$ and that $180 \leqslant r_i(\mathrm{wet}) \leqslant 1100\ \mathrm{s\ m^{-1}}$. Some of the variation in r_i for both the wet and dry soils may be related to natural daily variations in soil moisture or possibly the rate of soil drying during the periods of measurement. Variations in soil NO emissions and the associated chemical destruction of O_3 (e.g., Pilegaard, 2001) may also explain the variability of r_i. Nevertheless, to date there have not been enough studies of r_i and its relationship to soil porosity, soil moisture, and soil organic content to design a detailed model of r_i. Therefore, this study uses the following model of r_i:

$$r_i(\mathrm{dry}) = 100\ [\mathrm{s\ m^{-1}}], \quad (7)$$

$$r_i(\mathrm{wet}) = 500\ [\mathrm{s\ m^{-1}}]. \quad (8)$$

For modeling ozone deposition this study assumes that the soil at the vineyard site is dry due to lack of irrigation immediately before or during the experiment.

Table 1
Summary of soil boundary layer resistances to ozone deposition

Reference	Resistance (s m^{-1})	Comments
Galbally (1971)	$20 \leqslant r_{bs} \leqslant 70$	Model predictions to bare soil
Turner et al. (1973)	$r_{bs} \approx 10$–20	Inferred from data over bare soil
Garland (1976)	$r_{bs} \leqslant 40$	Inferred from data over bare soil
Garland and Penkett (1976)	$r_{bs} \leqslant 40$	Inferred from data over grass and soil
Leuning et al. (1979b)	$r_{bs} \approx 10$	Tobacco crop soil, model estimates
Massman (1993)	$r_{bs} \approx 70$	Inferred from data over shortgrass prairie
Güsten et al. (1996)	$r_{bs} = 10$–20	Model predictions to desert sand

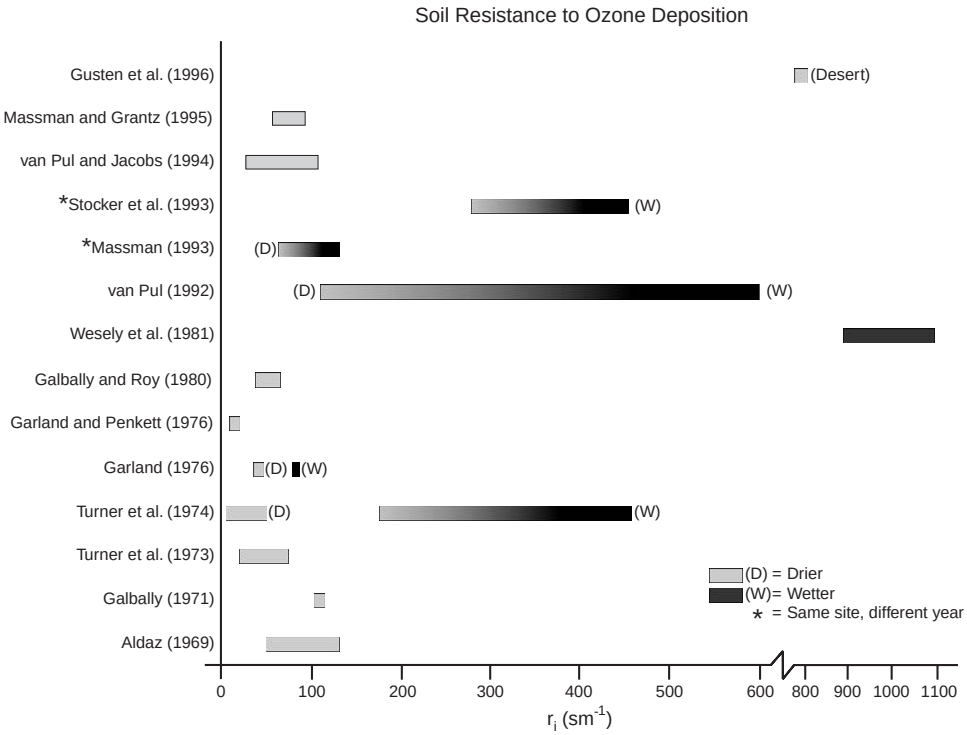

Fig. 3. Summary of observationally based inferences for the soil intrinsic resistance, r_i (see also Güsten et al., 1996; Massman and Grantz, 1995; van Pul and Jacobs, 1994; Stocker et al., 1993; Massman, 1993; van Pul, 1992; Wesely et al., 1981; Galbally and Roy, 1980; Garland and Penkett, 1976; Garland, 1976; Turner et al., 1973, 1974; Galbally, 1971; Aldaz, 1969).

2.3.4. The leaf surface resistance, r_{lsurf}

For a dry leaf the resistance of the (nonstomatal external) leaf surface to ozone deposition, r_{lsurf}, (which here includes the cuticular resistance), generally exceeds the stomatal resistance by at least three or four orders of magnitude (Kersteins and Lendzian, 1989). Nevertheless, this pathway is included in the model because plants tend to close their stomata at night which may cause this leaf surficial pathway to become an important sink for the destruction of nocturnal ozone. The following table, Table 2, summarizes much of the observational information on leaf cuticular or external surface resistance.

Before presenting our specific formulation for r_{lsurf} there are several important comments that should be considered. First, for comparative purposes data from plant chamber and canopy studies (i.e., Neubert et al., 1993; Massman and Grantz, 1995) have been scaled to the level of an individual leaf using measured or estimated LAIs. This was done by multiplying the canopy scale r_{lsurf} by 2LAI, which assumes that both the upper (adaxial) and lower (abaxial) sides of each leaf has the same r_{lsurf}. However, Kull and Moldau (1994) suggest this may not always be valid. Second, the results of Massman and Grantz (1995) are extremely uncertain and so they may not be significantly different statistically from the other studies. Third, except for Neubert et al. (1993) and Massman and Grantz (1995) no studies include the plant stem surfaces. Unfortunately, it is not possible from their studies to determine how much ozone was deposited to nonleaf plant surfaces. Fourth, r_{lsurf} can vary from plant to plant for a variety of reasons. For example, Kersteins and Lendzian (1989) note that (i) r_{lsurf} decreases with increasing relative humidity, (ii) the presence of leaf hairs and dust on the leaf reduces r_{lsurf}, and (iii) r_{lsurf} increases with increasing thickness of the cuticle. As a consequence of (ii) they also suggest that r_{lsurf} may depend upon the type and amount of epiphytes and microorganisms present on the leaf surface, which Schreiber and Schönherr (1993) have demonstrated. Finally, Kersteins and Lendzian (1989) also show that r_{lsurf} can change over time, suggesting that r_{lsurf} is influenced by the history of the leaf's exposure to pollutants and to ozone in particular.

These many large- and small-scale issues involving r_{lsurf} serve to underscore the large uncertainties inherent in any estimate of r_{lsurf} for ozone deposition at the canopy scale. With these issues in mind the plant canopy's surficial resistance is modeled as

$$r_{lsurf} = A_{lsurf}/\mathrm{LAI}, \tag{9}$$

Table 2
Summary of individual leaf surficial resistances to ozone deposition

Reference	Resistance (s m^{-1})	Plant Species
Rich et al. (1970)	$r_{lsurf} \approx 1900$	Bean leaf
Unsworth (1981)	$r_{lsurf} = 2180$	Corn leaf
Kersteins and Lendzian (1989)	$1100 \leqslant r_{lsurf} \leqslant 27,000$	Review of published literature
	$2500 \leqslant r_{lsurf} \leqslant 35,000$	Measurements from isolated cuticles
Neubert et al. (1993) (Chamber studies)	$r_{lsurf} = 11,500 \pm 6000$	Tobacco Plant (LAI = 3)[a]
	$r_{lsurf} = 4400 \pm 2400$	Sunflower Plant (LAI = 2)[b]
Kull and Moldau (1994)	$r_{lsurf} \approx 3200$ (adaxial)	White Birch leaf
	$r_{lsurf} \approx 1900$ (abaxial)	
Fuentes et al. (1994a)	$r_{lsurf} = 2200$	Poplar and Maple leaves
Massman and Grantz (1995) (eddy covariance)	$r_{lsurf} \approx 38,100$	Grape vineyard (LAI = 3.4)
	$r_{lsurf} \approx 400,000$	Cotton crop (LAI = 1.8–2.8)

Chamber and canopy studies have been scaled to the level of an individual leaf using observed or estimated values of LAI to account as necessary for both sides of the leaf.

[a] LAI estimate from David Raper (personal communication, 1996) and Avissar et al. (1985).

[b] LAI estimate from Saugier (1976).

Table 3
Summary of studies on the influence of surface wetness on dry deposition of ozone

Reference	Rain	Dew	Comments
Wesely et al. (1978)		−	Maize canopy, eddy covariance data
Leuning et al. (1979a)	−		Maize canopy after a thunderstorm
			Bowen ratio energy balance data
Fuentes et al. (1992)	+	+	Deciduous forest, eddy covariance data
Fuentes and Gillespie (1992)	+	+	Red maple leaves, chamber study
Fuentes et al. (1994b)	+	+	Red maple leaves, chamber study
	−	−	Poplar leaves, chamber study
Padro (1994)	−	+/0	Deciduous forest, eddy covariance data
Massman et al. (1994)		0	Cotton canopy and vineyard, eddy covariance data
Grantz et al. (1995)		+	Vineyard, eddy covariance data
Pleijel et al. (1995)	+	+	Chamber study, spraying of grass/clover canopy
Grantz et al. (1997)		−	Cotton canopy, eddy covariance data
Lamaud et al. (2002)		+	Pine forest, eddy covariance data
Zhang et al. (2002)	+	+	Eddy covariance data: mixed forest, pasture, deciduous forest, maize canopy, soyabean canopy

The plus sign (+) indicates that dry deposition rates are enhanced (relative to dry foliage) when the foliage is wet. The minus sign (−) indicates that dry deposition rates are reduced when the foliage is wet. 0 means no difference in dry deposition between wet and dry leaf or canopy surfaces.

where $A_{lsurf} = 5000$ s m^{-1} with an uncertainty again of about a factor of 2. This model basically assumes that the nonstomatal leaf surface is a passive receptor of ozone. However, Rondón (1993), Rondón et al. (1993), Granat and Richter (1995), and Coe et al. (1995) have hypothesized that ozone-destroying photochemical reactions may occur on the cuticle. At present the precise nature of this reaction is not known, but it does appear that this process is correlated with solar radiation and possibly with temperature and that the associated rate of ozone destruction is comparable in magnitude to that associated with the stomatal pathway. Because more specific information is lacking about this potentially important pathway for ozone destruction it is not included in the present model. However, it is important to be cognizant of the possibility that there may be an important pathway that has not been included in this or, to the author's knowledge, any ozone deposition model.

In the present formulation of ozone deposition no specific allowance is made for the presence of moisture on the nonstomatal canopy leaf surfaces. A review of the observational studies of the influence of surface wetness on ozone dry deposition rates, Table 3, indicates that surface wetness can enhance, reduce, or make very little

difference to the dry deposition of ozone to vegetation. Some of the reasons for this large range of variation are surface chemistry, presence or absence of leaf wax, occlusion of stomata by water drops, the position of stomata on upper and/or lower sides of leaves, the density of leaf hairs or trichomes, and mutual sheltering of leaves to wind (Schuepp, 1989; Brewer et al., 1991; Fuentes et al., 1994a; Grantz et al., 1995; Grantz et al., 1997). Again because of the paucity of observational and scientific data on which to construct a model the simplest (or null) approach is chosen for modeling the dry deposition of ozone to wet plant surfaces. The present model is intended to be specific to ozone and should not necessarily be used for the dry deposition of other gaseous species to wet foliage. A more general approach is required for other species and is beyond the intention of the present study.

2.4. Influences of possible chemical processes

Although chemical pathways for ozone destruction are not included in the model, they have been hypothesized as important under some conditions and as such deserve some discussion, particularly in regards to their potential impact on model parameterization and performance and their possible linkages to plant defense. As mentioned earlier, Rondón (1993), Rondón et al. (1993), Granat and Richter (1995), and Coe et al. (1995) have proposed that leaf surfaces may facilitate the chemical destruction of significant amounts of ozone. Kurpius (2001), who observed eddy covariance fluxes of ozone to a Ponderosa Pine forest that were larger than could be accounted for solely by stomatal and non-stomatal uptake, has suggested that a combination of ambient NO and hydrocarbons could have been as important as stomatal uptake in explaining the observed daytime ozone fluxes. Mikkelsen et al. (2000), suggested the same chemical pathway to explain the relatively high nighttime ozone depositional flux they observed at a conifer forest site dominated by Norway spruce. For many species of conifers hydrocarbon emissions can be substantial and they increase exponentially with increasing temperature (e.g., Harley et al., 1998; Shao et al., 2001). Furthermore, plant emissions of NO and some VOCs both appear to be possible plant responses to ozone exposure (e.g., Wildt et al., 1997; Heiden et al., 1999). Finally Gao et al. (1993) conclude from their modeling study of a coupled plant canopy biophysical and photochemical model that ozone fluxes can be influenced by reactive chemical processes. All this suggests (i) that a chemical pathway for ozone destruction may exist for some plant species and some situations and (ii) that emissions of some of these chemicals may be in response to ozone uptake. In the present context the existence of such a chemical pathway for ozone destruction serves to point out that a full description of the interactions between ozone and plants is likely to require coupling models of the plant's physical and (photo)chemical environment with biophysical and biochemical models of plant function and defense. Such a model is beyond the intention of the present (or any current) model. [Note that although the model of Gao et al. (1993) is a significant step in the necessary direction, it does not include processes associated with plant photosynthesis or plant defensive mechanisms.] However, there is still a need to find a simple parameterization for plant defense to include in a flux-based approach to setting ozone standards. This study develops a relatively simple and empirical approach to plant defense and parameterize it in terms of the rate of photosynthesis.

2.5. Modeling ozone injury to plants

Massman et al. (2000) and Matyssek et al. (2004) suggested that plant injury is cumulative and related to the difference between plant stomatal uptake and plant defense, i.e.,

$$\text{Injury} \propto \sum_i [F_{\text{stom}*}(t_i) - D(t_i)] \quad \text{(Hypothesis 1)},$$

where t is time, $F_{\text{stom}*}(t_i)$ is the plant stomatal ozone uptake rate or ozone flux (which includes both the stomatal and boundary layer effects, Fig. 1), $D(t_i)$ is the plant defense, and the summation is over a discrete time sampling index, i. Here this concept is extended by parameterizing plant defense in terms of the rate of photosynthesis, i.e.,

$$D(t) = \alpha A(t) \quad \text{(Hypothesis 2)},$$

where $A(t)$ is the gross canopy assimilation rate of CO_2, α is a proportionality constant with an assigned value of 0.20 $\mu g(O_3)\ mg(CO_2)^{-1}$. Because Hypotheses 1 and 2 are defined for plant canopies all the flux terms are m^{-2} of ground area.

Some justification and discussion of Hypothesis 2 should be useful here. First, Musselman and Massman (1999) suggested that $D(t)$ is likely to be, at least, an indirect function of the rate of photosynthesis. We make it explicit here because it is a reasonable (albeit heuristic) assumption. Second, this formulation for $D(t)$ is a continuously changing threshold which varies with time of day and season and is determined by the plants' ability to photosynthesize. As such, the parameter α is chosen so that the maximum possible ozone defense is about 0.36 $\mu g(O_3) m^{-2}\ s^{-1}$, which is lower than the value suggested by Massman et al. (2000) in accordance with their discussions about the ozone-flux/plant-response studies of Leuning et al. (1979b) and Amiro et al. (1984). Further, the ozone flux threshold studies of Pleijel et al. (2002) and Danielsson et al. (2003) suggest that the relative yield loss (damage) resulting from ozone uptake

will have occurred by the time the ozone uptake rate has reached a value of 0.30 ± 0.05 μg(O_3)m^{-2} s^{-1}, supporting the numerical estimates related to Hypothesis 2 and α. There is also some indication that no threshold or minimum level of ozone exists that will not reduce photosynthesis (e.g., Reich and Admundson, 1985; Weinstein et al., 1998), again tending to support our second hypothesis and the need to reduce the threshold estimate of Massman et al. (2000). Third, gross photosynthesis, rather than net photosynthesis, is used as part of an ozone metric primarily because gross photosynthesis was found to be slightly more sensitive to ozone uptake than net photosynthetic rate Grulke et al. (2002). Fourth, and maybe most importantly, this hypothetical defense parameterization does not include any reduction in the rate of photosynthesis resulting from ozone uptake. Such a feedback mechanism would in essence reduce defense capability with ozone uptake. It is possible to include this in a simple manner by including a reduction factor that modifies rate of photosynthesis, $A(t)$. For example,

$$A_r(t) = [1 - \beta_{O_3} F_{stom*}(t) \mathrm{LAI} \tau] A(t) \quad \text{(Hypothesis 3)},$$

where $A_r(t)$ is the reduced rate of photosynthesis, τ is the number of days the plant has been taking up ozone, and $\beta_{O_3} \approx 0.014$ μg$(O_3)^{-1}$ m^2 s day^{-1} for agricultural crops (Reich, 1987). (Note that Reich's (1987) analysis suggests that crops, hardwoods, and pines have different values of β_{O_3}.) Hypothesis 3 can be further adapted to include the special case of ozone-induced photoinhibition (e.g., Schmieden and Wild, 1995; Heath and Taylor, 1997), at least in a simple manner, by parameterizing β_{O_3} to increase at high light intensities, so that ozone injury increases when ozone and high light intensities act as synergistic stressors. In general, combining Hypotheses 2 and 3 to include a negative feedback on defense is possible with the present model. However, logically, Hypothesis 3 should be implemented on a leaf level, which would couple plant stomatal behavior and photosynthesis to ozone uptake. In turn, this would argue for the need to model within-canopy profiles of ozone concentration, in order to assess the importance of height-dependent within-canopy stomatal fluxes and plant defenses. While this approach is more realistic, it is also more complicated mathematically and is beyond the intent of this study. Fifth, and final, our model of plant defense, Hypothesis 2, does not include any possible interactions between ozone and other pollutants (e.g., Ormrod, 1982). Our intent with this brief discussion of plant response and Hypothesis 2 is to emphasize that the relationship between plant defense, plant response, and plant photosynthesis is potentially quite complicated; whereas, our model of plant defense is relatively, and intentionally, simple.

2.6. Estimating gross photosynthesis and plant defense with eddy covariance data

During CODE91 the measured CO_2 flux includes corrections for spectral attenuation and atmospheric density effects (Pederson et al., 1995). However, in general the resulting CO_2 flux is more closely related (during the daylight hours) to net photosynthesis than to gross photosynthesis, because this eddy covariance flux does not directly measure or include the plant uptake of CO_2 respired from the soil and plant itself. To compensate an additional respiratory flux term, $R_{CO_2}(t)$ given next, is added to the CODE91 CO_2 flux to better estimate gross photosynthesis.

$$R_{CO_2}(t) = R_0 e^{Q T_{soil}}. \tag{10}$$

Here T_{soil} is the measured half-hourly soil temperature [C] and $R_0 = 0.0088$ mg m^{-2} s^{-1}, and $Q = 0.1$ C^{-1} were determined by regressing the nighttime CO_2 flux data against the measured soil temperature. The nighttime CO_2 flux is comprised only of respiratory fluxes because photosynthesis is not active at night. Consequently, the modeled defense term, $D(t)$, is restricted to the hours between 7 a.m. to 8 p.m. local time. Otherwise $D(t) = 0$ is assumed. Again this is an intentional simplification. It is possible that plants have additional defensive capabilities that are active throughout both the day and night. Such a defense could be parameterized as a constant flux threshold. But for the present study, this possibility offers more complications than insights and so will not be considered here.

This is an admittedly simple method of estimating the respiratory flux, but again for the present purposes it should be quite adequate. A more complete soil/plant/atmosphere exchange model would likely include more detailed parameterizations of gross photosynthesis, net photosynthesis, and plant and soil respiration. Furthermore, if more were known about nighttime ozone defensive capabilities of plants it could also be included in a more complete model.

3. Results

3.1. The effective dose and the potential for plant injury

Fig. 4 displays the mean 24-h cycle of measured ozone concentration with the model's mean 24-h cycle of instantaneous effective ozone dose, $[F_{stom*}(t) - \alpha A(t)]$ at the vineyard site during the CODE91 (8 July through 6 August 1991), which is shown here as a negative quantity in accordance with the eddy covariance sign convention appropriate to ozone fluxes. For this convention any ozone flux is negative if it is downward or toward the surface. It is possible to make this ozone metric positive by taking the absolute value

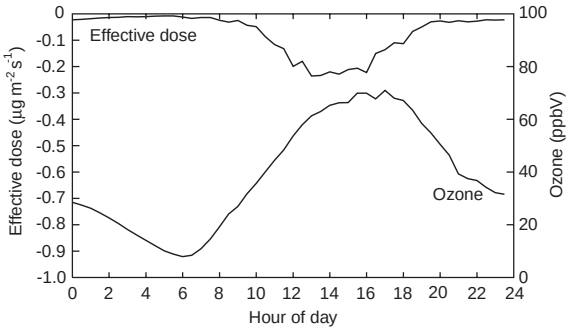

Fig. 4. Average daily cycle of the observed ozone concentration and model estimates of the flux-based instantaneous effective ozone dose, $[F_{\text{stom}*}(t) - \alpha A(t)]$, at vineyard site during the CODE91 (8 July through 6 August 1991). See Section 2.5 for a discussion of effective dose. The effective dose is negative by convention with ozone fluxes measured using eddy covariance, which are positive when they are upward or away from the surface and negative when they are downward or toward the surface.

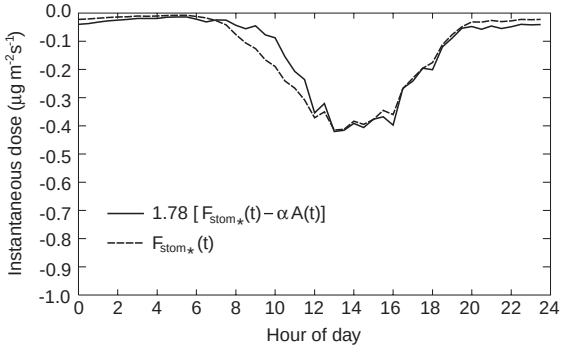

Fig. 5. Average daily cycle of the model estimates for the flux-based instantaneous ozone dose, $[F_{\text{stom}*}(t)]$, and instantaneous effective ozone dose $[F_{\text{stom}*}(t) - \alpha A(t)]$, at vineyard site during the CODE91 (8 July through 6 August 1991). The instantaneous effective ozone dose has been multiplied by 1.78 for ease of comparison between the two flux-based metrics.

of $F_{\text{stom}*}(t_i) - \alpha A(t_i)$ whenever the eddy covariance derived stomatal flux, $F_{\text{stom}*}(t_i)$, exceeds the defensive capabilities.

According to these results the period of greatest risk (highest effective dose) to the plant occurs between the hours of about 1 p.m. and 4 p.m. and the period of highest ozone mixing ratio is between 2:30 p.m. and 5 p.m. In other words there is a substantial overlap between the peak ozone concentrations and the potential for injury or damage. This temporal coincidence is of practical importance to exposure-based indices because some of them reflect this feature better than others. For example, SUM00 places too much emphasis on the low ozone concentrations typical of the early morning [8–10 a.m.]; whereas, the W126 and SUM06 are more realistic because they place greater emphasis on the higher concentrations characteristic of the mid-afternoon [2–4 p.m.] (US EPA, 1996b). Musselman and Massman (1999) and Massman et al. (2000) have reached similar conclusions.

Fig. 5 is a vineyard site comparison between the model's mean 24-h cycle of instantaneous ozone dose, $[F_{\text{stom}*}(t)]$, and the model's mean 24-h cycle of instantaneous effective ozone dose. Here the effective dose is multiplied by a factor of 1.78 so that the maximum effective dose is approximately the same as the maximum dose, which highlights a major difference between the simple dose-based metric and the effective dose-based metric. The primary difference between these two injury metrics is most obvious between the hours of 8 a.m. and noon. Relative to the simple dose metric, plant photosynthesis tends to reduce the contribution of the effective dose to the daily cumulative dose during this portion of the day. This demonstrates, as hypothesized by Massman et al. (2000), that plant defenses are likely to be greater during the morning hours precisely because photosynthesis is maximal during that time.

The difference shown in Fig. 5 results, at least in part, from the resistance model used to partition the measured ozone flux and from the soil respiration function, Eq. (10), used in the defense parameterization. A sensitivity analysis was performed to determine if this difference is an artifact of the particular choices that were made or if it is more general in nature. A comparison similar to Fig. 5 was performed after each of the following manipulations to the injury model: (i) multiplying all nonstomatal resistances by two, (ii) dividing all nonstomatal resistances by half, and (iii) deleting the respiration function altogether. In all three cases the temporal difference between the simple dose-based metric and the effective dose-based metric remained. However, more important to this difference is the numerical choice for the parameter α. As α increases so does the difference. In general, therefore, this temporal difference is a consequence of the formulation of the vegetation's defense to ozone.

3.2. The influence of nocturnal uptake of ozone

Fig. 6 shows the average daily cycle of cumulative effective ozone dose (normalized to unity) at the vineyard site during the CODE91. The figure indicates that between about noon and 4 p.m. the canopy accumulates some 50–60% of its daily effective dose. However, this figure also shows the importance of the nocturnal stomatal conductance to the hypothetical ozone injury index because about 15% of the daily total of the effective ozone dose accrues during the nighttime hours (8 p.m. to about 7 a.m.). A simple dose-based metric would not show as high a percentage because it does not include a specific daytime-only defense. This is

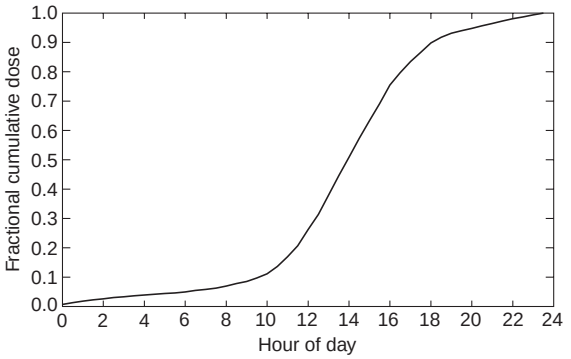

Fig. 6. Average daily cycle of cumulative effective ozone dose (normalized to unity) at the vineyard site during the CODE91 (8 July through 6 August 1991).

also an important difference between a simple dose-based metric and an effective dose-based metric. Over the course of the growing season this nocturnal ozone dose could play a significant role in plant injury. Massman et al. (2000), Musselman and Minnick (2000), and Matyssek et al. (2004) have also suggested this possibility.

4. Conclusions

This study is an extended example of the concepts, developed by Musselman and Massman (1999) and Massman et al. (2000), underlying the use of a flux-based metric for assessing plant injury. This study has, in essence, applied their concepts using an ozone deposition model (developed for this study) to eddy covariance (O_3 and CO_2 flux) data from the California Ozone Deposition Experiment (CODE91: Pederson et al., 1995; Massman et al., 1994). This model/data combination is used to partition observed fluxes into stomatal and nonstomatal components, to develop a simple parameterization of plant defense to ozone uptake, and to examine the temporal behavior of a flux-based metric for assessing ozone injury or damage to plant canopies. This flux-based metric, which employs the concept of effective dose, is defined as the difference between the canopy stomatal ozone uptake rate and a plant defense function, which is taken to be proportional to the canopy gross photosynthesis. For this study, the constant of proportionality is assumed to be nonvarying; however, it is quite likely to prove to be species dependent. Nocturnal stomatal conductance, strongly suggested by the eddy covariance data (Massman and Grantz, 1995), is included as part of the deposition model.

In addition, this study also develops a simple model to describe ozone deposition to nonstomatal surface pathways based on a summary and synthesis of the available data relating to the nonstomatal plant and soil ozone depositional pathways (see Fig. 1). These (five) additional resistances are parameterized, as much as possible, in terms of the friction velocity, u_*, and plant LAI. This deposition model includes separate parameterizations of leaf and soil boundary layer resistances. The stomatal conductance model is largely data based and, as such, is site specific. No coupling between the leaf stomatal and the boundary layer resistances (Collatz et al., 1991, Nikolov et al., 1995) is included in the present model. The nonstomatal resistances developed for this study could have applications beyond just the present study. However, the stomatal conductance is unlikely to be as broadly useful. For other applications, particularly those involving remote sensing, a more complete soil/leaf/plant/atmosphere model will ultimately be needed in order to include the influence that edaphic conditions, such as, soil moisture, vapor pressure deficit, solar radiation, etc., can have on stomata, stomatal ozone flux, plant defense, and effective dose.

Finally, the comparison between the measured average 24-h cycle of ozone concentration and the modeled mean 24-h cycle of instantaneous effective ozone dose predicts that the maximum (instantaneous) effective ozone dose occurs at the time that the ozone concentration is at or near its daily maximum value. Although some exposure-based indices capture this crucial temporal co-occurrence better than others, none of them include the edaphic conditions that control stomatal behavior, photosynthesis, ozone flux, and plant defenses. A comparison of the temporal behavior of a simple dose-based metric and an effective dose-based metric highlights the importance of the modeled plant defense in defining a flux-based metric. Nocturnal stomatal ozone uptake also accounted for about 15% of the cumulative daily effective ozone dose. In total the present results serve to emphasize the importance of a flux-based ozone metric and a dynamic formulation of plant defense to ozone uptake.

Results of the present study also suggest several areas that need further investigation. These include (i) species specific studies of plant defensive mechanisms for minimizing ozone injury and simple methods of parameterizing them, (ii) empirical studies relating flux-based metrics to plant injury and damage, (iii) further studies aimed at developing some of the concepts outlined in the present study for application to remote sensing, and (iv) use of more general soil/leaf/plant/atmosphere models for estimating stomatal ozone uptake and plant defense.

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