



1352-2310(95)00129-8

EFFECTS OF STOMATAL CONDUCTANCE AND SURFACE WETNESS ON OZONE DEPOSITION IN FIELD-GROWN GRAPE

D. A. GRANTZ,* X. J. ZHANG,* W. J. MASSMAN,† G. DEN HARTOG,‡
 H. H. NEUMANN† and J. R. PEDERSON§

*Department of Botany and Plant Sciences and Statewide Air Pollution Research Center, University of California at Riverside, Kearney Agricultural Center, 9240 S. Riverbend Avenue, Parlier, CA 93648, U.S.A.; †USDA, Forest Service, Rocky Mountain Forest and Range Experiment Station, Ft. Collins, CO 80526, U.S.A.; ‡National Research Council of Canada, Ontario, Canada; and §Technical Support Division, California Air Resources Board, Sacramento, CA 95812, U.S.A.

(First received 24 November 1993 and in final form 2 October 1995)

Abstract—Surface deposition is an important sink that removes ozone from polluted air basins, and leads to crop damage and ecosystem decline. Physiological and physical processes controlling deposition to vegetated surfaces are incompletely understood. We investigate the relationship between ozone flux to trellised grape, F , and canopy stomatal conductance to ozone, g_c , under dew-wetted and dry conditions. Empirically measured stomatal conductance was scaled to g_c using empirical measurements of leaf area index, L , single leaf stomatal response to photon flux density, I , and bulk canopy radiation extinction coefficient, K . Leaf wetness was determined with surrogate leaves covered with electrical impedance grids. Deposition velocity, V_d , and surface conductance, g_{surf} , were positively and highly significantly related to g_c . Surface wetness substantially increased V_d and g_{surf} . Under all conditions, $g_c < g_{surf}$, suggesting a significant non-stomatal (residual) pathway for ozone deposition, g_r . This residual term, g_r , was increased under wet conditions by a constant amount over the full range of g_c . Expected errors of $\pm 20\%$ in the single leaf model, in L , or in K , did not influence these conclusions. We conclude that V_d and g_{surf} were dominated by g_c , which may be used effectively to predict ozone deposition to physiologically active vegetated surfaces. Dew formation enhanced ozone deposition to the hypostomatous leaves of this grape canopy by a non-stomatal pathway.

Key word index: Canopy, conductance, dew, deposition, ozone.

INTRODUCTION

The San Joaquin Valley of California (SJV) is a region of rapid population increase that is subject to violations of federal air quality standards for tropospheric ozone. The SJV is a nearly closed air basin that is heavily agricultural. Ozone removal by deposition to crops is thus of central importance to regional ozone modelling efforts, and potentially to land use planning decisions.

The present study tests the hypotheses that canopy stomatal conductance predicts ozone deposition velocity to physiologically active vegetation such as irrigated grape (supported) and that surface wetness reduces ozone uptake to hypostomatous species such as grape below the level predicted by stomatal conductance (not supported).

Empirical field measurements of stomatal conductance, photon flux density above and below the canopy, dew formation on surrogate leaves, and canopy level ozone fluxes were obtained during the California ozone deposition experiment (CODE; Pederson *et al.*,

1992, 1995). For clarity, and unlike our previous treatments of these data (e.g. Massman *et al.*, 1994), we restrict the analysis to morning and evening hours with non-zero but less than half-maximal sunlight, when dew was sometimes present, stomatal conductance most rapidly changing, and surface properties likely to be controlling deposition. We apply a physiologically relevant single leaf stomatal light response function, exhibiting saturation kinetics over this range of photon fluxes. Previous treatments addressed modelling issues involving deposition to irrigated western crop canopies and discrepancies in alternative estimates of surface conductance. Here, we evaluate the interaction of dew formation with stomatal and non-stomatal pathways of ozone deposition, and the potential application of stomatal properties to infer ozone deposition in the field.

BACKGROUND

Distinguishing between stomatal and non-stomatal ozone deposition is important for airshed modelling

of photochemical oxidant budgets, and for prediction of agricultural and ecosystem productivity. Tropospheric ozone is a serious threat to human and plant health. Removal of ozone from the mixed atmospheric layer by vegetation may benefit human health by reducing ambient concentrations, while mediating deleterious direct effects on the vegetation (e.g. for grape, Roper and Williams, 1989a). The most severe phytotoxic effects of ozone involve uptake of ozone through stomata in the leaf surface, with consequent access and oxidative damage to photosynthetic tissue in the leaf mesophyll (Roper and Williams, 1989a; Thomson *et al.*, 1966). Additional damage by a non-stomatal pathway to the cuticle and trichomes on the leaf surface (e.g. Barnes *et al.*, 1988) may have consequences for tissue water loss. Grape has been shown to exhibit substantial yield losses due to ambient ozone in the San Joaquin Valley (SJV; Brewer and Ashcroft, 1983; Rowe and Chestnut, 1985) and in other grape producing regions (Musselman *et al.*, 1978, 1985; Shaulis *et al.*, 1972).

Stomatal conductance

Dry deposition of ozone over vegetated surfaces is mediated by turbulent exchange between the atmosphere and the surface boundary layer, in conjunction with surface properties (Baldocchi *et al.*, 1987; Fuentes *et al.*, 1992; Hicks *et al.*, 1987; Padro *et al.*, 1991). The surface conductance consists of canopy stomatal conductance, reflecting aggregate physiological attributes of the plant species present, and of physical surface conductances determined by the physicochemical properties of soil and external plant surfaces. Surface conductance is usually smaller than the atmospheric components and effectively controls ozone removal from the atmosphere (Baldocchi *et al.*, 1987; Fuentes and Gillespie, 1992; Massman *et al.*, 1994).

In isolated leaves and plants (Butler and Tibbitts, 1979) ozone deposition is closely related to stomatal conductance. In intact canopies, however, problems of scaling (Jarvis and McNaughton, 1986; Massman *et al.*, 1993; Meinzer and Grantz, 1989) make this conclusion less certain. Degradation of ozone by bare soil (e.g. Turner *et al.*, 1973) may approach 40% of total deposition (Leuning *et al.*, 1979b). Soil activity will depend on vegetation cover, including short understory species, and soil moisture. Reduced surface evaporation at night could lead to subsurface moisture wetting the soil surface by capillary action, thereby increasing ozone decomposition activity. This issue has not been explored.

Diurnal patterns of turbulence parameters may lead to covariance of atmospheric and stomatal conductances, both obscuring the role of stomatal regulation, but also strengthening the relationship between deposition and stomatal conductance. Under daylight conditions stomatal conductance generally dominates surface conductance of physiologically active plant canopies (e.g. Baldocchi *et al.*, 1987; Grantz *et al.*, 1994; Wesely *et al.*, 1978). Ozone deposition might

then be estimated only from knowledge of canopy-scaled stomatal behavior, without measurement or calculation of additional micrometeorological parameters. Canopy stomatal conductance of well-irrigated vegetation may be predicted from tabulated timecourses of radiation interception.

Dew

Other factors confound the dominant effect of canopy stomatal conductance on ozone deposition. Canopy wetness associated with dew formation could facilitate chemical interaction of ozone and surface solutes, increasing ozone deposition, or it could occlude stomatal pores, decreasing ozone deposition. Available experimental evidence is inconsistent.

Ozone deposition by a non-stomatal pathway was enhanced in a deciduous forest when the foliage became wetted with dew (Fuentes *et al.*, 1992). Under conditions favoring dew persistence, but low levels of stomatal conductance, significant ozone deposition was measured. After evaporation of the dew, but prior to substantial light-induced stomatal opening, ozone flux decreased. Similarly, single leaf gas exchange data have demonstrated enhanced ozone deposition on leaves misted with water at pH 6 (Fuentes and Gillespie, 1992). A mechanism for enhancement of ozone deposition by dew is provided by chemical arguments involving codeposition with acidic and acidifying species to leaf surface moisture (Chameides, 1987).

In contrast, ozone uptake was reduced by dew formation in maize and wheat (Hicks *et al.*, 1987; Wesely *et al.*, 1978). Deposition was also reduced in senescent maize plants, in which occlusion of stomatal pores would not be expected to obstruct deposition. A mechanism for suppression of deposition by dew is provided by the lower aqueous solubility of ozone than some other depositing species (e.g. SO₂; Fowler, 1985) which suggests that surface wetness could restrict access to reactive surface sites and physically block stomatal pores.

Differences between contrasting studies in the nature of stomatal control and in the direction and magnitude of observed surface wetness effects may reflect uncharacterized differences between experiments in leaf structure or surface chemistry, stomatal distribution, canopy morphology, or experimental methods. We analyze the most relevant portion of the CODE data set to address these persistent questions regarding ozone deposition in grape.

FIELD MEASUREMENTS

Site description

The California ozone deposition experiment (CODE; see Pederson *et al.*, 1995) was conducted in the San Joaquin Valley (SJV) of California between 8 July and 6 August 1991. The mature grape vines (cv. Thompson Seedless) were in trellised rows oriented eastwest, spaced ca. 3 m apart. Canopy height

was ca. 1.7 m. The experimental site (36°51'36" N, 120°6'7" W) was located ca. 40 km west of Fresno, ca. 100 m above sea level, and with fetch greater than 1 km. Clear skies, high temperatures, and low winds (1–6 m s⁻¹, from the northwest) were consistent during the study. Detailed micrometeorological, physiological, and microenvironmental data for this site over this period are available (den Hartog *et al.*, 1992; Grantz, 1992).

Canopy structure and photon penetration

Leaf area index, L , was measured near sunset on two occasions during the experimental period using a Plant Canopy Analyzer (LAI-2000, LiCor, Inc., Lincoln, NE), which is based on the gap inversion method (Wells and Norman, 1991). A modified protocol developed for grape (Grantz and Williams, 1993) was employed. Based on these data from nearby vineyards (Grantz, 1992), L was taken as the average value obtained on two dates ($L = 3.39$) over the relatively brief experimental period. L was considered on a total ground area basis, even though rows did not fully cover the ground at either measurement date. Short grasses growing in the inter-row spaces were not considered in the determination of L .

Photosynthetically active photon flux density, I , was measured on a horizontal plane above the canopy. An apparent bulk photon extinction coefficient, K , was determined empirically from photon penetration through the entire canopy at mid-row, over two bands of zenith angles, $\theta = 0$ –13° and $\theta = 16$ –28°, under conditions of low radiation. These data were obtained using intermediate calculations involved in the determination of L . The instrument contains optical filters to remove all but the blue portion of the photosynthetically active spectrum. The current analysis is restricted to morning and evening hours so that no attempt was made to model diurnal changes in K as required for a complete diurnal analysis.

Dew formation

Surface wetness of surrogate leaves was measured using electrical impedance sensors coated with a light green latex paint (Gillespie and Kidd, 1978) and located within the canopy as described (Grantz, 1992). Values of impedance were recorded with a data logger (21X, Campbell Scientific, Inc.; Logan, UT) every 5 s, and 30 min means calculated. Sensor readings exhibited a sharp cutoff between wet and dry conditions. Low mean values were rounded to 0, indicating a dry canopy, while high readings were rounded to 1, indicating a wet canopy. As there was no rainfall during the experimental period, and irrigation was by furrow, a positive leaf surface wetness reading represented only dew. Correlations during CODE in this grape canopy, between leaf wetness sensor readings, independent measurements of leaf to air vapor pressure gradient, and visual assessments of dew persistence, were consistent with valid indications of dew presence (Grantz, 1992).

Gas exchange

Single leaf stomatal conductance to water vapor, g_{sw} , was measured on exposed, sunlit leaves using a transient, clamp-on gas exchange system (LI 6200; LiCor Inc., Lincoln, NE) with a 1.0 L cuvette and manufacturer-supplied pads to limit the leaf area exposed to the airstream. Errors in these measurements are generally ca. $\pm 10\%$ when appropriately performed. Limited sampling from the highly heterogeneous leaf population was a more substantial source of uncertainty. For comparison, probable errors in a micrometeorological estimate of surface conductance in this vineyard during CODE (Massman *et al.*, 1993) were ca. $\pm 28\%$.

Stomatal conductance data are presented as means of the 3–20 individual leaves sampled within each half hour period corresponding to each averaging period used for micrometeorological data. Stomatal conductance was recorded in molar units and converted to velocity units (cm s⁻¹) using measured values of barometric pressure and temperature (Jones, 1992). Single leaf conductance to water vapor, g_{sw} , was scaled to canopy conductance to water vapor, g_{cw} , and then to canopy conductance for ozone, g_c , as described below.

Ozone deposition

Ozone flux, F , and concentration, and micrometeorological parameters were measured with an installation designed by the Air Quality Processes Research Division of the Canadian Atmospheric Environment Service (den Hartog *et al.*, 1992). Fluxes were calculated using an eddy covariance protocol, at 9.4 m above the soil surface, with data logged at 10–20 Hz, and recorded as half hourly means. Appropriate coordinate transformations and sensor corrections were applied (Massman *et al.*, 1994) as well as correction for density effects due to water vapor transfer (after Webb *et al.*, 1980).

Total conductance for ozone flux to the surface (deposition velocity, V_d (cm s⁻¹)) was calculated as the (negative) ratio of F to ozone concentration at measurement height (the total gradient from source to sink, since concentration is assumed to be zero at the sites of deposition). Aerodynamic, g_a , and quasi-laminar boundary layer, g_b , conductances were calculated from micrometeorological measurements as described by Massman *et al.* (1994), using atmospheric stability functions as presented by Brutsaert (1984). All parameters were calculated as half-hourly averages.

MODELLING CANOPY CONDUCTANCE

Single leaf stomatal conductance

Stomatal conductance to water vapor, g_{sw} , was measured on individual sunlit leaves, as means over discrete half-hourly sampling periods (Fig. 1; data points). Measurements of I were available whenever g_{sw} was measured and additionally whenever ozone

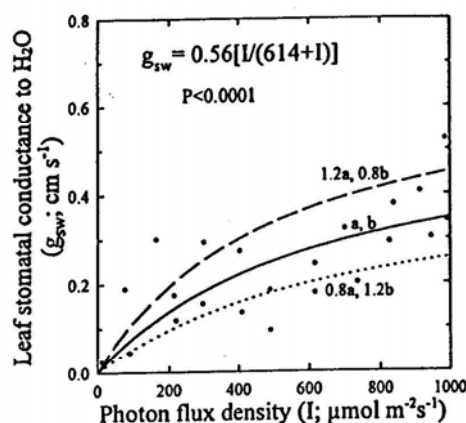


Fig. 1. Relationship between measured leaf stomatal conductance to water vapor, g_{sw} , and photosynthetically active photon flux density, I , in field-grown grape. Points represent 30 min averages of I and g_{sw} . Solid line, equation, and statistics characterize the regressions ($n = 22$; $r^2 = 0.46$) used to relate the infrequently obtained g_{sw} and the more frequently obtained I . Dotted and dashed lines indicate the maximum sensitivity of this single leaf model to combined $\pm 20\%$ errors in the parameters ($a = 0.56$; $b = 614$).

deposition was measured throughout the experiment. Stomatal conductance was generalized by fitting a highly significant hyperbolic function to these data (equation (1)) showing saturation kinetics with respect to I (Fig. 1; solid line). Data were excluded from analysis in darkness or greater than 50% full sunlight. This removed nocturnal measurements when stomata were closed and turbulent transport suppressed, and midday measurements when leaf wetness was not observed. Remaining data ($0 < I < 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$) corresponded approximately to $< 08:30$ and $> 17:30$ Pacific Daylight Time. The fitted equation for g_{sw} per unit leaf area was

$$g_{sw} = \frac{0.56I}{614 + I} \quad (1)$$

As implied by equation (1) and the data points (Fig. 1), g_{sw} exhibited a minimum value near 0 cm s^{-1} , suggesting tight stomatal closure at night. The line was constrained to pass through the origin, consistent with previous single leaf field data for grape in the SJV (Roper and Williams, 1989b) and elsewhere (Chaves *et al.*, 1987), with lysimeter measurements indicating minimal nocturnal transpiration by grape in the SJV (L. E. Williams, personal communication), and with a current model of grape canopy processes developed in the SJV (Williams *et al.*, 1993). This is not consistent with measurements by eddy covariance during CODE of nocturnal fluxes of water vapor up to 30 W m^{-2} (Massman *et al.*, 1994) and of ozone up to ca. $0.1 \text{ ppb V m s}^{-1}$ (Fig. 3, below). Both fluxes are equally consistent with limited stomatal opening and parallel cuticular conductance in grape, or with sub-

stantial, unmeasured, stomatal activity in the inter-row grasses and parallel deposition to soil and other non-varying surface sites. This feature of the diurnal course is important and merits further examination, but lies outside the scope of the present analysis. It is unlikely that substantial evaporation from the soil is occurring, in the absence of solar heating and convective, within-canopy, turbulence. However, vertical migration of water through the soil profile could moisten the surface, maintaining some water loss through the night in this irrigated vineyard.

Error analysis. The estimated uncertainty in the single leaf gas exchange measurements is $\pm 10\%$. Errors of twice this magnitude ($\pm 20\%$) in the fitted parameters of equation (1) are presented in Fig. 1 (dotted, dashed lines), and their impact on conclusions is considered below. Errors of this magnitude encompass most of the leaf to leaf variability in the field measurements (Fig. 1).

The model parameters of equation (1) imply lower levels of g_{sw} in Thompson Seedless grape than suggested in some other studies in well-irrigated, well-fertilized research vineyards in the SJV (e.g. Williams *et al.*, 1993). The current model (equation (1)) is entirely consistent with another comprehensive, and independent, single leaf data set (den Hartog *et al.*, 1992), collected with a different type of instrument (steady-state diffusion parameter) in this same vineyard during CODE. Reduced stomatal conductance and gas exchange activity in these vines could be associated with differences in irrigation or fertilization, or in vineyard age, soil or other environmental factor. These levels of stomatal conductance may indicate that the ozone fluxes measured at this location are lower than those occurring at other irrigated vineyard sites. This could have significant implications for regional estimates of deposition based on the CODE data set.

Canopy stomatal conductance

Canopy stomatal conductance to water vapor, g_{cw} , was evaluated with equation (1), using a constant $L = 3.39$, half-hourly value of horizontal I at the top of the canopy, and propagation of I through the canopy using a simplified radiative transfer model. This model (after Monsi and Saiki (1953) in Jones (1992)) assumes a unidirectional, downward quantum flux with simple exponential photon extinction through the canopy according to the empirically determined extinction coefficient $K = -0.92$. Thus, I at each leaf layer (i) was calculated as

$$I_i = I_0 \exp(-0.92i) \quad (2)$$

where i goes in integer steps from 0 to L , and I_0 is I at the top of the canopy. Single leaf stomatal conductance at each leaf level, g_i , was calculated from I_i using equation (1), assuming a similar stomatal response to photon flux density in sun and shade leaves. Total canopy conductance to water vapor, g_{cw} , was then

obtained as

$$g_{cw} = \sum_{i=0}^L g_i \quad (3)$$

Canopy conductance for the partial leaf layer below $i = 3$ was calculated as for a complete layer, then scaled by the fraction remaining at the bottom of the canopy ($\times 0.39$). The rapidly decreasing levels of I and of stomatal conductance with increasing canopy depth are consistent with the rapid declines of ozone uptake with canopy depth observed in a forest canopy (Fuentes *et al.*, 1992) and of stomatal conductance observed previously in grape (Williams *et al.*, 1993).

Total canopy stomatal conductance to water vapor, g_{cw} , was converted to ozone according to Graham's law (Jones, 1992) as

$$g_e = g_{cw}(D_{O_3}/D_{H_2O}) \quad (4)$$

where D is molecular diffusivity.

The modelled relationship between g_e and I is shown in both Figs 2A and B (solid lines). Consistent

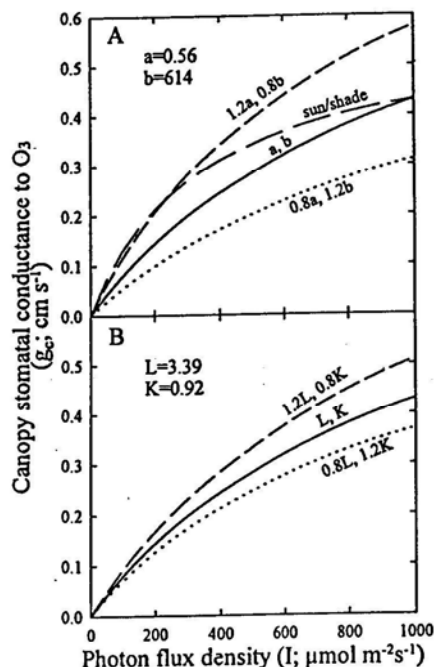


Fig. 2. Model relationship between canopy stomatal conductance to ozone, g_e , and I using equation (1) of Fig. 1 and the constant leaf area index, L and extinction coefficient, K , observed during the experiment (solid lines in Figs 2A and B). Dotted and short dashed lines represent the maximum sensitivity of this canopy model to combined $\pm 20\%$ errors in (A) the single leaf model parameters (a and b) or (B) the observed values of L and K . Long dashed line in (A) represents an alternative model of canopy stomatal conductance, using equation (1) with the same constant L and K , but with more complex radiative transfer function distinguishing sun and shade leaves (after Williams *et al.*, 1993).

with the single leaf model, the dark value is zero, and the value at $I = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ is ca. 0.42 cm s^{-1} .

Error analysis. The potential $\pm 20\%$ errors in the single leaf model parameters shown in Fig. 1 (broken lines) are larger than expected from measurement uncertainties. The impact of errors of this magnitude on the model of canopy conductance is shown in Fig. 2A (dotted and short-dashed lines). The maximal propagated error at $I = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ is ca. $\pm 28\%$ (Fig. 2A).

Aside from these possible errors associated with the single leaf model, the major empirical sources of error in the canopy formulation are the measured values of L and K . Two estimates of L obtained in this vineyard varied by $< 11\%$. The effect on g_e of a potential error of $\pm 20\%$ in L is evaluated in combination with a potential error of $\pm 20\%$ in K (Fig. 2B; broken lines). The combinations of errors in L and K yielding maximum absolute errors are shown. The negative error of ca. -14% at $I = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ (Fig. 2B; dotted line) is attributed nearly evenly to the effects of the 20% errors in L and K (not shown). The larger positive error of ca. $+19\%$ (Fig. 2B; dashed line) is dominated by the effect of the 20% error in K .

Alternative models. An additional source of uncertainty in the canopy model is the radiative transfer model of equation (2). An alternative model of g_e (Fig. 2A; long dashes) was derived using a far more complex radiative transfer treatment, involving partitioning of the leaves into sun and shade populations, radiation into diffuse and direct components, and the grape canopy into north-facing, south-facing, and horizontal sections (after Williams *et al.*, 1993).

Briefly, this alternative model weighted I by the fractions of sunlit and shaded leaf areas (Baldocchi *et al.*, 1987; Norman, 1982; Kim and Verma, 1991; Singh and Szeicz, 1980) such that

$$g_{cw} = L_{\text{sun}} g_{sw, \text{sun}} + L_{\text{shade}} g_{sw, \text{shade}} \quad (5)$$

in which L_{sun} and L_{shade} are sunlit and shaded leaf area indices and $g_{sw, \text{sun}}$ and $g_{sw, \text{shade}}$ are single leaf stomatal conductances of sun and shade leaves to water vapor, evaluated using equation (1) as a function of I incident on sunlit, I_{sun} , and shaded, I_{shade} , leaves. L_{sun} and L_{shade} were obtained according to Norman (1979) and values for I_{sun} and I_{shade} were computed according to Norman (1982) using measured values of I , ratios of diffuse to direct I presented by Smart (1973; Fig. 2), and ratios of I on horizontal and vertical sections of grapevines determined by L. E. Williams (unpublished SJV data obtained in August 1993).

Values of canopy conductances to O_3 derived from this sun/shade model (Fig. 2A; long-dashed line) were almost entirely within the boundaries described by the propagated $\pm 20\%$ single leaf errors of the previous, much simpler, canopy model (Fig. 2A; dotted and short-dashed lines). The more complex model exceeded these boundaries by (at most) ca. 10% , at $I = 200 \mu\text{mol m}^{-2} \text{s}^{-1}$, and was equivalent to the

simpler model at $I = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$. The substantial consistency between the two approaches suggested that the unique canopy geometry of a trellised vineyard did not invalidate these radiative transfer formulations. The simpler model of g_e is utilized throughout the following discussion.

CONTROL OF OZONE DEPOSITION

Relationships between ozone deposition and canopy conductance

Ozone flux. Measured ozone flux, F , increased in absolute magnitude (more negative; $P < 0.0001$) with increasing canopy stomatal conductance under both wet (Fig. 3A) and dry (Fig. 3B) conditions. These relationships do not consider potentially covarying changes in radiation and turbulence parameters, but suggest a significant dependence of F on g_e under both wet and dry conditions. There are substantially more data points under dry than wet conditions, even with the analysis restricted to $0 < I < 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$.

Deposition velocity. A more robust test of the role of g_e in ozone deposition is the relationship between deposition velocity, V_d , and g_e (Fig. 4). V_d increased significantly ($P < 0.0001$) with g_e under both wet (Fig. 4A) and dry (Fig. 4B) conditions. This strong relationship between scaled empirical measurements of stomatal conductance and direct empirical measurements of ozone deposition velocity supports earlier conclusions (e.g. Baldocchi *et al.*, 1987; Fuentes and Gillespie, 1992; Wesely, 1989) that internal leaf

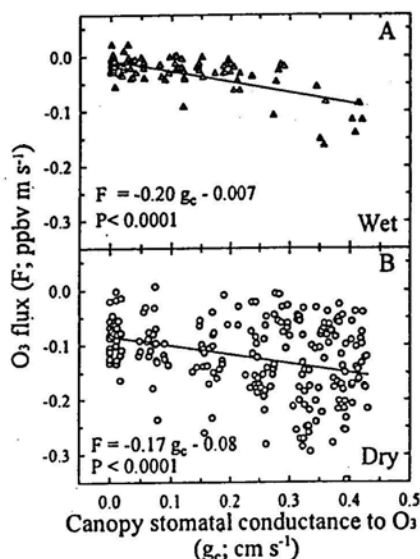


Fig. 3. Relationship between measured ozone flux to the canopy, F , and g_e under wet (A; $n = 102$; $r^2 = 0.49$; $P < 0.0001$) and dry (B; $n = 225$; $r^2 = 0.12$; $P < 0.0001$) conditions. Points represent 30 min averages. Solid lines, equations, and statistics characterize the linear regressions.

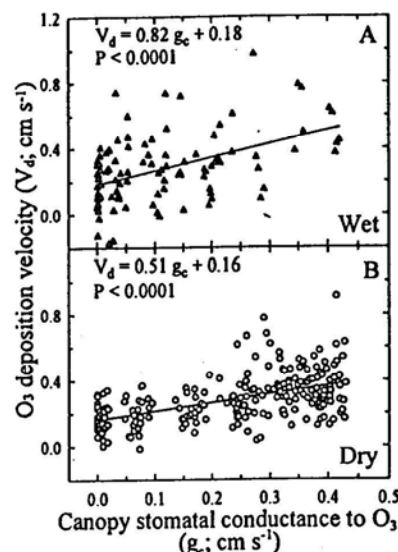


Fig. 4. Relationship between measured ozone deposition velocity, V_d , and g_e under wet (A; $n = 102$; $r^2 = 0.22$; $P < 0.0001$) and dry (B; $n = 225$; $r^2 = 0.26$; $P < 0.0001$) conditions. Points represent 30 min averages. Solid lines, equations, and statistics characterize the linear regressions.

sites represent significant canopy-scale sinks for ozone.

Under wet conditions the relationship between V_d and g_e (Fig. 4A) deviated from the 1:1 relationship (not shown) due to a substantial intercept of ca. 0.2 cm s^{-1} and a slope somewhat below unity. Under dry conditions (Fig. 4B), the intercept was similar to that under wet conditions, but the slope was well below the 1:1 line (not shown), with $V_d < g_e$ when $g_e > 0.35 \text{ cm s}^{-1}$.

Role of above-canopy turbulence

The strong relationship between V_d and g_e reflected a functional relationship between deposition and stomatal conductance. It was strengthened by a general covariance of g_e with turbulent transport efficiency, as both varied diurnally. To test the contribution of these factors, a total atmospheric conductance parameter, g_{atm} , was calculated from half-hourly averages as

$$g_{\text{atm}} = \frac{1}{1/g_a + 1/g_b} \quad (6)$$

This parameter, g_{atm} , increased significantly with I and thus with g_e (not shown) but remained much larger than g_e , so that diurnal responses of g_e to I dominated control of ozone deposition. Similarly covarying leaf and atmospheric processes contributed to diurnal patterns of ozone deposition in an eastern forest (Fuentes *et al.*, 1992).

Deposition velocity encompasses stomatal and atmospheric components, as well as non-stomatal sur-

face pathways for ozone deposition. Canopy stomatal conductance, on the other hand, reflects only the stomatal portion of the surface. By incorporation of both V_d and g_{aim} (equation (7)), a residual measure of total surface conductance, g_{surf} , may be obtained, completely independently of g_c , as

$$g_{\text{surf}} = \frac{1}{1/V_d - 1/g_a - 1/g_b} \quad (7)$$

The relationships of V_d (Fig. 5A) and g_{surf} (Fig. 5B) to g_c were similar, reflecting the large contribution of stomatal conductance to both. Use of g_c alone to predict V_d , where stomatal responses are known, removes the need for expensive *in situ* measurements and uncertain calculations of g_a and (particularly) g_b .

The effective quasilaminar boundary layer conductance, g_b , depends on the above canopy wind profile as parameterized, but also on canopy geometry and turbulence and gust penetration within the canopy, which are less well characterized. The magnitude of

g_b in the present case (Massman *et al.*, 1994) may be underestimated because of possible effects of the roughness sublayer (e.g. Cellier and Brunet, 1992) which was not incorporated here. Underestimation of g_b would increase g_{aim} and further emphasize the stomatal control of V_d and g_{surf} .

EFFECT OF SURFACE WETNESS ON OZONE DEPOSITION

Canopy stomatal conductance

Ozone flux. The sensitivity of ozone flux to changing g_c was similar under wet and dry conditions. In general, F was smaller (less negative) under conditions of surface wetness (cf. Figs 3A and B), partially reflecting lower mean O_3 concentrations during periods characterized by surface wetness.

Deposition velocity. Normalization of fluxes by ambient ozone concentration to yield V_d (Figs 4A and B) reversed the apparent reduction of ozone deposition under conditions of leaf wetness, revealing a substantial increase in V_d at high g_c (Fig. 5A).

Overall (Fig. 5A, Table 1), surface wetness increased V_d significantly under all conditions, consistent with our previous analysis using a linear leaf response model and the full range of I (Massman *et al.*, 1994). These data support earlier conclusions (e.g. Fuentes *et al.*, 1992) that surface wetness enhanced ozone deposition to plant canopies, despite the low aqueous solubility of ozone. The presence of dew in this vineyard also increased the apparent sensitivity of V_d to increasing g_c . This, however, reflected the covariance of atmospheric transport parameters. At low g_c the values of V_d under wet and dry conditions converged, but this was not observed for g_{surf} (Fig. 5B). Wet and dry values of g_{surf} exhibited a nearly constant separation, with parallel slopes indicating similar sensitivity to stomatal opening, and a nearly constant increment of non-stomatal conductance attributed to surface wetness. The relative increase in V_d and in g_{surf} by surface wetness was similar at high levels of g_c , though the variability of the calculated g_{surf} was large under wet conditions.

Non-stomatal surface conductance

A non-stomatal pathway for ozone deposition was suggested when $g_c < V_d$ (Fig. 5A). This was the case when g_c was below ca. 0.35 cm s^{-1} under dry conditions, and over all levels of g_c under wet conditions.

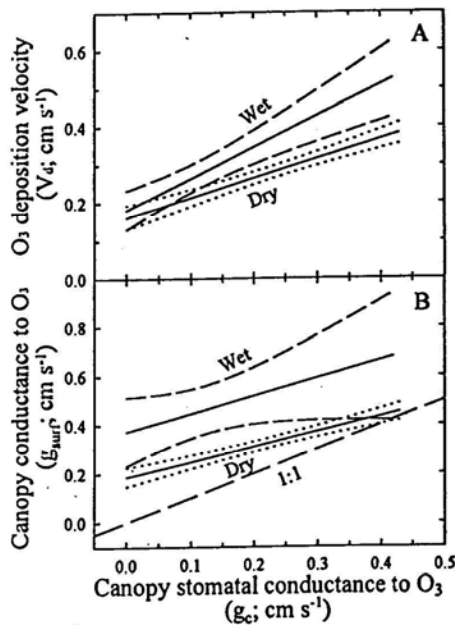


Fig. 5. Effect of leaf wetness on the relationship between V_d (A) or g_{surf} (B) and g_c . Solid lines characterize the linear regressions; dashed and dotted lines characterize the 95% confidence limits.

Table 1. Effect of surface wetness on mean ozone deposition, surface conductance, and residual conductance in grape. Data represent mean \pm S.E. Means within a single wet-dry comparison are different ($p < 0.0001$) when followed by different letters

V_d		g_{surf}		g_c	
Wet	Dry	Wet	Dry	Wet	Dry
$0.302a \pm 0.021$ $n = 86$	$0.272b \pm 0.009$ $n = 211$	$0.463a \pm 0.051$ $n = 86$	$0.328b \pm 0.012$ $n = 211$	$0.343a \pm 0.051$ $n = 86$	$0.098b \pm 0.011$ $n = 211$

Similarly, $g_e < g_{surf}$ (Fig. 5B) under all conditions. To evaluate the characteristics of the non-stomatal pathway, a residual component of surface conductance g_r , was calculated from the difference between g_{surf} and g_e , as

$$g_r = \frac{1}{1/V_d - 1/g_a - 1/g_b} - g_e \quad (8)$$

recognizing that the magnitude of g_r reflects not only non-stomatal ozone deposition but also cumulative errors in the calculated and measured parameters.

The values of V_d and g_{surf} were greater under wet than dry conditions (Fig. 5, Table 1). In particular, g_{surf} exhibited similar increases with g_e , under wet and dry conditions, reflecting the increasing stomatal pathway. It also exhibited a nearly constant increment of surface conductance caused by dew, over the entire range of g_e . This increment is likely to consist of heterogeneous ozone decomposition reactions, occurring on surfaces of the soil, leaves and stems, cuticles, and debris collecting below the canopy. These sinks may be important in removing ozone from the atmospheric surface layer (e.g. Baldocchi, 1988; Leuning *et al.*, 1979a,b; Turner *et al.*, 1973; Wesely, 1989).

The value of g_r declined with increasing g_e under both dry and wet conditions (Fig. 6). This may represent local depletion of O_3 near the sites of deposition. Data of vertical O_3 gradients and concentrations within the canopy are not available during CODE to test this hypothesis. Increasing errors in calculated values of g_b with increasing radiation could also contribute.

Error analysis. The magnitude of g_r (equation (8)) is sensitive to the model used to describe g_e (equations (1)–(4)). The potential $\pm 20\%$ errors in g_e (Figs 1 and 2) are directly reflected in estimates of g_r (not shown).

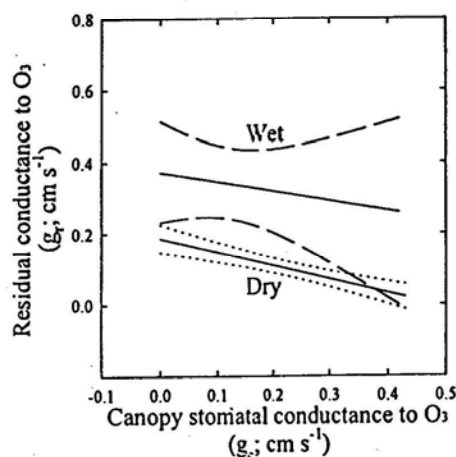


Fig. 6. Effect of leaf wetness on the relationship between residual conductance to ozone deposition, g_r , and g_e . Solid lines characterize the linear regressions; dashed and dotted lines characterize the 95% confidence limits.

and lie within the 95% confidence limits (Fig. 6). The relative comparisons of slopes and magnitudes of the relationships under wet and dry conditions are unchanged by potential errors in the single leaf or canopy modules.

The values of g_r remained positive, consistent with a substantial parallel, non-stomatal deposition pathway over the entire range of g_e considered. These data do not suggest a limiting intercellular, or mesophyll, conductance, g_m , to ozone deposition inside the stomatal pores (see Taylor *et al.*, 1982). A modest limitation by g_m would probably not be resolved by the current techniques and is not precluded (see Massman *et al.*, 1994).

CONCLUSIONS

Empirical measurements of stomatal conductance and photon penetration through a grape canopy were used to construct a simple model of canopy stomatal conductance to ozone over the range of photosynthetically active photon flux density, I , of $0 < I < 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$. The hypothesis that ozone deposition is a strong function of canopy stomatal conductance, g_e , was supported under all conditions. While g_e was the controlling factor, the generally parallel diurnal courses of g_e and atmospheric conductance strengthened the relationship between deposition velocity, V_d , and g_e . The hypothesis that surface wetness decreased ozone deposition to grape was not supported, as wetness substantially increased V_d and the calculated surface conductance, g_{surf} . This result may be uniquely valid for grape and other plant species with hypostomatous leaves, on which dew formation might increase surface reactivity on the upper leaf surfaces without occluding stomatal pores on the lower surfaces. Calculation of a residual conductance term reflecting non-stomatal components of surface conductance demonstrated a relatively constant wetness effect, by a non-stomatal pathway, over all levels of I and g_e . The magnitude of g_r declined with increasing g_e , possibly reflecting depletion of O_3 near sites of deposition. Stomatal conductance is a dominant pathway for ozone deposition to agricultural canopies, and in grape, surface wetness enhances ozone deposition by a non-stomatal pathway.

Acknowledgements—The authors thank Dr L. E. Williams for numerous helpful discussions and provision of unpublished data and the San Joaquin Valley Air Pollution Study Agency for financial support during CODE.

REFERENCES

- Baldocchi D. D. (1988) A multilayer model for estimating sulfur dioxide deposition to a deciduous oak forest canopy. *Atmospheric Environment* 22, 869–884.
- Baldocchi D. D., Hicks B. B and Camara P. (1987) A canopy stomatal resistance model for gaseous deposition to vegetated surfaces. *Atmospheric Environment* 21, 91–101.

Similarly, $g_e < g_{surf}$ (Fig. 5B) under all conditions. To evaluate the characteristics of the non-stomatal pathway, a residual component of surface conductance g_r , was calculated from the difference between g_{surf} and g_e , as

$$g_r = \frac{1}{1/V_d - 1/g_a - 1/g_b} - g_e \quad (8)$$

recognizing that the magnitude of g_r reflects not only non-stomatal ozone deposition but also cumulative errors in the calculated and measured parameters.

The values of V_d and g_{surf} were greater under wet than dry conditions (Fig. 5, Table 1). In particular, g_{surf} exhibited similar increases with g_e , under wet and dry conditions, reflecting the increasing stomatal pathway. It also exhibited a nearly constant increment of surface conductance caused by dew, over the entire range of g_e . This increment is likely to consist of heterogeneous ozone decomposition reactions, occurring on surfaces of the soil, leaves and stems, cuticles, and debris collecting below the canopy. These sinks may be important in removing ozone from the atmospheric surface layer (e.g. Baldocchi, 1988; Leuning *et al.*, 1979a,b; Turner *et al.*, 1973; Wesely, 1989).

The value of g_r declined with increasing g_e under both dry and wet conditions (Fig. 6). This may represent local depletion of O_3 near the sites of deposition. Data of vertical O_3 gradients and concentrations within the canopy are not available during CODE to test this hypothesis. Increasing errors in calculated values of g_b with increasing radiation could also contribute.

Error analysis. The magnitude of g_r (equation (8)) is sensitive to the model used to describe g_e (equations (1)–(4)). The potential $\pm 20\%$ errors in g_e (Figs 1 and 2) are directly reflected in estimates of g_r (not shown).

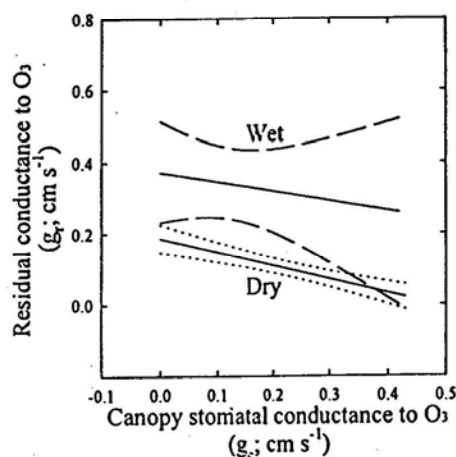


Fig. 6. Effect of leaf wetness on the relationship between residual conductance to ozone deposition, g_r , and g_e . Solid lines characterize the linear regressions; dashed and dotted lines characterize the 95% confidence limits.

and lie within the 95% confidence limits (Fig. 6). The relative comparisons of slopes and magnitudes of the relationships under wet and dry conditions are unchanged by potential errors in the single leaf or canopy modules.

The values of g_r remained positive, consistent with a substantial parallel, non-stomatal deposition pathway over the entire range of g_e considered. These data do not suggest a limiting intercellular, or mesophyll, conductance, g_m , to ozone deposition inside the stomatal pores (see Taylor *et al.*, 1982). A modest limitation by g_m would probably not be resolved by the current techniques and is not precluded (see Massman *et al.*, 1994).

CONCLUSIONS

Empirical measurements of stomatal conductance and photon penetration through a grape canopy were used to construct a simple model of canopy stomatal conductance to ozone over the range of photosynthetically active photon flux density, I , of $0 < I < 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$. The hypothesis that ozone deposition is a strong function of canopy stomatal conductance, g_e , was supported under all conditions. While g_e was the controlling factor, the generally parallel diurnal courses of g_e and atmospheric conductance strengthened the relationship between deposition velocity, V_d , and g_e . The hypothesis that surface wetness decreased ozone deposition to grape was not supported, as wetness substantially increased V_d and the calculated surface conductance, g_{surf} . This result may be uniquely valid for grape and other plant species with hypostomatous leaves, on which dew formation might increase surface reactivity on the upper leaf surfaces without occluding stomatal pores on the lower surfaces. Calculation of a residual conductance term reflecting non-stomatal components of surface conductance demonstrated a relatively constant wetness effect, by a non-stomatal pathway, over all levels of I and g_e . The magnitude of g_r declined with increasing g_e , possibly reflecting depletion of O_3 near sites of deposition. Stomatal conductance is a dominant pathway for ozone deposition to agricultural canopies, and in grape, surface wetness enhances ozone deposition by a non-stomatal pathway.

Acknowledgements—The authors thank Dr L. E. Williams for numerous helpful discussions and provision of unpublished data and the San Joaquin Valley Air Pollution Study Agency for financial support during CODE.

REFERENCES

- Baldocchi D. D. (1988) A multilayer model for estimating sulfur dioxide deposition to a deciduous oak forest canopy. *Atmospheric Environment* 22, 869–884.
- Baldocchi D. D., Hicks B. B and Camara P. (1987) A canopy stomatal resistance model for gaseous deposition to vegetated surfaces. *Atmospheric Environment* 21, 91–101.

- to gaseous dry deposition in regional-scale numerical models. *Atmospheric Environment* **23**, 1293–1304.
- Wesely M. L., Eastman J. A., Cook D. R. and Hicks B. B. (1978) Daytime variations of ozone eddy fluxes to maize. *Boundary-Layer Met.* **15**, 361–373.
- Williams L. E., Williams D. W. and Phene C. J. (1993) *In Modeling grapevine water use.* (edited by Stockley C. S., Johnstone R. S., Leske P. A. and Lee T. H.) *Proc. 8th Australian Wine Industry Technical Conf.*, pp. 29–23. Melbourne, Winetitles, Adelaide.