

## Ozone deposition to a cotton (*Gossypium hirsutum* L.) field: stomatal and surface wetness effects during the California Ozone Deposition Experiment

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### Abstract

Removal of tropospheric ozone from polluted airbasins by deposition to vegetation may be an important determinant of regional air quality. The physiological and physical processes that determine the magnitude of deposition, and the relative contributions of uptake by photosynthetic tissues versus ozone destruction on plant and soil surfaces, are not well understood. The California Ozone Deposition Experiment (CODE) demonstrated substantial deposition of ozone to several vegetated surfaces in the San Joaquin Valley. Using data collected during CODE, we examine the roles of stomatal conductance and leaf wetness from dew in mediating ozone deposition to an extensive field of irrigated cotton. Stomatal conductance, photon flux density, leaf area index ( $L$ ), leaf wetness, ozone deposition, and canopy photon extinction coefficient ( $K$ ) were measured. Single leaf measurements were scaled to canopy values of stomatal conductance to ozone ( $g_c$ ). Deposition velocity ( $V_d$ ) and surface conductance ( $g_{surf}$ ) were strongly positively correlated with  $g_c$ . Under dry canopy conditions  $g_c < g_{surf}$  indicating a significant residual conductance of a non-stomatal pathway for ozone deposition ( $g_r$ ), possibly reflecting reaction of  $O_3$  with nitric oxide emitted from fertilized soil. Dewfall reduced ozone deposition and eliminated  $g_r$ . However,  $g_r$  may actually have been increased by dew in amphistomatous cotton, as it was in hypostomatous grape during CODE. If so, canopy wetness reduced the stomatal pathway ( $g_c$ ) by occlusion of adaxial pores sufficiently to offset both the nitric oxide titration and the true wetness enhancement of  $g_r$ . We conclude that ozone deposition to cotton is largely controlled by stomatal responses. Stomatal responses may readily be modelled, potentially providing sufficient information to infer ozone deposition. In contrast to the case for hypostomatous grape, ozone uptake (particularly by the stomatal pathway) is reduced by leaf surface wetness in amphistomatous cotton. Alternative models of single leaf stomatal conductance and expected errors of  $\pm 20\%$  in model parameters did not affect these conclusions. © 1997 Elsevier Science B.V.

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## 1. Introduction

### 1.1. Regional context

The southern Central Valley of California (the San Joaquin Valley, SJV) is a highly productive agricultural region that is threatened by increasing population and the resultant anthropogenic, oxidant air pollution. The region is in violation of state and federal air quality regulations for the photochemical oxidant, ozone. As a result, extensive research efforts are under way to characterize the sources and sinks of ozone in the SJV. The present study was conducted as part of the California Ozone Deposition Experiment (CODE), whose objectives are to characterize the role of agricultural surfaces in removing ozone from the atmospheric surface layer (Pederson et al., 1992; Pederson et al., 1995). Discriminating between stomatal and non-stomatal deposition to these surfaces is relevant to modelling of airbasin pollutant concentrations and to predictions of uptake by and oxidant damage to specific plant species.

### 1.2. Role of stomata

Surface conductance for ozone deposition ( $g_{\text{surf}}$ ) is in series with an aerodynamic conductance associated with atmospheric turbulence characterized by an eddy diffusivity, and with a quasi-laminar boundary layer conductance characterized by a molecular diffusivity (Baldocchi et al., 1987; Fuentes et al., 1992; Hicks et al., 1987; Padro et al., 1991). The surface conductance consists of plant and non-plant components, and depends on physical, physiological and biochemical factors (Baldocchi et al., 1987; Grantz et al., 1995; Hicks et al., 1987; Massman et al., 1993; Padro et al., 1991). During daylight hours, the surface, or canopy conductance is usually smaller than the atmospheric components and controls the rate of ozone removal from the atmosphere (Baldocchi et al., 1987; Fuentes and Gillespie, 1992; Grantz et al., 1994, 1995; Massman and Grantz, 1995; Massman et al., 1993, 1994; Wesely et al., 1978) and is dominated by stomatal conductance.

Ozone removed from the atmosphere over vegetated surfaces is probably taken up mostly by photosynthetic organs through stomata, although this may not always be the case (Leuning et al., 1979a,b; Van Pul and Jacobs, 1994). Oxidant damage to vegetation

is typically mediated by uptake of ozone through the stomata for access to the leaf mesophyll (Roper and Williams, 1989; Thomson et al., 1966) including evidence obtained specifically with cotton (Temple, 1988; Temple et al., 1988). In isolated leaves, stomatal closure substantially reduces ozone uptake and largely prevents ozone damage to foliage (Butler and Tibbitts, 1979). Cotton exhibits sufficient yield losses due to ambient ozone under field conditions in the SJV (Olszyk et al., 1993) that substantial stomatal uptake seems likely.

The relative magnitudes of stomatal and other competing sinks throughout the canopy environment are not clear from large-scale field measurements. Heterogeneous reactions lead to ozone destruction throughout the canopy, and degradation of ozone by bare soil (Turner et al., 1973) may approach 40% of total deposition (Leuning et al., 1979b). These uncertainties regarding the distribution of sinks for ozone within the canopy, and additional uncertainties regarding scaling of leaf level responses to the canopy level (e.g. Baldocchi, 1989; Grantz et al., 1995; Grantz and Meinzer, 1990; Jarvis and McNaughton, 1986; Massman and Grantz, 1995; Massman et al., 1993; Meinzer and Grantz, 1989) complicate the partitioning of deposition between uptake of  $\text{O}_3$  by photosynthetically competent vegetative tissues and decomposition of  $\text{O}_3$  on plant and soil surfaces. This impacts both efforts to model the sink component of regional ozone budgets, and efforts to predict the magnitude of crop or ecosystem damage to be expected from prevailing concentrations of ambient ozone. Non-stomatal deposition may cause additional damage to cuticles and trichomes on leaf surfaces, which may increase non-stomatal, cuticular water loss (Barnes et al., 1988).

To the extent that stomatal uptake dominates ozone deposition to an extensive canopy, deposition may be approximated as a function of stomatal responses. These may be modelled under well-irrigated conditions as mechanistic or empirical functions of environmental parameters, allowing a straightforward method of evaluating vegetative effects on regional ozone budgets.

### 1.3. Role of surface wetness

Hydration of surface solutes and enhanced deposition of acidic gases might be expected to increase the

rates of the heterogeneous ozone decomposition reactions that occur throughout the canopy (e.g. Chameides, 1987). Alternatively, ozone is only weakly soluble in aqueous solution, so that a water film might mask reactive surface sites. In a model of surface deposition (Wesely, 1989) deposition is reduced by dew because putative occlusion of stomatal pores offsets any increases in surface reactivity.

Experimental evidence is mixed (Schuepp, 1989). Ozone deposition was reduced in maize and wheat when the foliar surfaces became wetted with dew (Hicks et al., 1987; Wesely et al., 1978). However, deposition was also reduced in senescent maize, in which the occlusion of stomata might not exert a substantial effect. Restriction of ozone access to reactive surface sites could be imposed by a water film on leaf and other surfaces.

Ozone deposition was increased in a deciduous forest, by a non-stomatal pathway when foliar surfaces became wetted with dew (Fuentes et al., 1992). Ozone deposition was significant at night and early in the morning when stomatal conductance was low, but foliar surfaces were wet with dew. Evaporation of the dew decreased ozone fluxes. Ozone deposition was increased to a trellised grape vineyard (Grantz et al., 1995) following dewfall, and to single leaves misted with water at pH 6 (Fuentes and Gillespie, 1992). The factors that lead to increased or decreased ozone deposition following dewfall remain to be characterized.

#### 1.4. Present investigation

We have previously addressed the relevance of current modelling assumptions to deposition of ozone to cotton in the arid west (Massman et al., 1994) and have evaluated the strengths and weaknesses of alternative means of scaling stomatal conductance to ozone from leaf to canopy in cotton (Massman and Grantz, 1995). The present study is narrowly focused on the role of leaf wetness and stomatal response in controlling ozone deposition to extensive vegetative surfaces such as cotton. To this end, the analysis is restricted to morning and evening hours when the photosynthetically active photon flux density was below half-maximal. These are the conditions when dew was sometimes observed on leaves, when stomatal conductance is most limiting to deposition, and

stomatal responses are most dynamic. Midday periods when ozone deposition is maximal are thus not considered. We have presented a similar treatment of stomatal and wetness effects on ozone deposition to a grape (*Vitis vinifera* L.) canopy, also using data obtained during CODE (Grantz et al., 1995). Differences in leaf morphology and in canopy structure between grape and cotton lead to contrasting conclusions from the two analyses.

In the present study, we have investigated the interaction between canopy conductance and leaf surface wetness in determining canopy level ozone deposition velocity to cotton. Stomatal conductance, photon flux density above and below the canopy, dew formation on surrogate leaves, and canopy level ozone fluxes and concentrations were all determined empirically in the field. A simple hyperbolic stomatal conductance–photon flux response curve was developed for single exposed leaves of cotton. Using these data and a simple model of canopy conductance, we test two hypotheses: that ozone deposition to extensive cotton fields is controlled by, and may be modelled as a function of stomatal conductance; and that surface wetness reduces ozone deposition to cotton below levels that would otherwise be predicted by prevailing canopy stomatal conductance. Both hypotheses are supported by the available data.

## 2. Materials and methods

### 2.1. Location

The California Ozone Deposition Experiment (CODE) was conducted in the San Joaquin Valley of California between 8 July and 6 August 1991 (DOY 189–218). The irrigated cotton field (*Gossypium hirsutum* L., cv. Delta Pine 6166), in which the present study was conducted, was located about 80 km west of Fresno (36°48'50"N, 120°40'38"W) at about 100 m above sea level, and with uniform fetch greater than 1 km. The crop was planted in rows oriented east–west, spaced about 1 m apart.

Clear skies, hot days and warm nights characterized the study area. Winds were northwest at 1–6 m s<sup>-1</sup>. Complete micrometeorological and microenvironmental data for the site are available through CODE (Delany et al., 1992; Grantz, 1992).

## 2.2. Leaf area and radiative transfer

The canopy height increased from 0.4 to 0.9 m during the study. The leaf area index ( $L$ ;  $\text{m}^2$  projected leaf per  $\text{m}^2$  ground) was determined several times during the experiment using a Plant Canopy Analyzer (LiCor LAI-2000, LiCor Inc., Lincoln, NE). This method is based on the gap inversion method (Wells and Norman, 1991). A non-standard measurement protocol was developed for cotton (Grantz et al., 1993) and was used in this canopy. All measurements of  $L$  were conducted at dusk, under conditions of low diffuse radiation. Values of  $L$  determined in this manner ranged from 1.7 to 3.2 during the experiment.

Photosynthetically active photon flux density ( $I$ ;  $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ ) was measured on a horizontal plane above the canopy, using a quantum sensor (LI 190-SA; LiCor, Inc., Lincoln NE). During a brief period when the quantum sensor was not functional,  $I$  was calculated from a regression of  $I$  on short-wave solar radiation ( $r^2 = 0.999$ ;  $n = 522$ ) obtained with a pyranometer.

The analysis is restricted to morning and evening hours when  $0 < I \leq 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ , i.e. the period before 08:30 and after 17:30 Pacific Daylight Time. This excluded periods of darkness when the stomata were closed and turbulent transport was suppressed, and midday periods with greater than 50% of full sunlight when leaf wetness was not observed.

A bulk canopy photon extinction coefficient ( $K$ ) was determined from measurements of photon flux with the LAI-2000 above and below the canopy during the determination of  $L$  (Grantz et al., 1993, 1995). The value of  $K = 0.7$  was determined from the measured photon penetration through the entire depth of this canopy over a range of zenith angles of  $\theta = 0\text{--}43^\circ$ . A single value of  $K$  was used with no attempt to model diurnal changes in  $K$ , as was done previously for a complete diurnal analysis (e.g. Massman and Grantz, 1995).

## 2.3. Canopy wetness

Canopy wetness was determined using electrical impedance grids coated with light green latex paint (Gillespie and Kidd, 1978). These were arrayed near

the surface of the canopy, and oriented with the sensing grid facing up, down, into and away from the middle of the row (Grantz, 1992). The impedance was recorded at 0.2 Hz and means calculated every 30 min with a data logger (21X, Campbell Scientific, Inc., Logan, UT).

Sensor readings exhibited a sharp cutoff between wet and dry conditions. Low readings were quantized to "0", indicating a dry leaf, and high readings to "1", indicating a wet leaf. Sensors in all four orientations were averaged for determination of periods of canopy wetness. Rainfall was not observed during the experiment, and the crop was furrow irrigated. Therefore an average sensor value near 1 indicated dew. These values correlated well with visual observations of dew and with minimal or negative values of leaf to air water vapor pressure gradients (Grantz, 1992).

## 2.4. Single leaf conductance

Stomatal conductance of single exposed, fully expanded leaves to water vapor ( $g_{\text{sw}}$ ) was determined using a transient, clamp-on gas exchange system (LI 6200; LiCor, 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 about  $\pm 10\%$  when appropriately performed. This is less than the expected variability among the sample population of leaves. In contrast, expected errors in a micrometeorological estimate of surface conductance in this cotton field are about  $\pm 39\%$  (Massman and Grantz, 1995; Massman et al., 1994).

Stomatal conductance was obtained quasi-hourly. To express the average stomatal conductance over the half-hour averaging periods for the micrometeorological measurements, the conductance data represent means of the 3–30 individual leaves that were sampled within each half-hour period.

Stomatal conductance was recorded in molar units, using the software of the LI 6200, and subsequently converted to velocity units ( $\text{cm s}^{-1}$ ), using measured values of barometric pressure and temperature. Single leaf conductance to water vapor ( $g_{\text{sw}}$ ) was scaled to canopy conductance to water vapor ( $g_{\text{cw}}$ ), and then to canopy conductance for ozone ( $g_{\text{c}}$ ), as described below.

## 2.5. Ozone deposition

The ozone flux ( $F$ ) and concentration, and the associated micrometeorological parameters, were measured using the Atmosphere–Surface Turbulent Exchange Research (ASTER) facility of the National Center for Atmospheric Research (Delany et al., 1992). Ozone concentrations and flux were measured at 5 m above the soil (about 4 m above the canopy) using a prototype  $O_3$  sensor provided by NASA Ames Research Center (Pearson et al., 1990) and a one-dimensional sonic anemometer (Applied Technologies). Fluxes were calculated using an eddy covariance protocol.

The data were logged at 10–20 Hz, and averaged half-hourly. Appropriate coordinate transformations and sensor and density corrections were applied (Massman et al., 1994; Webb et al., 1980).

Total conductance (deposition velocity,  $V_d$ ;  $\text{cm s}^{-1}$ ) for ozone flux to the surface was calculated from the ratio of ozone flux to ozone concentration at the measurement height (equivalent to the ozone gradient from source to sink assuming zero concentration within the leaf or at other sites of ozone decomposition).

The aerodynamic ( $g_a$ ) and quasi-laminar boundary layer ( $g_b$ ) conductances were calculated from measured micrometeorological parameters, as described by Massman et al. (1994), using functions presented by Brutsaert (1984). All parameters were calculated as half-hourly averages.

## 3. Results and discussion

### 3.1. Modelling surface conductance

#### 3.1.1. Single leaf stomatal conductance

Single leaf stomatal conductance to water vapor ( $g_{sw}$ ;  $\text{cm s}^{-1}$ ) was measured with a hand-held cuvette at discrete sampling times (data points, Fig. 1), whereas measurements of photosynthetically active photon flux density ( $I$ ) were sampled automatically and nearly continuously, fully characterizing the experimental period. The available values of  $g_{sw}$  were used to generalize stomatal response over all times when ozone flux data were available (Fig. 1, solid

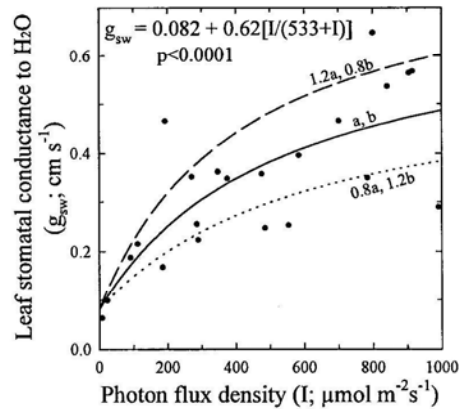


Fig. 1. Relationship between leaf stomatal conductance to water vapor ( $g_{sw}$ ) and photosynthetically active photon flux density ( $I$ ) in field-grown cotton. Points represent 30 min averages of both  $I$  and  $g_{sw}$ . Solid line, equation, and statistics characterize the nonlinear regression ( $n = 22$ ;  $r^2 = 0.65$ ). Dotted and dashed lines indicate maximum sensitivities of this single leaf model to combined  $\pm 20\%$  errors in the regression parameters ( $a = 0.62$ ;  $b = 533$ ).

line), by modelling  $g_{sw}$  as a simple hyperbolic function of  $I$  as

$$g_{sw} = 0.082 + \frac{0.62 I}{533 + I} \quad (1)$$

The single leaf values of stomatal conductance for this cotton canopy exhibited a nonzero minimum value of  $g_{sw} = 0.082 \text{ cm s}^{-1}$  (Eq. (1)), implying that the cotton leaf stomata did not close completely in darkness. This is consistent with growth chamber data for cotton (e.g. Harley et al., 1992) indicating minimum  $g_{sw} \approx 0.2 \text{ cm s}^{-1}$ . Eddy covariance data obtained in this field during CODE suggested that fluxes of ozone and water vapor were small at night when  $g_{sw}$  was minimal (Massman et al., 1994; Massman and Grantz, 1995). The non-steady state measurement system used in this study is subject to some uncertainty near  $g_{sw} = 0$ , and the standard error of the estimate of minimum  $g_{sw}$  in cotton was  $\pm 0.05 \text{ cm s}^{-1}$ . However, the same instrument indicated nearly complete nocturnal stomatal closure in grape during CODE (Grantz et al., 1995).

During daylight hours, stomatal conductance in cotton was generally greater than that measured in grape. This is consistent with greater water vapor

and ozone fluxes determined during CODE in cotton than in grape, and greater irrigation requirements for cotton than grape. Single leaf stomatal conductance over the experimental period in this well-irrigated field was modelled from values of  $I$  using Eq. (1).

### 3.1.2. Error analysis

The estimated maximum error in stomatal conductance is about  $\pm 10\%$ . The impact of combined errors of twice this magnitude in each of the parameters of the single leaf stomatal conductance model is presented in Fig. 1 (dotted, dashed lines). Maximum propagated errors in  $g_{sw}$  are about  $+24.1\%$  and about  $-20.9\%$  at  $I = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ . The variability among exposed leaves under field conditions is likely to contribute an uncertainty of at least this magnitude.

### 3.2. Modelling canopy stomatal conductance

Modelled values of  $g_{sw}$  as a function of  $I$  were used to incorporate diurnal effects, while the leaf area index ( $L$ ) as a function of day of year (Grantz, 1992) was used to incorporate seasonal trends in canopy development in developing a simple model of whole canopy stomatal conductance to water vapor ( $g_{cw}$ ).

We assume a unidirectional photon flux, decreasing exponentially through the canopy (Jones, 1992), with an empirically determined absorption of 50% by each unit of  $L$ . This corresponds to a bulk extinction coefficient of  $K = 0.7$ .  $I$  at the base of each full layer ( $i$ ) of foliage ( $I_i$ ) was calculated (after Monsi and Saiki, 1953; cited in Jones, 1992) as

$$I_i = I_0 \exp(-0.7i), \quad (2)$$

with half-hourly average values of  $I_0$  representing  $I$  on a horizontal plane at the top of the canopy.

Single leaf stomatal conductance to water vapor at each leaf level ( $g_i$ ) was calculated from these half-hourly values of  $I_i$  using Eq. (1), assuming the same stomatal responses to photon flux density in upper and lower leaves. Total canopy stomatal conductance to water vapor ( $g_{cw}$ ) was then obtained as

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

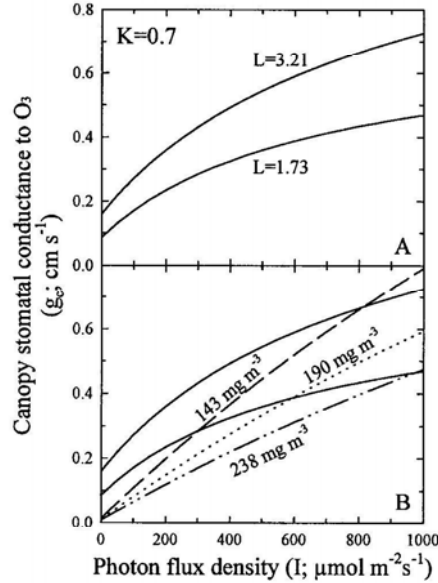


Fig. 2. Relationship between canopy stomatal conductance to ozone ( $g_c$ ) obtained from Eqs. (1–4), and  $I$ , at the maximum ( $L = 3.21$ ) and minimum ( $L = 1.73$ ) leaf area indices observed during the experiment (A,B, solid lines). The dotted line in (B) represents an alternative approach in which  $g_c$  is calculated from measurements of  $\text{CO}_2$  uptake (Baker et al., 1972) and  $\text{CO}_2$  concentration gradient (Harley et al., 1992). The dashed and broken lines in (B) represent the effect of altering the  $\text{CO}_2$  concentration gradient in this alternative calculation by  $\pm 25\%$ .

Canopy conductance of the lowest layer of foliage was calculated as for a complete layer, and then scaled by the fractional  $L$  remaining at the bottom of the canopy. Finally,  $g_{cw}$  was converted to canopy stomatal conductance to ozone ( $g_c$ ) according to Graham's law (after Jones, 1992) as

$$g_c = g_{cw} (D_{\text{O}_3} / D_{\text{H}_2\text{O}}), \quad (4)$$

where  $D$  is the molecular diffusivity at canopy temperature.

The magnitude of  $g_c$  increased both diurnally with increasing  $I$  and with increasing  $L$  due to canopy growth (cf. upper and lower lines in Fig. 2A). The full range of modelled  $g_c$  values throughout the CODE field campaign is contained within the solid lines in Fig. 2(A). Half-hourly averages of  $g_c$  obtained from values of  $I$  and  $L$  prevailing during individual half-hourly averaging periods for ozone

Table 1

Effects of maximum expected measurement errors ( $\pm 20\%$ ) in single leaf model parameters ( $a$ ,  $b$ ), leaf area index ( $L$ ) and radiation extinction coefficient ( $K$ ) on the estimates of canopy stomatal conductance at  $I = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ . Errors are combined to maximize the effects on  $g_c$

20% Error	Effect on $g_c$
1.2 $a$ , 0.8 $b$	+24.1%
0.8 $a$ , 1.2 $b$	–20.6%
1.2 $L$ , 0.8 $K$	+18.7%
0.8 $L$ , 1.2 $K$	–17.8%

deposition were used to derive the relationships below (e.g. Figs. 3–5).

### 3.2.1. Error analysis

Canopy stomatal conductance is calculated from the incoming photosynthetically active photon flux density ( $I$ ), the single leaf stomatal conductance model (Eq. 1), and the radiative transfer and scaling models (Eqs. (2–4)). The potential  $\pm 20\%$  errors in the single leaf model parameters (Fig. 1, dotted and dashed lines) are larger than those actually expected from measurement uncertainties.

The impact of combined errors of this magnitude on the modelled canopy conductance are shown in Table 1. The maximum propagated error due to combined uncertainties in the single leaf model parameters ( $a$  and  $b$ ) is +24.1% and –20.6% at  $I = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ . The propagated error derived from combined uncertainties in the radiative extinction coefficient ( $K$ ) and in the leaf area index ( $L$ ) is +18.7% and –17.8% at  $I = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ . These uncertainties in canopy stomatal conductance ( $g_c$ ) increase with increasing  $I$ , as expected from the behavior of the single leaf model (Fig. 1). These errors of about  $\pm 20\%$  represent the likely uncertainty in the relationships considered in this study.

### 3.2.2. Alternative models of canopy stomatal conductance

An additional source of uncertainty in the canopy stomatal conductance model (Fig. 2A,B, solid lines) is the simplified radiative transfer model of Eq. (2) and the assumption of a constant value of  $K$ . To test the sensitivity of  $g_c$  to these assumptions, we evalu-

ate an alternative and completely independent model of  $g_c$  (Fig. 2; dotted line). This model was derived from a published relationship between carbon assimilation and solar radiation in a mature cotton canopy (Baker et al., 1972; Fig. 3B) exhibiting a similar stature ( $h > 1$  m) and slightly greater (98%) radiation interception than in the present canopy (about 89%).

To develop a model from the radiation response functions of Baker et al. (1972), that is consistent in form with our model (Fig. 2), we transform short-wave solar radiation into photosynthetically active photon flux density ( $I$ ) according to the relationship determined in the present study ( $r^2 = 0.999$ ). We then calculate canopy stomatal conductance to  $\text{CO}_2$  from  $\text{CO}_2$  flux (mass per ground area per time) taken from Baker et al. (1972), and a  $\text{CO}_2$  concentration gradient ( $\Delta C$ ) between the ambient environment and the (canopy mean) leaf intercellular space of about  $190 \text{ mg m}^{-3}$ , obtained from Harley et al. (1992, Fig. 8). Conductance to  $\text{CO}_2$  is converted into canopy conductance to  $\text{O}_3$  ( $g_c$ ) using the appropriate analogue of Eq. (4). A model relationship between this estimate of  $g_c$  and  $I$ , following the form of Eq. (1), is then obtained as

$$g_c = 0.0112 + \frac{3.039I}{4216 + I}, \quad (5)$$

and presented as the dotted line in Fig. 2(B). This curve lies within the uncertainty of our original model when  $I > 600 \mu\text{mol m}^{-2} \text{s}^{-1}$ , and underestimates  $g_c$  when  $I < 600 \mu\text{mol m}^{-2} \text{s}^{-1}$ . This underestimation at low values of  $I$  reflects the decline of  $\text{CO}_2$  flux (Baker et al., 1972; Fig. 3) to near-zero under dark conditions, while our field data indicate significant stomatal conductance to  $\text{O}_3$  even under dark conditions.

A major uncertainty in this latter modelling approach is the assumption of  $190 \text{ mg m}^{-3}$  as the  $\text{CO}_2$  concentration gradient. To test the sensitivity of modelled  $g_c$  to this assumption, we vary  $\Delta C$  by  $\pm 25\%$  ( $143 \text{ mg m}^{-3}$ , dashed line;  $238 \text{ mg m}^{-3}$ , broken line; Fig. 2B). The lower estimate of  $\Delta C$  improves the agreement at lower levels of  $I$ , whereas the greater estimate of  $\Delta C$  consistently underestimates our modelled  $g_c$  over the range of  $I$  considered in this study, but agrees well at higher values of  $I$  (not shown).



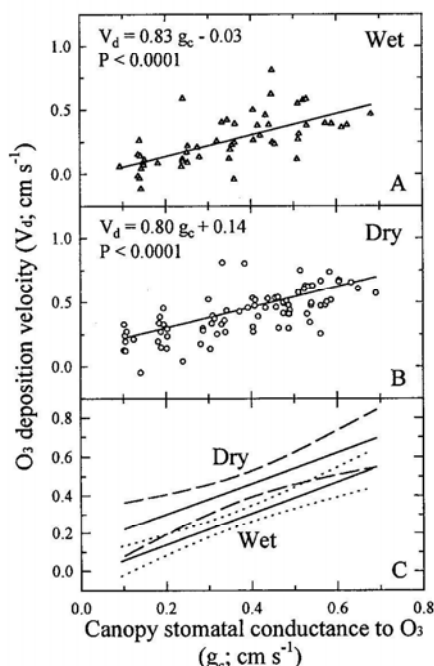


Fig. 4. Relationship between ozone deposition velocity ( $V_d$ ) and  $g_c$  under (A) wet ( $n = 53$ ;  $r^2 = 0.44$ ;  $p < 0.0001$ ) and (B) dry ( $n = 83$ ;  $r^2 = 0.14$ ;  $p < 0.0001$ ) conditions. Points represent 30 min averages. Solid lines, equations, and statistics characterize the linear regressions. Solid lines in (C) represent the same regressions for dry and wet conditions; dashed and dotted lines characterize the 95% confidence limits.

This parameter ( $g_{atm}$ ), considered here in series with  $g_c$ , increased with increasing  $I$  and  $g_c$  (not shown). However, since  $g_{atm}$  remained much larger than  $g_c$  throughout the experimental period, the responses of  $g_c$  to  $I$  represented the limiting conductance to deposition of ozone. The covariance of  $g_{atm}$  with  $g_c$  further strengthened the apparently mechanistic relationship between ozone deposition and  $g_c$  considered in Fig. 3. Under many conditions this could enhance the general utility of using the modelled values of  $g_c$  to infer ozone deposition. Similarly, the covariance of leaf and atmospheric processes have been found to contribute to diurnal patterns of ozone deposition in an eastern forest (Fuentes et al., 1992). Any underestimation of  $g_b$  would lead to an underestimation of  $g_{atm}$  (Eq. (6)), and subsequently to an underestimation of the role of stomatal regulation in

controlling ozone deposition. The magnitude of  $g_b$  may be underestimated in this analysis because of possible effects of a roughness sublayer (e.g. Cellier and Brunet, 1992), which was not incorporated in this analysis (Massman et al., 1994).

The strong relationships observed between measured values of canopy stomatal conductance and ozone deposition support earlier conclusions (Baldocchi et al., 1987; Fuentes and Gillespie, 1992; Grantz et al., 1995; Massman and Grantz, 1995; Wesely, 1989) that internal leaf sites represent significant regional sinks for ozone, controlled by the physiologically modulated stomatal response. The use of modelled stomatal behavior ( $g_c$ ) to predict  $V_d$  on a regional basis could reduce the data requirements for in situ measurements of ozone flux and uncertain calculations of  $g_a$  and (particularly)  $g_b$ .

### 3.3.3. Surface conductance

Removal of the effects of variable atmospheric mixing near the canopy ( $g_{atm}$ ; Eq. (6)) allows characterization of a true surface conductance ( $g_{surf}$ ) as

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

Whereas canopy stomatal conductance is scaled upwards from single leaf behavior, and reflects only the stomatal portion of the surface conductance,  $g_{surf}$  is scaled downward from canopy-scale measurements of  $V_d$  and  $g_{atm}$ , and is completely independent of  $g_c$ . Under both wet (Fig. 5A) and dry (Fig. 5B) canopy conditions,  $g_{surf}$  was very closely related to  $g_c$ , reflecting the dominance of stomatal conductance in controlling the total surface conductance ( $g_{surf}$ ). However, other non-stomatal modes of ozone deposition and decomposition may be present within the cotton canopy. Refining the analysis of ozone deposition to the surface allows explicit consideration of the parallel stomatal and non-stomatal pathways, and possible microenvironmental effects, such as wetness, on their relative contributions to ozone deposition.

### 3.4. Effects of surface wetness on ozone deposition

#### 3.4.1. Canopy stomatal conductance

Ozone fluxes to cotton ( $F$ ) were generally reduced in magnitude under wet conditions (cf. Fig.



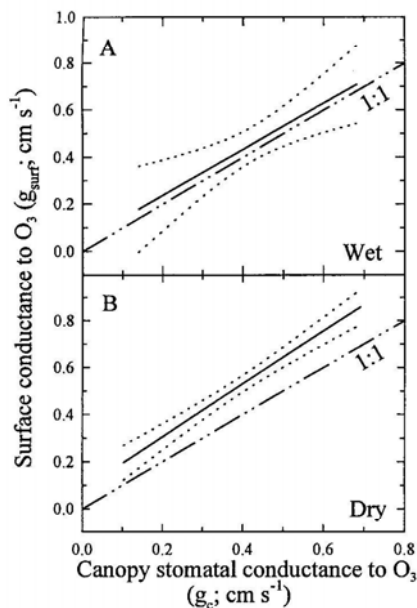


Fig. 5. Relationship between total surface conductance to ozone ( $g_{\text{surf}}$ ) and  $g_c$  under (A) wet and (B) dry conditions. Solid lines characterize the linear regressions; dotted lines, the 95% confidence limits; broken lines represent the 1:1 relationships.

3A,B). This result is consistent with assumptions made in some deposition models (Hicks et al., 1987; Wesely, 1989; Wesely et al., 1978), but contradicts some other reported results (e.g. Fuentes et al., 1992; Fuentes and Gillespie, 1992; Grantz et al., 1995).

Ozone deposition velocity ( $V_d$ ) was reduced under wet conditions (cf. Fig. 4A,B). Over the range of conditions considered in this analysis, surface wetness significantly decreased  $V_d$  by about 20% (Table 2). The relationships between  $V_d$  and  $g_c$  under wet and dry conditions were parallel (Fig. 4C), indicating no significant influence of wetness on the sensitivity of  $V_d$  to  $g_c$ . This contrasts with the enhancement of ozone deposition by leaf wetness observed in grape (Grantz et al., 1995).

### 3.4.2. Non-stomatal surface conductance

In grape the major effect of surface wetness was found to be on the non-stomatal component of surface conductance. This residual conductance ( $g_r$ ), in parallel with  $g_c$ , calculated as

$$g_r = g_{\text{surf}} - g_c \quad (8)$$

was generally positive in both grape and cotton (Table 2). These data do not suggest a limiting intercellular, or mesophyll, conductance to ozone deposition inside the stomatal pores, although this is not precluded by the precision of the available data (Massman and Grantz, 1995). On the contrary, the observation that  $g_{\text{surf}} > g_c$  suggests that the stomatal uptake pathway is not sufficient to account for the ozone deposition measured to the cotton canopy under dry conditions. An alternative sink, at the surface (i.e. below the deposition measurement height) and in parallel with the stomatal conductance, may be implicated.

The value of  $g_r$  was about 30% greater in cotton than in grape (Table 2). This could reflect greater soil emissions of nitric oxide (NO) from the heavily fertilized cotton field (Massman and Grantz, 1995). Titration of ozone by NO within and above the canopy would be indistinguishable from surface ozone deposition as determined by eddy covariance above the canopy, but would not be predicted from stomatal responses. At present there is no evidence of high rates of NO emission from these fields. Alternatively, deposition pathways associated with the residual, non-stomatal conductance,  $g_r$ , may consist of heterogeneous reactions on surfaces of the soil, leaf and stem, cuticles, and debris collecting below the canopy. These may be substantial sinks in removing ozone from the atmospheric surface layer (Baldocchi, 1988; Leuning et al., 1979b; Turner et al., 1973; Wesely, 1989). It is significant that the residual component of conductance to ozone ( $g_r$ ) is essentially independent of  $I$  and  $g_c$ , under both dry and wet conditions (cf. 1:1 line, solid line; Fig.

Table 2

Effects of surface wetness on mean ozone deposition velocity and residual conductance over the range  $0 < I \leq 1000 \mu\text{mol photons m}^{-2} \text{ s}^{-1}$  in cotton and in grape. Data represent mean  $\pm$  S.E. Means within a single wet-dry comparison are highly significantly different ( $p < 0.0001$ ) when followed by different letters

Cotton $V_d$		Cotton $g_r$		Grape $g_r$ <sup>a</sup>	
Wet	Dry	Wet	Dry	Wet	Dry
0.318a	0.403b	0.033a	0.130b	0.343a	0.098b
$\pm 0.0258$	$\pm 0.018$	$\pm 0.036$	$\pm 0.018$	$\pm 0.051$	$\pm 0.011$
n = 34	n = 75	n = 34	n = 75	n = 86	n = 211

<sup>a</sup> Data from Grantz et al., 1995.

5A,B). Under dry conditions,  $g_c < g_{surf}$  (Table 2) over the entire range of conditions considered (Fig. 5B). Under wet conditions (Fig. 5A), however,  $g_c \approx g_{surf}$  over this range of observations.

As a residual term,  $g_r$  is sensitive to expected errors in the single leaf stomatal conductance model parameters ( $a$  and  $b$ ), in the estimates of the leaf area index ( $L$ ), and in the radiation extinction coefficient ( $K$ ). Varying these parameters by  $\pm 20\%$  (above) altered the values of  $g_r$  in cotton to some extent, but  $g_r$  remained positive, indicating a substantial, non-stomatal deposition pathway over the entire range of  $g_c$  considered (not shown).

### 3.5. Contrasting cotton and grape canopies

The residual, non-stomatal conductance,  $g_r$ , was not different in the two contrasting canopies under dry conditions. In grape, following dew-wetting of the canopy,  $g_r$  increased by about  $0.245 \text{ cm s}^{-1}$  (Table 2). If  $g_r$  in cotton increased by a similar amount following dew-wetting, then we would expect values of  $g_r$  under wet conditions to be about  $0.375 \text{ cm s}^{-1}$ , rather than the very small value of  $0.033 \text{ cm s}^{-1}$  actually observed in cotton (Table 2). This difference of about  $0.342 \text{ cm s}^{-1}$  could represent an obscured decrease in another component of surface conductance that was not enhanced by wetness. This could include plant and soil surface sites of high reactivity, that were masked by an aqueous film in which ozone is only slightly soluble. However, an offsetting decrease of this magnitude is likely to represent an effect on the dominant component of surface conductance,  $g_c$ .

Such a decrease in  $g_c$  would be likely to occur through occlusion of stomatal pores by dew droplets, as suggested in models of ozone deposition (e.g. Wesely, 1989), perhaps occurring preferentially on the upper, adaxial surface of exposed leaves. The low value of  $g_r$  observed in cotton under wet conditions may reflect the blockage of a sufficient fraction of the stomatal pathway to offset any unmeasured NO titration or other non-stomatal component of  $g_r$  observed under dry conditions in cotton, as well as to offset the probable effect of wetness itself in enhancing the conductance of the non-stomatal pathway.

The difference between the cotton and grape

canopies (Grantz et al., 1995) is likely due to the differences in their physiological and morphological properties. Cotton is grown as a physiologically active annual plant, has amphistomatous leaves (i.e. stomatal pores on both surfaces), and displays a continuous canopy which completely covered the ground during most of CODE. Grape is a long-lived, woody perennial plant, with lower metabolic activity, hypostomatous leaves (i.e. stomatal pores on lower, abaxial leaf surfaces only), and presented a discontinuous, trellised canopy interspersed with a grass understory throughout the CODE study period.

### 4. Conclusions

Measured stomatal conductance and photon penetration through a cotton canopy have been used to construct a simple model of canopy stomatal conductance to ozone over the range of photosynthetically active photon flux density ( $I$ ) of  $0 < I < 1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ . This is the range of daytime conditions over which leaf wetness was observed. Our hypothesis that ozone deposition to an extensive cotton field is a strong function of canopy stomatal conductance ( $g_c$ ) was supported under conditions of both dry and wet foliage. The hypothesis that surface wetness decreases ozone deposition to amphistomatous cotton leaves was supported, as wetness decreased ozone flux, deposition velocity and surface conductance, determined independently of stomatal conductance, below levels predicted by  $g_c$  under dry conditions. This result contrasts with our previous analysis of a grape canopy during CODE, in which wetness increased the surface sink strength by a non-stomatal pathway. This is likely due to the occlusion of abaxial stomatal pores by surface dew in cotton, whereas these upward-facing leaf surfaces are free of stomata in grape. This inhibitory effect of wetness in cotton was sufficient to offset the non-stomatal conductance observed under dry conditions, associated with a possible titration of ozone by NO emitted from the cotton field, as well as a probable increase in the non-stomatal surface conductance associated with wetness in grape. Calculation of residual conductance terms under wet and dry conditions indicates a constant (i.e. independent of  $g_c$  and  $I$ )

non-stomatal component of surface conductance. This apparent  $g_r$  was lower under wet than dry conditions. Increasing dew deposition may decrease the stomatal pathway and increase the residual surface pathway by similar amounts. Further research into the determinants and properties of the residual conductance in contrasting vegetative and non-vegetative surfaces could enhance the utility of the relationship between stomatal properties and ozone deposition.

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