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Estimating canopy conductance to ozone uptake from observations of evapotranspiration at the canopy scale and at the leaf scale*

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Abstract

Stomatal uptake by vegetation is often the major sink for the destruction of tropospheric ozone. Using data obtained during the summer of 1991 at a grape vineyard and a cotton field in the San Joaquin Valley of California, we compare canopy (stomatal) conductances to ozone estimated (1) from eddy covariance ozone flux data (2) from eddy covariance evapotranspiration data and (3) by scaling leaf transpirational conductance to the canopy level using a canopy radiative transfer model. These simultaneous data, obtained at two levels of biological organization and for two trace gases, allow us to contrast the pathways for canopy–atmosphere exchange of water vapour and ozone, to evaluate limitations to scaling from leaf to canopy, and to predict ozone uptake parameters from those governing transpiration. At the vineyard site the eddy covariance ozone results underestimate the ET-based (eddy covariance and leaf scaling) approaches between 25% and 36%. At the cotton site the ozone-based results overestimate the ET-based approaches between 9% and 62%. A number of modelling and measurement uncertainties are of appropriate magnitude to reconcile these estimates. Some of the possible causes for these discrepancies that are discussed include NO effects, mesophyll resistances to ozone uptake and flaws in the K-theory (first-order closure) approach on which the canopy-scale analysis is based. Nevertheless, both canopy and single leaf measurements of conductance for water vapour provide acceptable estimates of conductance for ozone, but further experiments in which all are measured simultaneously are suggested.

Keywords: canopy conductance, leaf-to-canopy scaling, evapotranspiration, ozone deposition

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1 Introduction

Ozone, when taken up through plant stomata, can impair stomatal functioning, photosynthesis and a host of other plant physiological activities (Treshow & Anderson 1989). These plant responses in turn affect the release of water vapour, the uptake of CO_2 and the release of volatile organic hydrocarbons. Because plant stomata are often the major pathway for the dry deposition and removal of surface (tropospheric) ozone (Reich 1987; Lefohn 1992) and because tropospheric ozone is expected to increase (at least in the Northern Hemisphere) (Thompson 1992; Turco 1992), observational and modelling studies of dry deposition of ozone are likely to become increasingly important for understanding plant response to ozone and the impact that this can have on tropospheric chemistry.

The present study, part of the California Ozone Deposition Experiment (CODE), compares canopy (stomatal) conductances to ozone estimated from (a) eddy covariance ozone flux data, (b) eddy covariance evapotranspiration (ET) data, and (c) leaf-level measurements of transpirational conductance scaled to the canopy level using a radiative transfer model. We test the hypothesis that bulk canopy stomatal uptake of ozone scales in a predictable manner to canopy transpiration determined

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at canopy and single leaf levels. Although many previous leaf-level studies have demonstrated that ozone uptake is controlled by stomata in a manner similar to transpiration (Thorne & Hanson 1972; Laisk *et al.* 1989; Taylor & Hanson 1992), only few studies have examined this issue at the canopy scale (Wesely *et al.* 1978; Leuning *et al.* 1979; Grimm & Fuhrer 1992). Furthermore, none of these previous studies attempted to separate plant transpiration from soil evaporation when evaluating surface conductances to water vapour. To our knowledge this study is the first to compare all three measures of canopy conductance simultaneously.

In this study we analytically partition ozone and water fluxes between stomatal and non-stomatal pathways and evaluate the derived canopy conductances. Because the scaling methods used herein are model-based all bulk canopy conductances possess some uncertainty. We can reduce some of these uncertainties by comparing the different modelling approaches with each other. If the independently determined conductances agree with each other, then we should have greater confidence in the validity of the canopy conductances. Furthermore, the present methods do have the advantage of being relatively simple and yet incorporating most of the important physical processes that govern soil–plant–atmosphere exchange.

Ultimately this analysis should encourage the development of improved models of ozone deposition and tropospheric chemistry. Furthermore, this study may also provide enhanced techniques for ground-truthing of satellite and high-altitude remote sensing of canopy conductances (Gao 1994) and for deriving indices of canopy oxidative stress similar to leaf-level indicators currently available (e.g. Amiro *et al.* 1984; Reich 1987).

The rest of this study is divided into three sections. The next section discusses the experimental data, the models used to estimate canopy conductances and (in general terms) some of the strengths and weaknesses of those models. The third section discusses results and addresses several important issues regarding canopy stomatal control of transpiration and ozone uptake. This section presents a detailed sensitivity/uncertainty analysis of various model parameters and assumptions. The main purpose of this analysis is to estimate uncertainties in the canopy conductances. This allows us to explore the possibilities of using the three independent measures of canopy conductance to diagnose possible canopy mesophyll resistance to ozone and to evaluate the potential influence of soil NO emission on the conductances derived from ozone deposition data. This synthesis of results from the three independent estimates of canopy conductance has not been presented previously. The fourth and final section summarizes the main findings of this study.

2 Materials and methods

2.1 Site descriptions and supporting data

We present here only a brief summary of sites and supporting data. A complete description of the CODE, the experimental sites, the eddy covariance instrumentation and the data processing can be found in Massman *et al.* (1994) and Pederson *et al.* (1995).

The eddy covariance method was used to determine half-hourly estimates of the vertical fluxes of ozone, heat, water vapour and momentum at a grape vineyard (*Vitis vinifera* L. cv. Thompson seedless) site and cotton (*Gossypium hirsutum* L. cv. Delta Pine 6166) site in the San Joaquin Valley of California during July and August of 1991. Other half-hourly measurements made at each site include solar radiation, net radiation, soil heat flux, atmospheric temperature and humidity, horizontal wind speed and direction, soil temperature, infrared surface (soil plus vegetation) temperature, atmospheric ozone concentration and data from dew sensors placed within or near the plant canopies. The vineyard site was located about 40 km north-west of Fresno, California, and the cotton site was located about 80 km west of Fresno. During the CODE the cotton crop was actively growing (the leaf area index or LAI changed from 1.8 to 2.5 and the canopy height changed from 0.4 m to 0.9 m), while the vineyard had largely reached its maximum vegetative stage (LAI = 3.4, canopy height = 1.7 m).

The eddy covariance method has been used previously to study ozone deposition to maize (Wesely *et al.* 1978), soybean (Wesely *et al.* 1982), grasslands (Droppo 1985; Delany *et al.* 1986; Massman 1993), tundra (Jacob *et al.* 1992), a deciduous forest (Amthor *et al.* 1994), etc. However, the CODE is the first experiment to quantify the deposition of ozone to a cotton crop and a grape vineyard. Comparing the CODE eddy covariance ozone fluxes given by Massman *et al.* (1994) with these previous studies suggests that the ozone fluxes at the vineyard site are near the midrange of observed fluxes (–0.4 to –0.8 $\mu g\text{-}O_3\ m^{-2}\ s^{-1}$), but that the fluxes at the cotton site are relatively higher in magnitude (–0.8 to –1.2 $\mu g\text{-}O_3\ m^{-2}\ s^{-1}$).

In addition to the canopy-scale eddy covariance data, leaf physiological data from several individual sunlit leaves were also obtained at each site. Four fully expanded leaves from each of five plants were used to obtain hourly measurements of stomatal conductance to H_2O, carbon dioxide flux and intercellular CO_2 concentration. Each hourly datum is therefore the mean of 20 leaves. When possible, the same 20 leaves were used throughout a day of measurement. Any leaves damaged during measurement were replaced by similar leaves of the same plant. These data were obtained with a Portable Photosynthesis

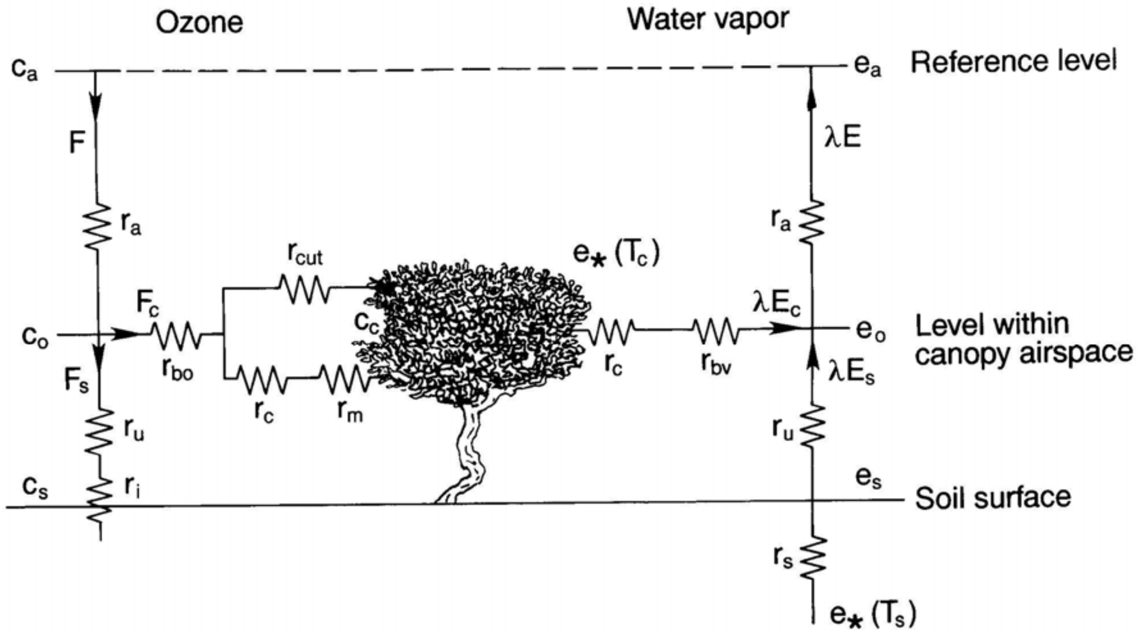

Fig. 1 Resistance network for the two-component (soil + canopy) Penman–Monteith model of evapotranspiration and ozone uptake. The arrows and associated capital letters refer to fluxes. All resistances are indicated by 'r'. Ozone concentration is denoted by 'c', while the partial pressure of water vapour is denoted by 'e'. The saturation vapour pressure is denoted by e_* and is a function of temperature, *T*. Table 1 provides a full discussion of the resistances.

System (LI-6200; LiCor Inc., Lincoln, NE) and consist of four (complete or partial) daytime time courses, each taken on separate days.

2.2 General discussion of models and conductances

This study uses three separate models to independently evaluate the canopy stomatal conductances. For the eddy covariance data (ozone and water vapour) we use slightly different formulations of the dual-source Penman–Monteith model. The dual-source model explicitly separates soil and plant exchange processes into two separate sources. Figure 1 shows the pathways and associated resistances of the dual-source model for ozone deposition (left side) and for evapotranspiration (right side). The more traditional (single-source) Penman–Monteith model combines both soil and plant exchange processes into one resistance. For the leaf-level water vapour conductance data we scale to the canopy level using leaf area index (LAI) and a radiative transfer model. This approach is inherently a single-source method and cannot provide any information on soil evaporation. All conductances derived from water vapour exchange are converted to ozone conductance by dividing by 1.65, the ratio of molecular diffusivities for water vapour and ozone. Table 1 summarizes the resistances, conductances and important modelling parameters and concepts used in each of these three models.

The major difference between the dual source water vapour and ozone models is that the water vapour model explicitly employs the surface energy balance and a physically based regression approach to partition the latent heat fluxes (λE) and the sensible heat fluxes (H) into plant and soil components (Massman & Ham 1994) and the ozone model does not. Once λE and H are partitioned, they are used in conjunction with measured soil and atmospheric temperatures and ambient atmospheric vapour pressures to estimate (*in situ*) the canopy temperature, the canopy conductance, the within-canopy aerodynamic resistance (r_u) and the soil evapourative resistance (r_s) (Massman 1992).

In contrast the ozone deposition model partitions the ozone flux by assuming that the canopy conductance is linearly related to solar radiation and that all non-transpiring surfaces take up ozone at a constant rate (similar to Massman *et al.* 1994). Consequently, the ozone model derives estimates of the canopy conductances from observed ozone deposition velocities and solar radiation, whereas the ET model derives *in situ* estimates of the canopy conductance without reference to solar radiation.

Table 1 Resistance/conductance notation and partial list of symbols with interpretation.

Symbol	Interpretation	Comments
r_a	bulk aerodynamic resistance	the same for both eddy covariance ET and ozone deposition models
r_b	bulk leaf boundary layer resistance	used with both eddy covariance ET and ozone deposition models, subscript o refers to ozone and subscript v refers to water vapour
r_c	bulk canopy stomatal resistance	used with (but not necessarily the same) for both eddy covariance ET and ozone deposition models
r_u	within-canopy aerodynamic resistance	used with (but not necessarily the same) for both eddy covariance ET and ozone deposition models
r_s	soil resistance to evaporation	used with eddy covariance ET model only
r_i	intrinsic soil resistance to ozone deposition	used with eddy covariance ozone deposition model only
r_m	bulk leaf mesophyll resistance to ozone deposition	used with eddy covariance ozone deposition model only
r_{cut}	plant bulk cuticular and epidermal resistance to ozone deposition	used with eddy covariance ozone deposition model, includes both plant leaves and stem surfaces
r_{surf}	bulk surface resistance	total surface (plants and soil) resistance to ozone deposition or ET, to be decomposed into its constituent parts with the dual-source eddy covariance models
g_{surf}	bulk surface conductance	$= 1/r_{surf}$
g_c	bulk canopy stomatal conductance	$= 1/r_c$
g_x, g_n	model parameters describing g_c	used as basis of comparison between all models, g_n is minimal or night-time bulk stomatal conductance, $g_x + g_n$ is maximal bulk stomatal conductance
g_0	total nonstomatal surface conductance for the ozone deposition model	$= 1/(r_b + r_{cut}) + 1/(r_u + r_i)$
$g_x{}'$, $g_n{}'$	parameters describing leaf level transpirational conductance	used as the basis of the radiative transfer model to scale to equivalent canopy conductances g_x and g_n
B	surface Stanton number	used for parameterizing bulk canopy boundary-layer resistance
LAI	canopy leaf area index	
L	cumulative leaf area downward from the top of the canopy	a measure of vertical position within the canopy
$M(L)$	leaf metabolic or photosynthesis parameter	used to describe possible reduction in maximum leaf stomatal conductance at saturating PAR of individual leaves at depth L within the canopy
κ	canopy light extinction coefficient for direct beam radiation	function of leaf angle distribution and solar zenith angle
v_d	ozone deposition velocity	defined as the negative ratio of the observed ozone flux (downward) to the observed ozone concentration

Nevertheless, we subsequently fit the inferred ET canopy conductances to the same linear model of stomatal response because it provides a convenient set of common parameters for comparisons between the various models. Specifically we fit all canopy stomatal conductances (g_c) with the following model:

$$g_c = g_x(R_s/R_{s0}) + g_n\,, \tag{1}$$

where R_s is the solar radiation (used here as a surrogate for PAR, the dominant regulator of stomatal opening), R_{s0} = 1000 Wm^{-2} is a convenient normalization factor approximating maximal radiation, g_n is the minimum conductance and corresponds to the night-time canopy stomatal conductance and g_x is the component of the canopy stomatal conductance that varies with solar radiation. The parameters g_x and g_n are determined by a least- squares technique from nearly four weeks of data and represent average canopy stomatal properties during the CODE.

For this study we use solar radiation as the sole linear regression variable to describe conductances primarily for ease of comparison. Although including ambient vapour pressure deficit or air temperature as regression variables or allowing curvilinear response to solar radiation might improve the description of the conductances (e.g. Grantz & Meinzer 1990; Massman 1992; McCaughey & Iacobelli 1994), they also introduce unnecessary and untestable complexity into the present models. Furthermore, as will be demonstrated later, solar radiation alone is an extremely good regression variable. Consequently (1) should be quite sufficient for the present purposes.

Finally, there are a few minor differences and similarities between the three models that need to be included in this general discussion. First, the ozone model includes (at least an optional) mesophyll resistance, but the ET models do not. Secondly, the ozone model uses both day and nighttime data, whereas the ET models are restricted to daylight periods ($R_s > 0$). Thirdly, the ozone model includes a cuticular (or more correctly a combination of epidermal and cuticular) resistance associated with ozone deposition to non-transpiring plant surfaces, but the ET models ignore water vapour loss through the plant cuticles. Fourthly, data collected when sensors indicated the presence of dew have been excluded from the present analysis to avoid complications of dew effects on canopy conductances (Fuentes *et al.* 1992; Massman *et al.* 1994; Grantz *et al.* 1995). Fifthly, to compare different methods of estimating the canopy conductance to ozone we estimate the uncertainties associated with the g_x values. The details of this uncertainty analysis are discussed later.

2.3 *Treatment of aerodynamic and boundary layer*

Aerodynamic resistance (r_a) is calculated as in Massman *et al.* (1994), as a function of the horizontal wind speed, atmospheric stability, displacement height, and roughness length, with a correction for a roughness sublayer (Massman *et al.* 1994) that reduces r_a by *c.* 33%.

The foliage boundary layer resistance, r_b, is estimated as $f_c[kB^{-1}_{03}]\,[ln(\{z-d\}/z_0) - \psi^m]/k^2u$, where f_c is a reduction factor associated with roughness sublayer effects on the wind speed profile (Massman *et al.* 1994), k is the von Karman constant, B_{03} is the canopy Stanton number for ozone, z is the measurement height, ψ_m is the Businger–Dyer stability function for momentum transfer, z_0 is the roughness length, d is the displacement height and u is the horizontal wind speed (Massman *et al.* 1994). For this study kB^{-1}_{03} is estimated for the CODE sites by adapting Massman's (1987) kB^{-1} model (which includes roughness sublayer effects) to amphistomatous leaves for cotton and hypostomatous leaves for grape and by incorporating a triangular leaf area density function with a maximum at 60% of the canopy height. As with r_a, incorporation of a roughness sublayer reduces r_b by *c.* 33% below the more traditional formulation (Massman *et al.* 1994). In addition to the difference in formulation for r_b, the usage of r_b is also different from Massman *et al.* (1994). In this study we place r_b in series with r_c and r_{cut} rather than in series with r_a in order to be more consistent with the dual-model formulation.

Nevertheless, the parameterization of kB^{-1}_{03}, and therefore, r_b remains very uncertain, particularly for sparse canopies such as those at all the CODE sites. For example, in the present study $kB^{-1}_{03} \approx 2–4$ which (assuming an analogue between ozone transfer and heat transfer) is common to closed canopies (Garratt & Hicks 1973). But, Kustas *et al.* (1989) report that kB^{-1} (for heat exchange)$\geqslant$ 5 over a sparse shrubland and Garratt & Hicks (1973) report that kB$^{-1} \approx 9$ over a grape vineyard. Consequently, the sensitivity of g_x and g_n to uncertainties in r_b is considered later.

2.4 *Canopy conductance from ozone eddy covariance data*

Ozone deposition is typically characterized by a deposition velocity v_d (defined as the negative of the ozone flux divided by the ambient ozone concentration), which in turn is interpreted using a multiple resistance model. For the present study the surface conductance, g_{surf} (defined as $1/r_{surf}$), is related to the deposition velocity as follows:

$$g_{surf} = v_d/(1{-}v_d r_a)\,. \tag{2}$$

The surface conductance model used in this study is comprised of a stomatal pathway in parallel with other pathways. In its simplest form this model is given as follows:

$$g_{\mathrm{surf}} = 1/(r_{\mathrm{b}} + r_{\mathrm{c}} + r_{\mathrm{m}}) + g_0\,, \tag{3}$$

where r_{m} is the canopy mesophyll resistance to ozone uptake and g_0 is the conductance associated with all the non-stomatal pathways, including deposition onto the leaf cuticles, the plant stem and branch surfaces and the soil.

For the present purposes the mesophyll resistance to ozone uptake is included for the sake of completeness and refers to any possible internal leaf resistance associated with the movement and destruction of ozone within the leaf mesophyll tissue. For this study we will concentrate on the case $r_{\mathrm{m}} = 0$, but we will discuss the influences that including r_{m} in the ozone model can have upon estimates of g_{x} as well.

Corresponding to Fig. 1, g_0 is given as $1/(r_{\mathrm{b}} + r_{\mathrm{cut}}) + 1/(r_{\mathrm{u}} + \mathrm{r_i})$; where r_{b} is the bulk canopy boundary layer resistance, r_{cut} is the total nontranspiring cuticular and epidermal resistance of the leaves and stems of the canopy, r_{u} is the within-canopy aerodynamic resistance and r_{i} is the intrinsic soil resistance to ozone destruction. For this study we will concentrate on the case g_0 = constant, but we also discuss model results associated with a more detailed model of g_0 which includes the effects of wind and turbulence on r_{u}.

Using observed data to calculate v_{d}, r_{a} and r_{b} and direct observations of R_{s}, a nonlinear least-squares regression approach is used to estimate g_{x}, g_{n}, g_0 (and r_{m} if desired) from the nearly four weeks of half-hourly data.

2.5 *Canopy conductance from eddy covariance ET data*

Canopy conductance to ozone is calculated from conductance to water vapour determined using the eddy covariance ET data, and a dual-source Penman-Monteith model (Massman 1992; Massman & Ham 1994). This technique is a physically based regression model that explicitly assumes surface energy balance closure (i.e. that net radiation (R_{n}) equals soil heat flux (G) plus sensible and latent heat fluxes). It analytically partitions water vapour flux between plant transpiration and soil evaporation (right side, Fig. 1), using the soil surface humidity and soil Bowen ratio as regression variables (after Massman & Ham 1994). Next, the foliage temperature and associated g_{c} are estimated (after Massman 1992) and finally g_{x} and g_{n} are found by regression against $R_{\mathrm{s}}/R_{\mathrm{s0}}$ using (1).

The major uncertainties in this partitioning approach are the ability of K-theory to adequately describe atmosphere–canopy exchange, and the possibility that the soil temperature data and the sensible and latent heat fluxes are not representative of the same portion of the surface (Massman & Ham 1994). Significant errors of either type could bias the partitioning and/or the computed foliage temperatures used to estimate g_{c}. These are considered in sections 3.1 and 3.2 below.

2.6 *Canopy conductance by scaling-up from leaf-level data*

Leaf stomatal conductance is scaled to the canopy level using methods developed for similar scaling of photosynthetic carbon assimilation. These models typically employ leaf-level measurements and canopy radiative transfer models (e.g. Gutschick 1991). A multitude of microenvironmental factors influence both photosynthesis and stomatal function, including light, water status, nutrition, etc. Though these may not always act in parallel on these two physiological processes, on average a general proportionality is maintained between photosynthesis and stomatal conductance (e.g. Wong *et al.* 1979).

In this study scaling-up is accomplished with an analytical evaluation of the following equation:

$$g_c = \int_0^{LAI} [g_{\mathrm{leaf}}^{\mathrm{sun}}(I_L)\, M^{\mathrm{sun}}(L)\, f^{\mathrm{sun}}(L) + g_{\mathrm{leaf}}^{\mathrm{shade}}(I_L)\, M^{\mathrm{shade}}(L)\, f^{\mathrm{shade}}(L)]\, dI, \tag{4}$$

where $g_{\mathrm{leaf}}^{\mathrm{sun}}$ ($g_{\mathrm{leaf}}^{\mathrm{shade}}$) is the leaf conductance of the sunlit (shaded) leaves, and is a function of the light intensity within the canopy (I_L); L is the cumulative leaf area from the top of the canopy downward; $M(L)$ describes a possible reduction in maximum leaf stomatal conductance at saturating PAR of individual leaves at depth L within the canopy; and f^{sun} ($f^{\mathrm{shade}} = 1 - f^{\mathrm{sun}}$) is the sunlit (shaded) leaf fraction at depth L within the canopy.

We parameterize $M^{\mathrm{sun}}(L)$ and $M^{\mathrm{shade}}(L)$ as $M(L) = [0.65 + 0.35\exp(-\kappa L)]$ following Johnson *et al.* (1989), $f^{\mathrm{sun}}(L)$ as $(1-\exp(-\kappa L))/\kappa L$ as discussed by Campbell (1977) and others, and g^{leaf} and $g_{\mathrm{leaf}}^{\mathrm{shade}}$ as follows:

$$g_{leaf}^{sun} = g'_x[R_s/R_{s0}][f_{\mathrm{D}}\kappa\exp(-\kappa L) - \partial I_{Ld}/\partial L]/(f_{\mathrm{D}} + f_d) + g'_n \tag{5a}$$

$$g_{leaf}^{sun} = g'_x[R_s/R_{s0}]\,[-\partial I_{Ld}/\partial L]\,(f_{\mathrm{D}} + f_d) + g'_n, \tag{5b}$$

where g'_{x} and g'_{n} are model parameters evaluated by linear regression from single leaf data obtained with the Portable Photosynthesis System; f_{D} is the fraction of solar radiation that is direct PAR and f_{d} is the fraction that is diffuse PAR (both of which are modelled following Choudhury 1987) and both are implicit functions of the time of day; κ is the extinction coefficient for direct beam radiation and equal to $G(\mu)/\mu$ where μ is the sine of the solar elevation angle (modelled as discussed in Spitters *et al.* (1986) and others as a function of latitude, time of year and time of day and $G(\mu)$ is the fractional direct-beam-projected leaf area averaged over all leaf orientations (modelled using the ellipsoidal leaf angle distribution function of Campbell 1986, 1990); and I_{Ld} is the diffuse radiation within the canopy [which results from the scattering of the direct and diffuse radiation incident at the top of the canopy and is modelled using the canopy two-stream approximation developed by Dickinson (1983) and Sellers (1985)].

It is necessary to include the normalization factor ($f_D + f_d$), in (5a) and (5b) because the visible portion of the incoming solar radiation contributes only about half of R_s. Therefore, to be consistent with the eddy covariance derived estimates of g_c we must assume that g_c is responding to 100% of the R_s variations rather than just a portion of R_s. I_{Ld} implicitly includes both f_D and f_d, as well as the soil albedo ($\rho_{soil} = 0.10$ in this study), the PAR leaf transmittance ($\tau_{leaf} = 0.06$ in this study), the PAR leaf reflectance ($\rho_{leaf} = 0.066$ in this study) and the canopy LAI. These values of τ_{leaf} and ρ_{leaf} are reasonable for cotton leaves (Stanhill 1976) and are used also for grape leaves. Except for performing the sensitivity analysis, all model calculations assume that the leaf angle parameter has a nominal value of 1.0 (spherical leaf angle distribution with $G(\mu) = 1/2$).

We also assume that g'_x and g'_n are the same for both sunlit and shaded leaves. We make this last assumption primarily for convenience because we have no gas exchange data on shade leaves during the day and no nighttime leaf-level gas exchange data. On the other hand, there is evidence to suggest that for photosynthesis the parameter equivalent to g'_x (P^o_m, Johnson *et al.* 1989) does not vary with depth in the canopy (Johnson *et al.* 1989).

After substituting the above expressions for g_{leaf} (sunlit and shaded), $M(L)$, $f^{sun}(L)$ and $f^{shade}(L)$, the integration over the canopy LAI (4) can be performed analytically. But, the results do require evaluating the exponential integral, E_1, using numerical techniques. For this we used the algorithm given by Press *et al.* (1992).

To evaluate g_x for the canopy we fit g_c from (3) with $g_x(R_s/R_{s0})$; i.e. $g_n \equiv 0.0$. This assignment for g_n was made because the leaf-level data suggested that the nighttime pathway for transpiration was not significant (i.e. $g'_n \equiv 0.0$).

2.7 Strengths and weaknesses of present methods

Both the dual-source eddy covariance models are based on K-theory which assumes that the flux of a quantity is directly proportional to the mean concentration gradient of that quantity. A major deficiency of K-theory is its inherent inability to simulate observed counter-gradient fluxes (Denmead & Bradley 1985; Wilson 1989). Consequently, there has been much effort recently to develop canopy models based on higher-order closure methods (Wilson & Shaw 1977; Meyers & Paw U 1986) and on the Lagrangian transport approach (Wilson *et al.* 1981; Raupach 1987). However, use of either of these potentially more realistic approaches would not necessarily have reduced the uncertainties in the canopy conductances.

For example, higher-order closure models do not always accurately reproduce profiles of within-canopy turbulent statistics (Raupach 1988; Wilson 1988), nor are the basic closure assumptions any more valid than those employed with the simpler first order closure (K-theory) models (Deardorff 1978). Furthermore, higher-order closure models are not necessarily any more accurate than first-order closure models when used to estimate the bulk surface conductances (Watanabe 1993). Langrangian models also have some inherent flaws. In particular, they do not necessarily reproduce within-canopy concentration profiles very well (Baldocchi 1992). Consequently, we cannot assume that inverting a Lagrangian model using measured within-canopy concentration profiles (Raupach 1989) would result in an accurate representation of the vertical source distribution or the bulk surface conductances. The CODE data lack any within-canopy profiles with which to test either a Lagrangian or a higher-order closure model.

On the other hand, the dual-source approach to estimating conductances is a significant improvement over the traditional single-source (K-theory based) Penman–Monteith model. With the single source approach the inferred surface conductance is a combination of aerodynamic, soil and plant physiological effects. Consequently, they are not necessarily purely physiological parameters (Finnigan & Raupach 1987) and they may not be valid beyond the site for which they were derived (Raupach & Finnigan 1988). On the other hand, these concerns may not be too serious if both soil and vegetation are modelled separately (as is the case in this study) and if plant conductance (rather than turbulent atmospheric transport) is the limiting factor for canopy trace gas exchange. This last condition is usually valid for most canopies and most meteorological conditions.

The dual-source Penman–Monteith models also have the advantages of invertability. By invertability we mean that they can be used to solve for canopy conductances given the appropriate micrometeorological data. Therefore, they can be used either in a diagnostic mode to study surface conductances or in a prognostic mode to predict evapotranspiration given a model of the component surface conductances.

Like the dual-source models, the radiative transfer model used in this study is also based on some important assumptions that need to be discussed. First, the canopy is being treated as a horizontally homogeneous turbid medium. Secondly, transients in irradiance associated with leaf movement or clouds are not included. For light interception the first approximation has little influence, but could be important for photosynthesis (Gutschick 1991) and consequently for canopy conductance as well. The second approximation may represent a severe limitation (Gutschick 1991). However, there were no clouds

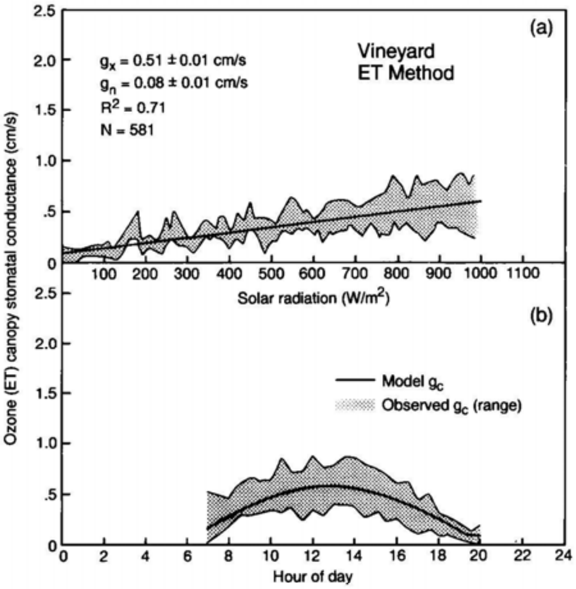

Fig. 2 Range of inferred and modelled vineyard ozone canopy conductances from eddy covariance ET data as a function of solar radiation (a) and time of day (b).

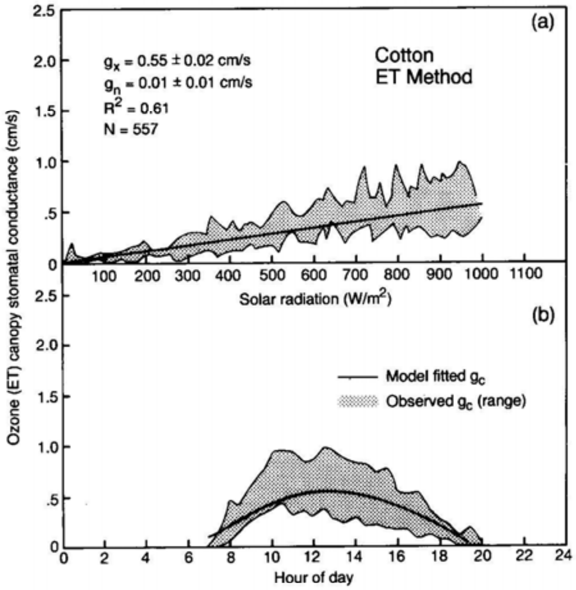

Fig. 3 Range of inferred and modelled cotton ozone canopy conductances from eddy covariance ET data as a function of solar radiation (a) and time of day (b).

during CODE and both wind speed (3–6 m s^{-1}) and direction were also nearly constant. Thirdly, $M(L)$ does not include the within-canopy variations of leaf temperature and leaf-to-air vapour pressure deficit. Although the variations of these within-canopy environmental variables are probably considerably less important than the variation in light intensity, they can nonetheless influence stomatal conductance. Furthermore, the need for $M(L)$ ultimately results from plant physiological activity; in which case using $G(\mu)/\mu$ in the present formulation suggests that plants can optimize their photosynthetic resources on an hour by hour basis (which is far too fast for most plants). Logically, $M(L)$ should not be parameterized in terms of $G(\mu)/\mu$, but rather in terms of a function that varies more slowly in time. On the other hand, this formulation is unlikely to introduce a significant error (Gutschick, personal communication).

3 Results and discussion

3.1 General results

Figures 2–6 summarize the results of the three models. Included on each of these figures are the range of variation in the inferred conductance data, the optimal parameter values (± SE), the R^2 of the regression relationships and the sample size, N. The R^2, defined as 1 – (the model's residual sum of squares)/(the variance of the data about its mean), is interpreted as that fraction of the data variance explained by the model.

Figures 2 (vineyard) and 3 (cotton) are the eddy covariance ET-based results. These figures suggest that the vineyard and cotton canopies should be relatively similar in their stomatal uptake of ozone except possibly at night when g_n is much larger for the vineyard than for cotton. Consequently, canopy night-time transpiration is much more significant with grape leaves than with cotton leaves. A comparison of the nighttime eddy covariance ET fluxes at each site supported this daytime result. At night λE was typically about 30 Wm^{-2} at the vineyard site, but it was usually less than 10 Wm^{-2} at the cotton site.

Figures 4 (vineyard) and 5 (cotton) are the ozone eddy covariance results for the model without a mesophyll resistance. Gaps in the diurnal cycle between 04.00h and 07.00h were produced by the elimination of dew events from the observations. The values of g_n used for this analysis were taken from the ET eddy covariance result, because, we found no statistically significant differences in the model performance or in the values of the parameters whether g_n was fixed at its present value or allowed to vary when fitting the data. Consequently, both the ozone and ET eddy covariance data are consistent with the interpretation that the vineyard canopy shows a significantly greater night-time stomatal conductance than does the cotton canopy. Since r_b is not limiting ozone fluxes in these canopies these plots of g_{surf} are essentially equivalent to the plots of g_c (Figs 2 and 3) except that

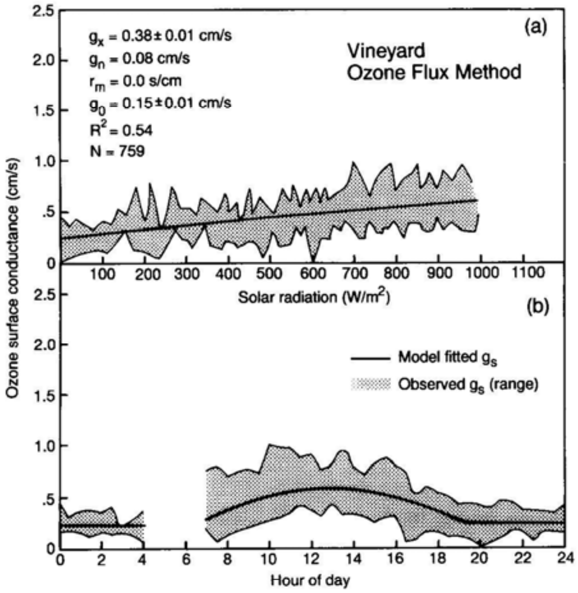

Fig. 4 Range of inferred and modelled vineyard ozone surface conductances from ozone eddy covariance data as a function of solar radiation (a) and time of day (b).

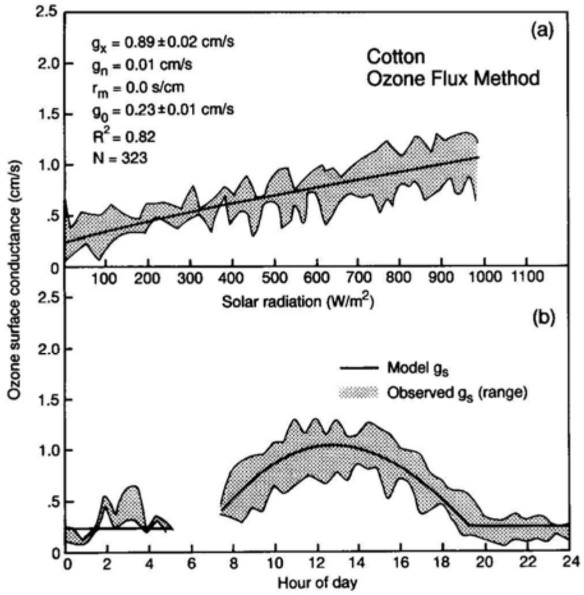

Fig. 5 Range of inferred and modelled cotton ozone surface conductances from ozone eddy covariance data as a function of solar radiation (a) and time of day (b).

they are adjusted upward by g_0. Nevertheless, Figs 4 and 5, unlike the earlier ET results, show significant differences in ozone uptake between these two canopies during the day. The cotton canopy conductance to ozone, g_x, is more than twice that of the grape canopy.

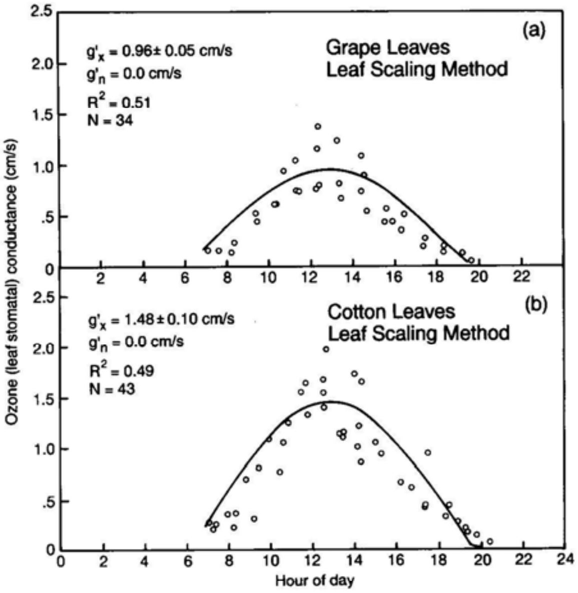

Fig. 6 Observed and modelled leaf stomatal conductance as a function of time of day at the vineyard site (a) and at the cotton site (b).

Figure 6 shows the diurnal course of the leaf-level stomatal conductance and the model fit to that data at both the vineyard and cotton sites. In these figures g'_n corresponds to the night-time pathway for transpiration and was assigned a value of 0.0 because the daytime gas exchange data did not suggest significant night-time transpiration. Although this contradicts $g'_n \neq 0.0$ from the eddy covariance ET analysis (Figs 2 and 3) and the night-time ET fluxes discussed earlier, model performance did not differ significantly between the two cases.

Table 2 lists the parameter values and their associated standard error of the estimates for the ozone eddy covariance model without a mesophyll resistance, for the dual-source ET model with and without night-time transpiration and for the leaf-to-canopy scaling model without the night-time transpiration pathway.

Figure 7 shows the uncertainty estimates in g_x that result from uncertainties in model parameters. For this evaluation of the models' uncertainties all results are presented in a two-tiered manner.

For the eddy covariance ET model we independently computed the variations in g_c (and/or g_x) that resulted from (i) a ± 3 °C change in the (model-computed) foliage temperatures and (ii) by allowing g_n to be zero.

For the leaf-to-canopy scaling model we first independently varied τ_{leaf} and ρ_{leaf} by ± 0.02, ρ_{soil} between 0.05 and 0.20, the measured values of LAI by ± 20%, the leaf angle parameter (x; Campbell 1990) between 0.5 (erectophile leaves) and 5.0 (planophile leaves), g'_x by ±

Table 2 Parameter values (± SE of the estimate) for canopy ozone uptake by vineyard and cotton fields during the CODE. Values without a standard error of the estimate were not directly determined by the least-squares regression technique.

	Vineyard	Cotton	Comments
g_x (s cm^{-1})	0.38 ± 0.01	0.89 ± 0.02	Eddy covariance
g_n (s cm^{-1})	0.08	0.01	ozone analysis
r_m (s cm^{-1})	0.0	0.0	without r_m
g_0 (s cm^{-1})	0.15 ± 0.01	0.23 ± 0.01	
R^2	0.54	0.82	
g_x (s cm^{-1})	0.51 ± 0.01	0.55 ± 0.02	Eddy covariance ET analysis
g_n (s cm^{-1})	0.08 ± 0.01	0.01 ± 0.01	Dual-source model with g_n
R^2	0.71	0.61	
g_x (s cm^{-1})	0.62 ± 0.01	0.56 ± 0.01	Eddy covariance ET analysis
g_n (s cm^{-1})	0.0	0.0	Dual-source model without g_n
R^2	0.67	0.61	
g_x (s cm^{-1})	0.59 ± 0.001	0.82 ± 0.002	Leaf-to-canopy scaling
g_n (s cm^{-1})	0.0	0.0	analysis without g_n
R^2	0.996	0.972	$M(L) = 0.65 + 0.35e^{-\kappa L}$

one standard error of the estimate and $M(L)$ between 1.0 (maximum limit) and $\exp(-\kappa L)$ (minimum limit) as discussed by Johnson *et al.* (1989). We then combined these variations simultaneously in such a way as to maximize the range of the variation in g_c. The uncertainties associated with the radiative transfer model are a result of (i) variations in $M(L)$ alone and (ii) variations in $M(L)$ combined with variations in all other parameters. (It is important to point out here that although other methods or models could have been used for $M(L)$ (e.g. Hirose & Werger 1987; Gutschick & Weigel 1988; Sellers *et al.* 1992), none of these other approaches yielded results outside the range of uncertainty in the present analysis.)

For the uncertainty in g_x associated with the ozone eddy covariance model we include (i) ± 40% errors resulting from random uncorrelated errors in the data and in the parameter values used to derive g_c (Massman *et al.* 1994) and (ii) ± 10% error associated with possible NO emissions from soils (Gao *et al.* 1991). Massman *et al.* (1994) showed that the expected error for grape vineyard is ± 28% and that it is ± 39% for cotton. For the present study we assumed the worse case and used ± 40% for the random errors for both canopies. Although we use a nominal ± 10% variation for the NO effects in Fig. 7, we suggest below that when NO soil emissions are very large g_x values can be affected much more significantly than ± 10%.

Table 2 and Fig. 7 suggest that canopy stomatal uptake of ozone does not scale to transpiration. The vineyard value of g_x from the ozone deposition data is about 25% less than the dual source ET model estimate and it is 36% less than the leaf to canopy scaling estimate. The ozone deposition data at the cotton site yields an estimate of g_x that is 9% higher than the leaf to canopy scaling value but more than 60% greater than the dual source ET estimate.

Figure 7 indicates that estimates of g_x derived from the model used to scale-up from the leaf to the canopy can be reconciled to either of the dual-source model estimates, but not to both simultaneously. In other words, in the leaf scaling approach there is enough uncertainty in the present parameterization of $M(L)$ and the nominal values of the soil albedo, the PAR leaf transmittance and reflectance, the leaf angle distribution function and the measured LAI to account for either a positive or negative bias in g_x. We cannot therefore use the leaf-scaling model to elucidate the cause (or causes) of the large difference between the eddy covariance based models of g_x for the two sites. Consequently, these results suggest that either one or more of the dual source model assumptions is false or that there are significant biases in either the cotton ET data set or the corresponding ozone data or both.

Although, it is possible that the eddy covariance data sets are biased, it is unlikely for two reasons. First, we have confirming evidence from independent aircraft eddy covariance data that ozone fluxes over cotton are relatively large (Massman *et al.* 1995); second, the cotton and vineyard eddy covariance ET and surface energy balance data sets are consistent with one another.

We conclude that the measured fluxes are unbiased and that either the eddy covariance ET-based modelling estimates of g_x are reasonably accurate and the ozone analysis is somehow in error, or the dual-source ET model fails to partition fluxes correctly. Available data are not sufficient to resolve this issue directly. But we can test several of the dual-source ET and ozone models' assumptions using a detailed sensitivity analysis.

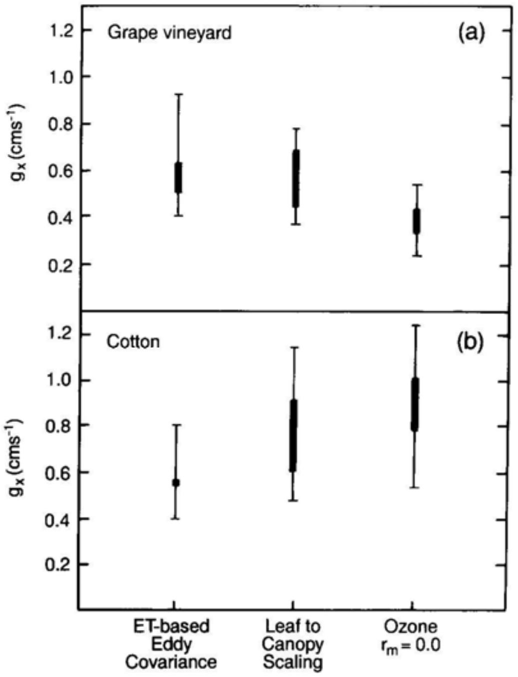

Fig. 7 Uncertainties in estimates of canopy conductance to ozone uptake for the vineyard site (a) and for the cotton site (b). For the eddy covariance ozone estimates the thick bar results from a ± 10% variation in the observed deposition velocity (presumed to result from photochemical effects), while the thin bars represent the ± 40% uncertainty in g_x based on the expected error analysis of Massman *et al.* (1994). For the eddy covariance ET estimate the thick bar gives the range of g_x values with and without a canopy night-time pathway for transpiration, while the thin bars give the variation in g_x resulting from a ± 3 °C variation in the computed canopy temperature. For the leaf-to-canopy scaling approach the thick bar results from uncertainties in $M(L)$ only and the thin bars result from the combined uncertainties in $M(L)$, the soil albedo, the leaf PAR transmittance and reflectance, the canopy LAI, the canopy leaf angle distribution and the standard error of the estimate for g'_x from the leaf measurements.

3.2 Uncertainties in the dual-source models assumption

3.2.1 Possible mesophyll resistances to ozone uptake. Including a canopy mesophyll resistance, r_m, in the ozone deposition model increased the g_x estimates for both canopies. The optimal value for r_m at the vineyard site was found to be 0.43 ± 0.30 (s cm^{-1}) and the corresponding value for g_x was 0.49 ± 0.09 (cm s^{-1}). For cotton they were r_m = 0.13 ± 0.11 (s cm^{-1}) and g_x = 1.00 ± 0.10 (cm s^{-1}). Changes in the other model parameters or the R^2 values were not significantly different from those shown in Table 2 for the deposition model without r_m. For the vineyard the introduction of r_m into the ozone deposition model eliminated much of the discrepancy with the ET-based estimates. However, for the cotton canopy the discrepancy worsened.

It has been suggested that r_m is related to how fast ozone reacts within the plant tissue and how efficient plant detoxification systems are at eliminating ozone after it has passed through the stomata (Plöchl *et al.* 1993; Heath 1994). If this is true then r_m for the vineyard canopy could be indicating that the vineyard is experiencing some ozone-induced stress. A more detailed analysis of the leaf-level transpiration data has suggested that the vineyard site is in fact suffering greater stress than the cotton site (Grantz *et al.* 1995). This latter study does not cite a specific cause for the stress. Furthermore, as discussed earlier, the vineyard ET data suggest incomplete stomatal closure at night and significant night-time transpiration. Similar behaviour in at least three species of conifers has been shown to be the result of ozone exposure (Skärby *et al.* 1987; Barnes *et al.* 1990; van Hove & Bossen 1994). Finally, because ozone concentrations are chronically higher at the vineyard site than at the cotton site (Massman *et al.* 1994), the vineyard is exposed to much more ozone than is the cotton crop.

Although all evidence is largely indirect, we suggest that the vineyard mesophyll resistance is real and that it is symptomatic of chronic ozone stress. Nevertheless, r_m in general is highly uncertain and could be the result of other model weaknesses and/or deficiencies. In the case of the cotton canopy, r_m not only fails to explain any of the discrepancies associated with the dual source models, but in fact suggests that there may be processes that are completely missing from the ozone deposition model.

3.2.2 Failure to correctly partition ET data. Overestimation of soil evaporation could cause g_x to be underestimated. The present ET model partitioning suggests that 18% of total ET at the cotton site originates from the soil. This is much higher than estimated at the vineyard with the same model. We estimate an upper limit on g_x at the cotton site by eliminating soil evaporation. Then the dual-source ET model predicts g_x to be 0.68 (± 0.01) cm/s with negligible night-time transpiration. This value of g_x, which is the upper limit g_x can have that is consistent with the foliage temperature derived from the dual-source model, is still about 25% less than the value of 0.89 cm s^{-1} derived from the ozone eddy covariance data. Even the worst case scenario (which is that the foliage temperature as estimated by the ET partitioning model is overestimated by 3 °C) yields a value of g_x of 0.8 cm s^{-1} (and negligible g_n) which again is below the lowest ozone eddy covariance estimate.

We can only conclude that either the present eddy covariance ET-based estimates of g_x are reasonably accurate and that the ozone analysis is in error or that the dual-source ET model has failed to partition total ET and/or estimate foliage temperature correctly. We feel that the present estimate for g_x from the ozone model is too high at the cotton site. Because the ozone fluxes themselves appear to be accurate, it would seem that there maybe other processes that are correlated with R_s which contribute to high ozone fluxes at the level of measurement or destroy the ozone before it can enter the stomata.

3.2.3 Possible NO effects. The presence of NO is known to affect ozone fluxes and is not explicitly included in the ozone deposition model. The ± 10% variation in v_d due to soil NO emissions was estimated from the model results of Gao *et al.* (1991) who used a maximum soil NO emission rate of about 25 ng-N m^{-2} s^{-1}. However, the model of Williams *et al.* (1992) suggest that for the heavily fertilized crops, like cotton in the San Joaquin Valley, NO emissions are about to 40–100 ng-N m^{-2} s^{-1} during most of the daylight hours. We arrived at this estimate of the flux by using the soil temperatures at the cotton site during the CODE and using the fertilization coefficient $A = 9$ from the model of Williams *et al.* (1992). Consequently, the influence of soil NO emissions at the cotton site may exceed ± 10%. Using the same algorithm to estimate NO emissions from the vineyard site yields about 18–44 ng-N m^{-2} s^{-1}. (Here we use the observed soil temperatures at the vineyard site & $A = 4$ from the model of Williams *et al.* (1992) because the vineyard is typically fertilized with no more than 50 kg ha^{-1} of fertilizer but cotton is typically fertilized with about 250 kg ha^{-1}). Such a significant difference in NO emissions may explain why the ozone conductances agreed more closely with their ET-based counterparts at the vineyard site than at the cotton site.

By partitioning the observed ozone flux into a component associated with dry deposition onto plant and soil surfaces and another component associated with chemical destruction by an opposing NO flux, we can quantitatively evaluate the influence that soil NO emissions have upon the estimates of g_x, g_n and g_0 of the ozone deposition model. The dry deposition component of the ozone flux can be used to evaluate the model parameters once the NO titration component of the ozone flux has been removed. We partition to observed ozone flux in the following manner.

Assuming steady-state conditions, the following flux difference conservation equation is valid for NO–NO_2–O_3 photochemically driven reactions between the canopy height (h) and the level of flux measurements (z_m, the reference level of Fig. 1) (Fitzjarrald & Lenschow 1983):

$$\partial(F_O - F_{NO})/\partial z = 0\ , \tag{6}$$

where F_O is the ozone flux and F_{NO} is the NO flux. (Henceforth we are assuming that F_{NO} is directed upward from the soil and that F_O is directed downward and that all flux units are assumed to be ppmV-m s^{-1}.) Integrating between z_m and h yields:

$$F_O(h) = F_O(z_m) + F_{NO}(h) - F_{NO}(z_m)\ . \tag{7}$$

We use this equation to partitioning the ozone flux, $F_O(h)$ into a deposition component, $F_{O,dep}$, and an NO titration component, $F_{O,titr}$; i.e. $F_O(h) = F_{O,dep} + F_{O,titr}$. We also parameterize $F_{NO}(h)$ and $F_{NO}(z_m)$ in terms of the soil NO flux, $F_{NO}(0)$. First we assume that $F_{NO}(z_m) = q_1F_{NO}(0)$, where q_1 is that fraction of $F_{NO}(0)$ that reaches the measurement height z_m. Next we assume that $F_{NO}(0)$ can be partitioned into three components: i.e. $F_{NO}(0) = F_{NO}(h) + F_{NO,dep} + F_{NO,titr}$. Here $F_{NO}(h)$ is the portion of $F_{NO}(0)$ reaching the canopy top, $F_{NO,dep}$ is the portion of $F_{NO}(0)$ taken up by the canopy and $F_{NO,titr}$ is the portion of $F_{NO}(0)$ that is destroyed by the opposing ozone flux within the canopy air space between the soil surface and the canopy top. (Note that $F_{NO,titr} + F_{O,titr} = 0$.) Combining these last four equations with (7) and solving for $F_{O,dep}$ yields:

$$F_{O,dep} = F_O(z_m) + (1\text{-}q_1)F_{NO}(0) - F_{NO,dep}\ . \tag{8}$$

We next set $q_1 = 0.25$. That is we assume that 25% of the soil NO flux reaches the measurement height. This is in reasonable agreement with the observations of Bakwin *et al.* (1990) who found that $q_1 = 0.40$ above the Amazon forest and the model calculations of Jacob and Wofsy (1990) who found that $q_1 \leq 0.20$ for the same Amazon forest experiment. From Williams *et al.* (1992) we take $F_{NO}(0) = 0.016\exp(0.071T_s)$ (ppmV-m s^{-1}) as appropriate for heavily fertilized soils. (Here T_s is the measured soil temperature in °C). To estimate $F_{NO,dep}$ we assume: (i) an NO deposition velocity (per leaf surface area) of 0.3 mm s^{-1} (e.g. Law & Mansfield 1982; Saxe 1986); (ii) LAI = 2 for the cotton canopy; and (iii) that the within-canopy NO concentration is 10 ppbV. [Pederson *et al.* (1995) report that ambient NO concentrations near the cotton site as ≤ 3 ppbV most of the time. Consequently, we assume that the within-canopy NO concentration will be significantly higher than ambient because the within-canopy air space is much closer to the soil surface, which for this exercise is taken to be a strong NO emitter.] Therefore, we estimate that $F_{NO,dep} = 0.006$ ppmV-m s^{-1}.

After correcting the observed ozone flux for possible NO effects using this simple model, g_x and g_0 were recomputed with the ozone deposition model and yielded $g_x = 0.68 \pm 0.02$ (cm s^{-1}) and $g_0 = 0.01 \pm 0.01$ (cm s^{-1}). (We fit only these two parameters and not other conductances mainly for illustrative purposes.) We conclude that NO effects can have a dramatic effect on estimates of canopy stomatal conductance, g_x, as well as g_0 when soil NO fluxes are large. These new estimates of g_x now differ from the ET values for cotton by less than 24%. While these arguments are not to be taken as conclusive proof that soil emissions at the cotton site are responsible for the lack of scaling between the ozone and ET-based conductances, they are nevertheless strongly supportive of this possibility.

3.2.4 Results from including a detailed g_0 *model in the ozone deposition model.* All prior results for the ozone model have assumed that g_0 = constant, but in general this assumption is probably not valid. For example, because g_0 is composed of all nontranspiring portions of the surface (plant epidermis and cuticle, soil and the within-canopy turbulent transfer) it is likely to vary with soil moisture and soil microbial activity which can influence r_i and atmospheric turbulence which can influence r_u and r_b. It is therefore important to evaluate how lumping these processes into one constant may influence the previous results. However, this evaluation is neither straightforward nor simple for three reasons. First, the K-theory description of the transfer processes is weakest in the understorey region of the canopy. This is particularly true for r_u. In general r_u is not controlled by understorey gradients, but rather by large-scale eddies above the canopy that periodically flush the understorey region (Denmead & Bradley 1985). Second, as previously shown, soil NO emissions can influence the numerical estimates of g_0 and consequently its constituent parts as well. Third, in order to decompose g_0 into its constituent parts it is necessary to parameterize r_u, r_i or r_{cut} in terms of a measured variable. This increases the number of free parameters used in the diagnostic model, and thereby increases the standard errors of all fitting parameters.

We decomposed g_0 by parameterizing the within-canopy conductance, g_u ($= 1/r_u$) in terms of measured wind speed above the canopy (namely $g_u = g_1 + g_2u$; where g_1 and g_2 are fitting parameters). (We also used the measured friction velocity and the Monin–Obuhkov stability parameter, z/L, in place of u and found no difference in the results.) Next we regressed the ozone data against the dual-source model using all free parameters. Model performance with g_0 = constant was not statistically different from that associated with the more complex model of g_0. Consequently we fixed g_x and g_n to the values given in Table 2 and refit all the remaining model parameters.

In this manner we estimated that the intrinsic soil resistance r_i is about 0.73 s cm^{-1} at the vineyard site and 0.90 cm^{-1} at the cotton site. The total plant epidermal and cuticular resistance (r_{cut}) was estimated to be about 56 s cm^{-1} at the vineyard site and greater than 1000 cm^{-1} at the cotton site; while the within-canopy conductance ($g_u = 1/r_u$) was estimated to vary between 0.12 and 0.18 cm s^{-1} at the grape vineyard and between 0.14 and 0.43 cm s^{-1} at the cotton site. These estimates are sufficiently uncertain that the r_{cut} estimate of 56 s cm^{-1} at the vineyard site is not significantly different from the r_{cut} value of 1000 s cm^{-1} estimated for the cotton site.

Nevertheless, the intrinsic soil resistances are similar to values found in previous studies (Massman 1993; Van Pul & Jacobs 1994) and the cuticular resistances are large, as expected. However, comparing the ozone within-canopy conductances to the ET-based within-canopy conductances suggests some differences. (See Massman 1992 for a discussion of the methodology for estimating the ET-based within-canopy conductances). The estimates for g_u from the ET-based model yields values for both canopies that are concentrated between 0.0 and 0.30 cm s^{-1}. On the average these ET-based values are slightly greater than the ozone-based estimates at the vineyard site and slightly below the ozone-based estimates at the cotton site. However, the uncertainties in all the estimates of g_u are large so that these discrepancies may not be too important. Furthermore, as shown in the previous section, possible NO effects can influence the numerical values of g_0 which only adds to the already large uncertainties associated with estimates of g_0 from the ozone deposition model.

3.2.5 Lack of energy balance closure in the ET model. The measured surface energy fluxes do not balance at either CODE site. In general (R_n–G) exceeds ($\lambda E + H$) by several percent (Pederson *et al.* 1995). Because the greatest uncertainty in the energy balance is associated with R_n and G (Pederson *et al.* 1995) we evaluated the potential contribution from the lack of energy closure by reducing (R_n–G) in the ET model by 25% and recomputing all conductances. Results indicate that the ET model's estimates of g_x or g_n were not significantly affected at either site. However, lack of closure could affect estimates of r_u. Since r_u is fairly uncertain anyway (see previous section, 3.2.4) we conclude that the lack of energy balance does not compromise any previous conclusions.

3.2.6 Canopy boundary layer resistance. The canopy boundary layer resistance, r_b, is quite uncertain because observed values of kB^{-1} in general are extremely variable. The ± 40% uncertainty associated with the ozone eddy covariance value of g_x quoted earlier results in part from an estimated ± 100% uncertainty in kB^{-1} (Massman *et al.* 1994). However, it is still possible that the formulation for r_b significantly underestimates the actual value. We performed a sensitivity analysis by recomputing g_x after increasing r_b by a factor 5. This was done for both the ozone and the ET eddy covariance models. In general we found that g_x increased in all cases. But this larger value of r_b only increased the differences between g_x values inferred from the ET and ozone eddy covariance data sets. We conclude either that possible uncertainties in r_b are not sufficient to explain the differences in g_x outlined in Table 2 and Fig. 7 or that r_b for heat, water vapour and ozone associated with the same canopy differ from one another much more than can be accounted for by present models of kB^{-1}.

4 Conclusions

The three methods outlined in this study provide estimates of canopy stomatal conductance that agree to within about 60% or better and that they (either separately or together) can yield a reasonably reliable partitioning of water vapour and ozone fluxes between transpiring and nontranspiring portions of a surface. But, as the present study indicates, they would appear to be more useful (at least diagnostically) when employed together.

For example, for the grape canopy both the dual source ET model and the leaf-to-canopy scaling model yielded similar estimates for the canopy stomatal conductance to ozone uptake and within 36% the ozone deposition model agreed with the other two approaches. Adding a mesophyll resistance in the dual source ozone deposition model yielded an estimate of the canopy stomatal conductance to ozone, g_x, within 20% of the other two models. We interpret the mesophyll resistance at the vineyard site as an indication of ozone-induced stress.

For the cotton canopy, the ET dual source model yielded a value for the canopy stomatal conductance (g_x) of about 0.55 cm s^{-1}, while the leaf-to-canopy scaling model gave a value of about 0.82 cm s^{-1}. However, the ozone deposition model suggested that it was about 0.89 cm s^{-1} which was higher than either of the other estimates of canopy stomatal conductance. A model sensitivity/uncertainty analysis suggested that at the cotton site ET was incorrectly partitioned between the soil and plant components and that the observed ozone fluxes were strongly influenced by soil NO emissions. Because the soil evaporation rate was overestimated the canopy transpiration rate was underestimated, resulting in a value for the canopy stomatal conductance that may have been too low. In contrast the ozone dual-source model without correction for NO titration resulted in values for the canopy stomatal conductance that may have been too high. After correcting each of the eddy covariance dual-source models their associated canopy stomatal conductances were in nearly perfect agreement with each other and both agreed with the leaf to canopy scaling model to within about 20%.

In addition to these general conclusions, the uncertainty/sensitivity analysis included in the previous section of this study allows two other important conclusions to be drawn. First, although scaling conductance from leaf to canopy using (4) is fairly sensitive to $M(L)$ and to canopy and soil radiative properties, we conclude, as have others (e.g. Baldocchi 1989), that it provides a reasonably accurate estimate of canopy conductance. Nevertheless, the sensitivity/uncertainty analysis also indicated that accurate evaluations of $M(L)$ and of the plant and soil radiative properties are required for obtaining accurate estimates of canopy conductances from leaf-level conductances. Second, although the dual source models in general can be used diagnostically to study understorey and soil conductances, all conclusions reached concerning these parameters were highly uncertain. Specifically numerical values of these conductances are quite sensitive to lack of energy balance closure, possible NO effects and almost certainly to the inability of first-order closure methods to adequately describe understorey exchange processes.

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References

Amiro BD, Gillespie TJ, Thurtell GW (1984) Injury response of *Phaseolus Vulgaris* to ozone flux density. *Atmospheric Environment*, **18**, 1207–1215.

Amthor JS, Goulden ML, Munger JW, Wofsy SC (1994) Testing a mechanistic model of forest-canopy mass and energy exchange using eddy correlation: carbon dioxide and ozone uptake by a mixed oak-maple stand. *Australian Journal of Plant Physiology*, **21**, 623–651.

Bakwin PS, Wofsy SC, Fan S-M, Keller M, Trumbore SE, DaCosta JM (1990) Emission of nitric oxide (NO) from tropical forest soils and exchange of NO between the forest canopy and atmospheric boundary layers. *Journal of Geophysical Research*, **95** (16), 755–16, 764.

Baldocchi DD (1989) Canopy-atmosphere water vapour exchange: can we scale from a leaf to a canopy? In: *Estimation of Areal Evapotranspiration* (eds Block TA, Spittlehouse DL, Novak MD, Price DT), pp. 21–41. IAHS Press, Wallingford.

Baldocchi D (1992) A Langrangian random-walk model for simulating water vapor, CO_2 and sensible heat flux densities and scalar profiles over and within a soybean canopy. *Boundary-Layer Meteorology*, **61**, 113–144.

Barnes JD, Eamers D, Brown KA (1990) The influence of ozone, acid mist and soil nutrient status in Norway spruce [*Picea abies* (L.) Karst.] I. Plant–water relations. *New Phytologist*, **114**, 713–720.

Campbell GS (1977) *An Introduction to Environmental Biophysics.* Springer-Verlag, New York, 159 pp.

Campbell GS (1986) Extinction coefficients for radiation in plant canopies calculated using an ellipsoidal inclination angle distribution function. *Agriculture and Forest Meteorology*, **36**, 317–321.

Campbell GS (1990) Derivation of an angle density function for canopies with ellipsoidal leaf angle distributions. *Agriculture and Forest Meteorology*, **49**, 173–176.

Choudhury BJ (1987) Relationships between vegetation indices, radiation absorption, and net photosynthesis evaluated by a sensitivity analysis. *Remote Sensing Environment*, **22**, 209–233.

Deardorff JW (1978) Closure of second- and third-moment rate equations for diffusion in homogeneous turbulence. *Physics of Fluids*, **21**, 525–530.

Delany AC, Fitzjerrald DR, Lenschow DH, Pearson JR R, Wendel GJ, Woodruff B (1986) Direct measurements of nitrogen oxides and ozone fluxes over grassland. *Journal of Atmospheric Chemistry*, **4**, 429–444.

Denmead OT, Bradley EF (1985) Flux-gradient relationships in a forest canopy. In: *The Forest–Atmosphere Interaction* (eds Hutchinson BA, Hicks BB), pp. 421–49. Reidel, Dordrecht.

Dickinson RE (1983) Land surface processes and climate-surface albedos and energy balance. *Advances in Geophysics*, **25**, 305–353.

Droppo Jr JG (1985) Concurrent measurements of ozone dry deposition using eddy correlation and profile flux methods. *Journal of Geophysical Research*, **90**, 2111–2118.

Finnigan JJ, Raupach MR (1987) Transfer processes in plant canopies in relation to stomatal characteristics. In: *Stomatal Function* (eds Zeiger E, Farquhar GD, Cowan IR), pp. 385–429. Stanford University Press, Stanford.

Fitzjarrald DR, Lenschow DH (1983) Mean concentration and flux profiles for chemically reactive species in the atmospheric surface layer. *Atmospheric Environment*, **17**, 2505–2512.

Fuentes JD, Gillespie TJ, den Hartog J, Neumann HH (1992) Ozone deposition onto a deciduous forest during wet and dry condition. *Agricultural and Forest Meteorology*, **62**, 1–18.

Gao W (1994) Atmosphere-biosphere exchange flux of carbon dioxide in a tallgrass prairie modeled with satellite spectral data. *Journal of Geophysical Research*, **99**, 1317–1327.

Gao W, Wesely ML, Lee IY (1991) A numerical study of the effects of air chemistry on fluxes of NO, NO_2, and O_3 near the surface. *Journal of Geophysical Research*, **96**, 18761–18769.

Garratt JR, Hicks BB (1973) Momentum, heat and water vapor transfer to and from natural and artificial surfaces. Quarterly *Journal of the Royal Meteorological Society*, **99**, 680–687.

Grantz DA, Meinzer FC (1990) Stomatal response to humidity in a sugar cane field: simultaneous porometric and micrometeorological measurements. *Plant, Cell and Environment*, **13**, 27–37.

Grantz DA, Zhang XJ, Massman WJ, den Hartog H, Neumann HH, Pederson JR (1995) Effects of stomatal conductance and surface wetness on ozone deposition in field-grown grapes. *Atmospheric Environment* (in press).

Grimm AG, Fuhrer J (1992) The response of spring wheat (*Triticum aestivum* L.) to ozone at higher elevations, I. Measurement of ozone and carbon dioxide fluxes in open-top field chambers. *New Phytologist*, **121**, 201–210.

Gutschick VP (1991) Joining leaf photosynthesis models and canopy photon-ransport models. In: *Photon-Vegetation Interactions* (eds Myneni RB, Ross J), pp. 501–535. Springer, Berlin.

Gutschick VP, Wiegel FW (1988) Optimizing the canopy photosynthetic rate by patterns of investment in specific leaf mass. *American Naturalist*, **132**, 67–86.

Heath RL (1994) Possible mechanisms for the inhibition of photosynthesis by ozone. *Photosynthesis Research*, **39**, 439–451.

Hirose T, Werger MJA (1987) Maximizing daily canopy photosynthesis with respect to leaf nitrogen allocation pattern in the canopy. *Oecologia*, **75**, 520–526.

Jacob DJ, Wofsy SC (1990) Budgets of reactive nitrogen, hydrocarbons, and ozone over the Amazon forest during the wet season. *Journal of Geophysical Research*, **95**, 16737–16754.

Jacob DJ, Fan S-M, Wofsy SC, Spiro PA, Bakwin PS (1992) Deposition of ozone to tundra. *Journal of Geophysical Research*, **97**, 16473–16479.

Johnson IR, Parsons AJ, Ludlow MM (1989) Modelling photosynthesis in monocultures and mixtures. *Australian Journal of Plant Physiology*, **16**, 501–516.

Kustas WP, Choudhury BJ, Moran MS, Reginato RJ, Jackson RD, Gay LW, Weaver HL (1989) Determination of sensible heat flux over sparse canopy using thermal infrared data. *Agricultural and Forest Meteorology*, **44**, 197–216.

Laisk A, Kull O, Moldau H (1989) Ozone concentration in leaf intercellular air spaces is close to zero. *Plant Physiology*, **90**, 1163–1167.

Law RM, Mansfield TA (1982) Oxides of nitrogen and the greenhouse atmosphere. In: *Effects of Gaseous Air Pollution in Agriculture and Horticulture* (eds Unsworth MH, Ormrod DP), pp. 93–112. Butterworth Scientific, London.

Lefohn AS (Ed) (1992) *Surface Layer Ozone Exposures and their Effects on Vegetation.* Lewis, Chelsea, 366 pp.

Leuning R, Unsworth MH, Neumann HN, King KM (1979) Ozone fluxes to tobacco and soil under field conditions. *Atmospheric Environment*, **13**, 1155–1163.

Massman WJ (1987) Heat transfer to and from vegetated surfaces: an analytical method for bulk exchange coefficients. *Boundary-Layer Meteorology*, **49**, 295–307.

Massman WJ (1992) A surface energy balance method for partitioning evapotranspiration data into plant and soil components for a surface with partial canopy cover. *Water Resources Research*, **28**, 1723–1732.

Massman WJ (1993) Partitioning ozone fluxes to sparse grass and soil and the inferred resistances to dry deposition. *Atmospheric Environment*, **27 A**, 167–174.

Massman WJ, Ham JR (1994) An evaluation of a surface energy balance method for partitioning ET data into plant and soil components for a surface with partial canopy cover. *Agricultural and Forest Meteorology*, **67**, 253–267.

Massman WJ, Pederson J, Delany A, Grantz D, den Hartog G, Neumann HH, Oncley SP, Pearson Jr R, Shaw R (1994) An evaluation of the RADM surface module for ozone uptake at three sites in the San Joaquin Valley of California. *Journal of Geophysical Research*, **99**, 8281–8294.

Massman WJ, MacPherson JI, Delany A, den Hartog G, Neumann HH, Oncley SP, Pearson Jr R, Pederson J, Shaw R (1995) Surface conductances for ozone uptake derived from aircraft eddy correlation data. *Atmospheric Environment* (in press).

McCaughey JH, Iacobelli A (1994) Modelling stomatal conductance in northern deciduous forests, Chalk River, Ontario. *Canadian Journal of Forest Research*, **24**, 904–910.

Meyers T, Paw U KT (1986) Testing a higher order closure model for modelling airflow within and above plant canopies. *Boundary-Layer Meteorology*, **37**, 297–311.

Pederson JR, Massman WJ, Delaney A, den Hartog G, Desjardins R, Grantz DA, Mahrt LJ, MacPherson JI, Neumann HH, Oncley S, Pearson Jr R, Roth PR, Schuepp PH, Shaw RH (1995) California ozone deposition experiment, methods, results and opportunities. *Atmospheric Environment* (in press).

Plöchl M, Ramage P, Badeck F-W, Kohlhammer GH (1993) Modeling of deposition and detoxification of ozone in plant leaves. In: *Proceedings of EUROTRAC Symposium* (eds Borrell PM, Borrel P, Cvitas T, Seiler W), pp. 748–752. SPB Academic Publishing bv, The Hague.

Press WH, Teukolsky SA, Vetterling WT, Flannery BP (1992) *Numerical Recipes*, 2nd edn. Cambridge University Press, Cambridge, 963 pp.

Raupach MR (1989) Applying Langrangian fluid mechanics to infer scalar source distributions from concentration profiles in plant canopies. *Agricultural and Forest Meteorology*, **47**, 85–108.

Raupach MR, Finnigan JJ (1988) Single-layer models of evaporation from plant canopies are incorrect but useful, whereas multilayer models are correct but useless: discuss. *Australian Journal of Plant Physiology*, **15**, 705–716.

Raupach MR (1988) Canopy transport processes. In: *Flow and Transport in the Natural Environment: Advances and Applications* (eds Steffan WL, Denmead AD), pp. 95–127. Springer, Berlin.

Raupach MR (1987) A Langrangian analysis of scalar transfer in vegetation canopies. *Quarterly Journal of the Royal Meteorological Society*, **113**, 107–120.

Reich PB (1987) Quantifying plant response to ozone: a unifying theory. *Tree Physiology*, **3**, 63–91.

Saxe H (1986) Stomatal-dependent and stomatal-independent uptake of NO_x. *New Phytologist*, **103**, 199–205.

Sellers PJ (1985) Canopy reflectance, photosynthesis and transpiration. *International Journal of Remote Sensing*, **6**, 1335–1372.

Sellers PJ, Berry JA, Collatz GJ, Field CB, Hall FG (1992) Canopy reflectance, photosynthesis, and transpiration. III. A reanalysis using improved leaf models and a new canopy integration scheme. *Remote Sensing Environment*, **42**, 187–216.

Skärby L, Troeng E, Boström C-Å (1987) Ozone uptake and effects on transpiration, net photosynthesis, and dark respiration in Scots Pine. *Forest Science*, **33**, 801–808.

Spitters CJT, Toussaint HAJM, Goudriaan J (1986) Separating the diffuse and direct component of global radiation and its implication for modeling canopy photosynthesis. *Agricultural Forest Meteorology*, **38**, 217–229.

Stanhill G (1976) Cotton. In: *Vegetation and the Atmosphere*, Vol. 2 *Case Studies* (ed. Monteith JL), pp. 121–150. Academic Press, New York.

Taylor GE Jr, Hanson PJ (1992) Forest trees and tropospheric ozone: role of canopy deposition and leaf uptake in developing exposure-response relationships. *Agriculture, Ecosystems and Environment*, **42**, 255–273.

Thom AD (1975) Momentum, mass and heat exchange. In: *Vegetation and the Atmosphere*, Vol. 1 *Principles* (ed. Monteith JL), pp. 57–109. Academic Press, New York.

Thompson AM (1992) The oxidizing capacity of the earth's atmosphere; probable past and future changes. *Science*, **256**, 1157–1165.

Thorne L, Hanson GP (1972) Species differences in rates of vegetal ozone adsorption. *Environmental Pollution*, **3**, 303–312.

Treschow M, Anderson FK (1989) *Plant Stress from Air Pollution*. John Wiley, New York, 283 pp.

Turco RP (1992) Atmospheric chemistry. In: *Climate System Modeling* (ed. Trenberth KE), 788 pp. Cambridge University Press, Cambridge.

van Hove LWA, Bossen ME (1994) Physiological effects of five months exposure to low concentrations of O_3 and NH_3 on Douglas Fir (*Pseudotsuga menziesii*). *Physiologia Plantarum*, **92**, 140–148.

VanPul WAJ, Jacobs AFG (1994) The conductance of a maize crop and the underlying soil to ozone under various environmental conditions. *Boundary-Layer Meteorology*, **69**, 83–99.

Watanabe T (1993) The bulk transfer coefficients over a vegetated surface based on k-theory and a 2nd-order closure model. *Journal of the Meteorological Society of Japan*, **71**, 33–42.

Wesely ML, Eastman JA, Cook DR, Hicks BB (1978) Daytime variation of ozone eddy fluxes to maize. *Boundary-Layer Meteorology*, **15**, 361–373.

Wesely ML, Eastman JA, Stedman DH, Yalvac ED (1982) An eddy-correlation measurement of NO_2 flux to vegetation and comparison to O_3 flux. *Atmospheric Environment*, **16**, 815–820.

Williams EJ, Guenther A, Fehsenfeld C (1992) An inventory of nitric oxide emissions from soils in the United States. *Journal of Geophysical Research*, **97**, 7511–7519.

Wilson JD (1989) Turbulent transport within plant canopies. In: *Estimation of Areal Evapotranspiration* (eds Black TA, Spittlehouse DL, Novak MD, Price DT), pp. 43–80. IAHS Press, Wallingford.

Wilson JD (1988) A second-order closure model for flow through vegetation. *Boundary-Layer Meteorology*, **42**, 371–392.

Wilson JD, Thurtell GW, Kidd GE (1981) Numerical simulation of particle trajectories in inhomogeneous turbulence, II: Systems with variable turbulent velocity scales. *Boundary-Layer Meteorology*, **21**, 423–441.

Wilson NR, Shaw RH (1977) A higher order closure model for canopy flow. *Journal of Applied Meteorology*, **16**, 497–1205.

Wong SC, Cowan IR, Farquhar GD (1979) Stomatal conductance correlates with phytosynthetic capacity. *Nature*, **282**, 424–426.