Ozone transport during the California Ozone Deposition Experiment

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Abstract. The high correlation between the canopy stomatal uptake and ozone deposition velocity is found to be strongly dominated by their diurnal variations. By averaging observed variables over the daytime periods to remove the correlations simply due to their individual diurnal variations, we found that the ozone deposition velocity is highly correlated with the buoyancy flux during the daytime. As canopy stomata are closed at night, the ozone deposition velocity is found to be related to the friction velocity. Interpretation of the derivation of the ozone deposition velocity, expressed in terms of the traditional three resistances, is reanalyzed to explain the role of the turbulence strength in the ozone deposition velocity. We find that the resistance $r_c$ is the dominant resistance for the ozone deposition, not only due to the ozone uptake through biophysical processes, but also due to its role in the turbulent ozone transport.

1. Introduction

Monin-Obukhov (M-O) similarity theory states that within the surface layer (or the inertial sublayer), stationary and horizontally homogeneous turbulent flux of a trace gas, and the vertical gradient of the mean gas concentration are related through a stability function, $\phi_s(z/L)$ [Monin and Obukhov, 1954]. Here $z$ is the observational height in the surface layer and $L = -(\theta_v u^3)/(k g w \theta_v^c)$ is the Obukhov length, where $\theta_v$ is the virtual potential temperature, $g$ is the gravitational constant, $w$ is the vertical velocity, $u^*$ is the friction velocity, and $w' \theta_v^c$ is the buoyancy flux in the surface layer [Garratt, 1992; Kaimal and Finnigan, 1994]. Based on M-O similarity theory, the turbulent flux can be obtained with known mean variables in the surface layer by vertically integrating the stability function, $\phi_s(z/L)$, leading to the bulk formula

$$F_c = CV(c_0 - c_z).$$  

Here $F_c$ is the turbulent flux of the trace gas, $C$ is the turbulent transfer coefficient based on the M-O stability function, expressed as

$$C = \frac{k u^*}{V \ln(z/z_c) - \Psi(z/L)}.$$  

$V$ is the mean wind speed, $c_z$ is the mean gas concentration observed at $z$, which is normally within the surface layer, $c_0$ is the gas concentration at a known height $z_c$, $u^*$ is the friction velocity at $z_c$, and $\Psi(z/L)$ is the vertical integral of $\phi_s$. Since $z_c$ is normally below the surface layer, where the M-O stability function is not valid, the gas concentration $c_0$ in (1) is actually the gas concentration extrapolated down to $z_c$ assuming the stability function is valid between $z$ and $z_c$. Therefore $c_0$ is the aerodynamic gas concentration and is not equal to the actual gas concentration at $z_c$ [Fleagle and Businger, 1980; Huband and Monteith, 1986; Norman and Becker, 1995; Mahrt, 1996; Sun et al., 1999]. Use of the aerodynamic gas concentration $c_0$ ensures the correct turbulent flux if the transfer coefficient $C$ is applied in (1). Relationship (1) must be applied in the surface layer above the roughness sublayer. In the roughness sublayer the flux-gradient relationship is not universal as in the surface layer [Raupach et al., 1980]. Variables within the roughness sublayer are horizontally inhomogeneous due to the influence of individual roughness elements [Fazu and Schwerdtfeger, 1989; Cellier and Brunet, 1992; Wieringa, 1993; Hopwood, 1996; Bosveld, 1997].

The turbulent transport of ozone in the surface layer is traditionally parameterized in terms of the ozone deposition velocity $v_d$, defined as

$$F_{O_3} = -v_d [O_3].$$  

Here $F_{O_3}$ is the turbulent ozone flux in the surface layer and $[O_3]$ is the mean ozone concentration at the observation height $z$. Numerous studies have focused on the relationship between the ozone deposition velocity and the physical capture of ozone by surfaces or chemical reactions of ozone over different types of canopy and ground surfaces [Wesely and Hicks, 1977; Garland and Derwent, 1979; Galbally and Roy, 1980; Lenschow et al., 1982; Baldocchi et al., 1987; Coe et al., 1995; Massman et al., 1995; Grantz et al., 1995]. The most common approach for the physical capture of ozone by plants is to assume that the ozone transport is analogous to water vapor transport through canopy stomata [Rich et al., 1970; Turner et al., 1974; Massman and Grantz, 1995]. Laboratory studies with individual leaves have indicated that the canopy efficiently removes ozone from the air through opened stomata [Rich et al., 1970]. As a result, the resistance of the stomatal uptake of ozone is commonly parameterized by measured stomatal resistance from individual leaves with assumed relationships between stomatal resistance and canopy resistance over large
areas. Chemical ozone removal is also investigated by Fitzjarraud and Lenschow [1983], Bakwin et al. [1990], Kramm et al. [1991], Hargreaves et al. [1992], Guo et al. [1995], Manger et al. [1996], and Kristensen et al. [1997].

In this study, we focus on the relative importance of turbulent transfer of ozone and the ozone surface removal mechanism to the ozone deposition velocity. The relationship between the ozone deposition velocity and all related variables is derived in section 2. The field data used in this study are described in section 3. The ozone deposition velocity and its correlation with turbulent fluxes are investigated separately for day and night in section 4. The conclusions are presented in section 5.

2. Ozone Deposition Velocity

2.1. Derivation

Following Wesely and Hicks [1977] and assuming that the ozone photochemical reaction can be neglected and the turbulent transfer of ozone is similar to that of heat, the ozone deposition velocity can be derived by relating the turbulent ozone transfer \((1; \text{ where } c = [\text{O}_3])\) to the turbulent heat transfer \((1; \text{ where } c = \theta)\). We have

\[
\frac{[\text{O}_3] - [\text{O}_3i]}{F_{O_3}} = \frac{\theta_0 - \theta_s}{w' \theta'} = -r_o + 1/\nu_d, \quad (4)
\]

where

\[
r_o = -[\text{O}_3i]/F_{O_3}, \quad (5)
\]

and \((3)\) is used in the derivation of \((4)\). Here \(\theta\) is the potential temperature and \(w' \theta'\) is the sensible heat flux. Substituting the turbulent heat transfer coefficient for \(C\) in \((2)\) into \((4)\), we have

\[
\frac{\theta_0 - \theta_s}{w' \theta'} = (\kappa u_*)^{-1} \left[ \ln (z/z_0) - \Psi_s \right]
\]

\[
= (\kappa u_*)^{-1} \left[ \ln (z/z_0) + \ln (z_0/z_h) - \Psi_s \right]
\]

\[
= (\kappa u_*)^{-1} \left[ \ln (z/z_0) - \Psi_s \right] + (\kappa u_*)^{-1} \ln (z_0/z_h)
\]

\[
= r_a + (\kappa u_*)^{-1} \kappa B^{-1}
\]

\[
= r_a + r_b, \quad (6)
\]

where

\[
r_a = (\kappa u_*)^{-1} \left[ \ln (z_0/z_h) - \Psi_s \right], \quad (7)
\]

\[
\kappa B^{-1} = \ln (z_0/z_h) = \kappa u_* r_b. \quad (8)
\]

Here \(B^{-1}\) is commonly called the sublayer-Stanton number [Owen and Thomson, 1963]; \(z_0\) is the roughness length for momentum, which is the height where the extrapolated wind following the M-O wind profile vanishes; and \(z_h\) in \((1)\), where \(c = \theta\) is the thermal roughness height for heat, which is the height where the extrapolated potential temperature equals the aerodynamic temperature \(\theta_a\). Owing to the assumed similarity between the ozone concentration and the potential temperature, \(z_h\) is also the height where the extrapolated ozone concentration equals the aerodynamic ozone \([\text{O}_3i]\). \(\Psi_h\) is the vertical integral of the stability function for heat \(\phi_h\). Substituting \((6)\) into \((4)\), we can write

\[
1/\nu_d = r_a + r_b + r_c. \quad (9)
\]

The above derivation indicates that the sum of the resistances \(r_a\) and \(r_b\) is equal to the resistance for the sensible heat transfer between \(z\) and \(z_h\) \((6)\), where \(r_a\) is the resistance for heat or ozone transfer from \(z\) to \(z_0\) and \(r_b\) is the resistance from \(z_0\) to \(z_h\) because the distance between \(z\) and \(z_0\) is much larger than that between \(z_0\) and \(z_h\). The resistance \(r_c\) can be negative if \(z_0\) is smaller than \(z_h\) \((8)\) [Verhoef et al., 1997]. The resistance \(r_c\) is the ratio of the aerodynamic ozone concentration to the turbulent flux of ozone in the surface layer. The three resistances are all related to the turbulent transfer in the surface layer, although \(z_0\) and \(z_h\) are in the roughness sublayer.

2.2. Interpretation of the Three Resistances

The ozone deposition velocity has been commonly considered as the ozone transport in three vertical layers: \(1\) transport by atmospheric turbulence between the observational level and the top of the canopy layer (actually the effective height \(z_h\) \((r_a)\); \(2\) mixing by atmospheric turbulence through the canopy layer and by molecular diffusion through the molecular sublayer of the leaf and ground surfaces \((r_b)\); and \(3\) physical capture or chemical reactions at the canopy and ground surfaces \((r_c)\). Based on the derivation of \((9)\), the interpretation of these three resistances can be further clarified. The connection between the resistances is demonstrated in this subsection.

2.2.1. Resistance \(r_a\) As shown in the derivation of \((9)\), the turbulent transfer of ozone is assumed to be analogous to that of heat, not that of momentum. Sometimes, \(r_a\) is estimated as \(r_{am} = V/\nu_w^2\) [Georgiadis et al., 1995; Coe et al., 1995; Hargreaves et al., 1992; Pilegaard et al., 1995], which is similar to \(r_a\) except \(\Psi_s\) in \((7)\) is replaced by \(\Psi_m\), the integral of the stability function for momentum. The turbulent transfer of heat and momentum is significantly different in the unstable boundary layer (more in section 4), although estimating \(r_a\) in terms of \(r_{am}\) greatly simplifies the calculation of the resistance \(r_a\). The value of the resistance \(r_{am}\) equals that of the resistance \(r_a\) only under neutral and stable conditions based on the stability functions for heat and momentum, although the physics involved in the two resistances are different.

2.2.2. Resistance \(r_b\) Although the distance between \(z_0\) and \(z_h\) could be the same order of magnitude as the depth of the molecular sublayer of leaf surfaces, \(r_b\) represents the resistance to the turbulent heat transfer in the surface layer across a distance between \(z_0\) and \(z_h\) as if the flux-gradient relationship were valid in the roughness sublayer. Within the canopy layer, the microclimate is substantially influenced by details of plant surfaces nearby. The flux-gradient relationship is sensitive to the exact horizontal location of measurements. Therefore the resistance \(r_b\) derived in section 2.1 is not directly related to the turbulent transfer or molecular diffusion across the molecular sublayer of the canopy surface.

The difference between the turbulent transfer of momentum and heat is traditionally parameterized by analogy between the kinematic viscosity and the thermal molecular diffusivity close to a smooth ground surface. The ratio of the two is the Prandtl number. Hypothetically assuming that the difference between the roughness length for momentum and the thermal roughness height is associated with the difference between molecular transfer of momentum and heat in the molecular sublayer close to the ground surface, then \(\kappa B^{-1}\) \((8)\) can be related to
the constant Prandtl number. In addition, the roughness Reynolds number, \( Re = u_z z / v \), where \( v \) is the air viscosity, is related to \( k B^{-1} \) to account for pressure form drag associated with bluff roughness elements [Owen and Thomson, 1963; Garrett and Hicks, 1973; Brutsaert, 1982].

In contrast to homogeneous surfaces with uniform surface temperature, heterogeneity of the surface temperature leads to variation of the turbulent transfer of heat, resulting in variation of the thermal roughness height (J. Sun, thermal and momentum roughness lengths, submitted to Boundary Layer Meteorology, 1999; hereinafter referred to as submitted paper). The turbulent momentum transfer is sensitive to physical variation of ground surfaces. The heat transfer, on the other hand, is sensitive to variations of the surface temperature caused by a variety of factors, such as solar angle, surface canopy structure, and cloudiness [Kustas et al., 1989; Kubota and Sugita, 1994; Sugita and Kubota, 1994; Qualls and Brutsaert, 1996; Mahrt et al., 1997; Qualls and Hopson, 1998]. In addition, efficiency of heat release depends on canopy structure [Sun and Mahrt, 1995a]. Natural swinging motions of tree branches can lead to more efficient ventilation and heat release compared to tree trunks. After each wind gust, the spatial distribution of the surface temperature changes. Since the variation of the thermal roughness height does not solely depend on the roughness length for momentum, \( k B^{-1} \) and thus \( r_p \), (8) are found to vary substantially over different surface conditions [Kustas et al., 1989; Sun and Mahrt, 1995b; Brutsaert and Sugita, 1996] and to vary with time of day due to variations of both \( z_0 \) and \( z_h \) (J. Sun, submitted paper, 1999).

Since the surface radiation temperature is usually the only surface temperature available in observations and numerical models, the aerodynamic temperature is sometimes replaced by the surface radiation temperature in the bulk formula. In this situation, \( z_h \) is the height where the M-O similarity temperature profile equals the surface radiation temperature [Sun et al., 1999]. Since the surface radiation temperature is not uniquely defined [Norman and Becker, 1995], \( z_h \) is sometimes chosen as the roughness length for momentum \( z_{0_m} \), which is easier to determine [Huband and Monteith, 1986; J. Sun, submitted paper, 1999]. Then the aerodynamic potential temperature is the air temperature at \( z_0 \), following the M-O temperature profile, and the resistance \( r_p \) in (9) is zero. Under this situation, the sum of the resistances \( r_p \) and \( r_h \) still represents the resistance for heat transfer, but between \( z \) and \( z_0 \) rather than between \( z \) and \( z_h \). In consequence, the aerodynamic ozone concentration ([O₃₀] in (5)) is the ozone concentration at \( z_0 \) instead of \( z_h \), and the value of the resistance \( r_p \) changes correspondingly. However, the fundamental physics for the derivation of the three resistances remains intact, i.e., the analogy between the ozone turbulent transfer and the turbulent heat transfer, and M-O similarity theory (more in section 2.2.3).

The derivation of (6) and (8) demonstrates that \( z_h \) is the height where the M-O temperature profile coincides with \( \theta_p \) and the flux-gradient relationship described by the temperature difference, \( \theta_p - \theta_a \), satisfies M-O similarity theory. In the literature, another definition of the roughness length for heat is also used [Sheppard, 1958; Kramm et al., 1995], where the thermal roughness height \( z_p \) is defined to be related to the molecular diffusion in the roughness sublayer. With this definition, the relationship between the Stanton number \( B^{-1} \) and \( z_p \) is different than that between \( B^{-1} \) and \( z_h \) in (8).

### 2.2.3. Resistance \( r_c \)

Since the difference between \([O₃₀]\) and \([O₃_a]\) is normally much smaller than either \([O₃₀]\) or \([O₃_a]\), the combination of (4) and (6) implies that the sum of \( r_p \) and \( r_c \) is a small difference between two larger terms, \( 1/w \) and \( r_c \). Therefore the ozone deposition velocity mainly depends on the resistance \( r_c \) in terms of magnitude, although there are some correlations between the sum of the resistances of \( r_p \) and \( r_h \), and the ozone deposition velocity. The large difference between \( r_c \) and the sum of \( r_p \) and \( r_h \) is also demonstrated by Wesely [1983] (more in section 4).

As demonstrated in the Introduction, \( z_c \) and \( c_o \) in (1) cannot be specified independently, since the two are constrained by M-O similarity theory. This result implies that the value of \( z_b \) influences both the values of \( r_c \) and \( r_p \), where \( r_c \) is associated with the aerodynamic ozone at \( z_b \), and \( r_p \) is connected to \( z_h \) by definition (8). In contrast, the resistance \( r_a \) can normally be estimated without ambiguity, since the roughness length for momentum is associated with the physical structure of the canopy [Brutsaert, 1982; J. Sun, submitted paper, 1999].

There is no doubt that the ozone removal at ground surfaces, in addition to photochemical ozone production [Leighton, 1961; Finlayson-Pitts and Pitts, 1986; Wayne, 1991; DeMuer et al., 1997], affects the ozone concentration in the surface layer, which in turn, affects the resistance \( r_c \) in (5). However, the ozone removal at ground surfaces cannot influence the strength of turbulent vertical motions, which partially determines the intensity of the downward transport of ozone. Therefore the resistance \( r_c \) should depend on both the strength of the turbulent transfer and all the ozone removal mechanisms (section 4). The influence of the turbulence in the surface layer is not confined to \( r_a \).

### 3. Data

The data used in this study were collected during the California Ozone Deposition Experiment (CODE) between the middle of July and the middle of August 1991 [Pederson et al., 1995], a total of 26 days. The CODE was conducted in San Joaquin Valley of California.

The weather was persistently sunny with similar wind patterns every day. A tower, equipped to measure micrometeorological variables and operated by the Atmospheric Environment Service of Canada, was located in a vineyard [den Hartog et al., 1992], which contained rows of grapes oriented in the east-west direction with short grass between the rows. The vines were about 1.7 m tall, and the distance between rows was about 3 m [den Hartog et al., 1992]. Air temperature was measured at 9.1 m, and wind speed at 10.8 m. Turbulence fluxes at 9.4 m were calculated by the eddy-correlation method and averaged over 30 min periods.

Local NO sources did not have much influence on ozone. The concentrations of NO and NO₂ were less than 2 and 10 ppb, respectively [Arcado, 1991]. Therefore ozone can be treated as a trace gas, and the analogy between the ozone and heat transport in section 2.1 is valid [Lenschow, 1982; Fitzjarald and Lenschow, 1983; Kristensen et al. 1997].

Leaf stomatal resistance was estimated using the measurements from a LiCor (LI-1600) steady state porometer (SSP806) by the Atmospheric Environment Service of Canada [den Hartog et al., 1992]. There were three sets of readings at 0900, 1300, and 1700 local standard time (LST) for most days. On July 16 and 26, hourly readings were taken from 0800 to 1900 LST. Leaf stomatal resistance was also estimated using...
the measurements from a transient, clamp-on gas exchange system [Gratz, 1992; Grantz et al., 1995]. The corresponding leaf stomatal resistances were only available for four days: July 12, 19, and 29 and August 5, from 0700 to 2000 LST. The leaf stomatal resistance from the two measurements compared well for the overlapping days, and the two data sets are combined into one for the entire field experiment. The canopy stomatal resistance is calculated as

\[ r_{\text{canopy}} = r_s / \text{LAI}. \] (10)

Here \( r_{\text{canopy}} \) is the canopy stomatal resistance, \( r_s \) is the leaf stomatal resistance, and LAI is the leaf area index. Using a LAI-2000 plant canopy analyzer, the LAI was measured as approximately 3.39 during the entire field experiment period [Grantz et al., 1995].

The resistance \( r_a \) defined in (7) is calculated by applying observed friction velocity with the roughness length for momentum derived from the bulk formula,

\[ u_* = C_d^{1/2} \frac{\kappa}{\text{z}_0}. \] (11)

where

\[ C_d^{1/2} = \frac{\kappa}{\ln \left( \frac{z_0}{z_0} \right) - \Psi(z/L) \right]}. \] (12)

Because of the variation of the surface radiation temperature and complexity of \( z_h \) (section 2.2.2), one approach is to assume that the thermal roughness height equals the roughness length for momentum. This assumption implies that the aerodynamic potential temperature \( \theta_a \) corresponds to the M-O potential temperature profile at the roughness length for momentum. Furthermore, the aerodynamic ozone concentration \([O_3]_0\) corresponds to the M-O ozone profile at \( z_0 \). With this assumption, the resistance \( r_a \) (8) is zero, and the resistance \( r_c \) can be calculated as the difference between \( 1/ \nu_d \) and \( r_s \) (9).

Following the approach described in section 2.2, another set of resistances are calculated as

\[ r_{am} = \frac{V}{U_*^2}, \] (13)

\[ r_{bm} = \frac{\kappa B^{-1}}{\kappa U_*^{-1}}, \] (14)

\[ r_{cm} = 1/ \nu_d - (r_{am} + r_{bm}). \] (15)

Here \( \kappa B^{-1} = 2.6 \) is used as done by Massman et al. [1994]. The implicit assumption of this approach is that the thermal roughness height is not equal to the roughness length for momentum; and the corresponding resistance \( r_{cm} \) is simply a residual resistance such that the sum of \( r_{am}, r_{bm}, \) and \( r_{cm} \) balances the total ozone resistance \( 1/ \nu_d \) (15). The subscript \( m \) in (13)-(15) is used to distinguish the commonly used resistances, (13)-(15), from the derived resistances, (5), (7), and (8).

In the present data set, 1% of the data are characterized as weak upward transport of ozone and are neglected. In addition, less than 2% of the data are associated with very weak turbulence (\( U_* < 0.065 \text{ m s}^{-1} \)) and are not considered in this study either.

4. Ozone Transport

Diurnal variations of the ozone concentration, ozone deposition velocity, the fluxes of heat, moisture, ozone, carbon dioxide, and the resistances are composited over the entire field campaign for each half-hour period of the diurnal cycle (Figure 1). The traditional resistance \( r_{am} \) (13) is larger than the resistance \( r_a \) (7) during the daytime and is the same as \( r_a \) at night due to the difference between the stability functions for heat and momentum under unstable conditions (section 2.2.1). Physically, this means that the resistance for the turbulent heat transfer is smaller than that for the turbulent momentum transfer under buoyant conditions. Although the values of \( r_c \) (5) and \( r_{cm} \) (15) are different due to the two different parameterizations, the total ozone resistance \( 1/ \nu_d \) is dominated by the resistance \( r_{cm} \) in (9) and by the resistance \( r_{cm} \) in (15). As a result, the correlation coefficient between \( 1/ \nu_d \) and \( r_s \) or between \( 1/ \nu_d \) and \( r_{cm} \) is the highest among those between \( 1/ \nu_d \) and other resistances (Table 1, Figure 2a). Considering the interaction between the atmospheric ozone and the soil and plant surfaces, especially stomatal ozone uptake, we separately study the ozone deposition during daytime and nighttime.

4.1. Nighttime

At night, the correlation of the total ozone resistance \( 1/ \nu_d \) with \( r_s \) (linear correlation coefficient, \( R = 0.78 \)) is almost the same as its correlation with the sum of \( r_{cm} \) and \( r_{cm} \) (\( R = 0.77 \)). Since \( r_s = r_{am} \) at night, the above correlations indicate that including \( r_{am} \) through \( \kappa B^{-1} \) (13)-(15) does not change the variance of the ozone deposition velocity explained by the resistance \( r_s \) (notice here \( r_c = r_{cm} \) at night). This result further proves that by choosing \( z_h = z_0 \), then \( r_s \) as defined in (8) is not necessary. In addition, \( z_h \) is more ambiguous to define than \( z_0 \).

The turbulent fluxes of moisture, sensible heat, carbon dioxide, and ozone are strongly correlated to the momentum flux due to wind shear generation of turbulence at night (Figure 3). Higher turbulent transport of ozone leads to larger ozone deposition velocity, and smaller ozone resistance. Therefore the high correlation between the friction velocity and the total ozone resistance \( 1/ \nu_d \) (\( R = 0.87 \)) indicates that the turbulence strength controls the downward transport of ozone at night. The significant nighttime ozone deposition also indicates that surface ozone uptake other than the stomatal uptake during the daytime plays an important role in the downward ozone transport. Ozone is a highly reactive gas and is efficiently captured when it reaches the ground surface or canopy surfaces due to intermolecular forces between leaf cuticles or soil surfaces and ozone molecules [Businger, 1986].

4.2. Daytime

During the daytime, diurnal variation of the solar radiation significantly influences all turbulent fluxes, the photochemical generation of the ozone [Leighton, 1961; Finlayson-Pitts and Pitts, 1986; Wayne, 1991; DeMuer et al., 1997], and stomatal activity. Two aspects of the ozone deposition velocity are studied in this subsection: the diurnal variation of the ozone deposition based on the hourly data (section 4.2.1) and the variation of the ozone deposition velocity between days based on daytime averaged data (section 4.2.2).

4.2.1. Diurnal variation of the ozone deposition velocity

During the daytime, the turbulence strength is mainly controlled by thermals associated with upward buoyancy flux (\( w' B' \)). The buoyancy flux is related to the heat flux (\( w' q' \)) and moisture flux (\( w' q' \)) as
Figure 1. (a) The composited diurnal variation of the fluxes of downward solar radiation (SWI, solid line), sensible heat flux (H, line with circles), latent heat flux (LE, line with triangles); (b) carbon dioxide flux (FCO₂, line with circles), ozone flux (FO₃, line with diamonds), ozone concentration ([O₃], line with solid triangles), and ozone deposition velocity (v_d, line with open triangles). The standard deviations of each variable during the entire field program are shown as vertical bars.

\[ \overline{w'q'} = \overline{w'q'} + 0.61 \overline{\theta}, \overline{w'q'}, \]  

where \( q \) is the specific humidity. In the present data, the buoyancy flux is dominated by the sensible heat flux.

The diurnal variations of the fluxes of sensible heat, latent heat, carbon dioxide, and ozone composited over 26 days show phase differences, i.e., each flux reaches its maximum value at different times (Figure 1). A similar result was also observed by Desjardins et al. [1995]. The ozone deposition velocity is a bulk measure of the effective ozone removal. It depends on the ozone concentration and the turbulent transport of ozone measured at a certain height, which in turn, depends on the strength of the turbulence, the ozone generation, and the ozone removal ability at the soil and plant surfaces. Each has its own diurnal cycle, although they are all related.

The strength of the turbulence, dominated by the buoyancy flux, reaches its maximum in the late morning due to the heat release from the absorption of the solar radiation of the canopy, small heat transfer into the soil, and small canopy photosynthesis indicated by the relatively weak downward carbon dioxide flux in the early morning (Figure 1). The increase of the canopy transpiration in the afternoon reduces the energy available for the sensible heat flux, resulting in the maximum downward carbon dioxide flux and upward moisture flux around 1400 LST.

The ozone concentration is modified by downward transport of ozone and photochemical production and reaches its maximum in the late afternoon. In the early morning, the vertical

| Table 1. Linear Correlation Coefficients Between 1/v_d and Different Resistances |
|-----------------|--------|
| 1/v_d           |        |
| r_a             | 0.68   |
| r_c             | 0.99   |
| r_am            | 0.62   |
| r_cm            | 0.37   |
| r_crm           | 0.99   |
gradient of the ozone concentration is small due to the low ozone concentration close to the soil and plant surfaces from the ozone removal at night. In addition, the limited ozone uptake by the partially closed stomata leads to relatively weak downward ozone flux even though the turbulence intensity is strong. In the early afternoon, the weaker turbulence due to enhanced canopy transpiration, implied by the reduced canopy resistance, prevents strong downward ozone flux, although the vertical gradient of the ozone concentration is larger. As the net effect of all these influences, the downward turbulent transport of ozone reaches its maximum in the middle afternoon, lagging behind the maximum strength of turbulence and the maximum uptake by stomata, but ahead of the maximum ozone concentration.

The combination of diurnal variations in the turbulent transport of ozone and the ozone concentration leads to the diurnal variation of the ozone deposition velocity, which reaches a plateau around 0900 LST and starts to decrease around 1600 LST (Figure 1). The large ozone deposition velocity in the morning is related to strong turbulence but low ozone concen-
tration, indicating the efficient removal of ozone by partially opened stomata, leaf cuticles [Rondon et al., 1993; Coe et al., 1995], and soil surfaces. The large ozone deposition velocity in the afternoon is related to the offsetting influences of decreasing turbulence and increasing ozone concentration, indicating the efficient ozone removal by fully opened stomata, leaf cuticles, and soil surfaces. The most efficient stomatal removal of ozone occurs only when the ozone concentration close to the leaf surface is the highest and the stomata are completely open. This does not occur in CODE due to the phase differences between the ozone transported down to the canopy surface and the stomatal activity.

Commonly, the resistance $r_c$ is associated with the canopy resistance. The linear correlation between the two is 0.85 based on the composited half-hourly data during the day. However, the relatively large correlation between the two is dominated by their diurnal cycles (more in section 4.2.2). Assuming the resistance $r_{cm}$ is linearly correlated with the canopy resistance $r_{canopy}$, the total ozone resistance $1/v_d$ can be parameterized based on (15):

\[ 1/v_d(\text{model}) = a_0 + a_1(r_{am} + r_{bn}) + a_2r_{canopy} \]  \hspace{1cm} (17)

where the regression constants $a_0 = 243$ s m$^{-1}$, $a_1 = -0.57$, and $a_2 = 0.62$. We find that the above model can explain 76% of the variance of the observed total ozone resistance $1/v_d$, implying that a linear function of the canopy resistance ($r_{canopy}$) cannot explain all the physics involved in $r_c$. Since the ozone deposition velocity is related to the turbulence strength, which influences all the turbulent fluxes, the ozone deposition velocity is found to be highly correlated with all the turbulent fluxes, especially the buoyancy flux and the carbon dioxide flux (Table 2). As the energy source of all the turbulent fluxes, the ozone deposition velocity is also highly correlated with the downward solar radiation (SWI in Table 2).

4.2.2. Variations of the ozone deposition velocity between days. Each variable in Figure 1 has its diurnal cycle. Correlations between any two variables are partly due to their physical connections and partly due to their independent connection to the variation of the solar radiation. Blind correlations between any two variables with diurnal cycles can always lead
to reasonable correlation coefficients, although the phase difference between the two leads to large scatter in their correlation. Therefore correlation coefficients between the 30 min averaged ozone deposition velocity and other fluxes in Table 2 may not reveal the physical mechanism of the ozone deposition. In order to investigate the physical connection between the ozone deposition velocity and the fluxes, the diurnal variation of all the variables in Table 2 is removed by averaging the variables over the daytime hours, and the daytime averaged ozone deposition velocity is then correlated with the daytime averaged fluxes in Table 2.

Due to elimination of individual time series with large random flux sampling errors, and instrument errors, measurements of some variables in Table 2 are "missing" at times. To ensure that all the variables are daytime-averaged over the same numbers of hours, we assign all the variables as missing at a given hour if one variable is missing at that hour. Due to the limited data for the stomatal resistance, the daytime-averaged canopy resistance cannot be obtained. Since the composite half-hourly stomatal resistance is best correlated with the carbon dioxide flux with a linear correlation coefficient of 0.75, we use the daytime-averaged carbon dioxide flux to indicate the variation of stomata activity between days during CODE.

The poor correlation between the daytime-averaged ozone deposition velocity and the daytime-averaged CO₂ flux in Table 2 implies that the variation of the daytime-averaged ozone deposition velocity between days is not correlated with the variation of the stomatal activity. The high correlation between the half-hourly ozone deposition velocity and the half-hourly CO₂ flux in Table 2 only indicates that the correlation is dominated by their diurnal variations. Both daytime-averaged and half-hourly-averaged ozone deposition velocities are highly correlated with the corresponding sensible heat flux or buoyancy flux (Table 2), further indicating the influence of the turbulence strength on the ozone deposition. The correlations in Table 2 also imply that more open stomata do not increase the ozone deposition velocity if the turbulence is weak and the ozone cannot be transported downward efficiently.

The variation of the buoyancy flux between days is mainly due to two irrigation events during the field campaign. The buoyancy flux was small when the field was wet. Because the soil moisture in the root zone was not seriously depleted when the ground was dry, substantial stomatal stress was not observed. Therefore the variation of the daytime-averaged buoyancy flux only implies the variation of the strength of the vertical ozone transport, not the variation of stomatal activities.

In contrast to the half-hourly correlation between the ozone deposition velocity and the downward solar radiation, the correlation between the daytime-averaged ozone deposition velocity and the downward solar radiation is poor, indicating that the incoming solar radiation is not the controlling factor for the ozone deposition velocity. The turbulent ozone transport can be weak if most of the net radiative energy is used for evapotranspiration even though the incoming solar radiation is high. Furthermore, the day-to-day variation of the solar radiation is small in this field program.

Rondon et al. [1993] and Coe et al. [1995] found that the extra ozone uptake beyond the stomatal uptake occurred only during daylight periods when leaf cuticles could provide a photochemical sink for ozone. Our results are consistent with their observations, further indicating that the ozone deposition in the morning is associated with the strong downward transport of ozone, which is partly absorbed at leaf cuticles. Nonstomatal uptake of ozone is also observed by Wesely [1983], Garland and Derwent [1979], Leuning et al. [1979], Fontan et al. [1992], Rondon et al. [1993], Coe et al. [1995], Granat and Richter [1995], Pilegaard et al. [1995], and Labatut [1997].

5. Conclusions

The data at the vineyard site in CODE demonstrate that the ozone deposition velocity is significantly influenced by the strength of the turbulence transport, which is characterized by the friction velocity at night and the buoyancy flux during the day. As a consequence of the partitioning of the surface energy balance, there is a phase difference between the diurnal variation of the stomatal resistance and the turbulence, which limits the potential stomatal uptake of ozone. The buoyancy flux peaks in the morning before the stomata are fully open. By the time the stomata are fully open, the strength of the buoyancy flux and the turbulence have declined due to increased evapotranspiration. Strong buoyancy flux leads to strong downward transport of ozone. At the same time, the strong solar radiation may lead to active photochemical reaction on leaf cuticles [Rondon et al. 1993; Coe et al., 1995]. Together, the two processes can remove ozone efficiently even without the stomatal uptake. Similar observations were noticed in seasonal variations of turbulent ozone fluxes in the Boreal Ecosystems Atmosphere Study (BOREAS), where the downward carbon dioxide flux increased substantially during the summer of 1994 without a significant simultaneous increase of the downward ozone flux [Oncley et al., 1997].

The high correlation between time series of the ozone deposition velocity and the stomatal activity is strongly influenced by their diurnal cycles, and the former is only partly related to the latter. The between-day variation of the ozone deposition velocity is not related to the between-day variation of stomatal activity, as indicated by the CO₂ flux, but to the between-day variation of the buoyancy flux.

The influence of the turbulence strength on the ozone deposition velocity is dominated by the traditional resistance \( r_e \), which is different from the usual interpretation of the three-resistance model ((13)–(15)) for the parameterization of the ozone deposition velocity. The resistance \( r_e \) is normally formulated as the turbulent transfer for momentum, and the resistance \( r_p \) is traditionally interpreted as the turbulent transfer through the canopy layer, and molecular diffusion through the molecular sublayer of the leaf and soil surfaces. Our analysis of the traditional derivation of the ozone deposition velocity demonstrates that both \( r_p \) and \( r_e \) are related to the turbulent heat transfer in the surface layer since M-O similarity theory used in the derivation is only valid in the surface layer along with extrapolated surface variables.
The turbulent transfer associated with $r_e$ does not represent the true turbulent transfer within the canopy layer or the molecular diffusion through the molecular sublayer of the leaf and the soil surfaces. Instead it refers to the turbulent heat transfer across the distance corresponding to the difference between the roughness height for momentum and the thermal roughness height. The magnitude of the resistance $r_e$ depends on the specification of the thermal roughness height, which can behave erratically if the surface radiation temperature is used.

By definition ((3)-(6)), the difference between the resistance $r_c$ and the sum of the resistances $r_a$ and $r_t$ is in their numerators. The numerator for $r_c$ is the aerodynamic ozone concentration, while the numerator for the sum of $r_a$ and $r_t$ is the difference between the aerodynamic ozone concentration and the observed ozone. Since the aerodynamic ozone is always larger than the difference between the aerodynamic ozone and the ozone concentration observed in the surface layer, $r_e$ is always much larger than the sum of $r_a$ and $r_t$. As a result, the ozone deposition velocity is strongly dominated by the resistance $r_e$, and in terms of magnitude, the influences of the resistances $r_a$ and $r_t$ are generally small.

From the derivation of the three resistances, the resistance $r_e$ represents the net effect of the downward turbulent ozone transport in the surface layer, although the strength of the ozone removal can be influenced by canopy stomatal uptake, leaf cuticle uptake, and chemical reactions as traditionally pursued. Therefore the high correlation between the sensible heat flux and the ozone deposition is mainly due to the connection between the sensible heat flux and the resistance $r_e$ during the daytime.

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