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Trace Gas Exchange Above the Floor of a Deciduous Forest 2. SO_2 and O_3 Deposition

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The pollutant uptake capacity of the surface beneath forest canopies is poorly understood. In this study we show that the eddy correlation method can be applied within a canopy. Direct measurements of SO_2 and O_3 deposition to the forest floor of two deciduous forests were made with the eddy correlation method. For dry periods the surface uptake resistance for SO_2 was of the order of 700 s m^{-1}. When the soil and litter were moist, the SO_2 surface uptake resistance was small, resulting in deposition velocities at the forest floor that were about 2 times greater than during dry periods. SO_2 deposition to the forest floor constitutes between 20 and 30% of total uptake to the forest ecosystem when the surface is moist. Soil surface uptake resistances for O_3 were about 2000 s m^{-1} for both wet and dry periods.

INTRODUCTION

Recent assessments of the total deposition (wet and dry) of nitrates and sulfur compounds suggest that dry deposition can comprise between 30 and 70% of the total atmospheric input (not including cloud water interception) to ecosystems [*Meyers et al.*, 1991; *Sirois and Barrie*, 1988]. These assessments are based on inferred deposition rates that are derived from measurements of ambient pollutant concentrations and estimates of the deposition velocity (V_d). With this approach, the flux (F) is determined as $F = V_d(z)C(z)$. Various schemes have been used to estimate V_d. In simple schemes, V_d is specified according to the land use and time of year [*Wesely*, 1989]. In more detailed schemes like those described by *Hicks et al.* [1987] and *Wesely and Lesht* [1989], the deposition velocity for the various pollutants of interest are modeled using standard meteorological data and detailed information about the site. This includes an estimate of the leaf area index (LAI) and specification of the various plant species that comprise a particular site. Deposition of pollutants to ecosystems includes not only uptake by the vegetative components but also uptake by the ground surface that lies beneath the canopy. The ground surface is not usually bare soil (with the exception of tilled agricultural systems) but is covered with detritus from decaying organic matter and understory vegetation. The chemistry which governs the overall sink potential for a surface also depends on the amount and existence of either liquid or frozen (snow) H_2O covering the surface. For example, *Cadle et al.* [1985] found that the SO_2 deposition velocity over snow depends on the snow surface temperature. Despite these effects the surface resistance is generally assumed to be a static quantity.

The diffusion of material from the atmosphere to soil surfaces takes a tortuous path that is comprised of three pathways: from the atmosphere (concentration C_a) to just outside a quasi-laminar layer above the ground surface (concentration C_b), across an unsteady viscous layer to the soil surface (concentration C_{sfc}), and finally from surface to reaction sites within the soil surface (concentration C_i). This framework for transport is analogous to flow through an electrical circuit in which the three serial pathways can be represented as resistances to diffusion across concentration differences. That is,

$$\text{Flux} = \frac{C_a(z) - C_b}{R_a(z)} = \frac{C_b - C_{sfc}}{R_b} = \frac{C_{sfc} - C_i}{R_s} = \frac{C_a(z) - C_i}{R_a(z) + R_b + R_s} \quad (1)$$

R_a is the atmospheric diffusive resistance and is characterized by the level of vertical turbulent mixing. The near-surface transport, which is mainly controlled by molecular diffusion processes is characterized by R_b. The surface uptake resistance (R_c), also called the bulk canopy resistance, quantifies the overall pollutant uptake capacity for a given surface or surfaces, including both soil and vegetative components. This is generally not constant as it can depend on surface wetness, and how the surface was wetted (rainfall or dew). Equation (1) reduces to the commonly used deposition velocity concept, where $F = (R_a(z) + R_b + R_s)^{-1} \cdot C_a(z) = V_d(z) \cdot C_a(z)$ when the internal pollutant concentration (C_i) is assumed to be zero.

Measurements of SO_2 uptake by calcareous soil surfaces have been reported to be large [*Garland*, 1977], with surface uptake resistances that were not significantly different from zero. No significant effect of soil moisture was observed. In laboratory experiments, *Abelles et al.* [1971] and *Terraglio and Manganelli* [1966] found that SO_2 uptake was strongly influenced by the availability of soil moisture. Average deposition velocities ranged from 0.3 to 0.6 cm s^{-1} for wet soils compared to 0.2 cm s^{-1} for dry soils.

Garland [1977] found an increase in the deposition velocity to soils with higher pH. *Payrissat and Beilke* [1974] report that a pH increase from 4.5 to 7.7 corresponds to a 10-fold decrease in the soil surface resistance to SO_2 uptake. *Petit et al.* [1977] found that the surface soil resistance ranged between 300 and 400 s m^{-1} for soils with a pH of 3 and were roughly a factor of 10 lower for soils with higher values of pH.

Early studies suggested that deposition to soils beneath vegetation was relatively small compared to the uptake of an active canopy. For example, *Fowler and Unsworth* [1979]

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estimate that the deposition to the soil beneath a cereal canopy is only 5 to 10% of the total flux to the agricultural plot. However, direct measurements of sulfur deposition to the forest floor have yet to be made.

Deposition rates of similar magnitudes to soils have been found for O_3. In laboratory experiments, *Turner and Waggoner* [1973] found surface uptake resistances for cultivated and sandy loam soils were of the order of 0.4 s cm^{-1}, with lower resistances reported for dryer soils. From the same study, the combined resistances below a height of 2.5 cm above the soil surface yielded a total resistance of about 200 s m^{-1} (i.e., V_d = 0.4 cm s^{-1}). An analysis by *Galbally* [1971] yielded similar results with combined resistances that were of the order of 150 s m^{-1}. Using measured gradients above a tobacco field and accounting for uptake by the vegetative elements, *Leuning et al.* [1979] estimated the soil surface resistance to be 100 s m^{-1}, which accounted for 50% of the total flux measured above the tobacco field. Much larger resistances (1000 s m^{-1}) were reported by *Wesely et al.* [1981] from measurements obtained over cold bare soil saturated with water, which yielded a maximum V_d of $\approx$ 0.1 cm s^{-1}.

In any case, uptake of SO_2 by the ground surface can constitute a significant fraction of the overall deposition to an ecosystem. Dry deposition to the soil or litter surface represents a component of the total deposition that cannot be measured using either leafwashing or throughfall methods. Models which are used to infer seasonal and annual deposition rates of O_3 and SO_2 have relied upon the aforementioned studies to parameterize the sink capacity of the forest floor for pollutants. However, actual measurements of dry deposition to ground surfaces within forests are lacking. The direct input to soils is important in the characterization of biogeochemical recycling in forest ecosystems. As a result, several experimental investigations were conducted to evaluate the role of the forest floor as a sink for O_3 and SO_2. Results from experiments conducted at two research sites are presented and discussed. The effect of water availability on the magnitudes of the dry deposition rates is also explored. The implications regarding the effect these results have on estimated seasonal and annual SO_2 deposition budgets are discussed.

SITE CHARACTERISTICS AND DATA ACQUISITION

Walker Branch Watershed, Oak Ridge, Tennessee

The data and analysis presented in this report were taken from three studies. The first study period ran from April 29 to May 10, 1988. The second experiment was conducted between September 14 and 30, 1988. Both of these experiments were conducted at Walker Branch Watershed, located on the U.S. Department of Energy's Reservation near Oak Ridge, Tennessee (35°57'30"N, 84°17'15"W). The field site is located on a gentle ridge in moderately complex terrain at 365 m above mean sea level. The site is a forested, mixed, uneven-aged stand of oak and hickory (spp. *Quercas*, *Carya*) with some small patches of loblolly pine (spp. *Pinus*) dispersed within the area. The average tree height is about 23 m with LAI of 5 [*Hutchison et al.*, 1986] during years that are not affected by drought. The first experimental period was preceded by a multiyear drought that resulted in a lower LAI (3.2) than what is normally expected (4.9) for this forest based on the methodology presented by *Baldocchi et al.* [1984]. The LAI for the second study was estimated to be 4.1 based on radiation transect measurements near the forest floor.

The soil at the site is classified as a cherty silt loam (Typic Paleudult) with a bulk density of 1.3 g cm^{-3} in the upper 10 cm of the soil profile. The soil is acidic (pH 4.2–4.6) and is low in exchangeable bases, nitrogen and phosphorus [*Johnson*, 1989]. Because the site is near the top of a ridge, the soils are very well drained. The O_1 litter in the watershed is comprised of decaying leaves (8.7 Mg/ha), twigs (1.8 Mg/ha), and wood (3.8 Mg/ha) and when combined with the litter in the O_2 horizon yields a total litter mass of 32 Mg/ha [*Edwards et al.*, 1989].

The eddy correlation method was employed to measure the turbulent exchange of sensible heat, H_2O, CO_2, O_3, and SO_2 between the air and the forest floor. A companion paper by *Baldocchi and Meyers* [1991] provides a detailed analysis of the measurements and interpretation of the exchange of H_2O and CO_2 above the forest floor. The application of the eddy correlation method requires fast response instrumentation to measure the three components of the wind vector and the scalars of interest [see *Businger*, 1986; *Baldocchi et al.*, 1988]. A three-dimensional sonic anemometer (model BH-478B/3; Applied Technology, Incorporated), mounted at 2 m, was used to measure the components of the wind vector. Fast response measurements of O_3 during the first two studies were determined with a highly modified version of the model 560 O_3 analyzer made by Analytical Instruments Development, Incorporated. The measurement of O_3 is based on a chemiluminescent reaction using ethylene in a gas phase titration. The time response of this analyzer has been determined to be 0.2 s. Rapid measurements of SO_2 were determined with a flame photometric detector (Meloy SA285, Meloy Laboratories Incorporated, Springfield, Virginia), using a SF_6-H_2 mixture for increased sensitivity [*D'Ottavio et al.*, 1981]. The response time of the analyzer used in this study has been determined to be less than 0.5 s. Because the response times of the chemical analyzers may limit applicability of the eddy correlation, a cospectral analysis will be done to determine the adequacy of these sensors. The intake lines were short (1.5 m of Teflon tubing) to minimize smearing of the concentration signal [*Lenschow and Raupach*, 1991]. Both O_3 and SO_2 analyzer intake lines were fitted with filters to remove unwanted particulates. The inlets were positioned within the sampling volume of the sonic anemometer. Mean concentrations of SO_2 and O_3 (2.0-m Teflon intake lines) were determined with Monitor Labs (model 8850) and Dasibi (1003 AH) monitors, respectively. Fast response measurements of temperature (for sensible heat flux) were performed with a microbead thermistor (Victory Engineering Corporation, Springfield, New Jersey, model E45A401C) that was placed within a few centimeters of the averaging path of the sonic anemometer. A krypton hygrometer (model KH20, Campbell Scientific, Logan, Utah) was used to measure fluctuations in water vapor density for the determination of evaporation.

The fast response instruments were sampled and digitized at 3 Hz with a desktop computer-controlled data acquisition system using a 12-bit analog to digital conversion board (Data Translation model DT2806, Marlboro, Massachusetts). Soil and litter gravimetric water content (θ_w) was measured daily [see *Baldocchi and Meyers*, 1991]. During

the first experiment at Oak Ridge, the soil and litter layer was moist with four rain events occurring over the course of 10 days. The soil gravimetric water content was never less than 0.3 g g^{-1}. During the fall study, the soil was moist at the beginning of the experiment ($\theta_w = 0.23$). With only 9 mm of rain over a 12-day period, θ_w dropped to 0.14 g g^{-1}.

Huntington Forest, Newcomb, New York

The third study was conducted during July 20–30, 1990, at Huntington Forest (43°59'N, 74°14'W). Located near Newcomb, New York (Essex County), Huntington Forest is a property of the State University of New York, College of Environmental Science and Forestry. As part of the Adirondack State Park of New York, the site is used as a research facility for long-term studies of wildlife ecology, forest ecosystem biogeochemical cycling studies, and silviculture. The elevation within Huntington forest ranges from 466 to 806 m. The site can be classified as a northern deciduous forest dominated by *Acer saccharum* Marsh. (sugar maple) and *Fagus grandifolia* Ehrh. (American beech). The leaf area index in the area where the eddy flux measurements were made is about 6.5 (70% maples, 30% beech) with an average tree height of 21 m. The total woody biomass (stems, branches, boles) is about 190 kg m^{-2}.

The soil at Huntington Forest is classified as a coarse-loamy, mixed, frigid, Typic Haplorthod. The soil profile (about 1 m in depth) overlies a bedrock of gneiss which contains a hardpan derived from parent material of glacial till. The soil contains a considerable fraction of coarse fragments with high organic matter concentrations in the mineral horizons. The *p*H of solution in the litter layer is 4.42 and increases to 4.9 at a depth of 50 cm [*Johnson and Lindberg*, 1992]. Two instrumented towers are currently in use at the Huntington Forest research site. A 30-m triangular tower (18-inch base), instrumented with meteorological and chemical samplers, has until recently been operated as part of the Integrated Forest Study (IFS) [see *Lindberg and Johnson*, 1989]. A walk-up scaffolding tower (38 m) was recently erected for the purpose of making micrometeorological measurements.

The topography at Huntington Forest is considered complex. In the azimuth window from about 90° to 180° the terrain is moderately rolling and the land use is generally homogeneous (hardwood forest) for at least 2 km. This window was considered the best possible fetch. To the north, the elevation increases significantly. There is also a large body of water (Arbutus Pond) located about 300 m northeast of the tower. An eddy correlation system was operated at 2 m above the forest floor on a portable platform. Air temperature and the three components of the wind vector were determined with a commercial version of the sonic anemometer/thermometer described by *Coppin and Taylor* [1983]. Water vapor density was measured with an open path, fast response infrared gas analyzer [*Auble and Meyers*, 1992]. Fast response measurements of O_3 were determined with a chemiluminescent method based on the design by *Ray et al.* [1986]. Experiments conducted earlier indicate a frequency response of better than 5 Hz. Measurements of SO_2 were in a similar fashion as previously described. Mean concentrations of SO_2 and O_3 (2.0-m Teflon intake lines) were determined with a Monitor Labs model 8850 and a TECO (model 49), respectively.

The analog signals from the fast response instrumentation were sampled and digitized at 20 Hz (Campbell Scientific Instruments, model 21X, Logan, Utah) before being sent to a desktop computer via RS-232 communication protocols. Short-haul modems were used to insure the integrity of the RS-232 signals over a distance of 200 m. The incoming data were written to portable storage media for post processing.

Determination of Vertical Fluxes

Vertical turbulent fluxes were computed in real time using a digital recursive filter (200-s time constant). Tests have shown that the computed flux is not sensitive to the choice of the filter time constant [see *Baldocchi et al.*, 1988]. The recursive filter allows for a determination of average values from which the instantaneous values were subtracted to obtain the fluctuations. The real-time vertical turbulent eddy fluxes were determined as

$$\overline{w'\chi'} = \frac{\sum_{i=1}^{n} (w - \langle w \rangle)(\chi - \langle \chi \rangle)}{n} \qquad (2)$$

where w is the vertical velocity and χ is the scalar of interest. Here, the bracketed quantities denote a running mean that is being subtracted from the instantaneous values. The averaging period of 30 min was used during all experiments. For experimental sites that are not perfectly flat, the coordinate system of the sonic anemometer can be mathematically rotated to obtain a zero mean vertical and transverse velocity ($\bar{w} = \bar{v} = 0$). This is usual practice to correct for small misalignment errors of the sonic anemometer as well as to determine the vertical turbulent flux across the mean horizontal streamline, which generally follows the contour of the land surface. Since the fast O_3 and SO_2 analyzers were not open path systems but were fitted with sampling tubes with intakes in the vicinity of the sonic anemometer, a 2-s time lag was introduced. Computer software compensated for these time lags during data acquisition and in the calculation of the fluxes.

RESULTS AND DISCUSSION

Micrometeorological Considerations

The validity of the flux measurements at 2 m above the forest floor can be addressed by examining the heat balance. That is, on average, do the measured sensible (H) and latent energy (LE) fluxes balance the sum of net radiation (R_n) and ground storage (S) fluxes? For the first two experiments at Walker Branch Watershed, *Baldocchi and Meyers* [1991] concluded from independent measurements of all the components that the energy balance was closed. The energy balance residual was not significantly greater than zero. Evaporation from the forest floor with a wet litter surface often exceeded 40 W m^{-2} and was closely linked to available energy ($R_n - S$). For dry surface conditions, evaporation was well correlated but weakly driven by available energy and LE values never exceeded 40 W m^{-2}.

During the experiment conducted at Huntington Forest, net radiation was measured above the canopy but not at the forest floor. For proper measurements of radiation within forest canopies, traversing tram systems are required to

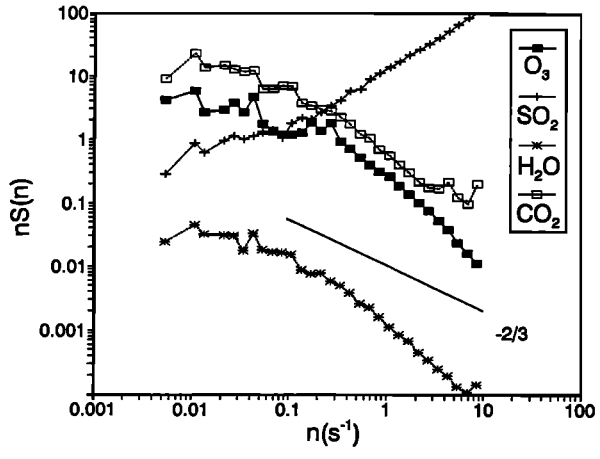

Fig. 1. Power spectral estimates ($nS(n)$) for H_2O, CO_2, O_3, and SO_2. Units are $(g/m^3)^2\ s^{-1}$ for H_2O, $(mg/m^3)^2$ for CO_2, $ppbv^2\ s^{-1}$ for O_3, and $(\mu g/m^3)^2\ s^{-1}$ for SO_2.

insure adequate spatial sampling. Because a tram system was not available, R_n at the forest floor was approximated as

$$R_n(f) = R_{n,0} \exp(-\gamma f) \quad (3)$$

where $R_{n,0}$ is the net radiation measured above the canopy, f is the LAI, and γ is an extinction coefficient. The value of γ was determined from published values for canopies of similar plant species and canopy structure [*Baldocchi et al.*, 1984]. The ratio of $(R_n - S)/(H + LE)$ from the Huntington Forest study (0.94 ± 0.11) was not significantly different from 1. The surface was very moist (gravimetric water content in the litter layer, $\theta_w > 0.5\ g\ g^{-1}$). During the period of the experiment, most of the available energy was used for surface evaporation. This observation is consistent with the observations reported by *Baldocchi and Meyers* [1991] for wet surface conditions.

Recording of the raw time series allows for spectral analyses to be performed with the data. Continuous data were not recorded during the first two experiments at Oak Ridge. However, continuous data were periodically recorded during the third experiment at Huntington Forest. Power spectra for O_3, SO_2, H_2O, and CO_2 were generated by averaging six time series segments, each containing 4096 data points. The spectral estimates were then block averaged with a relative bandwidth of 0.1.

The power spectra ($S(n)$) for H_2O, CO_2, and O_3 (Figure 1) show a roll-off at higher frequencies (n) with a slope of nearly -1. This slope is steeper than what is typically observed ($-2/3$) for power spectra in the inertial subrange for turbulence data in the atmospheric surface layer [*Kaimal et al.*, 1972]. However, such features in the power spectra have been observed for the vertical velocity variances measured within a black spruce forest [*Amiro and Davis*, 1988], tropical Amazon forest [*Fitzjarrald et al.*, 1990], and an eastern hardwood forest [*Baldocchi and Meyers*, 1988*a*, *b*]. Power spectral estimates from H_2O and CO_2 data collected at 2 m above the forest floor from a recent experiment that was conducted during the summer of 1992 at the Walker Branch Watershed in Oak Ridge show a slope of -1 in the inertial subrange (unpublished data). It was suggested by *Fitzjarrald et al.* [1990] that this feature is a result of the upper canopy acting as a low-pass filter, only allowing the large scales to penetrate to the lower canopy. However, a recent study by *Shaw and Zhang* [1992] suggest that turbulence in the lower canopy levels is generated mainly by pressure perturbations created aloft.

A slope of $+1$, which is observed for the data from the SO_2 analyzer, is typical of a white noise spectrum when $nS(n)$ is plotted against n on a log-log plot. This feature is expected when trace gas analyzers are operated during periods when the ambient concentrations are low and electronic noise represents a sizable fraction of the signal variance [*Wesely and Hart*, 1985].

The normalized cospectral estimates ($nC_{wx}(n)$) between the scalar quantities and the vertical velocity w, in general, show spectral peaks that occur at or near the same frequency. This includes the cospectral estimates for SO_2 (Figure 2) which for the same periods, had a signal that was dominated by noise (Figure 1). Although the noise constitutes a sizable fraction of the overall variance for SO_2, the cospectral estimates of SO_2 with w (i.e., the flux) are consistent with the spectral estimates from the more noise-free scalars (H_2O and CO_2) since the noise that is superimposed on the signal does not correlate with w. This illustrates the noise rejection capability that is inherent in the eddy correlation method. The strong similarity in the normalized cospectra for the fast response open-path analyzers (H_2O and CO_2) and the closed-path slower-responding sensors (SO_2 and O_3) demonstrates that these sensors were adequate for flux measurements within the canopy. The flux contribution at frequencies >1 Hz is minimal.

The two prominent peaks observed in Figure 2 suggest a strong similarity in the turbulent transfer mechanisms for scalars with upward fluxes (H_2O and CO_2) as well as for trace species that are taken up by the surface (O_3 and SO_2). From Figure 2 the majority of the covariance occurs at frequencies less than 0.05 Hz, indicating that a large fraction of vertical fluxes are dominated by infrequent coherent turbulent structures. This supports the hypothesis suggested by *Shaw and Zhang* [1992] that turbulence in the subcanopy trunk space is a consequence of pressure perturbations imposed on the canopy from above. These pressure fluctuations are of lower frequency than velocity [*Sigmon et al.*, 1983], resulting in a larger fraction of the power and cospectral energy occurring in the low-frequency range.

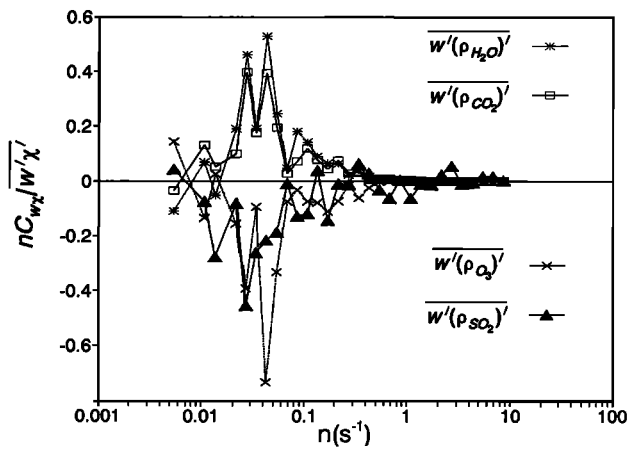

Fig. 2. Cospectral estimates (C_{wx}) of H_2O, CO_2, O_3, and SO_2. Cospectra are normalized by the average flux for the period.

TABLE 1. Desciption of the Quadrants

Quadrant	Plane, $w - c$	Emission, $\overline{w'c'} > 0$	Deposition, $\overline{w'c'} < 0$
1	($w' > 0$, $c' > 0$)	burst/ejection	outward interaction
2	($w' > 0$, $c' < 0$)	outward interaction	burst ejection
3	($w' < 0$, $c' < 0$)	sweep/gust	inward interaction
4	($w' < 0$, $c' > 0$)	inward interaction	sweep/gust

Quadrant Analysis

Conditional sampling is another analysis technique that is used to evaluate the turbulent events and processes that contribute to the time average vertical covariance. In particular, contributions from infrequent turbulent events such as a downward sweep of fast moving air or an ejection of slower air moving away from the surface can be evaluated. Most applications of quadrant analysis to canopy flows have focused on the structure of the kinematic Reynolds stress. For this quadrant analysis, the scalar fluxes of H_2O, CO_2, O_3, and SO_2 from the Huntington study will be examined.

In quadrant analysis, individual components of the vertical turbulent scalar flux ($\overline{w'c'}$) are examined on a w'-c' plane, where the y axis represents positive and negative w' fluctuations and the x axis represents the positive and negative c fluctuations. For scalar fluxes the definitions of the quadrants depend upon whether the flux is positive (surface is a source) or negative (surface is a sink). Table 1 describes the quadrants.

From the raw data time series, the relative importance of each turbulent event is assessed from

$$H = |w'c'|/|\overline{w'c'}| \tag{4}$$

where H represents a hyperbolic hole size in the w'-c' plane. By increasing the value of H, the importance of individual turbulent events relative to the mean can be determined. Following the notation of *Shaw et al.* [1983], the stress fraction $S_{i,H}$, for quadrant i and hole size H, can be determined as

$$S_{i,H} = \langle w'c' \rangle_{i,H}/\overline{w'c'} \tag{5}$$

where

$$\langle w'c' \rangle_{i,H} = \frac{1}{T}\int_0^T w'c'(t) I_{i,H}(t)\, dt$$

$I_{i,H}$ is equal to 1 if the product $w'c'$ lies in the ith quadrant and $|w'c'| \geq H|\overline{w'c'}|$. Otherwise, $I_{i,H}$ is set equal to 0. When the stress fractions are normalized by the average covariance, then

$$\sum_{i=1}^{4} S_{i,0} = 1 \tag{6}$$

Similarly, the fraction of time ($F_{i,H}$) for each flux fraction ($S_{i,H}$) is determined as

$$F_{i,H} = \frac{1}{T}\int_0^T I_i(t)\, dt \tag{7}$$

For all the gases (H_2O, CO_2, O_3, and SO_2), at least 50% of the total flux consists of turbulent events that are 10 times greater ($H = 10$) than the mean flux for the period (Figure 3). Yet, these events occur less than 10% of the time during the averaging period (Figure 4). Ejection and sweep events comprise at least 75% of the turbulent events for values of $H > 10$. Almost identical results were obtained by *Baldocchi and Meyers* [1988*a*, *b*] from a momentum flux study conducted at Oak Ridge with measurements at 2 m above the forest floor. Similar results were obtained by *Shaw et al.* [1983] for momentum flux within a corn canopy. In their study, about 50% of the momentum flux occurred from events ($H > 4$) that occupied only 6% of the time in the averaging period.

SO_2 Deposition to the Forest Floor

The SO_2 deposition velocities from all the experiments were classified into "wet" and "dry" periods. Soils with gravimetric water contents less than 0.15 were considered dry. The deposition velocities (V_d) at 2 m above the forest floor, shown in Figure 5, are plotted against the standard deviation of the vertical wind velocity (σ_w) measured at 2 m above ground level. From Figure 5 it is evident that the deposition velocities measured during the dry periods are significantly lower than those from the other periods, even though turbulent mixing (as indicated by σ_w) tended to be greater during the dry periods. Because the surface uptake resistance for SO_2 appears to be small for moist soil conditions, the level of turbulence in the canopy flow field becomes a controlling factor in characterizing the deposition rate. The strong dependency of deposition on the level of turbulence is observed for HNO_3 [*Huebert and Robert*, 1985; *Meyers et al.*, 1989], which is known to have a negligible surface uptake resistance when compared to the aerodynamic and boundary layer terms. For significant surface resistances, as evident in the dry periods, the depo-

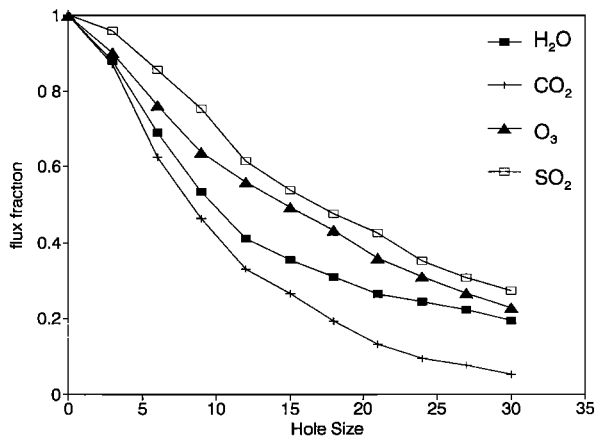

Fig. 3. Plot of the fraction of the total flux that exceeds a given hole size.

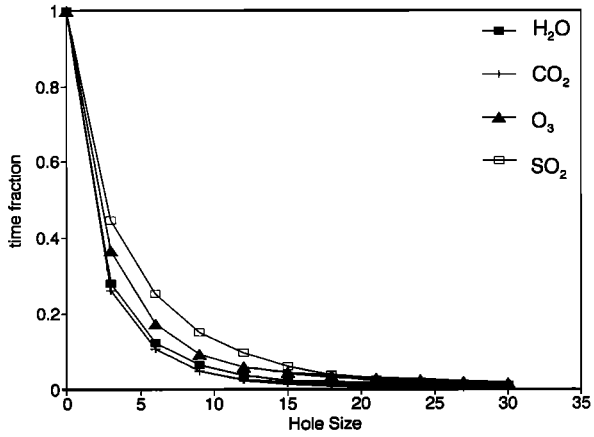

Fig. 4. Plot of the time fraction of the flux fractions that exceed a given hole size.

sition velocities are relatively insensitive to the local turbulent flow field.

The large deposition velocities observed during moist surface conditions indicate a negligible surface resistance for uptake for SO_2. If we assume that $R_s = 0$ for moist conditions, an estimate of the SO_2 surface uptake resistance for dry periods can be obtained. For periods when the surface was wet, and assuming $R_s \ll R_a$ or R_b, the deposition velocity can be determined as $V_d = (R_a + R_b)^{-1}$. From Figure 5, V_d can be approximated as a linear function of σ_w. By including this parameterization of V_d (and therefore $R_a + R_b$) into a complete resistance equation, the residual or surface uptake resistance can be determined. Upon substitution, the average surface uptake resistance for dry periods was 660 s m^{-1} ± 280 s m^{-1}. This finding is consistent with the laboratory studies by *Payrissat and Beilke* [1975] who found surface uptake resistances of the order of 400 s m^{-1} for soils of similar *p*H. *Garland* [1977], using the gradient method inside a wind tunnel, determined the surface uptake resistance for a dry, low *p*H soil to be 0.4 s cm^{-1}, much lower than the numbers reported here. The deposition velocities for dry, acidic soils (*p*H < 4)

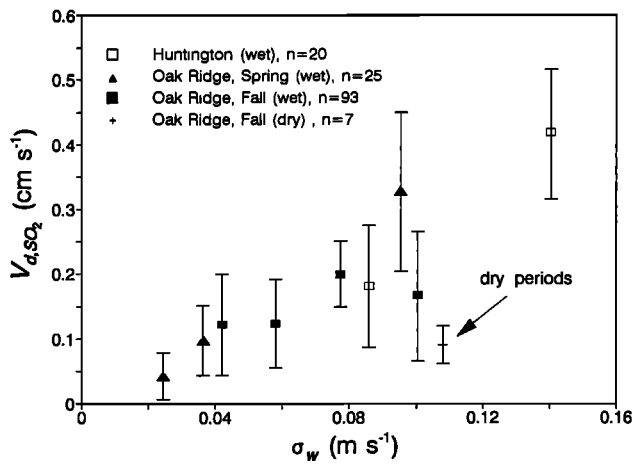

Fig. 5. The deposition velocity of SO_2 (V_{d,SO_2}) at Oak Ridge and Huntington Forest versus the standard deviation of the vertical velocity (σ_w) at 2 m above the forest floor; *n* is the number of half hourly periods (*n*) averaged together for each data point.

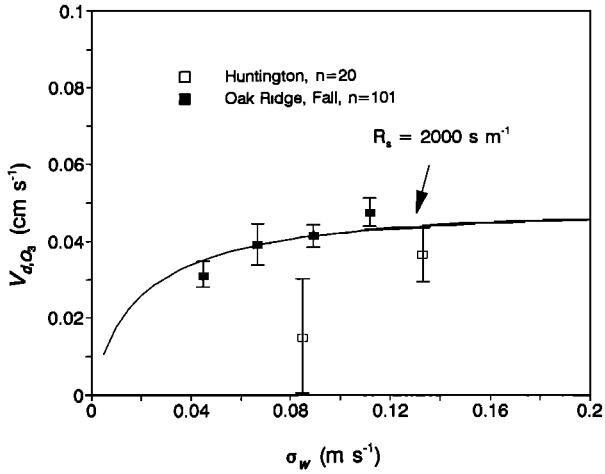

Fig. 6. The deposition velocity of O_3 (V_{d,O_3}) at Oak Ridge and Huntington Forest versus the standard deviation of the vertical velocity (σ_w) at 2 m above the forest floor; *n* is the number of half hourly periods averaged together for each data point.

reported by *Garland* [1977] were, on average, 1.3 cm s^{-1} with 20% larger values when these same soils were moist. Using a similar bulk resistance analogy as used here, *Fowler and Unsworth* [1979] found SO_2 soil uptake resistances of the order of 1000 s m^{-1} for a cultivated agricultural site. These resistances are consistent with our reported numbers for dry soils.

The differences in the surface uptake resistance between wet and dry surfaces results in a factor of ≈2 in the deposition velocity. This general conclusion is commensurate with findings from laboratory studies assessing the effect of moisture on SO_2 uptake on a variety of soil types and characteristics [*Terraglio and Manganelli*, 1966; *Payrissat and Beilke*, 1975; *Lockyer et al.*, 1978; *Judeikis and Stewart*, 1976; *Judeikis and Wren*, 1977].

O_3 Deposition to the Forest Floor

Ozone deposition velocities from all studies were plotted in a similar manner (versus σ_w) to SO_2 (Figure 6). The deposition velocities for O_3 show a slight dependency on turbulence (σ_w), similar to what was observed for SO_2 during dry conditions. In general, O_3 deposition appears to be limited by the surface uptake resistance for both moist and dry surface conditions. The surface resistance for O_3 was determined in a similar manner to that above for SO_2. The computed value from the Oak Ridge site (22 ± 8 s cm^{-1}) was in agreement with that determined for the Huntington Forest location (28 ± 11 s cm^{-1}). A plot of the deposition velocity against σ_w with R_s = 2000 s m^{-1} fits the observed data well with the exception of one point, although this value was associated with one of the largest standard deviations. The large surface resistance calculated for O_3 is consistent with measurements by *Wesely et al.* [1981] over bare wet soil. O_3, because of its low solubility in water, is not expected to have high deposition rates to moist surfaces. The average deposition velocity was 0.05 cm s^{-1} for this period. The trend displayed in Figure 6 is what would be expected for a diffusion process that is limited by a large surface uptake resistance. At low turbulence levels the aerodynamic and boundary layer resistance are relatively

large components of the overall resistance to diffusion. However, at higher turbulence levels, deposition is limited by the presumably constant surface uptake resistances. This can be contrasted to the results obtained for SO_2 (Figure 5), in which the forest floor was moist and the uptake resistance was negligible. As the turbulence levels increase (higher σ_w), the deposition velocity increases in an almost linear fashion (similar to HNO_3) because the aerodynamic and boundary layer resistances are believed to be the limiting factors in the diffusion process. However, this can only be true if the pH of these moist surfaces is well buffered. Measurements of soil litter leachate by *Lindberg and Johnson* [1989] found values of pH ranging from 5 to 6.

SUMMARY

Eddy correlation measurements of O_3 and SO_2 deposition were made at 2 m above the surface within two deciduous forests. A spectral analyses of the scalar quantities measured in the lower canopy at Huntington Forest indicate a much steeper roll-off in the inertial subrange than in the atmospheric surface layer (a slope of -1 compared to $-2/3$). Similar spectra have been observed for wind velocity spectra at the Oak Ridge site. This finding is consistent with recent suggestions that turbulence in the lower canopy is in part generated by low-frequency pressure perturbations. A quadrant analysis of the raw time series data showed that at least 50% of air-surface exchange at the forest floor is dominated by turbulent events that provide, on average, 10 times the mean flux. These events, however, only occupy less than 10% of the time during the averaging period.

The deposition of SO_2 was found to vary with surface moisture. When the surface was moist, the surface uptake resistance (R_s) for SO_2 was negligible which resulted in a deposition rate that was generally a factor of 2 higher than to dry surfaces. For dry surface conditions, R_s was estimated to be of the order of 700 s m^{-1}. The deposition of O_3 was invariant with surface moisture conditions and was associated with surface resistances that were of the order of 2000 s m^{-1}. For moist surface conditions, deposition of SO_2 to the forest floor comprises a significant fraction of the total flux to the ecosystem and during the dormant season has the potential to be a dominant sink for SO_2. Total deposition estimates based on throughfall measurements [*Lindberg and Lovett*, 1992] need to account for this additional fraction since it is not measured by the throughfall method.

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