PERGAMON

Atmospheric Environment 36 (2002) 4787–4799

ATMOSPHERIC ENVIRONMENT

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On ozone dry deposition—with emphasis on non-stomatal uptake and wet canopies

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Received 6 March 2002; accepted 1 July 2002

Abstract

Measurements of O_3 fluxes and concentrations over five different sites were used to study O_3 dry deposition. It was found that high humidity, dew and rain increase O_3 uptake by canopy cuticles. However, the increase by cuticle uptake maybe offset by a decrease in stomatal uptake due to weak solar radiation or stomatal blocking under wet conditions. Thus, during nighttime the overall canopy resistances (R_c) for O_3 uptake under wet conditions was usually smaller than under dry conditions, while in the daytime, R_c for wet canopies could be either larger or smaller compared to dry canopies. This will depend on the relative contributions of the decrease in cuticle resistance and the increase in stomatal resistance. The non-stomatal uptake of O_3 was found to be affected by friction velocity, relative humidity, canopy wetness, leaf area index, etc. Parameterizations for non-stomatal resistance for dry and wet canopies were developed based on the five site O_3 flux data. These equations were found to provide reasonable predictions of non-stomatal canopy resistance based upon comparisons with the nighttime and daytime measurements.

Keywords: Dry deposition; Non-stomatal uptake; Ozone; Surface resistance; Wet canopies

1. Introduction

Tropospheric ozone (O_3) is known to harm human health, damage vegetation and lead to deterioration of materials. Consequently, accurate determination of maximum acceptable concentrations is necessary. To evaluate the impact of O_3 on vegetation, there is presently a debate over whether ambient concentration-based exposures (e.g., AOT40) or fluxes are more appropriate. Although using flux has more physical meaning, measuring concentration is much simple. Clearly, it is important to obtain a better overall understanding of the relationship between O_3 concentration and/or various exposure indices and O_3 flux as a function of vegetation type. Estimating flux using models requires quantification of stomatal uptake and external leaf destruction of O_3.

Surface flux of O_3 is also a key loss pathway in air-quality models and thus must be treated as accurately as possible in order to predict O_3. There have been numerous measurement and modelling studies on O_3 flux over different surfaces and for different seasons (Wesely and Hicks, 2000). However, there is a lack of studies on O_3 flux over wet surfaces and less attention has been paid to deposition processes at night. These limitations need to be addressed in order to accurately determine the overall amount of O_3 deposition given how frequently surfaces can be wet, especially during certain time periods (e.g., nighttime) and over some areas.

Canopies wetted by rain and dew may have different behaviours of O_3 uptake (Padro, 1994; Finkelstein et al., 2000), most likely due to difference in the chemical composition of rain and dew (Klemm et al., 1999; Wesely et al., 1990; Sakugawa and Kaplan, 1993), or

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1352-2310/02/$ - see front matter
PII: S1352-2310(02)00567-8

differences in aerodynamic resistances. Both inhibition and enhancement of O_3 uptake by wetted surfaces compared to dry surfaces have been observed (Leuning et al., 1979; Fuentes et al., 1992; Massman et al., 1994; Grantz et al., 1995; Lamaud et al., 2002). The chemical composition of surface liquid layers can be further complicated by fluids exuding from the vegetative surface themselves (Wesely et al., 1990; Padro, 1994). However, no detailed modelling effort has been undertaken for O_3 deposition over wet canopies, although some studies have been done for SO_2 (Wesely et al., 1990; Erisman et al., 1994). Chameides (1987) studied dew effects on dry deposition to wetted surfaces, however, his model involves more information than is routinely available. In earlier models (e.g., Wesely, 1989), an increase in the resistance of O_3 uptake when the canopy was wet was assumed, due to ozone's low solubility. Our previous analysis of measurement data over a forest and our review of published information (Zhang et al., 2001b) suggested that wetness, either by dew or rain, would enhance O_3 cuticle uptake, but that this enhancement would be offset by full or partial stomatal closure.

In this paper, we have expanded the measurement base to include five different sites to quantitatively study O_3 fluxes from non-stomatal uptake, especially for wet canopies. The five sites include a mixed and a deciduous forest (Finkelstein et al., 2000), a corn, a soybean and a pasture field (Meyers et al., 1998). The data set not only covers a number of different canopies in different regions of eastern North America, but also covers a relatively long period (i.e., the whole growing season). During this period, wetness information at all five sites was recorded enabling a relatively extensive analysis of the effect of wetness on O_3 dry deposition. The result of this analysis, which we report in this paper, is the most broadly applicable parameterization of wetness and humidity effect to date. This parameterization is developed for application in relatively simple (i.e., bigleaf) dry deposition models.

2. Summary of O_3 flux and related measurements

The O_3 flux and concentration data used in the present study were collected over the following eastern USA sites: a mixed forest in New York State (Sand Flats, 43.565°N, 75.238°W) from 12 May to 20 October 1998, a deciduous forest in northwestern Pennsylvania (Kane, 41.595°N, 78.766°W) from 29 April to 23 October 1997 (Finkelstein et al., 2000), a corn field in Illinois (Bondville, 40.05°N, 88.37°W) from 18 August to 1 October 1994, a soybean field in Tennessee (Nashville, 36.65°N, 87.03°W) from 22 June to 11 October 1995, and a pasture field in Alabama (Sand Mountain, 34.29°N, 85.97°W) from 15 April to 13 June 1995 (Meyers et al., 1998).

The canopy wetness was measured with a wetness sensor similar to those used by wet-deposition buckets to sense when to open the lid. It consists of a fine grid of wires. Moisture from rain or dew on the grid reduces the resistence between two of the wires, which is sensed as a signal. When the moisture dries off, the resistance between the wires goes back up. The sensors were placed near the top of the canopy, among the top leaves at all five sites. Relative humidity was measured several meters above the canopy. The eddy correlation method was used in obtaining vertical turbulent fluxes of O_3. The details of these measurements and for other variables can be found in Meyers et al. (1998) and Finkelstein (2001). Discussion on the accuracy of flux measurements can be found in Finkelstein and Sims (2001). The flux data made available to this study have been pre-screened to meet all standard criteria (e.g., fetch, energy balance closure) and are believed to be reliable (P. Finkelstein, personal communications).

Here we use the flux and concentration measurements to calculate deposition velocity (V_d). Other measured variables that were used include friction velocity (u_*), relative humidity (RH), solar radiation (SR), canopy wetness (CW), stability (z/L) and precipitation information (PR). Note that the effect of NO_x emission and related photochemistry on the O_3 uptake cannot be considered, however, this effect is believed to be small due to the relatively large ambient O_3 concentrations compared to the total NO_x.

3. Methods

3.1. Theory

O_3 dry deposition is controlled not only by surface characteristics, but by meteorological conditions. To understand O_3 dry deposition over vegetated surfaces, it is practical to study the canopy resistance directly. Based on the theory of the big-leaf dry deposition model, the effects of the aerodynamic resistance R_a, and the quasi-laminar resistances R_b, which are determined by meteorological conditions, are small and can be excluded from the total deposition velocities (Fowler et al., 2001). The canopy resistance, R_c, can then be derived from the observed deposition velocity (V_d):

$$R_c = \frac{1}{V_d} - R_a - R_b. \qquad (1)$$

Observed dry deposition flux, the concentration of O_3 and meteorological measurements (i.e., friction velocity u_* and stability z/L, L is the Monin–Obukhov length) are used in Eq. (1) for calculating V_d, R_a and R_b and thus to determine the observed R_c. R_a and R_b are calculated using formulas described in Padro (1996).

To compare the magnitude of the different canopy resistance components, R_c can be decomposed according to

$$\frac{1}{R_c} = \frac{1 - W_{st}}{R_{st}} + \frac{1}{R_{ns}}, \quad (2)$$

where R_{st} is stomatal resistance, R_{ns} represents resistance for non-stomatal uptake and W_{st} is the fraction of stomatal blocking under wet conditions (Brook et al., 1999).

In our analysis, we assume that R_{ns} equals R_c during the nigttime (due to the very large value of R_{st}). Although there could be some stomatal uptake at night (Musselman and Minnick, 2000), it is not expected to be important for the plant species considered here. Thus, we can examine the processes affecting the canopy resistance by separating the data by day and night and further categorizing the data according to wetness conditions (i.e., dry, high humidity, dew and rain). To study these processes, it is necessary to identify the factors controlling the non-stomatal uptake (R_{ns}). The current big-leaf models (Wesely, 1989; Erisman et al., 1994) parameterize R_{ns} as

$$\frac{1}{R_{ns}} = \frac{1}{R_{ac} + R_g} + \frac{1}{R_{cut}}, \quad (3)$$

suggesting that R_{ns} is controlled by R_g, the ground (or soil) resistance; R_{ac}, the in-canopy aerodynamic resistance; R_{cut}, the cuticle resistance. These can also be the main non-stomatal components included in multi-layer models (e.g., Baldocchi, 1988). Focusing only on nighttime data allows us to study R_{ac}, R_g and R_{cut} more closely and to develop parameterizations for R_{ns}, for dry and wet canopies.

Daytime R_{ns} may be different from nighttime R_{ns}, but the difference is expected to be small, implying that the R_{ns} parameterization developed from night data should be applicable in the day. However, we independently test the parameterization developed from nighttime measurements using the daytime R_c and V_d measurements. The daytime R_c, obtained using this parameterized R_{ns} and R_{st}, calculated according to Zhang et al. (2001a), can then be compared with the observed R_c.

3.2. Data analysis approach

To develop and test the parameterization, the day is defined as 9:00–15:00 and night as $\geqslant$20:00 or $\leqslant$4:00. The day and night data are then further subdivided into different surface conditions defined as

- dry: CW$\leqslant$0.1, RH$<$80%,
- high humidity: CW$\leqslant$0.1, RH$\geqslant$90%,
- dew: CW$\geqslant$0.8, wetted by dew,
- rain: CW$\geqslant$0.8, wetted by rain.

The high RH group was defined because it was found from the available data that: based upon CW measurements, the canopy could still be dry even when the relative humidity (RH) was higher than 90% (CW = 1 represents canopy fully wet). It is worth noting that, from our available data, there is very little difference between R_c values during rain and after rain conditions. Thus, in the present study, the rain condition includes both rain and after rain (if CW$\geqslant$0.8) conditions.

Uncertainties in the measurement of fluxes and concentrations, and thus V_d, can cause errors in calculated R_c. Also, small errors in the measurement of u_* can affect both R_a and R_b, and thus R_c. Careful examination of the derived R_{ns} values under nighttime rain conditions at Sand Flats (mixed forest site) showed that a majority of the half-hourly measurements (129 out of 139) were smaller than $800\,s\,m^{-1}$. Seven measurements were between 800 and $2300\,s\,m^{-1}$ and one was $6500\,s\,m^{-1}$. This large value suggests that there were measurement errors or possibly a very uncommon condition. Uncertainties or error may be larger when u_* is small. For example, measured eddy fluxes of scalars are typically considered to be unrealistic for very small friction velocities. Shallow drainage flows, difficulties in measurement in light winds and atmospherically stable conditions contribute to this difficulty. To avoid misleading results, measurements associated with the smallest and largest u_* values (top and bottom 1–3%, depending on condition and site) were not included in the analysis when obtaining mean R_c values. This will not change the median, but does change the mean, both of which are given in the results. At each step of the analysis, a separate analysis was also done for larger friction velocity conditions (e.g., largest 60–70% u_*) to ensure the representatives of the conclusions drawn from using the full range of u_* values. Also, to avoid misleading results, data for any specific condition (i.e., dew, rain, etc.) having less than five measurements were not included.

4. Nighttime data and R_{ns} parameterization

4.1. Nighttime results

Table 1 is a summary of R_c values calculated from Eq. (1) using observed V_d, u_* and z/L. For comparison purposes, median values of R_c for all four conditions are presented in Fig. 1a. The frequency distribution of R_c for the mixed forest and soybean sites are presented in Figs. 1b and c by surface condition. R_c was largest under dry conditions for all five vegetation types. Dew, rain and high RH reduced R_c compared to dry conditions. R_c values under dew conditions only differed slightly from those under rain conditions for mixed forest, corn and pasture sites. For the other two sites, R_c under dew

Table 1
Observed nighttime canopy resistance ($s\,m^{-1}$) for O_3

Site	Dry				High humidity				Dew				Rain			
	Med	Ave	Std	*N*	Med	Ave	Std	*N*	Med	Ave	Std	*N*	Med	Ave	Std	*N*
Mixed forest	970	1375	1056	122	226	367	451	39	244	333	282	113	281	332	209	125
Deciduous forest	1831	2275	1656	193	711	1063	870	33	1055	1578	1508	261	397	628	613	122
Corn	1332	1347	615	23					308	474	487	132	391	409	114	7
Soybean	735	787	257	26	367	715	864	75	248	533	777	183	137	168	104	45
Pasture	823	1037	639	26	725	1242	1177	30	571	879	796	138	675	800	487	40

Med, Ave and Std represent median, average and standard deviation, respectively. *N* is the number of samples available for the specific conditions.

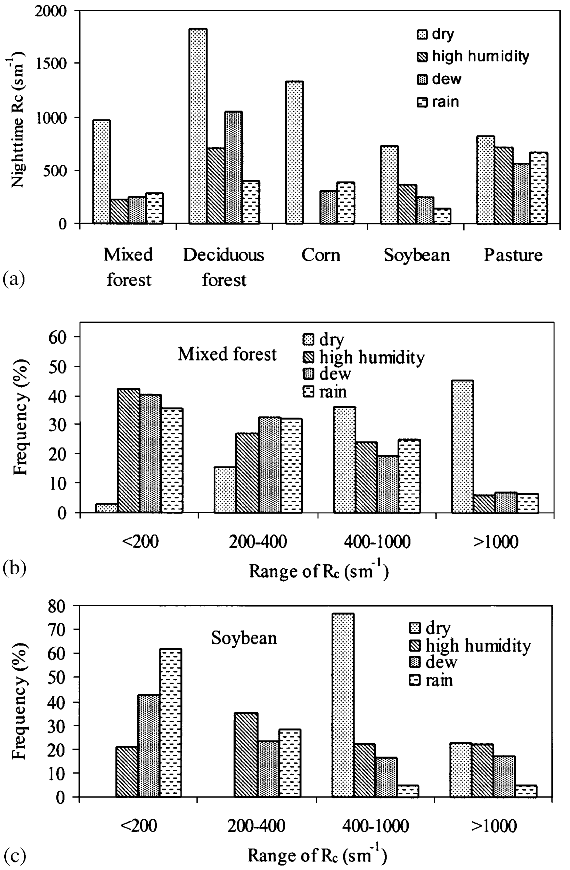

Fig. 1. (a) Median values of observed nighttime canopy resistance (R_c) under dry, high humidity, dew and rain conditions for five sites; (b) frequency distribution of R_c for Sand Flats (mixed forest); and (c) frequency distribution of R_c for Nashville (soybean).

conditions were higher than under rain conditions. One surprising result is that under high humidity conditions, R_c was found to be as small as, if not smaller than, when dew or rain occurred. This suggests that plant surfaces have a small amount of liquid water when RH is high. The only exception was the soybean site, where R_c for high humidity conditions (median value $367\,s\,m^{-1}$) was higher than for dew ($248\,s\,m^{-1}$) and rain conditions ($137\,s\,m^{-1}$). However, most of the measurements during high humidity conditions were collected in June and early in July when the leaf area index (LAI) was smaller than 1. Likewise, all the rain samples were obtained during 3 days (23–25 July) when the LAI was around 4. Thus, some of the differences in R_c for this site could have been caused by the temporal changes in LAI during the measurement period. The frequency distribution plot shows that for mixed forest more than 60% data samples have R_c values smaller than $400\,s\,m^{-1}$ under humid, dew and rain conditions, but only 20% under dry conditions. Over soybeans, more than 60% of the humid data, 70% of the dew data, 90% of the rain data and none of the dry data had R_c values smaller than $400\,s\,m^{-1}$. Similar behaviour was observed over the other vegetation types.

Fig. 2 is a plot of R_c versus RH for dry canopies (including the full range of RH but not dew or rain) during the night. For the mixed forest, corn and soybean, R_c decreases rapidly with increasing RH. For the deciduous forest, R_c did not decrease as rapidly with increasing RH, and over the pasture canopy resistance did not change much with RH. Although there is considerable scatter in the relationships, there was a clear tendency for smaller and less variable R_c for $RH \geqslant 95\%$. The exponential relations shown in Fig. 2 provide the strongest correlation coefficient between R_c and RH compared to other fits to the data (i.e., linear, power). Separate plots for limited ranges of RH (i.e., $RH < 60\%$, $RH \geqslant 80\%$, $RH \geqslant 90\%$) show the same tendency of R_c with increasing RH, but the best fit formulas and correlation coefficients varied slightly compared to those shown in Fig. 2. In addition, even when cases with smaller and potentially more uncertain u_* were neglected ($u_* < 0.3\,m\,s^{-1}$ for forests and $u_* < 0.1\,m\,s^{-1}$ for elsewhere) the results were similar to Fig. 2.

Fig. 3 shows R_c versus u_* for dry conditions for all five sites. R_c values tended to be smaller when u_* was larger.

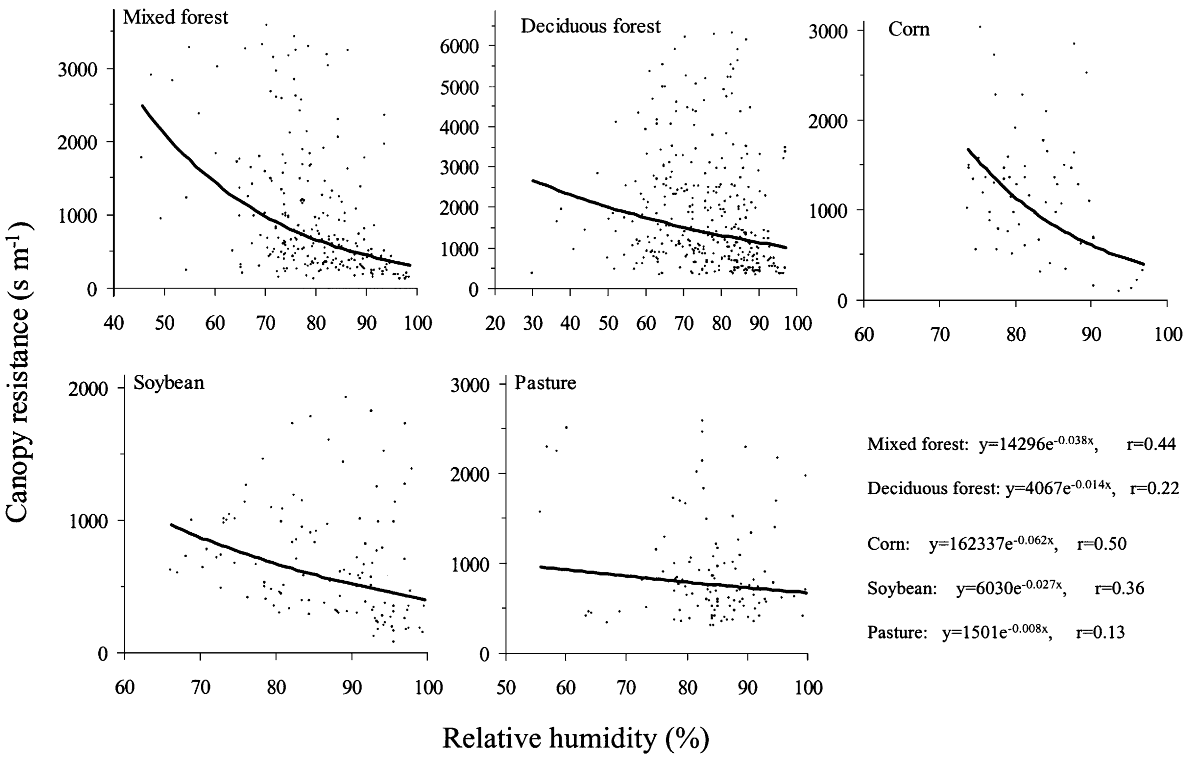

Fig. 2. Observed nighttime canopy resistance (R_c) versus relative humidity (RH) under dry conditions for five sites.

Large u_* values represent strong turbulence which can effectively transport O_3 down to the lower part of the canopy and the soil surface below the canopy (Hicks et al., 1989), thus enhancing uptake. During other conditions (high humidity, dew and rain), the situation was more complex because R_c was also affected by RH and wetness. Nonetheless, R_c was usually smaller when u_* was larger (figures not shown here), except for humid and rain conditions over soybean and rain conditions over pasture. Lamaud et al. (2002) also found that nighttime surface conductance (the reverse of surface resistance) for O_3 over a pine forest in Europe was higher when u_* was larger. The power relationships shown in Fig. 3 gave the strongest correlation coefficient compared to all other possible relationships. A separate analysis using only larger u_* values (as above) produced similar results. Note that 50% of the data had u_* values larger than $0.3\,\mathrm{m\,s^{-1}}$ for the mixed forest, but only 34% for the deciduous forest. The relationship between R_c and u_* for these large u_* cases are also shown in Fig. 3. For the other three sites (low canopy), most data have u_* values smaller than $0.3\,\mathrm{m\,s^{-1}}$ due to small roughness length and calmer conditions at night. Nevertheless, by excluding data with $u_* < 0.1\,\mathrm{m\,s^{-1}}$ the R_c to u_* relationships were very similar to those obtained using all the valid measurements.

The measurement data covered much of the growing period for most sites, allowing an investigation of the relationship between R_c and LAI. For most sites R_c increased with LAI under dry condition at night, but decreased with LAI under all other nighttime conditions. The increase of R_c with LAI can be explained by the in-canopy aerodynamic resistance (R_{ac}). A larger LAI may cause larger R_{ac} for high canopies (Erisman et al., 1994). The decrease of R_c under all other conditions implies that the decrease in cuticle resistance due to humidity and wetness dominated over the increase in R_{ac}, especially for canopies with more leaf area (large LAI). The correlation coefficient between R_c and LAI is not as large as that between R_c and u_*, implying less dependence of nighttime R_c on LAI than on u_*. The power relationship provided the best fit as measured by the correlation coefficient. A separate analysis based upon larger u_* values (as above) lead to similar R_c to LAI relationships. It is worth pointing out that the seasonal variation in R_c was small and could be explained mostly by the variation in LAI.

4.2. Parameterization of R_{ns}

The results discussed above indicate that the non-stomatal resistance, R_{ns}, is influenced by u_*, LAI, RH

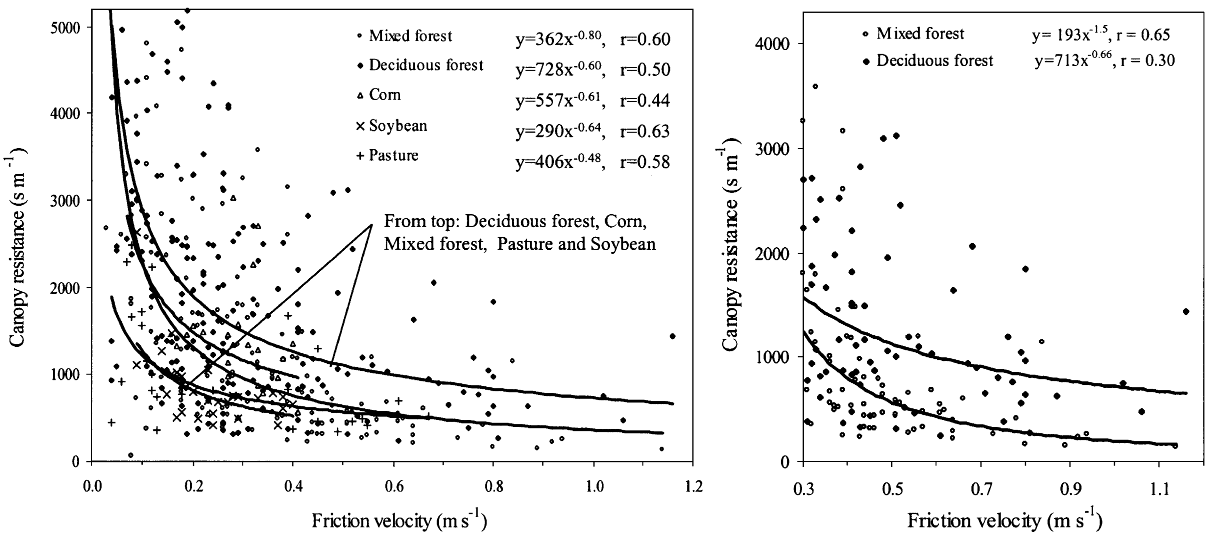

Fig. 3. Observed nighttime canopy resistance versus friction velocity under dry conditions: (a) for 5 sites using all u_* data; and (b) for two forest sites using larger u_* data.

and canopy wetness. The amount of scatter in Figs. 2 and 3 suggests that there are likely other unknown factors involved, such as chemical reactions on surfaces and/or surface wetness. For example, for most of the five sites, R_c was usually smaller when O_3 concentrations were smaller. However, the information needed to understand surface chemistry is not available. Thus, a simple parameterization only including factors available in the present data (i.e., RH, LAI, u_*, wetness) and expected to be available in the future is all that can be justified.

The theoretical basis for including u_* to parameterize R_{ns} can be found from the past multi-layer model framework (Baldocchi, 1988). In-canopy aerodynamic resistance (R_{ac}) and leaf boundary layer resistance (R_b) need to be considered for transporting pollutants onto individual leaves and underlying soil surfaces. R_{ac} is smaller when u_* is larger (Fig. 3) and when LAI is smaller. Our findings are consistent with this. Bulk R_{cut} is smaller under higher RH (Fig. 2), larger LAI and larger u_* (Fig. 3) conditions. Wet canopies are expected to have similar R_{ac} values compared to dry canopies, but cuticle resistance will be different. Given this physical and theroretical interpolation and the relations discussed above, numerical sensitivity tests were undertaken to derive formulas that are applicable to all five sites and all surface conditions. The objective of these tests was to determine the formula (parameterization) leading to the strongest correlation with the measured R_{ns} values and the smallest bias in median and mean values. The result was that R_{ns} for dry (including the full range of RH) and wet (dew and rain) canopies should be parameterized separately according to

For dry canopies,

$$\frac{1}{R_{ns}} = \frac{1}{R_{ac0}u_*^{-2}\,\mathrm{LAI}^{0.25} + R_{g0}} + \frac{1}{R_{cut0}\,\mathrm{e}^{(-0.03RH)}\,\mathrm{LAI}^{-0.25}u_*^{-1}}. \tag{4}$$

For wet canopies,

$$\frac{1}{R_{ns}} = \frac{1}{R_{ac0}u_*^{-2}\,\mathrm{LAI}^{0.25} + R_{g0}} + \frac{1}{R_{cut0}\,\mathrm{LAI}^{-0.5}u_*^{-1}}, \tag{5}$$

where R_{ac0}, R_{g0} and R_{cut0} are reference values for in-canopy aerodynamic resistance, soil resistance and cuticle resistance, respectively. Units are $\mathrm{s\,m^{-1}}$ for resistance, $\mathrm{m\,s^{-1}}$ for u_*, percentage for RH and $\mathrm{m^2\,m^{-2}}$ for LAI. The reference values are expected to change only slightly depending on plant species and season since most other factors (friction velocity, LAI, humidity and canopy wetness) are already explicitly considered in Eqs. (4) and (5). The first term on the denominator on the right-hand side contains a new parameterization for R_{ac} ($R_{ac} = R_{ac0}u_*^{-2}\,\mathrm{LAI}^{0.25}$). This is similar to Erisman et al. (1994) but differs in that the new R_{ac} depends even stronger on u_* (i.e., power of 2 versus 1).

The second term in Eqs. (4) and (5) represents cuticle uptake, which is equivalent to the overall effect of in-canopy aerodynamic resistance and quasi-laminar resistances to individual leaves and the subsequent leaf cuticle resistance. One important factor that is missing in Eqs. (4) and (5) is the canopy structure, which is likely to vary by type of canopy and season. Nonetheless, these equations are expected to be an improvement over most existing big-leaf model parameterizations (Wesely, 1989;

Zhang et al., 2002) because they only implicitly considered the factors included in Eqs. (4) and (5). Note that in these equations R_{ac0} is treated the same for dry and wet canopies, while consistent with physical expectations, R_{cut0} is treated differently. R_{g0} is likely to be different for dry and wet soils, but this process cannot be quantified given the data available at the present time. However, we expect that O_3 deposition will have less dependence on surface soil moisture compared to SO_2 (Meyers and Baldocchi, 1993).

4.3. Comparison of nighttime parameterized R_{ns} with observed R_c

In order to show how well Eqs. (4) and (5) fit the data, Fig. 4 compares the parameterized R_{ns} (from Eq. (4)) with observed nighttime R_c (from Eq. (1)) for dry canopies (including the full range of RH), with the assumption of $R_c = R_{ns}$ during nighttime. Th corn site is not shown due to the small number of dry canopy measurements. Statistical results associated with the data in Fig. 4 and the values determined for the parameters R_{ac0}, R_{g0} and R_{cut0} are listed in Table 2 for each site. The parameterized R_c values are in reasonably close agreement with the observed nighttime R_c values. Approximately 80% of the estimates are within a factor of 2 of the observed values. The median and mean values of the parameterized R_{ns} are mostly within 10% of the observed values for all four sites. The results for Nashville (soybean) are not as good as for other sites due to the rapid change of the canopy structure during the measurement period

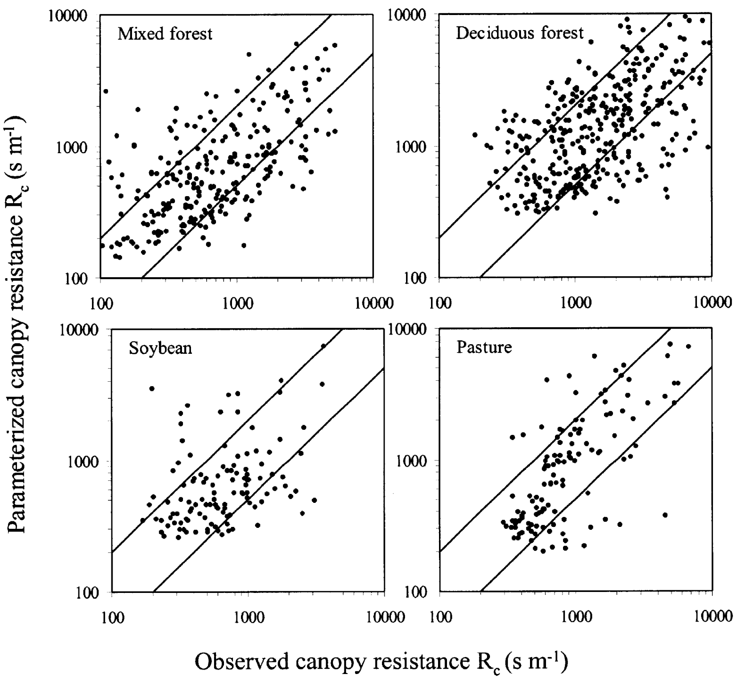

Fig. 4. Parameterized and observed nighttime canopy resistance for dry canopies for four sites. Two straight lines represent a factor of 2.

Table 2
Parameterized (P) and observed (O) nighttime canopy resistance R_c ($s\,m^{-1}$) and related input parameters for Eqs. (4) and (5)

Site	Dry canopy								Wet canopy						
	P_{Med}	P_{Ave}	O_{Med}	O_{Ave}	r	R_{cut0}	R_{g0}	R_{ac0}	P_{Med}	P_{Ave}	O_{Med}	O_{Ave}	r	R_{cut0}	R_{g0}
Mixed forest	596	941	635	1074	0.63	4000	200	100	236	340	272	332	0.37	200	200
Deciduous forest	1281	1800	1389	2075	0.51	6000	200	250	707	1088	723	1275	0.63	400	200
Soybean	550	865	647	839	0.46	5000	200	10–40	273	393	213	461	0.46	50	100
Pasture	873	1344	766	1238	0.69	4000	200	50	673	856	594	861	0.59	200	200

P_{Med} and P_{Ave} are median and averaged parameterized values, respectively. O_{Med} and O_{Ave} are median and averaged observed values, respectively. r is the correlation coefficient between parameterized and observed R_c data.

(Meyers et al., 1998). From the R_{ac} values listed in Table 2 we can see that high canopies (forests) were found to have a larger in-canopy aerodynamic resistance compared to lower canopies.

Fig. 5 shows the comparison of parameterized R_{ns} (Eq. (5)) with observed R_c for wet canopies. The related input parameters and statistical results are also listed in Table 2. Again, the parameterized estimates of R_{ns} are reasonably close to the observed R_{ns}, although the agreement is not as good as for dry conditions. This implies that O_3 dry deposition under wet conditions is more complex. In particular, the correlation between parameterized and observed R_c for nighttime wet conditions is not as large as for dry canopies for mixed forest and pasture, implying that there are other factors that have not been included in Eq. (5). These other factors may be related to differences in chemistry, precipitation and/or dew events, etc. However, overall the median values of the parameterized R_c are reasonably close to the observed values.

5. Daytime data analysis

5.1. Daytime results

Table 3 presents a statistical summary of the observed daytime R_c values. For the two forest sites and the

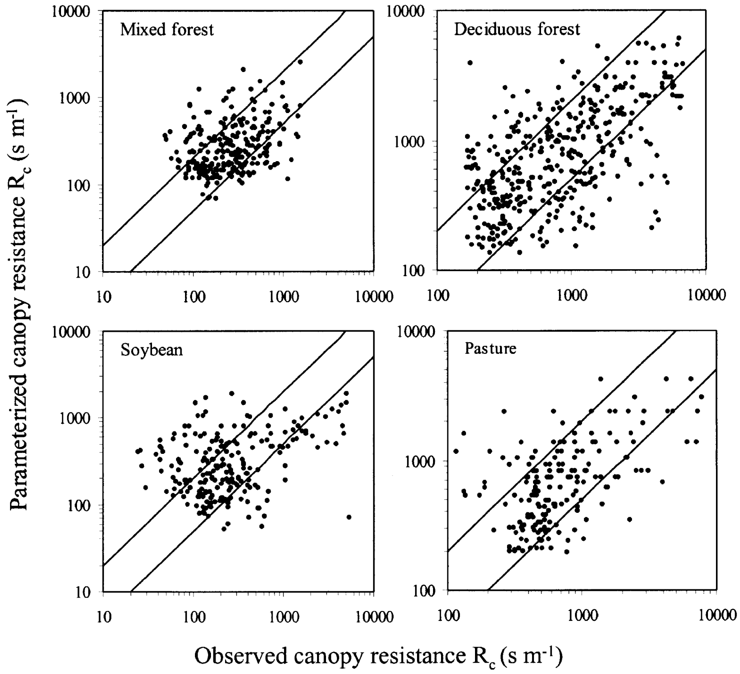

Fig. 5. Parameterized and observed nighttime canopy resistance for wet canopies for four sites. Two straight lines represent a factor of 2.

Table 3
Observed daytime canopy resistance ($s\,m^{-1}$) for O_3

	Dry				High humidity				Rain			
Site	Med	Ave	Std	*N*	Med	Ave	Std	*N*	Med	Ave	Std	*N*
Mixed forest	136	150	63	501	87	95	32	33	108	121	45	35
Deciduous forest	127	179	139	440	91	99	33	34	112	141	64	55
Corn	240	367	329	147								
Soybean	217	210	119	372	67	72	26	12	89	89	26	26
Pasture	197	208	65	308	210	257	123	12	518	523	129	9

Med, Ave and Std represent median, average and standard deviation, respectively. *N* is the number of samples available for the specific conditions.

soybean field, the R_c values under rain and high humidity are smaller compared to dry conditions. This is caused by the increased O_3 uptake by wet cuticles. Under rain conditions R_c is larger than under humid conditions, implying reduced stomatal uptake when rain occurs. For the pasture, the R_c for rain and humid conditions is actually larger than for dry conditions. This may be due to changes in LAI with season since most of the nine rain samples for this site were obtained during 1 day, 20 April, when LAI was small. It may also be due to stomata blocking under wet conditions. However, overall it appears that high humidity, dew and rain enhances O_3 deposition based on the mean and median values listed in Table 3.

5.2. Evaluation of stomatal blocking under wet conditions using daytime data

Daytime O_3 dry deposition under dry conditions is believed to be controlled by stomatal uptake, although a recent study suggests that non-stomatal uptake may be more important than stomatal uptake (Fowler et al., 2001). For wet conditions, some models have assumed that the stomata would be fully or partially blocked, so stomatal resistance was adjusted by increasing it by a factor of 2 or 3 (Wesely, 1989; Brook et al., 1999; Zhang et al., 2002). This assumption has not been verified. Therefore, we compared modelled and measured R_c for daytime wet conditions.

Eqs. (2), (4) and (5) were applied to estimate R_c with R_{st} calculated using a two-big-leaf stomatal resistance sub-model (Zhang et al., 2001a, 2002). Observed daytime R_c values were obtained from Eq. (1). First, we compared the modelled (parameterized) estimates of R_c with observed R_c under dry conditions. The values used for the unknown input parameters (e.g., minimum stomatal resistance) were constrained to be within a reasonable range compared to published information and to result in good agreement between estimated and observed R_c. Then we used these same input parameters to estimate R_c for wet canopies with W_{st} in Eq. (2) set to zero. The difference between these estimations and the observations were assumed to be indicative of the potential importance of W_{st}.

Table 4 lists the statistical results for parameterized and observed R_c for dry and wet canopies. Stomatal resistances were computed with a minimum stomatal resistance of $220\,s\,m^{-1}$ for mixed forest, $200\,s\,m^{-1}$ for deciduous forest and pasture and $180\,s\,m^{-1}$ for soybean. The agreement between the parameterized and observed mean and median R_c for dry canopies for four of the sites listed in Table 4, suggests that the input parameters selected for the stomatal resistance sub-model were reasonable. Approximately 80% of estimates were within a factor of 2 of the observed values.

In contrast, under wet conditions, the parameterized estimates of R_c were larger than the observed values (typically 50%) for three of the sites. The only exception was the pasture site, for which the parameterized R_c was smaller than the observed R_c. This suggests that stomatal blocking is unimportant since a non-zero value for W_{st} would increase the differences. The increase in R_c is a result of the small solar radiation values used in the model when conditions were wet (see Table 4) since the model for R_{st} is very sensitive to solar radiation (Baldocchi, 1988; Hicks et al., 1987; Wesely, 1989; Padro et al., 1991; Erisman et al., 1994; Zhang et al., 2001a). The average daytime solar radiation values were $>600\,W\,m^{-2}$ for all sites when conditions were dry, while the average daytime solar radiation during wet conditions (mostly rain conditions) was about $100\,W\,m^{-2}$. While these results suggested that W_{st} is 0 for most rain conditions, because O_3 uptake is reduced sufficiently due to closing stomata, there may be some exceptions. For example, morning dew or clear sky immediately after falling rain, when R_{st} is small because of relative strong solar radiation, uptake maybe inhibited due to partially or fully blocked stomata.

Recall that with W_{st} set to zero the R_c parameterization produces values that are too large (Table 4). This suggests that the R_{st} model is not reliable under low solar radiation with wet canopies or that R_{ns} from nighttime data is not approriate for daytime wet conditions. Fowler et al. (2001) suggested that for dry canopies the daytime R_{ns} may be smaller than nighttime R_{ns} due to higher temperatures and solar radiation during the day. This behaviour could also apply to wet canopies, but more studies are needed since it has thus

Table 4
Parameterized (P) and observed (O) daytime canopy resistance R_c ($s\,m^{-1}$), and observed solar radiation, SR ($W\,m^{-2}$)

Site	Dry canopy					Wet canopy				
	P_{Med}	P_{Ave}	O_{Med}	O_{Ave}	SR	P_{Med}	P_{Ave}	O_{Med}	O_{Ave}	SR
Mixed forest	116	126	126	146	611	172	185	108	121	91
Deciduous forest	130	142	122	172	604	162	216	112	141	79
Soybean	150	163	182	190	682	183	194	89	89	93
Pasture	181	190	203	217	695	306	320	518	523	121

far only been observed in one data set of measurements of R_c and calculated R_{st} of one location. Although aqueous phase reactions within thin liquid layers or leaf surfaces during the day could be different compared to the night, which could cause day–night difference in R_{ns}, we will assume Eqs. (4) and (5) apply at all times.

6. Evaluation of the O_3 dry deposition parameterization using all data

In order to assess how well the new R_{ns} parameterization performs along with removal of the stomatal blocking assumption (i.e., $W_{st} = 0$), we estimated deposition velocity for all time periods at four of the sites. Note that more than 60% data (dawn, day and dusk) were not used for model development, thus providing an independent test, albiet a relatively qualitative test, for Eq. (5). Note daytime measurements cannot be used to evaluate R_{ns} for dry conditions (i.e., Eq. (4)) because R_{st} is much smaller and is the controlling factor in the model. Statistical results, including a separate evaluation for wet periods, are given in Table 5. The agreement in mean values together with the relatively high correlation coefficients (Table 5) suggest that the model improvements presented in this paper should provide more realistic V_d values compared to earlier parameterizations (Wesely, 1989; Meyers et al., 1998; Brook et al., 1999; Finkelstein et al., 2000; Zhang et al., 2002).

Fig. 6 shows the observed mean diurnal cycle of half-hourly V_d for wet canopies along with the modelled estimates. On average, the agreement is closest at night. This is not surprising since nighttime R_{ns} was optimized using the same measurements. The slight underestimation of V_d during some daytime hours (deciduous forest, early morning for mixed forest, noon for soybean site) is mostly a result of a large R_c which could be due to either R_{st} or R_{ns} or both. Further research is needed to determine which of these factors is most responsible. There is a large overestimation of V_d during some daytime hours (late afternoon for soybean and pasture). However, the number of measurements was small (1 or 2) for most of these hours. For example, there was a short period of rain at 16:00 on Julian day 121 at the pasture site, but the canopy was kept wet from 16:00 to 20:00. The friction velocity during this period was around $0.5\,\mathrm{m\,s^{-1}}$ (Fig. 7), leading to a relatively small R_{ac} and R_{cut} (Eq. (5)) and thus, a relatively high V_d ($>0.5\,\mathrm{cm\,s^{-1}}$). However, the observed V_d was $<0.20\,\mathrm{cm\,s^{-1}}$ during this time period. One possible reason for the low observed V_d relative to the model estimates could have been that the lower part of canopy could have been dry since the wetness was only measured at the top of the canopy. The new parameterization may thus overestimate V_d under these types of situations. To solve this problem, the whole canopy could be divided into two portions, dry and wet, as has been done in some dry deposition models (Padro et al., 1991; Brook et al., 1999; Zhang et al., 2002), but then it would be necessary to estimate the relative proportion of dry and wet surfaces.

Comparing the diurnal pattern of friction velocity during wet conditions (Fig. 7) with V_d values (Fig. 6) shows that they were correlated. This is not surprising since the estimated stomatal resistances (controlled by solar radiation) are at least several times larger than the estimated cuticle resistance (controlled by friction velocity) for wet canopies. On the contrary, stomatal resistance are much smaller than cuticle resistance for dry canopies. Thus, in general, it is clear that in our new parameterization, daytime O_3 deposition to dry canopies is controlled by stomatal uptake (as before) while for wet canopies, cuticle uptake is the controlling factor.

7. Summary and conclusion

Ozone dry deposition measurements over five different canopies (mixed forest, deciduous forest, corn, soybean and pasture) were used to study the non-stomatal uptake and the effect of wetness on O_3 deposition. It was found that high humidity, dew and rain can all decrease canopy non-stomatal resistance (most possibly by altering cuticle uptake) compared to dry canopy conditions. The non-stomatal uptake is affected by friction velocity, relative humidity, canopy wetness and LAI. There may also be dependence upon

Table 5
Parameterized (P) and observed (O) deposition velocity ($\mathrm{cm\,s^{-1}}$)

Site	All data					Wet canopy				
	P_{Med}	P_{Ave}	O_{Med}	O_{Ave}	r	P_{Med}	P_{Ave}	O_{Med}	O_{Ave}	r
Mixed forest	0.52	0.50	0.45	0.51	0.66	0.41	0.44	0.40	0.47	0.52
Deciduous forest	0.31	0.36	0.28	0.40	0.75	0.20	0.26	0.24	0.31	0.68
Soybean	0.33	0.35	0.34	0.43	0.43	0.34	0.42	0.32	0.39	0.61
Pasture	0.33	0.31	0.25	0.27	0.63	0.15	0.20	0.15	0.16	0.25

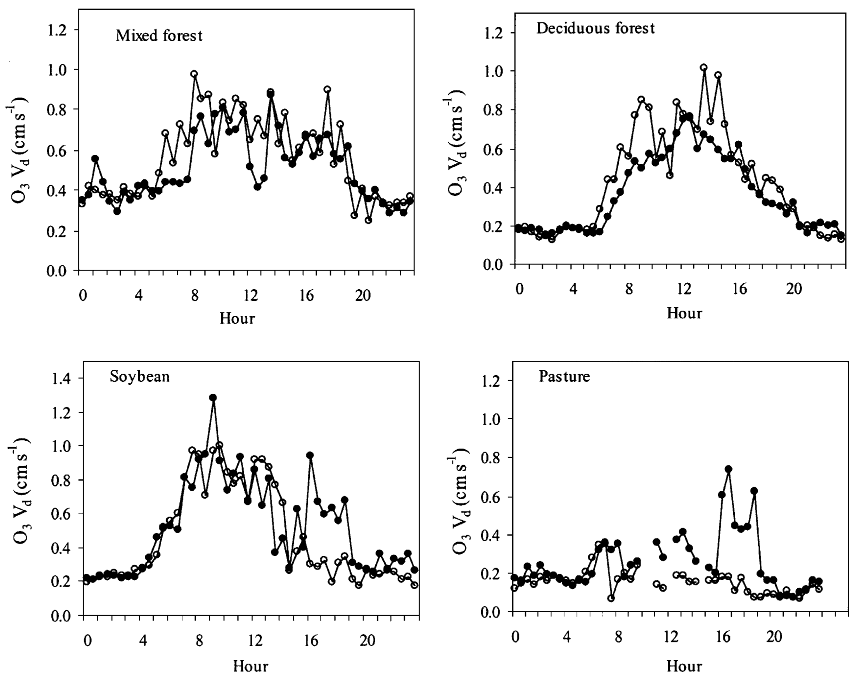

Fig. 6. Average diurnal cycle of parameterized (filled points) and observed (open points) deposition velocities under wet conditions for four sites.

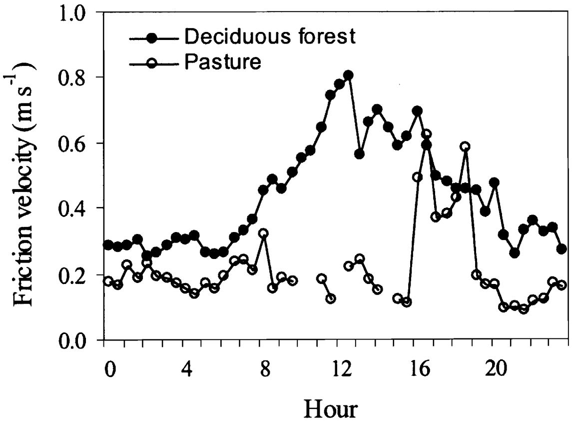

Fig. 7. Average diurnal cycle of friction velocity under wet conditions for two sites.

canopy structure, local chemistry and other factors that were not measured. The data indicate that wetness and high humidity tend to enhance O_3 uptake by cuticles. Based upon these observations, we developed a new paremeterization for non-stomatal uptake that can be applied to different canopy types and for different seasons. The new parameterization is expected to be an improvement over other existing models where a constant value is used for non-stomatal uptake. The median and mean values of the canopy resistance obtained from the new approach are close to the observations (within 10%), although for individual data samples (half-hourly value) the differences can be larger than a factor of 2. The average diurnal cycle of O_3 V_d estimated from the new parameterization is close to observed cycle, for both dry and wet canopies.

Inclusion of a parameter for stomatal blocking during rain conditions was not found to lead to an improvement in the canopy resistance model. This was because in most cases, assuming that the stomatal resistance model is correct, reduced solar radiation and its impact on overall stomatal resistance accounts for all of the observed reduction in V_d during rain. The consideration of stomatal blocking may only be necessary under wet conditions with strong solar radiation (i.e., morning dew, clear sky immediately after rain). Parameterized daytime R_c for wet conditions was found to be larger than observed values. This could have been caused by either the estimated R_{st} being too large or a difference in R_{ns} between day and night.

The present parameterization can be used in air-quality models for studying O_3 deposition and other gaseous species that have similar chemical characteristics. Given our present relatively limited knowledge about all the processes controlling on dry deposition, a well-developed big-leaf model can lead to flux estimates that are as good as some more sophisticated models. The simpler models have the advantage of requiring fewer assumptions regarding input parameters and less computation time, both of which are important for air-quality models. Development of more accurate dry deposition models may be possible if future measurements include solar radiation and wetness at multiple canopy levels and also possibly surface chemical composition (i.e., NO, NO_2, SO_2, H_2O_2, trace metals) at multiple levels. However, research on the effect of surface chemistry will likely require controlled experiments (e.g. chamber) in order to gain more understanding.

Acknowledgements

We greatly appreciate the US EPA (Dr. Peter Finkelstein and colleagues) for sharing their measurement data with us and Dr. Jacob Padro for helpful suggestions. Constructive suggestions from the anonymous reviewers are also greatly appreciated.

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