

Estimation of Atmospheric Deposition Velocities and Fluxes from Weather and Ambient Pollutant Concentration Conditions :

Part I. Application of multi-layer dry deposition model to measurements at north central Florida site

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The dry deposition velocities and fluxes of air pollutants such as SO₂(g), O₃(g), HNO₃(g), sub-micron particulates, NO₃⁻(s), and SO₄²⁻(s) were estimated according to local meteorological elements in the atmospheric boundary layer. The model used for these calculations was the multiple layer resistance model developed by Hicks *et al.*¹⁾. The meteorological data were recorded on an hourly basis from July, 1990 to June, 1991 at the Austin Cary forest site, near Gainesville FL. Weekly integrated samples of ambient dry deposition species were collected at the site using triple-filter packs.

For the study period, the annual average dry deposition velocities at this site were estimated as 0.87 ± 0.07 cm/s for SO₂(g), 0.65 ± 0.11 cm/s for O₃(g), 1.20 ± 0.14 cm/s for HNO₃(g), 0.0045 ± 0.0006 cm/s for sub-micron particulates, and 0.089 ± 0.014 cm/s for NO₃⁻(s) and SO₄²⁻(s). The trends observed in the daily mean deposition velocities were largely seasonal, indicated by larger deposition velocities for the summer season and smaller deposition velocities for the winter season. The monthly and weekly averaged values for the deposition velocities did not show large differences over the year yet did show a tendency of increased deposition velocities in the summer and decreased values in the winter. The annual mean concentrations of the air pollutants obtained by the triple filter pack every 7 days were 3.63 ± 1.92 μg/m³ for SO₄²⁻, 2.00 ± 1.22 μg/m³ for SO₂, 1.03 ± 0.59 μg/m³ for HNO₃, and 0.704 ± 0.419 μg/m³ for NO₃⁻, respectively. The air pollutant with the largest deposition flux was SO₂ followed by HNO₃, SO₄²⁻(s), and NO₃⁻(s) in order of their magnitude. The sulfur dioxide and NO₃⁻ deposition fluxes were higher in the winter than in the summer, and the nitric acid and sulfate deposition fluxes were high during the spring and summer.

Key words : dry deposition velocity, resistance model, deposition flux, triple-filter pack, meteorological elements

1. Introduction

The dry deposition of reactive gases and fine particles from the atmosphere by turbulent transfer and uptake on the earth's surface provides a major mechanism for cleaning the atmosphere and delivering chemical species to surfaces²⁾. These processes restrict the transport distance and lifetime of pollutants as well as control air pollutant con-

centrations in the atmosphere. Therefore, a detailed understanding of these processes of dry deposition is important in order to infer the nature and extent of environmental problems resulting from this form of anthropogenic air pollution³⁾.

Since the concept of estimating dry deposition fluxes by measuring ambient air pollution concentrations and inferring a deposition velocity was devised by Chamberlain in 1953, a large number

of dry deposition studies have been conducted. More recently, aerosol, ozone, and PAN deposition velocity estimates have been reported⁴⁻⁸.

Estimates of the amount of gases and particulate pollutants deposited are of great interest, because dry deposition may exert a large influence on the quality of local ecosystems⁹. The dry deposition of acid components from the atmosphere to the earth's crust and hydrosphere occurs continuously in the absence of precipitation, accordingly, since the annual magnitude is comparable to wet deposition¹⁰, the dry deposition of gases and particles in the air can be estimated using micrometeorological methods¹¹.

Numerous recent studies have indicated that out of the total(wet plus dry) atmospheric deposition, about 30-60% of sulfur and 30-70% of the nitrogen species are a result of dry deposition¹². These significant fractions suggest that over the northeastern United States about one half of the total acid deposition occurs in the absence of rainfall. In addition, the boundary layer concentrations of acid precursors can be modified due to dry deposition. However, these estimates are uncertain, because dry deposition is highly dependent on the local terrain, weather conditions, and sources¹³. Direct dry deposition measurements are difficult to make and apply reliably, plus they often require extensive and expensive instrumentation. To make up for this deficiency, models have been developed that infer removal rates calculated from meteorological parameters. One such model is the multiple layer resistance model developed by Hicks *et al.*¹¹ at the National Oceanic and Atmospheric Administration(NOAA). This is a one-dimensional model that assumes that the removal of a pollutant is the product of an ambient concentration and surface-specific deposition velocity.

The objectives of this paper are to provide data on the concentrations of acidic air pollutants observed at the Carry forest site in north central Florida, analyze the characteristics of this concentration data, and then estimate the atmospheric deposition velocities and fluxes from the weather and ambient pollutant concentration conditions using the Hicks model. It should be noted that validated concentrations and meteorological data were routinely and simultaneously observed at the same location by Allen and Sutton¹⁴.

1.1. Data

The field sampling site at Austin Cary forest is located approximately 15 km northeast(29.75°N, 82.21°W) of Gainesville, Florida. This inland rural site is situated within a two hectare cleared area surrounded by commercial slash pine plantations. In general, the summer seasons are long, warm, and relatively humid at this location. There is little day to day temperature variation. Afternoon temperatures reach 32°C (90°F) or higher with great regularity during the summer, but temperatures of 38°C (100°F) or higher only occur once or twice each year^{14,15}. The summer season, especially, June through September, is the rainy season, which on the average accounts for about half the total annual rainfall. Most of the summer rainfall results from frequent, short duration afternoon or early evening local thunderstorms, which occur on about half of the days in the quarter^{14,16}.

The nature and quality of the atmospheric environmental data collected from July, 1990 to June, 1991 at the Cary forest site are described in detail by Allen and Sutton¹⁴. The dry acid deposition sampling was performed following a combination of the Integrated Forest Study(IFS) and National Dry Deposition Network(NDDN) sampling protocols using triple-filter pack(TFP) systems^{14,16,17}. A filter pack system consisted of three filters mounted in succession. The first filter was 1 μm pore sized Teflon membrane for small(<5 μm) particle collection. The second filter was a 1 μm pore sized Nylon filter that primarily removed nitric acid vapor. The third filter was cellulose impregnated with K₂CO₃ and glycerin, that collected sulfur dioxide. In order to improve the sensitivity and accuracy of these trace gas and particle measurements, an integrated sampling time of one week was used. The air being sampled was drawn through the three filters at two liters per minute for seven days.

At Austin Cary forest, ambient air quality concentration measurements were simultaneously made for ozone(O₃), nitric oxide(NO), nitrogen dioxide(NO₂), nitrogen oxides(NO_x), sulfur dioxide(SO₂), particulate sulfate(P-SO₄), particulate nitrate(P-NO₃), and nitric acid vapor(HNO₃).

The hourly averaged meteorological data observed a 10 m height and included the temperature,

relative humidity, solar radiation, wind speed, wind direction, and standard deviation of the wind direction. The rainfall and surface wetness measurements (Vaisala Model DRD-11 sensor) for the period (7/90 to 6/91) were made near the ground (1m) at the same site.

1.2. Theory

The multi-layer resistance model assumes that biological processes are incorporated into the first generation 'big-leaf' model, as discussed by Hicks *et al.*,¹⁸⁾. The deposition velocity (V_d) is simply computed from the inverse of the total resistance to the transfer of a pollutant using equation (1).

$$V_d = \frac{1}{R_a + R_b + R_c} \quad (1)$$

where R_a is the aerodynamic resistance associated with the atmospheric turbulence, R_b is the quasi-laminar boundary layer resistance that is influenced by the molecular diffusivity of the material being transferred, and R_c is the surface/canopy resistance, which is a function of the environmental and physiological conditions, such as the leaf area index, chemical features, wetness of the surface, and diffusivity of the pollutant^{9,19-23)}. The pathways of resistance to the deposition of the gaseous pollutants and particles are shown in Figure 1.

1.3. Atmospheric Resistance (R_a)

The atmospheric resistance, R_a , illustrated in Figure 1, is computed from :

$$R_a = \frac{1}{\kappa u_*} \left[\ln \left(\frac{z}{z_0} \right) - \Psi_c(z/L) \right] \quad (2)$$

Equation (2) assumes that the pollutant flux is constant in the surface layer. The value z is the height at which the computation is performed, z_0 is the momentum roughness length, $\Psi_c(z/L)$ is the stability correction factor, κ is the von Karman constant, taken as 0.4, and u^* is the friction velocity.

The aerodynamic resistance is controlled by the atmospheric turbulence. The turbulence is measured based on the standard deviation of the wind direction (σ_θ). To a close approximation σ_θ can be written in terms of the cross-wind velocity component (σ_v) as in equation (3).

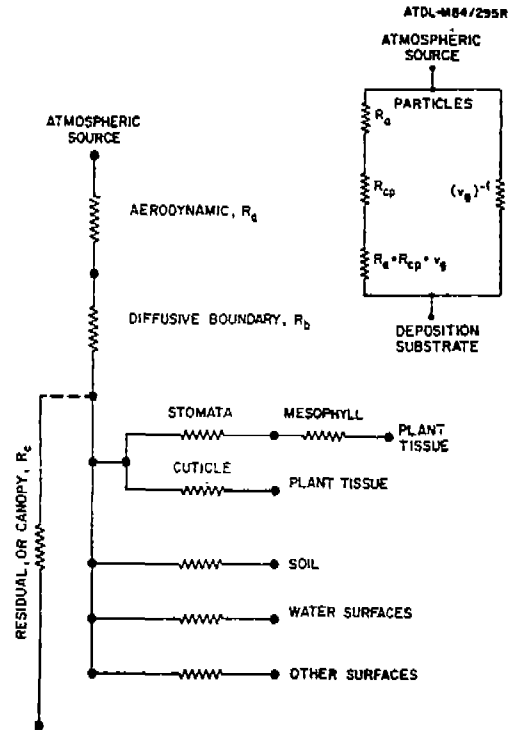


Fig.1. Resistance pathways to gaseous pollutant deposition.

$$\sigma_\theta \approx \sigma_v / u_* = \left[\sigma_v / u_* \right] \left[u_* / u \right] = \kappa \left[\sigma_v / u_* \right] \left[\ln(z/z_0) - \Psi_m(z/L) \right] \quad (3)$$

For stable and neutral conditions, it is assumed that the integrated stability correction factor for momentum $\Psi_m(z/L)$ is the same for all passive materials being transported ($\Psi_c(z/L)$).

Equations (2) and (3) can then be combined to give :

$$R_a \approx \left[\sigma_v / u_* \right]^2 / [u \sigma_\theta^2] \quad (4)$$

In near-neutral and stable stratification, the ratio (Ψ_v / u_*) is about two, however, it increases rapidly after the onset of instability to asymptotically approach a value of three²⁴⁾. Using this simplification, equation (4) is reduced to

$$R_a \approx 4 / [u \sigma_\theta^2]; (\neq \text{neutral and stable}) \quad (5a)$$

$$R_a \approx 9 / [u \sigma_\theta^2]; (\text{unstable}) \quad (5b)$$

1.4. Quasi-laminar boundary layer resistance (R_b)

The second atmospheric resistance R_b is com-

puted from :

$$R_b = \frac{2}{x \cdot u_*} \left(\frac{Sc}{Pr} \right)^{2/3} \quad (6)$$

where Sc is the Schmidt number (ν/D), ν is the kinematic viscosity of the air, and D is the molecular diffusivity of the air pollutant. The Prandtl number (ν/K) for air, $Pr(\approx 0.72)$, is present to account for the fact that the basic observations are primarily related to heat transfer²⁵⁾ and K is the thermal diffusivity of the air.

1.5. Surface/Canopy Resistance(R_c)

Many investigators have suggested that R_c depends on the photosynthetic activity, solar radiation, and surface type of each species that is deposited. Accordingly, canopy resistance is an important factor to be dealt with in deposition phenomena²⁶⁾.

First of all, stomatal resistance, r_{st} , is computed from equation (7), which takes account of photosynthetically active radiation (I_p).

$$r_{st} = r_{st}' \left[1 + \left(\frac{b'}{I_p} \right) \right] / (f_e f_w f_T f_s) \quad (7)$$

where r_{st}' is the constant that depends on the plant species, b' is the empirical constant^{18,27)}, f_e , f_w , and f_T are the correction terms for the effects of humidity, water vapor, and temperature, respectively, and all coefficients are within the range of 0 to 1.0²⁰⁾. f_s is the correction term to allow for differences in the molecular diffusivity between the pollutant of interest and water vapor. f_T is computed according to :

$$f_T = \left[\frac{T - T_e}{T_0 - T_e} \right] \left[\frac{T_h - T}{T_h - T_0} \right]^{B_t}$$

where

$$B_t = (T_h - T_0) / (T_0 - T_e) \quad (8)$$

Here, T_h , T_e are the higher and lower temperatures, respectively, at which the stomata are no longer open, which will vary depending on the plant species¹⁸⁾. T_0 is the temperature at which stomatal exchange is optimized. Other deposition pathways on a plant surface (see Figure 1) are on the cuticle and inside the mesophyll. Once pollutants gases pass the stomata, they have to transfer through the cell membranes. Thus, the total resistance to transfer through the stomatal opening is :

$$r_s = r_{st} + r_{mes} \quad (9)$$

This plant-canopy response modeling can be scaled up to an entire plant canopy, and the scaling can be made relative to the leaf area index (LAI). The net uptake resistance (R_{fol}) for the foliage per unit surface area, is calculated by combining the weighted parallel stomatal resistances of the sunlit (r_{sun}) and shaded (r_{sh}) leaf areas, and the cuticle resistance (r_{cut}). Then

$$R_{fol} = \left[\frac{1}{R_s} + \frac{LAI}{r_{cut}} \right]^{-1}$$

where

$$R_s = \left[\frac{L_s}{r_s} (K \cdot I_{psun}) + \frac{L_{sh}}{r_s} (0.5 I_{psh}) \right]^{-1} \quad (10)$$

$$L_s = [1 - \exp(-K \cdot LAI)] / K, \quad L_{sh} = LAI - L_s$$

K is the extinction coefficient ($0.5/\cos \alpha$), α is the zenith angle, and I_{psun} and I_{psh} are the photo-synthetically active radiances (PAR) on the sunlit foliage and shaded foliage, respectively²⁸⁾. The final canopy resistance, R_c , including the soil resistance (R_{soil}) is given by :

$$R_c = \frac{1}{R_{fol} + R_{soil}} \quad (11)$$

In the case of particulate sulfate and nitrate deposition, the boundary and surface resistances are computed from the experimental techniques parameterized by Wesely *et al.*²⁹⁾.

2. Results And Discussion

The data completeness for the observed hourly meteorological data at Austin Cary forest, Gainesville in north central Florida was 86%. The trends of the hourly, 24 hour average, monthly, and seasonal variations in the V_d 's and deposition fluxes were determined using the Hicks multiple resistance model. The weekly variations in these deposition velocities and deposition fluxes were then compared with the air quality data obtained for the same 7-day periods.

The weekly variations of each meteorological variable observed at Austin Cary forest, FL for the period (7/1/90 to 6/30/91) are displayed in Figure 2, where the week is displayed on the abscissa and the range of each weather element is given by the ordinate axis. The average air temperatures are displayed with normal values in

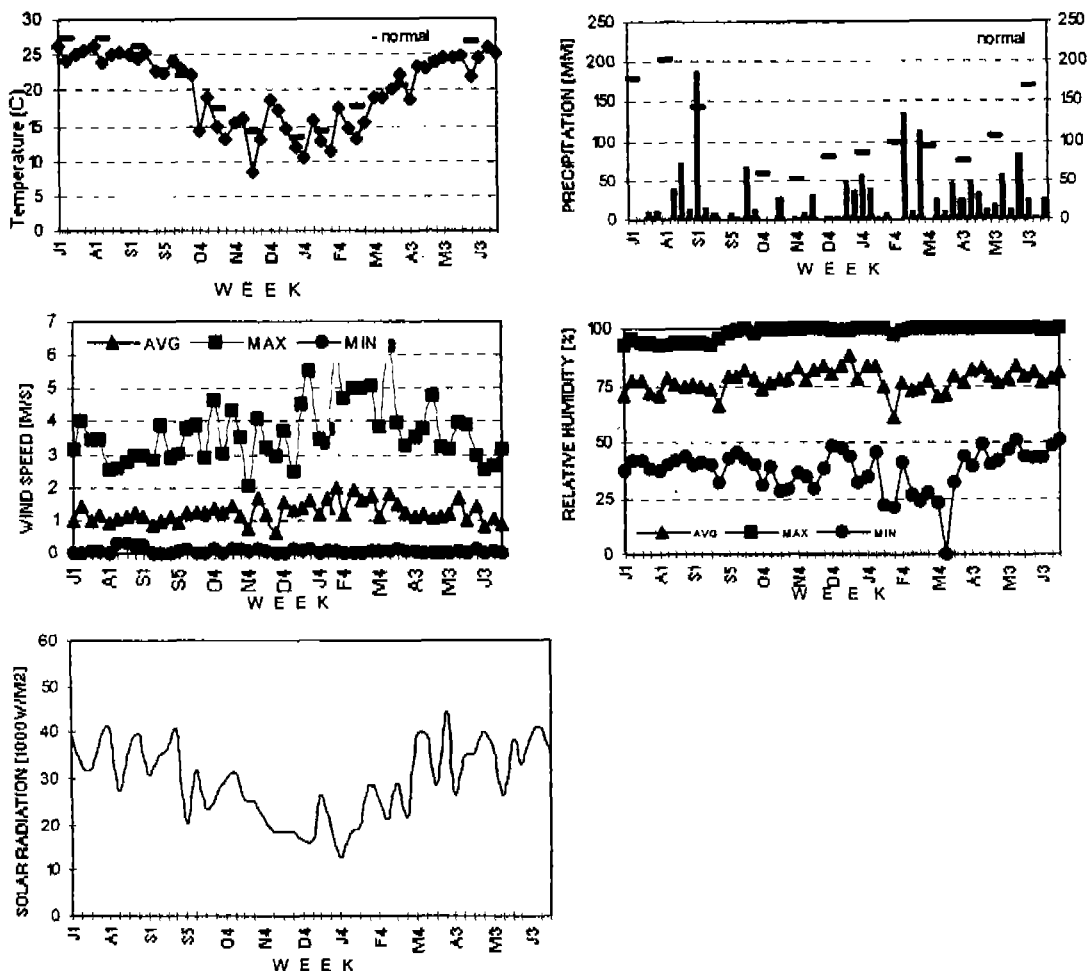


Fig. 2. Variations in local meteorological parameters at Cary forest, FL from July, 1990 to June, 1991.

Figure 2a, which showed a range of 8 °C to 27 °C, a decrease in the winter season(December - February), and an increase in the summer season (April - October). The temperatures in July and August, 1990 were lower than normal. The precipitation was distributed throughout the year, yet was greater in the spring and summer seasons than in the winter. In July and August, 1990, the rainfall was less than normal as was the temperature, thereby suggesting that the ambient air pollutant deposition by washout was small. The average wind speeds and relative humidities, described with weekly maximum and minimum values in Figures 2c and 2d, did not show large differences over the year. High weekly maximum wind speeds and

low weekly minimum relative humidities were seen in the spring. The distribution of solar radiation was similar to that of the temperature, higher during the spring and summer seasons.

The diurnal variations in the dry deposition velocities of the air pollutants(SO₂(g), O₃(g), HNO₃(g), sub-micron particulates NO₃⁻(s), and SO₄²⁻(s)) showed large deposition velocities during strong irradiance in the daytime and small deposition velocities at night, however, the daily mean deposition velocity data were used because the hourly data showed large fluctuations. The variations in the daily mean dry deposition velocities are shown in Figure 3. In the case of sulfur dioxide, the variations in the daily mean

deposition velocities were generally higher in the summer than in the winter. The daily mean deposition velocities for ozone, particulate sulfate, and nitrate showed a marked trend towards higher values in the summer, and these variations appeared to be closely connected with the seasonal variations in the air temperature and irradiation (see Figure 2). In the case of HNO_3 and sub-micron particulates, there were large differences in the magnitudes of the nitric acid and sub-micron particulate deposition velocities, yet their trends were similar. Therefore, the seasonal trends in the daily mean deposition velocities for the air pollutants were generally higher during the spring and summer and lower

during winter.

The monthly averages and medians of the pollutant deposition velocities are presented in Table 1. The monthly average deposition velocity was usually higher than the median value. The pollutant with the largest deposition velocity for the observation period was nitric acid, followed by SO_2 , O_3 , $\text{SO}_4^{2-}(\text{s})$, $\text{NO}_3^-(\text{s})$, and sub-micron particulates in a decreasing order of magnitude. The annual average deposition velocities were 1.20 ± 0.14 cm/s for HNO_3 , 0.87 ± 0.07 cm/s for SO_2 , 0.65 ± 0.11 cm/s for O_3 , 0.090 ± 0.014 cm/s for $\text{SO}_4^{2-}(\text{s})$, and 0.0045 ± 0.0006 cm/s for sub-micron particulates. When compared to the

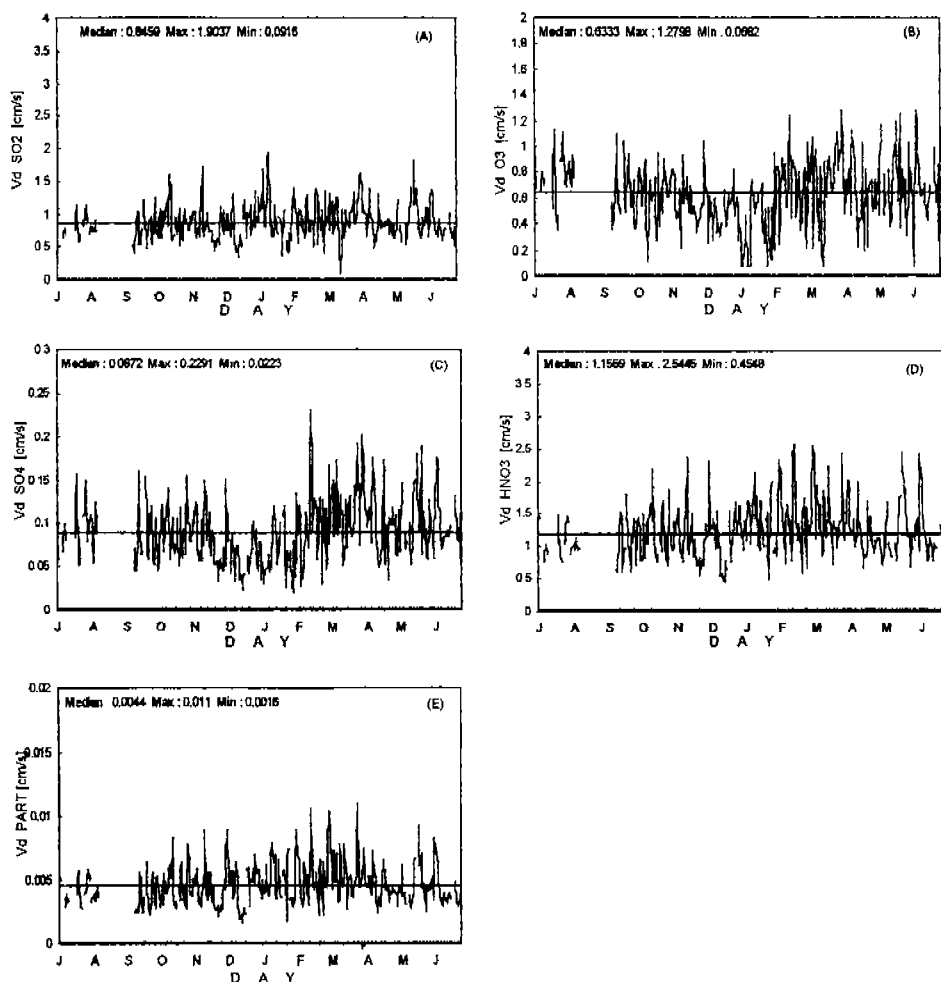


Fig. 3. 24 hour average deposition velocities for SO_2 (A), O_3 (B), SO_4^{2-} (C), NO_3^- (D), HNO_3 (D), and PART (E) at Cary forest, FL from July, 1990 to June, 1991.

deposition velocities reported in previous literature (see Table 2), the values for all the species, except for SO₂ were in the range of the values reported elsewhere, whereas the V_d for SO₂ was larger than the previously suggested values³⁰⁾. The range of annual average deposition velocities for Oak Ridge, TN, Penn State University, PA, and Whiteface Mountain, NY, reported by Wu and Davidson³¹⁾ and obtained using the resistance model of Hicks *et al.*¹⁾ were 0.07 to 0.13 cm/s for SO₄²⁻, 0.18 to 0.33 cm/s for SO₂, and 0.96 to 1.9 cm/s for HNO₃. In this study the V_d for SO₄²⁻(s) and HNO₃ were similar to the latter values yet the deposition velocity for SO₂ was higher than their value. Therefore, since the average SO₂ concentration at Cary forest was higher, the resulting higher

estimated V_d value would then be expected to increase the overall dry acidic deposition flux.

The weekly averaged concentrations of air pollutants obtained by the triple-filter pack sampling method are shown in Figure 4. An analysis of the seasonal variations in the SO₂ and SO₄²⁻(s) concentrations showed that the SO₂ concentrations were lowest whereas the SO₄²⁻(s) concentrations were highest during the summer season. The higher concentrations of SO₄²⁻(s) observed during the spring and summer season were probably strongly related to the chemical reactions involved in the conversion of SO₂ to SO₄²⁻. Conversely, the higher concentrations of SO₂ observed during the winter season were likely due to the slower conversion of SO₂ to SO₄²⁻ at the lower winter temperatures.

Table 1. Monthly mean deposition velocity(V_d) and medians(MED) for July, 1990 to June, 1991 at Cary forest, FL. SD is the standard deviation, PART is the submicron particulate, and the velocity unit is centimeters per second

MON	SO ₂ Vd	MED	O ₃ Vd	MED	HNO ₃ Vd	MED	PART Vd	MED	SO ₄ ²⁻ Vd	MED
JUL	0.8228	0.5706	0.7479	0.2265	1.0738	0.8230	0.0040	0.0032	0.0943	0.0276
AUG	0.7821	0.7723	0.8109	0.6817	1.0008	0.9347	0.0037	0.0035	0.0929	0.0310
SEP	0.7494	0.3978	0.6459	0.2043	1.0095	0.5884	0.0038	0.0024	0.0865	0.0224
OCT	0.8630	0.4750	0.6386	0.1447	1.1997	0.7653	0.0045	0.0033	0.0920	0.0261
NOV	0.8172	0.465	0.5764	0.0719	1.1438	0.6437	0.0043	0.0029	0.0781	0.0229
DEC	0.8084	0.4691	0.4991	0.0740	1.1302	0.7757	0.0043	0.0036	0.0605	0.0284
JAN	0.9745	0.5887	0.3731	0.0726	1.3273	0.9077	0.0050	0.0040	0.0650	0.0320
FEB	0.9291	0.4951	0.6775	0.2074	1.3797	0.9903	0.0054	0.0042	0.0970	0.0342
MAR	0.9240	0.4679	0.7058	0.1685	1.4763	1.2062	0.0057	0.0053	0.1079	0.0431
APR	0.9373	0.5840	0.6980	0.0755	1.2418	0.9545	0.0047	0.0039	0.1053	0.0339
MAY	0.9153	0.6052	0.6907	0.1642	1.2161	0.9188	0.0046	0.0037	0.0997	0.0357
JUN	0.8553	0.5053	0.6945	0.1371	1.1868	0.8810	0.0043	0.0035	0.0996	0.0316
AVG	0.8649		0.6465		1.1988		0.0045		0.0899	
SD	0.0677		0.1119		0.1375		0.0006		0.0144	

Table 2. Estimated deposition velocities for aerosols and gascs(ESE, 1991)

Species	Vd(cm/s)	References
SO ₄ ²⁻	0.1 - 0.2	Sehmel, 1980 ; Sheih <i>et al.</i> 1979 ; Voldner <i>et al.</i> , 1986 ; Wesely and Lesht, 1988 ; Wu and Davidson, 1988
NO ₃ ⁻	0.1 - 0.2	Assumed to be the same as SO ₄ ²⁻
SO ₂	0.2 - 0.4	Sehmel, 1980 ; Sheih <i>et al.</i> , 1979 ; Cadle <i>et al.</i> , 1987 ; Wesely and Lesht, 1988 ; Wu and Davidson, 1988
HNO ₃	1.0 - 2.0	Heubert, 1983 ; Wesely and Lesht, 1988 ; Wu and Davidson, 1988

The annual mean concentrations of $\text{SO}_4^{2-}(\text{s})$ and SO_2 were $3.63 \pm 1.92 \mu\text{g}/\text{m}^3$ and $2.00 \pm 1.22 \mu\text{g}/\text{m}^3$, respectively. These values were much lower than the annual mean concentrations of these species for the entire eastern United States ($2.4 \sim 23.2 \mu\text{g}/\text{m}^3$ for SO_2 , $5.0 \mu\text{g}/\text{m}^3$ for $\text{SO}_4^{2-}(\text{s})$). The annual mean particulate sulfate concentration for Florida was less than $5.0 \mu\text{g}/\text{m}^3$ ³⁰⁾.

The higher concentrations of HNO_3 observed in the summer season of 1990 would normally be expected to be lower due to removal by washout. However, in 1990 the summer rainfall was less than normal. The peak concentration of HNO_3 seen in February was probably due to an increase in the air temperature relative to the other weeks in that same month. The annual mean HNO_3 concentration was $1.03 \pm 0.59 \mu\text{g}/\text{m}^3$, which was lower than those values reported for the east central United States^{30,32)}.

The annual mean $\text{NO}_3^-(\text{s})$ concentration was $0.704 \pm 0.419 \mu\text{g}/\text{m}^3$ and the values were generally higher in the winter season than in the summer, a trend similar to that obtained for sulfur dioxide. The stability of $\text{NO}_3^-(\text{s})$ as a chemical species was affected by the air temperature and relative humidity. Ammonium nitrate (NH_4NO_3) was more stable in the lower winter air temperatures plus

the agricultural activity in spring influenced the generation of NH_3 and NO_3^- .

The annual trend in the weekly averaged SO_2 deposition velocities was not significant, however, the values were generally higher in the summer than in the winter (Figure 5). The variation of the weekly averaged deposition velocities for O_3 and $\text{SO}_4^{2-}(\text{s})$ showed a marked trend toward higher values during the summer season rather than in the winter. Even though HNO_3 and sub-micron particulates are quite different in their magnitude, their deposition velocities both tended to increase in the spring and summer seasons, with a peak in March. This result is consistent with the observations of Meyers *et al.*³³⁾, who showed that HNO_3 deposition velocities peak during the spring and are closely related to a variation in the maximum wind speed.

The weekly average dry deposition fluxes were obtained by multiplying the weekly average concentration and weekly average deposition velocity for each chemical species. This procedure to obtain the pollutant flux can cause a serious error in the estimated flux if the time series for the concentration and deposition velocity are correlated³³⁾. In this study, the correlation coefficient (r) between the two series was calculated to be less

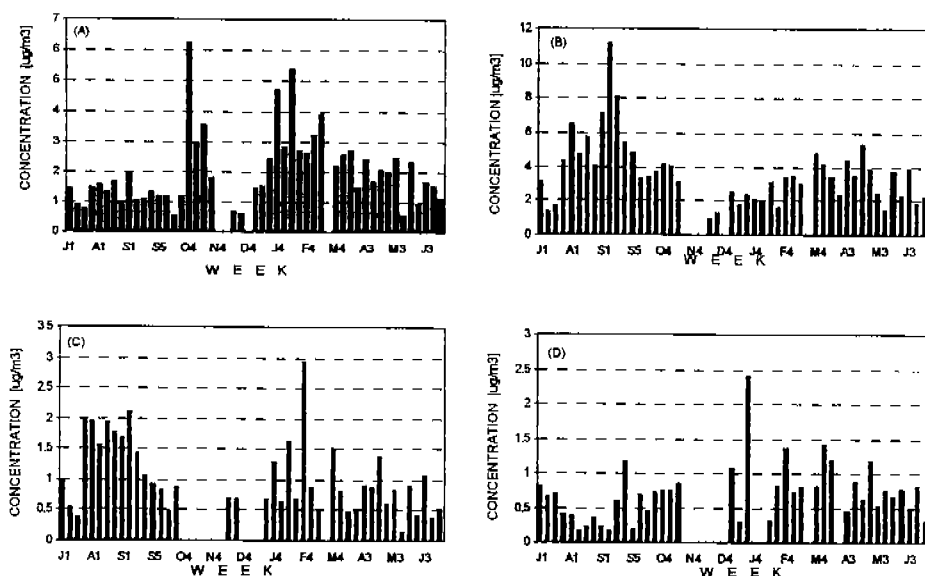
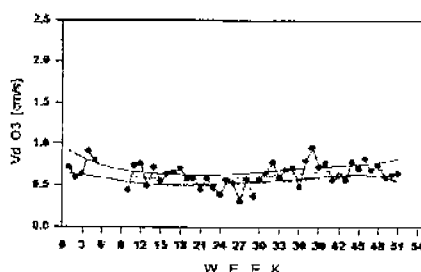
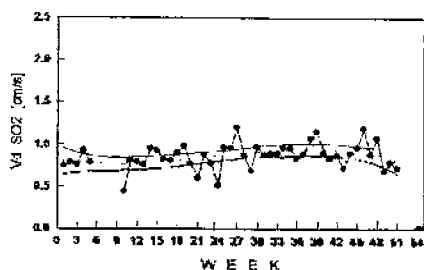
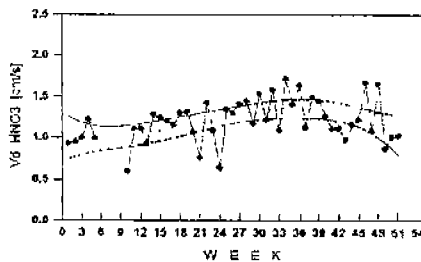
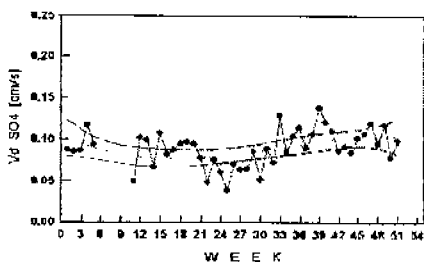


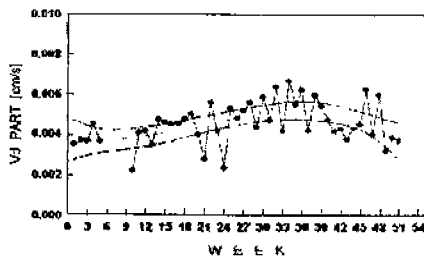
Fig. 4. Weekly concentration variations for SO_2 (A), SO_4^{2-} (B), HNO_3 (C), and NO_3^- (D) at Cary forest, FL from July, 1990 to June, 1991.



$$SO_2: Y = 0.81101 - 0.01264X + 0.00093X^2 - 0.00001X^3, R^2 = 0.16 \quad O_3: Y = -0.81147 - 0.02992X + 0.00109X^2 - 0.00001X^3, R^2 = 0.19$$



$$SO_4: Y = 0.10524 - 0.00386X + 0.00015X^2, R^2 = 0.21 \quad HNO_3: Y = 0.00383 - 0.00006X + 0.00001X^2, R^2 = 0.28$$



$$PART: Y = 0.00383 - 0.00006X + 0.00001X^2, R^2 = 0.28$$

Fig. 5. Weekly deposition velocities for (A) SO_2 , (B) O_3 , (C) SO_4^{2-} and NO_3^- , (D) HNO_3 , and (E) submicron particulates at Cary forest, FL from July, 1990 to June, 1991.

than 0.5.

The weekly pollutant deposition fluxes are shown in Figure 6. The deposition flux of SO_2 was the largest followed by HNO_3 , $SO_4^{2-}(s)$, and $NO_3^-(s)$ in decreasing order of magnitude. The weekly variations in the particulate sulfate and sulfur dioxide deposition fluxes showed that the sulfur dioxide deposition fluxes were highest whereas the particulate sulfate deposition fluxes were lowest during the winter. The nitric acid deposition fluxes, except for certain weeks in February, showed larger values during the spring

and summer. The weekly variations in the $NO_3^-(s)$ deposition fluxes over the year were not as clear as those for sulfur dioxide. Yet, during the winter, the $NO_3^-(s)$ deposition fluxes were high like those for sulfur dioxide. This was to be expected considering that deposition fluxes are more affected by the pollutant concentration than by the deposition velocity. Therefore, at Cary forest site, FL, a concentration dependence would tend to increase the HNO_3 and $SO_4^{2-}(s)$ deposition fluxes during the summer season and the SO_2 and $NO_3^-(s)$ deposition fluxes during the winter season.

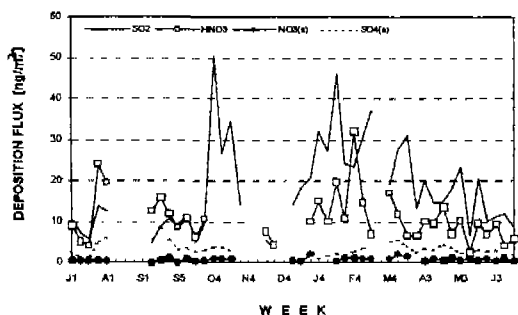


Fig. 6. Weekly deposition fluxes of ambient air pollutants at Cary forest, FL from July, 1990 to June, 1991.

3. Conclusions

The goals of this paper were to analyze the characteristics of acidic pollutant concentrations in rural and ambient air and estimate atmospheric deposition velocities and deposition fluxes from existing atmospheric conditions, such as local weather elements and ambient air quality, using the Hicks model.

The trend in the daily mean deposition velocities for air pollutants is a high deposition velocity during the spring and summer months and a low deposition velocity during the winter. For the study period (7/90~6/91) the pollutant with the largest deposition velocity was nitric acid (HNO_3) followed by SO_2 , O_3 , $\text{SO}_4^{2-}(\text{s})$, $\text{NO}_3^-(\text{s})$, and sub-micron particulates in a decreasing order of magnitude. The annual average deposition velocities were 1.20 ± 0.14 cm/s for HNO_3 , 0.87 ± 0.07 cm/s for SO_2 , 0.65 ± 0.11 cm/s for O_3 , 0.090 ± 0.014 cm/s for $\text{SO}_4^{2-}(\text{s})$ and $\text{NO}_3^-(\text{s})$, and 0.0045 ± 0.0006 cm/s for sub-micron particulates.

The annual mean concentrations of airborne pollutants obtained by the 7-day triple-filter pack samplings were 3.63 ± 1.92 $\mu\text{g}/\text{m}^3$ for $\text{SO}_4^{2-}(\text{s})$, 2.00 ± 1.22 $\mu\text{g}/\text{m}^3$ for SO_2 , 1.03 ± 0.59 $\mu\text{g}/\text{m}^3$ for HNO_3 , and 0.704 ± 0.419 $\mu\text{g}/\text{m}^3$ for $\text{NO}_3^-(\text{s})$, where the concentrations were strongly related to the weather elements and were lower than the annual mean concentrations for these species in the eastern United States^{30,32}.

The air pollutant with the largest deposition flux was SO_2 followed by HNO_3 , $\text{SO}_4^{2-}(\text{s})$, and $\text{NO}_3^-(\text{s})$ in a descending order of magnitude. The sulfur dioxide and $\text{NO}_3^-(\text{s})$ deposition fluxes were higher

in the winter than in the summer whereas the nitric acid and sulfate deposition fluxes were higher during the spring and summer seasons. These variations were to be expected considering that deposition fluxes are more affected by the pollutant concentration than the deposition velocity for these air pollutants. Accordingly, at this north central Florida site, this influence would tend to increase the HNO_3 and SO_4^{2-} deposition fluxes during the summer season and the SO_2 and $\text{NO}_3^-(\text{s})$ deposition fluxes during the winter season.

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References

- [1] Hicks B. B., D. Baldocchi, R. P. Hosker Jr., B. A. Hutchison, D. R. Matt, R. T. McMillen and L. C. Satterfield, 1985, On the use of monitoring air concentrations to infer dry deposition. NOAA Technical Memorandum ERL ARL-141. pp.65.
- [2] Wesely M. L., 1989, Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models. *Atmospheric Environment*, **23**, 1293~1304.
- [3] Jung J. Y., 1996, A study on the dry deposition model of air pollutants according to weather conditions. Master of Sciences Thesis. Inje University. Kimhae. Korea. pp.50.
- [4] Lee H. W., J. K. Park, and S. E. Moon, 1989, Simulation for the deposition velocity of the pollutants. *J. Korean Meteor. Soc.*, **25**, 121~128.
- [5] McMahon T. A., P. J. Denison, and R. A. Fleming, 1976, long-distance air pollution transportation model incorporating washout and dry deposition components, *Atmospheric Environment*, **10**, 751~761.
- [6] Whelpdale D. M. and P. W. Shaw, 1974, Sulphur dioxide removal by turbulent transfer over grass, snow and water surface. *Tellus*, **26**, 196~205.
- [7] Brimblecombe P. and D. J. Spedding, 1974, The absorption of low concentrations of

- sulphur dioxide into aqueous solutions. *Tellus*, **26**, 272~276.
- [8] Sehmel G. A., 1980, Particle and gas dry deposition : a review. *Atmospheric Environment*, **14**, 983~1011.
- [9] Beier C., P. Gundersen, and L. Rasmussen, 1992, A new method for estimation of dry deposition of particles based on throughfall measurements in a forest edge. *Atmospheric Environment*, **26**, 1553~1559.
- [10] Allen E. R., N. Cabrera, and J. C. Kim, 1994, Atmospheric Deposition Studies in Southern Commercial Forests of the Southern United States. *Proceedings of the 87th Annual Meeting of AWMA, Cincinnati, OH. Paper No. 94-W988.02*.
- [11] Hicks B. B., 1989, *Overview of deposition processes*. NORD. 3.1-3.21. Allen E. R. (1991) Atmospheric Exposure Monitoring in Austin Cary Forest, Gainesville, FL. *Final Report to Florida Department of Environmental Regulation*. Contact # SP210. Environmental Engineering Sciences Department. University of Florida. Gainesville, FL. p.94.
- [12] NAPAP, 1991, National Acid Precipitation Assessment Program. State of Science and Technology Report No.16, Washington, DC.
- [13] NAPAP, 1989, National Acid Precipitation Assessment Program. Models planned for use in NAPAP integrated assessment. Washington, DC.
- [14] Allen E. R. and R. L. Sutton, 1991, Atmospheric exposure monitoring in southern commercial forests. *Final Report to U. S. Environmental Protection Agency Cooperative Agreement CR-813613*. Environmental Engineering Sciences Department. University of Florida. Gainesville. FL. p.142.
- [15] Kim J. C. and E. R. Allen, 1996, Effects of filter pack sampling conditions on observed ambient concentrations of dry acid deposition species. *J. Chemosphere*, **34**, 587~610
- [16] Allen E. R., 1991, Atmospheric Exposure Monitoring in Austin Cary Forest, Gainesville, FL. *Final Report to Florida Department of Environmental Regulation*. Contact # Sp210. Environmental Engineering Sciences Department. University of Florida, Gainesville, FL. p.94
- [17] Kim J. C., 1995, Comparison study of dry acid deposition sampling at Austin Cary Forest, Gainesville, FL. Master of Engineering Thesis. University of Florida. Gainesville, FL.
- [18] Hicks B. B., Baldocchi D. D., Meyers T. P., Hosker R. P. Jr. and Matt D. R., 1987, A preliminary multiple resistance routine for deriving dry deposition velocities from measured quantities. *Water, Air, and Soil Pollution*, **36**, 311~330
- [19] Jarvis P. G., 1971, The estimation of resistances to carbon dioxide, In *Plant Photosynthetic Production : Manual of Methods*, pp.566~631.
- [20] Jarvis P. G., 1976, The interpretation of the variations in leaf water potential and stomatal conductance found in canopies in the field, *Phil. Trans. R. Soc. London ser. B*. **273**, 593~610.
- [21] Turner N. C., Rich C. and Waggoner P. E., 1973, Removal of ozone by soil, *J. Environ. Quality*, **2**, 259~264.
- [22] Unsworth M. H., 1982, The exchange of carbon dioxide and air pollutants between vegetation and the atmosphere. In *Plant and their Atmospheric Environment*(edited by Grace J., Ford E. D. and Jarvis P. G.). pp.111~138.
- [23] Hosker R. P. Jr. and Lindberg S. E., 1982, Review : atmospheric deposition and plant assimilation of gases and particles. *Atmospheric Environment*, **16**, 889~910.
- [24] Hicks B. B., 1981, An examination of turbulence statistics in the surface layer. *Boundary Layer Meteorology*, **21**, 389~402.
- [25] Wesely M. L. and Hicks B. B., 1977, Some factors that affect the deposition rates of sulfur dioxide and similar gases on vegetation. *Journal of the Air Pollution Control Association*, **27**, 1110~1116.
- [26] NCAR., 1985, The NCAR Eulerian Regional Acid Deposition Model. ADMP-85-3, NCAR/TN-256+STR. National Center for Atmospheric Research. Boulder, CO. 109~117.
- [27] Baldocchi D. D., Hicks B. B. and Camara P., 1987, A canopy stomatal resistance model

- for gaseous deposition to vegetated surfaces. *Atmospheric Environment*, **21**, 91 ~ 101.
- [28] Weiss A. and Norman J. M., 1985, Partitioning solar radiation into direct and diffuse visible and near-infrared components. *Agricultural and Forest Meteorology*, **34**, 205 ~ 213.
- [29] Wesely M. L., Cook D. R., Hart R. L. and Speer R. E., 1985, Measurements and parameterization of particulate sulfur dry deposition over grass. *Journal of Geophysical Research*, **90**, 2131 ~ 2143.
- [30] Edgerton E. S., Lavery T. F. and Prentice H. S., 1991, National Dry Deposition Network : Third Annual Progress Report (1989). Prepared for U. S. Environmental Protection Agency. EPA/600/3-91/018.
- [31] Wu Y. L. and Davidson C. I., 1989, Estimating dry deposition of SO_2 , HNO_3 , and SO_4 : The inconsequence of separate daytime and nighttime sampling. Prepared for : Office of Research and Development, U. S. Environmental Protection Agency, Washington, DC.
- [32] Edgerton E. S., Lavery T. F. and Prentice H. S., 1990, National Dry Deposition Network : Second Annual Progress Report (1988). Prepared for U. S. Environmental Protection Agency. EPA-600/3-90/020.
- [33] Meyers T. P., Hicks B. B., Hosker R. P. Jr ; Womack J. D. and Satterfield L. C., 1991, Dry deposition inferential measurement techniques-II. Seasonal and annual deposition rates of sulfur and nitrate. *Atmospheric Environment*, **25A**, 2361 ~ 2370.