

Measuring Air Pollutant Uptake by Plants: Nitrogen Dioxide¹

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ABSTRACT

Direct kinetic determinations of the uptake of nitrogen dioxide (NO₂) by selected plant species under various conditions were made using continuous stirred tank reactor (CSTR) techniques. Second-order rate constants with respect to exposure concentration and leaf area were obtained for corn [*Zea mays* (L.) 'Pioneer Brand 3369A'], soybean [*Glycine max* (L.) Merr. 'Davis'], loblolly pine (*Pinus taeda* L.), and white oak (*Quercus alba* L.). Mean rate constants in units of 10⁻³ dm⁻² min⁻¹ were: corn, 9.3; soybean, 13.6; loblolly pine, 13.7; and white oak, 2.8. On a mass basis, rates would be 3.5, 5.1, 5.2, and 1.1 × 10⁻² μg dm⁻² min⁻¹ pphm⁻¹ (pphm = parts per hundred million), respectively. Uptake rate constants remained the same over 5-hour exposure periods within the exposure concentration range of 0 to 58 pphm. The NO₂ uptake increased as the level of photosynthetically active radiation (PAR) increased. This effect of light was linearly correlated with the inverse of total diffusive resistance. Varying the level of tissue nitrogen (N) did not influence NO₂ uptake even though the leaves were smaller and chlorotic at the lower levels of tissue N. Photolysis of NO₂ occurred in controlled environment rooms under artificial light; the mean *k*₁ for photolysis was 0.03 min⁻¹.

Additional Index Words: air pollutant sorption, CSTR, corn, soybean, loblolly pine, white oak, total diffusive resistance, photolysis.

Knowledge of air pollution sorption by vegetation is important for several reasons. First, such knowledge would allow the impact of the entire flora of a region to be included in the diagnostic and predictive models of urban air pollution. Ideally, such models would permit an air pollution control policy or tactic to be evaluated before being instituted. Second, sorption data can be used in the quantitative evaluation of the efficacy of greenbelts (De Santo et al., 1976; Warren, 1973). Third, uptake information can contribute to the understanding of dose-response relationships that describe the phytotoxicity of pollutants. Fourth, the possibility that certain air pollutants may be significant sources of nutrients for some plant communities can be assessed. The last may be especially important in the case of nitrogen dioxide (NO₂) since nitrogen (N) is the most frequently deficient soil nutrient (Salisbury and Ross, 1969).

Tingey³ and Hill (1971) studied the sorption of NO₂ by alfalfa [*Medicago sativa* (L.) 'Ranger'] and oats [*Avena sativa* (L.) 'Park']. Measurement was indirect and was carried out by summing the amounts of pollutant added over time to maintain preset levels in a recirculating chamber. This work demonstrated significant NO₂ uptake, which was independent of ex-

posure concentration and which varied diurnally with net photosynthesis, transpiration, and light intensity. The authors' extrapolation indicated that in the Los Angeles area uptake of NO₂ by alfalfa could average as high as 279 g ha⁻¹ day⁻¹ as N, which could become significant in some ecosystems.

Srivastava et al. (1975a, 1975b) showed that the rate of NO₂ uptake with time was affected by the N supply for bush bean [*Phaseolus vulgaris* (L.) 'Pure Gold wax']. Uptake was enhanced by high temperature, low carbon dioxide (CO₂) concentration, and high humidity. O'Dell et al. (1977) presented a mass transfer model of pollutant uptake by plants that considered both meteorological and physiological factors.

We initiated this study to obtain direct real-time kinetic data for air pollutant uptake by vegetation because no published study contained such information.

MATERIALS AND METHODS

The continuous stirred tank reactor (CSTR) technique was chosen for use in this study. The system designed and constructed for this study is capable of providing direct kinetic data from which gas exchange rates can be conveniently computed. The system consists of two 200-liter chambers on a cart that is housed in a charcoal-filtered controlled environment room. Chamber configuration (cylindrical with three vertical 120° baffles) and stirring by an impeller produces uniform mixing. All internal surfaces are Teflon⁴ or glass; this minimizes reaction and loss of gases. Design details have been discussed⁵ and are available from the authors (Rogers et al., 1977).

Sequential measurement of the three sampling points in the system (common inlet and two outlets, I and II) allowed time sharing of the monitoring instruments. The manifold was wrapped with heat tape to prevent condensation of water vapor from transpiration. Samples were taken in 10-min repetitive cycles consisting of five 2-min steps. The inlet was sampled during the first step, outlet I during the second and fourth steps, and outlet II during the third and fifth steps.

The following instruments were used in the study: for NO₂ and nitric oxide (NO), Bendix Model 8101-B Oxides of Nitrogen Analyzer (chemiluminescent); for ozone (O₃), REM Model 612 Atmospheric Ozone Monitor (chemiluminescent); for dew point temperature, EG & G Model 880 Dew Point Hygrometer; for air temperature, 44203 Yellow Springs Thermistors; for leaf temperature; no. 36-Gauge, Type T thermocouples; for photosynthetically active radiation (PAR, 400 to 700 nm), Lambda Model LI-185 Quantum/Radiometer/Photometer; and for leaf area, Hayashi Denko Model AAM-5 Automatic Leaf Area Meter.

Soybean [*Glycine max* (L.) Merr. 'Davis'] and corn [*Zea mays* (L.) 'Pioneer Brand 3369A'] plants 12 to 20 days old were grown in a charcoal-filtered controlled environment room in these tests. Temperature was 29.5°C during the day and 24°C at night; PAR was 492 μeinsteins m⁻² sec⁻¹, and relative humidity ranged from 40 to 50%. Each plant was grown in a 177-ml Styrofoam cup containing a 1:1 peat-lite and gravel mixture watered daily with a nutrient solution. Loblolly pine (*Pinus taeda* L.) and white oak (*Quercus alba* L.) terminals were obtained from the field and cut ends immediately placed in Styrofoam cups of distilled water. During these experiments the soil-root or water and container system of each plant was isolated by placing it within a glass container with a split plate glass lid to accommodate the stem.

⁴Mention of trade or company name does not constitute a guarantee or warranty of the product by the USDA or the North Carolina State University and does not imply their approval to the exclusion of other products that may be suitable.

⁵H. H. Rogers. 1975. Uptake of nitrogen dioxide by selected plant species. Ph.D. Thesis. Univ. of North Carolina at Chapel Hill.

¹Contribution of SEA-AR, USDA, Botany Dep., North Carolina State Univ., Raleigh, NC 27650. Paper is no. 5808 of the Journal Series of the North Carolina Agric. Exp. Stn., Raleigh, N.C. Received 16 Oct. 1978.

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³D. T. Tingey. 1968. Foliar absorption of nitrogen dioxide. Master's Thesis. Utah Univ., Salt Lake City.

The glass interfaces and the area around the stem were sealed with fluorocarbon grease to prevent any loss of NO₂ to the cup and soil or water.

Total diffusive resistance (aerodynamic plus stomatal) was computed from measures of transpiration, leaf area (i.e., outline area of leaf profile), and temperatures and water vapor concentrations of the leaf and air.³

RESULTS AND DISCUSSION

General Principles

The uptake of NO₂ by plants was considered as a chemical kinetics problem that is analogous to the following reaction:



The rate of uptake may be defined as:

$$r = d\text{NO}_2/dt = k_{p1} [\text{NO}_2] \quad [2]$$

$$k_{p1} = k_{p2} [A] \quad [3]$$

where r = rate of NO₂ uptake; t = time; k_{p1} = pseudo first-order rate constant with respect to NO₂ concentration; k_{p2} = second-order rate constant with respect to NO₂ concentration and leaf area (A).

Rate computations begin with the mass balance equation for a CSTR (Jeffries et al., 1976; Levenspiel, 1972):

$$r = (f/V)(C_{\text{out}} - C_{\text{in}}) + (dC_{\text{out}}/dt) \quad [4]$$

where r = total NO₂ uptake rate for plants and walls (pphm min⁻¹ [pphm = parts per hundred million]); f = flow rate (liters min⁻¹); V = chamber volume (liters); C_{out} = outlet NO₂ concentration (pphm); C_{in} = inlet NO₂ concentration (pphm). At steady state, Eq. [4] reduces to $r = (f/V)(C_{\text{out}} - C_{\text{in}})$ since $dC_{\text{out}}/dt = 0$. If C_{in} is constant, this occurs around 6.6 residence times (V/f) when $C_{\text{out}} = 0.999 C_{\text{in}}$.

The value of flow rate (f) was 10 liters min⁻¹ and that of volume (V) was 200 liters. The values of C_{out} and C_{in} were available from these experiments. The NO₂ uptake rate for plants and walls (r) is divided by exposure concentration (C_{out}) to obtain a total (plants plus walls) pseudo first-order rate constant (k_t , min⁻¹):

$$k_t = r/C_{\text{out}} \quad [5]$$

where $r = (d[\text{NO}_2]_{\text{observed}})/dt = k_t [\text{NO}_2]$; $[\text{NO}_2]$ = concentration at outlet (C_{out}). This rate constant is pseudo first-order since the wall and leaf area are not consumed as uptake proceeds. The rate constant for plants and walls is next corrected for wall effects by subtraction of a value (k_w , min⁻¹) computed from Eq. [4] using data from a blank run:

$$k_{p1} = k_t - k_w \quad [6]$$

This difference is the pseudo first-order rate constant (k_{p1} , min⁻¹) for NO₂ uptake by the plants in the chamber. Division by leaf area (A , i.e., outline area of leaf profile) yields the second-order rate constant (k_{p2} , dm⁻² min⁻¹; defined by Eq. [3]):

$$k_{p2} = k_{p1}/A \quad [7]$$

Multiplying this second-order rate constant by chamber volume (200 liters), $\mu\text{g}/\mu\text{liter}$ (1.88 for NO₂ at 25°C and 760 mm Hg), and 10^{-2} $\mu\text{liter}/\text{liter}$ per pphm converts it to a mass rate ($\mu\text{g dm}^{-2} \text{min}^{-1} \text{pphm}^{-1}$ exposure concentration).

Effect of Various Factors on NO₂ Uptake

TIME

The uptake of NO₂ by corn and soybean has been reported to be stable over 5-hour exposure periods during buildup, steady state, and decay (Rogers et al., 1977). This suggests that a rate constant for NO₂ uptake exists for plants under a given set of conditions. Checking for the existence of the rate constant in transient phases of the experiment (i.e., build up and decay) is important when exposure concentrations are rapidly changing. One approach to showing the existence of the rate constant is to model the data. We developed a mass balance model of NO₂ outlet concentration assuming first-order behavior for NO₂ uptake by plants.

The predictive equation is:

$$C_{\text{out}} = [k_f/(k_f + k_t)] C_{\text{in}} + \{C_{\text{out}}^* - [k_f/(k_f + k_t)] C_{\text{in}}\} \exp[-(k_f + k_t)t] \quad [8]$$

where C_{out} = outlet NO₂ concentration; k_f = flow constant (flow rate/volume); k_t = pseudo first-order rate constant; C_{in} = inlet NO₂ concentration; C_{out}^* = outlet NO₂ concentration at time (t) = 0.

Stability and repeatability over time are illustrated by Fig. 1, which shows the graphical fitting of this model for corn and soybean. Data points for the experimental runs are plotted along with the fitted line. Calculations for the fitted line were made at 30-sec intervals. Time was the only transient variable; all other values except the inlet concentration (C_{in}) were held constant. Inlet concentration was changed to achieve decay. The fit during buildup, steady state, and decay means that the rate constant was about the same throughout a given run. This suggests that plants of a given species have a specific rate of NO₂ uptake under similar environmental conditions. In a few cases, a slight increase in the rate of NO₂ removal was observed as a very gradual decrease in outlet concentration. Physiological adaption by the plants to the exposure conditions or an increase in effective leaf area could account for this rise in the uptake rate.

Uptake of NO₂ by plants over the time periods tested, however, did not vary significantly. This finding suggests that NO₂ uptake (within certain concentration ranges) behaves according to the first-order rate law where one reactant (leaf area) is unconsumed.

EXPOSURE CONCENTRATION OF NO₂

The concentrations of NO₂ to which the plants were exposed in this study were below those that have been reported to impair plant function. Tingey³ found that the threshold levels for visible injury to plants in light

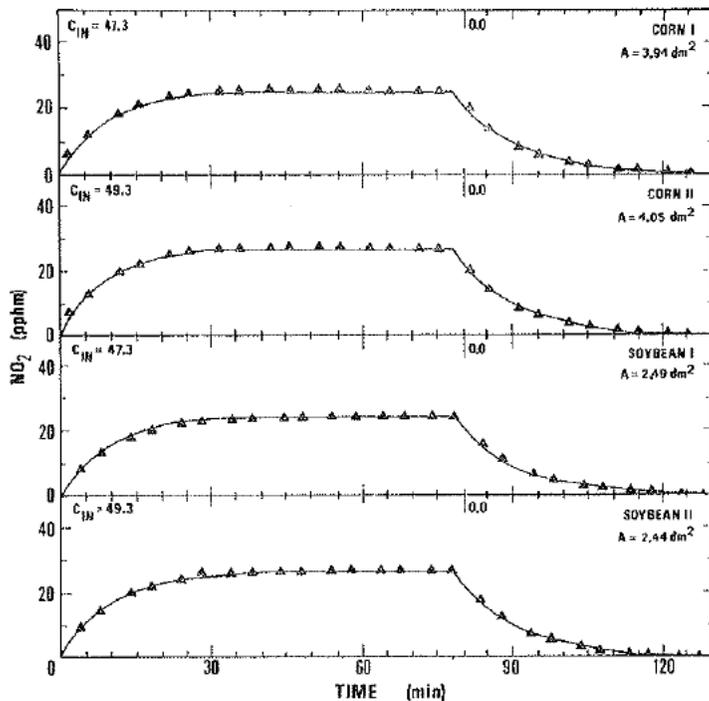


Fig. 1—Graphical fit of mass balance model.

(3-hour exposures) were 400 pphm NO₂ for alfalfa and 60 pphm for oats. Hill and Bennett (1970) reported a threshold of 60 pphm NO₂ (2-hour exposures) for depression of apparent photosynthesis in these same species. Most concentrations in our study ranged between 10 and 40 pphm, but none were greater than 60 pphm. In urban areas of the United States, ambient NO₂ values of 10 to 25 pphm are common; in nearly all areas, the values are below 50 pphm (USEPA, 1971).

For experimental runs made under stable environmental conditions, rate constants were determined for plants, and these constants were not influenced by NO₂ concentration in the range tested (0 to 58 pphm). This means that plant NO₂ uptake is first-order in nature with respect to concentration.

Kinetics data for NO₂ uptake were generated for corn and soybean in 5-hour runs with step concentration changes at 1-hour intervals. Uptake by both species was stable during these changes.

Means of duplicates for NO₂ uptake by corn and soybean are given in Table 1. For corn, the second-order rate constant k_{p2} did not change appreciably with concentration of NO₂ (C_{out}). The overall average of k_{p2} for corn was $0.0059 \pm 0.00008 \text{ dm}^{-2} \text{ min}^{-1}$. There was a slight downward trend for total diffusive resistance (R_{total} , based on water vapor diffusion from leaf to air) with increasing concentrations of NO₂, but the change did not seem to significantly affect uptake. The mean R_{total} for corn was $4.76 \pm 0.24 \text{ sec cm}^{-1}$. For soybean, as for corn, the second-order rate constant k_{p2} within

Table 1—Effect of concentration of NO₂ on its rate of uptake by corn and soybean; all values are means of duplicate experimental runs.

Concentration of NO ₂ pphm	Second-order rate constant (k_{p2})	Total diffusive resistance (R_{total})
	$10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$	sec cm^{-1}
	Corn†	
12.2	5.8	5.00
27.2	5.9	4.86
41.4	6.0	4.70
55.7	5.9	4.45
	Soybean‡	
8.4	11.4	3.23
16.8	12.4	3.04
24.9	12.6	3.40
34.6	12.0	3.30

† Mean leaf area = 5.16 dm².
‡ Mean leaf area = 7.34 dm².

the species seemed to be about the same regardless of NO₂ concentration; the average was $0.0121 \pm 0.00053 \text{ dm}^{-2} \text{ min}^{-1}$. The total diffusive resistance was similar at each level; the mean was $3.24 \pm 0.15 \text{ sec cm}^{-1}$. The mean k_{p2} value for soybean was about twice that for corn, probably because of the higher total diffusive resistance for corn.

The mass balance model (Eq. [8]) was fitted to all data from six stepped concentration runs.⁶ A nonlinear least squares curve fitting program developed by Daniel and Wood (1971) was used. The computer program used an iterative method that obtained estimates by Marquardt's Maximum Neighborhood Method which combines the Gauss (Taylor Series) Method and the Method of Steepest Descent.

The program was used to obtain best fit values for both the pseudo first-order rate constant for plants and walls (k_t) and flow constant (k_f , i.e., flow rate/volume) of Eq. [8]. Table 2 gives the results. Runs are designated I-I to 3-II; I and II represent the two separate exposure chambers. The program provided best fit values for the

⁶C. E. Feigley, 1975. Dep. of Environ. Sci. and Eng., School of Public Health, Univ. of North Carolina at Chapel Hill, N.C. Private communication.

Table 2—Nonlinear least squares fit of mass balance model (Eq. [8]) for pseudo first-order rate constant and flow constant.†

Run	Chamber	Species	k_t (min^{-1})‡		95% confidence interval
			Steady state	Fitted	
1	II	Corn	0.0375	0.0364	0.0364-0.0375
2	I		0.0363	0.0420	0.0408-0.0433
3	I	Soybean	0.0893	0.1030	0.1000-0.1060
3	II		0.1010	0.1008	0.0979-0.1040
1	I	Blank	0.0064	0.0062	0.0057-0.0066
2	II		0.0065	0.0052	0.0048-0.0056
			k_f (min^{-1})§		
			Experimental		
	I		0.050	0.050	0.049-0.051
	II		0.050	0.056	0.055-0.058

† Number of observations = 64 for each corn and blank run; 58 for each soybean run; total of 372. Number of coefficients = 8. Residual degrees of freedom = 364. $R^2 = 0.998$.

‡ Pseudo first-order rate constant for plants and walls.

§ Flow constant (flow rate/volume).

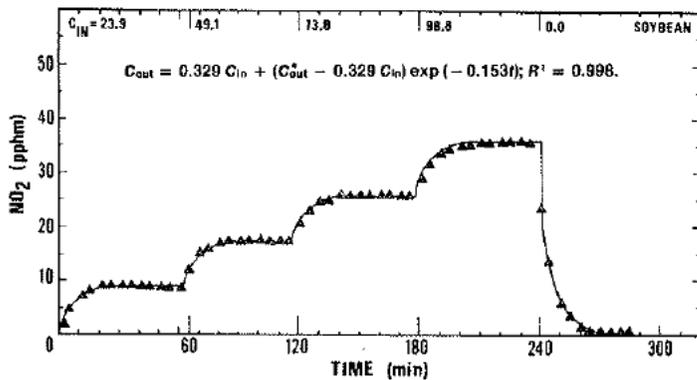


Fig. 2—Concentration of NO_2 at chamber outlet with six 13-day-old soybean plants having a total leaf area of 7.02 dm^2 (\blacktriangle). The inlet NO_2 concentration was stepped through five values in a step function as indicated. The solid line was computed from the equation as shown.

eight coefficients and their 95% confidence intervals. The rate constant (k_t) and the flow constant (k_f) were fitted simultaneously for appropriate data, which were selected by indicator variables. For example, the best fit value for k_t of Run 1-II was obtained simultaneously with k_f of the combined data for chamber II from all three runs in that chamber. This means that data from single runs were used to estimate k_t , whereas data from three runs were used to estimate k_f .

The steady state values are good estimates of the fitted values. The square of the multiple correlation coefficient is 0.998. Thus, it seemed that the model was quite appropriate for describing the process of NO_2 removal by both corn and soybean.

Figure 2 shows an example of the fit for soybean; results with corn were similar. The rate constant for uptake was held the same throughout the calculation of the fitted line. The agreement between the nonlinear regression line and the experimental data points is close, supporting the applicability of the first-order rate law.

This is further supported by data of Hill (1971) who reported that the specific rate of NO_2 uptake by an alfalfa canopy was $12 \mu\text{liters}/\text{m}^2$ ground area per pphm exposure concentration per min regardless of exposure concentration in the range 0 to 8 pphm. This rate may be converted to a leaf area basis (1.0 m^2 ground area = 9.5 m^2 leaf area of alfalfa, on the average); the value is $1.3 \mu\text{liter m}^{-2} \text{ pphm}^{-1} \text{ min}^{-1}$. In our study where the second-order rate constant for soybean has a mean value of $0.0121 \text{ dm}^{-2} \text{ min}^{-2}$, the value for specific rate, using the same units as those of Hill, is $2.4 \mu\text{liter m}^{-2} \text{ pphm}^{-1} \text{ min}^{-1}$.

LIGHT

Figure 3 shows the effects of step changes in light level. The inlet NO_2 concentration was stable over the experimental runs. As light was stepped through four levels—0, 71, 138, and $343 \mu\text{einsteins m}^{-2} \text{ sec}^{-1}$ —uptake by both corn and soybean increased, as shown by decreases in the outlet concentration.

Mean values of the second-order rate constant k_{p2} and the total diffusive resistance (R_{total}) at each PAR level are given in Table 3. With both corn and soybean,

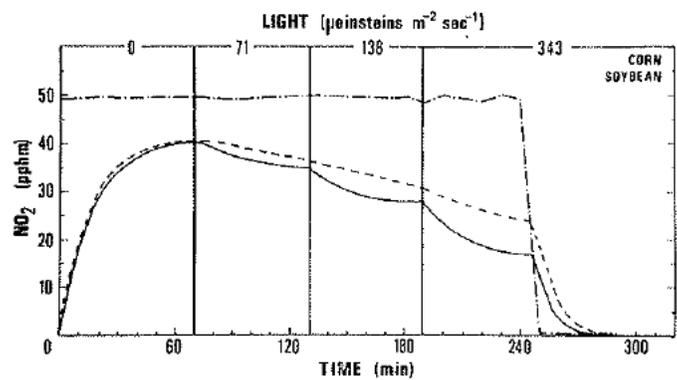


Fig. 3—Concentration of NO_2 at inlet (---), outlet of chamber with six 12-day-old corn plants having a total leaf area of 5.84 dm^2 (—), and outlet of chamber with six 12-day-old soybean plants having a total leaf area of 4.36 dm^2 (.....). PAR was increased through four levels as indicated.

k_{p2} increased and total diffusive resistance decreased with increasing PAR. This relationship between PAR and total diffusive resistance agrees with that observed by other investigators (De Michele and Sharpe, 1971; Shawcroft et al., 1973).

When the rate constant k_{p2} was regressed linearly on the reciprocal of total diffusive resistance R_{total} (Fig. 4), the second-order rate constant for NO_2 uptake by corn and soybean was a linear function of the inverse of the total diffusive resistance and the values of the regression coefficients indicated that the influence of total diffusive resistance was similar for both species.

The correlation between NO_2 uptake and total diffusive resistance agrees with the finding of Fowler and Unsworth (1974) that surface resistance was the controlling step in the removal of sulfur dioxide from the atmosphere by vegetation. The relationship is also supported by data of Rich et al. (1970), who found a high correlation between uptake of ozone and leaf resistance. Thus, increasing the PAR increases the rate of NO_2 uptake by decreasing the total diffusive resistance.

The patterns of increasing uptake were different for corn and soybean. Corn exhibited a stepped form of increase as PAR was raised. The initial rate of NO_2 uptake for corn seemed to increase rapidly within a given PAR

Table 3—Effect of PAR on NO_2 uptake by corn and soybean; all values are means of duplicate experimental runs.

Photosynthetically active radiation (PAR)	Concentration of NO_2 (C_{out})	Second-order rate constant (k_{p1})	Total diffusive resistance (R_{total})
$\mu\text{einsteins m}^{-2} \text{ sec}^{-1}$	pphm	$10^{-2} \text{ dm}^{-2} \text{ min}^{-1}$	sec cm^{-1}
Corn†			
0	38.6	0.6	27.04
71	33.3	2.5	10.73
138	23.4	7.7	5.96
343	17.8	13.4	2.74
Soybean‡			
0	40.6	1.2	21.88
71	37.5	2.6	9.42
138	30.4	6.4	5.44
343	25.4	10.2	3.62

† Mean leaf area = 5.92 dm^2 .

‡ Mean leaf area = 4.05 dm^2 .

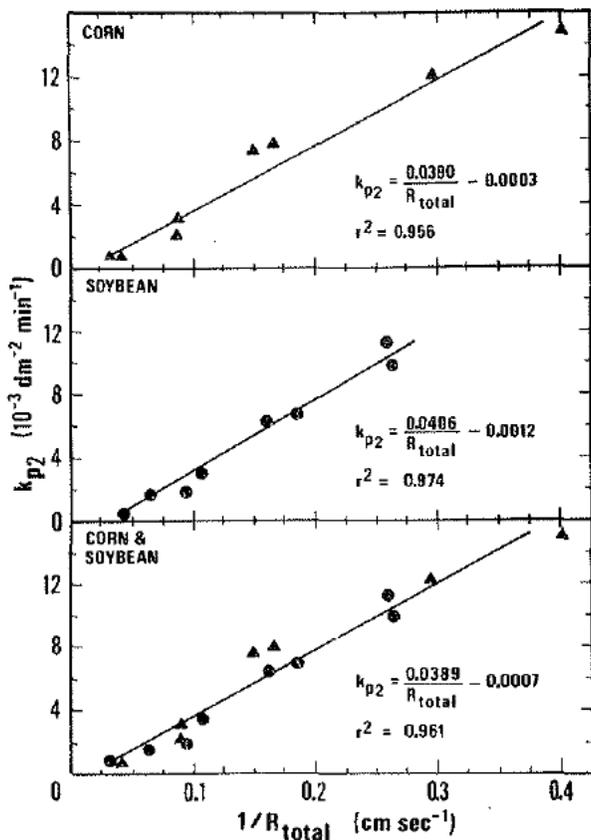


Fig. 4—Regression of second-order rate constant for NO_2 uptake (k_{p2}) on reciprocal of total diffusive resistance ($1/R_{\text{total}}$).

regime and then approach a steady state, whereas that for soybean increased gradually and constantly throughout the run. However, with soybean, it was not clear whether the two highest PAR levels influenced the rate, although it is likely that they did.

The different response patterns of corn and soybean to PAR changes may be due to differences in their stomatal function. The stomata of C_4 plants, such as corn, respond more rapidly to changes in light than do those of C_3 plants, such as soybean. Kanemasu (1974) reported that corn stomata move more rapidly than those of many other plants. Response time may be as short as 1 to 2 min.

SOIL NITROGEN

Plants were grown under three soil nitrogen regimes in order to assess the effect of varying levels of plant tissue nitrogen on NO_2 uptake.

Steady state values for the second-order rate constant k_{p2} and the total diffusive resistance R_{total} are given in Table 4. There was no significant variation in NO_2 uptake among the three tissue nitrogen contents for either corn or soybean. What small differences there were seemed to be related to total diffusive resistance. The total diffusive resistance was highest at the mid-levels of tissue nitrogen for both species. This could mean that an optimum level of nitrogen exists for greatest resistance.

Table 4—Effect of total N content of plant tissue on NO_2 uptake by corn and soybean; all values means of duplicate experimental runs.

Total N content	Leaf area	Concentration of NO_2	Second-order rate constant (k_{p2})	Total diffusive resistance (R_{total})
%	dm^2	pphm	$10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$	sec cm^{-1}
Corn				
1.65	2.13	32.0	9.5	3.13
2.94	2.88	26.9	8.8	3.36
3.95	4.00	25.8	9.3	2.73
Soybean				
3.30	1.76	28.6	14.4	2.87
5.18	1.62	27.0	13.0	3.44
5.80	2.46	25.4	13.6	3.01

For both species, leaf area was greatest at the highest nitrogen level. However, when the absolute rate was normalized for leaf area, uptake per unit area was similar for all nitrogen levels. Some chlorosis was noted for corn and soybean at the lowest nitrogen level, and chlorophyll was reduced, but this did not seem to influence the uptake rate constant. This finding was similar to that of Hutchinson et al. (1972) who reported that uptake of ammonia by soybean was unaffected by three different soil nitrogen fertility levels. At the lowest level, soybean plants were visibly stunted and very chlorotic, and at the highest, they were dark green and vigorous. However, ammonia uptake based on leaf area was not significantly different for the two groups.

Nitrogen deficiency is known to significantly increase leaf resistance (Ryle and Hesketh, 1969). However, resistance did not increase appreciably at the low soil nitrogen levels in our experiments. It may be that deficiency levels were not reached. The lowest total nitrogen value was 1.65% in corn. The level at which most higher plants are considered nitrogen deficient is 1.5% (Salisbury and Ross, 1969).

SPECIES

Table 5 shows the uptake rate constants for corn, soybean, loblolly pine, and white oak. Uptake for all species except white oak was of the same magnitude. The lower rate of white oak was apparently caused by the high total diffusive resistance. The relationship between the rate constant and the total diffusive resistance for white oak was similar in proportion to that for the other species.

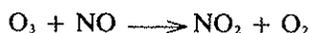
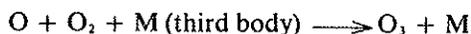
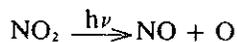
The similarity of uptake among the species tested suggest that NO_2 uptake is mediated primarily by physical exchange processes and not by metabolic processes.

Table 5—Uptake of NO_2 by corn, soybean, loblolly pine, and white oak; all values means of duplicate experimental runs.

Species	Leaf area	Concentration of NO_2	Second-order rate constant (k_{p2})	Total diffusive resistance (R_{total})
	dm^2	pphm	$10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$	sec cm^{-1}
Corn	4.00	25.8	9.3	2.73
Soybean	2.46	25.4	13.6	3.01
Loblolly pine	0.77	34.4	13.7	1.88
White oak	6.46	30.8	2.8	9.26

PHOTOLYSIS

Photolysis of NO₂ was considered in this study because it has been observed even under ordinary room light.⁷ This photolysis of NO₂ occurs in the near-ultraviolet portion of the spectrum (300 to 400 nm). The photochemistry may be expressed in three major reactions:



The k_1 (min⁻¹) for photolysis may be estimated (in clean air in the absence of competing reactions) from the following equation:

$$k_1 = [\text{O}_3] (24 \text{ ppm}^{-1} \text{ min}^{-1} [\text{NO}] + 0.046 \text{ ppm}^{-1} \text{ min}^{-1} [\text{NO}_2]) / [\text{NO}_2] \quad [9]$$

where $-r = k_1 [\text{NO}_2]$.

To assess photolysis, concentrations of NO₂, NO, and O₃ were followed over time. The average value for k_1 in exposures made in this study was 0.03 min⁻¹, under an irradiance of 343 μeinsteins m⁻² sec⁻¹. In full sunlight, where the ultraviolet would be much higher, the approximate value of k_1 would be 0.5 min⁻¹. In the current study where NO₂ concentrations ranged from about 15 to 20 pphm, O₃ ranged from 0.5 to 1.5 pphm and NO from 2 to 6 pphm.

Even though the level of photolytic products was low, their presence in plant exposure chambers (within controlled environment rooms) suggests that photolysis should be considered whenever NO₂ is handled in light. Outdoors, where full ultraviolet is available, this is particularly important. Formation of small quantities of NO and O₃ may become especially significant if they have synergistic effects on biological systems.

It was desirable to recognize the photolytic formation of O₃ and NO in the system. If photolysis had been appreciable, we would have had to take it into account in calculations of NO₂ uptake. However, the amount of NO₂ photolyzed was very small compared with that taken up by the plants.

Hill (1971) reported the accumulation of NO in a test chamber during exposures of alfalfa to NO₂. He did not determine the NO source, but suggested that some NO was formed within the plant after NO₂ uptake and was subsequently released into the atmosphere. The NO observed in our study seemed to be from the NO₂ tank, which is commonly contaminated by NO, and from photolysis.

SUMMARY AND CONCLUSIONS

The main objective of this study was to determine the rate of uptake of NO₂ by selected plant species. Using a continuous stirred tank reactor system, real time gas exchange rates were assessed under various conditions.

⁷L. D. Kornreich. 1973. Triangle Universities Consortium on Air Pollution, Chapel Hill, N.C. Private communication.

From experimental kinetics data, the following conclusions may be drawn. The first-order rate law applies to corn and soybean NO₂ uptake in the concentration range tested (0 to 58 pphm) over 5-hour exposure periods. For these plant species, a second-order rate constant with respect to leaf area and concentration may be computed. The exposure concentration in the range tested did not affect the specific rate of NO₂ uptake by corn and soybean. The uptake of NO₂ by plants can be modeled on the basis of first-order kinetic behavior.

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