

# Measuring Air Pollutant Uptake by Plants: A Direct Kinetic Technique

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Available chamber designs and experimental techniques have not permitted a critical appraisal of uptake of gaseous pollutants by plants. This work describes an approach that treats this process from a chemical kinetics viewpoint; it has led to the design of a chemical reactor system suitable for plant growth and exposure, while meeting criteria necessary to apply the concept of a continuous stirred tank reactor. Use of the system to study nitrogen dioxide uptake by corn [*Zea mays* (L.) 'Pioneer Brand 3369A'] and soybean [*Glycine max* (L.) Merr. 'Davis'] under several exposure conditions is presented. The system provided precise data that were readily amenable to mathematical modeling. The concept of a second-order rate constant for uptake is demonstrated, which is shown to be independent of nitrogen dioxide concentration and leaf surface area, but directly dependent upon inverse total diffusion resistance.

Several reviews deal with sorption of air pollutants by plants but chamber and experimental designs have not permitted uptake rates by vegetation to be appraised critically.<sup>1-6</sup> Uptake rates and total sorption by vegetation are important because this knowledge would permit including the predicted uptake rates for the flora of a region in diagnostic and predictive models of urban air pollution. These models could be

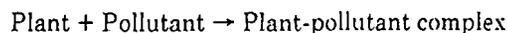
used to evaluate proposed control policies before they are enacted. Current data suggest that vegetation near monitoring stations might affect the measured pollutant concentrations. Uptake data could be used to evaluate the efficacy of green belts as buffer zones between pollutant sources and sensitive receptors. Also, pollutant uptake data could help to understand dose-response relationships and whether certain air contaminants (e.g. sulfur and nitrogen compounds) add significantly to the nutrient budget of some plant communities.

Determining uptake rates and total sorption of air pollutants by vegetation requires that plants be exposed to the test gas by a quantifiable technique. Generally, this has been accomplished in some type of chamber. Several field, greenhouse, and laboratory exposure chambers have been designed.<sup>7-10</sup> Hill<sup>11</sup> described a chamber for exposure and uptake studies where several environmental variables could be controlled. This chamber was used to determine uptake indirectly by recording absolute amounts of pollutant added over time to maintain constant concentrations within the chamber. This chamber is probably the best current design. However, many uptake studies use average exposure values over some set period, presuming uniformity, without controlling design characteristics, and often measurement methods are not direct.

Therefore, a system was developed so that real time data could be obtained using direct measurement methods and controlling all possible parameters. Such a system for studying gas exchange phenomena was derived from considering the uptake process as a chemical reaction and then applying the concept of a continuous stirred tank reactor (CSTR).<sup>12</sup>

## Theory

The uptake of gaseous pollutants by plants in a chamber can be considered as a problem in chemical kinetics, where one reactant is the pollutant and the other is the plant surface. Such a reaction can be expressed as:



A rate expression for this reaction could be:

$$-r_{\text{uptake}} = \frac{dC}{dt} = k_{p2}[C][S] \quad (1)$$

Where,  $-r_{\text{uptake}}$  is the rate of pollutant uptake (ppm/min),  $k_{p2}$  is similar to second-order rate constant for uptake

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( $\text{dm}^{-2}\text{min}^{-1}$ );  $C$  is the concentration of pollutant (ppm); and  $S$  is some function of plant surface (e.g.  $\text{dm}^2$ ).

Rate of pollutant uptake is influenced by the effective plant surface area and the density of its active sites, by total diffusion resistance (boundary layer plus stomatal resistance), and by metabolic activities. The last two factors are reflected in differing values for  $k_{p2}$ . To study uptake rates in terms of chemical kinetics, a reactor was needed that could also be used as a plant exposure chamber. Only three types of ideal reactors exist: batch, plug flow, and continuous stirred tank reactor (CSTR). All others are hybrids of approximations of these.

#### Batch Reactor

The batch reactor is the most common. In this type, reactants are initially introduced into a vessel and kept uniformly mixed. The progress of reactions within the reactor may be followed by analysis of the contents over time. In this closed system, factors which affect plants (e.g.  $\text{CO}_2$  and water vapor) would change during the course of an exposure and affect the sorption of gases.

#### Plug Flow Reactor

This standard pipeline reactor substitutes position along the reactor for time in the batch reactor by the continuous flowing of reactants and products through the vessel. Radial but no axial mixing is assumed. This reactor is not considered feasible for plant uptake studies since such a reactor containing plants would not satisfy plug flow requirements. The chamber designed by Hill acts as a modified high velocity laminar flow reactor.

#### Continuous Stirred Tank Reactor

The CSTR was chosen for developing a system design for studying pollutant uptake by vegetation. In the CSTR, the flow rate through the reactor is continuous; the reactor provides uniform (ideal) mixing; its performance is easily predictable over time; and it is the only type of reactor that yields direct kinetic rate data (i.e. it does not require integration of a rate expression.)

In CSTR systems, the basic assumption is that the composition of any elemental volume is uniform throughout the reactor and mixing is ideal.<sup>13</sup> Ideal mixing was defined empirically by van de Vusse as "once around the reactor under turbulent conditions."<sup>14</sup> This condition is approached if the ratio of mixing time to local homogeneity is much less than the average residence time (ratio of total volume to flow rate.) Instantaneous mixing requires two conditions: (a) the molecules at each point will leave at the same instant, and (b) points that have equal life expectancies are mixed, or at least have identical age distribution.<sup>15</sup> Perfect instantaneous mixing is obviously impossible since some time is needed for mixing. The time allowable for mixing before the assumption of "ideal mixing" no longer holds is a function of the reactor's purpose and depends on the time scale of events being observed. Thus, if it is assumed that mixing is ideal, a concentration gradient cannot exist long enough to influence measurably the rate of the process under study.

Assuming CSTR criteria are met, only five measurements are needed for calculating reaction rates: (1) time, (2) flow rate, (3) reactor volume, (4) concentration at inlet, and (5) concentration at outlet, which is the same as that at any point within the reactor.

Reactant mass entering an element of reactor volume can leave, react, or accumulate.<sup>17</sup> This can be stated simply as:

$$\begin{aligned} \text{Rate of accumulation} &= \text{Rate of flow in} \\ &- \text{Rate of flow out} - \text{Rate of reaction} \quad (2) \end{aligned}$$

If the composition within the reactor is uniform, as it is in the CSTR, this mass balance applies over the entire reactor.

If  $C$  represents the mass per unit volume (e.g.  $\text{g}/\text{m}^3$ ), then

$$V \frac{dC_{\text{out}}}{dt} = fC_{\text{in}} - fC_{\text{out}} - V(-r) \quad (3)$$

$V$  = reactor volume

$f$  = flow rate into and out of  $V$

$-r$  = rate of chemical reaction in units of mass/vol/time of process involving  $C$

or, by rearrangement and allowing  $f/V = Q$  in reciprocal time units where  $1/Q$  = residence time,

$$r = Q(C_{\text{out}} - C_{\text{in}}) + \frac{dC_{\text{out}}}{dt} \quad (4)$$

If  $C_{\text{in}}$  is constant, a steady state for  $C_{\text{out}}$  is reached after adequate time has passed (about  $6.6/Q$  time units to achieve 99.9% of final value.) Since  $C_{\text{out}}$  is essentially constant,  $dC_{\text{out}}/dt = 0$ , and

$$r = Q(C_{\text{out}} - C_{\text{in}}) \quad (5)$$

Once adequate mixing is achieved in a reactor volume, predicting how this volume will react to changes in the composition of the feed stream is possible. All reactor processes occur at the same value as the outlet concentration. Thus, any rate can be measured if an appropriate balance between the precision of the measurement method and the average residence time of the reactor is found. The stability and predictability of the CSTR can be used to investigate complex or dynamic behavior of a given system.

#### Design of a CSTR System for Use with Plants

The system design criteria were threefold—it had to meet requirements for CSTR behavior; be suitable for plant growth, and be capable of handling gaseous pollutants. The system was designed for use in controlled environment rooms rather than with self-contained environmental controls.

For suitable mixing, conditions within the CSTR must be turbulent yet not stress plants. Mixing needs to be independent of inlet flow rate so that the average residence time can be used to choose the desirable degree of reaction. The shape of the reactor determines the energy needed for uniform mixing. Spheres are ideally shaped for uniform mixing but not for plant exposure chambers. Cylinders can be well mixed and are suitable for plant chambers. In a cylinder, the stirrer needs to impart energy to the fluid without setting up a uniform flow pattern. A propeller is inadequate because it could establish a vortex down the cylinder axis. To achieve the desired uniform mixing an impeller in conjunction with three baffles set at  $120^\circ$  to generate shearing action was used.

Uhl and Gray<sup>15</sup> discussed general criteria for determining dimensions for CSTR gaseous systems where the basic tank is a cylinder: (1) the ratio of length to diameter should not exceed 1.5, (2) baffle width should be about 0.1 of tank diameter, and (3) peripheral impeller speed should usually range from 250 to 450 ft/min. Also, overall impeller width should be about 0.4 of tank diameter. For certain applications, these dimensional relationships can deviate from the general case.

#### Construction Design

The complete CSTR plant exposure system shown in Figure 1 is two 200 liter cylindrical chambers arranged side by side on a cart so it can be moved into a controlled environment room, whose air is charcoal filtered. All internal surfaces were made of Teflon or glass to minimize reaction and loss of gases

to surfaces.<sup>16</sup> Plants were placed inside by lifting the chambers from their gasketed bases. This was convenient for manipulating plants and for system maintenance. This was especially useful when fine thermocouples were being attached to the lower surfaces of leaves in some experiments.

Welded steel frames were commercially coated with Teflon. An open-ended cylinder of 5 mil FEP Teflon film was formed by heat sealing and was placed on the outside of the frame; the

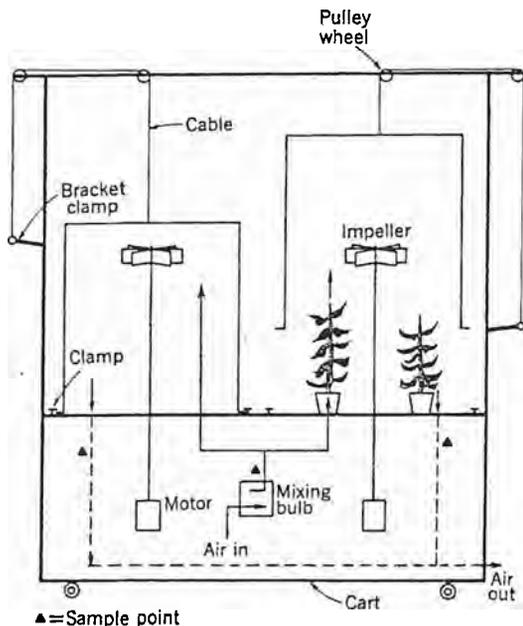


Figure 1. Schematic diagram of dual CSTR system.

top was a single circular sheet of film. Circular steel bands and rubber gaskets on the outside at the bottom, middle, and top of the frame secured the film to the frame and sealed the top sheet to the cylinder (Figure 2). Teflon-coated impellers were motor driven (120 rpm) from the lower level of the cart (Figure 1). The impeller shafts entered the chamber bases through Teflon-coated bearings. Inlet and outlet manifolds were fabricated from 3.18 cm glass tubing. There was a common inlet and separate outlets for the two chambers (Figures 1 and 3).

Flow through the system was maintained by a metal bellows pump on the downstream side (Figure 3). Flow was monitored by rotameters with adjustable valves and the pressure drop across the entire system was measured by a slant-tube manometer. During all experiments flow into the system was 22 liters/min (lpm) with a pressure drop of 0.02 in. (0.5 mm) of water. The main air stream entered the system through a glass fiber filter after which the treatment gas was injected. The gas stream entered a 4 liter mixing bulb and, after it was mixed, the inlet sample (2 lpm) was taken. 10 lpm flowed through each chamber and 2 lpm were taken as outlet samples as shown in Figure 3. All sampling lines were of 0.635 cm Teflon (FEP) tubing connected to a sampling manifold which supplied gas samples to the monitoring instruments. The manifold was wrapped with heat tape to prevent condensation of water vapor from transpiration of plants.

Sequential sampling of the three points (inlet and two outlets) and subsequent delivery of samples to the monitoring instruments was controlled by a set of 3-way Teflon solenoids (0.635 cm orifice) controlled by a digital timer. Air from all three sampling points was taken continuously, but only one

sample was analyzed; the other two samples were bypassed to exhaust. This flow scheme prevented changes in residence time in the reactors. Sequential measurement of the samples allowed time sharing of the monitoring instruments among the three sample points. Sampling was performed in 10 min repetitive cycles consisting of five 2 min monitoring 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.

### Physical Performance

To test initially for uniform mixing, a tracer smoke of titanium tetroxide was used. Mixing was visually uniform with no dead areas or plumbing. Dynamic flow tests with nitrogen dioxide ( $\text{NO}_2$ ) as a tracer gas were also used to verify uniform mixing. The  $\text{NO}_2$  was monitored with a Bendix Model 8101-B chemiluminescent analyzer.<sup>16</sup>

Eq. 4 can be solved for a tracer. Assuming  $C_{\text{out}} = 0$ , initially, and that  $C_{\text{in}}$  is a constant greater than zero, then

$$C_{\text{out}} = C_{\text{ss}}(1 - e^{-Qt}) \quad (6)$$

where  $C_{\text{ss}}$ , the concentration at steady state, would equal  $C_{\text{in}}$  without any losses of the tracer to chamber walls. If at some time after steady state has been reached,  $t^*$ ,  $C_{\text{in}}$  is changed stepwise to zero but flow is maintained, then

$$C_{\text{out}} = C_{\text{ss}}^* [e^{-Q(t-t^*)}] \quad (7)$$

where  $C_{\text{ss}}^*$  was the value of  $C_{\text{out}}$  at  $t^*$ . Thus, this system shows exponential dilution.

The solid line in Figure 4 represents  $C_{\text{out}}$  for an empty chamber when  $C_{\text{in}}$  was 50.5 pphm of  $\text{NO}_2$ .

Assuming ideal mixing, the time to reach 99.9 percent of the inlet concentration (Eq. 6) would be 132 min [6.6 residence times (volume/flow rate)]. In blank experimental runs, like the one in Figure 4, steady state was reached between 120 and

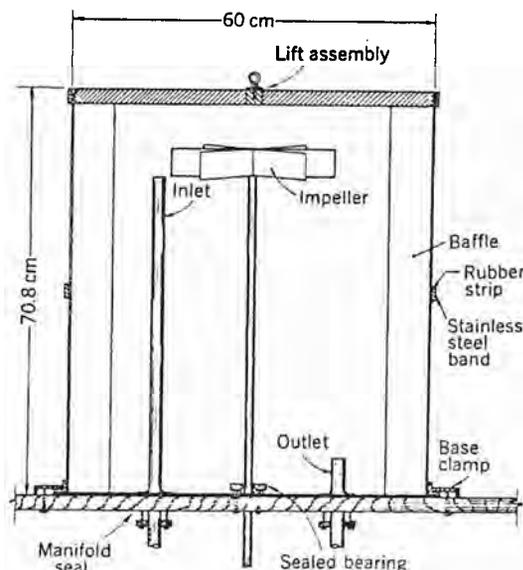


Figure 2. Cross-sectional view of chamber assembly.

130 min and  $C_{\text{ss}}/C_{\text{in}}$  was about 0.9. This decrease from the ideal time to steady state and the reduced value of  $C_{\text{ss}}$  were due to the small subtractive effect of the  $\text{NO}_2$  reaction with the chamber surfaces (see Eq. 10). Photolysis of  $\text{NO}_2$  was not significant in the system,  $k_1$  having a value of  $0.03 \text{ min}^{-1}$ .

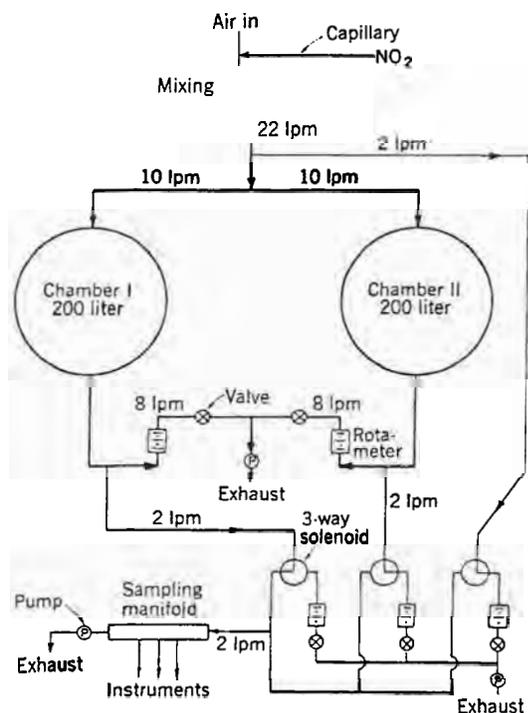


Figure 3. Flow path through dual CSTR system (liters/min = lpm).

Thus, mixing was nearly perfect in the reactor and its actual performance very closely approximated that of an ideal CSTR.

The inlet concentration of  $\text{NO}_2$  was maintained by a dynamic technique in which  $\text{NO}_2$  was injected through a stainless steel capillary (for flow control) from a high pressure calibration tank into the air stream. This injection system produced essentially constant  $\text{NO}_2$  levels over extended periods (see Table I and Figure 4 upper line.)

Air movement within the chamber caused some oscillation of plant leaves but did not seem to induce stress. Measurements of photosynthetically active radiation (PAR) inside the chambers indicated uniform lighting with a maximum value of  $343 \mu\text{einsteins m}^{-2} \text{sec}^{-1}$ . Teflon film has little effect on light quality and transmits about 95% of visible and infrared light.<sup>18</sup> The single pass flow scheme and the spectral properties of Teflon film prevented a large rise ( $<0.5^\circ\text{C}$ ) in the temperature of air moving through the system. Over a 200 min experiment, the average temperature ( $N = 40$ ) of the inlet gas stream was  $29.3^\circ \pm 0.1^\circ\text{C}$  while the outlet was  $29.7^\circ \pm 0.1^\circ\text{C}$ . Similar rises were seen in all other experiments.

Teflon, Teflon coating, or glass for all internal construction parts accounted for minimal loss of  $\text{NO}_2$  to chamber walls. On

Table I. Inlet  $\text{NO}_2$  concentrations for five experimental runs.

| Run no. | Duration (min) | No. observations | Mean $C_{\text{in}}$ (pphm) | Standard deviation (pphm) |
|---------|----------------|------------------|-----------------------------|---------------------------|
| 1       | 190            | 20               | 50.5                        | 0.56                      |
| 2       | 200            | 21               | 54.9                        | 0.57                      |
| 3       | 210            | 22               | 85.0                        | 1.07                      |
| 4       | 240            | 25               | 49.5                        | 0.35                      |
| 5       | 240            | 25               | 49.6                        | 0.43                      |

the average, the rate constant for  $\text{NO}_2$  loss ( $k_{\text{w}}$ ) was  $6.16 \times 10^{-3} \text{ min}^{-1}$ , assuming a first order loss of  $\text{NO}_2$  ( $d[\text{NO}_2]/dt = 6.16 \times 10^{-3} [\text{NO}_2] \text{ min}^{-1}$  for wall loss only). Thus, at an input concentration of 50 pphm and a flow rate of 10 lpm, about 10% would be lost to the chamber walls. As compared with other systems which report 40 to 60% loss of pollutant input during an experiment, this wall loss was small.<sup>19,20</sup> To make the system as free of leaks as possible in order to eliminate pollutant loss or random variation in residence time, negative pressure was used to effect flow, and gasketed seals of Teflon were used at the chamber bottom and at all entry points.

### Biological Performance

Preliminary tests with 2 to 6 soybean plants were made to determine the system's sensitivity to plant loading and the minimal loading which would provide usable kinetic data. Resolution of uptake was good with plant loadings having leaf areas (of one surface) as low as  $2.4 \text{ dm}^2$ .

Twelve to 20 day old soybean and corn plants were grown in a controlled environment room in these tests. Day temperature was  $29.5^\circ\text{C}$  and night  $24^\circ\text{C}$ ; PAR was  $492 \mu\text{einsteins m}^{-2} \text{sec}^{-1}$ ; and relative humidity ranged from 40 to 50%. Each plant was grown in a 177 ml styrofoam cup containing a peat-lite and gravel mixture watered daily with a nutrient solution. During experiments, the soil-root 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. The glass interfaces and around the stem were sealed with fluorocarbon grease to prevent any loss of  $\text{NO}_2$  to the cup or soil.

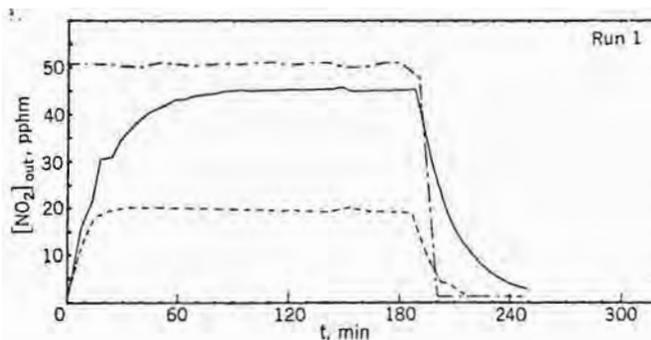


Figure 4. Nitrogen dioxide concentration in inlet (---), outlet of empty chamber (—), and outlet of chamber with six 20 day old soybean plants having a total leaf area of  $6.50 \text{ dm}^2$  (---). The inlet  $\text{NO}_2$  concentration had an average value of 50.5 pphm.

The first run made in this dual chamber system is shown in Figure 4 in which straight line segments were drawn between adjacent instrument readings for the three sample points. The blank portion of this run has already been discussed. Six 20 day old soybean plants with a total leaf area of  $6.50 \text{ dm}^2$  were placed in one chamber and a 10 lpm flow of air containing 50.5 pphm of  $\text{NO}_2$  was begun. The uptake by the plants and the small wall loss reduced this concentration to 19.0 pphm, reaching a steady state after about 30 min.

The air spent an average of 20 min in the reactor, during which 31.5 pphm of  $\text{NO}_2$  was lost. Therefore, the total loss rate,  $r$ , was  $31.5/20 = 1.58 \text{ pphm/min}$ . Some of this rate loss was due to chamber wall losses (Figure 4, blank run.) The long term average wall loss rate was  $6.16 \times 10^{-3} [\text{NO}_2]_{\text{out}}$ , or for this run, approximately 0.12 pphm/min. Thus, the plant uptake accounted for a loss rate of 1.46 pphm/min. This uptake rate remained constant from 30 to 180 min.

Since the concentration of  $\text{NO}_2$  in the reactor, the plant surface area, and the  $\text{NO}_2$  loss rate were constant, a rate constant for uptake by these soybean plants could be estimated using Eq. 1:

$$k_{p2} = \frac{-r_{\text{uptake}}}{[\text{NO}_2][S]} = \frac{1.46 \text{ pphm/min}}{(19.0 \text{ pphm})(6.50 \text{ dm}^2)} = 11.8 \times 10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$$

Another way to calculate  $k_{p2}$  is to use Eq. 5, where  $r$  is written out fully:

$$k_{p2} = \frac{(f/V)([\text{NO}_2]_{\text{out}} - [\text{NO}_2]_{\text{in}}) - k_w}{[\text{NO}_2]_{\text{out}}[S]} - \frac{k_w}{[S]} \quad (8)$$

For the data shown in Figure 4, this equation can be applied anytime between 30 and 180 min (the steady state region) for repeated determinations of  $k_{p2}$ . Rate on a mass basis can be obtained by multiplying  $k_{p2}$  by chamber volume (200 l),  $\mu\text{g}/\mu\text{l}$  (1.88 for  $\text{NO}_2$ ), and  $10^{-2} \mu\text{l/l}$  per pphm yielding a rate of  $44.4 \times 10^{-3} \mu\text{g dm}^{-2} \text{ min}^{-1} \text{ pphm}^{-1}$  exposure concentration. Rates at various exposure levels can then be estimated.

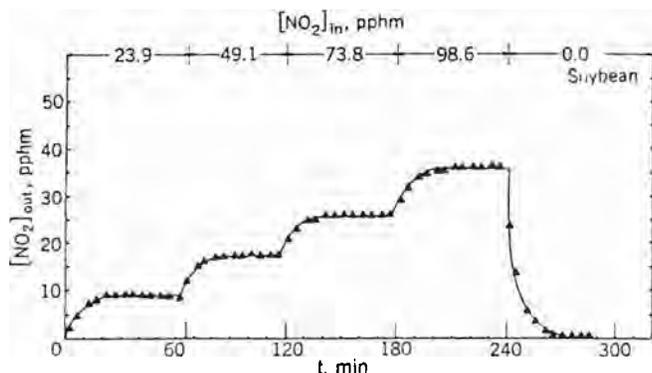
The above equations suggest that  $k_{p2}$  is independent of exposure concentration for a given set of environmental conditions and particular plant type. However, to test this hypothesis and demonstrate the versatility of this system, data shown in Figure 5a were obtained with six 13 day old soybean plants (leaf area =  $7.02 \text{ dm}^2$ ). Since it was shown in Figure 4 that steady state with plant uptake could be achieved in about 30 min,  $C_{\text{in}}$  was made a step function with each step lasting 60 min. The  $C_{\text{in}}$  values for each step are given in Figure 5a. For this system,  $C_{\text{out}}$  was a modified step function with exponential changes between one steady state level and the next.

Eq. 8 was applied to each steady state portion to calculate  $k_{p2}$  values. The results (in units of  $10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$ ) were: 11.2 (20–60 min), 12.2 (80–120 min), 12.4 (140–180 min), and 11.5 (200–240 min). The average value of  $k_{p2}$  was  $11.83 \times 10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$  with a standard deviation of  $0.57 \times 10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$  (4.8%). This value was almost identical with that obtained for 20 day old plants from the data shown in Figure 4.

An alternative method to applying Eq. 8 is to solve analytically Eq. 4 for  $C_{\text{out}}$ , given that  $C_{\text{in}}$  is a step function.<sup>21</sup> If we allow  $k_t = k_{p2}[S] + k_w$ , since  $[S]$  is essentially constant for any run, then

$$C_{\text{out}} = \frac{Q}{Q + k_t} C_{\text{in}} + \left[ C_{\text{out}}^* - \frac{Q}{Q + k_t} C_{\text{in}} \right] e^{-(Q+k_t)(t-t^*)} \quad (9)$$

where  $C_{\text{out}}^*$  is the value of  $C_{\text{out}}$  when  $t^* = 0$ , time 1, time 2 . . . where time 1, time 2 . . . are the times when  $C_{\text{in}}$  undergoes a



**Figure 5a.** Nitrogen dioxide concentrations at chamber outlet with six 13 day old soybean plants having a total leaf area of  $7.02 \text{ dm}^2$  ( $\blacktriangle$ ). The inlet  $\text{NO}_2$  concentration was increased through five values in a step function as indicated. The solid line was computed from Eq. 9 using values:  $Q = 0.050 \text{ min}^{-1}$ ,  $k_t = 0.1030 \text{ min}^{-1}$ , determined by nonlinear least squares fit with an  $R^2 = 0.998$ .

step increase. For only one initial step at  $t = 0$ , and assuming an initially purged reactor,  $C_{\text{out}}^* = 0$  and  $t^* = 0$ . For this case, Eq. 9 reduces to

$$C_{\text{out}} = \frac{Q}{Q + k_t} C_{\text{in}} [1 - e^{-(Q+k_t)t}] \quad (10)$$

This equation illustrates the shortening of time to steady state when a reactive component is used as compared with an inert tracer for which  $k_t = 0$  and explains why  $C_{\text{ss}}$  did not equal  $C_{\text{in}}$  in the blank run shown in Figure 4.

Using a nonlinear least squares program,<sup>22</sup> Eq. 9 was simultaneously fitted to the data given in Figure 5a, a duplicate soybean run, two corn runs (one illustrated in Figure 5b), and two blank runs. For each run, a single value of  $k_t$  was estimated using only the data from that run. All the data from a given chamber were lumped to estimate a single value of  $Q$  for each chamber over three runs. The results are plotted as solid lines in Figure 5.

Using fitted  $k_t$  values for the blank runs as  $k_w$ , for each reactor,  $k_{p2}$  values calculated by  $k_{p2} = (k_t - k_w)/[S]$ , were:

|                       |   |
|-----------------------|---|
| Data in Figure 5a     | $13.79 \times 10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$ |
| Duplicate soybean run | $12.50 \times 10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$ |
| Data in Figure 5b     | $6.82 \times 10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$  |
| Duplicate corn run    | $6.14 \times 10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$  |

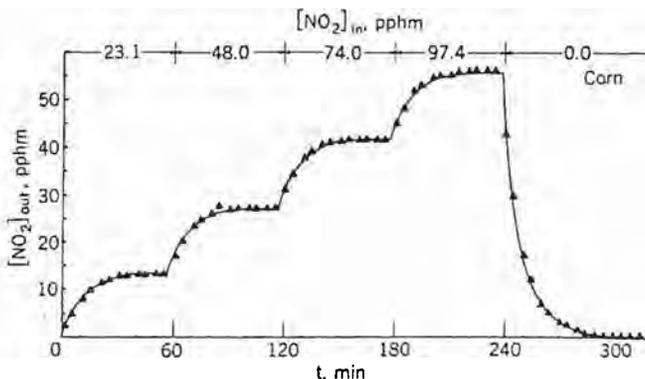
The overall  $R^2$  for these six runs (372 observations) was 0.998, demonstrating the consistent performance of this technique.

Figure 6 also illustrates the performance and versatility of this technique. In this run, the light level measured as photosynthetically active radiation (PAR) was increased stepwise, while the inlet  $\text{NO}_2$  concentration was kept constant at 49.5 pphm. As the light intensity was increased, the rate of uptake increased. The steady state values for  $k_{p2}$  with corn were: 0.4, 2.8, 7.6, and  $15.0 \times 10^{-3} \text{ dm}^{-2} \text{ min}^{-1}$ . Other data (not shown here) indicated that the total diffusion resistance,  $R_t$ , decreased from 23.8 to 10.7, 6.3, and finally to 2.3 sec/cm as the light level was increased. This resistance is based on water vapor diffusion from leaf to air. A regression of  $1/R_t$  against  $k_{p2}$  for these data gave the equation

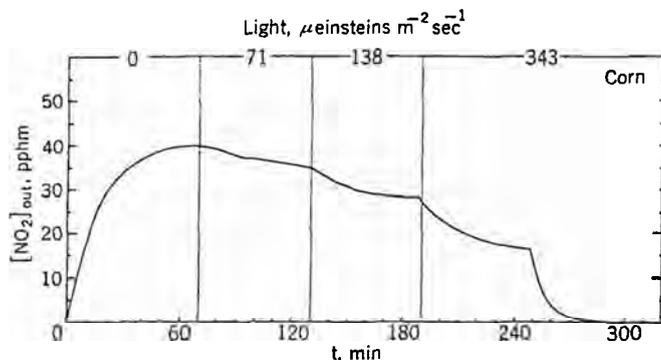
$$k_{p2} = 0.0380/R_t - 0.0003 \quad r^2 = 0.956 \quad (11)$$

Hence, as expected the second order rate constant for  $\text{NO}_2$  uptake by corn appears to be a linear function of the inverse total diffusion resistance.<sup>23,24</sup> Similar results were obtained for soybean.

Thus, considering the plant uptake of a gas as a type of chemical reaction characterized by a "rate constant" ( $k_{p2}$ ) seems quite reasonable:  $k_{p2}$  is independent of the concentra-



**Figure 5b.** Nitrogen dioxide concentrations at chamber outlet with six 12 day old corn plants with a total leaf area of  $5.25 \text{ dm}^2$  ( $\blacktriangle$ ). The inlet  $\text{NO}_2$  concentration was stepped through five values in a step function as indicated. The solid line was computed from Eq. 9 using values:  $Q = 0.56 \text{ min}^{-1}$ ,  $k_t = 0.042 \text{ min}^{-1}$ , determined by nonlinear least squares fit with an  $R^2 = 0.998$ .



**Figure 6.** Nitrogen dioxide concentration at chamber outlet with six 12 day old corn plants with a total leaf area of 5.84 dm<sup>2</sup>. The inlet NO<sub>2</sub> was constant with an average value of 49.5 pphm from 0 to 250 min and 0 thereafter. The light level was increased through four values as indicated.

tion of the gas and of the surface area of the plants exposed, but it is functionally dependent upon the inverse of total diffusion resistance, which is largely governed by stomatal function. The utility of  $k_{p2}$  is that there is a single value for a given set of plant conditions that characterizes the uptake process. Changes in the magnitude of  $k_{p2}$  with changes in environmental or physiological conditions may provide insight into the causative processes of uptake. This approach makes foliar gas uptake amenable to mathematical modeling, including a complete solution of systems of nonlinear differential equations describing the total chemistry by numerical techniques.

## Conclusions

The treatment of plant uptake of gaseous pollutants as a chemical reaction between the gas and the plant surface has proved valuable, and has led to improved chamber design easily characterizable and readily capable of mathematical modeling. Under experimental conditions, the chamber system met all design criteria. Data obtained from these chambers show a high precision for the measurement of kinetic and biological processes. A logical measure of the uptake process has been identified and quantified.

Although the inlet concentrations for the experimental runs of this study were controlled, they do not necessarily have to be controlled. That is, plant uptake rates using techniques based on CSTR function, may be calculated even if the input concentration varies randomly. Thus, such a system could be used in the field where air pollutant concentrations vary.

## Acknowledgments

We gratefully acknowledge financial support from: General Research Support (Dean's office) and Triangle Universities Consortium on Air Pollution, School of Public Health, University of North Carolina, Chapel Hill, NC, and Specific Cooperative Research Agreement, Agricultural Research Service, USDA, North Carolina State University, Raleigh, NC. We are indebted to F. Malcolm, R. Kamens, D. Fox, R. Philbeck, and to staff members of the North Carolina State University Phytotron, Raleigh NC, for their help.

## References

1. W. W. Heck, O. C. Taylor, and H. E. Heggstad, "Air pollution research needs: herbaceous and ornamental plants and agriculturally generated pollutants," *J. Air Poll. Control Assoc.* 23:257 (1973).
2. R. L. Kabel, R. A. O'Dell, M. Taheri, and D. D. Davis, "A Preliminary Model of Gaseous Pollutant Uptake by Vegetation," CAES Publication No. 455-76, Center for Air Environment Studies, Pennsylvania State University, University Park, PA, 1976.
3. J. H. Bennett and A. C. Hill, "Interactions of Air Pollutants with Canopies of Vegetation," in *Responses of Plants to Air Pollution*, Academic Press, New York, 1975, pp. 273-306.
4. Energy Research and Development Administration, Technical Information Center, Oak Ridge, TN, *Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants* (1974), ERDA Symposium Series 38, 1976.
5. K. H. Rasmussen, M. Taheri, and R. L. Kabel, "Sources and Natural Removal Processes for Some Atmospheric Pollutants," EPA-650/4-74-032, Office of Research and Development, EPA, June 1974.
6. W. H. Smith, "Air pollution effects on the structure and function of the temperate forest ecosystems," *Environ. Poll.* 6:111 (1974).
7. Y. K. Doshi, "Design of a Digitally Controlled Environmental Chamber for Air Pollution Effects Studies on Plants," Report EES-511x-1, Atmospheric Sciences Program and Department of Electrical Engineering, Ohio State University, Columbus, OH, Dec. 1975.
8. W. W. Heck, J. A. Dunning, and H. Johnson, "Design of a Simple Plant Exposure Chamber," APTD-68-6, National Center for Air Pollution Control, HEW, Cincinnati, OH, 1968.
9. S. B. McLaughlin, V. J. Schorn, and H. C. Jones, "A programmable exposure system for kinetic dose-response studies with air pollutants," *J. Air Poll. Control Assoc.* 26:132 (1976).
10. F. A. Wood, D. B. Drummond, R. G. Wilhour, and D. D. Davis, "An Exposure Chamber for Studying the Effects of Air Pollutants on Plants," Progress Report 335, College of Agriculture, Pennsylvania State University, University Park, PA, Nov. 1973.
11. A. C. Hill, "A special purpose plant environmental chamber for air pollution studies," *J. Air Poll. Control Assoc.* 17:743 (1967).
12. H. H. Rogers, "Uptake of Nitrogen Dioxide by Selected Plant Species," Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1975.
13. D. R. Mason and E. L. Piret, "Continuous flow stirred tank reactor systems," *Ind. Eng. Chem.* 42:317 (1950).
14. J. G. van de Vusse, "Mixing by agitation of miscible liquids," *Chem. Eng. Sci.* 4:178 (1958).
15. V. W. Uhl and J. B. Gray, eds., *Mixing: Theory and Practice*, Vols. I and II, Academic Press, New York, 1966.
16. Mention of trade or company name does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture, or the North Carolina State University and does not imply their approval to the exclusion of other products that may be suitable.
17. O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed., John Wiley and Sons, N.Y. 1972.
18. E. I. Du Pont De Nemours and Co. "Teflon FEP: Optical Properties," Technical Information Bulletin T-5, Fluorocarbons Division, Wilmington, DE.
19. M. W. Meyer, "Absorption and Release of Ammonia from and to the Atmosphere by Plants," Ph.D. Dissertation, University of Maryland, College Park, MD, 1973.
20. D. T. Tingey, National Ecological Research Laboratory, EPA, Corvallis, OR, private communication, 1975.
21. C. E. Feigley, Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina at Chapel Hill, N. C., private communication, 1975.
22. C. Daniel and F. Wood, *Fitting Equations to Data*, John Wiley, NY, 1971.
23. Saul Rich, P. E. Waggoner, and H. Tomlinson, "Ozone uptake by bean leaves," *Science* 169 (1970).
24. R. W. Shawcroft, E. R. Lemon, and D. W. Stewart, "Estimation of Internal Crop Water Status from Meteorological and Plant Parameters," in *Plant Response to Climatic Factors*, Proc. of Uppsala Symposium, 1970, UNESCO 1973.