DEPOSITION OF NITROGEN DIOXIDE TO POROUS BIOLOGICAL SURFACES

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ABSTRACT

For this study, a completely stirred tank reactor (CSTR) was constructed and used to study the deposition of NO_2 onto plant and soil surfaces. Spider plants were chosen for study because they are a common house plant and NO_2 was chosen because it is an indoor air pollutant of major importance. Four separate surfaces were tested in this project: the polyethylene surface of the reactor chamber, empty clay pots, pots with soil, and spider plants (with and without exposure of the pots and soil). Deposition to all of the surfaces was clearly observed. With chamber, pot, soil, and plant surfaces exposed, the inlet concentration of 0.54 ppm was reduced to 0.16 ppm. Based on linear relationships between concentration and deposition, the estimated deposition for the experiment with pots, soil, and plants was within 15% of the measured total. Evaluation of the results showed that the data were better explained by a non-linear model. For the run with the pots, soil, and plants, it was found that the predicted deposition based on the non-linear model was within 5% of the measured deposition. A computer simulation was used to determine if plants can be a significant mechanism to remove NO_2 from indoor air; however, it was found that the plants will not make a significant difference in indoor concentration.

INTRODUCTION

The problem of indoor air pollution can be traced to two main causes. First, people spend most of their time indoors. Second, indoor air can be more polluted than outdoor air, in some cases exceeding federal standards. Sources of indoor air pollutants can include outside air infiltrating in; the earth; building and furniture materials; and combustion appliances like kerosene heaters or gas stoves (Wadden and Scheff 1983). Some plants can take in air pollutants and metabolize them. For example, bean plants were shown to take in NO_2 through the stomata in the leaves, and then reduce the NO_2 to NH_4, which could then be used as a nutrient (Rogers et al. 1979).

For this study, a completely stirred tank reactor (CSTR) was constructed and used to study the deposition of NO_2 onto plant and soil surfaces. The objectives were to:

1. Confirm the completely stirred tank reactor as an effective method to measure sink rates;
2. Develop rates of pollutant uptake by a plant and soil; and
3. Determine if plants are a significant sink for indoor air pollutants.

Spider plants were chosen for study because they are a common house plant and have been used in similar studies (Wolverton et al. 1984). NO_2 was chosen for study because it is an indoor air pollutant of major importance, it is easy to produce and measure, and it is known that plants metabolize NO_2.

EXPERIMENTAL

CSTR Model

Batch reactors have been commonly used to measure source and sink rates of pollutants to and from materials. This method has several problems. The concentration of pollutants is not necessarily uniform throughout the reactor. Because of this, the measured concentration may not be the same as the concentration at the surface. Monitoring the concentration may disturb the system. Finally, it may be difficult to make accurate measurements from small sample volumes removed from a batch system.

The CSTR overcomes these problems. The CSTR (Figure 1) consists of a chamber with an input and output. A propeller or impeller is used to mix the fluid in the chamber. Within the chamber, there can be a reaction, in this case, a source or sink of pollutant gas. For a CSTR, the outlet concentration is equal to the chamber concentration. The mathematical representation of the CSTR is:

$$V \frac{dC}{dt} = Q C_o - Q C + S - R \qquad (1)$$

where V is the chamber volume (m³); C is the chamber or outlet concentration ($\mu g/m^3$); C_o is the inlet concentration ($\mu g/m^3$); S is the source rate ($\mu g/min$); R is the sink rate ($\mu g/min$); and t is time (min). The sink rate has been modeled as a first-order function of concentration (Wadden and Scheff 1983):

$$R = K_{dep} A C \qquad (2)$$

where K_{dep} is the deposition velocity (m/min) and A is the surface area (m²). The linear constant K_{dep} is what characterizes the deposition of a pollutant to a surface and, because it has dimensions of rate of decay of NO_2 ($\mu g/m^2 \cdot min$) per mean concentration of NO_2 at the surface ($\mu g/m^3$), it is referred to as a deposition velocity.
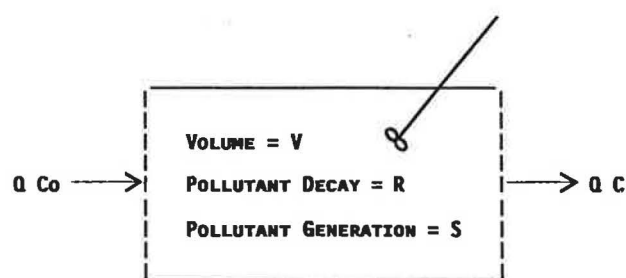

Figure 1 The completely stirred tank reactor

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Apparatus

The NO_2 was purchased from an industrial supply house. The gas was fed to a metering device which regulated the NO_2 flow and mixed it with filtered, dried air. Ambient NO and NO_2 were removed by the filtration system. The metering device fed the chamber inlet. The relative humidity of the air entering the chamber was 45%. The chamber was a polyethylene cylinder with a diameter of 55.7 cm, a height of 54.0 cm, and a total volume of 143.3 L. Polyethylene has been shown not to be a large sink for NO_2 (Spicer et al. 1986). Note that the later measurements were made in a batch reactor. Total flow through the chamber was 7.03 L/min, for a residence time of 20.4 min. The gas was mixed by an impeller turning at 370 rpm. Three 2.2-in-wide baffles at 120° created turbulence for better mixing. A 15 W fluorescent light provided 85 ± 13 footcandles (fc) of light at the base. The chamber is illustrated in Figure 2. Materials are inserted or removed by raising the chamber over the base. A mixing test was performed using a tracer gas and the system was found to be completely mixed (Bonem 1988). The chamber outlet was connected to an NO_2 analyzer, which used the chemiluminescent method to determine NO_x and NO concentrations. The output was recorded on a strip chart recorder.

Test Design

Four separate surfaces were tested in this project. The empty chamber was tested to characterize the deposition to the polyethylene surface. Empty clay pots were tested to characterize the deposition to the surface of the pots (correcting for the deposition to the chamber). Pots with soil were tested to characterize the deposition to the soil (correcting for removal by the chamber and pot surfaces). Plants were tested, with the pots and soil covered by plastic bags, to characterize the deposition to the plants. Finally, the plants were tested with the pots and soil exposed. This last test served as a check to see if the deposition of the sum of the surfaces would add up to the total deposition.

In each test, the concentration was raised and lowered in steps. Starting with zero concentration of NO_2, the concentration was raised to 0.25 ppm (463 $\mu g/m^3$) for six hours, 0.54 ppm (1003 $\mu g/m^3$) for six hours, down to 0.25 ppm for six hours, and back to zero for six hours. These levels were chosen to bracket typical acute values for a house with combustion sources (Wadden and Scheff 1983). Before each test,
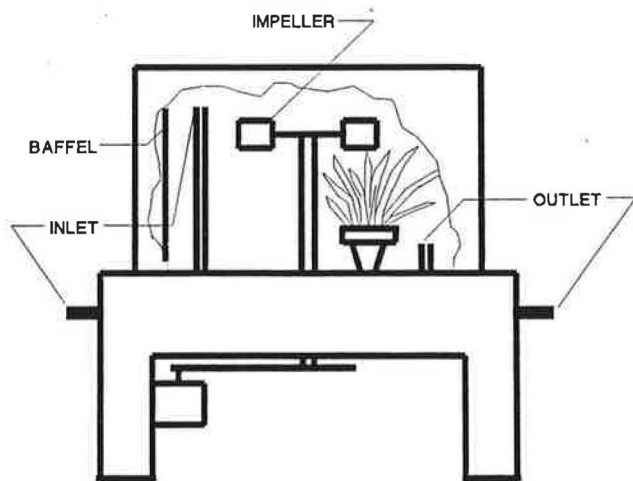
a calibration check was made using 0.4 ppm NO in N_2 calibration gas.

RESULTS

A graph of the inlet and outlet concentrations appears in Figure 3. Several things can be learned by a qualitative examination of this graph. It is clear that there is deposition to all surfaces. With chamber, pot, soil, and plant surfaces exposed, the inlet concentration of 0.54 ppm was reduced to 0.16 ppm.

There is also significant hysteresis in the system. The deposition at the first 0.25 ppm level (going up) is larger than the deposition at the second 0.25 ppm input (coming down). This might be explained by various parts of the system initially absorbing the NO_2 and desorbing the gas as the inlet concentration was decreased.

The figure also shows that with a 0.54 ppm input to the chamber, the uptake by the plants diminishes with time. This might be due to the toxic effects of the NO_2. The plants seem to recover after the concentration was reduced.

Linear Model

To determine the deposition velocities, several calculation steps were necessary, as illustrated in Table 1. The concentrations multiplied by the total gas flow rates gives the NO_2 mass flow rates. The total deposition or sink rates are then the difference between NO_2 mass flow into the chamber and the NO_2 mass flow out of the chamber. In the first experiment, the chamber is the only surface, so the total deposition is equal to the deposition to the chamber.

To separate the depositions to the other surfaces, it is necessary to use the relationship between deposition and concentration. For example, the deposition to the chamber is known only at the measured concentrations from the chamber-only experiment. However, there is deposition to the chamber at all other concentrations as well. Recall that as a surface was added, the chamber concentration decreased.

A linear model was developed from the empty chamber experiment and was used to determine the deposition to the chamber at all other concentrations. Thus, to determine the deposition to the pots, the deposition to the chamber is determined for the actual chamber concentration by the linear model, and the deposition to the pots calculated as the difference between the total deposition and deposition to the
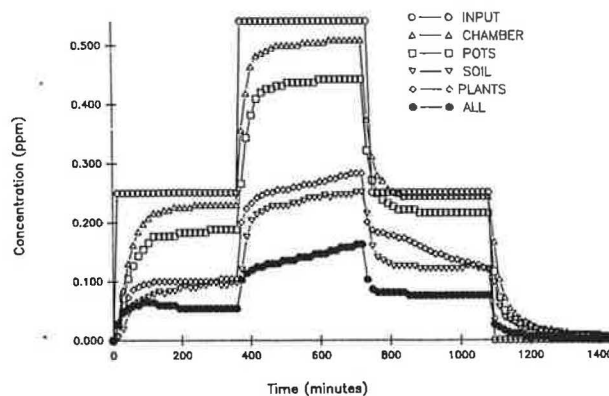

Figure 2 The chamber

Figure 3 Concentrations with surfaces

TABLE 1
Concentration, Mass Flow and Deposition Rates

Test	Conc.[a] in	out	Mass Flow[b] in	out	Deposition, μg/min total	chamber	pot	soil	plant
Chamber	469	425	3.30	2.99	0.307	0.307			
	1003	942	7.06	6.63	0.429	0.429			
	475	450	3.34	3.16					
Pot	462	358	3.25	3.52	0.733	0.283	0.477		
	1011	829	7.10	5.83	1.270	0.406	0.864		
	475	389	3.35	2.74					
Soil[c]	469	172	3.30	1.21	2.084	0.210	0.153	1.721	
	1009	464	7.11	3.26	3.840	0.319	0.333	3.188	
	469	231	3.30	1.63					
Plant	475	194	3.34	1.36	1.979	0.221	—	—	1.758
	1009	464	7.11	3.26	3.840	0.319	—	—	2.984
	469	231	3.30	1.63					
All	475	100	3.34	0.70	2.637	0.167	0.105	1.228	1.214
	1003	301	7.06	2.12	4.942	0.265	0.249	2.435	2.163
	475	150	3.35	1.06					
Soil[d]	313	118	2.02	0.83	1.371	0.180	0.114	1.077	
	503	207	3.54	1.45	2.081	0.227	0.177	1.677	
	767	352	5.40	2.48	2.917	0.284	0.268	2.365	
	1043	533	7.34	3.75	3.586	0.337	0.372	2.877	

[a]Concentration in μg/m³.

[b]Mass flow rate in μg/min.

[c]Sunshine Aggrate Plus, Fissons Western Corp, Vancover, BC.

[d]Hyponex Professional Mix, Hyponex Corp., Atlanta, GA.

TABLE 2
Linear Model Deposition Velocities

Surface	Area, cm²	Concentration, ppm Inlet	Outlet	K_{dep}, cm/min
Chamber	15,443	0.25	0.23	0.0468
		0.54	0.51	0.0295
Pot	2004	0.25	0.19	0.615
		0.54	0.45	0.522
Soil	265	0.25	0.09	36.6
		0.54	0.25	26.0
Plant	2406	0.25	0.10	3.70
		0.54	0.29	2.34

chamber. A linear model for the deposition to the pots was then developed to be used for subsequent calculations. In this way, the deposition to each surface was modeled.

The deposition velocity was then calculated by dividing the deposition to each surface (sink rate) by the concentration and the area of the exposed surface. The deposition velocities are presented in Table 2. The surface area of the plants represents the total area of one side of the leaves. Based on the linear relationships between concentration and deposition, the sum of estimated depositions to the four surfaces for the experiment with pots, soil, and plants was within 15% of the measured total.

Non-Linear Model

When the data points for each surface are plotted with the linear models, the lines do not pass through the origin (Figure 4). This is physically impossible, as the deposition
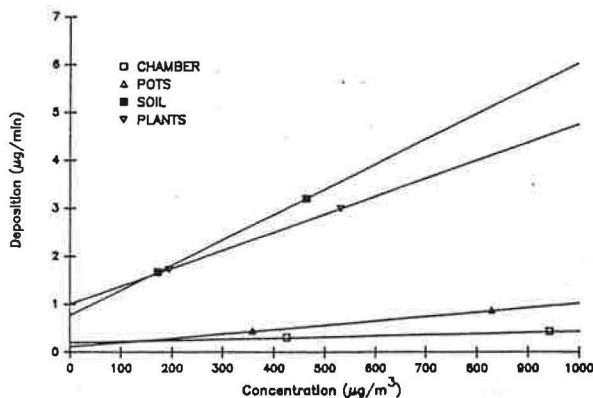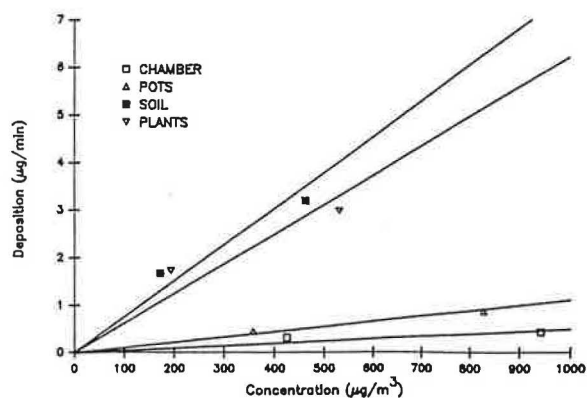

Figure 4 Data and linear models

Figure 5 Data and linear models through zero

TABLE 3
Non-Linear Model Deposition Constants

Surface	Area, cm²	K_{nl}	n
Chamber	15,443	0.0160	0.417
Pot	2004	0.0220	0.786
Soil	265	2.63	0.623
Plant	2406	0.458	0.525

must be zero for a zero chamber concentration. This observation calls the linear model into question. If least-squares linear models are constructed that force the line through the origin, it is seen that the data vary from the model in a consistent manner (Figure 5). The data are above the model at lower chamber concentrations, and below the model at higher chamber concentrations. These observations suggest that a non-linear model of concentration and deposition may be required. A non-linear model using the following parabolic relationship was used to model the deposition rate:

$$R = K_{nl} C^n \qquad (3)$$

where K_{nl} and n are fitted parameters. A new constant, K_{nl} (non-linear), is used because the constant is no longer a deposition velocity. Table 3 summarizes the results of calculations based on the parabolic model. For the run with the pots, soil, and plants, it was found that the agreement between the sum of the predicted deposition to the surfaces and the measured deposition to all of the surfaces was now within 5% for both inlet concentrations. This demonstrates the validity of
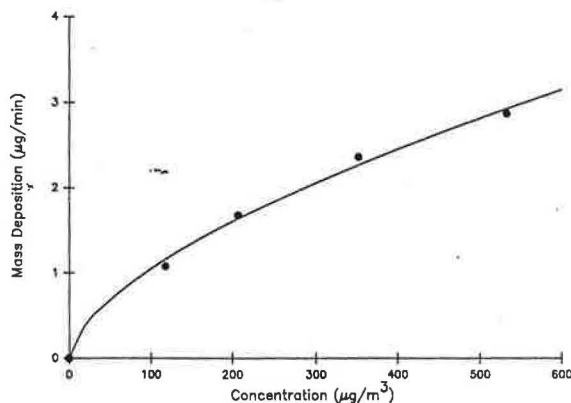

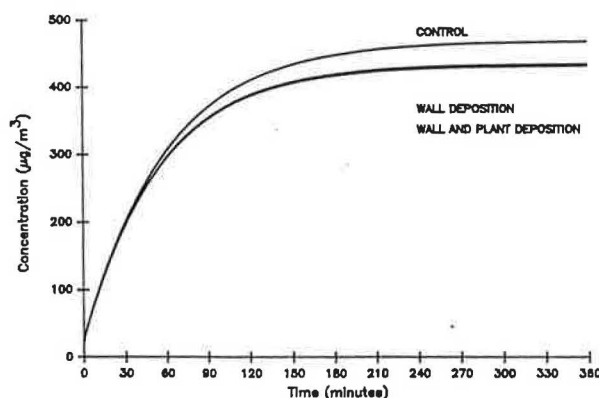Figure 6 Deposition vs. concentration for soil

the non-linear model and the effectiveness of the CSTR as a tool to develop sink rates.

Because non-linear deposition is a departure from previous work, it was felt that another test with more data points should be run to confirm the result. A test with a second soil using four steps up in concentration was made. Figure 6 shows the data points graphed with the fitted parabolic model. The r^2 for the curve is 0.999.

An unexplained phenomenon occurred during the soil tests. The soil covered NO_2 to large amounts of what appears to be NO. This is significant since NO is less toxic than NO_2. Another soil was tested with similar results. A sample of soil was sterilized with gamma radiation to determine if the reaction was biological in origin. The sterile soil, however, also generated the NO. Nishimura et al. (1986) reported conversion of NO_2 to NO by some plants. Spicer et al. (1986) and Yamanaka (1984) report similar reactions with building materials. Pitts et al. (1985) found nitrous acid (HONO) to be a decay product of NO_2. Either NO_2 is being chemically converted to NO, or NO_2 is being converted to HONO and is interpreted by the chemiluminescent reaction in the NO_x analyzer as NO.

Application

A computer simulation was used to determine if plants can be a significant mechanism to remove NO_2 from indoor air. The SIMBAS program, by H.R. Bungay and modified by C.N. Haas, solves differential equations over time. A living room with furniture and four spider plants was simulated using the deposition constants developed in this experiment. The plant deposition velocity was 0.0369 m/min (0.121 ft/min), the soil deposition velocity was 0.3361 m/min (1.102 ft/min), and the room deposition velocity was 0.0054 m/min (0.0177 ft/min) (Wadden and Scheff 1983). The room volume was 762.4 m³ (2500 ft³), and the airflow rate was 12.71 m³/min (1 ach). As illustrated in Figure 7, the plants do not make a significant difference. Another simulation, using 10 plants, is illustrated in Figure 8. Though the deposition is now observable, it is still not significant.

CONCLUSION

The CSTR is an effective tool to measure indoor pollutant source and sink rates. Plants and soil take up NO_2; however, the surface area is likely to be too small to be significant in an indoor environment. We also observed that when analyzed by a chemiluminescence analyzer, soil transforms NO_2 into another gas which appears to be NO. Our

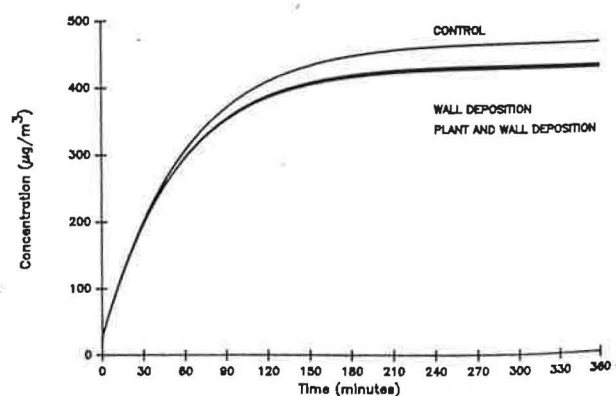Figure 7 Room simulation with four plants

Figure 8 Room simulation with ten plants

data suggest that the assumption of a linear relationship between concentration and deposition is not correct. For our data, a parabolic model more accurately represents this relationship.

REFERENCES

Bonem, M.L. 1988. "Plant deposition of nitrogen dioxide.". Masters thesis, Illinois Institute of Technology.

Bungay, H.R., and Stanzione, D.C. "SIMBAS, a simple language in BASIC for solving simultaneous differential equations." Unpublished.

Nishimura, H.; Hayamiza, T.; and Yanagisawa, Y. 1986. "Reduction of NO_2 to NO by rush and other plants." *Environmental Science and Technology*, Vol. 20, pp. 413–416.

Pitts, J.N.; Wallington, T.; Biermann, H.W.; and Winer, A.M. 1985. "Identification of nitrous acid in an indoor environment." *Atmospheric Environment*, Vol. 19, pp. 763–767.

Rogers, H.H.; Cambell, J.C.; and Volk, R.J. 1979. "Nitrogen-15 dioxide uptake and incorporation by phaseolus vulgaris (L)." *Science*, Vol. 206, pp. 333–335.

Spicer, C.W.; Coutant, R.W.; and Ward, G.F. 1986. "Investigation of nitrogen dioxide removal from indoor air." Final Report for the Gas Research Institute, Contract No. 5082-241-0772.

Wadden, R.A., and Scheff, P.A. 1983. *Indoor air pollution: characterization, prediction and control.* New York: John Wiley and Sons.

Wolverton, B.C.; McDonald, R.C.; and Watkins, E.A. 1984. "Foliage plants for removing indoor air pollutants from energy efficient homes." *Economic Botany*, Vol. 38, pp. 224–228.

Yamanaka, S. 1984. "Decay rates of nitrogen oxides in a typical Japanese living room." *Environmental Science and Technology*, Vol. 18, pp. 556–570.