Environ. Sci. Technol. **1995**, *29*, 2901–2903

Absorption of Formaldehyde by Oleander (*Nerium indicum*)

TAKAYUKI KONDO,
KIYOSHI HASEGAWA,* AND
RYUTARO UCHIDA

Chemical and Biochemical Engineering, Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama 930, Japan

MASANORI ONISHI AND
AKIHIRO MIZUKAMI

Toyama Prefectural Environmental Science Research Center, 17-1 Nakataikouyama, Kosugi, Toyama 939-03, Japan

KENJI OMASA

The National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305, Japan

Introduction

Vegetation is known to act as an important sink for gaseous air pollutants. Since Hill (*1*) demonstrated that alfalfa absorbed inorganic air pollutants such as SO_2, NO_2, O_3, and Cl_2, a number of investigators have repeatedly confirmed the absorption of SO_2 (*2, 3*), NO_2 (*4, 5*), and O_3 (*6, 7*) by plants. On the other hand, few studies have investigated the absorption of organic air pollutants by plants. Bacci *et al.* (*8*), and Simonich *et al.* (*9, 10*) observed the leaf–air partitioning of lipophilic organic chemicals such as chlorinated hydrocarbons and polycyclic aromatic hydrocarbons. Accordingly, the planting of trees is one strategy for reducing the concentration of air pollutants in polluted urban and industrial areas (*11*).

Atmospheric formaldehyde is given off as an exhaust gas from fuel combustion, solvent use, garbage incineration, and other activities (*12*). It is also produced by secondary reactions of hydrocarbons with O_3. Recently, the atmospheric levels and environmental fate of formaldehyde have attracted attention as a major volatile organic pollutant. Gabele (*13*) reported that atmospheric formaldehyde may increase as a result of switching from gasoline and diesel fuels to methanol fuels. On the other hand, the indoor concentration of formaldehyde has been found to be higher than outdoors because of indoor sources such as wood products and furniture (*14*).

Girard *et al.* (*15*) and Mutters *et al.* (*16*) observed the incorporation of atmospheric formaldehyde into sugars and amino acids in leaves of plants, although the absorption rate was not determined. To estimate the effect of tree-planting on atmospheric formaldehyde, it is necessary to determine the absorption rate of formaldehyde by trees. Therefore, the rate of formaldehyde absorption by oleander (*Nerium indicum*), which is popular as a street tree or garden tree in Japan, was measured.

This paper describes the development of a reliable method for measuring the absorption of formaldehyde by trees and the effects of light intensity, transpiration rate, and formaldehyde concentration on the rate of absorption by oleander.

* Fax: 764-41-8432.

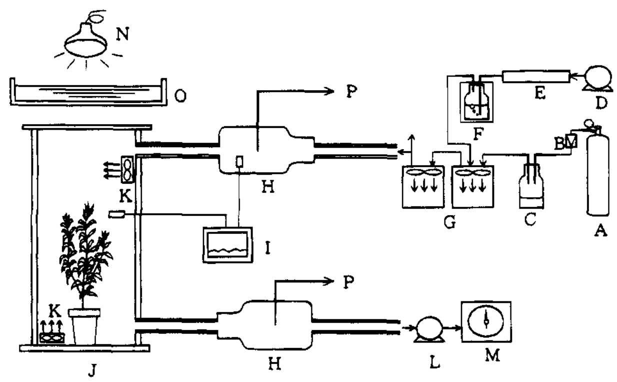

FIGURE 1. Apparatus for measuring the absorption of formaldehyde by trees: A, N_2 gas; B, mass flow controller; C, formaldehyde solution (37%); D, pump; E, activated charcoal; F, H_2O bubbler; G, mixing chamber; H, buffer tank; I, thermometer and hygrometer; J, exposure chamber; K, fan; L, pump; M, dry gas meter; N, lamp; O, water filter; P, to bubblers for sampling of formaldehyde gas.

Experimental Section

Apparatus. Figure 1 shows the apparatus used for measuring the rate of formaldehyde absorption by trees. Measurements of formaldehyde absorption were conducted using a chamber system placed in a temperature-controlled room. The system consisted of two major components: gas conditioning instrumentation (Figure 1, A–G) and a cylindrical exposure chamber (H–O).

Humidity-controlled pure air and formaldehyde-containing N_2 were introduced into a mixing chamber (G). Formaldehyde concentration in the gas mixture was controlled by the flow rate of N_2, and the humidity of the gas was regulated by the temperature of a H_2O bubbler (F).

The exposure chamber system consisted of a 120-L cylindrical acrylic chamber (J) equipped with 10-L buffer tanks (H) at its inlet and outlet. The rate of gas flow through the chamber was about 20 L min^{-1}. Mixing of the chamber gas, facilitated by two internally mounted fans (K), was adequate for creating a uniform distribution of the formaldehyde concentration.

Mean inlet temperature and relative humidity were 26 $\pm$ 0.6 °C and 70 $\pm$ 5%, respectively. The inlet concentrations of formaldehyde were within the range of 65–75 ppb and the photosynthetic photon flux density (PPFD) was 600 μmol of photons m^{-2} s^{-1} (Koito Co. Ltd., IKS-25; calibrated by Li-Cor Inc., Li-185A) at the height of the plant inside the chamber, except for the experiments in which the inlet concentrations of formaldehyde or PPFD were varied.

Measurement of Formaldehyde and Calculation of Absorption Rate. Gas samples in the inlet and outlet buffer tanks were drawn at a flow rate of 1 L min^{-1} for 4 h through two bubblers in series, each containing 10 mL of 0.5% boric acid solution (*17*). The solutions were combined, and the inlet and outlet concentrations of formaldehyde were measured using a AHMT (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole) procedure (*18*). The absorption rate of formaldehyde was corrected by a "blank" experiment performed with an empty chamber. The corrected absorption rate was calculated using the procedure of Hanson *et al.* (*5*).

0013-936X/95/0929-2901$09.00/0

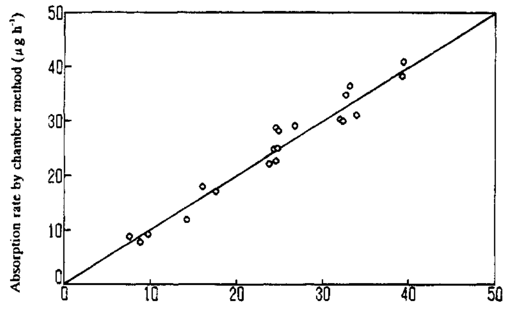

FIGURE 2. Relationship between the actual rate of formaldehyde absorption by filter papers and the rate of formaldehyde absorption using the chamber method.

Reliability of the Chamber System. The reliability of this chamber system was tested using cylindrical filter papers coated with trimethanolamine, which is an absorbent of formaldehyde. The absorption rates of formaldehyde using this chamber system were compared with those measured from the actual amount of formaldehyde absorbed on the filter papers. Prior to the experiments, the gas mixture was passed through the chamber for more than 30 min under the experimental conditions to equilibrate the system, then the filter papers were placed quickly in the chamber, and the experiment was started. After 4 h, the filter papers were extracted with distilled water by sonication for 15 min. A portion of the extracted solution was then analyzed using the AHMT procedure.

Absorption of Formaldehyde by Oleander. The effects of light intensity and formaldehyde concentration on the rate of absorption by oleander were examined. After conditioning for more than 30 min, the rate of absorption by oleander was measured while varying the light intensity from 100 to 600 μmol of photons m^{-2} s^{-1}. The transpiration rate was determined from the decrease in the weight of oleander planted in a pot, which was covered with a plastic bag. In the experiments whose inlet concentrations of formaldehyde were changed from 60 to 470 ppb, the rate of absorption of formaldehyde by oleander was measured for 8 h at a sampling flow rate of 0.5 L min^{-1}.

Results

The variation in the inlet concentration of formaldehyde was measured every hour for 8 h. The relative standard deviation was less than 5.0%. The outlet/inlet ratio of formaldehyde concentration was 98.2 ± 2.0% ($n = 9$) in the "blank" experiment. Figure 2 shows the results of absorption of formaldehyde with the filter papers. The relationship between the absorption rate determined by the chamber method and the actual absorption rate of formaldehyde was linear (1.01 ± 0.10, $n = 20$).

Table 1 shows the rate of formaldehyde absorption by oleander at various light intensities. The absorption rates were normalized for leaf area (one side) and the outlet concentration of formaldehyde. Since a uniform distribution of formaldehyde concentration in the chamber must be attained, the outlet concentration of formaldehyde was considered to be equal to that in the chamber itself (*4*). The absorption rates of formaldehyde by oleander were within the range 9.5–103 ng dm^{-2} h^{-1} ppb^{-1} and increased as the level of PPFD increased.

Figure 3 shows the linear relationship between the absorption rate of formaldehyde and the transpiration rate of oleander, obtained from the experiments in which the light intensity was varied ($r = 0.963$, $n = 16$). The transpiration rate was normalized for leaf area and the vapor pressure of water differential between the actual value and saturated value inside the chamber.

Figure 4 shows the relationship between the absorption rate and the concentration of formaldehyde. Within the concentration range of 35–245 ppb, the rate of formaldehyde absorption increased linearly with increasing formaldehyde concentration.

TABLE 1

Absorption Rate of Formaldehyde by Oleander

PPFD[a] (μmol of photons m^{-2} s^{-1})	absorption rate[b] (ng dm^{-2} h^{-1} ppb^{-1})
100	9.5 ± 1.8
200	28.7 ± 8.0
400	92.6 ± 21.1
600	103 ± 26.5

[a] Photosynthetic photon flux density. [b] Mean value and standard deviation of four measurements.

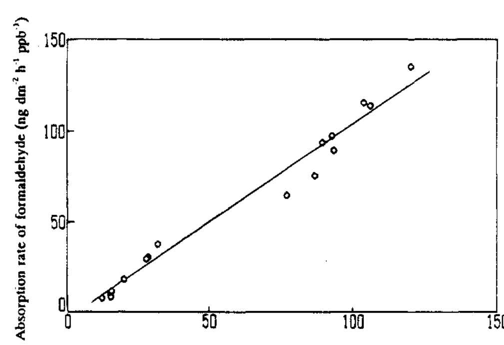

FIGURE 3. Relationship between the rate of formaldehyde absorption and the transpiration rate of oleander.

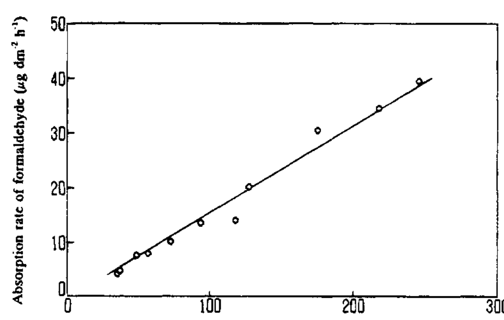

FIGURE 4. Relationship between the rate of formaldehyde absorption and formaldehyde concentration.

Discussion

The results of the "blank" experiment indicated that the adsorption of formaldehyde to the walls of the chamber and the formation or decomposition of formaldehyde in the chamber were very small using this system. From the results of formaldehyde absorption with the filter papers, it was confirmed that this chamber system was applicable to the measurement of formaldehyde absorption by trees.

The rate of formaldehyde absorption by oleander was 103 ng dm^{-2} h^{-1} ppb^{-1} at 600 μmol of photons m^{-2} s^{-1}. Rogers *et al.* (*4*) reported that the rates of NO_2 uptake by loblolly pine and white oak were 5.2×10^{-2} and 1.1×10^{-2}

$\mu g\ dm^{-2}\ min^{-1}\ pphm^{-1}$ at 492 μmol of photons $m^{-2}\ s^{-1}$, respectively. In our study, the absorption rate determined using the same units as those of Rogers *et al.* (*4*) was estimated to be $1.7 \times 10^{-2}\ \mu g\ dm^{-2}\ min^{-1}\ pphm^{-1}$ at 600 μmol of photons $m^{-2}\ s^{-1}$. Thus, it was confirmed that atmospheric formaldehyde was absorbed by oleander at an absorption rate similar to that of atmospheric NO_2.

The rate of formaldehyde absorption by oleander increased as the level of PPFD increased. This relationship agrees with the results obtained by Rogers *et al.* (*4*) for NO_2 uptake by corn and soybean. They explained that the increased rate of NO_2 uptake with increasing light intensity was due to a decrease in total diffusive resistance. In our results, a linear relationship between the rate of formaldehyde absorption and transpiration rate was observed. Since the wind speed inside the chamber was almost constant, it is reasonable to consider that the resistance of the leaf boundary layer was constant and that the increase in the transpiration rate was equal to the increase in stomatal conductance. Consequently, the absorption of formaldehyde increased as stomatal conductance increased. Thus, we can conclude that formaldehyde is absorbed through the stomata. It was found by Hanson *et al.* (*5*) and Johansson *et al.* (*19*) that NO_2 absorption by trees is strongly influenced by stomatal conductance. Omasa *et al.* (*20, 21*) concluded that the absorption rates of SO_2, NO_2, and O_3 can be explained by factors such as boundary layer and stomatal resistance, which are related to gaseous diffusion. The mechanism of formaldehyde absorption by trees is similar to that of inorganic air pollutants such as SO_2, NO_2, and O_3 because of its hydrophilic property.

As shown in Figure 4, increasing the concentration of formaldehyde did not affect the absorption ability of oleander, and no visible injury was observed during the 8-h exposure period even at a high concentration of 245 ppb. Singh *et al.* (*22*) showed that formaldehyde concentrations in urban sites in the United States were within the range of 6.6–45.9 ppb. Zhang *et al.* (*14*) found that indoor formaldehyde concentrations in six residential houses were within the range of 26.9–101.7 ppb. Therefore, trees have sufficient ability to absorb atmospheric formaldehyde in urban areas or within the home.

Mutters *et al.* (*16*) observed that plant growth was higher when plants were exposed to high concentrations of gaseous formaldehyde (400 ppb) and that higher concentrations of sucrose and glycine in leaf tissue were associated with formaldehyde treatment. They concluded that atmospheric formaldehyde would probably have no harmful effect on short-term growth of beans at 400 ppb. Krall *et al.* (*23*) reported that barley incorporated formaldehyde into sugars, amino acids, and choline in the leaves under light irradiation. Girard *et al.* (*15*) found that formaldehyde was incorporated predominantly into amino acids of younger leaves. From our experimental results, we cannot discuss the metabolism of formaldehyde in leaf tissue of oleander; however, it seems that similar metabolic pathways to those described above (*15, 16, 23*) play an important role in the absorption of formaldehyde. It is concluded that trees in general could act as an important sink for atmospheric formaldehyde.

Literature Cited

(1) Hill, A. C. *J. Air Pollut. Control Assoc.* **1971**, *21*, 341–346.
(2) Elkiey, T.; Ormrod, D. P.; Marie, B. *HortScience* **1982**, *17*, 358–360.
(3) Roberts, B. R. *Environ. Pollut.* **1974**, *7*, 133–141.
(4) Rogers, H. H.; Jeffries, H. E.; Witherspoon, A. M. *J. Environ. Qual.* **1979**, *8*, 551–557.
(5) Hanson, P. J.; Rott, K.; Taylor, G. E., Jr.; Gunderson, C. A.; Lindberg, S. E.; Ross-Todd, B. M. *Atmos. Environ.* **1989**, *23*, 1783–1794.
(6) Townsend, A. M. *J. Am. Soc. Hort. Sci.* **1974**, *99*, 206–208.
(7) Fujinami, Y.; Furukawa, T.; Totuka, T.; Tazaki, T. *Environ. Control Biol.* **1987**, *25*, 31–39.
(8) Bacci, E.; Gaggi, C. *Chemosphere* **1987**, *16*, 2515–2522.
(9) Simonich, S. L.; Hites, R. A. *Environ. Sci. Technol.* **1994**, *28*, 939–943.
(10) Simonich, S. L.; Hites, R. A. *Nature* **1994**, *370*, 49–51.
(11) Environment Agency Government of Japan. *Guide for Tree Planting to Reduce Atmospheric Contaminants*; Daiichi Hoki: Tokyo, 1989.
(12) Calvert, J. G.; et al. *Formaldehyde and Other Aldehydes*; National Academy Press: Washington, DC, 1981; pp 59–91.
(13) Gabele, P. A. *J. Air Waste Manage. Assoc.* **1990**, *40*, 296–304.
(14) Zhang, J.; He, Q.; Lioy, P. J. *Environ. Sci. Technol.* **1994**, *28*, 146–152.
(15) Girard, F.; Jolivet, P.; Belot, Y. *C. R. Acad. Sci.* **1989**, *309*, 447–452.
(16) Mutters, R. G.; Madore, M.; Bytnerowicz, A. *J. Air Waste Manage. Assoc.* **1993**, *43*, 113–116.
(17) Environment Agency Government of Japan. *Guide for Measurement of Air Pollutants*; Environmental Agency: Tokyo, 1988; pp 419–422.
(18) Dickinson, R. G.; Jacobsen, N. W. *Chem. Commun.* **1970**, 1719–1720.
(19) Johansson, C. *Tellus* **1987**, *39B*, 426–438.
(20) Omasa, K.; Abo, F. *J. Agric. Meteorol.* **1978**, *34*, 51–58.
(21) Omasa, K.; Abo, F.; Natori, T.; Totuka, T. *J. Agric. Meteorol.* **1978**, *35*, 77–83.
(22) Singh, H. B.; Salas, L. J.; Stiles, R. E. *Environ. Sci. Technol.* **1982**, *16*, 872–880.
(23) Krall, A. R.; Tolbert, N. E. *Plant Physiol.* **1957**, *32*, 321–326.

Received for review April 17, 1995. Revised manuscript received August 21, 1995. Accepted August 23, 1995.

ES950261M