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Absorption of Gaseous Air Pollutants By a Standardized Plant Canopy

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Concentration profiles for hydrogen fluoride(HF), sulfur dioxide(SO_2), ozone (O_3), nitrogen dioxide(NO_2), and nitric oxide(NO) generated in a standardized alfalfa canopy are presented. Wind, light, temperature, and carbon dioxide(CO_2) profiles, canopy pollutant uptake rates, and canopy structural data are also given. Canopy pollutant concentration profile characteristics were studied to evaluate the relative potentials for major air pollutants to penetrate into canopies. The study was conducted in an environmental growth chamber equipped to control automatically environmental conditions and monitor continuously gas exchange rates. HF, SO_2, and NO_2 profiles suggested that these gases were removed efficiently by the upper portion of the canopy as well as by the immediate subsurface vegetation. The steady state HF profile showed the greatest displacement within the canopy. The NO profile was displaced the least. The uptake rate of NO by plants was apparently too slow in comparison with gas transport and mixing within the canopy to affect the internal profile substantially. O_3 appeared to be readily deposited on the surface tissues, but the deeper tissues in the canopy had less effect on the concentration profile. Data are also presented to show the relationship between NO_2 concentration within the canopy and changes in the air concentration above the vegetation. The results indicated that gas transport between the atmosphere and canopy interior was rapid. The data presented should be of current interest to agriculturists, researchers, administrators, and environmental planners concerned with effects of air pollutants on plants and on the fate of pollutants in the microenvironment.

Evidence exists that vegetation may play an important role in cleansing certain toxic air pollutants from the atmosphere. Hill[1] recently reported investigations which compared relative uptake rates of nine major air pollutants by alfalfa canopies and discussed the importance of several environmental and chemical factors on the process. Factors and relationships affecting leaf penetration by air pollutants and their sorption by leaves have been incorporated into a model simulating the process by Bennett et al.[2] Reported in this paper are comparative data on canopy pollutant concentration profiles generated in a standardized alfalfa canopy under highly controlled conditions. The study sought to obtain basic information that might have predictive value in estimating pollutant concentrations within simple crop canopies. Such information should strengthen our knowledge of the relationship between atmospherically measured pollutant concentration and the effect of the ex-

posure on plants within canopies. The knowledge gained could also be a step toward evaluating the potential use of vegetation for removing air pollutants from the microenvironment.

The rates at which gaseous pollutants are removed from the air by plants depend upon a number of factors which affect gas transfer to plant sink sites within canopies (usually leaves) and pollutant reaction with the plant tissues. Atmospheric gases are transported to leaves by a combination of diffusion and air movement. Canopy air flow can largely determine the pollutant transport rate and to some extent the residence time at the sink sites. General air flow and gas exchange above and within simple crop canopies have been discussed by a number of authors.[3–10] Some general concepts, however, should be recounted here to orient the reader.

Canopy Air Flow and Gas Exchange Characteristics

Horizontal winds flowing over canopy surfaces are slowed by frictional drag on the vegetation. Immediately above a crop canopy a turbulent air boundary layer exists. Within the boundary layer the mean horizontal wind velocity is decreased logarithmically with decreasing height above the canopy surface. Outside the boundary layer wind velocity profiles are no longer logarithmic, but are characteristic of upwind conditions. Energetics (i.e. momentum, heat transfer, etc.) and canopy surface roughness influence the thickness and character of the boundary layer—hence, pollutant transfer and concentration gradients between the atmosphere and plant canopy. For a steady wind, the boundary layer thickness increases to a steady-state height with distance traversed from the leading edge of transition from one uniform surface to another. Temperature gradients, resulting from absorption of light by exposed vegetation, combined with plant geometric and elastic (plant waving) properties may influence turbulence, therefore, pollutant mixing, near the canopy. Inoue[5] discussed air flow adjacent and within simple crop canopies and separated the air layers into three characteristic parts: (1) a logarithmic wind profile layer (boundary-layer), (2) a canopy-eddy layer, and (3) the lowest part of the plant-air layer in which plants and the ground surface influence the wind profile. A logarithmic profile probably exists very close to the ground with the wind velocity decreasing to zero at ground level. In the immediate vicinity of individual leaves, gaseous pollutant transport to leaf external and internal surfaces occurs by molecular diffusion through leaf-air boundary layers adhering to each leaf (where a portion may react with surface substances), through the leaf epidermis (via stomata, breaks, etc.), and through the mesophyll free air spaces. Since mesophyll cells are bathed in aqueous media and are highly structured, pollutant solubility and reactive properties, solute transport, and site of attack influence cellular sink potentials and consequent effects.

The primary purpose of these investigations was to study steady-state canopy concentration profile characteristics of several major air pollutants having different chemical properties to evaluate their relative potential for penetrating into the standardized canopy. For reference purposes, therefore, air flow in the immediate canopy region should possess highly controlled air profile characteristics. In addition, the standardized environment should allow normal biological function to occur (see text for description of the system).

Methods

An environmental chamber designed to allow control of temperature, relative humidity, light, wind, and gaseous concentrations within the plant compartment was used in these studies. Chamber characteristics have been detailed in previous publications,[1,11] but will be briefly described here. The chamber interior was made of stainless steel welded at the seams to reduce surface reaction and leakage. Chamber air was recirculated with a portion (ca. 10%) passing each time through cold and hot water heat exchangers for temperature and humidity control. Temperature of the water circulated through each coil was automatically controlled by a system consisting of temperature and humidity sensing elements, bridge and proportional amplifier circuits, and three-way mixing valves that mixed water from cold and warm water tanks with return water from the coil. Specifically designed inlet and outlet diffusion walls, blocked off below the canopy surface, controlled air flow across the chamber above the canopy. Air was recirculated by a 4000 cfm capacity fan which could produce constant wind velocities above the plants ranging up to 5 mph. The study utilized alfalfa canopies carefully grown to desired dimensions in 25 cm deep flats (36 cm × 55 cm). The plants were planted in rows 15 cm apart. The rows were positioned in the chamber normal to the airflow. The chamber accommodated six flats.

Pollutant (with the exception of HF) and CO_2 concentrations were maintained at predetermined concentrations in the chamber with automatic analyzers connected to control systems. The analyzer varied with the gas to be measured, but the methods of addition and control were similar. Pressurized CO_2, SO_2, NO_2, NO (pollutants diluted with N_2), and electrostatically generated O_3 (at known concentrations) were added to the chamber through pressure-flow systems in line with solenoid valves. Flow rates were monitored with Hastings mass flow meters or rotameters. The continuous analyzers, connected to recorder controllers, operated the solenoid valves and regulated flow rates into the chamber. The times that the valves opened and closed were printed on a Simplex time event recorder. From the flow rate and flow time data, CO_2 and pollutant addition rates were calculated. Only approximate pollutant uptake data were simultaneously obtained from these experiments as the canopy could not be disturbed between runs for the proper preconditioning of the chamber. Therefore, chamber blanks were relatively high. The uptake data presented in Table I are averaged data from a number of previous runs with equivalent canopies. (During these runs preliminary pollutant profiles were obtained.)

Table I. Steady state uptake rates for pollutants, and CO_2, and transpiration water loss by alfalfa canopy.

Substance	Exchange rate/ min/m² canopy
NO	1 $\mu l_{(g)}$/pphm
O_3	10 " "
NO_2	12 " "
SO_2	17 " "
HF	22 " "
CO_2	35 $cc_{(g)}$/320 ppm
H_2O[a]	13 $cc_{(aq)}$

[a] Relative humidity in chamber atmosphere 48%. (For other plant and chamber conditions refer to Figures 1, 2, and Table II.)

Hydrogen fluoride fumigations were generated by the method of Hill et al.[12] Fluoride concentrations were monitored by absorbing HF in impingers containing 0.02 M KNO_3 and determining the F^- concentrations of sequentially obtained samples with an Orion Model 401 F^- analyzer.[13] Fluoride uptake was determined by F^- analysis of the treated plant tissue.[14]

Carbon dioxide, pollutant, temperature, and wind velocity profiles were obtained with stationary probes and sampling lines set above and into the canopy at specific depths. Carbon dioxide concentrations from the sampling lines were monitored with a Beckman IR215 infra-red CO_2 analyzer. Oxidants were measured with Mast oxidant meters (Model 724-2). Sulfur dioxide levels were monitored with a Beckman 906A SO_2 analyzer and a Meloy Model LL-1100-1B sulfur analyzer. Temperature measurements were made with a 12-channel Y.S.I. tele-thermometer (Model 44TD). Wind data were obtained with Hastings Model RF-1 air

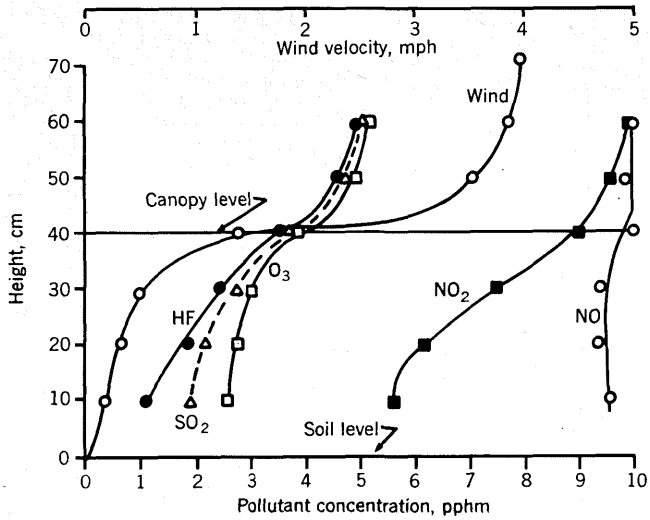

Figure 1. Pollutant concentration and wind profiles for alfalfa canopy

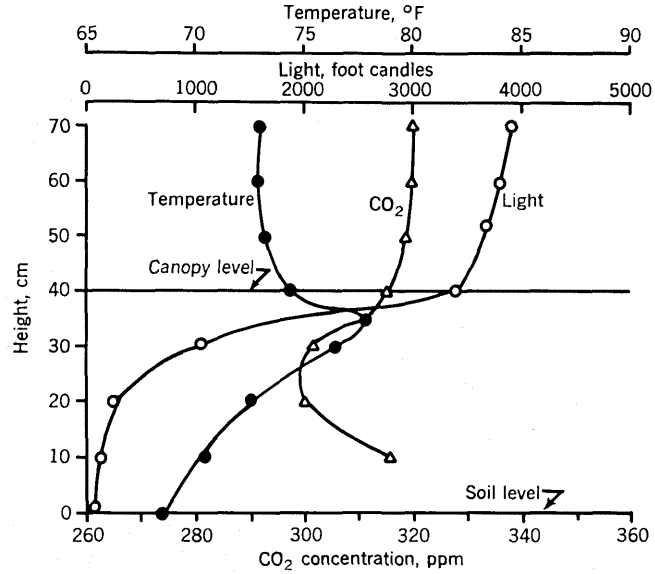

Figure 2. Light, temperature and CO_2 profiles for alfalfa canopy.

meters (Probe type N-7B). A Weston illumination meter (Model 756) was used for light measurements.

Results and Discussion

Pollutant concentration and wind velocity profiles for the defined alfalfa canopy are shown in Figure 1. Pollutant profiles, except for HF, were obtained from the same location in the canopy. The HF profile data were superimposed on Figure 1 and represent the average of two previous experiments using equivalent canopies. Ozone profiles also run on these two canopies compared very well with the O_3 profile presented. Preliminary runs with the other pollutants (SO_2, NO_2, and NO), using other canopies, also compared favorably with those presented.

Light, temperature, and CO_2 profiles are shown in Figure 2. These latter nonpollutant profiles resemble profiles, reported by Lemon,[7] which were obtained from a field study on a red clover crop. Steady-state uptake rates for each of the pollutants along with CO_2 and transpiration rates are presented in Table I. Table II gives integrated canopy leaf area data for each 10 cm stratum within the canopy. Judging from light and CO_2 profiles presented in Figure 2, some net photosynthesis occurred to a depth of 20–30 cm into the canopy. The tissues in the lowest 10 cm stratum were probably respiring. Air temperatures were warmest immediately beneath the average canopy surface level (4–5°F above the chamber air temperatures) due to local heating effects resulting from light energy absorption by the upper leaves.

An analysis of the canopy pollutant concentration profile data based upon pollutant chemical properties and plant uptake rates indicate that some predictable relationships were manifested. Displacement of the steady-state profiles within the canopy could be correlated in general with pollutant sorption rate, type of reactivity, and water solubility. The concentration profile generated by HF (the most soluble and readily sorbed pollutant) showed the greatest displacement, while the profile of the relatively insoluble and slowly sorbed NO was displaced the least. Hill[1] has reported data which show a close correlation between air pollutant uptake by alfalfa canopies and pollutant water solubility. For given air concentrations, highly water soluble pollutants may be expected to reach higher concentrations within the aqueous media bathing leaf cells than less soluble gases. This may produce greater solute concentrations in the vicinity of a potential sink. Nevertheless, the steady-state uptake rate depends upon the plant's capacity to maintain a continuous concentration gradient by depleting the absorbed pollutant solutes from the absorbing medium (i.e. through metabolism, translocation, pollutant reaction with cellular components, matrix, etc.). Some pollutants (notably HF and O_3), however, need not be absorbed internally to be substantially deposited. Deposition on leaf external surfaces may account for a significant part of the sorption of these pollutants.[2,15,16]

The HF, SO_2, and NO_2 profiles suggest that these gases were efficiently removed by plant tissues near the canopy surface as well as by those at deeper levels. A canopy overstory of 30 cm (cf. 10 cm height level in Figure 1) reduced the steady-state HF, SO_2, and NO_2 canopy-air concentrations to 20% 40%, and 55%, respectively, of the chamber air pollutant concentrations above the canopy. The steady-state NO profile was essentially vertical throughout the plant-air layer suggesting that plant removal was too slow compared with transport and mixing within the canopy to affect the internal concentration profile substantially. The NO concentration at the 30 cm depth level was reduced only 5% below the external concentration. The majority of this reduction occurred in the first few centimeters of the canopy. O_3 appeared to be almost as readily deposited on the surface tissues as HF and SO_2, but removal by lower tissues was relatively ineffective. The higher surface temperatures, combined with greater photosynthesis rates and probably more stomata in leaves near the surface, may have contributed to greater deposition near the canopy surface. Work by Bennett et al.[2] indicated that mesophyll tissues and epidermal

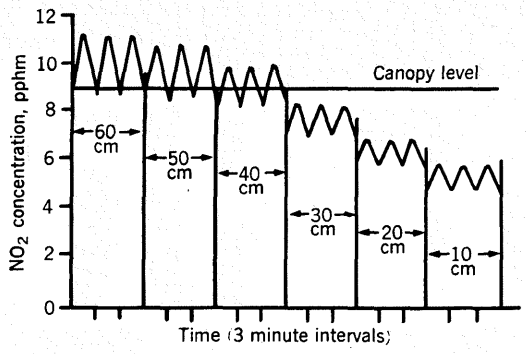

Figure 3. Chart showing oscillation and concentration damping of internal NO_2 for various levels within the alfalfa canopy. The NO_2 concentration was oscillated between 8.8 and 11.1 pphm in the air above the canopy. (Oscillation frequency 3 min/cycle).

Table II. Leaf area for 4 stratified layers within alfalfa canopy.

Canopy layer[a,b] height (cm)	Leaf area m^2/m^2 layer	Leaf area Percent
30–40	1.0	21
20–30	1.7	36
10–20	1.2	26
0–10	0.8	17
Total	4.7	100

[a] Canopy fresh wt. = 1420 gms/m^2.
[b] Leaf area calculated as 1 surface/leaf.

surfaces of some leaves could be effective sinks for O_3. Smooth leaf surfaces characteristic of alfalfa, however, which have little natural excrement or other reactable substances, pubescence, etc., are comparatively inefficient sinks. Some preliminary experiments showed that O_3 was very effectively sorbed by alfalfa canopies treated with certain pesticides. Ozone concentration profile curves indicated that most of the O_3 was deposited primarily at the canopy surfaces. Several reports of the use of sprays and dusts for protecting plants from O_3 by preferential surface reaction can be found in the literature.[17] This aspect was not pursued in this study. For this investigation, care was taken to utilize uncontaminated leaves.

Figure 3 presents observed NO_2 profile data showing concentration oscillations around mean pollutant concentration levels measured at various positions in the canopy and surrounding air. These data provide an indication of gas exchange rate between the external atmosphere and canopy air sublayers. The oscillations resulted from changes in pollutant concentrations in the chamber air. The amplitude and frequency could be set by adjusting the rate of addition, the concentration of pollutant added, and the interval between each addition. The oscillation amplitude observed for each subordinate position within the canopy was damped in proportion to the mean concentration measured at that level. Studies with more dense alfalfa canopies (greater densities than normally found from field studies) showed proportionally greater internal oscillation damping. Within these canopies, differential pollutant concentrations were less clearly coupled with concentration changes above the canopy. Pollutant exchange between the standardized canopy interior and atmosphere above was comparatively rapid. Reaction with plants was the major rate limiting factor determining uptake of the pollutants tested. Hill[1] previously reported data which showed that O_3 uptake by alfalfa canopies (equivalent to the standardized canopy reported here), treated in the experimental environmental chambers, reached maximal rates when the applied chamber wind velocity exceeded 3 mph. In experiments reported here, 4 mph chamber wind velocities were utilized.

Recent studies using other plant species (oats, barley, lawn grass) have shown canopy pollutant concentration profile characteristics corresponding in general to those described above for alfalfa. Study of the sink potentials for a variety of plants and canopies having differing geometrical structure and reactive properties are anticipated.

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