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Absorption of Ozone and Seven Organic Pollutants by *Populus nigra* and *Camellia sasanqua*

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Foliar absorption of seven organic pollutants (acetone, acetonitrile, acrolein, methyl ethyl ketone (MEK), isobutyl methyl ketone (IBMK), chloroform, and benzene), and ozone was examined. Two woody species (*Populus nigra* and *Camellia sasanqua*) were exposed to each pollutant at a concentration of 0.5 or 1.0 ppmv (μmol mol^{-1}), and gas absorption and transpiration rates were measured simultaneously. Ozone and acrolein were effectively absorbed by both species. MEK was absorbed by *C. sasanqua* only. A model analysis of gas exchange rates revealed that foliar absorption of the three pollutants was predominantly through the stomata, and cuticular contribution on gas removal is, if any, very small. The plant leaves showed no detectable absorption of the other five organic pollutants. We conclude that plant leaves act as an effective sink for some organic pollutants but not for others. The factor that determines whether plant leaves can effectively absorb pollutants in this study seems to be whether the pollutant is effectively metabolized in the leaf cells.

Introduction

Atmospheric pollutants such as SO_2, NO_2, and O_3 are effectively absorbed by plant leaves through the stomata (*1*−*6*). The stomatal absorption of these air pollutants proceeds in the following sequence (*1, 6*): (i) gas enters the leaf by gas-phase diffusion through the stomata; (ii) gas in the air space inside the leaf dissolves in the water on the surface of the plant cells; (iii) gas in the liquid-phase diffuses into the cells according to its concentration gradient; (iv) gas is metabolized or decomposed inside the cells, thus maintaining a concentration gradient of gas between the atmosphere and the interior of the plant cells. Recently, the importance of O_3 decomposition in the cuticle on the leaf surface in addition to the stomatal absorption have been reported by some researchers (*7, 8*). However, knowledge on the capacity and mechanism of cuticular ozone decomposition is lacking.

Among the organic pollutants, some reports indicate that formaldehyde (*9*−*11*) and phenol (*12*) are continuously absorbed by leaves through the stomata at high rates. These studies suggested that the metabolism of the absorbed pollutants maintains the concentration gradient between the atmosphere and the interior of the leaves and acts as the driving force that allows their continuous stomatal absorption. However, some organic pollutants absorbed by leaves remain inside them without being decomposed (*13*−*16*). In this case, the pollutants in plant leaves would eventually become equilibrated with those in the ambient air, and consequently the capacity of plants to remove these pollutants from the atmosphere would be very limited.

In the present paper we have reported foliar absorbency of seven notable atmospheric organic pollutants (acetone, acetonitrile, acrolein, methyl ethyl ketone (MEK), isobutyl methyl ketone (IBMK), chloroform, and benzene), of which the absorbency by plants and the absorption mechanisms are not yet understood clearly. The data were analyzed with a simple gas-diffusion model to investigate the foliar gas absorption mechanism in comparison with transpiration from stomata. Foliar absorption of O_3 was examined to compare with that of the organic pollutants. In addition, the capacity of cuticular contribution such as ozone decomposition was estimated through the analysis using the simple gas-diffusion model.

Experimental Section

Seedlings of *Populus nigra* (deciduous tree) and *Camellia sasanqua* (evergreen tree) of heights 0.4−0.7 m were used as plant materials. These seedlings were grown under ca. 25 °C air temperature and nonlimiting soil moisture conditions in a controlled greenhouse.

The gas exposure system used in this study is essentially the same as previously reported (*10*). Briefly, a potted plant was confined in a transparent acrylic box (45 cm × 40 cm in sides of the bottom × 80 cm in height), which was ventilated with air containing a pollutant. Air inside the acrylic box was mixed by two fans set on the bottom of the box. The pot was covered with a plastic film to avoid gas or water vapor transfer between soil/pot and the air inside the acrylic box. To measure transpiration rate, the potted plant was put on an electric balance installed in the acrylic box; transpiration rate was evaluated from the rate of decrease in the weight of the pot. The pollutant gas concentration at the air inlet made in a side near the bottom of the acrylic box was maintained at about 1 ppmv (organic pollutants) or 0.5 ppmv (O_3). Gas concentration of the pollutant at the inlet and the outlet made in a side near the top of the acrylic box was measured with a flame ionization detection gas chromatograph (organic pollutants) or a UV-absorption O_3 analyzer (O_3). Air temperature and relative humidity were kept at ca. 25 °C and 65% during the experiments. Light intensity was maintained at 500 μmol photons m^{-2} s^{-1} except an additional environment, for obtaining Figure 1c, of MEK exposure of *C. sasanqua*.

Foliar gas-phase conductance of water vapor (g^W; mmol m^{-2} s^{-1}) was calculated from transpiration rate, leaf temperature, humidity, and air temperature in the acrylic box. Foliar gas absorption rate on unit leaf area basis (Q) was determined from the difference in gas concentrations at the inlet and outlet of the box. There were no detectable differences in gas concentrations at the inlet and outlet of the empty box. Molar fraction of pollutant gas on the leaf-surface boundary layer (c_o) was assumed equal to the molar fraction of pollutant gas at the outlet of the box, and Q was normalized by dividing it by c_o to obtain q (mmol m^{-2} s^{-1}) (i.e., $q = Q/c_o$). The data were analyzed by a simple gas-

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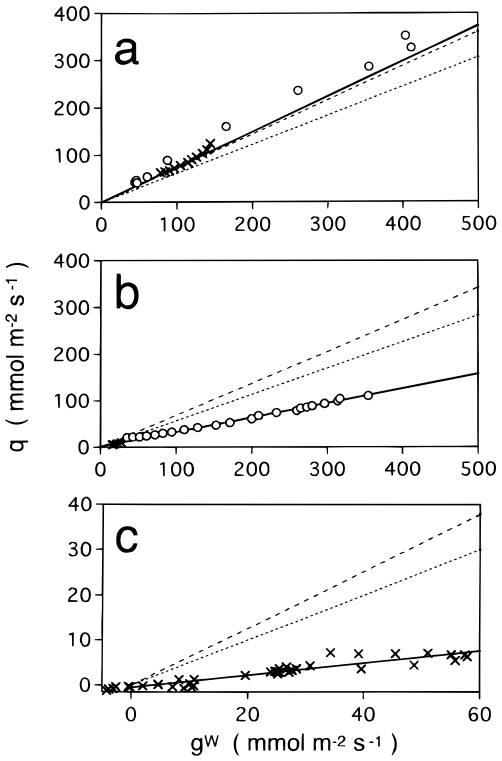

FIGURE 1. Relationships between g^W and q in *Populus nigra* (○) and *Camellia sasanqua* (×) when plants were exposed to 0.5 ppmv O_3 (a) or 1 ppmv acrolein (b) or MEK (c). Regression lines are shown by solid lines, and lines $q = k_b g^W$ and $q = k_s g^W$ are indicated by broken and dotted lines, respectively. Equations of the regression lines are as follows: O_3, $y = 0.746x + 0.035$ ($r = 0.981$); acrolein, $y = 0.312x + 1.479$ ($r = 0.997$); and MEK, $y = 0.134x - 0.478$ ($r = 0.938$). Note that the scales of the axes in c differ from those in a and b.

diffusion model previously published in other literatures (*2, 3, 11, 12*). Based on this model, q is related to g^W by the following equation

$$q = k(1 - c_i/c_o)g^W + \alpha/c_o \quad (1)$$

where c_i and α are the molar fraction of the pollutant gas in the air space inside a leaf and nonstomatal pollutant-gas sorption/decomposition rate on unit leaf area basis (mmol m^{-2} s^{-1}), respectively, and k is a constant, of which the range is

$$k_s < k < k_b \quad (2)$$

where k_s and k_b are constants calculated from molecular weights of water and the pollutant gas. For analysis of the experimental data, q was plotted against g^W, and α and c_i/c_o were evaluated from the y-intercept and slope of the regression line of this plot.

Results and Discussion

Acrolein and O_3 showed considerable absorption by *P. nigra* and relatively lower absorption by *C. sasanqua*; absorption of MEK was detected only in *C. sasanqua* (Table 1). Absorption by plants of any of the other five pollutants was not detected (Table 1). Both plant species exposed to acrolein or O_3 showed marked decreases in both q and g^W, indicating that exposure to either pollutant caused stomatal closure. MEK also caused decreases in both q and g^W in *C. sasanqua* but to a lesser extent than did acrolein or O_3. No detectable decreases in g^W resulted from exposure of *P. nigra* to MEK or from exposure of either species to acetone, acetonitrile, IBMK, chloroform, or benzene.

TABLE 1. Total Foliar Gas Sorption in 4 h (from 1 to 5 h after the Gas Exposure) by Unit Leaf Area Surface

pollutant	solubility in water[a] (mol kg^{-1})	cumulative foliar gas uptake (mol m^{-1})	
		Populus nigra	*Camellia sasanqua*
O_3	0.012	1.29	0.77
acetone	∞	nd[b]	nd[b]
acetonitrile	∞	nd[b]	nd[b]
MEK	4.95	nd[b]	0.05
acrolein	4.63	1.05	0.15
IBMK	0.017	nd[b]	nd[b]
chloroform	0.0069	nd[b]	nd[b]
benzene	0.0023	nd[b]	nd[b]

[a] From refs *6* and *17* and other literatures (at either 20, 22, or 25 °C). [b] nd indicates that gas sorption was not detected by this method and is less than 0.01 mmol m^{-1}.

Changes in stomatal opening are reported for leaves exposed to SO_2 and O_3 (*2, 3, 18, 19*). The concentration of pollutants to which the plants were exposed in this study was considerably higher (0.5 or 1 ppmv) than those in the ambient air. If plants were exposed to lower concentrations of O_3, acrolein, or MEK, the effects on stomatal opening would be less, thus a high gas absorption rate would be maintained for longer periods.

From the above measurements, q at various intervals was plotted against g^W for O_3 and acrolein (Figure 1a,b). The data show that the maximum g^W obtained under a constant light intensity (500 μmol photons m^{-2} s^{-1}) was considerably smaller in *C. sasanqua* than in *P. nigra*. For MEK, g^W in *P. nigra* kept at ca. 400 mmol m^{-2} s^{-1} during the exposure under the light intensity but q was not detected, and the variation of q and g^W in *C. sasanqua* was too small to permit investigation of the relationship between q and g^W. Thus, an additional experiment for MEK with *C. sasanqua* was carried out, in which light intensity was changed from 0 to 500 μmol photons m^{-2} s^{-1} to vary the stomatal opening, while the plant was exposed to MEK (Figure 1c).

In all the data (Figure 1a−c), q was found to increase linearly with increasing g^W, and the y-intercept was almost zero. The results indicate that absorption of all these pollutants by plants was predominantly through the stomata, and cuticular contribution on gas removal such as ozone decomposition is, if any, very small. For O_3, the slope of the regression line almost equaled the k_b value (Figure 1a). From eqs 1 and 2, it would be reasonable to interpret c_i as being close to zero for O_3. For acrolein and MEK, the slope of the regression line was considerably smaller than k_s. The range of c_i/c_o calculated from eqs 1 and 2 is $0.45 < c_i/c_o < 0.54$ for acrolein and $0.73 < c_i/c_o < 0.79$ for MEK.

In other reports (*2−5, 11, 12*), almost the same model was applied for the analysis of foliar absorption of SO_2, NO_2, O_3, formaldehyde, and phenol, and it was concluded that foliar absorption of these pollutants is predominantly through the stomata. For SO_2, NO_2, O_3, and formaldehyde, these reports state that $c_i \doteqdot 0$ even at a pollutant concentration of 1 ppmv. Compared with these results, c_i/c_o of acrolein and MEK is larger, indicating that the capacity to remove acrolein and MEK from the interior of leaves is lower than is the case for SO_2, NO_2, O_3, or formaldehyde.

Among the eight tested pollutants, no conspicuous relationship was found between solubility of a pollutant in water and its foliar absorbency (Table 1). Although the solubility of O_3 in water is relatively low, O_3 showed the smallest c_i value among the eight pollutants, suggesting that O_3 is most quickly scavenged inside the leaves. The c_i/c_o values

calculated for acrolein and MEK are both considerably larger than that estimated for O_3, although their solubility in water is 2 orders of magnitude higher than that of O_3. Furthermore, foliar absorption was not detected for acetone or acetonitrile, each of which is highly soluble in water (Table 1). These results show that solubility in water is not a critical factor in determining the foliar absorbency of a pollutant. The factor that determines whether plant leaves can effectively absorb pollutants in this study seems to be whether the pollutant is effectively metabolized in the leaf cells.

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