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Gas Diffusion Model Analysis of Foliar Absorption of Organic and Inorganic Air Pollutants

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Summary

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A simple gas diffusion model has analyzed the characteristics of foliar absorption of more than 20 organic and inorganic air pollutants. For SO_2, NO_2, O_3, PAN, and formaldehyde, the ratios (c_i /c_o) of gas concentration in the air at the gas-liquid interface of the stomatal cavity to that of the ambient air surrounding the leaf are almost zero, which indicates that these absorbed gases are very quickly scavenged from the air at the surface of the mesophyll cells, under favorable growing conditions. Hence, most of foliar absorption rates of these gases are governed solely by their gas-phase diffusion (i.e., mostly by stomatal conductance). For NH_3, c_i/c_o is between 0.05 and 0.1 at concentrations above the compensation point (0.4 - 15 ppb), but $c_i > c_o$ at concentrations below the compensation point, which indicates that NH_3 is emitted from the leaf into the atmosphere through the stomata. For some organic gases such as C_2-C_4 aldehydes and phenol, c_i /c_o is found to range between 0 and 1. For these gases, therefore, stomatal absorption appears to play an important role in foliar gas absorption, but the relating slow rates of metabolism of the gas in leaf tissues may act as a rate-limiting step. Consequently, for these pollutants, both stomatal conductance and metabolic rate determine the foliar gas absorption rate. For other organic pollutant gases (for example, acetone, chloroform, benzene, and trichloroethylene), foliar gas absorption could not be detected and so c_i /c_o is assumed to be unity. For NO and CO, c_i /c_o is above 0.9, suggesting that stomatal absorption is very small, thus indicating that metabolic capacity of these gases is very small.

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Introduction

Plant leaves effectively absorb a lot of organic and inorganic air pollutants through stomata (HILL 1971, BENNETT & al. 1973, OMASA 1979, 1990, KOZIOL & WHATLEY 1984, OMASA & al. 1985, OMASA & CROXDALE 1992, KONDO & al. 1996a, MANSFIELD & PEARSON 1996, DE KOK & STULEN 1998, OMASA & al. 2000a,b). The stomatal absorption proceeds in following sequence: (i) gas enters the leaf by gas-phase diffusion through the stomata; (ii) gas in the air space inside the stomatal cavity dissolves in the aqueous phase of the cell wall matrix, the so-called apoplastic fluid; (iii) gas in the aqueous phase reacts with components in apoplast and symplast of leaves, thus maintaining a concentration gradient of gas between the atmosphere and the interior of the plant cells. The gas flux into leaves also may be controlled by reactions with cuticular components.

Gas diffusion models have been widely used to analyze the exchange of water vapor and CO_2 between the atmosphere and plant leaves (MONTEITH 1973, JONES 1992). Hill, Bennett and colleagues (HILL 1971, BENNETT & HILL 1973, 1975, BENNETT & al. 1973) modified these models so as to describe the foliar absorption of atmospheric pollutant gases. Since then, considerable effort has focused on the quantitative analyses of foliar absorption of pollutant gases (O'DELL & al. 1977, OMASA 1979, 1990, HOSKER & LINDBERG 1982, OMASA & CROXDALE 1992, PARKHURST 1994, KONDO & al. 1996a, OMASA & al. 1981a,b, 2000a,b). Based on the gas diffusion model, it is possible to separately determine stomatal and non-stomatal components of gas absorption rates and to infer the foliar capacity for metabolism of the absorbed pollutant gases, whether inorganic or organic.

In present paper the characteristics of foliar absorption of more than 20 organic and inorganic air pollutants have been analyzed by a simple gas diffusion model.

A Simple Gas Diffusion Model for Analyzing Foliar Gas Absorption

Carbon dioxide (CO_2) in the atmosphere is absorbed by plant leaves through the stomata and used for photosynthesis in leaf cells. In a similar manner, atmospheric pollutants that can be metabolized inside the leaf tissue are absorbed through the stomata. Consequently, a concentration gradient of these gases is generated from the ambient air to the interior of the leaf (Fig. 1) and acts as a factor that regulates foliar gas absorption. Also, the evaporation of water through the stomata to the atmosphere (transpiration) is driven by the water vapor density gradient between the inside and outside of the leaf, although the direction of water vapor flux is opposite to that of CO_2 and pollutant gases. Therefore, the analysis of transpiration and gas absorption using a gas diffusion model aids us to understand the gas absorption phenomena taking place in the leaves.

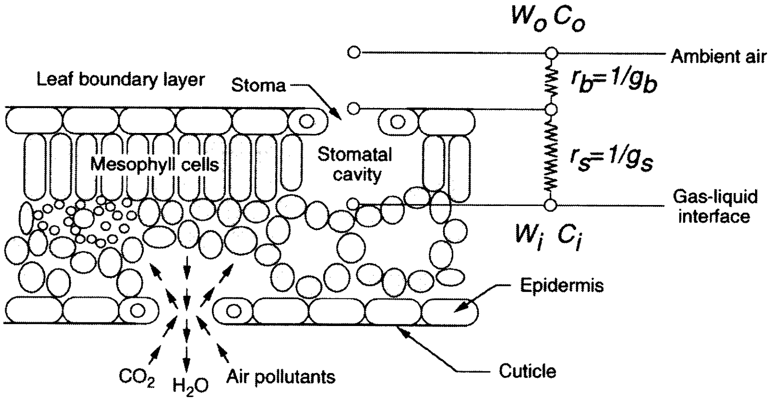

Fig. 1. Pathways for diffusion of gases and water vapor between ambient air and the interior of a leaf.

The gas and water vapor fluxes between ambient air and air at the gas-liquid interface, linking with the aqueous phase of the cell wall matrix, the so-called apoplastic fluid, in the stomatal cavity are regulated by two limiting sites, the leaf boundary layer and the stomata (Fig. 1). Resistance to the flow of gas or water vapor at the leaf boundary layer (r_b; leaf boundary layer resistance) depends on the thickness of the leaf boundary layer; the resistance and the thickness decrease with increasing wind velocity at the leaf surface, and are also dependent on leaf size and shape. Stomatal resistance to gas flow (r_s) depends on the density and size of the stomata and the degree of stomatal opening. Consequently, the total resistance (r) can be described as the sum of the two resistance components:

$$r = r_b + r_s \qquad (1)$$

The reciprocals of these resistances (r, r_b, and r_s) are referred to as the conductance. Thus, Eq.(1) can be rewritten:

$$1/g = 1/g_b + 1/g_s \qquad (2)$$

where g, g_b, and g_s are the total leaf conductance, the leaf boundary layer conductance, and the stomatal conductance, respectively.

The rate of water evaporation through the cuticle of matured leaves is usually very small compared with that through the stomata (OMASA & al. 1983, 1990, KRAMER & BOYER 1995). However, the cuticular deposition (adsorption and decomposition) of some pollutant gases may not be negligible and needs to be considered when modeling foliar gas absorption. Therefore, on a unit leaf area basis, the rates of cuticular gas deposition, total foliar gas absorption (to be exact, the total amount of absorption, adsorption, and decomposition), and transpiration can be represented by α, Q, and E, respectively, with the transpiration rate (E) and the stomatal gas absorption rate (Q - α) being approximated by Fick's law of diffusion:

$$E = g^W (w_i - w_o) \tag{3}$$

$$Q - \alpha = g^G(c_o - c_i) \tag{4}$$

where w_i and c_i, respectively, are the saturated water vapor density and the gas concentration in the air at the gas-liquid interface, linking with the apoplastic fluid, of the stomatal cavity, indicating the capacity to scavenge the gas in the leaves, and w_o and c_o, respectively, are the water vapor density and the gas concentration of the ambient air surrounding the leaf (Fig. 1). The respective W and G superscripts on g represent conductance for water vapor and the gas.

The total foliar gas absorption per unit gas concentration (q) is obtained from Eq. (4) as:

$$q = Q/c_o = (1 - c_i /c_o) g^G + \alpha/c_o \tag{5}$$

The ratio of g^G to g^W can be regarded as a constant, k. That is:

$$k = g^G /g^W \tag{6}$$

Thus, Eq. (5) can be rearranged as follows:

$$q = k (1 - c_i /c_o) g^W + \alpha/c_o \tag{7}$$

The leaf boundary layer conductance (g_b) and the stomatal conductance (g_s) can be regarded to be proportional to $D^{2/3}$ and D, respectively, where D denotes the diffusion coefficient (MONTEITH 1973). Therefore, the quotients g_b^G /g_b^W and g_s^G /g_s^W (k_b and k_s, respectively) are given by:

$$k_b = g_b^G /g_b^W = (D^G/D^W)^{2/3} \tag{8}$$

and

$$k_s = g_s^G /g_s^W = D^G/D^W \tag{9}$$

where the W and G superscripts on D indicate the diffusion coefficients for water vapor and pollutant gas, respectively.

The ratio of the diffusion coefficients can, in turn, be approximated by:

$$D^G /D^W = (M^G /M^W)^{-1/2} \tag{10}$$

where M^W and M^G are the molecular weights of water vapor and pollutant gas, respectively. This relationship indicates that the lower the molecular weight of a pollutant, the more diffusive the pollutant is through both the leaf boundary layer and the stomata.

From the relationships in Eqs. (2), (6), (8), and (9), it is deduced that the value k is a constant between k_s and k_b. Therefore, if $M^W < M^G$, as holds for many pollutant gases, then

$$k_s < k < k_b \quad (11)$$

or, from Eqs. (8)-(10)

$$(M^G / M^W)^{-1/2} < k < (M^G / M^W)^{-1/3} \quad (12)$$

Equation (7) indicates that by plotting q versus g^W and calculating the range of k from Eq. (8), c_i and α can be estimated from the gradient and the y-intercept of this plot, respectively. For this estimation, it is necessary to measure E, Q, w_o, and c_o, and to obtain w_i, which can be equated with saturated water vapor density at the leaf temperature (FARQUHAR & RASCHKE 1978).

It is clear from Eq. (7) that, at a given c_o, the stomatal absorption of a gas is governed by g^G ($= 1/g_b^G + 1/g_s^G$) and c_i. Because g_b is usually large and does not depend on physiological factors, the major changes in g^G can be attributed to changes in g_s^G, which in turn is determined by the density and size of the stomata on the leaves, as well as the degree of stomatal opening. Usually, to evaluate the conductance or resistance of gases through the stomata, g_s^W (instead of g_s^G) is utilized, and g_s^W is merely referred to as 'stomatal conductance.' Consequently, the regulation of stomatal gas absorption can be mainly attributed to two factors, g_s^W and c_i.

Model Analysis of Foliar Absorption of Pollutant Gases

HILL 1971 reported that O_3, NO_2, SO_2, Cl_2, HF, and peroxyacetyl nitrate (PAN) were absorbed continuously and at considerably high rates by an artificial alfalfa canopy, whereas absorption of NO and CO by the canopy was considerably smaller. He also reported that the absorption rates of all these gases by the canopy were proportional to the ambient gas concentration and were governed by the degree of stomatal opening. Subsequently, many researchers have focused on the foliar absorption of inorganic air pollutants by plants, and the results of these studies have been occasionally reviewed (for example, OMASA 1979, GARSED 1984, SMITH 1984, LANGE & al. 1989, DE KOK & STULEN 1998). Recently, studies of foliar gas absorption analysis have been extended to organic air pollutants. Consequently, it was found that four kinds of C_1-C_4 aldehydes (MUTTERS & al. 1993, KONDO & al. 1995, 1996a, 1998) as well as phenol (KONDO & al. 1996b, 1999) could be continuously absorbed by leaves through the stomata. More recently, OMASA & al. 2000b measured the foliar absorption of seven organic pollutants (acetone, acetonitrile, acrolein, methyl ethyl ketone [MEK], isobutyl methyl ketone [IBMK], chloroform, and benzene) by two woody species (*Populus nigra* and *Camellia Sasanqua*). Of these seven pollutants, acrolein was absorbed by both the tested species through the stomata, and MEK absorption was detected only in *C. Sasanqua*, whereas absorption of the other five pollutants could not be detected in either of the two species. Such finding suggests differences between species in absorption of different organic pollutants.

To investigate the mechanism of gas absorption by leaves, the gas diffusion model described in the previous section was applied to the results of foliar gas absorption measurements. Fig. 2 shows the relationship between the normalized O_3 absorption rate (q; see Eq. (7)) and total leaf conductance of water vapor diffusion (g^W) for 15 different woody species exposed to 0.5 ppm O_3. The *y*-intercept of this regression line is close to zero ($\alpha \cong 0$), indicating that the cuticular deposition (adsorption and decomposition) of O_3 was negligibly small. Based on Eq. (7), the slope of the regression line should have a value between k_s and k_b (Eq. (11)). Although the slope of the regression line is slightly larger than k_b, it would be reasonable to expect that c_i is close to zero, indicating all absorbed O_3 reacts rapidly apoplastic components such as ascorbate, polyamines, phenolics, etc. (POLLE 1998). The error may be due to either the incompleteness of the model applied or experimental errors. Because most of the changes in g^W can be regarded to result from changes in stomatal opening, this result would indicate that, for a wide range of species, foliar O_3 absorption is predominantly through the stomata and is strongly governed by stomatal conductance.

From gas absorption measurements of coniferous forests, it has been suggested that cuticular deposition also plays an important role in removing O_3 from the atmosphere (RONDON & al. 1993, COE & al. 1995, GRANT & RICHTER 1995). These reports indicated that the foliar gas absorption rate was approximately three fold that absorbed only through the stomata, and that the rate of cuticular gas deposition showed diurnal changes, being maximal at midday. However, other O_3 absorption studies (OMASA & al. 1979, 2000a,b, LAISK & al. 1989, MATYSSEK & al. 1997, POLLE 1998) do not support these findings, which may have been affected by inconstancies in environmental parameters that are inevitable in field experiments.

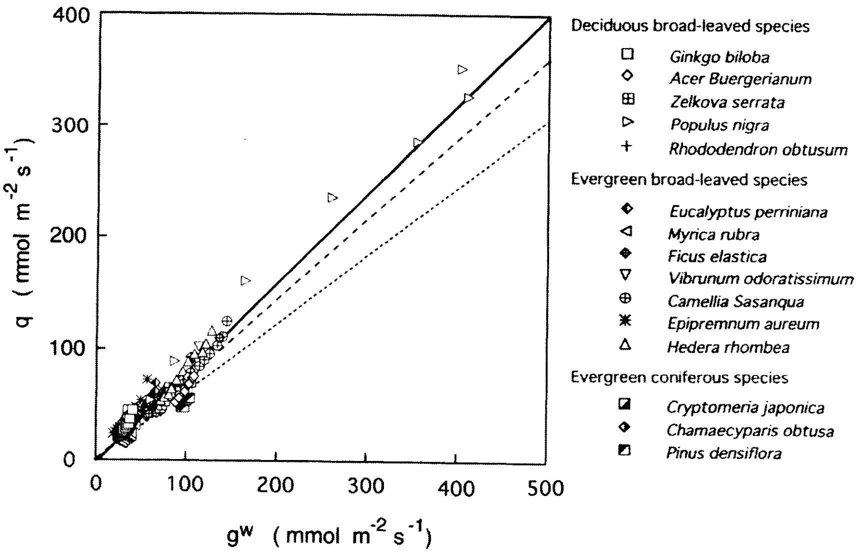

Fig. 2. Relationship between the normalized O_3 absorption rate (q) and total leaf conductance of water vapor diffusion (g^W) for 15 woody species which were exposed to 0.5-ppm O_3. Different symbols present measurements of different species. The regression line is shown by a solid line, and lines $q = k_b\, g^W$ and $q = k_s\, g^W$ are also indicated by broken and dotted lines, respectively. The equation of the regression line is $y = 0.804x - 0.002$ ($r = 0.972$) (from OMASA & al. 2000a).

For organic pollutants, the absorption rate varied with species of plants and gases. The relationship between the normalized formaldehyde absorption rate (q) and total leaf conductance of water vapor diffusion (g^W) for nine different woody species is shown in Fig. 3. The results indicate that both c_i and α were close to zero, as for O_3, suggesting that this pollutant is absorbed through the stomata and rapidly scavenged in the leaf tissues. This result is supported by reports demonstrating that formaldehyde is rapidly metabolized to sugars, amino acids, and other metabolites in leaf tissues and used for plant growth (KRALL & TOLBERT 1957, GIRARD & al. 1989, GIESE & al. 1994).

Fig. 4 shows a scheme of the possible metabolism of formaldehyde in leaves. Oxidation of formaldehyde to CO_2 is considered a major pathway of formaldehyde metabolism linked to photosynthetic C metabolism via the Calvin cycle in plants (KRALL & TOLBERT 1957, DOMAN & ROMANOVA 1963, UOTILA & KOIVUSALO 1979, KOIVUSALO & al. 1989, GIESE & al. 1994). This pathway is indicated by glutathione dependent formaldehyde dehydrogenase (FDH; EC 1.2.1.1), *S*-formylglutathione hydrolase (SFGH; EC 3.1.2.12) and formate dehydrogenase (FTDH; EC 1.2.1.2), in which glutathione and NAD^+ are required as obligatory cofactors. The glutathione adduct (HM-GSH; S-hydroxymethylglutathione) of formaldehyde occurs spontaneously, and subsequently FDH converts HM-GSH to *S*-formyl-glutathione (formyl-GSH) (STRITTMATTER & BALL 1955, UOTILA & KOIVUSALO 1983, HANSON & al. 2000). Secondarily, formate is formed from *S*-formylglutathione by SFGH, and finally converted to CO_2 by FTDH (HANSON & al. 2000, SCHMITZ & al. 2000). In dark, formaldehyde is presumably converted into CO_2 in same way as in the light, but CO_2 is not channeled into the Calvin cycle (SCHMITZ & al. 2000). As another pathway formaldehyde is converted to serine through the glycine adduct of 5,10-CH_2-THF (5,10-methylene-tetrahydrofolate). This reaction occurs spontaneously, therefore dissociation of 5,10-CH_2-THF formed from glycine or serine may occur; that is possible source of formaldehyde (GIESE & al. 1994, HANSON & al. 2000). Reactions between formate and 5,10-CH_2-THF are also reversible. The possibility of direct, nonenzymatic reactions of formaldehyde with NH_2 groups or SH groups of amino acids is not denied (SCHMITZ & al. 2000).

Table 1 shows the results of model analysis of foliar absorption of more than 20 organic and inorganic pollutant gases. For SO_2 (OMASA & ABO 1978, BLACK & UNSWORTH 1979), NO_2 (OMASA & al. 1979, NATORI & al. 1981, NEUBERT & al. 1993), O_3 (OMASA & al. 1979, 2000a, LAISK & al. 1989), PAN (NOUCHI 1980), and formaldehyde (KONDO & al. 1996a), c_i/c_o's are almost zero, which indicates that these absorbed gases are very quickly scavenged from the air at the surface of the mesophyll cells, under favorable growing conditions. Hence, most of foliar absorption rates of these gases are governed solely by their gas-phase diffusion (i.e., mostly by stomatal conductance). However, a part of the sulfur derived from SO_2 is emitted as H_2S (see KONDO 2002, DE KOK & al. 2002), and also NO_2 absorption depends on ascorbate concentrations in leaf apoplast. For NH_3, c_i/c_o is between 0.05 and 0.1 at concentrations above the compensation point (0.4 - 15 ppb), but $c_i > c_o$ at concentrations below the compensation point, which indicates that NH_3 is emitted from the leaf into the atmosphere through the stomata (FARQUHAR & al. 1980, GEßLER & RENNENBERG 1998). For NO and CO, c_i/c_o is above 0.9, suggesting that stomatal absorption is very small, thus indicating that metabolic capacity of these gases is very small.

For some organic gases such as C_2-C_4 aldehydes and phenol, c_i/c_o is found to range between 0 and 1. For these gases, therefore, stomatal absorption appears to play an important role in foliar gas absorption, but the relating slow rates of metabolism of the gas in leaf tissues may act as a rate-limiting step. Consequently, for these pollutants, both stomatal conductance and metabolic rate determine the foliar gas absorption rate. For other organic pollutant gases (for example, acetone, chloroform, benzene, and trichloroethylene), foliar gas absorption could not be detected and so c_i/c_o is assumed to be unity (Table 1).

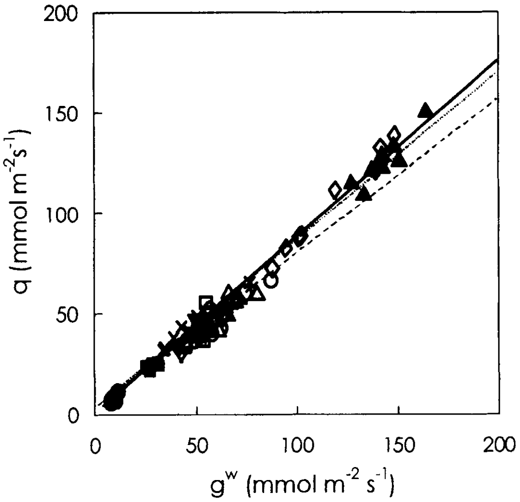

Fig. 3. Relationship between q and g^W in 9 woody species exposed to 0.07 ppm formaldehyde. Different symbols represent measurements of different species (▲, *Populus nigra* var. *Italica*; ◊, *Robinia pseudo-acacia* L.; Δ, *Acer palmatum* Thunb.; ○, *Ulmus davidiana* Planch var. *japonica* Naklai; □, *Ginkgo biloba* L.; X, *Camellia japonica* L.; ∇, *Quercus myrsinaefolia* Blume; ■, *Cedrus deopara* Loud; ●, *Pinus thunbergii* Parl.). The regression line is shown by a solid line, and lines $q = k_b g^W$ and $q = k_s g_w$ are also indicated by dotted and broken lines, respectively. The equation of the regression line is $y = 0.894x - 3.1$ ($r = 0.983$) (from Kondo & al. 1996a).

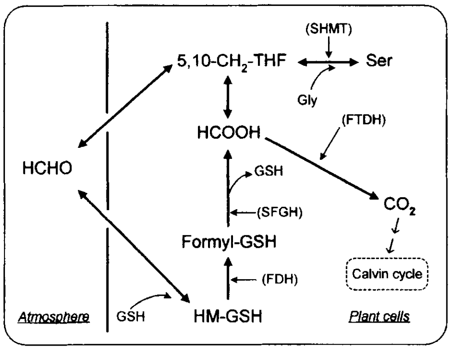

Fig. 4. Scheme of the possible metabolism of formaldehyde in leaves. Abbreviations: GSH, glutathione; Ser, serine; Gly, glycine; THF, tetrahydrofolate; 5,10-CH_2-THF, 5,10-methylene-THF; HM-GSH, *S*-hydroxymethylglutathione. Enzymes: FDH, formaldehyde-dehydrogenase; FTDH, formate dehydrogenase; SFGH, *S*-formylglutathione hydrolase; SHMT, serine hydroxymethyltransferase.

It has been reported that some organic pollutants absorbed by leaves exist in the leaves without being decomposed (Bacci & al. 1990a, Keymeulen & al.

1993, Simonich & Hites 1994a,b, Ockenden & al. 1998). In such cases, the foliar and ambient air pollutant levels will eventually become equilibrated, drastically limiting the capacity of the leaves to remove these pollutants from the atmosphere. Models describing the foliar absorption of such organic pollutants have been proposed (Bacci & al. 1990b, Riederer 1990, Trapp & al. 1990, Paterson & al. 1991, Deinum & al. 1995), and are used to estimate the partitioning and transport of organic pollutants between the atmosphere and different leaf parts.

Table 1. Solubility in water of gases and ci/co calculated from foliar gas absorption measurements under favorable growing conditions.

Gas	Solubility in water*)	Calculated c_i/c	C_0 and literature
CO_2	0.037	0.5-0.9 (light)	350 ppm; Zeiger & al. 1987
CO	0.00083	≅1	0.5 ppm; estimated from Hill 1971
NO_2	decomposes	≥ 0	0.1-6 ppm; Omasa & al. 1979
NO	0.0021	0.9-0.95	0.02-0.1 ppm; calc.from Neubert & al. 1993
NH_3	33	0.05-0.1	0.05 ppm; Farquhar & al. 1980
O_3	0.011	≥ 0	0.2-0.9 ppm; Omasa & al. 1979, 2000a°
SO_2	1.6	≥ 0	0.25-1.5 ppm; Omasa & Abo 1978
PAN	low	≥ 0	0.01-0.08 ppm; Nouchi 1980
Formaldehyde	18	≥ 0	0.05-1 ppm; Kondo & al. 1996a
Acetaldehyde	∞	0.4-0.5	0.1 ppm; calc. from Kondo & al. 1998
Propanal	3.8	0.35-0.45	0.1 ppm; calc. from Kondo & al. 1998
Butanal	0.56	0.3-0.5	0.1 ppm; calc. from Kondo & al. 1998
Pentanal	low	0.3-0.5	0.1 ppm; calc. from Kondo & al. 1998
Acrolein	4.6	0.2-0.6	1 ppm; Omasa & al. 2000b
Acetone	∞	≅1	1 ppm; Omasa & al. 2000b
Methylethylketone	5.0	0.7-0.8	1 ppm; Omasa & al. 2000b
Methylisobutylketon	0.017	≅1	1 ppm; Omasa & al. 2000b
Phenol	0.71	0.45-0.6	0.05 ppm; calc. from Kondo & al. 1999
Acetonitrile	∞	≅1	1 ppm; Omasa & al.2000b
Benzene	0.0023	≅1	1 ppm; Omasa & al. 2000b
Chloroform	0.0069	≅1	1 ppm; Omasa & al. 2000b
Trichloroethylene	0.0076	≅1	0.05 ppm; Kondo & al., unpubl.data

*) mol kg^{-1}; data from Richardson 1992-1994, Hill 1971.

Hill 1971 and Bennett & al. 1973 reported that stomatal absorbency of a gas is determined by its solubility in water and the effectiveness of its decomposition or metabolization in the leaf tissues. Among the pollutants listed in Table 1, no conspicuous relationship could be found between the solubility of a pollutant in water and its foliar absorbency. For example, although the solubility of O_3 in water is relatively low, the c_i /c_o for O_3 was close to zero. On the other hand, the foliar absorption of acetone or acetonitrile could not be detected, even though they are both highly soluble in water. These results imply that solubility in water is not a critical factor determining the foliar absorbency of a pollutant. However, there is a possibility that the foliar absorption of CO, chloroform, benzene, and trichloroethylene (Table 1) is limited by their solubility because their gas-liquid-phase transfer into the leaves is obstructed.

The fact that all the aldehydes (including acrolein) noted in Table 1 are absorbed by leaves indicates that leaves have a high capacity to metabolize aldehydes, although this capacity varies between the different kinds of aldehydes. However, different ketones show different levels of foliar absorbency (Table 1). For example, MEK absorbance is found in *C. Sasanqua* but is not detectable in *P. nigra* (Omasa & al. 2000b). Furthermore, although MEK and acetone have similar chemical structures and are both highly soluble in water, the leaves show no absorbance of acetone. Such variation may result from interspecific differences in the activity of metabolic enzymes or in the characteristics of the metabolic processes.

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