Controls on the emission of plant volatiles through stomata: A sensitivity analysis

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[1] According to experimental studies, plant emissions of volatile organic compounds (VOC) are controlled by stomata to a varying extent, but the differing responses could not be explained so far. A dynamic emission model developed in a previous study indicated that stomata may limit the emission rate in a nonsteady state conditions, whereas the rate of increase of liquid-phase volatile concentrations controls the degree to which stomata temporarily curtail the emission. Despite its large predictive capability, potentially large number of volatile physico-chemical and leaf structural variables are needed for parameterization of such dynamic models, limiting the usefulness of the approach. We conducted a sensitivity analysis to determine the effect of varying VOC distribution between gas- and liquid-phases (Henry's law constant, H, Pa m^3 mol^{-1}) and varying internal diffusion conductances in the liquid- and gas-phases. The model was parameterized for three contrasting leaf architectures (conifer, sclerophyll, and mesophytic leaves). The sensitivity analysis indicated that the volatile H value is the key variable affecting the stomatal sensitivity of VOC emissions. Differences in leaf architecture, in particular in leaf liquid volume to area ratio, also modified the emission responses to changes in stomatal aperture, but these structural effects were superimposed by compound gas/liquid phase partitioning. The results of this analysis indicate that major effort in parameterization of dynamic VOC emission models should be directed toward obtaining reliable gas/liquid-phase equilibria for various plant volatiles, and that these models may readily be applied for leaves with contrasting architecture. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* emission model, leaf architecture, Henry's law constant, liquid-phase conductance

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1. Introduction

[2] Plant leaves sensitively regulate water loss by decreasing the stomatal aperture in response to declining plant water status [*Jones*, 1996; *Tardieu and Simonneau*, 1998]. Such decreases in the openness of stomatal pores potentially also lead to limitations in the efflux of the volatiles from the leaves. Given that water limitations frequently occur in most environments, and water stress is the most significant factor limiting productivity at a global scale [*Schulze*, 1986], stomatal constraints may importantly alter stand, region and biome level estimates of volatile compound emission from the plants.

[3] Despite the potential importance of stomata, the emission responses of plant volatile compounds to changes in stomatal conductance are apparently different for various compounds. While stomata do affect the efflux rates of methanol [*Nemecek-Marshall et al.*, 1995], acetic acid [*Gabriel et al.*, 1999], acetaldehyde [*Kreuzwieser et al.*, 2000], and linalool [*Niinemets et al.*, 2002a], they do not control the isoprene [*Fall and Monson*, 1992] and α-pinene [*Loreto et al.*, 1996b] emission. Given that the volatile flux through the stomata is the product of stomatal conductance, G_S, and the difference in partial pressure between the leaf intercellular air space and ambient atmosphere, ΔP, the lack of stomatal sensitivity of isoprene and terpene emission has been explained by an increase of ΔP due to volatile build-up in leaf intercellular air space such that the emission flux remains unaltered despite of a lower value of stomatal aperture [*Sharkey*, 1991; *Fall and Monson*, 1992]. This mechanism explains the stomatal independence of isoprene and α-pinene fluxes, but does not allow for the strong stomatal sensitivity experimentally observed for the other compounds.

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[4] We have shown in the accompanying study [*Niinemets and Reichstein*, 2003] that compound-specific differences in gas/liquid-phase partitioning may provide an explanation for contrasting sensitivity of plant volatiles to modifications in stomatal conductance. Although it is true that stomatal closure leads to immediate increases in ΔP, and stomata cannot limit VOC emission in a steady state condition, the air-phase concentrations of more water-soluble compounds such as alcohols, aldehydes and carboxylic acids increase more slowly than those of isoprene and monoterpenes. For compounds with high solubility, large increases in aqueous-phase concentrations are needed to support a certain rise in gas-phase concentration. Thus, the rate constant for ΔP rise is smaller than the rate constant for stomatal movements, implying that in a nonsteady state situation, stomata may exert a temporal control over the emission rates of compounds with high solubility. Such effects on VOC emission can only be simulated by dynamic models.

[5] Although the dynamic models allow to gain fundamental insight into plant volatile emission mechanisms, and be potentially useful for improving current predictive algorithms of volatile emission, a great number of physico-chemical characteristics of volatiles, and anatomo-morphological leaf variables is needed to parameterize these models. Such extensive parameter requirement may mean that the dynamic models are of limited use for simulation of the field data. However, the physico-chemical characteristics of specific volatiles at various temperatures may be determined in the laboratory or derived from quantitative structure-property relationships. Once determined, they may be taken as constants for all situations. Thus, large variation in morphology and anatomy of plant leaves, implying widely differing diffusion pathway lengths and volatile liquid- and gas-phase pools may be the primary constraint limiting the simplification of dynamic emission algorithms for the field conditions.

[6] In the current study, we conduct a sensitivity analysis of the effects of various leaf architectures on the dynamics of volatile emission after changes in stomatal conductance. The dynamic emission model of *Niinemets and Reichstein* [2003] was parameterized for three species of contrasting leaf structure, allowing to determine the influence of varying distribution of total diffusion resistance between leaf internal liquid- and gas-phases on the stomatal constraints of VOC emission. Our analysis suggests that leaf structural differences have an impact on stomatal sensitivity of VOC emissions, but also that the overall effect is relatively minor, and is superimposed by the physico-chemical characteristics of volatiles, in particular, the VOC partitioning between gas- and liquid-phases.

2. Methods

2.1. Description of the Dynamic Model of Plant Volatile Emission

[7] The full details of the model are provided in *Niinemets and Reichstein* [2003], and here the basic characteristics are summarized. We use the mass balance approach, and describe the dynamics of the gas-phase (pool size S_G) and liquid-phase (pool size S_L) pools of a volatile as:

$$\frac{dS_G}{dt} = F_m - F \tag{1a}$$

$$\frac{dS_L}{dt} = I - F_m, \tag{1b}$$

where I is the rate of volatile production, F_m is the diffusion flux from the site of synthesis to outer surface of cell walls, and F is the diffusion flux from the gas-phase to ambient air. Because the gas-phase half-times are on the order of 10^{-2} to 10^{1} s even for very low finite stomatal conductances [*Niinemets and Reichstein*, 2003], but the half-times for stomatal opening and closure are on the order of minutes [*Tinoco-Ojanguren and Pearcy*, 1993; *Allen and Pearcy*, 2000], the gas-phase is considered as in a steady state in the current analysis. Thus, the extent to which the stomata may control VOC emissions depends primarily on the liquid-phase dynamics.

[8] Considering that $F = F_m$, and combining the flux equations for VOC diffusion from the site of synthesis to outer surface of the cell walls, and VOC flux from intercellular air space to ambient air, the liquid-phase pool dynamics is described as [*Niinemets and Reichstein*, 2003]:

$$\frac{dS_L}{dt} = I - k_L S_L, \tag{2}$$

where the first-order liquid-phase rate-constant, k_L, is given by:

$$k_L = G_L \frac{A}{f_w V}\left(1 + \frac{G_L P}{G_G H}\right)^{-1}. \tag{3}$$

In this equation, G_L is the liquid-phase conductance (m s^{-1}), A is the leaf surface area (m^2), V is the leaf volume (m^3), f_w is the liquid volume fraction in the leaf (m^3 m^{-3}), P is the air pressure (Pa), H is the equilibrium gas/liquid-phase distribution coefficient (Henry's law constant, Pa m^3 mol^{-1}), and G_G is the gas-phase diffusion conductance (mmol m^{-2} s^{-1}). Henry's law constant is numerically equal to compound saturated vapor pressure divided by compound's aqueous solubility [*Staudinger and Roberts*, 1996]. Equation (2) is integrated to determine the volatile compound flux rate for each time t [*Niinemets and Reichstein*, 2003].

[9] The model behavior is illustrated in Figure 1 for two compounds with relatively low H values. After a momentary simulated stomatal closure (half-time of stomatal closure $\tau = 0$ s), there is an immediate decline in the emission rate (Figures 1a and 1c), and gradual recovery as the liquid-phase pool size is increasing (Figures 1b and 1d). Because acetaldehyde has a larger H value (Figures 1a and 1b), it supports a greater gas-phase partial pressure for the same liquid-phase concentration than methanol (Figures 1c and 1d). Accordingly, the stomata may limit the emission of compounds with a higher H over a shorter time period than they can constrain the emission of more soluble compounds. As the simulations with realistic stomatal response half-times (1–5 min.; *Tinoco-Ojanguren and Pearcy* [1992]) demonstrate (Figures 1a and 1c), the effect of stomatal closure on the emission dynamics gradually decreases with increasing stomatal response time. In fact, stomata cannot control the emission of compounds, for which the liquid-phase dynamics is faster than the changes in stomatal aperture.

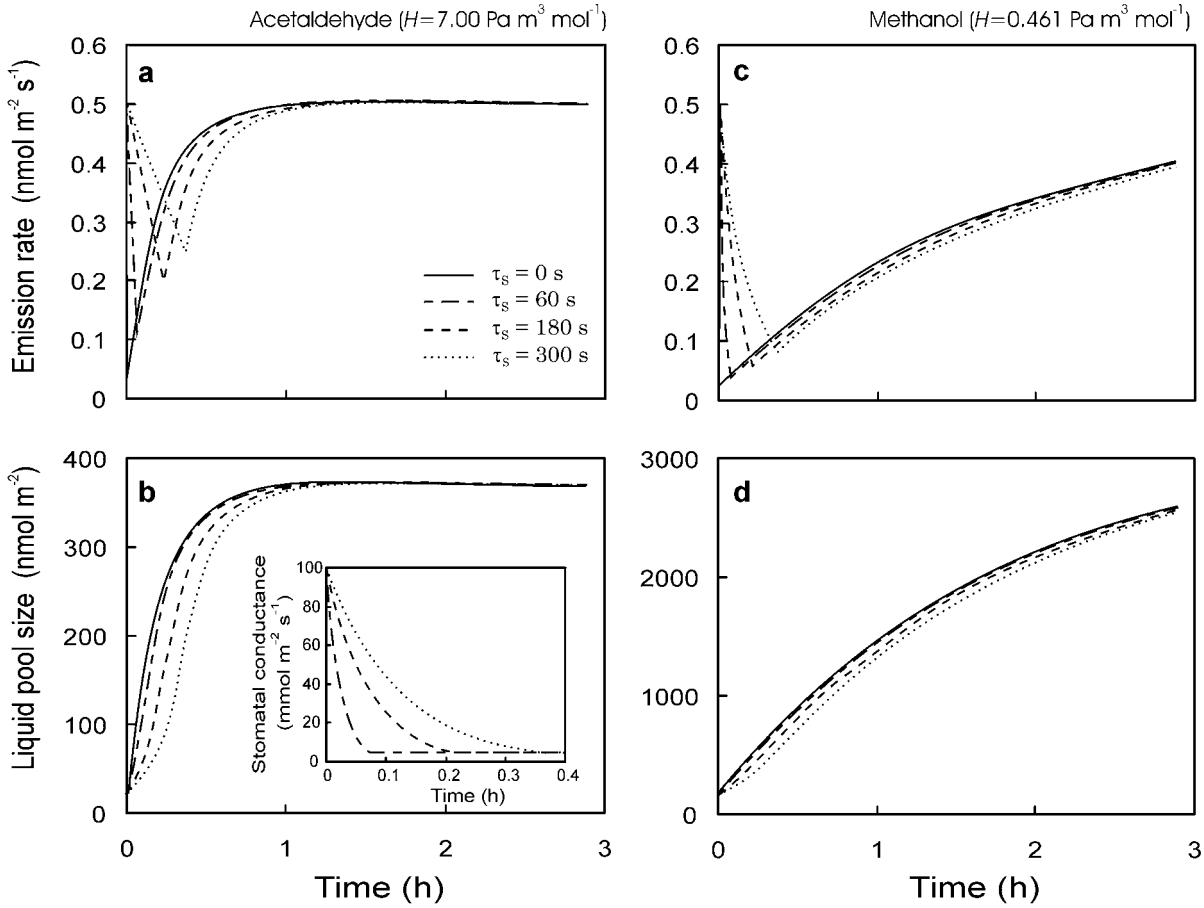

Figure 1. Illustration of the dynamics of volatile emission rate (Figures 1a and 1c) and the size of the volatile aqueous pool (Figures 1b and 1d) in response to changes in stomatal conductance to H_2O from 100 mmol m^{-2} s^{-1} to 5 mmol m^{-2} s^{-1} (G_V) at time $t = 0$ for acetaldehyde (Figures 1a and 1b) and methanol (Figures 1c and 1d). Methanol is a representative compound with a low value of Henry's law constant (H, the equilibrium gas/liquid-phase partition coefficient), and acetaldehyde with an intermediate H value. The volatile synthesis rate was set at 0.5 nmol m^{-2} s^{-1}, and the emission was in the steady state before changes in stomatal aperture. The internal diffusion conductances were calculated using the morphological characteristics of *Quercus ilex* (Table 1), and assuming the longest diffusion pathway. Decreases in stomatal conductance were simulated by an exponential relationship (inset in Figure 1b), and simulations for stomatal closure half-times of 0 s (momentary stomatal closure), 60 s, 180 s, and 300 s are depicted. The conductances and volatile physico-chemical characteristics were calculated for a leaf temperature of 25°C.

[10] Apart from the dependence of the liquid-phase dynamics on the compound Henry's law constant, equation (3) also indicates that the foliar structural differences may strongly alter the stomatal sensitivity of VOC emission rates. Leaf structure determines the liquid-phase conductance from the chloroplasts to the outer surface of mesophyll cell walls, G_L, and the amount of liquid volume per unit leaf area, $f_w V/A$ (equation (3)). In addition, leaf internal architecture also affects the gas-phase diffusion pathway length from outer surface of cell walls to substomatal cavities, thereby altering G_G. The exact extent to which leaf structure alters the emission dynamics after changes in stomatal conductance apparently depends on Henry's law constant and the initial volatile liquid pool size in a complex manner, and will be investigated in the following sensitivity analysis.

2.2. Characterization of the Gas-Phase Conductance

[11] The gas-phase conductance from the outer surface of cell walls to substomatal cavities (G_{ias}, m s^{-1}) is dependent on the fraction of intercellular air-space (f_{ias}, m^3 m^{-3}), the effective diffusion path length (ΔL_{ias}, m) in the gas-phase [*Syvertsen et al.*, 1995; *Terashima et al.*, 1995] and the binary air diffusion coefficient (D_A, m^2 s^{-1}) as:

$$G_{ias} = \frac{D_A f_{ias}}{\Delta L_{ias} \varsigma}, \quad (4)$$

where ς is the diffusion path tortuosity (m m^{-1}). An estimate of ς of 1.57 m m^{-1} was calculated as an average from measured leaf thickness and CO_2 internal gas-phase conductance for four woody thick-leaved species [*Syvertsen et al.*, 1995], and was not varied in the current

study. Because the other component of the gas-phase diffusion pathway, the stomatal conductance (G_S), is generally measured in molar units, we also convert G_{ias} to these units:

$$G_{ias}\left[\text{mol m}^{-2}\text{s}^{-1}\right] = \frac{G_{ias}[\text{m s}^{-1}]44.6 \cdot 273.16P}{(273.16+T)(101325)}, \quad (5)$$

where P (Pa) is air pressure, and T (°C) is leaf temperature. Total gas-phase conductance from outer surface of cell walls to ambient air, G_G, is given as the inverse of the sum of serial resistances:

$$G_G = \frac{1}{1/G_S + 1/G_{ias}}. \quad (6)$$

It is important that there is always a gas-phase limitation within the leaf, and thus, depending on the magnitude of the gas-phase internal conductance, shifts in liquid-gas phase-equilibrium may lead to modified emission dynamics even when the stomata are fully opened. The species may largely differ with respect to the distribution of the gas-phase conductance between the stomata and the intercellular airspace, and this may lead to different liquid-phase turnover times.

2.3. The Liquid-Phase Internal Conductance

[12] Depending on the site of synthesis of specific plant volatile, the components of the liquid diffusion pathway may differ. For compounds synthesized in chloroplast, the liquid-phase pathway includes cell wall, plasmalemma, cytosol, chloroplast envelope and chloroplast stroma (Figure 2), and the total conductance may be expressed as the inverse of the sum of the component serial resistances:

$$\frac{1}{G_L} = \frac{A_T}{A_{mes}}\left(\frac{1}{g_{cw}} + \frac{1}{g_{pl}} + \frac{1}{g_{ct}} + \frac{1}{g_{en}} + \frac{1}{g_{st}}\right), \quad (7)$$

where g_{cw} is the cell wall, g_{pl} the plasmalemma, g_{ct} the cytosol, g_{en} the chloroplast envelope, and g_{st} the chloroplast stroma conductance to the volatile. The ratio of mesophyll surface (A_{mes}) to total leaf surface area (A_T) corrects for the actual area available for diffusion [*Nobel*, 1991]. Implicit in the use of A_{mes}/A_T ratio to scale the conductances is the assumption that the cell wall, plasmalemma, and chloroplast exposed surface areas are essentially the same [*Nobel*, 1991]. The cell wall, cytosol and stroma conductances were calculated as (cf. *Tingey et al.* [1991] and equation (8.19) by *Nobel* [1991]):

$$g_i = \frac{r_f D_W p}{\Delta L_i}, \quad (8)$$

where g_i (m s^{-1}) is either g_{cw}, g_{ct} or g_{st}, D_W (m^2 s^{-1}) is the aqueous-phase volatile diffusion coefficient, ΔL_i (m) is the diffusion path length, and p (m^3 m^{-3}) is the effective porosity. Dimensionless coefficient r_f accounts for the decrease of the diffusion conductance in the cytosol and in the stroma ($r_f = 1$ for cell wall) because of greater viscosity and diffusion path length tortuosity of cytoplasm and chloroplast stroma than those of pure water [*Weisiger*, 1998]. An estimate of r_f of 0.294 for g_{ct} and g_{st} was determined as the ratio of effective water self-diffusion coefficients in duck embryo and in chemically pure water [*Weisiger*, 1998]. Effective porosity, p, was taken as 1 for g_{ct} and g_{st}, and 0.3 for cell walls. These are typical values for CO_2 liquid-phase diffusion [*Nobel*, 1991; *Evans et al.*, 1994; *Parkhurst*, 1994], and may actually be lower for larger molecules such as monoterpenoids.

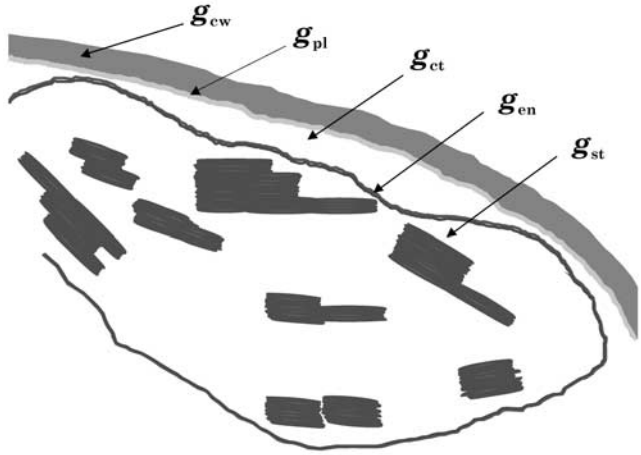

Figure 2. Components of the liquid-phase diffusion pathway in plant cells. Depending on the site of compound synthesis, and on whether equilibrium concentrations have been established among the cell compartments, various parts of the diffusion pathway may be relevant. For monoterpenes synthesized in chloroplasts, the total liquid-phase conductance (G_L) consists of chloroplast stroma (g_{st}), envelope (g_{en}), cytosol (g_{ct}), plasmalemma (g_{pl}) and cell wall (g_{cw}) conductances in series.

[13] The rate of passive diffusion through a cell membrane is limited by the movement of the molecule from the aqueous environment into the membrane lipid bilayer. Therefore, transport rate for a specific compound is proportional to the lipid solubility or hydrophobicity of that compound. The plasmalemma permeability to a VOC species may be expressed as:

$$g_{pl} = \frac{D_T^{pl} K_{pl/w}}{\Delta L_{pl}}, \quad (9)$$

where D_T^{pl} (m^2 s^{-1}) is the compound diffusion coefficient in the plasmalemma, ΔL_{pl} (m) is plasmalemma thickness, and $K_{pl/w}$ is the plasmalemma to water partition coefficient for specific VOC. $K_{pl/w}$ is the ratio of VOC concentration in the plasmalemma to the equilibrium concentration in the water-phase [*Nobel*, 1991]. Chloroplast envelope permeability, g_{en}, may be calculated analogously. Because of missing information of membrane lipid bilayer thickness as well as compound diffusion coefficients in plasmalemma and chloroplast envelope, we calculated the permeabilities of mesophyll cell membranes from the correlation between experimental permeabilities of mesophyll cell plasmalemma and chloroplast envelope in *Spinacia oleracea* [*Gimmler et al.*, 1981; *Daeter and Hartung*, 1993] with the compound diffusion volume (V_M, cm^3 mol^{-1}) [*Tucker and Nelken*, 1982] and octanol to assay medium partition coefficient ($K_{o/m}$). Because octanol to pure water partition coefficients

($K_{o/w}$) were only available from the literature [*Niinemets and Reichstein*, 2003, and the references therein], a correlation between $K_{o/m}$ used in the original study and $K_{o/w}$ was developed, allowing us to compute g_{pl} and g_{en} in relation to $K_{o/w}$:

$$g_{pl} = \frac{6.70 \cdot 10^{-4} K_{o/w}^{0.67}}{V_M^{0.918}}, \quad (10)$$

and

$$g_{en} = \frac{4.98 \cdot 10^{-5} K_{o/w}^{0.796}}{V_M^{0.543}} \quad (11)$$

($r^2 = 0.86$ for g_{pl} and $r^2 = 0.89$ for g_{en}). Data of *Gimmler et al.* [1981], and equations (10) and (11) predicted that the permeability of chloroplast envelope is one to two orders of magnitude greater than that of the plasmalemma. Values of all physico-chemical variables used in the current analysis are given by *Niinemets and Reichstein* [2003].

[14] Implicit in the calculations of G_L (equations (7)–(11)) is that environmental factors do not alter the liquid-phase conductance. However, there is recent evidence that G_L may respond to environment due to modification of membrane permeability as the result of changes in aquaporin (water-channels in membranes) conductance [*Terashima and Ono*, 2002]. Most of aquaporins are permeable only to water, and some specific aquaporins also to compounds with a small diffusion volume such as glycerol [*Borgnia et al.*, 1999]. Thus changes in aquaporin conductance unlikely alter the G_L for larger molecules such as terpenes, but may potentially influence the diffusion of smaller molecules such as methanol. Further experimental work is required to test for the possible effect of changing membrane permeabilities on the emission dynamics of plant volatiles with a small diffusion volume.

2.4. Leaf Structural Characteristics for Calculation of Transfer Resistances

[15] Foliar anatomical characteristics were compiled for three species of contrasting leaf structure [Table 1; *Niinemets*, 1999]. *Phaseolus vulgaris* L. is a species with mesophytic leaves having low internal diffusion limitations in both the gas- and liquid-phase. Previous research has indicated that it is a strong methanol emitter during leaf growth [*Nemecek-Marshall et al.*, 1995]. *Quercus ilex* L. is an evergreen Mediterranean sclerophyll species that has dense mesophyll with a low fraction of intercellular airspace. *Q. ilex* is a strong monoterpene emitter [*Loreto et al.*, 1996a], but may also emit aldehydes [*Kesselmeier et al.*, 1997; *Holzinger et al.*, 2000], carboxylic acids [*Kesselmeier et al.*, 1997, 1998; *Gabriel et al.*, 1999], and aliphatic alcohols and esters [*Loreto et al.*, 1996a]. *Pinus sylvestris* L. is an evergreen conifer with thick leaves, possessing the lowest diffusion conductances in the liquid- and gas-phase (Table 1). It is a representative conifer emitting monoterpenes [*Janson*, 1993; *Janson and de Serves*, 2001], but also acetone and aldehydes [*Janson and de Serves*, 2001].

[16] Because experimental data are available for the CO_2 mesophyll diffusion limitations [*Evans et al.*, 1994; *Evans and von Caemmerer*, 1996; *Evans and Loreto*, 2000], we computed the liquid- and gas-phase internal diffusion conductances for CO_2 to roughly estimate the reliability of our calculations (Table 1). Our estimates for *Quercus* and *Pinus* agree with the experimental values of 100–200 mmol m^{-2} s^{-1} for sclerophyllous leaves [*Syvertsen et al.*, 1995; *Evans and Loreto*, 2000]. Although the values for *P. vulgaris* may be somewhat underestimated, they are still above the lower limit of the mesophytic leaves [*Evans and Loreto*, 2000]. Thus we conclude that our calculations provide a representative description of the ranges of the internal diffusion pathway in field-grown plants.

3. Results and Discussion

3.1. Sensitivity of the Liquid-Phase Pool Dynamics to Henry's Law Constant

[17] The simulated half-times of the liquid pool size (τ_L), given as $\tau_L = \ln(2)/k_L$, strongly increase with decreasing Henry's law constant (Figures 3a–3c). There has been a broad debate over the extent to which stomata may control the volatile efflux from the leaves [*Sharkey*, 1991; *Fall and Monson*, 1992; *Kesselmeier and Staudt*, 1999]. Our sensitivity analysis indicates that stomata cannot control the emission rates in compounds with high H over a significant time-interval even in physiologically very unrealistic situations. The extent and kinetics of stomatal limitations of VOC emissions apparently depends on the rate constant for changes in stomatal openness (k_S, Figure 1). When k_S approaches k_L, the sensitivity of the emission rates to changes in stomatal openness progressively decreases (Figure 1). However, for compounds with low H such as methanol, the emission rates are only weekly affected by differences in k_S (Figure 1c), and the emissions are affected by stomatal changes over the entire physiologically relevant range of k_S. Given that k_S decreases in water-stressed leaves [*Aasamaa et al.*, 2002], for which the stomatal effects are most important in modifying the VOC emissions, stomatal effects also modify significantly the VOC emissions of compounds with intermediate H values in field conditions.

[18] The values of τ_L were larger at a common H for leaves with lower liquid-phase conductance (G_L, Figure 3a), and with lower surface area to volume ratio (A/V, Figure 3b), as well as for a situation with more closed stomata (Figure 3c). These effects of leaf structure on the emission dynamics are compatible with a limited rise in the gas-phase volatile partial pressure. A low G_L indicates a constrained rate of delivery from the site of synthesis, and in this case, the volatile pool sizes increase more slowly than in the case of a higher liquid-phase conductance. In a similar manner, high A/V ratio implies a greater liquid volume per unit leaf area, and accordingly a larger liquid pool size at a common liquid-phase volatile concentration (equation (3)).

3.2. Gas-Phase Diffusion Conductance and the Emission Dynamics

[19] Simulations with varying gas-phase conductances further demonstrate that the relevance of consideration of stomatal effects may depend on G_L (Figure 3d), A/V ratio (Figure 3e) and H (Figure 3f). Again, these effects result from the circumstance that these variables alter the VOC pool size at a common stomatal openness. The liquid-phase conductance has only a small effect at low and intermediate

Table 1. Leaf Structural Characteristics and Corresponding Internal Conductances to CO_2 in Three Species of Contrasting Leaf Architecture

Characteristic	Symbol (Unit)	Value (Reference[a])		
		Quercus ilex L.	*Phaseolus vulgaris* L.	*Pinus sylvestris* L.
Leaf Surface Area (A) to Volume Ratio (V)[b]	A/V ($m^2\ m^{-3}$)	3905 (4, 5, 9, 25–27)	5050 (2, 14, 15, 20, 21)	5840 (10, 19, 28)
Exposed Mesophyll Area to A Ratio[b,c]	A_{mes}/A ($m^2\ m^{-2}$)	30.5 (27)	22 (14)	15.4 (10, 12, 19, 28)
Fraction of Intercellular Air Spaces Within the Leaf	f_{ias} ($m^3\ m^{-3}$)	0.181 (27)[d]	0.271 (21)	0.228 (28)
Volumetric Foliar Water Fraction	f_w ($m^3\ m^{-3}$)	0.491 (6–8)	0.611 (18, 22, 23)	0.514 (28)
Diffusion Path Length in the Cell Wall	ΔL_{cw} (m)	$5.0 \cdot 10^{-7}$ (9, 17)	$1.2 \cdot 10^{-7}$ (1)	$1.1 \cdot 10^{-6}$ (11)
Diffusion Path Length in the Cytosol	ΔL_{ct} (m)	$9.7 \cdot 10^{-8}$ (17)	$2.1 \cdot 10^{-7}$ (1)	$1.2 \cdot 10^{-7}$ (24)
Effective Diffusion Path Length in the Gas-Phase[e]	ΔL_{ias} (m)	$1.22 \cdot 10^{-4}$ (4, 5, 9, 25, 27)	$5.12 \cdot 10^{-5}$ (2, 14, 15, 20, 21)	$4.74 \cdot 10^{-4}$ (19, 28)
Diffusion Path Length in the Chloroplast Stroma[f]	ΔL_{st} (m)	$1.65 \cdot 10^{-6}$ (17)	$1.5 \cdot 10^{-6}$ (1, 3)	$5.9 \cdot 10^{-7}$ (13, 24)
Leaf Dry Mass per Unit Area[b]	M_A ($g\ m^{-2}$)	181 (4, 5, 9, 25, 27)	32.0 (18, 20, 21, 23)	109 (16)
Internal Gas-Phase Conductance to CO_2	G_{ias} (mmol $m^{-2}\ s^{-1}$)	605	2160	197
Internal Liquid-Phase Conductance to CO_2[g]	G_L (mmol $m^{-2}\ s^{-1}$)	186	193	141
Total Internal Conductance to CO_2[h]	G_M (mmol $m^{-2}\ s^{-1}$)	142	177	82

[a](1) *Atabekova and Ustinova*, 1980; (2) *Barreiro et al.*, 1992; (3) *Bradbeer and Montes*, 1976; (4) *Castro-Díez et al.*, 1997; (5) *Christodoulakis and Mitrakos*, 1987; (6) *Gratani*, 1995; (7) *Gratani and Fiorentino*, 1988; (8) *Gratani et al.*, 1989; (9) *Grossoni et al.*, 1998; (10) *Jokela et al.*, 1998; (11) *Jokela et al.*, 1997; (12) *Kovalyev and Antipova*, 1984; (13) *Lewandowska and Öquist*, 1980; (14) *Longstreth and Nobel*, 1979; (15) *Morris and Arthur*, 1984; (16) *Niinemets et al.*, 2001; (17) *Paoletti*, 1998; (18) *Peñuelas et al.*, 1993; (19) *Perterer and Körner*, 1990; (20) *Radoglou et al.*, 1992; (21) *Radoglou and Jarvis*, 1992; (22) *Sõber*, 1992; (23) *Sõber and Rahi*, 1989; (24) *Soikkeli*, 1980; (25) *Terradas and Savé*, 1992; (26) *Tretiach et al.*, 1997; (27) *Wagner et al.*, 1993; (28) *Želawski et al.*, 1968. Whenever multiple references are given, an average value has been calculated.

[b]Because of three-dimensional needle shape, total leaf area, A_T, was used in *P. sylvestris*, and projected leaf area in *Q. ilex* and *P. vulgaris*. A representative A_T to projected area ratio of 2.53 $m^2\ m^{-2}$ may be used to convert A_T to projected leaf area [*Želawski et al.*, 1968; *Perterer and Körner*, 1990; *Niinemets et al.*, 2001].

[c]A_{mes}/A ratio was computed according to *Nobel* [1991], using the available sizes of palisade and spongy mesophyll cells, and approximating the cell shape to a prolate spheroid in *Q. ilex* and *P. vulgaris*, and to a sphere in *P. sylvestris*. A_{mes}/A calculations were corrected for the fraction of airspace in the leaves.

[d]The fraction of intercellular air-space in *Q. ilex* was calculated using available data on the size of mesophyll cells, and fraction of mesophyll in leaf cross-section. The volumes of palisade and spongy mesophyll cells were computed approximating cell shape by a prolate spheroid.

[e]ΔL_{ias} is an average diffusion path length that was taken equal to a half of leaf thickness for the hypostomatous species *Q. ilex*, and to a quarter of leaf thickness for the amphistomatous species *P. vulgaris*. In *P. sylvestris*, ΔL_{ias} was calculated from total needle thickness of $5.59 \cdot 10^{-4}$ m and accounting for the three-dimensional shape of the needles [*Niinemets et al.*, 2001].

[f]Half of the length of chloroplast side perpendicular to the cell-wall.

[g]Using the CO_2 permeabilities of plasmalemma and chloroplast envelope suggested by *Evans et al.* [1994].

[h]Calculated as $\frac{1}{G_M} = \left(\frac{1}{G_L} + \frac{RT_k}{G_{ias}H}\right)$, where R is the gas constant (J $mol^{-1}\ K^{-1}$), T_k is the absolute temperature (K), and H is the Henry's law constant (Pa m^3 mol^{-1}).

values of stomatal conductance, and has a minor effect in compounds with H values less than ca. 10 Pa m^3 mol^{-1} (Figure 3f). Yet, for volatiles with $H < 10$ Pa m^3 mol^{-1}, the emissions can be effectively controlled by stomata [*Niinemets and Reichstein*, 2003], because they have half-times of the liquid-phase on the order of at least minutes or more (Figure 1). Thus, this simulation suggests that large leaf-to-leaf differences in the internal liquid-phase diffusion conductance have a minor effect on the stomatal sensitivity of VOC emission.

[20] In contrast, the effects of A/V ratio on stomatal sensitivity of VOC emission did not depend on H (Figure 3b) or on gas-phase conductance (Figure 3e). For compounds with $H < 10$ Pa m^3 mol^{-1}, differences in A/V can affect τ_L by about a factor of four (Figures 3b and 3e). Nevertheless, the simulated leaf structural controls on the emission dynamics were superimposed by the effects of liquid/gas-phase partitioning (Figures 3b and 3e).

3.3. Dynamics of VOC Emission for Contrasting Leaf Architectural Types

[21] Because all foliar structural variables may vary simultaneously, we chose three contrasting leaf architectural types covering a realistic range of variation in leaf structure to gain insight into the potential implications of the combined influences of gas- and liquid-phase pathway lengths and leaf liquid volume to total area ratio. Sclerophyllous leaves of *Quercus* and mesophytic leaves of *Phaseolus* have similar liquid-phase conductance (G_L) but G_L is ca. 40% lower for the needles of *Pinus* (Table 1). The internal gas-phase conductance is the highest in *Phaseolus*, intermediate in *Quercus* and the lowest in *Pinus*, whereas the values of G_{ias} differ more than an order of magnitude between *Phaseolus* and *Quercus*. However, the needles of *Pinus* have a larger surface area to liquid-volume ratio $A/(f_wV)$ (11360 $m^2\ m^{-3}$), than the leaves of *Phaseolus* (8265 $m^2\ m^{-3}$) or *Quercus* (7950 $m^2\ m^{-3}$).

[22] Despite the lower liquid-phase conductance, the emission rate in *Pinus* responds faster (Figure 4) to an immediate decrease in stomatal conductance from 200 mmol $m^{-2}\ s^{-1}$ to 5 mmol $m^{-2}\ s^{-1}$ (τ_L = 0.117 h for acetaldehyde and τ_L = 1.43 h for methanol after simulated stomatal closure) than that in either *Phaseolus* (τ_L = 0.14 h for acetaldehyde and τ_L = 1.33 h for methanol) or *Quercus* (τ_L = 0.15 h for acetaldehyde and τ_L = 1.86 h for methanol). The species differences are larger for the compounds with a lower Henry's law constant (cf. Figures 4a and 4b).

3.4. Effects of Gas-Phase Distribution Between Stomata and Intercellular Air Space

[23] The faster recovery of emission rates after changes in stomatal openness in *Pinus* than in other species partly results from the higher $A/(f_wV)$ value in this species (Figure 3b). However, more rapid response after an immediate

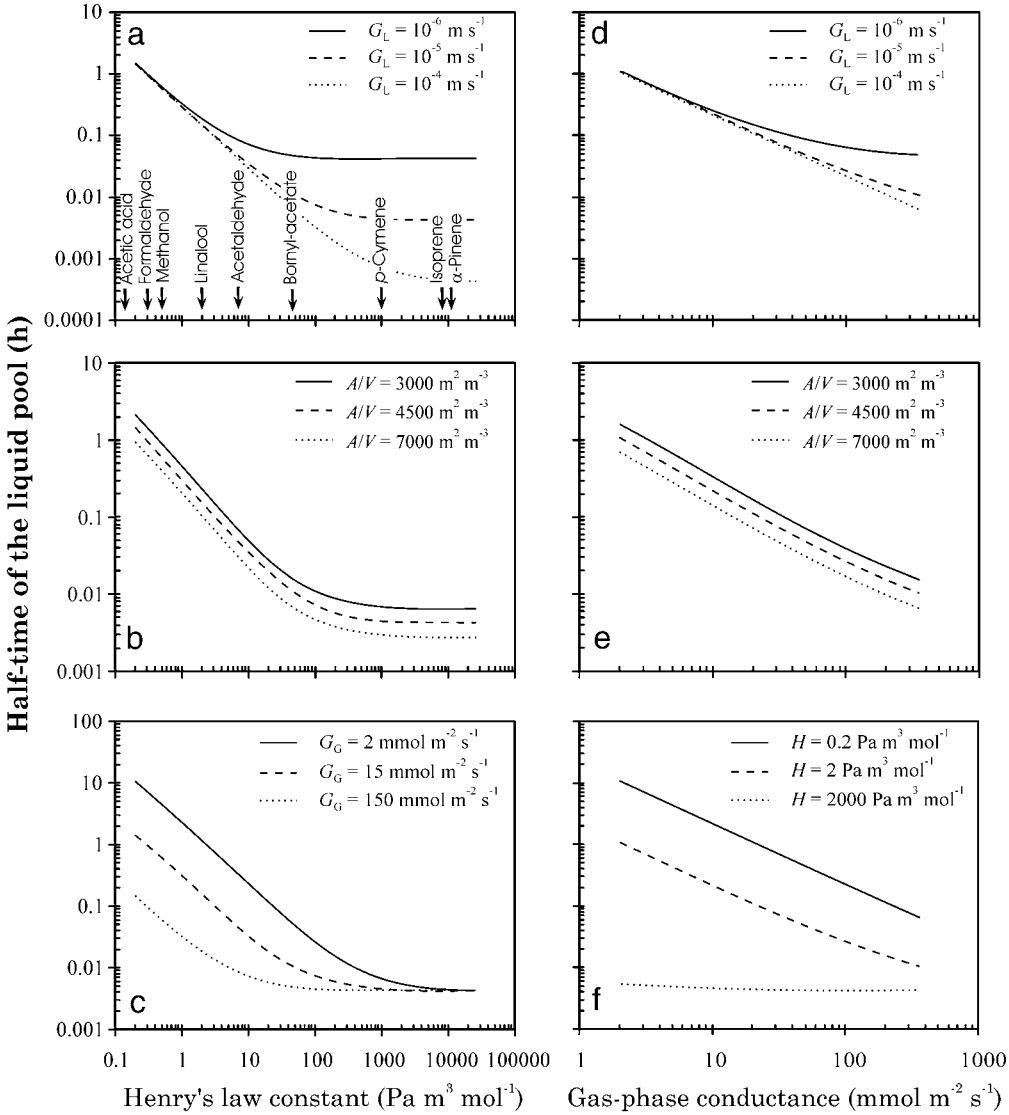

Figure 3. Dependence of the half-time of the VOC liquid pool (τ_L) on Henry's law constant (H, Figures 3a–3c) and its gas-phase conductance (G_G, equation (6), Figures 3d–3f) for different values of liquid-phase conductance from the site of synthesis to outer surface of cell walls (G_L, Figures 3a, 3d), area to volume ratio of the leaves (Table 1, Figures 3b, 3e), and G_G (Figure 3c) or H (Figure 3f). The half-time of the liquid pool (τ_L) was computed as $\ln(2)/k_L$, where k_L is the rate constant of the liquid pool (equation (3)). The variables not varied in the particular simulation were held constant at $G_L = 10^{-5}$ m s^{-1}, A/V = 4500 m^2 m^{-3}, H = 2 Pa m^3 mol^{-1}, G_G = 15 mmol m^{-2} s^{-1}. The gas-phase diffusion conductance to the compound vapor consists of a stomatal conductance and an intercellular transfer resistance from the outer surface of the cell walls to the substomatal cavities (equation (6)). Representative compounds with various H values are depicted in Figure 3a.

change in stomatal conductance may also be associated with its lower G_{ias}. This is because a smaller G_{ias} implies a lower total gas-phase conductance (G_G, equation (6)) for the same value of stomatal conductance (G_S). Accordingly, the same steady state volatile emission rate before the stomatal closure (Figure 4) can only be supported with a larger volatile liquid-phase pool size. This larger liquid-phase pool supports a greater VOC partial pressure after stomatal closure, and accordingly a greater VOC emission rate than that in the case of a smaller steady state pool size before the stomatal closure. In essence, the relative decline in the total gas-phase conductance for a common change in G_S is smaller in species with lower internal gas-phase conductance, and the new steady state will be reached faster.

[24] The effect of the steady state VOC liquid-phase pool size on the initial emission rate after stomatal closure is demonstrated in Figure 5. As the steady state pool size increases, the gas-phase VOC concentration also increases, and the sensitivity of the emission rate to a rapid decrease in G_S declines. Such an effect may play an important role during repeated changes in stomatal conductance. In particular, for compounds with low values of Henry's law

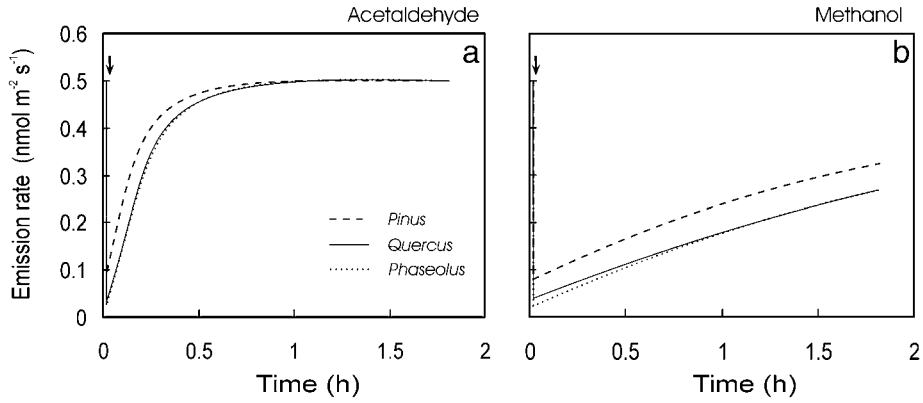

Figure 4. Variation in acetaldehyde (Figure 4a) and methanol (Figure 4b) emission dynamics after a change of stomatal conductance to H_2O from 200 mmol m^{-2} s^{-1} to 5 mmol m^{-2} s^{-1} (denoted by arrow) for three contrasting leaf architectures (Table 1). We assumed momentary stomatal closure (see Figure 1). All model parameters were calculated for a leaf temperature of 25°C.

constant, liquid-phase concentrations of which may reach a steady state in several hours (Figure 3). Thus, depending on whether or not the steady state has been reached before the stomatal closure, the sensitivity of the emission rates to changes in stomatal conductance may differ, and additional simulation studies are called for to address the significance of such effects on diurnal dynamics of VOC fluxes.

[25] A sensitivity analysis further indicates that the liquid-pool half-time is the larger the lower is the value of G_{ias} relative to G_S (Figure 6), because decreases in G_{ias} lead to a greater restriction of the gas-phase diffusion flux at a common stomatal openness. Thus, this analysis further underscores the potential relevance of species-specific structural characteristics that may affect the dynamic responses of the emission rates of volatiles to rapidly changing environmental conditions and compound synthesis rates.

[26] Because gas-phase rate coefficients for reaction with ozone and hydroxyl radicals vary more than several orders of magnitude for similar plant volatile compounds [*Fehsenfeld et al.*, 1992; *Guenther et al.*, 1994], a mechanistic prediction of the degree to which biological controls alter the emissions of specific compounds provides an important basis to determine diurnal changes in volatile composition and atmospheric reactivity. Furthermore, identification of

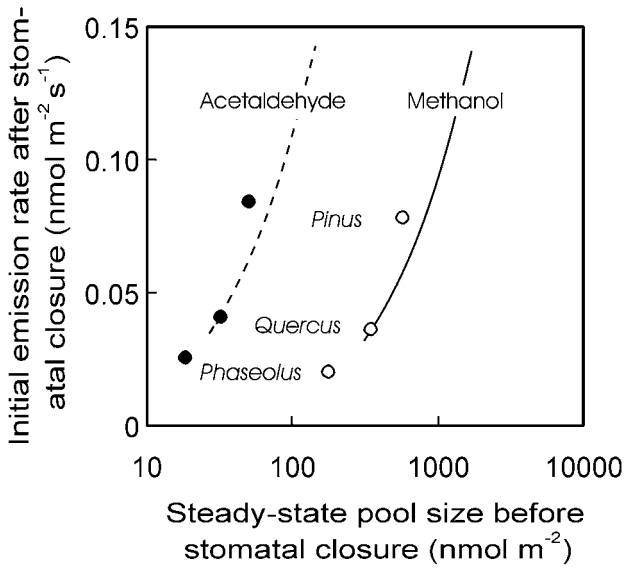

Figure 5. Relationship between the initial emission rate after the change of stomatal conductance to H_2O from 200 mmol m^{-2} s^{-1} to 5 mmol m^{-2} s^{-1}, and the steady state volatile liquid-phase pool size before stomatal closure. In the steady state, the volatile emission rate through the stomata equals the synthesis rate, I (0.5 nmol m^{-2} s^{-1}). The symbols correspond to the steady state pools and respective initial emission rates for thee contrasting leaf architectural types (Figure 4). The lines were simulated using the structural characteristics of *Q. ilex* and changing the liquid-phase pathway conductance.

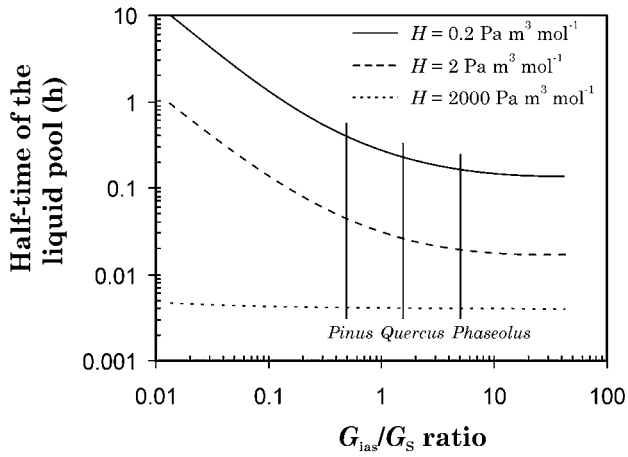

Figure 6. Changes in the half-time of the liquid pool of the volatile in dependence on the distribution of gas-phase conductance between stomata (G_S) and leaf intercellular airspace (G_{ias}) and on the value of the Henry's law constant of the volatile. Stomatal conductance to H_2O was held constant at 250 mmol m^{-2} s^{-1}, and G_{ias} was varied. The vertical lines indicate the corresponding estimates for three contrasting leaf structural types (Table 1).

the conditions for possible stomatal control allows to distinguish between gas-phase diffusion limitations, and secondary effects of stomatal closure on the production rate of specific compounds, making it possible to develop more mechanistic predictive models that rely on participating enzyme kinetics and regulation [*Niinemets et al.*, 2002b].

4. Conclusions

[27] The oxygenated compounds with low values of Henry's law constant are occasionally emitted in large quantities by the vegetation [*Gabriel et al.*, 1999; *Kesselmeier et al.*, 2000; *Kesselmeier*, 2001], but the physiological controls on the emission fluxes of these compounds are still poorly understood [*Kesselmeier*, 2001]. As our analysis demonstrates, the conflicting results may partly be explained by stomatal effects on the emission rates of these compounds as well as by different initial pool sizes before changes in stomatal conductance.

[28] Dynamic models are needed to simulate stomatal responses of VOC emissions, and a large number of leaf structural variables (Table 1) and physico-chemical characteristics of specific compounds [*Niinemets and Reichstein*, 2003] must be known for the model parameterization. Furthermore, a number of simplifications are required to determine the appropriate conductances of the diffusion pathway. This may suggest that our approach is of limited practical use for simulation of field data. However, our sensitivity analyses indicate that the stomatal effects on VOC emission are primarily driven by compound's H value, and only to a moderate extent by leaf structural differences. This demonstrates that the model is robust and is not very sensitive to the parameterization limitations. Leaf liquid volume per unit total area was identified as the most important leaf structural variable altering the emission kinetics. Given that this variable is easily measurable, we conclude that the dynamic models may provide an important tool for simulating the diurnal emission dynamics of oxygenated plant compounds. Combining the VOC emission model with a stand, landscape or biome level water use model, stomatal effects on VOC emission may be assessed at various scales of organization, thereby allowing to improve the correspondence between estimated and measured time-courses of oxygenated volatiles.

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