Review

Bidirectional exchange of biogenic volatiles with vegetation: emission sources, reactions, breakdown and deposition

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ABSTRACT

Biogenic volatile organic compound (BVOC) emissions are widely modelled as inputs to atmospheric chemistry simulations. However, BVOC may interact with cellular structures and neighbouring leaves in a complex manner during volatile diffusion from the sites of release to leaf boundary layer and during turbulent transport to the atmospheric boundary layer. Furthermore, recent observations demonstrate that the BVOC emissions are bidirectional, and uptake and deposition of BVOC and their oxidation products are the rule rather than the exception. This review summarizes current knowledge of within-leaf reactions of synthesized volatiles with reactive oxygen species (ROS), uptake, deposition and storage of volatiles, and their oxidation products as driven by adsorption on leaf surface and solubilization and enzymatic detoxification inside leaves. The available evidence indicates that because of the reactions with ROS and enzymatic metabolism, the BVOC gross production rates are much larger than previously thought. The degree to which volatiles react within leaves and can be potentially taken up by vegetation depends upon compound reactivity, physicochemical characteristics, as well as upon their participation in leaf metabolism. We argue that future models should be based upon the concept of bidirectional BVOC exchange and consider modification of BVOC sink/source strengths by within-leaf metabolism and storage.

Key-words: catabolism; compound breakdown; compound reactivity; emission controls; physicochemical characteristics; reactive oxygen species; volatile uptake.

INTRODUCTION

Biogenic volatile organic compound (BVOC) emissions play major roles in local and regional air quality by participating in ozone formation reactions, and in regional to global climate by contributing to aerosol and cloud formation, resulting in large-scale biosphere-atmosphere feedbacks (Heald et al. 2008; Arneth et al. 2009; Hallquist et al. 2009; Guenther et al. 2012; Kulmala et al. 2013). Reliable model-based integrations of BVOC fluxes are needed as inputs for these large-scale models. Traditionally, BVOC emission has been considered as a unidirectional flux of inert (i.e. non-reactive) molecules from the site of synthesis to the ambient atmosphere, and emission models use this simplified concept to directly relate the rate of emission to environmental drivers (e.g. Guenther et al. 1995, 2006; Monson et al. 2012). For BVOC produced de novo, it is generally assumed that the rate of emission is equal to the rate of production, whereas for those BVOC stored in specialized storage structures, the rate of emission is assumed equal to the rate of diffusion from the storage pools (for reviews, see Niinemets et al. 2010c; Monson et al. 2012; Grote et al. 2013). These assumptions likely reflect the circumstance that most of the interest in BVOC has, to date, been orientated towards non-oxygenated volatile isoprenoids (isoprene, monoterpenes and sesquiterpenes), and less research has dealt with oxygenated volatile compounds (OVCs) such as short-chained volatiles, for example, acetaldehyde, formaldehyde, acetone, methanol, ethanol, and formic and acetic acids, and the oxidation products of isoprenoids. In contrast to the volatile isoprenoids, OVC can be rapidly metabolized enzymatically and directly integrated into the central carbon and energy metabolism of plants.

Recent experimental and modelling work demonstrates that the assumption that BVOC emission rate always equals the rate of production at the site of synthesis or rate of vaporization at the site of emission is problematic, especially for OVC. Firstly, for several compounds, particularly those which partition strongly into the aqueous or lipid phases of the leaf, there can be significant time-lags between changes in BVOC production (or emission from storage pools) and emission from the leaf (Niinemets & Reichstein 2003a,b; Noe et al. 2010; Harley 2013). Secondly, a unidirectional emission flux can only be supported when ambient gas phase concentrations are lower than within-leaf concentrations. Although this can be the case when the rate of compound production is high such as in strong constitutive isoprenoid emitters, emitting species typically grow intermixed with non-emitting species that have inherently low leaf isoprenoid concentrations and can potentially take up emitted volatiles from the ambient air (Noe et al. 2008; Himanen et al. 2010), and this

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process can be sustained if there is a chemical sink (metabolization) within the plants (section Chemical sink heterogeneity). In addition, the rates of constitutive isoprene and monoterpene emissions in emitting species vary over several orders of magnitude in dependence on light conditions in the canopy (Harley et al. 1996, 1997; Niinemets et al. 2002a, 2010b; Grote 2007), suggesting that in turbulently mixed canopy air, low-emitting leaves could also constitute a sink of volatiles.

It has long been known that inorganic species in the atmosphere, such as ammonium (Farquhar et al. 1979, 1980), ozone (Laish et al. 1989) and SO$_2$ (Pfanz et al. 1987), can be rapidly deposited to vegetation (Wesely 1989). Laboratory experiments on individual leaves clearly illustrate the potential for bidirectional fluxes of a variety of BVOC, including short-chained aldehydes (Kesselmeier 2001; Rottenberger et al. 2004, 2005; Karl et al. 2005) and organic acids (Kesselmeier 2001; Kuhn et al. 2002), but uptake of larger alkenes such as monoterpenes (Copolovici et al. 2005; Noe et al. 2008) has also been observed. Furthermore, large canopy-scale BVOC deposition fluxes have recently been highlighted (Karl et al. 2010; Jardine et al. 2011; Park et al. 2013a,b), implying that the bidirectional exchange of volatiles is much more important than generally thought.

Recent evidence further suggests that the assumption of a non-reactive diffusion pathway from the site of synthesis and/or volatilization to the ambient atmosphere is not necessarily valid. Under oxidative stress, a large proportion of reactive isoprenoids might be oxidized along the diffusion pathway, generating volatile molecules previously thought to be found only in the atmosphere as a result of oxidative reactions (Jardine et al. 2012b, 2013). Thus, in addition to the rate of synthesis, within-leaf redox environment may importantly modulate the emission flux of reactive molecules.

This review analyses the recent evidence on within-leaf reactivity of volatiles, bidirectional emission controls and the significance of the ‘non-inert’ performance of BVOC at different scales of biological organization from cells to ecosystems. Firstly, we provide the basic framework of biophysical and physiological emission flux controls of different volatile compounds, and further analyse the importance of within-leaf redox environment on BVOC within-leaf reactivity. We then review the existing evidence on bidirectional emissions, the bidirectional emission controls and finally evaluate the significance of such controls at scales ranging from leaf to ecosystems. Overall, we emphasize the need to revise the concept of BVOC emission to include the enzymatic and non-enzymatic reactions of BVOC in planta and to include physicochemical controls on emission, storage, uptake and deposition. This review emphasizes the fundamentally different set of controls operating on the emission and uptake of non-oxygenated lipophilic volatiles, and oxygenated water-soluble volatiles, but also underscores that within-leaf and within-canopy reactions can oxidize a large part of non-oxygenated volatiles before they reach the leaf, canopy and atmospheric boundary layers.

**BASICS OF EMISSION OF VOLATILES: FROM UNIDIRECTIONAL TO BIDIRECTIONAL FLUX**

**Steady-state emission responses**

Except for those BVOCs that are stored in surface glands or trichomes and may escape directly to the atmosphere, exchange of plant-produced volatiles with the atmosphere occurs through the stomata (Fall & Monson 1992; Loreto et al. 1996; Städler & Reifenrath 2009). As cuticular conductances are low for most volatiles, cuticular emission flux can be neglected apart from conditions when stomata are closed (see also the section Deposition on surface for the discussion on surface deposition flux). The exchange of BVOC between plants and the atmosphere therefore obeys Fick’s first law, and the flux of a given BVOC ($J$, mol m$^{-2}$ s$^{-1}$) is directly proportional to the difference in BVOC gas phase concentration (or partial pressure or mole fraction) between the intercellular air space of the leaf (in the sub-stomatal cavity) and the air outside the leaf boundary layer, and inversely proportional to the sum of the resistances between them. Assuming little or no flux across the leaf cuticle, and assuming a low resistance across the leaf boundary layer, a reasonable assumption even at moderate wind speeds, this resistance pathway is dominated by the stomata, and

$$J_i = (X_{i,l} - X_{i,a})/r_{s,i} = (X_{i,l} - X_{i,a})g_{s,i},$$

where $X_{i,l}$ is the mole fraction of the given BVOC $i$ in the intercellular air space of the leaf and $X_{i,a}$ that in the ambient air (both in mol mol$^{-1}$), and $g_{s,i}$ is the stomatal conductance of the given volatile (mol m$^{-2}$ s$^{-1}$), whereas the inverse ($r_{s,i}$) is the stomatal resistance to the BVOC. For simplicity, Eqn 1 ignores the effect of mass flow of water vapour on the exchange flux (e.g. Ball 1987). The mass flow effect is generally relatively small and we refer to past studies for a full treatment of fluxes (e.g. Niinemets & Reichstein 2003a,b; Niinemets et al. 2011).

The stomatal conductance of any BVOC molecule can be conveniently linked to the stomatal conductance of water vapour ($g_w$) as

$$g_{s,i} = g_wD_{s,i}/D_{s,w},$$

where $D_{s,w}$ is the binary (air/water vapour) diffusion coefficient for water vapour and $D_{s,i}$ is that for the given volatile. Diffusivities of different volatiles are tabulated in chemical reference databases (e.g. Lugg 1968; Marrero & Mason 1972) but are still lacking for many plant volatiles. However, diffusivities at different temperatures can be predicted with minor errors using structure–function relationships, for example, based upon the predicted molar volumes (e.g. Niinemets & Reichstein 2003b). In fact, the ratio $D_{s,i}/D_{s,w}$ varies little with temperature for many volatiles (e.g. for isoprene, see Singsaas et al. 1997; Sun et al. 2013).

Whether or not a given BVOC is emitted or taken up at any given moment of time depends upon the direction of the concentration gradient, $X_{i,l} - X_{i,a}$, between the leaf intercellular air space and the ambient air. When $X_{i,l} = X_{i,a}$, there is no net flux and this concentration is known as the
chemo sources and sinks

Equation 1 indicates that at a given ambient BVOC concentration, the direction and the magnitude of the exchange are driven by BVOC source strength, which is given by the net rate of BVOC production within the leaf (i.e. the rate of production minus the rate of further metabolism). For some compounds, chemical conversion of the given compound into other metabolites has long been recognized, such as foliar conversion of ethanol transported from roots of flooded plants to acetaldehyde (Kreuzwieser et al. 1999, 2001; Kreuzwieser & Rennenberg 2013). However, for some other compounds such as isoprene, the rate of metabolism has been considered negligible until recently (Jardine et al. 2012b, 2013). In light of new evidence, within-leaf reactivity can have a major effect on X_u and thus the source strength of most volatiles. Furthermore, any atmospheric volatile that does not have a source within the leaf, including many anthropogenic volatiles and the whole range of products arising from BVOC oxidation, can be taken up by the leaves provided the compound can be metabolized (or go into solution). Understanding the capacity for BVOC degradation, metabolism and/or storage in the apoplastic and in the symplast is highly relevant as this capacity is a key factor that determines the BVOC compensation point.

Because the emission of a given BVOC has essentially no effect on the atmospheric concentration outside the leaf boundary layer, at least in turbulent conditions and over the timescale of minutes to hours, the emission can be sustained as long as the production continues and the within-leaf gas phase concentration exceeds the atmospheric concentration. Uptake, on the contrary, will cease as soon as an equilibrium is reached and the concentrations inside and outside the leaf reach the same value (X_comp). The fact that continuous uptake is frequently observed (e.g. Copolovici et al. 2005; Fowler et al. 2009; Stimler et al. 2010; Jardine et al. 2011; Stimler et al. 2011; Sandoval-Soto et al. 2012; Park et al. 2013a,b) therefore suggests the presence of significant sinks for BVOC within the leaves. In the case of inorganic atmospheric constituents such as O_3, which can diffuse through the stomata, it is clear that this highly reactive molecule is rapidly reduced upon contact with cellular metabolites or surface structures such that the concentration of O_3 within the leaf can be close to zero (Laisk et al. 1989), or is very low when atmospheric concentrations are high (Moldau & Bichele 2002; Loreto & Fares 2007). When the internal concentration is zero or very low, the rate of uptake is controlled primarily by stomatal conductance and the ambient concentration.

Until recently, all models of BVOC deposition assumed that, unlike O_3, BVOCs were largely non-reactive in plants. However, new evidence demonstrates that there are chemical BVOC sinks inside leaves such that, after entering the leaf, the compounds are rapidly metabolized, thereby maintaining a concentration gradient sufficient to drive the deposition flux (e.g. Copolovici et al. 2005; Stimler et al. 2010, 2011; Sandoval-Soto et al. 2012). The nature and magnitude of these enzymatic and non-enzymatic BVOC sinks within the leaf will vary for a given BVOC and with changing

compensation point (X_{comp}; Fig. 1). If the atmospheric concentration exceeds X_{comp}, uptake will occur, whereas when the within-leaf concentration is above the compensation point, emission results (Fig. 1).

In the literature, there often seems to be some misunderstanding about stomatal controls on volatile exchange. Stomata can sometimes control the emission rate under non-steady-state conditions (section Stomatal controls on emission), but we want to emphasize that when uptake occurs through the stomata, stomata will always control the deposition flux, even if the internal concentration X_u is zero. Such a dependence upon stomatal conductance has been demonstrated for numerous volatiles, including formaldehyde (Filella et al. 2006; Seco et al. 2008), acetone, acetonitrile, acrolein, methyl ethyl ketone (MEK), isobutyl methyl ketone (IBMK), chloroform, and benzene (Omasa et al. 2000), acetaldehyde (Cojocariu et al. 2004; Karl et al. 2005), methyl vinyl ketone (MVK), methacrolein (MACR) and croton aldehyde (Tani et al. 2010).

The strength of the stomatal control on uptake of different compounds depends upon the diffusivity of the given compound according to Eqn 2. When there is no apparent stomatal control over uptake, the emissions may be driven by deposition on leaf surfaces rather than by stomatal uptake (section Deposition on surface). As pointed out below, stomatal control on emission is more complex and is driven by different mechanisms.

Figure 1. Schematic illustration of the potential for bidirectional flux in three hypothetical situations. Curves (A) and (B) represent two leaves with similar rates of biogenic volatile organic compound (BVOC) production but different values of stomatal conductance, indicated by the different slopes. The balance between production and catabolism is such that they can maintain a gas phase concentration of 6 nmol mol⁻¹. When the BVOC ambient concentration exceeds 6 nmol mol⁻¹, the BVOC will be taken up by the leaf, and when the ambient concentration falls below 6 nmol mol⁻¹, emission will occur. The value of 6 nmol mol⁻¹, at which there is no net flux, is referred to as the compensation point. Curve (C) represents a case in which the stomatal conductance is identical to curve (A) but the net production of BVOC is much higher, resulting in a higher compensation point and a greater likelihood of emission over deposition.
environment, for example, light, temperature and stress level (see the section **Heterogeneity of biochemical sources and sinks and implications for the emission controls**).

**Stomatal controls on emission**

Although the compound uptake rate always depends upon stomatal conductance, Eqn 1 seems to suggest that the emission rate is also proportional to stomatal conductance. However, stomata can only control the emission flux when the within-leaf gas phase volatile mole fraction \(X_{il}\) is independent of stomatal conductance. When stomatal conductance decreases, \(X_{il} \rightarrow X_{ai}\) increases, balancing the reduction in \(g_{ai}\), such that in the steady state, stomata cannot limit the emission flux, provided the build-up of the volatile concentration does not inhibit its own synthesis rate (Niinemets & Reichstein 2003b; Harley 2013). It has been demonstrated that emission rates of isoprene (Fall & Monson 1992) and monoterpenes (Loreto et al. 1996) are independent of stomatal conductance. However, the rate of emission of oxidized compounds such as methanol (Nemecek-Marshall et al. 1995; Harley et al. 2007; Hüve et al. 2007) is reduced by stomatal closure. This enigmatic behaviour has been explained by the differences in compound physicochemical characteristics (Niinemets & Reichstein 2003b; Harley 2013), particularly by differences in compound equilibrium gas/liquid phase partition coefficient, the Henry’s law constant \(H_{pc}\) (Staudinger & Roberts 2001). The equilibrium gas phase concentration of a given compound is given as

\[
X_{il} = C_u H_{pc} / p,
\]

where \(C_u\) is the compound aqueous phase concentration (mol m\(^{-3}\)) and \(p\) is the air pressure (Pa). Compounds with a high \(H_{pc}\) support high gas phase concentration at a given liquid phase concentration, whereas compounds with low solubility (low \(H_{lc}\)) support a low gas phase concentration. Gas phase concentration of isoprene with a high \(H_{pc}\) of 7780 Pa m\(^3\) mol\(^{-1}\) at 25°C (Niinemets & Reichstein 2003b), that is, with a low solubility, increases essentially immediately, within seconds, after a change in stomatal conductance, and as a result, increases in \(X_{il} \rightarrow X_{ai}\) fully balance any change in stomatal conductance, maintaining the flux. However, methanol with a \(H_{pc}\) of only 0.46 Pa m\(^3\) mol\(^{-1}\) has four orders of magnitude greater aqueous phase solubility, and thus, gas phase concentrations increase much more slowly after reductions in stomatal conductance, resulting in temporary limitations of the emission flux that may last for up to several hours (Niinemets & Reichstein 2003b; Harley 2013). Thus, dissolution of compounds in the leaf water effectively uncouples the rate of emission of highly soluble compounds from their rate of production and allows stomata to control their flux in non-steady-state situations. In addition to methanol (Nemecek-Marshall et al. 1995; Geron et al. 2006; Harley et al. 2007; Hüve et al. 2007), such transient reductions of emission rates have been observed for a number of oxygenated compounds with low \(H_{pc}\) such as acetic acid (Gabriel et al. 1999), formaldehyde (Seco et al. 2008), linalool (Niinemets et al. 2002b) and methylbutenol (P. C. Harley, unpublished data).

However, it is important to recognize that even if stomata can limit the emission rate, the emission control is shared between the stomata and the rates of compound production and consumption (Jardine et al. 2008 for non-stomatal controls on acetaldehyde emission). Under exceptional circumstances such as in ozone-fumigated leaves, stomata actually close, but huge bursts of methanol are mainly driven by a rapid increase in methanol synthesis rate as the result of stress-dependent activation of pectin methyltransferases (Beauchamp et al. 2005). Thus, temporal dynamics in the emissions of oxygenated volatiles need to be carefully examined, ideally using dynamic models, to gain insight into the stomatal and non-stomatal factors altering the emission rate.

**Physicochemical sinks and sources**

From the perspective of compound uptake, the presence of a certain capacity for compound within-leaf storage is a physicochemical sink that helps sustain lower values of \(X_{il}\) and thus reduces the rate with which \(X_{il} \rightarrow X_{ai}\) approaches 0. This way deposition flux can be maintained when the compound ambient concentrations are relatively high (Omasa et al. 2000; Trapp & Karlson 2001; Copolovic et al. 2005). Thus, although the diffusion gradient, \(X_{il} \rightarrow X_{ai}\), ultimately will reach zero for compounds that are not metabolized within the leaf, this can take a very long time, depending upon the effective size of the ‘physicochemical’ storage pool.

In addition to the leaf liquid phase that can store watersoluble compounds, hydrophobic compounds can be sequestered in the leaf lipid phase (e.g. Niinemets & Reichstein 2002; Copolovic et al. 2005; Noe et al. 2010) with similar impacts on bidirectional fluxes. For example, Noe et al. (2008) demonstrated that several species of plants exposed to high concentrations of limonene were able to take up limonene from the surrounding air. The magnitude of the uptake was strongly correlated with the lipid content of the leaves, suggesting that limonene was being removed via dissolution into the lipid phase.

The capacity of the compound storage in the leaf lipophilic phase is often characterized by the compound octanol/water partition coefficient \(K_{ow}\), which is typically low for OVOC and high for non-substituted isoprenoids, although isoprene has a relatively low \(K_{ow}\) value (e.g. Copolovic & Niinemets 2005). Ultimately, the effective size of the storage depends upon the characteristics of the compound \((H_{pc} \text{ and } K_{ow})\) and the size of the leaf gas, liquid and lipid phase pools (Kirschbaum et al. 2007; Niinemets et al. 2011 for pertinent calculations).

Historically, Wesely (1989) recognized that dissolution of volatiles could represent a significant sink and lead to sustained deposition fluxes. However, he was concerned primarily with liquid water on surfaces or extracellular water in the sub-stomatal cavities. Furthermore, studies investigating the uptake of volatile and semi-volatile pollutants have defined the leaf bioconcentration factor \((F_m, \text{ leaf/gas phase})\).
partition coefficient) as the ratio of the compound concentration in the leaves ($C_{l}$) relative to that in the gas phase [mol m$^{-3}$ leaf (mol m$^{-3}$ air)$^{-1}$] (Simonich & Hites 1994; Hiatt 1998, 1999; Bakker 2000; Steyaert et al. 2009). Thus, analogous to Eqn 3, gas phase concentration can be expressed as

$$X_{i,l} = C_{i}/F_{i,ow}$$

(4)

The bioconcentration of a given compound depends upon its partitioning between leaf lipid and aqueous fractions, that is, on compound $K_{ow}$ and $K_{pc}$ values and on corresponding leaf volume fractions (Trapp et al. 1990). Typically, bioconcentration of persistent volatile and semi-volatile pollutants is strongly driven by partitioning to lipid phase such that there is a strong correlation between $F_{b}$ and $K_{ow}$ (Simonich & Hites 1994; McLachlan 1996; Hiatt 1998, 1999; Bakker 2000; Tao & Hornbuckle 2001) as well as correlation of $F_{b}$ with leaf lipid fraction (Simonich & Hites 1994; McLachlan 1996; Bakker 2000). Bioconcentration factors for many important volatile and semi-volatile pollutants have been determined and used in predicting the deposition flux (Hiatt 1998, 1999; Bakker 2000 for a review; Steyaert et al. 2009), but we argue that the concept coming from pollution research is of value for predicting emission and deposition kinetics of key BVOC as well.

In practice, whether the uptake flux is maintained due to the presence of a chemical sink or a physicochemical sink is not always obvious as the effect of a large physicochemical sink on the emission kinetics can be similar to that of a chemical sink. In fact, for a large physicochemical sink, the condition $X_{i,l} = X_{i,a}$ might be reached so slowly that there is no experimental evidence of reaching an equilibrium during the measurements. For instance, it has been demonstrated that for some persistent chlorinated hydrocarbons, it can take years to reach equilibrium with leaves (Jensen et al. 1992). However, the principal difference between a chemical and physicochemical sink is that physicochemically stored volatiles might be re-released upon increases in temperature (or increases in stomatal conductance for some compounds), whereas this is not the case for a chemical sink that permanently consumes molecules.

Another important difference among chemical and physicochemical sinks is how the sink strength changes with environmental conditions. Although the strength of a biochemical sink can depend upon any environmental driver that can modify the pathway flux rate, physicochemical sink strength depends upon compound physicochemical properties that determine compound volatility (partitioning coefficients) and diffusivity. Both the partitioning coefficients and the diffusivity depend upon temperature. For dissociable compounds such as organic acids, the physicochemical sink strength also depends upon pH in the given cellular or extracellular compartment. This is because for the liquid/gas phase equilibrium, only the concentration of the non-dissociated form matters, and accordingly, the apparent Henry’s law constant decreases exponentially with increasing pH (Niinemets et al. 2011). Although temperature can affect the strength of both the physicochemical and the chemical sinks, the effects are different. Temperature typically increases the rate of enzymatic processes up to the optimum temperature, and the rates decrease thereafter. In contrast, the rate of non-enzymatic, free-radical processes increases monotonically with increasing temperature. Analogously, compound volatility increases monotonically with increasing temperature, and thus, the physicochemical sink strength decreases with increasing temperature. These differences among temperature responses of biochemical and chemical and physicochemical processes can provide important insight into interpreting the processes driving bidirectional exchange in the field.

**Deposition onto and release from leaf surface**

Although stomatal uptake is a major sink for BVOC in leaves, hydrophobic BVOC and especially hydrophobic semivolatiles can adsorb directly onto the cuticle as a result of gas phase (dry) deposition (Bakker 2000; Riederer et al. 2002; Keyte et al. 2009; Burkhardt & Pariyar 2014). Diffusion of volatile and semi-volatile BVOC molecules into the cuticle and through the cuticle into the leaf can also occur (Bakker 2000; Keyte et al. 2009). However, the rate of diffusion into the cuticle is typically slow, especially for large BVOC and semi-volatile molecules and when the crystalline phase of the cuticle is high (Bakker 2000). Nevertheless, when stomatal conductance is low, uptake of hydrophobic compounds through the cuticle can be significant (Riederer et al. 2002; Keyte et al. 2009), and the rate of cuticular diffusion can be importantly enhanced by cuticular damage or modifications, for example, by salty aerosols (Burkhardt & Pariyar 2014).

What are the implications of potential cuticular exchange for plant BVOC? Characteristic plant hydrophobic BVOC such as mono- and sesquiterpenes can significantly adsorb onto and diffuse into cuticles and dissolve in the amorphous cuticle phase (Schmid et al. 1992). In fact, analysis of cuticles has demonstrated the presence of many BVOC including mono- and sesquiterpenes and their derivatives (Estell et al. 1994a,b). Recently, Himanen et al. (2010) demonstrated that leaves of birch (Betula) can take up and release semivolatiles from neighbouring plants and suggested that this process is driven by cuticular deposition. Thus, the cuticular exchange of hydrophobic BVOC seems to be a general phenomenon and clearly needs further experimental work to assess its importance.

Although predominantly hydrophobic, there can be hydrophilic regions on the leaf surface. In particular, aqueous cuticular pores can occur over anticlinal cell walls, in cuticular ledges and at the base of trichomes (Schönherr 2006). Furthermore, the outer guard cell surface is often hydrophilic, especially once subject to damage by abrasion or acidic deposition (Burkhardt & Eiden 1990; Burkhardt et al. 1999; Burkhardt & Pariyar 2014). Water-soluble volatiles can be exchanged through the aqueous pores and can also dissolve in water condensed on hydrophilic leaf regions. In fact, for short-chained OVOC, it has been demonstrated that cuticular deposition might be important during the dry season when stomatal conductance is low (Rottenberger et al. 2004).
However, dissolution of BVOC on leaf surface cannot serve as a long-term sink for BVOC. Compounds dissolved in the surface water will inevitably re-volatilize with the evaporation of dew or rain water, and the initiation of vertical transport driven by wind turbulence. Such ‘outgassing’ of volatiles from liquid water on leaf surface has been suggested to be responsible for the rapid increases in emission of oxygenated volatiles such as methanol in the morning (MacDonald & Fall 1993; Nemecek-Marshall et al. 1995), although the enhanced emission of these volatiles is also compatible with relaxation of stomatal controls on emissions in the morning when stomata open (Niinemets & Reichstein 2003b; Harley et al. 2007; Harley 2013). On the contrary, there is a plethora of epiphytic organisms living on leaf surface with bacteria being the most abundant group (Hirano & Upper 2000; Papen et al. 2002; Lindow & Brandl 2003; Redford et al. 2010). Methylo trophic bacteria on leaves are known to metabolize methanol produced by the host (Abanda-Nkpwatt et al. 2006). From a BVOC exchange point of view, these bacteria serve as a sink for methanol in the atmosphere, sustaining deposition to surfaces (Fall & Benson 1996). Depending upon bacterial populations on the leaves, many additional BVOC molecules could be consumed by foliar bacteria, potentially importantly contributing to BVOC exchange.

Overall, deposition and release of compounds from leaf surfaces are expected to be governed mainly by compound and cuticle physicochemical characteristics, and cuticular structure as well as by temperature. Thus, modelling such transfer processes might seem simple. However, there is a large variation in cuticular structural and chemical characteristics among species (Schreiber & Riederer 1996a,b) introducing important complications in modelling surface exchange. Furthermore, potential involvement of bacteria in surface exchange would imply that biological control mechanisms could exert an important control on surface BVOC exchange as well.

**HETEROGENEITY OF BIOCHEMICAL SOURCES AND SINKS AND IMPLICATIONS FOR THE EMISSION CONTROLS**

The previous section highlighted the fundamentals of BVOC emission and deposition fluxes in dependence on ambient and within-leaf concentrations, stomatal openness and strengths of sources and sinks. In particular, evidence for these sinks, resulting from BVOC metabolism or BVOC dissolution into the aqueous or lipid phases, has accumulated in recent years. Although simple principles govern volatile exchange between plants and atmosphere, complicated emission patterns can result from the huge physicochemical diversity of plant-emitted volatiles as well as from pathway heterogeneities that determine what compounds are being formed, when the various metabolic routes are activated, to which degree they are activated, and whether and when they are deactivated (Niinemets et al. 2004; Grote et al. 2013). These variations determine the strengths of sinks and sources, compound residence times within the leaves and probabilities of compound reaction within the leaves at different times during the day and in different locations in vegetation (Figs 2 & 3).

**Biochemical source heterogeneity**

Different pathways with contrasting regulatory mechanisms are responsible for the production of different classes of volatiles (for recent reviews on volatile production, see Li & Sharkey 2013; Monson 2013; Rajabi Memari et al. 2013). The rate of volatile isoprenoid synthesis in constitutively emitting species is often tightly linked to photosynthetic metabolism, and therefore, the emissions primarily respond to light and temperature, similarly to photosynthesis (for reviews, see Niinemets et al. 2010c; Grote et al. 2013; Li & Sharkey 2013; Niinemets et al. 2013a). The emissions also respond to CO₂ concentration, although often differently from photosynthesis (Niinemets et al. 2010c; Sun et al. 2012b; Grote et al. 2013; Li & Sharkey 2013). However, the rates of synthesis and emissions of monoterpenes and sesquiterpenes stored in specialized storage organs are typically uncoupled and not linked to photosynthetic metabolism (Kesselmeier & Staadt 1999; Niinemets et al. 2004, 2010c), although there may be a significant plasticity of environmental responses of storage
emissions, for example, during the season (Tarvainen et al. 2005; Holzinger et al. 2006). Finally, all plant species emit inducible volatile isoprenoids under stress conditions, often in light- and temperature-dependent manner (Paré & Tumlinson 1997; Hansen & Seufert 2003; Kask et al. 2013; Niinemets et al. 2013b).

Oxgenated volatiles are produced by multiple metabolic pathways. Only oxidized isoprenoids such as methylbutenol that is constitutively emitted similarly to isoprene in several pine species (e.g. Harley et al. 1998; Gray et al. 2003; Gray et al. 2011) and oxygenated monoterpenes such as linalool and 1,8-cineole that are classical components of induced emission mixtures (Paré & Tumlinson 1997; Niinemets et al. 2002b, 2010a) can be directly associated with photosynthetic metabolism. In fact, oxygenated volatiles are often by-products of central metabolic processes such as degradation of cell walls and turnover of cellular metabolites (for a review, see Seco et al. 2007). The rates of synthesis of these OVOCs can dramatically increase during specific developmental stages. For example, methanol emissions from cell walls in growing leaves reflect chemical transformations during relaxation and rigidification of cell walls in expanding tissues (Fall 2003; Hűve et al. 2007).

OVOC production can also drastically increase in response to a variety of stresses. Emissions of some stress-induced OVOC are associated with specific stresses. For example, acetaldehyde, ethanol and acetic acid emissions in flooded trees are indicative of cytosolic fermentation processes primarily in roots and the biosynthesis of acetyl-CoA (Jardine et al. 2010b, 2012a; Kreuzwieser & Rennenberg 2013). In general, this alternate route of acetyl-CoA production in various plant organs in response to different environmental cues is therefore tightly linked with the enzymatic production and consumption of these OVOC (Jardine et al. 2010b, 2012a).

Several ubiquitous stress pathways, associated with ROS formation, in particular the oxylipin pathway (Appendix), further lead to emission of a large number of OVOC (Seco et al. 2007 for a review of OVOC). Both enzymatic and non-enzymatic mechanisms can lead to the formation of characteristic fatty acid peroxidation biomarkers that may be detectable as gas phase emissions from plant tissues under stress (Appendix). Fatty acid peroxidation reactions produce a large array of volatile oxylipins that can be classified into distinct structural groups including alkanes (e.g. propanal, butanal, pentanal, hexanal), 2-alkenals (e.g. 2-propenal, 2-butenal, 2-pentenal, 2-hexenal), furans and furanones (e.g. tetrahydrofuran, 2-ethyl furan) and dicarbonyls (e.g. malondialdehyde, glyoxal, methyl glyoxal and diacetyl) (Matsui et al. 2010). In addition, the enzymatic peroxidation of plant fatty acids by lipoxygenase enzymes can lead to the formation and emission of characteristic oxidation products known as green leaf volatiles (GLVs) via the lipoxygenase pathway (Hatanaka 1993; Fall et al. 1999; Loreto & Schnitzler 2010). In this pathway, the formation of the classic C6 GLV in plants is initiated by the ubiquitous type 2 lipoxygenases (13-LOX) in chloroplasts that catalyse the oxygenation of α-linolenic acid (the dominant fatty acid in the aerial tissues of most plants) to form 13-hydroperoxy linolenic acid (HPLA) (Andreou & Feusner 2009). HPLA can be degraded by hydroperoxide lyase to form the primary GLV (Z)-3-hexenal, which is then reduced and acetylated to form the corresponding alcohol (Z)-3-hexen-1-ol and acetate ester (Z)-3-hexen-1-yl acetate (D’Auria et al. 2007).

Release of multiple classes of OVOC such as GLV, methanol, acetaldehyde and acetone from plants has been documented during processes known to be associated with ROS accumulation including programmed cell death during senescence (de Gouw et al. 1999; Holopainen et al. 2010; Sun et al. 2012a), and a wide variety of biotic and abiotic stresses including pathogen attack (Jansen et al. 2009; Toome et al. 2010), high ambient ozone concentrations (Heiden et al. 2003; Beauchamp et al. 2005; Cojocariu et al. 2005), herbivory (Arimura et al. 2009; Copolovici et al. 2011), desiccation (de Gouw et al. 2000), high light and temperature (Loreto et al. 2006; Copolovici et al. 2012), mechanical wounding (Fall et al. 1999; Karl et al. 2001; Loreto et al. 2006; Brilli et al. 2011) and freeze-thaw events (Fall et al. 2001). In addition, acids such as formic and acetic acid can also be emitted as a result of intercellular and often non-enzymatic degradations of carbohydrate and fats (Kesselmeier et al. 1998; Kesselmeier & Staudt 1999; Staudt et al. 2000).

Different from compounds produced in situ, the source strength of compounds transported from other organs can...
also be driven by the rate of compound transport. Such effects are important for flooding-driven emissions when ethanol produced in the roots is transported to the leaves and oxidized to the more volatile acetaldehyde (Kreuzwieser & Rennenberg 2013). Thus, acetaldehyde source strength in flooded trees is often driven by ethanol transport rate (Kreuzwieser et al. 1999, 2001; Cojocaru et al. 2004). Within-leaf production of acetaldehyde has also been recently discussed in the context of a pyruvate overflow hypothesis supporting acetyl-CoA production as a part of the pyruvate dehydrogenase bypass system (Jardine et al. 2010b, 2012a).

This huge heterogeneity of emission pathways including distinct tissue localization has important implications for the bidirectional emission controls. In particular, synchronization or non-synchronization of the timing of physiological changes in stomatal conductance and rates of formation of volatiles affect the pool size of volatiles. Differences in pool size imply modification in the compound residence times, which, in turn, will alter the rate of secondary within-leaf chemical reactions. In addition, changes in BVOC sink/source strengths also imply modifications in the compensation point of the volatiles. Complex kinetics of volatiles including oscillations and emission bursts have been observed, reflecting asynchronous rates of various key physiological processes (e.g. Beauchamp et al. 2005; Harley et al. 2007; Hüve et al. 2007). There might be an urge to link these emission kinetics immediately to the rate of compound synthesis. However, under inherently non-steady-state conditions, dynamic emission models are needed to deconvolute different physiological and physicochemical emission controls (Niinemets et al. 2004).

Chemical sink heterogeneity
The nature of the chemical sinks for oxygenated volatiles

Once produced or taken up, many oxygenated volatiles can enter into catabolic pathways, potentially leading to their complete oxidation to CO$_2$ (Oikawa & Lerdau 2013), but they may also be integrated into anabolic pathways involved in the biosynthesis of biologically relevant molecules. Although not all catabolic and anabolic pathways for different volatiles have been fully resolved, metabolism of volatile biogenic molecules can be an important carbon source for the plant such that evolution of novel biochemical pathways for consumption of volatiles clearly does contribute to plant survival (Oikawa & Lerdau 2013).

The metabolism including C$_3$ OVOC is well understood, and pathways involving ethanol, acetaldehyde and acetic acid are constitutively active in leaves and are further up-regulated under certain stress conditions such as flooding (Kreuzwieser et al. 1999; Kreuzwieser & Rennenberg 2013). Ultimately, C$_3$ OVOC can be converted to acetyl-CoA and enter primary metabolism or catabolized to CO$_2$. In contrast, the pathways responsible for C$_1$ OVOC consumption, particularly methanol reactions, are less well understood. It was recently shown that methanol can be directly acetylated by acetyl-CoA to produce the OVOC methyl acetate (Jardine et al. 2014). Formic acid can participate in the transfer of methyl and hydroxymethyl groups for the synthesis of other molecules (Kesselmeier & Staudt 1999; Kuhn et al. 2002) or oxidized to CO$_2$ in the mitochondria (Igamberdiev et al. 1999; Hanson & Roje 2001). Achkor et al. (2003) reported detoxification of formaldehyde by glutathione-dependent formaldehyde dehydrogenase (FALDH) in Arabidopsis.

Carbonyl sulphide (COS), a C$_3$ molecule, although oxygen-containing, is seldom considered together with other OVOC, but there is a strong chemical sink of COS inside leaves. This sink is dominated by carbonic anhydrase-driven reactions and to a lesser extent by ribulose 1,5-carboxylase/oxygenase (Rubisco)-driven reactions (Stimler et al. 2010) such that the atmospheric compensation point for COS is often very low (Kesselmeier & Merk 1993; Xu et al. 2002; Stimler et al. 2010, 2011; Sandoval-Soto et al. 2012).

Involvement of cytochrome P-450-dependent oxidases and glutathione-S-transferases (GSTS) has been postulated in detoxification of a variety of oxygenated and non-oxygenated BVOC molecules (Trapp & Karlson 2001). In addition, aldehyde dehydrogenase (ALDH) protein superfamily of nicotinamide adenine dinucleotide phosphate (NADP$^+$)-dependent enzymes, together with peroxidase families, can oxidize a wide range of aldehydes by oxidizing these to their corresponding carboxylic acids (Kirch et al. 2004). Non-enzymatic reactions involving reactive oxygen species (ROS) (Appendix) can also play a role for conversion of OVOC species with double bonds. Thus, a large number of metabolic and oxidative pathways can serve as important chemical sinks within the leaves.

Furthermore, the activity of oxidative pathways can be strongly enhanced under oxidative stress conditions induced by exposure to pollutants such as ozone or exposure to high temperatures (Karl et al. 2010). In fact, OVOC is taken up from the ambient atmosphere both under non-stressed and stressed conditions, but both apoplastic and symplastic concentrations of OVOC, particularly the concentrations of oxidation products of isoprene, MVK and MACR, are strongly reduced under stress (Karl et al. 2010). Similar behaviour is expected for oxidation products of monoterpenes and OVOC such as hydroxyacetone, glycolaldehyde, C$_5$ carboxyls and nopinone.

As noted earlier, chemical sinks and physicochemical storage (in leaf lipid and aqueous phases) cannot always be conclusively separated as leaves can support large equilibrium pools for many oxygenated volatiles (Niinemets & Reichstein 2003a,b). Thus, the pertinent question is to what extent physicochemical sinks contribute to the uptake of OVOC. In fact, within-leaf OVOC concentrations have seldom been estimated. Tani & Hewitt (2009) found that the total foliar uptake of aldehydes and ketones by a range of houseplants was 30–100 times greater than the amount dissolved in the leaves, suggesting that fast scavenging of these aldehydes is the primary sink maintaining the uptake flux. In another study, Tani et al. (2010) observed that MACR is taken up at a faster rate than MVK, and intercellular MACR concentration is lower than that for MVK. Given that the Henry’s law constant is actually larger for MACR
(15.6 Pa m⁻² mol⁻¹ at 25 °C) than for MVK (2.5 Pa m⁻² mol⁻¹ at 25 °C) (Iraci et al. 1999), this evidence suggests that the differences in the uptake rates are driven by greater within-leaf chemical scavenging of MACR rather than by differences in physicochemical sink strength.

**Chemical sinks for non-oxygenated volatiles**

Because of its high vapour pressure, isoprene exists as a gas under normal physiological conditions and can therefore escape plants and enter the surrounding atmosphere. This process occurs to such a large magnitude that terrestrial isoprene emissions account for an estimated one-third of global volatile organic compound emissions from all natural and human sources combined (Guenther et al. 1995, 2012). Although past research has highlighted the role of isoprene in the protection of photosynthesis during abiotic stress, the mechanisms still remain unclear. Nonetheless, a growing body of evidence suggests that isoprene safeguards plants under stress by functioning as an effective antioxidant (Vickers et al. 2009). In particular, isoprene protects the leaves against volatile oxidants from ambient air such as ozone (Loreto et al. 2001), and quenches nitrogen oxide (NO) in leaves followed by a decrease in isoprene emission and modification of the NO compensation point (Velikova et al. 2008). It has been argued for long that the oxidation of BVOC in leaves, especially under stress conditions, involves reactions with ROS generated by oxidative stress (Appendix; Loreto & Velikova 2001; Velikova et al. 2004, 2008). Recently, the first direct evidence that isoprene functions as an antioxidant by directly reacting with ROS was obtained by quantifying gas phase emissions of isoprene and its oxidation products MVK, MACR and 3-methyl furan from tropical (Jardine et al. 2012b, 2013) and desert (Jardine et al. 2010a) plants under abiotic stress. Increased emissions of isoprene oxidation products (£\textsubscript{\text{iso}}) relative to isoprene (£\textsubscript{i}) were stimulated by high temperature stress at the branch and ecosystem levels. \(^{13}\text{CO}_2\) and pyruvate-2-\(^{13}\text{C}\) leaf labelling showed a rapid incorporation of \(^{13}\text{C}\) into both isoprene and £\textsubscript{\text{iso}}, providing additional evidence for their production from isoprene peroxydation (Jardine et al. 2012b).

The evidence of chemical reactions of monoterpenes is scarce, but in Quercus ilex with fosmidomycin-inhibited monoterpen emission, the uptake of the reactive monoterpene \(\alpha\)-pinene increased with increasing temperature, whereas the uptake of the non-reactive \(\alpha\)-terpinene decreased with increasing temperature (Copolovici et al. 2005). Because the physicochemical gradient from ambient air to leaves decreases with increasing temperature due to greater volatility of terpenes, the increased \(\alpha\)-pinene uptake also suggests the presence of a chemical sink within the leaves (Copolovici et al. 2005).

In a similar fashion, exposure of photosynthetic microorganisms and vascular plants to photooxidative conditions resulted in the emission of volatile oxidation products of \(\beta\)-carotene, including the aldehyde \(\beta\)-cyclocitral and the ketone \(\beta\)-ionone (Walsh et al. 1998; Ramel et al. 2012). Similar to reactive electrophile species that mediate gene-level responses to ROS, including initiating the expression of an array of defence genes (Appendix), the biological activity of these isoprenoid peroxidation products is high (Havaux 2013). However, unlike \(\beta\)-carotene, which is tightly associated with pigment-binding complexes in photosynthetic membranes, isoprene and likely other volatile isoprenoids such as mono- and sesquiterpenes can freely diffuse through cell membranes where they can terminate fatty acid peroxidation chain reactions by oxidizing, diffusing away from the membrane, and either being emitted as an oxidation product to the atmosphere or being further metabolized (Appendix).

What is the implication of the findings of chemical sinks within the leaves for widespread volatiles such as isoprene that is produced at high rates between 20 and 100 nmol m⁻² s⁻¹ in isoprene-emitting plants? In emitting species, the concentrations in the intercellular air space (typically a few \(\mu\)mol mol⁻¹) far exceed the atmospheric concentrations (typically a few nmol mol⁻¹), and although a compensation point presumed exists, it is orders of magnitude above the ambient levels. Thus, the net flux of isoprene, at least during daytime, is from the leaf to the atmosphere in isoprene-emitting species. However, in the case of ‘non-emitting’ species, possible metabolism of isoprene within the leaf suggests that a deposition flux may be sustained, the rate of uptake being jointly determined by ambient concentrations, the rate of metabolism and the stomatal conductance.

The other important implication of oxidation of volatiles is that novel oxidized molecules with different physicochemical characteristics are generated, which can exhibit different exchange characteristics than the non-oxidized parent molecules. In particular, the emission rates of these volatiles can be modified by changes in stomatal conductance. Although the level of stomatal control over emissions is expected to be relatively weak for MACR and MVK owing to their moderate solubility, changes in stomatal conductance will still importantly alter the residence time of these compounds inside the leaves, thereby enhancing the probability of within-leaf metabolism. As several of the oxidation products of volatile isoprenoids are known to be toxic (Kai et al. 2012), a capacity for metabolization of these compounds is physiologically highly relevant.

**Variation of the BVOC compensation points: role of sinks, sources and environmental conditions**

Compensation point is an important concept of bidirectional exchange in atmospheric science and is widely employed in bidirectional exchange modelling as it allows for a convenient switch between emission and deposition (e.g. Pleim & Ran 2011). However, for plant/atmosphere exchange, there is a large uncertainty in compensation point values not only for different compounds but also for the very same compounds. For any given compound, variable compensation points for different plant species and for the same species under different conditions have been demonstrated in the literature. For example, Rottenberger et al. (2004) reported compensation points on the order of 0.6 nmol mol⁻¹ for acetaldehyde and formaldehyde for different Amazonian species, whereas Seco
et al. (2008) reported compensation points for formaldehyde of 20 nmol mol⁻¹ for the Mediterranean species *Q. ilex* and *Pinus halepensis*. Jardine et al. (2008) found different compensation points for acetaldehyde during light and dark periods for *Populus deltoides* and *Q. ilex* (Jardine et al. 2008), with the compensation points being much larger in the light than in the dark. In Rottenberger et al. (2004), there was a higher compensation point during dry versus wet season in tropical trees.

The reasons for such vast differences have been seldom addressed, and we argue that multiple factors can be responsible for changes in the compensation points (Figs 1 & 2). For ammonium, it has been demonstrated that differences in compensation points can reflect both physiological and physicochemical factors, but physicochemical factors, in particular, pH and temperature-dependent changes in its Henry’s law constant dominate modifications in the compensation point (Husted & Schjoerring 1996; Wang et al. 2013). For acetaldehyde emissions in *Pinus taeda*, Karl et al. (2005) observed that the compensation point increased exponentially with increasing leaf temperature. Temperature-dependent increase in the compensation point likely indicates enhanced within-leaf acetaldehyde source strength perhaps from cytosolic pyruvate (Karl et al. 2002a) and is also consistent with reduced physicochemical sink as acetaldehyde becomes increasingly volatile at higher temperatures. The evidence of a light-dependent increase in the acetaldehyde compensation point in the study of Jardine et al. (2008) further suggests that light-dependent changes in the source strength were driving the modifications in the compensation point (see Fig. 1 for theoretical calculations). On the contrary, in the Karl et al. (2005) study, the compensation point decreased after ozone fumigation, suggesting activation of an acetaldehyde chemical sink (e.g. activation of an aldehyde dehydrogenase) in this species. Interpretation of the seasonal changes and species differences in the compensation point is less clear-cut, although these differences might indicate environmentally driven seasonal and species differences in the sink/source strengths.

The evidence of a strong dependence of the compensation points on the sink strength highlights a major limitation of the compensation point concept as a basis for simulating bidirectional exchange. Owing to strong variations in sink/source strengths, compensation points will vary and assuming a fixed compensation point will lead to major bias in predicted emissions. In fact, using the available evidence of sink/source strength variations in dependence on environmental conditions within a simple modelling framework (Eqn 1), it becomes evident that the compensation points and the slopes of the relationships linking the ambient concentration to the flux rate should also vary during the day (Figs 1 & 2). Fitting daily and longer-term relationships of compound flux versus ambient concentration often results in highly scattered relationships (Cojocariu et al. 2004; Rottenberger et al. 2004, 2008; Karl et al. 2005; Seco et al. 2008; Graus et al. 2013). Thus, compensation points cannot be precisely derived from such relationships pooling multiple sources of variance. Therefore, compensation point estimates from regressions linking ambient concentration and flux rates over periods of time with fluctuating environmental conditions are potentially associated with large errors and inherent variability. These large variations likely reflect the key limitation that the compensation point is importantly driven by sink and source strengths that can vary due to inherent physiological regulation mechanisms characteristic to a given compound as well as due to non-enzymatic reactions and environmental controls on compound physicochemical characteristics. Although the use of compensation points has been successful for simulating bidirectional exchange kinetics for some compounds such as ammonium (Farquhar et al. 1980; Schjoerring et al. 1998; Fowler et al. 2009), we argue that it might be more appropriate to simulate the dynamics of BVOC sinks and sources rather than apply a given value of a compensation point in flux simulations. Bidirectional exchange models coupled to detailed measurements under different environmental conditions (e.g. Karl et al. 2005; Jardine et al. 2008) could be inverted to estimate the sink and source activities corresponding to any given value of the compensation point.

**BIDIRECTIONAL EXCHANGE AT THE CANOPY SCALE**

**How do canopies differ from leaves?**

Although the same principal chemical and physiological mechanisms operate at the leaf and canopy scales, canopies are characterized by strong variations in environmental characteristics (e.g. Niinemets 2007), differences in the proportion of constitutively emitting and non-emitting species, differences in the stress status of the trees and foliage at different positions in the canopy and variations in the concentrations of volatiles and oxidants (e.g. Noe et al. 2012). Thus, BVOC production rates and BVOC compensation points of leaves at different canopy positions may be expected to vary widely, complicating attempts to apply the compensation point methodology at the canopy scale. Indeed, the rates of BVOC exchange (Cojocariu et al. 2004; Niinemets et al. 2010b) and even the flux direction for oxidized volatiles (Cojocariu et al. 2004; Karl et al. 2004) can depend upon the foliage position within the canopy. Until recently, discrepancies between observed canopy fluxes and leaf-level fluxes have been attributed to within-canopy gas phase oxidation of leaf-released volatiles by atmospheric oxidants. However, evidence of within-leaf oxidation reactions of many volatiles has recently accumulated (see the section *Chemical sink heterogeneity*), raising the possibility that some volatiles released within the canopy may be taken up and oxidized by other leaves before exiting the canopy air space. Furthermore, oxidation reactions can take place in liquid and wax phases on the leaf surface. Although oxidation reactions may prove important both within and outside the leaf, differences in the suite of oxidizing species, physical phase (lipid, liquid, gas) of oxidation reactions and degree of volatile mixing imply that within-canopy and within-leaf oxidation processes may be very different.
The pertinent question is how increased understanding of leaf-level deposition processes can be used to improve our ability to understand and model canopy-level processes. Unravelling the controls at the canopy scale is further complicated by relatively sparse datasets and infrequent temporal data coverage, conventionally 30 min for micrometeorological techniques used for flux estimation (Karl et al. 2002b; Fares et al. 2012). Furthermore, flux measurements made at night, when deposition processes may predominate, are frequently unreliable because assumptions underlying the micrometeorological flux techniques are violated.

In fact, estimates of canopy-scale fluxes made by up-scaling fluxes measured with enclosures at leaf level often fail to agree with fluxes measured at ecosystem level with micrometeorological techniques. Bouvier-Brown et al. (2009) and Ciccioli et al. (1999) detected much lower fluxes of sesquiterpenes above plant canopies than predicted from branch enclosure measurements, revealing significant within-canopy losses of certain isoprenoids due to their high reactivity.

The situation is further complicated by the circumstance that canopy processes can differ for non-oxidized and oxidized molecules. In the ambient atmosphere, isoprenoids can react with ozone, and NO, and OH radicals (Atkinson & Arey 2003), with compound lifetimes ranging from a few seconds for some very reactive mono- and sesquiterpenes to a few hours for less reactive isoprenoids such as isoprene and α-pinene (for calculation of chemical lifetimes see, e.g. Arneth & Niinemets 2010; Holopainen et al. 2013). The reactive compounds can notably influence the oxidizing capacity and the ozone-forming potential of the atmosphere and the formation of secondary organic aerosol and contribute to the atmospheric source of OVOC (Andreae & Crutzen 1997; Fuentes et al. 2000). OVOCs have generally a longer lifetime in the atmosphere than non-saturated non-oxygenated volatiles, up to several days (e.g. acetone lifetime is 15 d). This means that they are retained longer and can be transported to greater distances from the emission source, where they can take part in photochemical reactions or be deposited (Goldstein & Galbally 2007).

**Canopy deposition velocity framework**

As discussed earlier, the magnitude and direction of BVOC flux depends upon the size and direction of the concentration gradient between the leaf intercellular air space and the ambient air. The concentration of a given BVOC in the ambient air outside the leaf and the capacity of plants to produce/metabolize that BVOC determine its leaf compensation point. In contrast to the compensation point formulation used in studies of bidirectional exchange in individual leaves, studies of canopy-level deposition flux, \( F \) (mol m^{-2} s^{-1}), have traditionally employed the concept of deposition velocity, using an analogy with Ohm’s law:

\[
F = v_d C_s, \tag{5}
\]

where \( v_d \) is the deposition velocity (m s^{-1}) and \( C_s \) is the compound ambient concentration (mol m^{-2}). Deposition velocity is given as the inverse of the sum of three resistances in series:

\[
v_d = \frac{1}{R_a + R_b + R_c}. \tag{6}
\]

In the present context, \( R_a \) (the sum of aerodynamic resistances) and \( R_b \) (the quasi-laminar sub-layer resistance) can be ignored, and the so-called surface resistance (\( R_c \)) is the major determinant of whether or not a given volatile species is deposited. \( R_c \) describes the effective resistance to uptake by surface elements, including vegetation, and incorporates a variety of factors, including stomatal and mesophyll resistance terms that include, among other things, the magnitude of both the within-plant source and within-plant sink for the volatile of interest. Wesely (1989) defined a reactivity factor \( f_0 \), which describes the oxidation rate of the volatile compound within the plant. The factor \( f_0 \) ranges from 1 for extremely reactive compounds like \( O_3 \) to 0 for non-reactive compounds. Those considered slightly reactive are assigned a value of 0.1.

The traditional deposition velocity framework (Wesely 1989) continues to be widely used in regional air quality models (e.g. Zhang et al. 2002; Pleim & Ran 2011). In application of the algorithm, the compound concentration within the leaf is assumed to be very small and the flux is therefore a function of the ambient concentration and modelled stomatal conductance (Eqn 5). This generally works well for extremely reactive species such as \( O_3 \) and \( SO_2 \) (Pleim & Ran 2011). Although, in principle, the same formulation can be applied to organic species, very few experimentally determined estimates of \( f_0 \) exist for such compounds, and recent evidence (Karl et al. 2010) suggests that the previously assumed values may be too low, significantly underestimating within-plant rates of destruction, and thus underestimating deposition velocities as well. For example, initially (Wesely 1989), values of \( f_0 \) of 0 were assigned to several BVOCs (e.g. formaldehyde, acetaldehyde and formic acid) which have subsequently been shown to be taken up by vegetation at both the leaf and the canopy scales. This underscores the need to re-evaluate the canopy resistance term for a wide range of BVOC, as we learn more about their metabolism within the plant. Thus, one approach to improve our ability to predict deposition rates would be to conduct detailed canopy-scale deposition studies (comparing deposition velocities to that of ozone for example) for a variety of BVOC to estimate values of \( f_0 \). However, difficulties associated with micrometeorological flux studies during the night when deposition fluxes may dominate, pose a technical obstacle to such a strategy.

**Bidirectional fluxes of BVOC at the ecosystem scale**

It is important to distinguish between BVOC species that are produced within the plant and others that can originate from BVOC oxidation processes in the ambient atmosphere. If there is no source for a given BVOC within the plant,
deposition is the only possibility, and the rate of deposition is jointly determined by the atmospheric concentration, the rate at which the compound is broken down within the plant and the stomatal conductance. For those BVOCs that are produced by the plant, the situation is far more complicated, as bidirectional fluxes are possible, and the rate of production also contributes strongly to both the size and the direction of the flux.

The atmospheric concentration of a given BVOC can fluctuate over a wide range during the diurnal cycle, and it plays a major role in determining whether leaves are a net sink or a net source of BVOC, because only when the atmospheric concentration falls below the compensation point, leaves can emit. Factors contributing to the diurnal variation in atmospheric concentrations include the emission source strengths for compounds produced within the plant, the atmospheric removal rates and the diurnal changes in boundary layer thickness. Thus, the expansion of the atmospheric boundary layer during the central hours of the day can lead to a decrease in atmospheric concentration of BVOC, whereas the nighttime collapse of the boundary layer can concentrate many BVOC within a much smaller volume, increasing the likelihood of leaf uptake (Fuentes et al. 2000; Betts et al. 2001). For those oxygenated BVOCs that arise from oxidation processes in the atmosphere, both the emission rates of their precursors and the rates of atmospheric oxidation affect the concentration. For some OVOCs, such as acetone or formaldehyde, there may be sources both within the plant and atmosphere. These photochemical processes that are maximized during periods of high light and warm temperature can significantly increase the atmospheric concentration of OVOC (Seco et al. 2007). When ambient air OVOC concentrations build up, the troposphere can represent a source of OVOC and generate a positive gradient, thus promoting deposition. This process has been indeed inferred to dominate the removal of BVOC from the atmosphere (Hallquist et al. 2009).

All of these interactions make it exceedingly difficult to predict the magnitude and direction of flux at any given time. In the tropical forest of Amazonia, the uptake of formic and acetic acids at the branch level was found to be controlled largely by changes in atmospheric concentration, as the measured compensation points were low and stayed within a fairly narrow range (0.16–0.30 nmol mol⁻¹), well below the usually observed atmospheric concentrations (Kuhn et al. 2002). In a tropical rain forest in Costa Rica, bidirectional exchange of methanol, acetaldehyde and acetone was observed, with emissions during the day and deposition at night (Karl et al. 2004). Although stomata have traditionally been assumed to close at night, there is now convincing evidence (Dawson et al. 2007) that many woody species maintain significant stomatal conductance at night, thus facilitating deposition processes for those compounds whose production in planta is dependent upon light and/or temperature. Although above-canopy emissions were generally observed during the day, within-canopy concentration profiles indicated that upper canopy leaves appeared to be a net source of acetaldehyde, whereas shade leaves within the canopy served as a sink (Karl et al. 2004). Deposition velocities were far higher than traditional deposition models predict, implying much lower values of Rₑ and fₑ than previously thought. In two studies in orange (Citrus aurantium) orchards, high concentrations in ambient air were associated with OVOC deposition to orange canopies (Staudt et al. 2000; Fares et al. 2012).

Apart from leaves, soil with litter and roots can constitute an important source (Hayward et al. 2001; Asensio et al. 2007a; Leff & Fierer 2008; Aaltonen et al. 2011; Greenberg et al. 2012; Horvath et al. 2012) or chemical and/or physicochemical sink (Minnich & Schumacher 1993; Pegoraro et al. 2006; Asensio et al. 2007a,b; Reid & Jaffe 2013) of different BVOCs. Although this review primarily focuses upon plant emissions, we note that consideration of soil processes might be important to close the ecosystem BVOC balance.

Recently, ecosystem-level compensation points for organic acids (1.4 nmol mol⁻¹ for formic acid and 2.1 nmol mol⁻¹ for acetic acid) in a central Amazonian forest were reported (Jardine et al. 2011). A seasonal switch between formic and acetic acid net emission in the wet season and net deposition during the dry season was observed and largely attributed to changes in atmospheric concentrations due to seasonal pollution from biomass burning (Jardine et al. 2011). Although the flux versus ambient concentration relationships were scattered as is often the case in estimations of leaf-level compensation points (Jardine et al. 2011), these results further underscore the importance of considering BVOC bidirectional exchange at the ecosystem level.

From a limited set of compounds to a full spectrum of atmospheric BVOC and OVOC

The vast majority of studies to date have focused upon BVOC emissions from plant canopies because of their importance in atmospheric processes. Much fewer studies have considered BVOC deposition, and even these few studies have focused on a narrow range of plant-produced and bidirectionally exchanged short-chained OVOC such as methanol, acetone, acetaldehyde, formic and acetic acids. As a result, little is known about deposition rates for the large number of BVOC oxidation products formed in the atmosphere. The limited evidence suggests that the rates of deposition of most OVOC are that high that they can significantly alter the composition of the atmosphere in ways not captured by existing models. Attempts to further our understanding of deposition processes have profited greatly from new advancements in BVOC measurement technology. The recently developed proton transfer reaction–time of flight–mass spectrometer (PTR-TOF-MS), for instance, can measure an unprecedented number of BVOC simultaneously with very high time resolution (Jordan et al. 2009). Recent eddy covariance applications revealed the presence of high concentrations and bidirectional fluxes of BVOC and their oxidation products (Park et al. 2013a,b). Although parent ions and their fragments could not be distinguished, more than 555 ions were measured in an orange
Implications for emission/deposition models

Recent evidence indicating the presence of significant chemical and physicochemical sinks for BVOC and OVOC within the leaves that can lead to overall complex bidirectional exchange dynamics calls for rethinking of how to best simulate trace gas exchange between plants and atmosphere (Figs 2 & 3). There is a growing consensus in atmospheric science that unidirectional flux modelling such as separate consideration of dry deposition and emissions should be replaced by bidirectional flux modelling (Pleim & Ran, 2011), and we argue that plant trace gas exchange should also follow this path. Current BVOC emission models such as the biogenic emission inventory system (BEIS; Pierce et al. 1998; Schwede et al. 2005; Hogrefe et al. 2011) and the model of emissions of gases and aerosols from nature (MEGAN; Guenther et al. 2006) still do not consider many BVOC species, which could be important in order to achieve an accurate estimate of ozone and SOA formation through regional photochemistry, although MEGAN2.1 (Guenther et al. 2012) deals explicitly with 138 different compounds. MEGAN2.1 recognizes the occurrence of bidirectional fluxes and includes a separate category for the short-chain oxygenated compounds ethanol, acetaldehyde, formaldehyde, acetic and formic acids. Millet et al. (2010) used a version of MEGAN2.1 to estimate terrestrial acetaldehyde flux, and recognized the bidirectional nature of that flux. Their approach was fairly crude, incorporating a leaf area index factor that resulted in emissions from upper canopy leaves and deposition to lower leaves, consistent with the observations of Karl et al. (2004) and Jardine et al. (2008). Clearly, a key implication of within-canopy variations in emission and deposition processes is that the canopy itself, particularly leaf area and leaf property distributions, should be better represented in the models.

Recent studies have shown that small changes in BVOC emission potential parameterization can lead to considerable changes of the prediction of physical and chemical properties of the atmosphere in the Mediterranean climate (Fares et al. 2013; Richards et al. 2013). The presence of still poorly explored BVOC in the atmosphere may also account for a sizable amount of the missing OH chemical reactivity and ozone chemical loss observed in plant environments (e.g. Di Carlo et al. 2004; Nölscher et al. 2012). Moreover, global chemistry and transport models should be finely parameterized to account for deposition of BVOC. Karl et al. (2010) demonstrated that altering the deposition scheme of the chemical transport model of Emmons et al. (2010) by incorporating the fast metabolic conversion of OVOC within leaves leads to substantially higher estimates of OVOC deposition, thus reducing OVOC concentrations in the lower troposphere and leading to changes in model predictions of SOA and tropospheric OH and ozone concentrations (Fig. 3). These pieces of evidence collectively indicate that next generation modelling schemes clearly provide more realistic temporal predictions, resulting in major improvements in simulations of biosphere-atmosphere exchange processes.

OUTLOOK FOR FUTURE RESEARCH

Depending upon the frequency of observations (minutes, hours, days), a plant ecosystem can behave as a BVOC source or sink. Based upon recent results, and considering the complexity of plant–atmosphere interactions (Fig. 3), more leaf-level investigations to determine the compensation point for a wider range of BVOC species than examined to date are clearly called for. In addition, studies to determine how compensation points vary in response to, among other factors, light, temperature and imposition of various stresses will be crucial. Studies on the deposition rate of a wide range of atmospheric organic constituents that have no source within leaves should also be examined, to determine whether their uptake is relatively slow, as older models predict, or rapid, implying much faster degradation processes within the leaf. If they are taken up at rates similar to ozone, for example, characterizing their deposition rates would be much more straightforward, depending largely upon stomatal conductance and ambient concentrations.

Although clearly useful and important for enhancing our understanding of the underlying physiological processes involved, it will be exceedingly difficult to apply such information at the canopy or ecosystem scale. Additional field studies, ideally at sites already equipped for micro-meteorological flux measurements of CO₂ and H₂O should be performed in order to capture the large suite of compounds exchanged with the atmosphere, and perhaps determine canopy-scale compensation points and examine how they vary with environmental conditions. Given that the spectrum of compounds emitted and their exchange characteristics vary considerably across different vegetation
types as a result of phenology and atmospheric variability (Keenan et al. 2009; Fares et al. 2010, 2012), long-term studies are likely particularly fruitful in bringing bidirectional BVOC modelling forward.

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environment, and plant alkanes with ages greater than one billion years have been detected in lake sediments (Oro et al. 1965). In contrast, unsaturated lipids including isoprenoids and fatty acids are highly susceptible to oxidation with their pools rapidly turned over under oxidizing conditions. Moreover, the oxidative power of the lower atmosphere is strongly influenced by the emission of unsaturated volatile lipids from vegetation, especially isoprenoids and other reactive volatile lipids, which are emitted from many plant species at high rates and which fuel atmospheric chemistry through photooxidation reactions.

Reactive oxygen species (ROS) including singlet oxygen (O2), superoxide anion (O2·−), hydrogen peroxide (H2O2) and the hydroxyl radical (OH) are continuously generated in plants by the incomplete reduction of oxygen (O2). Although ROS concentrations within the plants are generally kept low by ROS quenching and scavenging systems, excessive ROS accumulation can result in extensive oxidation of plant lipids (Apel & Hirt 2004; Jardine et al. 2010a). Although traditionally described as the ‘oxygen paradox’ where ROS are simply a toxic by-product of aerobic metabolism (Davies 1995), ROS-lipid signalling is now recognized as an integral component of plant response to abiotic and biotic stresses as well as a driver in regulation of growth, development and programmed cell death (Mittler et al. 2011; Suzuki et al. 2011).

Furthermore, oxidation products of volatiles themselves can be highly reactive. In particular, oxygenated volatiles (OVOCs) that contain an α-β unsaturated carbonyl group are classified as reactive electrófilo species (RES). RES are biologically very active due to their extremely high chemical reactivity with nucleic acids, proteins and metabolites (Farmer & Davoine 2007). Therefore, oxidative stress generated by RES can lead to gene expression patterns at all levels (Farmer & Davoine 2007).

ROS-initiated lipid peroxidation

Like all radical reactions, lipid peroxidation reactions involve an initiation, propagation and termination stage (Wheatley 2000). Lipid peroxidation is initiated when a ROS-lipid encounter leads to the formation of a lipid radical, which then combines with molecular oxygen to form a lipid peroxy radical. The propagation stage is characterized by a chain reaction where lipid peroxo radicals react with other nearby lipids to form additional lipid radicals. Finally, the termination stage occurs when lipid radicals react with other lipid radicals or when they react with antioxidants that can terminate lipid peroxidation processes by converting lipid peroxy radicals into more benign lipid hydroperoxides. Given the typical close physical proximity of lipids in biological structures including membranes, storage vesicles and glands, the rapid termination of lipid peroxidation is critical to avoid massive oxidative damage, loss of biological functions and cell death.

Plant oxylipins

The oxidation of plant fatty acids via non-enzymatic (Durand et al. 2009; Mene-Saffrane et al. 2009) and enzymatic (Heiden...
mechanisms produces a broad range of oxidation product biomarkers termed oxylipins. The accumulation of ROS in plant tissues initiates fatty acid (e.g. α-linolenic acid) peroxidation, yielding a large array of ‘oxidative stress’ biomarkers (Table A1). Lipid peroxidation generates a number of products that have been extensively used as quantitative indicators of oxidative damage in plants (Gutteridge 1995; Shulaev & Oliver 2006). For example, 4-hydroxy-2-nonenal (HNE), 4-hydroxy-2-hexenal (HHE) and malondialdehyde are widely used as biomarkers of non-enzymatic lipid peroxidation (Halliwell & Gutteridge 1999; Hartley et al. 1999; Long & Picklo 2010). However, the extraction from plant tissues, derivatization and compound-specific analysis (GC-MS or HPLC) of these reactive carbonyl compounds remains a challenge due to their trace abundances, high reactivity, water solubility and volatility (Shibamoto 2006). Nonetheless, a number of classes of lipid peroxidation products have been identified, including hydrocarbons, ketones, furans, alkanals, 2-alkenals, 2,4-alkadienals, 2-hydroxyalkanals, 4-hydroxy-2-alkenals and dicarbonyls (Frankel et al. 1989; Mark et al. 1997; Nielsen et al. 1997; Moseley et al. 2003; Shibamoto 2006; Steeghs et al. 2006; Kawai et al. 2007).

Table A1. Example of isoprene (italic) and fatty acid (roman) peroxidation biomarkers from plants under oxidative stress.

<table>
<thead>
<tr>
<th>Parent lipid</th>
<th>Class</th>
<th>Oxidation biomarkers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene</td>
<td>Isoprene</td>
<td>Methacrolein, methyl vinyl ketone</td>
</tr>
<tr>
<td>Isoprene</td>
<td>GLVs</td>
<td>3-Hexenal, 3-hexen-1-ol, 3-hexen-1-yl acetate</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>Furans and furanones</td>
<td>Tetrahydrofuran, 2-ethyl furan, 5-ethyl-(SH)-furanone</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>Alkanes</td>
<td>Propane, butane, pentane, . . . , undecane</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>2-Alkenes</td>
<td>2-Propene, 2-butene, 2-pentene . . . , 2-undecene</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>Alkanals</td>
<td>Propanal, butanal, pentanal, . . . , undecanal</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>2-Alkenals</td>
<td>2-Propenal, 2-butenal, 2-pentenal, . . . , 2-undecenal</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>2,4-Alkadienals</td>
<td>2,4-Hexadienal, 2,4-heptadienal, 2,4-octadienal</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>2-Ketones</td>
<td>2-Butanone, 2-pentanone, . . . , 2-undecanone</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>Alkenones</td>
<td>1-Hexen-3-one, 1-penten-3-one, 1-octen-3-one, 6-methyl-5-hepten-2-one</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>4-Hydroxy 2-alkenals</td>
<td>4-Hydroxy-2-hexenal, 4-hydroxy-2-nonenal</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>Dicarbonyls</td>
<td>Malondialdehyde, glyoxal, methyl glyoxal, diacetyl</td>
</tr>
</tbody>
</table>