Journal of Experimental Botany, Vol. 68, No. 19 pp. 5293–5306, 2017
doi:10.1093/jxb/erx302 Advance Access publication 26 August 2017

REVIEW PAPER

Physico-chemical properties of plant cuticles and their functional and ecological significance

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Editor: José Heredia-Guerrero, Istituto Italiano di Tecnologia, Italy

Received 2 May 2017; Editorial decision 3 August 2017; Accepted 3 August 2017

Abstract

Most aerial plant surfaces are covered with a lipid-rich cuticle, which is a barrier for the bidirectional transport of substances between the plant and the surrounding environment. This review article provides an overview of the significance of the leaf cuticle as a barrier for the deposition and absorption of water and electrolytes. After providing insights into the physico-chemical properties of plant surfaces, the mechanisms of foliar absorption are revised with special emphasis on solutes. Due to the limited information and relative importance of the leaf cuticle of herbaceous and deciduous cultivated plants, an overview of the studies developed with Alpine conifers and treeline species is provided. The significance of foliar water uptake as a phenomenon of ecophysiological relevance in many areas of the world is also highlighted. Given the observed variability in structure and composition among, for example, plant species and organs, it is concluded that it is currently not possible to establish general permeability and wettability models that are valid for predicting liquid-surface interactions and the subsequent transport of water and electrolytes across plant surfaces.

Key words: Contact angles, cuticle, deliquescence point, foliar uptake, leaf absorption, stomata, surface free energy, wettability.

Introduction

Plant surfaces play a major role for plant survival and protection against multiple abiotic and biotic stress factors such as dehydration (Kerstiens, 1996; Riederer and Schreiber, 2001), excess UV irradiation (Krauss *et al.*, 1997), increased vapour pressure deficits (Fernández *et al.*, 2014a), and pathogen (Serrano *et al.*, 2014) or insect attacks (Eigenbrode and Jetter, 2002). Most aerial plant parts such as leaves, fruits, flowers or stems are covered with a cuticle, which is the interface between organs and the surrounding atmosphere (Riederer and Schreiber, 2001). While the definition of a bi-layered cuticle *sensu* Brongniart (1830) and von Mohl's (1847) has been recently challenged (Fernández *et al.*, 2016; Segado *et al.*, 2016), several studies determined the ultrastructure of cuticles from different organs and species (as revised by Jeffree, 2006). The link between internal structure, chemical composition, and functionality still remains in parts obscure (Fernández *et al.*, 2016).

Abbreviations: δ, solubility parameter; γs, surface free energy; Θ, contact angle; DRH, deliquescence relative humidity; g_{min}, minimum conductance; RH, relative humidity

During the last fifty years, significant research efforts have been made towards improving our understanding of, for example, the processes of cuticle and wax formation (Kunst and Samuels, 2009; Segado *et al.*, 2016; Jacq *et al.*, 2017; Mazurek *et al.*, 2017), cuticle barrier properties to transpiration (Jetter and Riederer, 2016; Zeisler and Schreiber, 2016), cutin genesis (Dominguez *et al.*, 2015; Fich *et al.*, 2016) and cuticle responses to biotic and abiotic stress factors (Isaacson *et al.*, 2009; Kosma *et al.*, 2010). Furthermore, the composition, structure, formation, and functionality of plant cuticles of several plant species and organs have been assessed in several reports (Riederer and Müller, 2006). However, most of those studies were performed with the leaves of just a few species, such as *Clivia miniata*, *Agave americana*, *Populus* x *canescens*, and *Arabidopsis thaliana*, in addition to tomato and pepper fruits (Riederer and Müller, 2006; Schreiber and Schönherr, 2009). For other plant species, a limited number of investigations examined the cuticles of leaves (Gouret *et al.*, 1993; Guzman *et al.*, 2014a,b,c), fruits (Peschel *et al.*, 2007; Martin and Rose, 2014, Lara *et al.*, 2015; Guzmán-Delgado *et al.*, 2017), and flower petals (Goodwin *et al.*, 2003; Kwiatkowska *et al.*, 2014; Buschhaus *et al.*, 2015).

On the other hand, comparably more research has been devoted to characterize the wettability of plant surfaces, focussing on plant ecophysiology (Brewer *et al.*, 1991; Holder and Rosado, 2013; Matos and Rosado, 2016) and an adaptive relationship between leaf surface wettability, stomatal density, and photosynthetic performance has been suggested to occur (Smith and McClean, 1989).

The main aim of the review is to provide a broad overview of the significance of the cuticle as barrier for the deposition and potential absorption of water and electrolytes by leaves of cultivated, namely forest and crop species, and wild species. Provided the limited information available on the ecophysiological role of the leaf cuticle of herbaceous and deciduous species, emphasis is made on the paramount role attributed to the cuticles of needles of Alpine conifers and treeline species. The major degree of variability in plant surface structure and composition is highlighted, also considering stomatal pores and trichomes.

Plant surface physico-chemical properties

Plant surface structure and composition

The structure and composition of the surface of aerial plant organs, which are generally covered with a cuticle, determines the contact phenomena with surface-deposited liquids or solid particles (Fernández *et al.*, 2011; Fernández and Khayet, 2015). Glabrous or pubescent surfaces (see TEM images in Fig. 1) are covered with a cuticle similar to guard cells (Fig. 2) or trichomes (Fig. 1E). The base of the trichomes of leaves of some xeromorphic species have been observed to be cutinised (Fahn, 1986; Fernández *et al.*, 2014a),

The cuticle can be considered as a composite material made of lipophilic components, namely apolar compounds such as waxes and cutin, and hydrophilic components, namely polar compounds such as polysaccharides. An example of the chemical and structural heterogeneity of plant cuticles is shown in Fig. 1. The adaxial cuticle of beech (*Fagus sylvatica* L.) (Fig. 1A) and wheat (*Triticum aestivum* L.) (Fig. 1D) leaves can be observed as a smooth, continuous, whitish layer significantly different from the cell wall underneath, while the lower leaf cuticle of poplar (*Populus bolleana* Carr.) has a sinuous topography (Fig. 1B). The entire adaxial epidermal cell wall of sessile oak (*Quercus petraea (Matt.) Liebl.*) appears to be lipidised but an upper continuous, whitish layer can be distinguished (Fig. 1C). The upper leaf cuticle of Magellan's beech (*Nothofagus betuloides* (Mirb.) Oerst) appears to be a continuous layer containing patches of an electron-dense material located underneath the epicuticular wax layer (Fig. 1F). A thin cuticle with a layer of an electron-dense material underneath can also be observed in the cross-section of trichomes of the abaxial leaf surface of holm oak (*Quercus ilex* L.) Fig. 1E. Such trichomes were observed to yield highly hydrophobic surfaces in contrast to the wettable trichomes found on the upper leaf side of young leaves of this species (Fernández *et al.*, 2014a).

An example of the variability of guard cell and stomatal pore structure is provided in Fig. 2. The presence of cuticular ledges can be observed in all four species, while the overall guard cell shape, topography, and cuticle thickness in the leaf surface and within the stomatal pore greatly differ between species. The inner cell wall of guard cells, that is the upper part of the pore wall, of holm oak (Fig. 2A), elm (*Ulmus minor* Mill.), and Magellan's beech leaf stomata are covered with a continuous cuticle that is sinuous in elm stomata (Fig. 2B) and has some pegs at the base in the case of Magellan's beech stomata (Fig. 2D). However, the guard cells of poplar leaf stomata have a thicker cuticle on the ledges, which thins out towards the inner part of the stomatal pore (Fig. 2C). The major degree of cuticular structural and chemical heterogeneity (as shown in Figs 1 and 2) will cause major differences in surface contact phenomena and transport processes across the cuticle. The functional implications of such differences are not yet fully understood (Fernández *et al.*, 2016).

Plant surface physico-chemistry

Since the 1990s when the major water drop repellence of *Nelumbo nucifera* leaves was described to provide self-cleaning properties (Barthlott and Neinhuis, 1997), several studies were carried out to characterize the performance of plant surfaces from a materials science viewpoint (Koch *et al.*, 2008).

For analyzing plant cuticle-liquid or cuticle-solid contact phenomena, it is crucial to consider the chemical nature of the plant surface and the liquids or solids deposited onto it (Fernández and Khayet, 2015; Nairn *et al.*, 2016). The potential occurrence of dispersive, non-dispersive or hydrogen-bonding interactions between plant surfaces and surface-deposited liquids or solids may provide *a priori* insights into potential surface-related processes, such as leaf absorption of water or agrochemicals, particle deposition or water loss. In this review, we will refer to wettable surfaces when the contact angle (θ) with water is <90° and with unwettable or non-wettable surfaces is >90°. The water wettability of

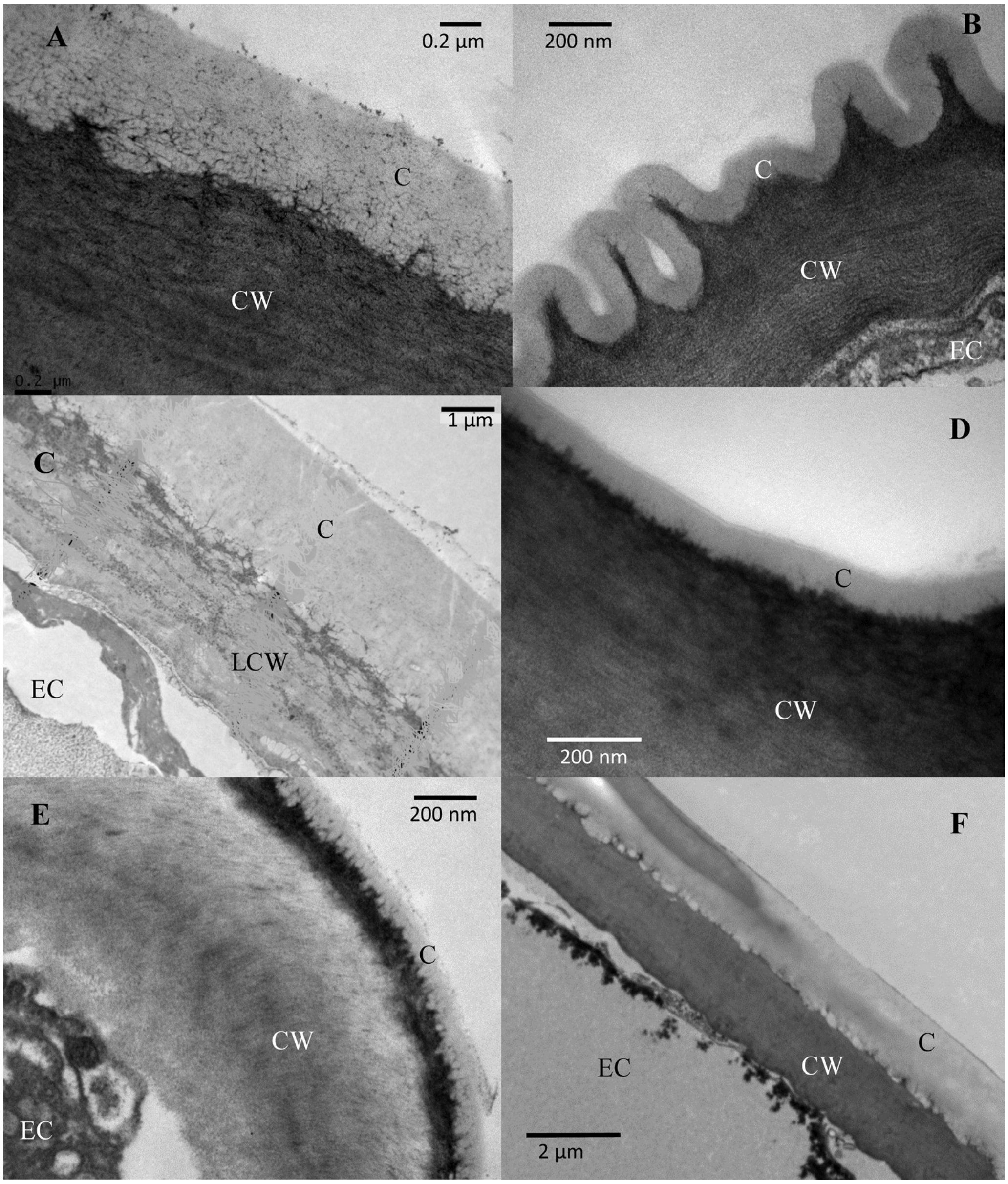

Fig. 1. Structural variability of leaf cuticle cross-sections. Cuticle cross-sections of (A) adaxial side of beech, (B) abaxial leaf cuticle of poplar, (C) adaxial leaf cuticle of sessile oak, (D) adaxial leaf cuticle of wheat, (E) cuticle of a holm oak trichome of the abaxial leaf side, (F) adaxial cuticle of Magellan´s beech. Samples were prepared for TEM as described by Guzmán *et al*. (2014a). C, cuticle; CW, cell wall; EC, epidermal cell; LCW, lipidised cell wall.

leaf surfaces of many species has been measured in a number of studies (Aryal and Neuner, 2016; Goldsmith *et al.*, 2017). These values however provide limited information on potential plant surface-liquid/solid interactions because they neglect the role of surface chemistry (Fernández and Khayet, 2015; Nairn *et al.*, 2016). The importance of quantifying the contribution of structural and chemical interactions between plant surfaces and agrochemical formulations has been recently examined (Nairn *et al.*, 2011; Nairn *et al.*, 2016; Nairn and Forster, 2017). A method for estimating the degree of leaf polarity using a wetting tension dielectric technique based on measuring contact angles has been introduced by Nairn *et al.* (2011, 2016). This procedure may facilitate the estimation of the contribution of leaf surface chemical composition to drop wetting and adhesion and may be useful for developing agrochemical spray formulations targeted for specific plant species (Nairn *et al.*, 2011; Nairn *et al.*, 2016).

A membrane science approach for analyzing the surfaces of several plant species, intact organs, and enzymatically-isolated cuticles has also been implemented (Fernández *et al.*, 2011; Fernández *et al.*, 2014a,b; Guzmán-Delgado *et al.*, 2016). This involves the estimation of the surface free energy (γ_s) of plant surfaces via measurement of contact angles of drops of liquids with different degrees of polar and apolar surface tension components (Fernández *et al.*, 2011; Wang *et al.*, 2014). Fernández and Khayet (2015) applied the most common γ_s calculation methods to plant leaves and concluded that due to their heterogeneity, at least three different liquids should be measured.

Another parameter that can be either calculated theoretically from molecular structures or empirically as derived from

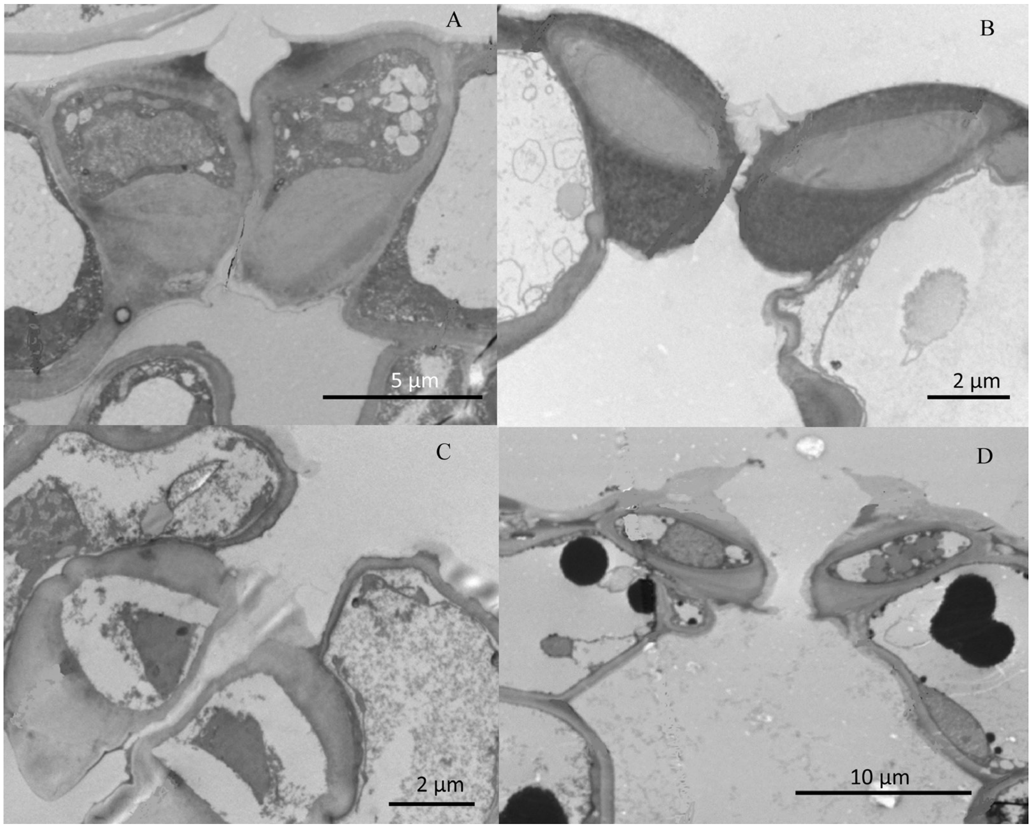

Fig. 2. Variability of guard cell walls among plant species. Cross-sections of guard cells of the abaxial leaf side of (A) holm oak with guard cells completely covered with a cuticle, (B) elm with sinuous cuticular surface in the cell wall pore, (C) poplar with limited cuticle deposition on the stomatal pore, and (D) Magellan´s beech with guard cells completely covered with a cuticle with a basal peg at the end of the pore. Samples were prepared for TEM as described by Guzmán *et al*. (2014a).

γ_s estimations (Khayet and Fernández, 2012), is the solubility parameter (δ). While the Theory of Solubility was proposed a century ago (Hildebrandt, 1916), δ, its components, and applications were described by Hildebrand and Scott (1950) and further developed in subsequent studies (van Krevelen and Hoftyzer, 1976; Hildebrandt, 1979; Hansen, 2004). The solubility parameter is based on quantifying the cohesive properties of a molecule and the degree of interaction or affinity between different molecules (van Krevelen and Nijenhuis, 2009). Prediction of δ is often used in membrane science (Khayet *et al.*, 2007), the coating industry (Hansen, 2004) or in pharmacology (Bustamante *et al.*, 2011), and it has also been applied to plant surfaces (Khayet and Fernandez, 2012). Apart from calculating the affinity between model agrochemicals and plant surfaces (Khayet and Fernández, 2012), potential interactions between cuticle chemical constituents and TEM sample preparation chemicals (Guzmán *et al.*, 2014c) and the effect of plant surface roughness and chemical composition (Fernández and Khayet, 2015; Guzmán-Delgado *et al.*, 2016) have also been interpreted by comparing δ values.

In Table 1, θ values of drops of water, glycerol, and diiodomethane on the adaxial and abaxial leaf side of orange, olive, maize, and wheat leaves (Fig. 3) are provided as an example. The corresponding total γ_s, γ_s components, polarity, and solubility parameter values of such surfaces are shown in Table 2. At a first sight it can be observed that the θ values of the three liquids may vary between species for the same leaf side, for example the adaxial side of highly water wettable maize versus the almost super-hydrophobic wheat leaf, and/or when comparing the adaxial and abaxial leaf surface of the same species, for example diiodomethane θ values in wheat. Such liquid drop-surface interactions will be related to the combined effects of surface chemistry and physical structure (Fernández and Khayet, 2015). The upper leaf side of wheat (Table 1) is not wettable for any of the three liquids and this has been associated with

Table 1. *Wettability of plant surfaces by liquids with different polar and apolar surface tension components. Contact angles of water* (θ_w), *glycerol* (θ_g) *and diiodomethane* (θ_d) *with adaxial and abaxial leaf surfaces of orange* (Citrus sinensis *(L.) Osbeck cv. Washington navel), maize (*Zea mais*, population EPS14(FR)C3), olive (*Olea europaea *L. cv. Arbequina), and wheat (*Triticum aestivum *L. cv. Axe) leaves. Data are means ± standard deviation. Contact angles were measured as described by* Revilla et al. *(2016).*

Species	Leaf side	θ_w (°)	θ_g(°)	θ_d(°)
orange	Adaxial	91.5 ± 8.6	92.3 ± 3.7	66.9 ± 5.9
	Abaxial	98.4 ± 6.4	98.8 ± 4.1	71.6 ± 3.4
maize	Adaxial	53.2 ± 11.5	76.5 ± 5.9	47.8 ± 5.5
	Abaxial	63.2 ± 12.6	80.4 ± 5.5	52.8 ± 5.9
olive	Adaxial	65.3 ± 7.5	63.9 ± 11.2	55.8 ± 6.2
	Abaxial	68.8 ± 9.2	90.0 ± 6.0	59.8 ± 5.9
wheat	Adaxial	143.2 ± 5.1	125.1 ± 8.8	104.0 ± 5.9
	Abaxial	117.7 ± 10.7	110.1 ± 7.1	75.3 ± 5.4

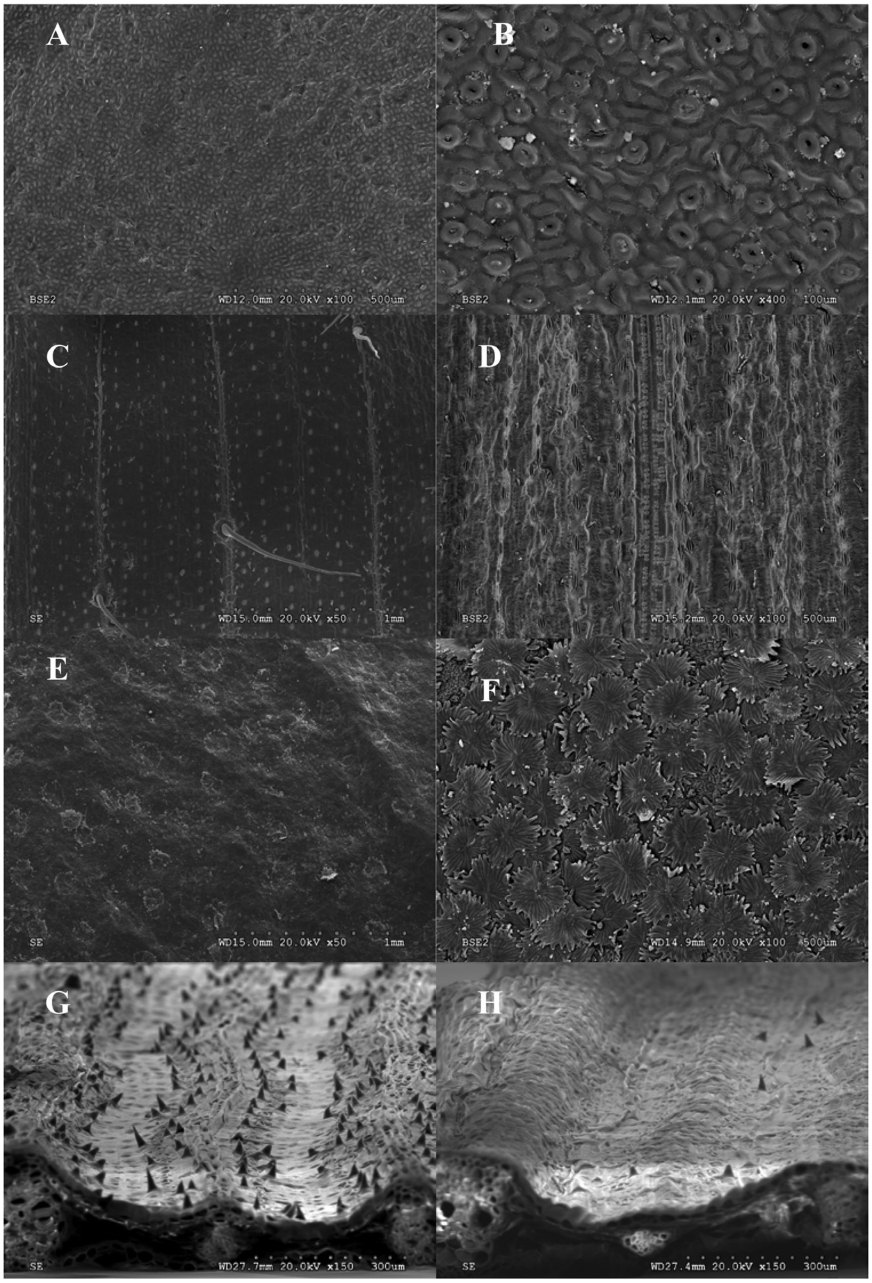

Fig. 3. Variability of surface topography among plant species. Adaxial (A, C, E, G) and abaxial (B, D, F, H) leaf surfaces of (A, B) orange, (C, D) maize, (E, F) olive, and (G, H) wheat. Front views highlight the presence of trichomes. Fresh tissue samples were gold-sputtered and observed by SEM.

the roughness provided by trichomes (Fernández *et al.*, 2014b; Fig. 3G). Consequently, this surface has a low total γ_s at 8.6 mJ m^{-2} and polarity ($\gamma_s^{AB}\gamma_s^{-1}$), as well as a total δ that is below the theoretical value of epicuticular waxes of 16 to 17 MJ$^{1/2}$ m$^{-3/2}$ (Khayet and Fernández, 2012). On the other hand, smoother but very lipidic surfaces such the upper and lower side of orange leaf (Fig. 3A, B) or the adaxial side of olive leaf (Fig. 3E) have higher γ_s values, from 28 to 33 mJ m^{-2}, and a δ within the range determined for waxes (Khayet and Fernández, 2012). Such γ_s values are within the average range estimated for paraffin wax surfaces of 23 to 35 mJ m^{-2} (Jańczuk and Białopiotrowicz, 1989; Jańczuk and Białopiotrowicz, 1990).

Different physico-chemical performance is observed for the lower leaf side of olive leaf (Fig. 3F) and both maize leaf sides (Fig. 3C, D; Table 1; Revilla *et al.*, 2016), rendering them all fairly wettable for all the liquids. This implies higher γ_s, increased polarity and δ values that may be related to an irregular deposition of lipids over the epidermal cell wall. The fact that some plant surfaces may not have completely homogeneous wax coverage has been suggested in several studies (Holloway, 1970; Nairn *et al.*, 2011; Fernández *et al.*, 2014a; Revilla *et al.*, 2016). This may be seen by high electron donor component (γ_s^-) values (Table 2; maize and olive leaves), which like in cellulose (Dourado *et al.*, 1998) may be related to the presence of functional groups that are prone to hydrogen-bonding and polar interactions, for example hydroxyl, acid or alcohols (Khayet and Fernández, 2012).

Table 2. *Total surface free energy (γ) of adaxial and abaxial leaf surfaces of orange, maize, olive, and wheat leaves. Also included are corresponding Lifshitz van der Waals (γ^{LW}; apolar), electron donor (γ_s^-) and acid-base (γ^{AB}; polar) components, polarity ($\gamma^{AB}\gamma_s^-$) and solubility parameter (δ). Values were calculated from the θ in Table 1 as described by Fernández and Khayet (2015).*

Species	Leaf side	γ_s^{LW} (mJ m^{-2})	γ_s^- (mJ m^{-2})	γ_s^{AB} (mJ m^{-2})	γ_s (mJ m^{-2})	$\gamma_s^{AB}\gamma_s^{-1}$ (%)	δ (MJ$^{1/2}$ m$^{-3/2}$)
orange	Adaxial	20.4	18.2	12.2	32.6	37.4	16.9
	Abaxial	18.4	14.2	12.0	30.4	39.5	16.1
maize	Adaxial	23.6	110.3	72.8	96.4	75.5	23.6
	Abaxial	22.8	81.6	54.0	76.8	70.3	22.8
olive	Adaxial	22.6	28.2	5.4	28.1	19.2	15.1
	Abaxial	18.9	91.8	72.6	91.6	79.3	36.7
wheat	Adaxial	8.1	1.9	0.5	8.6	5.8	6.3
	Abaxial	18.8	1.6	3.6	22.4	16.1	12.8

By measuring contact angles of liquids with different dielectric constants on leaves of different plant species, Nairn *et al.* (2016) quantified the contribution of roughness and chemical composition and found that bean and ryegrass leaves were polar. The authors hypothesise that the more polarized the leaf surface, the less solutions with antagonistic polarity are likely to stick to it. The effect of surface polarity and apolarity on the deposition of liquids, for example water or agrochemicals, and solids, for example aerosol particles or pathogens, of different chemical natures still needs to be further elucidated.

According to Koch and Barthlott (2009), superhydrophilic, that is extremely wettable, plant surfaces can be divided into those that are permanently wet, such as aquatic plant organs, those that absorb water over their surfaces, and those that let water spread over their surfaces. Based on their particular physico-chemical characteristics, foliar uptake of pure water solutions may be expected *a priori* in rather wettable and polar surfaces compared with extremely hydrophobic and apolar plant surfaces.

The physico-chemical properties of plant surfaces that are determined by their chemical composition and structure as described above will for example, affect their rate of wettability, adhesion or repulsion of water drops, and influence transport phenomena across the cuticle. The significance of the cuticle as barrier for the loss and absorption of water and hydrophilic solutes will be subsequently discussed.

Leaf surface permeability to agrochemicals, particularly hydrophilic solutes

Penetration of foliar-applied solutes by diffusion

Agrochemicals, such as plant protection products or mineral nutrients, are often applied to foliage to deliver the ingredients directly to the target organs (Fernández and Eichert, 2009). Foliar-applied substances penetrate the leaf surface by diffusion (Eichert and Fernández, 2012), and therefore this process can be described based on the principles of Fick's laws. There are thus two paramount parameters governing the rate of solute penetration across leaf surfaces after the initial contact surface phenomena: (i) the concentration gradient across the leaf surface acting as the driving force, and (ii) the permeability of the leaf surface determining the resulting rate of penetration.

The actual concentration gradient, acting as driving force of foliar penetration, is initially dynamic due to the equilibration of the foliar-applied aqueous solutions with the environmental conditions. The initial phase, immediately after spray application of agrochemicals, is usually characterized by the dynamics of water evaporation and the resulting increase in solute concentrations on the leaf surface. Temperature, wind speed, and the degree of water saturation of the air determine the duration until equilibrium with the atmosphere is reached. In the state of equilibrium, the resulting spray residues may either be dry or liquid, both depending on the nature of the solutes and the prevailing air humidity (Fernández and Eichert, 2009). These processes also apply for the deposition of salts on to foliage due to, for example natural phenomena as in mangroves (Lovelock *et al.*, 2017), atmospheric particles (Burkhardt and Hunsche, 2013) or sprinkler irrigation (Isla and Aragués, 2009).

In the dissolved state, foliar-applied substances may penetrate the leaf surface at least via the cuticle and stomata (Eichert *et al.*, 1998, Eichert and Burkhardt, 2001) and the relative importance of these pathways will depend, amongst other factors, on the physico-chemical properties of the solute and the plant surface. Whereas the permeability of the cuticle to lipophilic solutes, such as many pesticides or herbicides (Khayet and Fernández, 2012), is relatively high (Schönherr, 2006), the cuticle may be an effective barrier against the penetration of solutes like mineral fertilizers. However, this will certainly depend on the physico-chemical characteristics of the leaf surfaces as described above. In the following sections, the processes on the leaf surface controlling solute concentrations and thus the driving force of penetration, as well as the specific features of both available penetration pathways will be summarized, focusing mainly on hydrophilic solutes, with some new aspects addressed.

Processes affecting solute concentrations on the leaf surface

The equilibrium concentration of applied solutions on the leaf surface depends both on external air relative humidity (RH) and the type of solute. During equilibration with the atmosphere, the solutions on the leaves may either dry out completely or remain liquid. For any given pure solute, there is a defined threshold RH, above which the solution remains liquid and below which it will dry out, named the deliquescence relative humidity (DRH) or deliquescence point (Burkhardt and Eiden, 1994). When DRH equals RH, the solute concentration is at its maximum. When ambient RH rises above the DRH, solute concentrations will decrease and approach zero when water saturation of the atmosphere is reached. On the other hand, below DRH uptake will cease due to complete drying of the solution (Fig. 4).

Since the concentration gradient between the solution on the leaf surface and the leaf interior is the driving force for foliar uptake, RH will have a strong effect on penetration rates of foliar applied solutes. Fluctuating RH levels, for example due to diurnal rhythms of RH and temperature, will result in changing solute concentrations on the leaf surfaces and thus in varying penetration rates. If RH rises above the DRH of the solute, for example during the night, previously dried out solutions may even become re-moisturized resulting in resumption of foliar uptake.

The DRH values of different salts span a broad range. The DRH values of Mg salts, for example, range from 33% RH for $MgCl_2$ to 86% for $MgSO_4$ (Fountoukis and Nenes, 2007). Salts with low DRH, such as $MgCl_2$, will thus stay humid even under rather dry atmospheric conditions, whereas salts with high DRH, such as $MgSO_4$, will dry out even at relatively high ambient RH. The type of mineral salt chosen for foliar fertilization will therefore affect the resulting penetration rates under the prevailing levels of ambient RH. Generally speaking, the application of salts with low DRH will thus result in much higher penetration rates than of salts with high DRH.

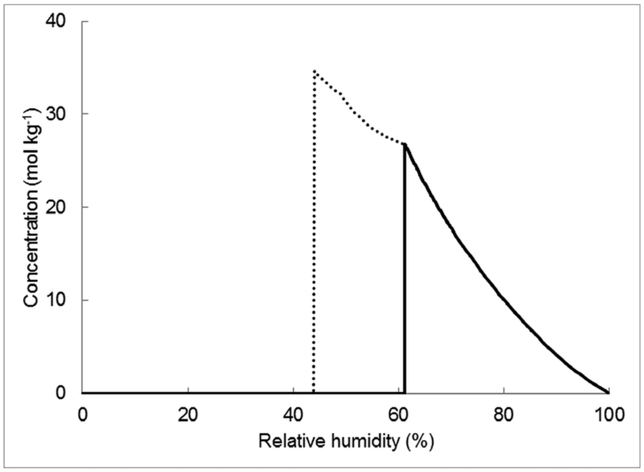

Fig. 4. Effect of relative humidity on the equilibrium concentrations of NH_4^+ in a solution of NH_4NO_3. Concentration is given as mol cations per kg of water. The solid line represents the concentrations in a pure solution, the dotted line in a solution with a small amount (1‰ of NH_4NO_3) of NaCl added. The vertical sections of the graphs correspond to the respective deliquescence relative humidities (DRH). Data were calculated using the Extended AIM Aerosol Thermodynamics Model of Clegg, Brimblecombe and Wexler (Clegg et al. 1998, http://www.aim.env.uea.ac.uk/aim/aim.php) using starting values of 1 mol NH_4NO_3 m^{-3} or 1 mmol NaCl m^{-3} air.

It has to be considered, however, that tabulated values of DRH are only valid for the pure solutions of defined salts. Even minute admixtures of other components, for example with formulation additives, impurities contained in the fertilizer salt or atmospheric deposits present on the leaf surface, may substantially affect the resulting deliquescence behaviour of the liquid system. This is exemplified in Fig. 4, where the effect of the addition of a small amount of NaCl to a solution of NH_4NO_3 is shown. The contamination with 1% NaCl lowered the DRH from 61% to 44% and increased the maximum NH_4^+ concentration from 27 mol kg^{-1} to 35 mol kg^{-1}, namely by 30%.

If the spray solution consists of a combination of different nutrient salts in similar concentrations, the effects of mixing of salts on DRH may be even more pronounced. An example is given in Fig. 5. Here, the theoretical deliquescence curves are displayed for Na_2SO_4, NH_4NO_3, and of an equimolar mixture of both based on the cations. The mixture has a DRH of 49% as compared with 61% for NH_4NO_3 and 94% for Na_2SO_4 as single salts. The maximum cation concentrations in the mixture reach 28 mol kg^{-1} for NH_4^+ and 11 mol kg^{-1} for Na^+ as compared with 24 mol kg^{-1} and 3.4 mol kg^{-1} for the single salt solutions of NH_4NO_3 and Na_2SO_4, respectively.

These examples emphasize that the deliquescence properties of nutrient salts may be significantly modified by any kind of additional solute contained in the aqueous spray solution or present on the leaf before spraying. This has two important practical consequences for foliar fertilization: first, tabulated values of DRH are not suited for the prediction of the deliquescence properties of nutrient salts as soon as additional compounds are present in the spray solution. These may be contaminations contained in the fertilizer or already present on the leaf surface due to atmospheric deposition. Second, specific additives may be used for modifying the

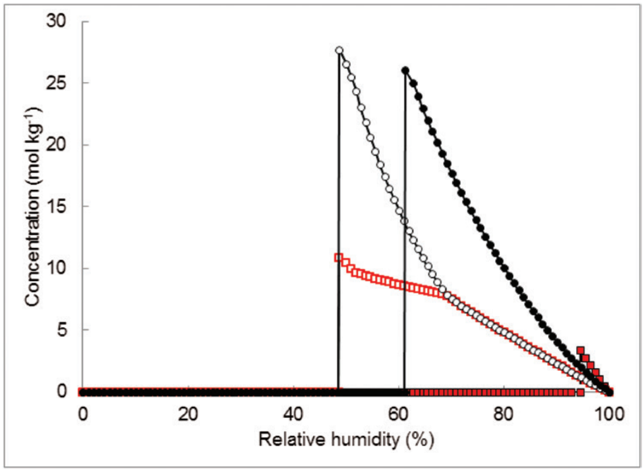

Fig. 5. Effect of relative humidity on the equilibrium concentrations of cations in solutions of NH_4NO_3 (filled circles) and Na_2SO_4 (filled squares) and in the equimolar mixture (based on the cations) of both salts (NH_4^+: open circles, Na^+: open squares). Concentration is given as mol cations per kg of water. Data were calculated using the Extended AIM Aerosol Thermodynamics Model of Clegg, Brimblecombe and Wexler (Clegg et al. 1998; http://www.aim.env.uea.ac.uk/aim/aim.php) using starting values of 1 mol NH_4NO_3 m^{-3} or 0.5 mol Na_2SO_4 m^{-3} air.

deliquescence properties of spray solutions, for example for lowering the DRH to increase the rate of foliar absorption.

Cuticular penetration pathways

The penetration of cuticles by lipophilic molecules has been described by the solution-diffusion model (Riederer and Friedmann, 2006). This model predicts penetration rates of a given molecule from its solubility and mobility, described by the partition coefficient of the molecule between the external solution and the cuticle and its diffusion coefficient in the cuticle (Schreiber, 2006).

Whereas the penetration of lipophilic solutes fits this model, the solubility of ions in the cuticle is too low to account for the observed transport rates (Schönherr, 2000; Schönherr, 2006). It was therefore suggested that the cuticle provides an alternative penetration pathway for these hydrophilic substances, called 'polar pores' (Schönherr, 1976), 'aqueous pores' (Schönherr, 2000; Schönherr and Schreiber, 2004) or 'water-filled pores' (Schreiber, 2005). It was proposed that these pores are created by sorption of water in the cuticle, which may form clusters allowing the movement of hydrophilic solutes across the leaf surface (Tyree *et al.*, 1990). In the cuticle, hydrophilic cell wall material such as cellulose, pectins, and hemicelluloses are thought to be the main sites of water absorption (Schönherr and Huber, 1977). Additionally, polar moieties of the cutin network (Schönherr, 2000; Schreiber, 2005), such as unesterified carboxylic groups (Schönherr and Bukovac, 1973), ester and hydroxylic groups (Chamel *et al.*, 1991) may present sites of water sorption. Chamel *et al.* (1991) reported the water content of isolated *Citrus aurantium* leaf cuticles of up to 8% of their dry weight at 85% RH and for *Abies alba* even higher values of up to 17% at 80% RH were reported (Chamel *et al.*, 1992). Absorption of substantial amounts of water will increase the volume of the cuticle, a process called swelling of the cuticle (Chamel *et al.*, 1991; Luque *et al.*, 1995; Arand *et al.*, 2010). With isolated cuticles it was shown that the degree of swelling increases with increasing RH in a non-linear fashion and that the strongest increase in water sorption takes place at high values of RH (Chamel *et al.*, 1991).

Whereas in the hydration studies with isolated cuticles developed by Chamel *et al.* (1991, 1992), the surrounding air was the only source of absorbed water, the situation in intact leaves will be different. Here, the underlying epidermal cells provide an additional water source, which is not dependent on the external RH. It is therefore very likely that the cell wall constituents within the cuticle (Guzmán *et al.*, 2014a; Fernández *et al.*, 2016) are continuously supplied with water by the underlying epidermal cells, whereas the sorption of water vapour from the outer side of the cuticle facing the atmosphere will still strongly depend on the humidity of the surrounding air (Fig. 6). Under dry atmospheric conditions, only low amounts of water will be absorbed by the outer cuticle and hence only a few functional aqueous connections traversing the cuticle will exist. With increasing air humidity or after wetting of the leaf surface by precipitation or spraying with agrochemicals, more water will be absorbed by the cuticle from the outer side. This increases the probability that water clusters will form a continuous connection between the outer and inner side of the cuticle (Fig. 6) in which hydrophilic solutes can diffuse across the cuticle, a structure previously called pore.

This model is not only supported by the reported effects of RH on water sorption and swelling of isolated cuticles (see above), but also by the observation that penetration rates of ions across isolated cuticles strongly increased with increasing relative air humidity (Schönherr, 2000; Schönherr, 2001; Schönherr and Luber, 2001; Schönherr, 2002). As shown by Fernández and Eichert (2009), high levels of relative

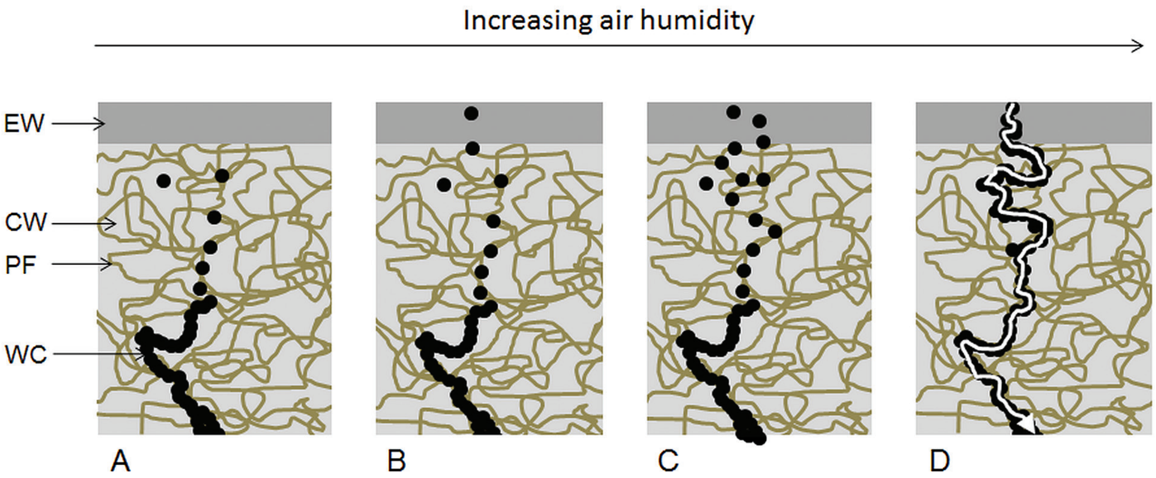

Fig. 6. Model of the formation of an aqueous connection traversing the cuticle. In this simplified model, the cuticle consists of a matrix of cutin and waxes (CW) interspersed with hydrophilic domains provided by polysaccharides; PF, polysaccharides fibrils for depicting cellulose and other hydrophilic constituents of the cuticle, such as pectins and polar moieties of the cutin matrix. The overlying layer of epicuticular waxes (EW) facing the outer side is devoid of polysaccharides. Water clusters (WC) are formed by adsorption of water by the hydrophilic domains. If air humidity is low water clusters mainly originate from the epidermal cells underneath the cuticle (A). With increasing external air humidity, more water is sorbed by the cuticle from the outer surface (A–C). At high humidity a tortuous connection between the leaf surface and the leaf interior emerges (D). Externally applied solutes may diffuse in these connections through the cuticle (white arrow in D). For clarity, other water clusters in the cuticle adjacent to the depicted emerging connection are not shown.

humidity, that is > 90%, are required before cuticular permeability to ions increases significantly.

According to the model suggested in Fig. 6, the aqueous connections between the leaf surface and interior are associated with hydrophilic domains present in the cuticle. They are therefore highly tortuous, probably often dendritic and may form a more or less continuous network in the cuticle. As a result of the RH-dependent, dynamic sorption and desorption of water, they are also probably randomly distributed. Since their appearance is strongly dependent on the hydration status of the cuticle, these aqueous structures randomly forming trans-cuticular connections are most probably unsteady in time and space, and they are thus characterized by their ghostliness. It is also clear that dried cuticles, for example following enzymatic isolation or sample preparation before microscopy, will not contain water clusters and hence the direct proof of these aqueous networks will be difficult.

The aqueous connections may not be created by filling previously empty spaces with water. They rather lodge themselves in the cuticle by docking at hydrophilic domains, a process related to cuticle swelling (Chamel *et al.*, 1991; Luque *et al.*, 1995; Arand *et al.*, 2010). However the common perception of the previously applied term of pore rather implies the opposite, namely a permanent, more or less straight opening admitting the passage of matter through a solid. Instead of pores, Beyer *et al.* (2005) used the term 'aqueous continuum', which reflects the network-like distribution of water within the cuticle. In order to account for the dynamics of formation and vanishing of functional aqueous connections, we suggest expanding this term to 'dynamic aqueous continuum'.

One important practical aspect with regard to the penetration of solutes through cuticles is the question of whether or not the diffusion of molecules through this compartment may be hindered or restricted by their size. Since the cuticle can be considered as a composite material formed of heterogeneous chemical constituents with chiefly apolar components, for example waxes or cutin, or polar components, for example polysaccharides, size restriction may occur both in the lipophilic and hydrophilic cuticular transport pathways, since penetrating molecules must diffuse within and between potentially formed matrix voids and water clusters following a tortuous pathway (Eichert and Fernández, 2009). Early estimations of pore sizes, based on experiments with isolated cuticles, yielded average pore diameters of about 1 nm or less (Schönherr 1976; Popp *et al.*, 2005), whereas considerably larger sizes of 4–5 nm were later reported in experiments with intact leaves (Eichert and Goldbach, 2008). It is not clear, whether these differences are caused by the different experimental approaches, for example by alterations of the cuticles during the isolation process, or are simply reflecting differences between species.

The stomatal penetration pathway

For a long time, it was unclear, whether or not stomata may enable the uptake of foliar-applied solutes into leaves. At the start of research on this subject, it was assumed that solutions may enter stomata by infiltration, that is by mass flow through the stomatal pore. Later it was shown that stomata are protected against capillary infiltration of aqueous solutions, mainly due to their specific architecture (Schönherr and Bukovac, 1972) and that only by means of low surface tension surfactants, for example organo-silicons, will stomatal infiltration be induced (Field and Bishop, 1988; Zabkiewicz *et al.*, 1993).

Nevertheless, many studies showed a clear promoting effect of stomata on foliar solute uptake even without adding surfactants (Schönherr and Bukovac, 1978; Eichert *et al.*, 1998; Eichert and Goldbach, 2008, Burkhardt *et al.*, 2012), but the underlying mechanism was for a long time not understood. Meanwhile, evidence was provided that solutes and even small particles may penetrate the stomatal pore by diffusion along the surface of the guard cells (Eichert *et al.*, 2008; Eichert and Goldbach, 2008). It was shown that not all stomata contribute to the uptake of foliar-applied solutes, making it most likely that external processes may reduce the native hydrophobicity of the guard cell cuticle of individual stomata activating them for solute transport (Eichert and Burkhardt, 2001; Eichert *et al.*, 2008; Fernández and Eichert, 2009; Burkhardt *et al.*, 2012). The increase in wettability of the pores may lead to the formation of continuous liquid water films on the stomatal walls that enable diffusive solute transport into and out of the leaf interior (Eichert *et al.*, 2008; Burkhardt *et al.*, 2012). Different mechanisms were suggested that may be responsible for the emergence of water films in pores: growth of bacteria (Eichert *et al.*, 2008) or fungal hyphae (Burgess and Dawson, 2004), epistomatal mucilage (Westhoff *et al.*, 2009) and deposited hygroscopic particles (Burkhardt *et al.*, 2012; Basi *et al.*, 2014). Nevertheless, the structural and chemical composition of guard cells and stomatal pores (see Fig. 2 and paragraphs above) will determine the prevailing liquid-solid interactions onto such surfaces. In this regard, Fernández *et al.* (2014a) highlighted that dropwise condensation will occur on unwettable surfaces while film condensation will take place on wettable surfaces. Similar wetting phenomena can be expected to occur depending on the roughness and chemical composition of stomatal pore wall surfaces. Besides the identification of the nature and basis of water film formation in stomatal pores, the question remains to be elucidated if and how the interspecific differences in cuticle composition, structure, wettability, and extension into the substomatal cavity (see Fig. 2 as an example) affect this phenomenon. In theory, more hydrophobic and/or deeper extending cuticles with increased surface roughness should provide better protection against water film formation but this still needs to be confirmed experimentally.

Significance of the cuticle for limiting water loss and enabling water uptake

The importance of the cuticle for protection against water loss is widely recognized (Kerstiens, 1996; Schreiber and Riederer, 1996). However, the potential role of leaf surface wettability as an adaptation for enhancing gas exchange, limiting transpiration, and improving water use efficiency has been comparably less explored (Smith and McClean, 1989). Adhesion, namely drops or films, or repulsion of water may favor or prevent the transport of water and gases, largely CO_2, across the surfaces, and this may be related to the habitat conditions of each particular plant species. In the following paragraphs, the ecophysiological importance attributed to the needle cuticle of Alpine conifers and treeline species is discussed, followed by the relevance of leaf wetting and water absorption.

Role of the needle cuticle of Alpine conifers and treeline species

The role of water loss through the epidermis, so-called 'cuticular transpiration', 'minimum transpiration' or 'minimum conductance', has been considered key for explaining vegetation processes of ecological significance, such as the conifer forest to alpine tundra transition, or the alpine treeline. Comparably few ecophysiological studies analyzed the importance of the cuticle for protection against water loss, and they were largely developed with perennial leaves, namely conifer needles. Plants growing at the alpine treeline are exposed to various stress factors including a short growing season due to low temperatures (Körner, 2003; Mayr *et al.*, 2006). Moreover, during winter water uptake is limited by low soil temperatures, while warm atmospheric temperatures and solar radiation may increase evaporative demand, leading to a condition known as 'frost drought' (Michaelis, 1934; Tranquillini, 1976). Under these conditions when stomata are mostly closed and photosynthesis is impaired, minimizing water loss through a reduced minimum conductance (g_{min}) may be critical for needle water status (Anfodillo *et al.*, 2002). Several studies showed that g_{min} increased with elevation but the underlying factors remain unclear (Kerstiens, 1996).

Wardle (1974) and Tranquillini (1979) suggested that the treeline constitutes an environmental limit for the maturation of aerial tissues because of low summer temperatures. These authors proposed that the growing season needs to be long enough for plant cuticles to fully develop and that unripened cuticles are unable to prevent water loss during winter (hypothesis of Michaelis, 1934), compared with those from lower altitudes (Baig and Tranquillini, 1976; Tranquillini, 1979). Working at high elevations in the Austrian Alps, Kerstiens (1996) observed that *Picea abies* needles significantly increased g_{min} when subjected to an artificial shortening of the growing season. This again supported the idea that *P. abies* and other tree species require a growing period of at least three months to complete their maturation (Tranquillini, 1974). Tranquillini (1982) suggested that the combination of elevated g_{min} associated with unripe cuticles could be a contributing factor for foliage damage by frost drought. Furthermore, with rising elevation DeLucia and Berlyn (1984) measured a 59% cuticular transpiration increase and a decrease in adaxial needle cuticle thickness of *Abies balsamea*. The authors related these phenomena to the shortened growing season and increased frost drought risk at higher elevations (Tranquillini, 1979).

In other studies, the high g_{min} values determined for alpine conifers have been alternatively associated with physical damage of needle surfaces caused, for example by wind or snow. The extreme damage caused by wind perhaps through cuticle abrasion may induce severe needle dehydration and mortality (Hadley and Smith, 1983; Hadley and Smith, 1986). Similarly, Hadley and Smith (1989) hypothesized that the loss of leaf surface wax due to wind erosion during winter may contribute to needle desiccation and mortality of timberline conifers. Van Gardingen *et al.* (1991) also recorded an effect of strong winds in increasing needle g_{min} in *Pinus sylvestris* and *Picea sitchensis*. Grace (1990) chiefly attributed the increased needle water loss of treeline *P. sylvestris* in Scotland to stomatal failure caused by leaf mechanical damage. However, it was concluded the small increase in g_{min} measured was unlikely to cause frost drought (Grace, 1990).

The increase in g_{min} with higher altitudes could not be confirmed by Anfodillo *et al.* (2002), who studied the performance of *Picea abies* and *Pinus cembra* needles along an altitudinal gradient in the Dolomites. In disagreement with previous reports, the authors found that the cuticle was thicker in needles of high altitude trees compared with low altitude trees, with no significant correlation between g_{min} and cuticle thickness. More recently, Nakamoto *et al.* (2012) obtained similar results when analyzing needle death in *Pinus pumila* in the alpine region of Japan during early springtime. The authors failed to find a significant relationship between cuticular resistance and thickness, concluding that needle death was not caused by cuticle mechanical damage, or a thinner cuticle, as also noted by Nakamoto *et al.* (2013) for *Abies mariesii* needles. These authors suggested that needle desiccation may rather relate to changes in cuticle composition and structure. In this regard, Gil-Pelegrín (1988) reported that cuticular waxes from needles of *Pinus uncinata* treeline populations of the Spanish Pyrenees had more polar compounds, namely alcohols and fatty acids, and esters than those belonging to lower altitude populations. This may increase the permeability of the cuticle to water (Haas and Schönherr, 1979) and yield the surfaces more polar (Khayet and Fernández, 2012). Consequently, a decrease in the cuticular resistance for *P. uncinata* needles at the treeline may occur due to qualitative, rather than quantitative, wax variations between populations (Gil-Pelegrín, 1993). The lack of relationship between cuticle thickness, wax amounts, and cuticular permeability has also been emphasised in several studies (Norris, 1974; Riederer and Schreiber, 2001; Kerstiens, 2006; Jetter and Riederer 2016).

Ecophysiological implications of foliar absorption of water

Several studies examined the potentially positive or negative physiological effects associated with leaf surface wettability and water retention or repulsion (Smith and McClean, 1989; Brewer *et al.*, 1991; Brewer and Nuñez, 2007; Holder, 2007; Rosado *et al.*, 2010; Rosado and Holder, 2013; Goldsmith *et al.*, 2017). Leaf water repellency or adhesion may, for example, favour leaf water uptake by increased surface wetting and drop retention (Eller *et al.*, 2013; Fernández *et al.*, 2014a) or increased photosynthetic rates in non-wettable leaves (Smith and McClean, 1989; Hanba *et al.*, 2004; Urrego-Oereira *et al.*, 2013). Working with leaves of 57 native species, Smith and McClean (1989) observed that higher water contact angles were normally determined in the surfaces containing the most stomata. Sharp declines in photosynthesis were measured for species having wettable leaf surfaces, while the deposition of water beads onto non-wettable surfaces led to increases in photosynthesis, major transpiration reductions, and significantly improved water use efficiencies. Smith and McClean (1989) suggested the occurrence of an adaptive relationship between leaf wettability, stomatal densities, and gas exchange parameters. Recently, Goldsmith *et al.* (2017) found neither an apparent relationship between increased precipitation and leaf water repellency, nor a clear phylogenetic signal for leaf wettability traits.

Increased hydrophobicity and variable surface-related phenomena have also been reported in relation to pubescent surfaces (as revised by Bickford, 2016). On the other hand, the occurrence of hydrophilic trichomes may yield leaf surfaces highly wettable and even lead to direct water absorption (Grammatikopoulos and Manetas, 1994; Pina *et al.*, 2016).

Leaf water uptake may play an important ecophysiological role for plant performance during drought (Breshears *et al.*, 2008; Eller *et al.*, 2013) but the mechanisms involved are still not fully characterised (Eichert and Fernández, 2012). Water deposited onto a leaf surface may penetrate through stomata (Eichert *et al.*, 1998; Burkhardt *et al.*, 2012), the cuticle (Yates and Hutley, 1995; Kerstiens, 1996; Kerstiens, 2006), specialized epidermal structures such as trichomes (Pina *et al.*, 2016; Nguyen *et al.*, 2017), and scales (Wang *et al.*, 2016; John and Hasenstein, 2017), or the stem base (Uematsu *et al.*, 2017).

Foliar water uptake due to natural phenomena, such as fog or dew, is considered especially important in areas of the world subjected to temporary drought, where leaf wetting events frequently occur (Simonin *et al.*, 2009; Eller *et al.*, 2013; Eller *et al.*, 2016). Several studies provided evidence for the uptake of water via foliage in a variety of ecosystems, such as deserts (Martin and von Willert, 2000), tropical montane cloud forests (Gotsch *et al.*, 2014; Eller *et al.*, 2013; Eller *et al.*, 2016), cloud-immersed mountain habitats (Berry and Smith, 2012; Berry *et al.*, 2014), and coastal mountain regions where fog is a significant climatic contributor (Burgess and Dawson, 2004; Simonin *et al.*, 2009).

Fernández *et al.* (2014a) analysed the process of foliar water uptake in holm oak and recorded significant water potential changes in response to leaf hydration. The increased wettability of the adaxial side of holm oak leaves facilitated leaf rehydration, possibly through the trichomes and the remaining scars after trichome shedding. Fernandez *et al.* (2014a) emphasised the potential significance of foliar water uptake in the climatic context of this Mediterranean species, which is normally exposed to dry and hot summers with occasional storms (Peguero-Pina *et al.*, 2014). The authors suggested that plant surface wetness, for example due to storms, or dew formation may favour foliar water absorption all year round, such process being especially important for plant water economy during the summer season (Fernández *et al.*, 2014a).

Concluding remarks

In this article, an overview of plant surface physico-chemical properties and permeability to water and solutes has been provided, also considering the importance of leaf wettability, foliar uptake, and transpiration, from an ecophysiological viewpoint. Given the major structural and chemical variability of plant cuticles and the current state of knowledge, it is not possible to suggest a general model for cuticular and stomatal permeability that would be valid, for example, for all species, organs or environmental conditions. However, a potential mechanism of cuticular diffusion of water and solutes likely related to hydrophilic cuticular components, namely polysaccharides, and cuticle swelling is suggested and named the 'dynamic aqueous continuum'.

It is now clear that wettability, retention or repulsion, and the degree of polarity and apolarity of plant surfaces and surface-deposited liquids will affect contact and subsequent transport phenomena across the foliar surface. However, the role of leaf wettability for plant ecophysiology including gas exchange, and in relation to plant phylogeny needs to be further explored. It is concluded that more research is required for elucidating the physico-chemical properties, permeability, and functional significance of plant surfaces for improving, for example, our understanding of plant ecophysiology and optimizing the performance of foliar agrochemical sprays.

Acknowledgments

This study was partially supported by the Spanish Ministry of Economy and Competitiveness (RTA2015-00054-C02-01) and by Gobierno de Aragón (H38 research group). The work of DSK is supported by a DOC INIA contract co-funded by the Spanish National Institute for Agriculture and Food Research and Technology (INIA) and the European Social Fund (ESF).

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