Appendix S1. Gradients in water potential of water vapor in leaf airspaces

Liquid water in equilibrium with a body of air with relative humidity h has a water potential, ψ, given by

(S1) $\qquad \psi = \dfrac{RT}{v_w} \ln(h),$

where v_w is the molar volume of water ($1.8 \cdot 10^{-5}$ mol m^{-3}) and R is the gas constant ($8.314 \cdot 10^{-6}$ MPa m^3 mol^{-1} K^{-1}) and T is temperature in kelvins. This is Eq. 1 in the main text, with RH rewritten as a dimensionless quantity, h = RH/100. Water at evaporating surfaces in a transpiring leaf is not in equilibrium with the adjacent air, however, because vapor diffusion away from the surface generates a gradient in vapor concentration, c (mol m^{-3}). Thus, ψ at the evaporating surface is greater than the value predicted by Eq. S1 for a value of h measured at some finite distance away from the surface. By Fick's first law of diffusion, the steady state gradient in concentration equals the ratio of the vapor flux, J (mol m^{-2} s^{-1}), to the binary diffusivity of water vapor in air (D_{wa} /[m^2 s^{-1}] = $2.178 \cdot 10^{-5} \cdot (T/273.15)^{1.81}$ at sea level for T in kelvins):

(S2) $\qquad \dfrac{\partial c}{\partial x} = \dfrac{J}{D_{wa}}.$

where x denotes position along a diffusion path of constant area (m). The flux J is proportional to the leaf transpiration rate, E (mol m^{-2} s^{-1}), by an unknown dimensionless factor f, discussed below. As we are interested in water potential rather than vapor concentration, we can convert $\partial c / \partial x$ to an equivalent water potential gradient using the chain rule:

(S3) $\qquad \dfrac{\partial \psi}{\partial x} = \dfrac{\partial c}{\partial x} \dfrac{\partial p}{\partial c} \dfrac{\partial h}{\partial p} \dfrac{\partial \psi}{\partial h},$

where p is vapor pressure (Pa). By Dalton's Law and the Ideal Gas Law, $p = cRT$, so $\partial p / \partial c = RT$. For any p, $h = p/p_{sat}$, so $\partial h / \partial p = 1/p_{sat}$, where p_{sat} is the saturation vapor pressure (Pa). Differentiation of Eq. S1 gives $\partial \psi / \partial h$ as $RT/(v_w h)$. Applying these results to Eq. S2 and S3, and noting that $h = p_{leaf}/p_{sat}$, gives the diffusional gradient in ψ near an evaporating surface as

(S4) $$\frac{\partial \psi}{\partial x} = \frac{fE(RT)^2}{D_{wa} v_w p_{leaf}}.$$

For diffusion very close to the evaporating surfaces, f (the ratio of J to E) is equal to the ratio of leaf area to evaporating surface area. If all interior leaf surfaces support evaporation, then the latter ratio is likely no greater than 0.1 (e.g., Evans et al., 1994; Tomás et al., 2013). We assumed $f = 1$ for the sake of argument; this overestimates $\partial \psi/\partial x$ near evaporating surfaces to the extent that those surfaces are greater in area than the underlying leaf area.

Applying Eq. S4 to the data of Cernusak et al. (2018) gives $\partial \psi/\partial x \leq 0.008$ MPa μm^{-1} for *P. edulis*, and $\partial \psi/\partial x \leq 0.011$ MPa μm^{-1} for *J. monosperma*. In words, this means that free diffusion away from an evaporating surface causes a drop of less than 0.27 MPa at a distance 25 μm from the surface (similar to the size of a typical mesophyll cell). This suggests that the water potential of liquid water at the evaporating surfaces is fairly close to the value predicted by the equilibrium relationship given by Eq. S1 (Eq. 1 in the main text), for h in the adjacent airspaces.

Effective diffusion over much greater distances – for example, from an evaporating site near the xylem to a pocket of airspace adjacent to a stomatal pore – could potentially generate a much greater water potential drawdown. However, the cell wall solution (CWS) of cells along that pathway must either (1) themselves evaporate water, in which case they would be separated from the adjacent airspaces by a very short diffusion path; (2) be in equilibrium with the vapor in the adjacent airspaces; or (3) not exchange water at all with the airspaces, in which case all evaporation must occur from the proximal evaporating site. In any of these scenarios, the water potential of the CWS at the evaporating site cannot be very far from that of the vapor in the adjacent airspaces.

References

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