Evaporation from Micro-Reservoirs
Supplementary Information

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APPENDIX I - **Geometrical determination of meniscus shape**

The geometrical definitions defining the shape of a meniscus in an expanding reservoir ($2\alpha > \pi/2$) are shown in figure S1. The same definitions associated with cylindrical ($2\alpha = \pi/2$) or contracting ($2\alpha < \pi/2$) reservoirs are very similar and not shown here. The reservoir walls can be described by the line $r = F(z) = a_1 z + a_2$. Additional geometric information for this system are the angles

$$\beta_1 = 2\alpha - \frac{\pi}{2}, \qquad \textbf{(1)}$$

$$\beta_2 = \pi - 2\alpha - \theta_2, \qquad \textbf{(2)}$$

$$\beta_3 = 2\alpha + \theta_2 - \frac{\pi}{2}, \qquad \textbf{(3)}$$

as shown in figure S1.

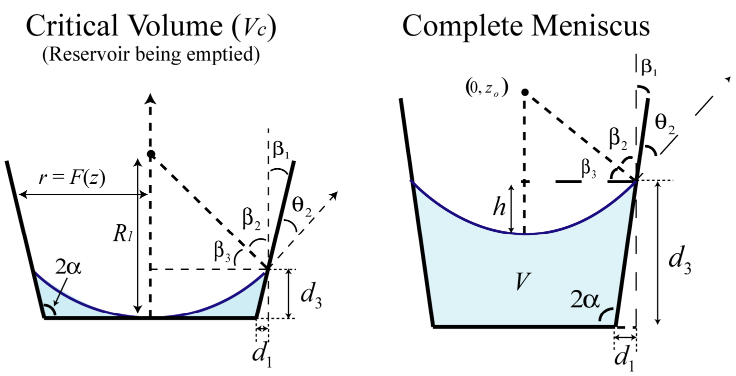

Figure S1. Geometries used in the calculation of the meniscus shape.

Critical volume (V_c)

The critical volume is the volume at which the meniscus will rupture from a continuous state to form a moving contact line. This event occurs at the liquid volume for which the bottom of the meniscus reaches the reservoir floor ($z_o = R_1$), and depends only on the reservoir geometry and θ_2. The first radius of curvature for this system can be found by equating two relationships for the z-position of the meniscus intersection with the reservoir sidewalls,

$$d_3 = \frac{2R_1\cos(\beta_3) - D_1}{2\tan(\beta_1)}, \quad \textbf{(4)}$$

$$d_3 = R_1\left(1 - \sin(\beta_3)\right), \quad \textbf{(5)}$$

which leads to

$$R_1 = \frac{D_1}{2\left(\cos(\beta_3) + \tan(\beta_1)\sin(\beta_3) - \tan(\beta_1)\right)}. \quad \textbf{(6)}$$

From this value of R_1, the critical volume can be obtained by $V_c = V_2 - V_1$, where

$$V_2 = \pi\int_0^{d_3} F^2 dz = \frac{\pi}{3a_1}\left((a_1 d_3 + a_2)^3 - a_2^3\right), \quad \textbf{(7)}$$

$$V_1 = \frac{\pi}{6}h\left(3R_m^2 + h^2\right), \quad \textbf{(8)}$$

using the relationships $R_m = R_1\cos(\beta_3)$ and $h = R_1\left(1 - \sin(\beta_3)\right)$.

Complete Mensiscus

This case arises when $V > V_c$ and $d_3 < H$. From the trigonometric relationships

$$d_1 = R_1\cos(\beta_3), \quad \textbf{(9)}$$

$$d_3 = \frac{d_1}{\tan(\beta_1)}, \quad \textbf{(10)}$$

we solve the equation $V = V_2 - V_1$ for R_1, where V_2 and V_1 are given above. The explicit solution for R_1 is very complicated and will not be repeated here. The center of curvature for the meniscus will then be $(0, z_o)$, where $z_o = d_3 + R_1\sin(\beta_3)$.

Incomplete Meniscus

This case arises when $0 < V < V_c$ (as well as the additional criteria that $d_3 < H$). No analytical solution can be found for R_1 for this geometry, thus the solution must be found iteratively. Using the trigonometric relationships

$$d_2 = R_1\sin(\beta_3), \quad \textbf{(11)}$$

$$d_3 = R_1\cos(\theta_1) - d_2, \quad \textbf{(12)}$$

$$d_1 = d_3\tan(\beta_1), \quad \textbf{(13)}$$

the equation $V = V_2 - V_1$ is solved for R_1, where V_2 is given above, and V_1 may be written as

$$V_1 = \pi \int_0^{d_3} F^2 dz = \pi \int_0^{d_3} \left(r_o + (R_1^2 - (z - z_o)^2)^{\frac{1}{2}} \right)^2 dz\,. \tag{14}$$

Here, r_o and z_o are the center of curvature of the meniscus, and can be found via

$$r_o = \frac{D_1}{2} + d_1 - R_1 \cos(\beta_3)\,, \tag{15}$$

$$z_o = d_3 + d_2\,. \tag{16}$$

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APPENDIX II – one dimensional diffusion in a reservoir

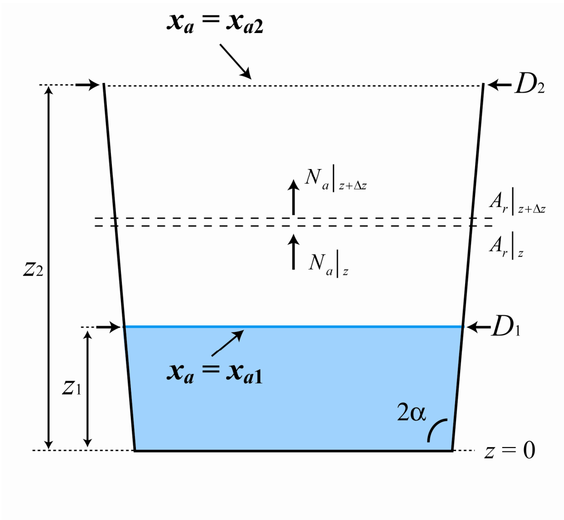

Figure S2. Geometric parameters describing the system.

Consider a well with height $H = z_2$ and liquid level positioned at $z = z_1$ with upper diameter (D_2) and diameter at the meniscus (D_1) as shown in Figure S2. Assuming the average interface position (z_1) is not moving very fast, we can perform a quasi steady-state mass balance between the plane z and $z + \Delta z$ to find

$$\frac{d}{dz}(A_r N_a) = 0, \tag{17}$$

where A_r is the cross-sectional area of the reservoir and N_a is the molar flux of water vapor in the z-direction. Using Fick's first law of binary diffusion, we can also express the molar flux as

$$N_a = -\frac{c\mathcal{D}}{1 - x_a}\frac{dx_a}{dz}. \tag{18}$$

Where c is the molar concentration of the gas phase, $\mathcal{D}$ is the diffusion coefficient of water vapor, and $x_a = x_a(z)$ is the mole fraction of water vapor. Again, the reservoir walls can be described by the line $r = F(z) = a_1 z + a_2$, thus A_r can be expressed as a function of z

$$A_r = \pi(a_1 z + a_2)^2. \tag{19}$$

Assuming that both the molar concentration and diffusion coefficient are constant with dilute values of x_a, substitution of equations (18) and (19) into equation (17) and simpifying yields

$$\frac{d}{dz}\left(\frac{(a_1 z + a_2)^2}{1 - x_a}\frac{dx_a}{dz}\right) = 0. \tag{20}$$

Integration of equation (20) twice with respect to z yields

$$\ln(1 - x_a) = \frac{C_1}{a_1(a_1 z + a_2)} + C_2. \tag{21}$$

The boundary conditions for this problem are then

$$x_a = x_{a1} \ \text{ at } \ z = z_1, \tag{22}$$
$$x_a = x_{a2} \ \text{ at } \ z = z_2, \tag{23}$$

where x_{a1} and x_{a2} represent the mole fraction of water vapor at the air/liquid interface and reservoir entrance, respectively. Noting that $D_1 = 2(a_1z_1+a_2)$ and $D_2 = 2(a_1z_2+a_2)$, the mole fraction distribution can then be found as

$$x_a = 1 - \exp(Y), \tag{24}$$

where

$$Y = \frac{D_1 D_2}{2(D_2 - D_1)(a_1 z + a_2)}\ln\left(\frac{1 - x_{a1}}{1 - x_{a2}}\right) + \frac{D_1 \ln(1 - x_{a2}) - D_1 \ln(1 - x_{a1})}{D_2 - D_1}. \tag{25}$$

Eqn. (25) can be used with Eqn. (18) to calculate the overall one-dimensional evaporation rates. Figure S3 displays the liquid evaporation rate $Q_e = N_a A_r M_w / \rho$ as a function of the dihedral angle 2α for several different reservoir geometries, where M_w and ρ correspond to the molecular weight and density of water, respectively. It can be seen that for all reservoir geometries, Q_e increases with increasing α and increasing values of D_1, consistent with the results of this study.

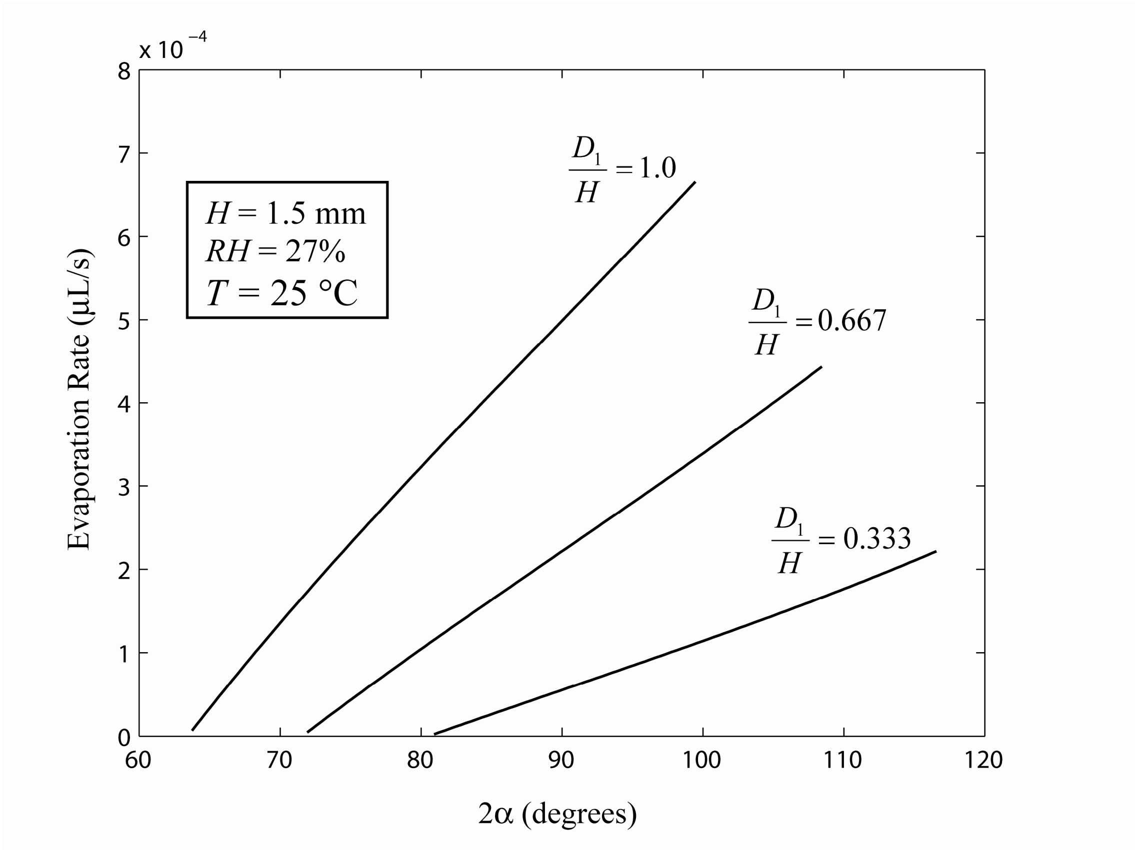

Figure S3. Overall evaporation rate (Q_e) vs. the dihedral angle 2α for three different reservoirs with varying values of D_1.