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

\[
\beta_1 = 2\alpha - \frac{\pi}{2}, \quad (1)
\]
\[
\beta_2 = \pi - 2\alpha - \theta_2, \quad (2)
\]
\[
\beta_3 = 2\alpha + \theta_2 - \frac{\pi}{2}, \quad (3)
\]
as shown in figure S1.

![Figure S1](image)

**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 \((z_0 = R_1)\), and depends only on the reservoir geometry and \(\theta_2\). 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,
\[ d_3 = \frac{2R_1 \cos(\beta_3) - D_1}{2 \tan(\beta_1)}, \]  
\[ d_3 = R_1(1 - \sin(\beta_3)), \]  
which leads to
\[ R_1 = \frac{D_1}{2(\cos(\beta_3) + \tan(\beta_1) \sin(\beta_3) - \tan(\beta_1))}. \]

From this value of \( R_1 \), the critical volume can be obtained by \( V_c = V_2 - V_1 \), where
\[ V_2 = \pi \int_0^{d_1} F^2 dz = \frac{\pi}{3a_1} \left( a_1 d_3 + a_2 \right)^3 - a_2^3, \]  
\[ V_1 = \frac{\pi}{6} h(3R_m^2 + h^2), \]
using the relationships \( R_m = R_1 \cos(\beta_3) \) and \( h = R_1(1 - \sin(\beta_3)) \).

**Complete Meniscus**

This case arises when \( V > V_c \) and \( d_3 < H \). From the trigonometric relationships
\[ d_1 = R_1 \cos(\beta_3), \]  
\[ d_3 = \frac{d_1}{\tan(\beta_1)}, \]
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 \((0, z_0)\), where \( z_0 = d_3 + R_1 \sin(\beta_3) \).

**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
\[ d_2 = R_1 \sin(\beta_3), \]  
\[ d_3 = R_1 \cos(\theta_1) - d_2, \]  
\[ d_1 = d_3 \tan(\beta_1), \]
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
\[
V_1 = \pi \int_0^{d_1} F^2 \, dz = \pi \int_0^{d_1} \left( r_o + (R_i^2 - (z - z_o)^2)^{\frac{1}{2}} \right)^2 \, dz. \tag{14}
\]

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

\[
r_o = \frac{D_1}{2} + d_1 - R_i \cos(\beta), \tag{15}
\]
\[
z_o = d_3 + d_2. \tag{16}
\]
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APPENDIX II – one dimensional diffusion in a reservoir

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

$$d \left( A_r N_a \right) / dz = 0 ,$$

(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

$$N_a = - c \mathcal{D} \frac{dx_a}{dz} .$$

(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 $z$

$$A_r = \pi (a_1 z + a_2)^2 .$$

(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 simplifying yields

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

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

\[
\ln(1 - x_a) = \frac{C_1}{a_1(a_1 z + a_2)} + C_2.
\]  \hfill (21)

The boundary conditions for this problem are then

\[
\begin{align*}
x_a &= x_{a1} \text{ at } z = z_1, \quad \text{(22)} \\
x_a &= x_{a2} \text{ at } z = z_2, \quad \text{(23)}
\end{align*}
\]

where \( x_{a1} \) and \( x_{a2} \) represent the mole fraction of water vapor at the air/liquid interface and reservoir entrance, respectively. Noting that \( D_1 = 2(a_1 z_1 + a_2) \) and \( D_2 = 2(a_1 z_2 + a_2) \), the mole fraction distribution can then be found as

\[
x_a = 1 - \exp(Y),
\]  \hfill (24)

where

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

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

$H = 1.5$ mm  
$\text{RH} = 27\%$  
$T = 25\,^\circ\text{C}$