SUPPLEMENTAL INFORMATION

The transient model derivation is provided below. The model was derived to be applicable to other diffusive sampling scenarios (including e.g. solid-phase microextraction, where r_1 would be non-zero), but is equally suited to the current application. The governing equations are:

Concentration in the gas phase within the void space $c_g(r,t)$;

$$\frac{\partial c_g}{\partial t} - D_{air}\left[\frac{\partial^2 c_g}{\partial r^2} + \frac{1}{r}\frac{\partial c_g}{\partial r}\right] = 0 \qquad 0 \le r < r_2 \tag{S1}$$

Concentration in the soil vapor surrounding the void space $c_s(r,t)$;

$$\frac{\partial c_s}{\partial t} - D_{eff}\left[\frac{\partial^2 c_s}{\partial r^2} + \frac{1}{r}\frac{\partial c_s}{\partial r}\right] = 0 \qquad r_2 \le r < r_3 \tag{S2}$$

with the following initial and boundary conditions:

$$c_g(r_2,t) = c_s(r_2,t) \tag{S3}$$

$$c_g(r,0) = 0 \tag{S4}$$

$$c_s(r,0) = c_{s_0} \tag{S5}$$

$$\frac{\partial c_g}{\partial r}(r_1,t) = 0 \tag{S6}$$

$$\frac{\partial c_s}{\partial r}(r_3,t) = 0 \tag{S7}$$

$$D_{air}\frac{\partial c_g}{\partial r}(r_2,t) = D_{eff}\frac{\partial c_s}{\partial r}(r_2,t) \tag{S8}$$

Applying the Laplace transform to Equation (S1) to transform the time derivative in order to convert the partial differential equation (PDE) into an ordinary differential equation (ODE):

$$L\left[c_g(r,t)\right] = \bar{c}_g(r,p) \tag{S9}$$

$$L\left[\frac{\partial c_g}{\partial t}\right] = -c_g(r,0) + p\bar{c}_g(r,p) = p\bar{c}_g(r,p) \tag{S10}$$

$$D_{air}\left[\frac{\partial^2 \bar{c}_g}{\partial r^2}+\frac{1}{r}\frac{\partial \bar{c}_g}{\partial r}\right]-p\bar{c}_g=0 \tag{S11}$$

where p is the Laplace transform variable and is complex-valued.

Applying the Laplace transform to Equation (S2):

$$L[c_s(r,t)]=\bar{c}_s(r,p) \tag{S12}$$

$$L\left[\frac{\partial c_s}{\partial t}\right]=-c_s(r,0)+p\bar{c}_s(r,p)=\ -c_{s_0}+p\bar{c}_s(r,p) \tag{S13}$$

$$D_{eff}\left[\frac{\partial^2 \bar{c}_s}{\partial r^2}+\frac{1}{r}\frac{\partial \bar{c}_s}{\partial r}\right]-p\bar{c}_s=-c_{s_0} \tag{S14}$$

Applying the Laplace transform to initial and boundary Equations (S3), (S6), (S7) and (S8),

$$\bar{c}_g(r_2,p)=\bar{c}_s(r_2,p) \tag{S15}$$

$$L\left[\frac{\partial c_g}{\partial r}(r_1,t)\right]=\int_0^\infty \frac{\partial c_g}{\partial r}(r_1,t)\ e^{-pt}dt=\frac{\partial}{\partial r}\int_0^\infty c_g(r_1,t)\ e^{-pt}dt \tag{S16}$$

$$=\frac{\partial \bar{c}_g}{\partial r}(r_1,p)=0$$

$$L\left[\frac{\partial c_s}{\partial r}(r_3,t)\right]=\frac{\partial \bar{c}_s}{\partial r}(r_3,p)=0 \tag{S17}$$

$$D_{air}\frac{\partial \bar{c}_g}{\partial r}(r_2,p)=D_{eff}\frac{\partial \bar{c}_s}{\partial r}(r_2,p) \tag{S18}$$

The transformed governing equation (Equation S11) is a linear, second-order homogeneous ODE that has a solution of the general form:

$$\bar{c}_c=AI_0\left(q_g r\right)+BK_0(q_g r) \tag{S19}$$

where ${q_g}^2 = \left|-\frac{p}{D_{air}}\right| = \frac{p}{D_{air}}, if\ p > 0$, I_0 is the modified Bessel function I of order zero and K_0 is the modified Bessel function of K of order zero.

Differentiating $\bar{c}_g$ with respect to r, we obtain

$$\frac{\partial \bar{c}_g}{\partial r} = q_g A I_1(q_g r) - q_g B K_1(q_g r) \tag{S20}$$

where I_1 is the modified Bessel function I of order one and K_1 is the modified Bessel function of K of order one. Using Equation (S16),

$$q_g A I_1(q_g r_1) - q_g B K_1(q_g r_1) = 0 \tag{S21}$$

$$A = \frac{B K_1(q_g r_1)}{I_1(q_g r_1)} \tag{S22}$$

$$\bar{c}_c = B\left[\frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_0(q_g r) + K_0(q_g r)\right]. \tag{S23}$$

The general form solution of Equation (S14) is

$$\bar{c}_s = \frac{c_{s_0}}{p} + E I_0(q_s r) + F K_0(q_s r) \tag{S24}$$

where ${q_s}^2 = \frac{p}{D_s}$.

Differentiating $\bar{c}_s$ with respect to r, we obtain

$$\frac{\partial \bar{c}_s}{\partial r} = q_s E I_1(q_s r) - q_s F K_1(q_s r) \tag{S25}$$

and using Equation (S17),

$$q_s E I_1(q_s r_3) - q_s F K_1(q_s r_3) = 0 \tag{S26}$$

$$E = \frac{FK_1(q_s r_3)}{I_1(q_s r_3)} \tag{S27}$$

$$\bar{c}_s = \frac{c_{s_0}}{p} + F\left[\frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r) + K_0(q_s r)\right]. \tag{S28}$$

In order to solve the constant F based on Equation (S18), differentiate $\bar{c}_s$ with respect to r again

$$\frac{\partial \bar{c}_s}{\partial r} = F q_s \frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_1(q_s r) - F q_s K_1(q_s r) \tag{S29}$$

and do the same to Equation (S23),

$$\frac{\partial \bar{c}_g}{\partial r} = B q_g \frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_1(q_g r) - B q_g K_1(q_g r). \tag{S30}$$

Substituting Equation (S18) with the two equations above,

$$F D_s q_s [\frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_1(q_s r_2) - K_1(q_s r_2)] = B D_{air} q_g [\frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_1(q_g r_2) - K_1(q_g r_2)] \tag{S31}$$

$$F = B \frac{\overbrace{D_{air} q_g}^{\varphi_3}}{D_{eff} q_s} \frac{\overbrace{[\frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_1(q_g r_2) - K_1(q_g r_2)]}^{\varphi_1}}{\underbrace{[\frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_1(q_s r_2) - K_1(q_s r_2)]}_{\varphi_2}}$$

$$F = B \frac{\varphi_1 \varphi_3}{\varphi_2}$$

$$\therefore \quad \bar{c}_s = \frac{c_{s_0}}{p} + B \frac{\varphi_1 \varphi_3}{\varphi_2}\left[\frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r) + K_0(q_s r)\right]. \tag{S32}$$

In order to determine the constant B in Equation (S23) and (S32), Equation (S15) is applied:

$$B\left[\frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_0(q_g r_2) + K_0(q_g r_2)\right] = \frac{c_{s_0}}{p} + B\,\frac{\varphi_1\varphi_3}{\varphi_2}\left[\frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r_2) + K_0(q_s r_2)\right]$$

$$B = \frac{c_{s_0}}{p}\{\underbrace{\left[\frac{K_1(q_c r_1)}{I_1(q_c r_1)} I_0(g r_2) + K_0(q_g r_2)\right]}_{\varphi_4} - \frac{\varphi_1\varphi_3}{\varphi_2}\underbrace{\left[\frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r_2) + K_0(q_s r_2)\right]}_{\varphi_5}\}^{-1}$$

$$B = \frac{c_{s_0}}{p}\frac{1}{\varphi_4 - \frac{\varphi_1\varphi_3\varphi_5}{\varphi_2}} = \frac{c_{s_0}}{p}\frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}. \tag{S33}$$

Finally, arranging the constant B into the governing equations, we obtain

$$\bar{c}_g = \frac{c_{s_0}}{p}\frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}\left[\frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_0(q_g r) + K_0(q_g r)\right] \tag{S34}$$

for $0 \le r < r_2$

$$\bar{c}_s = \frac{c_{s_0}}{p} + \kappa\frac{c_{s_0}}{p}\frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}\frac{\varphi_1\varphi_3}{\varphi_2}\left[\frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r) + K_0(q_s r)\right] \tag{S35}$$

for $r_2 \le r < r_3$

To find the total mass $M(t)$ per unit area in the thin film when $r = r_2$ as a function of time, we have:

$$M(t) = D_c \int_0^t \left.\frac{\partial c_g}{\partial r}\right|_{r=r_2} \partial\tau \tag{S36}$$

Therefore,

$$\bar{M}(p) = \frac{D_{air}}{p}\left.\frac{\partial \bar{c}_g}{\partial r}\right|_{r=r_2} \tag{S37}$$

$$\text{or } \bar{M}(p) = \frac{D_{eff}}{p}\frac{\partial \bar{c}_s}{\partial r}\bigg|_{r=r_2} \tag{S38}$$

Differentiating Equation (S34) with respect to r,

$$\frac{\partial \bar{c}_g}{\partial r} = \frac{c_{s_0}}{p}\frac{\varphi_2}{\varphi_2\varphi_4-\varphi_1\varphi_3\varphi_5}\left[\frac{K_1(q_g r_1)}{I_1(q_g r_1)}q_g I_1(q_g r) - q_g K_1(q_g r)\right] \tag{S39}$$

And then rearranging the mass function, we obtain,

$$\begin{aligned}\bar{M}(p) &= \frac{D_{air}c_{s_0}}{p^2}q_g\frac{\varphi_2}{\varphi_2\varphi_4-\varphi_1\varphi_3\varphi_5}\left[\frac{K_1(q_g r_1)}{I_1(q_g r_1)}I_1(q_g r_2) - K_1(q_g r_2)\right] \\ &= \frac{D_{air}c_{s_0}}{p^2}q_g\frac{\varphi_2\varphi_1}{\varphi_2\varphi_4-\varphi_1\varphi_3\varphi_5}.\end{aligned} \tag{S40}$$

Equation (S40) allows the calculation of the mass in the void space based on the mass flux across the borehole wall from the void side.

Again, differentiating Equation (S35) with respect to r,

$$\frac{\partial \bar{c}_s}{\partial r} = \frac{c_{s_0}}{p}\frac{\varphi_2}{\varphi_2\varphi_4-\varphi_1\varphi_3\varphi_5}\frac{\varphi_1\varphi_3}{\varphi_2}\left[\frac{K_1(q_s r_3)}{I_1(q_s r_3)}q_s I_1(q_s r) - q_s K_1(q_s r)\right]$$

$$\begin{aligned}\bar{M}(p) &= \frac{D_s c_{s_0}}{p^2}q_s\frac{\varphi_2}{\varphi_2\varphi_4-\varphi_1\varphi_3\varphi_5}\frac{\varphi_1\varphi_3}{\varphi_2}\left[\frac{K_1(q_s r_3)}{I_1(q_s r_3)}I_1(q_s r_2) - K_1(q_s r_2)\right] \\ &= \frac{D_s c_{s_0}}{p^2}q_s\frac{\varphi_2\varphi_1\varphi_3}{\varphi_2\varphi_4-\varphi_1\varphi_3\varphi_5}.\end{aligned} \tag{S41}$$

Equation (S41) allows the calculation of the mass in the void space based on the mass flux across the borehole wall from the soil side.

The inverse Laplace transforms of Equation (S34), (S35), (S40) and (S41) are computed numerically using the algorithm developed by DeHoog et al.[37].

Bessel functions

The modified Bessel functions I_α and K_α used for Equations (S34), (S35), (S40) and (S41) are defined by:

$$I_\alpha(x) = i^{-\alpha} J_\alpha(ix) = \sum_{m=0}^{\infty} \frac{1}{m!\,\Gamma(m+\alpha+1)} \left(\frac{x}{2}\right)^{2m+\alpha} \tag{S42}$$

$$K_\alpha(x) = \frac{\pi}{2} \frac{I_{-\alpha}(x) - I_\alpha(x)}{\sin(\alpha\pi)} = \frac{\pi}{2} i^{\alpha+1} H_\alpha^{(1)}(ix) = \frac{\pi}{2} (-i)^{\alpha+1} H_\alpha^{(2)}(-ix) \tag{S43}$$

For this application, the axis of symmetry at r = r_1 was assigned a very small radius (10^{-6} cm). The radius of the borehole or void space is assigned to be r_2. Nominal 1-inch (2.54 cm) and 4-inch (10.2 cm) diameter holes were considered because these are common for hand tools used in passive sampler deployment. The radial distance at which concentrations remain essentially unaffected throughout the passive sampling duration (r_3) was assigned to be 1 m. The sensitivity of the value assumed for r_3 was evaluated using the steady-state model. Where needed for calculating the volume of the void space, the vertical height of the void space was assumed to be 10 cm.