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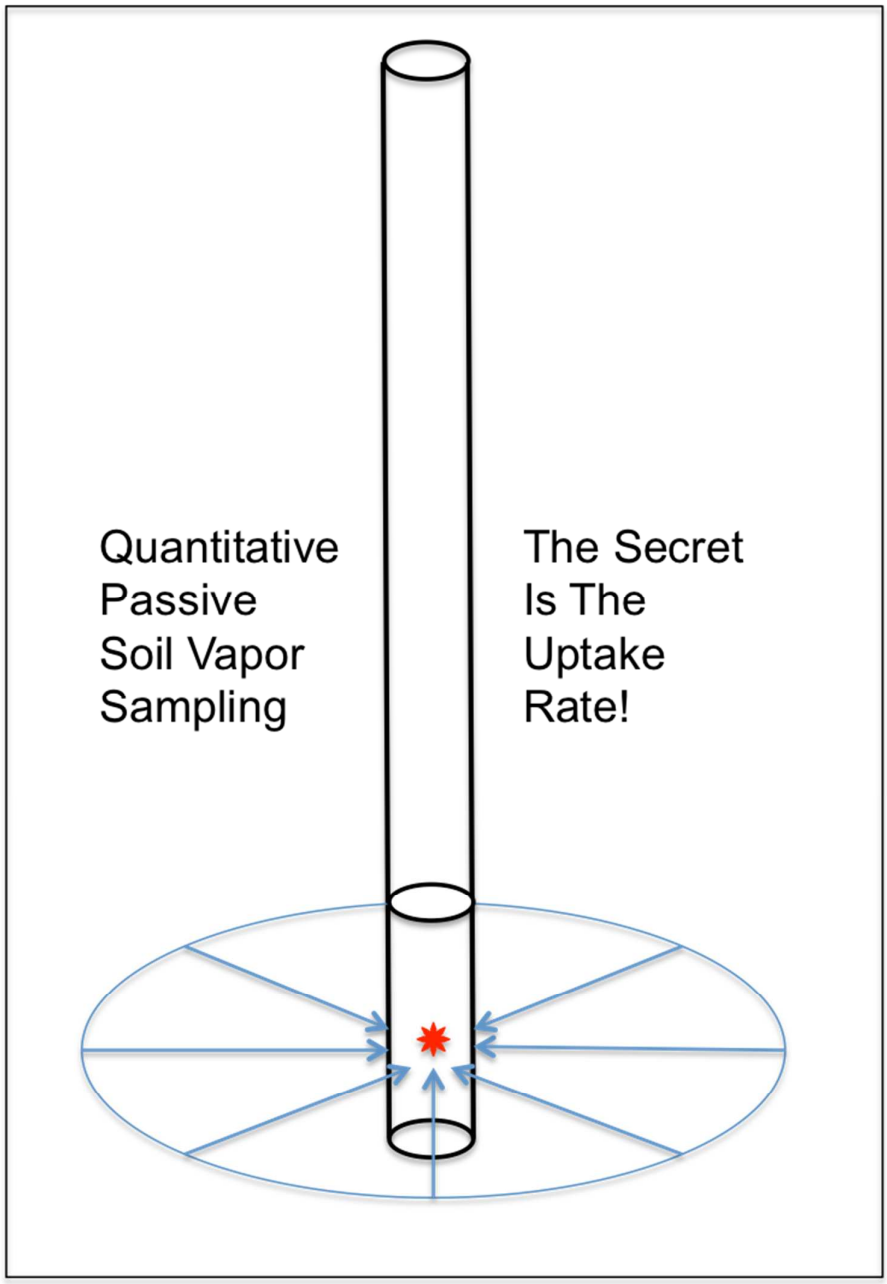

Environmental Impact Statement
To accompany the submission of the draft paper entitled: Quantitative Passive Soil Vapor Sampling for VOCs – Part 1: Theory
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Conventional soil vapor sampling for VOC analysis can be time-consuming if quality control measures are implemented to verify the absence of leaks and sample collection may be impractical in low-permeability soils. Passive adsorptive sampling has been an alternative to conventional active sampling for decades, but the uptake rate of the sampler has never been well understood or controlled, so passive sampling has been considered a qualitative or semi-quantitative method. This paper provides a theoretical framework using a combination of steady-state and transient mathematical models to support an improved design for passive diffusive samplers for soil vapor monitoring, which minimizes the starvation effect, maximizes the sensitivity and provides quantitative concentration measurements for a wide range of soil types.

Quantitative Passive Soil Vapor Sampling for VOCs: Theory

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ABSTRACT

Volatile organic compounds are the primary chemicals of concern at many contaminated sites and soil vapor sampling and analysis is a valuable tool for assessing the nature and extent of contamination. Soil gas samples are typically collected by applying vacuum to a probe in order to collect a whole-gas sample, or by drawing gas through a tube filled with an adsorbent (active sampling). There are challenges associated with flow and vacuum levels in low permeability materials, and leak prevention and detection during active sample collection can be cumbersome. Passive sampling has been available as an alternative to conventional gas sample collection for decades, but quantitative relationships between the mass of chemicals sorbed, the soil vapor concentrations, and the sampling time have not been established. This paper presents transient and steady-state mathematical models of radial vapor diffusion to a drilled hole and considerations for passive sampler sensitivity and practical sampling durations. The results indicate that uptake rates in the range of 1 to 0.1 mL/min will minimize the starvation effect for most soil moisture conditions and provide adequate sensitivity for human health risk assessment with a practical sampling duration. This new knowledge provides a basis for improved passive soil vapour sampler design.

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INTRODUCTION

Knowledge of the spatial distribution of volatile organic compound (VOC) vapors in the subsurface is essential for assessing human health risks associated with subsurface vapor migration and intrusion to indoor air, as well as for monitoring the performance of related mitigation and remediation systems (sub-slab venting, soil vapor extraction, multiphase extraction, air sparging, bioventing, etc.). There are a wide variety of different methods and guidance available for soil vapor sampling and analysis[1,2,3,4,5,6,7,8], but few comparative studies that evaluate the relative performance between various active soil vapor sampling methods[9]. Currently, the most common method for collection and analysis of sub-slab or soil vapor samples during vapor intrusion investigations in North America (and to varying degrees elsewhere) is an active method whereby soil gas is drawn into an evacuated, passivated stainless steel container (e.g., SilcoTek™ SilcoCan® or Summa® canisters) through a flow controller, followed by shipment to a laboratory for analysis by EPA Method TO-15[10]. Sampling protocols for canisters are complicated because subsurface permeabilities and soil vapor concentrations can both vary over many orders of magnitude and care is needed to prevent and document the absence of leaks of atmospheric air into the sample train[11]. Passive sampling does not involve applying a vacuum to draw a volume of gas as a sample, and with no induced pressure gradient, the potential for low bias attributable to leakage is dramatically reduced or eliminated.

At the present time, there are varying opinions regarding the reliability of soil vapor sampling for assessing human health risks posed by VOCs. For example, the ITRC vapor intrusion guidance[6] states: “Soil gas data are recommended over other data, specifically soil matrix and groundwater data, because soil gas data represent a direct measurement of the contaminant that can potentially migrate into indoor air”. However, the empirical database of soil vapor and indoor air

concentrations compiled by the USEPA[12] shows a worse correlation between soil vapor and indoor air VOC concentrations than the corresponding comparison between groundwater and indoor air VOC concentrations. It is not clear what role sampling errors or biases play in the relatively poor correlation between soil vapor and indoor air concentrations; however, protocols using passive sampling devices are considerably simpler than active sampling protocols, and simpler protocols are likely to reduce variability attributable to operator error, which provides an incentive to advance the science of passive soil vapor sampling.

Passive sampling is an alternative approach with several potential advantages over conventional whole-gas sampling, including simpler protocols, smaller size for ease of shipping and handling, and lower overall cost (including the labor cost for sample collection). Much of the historic application of passive sampling has been indoor and outdoor air quality monitoring and industrial hygiene applications[13,14,15,16,17]. Several passive soil gas sampling methods have been developed over the past quarter century since the earliest efforts[18], including Petrex tubes[19,20], EMFLUX® cartridges[21], Beacon B-Sure Sample Collection Kits™[22] and Gore™ Modules (formerly known as the Gore-Sorber®)[23]. Each of these methods provides results in units of the mass adsorbed over the duration of the sample; however, the correlation between the mass adsorbed and the soil vapor concentration has not been quantitatively established[24,21,23]. Concentration values are needed for comparison to risk-based screening levels when assessing human health risks via vapor intrusion, so many regulatory guidance documents caution that passive soil gas sampling should only be used as a qualitative or semi-quantitative screening tool[24,25]. Overcoming this limitation was the primary motivation of this research.

THEORY

Quantitative passive samplers are of two general varieties: equilibrium samplers (where the sampler equilibrates with the surrounding medium), and kinetic samplers (where the sampler is designed to have a constant uptake rate throughout the sample duration). This paper deals exclusively with kinetic passive samplers because the focus of this research was human health risk assessment associated with subsurface vapour intrusion to indoor air, where time-weighted average concentrations are preferred.

The basic principles of operation for quantitative passive samplers are as follows. Each device is supplied by the laboratory certified clean and sealed in air-tight packing. The sampler is exposed to the air or soil gas being investigated for a measured amount of time (t), during which VOCs diffuse or permeate into the device from the surrounding gas or air in response to the chemical potential (i.e. concentration) gradient[26]. A certain mass of VOCs is trapped by the sorptive medium within the device. After sampling, the device is shipped in an air-tight container to the analytical laboratory, where the mass sorbed is quantified. The time-weighted average (TWA) concentration (c) of a particular analyte in the medium being sampled is then calculated as follows[26]:

$$c = \frac{Mk}{t} \qquad (1)$$

where:

c = TWA concentration of a particular analyte in the sampled air [μg/m^3]

M = mass of analyte on the sorbent, blank-corrected if needed [pg]

k = calibration constant [min/mL]

t = sampling time [min]

(note that there are two offsetting conversion factors from pg to μg and mL to m^3)

The reciprocal of the calibration constant (1/k) is referred to as the uptake rate (UR), which has units of mL/min. Even though the uptake rate has units of [volume/time], it is important to

emphasize that it does not represent a real flow; rather, it is simply a number equivalent to the flow that would produce the same mass loading on an active adsorptive sampler that had air pulled through it for the same *c* and *t*. The mass adsorbed and the sample duration can both be measured very accurately (commonly within 5% to 15%), so the accuracy of the uptake rate is the key factor controlling the accuracy of the calculated concentration. Quantitative kinetic passive samplers are designed to control the uptake rate of chemicals during sampling using well-defined barriers between the sorbent and the media being sampled of a fixed cross-sectional area and known diffusion or permeation characteristics for the chemicals of interest. The uptake rates of kinetic samplers are typically measured in controlled exposure chamber experiments or calculated from first principles based on the free-air diffusion coefficient or permeation rate of the particular compound of interest[27,28,29,30,31,32,33].

High uptake rates allow lower concentrations to be quantified with shorter sample durations, which can be an advantage in some instances. Lower uptake rates reduce the risk of the "starvation effect", which occurs when the rate-limiting step is transport of chemicals to the sampler instead of the uptake rate of the sampler itself. This situation results in a reduction in vapor concentrations near the sampler, and a negative bias in the calculated passive sampler concentrations compared to the conditions under which the passive sampler uptake rate was measured. Advection from wind and ventilation during indoor and outdoor air sampling is often sufficient to minimize or eliminate the starvation effect completely. For soil gas sampling, advection is likely to be minimal and the rate of contaminant vapor replenishment in the gas-filled void space surrounding the sampler is likely to be dominated by diffusive transport, which is the focus of the mathematical models presented in this paper. The uptake rate of a passive sampler can be increased or decreased by design, and the calculations presented here support the selection of appropriate uptake rates for quantitative passive soil vapor sampling.

Conceptual Model For Quantitative Passive Soil Vapor Sampling

Passive soil vapor sampling is usually performed by drilling a hole in the ground, removing soil, placing a passive sampler in the void-space created by drilling, sealing the hole from the atmosphere for the duration of the sample, then retrieving the sampler and backfilling or grouting the hole. A simple conceptual model of this scenario is as follows:

- Immediately after the hole is drilled and the soil is removed, the void space fills with air. Assuming atmospheric air can enter the void space with less resistance than gas flowing through the surrounding soil, the initial concentration of vapors inside the void space would be expected to be much lower than that in the surrounding soil, and at worst could be assumed to be essentially zero (if atmospheric air is contaminant-free).
- In most cases, passive samplers are placed in the borehole and the space above the sampler is sealed without purging to remove atmospheric air from the void space around the sampler (purging is feasible during passive soil vapor sampling, but not common).
- During the period of sampling, vapors diffuse into the void space from the surrounding soil. If the void space is long relative to its diameter and short enough that the geologic properties and vapor concentrations are relatively uniform over the vertical interval of the void space, then the diffusion will be essentially radially symmetric (this has been assumed for the remainder of this paper).
- The rate of diffusive mass transport into the void space over time will depend on the concentration gradient and effective diffusion coefficient, and will gradually diminish as the concentration in the void space increases toward equilibration with the surrounding soil. If a passive sampler is present in the void space, the concentration in the void space will remain somewhat below the concentration in the surrounding soil depending on the uptake rate of the passive sampler.

- If the uptake rate of the sampler is small relative to the rate of diffusion into the void space (a goal if the starvation effect is to be small), then the steady-state concentration in the void space will be similar to the concentration in the surrounding soil and passive sampling will be able to provide a quantitative measure of the soil vapor concentration.

Mathematical Modeling of Quantitative Passive Sampling

Passive soil vapor sampling involves transport of vapors through the soil surrounding the drillhole into the void space in which the sampler is deployed, diffusion through the air inside the void-space, and uptake by the sampler. The free-air diffusion coefficient through the air inside the void space will be roughly one to several orders of magnitude higher than the effective diffusion coefficient in the surrounding soil, so vapor transport through the air inside the void space is not expected to be the rate-limiting step. This allows the mathematical analysis to focus on two components: the rate of vapor diffusion into the void space (the "diffusive delivery rate", or DDR) and the rate of vapor uptake by the passive sampler ("passive sampler uptake rate" or UR). Understanding the rate of diffusion of vapors into the void space is necessary to design an uptake rate for the passive sampler that is low enough to minimize the starvation effect. However, the uptake rate must also be high enough to provide adequate sensitivity (ability to meet target reporting limits with an acceptable sampling duration), so both constraints must be considered.

Influence of Soil Moisture on the Effective Diffusion Coefficient in Soil

The effective diffusion coefficient depends strongly on the total porosity (volume of pores divided by total volume of soil) and water-filled porosity (volume of water divided by total volume of soil, otherwise known as the volumetric water content). Understanding this relationship is helpful for context in the theory of passive soil gas sampling if diffusion is the

main process delivering vapors to the void space in which the sampler is deployed. Johnson and Ettinger[34] adopted the Millington-Quirk[35] equation in their well-known model for assessing the potential for subsurface vapor intrusion to indoor air. Their formulation of the effective diffusion coefficient also includes diffusion in the aqueous phase, assuming the Millington-Quirk empirical relationship is equally valid for both the gas and water phases:

$$D_{eff} = D_{air}\frac{\theta_a^{10/3}}{\theta_T^2} + \frac{D_w}{H}\frac{\theta_w^{10/3}}{\theta_T^2} \qquad (2)$$

where the parameters are defined in Table 1. Parameter values used for all calculations in this paper were selected to be representative of trichloroethene (TCE), one of the most common VOCs of interest for human health risk assessment associated with contaminated land. Many other VOCs have similar diffusion coefficients and Henry's Law constants, so the general trend applies for a range of VOCs of interest for human health risk assessments. Equation (2) was used to calculate D_{eff} for both the transient and steady-state models in this paper.

TABLE 1

A series of calculations were performed using Equation (2) and the parameter values in Table 1 to show the relationship between the effective diffusion coefficient and the water-filled porosity. The calculated D_{eff} values span a range from about 0.01 to about 0.00001 cm^2/s over a range of water-filled porosities from 1% to 36% in a soil with 36% porosity (Figure 1). These values are indeed much lower than the free-air diffusion coefficient (0.069 cm^2/s), which supports the assumption that diffusion through the air in the void space in which the sampler is deployed is not rate-limiting.

FIGURE 1

Two models (transient and steady-state) are presented to simulate the passive sampling process.

TRANSIENT MODEL

The conceptualization for a transient mathematical model of radial diffusion of vapors from soil into the void space is shown in Figure 2. For simplicity, the transient model simulates an empty void space (i.e, no passive sampler), which is a reasonable approximation because a passive sampler with an uptake rate low enough to minimize the starvation effect would only become significant as the concentration inside the void space approached steady-state. The derivation of the transient model is provided in Supplemental Information. In summary, the governing equations are:

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

$$\frac{\partial c_g}{\partial t} - D_{air}\left[\frac{\partial^2 c_g}{\partial r^2} + \frac{1}{r}\frac{\partial c_g}{\partial r}\right] = 0 \qquad 0 \le r < r_2 \tag{3}$$

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

$$\frac{\partial c_s}{\partial t} - D_{eff}\left[\frac{\partial^2 c_s}{\partial r^2} + \frac{1}{r}\frac{\partial c_s}{\partial r}\right] = 0 \qquad r_2 \le r < r_3 \tag{4}$$

The initial and boundary conditions are also shown in Figure 2. A Laplace transform is applied to convert the partial differential equations into ordinary differential equations and other operations are performed as described in the Supplemental Information to obtain:

$$\bar{c}_g = \frac{c_{s_0}}{p}\frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}\left[\frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_0(q_g r) + K_0(q_g r)\right] \tag{5}$$

for $0 \le r < r_2$

$$\bar{c}_s = \frac{c_{s_0}}{p} + \kappa\frac{c_{s_0}}{p}\frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}\frac{\varphi_1\varphi_3}{\varphi_2}\left[\frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_0(q_s r) + K_0(q_s r)\right] \tag{6}$$

for $r_2 \le r < r_3$

Equations (7) and (8) allow the calculation of the mass in the void space based on the mass flux across the borehole wall from the void side and soil side, respectively.

$$\bar{M}(p) = \frac{D_{air}c_{s_0}}{p^2} q_g \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}\left[\frac{K_1(q_g r_1)}{I_1(q_g r_1)} I_1(q_g r_2) - K_1(q_g r_2)\right] \tag{7}$$

$$= \frac{D_{air}c_{s_0}}{p^2} q_g \frac{\varphi_2\varphi_1}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}.$$

$$\bar{M}(p) = \frac{D_s c_{s_0}}{p^2} q_s \frac{\varphi_2}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}\frac{\varphi_1\varphi_3}{\varphi_2}\left[\frac{K_1(q_s r_3)}{I_1(q_s r_3)} I_1(q_s r_2) - K_1(q_s r_2)\right] \tag{8}$$

$$= \frac{D_s c_{s_0}}{p^2} q_s \frac{\varphi_2\varphi_1\varphi_3}{\varphi_2\varphi_4 - \varphi_1\varphi_3\varphi_5}.$$

The inverse Laplace transforms of Equation (5), (6), (7) and (8) are computed numerically using the algorithm developed by DeHoog et al.[37]. The modified Bessel functions I_α and K_α used for Equations (5), (6), (7) and (8) are defined by:

$$I_\alpha(x) = i^{-\alpha} J_\alpha(ix) = \sum_{m=0}^{\infty} \frac{1}{m!\,\Gamma(m+\alpha+1)} \left(\frac{x}{2}\right)^{2m+\alpha} \tag{9}$$

$$K_\alpha(x) = \frac{\pi}{2}\frac{I_{-\alpha}(x) - I_\alpha(x)}{\sin(\alpha\pi)} = \frac{\pi}{2} i^{\alpha+1} H_\alpha^{(1)}(ix) = \frac{\pi}{2}(-i)^{\alpha+1} H_\alpha^{(2)}(-ix) \tag{10}$$

The meaning of the symbols in the equations is explained in the Supplementary Information.

FIGURE 2

STEADY-STATE MODEL

If the duration of passive sampling is long compared to the time required for the vapor concentrations in the void space to approach equilibrium with the surrounding soils, then a steady-state model would also provide insight into the passive sampling mechanisms. For this case, the conceptual model is as follows:

- The vapor concentration in the soil surrounding the void space is uniform at c_s beyond a radial distance of r_3,
- Diffusion occurs in the region between the outer wall of the drillhole (radius = r_2) and r_3,

through a cylinder of height, h,

- The concentration in the gas inside the void space of the borehole (c_g) is lower than c_s by a factor $\delta = c_g/c_s$ (this value should be close to 1.0 in order for the sampler to be exposed to vapor concentrations very similar to the surrounding soil),
- Radial diffusion occurs from the soil to the void space at a diffusive delivery rate equal to the passive sampler uptake rate for the majority of the sample deployment interval (i.e., the sampling period is long compared to the time required for steady-state diffusion to be established).

The rate of mass transfer (R_{MT}) of vapors into the borehole via vapor diffusion through the surrounding soil ($R_{MT}1$) is given by Carslaw and Jaeger (1959):

$$R_{MT}1 = \frac{2\pi h D_{eff}(C_s - C_g)}{\ln(\frac{r_3}{r_2})} \quad (11)$$

The rate of mass uptake by the sampler ($R_{MT}2$) is given by:

$$R_{MT}2 = c_g \; x \; UR \quad (12)$$

Setting $R_{MT}1 = R_{MT}2$ gives:

$$UR\left[\frac{mL}{min}\right] = \frac{2\boldsymbol{\pi} h[cm] D_{eff}[\frac{cm^2}{s}](1-\boldsymbol{\delta})}{\ln(\frac{r_3}{r_2})\boldsymbol{\delta}} \; x \; 60[s/min] \quad (13)$$

RESULTS AND DISCUSSION

TRANSIENT MODEL SIMULATIONS

A series of simulations were performed using the transient model to show the relationship between the mass entering the void space from the surrounding soil and time for a 2.54 cm (1-inch) diameter drillhole, a soil vapor concentration (c_s) of 100 μg/m^3 and a vertical interval of 10 cm. Figure 3 shows simulations for a variety of different water-filled porosities (θ_w) and the corresponding effective diffusion coefficients calculated using Equation 2. For all water contents

simulated, the mass of TCE in the void space eventually reaches the same steady value as the concentration inside the void space equilibrates with the surrounding soil. These simulations are instructive because they indicate the time required for the void space to equilibrate with the surrounding soil as a function of the moisture content. For relatively dry soils (e.g., $\theta_w < 0.1$), the void space concentration would be within 10% of the soil vapor concentration in as little as about 10 minutes. For wet soils (e.g., $\theta_w = 0.30$), a similar level of equilibration may require up to about 1 day.

FIGURE 3

Equilibration occurs more slowly with larger diameter boreholes. A comparison of the equilibration time for a nominal 1-inch and 4-inch diameter voids of 10 cm height are shown in Table 2, which shows that the difference in equilibration time is proportional to the difference in the volume of the void space (i.e., varies in proportion to the square of the borehole radius). Most passive samplers can fit within a borehole of 2-inch diameter or less, so the equilibration time would be less than 1 day for most soil moisture contents.

TABLE 2

The transient model simulations do not account for mass removed by a passive sampler in the borehole, which would draw a small but not insignificant amount of mass from the surrounding soil over time. At steady-state, the uptake rate of the passive sampler (UR) and the diffusive delivery rate from the surrounding soil (DDR) would be equal; therefore, Equation (1) can be re-arranged to:

$$DDR = \frac{M}{C\,t} \tag{14}$$

In the period of time before steady-state is achieved, the diffusive delivery rate (DDR) would not be constant and equal to the uptake rate of the sampler, rather, it would be high initially when the concentration gradient is the largest, and gradually slow down as the concentration inside the

void space equilibrates with the surrounding soil. Equation 14 can be used to calculate DDR values as a function of time where M is calculated using Equation 8 for a given period of time (t) and a c_s value of 100 μg/m^3, as shown in Figure 4. The DDR diminishes to less than about 1 mL/minute within about 30 minutes for all moisture contents. Quantitative passive samplers for indoor air quality monitoring typically have uptake rates of 10 to 100 mL/min[27,28,29,30,31,32,33], so these simulations demonstrate that a customized sampler with a lower uptake rate would be needed to minimize the starvation effect to enable reliable quantitative soil vapor sampling for all but very short sample durations and dry soils.

FIGURE 4

The DDR decreases as the concentration in the void space approaches equilibrium with the surrounding soil vapor, as shown in Figure 5. For very dry soils, the average DDR is greater than 10 mL/min until about 90% of the mass has entered the void-space (which occurs within 10 minutes according to Figure 3). In this scenario, a passive sampler with an uptake rate as high as 10 mL/min may still provide data with an acceptably small starvation effect. In other words, the sampler uptake rate remains below the diffusive delivery rate from the soil until the mass delivered to the void space is about 90% of the steady-state value, so a negative bias of about 10% may be expected, which would meet the data quality objectives typically used for soil vapor monitoring (precision within 25% RPD[36]). For very wet soils (θ_w = 0.30), the average DDR is about 0.01 mL/min by the time the void space has nearly equilibrated with the surrounding soil (roughly 1 day). For moisture contents typical of most vadose zone soils ($0.10 < \theta_w < 0.25$), Figure 5 shows that an uptake rate of about 1 mL/min would be expected to result in an acceptably small starvation effect (i.e., for a water-filled porosity of up to 25% in a soil with 36% porosity, the bias due to the starvation effect for a sampler with an uptake rate of 1 mL/min would be expected be less than -20%).

FIGURE 5

Superposition of Diffusive Delivery Rate and Uptake Rate

The transient mathematical model presented in the previous section must be processed further to demonstrate the effect of adding a passive sampler to the void space. A mathematical model including 2-dimensional radial diffusion to the void space (diffusive delivery), 3-dimensional diffusion through the void-space to the passive sampler, and uptake by a variety of possible passive sampler designs and geometries is challenging to formulate mathematically. However, an approximate model can be derived by adding the diffusive delivery rate (Figure 4) and the sampler uptake rate to estimate the effect of both processes occurring at the same time, using the principle of superposition. As long as the uptake rate of the sampler is small, the combined model will differ from the transient analytical model of radial diffusion only after the diffusion into the void space has very nearly attained steady-state, at which time the diffusive delivery rate of vapors into the void space will stabilize at the same value as the uptake rate of the sampler. Figure 6 shows an example of the diffusive uptake rate that would be expected if a passive sampler with an uptake rate of 1 mL/min was placed in the void-space simulated in Figures 3, 4 and 5. Within about 1 hour, the delivery rates for all water-filled porosities approach the uptake rate of the sampler (within about a factor of 2). The delivery rate becomes equal to the uptake rate for all soil moisture contents within about 1 day.

FIGURE 6

It should be noted that for very wet soils (water-filled porosity greater than 0.25), the steady-state delivery rate may be less than 1 mL/min, in which case there are two possibilities: 1) a lower uptake rate sampler could be used with a proportionately longer sample duration, or 2) a negative bias attributable to starvation may still be experienced. If the negative bias is predictable or acceptably small, the data may still be useful and this may be reasonably evaluated using the

models presented here as long as the porosity and moisture content are known or can be reasonably estimated. From a practical perspective, very wet soils have an effective diffusion coefficient about two orders of magnitude lower than dry soils (Figure 1), which would reduce the risk to human health from subsurface vapor intrusion to indoor air by a similar amount. Therefore, a slight negative bias in the passive sampler result may still result in protective decision-making if the results are compared to screening levels derived to be protective of dry soil conditions. Also, it may be possible to avoid low bias associated with wet soils by design via either: 1) coring the soil and selecting coarse-textured, well-drained intervals for monitoring; 2) sampling during dry seasons; or 3) sampling within the rain-shadow below buildings (a.k.a., sub-slab samples).

STEADY STATE MODEL SIMULATIONS

For a passive sampler deployed in a borehole with a nominal diameter of 1-inch (r_1 = 1.25 cm) and sealed within a 10 cm void space (h = 10 cm), the uptake rates calculated using Equation (13) are shown in Figure 7 for δ values of 0.5, 0.75 and 0.95. The r_3 value for these calculations was assumed to be 1 m. Figure 7 shows that an uptake rate of 10 mL/min might be acceptable for very dry soil if the data quality objective was to quantify concentrations within a factor of 2 (i.e., δ = 0.5), however; an uptake rate of 1 mL/min would be more suitable for soils with water-filled porosity of up to about 15%, assuming a more stringent data quality objective of +/-25% (i.e., δ = 0.75). Progressively lower uptake rates would be required to further reduce the negative bias or meet typical data quality objectives in very wet soils.

FIGURE 7

A sensitivity analysis on the r_3 value is shown in Figure 8 for the same conditions as in Figure 7 and a δ value of 0.75. This plot shows that the value assumed for r_3 does not affect the conclusions in a significant way even when it is varied by an order of magnitude.

FIGURE 8

PRACTICAL CONSTRAINTS ON THE UPTAKE RATE

There is a practical lower limit to the uptake rate for passive sampling, which is imposed by the sample duration needed to achieve a specified reporting limit. Equation (1) can be rearranged to calculate the sample duration required to achieve a target reporting limit if the uptake rate of the sampler and the laboratory mass reporting limit (M_{RL}) are known:

$$t = \frac{M_{RL}}{c\ x\ UR} \tag{14}$$

For example, consider an initial soil vapor concentration of 100 μg/m^3 of TCE and a sampler with an uptake rate of 1 mL/min. A detectable mass of TCE (M_{RL} ~ 0.05 μg via solvent extraction, GC/MS) would be adsorbed by the sampler in 500 min (0.35 day). This demonstrates that a low-uptake rate sampler can provide practical sensitivity within a reasonable amount of time and still avoid or minimize the starvation effect. However, if the uptake rate was reduced to 0.1 or 0.01 mL/min, the sample duration would need to increase to 3.5 or 35 days, respectively. There are logistical challenges with long sample durations (costs of return travel to field sites, security, etc.). The sensitivity can be increased using thermal desorption instead of solvent extraction (M_{RL} ~ 0.002 μg); however, weaker sorbents are typically used with thermal desorption, hence less-strongly sorbed analytes may not be effectively retained, especially for longer sampling durations.

CONCLUSIONS

In order for a kinetic passive sampler to provide quantitative soil vapor concentration data, it must have a known and reliable uptake rate for all of the compounds of interest. The passive sampler uptake rate should be low enough to allow the rate of diffusive delivery of vapors into the void space from the surrounding soil to sustain vapor concentrations in the void space similar

to those of the surrounding soil in order to minimize the starvation effect. The uptake rate must also be high enough to provide the ability to detect concentrations at or below risk-based screening levels with acceptable sampling duration. This paper demonstrates that kinetic samplers with the uptake rates in the range of ~0.01 to ~10 mL/min can deliver quantitative passive soil vapor concentration data with only a small bias, depending on the soil moisture, and that an uptake rate of about 1 mL/min provides acceptable accuracy and sensitivity for most commonly-encountered water-filled porosities in unsaturated soils. These conclusions are supported by both transient and steady-state models. The knowledge gained from the mathematical modeling in this paper allows passive samplers to be modified as needed to achieve an uptake rate small enough to minimize starvation and high enough to provide adequate sensitivity, which will simplify and improve the cost-effectiveness of quantitative soil vapor concentration measurement and monitoring for VOCs.

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Table 1: Parameter Values used in Model Simulations (representative for TCE)

Parameter name	Symbol	Units	Value
Free air diffusion coefficient	D_{air}	cm^2/s	0.069
Aqueous diffusion coefficient	D_w	cm^2/s	0.00001
Henry's Law constant	H	dimensionless	0.35
Total porosity	θ_T	Volume of voids / total volume of soil	0.375
Water-filled porosity	θ_w	Volume of water / total volume of soil	Various values from 0.01 to 0.36
Air-filled porosity	θ_a	$\theta_T - \theta_w$	Various values from 0.365 to 0.015

Table 2: Comparison of time to reach 95% of steady-state concentration in the void space comparing nominal 1-inch and 4-inch diameter boreholes (total porosity 37.5%)

Water-filled porosity (-)	D_{eff} (m^2/day)	Time to reach 95% Cs0 (day)		t_4/t_1
		t_1 $(r_2 = 0.5inch)$	t_4 $(r_2 = 2inch)$	
0.01	0.15	0.0048	0.076	16
0.05	0.10	0.0070	0.11	
0.1	0.058	0.012	0.19	
0.15	0.030	0.024	0.38	
0.2	0.013	0.055	0.87	
0.25	0.0042	0.17	2.7	
0.3	0.00080	0.87	13	
0.31	0.00052	1.3	21	
0.32	0.00033	2.1	34	
0.33	0.00020	3.5	56	
0.34	0.00013	5.5	88	
0.35	0.000093	7.5	120	
0.36	0.000084	8.3	130	

Figure 1: Effective diffusion coefficient versus water-filled porosity for TCE in a soil with 37.5% total porosity, typical of a sandy soil.

Figure 2: Schematic of transient mathematical model domain including boundary and initial conditions

Figure 3: Simulated mass delivered by diffusion from surrounding soil to the void space versus time for a 2.5 cm diameter borehole in a sandy soil with 37.5% total porosity and an initial soil vapor concentration of 100 $\mu g/m^3$, assuming no removal of mass by a passive sampler.

Figure 4: Diffusive delivery rate versus time for mass entering the void space of a 2.5 cm diameter, 10 cm tall void space in a soil with 37.5% total porosity and an initial soil vapor concentration of 100 $\mu g/m^3$, assuming no removal of mass by a passive sampler.

Figure 5: Relationship between the instantaneous diffusive delivery rate of vapors into the void space versus the percentage of the analyte mass at steady-state ($100 \times M_t/M_{ss}$, where M_t is the analyte mass in the borehole at time t, and M_{ss} is the analyte mass at steady state), assuming a 2.5 cm diameter borehole in a soil with 37.5% total porosity, initial soil vapor concentration of 100 $\mu g/m^3$, and no removal of mass by a passive sampler.

Figure 6: Superimposed diffusive delivery rate plus uptake rate for a 10 cm tall and 2.5 cm diameter void space in a soil with 37.5% porosity and an initial soil vapor concentration of 100 $\mu g/m^3$ containing a passive sampler with an uptake rate of 1 mL/min.

Figure 7: Calculated uptake rate corresponding to various δ values as a function of water-filled porosity for a 10 cm tall and 2.54 cm diameter void space assuming $r_3 = 1m$

Figure 8: Calculated uptake rate corresponding to various r_3 values as a function of water-filled porosity for a 10 cm tall and 2.54 cm diameter void space assuming $\delta = 0.75$.

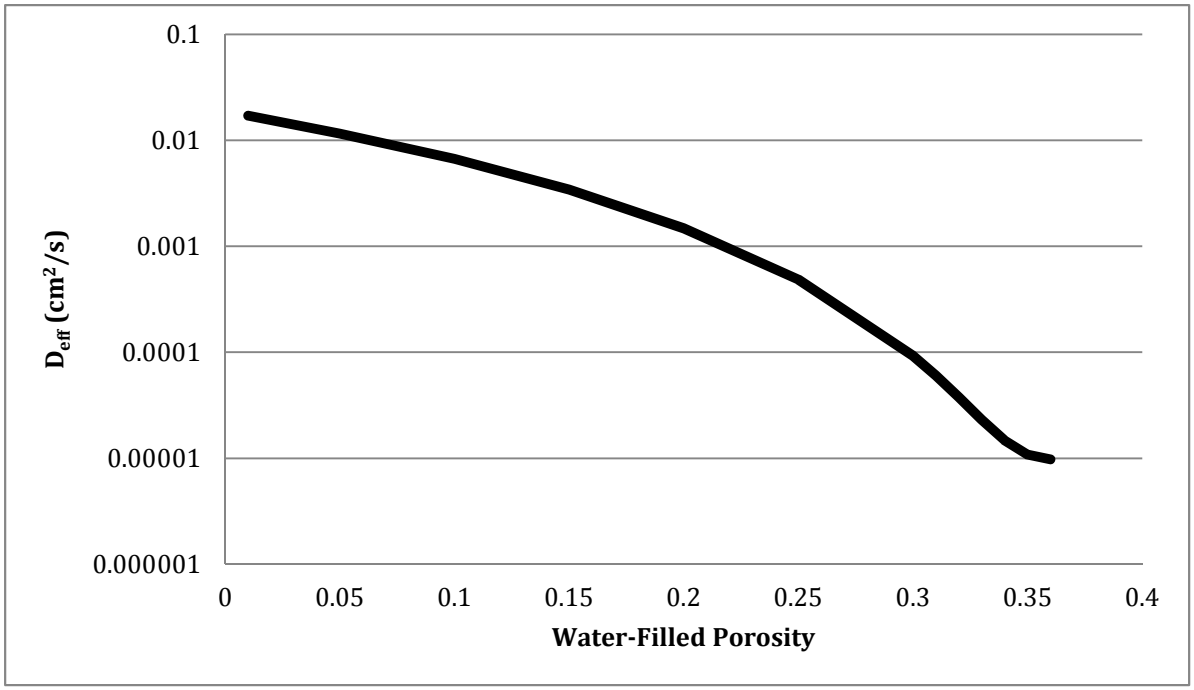
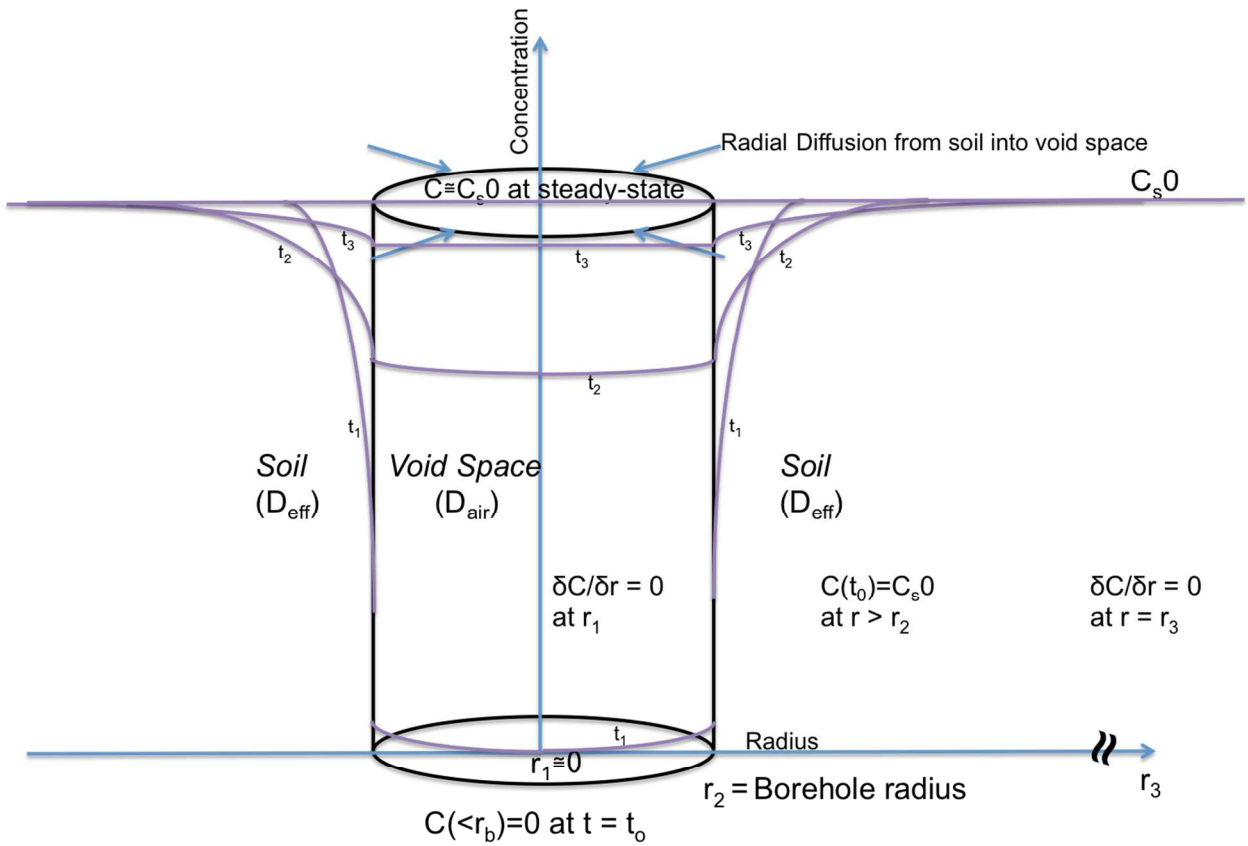


Figure 1



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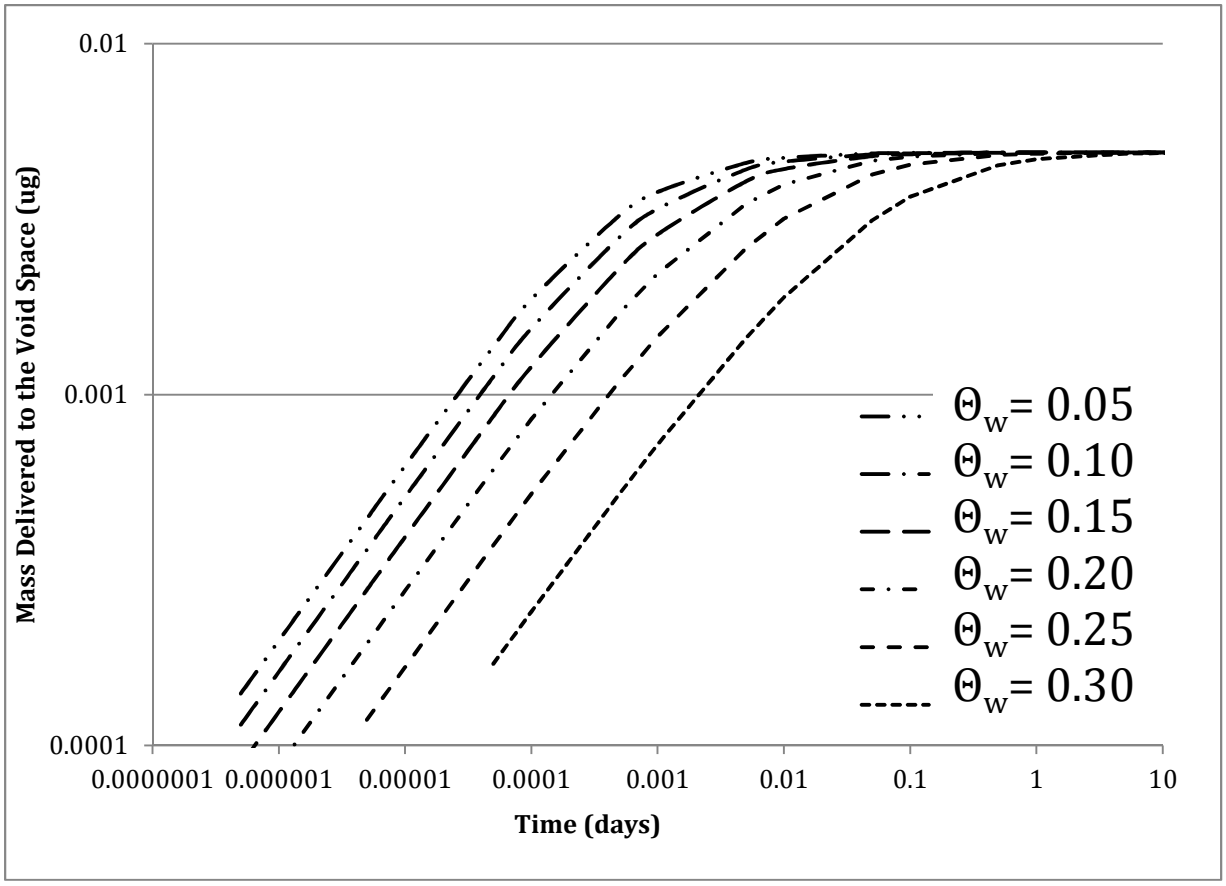

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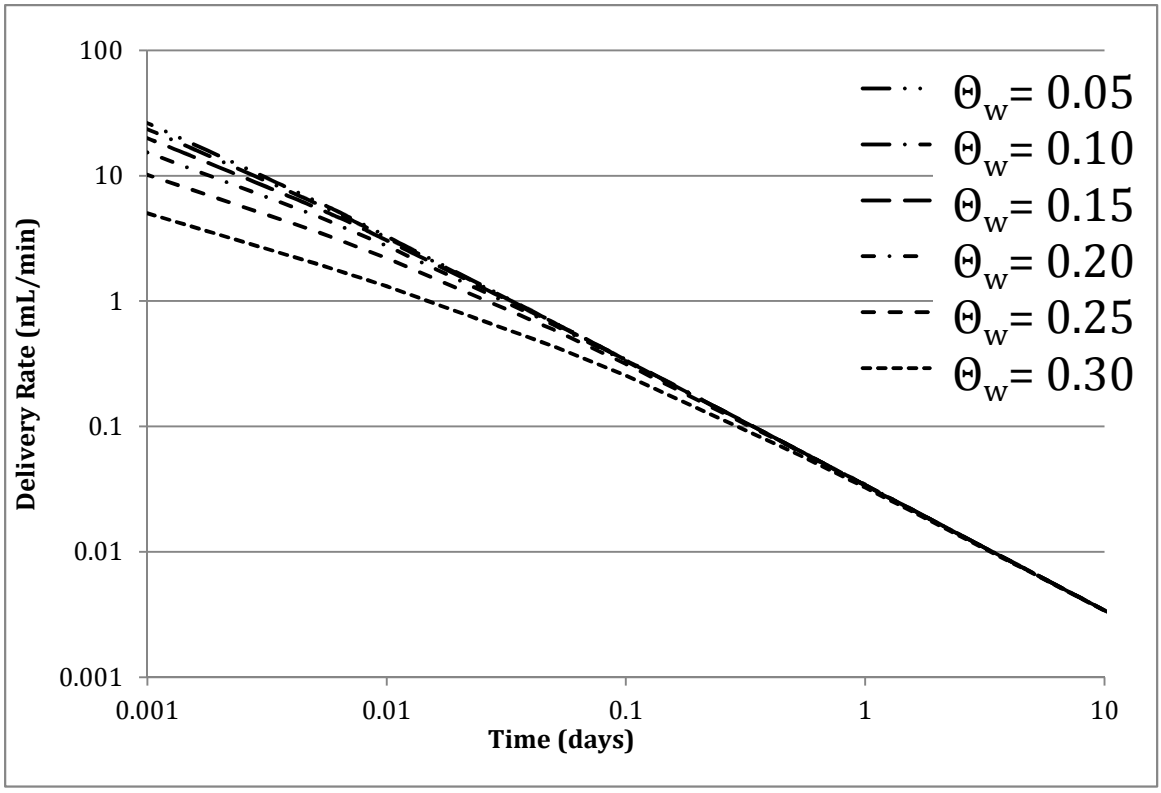

Figure 4

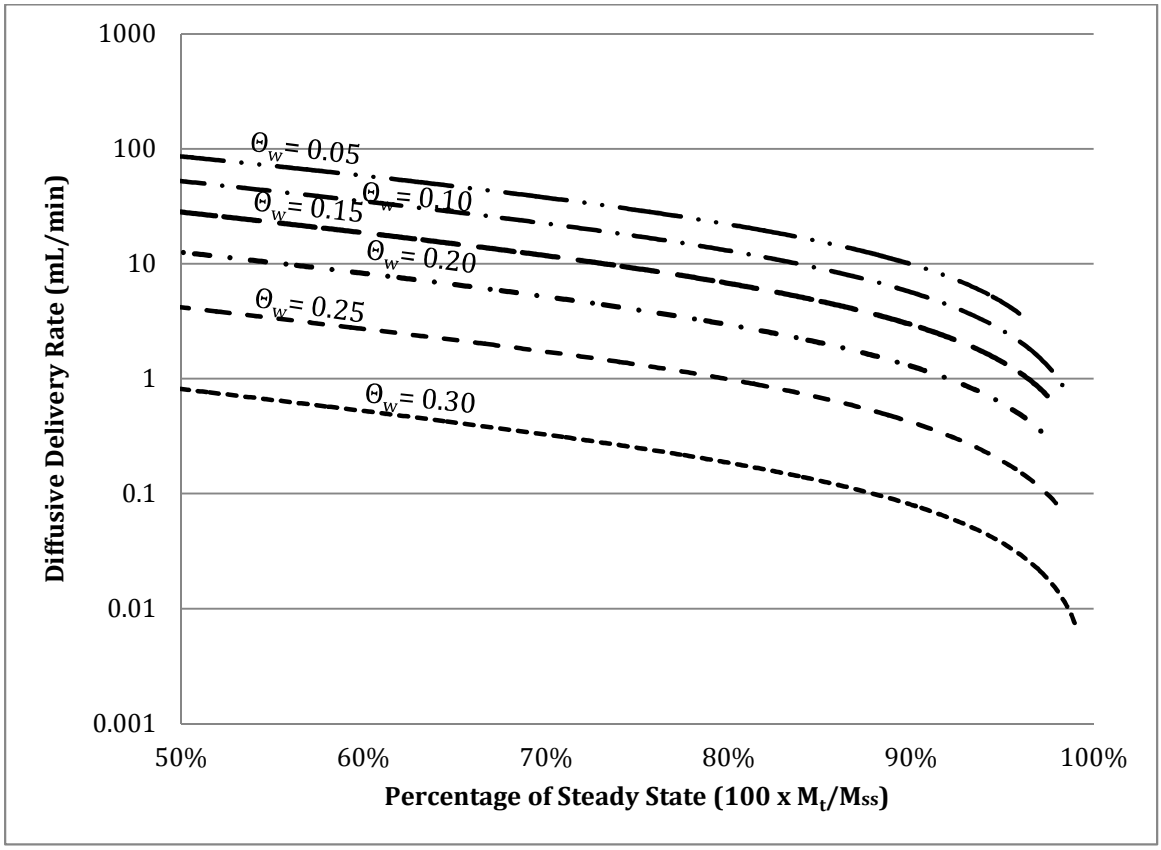

Figure 5

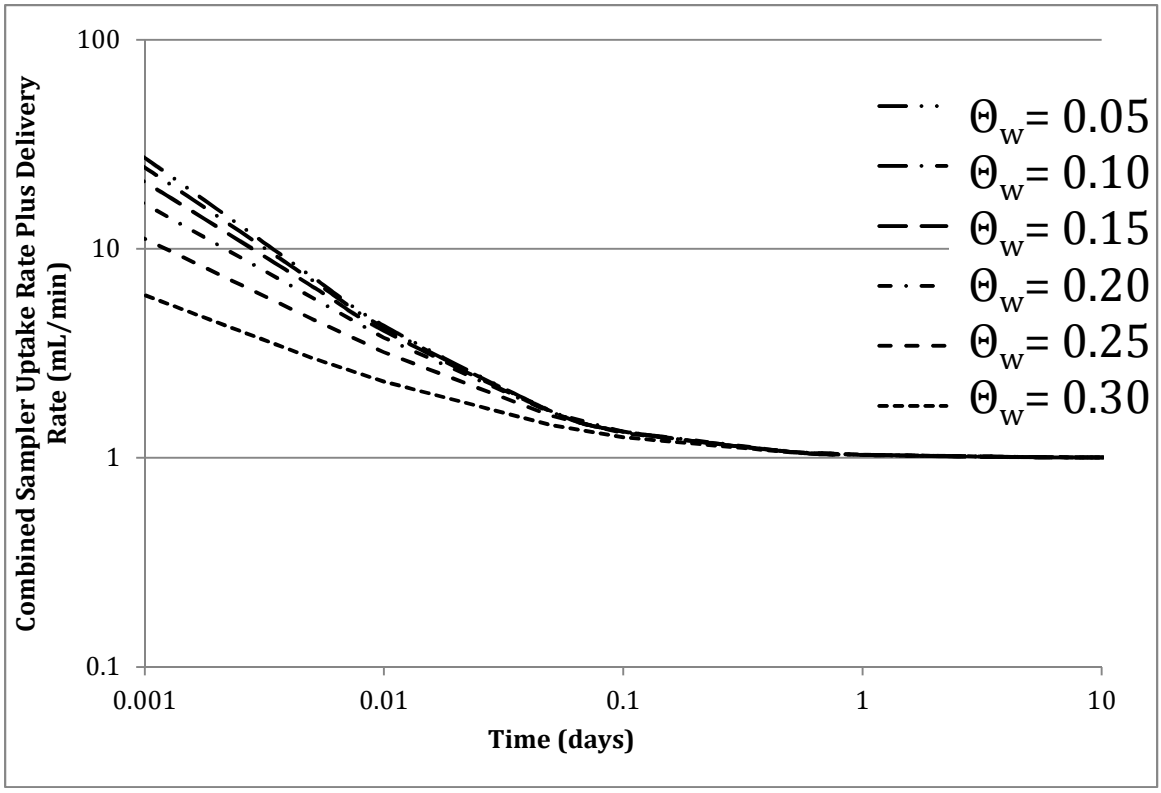

Figure 6

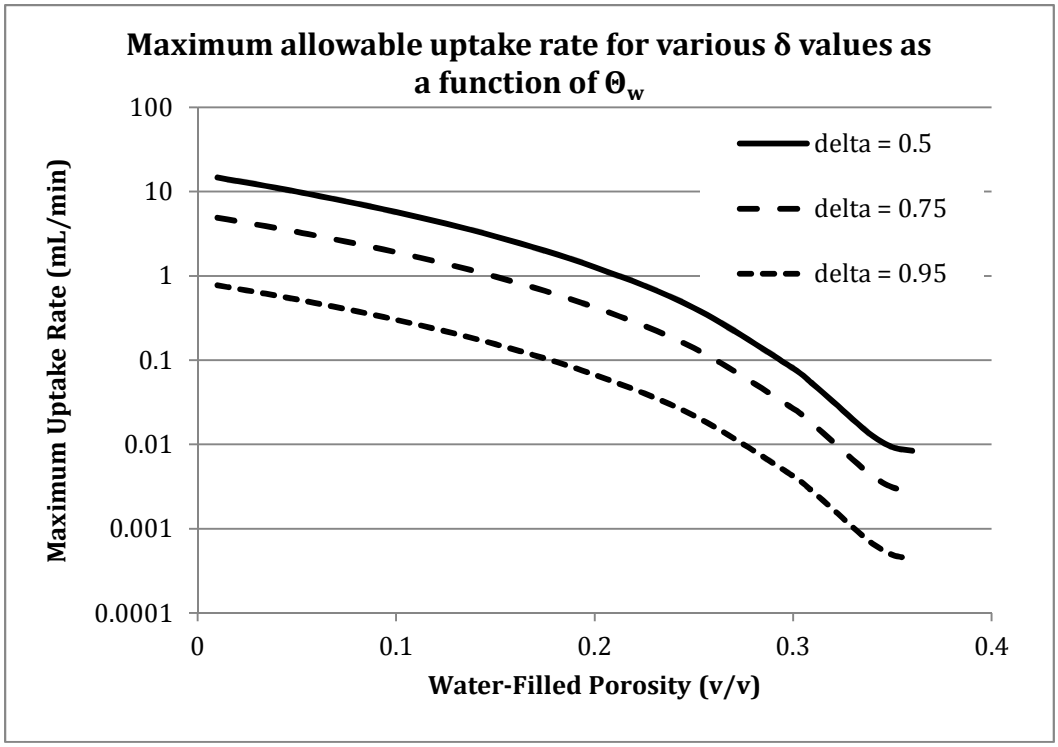

Figure 7

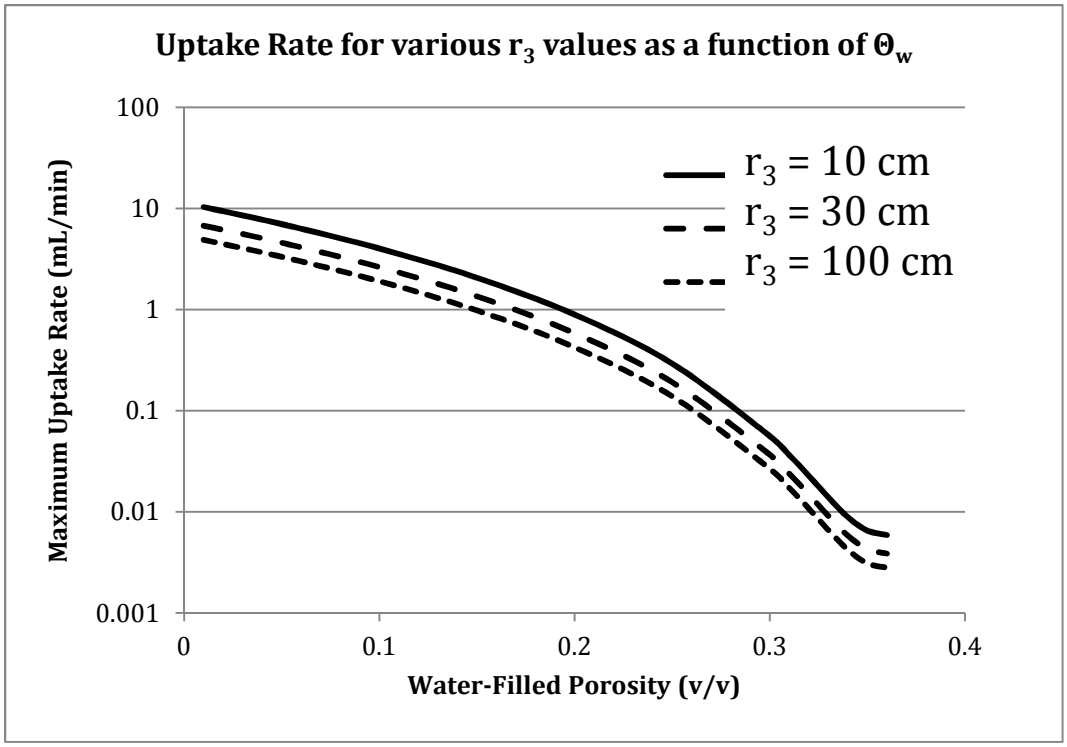

Figure 8