AA GeoEnvironmental Technical White Paper
PFAS Vadose-Zone Fate and Transport (Leach) Modeling

Governing Equations, Calibration, Sensitivity Analysis, Uncertainty Evaluation, and Defensibility Considerations

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Executive Summary

PFAS leaching from the vadose zone to groundwater is governed by a coupled set of hydrologic and geochemical processes that include variably saturated flow, aqueous advection and dispersion, adsorption to solids, adsorption at air-water interfaces, kinetic mass transfer, preferential flow, and, where warranted, precursor transformation. A technically defensible model must match the conceptual site model to the problem being solved. For many PFAS sites, the most load-bearing issue is not whether a model reproduces one concentration profile, but whether it realistically represents the mechanisms controlling long-term source persistence and groundwater mass discharge.

This white paper presents a unified framework for PFAS vadose-zone leach and fate & transport modeling. It explains the governing equations, defines the terms in each equation, interprets each mathematical relationship in real-world language, and summarizes how those equations are calibrated, stress-tested, and bounded through sensitivity and uncertainty analysis. The paper also addresses the defensibility of precursor transformation modeling and explains why precursor terms should usually be framed as lumped reactive-transport approximations rather than universal PFAS reaction laws.

Contents

Abstract

Per- and polyfluoroalkyl substances (PFAS) in the vadose zone can remain a long-term source to groundwater because transport is controlled not only by advection and dispersion, but also by solid-phase adsorption, adsorption at air-water interfaces, transient unsaturated flow, and, in some settings, kinetic desorption, precursor transformation, and preferential flow. Reviews and recent field/modeling studies show that these coupled processes can produce decadal persistence in shallow soils, delayed mass discharge to groundwater, and large differences in mobility between shorter- and longer-chain PFAS.

This white paper presents a continuous mathematical and practical framework for PFAS vadose-zone modeling. It covers the governing flow and transport equations, equilibrium and nonequilibrium retention processes, preferential-flow and precursor-transformation formulations, and a defensible workflow for calibration, sensitivity analysis, and uncertainty analysis. The central modeling position advanced here is that PFAS vadose-zone predictions are most defensible when the conceptual site model is explicit, PFAS-specific retention processes are represented where warranted, calibration is tied to both hydraulic and chemical observations, and uncertainty is communicated as part of the core result rather than as an afterthought.

1. Introduction

Vadose-zone PFAS modeling matters because soil and unsaturated sediment may serve as the controlling reservoir for long-term groundwater loading. Field evidence from AFFF-impacted sites shows that most PFAS mass can remain concentrated in shallow intervals for long periods, while a smaller but important fraction continues to migrate downward and sustain groundwater impacts. Broader reviews conclude that the vadose zone is a critical PFAS compartment where adsorption, interfacial retention, evapotranspiration, source aging, and precursor transformation can all influence long-term fate.

PFAS differ from many conventional groundwater contaminants because transport in unsaturated systems is strongly affected by air-water interfacial adsorption. That process is often comparable to or larger than solid-phase adsorption, especially under partial saturation. As a result, conventional leaching approaches based only on a soil-water partition coefficient can materially underpredict PFAS retention or misrepresent the timing of groundwater impacts.

The aim of this white paper is to present a rigorous but practical framework for evaluating PFAS leaching from the vadose zone to groundwater. The discussion is organized around four questions:

- What equations govern PFAS flow and transport in the vadose zone?
- What do those equations mean in real site settings?
- How should such models be calibrated and tested?

- How should uncertainty be represented so the final conclusions remain technically defensible?

2. Conceptual Model for PFAS Fate and Transport in the Vadose Zone

At site scale, PFAS fate and transport in the vadose zone is controlled by a coupled set of hydrologic and geochemical processes:

- transient unsaturated flow
- aqueous advection and dispersion
- adsorption to solids
- adsorption at air-water interfaces
- kinetic mass transfer and desorption tailing
- preferential flow caused by heterogeneity, macropores, or textural contrasts; and
- transformation of precursor compounds into daughter PFAAs where relevant.

A robust conceptual site model therefore begins with several questions. Is the source dominated by terminal PFAAs or are precursors likely? Is the vadose zone relatively homogeneous, or is there evidence of preferential flow, perched water, or textural contrasts? Are recharge and evapotranspiration strong enough to create major wetting-drying cycles? Is the groundwater table stable or seasonally fluctuating? The equations that follow should be selected and simplified only after these questions are addressed.

3. Governing Water-Flow Equations

3.1 Richards equation for variably saturated flow

The standard governing equation for one-dimensional variably saturated flow is the mixed-form Richards equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial z} + 1\right)\right] - S_w \qquad (1)$$

Terms in the equation

- θ = volumetric water content [dimensionless]
- t = time [T]
- z = vertical coordinate [L]
- $K(h)$ = unsaturated hydraulic conductivity [length/time]
- h = pressure head [L]

- S_w = water sink/source term [T or equivalent volumetric rate]

This equation determines when, how fast, and through which portion of the pore space PFAS-bearing water moves downward. In humid settings, frequent infiltration can flush mobile PFAS more rapidly. In semi-arid settings, evapotranspiration and upward water flux can slow or temporarily reverse aqueous movement, enhancing shallow retention.

3.2 Soil-water retention: van Genuchten relationship

A common constitutive relationship for water retention is:

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{(1 + |\alpha h|^n)^m}, \qquad h < 0 \tag{2a}$$

with

$$m = 1 - \frac{1}{n} \tag{2b}$$

and effective saturation:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{2c}$$

Terms in the equations

- $\theta(h)$ = water content as a function of pressure head
- θ_r = residual water content
- θ_s = saturated water content
- α = inverse air-entry or fitting parameter [1/length]
- n, m = shape parameters
- S_e = effective saturation [dimensionless]

Water retention determines how much of the pore space is water-filled versus air-filled. That matters enormously for PFAS because air-water interfacial area is a strong function of saturation. The same recharge rate can therefore produce different PFAS retardation depending on the shape of the soil-water retention curve.

3.3 Unsaturated hydraulic conductivity: Mualem–van Genuchten form

A common conductivity function is:

$$K(h) = K_s S_e^l \left[1 - \left(1 - S_e^{\frac{1}{m}}\right)^m\right]^2 \tag{3}$$

Terms in the equation

- $K(h)$ = unsaturated hydraulic conductivity
- K_s = saturated hydraulic conductivity [length/time]
- S_e = effective saturation
- l = pore-connectivity parameter
- m = van Genuchten parameter

Hydraulic conductivity controls how efficiently recharge pulses move through the vadose zone. A layered or structured profile can direct flow into specific pathways, reducing contact with much of the matrix and accelerating PFAS leaching.

4. Governing PFAS Transport Equations

4.1 General aqueous-phase PFAS transport

A general one-dimensional PFAS mass-balance equation in a variably saturated porous medium is:

$$\frac{\partial(\theta C_i)}{\partial t} + \rho_b \frac{\partial S_i}{\partial t} + \frac{\partial(A_{aw}\Gamma_i)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D_i \frac{\partial C_i}{\partial z}\right) - \frac{\partial(qC_i)}{\partial z} + \sum R_i \tag{4}$$

Terms in the equation

- C_i = aqueous concentration of PFAS species i [mass/volume]
- ρ_b = bulk density of porous medium [mass/volume]
- S_i = sorbed concentration on solids [mass/mass]
- A_{aw} = specific air-water interfacial area [1/length]
- Γ_i = adsorbed PFAS mass per interfacial area [mass/area]
- D_i = hydrodynamic dispersion coefficient [length^2/time]
- q = Darcy flux [length/time]
- $\sum R_i$ = reaction/source-sink term [varies by formulation]

This equation is the core statement that PFAS mass in the vadose zone is partitioned among porewater, the solid phase, and air-water interfaces while being redistributed by flow and spreading. For PFAS, the interfacial-storage term often separates realistic models from oversimplified ones.

4.2 Advection and dispersion

The advective and dispersive components are:

$$-\frac{\partial(qC_i)}{\partial z} \quad (5a)$$

$$\frac{\partial}{\partial z}\left(\theta D_i \frac{\partial C_i}{\partial z}\right) \quad (5b)$$

with pore-water velocity:

$$v = \frac{q}{\theta} \quad (5c)$$

and hydrodynamic dispersion often represented as:

$$D_i = \alpha_L v + \tau D_{m,i} \quad (5d)$$

Terms in the equations

- v = pore-water velocity [length/time]
- α_L = longitudinal dispersivity [L]
- τ = tortuosity factor [dimensionless]
- $D_{m,i}$ = molecular diffusion coefficient in water [length^2/time]

Advection determines travel speed with moving water. Dispersion determines how the PFAS front spreads and how concentration gradients evolve. In layered or heterogeneous soils, effective dispersion and mixing can differ substantially from homogeneous-column expectations.

5. Solid-Phase Adsorption and Rate-Limited Desorption

5.1 Equilibrium solid-phase adsorption

The simplest solid-phase retention model is linear equilibrium adsorption:

$$S_i = K_{d,i} C_i \quad (6a)$$

A common nonlinear alternative is the Freundlich relation:

$$S_i = K_{f,i} C_i^{N_i} \tag{6b}$$

Terms in the equations

- $K_{d,i}$ = linear distribution coefficient for species i [volume/mass or equivalent]
- $K_{f,i}$ = Freundlich adsorption coefficient
- N_i = Freundlich exponent [dimensionless]

Executive interpretation

Solid-phase adsorption slows PFAS movement, but the degree of slowing varies widely by compound and site. Longer-chain and sulfonated PFAS commonly show stronger retention than many shorter-chain compounds, but field predictions should not rely on chain length alone because water content, interfacial effects, and heterogeneity also matter.

5.2 Two-site sorption model for rate-limited desorption

A common nonequilibrium representation is:

$$S_i = S_{i,1} + S_{i,2} \tag{6c}$$

$$S_{i,1} = f_i K_{d,i} C_i \tag{6d}$$

$$\frac{\partial S_{i,2}}{\partial t} = \alpha_{s,i}\left[(1 - f_i) K_{d,i} C_i - S_{i,2}\right] \tag{6e}$$

Terms in the equations

- $S_{i,1}$ = equilibrium sorbed concentration component
- $S_{i,2}$ = kinetic sorbed concentration component
- f_i = fraction of equilibrium sites [dimensionless]
- $\alpha_{s,i}$ = first-order mass-transfer coefficient for kinetic sites [1/time]

This formulation is the mathematical basis for long PFAS tailing even after source input stops. A model that fits early breakthrough but omits rate-limited release may severely underpredict long-term mass discharge to groundwater.

6. Air-Water Interfacial Adsorption

6.1 Equilibrium interfacial adsorption

A common linearized form is:

$$\Gamma_i = K_{aw,i} C_i \qquad (7a)$$

Terms in the equation

- $K_{aw,i}$ = effective air-water interfacial adsorption coefficient for species i

This equation expresses the tendency of amphiphilic PFAS molecules to accumulate where air and water meet in the pore network. For many PFAS, especially under partial saturation, this is a major retention mechanism.

6.2 Kinetic interfacial adsorption

Under transient or heterogeneous flow conditions, equilibrium may be insufficient. A kinetic representation is:

$$\frac{\partial \Gamma_i}{\partial t} = \alpha_{aw,i}\left(K_{aw,i} C_i - \Gamma_i\right) \qquad (7b)$$

Terms in the equation

- $\alpha_{aw,i}$ = interfacial mass-transfer coefficient [1/time]

This equation allows for delayed adsorption or release at the air-water interface. It can become important during wetting and drying cycles, rapid transient infiltration, and heterogeneous saturation changes.

6.3 Interfacial mass balance

Because both interfacial concentration and interfacial area change with saturation, the storage term expands to:

$$\frac{\partial (A_{aw}\Gamma_i)}{\partial t} = A_{aw}\frac{\partial \Gamma_i}{\partial t} + \Gamma_i \frac{\partial A_{aw}}{\partial t} \qquad (7c)$$

Terms in the equation

- $\partial A_{aw} / \partial t$ = rate of change of interfacial area with time

For PFAS, interfaces are not static. This equation recognizes that interfacial storage changes because PFAS adsorbs or desorbs and because the geometry of the air-water interface changes as soils wet or drain.

7. Air-Water Interfacial Area

A physically based thermodynamic expression for specific interfacial area is:

$$A_{aw}(\theta) = \frac{\rho_w g}{\sigma_0} \int_{\theta}^{\theta_s} h\,(\theta)\,d\theta \qquad (8)$$

Terms in the equation

- ρ_w = density of water [mass/volume]
- g = gravitational acceleration [length/time^2]
- σ_0 = surface tension of pure water [mass/time^2]
- $h(\theta)$ = pressure head expressed as a function of water content

A_{aw} is one of the most load-bearing variables in PFAS vadose-zone models. If the interfacial area is underestimated, PFAS retention is often underestimated; if the wrong saturation relationship is chosen, both leaching timing and groundwater mass discharge can shift materially.

8. Simplified Retardation Factor

Under linear equilibrium assumptions for both solid-phase and air-water interfacial adsorption, the retardation factor can be written as:

$$R_{f,i} = 1 + \frac{\rho_b K_{d,i}}{\theta} + \frac{A_{aw} K_{aw,i}}{\theta} \qquad (9a)$$

The simplified transport equation becomes:

$$R_{f,i} \frac{\partial C_i}{\partial t} = \frac{1}{\theta} \frac{\partial}{\partial z}\left(\theta D_i \frac{\partial C_i}{\partial z}\right) - \frac{1}{\theta} \frac{\partial (q C_i)}{\partial z} - \lambda_{w,i} C_i \qquad (9b)$$

Terms in the equations

- $R_{f,i}$ = retardation factor [dimensionless]
- $\lambda_{w,i}$ = aqueous-phase first-order decay or loss term [1/time]

The important point is that PFAS retardation in the vadose zone is not just a K_d problem. The interfacial term can dominate, especially for longer-chain compounds and intermediate saturations. That is why conventional leaching approaches based only on soil adsorption can misrepresent PFAS behavior.

9. Preferential Flow and Heterogeneous Media

A dual-domain representation for matrix and preferential-flow domains can be written as:

$$\frac{\partial(\theta_m C_{i,m})}{\partial t} + \rho_b \frac{\partial S_{i,m}}{\partial t} = \frac{\partial}{\partial z}\left(\theta_m D_{i,m} \frac{\partial C_{i,m}}{\partial z}\right) - \frac{\partial(q_m C_{i,m})}{\partial z} + \omega_i(C_{i,f} - C_{i,m}) \tag{10a}$$

$$\frac{\partial(\theta_f C_{i,f})}{\partial t} + \rho_b \frac{\partial S_{i,f}}{\partial t} = \frac{\partial}{\partial z}\left(\theta_f D_{i,f} \frac{\partial C_{i,f}}{\partial z}\right) - \frac{\partial(q_f C_{i,f})}{\partial z} - \omega_i(C_{i,f} - C_{i,m}) \tag{10b}$$

Terms in the equations

- subscript m = matrix domain
- subscript f = preferential-flow domain
- ω_i = interdomain mass-transfer coefficient [1/time]
- q_m, q_f = Darcy fluxes in matrix and preferential domains
- $D_{i,m}, D_{i,f}$ = dispersion coefficients in matrix and preferential domains

Preferential flow can produce early PFAS arrival to depth, especially where a homogeneous one-dimensional model would otherwise predict strong retardation. Heterogeneity can also reduce accessible air-water interfaces and thereby accelerate leaching.

10. PFAS Precursor Transformation

10.1 Lumped precursor transport and loss

A practical precursor equation is:

$$\frac{\partial(\theta C_p)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D_p \frac{\partial C_p}{\partial z}\right) - \frac{\partial(q C_p)}{\partial z} - \lambda_p \theta C_p \tag{11a}$$

Terms in the equation

- C_p = precursor concentration in pore water [mass/volume]
- D_p = precursor dispersion coefficient [length^2/time]
- λ_p = lumped first-order precursor transformation coefficient [1/time]

10.2 Daughter-PFAS generation term

A corresponding daughter-production term may be written as:

$$R_{p\to i} = Y_i \lambda_{p,i} \theta C_p \tag{11b}$$

For multiple daughters or precursor classes:

$$\sum_j Y_{ij}\, \lambda_{p,j} \theta C_{p,j} \tag{11c}$$

Terms in the equations

- $R_{p\to i}$ = generation rate of daughter species i
- Y_i or Y_{ij} = effective yield term [dimensionless]
- $\lambda_{p,i}$ = pathway-specific or effective first-order transformation coefficient
- $C_{p,j}$ = concentration of precursor class j

These equations are most defensible when presented as lumped reactive-transport approximations of net precursor loss and daughter-PFAA generation, not as universal mechanistic laws for all PFAS precursor chemistry. Real precursor transformation can involve multiple intermediates, pathway branching, variable yields, and strong dependence on hydraulic residence time and microbiological conditions.

11. Integrated PFAS Vadose-Zone “Master” Equation

A practical advanced PFAS equation that combines the main processes is:

$$\frac{\partial(\theta C_i)}{\partial t} + \rho_b \frac{\partial\left(S_{i,1} + S_{i,2}\right)}{\partial t} + \frac{\partial(A_{aw}\Gamma_i)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D_i \frac{\partial C_i}{\partial z}\right) - \frac{\partial(qC_i)}{\partial z} + \omega_i\left(C_{i,f} - C_{i,m}\right) + \sum_j Y_{ij}\, \lambda_{p,j} \theta C_{p,j} - \lambda_{w,i} \theta C_i \tag{12a}$$

with the kinetic relations:

$$S_{i,1} = f_i K_{d,i} C_i \tag{12b}$$

$$\frac{\partial S_{i,2}}{\partial t} = \alpha_{s,i}\left[(1 - f_i) K_{d,i} C_i - S_{i,2}\right] \tag{12c}$$

$$\frac{\partial \Gamma_i}{\partial t} = \alpha_{aw,i}\left(K_{aw,i}C_i - \Gamma_i\right) \qquad (12d)$$

Terms in the equations

- $C_{i,m}, C_{i,f}$ = species i concentrations in matrix and preferential domains
- f_i = equilibrium sorption fraction
- $\alpha_{s,i}$ = kinetic solid-phase mass-transfer coefficient
- $\alpha_{aw,i}$ = interfacial mass-transfer coefficient

all other terms retain the meanings defined above

This integrated framework states that PFAS leaching is usually a competition between processes that accelerate downward transport, such as recharge and preferential flow, and processes that retain PFAS, such as solid sorption, interfacial adsorption, and kinetic release from immobile domains. A defensible model includes the processes that materially control the decision at hand; it does not include complexity merely for appearance.

12. Calibration Framework

12.1 Weighted least-squares objective function

A standard inverse-model calibration objective is:

$$\Phi(\mathbf{p}) = \sum_{i=1}^{n} w_i \left[y_i^{obs} - y_i(\mathbf{p})\right]^2 \qquad (13)$$

with common weighting choice:

$$w_i = \frac{1}{\sigma_i^2}$$

Terms in the equations

- $\Phi(\mathrm{p})$ = weighted objective function
- p = parameter vector
- n = number of observations
- w_i = weight assigned to observation i
- y_i^{obs} = observed value for observation i

- $y_i(\mathrm{p})$ = simulated value associated with parameter vector p
- σ_i^2 = variance of observation error

This is the mathematical statement of calibration. It measures the mismatch between observed and simulated values and seeks the parameter set that minimizes that mismatch. For PFAS, calibration is strongest when it includes both hydraulic observations and chemical observations.

12.2 Regularized objective function

When PFAS models include weakly identifiable parameters, regularization is often necessary:

$$\Phi_{total} = \Phi_{obs} + \mu\Phi_{reg} \qquad (14a)$$

$$\Phi_{reg} = \sum_{j=1}^{m}\left(\frac{p_j - p_{j,prior}}{\sigma_{p_j}}\right)^2 \qquad (14b)$$

Terms in the equations

- Φ_{total} = total objective function including regularization
- Φ_{obs} = observation misfit objective function
- Φ_{reg} = regularization penalty term
- μ = regularization weight
- m = number of estimated parameters
- p_j = estimated parameter j
- $p_{j,prior}$ = preferred or prior parameter value
- σ_{p_j} = allowed deviation or prior standard deviation

Regularization keeps the model from drifting into unrealistic parameter combinations just to fit the data. It is especially useful for PFAS-specific parameters such as, interfacial-area functions, kinetic transfer coefficients, and precursor terms.

12.3 Parameter-update equation

A common Gauss-Newton or Levenberg-Marquardt update is:

$$(\mathrm{J}^T\mathrm{WJ} + \lambda\mathrm{I})\Delta\mathrm{p} = \mathrm{J}^T\mathrm{Wr} \qquad (15)$$

Terms in the equation

- J = Jacobian or sensitivity matrix
- W = weighting matrix
- λ = damping factor
- I = identity matrix
- Δp = parameter correction vector
- r = residual vector = $y^{obs} - y(p)$

This equation is the mathematical engine of inverse calibration. It tells the model how to adjust parameters step by step so simulated outputs move closer to observed site data while avoiding unstable jumps.

12.4 Residuals and fit metrics

Residuals are:

$$e_i = y_i^{obs} - y_i(\mathbf{p}) \tag{16a}$$

Weighted residuals are:

$$e_{w,i} = \sqrt{w_i}\, e_i \tag{16b}$$

Common performance metrics include:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(y_i^{obs} - y_i\right)^2}$$

$$MAE = \frac{1}{n}\sum_{i=1}^{n}\left|y_i^{obs} - y_i\right|$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n}\left(y_i^{obs} - y_i\right)^2}{\sum_{i=1}^{n}\left(y_i^{obs} - \bar{y}^{obs}\right)^2}$$

$$NSE = 1 - \frac{\sum_{i=1}^{n}\left(y_i^{obs} - y_i\right)^2}{\sum_{i=1}^{n}\left(y_i^{obs} - \bar{y}^{obs}\right)^2}$$

$$PBIAS = 100\,\frac{\sum_{i=1}^{n}\left(y_i - y_i^{obs}\right)}{\sum_{i=1}^{n} y_i^{obs}}$$

Terms in the equations

- e_i = residual for observation i

- $e_{w,i}$ = weighted residual for observation i
- $RMSE$ = root mean square error
- MAE = mean absolute error
- R^2 = coefficient of determination
- NSE = Nash–Sutcliffe efficiency
- $PBIAS$ = percent bias
- $\bar{y}^{obs}$ = mean of observed values

Fit metrics are useful summaries, but a statistically acceptable fit does not guarantee conceptual correctness. For PFAS, a model may reproduce one dataset while still omitting critical processes such as AWI adsorption, preferential flow, or rate-limited release.

13. Validation

13.1 Split-Sample Validation

$$\mathbf{p}^* = \arg\min_{\mathbf{p}} \quad \Phi_{cal}(\mathbf{p}) \tag{17a}$$

With calibration objective:

$$\Phi_{cal}(\mathbf{p}) = \sum_{i=1}^{n_{cal}} w_i \left(y_i^{obs} - y_i^{sim}(\mathbf{p})\right)^2 \tag{17b}$$

Validation with independent data is then evaluated:

$$\Phi_{val}(\mathbf{p}^*) = \sum_{j=1}^{n_{val}} w_j \left(y_j^{obs} - y_j^{sim}(\mathbf{p}^*)\right)^2 \tag{17c}$$

Terms in the equations

- $\mathbf{p}$= parameter vector
- $\mathbf{p}^*$= calibrated parameter set
- Φ_{cal}= calibration objective function
- Φ_{val}= validation objective function
- n_{cal}= number of calibration observations
- n_{val}= number of validation observations

This is one of the strongest validation approaches because the model is tested using observations not used during calibration.

13.2 Multi-objective hydraulic and PFAS behavior validation

A combined validation expression may be written as:

$$\Phi_{val,total} = \Phi_{val,hydraulic} + \Phi_{val,chemical} \tag{18a}$$

With

$$\Phi_{val,hydraulic} = \sum w_i^{\theta}\left(\theta_i^{obs} - \theta_i^{sim}\right)^2 + \sum w_i^{h}\left(h_i^{obs} - h_i^{sim}\right)^2 \tag{18b}$$

$$\Phi_{val,chemical} = \sum w_i^{C}\left(C_i^{obs} - C_i^{sim}\right)^2 \tag{18c}$$

Terms in the equations

- $\Phi_{val,total}$= total validation objective
- $\Phi_{val,hydraulic}$= hydraulic validation component
- $\Phi_{val,chemical}$= PFAS concentration validation component
- $\theta_i^{obs}, \theta_i^{sim}$= observed and simulated water content
- h_i^{obs}, h_i^{sim}= observed and simulated pressure head
- C_i^{obs}, C_i^{sim}= observed and simulated PFAS concentration
- $w_i^{\theta}, w_i^{h}, w_i^{C}$= observation weights

For PFAS vadose-zone models, validation is strongest when the model reproduces both the water-flow system and the PFAS transport system.

13.3 Cumulative mass-discharge validation

For long-term PFAS leaching, cumulative mass discharge may be defined as:

$$M(t) = \int_0^t Q(\tau)\, C(\tau)\, d\tau \tag{19a}$$

Discrete data:

$$M(t_k) \approx \sum_{j=1}^{k} Q_j\, C_j \Delta t_j \tag{19b}$$

Terms in the equations

- $M(t)$= cumulative mass discharge by time t
- $Q(\tau)$= flow rate at time τ
- $C(\tau)$= concentration at time τ
- Δt_j= time increment for observation interval j

This is particularly important for PFAS because the practical question is often the total mass leached over time, not just concentration at one time step.

14. Sensitivity Analysis

14.1 Local sensitivity

For an output and parameter :

$$S_j^{local} = \frac{\partial Y}{\partial p_j} \tag{20a}$$

and a normalized local sensitivity is:

$$S_j^* = \frac{p_j}{Y}\frac{\partial Y}{\partial p_j} \tag{20b}$$

A finite-difference approximation is:

$$\frac{\partial Y}{\partial p_j} \approx \frac{Y(p_j + \Delta p_j) - Y(p_j - \Delta p_j)}{2\Delta p_j} \tag{20c}$$

Terms in the equations

- S_j^{local} = local sensitivity of output Y to parameter p_j
- S_j^* = normalized local sensitivity
- Δp_j = small perturbation applied to parameter p_j

Local sensitivity evaluates how strongly a model prediction changes when one parameter is perturbed near the calibrated solution. It is useful for ranking which parameters matter most in the neighborhood of the preferred parameter set.

14.2 Composite scaled sensitivity

A regression-style metric is:

$$CSS_j = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\partial y_i}{\partial p_j}\, p_j \sqrt{w_i}\right)^2} \tag{21}$$

Terms in the equation

- CSS_j = composite scaled sensitivity for parameter p_j
- $\partial y_i / \partial p_j$ = sensitivity of simulated observation i to parameter p_j

Composite scaled sensitivity indicates which parameters the calibration dataset can actually "see." Parameters with very low sensitivity may remain weakly identifiable even if they are conceptually important.

14.3 Morris elementary effects

For a model with inputs , the elementary effect of factor is:

$$EE_i(\mathrm{X}) = \frac{Y(X_1, \dots, X_i + \Delta, \dots, X_k) - Y(\mathrm{X})}{\Delta} \qquad (22a)$$

with summary measures:

$$\mu_i = \frac{1}{r}\sum_{j=1}^{r} EE_{i,j} \qquad (22b)$$

$$\mu_i^* = \frac{1}{r}\sum_{j=1}^{r} \left|EE_{i,j}\right| \qquad (22c)$$

$$\sigma_i = \sqrt{\frac{1}{r-1}\sum_{j=1}^{r} \left(EE_{i,j} - \mu_i\right)^2} \qquad (22d)$$

Terms in the equations

- EE_i = elementary effect for factor i
- X_i = model factor or input variable
- Δ = perturbation step in normalized input space
- r = number of Morris trajectories
- μ_i = mean elementary effect
- μ_i^* = mean absolute elementary effect
- σ_i = standard deviation of elementary effects

Morris screening is a practical first-pass method for larger PFAS models. A high indicates a parameter is influential, while a high suggests nonlinearity or parameter interaction.

14.4 Sobol variance-based sensitivity

Variance decomposition is:

$$Var(Y) = \sum_{i} V_i + \sum_{i<j} V_{ij} + \sum_{i<j<k} V_{ijk} + \cdots \qquad (23a)$$

with first-order Sobol index:

$$S_i = \frac{V_i}{Var(Y)} \qquad (23b)$$

and total-effect index:

$$S_{T_i} = 1 - \frac{Var_{X_{\sim i}}\left(E_{X_i}[Y \mid X_{\sim i}]\right)}{Var(Y)} \qquad (23c)$$

Terms in the equations

- $Var(Y)$ = total variance of model output Y
- V_i = variance contribution from factor i
- V_{ij}, V_{ijk} = interaction contributions
- S_i = first-order Sobol index
- S_{T_i} = total-effect Sobol index
- $X_{\sim i}$ = all input factors except i
- $E_{X_i}[\cdot]$ = expectation over factor X_i

Sobol analysis provides the strongest picture of parameter importance because it separates direct effects from interaction effects across the full parameter space. In PFAS work, it can reveal whether predictions are controlled mostly by one parameter or by interactions among flow, retention, and release processes.

15. Uncertainty Analysis

15.1 Parameter covariance

Near the optimum parameter set, the parameter covariance matrix is approximated as:

$$\mathbf{C_p} = s^2(\mathrm{J}^T\mathrm{W}\mathrm{J})^{-1} \qquad (24a)$$

with residual variance estimate:

$$s^2 = \frac{\Phi(\mathbf{p}^*)}{n - m} \tag{24b}$$

and approximate standard error:

$$SE(p_j) = \sqrt{C_{p,jj}} \tag{24c}$$

Terms in the equations

- $\mathbf{C_p}$ = parameter covariance matrix
- s^2 = residual variance estimate
- $\mathbf{p}^*$ = optimum parameter vector
- $SE(p_j)$ = standard error of parameter p_j
- $C_{p,jj}$ = diagonal covariance element for parameter p_j

This provides the first formal estimate of how uncertain each calibrated parameter remains. Large standard errors indicate weak parameter identifiability.

15.2 First-order prediction uncertainty

For a scalar prediction :

$$Var(Z) \approx \mathrm{g_p}^T \mathrm{C_p} \mathrm{g_p} \tag{25a}$$

with

$$\mathbf{g_p} = \left[\frac{\partial Z}{\partial p_1}, \frac{\partial Z}{\partial p_2}, \ldots, \frac{\partial Z}{\partial p_m}\right]^T \tag{25b}$$

and

$$\sigma_Z = \sqrt{Var(Z)} \tag{25c}$$

Terms in the equations

- $Var(Z)$ = approximate variance of prediction Z
- $\mathbf{g_p}$ = gradient of prediction with respect to parameters
- σ_Z = standard deviation of prediction

This is the simplest way to translate parameter uncertainty into a prediction such as groundwater arrival time, peak leachate concentration, or long-term mass discharge.

15.3 Monte Carlo uncertainty propagation

Parameter realizations are sampled as:

$$\mathbf{p}^{(\boldsymbol{k})} \sim f_{\mathrm{p}}(\mathrm{p}), \qquad k = 1, \dots, N \tag{26a}$$

and propagated through the model:

$$\boldsymbol{Y}^{(\boldsymbol{k})} = f\left(\mathrm{p}^{(k)}\right) \tag{26b}$$

with summary statistics:

$$\bar{Y} = \frac{1}{N}\sum_{k=1}^{N} Y^{(k)} \tag{26c}$$

$$Var(Y) \approx \frac{1}{N-1}\sum_{k=1}^{N}\left(Y^{(k)} - \bar{Y}\right)^2 \tag{26d}$$

and percentile interval:

$$PI_{95\%} = [Q_{2.5}(Y), Q_{97.5}(Y)] \tag{26e}$$

Terms in the equations

- $f_{\mathrm{p}}(\mathrm{p})$ = probability distribution assigned to uncertain parameters
- N = number of simulations
- $\boldsymbol{Y}^{(\boldsymbol{k})}$ = output from the kth simulation
- $\bar{Y}$ = mean of simulated outputs
- $PI_{95\%}$ = 95% prediction interval

- $Q_{2.5}, Q_{97.5}$ = 2.5th and 97.5th percentiles

Monte Carlo analysis shows how predictions spread when uncertain parameters vary across realistic ranges. For PFAS, this is especially important because long-term leaching can be highly nonlinear and strongly affected by AWI adsorption, transient saturation, and kinetic release.

15.4 Latin Hypercube Sampling

A more efficient sampling design is:

$$\mathbf{p}^{(k)} \sim \mathrm{LHS}\left(f_{\mathbf{p}}\right) \tag{27}$$

Terms in the equation

- LHS = Latin Hypercube Sampling, a stratified sampling scheme for efficient parameter-space exploration

LHS does not change the uncertainty framework; it changes how efficiently the parameter space is sampled. It is often preferable for PFAS models with many uncertain variables.

15.5 Likelihood and posterior-style updating

A likelihood-style weighting is:

$$L(\mathbf{p}) \propto \exp\left(-\frac{1}{2}\Phi(\mathbf{p})\right) \tag{28a}$$

with posterior-style form:

$$f\left(\mathbf{p} \mid \mathbf{y}^{obs}\right) \propto L(\mathbf{p})\, f(\mathbf{p}) \tag{28b}$$

Terms in the equations

- $L(\mathbf{p})$ = likelihood assigned to parameter vector **p**
- $f(\mathbf{p})$ = prior distribution of parameters
- $f\left(\mathbf{p} \mid \mathbf{y}^{obs}\right)$ = posterior distribution conditioned on observations

This framework updates prior parameter information using site data rather than only a single optimum estimate. It is useful when the goal is not just one best-fit model, but a probability-weighted ensemble of plausible models.

15.6 Null-space Monte Carlo concept

In highly parameterized inverse modeling, uncertainty can be explored through weakly informed directions of parameter space:

$$\mathbf{p}^{(k)} = \mathbf{p}^* + \mathbf{V_n}\mathbf{a}^{(k)} \tag{29}$$

Terms in the equation

- $\mathbf{V_n}$ = basis for the null space of the sensitivity matrix
- $\mathbf{a}^{(k)}$ = random coefficient vector for realization k

This method explores prediction uncertainty by varying parameters in directions that remain informed by the data while preserving acceptable calibration.

14.7 Total predictive uncertainty

A practical decomposition is:

$$Var_{total}(Z) = Var_{param}(Z) + Var_{obs}(Z) + Var_{scenario}(Z) + Var_{structure}(Z) \tag{30}$$

Terms in the equation

- $Var_{total}(Z)$ = total prediction variance
- $Var_{param}(Z)$ = variance due to parameter uncertainty
- $Var_{obs}(Z)$ = variance due to observation or measurement error
- $Var_{scenario}(Z)$ = variance due to future forcing scenarios
- $Var_{structure}(Z)$ = variance due to model structural uncertainty

A single best-fit PFAS run is rarely enough. Total predictive uncertainty reflects not only uncertain parameters, but also uncertain measurements, future recharge or source scenarios, and the possibility that the model itself omits relevant processes.

16. Key Assumptions for a Defensible PFAS Vadose-Zone Model

A defensible PFAS model usually rests on a limited but explicit set of assumptions:

The conceptual site model is approximately correct and identifies the dominant source, transport pathway, and controlling PFAS processes.

The selected equations match the purpose of the model. A screening model can justify simplifications that would be inadequate for a remedial-design model.

Adsorption and interfacial parameters are treated as effective site-scale model parameters, not immutable constants.

Precursor transformation, if included, is represented as a lumped approximation unless the data justify more mechanistic detail.

Recharge, evapotranspiration, and water-table conditions are represented using defensible boundary conditions and scenarios.

Calibration targets are relevant to the decisions the model is intended to support.

17. Key Limitations

PFAS vadose-zone models remain limited by parameter non-uniqueness, scale effects, and data scarcity. Laboratory-derived adsorption or interfacial parameters may not transfer directly to field conditions. Air-water interfacial area remains difficult to estimate robustly at field scale. Preferential flow may be invisible in sparse datasets but still dominate arrival timing. Precursor transformation pathways can be oversimplified if represented too mechanistically. A strong calibration to one observation type does not guarantee robust prediction of other outputs, particularly long-term mass discharge.

18. Conclusions

PFAS vadose-zone modeling is defensible when it reflects what is now well established in the literature: PFAS mobility in unsaturated media is governed by transient flow, adsorption to solids, adsorption at air-water interfaces, and depending on site conditions, kinetic retention, preferential flow, and precursor transformation. Models that neglect these processes may be useful only for very rough screening and can materially underpredict or misrepresent groundwater impacts.

AA GeoEnvironmental emphasizes conceptual-model consistency, process-appropriate model formulation, calibration to relevant observations, independent dataset validation, transparent evaluation of assumptions, sensitivity, and uncertainty as the foundation of defensible PFAS fate and transport modeling.

The strongest PFAS white papers do not merely provide equations. They show why the selected equations are appropriate for the site, what the controlling parameters are, how well the model matches evidence, and how much uncertainty remains in the predictions.

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Appendix A. 3-D Governing Equations for PFAS Vadose-Zone Modeling

This appendix extends the primary one-dimensional governing equations into three dimensions. The governing physics remain the same, but water flow and PFAS transport are represented in the x, y, and z directions using vector fluxes, gradients, divergence operators, and dispersion tensors. Three-dimensional formulations are most useful when the site has irregular source geometry, lateral spreading, stratigraphic heterogeneity, capillary barriers, textural contrasts, perched water, groundwater-table fluctuations, or localized preferential pathways.

The notation below is intentionally explicit so the equations can be read as a stand-alone technical appendix.

A.1 3-D variably saturated flow (Richards equation)

$$\frac{\partial \theta}{\partial t} = \nabla \cdot [K(h)\nabla H] - S_w$$

$$H = h + z$$

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left(K_x \frac{\partial H}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial H}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial H}{\partial z}\right) - S_w$$

Definitions: θ = volumetric water content; t = time; ∇ = gradient operator; ∇· = divergence operator; K(h) = unsaturated hydraulic conductivity tensor or directional conductivity; H = total hydraulic head; h = pressure head; z = elevation head; Kx, Ky, Kz = directional unsaturated hydraulic conductivity components; Sw = sink/source term for water, including extraction or root uptake if represented.

Practical meaning: This equation describes how water moves through unsaturated porous media in all spatial directions. In real PFAS sites, infiltration may move downward and then spread laterally along lower-permeability layers or perched horizons.

A.2 3-D aqueous-phase PFAS transport equation

$$\frac{\partial (\theta C_i)}{\partial t} + \rho_b \frac{\partial S_i}{\partial t} + \frac{\partial (A_{aw}\Gamma_i)}{\partial t} = \nabla \cdot (\theta \mathbf{D}_i \nabla C_i) - \nabla \cdot (\mathbf{q} C_i) + \sum R_i$$

$$-\nabla \cdot (\mathbf{q} C_i) = -\frac{\partial (q_x C_i)}{\partial x} - \frac{\partial (q_y C_i)}{\partial y} - \frac{\partial (q_z C_i)}{\partial z}$$

Definitions: Ci = aqueous concentration of PFAS species i; ρb = bulk density; Si = sorbed concentration on solids; Aaw = specific air-water interfacial area; Γi = PFAS mass adsorbed per unit air-water interfacial area; Di = three-dimensional hydrodynamic dispersion tensor; q = Darcy flux vector; qx, qy, qz = directional Darcy flux components; ΣRi = net reaction, source, and sink terms, including transformation or decay terms where relevant.

Practical meaning: This is the three-dimensional PFAS mass-balance equation. It allows PFAS to migrate vertically, laterally, and diagonally through heterogeneous vadose zones.

A.3 3-D dispersion tensor

$$\mathbf{D}_i = \begin{bmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{bmatrix}$$

$$D_{ij} = \alpha_T |\mathbf{v}| \delta_{ij} + (\alpha_L - \alpha_T)\left(\frac{v_i v_j}{|\mathbf{v}|}\right) + \theta \tau D_m \delta_{ij}$$

Definitions: Dxx, Dxy, … , Dzz = tensor components of hydrodynamic dispersion; αL = longitudinal dispersivity; αT = transverse dispersivity; |v| = magnitude of pore-water velocity; δij = Kronecker delta; vi and vj = pore-water velocity components; τ = tortuosity factor; Dm = molecular diffusion coefficient in water.

Practical meaning: In three dimensions, PFAS spreading is not only forward in the principal flow direction; it also occurs laterally and vertically because of heterogeneity and velocity variations.

A.4 3-D pore-water velocity

$$\mathbf{v} = \frac{\mathbf{q}}{\theta}$$

$$v_x = \frac{q_x}{\theta}, \qquad v_y = \frac{q_y}{\theta}, \qquad v_z = \frac{q_z}{\theta}$$

Definitions: v = pore-water velocity vector; q = Darcy flux vector; θ = volumetric water content; v_x, v_y, v_z = directional pore-water velocity components.

Practical meaning: This converts Darcy flux into the actual transport velocity of PFAS in the water-filled pore space.

A.5 Solid-phase adsorption in 3-D

$$S_i = K_{d,i} C_i$$

$$S_i = K_{f,i} C_i^{N_i}$$

Definitions: Si = sorbed concentration of PFAS species i on the solid phase; Kd,i = linear distribution coefficient; K_f,i = Freundlich coefficient; Ni = Freundlich exponent; Ci = aqueous concentration of PFAS species i.

Practical meaning: Adsorption is evaluated locally in each grid cell or finite element. In a 3-D model, each spatial location can have different geologic, geochemical, and saturation conditions, so adsorption can vary laterally and vertically.

A.6 Two-site sorption and kinetic desorption in 3-D

$$S_i = S_{i,1} + S_{i,2}$$

$$S_{i,1} = f_i K_{d,i} C_i$$

$$\frac{\partial S_{i,2}}{\partial t} = \alpha_{s,i}\left[(1 - f_i) K_{d,i} C_i - S_{i,2}\right]$$

Definitions: Si,1 = equilibrium sorbed concentration; Si,2 = kinetic sorbed concentration; fi = fraction of instantaneous equilibrium sites; αs,i = first-order solid-phase mass-transfer coefficient; K_d,i = linear distribution coefficient; Ci = aqueous PFAS concentration.

Practical meaning: This formulation captures slow desorption and mass-transfer limitations that can sustain long-term PFAS release after the original source has diminished.

A.7 Air-water interfacial adsorption in 3-D

$$\Gamma_i = K_{aw,i} C_i$$

$$\frac{\partial \Gamma_i}{\partial t} = \alpha_{aw,i}\left(K_{aw,i} C_i - \Gamma_i\right)$$

$$\frac{\partial (A_{aw} \Gamma_i)}{\partial t} = A_{aw} \frac{\partial \Gamma_i}{\partial t} + \Gamma_i \frac{\partial A_{aw}}{\partial t}$$

Definitions: Kaw,i = air-water interfacial adsorption coefficient for PFAS species i; αaw,i = first-order interfacial mass-transfer coefficient; Aaw = specific air-water interfacial area; Γi = PFAS mass adsorbed per unit interfacial area; Ci = aqueous PFAS concentration.

Practical meaning: These equations allow the model to account for strong PFAS retention at air-water interfaces under unsaturated conditions, including transient changes caused by wetting and drying.

A.8 Air-water interfacial area in 3-D

$$A_{aw}(\theta) = \frac{\rho_w g}{\sigma_0} \int_{\theta}^{\theta_s} h\,(\theta)\, d\theta$$

Definitions: A_{aw} = specific air-water interfacial area; ρ_w = water density; g = gravitational acceleration; σ_0 = surface tension of pure water; θ = volumetric water content; θs = saturated water content; h(θ) = pressure head expressed as a function of water content.

Practical meaning: In three-dimensional media, saturation can vary laterally and vertically, so the available air-water interfacial area can also vary strongly across the domain.

A.9 Preferential-flow / dual-domain formulation in 3-D

$$\frac{\partial\left(\theta_m C_{i,m}\right)}{\partial t}+\rho_b\frac{\partial S_{i,m}}{\partial t}+\frac{\partial\left(A_{aw,m}\Gamma_{i,m}\right)}{\partial t}=\nabla\cdot\left(\theta_m\mathbf{D}_{i,m}\nabla C_{i,m}\right)-\nabla\cdot\left(\mathbf{q}_m C_{i,m}\right)+\omega_i\left(C_{i,f}-C_{i,m}\right)$$

$$\frac{\partial\left(\theta_f C_{i,f}\right)}{\partial t}+\rho_b\frac{\partial S_{i,f}}{\partial t}+\frac{\partial\left(A_{aw,f}\Gamma_{i,f}\right)}{\partial t}=\nabla\cdot\left(\theta_f\mathbf{D}_{i,f}\nabla C_{i,f}\right)-\nabla\cdot\left(\mathbf{q}_f C_{i,f}\right)-\omega_i\left(C_{i,f}-C_{i,m}\right)$$

Definitions: θ_m, θ_f = volumetric water contents of matrix and preferential-flow domains; Ci,m, Ci,f = aqueous PFAS concentrations in matrix and preferential-flow domains; Si,m, Si,f = sorbed concentrations in the two domains; A_{aw},m, A_{aw},f = specific air-water interfacial areas in the two domains; Γi,m, Γi,f = interfacially adsorbed PFAS; Di,m, Di,f = dispersion tensors; qm, qf = Darcy flux vectors; ωi = interdomain mass-exchange coefficient.

Practical meaning: This framework captures rapid PFAS movement through fractures, fingers, root channels, macropores, or textural contacts while also allowing exchange with the slower matrix domain.

A.10 Precursor transformation in 3-D

$$\frac{\partial\left(\theta C_p\right)}{\partial t}=\nabla\cdot\left(\theta\mathbf{D}_p\nabla C_p\right)-\nabla\cdot\left(\mathbf{q}C_p\right)-\lambda_p\theta C_p$$

$$R_{p\to i}=Y_i\lambda_{p,i}\theta C_p$$

$$\sum_j Y_{ij}\,\lambda_{p,j}\theta C_{p,j}$$

Definitions: Cp = precursor concentration in pore water; Dp = precursor dispersion tensor; λp = lumped precursor transformation coefficient; Rp→i = daughter-PFAS production rate; Yi or Yij = effective yield coefficient; Cp,j = concentration of precursor class j.

Practical meaning: In three dimensions, precursor pools can follow different flow paths, residence times, and geochemical environments before producing daughter PFAS. The formulation is best interpreted as a lumped reactive-transport approximation of net precursor loss and daughter-PFAS generation.

A.11 Full 3-D PFAS vadose-zone master equation

$$\frac{\partial(\theta C_i)}{\partial t}+\rho_b\frac{\partial\left(S_{i,1}+S_{i,2}\right)}{\partial t}+\frac{\partial(A_{aw}\Gamma_i)}{\partial t}$$
$$=\nabla\cdot(\theta\mathbf{D}_i\nabla C_i)-\nabla\cdot(\mathbf{q}C_i)+\omega_i\left(C_{i,f}-C_{i,m}\right)+\sum_j Y_{ij}\,\lambda_{p,j}\theta C_{p,j}-\lambda_{w,i}\theta C_i$$

$$S_{i,1}=f_iK_{d,i}C_i$$

$$\frac{\partial S_{i,2}}{\partial t}=\alpha_{s,i}\left[(1-f_i)K_{d,i}C_i-S_{i,2}\right]$$

$$\frac{\partial \Gamma_i}{\partial t} = \alpha_{aw,i}\left(K_{aw,i}C_i - \Gamma_i\right)$$

$$A_{aw} = A_{aw}(\theta)$$

$$\mathbf{v} = \frac{\mathbf{q}}{\theta}$$

$$\frac{\partial \theta}{\partial t} = \nabla \cdot [K(h)\nabla H] - S_w$$

Definitions: λw,i = first-order aqueous-phase loss or transformation coefficient for PFAS species i; all other terms are defined above.

Practical meaning: This integrated equation set is appropriate for realistic field sites where PFAS migration is affected by multidirectional flow, heterogeneity, interfacial retention, kinetic release, preferential pathways, and precursor transformation.

A.12 Practical note on when 3-D modeling is warranted

Three-dimensional modeling is generally most warranted when the site has irregular source geometry, strong stratigraphic heterogeneity, lateral spreading along layers, capillary barriers, perched water, groundwater-table fluctuations, variable recharge, or preferential pathways that cannot be represented adequately in a one-dimensional framework.

In contrast, one-dimensional models are often adequate for screening-level vertical leaching estimates, homogeneous column studies, and simple preliminary assessments where lateral spreading and heterogeneity are not central to the decision.