

Extent of Air-water and Solid-phase Adsorption of PFAS in the Vadose Zone within Heterogeneous Systems

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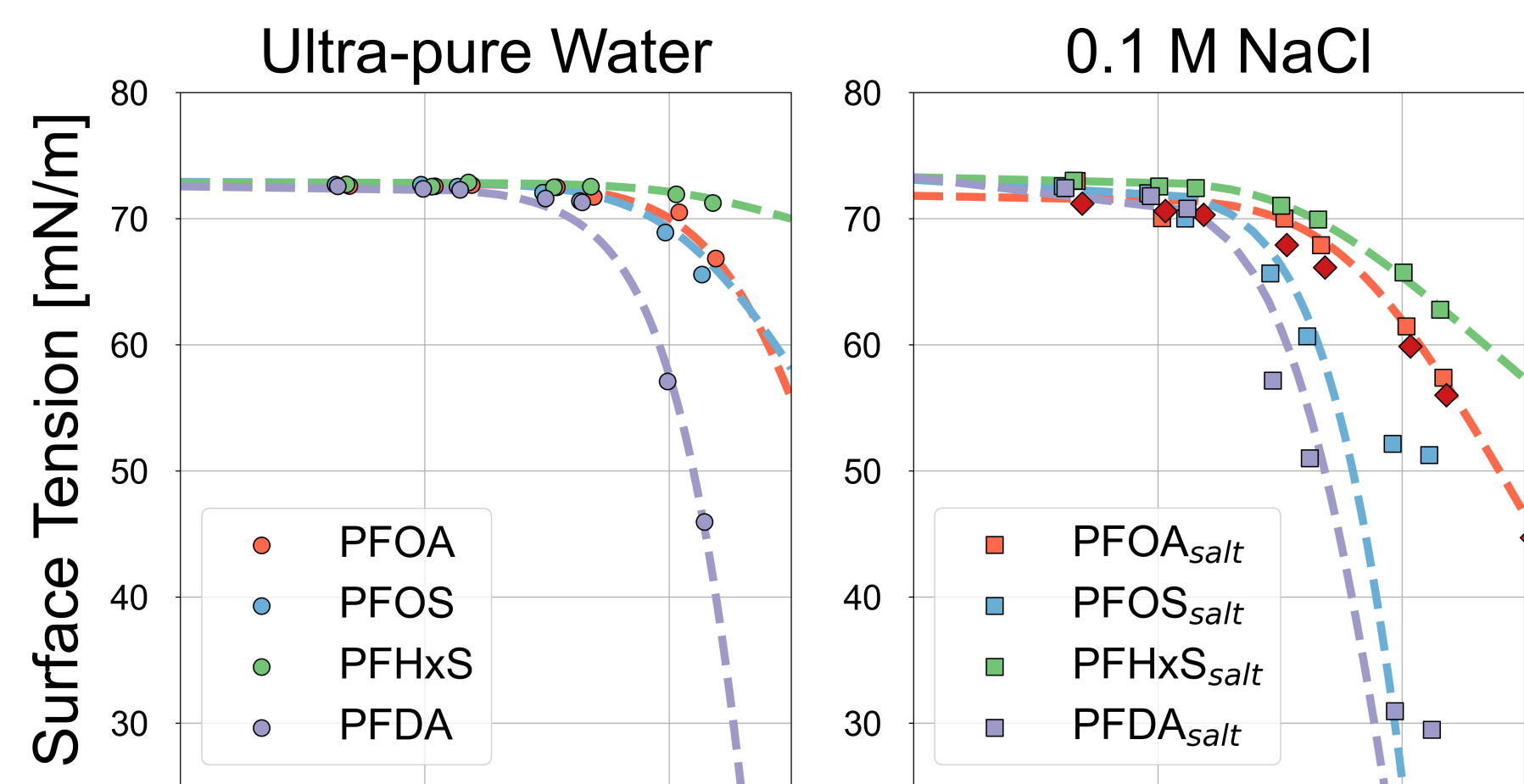
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2 Quantifying PFAS adsorption



$$R = 1 + \frac{K_d \rho_b}{\phi S_w} + \frac{K_{aw} A_{wi}}{\phi S_w}$$

PFAS retardation described in terms of solid-phase adsorption and air-water interfacial adsorption

Figure 1: Surface tension and K_{aw} in ultrapure water and 0.1 M NaCl solution plotted against molar concentration. Dashed lines represent Langmuir-Syszkowski best fits. Note, because the CMC boundary was heavily influenced by the addition of 0.1 M NaCl, fits were performed for concentrations of 10 mg/L and under. Additionally, PFOA measurements in saline solution were compared with previously measured data (diamonds)^[2]. Air-water adsorption coefficients are shown to increase with increasingly saline conditions.

3 Capillary heterogeneity

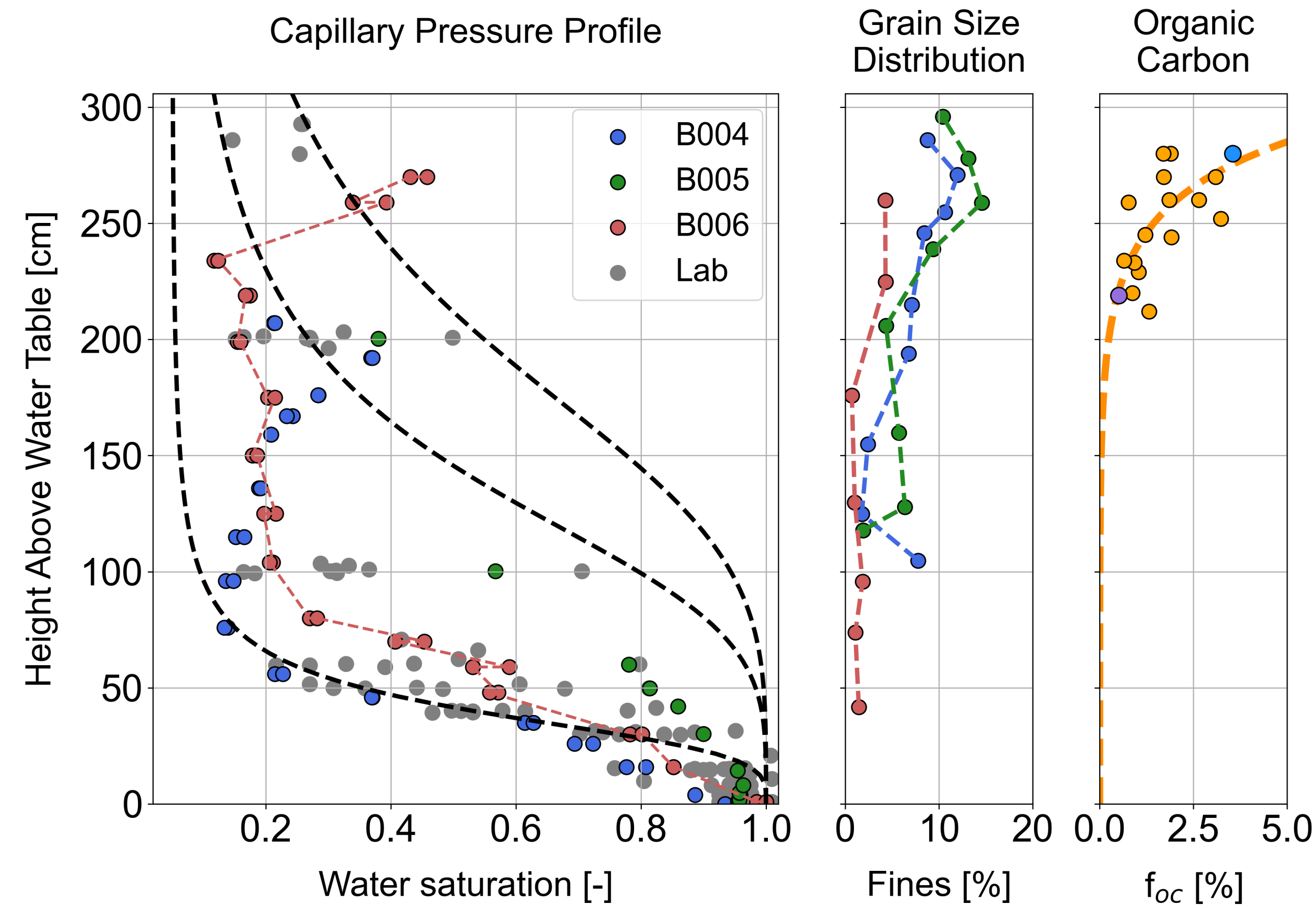


Figure 2: (Left) In-situ (B004, B005, B006) and laboratory measured soil-water retention profiles. ORA is primarily composed of glacial outwash sediments, coarsening with depth. Dashed black lines correspond to capillary pressure curve fits to measured data while the red dashed line traces the in-situ curve of B006.

8 References and acknowledgements

[1] Sharifan, et al. Fate and transport of per- and polyfluoroalkyl substances (PFASs) in the vadose zone. Science of the Total Environment 2021, 771, 145427.

[2] Brusseau, M. L. Assessing the potential contributions of additional retention processes to PFAS retardation in the sub-surface. Science of the Total Environment 2018, 613-614, 176–185

[3] Heisler, A. et al. Leaching and transport of PFAS from aqueous film-forming foam (AFFF) in the unsaturated soil at a firefighting training facility under cold climatic conditions. Journal of Contaminant Hydrology 2019, 222, 112–122.

[4] Weber, A. K. et al. Geochemical and Hydrologic Factors Controlling Subsurface Transport of Poly- and Perfluoroalkyl Substances, Cape Cod, Massachusetts. Environmental Science and Technology 2017, 51, 4269–4279.

[5] Valocchi, A. J. Spatial moment analysis of the transport of kinetically adsorbing solutes through stratified aquifers. Water Resources Research 1989, 25, 273–279

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1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of emerging and environmentally persistent contaminants known to be toxic to humans and ecosystems^[1]. Numerous field investigations have demonstrated long-term leaching behavior decades after the most recent applications. A number of mechanisms control the environmental fate and transport properties of PFAS, namely solid-phase adsorption and air-water interfacial adsorption^[2]. These mechanisms are the dominant processes hypothesized to explain observations of long-term leaching to groundwater^[3,4]. In this work, a semi-analytical framework to estimate PFAS adsorption in the vadose zone was developed and tested at a contaminated site in Northern Wisconsin.

4 Heterogeneous PFAS adsorption

PFAS Vadose Zone Adsorption Maps ($C_0 = 100$ ppt)

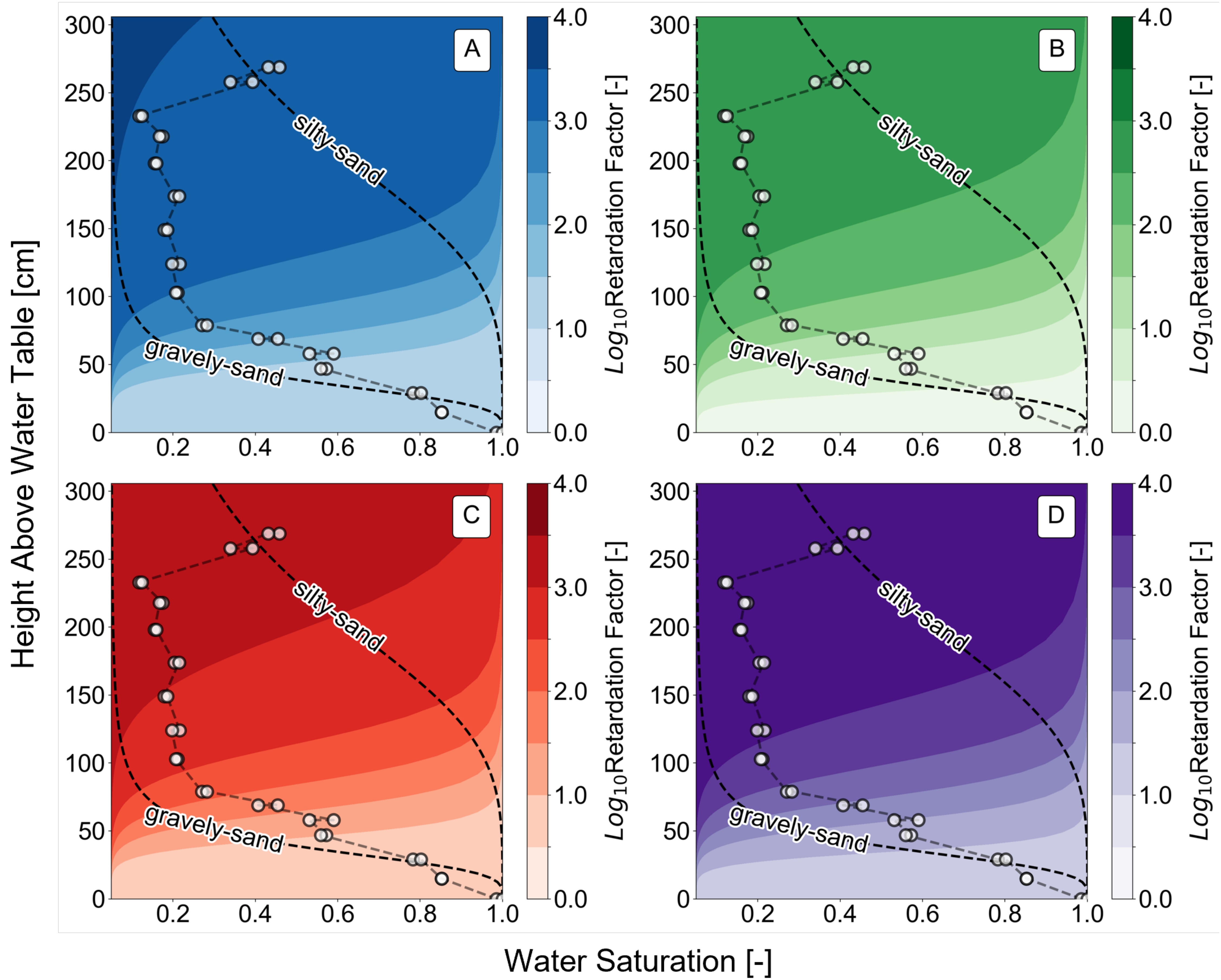
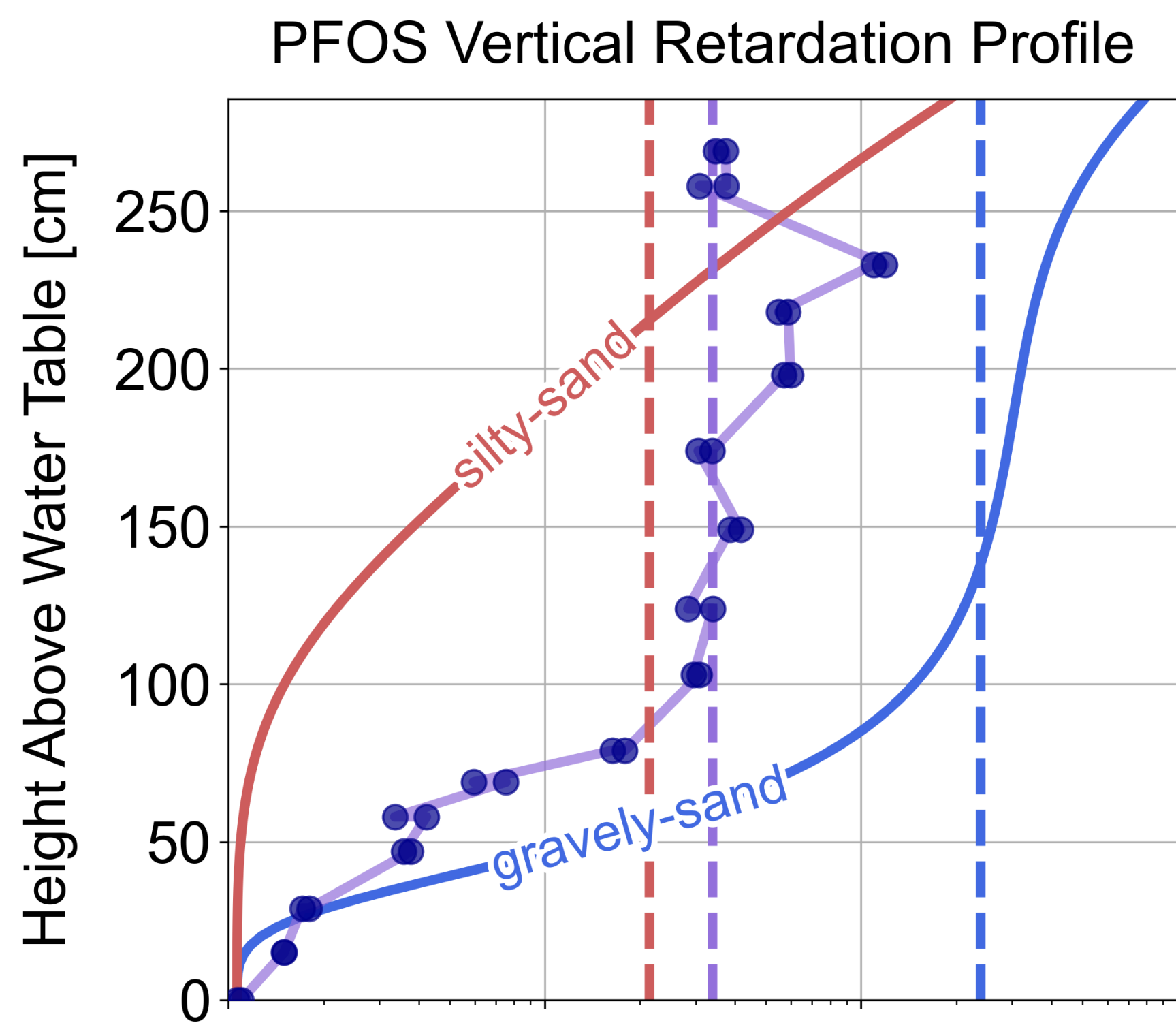


Figure 3: First order approximations of the possible range of retardation experienced by PFOS (A), PFHxS (B), PFOA (C), and PFDA (D) in the vadose zone at a concentration of 100 [ppt]— derived from ultrapure water measurements. Two representative capillary pressure characteristic curves are shown constraining site-wide heterogeneity. The measured capillary pressure profile of one sampled borehole (B006) is plotted to illustrate the effect of capillary heterogeneity on PFAS retardation. Log₁₀ retardation factors are experienced throughout the vadose zone suggesting nearly complete immobilization of PFAS.

5 Vertical integration methods



$$\bar{R} = \frac{1}{H} \int_0^H R(z) dz$$

Vertical integration method originally proposed by Valocchi (1989)^[5]. The depth averaged retardation factor, \bar{R} , results from integrating the spatially variable retardation factor across the height of the vadose zone. This method synthesizes the complex retardation profile of PFAS to a single value for implementation into transport models.

Figure 4: Application of semi-analytical framework for PFOS at a concentration of 100 ppt. Depth dependent retardation calculated based on ORA representative capillary pressure curves and borehole measurements (solid lines). Estimations of the upper and lower bounds on PFOS retardation is constructed by applying the vertical integration framework (corresponding vertical dashed lines). Additional discrimination of air-water and solid-phase retardation contributions are shown in relation to the combined retardation range in the lower bar plot.

6 Future work: Geostatistical Models

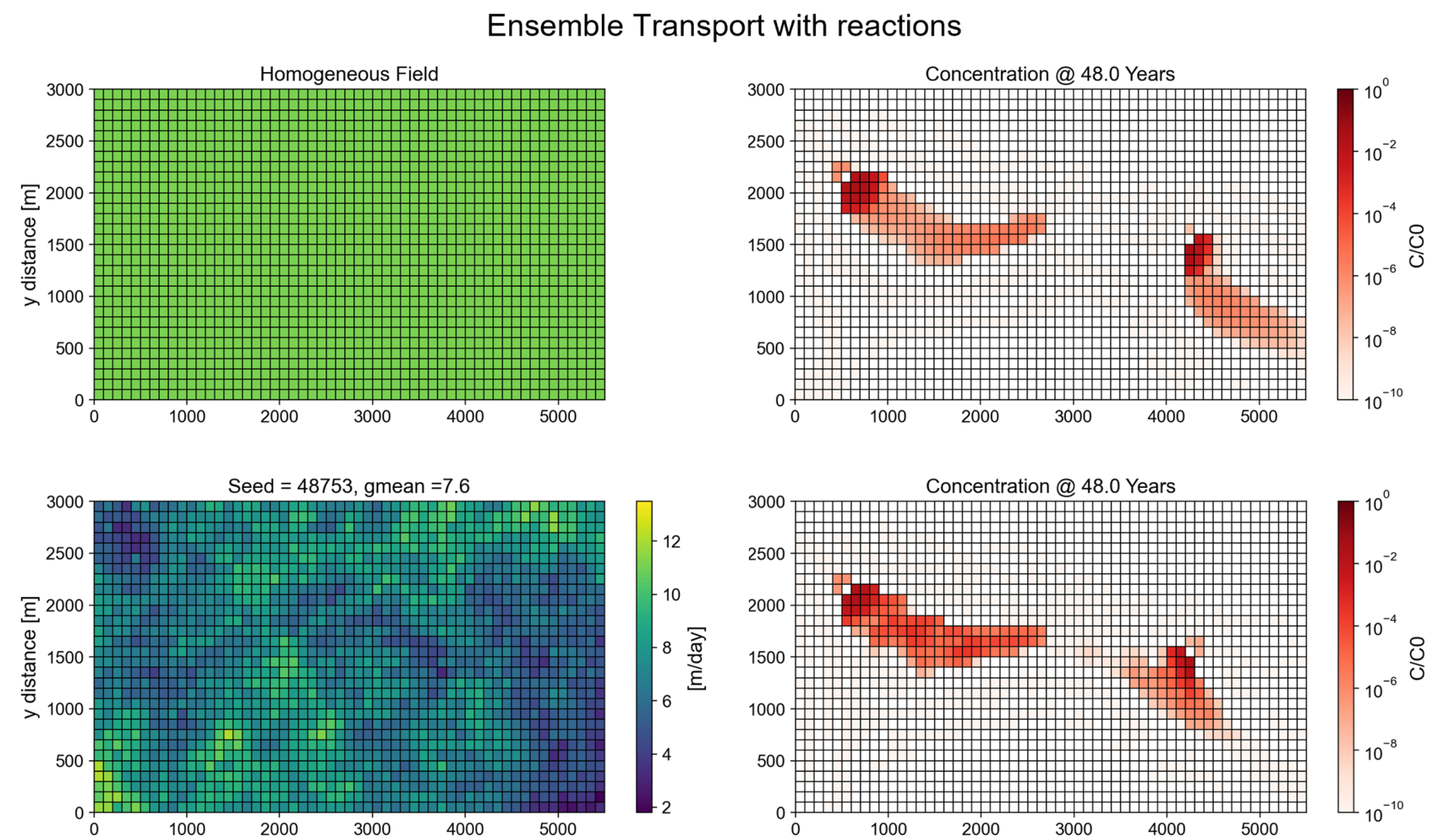


Figure 5: Preliminary 3D PFAS transport models in saturated homogeneous (top) and heterogeneous (bottom) realizations of the subsurface. Hydraulic conductivity and organic carbon content maps were used to spatially model heterogeneity across the field site. The introduction of heterogeneous transport and adsorption mechanisms alters the migration path of PFAS. Future studies will involve unsaturated models relying on vertical integration simplifications

7 Conclusions

- Under hydrostatic conditions, PFAS are **nearly immobile** in unsaturated systems
- The proposed semi-analytical framework allows for **first-order approximations** of PFAS adsorption in heterogeneous systems
- Vertical integration methods **synthesize complex retardation profiles** for implementation into unsaturated transport models