Multiscale approaches to investigate **PFAS** transport and adsorption in the **unsaturated zone**

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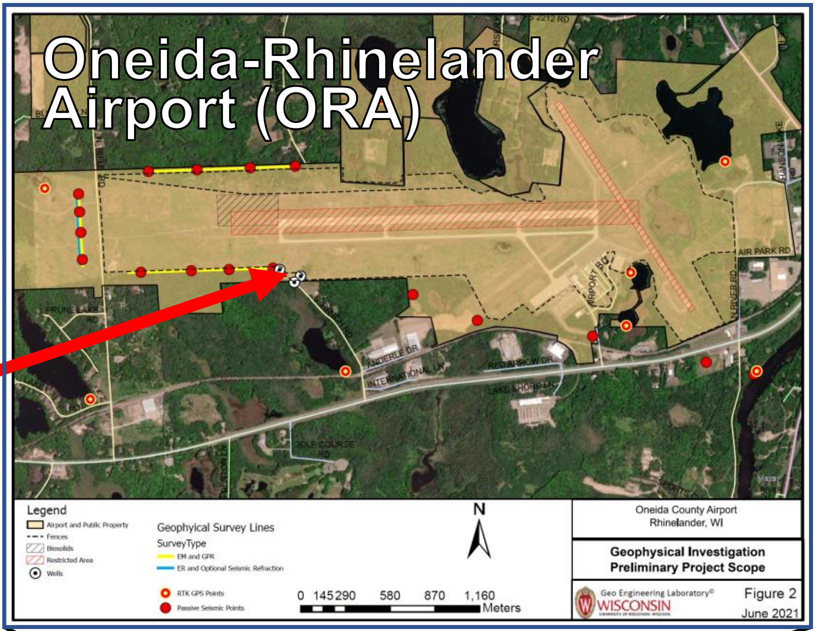
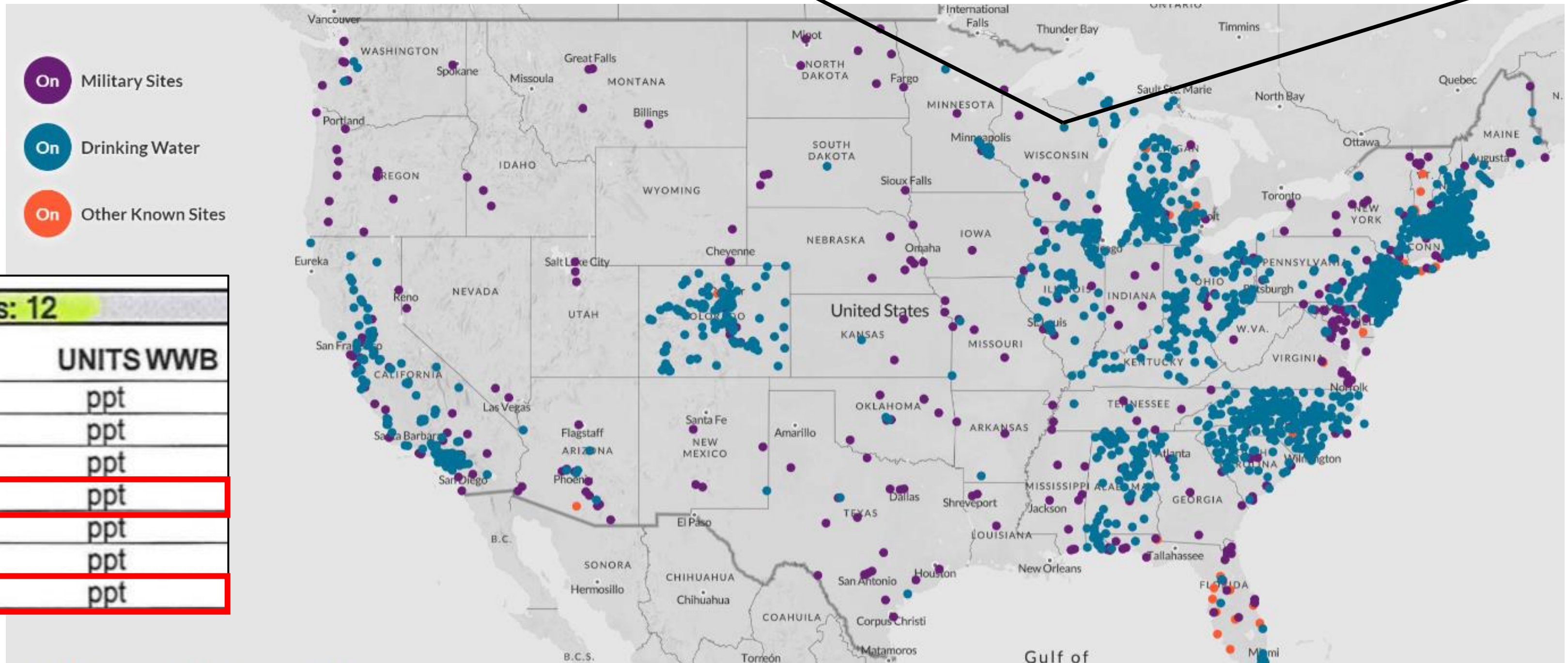
Per- and Polyfluoroalkyl Substances (PFAS) are a growing problem nationally and throughout Wisconsin



Shut down municipal wells

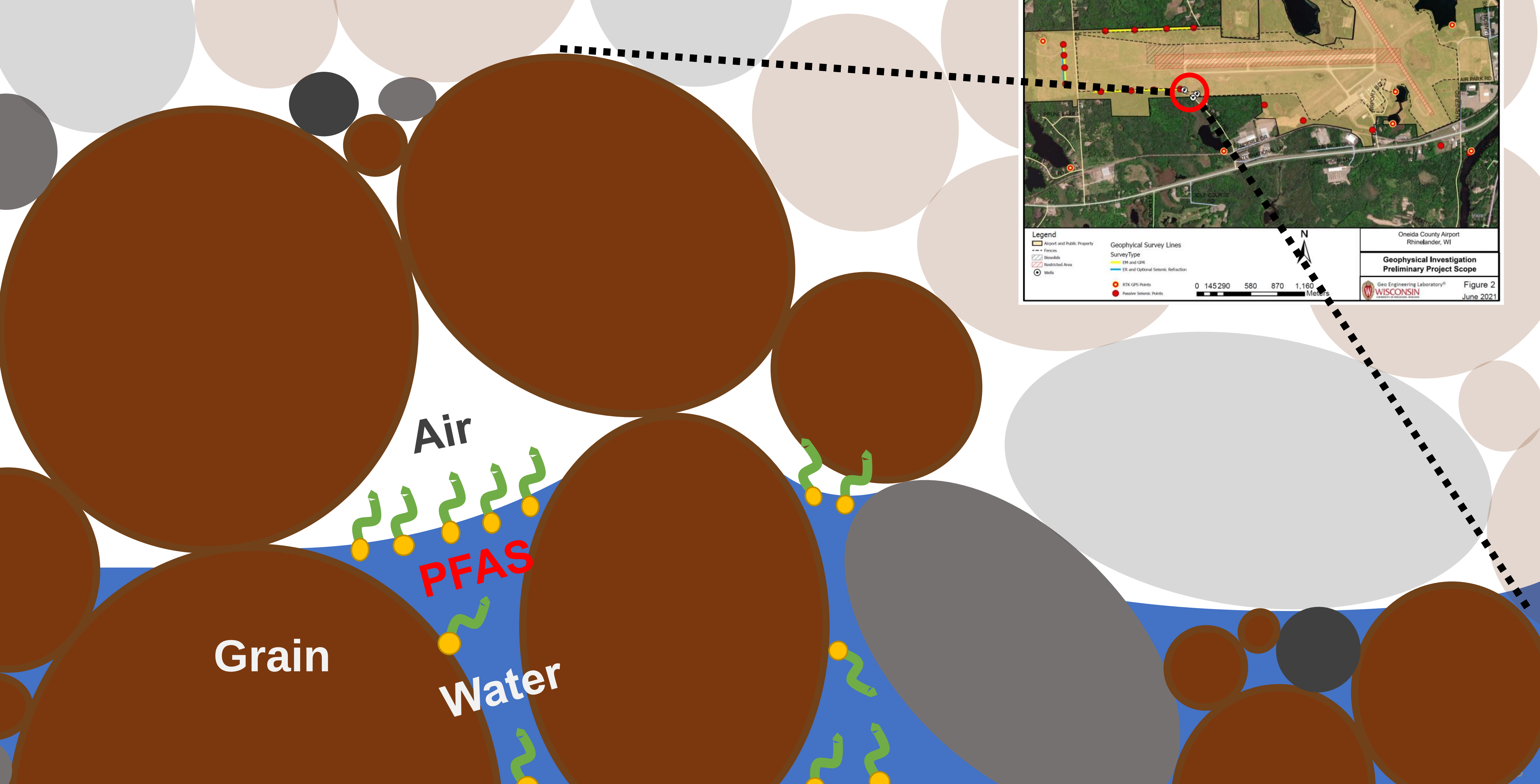
EPA health advisory:
70 ppt PFOA + PFOS

Sample: 1124000 3401 Fox Ranch R	06/14/19 - Analytes: 12	
ANALYTE NAME	RESULT	UNITS WWB
perfluorobutanesulfonic acid (PFBS)	28.4	ppt
perfluorohexanoic acid (PFHxA)	49.9	ppt
perfluoroheptanoic acid (PFHpA)	15.9	ppt
perfluorohexanesulfonic acid (PFHxS)	590	ppt
perfluorooctanoic acid (PFOA)	25.2	ppt
perfluorononanoic acid (PFNA)	ND	ppt
perfluorooctanesulfonic acid (PFOS)	79.6	ppt

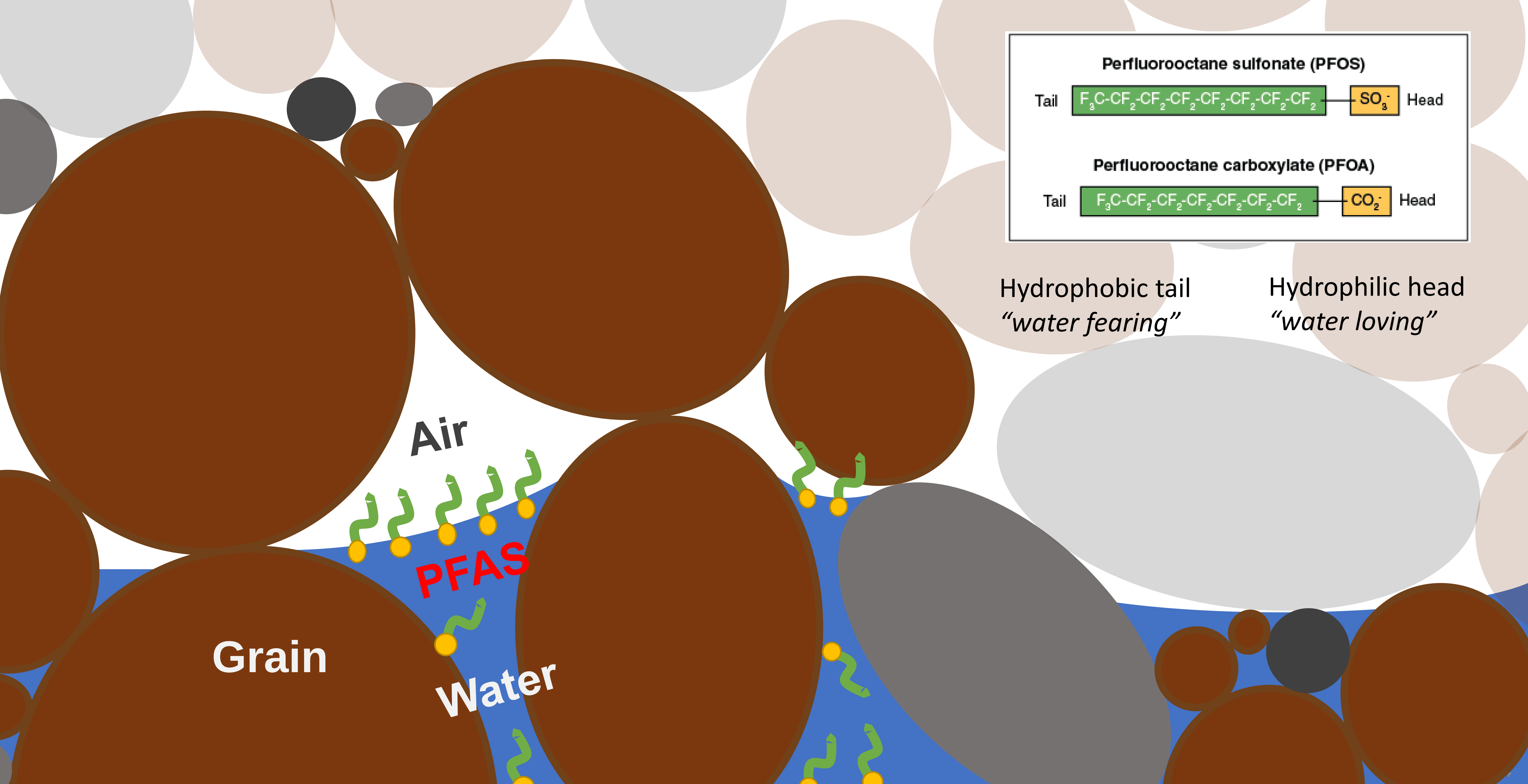


[EWG.org, October 2021]

Pore scale view of PFAS in the vadose zone



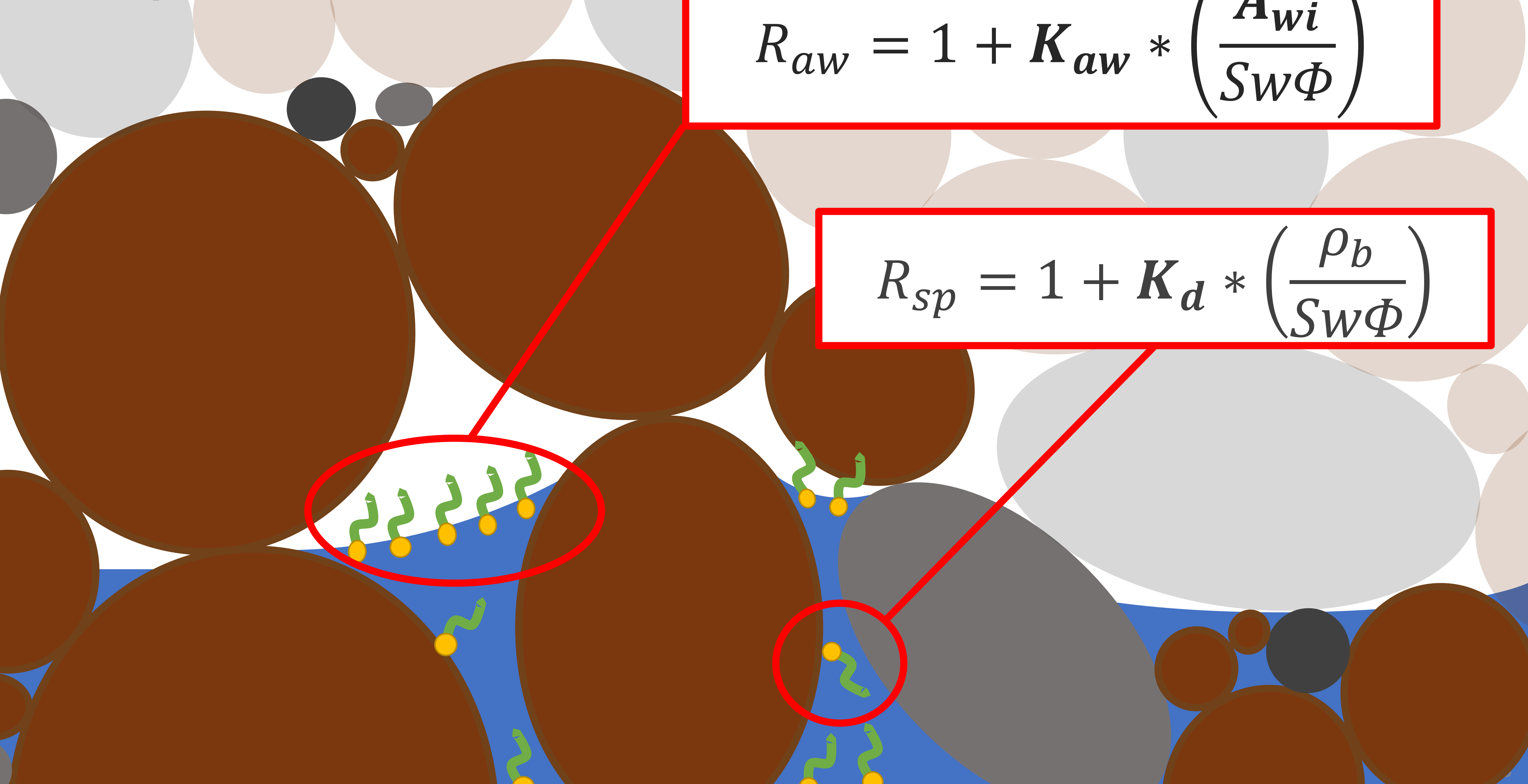
Properties driving long-term PFAS behavior



Adsorption Mechanisms

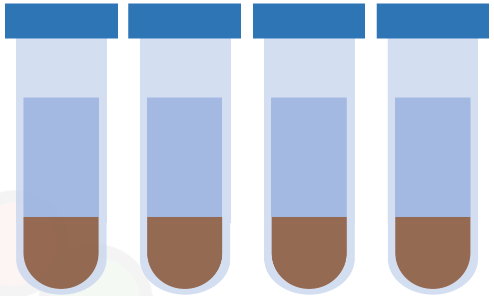
$$R_{aw} = 1 + \boldsymbol{K_{aw}} * \left(\frac{\boldsymbol{A_{wi}}}{Sw\Phi}\right)$$

$$R_{sp} = 1 + \boldsymbol{K_{d}} * \left(\frac{\rho_b}{Sw\Phi}\right)$$

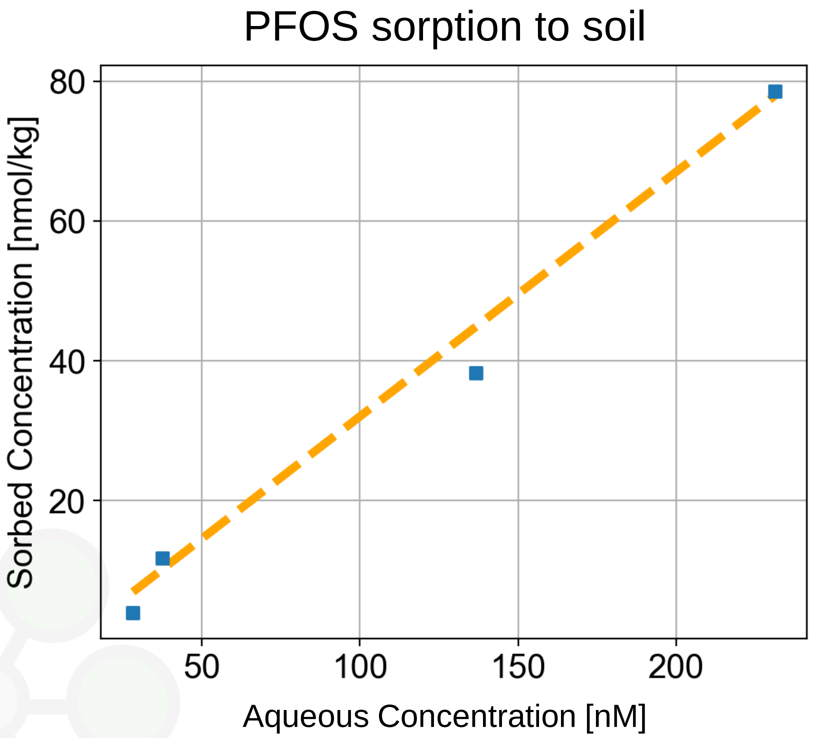


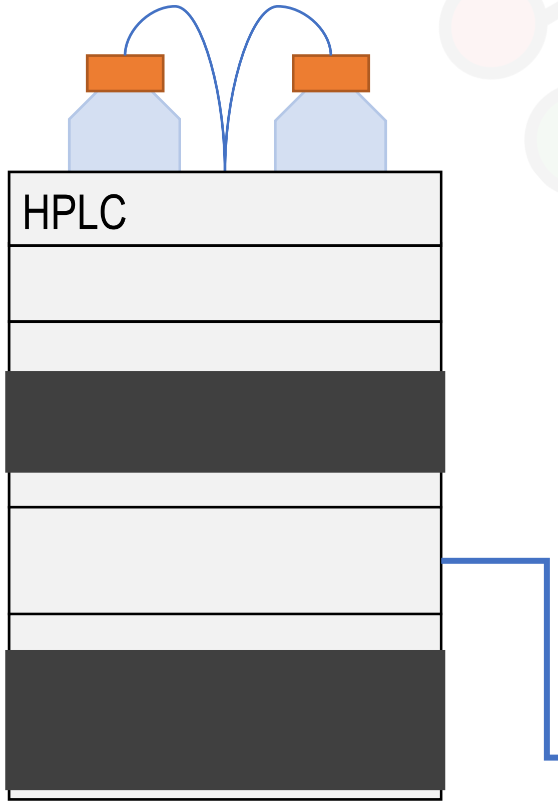
K_d Quantifying Solid-Phase Adsorption by batch-methods

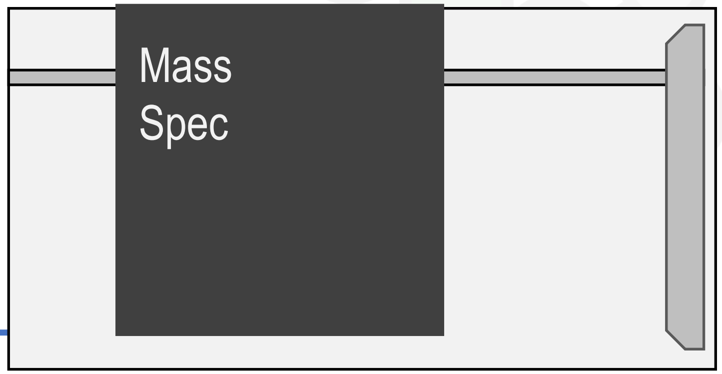
$$R_{sp} = 1 + \boldsymbol{K_d} * \left(\frac{\rho_b}{Sw\Phi}\right)$$



Batch-Type Procedures for Estimating Soil Adsorption of Chemicals

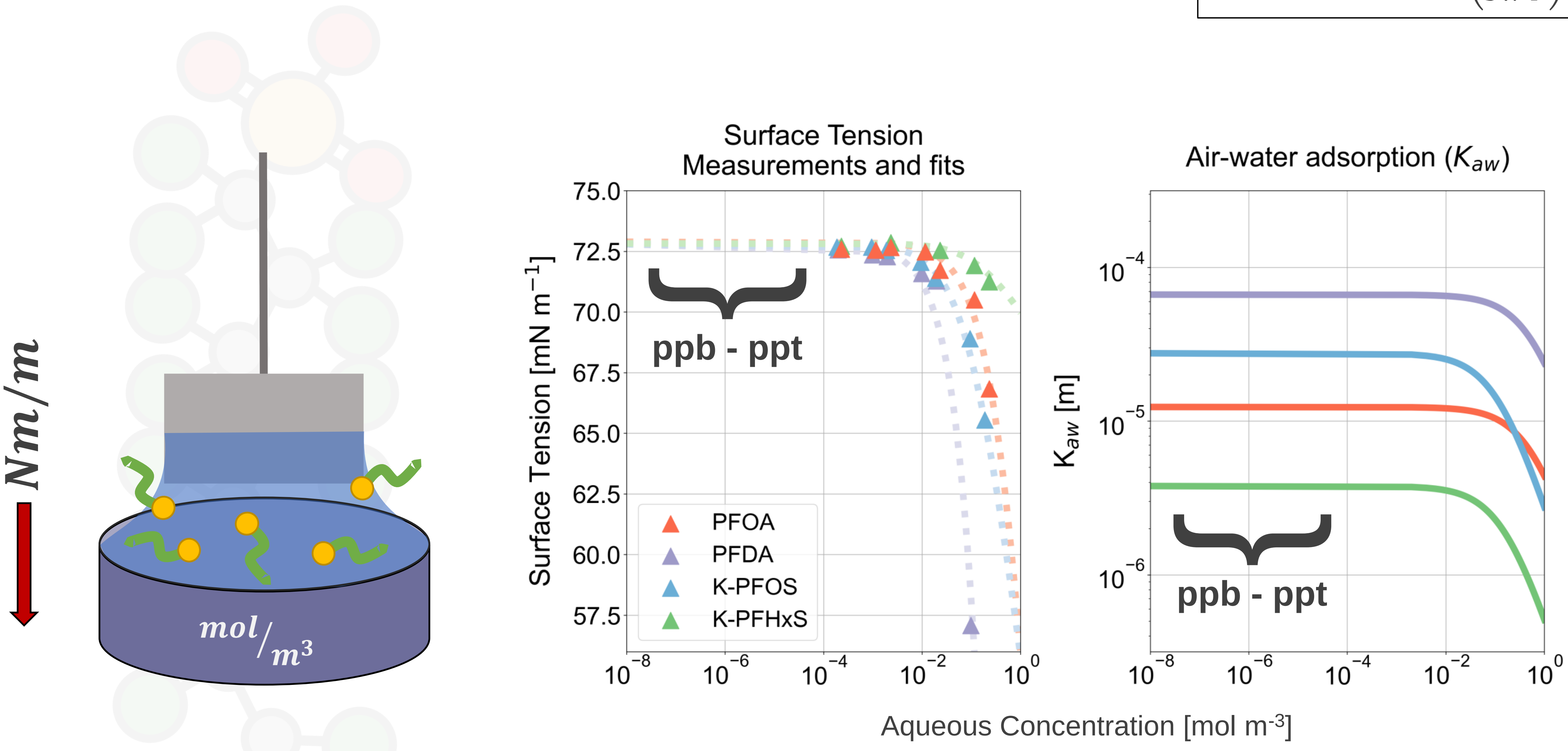






K_{aw} - Quantifying Air-Water Interfacial Adsorption

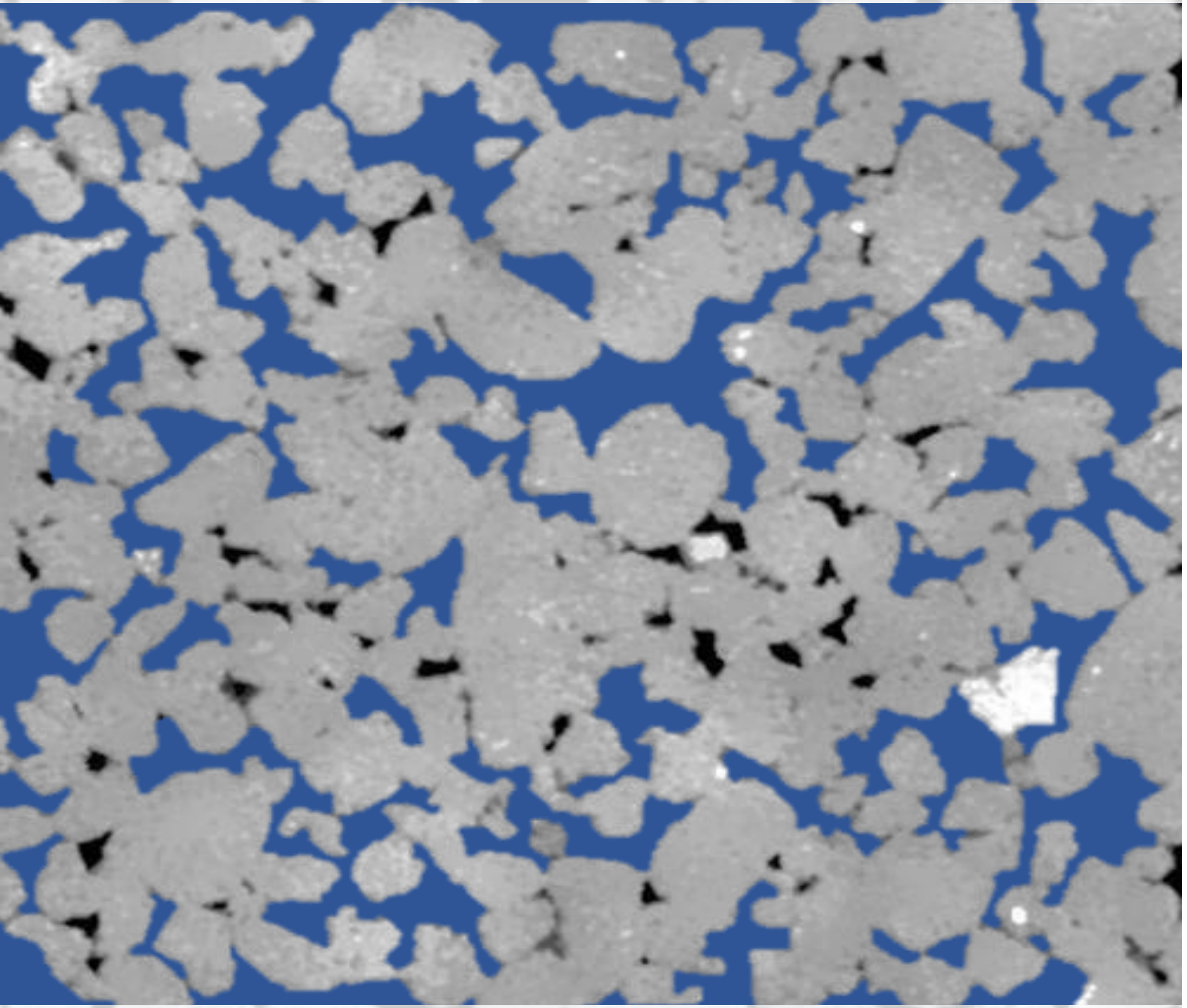
$$R_{aw} = 1 + K_{aw} * \left(\frac{A_{wi}}{Sw\Phi}\right)$$

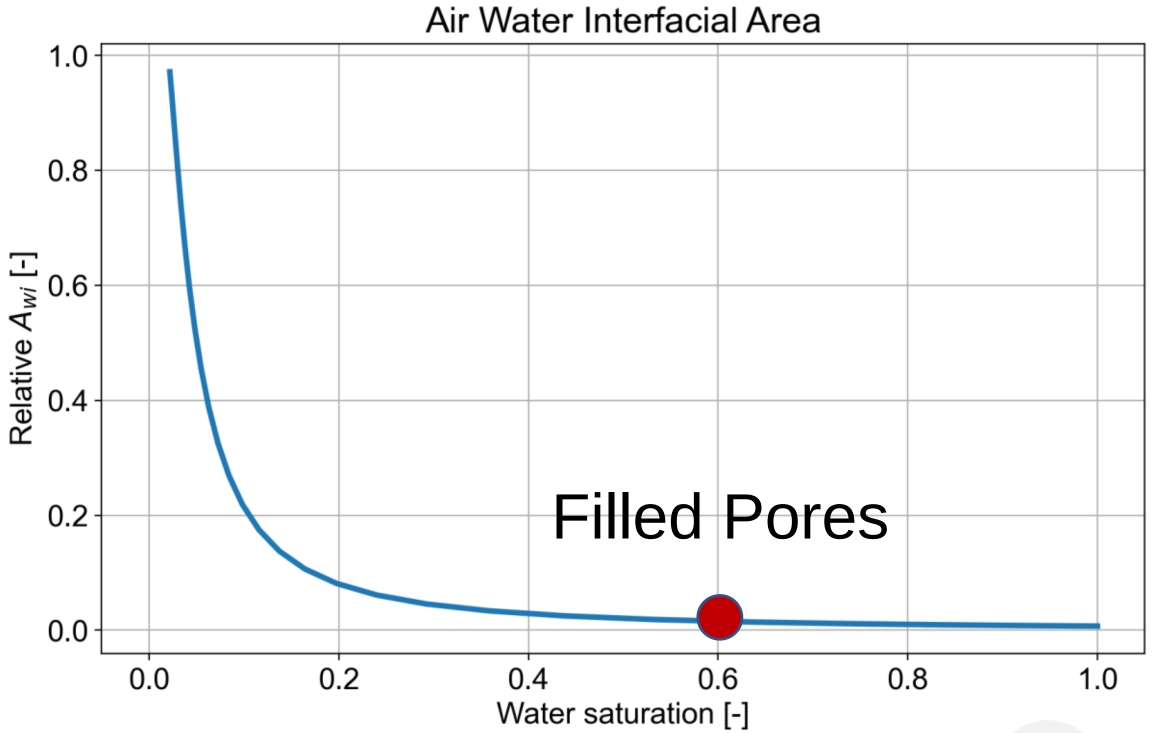


Goal: Approximate K_{aw} at concentrations below 10E-4 mol/m^3 (~ ppt – ppb range)

A_{wi} - Quantifying Air-water Interfacial Area

$$R_{aw} = 1 + K_{aw} * \left(\frac{A_{wi}}{Sw\Phi}\right)$$

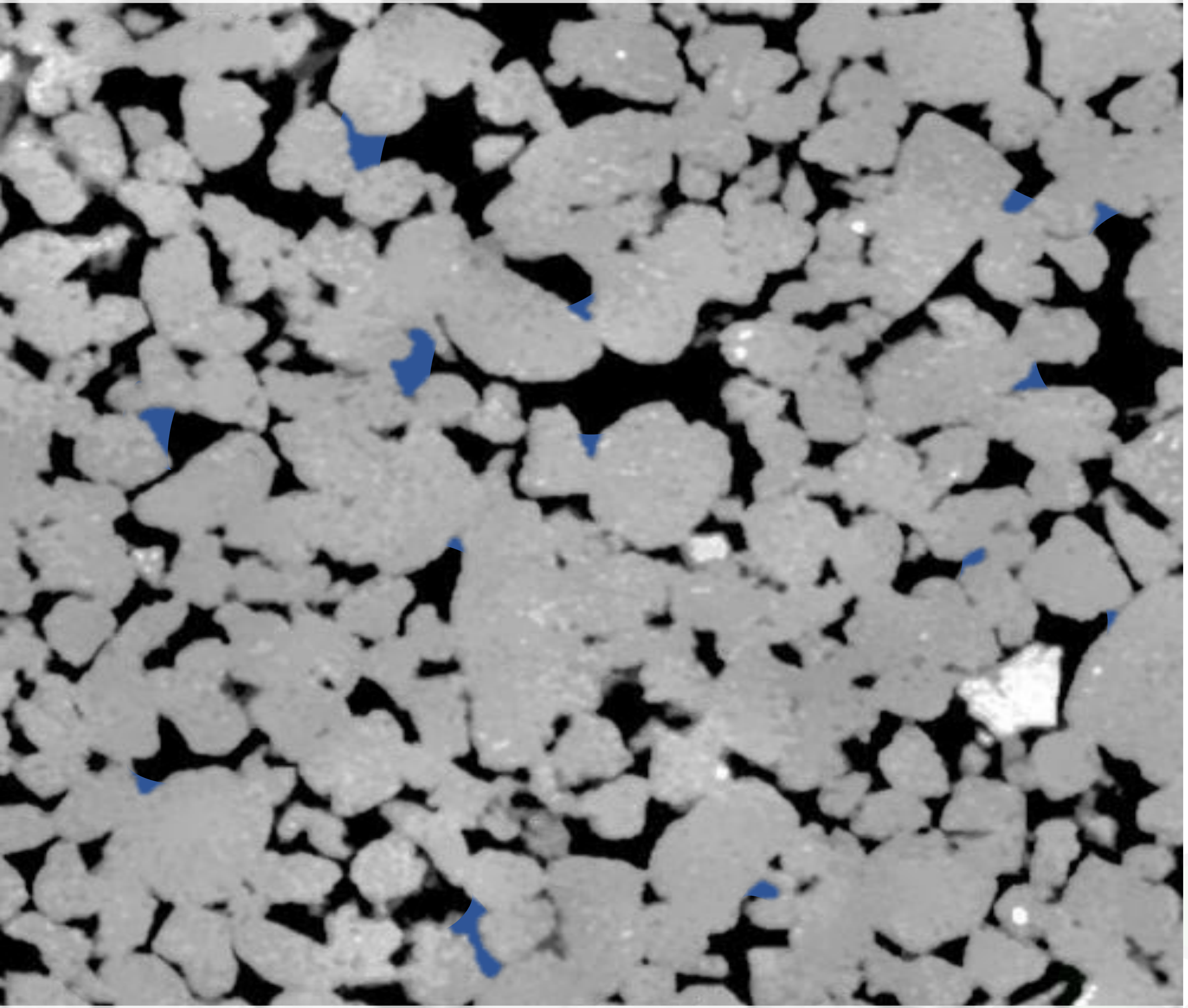


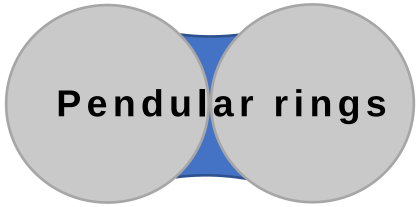


- How does water/fill drain pore space?
- How much water is left behind?
- What is the distribution of residual water

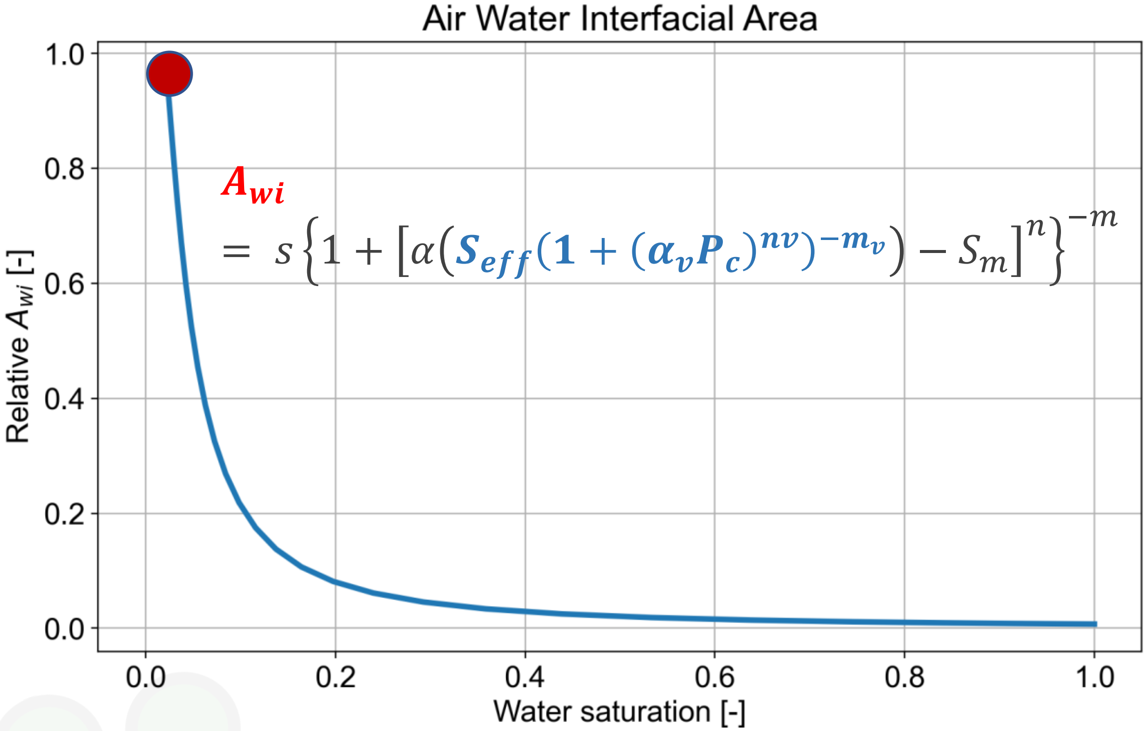
Peng and Brusseau 2005; 2012

A_{wi} - Quantifying Air-water Interfacial Area





$$R_{aw} = 1 + K_{aw} * \left(\frac{A_{wi}}{Sw\Phi}\right)$$



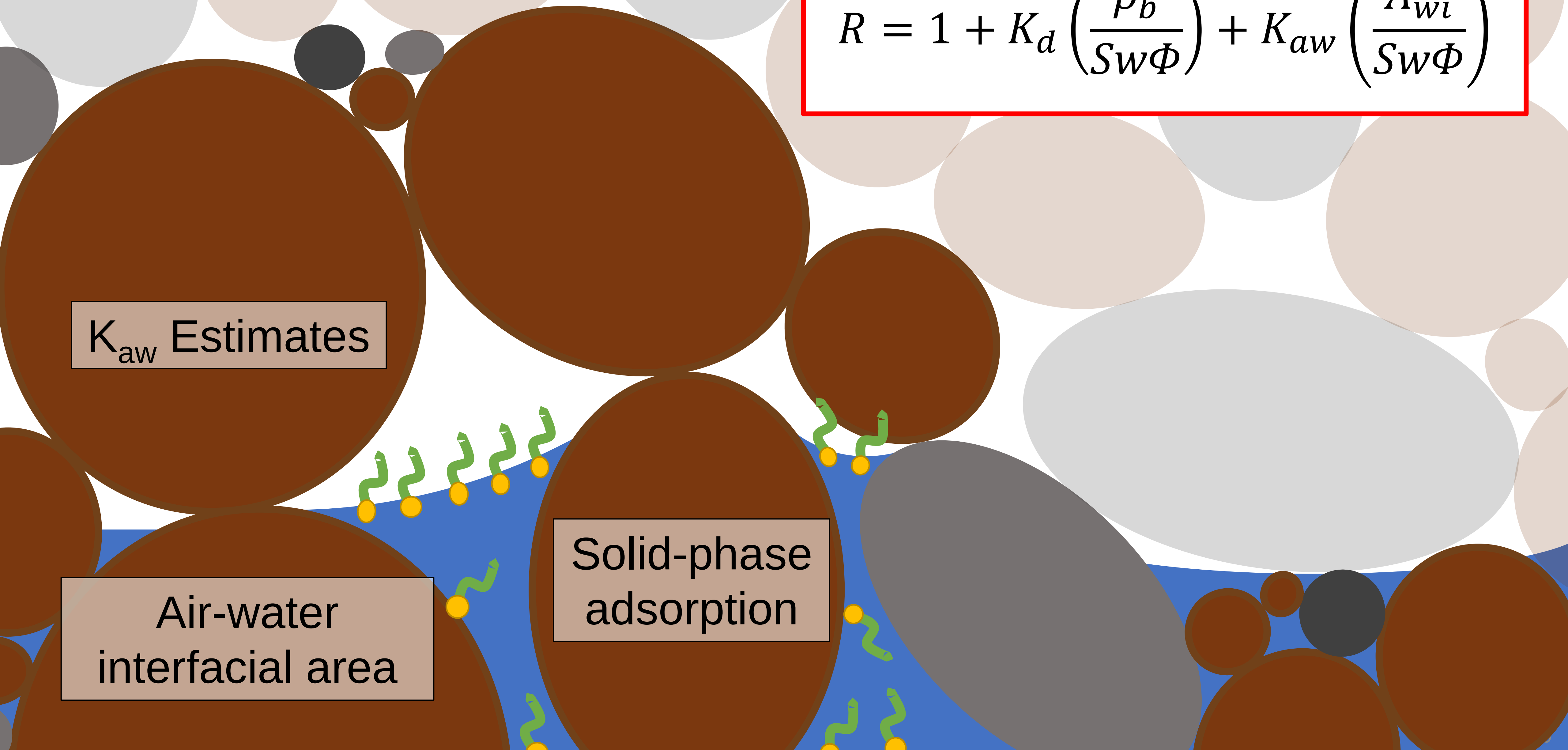
- How does water/fill drain pore space?
- How much water is left behind?
- What is the distribution of residual water

Peng and Brusseau 2005; 2012

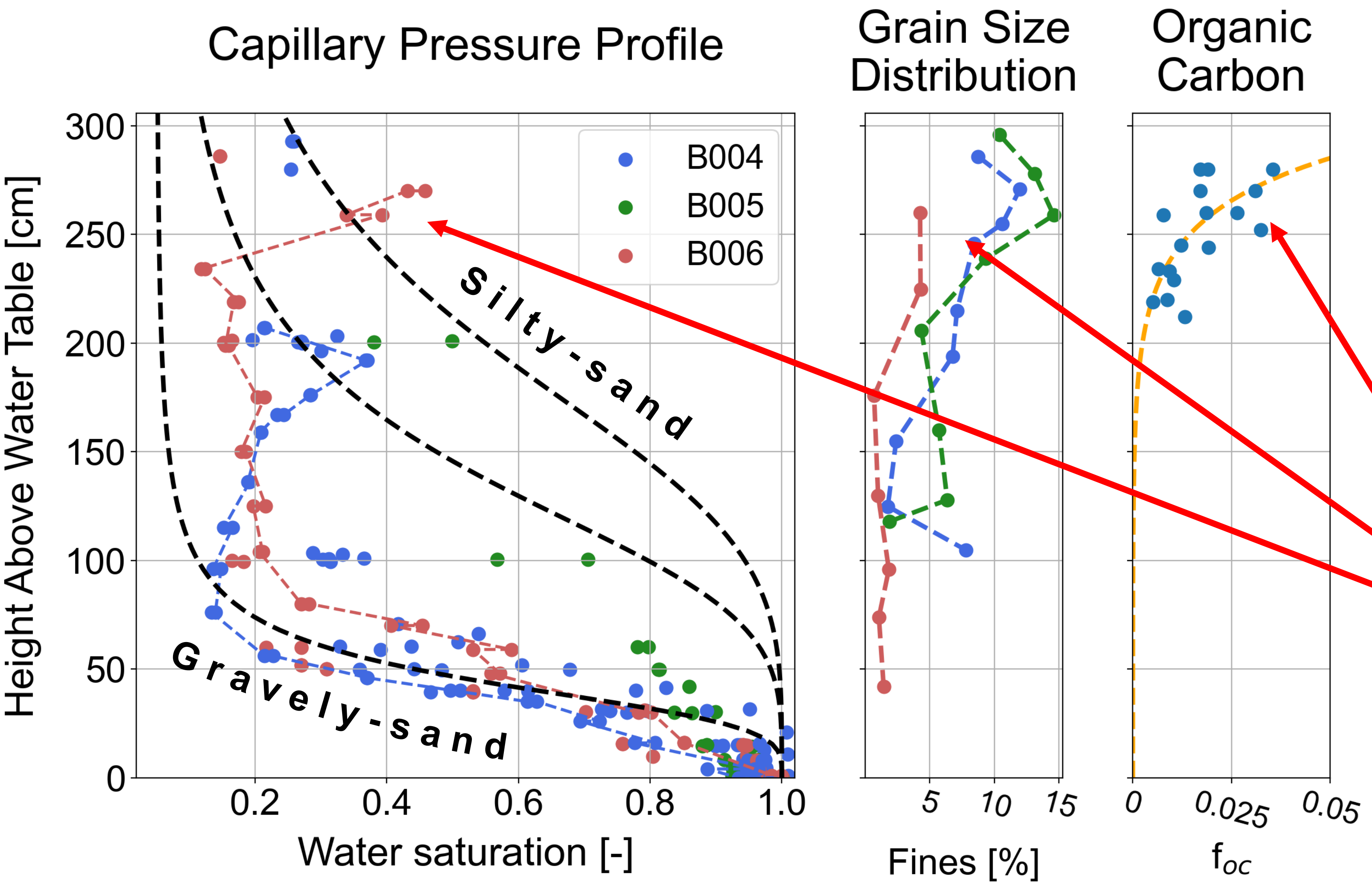
Vadose Zone Adsorption Model

The complete Picture

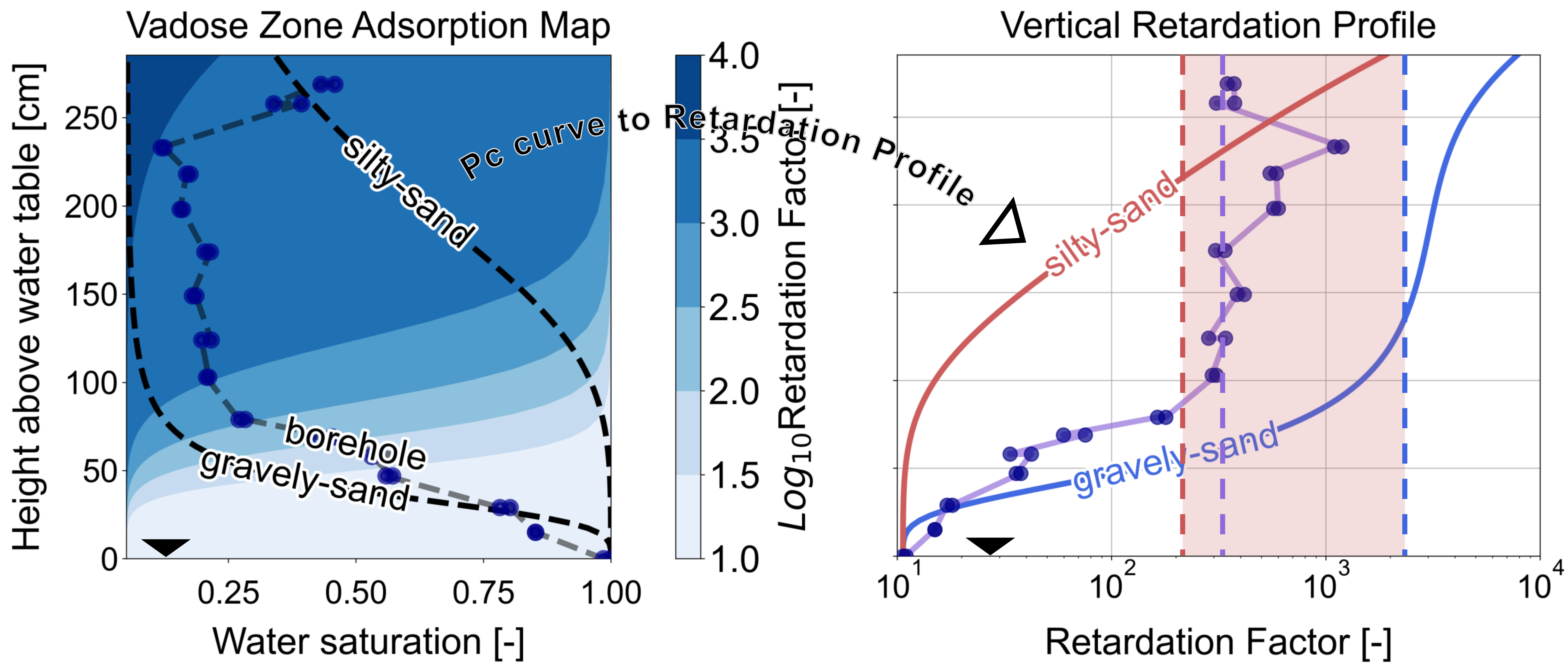
$$R = 1 + K_d\left(\frac{\rho_b}{Sw\Phi}\right) + K_{aw}\left(\frac{A_{wi}}{Sw\Phi}\right)$$



Field-scale heterogeneity introduces complexity



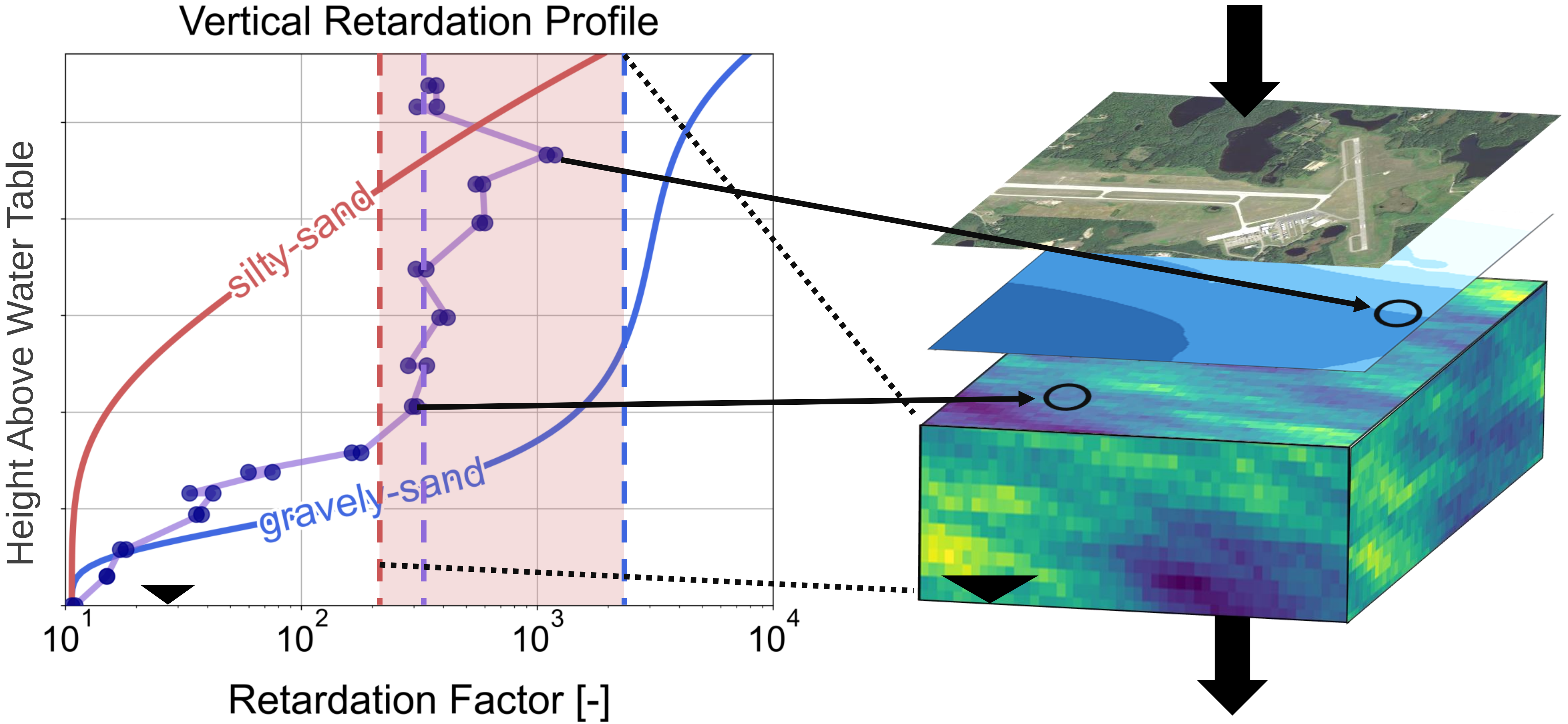
Merging lab and field measurements
Assessing adsorption across heterogeneity



Synthesize complex retardation profiles in the vadose zone

Future Work: Geostatistical Approaches, transience, etc.

From generalizations to **predictive transport models**



Take aways

- With a few **routine site parameters,** PFAS retention in the vadose zone can be assessed

- Vadose zone transport of PFAS may be subject to periodic immobilization due to adsorption at **air-water interfaces**, explaining observations of long-term leaching

"This finding suggests that the unsaturated zones beneath fire training areas and wastewater infiltration beds at other sites can act as long-term PFAS sources to groundwater over several decades" – Weber et al. 2017

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