The Sentinel™ Sampler for Measurement of PFAS in Environmental Waters

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USGS Toxic Contaminants Working Group
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Recent DoD Support for PFAS Passive Samplers

Size/Dimensions

Ease of use and analysis

- Can it be analyzed by commercial lab?

Integrative or equilibrium

Sensitivity to environmental conditions (temp, pH, TDS, etc.)

Detection limit

Deployment time

Degree of field testing/application

Commercial availability and cost

SW	Surface Water	$\int dx$	Integrative
GW	Groundwater	⇌	Equilibrium
SPW	Sediment or Pore Water	🛒	Commercially Available

ER20-1127

SW GW $\int dx$ 🛒

ER20-1293

SW $\int dx$

ER20-1156

SW GW $\int dx$ 🛒

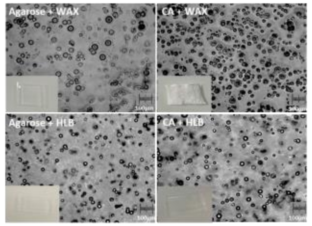
ER23-7741 PFASsive™

SW SPW ⇌ 🛒

ER23-7696

SPW $\int dx$ 🛒

ER20-1336



SW GW SPW ⇌

ER21-5104

SW GW SPW ⇌ 🛒

ER20-1363

SW* GW* $\int dx$ 🛒

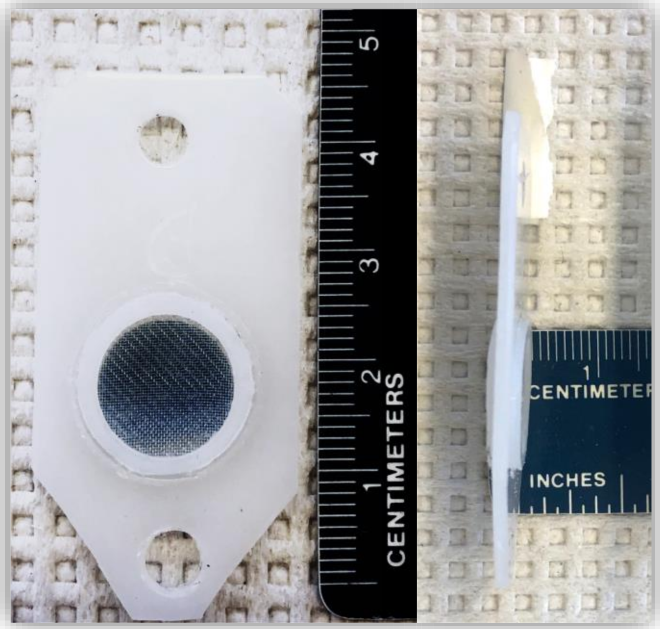
ER20-1073

SW GW SPW* ⇌ 🛒

Sentinel™ PFAS Sampler Development

Introduction

- Prototype designed and field-tested in SERDP project ER20-1127
- Commercial manufacture by Aquanex Technologies, LLC*
- Cu(II)-polyethyleneimine-Osorb® adsorbent
  - Mesoporous organosilica resin
  - Weak anion-exchange groups
  - Cu(II) for high affinity binding of short chain PFAS



Prototype - Polyethylene construction with 80-mesh granular Cu(II)-polyethyleneimine-Osorb® sorbent

* Sentinel™ PFAS passive samplers for water and sediment are now commercially available and discounts are offered for research applications https://aquanextech.com/collections/passive-samplers

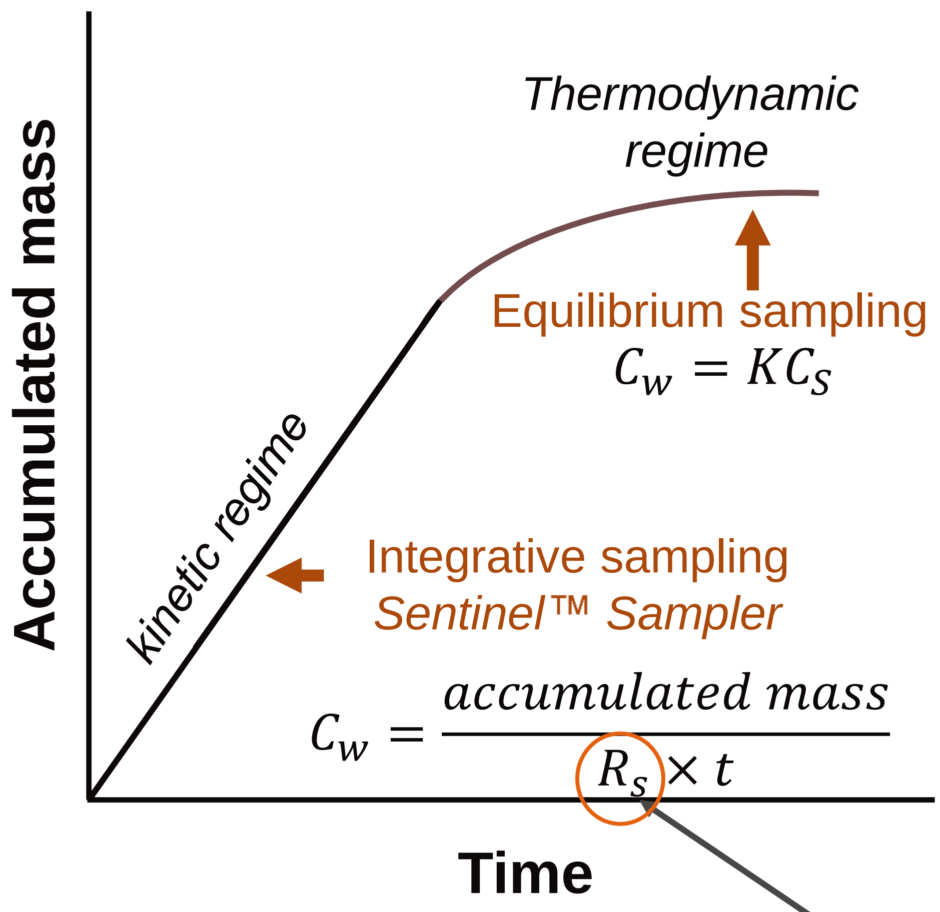
Sentinel™ Sampler Advantages

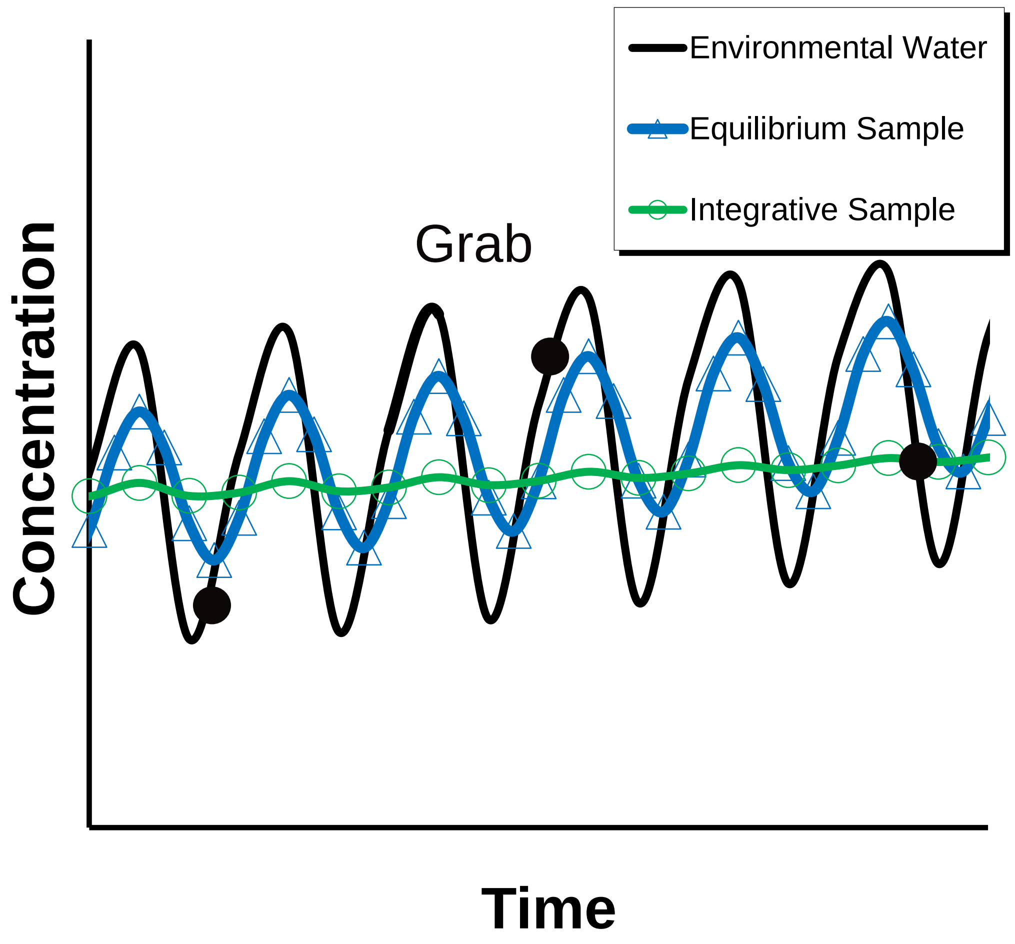
- Small size with high durability allows for easy installation and shipping, lowering costs.
- Consistent and fast uptake rates show applicability to a wide range of environmental water types
- Integrative sampling nature useful for providing concentration values that are time-averaged
- Uses isotopically labeled surrogates for QA/QC evaluation (compatible with EPA Methods)
- Flexible deployment options and durations
- Compact thin design enables vertical profiling in sediment
- Membrane-less design with Cu^{2+} to inhibit biofouling
- Sorptive mode of action captures dissolved PFAS – less capture of solids in samples than grab samples

Stainless steel for sediment

HDPE for water applications

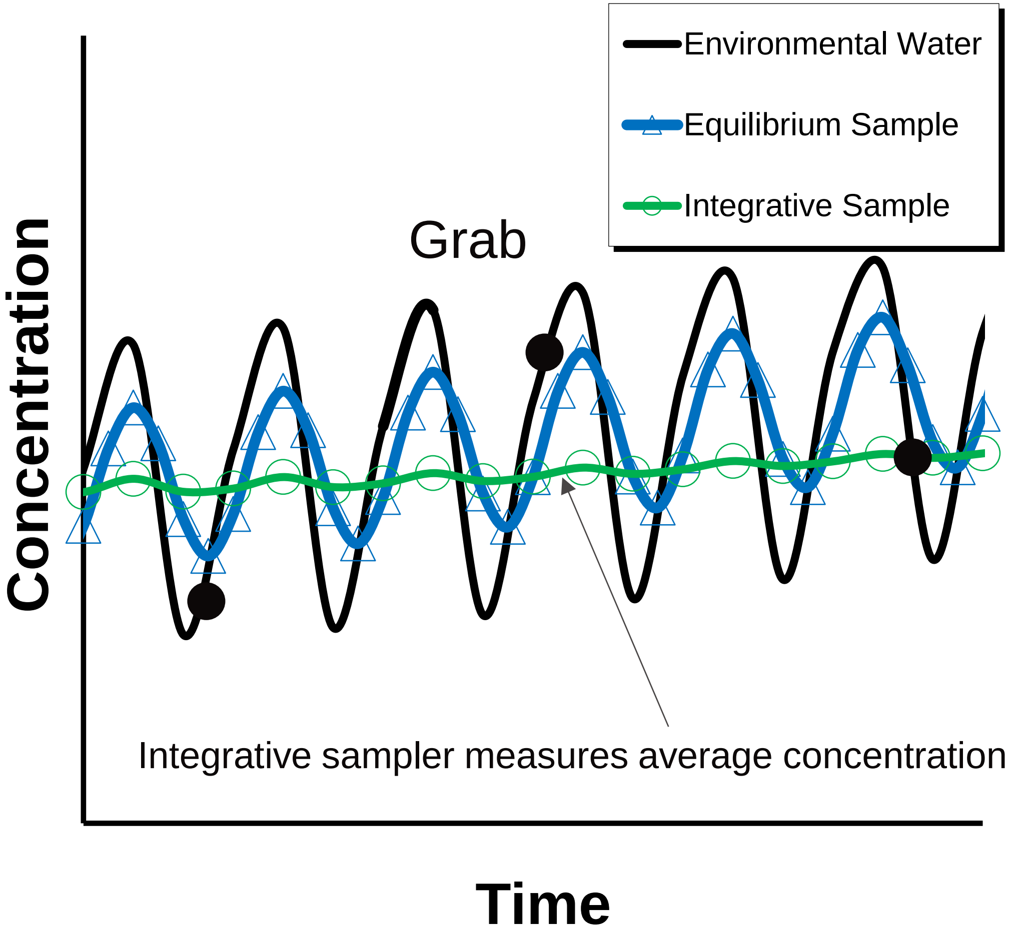
Modes of Passive Sampling



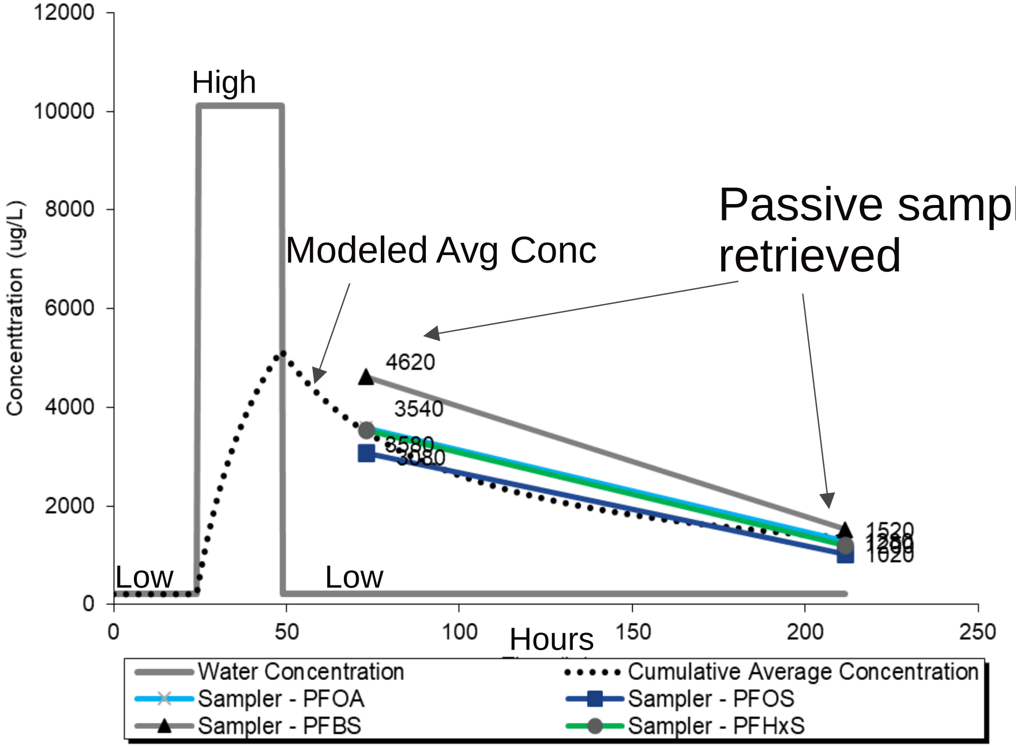


R_s value (Sampling Rate) empirically derived for each analyte

Lab Measurement of Integrative Behavior

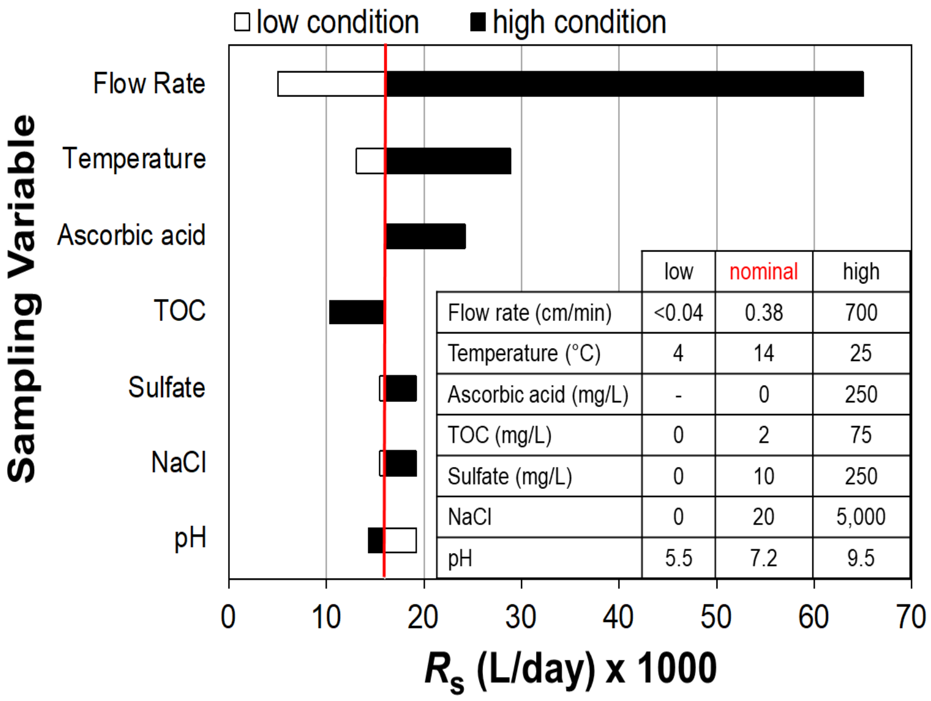


Variable Concentration Experiment



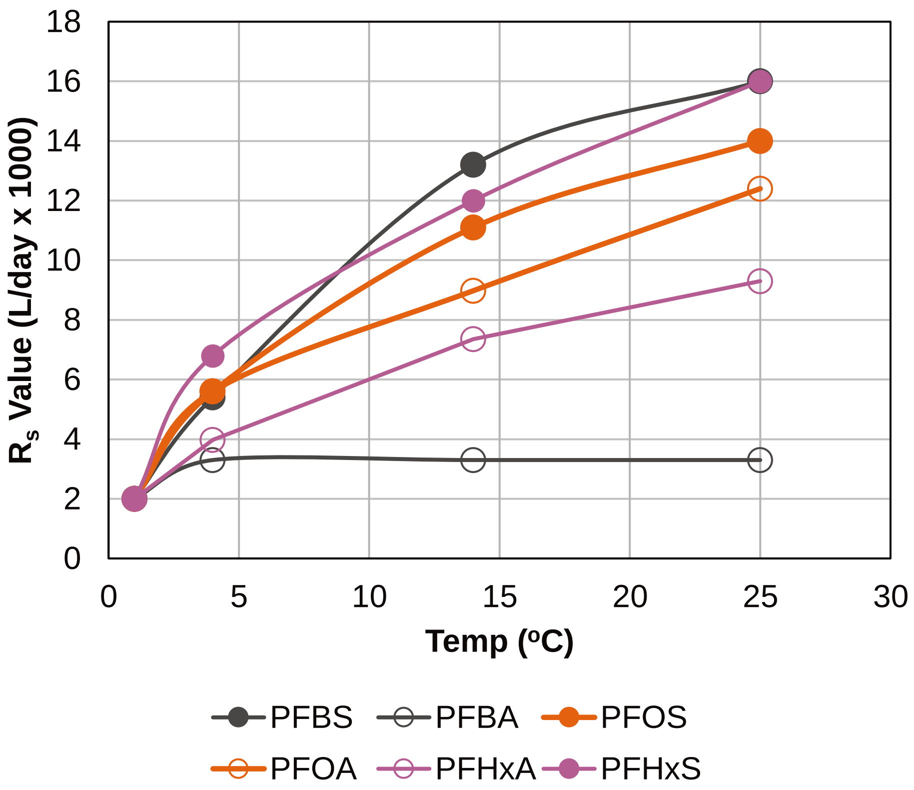
Measured passive sampler concentration matches modeled cumulative average water concentration. Binding to sampler is ~ unidirectional (on >>> off).

R_s Sensitivity to Environmental Conditions



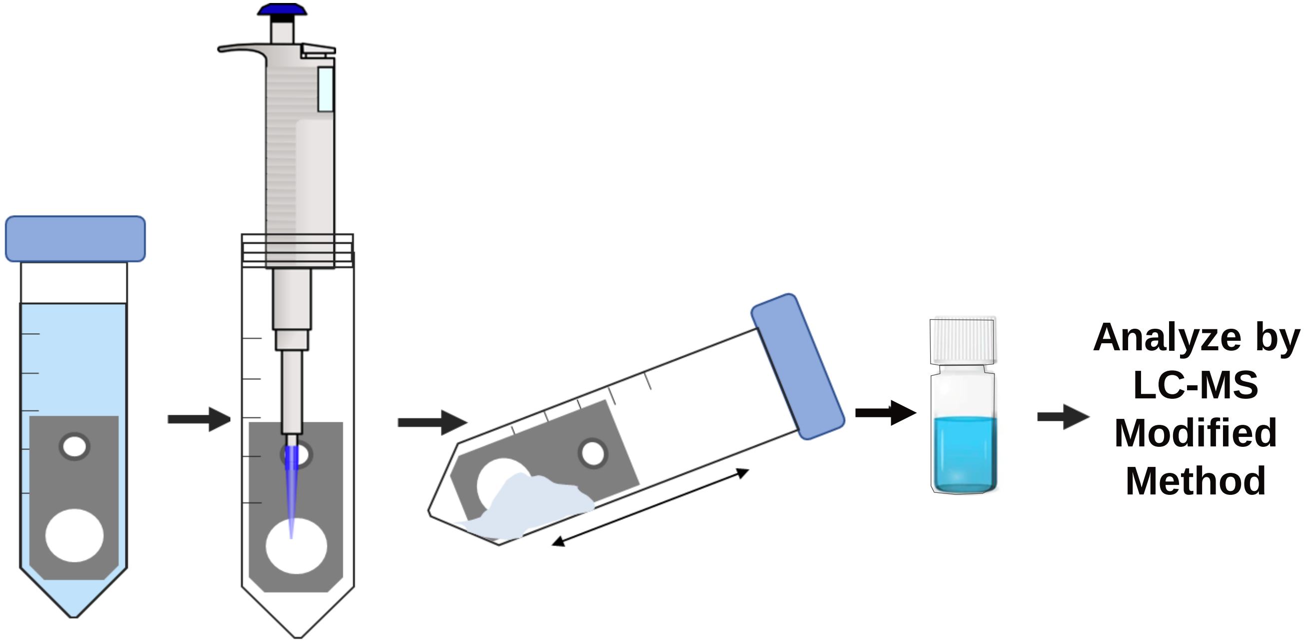
	low	nominal	high
Flow rate (cm/min)	<0.04	0.38	700
Temperature (°C)	4	14	25
Ascorbic acid (mg/L)	-	0	250
TOC (mg/L)	0	2	75
Sulfate (mg/L)	0	10	250
NaCl	0	20	5,000
pH	5.5	7.2	9.5

R_s is most sensitive to flow rate and temperature



R_s is corrected for temperature with Langmuir-style curve fitting

Passive Sampler Deployment and Analysis



Steps 1-2: Rinse in DI water, centrifuge

Step 3: Apply 50 µL surrogate solution

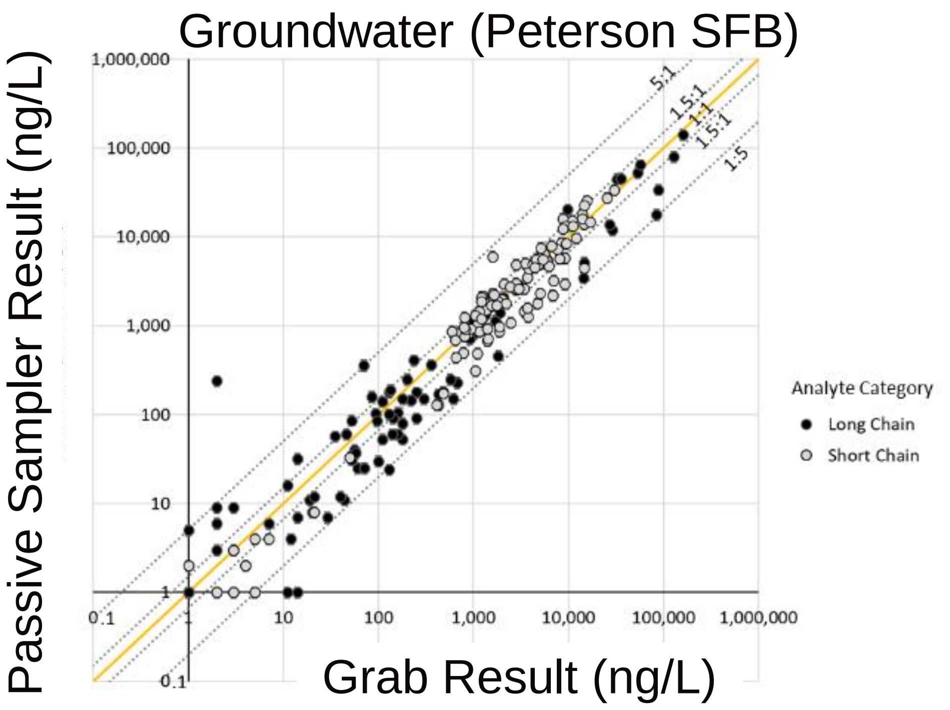
Step 4: Extract with 2.0 mL of methanol, agitate on shaker.

Steps 5-7: Decant methanol extract, add internal standards, run on LC-MS.

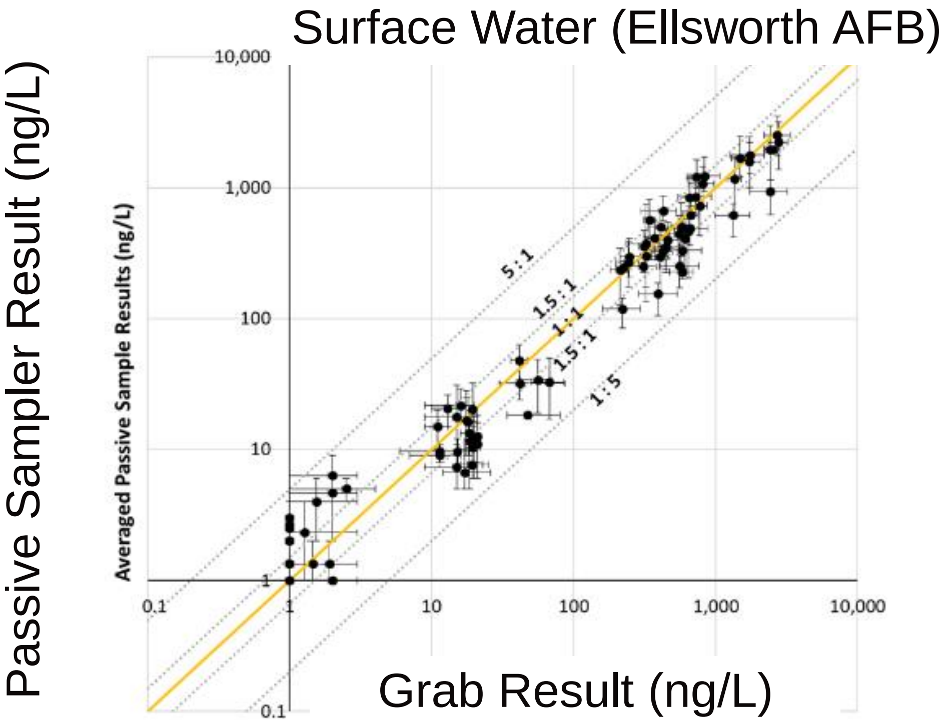
Current Labs:

- EPA 1633 by Sentinel™ Passive Sampler (Enthalpy Labs - 2025)
- PFAS by Sentinel™ Passive Sampler - Pacific Rim Labs, RTI Labs, SGS–Fellbach Germany, ALS UK

Pilot Demonstrations Results in Groundwater and Surface Water



- 56% within 1.5X
- 71% within 2X
- Short and long chain performed similarly
- 14% RSD passive sampler replicates



Performance over 5 OoM PFAS concentration range

- 58% within 1.5X
- 80% within 2X
- 30% RSD passive sampler replicates

Edmiston et al. (2023) GWMR

Key Points

Fast sampling (>0.01 L/d) with high capacity

Time-averaged concentration with DLs ~1-2 ng/L

Variable deployment times – days to weeks

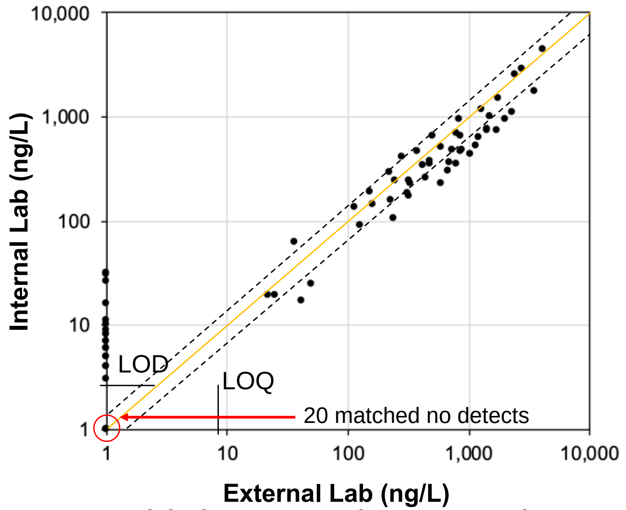
Strong correlation to grab data and good precision

Relatively insensitive to environmental variables (TOC, pH, TDS)

Commercially avail. ($100; discounts for research)

Commercial labs report mod method – 49 PFAS analytes

- EPA Method 1633 (40 analytes)
- EPA Method 533 (25 analytes)
- EPA Method 537.1 (18 analytes)
- Ultrashort chains in progress



Third Party Lab Comparison

www.aquanextech.com
for more information

Labs qualified by Aquanex:

Enthalpy Analytical (Wilmington, NC), seeking DoD ELAP

Pacific Rim Labs (Vancouver, BC, Canada)

RTI Laboratories (Livonia, MI)

SGS – Germany (Fellbach)

ALS – UK (Manchester)

In progress:

Pace Analytical

SGS - Orlando

Additional Resources

Edmiston, Carter, Toth, Hershberger, Hill, Divine, 2023. Field Evaluation the Sentinel™ Integrative Passive Sampler for the Measurement of Per- and Polyfluoroalkyl Substances in Water Using a Modified Organosilica Adsorbent. GWMR 43(4), https://doi.org/10.1111/gwmr.12574

Edmiston, Hill, Hershberger, Hartmann, Carter, Divine, 2023. Laboratory Validation of an Integrative Passive Sampler for Per- and Polyfluoroalkyl Substances in Water. Environmental Science: Water Research & Technology, 9, 1849 – 1861. https://doi.org/10.1039/d3ew00047h

Hartmann, Hefner, Carter, Liles, Divine, Edmiston, 2021. Passive Sampler Designed for PFAS Using Polymer-Modified Organosilica Adsorbent. AWWA Water Science, 3(4) https://doi.org/10.1002/aws2.1237

Project Video: https://youtu.be/xaYb_1Jh64w

Two US Patents issued (11,650,138 B2; 11,703,426 B2)

- Additional EPA-led demonstrations with other passive samplers
- 6-site AFCEC demonstration project underway

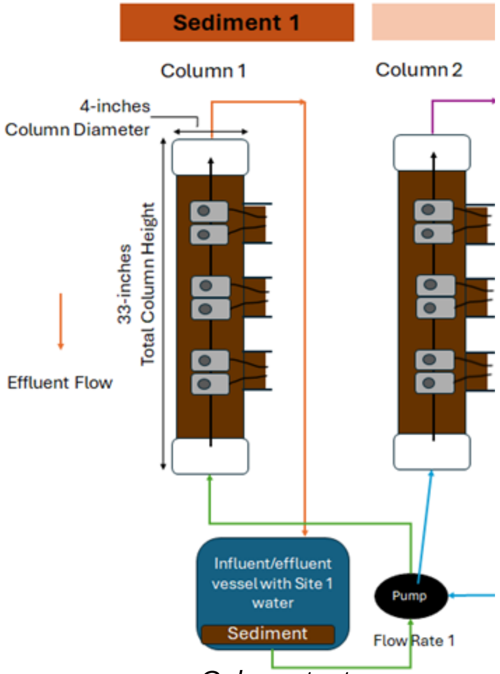
New Research Demonstration:
ESTCP 23-7696

ESTCP 23-7696 – Sediment Porewater

Primary Objective: Lab- and field-validate application of the Sentinel™ PFAS passive sampler to determine concentrations of PFAS in pore water at contaminated sediment sites. Focus on sites where flow through sediment is expected.

- Lab (Yr 1): Verify calibration of passive sampler for sediment pore water sites, where flow rates through sediment are expected to be lower than in previous field deployments.
  - Calibrate the passive sampler for integrative (time-averaging) deployment in sediment, using different sediment types and laboratory-controlled flow rates
  - Static tank tests (no flow), column tests (3 flow rates)
  - Determine precision in homogenized sediment; evaluate deployment duration

Static tank test



Column test

Field Demonstration (Yr 2-3 2025-2026)

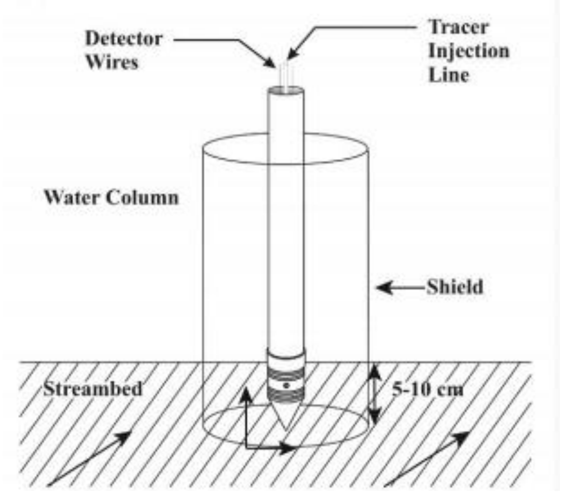
- Field: Demonstrate that the previously developed passive sampler can be field-deployed in sediment environments.
  - Construct tools for sediment deployment and develop recommendations on additional design modifications for sediment
  - Deploy samplers in 2 field sites (sediment) and determine the accuracy of passive samplers relative to matched grab samples, and sampler precision (~20 locations per site). A passive sampling stake will be designed to hold multiple samplers to push into the upper 12-18 inches of sediment
  - Deployment duration 2-4 weeks, multiple time steps per site
  - Paired grab porewater samples using conventional methods (e.g., push-point samplers)
  - ~250 passive, 100 grab samples per site

Conventional push-point sampler (MHE Products)

Prototype passive sampler deployment stake

Field Demonstration (Yr 2-3 2025-2026)

- Field: Use of passive samplers in flux measurements
    - Temperature/conductivity probes, point velocity probes prior to passive sampler deployment to identify groundwater discharge zones for sampler placement
    - Flux measurement to verify flow regime range (versus lab calibrations) and provide estimates of PFAS flux to surface water
    - Passive flux meters buried over passive sampler deployment
    - Point velocity probes to measure horizontal and vertical pore water velocity beneath sediment-water interface
    - Multi-level piezometers for gradient calculation



Schematics of the streambed point velocity probe (Courtesy Rick Devlin)

Streambed passive flux meter (Courtesy Rick Devlin)

ARCADIS

Sediment Porewater Takeaways

- Sentinel passive sampler shows promise for sediment porewater applications
- Linear uptake in impacted sediment over 20 days even in non-flowing condition
- R_s values anticipated to be lower in sediment porewater than streamwater. May overlap with groundwater R_s (e.g., zones of groundwater discharge). Non-flowing tank test brackets low range.
- Current study gathering R_s calibration data for several sediment types and assessing constraints on deployment duration
- Calibration will be tested in the field demonstration at two sites with contrasting characteristics

Presenter Information

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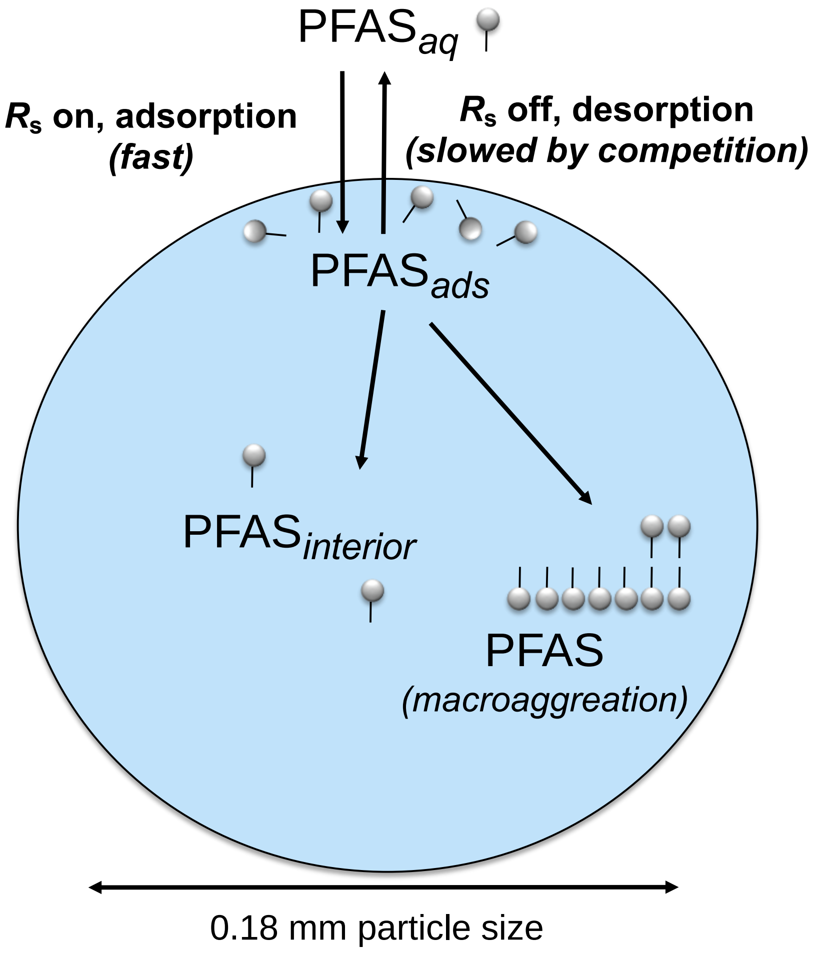
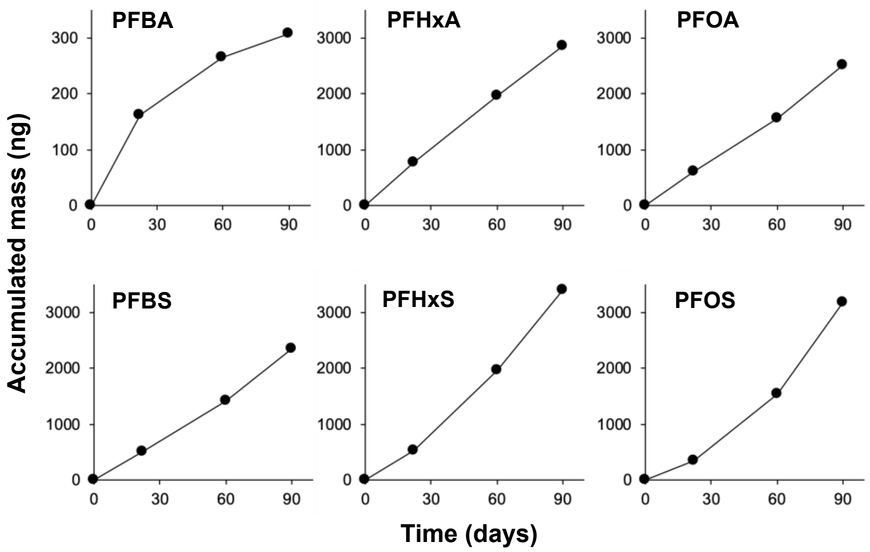
Extras

Hypothesized PFAS Adsorption Mechanism





Due to high capacity of adsorbent and other sinks to bind PFAS, equilibration time is many months and response is integrative

Laboratory Testing (Yr 1 – Fall 2024 in progress) Static Tank Tests

Objective: Evaluate whether site-specific sediment characteristics (e.g., organic muck, coarse-grained, brackish/saline) affects R_s constant

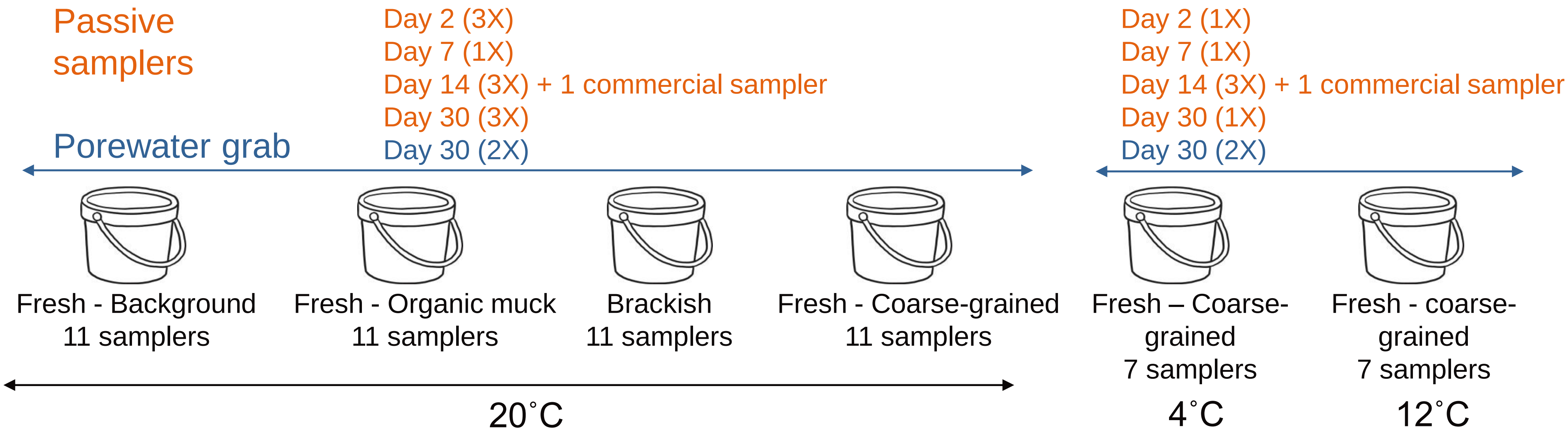
Site	Site 1		Site 2	Site 3
	A	B		
Laboratory Study	Fresh water background (low PFAS concentration)	Fresh water organic muck	Fresh water coarse-grained / sands	Brackish sediment

- Evaluate whether R_s behaves linearly with time in low-PFAS-concentration sediment (evaluate for depletion halo)
- Quantify R_s at endmember (0) flow rate
- 4 sediment types
- Calculate R_s over time (multiple deployment durations)
- Measure precision in homogenized sediment
- Assess temperature effect

Static tank test

Laboratory Testing (Yr 1 - Fall 2024 in progress) Static Tank Tests – Cont.

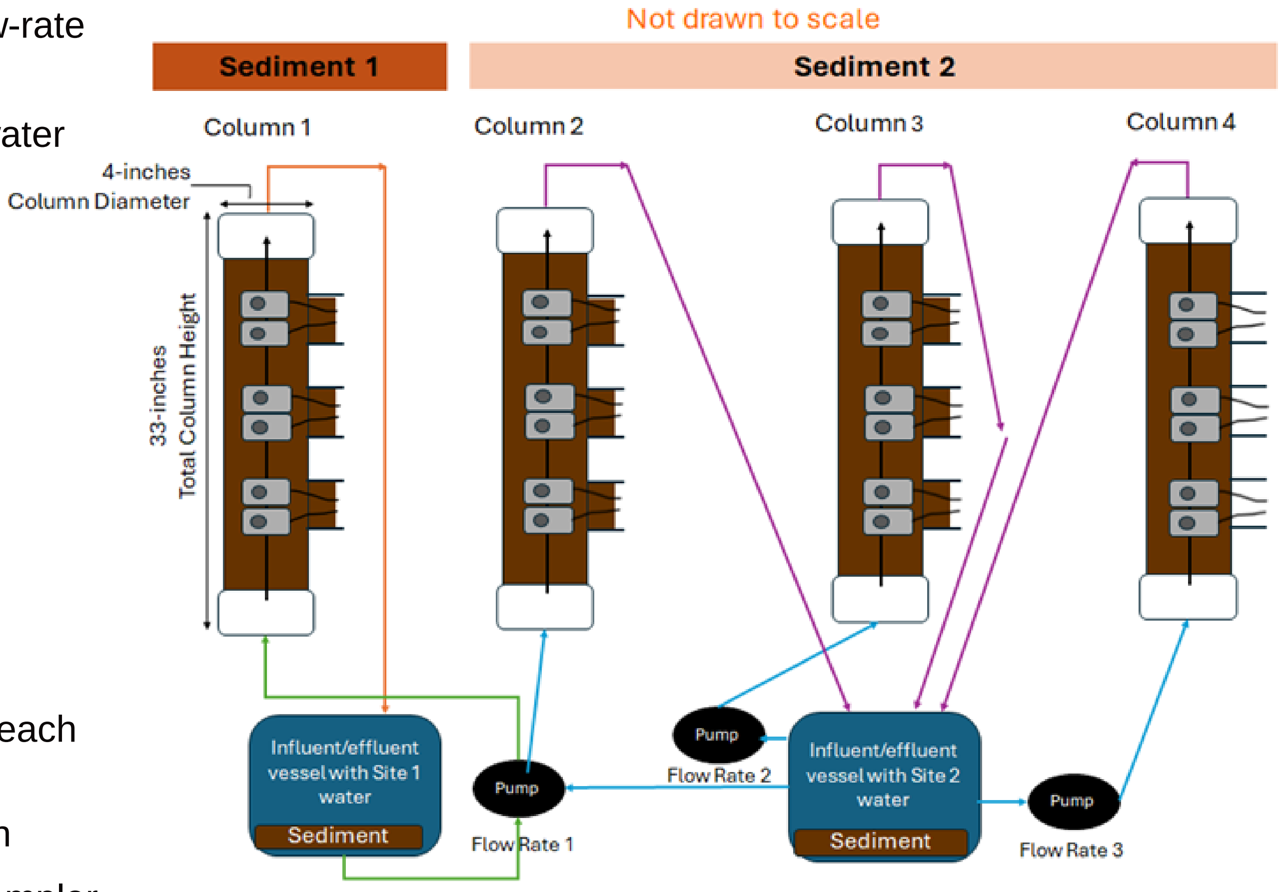
- 4 sediments tested at room temperature (20 ºC)
  1 sediment also at 4 ºC and 12 ºC
- Passive samplers deployed for 4 time periods:
  2, 7, 14, 30 days
- Precision measured with triplicate passive samplers in 3 of the time periods
- Grab porewater samples will be collected at the end of the experiment (30 days) using a push-point sampler



Laboratory Testing (Yr 2 – Spring 2025)
Flow-Through Packed Column Experiments

Objective: Evaluate the effect of flow on R_s under controlled low-flow-rate conditions and verify appropriate deployment duration

- Simulated porewater flow with recirculated pre-equilibrated site water
- Room temperature
- 2 sediment types (low or high-permeability)
- 4 columns (33 inches x 4-inch diameter) with site sediment
  - 3 columns - coarse-grained sediment, 3 flow rates
  - 1 column - fine-grained sediment, 1 flow rate
- Target Darcy velocity range: 0.001 to 0.01 cm/min
- 2 passive samplers at 3 separate heights within each column (n=6 per column)
- 2 deployment time periods TBD based on static tank test.
  At end of each time period, 3 passive samplers removed (1 from each height)
- Time-discrete effluent water samples for PFAS, from each column
- Grab porewater samples from each column using a push point sampler at the end of the experiment



Packed column experiment layout