TECHNOLOGIES AND METHODS FOR CHARACTERIZING PFAS MASS FLUX NEAR GROUNDWATER-SURFACE WATER INTERFACES

CRAIG DIVINE, PHD, PG

NOVEMBER 7, 2023

Outline

Important PFAS Transport & Fate Characteristics

Typical Fire Training Area Conceptual Model

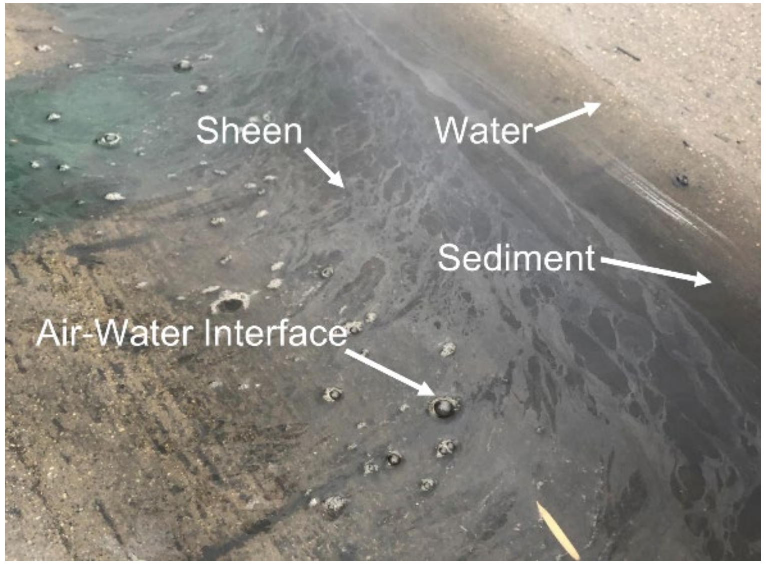
Example Vignettes Highlighting Importance of PFAS Transport at Groundwater-Surface Water Interfaces

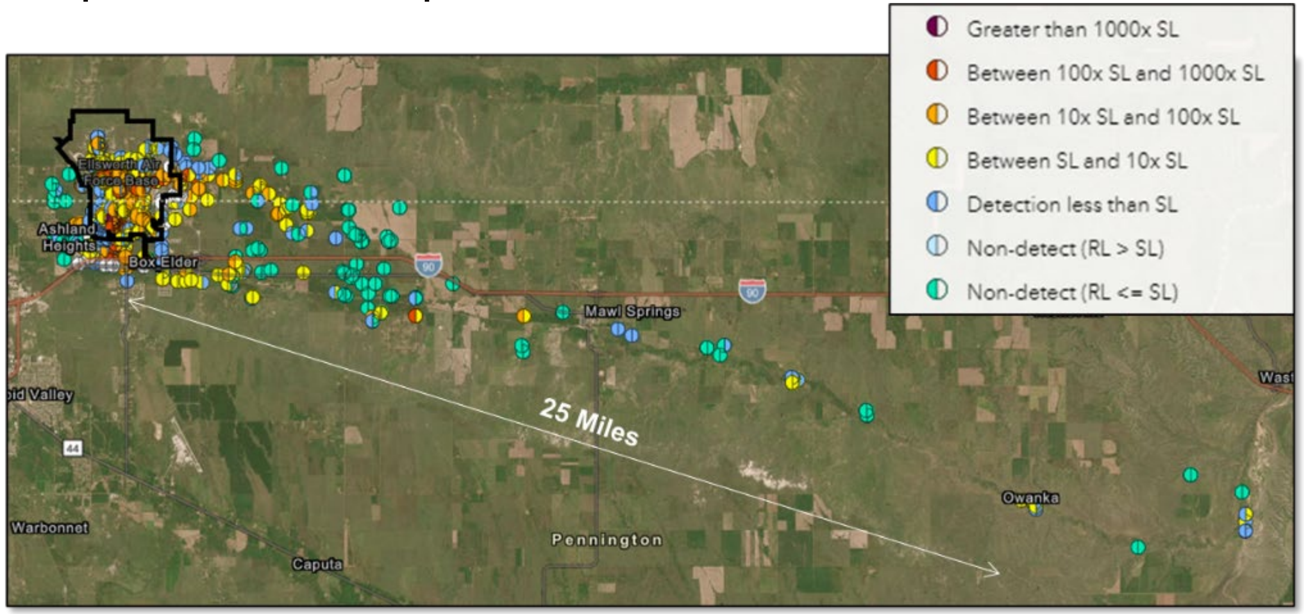
Characterization Tools and Techniques

Future Needs and Priorities

Behavior of PFASs in the Environment is Complex

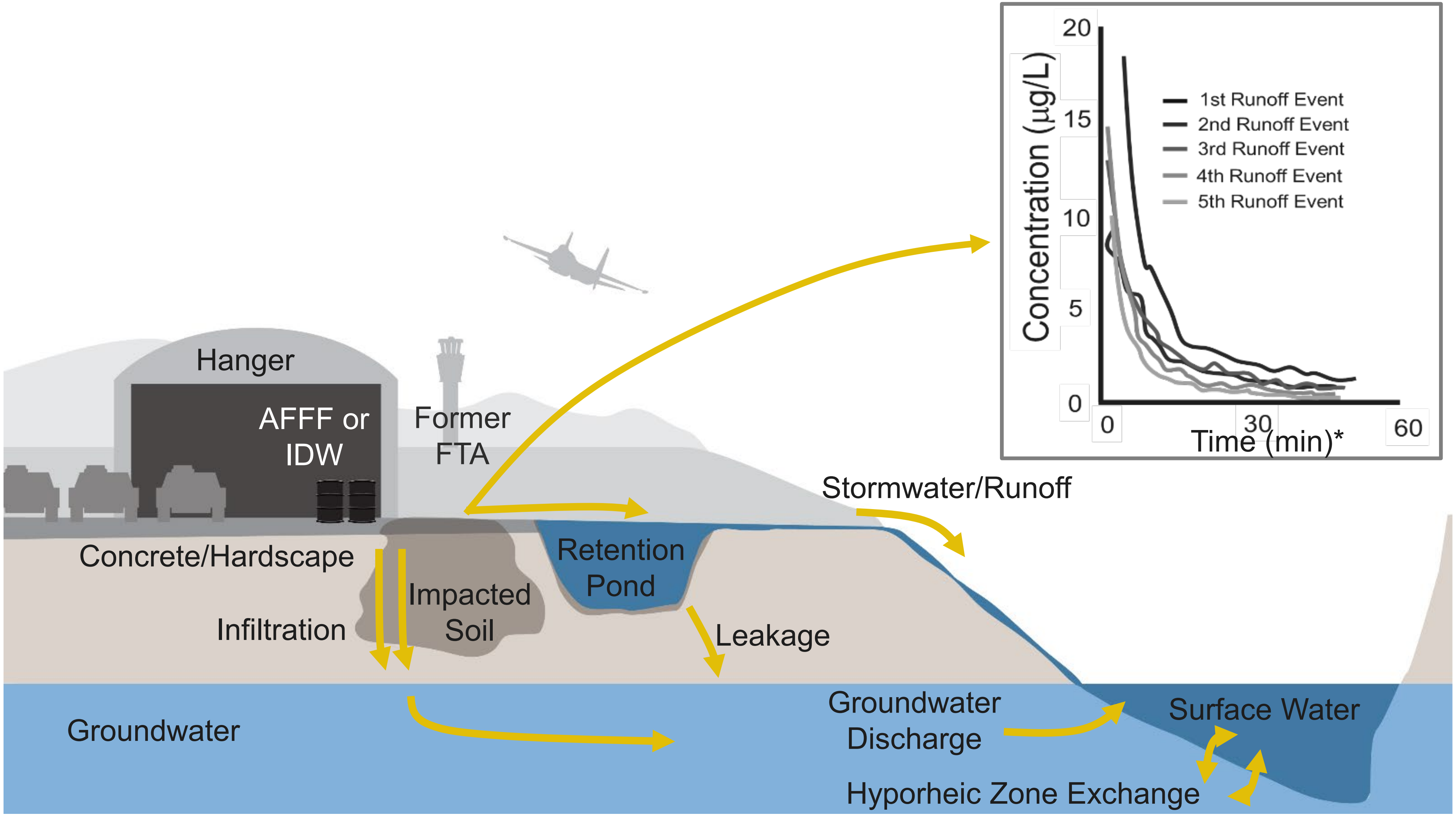
- Resistant to biological and abiotic degradation processes (Liou et al. 2010),
- Sorb to sediment and microplastics (Schaefer et al. 2021; Pramanik et al. 2020; Cheng et al. 2021; Scott et al. 2021)
- Exhibit self- assembly behavior (Dong et al. 2021)
- Partition into non-aqueous phase liquid (NAPL; Liao et al. 2022)
- Concentrate at air-water interfaces (Li et al. 2020; Brusseau and Guo 2022)
- Due to hyporheic exchange, PFAS plumes at multiple AFBs extend off-site >10 miles





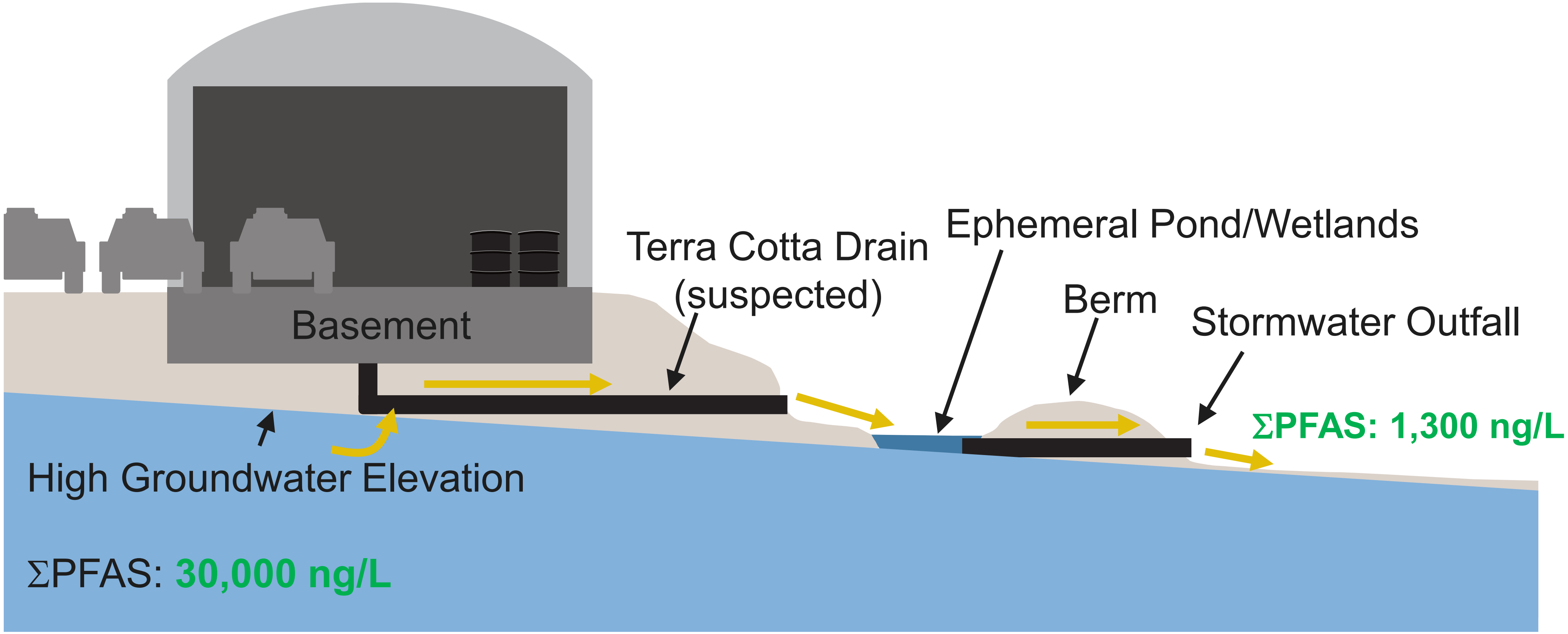
There will be many sites where assessment and management of PFASs at the groundwater- surface water interface will be necessary

Fire Training Area Conceptual Model



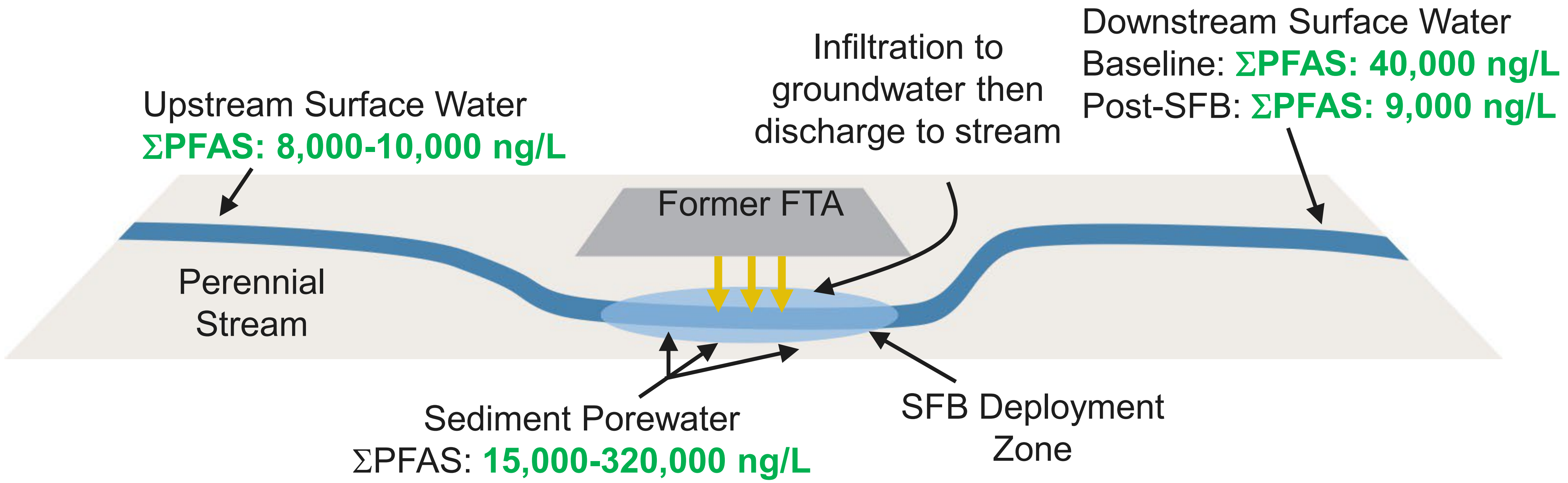
*Developed from data presented in Thai et al. (2022)

Vignette 1



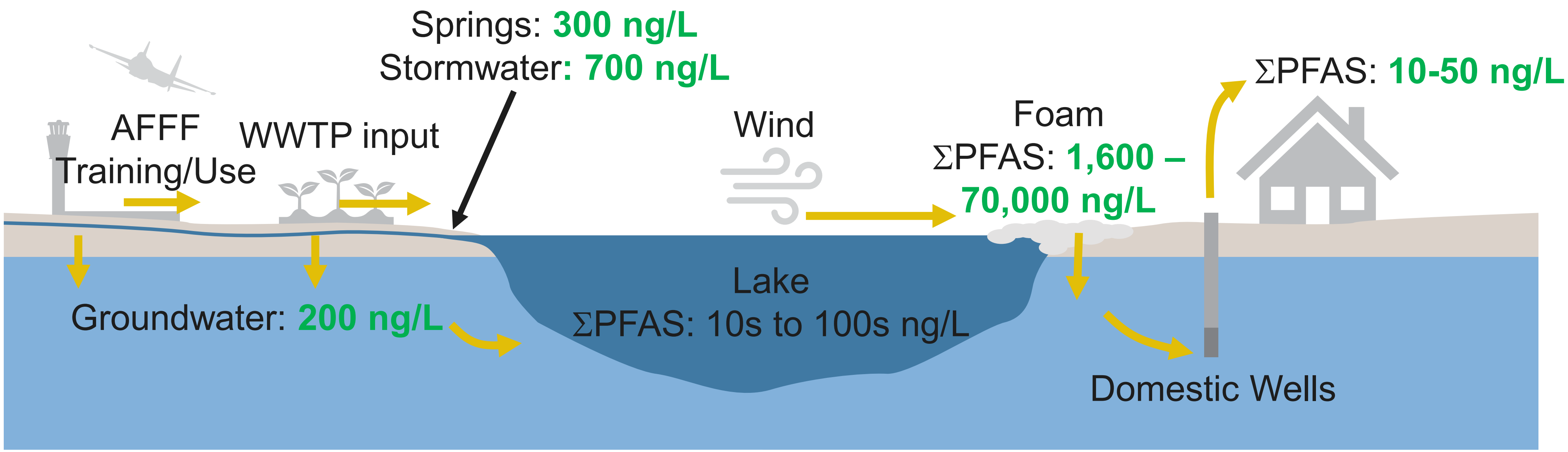
Terra Cotta Drain
(suspected)
Ephemeral Pond/Wetlands
Berm
Stormwater Outfall
Basement
ΣPFAS: 1,300 ng/L
High Groundwater Elevation
ΣPFAS: 30,000 ng/L

Vignette 2



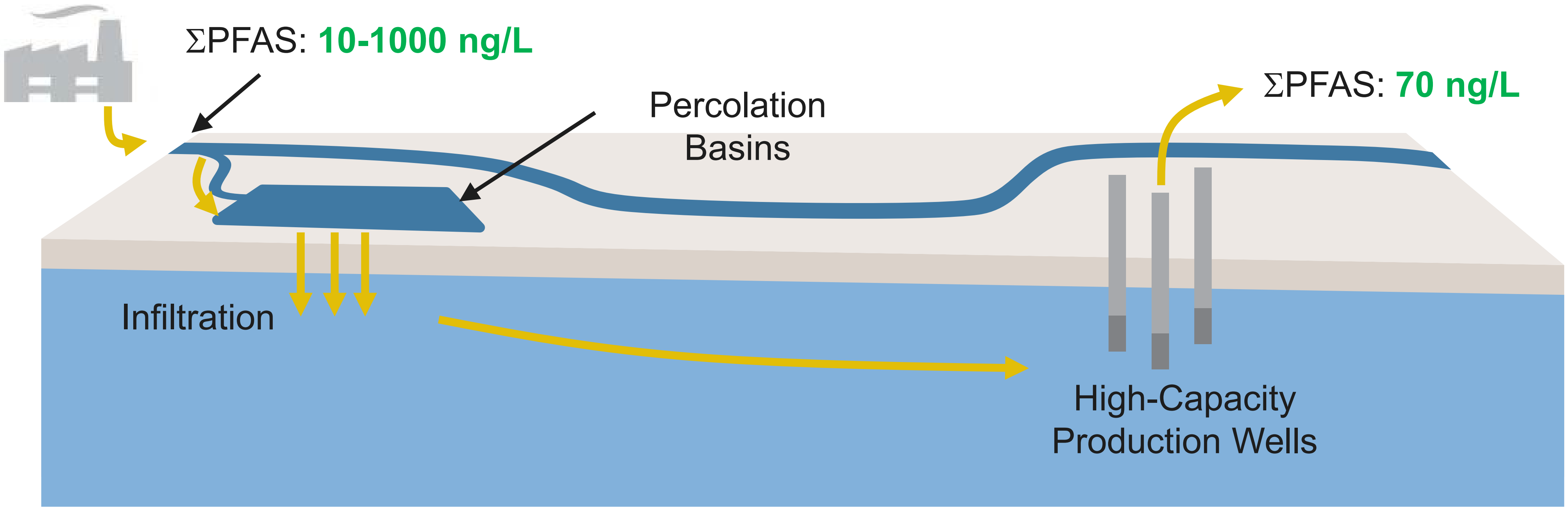
Upstream Surface Water
ΣPFAS: 8,000-10,000 ng/L
Infiltration to groundwater then discharge to stream
Downstream Surface Water
Baseline: ΣPFAS: 40,000 ng/L
Post-SFB: ΣPFAS: 9,000 ng/L
Former FTA
Perennial Stream
Sediment Porewater
ΣPFAS: 15,000-320,000 ng/L
SFB Deployment Zone

Vignette 3



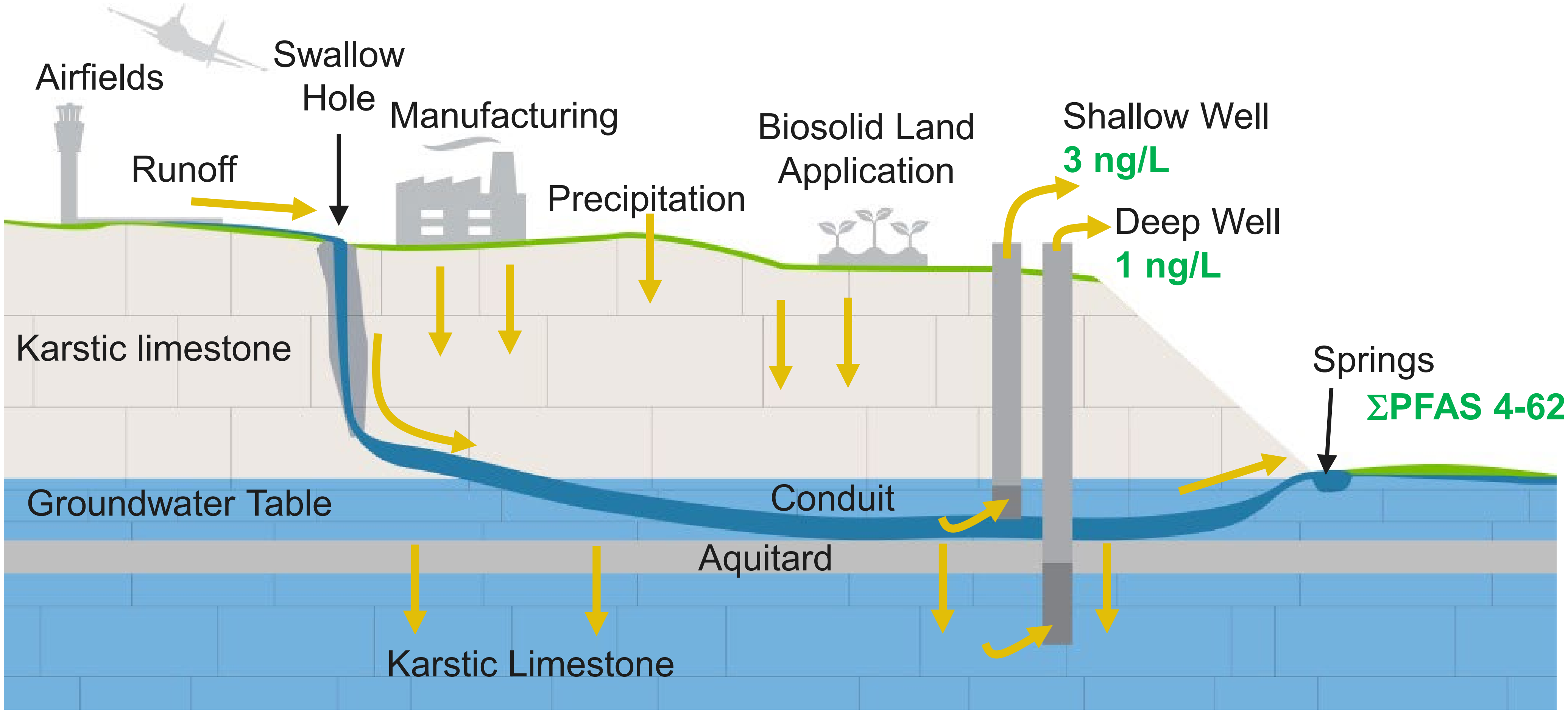
Springs: 300 ng/L
Stormwater: 700 ng/L
AFFF
Training/Use
WWTP input
Wind
Foam
ΣPFAS: 1,600 – 70,000 ng/L
ΣPFAS: 10-50 ng/L
Lake
ΣPFAS: 10s to 100s ng/L
Groundwater: 200 ng/L
Domestic Wells

Vignette 4



[1]Range of measurements from 2 sampling locations in (January 2020 to December 2021; Edmiston et al., 2022)
[2]Representative measurements from Bessie well (December 2019 to October 2020; OCWD 2021)

Vignette 5



Airfields
Swallow Hole
Manufacturing
Biosolid Land Application
Shallow Well
3 ng/L
Runoff
Precipitation
Deep Well
1 ng/L
Karstic limestone
Springs
ΣPFAS 4-62 ng/L
Groundwater Table
Conduit
Aquitard
Karstic Limestone

The Toolbox

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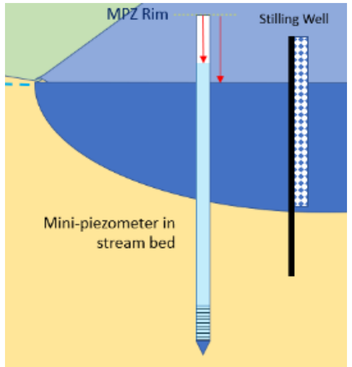
Multilevel Piezometers



Push-Point and Porewater Samplers

MHE Equipment

Porewater sampler

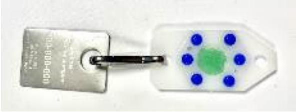
Seepage Meters

Rosenberry et al. (2008)

Passive Samplers

Sirem

Battelle



Aquanex

Streambed Passive Flux Meters (SBPFMs)

Streambed Point Velocity Probes (SBPVPs)

Courtesy Rick Devlin

TEFLUX

Courtesy Tim Johnson

Stream Tracer Testing

Vertebrae Horizontal Wells

ARCADIS

Sentinel™ Passive Samplers

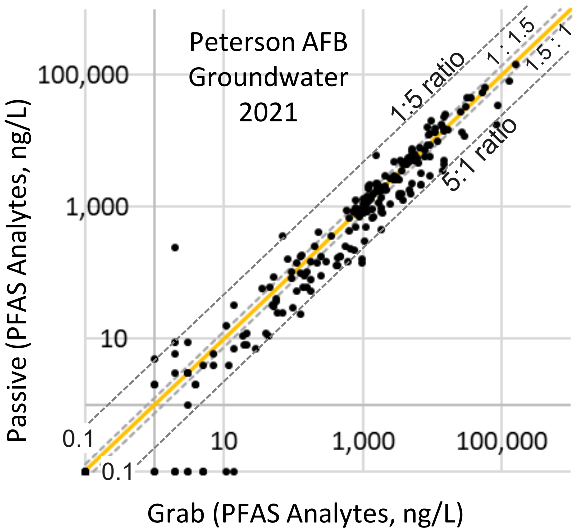
Field Testing Program

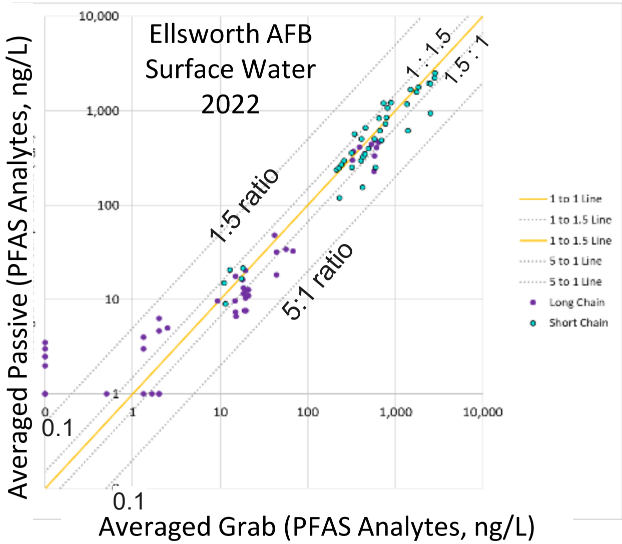




- ➢ >200 samplers at 7 sites (surface water and groundwater)
- ➢ Integrative response
- ➢ 2-30 day deployment time

SERDP project ER20-1127





Linear response over > 5 orders of magnitude in concentration (short- and long-chains)

Majority of data with 1.5:1 / 1:1.5 ratio (40% RPD)

Commercial availability

AQUANEX

https://aquanextech.com

- Available ~US$100
- Commercial labs will report the analysis as either a modified EPA Method 1633 or a modified EPA Method 537.1
- Mass of analytes (ng) sorbed on the Sentinel™ converted to ng/L

Sediment Porewater Passive Sampling

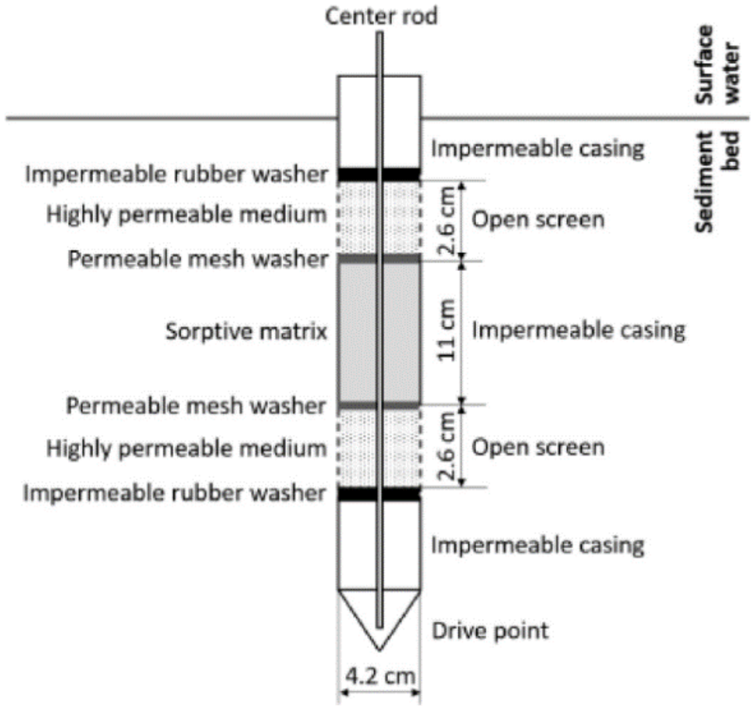
Sentinel™: Modified stainless steel version for sediment

Conceptual prototype frame for deployment of array of passive samplers in sediment.

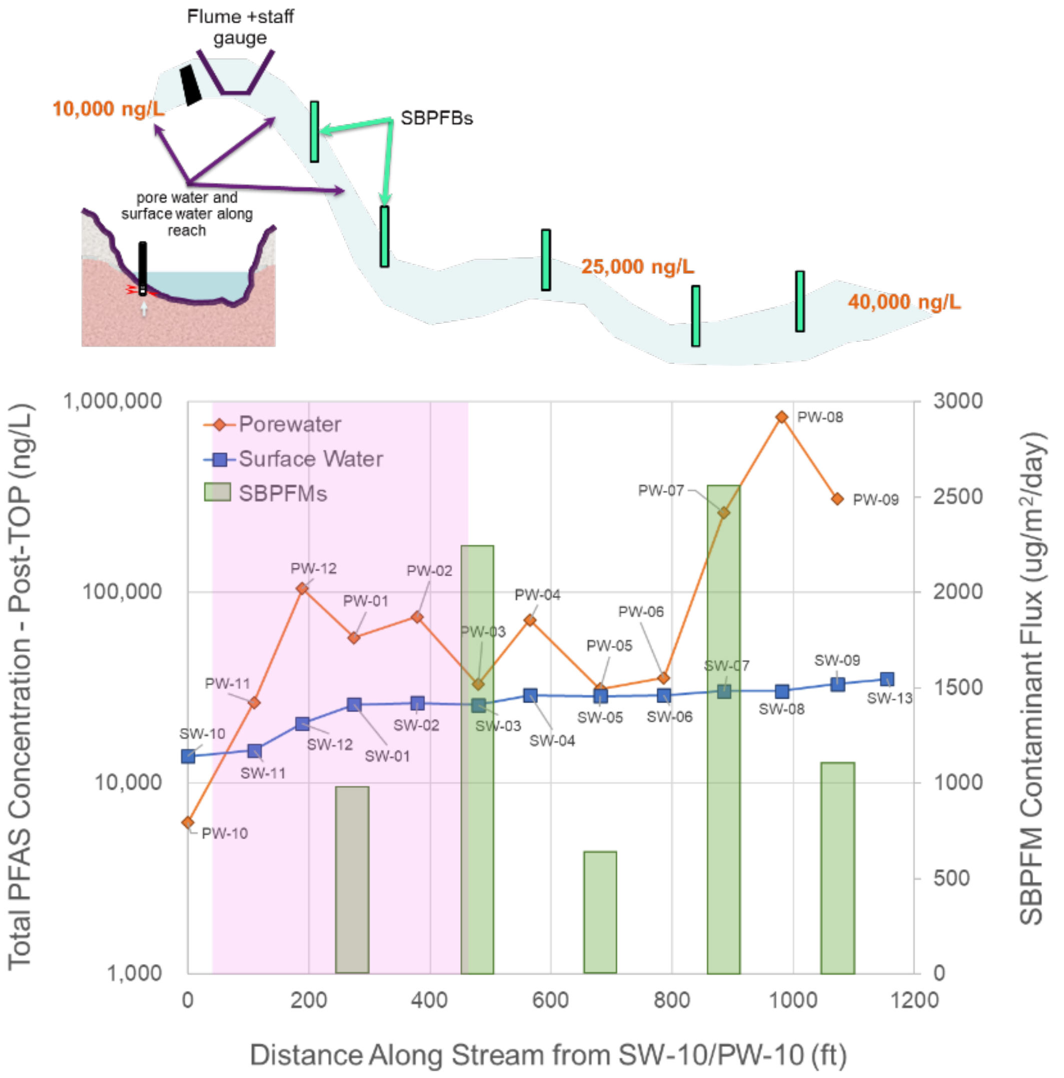
PFAS Insight™ (Battelle)

PFASsive™ (Sirem)

Streambed Passive Flux Meters (SBPFMs)

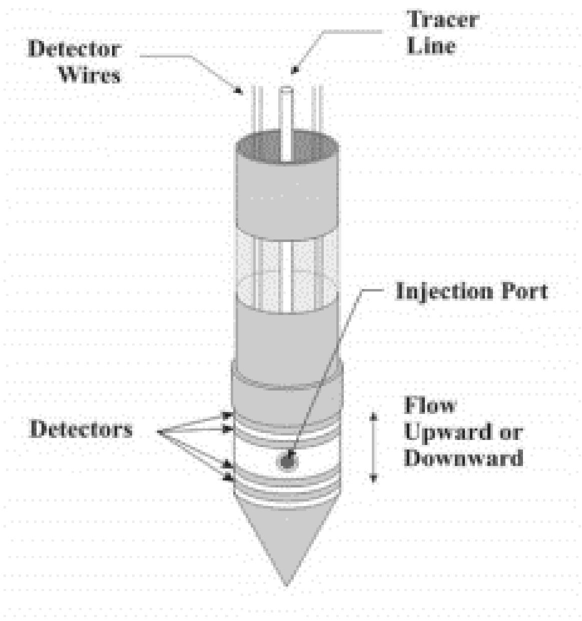


Layton et al. (2017)

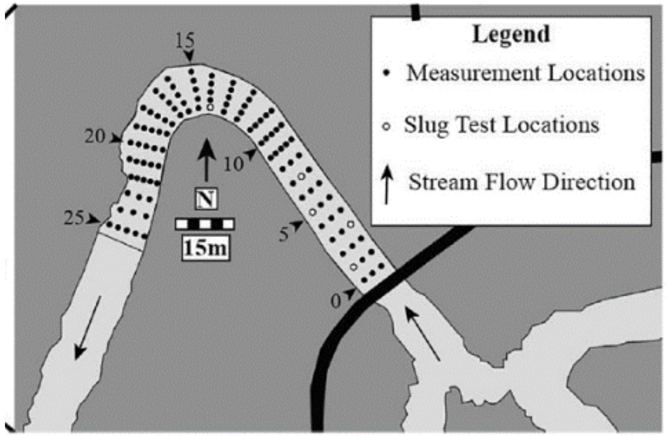


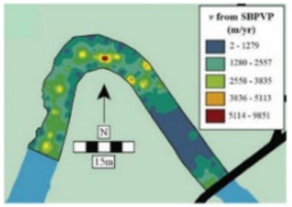
Commercially available from Enviroflux (https://enviroflux.com/technology/passive-flux-meter/) and iFLUX (https://ifluxsampling.com/en)

Streambed Point Velocity Probes (SPVPs)

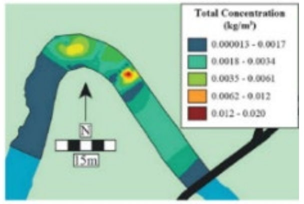


Schematics and photo of the SBPVP (Cremeans and Devlin, 2017). SPVP photo courtesy Rick Devlin



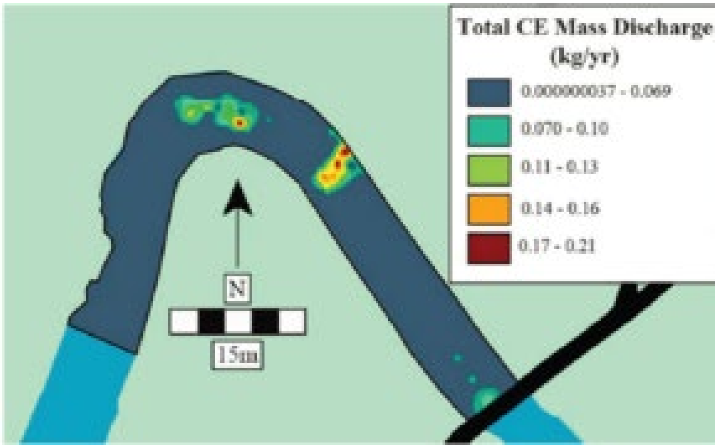


Groundwater flux



Contaminant distribution

Cremeans et al. (2018)



Contaminant flux

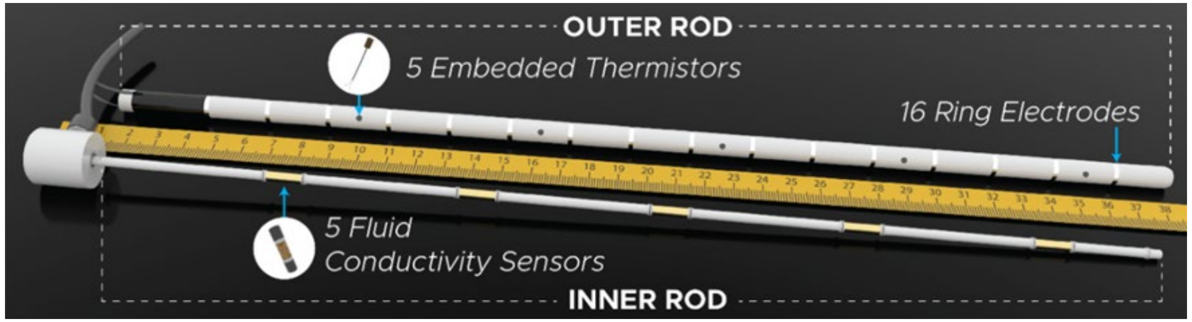
Available from Ozark Underground Laboratory: https://www.ozarkundergroundlab.com/assets/point-velocity-probe-handbook.pdf

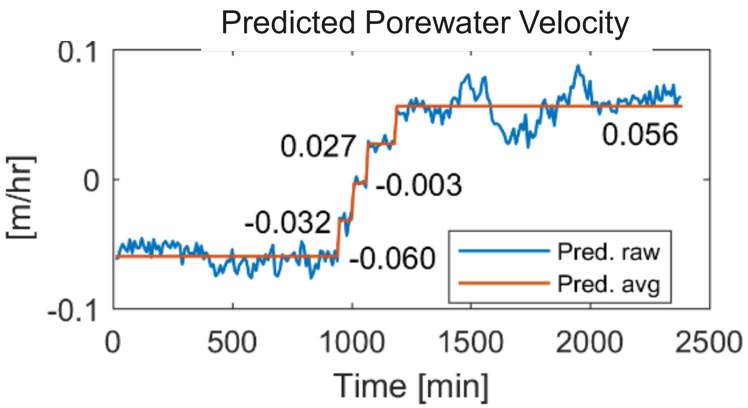
Thermo-Electric Water Flux Detection Probe (TEFLUX)

- Pressure, temperature, fluid conductivity, and bulk electrical conductivity sensors along axis
- Data time-series are collected during dynamic tidal or river stage variations
- Porosity is estimated from fluid and bulk conductivity via Archie's Law

➤ Estimates distribution of permeability and porosity

➤ Computes dynamic pore velocity and Darcy flux

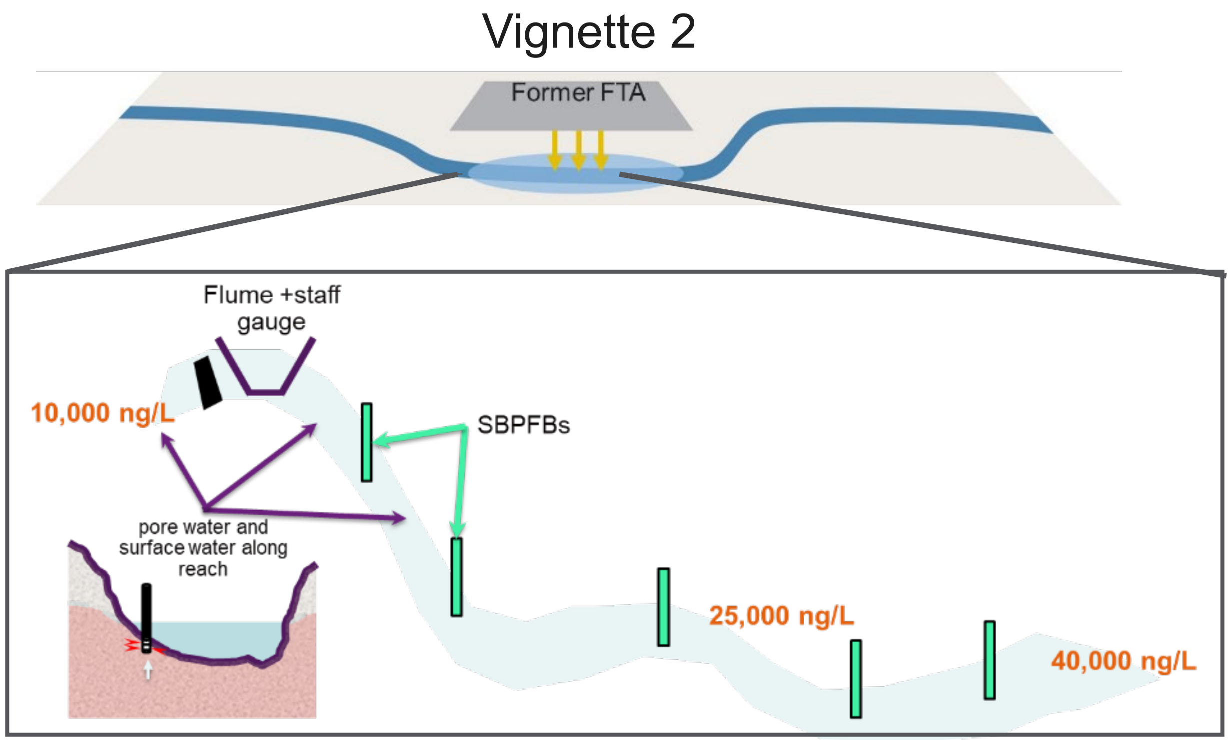




Courtesy Tim Johnson (PNNL)

Courtesy Tim Johnson (PNNL)

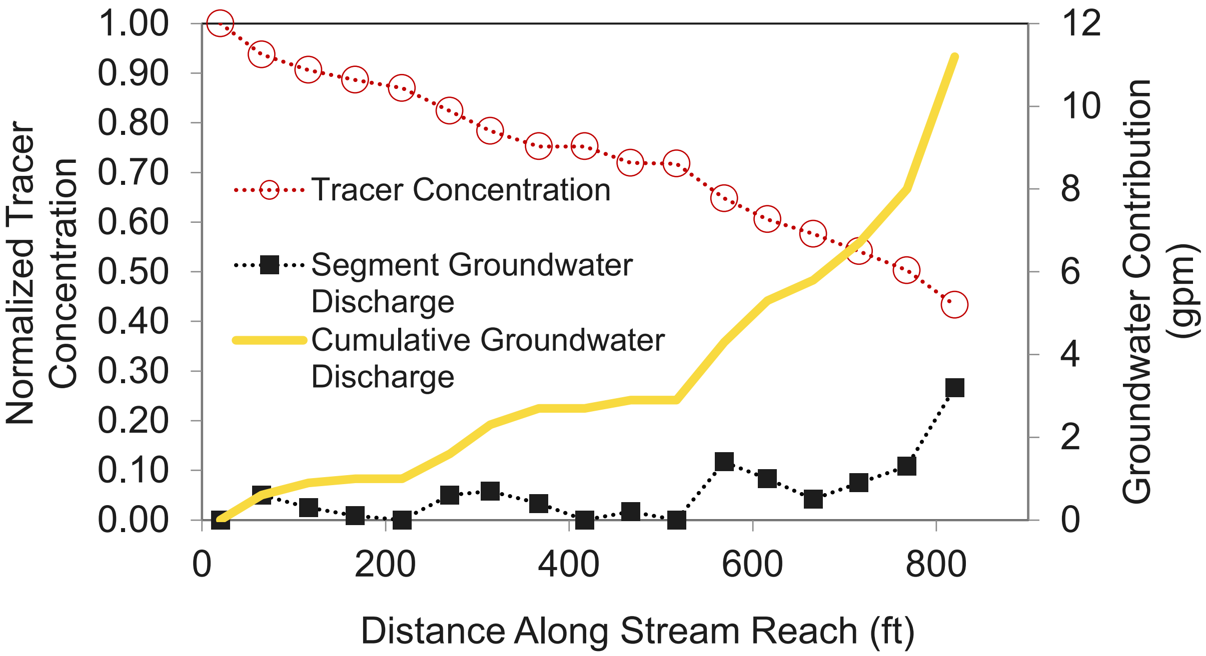
Stream Dilution Tracer Test



1. Add conservative tracer until steady state is achieved
2. Measure in-stream tracer concentrations along reach
3. Declines in tracer concentrations are assumed a result of groundwater flux

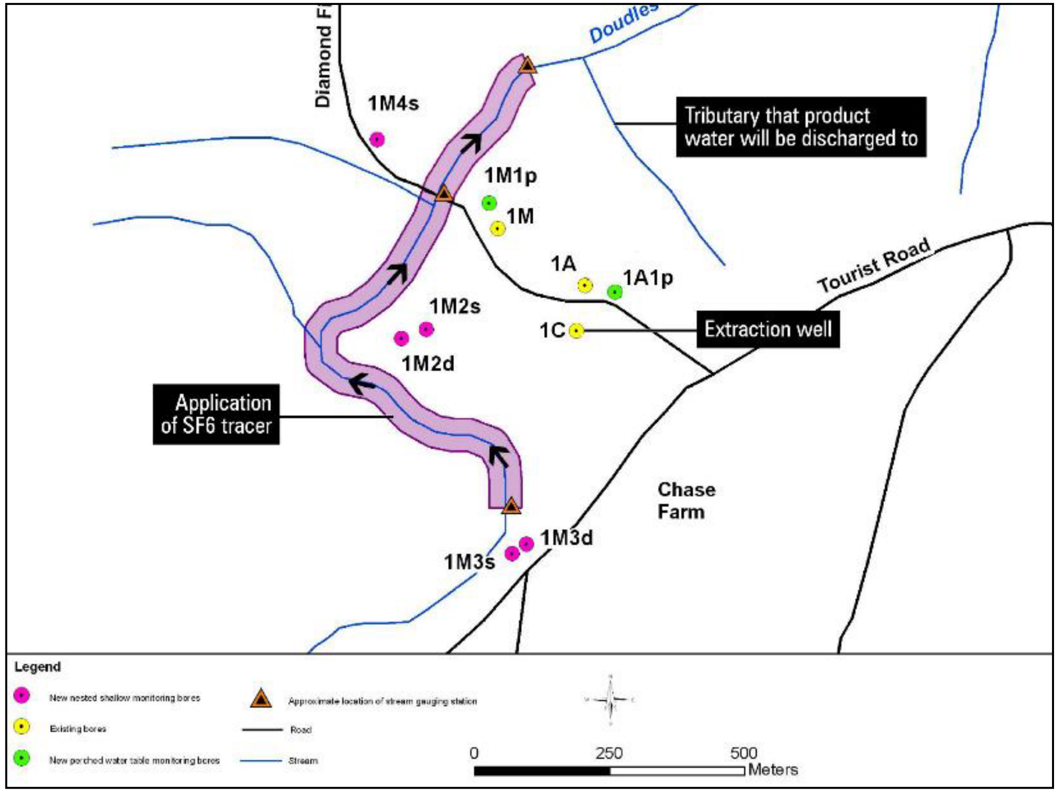
Mixed Tanks for Stream Tracer Test

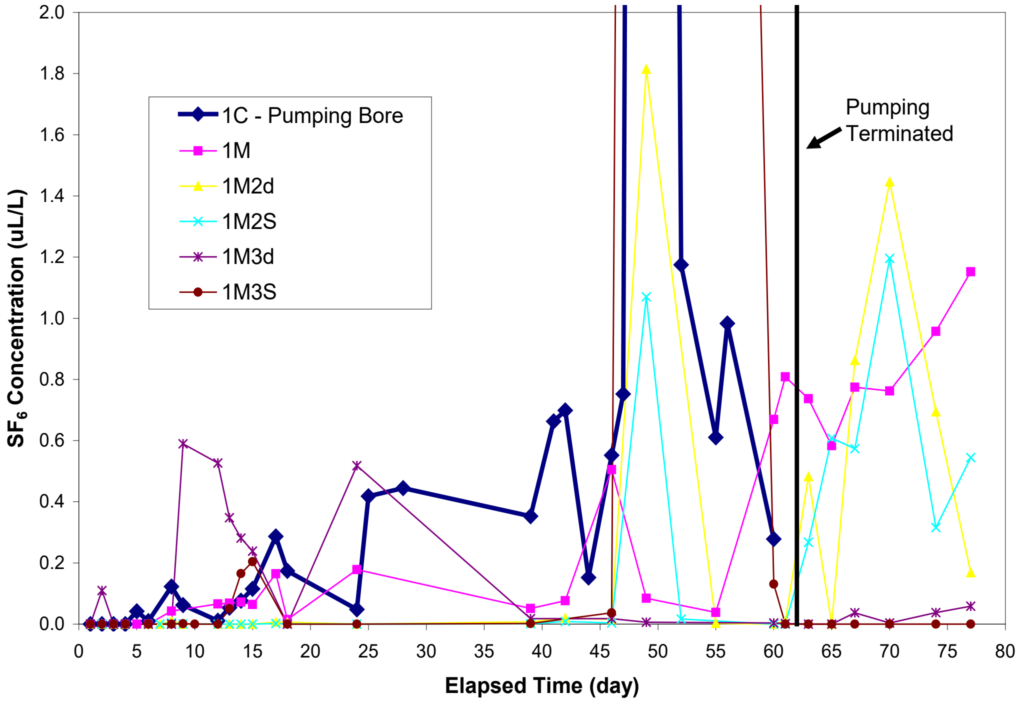
Tracer Addition Location



Stream Loss Tracer Test

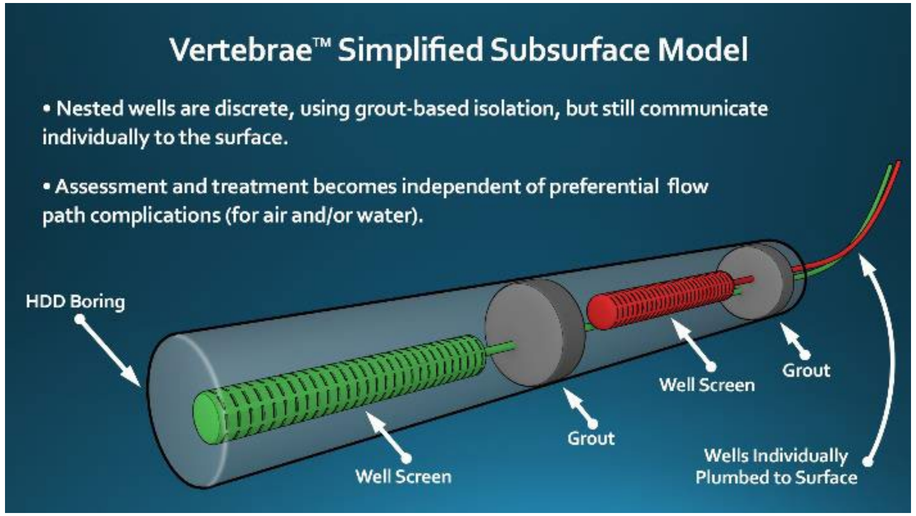
- SF_6 tracer applied to creek (~0.3% solubility)
- Breakthrough at pumping well (x=850 ft) at 5 days
- Tracer detected in all monitoring wells
- Transport velocity within primary pathways ~200 ft/day
- ~5% of water at production bore from the creek

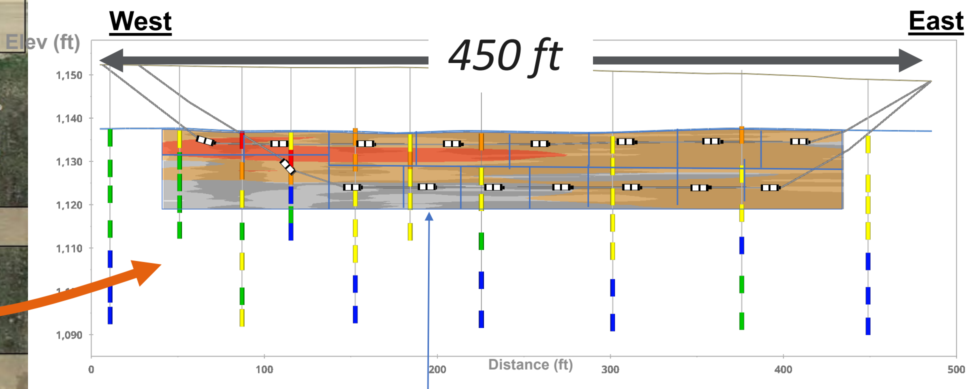




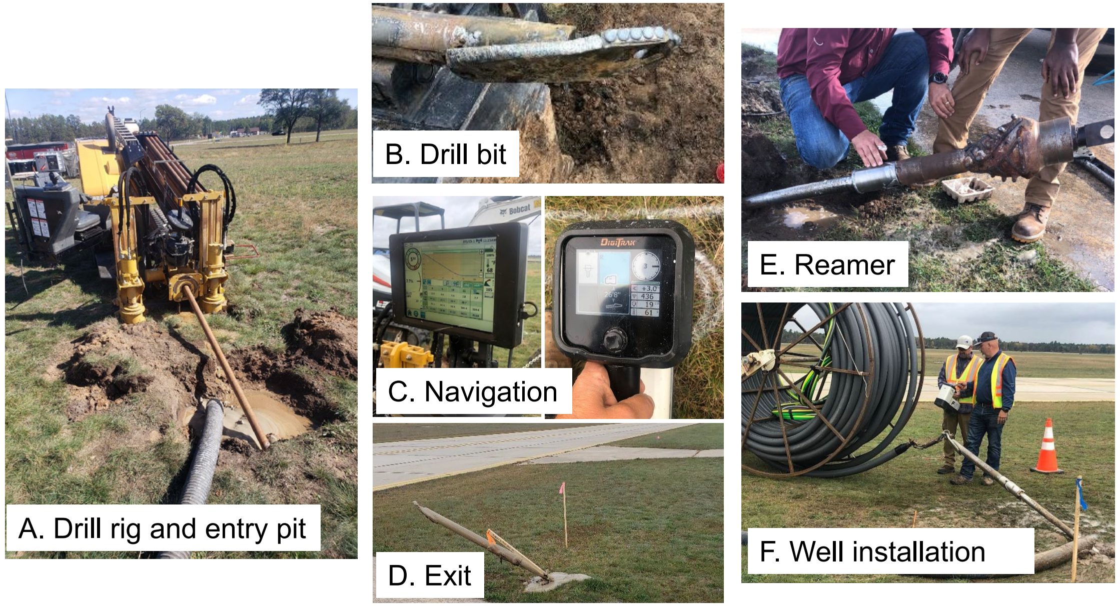
SF_6 Tracer breakthrough in pumping and monitoring wells

Vertebrae™ Segmented Horizontal Wells for PFAS Mass Discharge





$M_i = C_i \cdot q_i \cdot A_i$ $\qquad M_D = \sum M_i$



ESTCP project ER20-5026

- Vertebrae is commercially available and cost effective
- Easily installed, including under surface infrastructure
- Screen placement within +/- 1.5 feet of targets
- A-DTS and tracer testing yield reasonable flux values
- Spatial variability: >90% mass discharge from two subzones
- Can measured mass discharge changes over time
- Can support remedy performance evaluation, risk assessment, etc.

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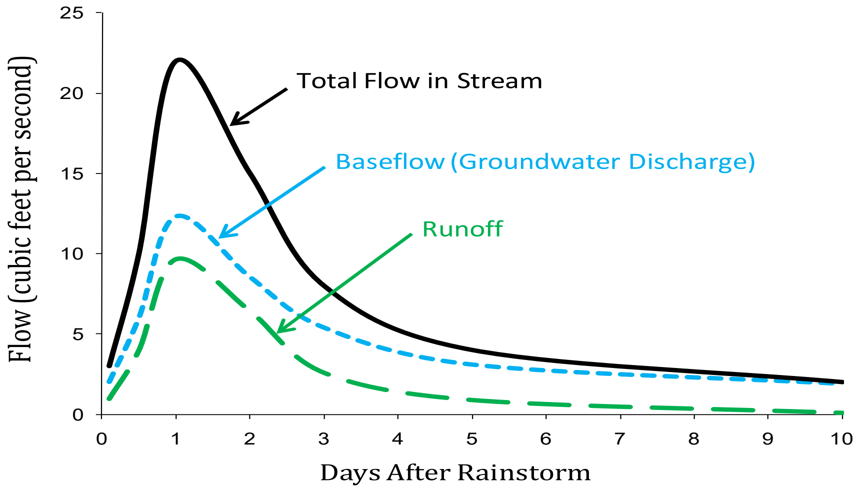
Future Needs and Priorities

Stormwater

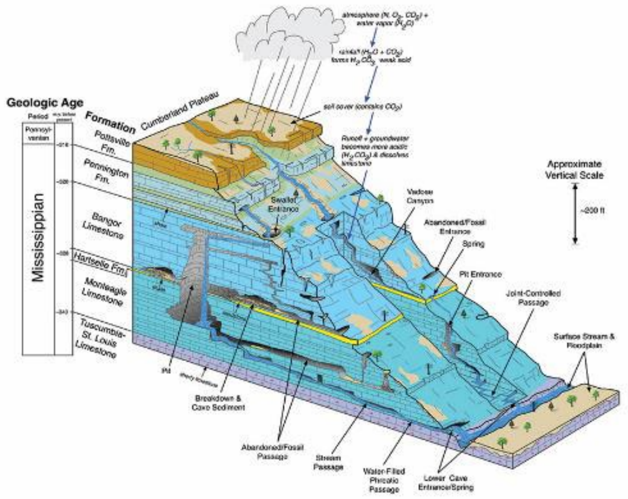
- High stage → drive hyporheic exchange
- Turbulent flow → Foaming potential and enhanced concentration of PFAS
- High sediment/microplastic → Enhanced PFAS transport
- PFAS chemograph may be complex → first flush?



Post-storm hydrograph. Baseflow and runoff components were separated using environmental tracers (e.g., ^{18}O, ^{2}H, TDS, silica)

Karst

- ~20% of US underlain by karst or pseudo karst
- Sinkholes → High loading potential from stormwater
- High heterogeneity and anisotropy → Complex and fingered plumes with changes in groundwater flow directions under various hydrologic conditions
- Rapid, long-distance transport → Large plumes
- Springs → convergence of flow integrates contamination, main exposure point



Left: Karst system conceptual model. Middle: Natural foam generated by turbulence. Right: ephemeral spring connected to conduits which only flow under high-flow conditions.

Contacts

CRAIG DIVINE PHD, PG

Principal Hydrogeologist, Nixa, MO

c 720 308 5367

e craig.divine@arcadis.com

Natural iron staining from reduced groundwater discharging from a sandstone aquifer to an oxic stream.

Summary of Flux Measurement Technologies and Methods

Method	Advantages	Limitations	Measurement time window	Measured Parameters
Multilevel piezometers	• Widely used and accepted • Quick and easy to install • Low in material cost	• Challenges related to obtaining accurate hydraulic gradients over small distances • Difficult to maintain in high energy water bodies	Point scale (can be continuously measured)	• Hydraulic gradient
Seepage meters	• Direct measure of flux • Widely used and accepted	• Less reliable in high energy water bodies • Not well-suited for coarse sediments • Often requires custom fabrication	Hours to days	• Groundwater flow
Single-well tracer tests (SWTTs)	• Direct measure of flux • Widely used and accepted	• Typically used for horizontal flux • Best performs in higher groundwater flux conditions	Hours to days	• Darcy flux
Streambed passive flux meters (SBPFMs)	• Provides long-term average estimates of groundwater flux	• Modest equipment, sampling, and materials cost • Difficult to maintain in high energy water bodies	Several days to a week	• Darcy flux • Contaminant flux
In-stream tracer tests	• Direct measure of flux • Learge measurement scale	• Typically limited to small streams	Hours to days	• Darcy flux
Streambed point velocity probes (SBPVPs)	• Estimates independent of Darcy's Law calculations • Wide range of operation	• Requires active injection and not capable of collecting continuous data • Moderate to high initial installation cost • Not yet commercially available	Point scale	• Groundwater velocity
TEFLUX	• High temporal resolution, continuous monitoring • Simple operation • Rugged construction suitable for difficult environments	• Not fully demonstrated in the field • Uncertainty in the effects of horizontal flow on the results	Point scale (can be continuously measured)	• Hydraulic gradient • Groundwater velocity • Hydraulic conductivity • Porosity

Some Commercially Available PFAS Passive Samplers

Sampling Device (Developer)	Description	Applications	Typical Deployment	Maturity	Resources
Sentinel™ Sampler	Granular organosilica sorbent in HDPE housing	Groundwater, surface water	1-2 Weeks, integrative	Field testing in progress.	Edmiston et al. (2023) https://aquanextech.com/collections/passive-samplers
POCIS (USGS)	Solid-phase sorbent (various) between two microporous polyethersulfone membranes, housed between metal rings. Originally developed for other organics and recently adapted for PFAS.	Surface water, groundwater (well diameter limitations).	Weeks to 1 month, integrative	Commercially available for other organic analytes, requires sorbent modification for PFAS	Kaserzon et al. (2014) https://est-lab.com/pocis.php
PFAS Insight™ (Battelle Laboratories)	Polymeric sorbent in metal housing	Groundwater, surface water, sediment porewater (in development)	1 Month, integrative	Commercially available	https://www.battelle.org/markets/environment/investigation-remediation/pfas-assessment-mitigation/pfas-insight-passive-sampling-technology
PE Sampler	Microporous PE tube containing sorbent (e.g., Strata X-AW).	Groundwater, surface water (in development)	~ 3 Months, integrative	Pilot field testing (groundwater) published. Additional field testing and development in progress.	Kaserzon et al. (2019) SERDP Project ER20-1156
DGT Sampler (DGT Research)	Filter membrane, diffusive gel layer, over sorbent phase within housing capsule. Originally developed for other analytes and adapted for PFAS.	Groundwater, surface water	Weeks, intrgrative	Commercially available. Field testing of modified designs in progress.	Wang et al. (2021)
Graphene Monolith (Univ. Rhode Island / Brown Univ.)	Surface-modified graphene hydrogel monolith	Groundwater, surface water	1 Week, equilibrium	Proof-of-concept field testing in surface water published	Becanova et al. (2021) SERDP project ER-1293
Dual-Membrane Passive Diffusion Sampler (DMPDB™) (EON Products)	No-purge sampler consisting of two separate semi-permeable membranes (one hydrophilic, one LDPE) around a single sample chamber for analysis of broad suite of analytes	Groundwater	2 Weeks, equilibrium	Commercially available	https://www.eonpro.com/dmpdb-case-studies-user-information/#1610739662295-3686640b-07fd
SNAP Sampler (QED Inc.)	No-purge sampler using double-ended bottles that "snap" closed in-situ within the well casing. Developed for other analytes but may be applied for PFAS	Groundwater (note, bottleware may contain Teflon parts)	Days to months, equilibrium	Commercially available	https://www.qedenv.com/en-us/products/snap-sampler/

SERPD-ESTCP PFAS Passive Sampler Projects

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Project Number	ER20-1127	ER23-7696	ER23-4022	ER20-1211	ER20-1293	ER20-1156	ER20-1363	ER21-5104	ER20-1073	ER20-1336	ER23-7741
PI or Contact	Craig Divine	Erika Carter	Paul Edmiston	Mei Sun	Rainer Lohman	Sarit Kazerzon	Julian Fairey	Andrew Jackson	Lee Blaney	Upal Ghosh	Jason Conder
Technology Readiness Level	9	7	3	4	7	8	Readiness for what? Field testing? Compliance monitoring?	8-9	3-4	5	9
Commercially Available (if yes, incl. hyperlink)?	Yes	Yes	No	No	No	Yes	Yes	Yes	Yes* (membranes)	No	Yes
Can be analyzed by commercial labs?	Yes	Yes	No	Yes	no	Yes	Yes	Yes	Yes	Yes	Yes
Number of field samples to-date	200	5	0	0	36	150	0	200	0	0	150
Integrative or Equilibrium	Integrative	Integrative	Integrative	Integrative	Integrative	Integrative	Kinetic	Equilibroum	Equilibrium	Equilibrium	Equilibrium
Sorbent Media	Organosilica (Osorb)	Organosilica (Osorb)	Organosilica (Osorb)	Fluorogel and functionalized resin	Oasis WAX	Strata XAW (Phenomenex), interchangeable to any sorbent	Weak Anion Exchange (WAX) resin	Water	Commercial anion-exchange membranes	Several	Water
Membrane	None	None	None	None	agarose	None	None	0.4um Stainless Steel	None	Several	0.4-μm polycarbonate
Dimention (cm, LxWxH)	4.5x2.5x0.3	4.5x2.5x0.3			3.75 x 3.75 x 0.8 cm	4x0.5x0.4	4 x 4 x 2	1,440 Length 6 OD	9.7 (diameter), 1.4 (height)	Variable	
Deployment Time (days)	2 to 30	TBD	TBD	TBD	TBD	3-180	≤ 90 (expected)	21-28	TBD	7-14 days	≥ ~2 to ∞ (water) ≥ ~7 to ∞ (sediment)
Typical Detection Limits (ng/L)	1	1	TBD	TBD	TBD	1	TBD	1-5	TBD	can be tailored to need	1
Range of detection (ng/L)	1 to >100,000	1 to >100,000	TBD	TBD	TBD	1 to >100,000	TBD	1 to >100,000	TBD	can be tailored to need	1 to > 100,000
Sampling Rate Range (L/day)	0.01 to 0.07	TBD	TBD	TBD	TBD	0.003-0.02	0.0025 to 0.017	Not Applicable	Not applicable	NA	Not applicable
Are mass transfer rates publicly available (Yes / No)	Yes	Yes	No		No	Yes (doi's below)	In progress (diffusion coefficients in diffusive gel layer)	Yes	No	NA	
Membrane Diffusion Coefficient Range (cm2/d)	Not applicable	Not applicable	Not applicable	Not applicable	0.1--0.8	Not applicable	Not applicable	0.5-1 cm/day^{1}	TBD	NA	ke (water) = ~ 0.5 day^{-1}
Performance reference compound used?	No	TBD	TBD	TBD	TBD	No	No	Possible	TBD	Yes	Yes
Surrogates used to assess recovery?	Yes	Yes	Yes	Yes	Yes	Yes	Yes - isn't this a requirement?	Yes	Yes	Yes	Yes
Compatible with non-target semi-quantification	Yes	Yes	TBD	Yes	TBD	Yes	Not Tested	Yes	Yes	Yes	Yes
Compatible with TOP assay	Yes	Yes	TBD	Yes	TBD	Yes	Not Tested	Yes	Yes	Yes	Yes
Capable of measuring mass flux	No	No	No	No	No	Yes (if this is mass loads?)	Yes	Yes	TBD	Yes	Yes
Sensitivity to Temperature (low, moderate, high)	Moderate	Moderate	TBD	TBD	TBD	TBD	Moderate; diffusion coefficient in Gel layer corrected to measured T using Stokes-Einstein equation	Low	TBD	Low	Low
Sensitivity to Salinity (low, moderate, high)	Low	Low	TBD	TBD	TBD	Low	TBD	Low	Low	TBD	Low
Sensitivity to pH (low, moderate, high)	Low	Low	TBD	TBD	TBD	Low	TBD	Low	Low	TBD	Low
Sensitivity to DOC (low, moderate, high)	Low	Low	TBD	TBD	TBD	Low	TBD	Low	TBD	TBD	Low
Sensitivity to flow velocity (low, moderate, high)	Moderate	Moderate	TBD			Low	TBD	Low	Low	Low	
Surface water (applicable/not applicable)	Applicable	Applicable	TBD	Applicable	Applicable	Applicable	Applicable, not tested	Applicable	Applicable	Applicable	Applicable, tested
Stormwater water (applicable/not applicable)	Applicable, not tested	Applicable, not tested	TBD	Applicable, not tested	TBD	Applicable	Applicable, not tested	Applicable	Applicable, not tested	Applicable	Applicable, not tested
Groundwater (applicable/not applicable)	Applicable	Applicable	TBD	Applicable	TBD	Applicable	Applicable, not tested	Applicable/tested	Applicable	Applicable	Applicable, tested
Sediment/porewater (applicable/not applicable)	Applicable, not tested	Applicable	TBD	Applicable, not tested	TBD	Not applicable	Applicable, not tested	Applicable/tested	Applicable, not tested	Applicable	Applicable, tested
Wastewater (applicable/not applicable)	Applicable, not tested	Applicable, not tested	Not applicable		TBD	Applicable	Applicable, not tested	Applicable	Applicable	Applicable	
Direct drive compatible	Not applicable	Yes	No	Yes	No	Not sure what this means	No	Yes	Yes	Yes	Yes
Air (applicable/not applicable)	Not applicable	Not applicable	TBD	Not applicable	no	Not applicable	Not applicable	Not Applicable	Not applicable	TBD	Not applicable
Firefighting Foam (applicable/not applicable)	Not applicable	Not applicable	Applicable	TBD	not applicable	Not applicable	Not Tested	Not Applicable	Not applicable	Why?	Not applicable
Photograph of current sampler				None							

Literature Cited

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