Optimization of equilibrium passive sampling for short-term surface water measurements.

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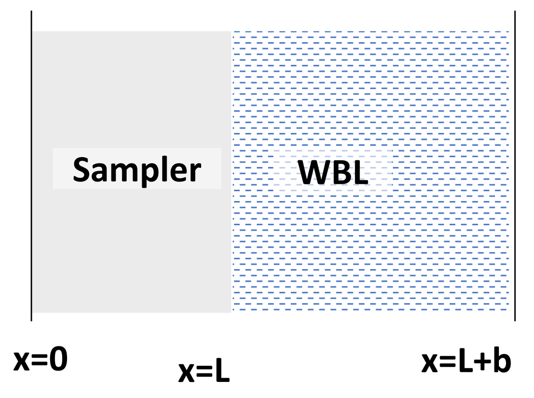
INTRODUCTION



- **Passive sampling** typically performed over an **extended period of time** provides **time-integrated concentration of HOCs**.
- **Short-term** measurements are critical in assessing **inputs from episodic events** and **delineating pollutant sources**.
- Primary factors that control the rate of uptake of pollutants in a passive sampler:
  1. **thickness of the polymer sheet** (mass transfer resistance within the polymer)
  2. flow velocity that controls the **hydrodynamic boundary layer thickness** (mass transfer resistance in the water side).

Research Aim: Explore the feasibility of performing short term measurements of PCBs in episodic events, with equilibrium passive samplers (polyethylene) by mathematical optimization followed by physical experiments and manipulation of sampler design.

MATERIALS AND METHODS

Two sets of experiments conducted:
1. Impact of forced vibration on passive sampling platform for slow flowing water column conditions.
2. Static PE sampler (25 µm) exposed to different flow velocities (6-30 cm/s)

Modeling framework for short term measurements in overlying water Fick's Diffusion:

Static mode:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE}\frac{\partial^2 C_{PE}}{\partial x^2} \quad \text{when } -L < x < L$$

$$\frac{\partial C_W}{\partial t} = D_W\frac{\partial^2 C_W}{\partial x^2} \quad \text{when } -L > x > -(L+b) \text{ and } L < x < (L+b)$$

Vibration mode:

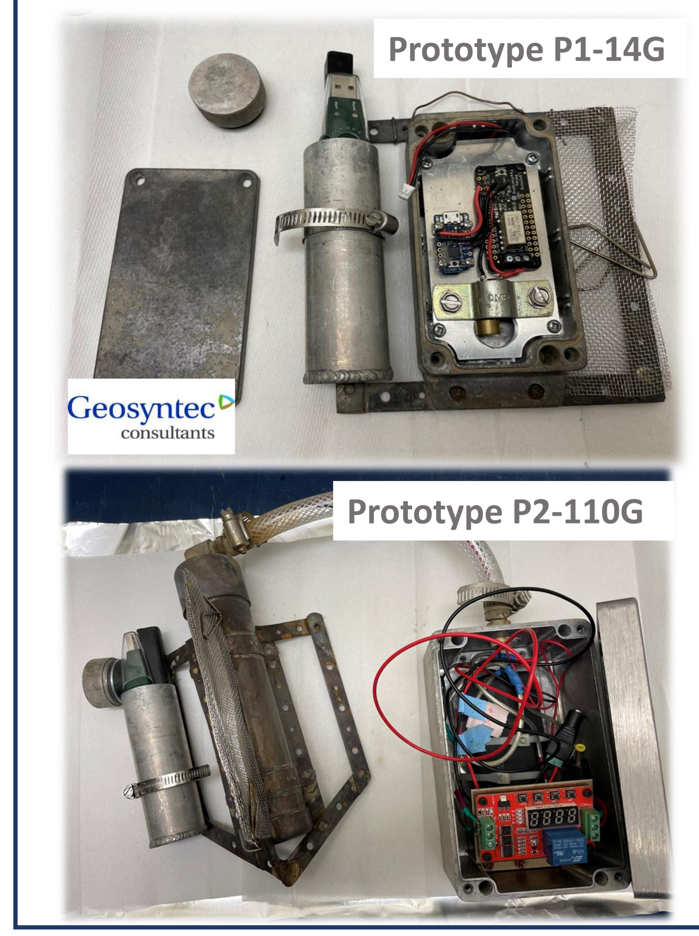
$$\frac{\partial C_{PE}}{\partial t} = D_{PE}\frac{\partial^2 C_{PE}}{\partial x^2} \quad \text{when } -L < x < L$$

$$C_W = C_{W,init} \quad \text{when } -L > x > -(L+b) \text{ and } L < x < (L+b)$$

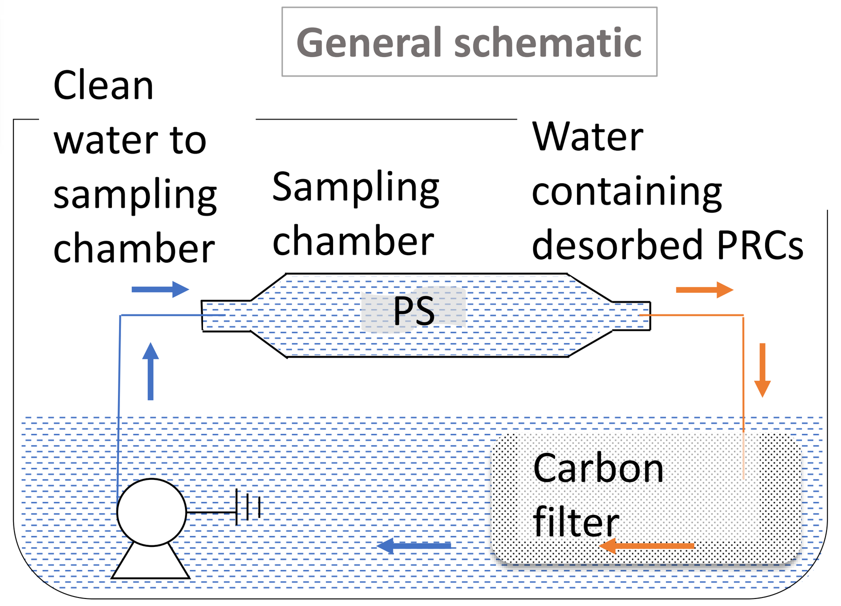
Physical experiments for short term measurements in overlying water:

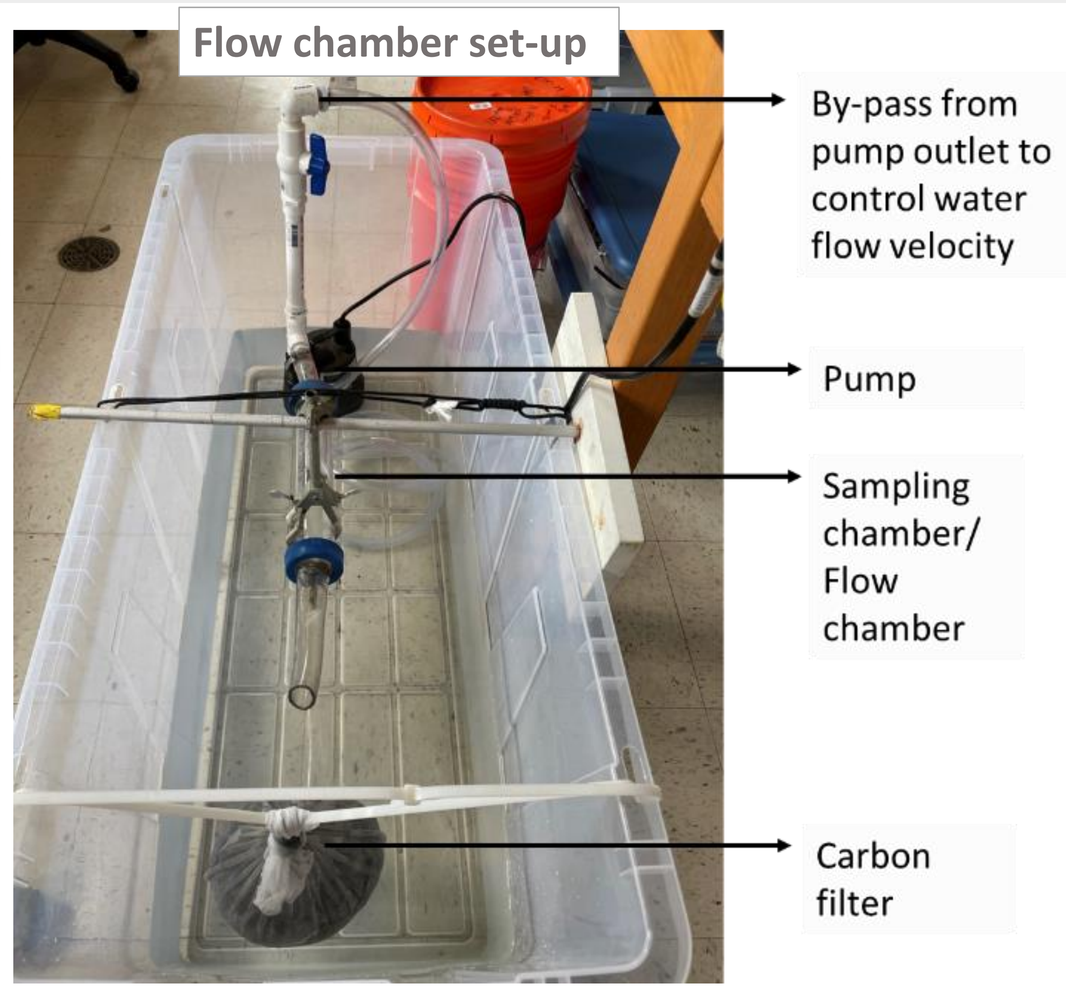
Passive sampler preparation: Cleaned PE sheets loaded with C13 labeled PCB compounds (*tetra-54*, tri-47*, tetra-37*, penta-111*, hexa-138*, hepta-178**).

Vibration induced passive sampling platforms:



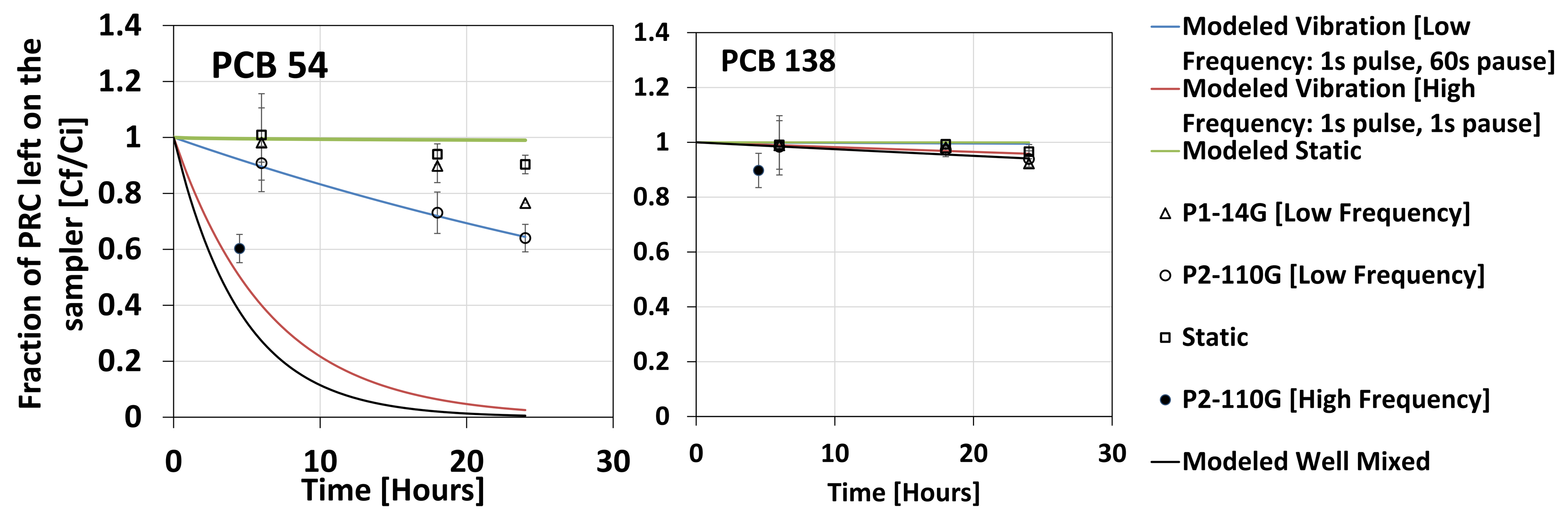
Laboratory flow chamber for controlled flow velocity:





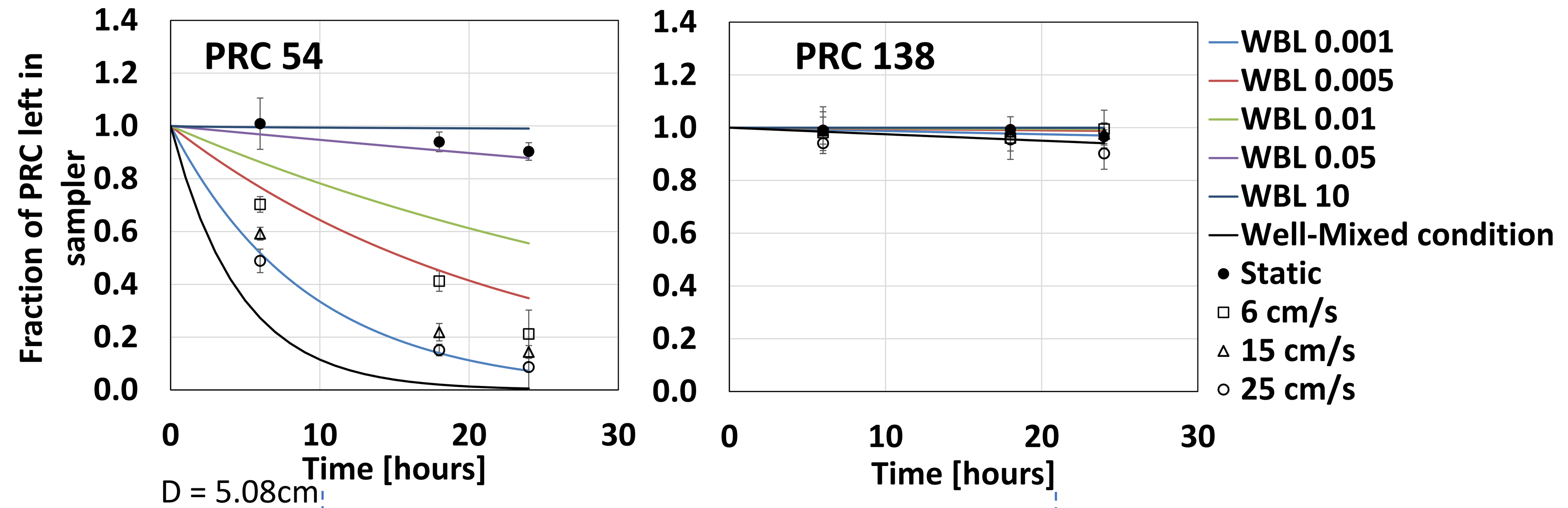
RESULTS

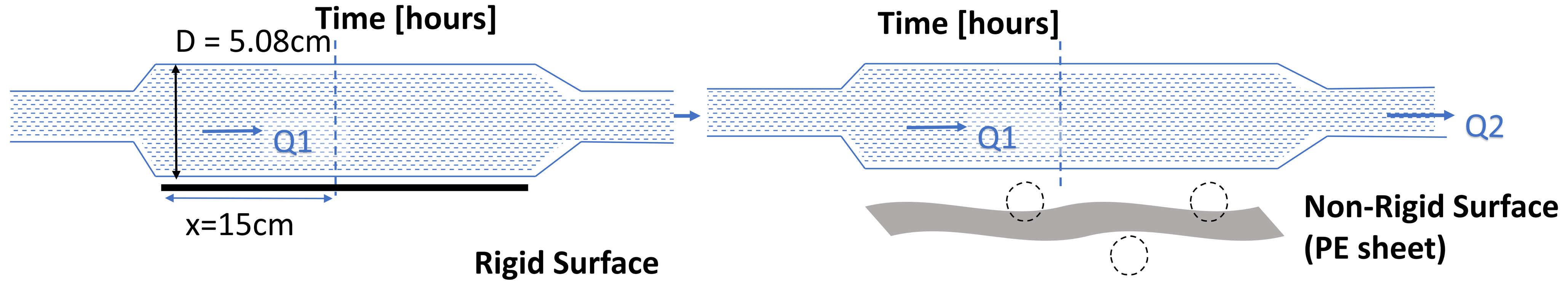
• Surface water experiments in the outer reservoir with vibrating sampler



- Induced vibration allows faster desorption of PRC compounds from PE sampler. Prototype P2 > Prototype P1.
- 15-50% loss of the tri-tetra homolog PRCs with low vibration frequency (1s pulse, 60s pause) within 24 hours.
- 10-40% loss of the tri-tetra and 2-8% loss of the penta-hepta homolog PRCs with the high frequency mode (1s pulse, 1s pause) in 4.5 hours.
- Not enough loss for the higher homologs for PRC correction purposes: Can we do other optimizations of PS choices / frequency of vibration?

• Flow velocity experiments in artificial flow chamber



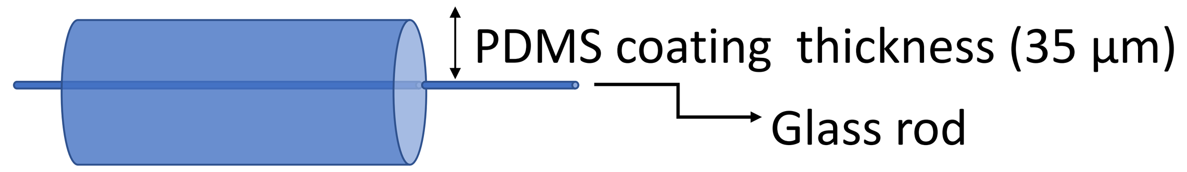


Re (within a pipe) = [Laminar flow when Re < 2300 and turbulent flow when Re> 2900]

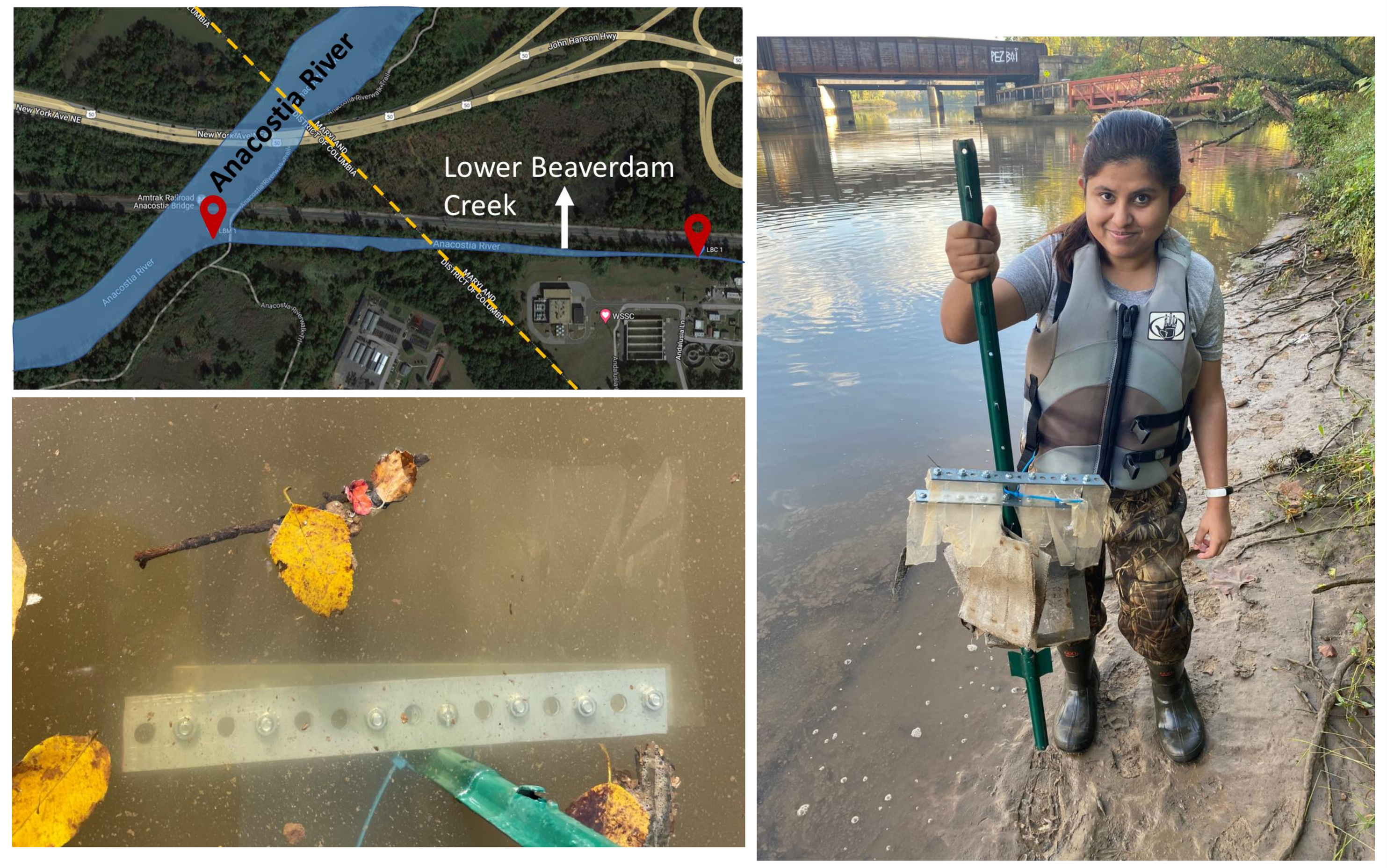
kinematic viscosity of water, v=			0.010023	cm2/s		
Water velocity, u [cm/s]	**Hydraulic Diameter, D [cm]**	**Re = uD/v**	**Laminar (L) OR Turbulent (T)**	**WBL/x =5/√Re (L) =0.37/(Re^0.2)(T)**	**Calculated WBL (cm) (WBL/x)*x**	**Measured WBL (cm)**
6	5	3041	T	0.07	1.1	0.001<WBL<0.005
15	5	7603	T	0.06	0.9	0.001<WBL<0.005
25	5	12671	T	0.06	0.8	0.001<WBL<0.005

ONGOING/FUTURE WORK

1. Varying PE thicknesses (7, 18, 25, 50 µm PE)
2. Establish correlation between water velocity and WBL thickness for flexible PE sheets
3. Determine parameters that would enable short-term measurements in the field (time, polymer material and thickness, and need for field vibration)
4. PDMS vs PE (Log D_{pdms}= -6.4 vs Log D_{PE}= -8.98 for PCB#47)



5. Field implementation of short-term PS to estimate pollutant discharge during a single storm-event:
   - Lower Beaverdam Creek and two storm outfalls (upstream and downstream at the confluence of LBC with Anacostia River, Washington DC).
   - Thinner polymer sheet and deployment for a much shorter period of time.
   - Compare freely dissolved concentrations measured over the high flow period after a major rainfall with concentrations measured over a longer duration time integration of 2-3 months.



ACKNOWLEDGEMENTS

- Sponsorship from SERDP and DOEE.
- Collaborators on this work include Mehregan Jalalizadeh (Geosyntec, now Exponent) and Louis Cheung (UMBC)

Sponsors
SERDP DOD • EPA • DOE
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Collaborator
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