



Use of LDPE Passive Samplers for Monitoring PAHs in the Water Column of a Suburban, Freshwater Oil-Spill Site

James W Rice¹, Travis Bals¹, Eric M Suuberg¹, Robert M Burgess², Kim Boekelheide¹

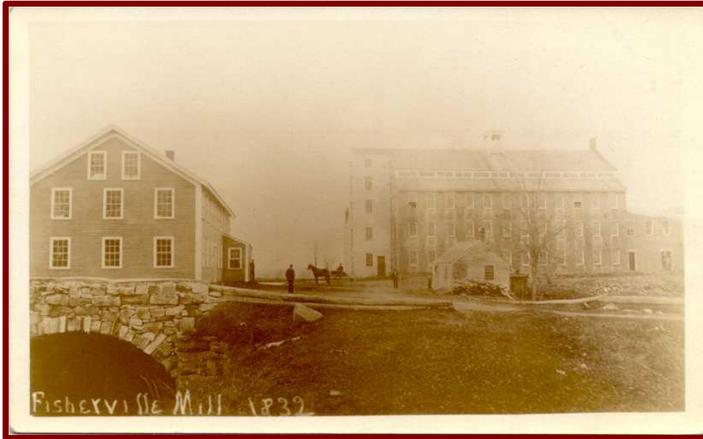
Post Doctoral Research Associate
Engineering State Agencies Liaison

¹Superfund Research Program, Brown University, Providence, RI, USA

²US Environmental Protection Agency, ORD/NHEERL, Narragansett, RI, USA

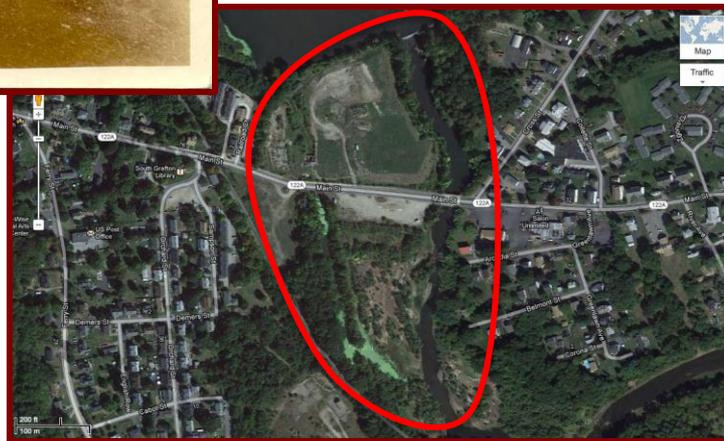
James_Rice@Brown.edu

Fisherville Mill Site, Grafton, MA



- Site of former textile mill
- Bounded by Blackstone River, which flows into RI
- Fire completely destroyed mill in 1999
- EPA “completed” cleanup in 2005
- Fisherville Redevelopment Corp. purchased site

Engaged developer wants to restore site for town benefit



No deep pockets for expensive remediation

Contaminants of Concern

- Petroleum – Current contaminant of concern in canal
- Heavy metals – In sediment and floodplains
- Chlorinated organic solvents - Subsurface
- Asbestos – removed in Emergency Action



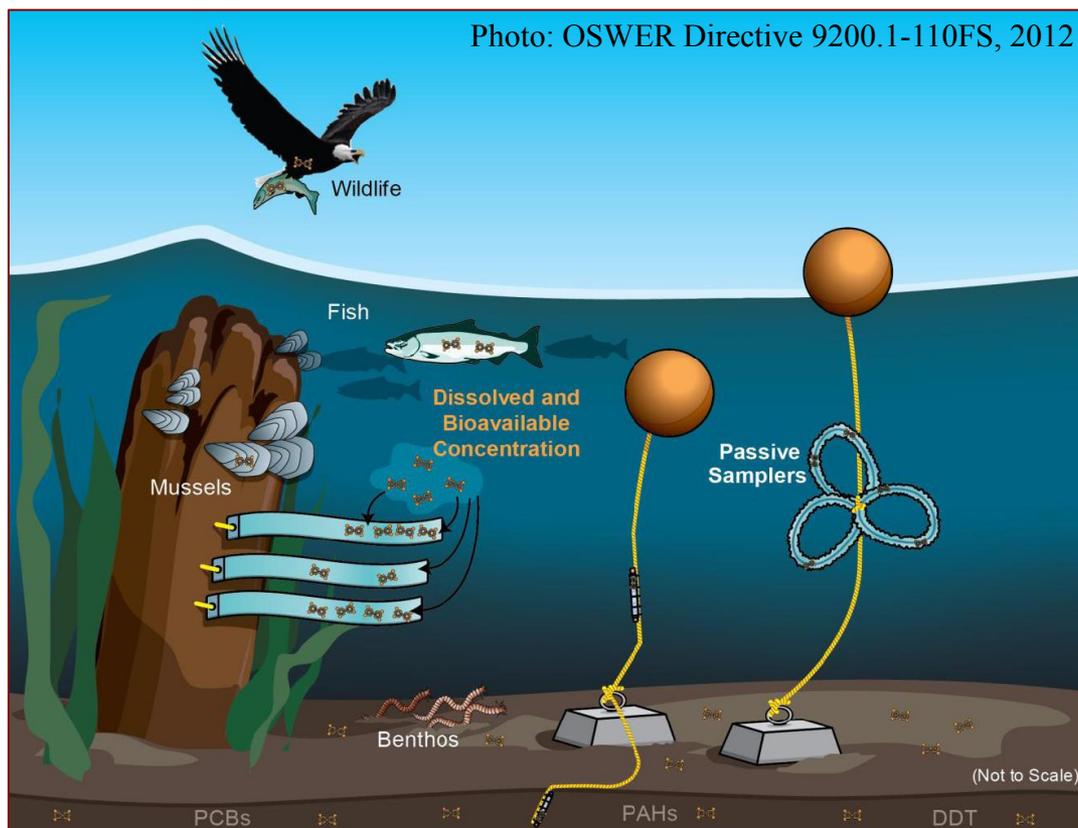
Fisherville is a Complicated Site



- Heavily contaminated oil spill (Bunker-C) site
- Shallow, warm, fresh water
- **Uncertainty regarding bioavailability of petroleum hydrocarbons, e.g., PAHs**
- PAHs in water column likely associated with natural organic carbon, particulates, colloidal suspensions, and free-phase oil
 - Not all PAHs are freely dissolved
 - “Grab” samples may not reflect freely dissolved PAH concentrations

What are Passive Samplers?

Solid materials (usually plastic) into which freely dissolved organic contaminants absorb



Contaminants extracted from samplers after lengthy deployment and measured in laboratory

Benefits of Passive Samplers

Traditional Grab Sampling Methods

Collection of large volumes of water and/or sediment

Results often affected by multiple phases (e.g., colloids, natural organic carbon, particulates) so concentrations do not always represent truly dissolved and bioavailable fractions

Dissolved phase concentration often so low that chromatographic methods are unable to detect hydrophobic contaminants (PAHs)

Involve large volumes of organic solvent that are expensive and environmentally harmful

Passive Samplers

Can be deployed in situ; not necessary to collect grab samples

Only freely dissolved and bioavailable contaminants of concern accumulate into samplers (surrogates for aquatic organisms?)

Contaminants concentrate to detectable levels for several days, providing time averaged representation of contamination

Typically \$100-200 less per sample than traditional methods

Our Passive Samplers



- Low density polyethylene (LDPE) sheets cut from commercially available painter's drop cloth that was pretreated before in situ deployment
- Housed inside fish cages weighted with cement blocks
- Deployed from a kayak and allowed to equilibrate with water for 28 days
- Collected and brought back to lab for solvent extraction and GC-MS analysis

Calculating Freely Dissolved PAH Concentration

At equilibrium: Freely dissolved PAH concentration ($C_{\text{PAH,free}}$) a function of PAH sampler concentration ($C_{\text{PAH,sampler}}$) and a literature-based partition coefficient ($K_{\text{PE/water}}$)

$$C_{\text{PAH, dissolved}} = C_{\text{PAH, free}} = \frac{C_{\text{PAH, passive sampler}}}{K_{\text{PE/water}}}$$

However, time to reach equilibrium varies by compound, from days to months.

An exchange rate coefficient (k_e) was used to adjust for non-equilibrium conditions.

k_e calculated using deuterated PAHs as performance reference compounds (PRC).

$$k_e = \ln \left(\frac{C_{\text{PAH, passive sampler, } t=0}}{C_{\text{PAH, passive sampler, } t}} \right) t^{-1}$$

$$C_{\text{PAH, free}} = \frac{C_{\text{PAH, passive sampler}}}{(1 - e^{-k_e t})(K_{\text{PE/water}})}$$

Do PAH Concentrations Change Along Canal?



Location	Tank	L1	L2	L3	L4	L5
July Deployment (ng/L)	2	97	191	84	74	NA
Aug. Deployment (ng/L)	ND	159	129	91	135	114

Passive Samplers vs. Grab Samples

Sampler data from 15 samplers at 5 locations, adjusted for non-equilibrium conditions

Researcher →	J. Rice	J. Rice	C. Peters	US EPA
Location/Description →	Fville (8/13)	Fville (7/12)	Aq. Solubility	MCL
Method →	PE Sampler	Grab (1L)	25 deg-C	N/A
Units →	ng/L or ppt	ng/L	ng/L	ng/L
Fluoranthene	18	731	260000	
Pyrene	75	1268	130000	
Benz[a]anthracene	4.9	150	11000	100
Chrysene	31	977	2000	200
Benzo[b]fluoranthene	15	740	1500	200
Benzo[k]fluoranthene	5.3	305	800	200
Benzo[a]pyrene	5.9	540	4000	200
Indeno[1,2,3-cd]pyrene	1.63	810	62000	400
Dibenz[a,h]anthracene	0.60	918	500	300
Benzo[g,h,i]perylene	1.4	1174	300	

Passive sampling detected **significantly lower** total PAH concentrations, suggesting that only 2% of these PAHs in water column (grab samples) are freely dissolved.

Take-Home Messages and Future Work

- Passive samplers are a promising option for measuring freely dissolved organic contaminants in heavily contaminated, shallow, fresh water.
- In environmental risk assessment, grab sampling is more commonly used but may overestimate the freely dissolved concentration in settings where natural organic carbon, particulates, and colloids exist.
- There are benefits to using both passive sampling and grab sampling techniques, but neither seems to be a silver bullet for holistic assessment of particularly egregious oil spill sites. Regulators should know this.
- Barriers to regulatory acceptance of passive sampling:
 - Limited understanding of advantages and limitations
 - Confusion about passive sampler selection and standardization
- Further studies needed to link toxicity, bioaccumulation, and passive sampler contaminant concentrations.



Thank You



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