Groundwater/Surface Water Interactions at the Transition Zone: Utilizing an *In-Situ* Passive Sampling Program to Evaluate Groundwater Upwelling

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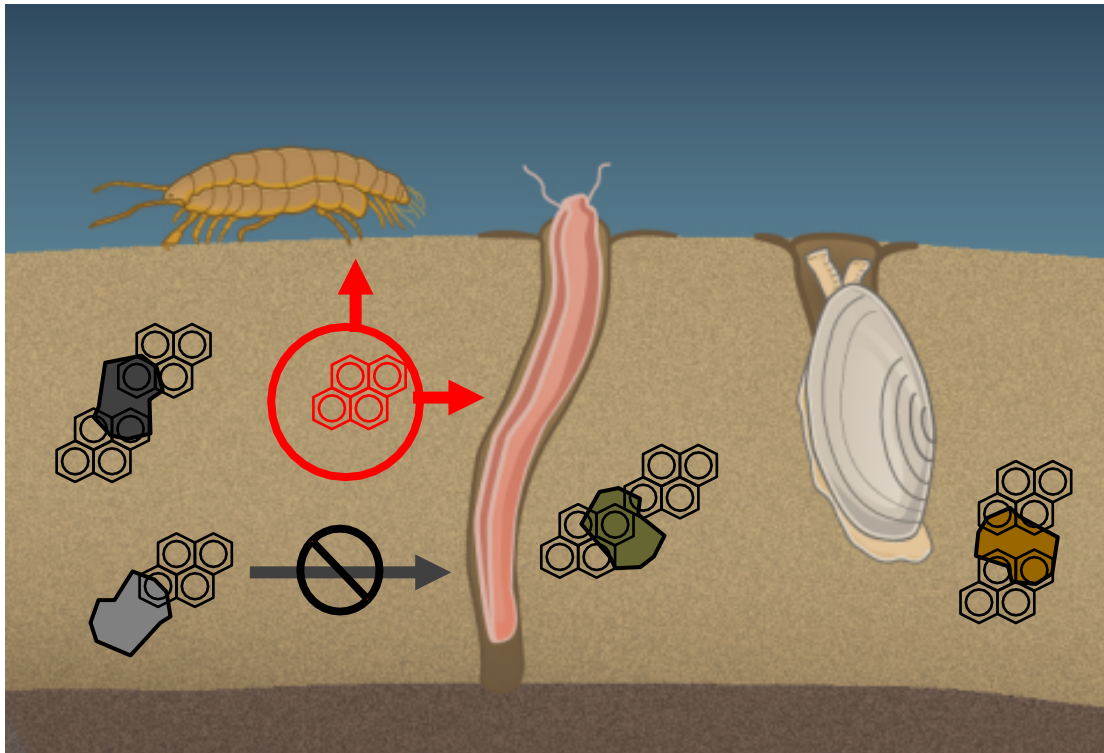Jason Conder & David Toler (Geosyntec Consultants Inc.)

Lance Fontenot (Integral Consulting Inc.)

Steven Aufdenkampe (Norfolk Southern Corporation)

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C_{free}: Core Concepts

- Only a small fraction of chemicals in sediment (or water, or soil) are **freely-dissolved** and available to organisms
  - Most **bound** to sediment solids (organic matter, clay, etc.)

freely-dissolved

bound

- Passive sampling allows us to measure the concentration of **freely-dissolved chemicals (C_{free})**

# SP3™: Passive Sampler for Hydrophobic Organics

- Polyethylene-based passive samplers for PCBs, PAHs, Dioxins and Furans, total petroleum hydrocarbons (TPH) and organochlorine pesticides (OCPs)

- Equilibrium-based partitioning sampler

- End to End service for supply of samplers, assist with deployment/retrieval (optional), analytical chemistry and C_{free} calculation
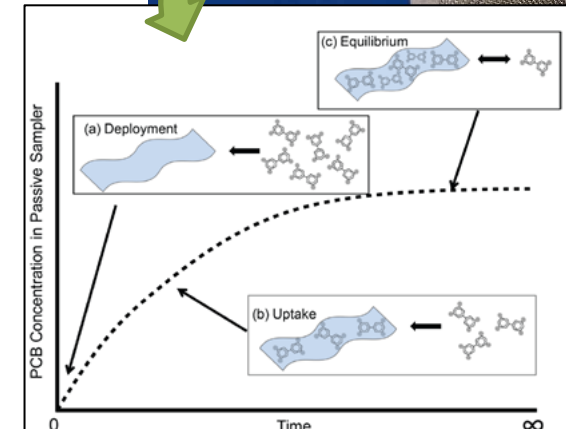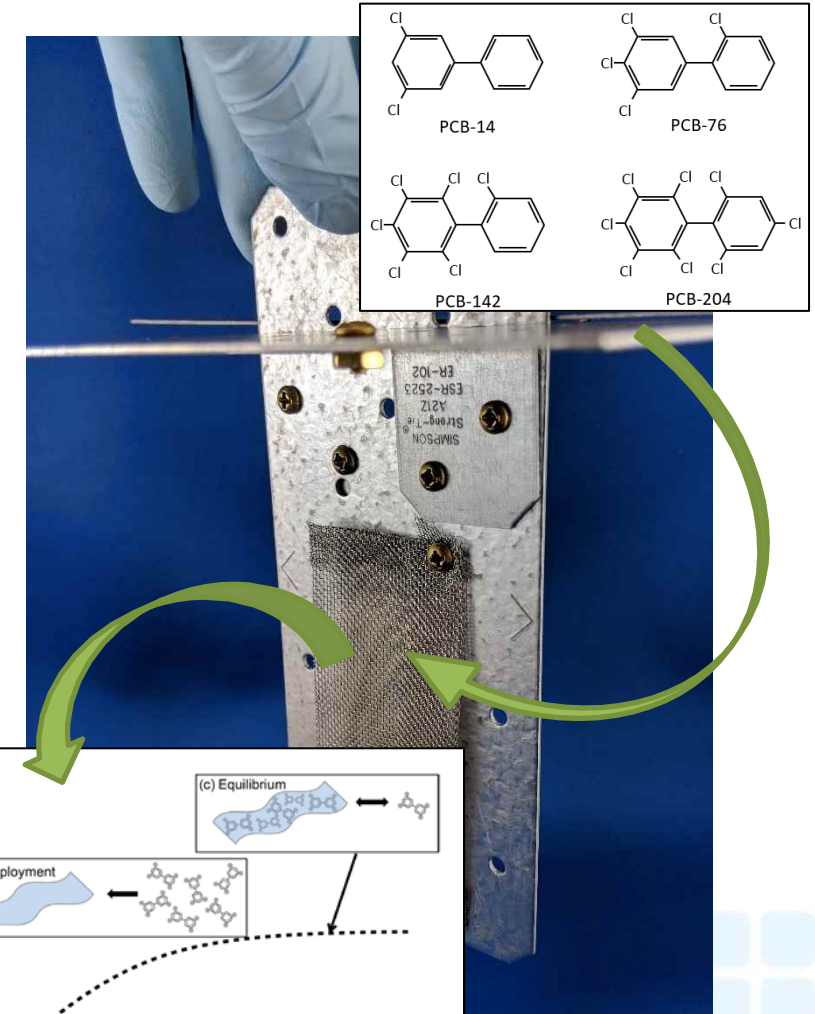
PRC Selection

- The most important factor when selecting PRCs is that the PRCs have similar hydrophobicities to the compounds of interest

- The K_{PE} values for the PRCs must have a range that extends past the range of the target compound's K_{PE} value

- They do not have to be of the exact same compound class

K_{PE} of PCB PRCs and MW

Range of K_{PE} values for Compounds of Interest

$\log K_{PE}$

MW
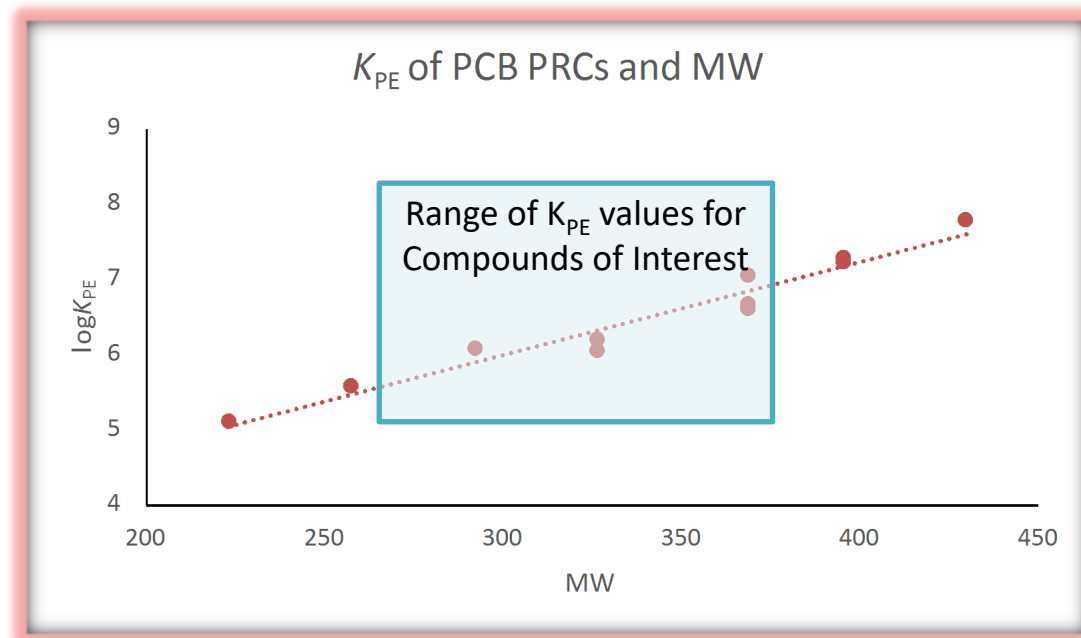
Analysis and Data Processing

- Concentration in polyethylene converted to liquid concentration (e.g., pg/L)

  → "available concentration"

  → "porewater concentration"

  → "freely-dissolved concentration (C_{free})"

  - **Food-web/risk models**
  - **Predict/understand bioaccumulation**
  - **Risk-based threshold concentrations**
  - **Fate/remediation models**
  - **Etc.**

$$C_{free} = \frac{C_{sampler}}{\left(1 - e^{-k_e t}\right) \times K_{sampler}}$$

$$k_e = \ln\left(\frac{C_{PRCi}}{C_{PRCf}}\right) \times \frac{1}{t}$$

$$COC_D = \frac{COC_{PS}}{K_{PS-D}} * 1000$$

pg/L
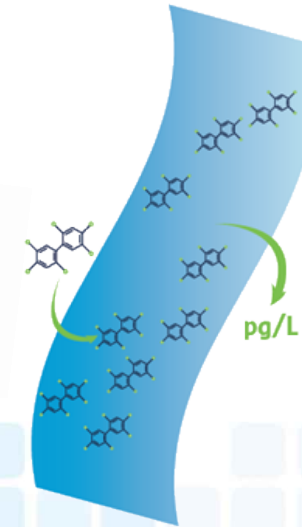
Former Wood Preserving Site, LA

- Parent and Alkylated PAHs detected in groundwater adjacent to and sediment in Pump Slough

- Horizontal and Vertical groundwater gradients suggested that the sands beneath the Pump Slough are in hydrogeologic communication with the Pump Slough

  - Groundwater primarily discharges to pump slough with brief period of recharge over the period of record

- Does contaminated GW discharge into sediment & surface water?

- Is the discharge significant or above acceptable levels?

Overall Goal – Ensure that there are **NO** surface water or sediment impacts on human health or ecosystem
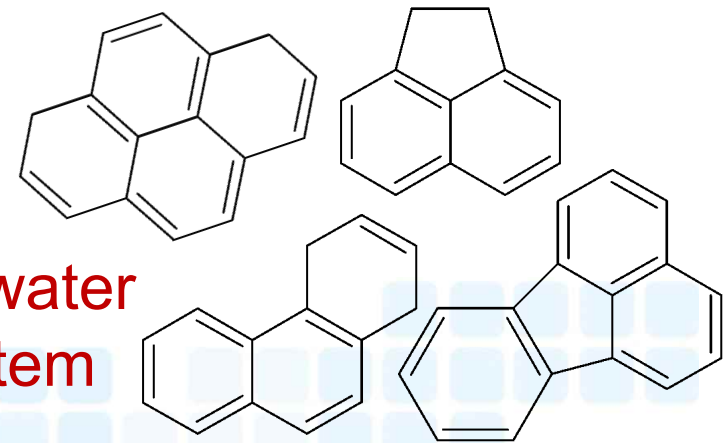
Approach

- Determine C_{free} of parent & alkylated PAHs
  - 24 SP3™ samplers (19 sediment, 2 surface water, 3 trip blanks)
  - Deployed 30 days
  - Analyzed by modified EPA 8270 method (ID-0016; PAHs by GC/MS Isotope Dilution)
- Use C_{free} values and USEPA final chronic values (FCVs) derived from the equilibrium partitioning (EqP) approach to determine toxic unit (TU)
- Use C_{free} values and multivariate statistics to cluster results and provide another line of evidence to EqP and TU approach
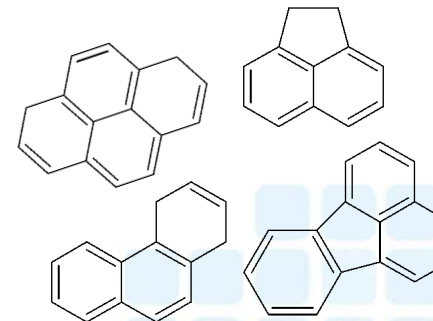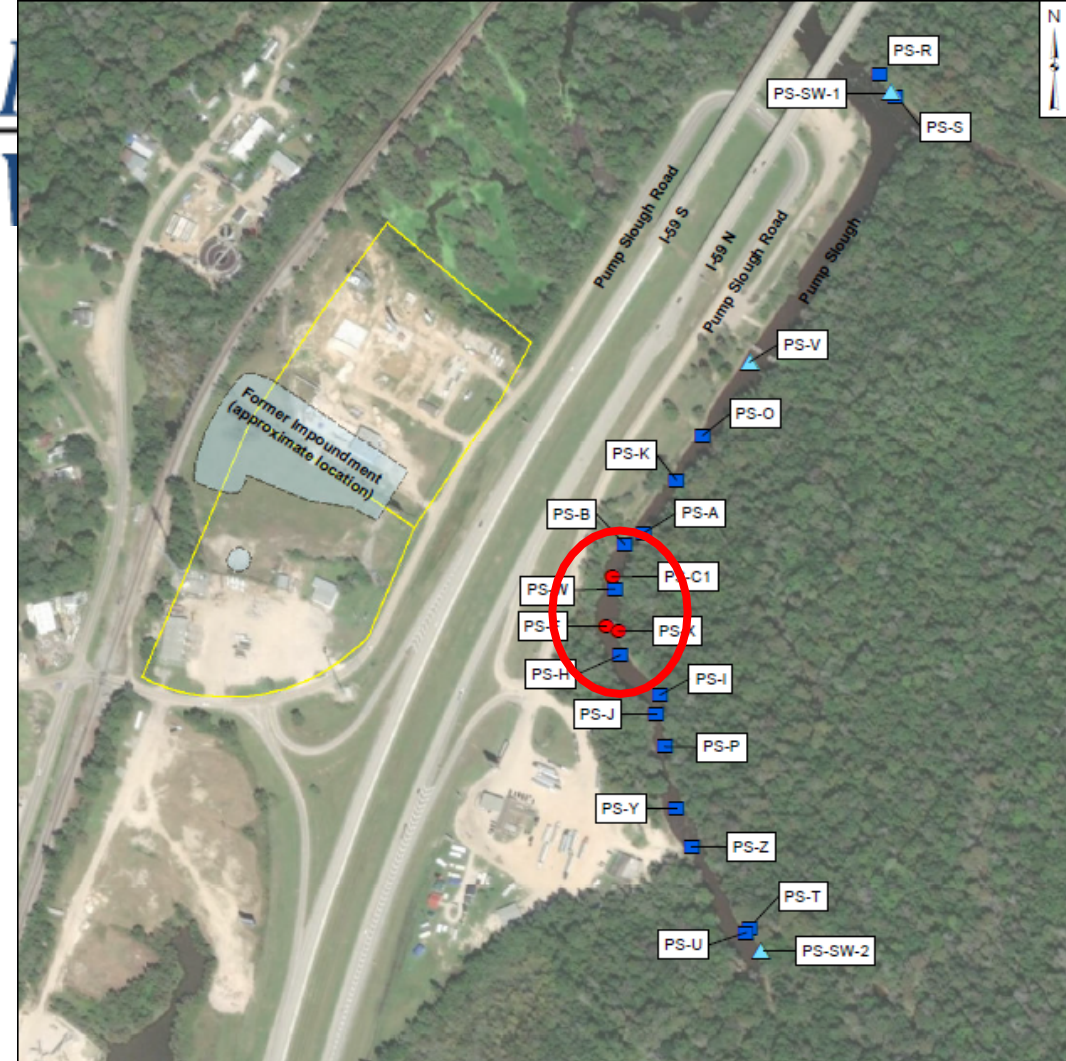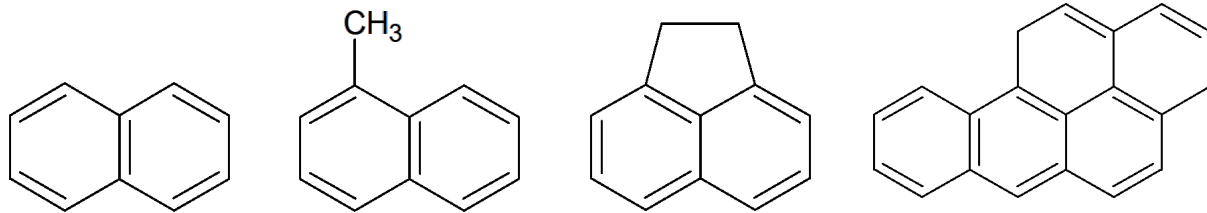
PAH Mixtures and Toxic Units

$$TU = \frac{[PAH_1]}{FCV_1} + \frac{[PAH_2]}{FCV_2} + ... + \frac{[PA}{FCV}$$

C_{free} data available from SP3^{TM}, TU data more representative estimate of potential toxicity than one-carbon EqP

PS-C1, PS-F, PS-X TU ranged from 1.84 – 3.88. (TU > 1 possible risk to benthos)

Analysis of Results – Multivariate Statistics

Hierarchical cluster analysis (HCA) that can identify common groups of samples (clusters) within a large data set based on PAH concentration compositions

1. Begin assuming each sample is own cluster

2. Identify the closest two clusters (based on similarity across PAH concentrations) and combine them into one cluster

3. Repeat the above step until all the data points are in a single cluster

Euclidean distance across PAH concentrations used for similarity/closeness quantification
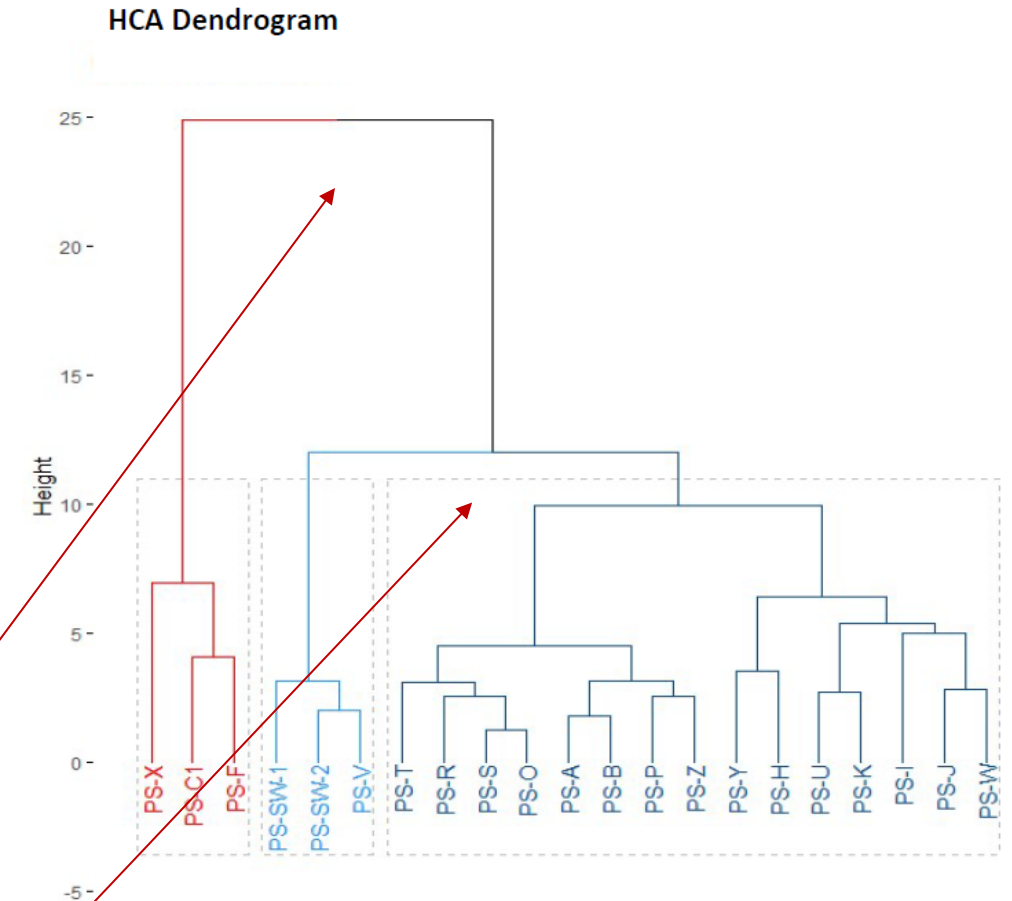
Two Distinct Clusters of passive sampler locations

Cluster 2 divided into two sub-groups

HCA Dendrogram

Analysis of Results – Multivariate Statistics

Principal Component Analysis (PCA) summarizes variation in the data set that consists of multiple correlated variables.

1. Reduces the number of variables by transforming them into smaller sets of uncorrelated variables without the loss of information

2. New variables correspond to a linear combination of the original variables called principal components (PC)

3. Samples that plot near each other in PC space have similar variable distributions, farther away have less similar distributions
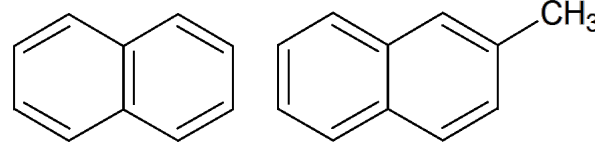

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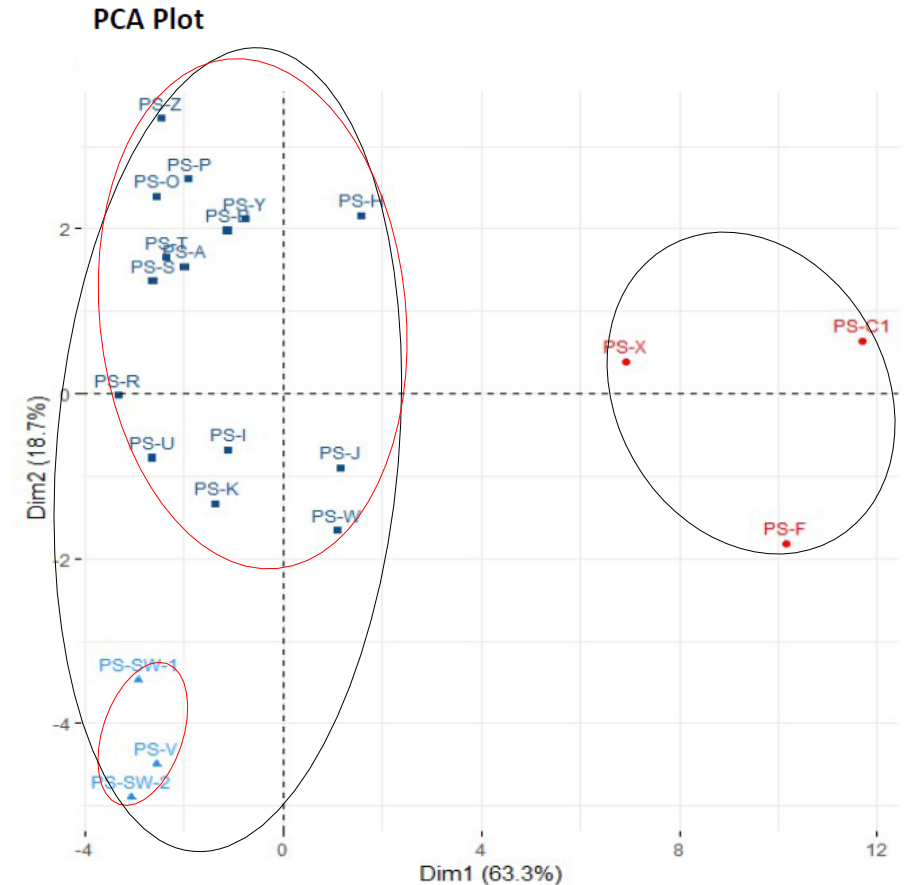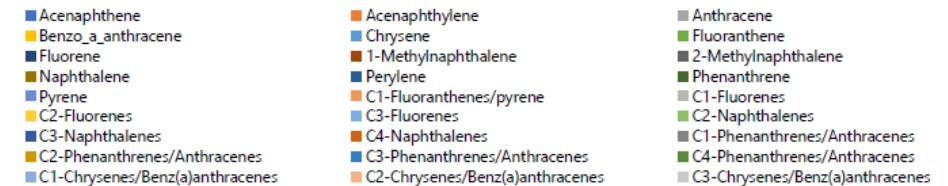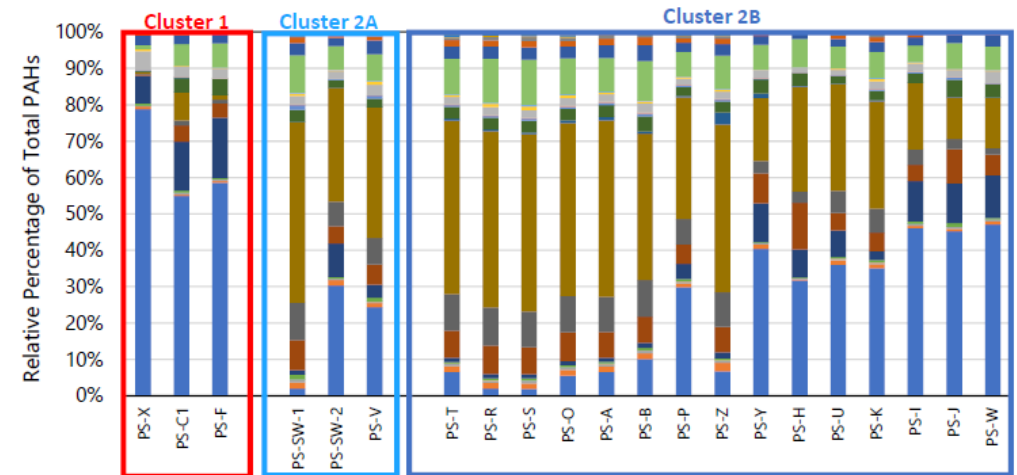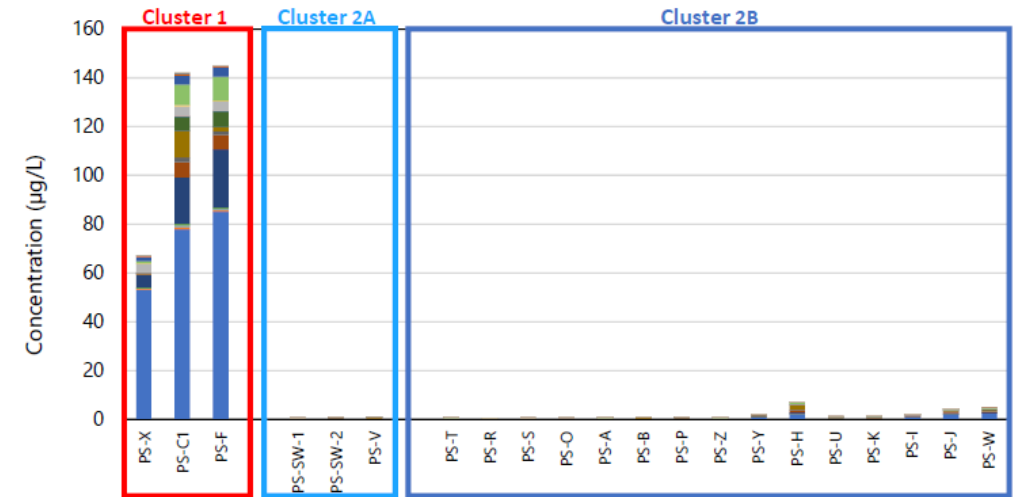
PAH Concentrations & Composition

Cluster 1 – Highest concentrations and major contributor: acenaphthene
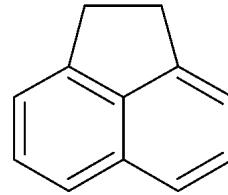
Cluster 2 – Total concentration are 1 to 2 orders of magnitude lower than cluster 1 and major contributors: naphthalene and 2-methylnaphthalene

Clustering consistent with TU > 1 (Cluster 1 samples), and are clearly distinguishable from remainder of samples

Recommendations

- Groundwater discharges into Pump Slough indicate that the discharge is contained along southern bend

- All other areas have very low C_{free}

  - Consistent with previous bulk chemistry sediment data in terms of totals

 - SP3^{TM} able to distinguish from background where bulk chemistry could not
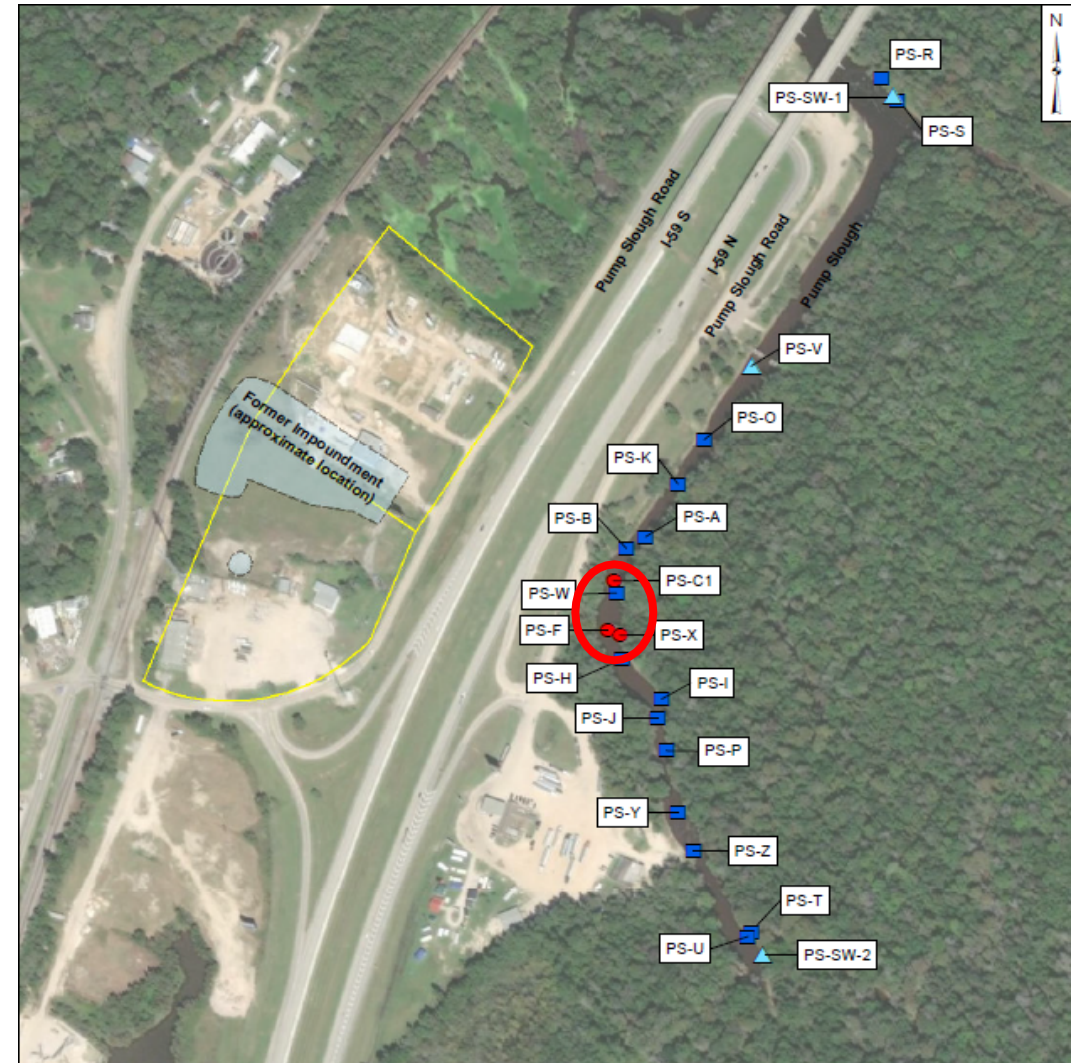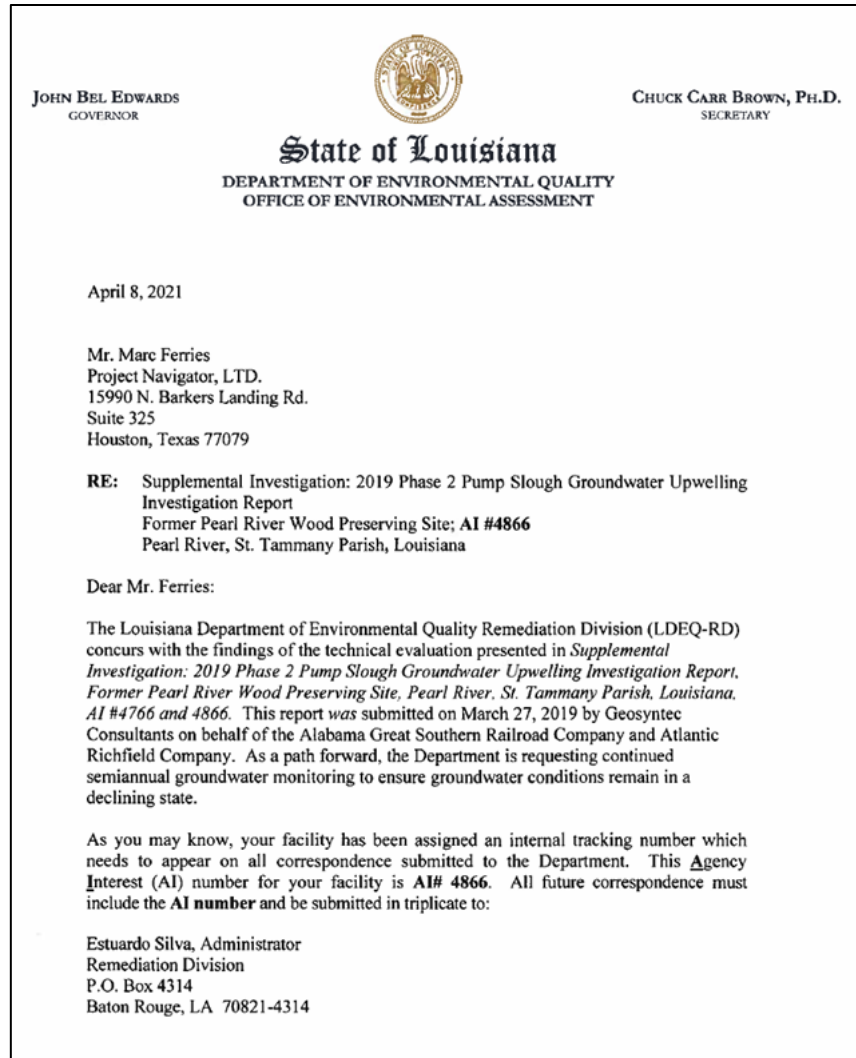
Summary

- SP3™ identified locations and concentrations of COC flux with multiple lines of evidence

- Previous work over-estimated the need for corrective action at this site
  - SP3™ able to reduce potential remediation costs and planning

If corrective action required, would be confined to a small area
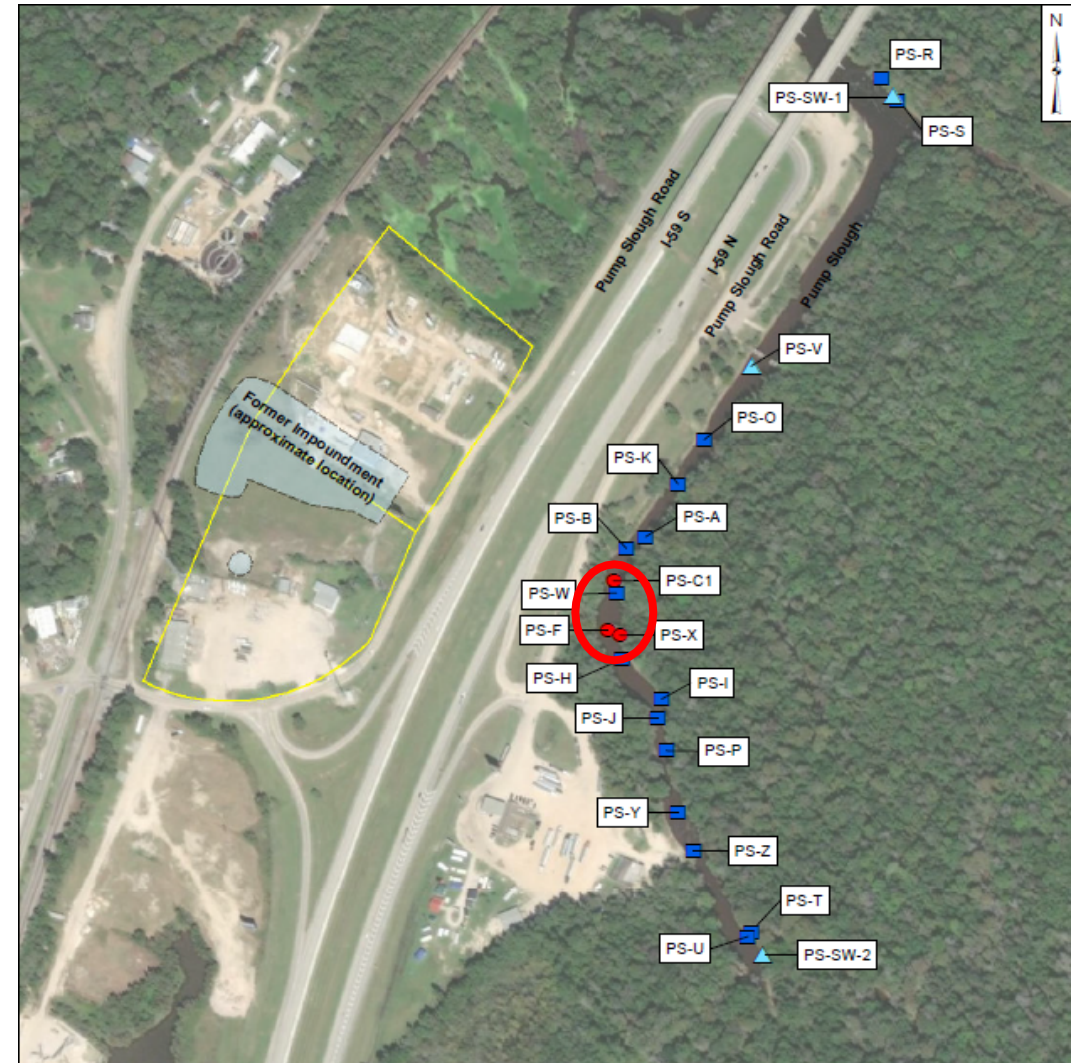
No Further Action!

Apr.8, 2021 State of Louisiana determined NO FURTHER ACTION is required at the site based on SP3™ results.

- $2M - $5M in cost savings to client

Questions?
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Why Porewater by Passive Sampling?

- Traditional approaches overestimate toxicity, mobility, fate, risk, etc.

- Passive sampling quantifies availability as the freely-dissolved concentration (C_{free}), and C_{free} relates well to bioavailability
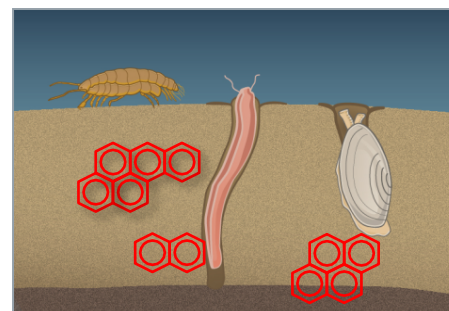
Passive Sediment Porewater Sampling Service

- Porewater sampler for dissolved organic and inorganic compounds

- Easy to use off the shelf sampler ready for deployment
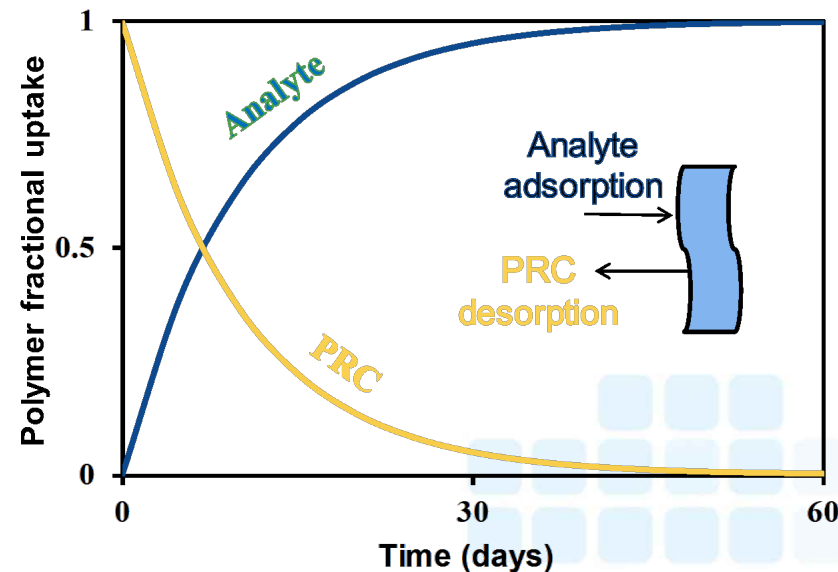
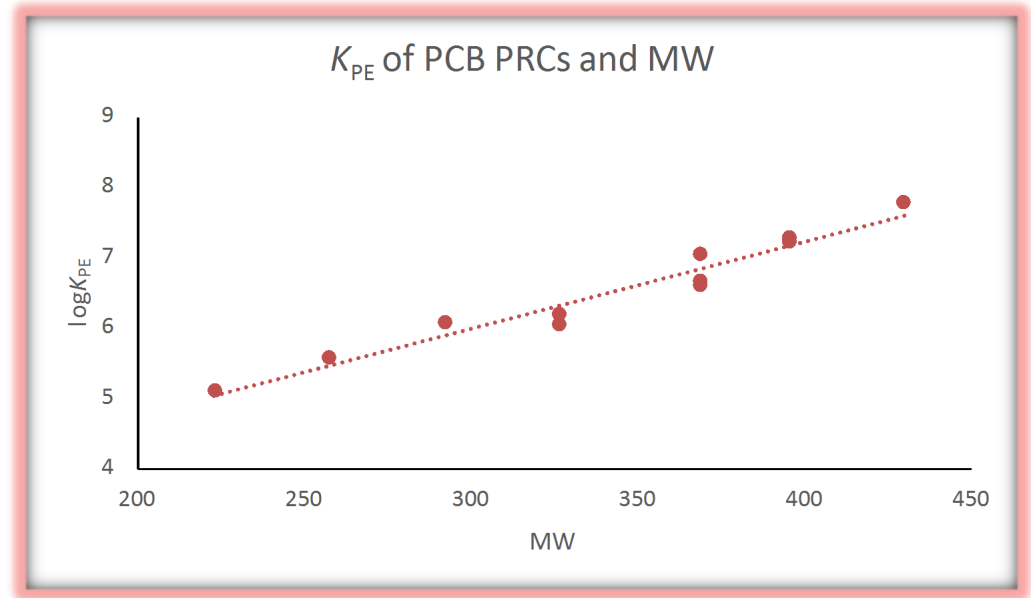- Includes Performance Reference Compounds

Performance Reference Compounds (PRCs)

- Standard PRCs for SP3™ are 10 rare PCB congeners

  – Specific congeners can be removed if they are incompatible with the analytical lab or present at the site

  – Used to correct for non-equilibrium

- Data analysis models are based on K_{PE} values

K_{PE} of PCB PRCs and MW

Quality Assurance/Quality Control

- Always include unexposed samplers (ideally 3) that travels to the site and then to the analytical laboratory

  - Provides initial concentrations of the PRCs / Br tracer

  - Identifies contaminants that may absorb into the sampler during shipment/handling

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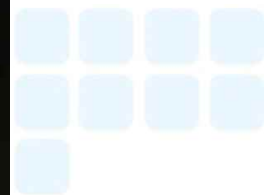
Field Preparations

Field SOP provided for preparing the samplers before they are deployed