

Pilot Study of Polycyclic Aromatic Hydrocarbons in Delaware Estuary Using Passive Diffusion Sampling Technology

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Introduction

- **Delaware Estuary highly industrialized**
- **Numerous petrochemical plants**
- **Legacy oil spills and runoff left PAH residues in the system**
- **Ecological risk to aquatic life & human consumption of fish**
- **PAH residues complicate Natural Resource Damage Assessments**

2010 Deepwater Horizon Spill

- **A 2011 National Aquarium Symposium on the Gulf oil spill submitted a recommendation to a US Senate subcommittee identifying the need for better baseline data and alternative approaches to obtain pre-spill conditions in aquatic ecosystems.**
- **Most of the grab samples analyzed for the BP oil spill revealed that concentrations of PAHs were below the analytical detection limits**
- **However, PAH values below detection limits and below predetermined benchmark values doesn't mean that PAHs are absent or present at levels which are not harmful.**

Background (cont.)

- **The symposium identified that passive sampling technology was a promising approach to determine extremely low concentrations of organic petroleum when conventional methods of sampling are not effective**
- **The symposium concluded that passive samplers, placed in the sediments and water column, could provide a representative picture of levels of pollutants over a period of time from days to months**

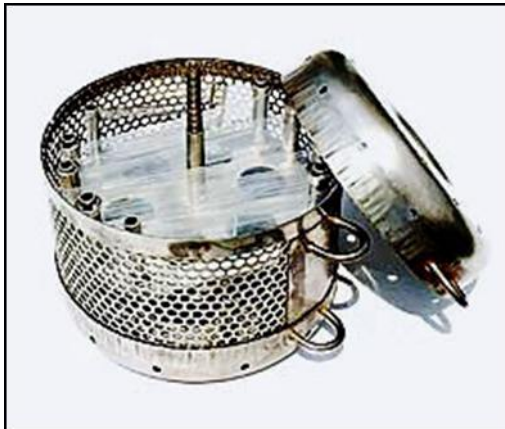
The Project

On behalf of DNREC's, Site Investigation and Restoration Section, Versar conducted a pilot study on the effectiveness of passive samplers (Semi-permeable Membrane Devices) to measure freely dissolved PAHs in the sediments and water column of the Delaware Estuary.

Study Objective

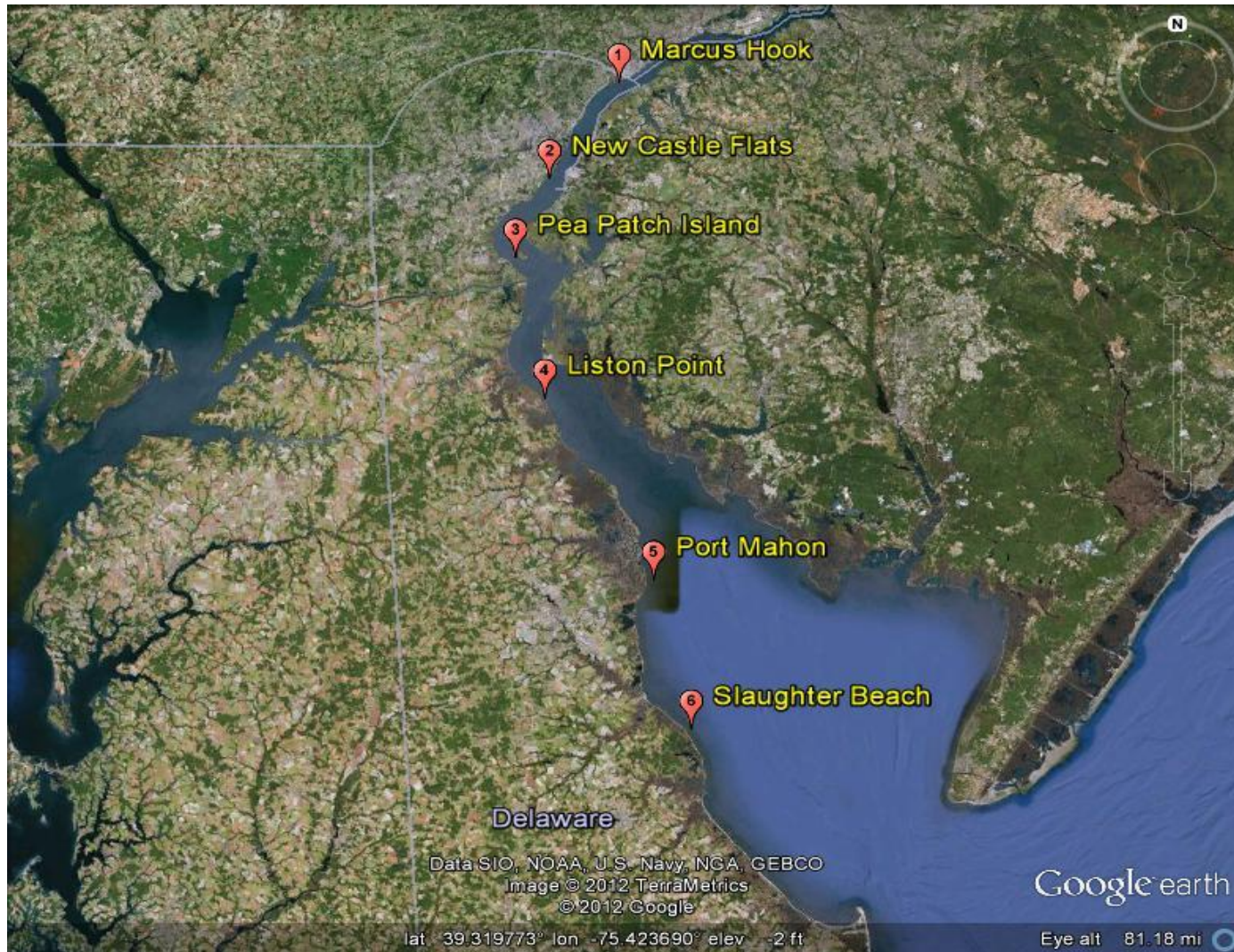
- **Study primarily intended to be used as a pilot/proof-of-concept towards establishing PAH baseline levels for Delaware Estuary for oil spill NRDA's**
- **Test the effectiveness of Semi-permeable Membrane Devices (SPMD) and potentially expand the program to characterize PAH baseline for the entire estuary**

SPMD



- **Commercially produced by EST, St. Louis, Missouri**
- **Flat tubing filled with lipid gel**
- **10 Angstrom transport corridors**
- **Absorbs PAHs much like fatty tissues but no metabolism**
- **After a deployment period PAHs extracted by EST and ampules sent to analytical lab**
- **Never used in the Delaware Estuary**

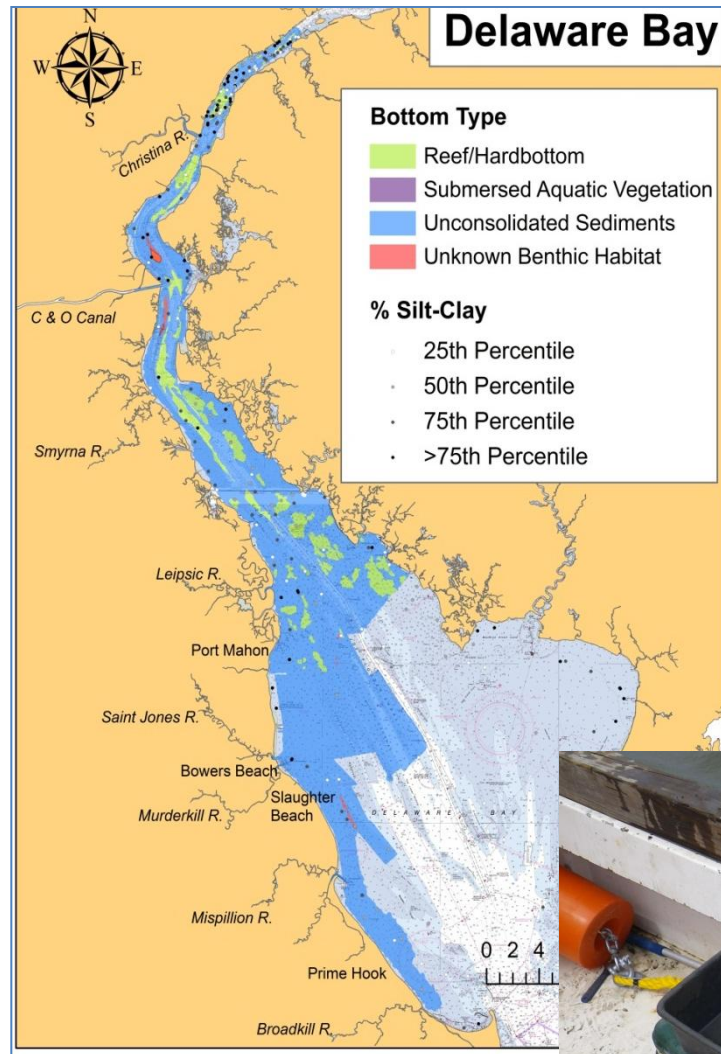
Selected a range of stations from high to low contaminant levels



Selected stations with high silt/clay content using Delaware Bay Benthic Mapping Data

>75% silt/clay sites targeted

Benthic grabs to confirm sed type upon deployment



Bottom and 1-meter above bottom SPMD canisters deployed for 1 month in August 2012



Bulk sediment sampling also conducted half way through the deployment



Parent and Alkylated PAH Analysis conducted on SPMD and Bulk Sediment

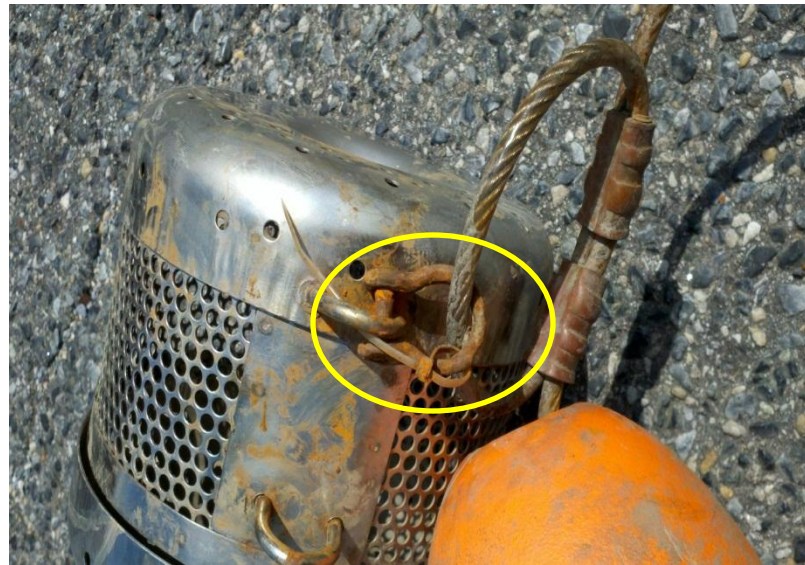
1,1'-Biphenyl	C1-Dibenzothiophenes	C3-Phenanthrenes/Anthracenes
1-Methylnaphthalene	C1-Fluoranthenes/pyrene	C4-Chrysenes
1-Methylphenanthrene	C1-Fluorenes	C4-Dibenzothiophenes
2,3,5-Trimethylnaphthalene	C1-Naphthalenes	C4-Naphthalenes
2,6-Dimethylnaphthalene	C1-Phenanthrenes/Anthracenes	C4-Phenanthrenes/Anthracenes
2-Methylnaphthalene	C2-Chrysenes	Chrysene
Acenaphthene	C2-Dibenzothiophenes	Dibenz(a,h)anthracene
Acenaphthylene	C2-Fluoranthenes/Pyrene	Dibenzothiophene
Anthracene	C2-Fluorenes	Fluoranthene
Benzo[a]anthracene	C2-Naphthalenes	Fluorene
Benzo[a]pyrene	C2-Phenanthrenes/Anthracenes	Indeno[1,2,3-cd]pyrene
Benzo[b]fluoranthene	C3-Chrysenes	Naphthalene
Benzo[e]pyrene	C3-Dibenzothiophenes	Perylene
Benzo[g,h,i]perylene	C3-Fluoranthenes/Pyrene	Phenanthrene
Benzo[k]fluoranthene	C3-Fluorenes	Pyrene
C1-Chrysenes	C3-Naphthalenes	Total compounds 47

Data Analysis

- **Dissolved PAH concentrations calculated from SPMD results using USGS estimator spreadsheet**
 - *Accounts for deployment days, loss using PRCs, and uses equilibrium coefficients*
- **Dissolved PAH concentrations in sediment pore water also calculated using bulk sediment results & Equilibrium Partitioning (EqP) accounting for TOC and black carbon absorption**
- **SPMD & Sediment EqP results for total dissolved PAH compared**
 - *½ DL used for non-detected compounds*
- **Fingerprints also compared**

Old Man Delaware....will get you every time

**5 of the 6 water column samplers lost due
to galvanic corrosion**



**Marcus Hook water column canister recovered
and all six sediment samplers recovered**

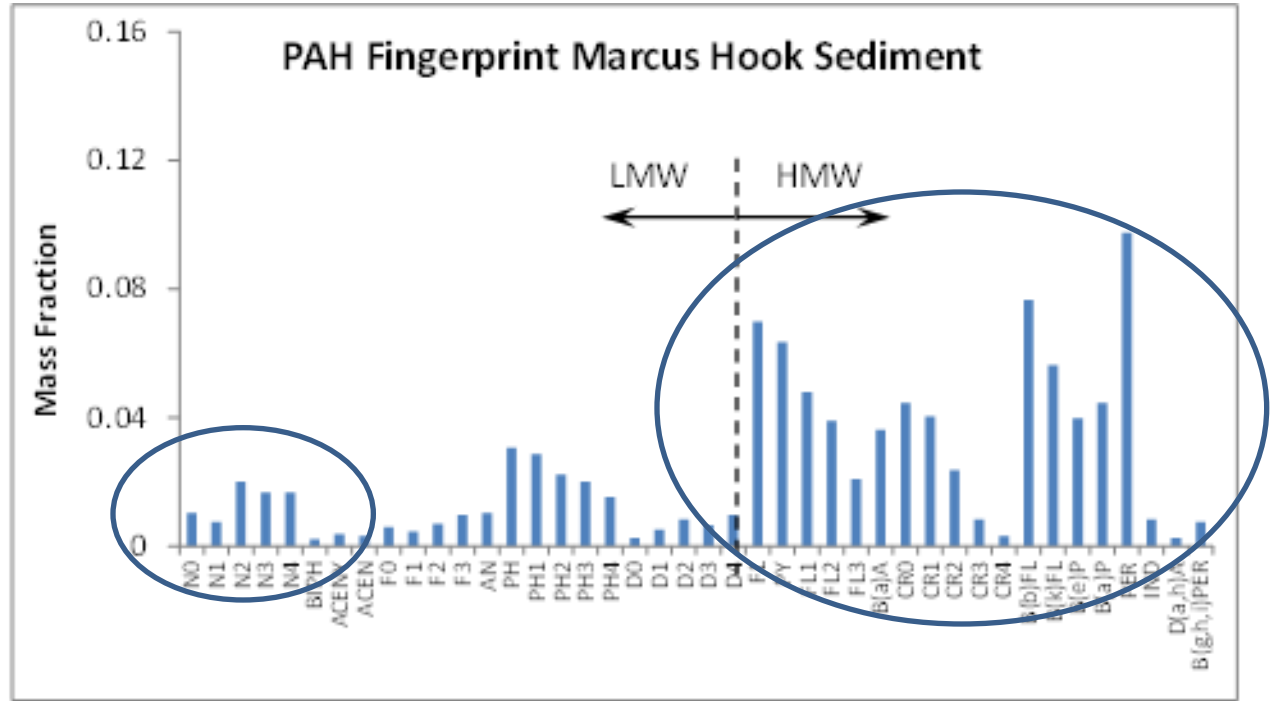
Results

Total PAH concentrations found sediment SPMDs and bulk sediment analysis

	Unit	Marcus Hook		New Castle Flats		Pea Patch Island		Liston Point		Port Mahon		Slaughter Beach	
		Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
Total	ng/mL	5738	5288	3405	2955	3544	3633	2626	2698	2802	2824	1680	1690
Ave	ng/mL	5,513		3,180		3,589		2,662		2,813		1,685	
# of SPMD non-detects		3	4	5	6	6	5	7	7	12	9	18	17
Sediment PAH Total	µg/Kg	1,469		3,987		2,704		1,408		473		548	
# of sediment non-detects		0		0		0		2		6		6	

Results

Bulk sediment PAH fingerprints dominated by pyrogenic PAHs, although naphthalenes (petrogenic) also present at all stations



Fingerprints are highly correlated among the 6 stations

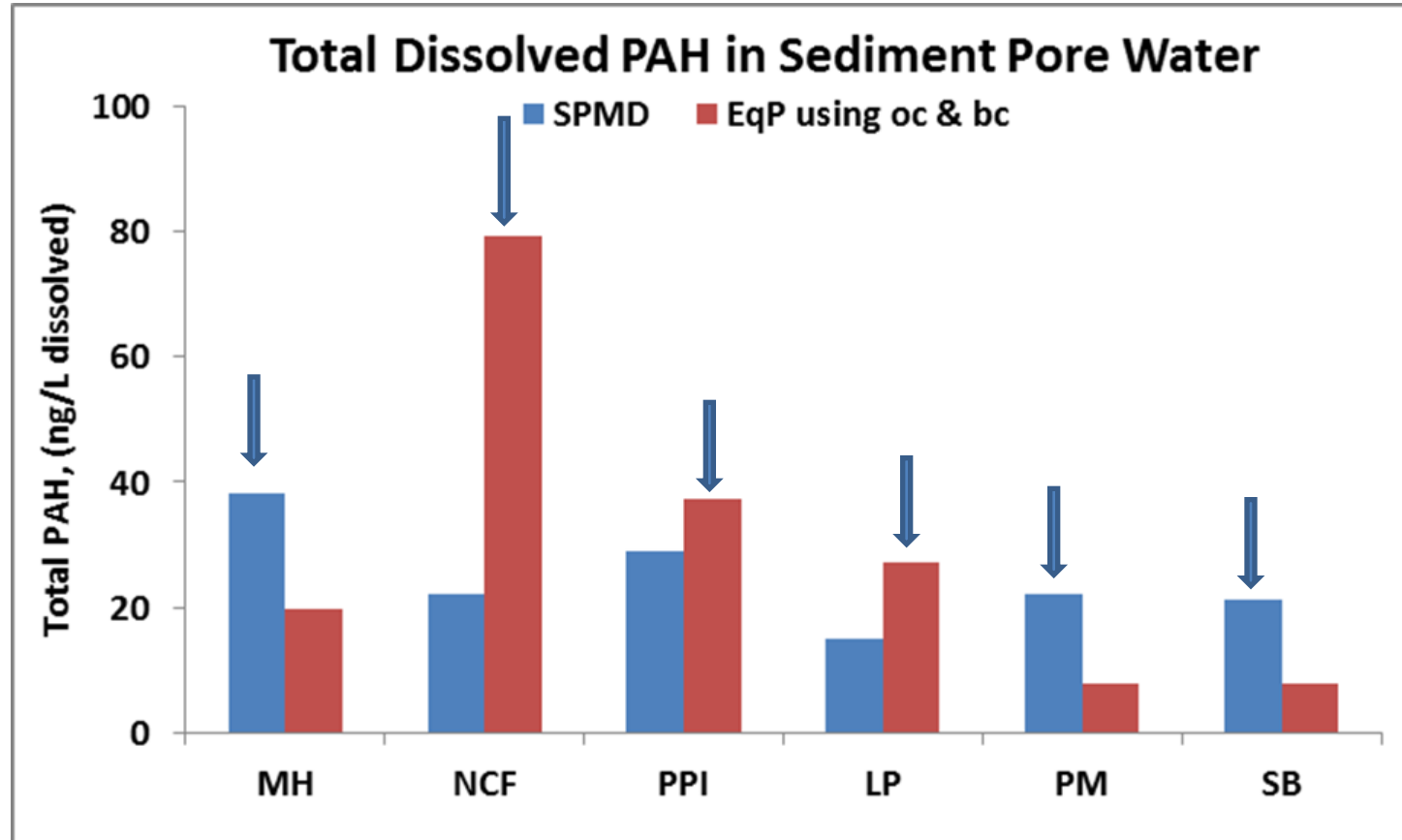
	Marcus Hook	New Castle Flats	Pea Patch Island	Liston Point	Port Mahon	Slaughter Beach
Marcus Hook	1					
New Castle Flats	0.89	1				
Pea Patch Island	0.97	0.95	1			
Liston Point	0.99	0.91	0.98	1		
Port Mahon	0.94	0.93	0.96	0.97	1	
Slaughter Beach	0.89	0.98	0.95	0.91	0.94	1

Results

Good agreement overall

Ave diff. = 2.3
(1.3 min, 3.6 max)

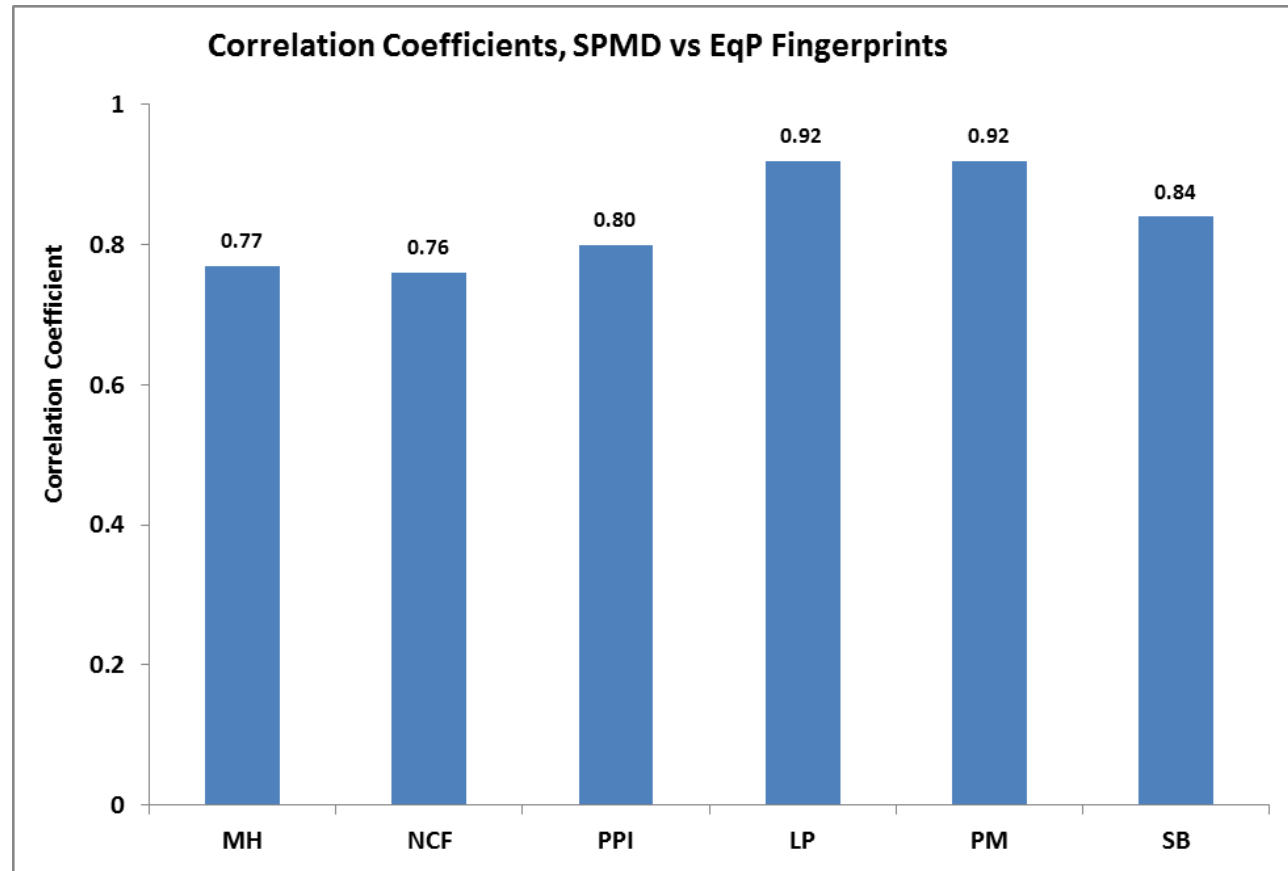
No systematic bias between the two approaches



Results

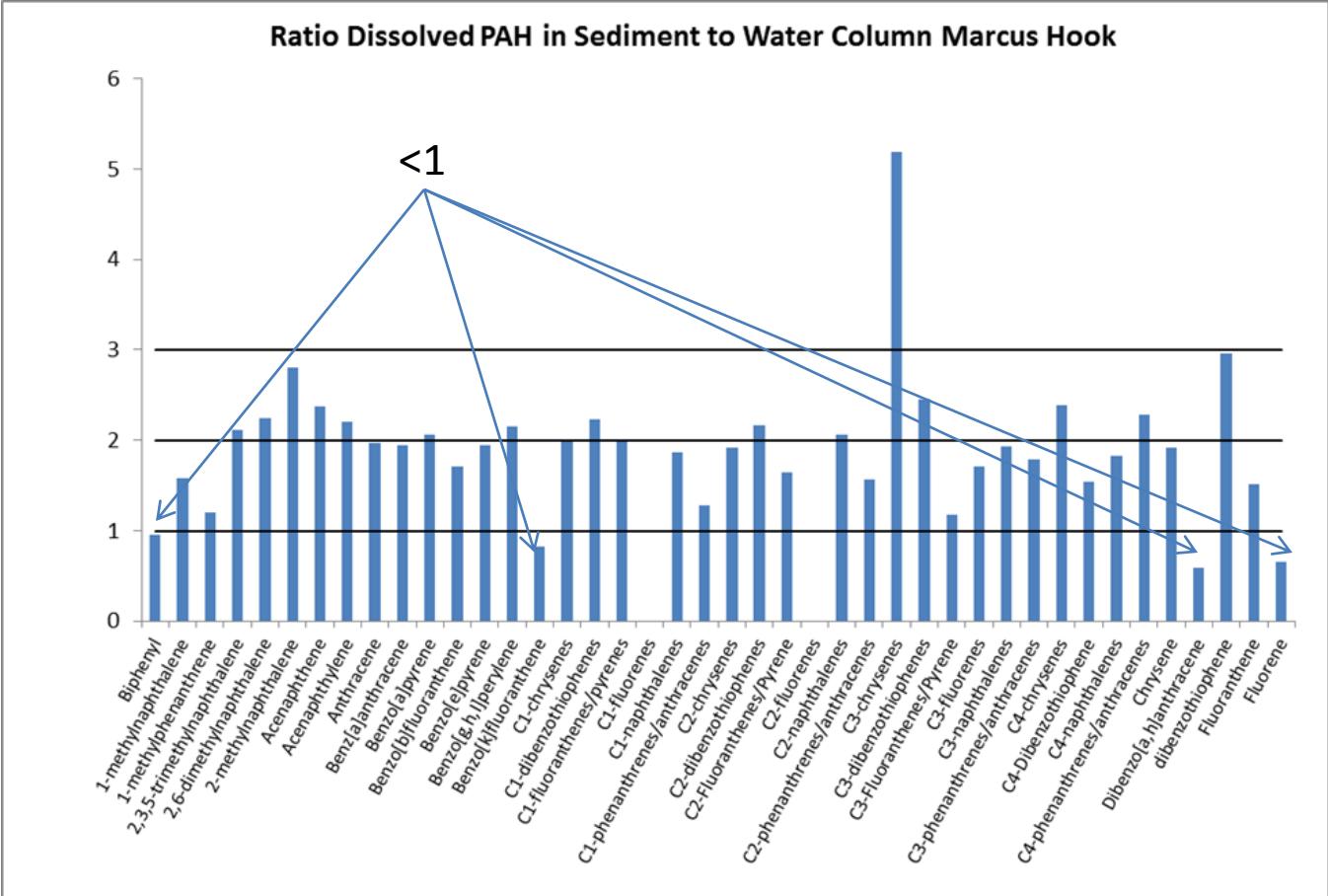
Not only are total dissolved PAH concentrations in good agreement between SPMD & EqP, the fingerprints are also well correlated

Hence, the 2 methods yield consistent results



Results

Slight flux from the sediments to the overlying water column suggested at Marcus Hook



Conclusions

- **Total dissolved pore water PAH concentration estimated from SPMDs and sediment EqP were similar**
- **Good agreement between the fingerprints calculated from the two different approaches**
- **Sediment SPMDs had higher frequency of non-detections**
- **Sediment pore water may best be estimated using bulk data**
- **Water column uses of SPMDs promising but needs further evaluation**

Follow on Work

- **Plan to repeat the study using better attachment hardware in 2013**
- **May add 1-meter above bottom and 1-meter below surface to further investigate sediment water column fluxes**
- **Include the sediment SPMDs**
- **Additional mooring sites in more sensitive habitats or different sediment types**