Assessment of bioavailable PAH compounds in water and air at near shore locations in the Gulf of Mexico pre- and post- shoreline oiling during the deepwater horizon oil spill

November 2010 Superfund Research Program Annual Meeting

Kim A. Anderson
Oregon State University

Sources of PAHs in the Environment

- Biogenic (minor)
- Petrogenic
  - Generated by geological processes
    - NATURAL- seeps, coal outcrops
    - ANTHROPOGENIC –fossil fuel release
- Pyrogenic
  - Generated by high temperature combustion of organic matter
    - NATURAL –forest fires
    - ANTHROPOGENIC- wood stoves, car exhaust, coal tar

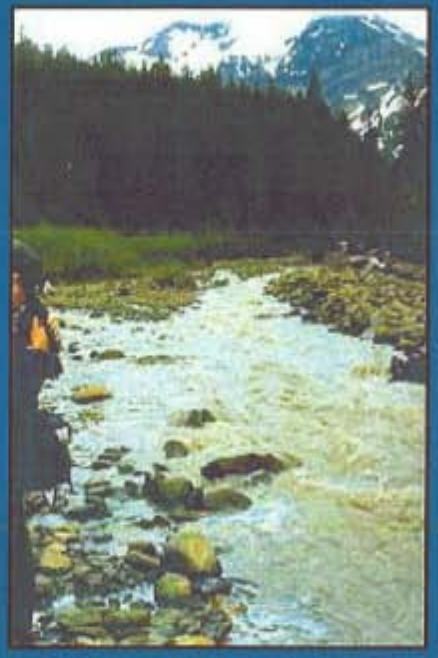
2010 June Sampling Campaign, FL, tar-ball

It Doesn't Take Much Seep Oil to Deliver a Lot of PAH

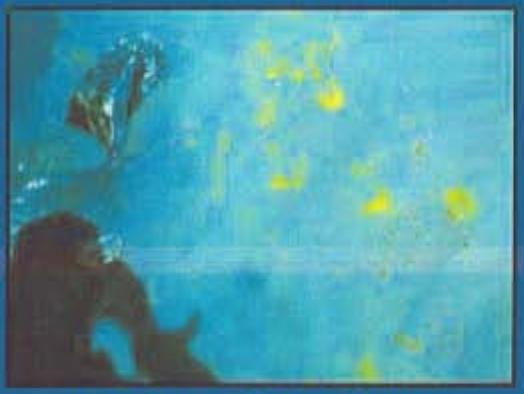
One kilogram of oil contains as much PAH as a metric ton of coal

Oil-Covered Pool at Johnston Creek Seep

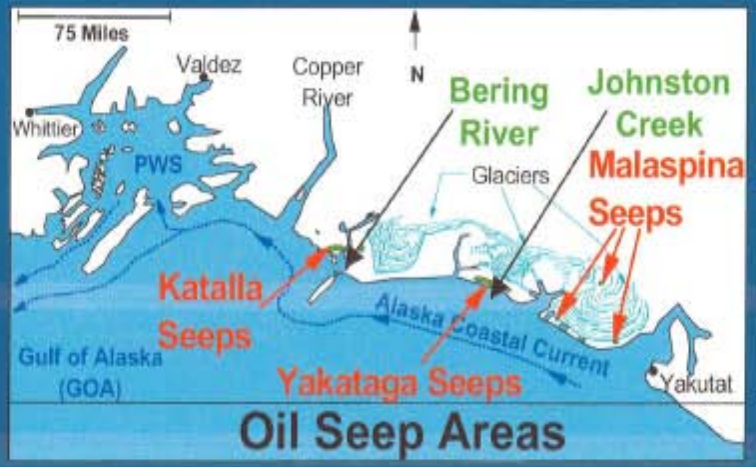
Sampling Johnston Creek Oil

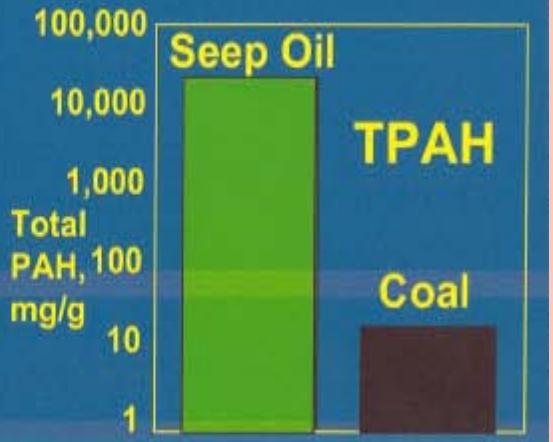


Sheens on Johnston Creek



Bering River Seep





http://www.valdezresearch.com/

The **SAME PAHs** Occur in both petrogenic and pyrogenic Sources just in DIFFERENT Proportions

- **Petrogenic** source material exhibit PAH homologue patterns where the **2- and 3- substituted alkyl groups are more abundant** than the parent (non-alkylated PAH)
- Weathering of PAH profile tends to convert a pyrogenic (skewed) profile towards a petrogenic (bell-shaped) profile

Nomenclature

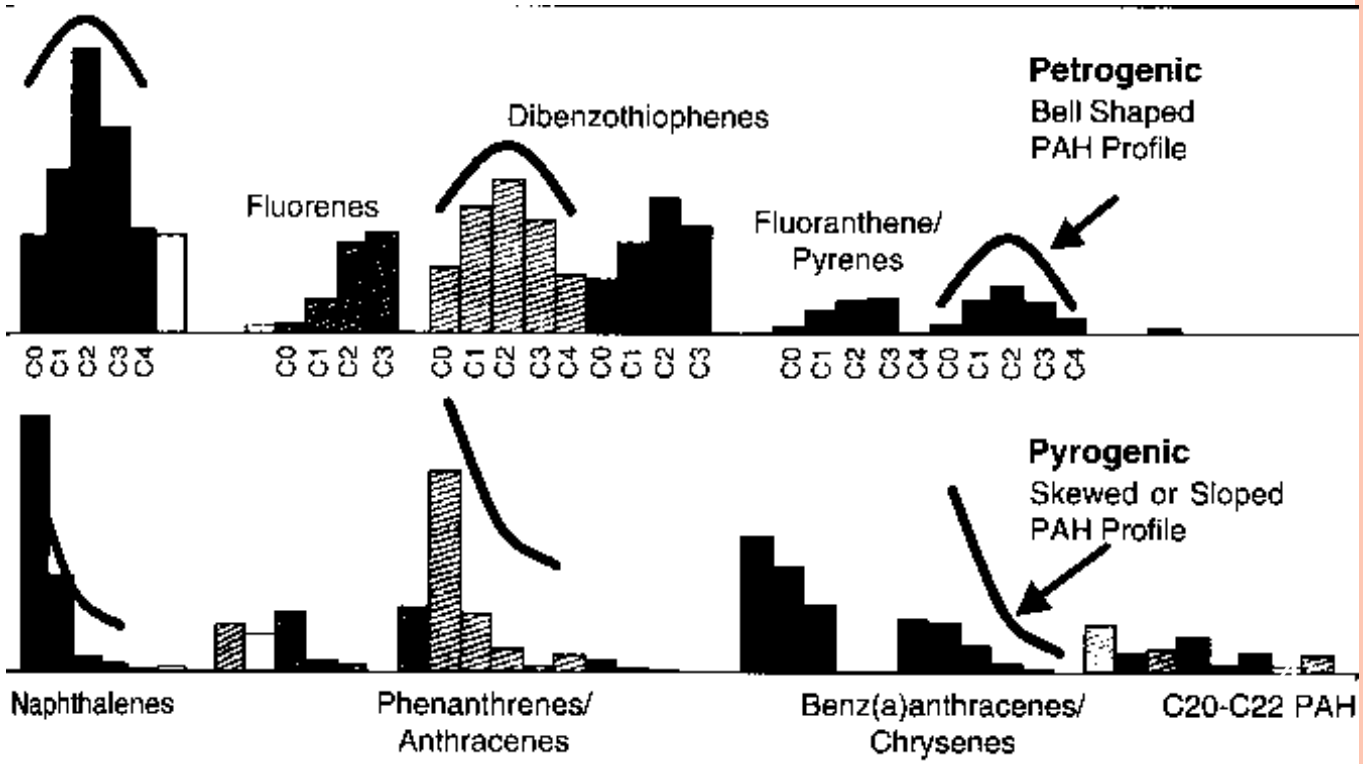
parent PAH =C0

1 methyl group subst on

PAH = C1

2 methyl groups subst on

PAH = C2



Polycyclic Aromatic Hydrocarbons (PAHs): Gulf of Mexico
Kim A. Anderson

PAH containing Spills

- **260,000 metric tons** of liquid petroleum into North American waters **annually**
- **1.3 *million* metric tons worldwide annually**
- US, 25 spills over 4000 L into waters ***per day***
- US, 75 spills onto lands, ***per day***

- ***READY Response (next disaster…)***

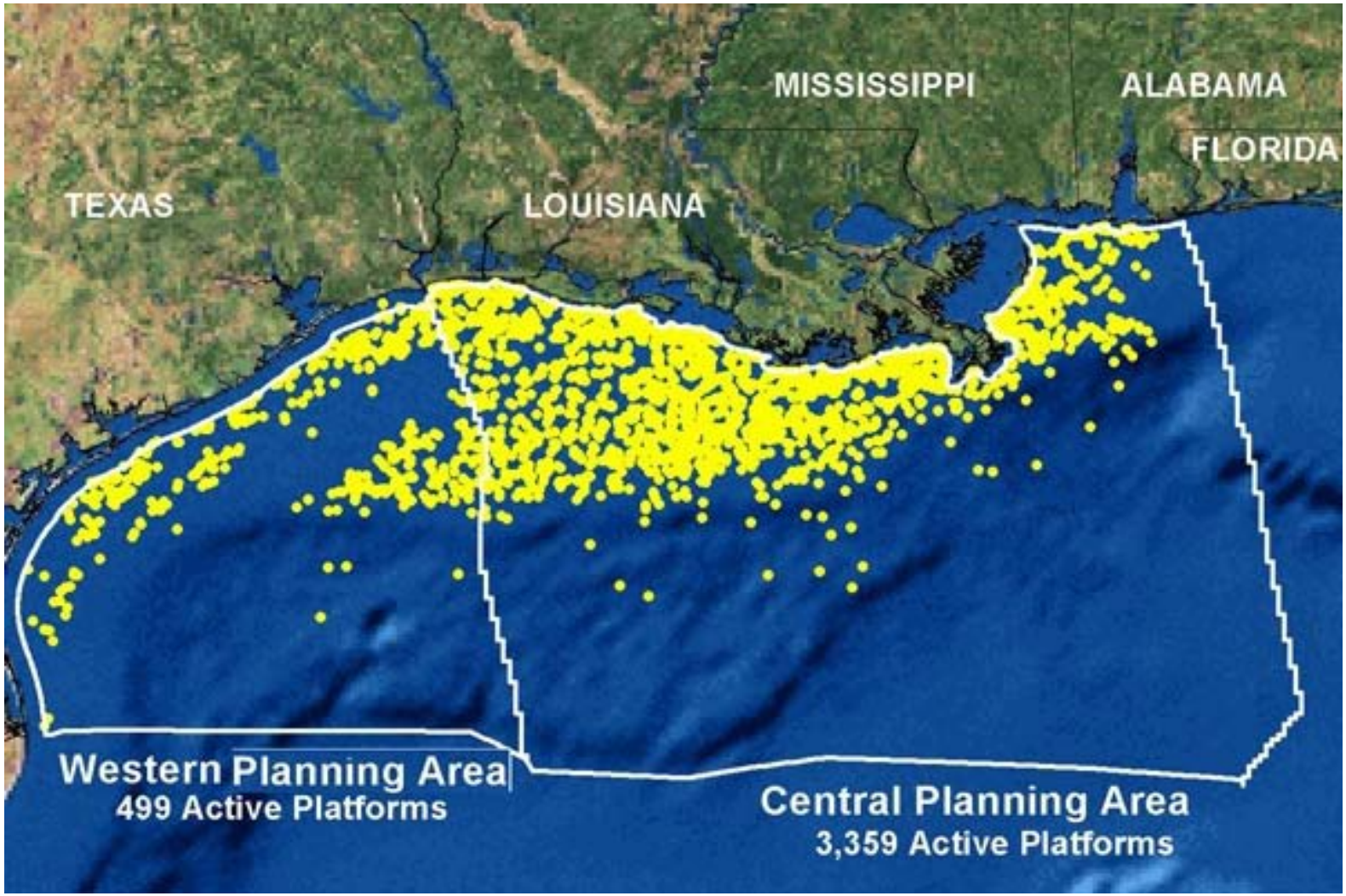
- Wang, Stout, Fingas, EF, 2006

PAH Context & Comparisons Deepwater Horizon Spill

- Horizon PAH* — 5,000– 7,000 **m Ton**
- World Trade Towers PAH — 100 - 1000 m Ton
- Total US **air** PAH — 715 – 2,700 m Ton
  - vapor & particulate
  - Average monthly sum *entire* US

- PAH in oil estimated from National Academy of Science report "Oil in the Sea III" (used 1%)
- Final (?) 2-4 million barrels of crude oil (~200,000,000 gallons)

May 1 Planning Started
Complicated Ops, multi-sources, sites, access



Goals: establish representative sites
Background: defensible, unbiased data

- Pre-spill
- Many sites oil present
- Quality Control
  - Trip blanks
  - Field blanks
  - Laboratory QC
- Quality Assurance
  - Established protocols
  - Documentation
  - Staff trained

Quality Assurance Program Plan
Defensible, Unbiased data

LFT Deployment Benchsheets

Deployment Date: 5/11/10

Project Number	Project Name
ROWH 10	Deepwater Horizon

Collecting Agency	Collector Name (print and sign)
FSES	Sarah E. Allan

Site Information

Site Name	Site Location		Water Body Type (optional)
Gulfport Public Pier	Gulfport, MS		Ocean - Gulf
Site Description (optional):	Latitude: 30.359306°N	Longitude: 89.086167°W	

Public pier in Gulfport Bay.
Near Construction site, marina and industrial center.

Sample Name (ID)	Environmental Media (Air/Water)	LFT Fortification (Spiked/Blank)	Complete deployment hardware preparations and load 5 LFT into Sampler	Deployment Start Time	Initials	Notes:
Gulfport Air Spiked	Air	Spiked	✓	11:15am	Sea	marked w/ ziptie samplers screwed to
Gulfport Air Blank	Air	Blank	✓	11:08am	Sea	boards under pier, above water level.
Gulfpor Water Spiked	Water	Spiked	✓	11:40am	Sea	marked w/ ziptie tied to pier.
Gulfport Water Blank	Water	Blank	✓	11:40am	Sea	

Environmental Conditions

Air Temp.	81° F
Water Temp.	75° F
Water Depth	~4 m
Other: Prevailing Wind S-SE	

Field QC

QC Type	Site	Description	Check
Field Blank	Grand Isle	N/A	✓
Trip Blank	N/A	1 LFT transported for field trip	✓

Chemist Review

Signature Date

Director Review

Signature Date

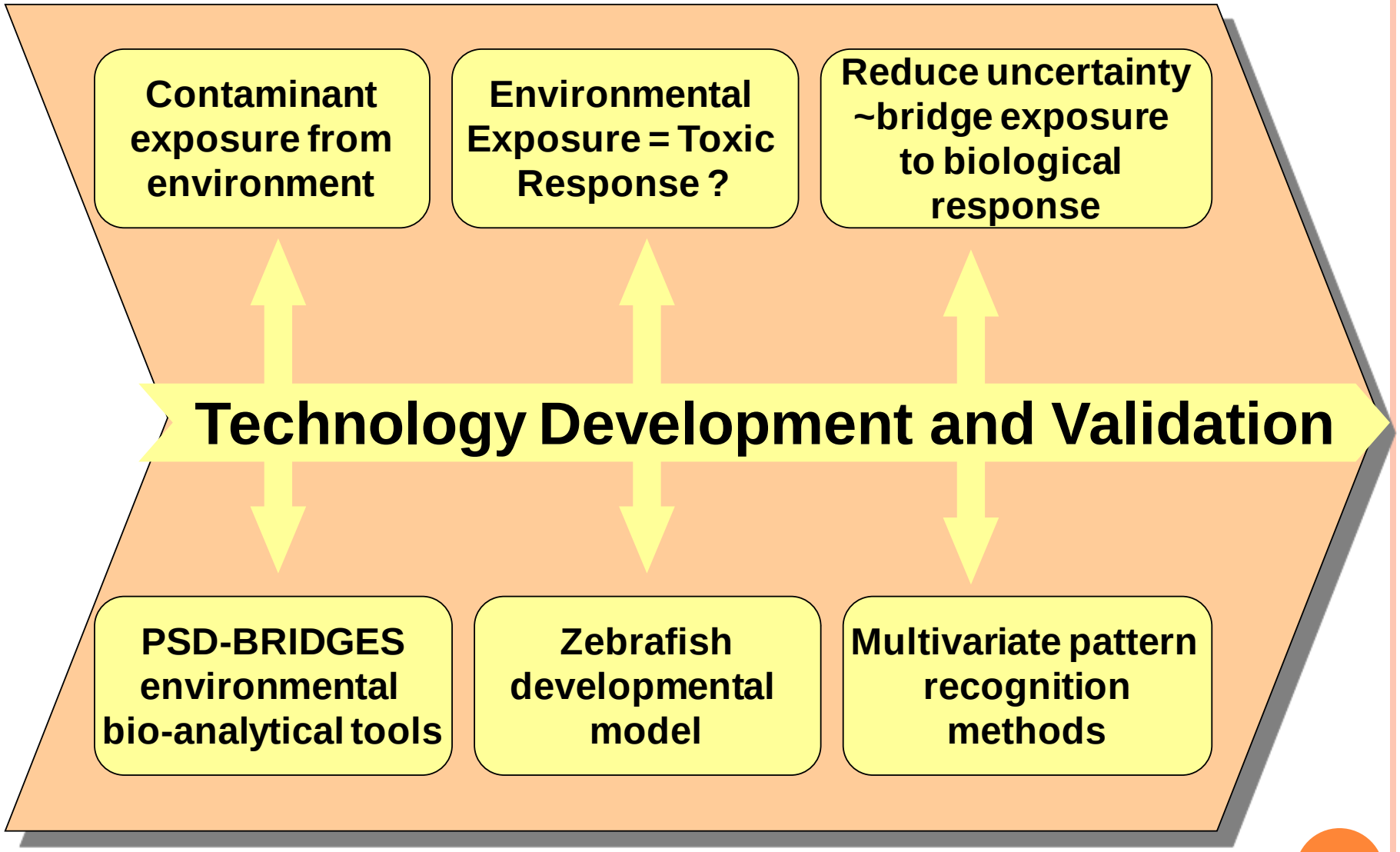
T:\EMT\ALS1036\Share\Allan, S\Research\Benchsheet Templates\LFT Deployment Benchsheet Template

Hypotheses:

- Complementary air and water PSD can be deployed in pre- and post-impact oil spill affected sites that selectively and quantitatively sequester *bioavailable:*
  - PAHs, (known toxicity and/or carcinogenic)
  - Oxygenated PAHs (possible environmental dead-end products, likely as toxic as PAHs), and
  - Alkylated PAHs (diagnostic of source)

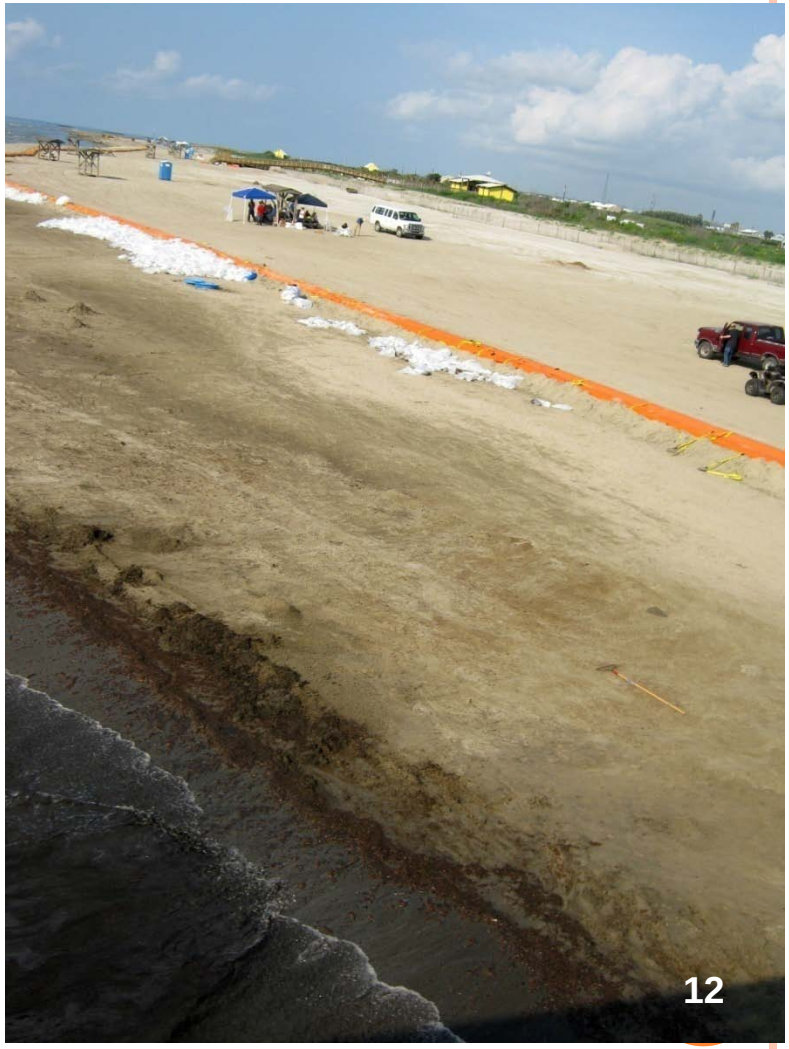
- Post-impact oil spill extracts from air and water Gulf of Mexico PSDs will elicit additional toxic response beyond pre-impact in bioassays such as zebrafish development model and Ames Assays.

Adapted from: Schwartz, D.A., *et al*, 2005



Goals: Many fold
Many Ideally suited to Passive Samplers

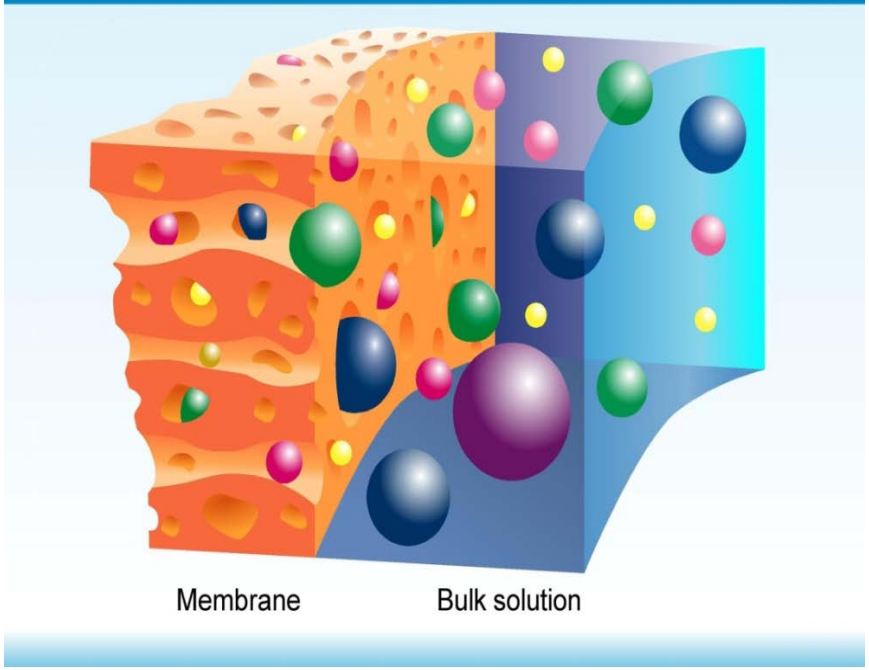
- Establish regional and *individual* relationships
- Gear – goals
  - Bioavailable passive samplers used for BRIDGES (biological response indicator devices for gauging environmental stressors)
  - Passive Sampler for **aquatic exposures**
  - ***NEW*** PSD **air** sampler
  - Both **chemical and bio-assays**
  - Quality Control, PRC
- Oil trajectory uncertain
- Broad geographic areas "at risk"
- PRE-spill conditions
- Time-scale
- **Defensible, Unbiased data**



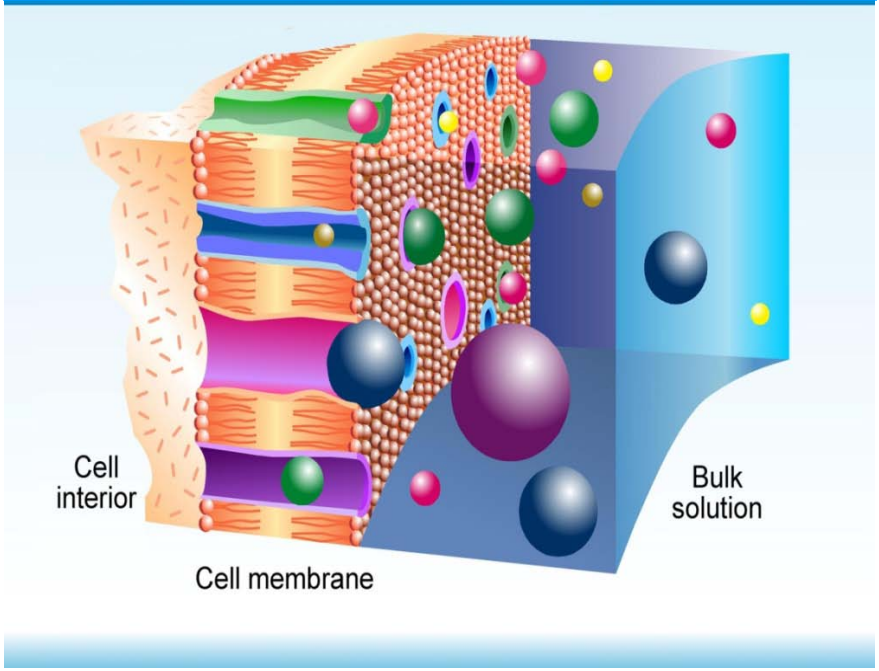
Grand Isle, LA, Anderson Research June 2010 Sampling Campaign

Passive Sampling Device
Adequate biological surrogate

LFT Membrane

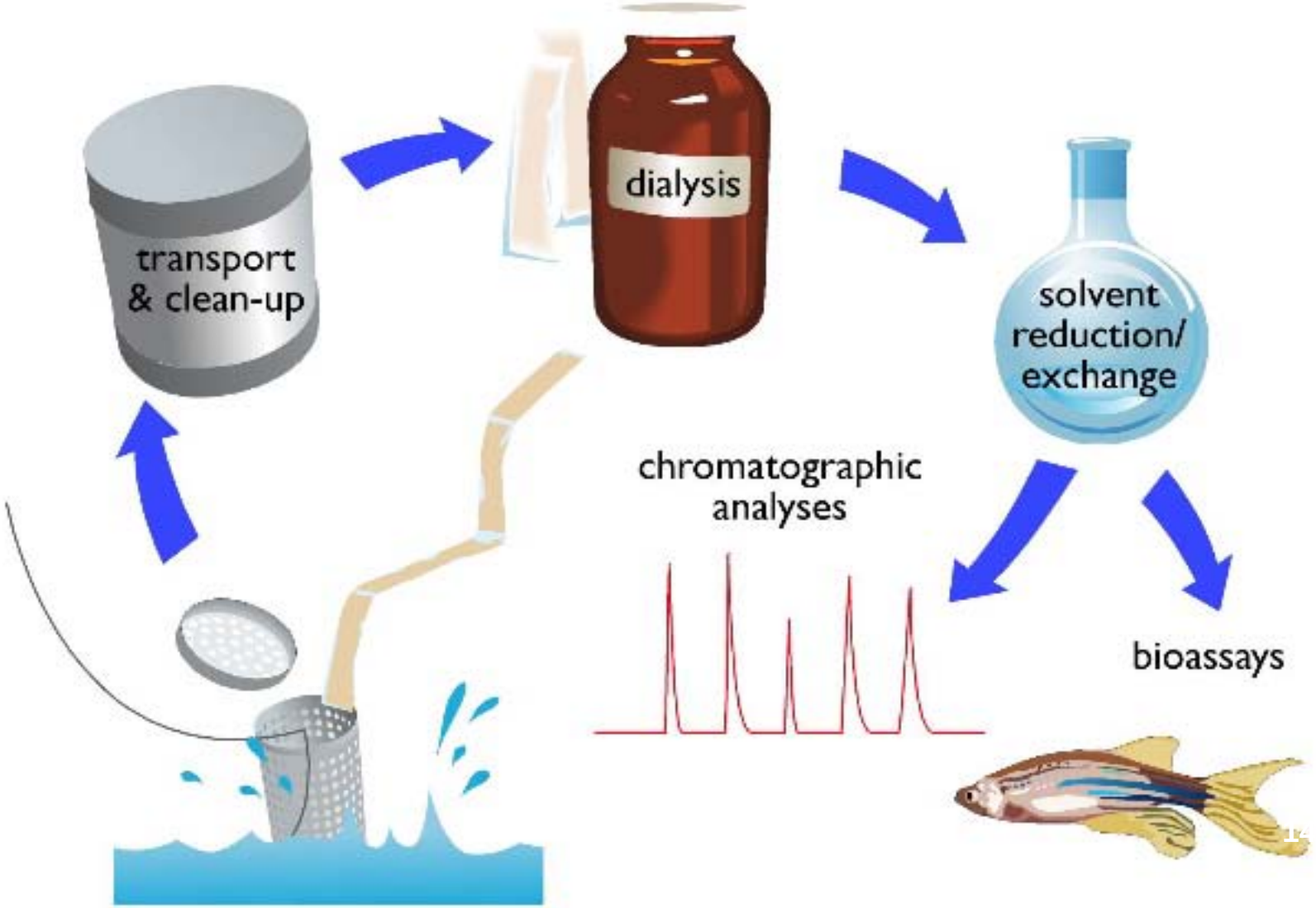


Cell Membrane



LFTs are polyethylene membranes that, similar to cell membranes, passively uptake freely dissolved (bioavailable) hydrophobic compounds.

Sampling - PSDs



Passive sampling devices Deployed at Superfund sites

- **PSD principle:** our LFTs are constructed of *modified* polyethylene strips which represent an organic lipid membrane. Like a membrane, LFTs discriminate against particulate bound material. As *in situ* time integrative passive samplers, LFTs may be deployed for extended periods of time to sequester contaminants. This **overcomes potential issues such as detection limits, bioavailable fraction collection and fluctuating contaminant concentrations**.

Sampling and analysis

- Sampling started May 11th – October 14th 2010
- Initial event, then **>130 days** of continuous sampling

- PSDs were extracted and analyzed by GC-MS:
  - **33 PAHs**
  - 16 OPAHs
  - Screened for 1,200 chemicals of concern
    - RTL DRS software.
- Calculation of concentration in water

Goals: establish regional and *Individual* contacts

- Florida
  - *Pensacola*, Gulf Islands National Seashore
    - Permit required, yes, State of FL
- Alabama
  - *Mobile*, Ben Secour National Wildlife Refuge
    - Permit required, yes, State of AL
- Mississippi
  - *Gulf Port,* Public Pier
    - currently closed due to construction
    - Gulf Port Harbor Master,
- Louisiana
  - *Grand Isle* State Park
    - Permit required, yes, State of LA

Gulf Port, MS

Bon Secour, AL

Grand Isle, LA

Gulf Shores, FL

Results: May – prior to shoreline

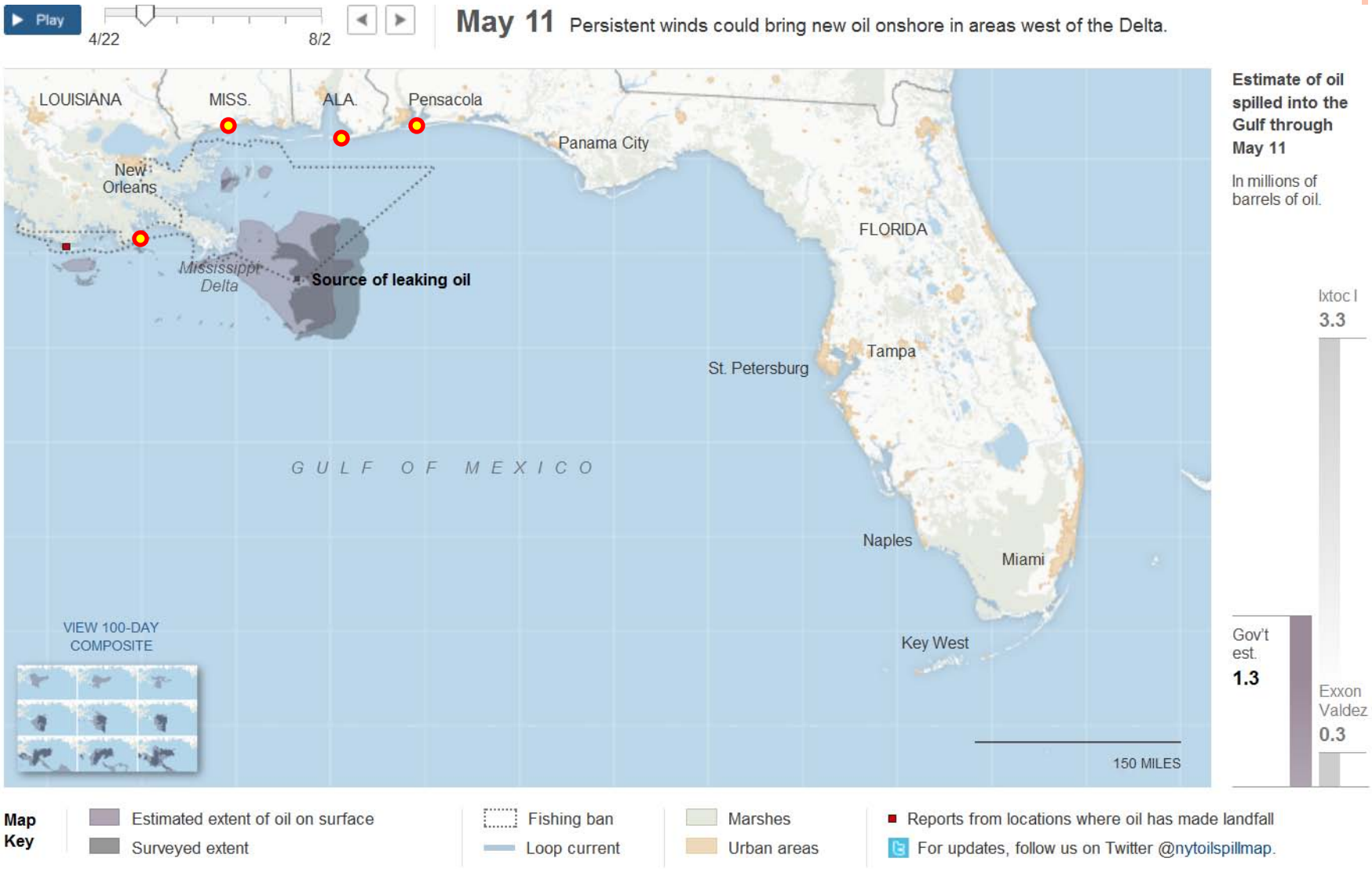


Image: http://www.nytimes.com

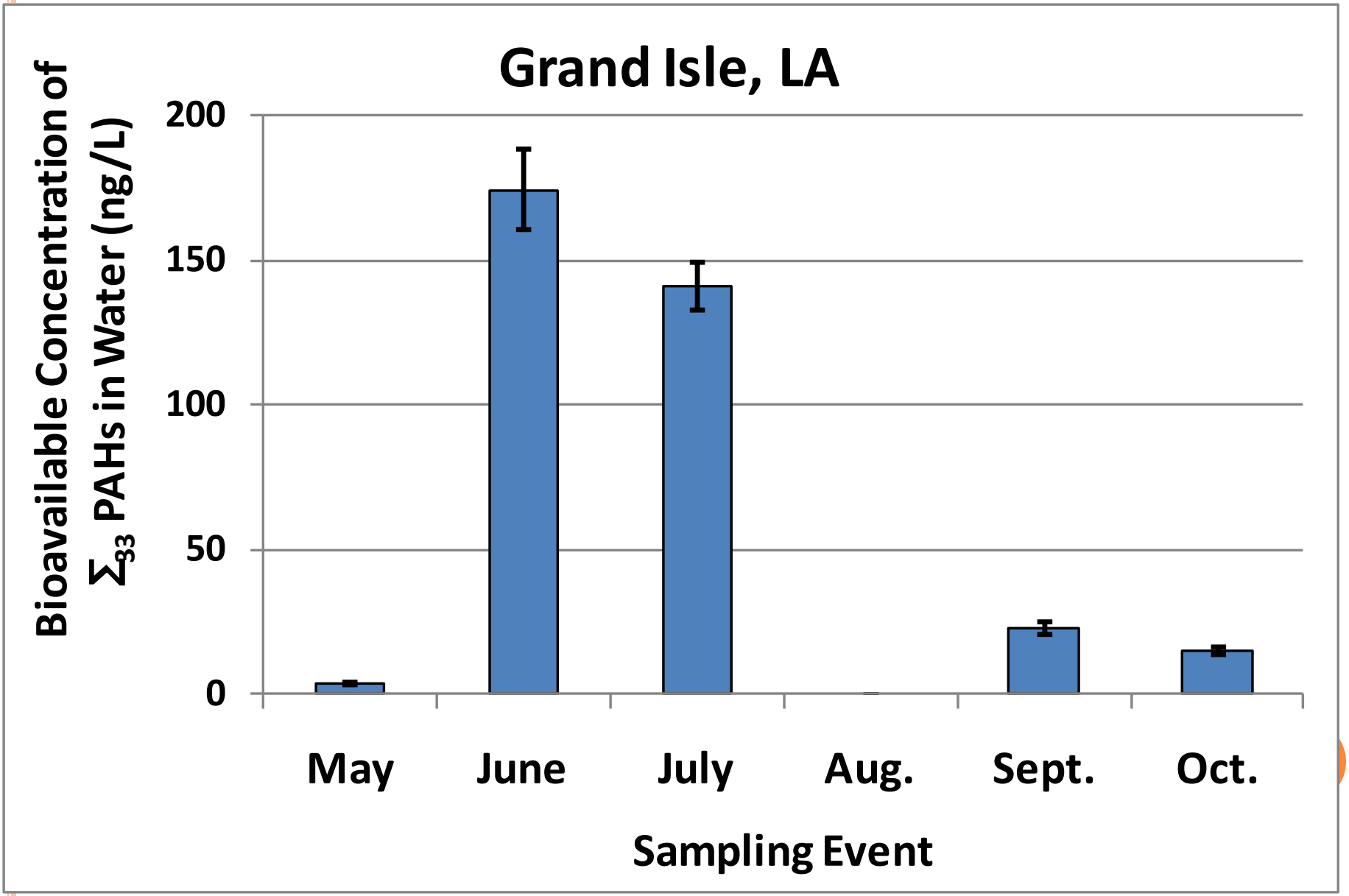
Spatial Results: May– prior to shoreline oiling

- Yes, bioavailable PAHs are present at ALL sites prior to shoreline oiling

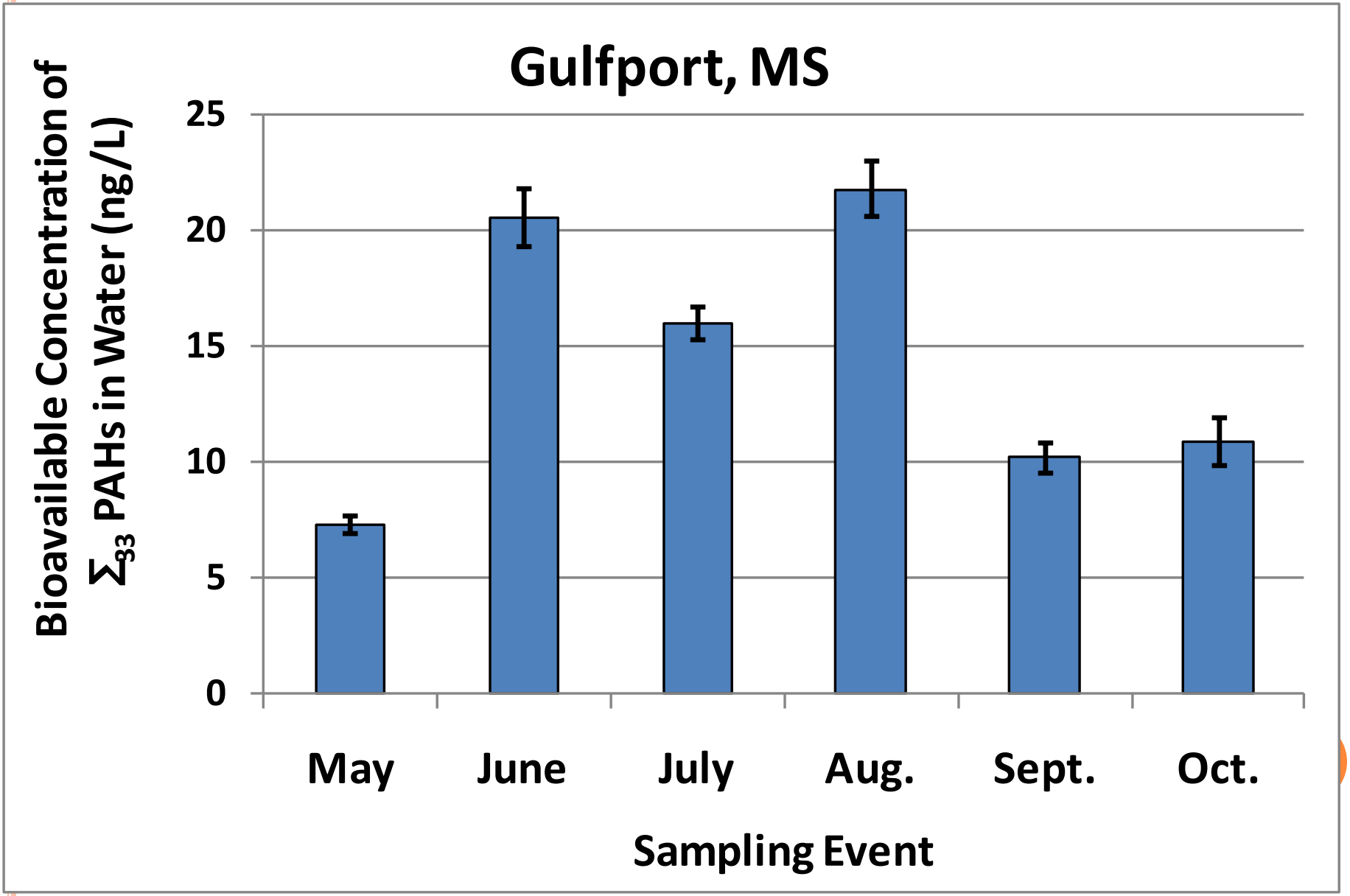
Results: June, July – during coastal oiling

- Bioavailable PAHs increased 40 fold at LA from May to June, and July
- LA sampler and gear loss during August sampling
- Sept and October bioavailable PAHs still **significantly above pre-shoring line** oiling conditions of May 2010

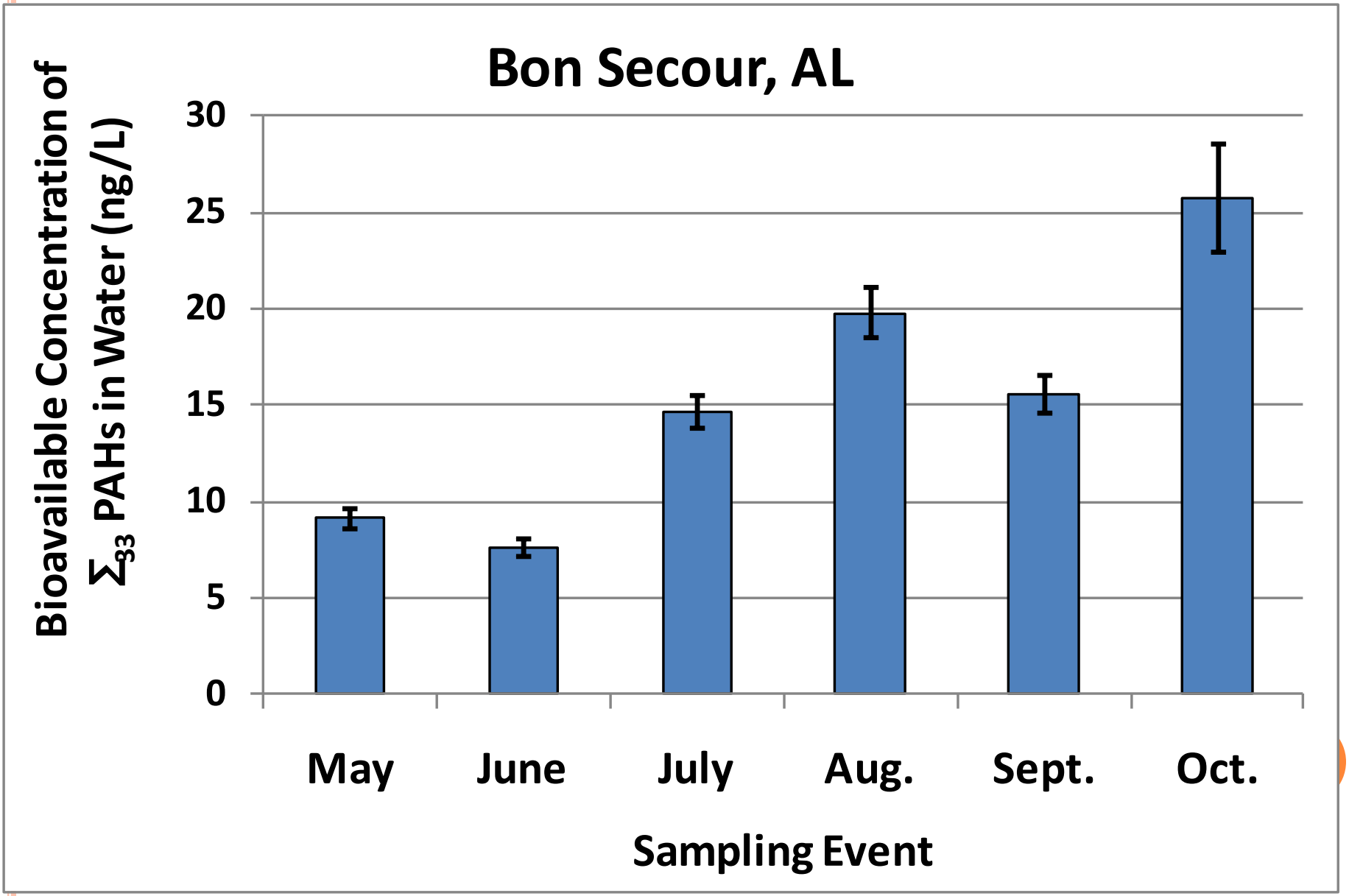
Temporal Results: Grand Isle, LA



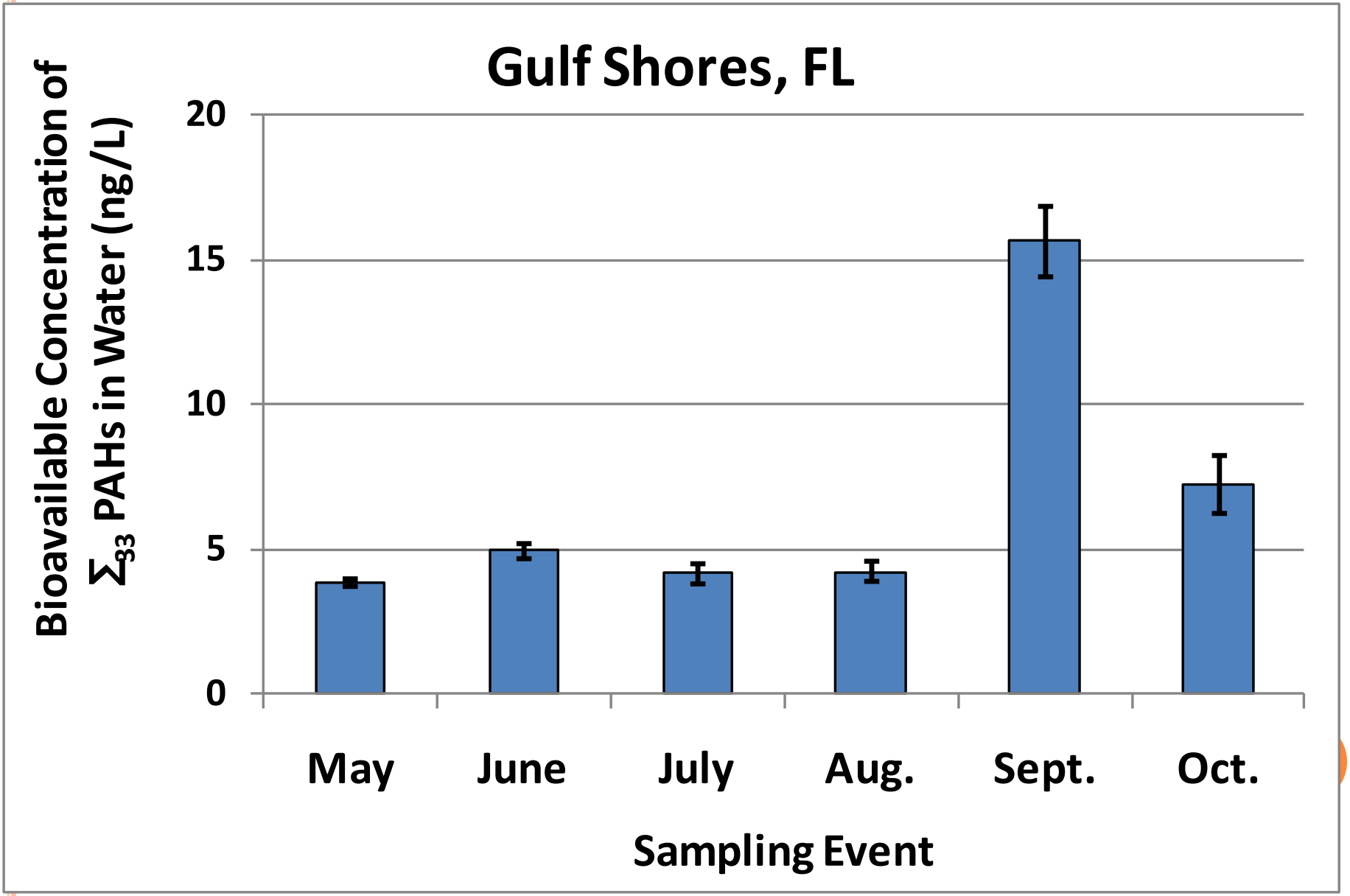
Results: Gulf Port, MS

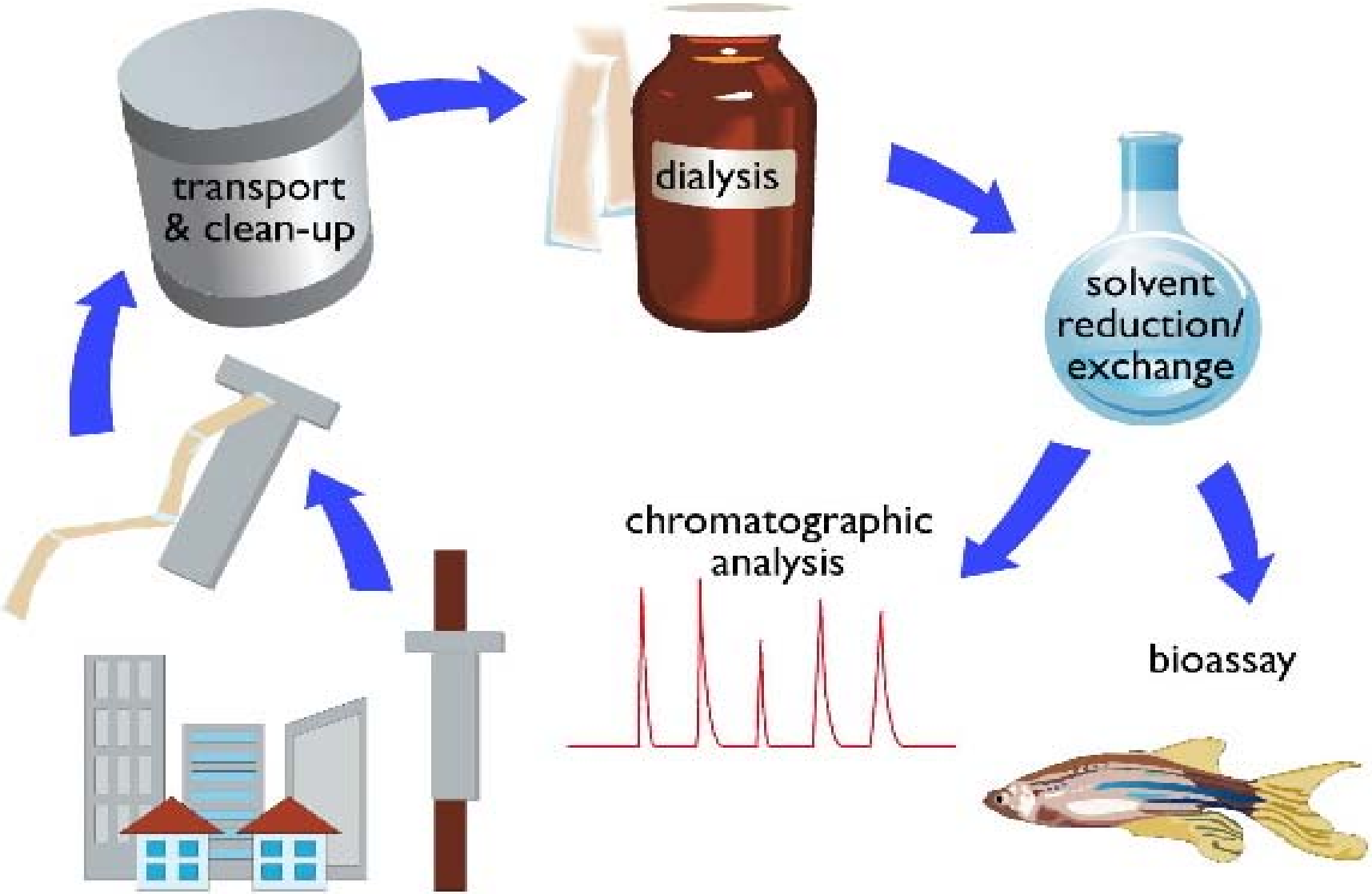


Results: Bon Secour, AL

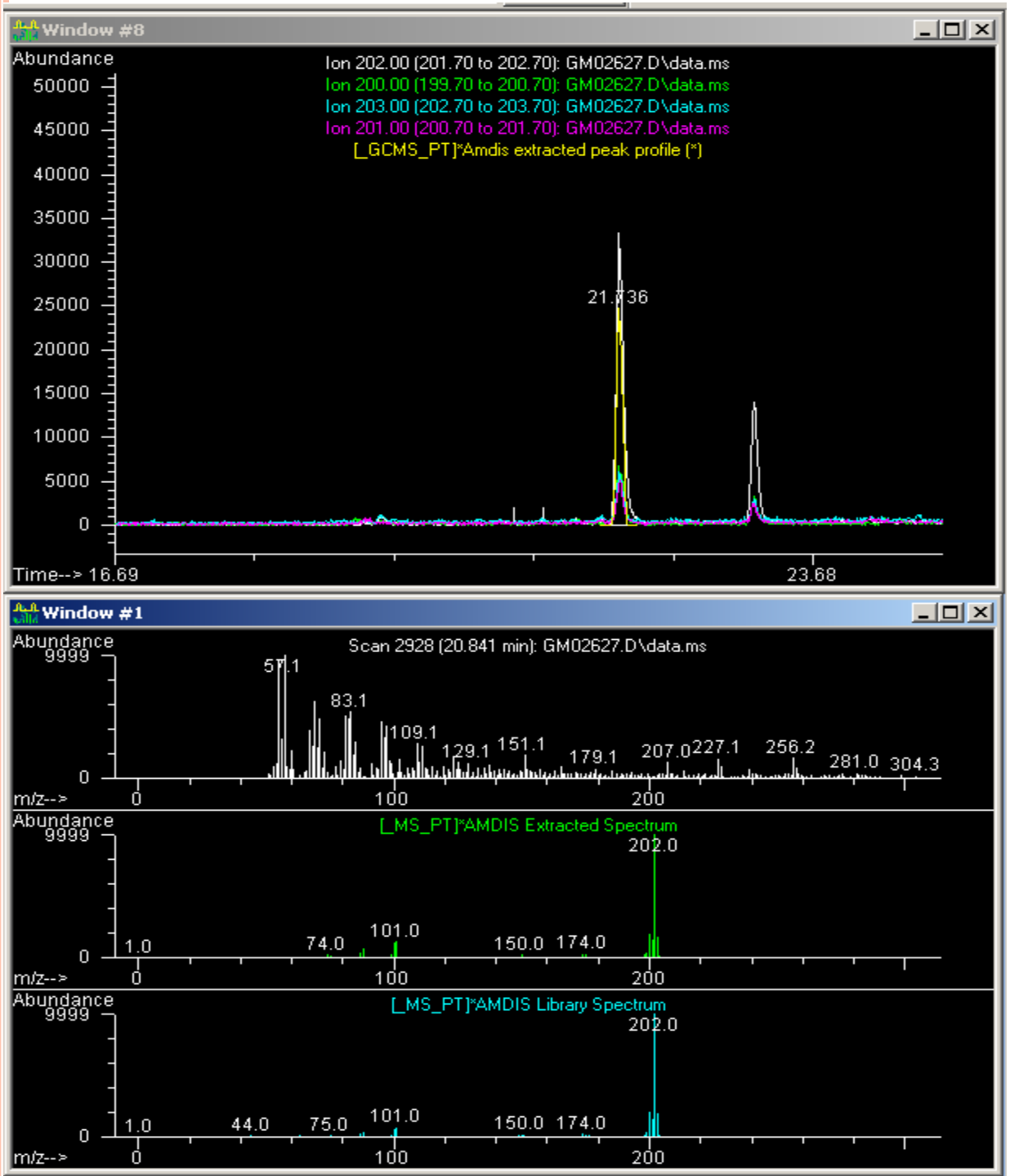


Results: Gulf Shores, FL





Beta Test Air Passive Sampler



Example of 1,200 screening method,

AMDIS extracted flouranthene in exposed AIR LFT extract from Louisiana

Abridged list of positively identified compounds from AIR exposed LFT extract:

- Ethiolate
- Biphenyl
- Bifenthrin
- Acenaphthene
- Phenanthrene
- Flouranthene
- Pyrene
- Retene
- Benzo(a)anthracene
- Chlorpyrifous
- Permethrin1
- Permethrin 2
- Chrysene
- Benzophenone
- 9-flouranone
- Benzylbenzoate

Goals: Next Chemistry and Biology

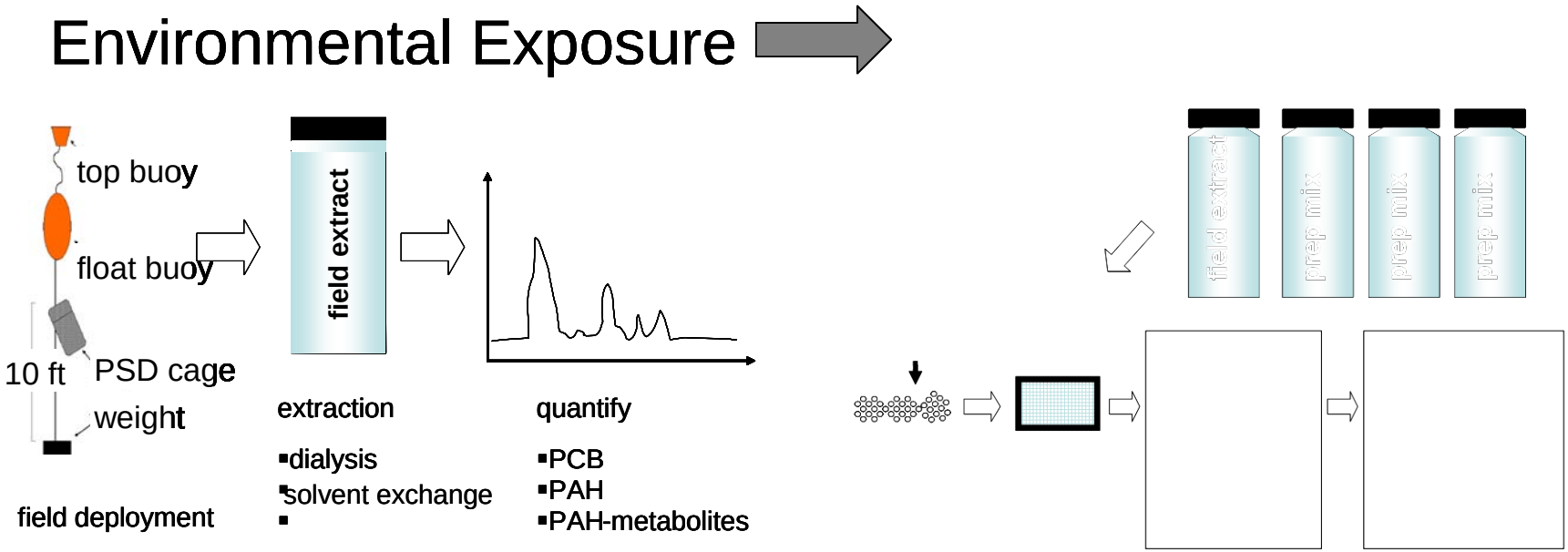
- 302 mw isomers, dibenzo-pyrenes
  - dibenzo(a,i) pyrene, dibenzo(a,e) pyrene and dibenzo(a,h)pyrene
  - are potent carcinogens[1,2]
- **Oxygenated PAHs**
  - formation of OPAHs during metabolism can lead to genotoxicity, promoting carcinogenesis[3,4]
- Alkylated PAHs, molecular fossils
  - total Nap=Naphthalene X 120[5]
- **Bio-assays**

- [1]Layshock et al, JEM, in press 2010, [2] Pufulete, et al R. Toxico Pharmaco, 2004, [3]Layshock et al, ET&C, in press 2010, [4] Burdick, et al, Cancer Res, 2003, D. Mount, EPA Duluth

Oxygenated PAH -Environmental Dead End Products of Toxicological Concern in Oil Spills

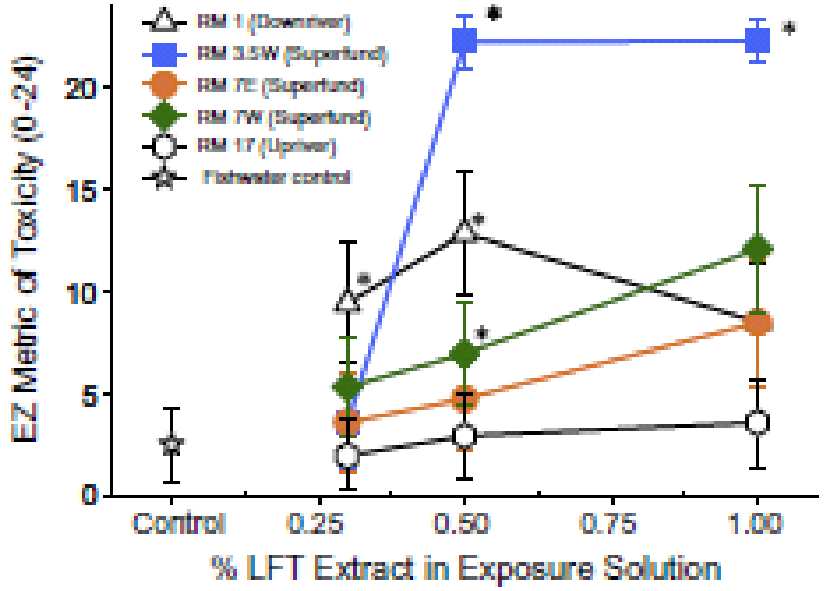
- There is evidence that OPAH compounds are more toxic than the unsubstituted parent PAHs
- The principal source of OPAHs to aquatic systems is currently thought to be biodegradation of parent PAH compounds by bacteria

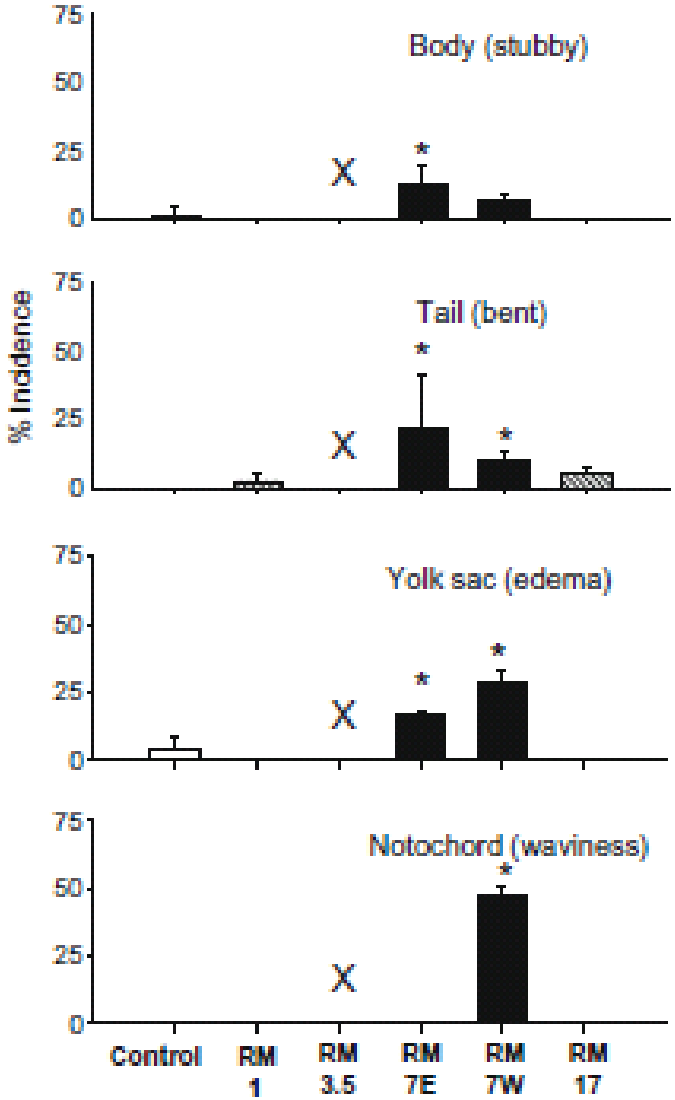
BRIDGES Bio-analytic Tool: Combines passive samplers with the **EMBRYONIC ZEBRAFISH MODEL**.



- BRIDGES: **Reduce Exposure Uncertainty by Analyzing Biological Responses**
- Provides a quantitative measure of the developmental toxicity of site-specific, environmentally relevant contaminant mixtures.

PSD successfully Bridged to bio-response Assay





Hillwalker, Allan, Tanguay, and Anderson Chemosphere, 2010, 79, 1-7

Anticipated IMPACT

Anticipated IMPACT

- Rapid generation of bioavailable PAHs data in air and water.
- High throughput, 1,200+ analyte screen, of both air and water PSD will have independent usefulness for examining environmental mixtures.
- First creation of bioavailable OPAH data in air and water will be invaluable to understanding effects on environmental and human health during and after an oil spill.
- Background PAH concentration data at the gulf sites will prove invaluable to understanding current and future effects from the Deepwater Horizon Spill

WEB OUTREACH
GULF OF MEXICO OIL SPILL, PAHS, AND HEALTH
[INFO LAST UPDATED: NOVEMBER 7, 2010]

- http://oregonstate.edu/superfund/oilspill
- http://oregonstate.edu/superfund/gulfvideo1

2010 June Sampling Campaign, Grand Isle LA, "Marvin" the Egret on park boom

Superfund Research Program

Navigation
SRP Home
People
Support Cores
Research Projects
News and Highlights
Gulf Oil Spill, PAHs, and Health
Outreach
Publications
Resources
Definitions
Site map
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Internal Communication

Gulf of Mexico Oil Spill, PAHs, and Health

[Info last updated: July 21, 2010]

Background

The *Deepwater Horizon* oil spill (also known as the Gulf of Mexico Oil Spill or the BP Oil Spill) is a large disastrous oil spill caused by an explosion April 20, 2010 on the *Deepwater Horizon* offshore oil platform about 50 miles southeast of the Mississippi River delta (28.74°N, 88.39°W). Oil gushed for 87 days (until July 15th) into the gulf from the wellhead 5,000 feet (1,500 m) below the ocean surface at an estimated 20,000 - 40,000 barrels a day. The total amount spilled is estimated to be approximately 184,755,550 gallons, which is enough oil to fill 307 olympic-size swimming pools. This environmental disaster has been devastating to marine and wildlife habitats, as well as the Gulf of Mexico fishing and tourism industries, which have been the livelihood of these coastal communities.

OSU SRP PAH Research at the Oil Spill

As part of SRP's focus on PAHs, we are sampling the **polycyclic aromatic hydrocarbons (PAHs)** in air and water in the Gulf of Mexico related to the oil spill. The level of PAHs in crude oil varies between 0.2 and 7%, depending on location. Although this seems like a small percent, PAHs are a significant toxicological health concern.

View a video introduction of the project showing sampling in the four Gulf locations.

- All About PAHs
- Oil Spill & Related Research Links
  - Public Health Issues and Resources
- Oil Spill & PAH Research Terms

WHY ARE WE SAMPLING?

The use of complementary bio-analytical tools that quantify bioavailability processes is important to understand disasters such as oil spill risk. The project goals will be to use air and water passive sampler devices (PSDs) in the Gulf of Mexico before, during and post impact from the Deepwater Horizon Spill of spring 2010.

The PSDs are biological response indicator devices for gauging environmental stressors (BRIDGES) developed as part of a Superfund Program grant (Project 4). They *bridge* environmental exposure and biological response/effect. They can provide for **rapid turnaround** of data.

The PSDs sequester PAHs, oxygenated PAHs (OPAHs) as well as other organic contaminants. **OPAHs are potentially more mobile, bioavailable and/or persistent than PAHs.**

Stay Connected and Updated!

Sign up for our Gulf Listserv to receive email updates when research and information is updated on our web site.

Next Outreach

Acknowledgements

Collaborators at:

- **Grand Isle State Park**
- **Bon Secour National Wildlife Refuge**
- **Gulf Islands National Seashore**
- **and Gulf Port Harbor Master DJ Ziggler**

Sampling May 2010, end of long day…

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Food Safety & Environmental Stewardship