

# **Advanced Petroleum Hydrocarbon Testing of the tissue and organs of the inshore fish of Pensacola Bay and offshore in the Gulf of Mexico**

2012 Mississippi-Alabama Bays and Bayous Symposium – Biloxi, MS

*Heather Reed- Ecological Consulting Services Inc.*



**ECS**

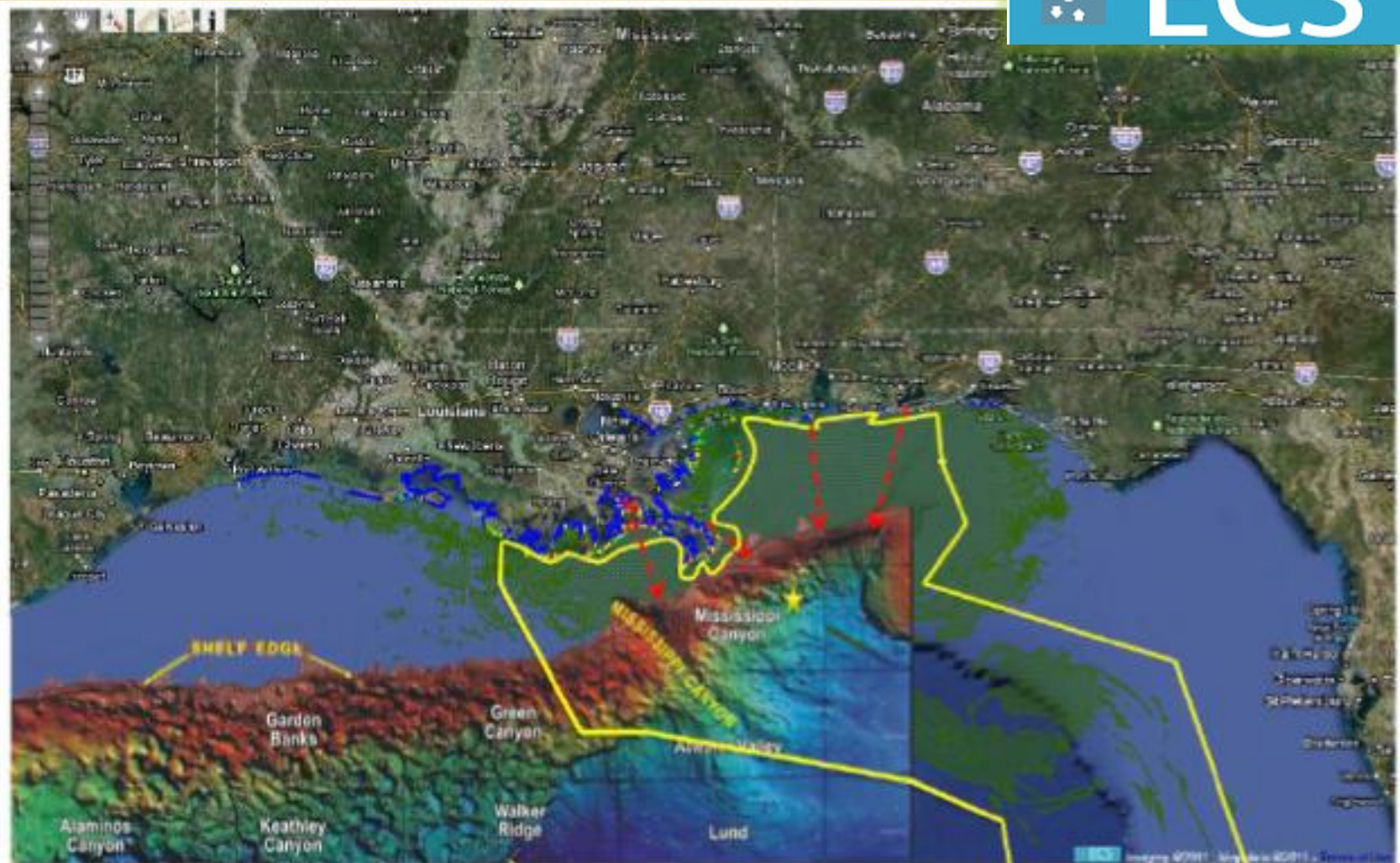
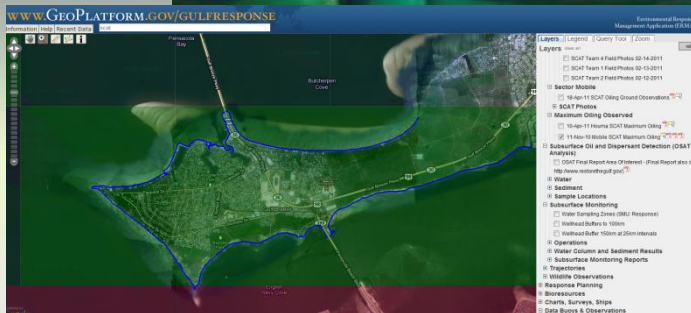
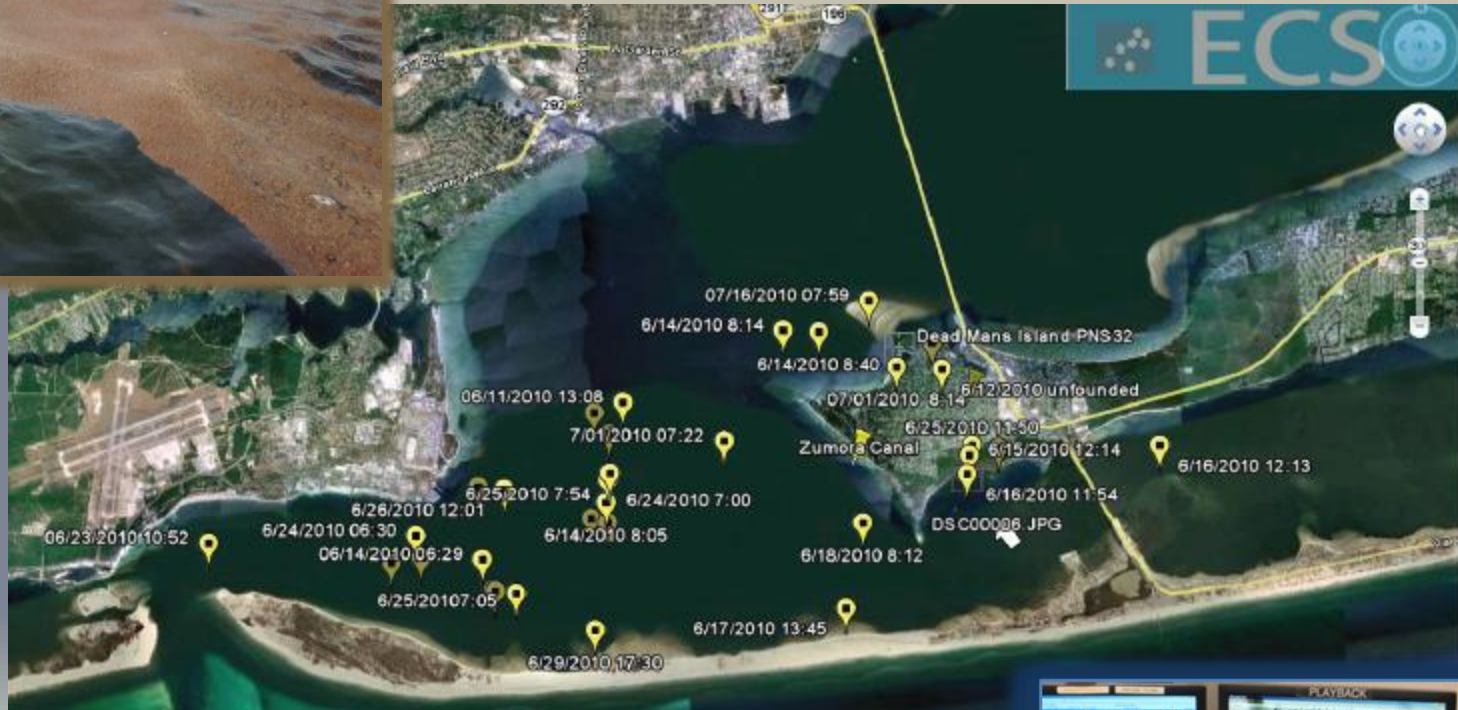


Figure 1: Overlays: Gulf of Mexico ocean floor bathymetry showing reef habitat for fisheries and reef inside the restricted zone. The yellow lined area shows the Federal fishery closure boundary (June 2010) which was impacted by oil continuously from April 20, 2010 to September 19, 2010. Notice the Mississippi Canyon is the closest area to the mainland for reef fish, upwelling zone for plankton which provides primary productivity for the reef, benthic and pelagic breeding grounds. The red dotted line are the commercial fishing routes. All reported fishing sites were impacted with oil to depths of 1000 fathoms.

## 2010 Pensacola Bay City of Gulf Breeze Oil Sightings



No Oil Ever? Really? Reported June 2010- Inspected OCTOBER 2010 –  
FDEP SCAT 2hrs to inspect six miles of rip rap (insufficient inspection)-Should be classified as “Not Determined”

*MidWay Fire Department demonstrating how to assemble a mobile decontamination station during HAZWOPER training for the oil spill response team*



## NOAA NMFS NWFSC-59 method

NOAA method is testing for certain components such as the individual PAH's and individual PCB congeners - mass spec

*The State of Florida - only required to test 13 out of the 60 compounds*

Total Petroleum Hydrocarbon

total hydrocarbon  
result NMFS  
NWFSC-59 method  
but it would be a  
combination of  
different tests  
(1668, 8270 PAH  
SIM or alkylated  
PAH's

EPA 8270, EPA  
8272,

Tests 60 of PAH including the 13

## Methods

- 83 samples of various species
- Tissue and organs
- Collection NRDA methods
- Oysters 20 per sample homogenized
- Analyzed – Mixture of EPA 8270, 3541,8015B and NOAA NMFS-NWFSC-59

Oysters are “windows” to Water Quality

*Bivalves are less complex organisms that do not have the ability to metabolize PAHs in the environment or to move from a contaminated area. All bivalves, including oysters, take up the PAHs that are in the water column. Their bodies cannot process the compounds, so the harmful pollutants accumulate in their tissues.*

*PAHs are made up of any-where between two and six benzene rings linked together. Smaller, lower molecular weight PAHs with fewer rings are more soluble; they are taken up by organisms in the water column readily, but are relatively harmless.*

*The larger molecular weight meaning PAHs with four or more rings are fat-soluble. When PAH is ingested by the bivalves, the molecules are stored in the tissue because they are hydrophobic and lipid-soluble.*

## The City of Gulf Breeze Deadman's Island Restoration Project



Prior May 2010 reef  
98% live oyster  
coverage  
to  
May 2012 1% live  
coverage



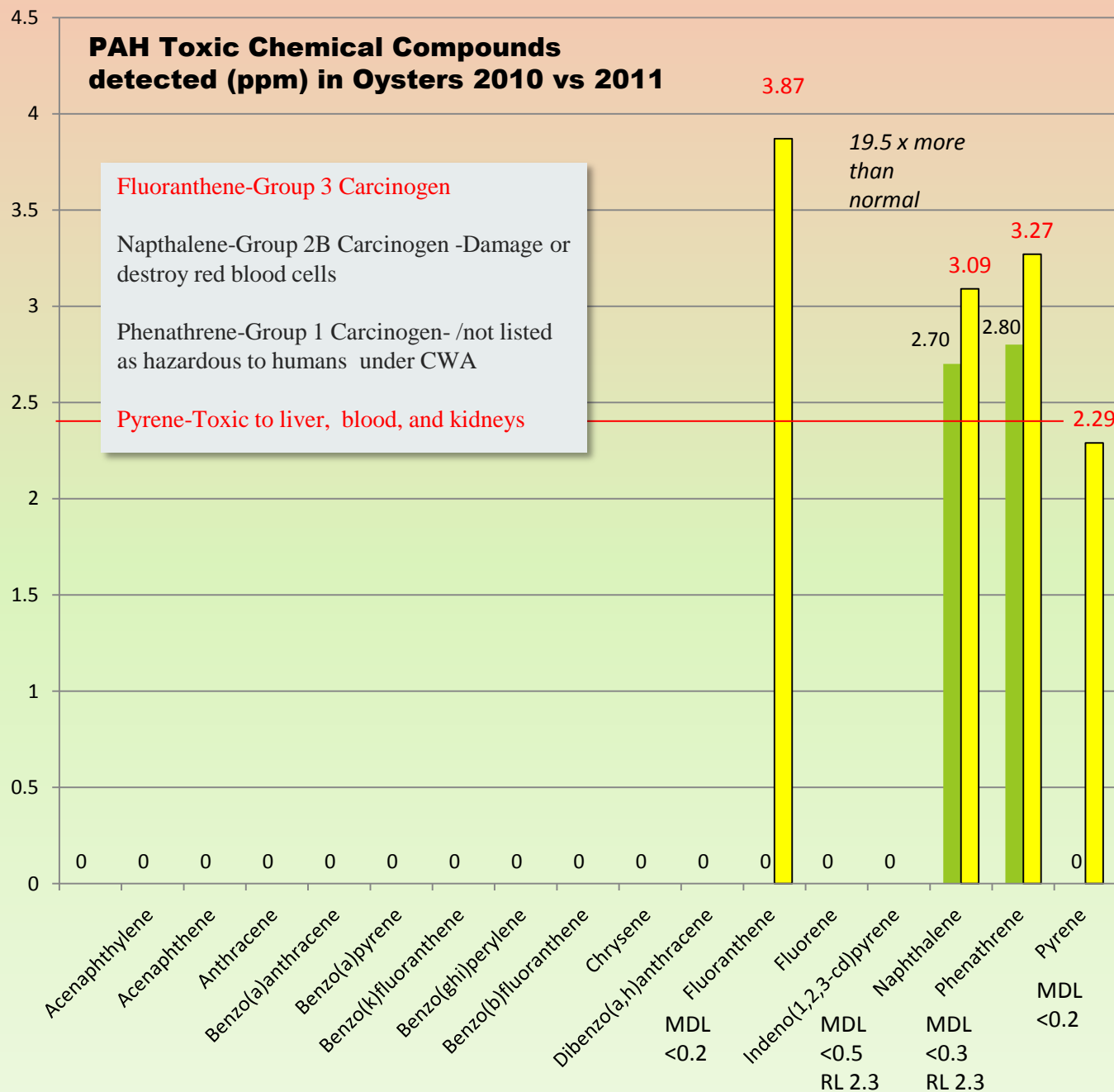
# PAH Toxic Chemical Compounds detected (ppm) in Oysters 2010 vs 2011

Fluoranthene-Group 3 Carcinogen

Napthalene-Group 2B Carcinogen -Damage or destroy red blood cells

Phenathrene-Group 1 Carcinogen- /not listed as hazardous to humans under CWA

Pyrene-Toxic to liver, blood, and kidneys

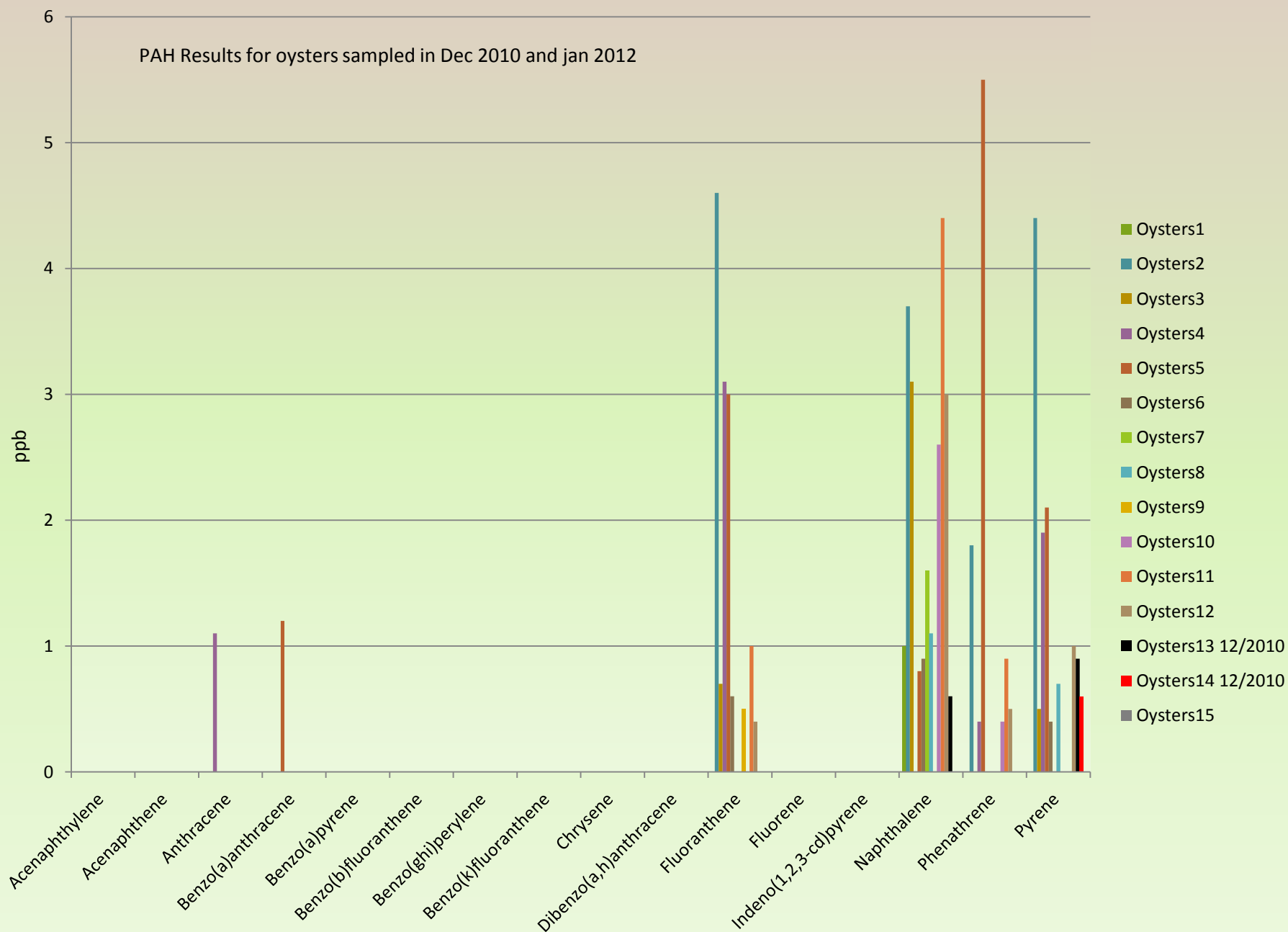


19.5 x more than normal

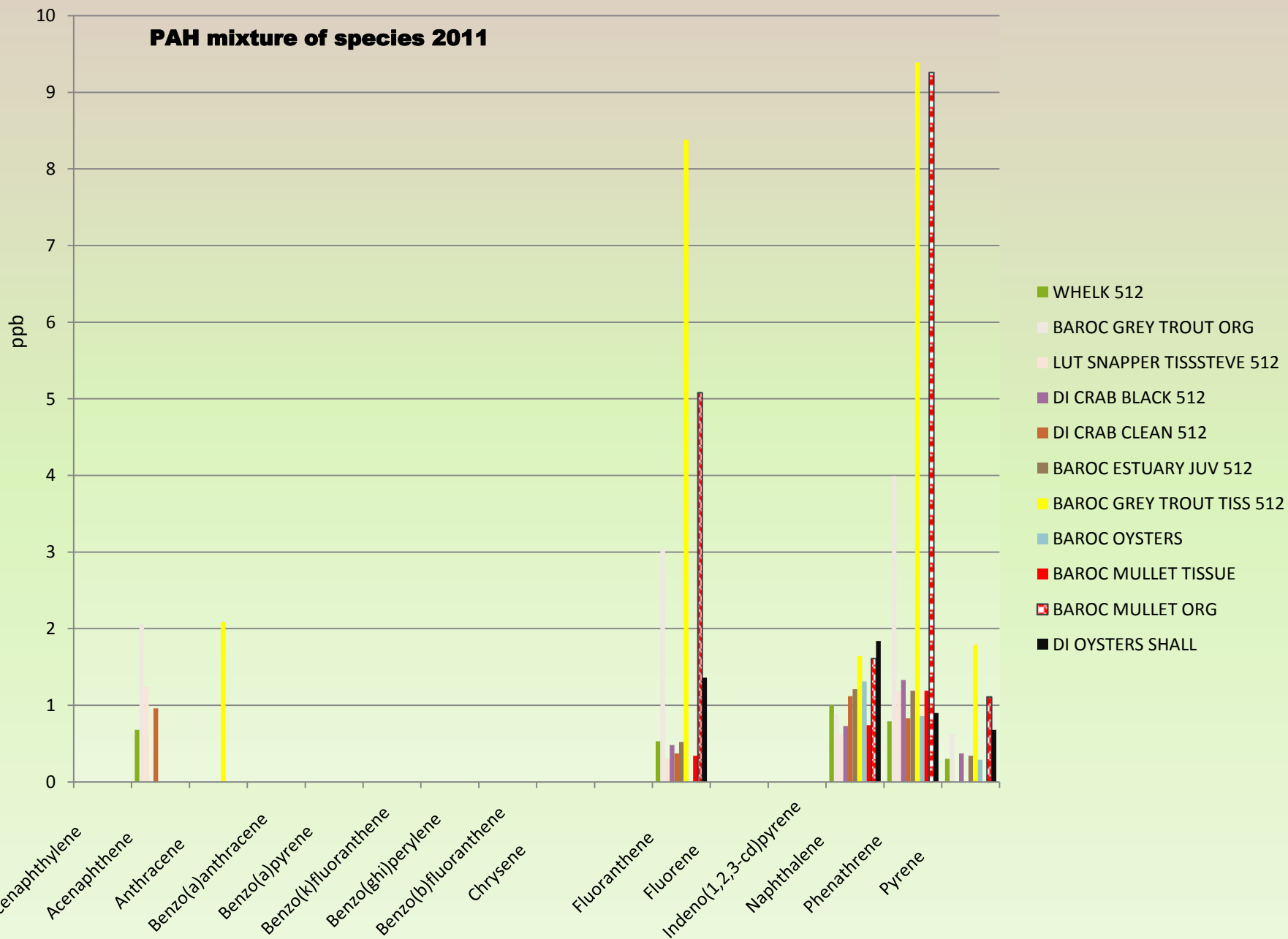
~10 x's more than normal

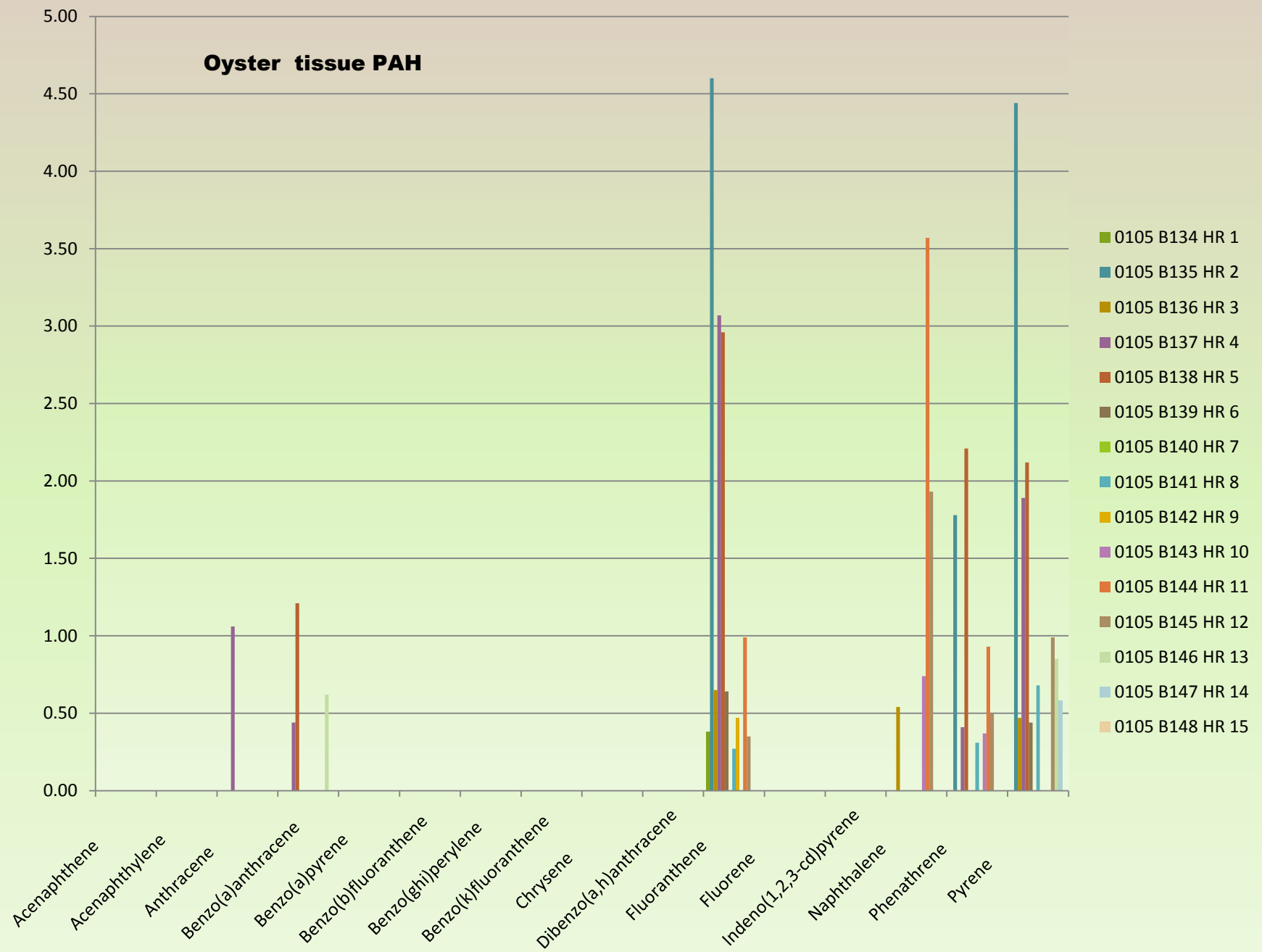
■ DI Oysters 5/2010  
■ DI Oysters 3/2011

PAH Results for oysters sampled in Dec 2010 and jan 2012

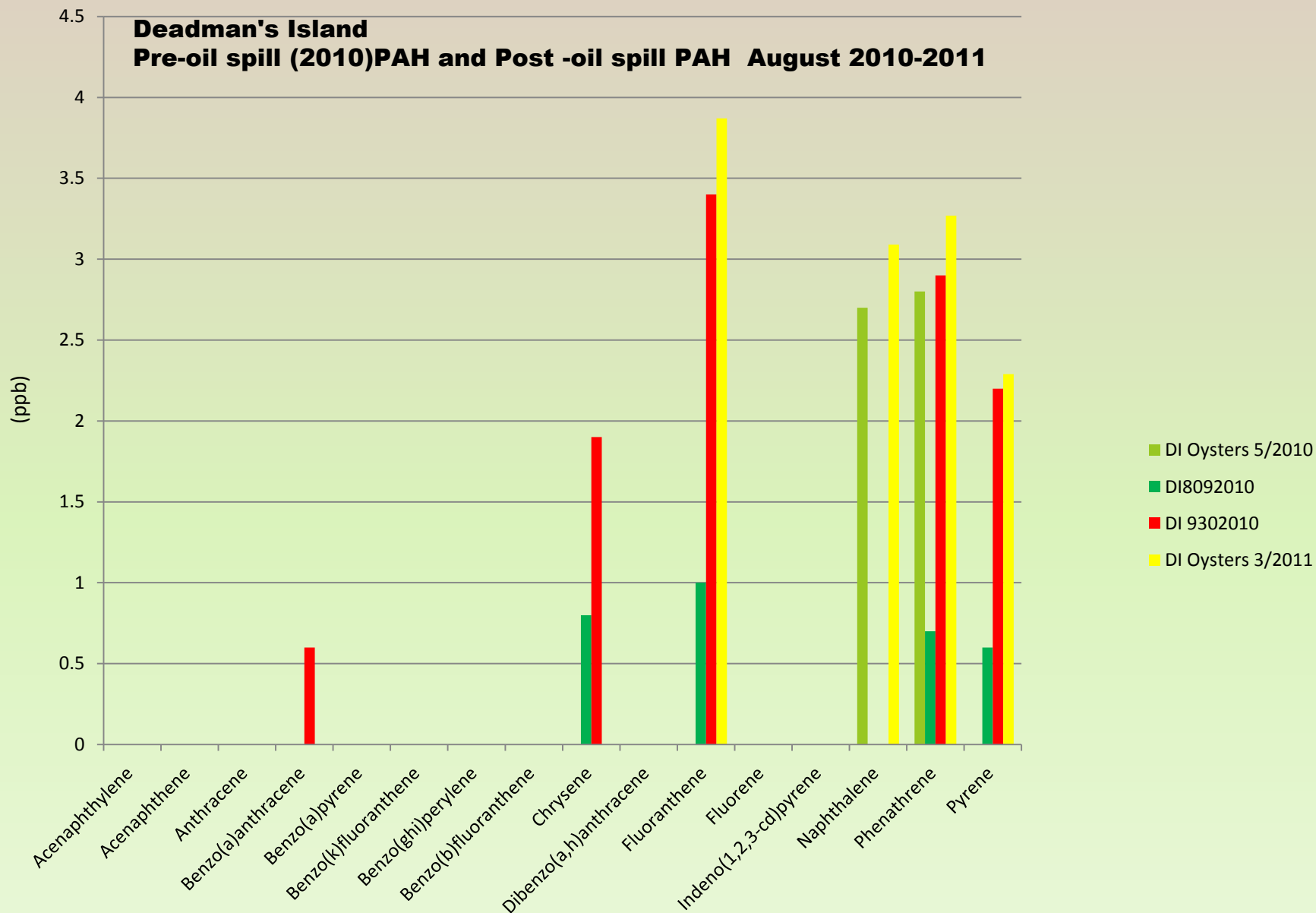


# PAH mixture of species 2011





**Deadman's Island**  
**Pre-oil spill (2010) PAH and Post -oil spill PAH August 2010-2011**



# Biological Impacts and Discoveries

## Cause of death of dolphin at Fort Pickens still pending

...of dolphin death is still unclear, ... is suspected

... seeking oil and recon is actively looking for oil, as ... to the impression

West F  
Preserva  
Noon, J.  
120 Chur  
Ann St  
mstalley!  
Com  
Park As  
Devlop  
2 p.m.



2 ... vigilant in its efforts ... shores and out of its w

10 CONNECTS  
NEWS

## Oil still washing up on Panhandle beaches

Christopher Collette 4 days ago



Heather Reed, a marine biologist and environmental advisor for Gulf Breeze, leads a team of volunteer Navy divers and Gulf Breeze Coastwatchers in a search for submerged oil in the Gulf.



Lubchenco said 52 days after the oil well was capped, "extreme" monitoring of offshore subsurface oil - which could measure a little less than four Alaskan Valdez oil spills - is underway by the public and private sector, including universities in Louisiana and Florida and Woods Hole



# Sunken Oil

Florida Department of Environmental Protection  
Central Laboratory  
2600 Blair Stone Road  
Tallahassee, FL 32399-2400  
DOH Accreditation E31780

Florida Department of Environmental Protection  
Innovation Park Laboratory  
2051 E. Paul Dirac Dr.  
Tallahassee, FL 32310  
DOH Accreditation E31640

Event Description: Proximity Sampling - Spoil Island off Ft McRae  
Request ID: RQ-2010-10-04-46  
Customer: NW-DIST  
Project ID: DH-OIL-PST

Methylene chloride	0.50	U	ug/L
1,1,2,2-Tetrachloroethane	0.50	U	ug/L
Tetrachloroethene	0.50	U	ug/L
Toluene	0.50	U	ug/L
1,1,1-Trichloroethane	0.20	U	ug/L
1,1,2-Trichloroethane	0.20	U	ug/L
Trichloroethene	1.0	U	ug/L
Trichlorofluoromethane	0.50	U	ug/L
Vinyl chloride	0.50	U	ug/L
Methyl-t-butyl ether	0.50	U	ug/L
o-Xylene	0.20	U	ug/L
m,p-Xylene	0.50	U	ug/L

Field ID: PROXIMITY

Sample ID 1303465 Ref. Meth: EPA 8260C

Sample: June 23 Pure Bay Lab ID: 3520885002 Collected: 10/22/10 14:30

Results reported on a "dry-weight" basis

Parameters	Results	Units	PQL	MDL	DF
FL-PRO Soil Microwave					
Analytical Method: FL-PRO Preparation Method: EPA 3					
Petroleum Range Organics	462000	mg/kg	3200	2040	20
C-39 (S)	113	%	60-118		20
o-Terphenyl (S)	572	%	62-109		20

Ref. Method and Comment:  
EPA 8260C: Insufficient sample to perform second matrix spike. QC failure(s) observed.

Sample Location: SPOIL ISLAND SIDE OFF FT McRAE

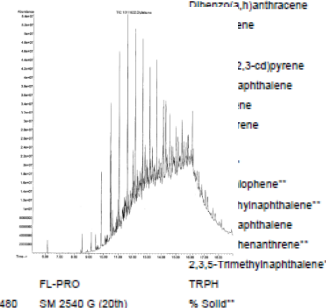
Collection Date/Time: 10/07/2010 12:00 PM

Field ID: PROXIMITY REP-1

Sample ID 1303446 Ref. Method: EPA 8270D

Matrix: SEDIMENT

Component	Result	Code	QC Failures	Units	Cert #
Acenaphthene	120	U		ug/kg	E31
Acenaphthylene	120	U		ug/kg	
Anthracene	120	U		ug/kg	
Benzo(a)anthracene	550	I		ug/kg	
Benzo(a)pyrene	240	U		ug/kg	
Benzo(b)fluoranthene	240	U		ug/kg	
Benzo(k)fluoranthene	240	U		ug/kg	
Benzo(g,h,i)perylene	240	U		ug/kg	
Chrysene	260	I		ug/kg	
Benzo(a,h,i)anthracene	240	U		ug/kg	
ene	120	U		ug/kg	
ene	120	U		ug/kg	
2,3-cdipyrene	240	U		ug/kg	
aphthalene	120	U		ug/kg	
ene	120	U		ug/kg	
ene	900	U		ug/kg	
ene	240	U		ug/kg	
ene	120	U		ug/kg	
lophenene	120	U		ug/kg	
vinaphthalene	120	U		ug/kg	
aphthalene	120	U		ug/kg	
nenanthrene	1.7E+03	U		ug/kg	
2,3,5-Trimethylnaphthalene	120	U		ug/kg	
TRPH	2.2E+04			mg/kg	
% Solid	54.6			%	



FL-PRO Soil Microwave

Analytical Method: FL-PRO Preparation Method: EPA 3

Petroleum Range Organics	124000	mg/kg	2250	1430	20
C-39 (S)	120	%	60-118		1
o-Terphenyl (S)	148	%	62-109		1

FL-PRO Soil Microwave

Analytical Method: FL-PRO Preparation Method: EPA 3

Petroleum Range Organics	20700	mg/kg	484	308	100
C-39 (S)	134	%	60-118		20
o-Terphenyl (S)	517	%	62-109		20

September 30, 2010



Field ID: PROXIMITY REP-1

Sample ID Ref. Method Component

Ref. Method and Comment:

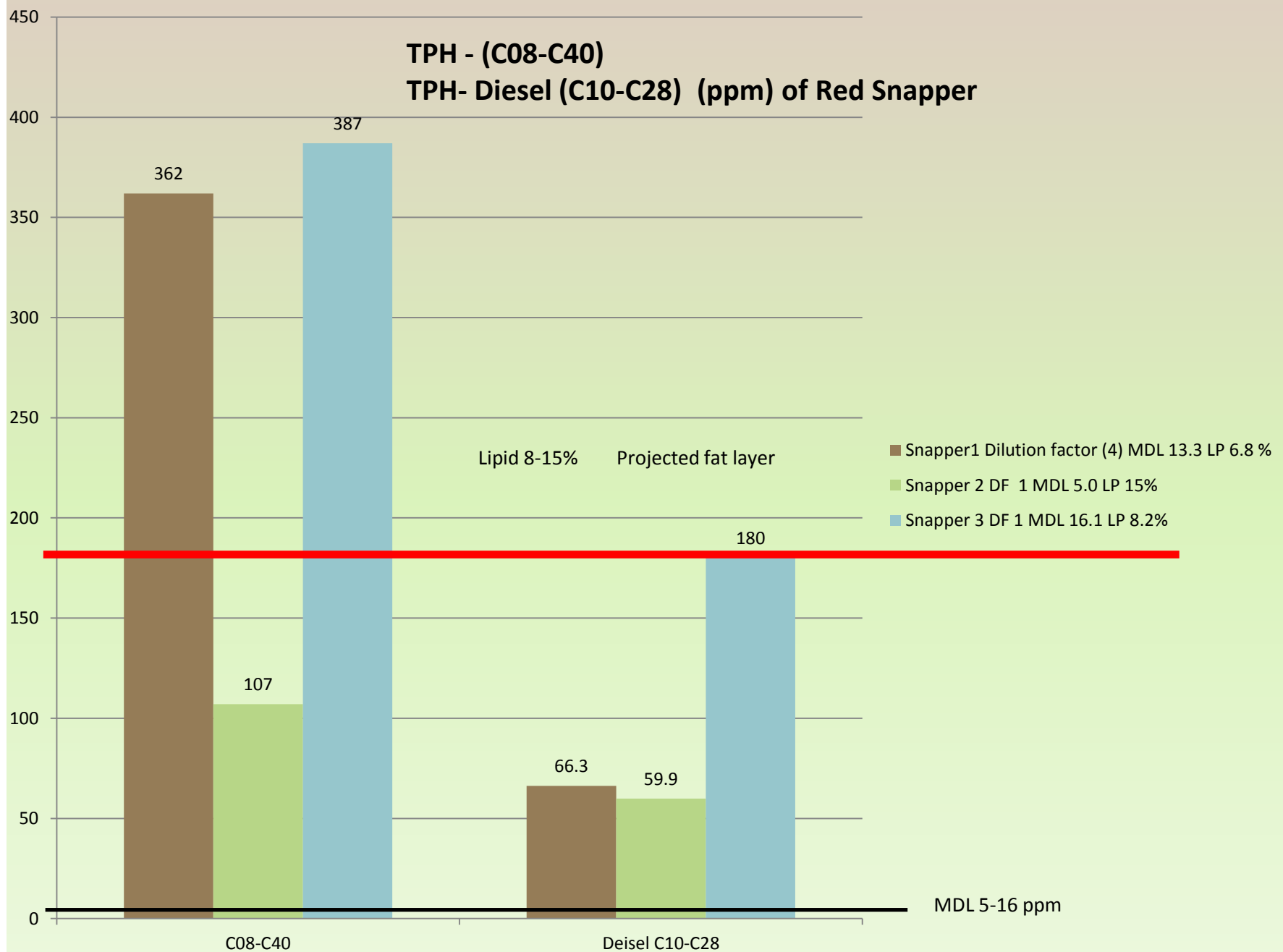
EPA 8270D: Detection limits have been elevated due to matrix interferences. A hydrocarbon pattern consistent to that of the Deepwater Horizon oil was observed in the sample.

FL-PRO: A hydrocarbon pattern consistent to that of the Deepwater Horizon oil was observed in the sample.

Sample Location: SPOIL ISLAND SIDE OFF FT McRAE

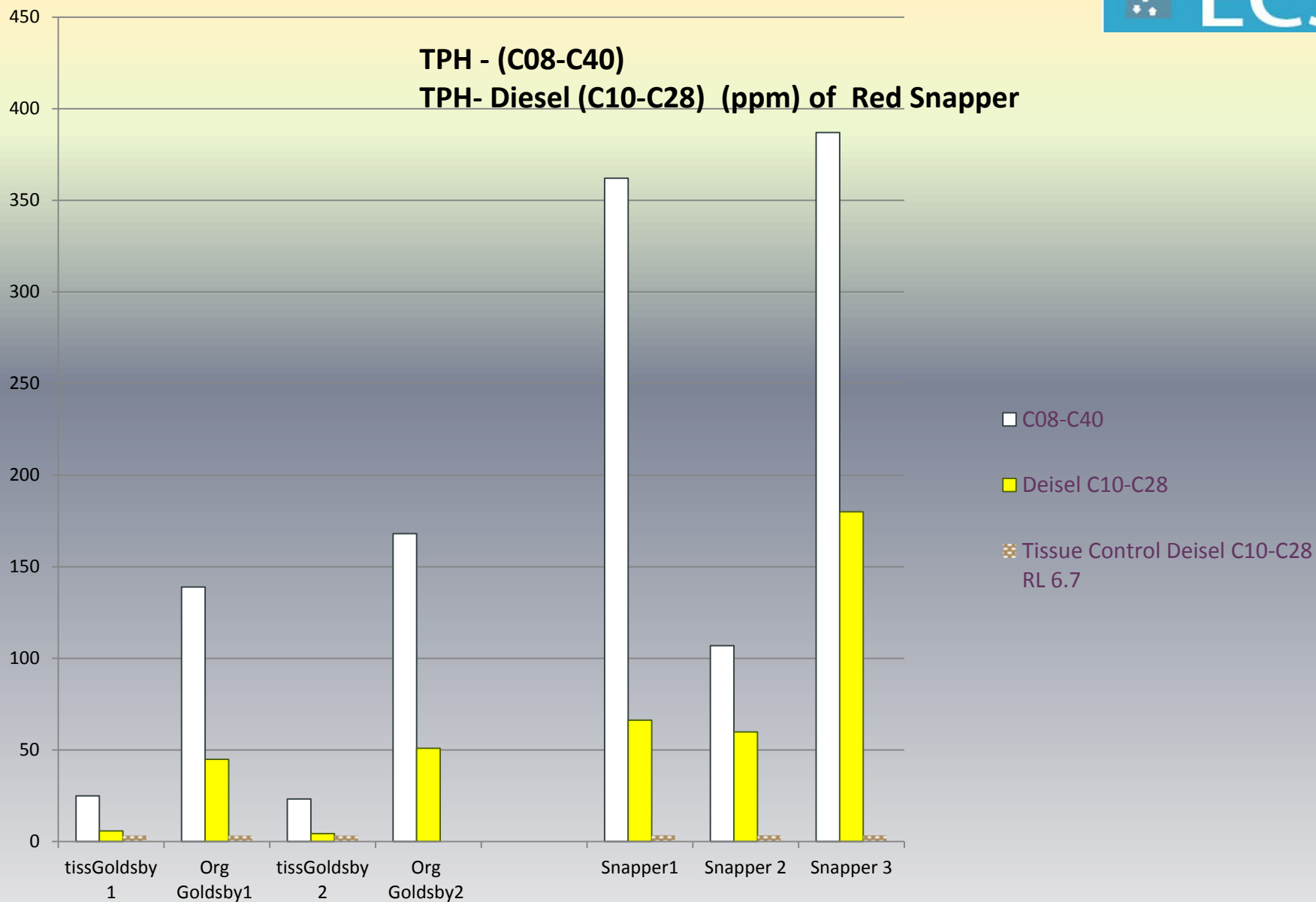
Collection Date/Time: 10/07/2010 11:50 AM

# TPH - (C08-C40) TPH- Diesel (C10-C28) (ppm) of Red Snapper

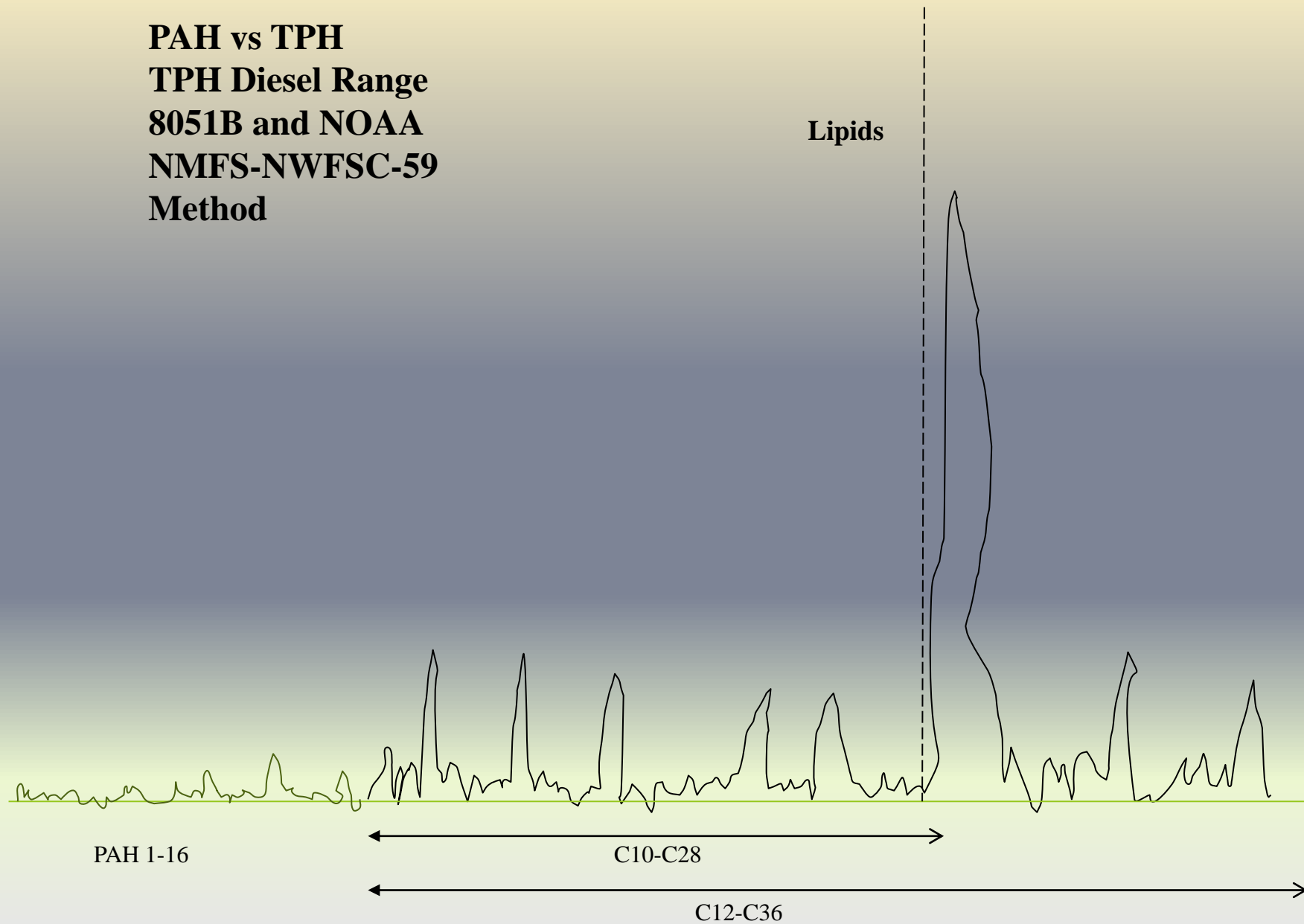


TPH - (C08-C40)

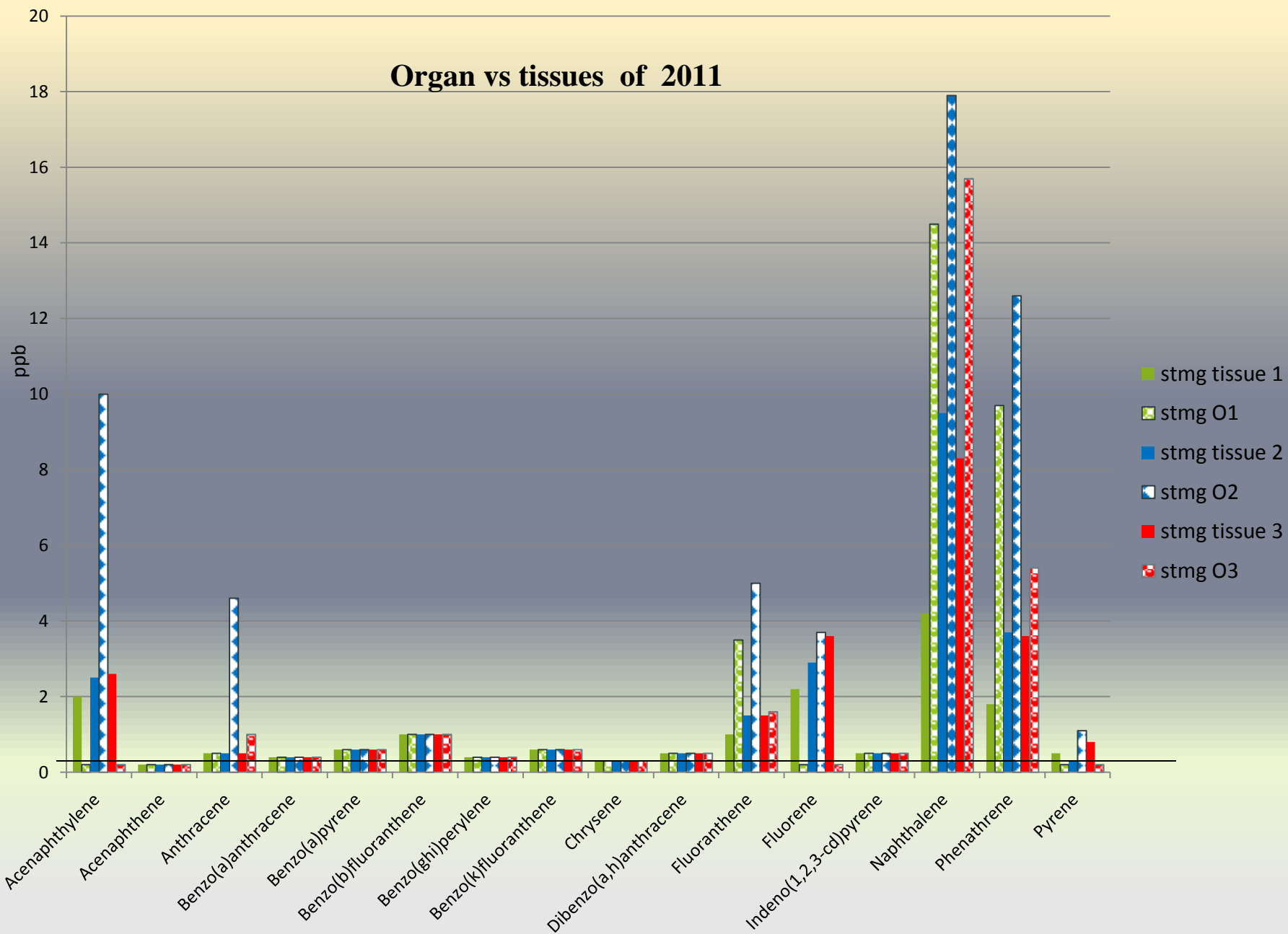
TPH- Diesel (C10-C28) (ppm) of Red Snapper



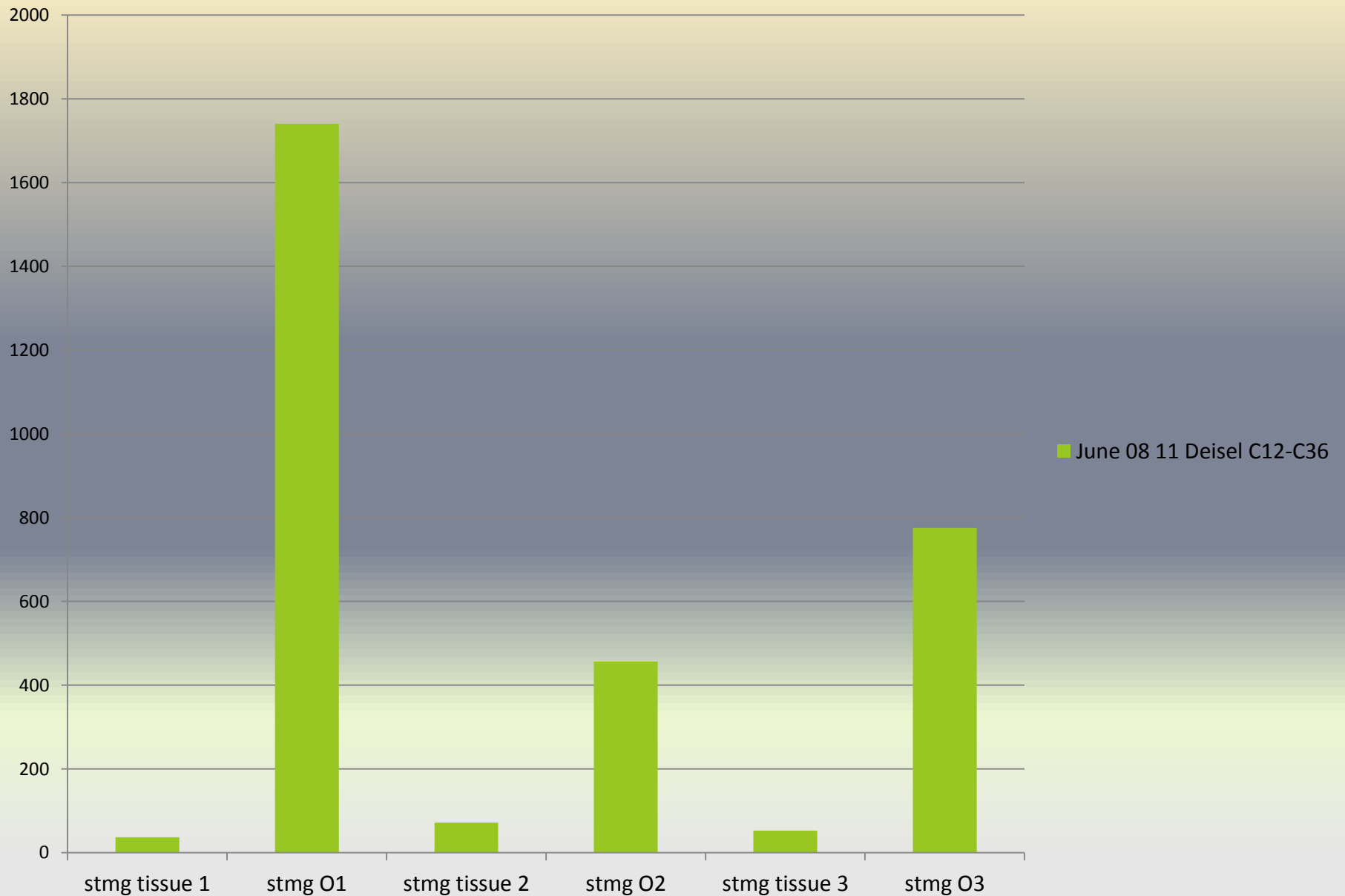
**PAH vs TPH**  
**TPH Diesel Range**  
**8051B and NOAA**  
**NMFS-NWFSC-59**  
**Method**



## Organ vs tissues of 2011



## June 08 11 Deisel C12-C36



# PAH

- ▣ “The FDA has determined, based on a large base of science, that the compounds of greatest concern to human health are the PAHs, and levels of concern have been determined for the PAHs,” Dr. John Stein, a seafood safety expert at NOAA, said in an email. “The methods used for testing are designed for PAHs.”
- ▣ Sniffers for PAH-2010
- ▣ Visual identifiers for MC252 (FLDEP Spring 2011)
- ▣ So far there is no MC252 oil

## Known Information

Oil from fish is common – oil from crude- not common


Fish oil does not contain carcinogenic hydrocarbons

Fish are not normally exposed to COREXIT –

Corexit has a half life of 45 days – you cannot see Corexit by UV lighting- many things in the Marine environment fluoresces

These tests are not longtem exposure -these are dose testing over a certain period of time

Seafood Testing needs to include TPH



BP  
Regional Oil Spill Response Plan – Gulf of Mexico

Section 18  
Dispersant Use  
Plan

ORGANISM TYPE	REPRESENTATIVE SPECIES	RISK FACTOR
Free-swimming shellfish	Brown Shrimp	Commercial species, planktonic eggs/larvae, during migration concentrate near surface at night
	White Shrimp	Commercial species, planktonic larvae, juveniles occur near water surface during offshore migration
Water column-spawning fish	Gulf Menhaden	Large commercial fishery, potential to affect planktonic eggs/larvae
Diving duck	Lesser Scaup	Recreationally managed, aggregate in large rafts floating on water surface, present over 10 miles from shore.

Toxicity values presented in the following summary represent the results of a bioassay used to determine dispersant toxicity to the species listed below (LC 50 test). The LC 50 value is the Lethal Concentration (LC in ppm) causing 50 percent mortality over a given period of time (i.e. 48-hour). The following is a summary for the dispersant COREXIT 9500/9527.

SPECIES	LC50 – COREXIT 9500	LC50 – COREXIT 9527
Menidia beryllina (inland silverside)	25.2 ppm @ 96-hrs	14.57 ppm @ 96-hrs
Fundulus heteroclitus (mummichog)	140 ppm @ 96-hrs	100 ppm @ 96-hrs
Artemia salina (brine shrimp)	21 ppm @ 48-hrs	50 ppm @ 48-hrs
Mysidopsis bahia (mysid shrimp)	32.23 ppm @ 48-hrs	24.14 ppm @ 48-hrs

A Material Safety Data Sheet for Corexit 9500 may be found in **Figure 18-9**. An MSDS for Corexit 9527 may be found in **Figure 18-10**.

#### D. Dispersant Effectiveness

Open water with sufficient depth and volume for mixing and dilution are the preferred conditions for dispersant application. Weathering of oil decreases the effectiveness of dispersants, therefore, initial application should be completed as soon as possible. Dispersants should be considered when the impact of floating oil on sensitive shoreline habitats is greater than the risk of mixing oil into the water column.

In the case of increased contact with an expanding slick after treatment, it should be noted that treated slicks may increase in size initially (10-17 hours) as the interfacial tension at the oil surface is reduced. However, by 18 hours post-treatment, the treated slick is broken up and becomes smaller in area. The net effect of dispersant application is

Title of Document: Regional Oil Spill Response Plan  
Authority: Dan R. Replogle,  
GoM EMG Mgmt Representative  
Scope: GoM EMG  
Issue Date: 12/01/00

UPS-US-SW-GOM-HSE-DOC-00177-2  
Custodian: Earnest Bush,  
Environmental Coordinator  
Document Administrator: Kristy McNease,  
GoM HSE Document Mgmt Administrator

Oil and Grease test- why? Fastest test to make money and not find anything..

Our water quality is constantly threatened by many different sources and types of pollution. Under the Clean Water Act, every must adopt water quality standards to protect, maintain and improve the quality of the nation's surface waters. These standards represent a level of water quality that will support the goal of "swimmable/fishable" waters. Water quality standards are ambient standards as opposed to discharge-type standards. These ambient standards, through a process of back calculation procedure known as total maximum daily loads or wasteload allocations form the basis of water quality based permit limitations that regulate the discharge of pollutants into surface waters under the National Pollutant Discharge Elimination System (NPDES) permit

# CLEAN WATER ACT

State Criteria reevaluation every three  
years

(so far PAH tests show there is no need to reevaluate)

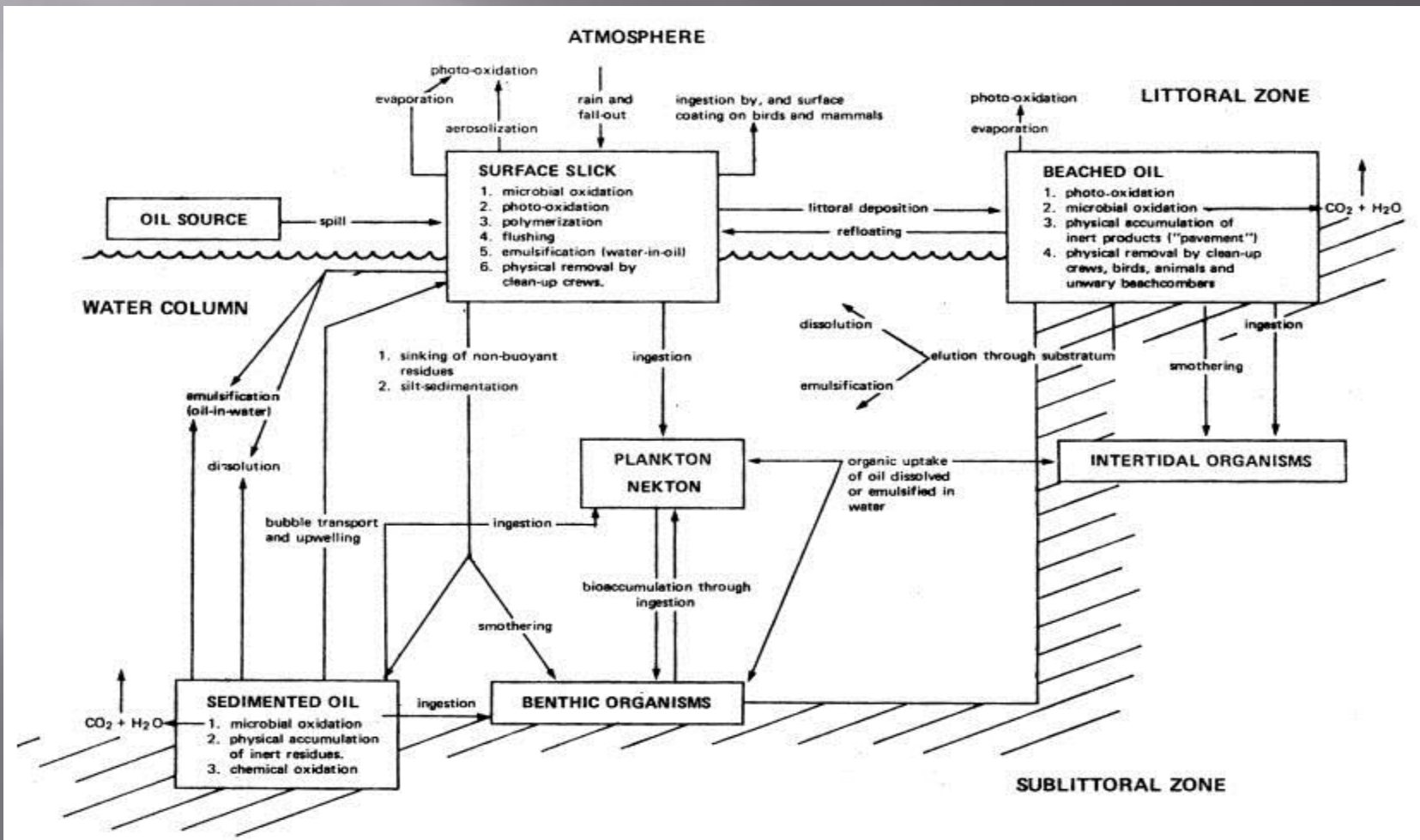
## Water Quality Standards Program

Water quality standards (WQS) are risk-based (also called hazard-based) requirements which set site-specific allowable pollutant levels for individual water bodies, such as rivers, lakes, streams and wetlands. States set WQS by designating uses for the water body (e.g., recreation, water supply, aquatic life, agriculture) and applying **water quality criteria** (numeric pollutant concentrations and narrative requirements) to protect the designated uses. An **antidegradation policy** is also issued by each state to maintain and protect existing uses and high quality waters.<sup>[21]</sup>

the "best available technology" (

Clean Water Act needs to be changed to include new technology and the State needs to except new technology in their methods.

- ❑ First order of effects-
- ❑ Second order of effects
- ❑ Third order of effects (Upwelling buried oil can cause the order of effects to repeat itself)



# First Order of Effects

## ▣ Physical and Internal

- Physical
- Current Observation from Universities in Louisiana and Alabama
- Sick Fish- Lesions and discoloration
- Internal Toxicity
- Supports current >C5- 35 petroleum hydrocarbon testing rather than current human health criteria of C1-C5 (PAH).
- Organs are containing the presence of Diesel range hydrocarbons.
- Organs are performing as needed but the processing of toxins are too high to support a healthy immune system in the fish- pathogens , diseases and cancers

# Second Order of Effects

- ▣ Include changes in populations of each species with respect to size-frequency and age structure, productivity, standing crop, reproductive abilities, etc.
- ▣ Some Principal Investigators are seeing less of the key species and more of the pioneer species
- ▣ These are generally intermediate-term effects which show up in weeks, months, and for some long-lived species, years.

# Third Order of Effects

- ▣ Include changes at the community or ecosystem level with respect to relationships within or between trophic levels, species composition and/or abundance, and other aspects of community dynamics.
- ▣ These changes are often the result of subtle, sub-lethal effects which may not show up for months or years.
- ▣ Disputable? Maybe but documented in other references post oil spill.

# Conclusion

- PAH is not designed to find crude compounds which can effect fish long term
- Fish with TPH in their tissue show higher amounts of TPH in the organs
- Since oysters do not process PAH, they make great windows to water quality over time – until 100% mortality such as the case of The City of Gulf Breeze's Deadman's Island vertical reefs in Gulf Breeze, Florida
- TPH needs to be a priority test in Human Health Seafood Testing instead of PAH or "sniff tests"
- The order of effects may continue with ongoing upwelling so recovery in primary production may take years as demonstrated in previous oil spills.
- CWA needs to reflect new technology in reevaluation

# Questions?

*Heather Reed*

*<http://www.linkedin.com/in/heatherreedpensacola>*

*[hreed@ecoconsultingservices.com](mailto:hreed@ecoconsultingservices.com)*

*Visit*

*[www.ecologicalconsultingservices.com](http://www.ecologicalconsultingservices.com)*



# ECS

38 S Blue Angel Parkway #346

Pensacola FL 32506

850-417-7008