

Responding to the Deepwater Horizon Oil Spill: Interlaboratory Comparisons, Sample Protocol Development and Sample Archival

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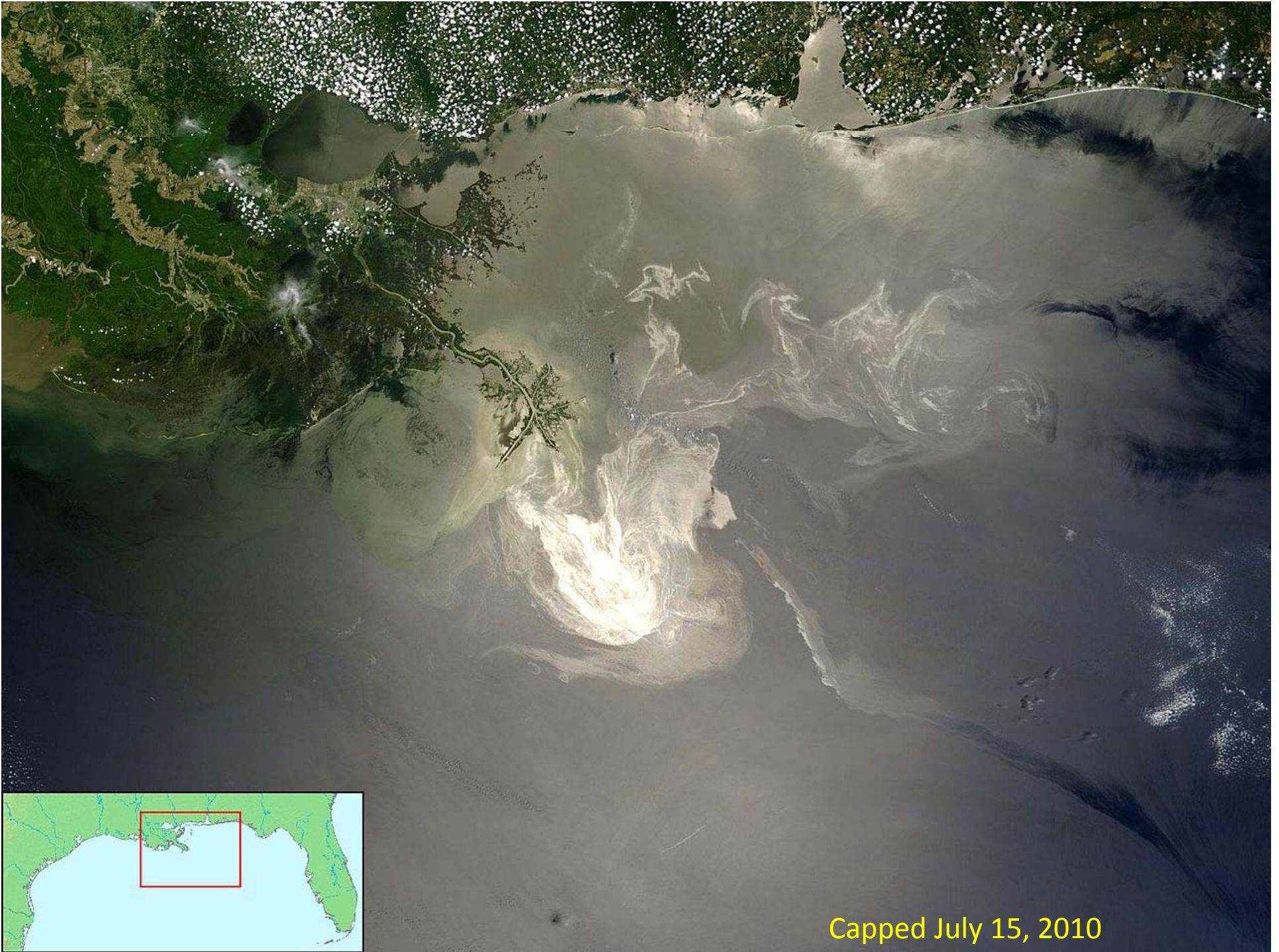
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

**HOLLINGS MARINE
LABORATORY**





April 20, 2010



Capped July 15, 2010



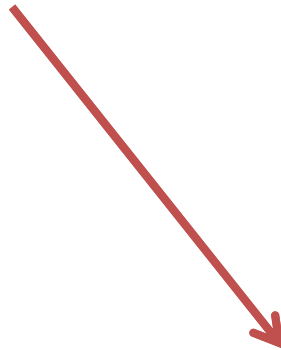
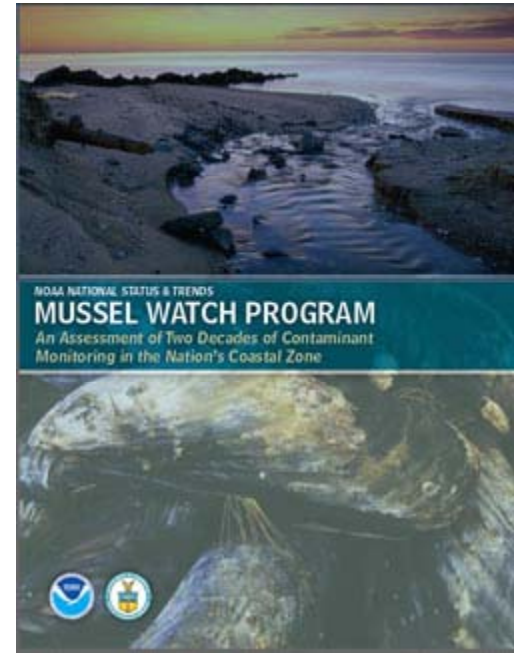
NOAA FISHERIES SERVICE
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION



Challenges

- What do you sample?
- What do measure?
 - Can we link oil in a sample to that from the Macondo Well?
 - How much oil is in a sample?
 - What about animals that ingest and metabolize oil (e.g. marine mammals?)
- How to take samples of marine organisms to gauge oil exposure?
- Legal issues, chain of custody etc.

Interlaboratory Comparison Exercises
Specimen Banking
Standard Reference Materials



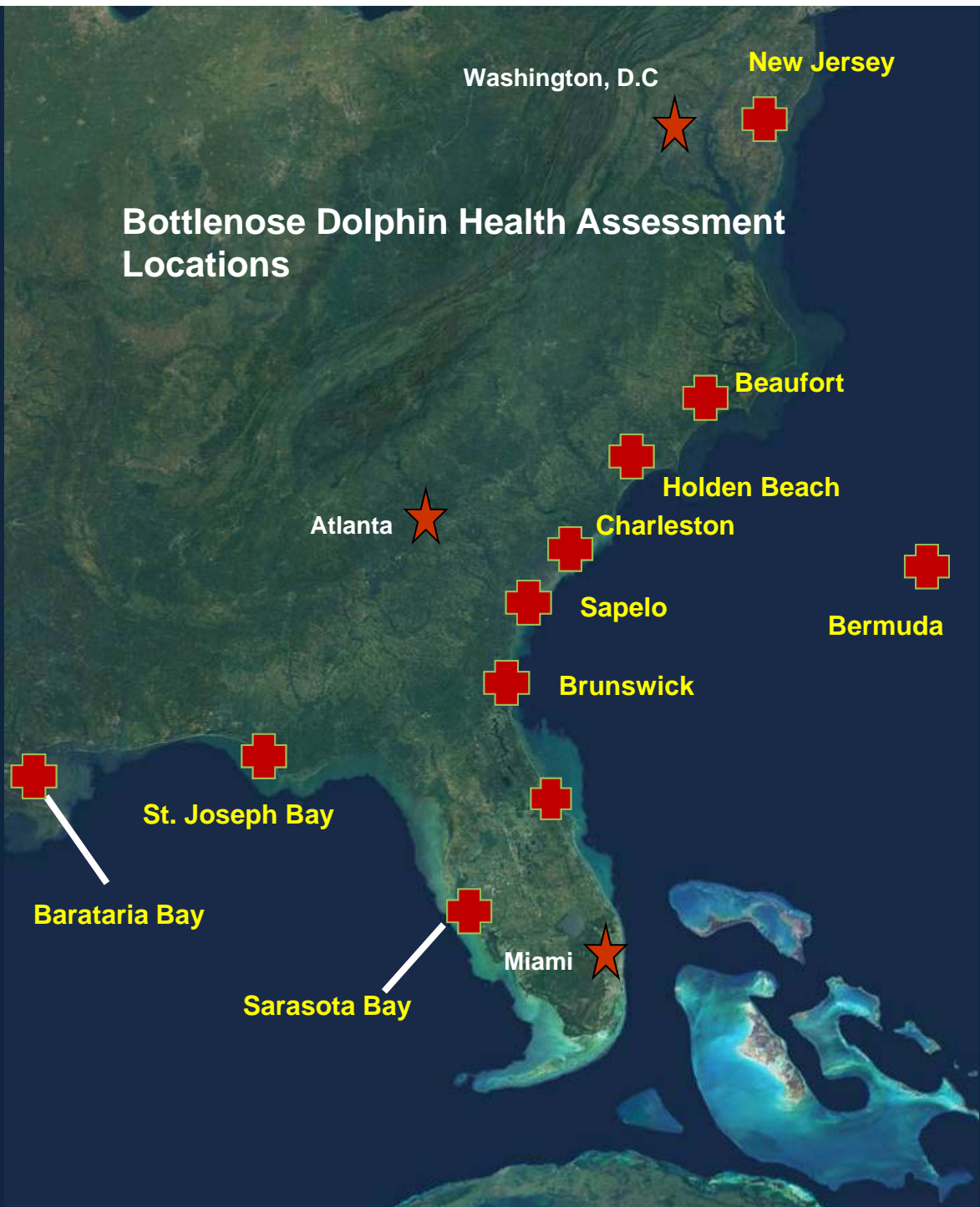
Interlaboratory Comparison Exercises
Specimen Banking
Reference Materials
Dolphin Health Assessments
Sample Analysis
Sampling Procedures and Protocols

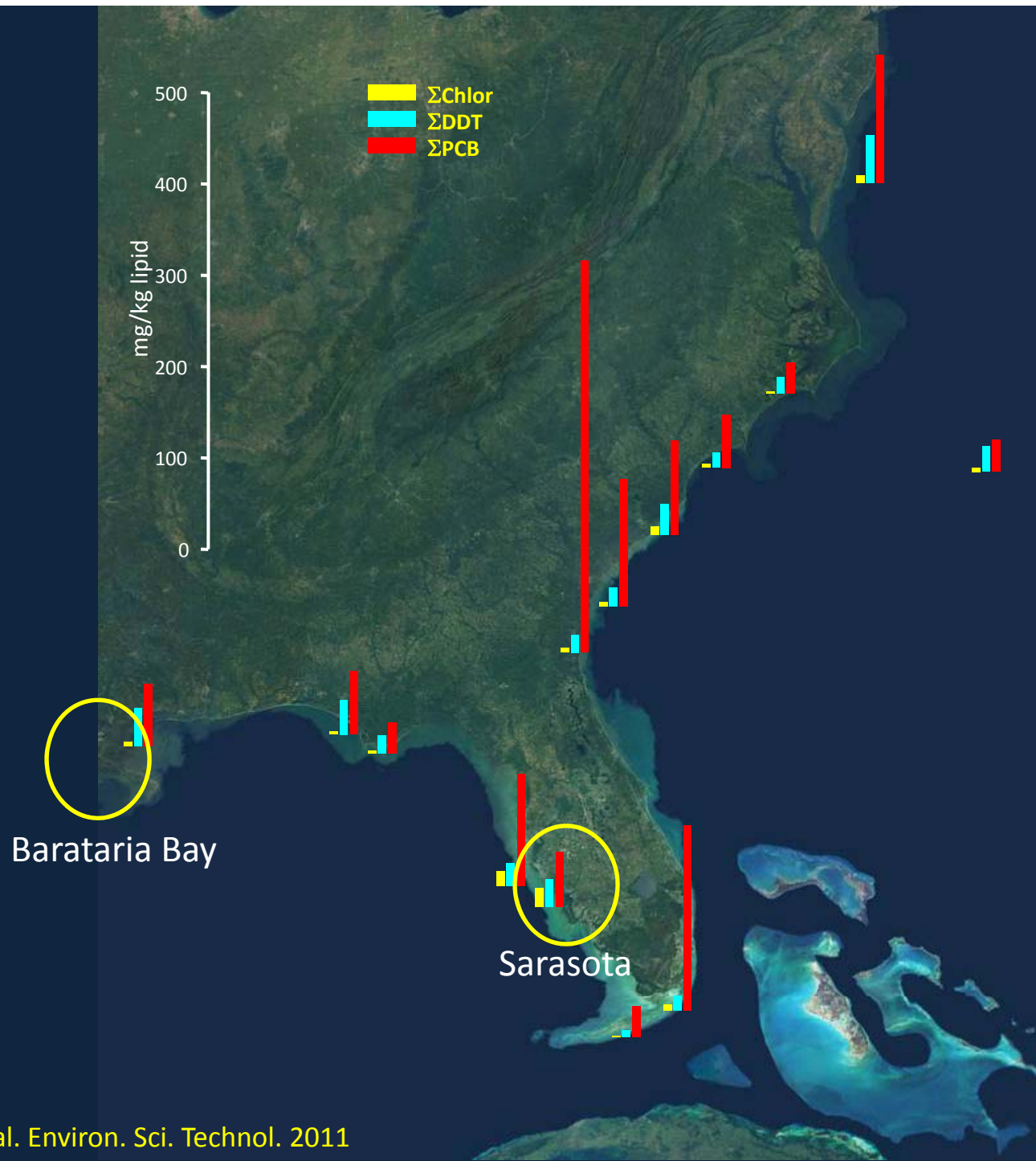


Collaborating with NOAA

- Developing sampling plans
 - Samples from living animals (health assessment/remote biopsy)
 - Stranded animals
- Providing for sample archival
 - Samples needed to be stored frozen in a secure facility
 - Chain of custody must be maintained
 - Sample distribution
- Assessing laboratory agreement

Bottlenose Dolphin Health Assessment Locations







NMFS Permit No. 932-1905/MA-009526



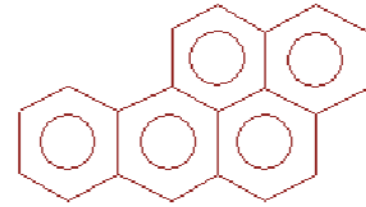
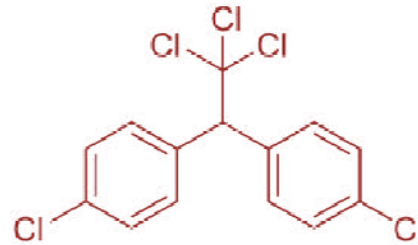
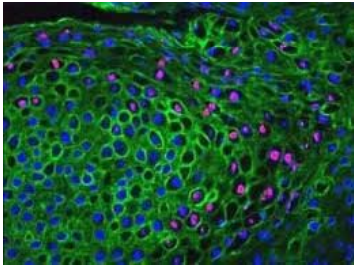
Photo by Sarasota Dolphin Research Program, taken under National Marine Fisheries Service Scientific Research Permit No. 15543



NOAA Permit 932-1905-MA-009526

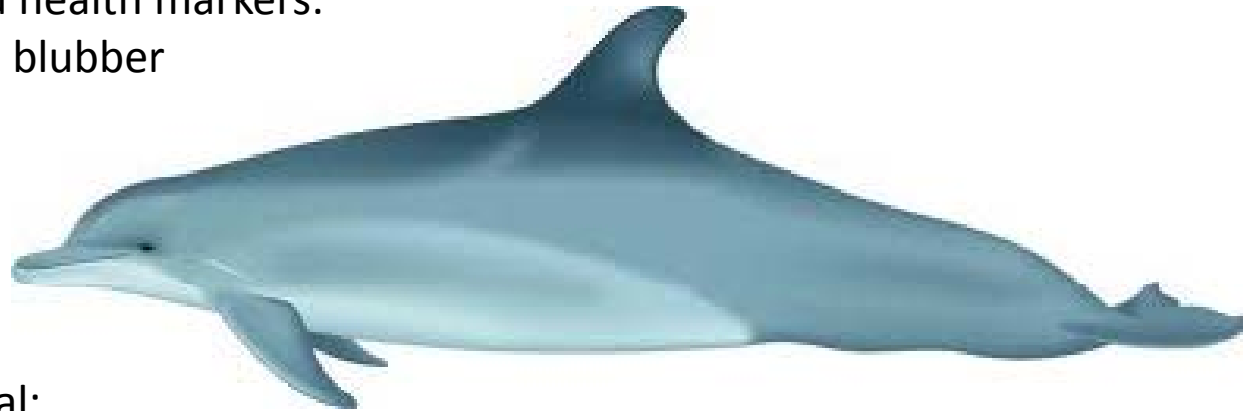


NOAA Permit 932-1905-MA-009526

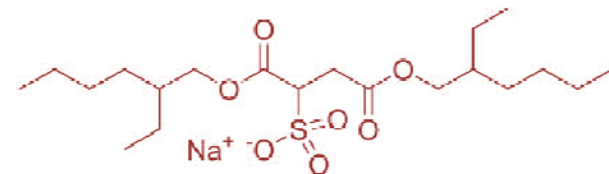
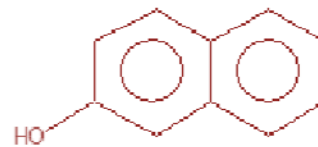


Parent PAHs, POPs: Blubber and plasma

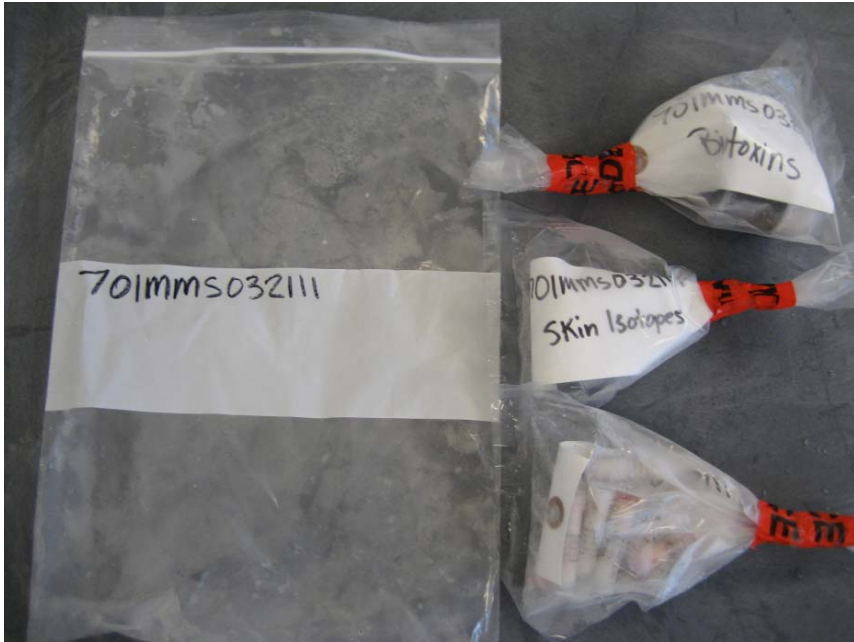
Biomarkers and health markers:
Blood, skin and blubber



Sample archival:
serum, plasma, blubber, whole blood



Metabolites/DOSS: Urine and plasma



Interlaboratory Comparison Exercises



Marine Sediment



Crude Oil

Standard
Reference Material
(SRM)
+
Unknown Sample



Mussel Tissue



Spiked Alligator Blood
(no SRM available)

Interlaboratory Comparison Exercises

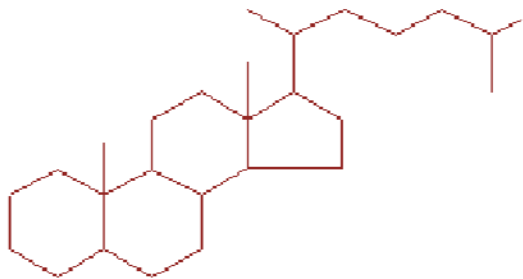
Exercise	Samples	Analytes	#Labs	Reference
Marine Sediment QA10SED01	QA10SED01 SRM 1941b Organics in Marine Sediment	PAHs, Alkyl PAHs, hopanes and steranes	33	NISTIR 7792
Crude Oil QA10OIL01	QA10OIL01 (→ SRM 2779) SRM 1582 Petroleum Crude Oil	PAHs, Alkyl PAHs, hopanes and steranes	26	NISTIR 7793
Tissue QA10TIS01	QA10TIS01 SRM 1974b Organics in Mussel Tissue (<i>Mytilus edulis</i>).	PAHs, Alkyl PAHs, hopanes and steranes	34	NISTIR 7819
Blood QA11Blood01	QA11Plasma, QA11WholeBlood, QA11Solution#1-PAH and QA11Solution#2-DOSS	parent PAHs, alkylated PAHs, hydroxylated PAHs and DOSS.	6	NISTIR 7869

SRMs Used

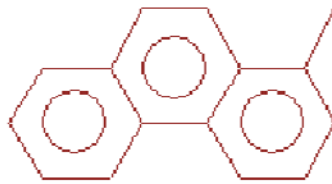
SRM	Certified PAHs	PAHs with reference values	Comments
SRM 1941b- Organics in Marine Sediment	24	44	Values for 10 hopanes and steranes
SRM 1582- Crude Oil	6	7	
SRM 1974b- Organics in Mussel Tissue (<i>Mytilus edulis</i>)	22	16	Being replaced by SRM 1974c

Target PAHs

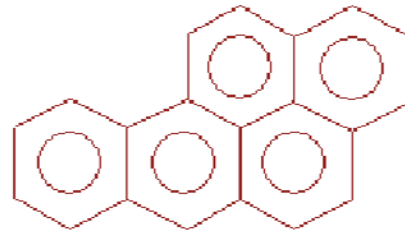
- Parent PAHs
- Alkyl PAHs
- Alkyl PAH Groups
- Oil “biomarkers” i.e., hopanes and steranes



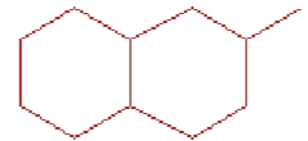
cholestane



1-methylphenanthrene



Bezo[a]pyrene



2-methyl decalin

Interlab 3: Mussel Tissue

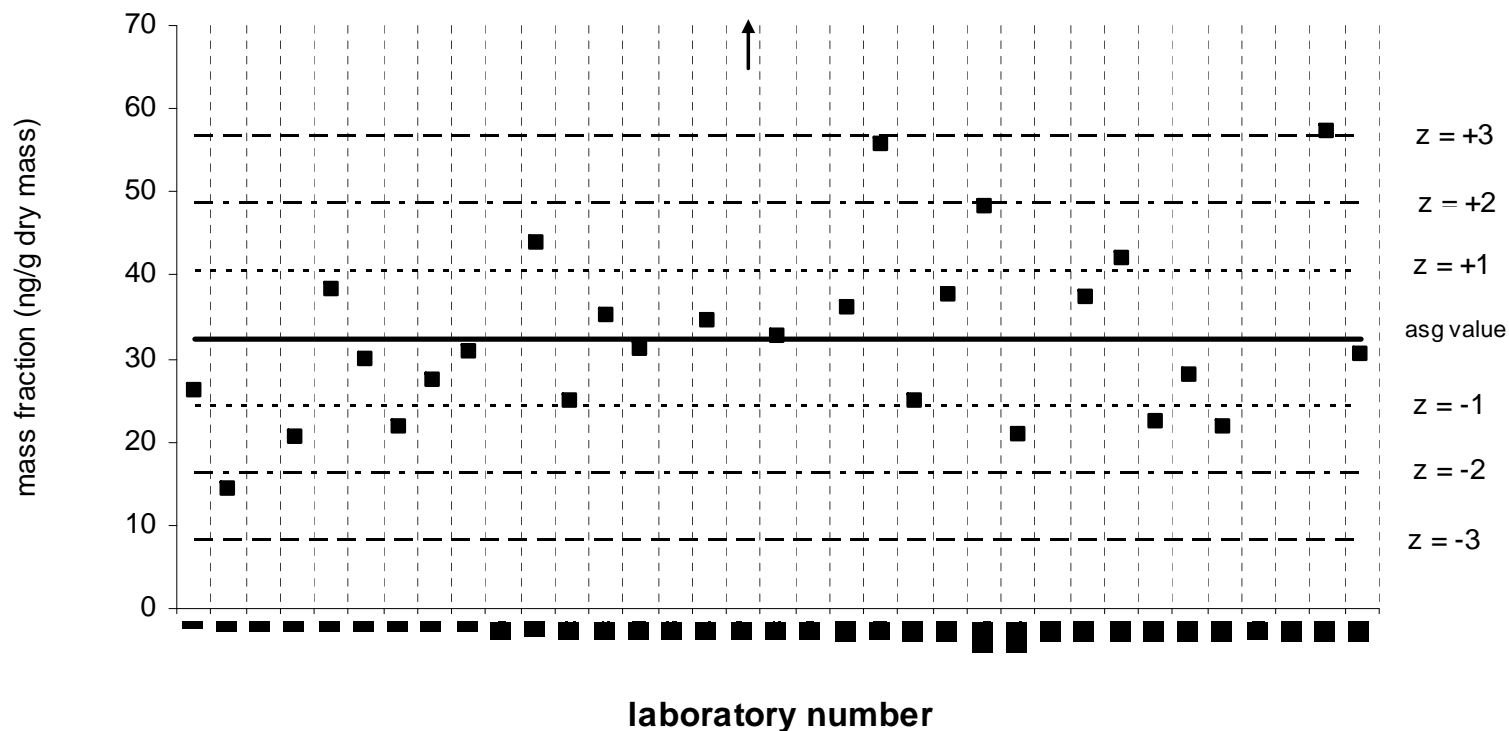
benzo[b]fluoranthene

QA10TIS01

Assigned value = 32.4 ng/g dry mass $s = 10.5$ ng/g dry mass 95% CI = 4.0 ng/g dry mass

Median value = 30.9 ng/g dry mass

Reported Results: 33 Quantitative Results: 28



Solid line : exercise assigned value (EAV); dotted line: $z = \pm 1$ (25% from EAV); dotted/dashed line: $z = \pm 2$ (50% from EAV); dashed line: $z = \pm 3$ (75% from EAV)

Interlab 3: Mussel Tissue

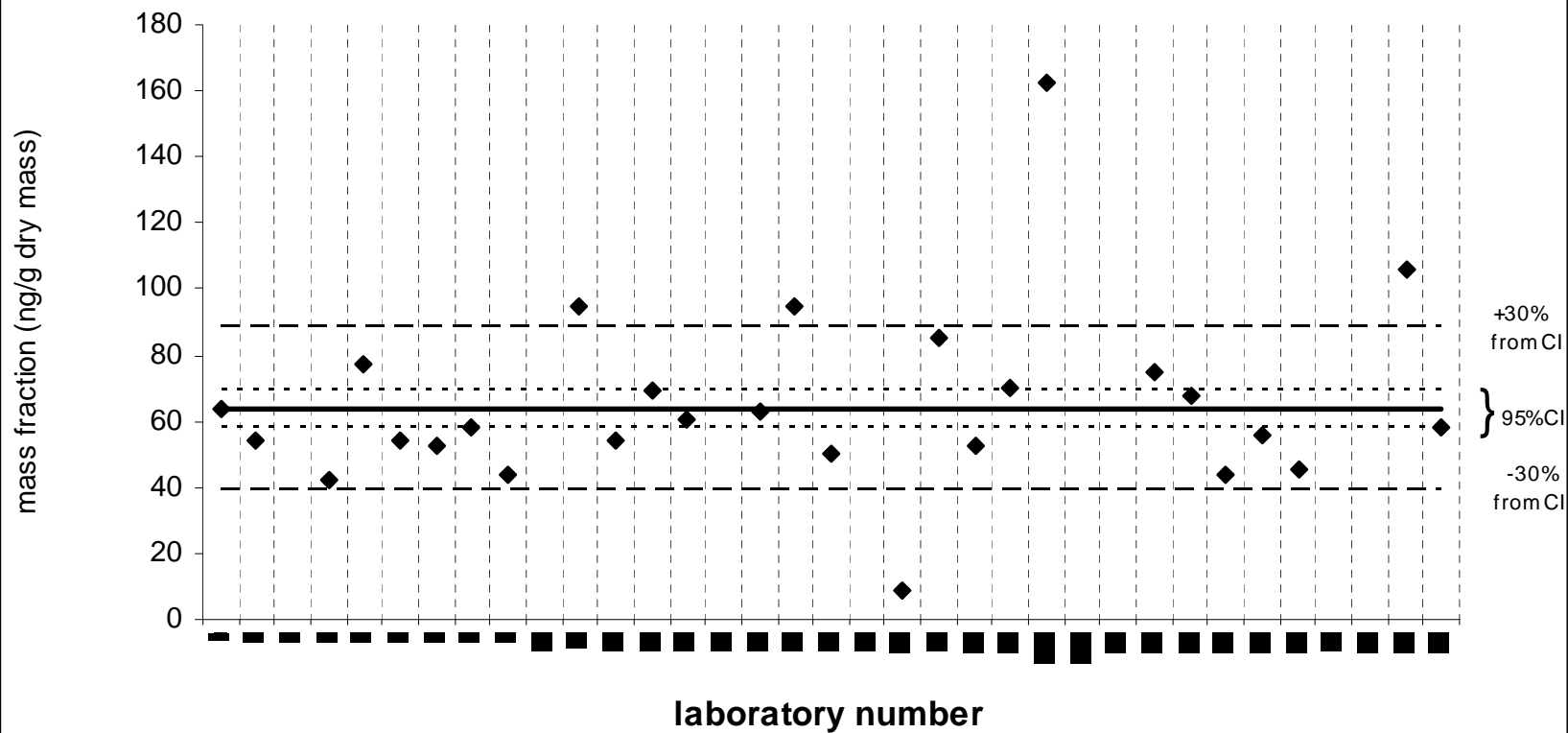
benzo[b]fluoranthene

SRM 1974b

Certified Value = 63.8 ng/g dry mass ; 95% CI 5.8 ng/g dry mass: Median value = 58.5 ng/g dry mass

Reported Results: 31

Quantitative Results: 27



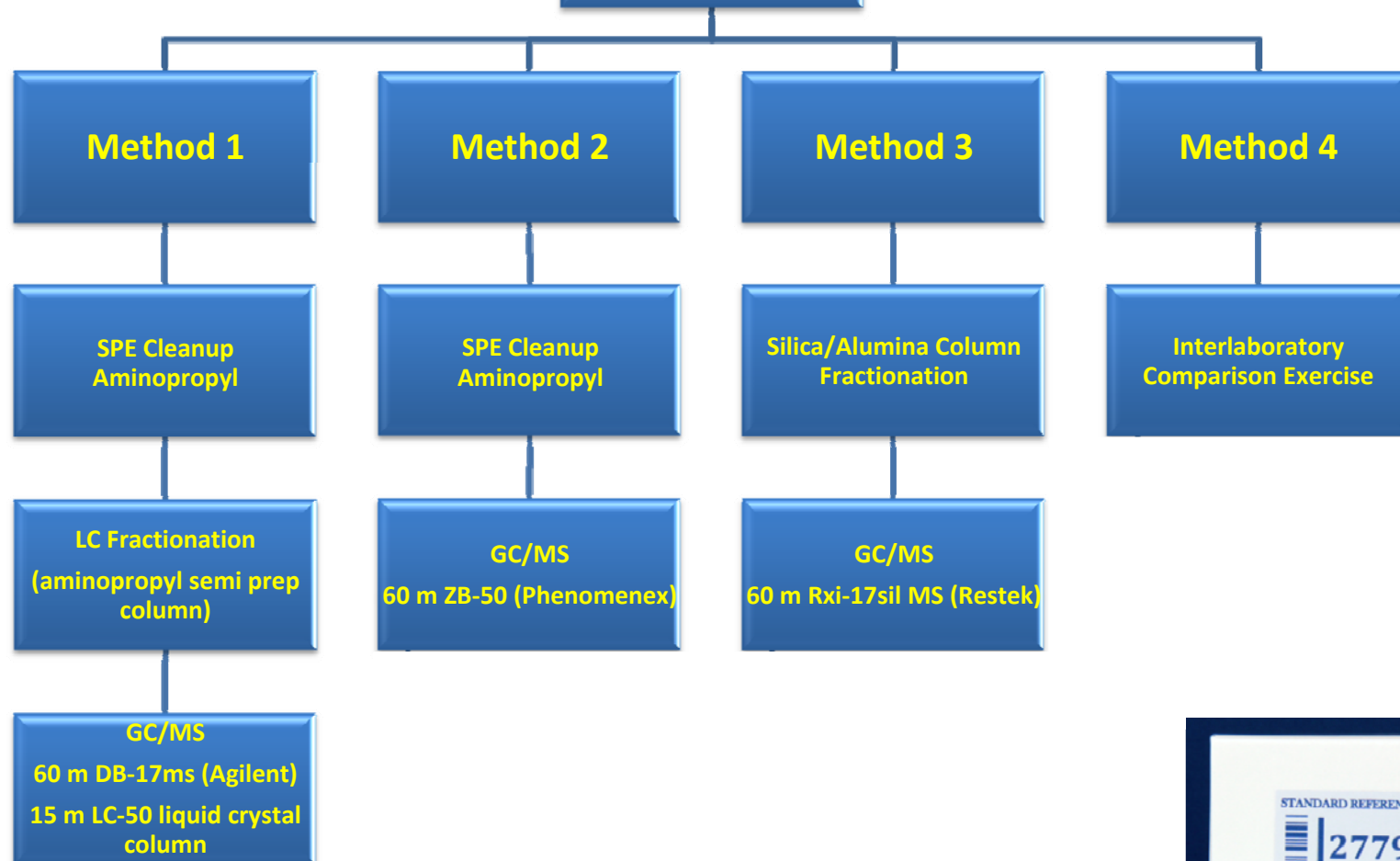
Solid line: value from Certificate of Analysis ; dotted line: 95% confidence limits; dashed line: 30% from 95% confidence limits

SRM 2779: A New Standard Reference Material

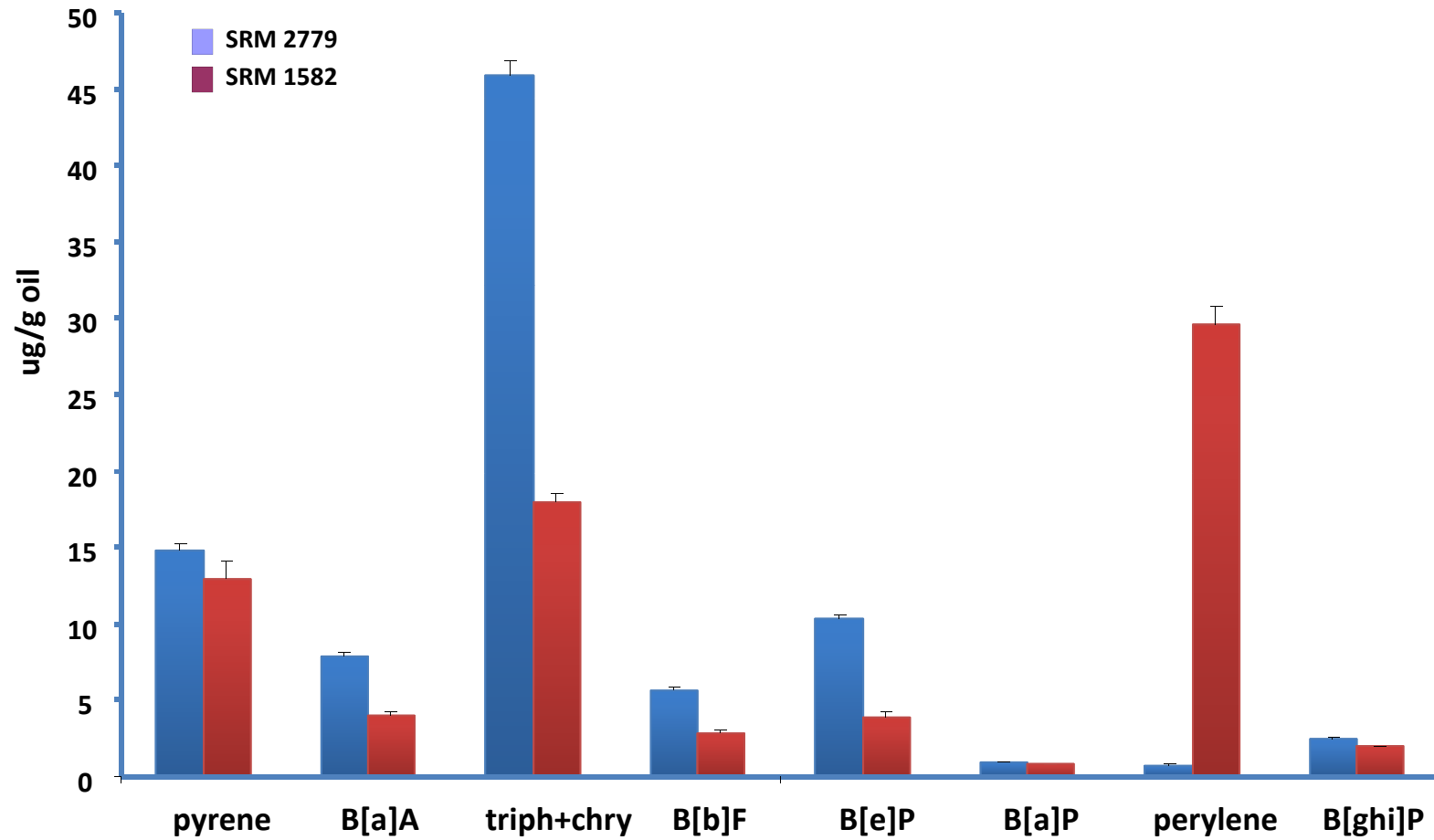
- Certified for 14 parent, 6 alkyl PAHs
- Reference values for
 - 12 Parent and 10 alkyl PAHs
 - 9 alkyl PAH groups
 - 13 hopanes and steranes.



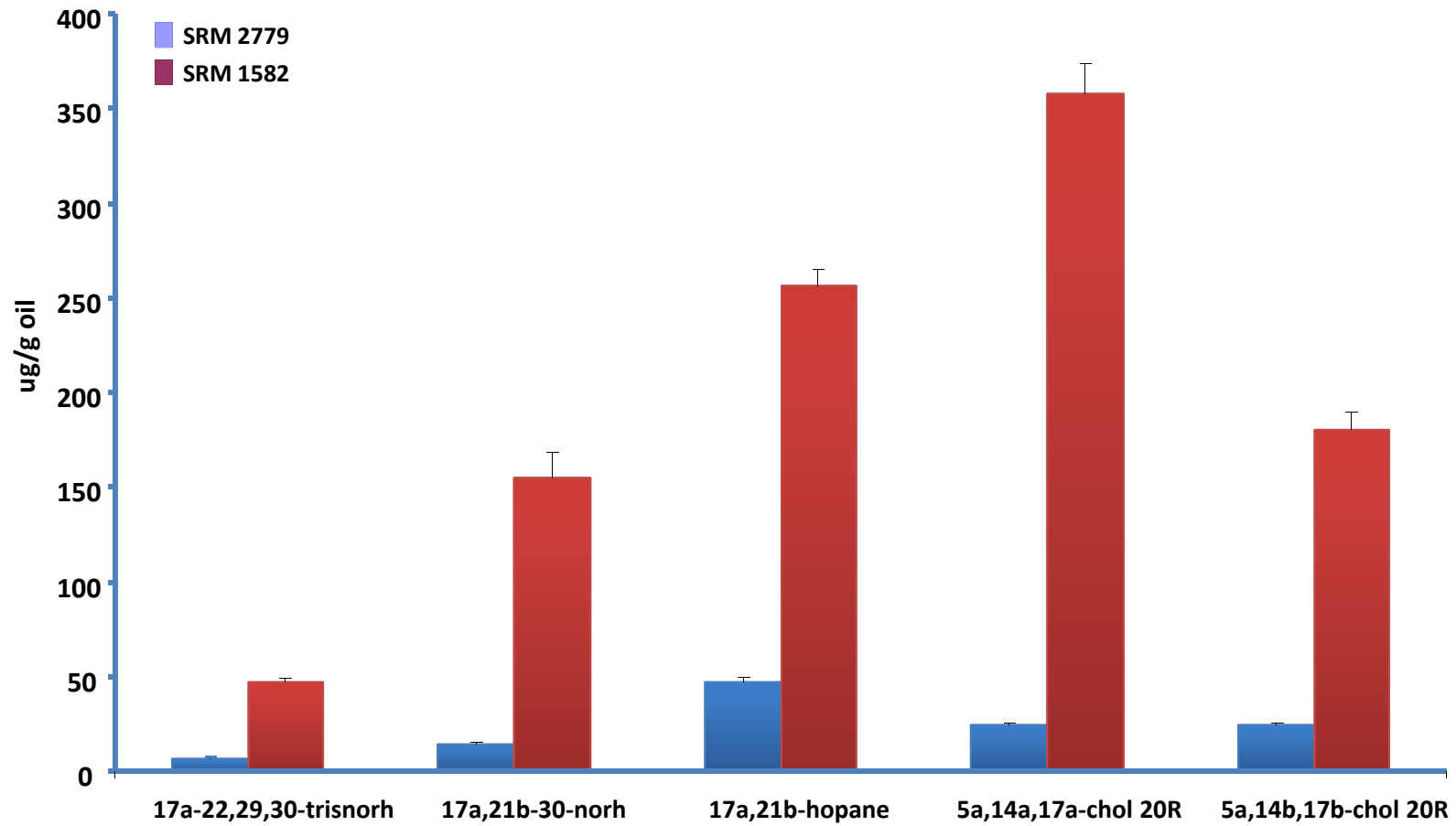
SRM 2779



SRM 2779 vs. SRM 1582

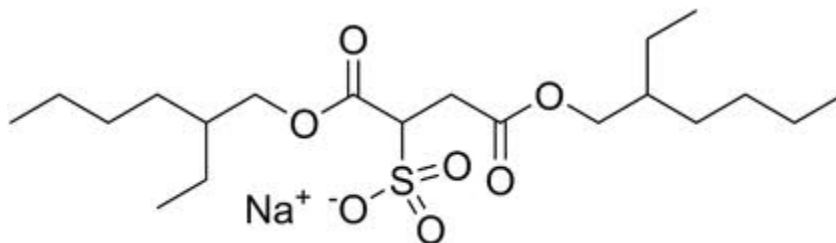


SRM 2779 vs. SRM 1582



Dioctyl Sodium Sulfosuccinate (DOSS; ng/g) in Amended Alligator Blood

Test Material	Laboratory			Mean	Target
	1	2	3		
Solution	116	110	116	114(3.5)	110
Plasma	293	303	330	309(19)	301
Whole Blood	276	272	282	277(5.0)	300



Summary and Conclusions

- NOAA depended heavily existing collaboration with NIST
 - Previous sampling procedures for POPs adapted for PAHs
 - NIST Environmental Specimen Bank=secure facility for sample storage
 - NIST interlaboratory comparison protocol applied to QC of Deepwater Horizon labs was valuable
- NOAA/DOI preparedness needs to be improved

NIST

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Acknowledgements

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