

A Biomarker-Based Approach Identifying Contaminated Sediments as the Primary Source of Oil Sheen at Mississippi Canyon Block 20

Christopher M. Reddy

Makepeace Environmental Solutions, LLC

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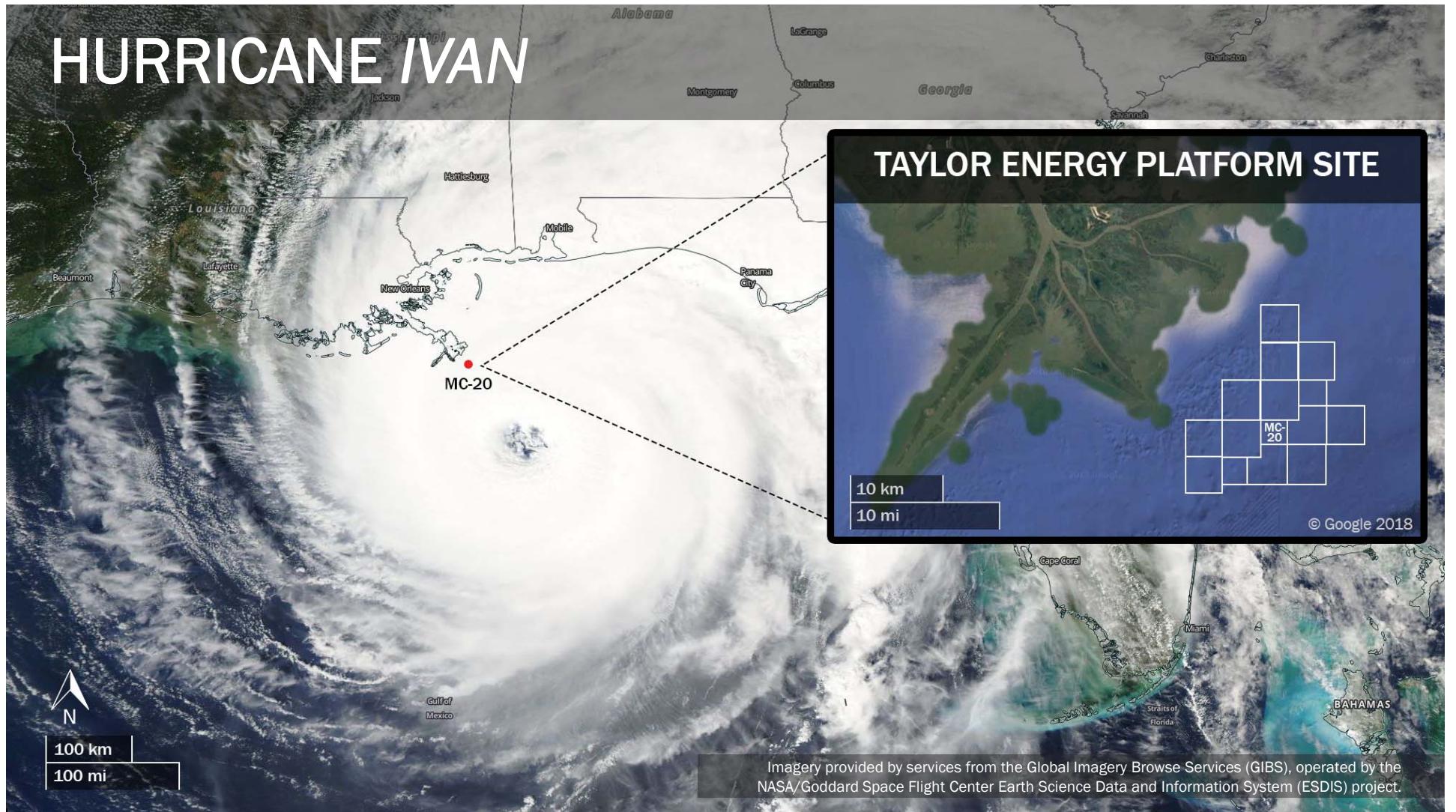
Co-authors:

- Edward Overton, Louisiana State University
- Richard Camilli, Navistry Corporation
- Wade Bryant, CK Associates

Taylor Platform, MC20; Pre-Hurricane Ivan (2004)

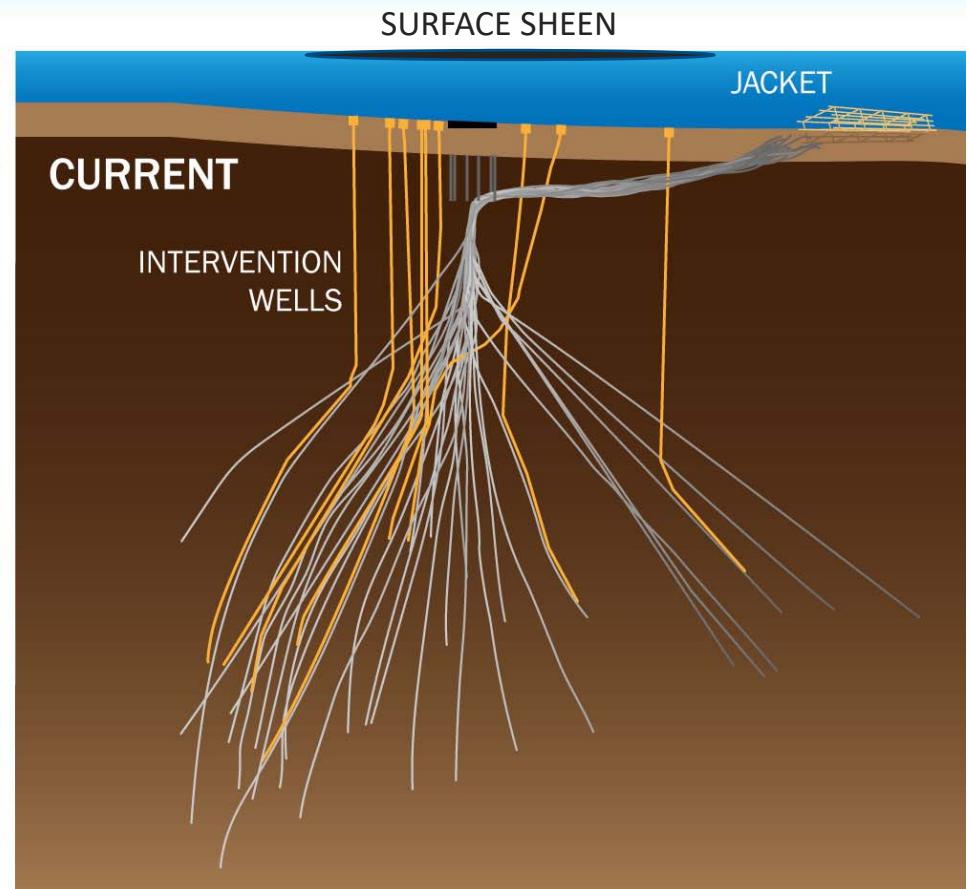
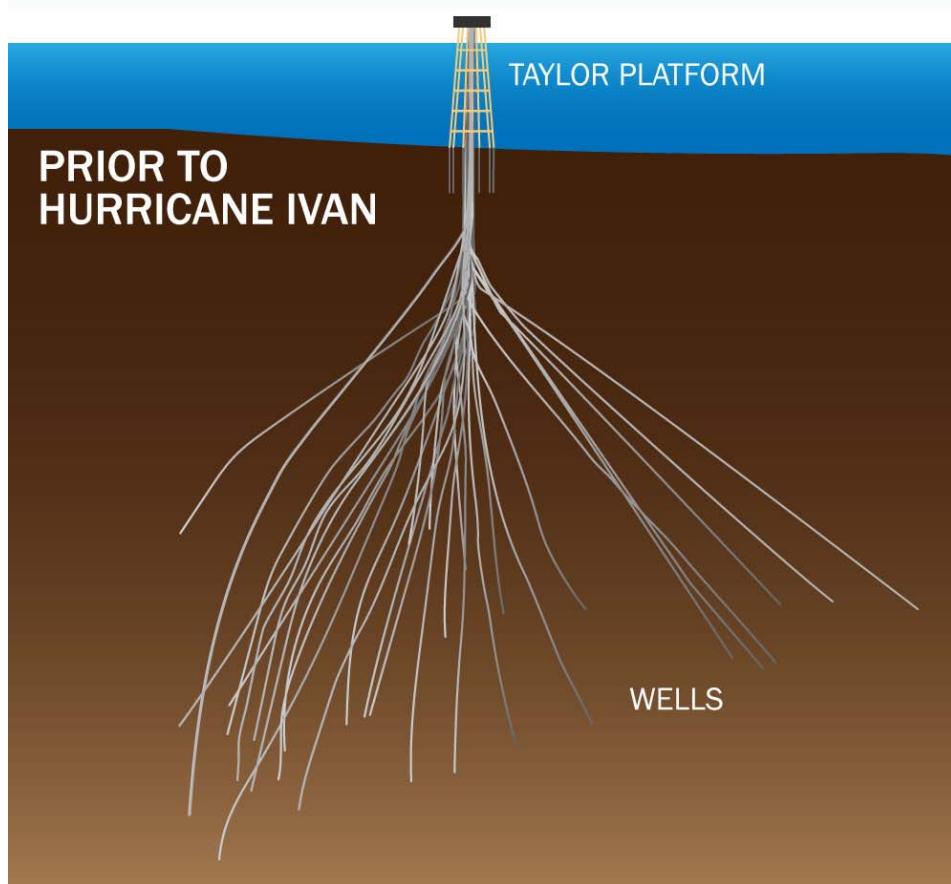


HURRICANE IVAN



“Waves generated by *Ivan* were the largest ever measured”

Teague, E. et al. (2007)



Two interagency and RP task-forces have considered the sheen-source location(s) with field operations

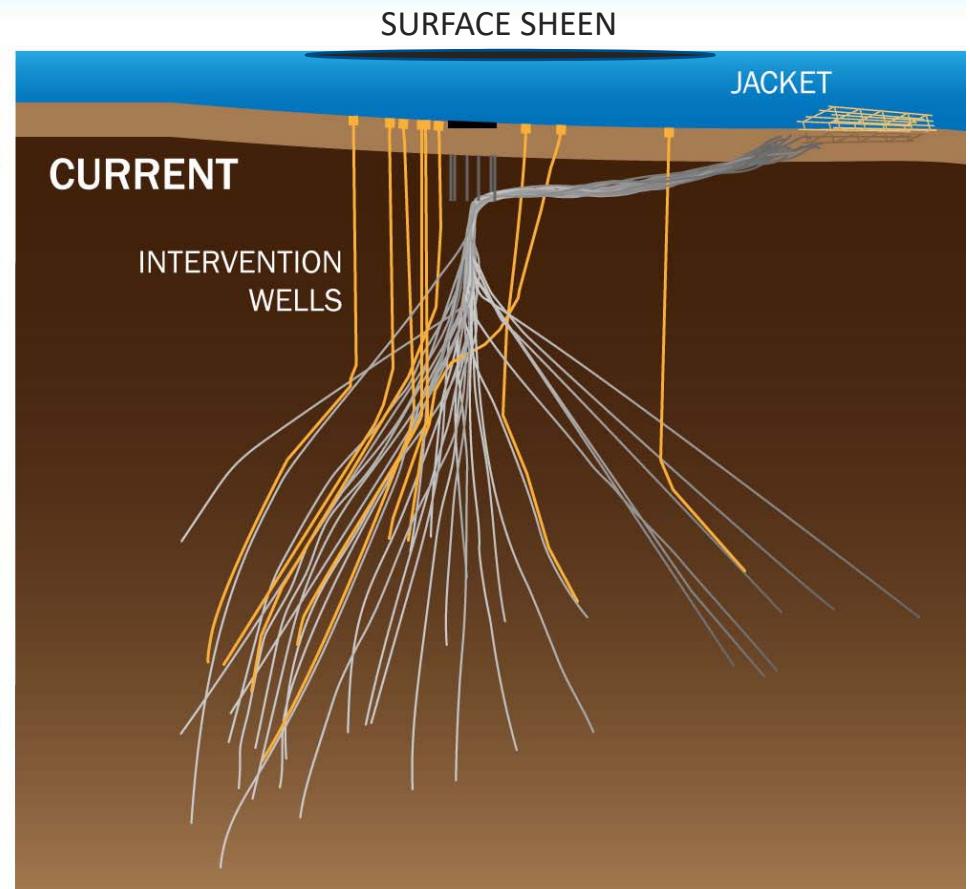
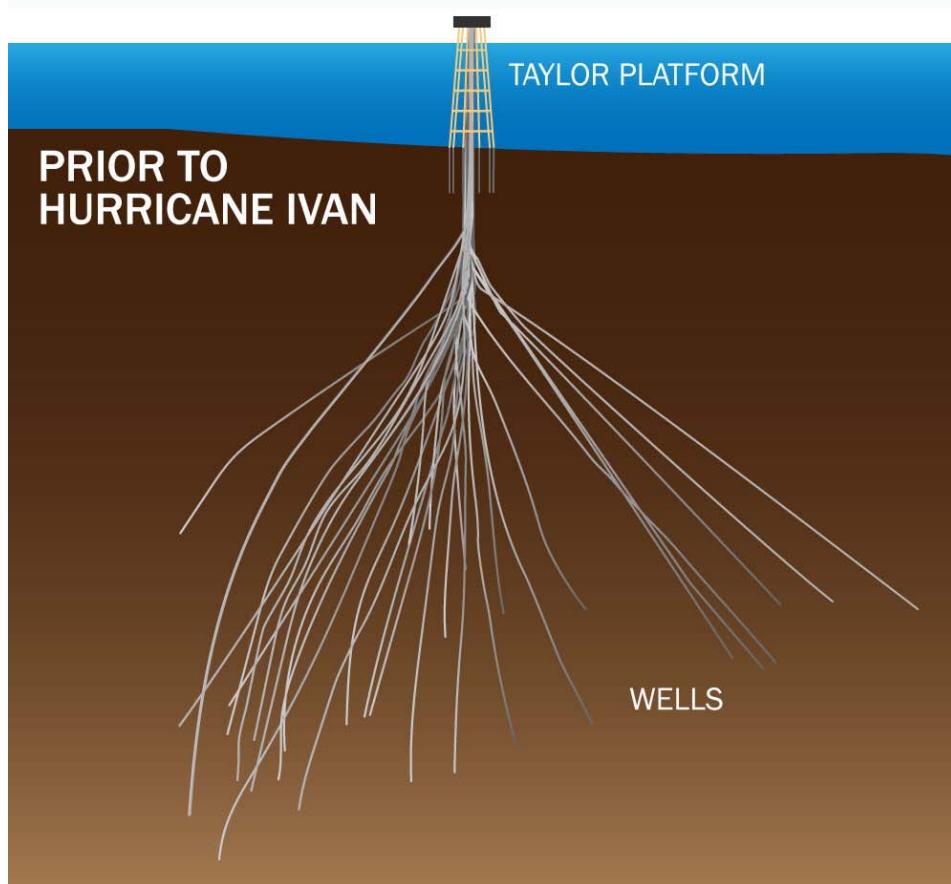
- Sheen Source Location Group (2012-2013)
- Sheen Source Location Working Group (2016-2017)

The results of these field studies and their interpretations will be used in this presentation.



“Waves generated by *Ivan* were the largest ever measured”

Teague, E. et al. (2007)

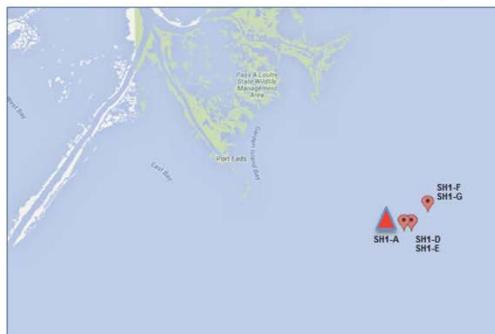


Sediment collection: July 2012 and Feb 2013

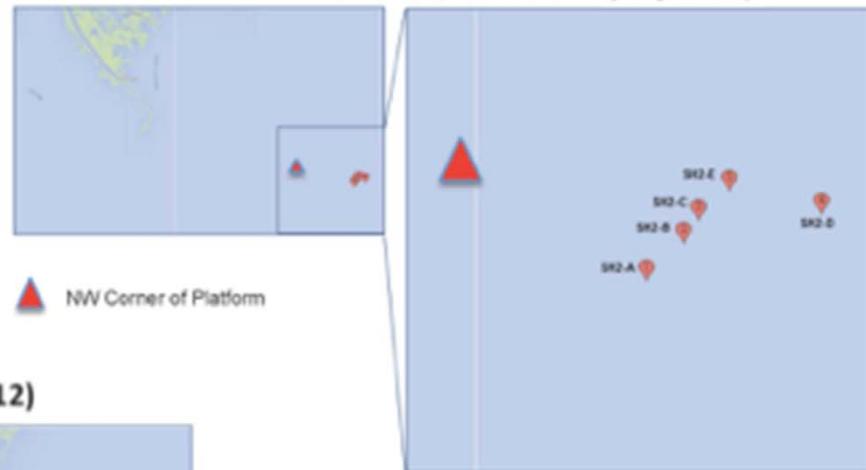


**Surface sheens: July 2012: three transects; Feb 2013:
one transect**

SH1 Sheen Track (July 2012)



SH2 Sheen Track (July 2012)



SH3 Sheen Track (July 2012)



SH4 Sheen Track (Feb 2013)



Key outcomes from Sheen Source Location Group (2012-2013)

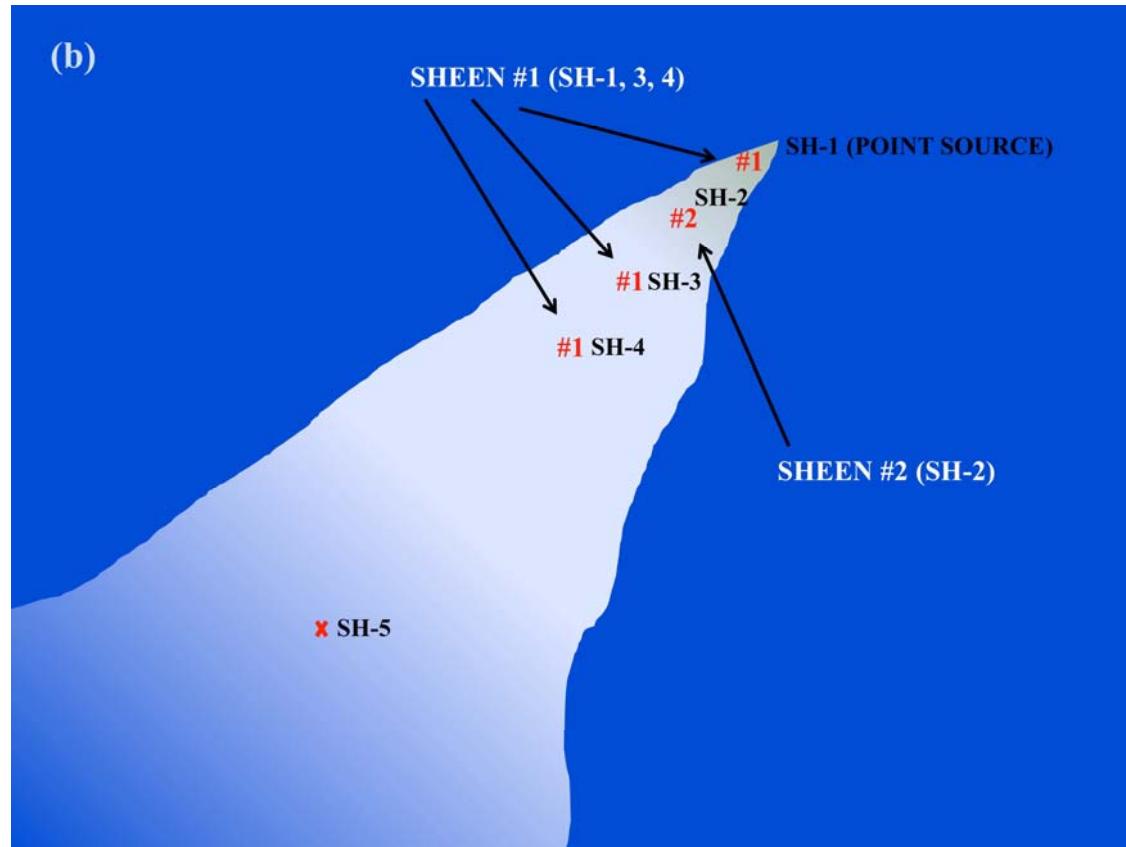
2012

- Coast Guard Marine Safety Laboratory (MSL), “....differences are very subtle....NOTE: Comparison of these samples [sheens] suggest the spilled oil is coming from a non-homogeneous source”.
- When compared to sediments collected near the former well bay, no matches to 2012 sheens (former well-bay).

2013

- MSL observed heterogeneity again in surface sheens.
- When compared to sediments collected near the jacket (diver cores), “somewhat similar” or “common source” to 2013 surface sheens.

February Sheen Transect 2013



Prepared by Jason Screws (USCG)

Charge of the SSLWG (2016)

Best captured by paraphrasing the Federal On-Scene Coordinator Captain Philip Schifflin (USCG),

“..I want the x/y/z coordinates on the ocean floor where the majority of oil is released, which are causing surface sheens...”

Research plan

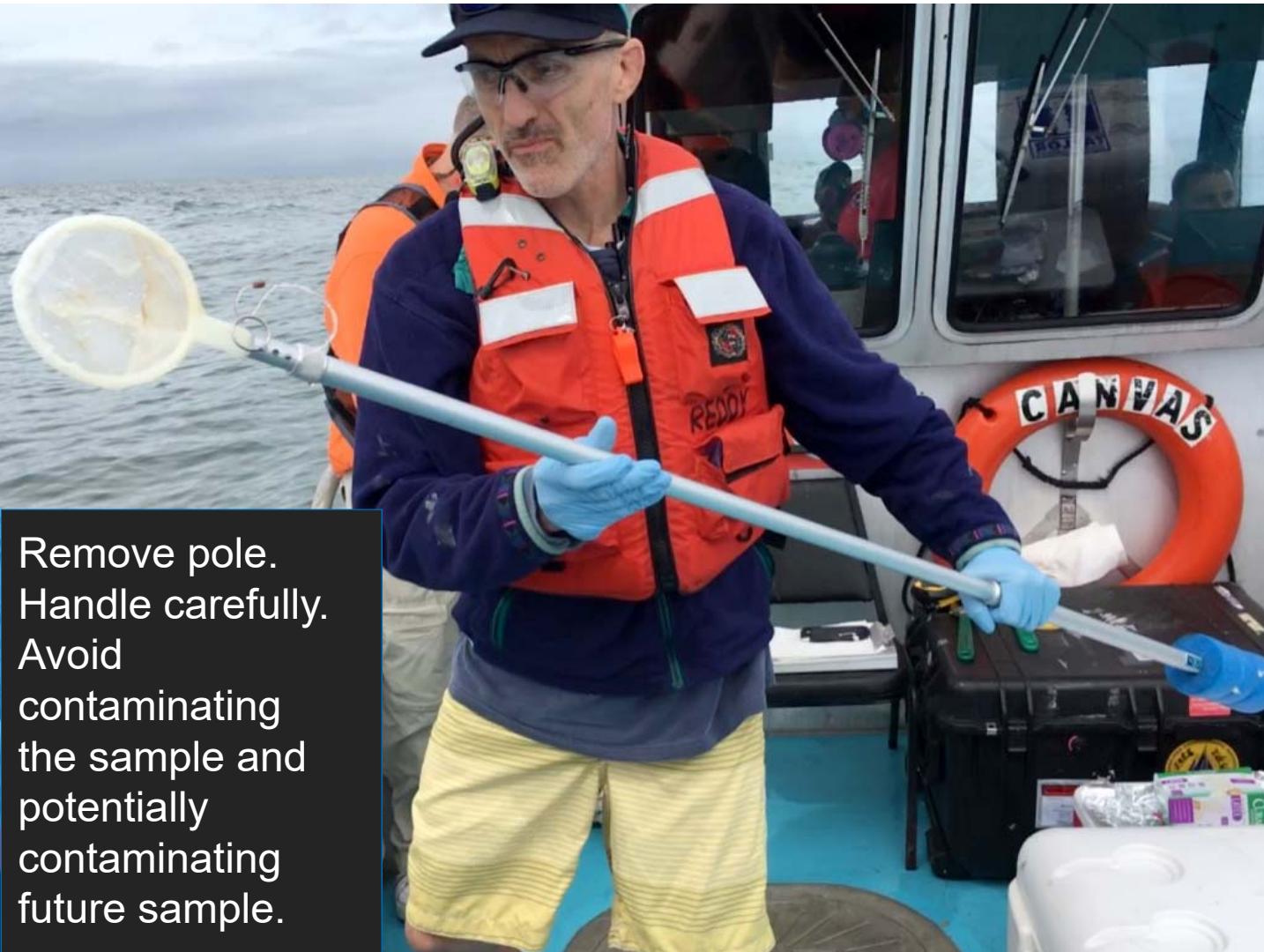
- Collect discrete, recently surfaced residue samples, time-stamped and geo-referenced.
- Geo-referencing with acoustic and physical observations, thus enabling integration of the chemical analyses with physical and visual field observations.
- Chemically analyze samples at Alpha Analytical (Mansfield, MA) with four-tier forensic approach.

Available samples

- 2012/2013/2017 surface sheens.
- 2012/2013 sediment cores.
- Crude oil from local block MC21 as a proxy for fresh oil (not discussed but no matches to surface sheens).

Skim the sheen.
Keep the net at
the very surface.
Avoid excessive
drag on the net.
It may rip. The
duration of
sampling should
be predefined or
with input from
others. Be
careful. Use the
telescoping
feature of the
pole.





Remove pole.
Handle carefully.
Avoid
contaminating
the sample and
potentially
contaminating
future sample.

Summary of Dr. Overton's Tier 1 (GC-FID) and 2 (GC-MS EICs) analysis

- Even with compositional similarities, every sample was distinct, underscoring the fact that the probable source has a heterogeneous composition.
- A heterogeneous source is scientifically reasonable when considering the base of the jacket was a mix of different oil residues.

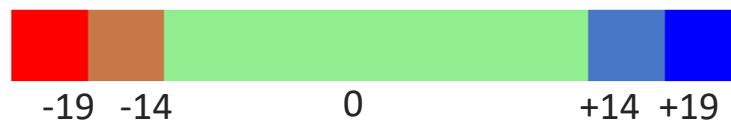
Tier 3 Analysis: Biomarkers

- Used a standard set of "diagnostic ratios".
- Analysis was done CEN/TR 15522-2.
- Due to the complexity of the MC20 wells and unusual nature of the site, we expanded this method to include “probable matches”.

We employed heat maps to present quantitative results to the number of comparisons for Tier 3 biomarkers.

Percent difference between samples

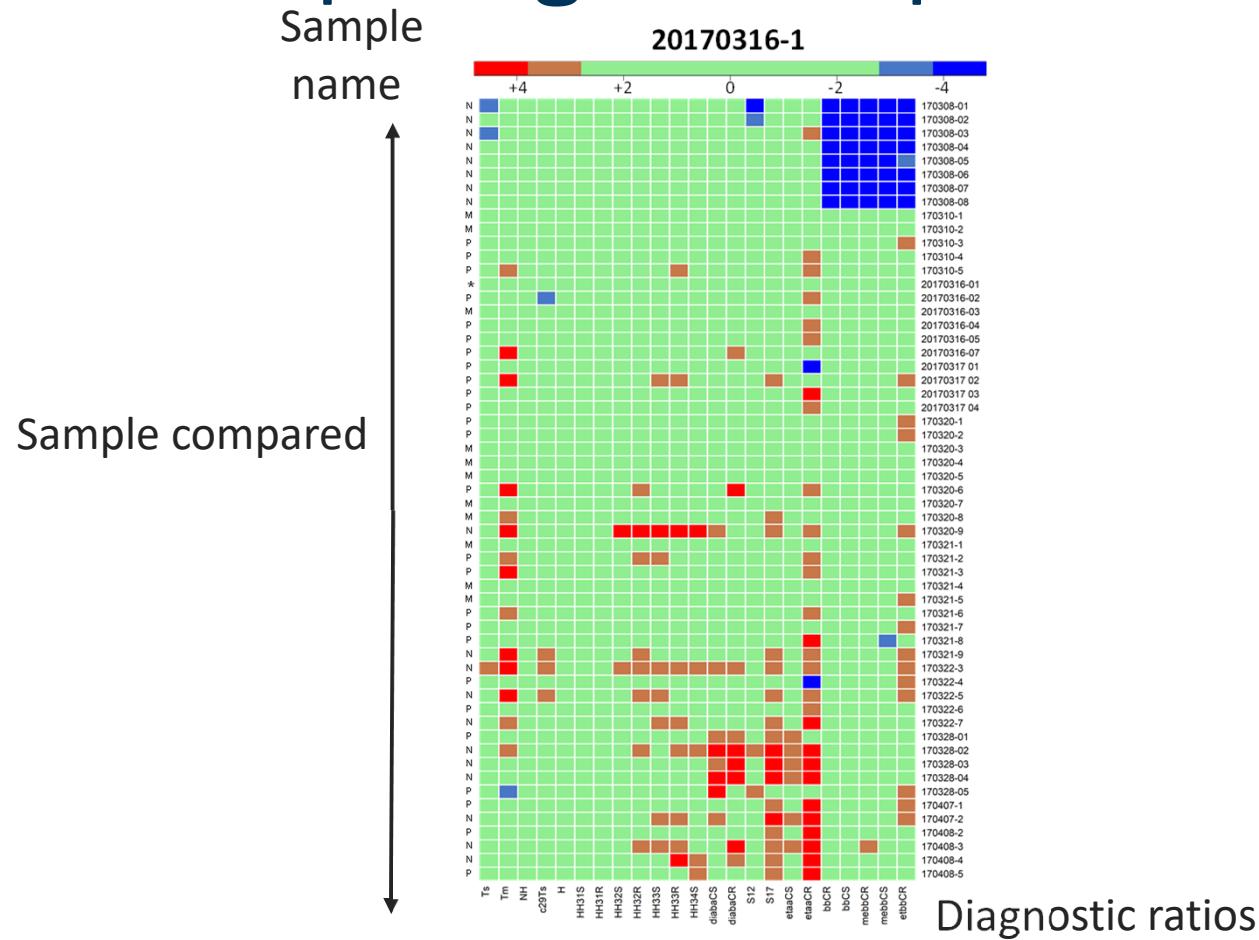
$$\frac{\left(\left(\frac{[X]}{[H]} \right)_{sample\ 1} - \left(\frac{[X]}{[H]} \right)_{sample\ 2} \right)}{\left(\frac{[X]}{[H]} \right)_{sample\ 2}} \times 100$$



Tier 3: Match, Probable Match, and No Match.

M	match	all 22 ratios match within 14%
P	probable match	at least 18 of the 22 ratios match within 14% and at least 20 of the 22 ratios match within 19%
N	non-match	more than 4 ratios differ by more than 14% or more than 2 ratios differ by more than 19%

Roadmap for interpreting heat maps for Tier 3



Tier 4: Hierarchical Cluster Analysis (HCA) from biomarker data

- HCA groups samples together based on the similarity of their overall diagnostic ratio profiles.
- Standard methodology was used where ratios were normalized to the mean value for each ratio and scaled to a variance of one.
- A Euclidean distance matrix was created and the HCA was performed using the complete linkage method.

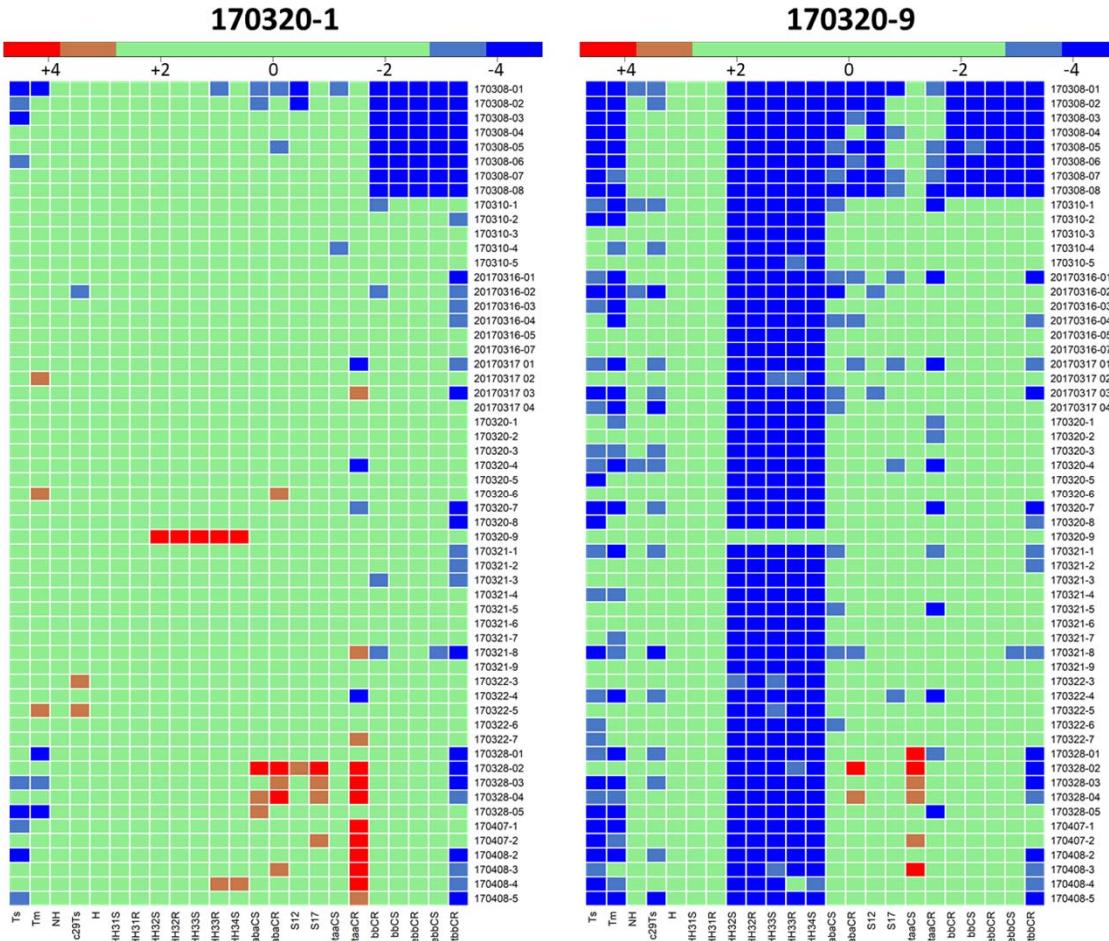
I. 2017 sheens versus 2017 sheens

Tier 3: Match, Probable Match, and No Match.

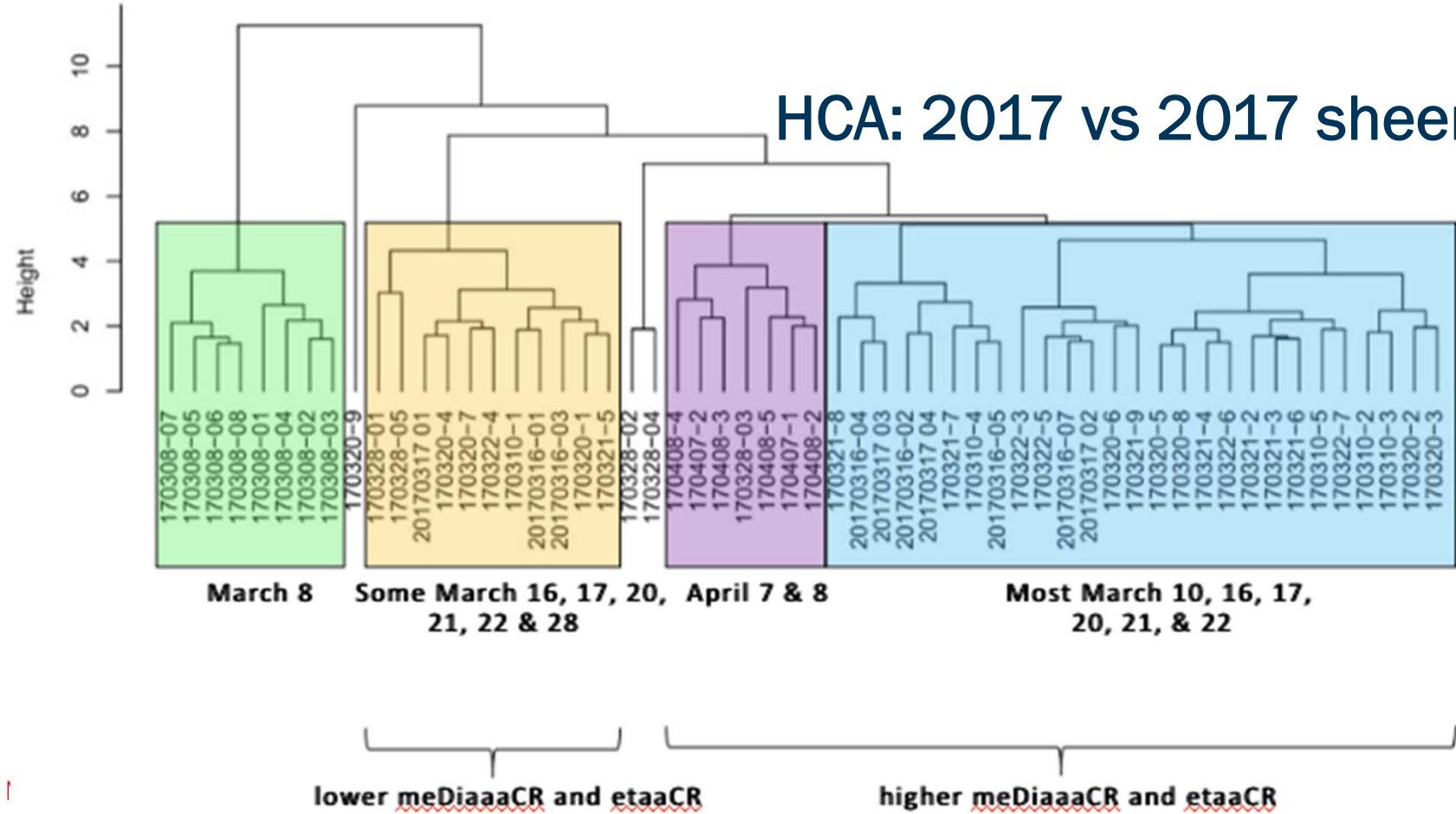
M	match	all 22 ratios match within 14%
P	probable match	at least 18 of the 22 ratios match within 14% and at least 20 of the 22 ratios match within 19%
N	non-match	more than 4 ratios differ by more than 14% or more than 2 ratios differ by more than 19%

March 20, 2017 sheens

- 170320-1 was a match or partial match for many samples.
- 170320-9 did not match any other sample from 2017.
- Collected within 30 m of each other separated by four hours.



HCA: 2017 vs 2017 sheens



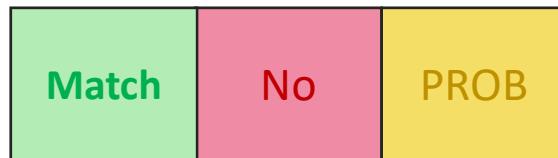
Summary: 2017 sheens were heterogeneous

II. 2017 sheens versus 2012/2013 sheens

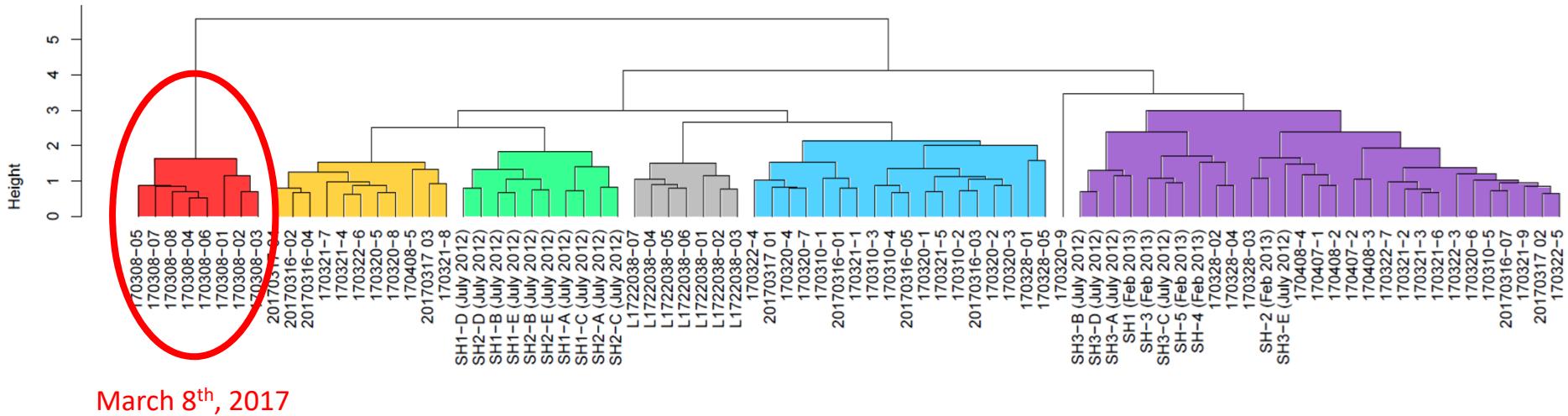
Biomarker: 2017 vs 2012/2013 sheens

Feb 2013 July 2012

	<u>3/8/17</u>	<u>3/10/17</u>	<u>3/16/17</u>	<u>3/17/17</u>	<u>3/20/17</u>	<u>3/21/17</u>	<u>3/22/17</u>	<u>3/28/17</u>	<u>4/7/17</u>	<u>4/8/17</u>	
SH1-A (July 2012)	N N N N N	17/03/08-01	17/03/08-03	17/03/08-04	17/03/08-05	17/03/08-06	17/03/08-07	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3
SH1-B (July 2012)	N N N N N	17/03/08-02	17/03/08-04	17/03/08-05	17/03/08-06	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3
SH1-C (July 2012)	N N N N N	17/03/08-03	17/03/08-05	17/03/08-06	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/10-4
SH1-D (July 2012)	N N N N N	17/03/08-04	17/03/08-06	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/10-4	17/03/10-5
SH1-E (July 2012)	N N N N N	17/03/08-05	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/10-4	17/03/10-5	2017/03/16-01
SH2-A (July 2012)	N N P P P	17/03/08-02	17/03/08-04	17/03/08-05	17/03/08-06	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/16-02
SH2-B (July 2012)	N N N N N	17/03/08-03	17/03/08-05	17/03/08-06	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/16-03
SH2-C (July 2012)	N N P N P	17/03/08-04	17/03/08-06	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/10-4	17/03/16-04
SH2-D (July 2012)	N N P N P	17/03/08-05	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/10-4	17/03/10-5	2017/03/16-05
SH2-E (July 2012)	N N P N P	17/03/08-06	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/10-4	17/03/10-5	17/03/11-01	2017/03/16-06
SH3-A (July 2012)	N N N N N	17/03/08-03	17/03/08-05	17/03/08-06	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/11-02
SH3-B (July 2012)	N N N N N	17/03/08-04	17/03/08-06	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/10-4	17/03/11-03
SH3-C (July 2012)	N N N N N	17/03/08-05	17/03/08-07	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/10-4	17/03/10-5	17/03/11-04
SH3-D (July 2012)	N N N N N	17/03/08-06	17/03/08-08	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/10-4	17/03/10-5	17/03/11-05	17/03/11-06
SH3-E (July 2012)	N N N N N	17/03/08-07	17/03/08-09	17/03/10-1	17/03/10-2	17/03/10-3	17/03/10-4	17/03/10-5	17/03/10-6	17/03/11-07	17/03/11-08
SH1 (Feb 2013)	N N N N N	17/03/08-08	17/03/08-10	17/03/08-11	17/03/08-12	17/03/08-13	17/03/08-14	17/03/08-15	17/03/08-16	17/03/08-17	17/03/08-18
SH2 (Feb 2013)	N N N N N	17/03/08-09	17/03/08-11	17/03/08-12	17/03/08-13	17/03/08-14	17/03/08-15	17/03/08-16	17/03/08-17	17/03/08-18	17/03/08-19
SH3 (Feb 2013)	N N N N N	17/03/08-10	17/03/08-12	17/03/08-13	17/03/08-14	17/03/08-15	17/03/08-16	17/03/08-17	17/03/08-18	17/03/08-19	17/03/08-20
SH4 (Feb 2013)	N N N N N	17/03/08-11	17/03/08-13	17/03/08-14	17/03/08-15	17/03/08-16	17/03/08-17	17/03/08-18	17/03/08-19	17/03/08-20	17/03/08-21
SH5 (Feb 2013)	N N N N N	17/03/08-12	17/03/08-14	17/03/08-15	17/03/08-16	17/03/08-17	17/03/08-18	17/03/08-19	17/03/08-20	17/03/08-21	17/03/08-22



HCA: 2017 vs 2012/2013 sheens



**Summary: No major changes in 2017 vs 2012/2013
sheens**

III. Sediment cores at MC20 (2012/2013)

Piston and box cores from 2012

	Piston 2-1	Piston 2-2	Piston 2-3	Piston 3-2	Piston 3-4	Piston 3-5	Piston 3-6	Piston 3-7	Piston 4-1	Piston 4-2	Piston 4-3	Piston 4-4	Piston 5-2	Piston 5-3	Piston 5-4	Piston 5-5	Piston 5-6	Piston 6-1	Piston 6-2	Piston 6-3	Piston 6-4	Piston 6-5	Piston 6-6	Piston 6-7
Piston 2-1	-																							
Piston 2-2	M	-																						
Piston 2-3	P	P	-																					
Piston 3-2	P	P	P	-																				
Piston 3-4	P	P	P	M	-																			
Piston 3-5	P	M	P	M	M	-																		
Piston 3-6	P	P	P	P	P	M	-																	
Piston 3-7	P	P	P	P	P	P	M	-																
Piston 4-1	P	P	P	M	M	M	P	P	-															
Piston 4-2	P	P	P	M	M	M	P	M	-															
Piston 4-3	P	P	P	M	M	M	P	P	M	M	-													
Piston 4-4	M	P	P	M	M	M	P	P	M	M	M	-												
Piston 5-2	P	N	P	M	M	M	P	P	P	M	M	P	-											
Piston 5-3	P	P	P	P	P	M	P	P	P	M	M	P	P	-										
Piston 5-4	P	P	P	M	M	M	P	P	M	M	M	M	M	-										
Piston 5-5	M	P	P	M	M	M	M	M	M	M	M	M	P	M	-									
Piston 5-6	M	P	P	M	M	M	M	M	M	M	M	M	P	M	M	M	-							
Piston 6-1	M	P	P	M	M	M	P	P	M	M	M	M	P	M	M	M	M	-						
Piston 6-2	M	M	P	M	M	M	P	M	M	M	M	M	P	M	M	M	M	M	-					
Piston 6-3	M	M	P	M	M	M	P	P	M	M	M	M	P	P	M	M	M	M	M	-				
Piston 6-4	P	P	P	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	-			
Piston 6-5	P	P	P	M	M	M	P	P	M	M	M	M	P	M	M	M	M	M	M	M	M	M	M	-
Piston 6-6	P	P	P	M	M	M	M	M	M	M	M	M	P	M	M	M	M	M	M	M	M	M	M	-
Piston 6-7	P	P	P	P	M	M	M	M	M	P	M	M	M	M	M	M	M	M	M	M	M	M	M	-

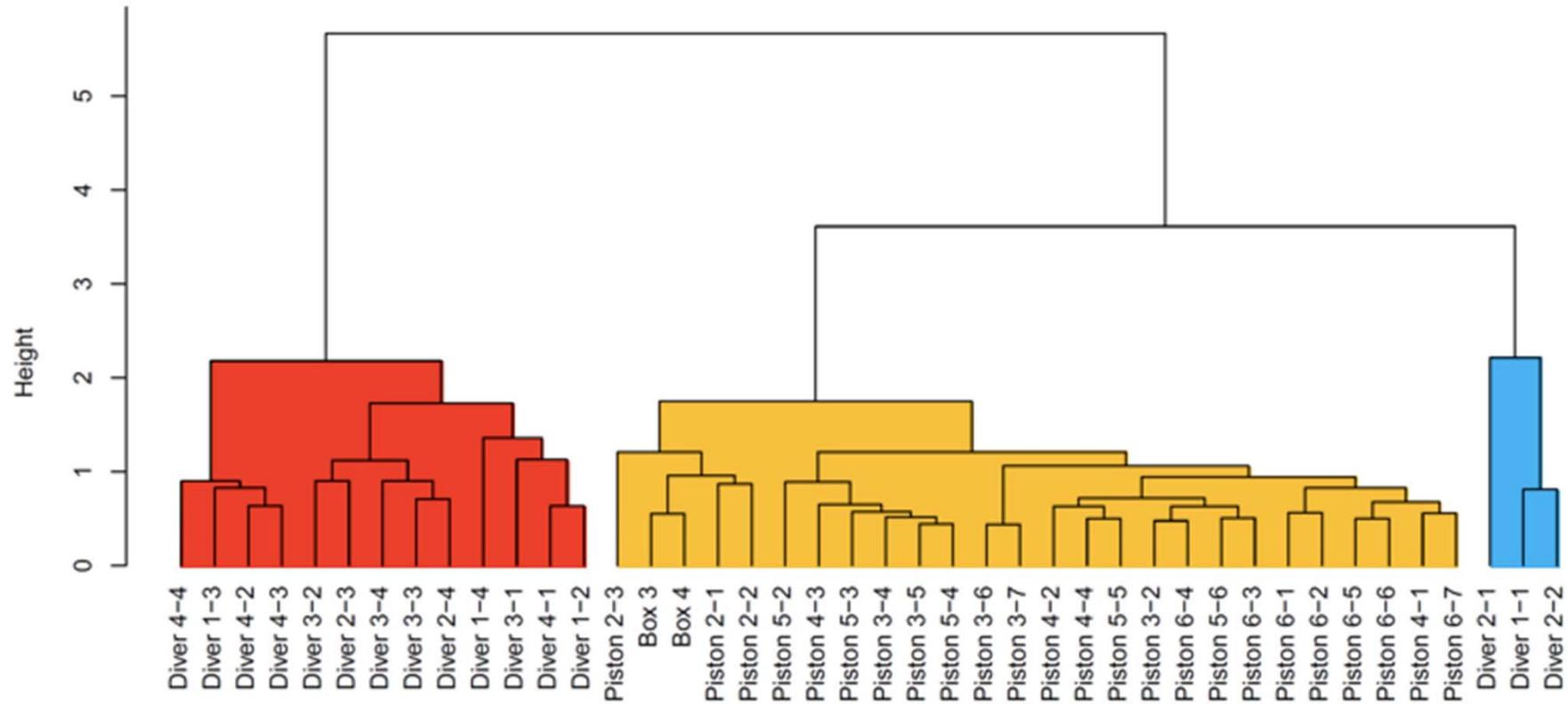
Match
No
PROB

Diver cores from 2013

	- Diver 3-1	Diver 3-2	Diver 3-3	Diver 3-4	Diver 4-1	Diver 4-2	Diver 4-3	Diver 4-4	Diver 1-1	Diver 1-2	Diver 1-3	Diver 1-4	Diver 2-1	Diver 2-2	Diver 2-3	Diver 2-4
Diver 3-1	-															
Diver 3-2	M	-														
Diver 3-3	M	M	-													
Diver 3-4	M	M	M	-												
Diver 4-1	M	M	M	M	-											
Diver 4-2	P	P	P	N	M	-										
Diver 4-3	M	M	M	M	M	M	-									
Diver 4-4	P	P	P	P	M	M	M	-								
Diver 1-1	P	P	N	P	P	N	N	N	-							
Diver 1-2	M	M	P	P	M	M	M	M	P	-						
Diver 1-3	P	P	P	N	P	M	M	M	N	M	-					
Diver 1-4	P	P	P	P	M	P	P	P	P	N	-					
Diver 2-1	N	N	N	N	N	N	N	N	N	N	N	N	N	-		
Diver 2-2	P	N	N	N	N	N	N	N	M	N	N	P	N	-		
Diver 2-3	P	P	M	P	M	M	M	M	P	M	M	P	N	N	-	
Diver 2-4	M	M	M	M	P	P	M	P	N	P	P	P	N	N	M	-



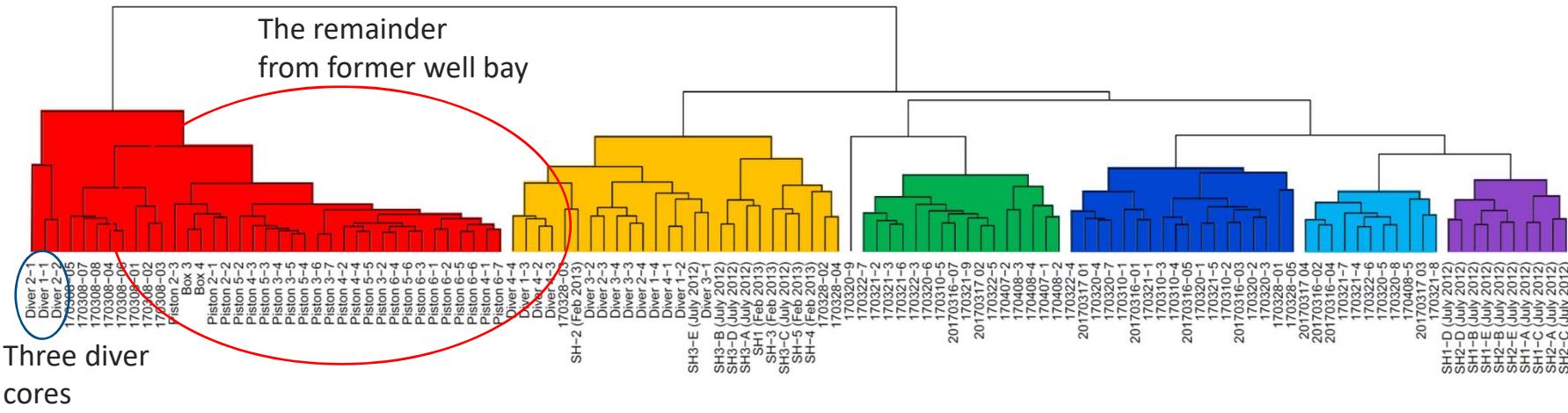
HCA: 2012 vs 2013 cores



Summary: 2012 sediment cores near former well bay were homogeneous; 2013 sediment cores were heterogeneous.

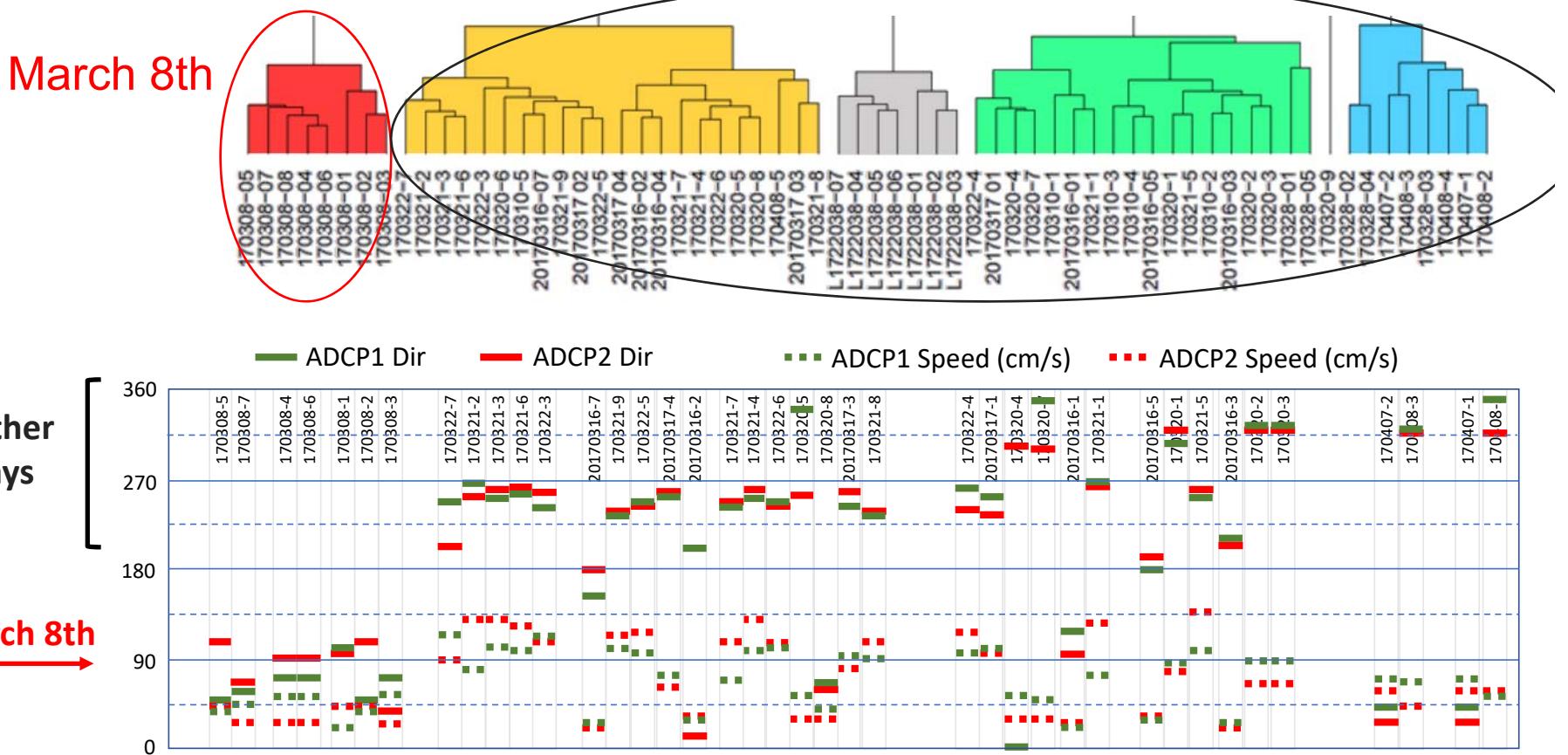
IV. 2017 Sheens vs. 2012/2013 sediment cores

HCA: 2012/2013/2017 sheens vs cores



Summary: Major source of sheens are sediments near fallen jacket (diver cores).

What happened on March 8, 2017? → Currents



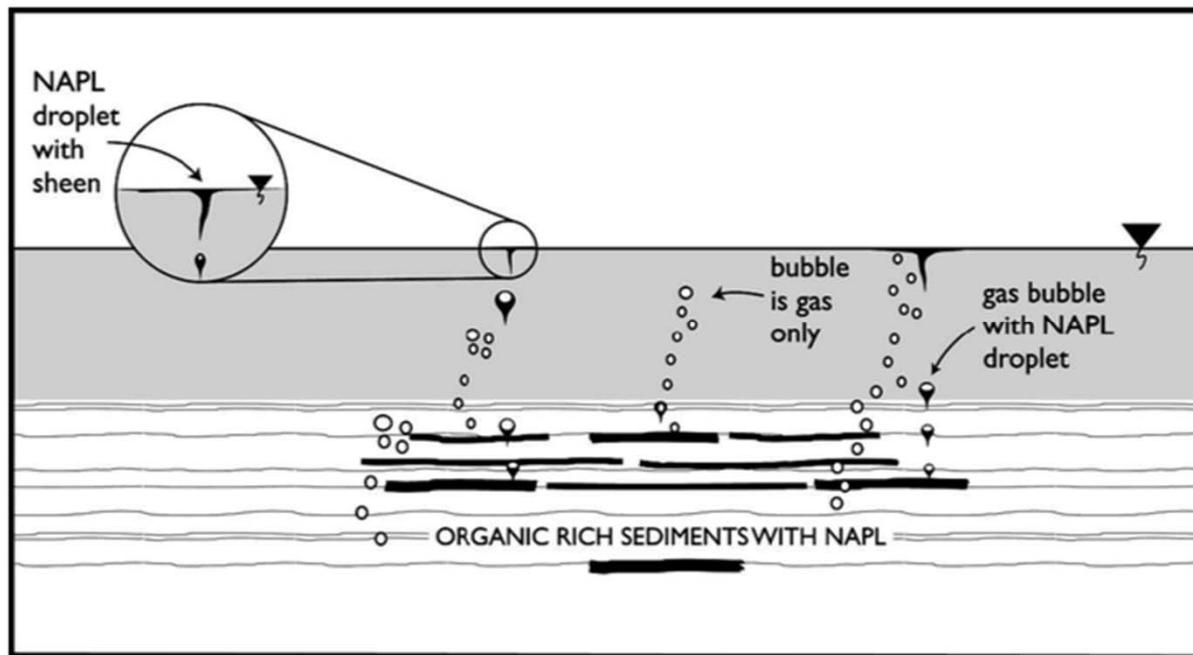
Is it reasonable that a contaminated sediment can create a sheen? – Yes.



Coal tar sheens are shown forming on the water surface at a former manufactured gas plant site.

Conceptual model for a contaminated site in Maine

Taylor site
also has
swirling
currents
around jacket.

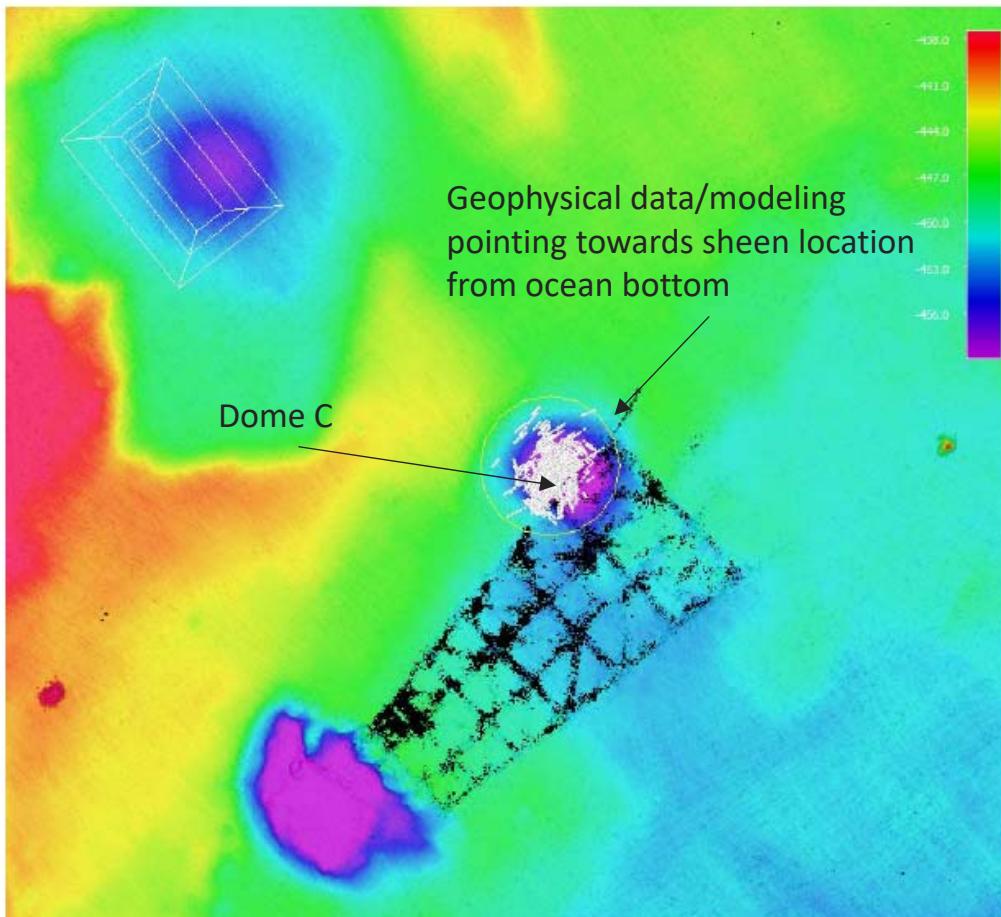


McLinn and Stolzenberg, *Env. Tox. Chem.* (2009)

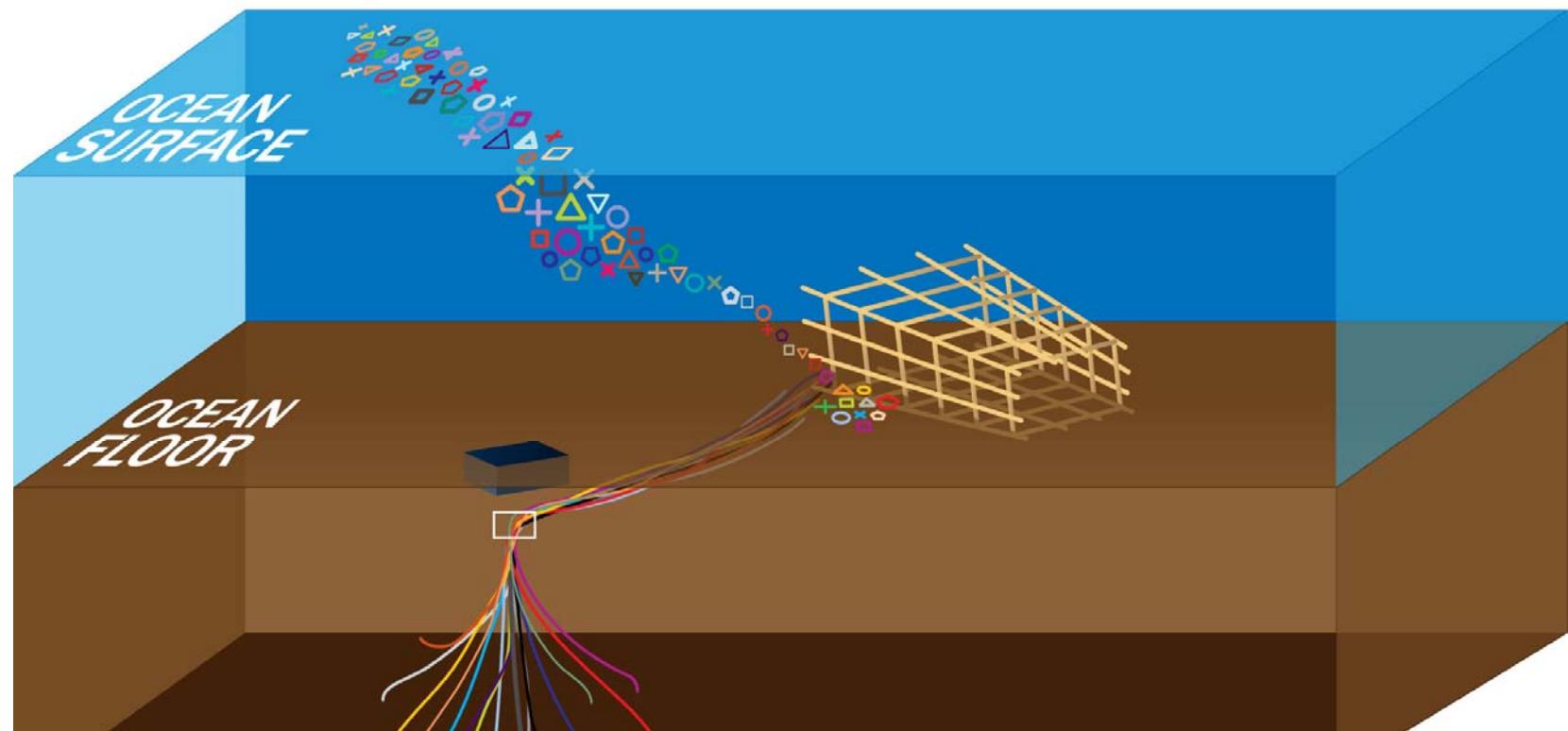
Diver core images



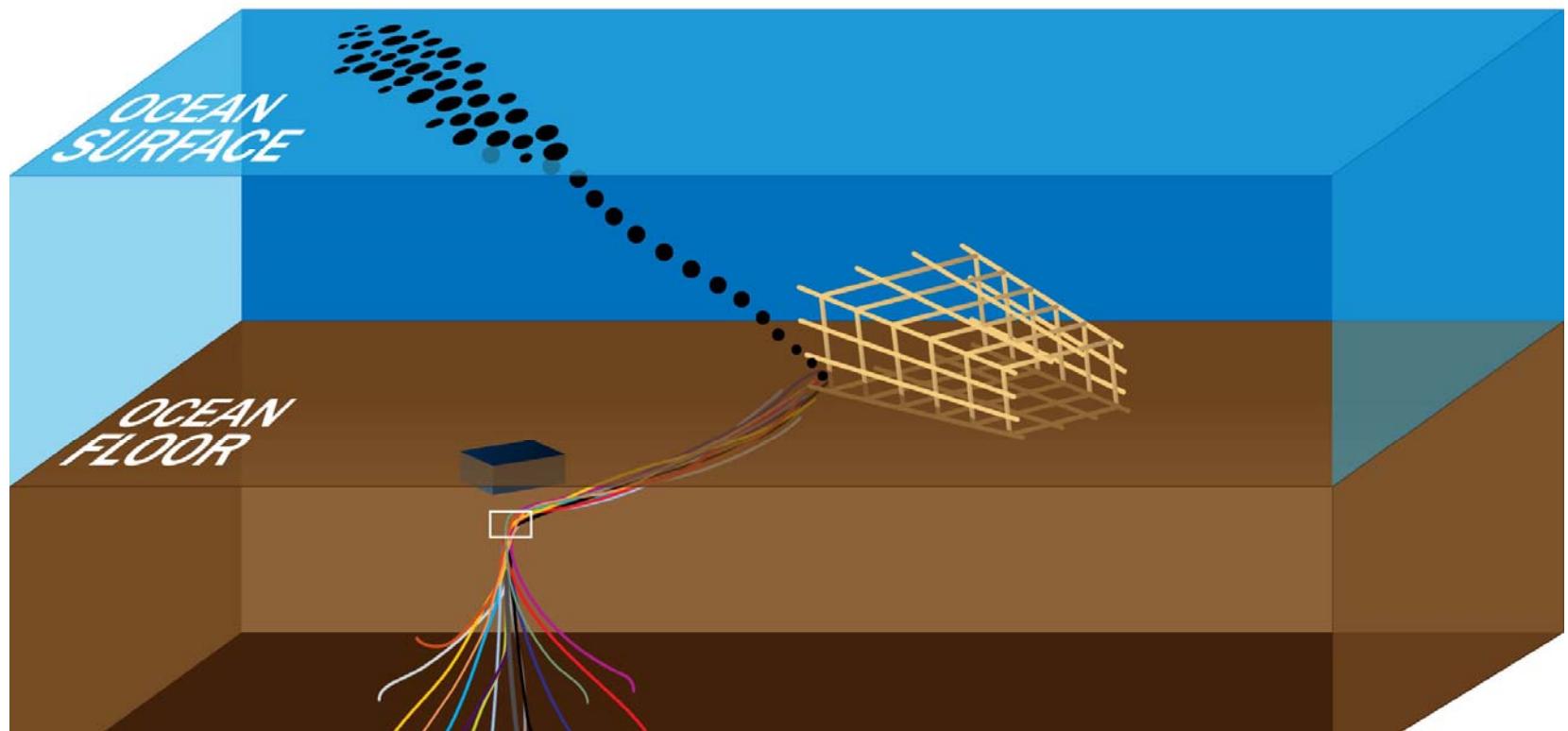
Highly contaminated sediments are being excavated



100% heterogeneous release from remnant sediments



100% release from a homogeneous well leak



Conclusions

- All four forensic-based Tiers point to 2017 surface sheens to be heterogeneous.
- Do not support a single source.
- **The most compelling scientific conclusion is that the contaminated sediments near the toppled jacket are supporting the majority (or all of the surface sheen).**
- Consistent with MSL's findings from 2012/2013.
- This conclusion is supported by other geophysical work on site and studies at other contaminated sites.
- Ocean currents play a critical role in this study.

STOP

- BACK-UP SLIDES

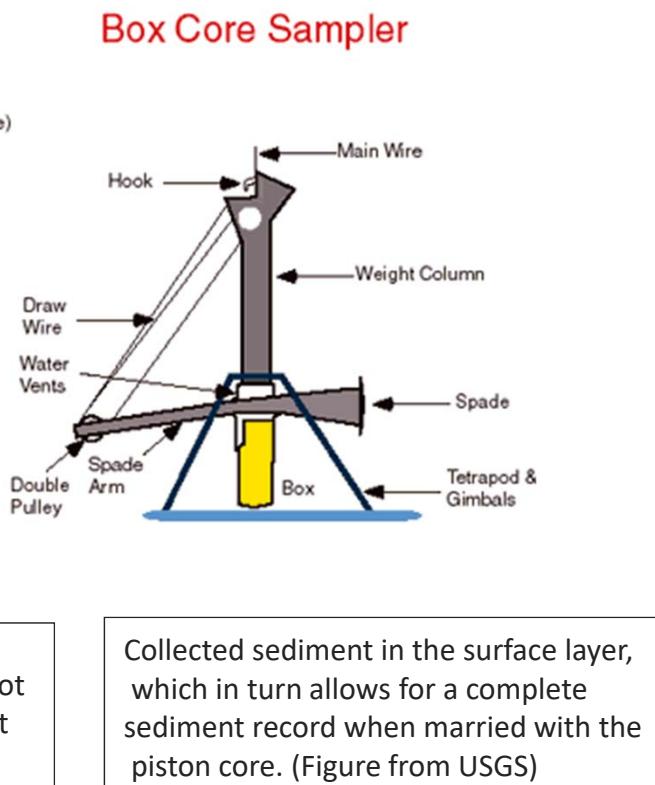
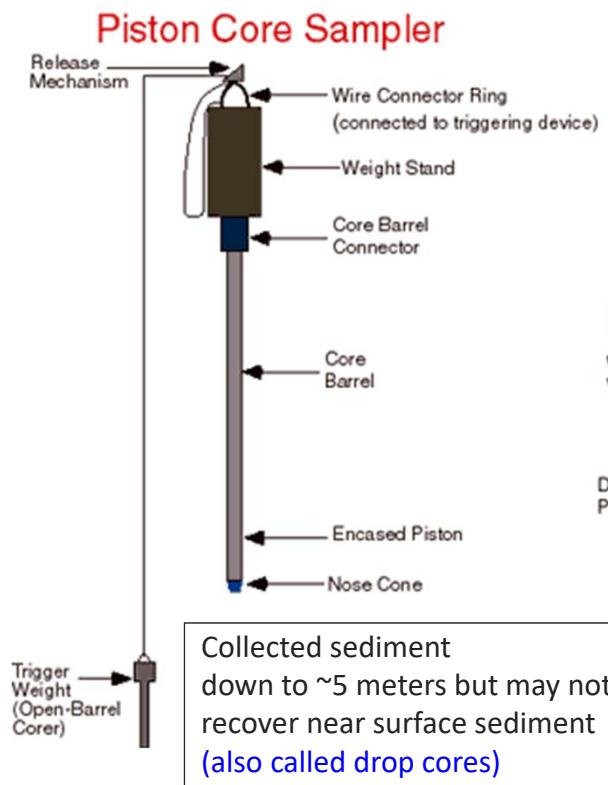
July 2012 sediment sampling

-12 locations

-Each location included ~10 samples

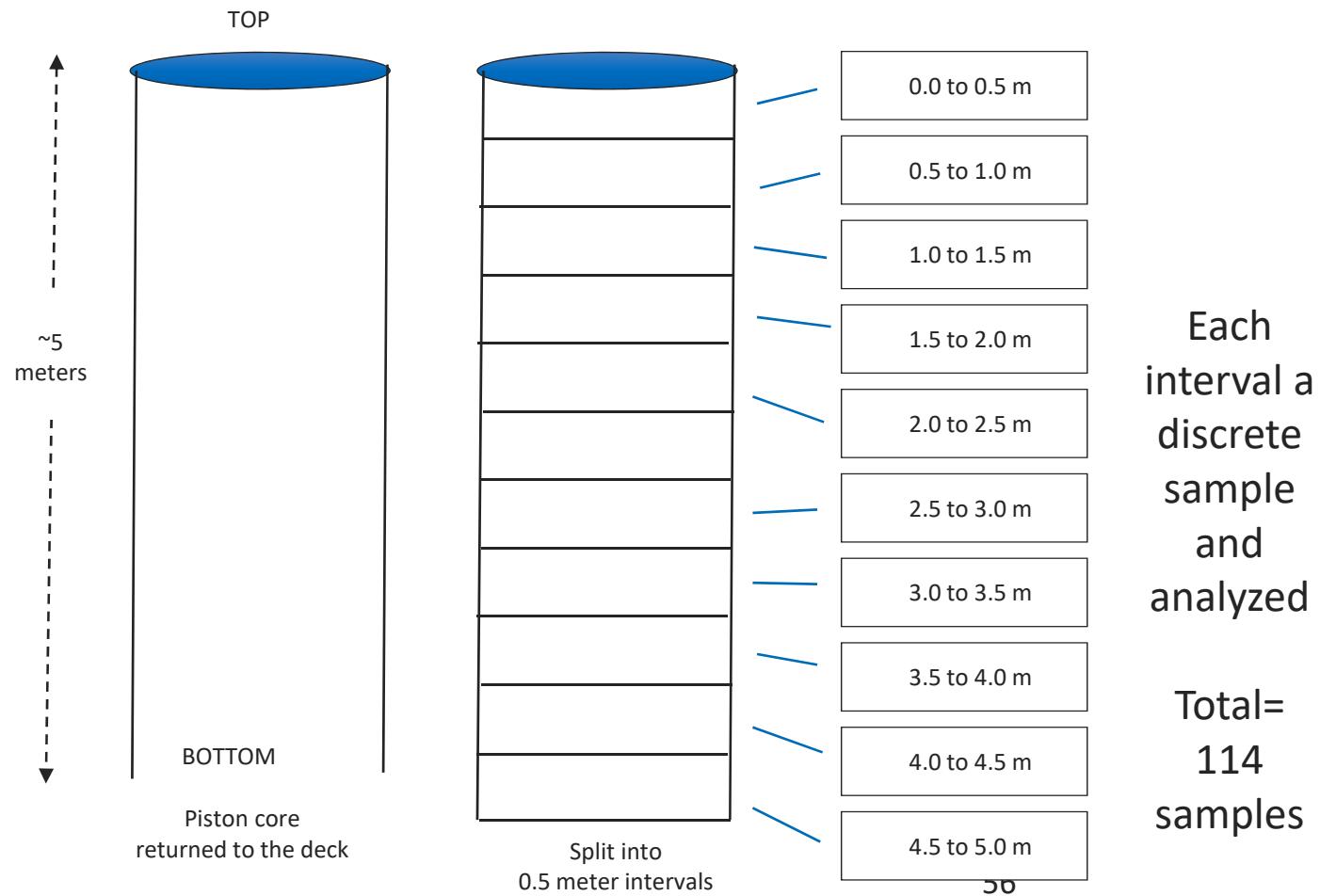
Total petroleum hydrocarbons (TPH)
values (uncertainty ~5%)

Sediment samplers used in July 2012

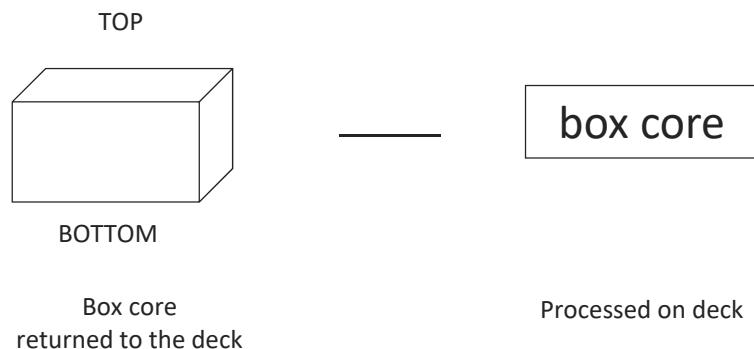


Twelve piston cores (July 2012): processing and analysis

1/21/16



Twelve box cores (July 2012): processing and analysis



Each
box core
produced
one
discrete
sample
that was
analyzed.

Total=12 box core
samples

February 2013 sediment sampling (diver)

- 4 locations
- Each location included ~4 samples

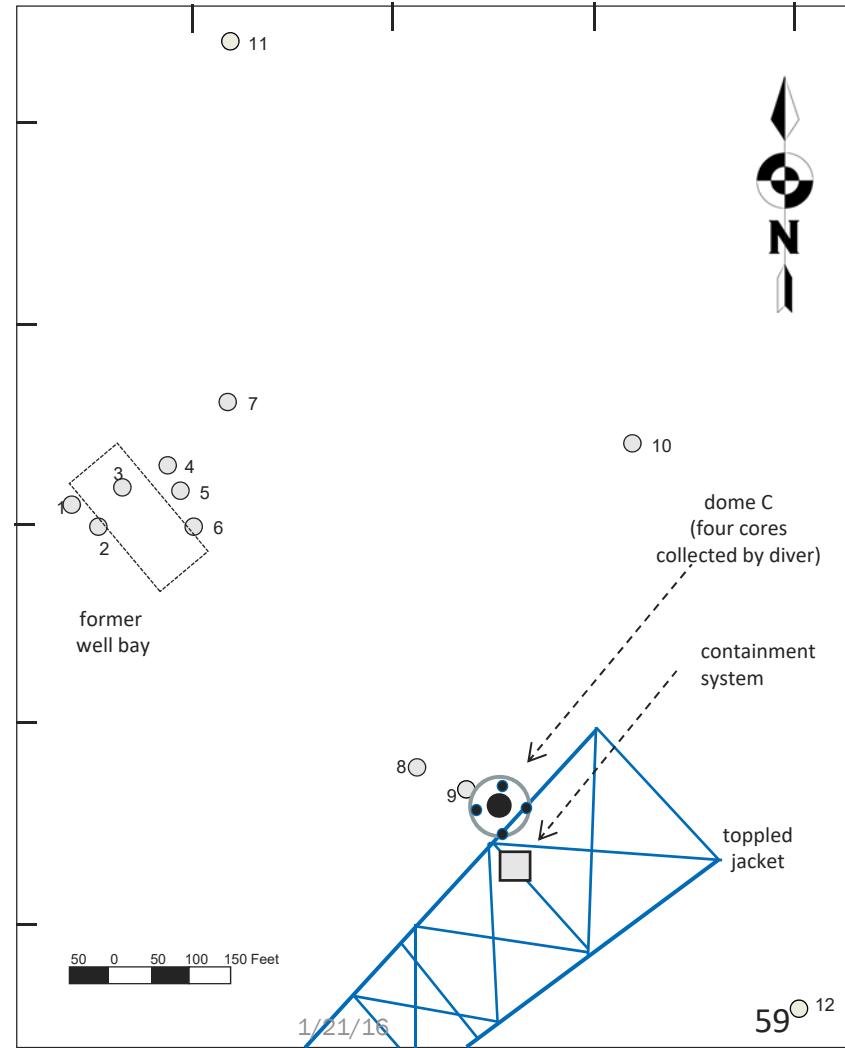
Sediment coring Locations

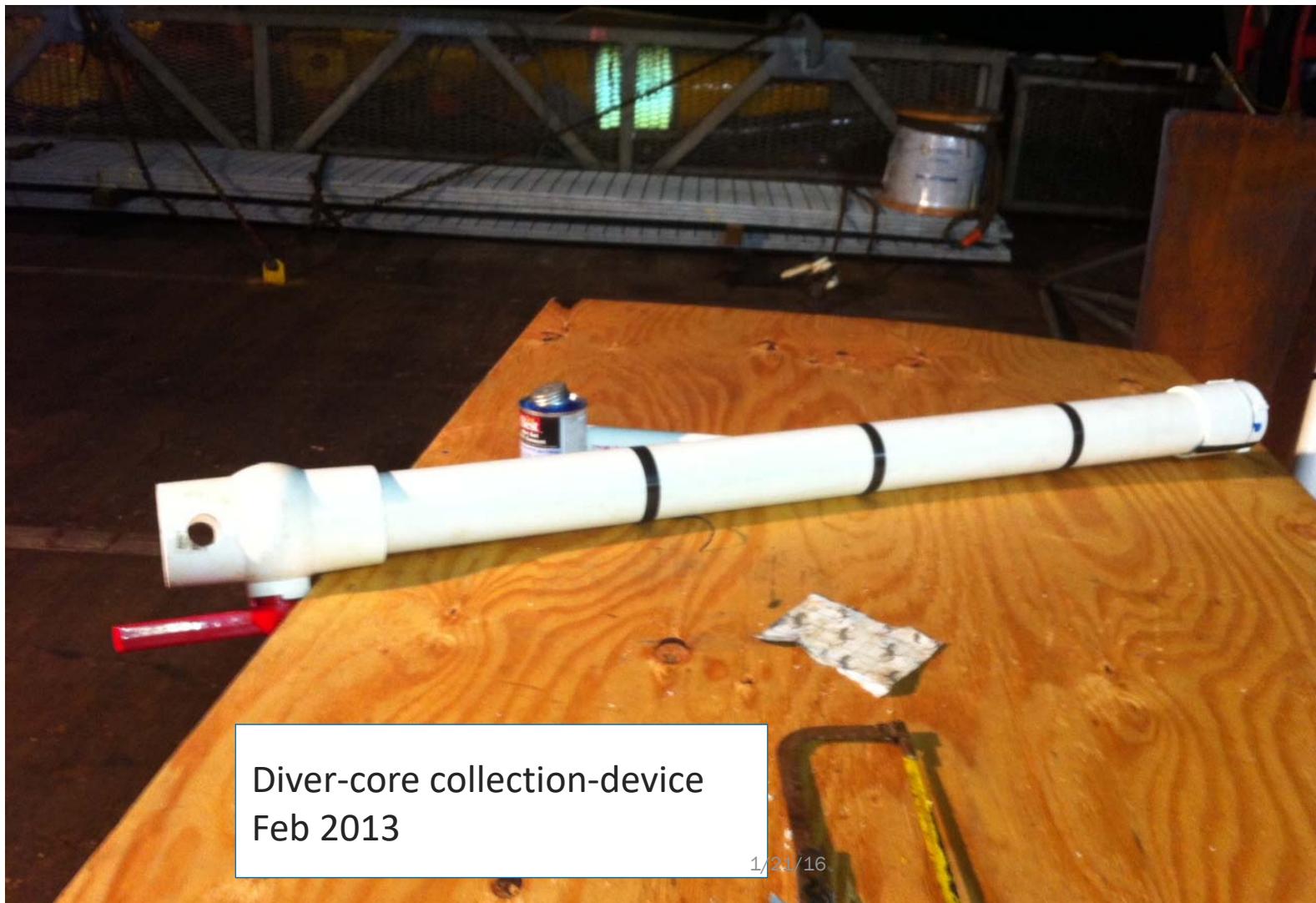
(July 2012*
and Feb 2013***)

*Sediment was collected at all 12 numbered sites with both box and piston corers. locations=

**Divers collected four cores along each side of the containment system only in February 2013. locations=

Note: The July 2012 piston cores were originally designated as "DC-x" for drop core. They are now "PC-x" so that the Feb 2013 diver cores's can be "DC-x".



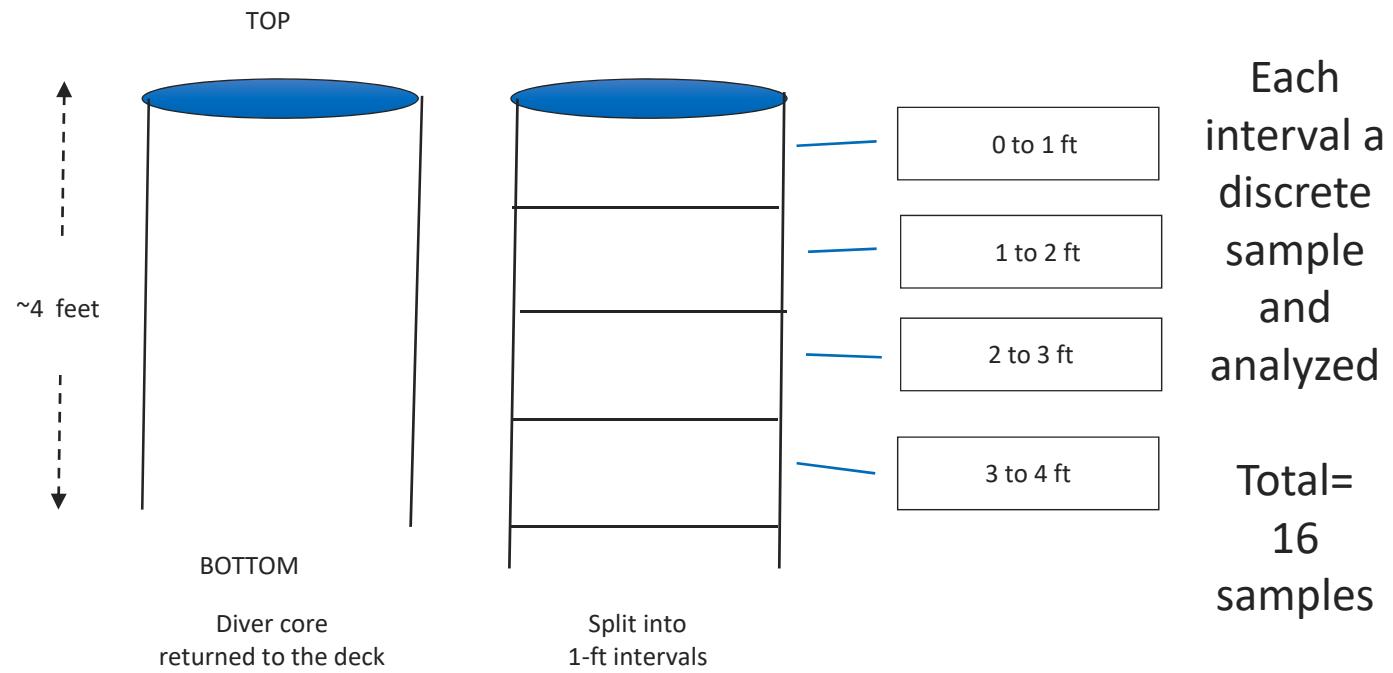


Diver-core collection-device
Feb 2013

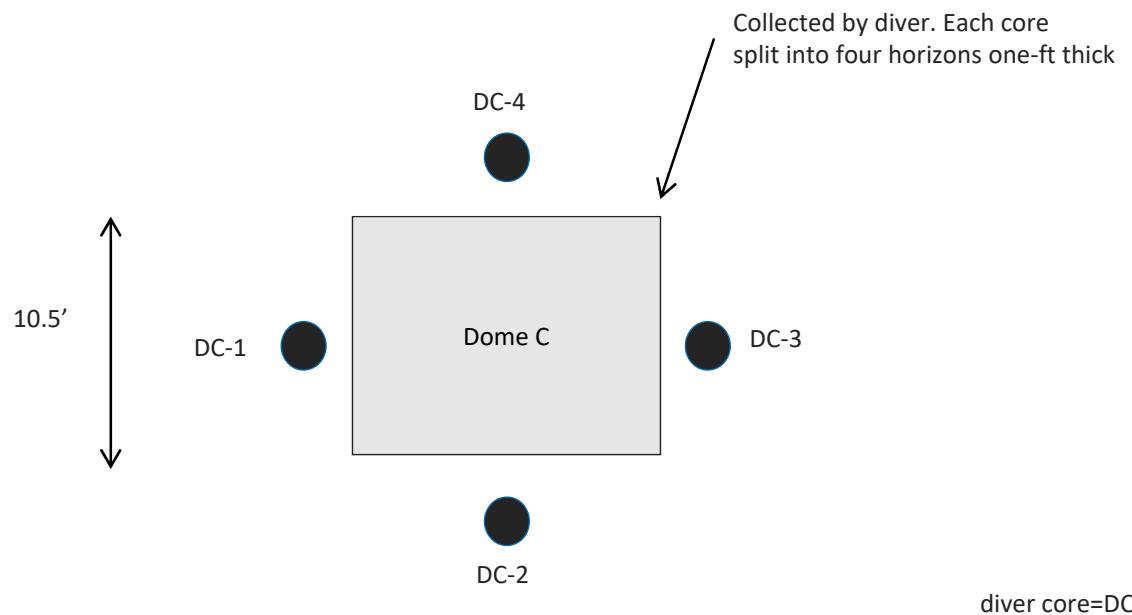
1/21/16

Four diver cores (Feb 2013): processing and analysis

1/21/16

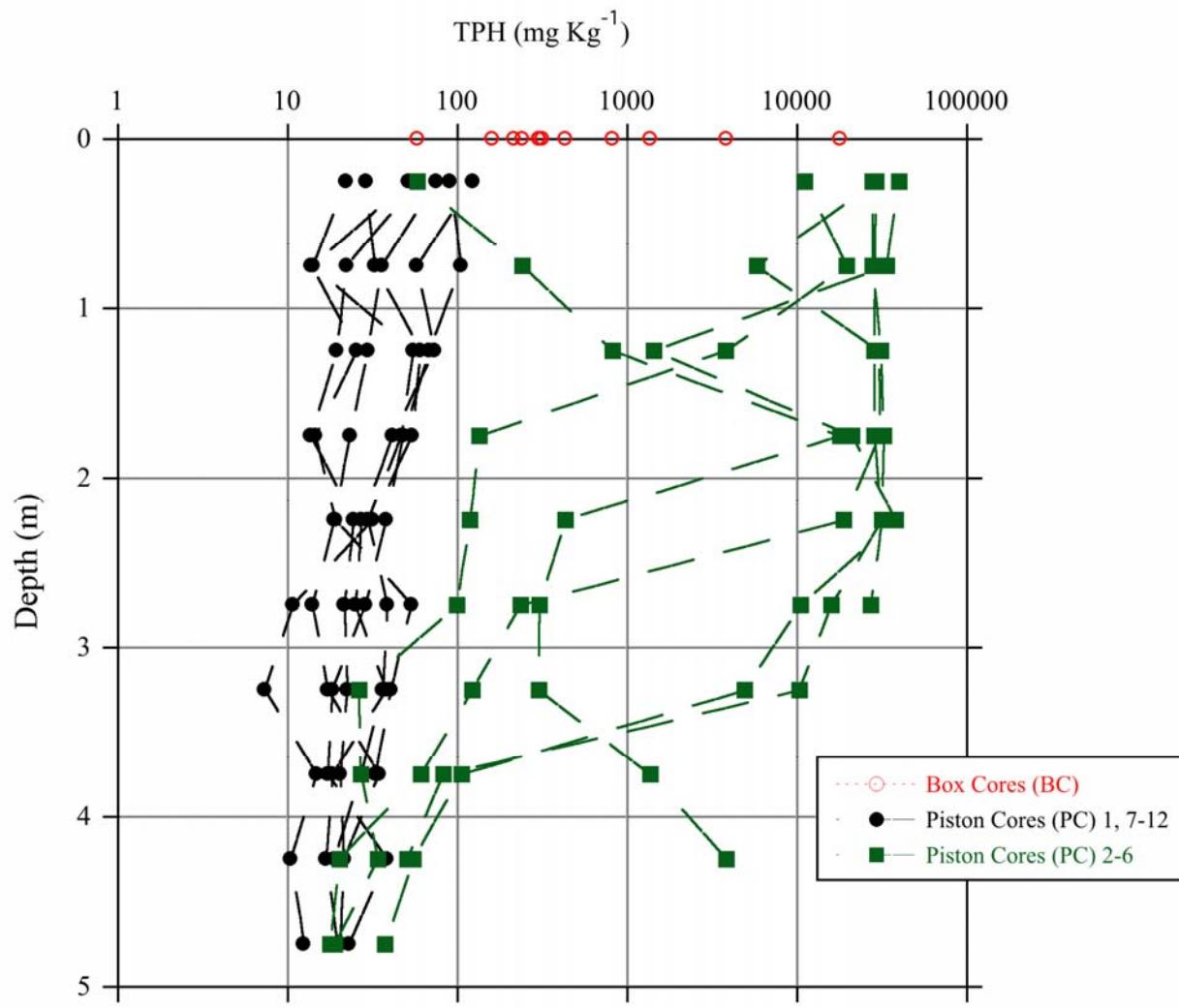


Blow-up of cores collected in February 2013 (DC-1 to 4)



Figures for total petroleum hydrocarbons (TPHs) from the piston cores (or drop cores) collected in July 2012

Twelve cores collected to mud depths of ~5m, split at 0.5 m intervals and analyzed



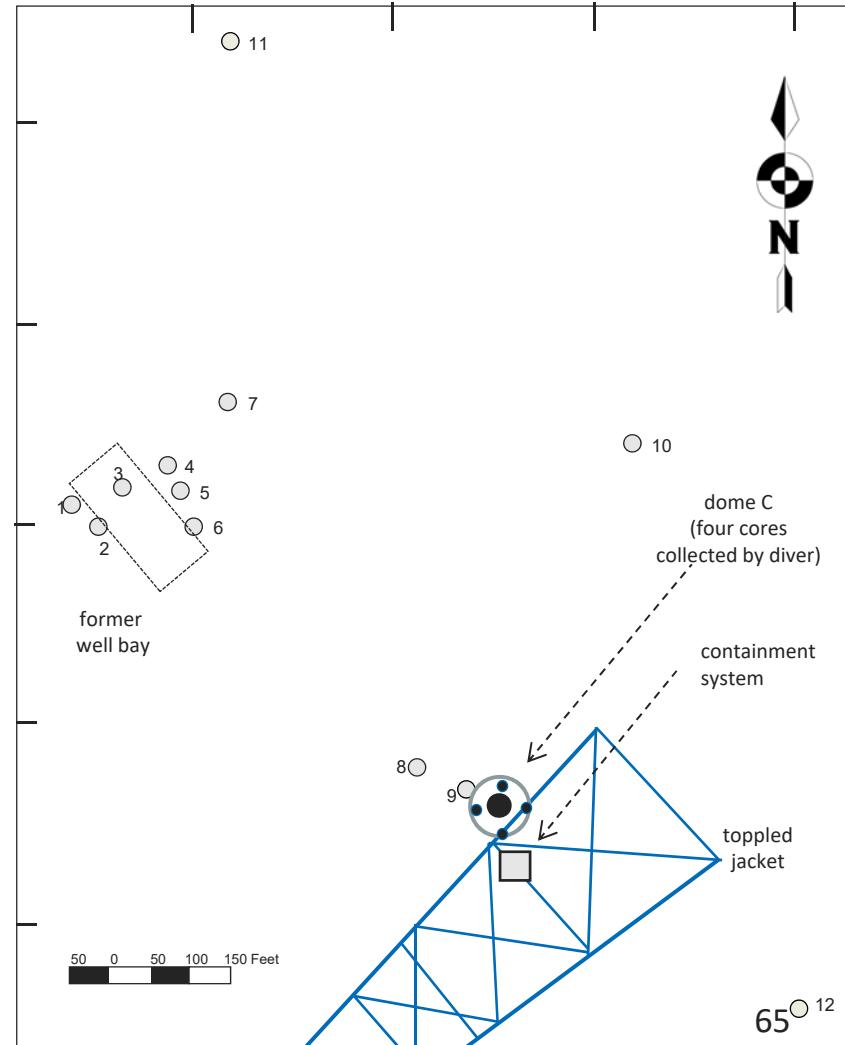
Sediment coring Locations

(July 2012*
and Feb 2013***)

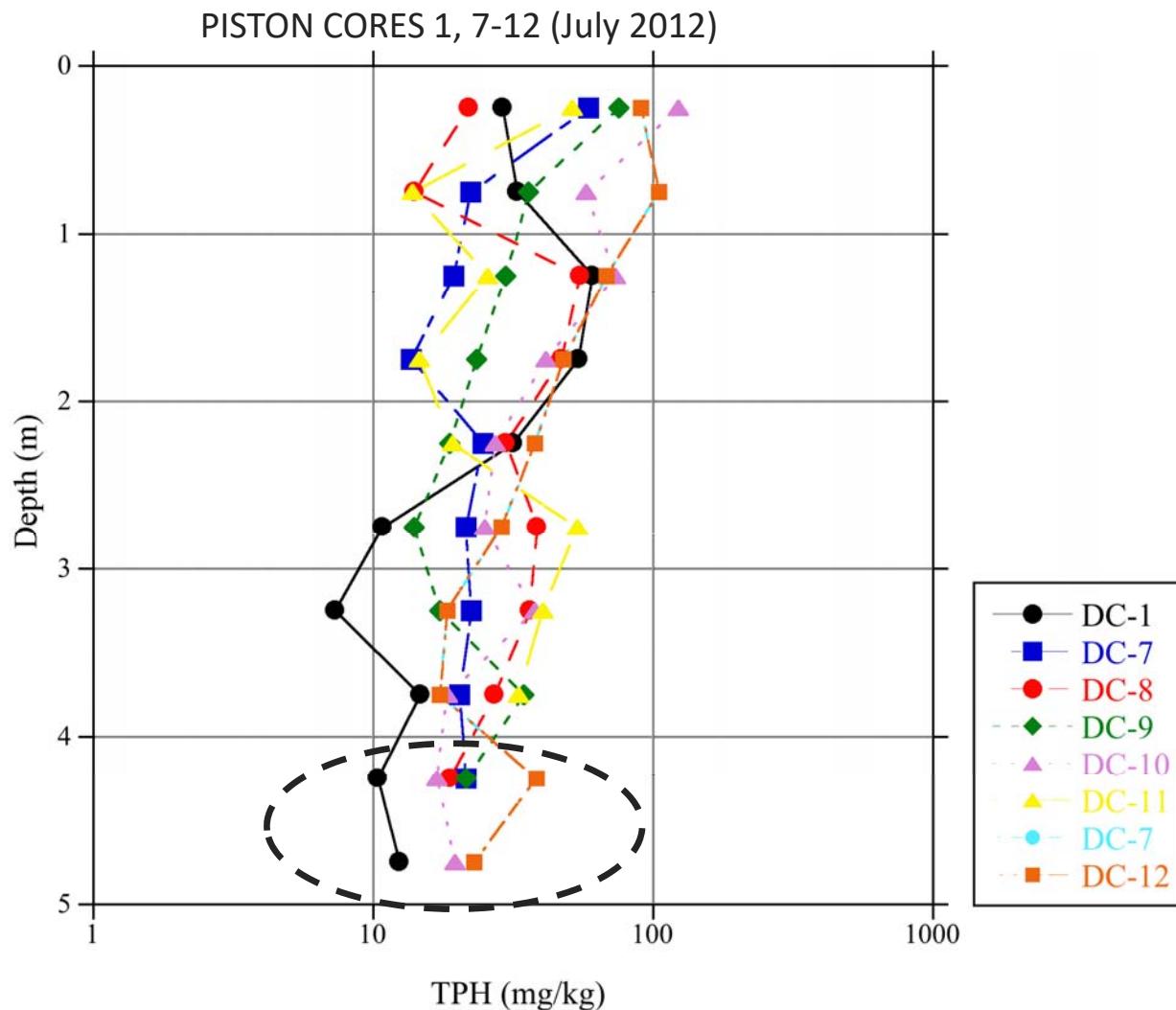
*Sediment was collected at all 12 numbered sites with both box and piston corers. locations=

**Divers collected four cores along each side of the containment system only in February 2013. locations=

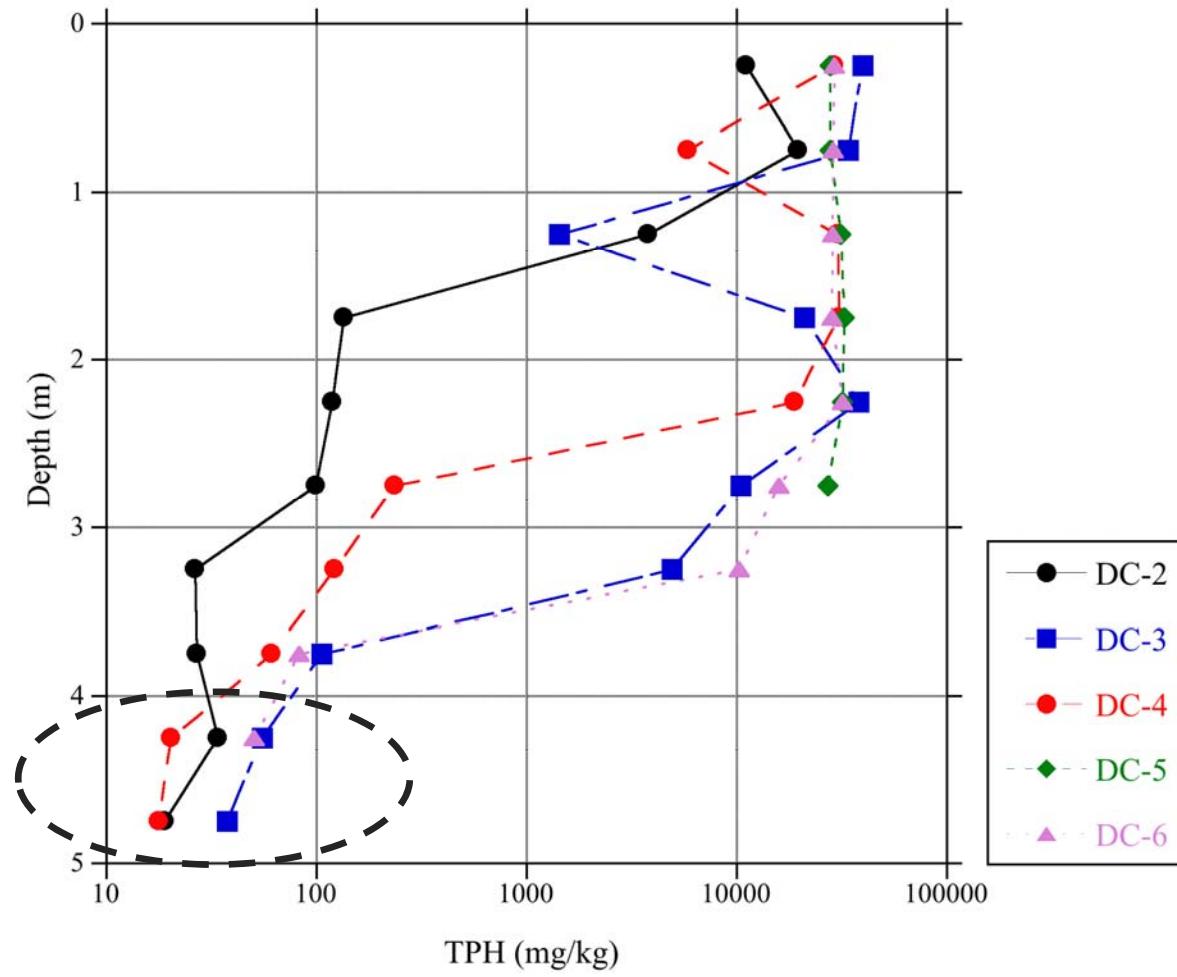
Note: The July 2012 piston cores were originally designated as "DC-x" for drop core. They are now "PC-x" so that the Feb 2013 diver cores's can be "DC-x".



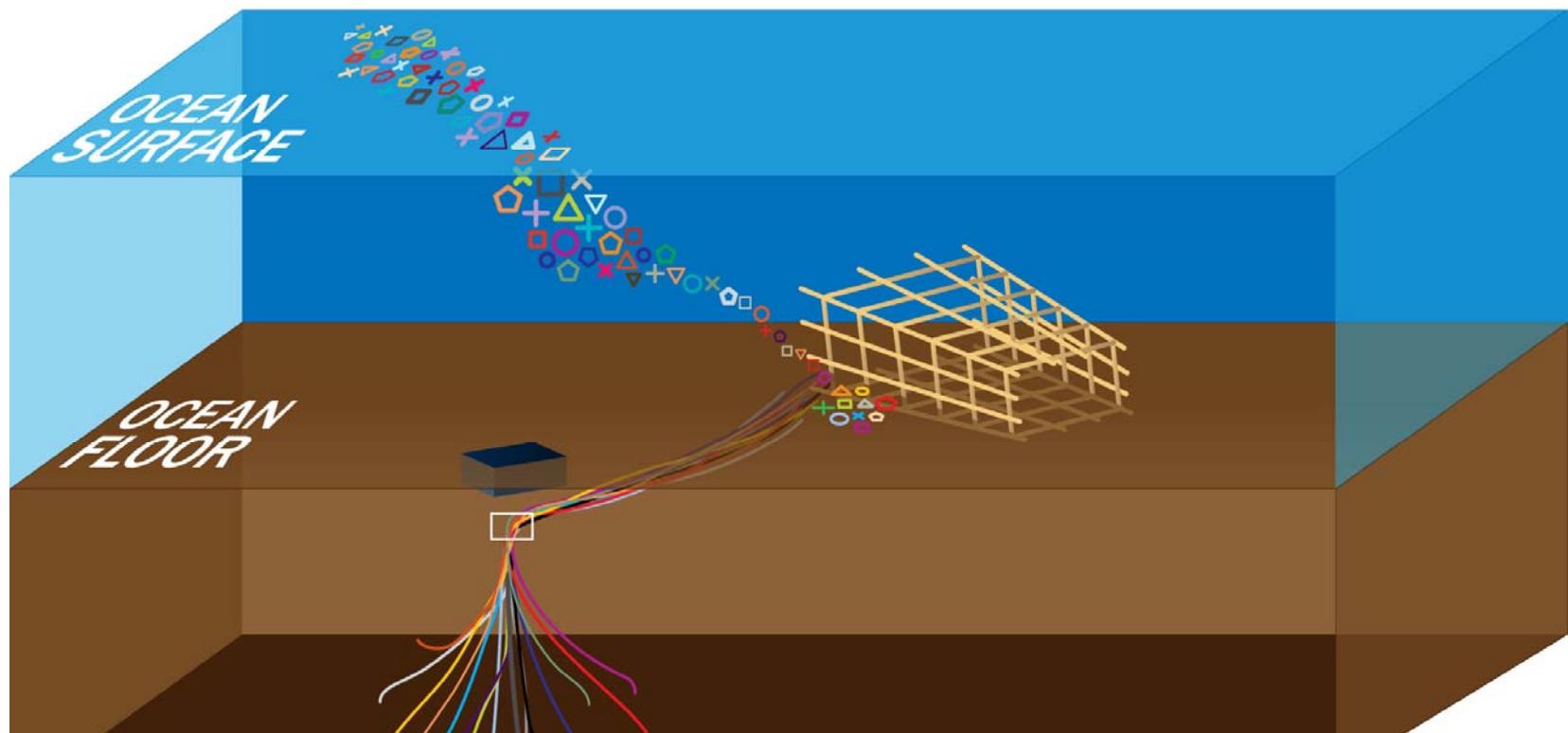
1/21/16



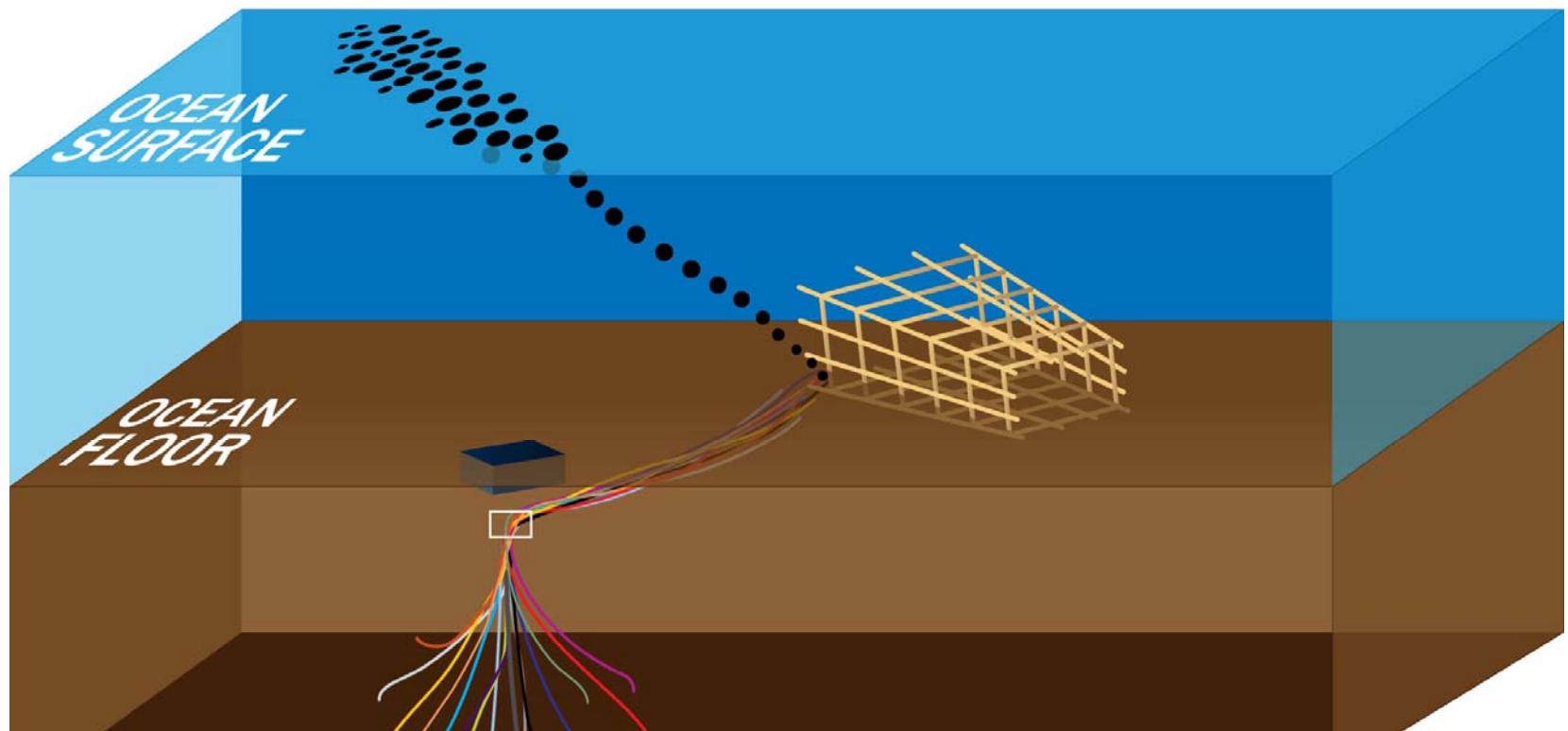
PISTON CORES 2 to 6 (July 2012)



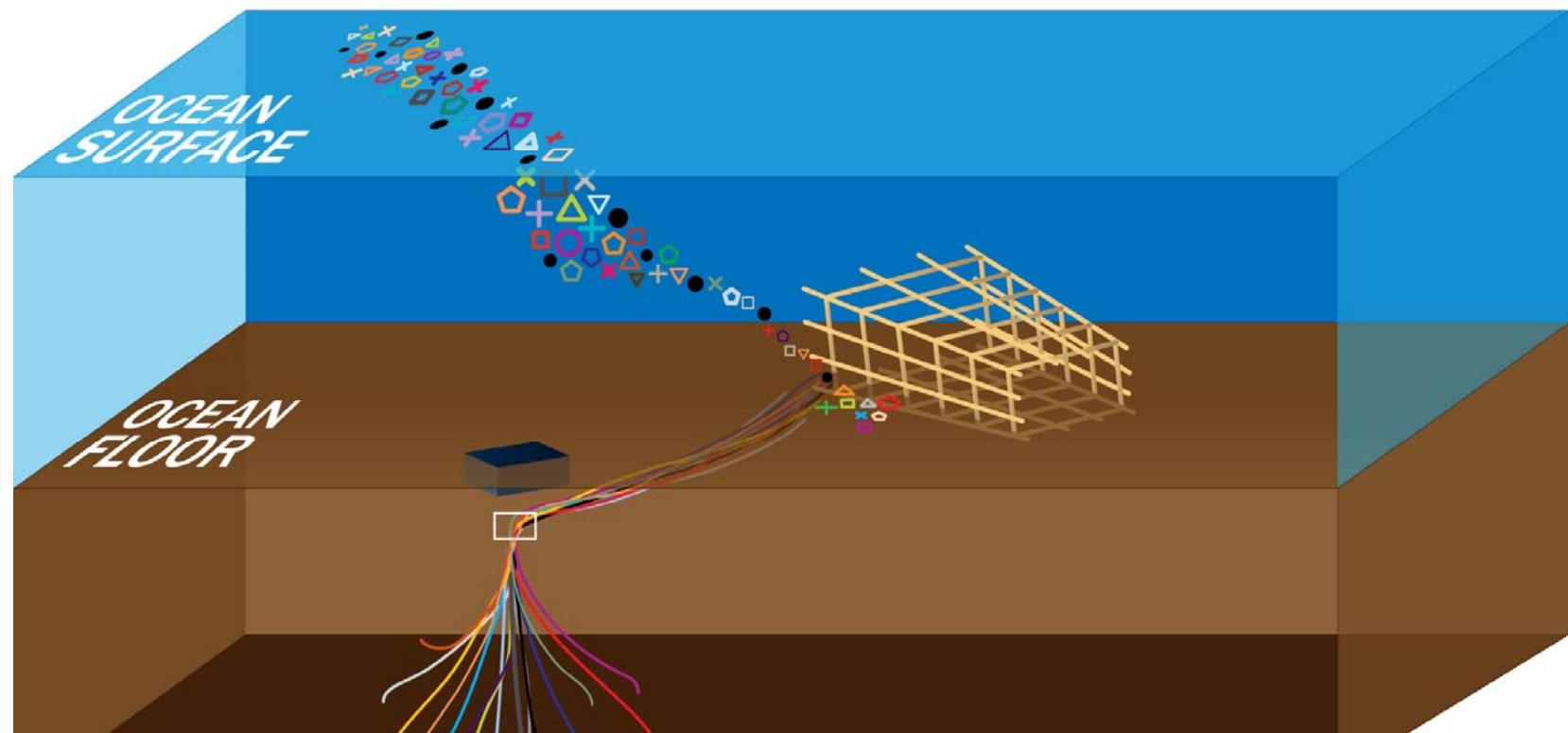
100% heterogeneous release from remnant sediments



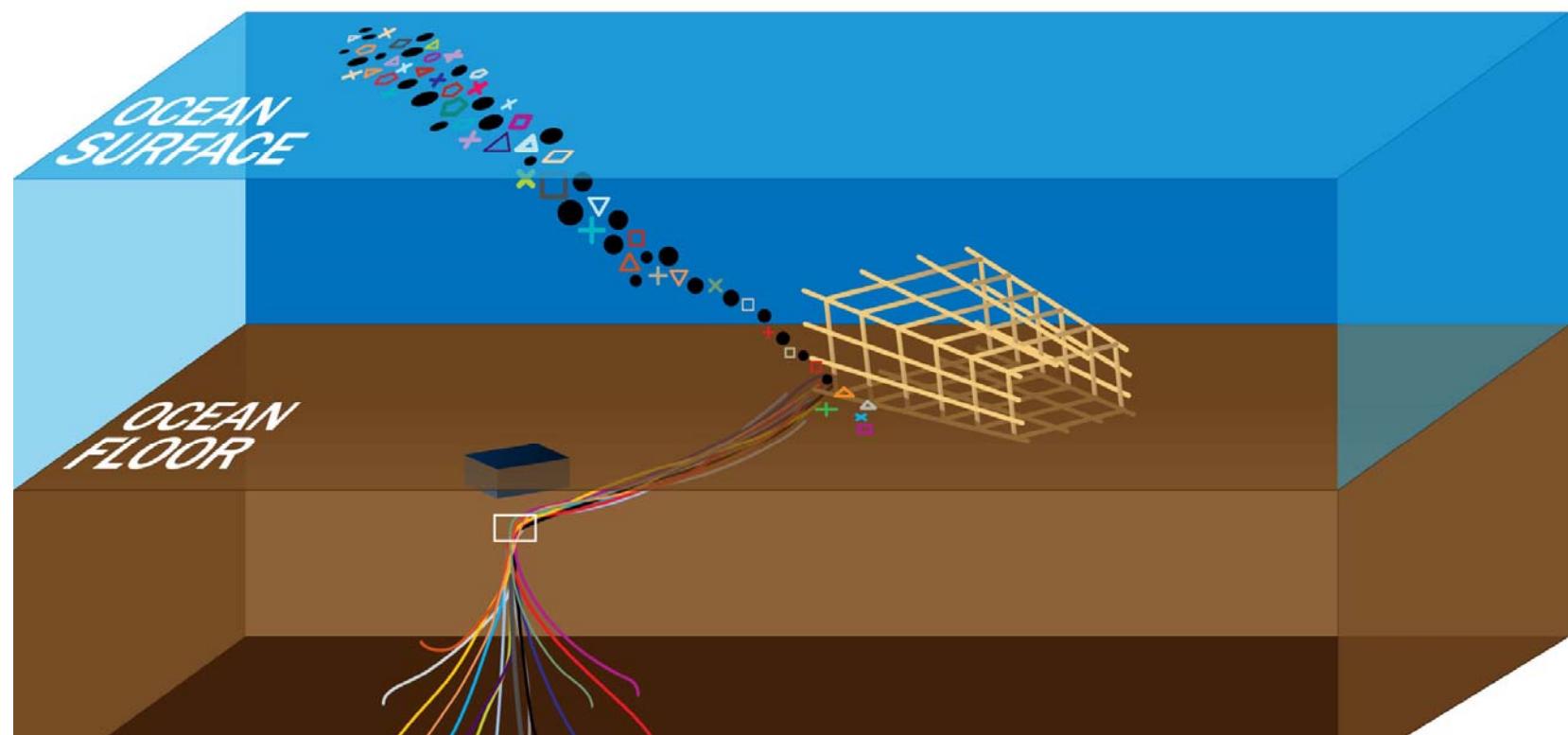
100% release from a homogeneous well leak



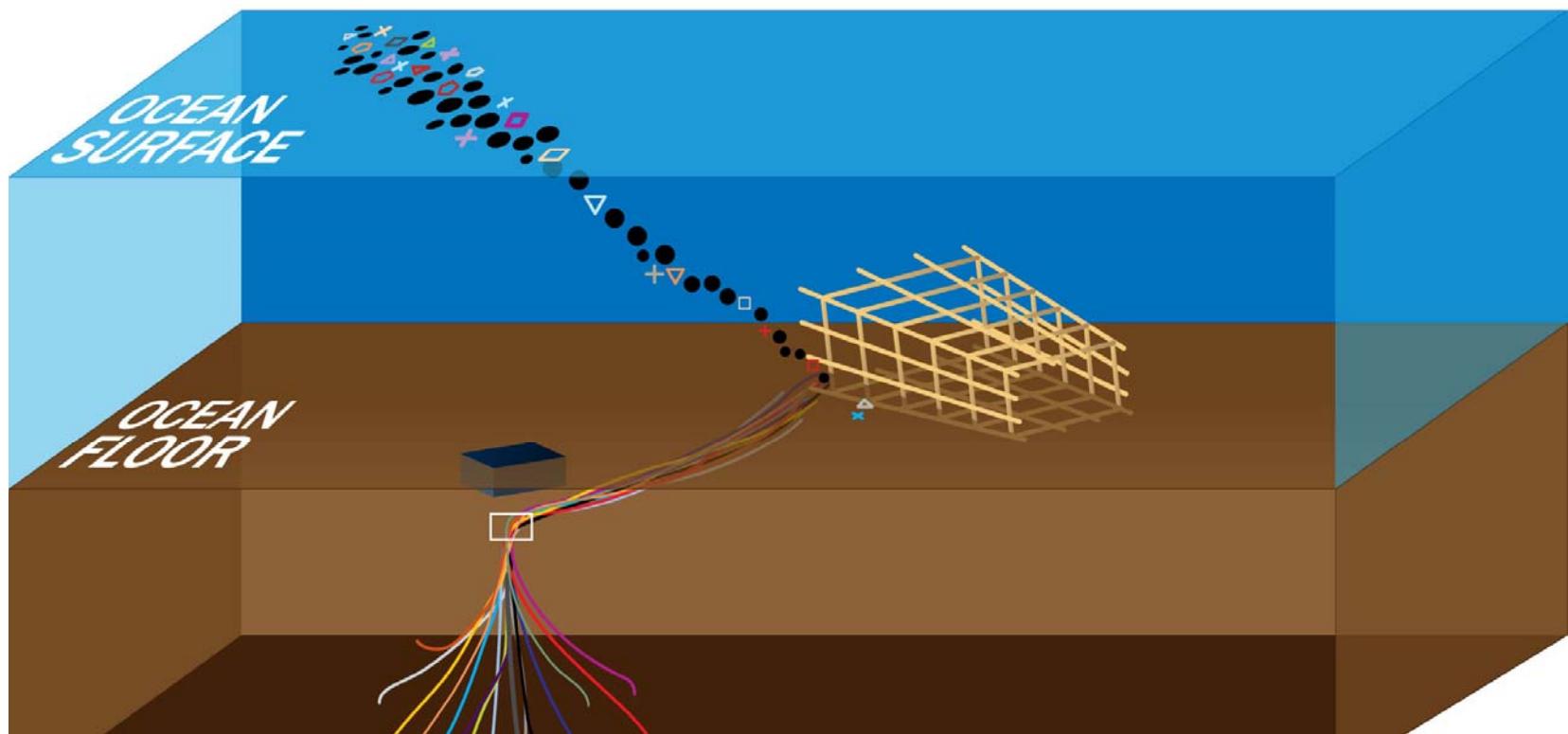
75% heterogeneous release from remnant sediments
and 25% release from a homogeneous well leak

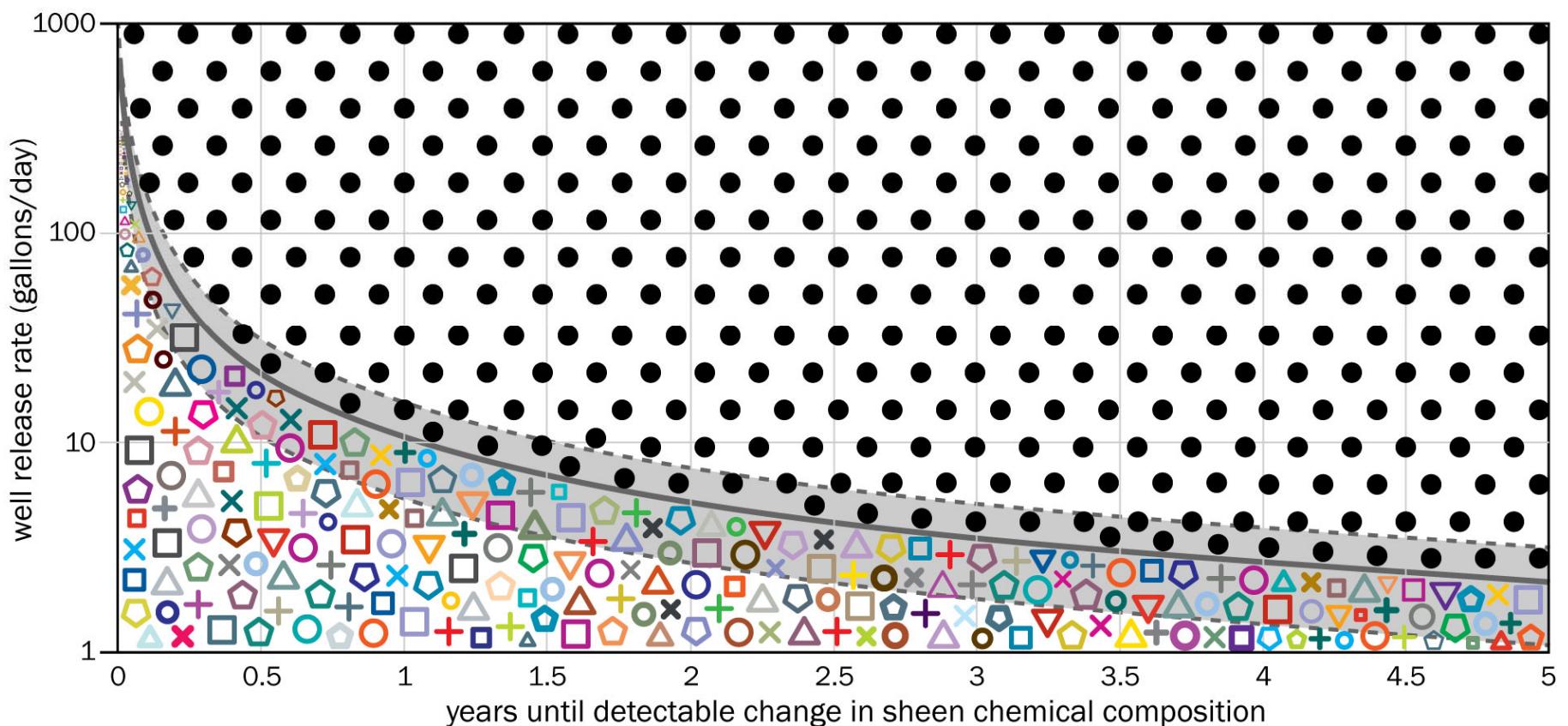


50% heterogeneous release from remnant sediments
and 50% release from a homogeneous well leak



25% heterogeneous release from remnant sediments
and 75% release from a homogeneous well leak





Summary of Tiers 3 and 4 FINDINGS

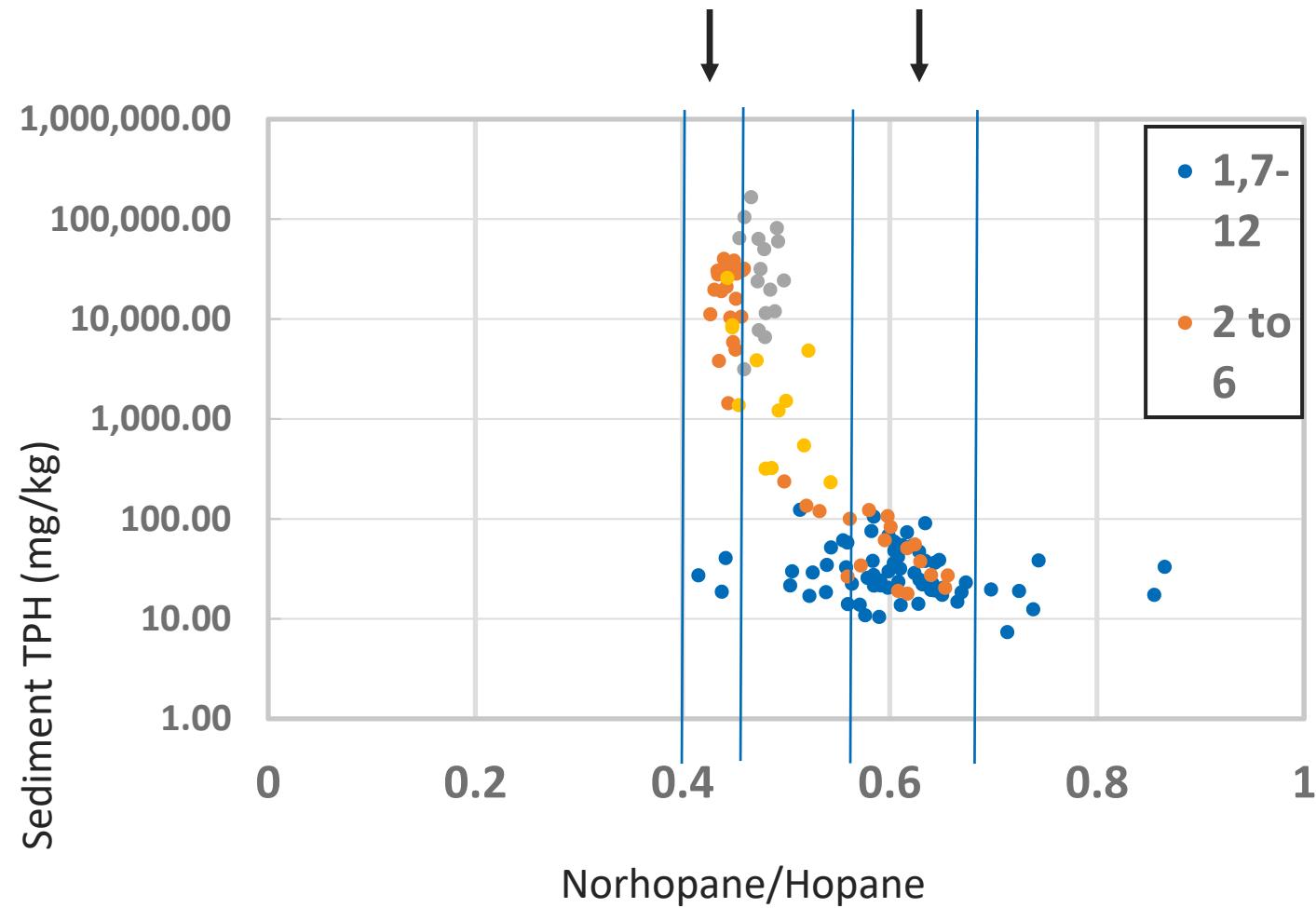
- Results from a Tier 3 (quantitative biomarker) and Tier 4 (cluster analysis) are consistent with Dr. Overton's findings.
- Surface sheens collected in 2017 are heterogeneous.
- Do not support a single source.
- The most compelling scientific conclusion is that the contaminated sediments near the toppled jacket are supporting the majority (or all of the sheen).
- Ocean currents play a critical role in this study.

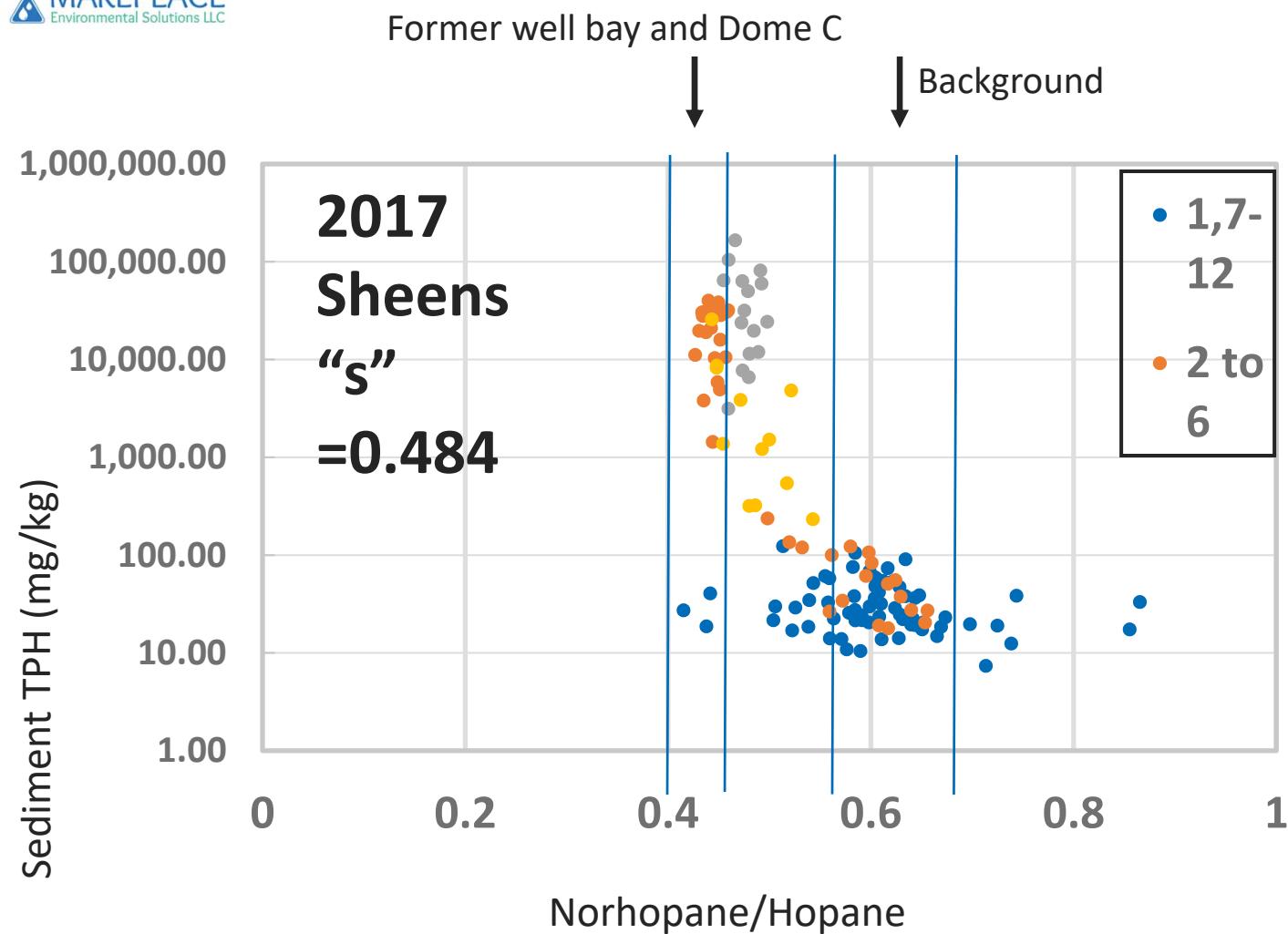
Consistent with MSL findings from 2012/2013

Biomarker compound	Abbreviation	Uncertainty
18a,22,29,30-Trisnorhopane-TS	Ts	3%
17a(H)-22,29,30-Trisnorhopane-TM	Tm	5%
30-Norhopane	NH	3%
18a(H)-30-Nornehopane-C29Ts	c29Ts	4%
30-Homohopane-22S	HH31S	2%
30-Homohopane-22R	HH31R	4%
30,31-Bishomohopane-22S	HH32S	3%
30,31-Bishomohopane-22R	HH32R	3%
30,31-Trishomohopane-22S	HH33S	5%
30,31-Trishomohopane-22R	HH33R	4%
Tetrakishomohopane-22S	HH34S	4%
13b(H),17a(H)-20S-Diacholestane	diabaCS	0%
13b(H),17a(H)-20R-Diacholestane	diabaCR	5%
14a(H),17a(H)-20S-Cholestane/13b(H),17a(H)-20S-Ethyldiacholestane (S12)	S12	2%
14a(H),17a(H)-20R-Cholestane/13b(H),17a(H)-20R-Ethyldiacholestane (S17)	S17	3%
14a,17a-20S-Methylcholestane ²	meaaCS	6%
14a,17a-20R-Methylcholestane ²	meaaCR	6%
14a(H),17a(H)-20S-Ethylcholestane	etaaCS	5%
14a(H),17a(H)-20R-Ethylcholestane	etaaCR	4%
14β(H),17β(H)-20R-Cholestane	bbCR	2%
14β(H),17β(H)-20S-Cholestane	bbCS	3%
14β,17β-20R-Methylcholestane	mebbCR	3%
14β,17β-20S-Methylcholestane	mebbCS	3%
14β(H),17β(H)-20R-Ethylcholestane	etbbCR	5%

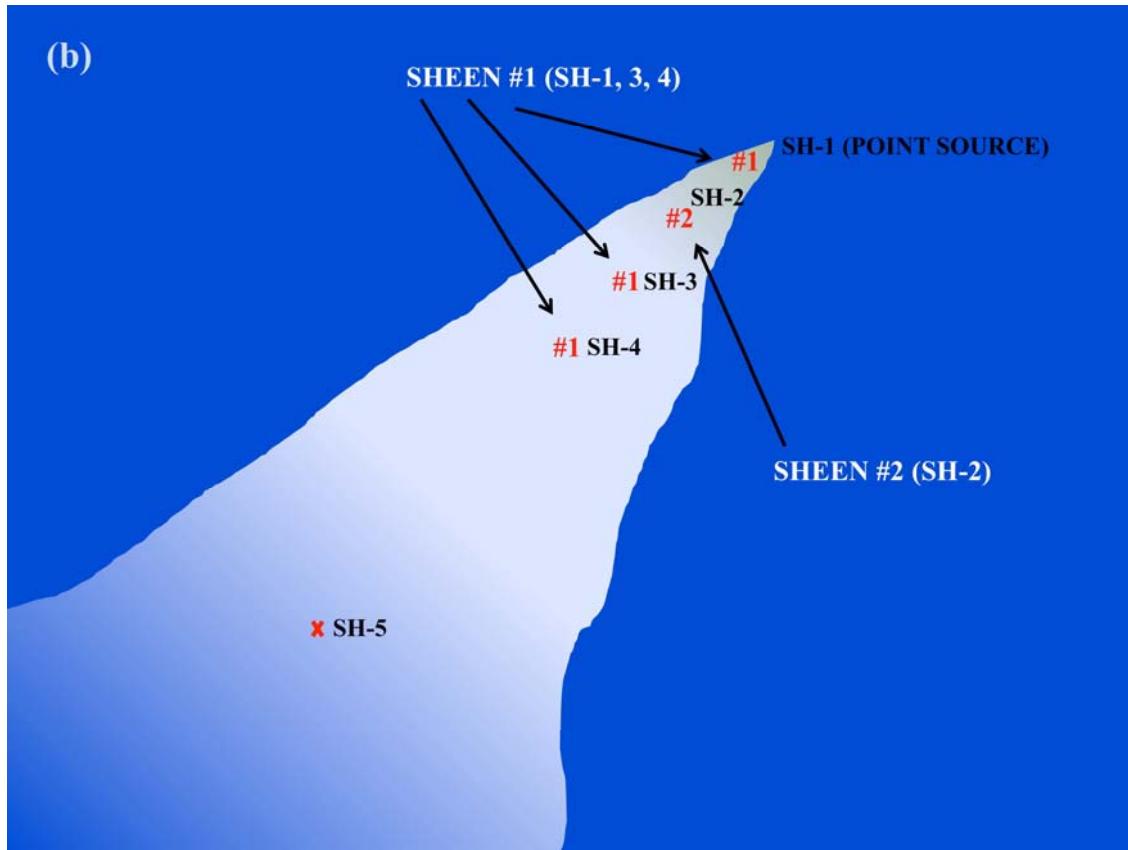
Former well bay and Dome C

Background





(b)



Prepared by Jason Screws (USCG)

