Geochemical Evaluation of Ocean Surface Slick Methods to Ground Truth Satellite Seepage Anomalies for Seepage Detection*

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Abstract

Synthetic Aperature Radar (SAR) has become a relatively standard tool for petroleum system validation in offshore frontier exploration areas. SAR sensors send out a radar signal and build an image from radiation reflected back to the satellite. The dampening of ocean surface capillary waves by films of oils (slicks), natural film from sea surface micro-layer, biological material, or physical processes such as current flow or wind will produce an anomalously low backscatter.

A field test program was undertaken to test a range of different sampling methods to determine the best way to ground truth ocean surface natural hydrocarbon seepage over a range of different sites and examine geochemical changes related to slick formation and aging. The field program was undertaken at the Coal Oil seep field using several ocean surface sampling methods; conventional headspace gas (C_1 to C_5) and gasoline plus range solid phase microextraction on ocean surface water sample in sealed containers; and surface contact methods which include the General Oceanics, Shell, and Gore samplers.

Our calibration studies have determined two sampling methods are required to properly collect both the lower boiling point (light hydrocarbons and gasoline plus range) and high molecular weight (C_{12} plus) hydrocarbons. The Gore Sorber slick sampler is a modified version of the soil sampling module which works best with fresh seepage that contains light hydrocarbon (C_2 to C_{26}) fractions. The General Oceanics Oil Sampler with a DCM solvent extraction works best for the higher molecular weight hydrocarbon (C_{15} plus) fraction including petroleum derived biomarkers.

References

Abrams, M.A., N.F. Dahdah, and E. Francu, 2009, Development of methods to collect and analyze gasoline plus range (C_5 to C_{12}) hydrocarbons from seabed sediments as indicators of subsurface hydrocarbon generation and entrapment: Applied Geochemistry, v. 24/10, p. 1951-1970.

Jones, A.T., G.A. Logan, J.M. Kennard, and N. Rollet, 2005, Reassessing potential origins of Synthetic Aperture Radar (SAR) slicks from the Timor Sea region of the North West Shelf on the basis of field and ancillary data: AAPEA Journal, p. 311-331.

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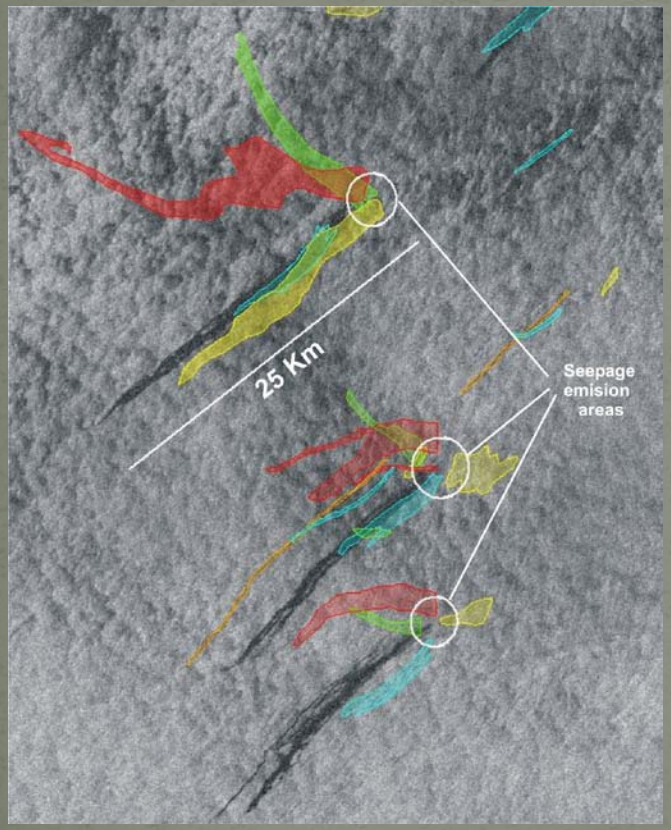
Goal: Develop collection and analysis protocols to ground truth ocean surface natural hydrocarbon seepage over a range of different seep zones and to examine geochemical changes related to hydrocarbon seepage slick formation and aging.

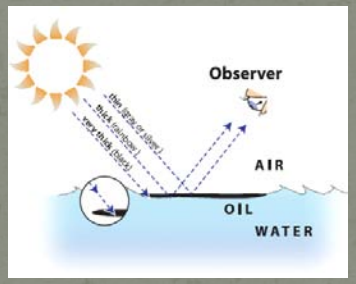
Talk Outline

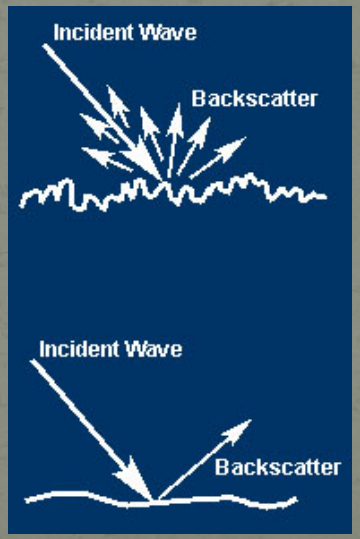
- Ocean surface slick satellite anomalies.
- Coal Oil Point seep field slick test program.
- Collection and analytical methods examined.
- Results from Coal Oil Point calibration survey.
- Summary and recommendations slick sampling.

Ocean Surface Slick Satellite Anomalies

Microwave backscatter from ocean surface is reduced in areas where capillary waves are dampened by hydrocarbon seepage or other non petroleum event providing a dark response in a brighter background.







SAR seepage analysis routine method to evaluate HC seepage

Contractors recognize not all wave dampening features are related to petroleum seepage since radar does not detect oil directly.

To overcome, several criteria are used to rank satellite anomaly;

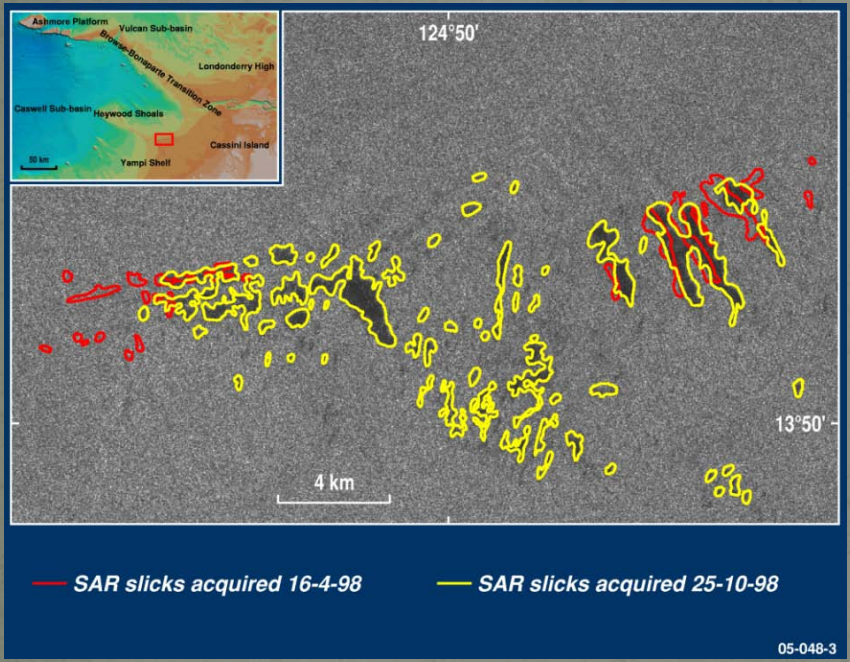
- **repeatability:**
  - **⇒ temporal repeatability**
- **shape (dog-leg, blob, or tadpole).**
- **dimensions (size).**
- **relationship to subsurface and near-surface geological features.**

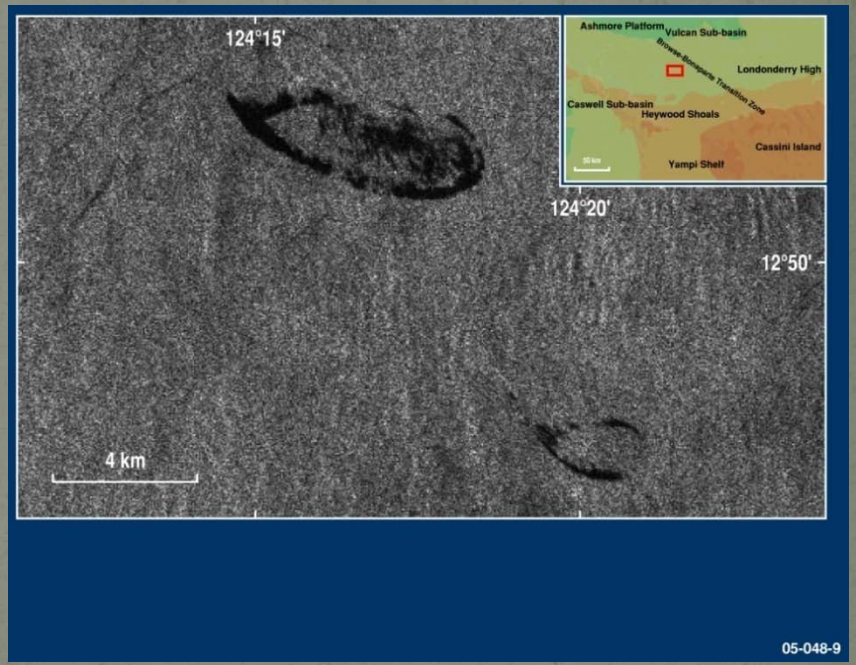
Indirect measurement → SAR measures wave dampening NOT hydrocarbons.

What are ocean surface slicks , cont.

SAR survey was undertaken to validate earlier anomalies clustered around seabed bathymetric edge and approximate edge of effective regional seal ⇒ concluded SAR anomalies related to petroleum leakage from seal failure. Later work demonstrated many of the SAR anomalies identified as high ranking were due to tidal current flows and coral spawning event.

SAR anomalies which correlate to subsurface geology may not always be related to petroleum seepage since seabed morphology will also affect surface micro-layers, distribution of ocean surface biological material, and current or wind flow which will also produce an anomalously low backscatter.

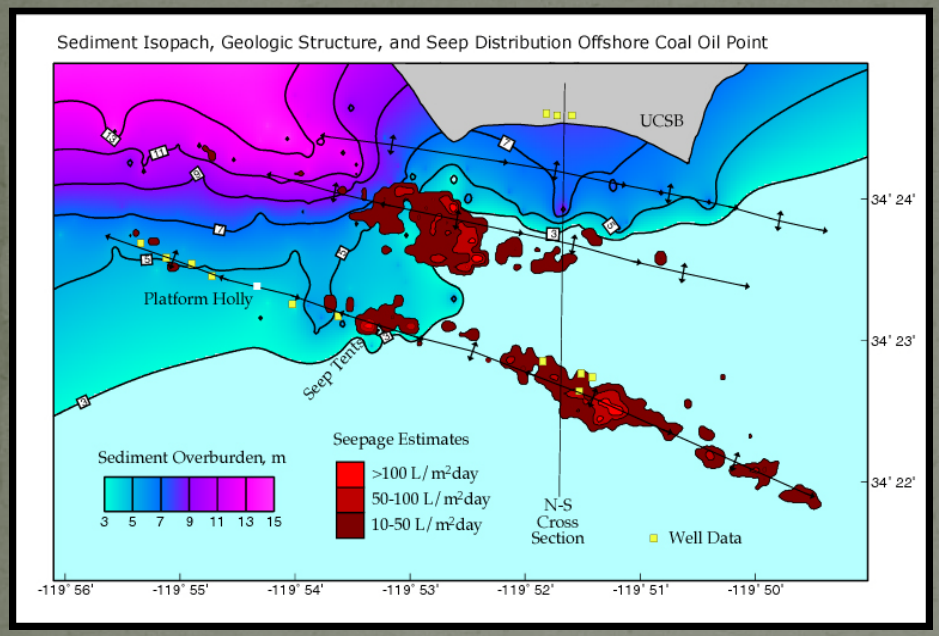


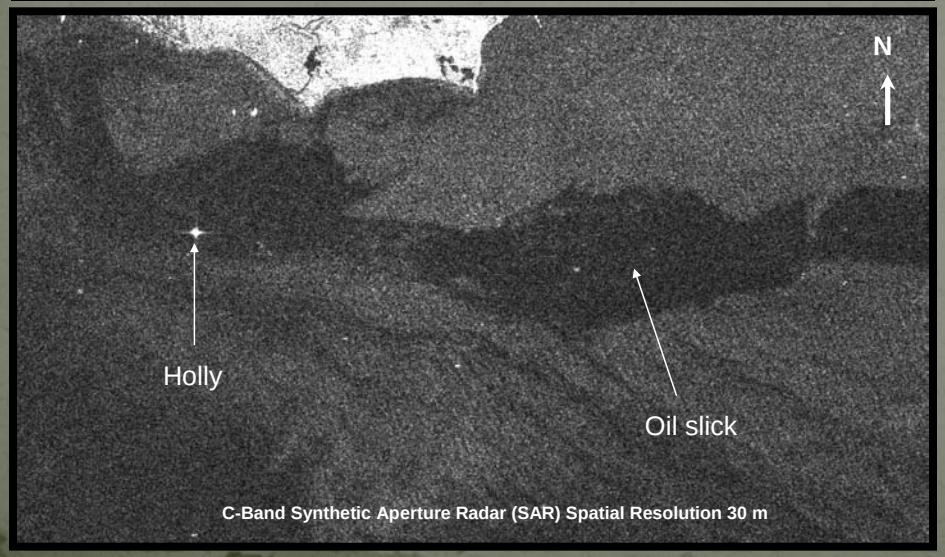


Not all SAR anomalies classified as high ranking related to HC seepage.

Jones et al. (2005) Reassessing potential origins of Synthetic Aperture Radar (SAR) slicks from the Timor Sea region of the North West Shelf on the basis of field and ancillary data. AAPEA Journal p. 311-331.

Coal Oil Point Ocean Surface Slick Test Program





GOAL

Evaluate sampling methods to ground truth SAR surface slick anomalies.

Study Area:

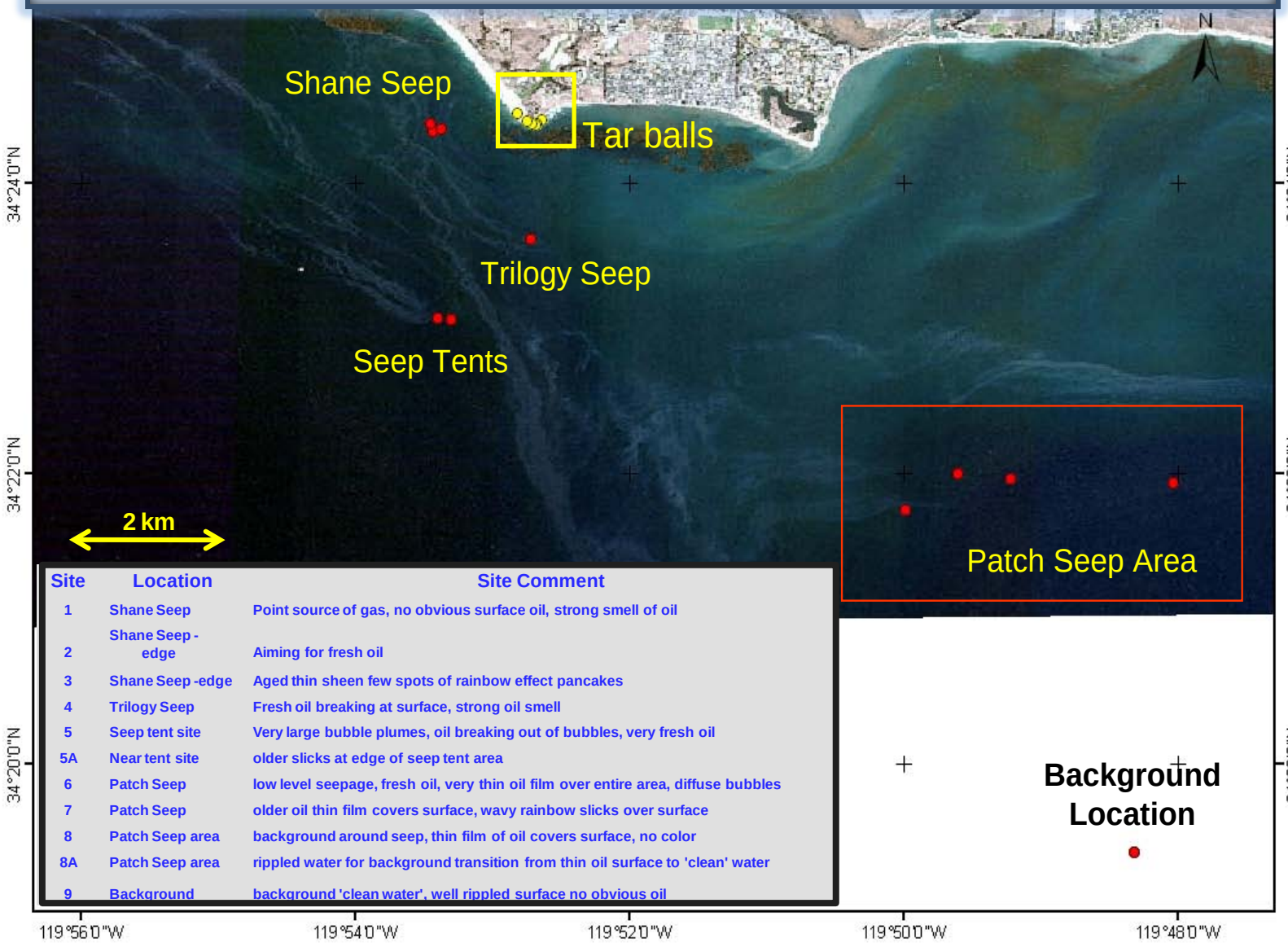
- Coal Oil Point seep field one of the most prolific and heavily studied offshore seep zones (well mapped seismic & sonar).
- known hydrocarbon origin (Monterey).
- full range seepage activity (fresh → relict).
- approximately 1.5 x 105 m^3 per day leaks from the sea floor to the ocean surface.
- located along linear trends above faults or fractured anticlines.

Sampling Program:

- Sample different seepage activity.
- Background sample location.

Coal Oil Point Ocean Surface Slick Test Program: Sample Locations

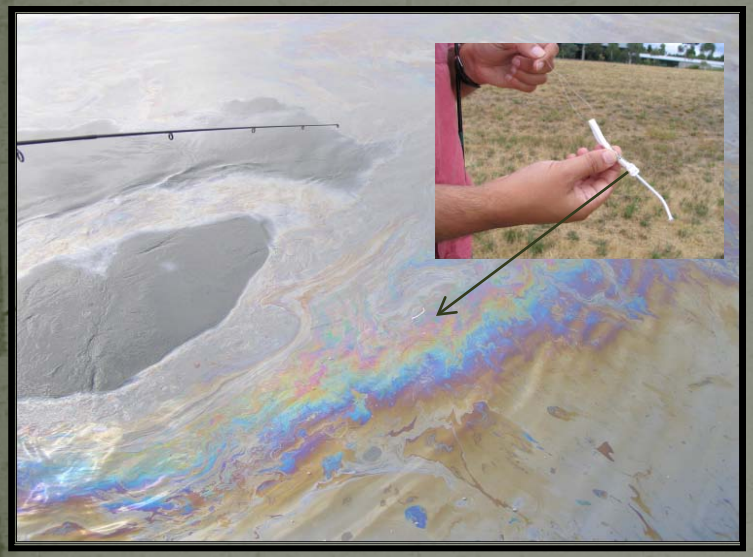
Goal: sample different types and stages of ocean surface HC seep slicks.



Site	Location	Site Comment
1	Shane Seep	Point source of gas, no obvious surface oil, strong smell of oil
2	Shane Seep - edge	Aiming for fresh oil
3	Shane Seep -edge	Aged thin sheen few spots of rainbow effect pancakes
4	Trilogy Seep	Fresh oil breaking at surface, strong oil smell
5	Seep tent site	Very large bubble plumes, oil breaking out of bubbles, very fresh oil
5A	Near tent site	older slicks at edge of seep tent area
6	Patch Seep	low level seepage, fresh oil, very thin oil film over entire area, diffuse bubbles
7	Patch Seep	older oil thin film covers surface, wavy rainbow slicks over surface
8	Patch Seep area	background around seep, thin film of oil covers surface, no color
8A	Patch Seep area	rippled water for background transition from thin oil surface to 'clean' water
9	Background	background 'clean water', well rippled surface no obvious oil

Collection and Analytical Methods Examined

Multiple methods were examined to evaluate ocean surface light to high molecular weigh hydrocarbons sampling and analysis methods.



Gore Sorber Slick Sampler®:

- GORE-TEX ePTFE® (polytetrafluoroethylene) and sorbent filled collectors.
- ePTFE chemically inert microporous hydrophobic structure allows HC vapor transfer and not water.
- Gore Sorber® placed in ocean surface slick then placed sealed special glass container for shipping.
- analyzed by thermal desorption coupled with GCMS for C_2 to C_{28}+ hydrocarbons.

Equilon-SEPCO Sheen Sorbent:

- Shell sheen/slick sampler chemically treated tetrafluoroethylene polypropylene strips.
- wrapped in destructible wrap (dissolves) then exposed to slick with maximum absorbent surface area
- oiled slick sheen sorbent placed in special container, frozen in field, then shipped for analysis.
- solvent washed with CH and MCH remove sorbed HC.
- extract analysis program:
  - whole extract GC-FID (gas chromatography)
  - GC-MS full-scan with ion chromatograms to identify components along with mass spectra.

CH = cyclohexane MCH = methylcyclohexane

Collection and Analytical Methods Examined, cont.

Disrupter Container

General Oceanics Oil Sampling Net Kit:

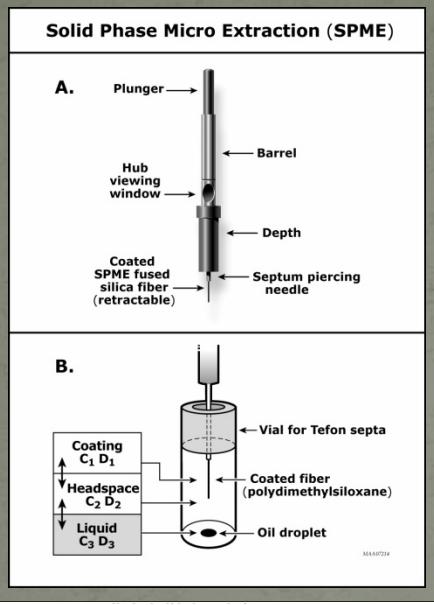
- drag net through ocean surface slick.
- method used by USCG for oil spill studies.
  - place oiled net in jar ship to laboratory.
  - add cyclohexane to jar and thoroughly shake.
  - transfer to test tube and remove water.
  - concentrated extract to GC and GCMS analysis.
- modified SGC analysis method:
  - place oiled net in disrupter container without blades
  - freeze onboard and ship to laboratory for analysis
  - analytical procedures for GO sampler net:
    1. disrupter syringe HS light hydrocarbons (C_1-C_5).
    2. disrupter HS SPME gasoline range HC (C_5-C_{10}).
    3. solvent (CH & MCH) extraction HMW HC (C_{12}+).

Surface water sample:

- collect surface water sample with disrupter container without internal blades plus chemical grade salt to prevent bacterial activity
  → 2/3 water sample and 1/3 air headspace
- seal container, freeze, then ship for laboratory analysis
- analytical procedures undertaken on disrupter sample
  1. disrupter syringe HS light hydrocarbons (C_1-C_5).
  2. disrupter HS SPME gasoline range HC (C_5-C_{10}).

HS = headspace SPME = solid phase microextraction

Collection and Analytical Methods Examined, cont.

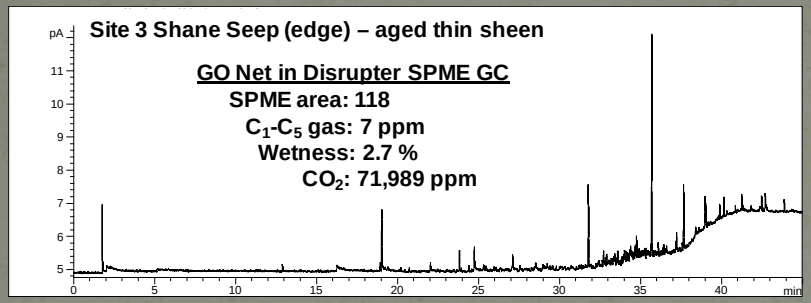


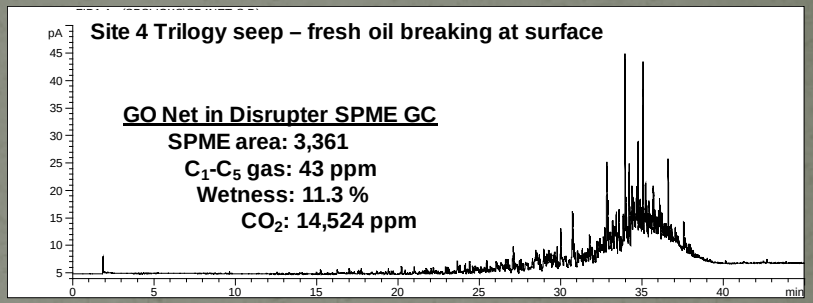
Headspace Solid Phase Microextraction (HSPME)

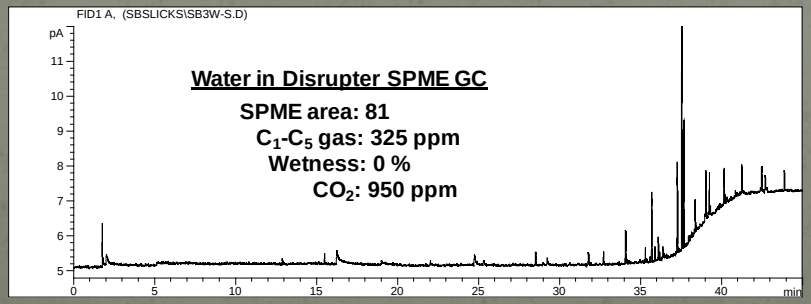
HSPME relies on an "equilibrium" between sample, container headspace, and fiber providing a representation of slick gasoline plus range (C_5-C_{10}) hydrocarbon relative concentrations.

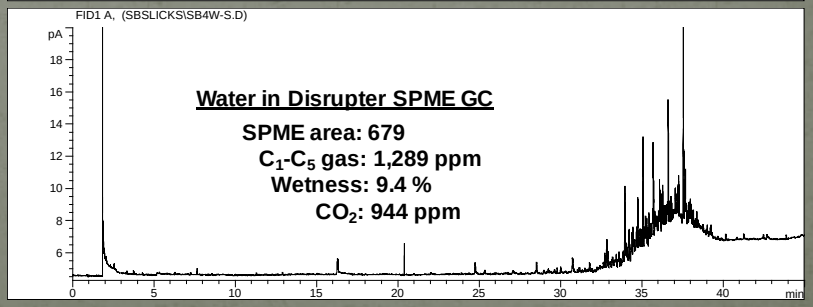
→ Disrupter water and GO net sample

Evaluated for sediment gasoline range analysis but untested to examine effectiveness in the detection ocean surface light hydrocarbons (less than C_{10}).







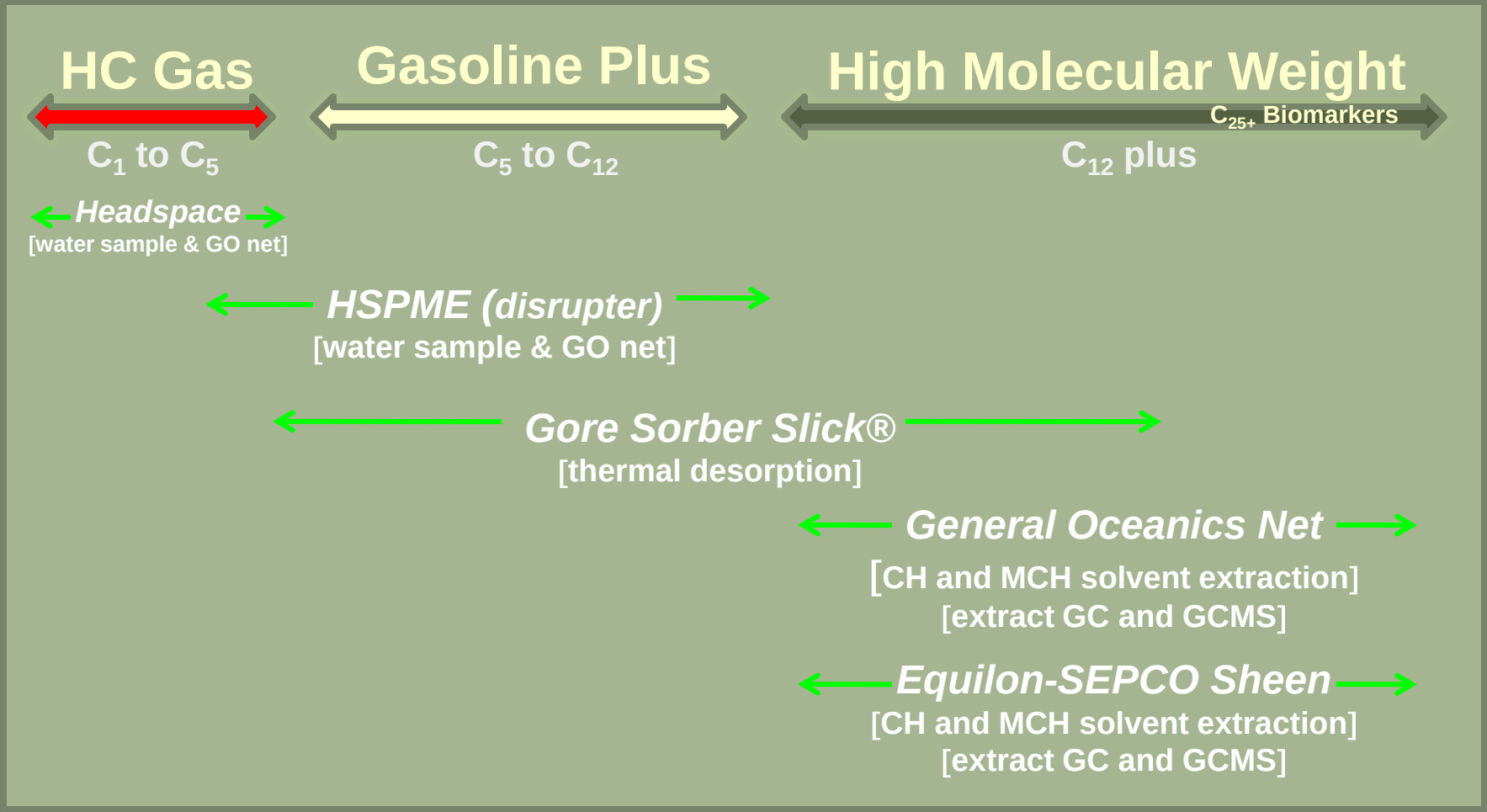


Abrams et al. (2009), Development of methods to collect and analyze gasoline plus range (C_5 to C_{12}) hydrocarbons from seabed sediments as indicators of subsurface hydrocarbon generation and entrapment, *Applied Geochemistry,* 24 p. 1951-1970.

Collection and Analytical Methods Examined, cont.

Sampling Method versus Hydrocarbon Range

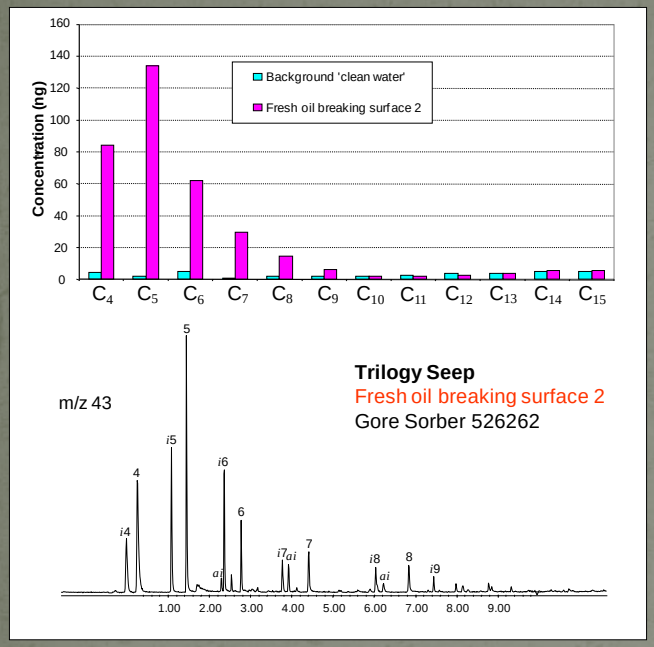
Each collection and analysis method examines different boiling point range.



Next: compare results from different methods on different types of slicks.

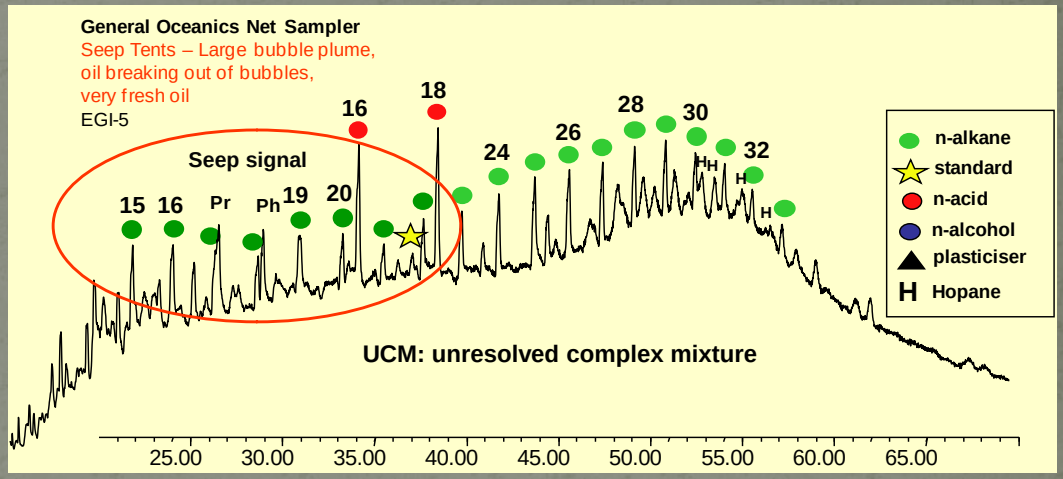
Changes in Slicks Signal With Time: Stage 1

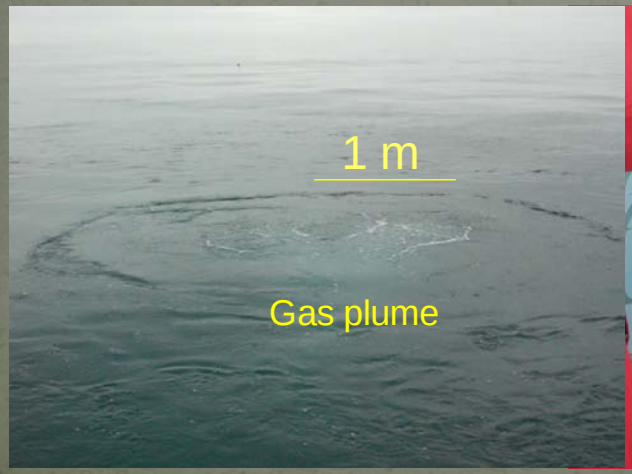
Fresh seep Volatiles Intact

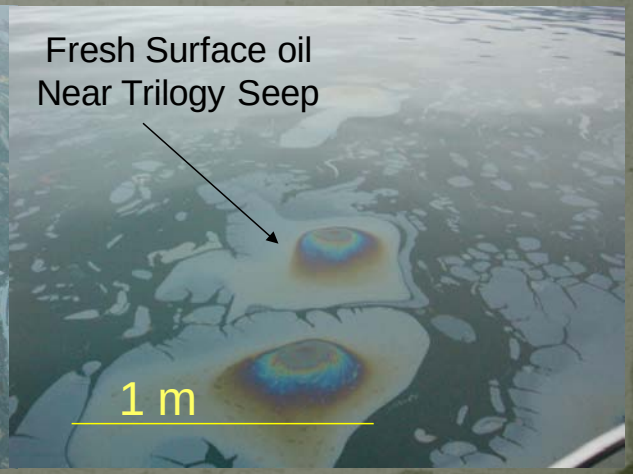


Directly over fresh seeps gas and gasoline range hydrocarbons can be detected using.

NOTE: volatiles detected Gore Sorber & HSPME only.

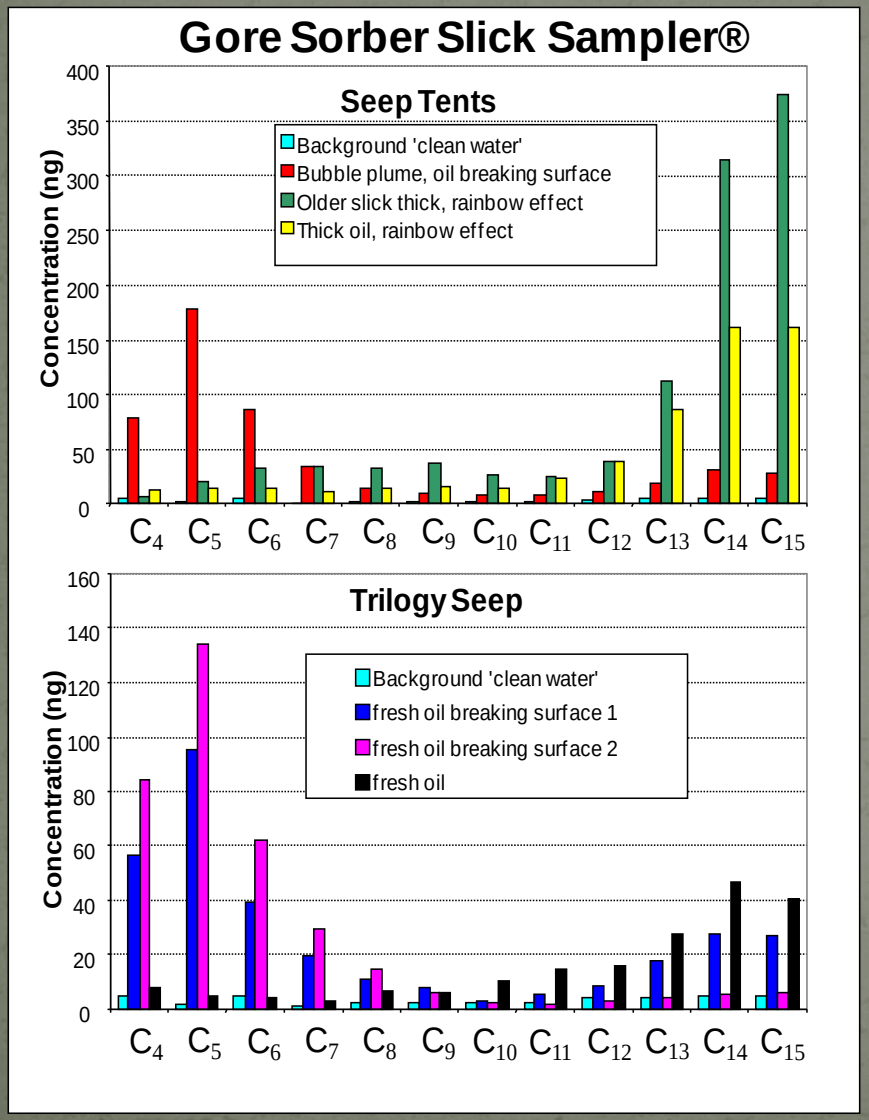






Changes in Slicks Signal With Time: Stage 2

Volatile Loss (very quickly)

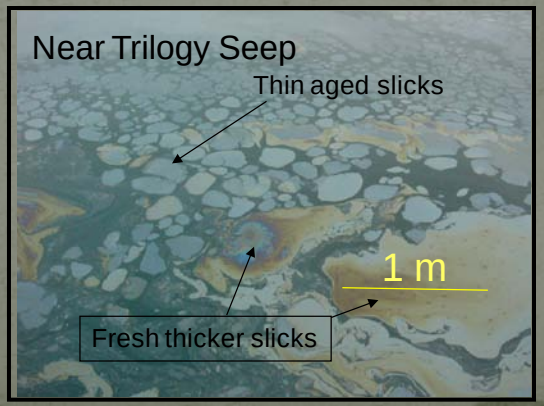


As ocean surface seeps age, they are subject to greater volatile loss, concentration of heavier hydrocarbons (C_{12} plus), and become relatively thin:

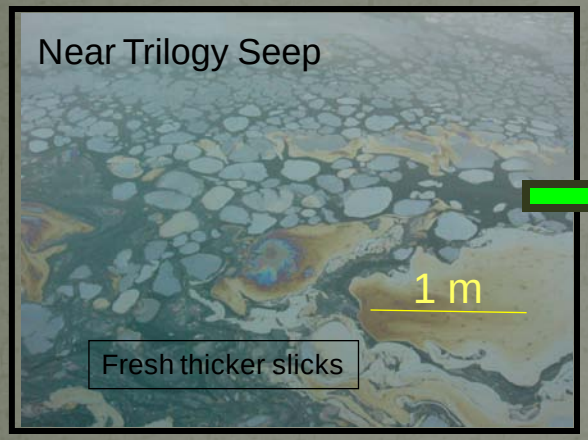
- very strong petroleum odor noted during sampling from volatile loss.
- changes in compound distribution from fresh to older slicks.

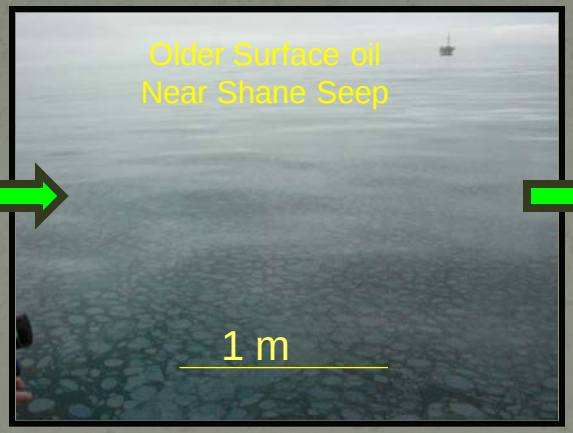
As HC seep related slicks become thin, it is increasingly difficult to collect and analyse the petroleum related slick:

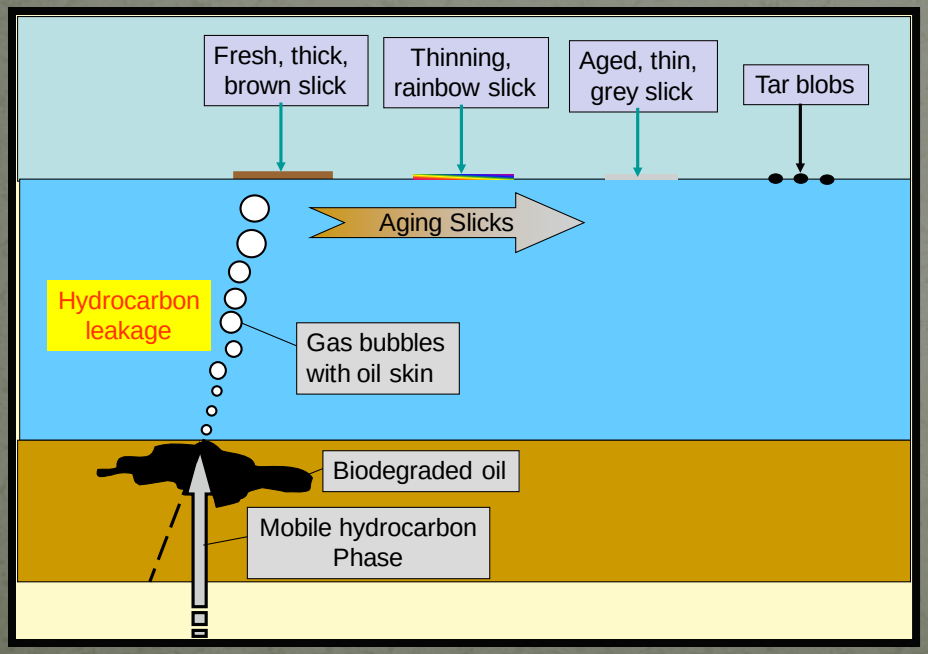
- Gore Sorber slick sampler is most sensitive in detection older slicks.

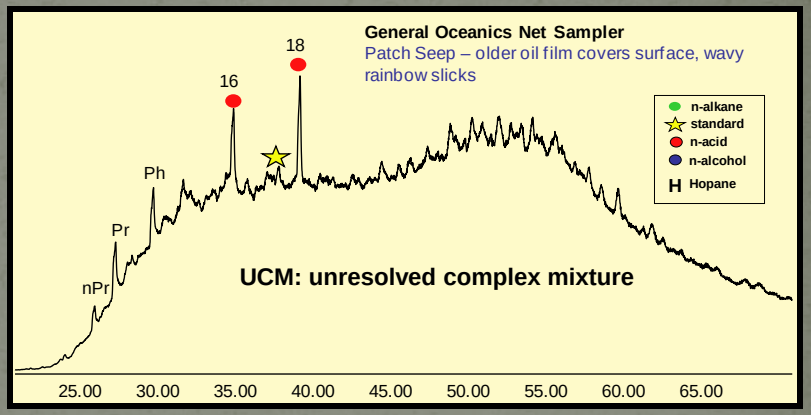


Changes in Slicks Signal With Time: Stage 3
Slicks become very thin and alteration occurs.



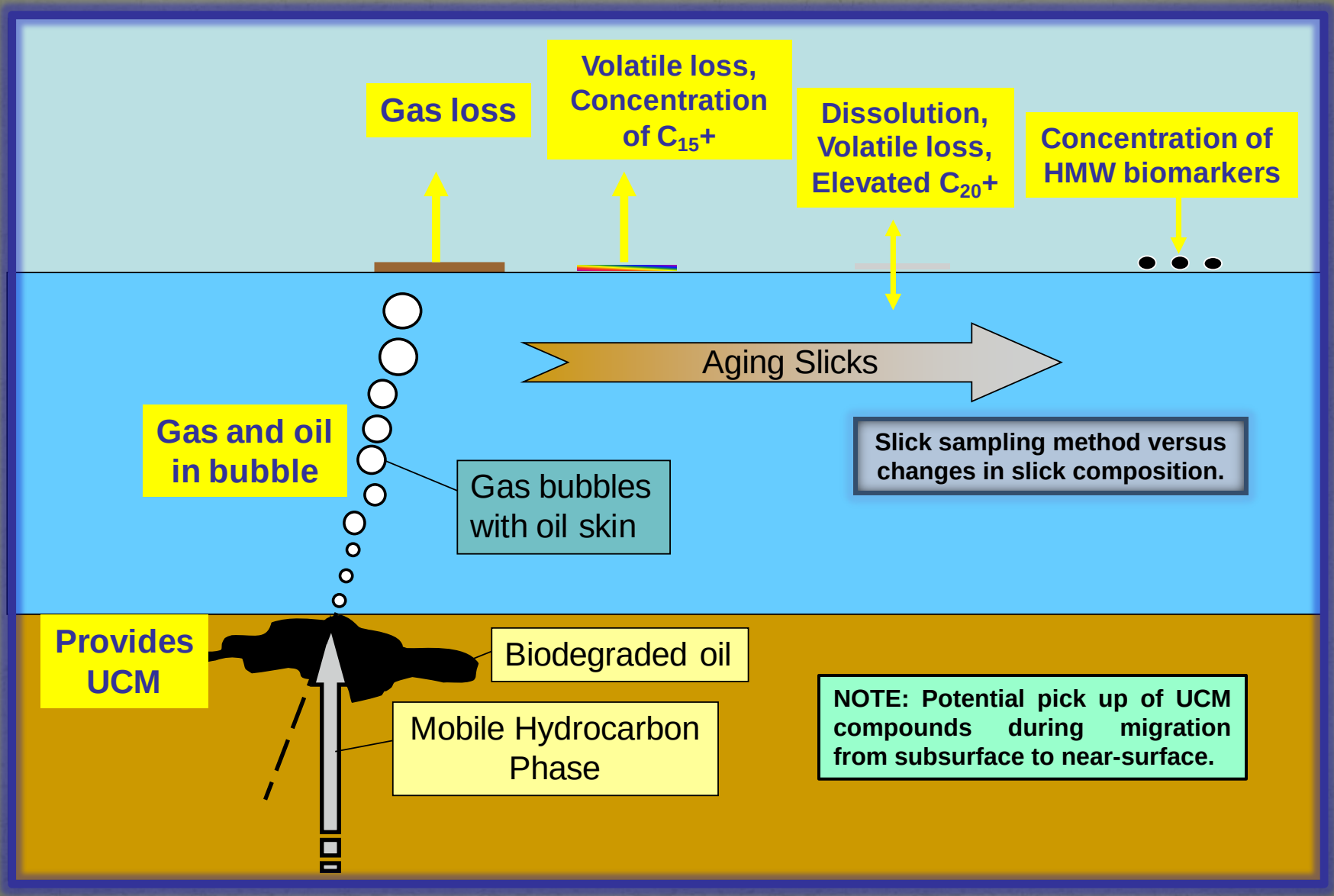






NOTE: Some oil slicks appear heavily biodegraded; where does this occur → within ocean surface or near surface sediments ?

Changes in Slicks Signal With Time



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Geochemical evaluation of ocean surface slick methods to ground truth satellite seepage anomalies for seepage detection

Important Observations

Detection Methods:

- Gore Sorber and HSPME (via GO nets and water) detect gasoline range hydrocarbons directly over active fresh hydrocarbon seepage/slicks.
- Only Gore Sorber detected hydrocarbons in thin/aged slicks with lower concentration light and HMW hydrocarbons or gas seepage only.
- GO Net and Equilon-SEPCO Sheen Sorbent with solvent extraction detect HMW hydrocarbons in fresh and less altered (thin) surface slicks.
  NOTE: problems as the slick becomes aged and very thin.
- GO Net enhances UCM signal (collection capture more polar compounds ?).
- GCMS analysis of extracted material from GO Net and Equilon-SEPCO Sheen Sorbent does provide usable results.
- No GCMS data from Gore Sorber and HSPME sample and removal process.
- Ocean surface slick water collection not an effective method to obtain slick hydrocarbon sample for geochemical analysis.

Changes in slick with time:

- As seep slicks age, loose volatiles and concentrate heavier hydrocarbons.
- Thin aged slicks are difficult to detect/analyse (Gore Sorber most sensitive).
- Some oil slicks appear heavily biodegraded (occurs subsurface).

Geochemical evaluation of ocean surface slick methods to ground truth satellite seepage anomalies for seepage detection, cont.

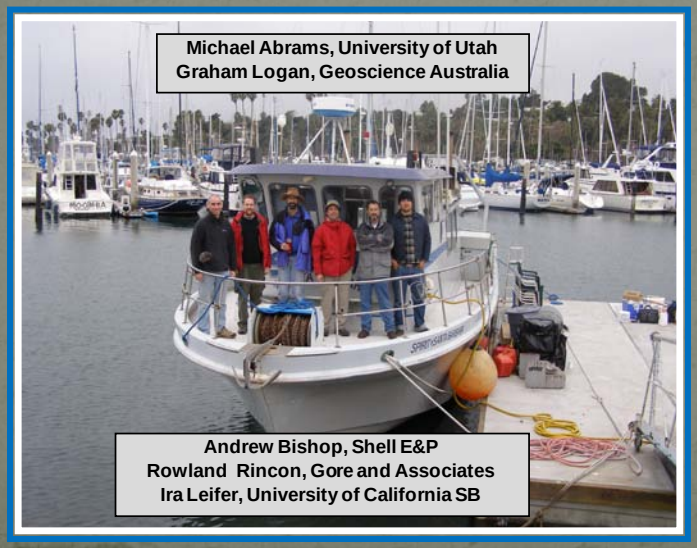
Recommendations

All ocean surface satellite anomalies MUST be ground truth no matter how high your confidence level is (correct shape, repeatability, or association with geological features such as migration pathways and/or seal failure).

We recommend two ocean surface hydrocarbon slick sampling methods to capture two different types/ranges of hydrocarbons:

- **Light hydrocarbons – *Gore Sorber Slick Sampler®***
- **High molecular weight HC*: *General Oceanics Oil Sampling Net***

*** with DCM solvent extraction to include biomarkers.**



Thank you,
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