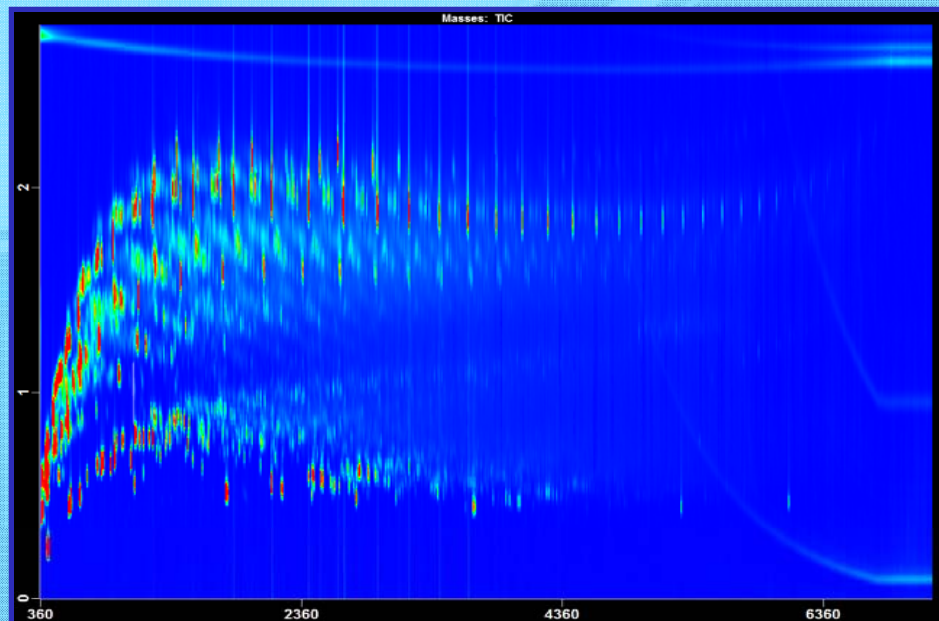


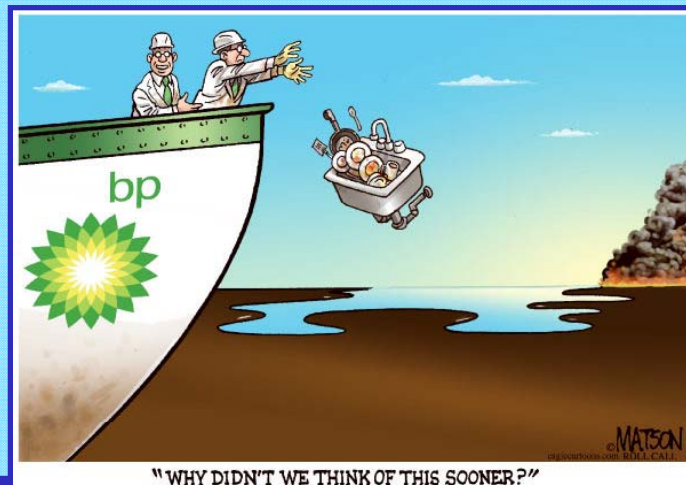
# *Characterization of Crude Oils and Tar Balls using Biomarkers and Comprehensive Two-Dimensional Gas Chromatography*



Michelle Misselwitz, Jack Cochran, Chris English, and Barry Burger

# Deepwater Horizon Oil Spill

April 20<sup>th</sup>, 2010



July 15<sup>th</sup>, 2010



# On going cleanup efforts Walton County, Florida 2011



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# How Restek got Involved


**ChromaBLOGraphy** Visit Restek.com

Topical and timely insights from top chromatographers.

Archive for the 'Oil Spill' Category

« Older Entries

### EcoRigs Non Profit Organization



**EcoRigs Data Collection**

Due to the location of offshore platforms immediately inshore to the source of the oil spill, the coral reef communities living on the platforms will experience the greatest exposure to various states of the oil coverage. In addition, the platforms occupy the entire water column, from the sea floor through the splash zone and shallow water and deep water organisms are present on the structures. This is a great scientific opportunity because very little is known about the impact of oil and dispersants on coral reef communities. This page will be updated as data arrives; written reports on each video are forthcoming. EcoRigs is self-funded non-profit so the process is slow.

facebook

### The Oil Spill and South Walton/Scenic Hwy 30A - CONNECT

Wall Info Discussions Photos Video Events

**Susan B. Forsyth** And we thought it was over...  
<http://www.youtube.com/watch?v=MMVIXhrK-zk>

**BP oil and froth in water: 9/14/11**  
[www.youtube.com](http://www.youtube.com)  
MC252 is present on the beaches of Florida. On September 14, 2011 UV light detected the unique fluorescent signature of BP's crude oil mixed with Corexit. Ta...

September 15 at 10:12am · Like · Comment · Share

Leigh Holmes likes this.

Write a comment...

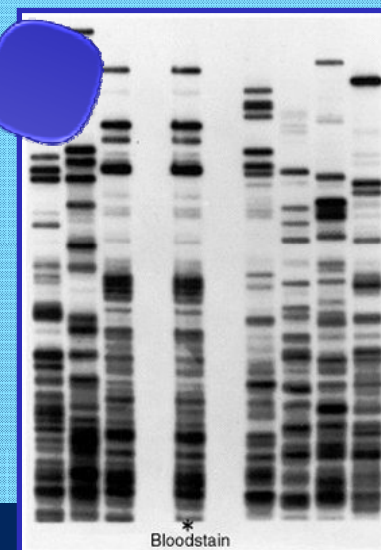
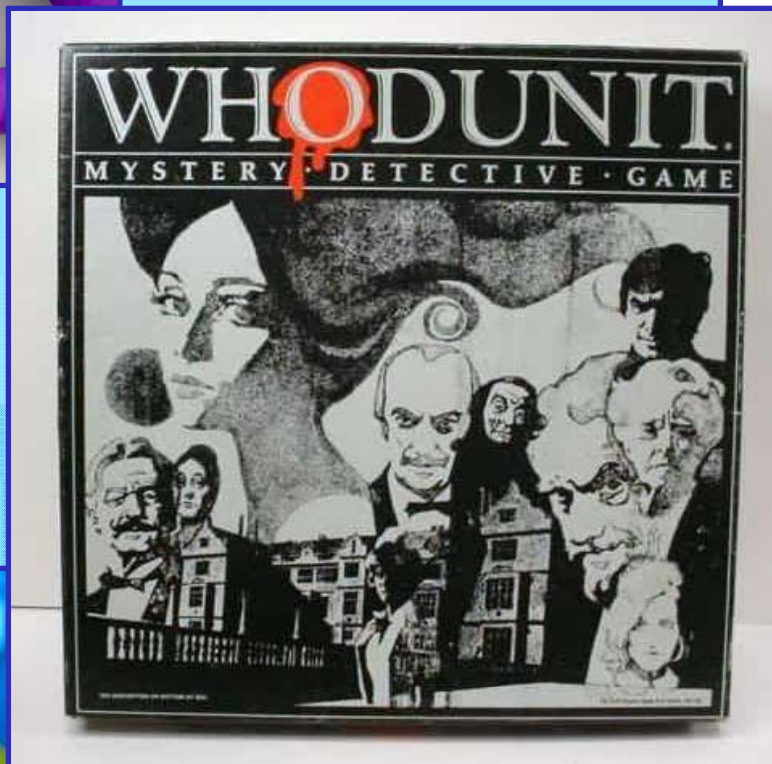
**Anna Hermina** <http://www.groupon.com/deals/dolphins-cove-miami>

**\$85 for a Shallow-Water Dolphin Encounter at Dolphins Cove in Key Largo (\$145 Value)**  
[www.groupon.com](http://www.groupon.com)  
The call of the wild is like a call from an elderly grandparent: though you can't quite make out what's being said, you feel better about yourself when you answer. Pick up nature's phone with today's Groupon: for \$85, you get a shallow-water dolphin encounter at Dolphins Cove in Key Largo (a \$145 va...

August 27 at 2:29pm · Like · Comment · Share

**Susan B. Forsyth** On CNN: Coastal geologist and a scuba team from EcoRigs find a dark lifeless seafloor along panhandle. Thanks to Emerald Coast SURFRIDER and Patagonia, the sediment samples are being extensively tested- results should be back in 2 weeks.  
<http://ireport.cnn.com/docs/DOC-637109>

# Criminal Forensics

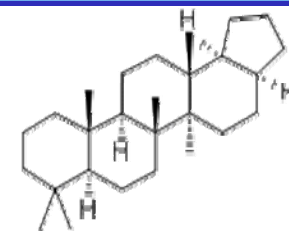
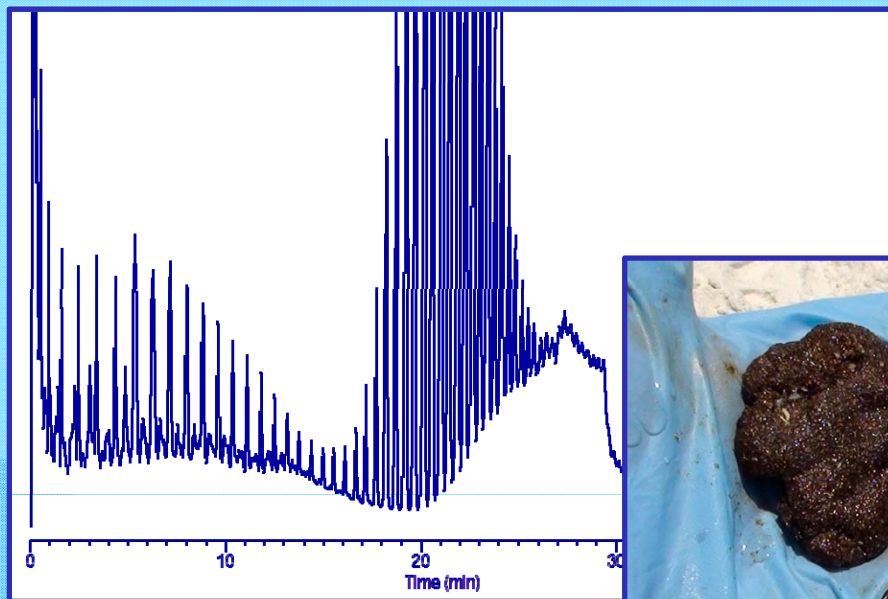


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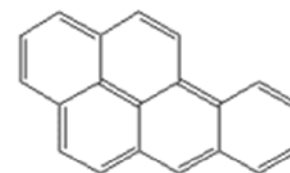
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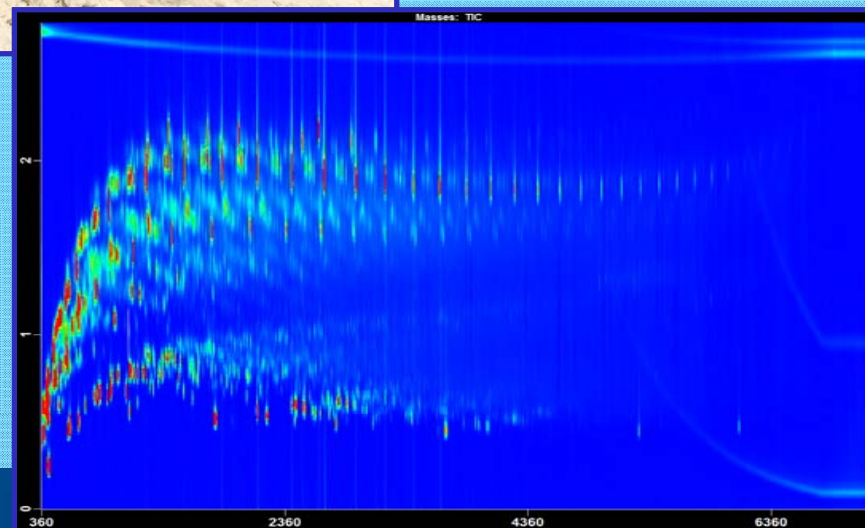
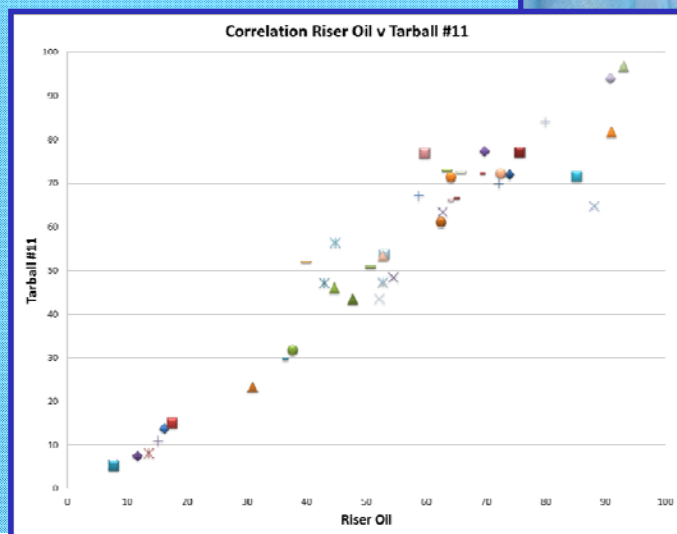
# Environmental Forensics



17 $\alpha$ (H)-22,29,30-Trisnorhopane



Benzo(a)pyrene



**RESTEK**

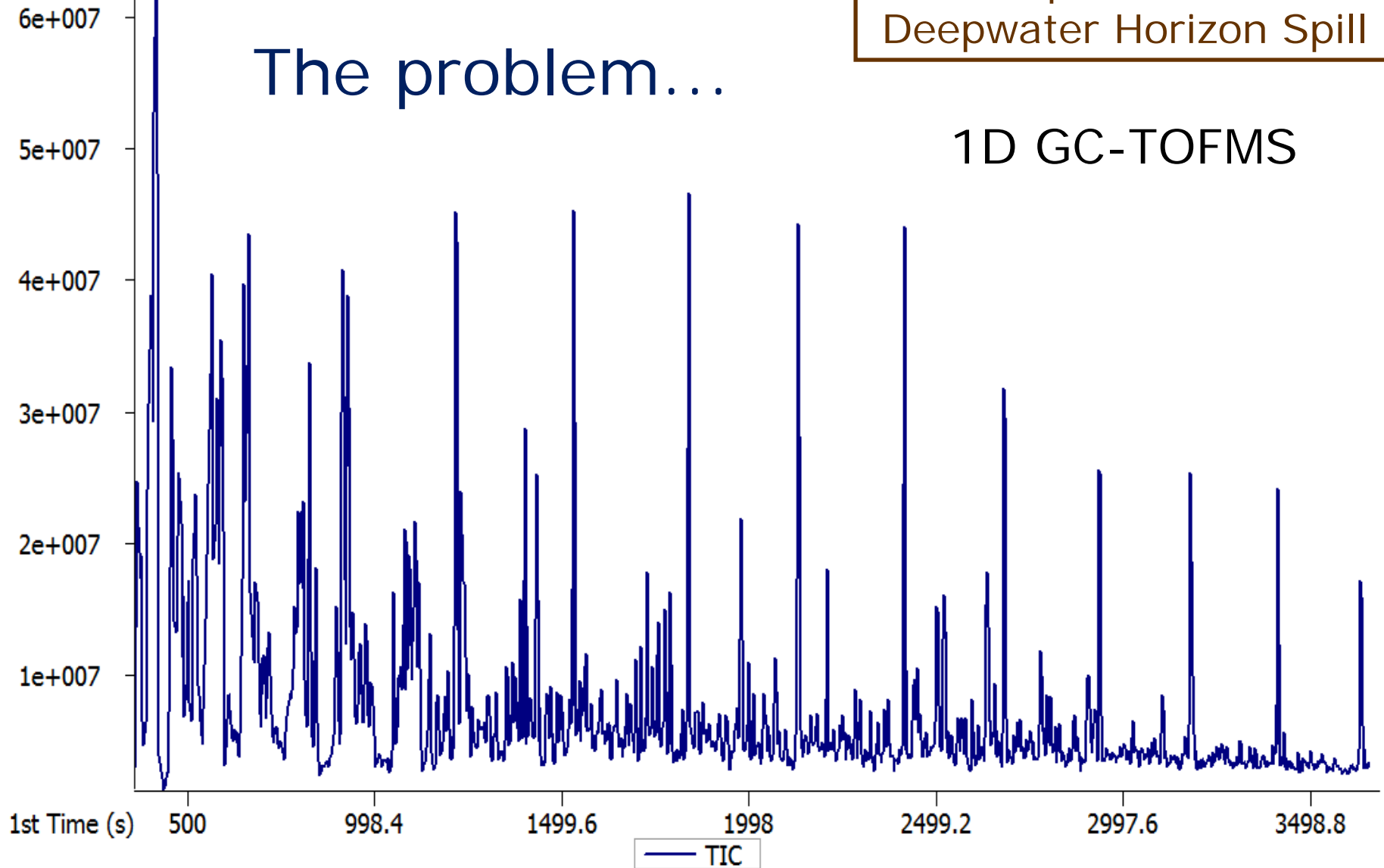
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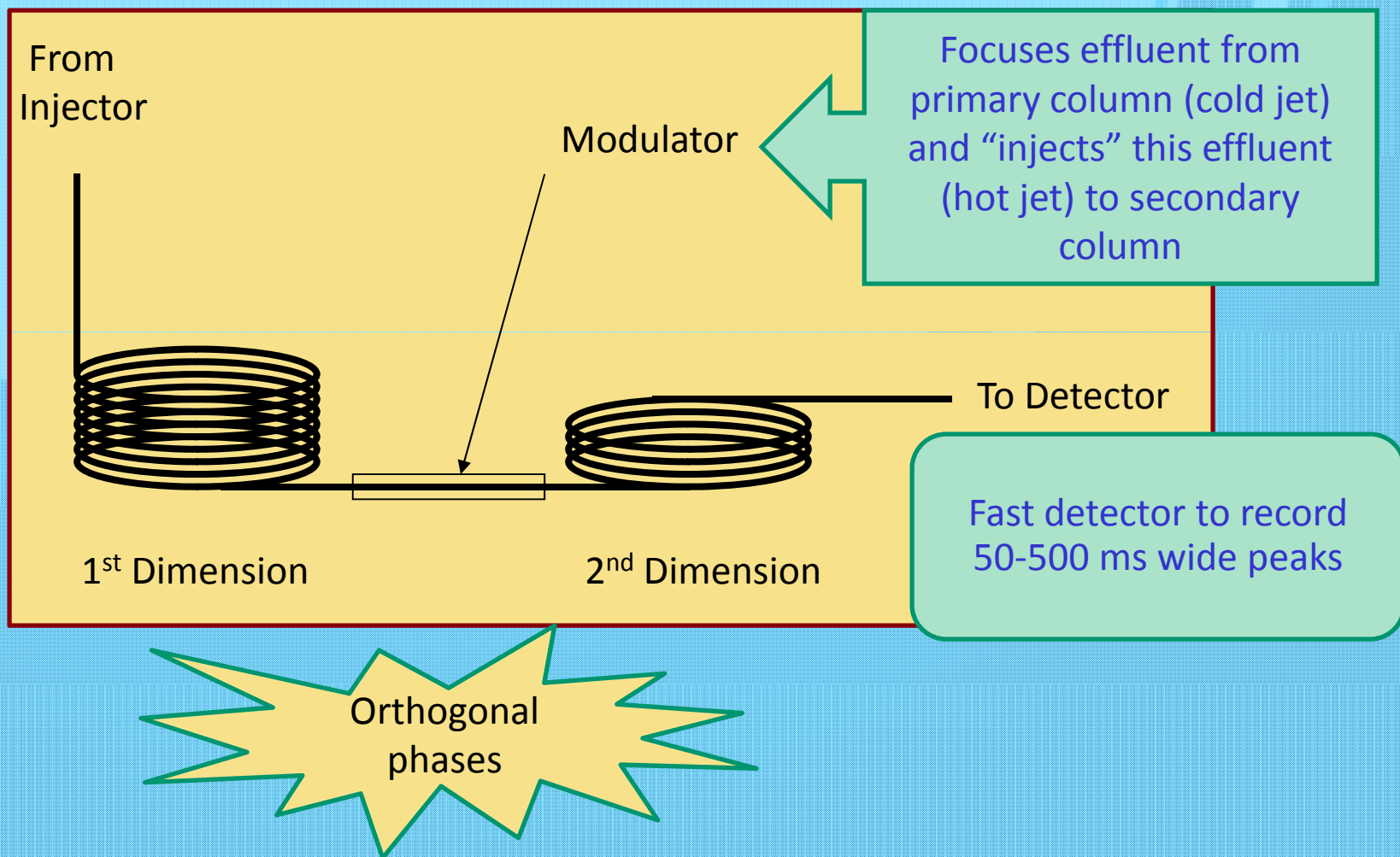
Riser Pipe Oil from the  
Deepwater Horizon Spill

The problem...

1D GC-TOFMS

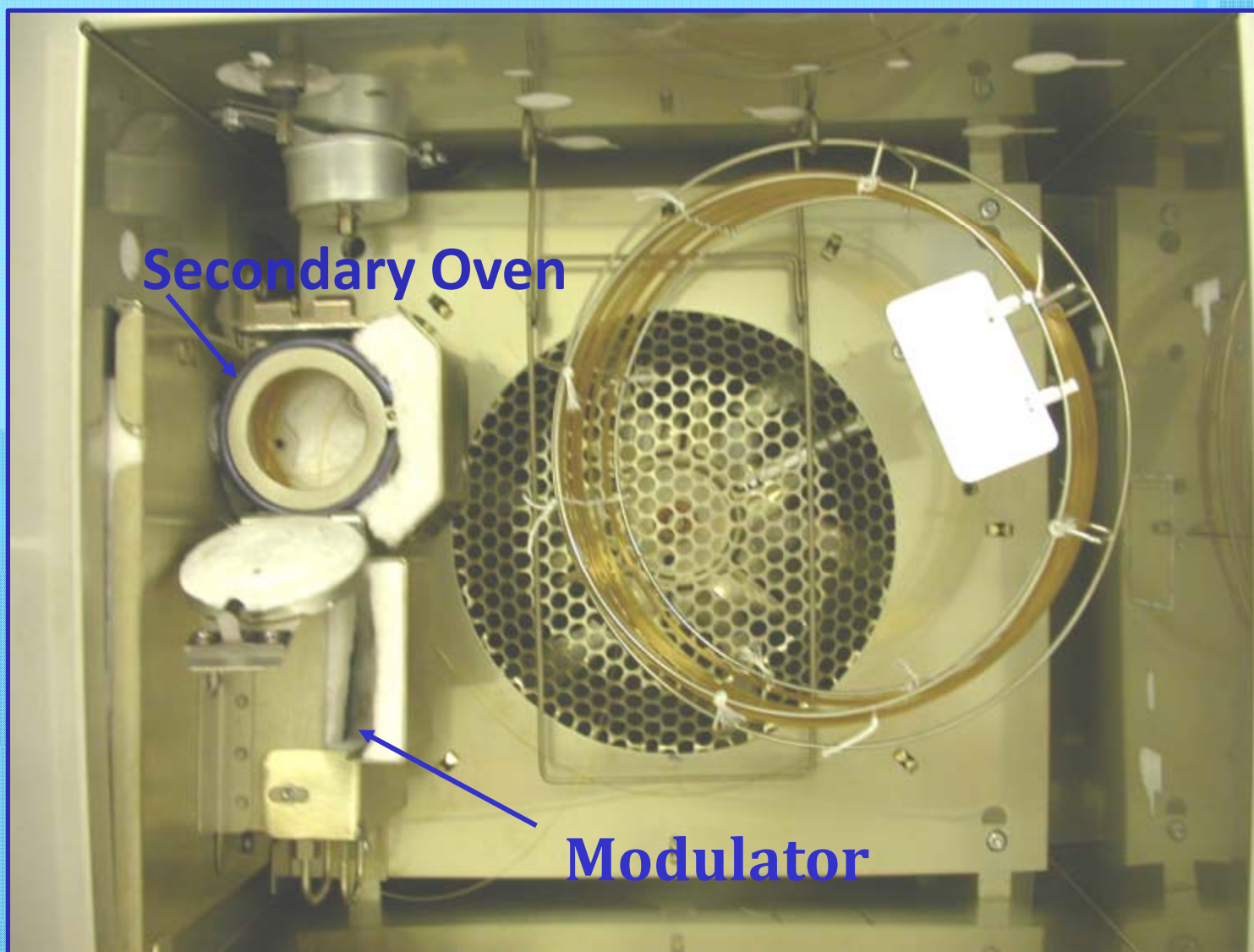


# Basics of GCxGC





# Modulator and Secondary



Masses: TIC

Pristane

Phytane

Riser Pipe Oil from the  
Deepwater Horizon Spill

<< Paraffins and iso-paraffins >>

<< Olefins and cyclo-paraffins >>

Steranes  
Hopanes

<< Aromatics, alkyl-aromatics >>

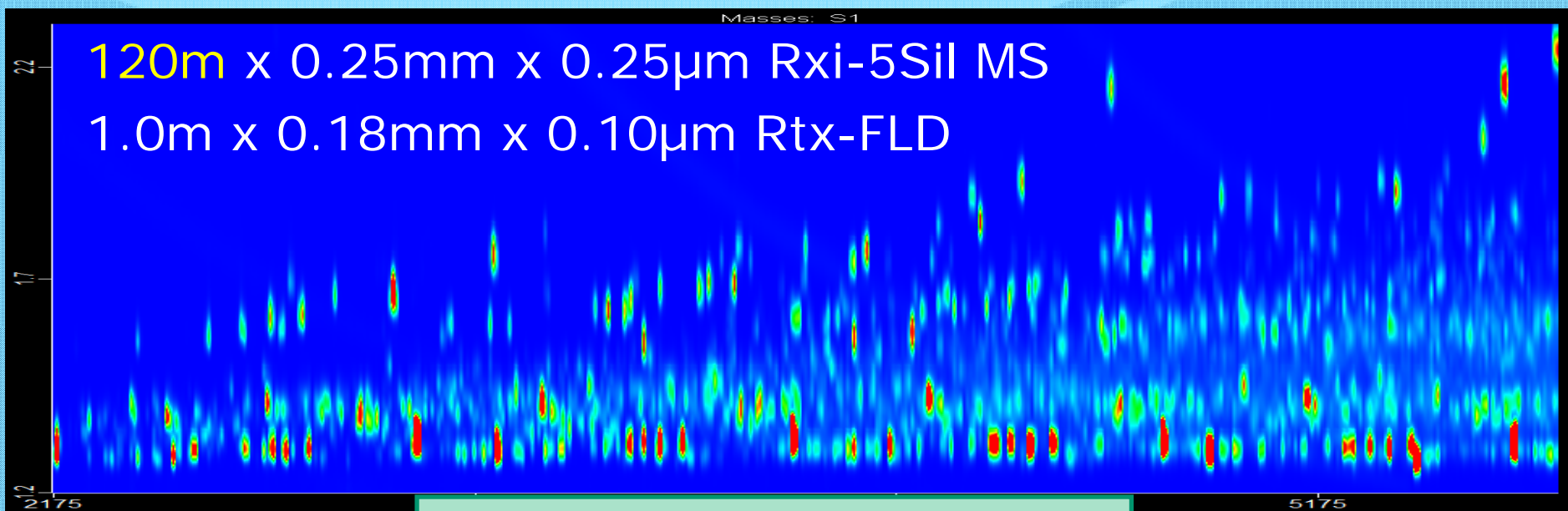
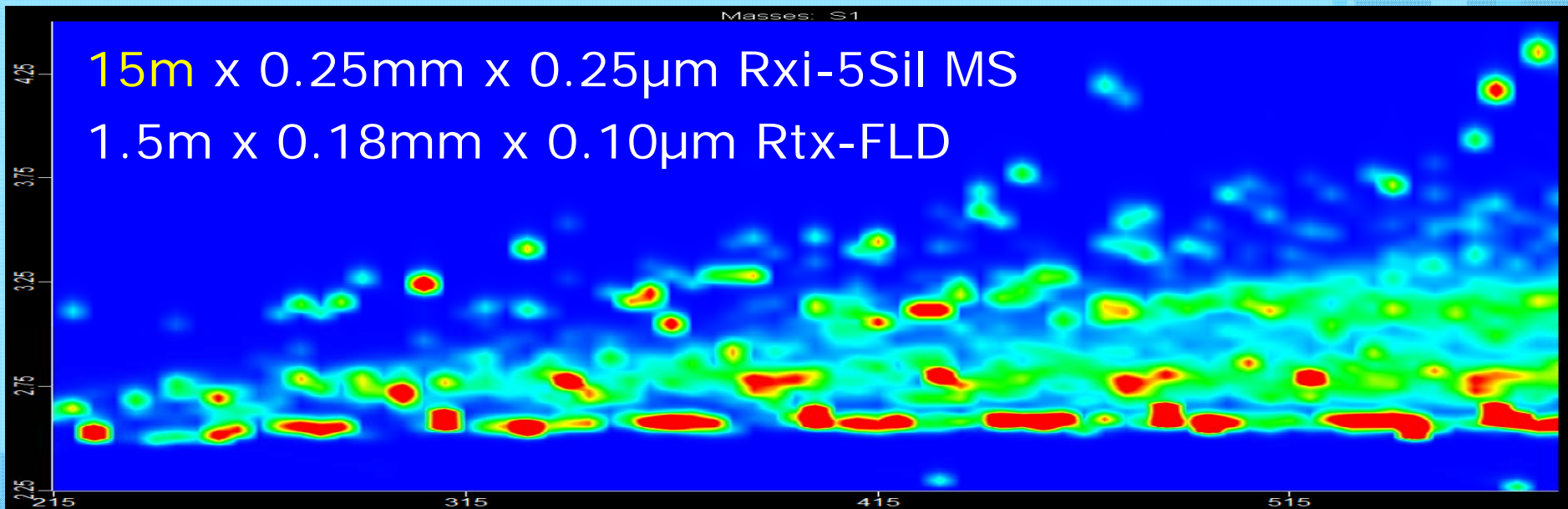
<< PAHs, alkyl-PAHs, dibenzothiophenes >>

Rxi-17Sil MS 60 m x 0.25 mm x 0.10  $\mu\text{m}$

Rxi-1HT 1 m x 0.25 mm x 0.10  $\mu\text{m}$

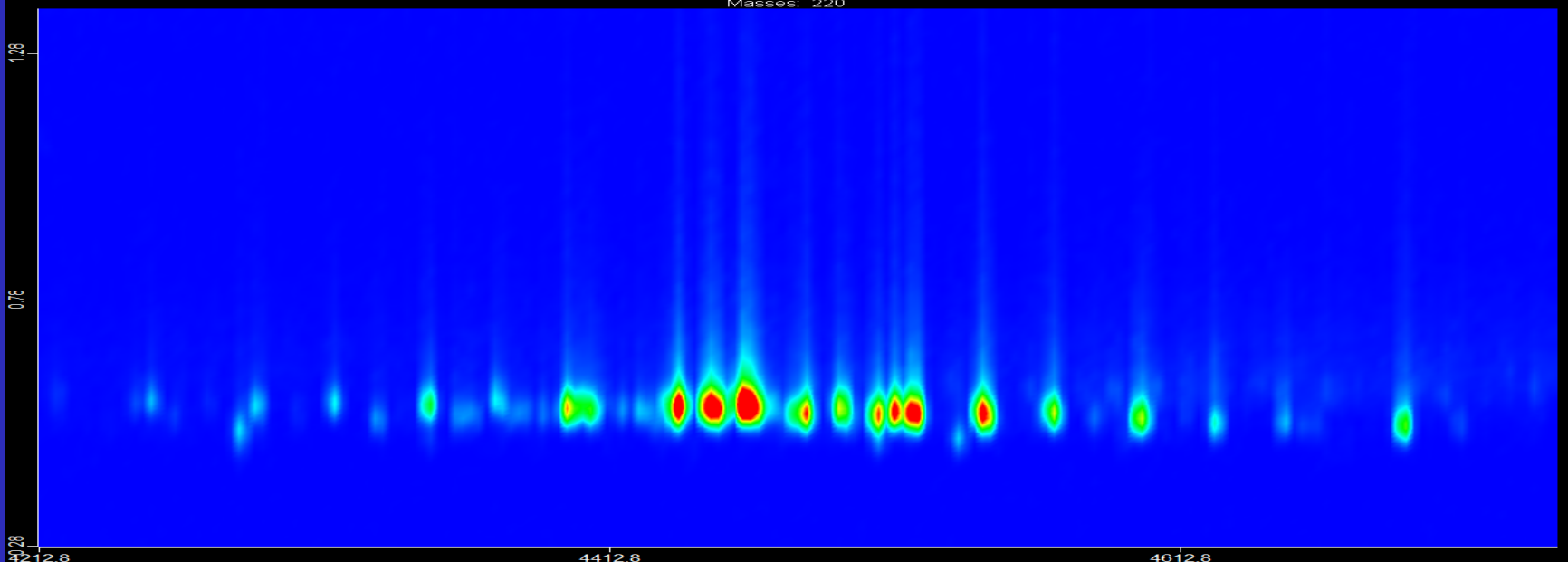
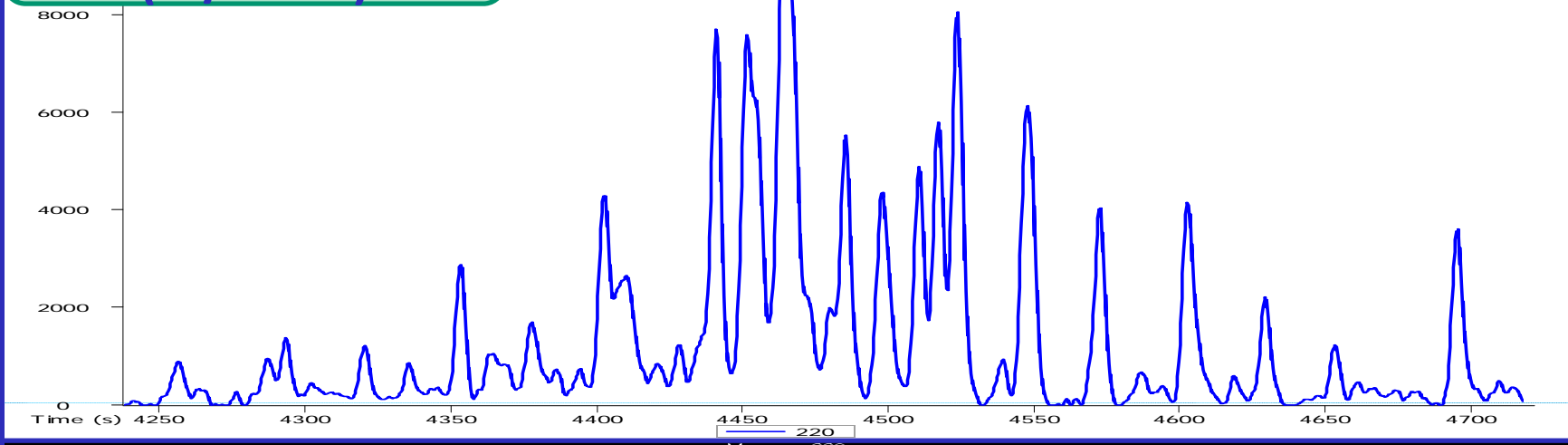
# Increasing Peak Capacity with Efficient Separations

- ✓ Optimal carrier gas velocity and GC oven heating rate
- ✓ Preservation of first dimension separation
- ✓ Second dimension separation (or modulation time) matched for 3-5 slices of first dimension peak
- ✓ Long first dimension columns that “naturally” generate wider peaks under efficient operation (60m x 0.25mm ID)



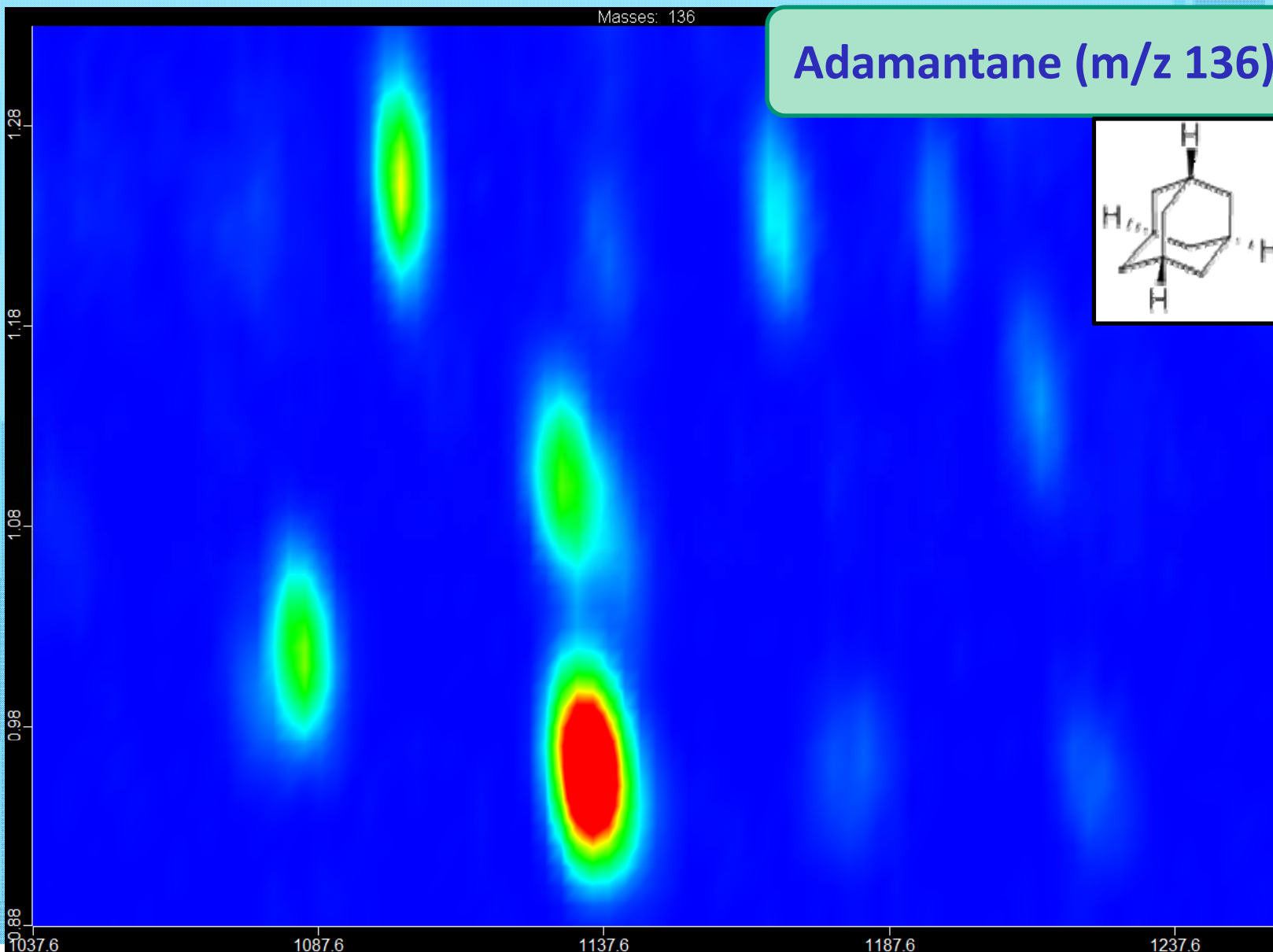
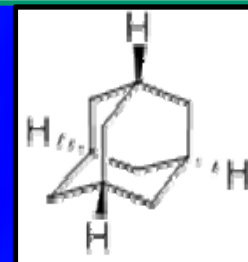
Fort Irwin Fog Oil (zoomed in)

# C3-phenanthrenes (m/z 220)

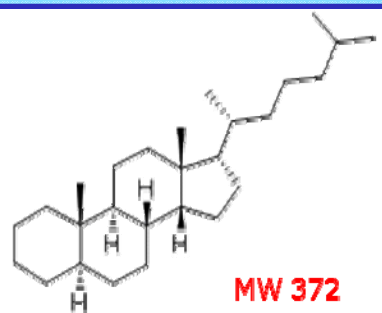


Masses: 136

Adamantane (m/z 136)



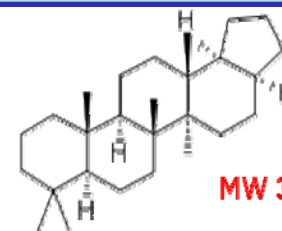
# Biomarkers



MW 372

$\alpha\beta$  20R-Cholestane

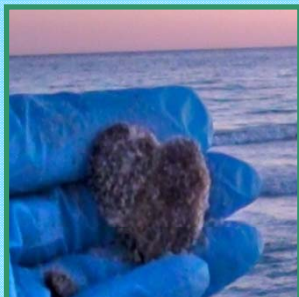
- ✓ Hydrocarbon groups in petroleum used for chemical fingerprinting
- ✓ Complex molecules from formerly living organisms
- ✓ Resistant to weathering, or degrading in the environment
- ✓ Every crude oil may exhibit unique biomarker fingerprint.
- ✓ Hopanes (m/z 191) and Steranes (m/z 217) are common biomarkers



MW 370

17 $\alpha$ (H)-22,29,30-Trisnorhopane

# Experimental



## Sample Preparation

Crude oil samples were diluted to 10mg/mL in methylene chloride. Tarball samples (100mg) were added to methylene chloride and soaked overnight. The samples were then filtered and further diluted in methylene chloride.



## GCxGC-TOFMS (LECO Pegasus® 4D)

**Column:** 60m x 0.25mm x 0.10µm Rxi-17Sil MS (primary);  
1m x 0.25mm x 0.10µm Rxi-1HT (secondary)

**Injection:** 1µL split injection (10:1) with a Sky Precision liner with wool  
He carrier gas, 1mL/min corrected constant flow

**Oven:** 40°C (1 min), 2.5°C/min to 320°C (7 min) primary oven , +5°C  
secondary oven offset

**Modulation period :** 2.8sec

**TOFMS source temperature :** 250°C

**Acquisition range:** 45 to 550u at 100 spectra/sec





Riser Oil

South Louisiana Crude

Basrah Light, Iraq

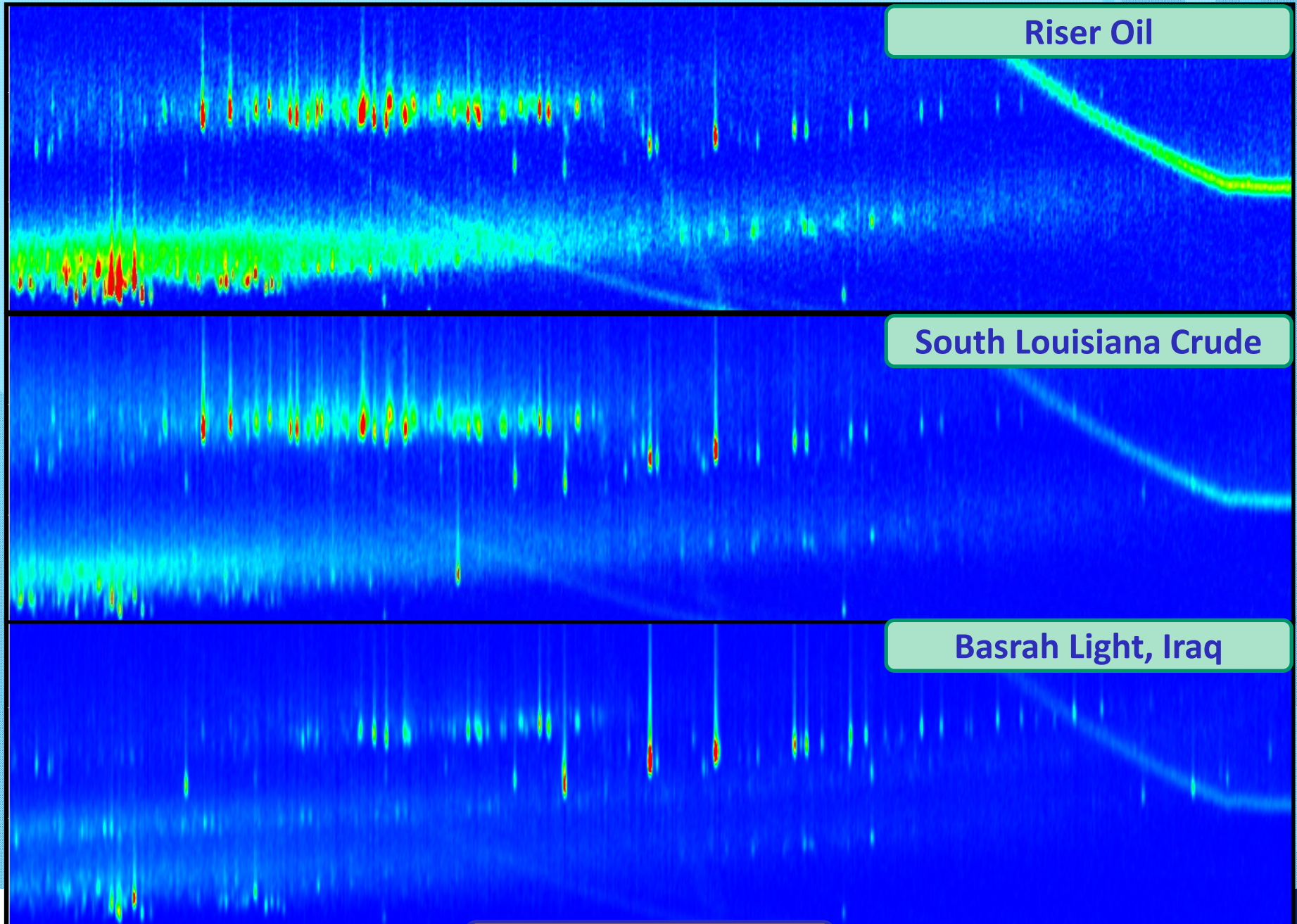
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Riser Oil

South Louisiana Crude

Basrah Light, Iraq

Riser Oil

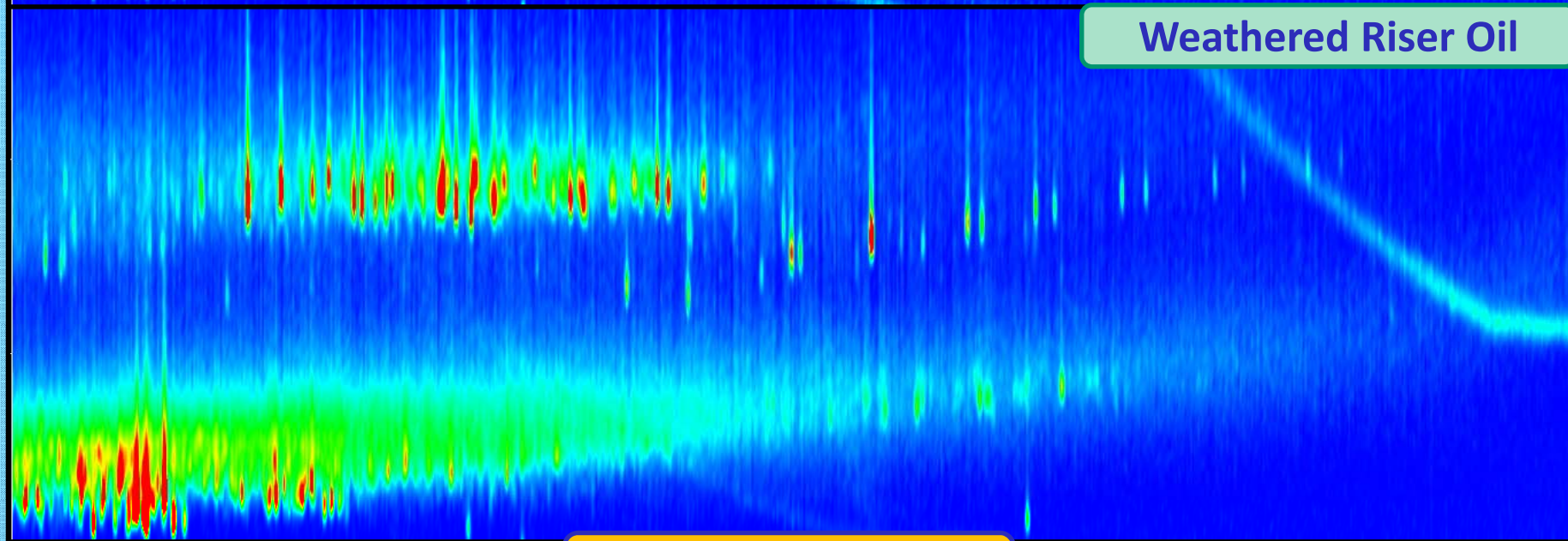
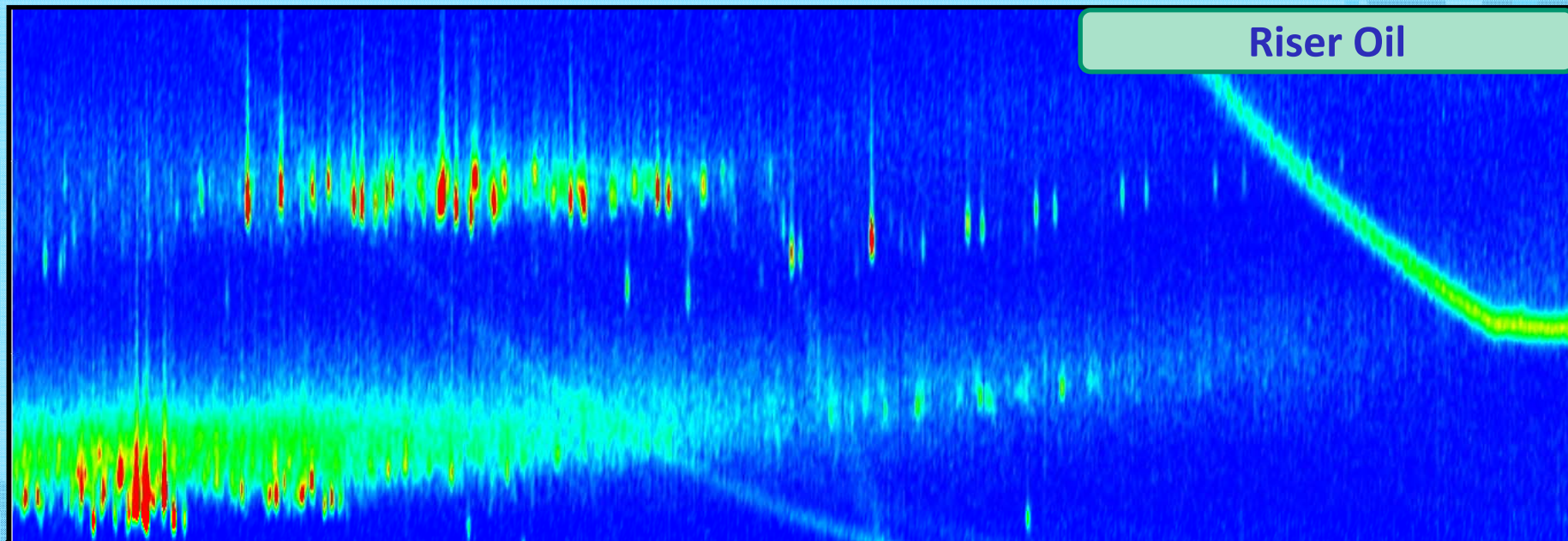
Weathered Riser Oil

TIC

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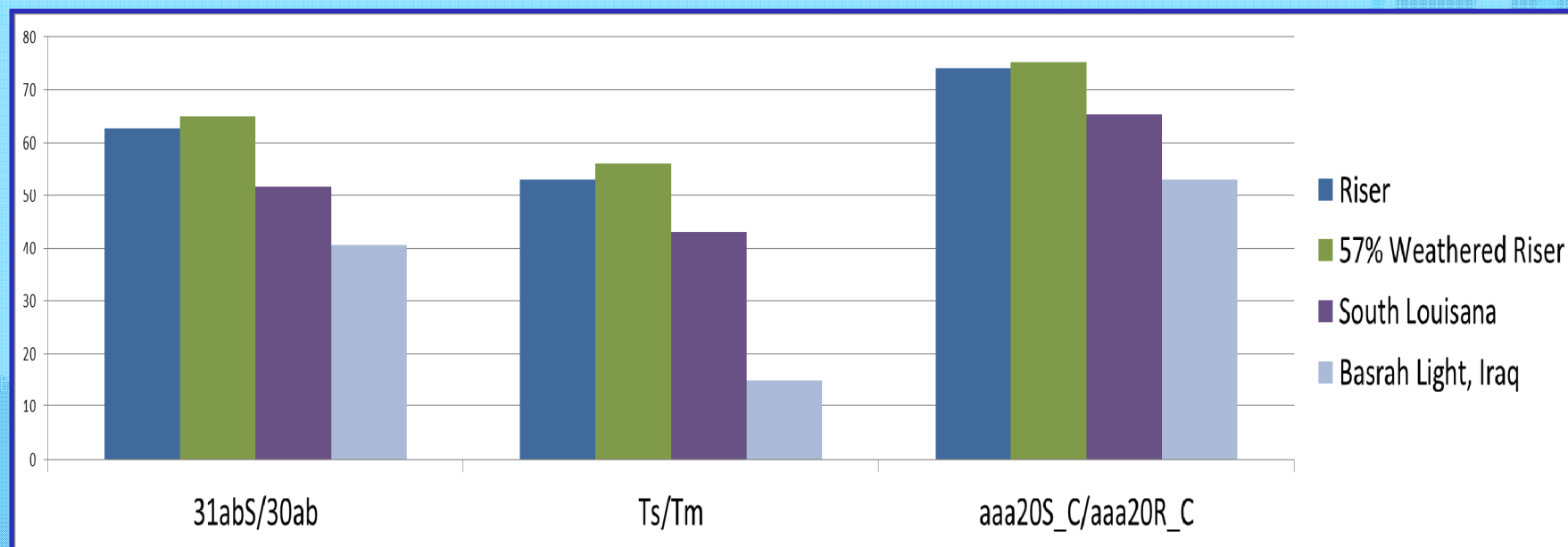
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**m/z 217, 218, 191**

# Hopanes and Steranes Diagnostic Ratios



## Hopanes (m/z 191)

31abS = 17 $\alpha$ (H), 21 $\beta$ (H)-22S-Homohopane

30ab = 17 $\alpha$ (H), 21 $\beta$ (H)-Hopane

Ts = 18 $\alpha$ (H)-22,29,30-Trisnorhopane

Tm = 17 $\alpha$ (H)-22,29,30-Trisnorhopane

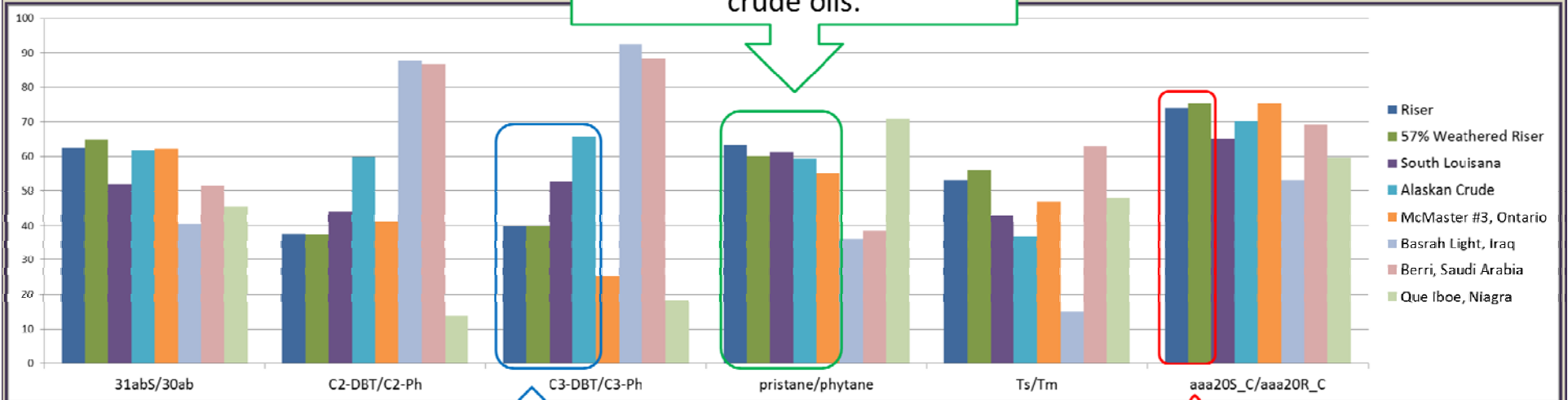
## Steranes (m/z 217)

aaa20S\_C =  $\alpha\alpha\alpha$  20S Cholestane

aaa20R\_C =  $\alpha\alpha\alpha$  20R Cholestane

$$\text{Ratio} = 100 \times A / (A+B)$$

Pristane/phytane ratio's are not enough to distinguish similar crude oils.



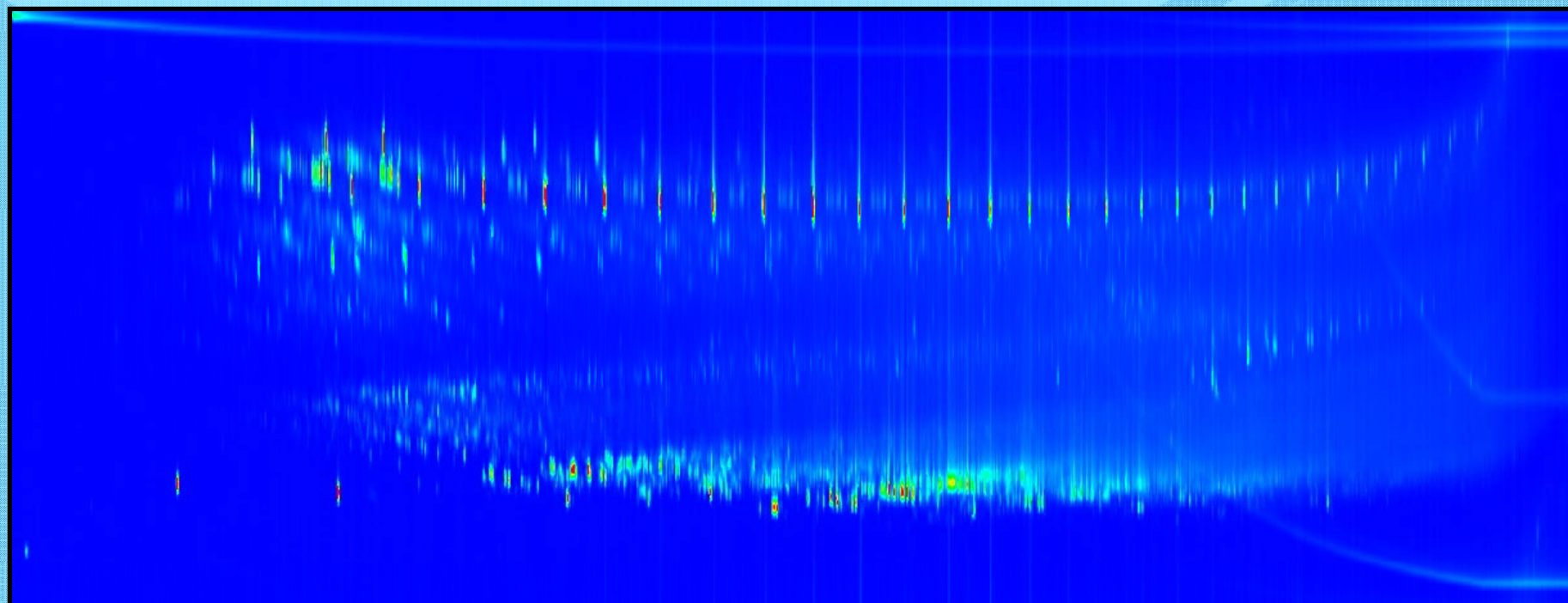
Alkylated dibenzothiophenes and phenanthrenes varies widely in different oils and is a good diagnostic source ratio.

Biomarkers are resistant to degradation. Weathered and non-weathered riser oil show the same diagnostic ratios.

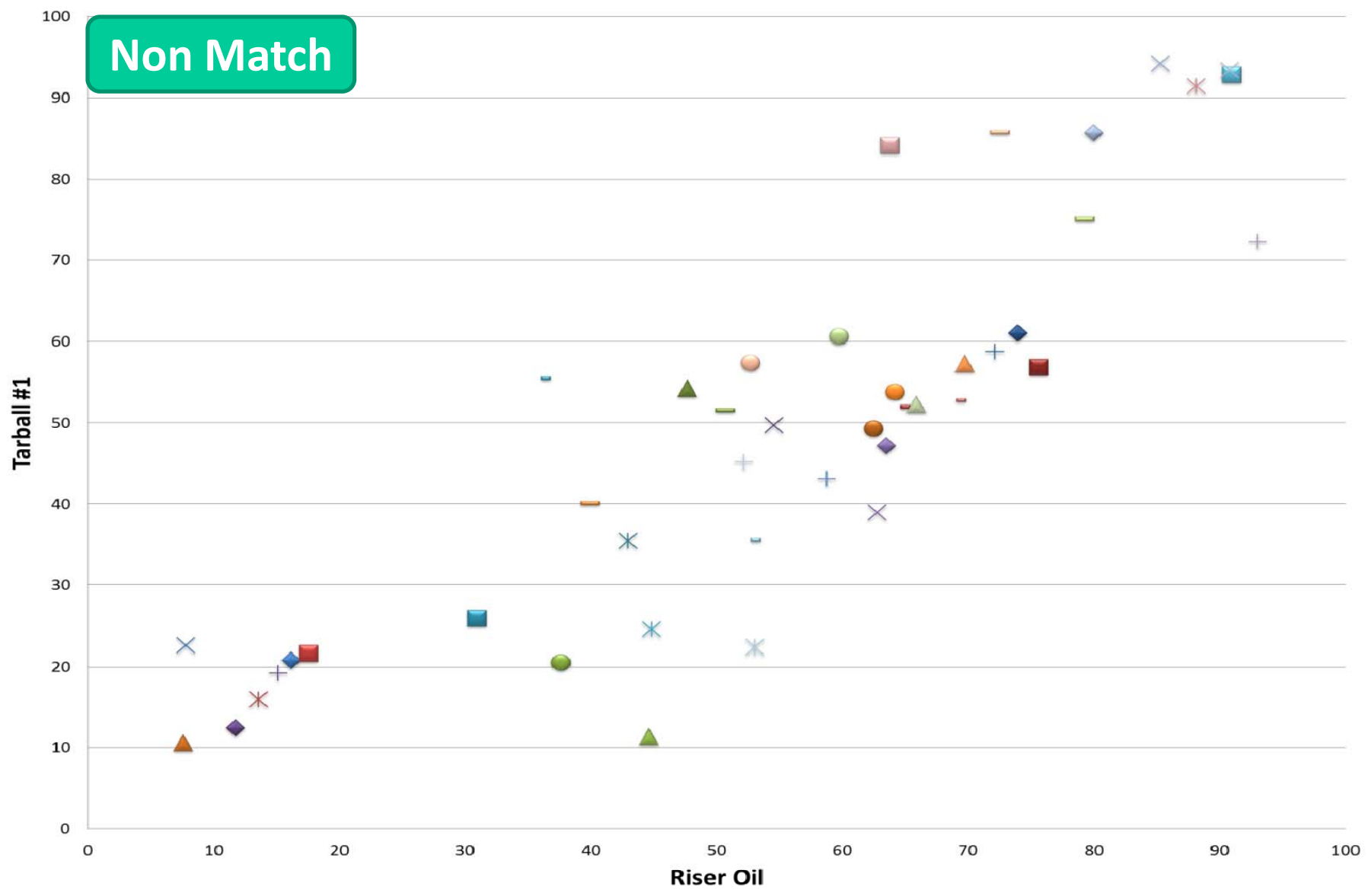
# Tarball #1



**Tarball # 1: Oily Mix**  
**Sampled: April 5<sup>th</sup> 2011**  
**Location: Ed Walline Park, FL**



Correlation Riser Oil v Tarball #1

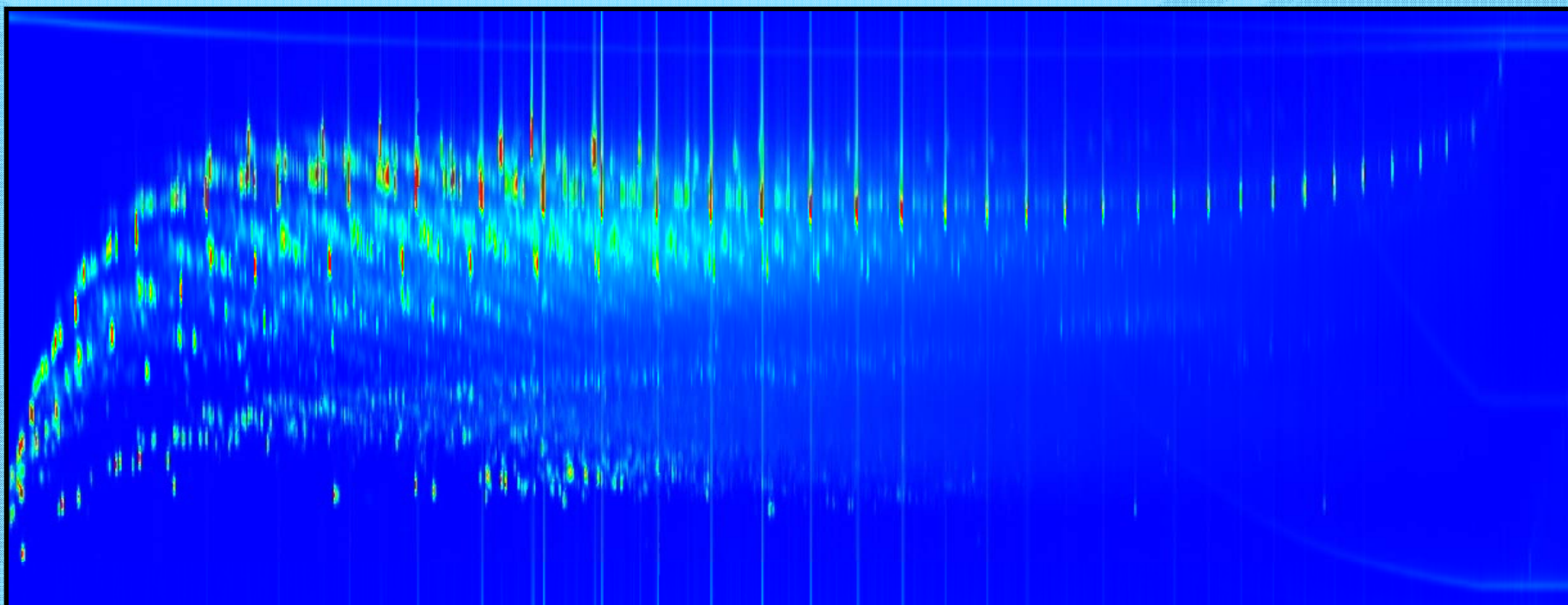




# Tarball #11

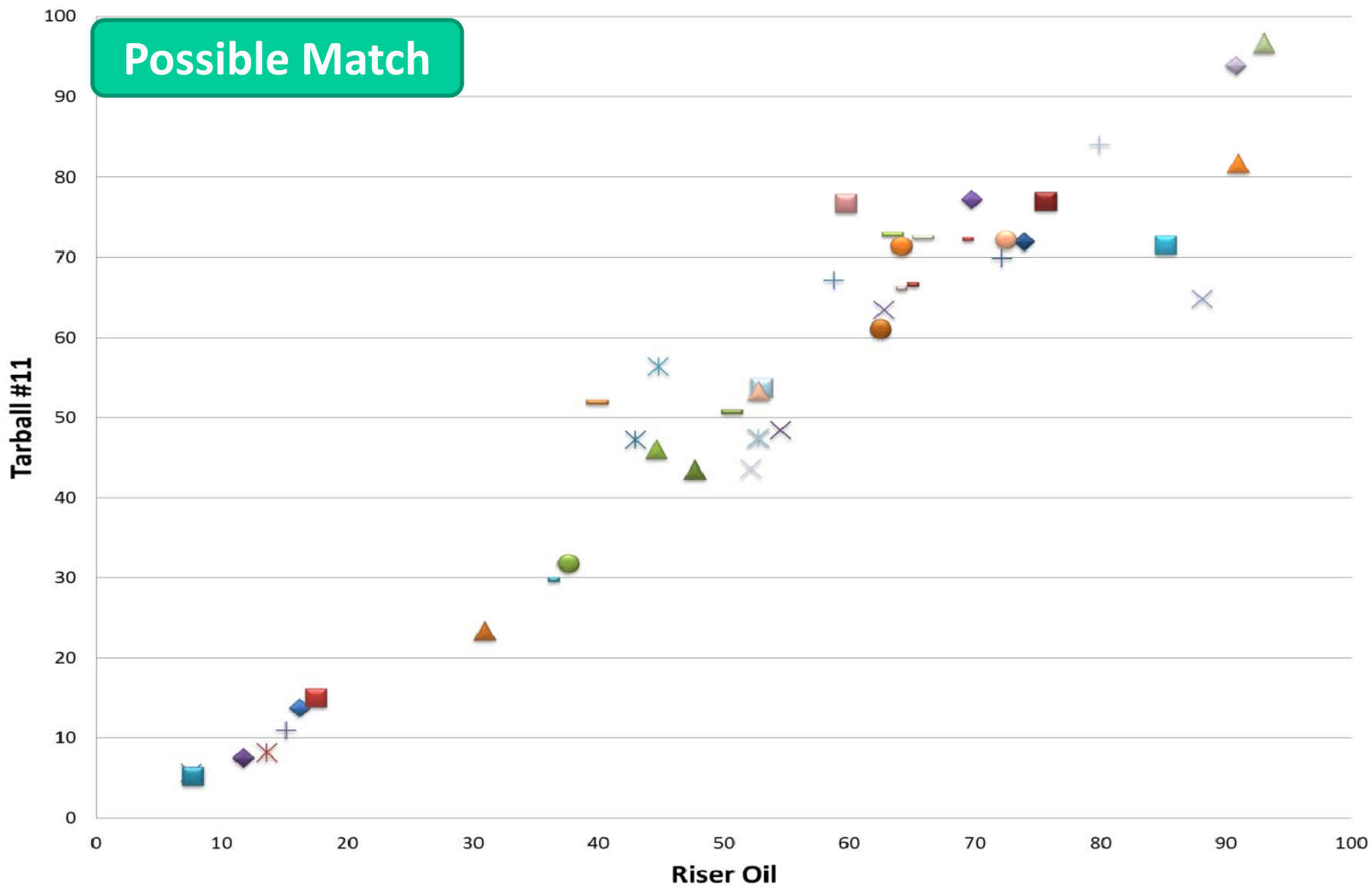


**Tarball # 11:** Core, 5lb chunk  
**Sampled:** July 16<sup>th</sup> 2011  
**Location:** Ed Walline SP, FL



### Correlation Riser Oil v Tarball #11

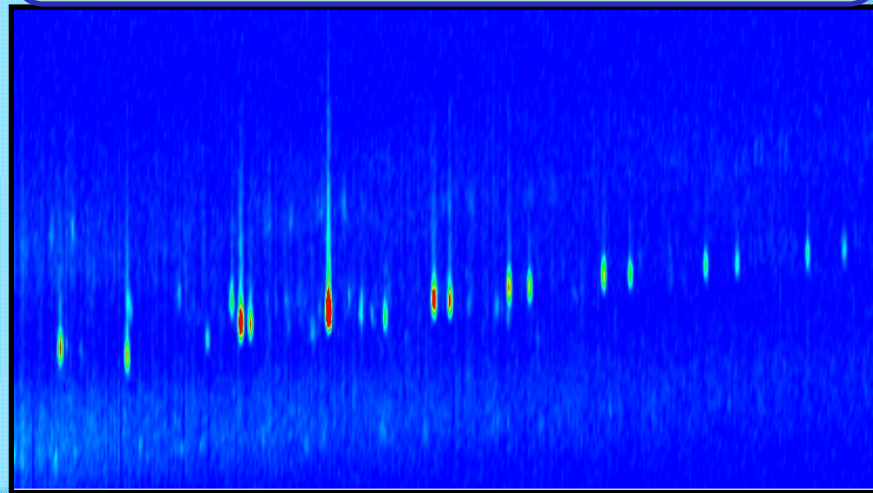
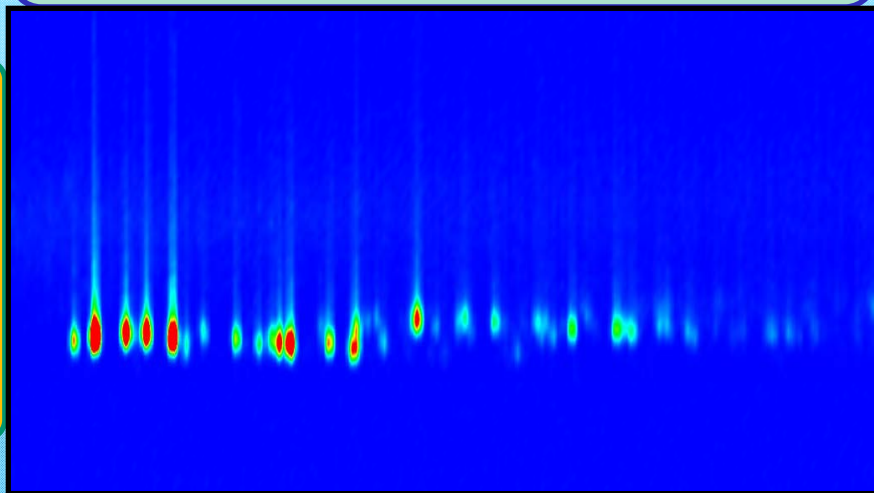
Possible Match



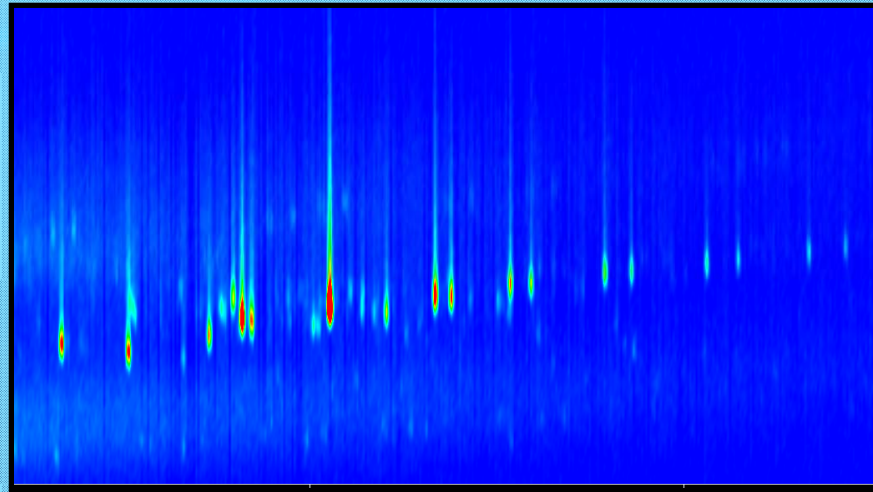
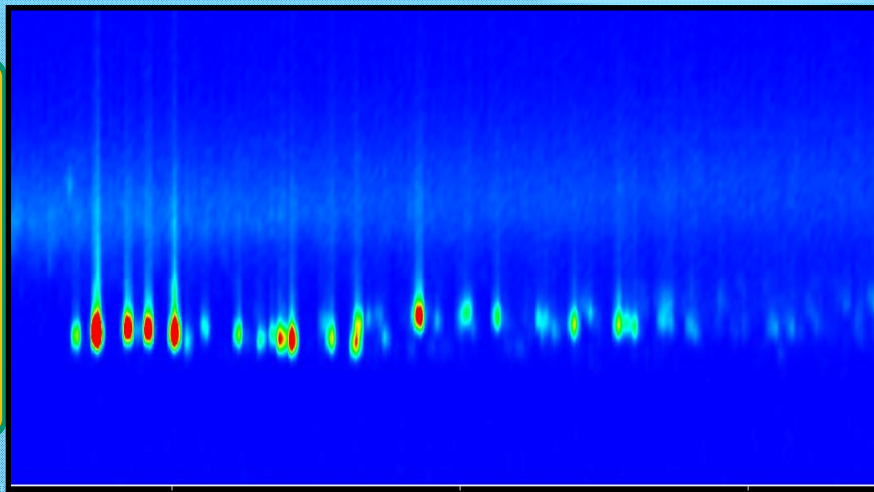
C2 and C3 dibenzothiophenes  
(m/z 212, 226)

Hopanes (m/z 191)

Riser oil



Tarball #11



# Thank You!

Ed Overton, Professor Emeritus at Louisiana State University, for  
the riser pipe oil sample

Susan Forsyth for the tarball samples.