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## Effects of Weathering on Aromatic Compounds in Beach Tars from the Deepwater Horizon Disaster, Gulf of Mexico Coast, USA

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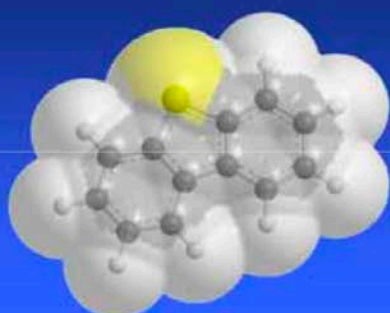
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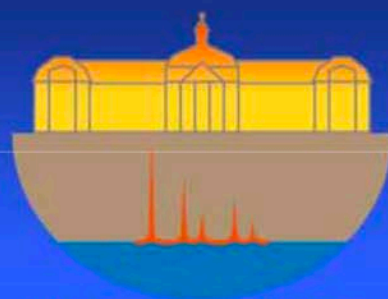
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Group of Prof. Jan Andersson - University of Münster



UNIVERSITY OF MÜNSTER  
APPLIED GEOLOGY

# 23<sup>rd</sup> International Symposium on Polycyclic Aromatic Compounds (ISPAC 23)

September 4 – 8, 2011  
Münster, Germany

<https://www.uni-muenster.de/GeoPalaeontologie/Geologie/Angewandte/ISPAC23/>

# Effects of weathering on aromatic compounds in beach tars from the *Deepwater Horizon* disaster, Gulf of Mexico coast, USA

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**ABSTRACT:** Operators aboard the *Deepwater Horizon* drilling platform lost control of the Macondo No. 1 well about 90 km southwest of the Louisiana coast on April 20, 2010, leading to a catastrophic release of ca. 550 Gg of crude oil over the next 86 days [1]. Oil from the spill soon found its way to nearby coastal areas, leaving tarry deposits on beaches and marshes. Oil was reported on the beach at Gulf Shores, Alabama (180 km northeast of the well) on June 5 and the relatively fresh sample discussed herein (GSA) was collected that same day. Oil reached the beach at Grand Isle, Louisiana (180 km east of the well) by May 24, 2010 and the sample (GIL) was collected on Jan. 15, 2011, i.e., about six months after the flow of oil was staunched at the well site. These two tar samples were analyzed directly, without preparation or clean-up, using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) in order to evaluate the usefulness of this technique for rapid forensic characterization of beach tars at spill sites. In this case, the pyrolysis temperature of 610 °C primarily induced vaporization of compounds present with relatively minor formation of pyrolytic artifacts. The analyses revealed a complex suite of polycyclic aromatic compounds, along with acyclic alkanes and both saturate and aromatic biomarkers.

The total ion current trace of the fresher sample (GSA) exhibits a series of  $C_{16}$ - $C_{32}$  *n*-alkanes above a pronounced hump due to an unresolved complex mixture (UCM) of hydrocarbons, whereas in the case of the more weathered sample (GIL), only the UCM is visible, indicating an advanced stage of biodegradation. Distributions of hopanes, tricyclic terpanes, and steranes in both samples show little evidence of degradation and correlate well, indicative of a common origin. The monoaromatic and triaromatic steroid distributions are also very similar in both samples. Differences are evident in the relative proportions of alkylated phenanthrene and dibenzothiophene isomer clusters, as well as in the proportions of individual isomers, particularly among the dimethyl. In contrast, the  $C_0$ - $C_3$  alkylchrysenes display only minor differences between the two samples. Given that the biomarkers indicate that both samples are of about the same thermal maturity, the observed variations most likely arise due to differences in the severity of degradation. Such alterations must be considered when undertaking forensic evaluations of weathered oil. The Py-GC/MS technique appears to adequately resolve the essential similarities and differences between the two samples.

1) New York Times, 2010. Tracking the oil spill in the Gulf of Mexico.  
<http://www.nytimes.com/interactive/2010/05/01/us/20100501-oil-spill-tracker.htm>

# OUTLINE

## *Deepwater Horizon* blow-out disaster

### Samples and analytical procedures

### Results – comparison of fresh & degraded samples

- *n*-Alkanes
- UCM (chromatographically-unresolved complex mixture of compounds)
- Biomarkers
- PACs (parent & alkylated polycyclic aromatic compounds)

### Conclusions

The loss of the  
*Deepwater Horizon*  
Gulf of Mexico, USA



<http://ecoeco.mx/resena-deepwater-horizon-bp/>

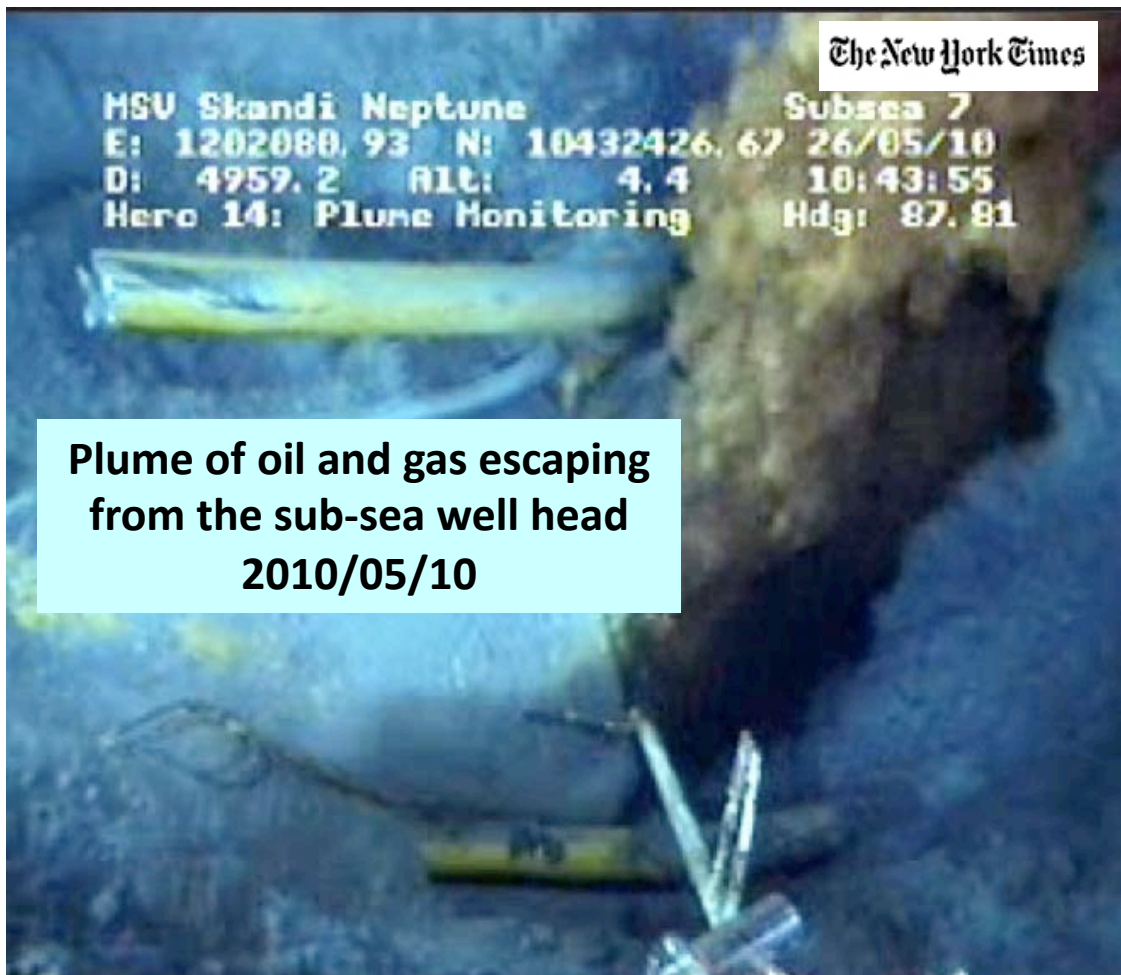


The *Deepwater Horizon* offshore oil platform caught fire and sank with the loss of 11 crew members, as the well was being closed pending later production.

2010/04/20



The New York Times



The New York Times

MSV Skandi Neptune Subsea 7  
E: 1202080.93 N: 10432426.67 26/05/10  
D: 4959.2 Alt: 4.4 10:43:55  
Hero 14: Plume Monitoring Hdg: 87.81

**Plume of oil and gas escaping  
from the sub-sea well head  
2010/05/10**

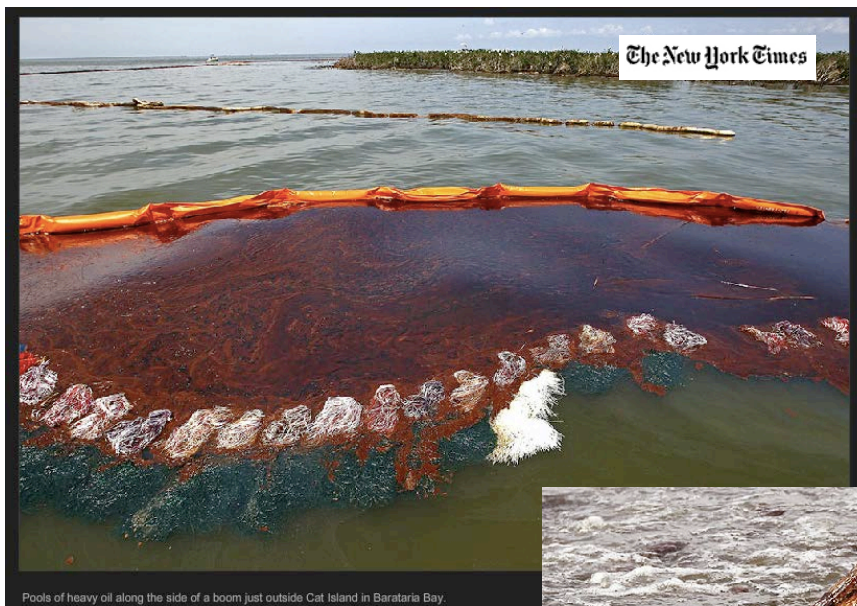




**Operation in water depth of ca. 1600 m.**

**Oil reservoir at about 4000 m below the sea bed.**

*The Macondo prospect is located on Mississippi Canyon Block 252 in the Gulf of Mexico.*

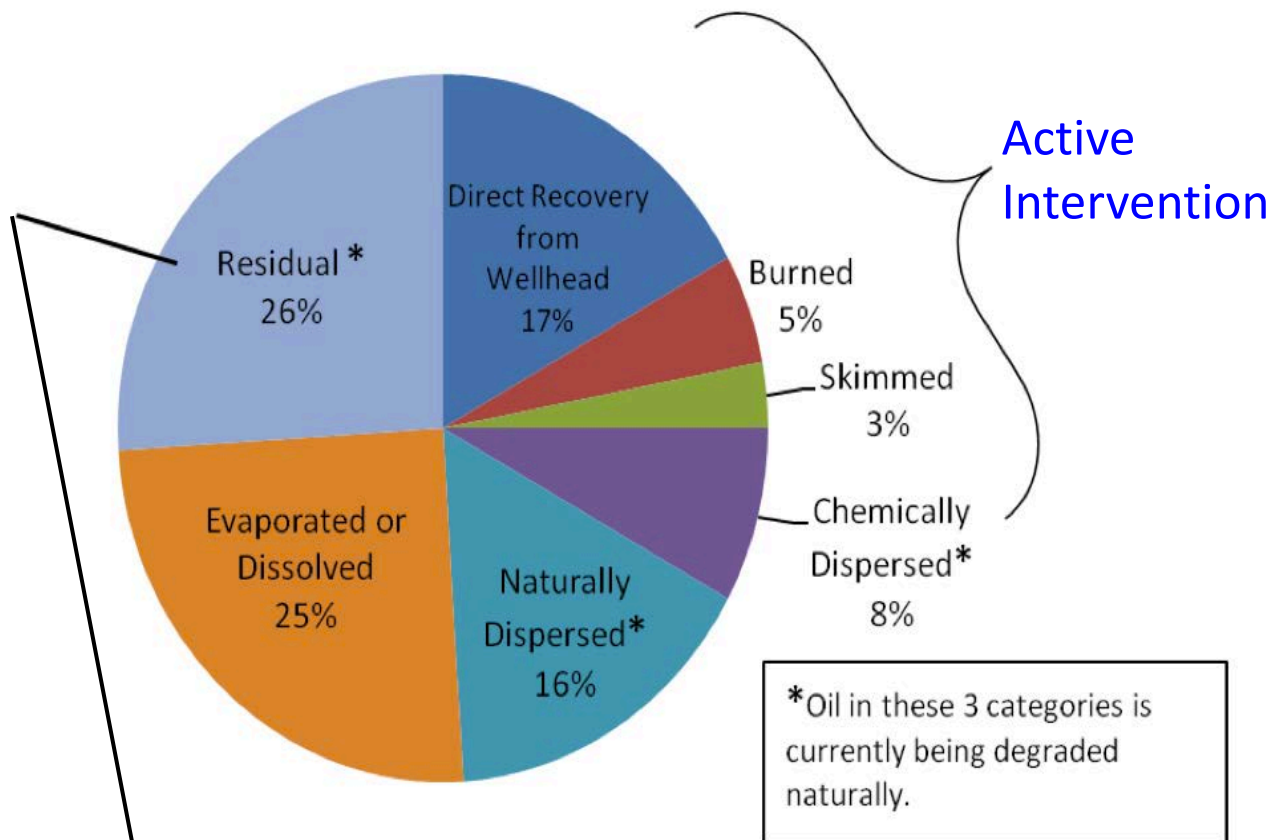


*Photos showing effects of the oil spill.*



# Deepwater Horizon Oil Budget

Based on estimated release of 4.9m barrels of oil

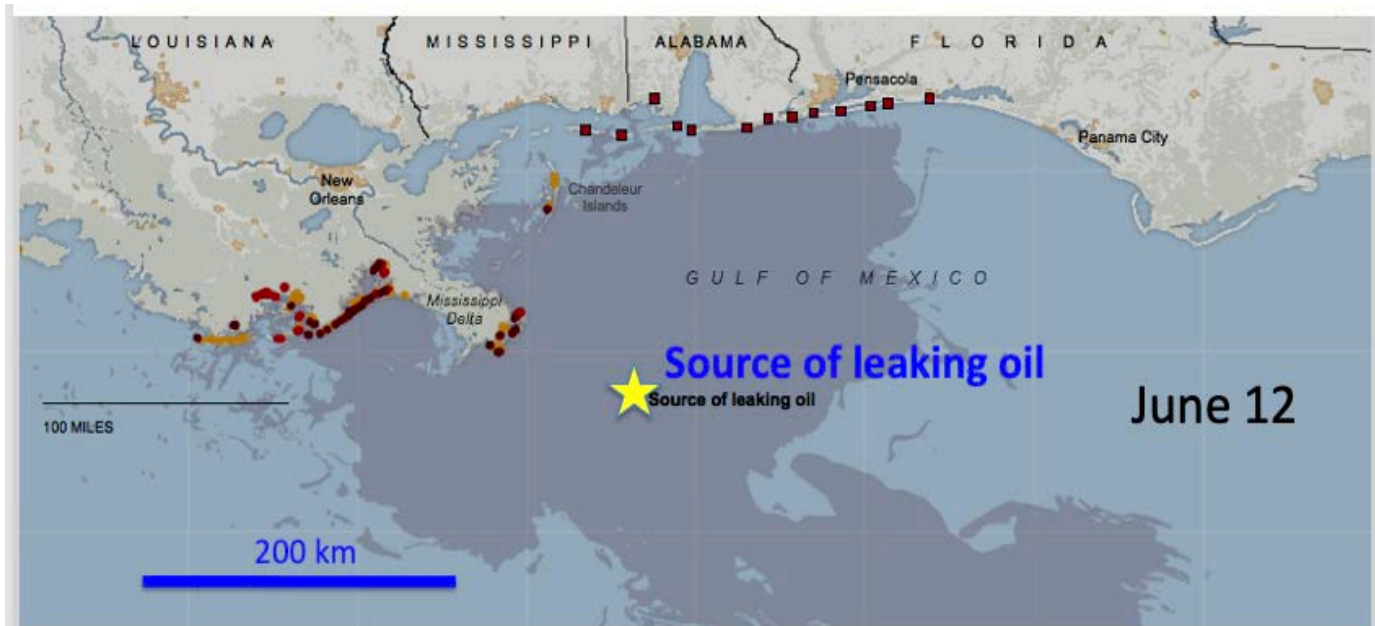
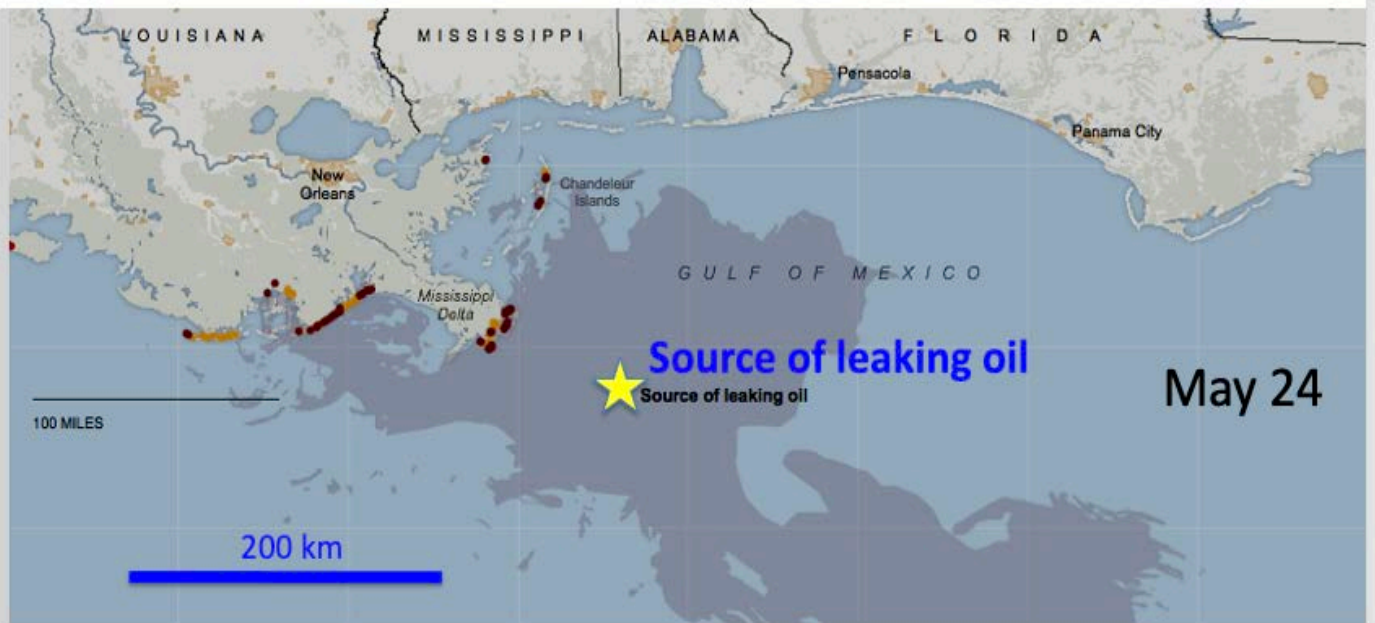


National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling  
THE AMOUNT AND FATE OF THE OIL, Staff Working Paper No. 3, 2010

*Two tarballs washed ashore were collected for this study.*



# Expansion of surface oil plume

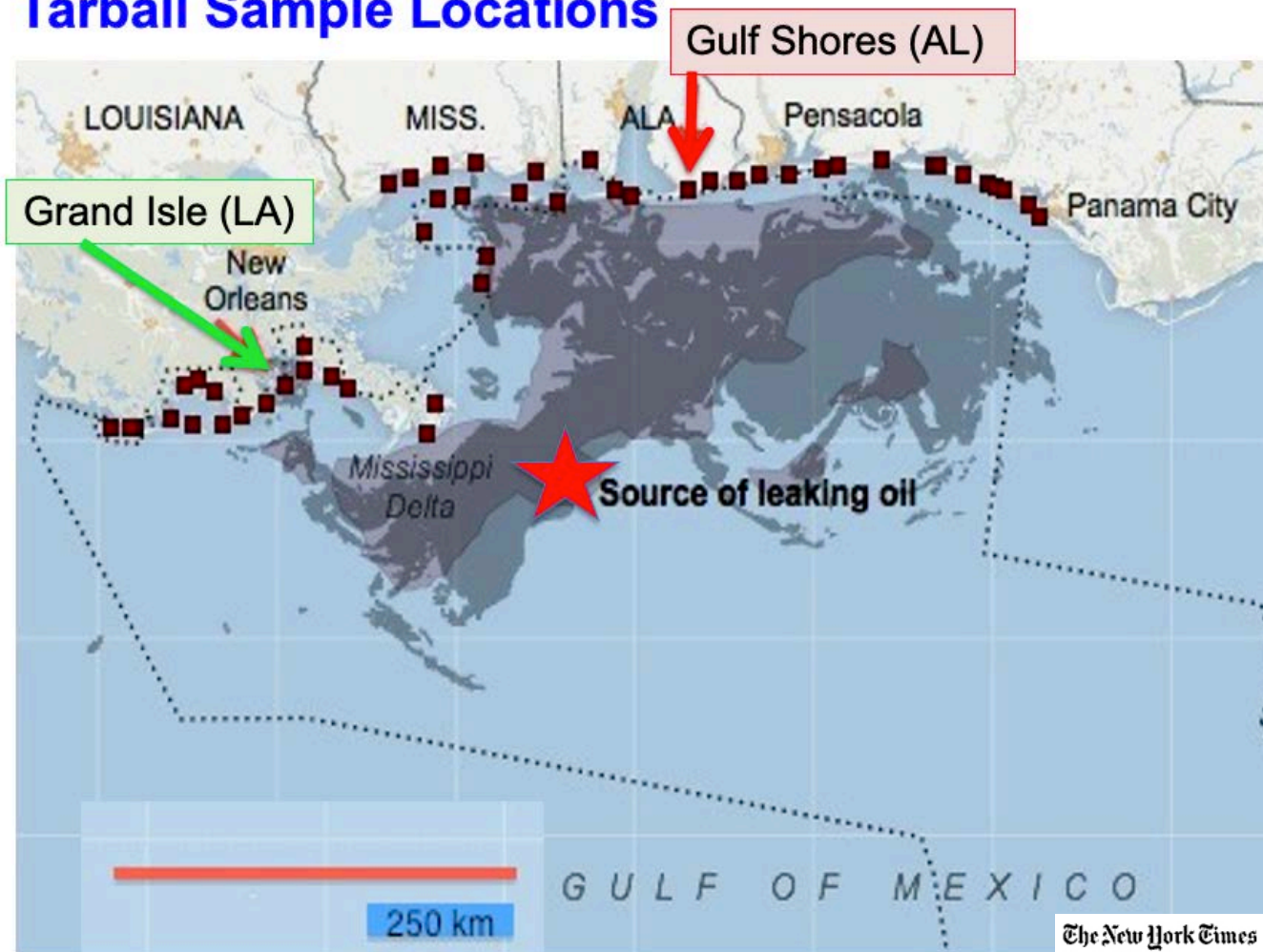


The New York Times

*The surface oil plume greatly expanded over these 19 days.*



# Tarball Sample Locations



**State of spill, June 26, 2010** (*composite spill map*)

## Timing of Tarball Sampling

- Explosion and initial release: **April 20, 2010**
- Flow stopped: **July 15**
- Sea surface oil largely dispersed: **August 2**

	Sample	Oil 1 <sup>st</sup> reached shore (approx.)	Sample taken
2 Samples →	Gulf Shores (AL)	June 5	June 5
	Grand Isle (LA)	May 24	January 15

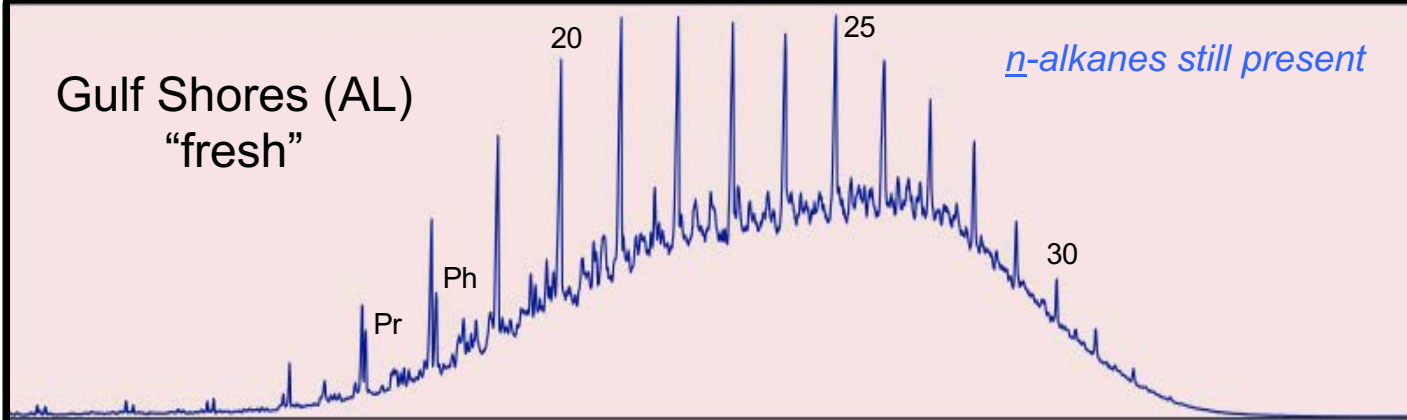
## Tarball analysis:

- Rapid screening by analytical pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)
- Tarballs analyzed directly without sample preparation
- Yielded predominantly thermodesorption products



Tarballs, Fort Walton Beach (FL), June 16, 2010 (Wikipedia).

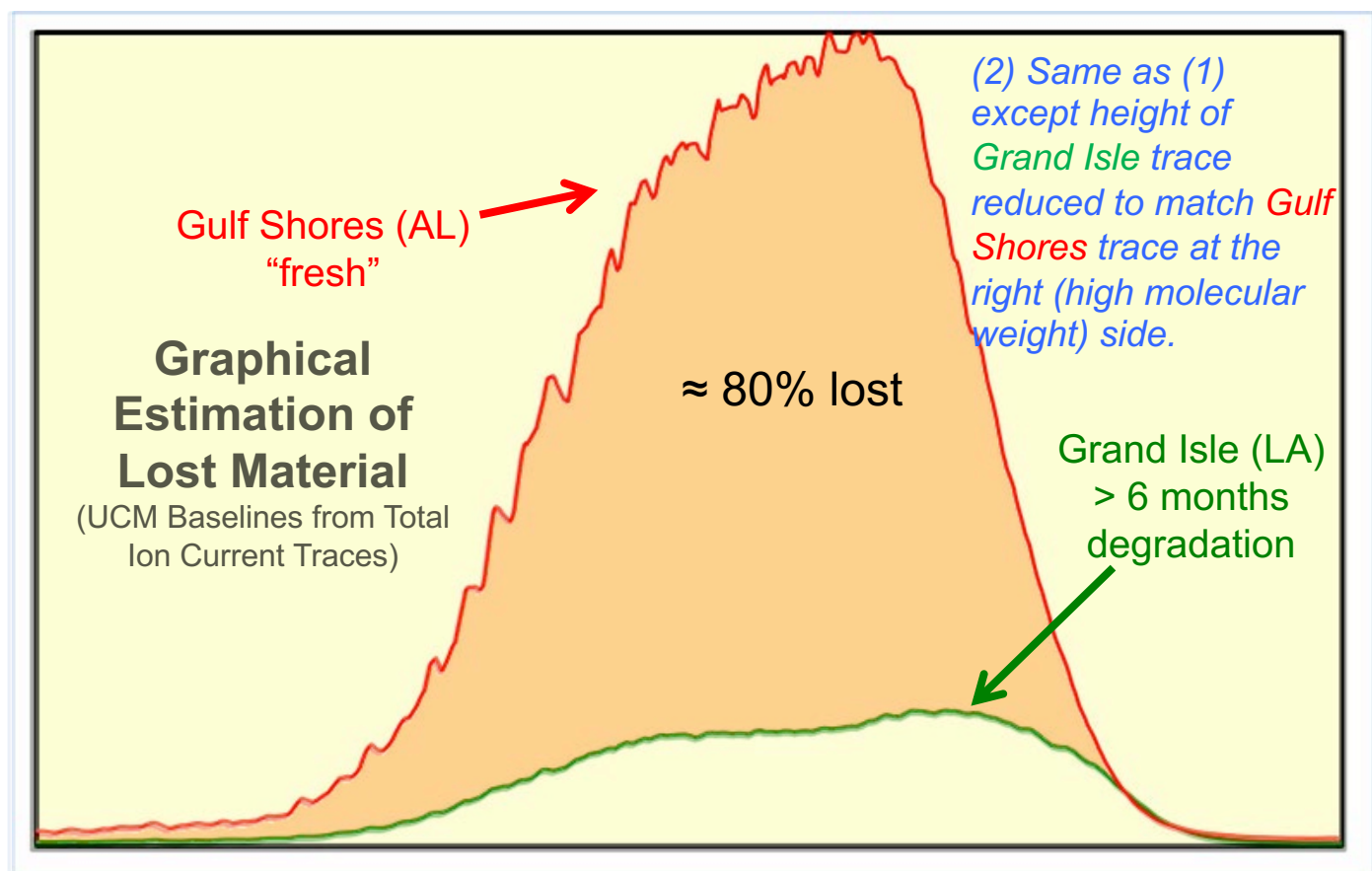
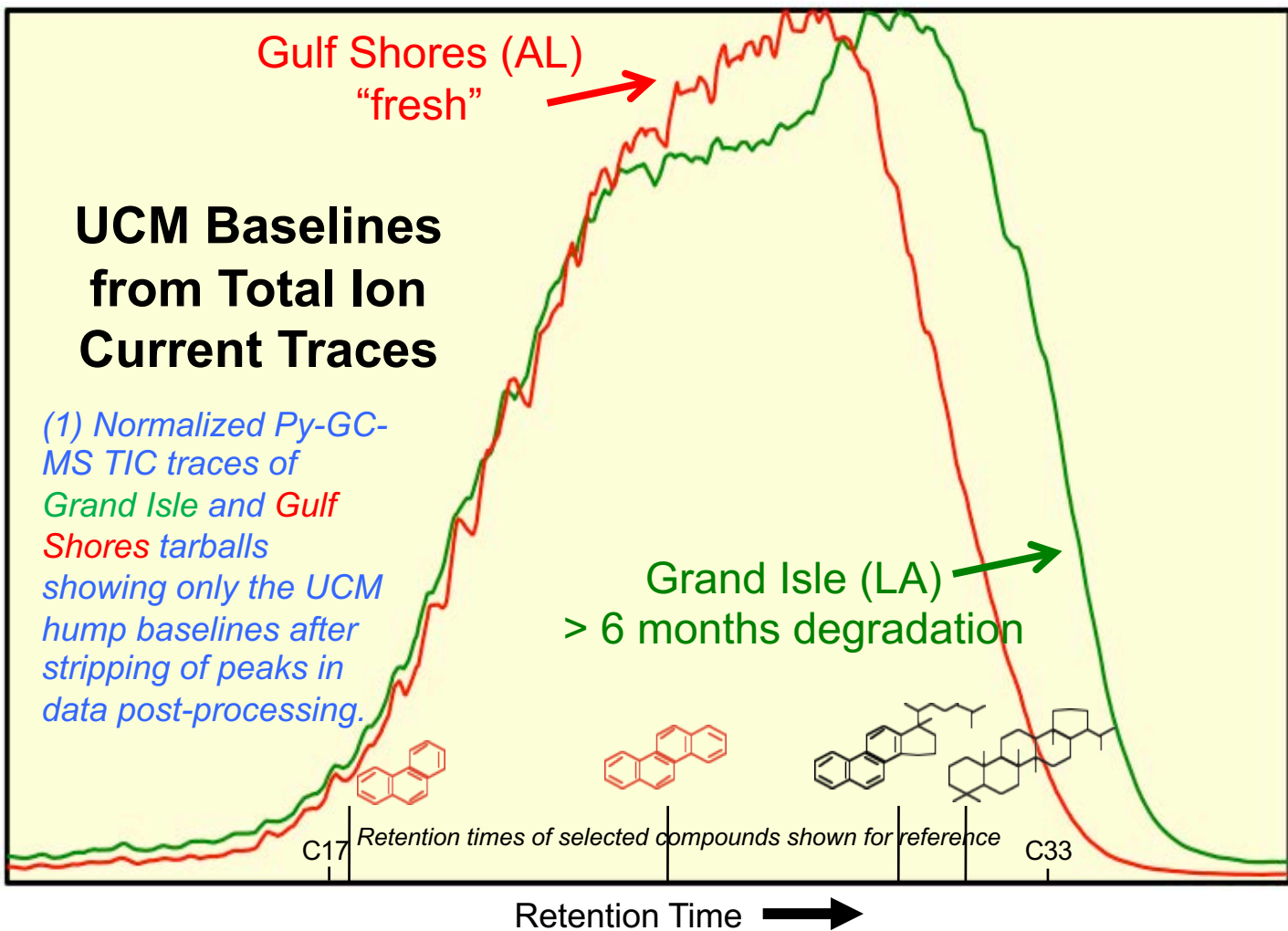
Gulf Shores (AL)  
“fresh”



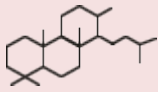
Pr  
Ph

Grand Isle (LA)  
> 6 months degradation

*n-alkanes absent*

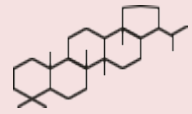






H30

Gulf Shores (AL)  
"fresh"



H33

T23

T26

**Tricyclic Terpane and Hopane  
Distributions (m/z 191)**

Grand Isle (LA)

> 6 months degradation

H30

T23

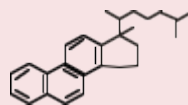
T26

H33

*Biomarker distributions are largely unaffected by the degradation.*

C21

Gulf Shores (AL)  
"fresh"



C26S

C28R

**Triaromatic Steroid Distributions (m/z 231)**

Grand Isle (LA)

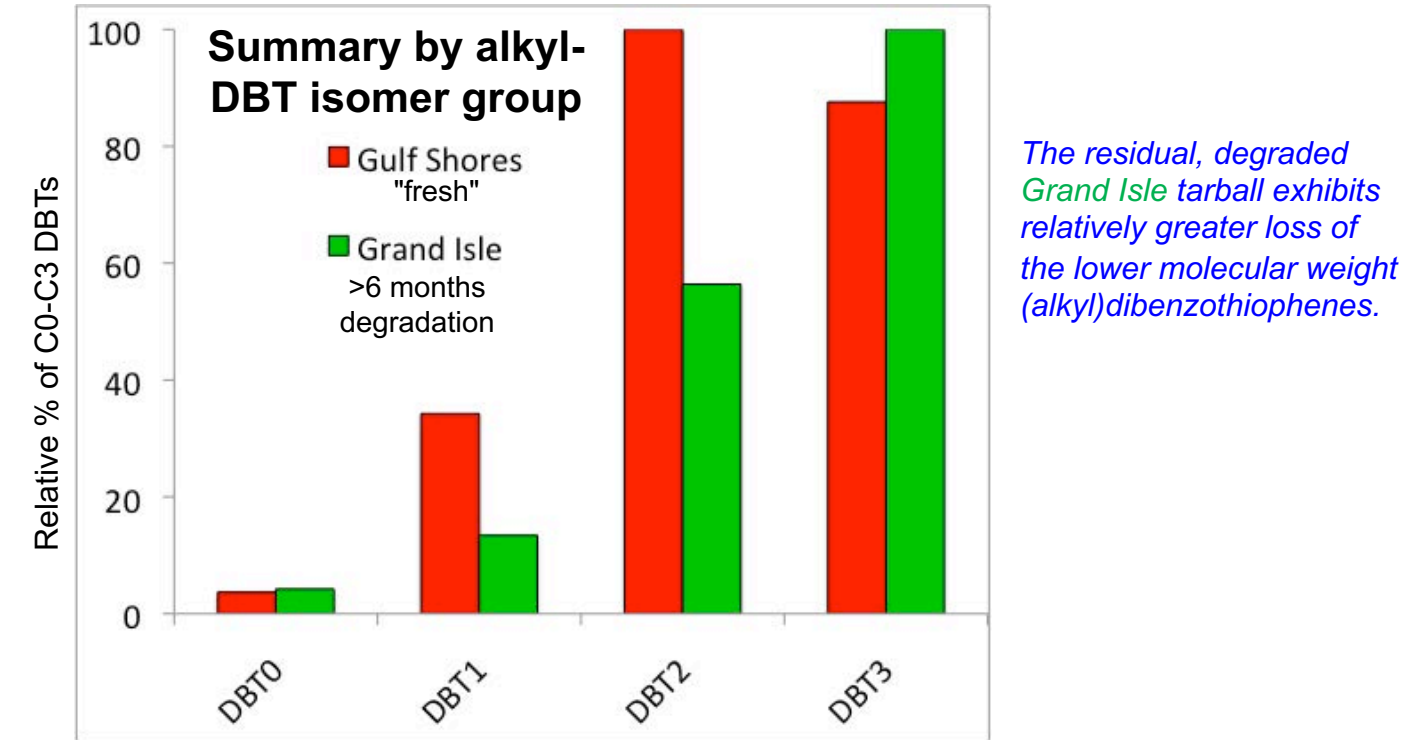
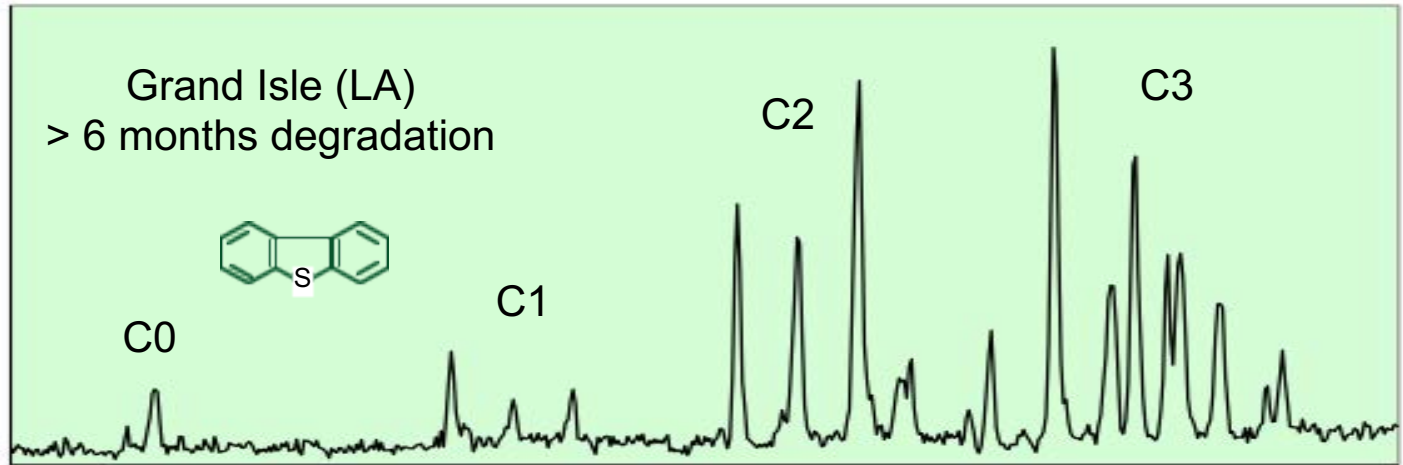
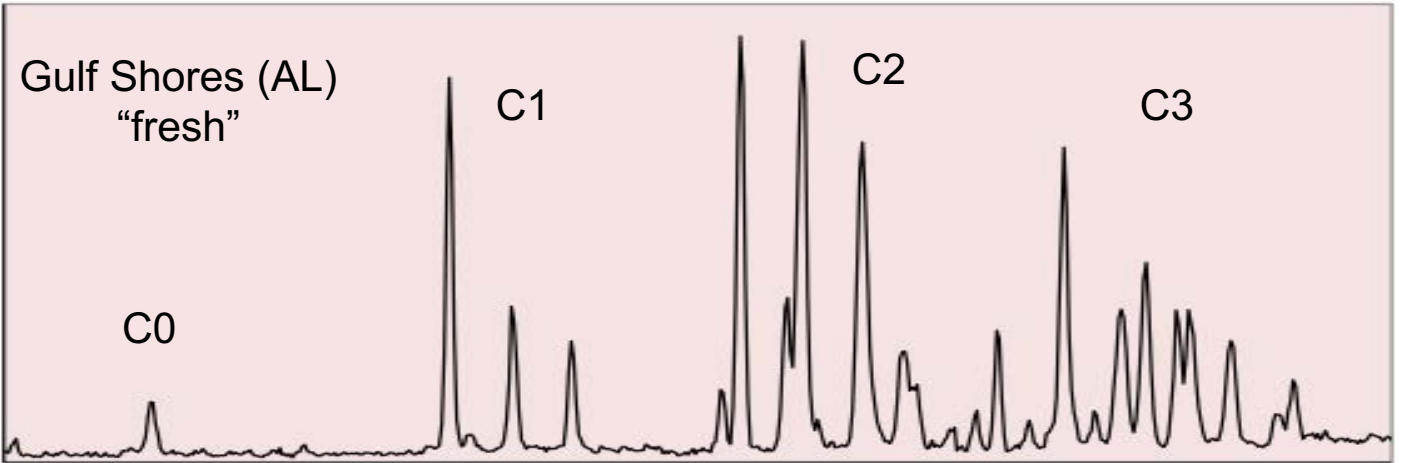
> 6 months degradation

C21

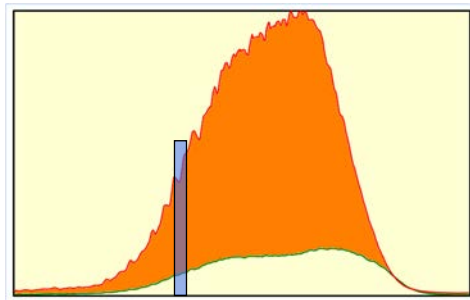
C26S

C28R

**C<sub>0</sub>-C<sub>3</sub> Dibenzothiophene Group Distributions (m/z 184, 198, 212, 226)**



## C<sub>2</sub> Dibenzothiophene Detailed Distributions (m/z 212)



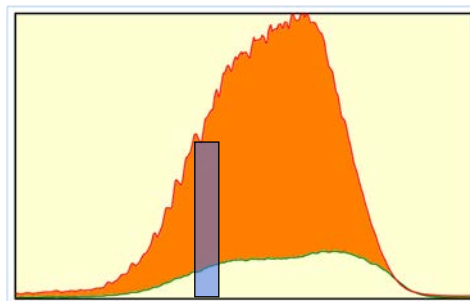
Retention Time

*Insets show the retention time range of the DBTs in the context of the UCM baselines.*

*The relative distribution of C<sub>2</sub>-alkyldibenzothiophene isomers is strongly affected by the degradation.*

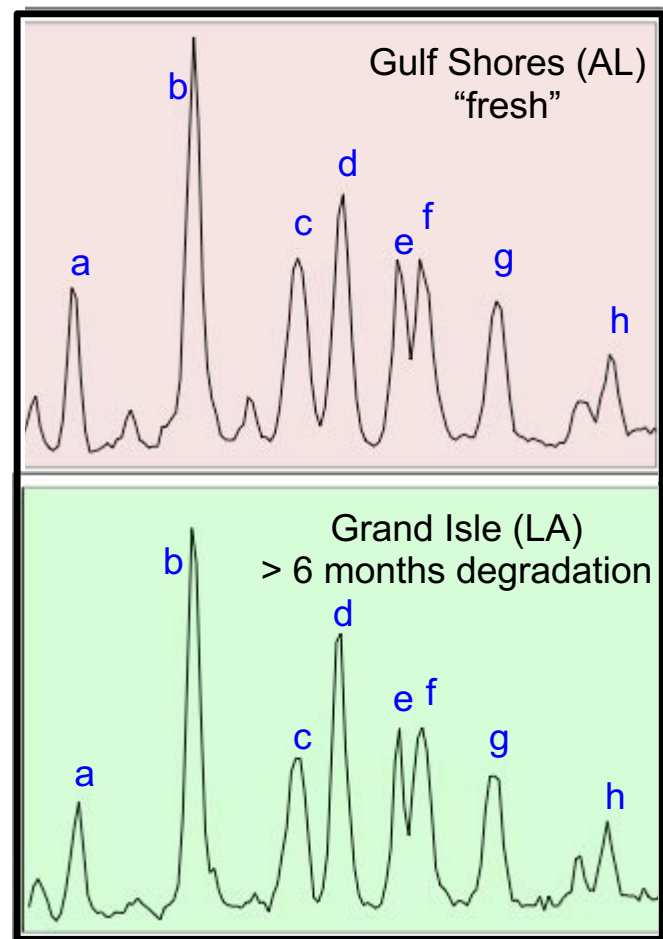
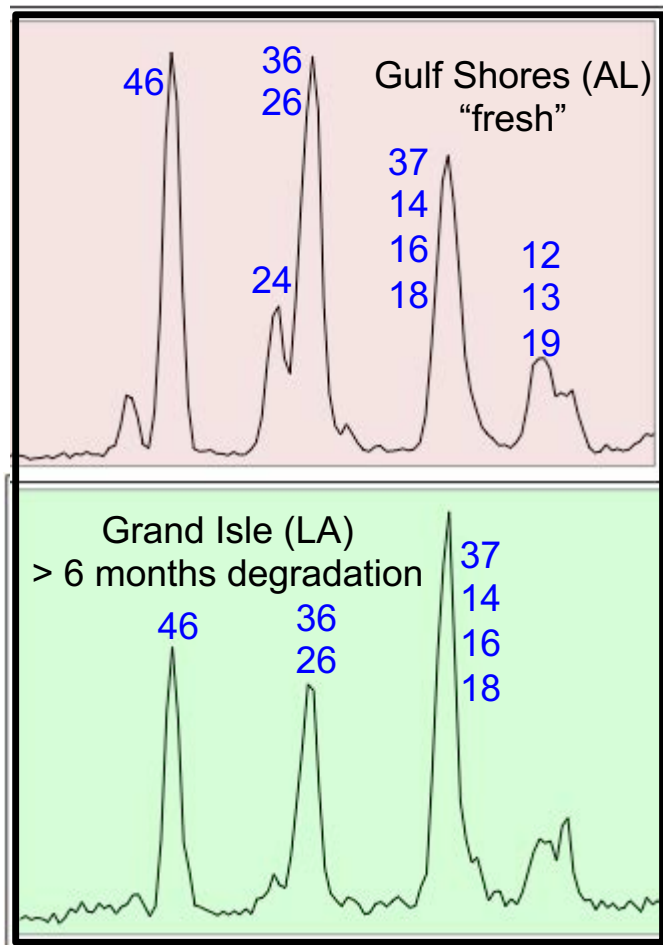
*Blue numerals denote the methyl group sites on the C<sub>2</sub>-DBT isomers.*

## C<sub>3</sub> Dibenzothiophene Detailed Distributions (m/z 226)



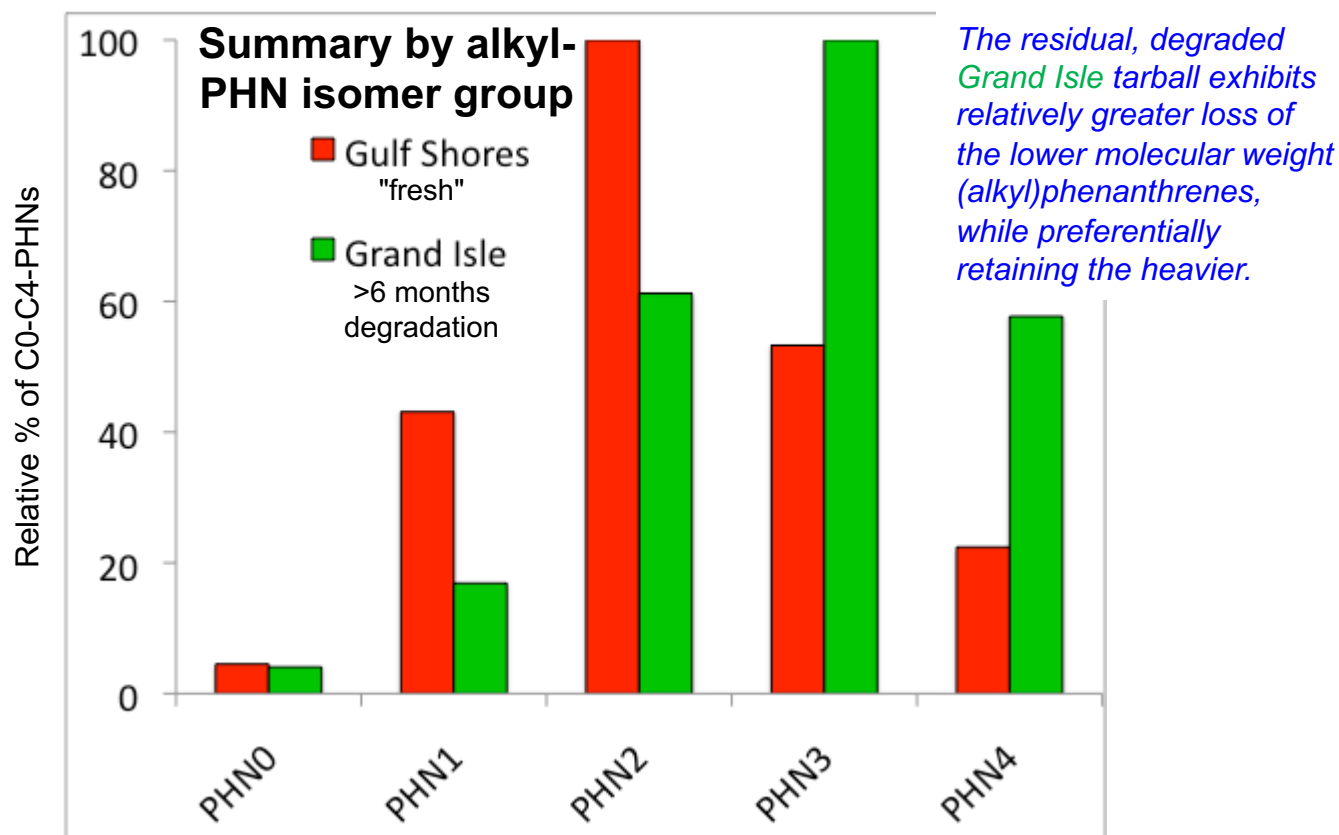
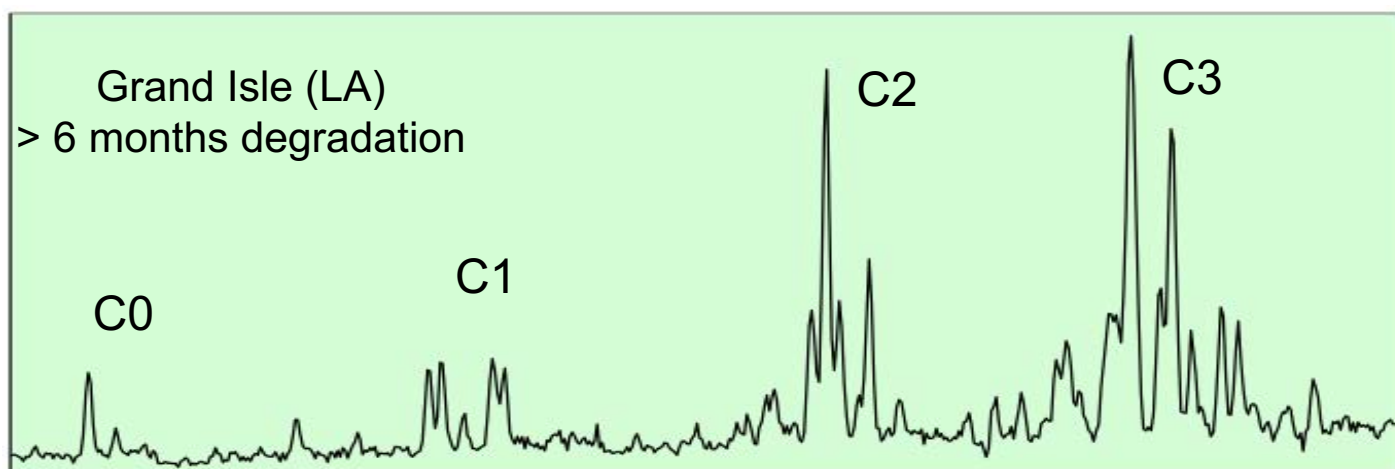
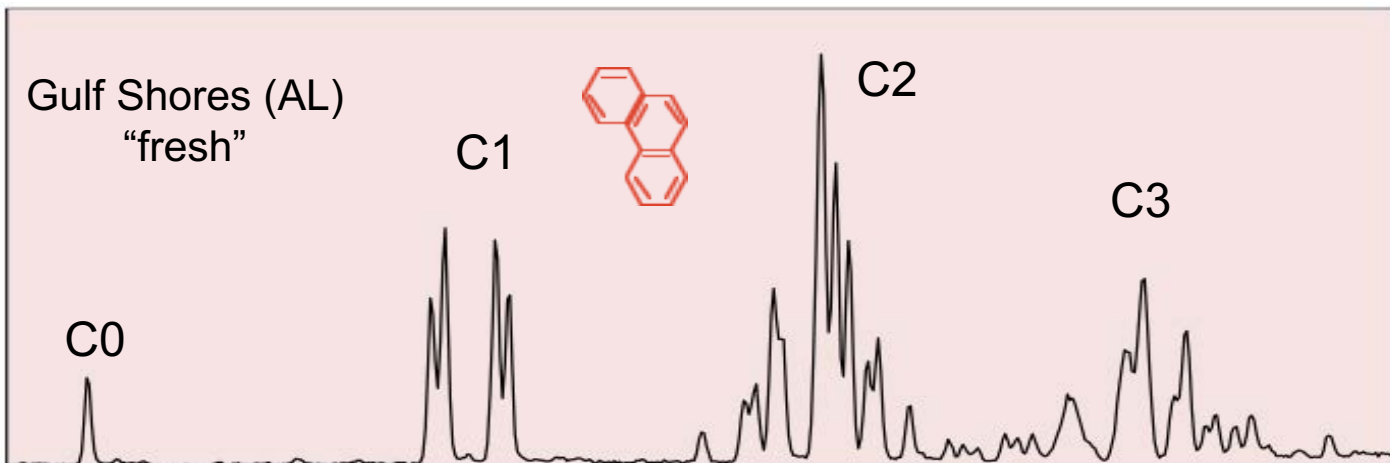
Retention Time

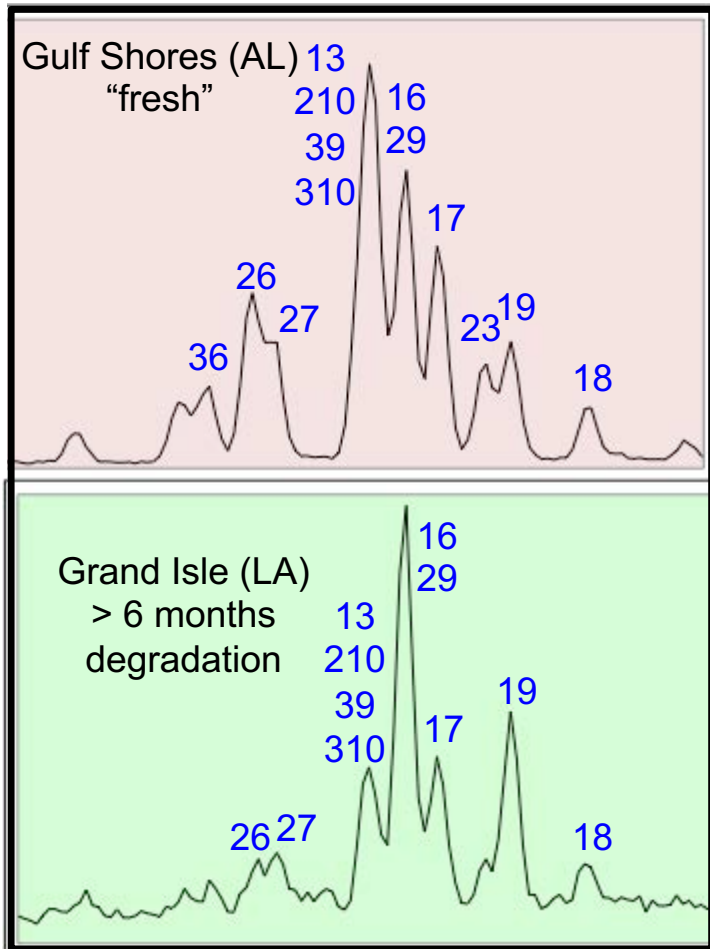
*In contrast, the relative distribution of heavier C<sub>3</sub>-alkyldibenzothiophene isomers is not much affected by the degradation.*



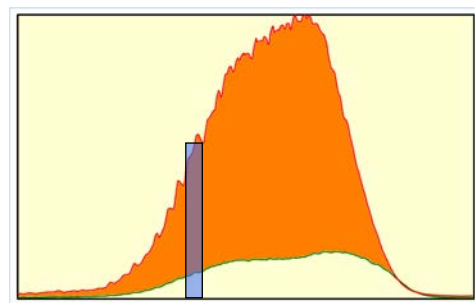


## C<sub>0</sub>-C<sub>3</sub> Phenanthrene Group Distributions (m/z 178, 192, 206, 220)





## C<sub>2</sub> Phenanthrene Detailed Distributions (m/z 206)

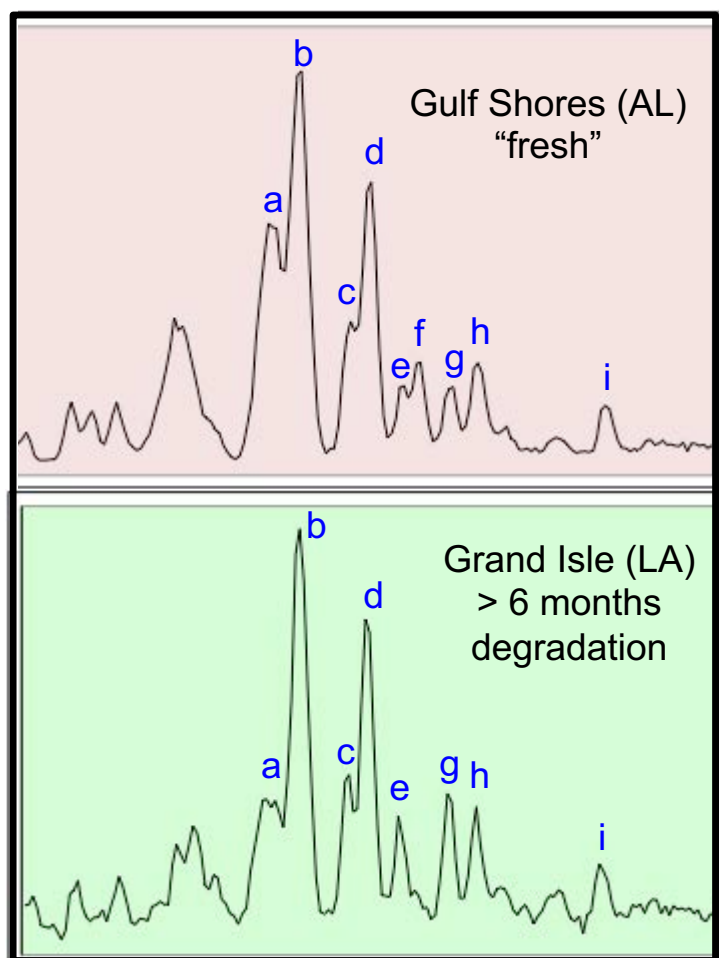


Retention Time

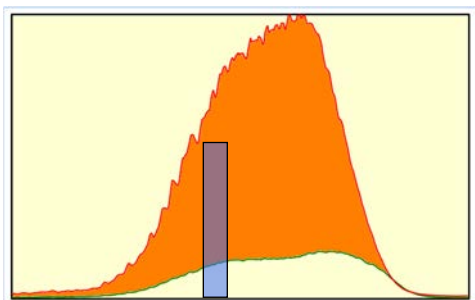
*Insets show the retention time range of the PHNs in the context of the UCM baselines.*

*The relative distribution of C<sub>2</sub>-alkylphenanthrene isomers is strongly affected by the degradation, with the preferential loss of certain individuals.*

*Blue numerals denote the methyl group sites on the C<sub>2</sub>-PHN isomers.*



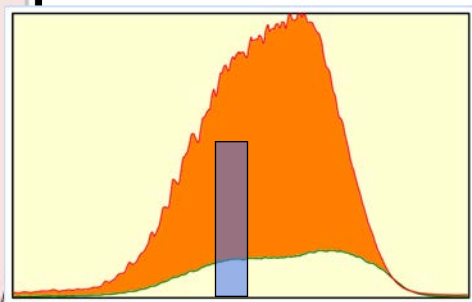
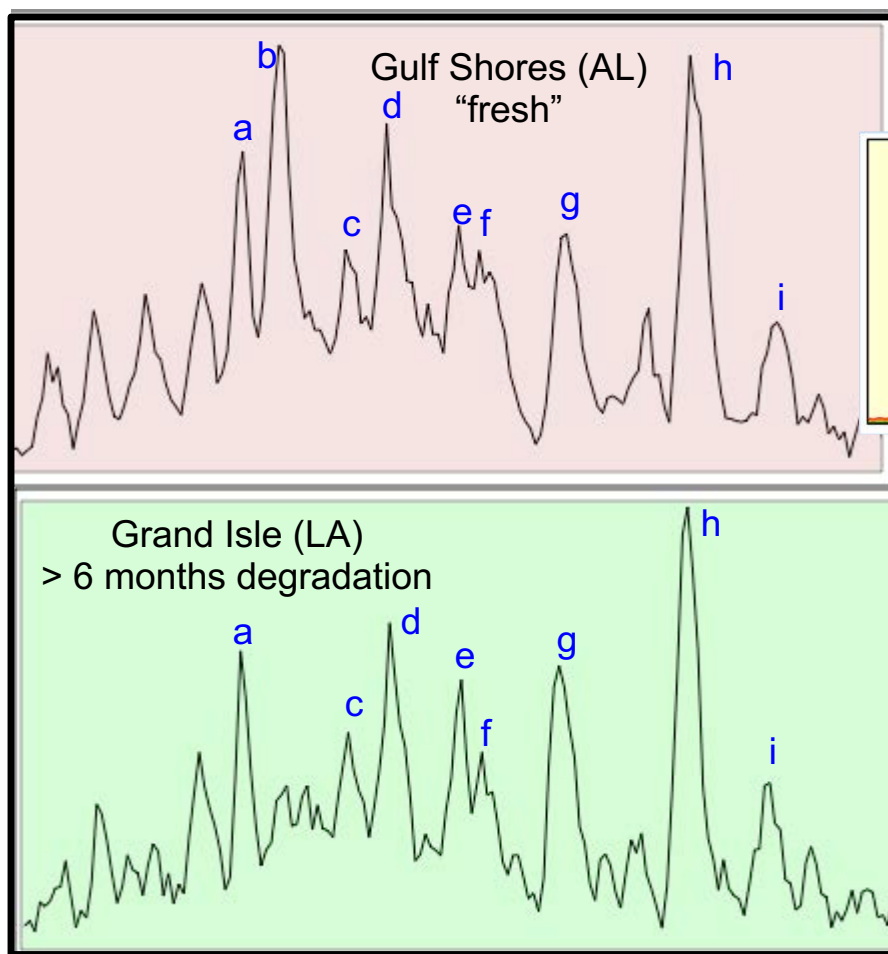
## C<sub>3</sub> Phenanthrene Detailed Distributions (m/z 220)



Retention Time

*In contrast, the relative distribution of heavier C<sub>3</sub>-alkylphenanthrene isomers is only slightly affected by the degradation.*

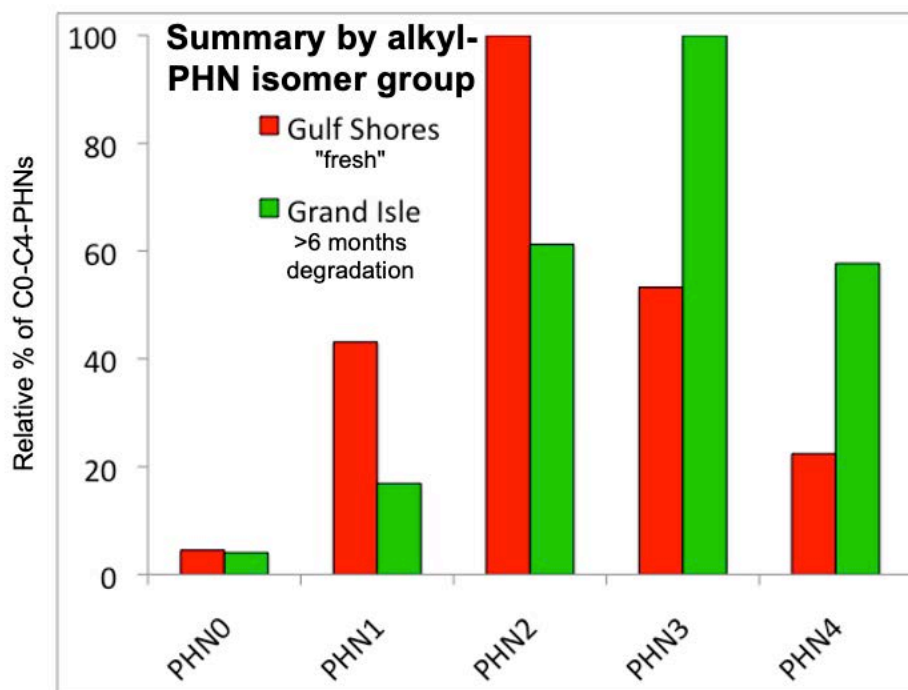
## C<sub>4</sub> Phenanthrene Detailed Distributions (m/z 234)



Retention Time

*Inset shows the retention time range of the C<sub>4</sub>-PHNs in the context of the UCM baselines.*

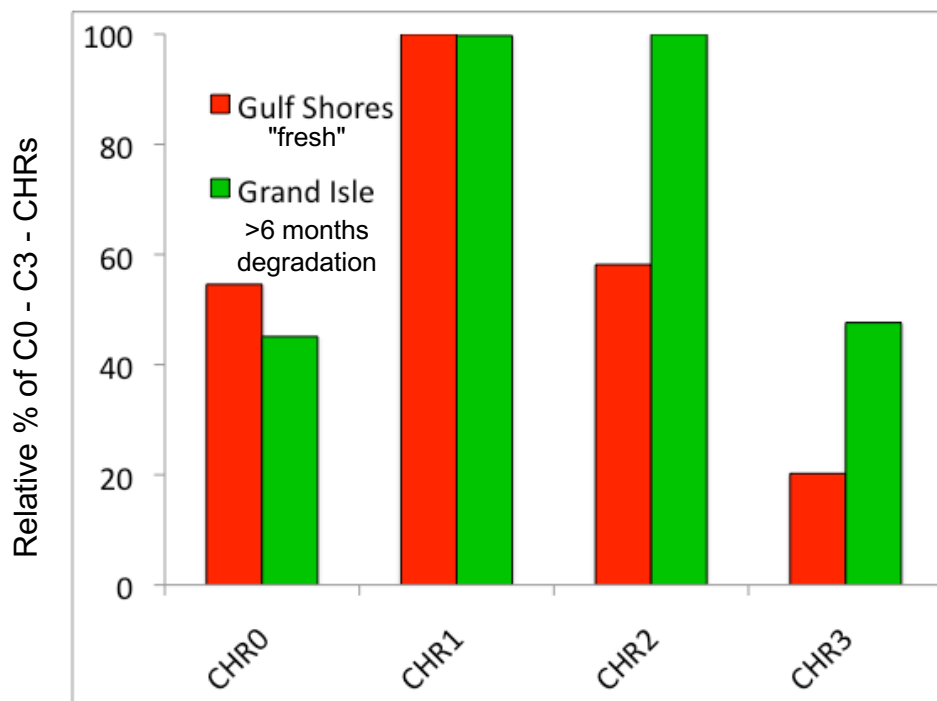
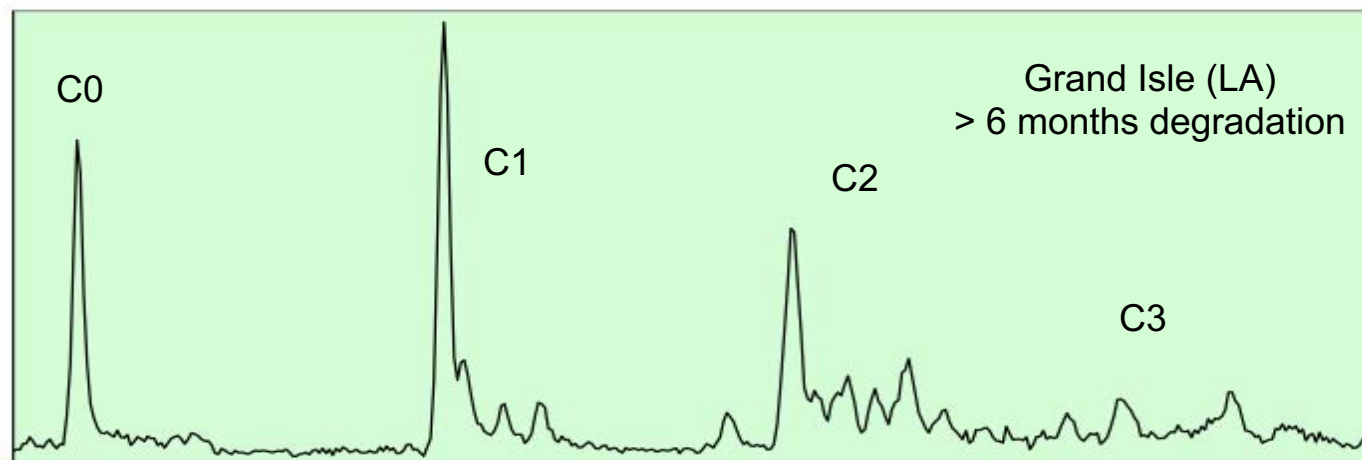
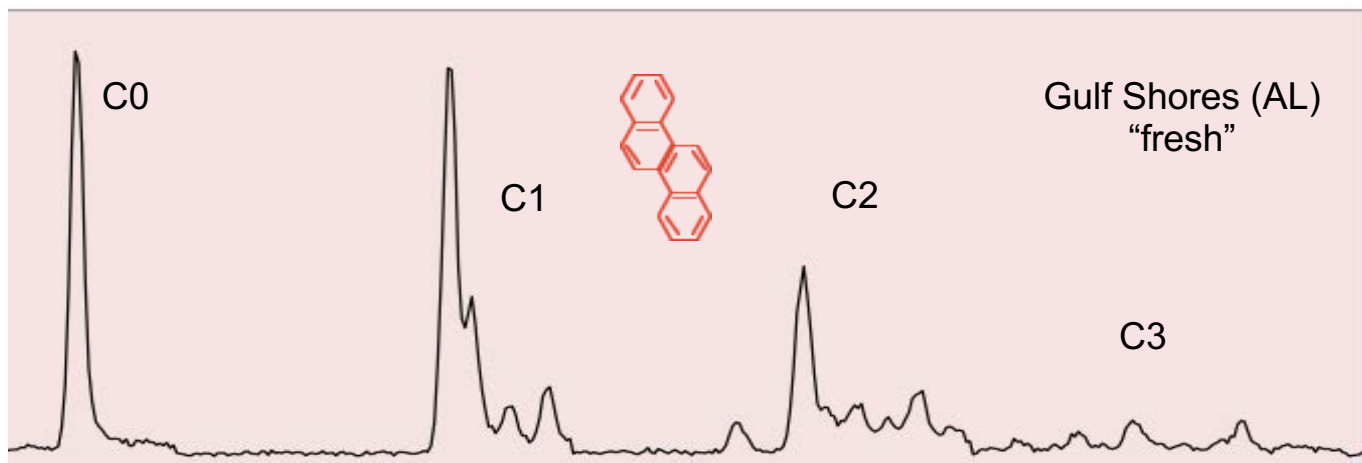
*As with the C<sub>3</sub>-PHNs, the relative distribution of the C<sub>4</sub>-alkylphenanthrene isomers is only slightly affected by the degradation.*



*Repeating the previously displayed chart, to emphasize that the residual, degraded **Grand Isle** tarball exhibits relatively greater loss of the lower molecular weight (alkyl)phenanthrenes, while preferentially retaining the heavier.*



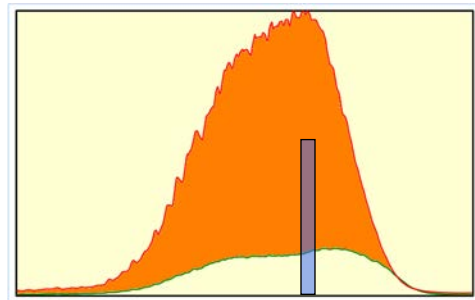
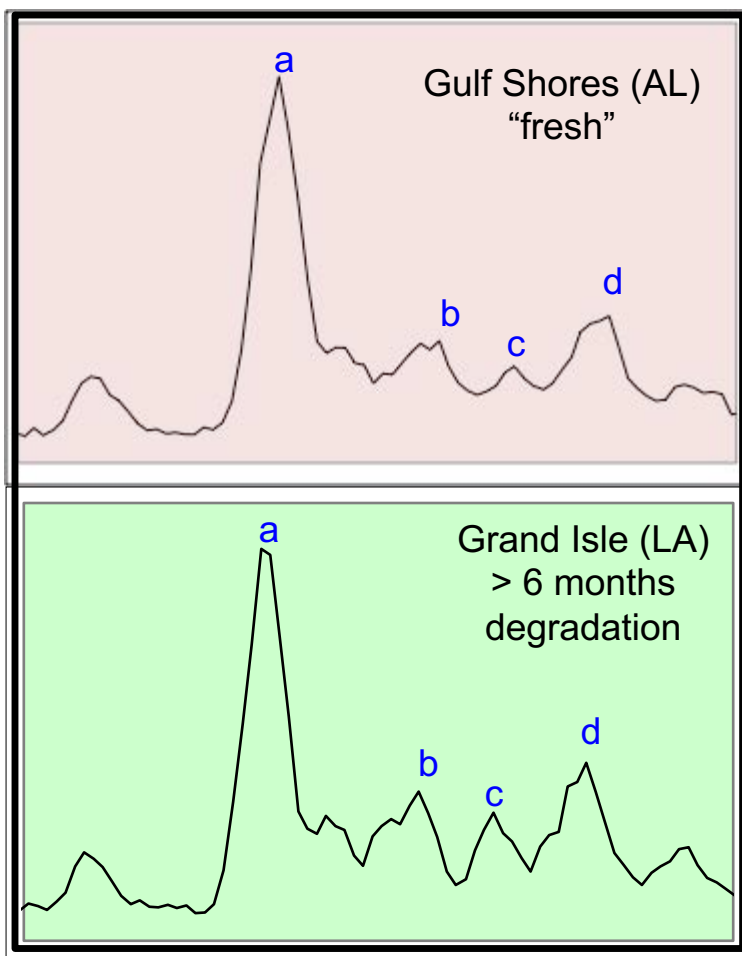
## C<sub>0</sub>-C<sub>3</sub> Chrysene Group Distributions (m/z 228, 242, 256, 270)



### Summary by alkyl-CHR isomer group

*The degraded Grand Isle tarball exhibits relatively little loss of the lower molecular weight (alkyl)chrysenes, while preferentially retaining the heavier.*

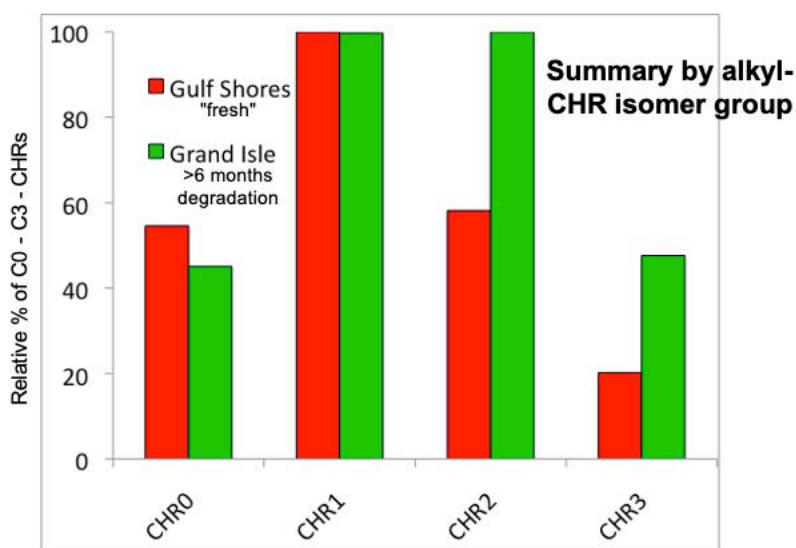
## C<sub>2</sub> Chrysene Detailed Distributions (m/z 256)



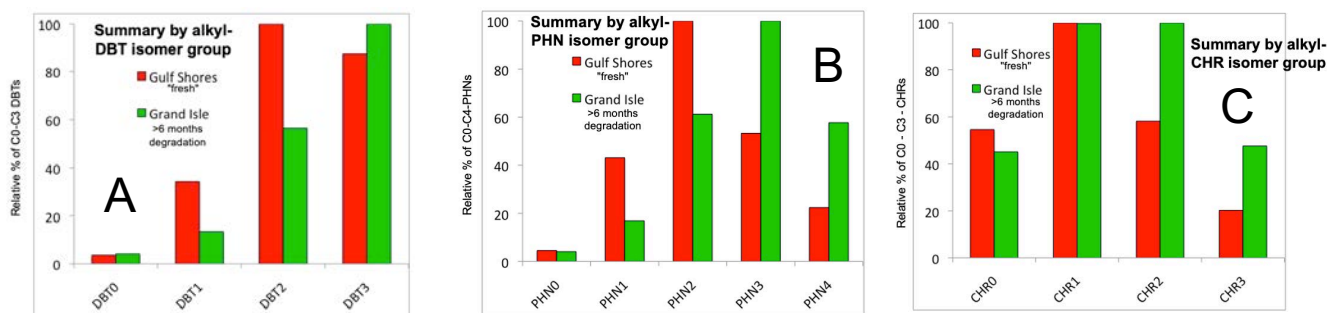
Retention Time

*Inset shows the retention time range of the C2-CHRs in the context of the UCM baselines.*

*The relative distribution of the C2-alkylchrysene isomers is only slightly affected by the degradation.*



*Repeating the previously displayed chart, to emphasize that the residual, degraded Grand Isle tarball exhibits relatively little loss of the lower molecular weight (alkyl)chrysenes, while preferentially retaining the heavier.*

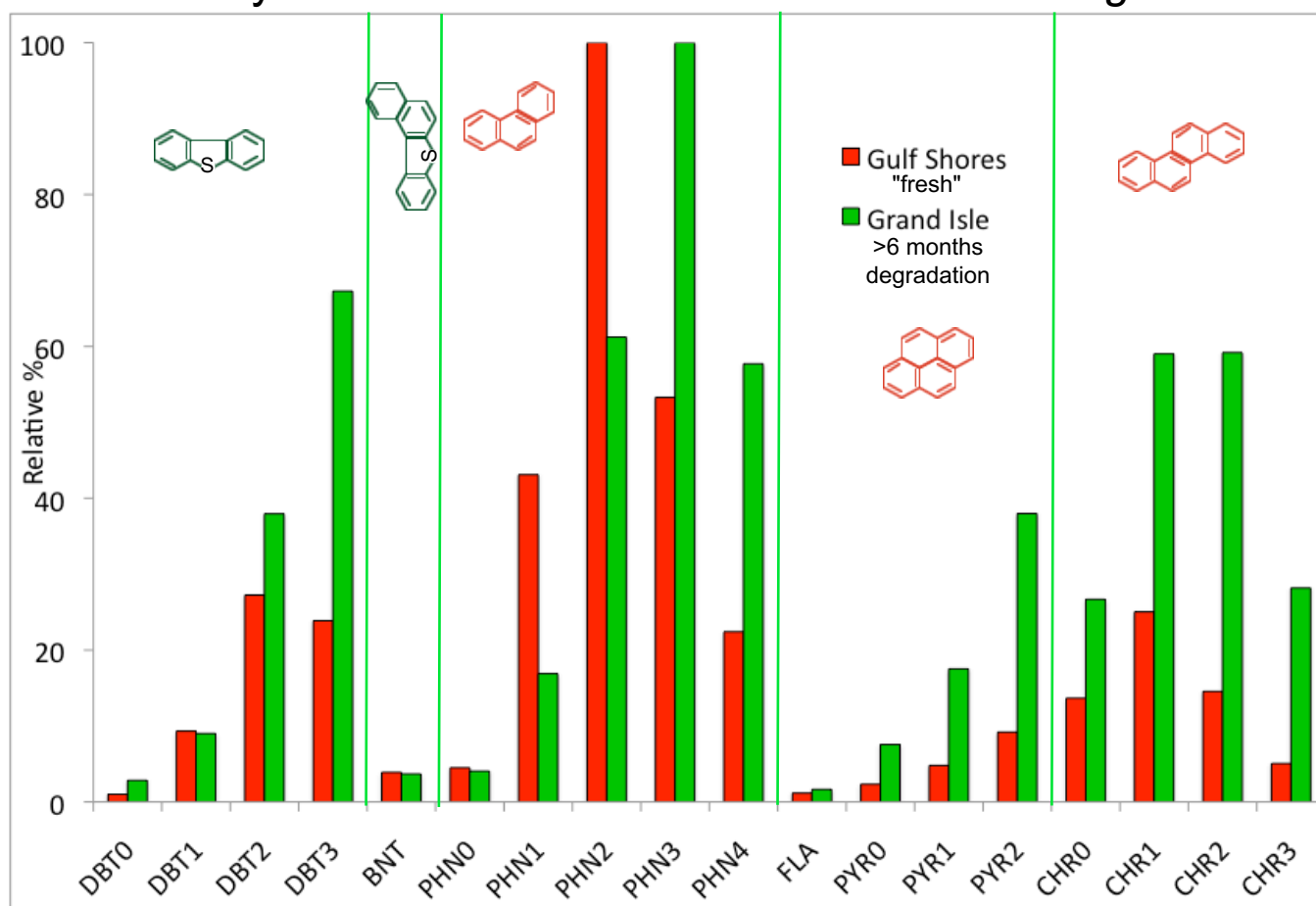


The charts in the previous slides (reproduced above) were normalized for each individual PAC series: (A) dibenzothiophenes, (B) phenanthrenes, and (C) chrysenes.

For an different perspective, the overview chart below shows the compounds normalized across the full suite of PACs (with the pyrene series and benzonaphthothiophene added).

For all PACs in this study, the quantitations used the respective molecular ions.

## Summary of Relative Concentrations: 3 and 4 Ring PACs



Within each PAC group as well as overall, the residual, degraded Grand Isle tarball has preferentially lost more of the lower molecular weight components, which retaining relatively more of the heavier compounds.



# Conclusions

More heavily alkylated PACs degraded more slowly than parent and monomethyl.

Degradation more strongly affects the relative distribution of isomers in methyl and dimethyl 3-ring PACs.

- Trimethyl+ and 4-ring compounds less affected.

Techniques of environmental forensics can assist in ascertaining sources of oil

- Even after severe degradation
- Must employ conservative compounds (e.g., hopanes, triaromatic steroids, alkylated chrysenes)

Pyrolysis-GC/MS effective for rapid tarball characterization: *n*-alkanes, UCM, petroleum biomarkers, PACs all were evident.



**New York City**

Real-Time  
Air Quality Analysis  
- on the Sidewalk!



## Acknowledgements:

Gulf Shores (AL) sample: Robert J. Martinez, University of Alabama

Grande Isle (LA) sample: Michael Pawlish, Montclair State University (with the assistance of B. Zagorski)