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

Michael A. Kruge

Montclair State University, krugem@mail.montclair.edu

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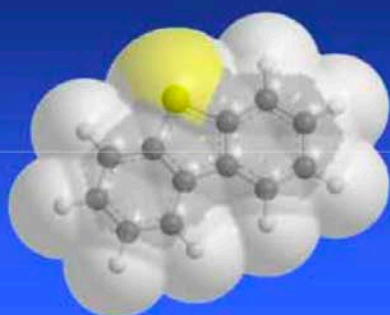
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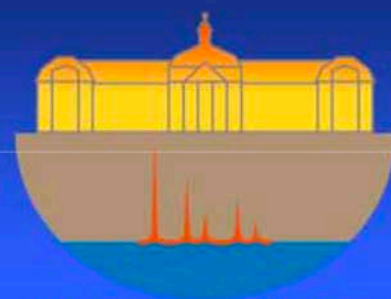
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Group of Prof. Jan Andersson - University of Münster



UNIVERSITY OF MÜNSTER
APPLIED GEOLOGY

23rd 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

Michael A. Kruge
Dept. of Earth & Environmental Studies
Montclair State University
New Jersey, USA



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/>

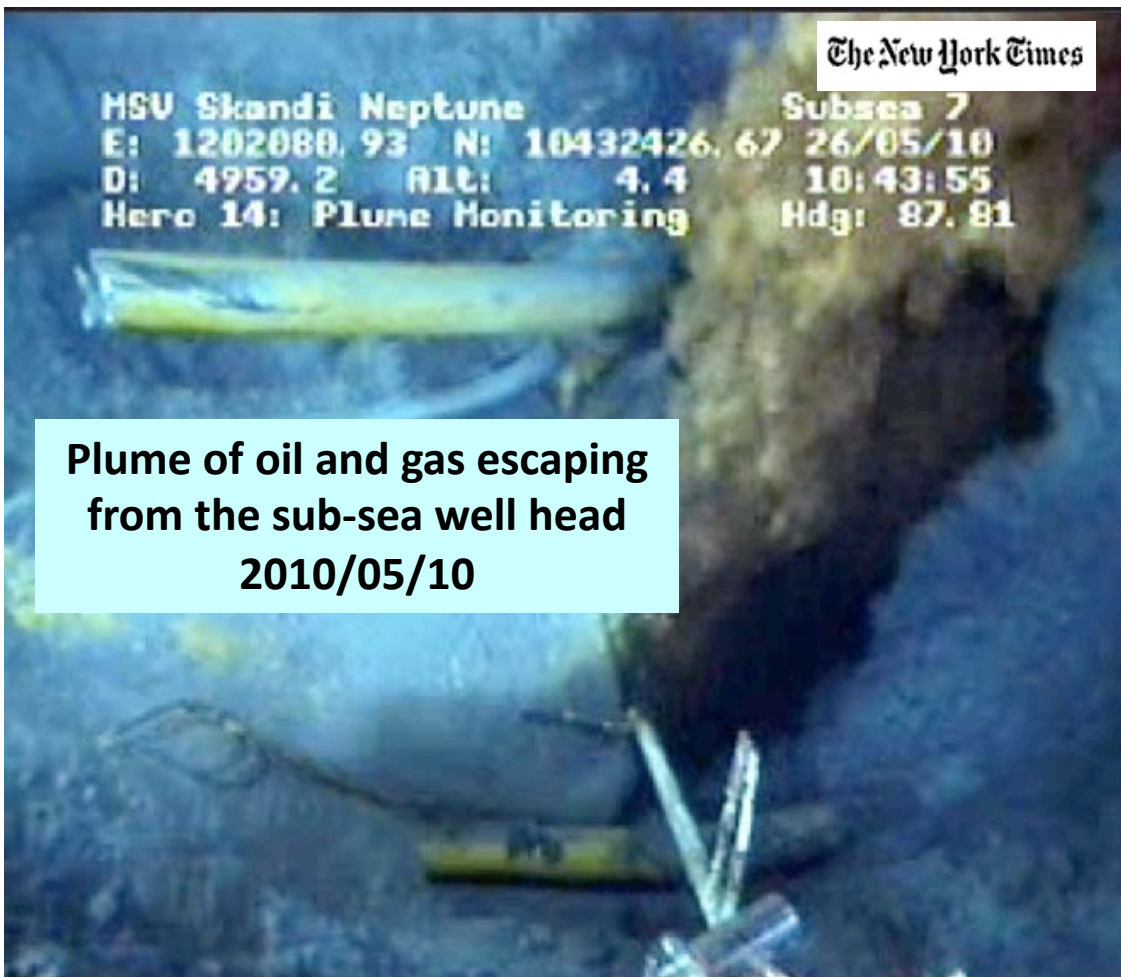
The *Deepwater Horizon* offshore oil platform caught fire and sank with the loss of 11 crew members, as the well was being closed pending later production.

2010/04/20



MSU 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**



The New York Times

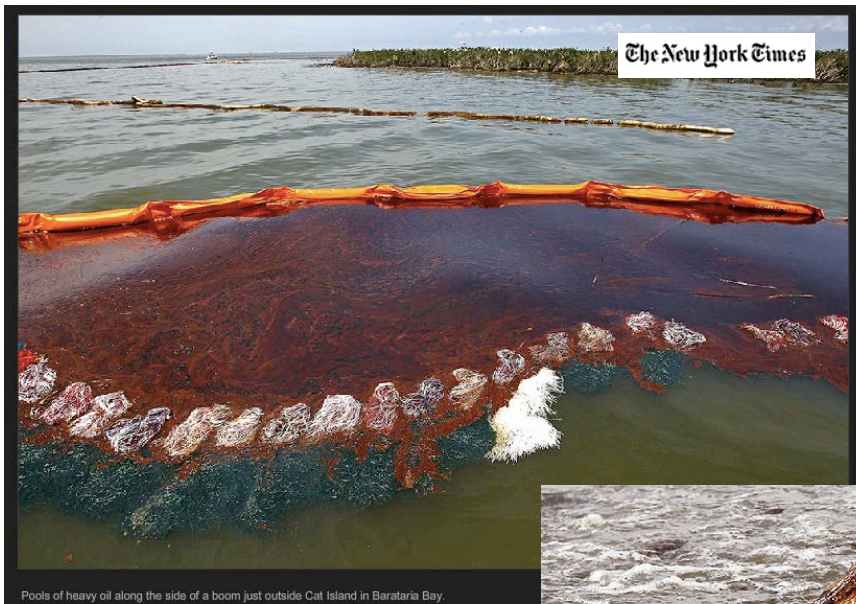


Operation in water depth of ca. 1600 m.

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.

The New York Times



Pools of heavy oil along the side of a boom just outside Cat Island in Barataria Bay.

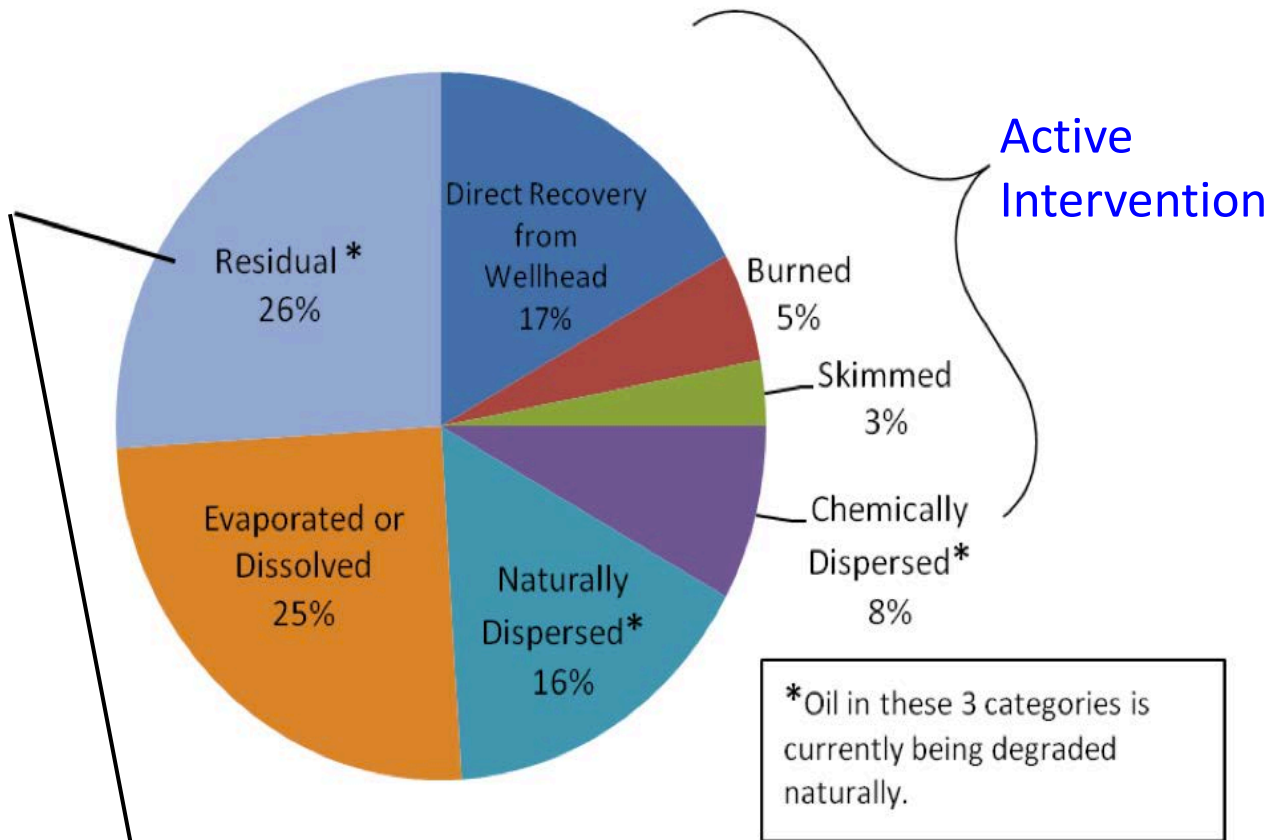
The New York Times



Photos showing effects of the oil spill.

Deepwater Horizon Oil Budget

Based on estimated release of 4.9m barrels of oil



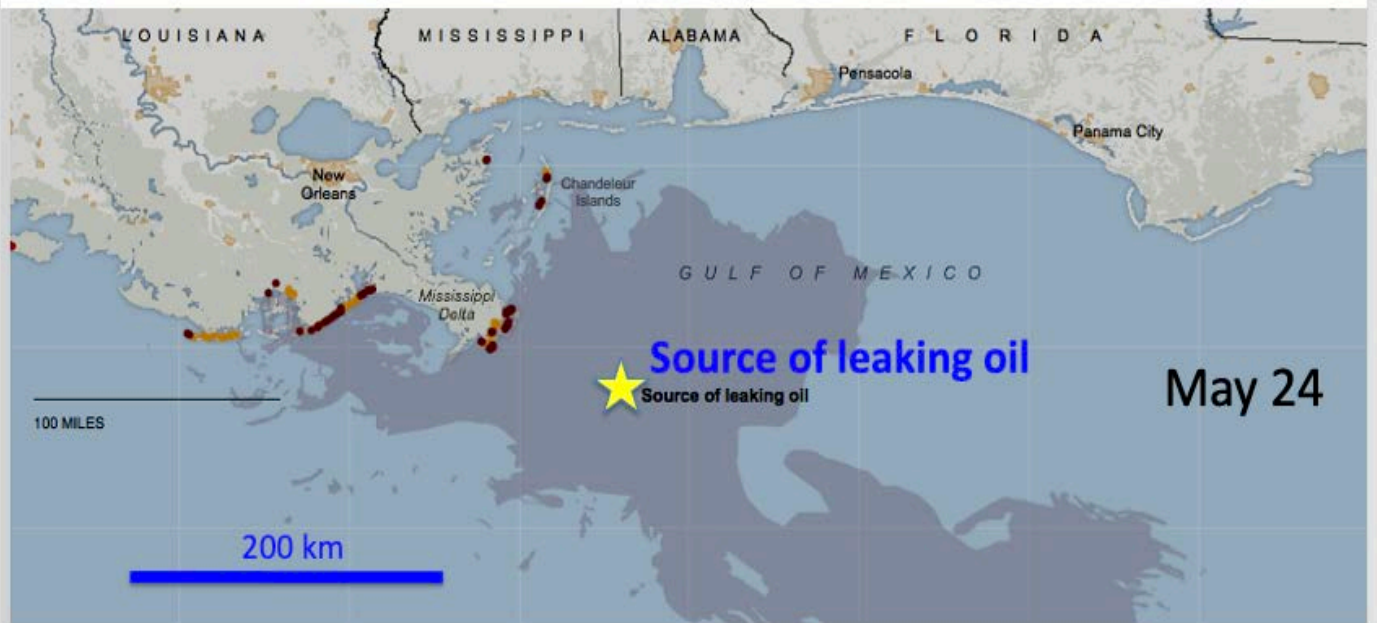
National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling
THE AMOUNT AND FATE OF THE OIL, Staff Working Paper No. 3, 2010

Residual includes

- oil that is on or just below the surface
- light sheen
- weathered tar balls
- washed ashore
- buried in sediment

Two tarballs washed ashore were collected for this study.

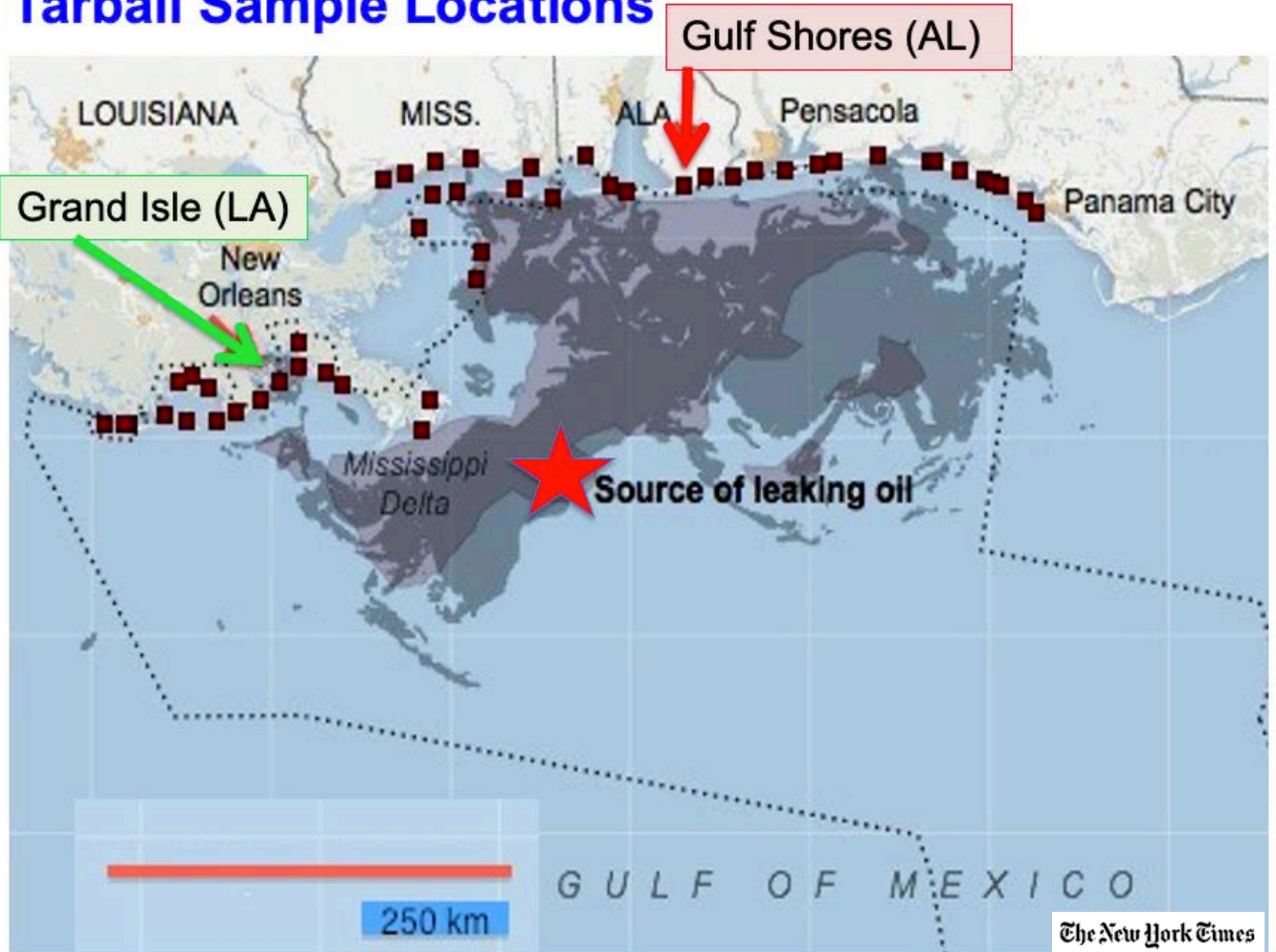
Expansion of surface oil plume



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 st reached shore (approx.)	Sample taken
Gulf Shores (AL)	June 5	June 5
Grand Isle (LA)	May 24	January 15

2 Samples

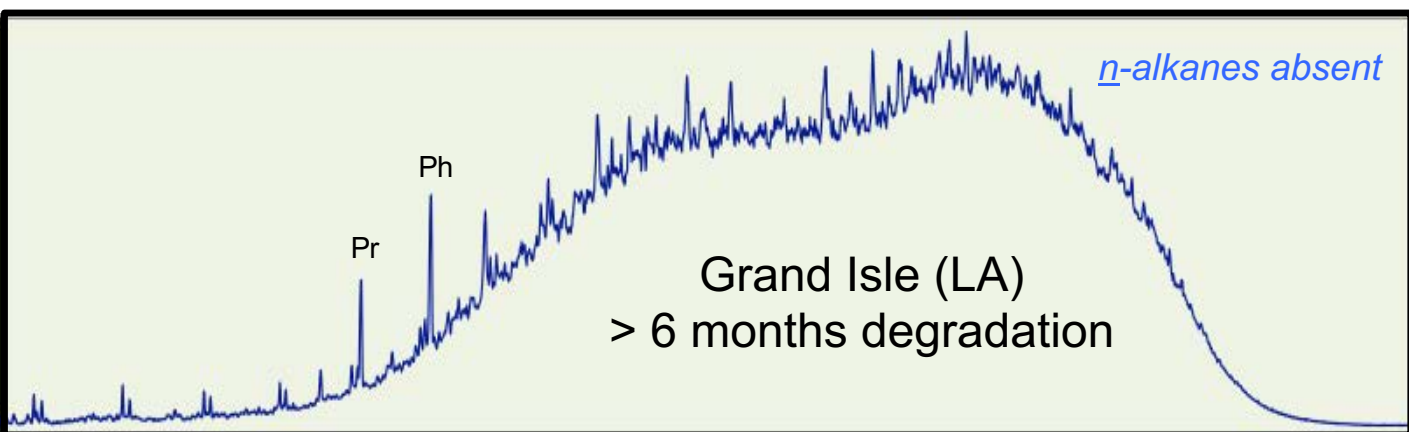
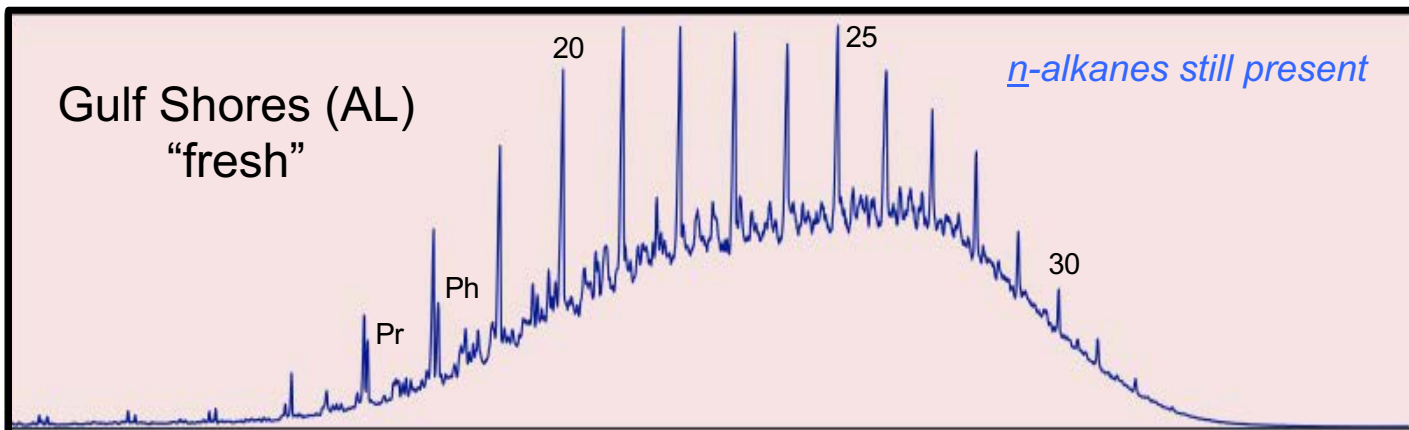


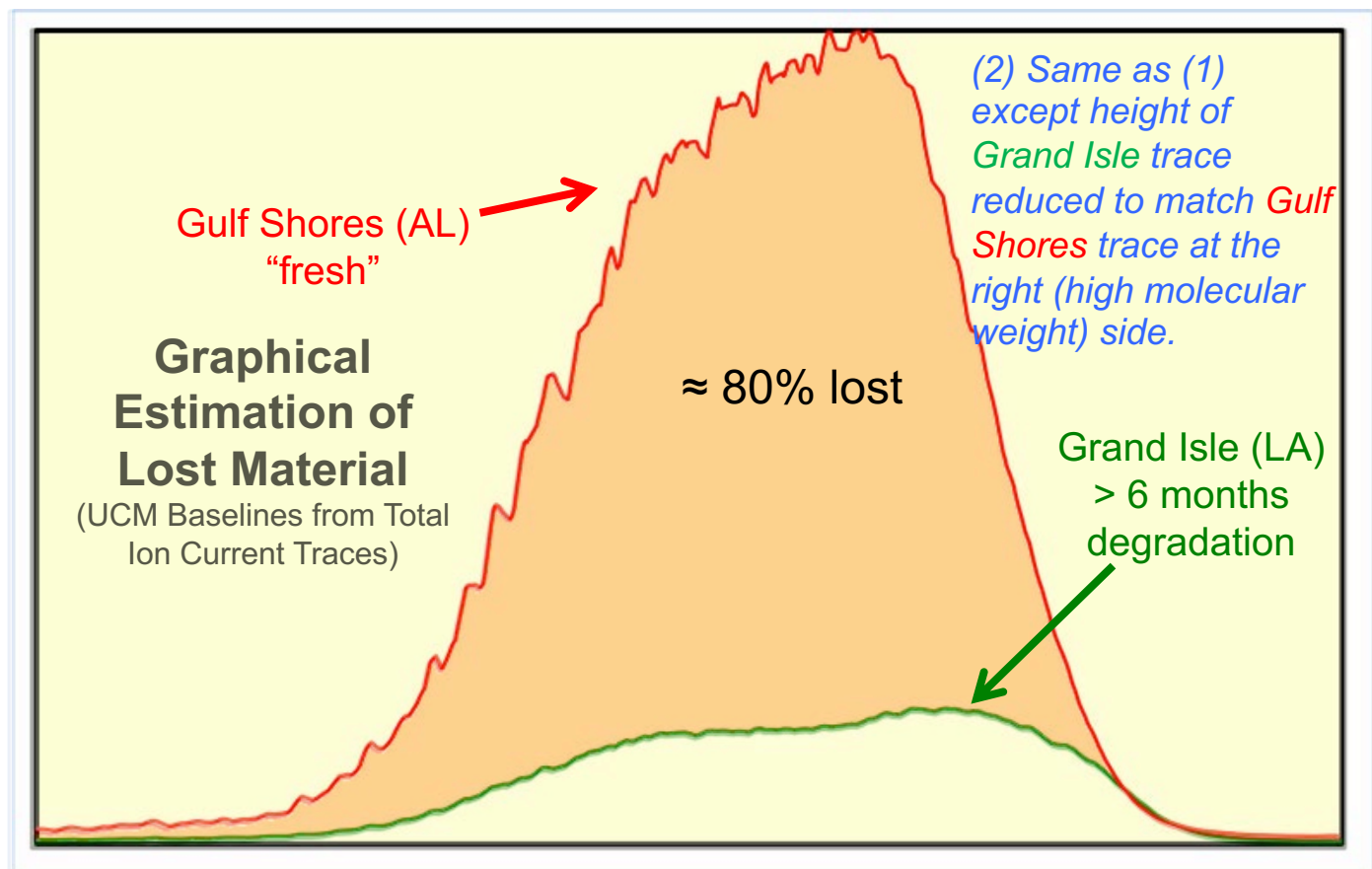
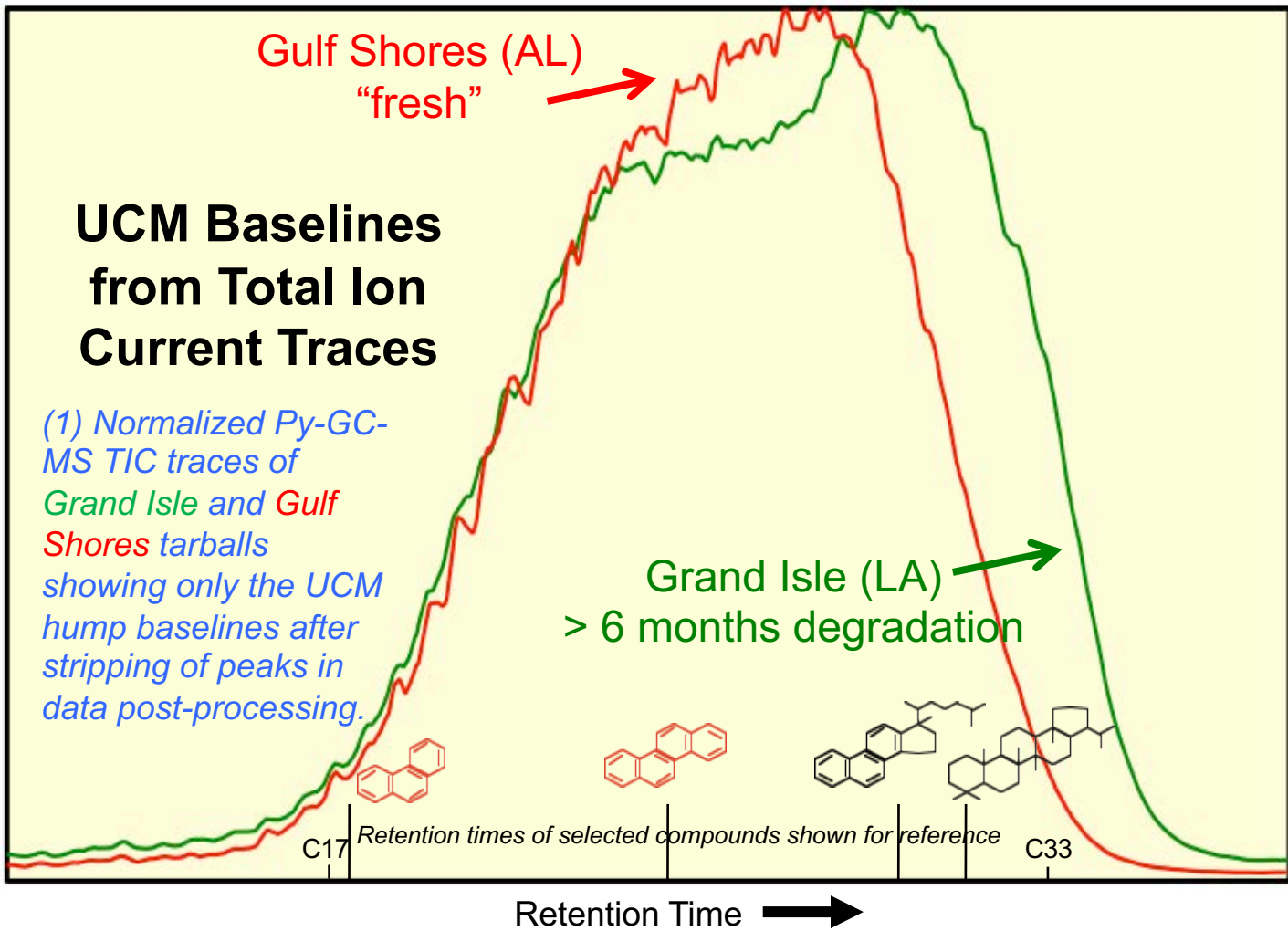
Tarball analysis:

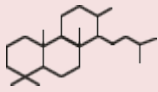
- Rapid screening by analytical pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)
- Tarballs analyzed directly without sample preparation
- Yielded predominantly thermodesorption products



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





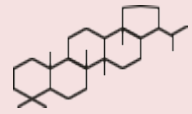


H30

Gulf Shores (AL)
"fresh"

T23

T26



H33

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

Grand Isle (LA)

> 6 months degradation

H30

T23

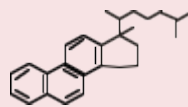
T26

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)

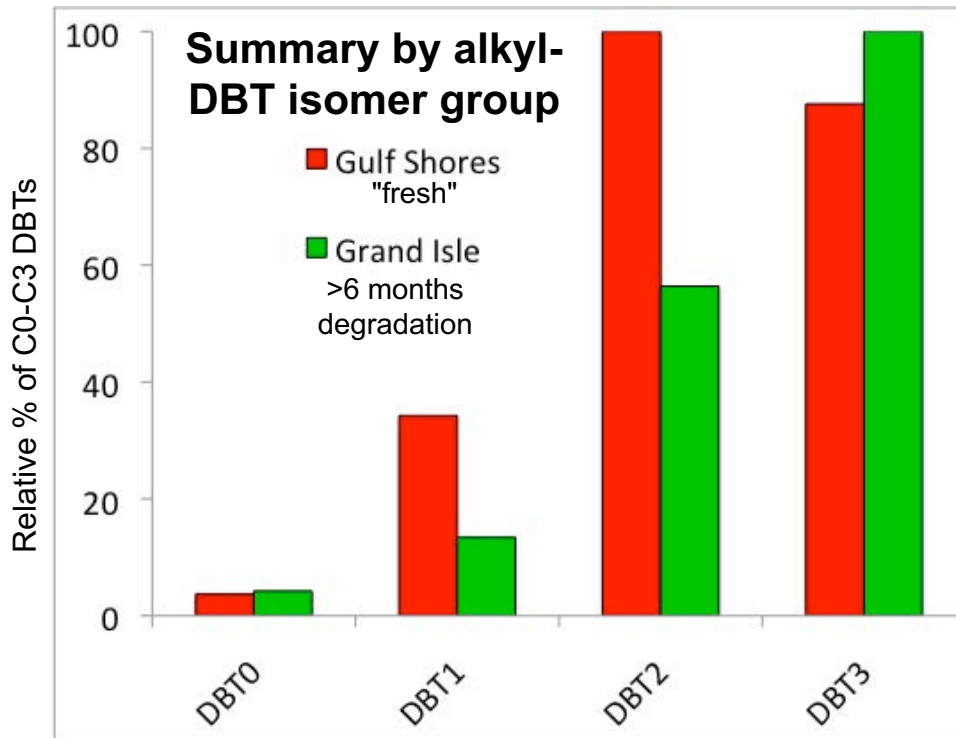
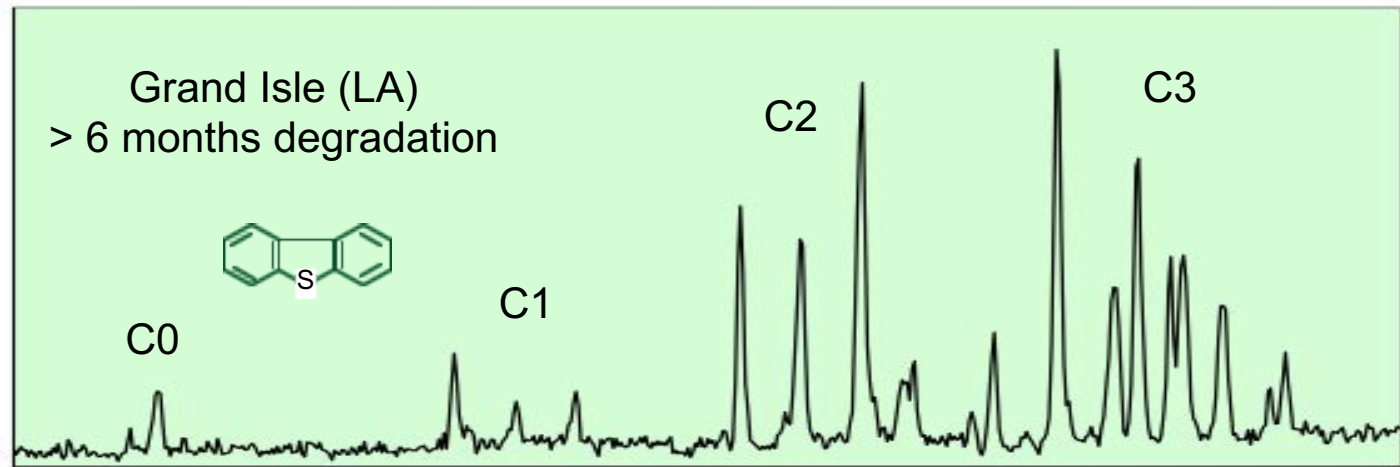
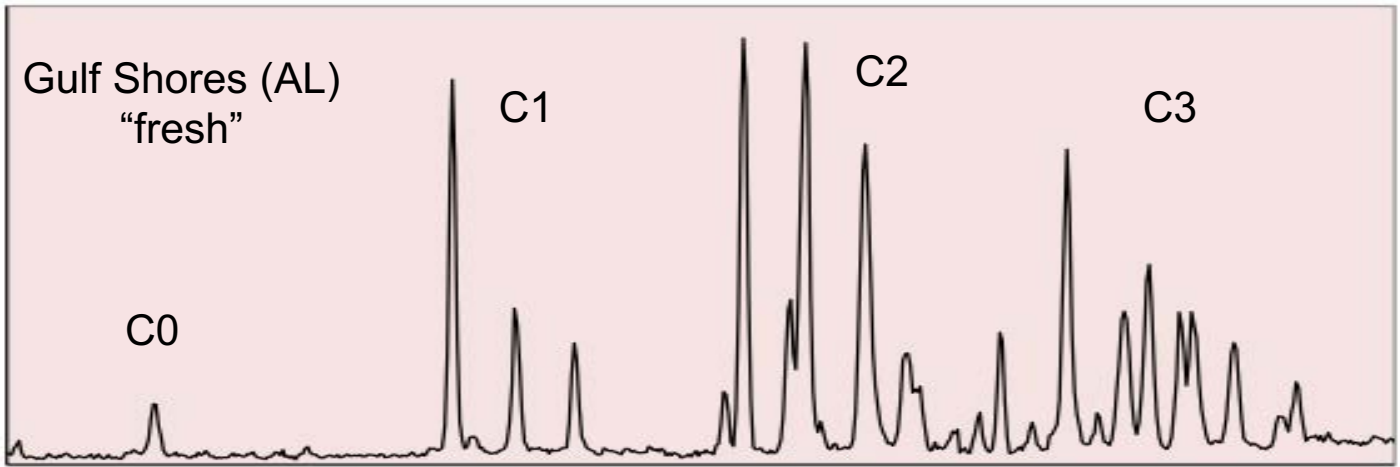
> 6 months degradation

C21

C26S

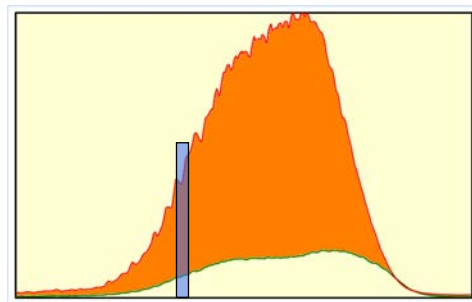
C28R

C₀-C₃ Dibenzothiophene Group Distributions (m/z 184, 198, 212, 226)



The residual, degraded Grand Isle tarball exhibits relatively greater loss of the lower molecular weight (alkyl)dibenzothiophenes.

C₂ Dibenzothiophene Detailed Distributions (m/z 212)

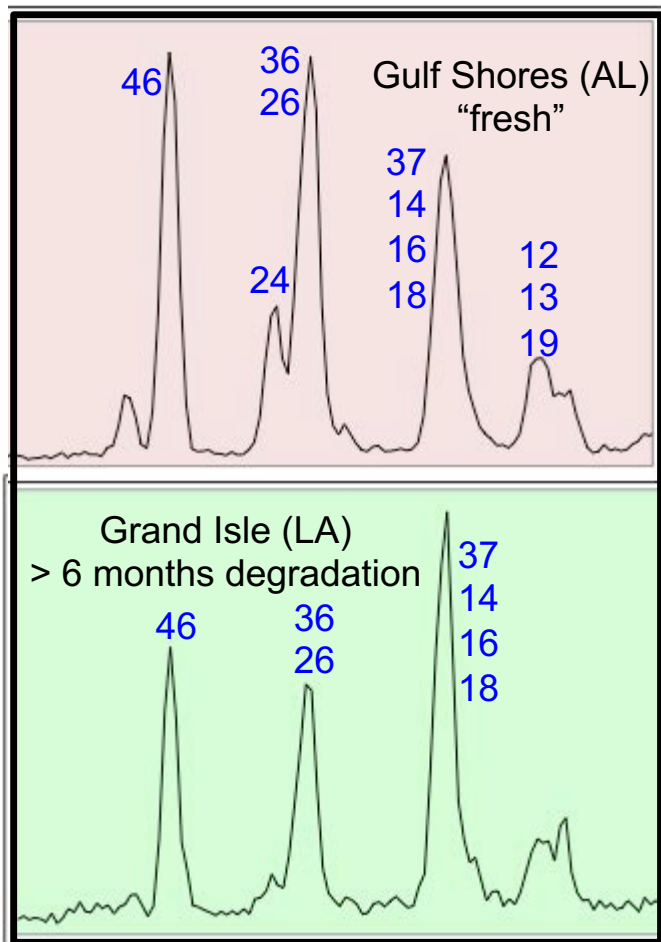


Retention Time

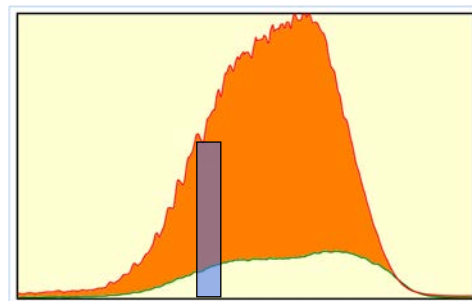
Insets show the retention time range of the DBTs in the context of the UCM baselines.

The relative distribution of C₂-alkyldibenzothiophene isomers is strongly affected by the degradation.

Blue numerals denote the methyl group sites on the C₂-DBT isomers.

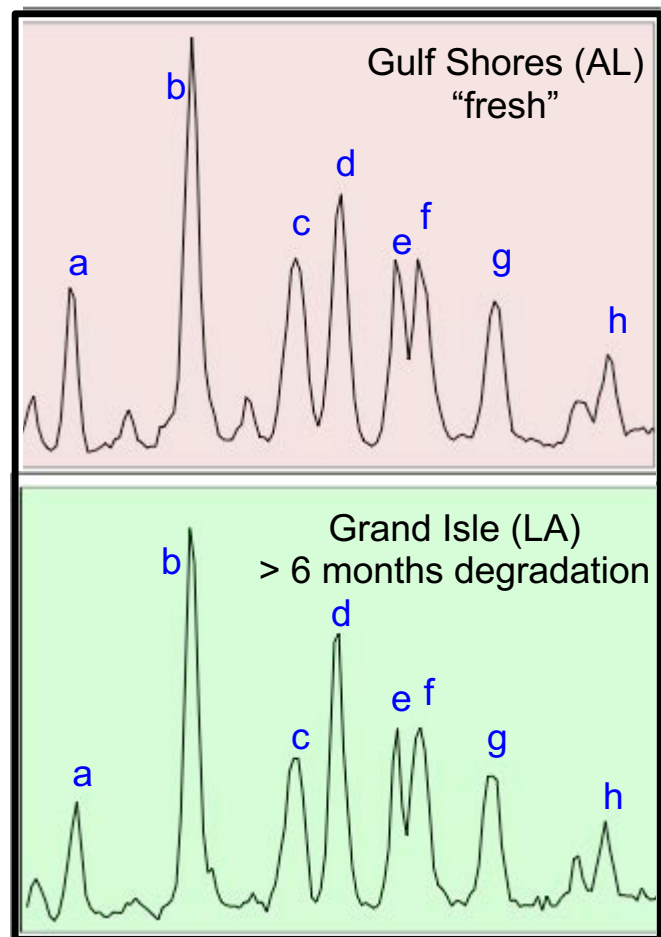


C₃ Dibenzothiophene Detailed Distributions (m/z 226)

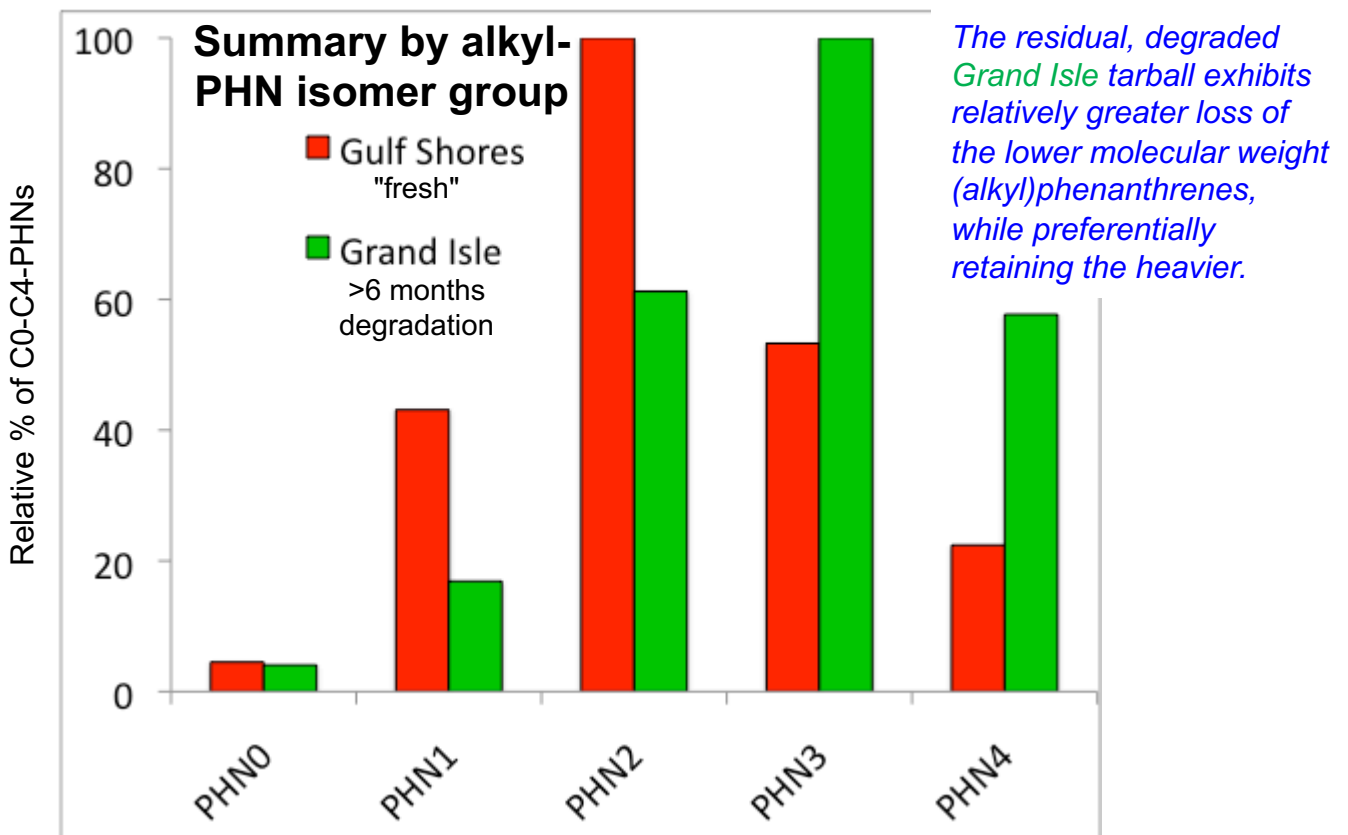
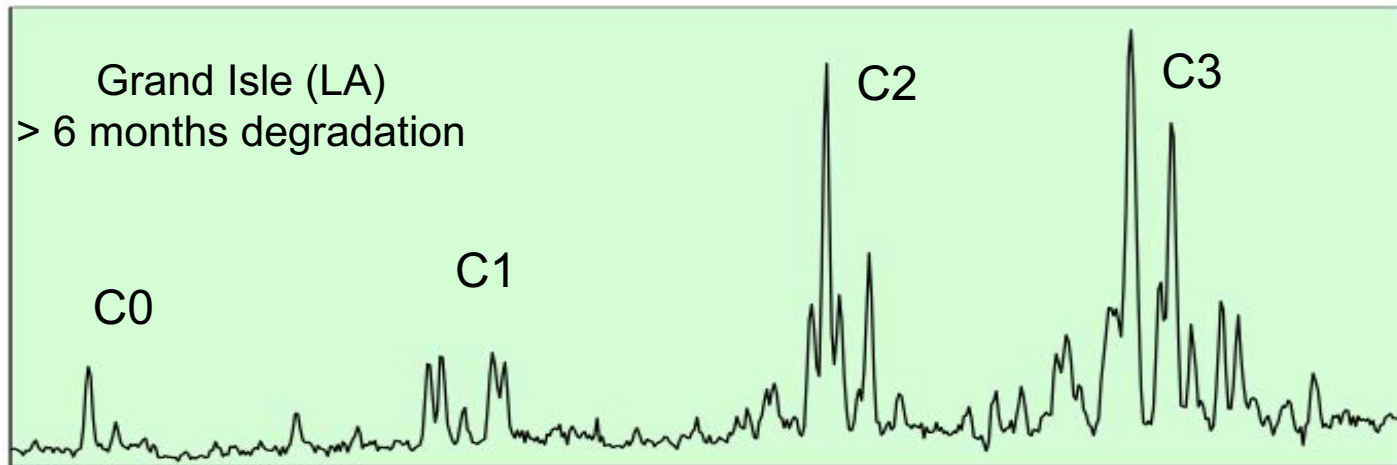
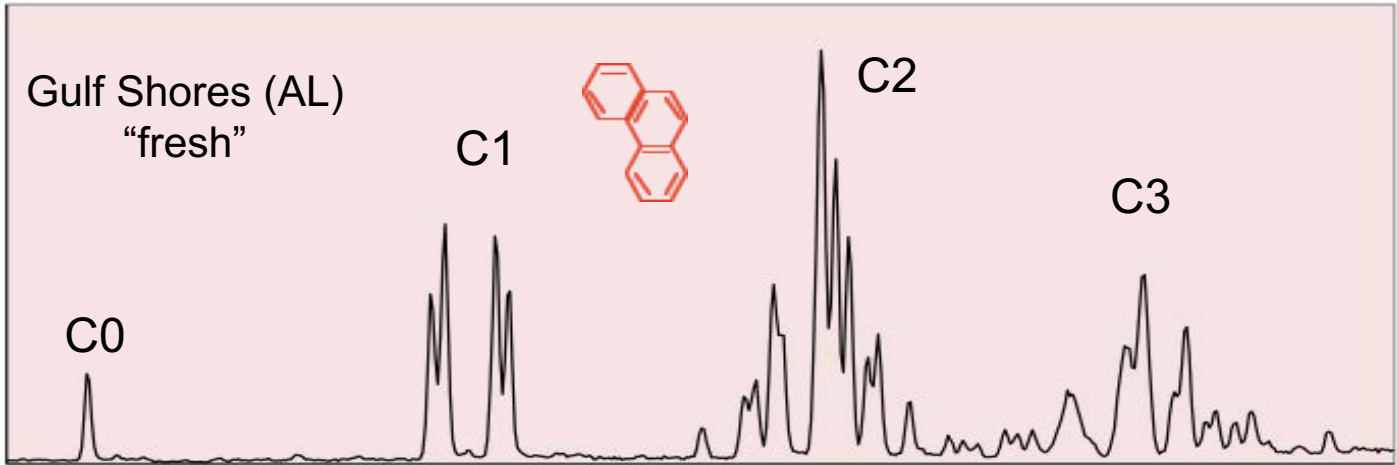


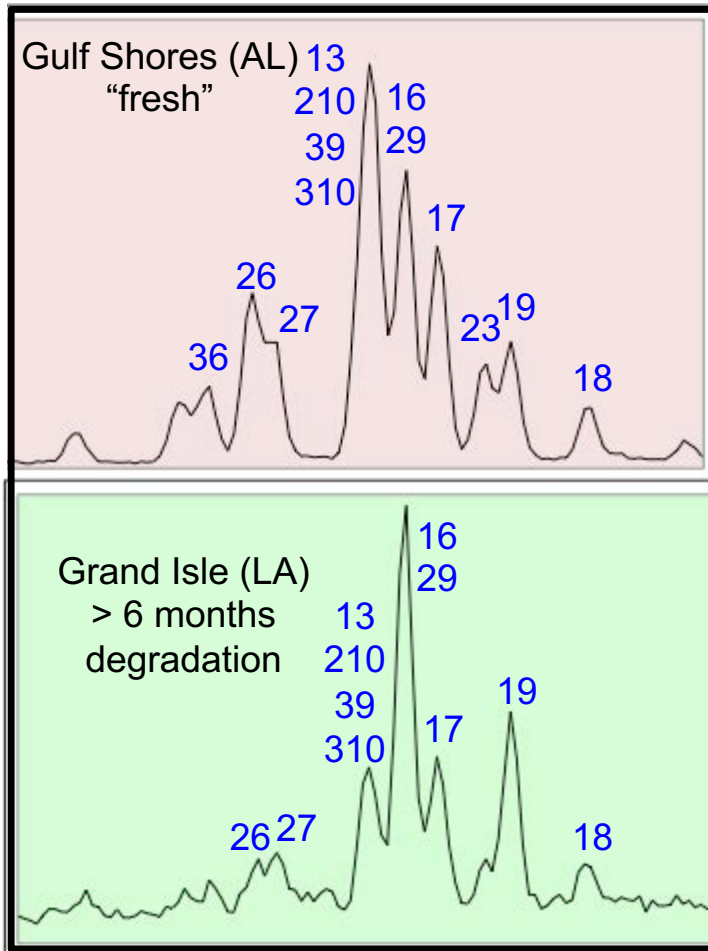
Retention Time

In contrast, the relative distribution of heavier C₃-alkyldibenzothiophene isomers is not much affected by the degradation.

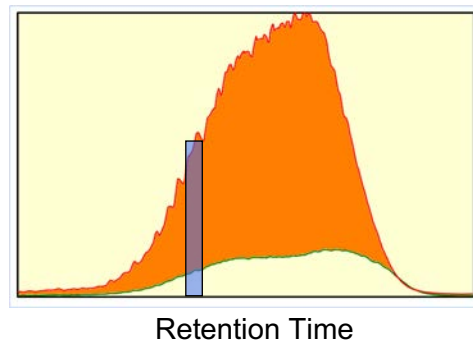


C₀-C₃ Phenanthrene Group Distributions (m/z 178, 192, 206, 220)





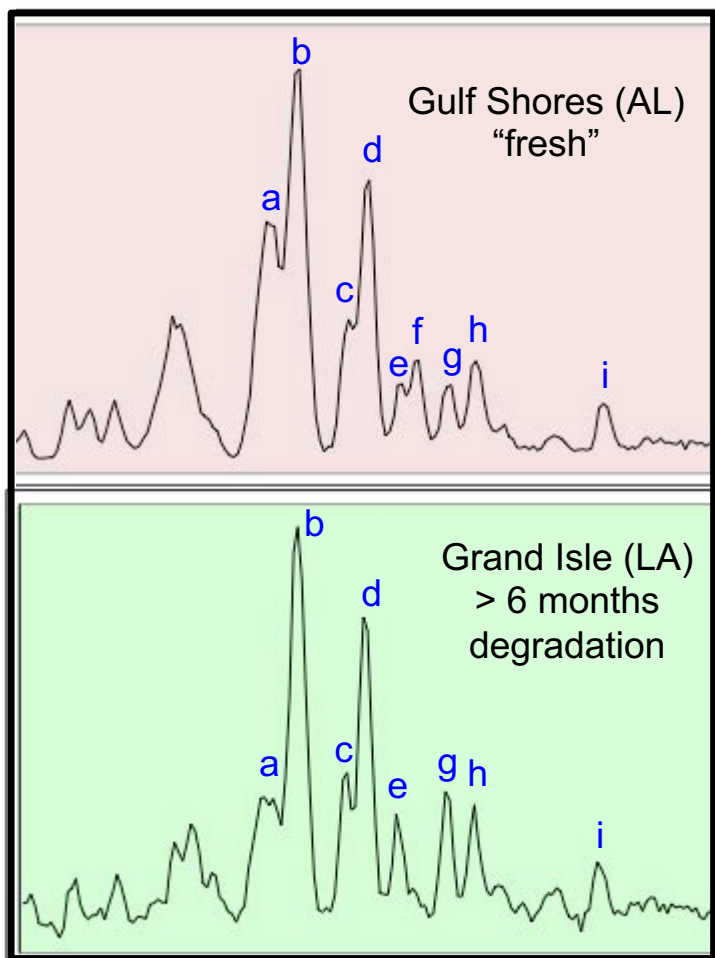
C₂ Phenanthrene Detailed Distributions (m/z 206)



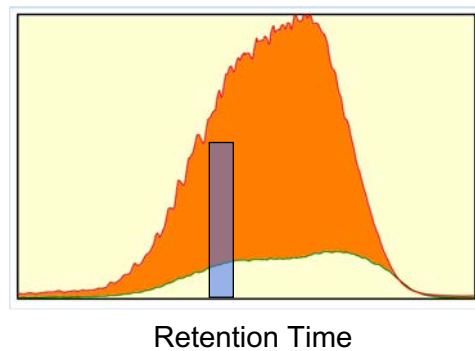
Insets show the retention time range of the PHNs in the context of the UCM baselines.

The relative distribution of C₂-alkylphenanthrene isomers is strongly affected by the degradation, with the preferential loss of certain individuals.

Blue numerals denote the methyl group sites on the C₂-PHN isomers.

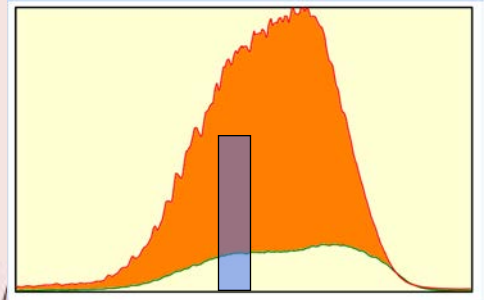
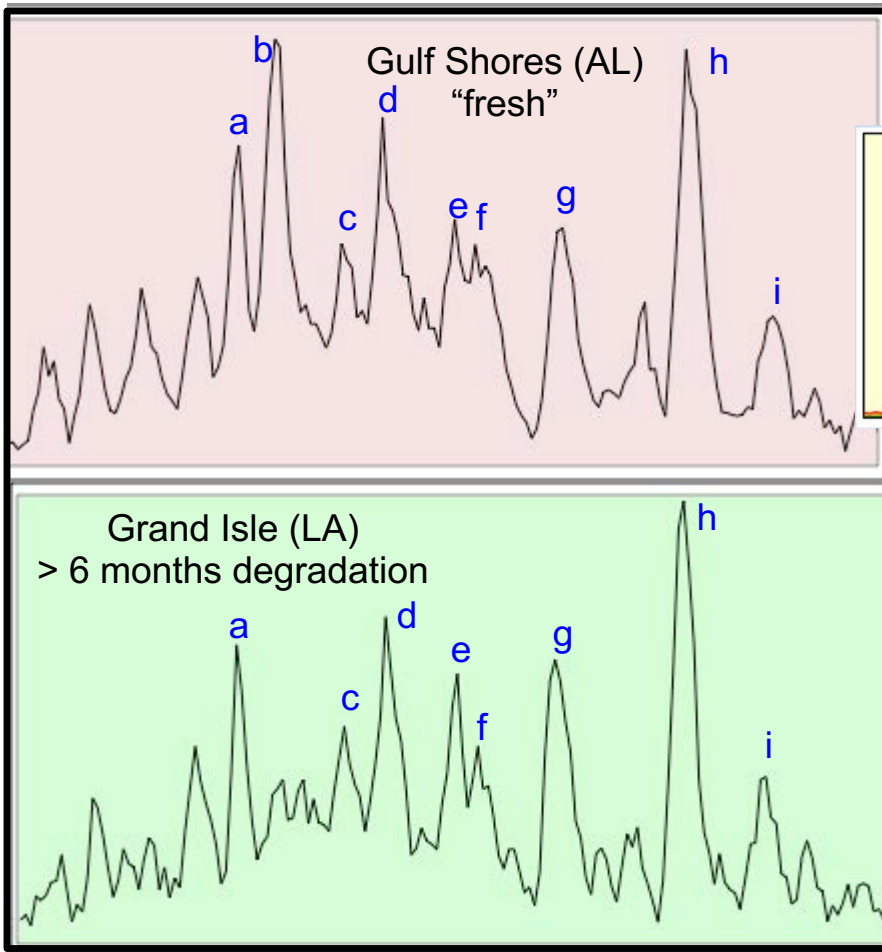


C₃ Phenanthrene Detailed Distributions (m/z 220)



In contrast, the relative distribution of heavier C₃-alkylphenanthrene isomers is only slightly affected by the degradation.

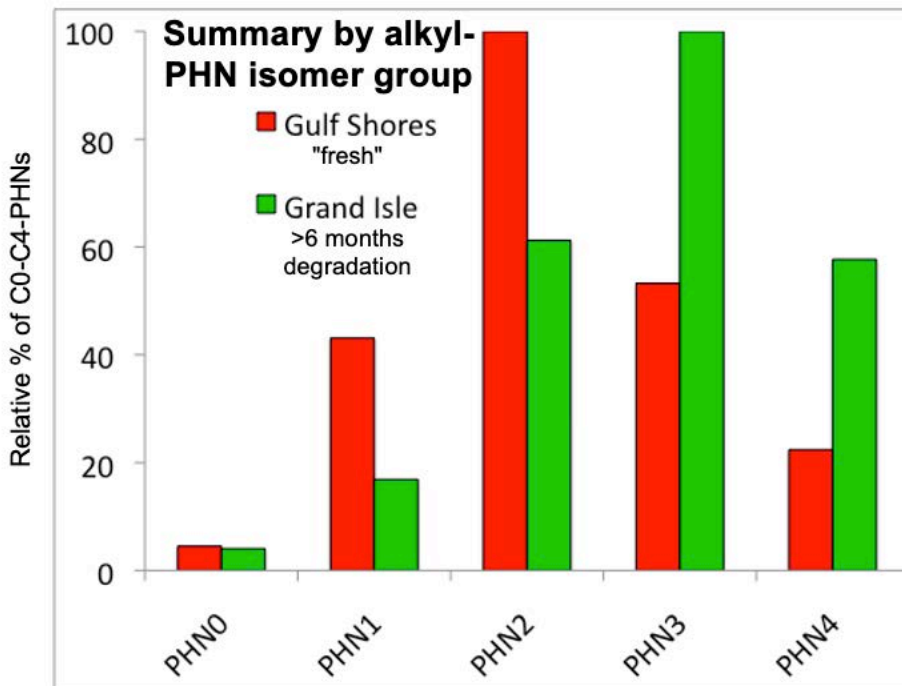
C₄ Phenanthrene Detailed Distributions (m/z 234)



Retention Time

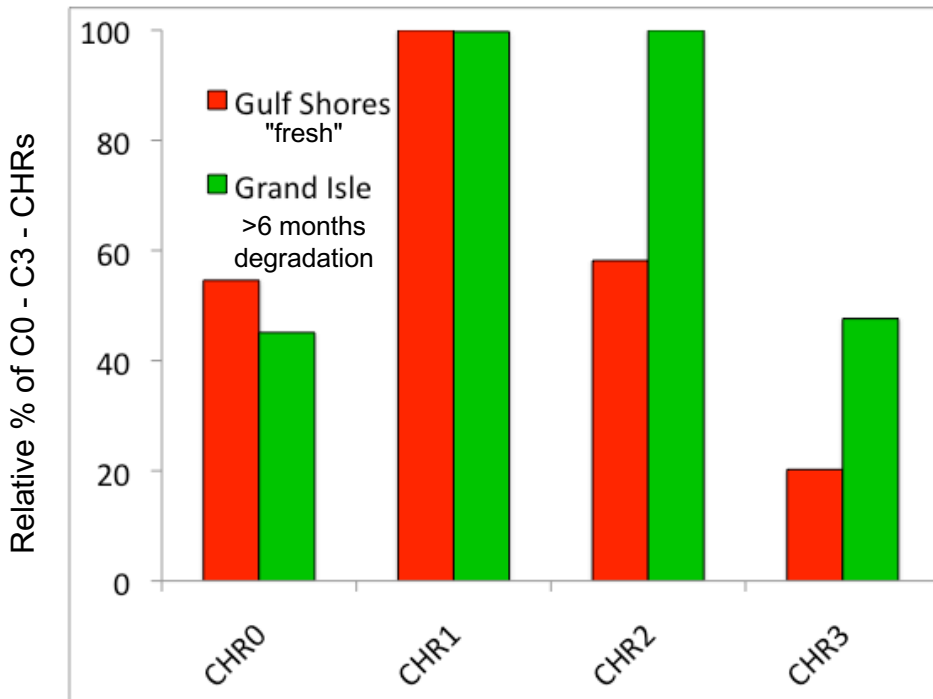
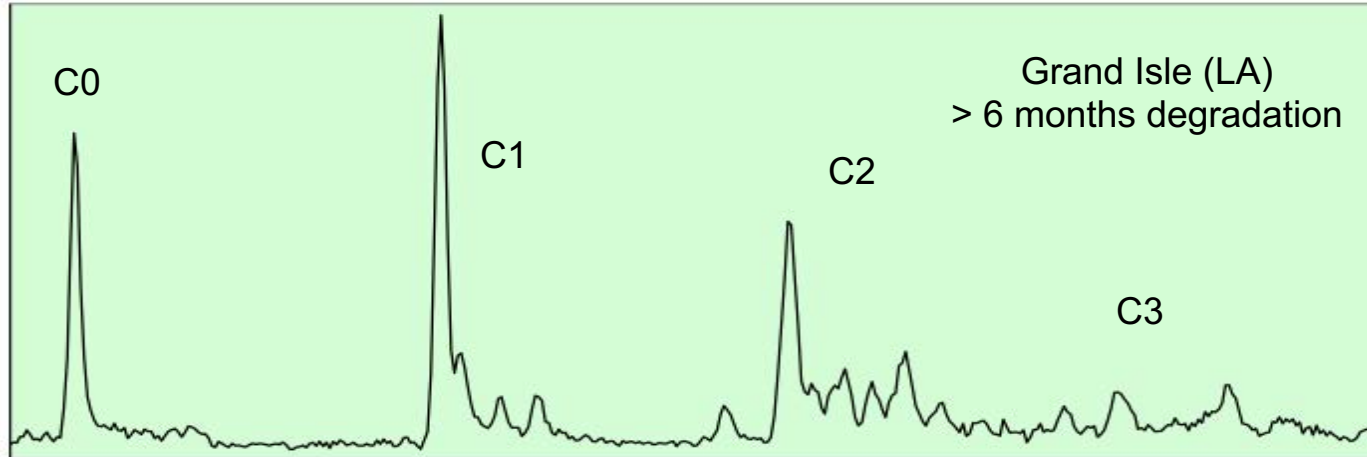
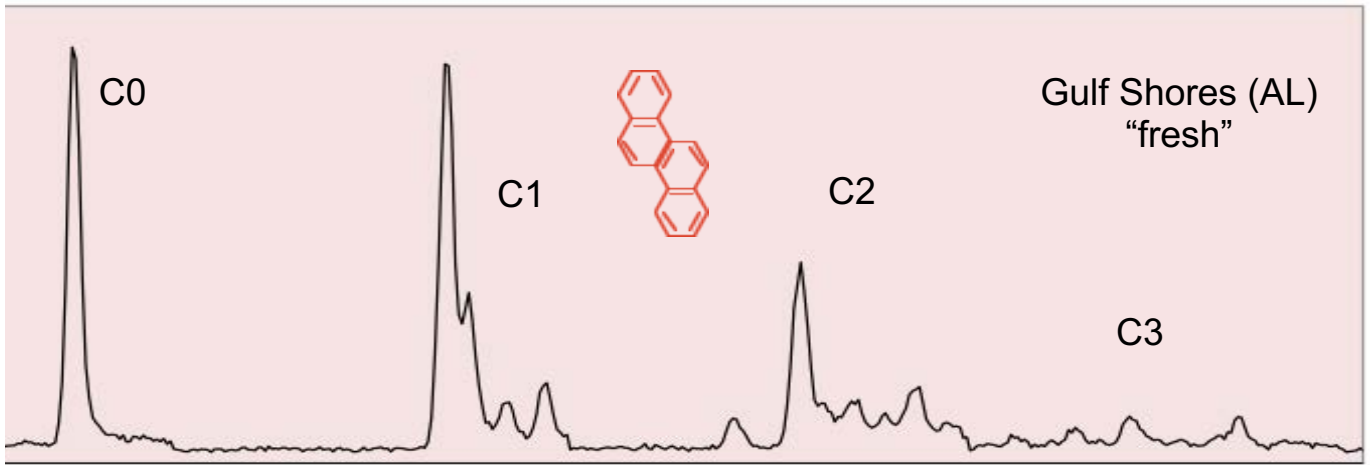
Inset shows the retention time range of the C₄-PHNs in the context of the UCM baselines.

As with the C₃-PHNs, the relative distribution of the C₄-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.*

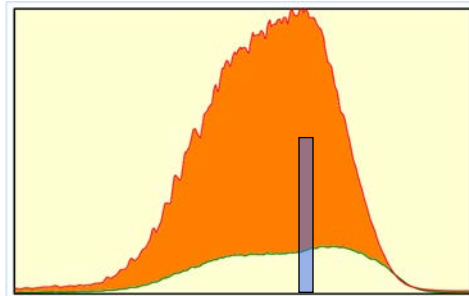
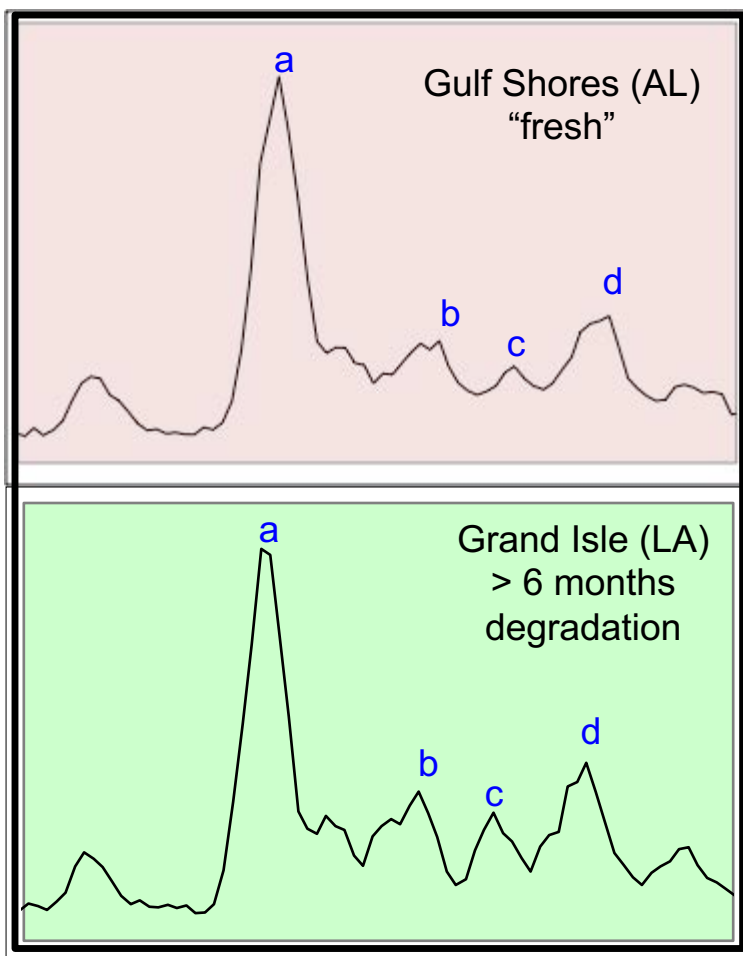
C₀-C₃ Chrysene Group Distributions (m/z 228, 242, 256, 270)



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.

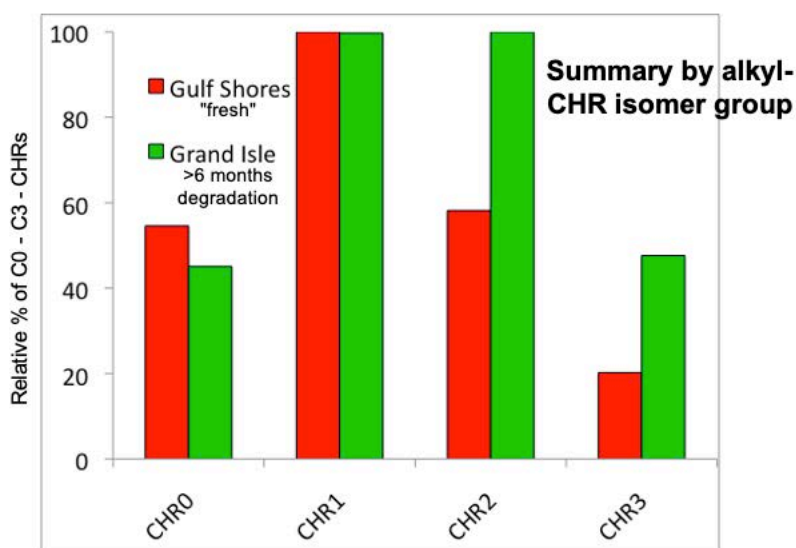
C₂ Chrysene Detailed Distributions (m/z 256)



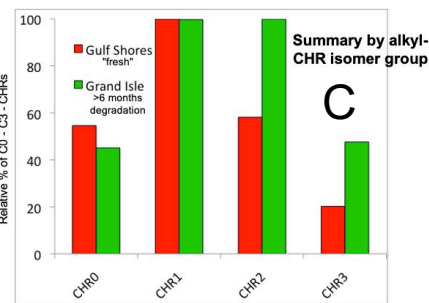
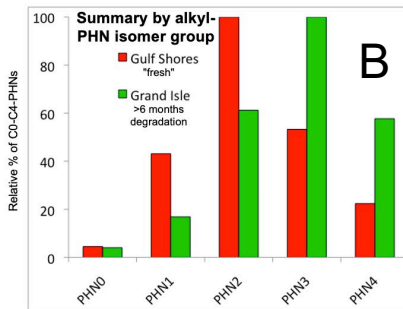
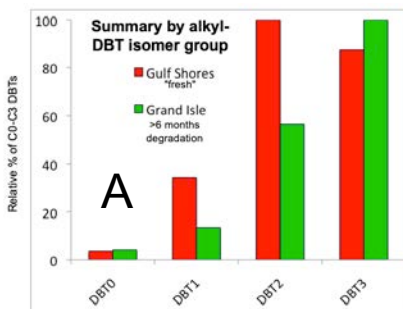
Retention Time

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.

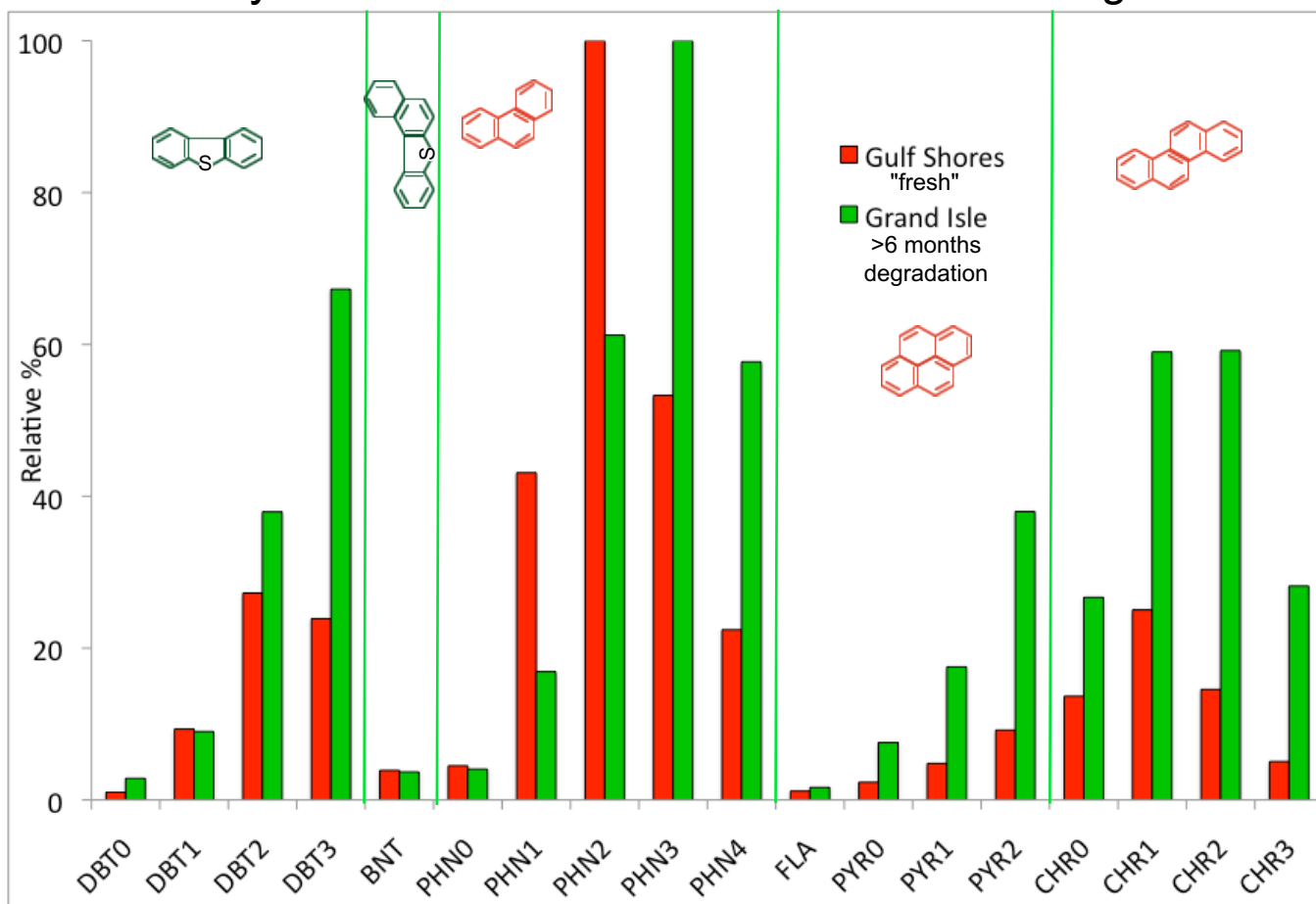


The charts in the previous slides (reproduced above) were normalized for each individual PAC series: (A) dibenzothiophenes, (B) phenanthrenes, and (C) chrysenes.

For a 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)