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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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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.

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

[Link](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

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.
Two tarballs washed ashore were collected for this study.

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

National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling

Active Intervention

Direct Recovery from Wellhead 17%
Burned 5%
Skimmed 3%
Chemically Dispersed* 8%

Residual * 26%
Evaporated or Dissolved 25%
Naturally Dispersed* 16%

*Oil in these 3 categories is currently being degraded naturally.
The surface oil plume greatly expanded over these 19 days.
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**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oil 1st reached shore (approx.)</th>
<th>Sample taken</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gulf Shores (AL)</td>
<td>June 5</td>
<td>June 5</td>
</tr>
<tr>
<td>Grand Isle (LA)</td>
<td>May 24</td>
<td>January 15</td>
</tr>
</tbody>
</table>

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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”

Py-GC-MS Total Ion Current

n-alkanes still present

Grand Isle (LA)

> 6 months degradation

n-alkanes absent
(1) Normalized Py-GC-MS TIC traces of Grand Isle and Gulf Shores tarballs showing only the UCM hump baselines after stripping of peaks in data post-processing.

(2) Same as (1) except height of Grand Isle trace reduced to match Gulf Shores trace at the right (high molecular weight) side.

Retention times of selected compounds shown for reference.

≈ 80% lost

Gulf Shores (AL) “fresh”

Grand Isle (LA) > 6 months degradation

≈ 80% lost

Gulf Shores (AL) “fresh”

Grand Isle (LA) > 6 months degradation

Graphical Estimation of Lost Material
(UCM Baselines from Total Ion Current Traces)
Biomarker distributions are largely unaffected by the degradation.
C₀-C₃ Dibenzothiophene Group Distributions (m/z 184, 198, 212, 226)

Gulf Shores (AL) “fresh”

Grand Isle (LA) > 6 months degradation

The residual, degraded Grand Isle tarball exhibits relatively greater loss of the lower molecular weight (alkyl)dibenzothiophenes.
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C\textsubscript{2} Dibenzothiophene Detailed Distributions (m/z 212)

Gulf Shores (AL) "fresh"

Grand Isle (LA) > 6 months degradation

C\textsubscript{3} Dibenzothiophene Detailed Distributions (m/z 226)

Grand Isle (LA) > 6 months degradation

In contrast, the relative distribution of heavier C\textsubscript{3}-alkyldibenzothiophene isomers is not much affected by the degradation.
**C₀-C₃ Phenanthrene Group Distributions (m/z 178, 192, 206, 220)**

**Gulf Shores (AL)**
- “fresh”

**Grand Isle (LA)**
- > 6 months degradation

**Summary by alkyl-PHN isomer group**

- **Gulf Shores** "fresh"
- **Grand Isle** >6 months degradation

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

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.
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.

Gulf Shores (AL) “fresh”

Grand Isle (LA) > 6 months degradation

Relative % of C0 - C3 - CHRs

0 20 40 60 80 100
CHR0 CHR1 CHR2 CHR3

Gulf Shores “fresh”

Grand Isle >6 months degradation

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Chrysene Detailed Distributions (m/z 256)

Inset shows the retention time range of the C2-CHRIs 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.
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.

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