Oil: What is it made of and how do we detect it in the environment

Ed Overton,
LSU Department of Environmental Sciences
Photosynthesis:

$$CO_2 + H_2O + \text{energy} = \{CH_2O\} + O_2$$

Reduction reactions create biomass and oxygen, stores energy in C-H bonds.

Elemental composition:

Plant biomass is mostly composed of three elements:

- 42%–47% of carbon (C),
- 40%–44% of oxygen (O), and
- 6% of hydrogen (H).

Biomass = 

- Lignin.
- Hemicellulose.
- Cellulose.
- Oils and fats.
Environmental Carbon Cycle

\[ \text{CO}_2 + \text{sun's energy} \rightarrow \{\text{CH}_2\text{O}\} \rightarrow \{\text{CH}_2, \text{CH}\} \]

<table>
<thead>
<tr>
<th>Carbon Dioxide</th>
<th>Plant biomass</th>
<th>Macondo Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 27%</td>
<td>C 42%–47%</td>
<td>C 86.6%</td>
</tr>
<tr>
<td>O 73%</td>
<td>O 40%–44%</td>
<td>H 12.6%</td>
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<tr>
<td></td>
<td>H 6%</td>
<td>N 0.38%</td>
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<tr>
<td></td>
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<td>S 0.39%</td>
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</tbody>
</table>
Hydrocarbon Structures in Oils

Alkyl Homologs of PAHs are the predominant aromatic species in oils
<4% aromatic content  
>90% Alkyl Homologs of PAHs (C1 to C4)  
Mostly Alkyl Naphthalenes and Phenanthrenes

EPA-Priority PAH

From Prof Trevor Penning
Non-Hydrocarbons Structures in Oil (NSO)

Figure 3. Chemical structures.
Typical Molecular Structures that make up all Crude Oils

- Saturates
- Low MW Aromatics
- High MW Aromatics & NSO compounds
- Resins
- Asphaltenes
- Porphyrins & metals
- NSO
- Metals

• Oil contains many thousands of compounds,
• All oils, regardless of source, contain the same molecular structures,
• It is the quantity of specific hydrocarbons that separates oils from different sources,
• It is the quantity of specific hydrocarbons that determines the oil’s physical and chemical properties
Macondo Well Petroleum

**Source Petroleum Fluid Composition**
- C1 to C10: ~87% (by Moles)
- C10 to C24: ~5% (by Moles)
- C25 & up: ~8% (by Moles)

**Liquid Source Oil Composition**
- C1 to C10: ~19% (by Mass)
- C10 to C24: ~27% (by Mass)
- C25 & up: ~5% (by Mass)

**Floating Oil Composition**
- C10 to C24: ~57% (by Mass)
- C25 & up: ~43% (by Mass)

**Legend**
- C1 to C4 HC: Natural gas
- C5 to C44+: Liquid oil

**C1-C10:** volatiles that readily loss to evaporation/dissolution

**C10 to C24:** liquid material that weathers in days to weeks

**C25 & up:** mostly solid material that weathers very slowly
Total Petroleum Hydrocarbon or TPH

Limited data ~0.1 $k

Much more definitive useful data ~1 $k

Analytical Steps

Extractions
Separations (GC, LC)
Mass Spect (Low & High Res)
UV-V, IR Spectrometry
Physical Properties (D, Vis, BP)

GC or GCMS and GCMSMS

Low & High Res Mass Spect
UV-V, IR Spectrometry
Physical Properties (D, Vis, BP)
1 to 40 Carbon Atoms

**GC-FID**
- Macondo Oil: FID
- Complex unresolved mixture (hump)

**GC-MS-FS**
- Macondo Oil: TIC
  - Resolvable compounds
  - Complex unresolved mixture (hump)

**GC-MS-SIM**
- Macondo Oil: TIC
  - Sensitivity
  - 30 meter DB-5 column
  - 2-4 ringed aromatics
1 to 40 Carbon Atoms

GCxGC-FID

GCxGC-MS

Reddy et al. 10.1073/pnas.1101242108
SARA
Saturates
Aromatics
Resins
Asphaltenes

Aeppli et al 2012
Ultra High Resolution Mass Spectrometry
electrospray ionization FT—ICR MS
Macondo Well Oil

Macondo Well Petroleum
Positive-ion APPI 9.4 T FT-ICR MS
28,721 peaks > 6σ Baseline RMS Noise

501.32 501.40

28,721 peaks

10 to ~100 Carbon Atoms