Gasoline in the groundwater

GEOL 304 - Hydrogeology
Erik Krogh
Applied Environmental Research Laboratories
Department of Chemistry, VIU
Outline

Chemical Composition
  complexity

Refining and Reforming
  additives

Physical Properties
  vapour pressure, water solubility

Environmental Fate and Distribution
  mobility, degradation, sorption
Chemical Composition

Major Hydrocarbon Components ($C_5 – C_{20}$)

Alkanes ($C_n H_{2n+2}$)
  e.g., hexane, isooctane

Alkenes & Cycloalkanes ($C_n H_{2n}$)
  e.g., isobutene, methylcyclohexane

Aromatics
  e.g., BTEX

PAHs
  e.g., naphthalene
Gas Chromatographic (GC) Separation
GC Analysis of Gasoline Vapours

1. Butane
2. 2-Methylbutane
3. Pentane
4. 2-Methylbutane
5. Hexane
6. Methylcyclopentane
7. Benzene
8. Methylcyclopentane
9. Toluene
10. Octane
11. Ethylbenzene
12. Xylene
13. Xylene
14. Xylene
15. Nonane
16. 1-Ethyl-2-methylbenzene
17. 1,2,4-Trimethylbenzene

Sample, dilution solvent and matrix modifier
Volatile analytes
GC Analysis of Gasoline (refined)
GC Analysis of Kerosene and Light Crude Oil
# Fuel Types

<table>
<thead>
<tr>
<th>Fuel Grade</th>
<th>#Carbons</th>
<th>BP Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>$C_4 - C_{12}$</td>
<td>0 – 225 ºC</td>
</tr>
<tr>
<td>Jet Fuel</td>
<td>$C_{12} - C_{18}$</td>
<td>150 – 320 ºC</td>
</tr>
<tr>
<td>Diesel Fuel</td>
<td>$C_{12} - C_{20}$</td>
<td>150 – 400 ºC</td>
</tr>
<tr>
<td>Lube Oil</td>
<td>$C_{20} - C_{40}$</td>
<td>350 – 500+ ºC</td>
</tr>
<tr>
<td>Crude Oil</td>
<td>$C_2 - C_{100+}$</td>
<td>0 – 700+ ºC</td>
</tr>
</tbody>
</table>
Fractional Distillation into Fuel Types

Refining & Reforming
Cracking, Isomerization
Fuel Additives
Crude Oils

Aliphatic Hydrocarbons

- Normal Alkanes (n-decane)
- Acyclic Isoprenoids (pristane)
- Bicyclic Sesquiterpanes (Eudesmane)
- Tricyclic Diterpanes (Abietane)
- Steranes (Cholestanate)
- (Hopane)
- Pentacyclic Triterpanes (Oleanane)

Aromatic Hydrocarbons

- Monoaromatics (toluene)
- Diaromatics (1,6-dimethylnaphthalene)
- Triaromatics (retene; 1-methyl-7-isopropylphenanthrene)
- Tetraaromatics (chrysene)
- 1,2-(3′-isopropyl)propane-methylchrysene
- Pentaaromatics (2,9-dimethylpicene)

Figure 1-3 Examples of aliphatic and aromatic hydrocarbons in crude oils.

Figure 1-4 Example of the disparate primary chemical fingerprinting features in crude oils from the North Slope of Alaska and the Niger Delta, Nigeria. (a–b) GC/FID chromatograms, (c–d) partial m/z 191 mass chromatograms, and (e–f) partial m/z 217 mass chromatograms. * = internal standards, left to right: o-terphenyl, 5α-androstanate and tetracosane-Δ5.
Gasoline Additives

Structures of some gasoline additives

**MTBE**  
(oxygenate)

**MMT**  
(organometallic)

**Ethanol**  
(oxygenate)
Fuel Type Markers

Pb / TEL: pre 1990 leaded gasoline and current Aviation Gasoline
Mn / MMT: 1970’s – 2004 gasoline
MTBE: late 1990’s gasoline
Sulphur content in gasoline vs diesel
Benzene content in gasoline
Ca, Ba, Mg, Zn, P, etc. in lube oils
Alternate Fuels

Ethanol
   e.g., typically E10

Fatty Acid Methyl Esters (FAMEs)
   e.g., biodiesel esters

GTL / Paraffinic diesel fuel (from CH$_4$)
Physical Properties – MPs & BPs

[Graph showing melting points and boiling points of hydrocarbons with labels for hexane, octane, and decane]
**Physical Properties – Vapour Pressure ($P^o$) & Water Solubility ($C_w$)**

Size matters – small hydrocarbons are more volatile (i.e., higher $P^o$)

Size matters – small hydrocarbons are more water soluble (i.e., higher $C_w$)

$\pi$’s matter – alkenes and aromatics are more water soluble (c.f. BTEX)
Environmental Fate & Distribution

Partition Constants

Air-Water ($K_{aw}$)

Octanol-Water ($K_{ow}$)

Sediment-Water ($K_{oc}$ or $K_d$)
## Physical Properties

<table>
<thead>
<tr>
<th>Compound</th>
<th>( P^o )</th>
<th>( C_w )</th>
<th>( K_{aw} )</th>
<th>( K_{ow} )</th>
<th>( K_{oc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylcyclohexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isooctane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Toluene</td>
<td></td>
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<td></td>
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<tr>
<td>Naphthalene</td>
<td></td>
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</tr>
</tbody>
</table>
Groundwater contamination by MTBE

[MTBE] < 20 ppb (taste/odour) health ? potential carcinogen not regulated (AWWA)

20% of the groundwater in areas where MTBE is used contaminated (USGS)

MTBE is highly water soluble low Kow, low sorbtivity to sediments
Non-Aqueous Phase Liquids (NAPL)

Light NAPLs – hydrocarbons, petroleum products
Dense NAPLs – chlorinated solvents
Attenuation and Transformations
Aerobic Microbial Degradation

**Alkane dioxygenase**

\[
\text{alkane} + O_2 \rightarrow \text{alkane} + \text{alkane hydroperoxide}
\]

**Naphthalene dioxygenase**

\[
\text{naphthalene} + 2e^- + 2H^+ + O_2 \rightarrow \text{naphthalene dihydrodiol}
\]

**Figure 11-2** Typical reactions catalyzed by hydrocarbon dioxygenases. The alkane dioxygenase of an *Acinetobacter* apparently converts alkanes to alkaneehdroperoxides (Maeng et al., 1996). Naphthalene dioxygenase of *Pseudomonas putida* oxidizes naphthalene to cis-naphthalene-1,2-dihydrodiol (Karlsson et al., 2003).
## Table 11-1: Comparison of Aerobic and Anaerobic Respiration Reactions

<table>
<thead>
<tr>
<th>e-Acceptor</th>
<th>Reaction (Toluene)</th>
<th>( \Delta G^\circ ), kJ/mol Toluene</th>
<th>Molar Ratio</th>
<th>Mass Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 )</td>
<td>( \text{C}_7\text{H}_8 + 9\text{O}_2 \rightarrow 7\text{CO}_2 + 4\text{H}_2\text{O} )</td>
<td>-3913</td>
<td>9</td>
<td>3.1</td>
</tr>
<tr>
<td>( \text{NO}_3^- )</td>
<td>( \text{C}_7\text{H}_8 + 7.2\text{NO}_3^- + 0.2\text{H}^+ \rightarrow 3.6\text{N}_2 + 7\text{HCO}_3^- + 0.6\text{H}_2\text{O} )</td>
<td>-3554</td>
<td>7.2</td>
<td>4.8</td>
</tr>
<tr>
<td>Mn(IV)</td>
<td>( \text{C}_7\text{H}_8 + 21\text{MnO}_2 + 14\text{H}^+ \rightarrow 7\text{MnCO}_3 + 14\text{MnO} + 7\text{H}_2\text{O} )</td>
<td>-3502</td>
<td>21</td>
<td>27</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>( \text{C}_7\text{H}_8 + 94\text{Fe(OH)}_3 \rightarrow 7\text{FeCO}_3 + 29\text{Fe}_3\text{O}_4 + 145\text{H}_2\text{O} )</td>
<td>-3398</td>
<td>94</td>
<td>109</td>
</tr>
<tr>
<td>( \text{SO}_4^{2-} )</td>
<td>( \text{C}_7\text{H}_8 + 4.5\text{SO}_4^{2-} + 3\text{H}_2\text{O} \rightarrow 7\text{HCO}_3^- + 2.5\text{H}^+ + 4.5\text{HS}^- )</td>
<td>-205</td>
<td>4.3</td>
<td>4.5</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) (( \text{CO}_2 ))</td>
<td>( \text{C}_7\text{H} + 7.5\text{H}_2\text{O} \rightarrow 2.5\text{HCO}_3^- + 2.5\text{H}^+ + 4.5\text{CH}_4 )</td>
<td>-131</td>
<td>7.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Complex Hydrocarbon Mixtures

Composition depends on source, refining (additives), ‘weathering’, degradation & mixing

Range of Physical-Chemical Properties

Migration & Attenuation depends on vapour pressure, water solubility, partitioning (i.e., $K_{aw}$, $K_{ow}$ and $K_d$)