Some effects of oil and dispersed oil on coastal ecosystems (grass, microbes, and animals)

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School of Renewable Natural Resources
Background info

• Crude oil
  • Tens of thousands of different chemicals in crude oil
    (McKenna A.M. et al. 2013. Environmental Science and Technology 47:7530-7539)
  • Chemists can measure the concentration of only about 150 of those chemicals even using oil “fingerprinting”
  • Oil spill dispersant: a mixture of chemicals designed to break up oil (make oil dissolve in water). Ex: COREXIT 9500
Why care about marsh grasses?

• **Photosynthesis:** source of all energy flowing into ecosystem

• **Aboveground parts:** Provides nesting, foraging and escape habitat for wildlife

• **Belowground parts:**
  • Provide soil strength, which slows erosions
  • Can contribute to vertical accretion, which allows coastal wetlands to survive subsidence and sea-level rise
Effects of oil on marsh grass

Rouseu Cane (*Phragmites australis*), May 2010, Pass A Loutre WMA
Dozens of published experiments describing effects of oil on wetland plants

- Oil on/in soil is more toxic than oil on plant stem/leaves
- Often 3 zones of contamination

Dozens of published experiments describing effects of oil on wetland plants

Why care about bacteria in marsh mud?

- Soil organic matter decomposition
  - supplies nutrients to plants (i.e., composting)
  - but also consumes peat (which helps offset subsidence and sea-level rise)
- Crude oil disappearance (biodegradation)
  - Reduces toxicity to plants, animals, and other microbes
Effects of oil on marsh mud

• Soil organic matter decomposition
  • microbial activity temporarily increased
  • Fertilizers, COREXIT 9500, 9550, and 9580 generally failed to reduce the increase

• Hydrocarbon disappearance
  • In fresh marsh soils, COREXIT 9550 & 9580 may have accelerated hydrocarbon disappearance
  • In saline marsh soils, COREXIT 9500 slowed disappearance

Why care about marsh animals?

• Ecologically important
• Economically important
• Recreationally important
• Emotionally important
• People probably affected by oil more like animals than like plants and microbes
Effects of oil on marsh animals

• Diesel was more toxic than crude oils
• Toxicity declined over time
• Toxicity of soil-water and flood-water were unrelated


Effects of oil on marsh animals

- When there were differences, dispersed oil was more toxic than oil or dispersant.
- Toxicity prolonged by dispersants.
  - Low salinity prolonged toxicity more than high salinity.
- Toxicity could not be predicted from hydrocarbon concentrations.


• Which chemical measurement of oil is the best?
  • I believe the best is the one that most closely matches the toxicity to animals.

• I trust toxicity data over chemical data; I trust GC/MS chemical fingerprinting over all other chemical tests commonly used.
**Surfactant:** a chemical that helps oil and water mix. Thousands currently on the market and used in oil spill dispersants, personal care products, food, medicine, herbicides, etc.

- **Antiquity:** animal fats and ash, plant oils and ash,
- **Late 1800s-now:** designed and made using organic chemistry
- **Late 1900s-now:** designed and brewed using designer microbes

**Examples:** Sodium Lauryl Sulfate (SLS), Dioctyl Sodium Sulfosuccinate (DOSS), Surfactin, Fa-Glu
<table>
<thead>
<tr>
<th>traditional organic chemistry</th>
<th>synthetic biology and green chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>building blocks</td>
<td>petroleum</td>
</tr>
<tr>
<td>technology of production</td>
<td>catalysts, pressure, heat, pH</td>
</tr>
<tr>
<td>technology of purification</td>
<td>traditional solvents, pressure, heat, pH</td>
</tr>
<tr>
<td></td>
<td>solvents produced from agriculture or fermentation, pH</td>
</tr>
</tbody>
</table>
The Collaborators

U.S. EPA

microbes and surfactants

modular

genetics

STATE

LSU AgCenter

Columbia University

$
Toxicity of surfactants to fish

- **petroleum-based surfactant:**
  - Sodium lauryl sulfate (SLS)
  - Dioctyl Sulfosuccinate Sodium (DOSS)

- **microbial-based surfactants:**
  - Surfactin (natural)
  - FA-Glu (designed)
DOSS is in COREXIT 9500A at 10% by weight


COREXIT® Ingredients

Several weeks ago, Nalco responded to US EPA requests by providing the agency with detailed formulation and ingredient information on our COREXIT® dispersants. We further agreed that this information could be shared with any other federal agency and with third party laboratories; EPA has been using for its Gulf monitoring and assessment program to allow them to monitor any potential for risks to the environment or public health.

The table below outlines the same ingredient list for our COREXIT dispersants as provided to the EPA.

<table>
<thead>
<tr>
<th>CAS #</th>
<th>Name</th>
<th>Common Day-to-Day Use Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1338-43-8</td>
<td>Sorbitan, mono-(9Z)-9-octadecenoate</td>
<td>Skin cream, body shampoo, emulsifier in juice</td>
</tr>
<tr>
<td>6005-65-6</td>
<td>Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.</td>
<td>Baby bath, mouth wash, face lotion, emulsifier in food</td>
</tr>
<tr>
<td>6005-70-3</td>
<td>Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs.</td>
<td>Body/Face lotion, tanning lotions</td>
</tr>
<tr>
<td>577-11-7</td>
<td>* Butanediolic acid, 2-sulfo-, 1,4-bis(2-ethylhexyloxy) oster, sodium salt (1:1)</td>
<td>Wetting agent in cosmetic products, gelatin, beverages</td>
</tr>
<tr>
<td>28911-20-2</td>
<td>Propanol, 1-(2-butoxy-1-methoxy)</td>
<td>Household cleaning products</td>
</tr>
<tr>
<td>04742-47-8</td>
<td>Disilllates (petroleum), hydrotreated light</td>
<td>Air freshener, cleaner</td>
</tr>
<tr>
<td>111-76-2</td>
<td>** Ethanol, 2-butoxy</td>
<td>Cleaners</td>
</tr>
</tbody>
</table>

** Ethanol, 2-butoxy is NOT included in the composition of COREXIT® 9500A. This solvent component has been removed from Dispersants since the spill began. Limited quantities of Ethanol, 2-butoxy are occasionally added to COREXIT 9500A to assist with Formulation of the dispersion. This solvent is not included in the ingredient list for COREXIT 9500A.
- Salinity altered toxicity of DOSS
- DOSS was less toxic at moderate salinity than at fresher and saltier salinities.

Since its creation in 1973, Dawn dishwashing liquid has been known for superior grease-fighting power. It’s so effective on dishes, pots and pans, that over the years, consumers have used Dawn on other greasy messes around their homes, from kitchen appliances to oily spots in the garage.

Animal rescuers have even discovered that it’s a great way to remove grease from animals in oil spill cleanups. As a result, Dawn has helped conservation organizations save thousands of animals for over 30 years.

Today, Dawn has grown into an international family of products that is dedicated to innovation and that answers consumers’ ever-changing needs.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>solvent</td>
</tr>
<tr>
<td>sodium lauryl sulfate</td>
<td>cleaning agent</td>
</tr>
<tr>
<td>sodium laureth sulfate</td>
<td>cleaning agent</td>
</tr>
<tr>
<td>alkyl dimethyl amine oxide</td>
<td>cleaning agent</td>
</tr>
<tr>
<td>SD alcohol</td>
<td>solvent</td>
</tr>
<tr>
<td>sodium chloride</td>
<td>process aid</td>
</tr>
<tr>
<td>PPG-26</td>
<td>viscosity control</td>
</tr>
<tr>
<td>PEI-14 PEG-10/PPG-7 copolymer</td>
<td>cleaning enhancer</td>
</tr>
<tr>
<td>cyclohexanediamine</td>
<td>solvent</td>
</tr>
<tr>
<td>magnesium chloride</td>
<td>suds enhancer</td>
</tr>
<tr>
<td>phenoxyethanol</td>
<td>process aid</td>
</tr>
<tr>
<td>methylisothiazolinone</td>
<td>preservative</td>
</tr>
<tr>
<td>fragrance</td>
<td>fragrance</td>
</tr>
<tr>
<td>FD&amp;C Blue 1</td>
<td>colorant</td>
</tr>
</tbody>
</table>
• Surfactin was most toxic, Fa-Glu was least toxic.
• Salty water made all more toxic, but Fa-Glu less so.

Fig. 4. Effect of salinity on the toxicity of surfactin, SLS, and FA-Glu. The concentration of each surfactant was set at 96 h-LC50, the amount required to kill 50% of the fish within 96 h, at a salinity of 12 parts per thousand (ppt). Control is without surfactant. Means and standard errors of the mean are presented for each treatment substance and control group.

Ongoing Research to Determine If Molecular Shape of Surfactant is Related to Toxicity

Reznik, GO; Vishwanath, P; Pynn, MA; et al. 2010, Appl. Microbiol. Biotech. 86, 1387
How toxic is the dispersant?

- COREXIT 9500 was less toxic than Dawn Dishwashing Detergent (product A).
- COREXIT 9500 was more toxic than Johnson’s Baby Shampoo (product F) and GreenWorks All Purpose Cleaner (product H).

Questions?

• If now, raise your hand

• If later, …
  
  • Chris: CGreen@lsuagcenter.lsu.edu
  
  • Andy: JNyman@lsu.edu
  
  • Facebook:
    
    https://www.facebook.com/toxicologistLSU
Table 4. Mean LC50 results from standard 96-h testing conducted with the fish, *Menidia beryllina*, and common household products.

<table>
<thead>
<tr>
<th>Product ID</th>
<th>Product</th>
<th>Mean LC50 (95%CI) (ppm)</th>
<th>EPA toxicity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Dawn</td>
<td>8.9 (7.05–10.4)</td>
<td>MT</td>
<td>Lab A (EE)</td>
</tr>
<tr>
<td></td>
<td>Dish Soap</td>
<td>8.3 (0.0–13.4)</td>
<td>MT</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td>B</td>
<td>Restore the Earth</td>
<td>26.9 (24.4–29.8)</td>
<td>MT</td>
<td>Lab A (EE)</td>
</tr>
<tr>
<td></td>
<td>Dish Soap</td>
<td>21.2 (19.9–22.5)</td>
<td>MT</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td>C</td>
<td>Palmolive</td>
<td>7.1 (5.53–8.26)</td>
<td>MT</td>
<td>Lab A (EE)</td>
</tr>
<tr>
<td></td>
<td>Dish Soap</td>
<td>5.4 (2.5–6.5)</td>
<td>MT</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td>D</td>
<td>Green Works Dish</td>
<td>7.8 (6.8–9.0)</td>
<td>MT</td>
<td>Lab A (EE)</td>
</tr>
<tr>
<td></td>
<td>Soap</td>
<td>9.0 (8.0–11.2)</td>
<td>MT</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td>E</td>
<td>Cascade</td>
<td>56.6 (42.7–65.7)</td>
<td>MT</td>
<td>Lab A (EE)</td>
</tr>
<tr>
<td></td>
<td>Dish Detergent</td>
<td>55.6 (52.6–57.0)</td>
<td>MT</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td>F</td>
<td>Johnson’s</td>
<td>38.8 (28.2–53.3)</td>
<td>MT</td>
<td>Lab A (EE)</td>
</tr>
<tr>
<td></td>
<td>Baby Shampoo</td>
<td>42.0 (40.4–43.5)</td>
<td>MT</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td>G</td>
<td>Tide</td>
<td>4.0 (3.15–4.58)</td>
<td>MT</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td></td>
<td>Laundry Detergent</td>
<td>11.8 (11.3–12.1)</td>
<td>MT</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td>H</td>
<td>Green Works</td>
<td>386 (365–409)</td>
<td>MT</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td></td>
<td>Corexit Dispersant</td>
<td>421 (342–491)</td>
<td>MT</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td>9500-A</td>
<td>CRXVS60132</td>
<td>105 (87.0–112.0)</td>
<td>ST</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td>9500-B</td>
<td>Corexit Dispersant</td>
<td>35.4 (12.6–40.6)</td>
<td>ST</td>
<td>Lab B (SM)</td>
</tr>
<tr>
<td></td>
<td>20100619-CRXU087</td>
<td>110 (106.7–112.7)</td>
<td>ST</td>
<td>Lab B (SM)</td>
</tr>
</tbody>
</table>

MT = Moderately toxic; ST = slightly toxic; PNT = practically non toxic.

Figure 1. Results from toxicity tests with common household products and Corexit® 9500 conducted in parallel by two independent laboratories. (USEPA and NCP test results added for reference [Hemmer et al. 2010; USEPA NCP b, respectively].)

References to some peer-reviewed studies...


