Tier II Results for Multimedia Risk Assessment of Biodiesel: Relative Mobility, Biodegradation, and Aquatic Toxicity

8 December 2010 MMRA Workshop

TR Ginn¹, ML Johnson², KM Scow³, J Miller⁴, L Rastegarzadeh¹, T Hatch¹, A Epple¹, V Nino¹, T Schetrit¹, T Barkouki¹, D Rice⁵, T McKone⁶

¹ UC Davis Civil & Environmental Engineering
² UC Davis Aquatic Ecosystems Analysis Laboratory
³ UC Davis Department of Land, Air, and Water Resources
⁴ Aquascience Inc., Davis CA
⁵ Consultant to UC
⁶ UC Berkeley, Environmental Health Sciences
Multimedia Risk Assessment

Tier 1
Tier II
Tier III

Tier 1
Preliminary Review
- Define framework and approach
- Identify information needs and gaps
- Peer review

Tier 2 Multimedia Risk Assessment
Design Review
- Experimental design developed and submitted
- Design peer reviewed, feedback provided for Tier 3

Tier 3
Final Multimedia Risk Review
- Final report is used as the basis for recommendations submitted to the Environmental Policy Council
- Final report is peer reviewed
Multimedia Risk Assessment

Tier 1

Tier II

Tier III

Tier 1
Preliminary Review

- Define framework and approach
- Identify information needs and gaps
- Peer review

Tier 2 Multimedia Risk Assessment
Design Review

- Experimental design developed and submitted
- Design peer reviewed, feedback provided for Tier 3

Tier 3

- Final report is used as the basis for recommendations submitted to the Environmental Policy Council
- Final report is peer reviewed

1 http://www.arb.ca.gov/fuels/multimedia/multimedia.htm
2 http://www.arb.ca.gov/fuels/diesel/altdiesel/biodiesel.htm
Multimedia Risk Assessment\textsuperscript{1}
Tier II\textsuperscript{2}
Experiments Performed

\begin{itemize}
  \item Mobility
    \begin{itemize}
      \item Side-by-side infiltration in 2D “ant farm” flow cells
    \end{itemize}
  \item Biodegradation Tests
    \begin{itemize}
      \item Microcosm respirometry in soil slurry, 29 day
    \end{itemize}
  \item Aquatic Toxicity
    \begin{itemize}
      \item Suite of freshwater/estuarine toxicity tests
    \end{itemize}
\end{itemize}

\textsuperscript{1} http://www.arb.ca.gov/fuels/multimedia/multimedia.htm
\textsuperscript{2} http://www.arb.ca.gov/fuels/diesel/altdiesel/biodiesel.htm
## Mobility

### Fuel Blends

**Sandbox Experimental Matrix**

<table>
<thead>
<tr>
<th>Type</th>
<th>Feedstock</th>
<th>Totals</th>
<th>Additization</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>None</td>
<td>Bioextend</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td># Quantity</td>
<td># Quantity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B100</td>
<td>Animal-fat</td>
<td>6</td>
<td>3</td>
<td>50 mL/test</td>
<td>3</td>
<td>50 mL/test</td>
</tr>
<tr>
<td>B100</td>
<td>Soy</td>
<td>3</td>
<td></td>
<td></td>
<td>3</td>
<td>50 mL/test</td>
</tr>
<tr>
<td>B20</td>
<td>Animal-fat</td>
<td>3</td>
<td></td>
<td></td>
<td>3</td>
<td>50 mL/test</td>
</tr>
<tr>
<td>B20</td>
<td>Soy</td>
<td>3</td>
<td></td>
<td></td>
<td>3</td>
<td>50 mL/test</td>
</tr>
<tr>
<td>ULSD</td>
<td>petroleum</td>
<td>15</td>
<td>15</td>
<td>50 mL/test</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Note:** Experiments involve include side by side comparison between ULSD and Biodiesel within the same sandbox for consistency of sand compaction.
Mobility

- Image analysis of biodiesel vertical infiltration in Sandbox
- 30x20x2cm, #20 (coarse) sand, water table
- Soy- and Animalfat-based 100% and 20% blends, 1 additive

- Sandbox preparation
  - Wet-pluviated sand
  - Drain to water table
  - simultaneous 50mL ULSD#2 and biodiesel side-by-side, both dyed

- Data collected
  - infiltration rate in vadose zone
  - redistribution
  - lens form & surface area, on water table
Sample Results
Final Lenses

• Soy B20 least different
Sample Results
Final Lenses

- **Animalfat B100**
  - strongest effect
  - similar traveltimes
  - Less lateral dispersion
  - thicker, deeper lens
  - more residual, less sfc area
Mobility

Summary

• Minor differences in travel times
• AF B100a only shows Moderate differences
  - thicker lens formation
  - more residual
Mobility

Summary

• Minor differences in travel times

• AF B100a only shows Moderate differences
  - thicker lens formation
  - more residual

• Interfacial Tensions\(^1\) (mN/m):
  ULSD:  7.4
  Soy (B20/B100):  8.5/12.0
  AF (B20/B100):  15.0/19.5

• Viscosity\(^1\)

Biodegradation Tests

- 29-day Respirometry using soil slurry inoculum
  - Soy- and Animalfat-based 100% and 20% blends, 2 additives
- Microcosm preparation
  - 250 mL flask that consists of 200 ml mineral medium
  - 2 g soil (Yolo silt loam) as bacterial inoculums
  - 5uL of test substrate
- For each fuel type:
  - triplicate batch
  - one sterilize control (1% sodium azide) - showed no CO2.
# Biodegradation Tests

## Fuel Blends

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
<th>Fuel Type</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diesel</td>
<td>ULSD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soy biodiesel 20% blend + bioextend</td>
<td>Soy B-20 A</td>
<td></td>
</tr>
<tr>
<td>#1</td>
<td>Animal fat biodiesel 20% blend + bioextend</td>
<td>AF B-20 A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soy biodiesel 20% blend - no additives</td>
<td>Soy B-20</td>
<td></td>
</tr>
<tr>
<td>#2</td>
<td>Diesel</td>
<td>ULSD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soy biodiesel 100% - no additives</td>
<td>Soy B-100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Animal fat biodiesel 20% blend - no additives</td>
<td>AF B-20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Animal fat biodiesel 100% - no additives</td>
<td>AF B-100</td>
<td></td>
</tr>
<tr>
<td>#3</td>
<td>Diesel</td>
<td>ULSD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soy biodiesel 20% blend + bioextend + biocide</td>
<td>Soy B-20 AA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Animal fat biodiesel 20% blend + bioextend + biocide</td>
<td>AF B-20 AA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soy biodiesel 100% + bioextend + biocide</td>
<td>Soy B-100 AA</td>
<td></td>
</tr>
<tr>
<td>#4</td>
<td>Diesel</td>
<td>ULSD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Animal fat biodiesel 100% + bioextend + biocide</td>
<td>AF B-100 A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Animal fat biodiesel 100% + bioextend</td>
<td>AF B-100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Soy biodiesel 100% + bioextend</td>
<td>Soy B-100</td>
<td></td>
</tr>
</tbody>
</table>
Biodegradation Tests

Results
Biodegradation Tests

29Day Cumulative degradation percentages

![Bar chart showing cumulative degradation percentages for different blends of ULSD and biodiesel over three runs.](chart.png)
Biodegradation Tests

Summary

- All fuel blends more readily degradable than ref. fuel
- Soy-based blends somewhat more degradable than Animalfat-based blends
- 20% biodiesel blends somewhat more degradable than 100% biodiesel
- Additives effect are minor
Aquatic Chronic Toxicity Tests

- 6 fuel blends
- 3 freshwater and 3 estuarine organisms
- 6 dilutions plus a control per species/fuel
- Using published USEPA chronic toxicity testing protocols
- “100% solutions” produced using the “slow stir” method, defining equilibrium solubility conditions
- All tests met protocol QA/QC requirements
Aquatic Chronic Toxicity Tests

Details

6 Blends in addition to reference fuel (ULSD)
- Animalfat biodiesel (100% 20%, 20% w/additive)
- Soy biodiesel (100% 20% 20% w/additive)

100% solubility solution by slow stir method
- solutions 100%, 50%, 25%, 10%, 5%, and 1%, w/stock
# 2 samples/test archived frozen for later analysis
# Replicates for particular combinations.

Interpolate among dilutions to determine EC$_{25}$
- “Toxicity” as TU = 100/EC$_{25}$
# TU<1 no effects
# TU = 1 effects seen only at 100% solution
# TU = 100 effects seen at 1% solution
## Aquatic Chronic Toxicity Tests

### Fuel Blends

<table>
<thead>
<tr>
<th><strong>Fuel Type</strong>&lt;sup&gt;a&lt;/sup&gt;</th>
<th><strong>Code</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Ultra-Low Sulfur Diesel</td>
<td>ULSD</td>
</tr>
<tr>
<td>100% Soy Biodiesel</td>
<td>Soy B-100</td>
</tr>
<tr>
<td>20% Soy Biodiesel + 80% ULSD (w/w)</td>
<td>Soy B-20</td>
</tr>
<tr>
<td>20% Soy + 80% ULSD (w/w) amended with additive&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Soy B-20A</td>
</tr>
<tr>
<td>100% Animal Fat Biodiesel</td>
<td>AF B-100</td>
</tr>
<tr>
<td>20% Animal Fat Biodiesel + 80% ULSD (w/w)</td>
<td>AF B-20</td>
</tr>
<tr>
<td>20% Animal Fat + 80% ULSD (w/w) amended with additive</td>
<td>AF B-20A</td>
</tr>
</tbody>
</table>
## Aquatic Chronic Toxicity Tests

### Test Species

<table>
<thead>
<tr>
<th>Category</th>
<th>Test Species</th>
<th>Test Type</th>
<th>Test Endpoints</th>
<th>Replicates</th>
<th>Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater</td>
<td>Green algae (S. capricornutum)</td>
<td>96-hour static</td>
<td>Cell growth</td>
<td>10,000 cells/rep</td>
<td>25 ± 1 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4 reps/conc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water flea (C. dubia)</td>
<td>7-day daily renewal</td>
<td>Survival Reproduction</td>
<td>1 flea/rep</td>
<td>25 ± 1 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 reps/conc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fathead minnow (P. promelas)</td>
<td>7-day daily renewal</td>
<td>Survival Growth</td>
<td>10 fish/rep</td>
<td>25 ± 1 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4 reps/conc</td>
<td></td>
</tr>
<tr>
<td>Estuarine/Marine</td>
<td>Red abalone (H. rufescens)</td>
<td>48-hour static</td>
<td>Normal shell development</td>
<td>5 reps/conc</td>
<td>15 ± 1 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2000 embryos/rep</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mysid shrimp (M. bahia)</td>
<td>7-day daily renewal</td>
<td>Survival Growth Fecundity</td>
<td>5 fish/rep</td>
<td>25 ± 1 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8 reps/conc</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Topsmelt (A. affinis)</td>
<td>7-day daily renewal</td>
<td>Survival Growth</td>
<td>5 fish/rep</td>
<td>20 ± 1 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5 reps/conc</td>
<td></td>
</tr>
</tbody>
</table>
Aquatic Chronic Toxicity Tests

Results

- ULSD - low but detectable toxicity on mysid growth (1.0 TU) and *Ceriodaphnia* reproduction (1.8 TUc) only.

- No unadditized Animalfat or Soy Biodiesel blends produced detectable toxicity to the mysid, topsmelt or fathead minnow.

- Animal Fat and Soy B-100 and B-20 mixtures caused toxicity to algae cell growth, abalone shell development, and *Ceriodaphnia* survival and/or growth.

- Except for algae, the additized Biodiesel B-20 test materials were substantially more toxic than the corresponding unadditized material.
Aquatic Chronic Toxicity Tests

Examples

Red Abalone (*Haliotis Rufecens*) shell development
Aquatic Chronic Toxicity Tests

Examples

Water flea (*Ceriodaphnia dubia*) survival and reproduction
Aquatic Chronic Toxicity Tests

Summary Toxicity with additive

Toxicity apparent in all 6 species per growth endpoint
Aquatic Chronic Toxicity Tests

Summary

• Biodiesel blends are significantly more toxic than CARB ULSD#2
  - algae cell growth
  - abalone shell development
  - *Ceriodaphnia* survival and growth

• Biodiesel 20% blends with antioxidant additive were substantially more toxic than the corresponding unadditized blend
  - abalone shell development
  - *Ceriodaphnia* survival and growth
Tier II for Biodiesel Blends Tested

Summary

- **Mobility**
  - AFB100a shows thicker lens, more residual
  - due to higher viscosity, IFT

- **Biodegradation**
  - All biodiesel blends more readily degradable than ULSD
  - Soy-based blends, or 20%, somewhat more degradable
  - Additives effect are minor

- **Aquatic Toxicity**
  - Biodiesel blends are more toxic than ULSD#2
  - Biodiesel 20% blends with antioxidant additive are more toxic than the corresponding unadditized blend
Tier II for Biodiesel Blends Tested

Summary

• Mobility
  - AFB100a only shows smaller lens, more residual

• Biodegradation
  - All biodiesel blends more readily degradable than ULSD
  - Soy-based blends, or 20% s, somewhat more degradable
  - Additives effect are minor

• Aquatic Toxicity
  - Biodiesel blends are more toxic than ULSD#2
  - Biodiesel 20% blends with antioxidant additive are more toxic than the corresponding unaddititized blend