# Tier II Results forMultimedia Risk Assessment of Biodiesel: Relative Mobility, Biodegradation, and Aquatic Toxicity

## 8 December 2010 MMRA Workshop

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## 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**

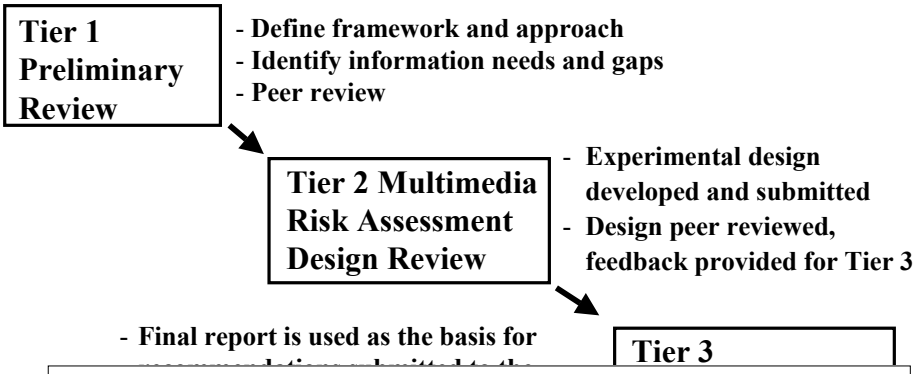
- **Final report is used as the basis for recommendations submitted to the Environmental Policy Council**
- **Final report is peer reviewed**

## Multimedia Risk Assessment[1]

Tier 1

**Tier II**[2]

Tier III




[1] http://www.arb.ca.gov/fuels/multimedia/multimedia.htm
[2] http://www.arb.ca.gov/fuels/diesel/altdiesel/biodiesel.htm

## Multimedia Risk Assessment[1]
## Tier II[2]
## Experiments Performed

- Mobility
  - Side-by-side infiltration in 2D "ant farm" flow cells
- Biodegradation Tests
  - Microcosm respirometry in soil slurry, 29 day
- Aquatic Toxicity
  - Suite of freshwater/estuarine toxicity tests

[1] http://www.arb.ca.gov/fuels/multimedia/multimedia.htm
[2] http://www.arb.ca.gov/fuels/diesel/altdiesel/biodiesel.htm

# Mobility

## Fuel Blends

Sandbox Experimental Matrix

| Type | Feedstock | Totals | Additization | | | |
|---|---|---|---|---|---|---|
| | | | None | | Bioextend | |
| | | | # | Quantity | # | Quantity |
| B100 | Animal-fat | 6 | 3 | 50 mL/test | 3 | 50 mL/test |
| B100 | Soy | 3 | | | 3 | 50 mL/test |
| B20 | Animal-fat | 3 | | | 3 | 50 mL/test |
| B20 | Soy | 3 | | | 3 | 50 mL/test |
| ULSD | petroleum | 15 | 15 | 50 mL/test | | |

**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

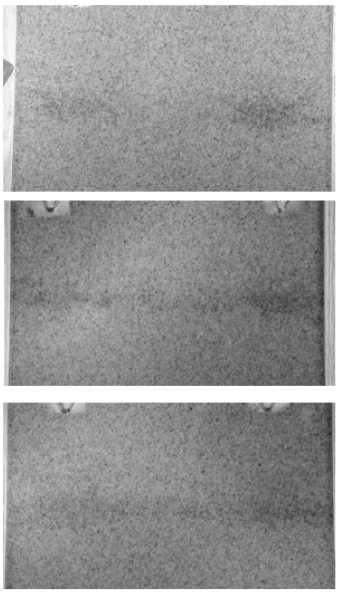
- Sandbox preparation
  - Wet-pluviated sand
  - Drain to water table
  - simultaneous 50mL ULSD#2 and biodiesel side-by-side, both dyed

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

## Mobility

**Sample Results**
**Final Lenses**

Soy B20a CARB ULSD#2

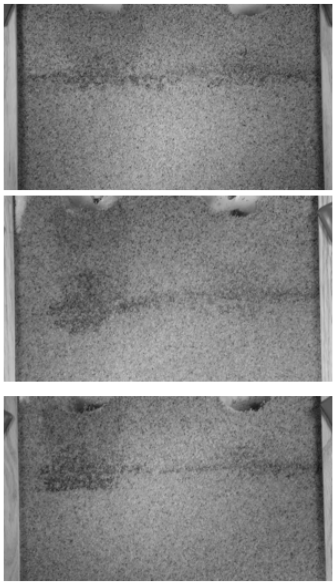


- Soy B20 least different

## Mobility

**Sample Results**
**Final Lenses**

AF B100a CARB ULSD#2



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

## Mobility

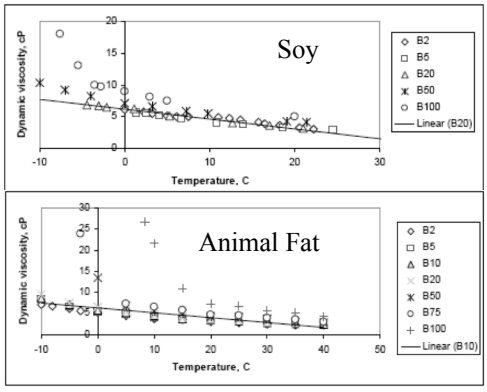
**Summary**

- Minor differences in traveltimes
- AF B100a only shows Moderate differences
  - thicker lens formation
  - more residual

## Mobility

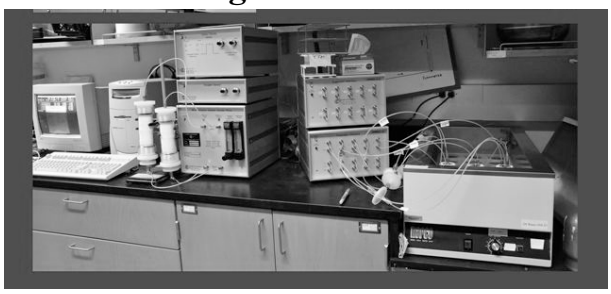
**Summary**

- Minor differences in traveltimes
- 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]




1.Yang et al., ULSD/Biodiesel blend and its effect on fuel/ water separation, Amer. Filtration & Separation Soc. Annual Conf., May 19-22 (2008), Valley Forge, PA

## 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 $CO_2$.

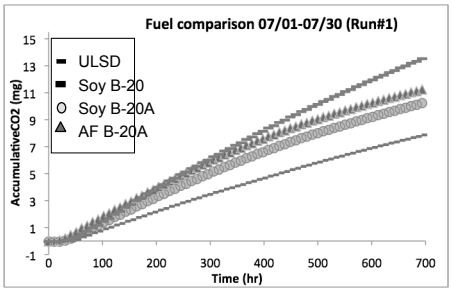
## Biodegradation Tests

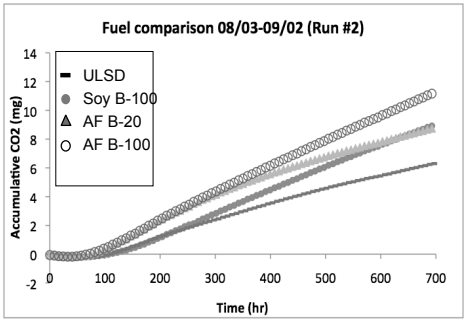
### Fuel Blends

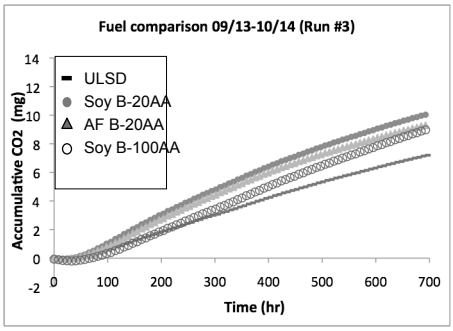
| Experiment | Fuel Type | |
|---|---|---|
| | Description | Abbreviation |
| #1 | Diesel | ULSD |
| | Soy biodiesel 20% blend + bioextend | Soy B-20 A |
| | Animal fat biodiesel 20% blend + bioextend | AF B-20 A |
| | Soy biodiesel 20% blend -no additives | Soy B-20 |
| #2 | Diesel | ULSD |
| | Soy biodiesel 100% - no additives | Soy B-100 |
| | Animal fat biodiesel 20% blend - no additives | AF B-20 |
| | Animal fat biodiesel 100% - no additives | AF B-100 |
| #3 | Diesel | ULSD |
| | Soy biodiesel 20% blend + bioextend + biocide | Soy B-20 AA |
| | Animal fat biodiesel 20% blend + bioextend + biocide | AF B-20 AA |
| | Soy biodiesel 100% + bioextend + biocide | Soy B-100 AA |
| #4 | Diesel | ULSD |
| | Animal fat biodiesel 100% + bioextend + biocide | AF B-100 A A |
| | Animal fat biodiesel 100% + bioextend | AF B-100 |
| | Soy biodiesel 100% + bioextend | Soy B-100 |

# Biodegradation Tests

## Results

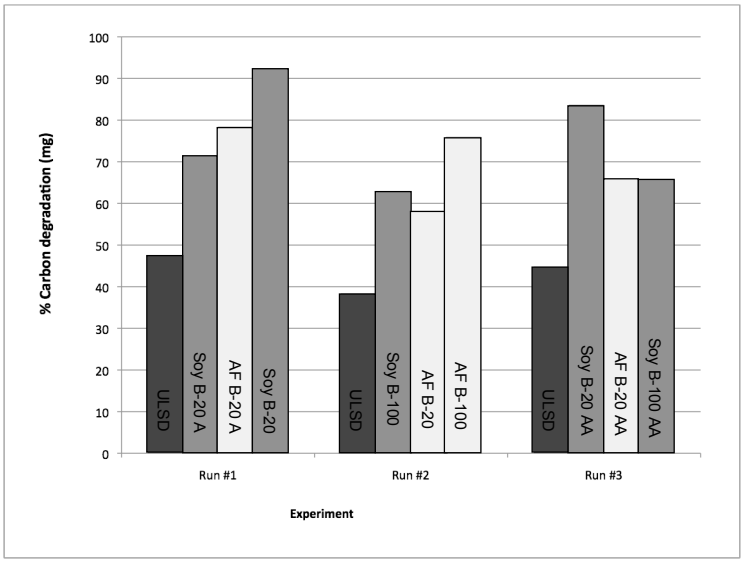



# Biodegradation Tests

## 29Day Cumulative degradation percentages

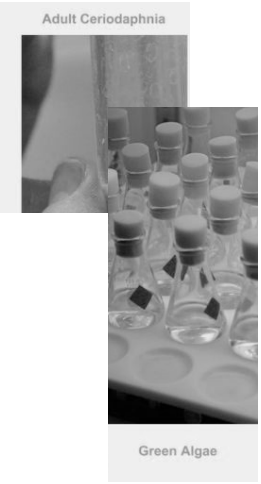


## Biodegradation Tests

**Summary**

- All fuel blends more readily degrable than ref. fuel
- Soy-based blends somewhat more degrable than Animalfat-based blends
- 20% biodiesel blends somewhat more degrable 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

| *Fuel Type*[a] | *Code* |
|---|---|
| 100% Ultra-Low Sulfur Diesel | ULSD |
| 100% Soy Biodiesel | Soy B-100 |
| 20% Soy Biodiesel + 80% ULSD (w/w) | Soy B-20 |
| 20% Soy + 80% ULSD (w/w) amended with additive[b] | Soy B-20A |
| 100% Animal Fat Biodiesel | AF B-100 |
| 20% Animal Fat Biodiesel + 80% ULSD (w/w) | AF B-20 |
| 20% Animal Fat + 80% ULSD (w/w) amended with additive | AF B-20A |

## Aquatic Chronic Toxicity Tests

### Test Species

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

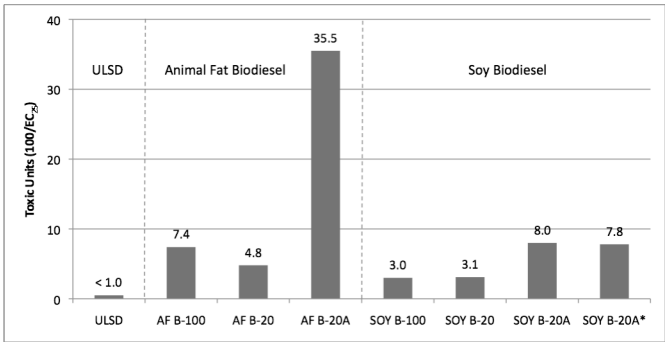
## Aquatic Chronic Toxicity Tests

### 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

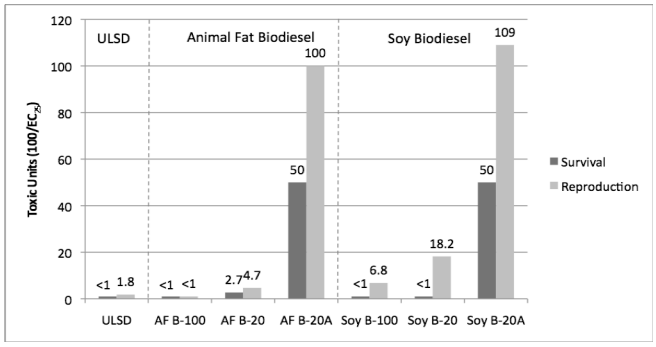
**Examples**




Red Abalone (*Haliotis Rufecens*) shell development

## Aquatic Chronic Toxicity Tests

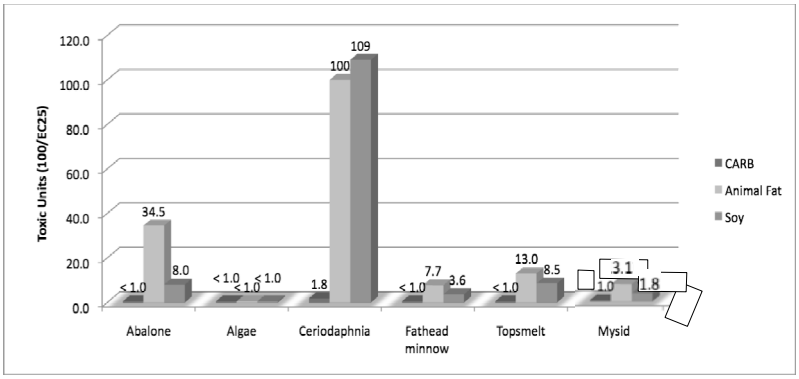
**Examples**




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 degrable than ULSD
  - Soy-based blends, or 20%s, somewhat more degrable
  - 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 degrable than ULSD
  - Soy-based blends, or 20%s, somewhat more degrable
  - 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