

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



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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

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

**Tier 3 Final Multimedia Risk Review**

## Multimedia Risk Assessment<sup>1</sup>

Tier 1

**Tier II<sup>2</sup>**

Tier III

**Tier 1  
Preliminary  
Review**

- Define framework and approach
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**Tier 2 Multimedia  
Risk Assessment  
Design Review**

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

- Final report is used as the basis for

**Tier 3**

<sup>1</sup> <http://www.arb.ca.gov/fuels/multimedia/multimedia.htm>

<sup>2</sup> <http://www.arb.ca.gov/fuels/diesel/altdiesel/biodiesel.htm>

## Multimedia Risk Assessment<sup>1</sup>

**Tier II<sup>2</sup>**

### 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

<sup>1</sup> <http://www.arb.ca.gov/fuels/multimedia/multimedia.htm>

<sup>2</sup> <http://www.arb.ca.gov/fuels/diesel/altdiesel/biodiesel.htm>

## Mobility

### Fuel Blends

Sandbox Experimental Matrix

Type	Feedstock	Totals	Additization			
			#	None Quantity	#	Bioextend 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

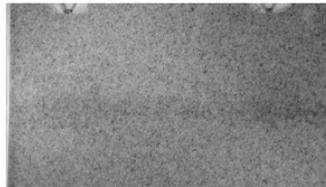
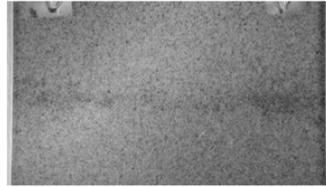
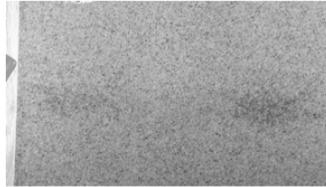


## Mobility

Soy B20a CARB ULSD#2

### Sample Results Final Lenses

- Soy B20 least different

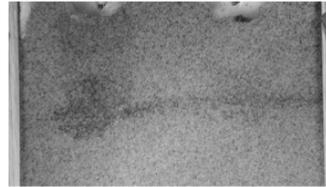
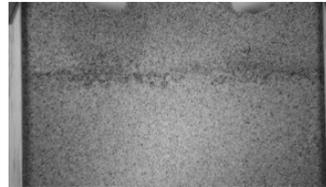


## Mobility

AF B100a CARB ULSD#2

### Sample Results Final Lenses

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



## Mobility

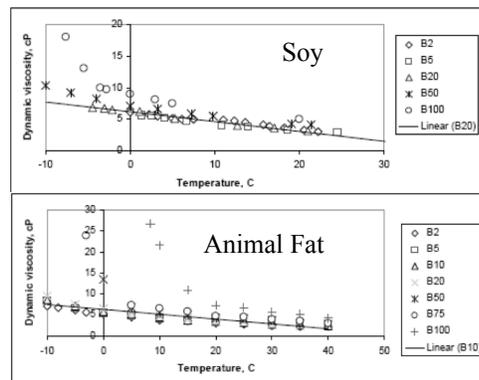
### Summary

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

## Mobility

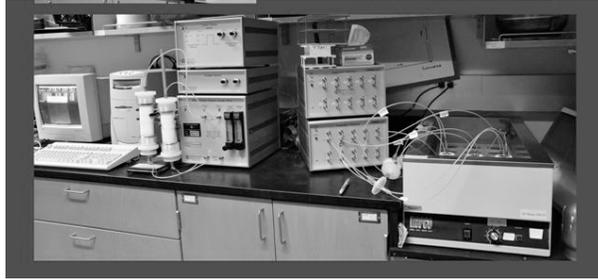
### Summary

- Minor differences in traveltimes
- AF B100a only shows Moderate differences
  - thicker lens formation
  - more residual
- Interfacial Tensions<sup>1</sup> (mN/m):
  - ULSD: 7.4
  - Soy (B20/B100): 8.5/12.0
  - AF (B20/B100): 15.0/19.5
- Viscosity<sup>1</sup>



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<sub>2</sub>.

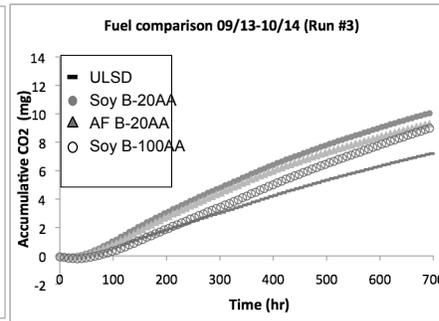
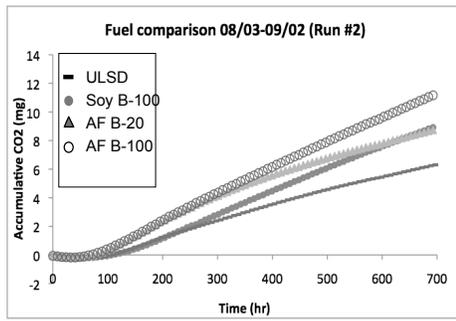
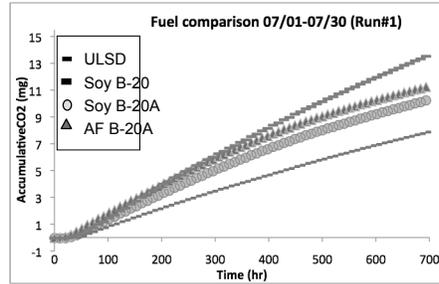
## Biodegradation Tests

### Fuel Blends

Experiment	Description	Fuel Type	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
	Animal fat biodiesel 100% + bioextend		A
	Soy biodiesel 100% + bioextend		AF B-100

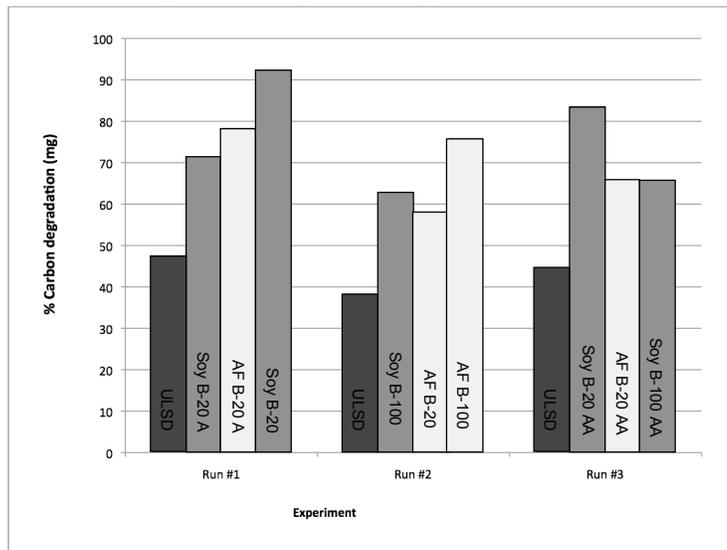
## Biodegradation Tests

### Results



## Biodegradation Tests

### 29Day Cumulative degradation percentages

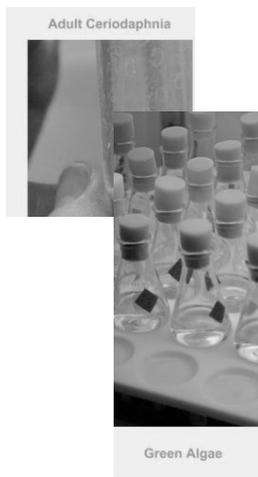


## Biodegradation Tests

### 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

<i>Fuel Type</i> <sup>2</sup>	<i>Code</i>
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 <sup>3</sup>	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 ( <i>S. capricornutum</i> )	96-hour static	Cell growth	10,000 cells/rep 4 reps/conc	25 ± 1 °C
	Water flea ( <i>C. dubia</i> )	7-day daily renewal	Survival Reproduction	1 flea/rep 10 reps/conc	25 ± 1 °C
	Fathead minnow ( <i>P. promelas</i> )	7-day daily renewal	Survival Growth	10 fish/rep 4 reps/conc	25 ± 1 °C
Estuarine/ Marine	Red abalone ( <i>H. rufescens</i> )	48-hour static	Normal shell development	5 reps/conc 2000 embryos/rep	15 ± 1 °C
	Mysid shrimp ( <i>M. bahia</i> )	7-day daily renewal	Survival Growth Fecundity	5 fish/rep 8 reps/conc	25 ± 1 °C
	Topsmelt ( <i>A. affinis</i> )	7-day daily renewal	Survival Growth	5 fish/rep 5 reps/conc	20 ± 1 °C

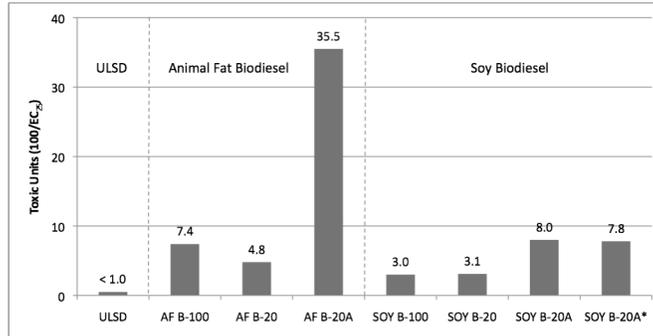
## Aquatic Chronic Toxicity Tests

### 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

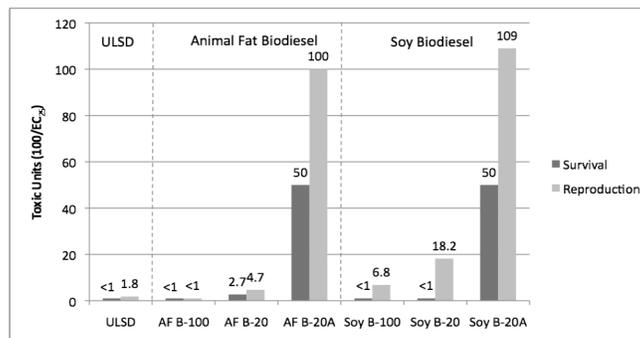
### Examples



Red Abalone (*Haliotis Rufecens*) shell development

## Aquatic Chronic Toxicity Tests

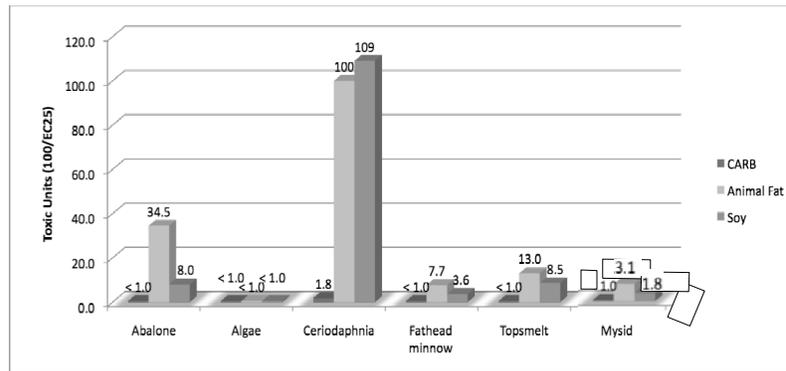
### Examples



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 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 unadditized blend

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  - **Biodiesel blends are more toxic than ULSD#2**
  - Biodiesel 20% blends with antioxidant additive are more toxic than the corresponding unadditized blend