# Biodiesel and Renewable Diesel Workgroup

# California Biodiesel Multimedia Revised Tier II Report

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UCDAVIS
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# Tiered Approach Refresher

**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

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# Conclusions About Key Information Gaps

- **Additives composition, use, and impact**
  - **How biocides and anti-oxidants impact biodegradation**
  - **How priority additive impact human and ecosystem health**
  - **How cold flow property controllers impact multiphase transport, etc.**
  - ***toxicity***
- **Subsurface fate and transport properties**
- **Releases - Material Compatibility**
- **Biodegradation of all biodiesel components in soils and aquifers**
- **More information on air emissions**
- **Missing toxicological data**

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  - How cold flow property controllers impact multiphase transport, etc.
  - *toxicity*
- **Subsurface fate and transport** properties
- Releases - **Material Compatibility**
- **Biodegradation** of all biodiesel components in soils and aquifers
- More information on **air emissions**
- Missing **toxicological** data

- **biocides and anti-oxidants**
  - cold flow, cetane booster, NOx reducer…

- **Subsurface fate and transport**
- **Material Compatibility**
- **Biodegradation**

- **Air emissions**
- **Toxicological**

# Overview of the Biodiesel Tier II Plan

- **>Solubility of components<**
- **biocides and anti-oxidants**
  - cold flow, cetane booster, NOx reducer… >solubility<

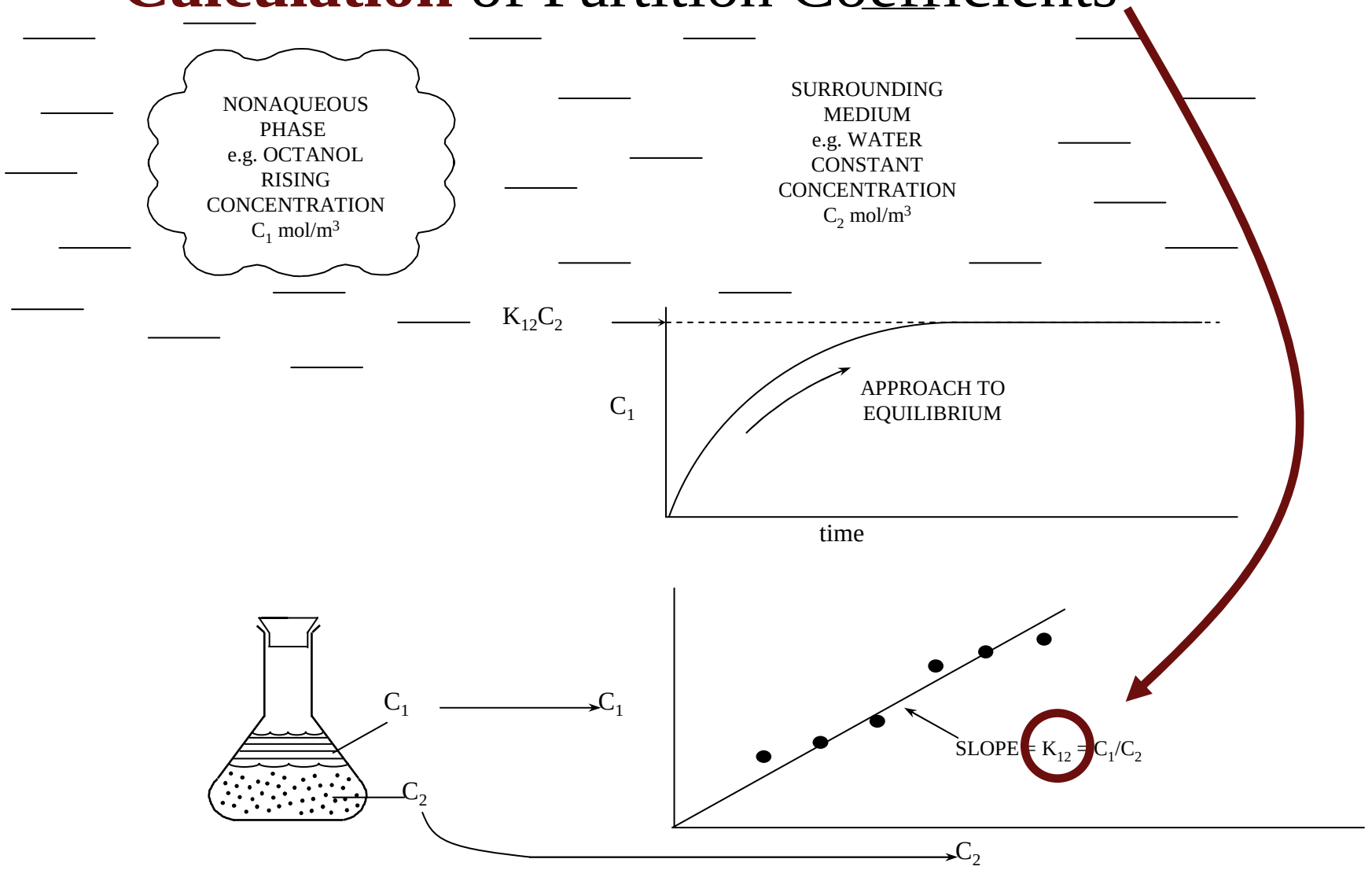
- **Subsurface fate and transport**
- **Material Compatibility**
- **Biodegradation**

- **Air emissions**
- **Toxicological**

**Relative to ULSD**

# Experimental Determination (coming)

## **Calculation** of Partition Coefficients



# Solubility Calculations

- **Assumptions:**
  - **Raoult's law**
    - **Solubility proportional to mole fractions in biodiesel**
  - **Assume activities =1**
    - **(conservatively assumed based on knowing that the greatest partitioning of oil into the water phase will be achieved through this assumption).**
  - **FAMES and additives partition according to Raoult's Law**
  - **Raoult's law implies the absence of cosolvency effects.**
    - **(This may not be a conservative assumption when additives are involved, some of which are completely soluble in water and may affect solubility of other components of biodiesel)**

# Solubility Calculations

**Biodiesel-water Partition Coefficient, $K_o$ for kth component from Raoult's law**

$$K_o = \frac{\omega_k \sum_{j=1}^{N} \frac{c_{oj}}{\omega_{oj}}}{S_k \gamma_k}$$

**Where, per kth component:**

- **$\omega_o$= the molecular weight (g/mol)**
- **$c_o$ = component concentration in biodiesel (g/L)**
- **S = the solubility of the component in water (g/L)**
- **$\gamma$ = the activity coefficient of the component (assumed to be 1)**
- **component = FAME or additive compound.**

**…Will Compare with GC-MS**

# Experimental Plan Summaries

**Subsurface Fate & Transport**

- Ant Farm

**Material Compatibility**

- Immersion batch

**Biodegradation**

- Multi-batch respirometry

**Aquatic Toxicity**

- 6 species marine & freshwater

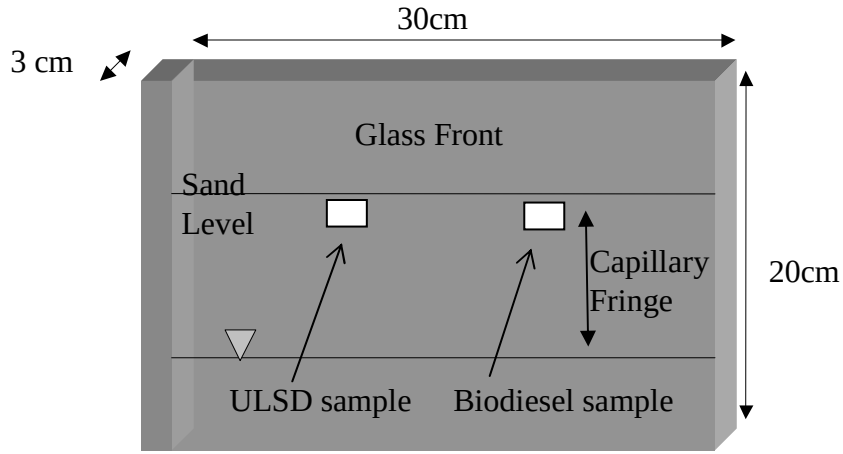
# Subsurface Fate & Transport

## Approach:

- Ant Farm
- 2D infiltration vadose zone
  - Visual observation, dyes
- Lens formation

## Permutations:

- Two soils
  - Medium sand
  - Silty-sand-loam
- B100 (Soy and animalfat)
  - antioxidant+biocide
- B20 (Soy and animalfat)
  - antioxidant+biocide
- ULSD



# Subsurface Fate & Transport

## Experimental Matrix

| | ULSD | Animalfat B100 | Animalfat B20 | Soy B100 | Soy B20 |
|---|---|---|---|---|---|
| Reference | 50-200 mL | | | | |
| biocide and antioxidant | | 50-200 ml two soils | 50-200 ml | 50-200 ml two soils | 50-200 ml |
| | | | | | |
| Totals | 50-200mL | 200-800 ml | 100-400 ml | 200-800ml | 100-400ml |

# Subsurface Fate & Transport

# Material Compatibility

## Approach:

- Prelude to anticipated UL testing
  - Broad indicators
- Batch exposures
  - 1-4 months
  - Aerobic immersions

## Permutations:

- B100, B20, B5 x Animalfat, Soy
  - With/without low salinity water
  - All with antioxidant additive
- Materials
  - Bimetal copper-steel coupons
  - Fiberglass
  - elastomers

# Material Compatibility

## Experimental Matrix

Low-salinity water

| Material | ULSDx2 | Animalfat | | | Soy | | |
|---|---|---|---|---|---|---|---|
| | | B100 | B20x2 | B5 | B100 | B20x2 | B5 |
| Copper-steel | .2 L | .2 L | .2 L | .2 L | .2 L | .2 L | .2 L |
| Fiberglass 1 | .2 L | .2 L | .2 L | .2 L | .2 L | .2 L | .2 L |
| Fiberglass 2 | .1 L | .1 L | .1 L | - | .1 L | .1 L | - |
| Elastomer 1 | .2 L | .2 L | .2 L | .2 L | .2 L | .2 L | .2 L |
| Elastomer 2 | .1 L | .1 L | .1 L | .1 L | .1 L | .1 L | .1 L |
| Elastomer 3 | .1 L | .1 L | .1 L | - | .1 L | .1 L | - |
| Elastomer 4 | .1 L | .1 L | .1 L | - | .1 L | .1 L | - |
| Totals | 2 L | 1 L | 2 L | 1 L | 1 L | 2 L | 1 L |

# Biodegradation

## Approach:

- OECD (2004) recommended testing
- Batch respirometry (CO2)
  - Mineral medium,
  - inoculumn activated sludge
  - Tested substrate (same slow stir method as aquatic tox)

## Permutations:

- B100 (Soy and animalfat)
  - Antioxidant, antioxidant+biocide
- B20 (Soy and animalfat)
  - Antioxidant, antioxidant+biocide
- ULSD

# Biodegradation

## Experimental Matrix

| | ULSD | | Animalfat B100 | Animalfat B20 | Soy B100 | Soy B20 |
|---|---|---|---|---|---|---|
| Reference | .2 L | | | | | |
| antioxidant | | | .2 L | .2 L | .2 L | .2 L |
| antioxidant and biocide | | | .2 L | .2 L | .2 L | .2 L |
| | | | | | | |
| subTotals | .2 L | | .4 L | .4 L | .4 L | .4 L |
| Replication factor | 3 | | 3 | 3 | 3 | 3 |
| Totals | .6 L | | 1.2 L | 1.2 L | 1.2 L | 1.2 L |

# Biodegradation

## Experimental Matrix And submatrix

| | ULSD | | Animalfat B100 | Animalfat B20 | Soy B100 | Soy B20 |
|---|---|---|---|---|---|---|
| Reference | .2 L | | | | | |
| antioxidant | | | .2 L | .2 L | .2 L | .2 L |
| antioxidant and biocide | | | .2 L | .2 L | .2 L | .2 L |
| | | | | | | |
| subTotals | .2 L | | .4 L | .4 L | .4 L | .4 L |
| Replication factor | 3 | | 3 | 3 | 3 | 3 |
| Totals | .6 L | | 1.2 L | 1.2 L | 1.2 L | 1.2 L |

| **Description** | **Content** | | | | **# of Rep.** | **# of Microcosm** |
|---|---|---|---|---|---|---|
| | *Substrate* | *Inoculum* | *Mineral* | *Reference* | | |
| Test suspension | X | X | X | | 3 | 3x9 = 27 |
| Inoculum blank | | X | X | | 3 | 3 |
| Procedure control | | X | X | X | 1 | 1 |
| Abiotic + Adsorption control | X Sterilized | X Sterilized | X Sterilized | | 1 | 1x9 = 9 |
| | | | | **TOTAL Microcosms:** | | 50 |

# Aquatic Toxicity

## Approach: 6 Species

**EPA methods for Chronic Toxicity**

- W Coast Marine EPA 600/R-95-136, 1995
- Marine and Estuarine, EPA 821-R-02-014, 2002
- Freshwater EPA 821-R-02-013, 2002.

**Slow-stir aqu. prep (Schluep et al. 2001)**

- 10:1 aqu:biodiesel, 24hrs, 2 hrs, decant
- GC-MS for solubility, stability
- 100%, 50%, 25%, 10%, 5%, 1%, 0% dilutions

**Multiple chronic and Acute endpoints**

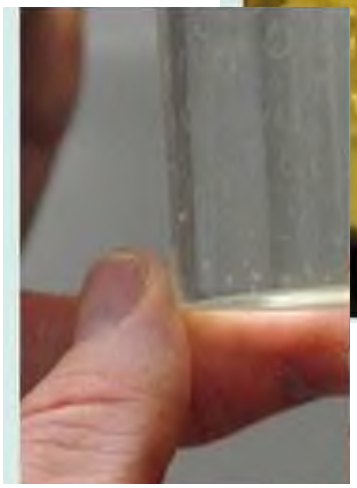
## Permutations:

**B20 Soy, B20 Animalfat**

Antioxidant and biocide

**B100/no biocide as feasible**

**ULSD**



**Green Algae**

**Ceriodaphnia Dubia**

# Aquatic Toxicity

## Experimental Matrix

| Test Species | Test Type | Test chemical | | | | |
|---|---|---|---|---|---|---|
| | | ULSD | B20S A | B20S A+B[a] | B20A A | B20A A+B |
| Green algae *(Selenastrum capricornutum)* | 96-hr chronic cell growth | 1L | 1L | 1L | 1L | 1L |
| Water flea *(Ceriodaphnia dubia)* | 7-day chronic (survival and reproduction) | 1L | 1L | 1L | 1L | 1L |
| Fathead minnow *(Pimephales promelas)* | 7-day chronic (survival and growth) | 1L | 1L | 1L | 1L | 1L |
| Red Abalone (*Haliotis rufescens*) | 48-hr chronic (shell development) | 1L | 1L | 1L | 1L | 1L |
| Mysid *(Mysidopsis bahia)* | 7-day chronic (survival and growth) | 1L | 1L | 1L | 1L | 1L |
| Topsmelt (*Atherinops affinis*) | 7-day chronic (survival and growth) | 1L | 1L | 1L | 1L | 1L |
| | | | | | | |
| Totals | | 6L | 6L | 6L | 6L | 6L |

# Summary

**Relative to ULSD**

**Broad Scope - Limited depth (time, $)**

- **Conservative design**
  - **Potential risk = potential impact x potential frequency of use**

**Present**

- **Soy, animalfat feedstocks**
- **B100 storage, B20 storage & use, B5 use**
- **Biocide, antioxidant**

**Absent**

- **Other feedstocks (yellowgrease, canola, etc.)**
- **Other additives (coldflow, cetane booster, NOx reducer)**
- **Anaerobic biodegradation, NAPL biodegradation**
- **Coupled processes (SRB in UST)**