Environment Canada Environnement Canada

Canada

Biofuels in the Environment

A Review of Behaviors, Fates and Effects & Remediation Techniques

Bruce Hollebone
Environment Canada
Freshwater Spills Symposium
St. Louis, MO, 2009

Where does the spill go?

Does it mix into/with water?

- Aquatic: partitioning, solubility, emulsification
- Soil: ground water partitioning and solubility

How does it spread?

- Aquatic: density and viscosity, solubility
- Soil: infiltration, movement in soil zones

What is the end-state?

- Evaporation
- Dissolution/emulsification
- Degradation

What does the spill affect?

Health and Safety
- Fire risks
- Chemical: Vapour
  - Oral (Drinking water)
  - Contact

Ecotoxicology
- Acute (lethality)
- Chronic (accumulation)
- Indirect (intermediates, breakdown products, side effects of degredation)

What can we do about a spill?

Response & Countermeasures

- Mechanical
- Chemical
- Other countermeasures

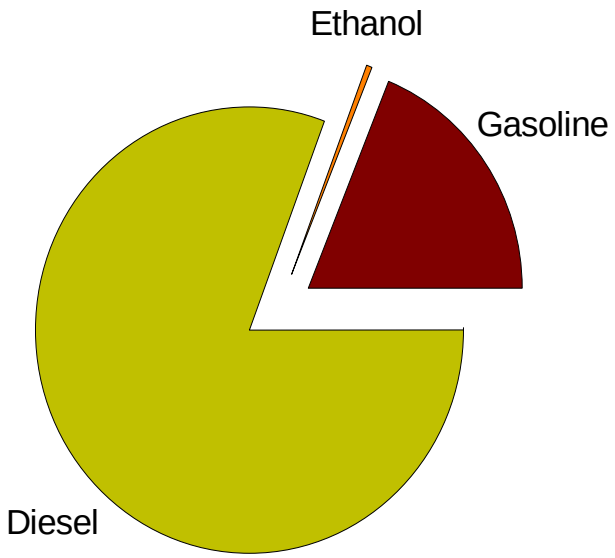
Restoration

- Site remediation
- Land-farming
- Vapour stripping

Spills of Road Fuels by Volume

For 2005-2006

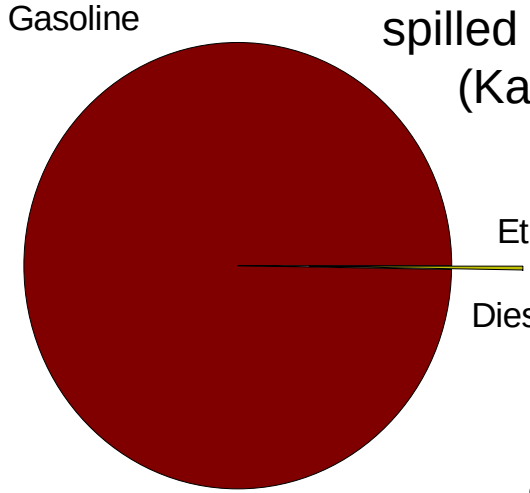
CANADA



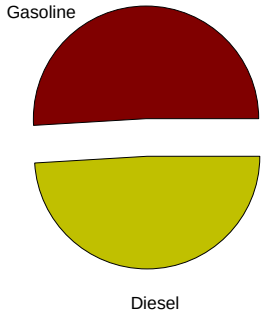
1,000,000 L spilled/year

US

6,000,000,000 L spilled in 1 year (Katrina)



US Near Water Only



7,000,000 L spilled/year near/on water

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Biodiesel

Biodiesel Basics

Made from animal or vegetable oils with an alcohol:

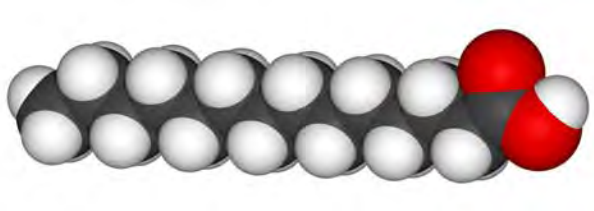
10 parts Oil + 1 part Methanol

gives

10 parts biodiesel + 1 part glycerine

- Not very miscible with water
- Completely miscible with diesel

- Less dense than water
- More viscous than water or diesel
- Gels at high temperatures
- Very low vapour pressure
  - Low fire risk



C14 Fatty Acid

Transport and Market of Biodiesel

- Biodiesel is mildly corrosive to metals, plastics and other synthetic materials
- Producers supply B100 from biological stocks
- B100 transported to blending facility by rail, truck
- Blended at pipeline rack in distribution terminal to B5/B20
- Blends transported to retailers by truck
- B5/B20 blends stored by retailers

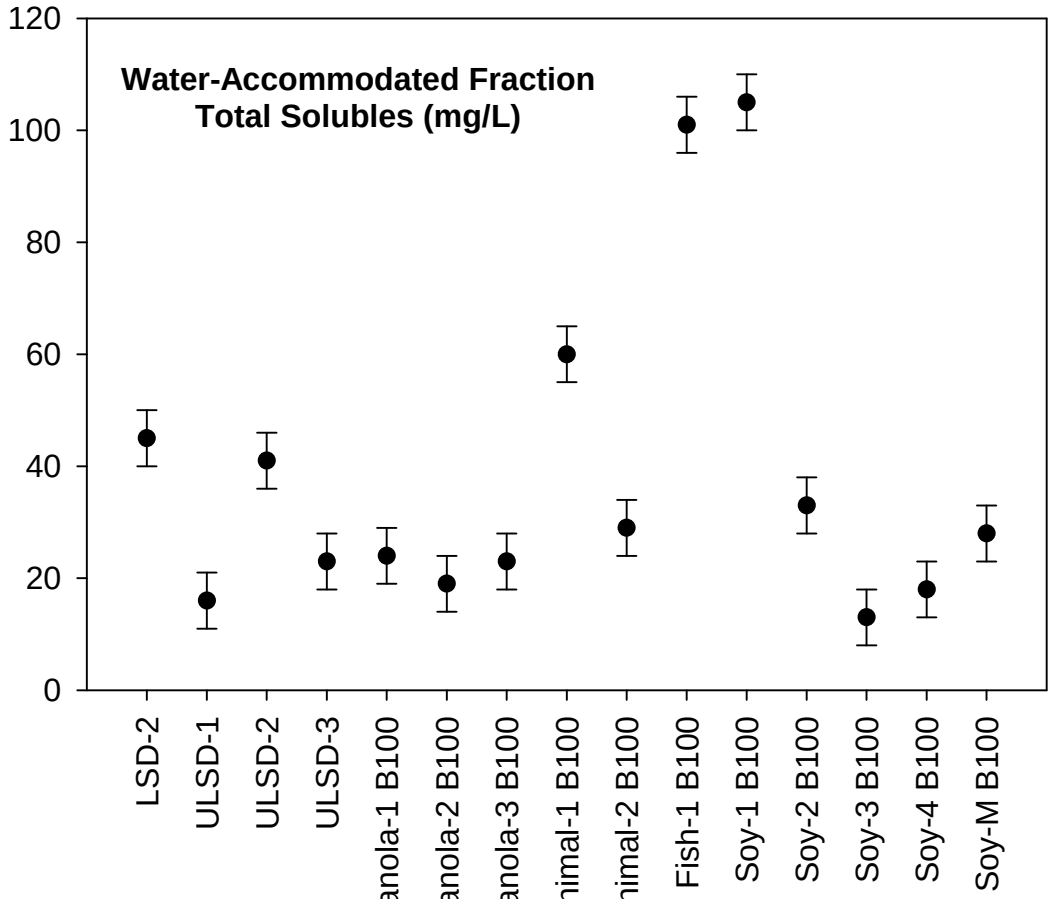
“Solubility” of Biodiesels

Water Accommodated Fraction

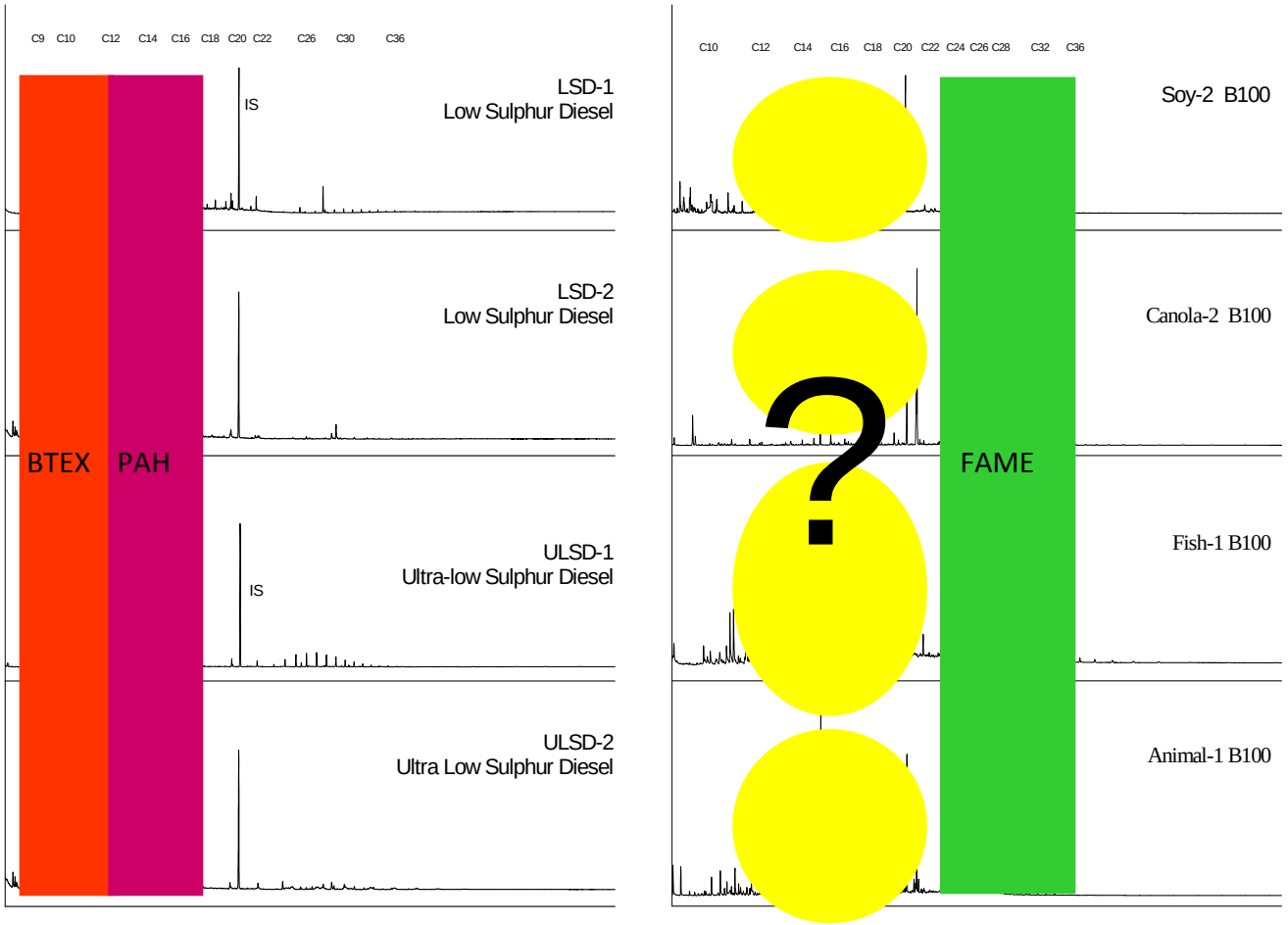
Extract

Analyze

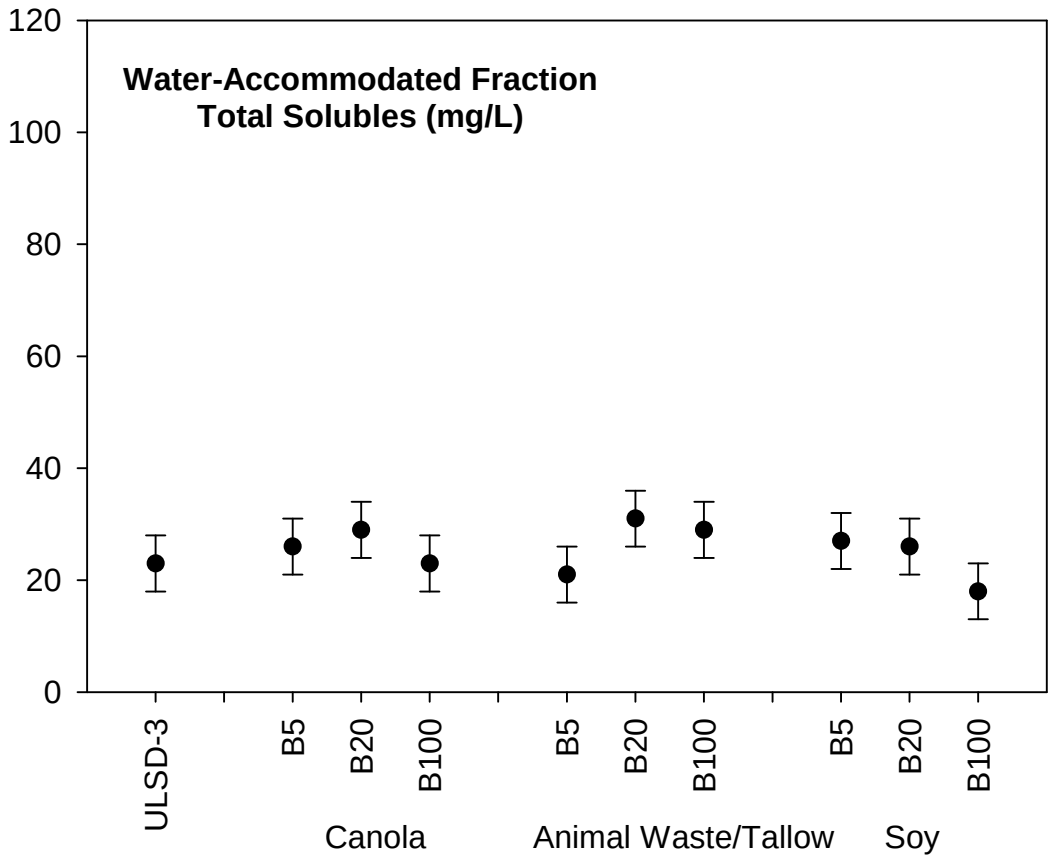
Aqueous Solubilities



Aqueous Extract Chromatograms



Blend WAF “Solubility”



Aquatic “Solubility”

- Petroleum diesel “solubilities”: 20-40 ppm.
  - Most soluble components are alkyl-benzenes (including BTEX) and PAHs (mostly naphthalenes).
- Biodiesel water fractions highly variable 20—100ppm
  - Characteristic FAME peaks do not change much
  - Mostly early eluting (light) compounds which cause variability in biodiesel “solubility”
- No measurable cosolvent effects between biodiesel and petrodiesel

Dispersibility

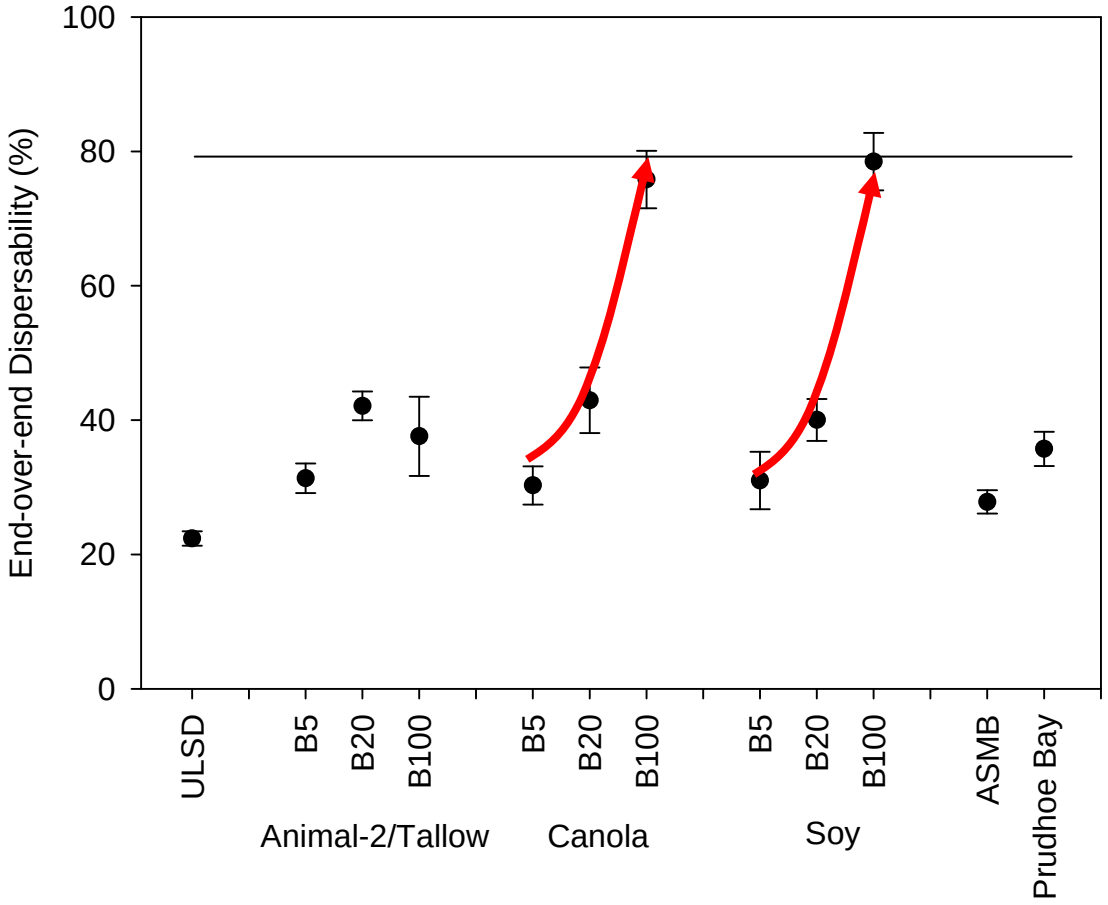
Low Energy Mixing

Swirling Flask Test

Higher Energy Mixing

End-over-end Rotary Mixer

Biodiesel in Water Dispersions



Total Dispersion

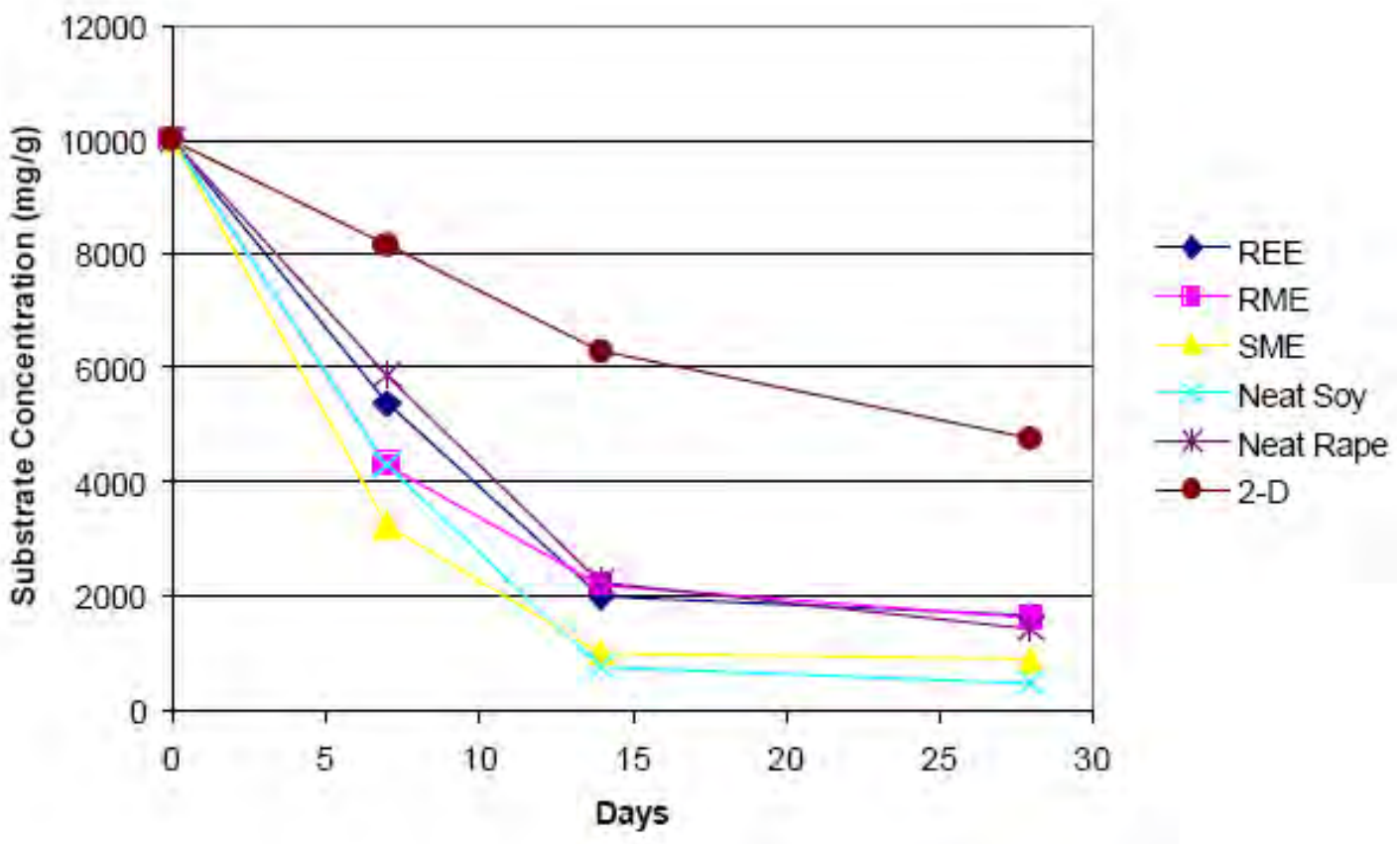
Biodiesel Dispersability

- Biodiesels will naturally disperse much more easily than petroleum diesels
  - Biodiesels are mild surfactants
  - Form a white, milky emulsion.
- Biodiesel blended with diesel can cause dispersion of diesel into the water column in blends as low as B10 to B20

Degradation of Biodiesel

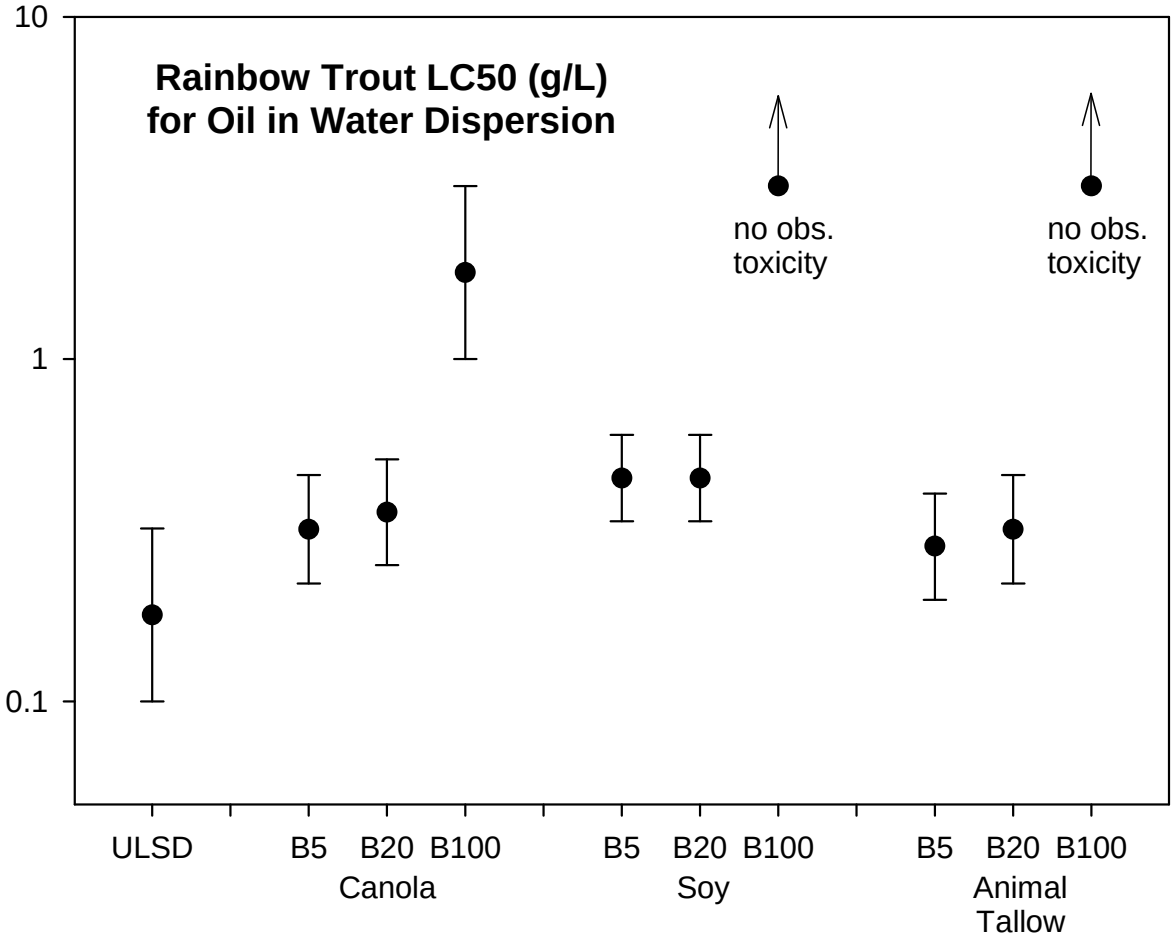
- Biodiesel will auto-degrade.
  - light, high temperatures, presence of oxidizers.
- In optimal conditions, pure biodiesel can biodegrade in 8 days or less.
  - No lack of nutrients or oxygen
  - Activated sludge medium
- In more normal conditions, biodegradation limited by electron acceptors/oxygen and nutrients:
  - Biodiesel degrades 80-90% / 28 days
  - Petrodiesel degrades 50% / 28 days
- Biodiesel biodegrades 2-2.5 times faster than petrodiesel in typical conditions

Biodiesel Degradation in Soil



Peterson and Moller 2004

Rainbow Trout Toxicity of Biodiesel



Toxicity Ranking

B20 Soy

B5 Tallow

B20 Canola

B20 Tallow

B5 Soy

ULSD

B5 Canola

B100 Tallow

B100 Canola

B100 Soy

More Toxic

Less Toxic

ULSD

B5 Tallow

B20 Tallow

B5 Canola

B20 Canola

B20 Soy

B5 Soy

B100 Canola

B100 Tallow

B100 Soy

"Diesel" Toxicity

Native Biofuel

Aquatic Toxicity

- Pure biodiesels are at least 5 times less acutely toxic than petroleum diesels.
- Biodiesel/petrodiesel blends up to 20% are similarly toxic to petrodiesel
- Toxicity for blends is not linear with blend concentration
- No strong correlations between solubility and toxicity
- Weak correlations observed between organism toxicities
- Large differences in sensitivity
  - Microtox > R. Trout > D. Magna (non smothering)

Relative toxicities of diesels to rats

28 days oral administration of 500mg/kg/day

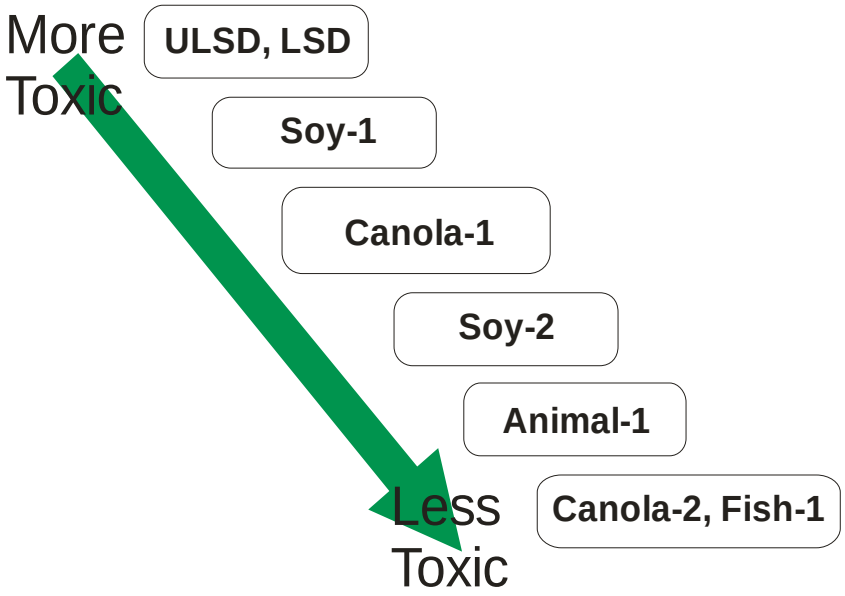
	LSD	ULSD	Soy-1	Canola-1	Soy-2	Animal-1	Canola-2	Fish-1
Inc. liver wt.	+	+	+	+				
Thyroid changes	++	++	+	+	+	+	+	+
Distended cecum, colon, rectum					+			
Inc. urinary ascorbic acid	++	+++	++					
Inc. peroxisome proliferating enzyme	+	+	+		+	+	+	+
Inc. liver Phase I Drug metabolizing enzyme	++	++	+					
Inc. liver GST	+	+	+			+		
Inc. liver UDPGT	+							

Courtesy of R. Poon, Health Canada

Animal Oral Toxicity

Animal Tests

- Biodiesels less toxic than LSD and ULSD in animal tests
- Toxicity varied widely among biodiesels (feedstock? additives?)

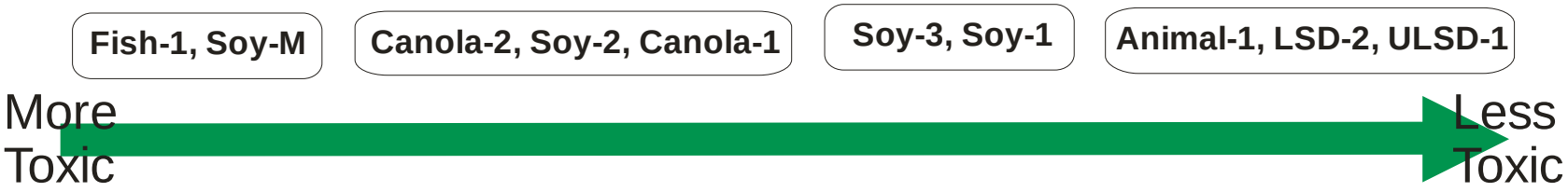


Courtesy of R. Poon, Health Canada

Human Lung Cells

Cellular Assays

- Tests inhalation toxicity
- Fish-1 and Soy-M most toxic to alveolar macrophages
- Biodiesel a higher inhalation risk than petrodiesel



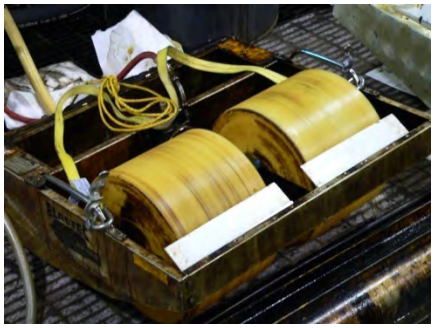
Courtesy of R. Poon, Health Canada

Environmental Toxicity

Biodiesels compared to petroleum diesel:

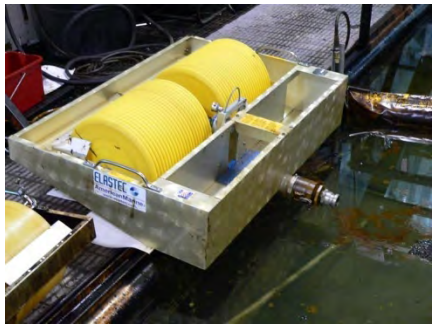
- Less acutely toxic to aquatic life
  - Little correlation between feedstock and toxicity
- Readily disperses at high energy
  - Acts as a surfactant to increase diesel concentrations in water column.
  - Toxicity very different between “soluble” (WAF) and dispersible component exposures.

Skimmer Testing with Biodiesels



Smooth Drum

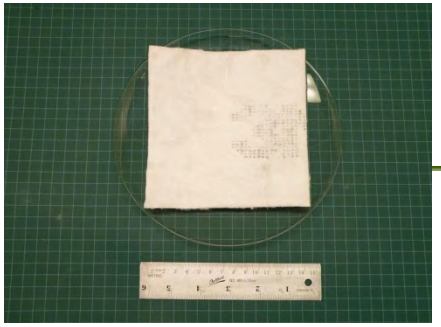
Belt



Grooved Drum

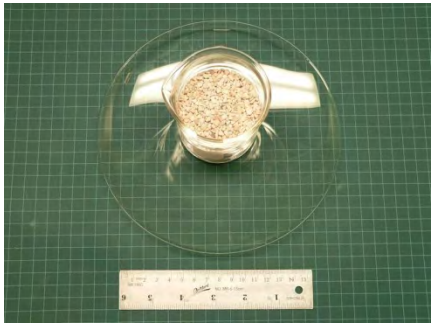
- Skimmer pick-up of biodiesel slightly better than petrodiesel
- Even better for vegetable oil stock
- Related to viscosity increase

Sorbents & Biodiesel



Polypropylene

Peat Moss



Diatomaceous Earth

- Biodiesel pick-up very similar to that of fuels of same viscosity for most sorbent types.
- Not tested on emulsified products
- Not tested near gel point
- Problems with diatomaceous earth products: emulsification ?

Biodiesel Knowledge Gaps

Fate & Behaviour

- Partitioning vs emulsification
- Long-term stability of dispersions/emulsions
- Rates of infiltration and migration in soils not well known
- Factors affecting biodegredation

Effects and Toxicities

- Only know lethal levels for some sentinel species
- Sublethal effects unknown
- Levels of concern for eutrophication?

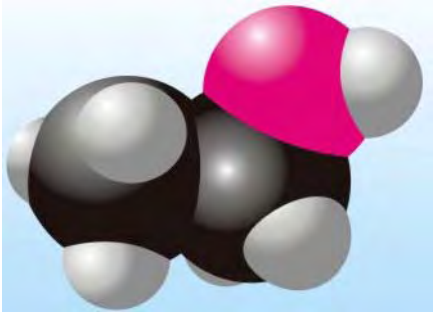
Response and Remediation

- Chemical agents (SWA, Gelling agents)
- Mechanical agents in current use (sorbent booms, skimmer tech)
- Monitoring?
- Optimal parameters for biodegredation

Gasohol & Ethanol

Ethanol Basics

- A small, polar molecule
  - Completely miscible in water
  - Completely miscible in gasoline
  - Much prefers water to gasoline



- Less dense than water
- Viscosity slightly less than water
- High vapour pressure

Ethanol Market and Transport

- Ethanol rapidly degrades or corrodes metals plastics, synthetic materials
- Pure ethanol produced, but shipped denatured: E95
- Transport by barge, rail and truck
- Pipeline terminals store E95 and mix blends for retailers: E10-E15, E85
- Blends distributed by truck.

Ethanol Evaporation Rate

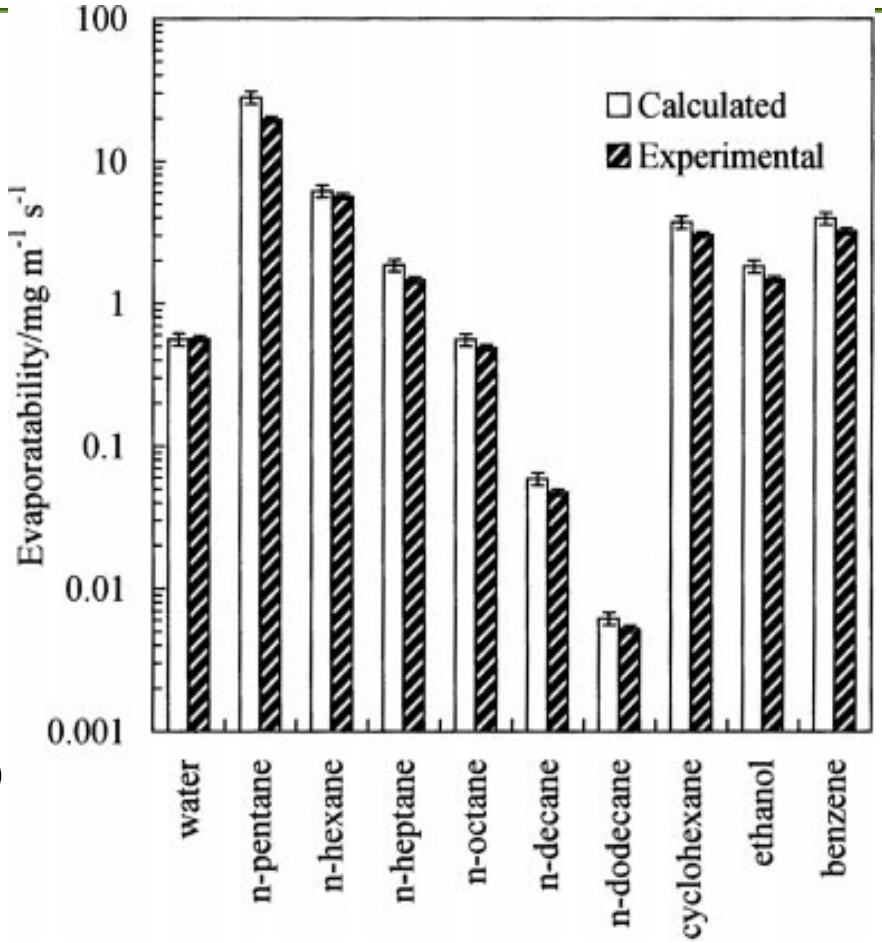
- Ethanol evaporates at approximately the same rate as gasoline, about 8 times faster than water

- Wider combustion range

  E100: LEL 3.3% UEL 19%

  E85: LEL 1.4% UEL 19%

  Gas: LEL 1.4% UEL 7.7%

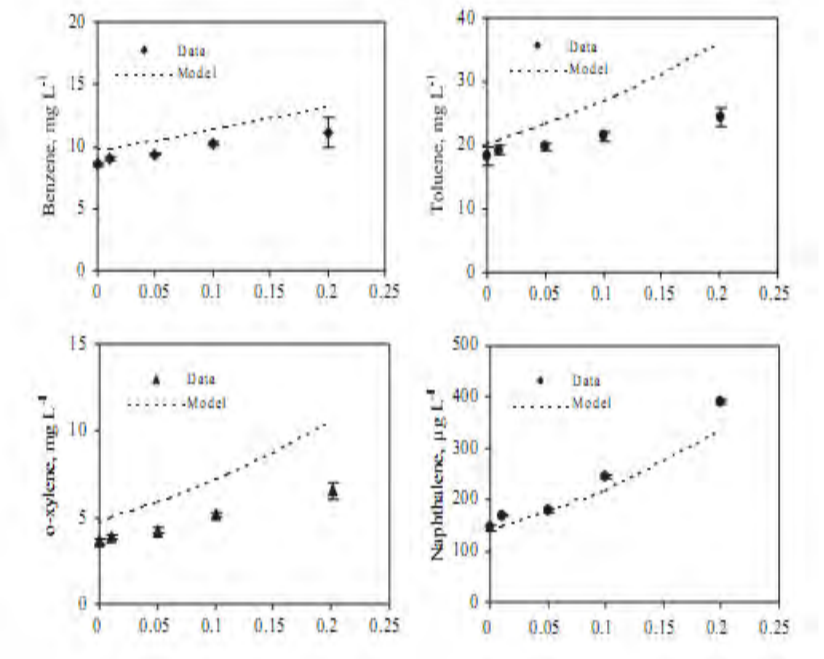


Gasoline/Ethanol Co-solubility

- Ethanol can increase solubility of BTEX and PAH compounds
- Requires high levels of ethanol (ie E85 not E15)

BUT

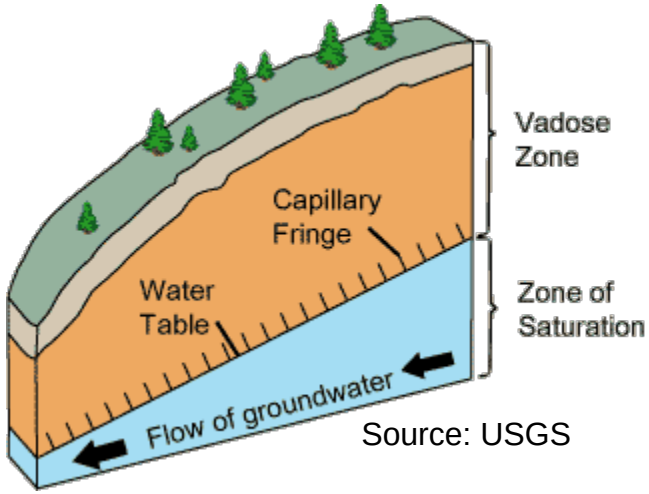
- Many case studies report very low levels of ethanol at water interface
- Estimated maximum of 0.05



Corseuil et al., 2004

Groundwater Fate

- Gas/alcohol traps at interface of water table in capillary fringe
- Alcohol mostly partitions into saturated zone, but some remains in capillary fringe. Ethanol can be retained for long periods (>100 d) in saturated zone.
- Ethanol in capillary fringe reduces surface tension---less gasoline stored in vadose zone
- Ethanol vapours not measurable



Source: USGS

Degradation of Gasohol

- Ethanol degrades very quickly in both soil and water
  - No abiotic, all degradation is microbial
  - More rapid than BTEX compounds, 100% in 5 days
- In water:
  - Enhances BOD/COD, causes eutrophication
- In soil:
  - Preferential degradation of ethanol hinders natural attenuation of BTEX.
    - Alters microbial conditions and reduces electron-acceptors
  - BTEX and ethanol typically degrade more rapidly in soils that have been previously contaminated
  - Reduced degradation allows for greater travel of BTEX plumes, 1.5 to 2.5x farther.

(Responder) Health and Safety

- Gasohols are flammable and evaporate easily
  - High fire risk
  - Low flashpoints/low LEL/ High UEL
- Ethanol and gas vapours are heavier than air
  - Vapours are OD and toxic (1000 ppm TWA for EtOH)
  - Confined/restricted space entry problems
- Gasohol is carcinogenic

Ecotoxicity of Gasohol

- Ethanol is acutely toxic to most organisms
  - LC50 9,000 to 11,000 milligrams per liter for many fish
  - Does not bioaccumulate
- Gasohol
  - Considered carcinogenic
- Oxygen depletion
  - Widely reported in case studies
  - Lab studies indicate can be very high
  - Not well modelled

Response

- Containment and prevention
- Mitigation and monitoring
  - Monitoring: BOD/COD, TPH, BTEX
  - Mitigation: ?

Remediation

- Enhanced Degradation
  - addition of nitrate as an electron acceptor for *in situ* bioremediation of gasohol.
- Vapour stripping/sparging

Gasohol Knowledge Gaps

Fate and Behaviour

- Partitioning and cosolvent behaviour, both in surface and ground water. When is cosolubility really important?
- Transport in soil: interactions in the capillary fringe, degradation rate

Toxicology

- Cosolvent effects
- Sub lethal effects
- Terrestrial organisms

Response and Restoration

- Monitoring?
- Factors affecting biodegradation of ethanol and gasoline mixtures.
  - Most effective soil amendments
- Soil vapour extraction, stripping.

Merci/Thank You!

Questions?