Biofuels in the Environment
A Review of Behaviors, Fates and Effects & Remediation Techniques

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Environment Canada
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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 degradation)
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**
- Diesel: 1,000,000 L spilled/year
- Gasoline
- Ethanol

**US**
- Gasoline
- Diesel
- Ethanol

- 6,000,000,000 L spilled in 1 year (Katrina)
- 7,000,000 L spilled/year near/on water

**US Near Water Only**
- Gasoline
- Diesel
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

Water-Accommodated Fraction
Total Solubles (mg/L)
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

End-over-end Dispersability (%)

Total Dispersion

ULSD  B5  B20  B100  B5  B20  B100  B5  B20  B100  ASMB
Animal-2/Tallow  Canola  Soy  Prudhoe Bay
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

Rainbow Trout LC50 (g/L) for Oil in Water Dispersion

- ULSD
- B5
- B20
- B100
- Canola
- B5
- B20
- B100
- Soy
- B5
- B20
- B100
- Animal Tallow

- no obs. toxicity
- no obs. toxicity
Toxicity Ranking

B20 Soy
B5 Tallow
B20 Canola
B20 Tallow
B5 Soy
ULSD
B5 Canola
B100 Tallow
B100 Canola
B100 Soy

More Toxic
ULSD
B5 Tallow
B20 Tallow
B5 Canola
B20 Canola
B20 Soy
B5 Soy
B100 Canola
B100 Tallow
B100 Soy

 Less Toxic
“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

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<th>ULSD</th>
<th>Soy-1</th>
<th>Canola-1</th>
<th>Soy-2</th>
<th>Animal-1</th>
<th>Canola-2</th>
<th>Fish-1</th>
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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?)

More Toxic: ULSD, LSD, Soy-1, Canola-1, Soy-2, Animal-1

Less Toxic: Canola-2, Fish-1

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

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

- 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 biodegradation

**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 biodegradation
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

Ethanol fraction (1=100%)

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 groundwater. *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?