Composition and Behavior of Ethanol Gasolines

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For
Freshwater Spills 2009
St. Louis, Missouri
April 27-30, 2009

Outline

- Historical Usage of Ethanol
- Phase behavior of ethanol/gasoline blends
- Composition of Fuel Ethanol Samples
- Field Examples: Land and Water
- Modeling Examples

Overview from producers to consumers

- Producers
  - Distill to 190 proof – 95% alcohol
  - Dry to 200 proof (molecular sieve)
  - Denature
- Transport
  - Not to go in U.S. pipelines,
    - 1 exception (Florida)
  - Therefore: barges, trucks, trains
- Distribute
  - (Terminals) Separate Ethanol Tank
  - Splash Blending at rack
- Use
  - Compatible Tanks, Pipes, Dispensers?
  - Water Bottoms?

Alternate Marketing Strategies

Terminology

- Following **ASTM D 4806 – 08a Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel.**
  - ***Denaturant*** -- a material added to fuel ethanol to make it unsuitable for beverage use, but not for unsuitable for automotive use.
  - ***Fuel Ethanol*** -- ethanol with impurities common to its production including water but not denaturants.
  - ***Denatured Fuel Ethanol*** – fuel ethanol made unfit for beverage use by the addition of denaturants.
  - ***Higher Molecular Weight Alcohols*** – aliphatic alcohols of general formula CnH2n+1OH with n from 3 to 8.

Ethanol and Gasoline Blends

- E100: Non-denatured fuel ethanol
- E95: Denatured fuel ethanol
  - ASTM 4806
    - Min 92% ethanol
    - Denaturants: 2% to 5%
      - Natural gasoline
      - Gasoline components
      - Unleaded gasoline
- E85: “Flex Fuel” ASTM D 5798
  - Three ethanol classes: min. 70%, 74%, 79%
- E10: “may contain 10% ethanol”
  - ~90% gasoline

ASTM SPEC

- Ethanol > 92.1%
- Water < 1%
- Methanol < 0.5%
- Solvent-wasted gum < 5 mg/100 mL
- Denaturant 1.96% to 5%
- Inorganic Chloride < 10 mg/L

A Word on Taxes

- 2008 Food, Conservation, and Energy Act (Public Law 110-123)
  - January 1, 2009
  - full ethanol production credit only if denaturant content < 2%.
- U.S. Internal Revenue Service
  - temporarily allowing credits for denaturant(s) < 2.5% of the fuel ethanol
  - Notice 2009-06

Denaturants

- ASTM also specifies prohibited denaturants:
  - (adverse effects on fuel stability, automotive engines, and fuel systems)
  - hydrocarbons with an end boiling point above 225 ^{o}C,
  - methanol not meeting ASTM D1152,
  - pyrroles, turpentine, ketones, and tars.

Ethanol Usage in Gasoline

- Historic
  - Known as an octane booster since the 1920s
  - Oxygenates required in reformulated gasoline 1995-2006
- Mandated
  - Energy Policy Act 2005
  - Energy Independence and Security Act of 2007
  - Some state rules

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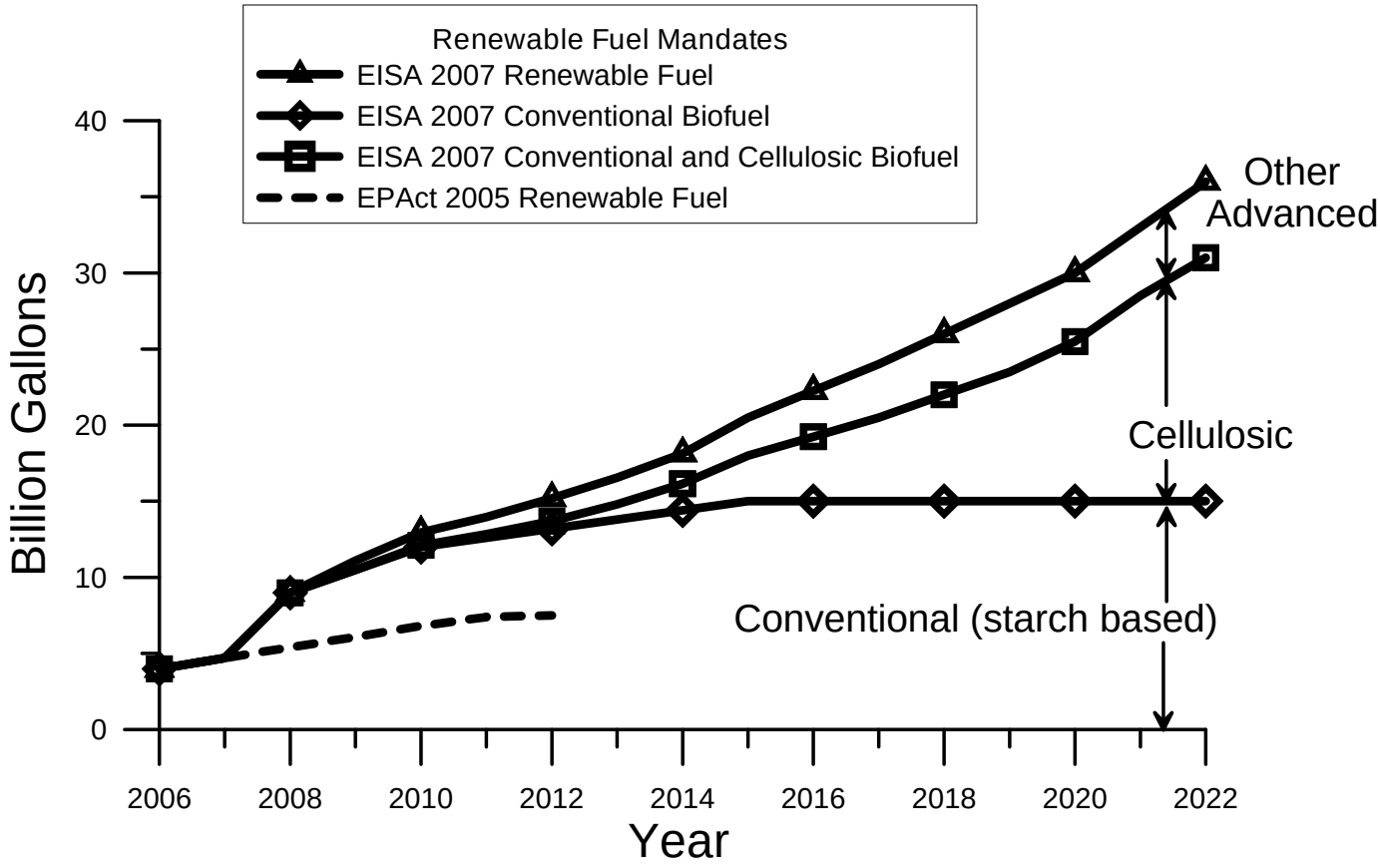
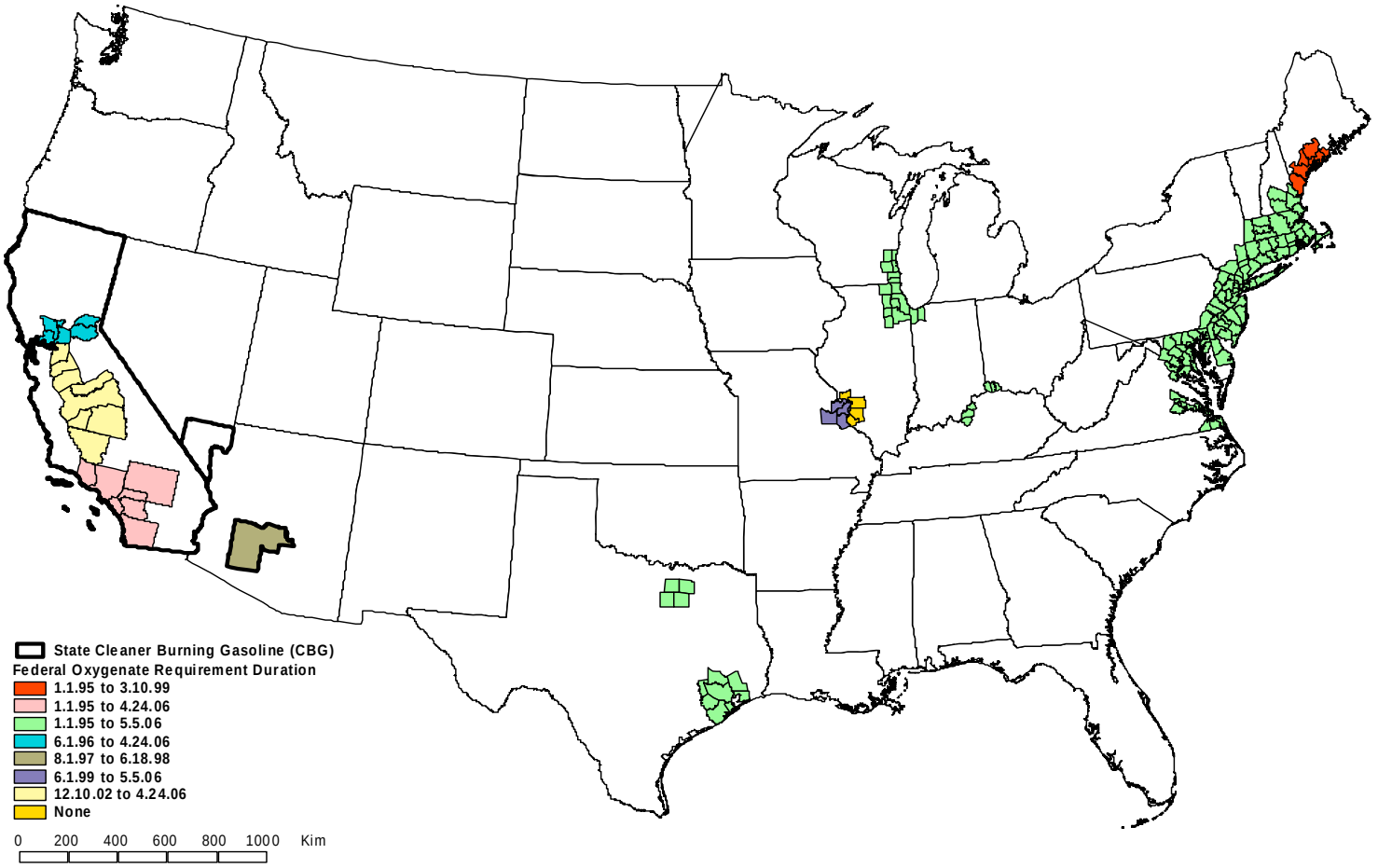


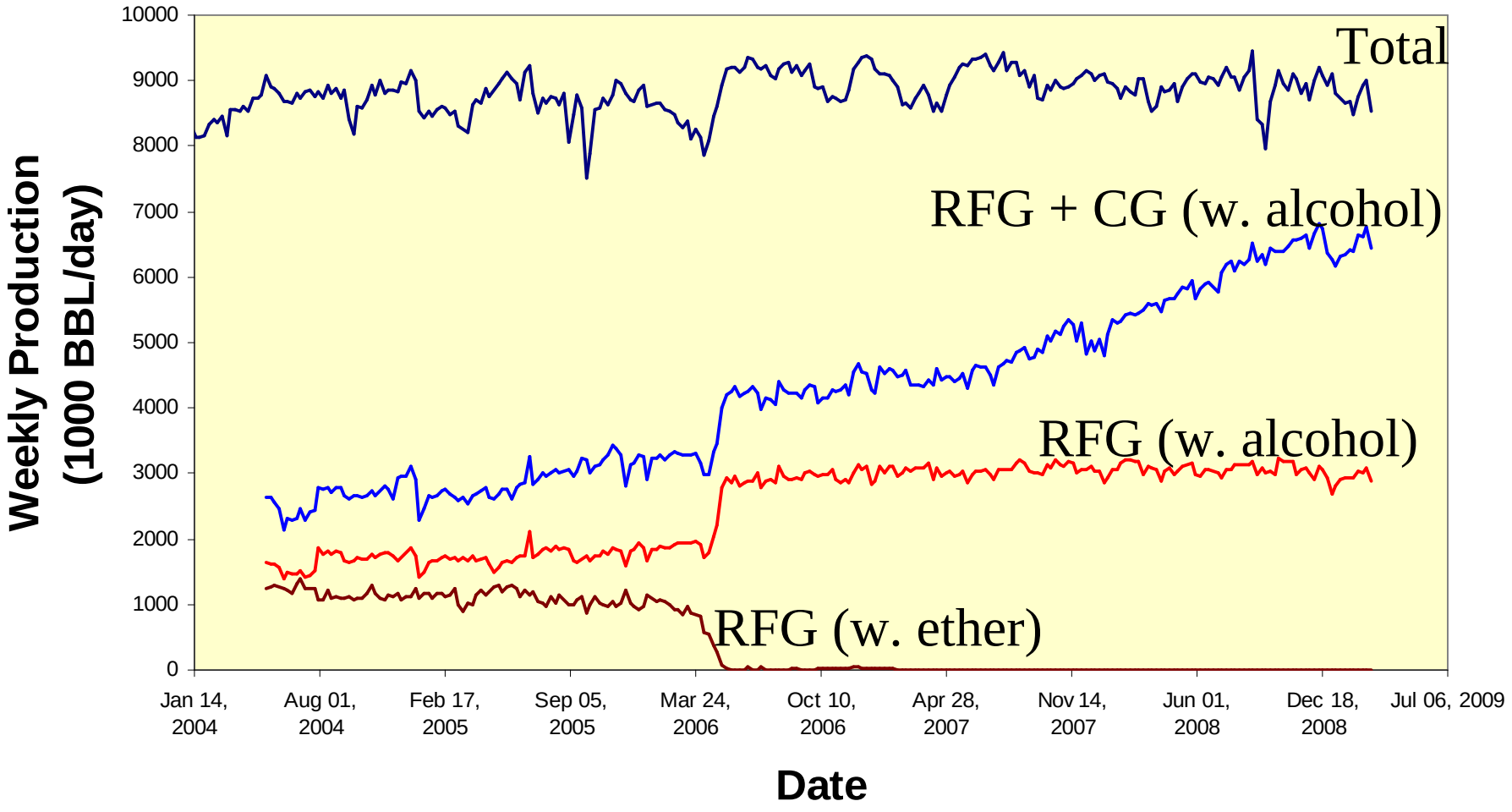
Terminology

- Following the **Code of Federal Regulations (40 CFR) Part 80 – Regulation of Fuels and Fuel Additives**:
  - ***Reformulated Gasoline (RFG)*** is any gasoline whose formulation has been certified under 40 CFR § 80.40 and which meets each of the standards and requirements prescribed under 40 CFR § 80.41.
    - From 1995 until 2006, RFG was required to contain 2 % by weight oxygen-containing compounds (“oxygenates”)
    - *Benzene < 1%*
  - ***Conventional Gasoline (CG)*** is any gasoline which has not been certified under 40 CFR § 80.40.
  - ***Oxygenated Gasoline (OG)*** is any gasoline which contains a measurable amount of oxygenate.

Reformulated and Conventional Gasoline in the US



DOE Production Data



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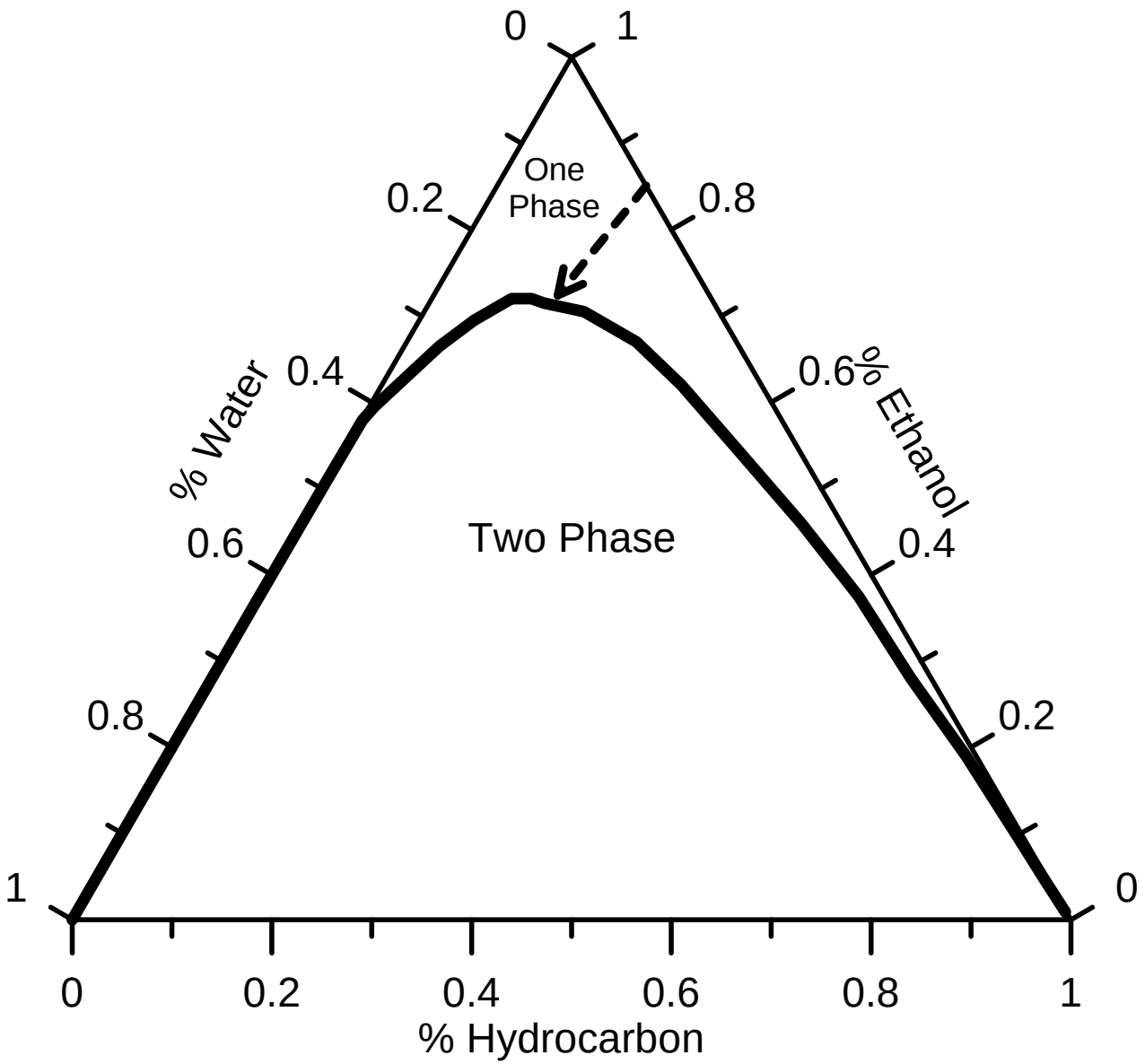
Phase Behavior

- Phase Separation
  - Gasoline adsorbs water up to a point where phase separation occurs
    - Gasoline ~0.1%
- Volume Changes
  - Ethanol/E85 volume reduction with water addition



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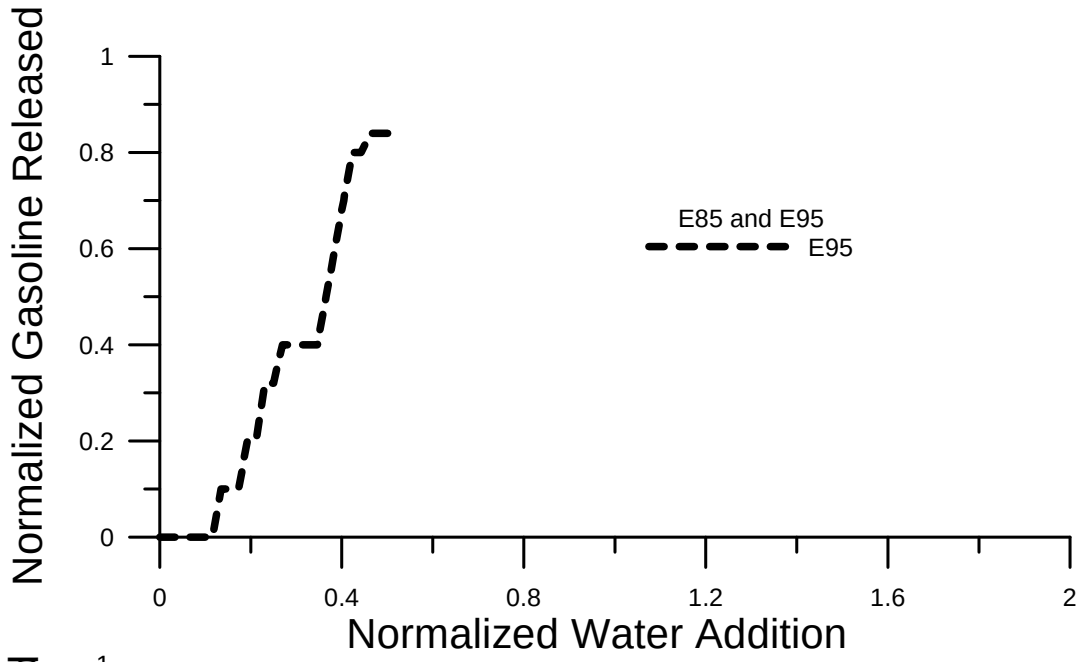

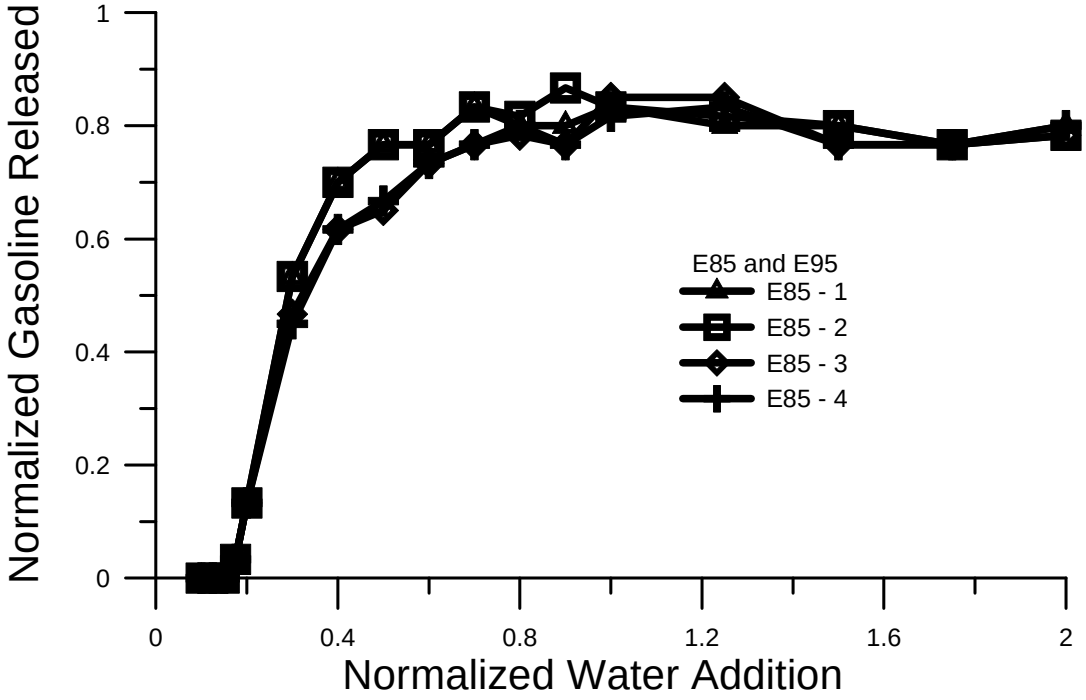

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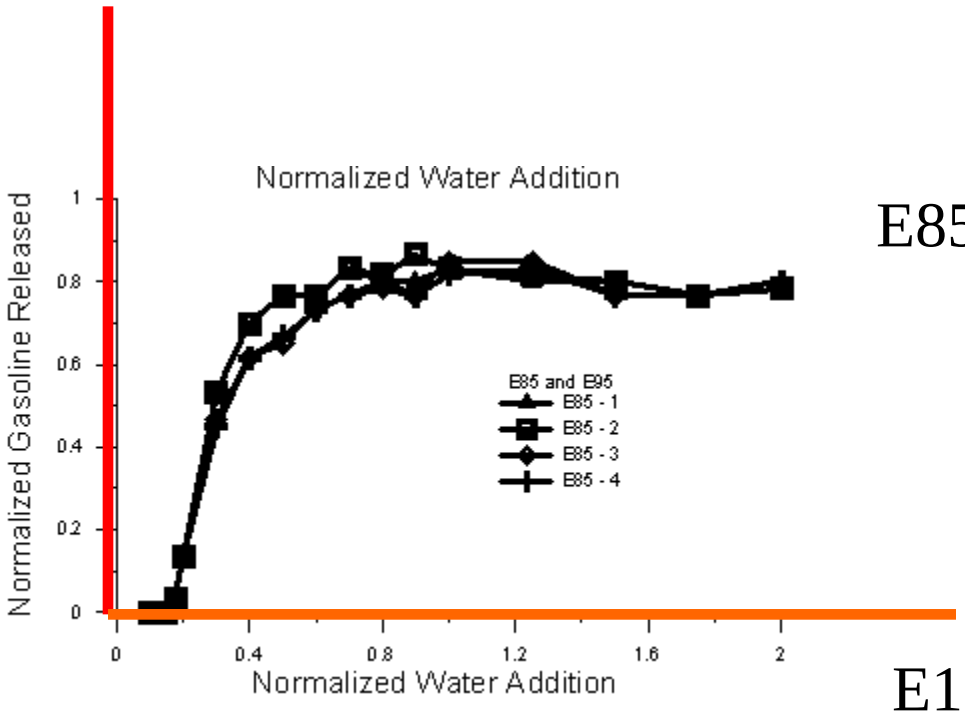
E10 Gasoline



E85 and E95

E100 Ethanol

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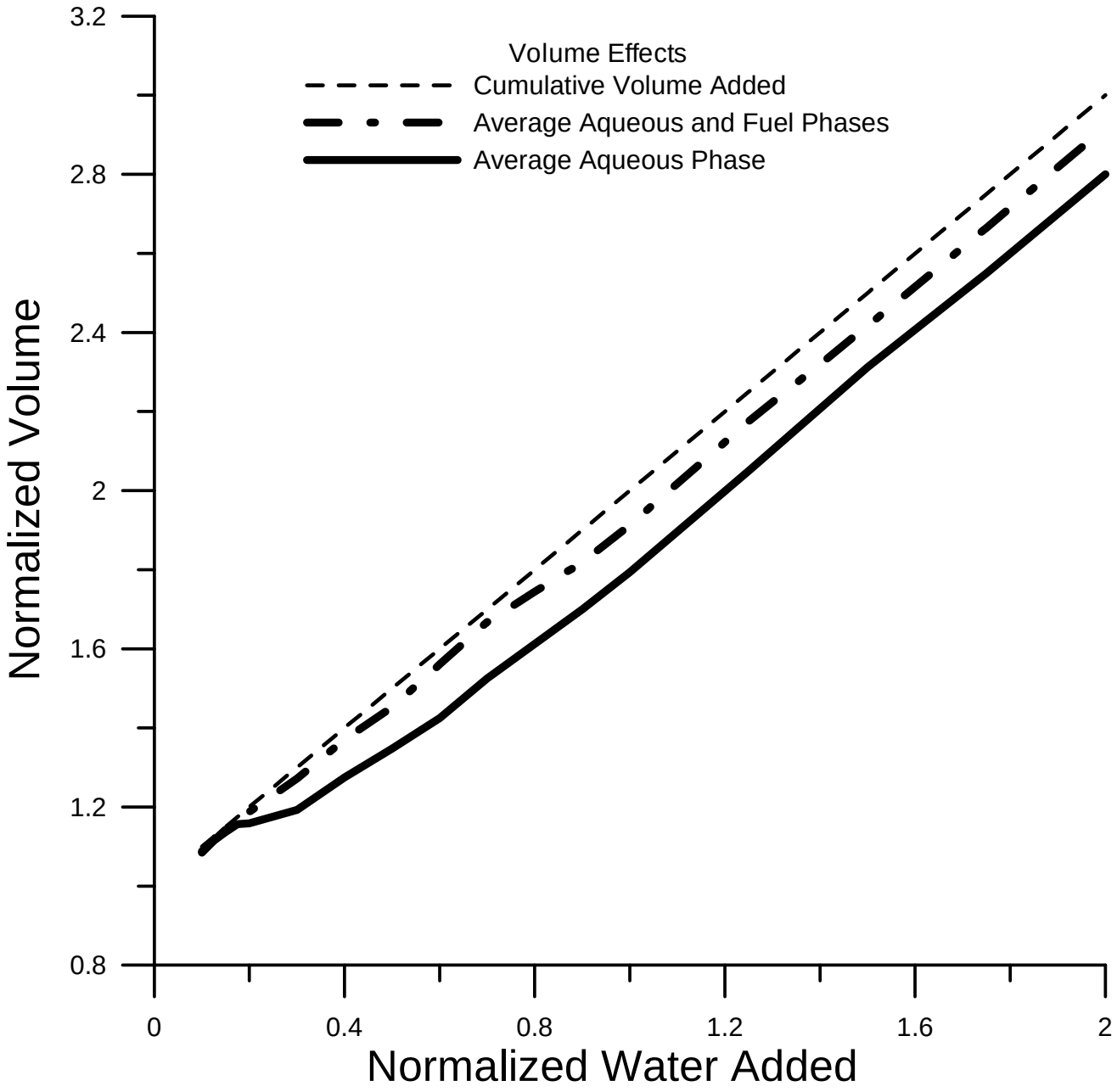
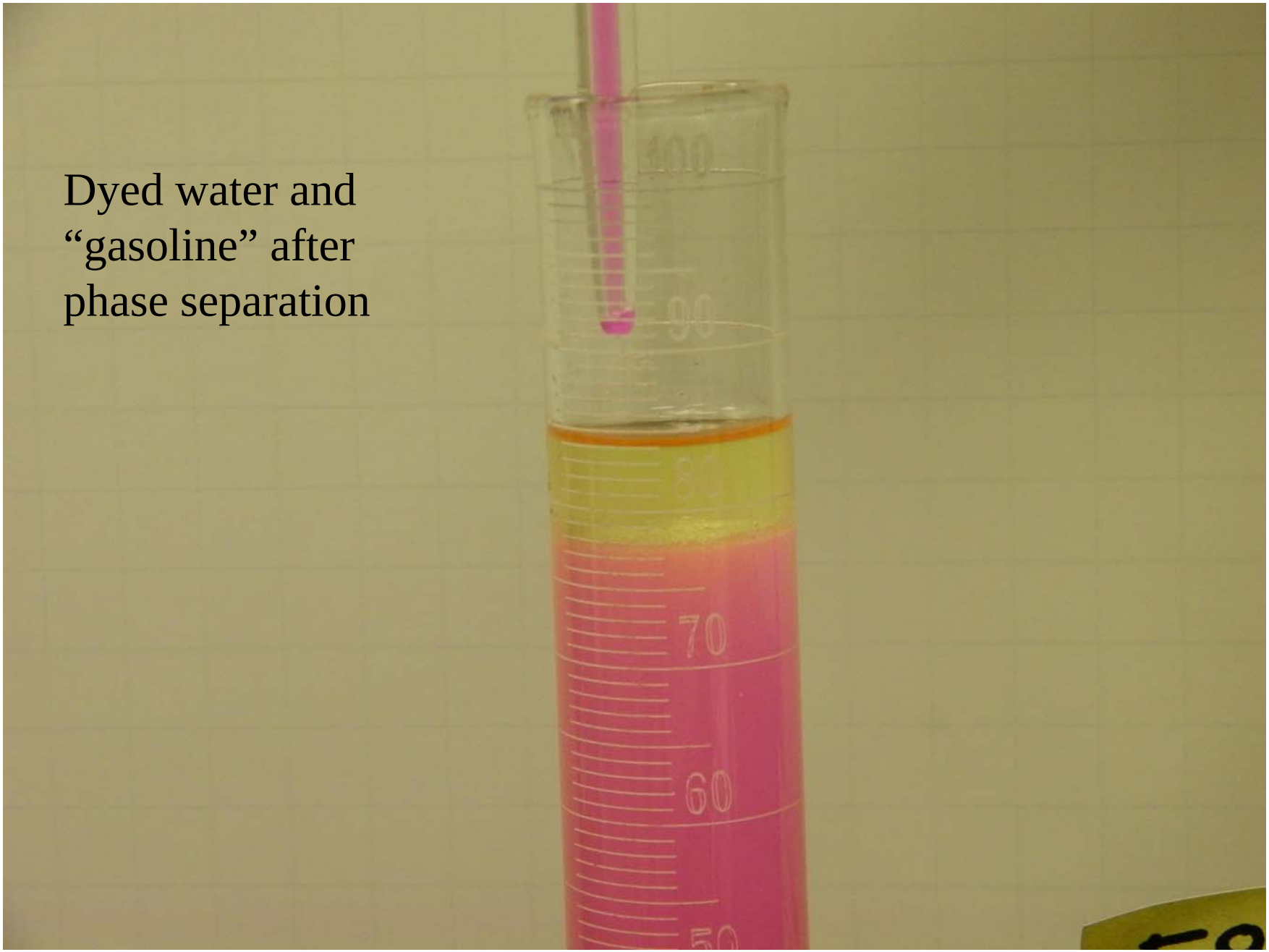


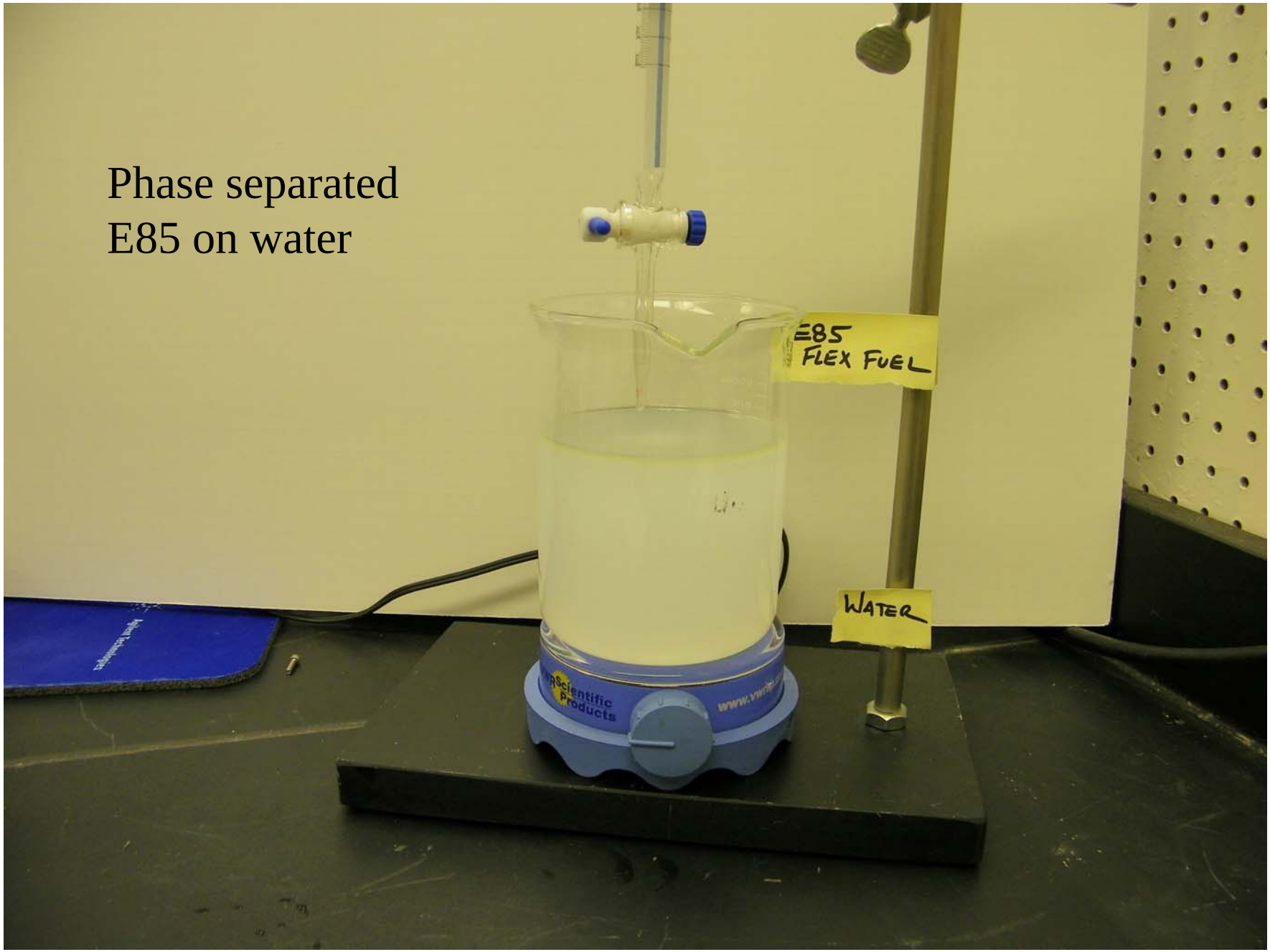
Videos

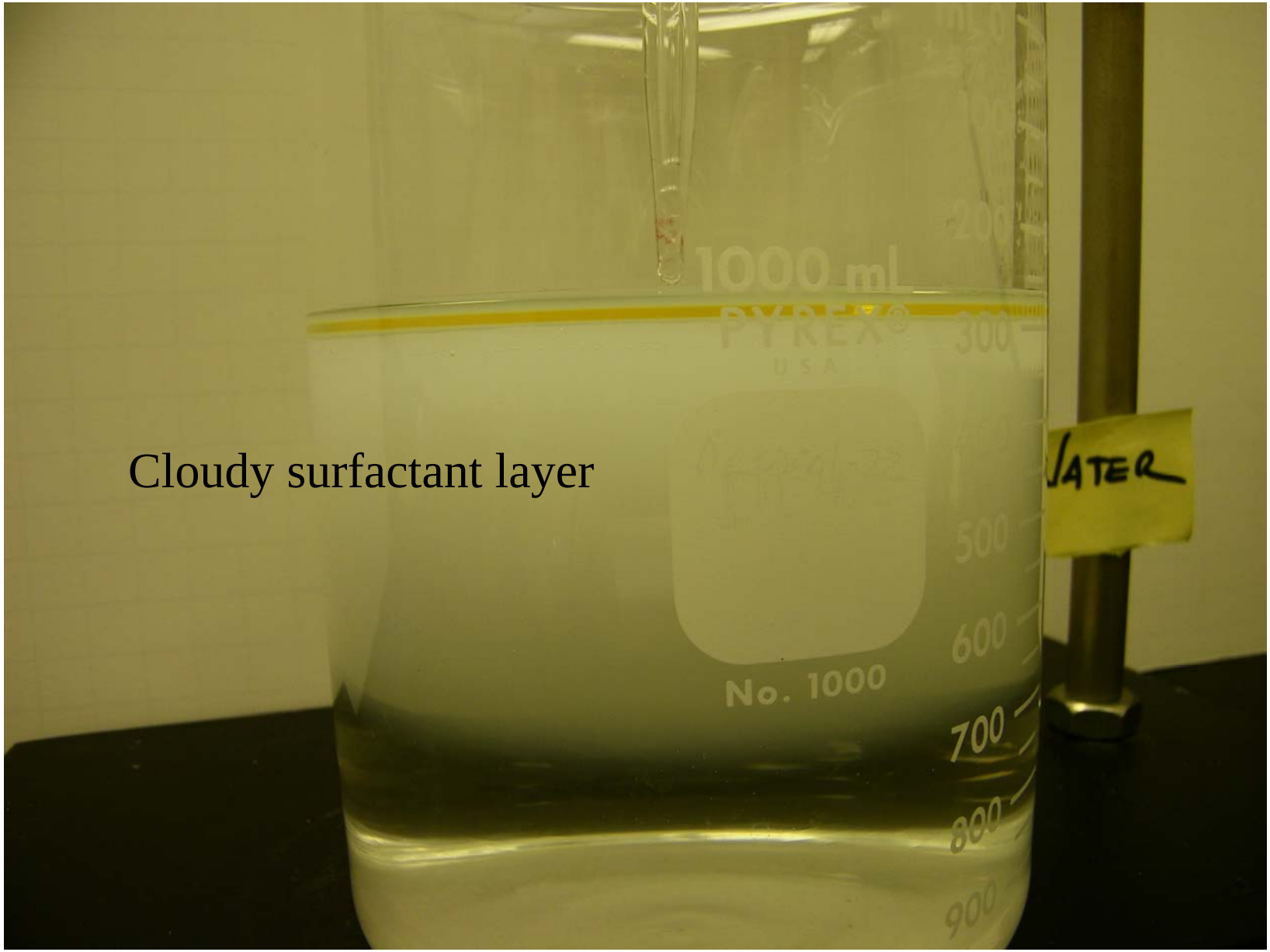
- Dyed Water Added to E85
  - Initially water is absorbed by E85
  - Initially no increase in volume
  - E85 breaks into “gasoline” and aqueous/ethanol phase
- E85 added to water
  - Quiescent E85 jets into water
  - Cloudy surfactant layer over clear water
  - Gasoline accumulates on surface
  - In moving system gasoline “rides” surface

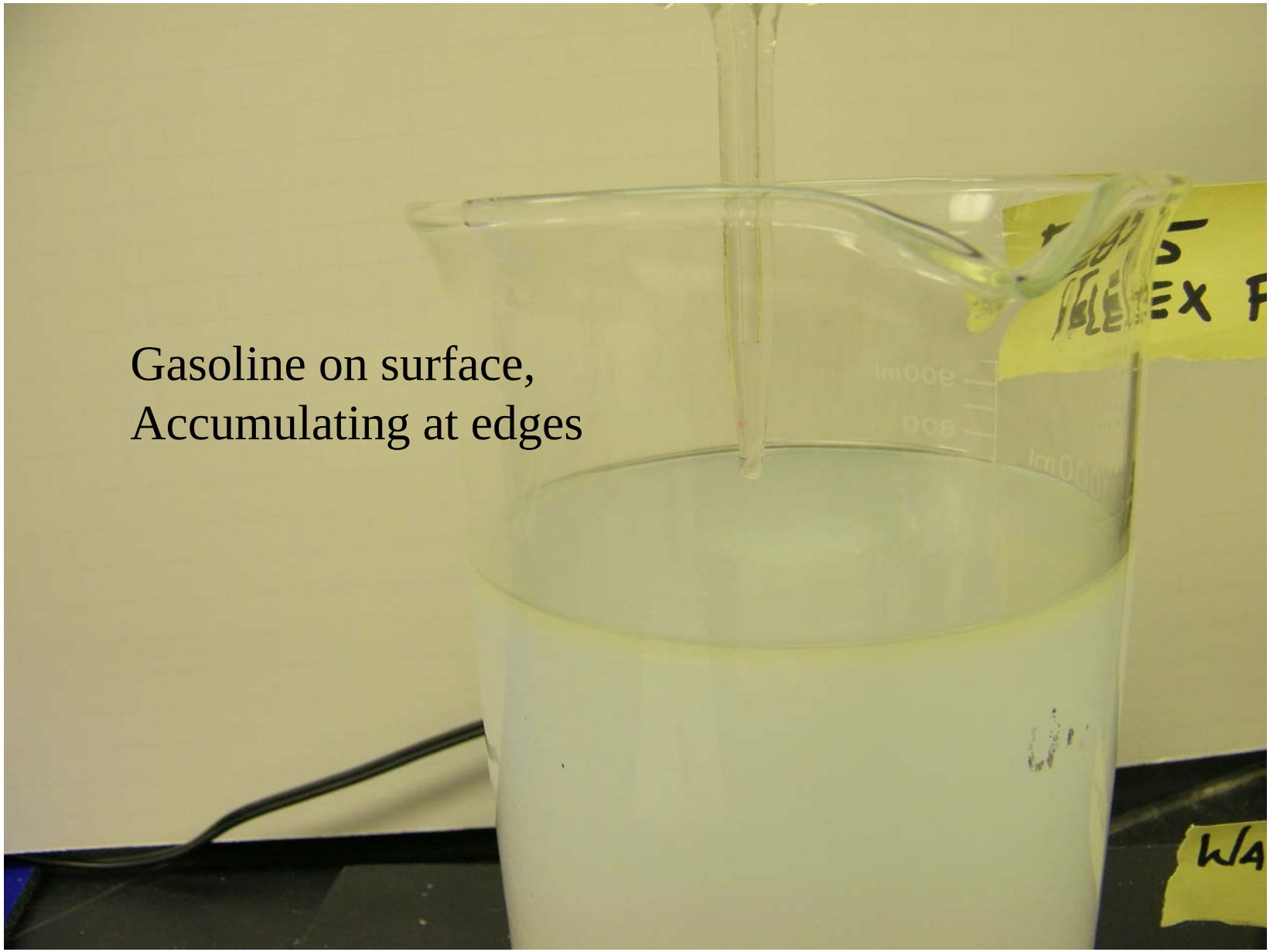
Dyed water and
“gasoline” after
phase separation

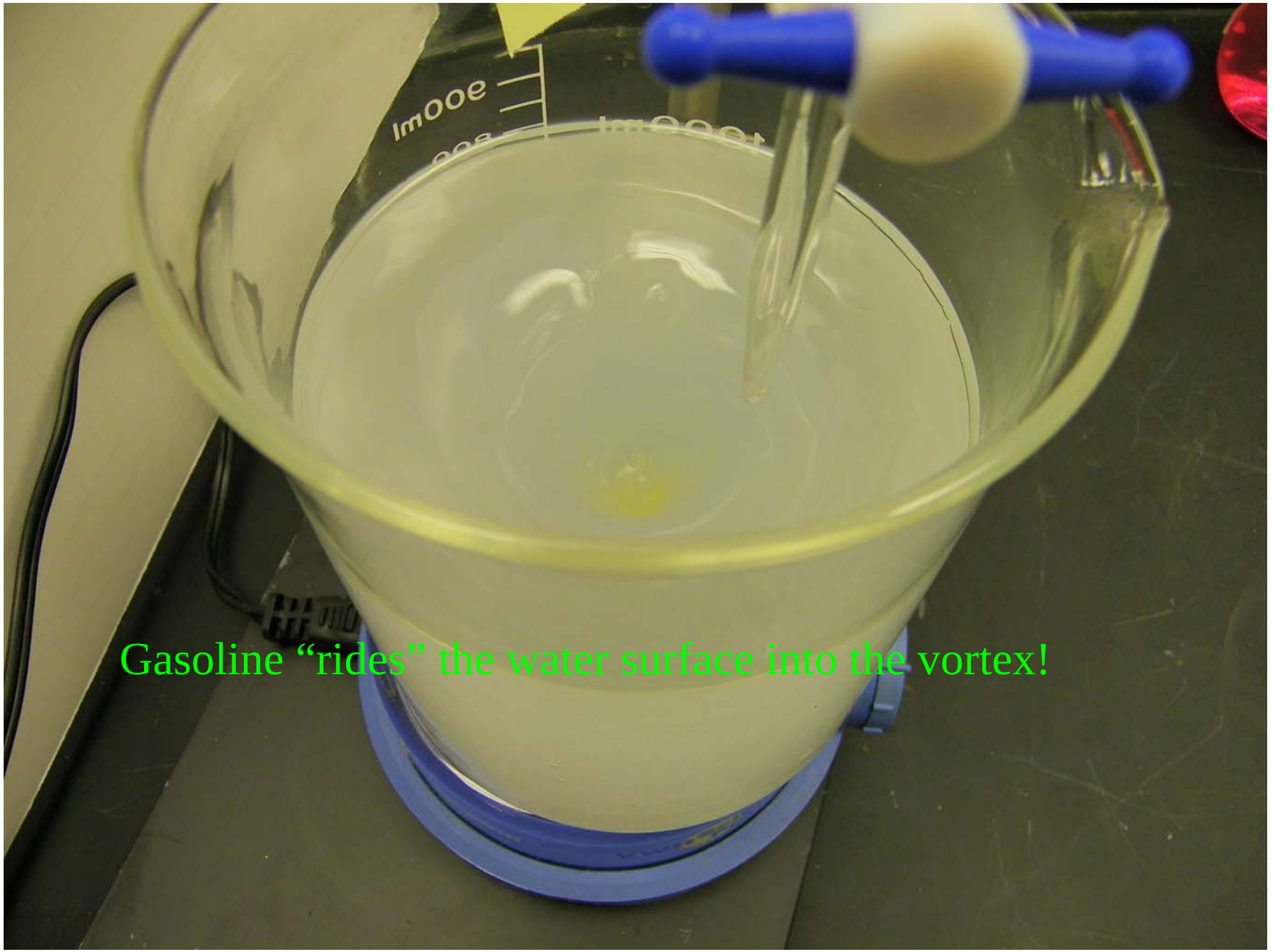


Phase separated
E85 on water

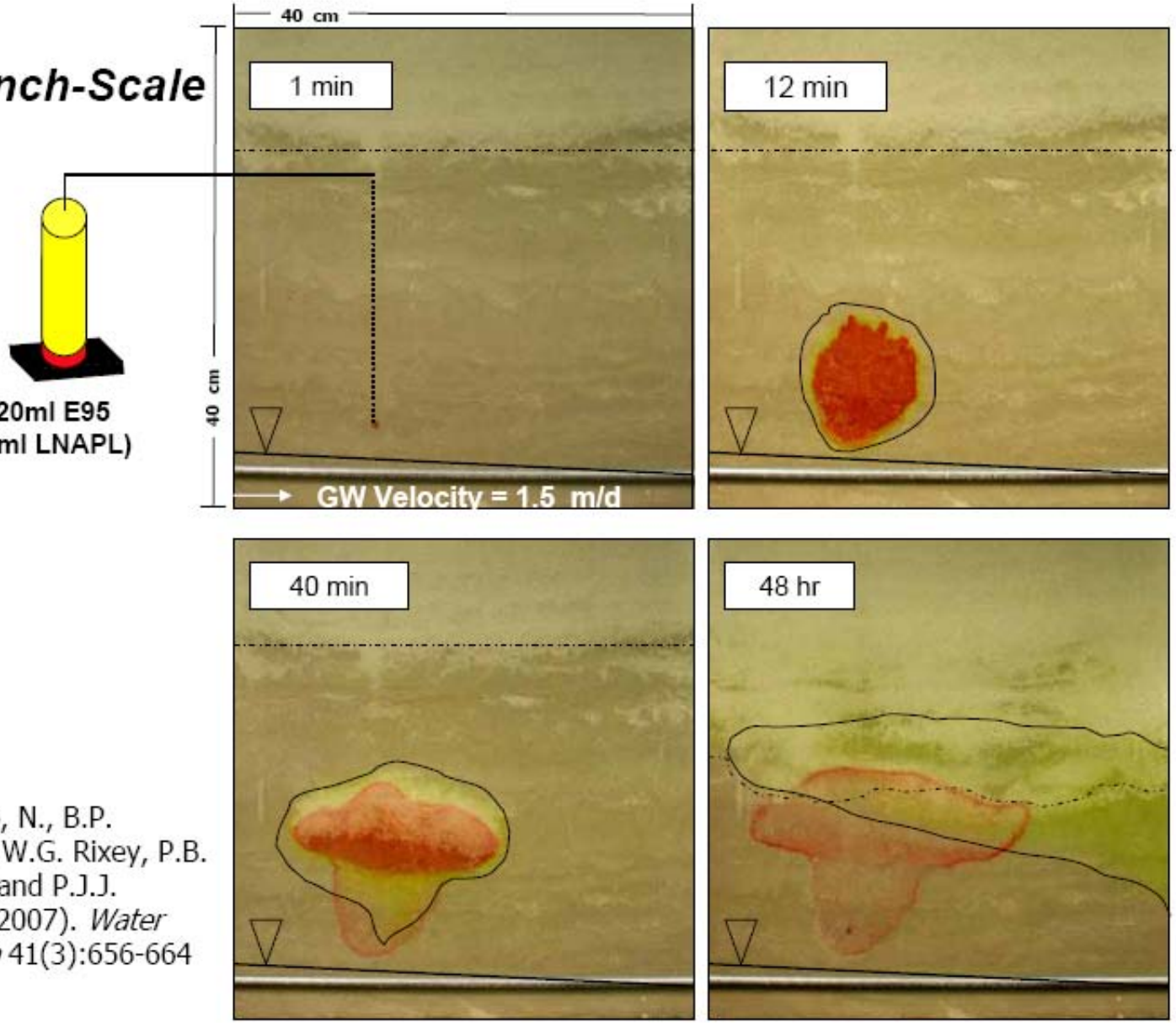






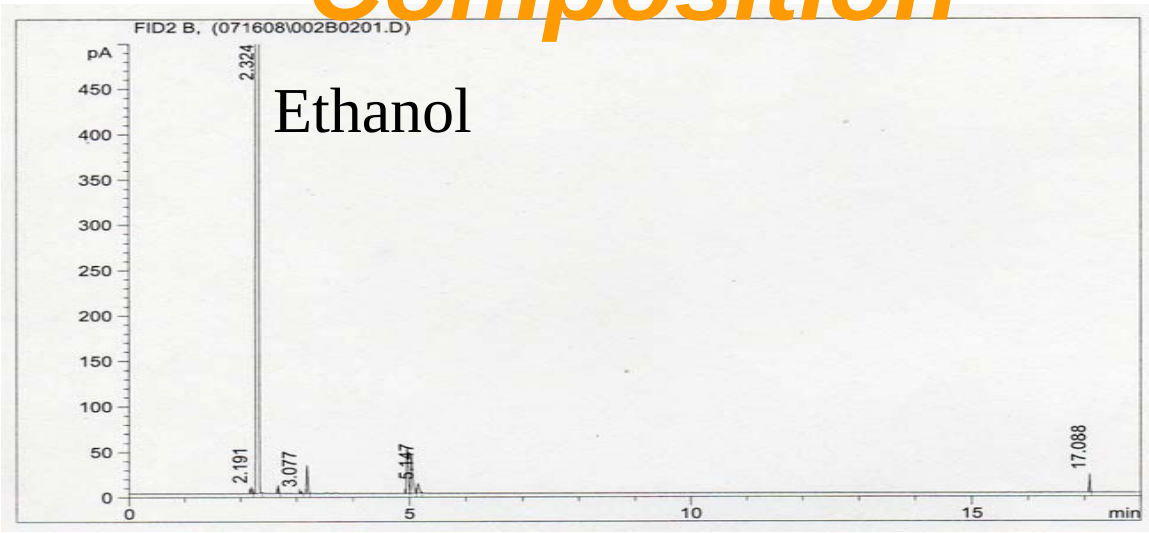


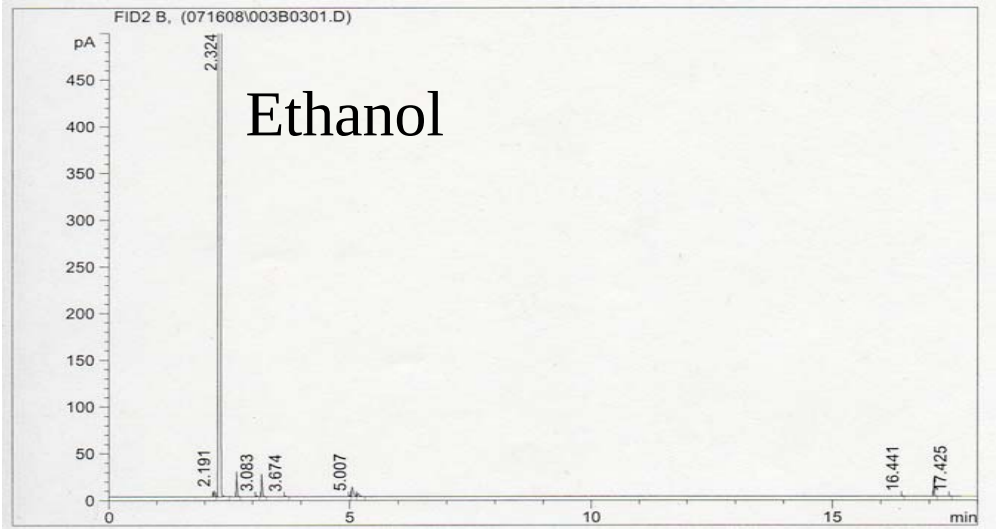
2D Bench-Scale



In Cápiro, N., B.P. Stafford, W.G. Rixey, P.B. Bedient, and P.J.J. Alvarez (2007). *Water Research* 41(3):656-664

Composition





Ethanol Components

Name	Formula	CAS. Number	Concentration (wt. %)	
			Wet Mill Sample	Dry Mill Sample
Water[1]	H_2O	7732-18-15	0.65	0.08
Methanol	CH_4O	67-55-1	0.07	0.06
Ethanol[2]	C_2H_6O	64-17-5	97.89	99.75
1-Propanol	C_3H_8O	71-23-8	0.03	0.08
Isobutyl Alcohol	$C_4H_{10}O$	78-83-1	0.10	0.08
2-Methyl 1-Butanol	$C_5H_{12}O$	137-32-6	0.06	0.01
3-Methyl 1-Butanol	$C_5H_{12}O$	123-51-3	0.21	0.02
Ethyl Acetate	$C_4H_8O_2$	141-78-6	0.02	--
1,1-Diethoxyethane	$C_6H_{14}O_2$	105-57-7	0.28	--

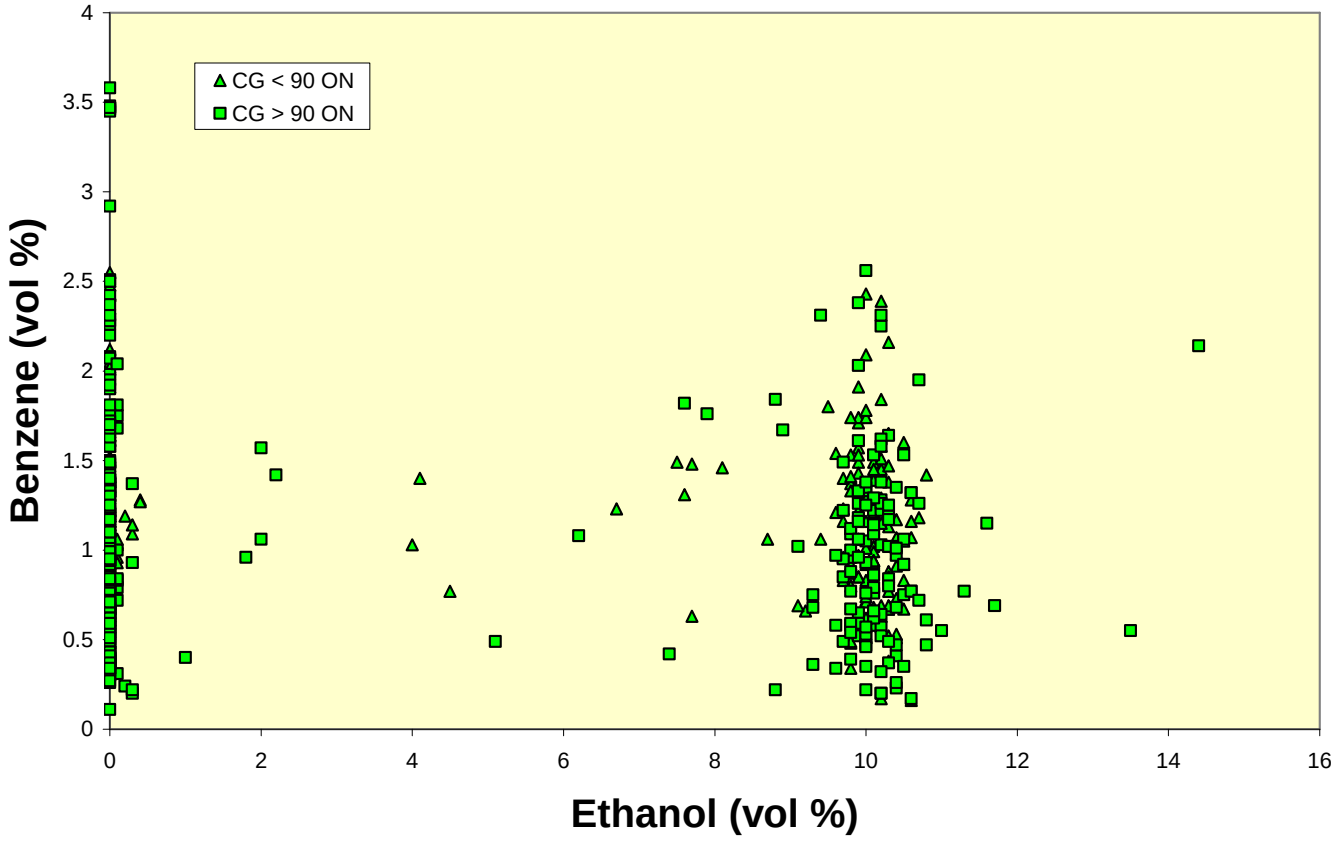
[1] Determined by Karl Fischer titration

[2] Determined by remainder of other compounds

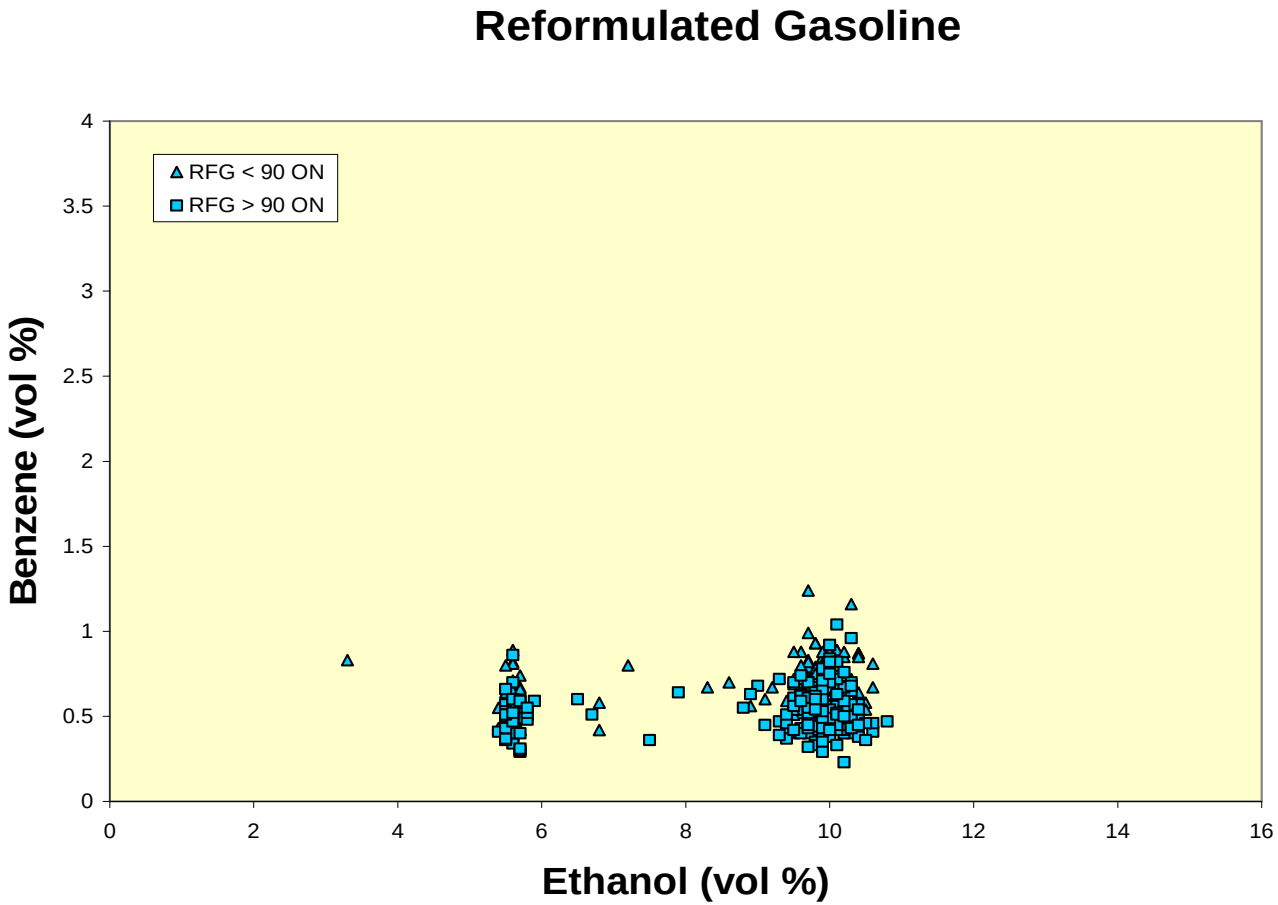
Observed Ethanol Concentrations in Gasoline

Northrop-Grumman (successor to NIPER) Bartlesville, Oklahoma Summer 07

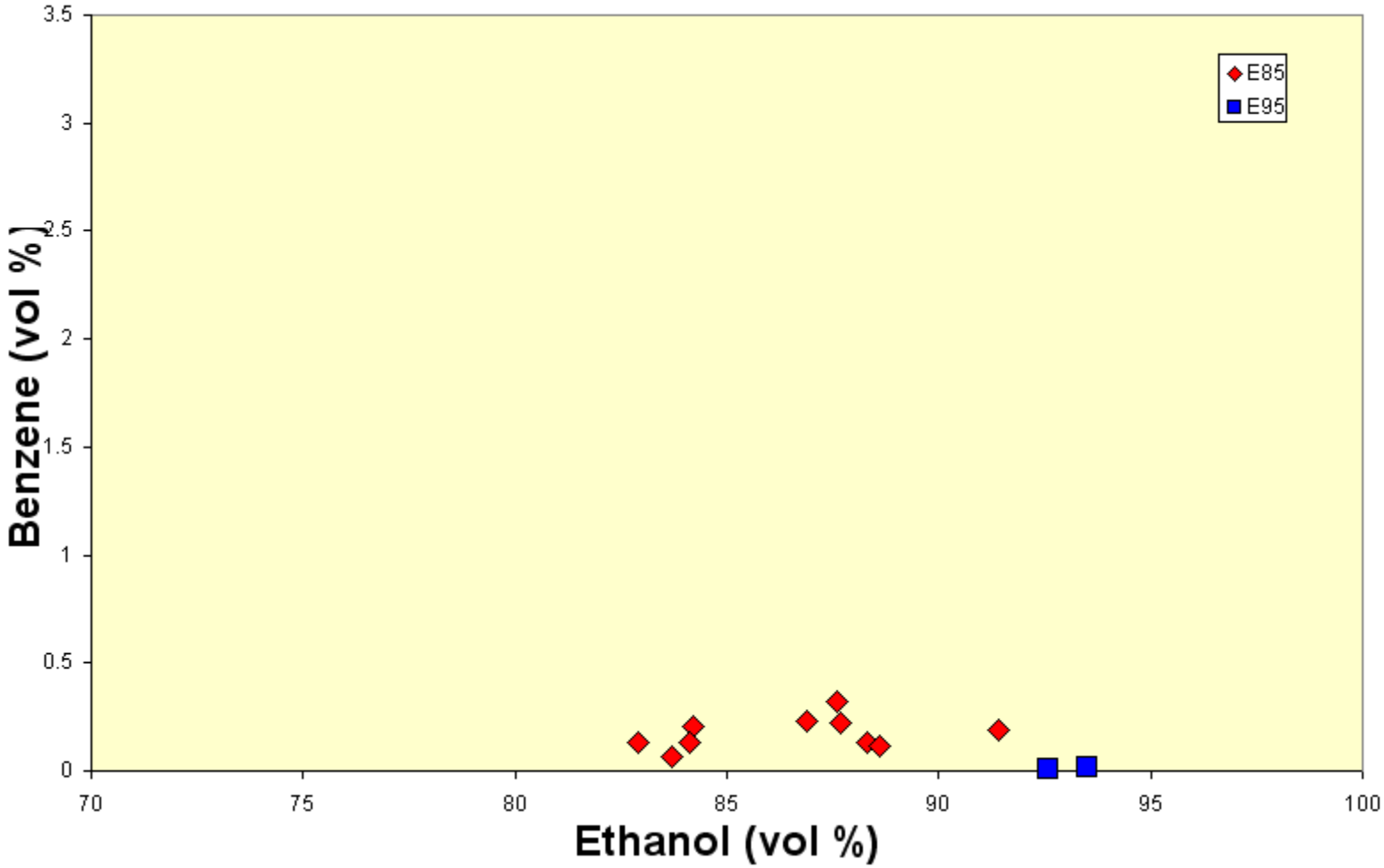
Conventional Gasoline



Northrop-Grumman (successor to NIPER) Bartlesville, Oklahoma



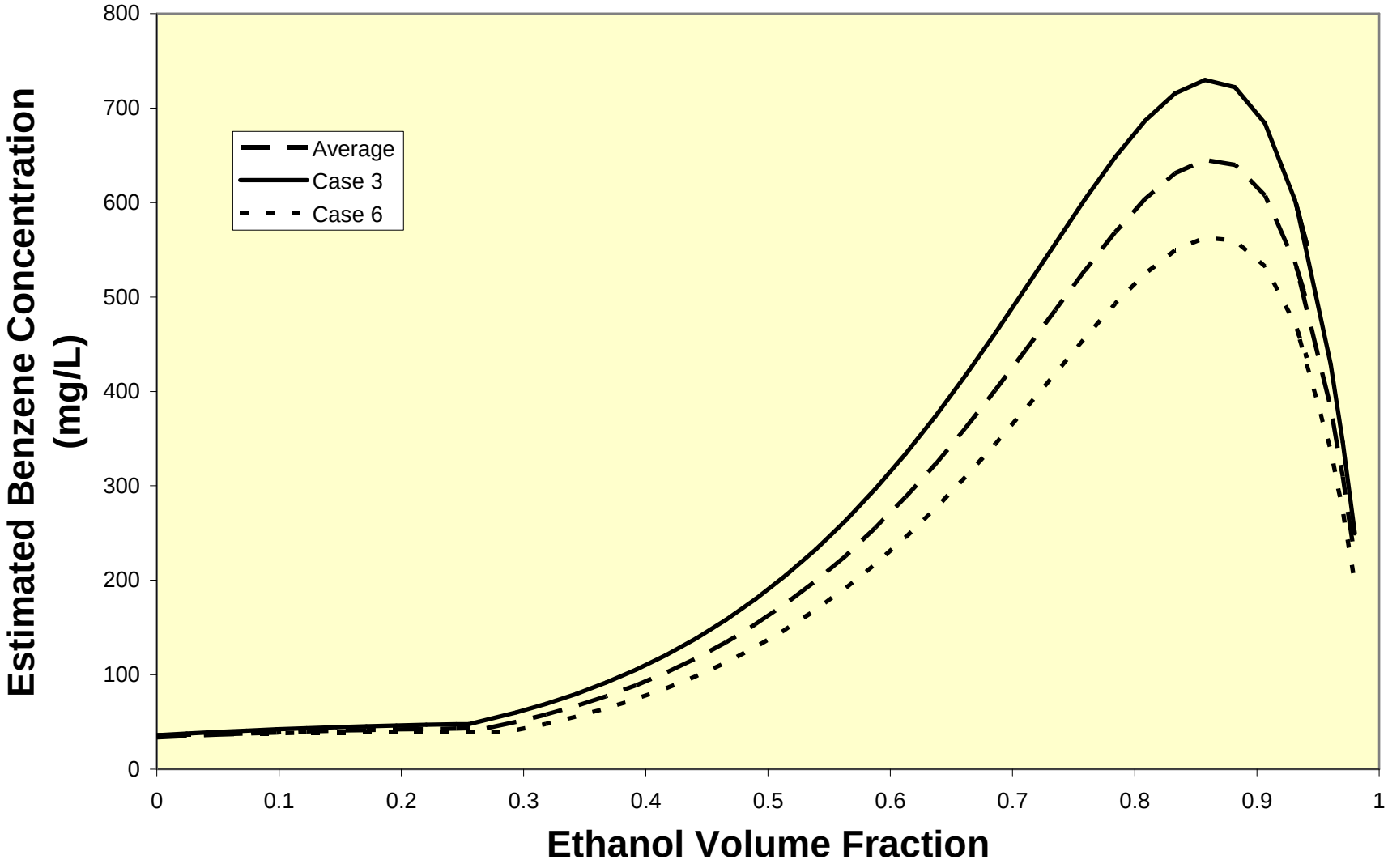

E85
TM
85% Ethanol
11
E-85
MINIMUM
85%
ETHANOL
$
Price per gallon
All taxes included
Ethanol
PRESS


E85
E95
Benzene (vol %)
Ethanol (vol %)
3.5
3
2.5
2
1.5
1
0.5
0
70
75
80
85
90
95
100

Cosolubility

- Ethanol increases the aqueous solubility of petroleum hydrocarbons
  - Dependent on
    - Ethanol concentration in water
    - Petroleum hydrocarbon concentration in gasoline
  - Theory developed by Heerman and Powers, 1998
    - Example:
      - Gasoline containing 1% benzene, mixed with denatured alcohol
      - Alcohol denatured with gasoline containing 1% benzene
      - Benzene mass not limiting

Estimated Benzene Concentration



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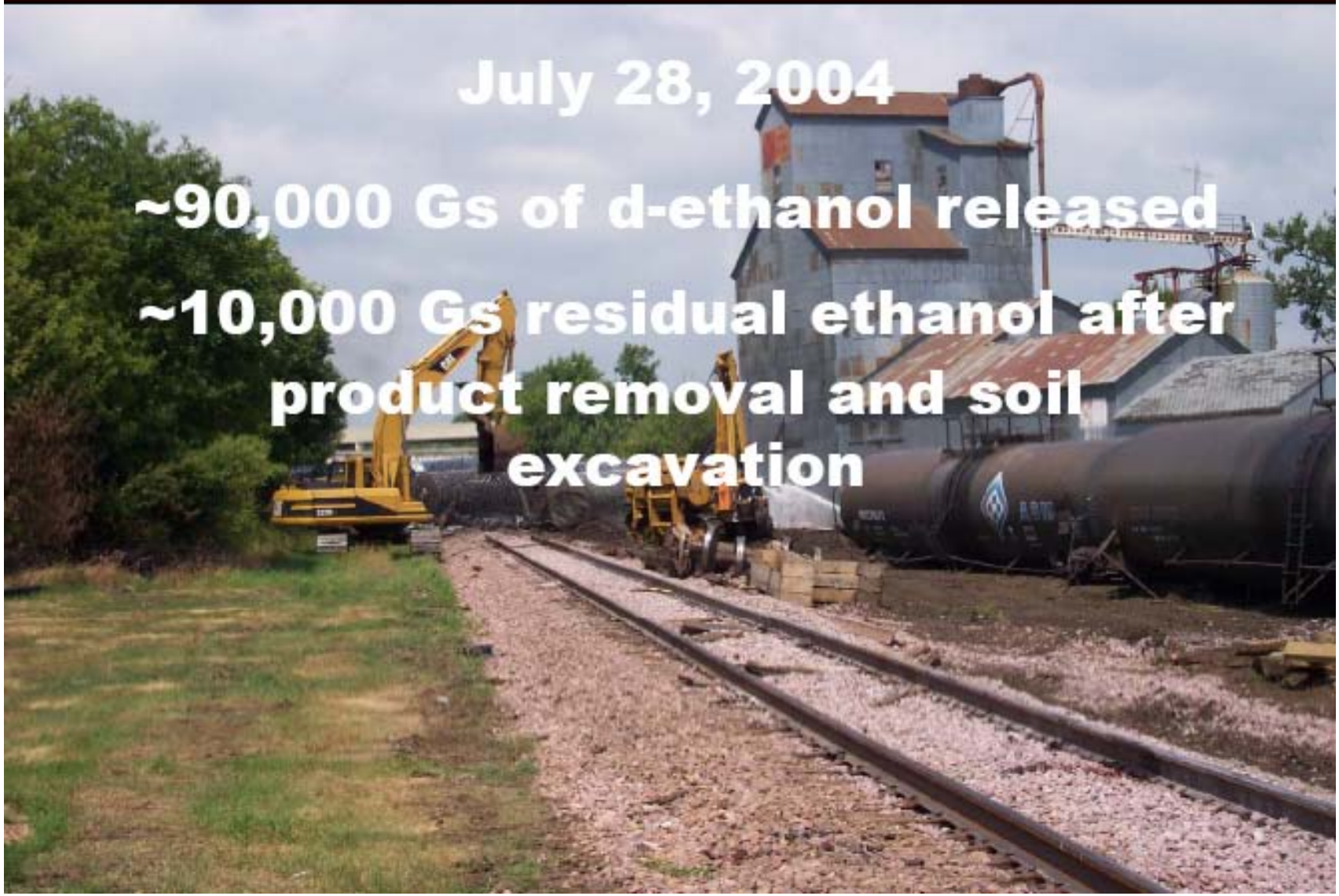
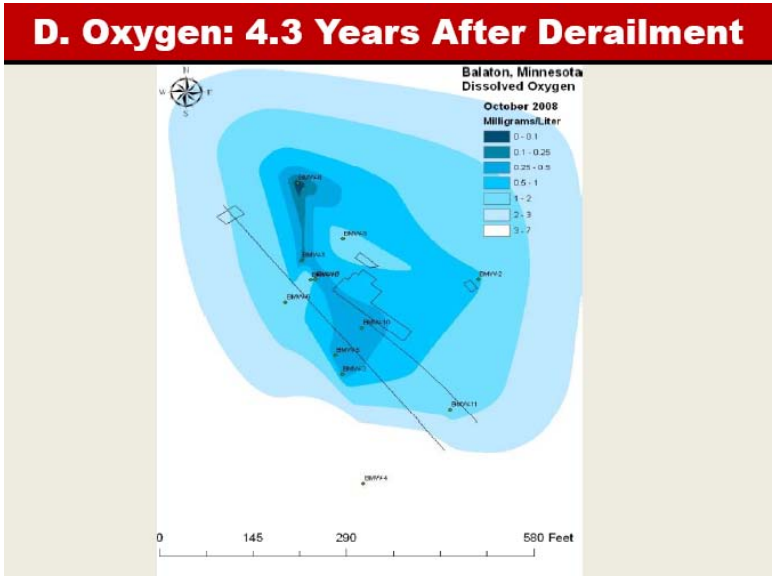
Spill to Land, Info. Courtesy of Dr. Roy Spalding, U of Nebraska

Balaton, Minnesota

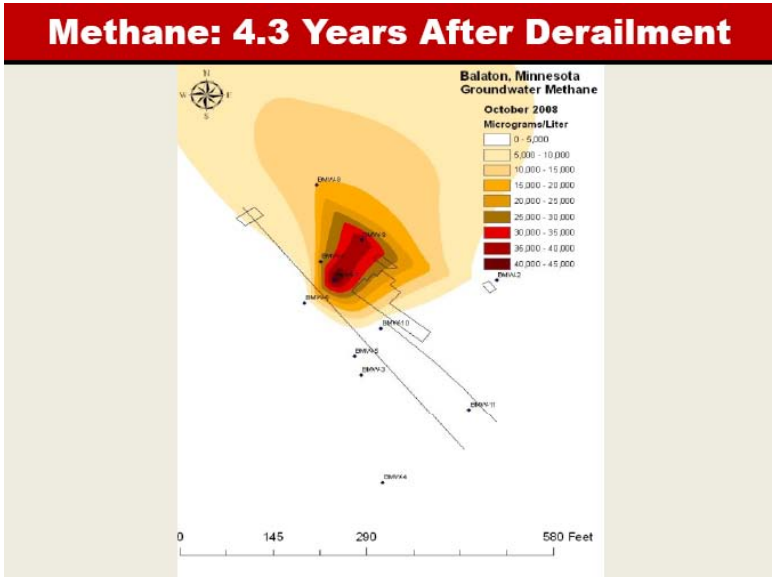
Balaton, Minnesota



D. Oxygen: 4.3 Years After Derailment

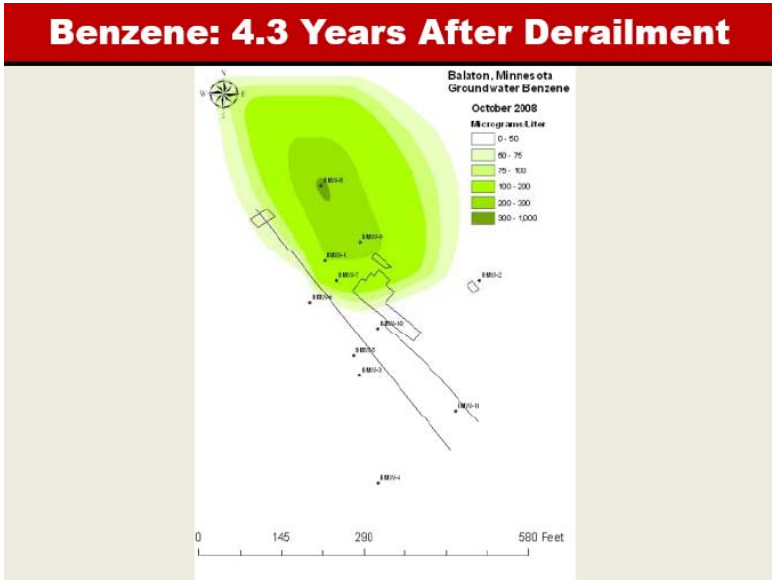


Methane: 4.3 Years After Derailment



- Long delay in ground water impact
- Ethanol hanging up in vadose zone for undetermined reasons
- Methane at water solubility
- Similar behavior to two other sites under investigation

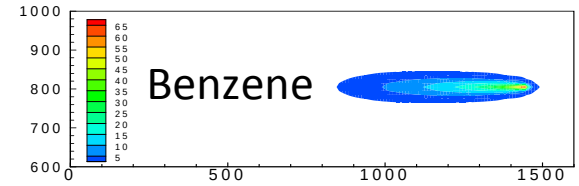
Benzene: 4.3 Years After Derailment

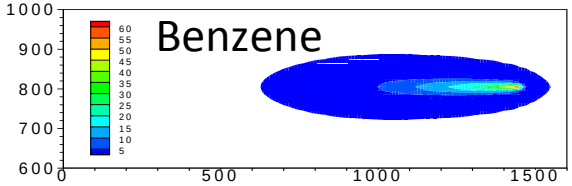


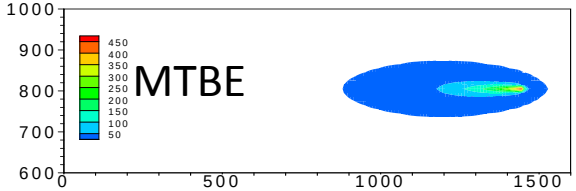
E10 Releases to Land

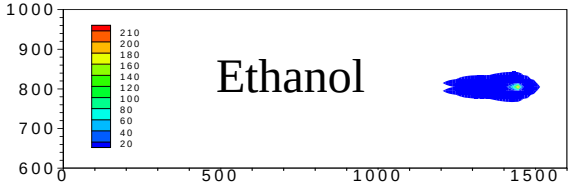
- Formation of groundwater plumes
- Biotransformation of ethanol causes extension of BTEX plumes
  - Order of 2x length
- Simulation (next slide) requires accounting for electron acceptors/donors: O_2, NO_2, Fe^{+++}, SO_4, CO_2

Modeled RFG (w MTBE) vs E10









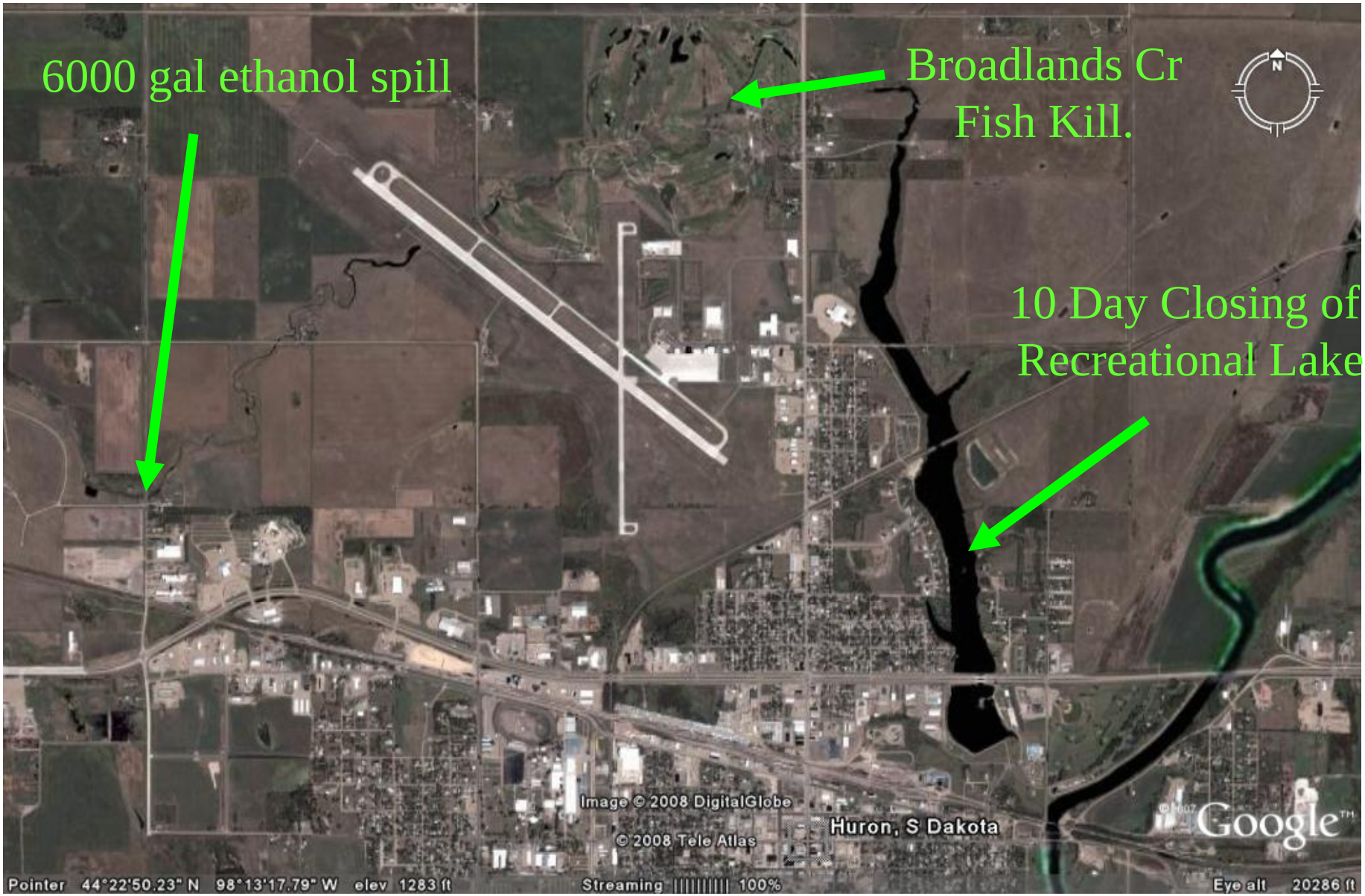
Spill to Broadland Creek May 17, 2008 Info. Courtesy of Kim McIntosh, SD-DENR

- Dry Mill plant in Huron, South Dakota
- Transfer line hose broke during filling of tank car
- Approx. 6000 gallons of ethanol released
- 100s of fish killed in creek
  - Minnows, bullhead, carp
- Recreational lake closed for 10 days

Response

- Deploy boom and aerators 3 mi downstream
- Daily check of temperature, dissolved oxygen, pH, conductivity
  - 5/20/2008 am D.O. 0.2 to 10.6 mg/L
  - 5/21/2008 am D.O. 0.3 to 5.4 mg/L
  - 5/21/2008 pm D.O. 1.0 to 7.6 mg/L
  - 5/22/2008 am D.O. 1.0 to 6.0 mg/L
  - 5/22/2008 pm D.O. 1.2 to 5.7 mg/L (downstream)
  - 5/22/2008 pm D.O. 0.4 to 8.0 mg/L
  - 5/23/2008 am D.O. 1.0 to 6.6 mg/L (upstream)
  - 5/23/2008 pm D.O. 0.3 to 5.8 mg/L
  - 5/23/2008 pm D.O. 0.1 to 5.6 mg/L (downstream)
  - 5/24/2008 am D.O. 0.2 to 5.9 mg/L
  - 5/27/2008 am D.O. 1.0 to 8.0 mg/L
- Moved aerators as plume moved downstream

Huron, S.D., May 17, 2008



Comments

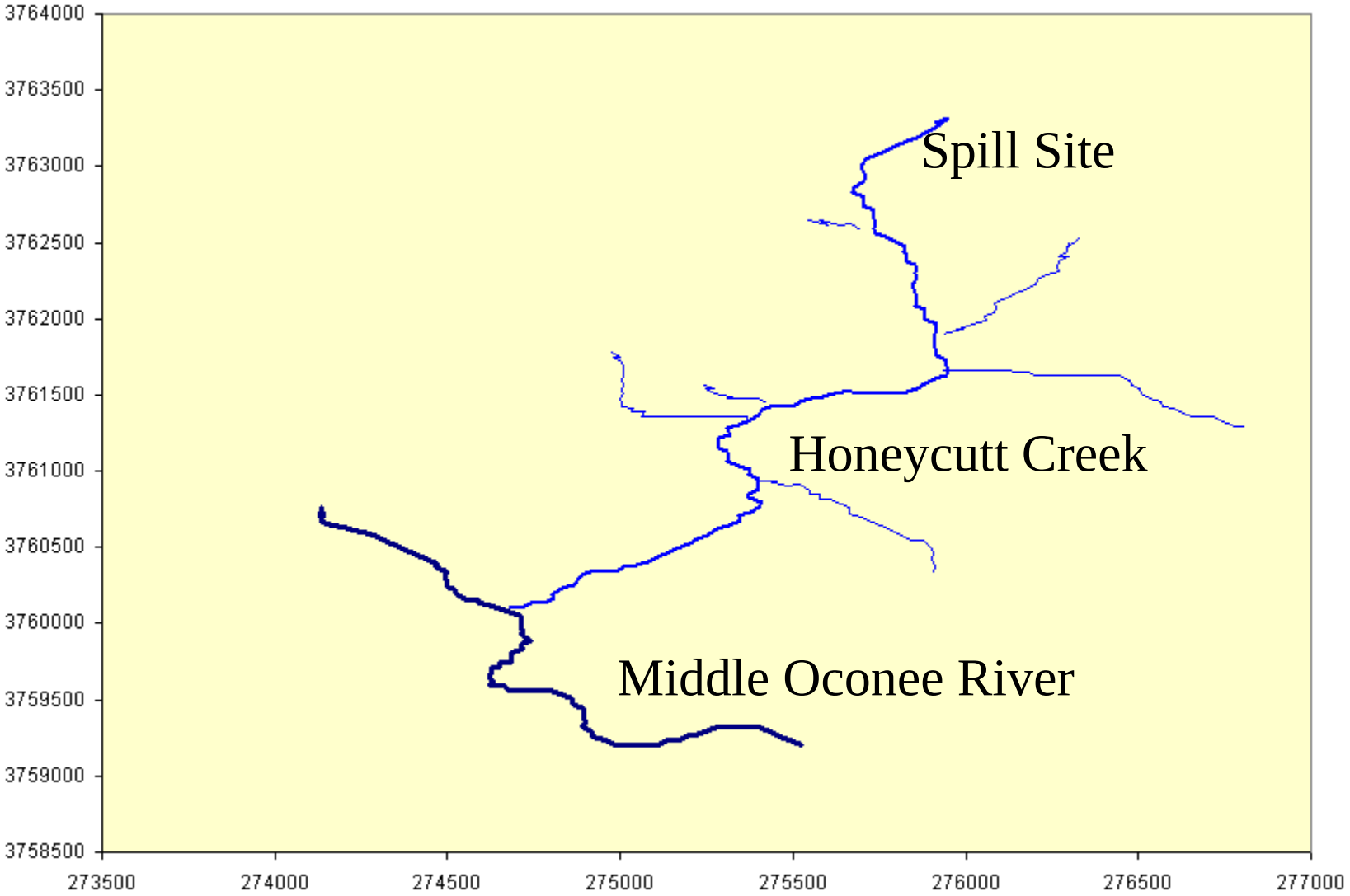
- No gasoline obeserved
- 4 water samples for VOCs 5/21
  - BTEX, tri-methylbenzenes, ethanol, methanol
  - Most results ND, one sample ethanol at 6800 ppb
- Generally increased D.O. by 5/27/2008

Honeycutt Creek/Middle Oconee River Athens, Georgia

- Scenario:
  - Small creek that drains area near fuel terminal
  - Oil spill in 2003 (14K gallons mixed gasoline, diesel, waste oil)
  - Approx 3 miles downstream intercepts Middle Oconee River
  - Drinking Water Intake for Athens, Georgia

Data

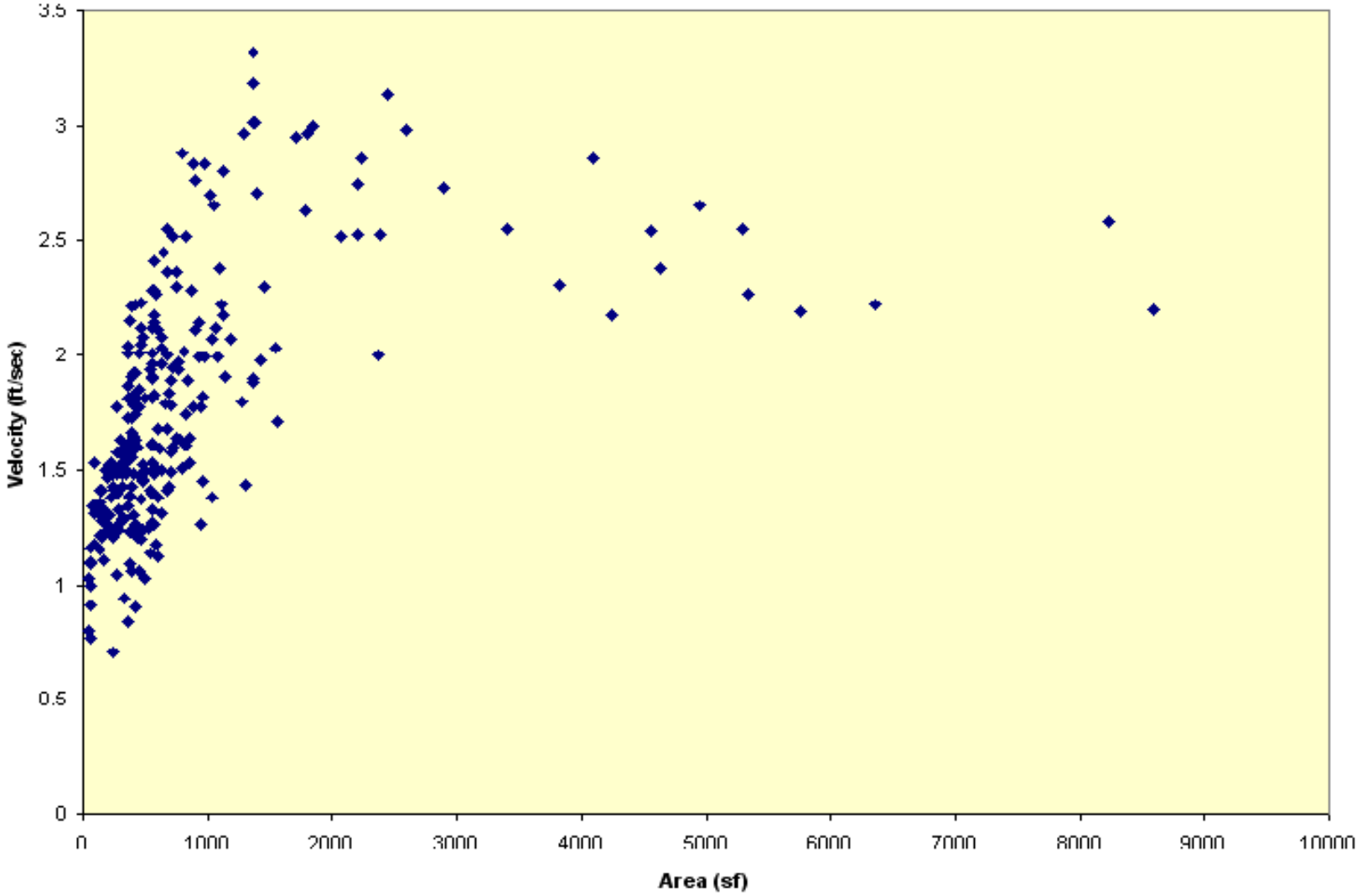
- Hypothetical Release Scenario
- Composition and Phase Separation Data from Laboratory
- Stream network geometry from USGS DEMs
- Flows
  - Honeycutt Creek flow and geometry from a day's work
  - Middle Oconee River flows and discharge stage from USGS gages



USGS Station Geometry

- Depth and Width of River/Streams are necessary
  - Determines dilution of dissolved chemicals
- Velocity
  - Determines transport rate
- USGS surveys stations each year
  - Continual change due to scouring and sedimentation
  - Our protocol is to use the latest data for a given channel size

USGS Velocity/Area Data



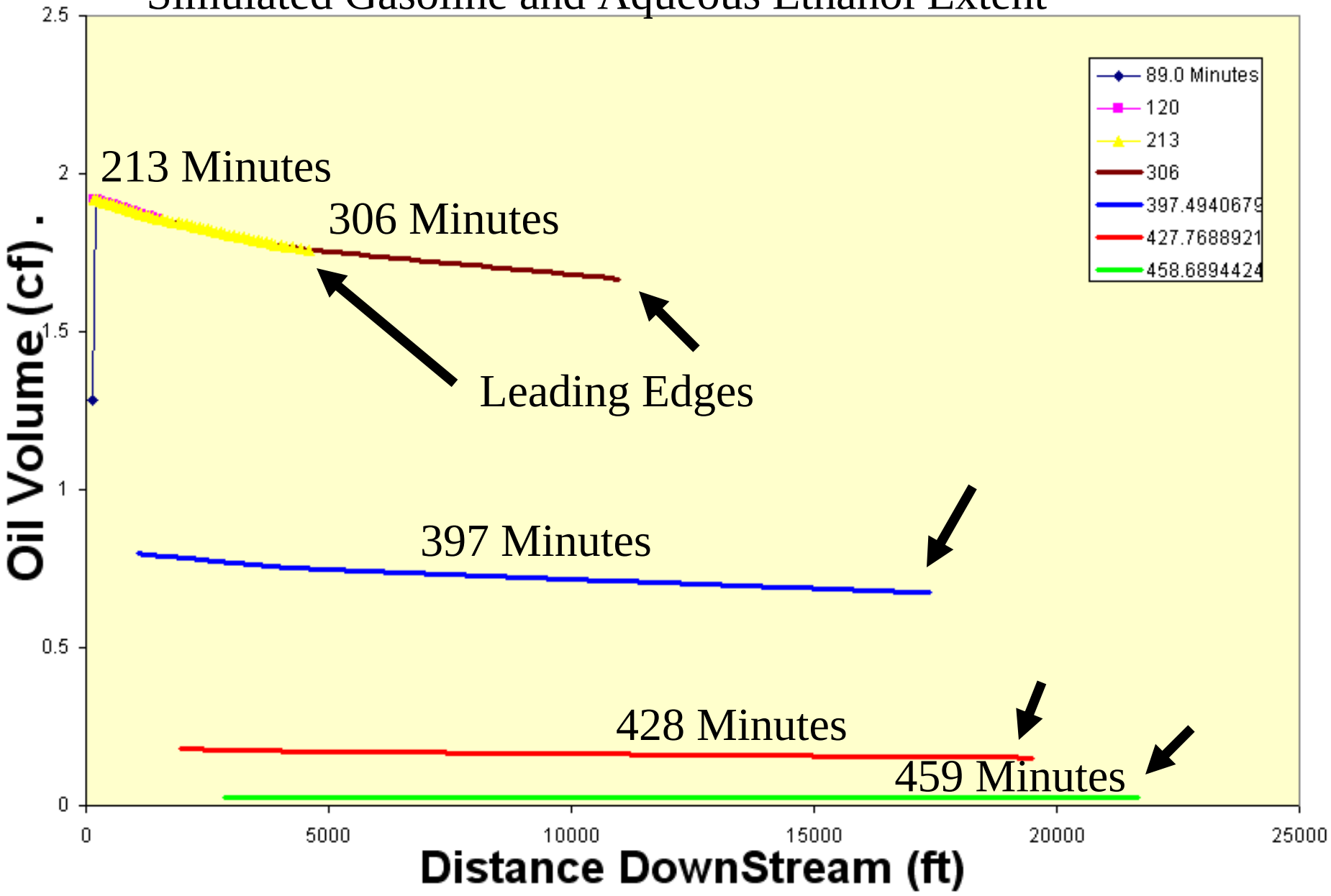
Model Approach

- Use measured flows to drive Lagrangian transport model
  - Flow ~ spill rate
    - Assume complete mixing
    - Adjust velocity via Manning formula
  - Flow >> spill rate
    - Mixing zones defined from turbulent diffusion coefficients

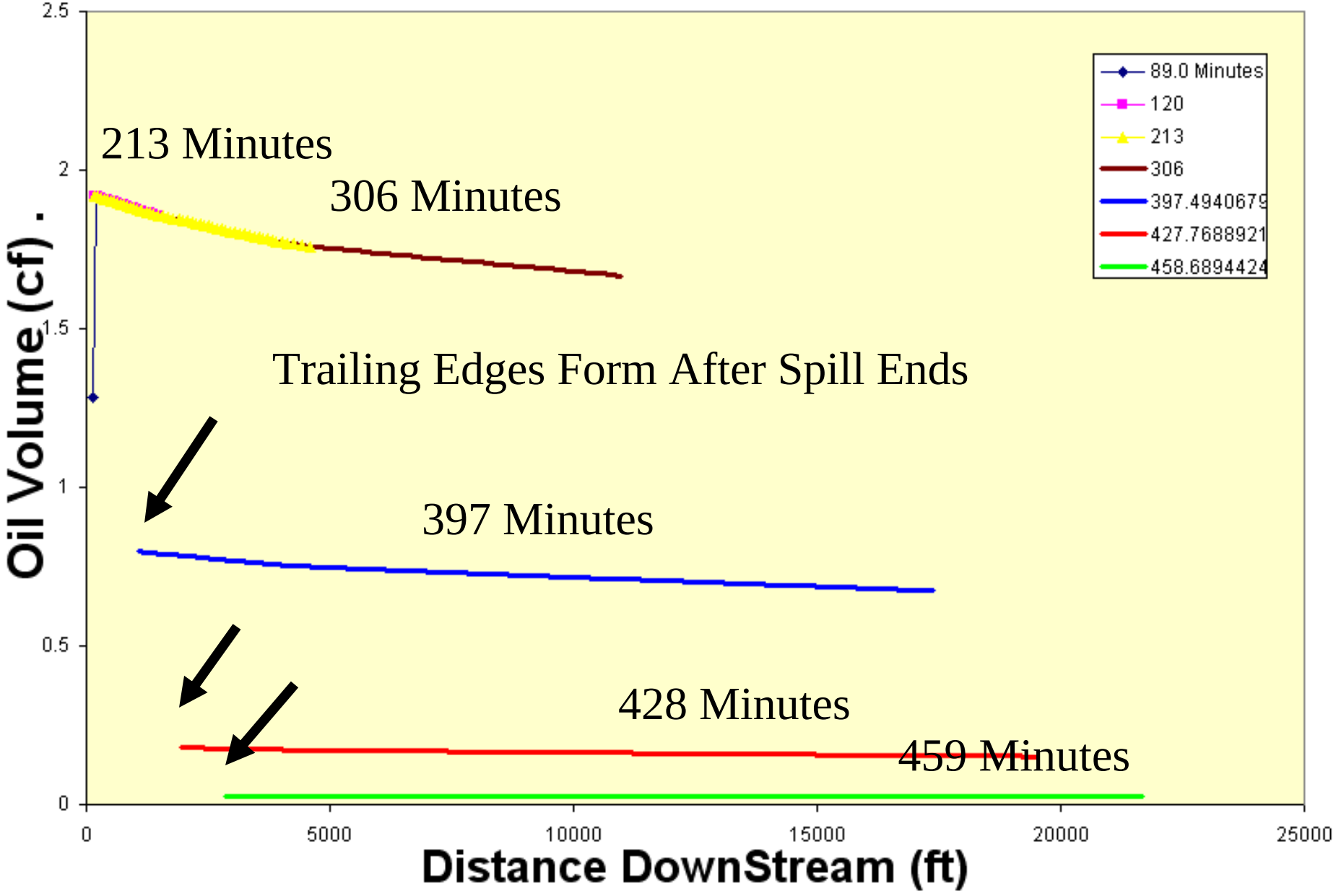
Spill Chacteristics

- 10,000 Gal Spill of E-85
- 5 hour spill duration

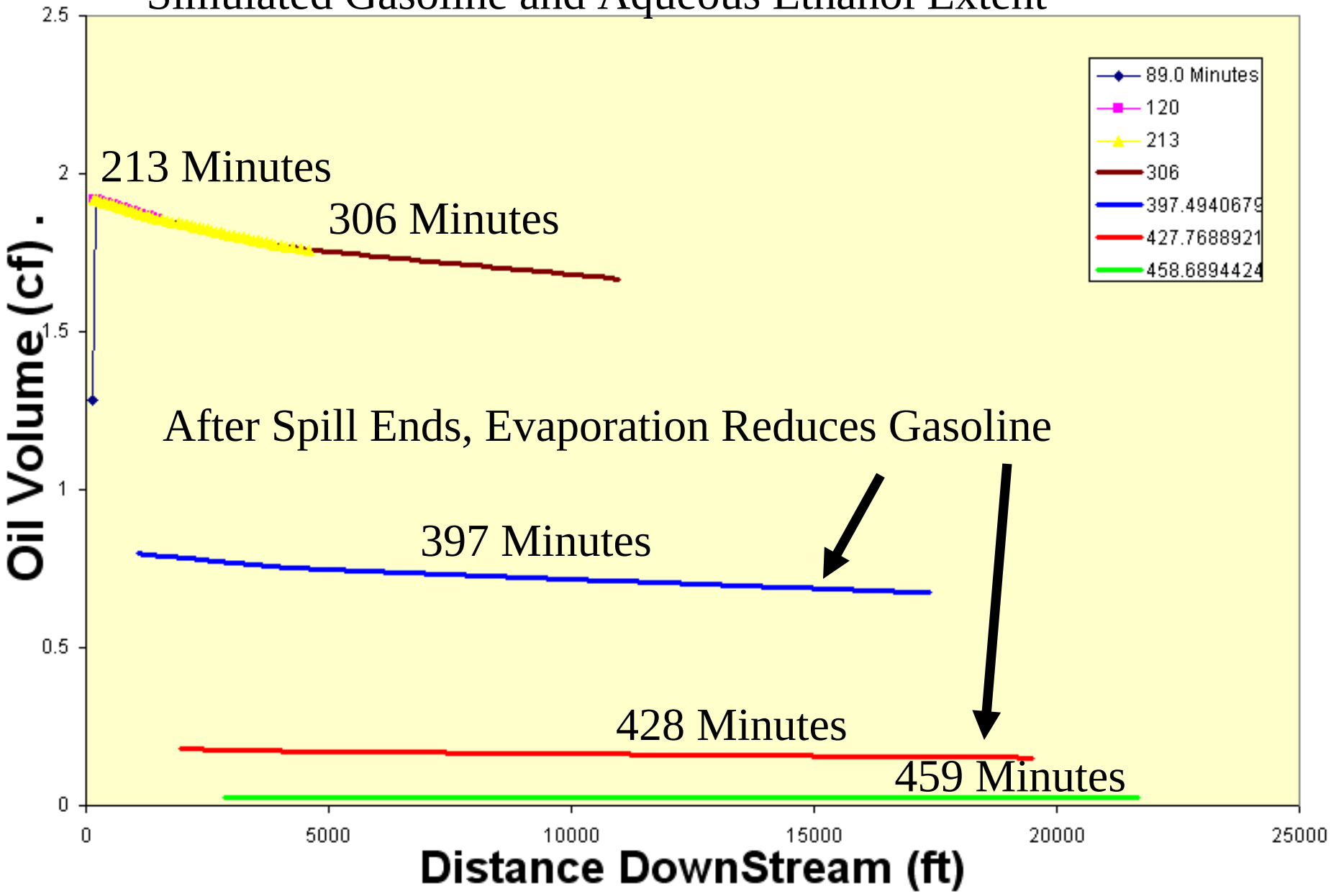
Simulated Gasoline and Aqueous Ethanol Extent



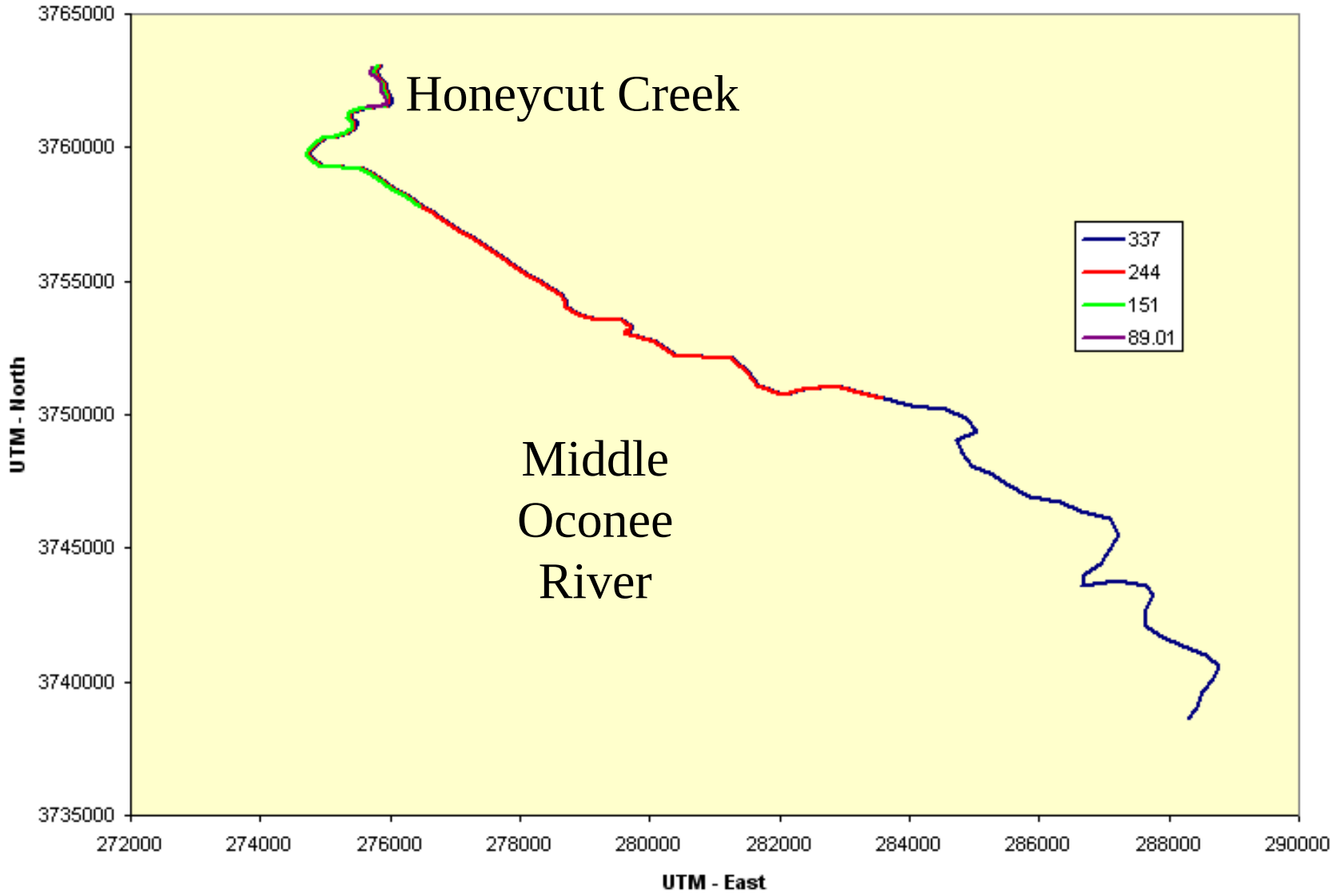
Simulated Gasoline and Aqueous Ethanol Extent



Simulated Gasoline and Aqueous Ethanol Extent



Oil Slick Extent



Conclusions

- Ethanol rapidly replaced ethers in mid 2006 in reformulated gasoline
- Ethanol is used in about 75% of U.S. gasoline.
- Fuel ethanol contains several impurities including higher molecular weight alcohols
  - 3 to 5 carbon atoms
  - …But at concentrations < 1/4 percent

Conclusions

- E85 and E95 adsorb about 20%-30% of own volume in water before phase separating
  - Fuel Ethanol doesn't phase separate
  - E10 phase separates at about 0.5% water

Conclusions

- Spills of denatured alcohol to land based on three field studies:
  - Hangs up in the vadose zone
  - Methane at max solubility
  - Impacts to ground water delayed
- E10 Releases cause extended BTEX plumes
- Spills to water (Broadlands Ck)
  - No observed gasoline slick from denatured alcohol
  - Loss of dissolved oxygen major impact

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National Exposure Research Laboratory

- Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy.
- Thanks to:
  - Mark Toso, Minnesota PCA,
  - Cheryl Dickson, Northrop-Grumman
  - Kim McIntosh, South Dakota DENR,
  - Dr. Roy Spalding, University of Nebraska,
  - Dr. Illena Rhodes, Shell Global Solutions
- Contact: *weaver.jim@epa.gov*
- EPA report, April 2009:
  - ***Composition and Behavior of Fuel Ethanol, EPA 600/R-09/037***
  - ***from www.epa.gov/athens/publications***