

Composition and Behavior of Ethanol Gasolines

Jim Weaver

US Environmental Protection Agency
National Exposure Research Laboratory
Athens, Georgia

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 $C_nH_{2n+1}OH$ 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

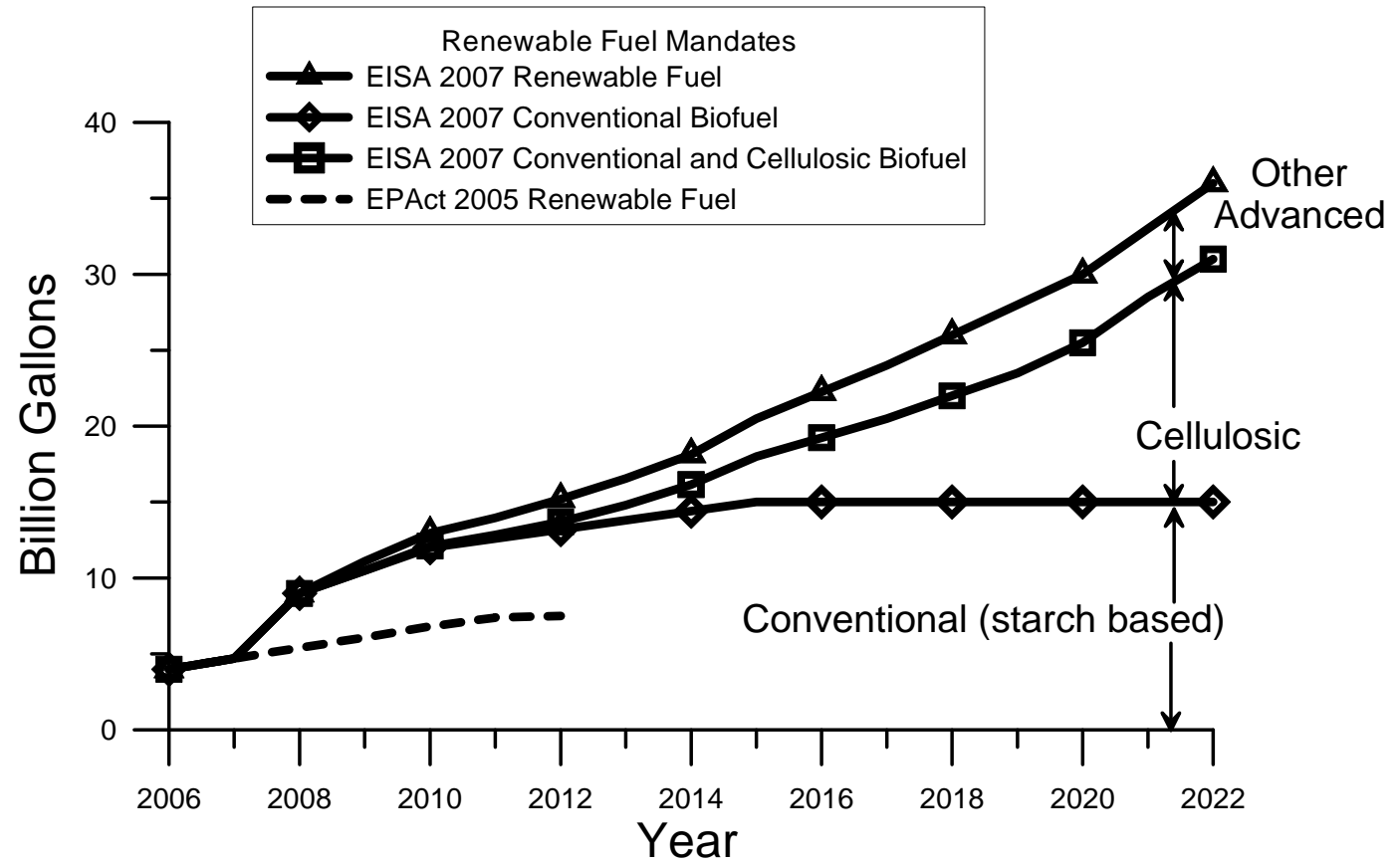
- ASTM also specifies prohibited denaturants:
 - (adverse effects on fuel stability, automotive engines, and fuel systems)
 - hydrocarbons with an end boiling point above 225 °C,
 - methanol not meeting ASTM D1152,
 - pyrroles, turpentine, ketones, and tars.

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

**RESEARCH &
DEVELOPMENT**

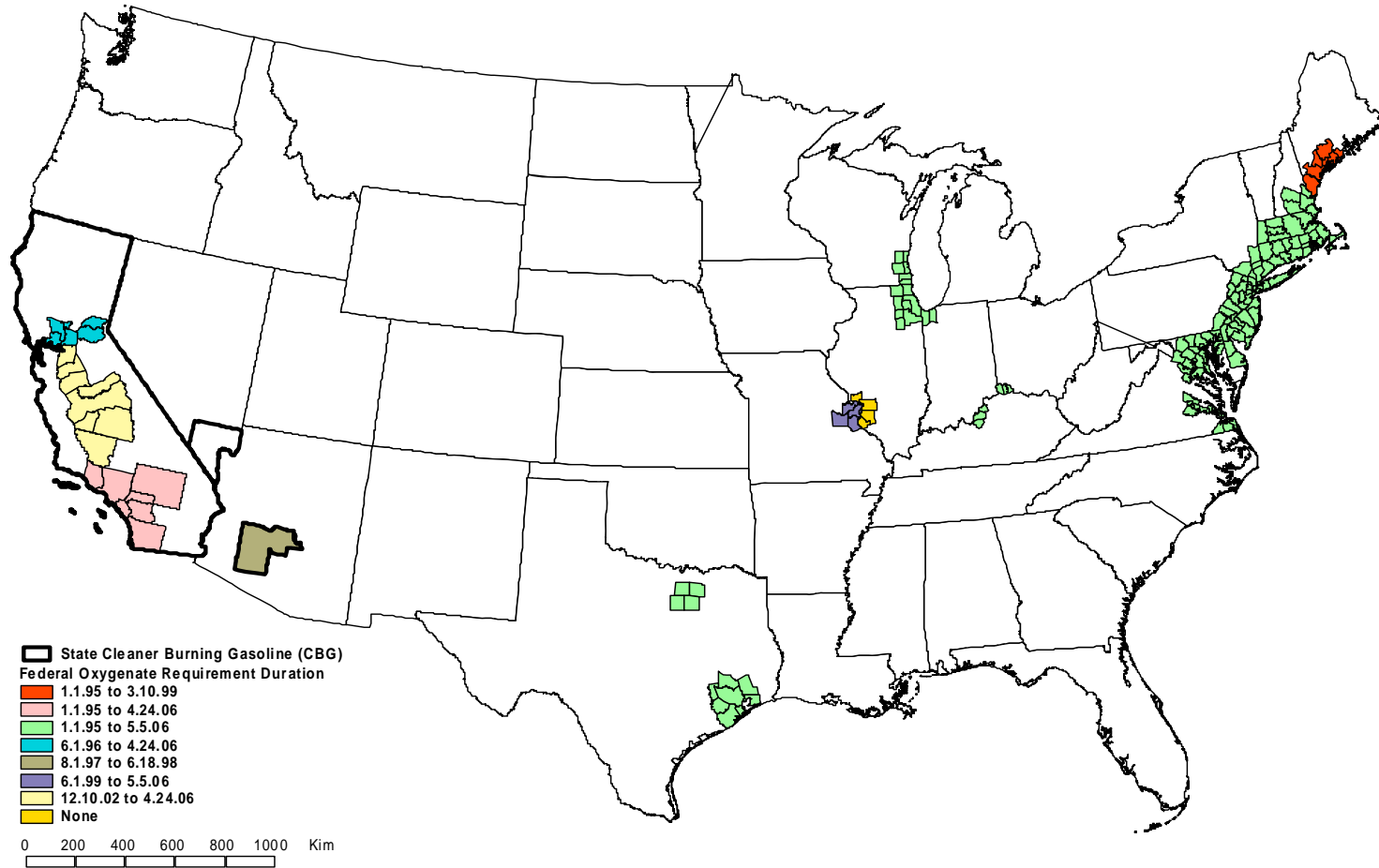
*Building a
scientific
foundation
for sound
environmental
decisions*



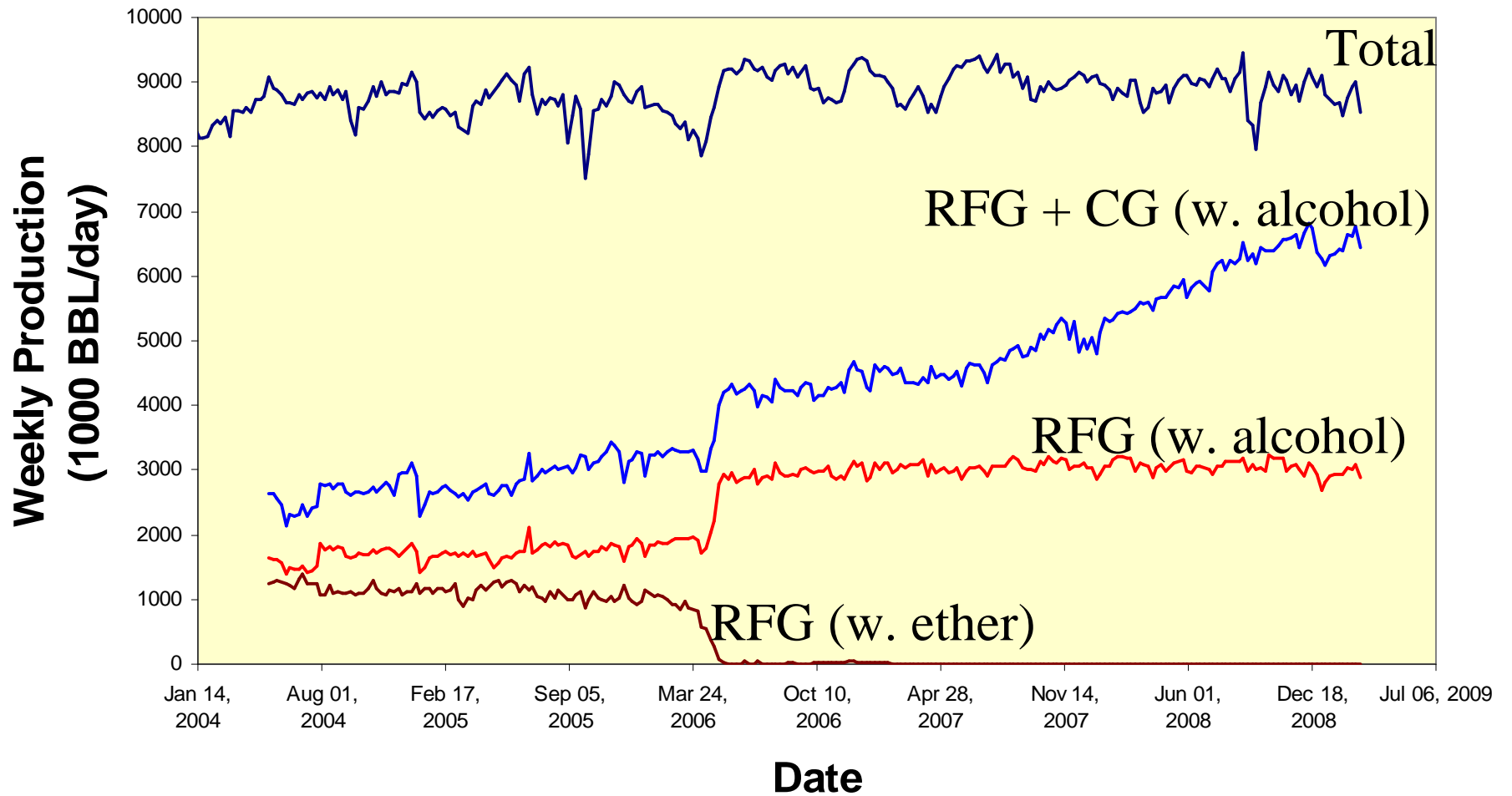
Terminology

- 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



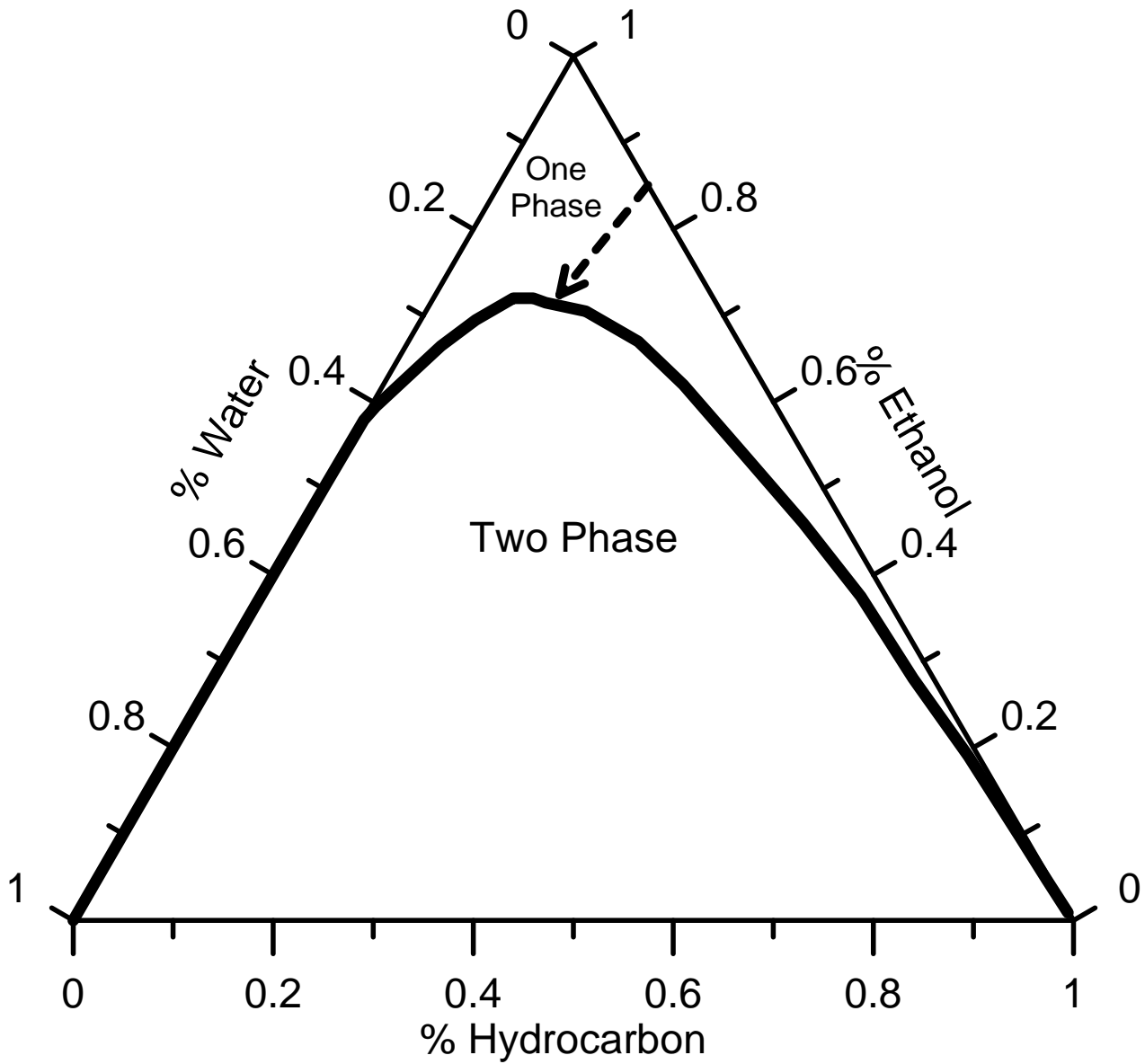
DOE Production Data



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

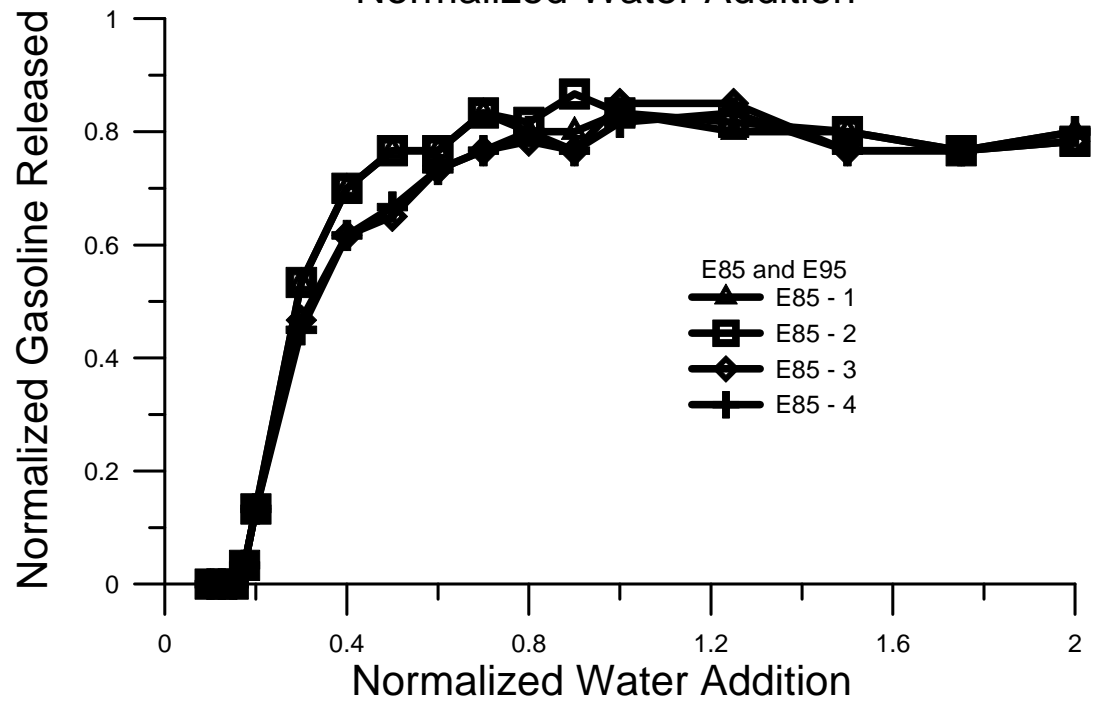
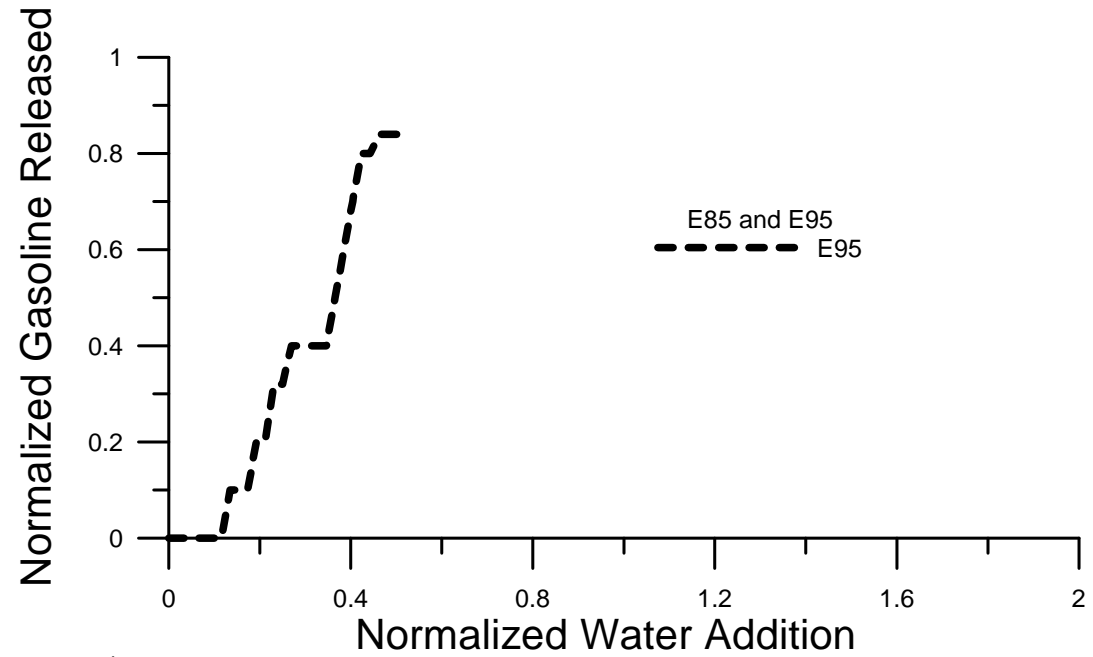




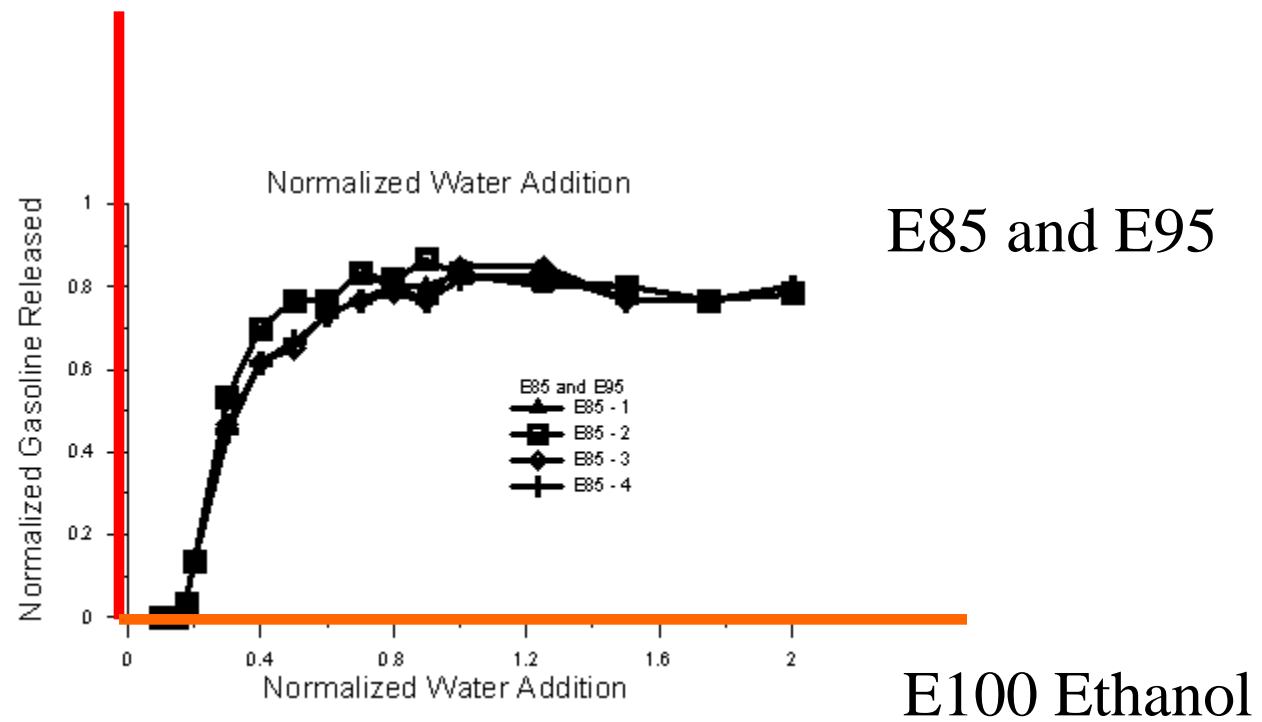


**RESEARCH &
DEVELOPMENT**

*Building a
scientific
foundation
for sound
environmental
decisions*

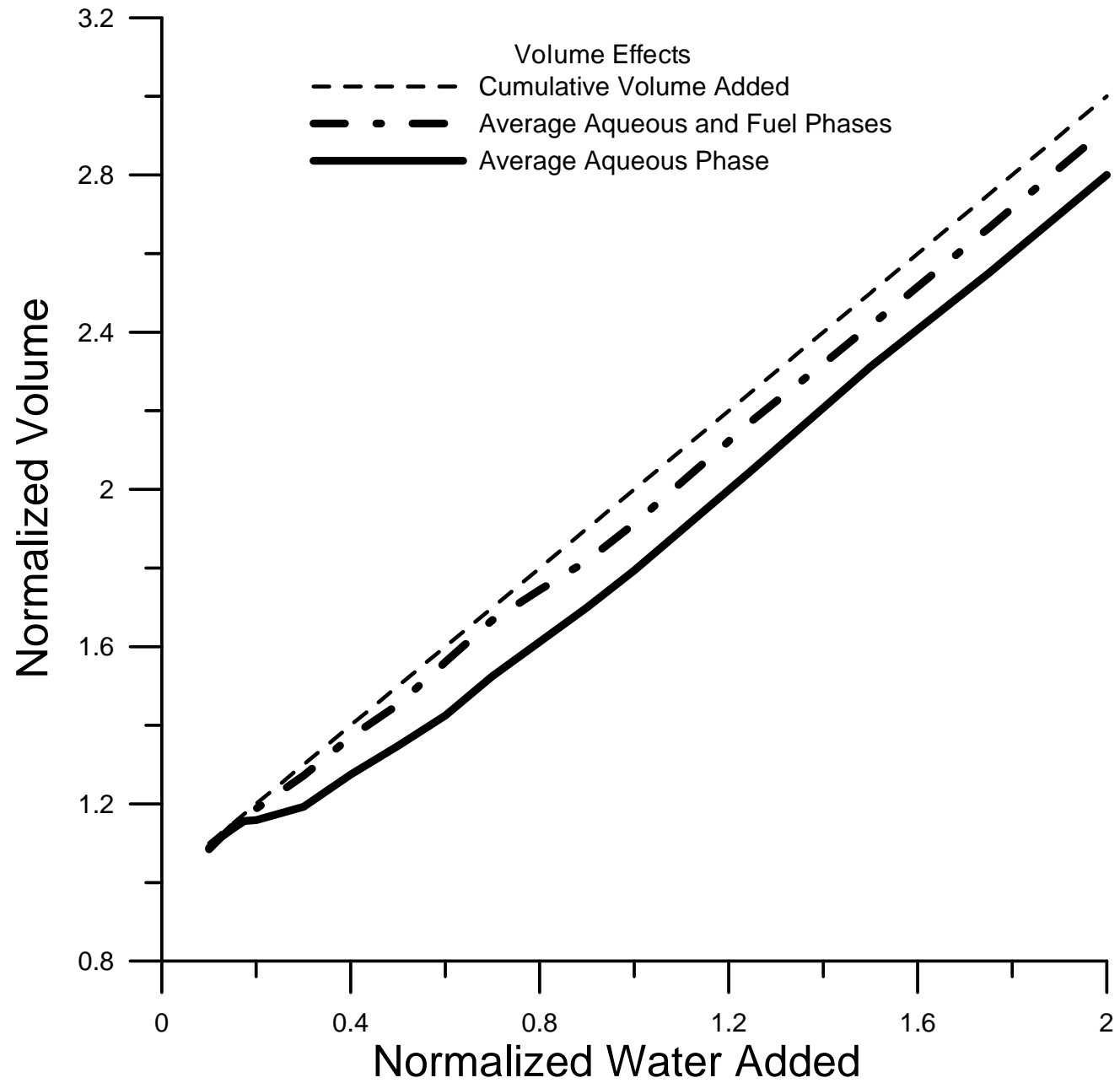


E10 Gasoline



**RESEARCH &
DEVELOPMENT**

*Building a
scientific
foundation
for sound
environmental
decisions*



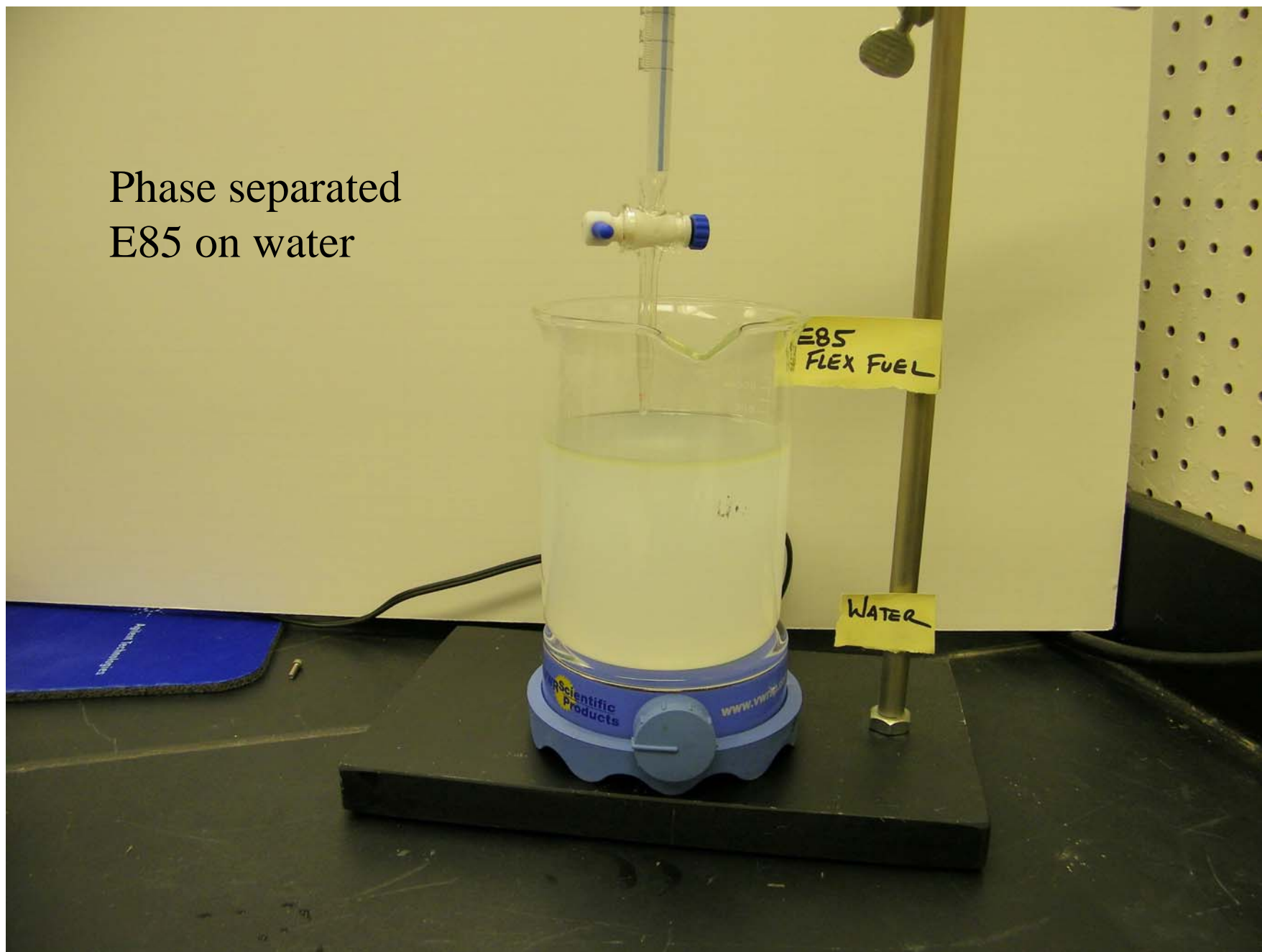
Videos

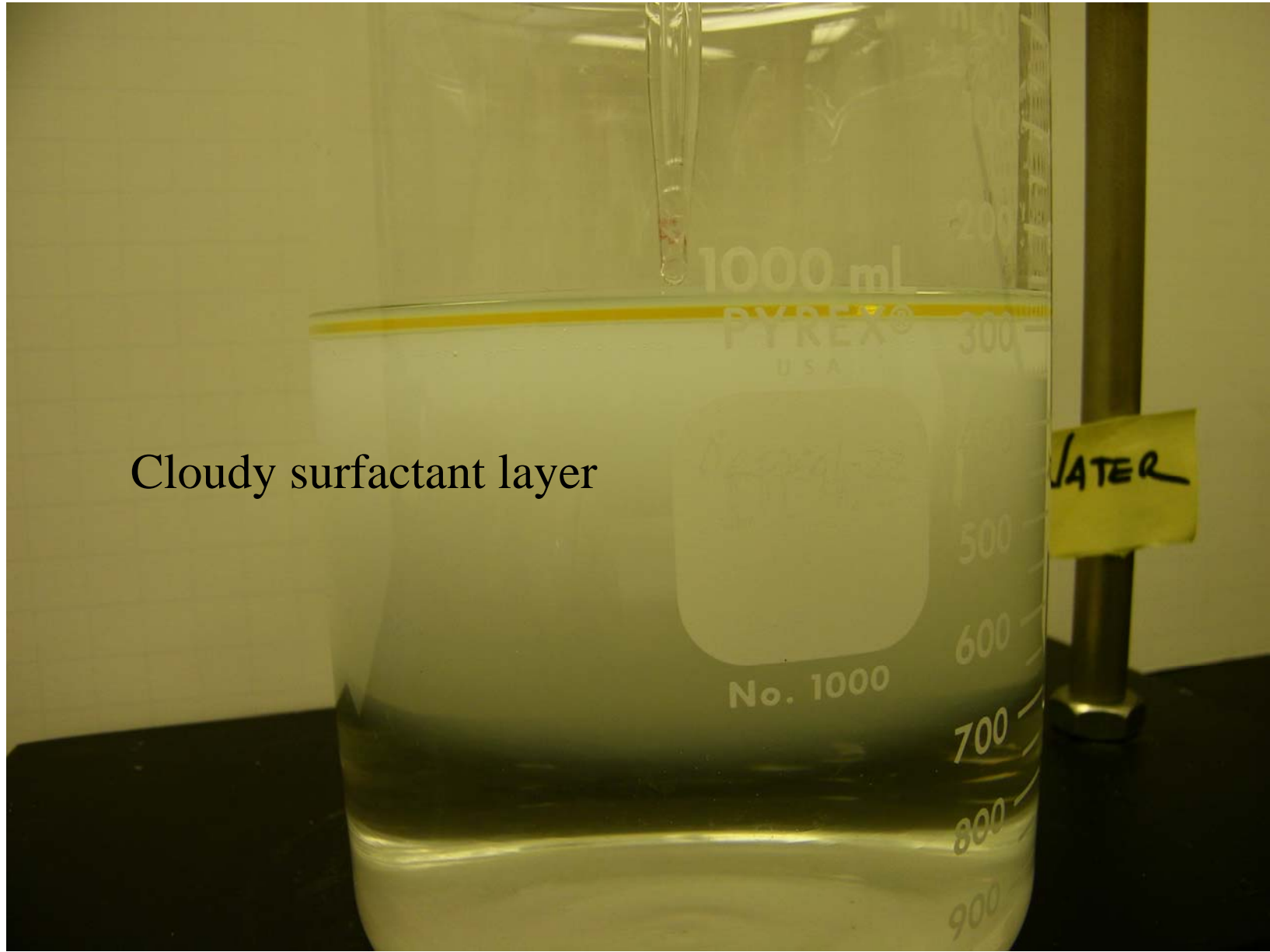
- Dyed Water Added to E85
 - Initially water is absorbed by E85
 - Initially no increase in volume
 - E85 breaks into “gasoline” and aqueous/ethanol phase
- E85 added to water
 - Quiescent E85 jets into water
 - Cloudy surfactant layer over clear water
 - Gasoline accumulates on surface
 - In moving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

Dyed water and
“gasoline” after
phase separation



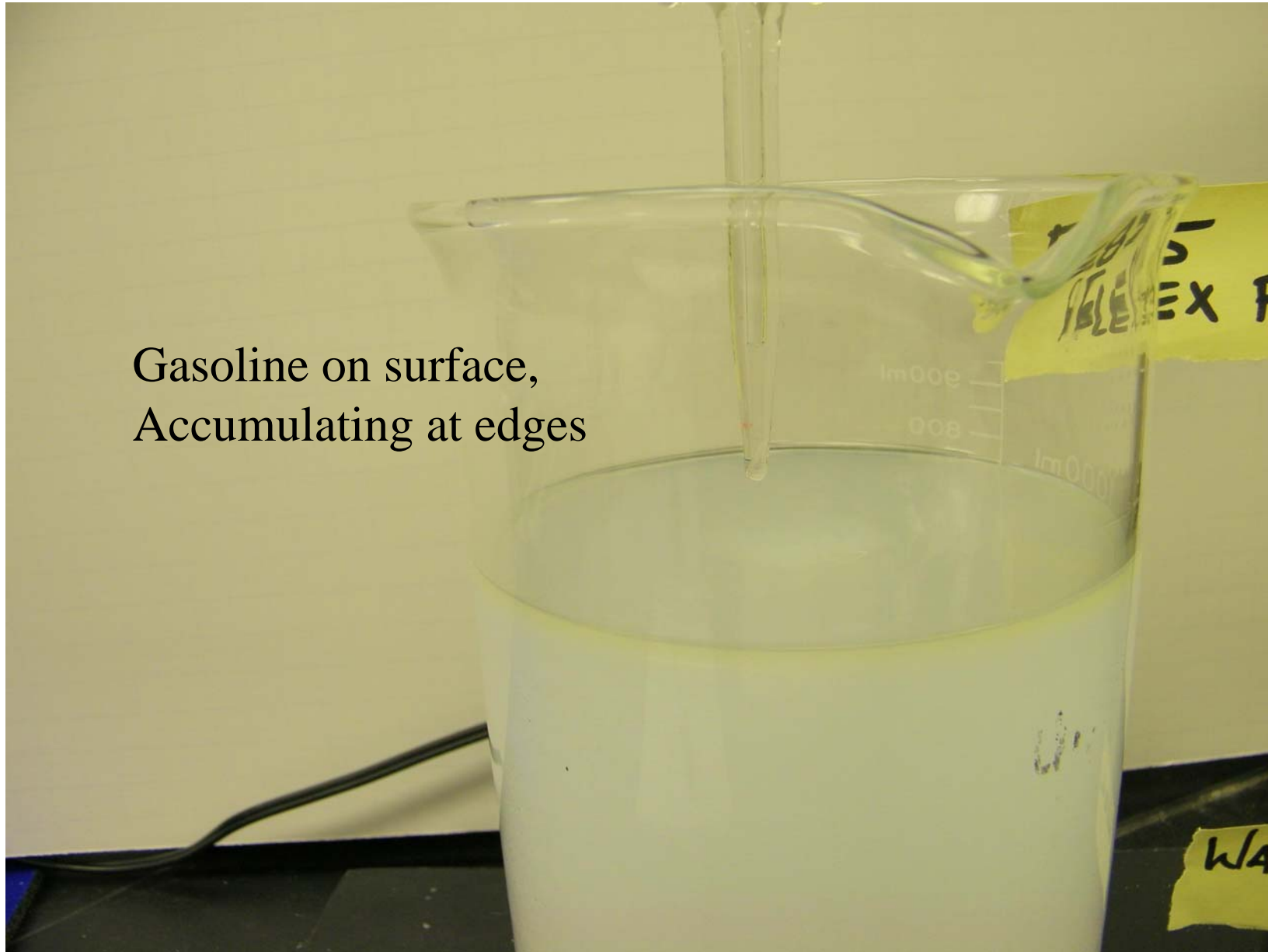
Phase separated
E85 on water

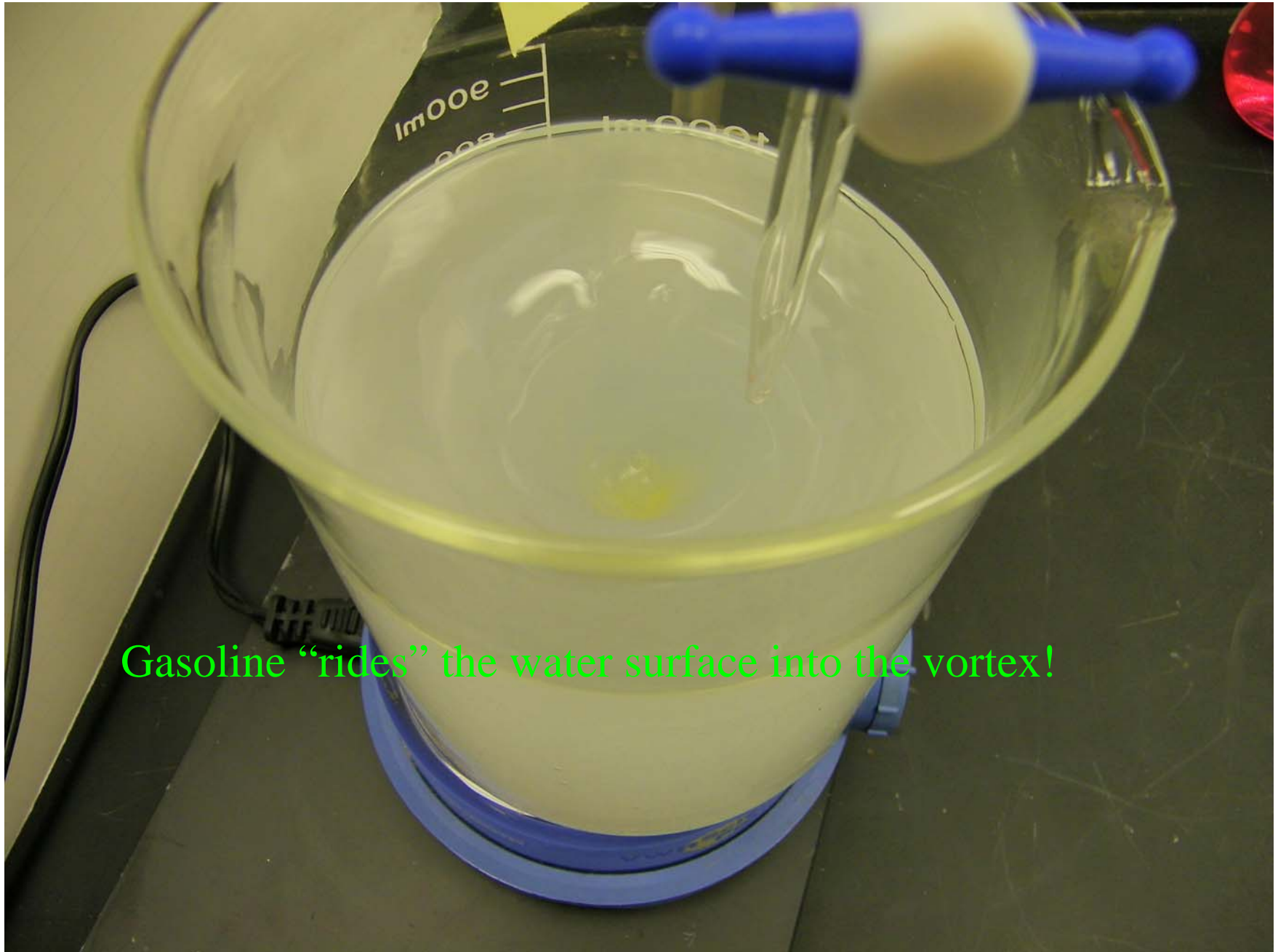




Cloudy surfactant layer

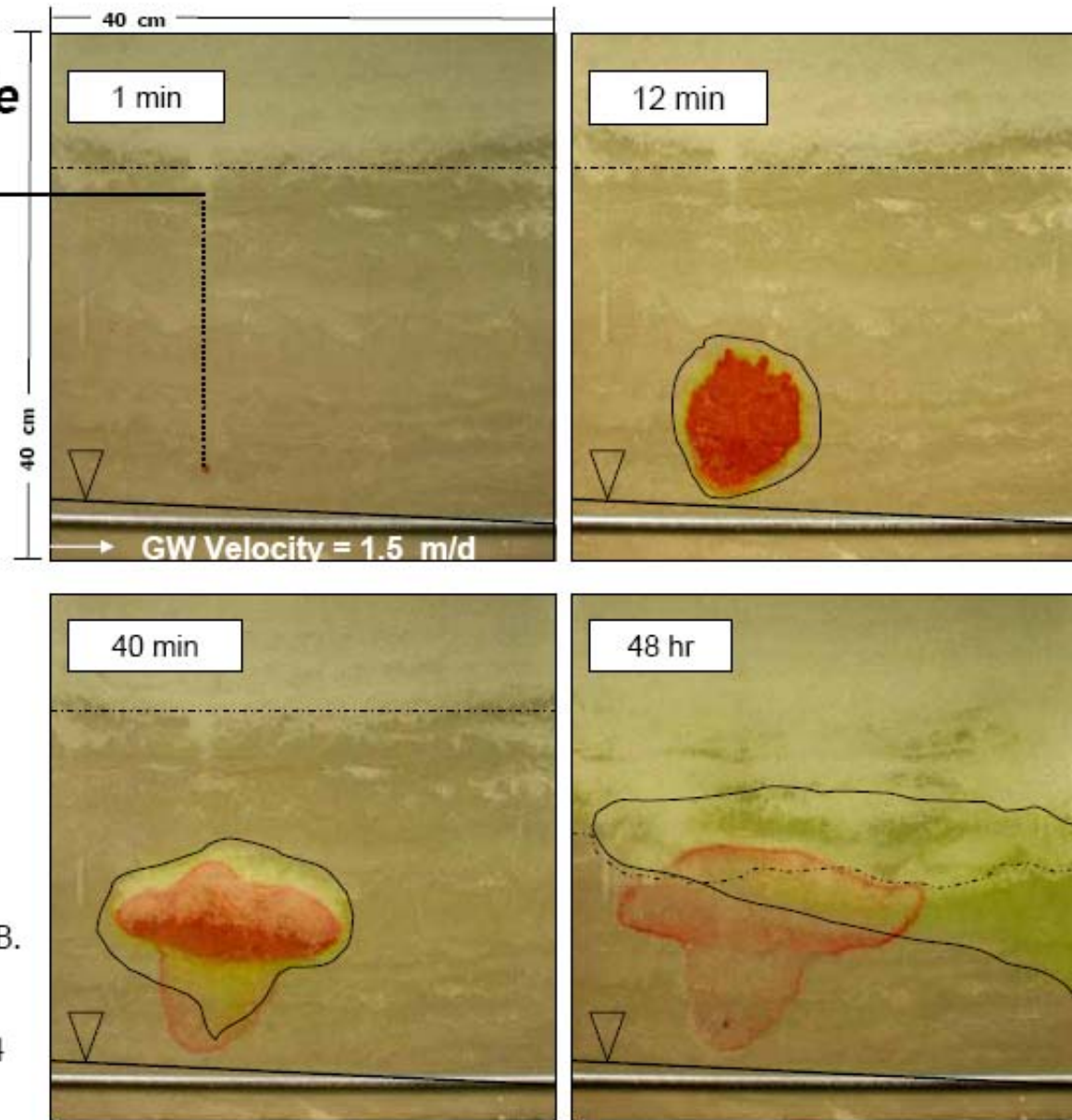
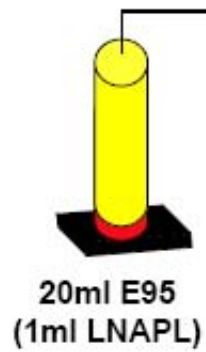
Gasoline on surface,
Accumulating at edges





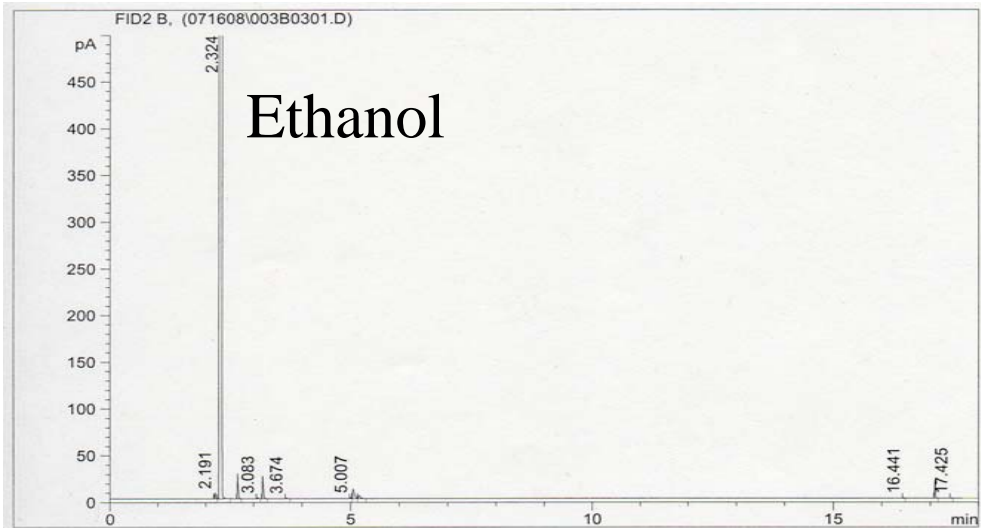
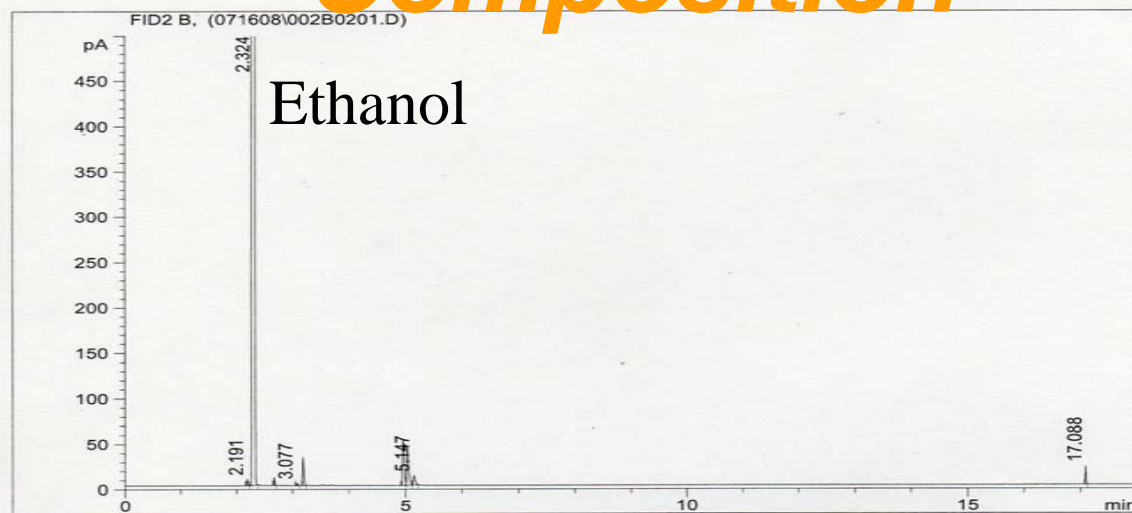
Gasoline "rides" the water surface into the vortex!

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 ₂ O	7732-18-15	0.65	0.08
Methanol	CH ₄ O	67-55-1	0.07	0.06
Ethanol ⁽²⁾	C ₂ H ₆ O	64-17-5	97.89	99.75
1-Propanol	C ₃ H ₈ O	71-23-8	0.03	0.08
Isobutyl Alcohol	C ₄ H ₁₀ O	78-83-1	0.10	0.08
2-Methyl 1-Butanol	C ₅ H ₁₂ O	137-32-6	0.06	0.01
3-Methyl 1-Butanol	C ₅ H ₁₂ O	123-51-3	0.21	0.02
Ethyl Acetate	C ₄ H ₈ O ₂	141-78-6	0.02	--
1,1-Diethoxyethane	C ₆ H ₁₄ O ₂	105-57-7	0.28	--

⁽¹⁾ Determined by Karl Fischer titration

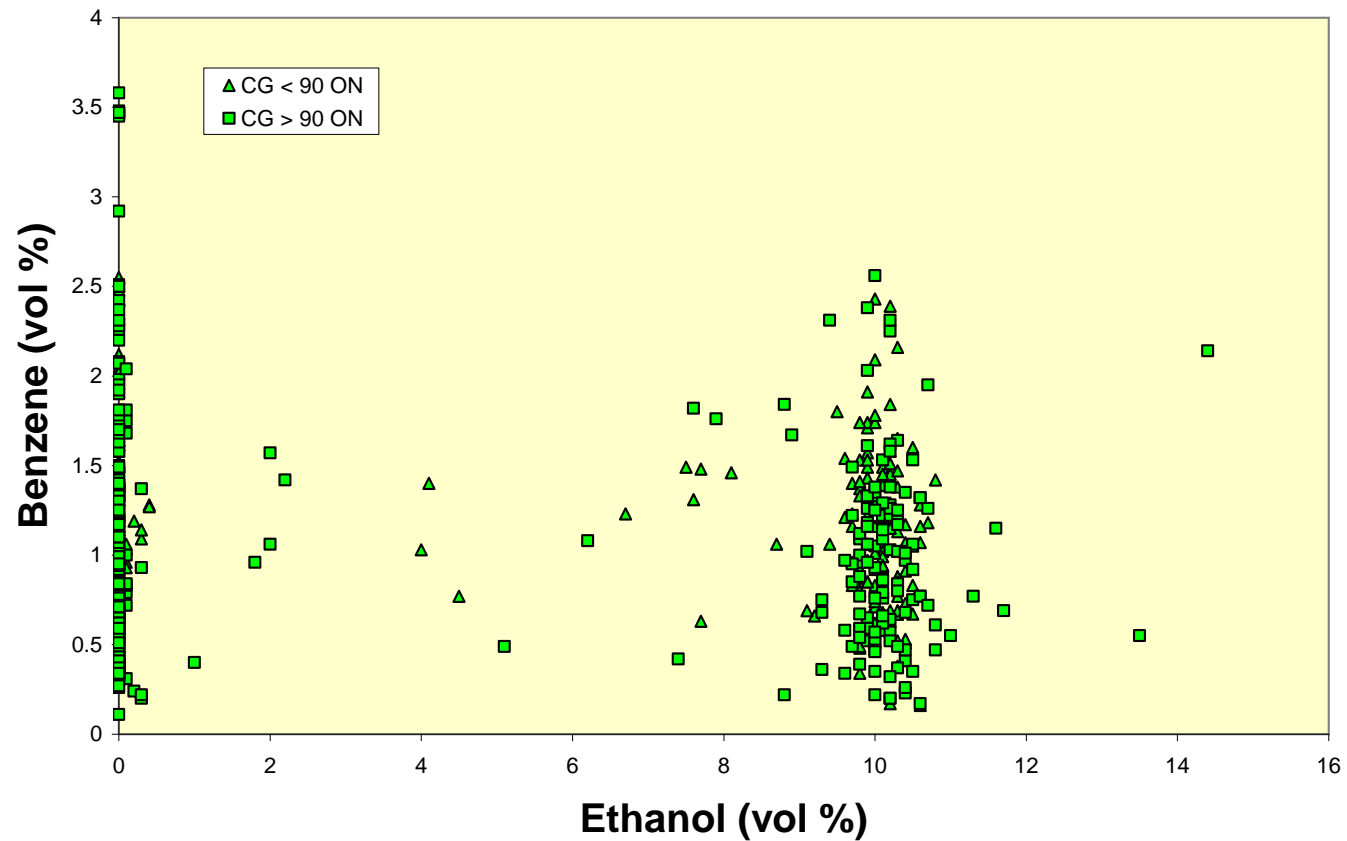
⁽²⁾ Determined by remainder of other compounds

Observed Ethanol Concentrations in Gasoline



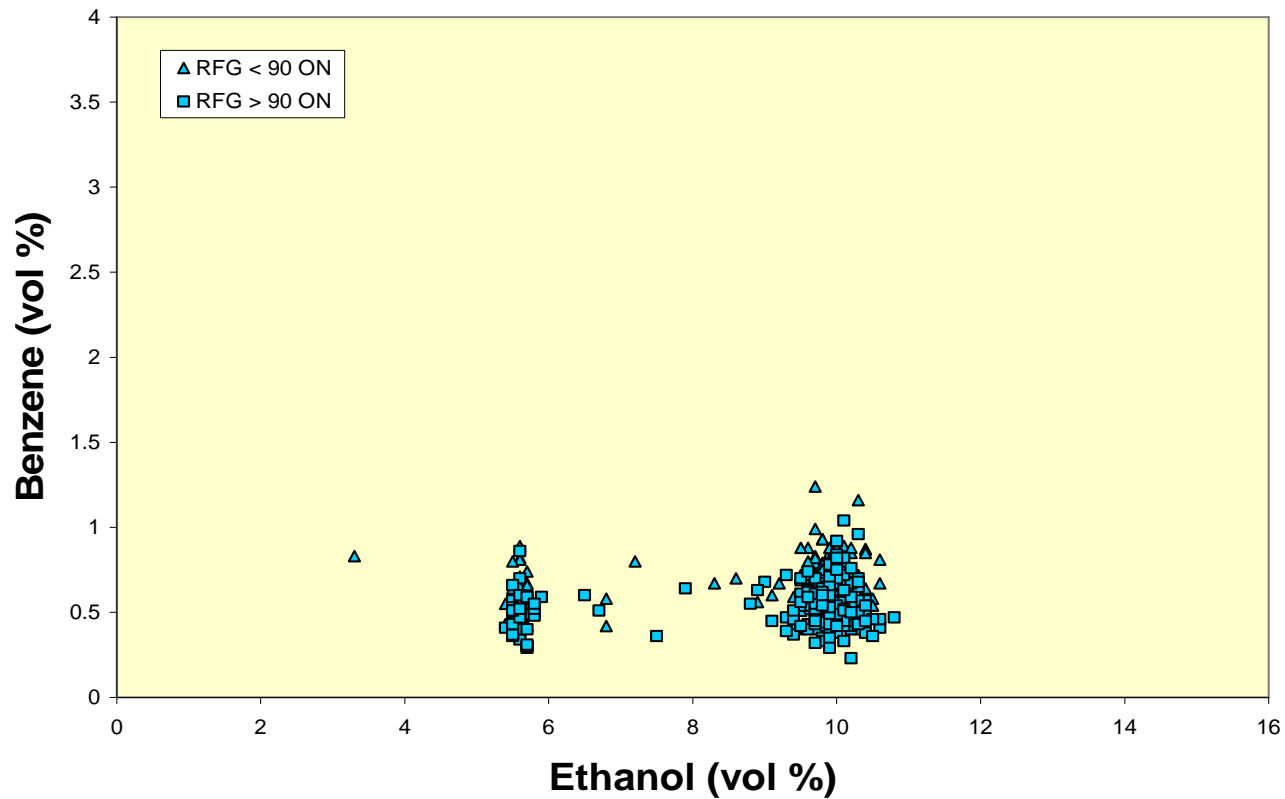
**Northrop-Grumman
(successor to NIPER)
Bartlesville, Oklahoma
Summer 07**

Conventional Gasoline



Northrop-Grumman (successor to NIPER) Bartlesville, Oklahoma

Reformulated Gasoline



E85TM

85% Ethanol

11

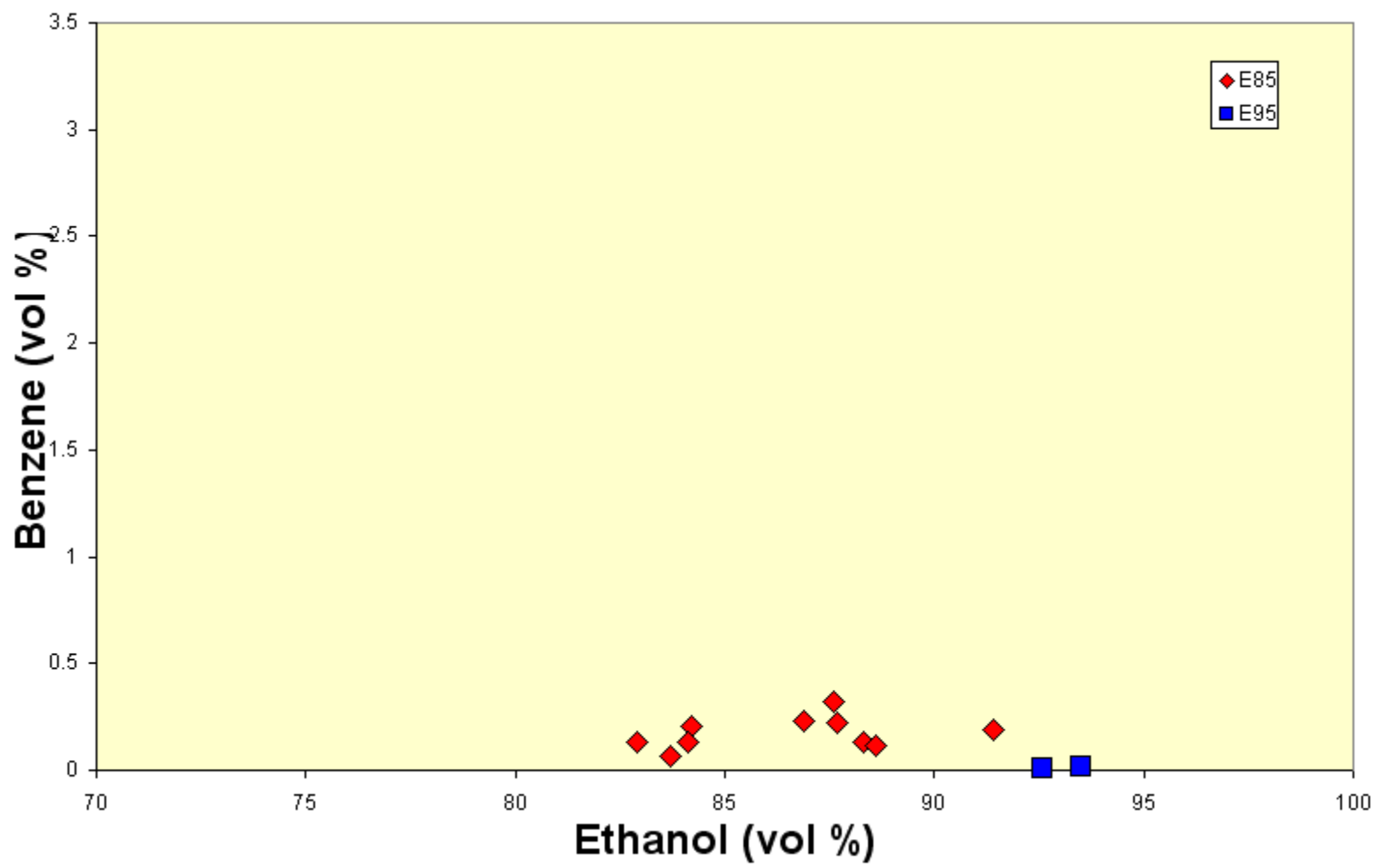
E-85
MINIMUM
85%
ETHANOL



2.899

Price per gallon
All taxes included

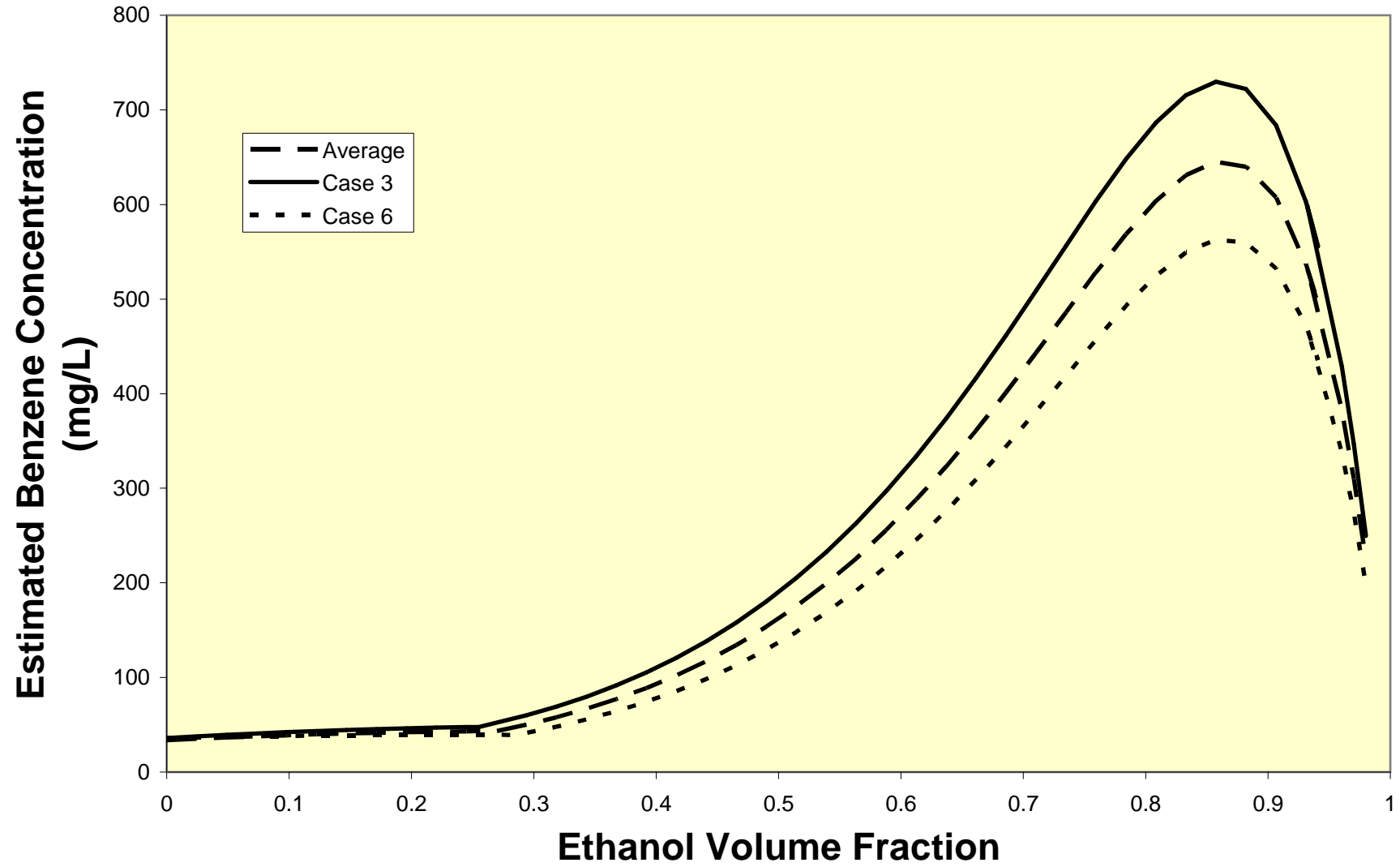
Ethanol
P R E S S



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



RESEARCH &
DEVELOPMENT

*Building a
scientific
foundation
for sound
environmental
decisions*

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

Balaton, Minnesota



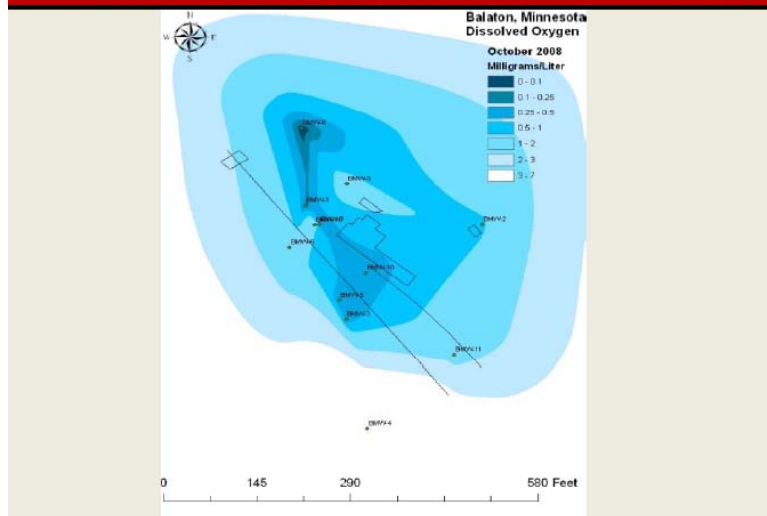
Balaton, Minnesota

July 28, 2004

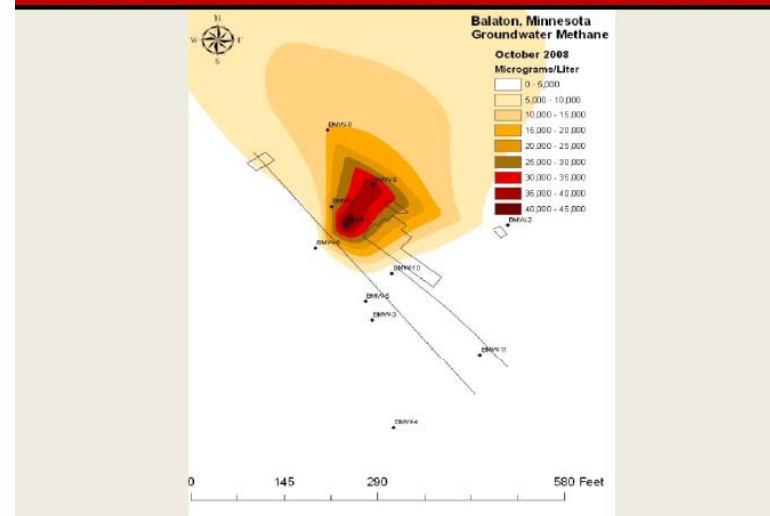
~90,000 Gs of d-ethanol released
~10,000 Gs residual ethanol after
product removal and soil
excavation



D. Oxygen: 4.3 Years After Derailment

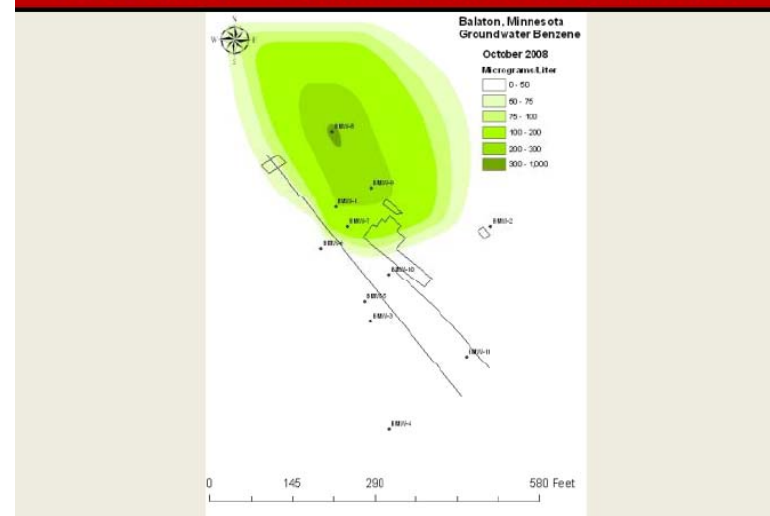


Methane: 4.3 Years After Derailment



- 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

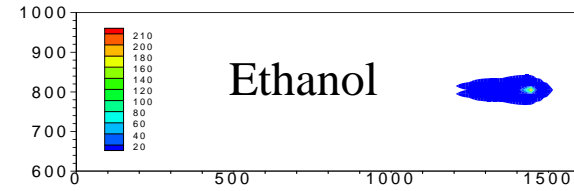
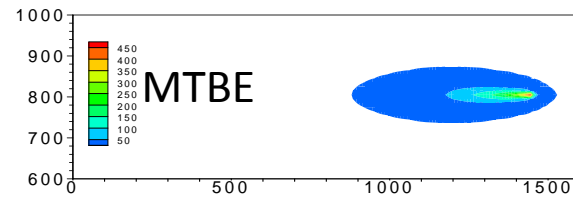
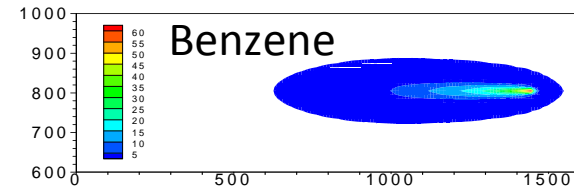
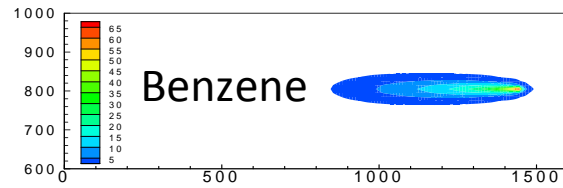
Benzene: 4.3 Years After Derailment



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

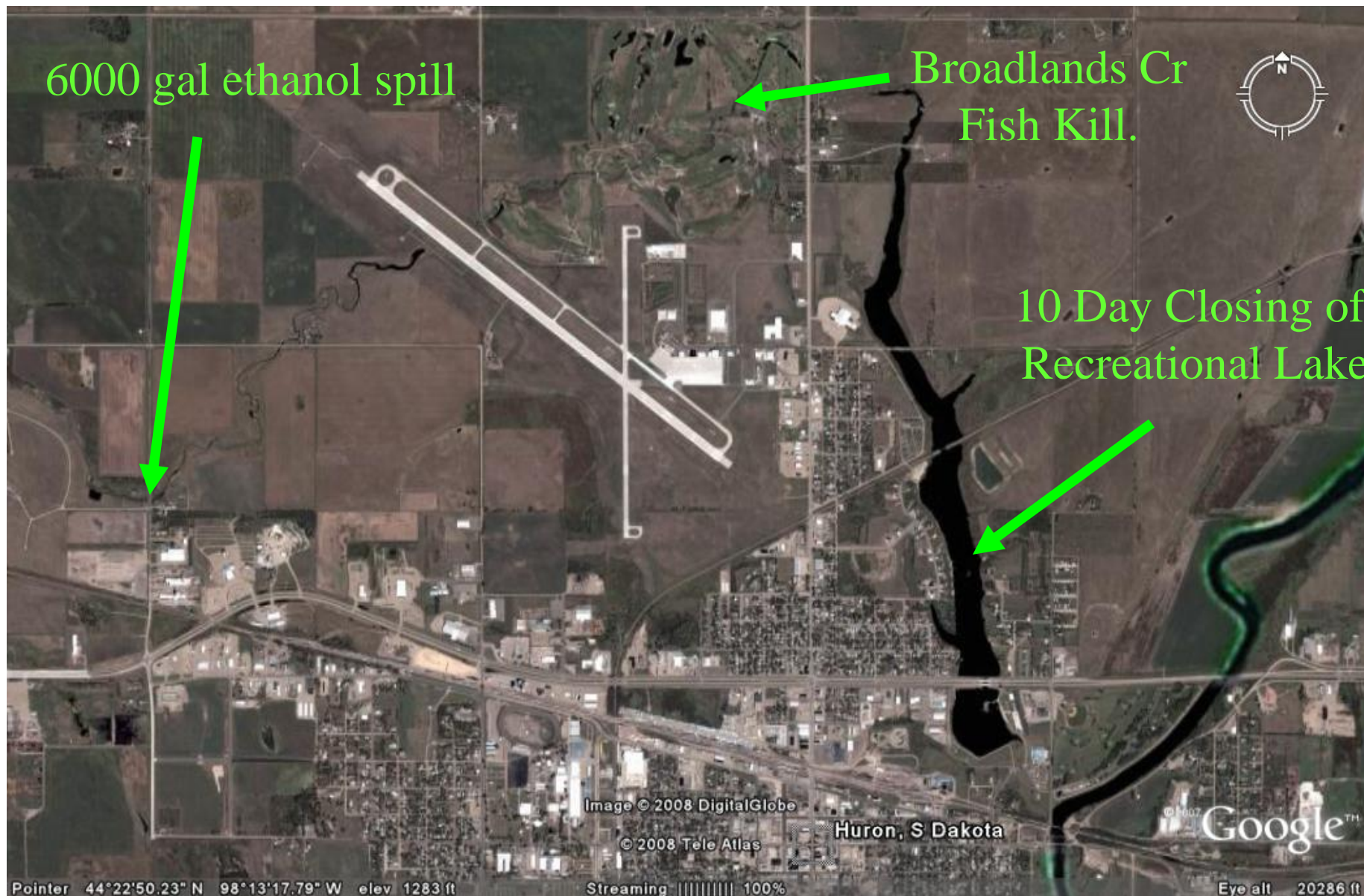
Info. Courtesy of Kim McIntosh, SD-DENR

- 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

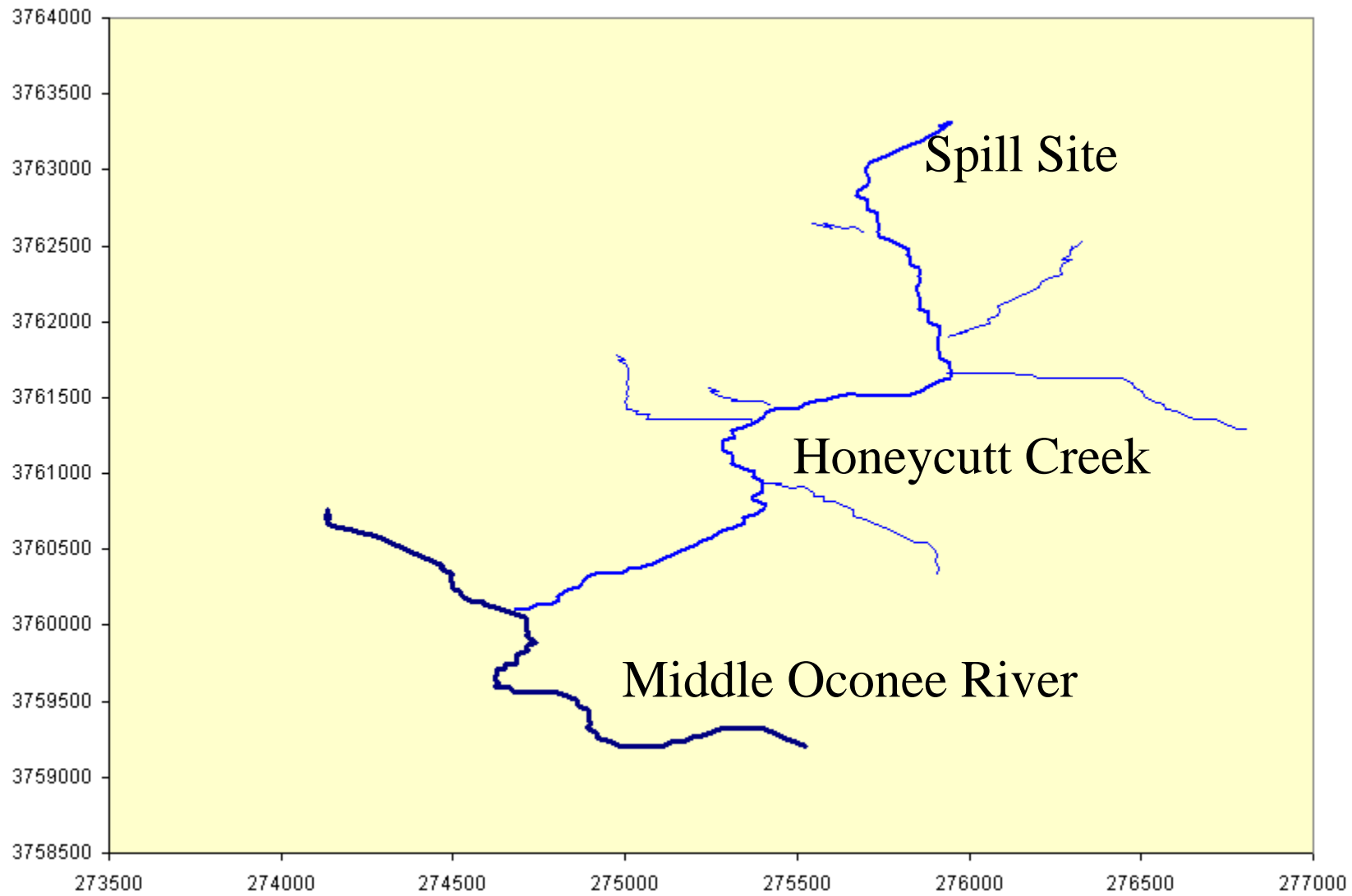
- No gasoline observed
- 4 water samples for VOCs 5/21
 - BTEX, tri-methylbenzenes, ethanol, methanol
 - Most results ND, one sample ethanol at 6800 ppb
- Generally increased D.O. by 5/27/2008

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

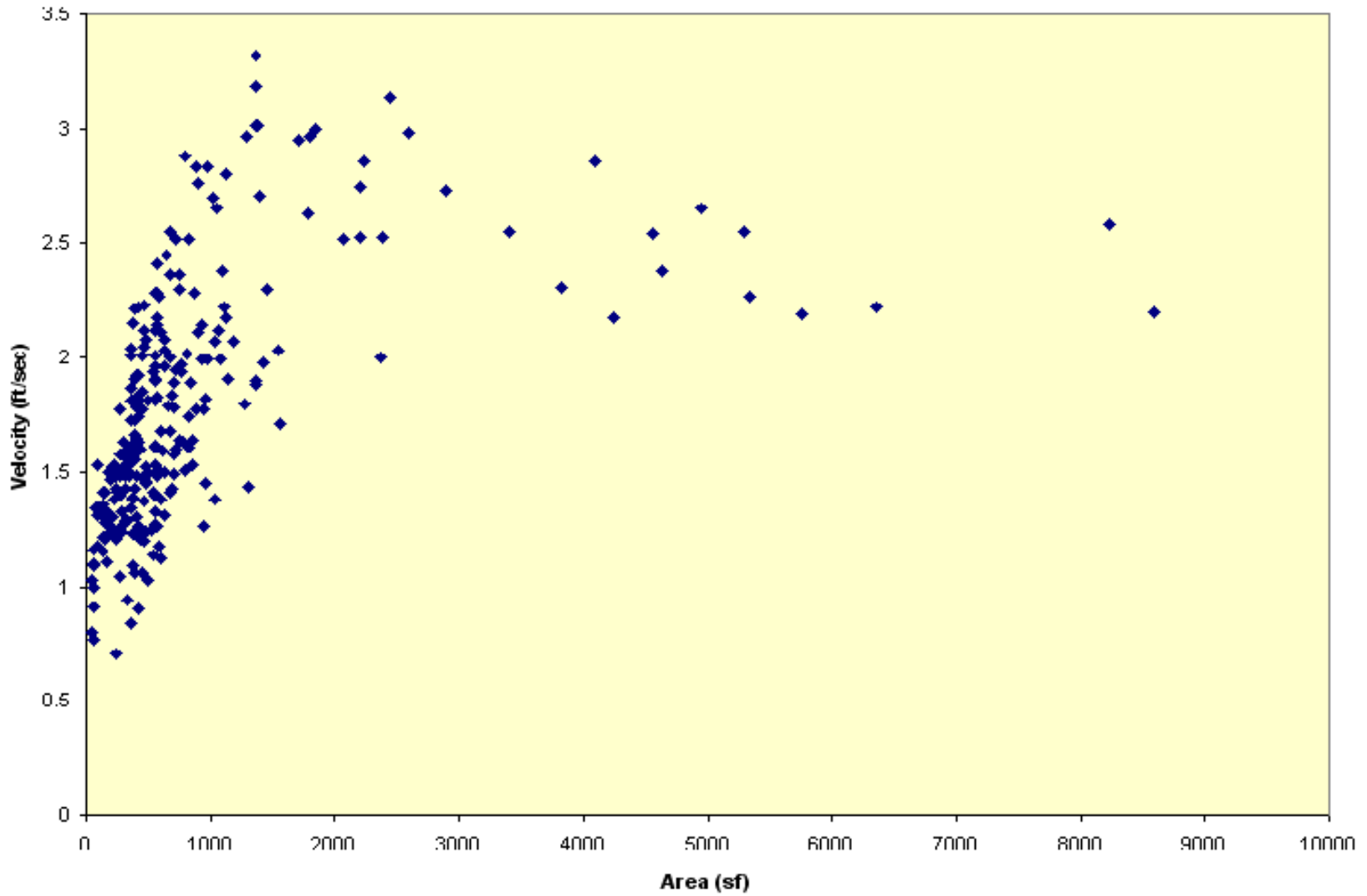
- Hypothetical Release Scenario
- Composition and Phase Separation Data from Laboratory
- Stream network geometry from USGS DEMs
- Flows
 - Honeycutt Creek flow and geometry from a day's work
 - Middle Oconee River flows and discharge stage from USGS gages



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



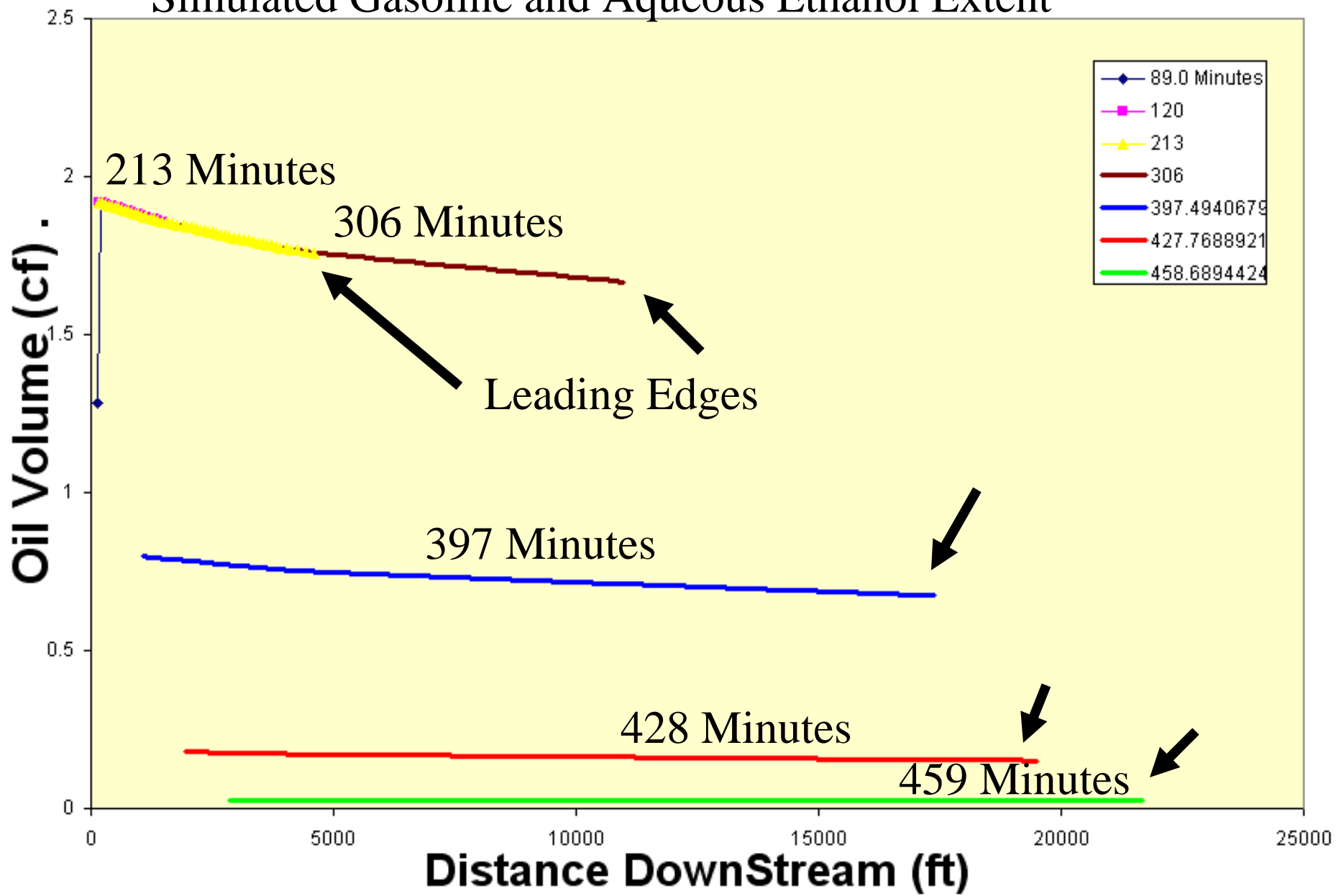
Model Approach

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

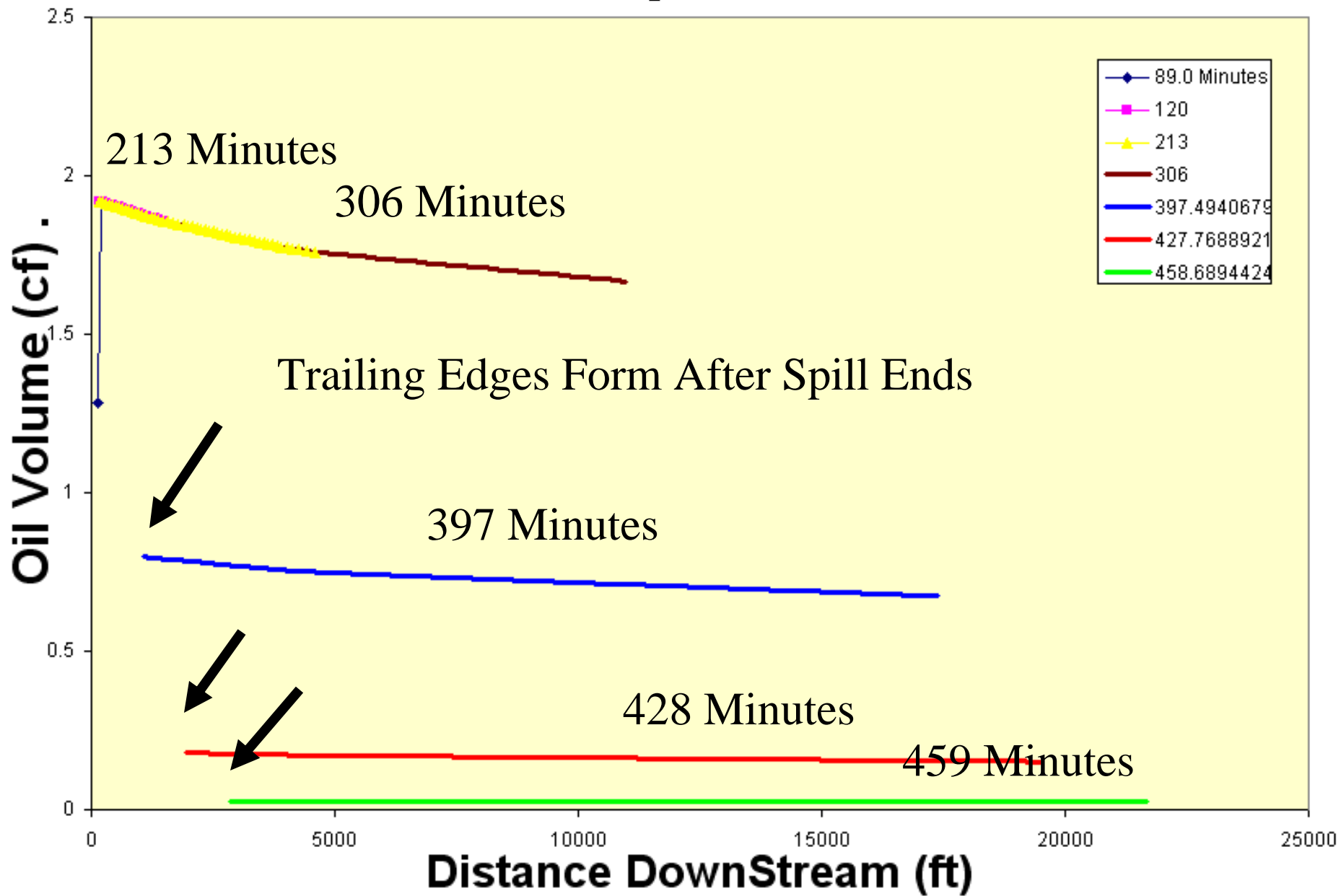
Spill Characteristics

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

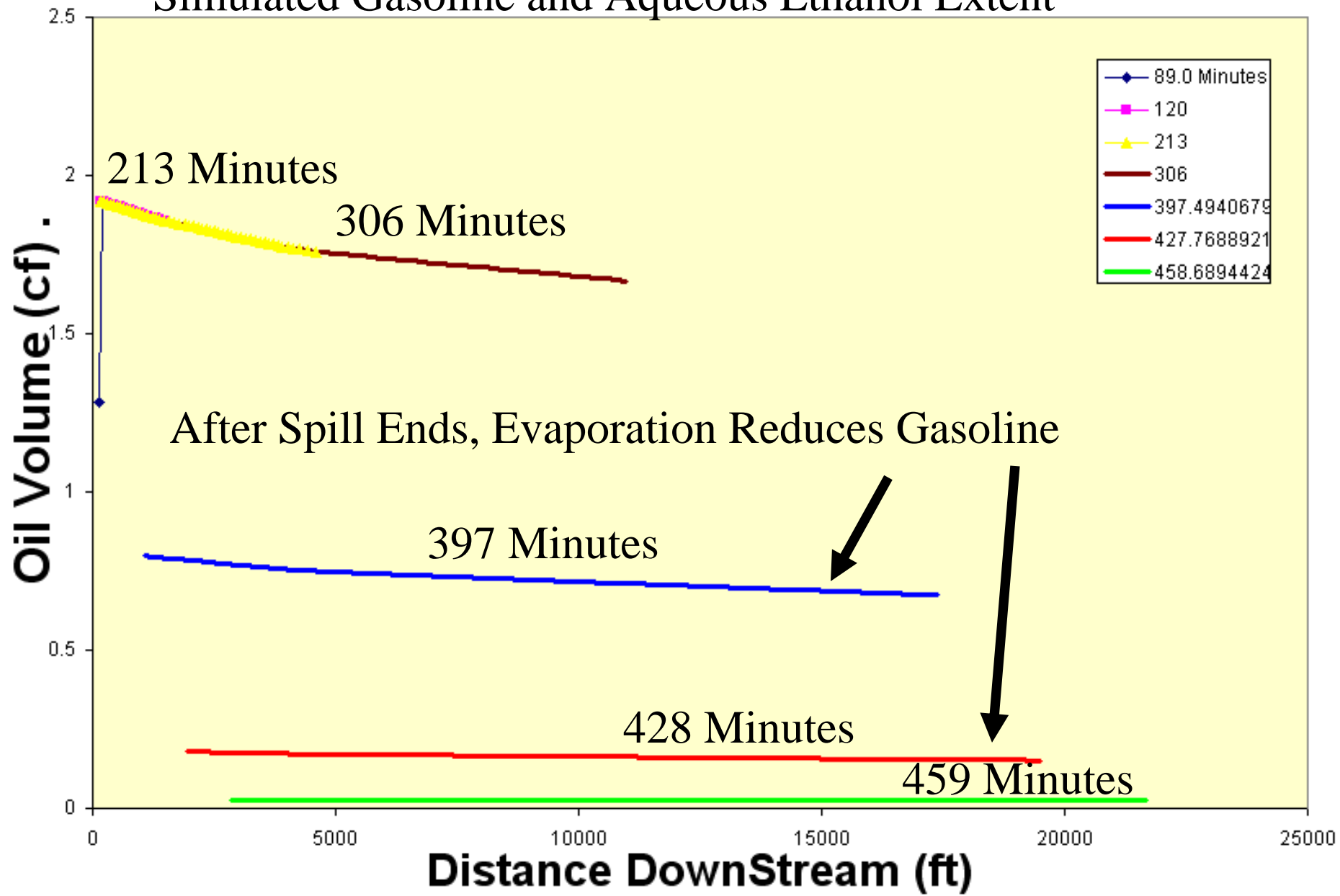
Simulated Gasoline and Aqueous Ethanol Extent



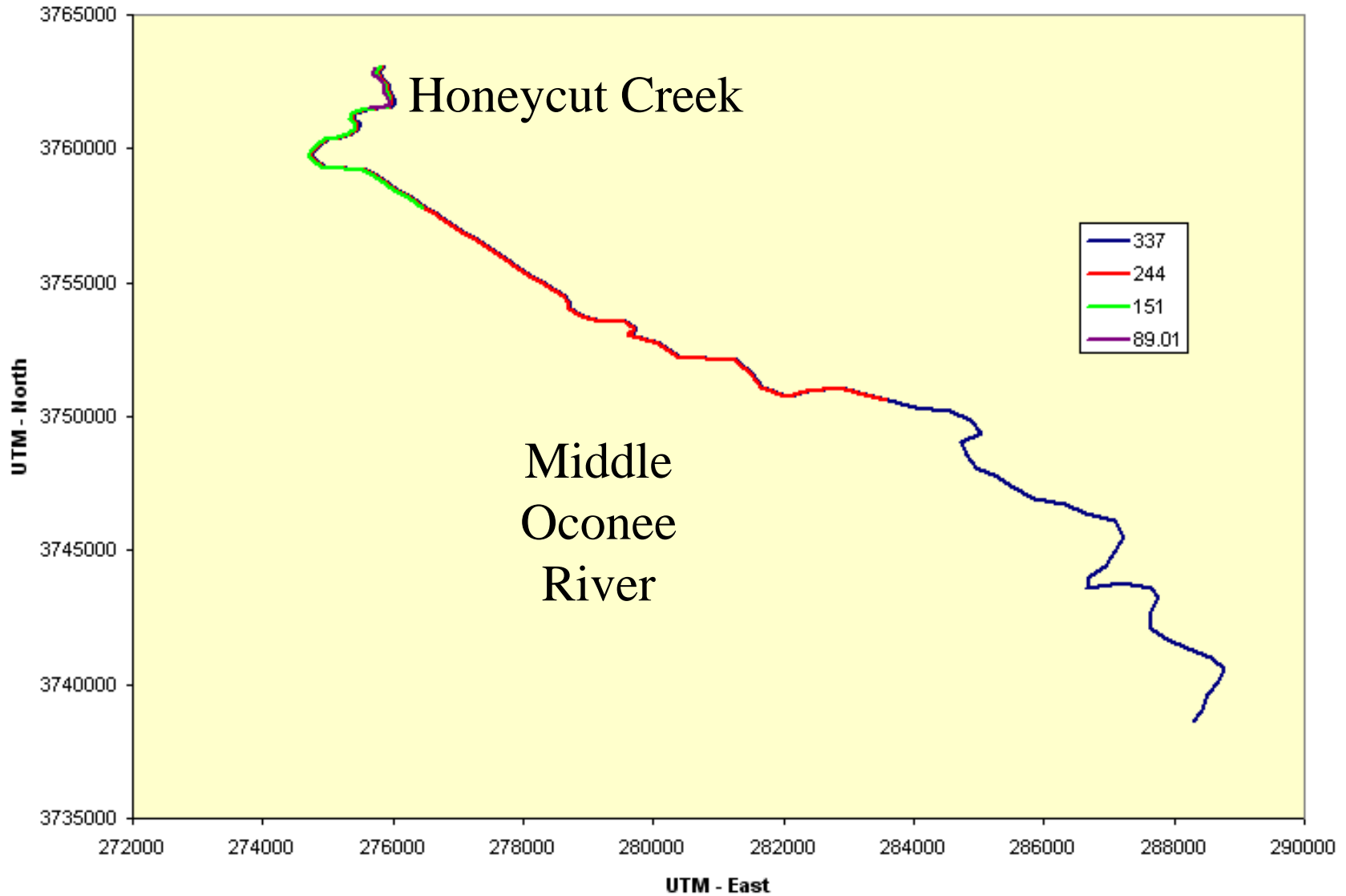
Simulated Gasoline and Aqueous Ethanol Extent



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

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***