13th Annual OSC Readiness Training Program

Composition and Behavior of Ethanol Gasolines

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US Environmental Protection Agency
National Exposure Research Laboratory
Athens, Georgia

Training by OSCs for OSCs

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www.oscreadiness.org

Outline

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

Alternate Marketing Strategies

Ethanol Usage in Gasoline

- Historic
  - Known as an octane booster since the 1920s
  - Used in upper mid west at least during 90s
  - Oxygenates required in reformulated gasoline 1995-2006
  - Increased usage because of MTBE bans after 2000
- Mandated
  - Energy Policy Act 2005
  - Energy Independence and Security Act of 2007
  - Some state rules

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.

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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: 70%, 74%, 79%
- E10: “may contain 10% ethanol”
  - ~90% gasoline
- “E00” “ethanol free gasoline”

Overview from producers to consumers

- Producers
  - o Distill to 190 proof
  - o Dry to 200 proof (molecular sieve)
  - o Denature
- Transporters
  - o Not to go in U.S. pipelines (exception for Central Florida)
  - o Therefore: barges, trucks, trains
- Distributers (from terminals)
  - o Separate Ethanol Tank
  - o Splash Blending
    - Add gasoline blending component (“RBOB”), ethanol, and additives let mix in tanker as delivery is made
- Users
  - o Compatible Tanks, Pipes, Dispensers?
  - o Water Bottoms?
  - o Auto issues?

ASTM SPEC

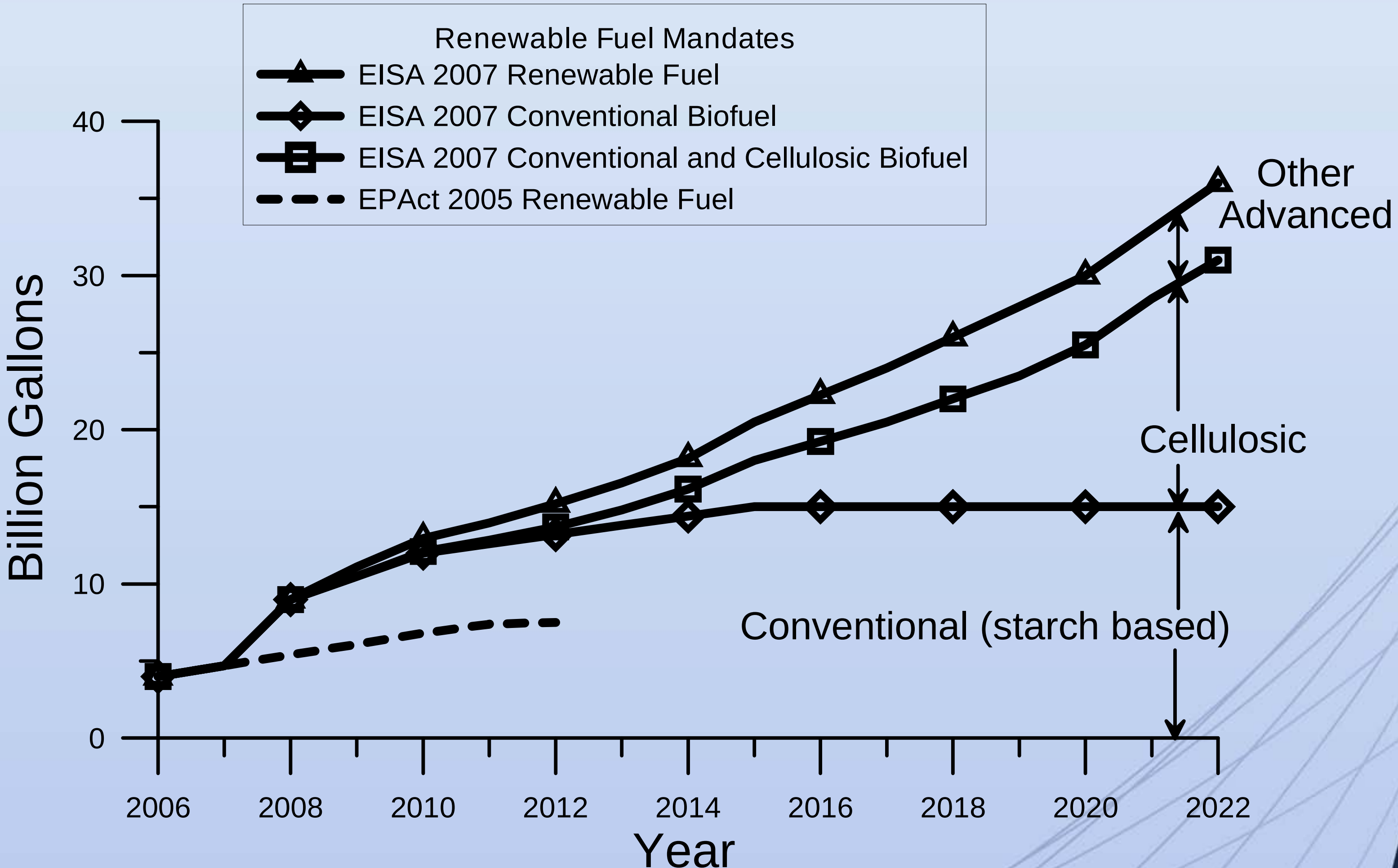
- Ethanol > 92.1%
- Water < 1%
- Methanol < 0.5%
- Solvent-wasted gum < 5 mg/100 mL
- Denaturant 1.96% to 5%
- Inorganic Chloride < 10 mg/L

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

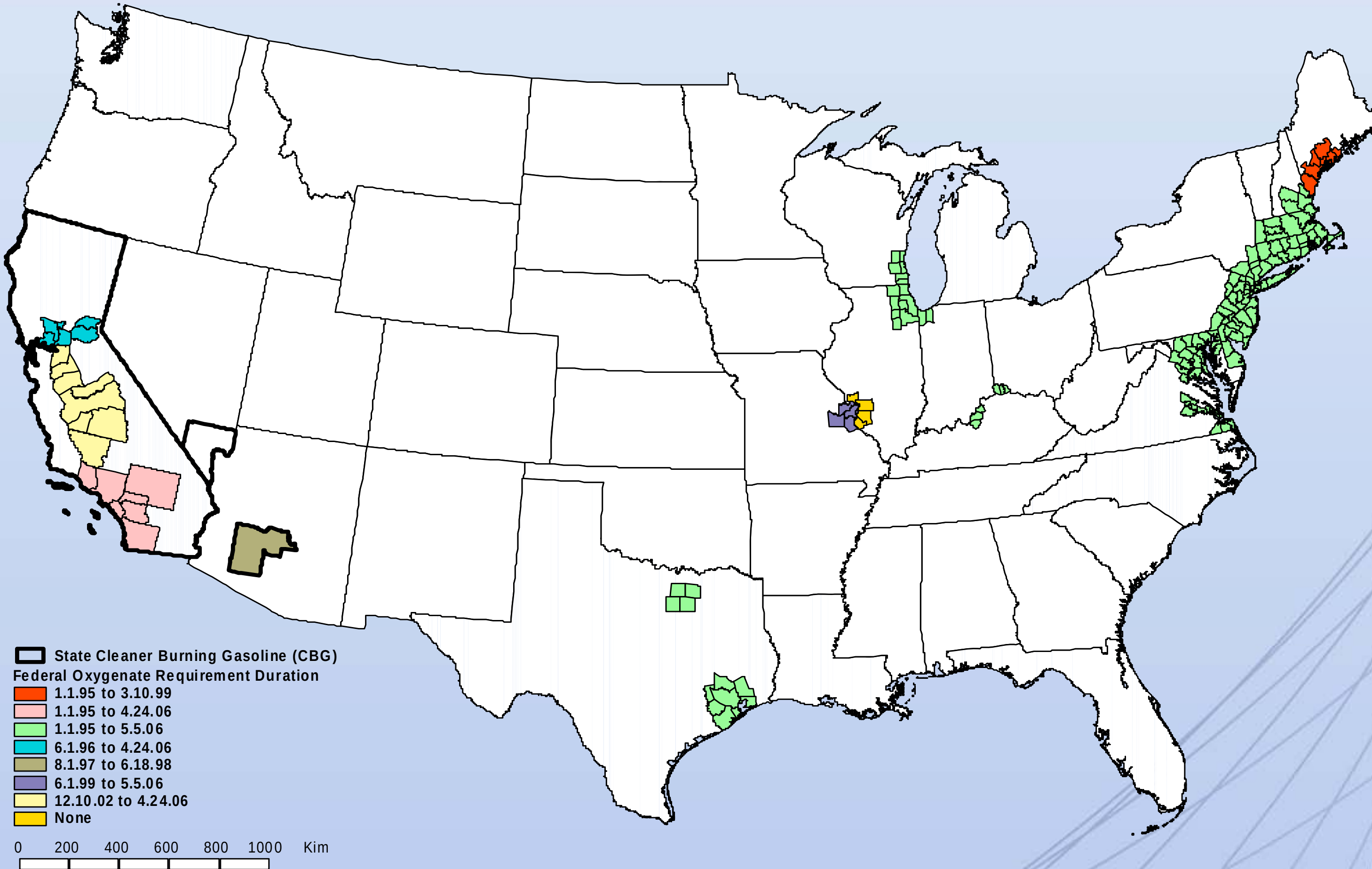
- ASTM also specifies **prohibited** denaturants:
  - (adverse effects on fuel stability, automotive engines, and fuel systems)
  - hydrocarbons with an end boiling point above 225 ^{o}C,
  - methanol not meeting ASTM D1152,
  - pyrroles, turpentine, ketones, and tars.


Renewable Fuel Mandates
EISA 2007 Renewable Fuel
EISA 2007 Conventional Biofuel
EISA 2007 Conventional and Cellulosic Biofuel
EPAct 2005 Renewable Fuel
Billion Gallons
0
10
20
30
40
2006
2008
2010
2012
2014
2016
2018
2020
2022
Year
Other Advanced
Cellulosic
Conventional (starch based)

Terminology

- Following the **Code of Federal Regulations (40 CFR) Part 80 – Regulation of Fuels and Fuel Additives**:
    - o ***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%*
    - o ***Conventional Gasoline (CG)*** is any gasoline which has not been certified under 40 CFR § 80.40.
    - o ***Oxygenated Gasoline (OG)*** is any gasoline which contains a measurable amount of oxygenate.

Reformulated and Conventional Gasoline in the US



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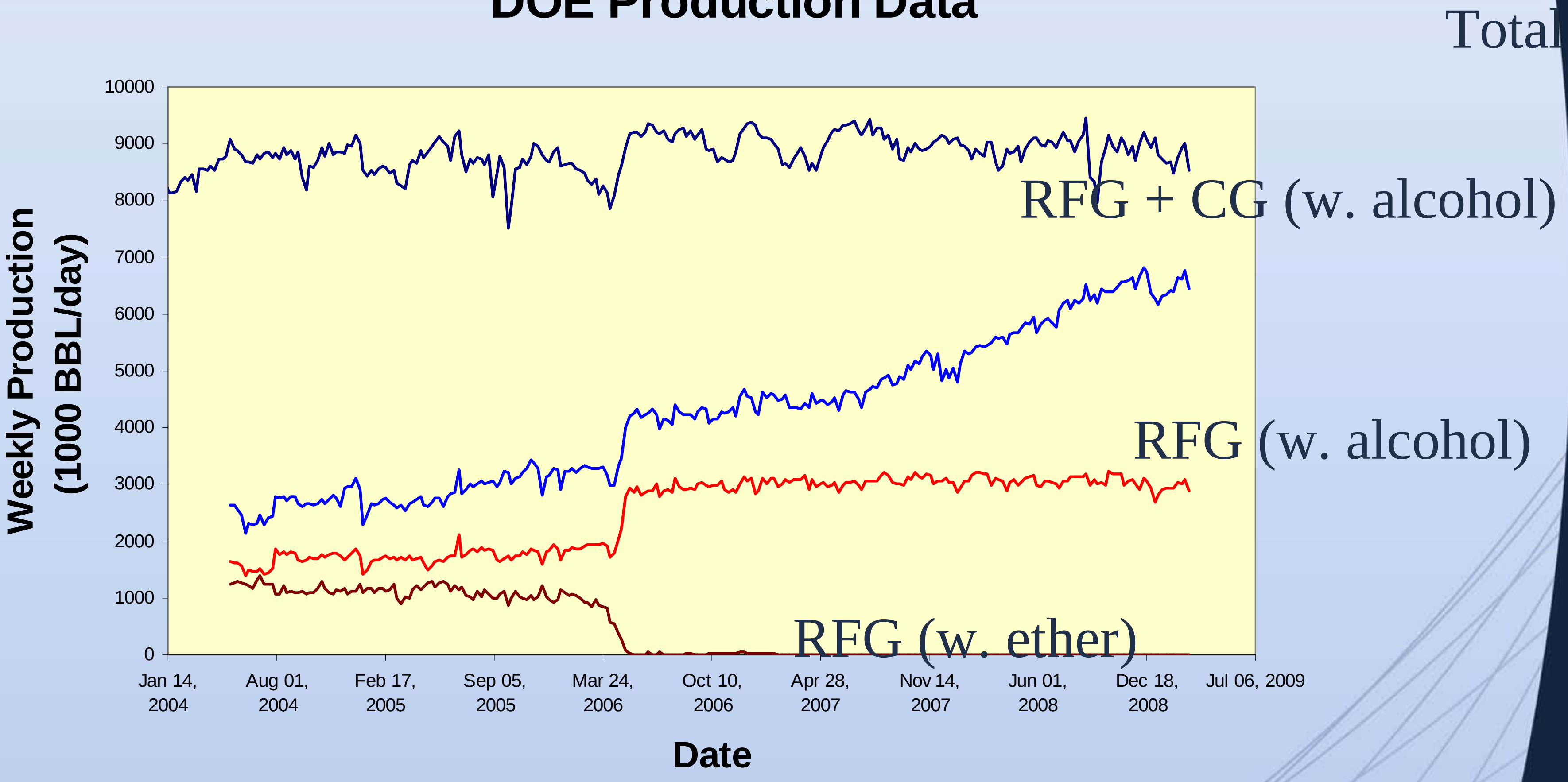
DOE Production Data



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

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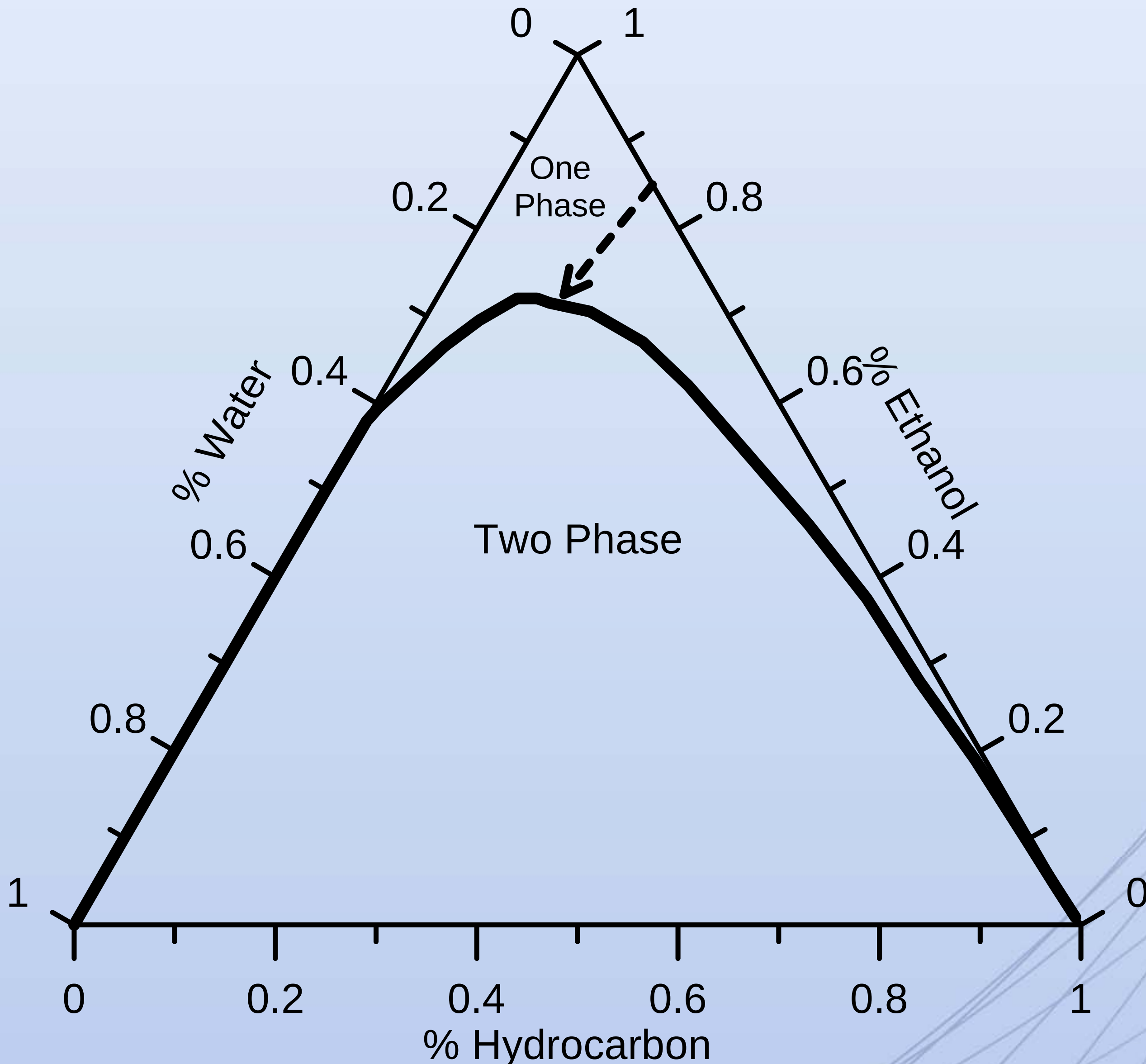
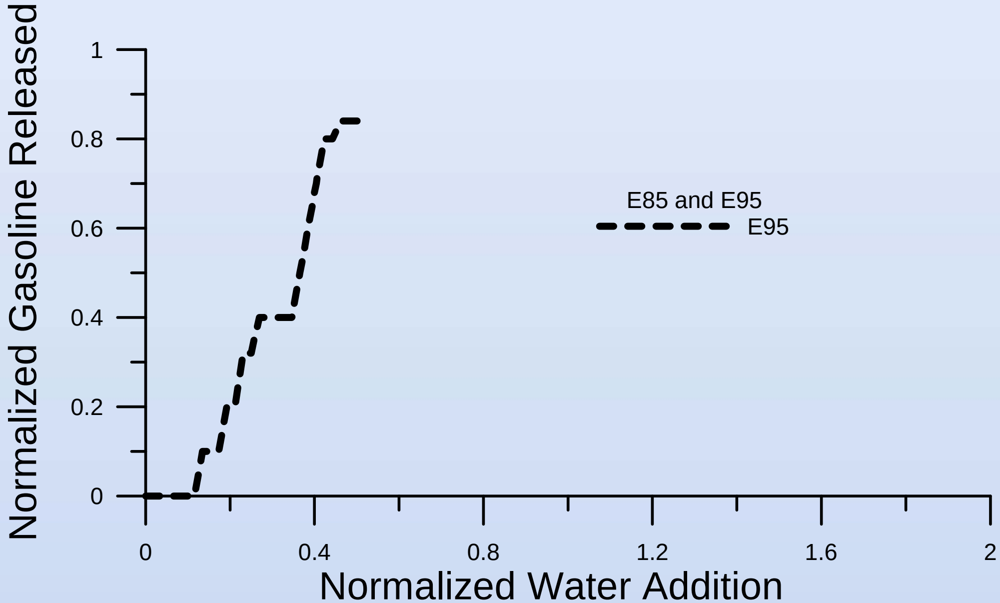
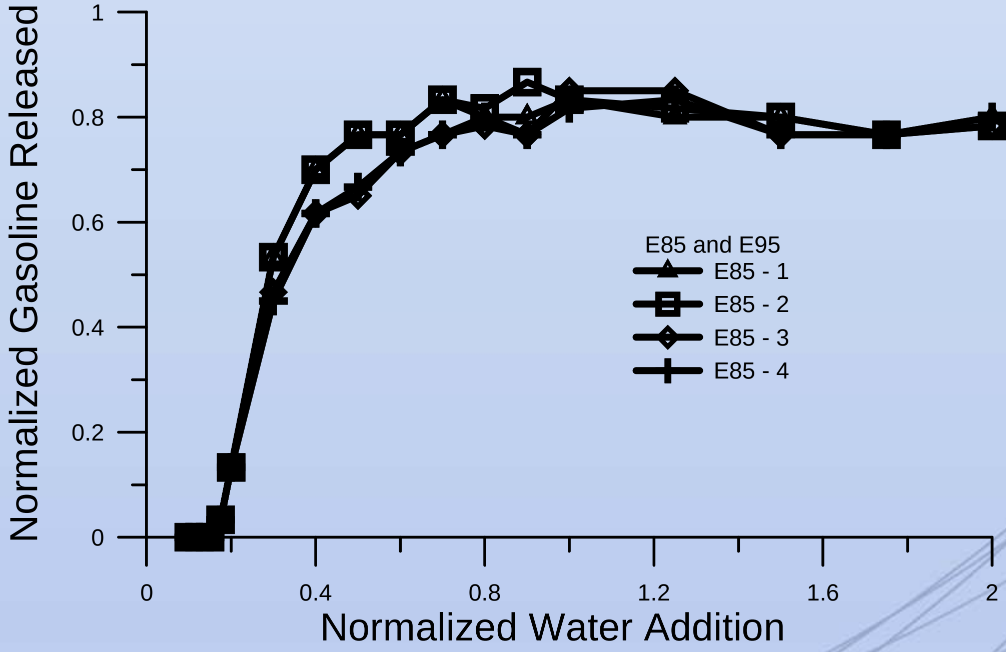
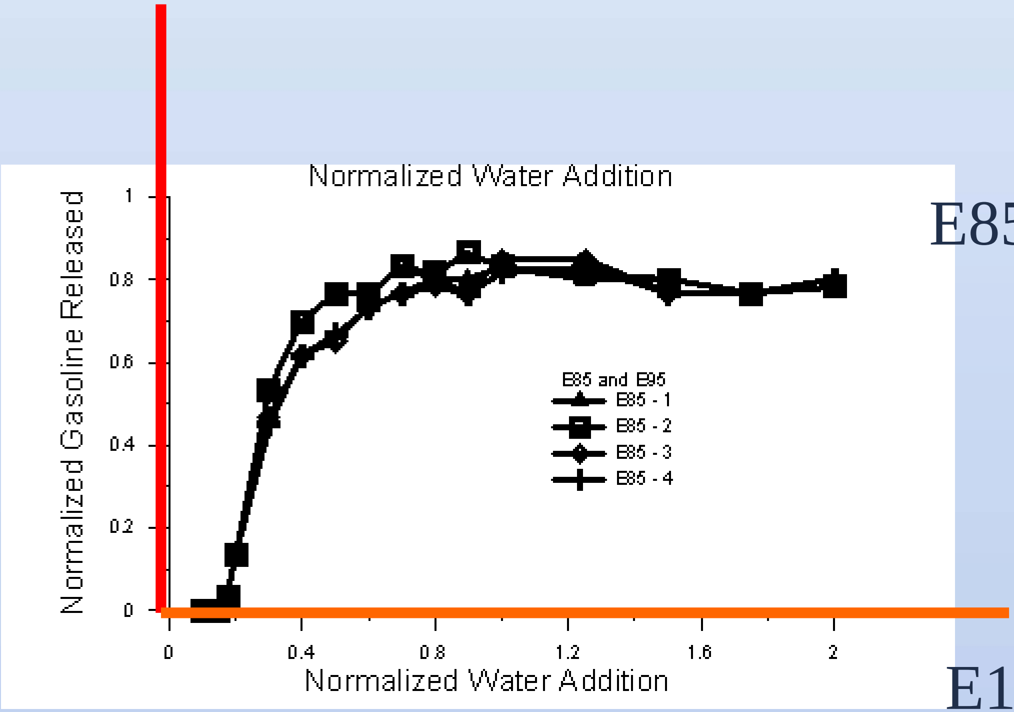


0
1
One
Phase
0.2
0.8
0.4
0.6
% Water
% Ethanol
Two Phase
0.6
0.4
0.8
0.2
1
0
0
0.2
0.4
0.6
0.8
1
% Hydrocarbon


Normalized Gasoline Released
1
0.8
0.6
0.4
0.2
0
0
0.4
0.8
1.2
1.6
2
Normalized Water Addition
E85 and E95
E95

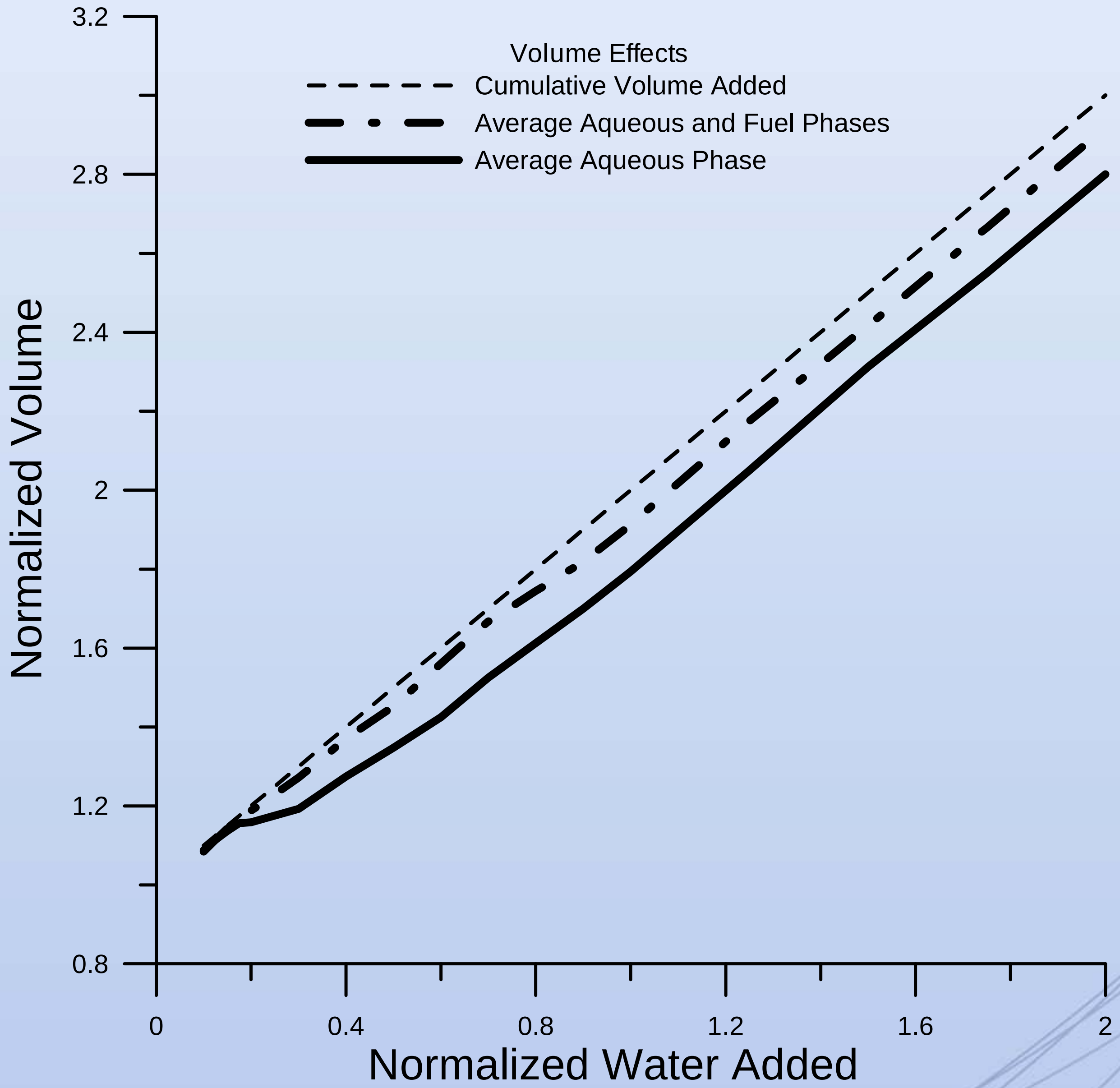

Normalized Gasoline Released
1
0.8
0.6
0.4
0.2
0
0
0.4
0.8
1.2
1.6
2
Normalized Water Addition
E85 and E95
E85 - 1
E85 - 2
E85 - 3
E85 - 4

E10 Gasoline



E85 and E95

E100 Ethanol

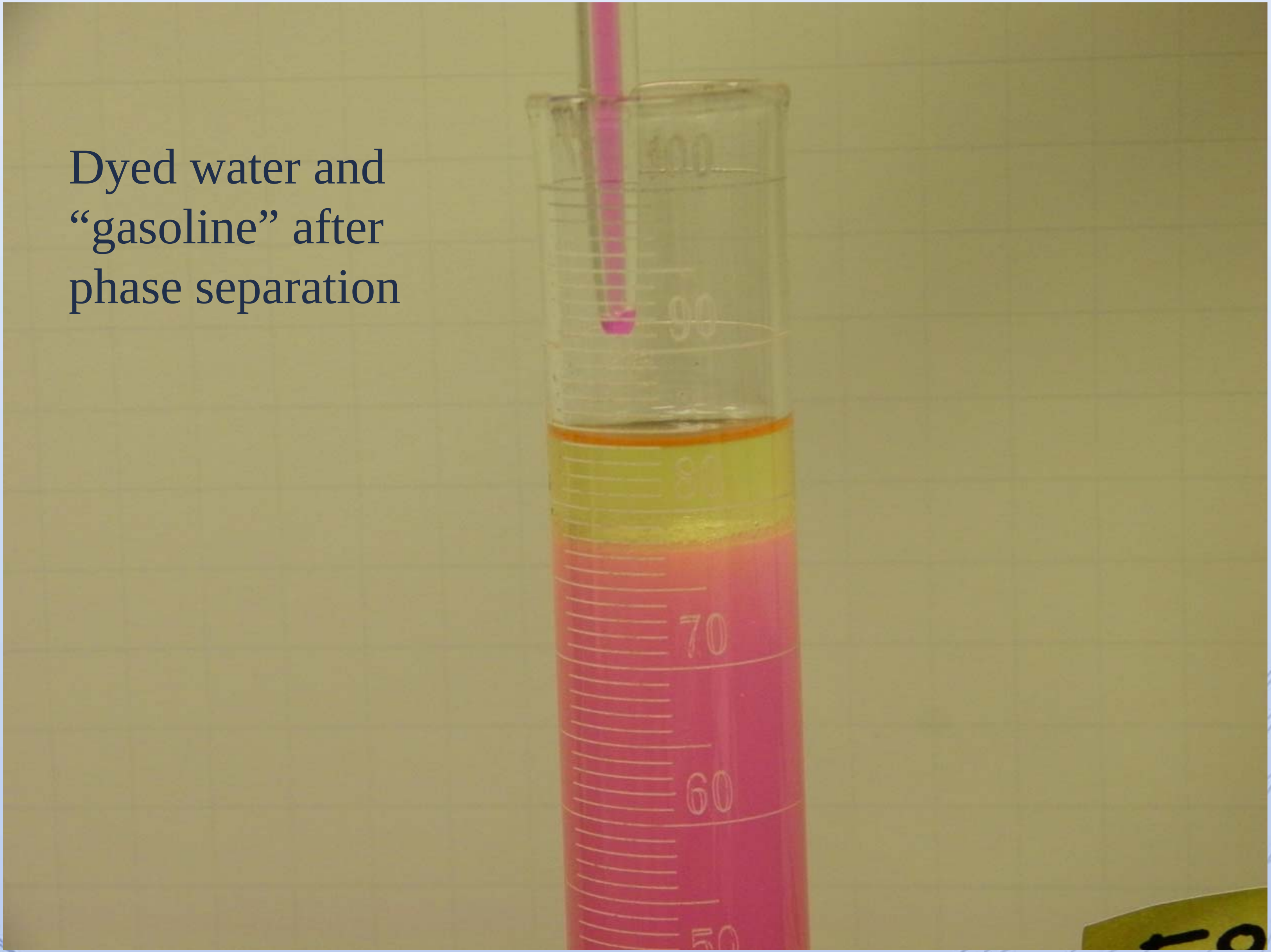


Volume Effects
Cumulative Volume Added
Average Aqueous and Fuel Phases
Average Aqueous Phase
Normalized Volume
Normalized Water Added
3.2
2.8
2.4
2
1.6
1.2
0.8
0
0.4
0.8
1.2
1.6
2

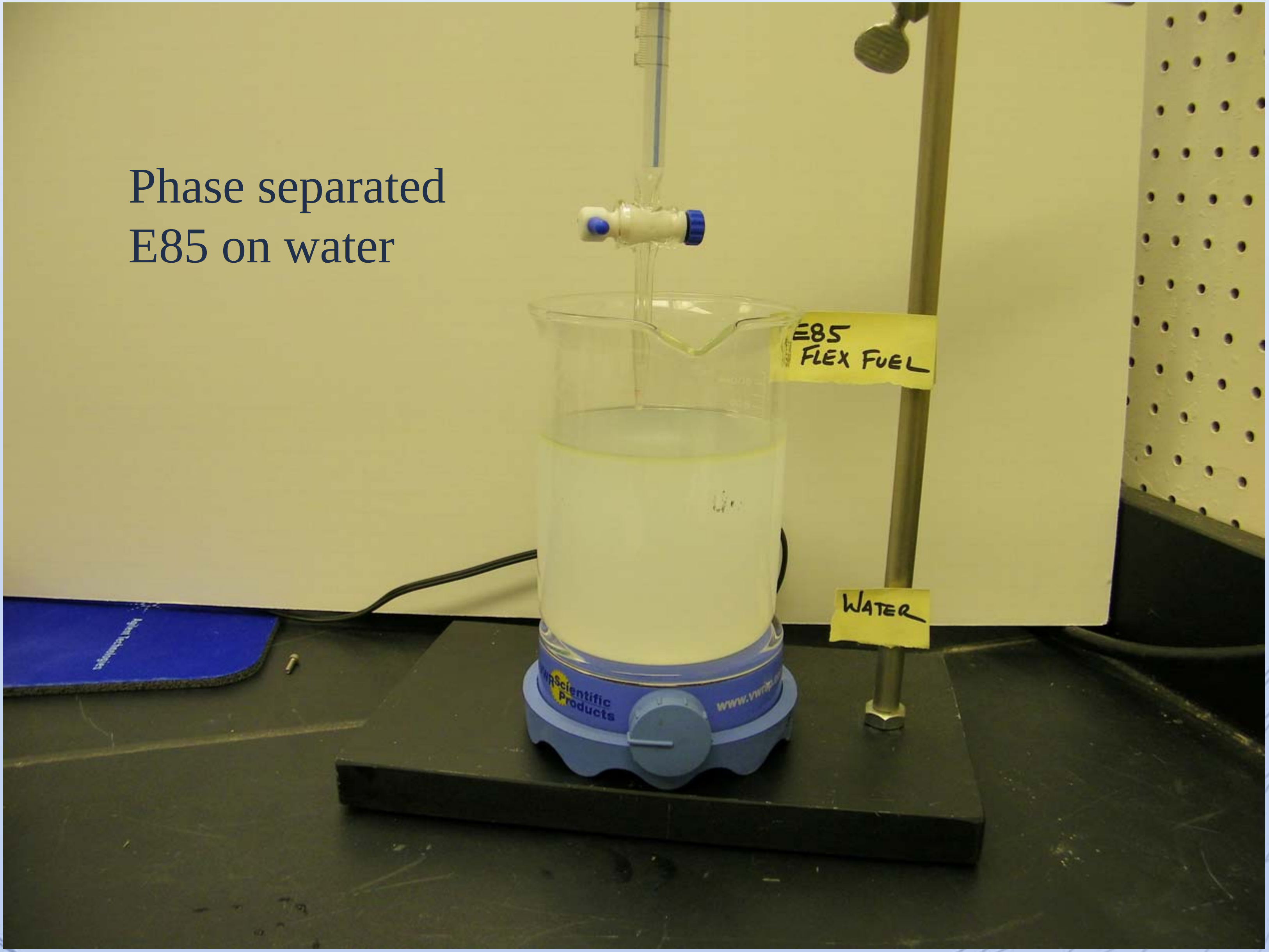
Videos

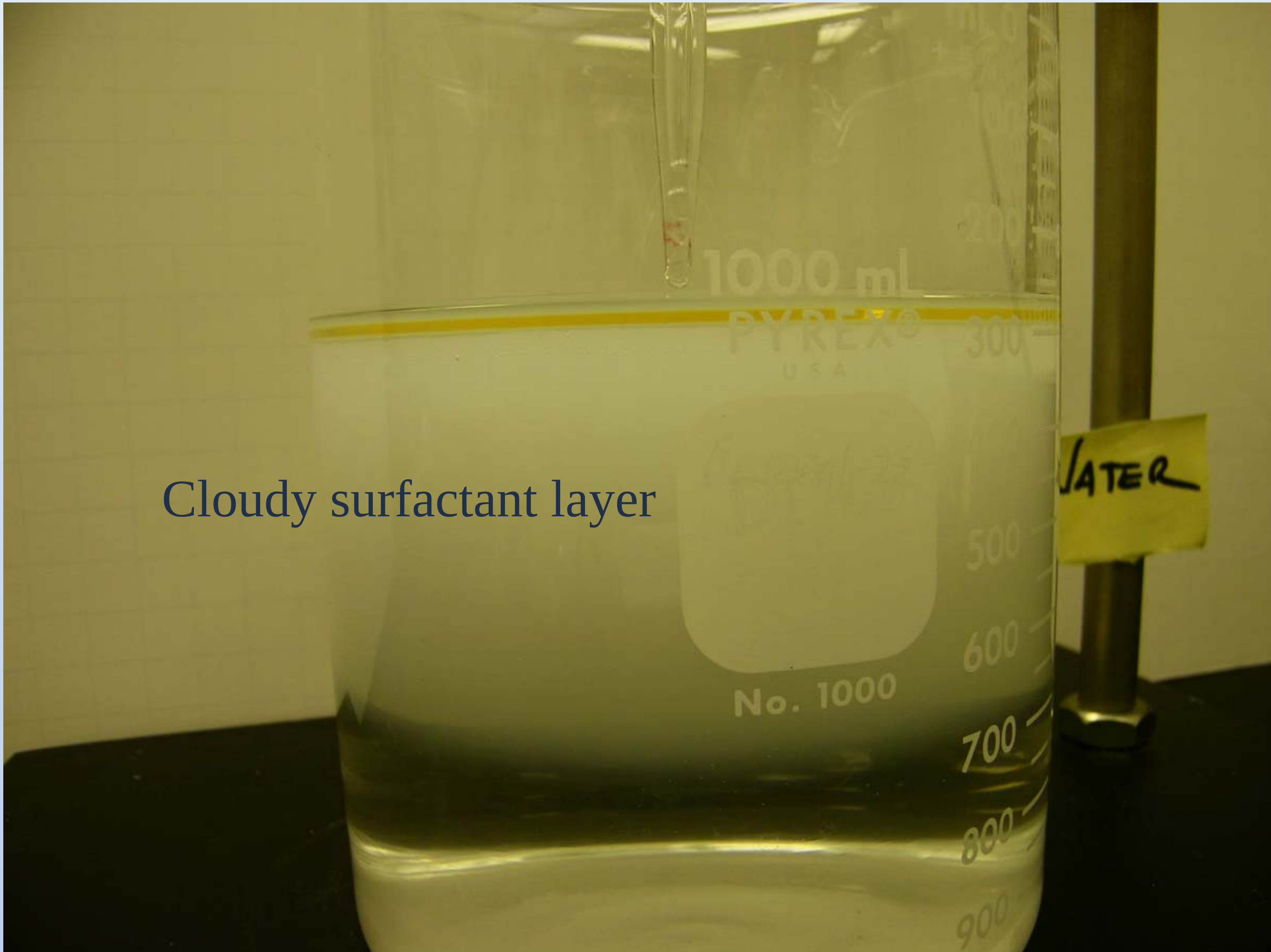
- Dyed Water Added to E85
  - Initially water is absorbed by E85
  - Initially no increase in volume
  - E85 breaks into “gasoline” and aqueous/ethanol phase
- E85 added to water
  - Quiescent E85 jets into water
  - Cloudy surfactant layer over clear water
  - Gasoline accumulates on surface
  - In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

Dyed water and "gasoline" after phase separation

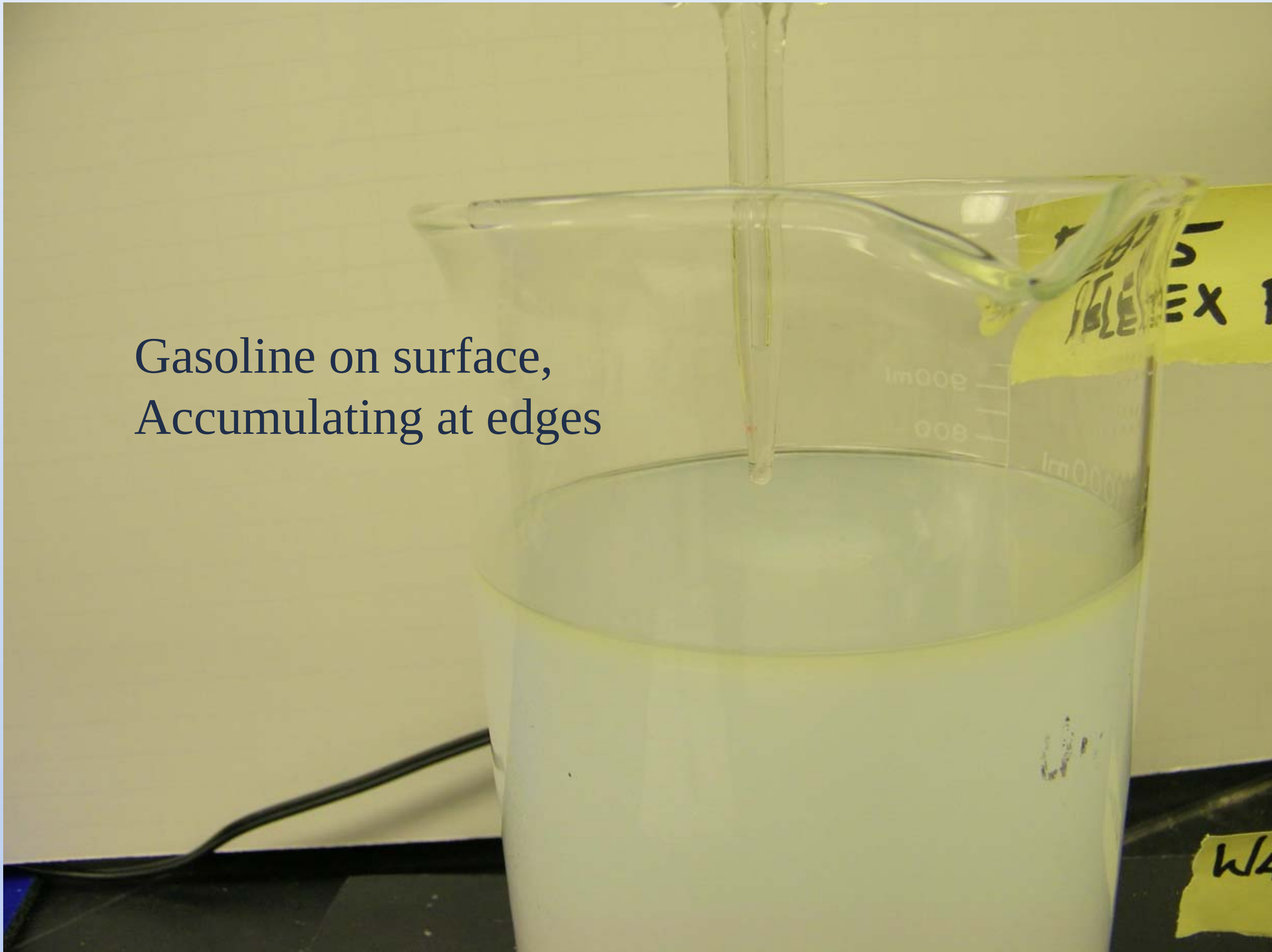


Phase separated
E85 on water

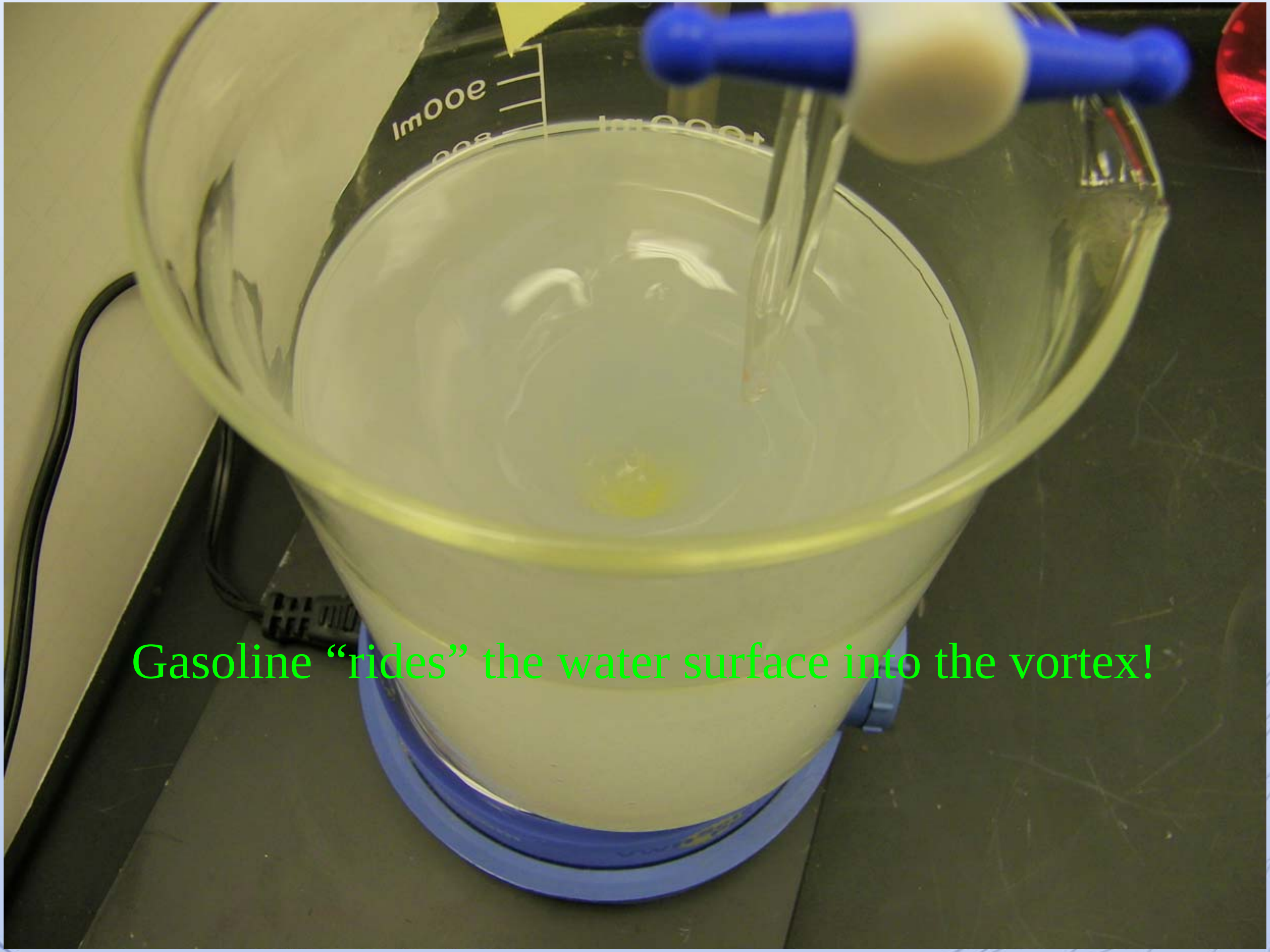




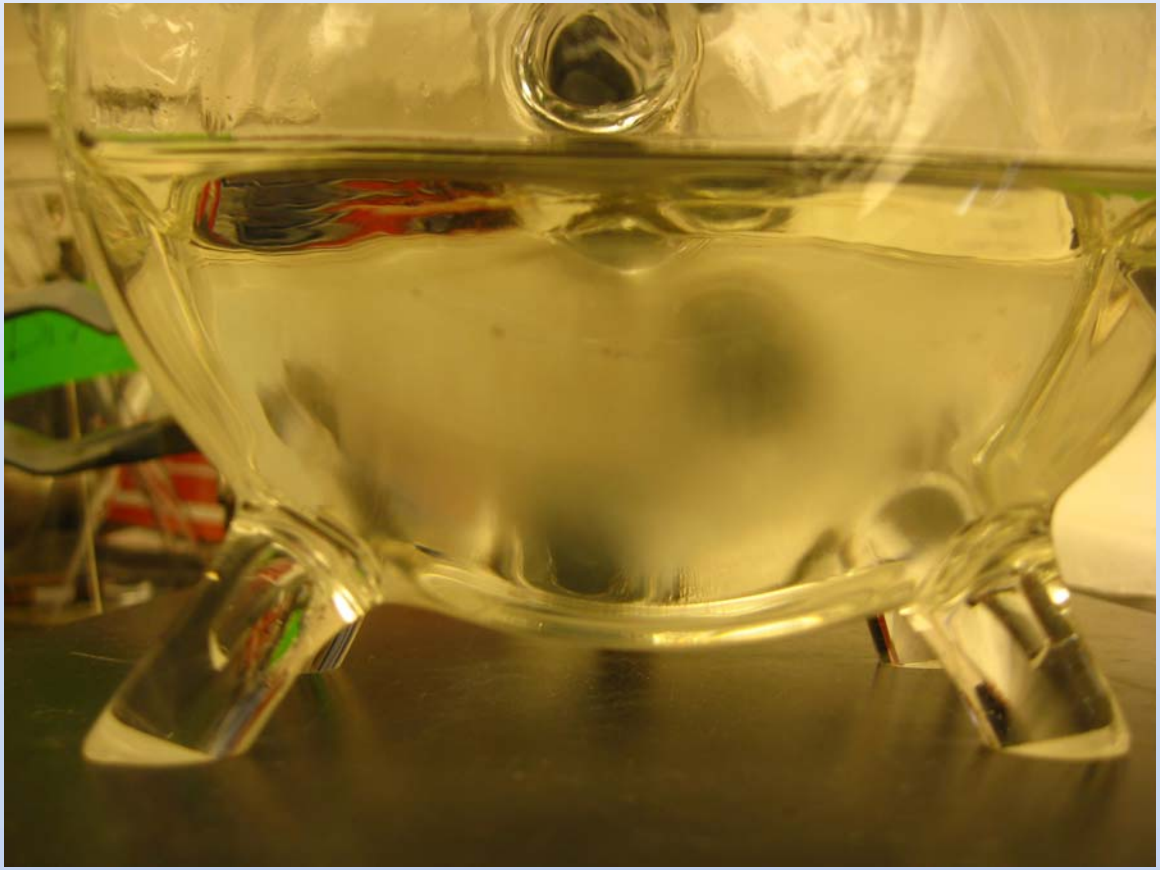
Cloudy surfactant layer



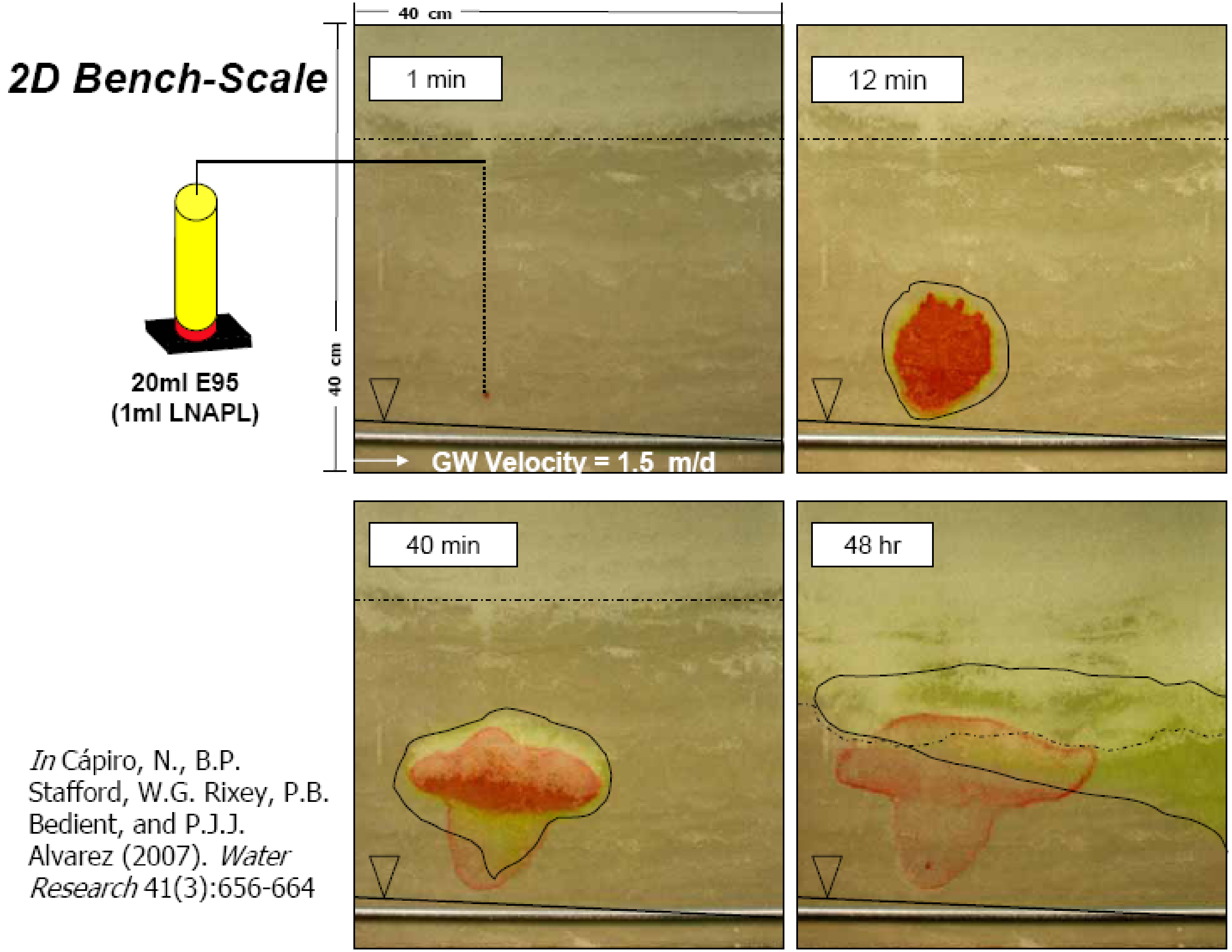
Gasoline on surface,
Accumulating at edges



Gasoline "rides" the water surface into the vortex!




After
2 min
Shaking

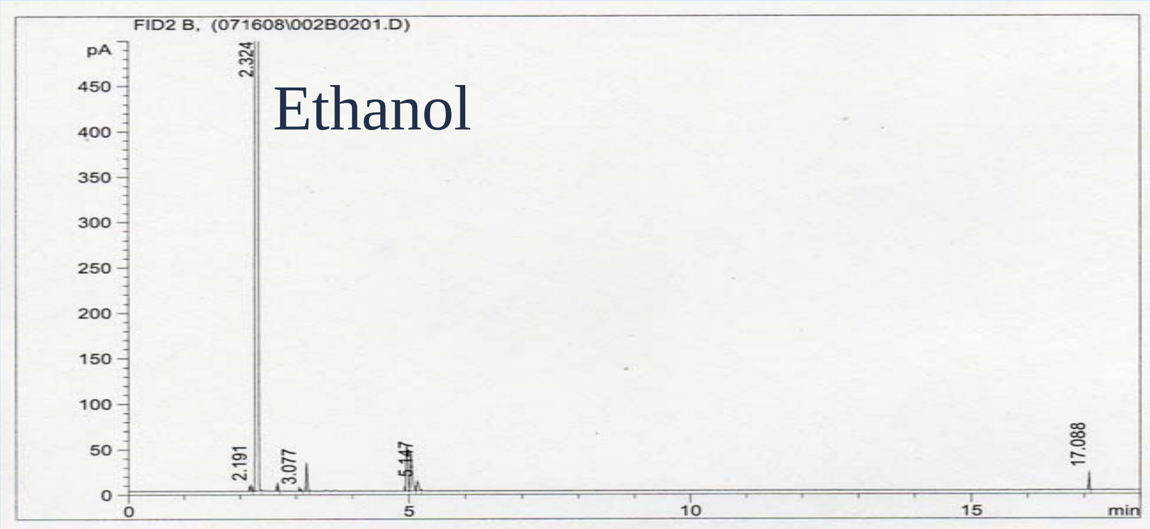


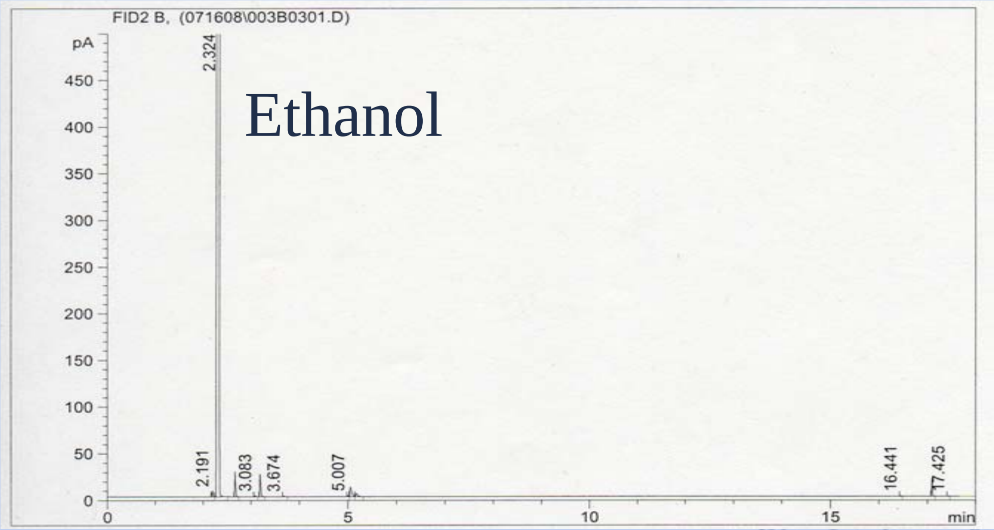
In Cápiro, N., B.P. Stafford, W.G. Rixey, P.B. Bedient, and P.J.J. Alvarez (2007). *Water Research* 41(3):656-664

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	--

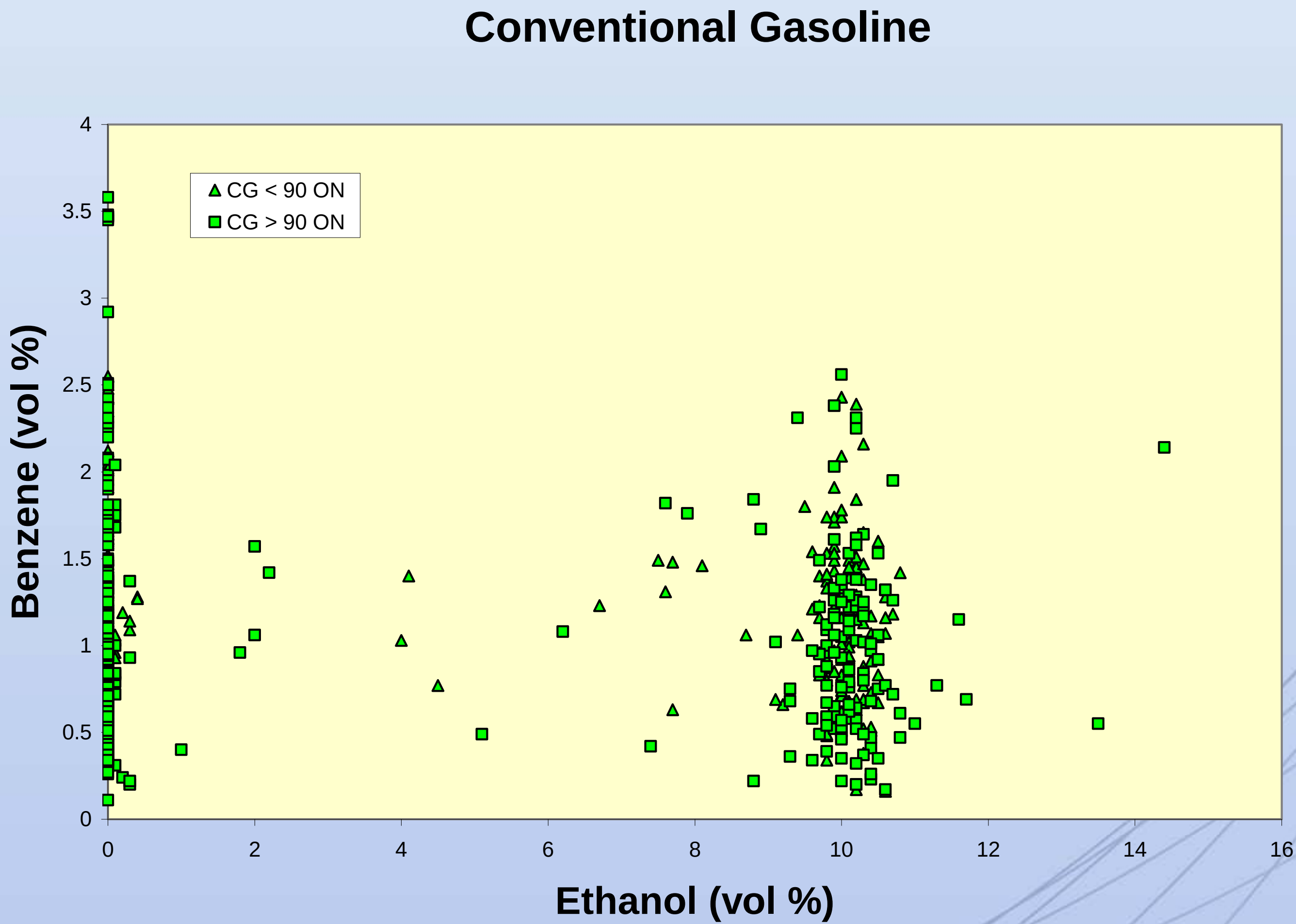
(1) Determined by Karl Fischer titration
(2) Determined by remainder of other compounds


FID2 B, (071608\002B0201.D)
pA
Ethanol
2.324
2.191
3.077
5.147
17.088
min

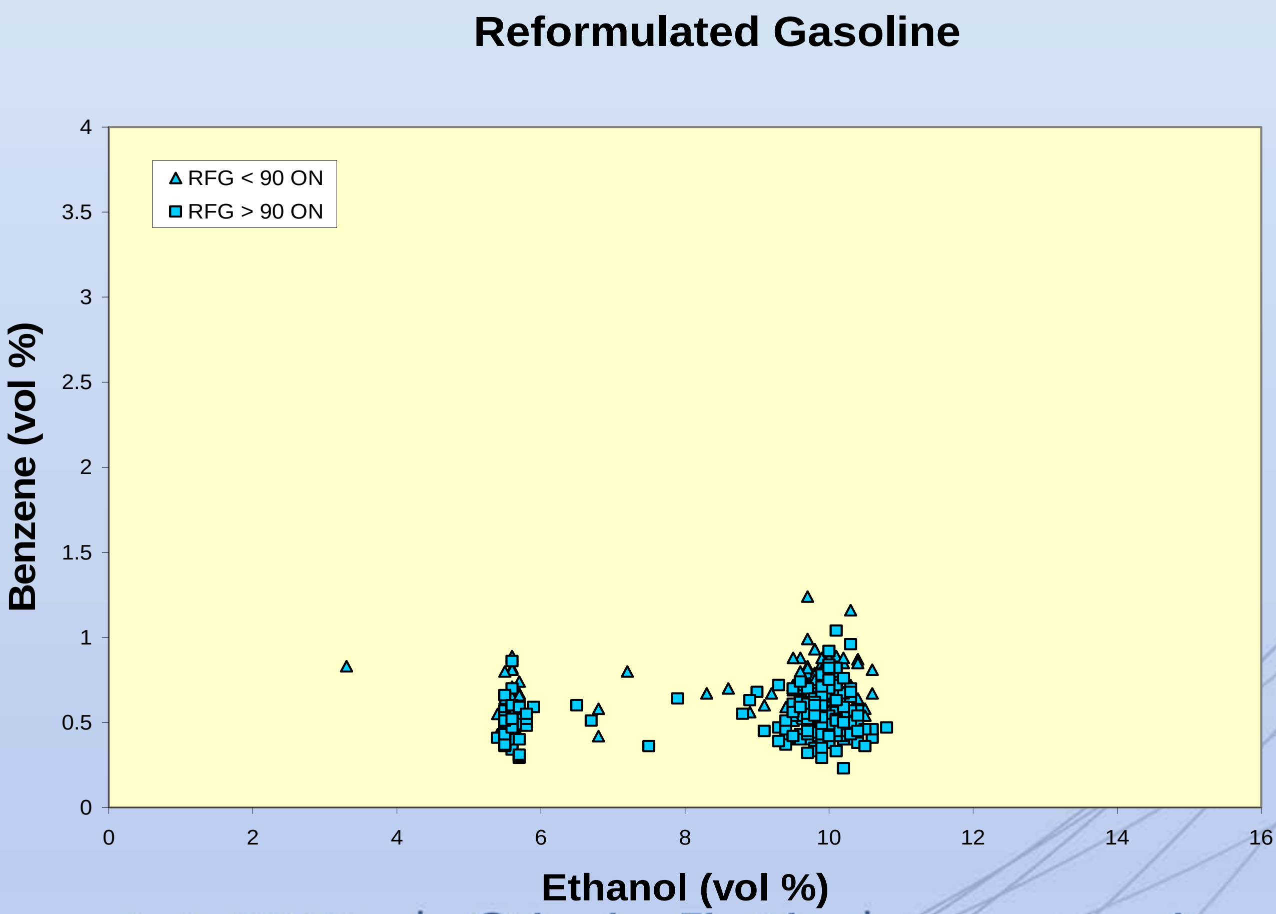

FID2 B, (071608\003B0301.D)
pA
Ethanol
2.324
2.191
3.083
3.674
5.007
16.441
17.425
min

Observed Ethanol Concentrations in Gasoline

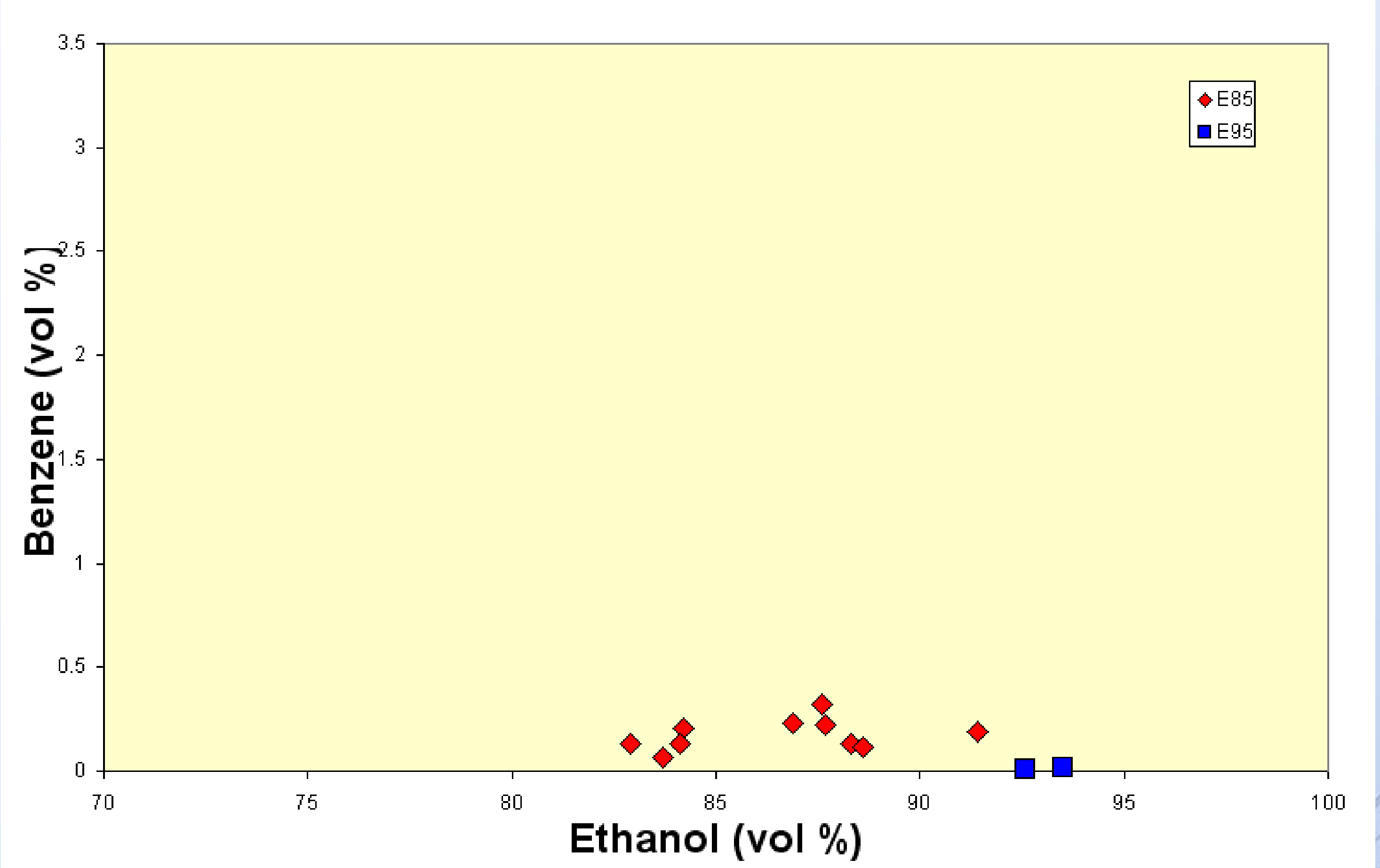
Northrop-Grumman (successor to NIPER) Bartlesville, Oklahoma



Northrop-Grumman (successor to NIPER) Bartlesville, Oklahoma



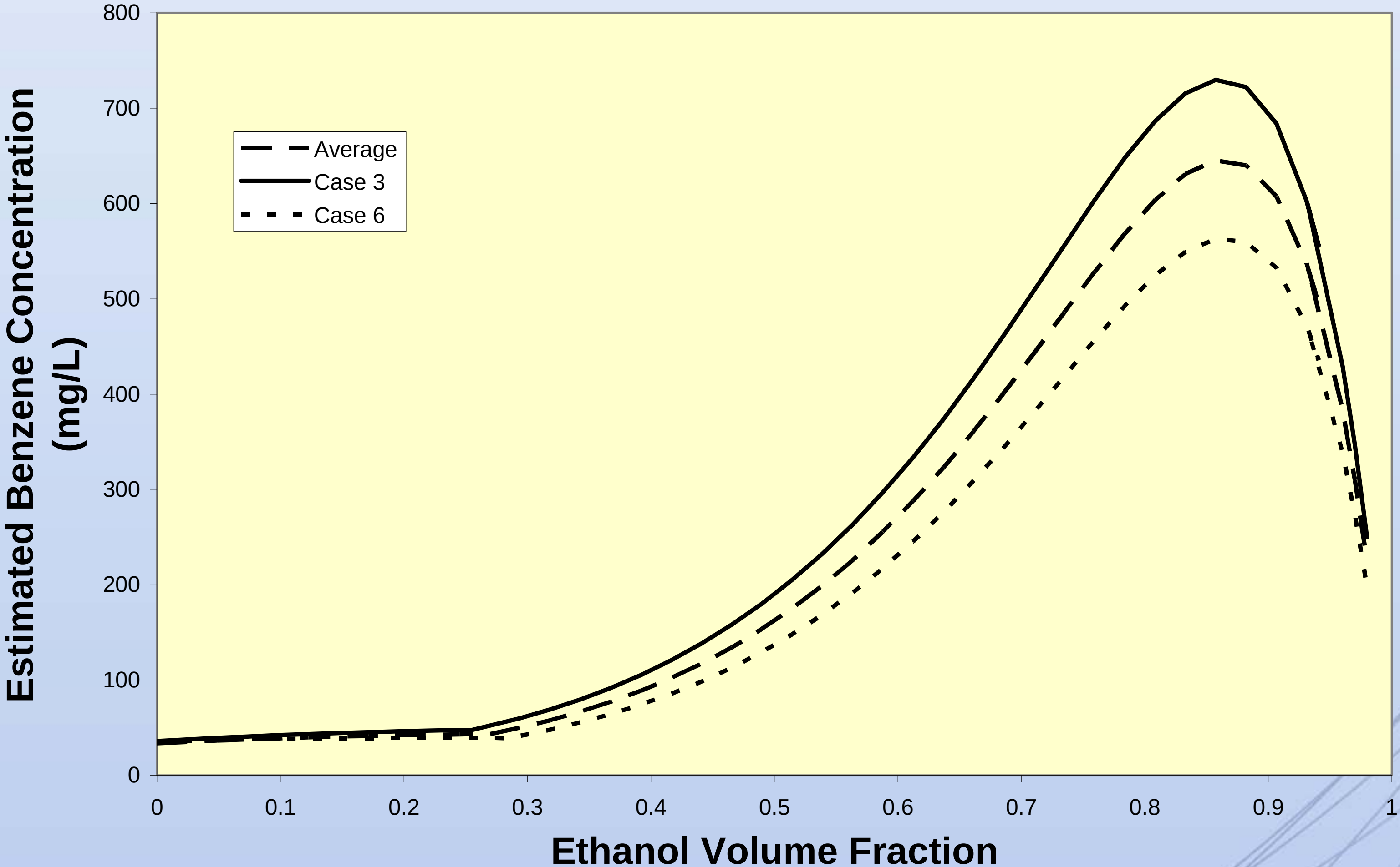

E85
TM
85% Ethanol
11
E-85
MINIMUM
85%
ETHANOL
$
Price per gallon
All taxes included
Ethanol
PRESS


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

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



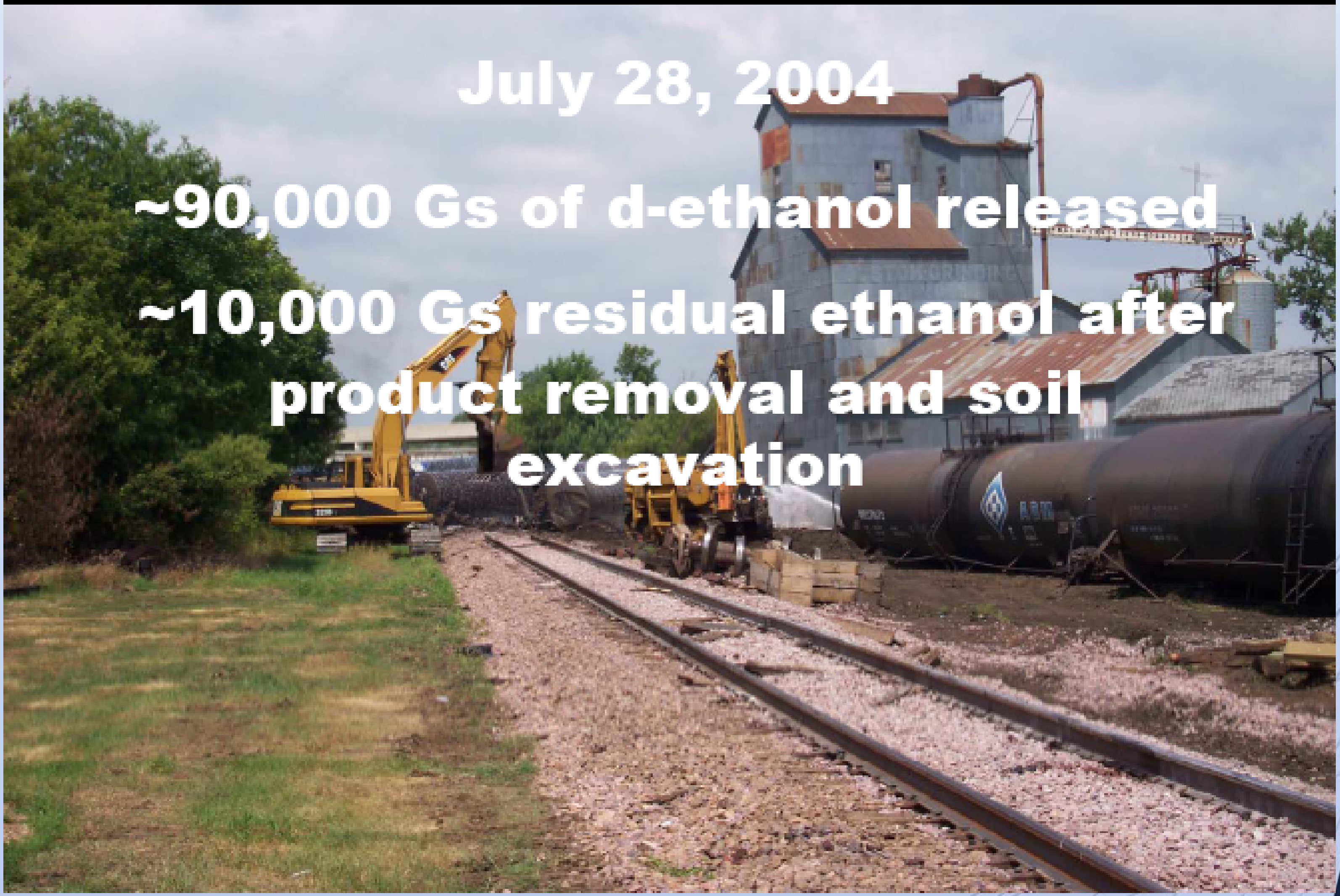
Spill to Land, Info. Courtesy of Dr. Roy Spalding, U of Nebraska

Balaton, Minnesota

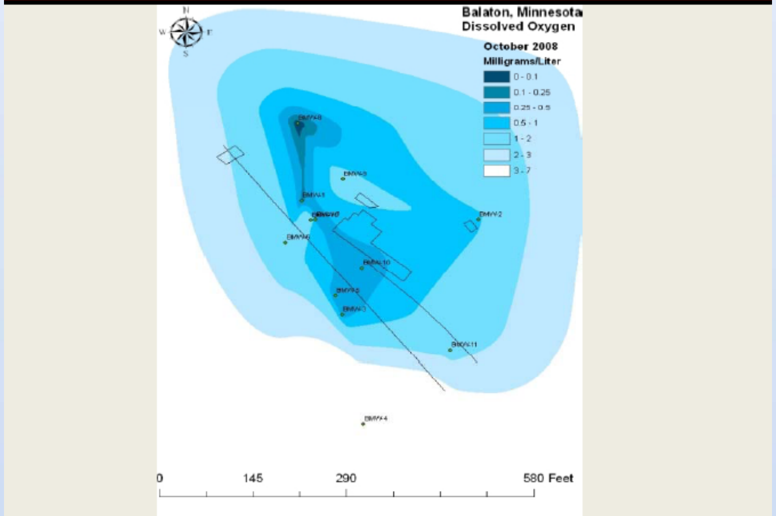
July 28, 2004

~90,000 Gs of d-ethanol released

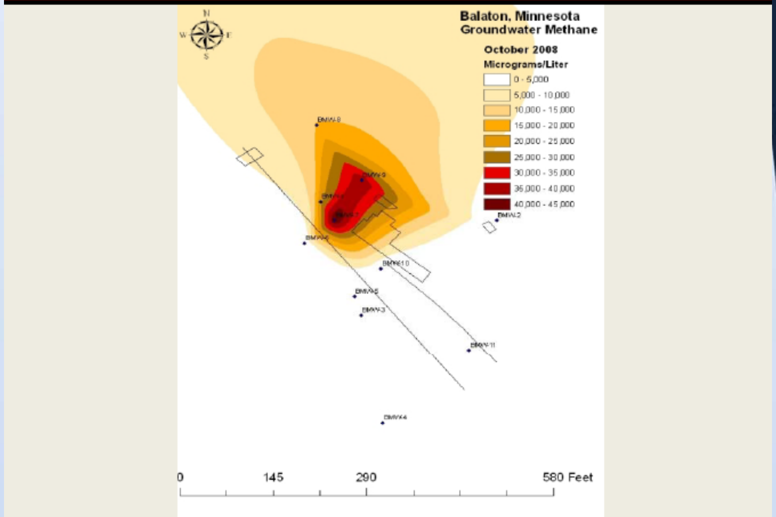
~10,000 Gs residual ethanol after product removal and soil excavation



D. Oxygen: 4.3 Years After Derailment

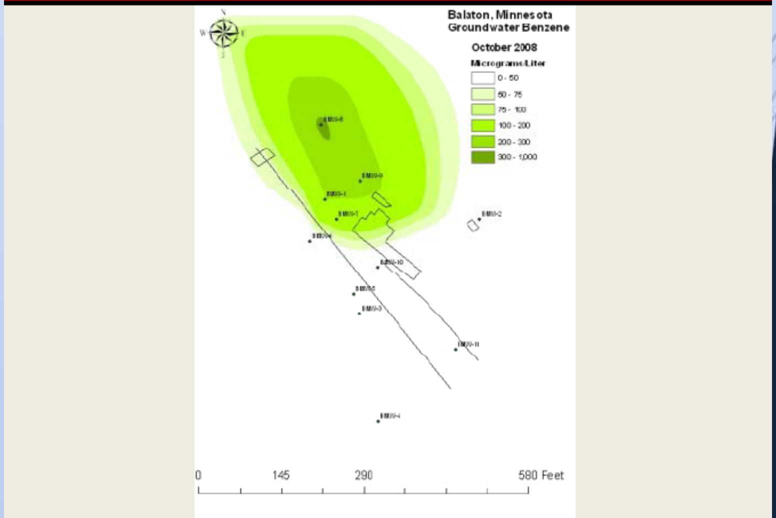


Methane: 4.3 Years After Derailment



- 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

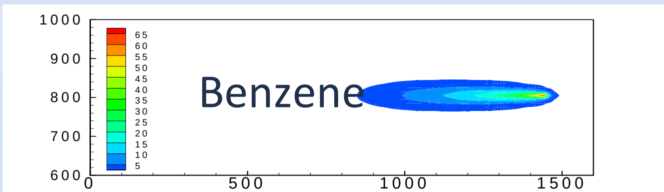
Benzene: 4.3 Years After Derailment

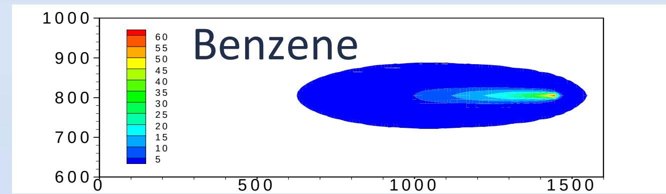


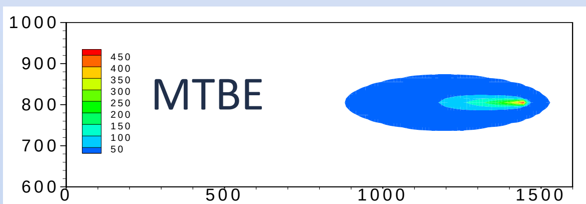
E10 Releases to Land

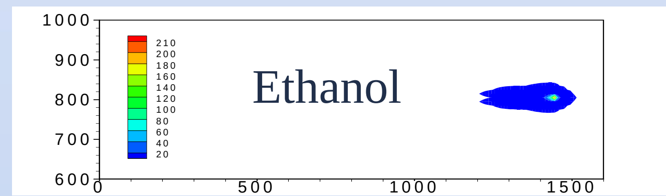
- Formation of groundwater plumes
- Biotransformation of ethanol causes extension of BTEX plumes
  - Order of 2x length
- Simulation (next slide) requires accounting for electron acceptors/donors: O_2, NO_2, Fe^{+++}, SO_4, CO_2

Modeled RFG (w MTBE) vs E10









- Plan views:
- Flow is to the left
- MTBE/Benzene: low biodegradation of MTBE, benzene plume is degraded, and limited in extent
- E10/Benzene, High degradation of ethanol, benzene plume is expanded in extent

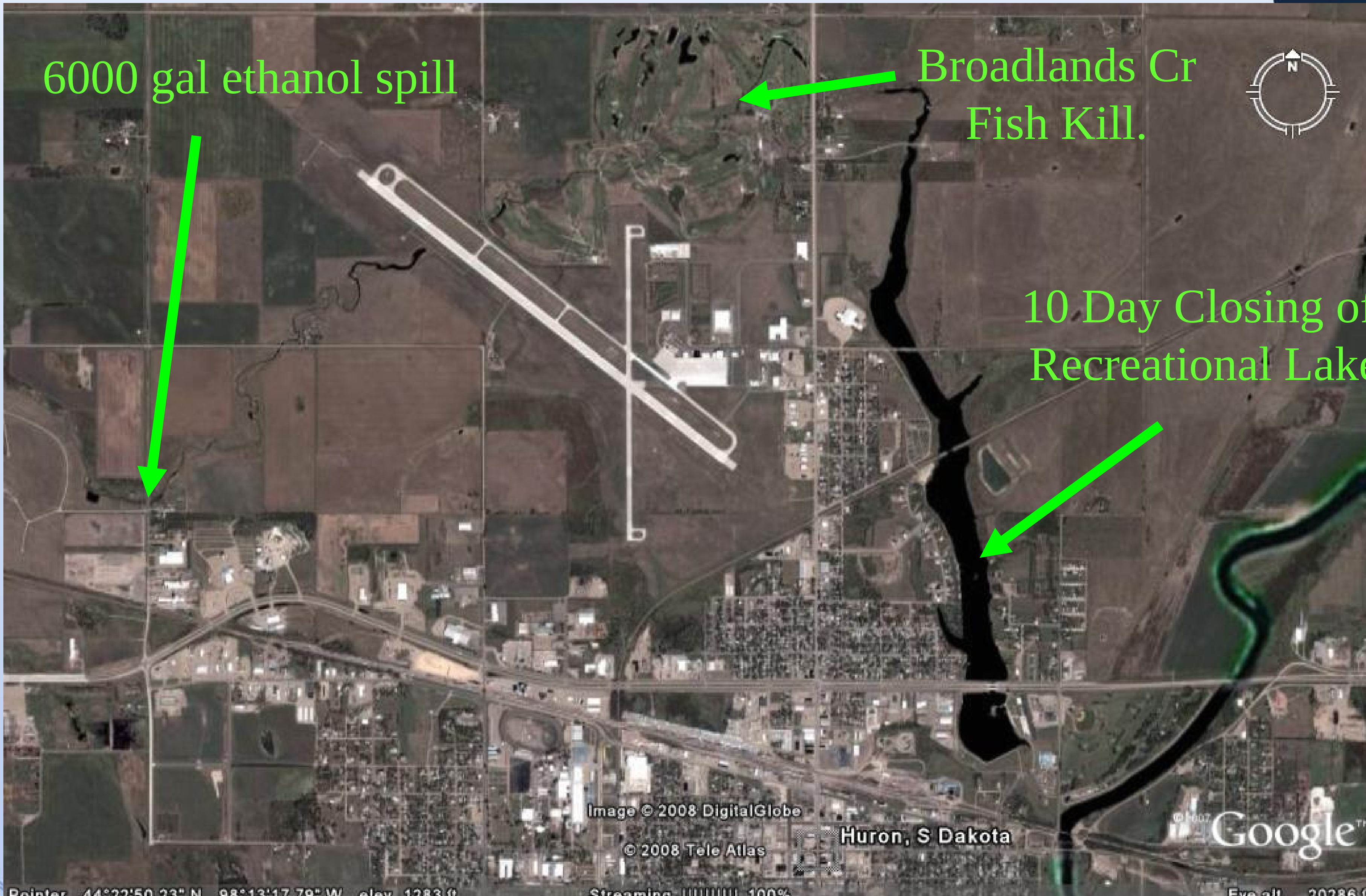
Spill to Broadland Creek May 17, 2008 Info. Courtesy of Kim McIntosh, SD-DENR

- 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
  - o BTEX, tri-methylbenzenes, ethanol, methanol
  - o Most results ND, one sample ethanol at 6800 ppb
- Generally increased D.O. by 5/27/2008
- Fish kill happened before oxygen sparging
  - o Does the depletion of oxygen kill the fish?
  - o Does the ethanol + hydrocarbons kill the fish?
    - (replenishing the D.O. may not save the fish)

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

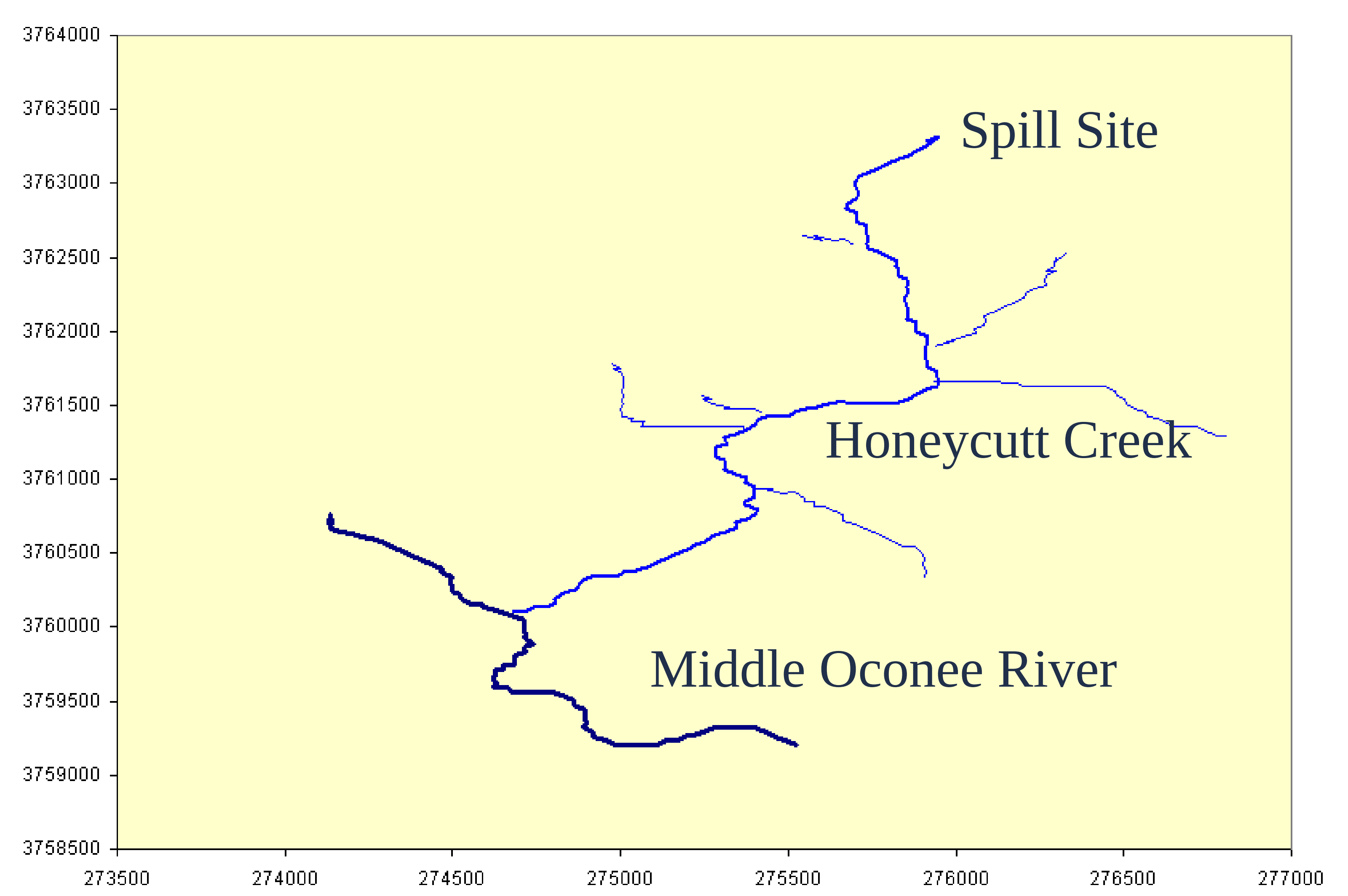
- Spills of denatured alcohol to land based on three field studies:
  - Hangs up in the vadose zone
  - Methane at max solubility
  - Impacts to ground water delayed
- E10 Releases cause extended BTEX plumes
- Spills to water (Broadlands Ck)
  - No observed gasoline slick from denatured alcohol
  - Loss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

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 at confluence of Honeycutt Creek and Middle Oconee River
  - River continues to Lake Oconee 27 miles down river
    - Recreational lake – lots of fishing

Data

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



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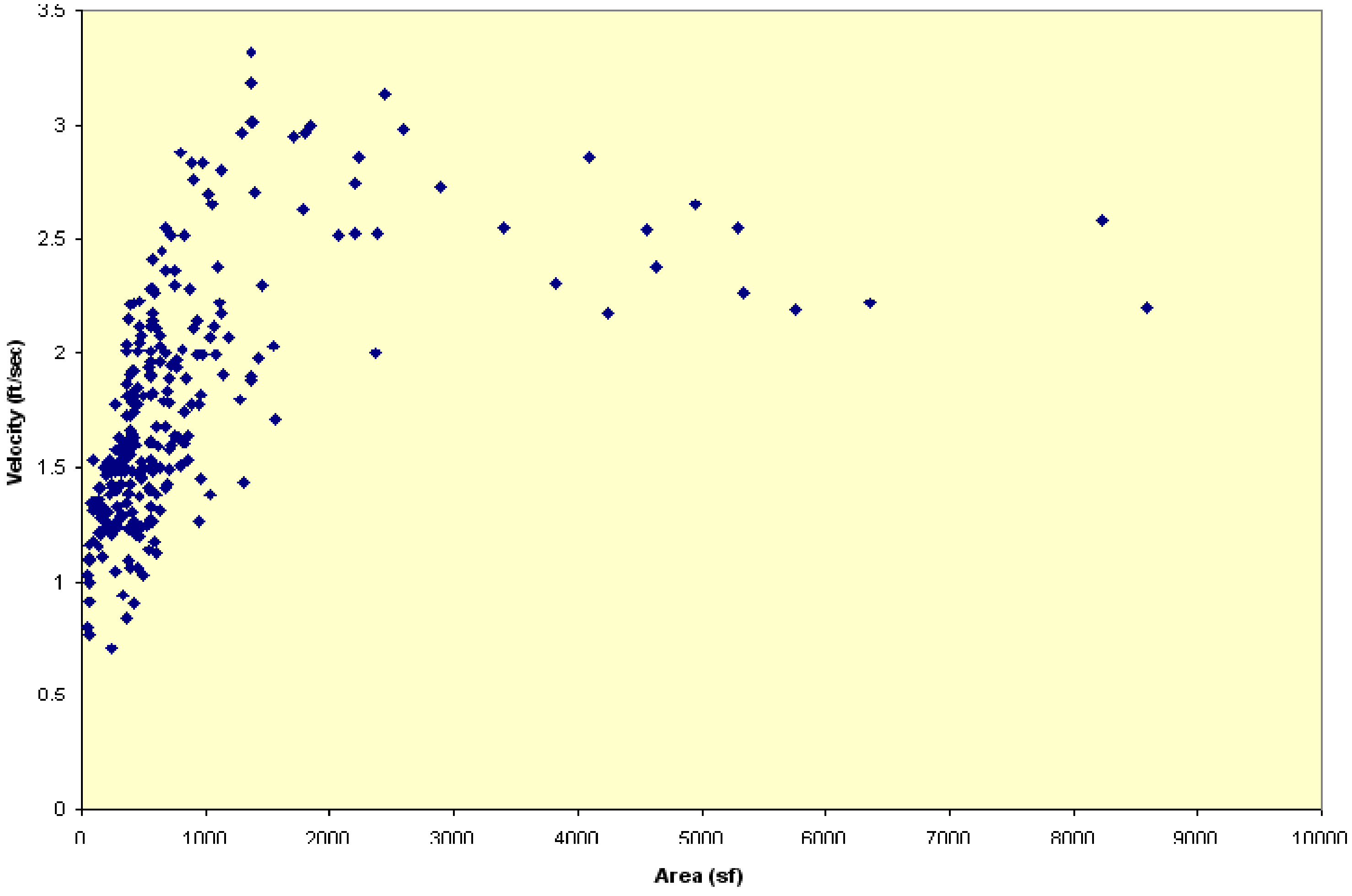
USGS Station Geometry

- 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

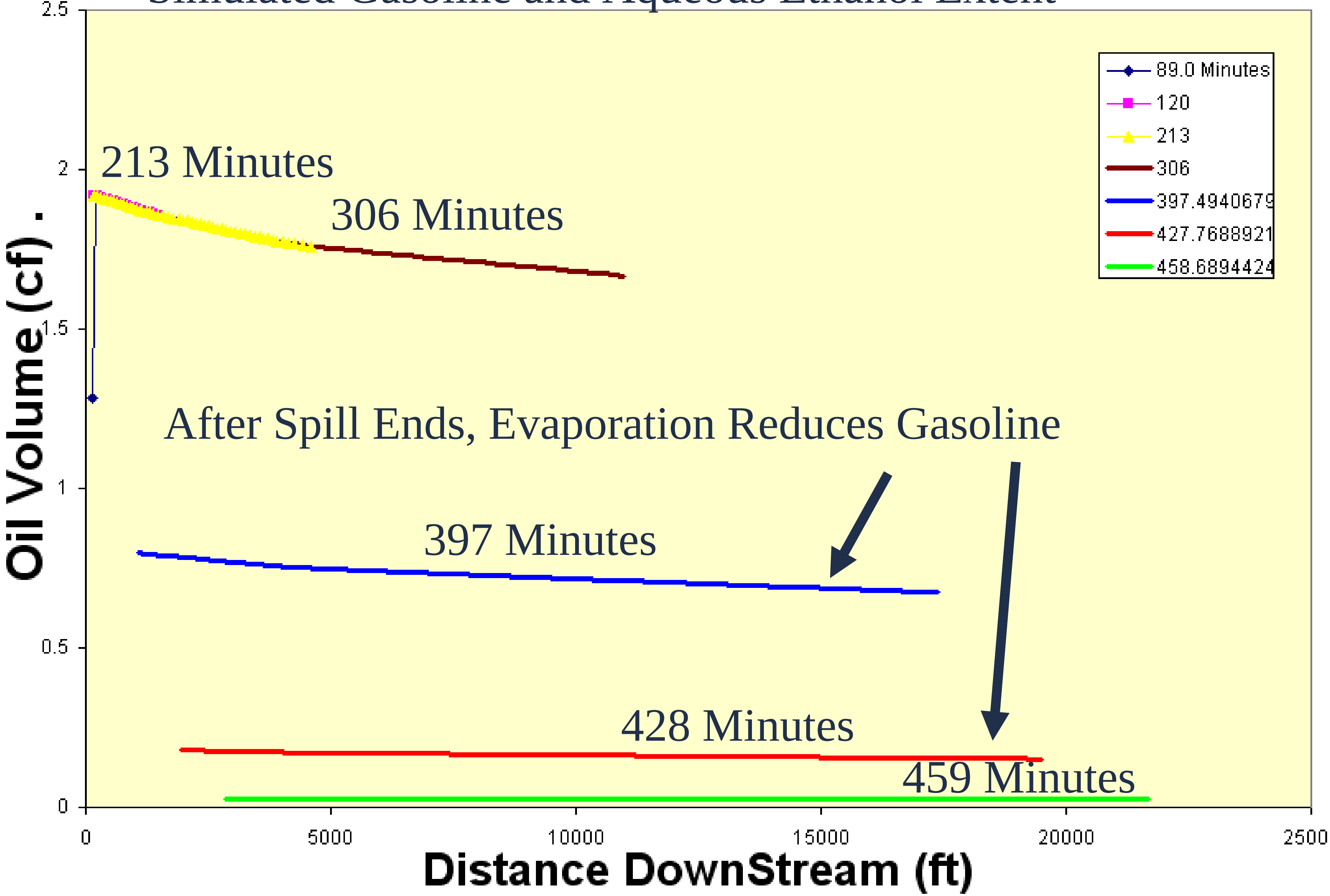
USGS Velocity/Area Data



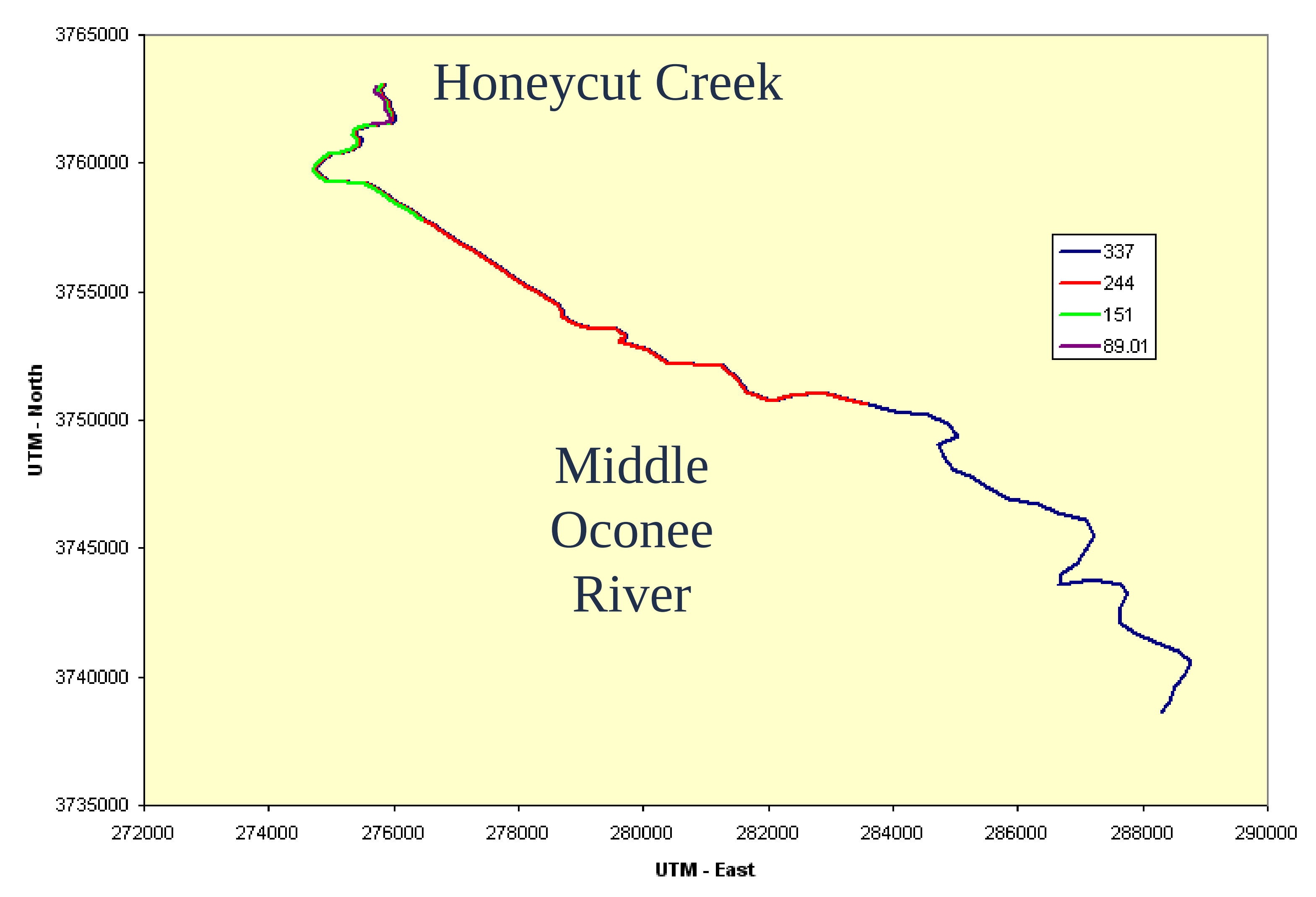
Model Approach

- Use measured flows to drive transport model
- Lagrangian approach to gasoline slick transport
  - Cosolvancy calculation for BTEX and other petroleum hydrocarbons
  - All ethanol washes out of fuel
    - Supported by experimental results
  - Gasoline evaporates based on time on river
- Eulerian-lagrangian approach to ethanol/BTEX/oxygen transport
  - Accurate solution of the transport equation necessary to correctly simulate reaction
  - Implemented via a flexible/extensible approach

Simulated Gasoline and Aqueous Ethanol Extent



Oil Slick Extent



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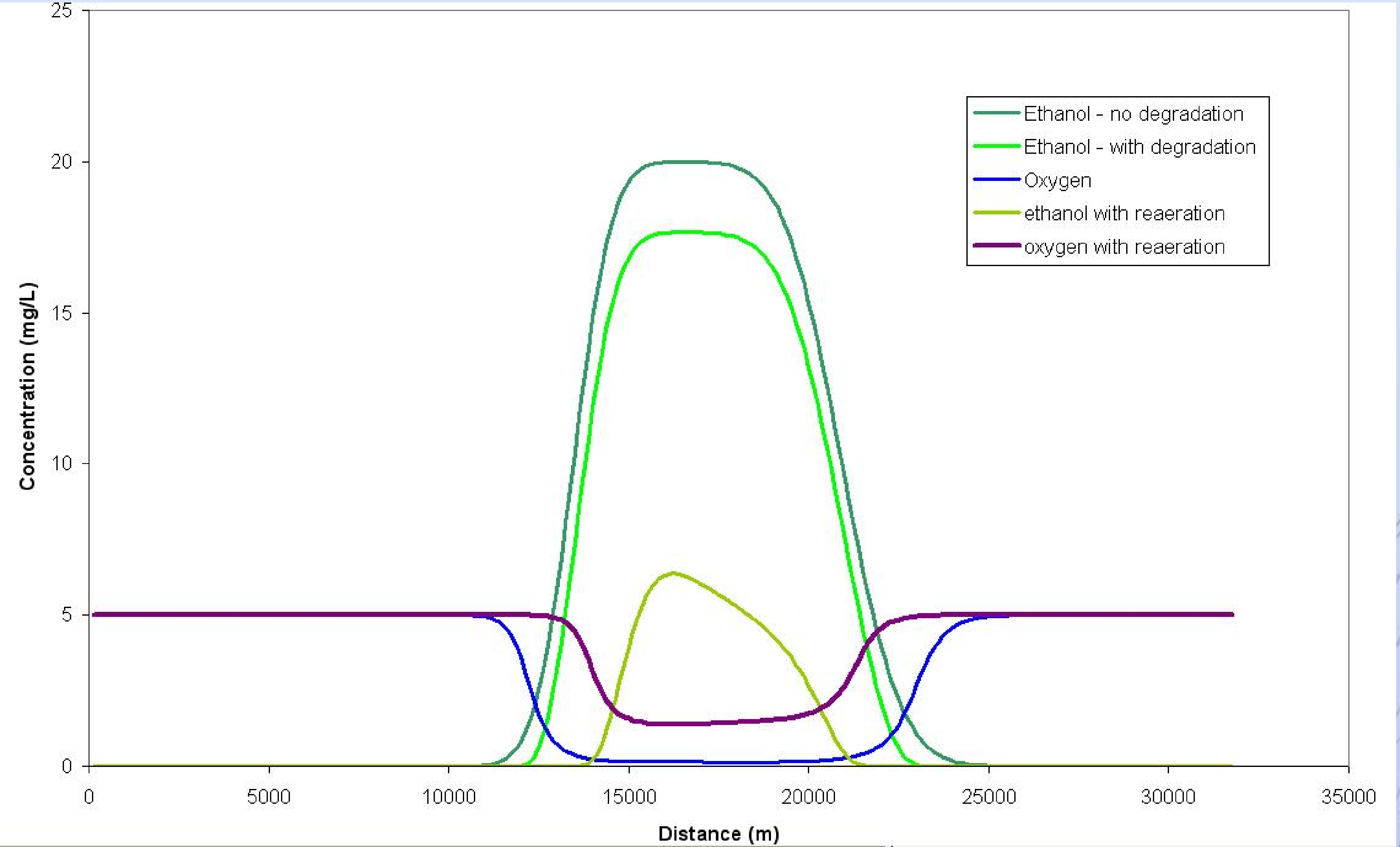
Reactive Transport for Ethanol/BTEX and oxygen

- Ethanol degrades aerobically in the presence of oxygen
- Approximately 2 g of O_2 required to mineralize 1 g of ethanol
- Oxygen is supplied from
    - Ambient dissolved oxygen concentration in water
    - Re-aeration from the atmosphere
    - Oxygenated inflows

Test Problem to Illustrate Appropriate Stoichiometry



Next Steps

- Assembling data for Rockford, Ill spill
- Increased efficiency in the model is needed in order to simulated 100+ river miles
- Linkage with bioaccumulation/toxicity model to estimate fish kill due to ethanol + hydrocarbon toxicity
- Others

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*
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