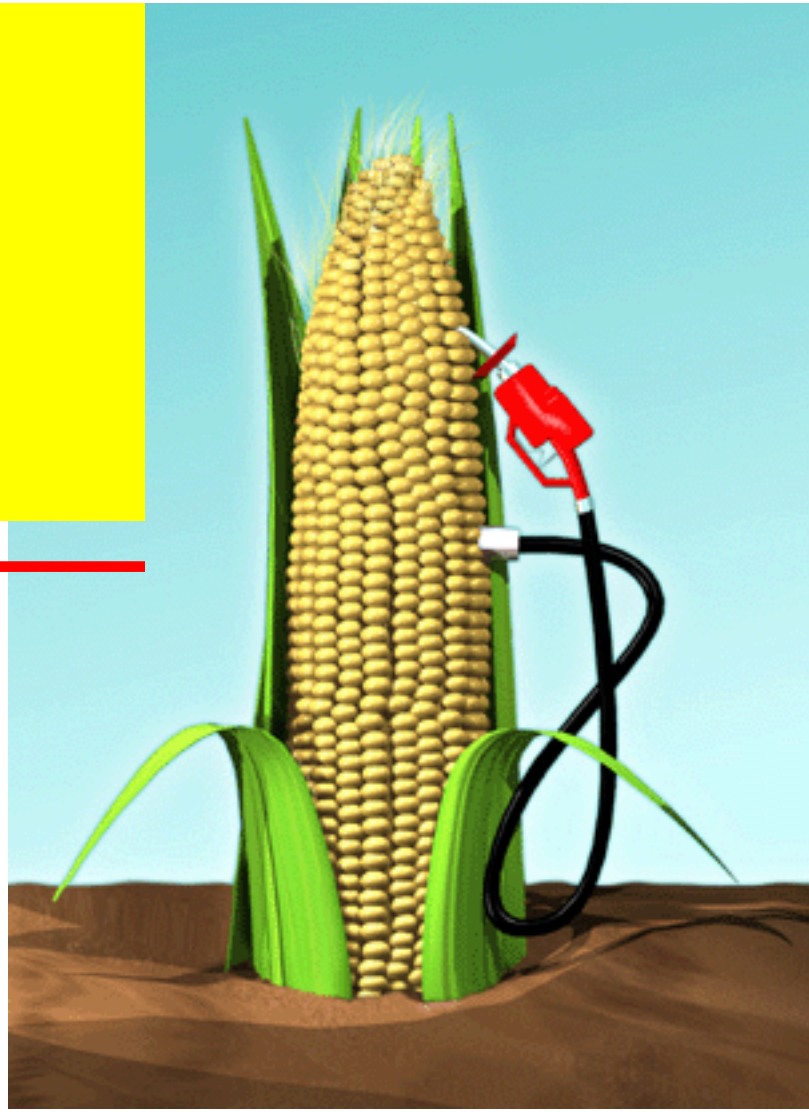
Ethanol in Fuel: Implications for Groundwater Pollution



Pedro J.J. Alvarez

RICE

Background

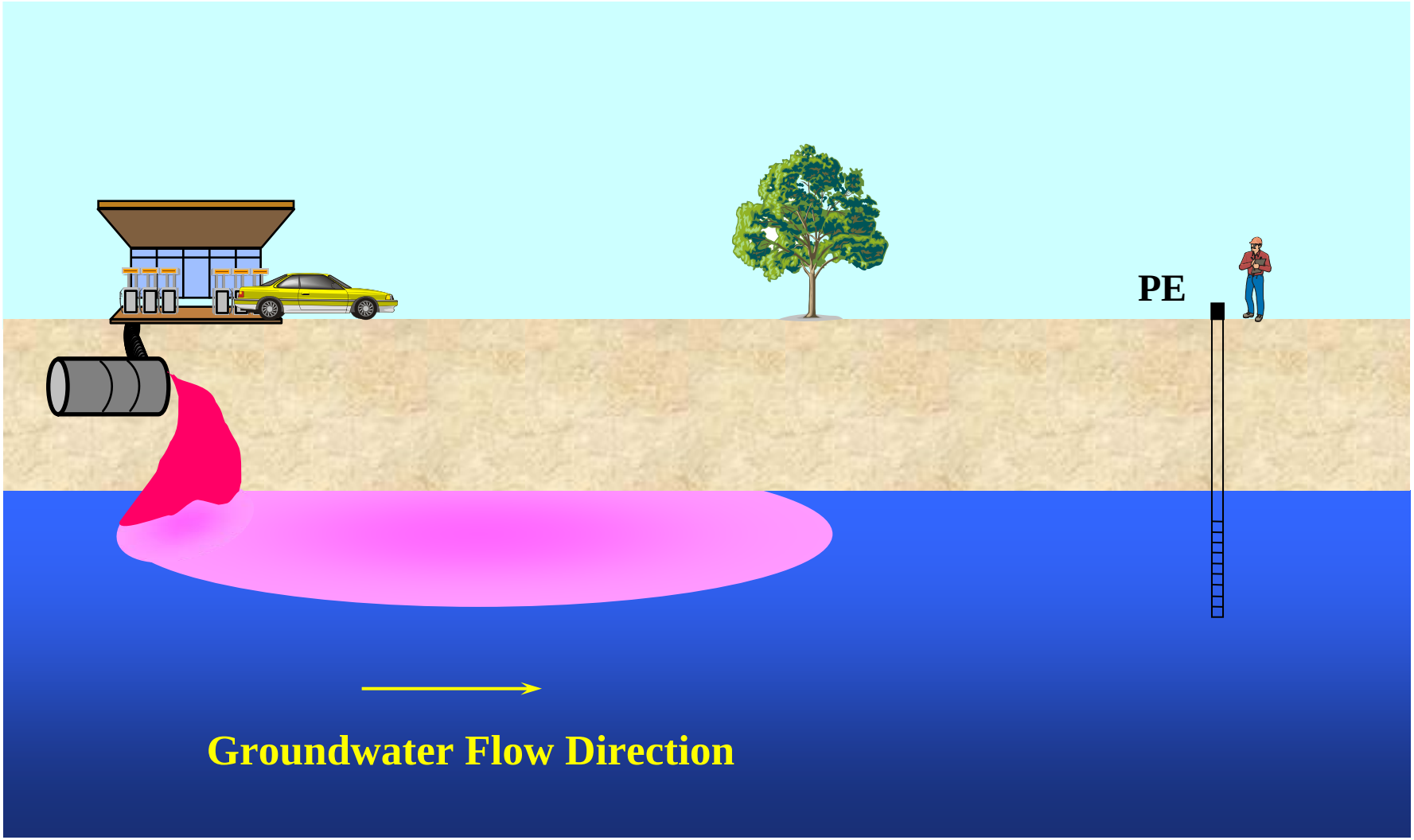
Ethanol is a good oxygenate (reduces air pollution from combustion), renewable, biodegradable, non-toxic, and can serve as substitute fuel for imported oil (good for trade balance). But...

Food for fuel?

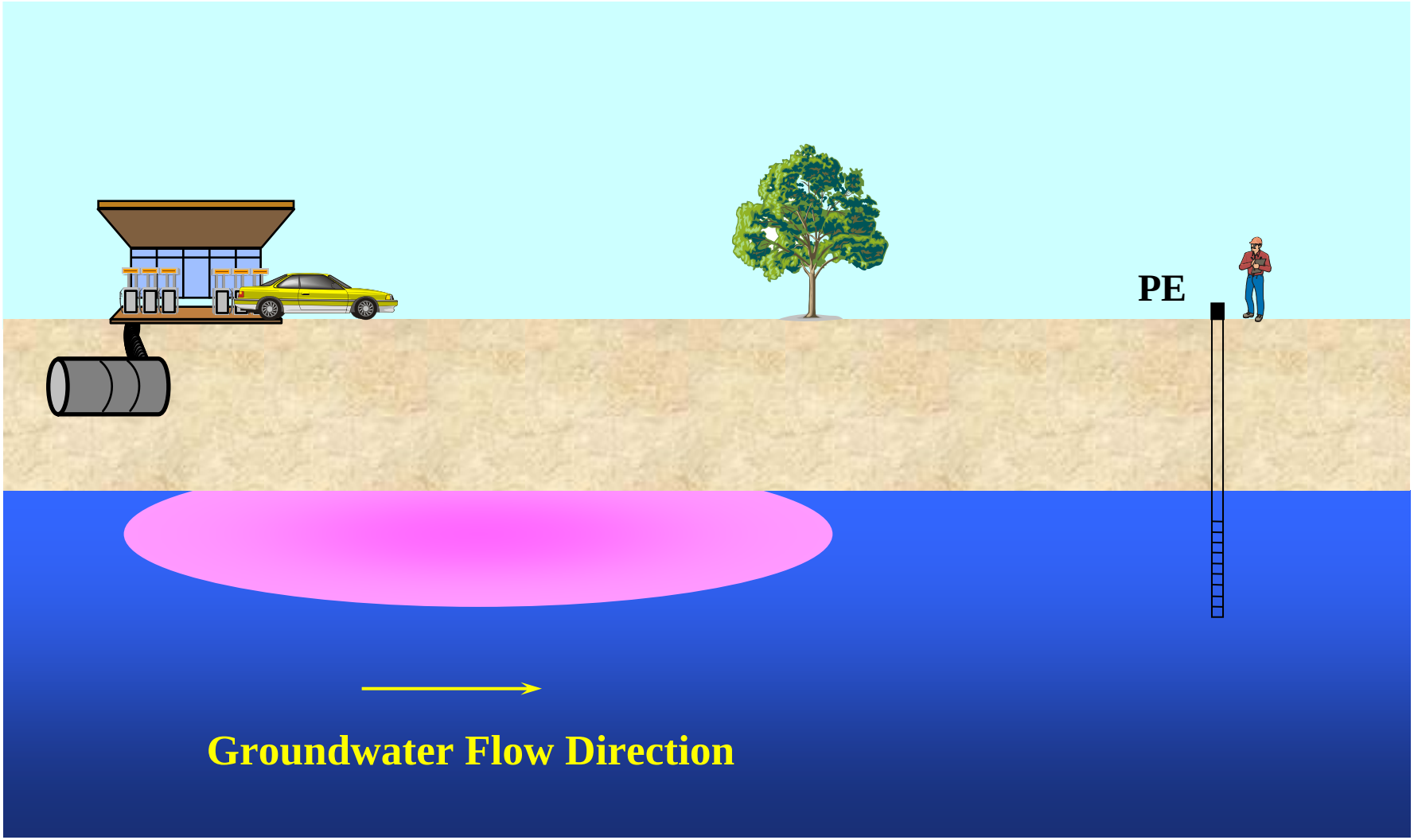
Tax subsidy ($0.51/gal) = corporate welfare for corn growers and ethanol producers?

- How does ethanol affect benzene migration, degradation and natural attenuation, and what is the overall effect on the resulting plume length?

Natural Attenuation

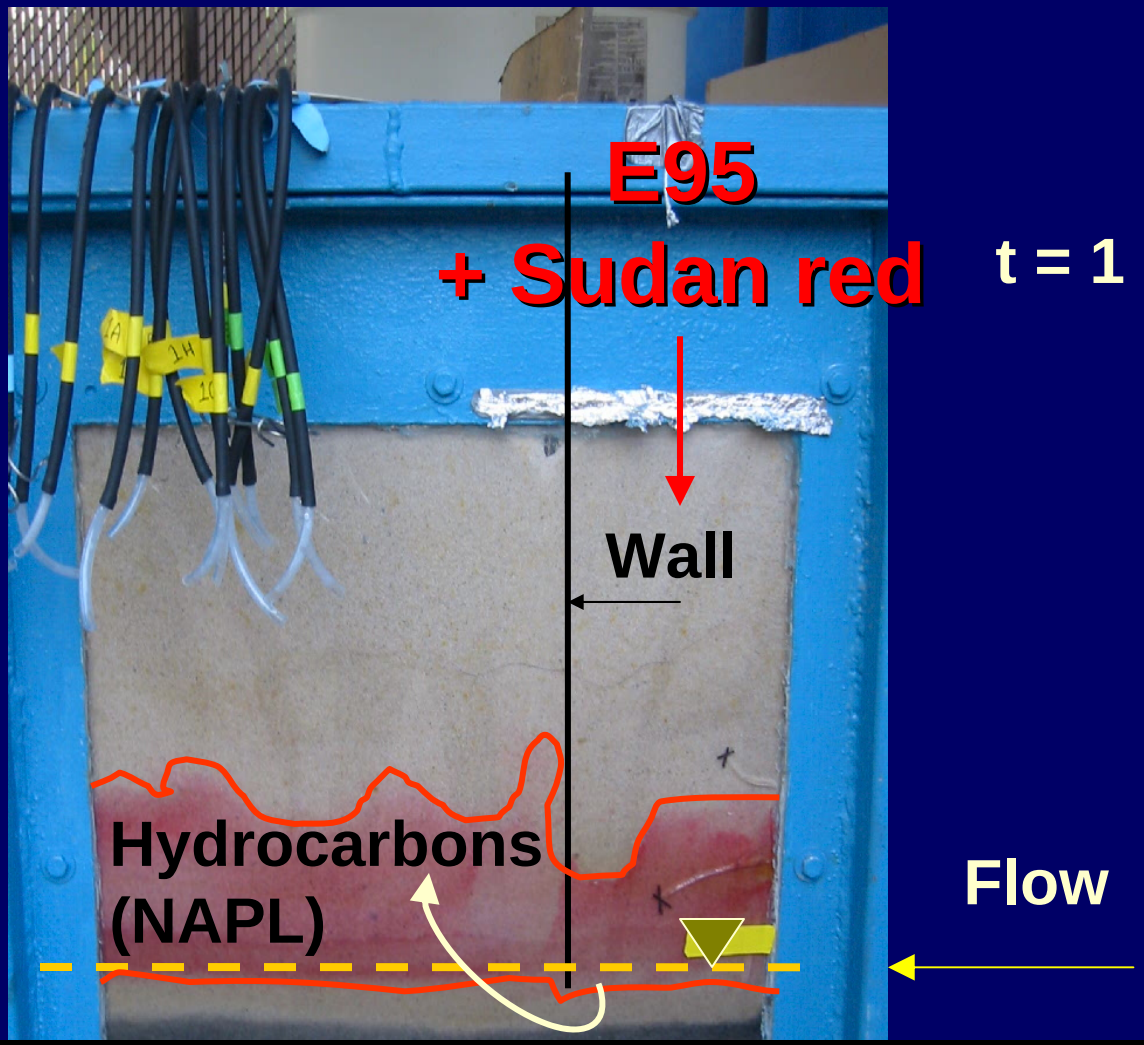


Natural Attenuation



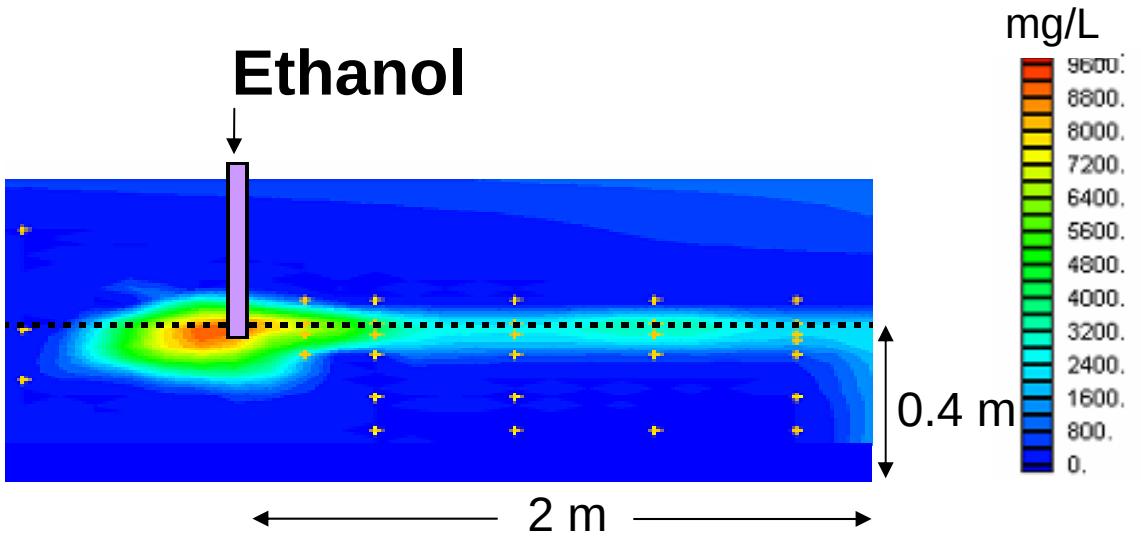
Pilot Ethanol Spill Tank (PEST)

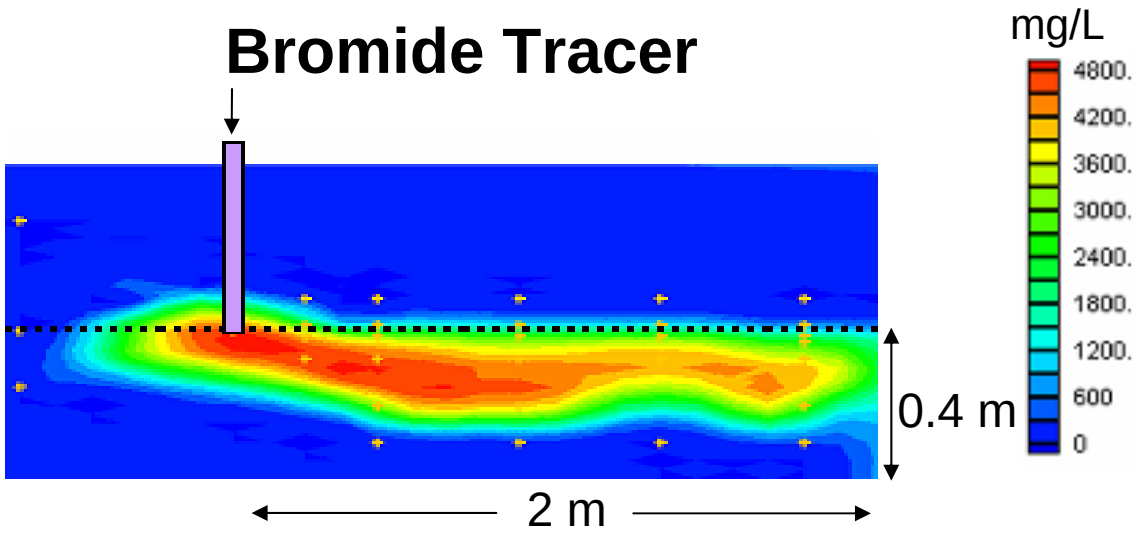
Hydrocarbon NAPL Formation & Movement



EtOH decreases interfacial tension & capillary forces, facilitating flow through the capillary zone. As EtOH is diluted by water, its co-solvent effect decreases and hydrocarbons separate (NAPL).

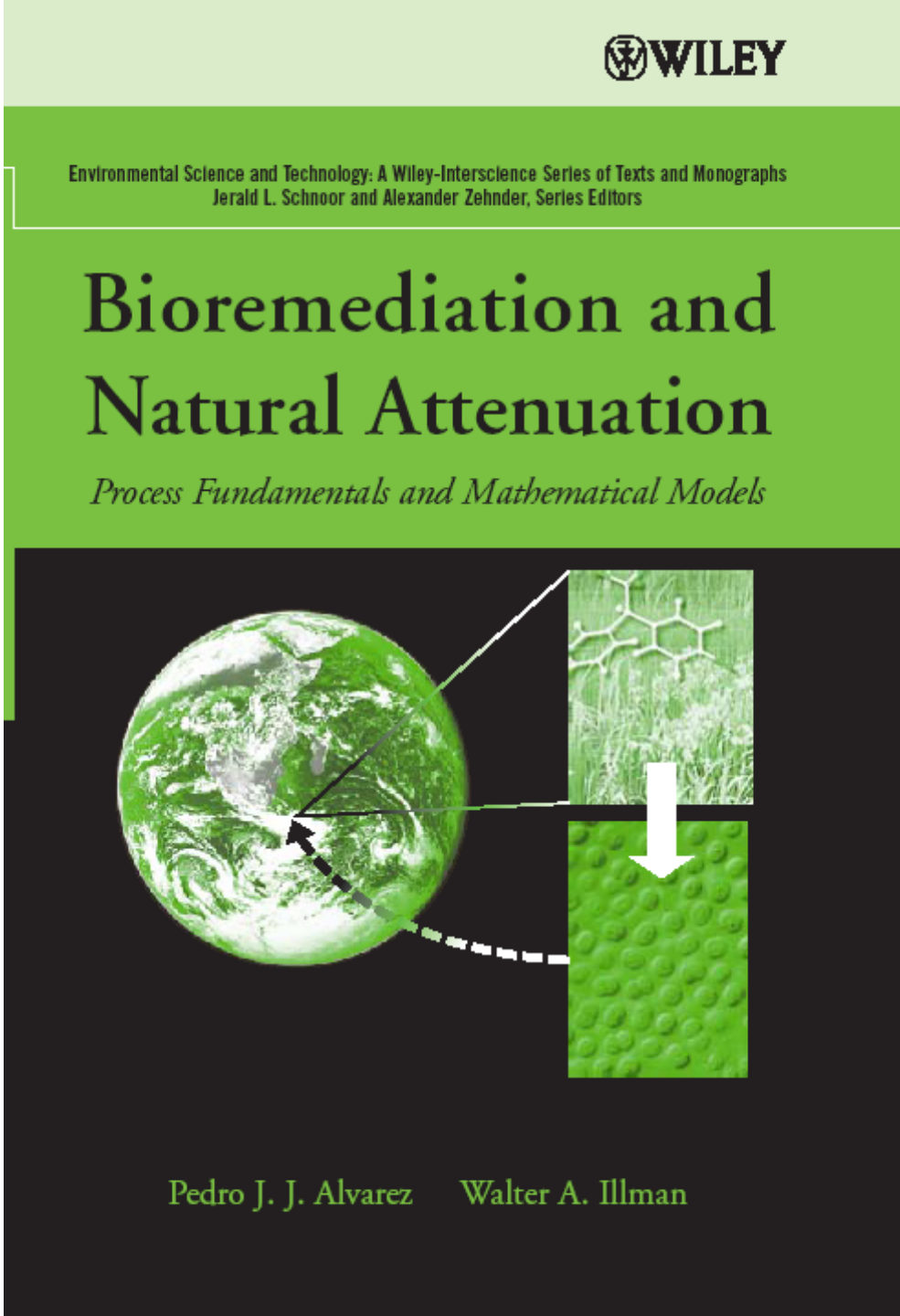
Concentration profiles show that EtOH migrated in a thin layer at the water table interface (little vertical dispersion compared to tracer)



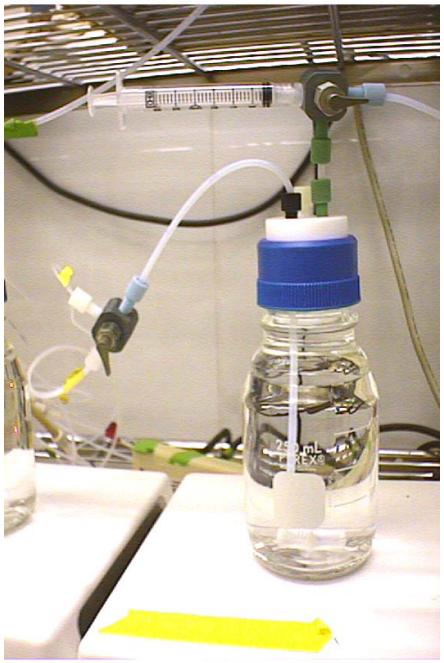


Cápiro N, B. Stafford, W. Rixey , P. Bedient, and P.J.J. Alvarez (2007). *Water Research.* 41(3):656-664

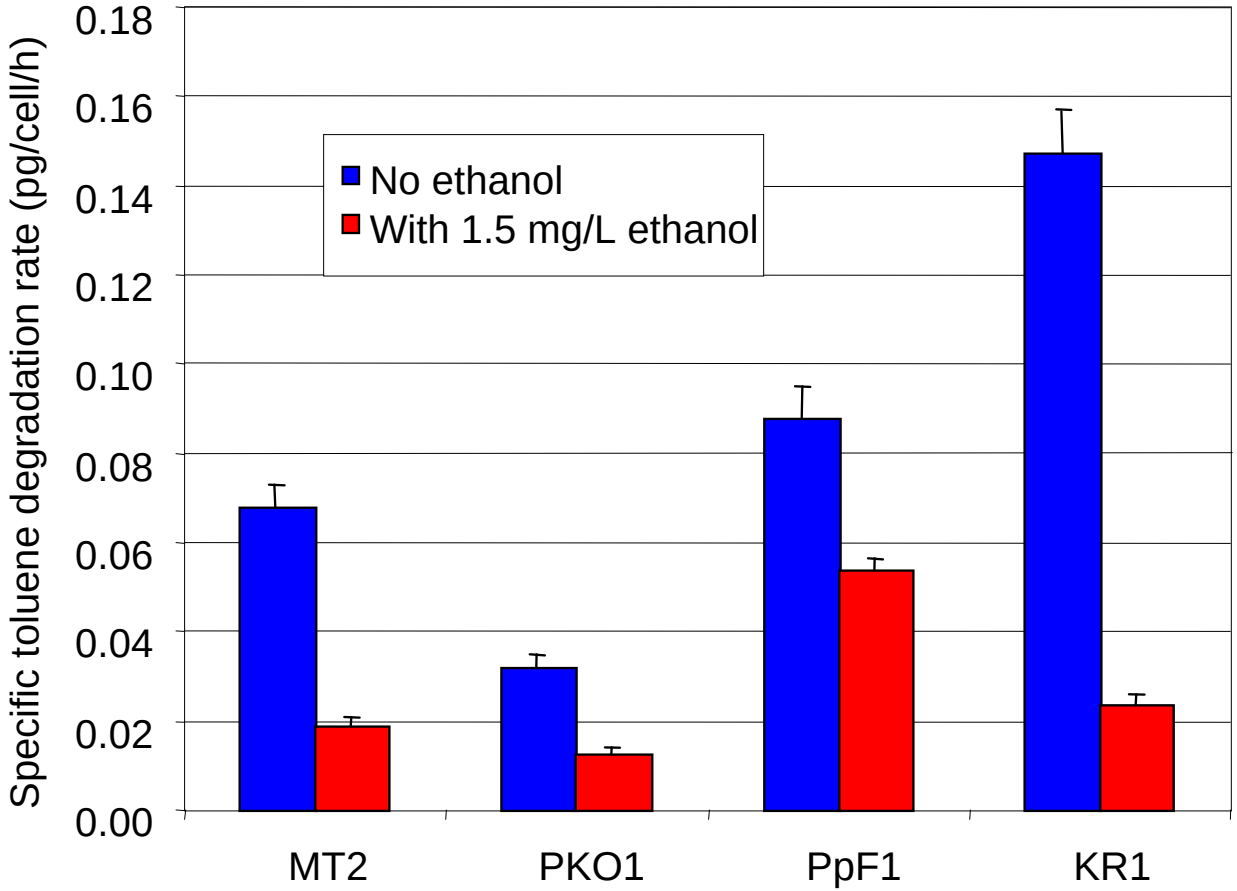
Microbial Impacts and Response: Effect on BTX Biodegradation



Effect of Ethanol on Aerobic Toluene Degradation Activity in Chemostats with Different Archetypes



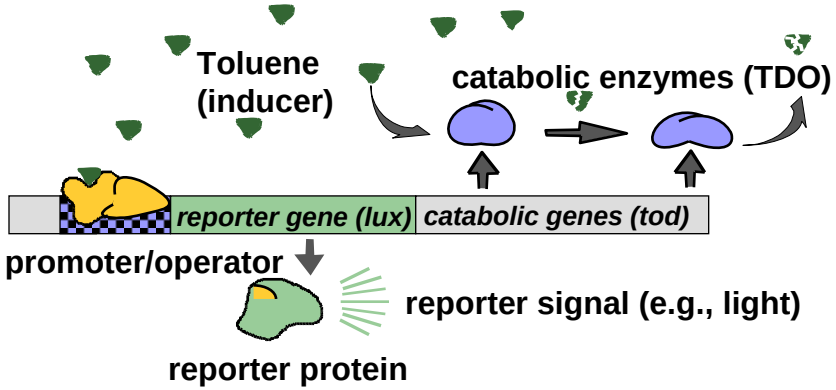
C_0 = 1 mg/L toluene



Lovanh N., C.S. Hunt, and P.J.J. Alvarez (2002). *Water Research*. 36:3739-3746.

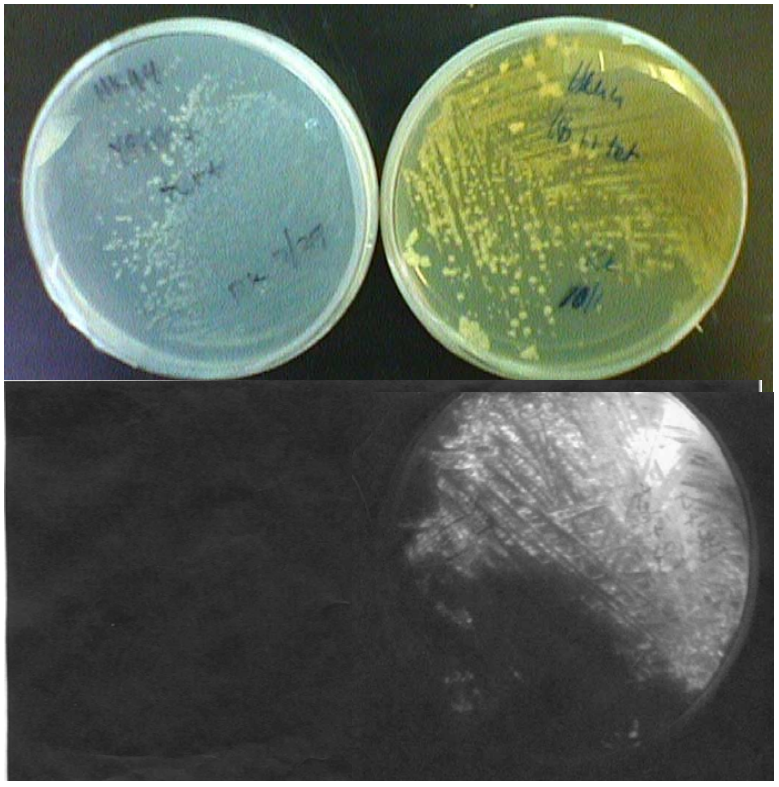
Bioreporter Strain

Pseudomonas putida F1 with *tod-lux*

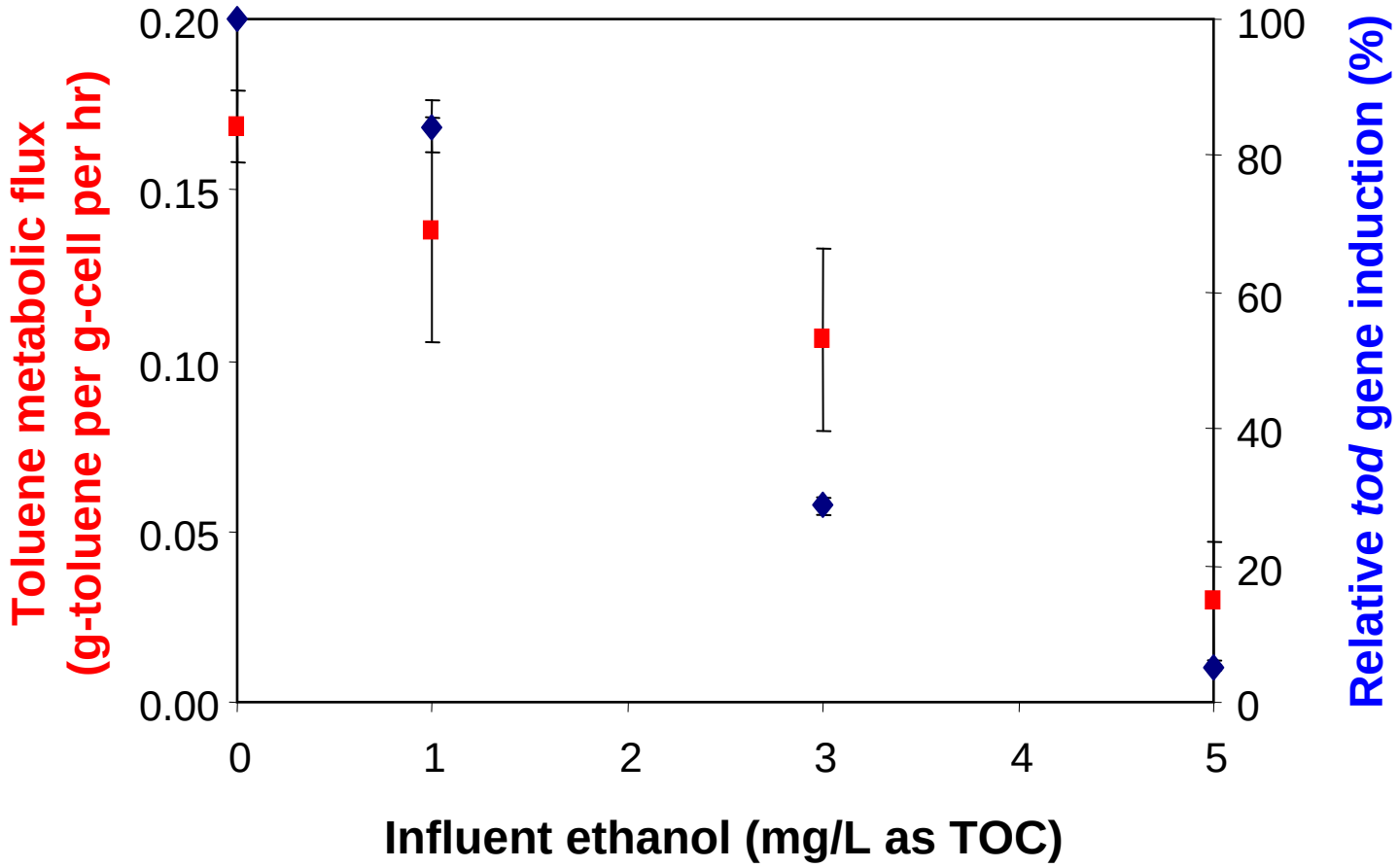


- Fused a reporter gene (*lux*) with the *tod* catabolic gene
- When the *tod* gene is induced, the reporter gene is also expressed producing luciferase, which emits a signal (e.g., light)
- The signal (measured with a luminometer) is proportional to the level of induction

PpF1 with *tod-lux* fusion

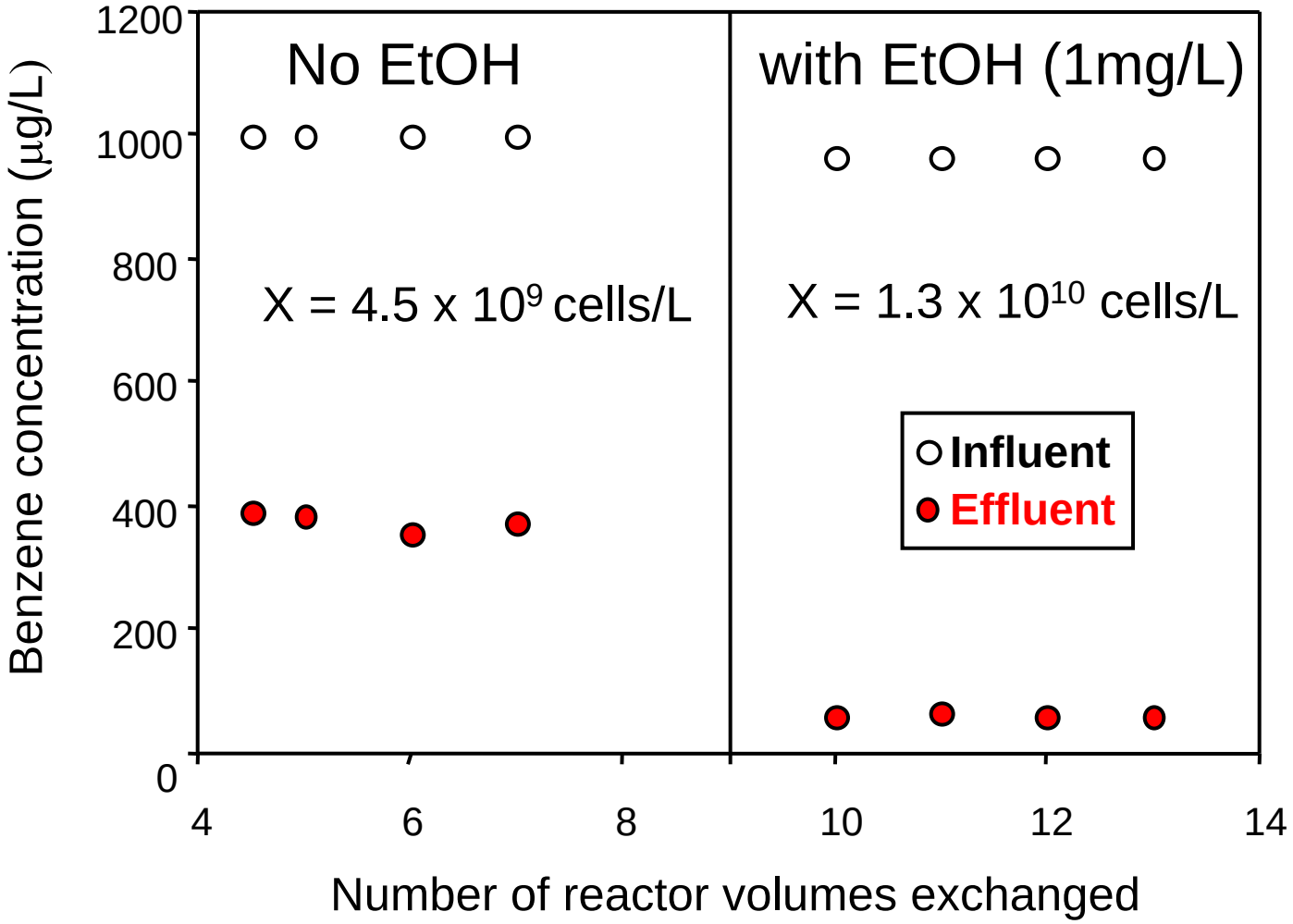


Enzyme induction and toluene metabolic flux *decreased* with increased ethanol availability



Lovanh N. and P.J.J. Alvarez (2004). *Biotechnol. Bioeng*. 86(7):801-808.

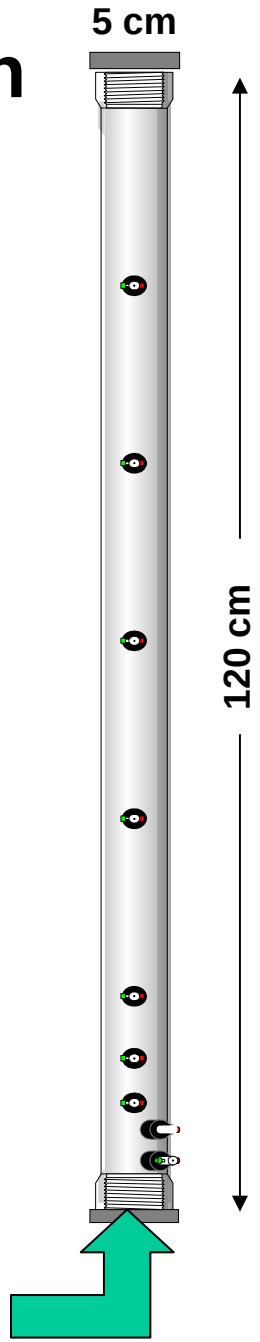
Adding 1 mg/L ethanol enhanced benzene degradation by PpF1 due to an increase in the microbial concentration



Lovanh N., C.S. Hunt, and P.J.J. Alvarez (2002). *Water Research*. 36:3739-3746.

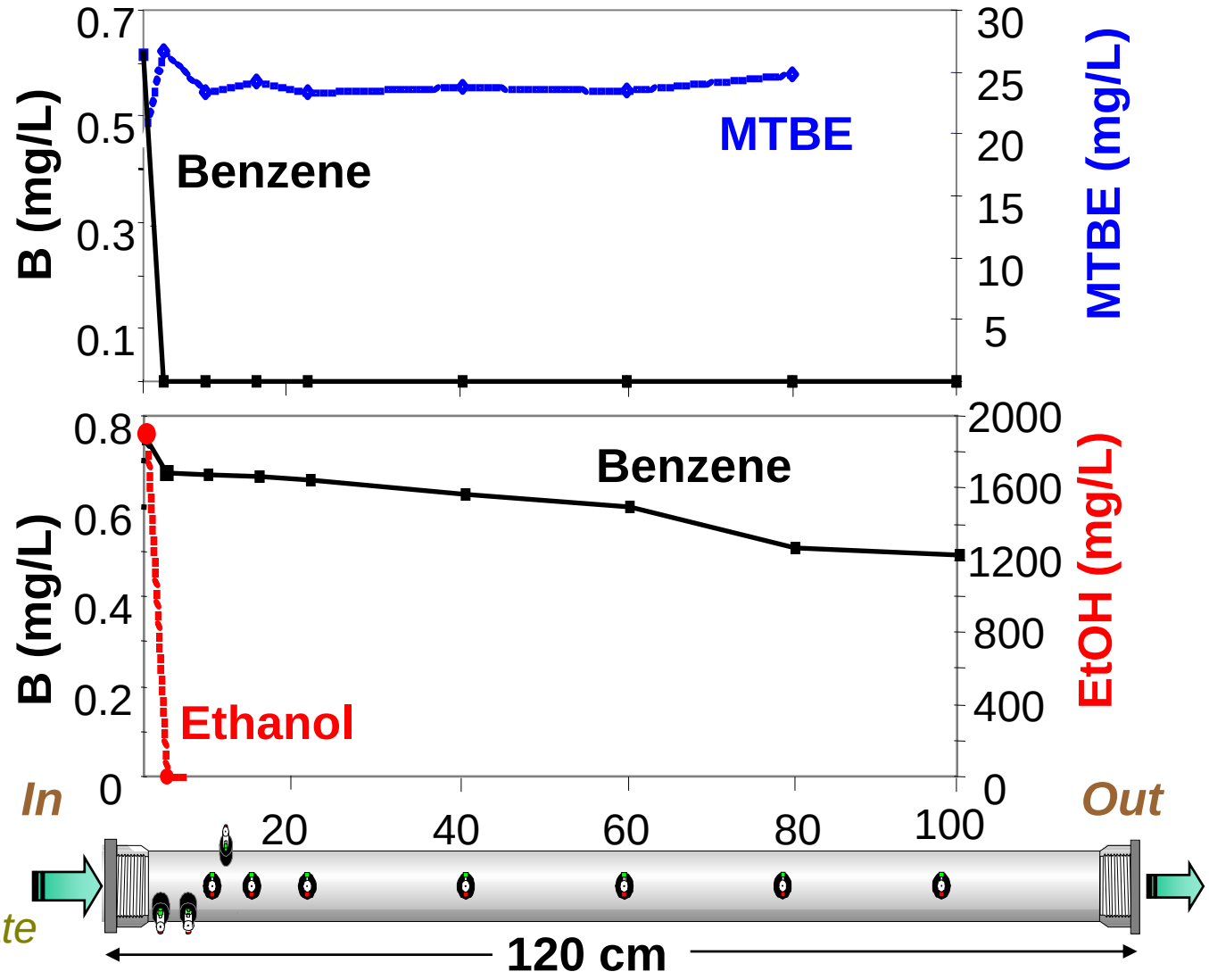
Aquifer Column Experiments

Effective Porosity: 0.37
Dispersion: 0.7 $cm^2\ h^{-1}$
Pore velocity: 2 $cm\ h^{-1}$
HRT = 6 days



Synthetic GW
BTEX alone or
with Ethanol

Effect of Ethanol versus MTBE on Benzene Attenuation

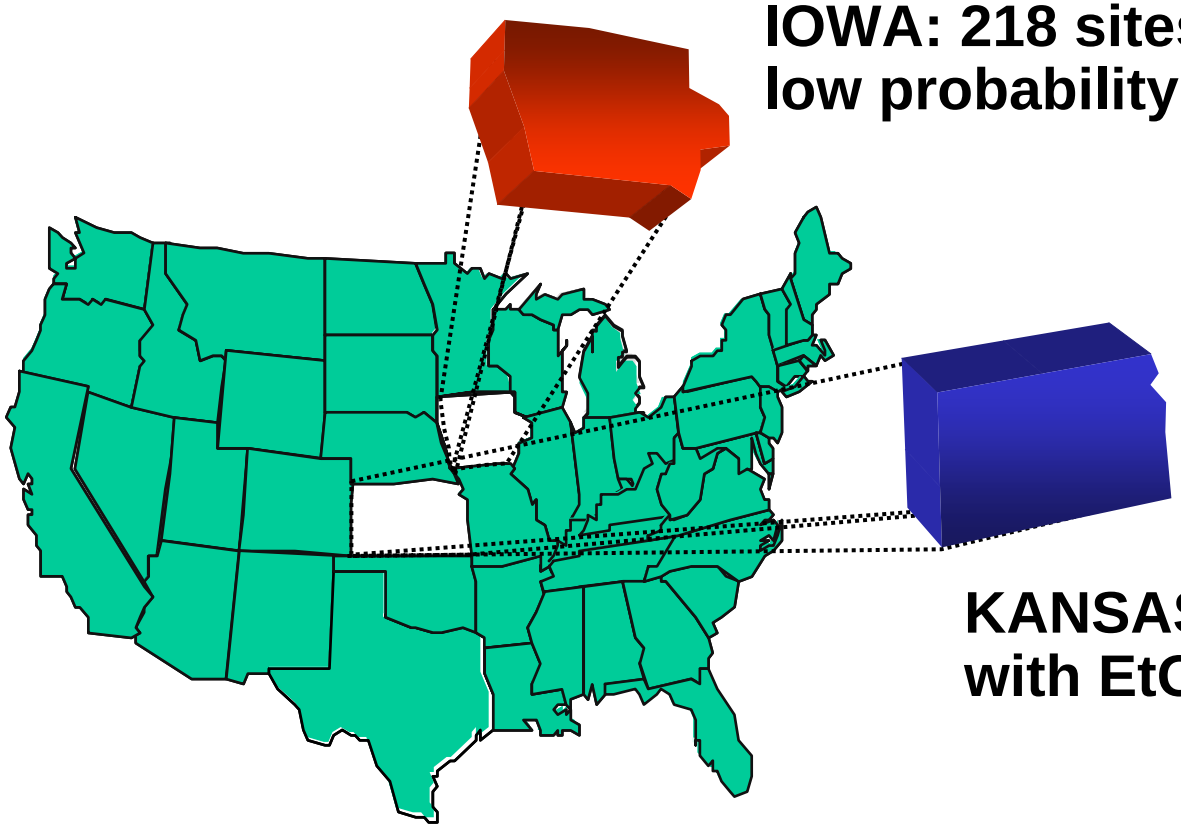


HRT = 5.5 days
8 ppm DO
30 ppm nitrate
100 ppm sulfate
1000 ppm bicarbonate

Da Silva M.L. and P.J.J. Alvarez (2002). *J. Env. Engrg.* 128(9):862-867.

The Midwest Plumathon

Is the elongating effect of ethanol on BTEX plumes significant?

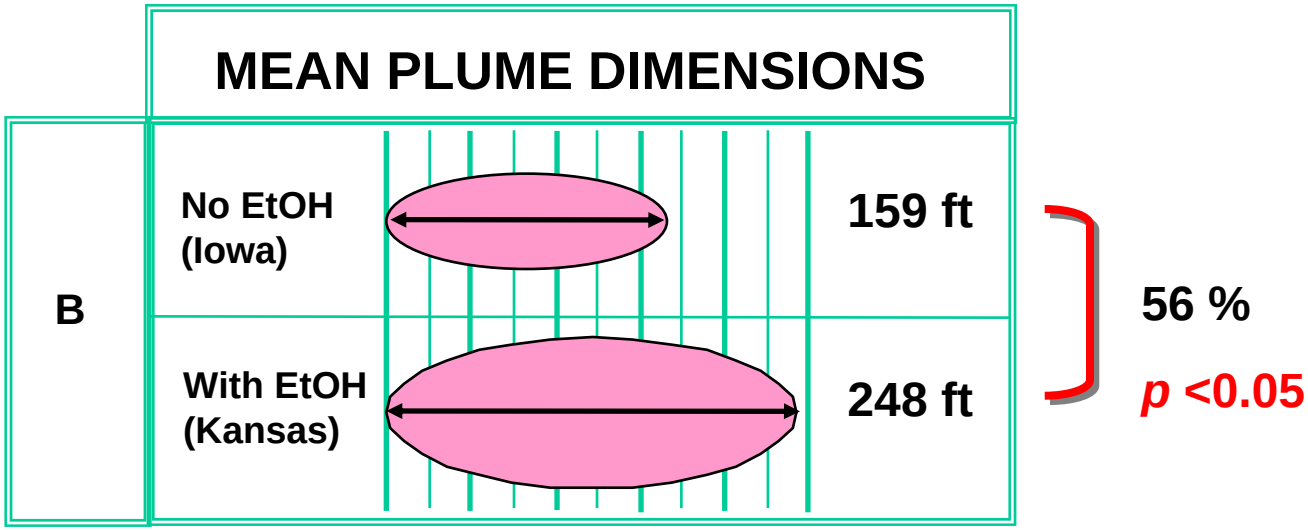


IOWA: 218 sites
low probability of EtOH

KANSAS: 29 sites
with EtOH (10% v:v)

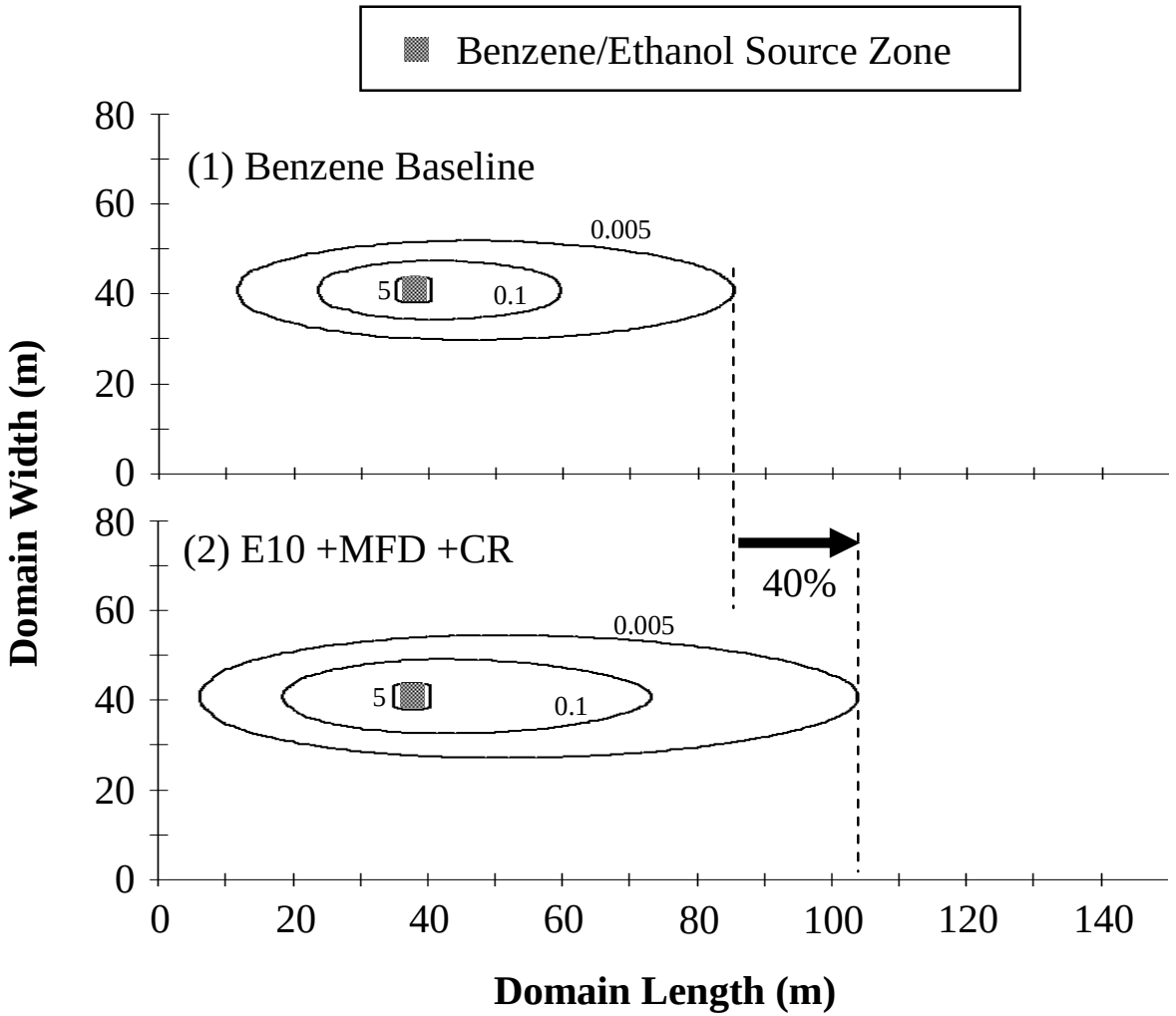
For each site, determined benzene & toluene plume lengths

What is the Overall Effect of Ethanol?



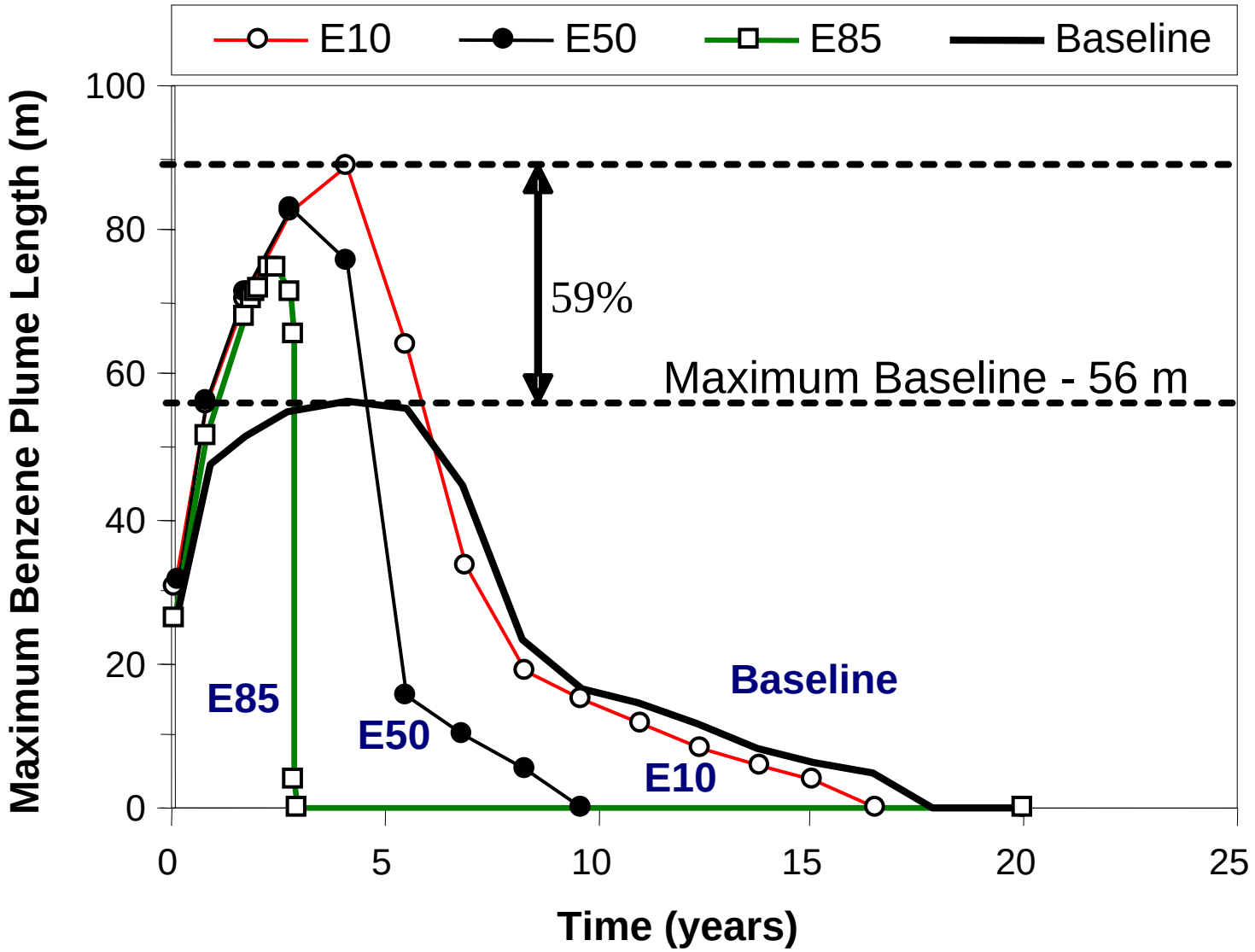
Ruiz-Aguilar G.M, K. O'Reilley, and P.J.J. Alvarez (2002). *Ground Water Monitoring and Remediation.* 23(1):48-53

RT3D with GISM Model Simulations Agree with Survey



Gomez D., P. Leblanc P. Bedient. W. Rixey and P.J.J. Alvarez* (2008). Wat. Resour. Res. 44(5), W05405.

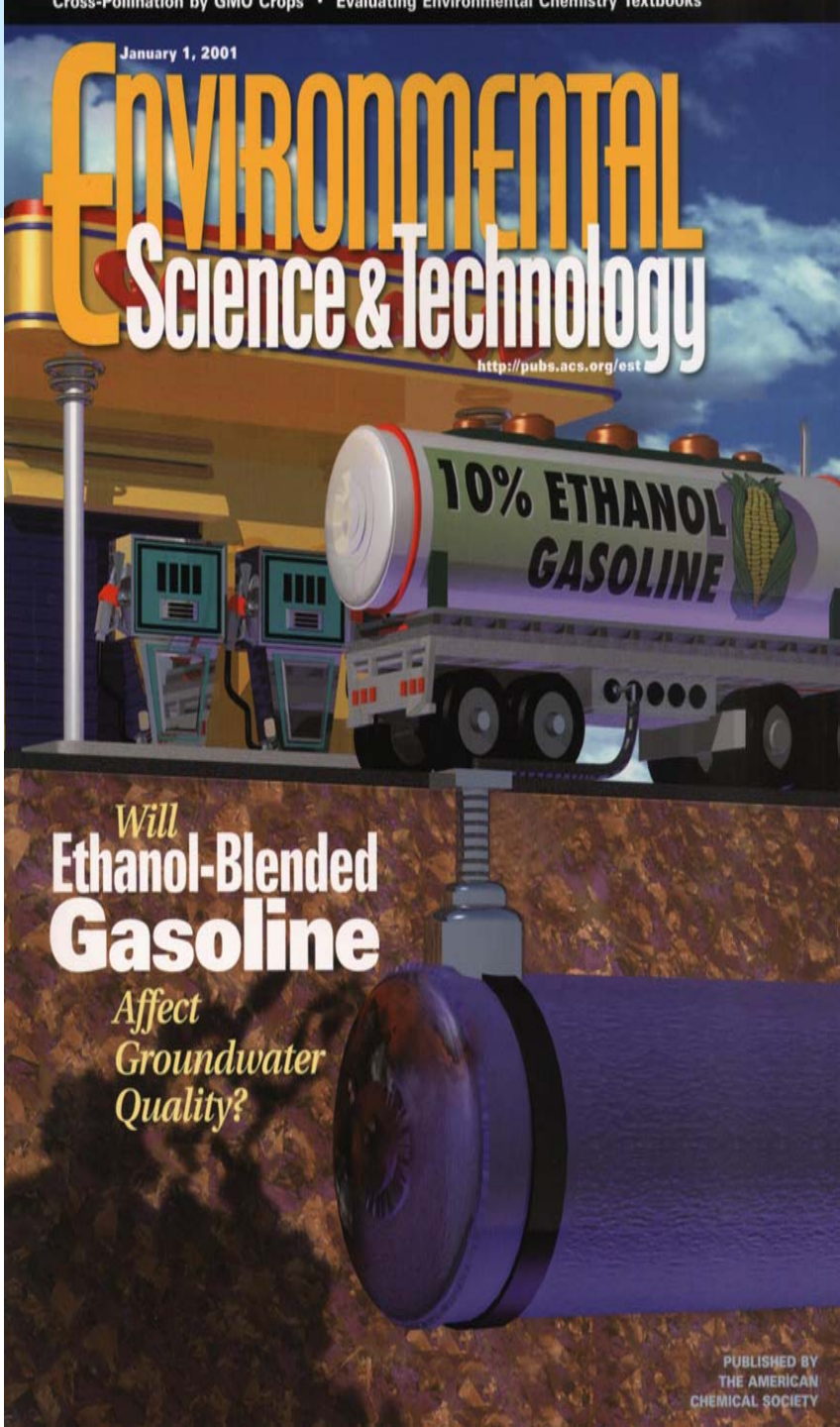
Benzene plume lengths for different ethanol mixtures



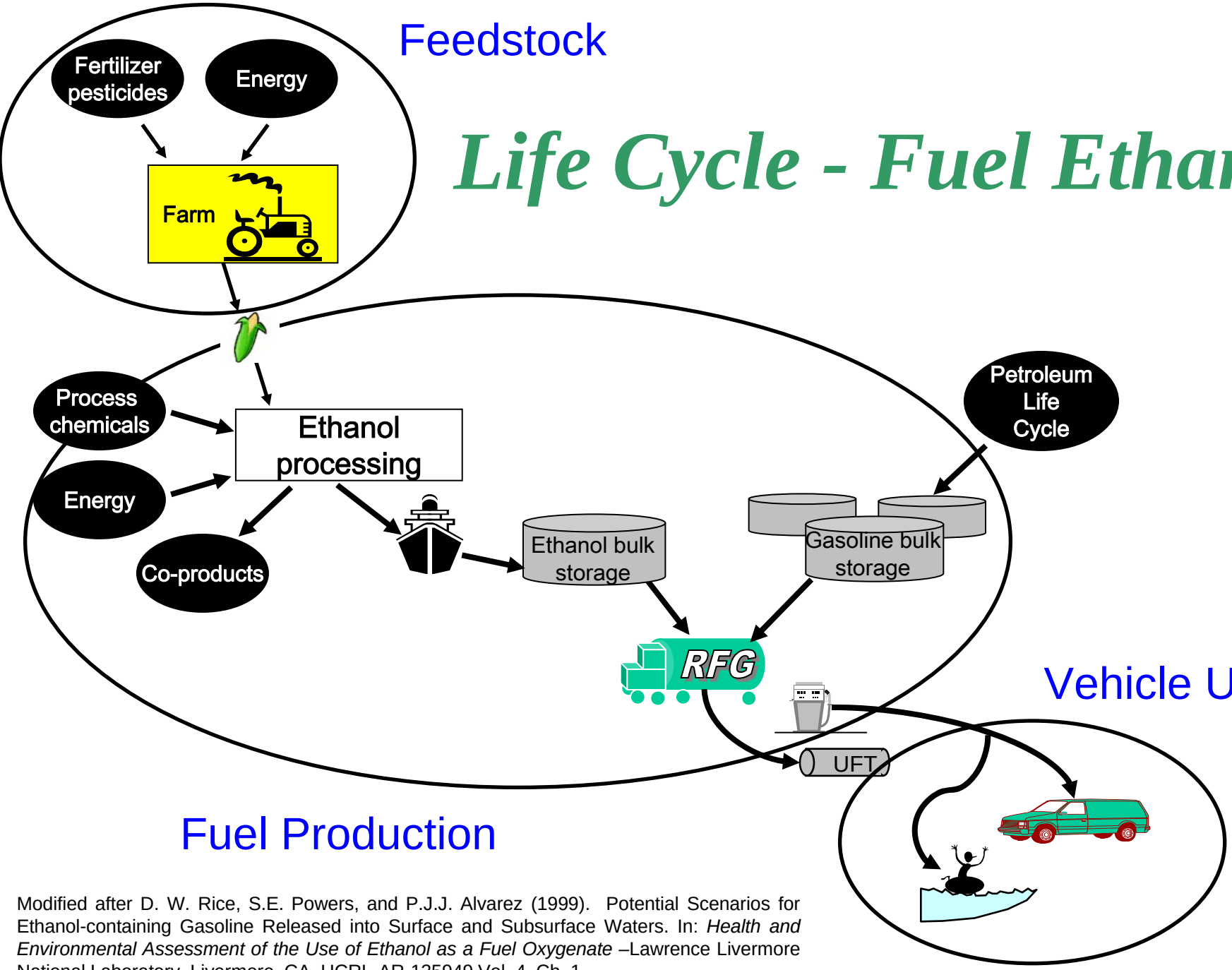
Conclusion

Ethanol can hinder the natural attenuation of benzene (MFD> CR> BOD), which could result in longer plumes and a higher risk of exposure.

However, the significance of this effect is probably site-specific, largely depending on the release scenario and the available e^- acceptor pool.

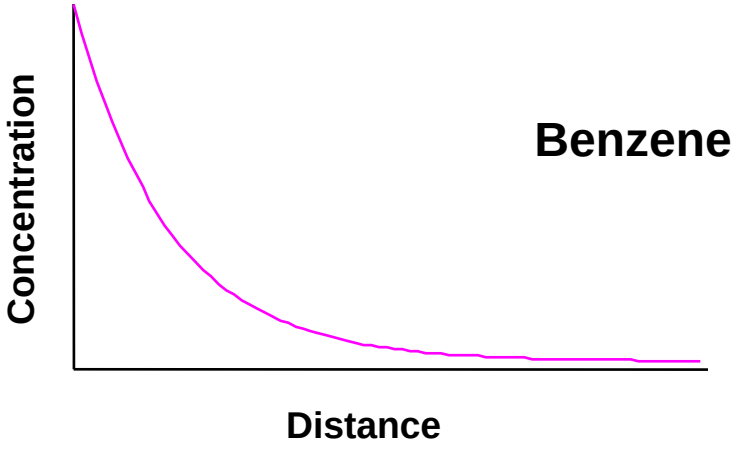


Life Cycle - Fuel Ethanol

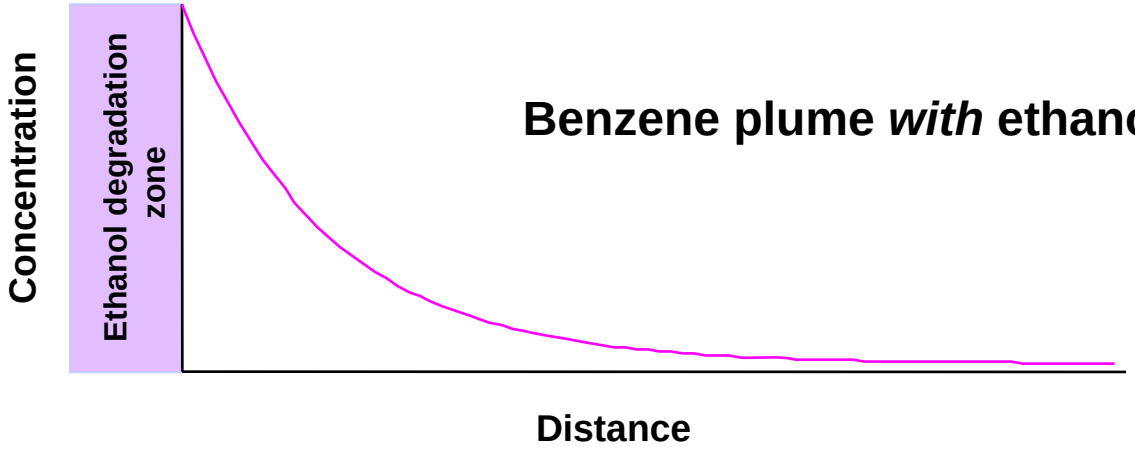


Modified after D. W. Rice, S.E. Powers, and P.J.J. Alvarez (1999). Potential Scenarios for Ethanol-containing Gasoline Released into Surface and Subsurface Waters. In: *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate* –Lawrence Livermore National Laboratory, Livermore, CA, UCRL-AR-135949 Vol. 4, Ch. 1.

Potential Ground Water Impacts of EtOH-Plume Conceptual Model

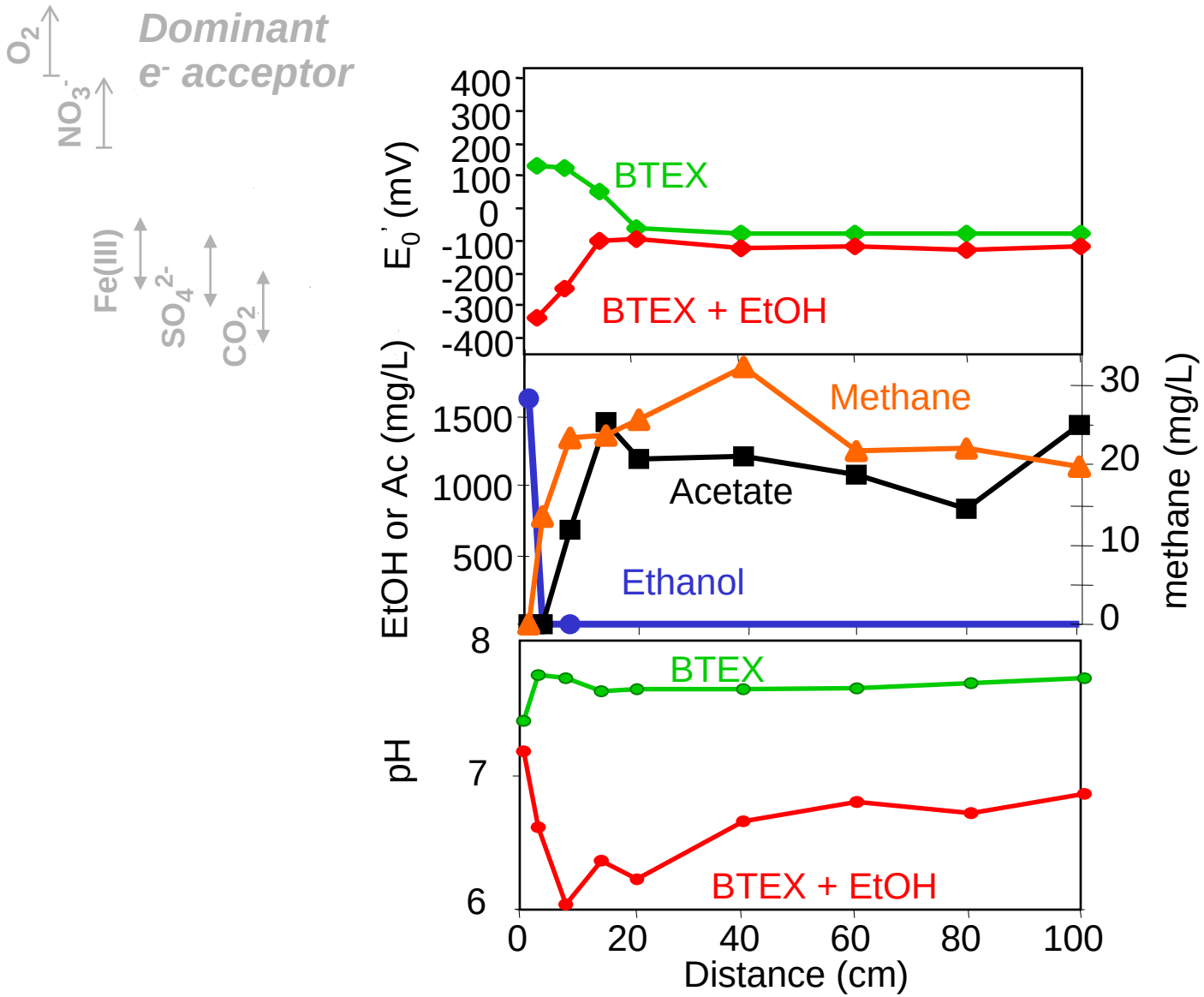


Benzene plume *without* ethanol.



Benzene plume *with* ethanol.

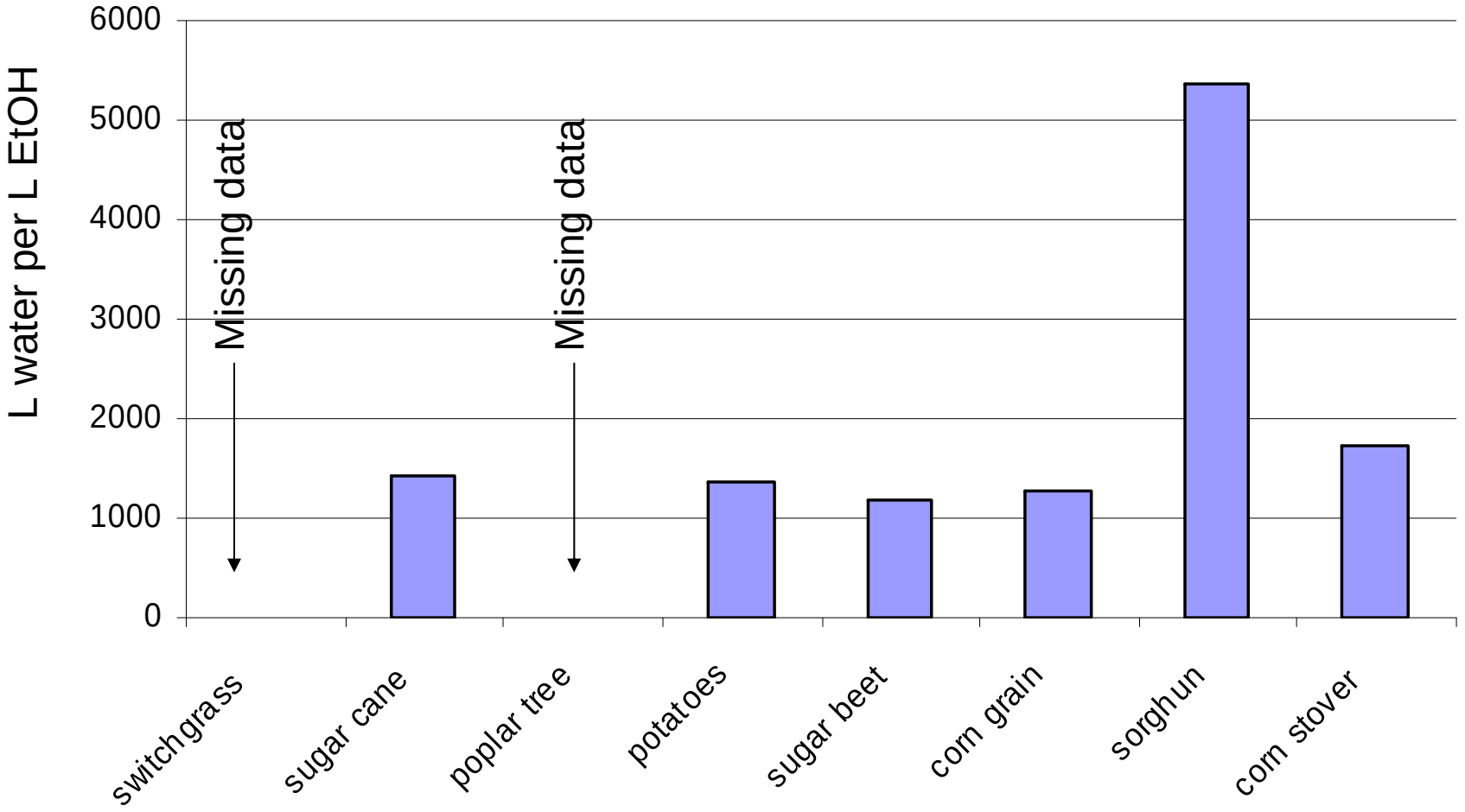
Effect of ethanol on ORP, acetate production and pH



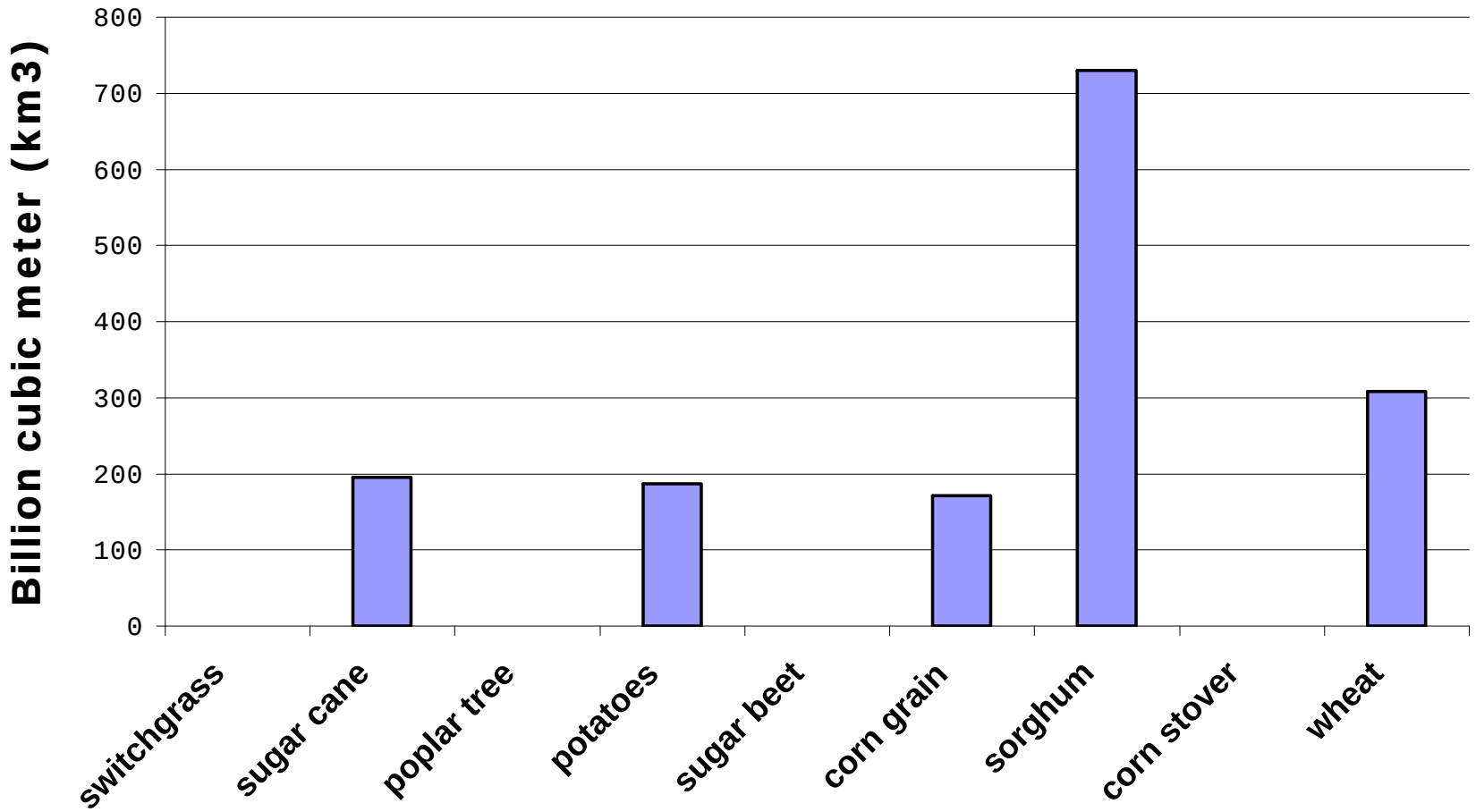
Da Silva M.L. and P.J.J. Alvarez (2002). *J. Env. Engrg.* 128(9):862-867.

Water and land footprint for different crops

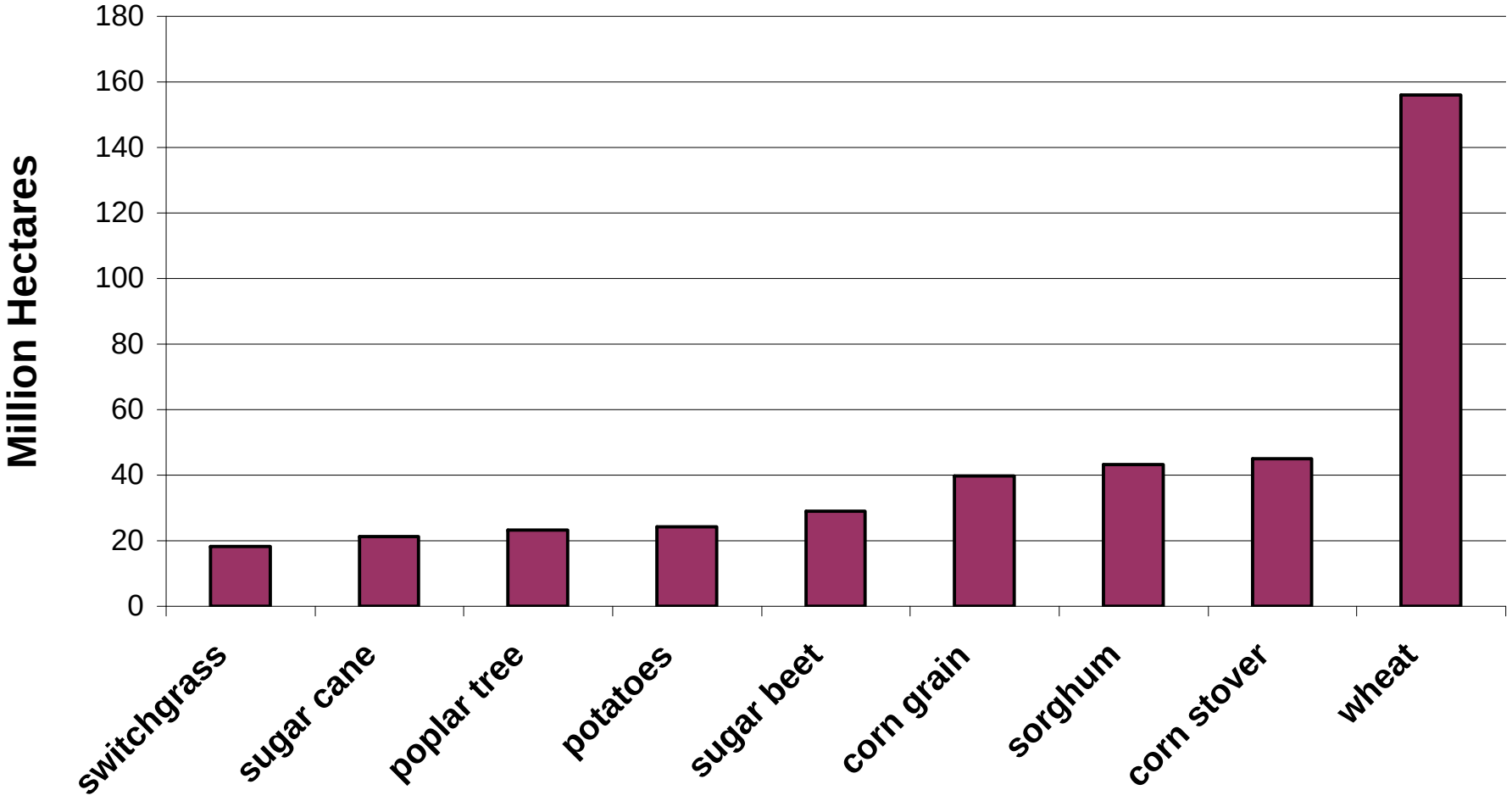
Agricultural water requirement to make ethanol (based on CWP)



Total water required to meet the 36 billion gal goal Ethanol by 2020



Total land requirements to meet the 36 billion gal goal Ethanol by 2020



Cellulosic Ethanol Roadmap

75 million acres

~57% of non-harvested cropland

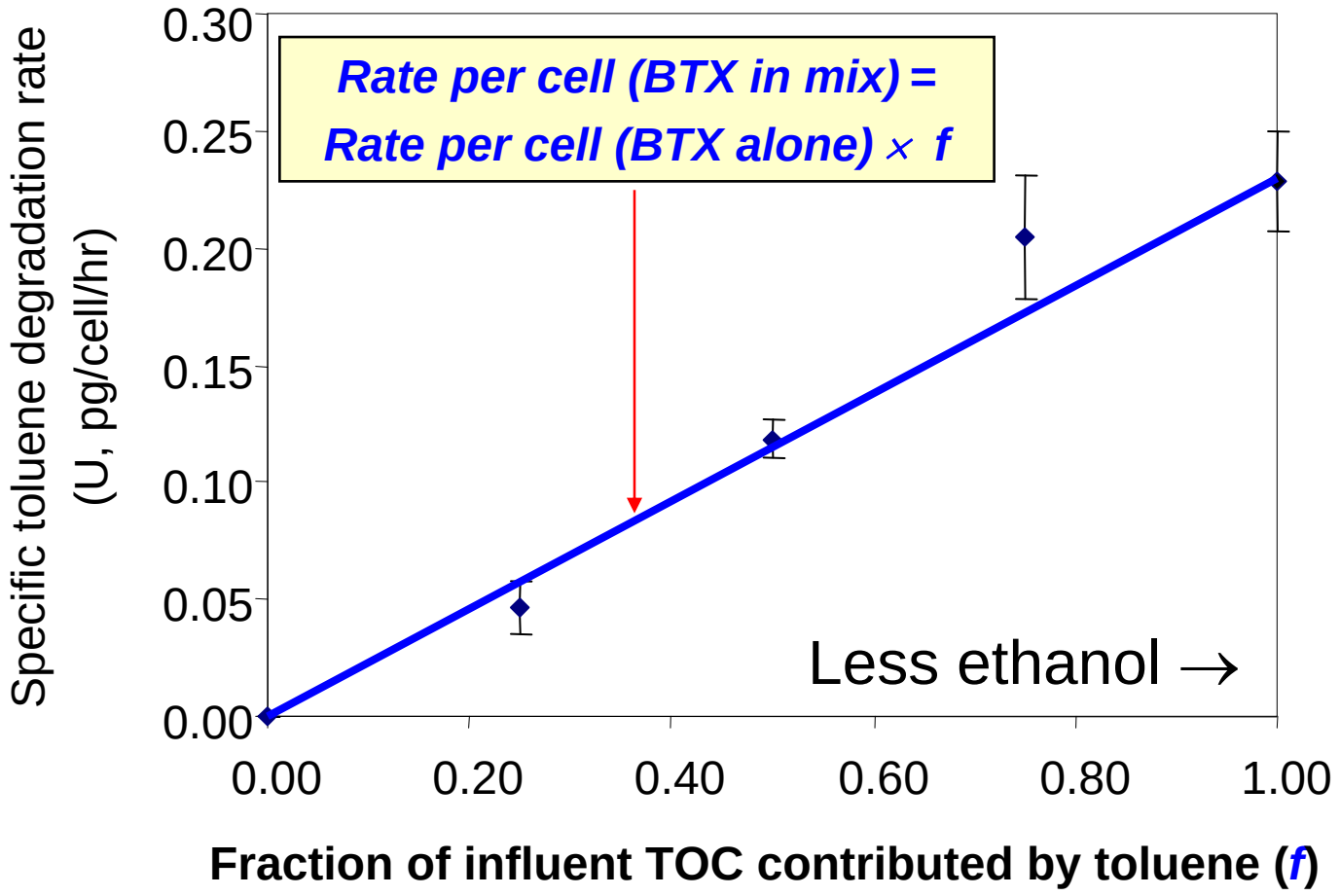
US Statistics

Total Farmland = 938 million acres
Total Cropland = 434 million acres
Harvested Cropland = 303 million acres

Any Questions?

Metabolic flux dilution model

The metabolic flux of a substrate in a mixture is proportional to its relative availability (expressed as its fraction of the influent TOC, ***f***).



Lovanh N., C.S. Hunt, and P.J.J. Alvarez (2002). *Water Research*. 36:3739-3746.

Plume Elongation Mechanisms

Oxygen Depletion → **+180%**

Fortuitous Growth → **- 53%**

Catabolite Repression → **+36%**

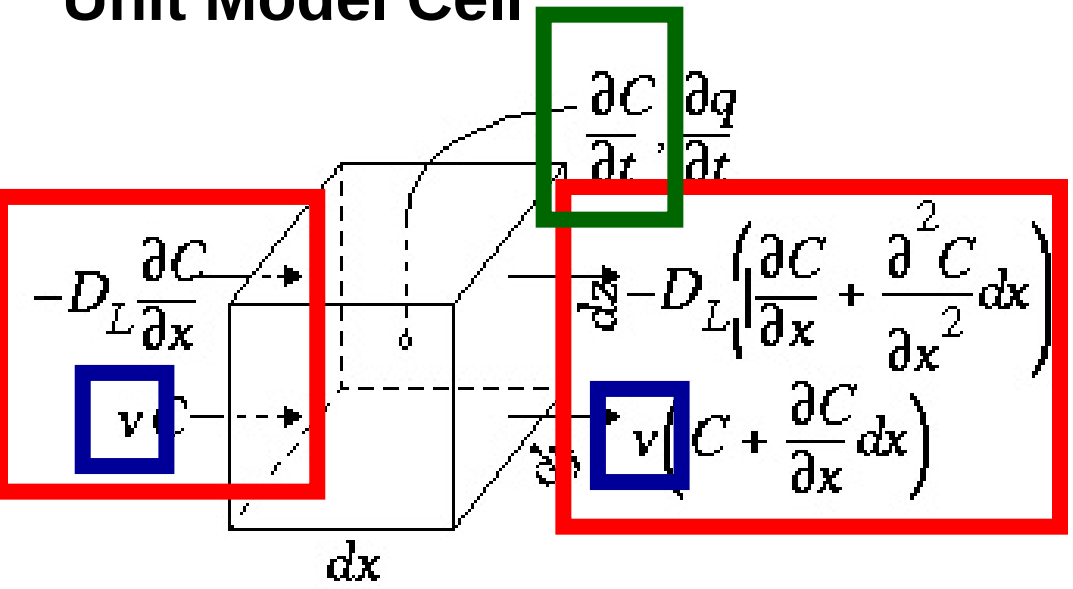
Metabolic Flux Dilution → **+109%**

Cosolvency (For E10) → **0%**

Overall ethanol effect on benzene → +38%

Model to Evaluate Plume Elongation Mechanisms

Unit Model Cell

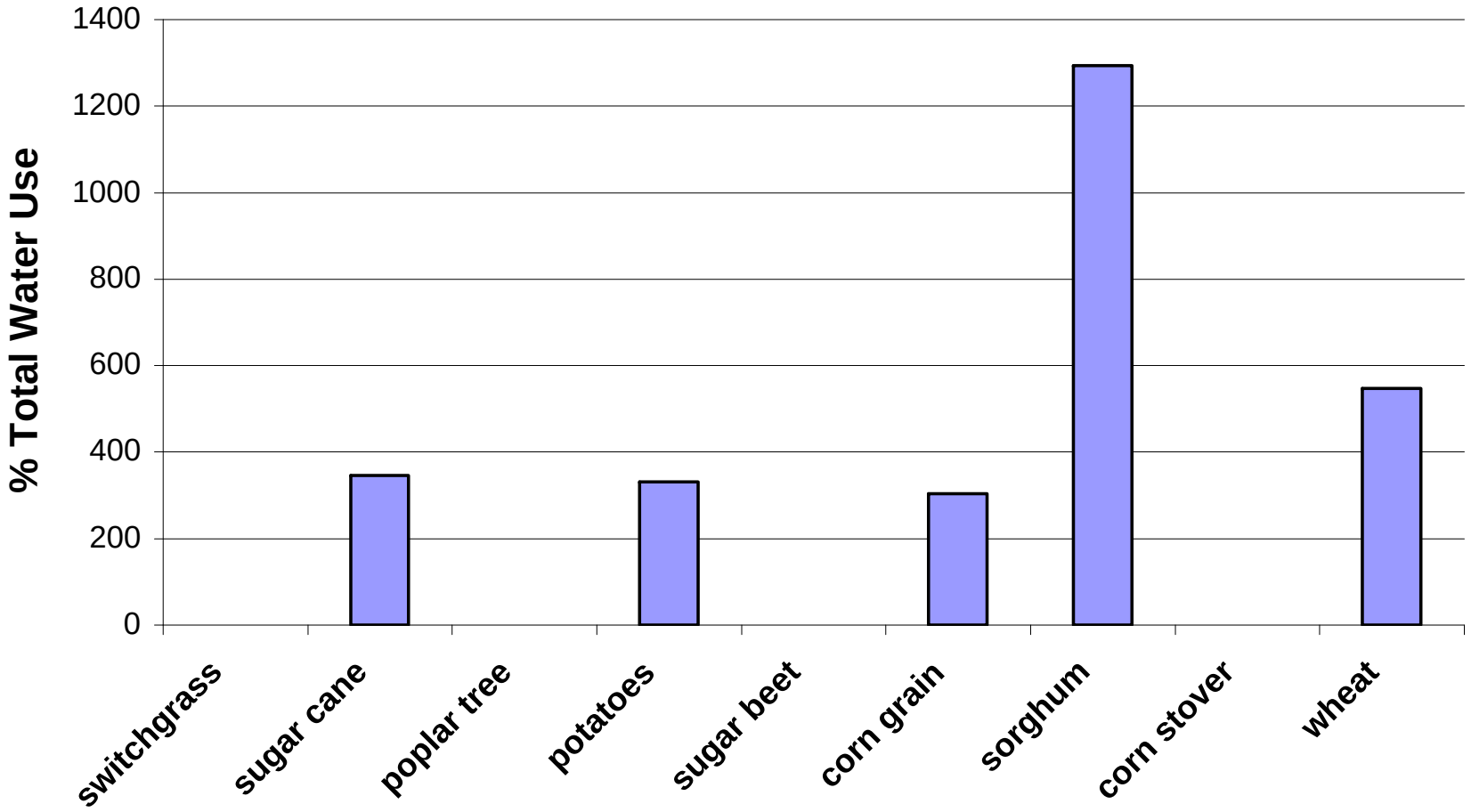


Groundwater velocity:
h, K, n, I (MODFLOW)

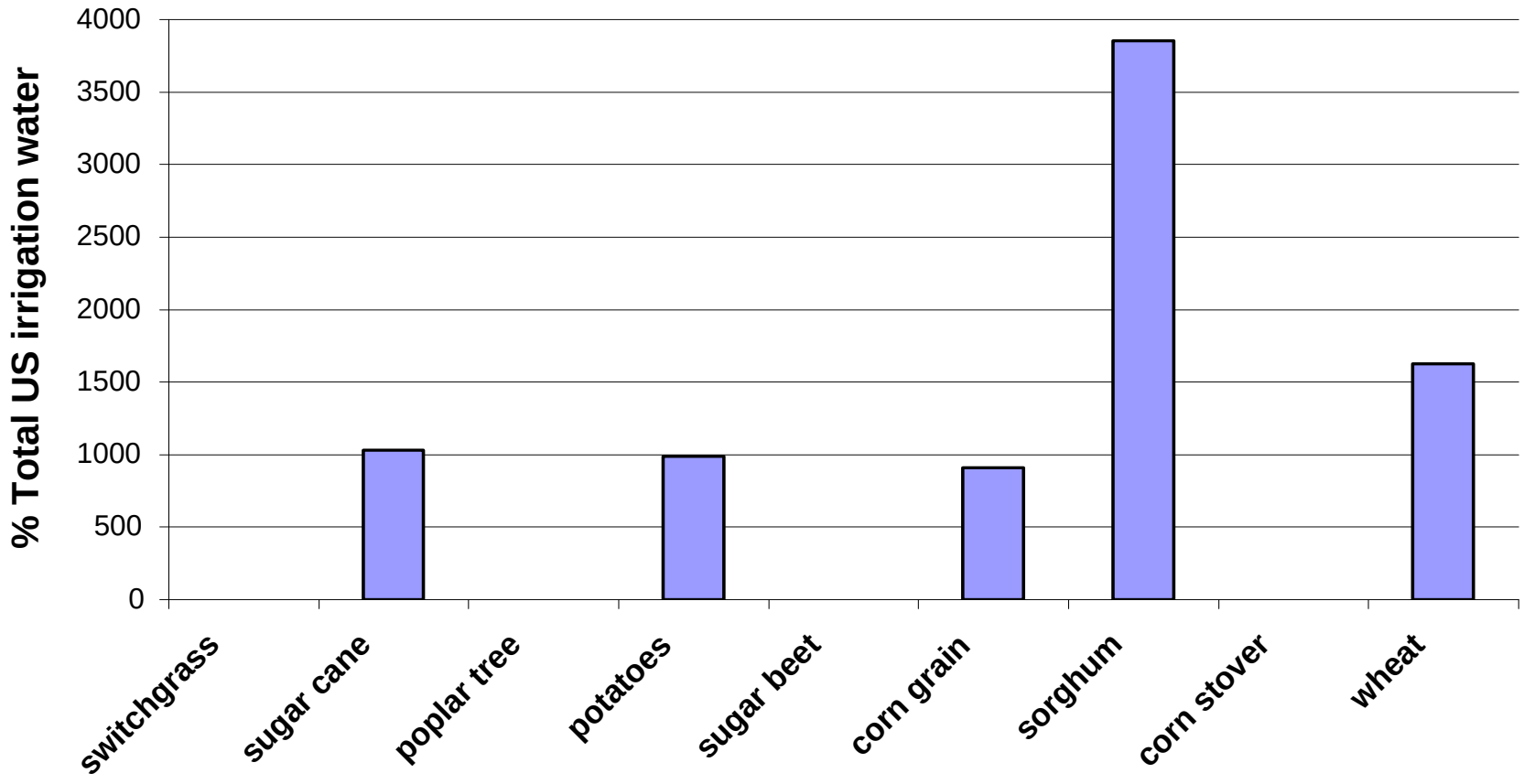
Advection and dispersion:
v, S, α, D_L (RT3D)

Degradation, microbial growth and substrate interactions (catabolite repression, MFD)

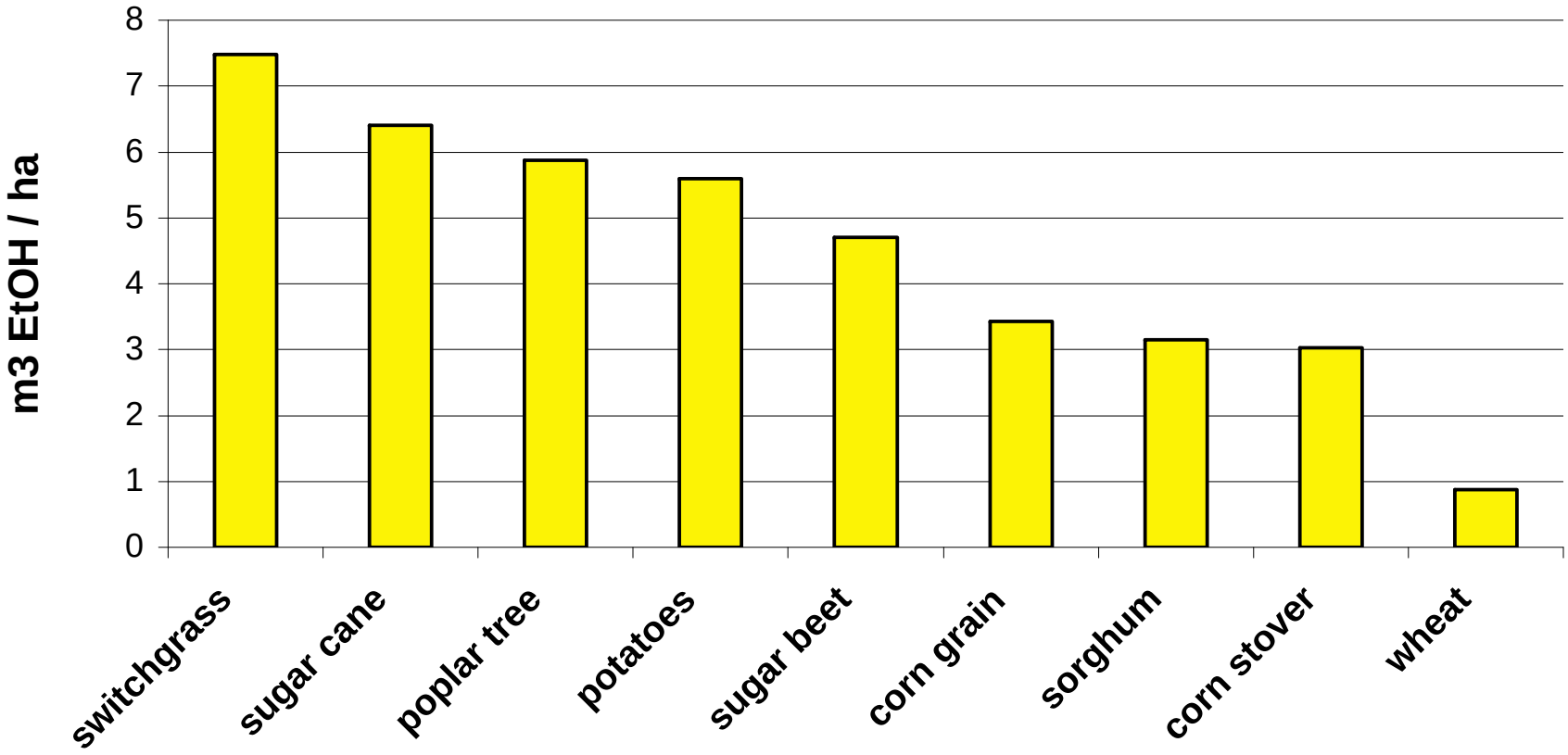
% US Water (all uses) for single crops in 2020



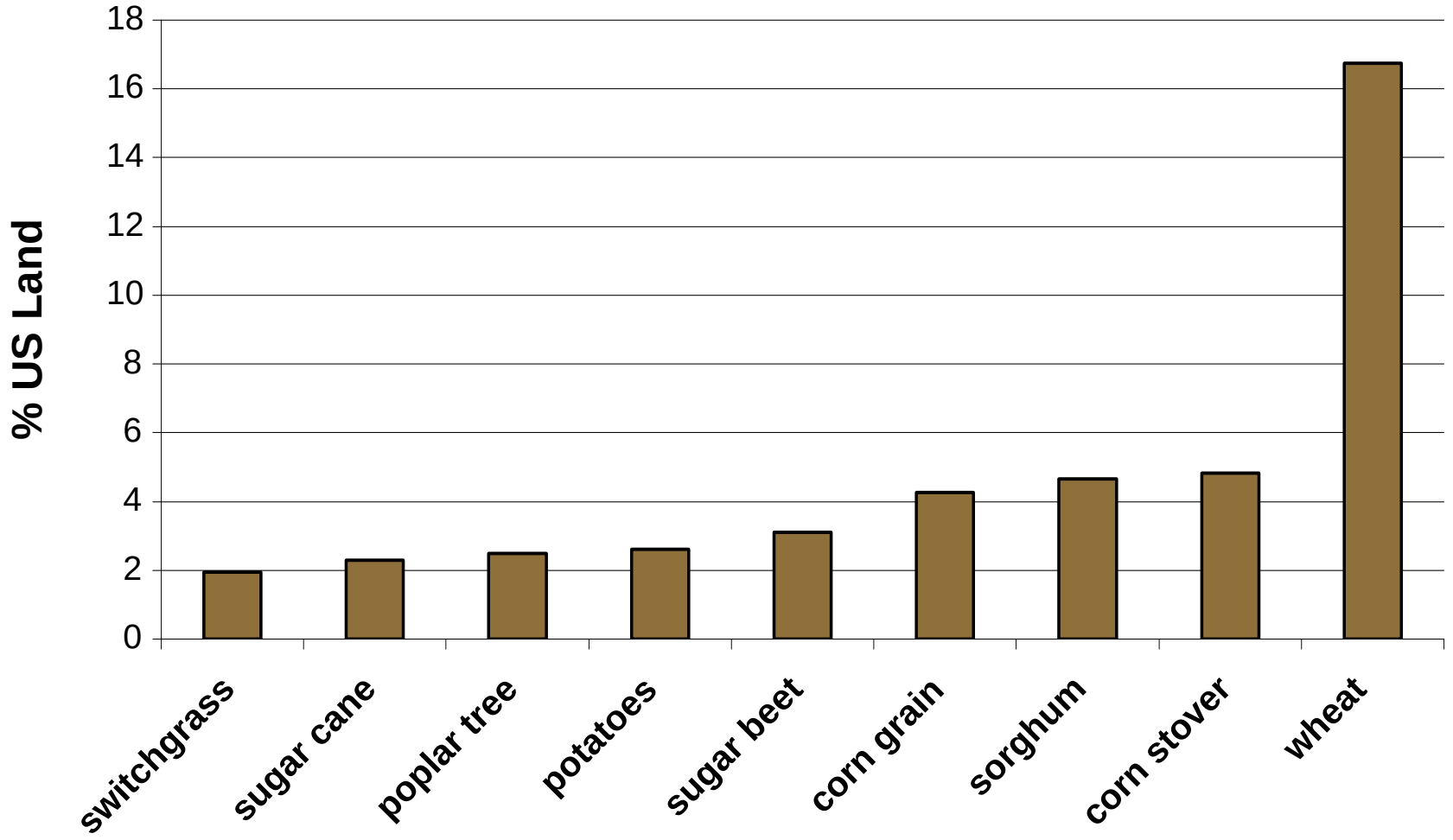
% US irrigation water for single crops in 2020



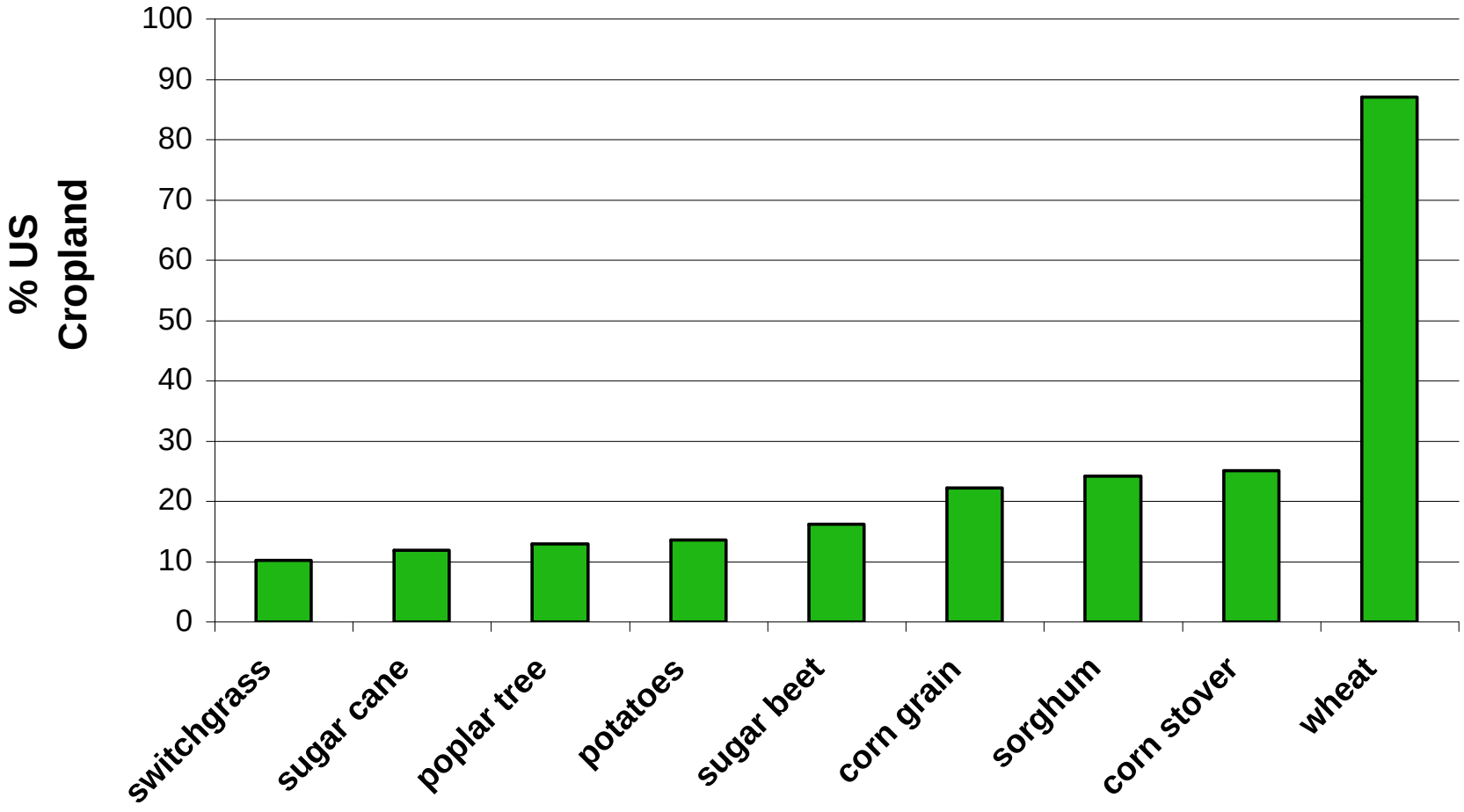
Ethanol yield for single crops (m^3/ha)



% US land in 2020 for single crops



% US cropland for single crops by 2020



DATA USED

- Goal for 2020 = 36 B gal ethanol = 3.6E+10 gallons
- Total US land = 2300 Million ac
- Total US arable land in 2002 = 442 Million ac
- Total Water Consumption in the US (2002) = 148,920 Mgal/year
- Irrigation Water Use in the US (2002) = 50,005 Mgal/year

Research Needs and Opportunities

- *Develop a comprehensive LCA framework for environmental impact evaluation and pollution prevention* :
  - Surface water pollution by increased fertilizer and pesticide use (Gulf hypoxia)
  - Increased water consumption (e.g., for irrigation) and impact on water security
  - Changes in land use and impact on soil erosion and soil health
  - Changes in urban air quality
  - Atmospheric decarbonization and global climate.
  - Increased energy demand (e.g., for processing) and impact on net energy value.
  - Impacts to plant biodiversity due to dispersal of exogenous genes from genetically modified crops.
  - Groundwater impacts of biofuel releases
  - Potentially problematic fuel components, byproducts and impurities

Research Needs and Opportunities

- *Major logistical challenges for the biofuel industry*:
  - Robustness in the event of a drought, and management of related uncertainty and interdependence of systems (including related impact on food prices).
  - Adequacy of existing biofuel distribution and storage infrastructure

- *Framework for analyzing the overall costs and benefits :*
  - The costs of biofuels production including the effect of system perturbations on costs.
  - The competitiveness of biofuels with alternative sources of transportation fuels.
  - Methodology for costing the externalities associated with biofuels production.

Research Needs and Opportunities

- *Enhance economic and environmental feasibility of biofuels production:*
  - Energy audits to increase the net energy value
    - Transportation and distribution logistics and implications on NEV
    - Alternative energy distribution options, such as using biofuels to generate electricity.
    - N_2-fixing genes into plants to reduce the need for energy-intensive fertilizers
    - Altering cell wall properties abs stress tolerance to enhance biofuel yield
  - Conversion of waste glycerol into fuel and reduced chemicals.
  - Replace hazardous substances used in biofuel production (*e.g.*, integrative pest management and bioinsecticides instead of synthetic pesticides; novel reaction media and/or biocatalysts instead of acids in biomass pretreatment).
  - Plant-derived enzymes that naturally modify plant cell walls for easier hydrolysis and fermentation.
  - Alternative sources of biomass (e.g., biodiesel from algae, H_2 from cellulosic agricultural waste) and their effect on water consumption and NEV.
  - CO_2 emission credits for replacing hydrocarbons by renewable fuels.
  - Identifying and addressing process scale up challenges.

Choosing Suitable Fuels: Current Approach

- Primary criteria for fuel policy decisions
  - Energy value and cost of fuel
  - Availability of feedstock
  - Required distribution infrastructure
- Secondary criteria (in USA)
  - Urban air pollution
    - Lead to use of MTBE as an oxygenate
  - Groundwater impacts during use of fuel
    - Lead to replace MTBE with ethanol

Fuel-Related Global Problems

Annual Growth Rates:

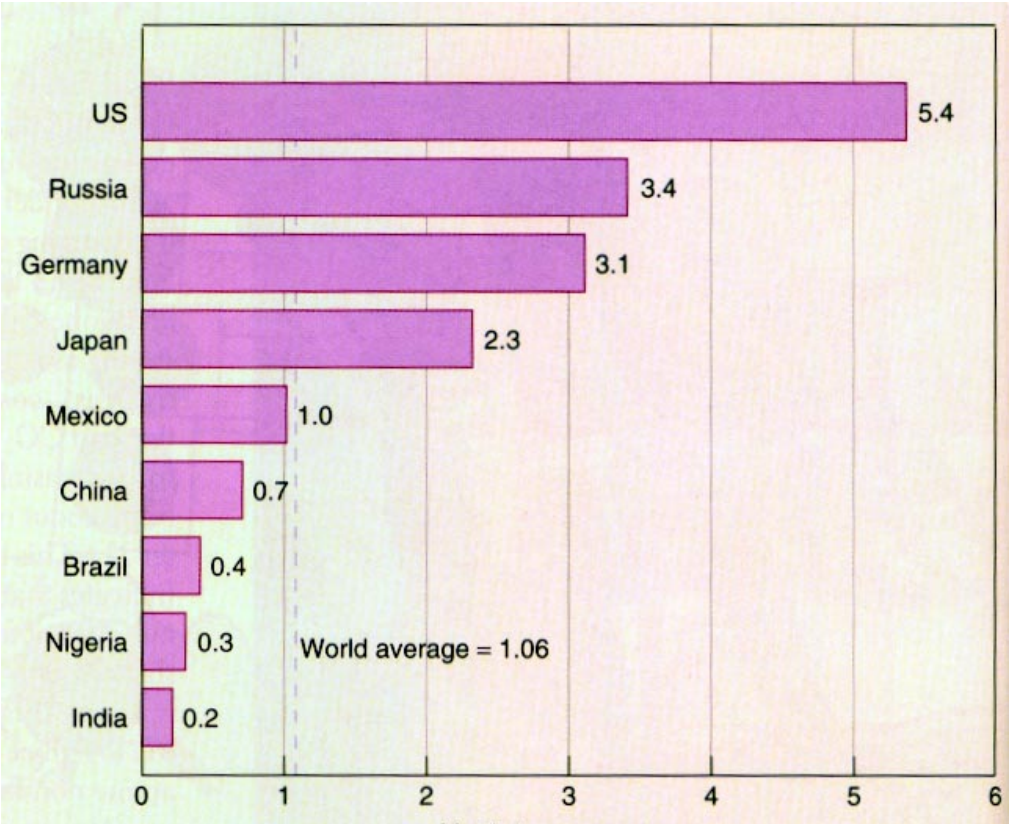
- 2% for world population
- 4% per capita fuel consumption

Petroleum:

- ~ 200 million years to form
- Depleted in < 300 years

USA's Contribution:

- 4% of world's population
- Uses 25% of energy produced
- Emits 25-30% of GHGs



CO_2 Emissions (tons/person)

“The use of (biofuels) may seem insignificant today, but it may become, in the course of time, as important as petroleum and the coal tar products of the present time.“

Rudolf Diesel, 1912.

Fuels from Biomass Feedstock

1850	Transesterification of vegetable oils (bodiesel)
1898	Rudolph Diesel demonstrates compression ignition engine using peanut oil. Vegetable oils were used in diesel engines until the 1920's
1908	Henry Ford used hemp-derived ethanol for Model T.
1930	Biofuel sales are undercut by petroleum industry and the interests of some industrialists (Hurst, Rockefeller)
1978	Second oil crisis renews interest in biofuels
2000	Grease car

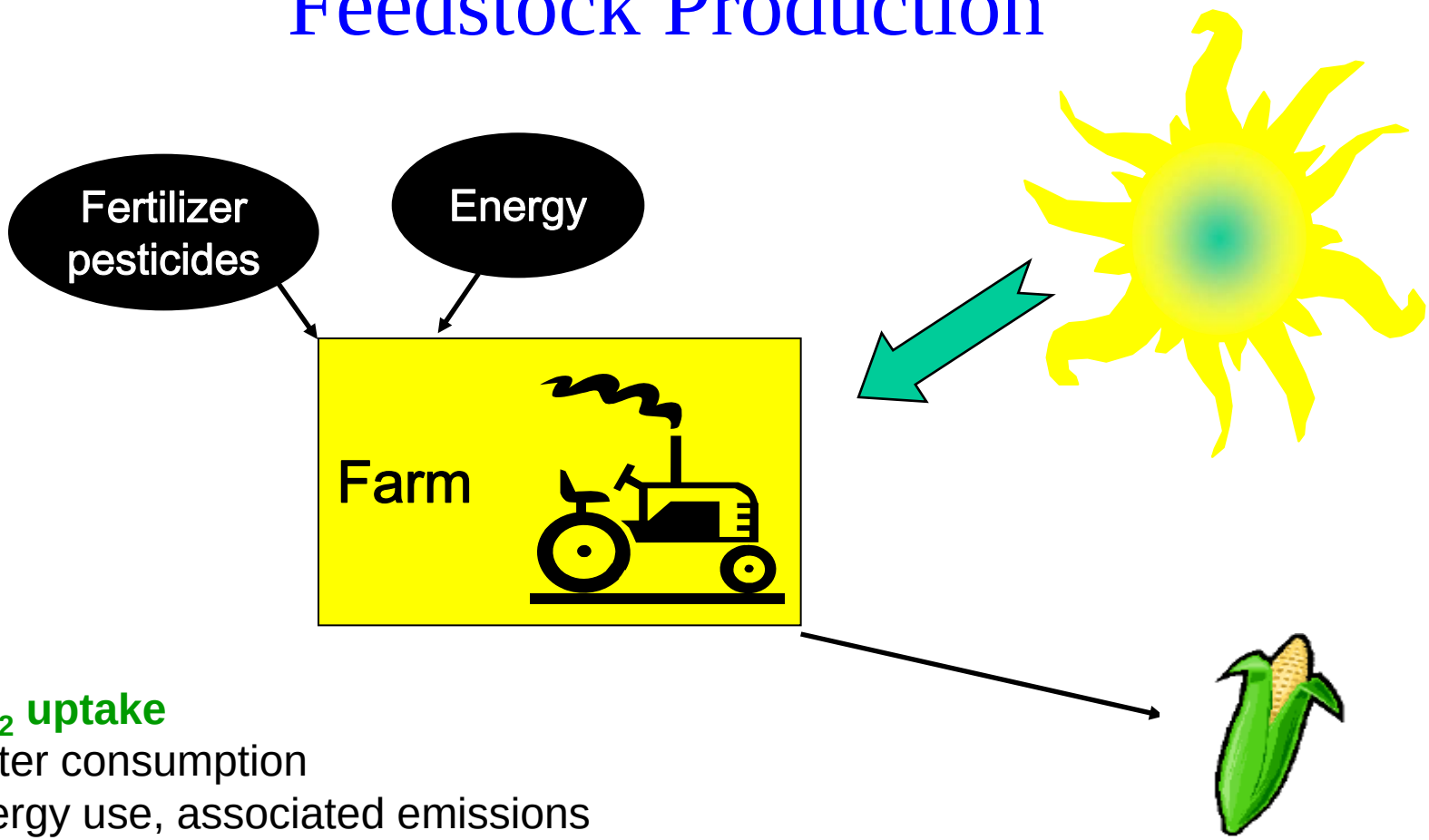
Plant-Based Fuels (biodiesel, EtOH, & H_2) Can Address Three National Interests

(1) Minimize dependence on foreign oil and improve our trade balance

(2) Steer the impending growth of biomass-based industries to protect environmental quality, and

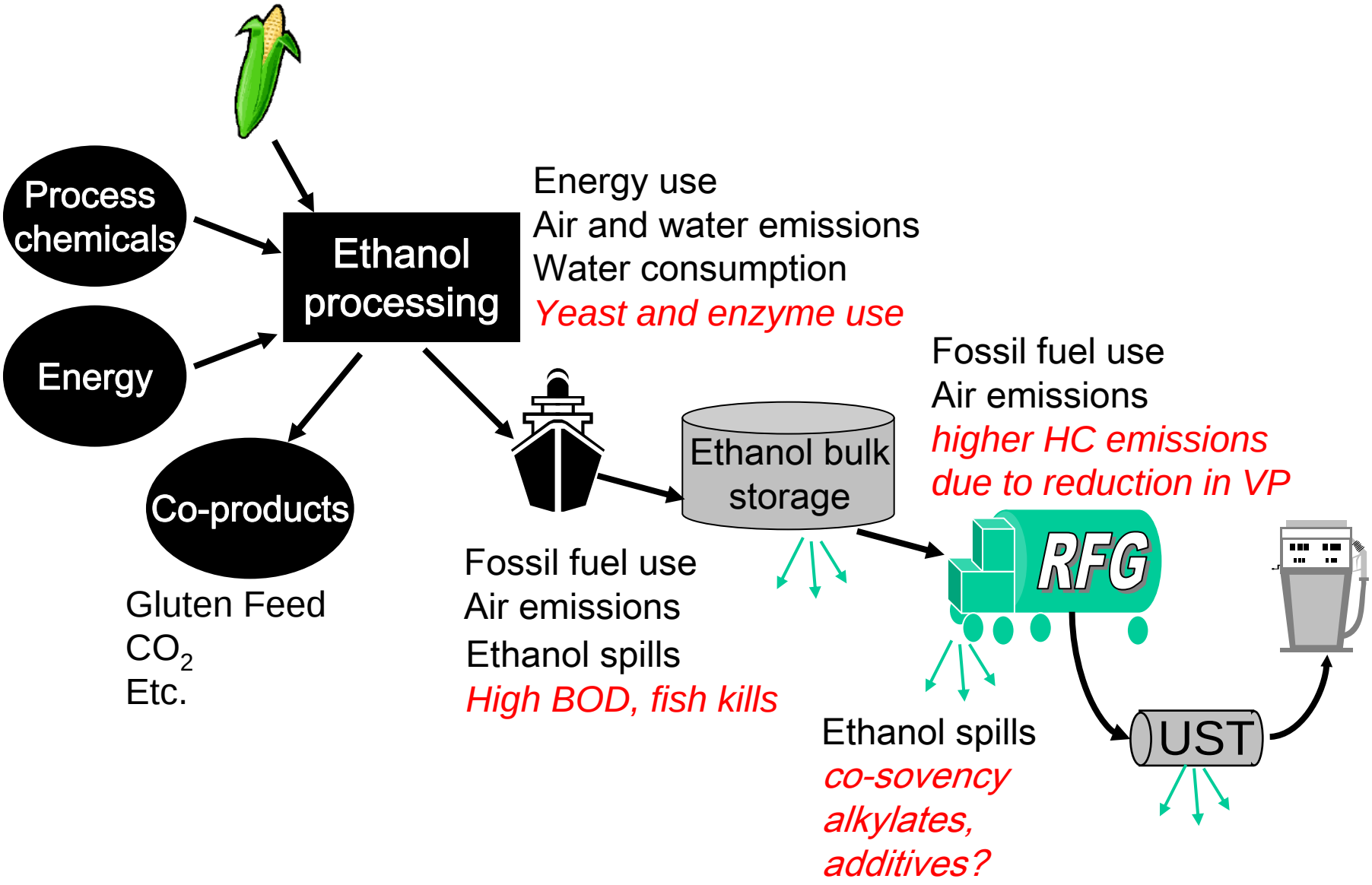
(3) Invigorate agricultural activity and rural economy for food security.

Feedstock Production

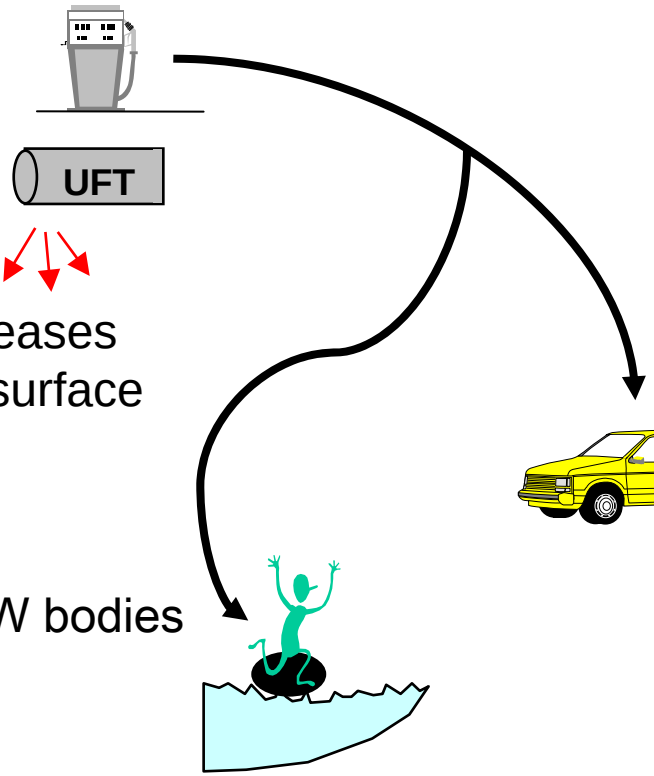


CO_2 uptake
Water consumption
Energy use, associated emissions
Land use
Fertilizer & pesticide use and associated soil/water contamination
Biodiversity and genetic drift issues if genetically engineered corn is used
Erosion and Soil health
Food versus fuel?

Fuel Processing & Transportation



Vehicle Use



Unintended releases
to soil and subsurface
co-solvency,
MNA inhibition

Direct discharge to SW bodies

Decreased fossil fuel use
Reduced CO air emissions
(oxygenate)

Potentially higher HC emissions due to reduction in VP
Increased amount of alkylates, decreased amount of BTEX
Impacts to vehicle lifecycle?

Life Cycle Engineering of Biofuels

1) Develop framework for life cycle impact evaluation and pollution prevention.

- Water pollution by higher fertilizer and pesticide use, (hypoxia problem in the Gulf of Mexico?).
- Changes in land use and impact on soil health
- Changes in air quality as a result of replacing hydrocarbons by biomass-based renewable fuels.
- Changes in CO_2 emissions to and from the atmosphere, and its net effect on atmospheric decarbonization and global climate.
- Increased water consumption (e.g., for irrigation) and impact on water security.

Life Cycle Engineering of Biofuels

2) Identify major logistical challenges for the biofuel industry.

- Robustness in the event of a drought, and management of related uncertainty
- Adequacy of existing biofuel distribution and storage infrastructure.

Life Cycle Engineering of Biofuels

3) Develop a framework for analyzing the overall costs and benefits of biofuels.

- Examine the costs of biofuels production including the effect of system perturbations on costs.
- Examine the competitiveness of biofuels with alternative sources of transportation fuels.
- Develop methodology for costing the externalities associated with biofuels production

Life Cycle Engineering of Biofuels

4) Enhance the economic and environmental feasibility of biofuels production.

- Characterize energy flows & opportunities for increasing the net energy value (biocatalysis, genetic modification of plants & bugs)
- Replace hazardous substances used in the life cycle with "greener" alternatives (bioinsecticides?)
- Alternative biomass sources (e.g., biodiesel from algae, fuel alcohols from lignocellulosic waste) and effect on water consumption & competitiveness
- Framework for CO_2 emission credits (or subsidies if CO_2 emissions are taxed)

Sustainable Biofuels: Research Needs

1. Develop a comprehensive, comparative LCA framework for the production, storage, distribution, and use of biomass-based renewable fuels (e.g., H_2, biodiesel, and ethanol)

2. Enhance biofuels economic feasibility and environmental viability (e.g., biocatalysis, NEV, CO_2 emissions trading)

Sustainable Biofuels: Research Needs

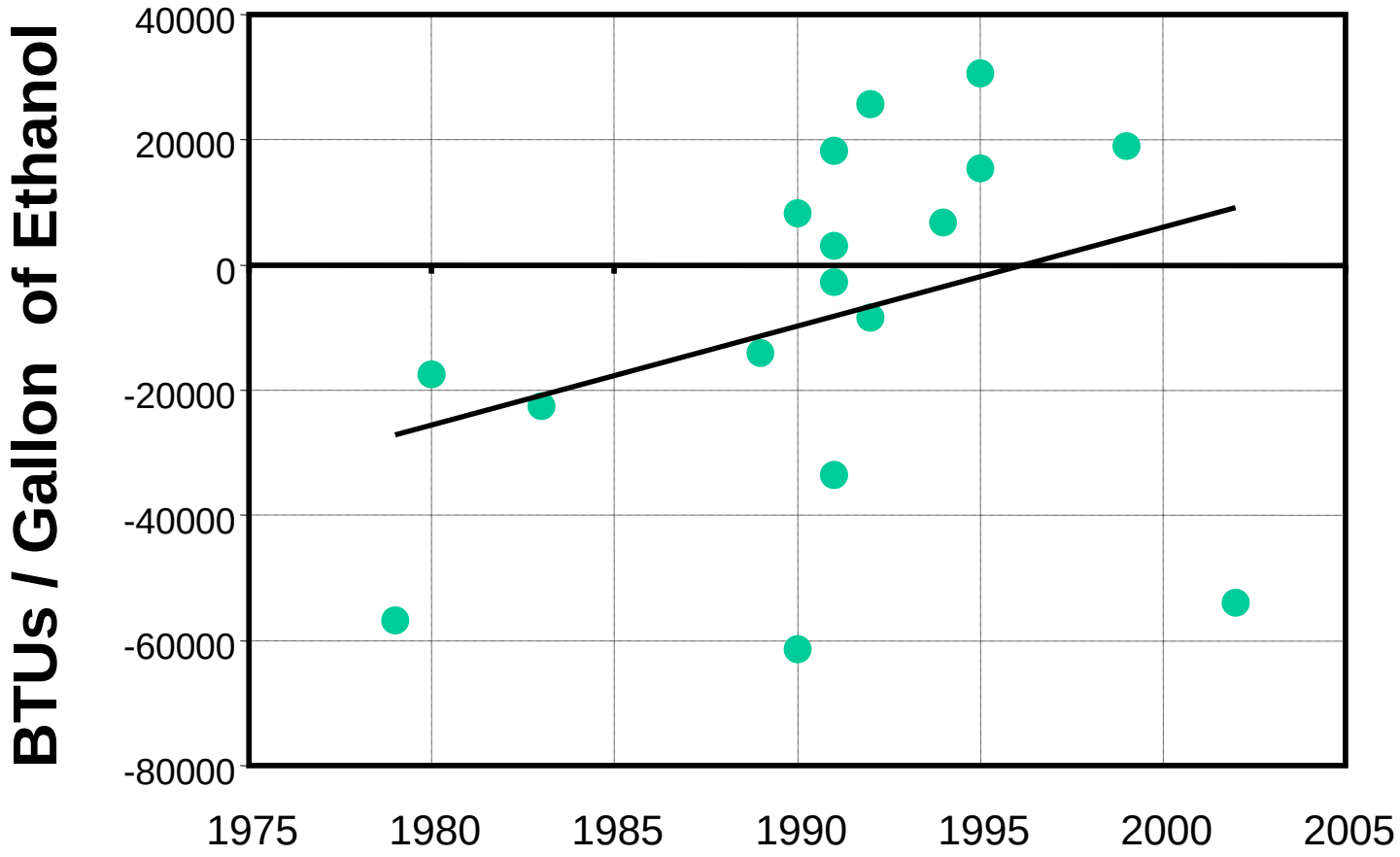
1. Develop a comprehensive (comparative) LCA framework for the production, storage, distribution, and use of biomass-based renewable fuels (biodiesel, H_2, and ethanol); e.g.,

- Changes in urban air quality (+ or -)?
- Carbon balances (decarbonization, soil health and global climate implications)?
- Potentially problematic fuel components and impurities? (environmental analysis, ecotoxicology, fate and transport)
- Changes in land use, erosion, pesticide and fertilizer application and implications on environmental quality?

Biofuel Research Needs (cont'd)

- Control energy flows and increase net energy value
- "Greener" replacements for hazardous substances used in life cycle (*e.g.*, bioinsecticides; biocatalysis).
- Decrease biodiesel melting point for enhanced winter performance (shorter, saturated fatty acids).
- Alternative biomass sources for H_2 and biodiesel (algae, lignocellulosic agricultural waste).
- CO_2 emission credits for replacing petroleum

Reported NEV Corn Ethanol



Potential Environmental Impacts

Emissions to Soil, Air, Water
Fossil fuel consumption
CO_2 – climate change
Material consumption
Land use
Soil quality

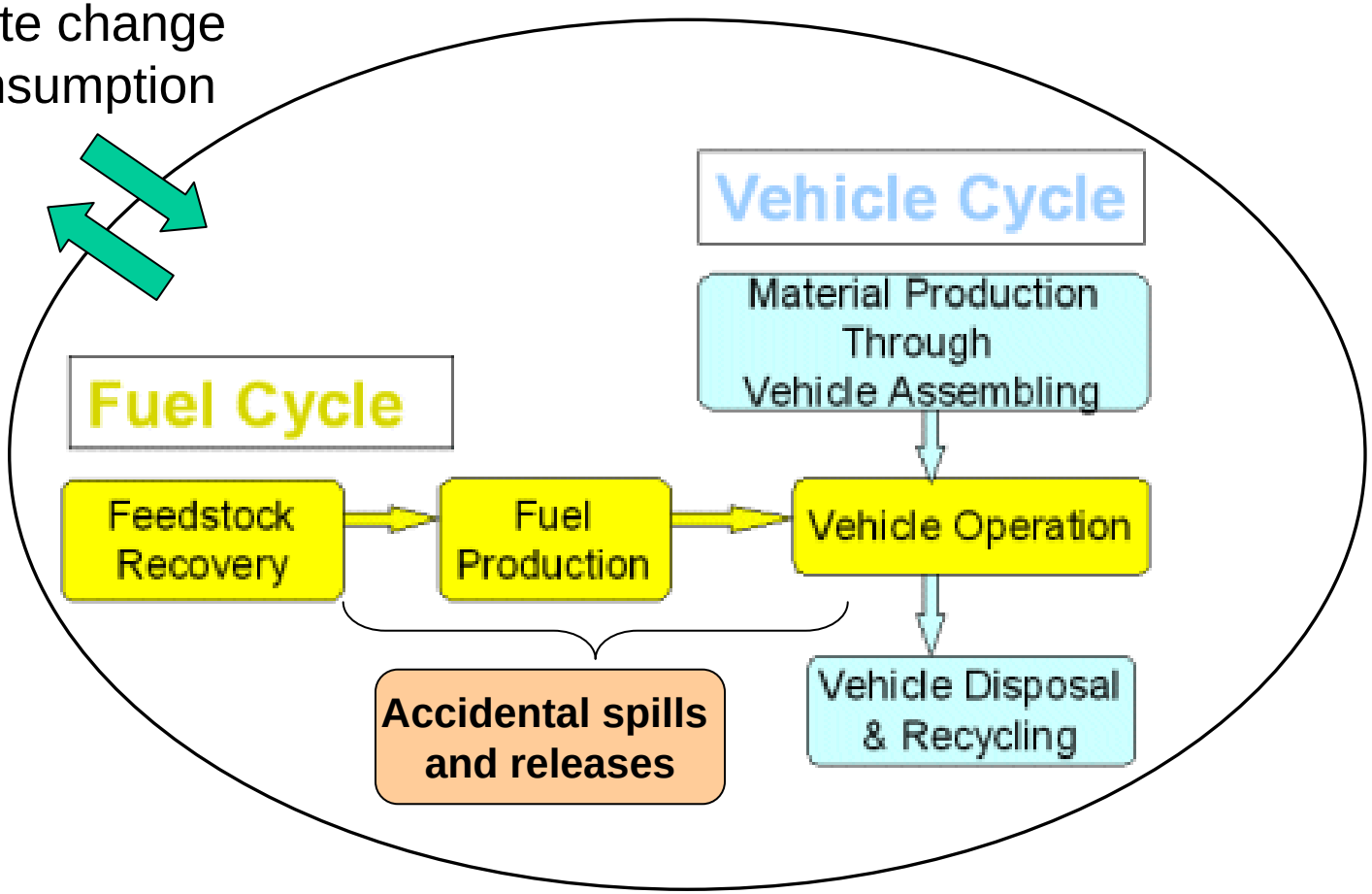


Figure adapted from GREET, Argonne Nat'l Lab