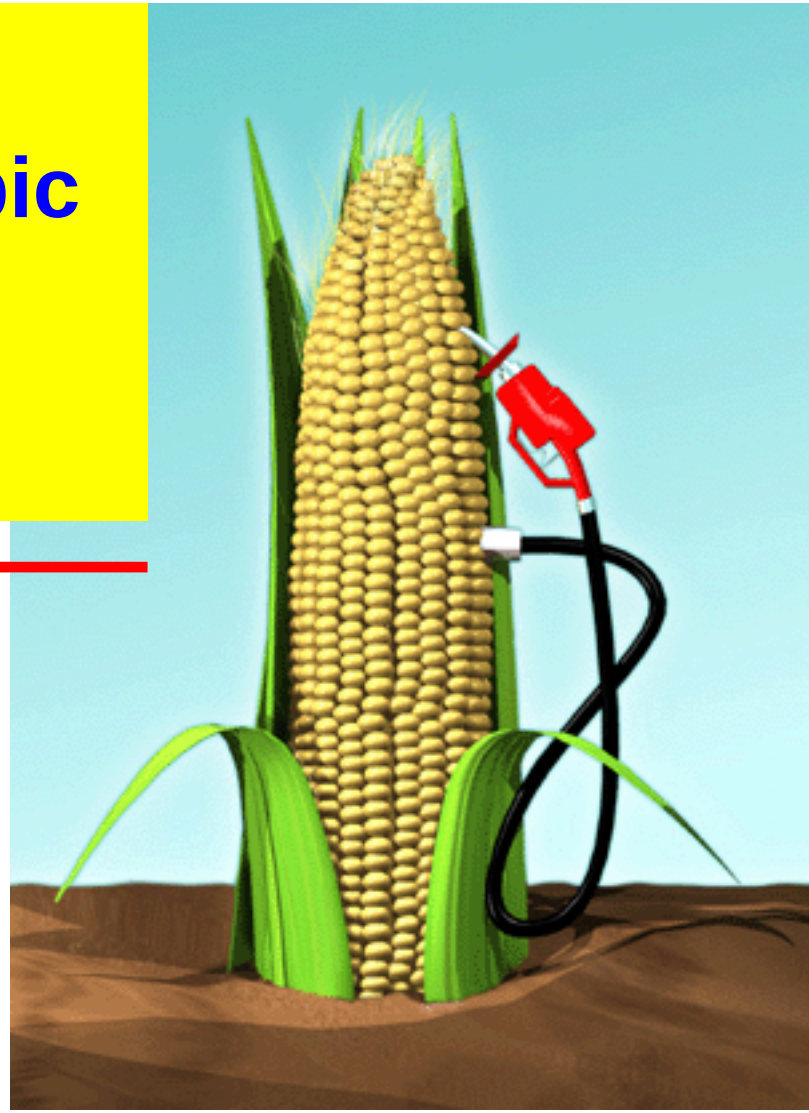
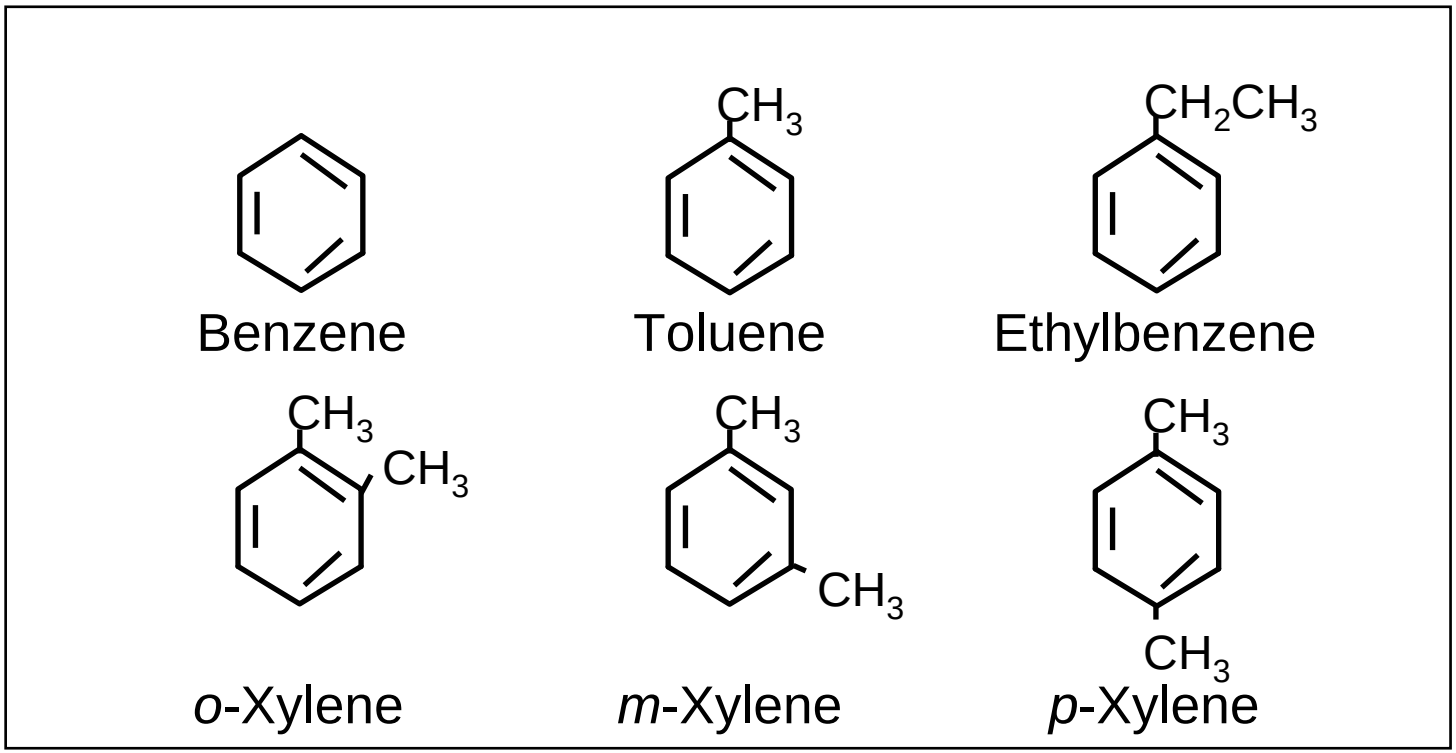
Ethanol in Fuel: Microscopic & Macroscopic Implications for Groundwater Pollution



Pedro J.J. Alvarez

RICE

Contaminants of Concern with Fuel Spills: BTEX



Two Potential Effects of EtOH on BTEX Fate and Transport:

- Physico-chemical (Co-solvency and mobilization of BTEX)
- Microbial (Effect on BTEX biodegradation)

Acknowledgments

Former students:

Marcio Busi da Silva

Natalie Capiro

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Jim Barker (Waterloo)

Greg Hattan (KDHE)

Bruce Bauman (API)

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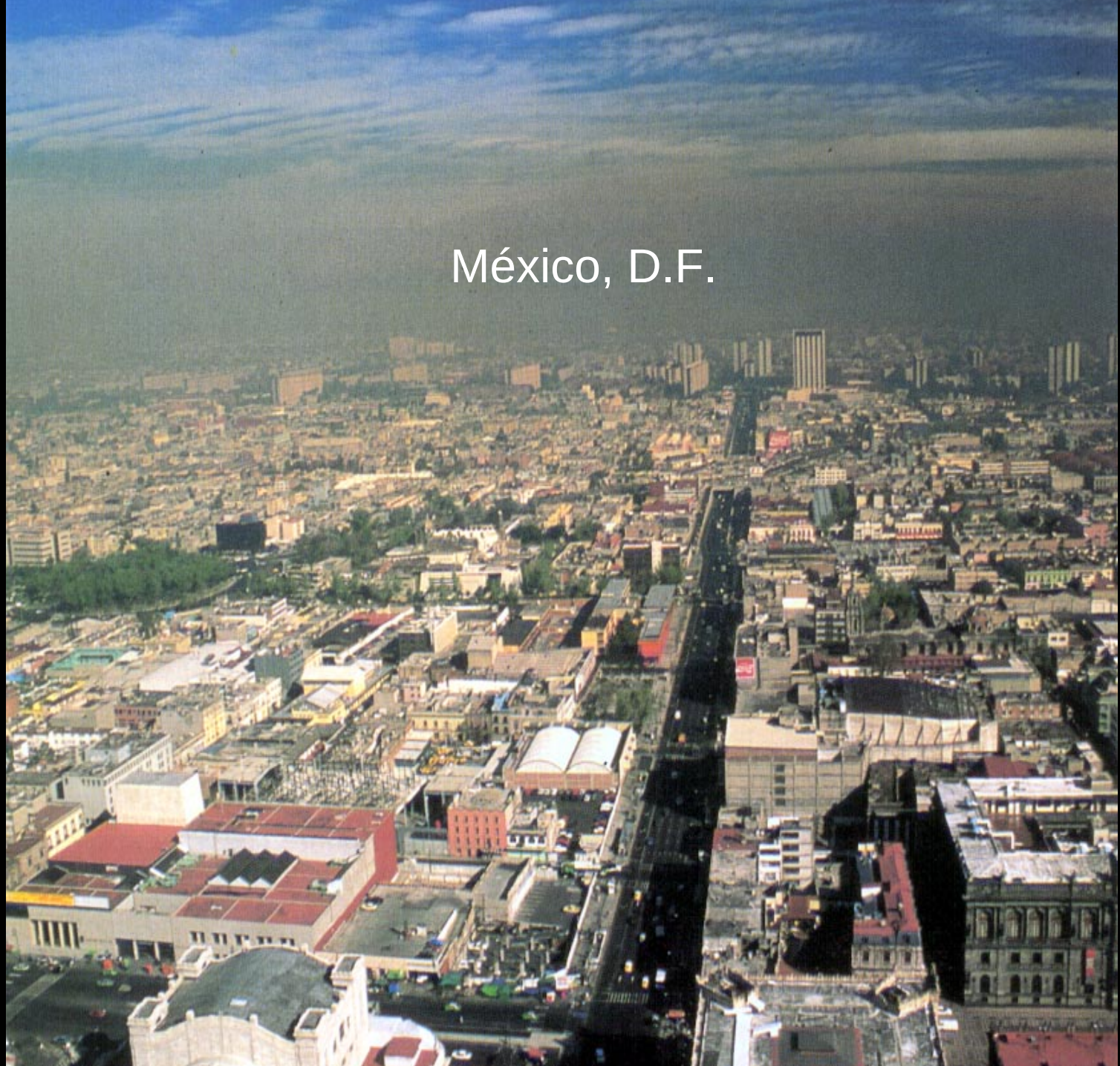
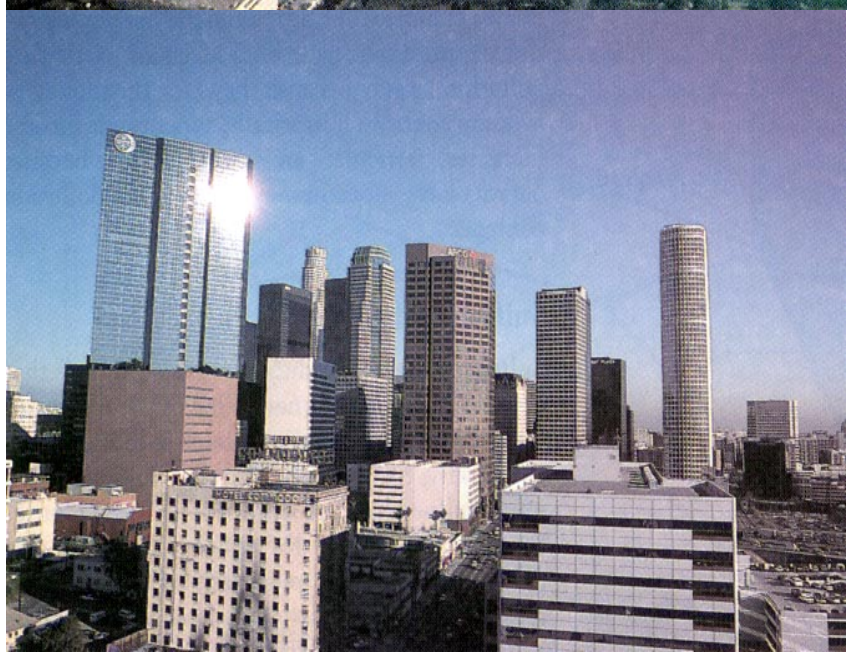

México, D.F.

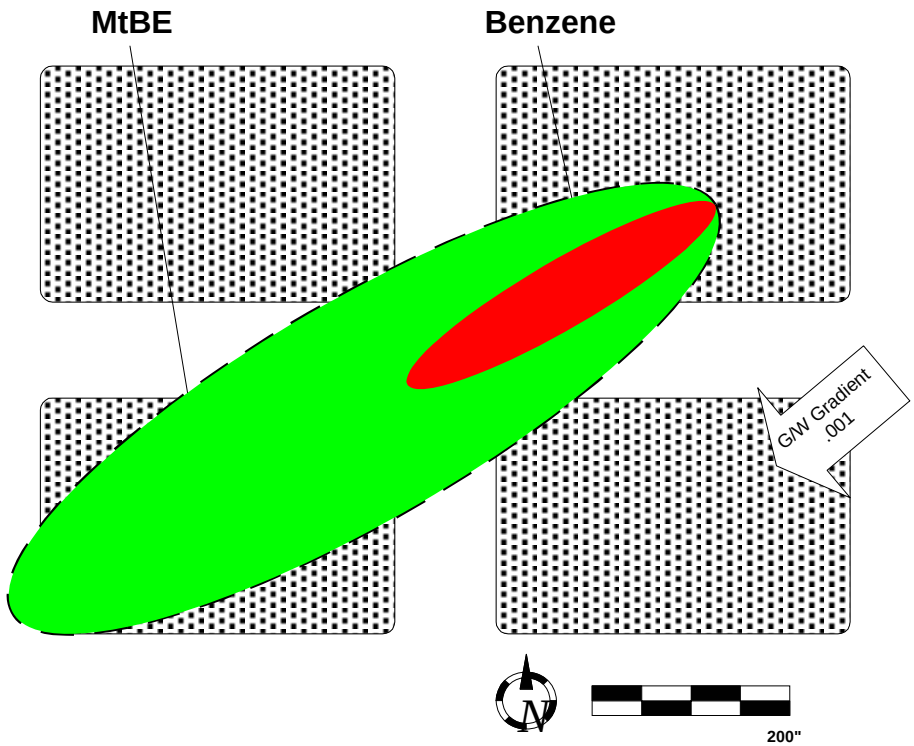
Gasoline reformulation (MTBE) and catalytic converters improved air quality in urban areas

~10 years

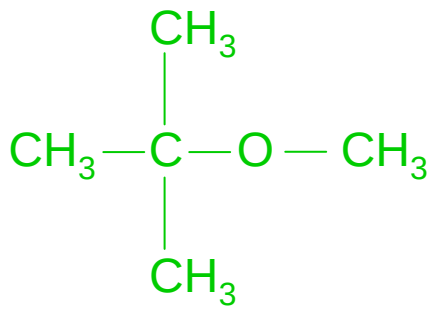


Soil and Groundwater Pollution

Distribution of Key Constituents in Gasoline-Contaminated Groundwater



MTBE



A potential carcinogen that smells and tastes like turpentine

Background

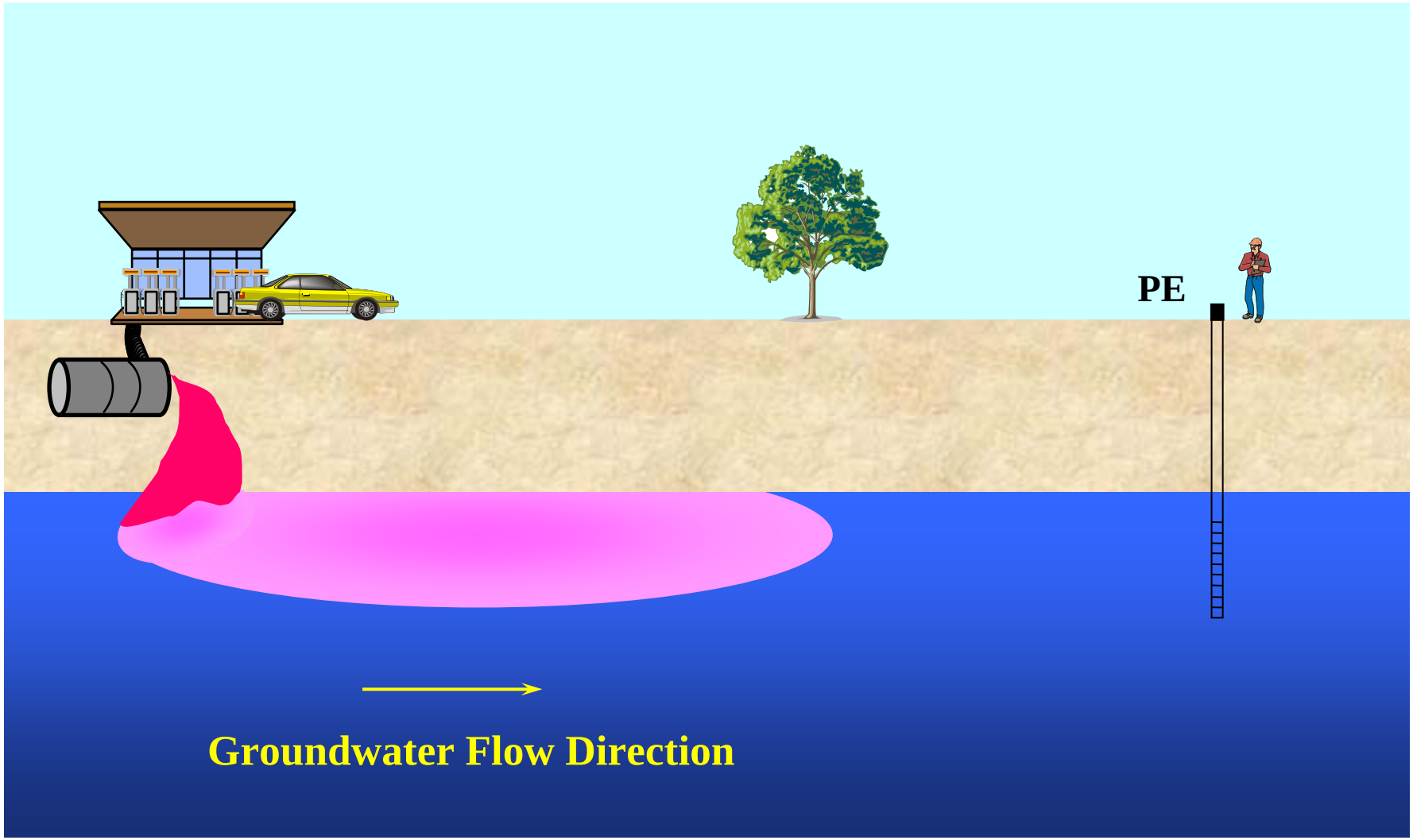
Ethanol is a good oxygenate (reduces air pollution from combustion), renewable, biodegradable, non-toxic, and can serve as substitute fuel for imported oil (good for trade balance and food security). But...

Food for fuel?

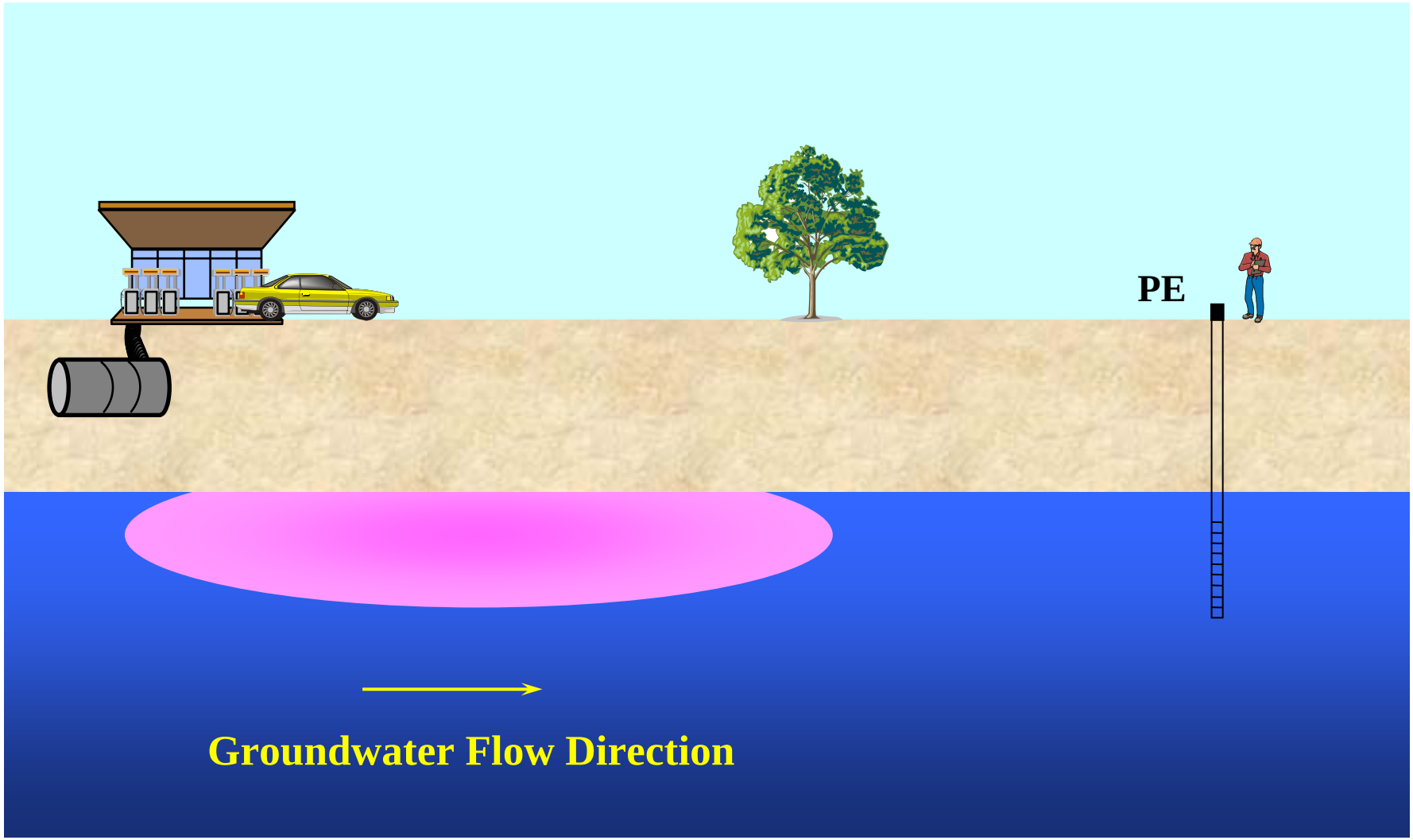
Tax subsidy ($0.51/gal) = corporate welfare for corn growers and ethanol producers?

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

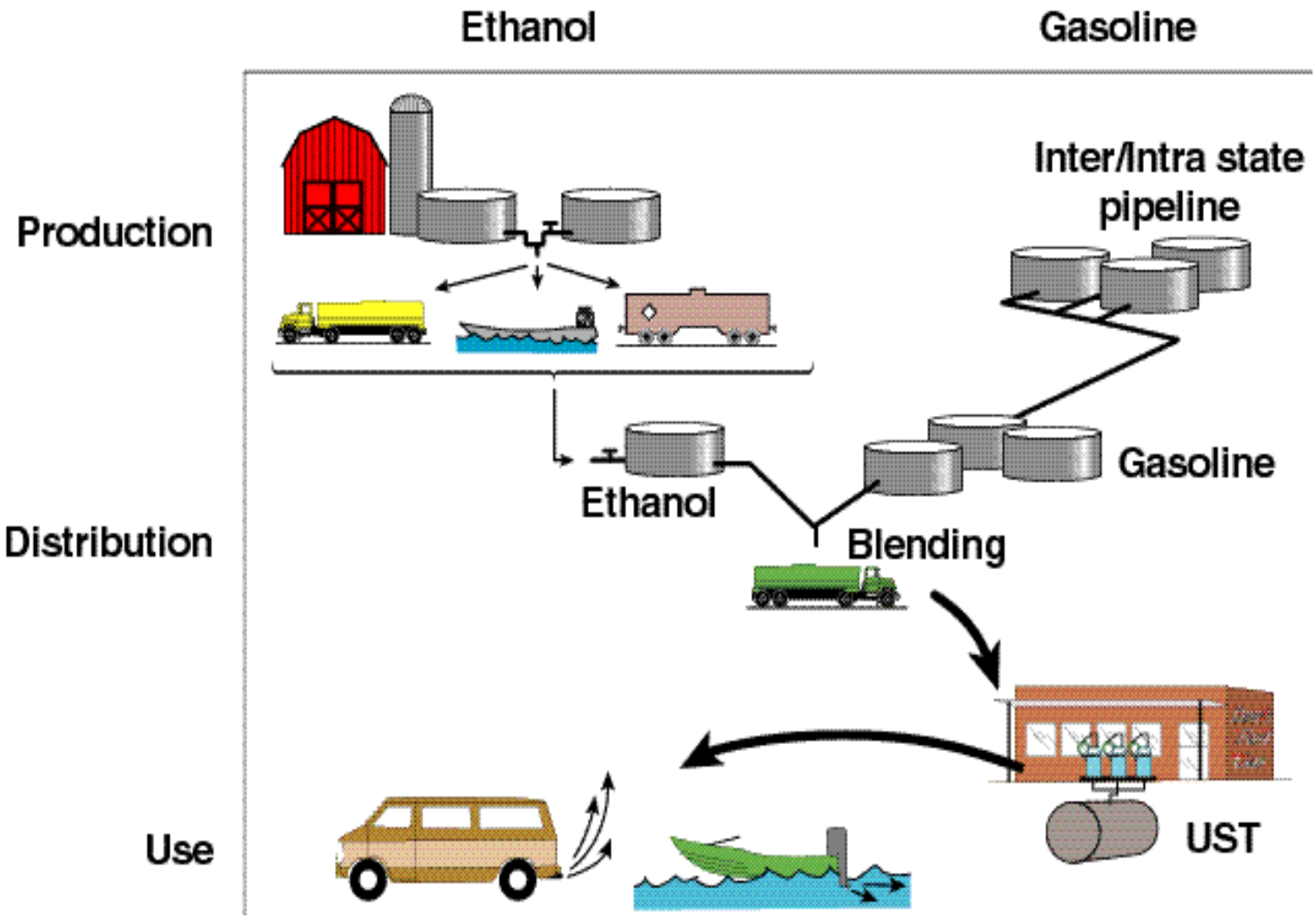
Natural Attenuation



Natural Attenuation

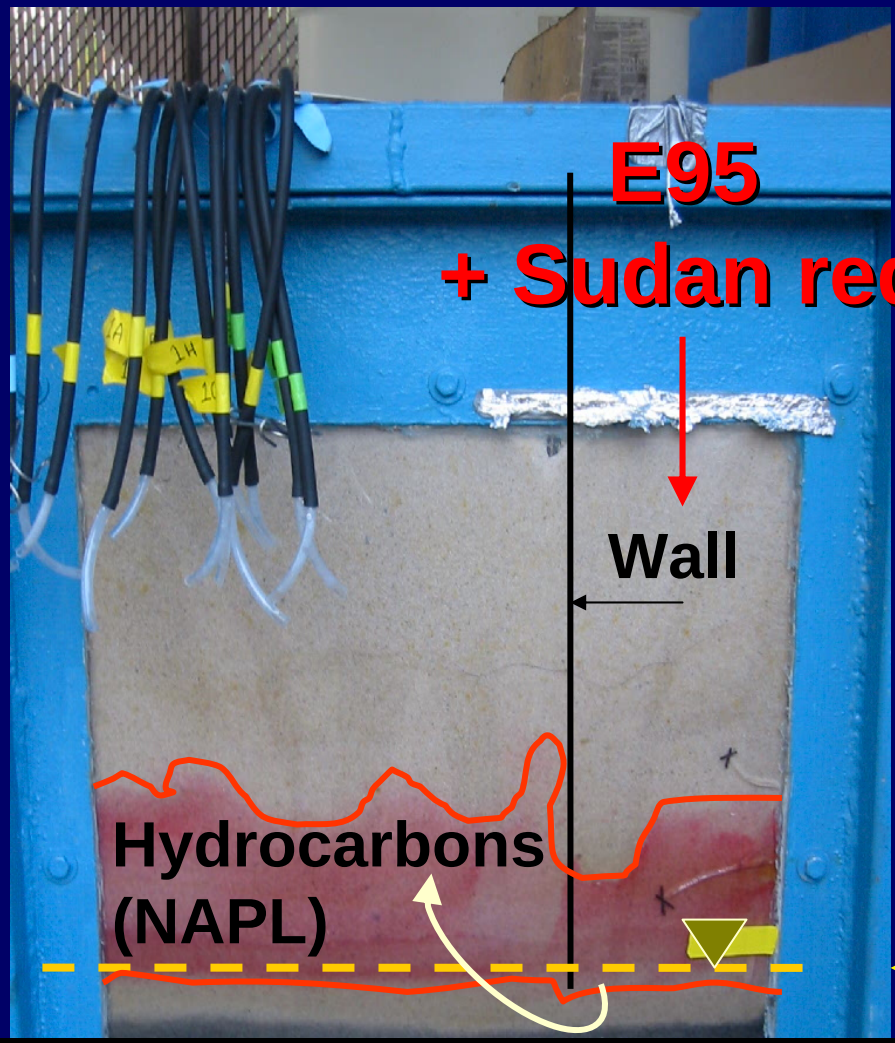


Simplified Life Cycle of Fuel Ethanol



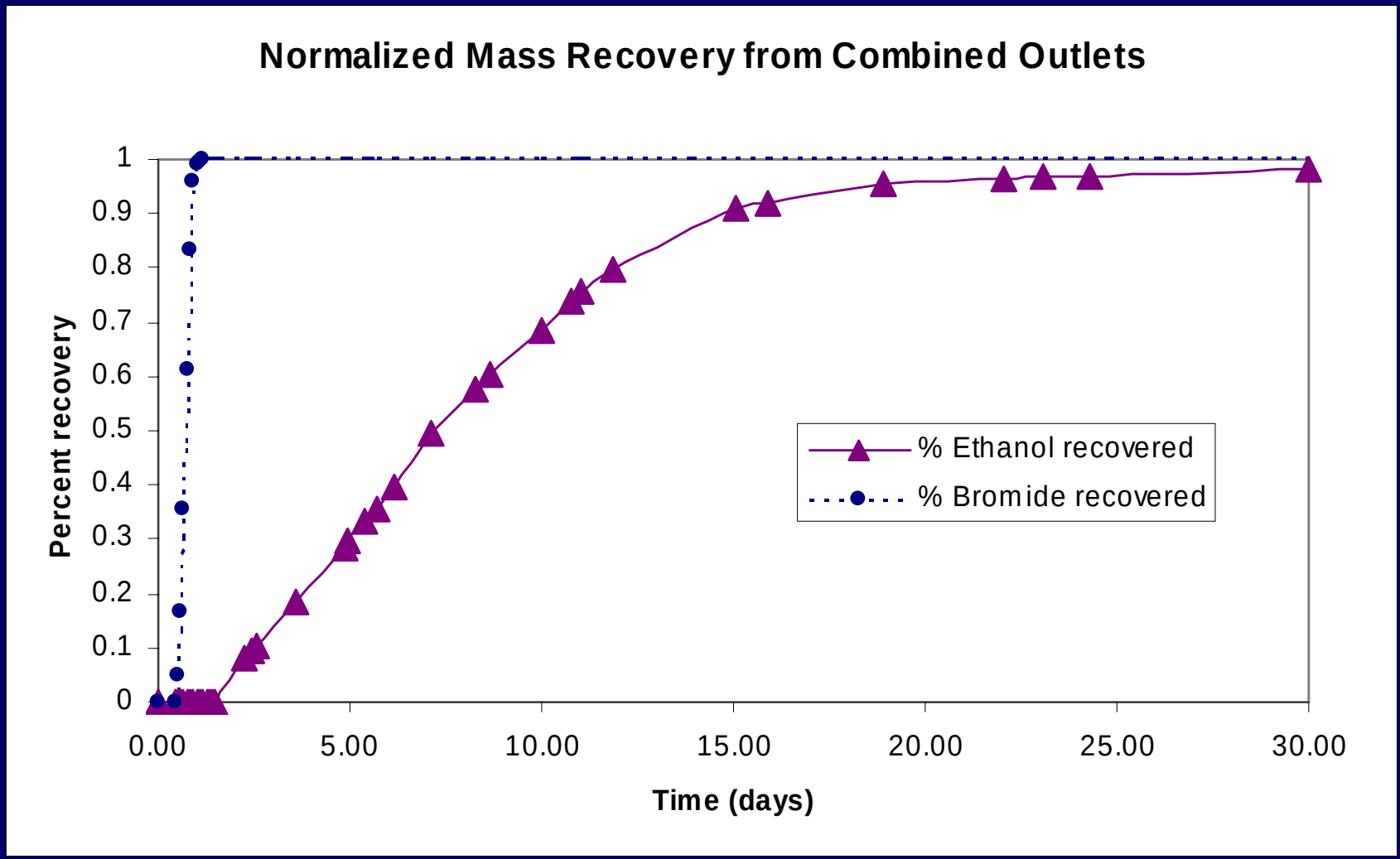
Pilot Ethanol Spill Tank (PEST)

Hydrocarbon NAPL Formation & Movement



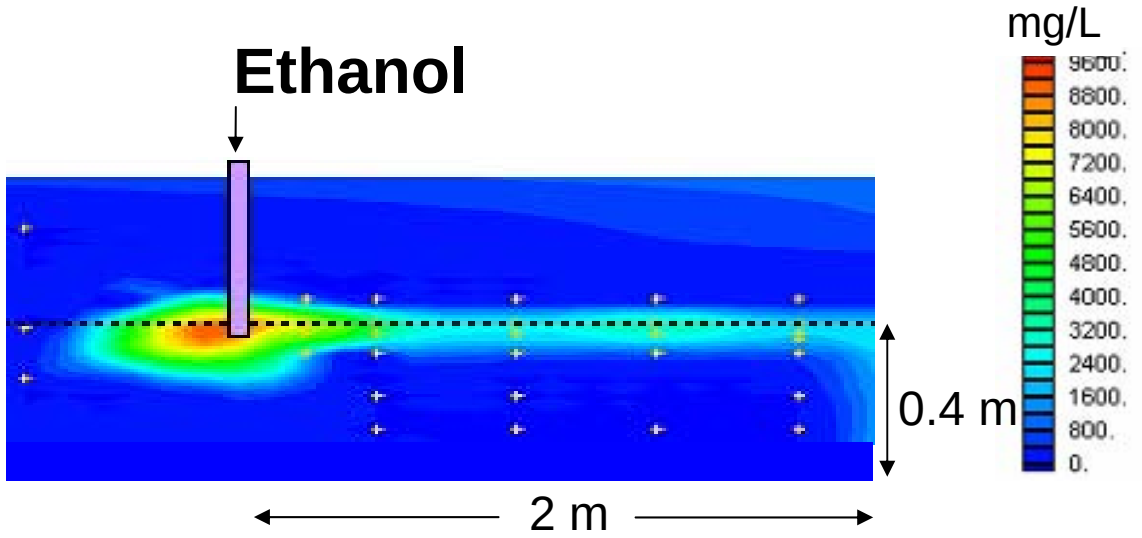
Ethanol decreases the surface tension and the capillary forces, which facilitates flow through the capillary zone. This spreads out the oily phase (Non-Aqueous Phase Liquid - NAPL)

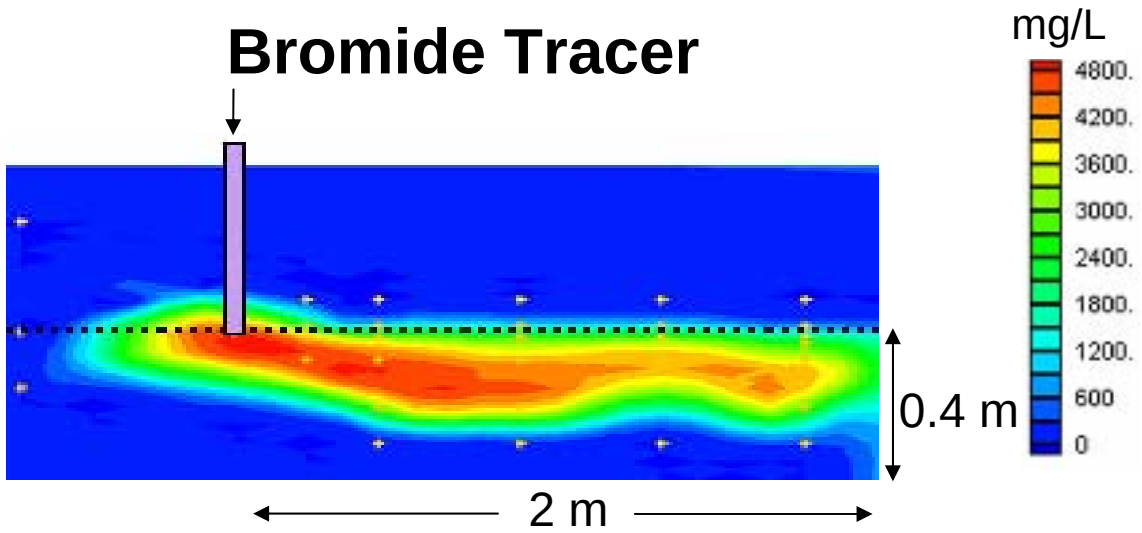
Cumulative Breakthrough Shows Excellent EtOH Mass Balance + Retardation



Cápiro N.L, B. P. Stafford, W.G. Rixey, P.J.J. Alvarez, and P.B. Bedient (2006). *Water Research* (In Press)

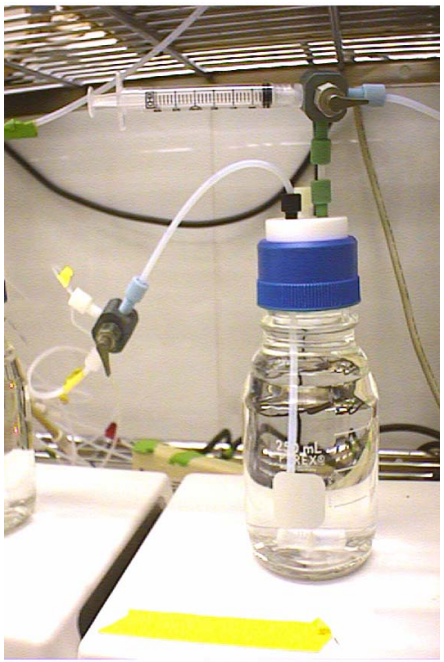
Concentration profiles show that EtOH migrated in a thin layer at the water table interface (little vertical dispersion compared to tracer)



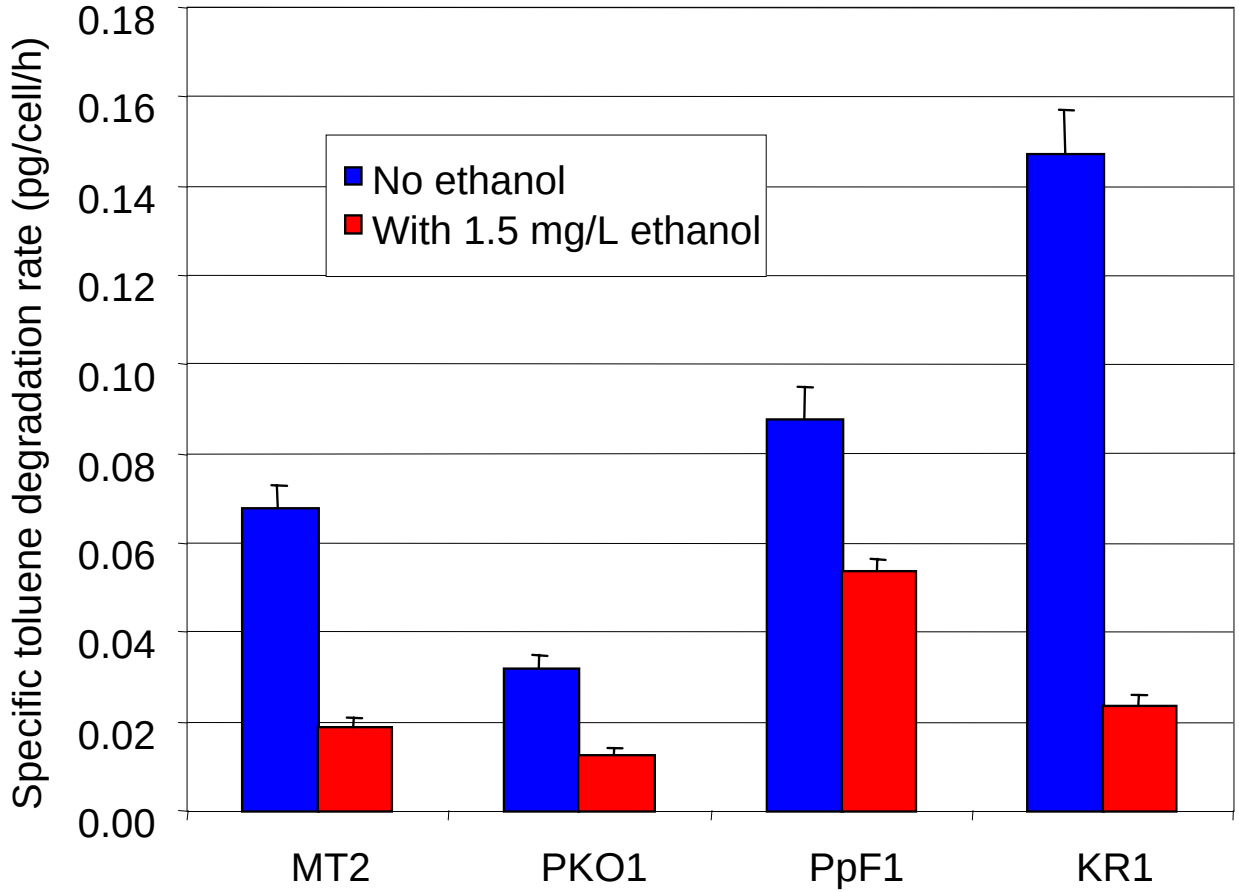


Cápiro N.L, B. P. Stafford, W.G. Rixey, P.J.J. Alvarez, and P.B. Bedient (2006). *Water Research* (In Press)

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



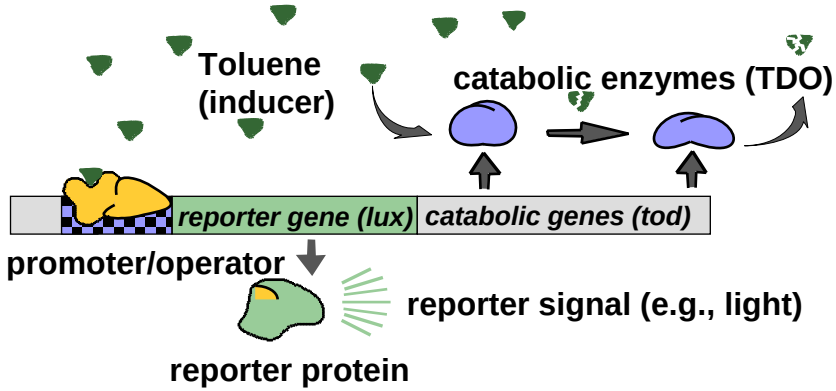
C_0 = 1 mg/L toluene



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

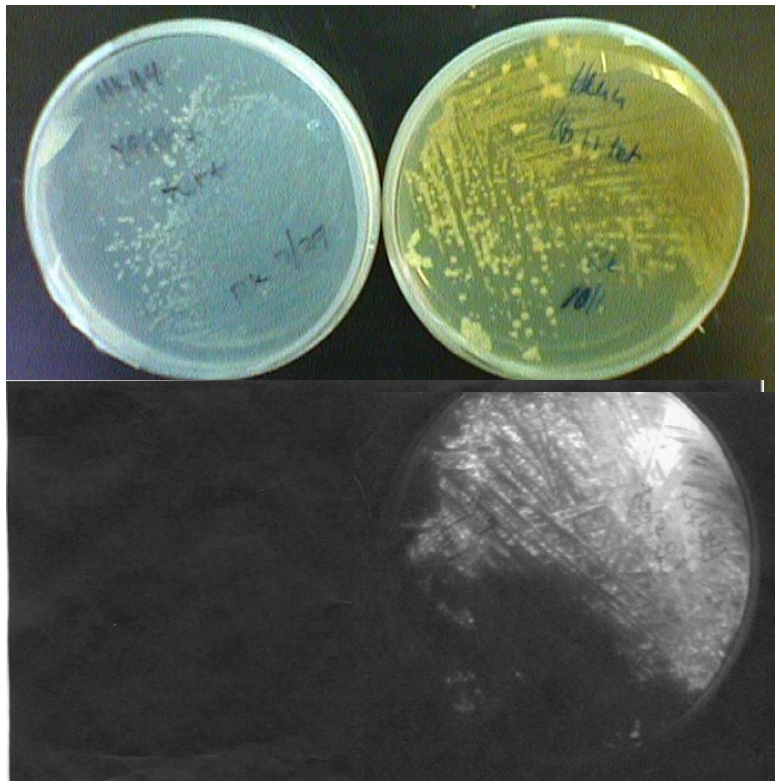
Bioreporter Strain

Pseudomonas putida F1 with *tod-lux*

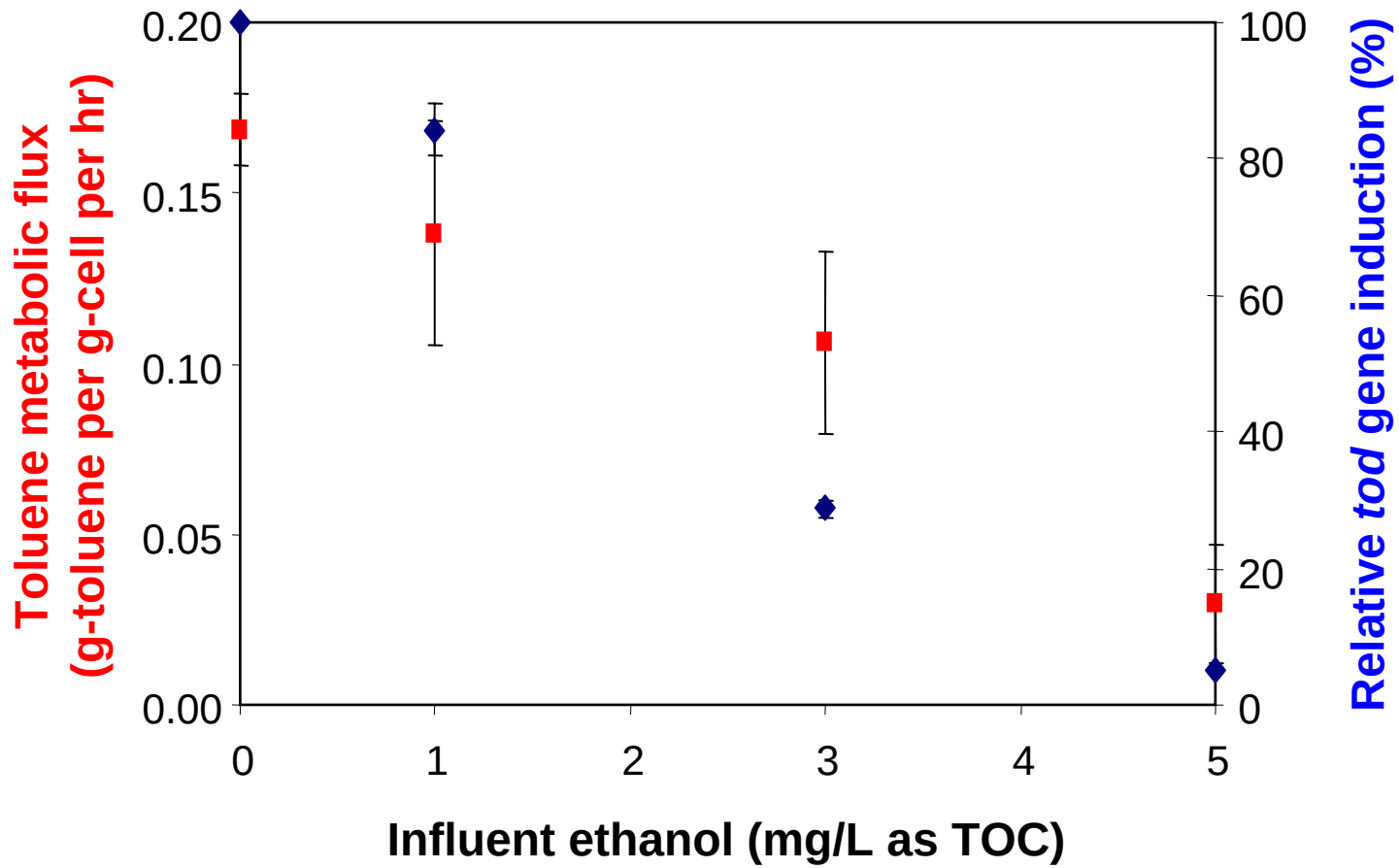


- Fused a reporter gene (*lux*) with the *tod* catabolic gene
- When the *tod* gene is induced, the reporter gene is also expressed producing luciferase, which emits a signal (e.g., light)
- The signal (measured with a luminometer) is proportional to the level of induction

PpF1 with *tod-lux* fusion

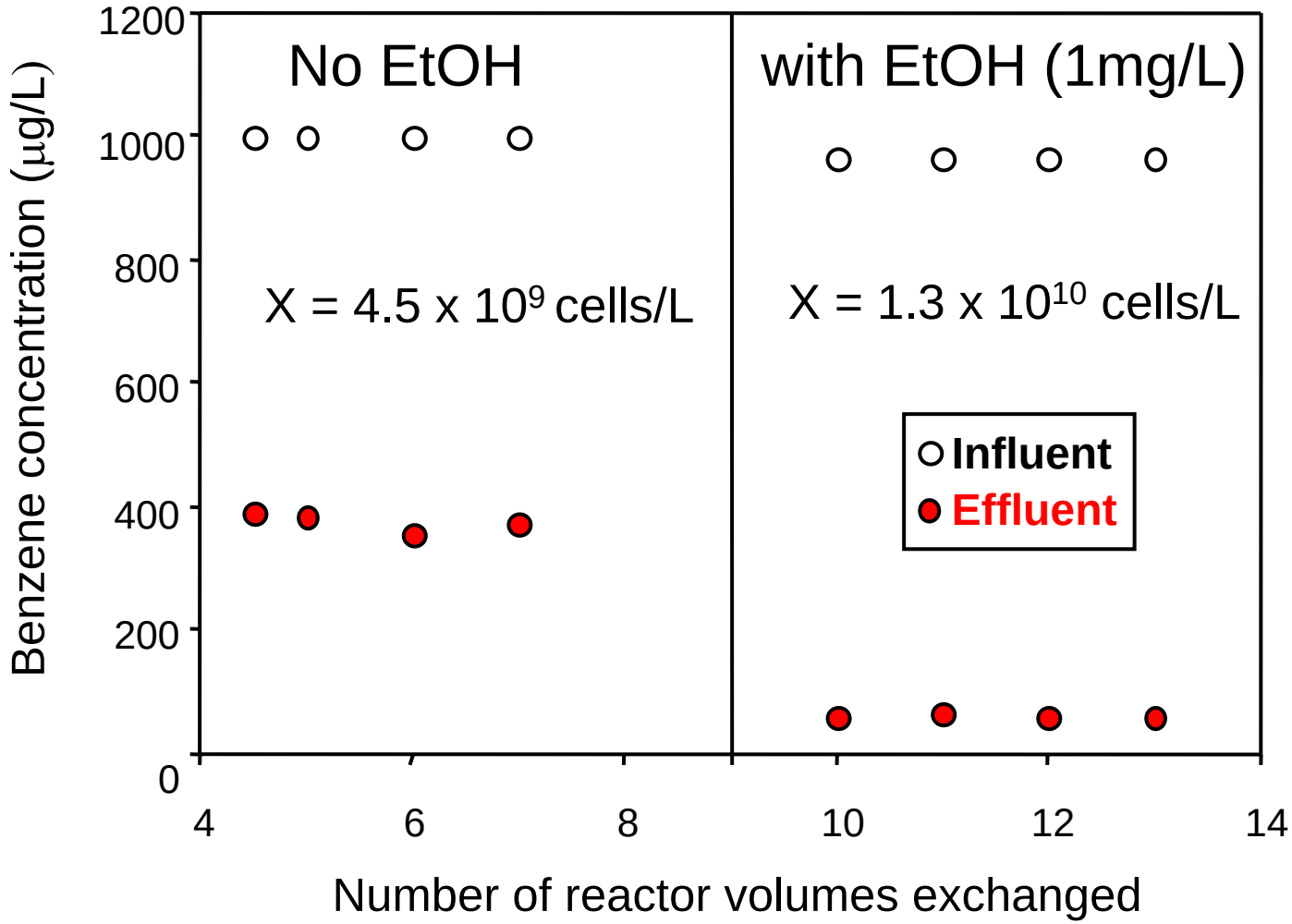


Enzyme induction and toluene metabolic flux *decreased* with increased ethanol availability



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



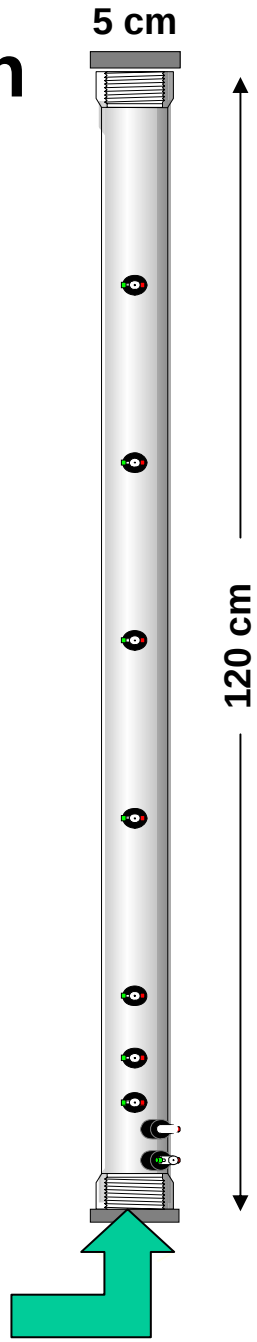
Lovanh N., C.S. Hunt, and P.J.J. Alvarez (2002). *Water Research*. 36:3739-3746.

Implications of Chemostat Results

- The inhibitory effect of ethanol on specific BTEX degradation activity (catabolite repression and metabolic flux dilution) can be offset by additional cell growth. However, ethanol-driven depletion of nutrients and electron acceptors (e.g., O_2) is likely to hinder the natural attenuation of BTEX.

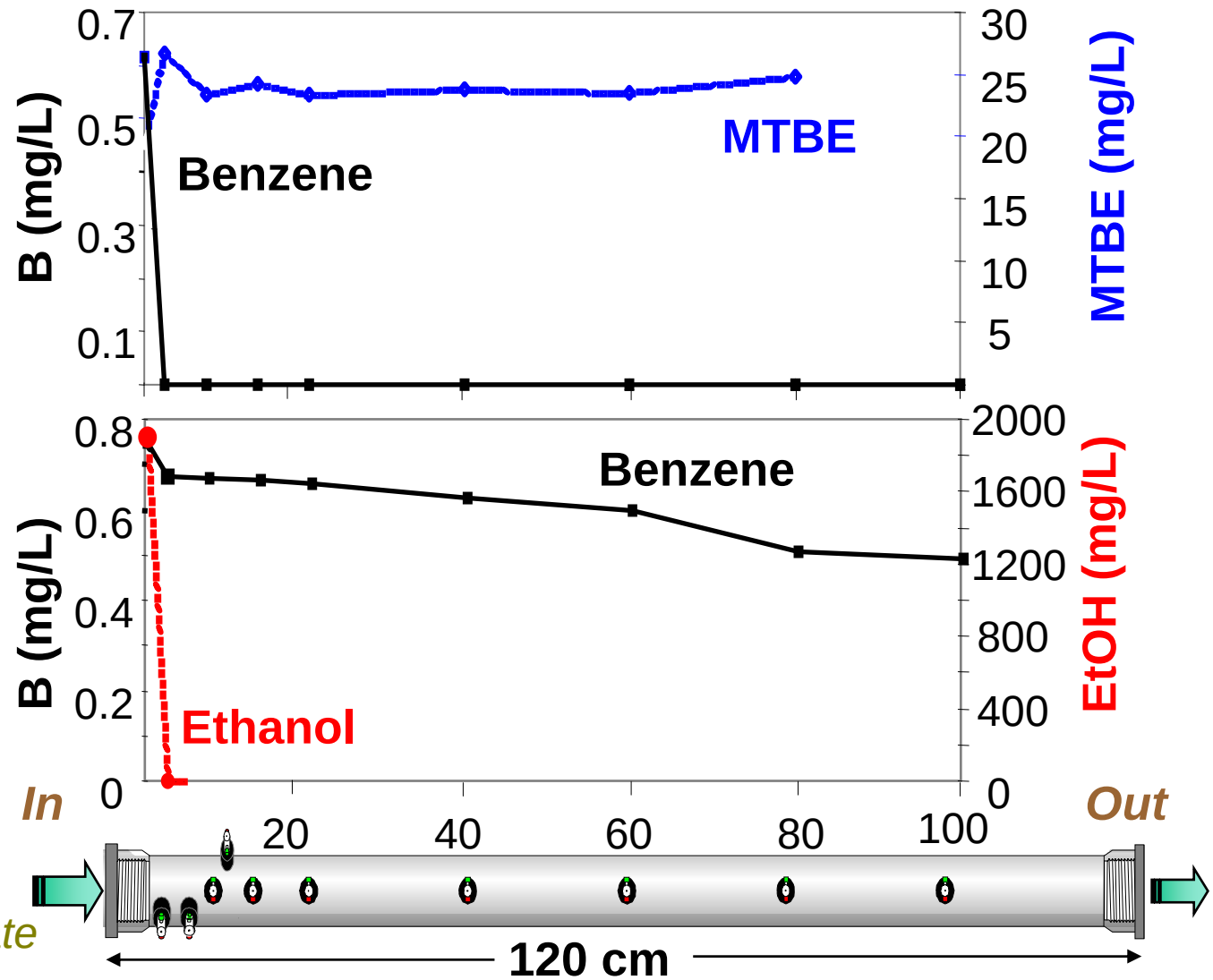
Aquifer Column Experiments

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

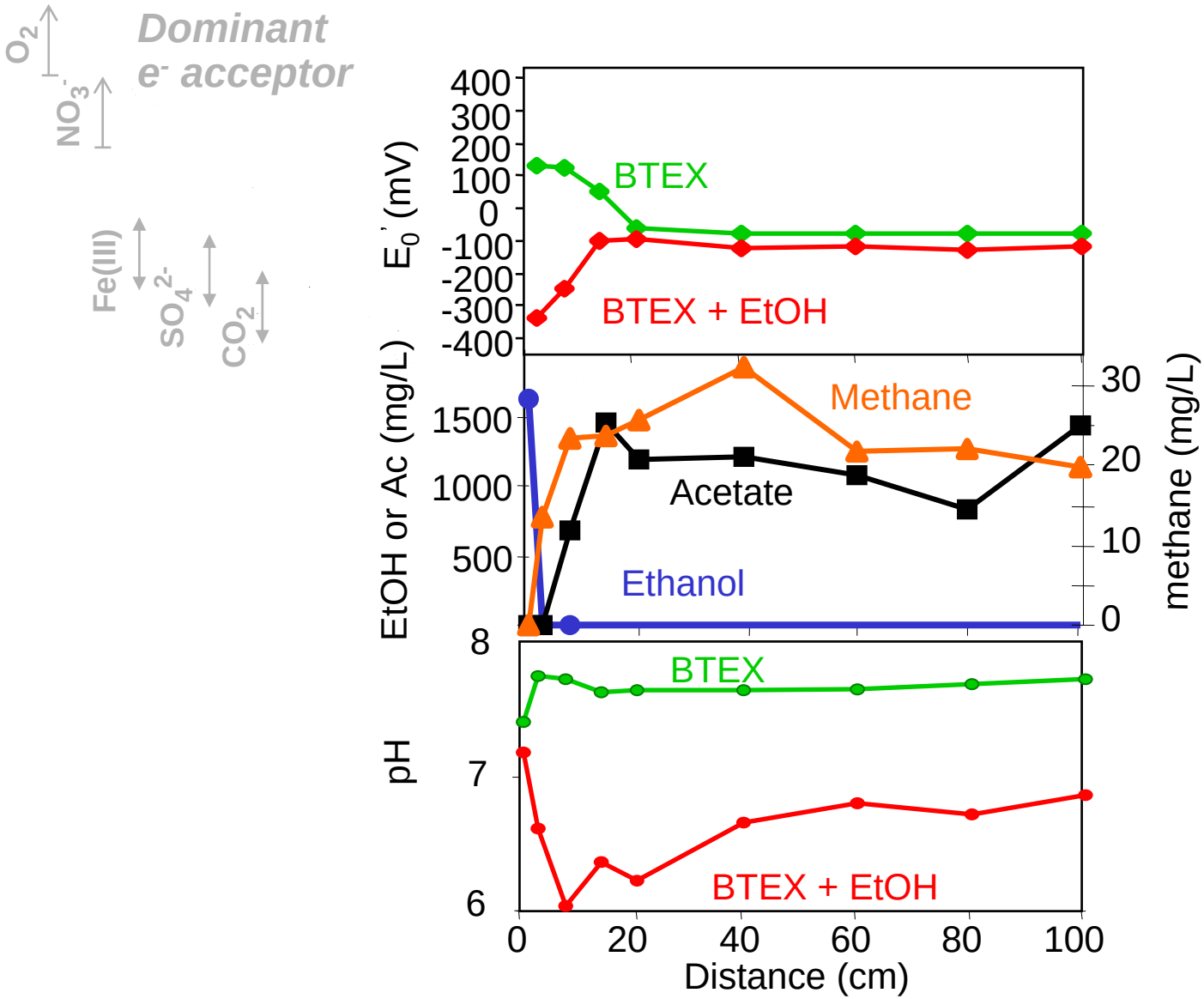
Effect of Ethanol versus MTBE on Benzene Attenuation



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

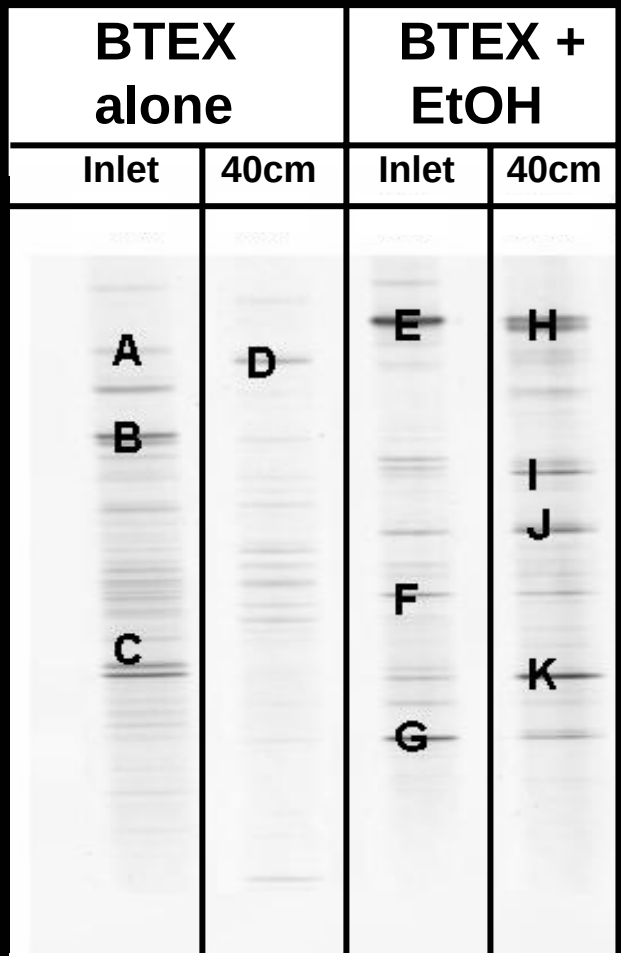
Da Silva M.L. and P.J.J. Alvarez (2002). *J. Env. Engrg.* 128(9):862-867

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.

DGGE Analysis of the Effect of EtOH on Microbial Community Structure

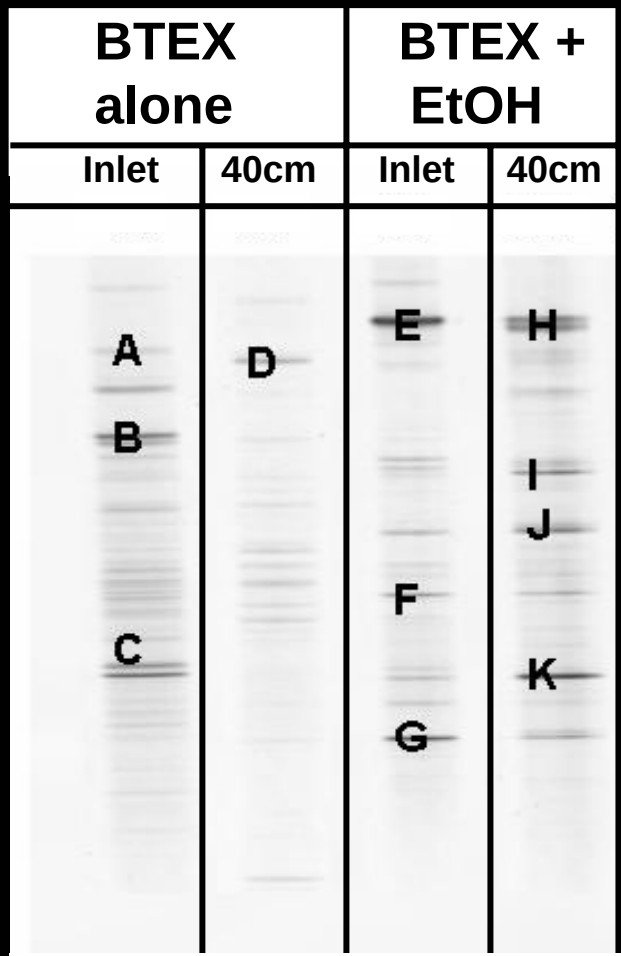


Dominant Species

A - *Geobacter akaganeitreducens*
B - *Geobacter sp.*
C - *Clostridium sp.*
D - *Azoarcus sp.*
E - *Campylobacter sp.*
F - *Clostridium sp.*
G - *Desulfovibrio burkinensis*
H - *Sporomusa sp.*
I - *Clone WCHB1-71*
J - Failed
K - Clone SJA-181

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

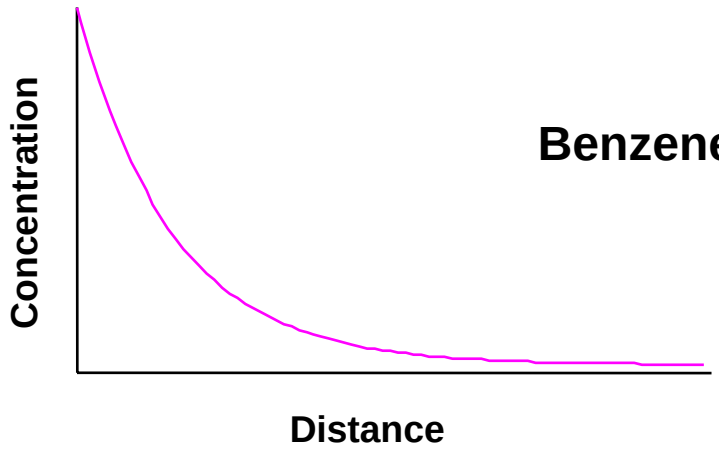
DGGE Analysis of the Effect of EtOH on Microbial Community Structure



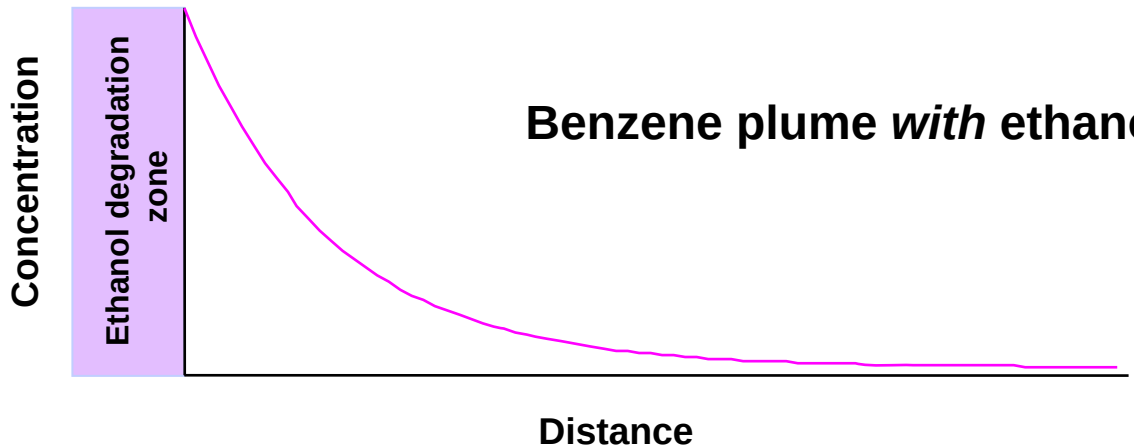
= Genotypic Dilution

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

Potential Ground Water Impacts of EtOH-Plume Conceptual Model



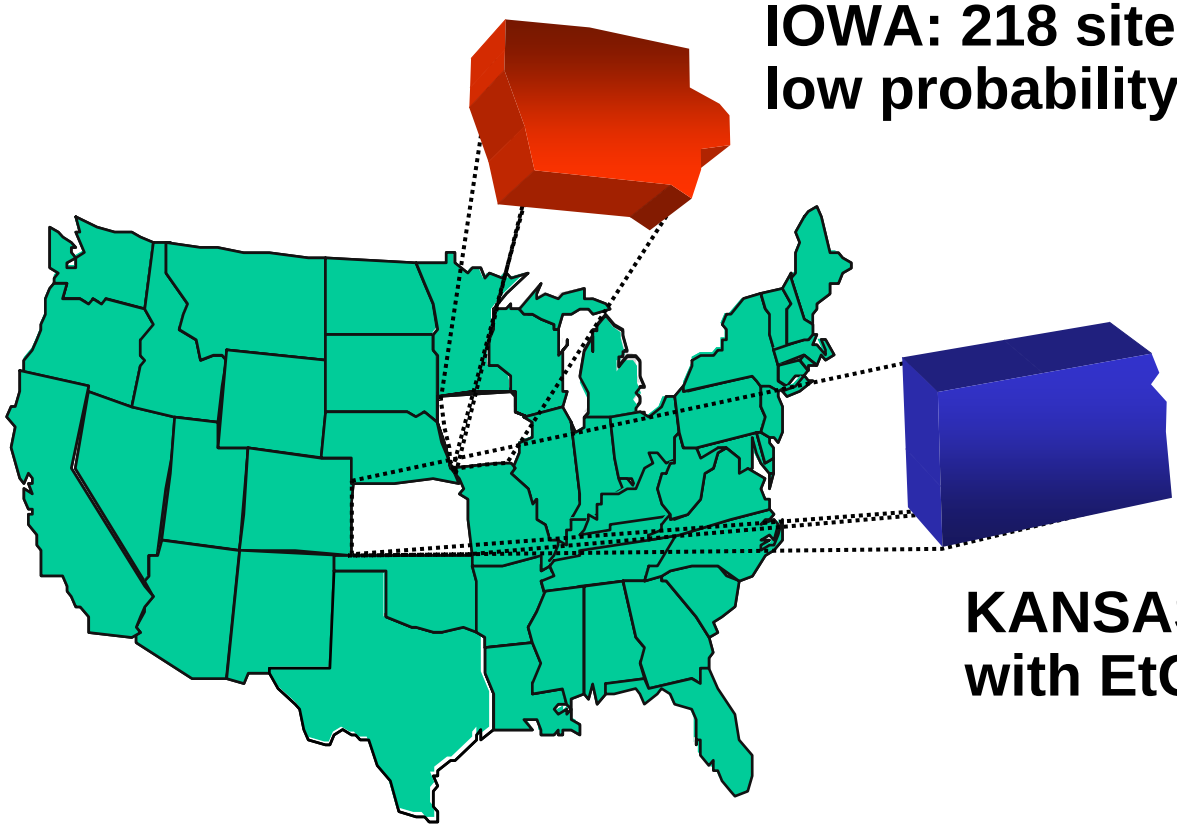
Benzene plume *without* ethanol.



Benzene plume *with* ethanol.

The Midwest Plumathon

Is the elongating effect of ethanol on BTEX plumes significant?

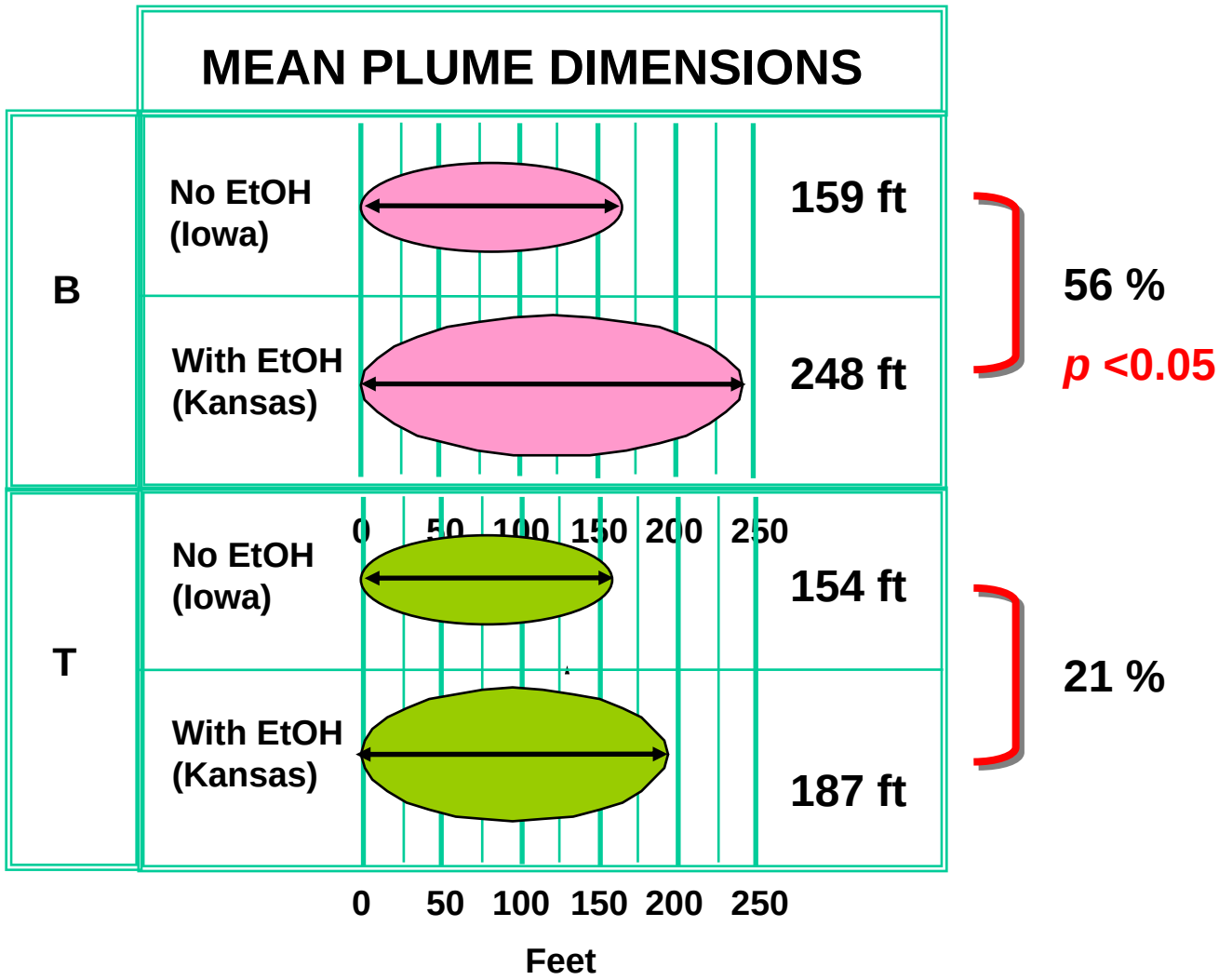


IOWA: 218 sites
low probability of EtOH

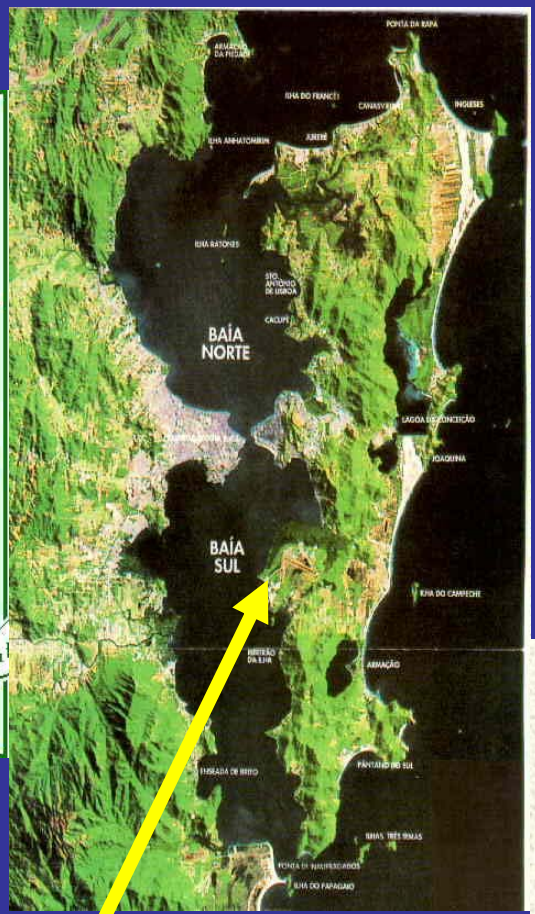
KANSAS: 29 sites
with EtOH (10% v:v)

For each site, determined benzene & toluene plume lengths

What is the Overall Effect of Ethanol?

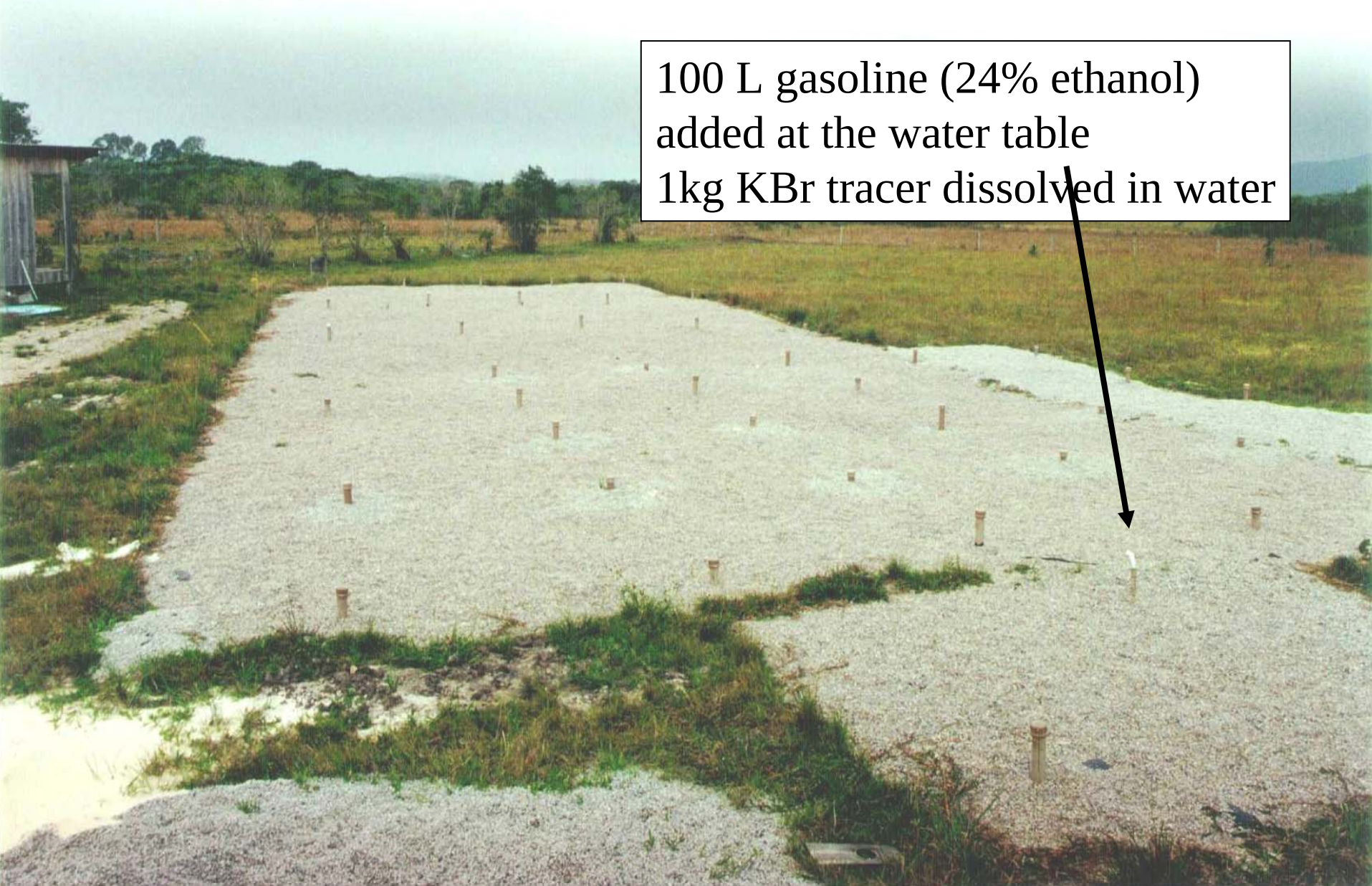


Ruiz-Aguilar G.M, K. O'Reilley, and P.J.J. Alvarez (2002). *Ground Water Monitoring and Remediation.* 23(1):48-53



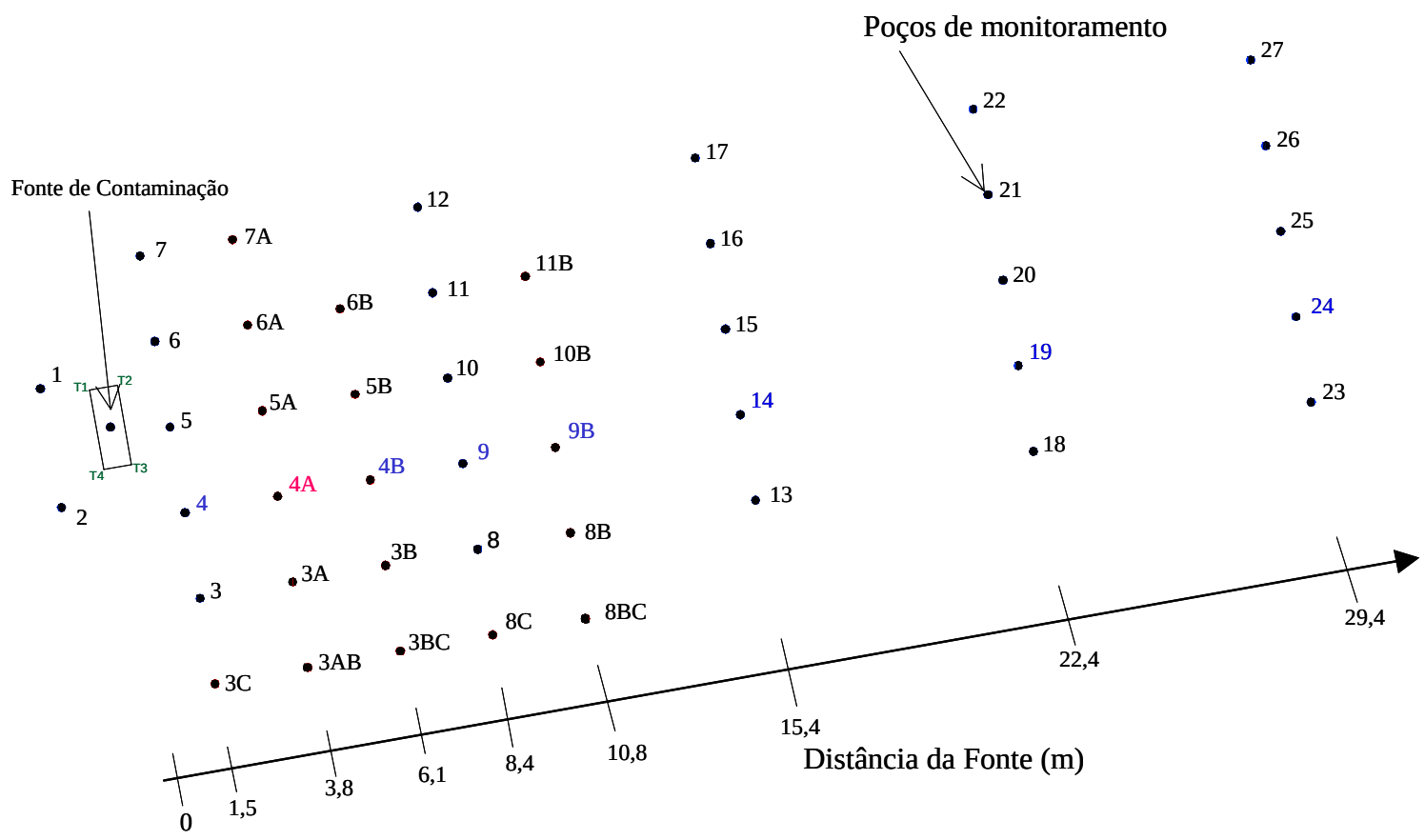
Fazenda Ressacada

Field Experiment (sandy, homogeneous aquifer)



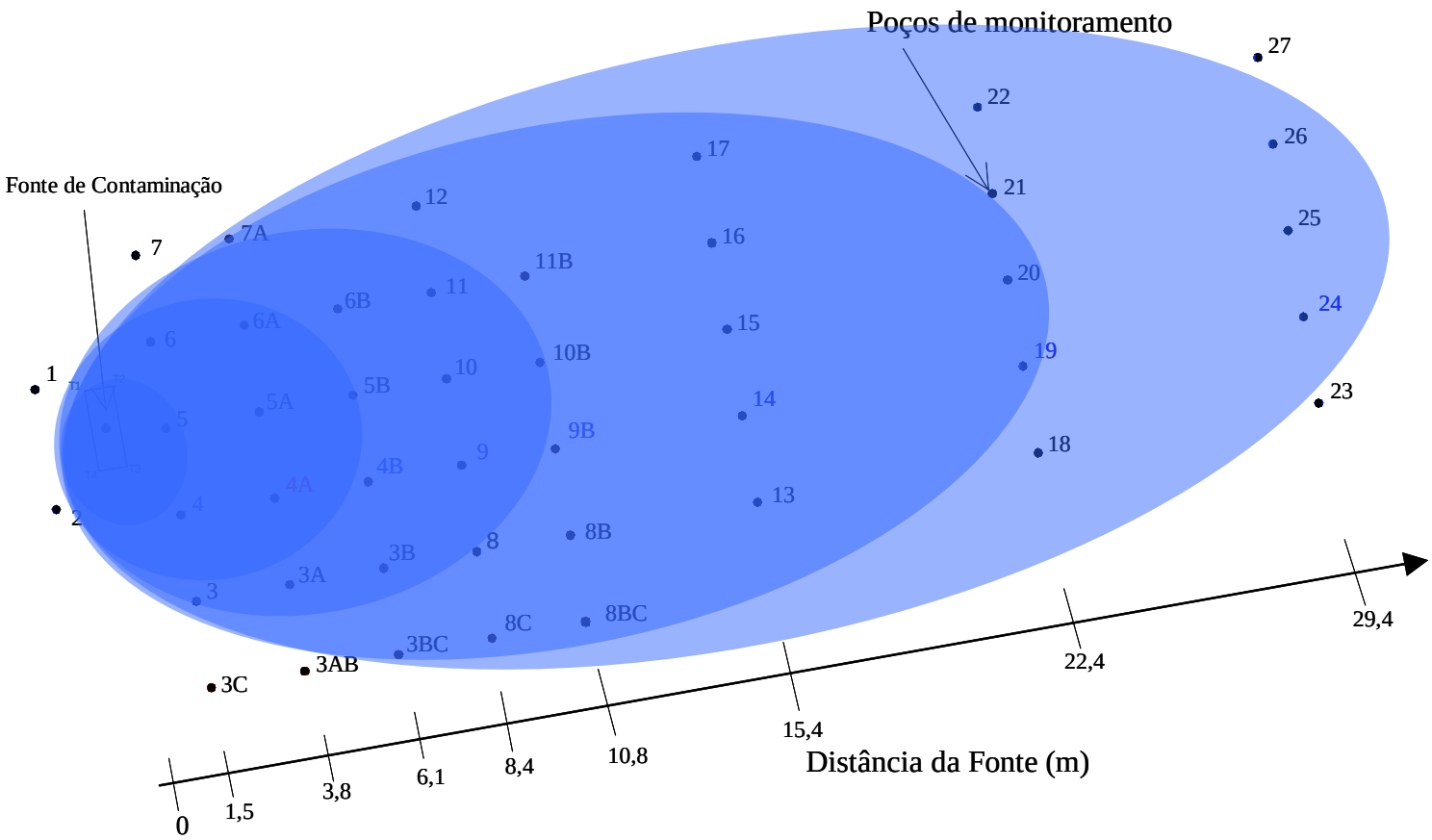
45 Monitoring Well Clusters

Sampling depths: 1; 2; 2.5; 3.5 & 4.5 m



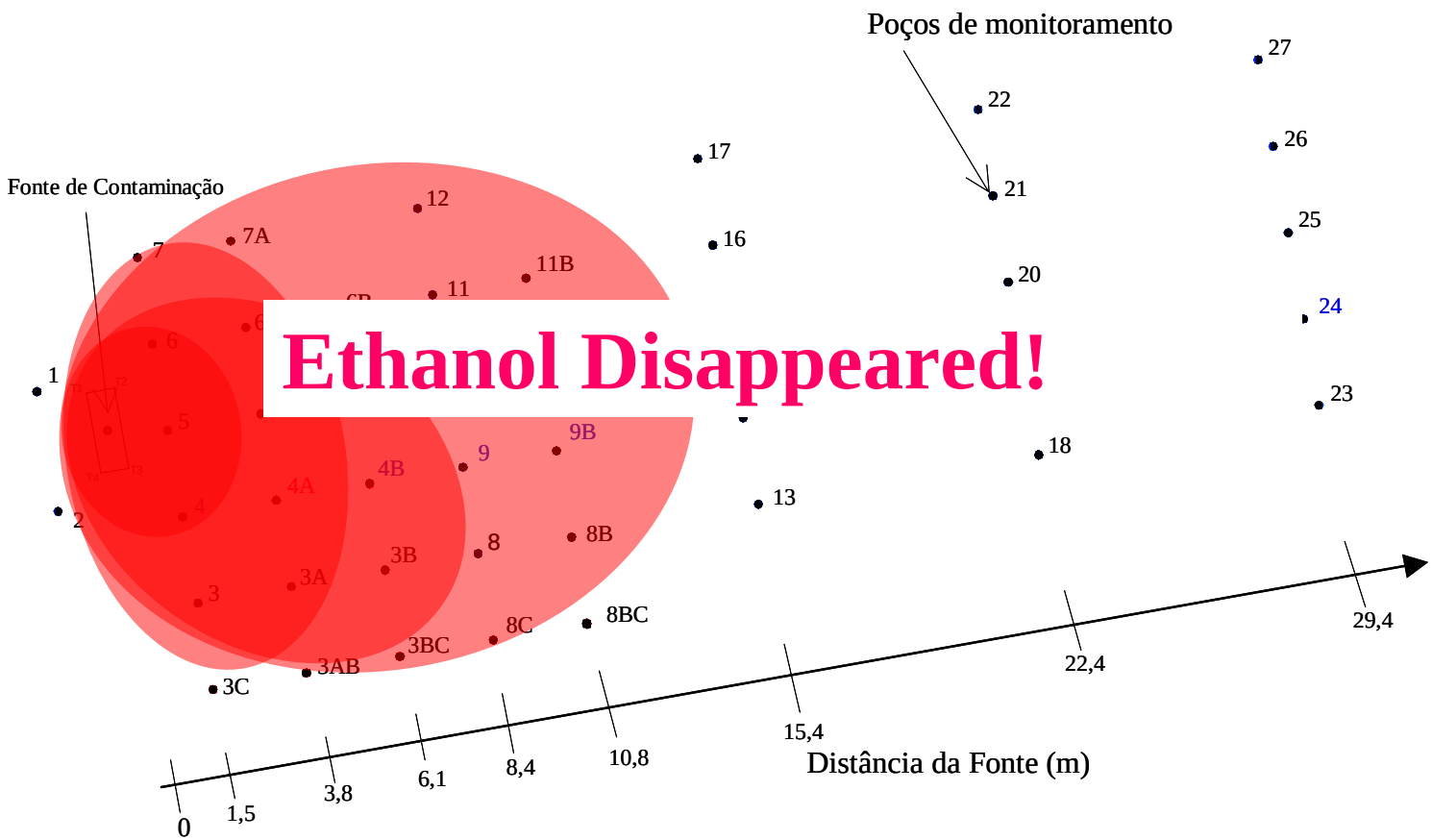
Migration of Bromide Tracer

Days: 980



Evolution of Etanol Plume

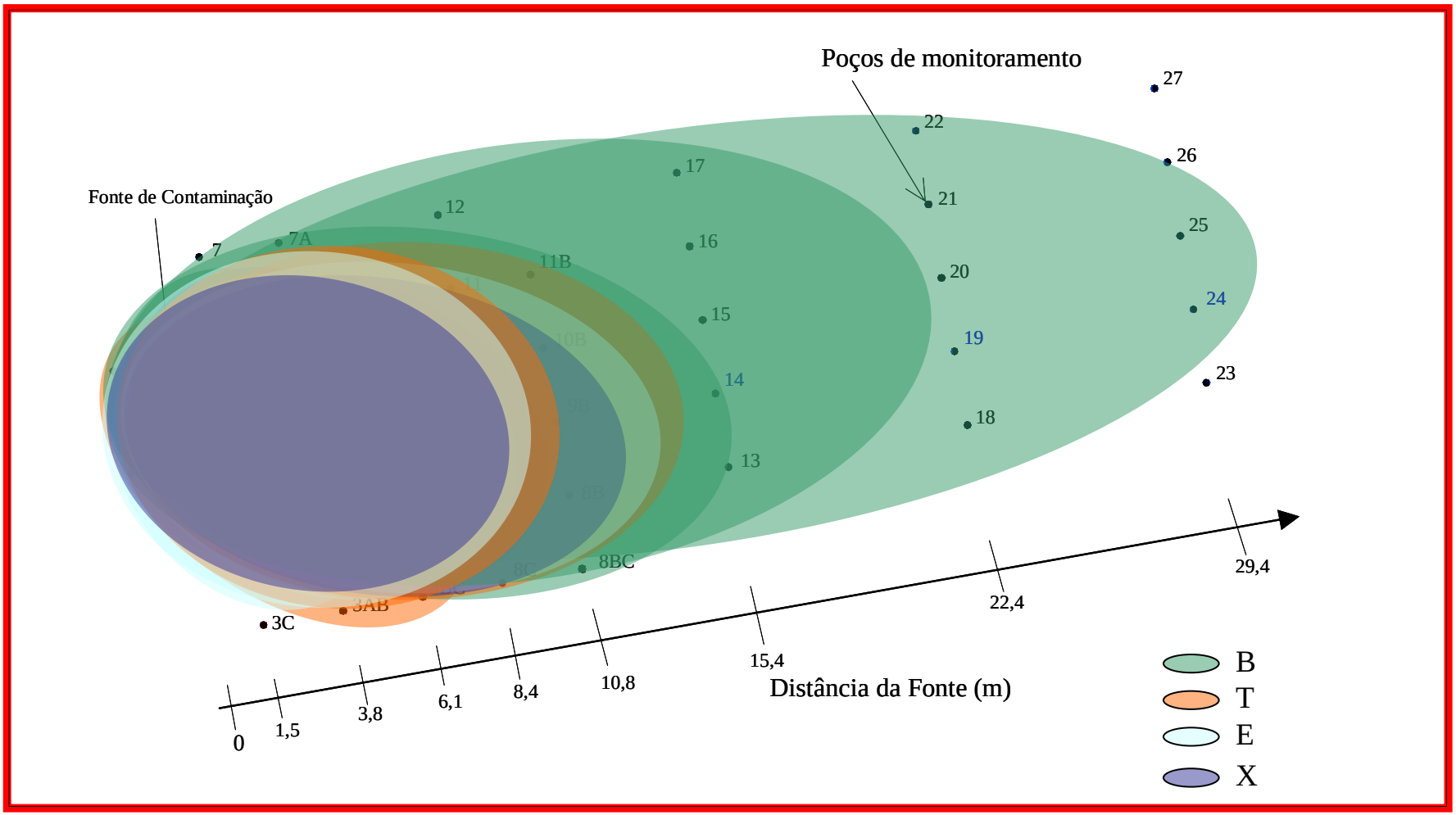
Days: 974




Maximum, extension of ethanol plume
15 m (2 years)
Disappeared in less than 3 years

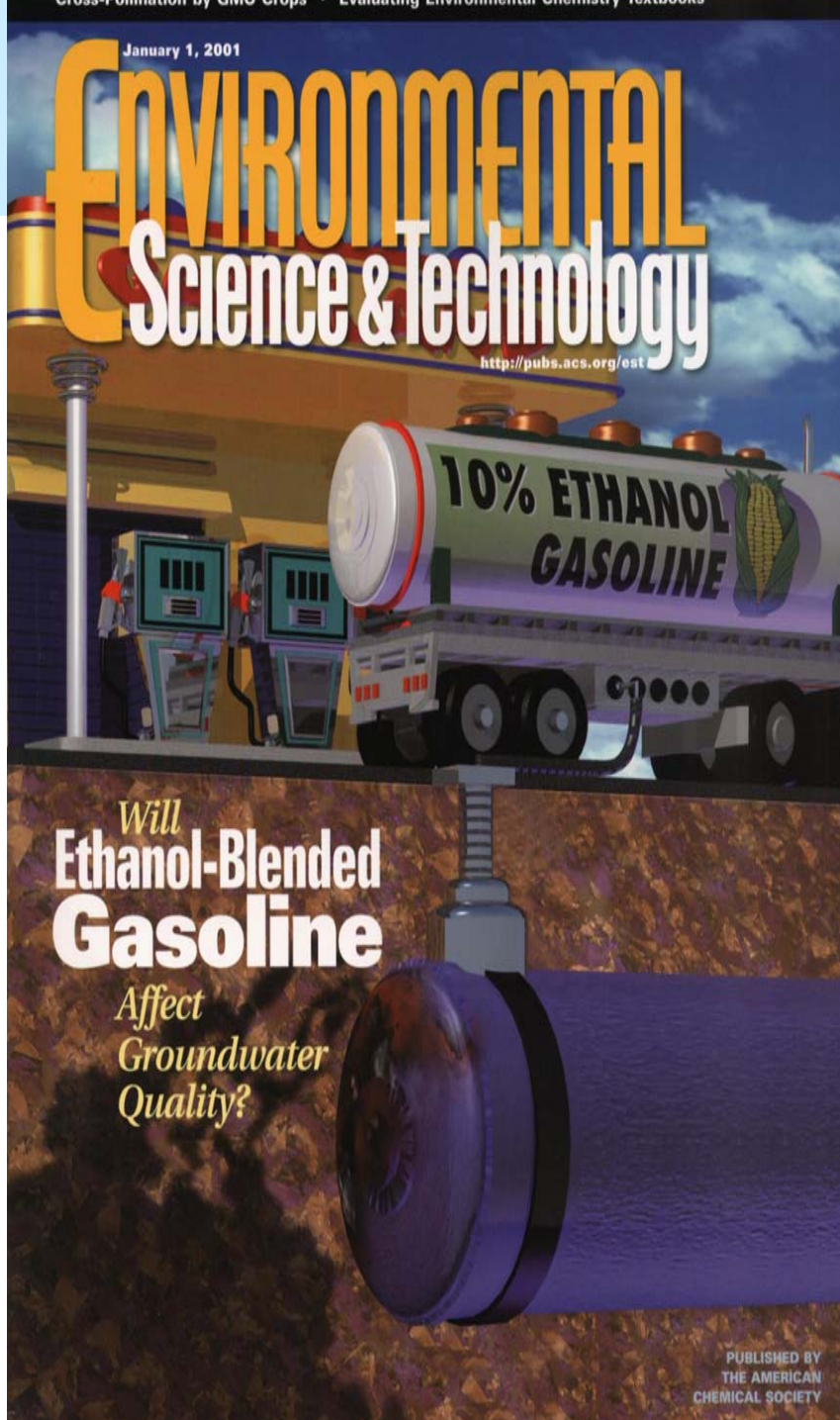
Evolution of BTEX Plume

Days: 1150



Conclusion

Ethanol can hinder the natural attenuation of benzene, 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.



Any Questions?

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

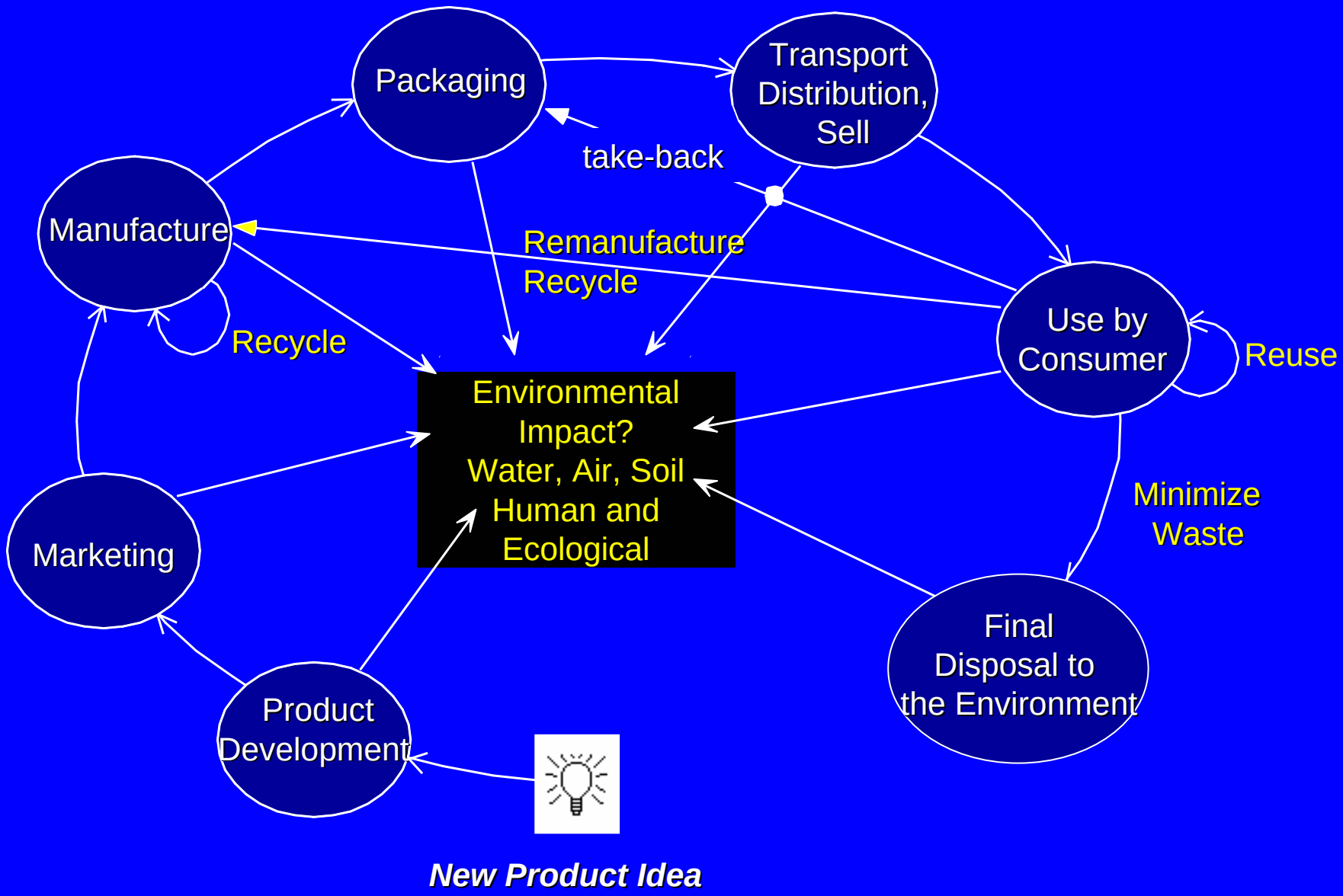
Plant-Based Fuels (biodiesel, EtOH, & H_2) Can Address Three National Interests

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

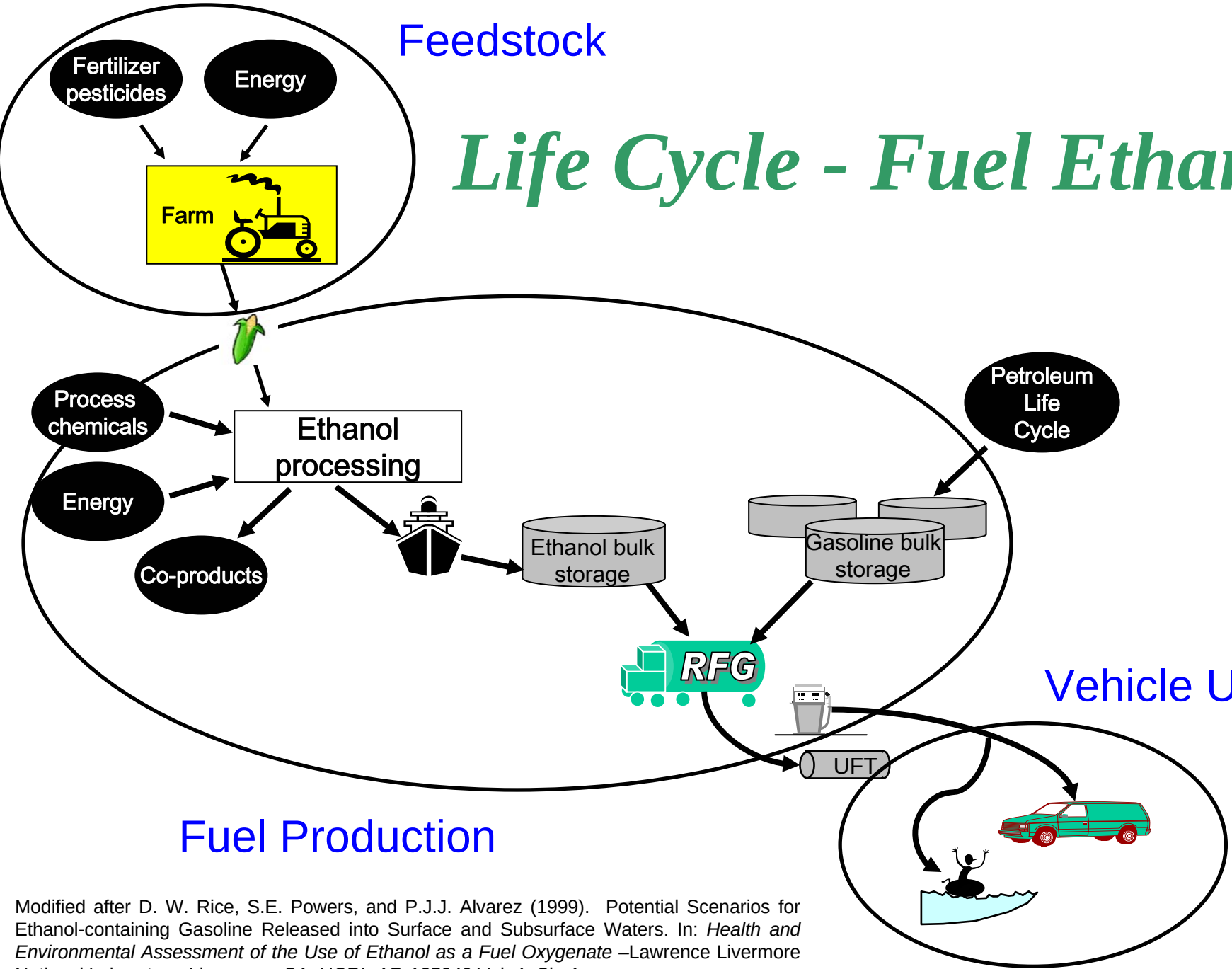
(2) Steer the impending growth of biomass-based industries to protect environmental quality, and

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

Life Cycle Assessment and Engineering Is Needed

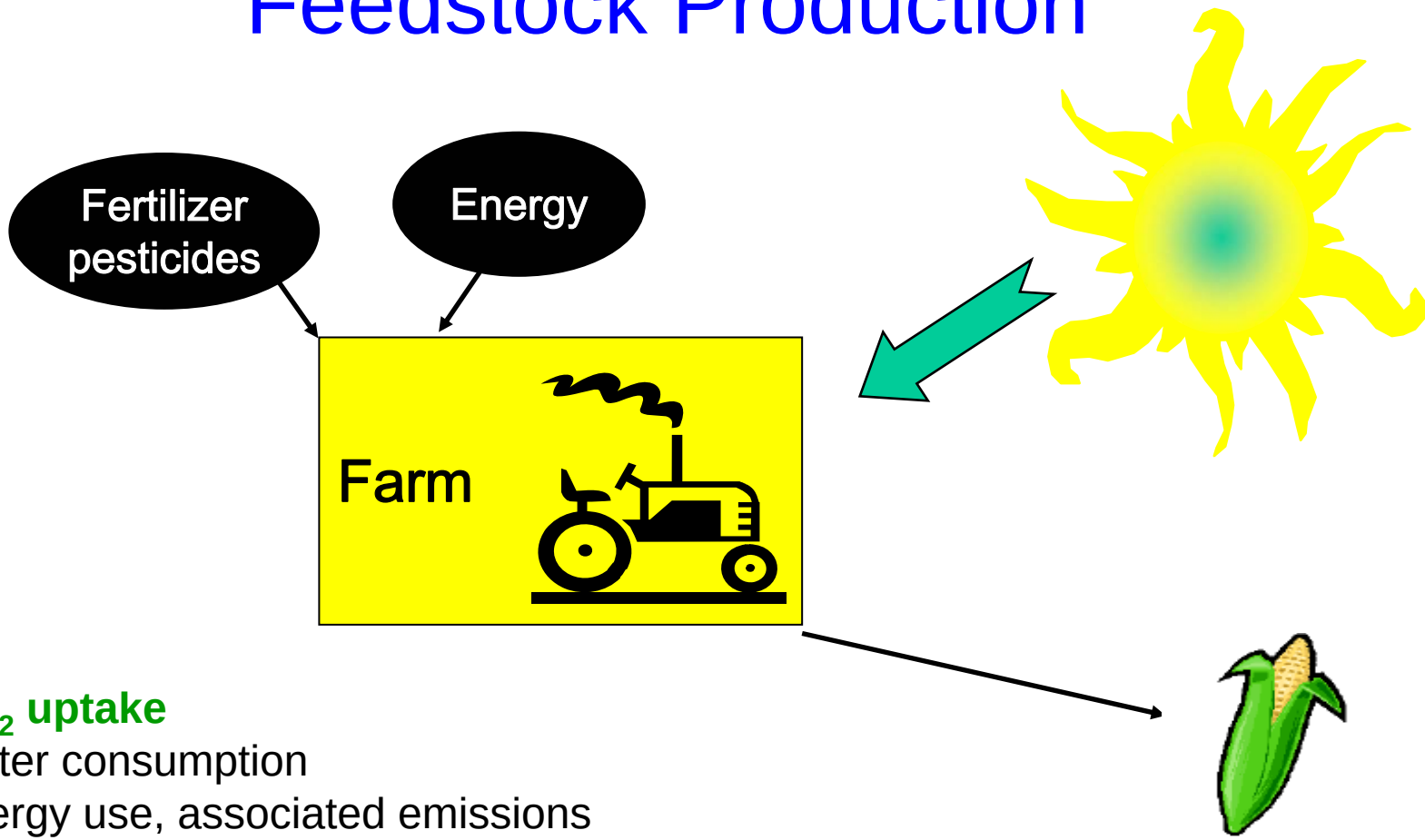


Life Cycle - Fuel Ethanol



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.

Feedstock Production



CO_2 uptake

Water consumption

Energy use, associated emissions

Land use

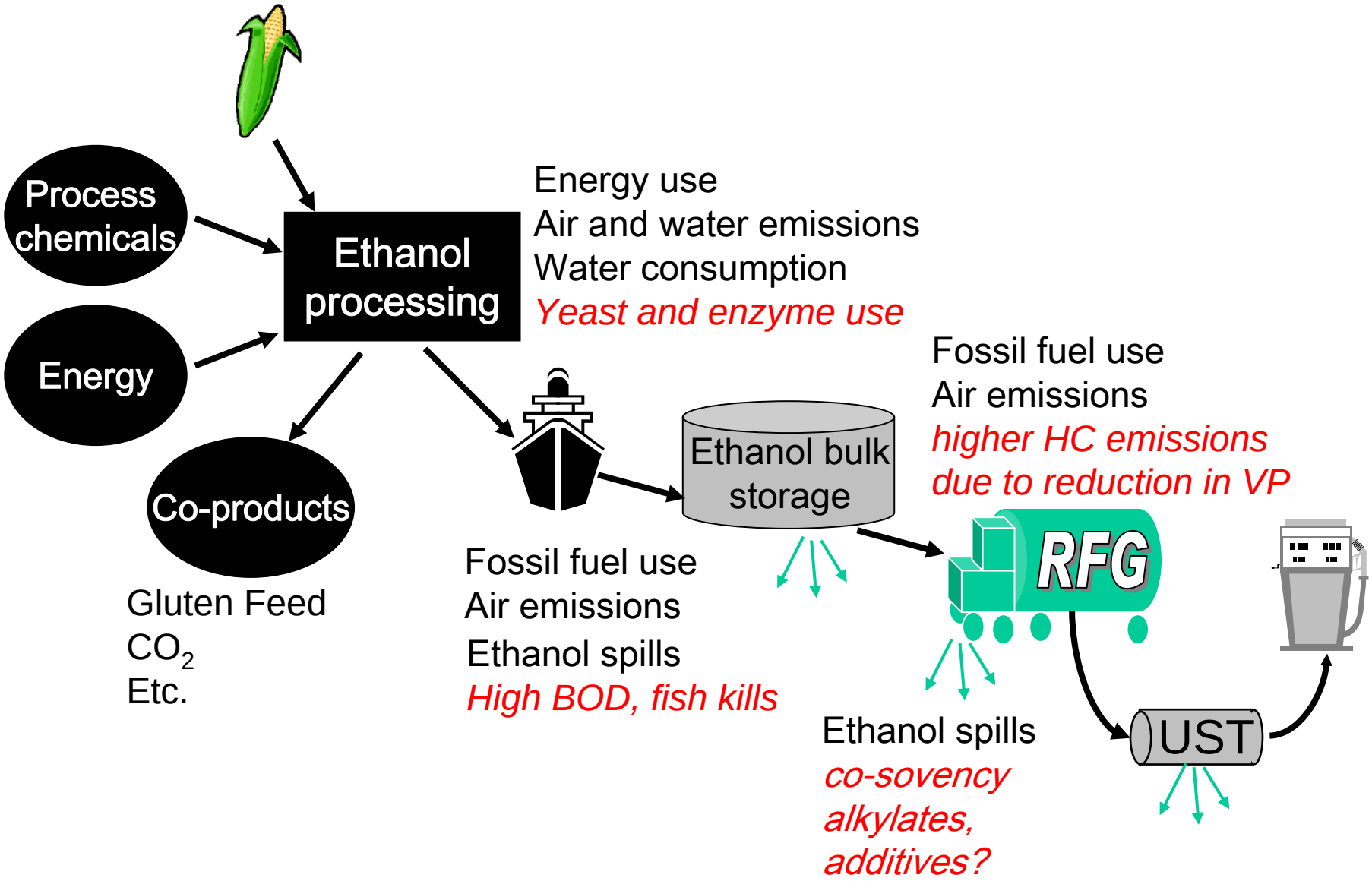
Fertilizer & pesticide use and associated soil/water contamination

Biodiversity and genetic drift issues if genetically engineered corn is used

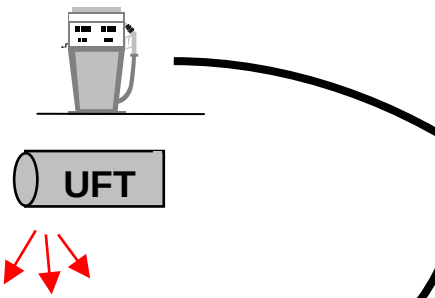
Erosion and Soil health

Food versus fuel?

Fuel Processing & Transportation



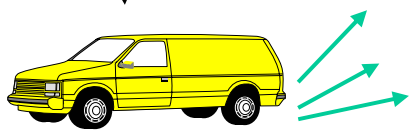
Vehicle Use



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?

Sustainable Biofuels: Research Needs

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

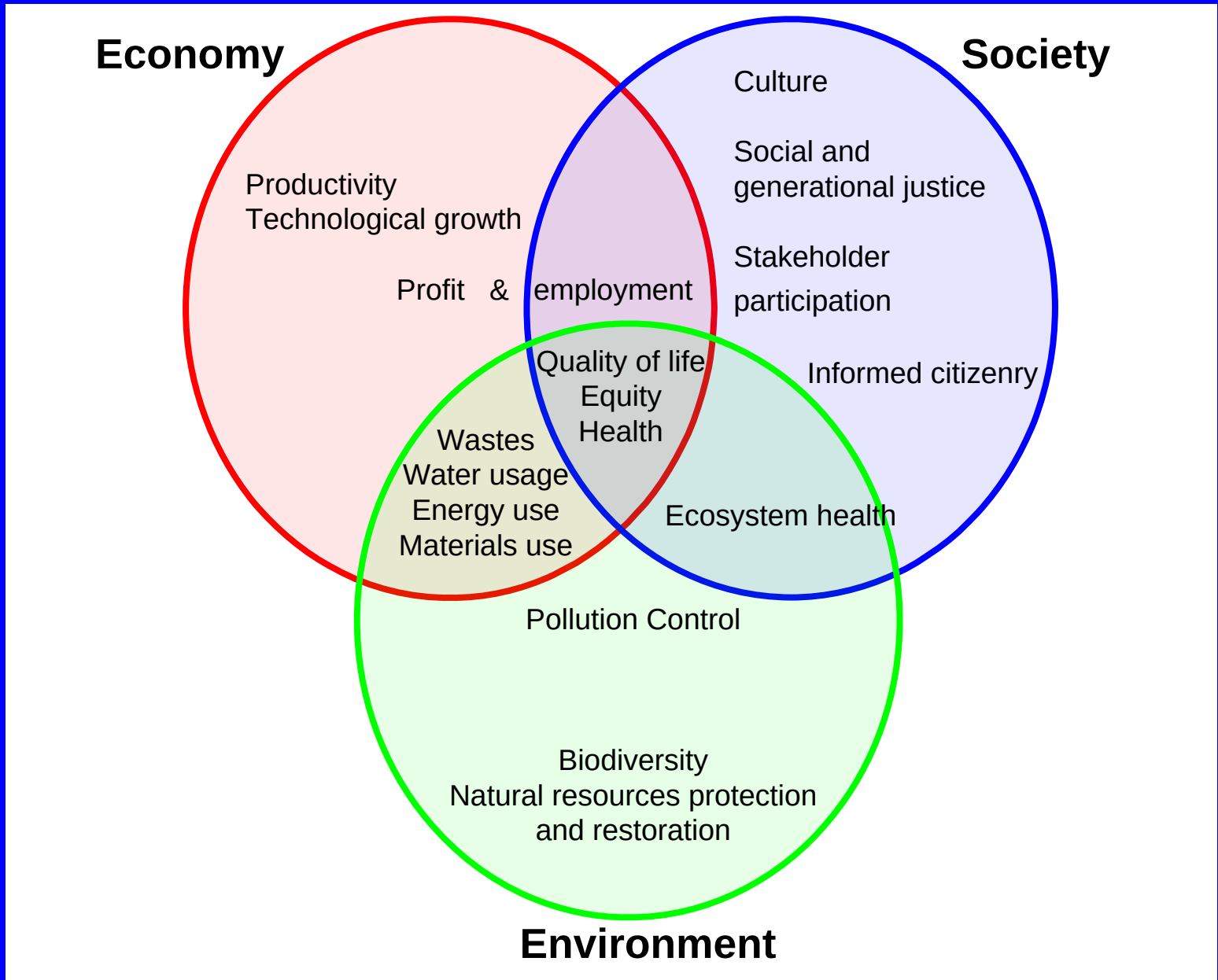
- Changes in urban air quality (+ or -)?
- Carbon balances (decarbonization, soil health and global climate implications)?
- Potentially problematic fuel components and impurities? (environmental analysis, ecotoxicology, fate and transport)
- Changes in land use, erosion, pesticide and fertilizer application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

Biofuel Research Needs (cont'd)

2. Enhance biofuels economic feasibility and environmental viability (e.g., biocatalysis, NEV, CO2 emissions trading)

- Control energy flows and increase net energy value (N_2 fixation)
- "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

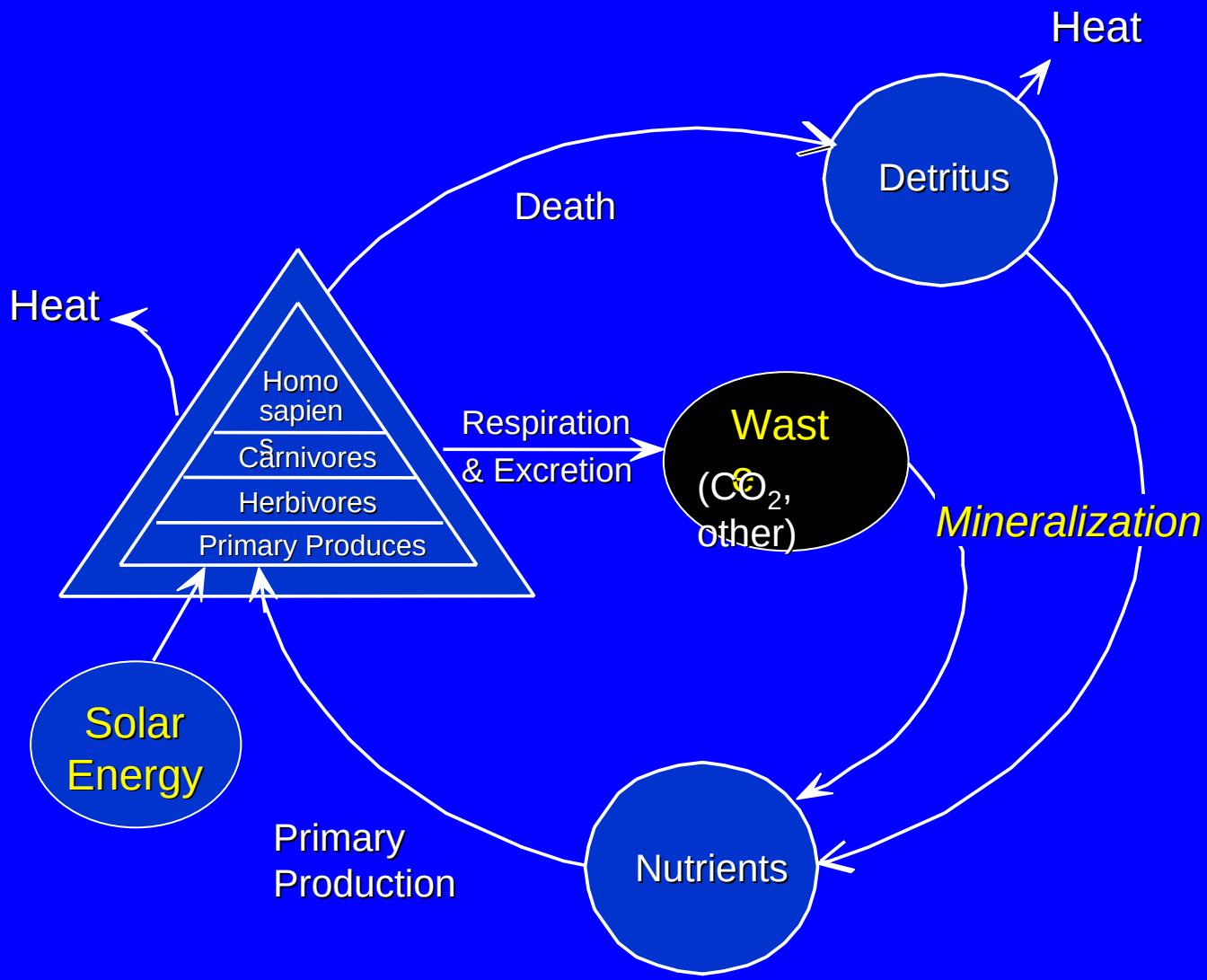
Sustainable ≠ Green



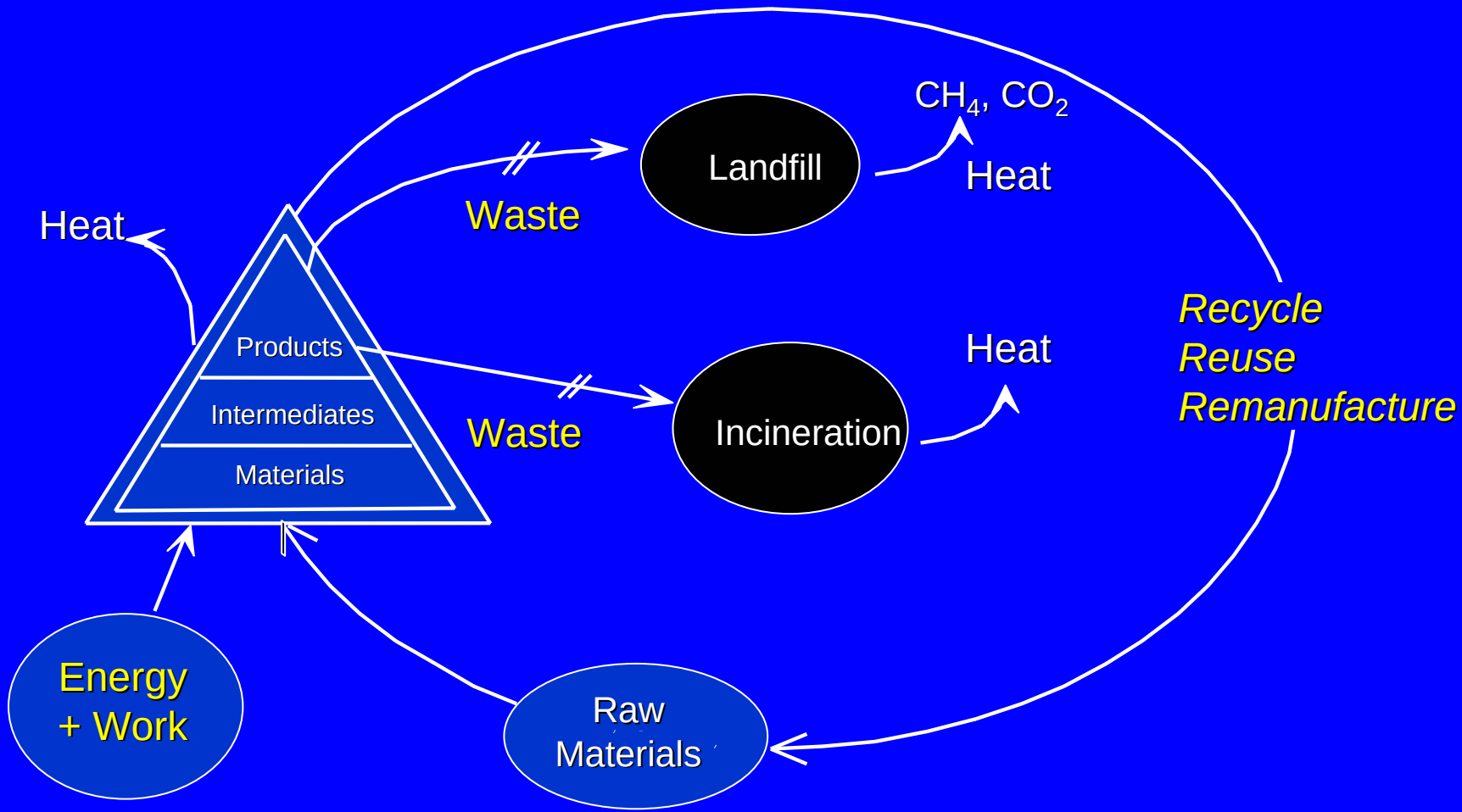
Industrial Ecology

- It is a multidisciplinary framework to design and operate industries as if they were living entities interacting with ecosystems.
- Seeks to attain a balance between economic gains and ecological and global interests.
- It is the science behind sustainable development.

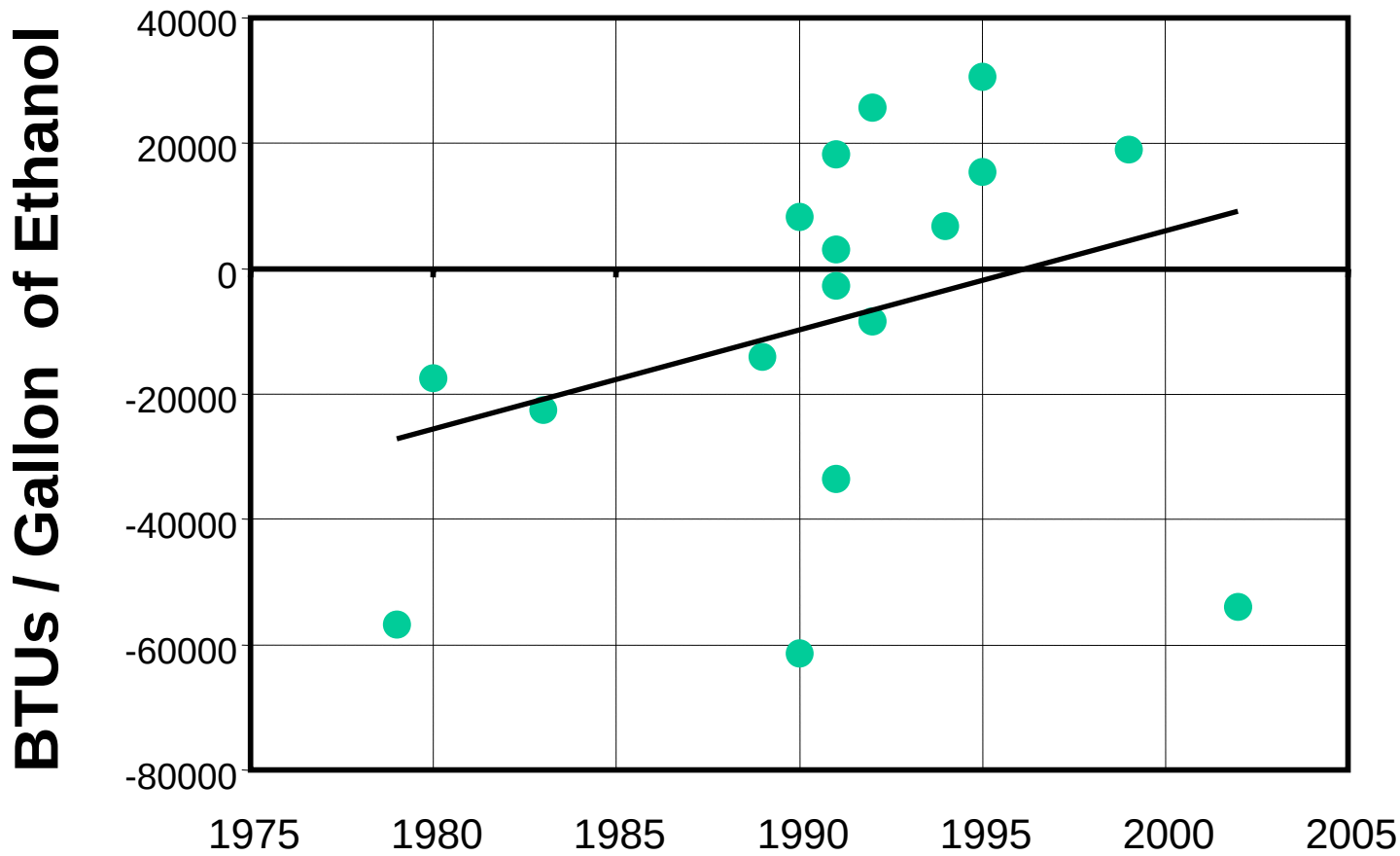
Natural Ecology



Industrial Ecology



Reported NEV Corn Ethanol



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)

Potential Environmental Impacts

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

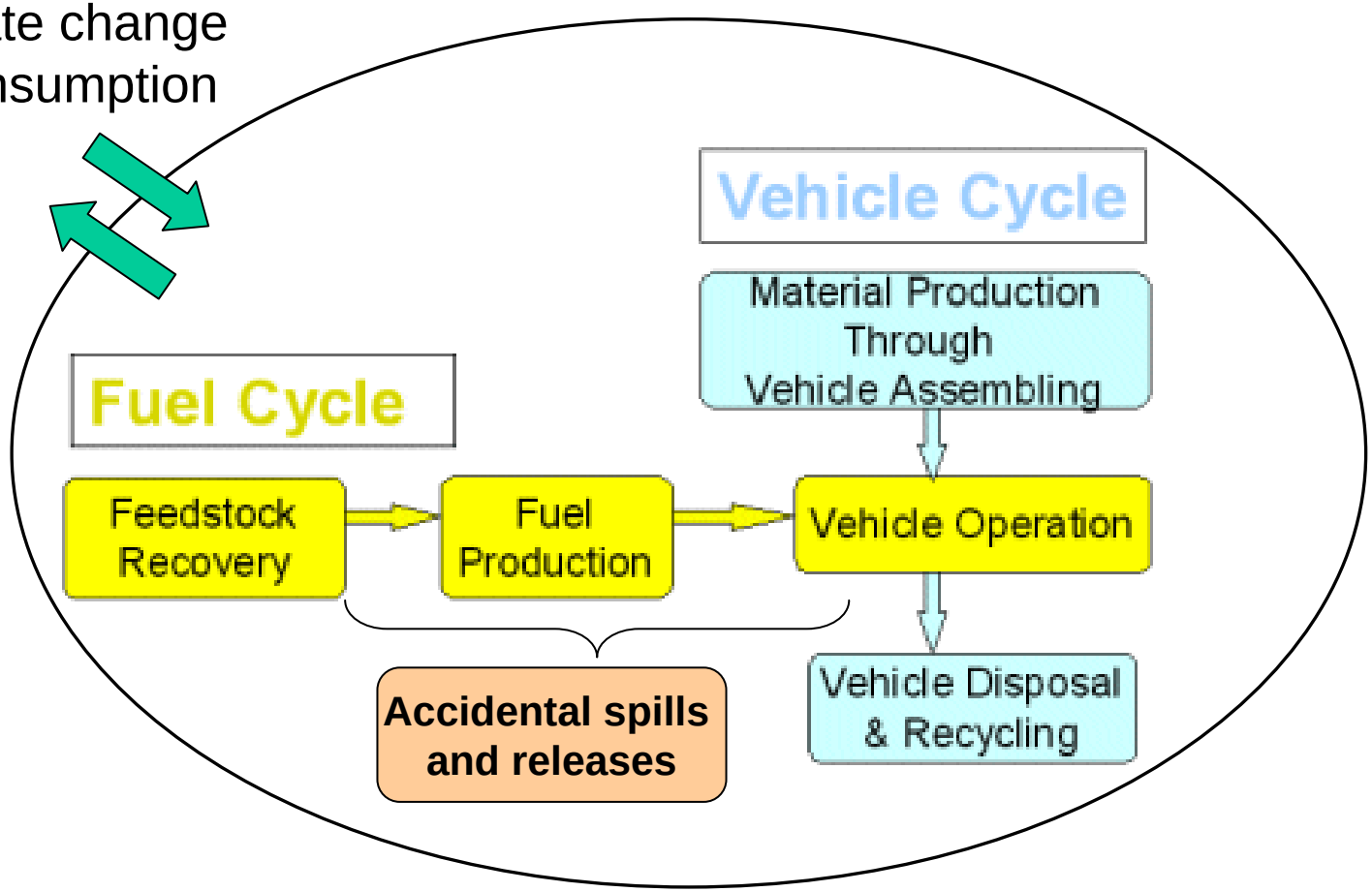
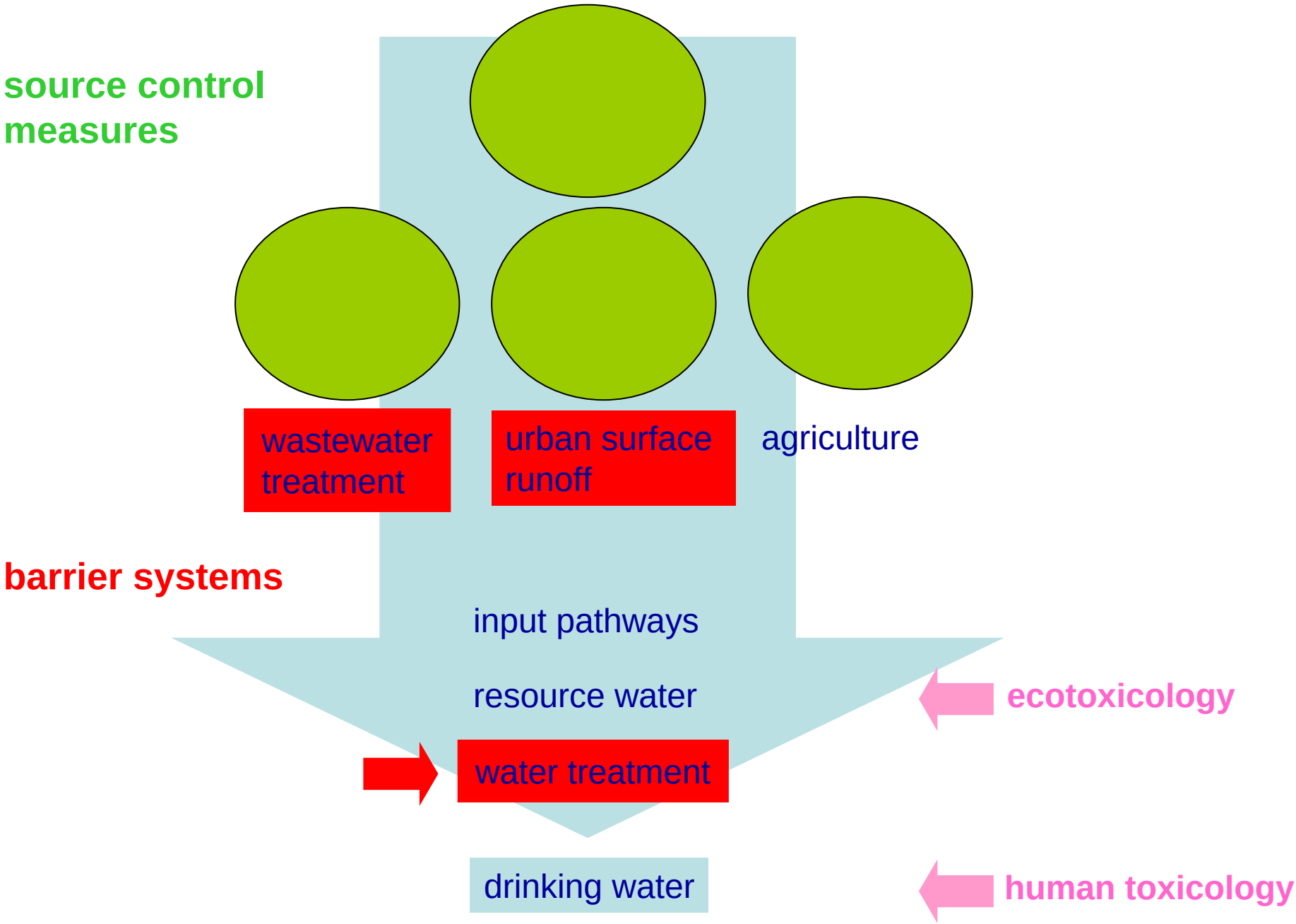
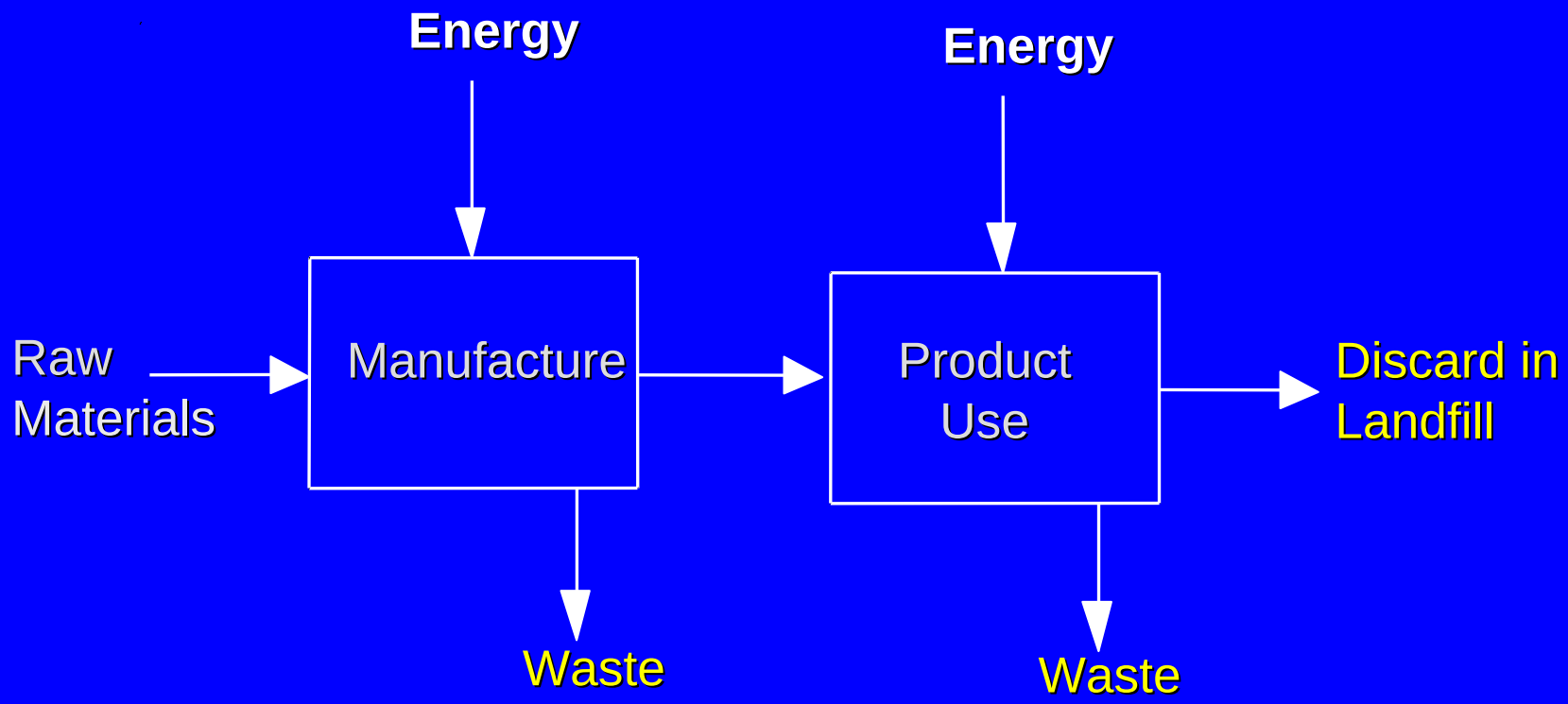


Figure adapted from GREET, Argonne Nat'l Lab

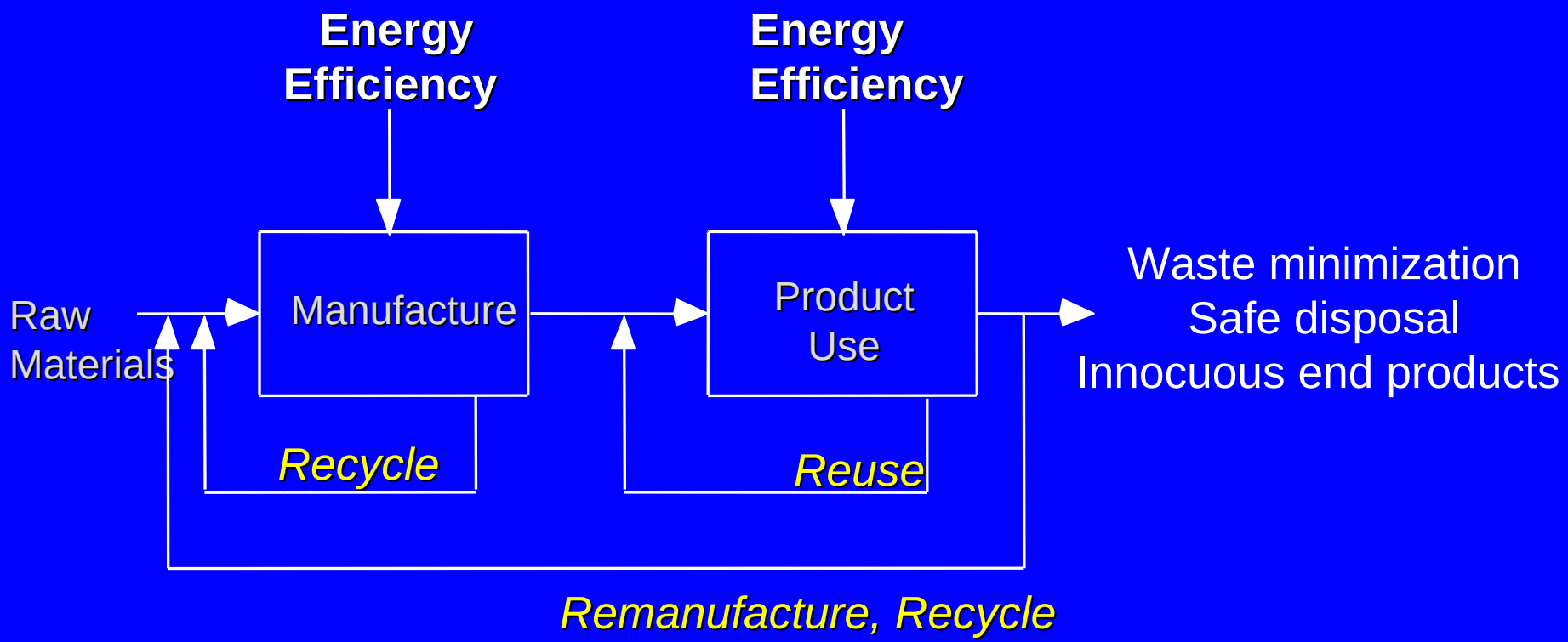
Future: from barrier systems to source control

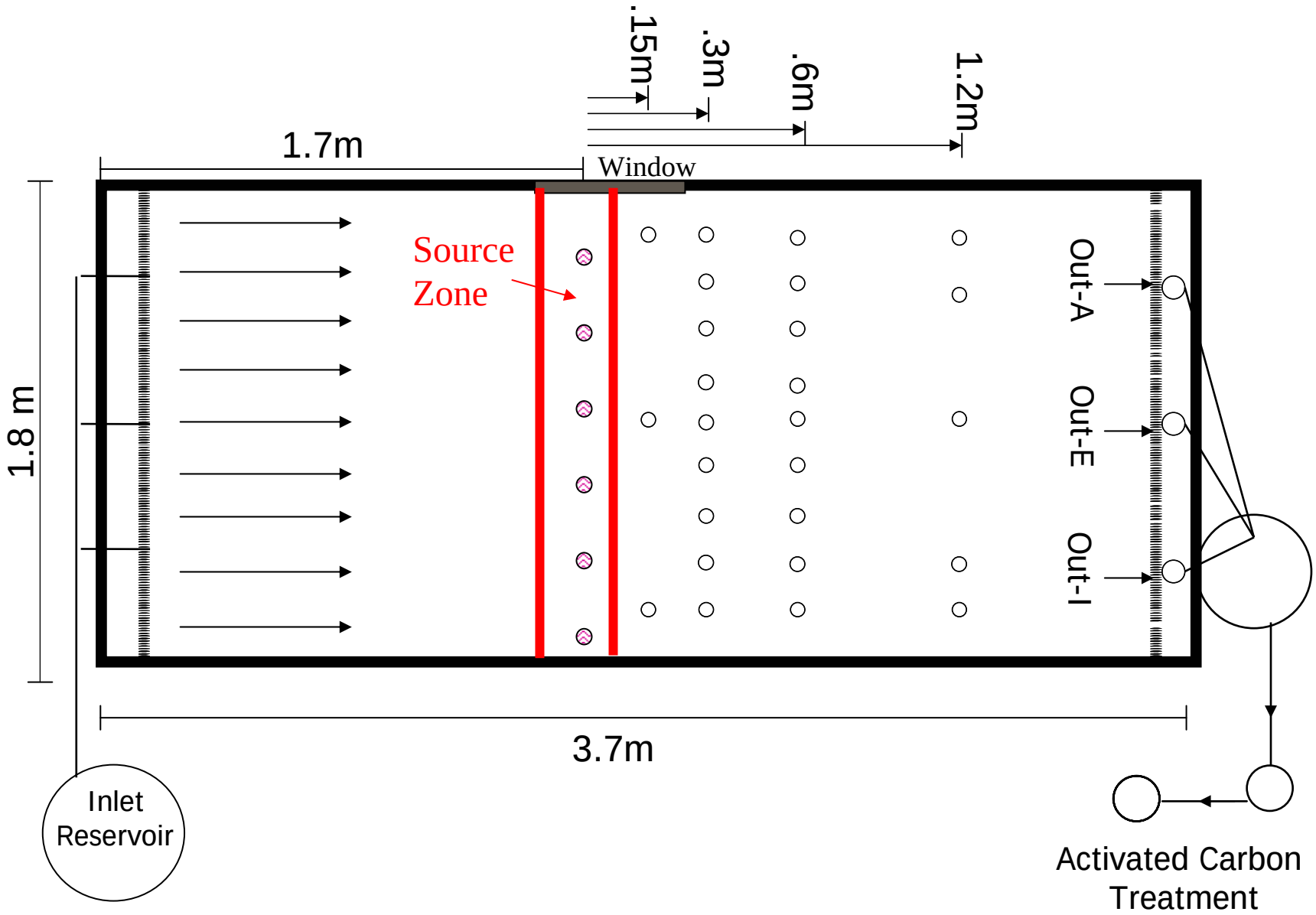


Conventional Design



Green Design



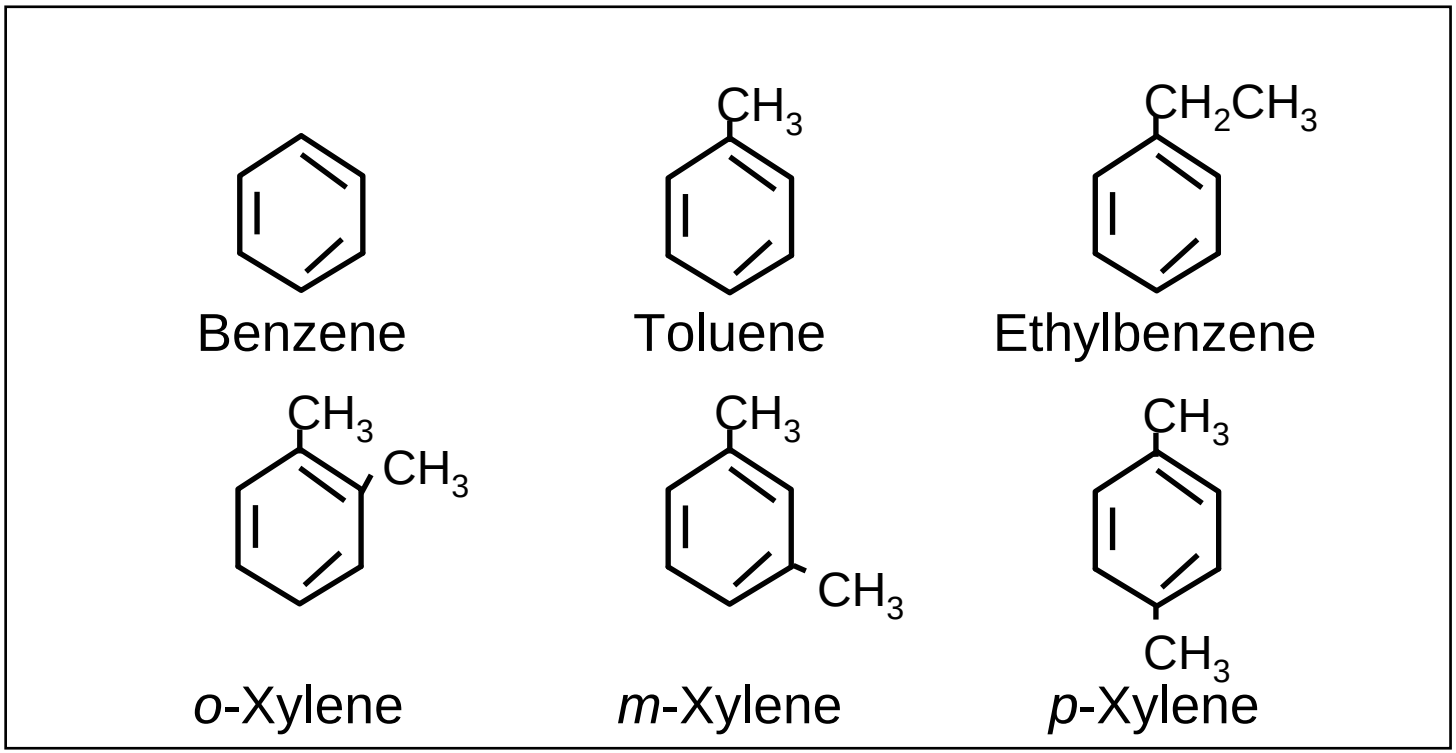


Plan View and Sampling Distribution

E95 Addition

- Six ¼ inch stainless steel injection wells at water table.
- 20-gallons of E95 was injected over a 3-h period.
- The 5% NAPL in E95 contained B (0.5%), T (5.7%), m-X (11.9%), OCT (52%) & TMB (29.9%).
- Plexiglas walls down to the water table on either side of the source wells to try contain spreading in vadose zone.

Contaminants of Concern: BTEX



- Benzene can cause leukemia (of most concern)