UCRL-ID-143717

Workshop on the Increased use of Ethanol and Alkylates in Automotive Fuels in California

D.W. Rice

May 4, 2001

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

DISCLAIMER

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (423) 576-8401
http://apollo.osti.gov/bridge/

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161
http://www.ntis.gov/

OR

Lawrence Livermore National Laboratory
Technical Information Department's Digital Library
http://www.llnl.gov/tid/Library.html

Workshop Welcome

Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California

Oakland, California
April 10 - 11, 2001

David W. Rice

Environmental Protection Department
Lawrence Livermore National Laboratory

Background

- Legislatively mandated University of California Study to evaluate impacts of MTBE.
- California Governor Davis issued Executive Order D-5-99 in March, 1999 calling for removal of MTBE from gasoline no later than December 31, 2002.
- The Executive Order required the Air Board, Water Board and Office of Environmental Health Hazard Assessment to prepare an analysis of potential impacts and health risks that may be associated with the use of ethanol as a fuel oxygenate.
- A copy of this report is included in your workshop package.
- Full report also available at: www-erd.llnl.gov/ethanol.

Background - Continued

- **11 States have passed legislation to ban or limit the use of MTBE.**
  - **Arizona, California, Colorado, Connecticut, Iowa, Maine, Michigan, Minnesota, Nebraska, New York, and S. Dakota**
- **California has asked for a waiver of the fuel oxygenate mandate.**
- **Bottom line:**
  - **The composition of gasoline will change.**
  - **There will likely be an increased use of both ethanol and alkylates in gasoline**

Background - Continued

? Conclusion presented to the California Environmental Policy Council:

— The water resource impacts associated with the use of ethanol will be significantly less and more manageable than those associated with the continued use of MTBE

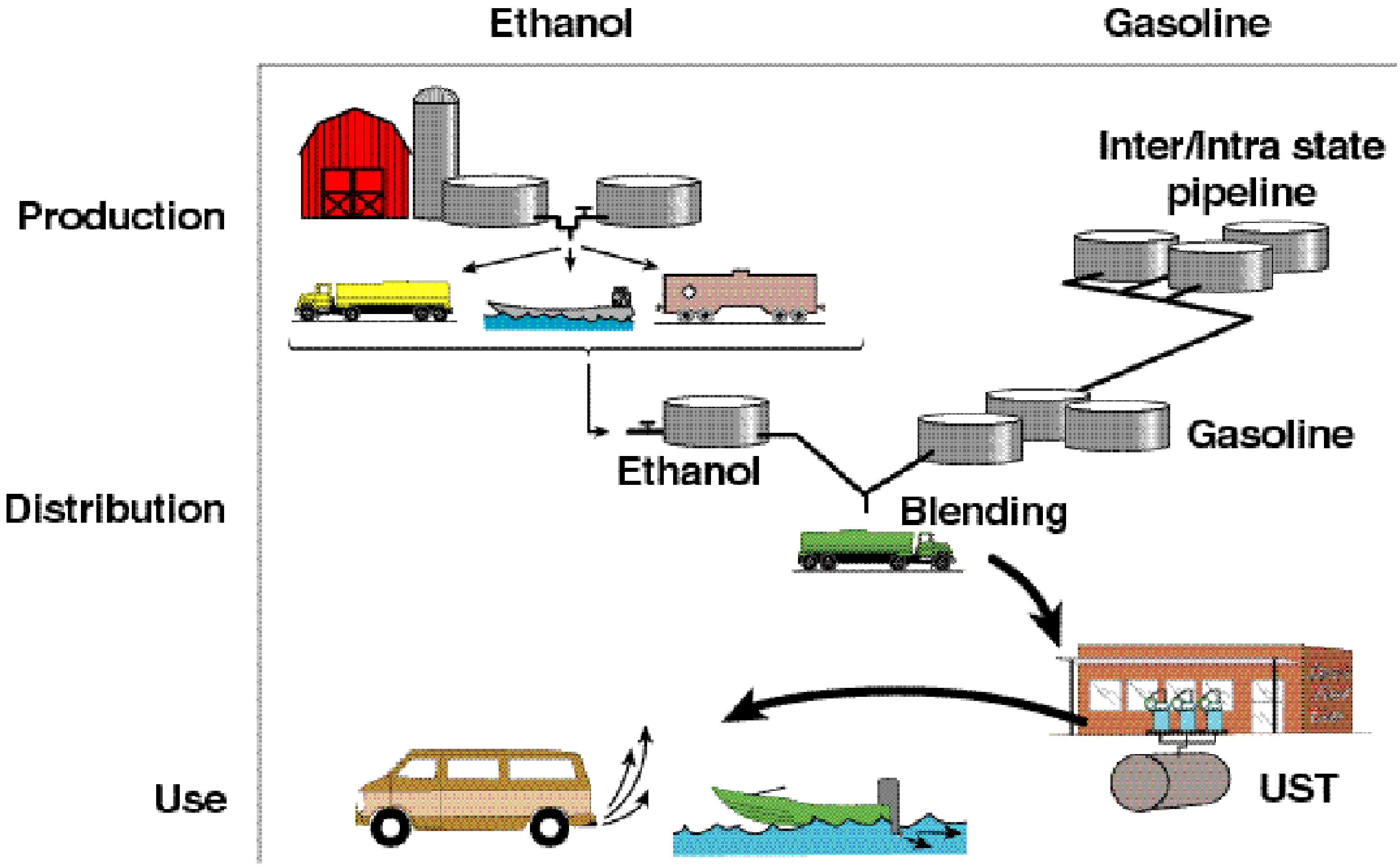
— The key factor is the biodegradability of ethanol compared to MTBE.

— A complete life cycle analysis that examines potential environmental trade-offs is needed for both ethanol and alkylates

Background - Continued

- ? This workshop follows up on commitment to the California Environmental Policy Council to continue to examine life cycle environmental and resource management consequences of the increased use of ethanol and alkylates in gasoline
- ? Release scenarios were developed based on the production, distribution, and use of ethanol as a fuel oxygenate.
  - — Not all release scenarios were evaluated.
- ? Need to evaluate the release scenarios for the production, distribution, and increased use of alkylates in gasoline.

Potential Ground and Surface Water Impacts – Ethanol Life Cycle



Goals of the Workshop

- Review the existing state of knowledge on
  - — physicochemical properties, multi-media transport and fate, exposure mechanisms
  - — release scenarios associated with the production, distribution, and use of ethanol and alkylates in gasoline.
- Identify key regulatory, environmental, and resource management issues and knowledge gaps associated with anticipated changes in gasoline formulation in California.
- Develop a roadmap for addressing issues/knowledge gaps

Workshop Attendees

- This is a workshop, not a conference,
  - We encourage your active participation
  - Discussions that occur during this workshop will provide valuable information to decision-makers who must plan and prepare the infrastructure changes needed to safely and cost-effectively provide transportation fuels without MTBE.
- Major interest groups attending the workshop
  - Fuels-related companies
  - Regulatory Agencies
  - Universities/National Laboratories

Welcome - Lets get started!

- David Rice, Workshop Director
- David Layton, Co-Workshop Director
- Cheryl Kuks, Workshop Coordinator
- Karen Pangelina, Co-workshop Director

Workshop on Ethanol and Alkylates in Fuels

Overview of

Office of Fuels Development

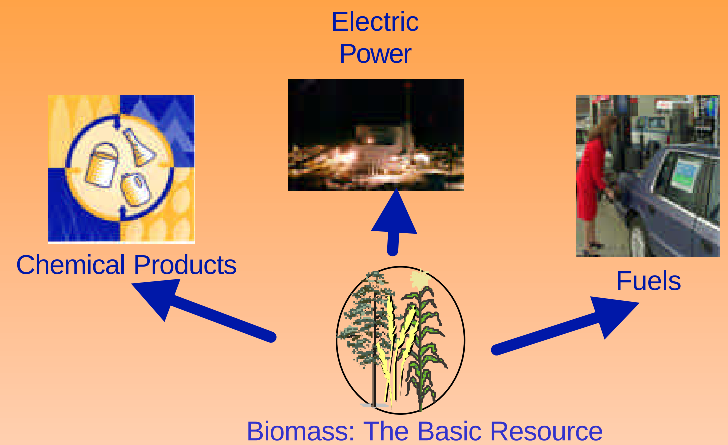
Energy Efficiency and Renewable Energy

April 2001

Tien Nguyen

Mission

Perform R&D to enable and support the establishment of a large integrated biomass-based bioenergy industry that supplies fuels, chemicals, and electricity



Foster new domestic jobs, and reduce carbon emissions and reliance on imported fuels

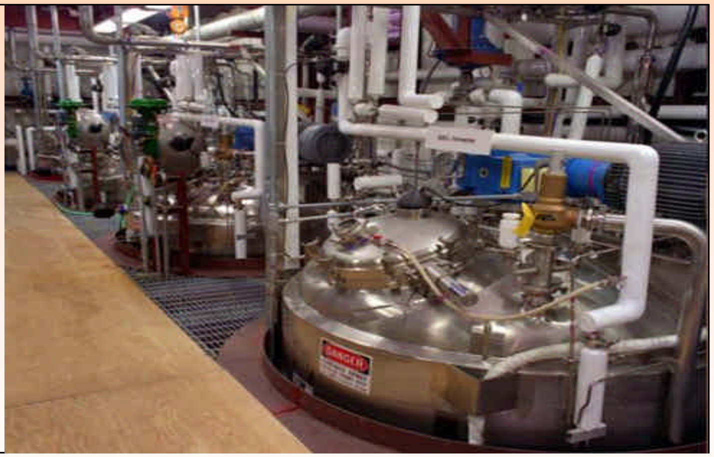
Scope

- **Program Areas ($40 Million per year total)**
  - **Biomass Feedstock Development**
  - **Biomass Conversion Technology R&D**
  - **Renewable Diesel Alternatives R&D**
  - **Regional Biomass Energy Program**
  - **Bioenergy Initiative**

Objectives

Feedstock Production
Develop cost competitive feedstock supply systems to support large-scale wide-spread production of fuels, chemicals, and power

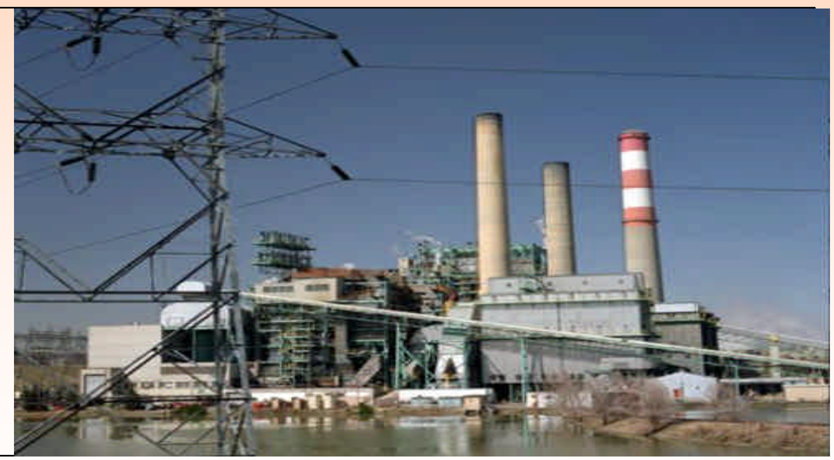
Biomass Conversion
Develop integrated bioengineering systems to increase conversion yields and reduce ethanol and chemicals production cost



Objectives (continued)

Renewable Diesel Alternatives
Support the development, testing, and deployment of diesel alternatives.

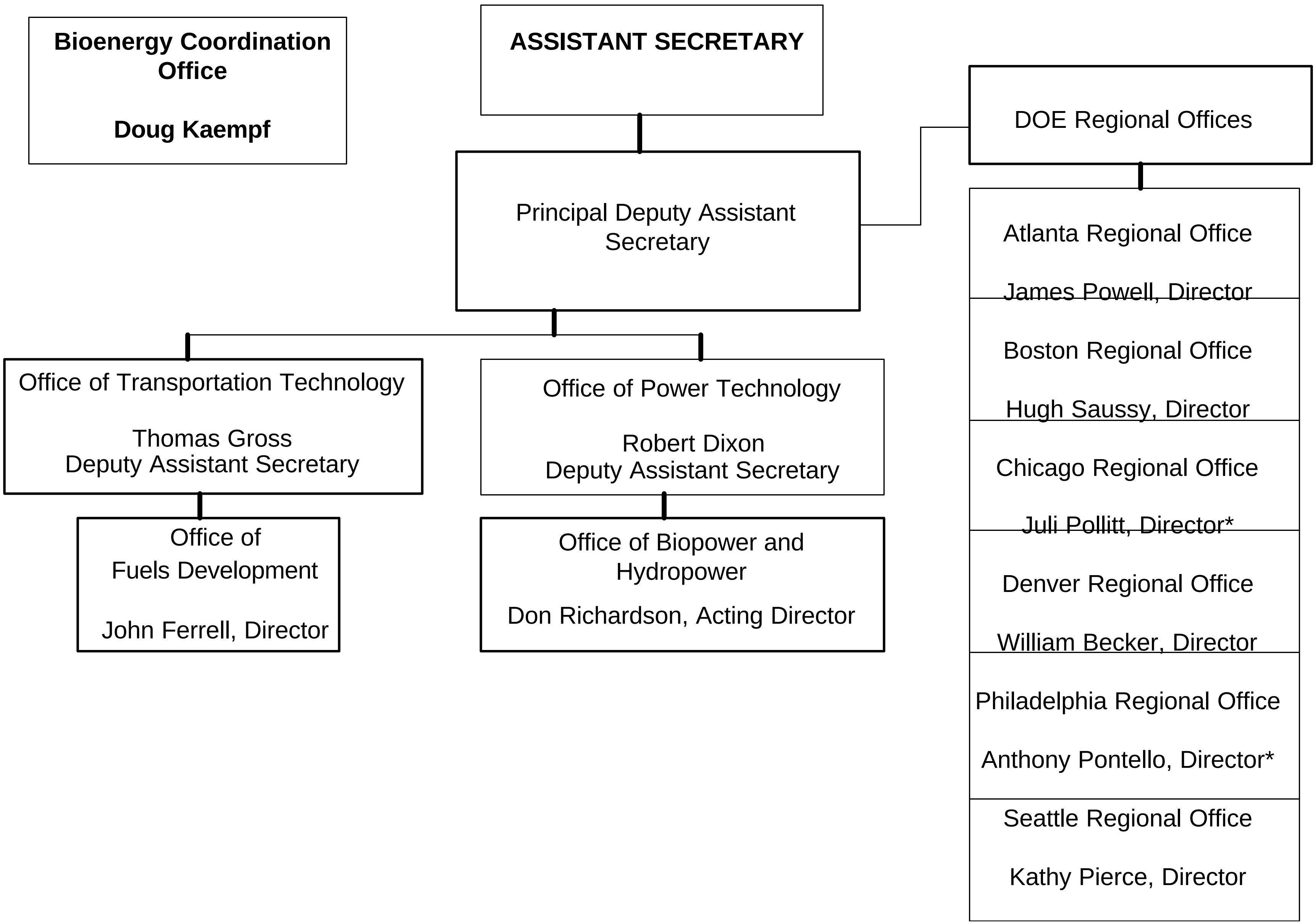
Regional Program
Foster the use of bioenergy alternatives through technology transfer and industry support at regional and state levels.



Strategic Approach

- Focus on ethanol production research, development and deployment as most promising option
- Partner with industry to build demonstration facilities
- Core research and development to reach program cost goals and proceed beyond first demonstration facilities

Office of Energy Efficiency and Renewable Energy



Implementation of California Phase 3 Reformulated Gasoline

Workshop on Ethanol & Alkylates in Fuels

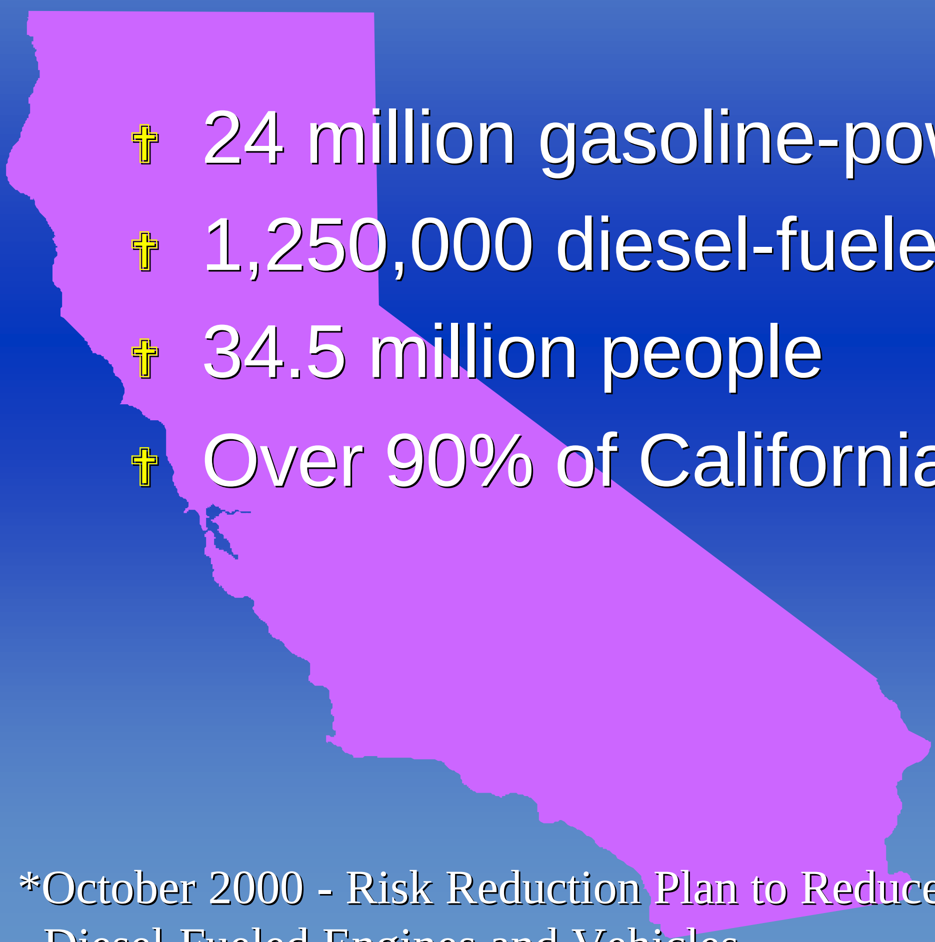
April 10, 2001

Dean Simeroth

California Environmental Protection Agency

Air Resources Board

California's Air Quality Problem



- 24 million gasoline-powered vehicles
- 1,250,000 diesel-fueled vehicles and engines*
- 34.5 million people
- Over 90% of Californians breath unhealthy air

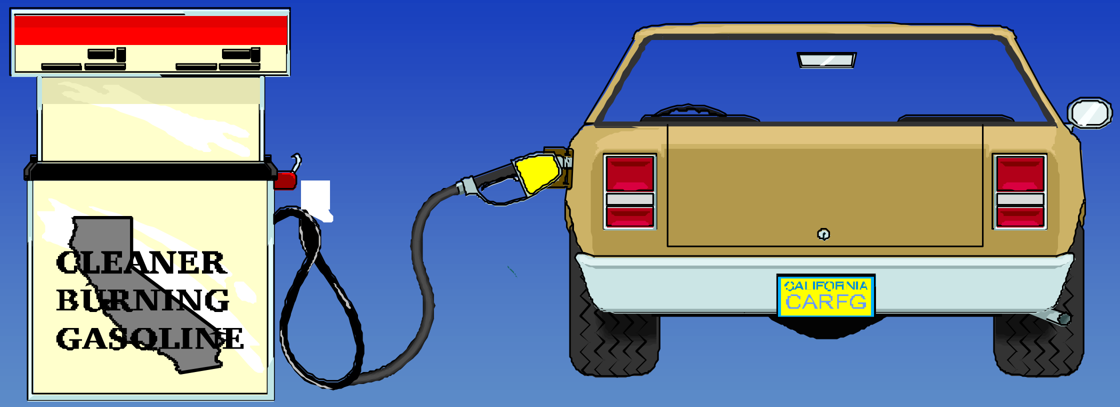
*October 2000 - Risk Reduction Plan to Reduce PM Emissions from Diesel-Fueled Engines and Vehicles

California Clean Air Act
Requirements for Mobile Sources

- Achieve maximum feasible reductions in PM, CO, and toxic air contaminants
- Achieve maximum emission reductions of VOC and NOx by earliest practicable date
- Adopt most effective combination of control measures on all classes of motor vehicles and their fuels

Motor Vehicle Fuels Control Strategy

- Treat vehicles / fuels as a system
  - Vehicle emission standards
  - Fuel standards
- Flexible



California's Vehicle Fuels Programs

Year Adopted	Gasoline	Diesel	Alternative Fuels
1971	Reid Vapor Pressure	-------	-------
	Bromine Number	-------	-------
1975	Sulfur	-------	-------
	Manganese/Phosphorus	-------	-------
1976	Lead	-------	-------
1981	-------	Sulfur (SCAB)	-------
1982	Lead	-------	-------
1988	-------	Sulfur/Arom. HC	-------
1990	Phase 1 RFG	-------	-------
	-------	-------	Clean Fuels/LEV
1991	Phase 2 RFG	-------	-------
	Wintertime Oxygenates	-------	-------
1992	-------	-------	Commercial and Certification Specs
1994	Phase 2 RFG Predictive Model	-------	-------
	-------	-------	LPG (amended)
1998	Combustion Chamber Deposits (amended)	-------	-------
	Wintertime Oxygenates (amended)	-------	-------
	-------	-------	LPG (amended)
1999	Wintertime Oxygenates (amended)	-------	-------
	-------	-------	Clean Fuels (amended)
2000	Phase 3 RFG(eliminates MTBE)		

Summary of Fuels Program Benefits

	Emissions Reductions (tpd)					
Program	HC	NOx	PM	SOx	CO	Toxics
Diesel (1993)	--	70	20	80	--	25%
CaRFG1 (1992)	210	--	--	--	--	--
CaRFG2 (1996)	190	110	--	30	1300	40%
CaRFG3 (2003)	0.5	19	--	4	--	7%
Total (tpd)	400	190	20	114	1300	na

California Phase 2 Gasoline (CaRFG2) Program

- Adopted in 1991
- Implemented March 1996

- Limits on the following parameters:

Sulfur	RVP (Summertime)
T50	Benzene
T90	Aromatic Hydrocarbons
Olefins	Oxygen Content

CaRFG2 Specifications

	Typical Before CaRFG2	Flat Limit Standard	Average Standard	Cap for All Gasoline
RVP, psi	7.8	7.0	-	7.0
Sulfur, ppmw	150	40	30	80
Aromatic HC, vol%	32	25	22	30
Benzene, vol%	2.0	1.0	0.8	1.2
Olefins, vol%	9.9	6.0	4.0	10.0
Oxygen, wt%	0	1.8-2.2	--	1.8[1]-2.7
T90, deg F	330	300	290[2]	330
T50, deg F	220	210	200	220

[1] **Wintertime only**
[2] **Refinery cap = 310 deg F**

Typical Properties[1] of CaRFG2

RVP, psi	6.8
Sulfur, ppmw	22
Aromatic HC, vol%	23
Benzene, vol%	0.6
Olefins, vol%	4.5
Oxygen, wt%	2.0
T90, deg F	310
T50, deg F	201

[1] **Based on 1999 CEC ARB survey of California refiner's summertime fuel**

Compliance Options

- Meet “flat” limit standards
- Meet “average” limit standards
- Produce formulation certified as equivalent through:
  - Emissions testing
  - Predictive model (flat or average limits)

- Essentially all California reformulated gasoline is now being marketed using the Predictive Model

Benefits of CaRFG2

- Emission reductions equivalent to removing 3.5 million vehicles from region's roads
- Reduces smog forming emissions from motor vehicles by 15%
- Reduces potential cancer risk from vehicle emissions by 40%
- 1/4 of SIP reductions in 1996
- Reduces benzene emissions by half

Federal Reformulated Gasoline (RFG) Program

- Required by 1990 CAAA in severe and extreme ozone non-attainment areas
- Minimum oxygen requirement of 2.0 weight percent
- Performance based fuel standards
- Phase 1 federal RFG
  - Required as of January 1, 1995
- Phase 2 federal RFG
  - Required January 1, 2000
- Sulfur reduced to an average of 30 ppm in 2004

The Governor Directed the Use of MTBE to Be Phased Out of Gasoline

- Based on study by University of California, and public hearings Governor found:
  - MTBE in small amounts presents threat to groundwater, surface water, and drinking water
    - Underground gasoline storage tanks are not leak proof
    - MTBE is highly soluble in water and transfers to groundwater faster than other constituents in gasoline
  - MTBE potential but not proven health problem
  - MTBE not essential to cleaner-burning gasoline

Governor's Executive Order

- Directed that the use of MTBE be phased out by December 31, 2002
- Adopt CaRFG regulations to:
  - Provide additional flexibility in removing oxygen
  - Preserve benefits
- Directs ARB to request waiver from Federal Oxygen Requirement from U.S. EPA

State Legislation

- Senate Bill 989 (Sher)
  - Ensure the CaRFG3 regulations maintain or improve upon emissions and air quality benefits
- Senate Bill 529 (Bowen)
  - Multi-media review of revisions to ARB's CaRFG standards

Air Resources Board Took Action to Implement the Governor's Directive to Phase Out MTBE

- In 1999, the ARB amended California's gasoline regulations to phase out the use of MTBE by December 31, 2002

CaRFG3 Regulations

- Approved on December 9, 1999
- Implemented the Governor's Executive Order
- Meets requirements of the Sher Bill and the Bowen Bill
- Removes MTBE from California gasoline December 31, 2002
- Provides additional flexibility to remove MTBE
- Enhances emission benefits of current program
- Accommodates need for imports on routine basis
- Additional follow-up needed
- Flexible

Approved CaRFG3 Specifications Compared to CaRFG2

Property	Flat Limits		Cap Limits	
	Current	Approved	Current	Approved
RVP, psi	7.0	7.0(1)	7.0	6.4-7.2
Benzene, vol%	1.00	0.80	1.20	1.10
Sulfur, ppmw	40	20	80	60/30(2)
Aromatic HC, vol%	25	same	30	35
Olefins, vol. %	6.0	same	10	same
Oxygen, wt. %	1.8 to 2.2	same	0-3.5	0-3.7(3)
T50 ^{o}F	210	213	220	220
T90 ^{o}F	300	305	330	330

1) Equal to 6.9 psi. if using the evaporative element of the Predictive Model

2) 60 ppmw. will apply December 31, 2002; 30 ppmw. will apply December 31, 2004

3) Allow 3.7 for gasoline containing no more than 10 volume percent ethanol

CaRFG3 Program Preserves Emissions Benefits

- CaRFG3 designed to eliminate the use of MTBE while providing refiner flexibility, preserving the existing air quality benefits of the CaRFG2 program
- The CaRFG3 specifications result in no greater emissions of hydrocarbons, NOx and potency-weighted toxics than the CaRFG2 specifications

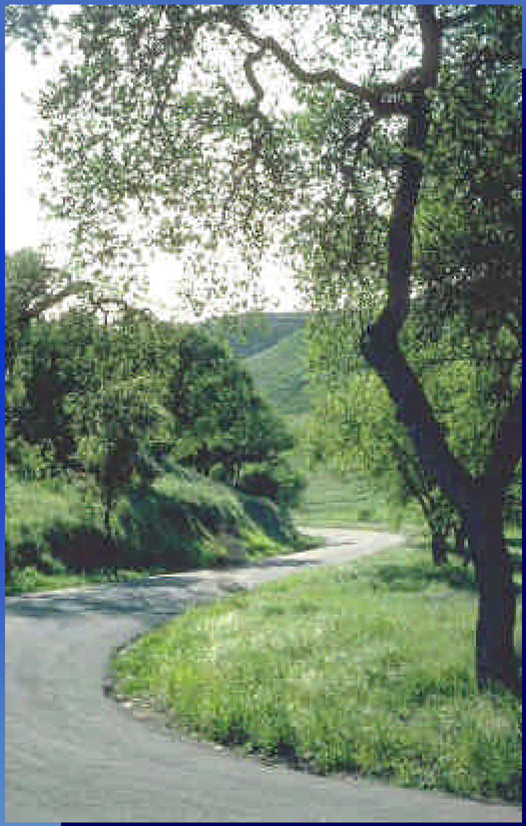
Expected Changes to Gasoline

- No MTBE
- Increased use of ethanol
- Increased use of alkylate blending components
- Less benzene
- Lower sulfur content
- Blending components similar to today's

Environmental Impacts of CaRFG3

- MTBE contamination of water resources will be limited to pre-existing MTBE contamination prior to implementation of CaRFG3
- Less benzene contamination of surface and ground water
- No net increase in greenhouse gas emissions
- Decreases in NOx, potency weighted toxics and equivalency on hydrocarbon emissions

Environmental Policy Council Findings

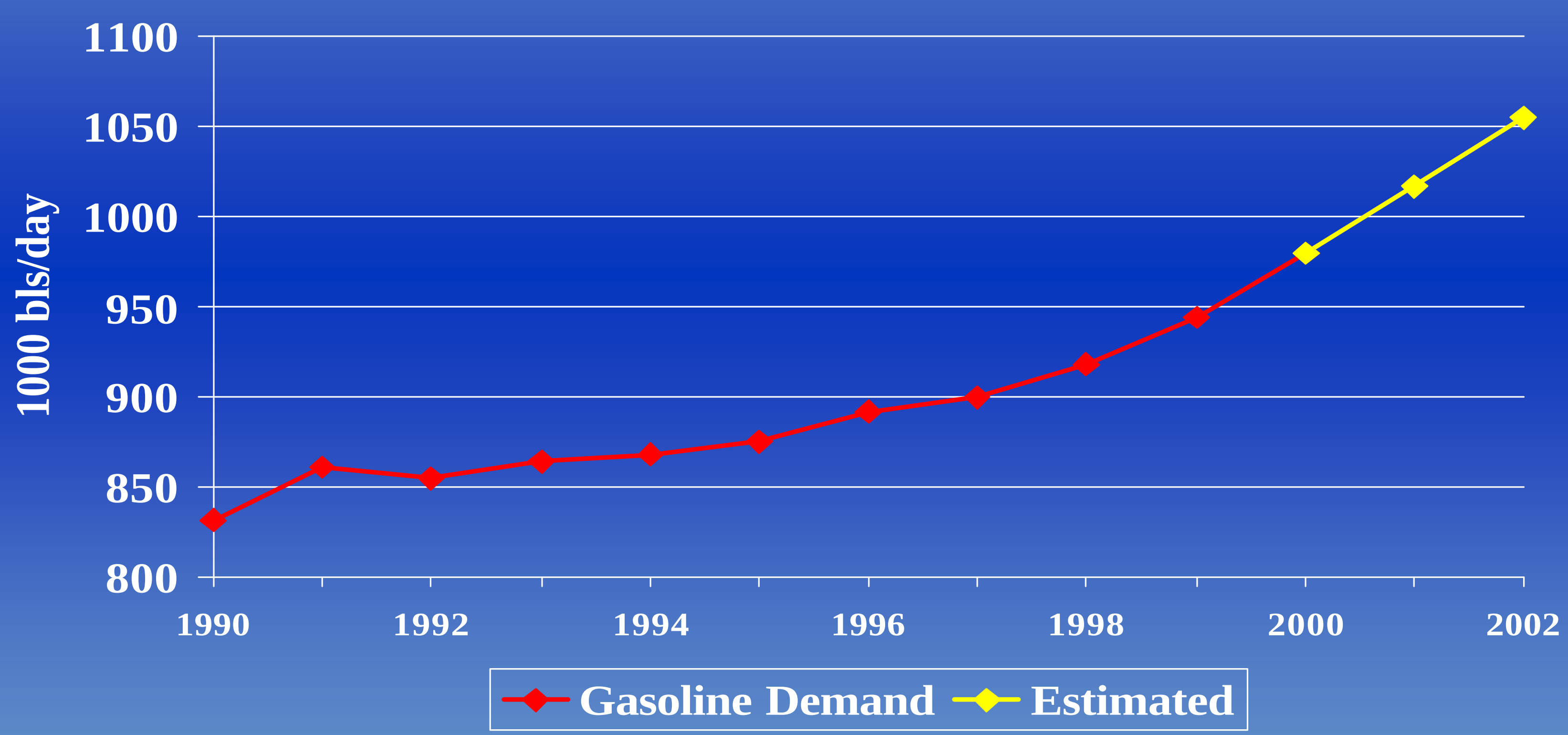


- Found that there will be no significant adverse impact on public health or the environment, including any impact on air, water or soil, that is likely to result from the change in motor vehicle gasoline that is expected to be produced in the future

Progress to Date

- CaRFG3 regulations approved by Environmental Policy Council on January 18, 2000
- Submitted supplemental information for oxygenate waiver request to US EPA
- Transmitted letter to the US EPA recommending a nationwide driveability index standard

Demand for Gasoline has Increased by 20% Since 1990



Compliance Plans

- Initial compliance plans received
  - From refiners and pipeline distributors
- Proposed schedules show refiners are on track for December 31, 2002
- South Coast refiners have begun CEQA process
- San Joaquin Valley and Bay Area refiners on track for CEQA this quarter

Future Gasoline Will Be Similar to Today's Gasoline

- Generally gasoline will look like today's gasoline except:
  - No MTBE
  - Increased use of ethanol
  - Less benzene
  - Lower sulfur content

Trends in California Gasoline Properties and Motor Vehicle Emissions

Robert Harley
Civil & Environmental Engineering Dept.
University of California at Berkeley

Workshop on Ethanol & Alkylates in Fuels
April 10-11, 2001

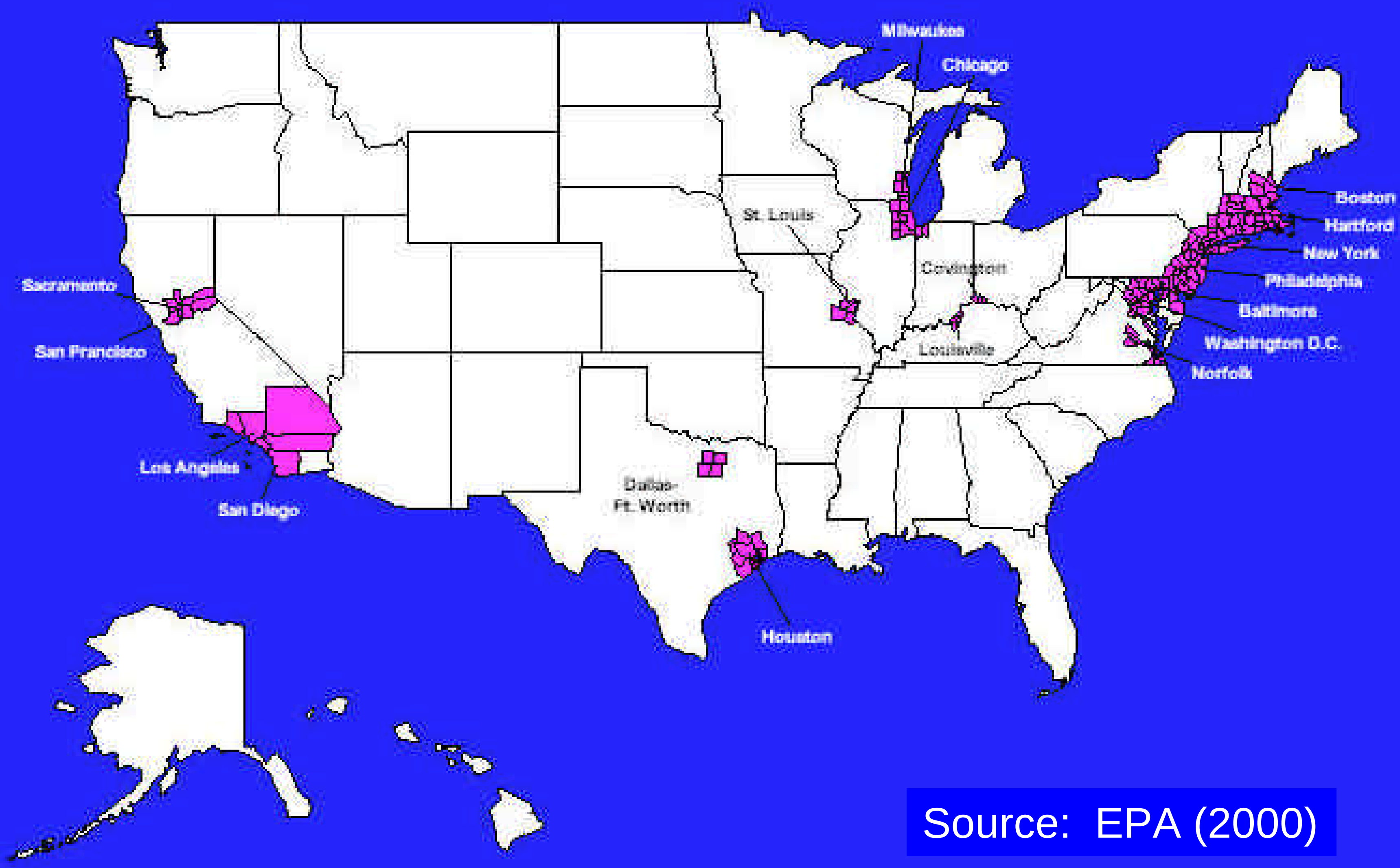
Acknowledgments

- Tom Kirchstetter, Brett Singer, and Andrew Kean (UC Berkeley)
- Gary Kendall (Bay Area AQMD)
- Kent Hoekman & David Kohler (Chevron)
- Financial support:
  - Caltrans & US DOT
  - California Air Resources Board

Introduction

- Major changes to gasoline since 1990:
  - Wintertime use of oxygenates (1992)
  - California RFG (1992, 1996)
  - Federal RFG (1995, 2000)
- Further changes are underway!
  - MTBE will be phased out in California by end of 2002

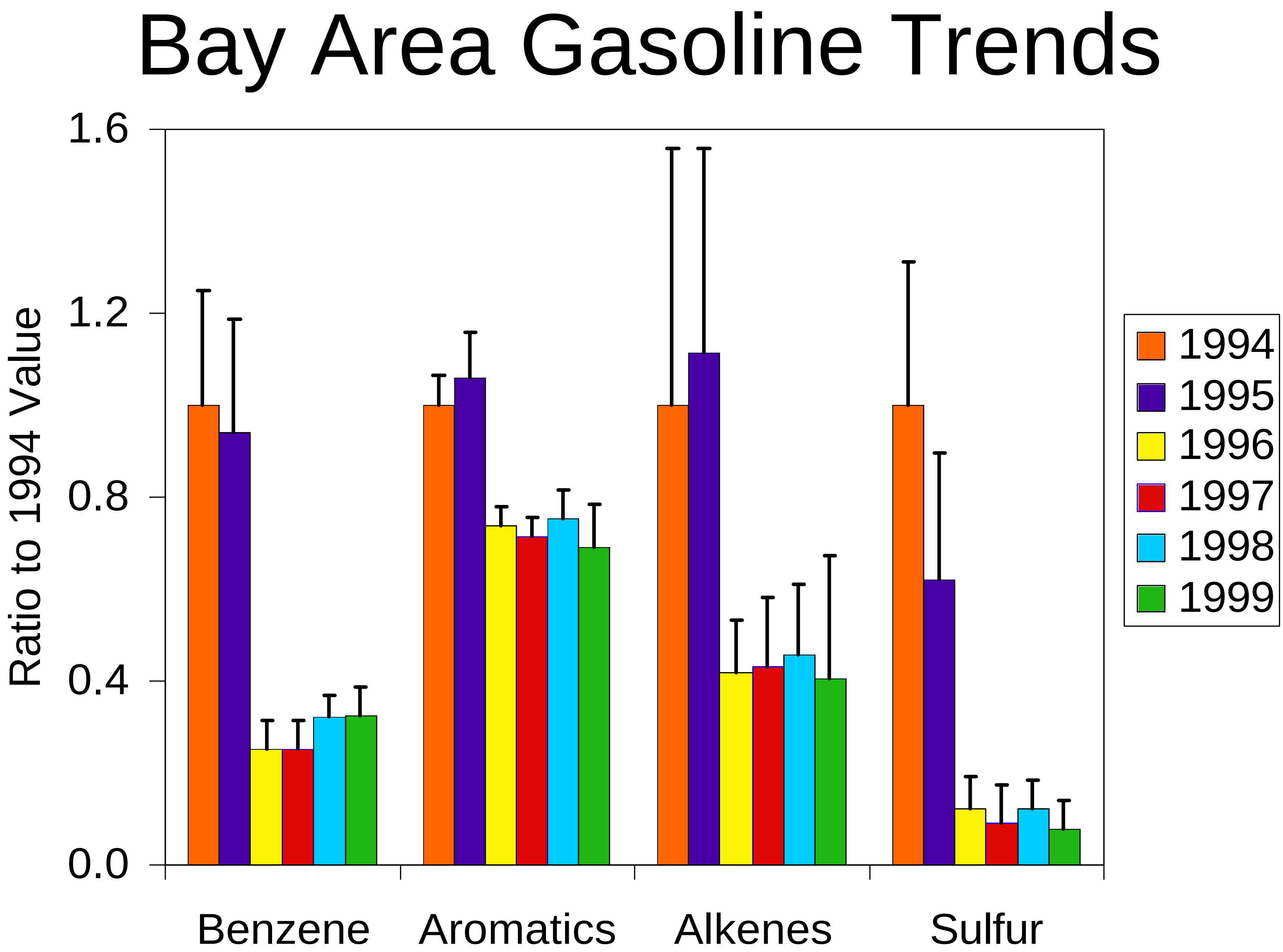
Federal Reformulated Gasoline Areas



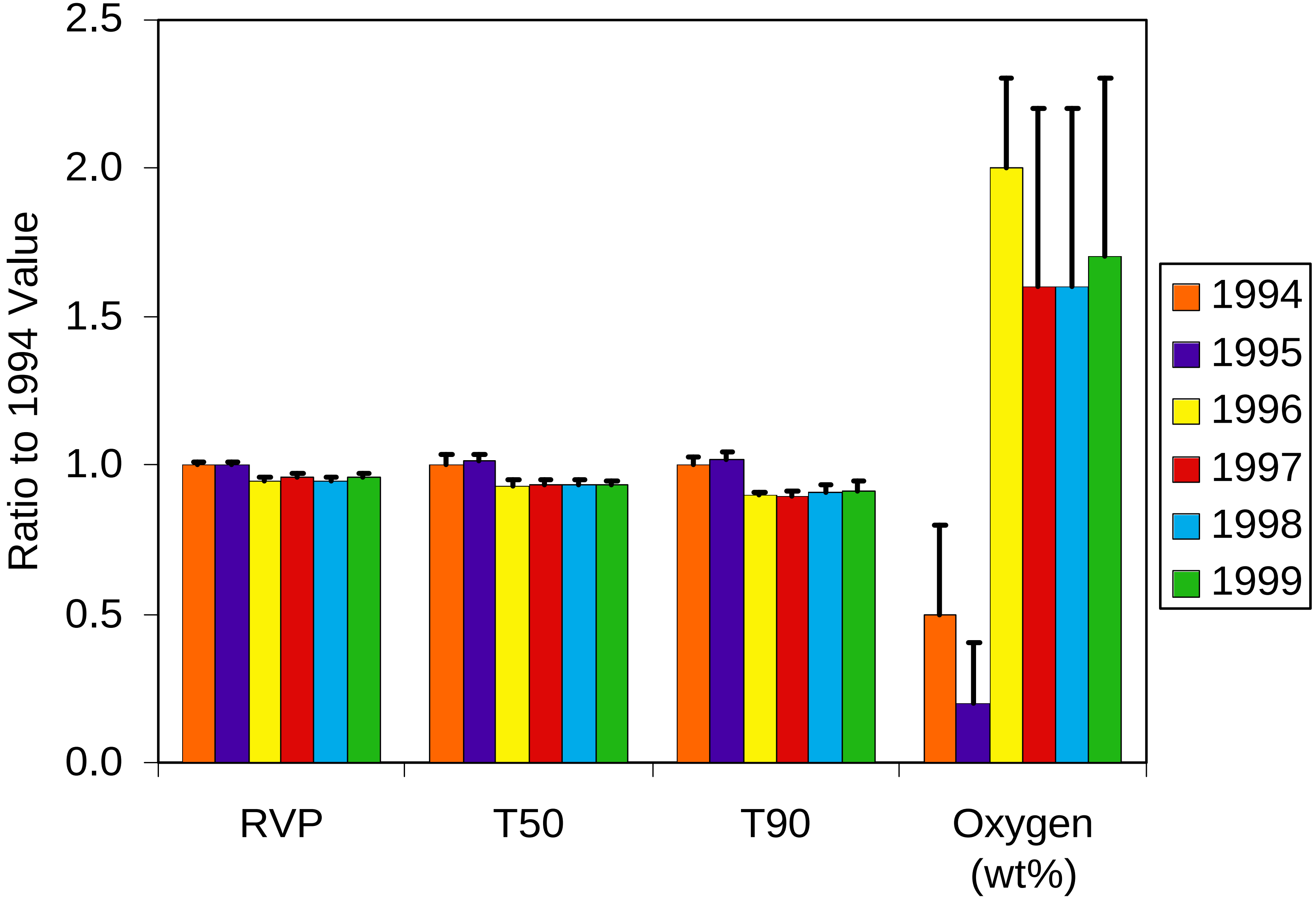
Source: EPA (2000)

Bay Area Gasoline (1994)

Benzene (vol%)	1.6 $\pm$ 0.4	RVP (psi)	7.4 $\pm$ 0.1
Aromatics (vol%)	31.9 $\pm$ 2.1	T_{50} (°F)	214 $\pm$ 8
Alkenes (vol%)	7.9 $\pm$ 4.4	T_{90} (°F)	334 $\pm$ 8
Sulfur (ppmw)	131 $\pm$ 41	Oxygen (wt%)	0.5 $\pm$ 0.3


Bay Area Gasoline Trends
1.6
1.2
0.8
0.4
0.0
Ratio to 1994 Value
Benzene
Aromatics
Alkenes
Sulfur
1994
1995
1996
1997
1998
1999

Bay Area Gasoline Trends



Vehicle Emissions

- Most studies of fuel effects have relied on laboratory dynamometer testing
  - Test one vehicle at a time
  - Simulate stop-and-go city driving
  - Repeat using different fuel formulations
- For example, see Auto/Oil study (Hochhauser *et al.*, SAE 912322)

Caldecott Tunnel

- Tunnel on hwy. 24 east of Oakland, CA
  - 1100 meters (0.7 mile) long
  - Three two-lane traffic tubes
  - Sample in middle bore (no diesel trucks)
  - Sample 10 days each summer 1994-99
  - Sample 4-6 PM (>4000 vehicles/hour)
  - Traffic is eastbound/uphill on 4.2% grade

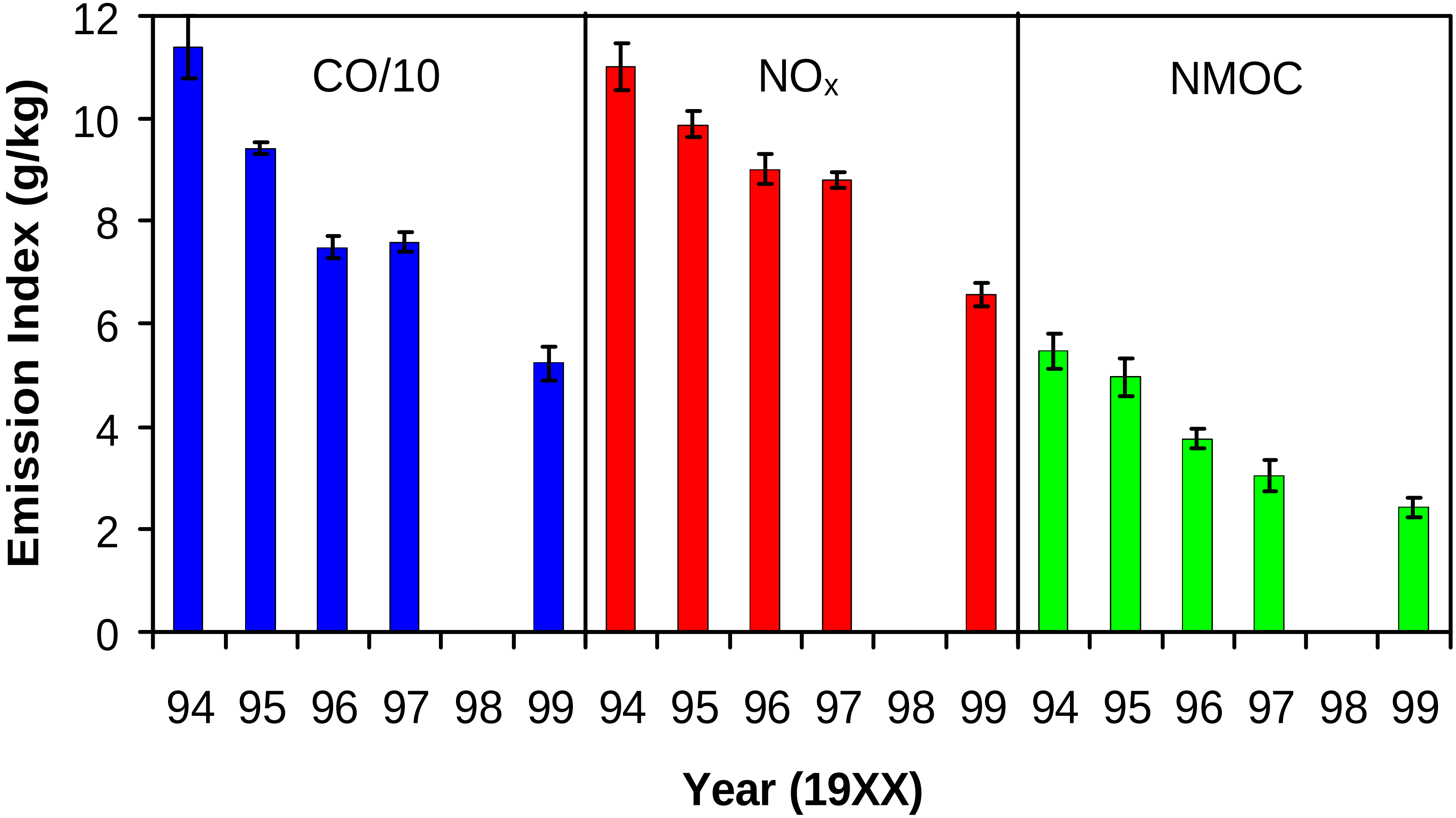
Pollutant Measurements

- Carbon dioxide (CO_2)
- Carbon monoxide (CO)
- Nitrogen oxides (NO_x)
- Non-methane hydrocarbons (NMHC)
- Methyl tert-butyl ether (MTBE)
- Methane (CH_4)
- Aldehydes

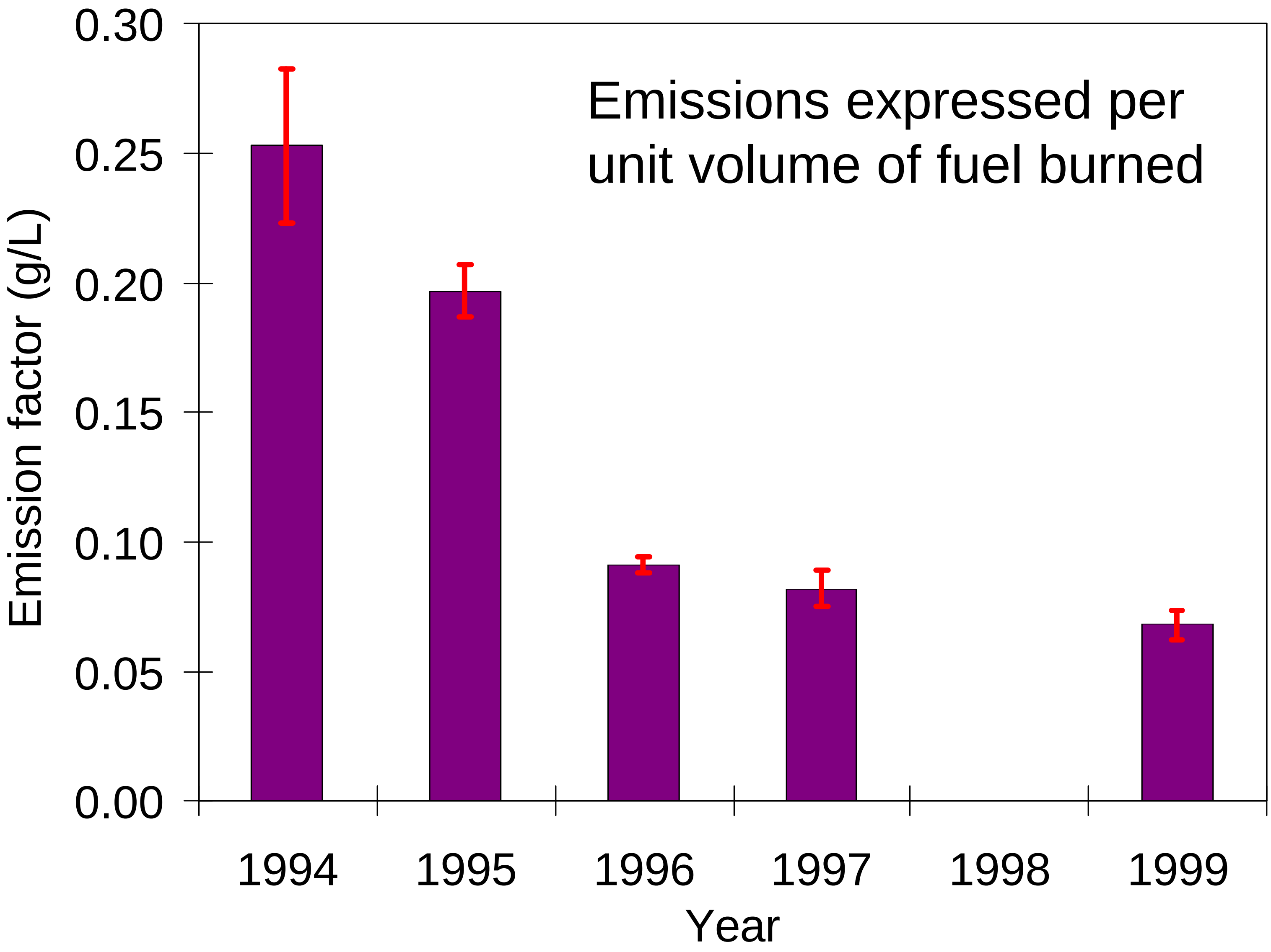
Pollutant Measurements

Emission Factor Trends

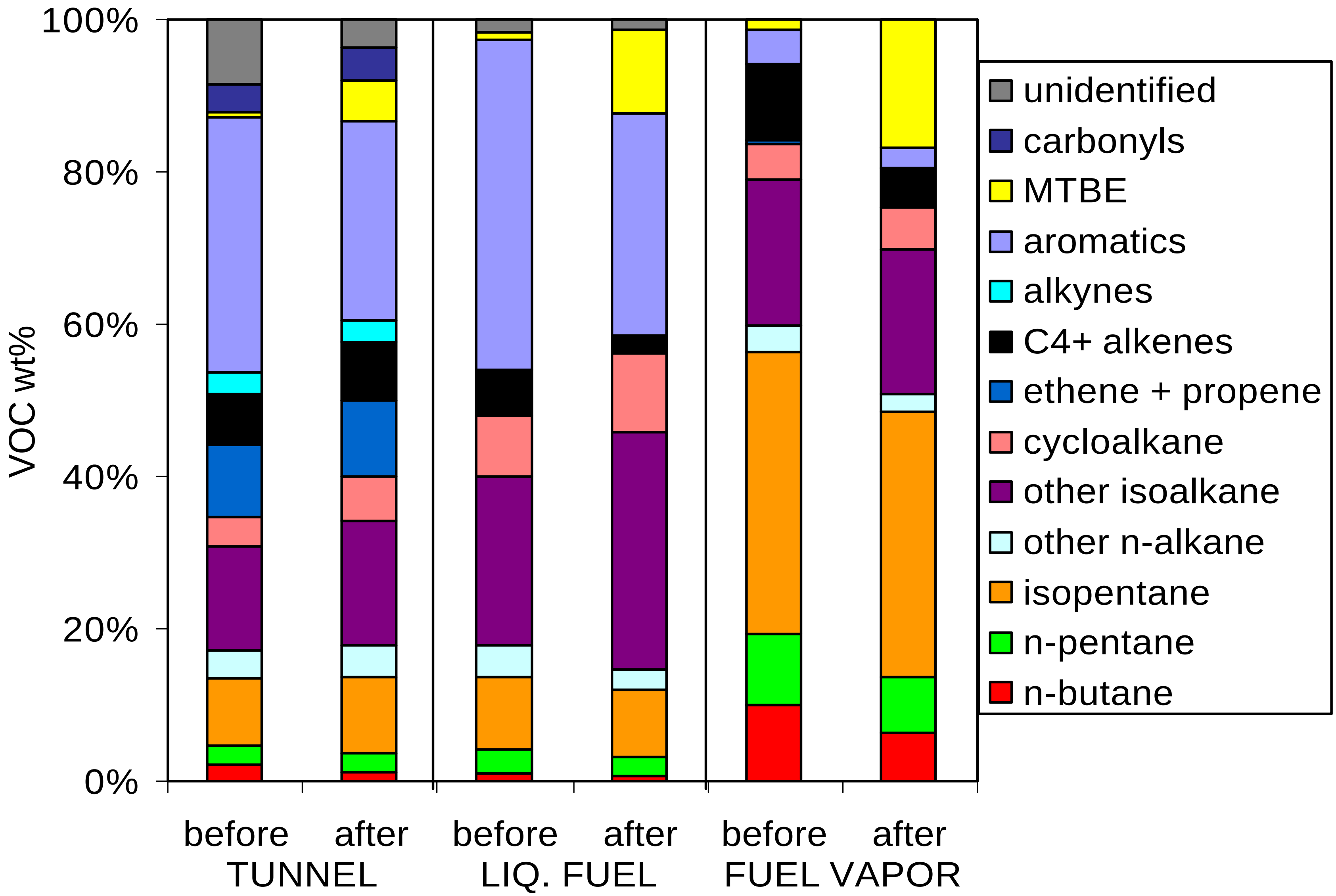
Emissions expressed per unit mass of fuel burned



Benzene Emission Trends



Effects of Fuel Change on VOC



Summary

- Emission factors decreased between 1994 and 1999:
  - Benzene down by 73 ±12%
  - NMOC down by 55 ± 7%
  - CO down by 54 ± 6%
  - NO_x down by 41 ± 4%
- Improved vehicle technology more important than fuel changes, except benzene where contribution due to fuel changes is 30-40%

Air Quality Issues: Ethanol

- Acetaldehyde (CH_3CHO) emissions will increase by ~150% if ethanol added to gasoline at 10 vol% (SAE 920326)

$$CH_3CHO + OH^{\bullet} \xrightarrow{O_2} CH_3C(O)O_2^{\bullet} + NO_2$$

$$\updownarrow$$

$$CH_3C(O)OONO_2$$

Peroxyacetyl nitrate (PAN)

Vapor Pressure

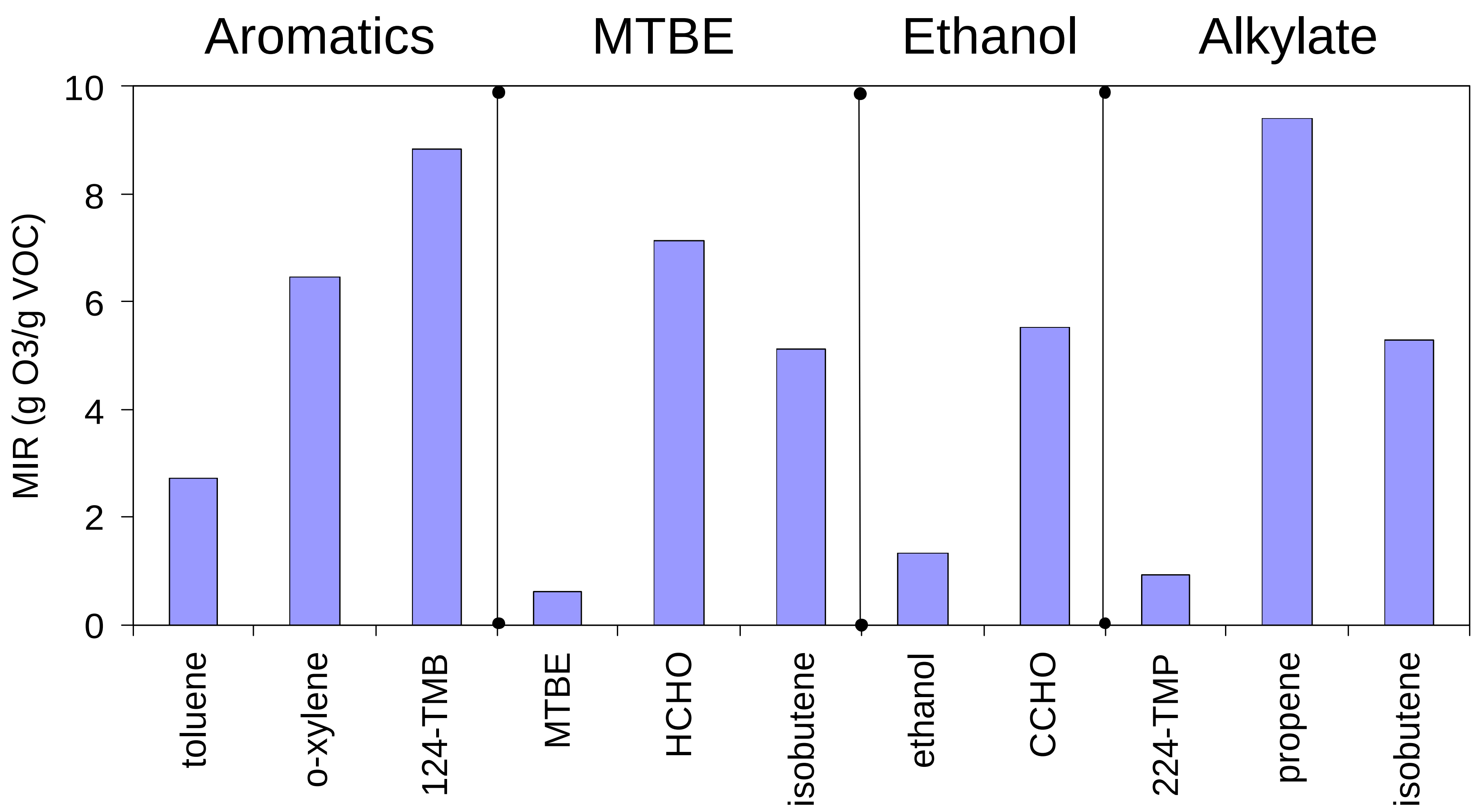
- Affects tendency of gasoline to evaporate in hot weather
- Gasoline v.p. limit 48 kPa at 38°C
- Ethanol has v.p. of 16 kPa at 38°C
- Adding ethanol should lower v.p. of gasoline… right?

No! It forms non-ideal solution and vapor pressure increases.

Air Quality Issues: Alkylate

- Strong acid catalysts (HF, H_2SO_4) used in refinery alkylation process are hazardous
- Alkylate in gasoline is a precursor to emissions of C_3-C_4 alkenes (highly reactive) in vehicle exhaust
- Higher energy content than oxy-fuels

VOC Reactivity



Conclusions

- Reactivity of exhaust VOC with respect to ozone formation is unlikely to change for MTBE vs. ethanol vs. alkylate
- Potential air quality impacts:
  - Vapor pressure problems, increased acetaldehyde & PAN formation (for EtOH)
  - Hazardous strong acid catalysts used in refineries to make alkylate

References:
Environ. Sci. Technol.

- Kirchstetter *et al.*, vol. 33, pp. 318-28, 1999a.
- Kirchstetter *et al.,* vol. 33, pp. 329-36, 1999b.
- Kean *et al.,* vol. 34, pp. 3535-39, 2000.
- Harley *et al.,* vol. 34, pp. 4088-94, 2000.

ALKYLATION CURRENT EVENTS

PRESENTED AT THE
LAWRENCE LIVERMORE NATIONAL LABORATORY
WORKSHOP ON ETHANOL & ALKYLATES IN FUELS

APRIL 10-11, 2001

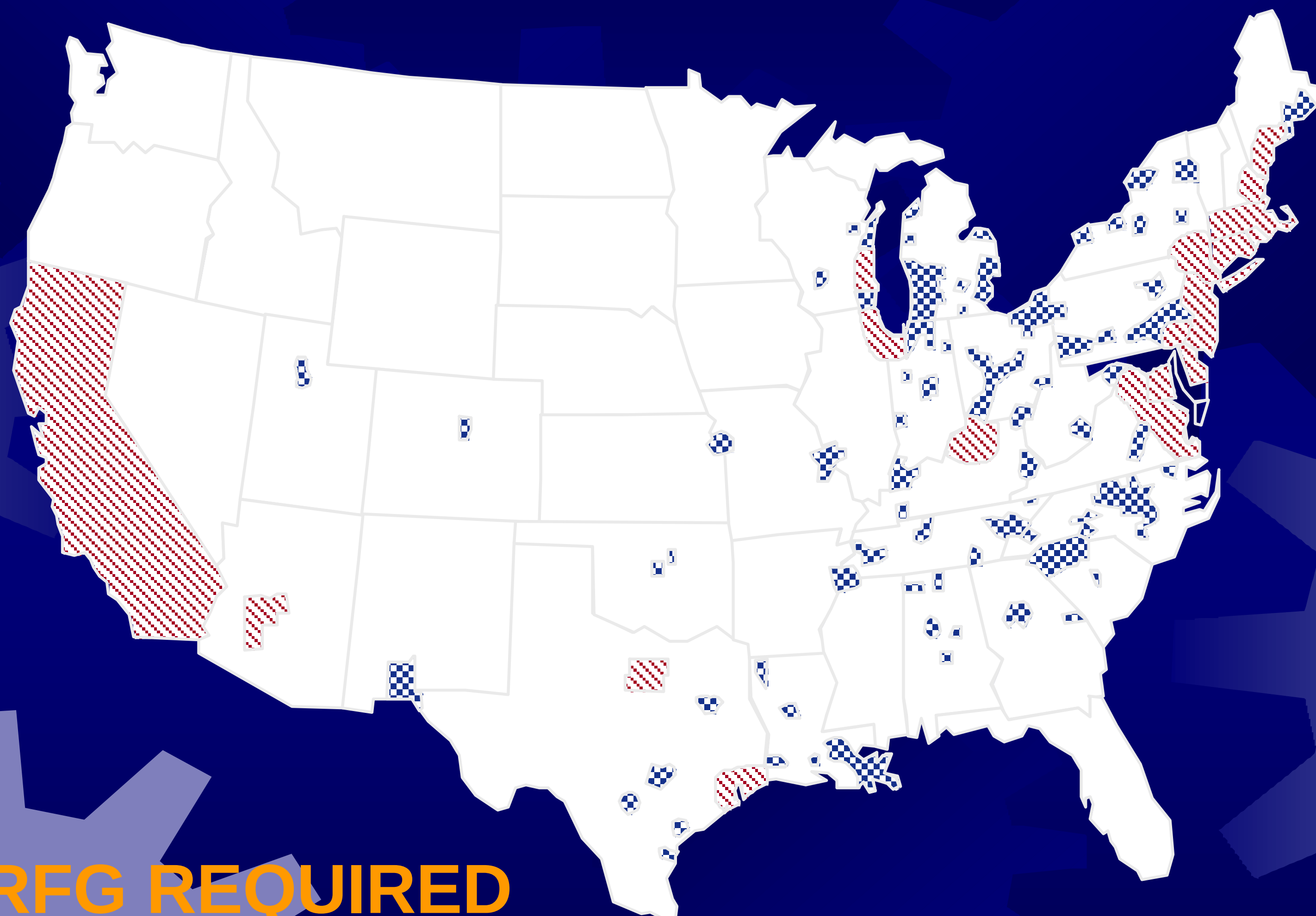
Presented By:
Pam Pryor
STRATCO, Inc.
Manager of Technical Sales

STRATCO
The Engineering and Technology Company

AGENDA

- REGULATORY/LEGISLATIVE ISSUES
- MTBE
- DRIVEABILITY INDEX
- ALKYLATE'S ROLE IN RFG

U.S REFORMULATED GASOLINE



RFG REQUIRED

NEEDS OZONE CONTROLS

RFG REQUIREMENTS

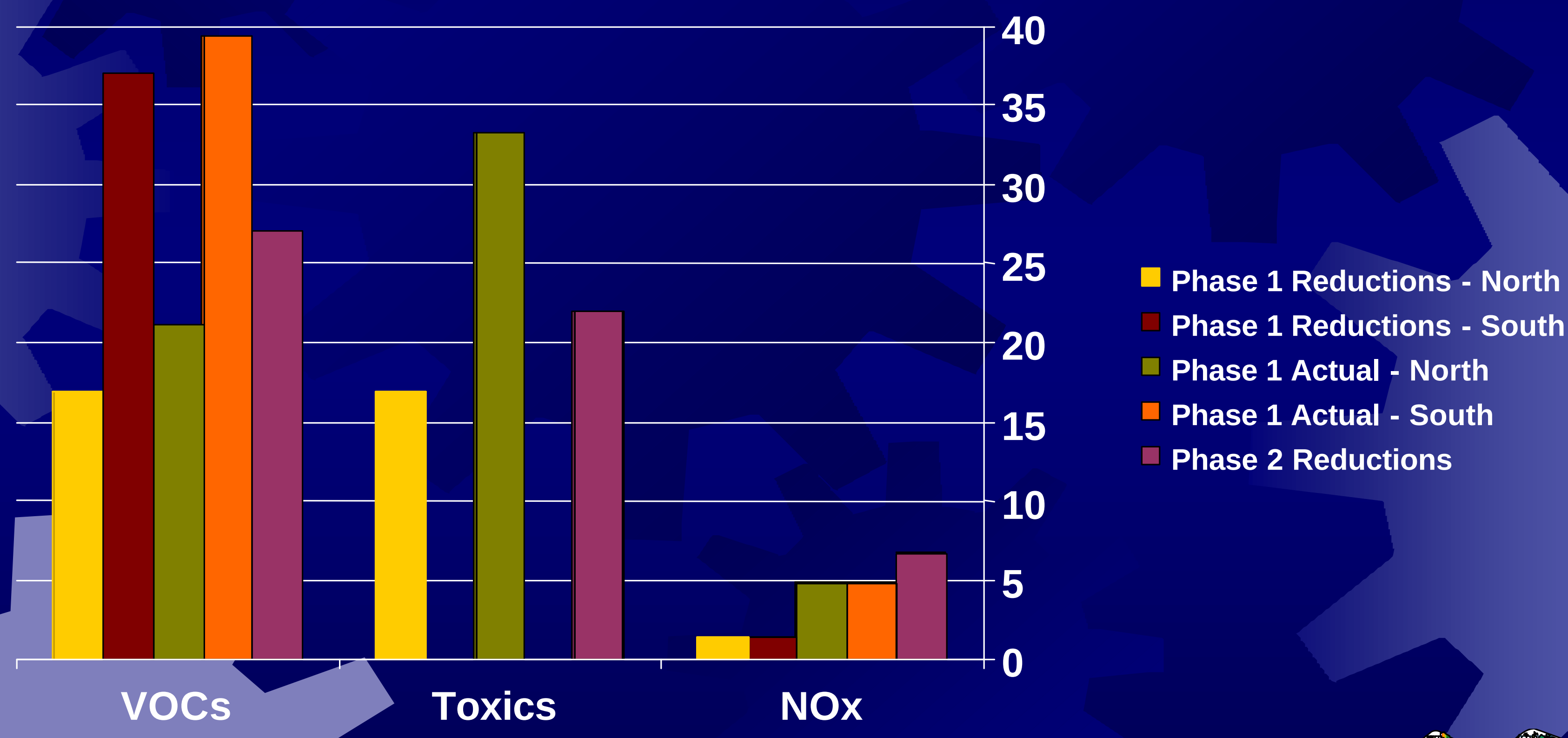
- U.S. NON-ATTAINMENT AREAS
  - PHASE 1 COMPLEX MODEL 1998-1999
  - PHASE 2 COMPLEX MODEL 2000+
- CALIFORNIA NON-ATTAINMENT AREAS
  - CA RFG PHASE 2 1996+
  - CA RFG PHASE 3 2003

STRATCO
The Engineering and Technology Company

Ca RFG PHASE 2 & 3

FUEL PARAMETER	PHASE 2/3 ALLOWABLE LEVEL
SULFUR	40/20 WT PPM
AROMATICS	25/25 VOL%
BENZENE	1.0/0.8 VOL%
OLEFINS	6.0/6.0 VOL%
OXYGEN	2.0/2.0 WT%
T_{90}	300^{O}F (149^{O}C)/305^{O}F (152^{O}C)
T_{50}	210^{O}F (99^{O}C)/213^{O}F (101^{O}C)
RVP	7.0/7.0 PSI (0.49 KG/CM^2)

RFG PHASE 1 & 2 REDUCTIONS



MTBE

- FEDERAL OXYGEN MANDATE
  - Over 18 bills introduced during 106^{th} Congress.
  - May revert to a state by state decision.
- OCTANE AND VOLUME LOSS HARD TO REPLACE
- ETHANOL
  - If the oxygen mandate continues, ethanol is the most likely replacement.
  - Ethanol requires special handling considerations.
    - To prevent groundwater contamination
    - To offset NO_x emissions according to CA Predictive Model
    - Alkylate to balance ethanol's blending RVP

DRIVEABILITY STANDARD

DRIVEABILITY INDEX:

$$DI\ (^{O}F) = 1.5\ (T_{10}) + 3(T_{50}) + T_{90} + (20 \times wt\%\ Oxygen)$$

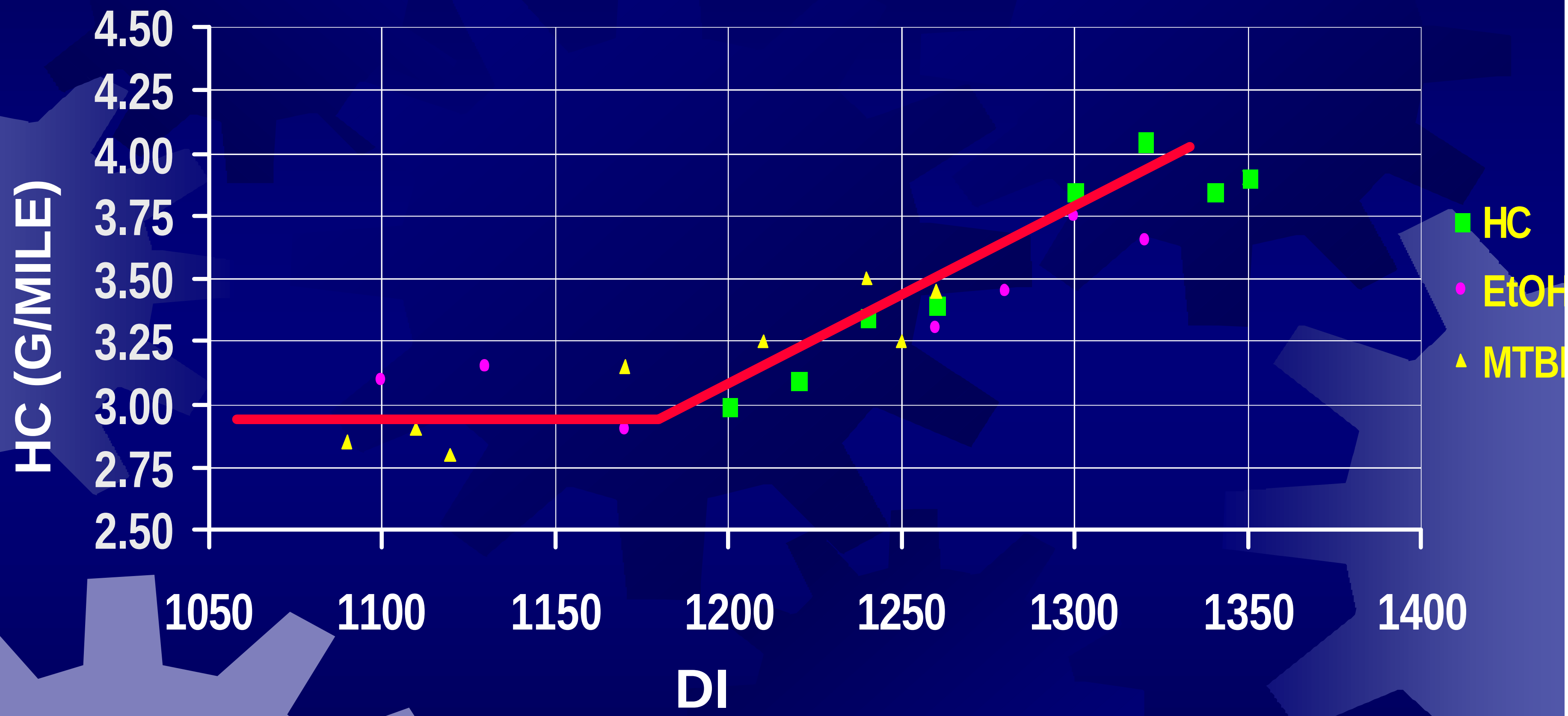
T_{50} = 170 ^{O}F MINIMUM

DI = 1200 ^{O}F MAXIMUM

STRATCO

The Engineering and Technology Company

EMISSIONS vs. DI



Source: GM

ALKYLATE'S ROLE IN RFG

- IDEAL BLENDSTOCK
  - 100% PARAFFINIC
  - LOW RVP
  - HIGH OCTANE
  - GOOD DISTILLATION CHARACTERISTICS
  - NO/LOW SULFUR
- DILUTION EFFECT

STRATCO
The Engineering and Technology Company

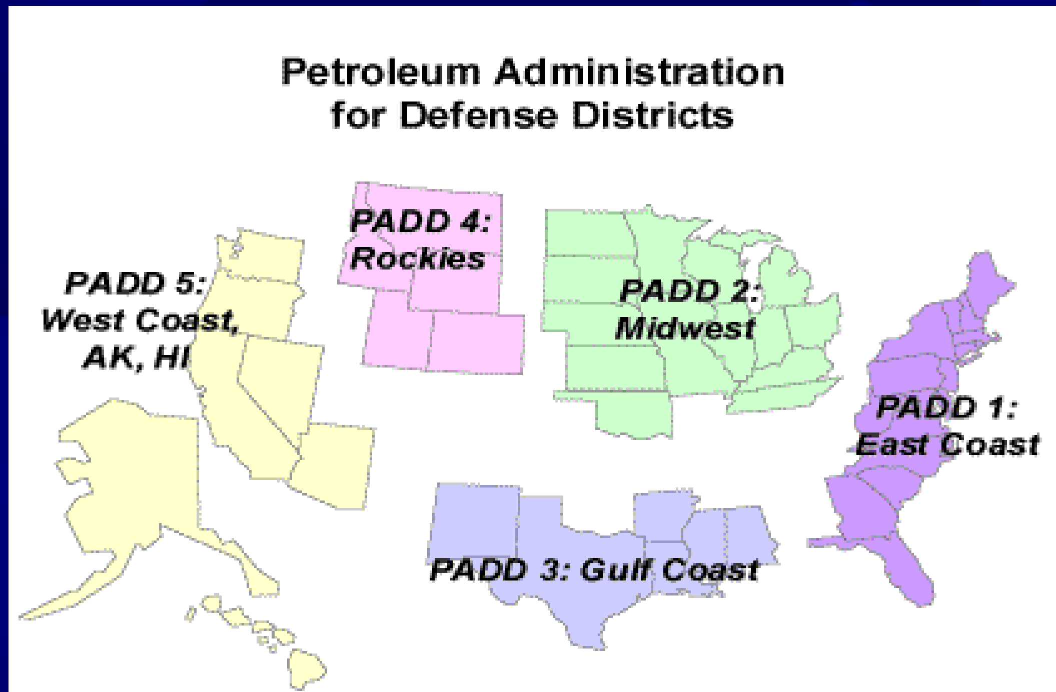
GASOLINE BLENDSTOCKS

	ALKY	FCC	REFORMATE	POLY
AROMATICS	0	29	63	0
OLEFINS	0	29	1	95
SULFUR	~0	756	~0	~0
MON	92	81	87	82
RON	94	92	98	94
DI	1134	1223	1299	1251

SOURCE: NPRA

STRATCO

RFG BLENDING PROPERTIES BY PADD



PADD 2

FCC Gasoline-33%
Reformate-29%
Alkylate-12%
Oxygenate-10%
Hydrocrackate-3%

ALKY CAPACITY
295,000 BPD

PADD 5

FCC Gasoline-26%
Reformate-23%
Alkylate-15%
Oxygenate-11%
Hydrocrackate-10%

ALKY CAPACITY
196,900 BPD

PADD 1 & 3

FCC Gasoline-40%
Reformate-25%
Alkylate-11%
Oxygenate-11%
Hydrocrackate-3%

ALKY CAPACITY
600,000 BPD

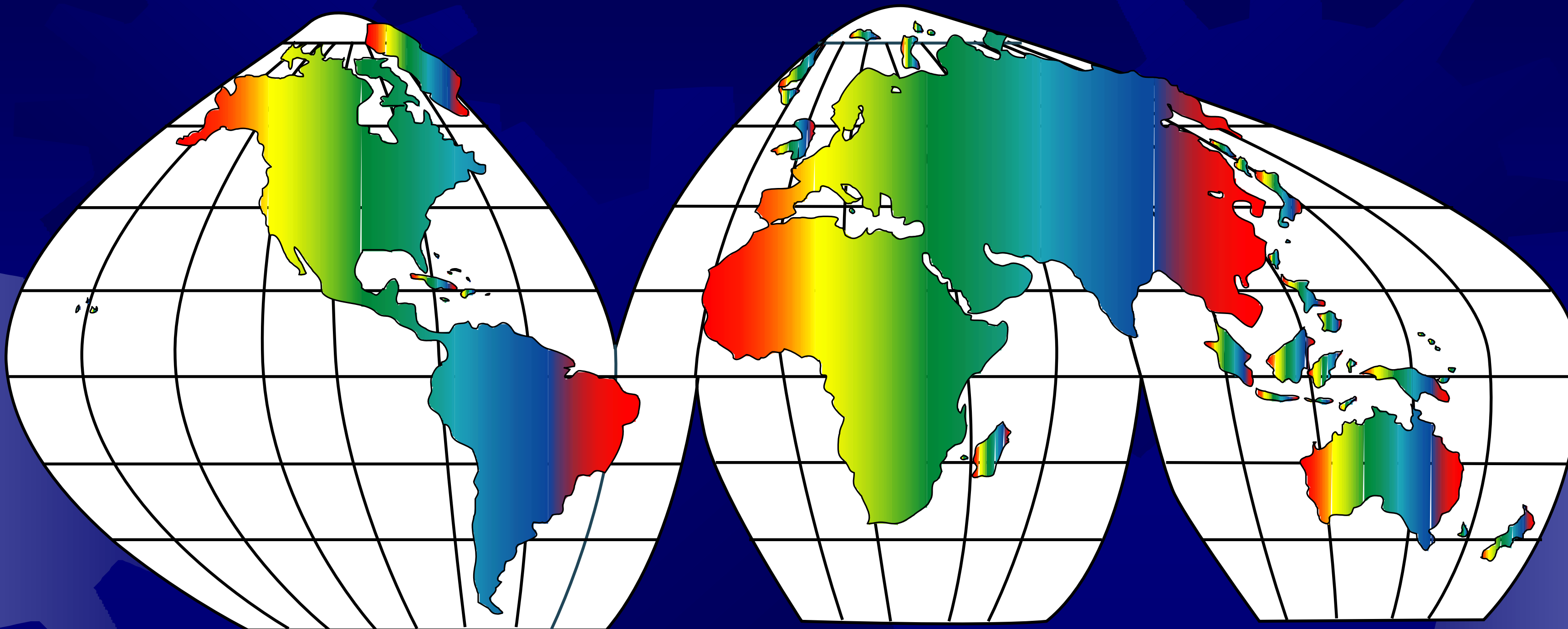
ALKLYATION – PROVEN TECHNOLOGY

- **NOT NEW TECHNOLOGY**
  - **Molecules in gasoline from beginning.**
  - **On-purpose production began in 1930's.**
- **ALKYLATE CURRENTLY ACCOUNTS FOR 15-30% OF THE FINISHED GASOLINE POOL.**
- **PERRY'S CHEMICAL ENGINEER'S HANDBOOK LISTS ALKYLATES MOLECULES AS INSOLUBLE IN WATER**

SUMMARY

- RFG LEGISLATION, MTBE PHASEOUT AND THE OXYGEN MANDATE UNCERTAINTY ARE MAJOR FACTORS INFLUENCING REFINING INDUSTRY.
- ALKYLATION GROWTH CONTINUES TO BE ENVIRONMENTALLY DRIVEN.
- TREMENDOUS SYNERGY BETWEEN ALKYLATE AND ETHANOL.

STRATCO
The Engineering and Technology Company



STRATCO®

The Engineering and Technology Company

Production of Ethanol & Update on Ethanol Current Events

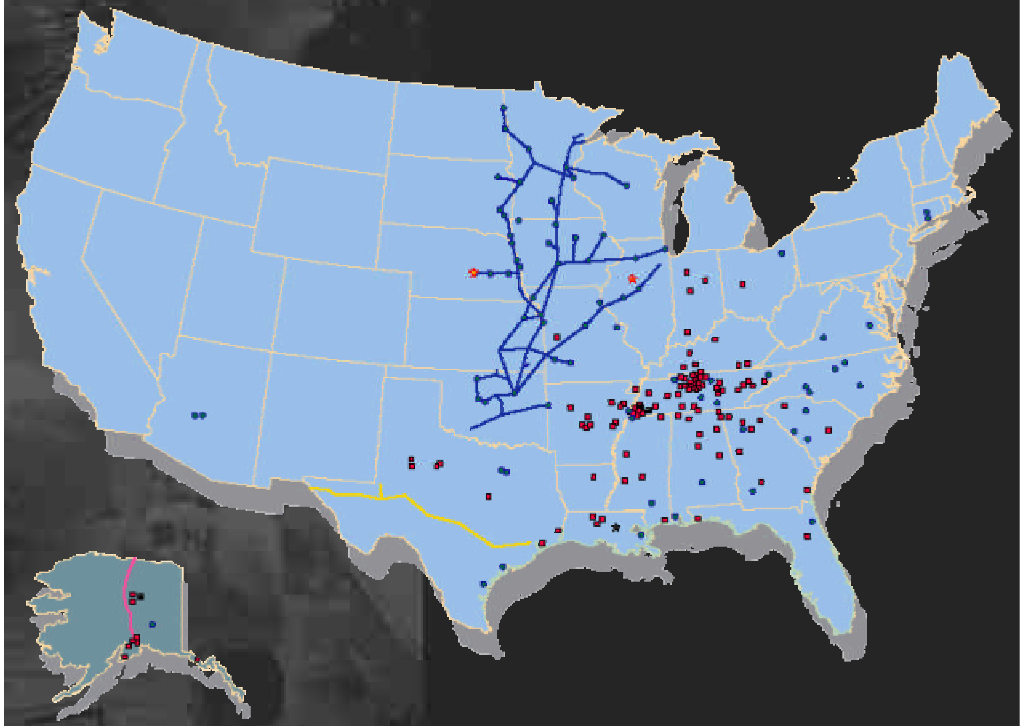
Williams

Ron Miller
President, Williams Bio-Energy
April 10, 2001
Oakland, California

Our Message

- California oxygenate waiver - Clean Air Act oxygen requirement
- Ethanol is a viable alternative to MTBE and neat ethanol can be shipped in pipelines
- Ethanol production capacity continues to increase.
- CARB's Phase III rules and the market implications for ethanol in California.

Diverse Petroleum Services Network



- **Bio-Energy leader**
- #1 Petroleum storage company in North America
- Largest petroleum transportation provider in the Midwest
- True niche refiner
- Creating 1st "Virtual Supply Network"

Williams Bio-Energy

Fuel ethanol

- *Gasoline blending*
- *Clean Burning "Oxygenate"*

Beverage alcohol

- *Vodka, Bourbon, Tequila production*

Industrial Alcohol

- *Specialty chemicals*
- *Vinegar*

Co-Products

- *Corn gluten meal*
- *Corn gluten feed*
- *Distillers Dried Grains*
- *Brewers yeast*
- *Carbon Dioxide*

California Ethanol Issues

- California oxygenate wavier has not been granted or denied
- Clean Air Act oxygen standard
- The California MTBE phase out is only 15,037 hours away

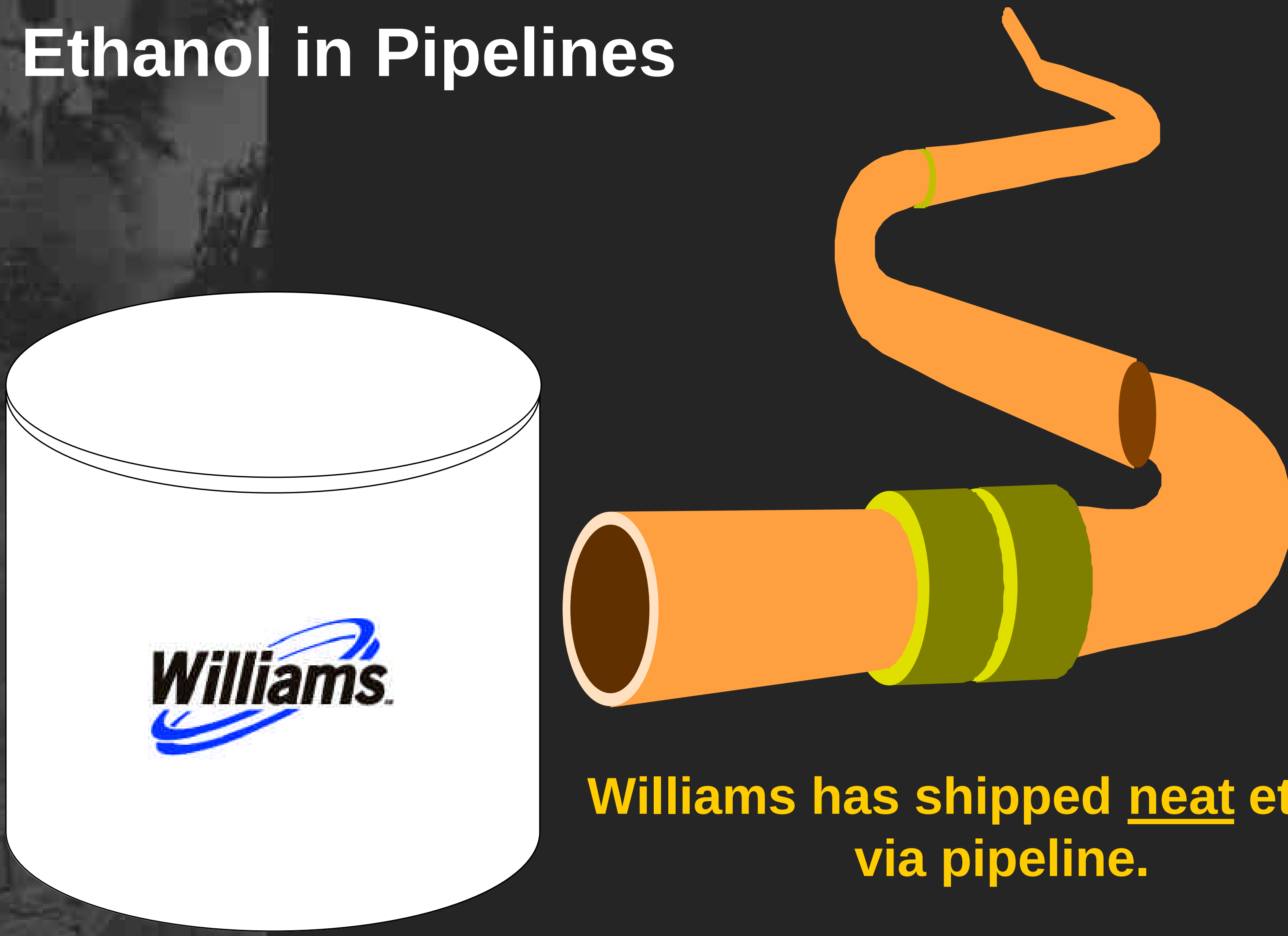
Health & Environment

"The substitution of ethanol and alkylates for MTBE in California's fuel supply will not have any significant air-quality impacts. This finding is supported by theoretical calculations in the South Coast Air Basin using state-of-the-art science tools, an analysis of the impact of uncertainties, air quality measurements in areas that have already introduced ethanol into their fuel supply, and an independent scientific peer review by the University of California".

California Issues - Logistics

- Ethanol storage capacity in place in Los Angeles and San Francisco area terminals
- Current California ethanol market
- Vessel and railcar deliveries available
- We believe ethanol will be transported in “non-traditional” ways

Ethanol in Pipelines



Williams has shipped <u>neat</u> ethanol via pipeline.

Williams Neat Ethanol Test

- Conducted in the early 1980's
- 4,600 barrels of ethanol was shipped in an 8 inch line from Kansas City to Des Moines
- Pipeline constructed in 1930
- Pipeline operated in multi-product service
- Changed to gasoline 10 days prior to ethanol test
- Pigs were used prior to the test
- Ethanol batch profiled & tank tested on receipt

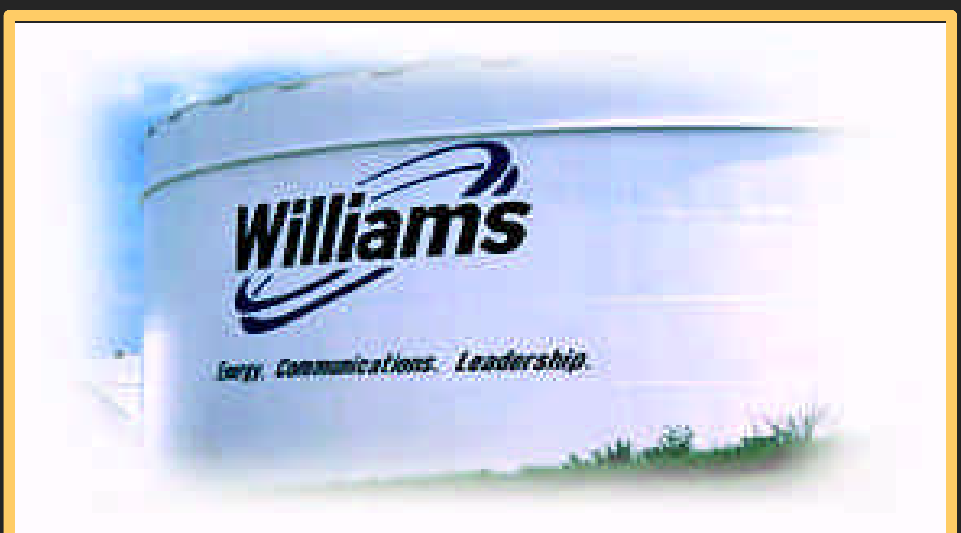
What Happened to Ethanol Quality?

Good

- Moisture (Water)
- Apparent Proof
- Interfaces

Areas of Concern

- Color
- Gum
- Interface handling



We Suggest the Following for Routine Ethanol / Pipeline Shipments

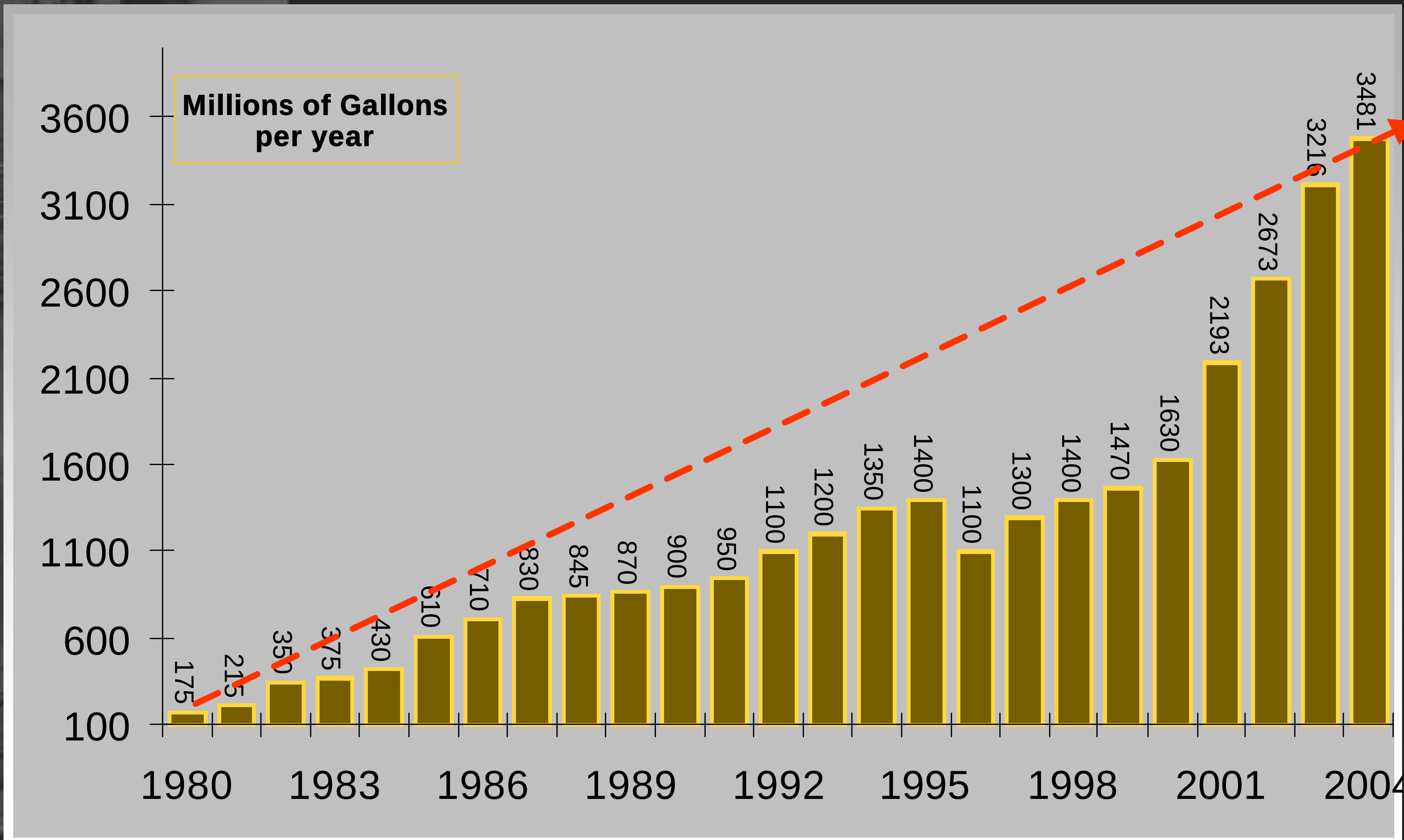
- Frequent dewatering of mainlines using pigs and spheres
- Use closed floater storage tanks to prevent rainwater ingestion
- A commitment to dry storage tanks
- Installation of inline corrosion monitoring
- Possible installation of filtration system
- Ethanol QA oversight program
- Materials compatibility review
- Updated safety documentation & training

Ethanol Pipeline Shipments

- "… our experimental pipeline tests indicate that fuel grade ethanol can be successfully transported in a multi-products pipeline system under controlled conditions. The greater the frequency of batches through any system through any given line segment, the fewer the quality problems that we would expect to experience."

* Williams Presentation, March, 1982, Alcohol Week Conference, San Antonio, TEXAS

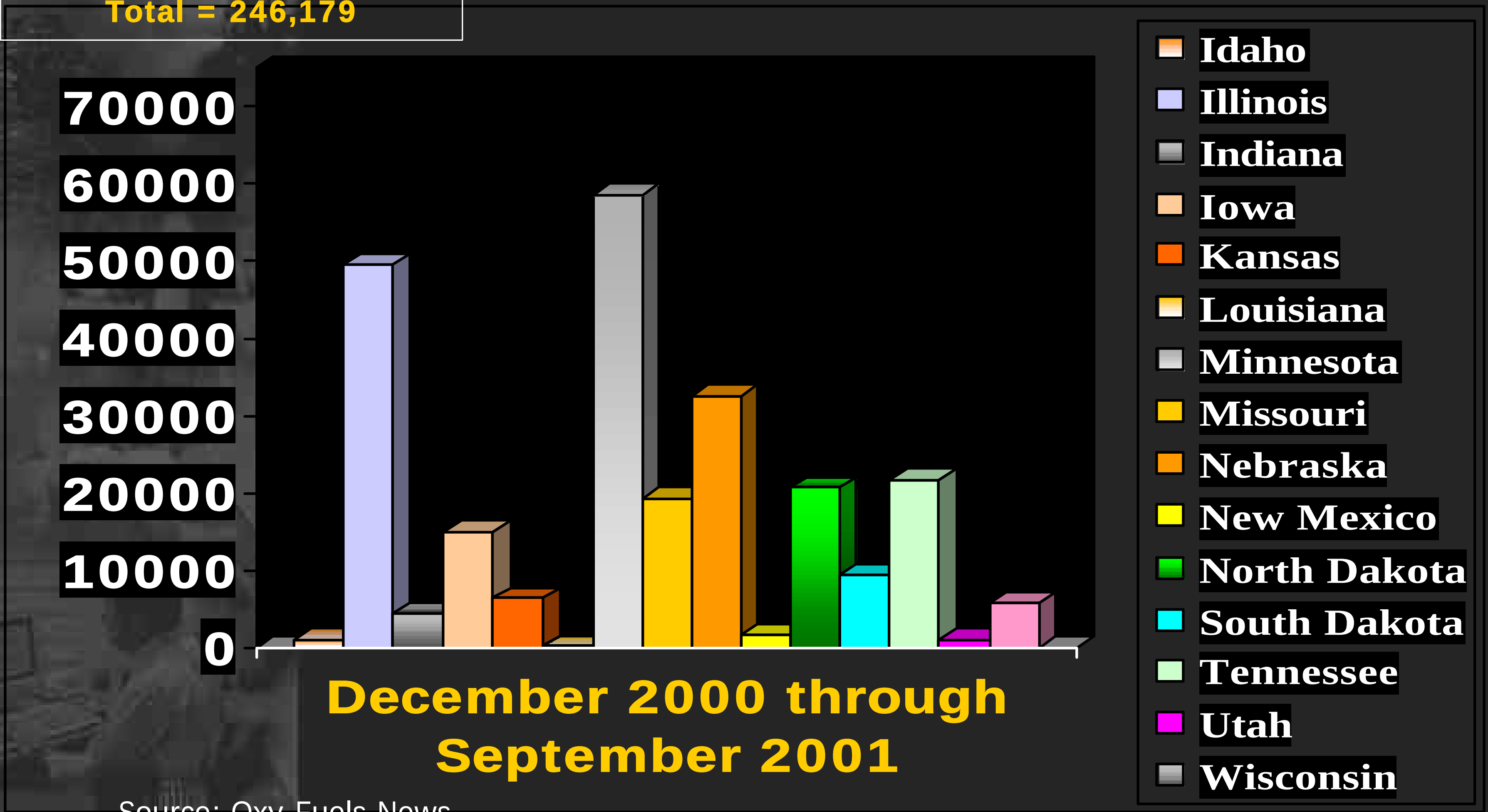
Historical & Projected Ethanol Production



Source: Renewable Fuels Association & AUS Consultants

Anticipated Increase in Ethanol Production - Commodity Credit Corporation Program (By State)

Increased Thousand Gallons
Eligible for Payment
Total = 246,179

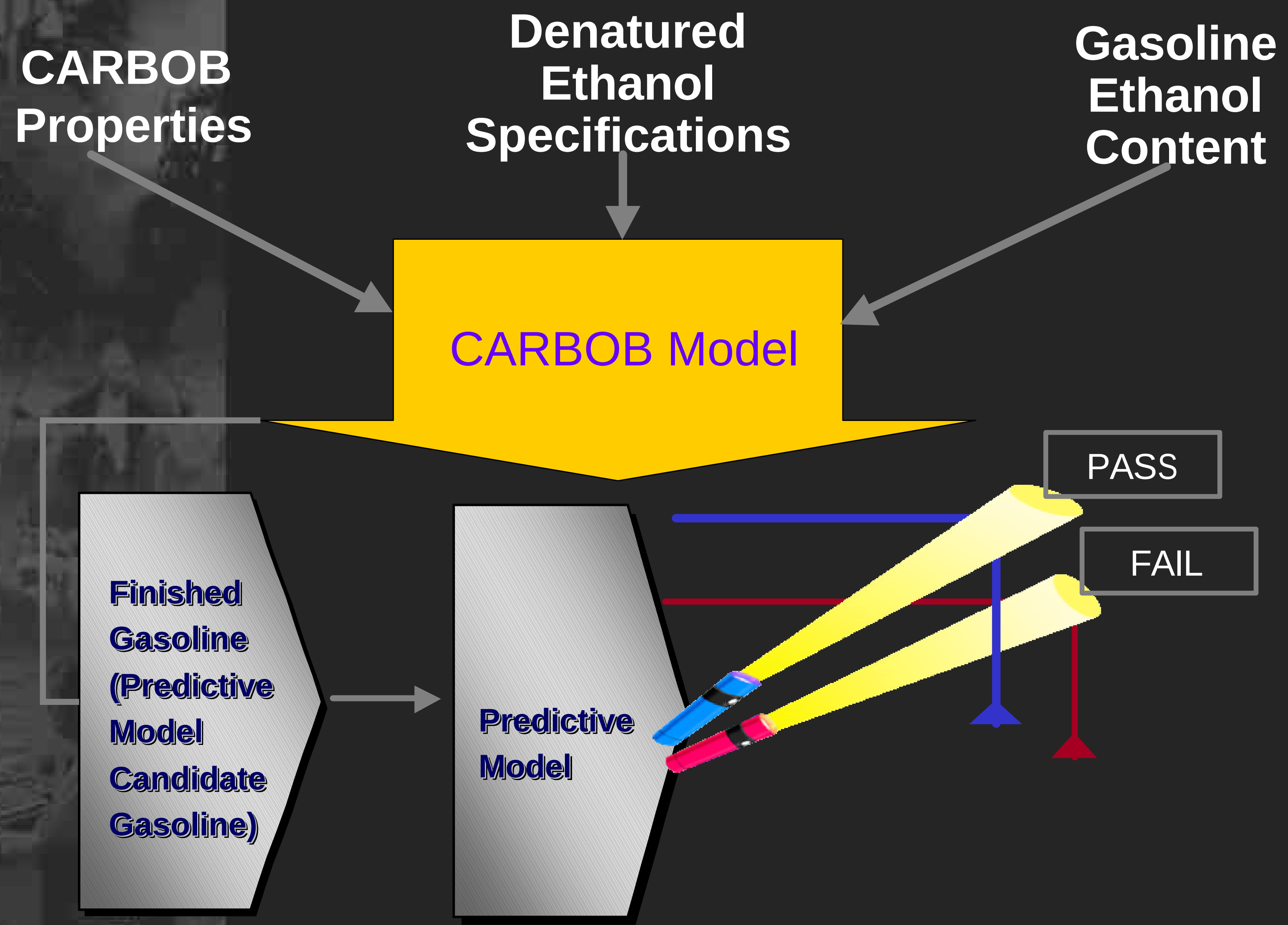


Source: Oxy-Fuels News

California Regulatory Leadership

- The ethanol industry will continue to develop partnering relationships with California agencies & stakeholders to ensure a smooth transition from MTBE to ethanol

California Reformulated Blendstock for Oxygenate Blending



Williams

California Phase III Rulemaking

California Air Resources Board
Specifications for Denatured Ethanol

Property	Specifications for Denatured Ethanol	Specifications for Denaturants
Sulfur, ppm	10	n/a
Benzene, vol %	0.06	1.1
Olefin, vol %	0.5	10
Aromatics, vol %	1.7	35
Others	ASTM 4806	n/a

Ethanol Producer Challenge

Takeaways

- The ethanol industry has encouraged EPA to deny ARB's waiver request
- Ethanol will meet the high environmental expectations of California policymakers
- Supply capacity will grow to over 2 billion USG per year in 2001
- Refiners can switch oxygenates "when ready"
- Ethanol can be shipped in untraditional ways
- CARB has imposed cleaner specifications for ethanol than gasoline

With Upgraded USTs, Are We Still Concerned About Groundwater?

Yes

Workshop on Increased Use of Ethanol and Alkylates in Automotive Fuels in California

April 10 & 11, 2001

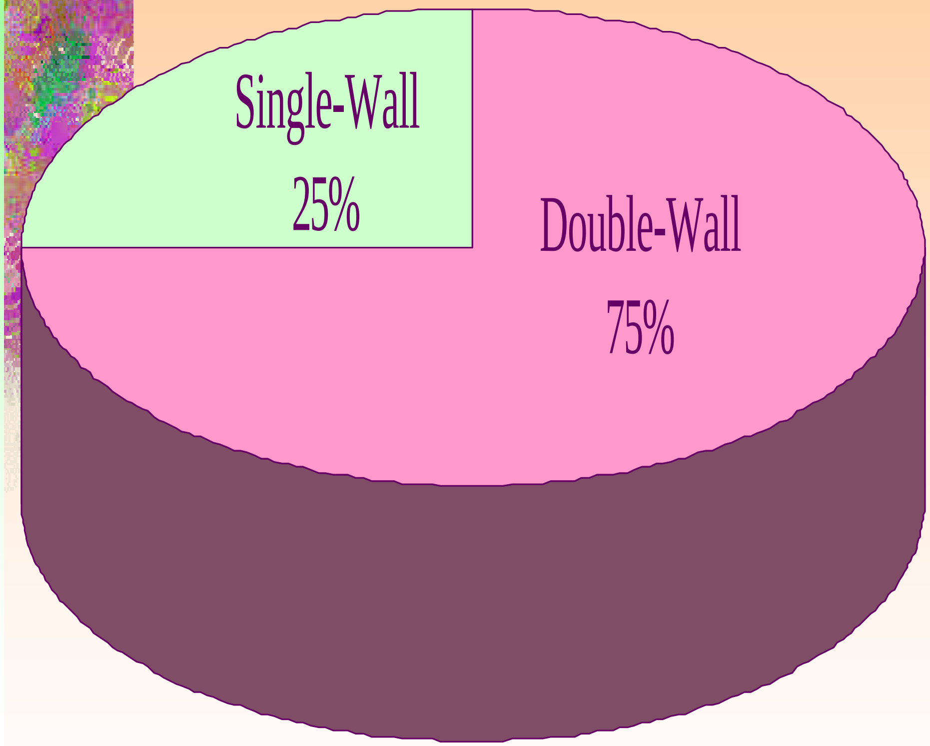
California's UST Program

- State law and federal regulations required all operating USTs to be upgraded or replaced by 12/22/98.
- It is 2+ years later.
- Are we still concerned about leaking underground fuel tanks?

Upgraded vs. Replaced

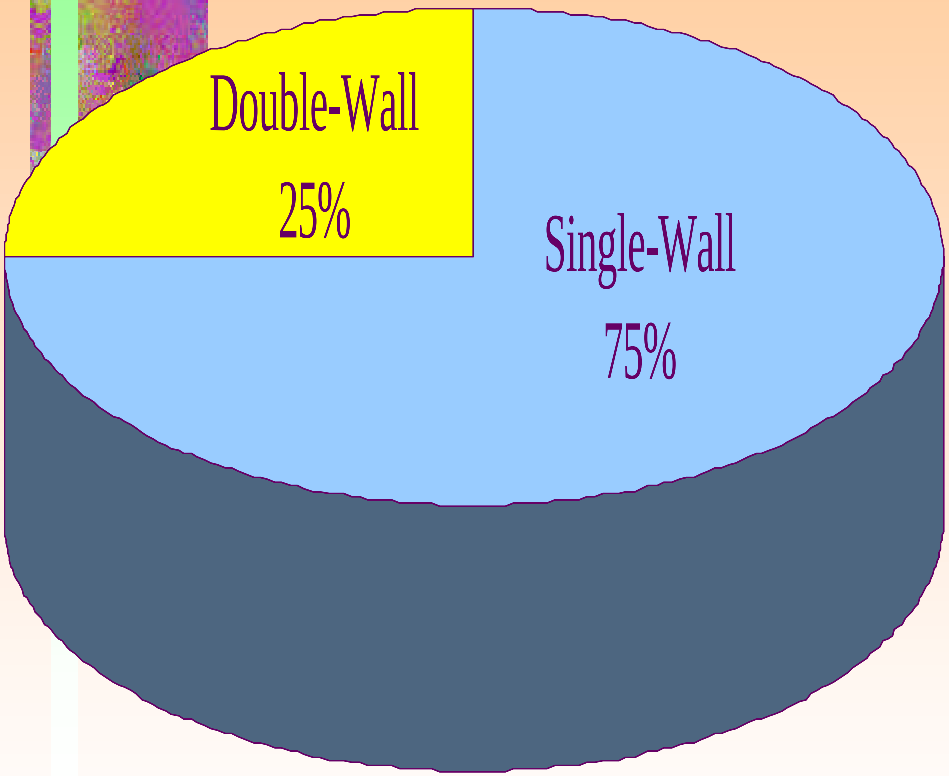
- An “upgraded” system has single-wall components.
- “Replaced” systems in California must have secondary containment.
- There are >2,300 single-wall systems within 1,000 feet of a public drinking water well.

Estimated Breakdown of UST Tanks in California



- Approximately 49,000 active USTs in California
  - 12,000 sw USTs
  - 37,000 dw USTs

Estimated Breakdown of UST Systems in USA



- Approximately 743,000 active UST systems in USA
  - 186,000 dw systems
  - 557,000 sw systems

Upgraded Systems Violations

- Turbine sumps not liquid tight
- Sensors in turbines raised
- Mechanical float (bead chain) set incorrectly
- Mechanical line leak detectors on S/W piping
- Numerous small leaks found at turbine and dispenser ends
- Systems operating in an alarm condition for extended periods
- Unprotected steel piping/fittings

Pipe dreams

- Single-wall steel piping can have cathodic protection added, but what was the condition of the piping?
- A reportable leak rate is over 0.1 gph for a once a year test. The leak rate for line leak detectors is 3 gph.
- Do the math.
- What really is buried?


AUG 2 2000


2001 2 20


JUN 28 2000

Replaced System Problems

- Are they really liquid tight?
- Are they vapor tight?

Legislature to the Rescue: SB 989 (1999, Sher)

- Field-Based Research
- Enhanced Leak Detection
- Secondary Containment Testing

Field-Based Research

- Quantify releases from upgraded and replaced UST systems
- Complete by June, 2002
- Contractor: UC Davis
- Relies on methodology used by Tracer Research, Inc.

Enhanced Leak Detection

- Applies to single-wall systems within 1,000 feet of a public drinking water well.
- Test method introduces an inert nonfuel substance into UST system with external detection.
- Leak rate detection at 0.005gph.
- Conduct every three years.

Secondary Containment Testing

- Test every three years.
- Must perform as well as it did upon installation.
- Can use enhanced leak detection.
- If cannot be tested, must be replaced.

Likely Findings

- Some liquid releases
- Many vapor releases

Commandment for Groundwater Protection

- Thou shalt neither discharge nor release any substance to the ground which is water soluble and resistant to biodegradation and would impart toxicity, taste, or odor at low concentrations in water.

Constituents of Concern?

- Salts
- Nitrates
- DBCP
- Solvents
- Benzene
- MTBE/Ethers
- Ethanol
- Alkylates

Commandment for Groundwater Protection

- Thou shalt neither discharge nor release any substance to the ground which is water soluble OR HAS A SPECIFIC GRAVITY GREATER THAN WATER and resistant to biodegradation and would impart toxicity, taste, or odor at low concentrations in water.

The Plusses and Minuses of Ethanol and Alkylates for Gasoline blending A Carmaker's Perspective

Lawrence Livermore National Laboratory Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California

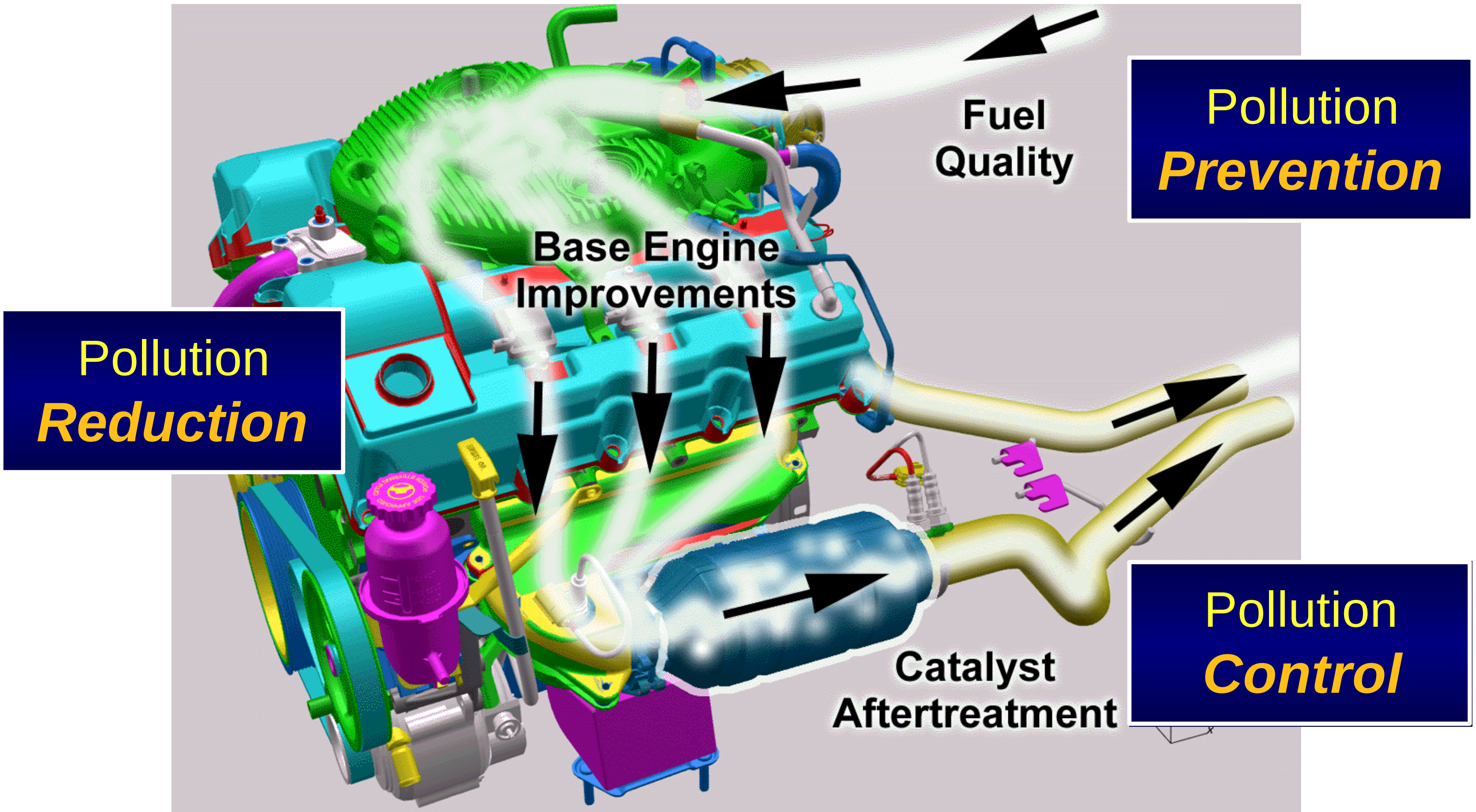
April 10-11, 2001

Loren K. Beard, DaimlerChrysler Corporation

The Vehicle/Fuel as a System Approach

- Throughout the process of the development of low emission vehicles and reformulated gasoline, the ARB has treated the vehicle and its fuel as a system
- Considerations of neither vehicle emissions standards nor fuel properties should be undertaken without consideration of impacts on the other
- The MtBE/groundwater issue in California brings another component to the system -- the environment in which fuels are transported and stored

Systems Approach - Pollution Prevention



The Success of California CBG

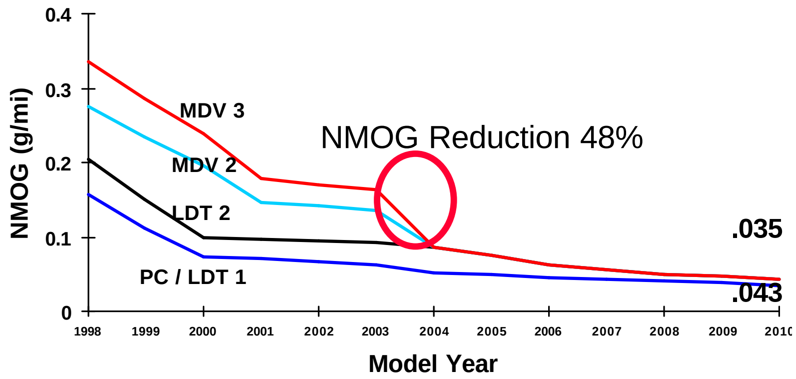
- LEV II Staff Report states, “ … tenet of the original LEV program is that the vehicle technology and fuels must be linked to achieve the greatest emission reductions”, i.e., improvements in vehicle hardware should be accompanied by improvements in fuel quality

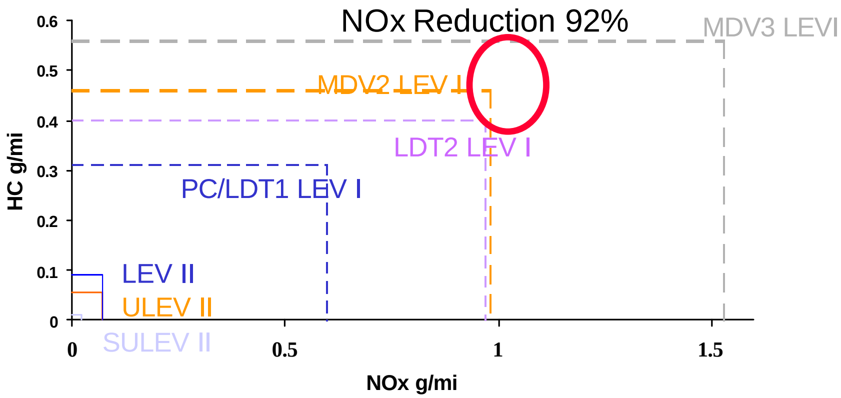
- “Cleaner-burning gasoline is the single biggest smog-reduction measure in California since the introduction of the catalytic converter in 1975 … No single measure in our history has reduced pollution by such a large amount in such a short time. California gasoline now is the cleanest in the world.” -- ARB, October, 1996

ARB Found Need for and Adopted LEV II Standards - ARB Staff Report November 15, 1998

- "State and federal air quality standards continue to be exceeded in regions throughout California"
- SIP called for adoption of technology-based emission control strategies for light-duty vehicles beginning in 2004 MY
  - Emission reductions of 25 tpd ROG+NOX by 2010 in South Coast
  - Additional technology measures, mobile source "Black Box", needs of 75 tpd
  - LEV II "make(s) progress on the Black Box"
- "Emission reductions are needed statewide."
- "The exhaust standards proposed in this rulemaking present a significant challenge to automobile manufacturers over the next ten years."

ARB LEV-II Vehicle TP Emission Requirements





- The LEV II vehicle emission standards cut emissions from some vehicles by over 92%, and all tailpipe and evaporative standards are tightened

Fuel / Vehicle System Synergies for Improved Air Quality

GASOLINE PROPERTIES FOR LEV II

CALIFORNIA LEV II ISSUE	GASOLINE PROPERTY ENABLER
0.010 g/mi NMOG (SULEV)	Lower Sulfur Aromatics Control Volatility Control
0.05 g/mi NOx (LEV/ULEV)	Lower Sulfur, Lower Olefins Deposit Control Narrow band of oxygen content
0.01 g/mi PM_{10}	Lower Sulfur Deposit Control Heavy Aromatics
120,000 Mile Durability (150,000 Mile Optional)	Lower Sulfur Deposit Control
Trucks to Car Standards	Lower Sulfur Deposit Control Volatility Control
OBD II Monitors	Lower Sulfur Volatility Control
SFTP	Lower Sulfur Volatility Control Narrow band of oxygen content
"Zero" Evap. and Refueling	Control of RVP, T_{10}, T_{50} No Waivers for RVP, T_{50}, T_{10}, or $T_{(V/L)=20}$ for EtOH
Exhaust Reactivity	Lower olefins Poly-substituted aromatics control

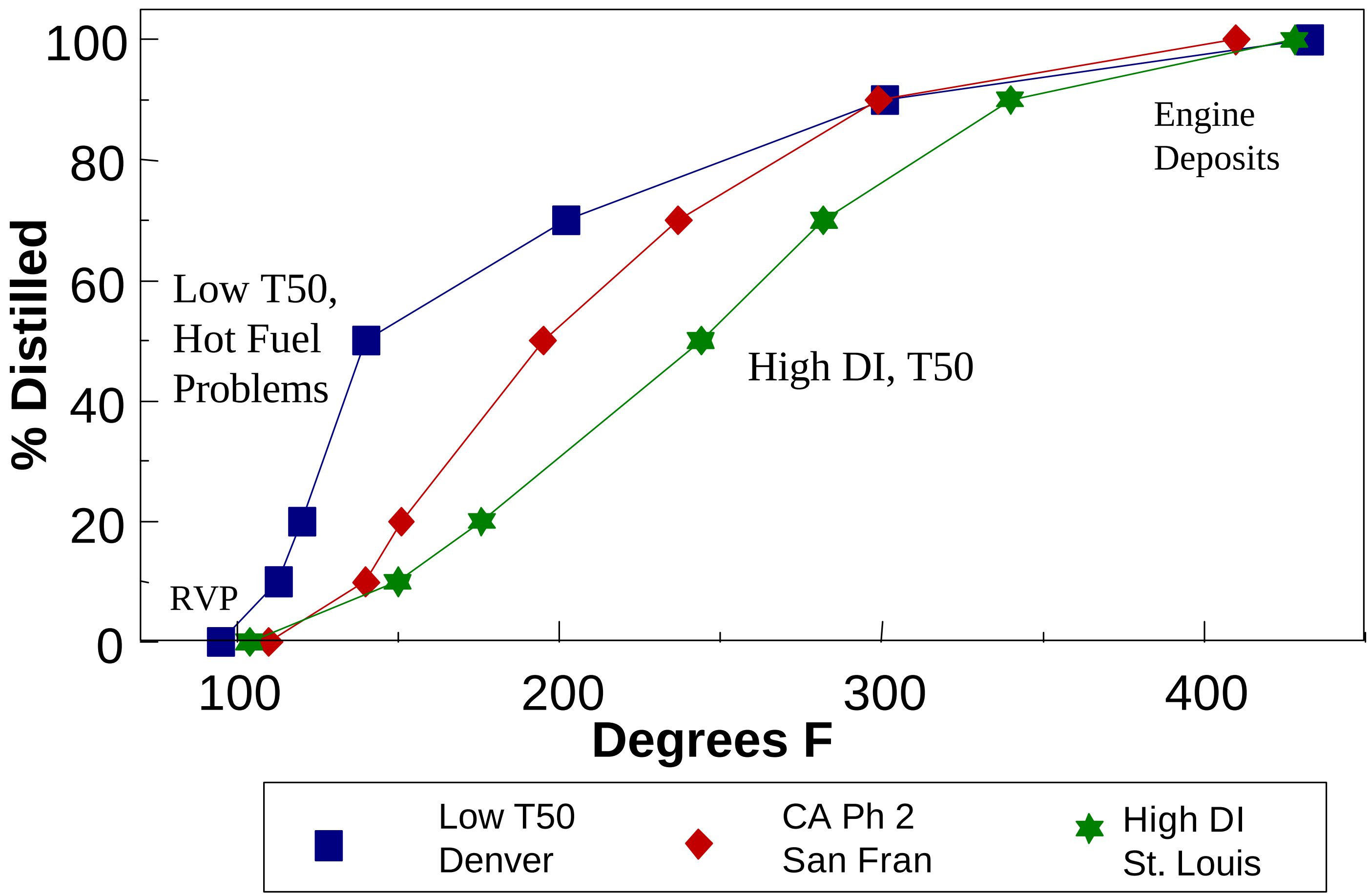
Gasoline Volatility

- Reid Vapor Pressure (RVP) of gasoline has been controlled as a means of reducing evaporative emissions
- However, other aspects of gasoline volatility, as measured by the distillation curve are important with respect to combustion. Unless constrained, these other volatility parameters (T-numbers) will increase as RVP is decreased
- Predictable gasoline volatility, as expressed in the distillation index (DI) is critical in maintaining a stoichiometric F/A ratio, which in turn is critical in reducing exhaust emissions. EPA recognizes that extremely tight control of F/A ratio is an enabler for tighter Tier 2 emissions standards

Gasoline Volatility (cont.)

- **RVP is important to**
  - **Cold Weather starting**
  - **Hot weather vapor lock**
  - **Evaporative Emissions**
- **ASTM D86 Distillation**
  - **Defines entire gasoline boiling range**
    - **T_{10}, T_{50}, T_{90} are the temperatures at which 10%, 50%, and 90% of a gasoline sample boils**
  - **The Distillation Index (DI) defines an empirical relationship between gasoline volatility and engine performance (driveability and emissions)**
- **DI = 1.5 X T_{10} + 3 XT_{50} + T_{90} + 20 (wt%oxy from EtOH)**

Three Typical Gasoline Distillation Curves



San Francisco and St. Louis from AAMA Summer '97 Survey
Denver from AAMA Fall '97 Shoulder Survey

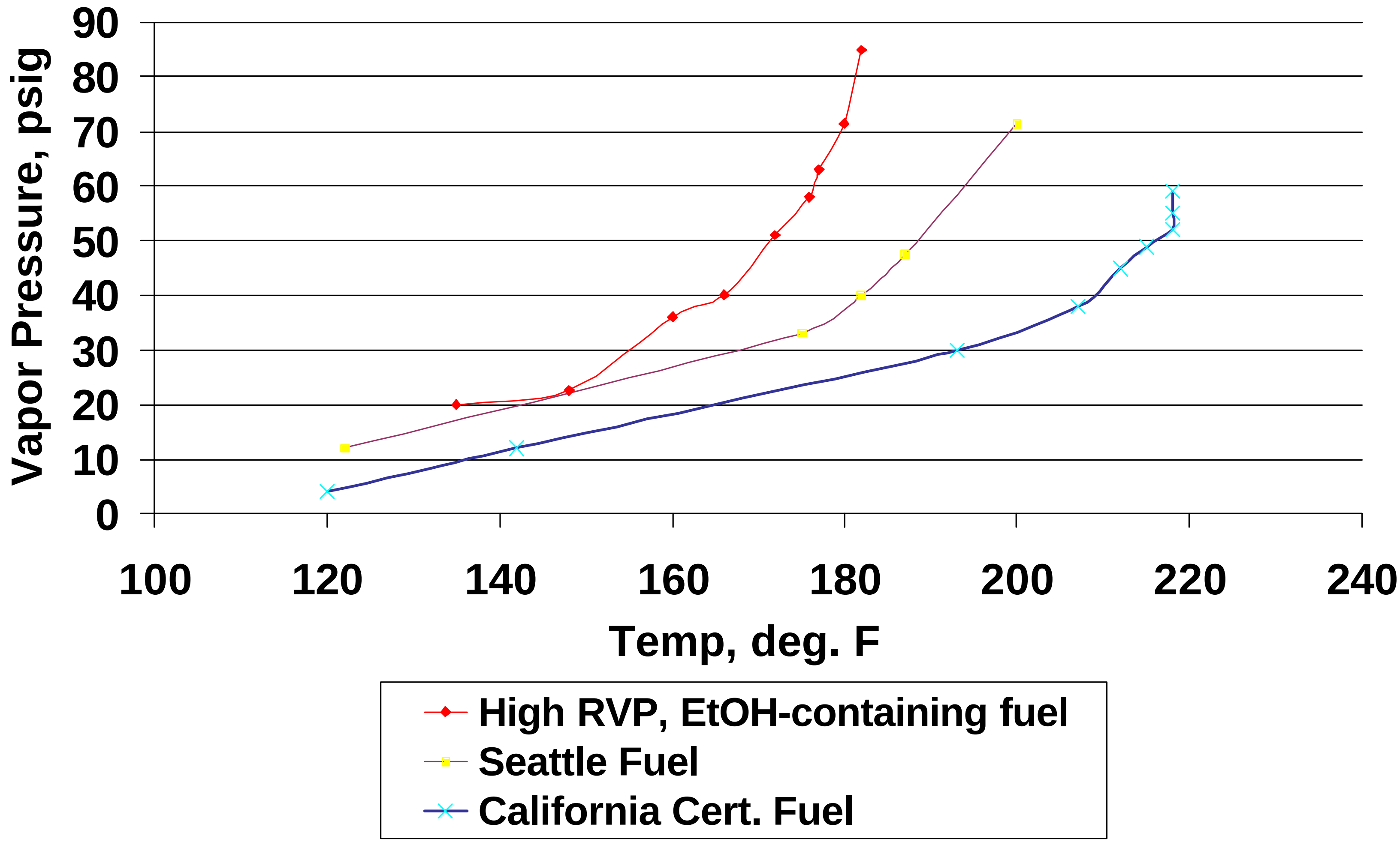
The Impacts of Ethanol and alkylates on Gasoline Volatility

- C-8 alkylates boil higher than the current T_{50} of California gasoline, thus, their increased use will lead to higher T_{50}, and the associated problems
- Ethanol does not blend ideally with gasoline with respect to volatility. i. e. it does not follow the Clausius-Clapeyron behavior
- Ethanol raises RVP, and depresses T_{50}, but not the DI, which is related to engine performance
- The polarity of ethanol may lead to increased permeation of fuel compounds through plastics and elastomers in the fuel system

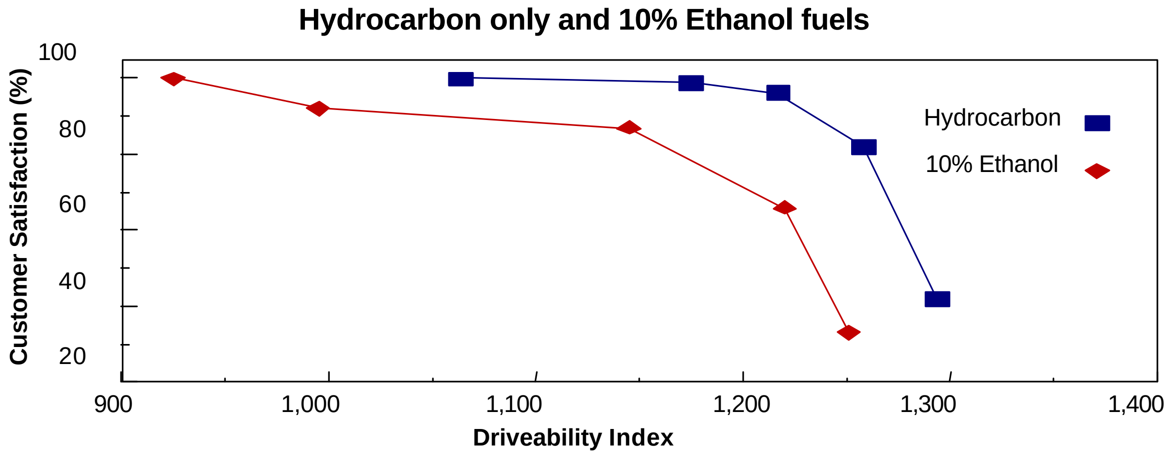
Fuel System Requirements for EtOH-Containing Fuels

- At any temperature where the fuel Vapor Pressure is greater than the system operating pressure, vapor will form.
- Thermodynamics predicts when vapor will form, but not how much or where.
- Coordinating Research Council Work suggests that fuels should be limited to a vapor pressure of no more than 450 kPa at 250 degrees F.

Vapor Pressure vs. Temp. for EtOH-Containing, and non-EtOH-containing Fuels



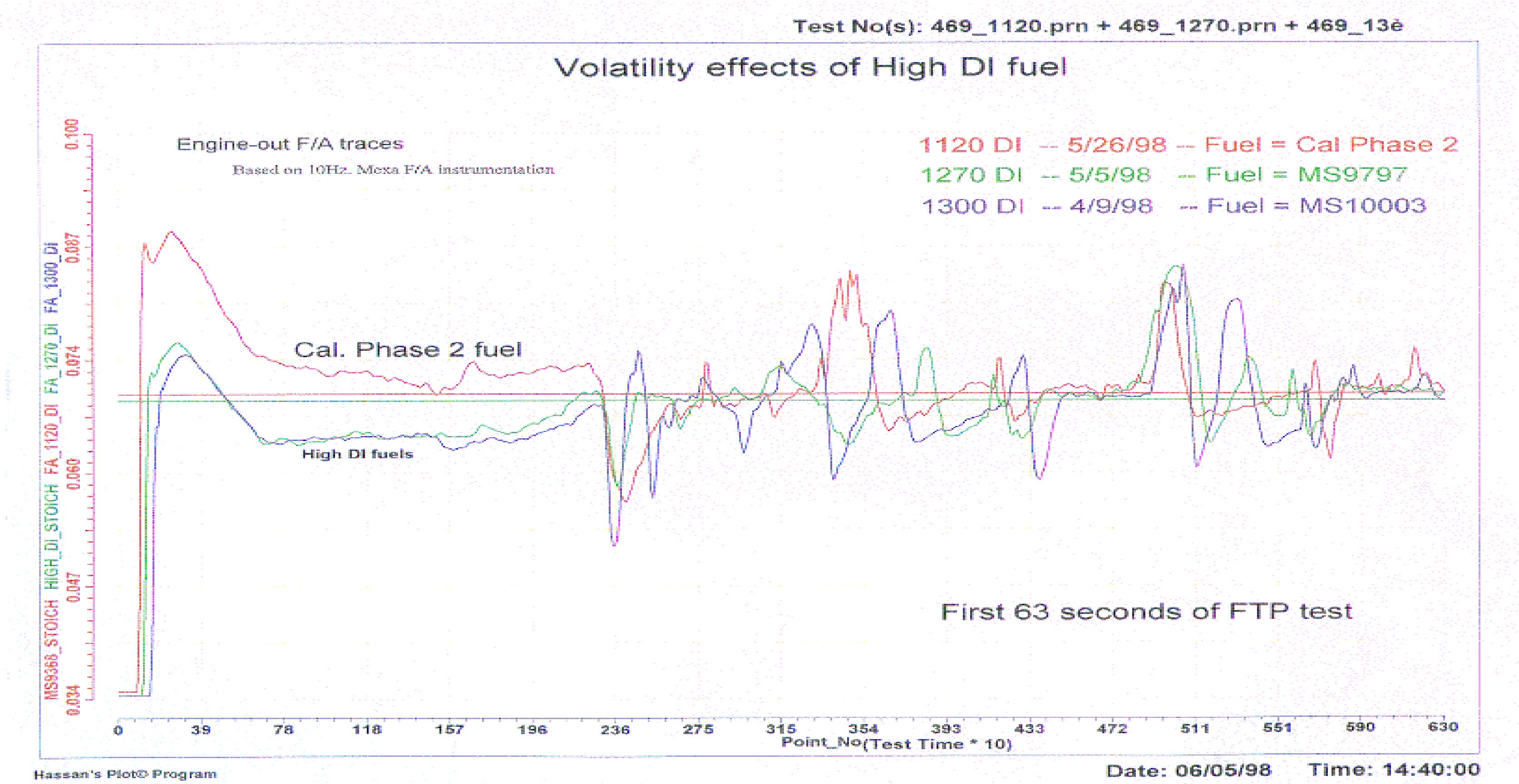
Volatility Control Very Important to Vehicle Owners and Air Quality



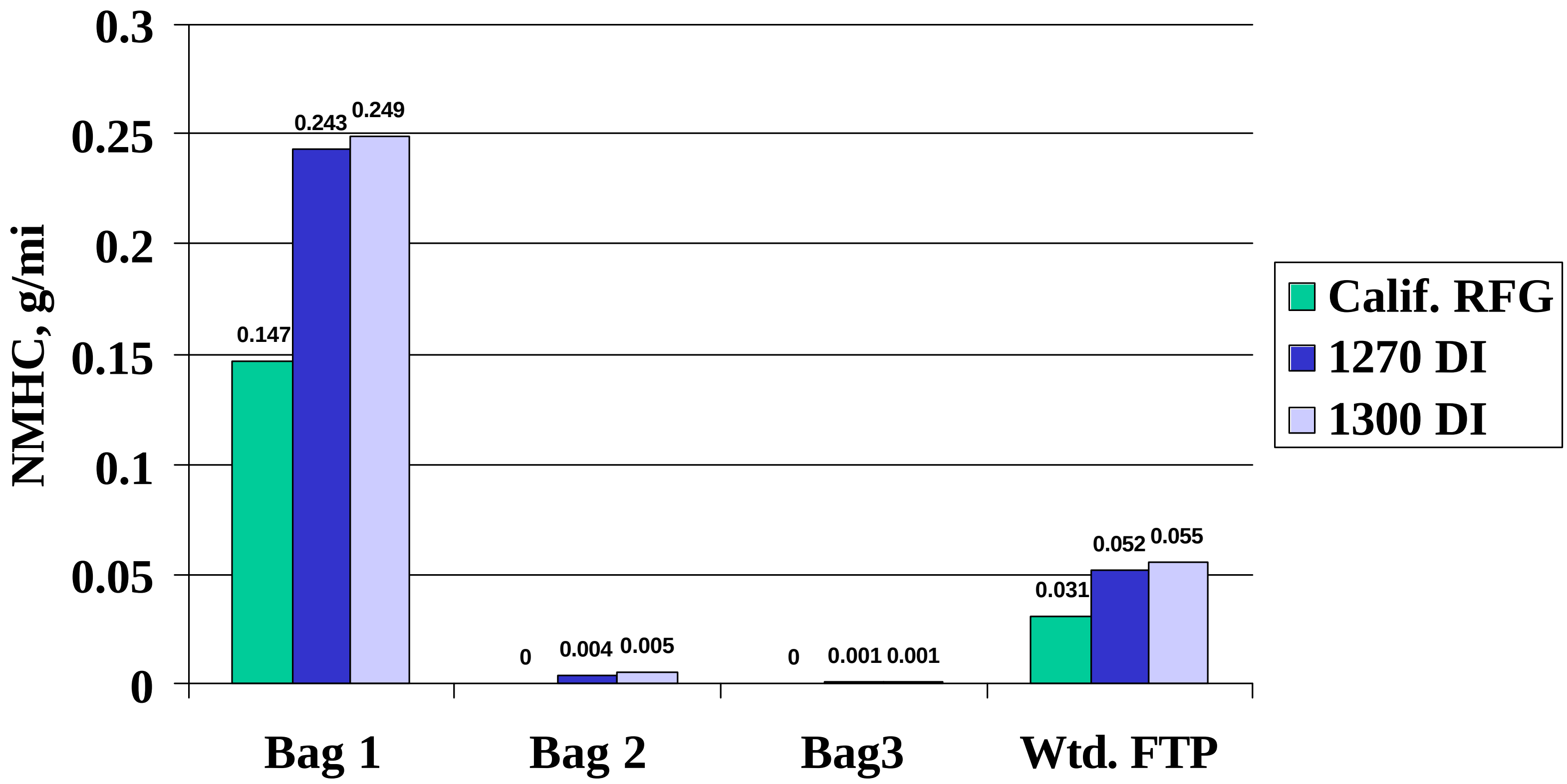
1993 CRC Driveability Study

- Distillation Index = 1.5* T_{10} + 3* T_{50} + T_{90} + 20* wt oxygen from ethanol
- Equation based on CRC studies derived from consensus auto and oil industry research
- Worldwide Fuel Charter recommends 1200 maximum - endorsed by over 60 companies

DI Effects on F/A Ratio Emissions from a 1998 ULEV



DI Effects on NMHC Emissions from a 1998 ULEV



Plusses and Minuses of Ethanol and C-8 Alkylate vs. MtBE

	Ethanol	C-8 alkylate
Sulfur, Aromatics, Olefins	0	0
Octane	0	0
Minimum T50, Hot fuel handling	-	+
DI	0	-
Evap. Emissions	-	0
Permeation	-	+

Summary

- New vehicle standards must be accompanied by improvements in fuel quality, both to enhance the performance of existing technology for air quality improvements and to enable new technologies.
- Statewide, ARB has acknowledged the need for further emission reductions.
- Gasoline volatility plays a major role in vehicle performance and emissions
- Alkylates, although sulfur-, aromatic-, and olefin-free, C-8 alkylate as a replacement for MtBE will raise T_{50}, and the distillation index, thereby increasing emissions, and reducing vehicle performance, unless, some other heavy component is removed (heavy reformate?).
- Ethanol, reduces T_{50}, but not DI, and its impact on RVP will lead to higher evaporative emissions. Permeation needs to be studied further, but available data suggest a need for concern. Hot fuel handling can be managed, but only if the proper parameters are controlled.

California Issues - Expanded Use of Ethanol and Alkylates

LLNL Workshop
Oakland, Ca
April 10-11, 2001

Gordon Schremp
California Energy Commission

Introduction

- Supply Concerns
- Logistics
- Cost Impacts
- Closing Remarks

Supply Concerns

- Refinery Production
- Ethanol Availability
- Alkylate Availability

Supply Concerns - Refinery Production

- California Gasoline Production
  - Will not meet demand by 2003, at least a 6-10 % shortfall
  - Production capacity will decline slightly
  - Demand will be over a million barrels per day by 2003, 6 % greater than 2000

Supply Concerns - Refinery Production (cont.)

- California Gasoline Supply
  – Ethanol provides little, if any, supply benefit during the majority of the year
  – During the low Rvp season (8 months of the year), ethanol in and pentanes out
  – During the winter months, refiners can use butanes and pentanes
  – California will continue to meet demand through increased imports, if the clean components can be obtained

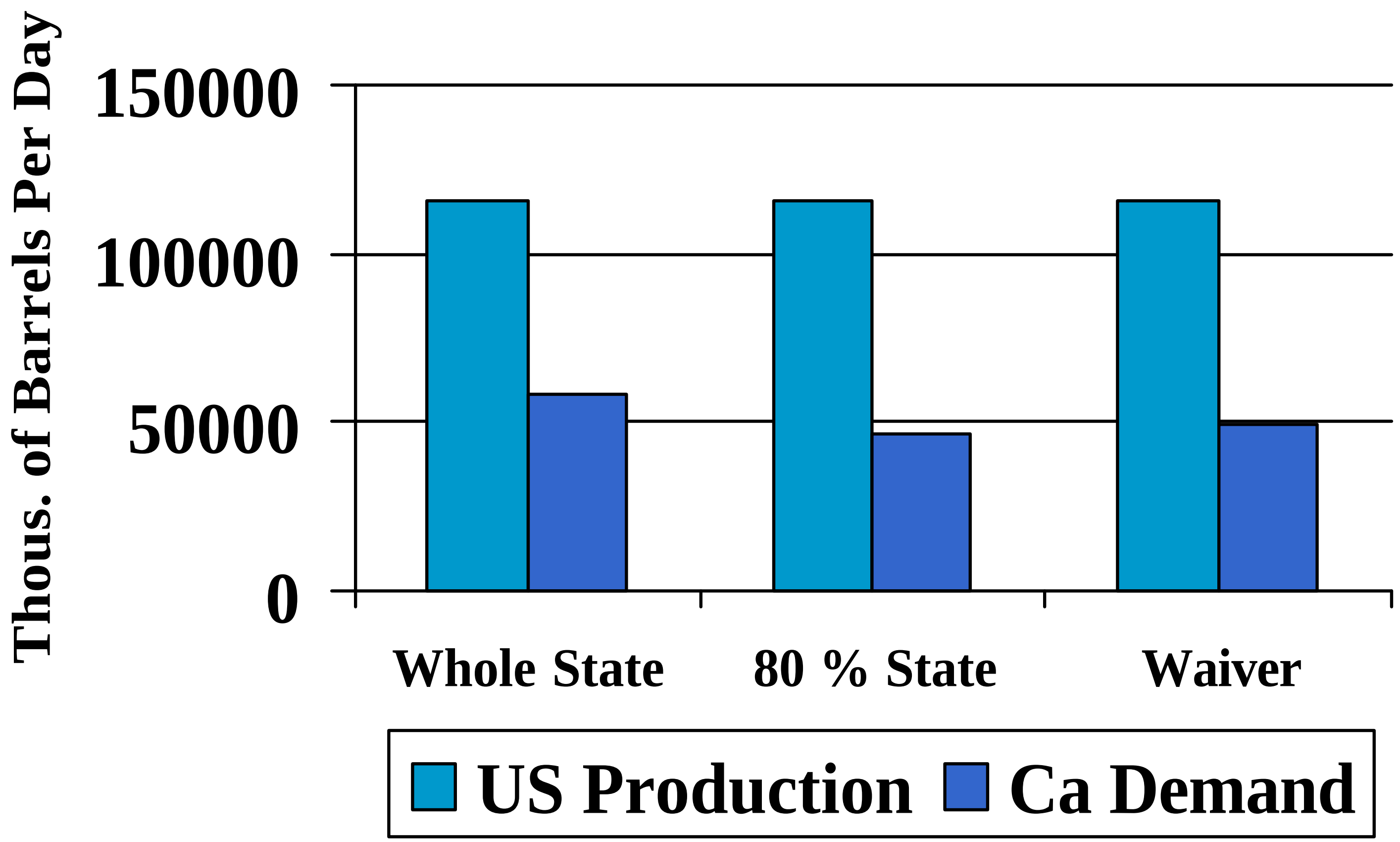
Supply Concerns - Ethanol Availability

- Ethanol Concentration
  - Refiners will use 5.7 % ethanol by volume
  - Some ethanol in use now, but MTBE use will continue until 4th quarter of 2002
  - Most refiners must complete modifications to facilities to be able to blend ethanol during the low Rvp season

Supply Concerns - Ethanol Availability (cont.)

- Ethanol Demand
  - – California will require significant quantities of ethanol
  - – Without a waiver, 50 percent of current US production, 42 percent with a waiver
  - – Expansion of ethanol production capacity must be significant and on line by the Fall of 2002
  - – Ethanol from California biomass will not be available prior to 2004 - 2005

US Production vs. Calif. Demand



Supply Concerns - Alkylate Availability

- Alkylate Concentration
  - Already in California gasoline
  - Concentration expected to grow from 15 to 25 percent by volume
  - No equivalent replacement available with similar blending properties

Supply Concerns - Alkylate Availability (cont.)

- Alkylate Demand
  - – Imports could top 50 KBPD
  - – Critical blending component during the low Rvp season
  - – Demand increasing outside California to help achieve complying blends of Federal RFG with ethanol
  - – Demand will continue to grow if other areas of the US phase out the use of MTBE

Supply Concerns - Alkylate Availability (cont.)

- Alkylate Supplies
  - Availability a concern, supplies are limited
  - Prices have reached extraordinary levels this year, 35 to 40 cents over USGC clear
  - Sufficient conversions of merchant MTBE facilities unlikely prior to end of 2002
  - “Wait-and-see” stance will contribute to rough transition away from MTBE

Logistics

- Movement of Ethanol to California
- Ethanol Logistics Within the State
- Fungibility & Flexibility Issues
- Alkylate Logistics

Logistics - Ethanol to California

- Marine Vessels
  - US Jones Act vessels will be necessary
  - Fleet size is declining
  - Freight rates could exceed 20 cents per gallon
- Rail Cars
  - Many terminals unable to receive rail
  - Unit car use should evolve, but where?
  - Rolling stock availability and scheduling delays could become issues

Logistics - Within California

- Pipeline Movement
  - Petroleum product pipelines will not be used to transport ethanol or blends
  - Some dedicated pipelines will transport neat ethanol to tankage from tankers
- Terminals
  - Ethanol will be blended at the tanker truck
  - Majority of terminals will receive ethanol from tanker trucks
  - Truck traffic will increase, especially in proximity to terminals

Logistics - Fungibility & Flexibility

- Fungibility
  - – Phase 3 CaRFG with ethanol and non-oxy blends cannot be combined
  - – Segregation needs will grow
  - – Adequacy of tankage, especially at terminals, will be a concern

Logistics - Fungibility & Flexibility (cont.)

- Flexibility
  - Today, refiners can increase concentration of MTBE to ensure adequacy of supplies
  - This practice will be severely diminished or impractical with ethanol blends
  - Failure to receive a waiver from the Federal minimum oxygen requirement will reduce flexibility for refiners
  - Reduced flexibility will translate to higher prices at the pump

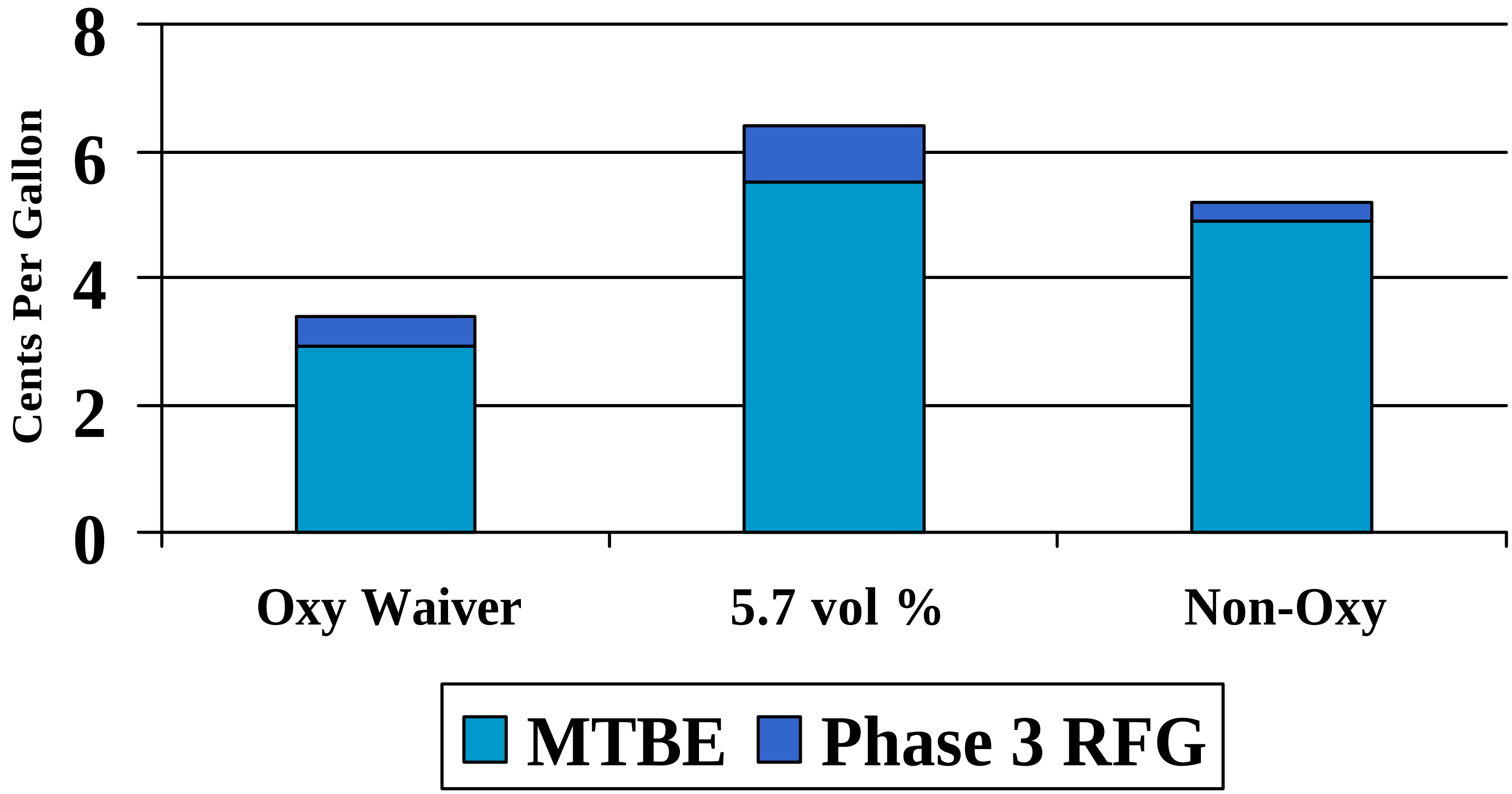
Logistics - Alkylate

- Transportation Less of an Issue
  - Can use product pipelines
- Alkylates Blended at the Refinery

Cost Impacts

- Ethanol & Non-Oxy Blends
- Ethanol & Alkylate Pricing

Impacts of MTBE Removal and Phase 3 RFG - Average Cost



Cost Impacts - Ethanol & Non-Oxy Blends

- Comparison
  - Waiver scenario least expensive
  - Ethanol case most expensive
  - Failure to issue waiver will cost California consumers at least $450 million per year
  - Loss of fungibility and flexibility associated with the use of ethanol will likely result in costs to consumers well in excess of the original 3 to 6 cent per gallon estimate

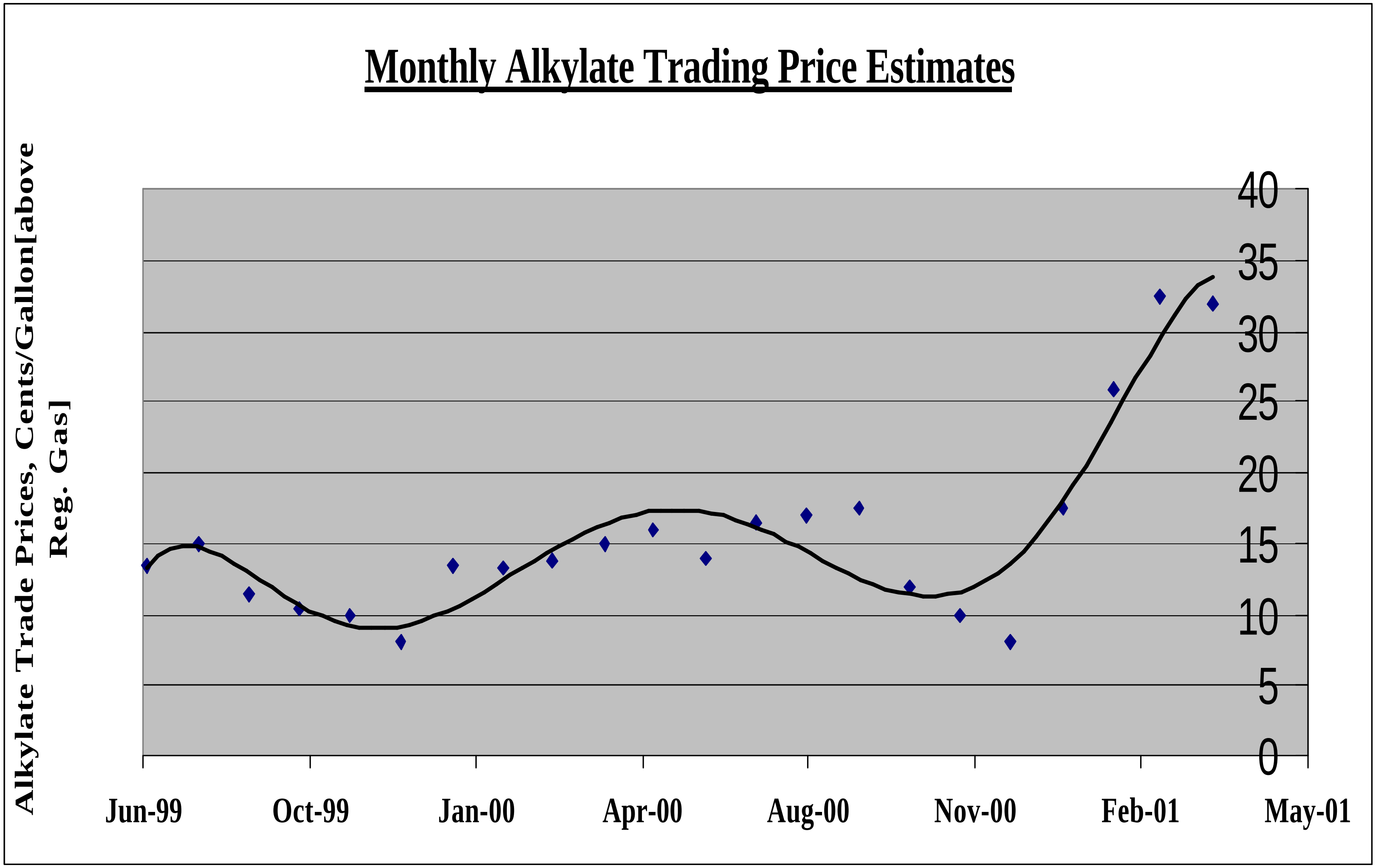
Cost Impacts - Ethanol Pricing

- Ethanol Price Increases
  - Previous estimates too low
  - Recent market prices were reflecting jump in demand
  - Without additional capacity, future prices could be even greater than highest estimates

Cost Impacts - Alkylate Pricing

- Alkylate Price Increases
  - Previous estimates too low
  - High natural gas prices have contributed to recent price spike
  - Market is reflecting desirability of clean components in US and other countries
  - Without additional alkylate capacity build through MTBE plant conversions, future prices could be even greater than today

Cost Impacts - Alkylate Pricing



Other Concerns

- Availability of Imports for California
- Marine Transportation
- MTBE Removal Outside the US
- Renewable Mandate
- Price Spikes

Other Concerns - Availability of Imports

- Outside Sources Could Decline
  - Not all refiners that currently supply the California market will be in a position to produce low volatility base gasoline
  - Import potential for CARBOB could drop
  - Competition for existing production would increase
  - Alkylate and iso-octane supplies would increase in value and importance

Other Concerns - Marine Transportation

- US Jones Act Unduly Increasing Costs
  - Most waterborne ethanol deliveries will need US vessel
  - All alkylate and CARBOB shipments from USGC must arrive via Jones Act ships
  - Cargo movements have been constrained and shipping costs have jumped
  - Situation will deteriorate over the near term
  - Suspension of Jones Act for product movements would directly benefit California consumers

Other Concerns - MTBE Removal Outside The US

- Demand for Premium Blending Components Will Increase
  – Alkylate supplies could be critical
- Ethanol Demand Will Surge
  – Excluding California, demand for rest of U.S could total 150 to 200 thousand barrels for day by 2004
  – Logistical challenge, especially in the Northeast
- Gasoline Will Become More Expensive

Other Concerns - Renewable Mandate

- Renewable Ethanol Mandate Will Not Benefit Gasoline Supplies
  - Flexibility will be diminished if ethanol use required during the low Rvp season
  - Costs will rise if ethanol demand increases beyond today’s production levels
  - Demand for alkylates will be higher

Other Concerns - Price Spikes

- Frequency and Magnitude of Price Spikes Could Increase
  - Reduced flexibility
  - Potential decline of import availability
  - Difficulty in obtaining replacement supplies quickly
- Ultimate Pump Price to Consumers Could be Significantly Greater than the Projected Production Cost Increases of an MTBE Phaseout

Closing Remarks

- Producing and Dispensing Gasoline Will be More Challenging
- Removal of Oxygen Mandate Would Minimize Cost Impacts of MTBE Removal and Restore Some Flexibility
- Failure to Resolve the Oxy Waiver Issue is Delaying Some Investment Decisions
  - Ethanol producers
  - Potential MTBE plant conversions

Closing Remarks (cont.)

- Additional MTBE Phaseouts Throughout the U.S. Could Imperil the Adequate Availability of Ethanol and Blending Component Supplies for California and the Rest of the Country
- The Decision to Phaseout MTBE Should Not be Taken Lightly

KINDER MORGAN ENERGY PARTNERS

Distribution Implications For California With Increased Use Of Ethanol

Who Is Kinder Morgan ?

- KMEP owns and operates one of the largest product pipeline and terminal systems in the country.
- Operating more than 30,000 miles of natural gas and products pipelines.
- The nations leading provider of CO_2 for use in enhanced oil recovery projects.

Who Is Kinder Morgan

Kinder Morgan's Pacific Region

- Over 3,300 miles of pipeline.
- Transporting over 1 million barrels of refined products (gasoline, diesel, commercial and military turbine) per day.
- Terminal Locations in California, Arizona, Nevada, Oregon, Texas and New Mexico.

WASHINGTON
MONTANA
OREGON
IDAHO
WYOMING
CALIFORNIA
NEVADA
UTAH
COLORADO
ARIZONA
NEW MEXICO
TEXAS
MEXICO
PACIFIC OCEAN
PORTLAND
ALBANY
EUGENE
CHICO
ROCKLIN
RENO
FALLON
SACRAMENTO
BRADSHAW
LAKE TAHOE
RICHMOND
CONCORD
STOCKTON
SAN FRANCISCO
BRISBANE
SAN JOSE
ATWATER
FRESNO
LEMOORE
BAKERSFIELD
LOS ANGELES
NORWALK
COLTON
WATSON
ORANGE
NILAND
MISSION VALLEY
IMPERIAL
SAN DIEGO
YUMA
PHOENIX
TUCSON
EL PASO

Current Conditions Under CARB Phase 2

- Refineries Blend MTBE into gasoline to meet state and federal oxygen requirements (approximately 11% volume).
- With MTBE, refineries benefit from octane which helps in production of premium gasoline.
- Gasoline meets all of the fuel specifications prior to shipment.

Increasing Use Of Ethanol Talking Points

- Volume loss of 11% in pipeline shipments.
- Terminals do not have access for bulk receipt of ethanol (rail car and/or barge).
- Gasoline must be blended with ethanol at the terminal racks to meet final specifications.
- Environmental Issues?

Reduction In Pipeline Volumes

Why not ship ethanol by pipeline

- Ethanol removes oxide scale from the internal pipe wall exposing fresh metal.
- Internal pipe wall is then subject to internal corrosion.
- Little evidence that corrosion inhibitors would be effective over long distances.
- Internal corrosion leads to leaks.

Terminal Access For Bulk Ethanol Shipments

Pipelines and associated terminals were originally constructed in late 1950's and early 1960's in remote locations.

Urban sprawl has surrounded the terminals.

- Orange Terminal Neighbors: Arrowhead Pond, Anaheim Stadium, 16-Screen movie & restaurant complex.
- San Diego Terminal Neighbors: Qual-Com Stadium and luxury homes.

Terminal Access For Bulk Ethanol Shipments

- Sacramento Terminal Neighbors: Homes, businesses and restaurants.

What's The Bottom Line:

- The only method for getting ethanol into terminals will be by truck.

Rack Blending Of Ethanol

Currently Under CARB Phase 2

- Refinery testing and certification of fuel quality.
- Kinder Morgan random testing upon receipt.
- Kinder Morgan tank testing to ensure quality.

With ethanol blending, we have one opportunity to get it correct (you can't test every truck).

Environmental & Safety Issues

The Key Is: Prevention – Prevention – Prevention

Materials Compatibility Issues:

- Epoxy Tank Coatings
- Teflon Seals & Rings

Water Treatment Systems: Future Standards?

Fire Hazards & Prevention

What's The Impact On The Distribution System

We All Have To Work A Little Harder

- Industry coordination with ethanol producers and distributors for adequate supply.
- Coordination with transporters for efficient truck utilization and terminal off-loading of ethanol.

What's The Impact On The Distribution System

We All Have To Work A Little Harder.

- Agency development and approval of standardized test methods to ensure ethanol quality.
- Engineer more effective methods to keep chemicals (petroleum, ethanol, MTBE) out of the environment.

The Message Of The Day

- The distribution system can handle the increasing use of ethanol.
- Currently blend ethanol in Phoenix and Tucson Arizona, Reno and Las Vegas Nevada as well as Portland and Eugene Oregon.
- In regards to California, it will take a cooperative effort by everyone.

We All Have To Work A Little Harder.

Environmental Consequences of Increased Use of Ethanol and Alkylates in California Fuels

April 10-11, 2001

Framework for Comparative Evaluation of Environmental Impacts of Fuel Options

J. Michael Davis, Ph.D.

National Center for Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC

US EPA Office of Research and Development

NCEA
National Center For Environmental Assessment

“Compared to gasoline, the ethers MTBE and ETBE have relatively large aqueous solubilities and would likely leach more rapidly through soil and groundwater. Also, limited data suggest that ethers may be persistent in sub-surface environments.”

U.S. EPA (1992)

“Very little is known about emissions and releases from MTBE and ETBE storage and distribution, making this area an appropriate target for research.”

U.S. EPA (1992)

“Research Objectives:

1. Assess the impact of reformulated gasolines on the potential for groundwater contamination and resultant pollutant exposure.”

U.S. EPA (1992)

U.S. EPA (1992):

Alternative Fuels Research Strategy

US Environmental Protection Agency

Office of Research and Development
Report EPA/600/AP-92/002

www.epa.gov/ncea/pdfs/mtbe/altfuel.pdf

Risk Assessment

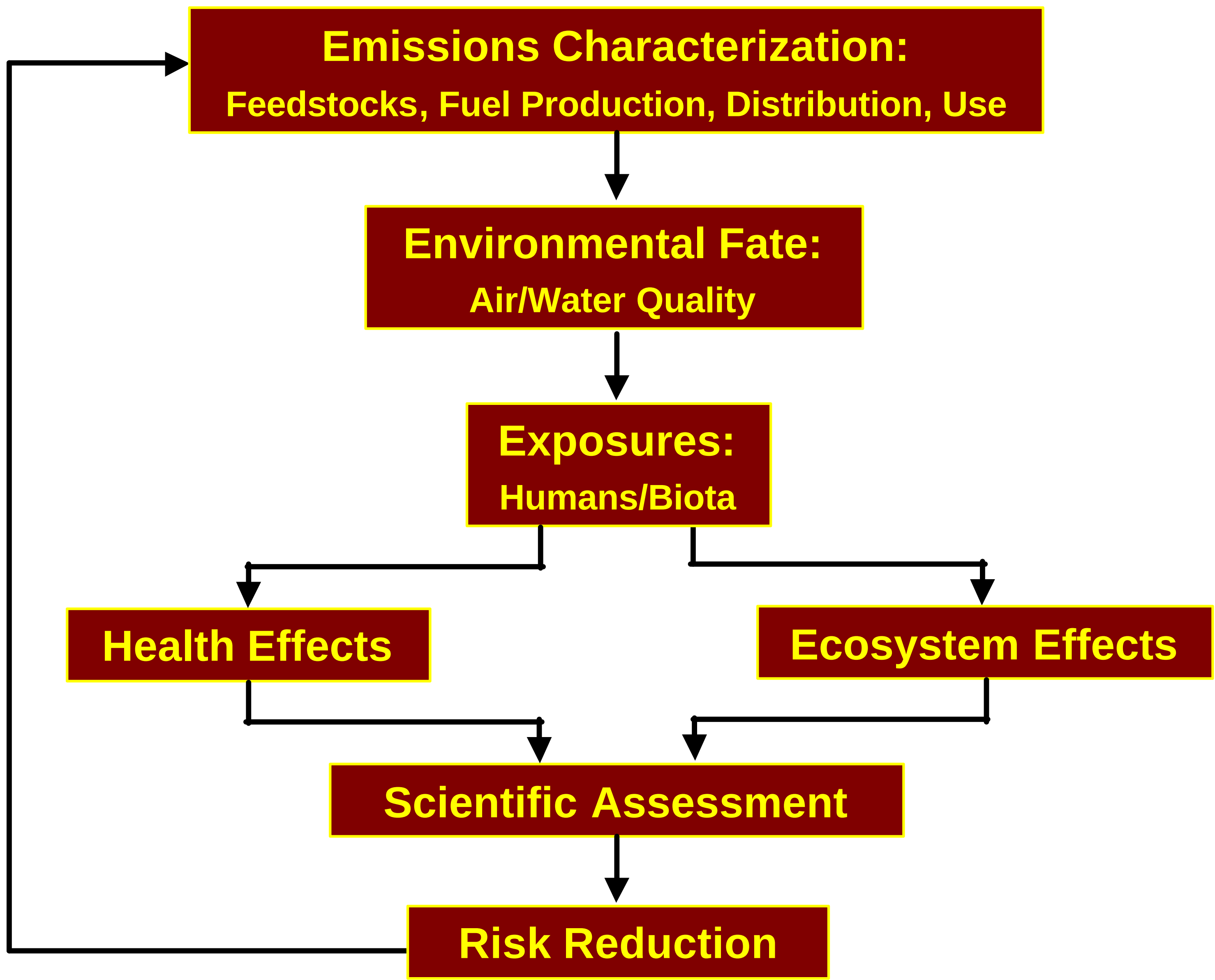
Hazard Identification
(Qualitative)

Dose-Response
(Quantitative)

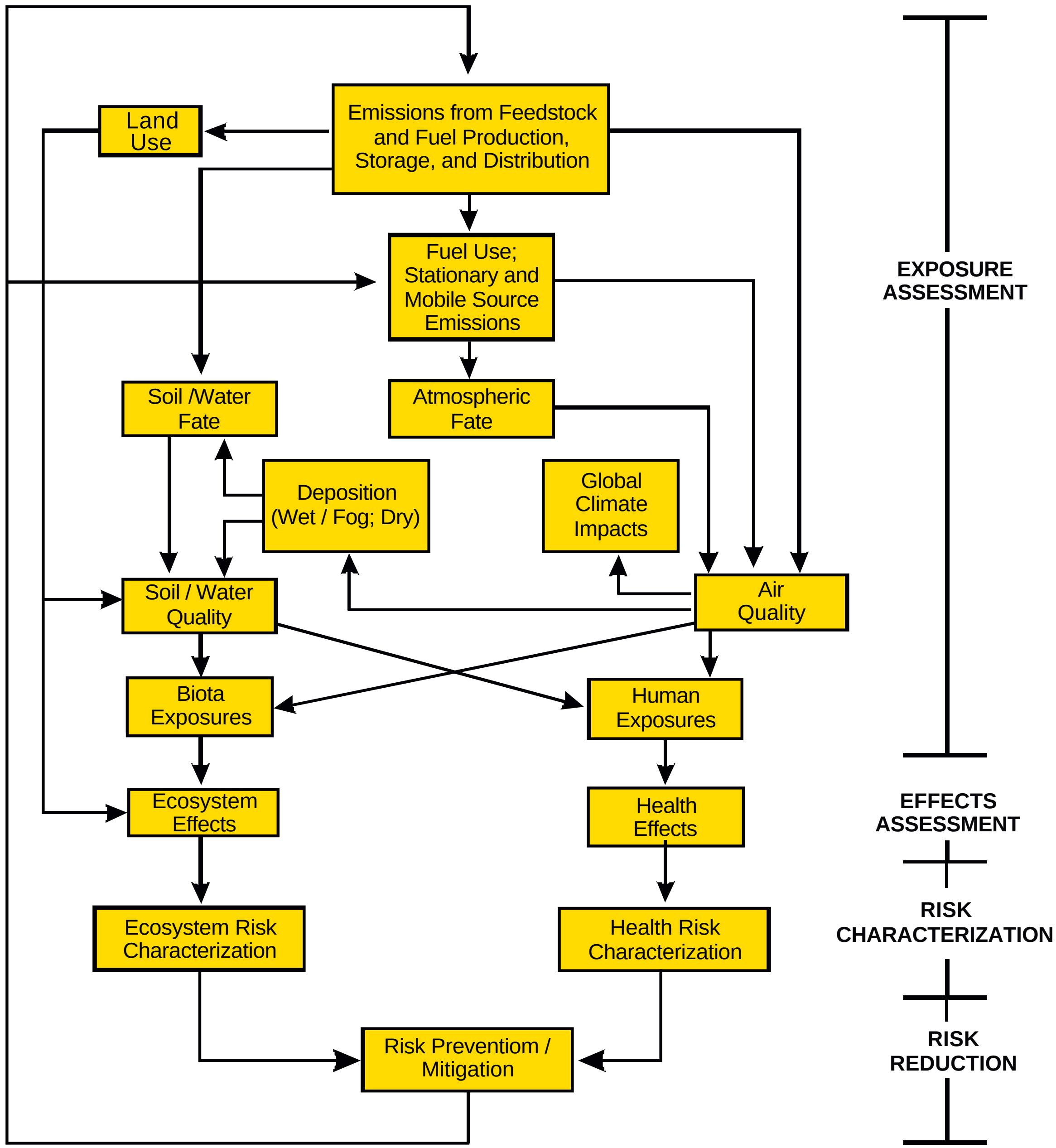
Exposure
(Population contact)

Risk Characterization

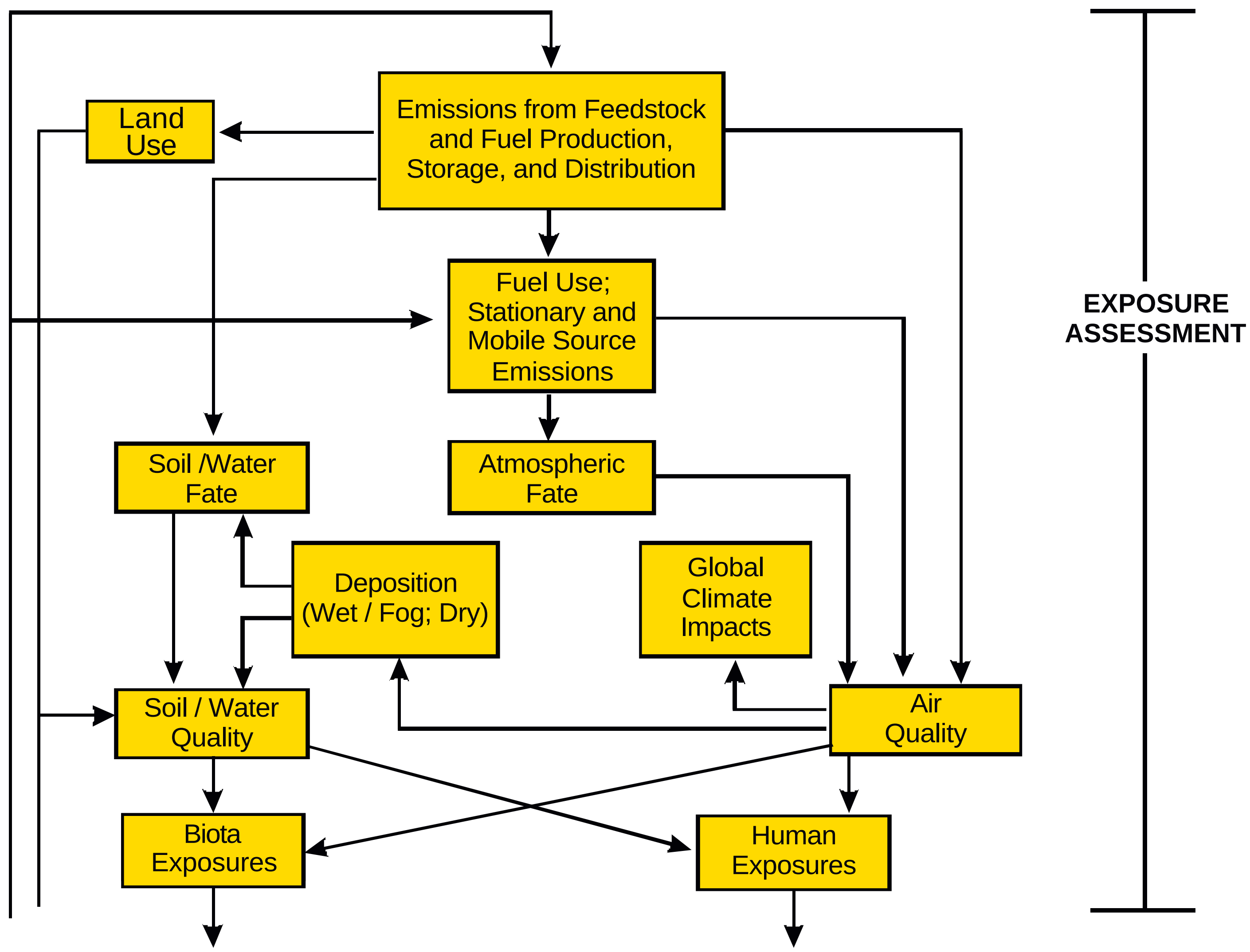
(Incidence of adverse effect)


Emissions Characterization:
Feedstocks, Fuel Production, Distribution, Use
Environmental Fate:
Air/Water Quality
Exposures:
Humans/Biota
Health Effects
Ecosystem Effects
Scientific Assessment
Risk Reduction

LCA / Risk Assessment Framework



LCA / R.A. Framework: Exposure Component



Some Possible Fuel Options for Comparative Assessment

- RFG/MTBE
- RFG/Ethanol
- RFG/nonOxygenate
- NOTE: These fuel options and the specific issues identified on the following pages are for illustrative purposes. They do not represent a judgment that these are necessarily the only options or the most important issues for consideration.

Source/Emissions Characterization

	RFG with:		
	MTBE	**EtOH**	**No Oxy**
Feedstock	Methane	Pesticides	Ref. Pt.?
Production	-- VOCs, GHGs --		”
Distribution	Small/chronic	Large/acute	”
Storage	-- Materials compatibility --		”

Source/Emissions Characterization (cont.)

	RFG with:		
	MTBE	**EtOH**	**No Oxy**
Use (evap. & combust.)	Air toxics, NOx, CO, etc.	CH_3CHO, alkylates, etc.	Alkylates, toluene, ??

Environmental Fate

	RFG with:		
	MTBE	**EtOH**	**No Oxy**
Air	HCHO, TBF	PAN	?
Subsurface	TBA	BTEX incrs.?	Alkylates
Surface Water	?	?	?

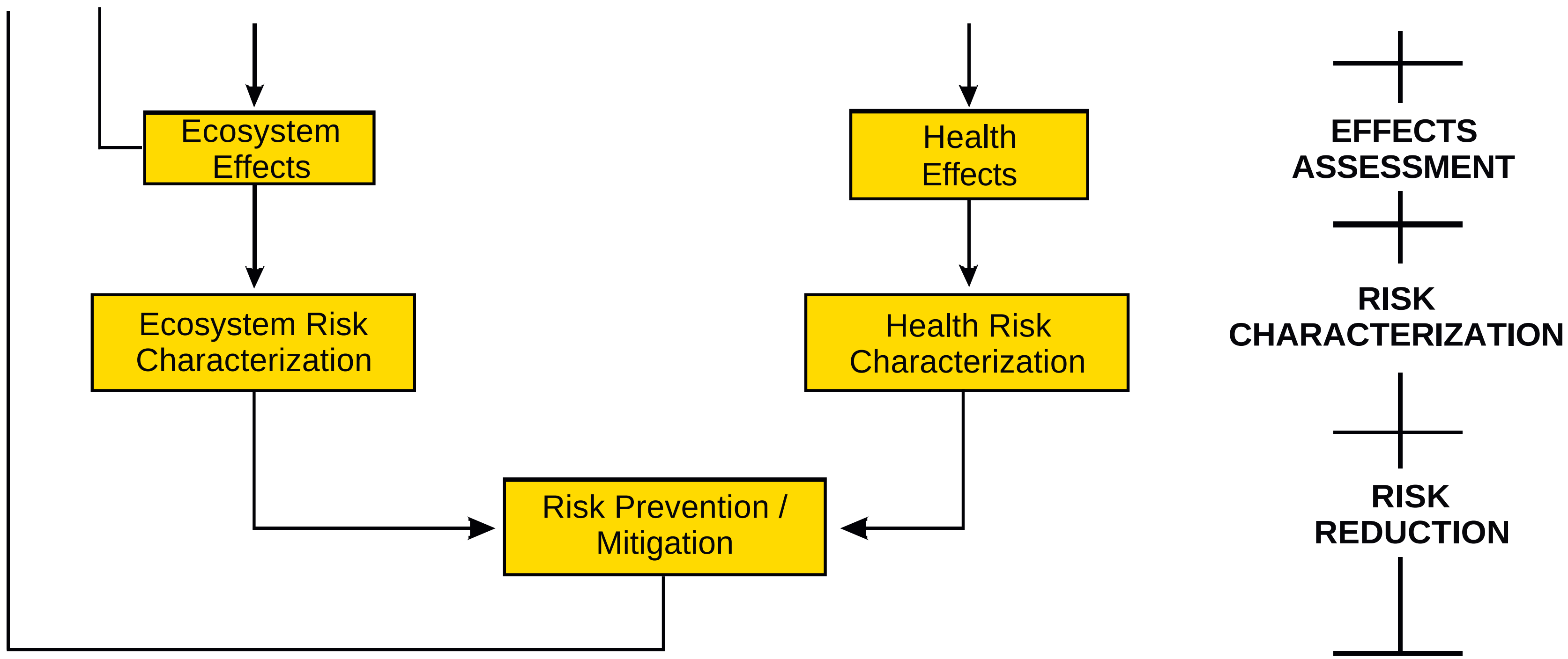
Environmental Quality

	RFG with:		
	MTBE	**EtOH**	**No Oxy**
Air	--	Air toxics, CO, O_3, GHGs	--
Subsurface	MTBE	EtOH, BTEX, alkylates	Alkylates
Surface Water	”	”	”

Exposure Assessment

	RFG with:		
	MTBE	**EtOH**	**No Oxy**
Human	---	Acute/Chronic	---
	--	Personal & Population Exposures	--
	---	Cumulative & Mixtures	---
Biota	---	Acute/Chronic	---
	---	Aquatic/Terrestrial	---

LCA / R.A. Framework: Cont'd.



Risk Assessment

Hazard Identification
(Qualitative)

Dose-Response
(Quantitative)

Exposure
(Population contact)

Risk Characterization

(Incidence of adverse effect)

Health Effects

	RFG with:		
	MTBE	**EtOH**	**No Oxy**
Acute	Neurobehavioral, Respiratory, Organoleptic, etc.?		
Chronic	Cancer Potency Inhalation RfC Oral RfD		

Ecosystem Effects

	RFG with:		
	MTBE	**EtOH**	**No Oxy**
Terrestrial			
Aquatic	--	Organism	--
Freshwater	--	Population	--
Marine	--	Community/Ecosystem	--

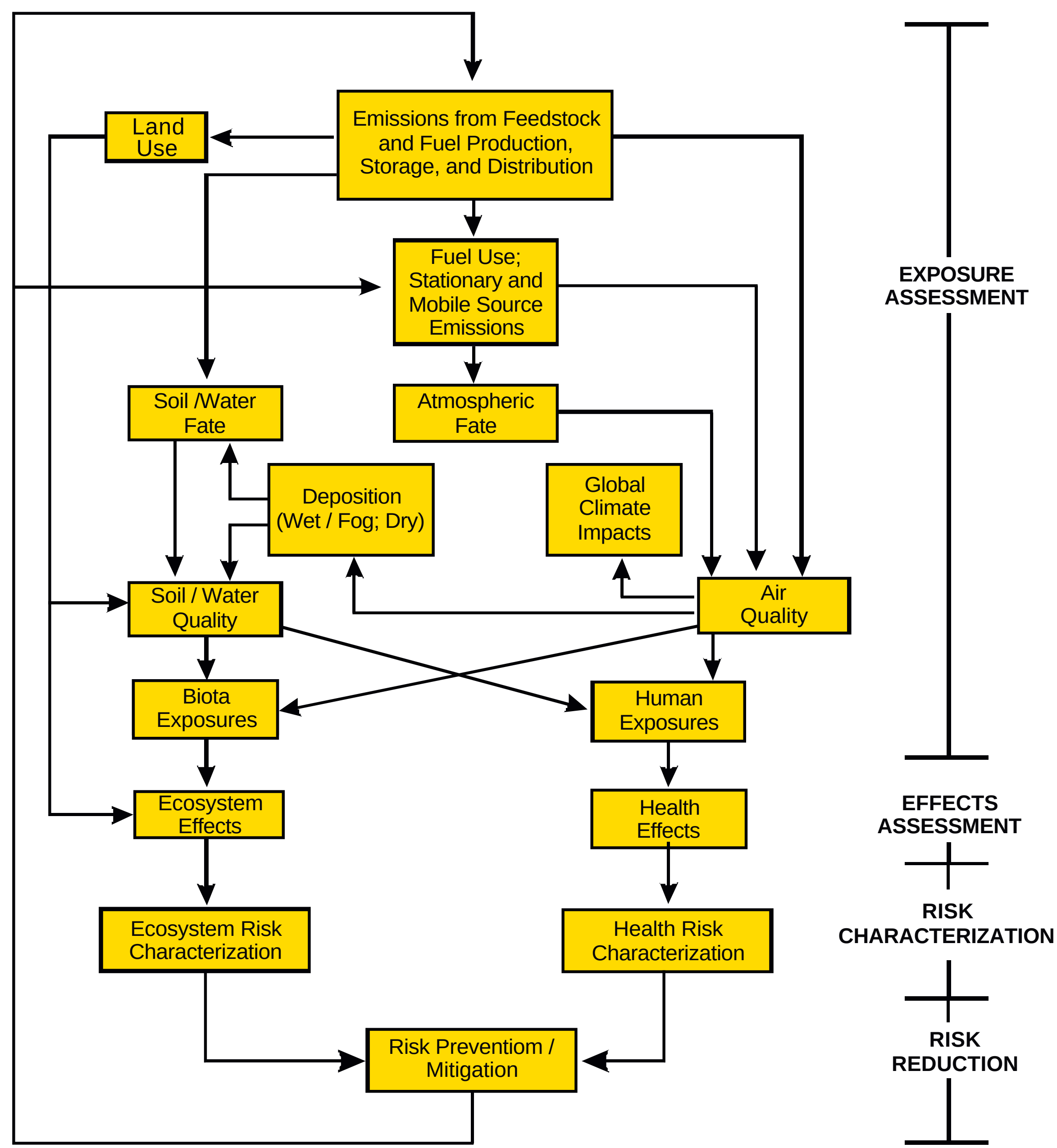
Global Climate Change

	RFG with:		
	MTBE	**EtOH**	**No Oxy**
CO_2			
Methane	Increases?		
N_20		Decreases?	
CO			No Net Change?
NOx			
VOCs			

Risk Characterization

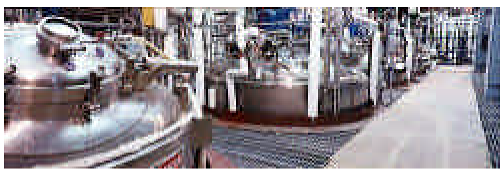
	RFG with:		
	MTBE	**EtOH**	**No Oxy**
Human Health	Increased / decreased risks?	Increased / decreased risks?	Increased / decreased risks?
Ecosystem Impacts	”	”	”

LCA / Risk Assessment Framework



Risk Management

- Risk assessment feeds into risk management
- Risk management feeds back, e.g., emission controls may reduce exposure and hence risk
- LCA "sensitivity" analysis may identify critical points in life cycle where risk management efforts can be focused



Is bioethanol sustainable?

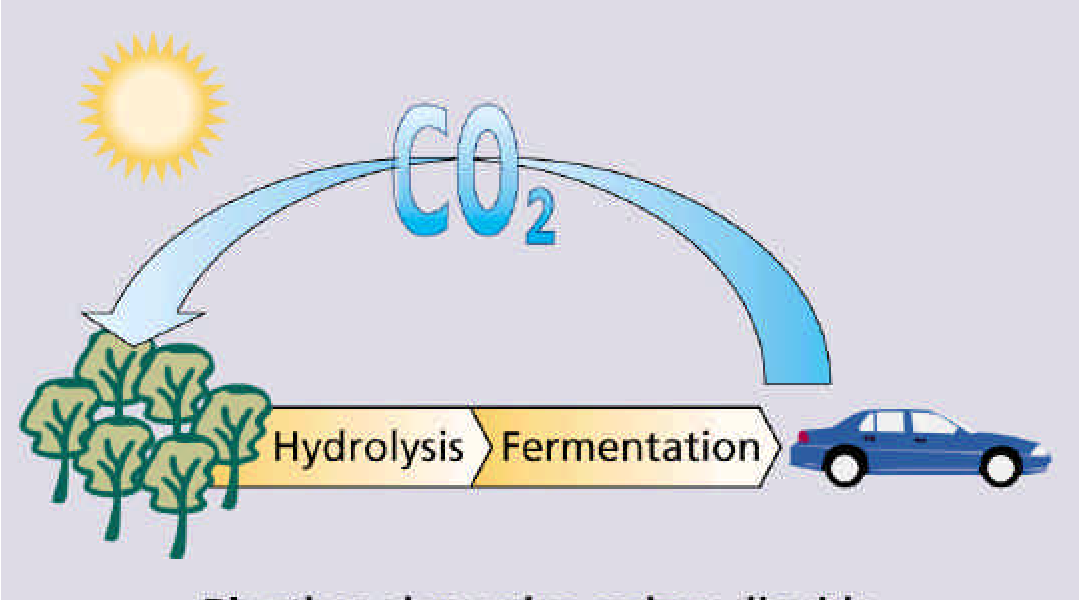
John Sheehan
Biotechnology Center for Fuels and Chemicals
National Renewable Energy Laboratory

April 10, 2001
Ethanol Alkylates Workshop
Oakland, California

Outline

- What is bioethanol?
- Sustainability
  – a goal or a direction?
  – a framework for choosing among risks
  – Life cycle analysis and a systems approach
- Bioethanol and Sustainability
  – Resources impacts
  – Economics—cost and impact
  – The environment
  – Technology risk and availability
- Dialogue

What is bioethanol?



Bioethanol recycles carbon dioxide

- Fuel ethanol made from non food biomass sources
- Requires "new" technology:
  - To break down (hydrolyze) cellulose and hemicellulose to sugar
  - To ferment unusual sugars

Sustainability—a goal or a direction?

"Sustainable (adj.) capable of being sustained or maintained"

Webster's New Twentieth Century Dictionary

Sustainability—a goal or a direction?

- From Webster's point of view, understanding sustainable development should be simple
- In practice, it is not
- Underlying this simple concept are some difficult questions. To name a few:
  - *What* should be maintained?
  - *At what cost* should we maintain "it"?
  - *Why* should we maintain "it"?
  - *For how long* should we maintain "it"?

Sustainability—a politically correct goal

"[S]ustainable development meets the needs of the present without compromising the needs of the future generations."

Our Common Future. United Nations' World Commission on Environment and Development (1987)

Sustainable development—an unattainable utopian goal

"...the great question is now at issue, whether man shall henceforth start forwards with accelerated velocity towards illimitable, and hitherto unconceived improvement; or be condemned to a perpetual oscillation between happiness and misery, and after every effort remain still at an immeasurable distance from the wished-for goal."

Thomas Malthus
An Essay on the Principle of Population (1798)

Sustainability—a way of life and an ethos

"The common aim must be to expand resources and improve quality of life for as many people as heedless population growth forces upon Earth, and do it with minimal prosthetic dependence. That, in essence is the ethic of sustainable development."

E.O. Wilson in
Consilience: The Unity of Knowledge (1998)

Sustainability—a framework for making choices

- Gloomy tone aside, Wilson's view of sustainability offers several key terms:
  - "Expanding Resources"—stewardship of natural resources, both renewable and nonrenewable
  - "Quality of life"—economic and moral attributes of a "good life"
  - "Earth"—the environment we live in
  - "Minimal prosthetic dependence"—a balanced role for technology and technological risk
  - "Ethic"—the political values of our community and the moral values of individuals

Sustainability—a framework for making choices

“[Sustainable agriculture] has all the makings of an ideal concept that requires a holistic, integrated, interdisciplinary, or systems-oriented approach that can be talked about but not easily translated into practical research.”

Rattan Lal, in preface to *Soil Management for Sustainability* (1991)

NREL

Talking about sustainability

- "Systems oriented"
- "Expanding Resources"
- "Quality of Life"
- "Earth"
- "Minimal prosthetic dependence"
- "Ethic"

→

- Life Cycle
- Renewable Resources
- Economics
- Environment
- Technology risks
- Dialogue

Bioethanol and sustainability

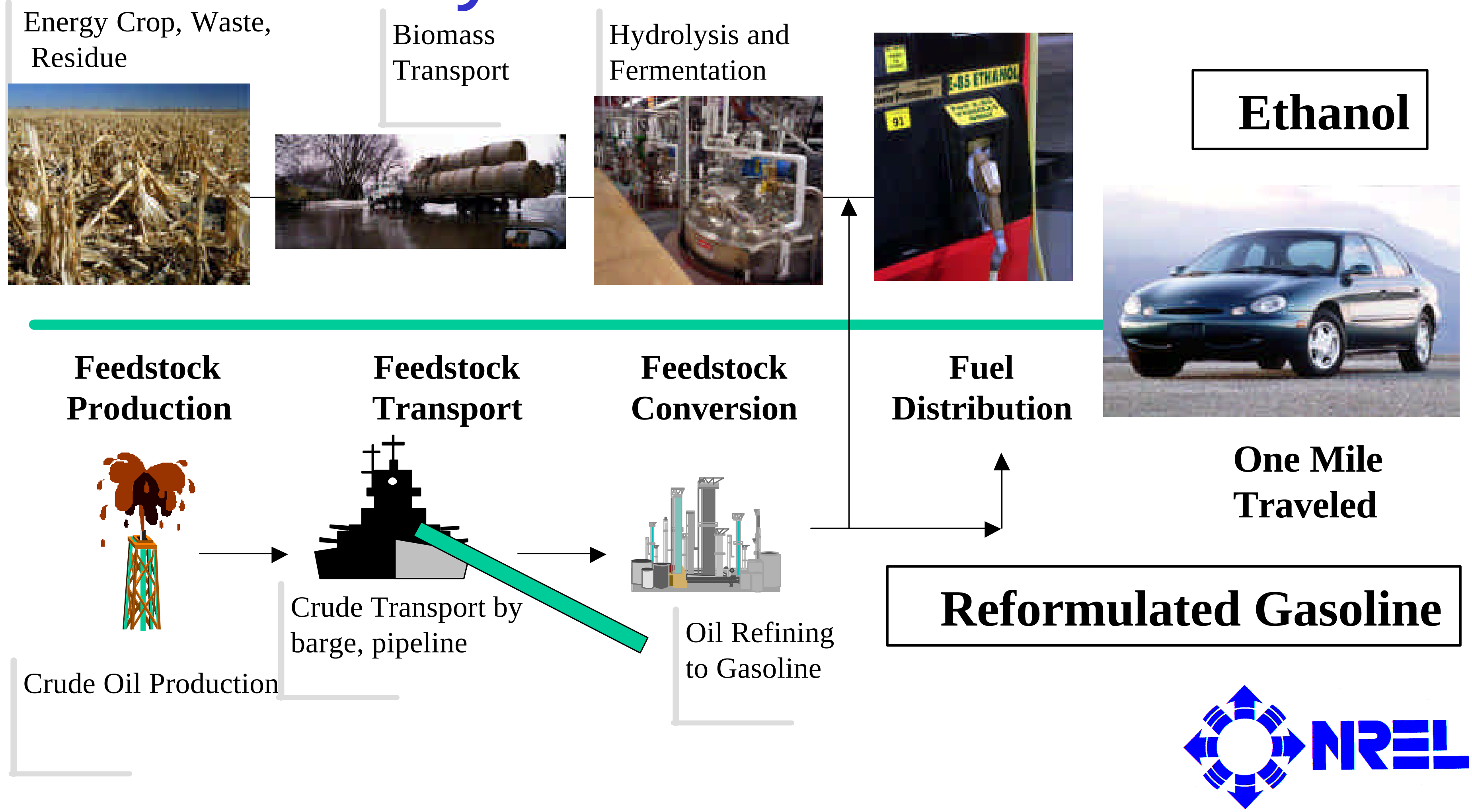
- “Systems oriented”
- “Expanding Resources”
- “Quality of Life”
- “Earth”
- “Minimal prosthetic dependence”
- “Ethic”

- Life Cycle
- Renewable Resources
- Economics
- Environment
- Technology risks
- Dialogue

Life Cycle Assessment—a framework for making choices that support a sustainable society

- A “comprehensive” accounting of a product’s flows to and from the environment
  - Air, water and solid waste emissions
  - Energy resources
  - Other primary resources extracted from the environment
- “Cradle to grave”

Sustainability: the life cycle of fuels



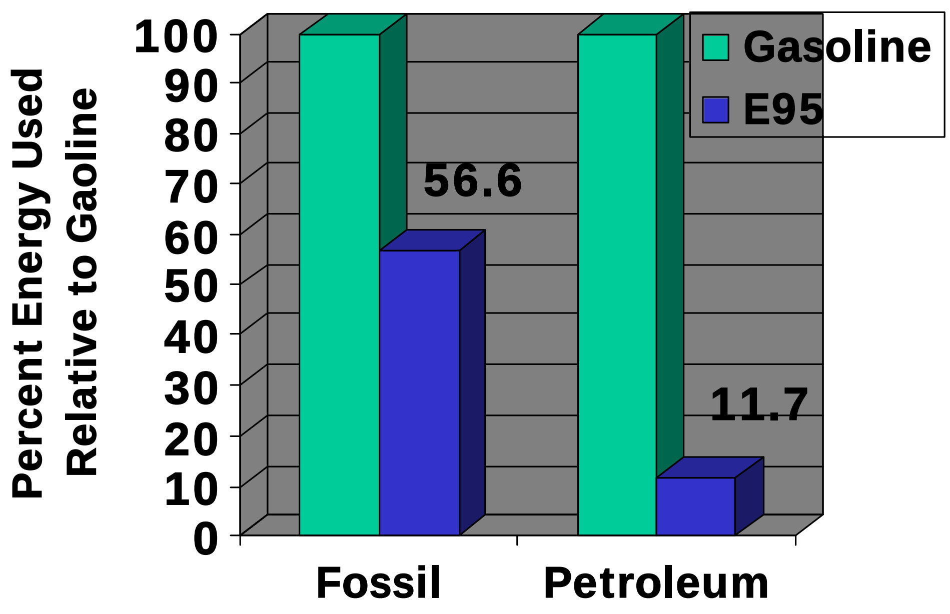
Bioethanol and sustainability

- "Systems oriented"
- "Expanding Resources"
- "Quality of Life"
- "Earth"
- "Minimal prosthetic dependence"
- "Ethic"

- Life Cycle
- Renewable Resources
- Economics
- Environment
- Technology risks
- Dialogue

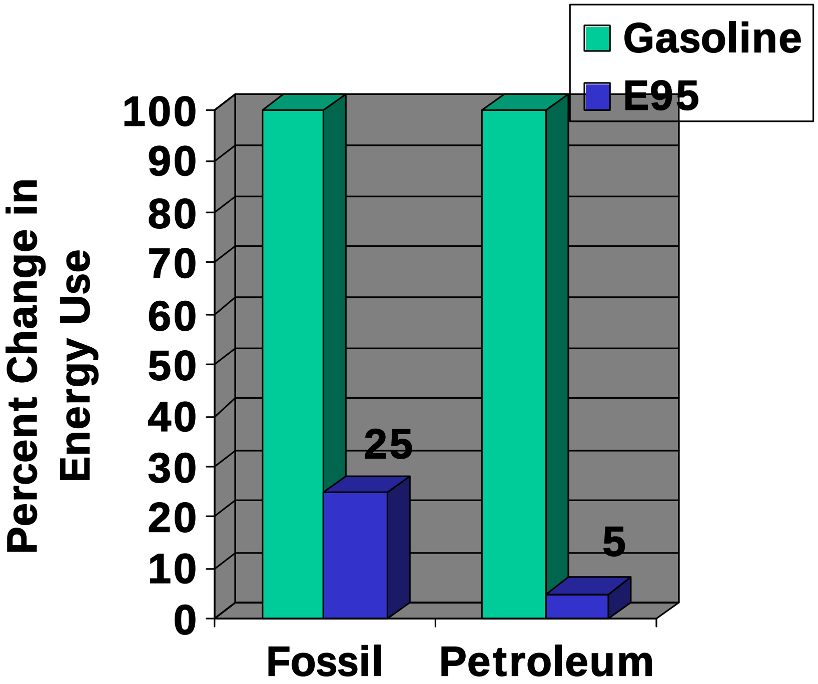
Resources: Life cycle energy use for corn ethanol

- Despite many early reports to the contrary, corn ethanol moves us in the right direction in terms of sustainability
- 43% drop in fossil energy use relative to gasoline
- 88% drop in petroleum use



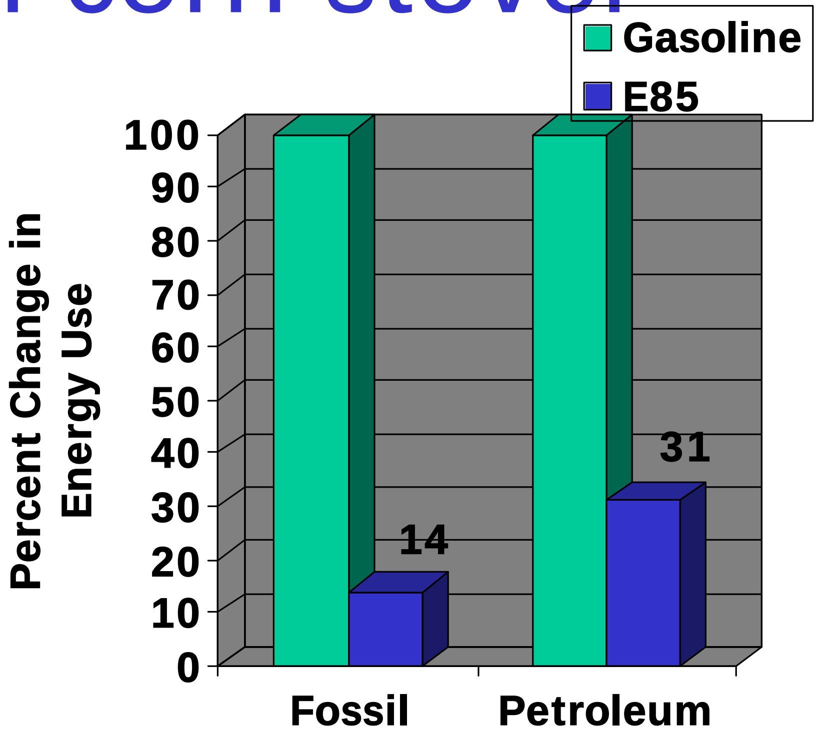
Resources: Life cycle energy use for bioethanol from energy crops

- Energy crops look even better in terms of sustainability
- 75% drop in fossil energy inputs relative to gasoline
- 95% drop in petroleum use



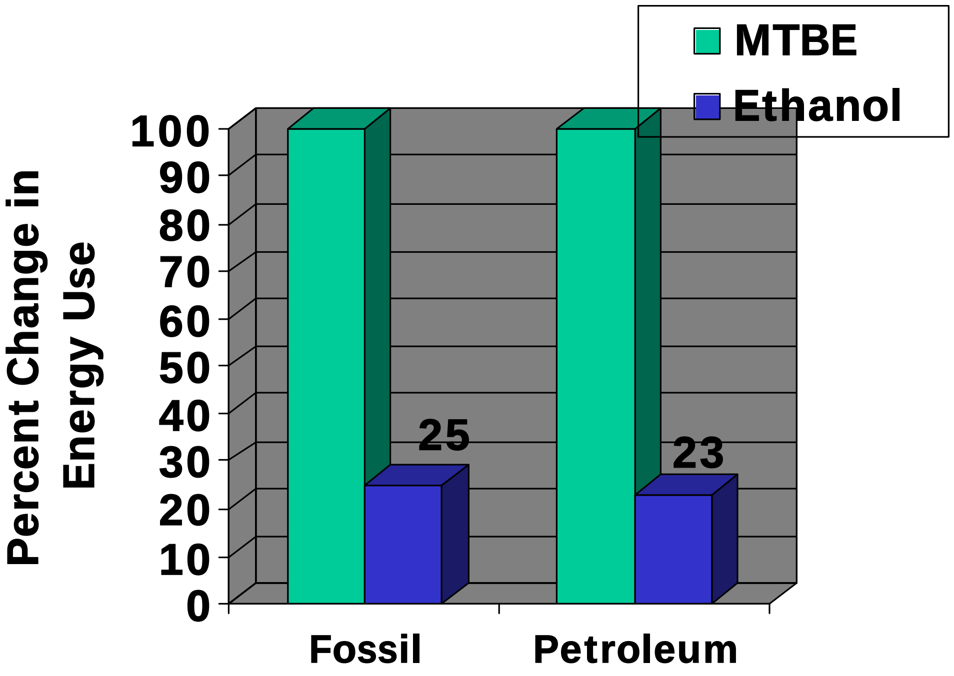
Resources: Life cycle energy use for bioethanol from corn stover

- Residues from corn harvests are attractive as mid term energy supplies
- 86% drop in fossil energy inputs relative to gasoline
- 69% drop in petroleum use



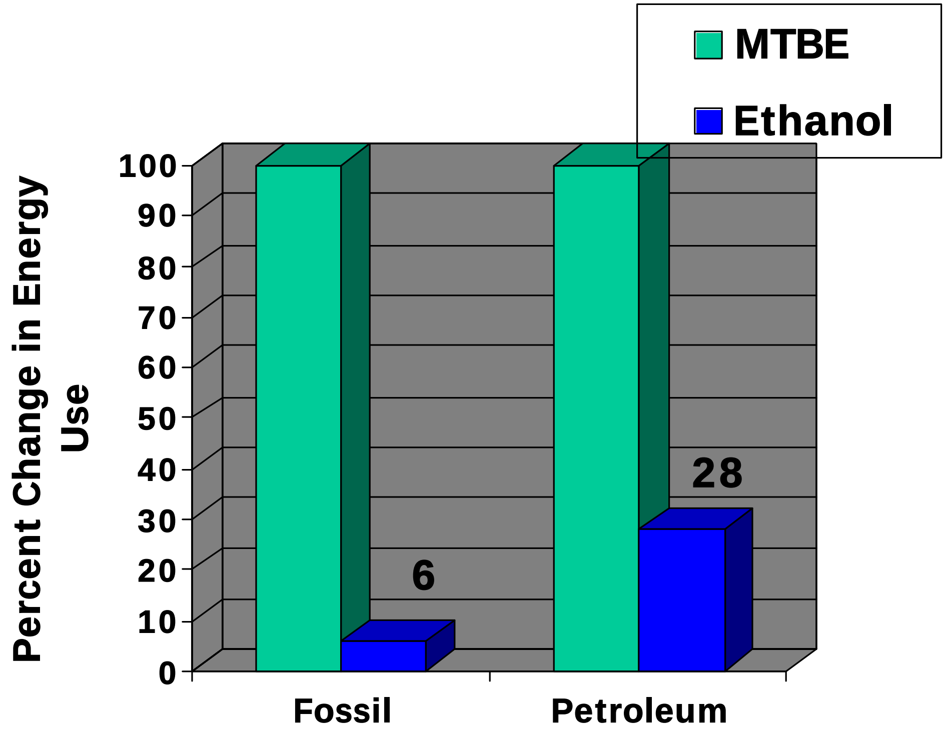
Resources: Life cycle energy use for rice straw in CA

- Making ethanol is a more sustainable alternative to open burning of rice straw
- 75% drop in fossil inputs relative to MTBE
- 77% drop in petroleum inputs relative to MTBE



Resources: Life cycle energy use for forest residue ethanol in CA

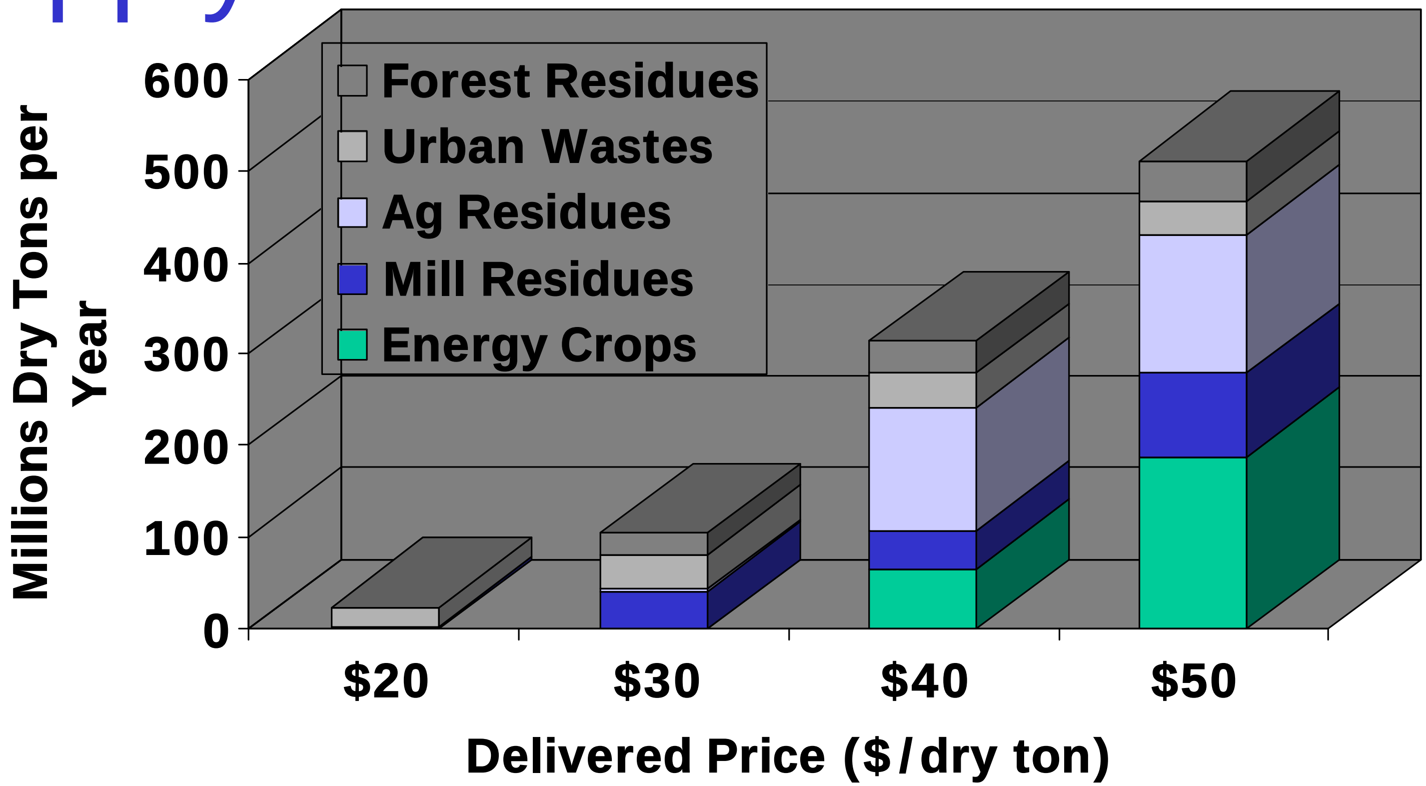
- Making ethanol is a more sustainable alternative to controlled burning in forests
- 94% drop in fossil energy inputs relative to MTBE
- 72% drop in petroleum inputs



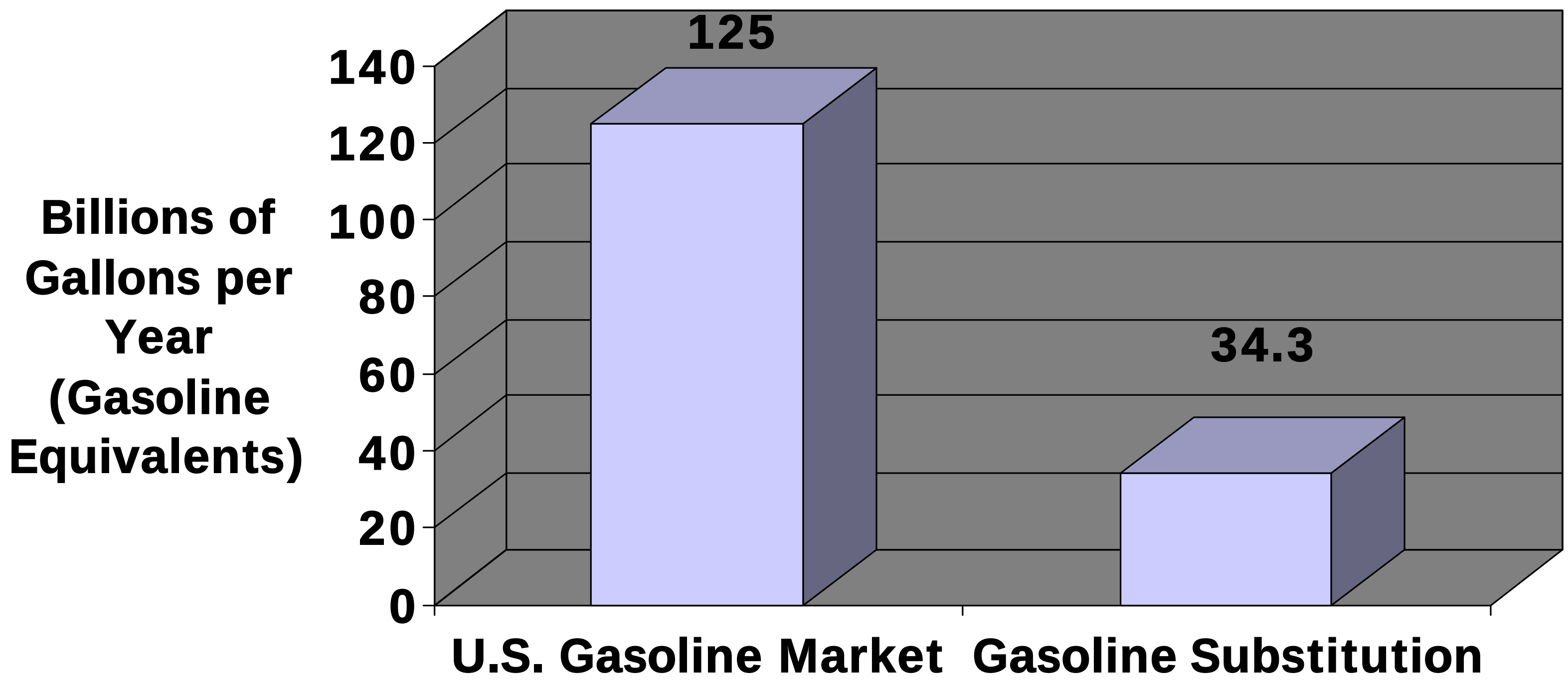
Resources: Can bioethanol make a difference?

- Joint study by U.S. Department of Agriculture and U.S. Department of Energy to estimate future production of grasses and trees as dedicated energy crops
- 42 million acres (10% of total cropland) could switch to bioenergy crops
- Includes 13 million acres of Conservation Reserve Program (CRP) land
- 181 million dry tons of switchgrass per year at $50 per ton or less.

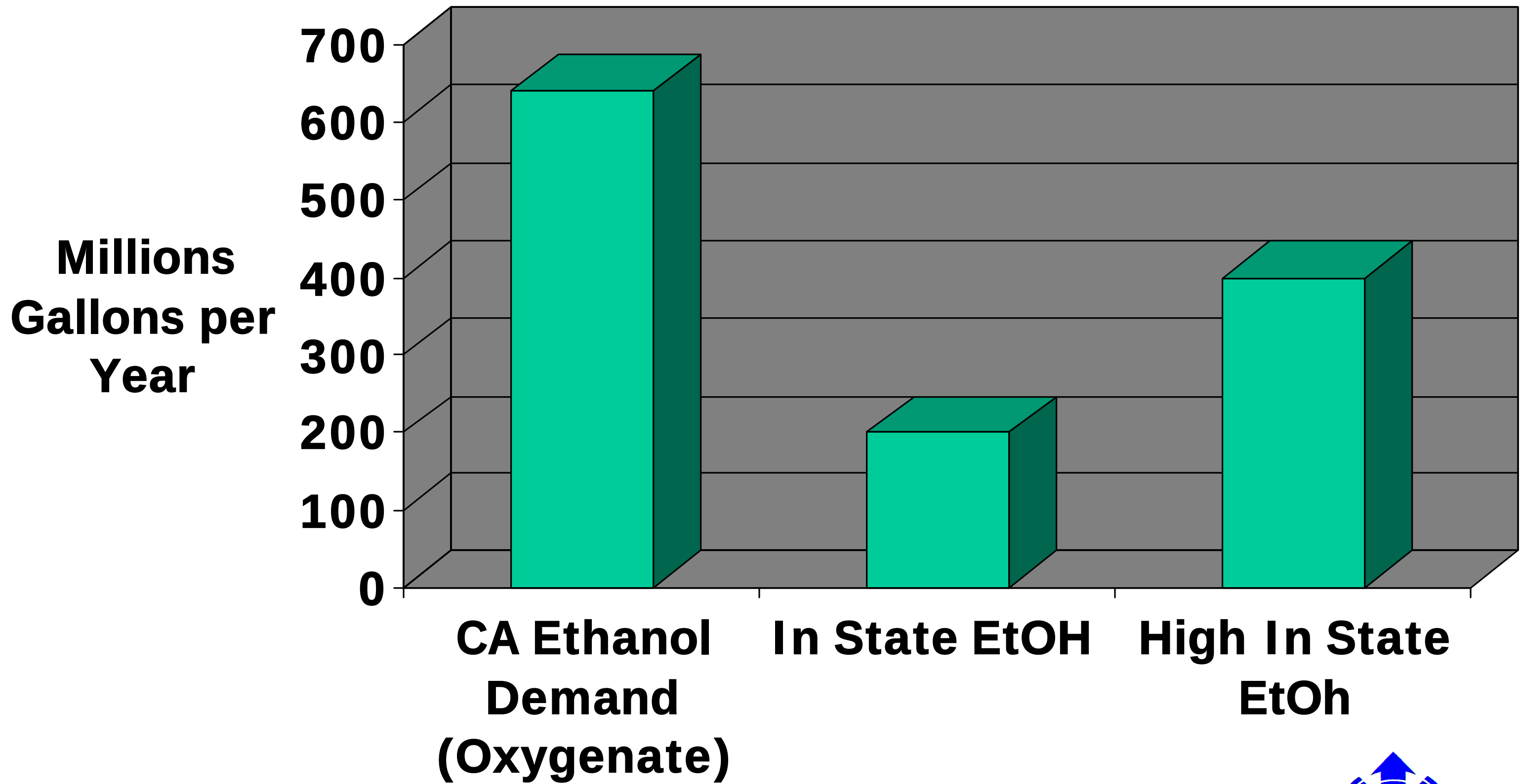
Resources: Potential U.S. Biomass Supply



Resources: Maximum Impact of Bioethanol on U.S. Gasoline



Resources: Maximum Impact of Bioethanol on CA Gasoline



Bioethanol and sustainability

- “Systems oriented”
- “Expanding Resources”
- “Quality of Life”
- “Earth”
- “Minimal prosthetic dependence”
- “Ethic”

- Life Cycle
- Renewable Resources
- Economics
- Environment
- Technology risks
- Dialogue

NREL

Economics: A new industry for California and the U.S.

- The CEC's recent findings on ethanol
  - "The benefits of biomass-to-ethanol...for California's economy are potentially greater than the cost of state support for such an industry"
  - $1 billion in economic benefits from $500 million in incentives for a 200 million gallon industry in CA
    - Includes benefits across the life cycle

Bioethanol and sustainability

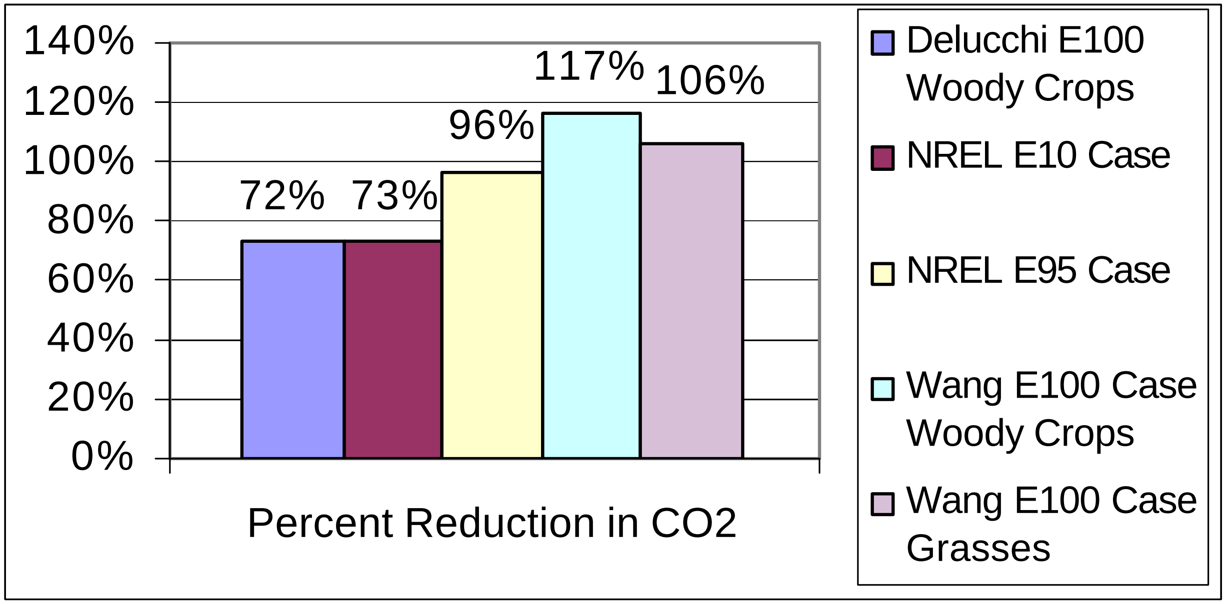
- “Systems oriented”
- “Expanding Resources”
- “Quality of Life”
- “Earth”
- “Minimal prosthetic dependence”
- “Ethic”

→

- Life Cycle
- Renewable Resources
- Economics
- Environment
- Technology risks
- Dialogue

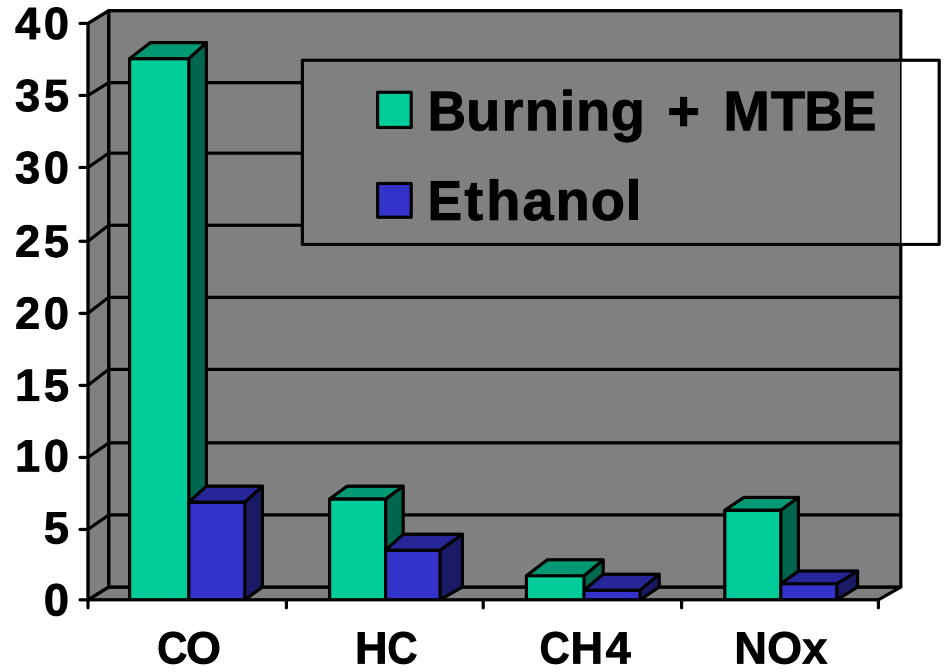
Environment: Climate change as a case study in sustainability

- The fossil energy benefits of bioethanol translate directly into greenhouse gas reductions



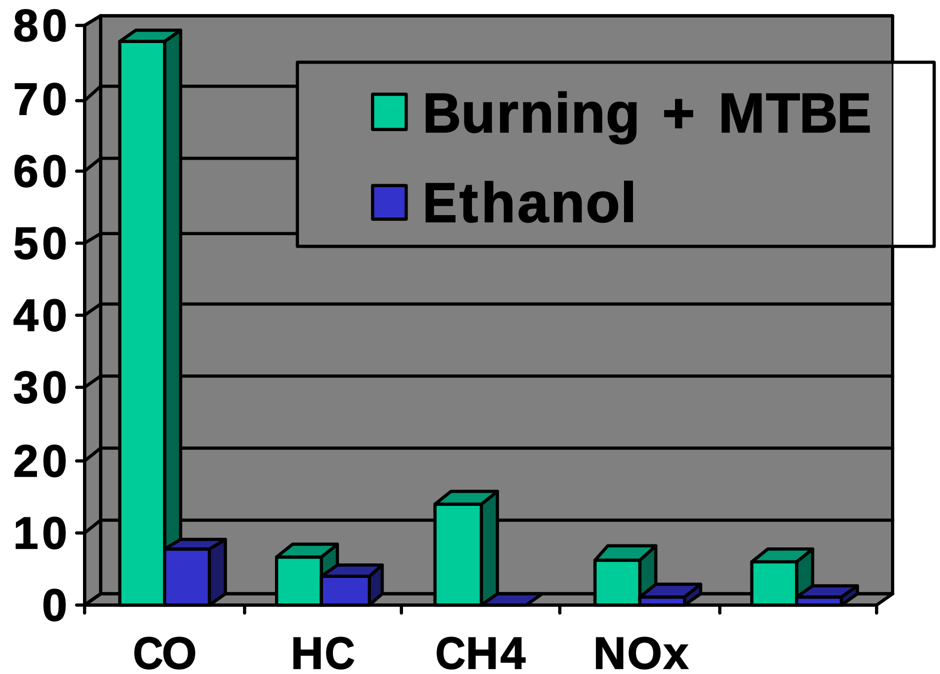
Environment: A holistic approach leads to multiple benefits

- Avoided emissions from open burning of rice straw



Environment:
A holistic approach leads to multiple benefits

- Avoided emissions from controlled burning to remove excess fuel in forests



Environment: The risks of genetically engineered organisms

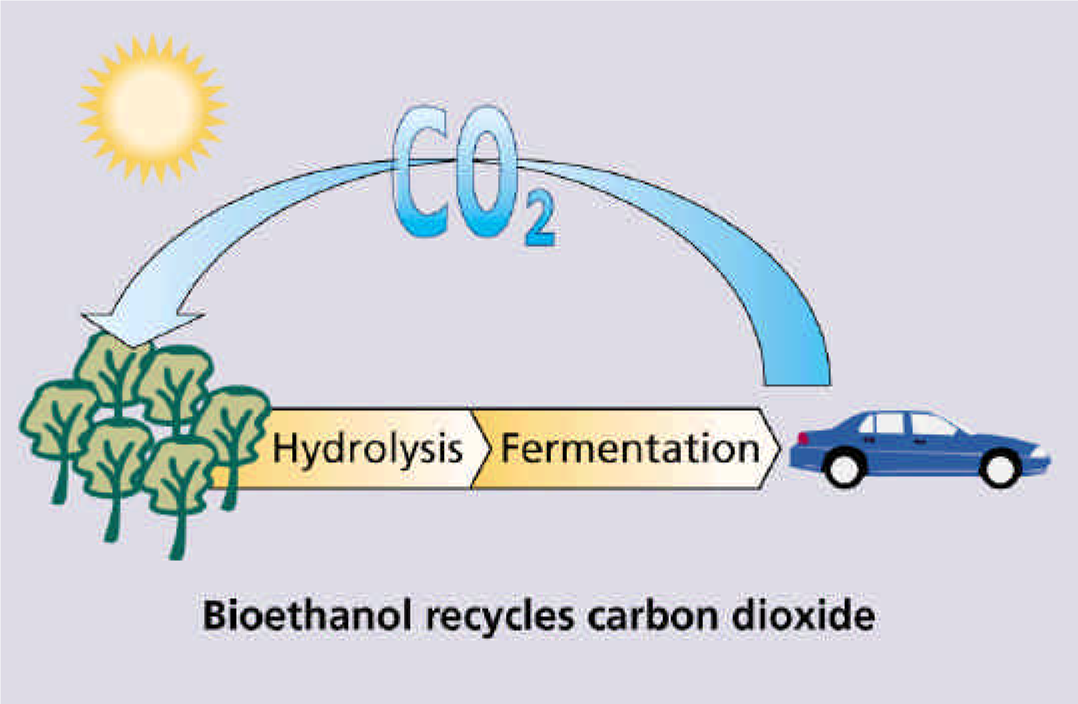
- The "inside/out" view
  - While the use of genetically engineered organisms does carry with it some risk, we focus on the use of GMOs *only* in the process operation
  - As we learn more, we may explore genetically modified crops as well, but this is in the future

Bioethanol and sustainability

- "Systems oriented"
- "Expanding Resources"
- "Quality of Life"
- "Earth"
- "Minimal prosthetic dependence"
- "Ethic"

- Life Cycle
- Renewable Resources
- Economics
- Environment
- Technology risks
- Dialogue

The Technology: today...



Everything that has been done or could be done to improve production of bioethanol from biomass can be categorized in terms of sugar production or fermentation

The Technology: today…

- 1st Generation Technology
  - Concentrated Sulfuric Acid
    - Masada
  - Two Stage Dilute Sulfuric Acid
    - BC International
  - Pioneer plants using “niche” feedstocks and new engineered organisms for cofermentation of C5 and C6 sugars
  - We anticipate that the first plants will be on line in 2003 to 2005 timeframe

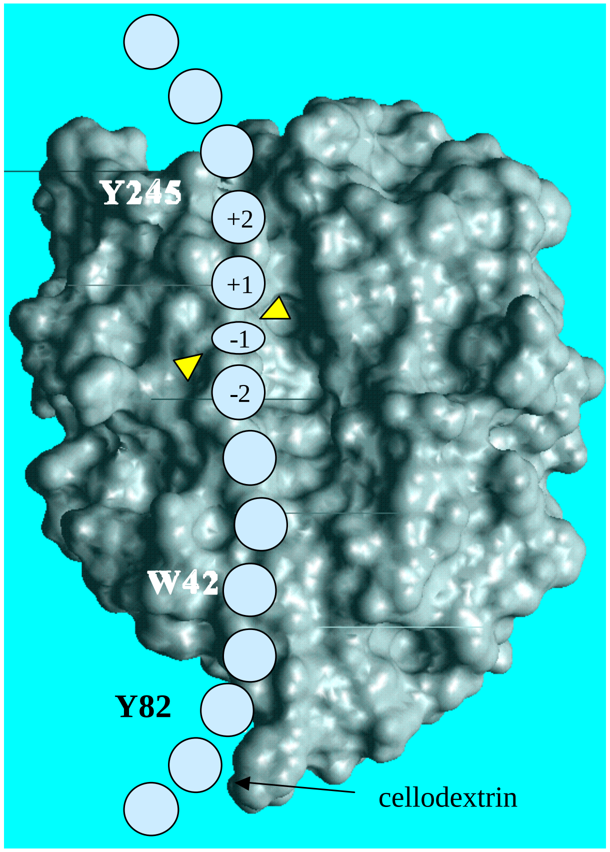
The Technology: tomorrow...

- 2nd Generation Technology
  - Enzymatic Hydrolysis.
  - By comparison, enzyme technology is not nearly as well developed as acid technology.
  - but enzymes offer greater opportunities for cost reduction in the long term

The Technology: tomorrow...

We are relying on the exploding advances in biotechnology to achieve the long term cost competitiveness of bioethanol

For many, the benefits of biotechnology must be carefully weighed against the environmental risks of genetically engineered organisms

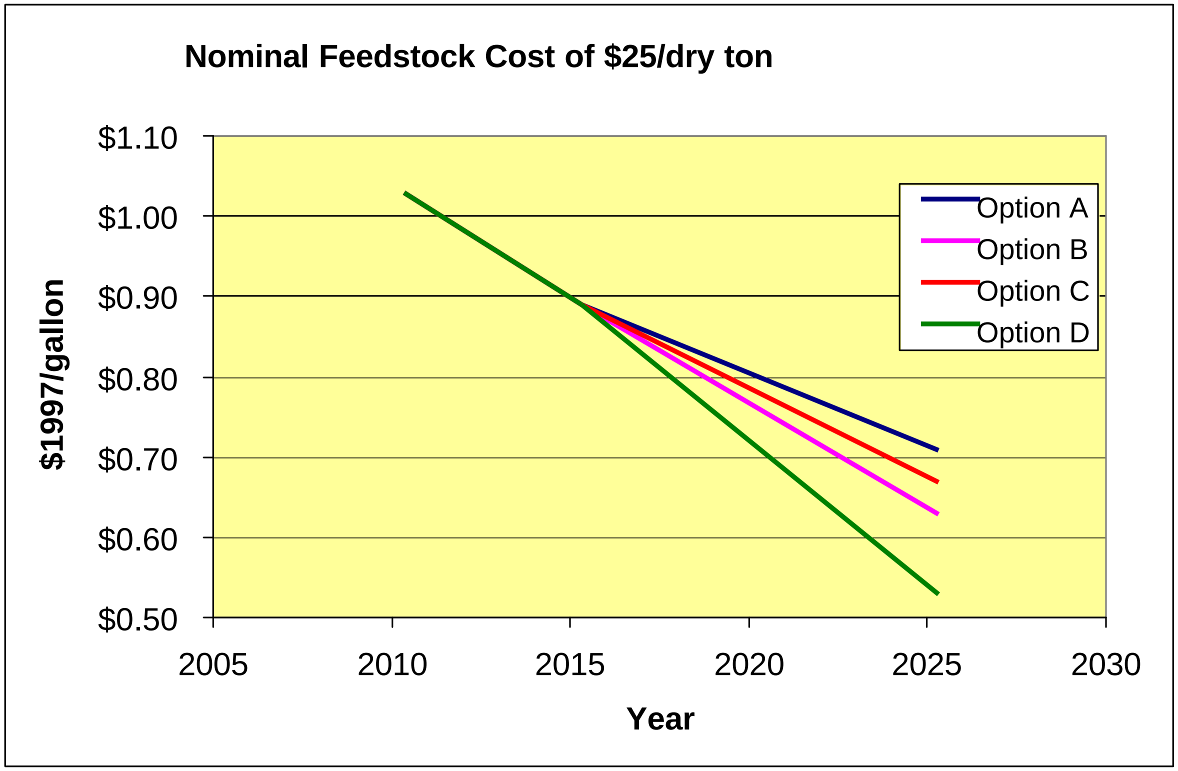


The Technology: Risks

- Market uncertainty

The Technology: Risks

- Technical uncertainty for new enzyme technology
- The rewards are great, but this is high risk research
- We need to be in the game for the long haul



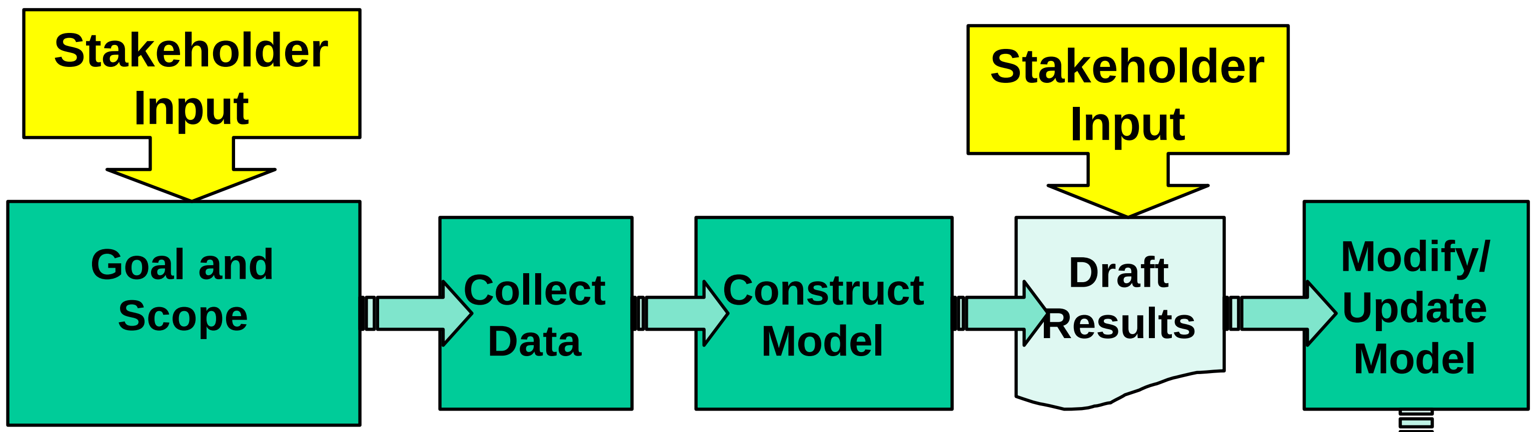
The Technology: The risks of using biomass

- New crops and new management practices always have some risk of “unintended consequences.”
- We must continue to look at issues such as
  - Biodiversity
  - Natural Habitats
  - Soil health and sustainability

The Technology:
The risks of using biomass

- Our latest life cycle study considered the effects of collecting corn stover on the long term health of soil
- Preliminary findings show that—*when done responsibly*—residue collection can offset petroleum fossil CO2, reduce our dependence on petroleum and still allow carbon sequestration in soils

Life cycle analysis—a tool for dialogue



Involving stakeholders at the start and throughout such studies builds trust and confidence. It also helps to sort out the uncertainties of the science from the uncertainties of the moral and ethical choices we need to make

Bioethanol's future

- The next few years will see the first cellulose-to-ethanol plants since World War I
- Solving environmental problems like rice straw burning and using hitherto unvalued residues like corn stover represent a huge untapped resource for fuel production
- Using biotechnology responsibly, we can develop bioethanol technology that contributes to the overall sustainability of our transportation sector

Cost/Benefit Analysis of the Health and Environmental Issues of Oxygenated and Non-Oxygenated Gasoline Formulations

Dr. Arturo Keller

University of California, Santa Barbara

Presented at:

Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California, April 10-11, 2001

Components of the Analysis

- Air Quality Benefits of Reformulated Gasoline
- Human Health Effects
- Ecological Effects
- Exposure Assessment
- Extent of Contamination of Drinking Water Supplies
- Water Treatment
- Cost-Benefit Analysis of Gasoline Alternatives
- Policy Recommendations

Gasoline Formulations

- Reference point: Conventional gasoline
- Reformulated Gasoline with MTBE
- Reformulated Gasoline with Ethanol
- Non-oxygenated Reformulated Gasoline
  - Toluene increased (e.g. Chevron)
  - Alkyls added (e.g. iso-octane)

Air Quality Considerations

- RFG (Reformulated Gasoline)
  - Reduced benzene emissions
  - Reduced CO, NOx, VOC and toxic emissions
  - Lower ozone forming potential
- RFG with MTBE
  - Useful for older vehicles (~pre-1990): reduce CO
  - No significant difference for newer vehicles
  - MTBE emissions to atmosphere
  - Increased formaldehyde emissions

Air Quality Considerations

- RFG with Ethanol
  - Same benefits as gasoline with MTBE
  - Ethanol emissions to atmosphere
  - Increased acetaldehyde emissions
- Non-oxygenated RFG (with more Toluene or alkyl)
  - Same benefits as gasoline with MTBE or Ethanol
  - Increased toluene or alkyl emissions to atmosphere
  - No additional combustion by-products

Human Health Effects of MTBE

- MTBE is an animal carcinogen at high doses; potential to cause cancer in humans (CAL-DHS level at 13 ppb)
- Mechanisms by which MTBE causes cancer is not understood, but either TBA or formaldehyde may play a role
- Laboratory animal experiments indicate reproductive or developmental toxicity at very high exposure levels
- Acute effects at high concentrations (> 100 ppm)
- Taste and odor are a significant concern at low levels (5-20 ppb)
- Formaldehyde as a Product of Incomplete Combustion

Human Health Effects of Ethanol

- Acute and Chronic Toxicity at high concentrations (several percent by volume)
- Little information at low concentrations expected in environment (ppb to ppm)
- Taste and odor probably not a major issue at low concentrations: may be noticeable and objectionable at higher concentrations (**RESEARCH NEEDED**)
- Acetaldehyde as a Product of Incomplete Combustion

Human Health Effects of Toluene

- Acute and Chronic Toxicity at high levels
- Reference Concentration (RfC) in air of 0.4 mg/m^3 or 400 ?g/m^3 (USEPA, 1993d)
- In California, the mean concentration of toluene in air is 8.5 ?g/m^3
- Not proven to be a carcinogen (animal studies have proven negative)
- Toluene in tap water would require treatment to bring risk to acceptable level (below RfD)

Human Health Effects: Alkylates

- Isooctane not classified as a hazardous air pollutant by USEPA
- Isooctane not considered by Agency for Toxic Substances and Disease Registry (ATSDR) within their priorities
- Acute toxicity at high concentrations in air
- **RESEARCH NEEDED**

Ecological Effects of MTBE

- Acute toxicity only at very high concentrations (44 to 1000 mg/L)
- Chronic toxicity at high levels (200 mg/L and higher)
- No developmental effects detected in fish at concentrations between 10 ug/L and 700 mg/L
- No effect on mammalian reproduction at levels up to 2000 mg/kg-day
- Very few species have been studied

Ecological Effects

- Ethanol, Toluene, Iso-octane
  - As with any gasoline constituent, high damage near the spill
  - Expect damages to be similar to conventional gasoline once the concentrations are diluted in a river or groundwater
  - **RESEARCH NEEDED** on Ecotoxicity

Fate and Transport of MTBE

- Very high solubility => transfers to water easily
- Volatile => can evaporate from spills and can be removed from surface water reservoirs to atmosphere
- Very low sorption => doesn't slow down in groundwater
- Very slow biodegradation under natural conditions => persistent, will travel far

Fate and Transport of Ethanol

- Very high solubility => transfers to water easily
- Volatile => can evaporate from spills and can be removed from surface water reservoirs to atmosphere (slower than MTBE)
- Very low sorption => doesn't slow down in groundwater
- Very FAST biodegradation under natural conditions => will be used first by microbes
- May use up all the oxygen before BTEX, extending benzene plume **(RESEARCH NEEDED)**

Fate and Transport of Toluene

- Soluble => transfers to water
- Volatile => can evaporate from spills and can be removed from surface water reservoirs to atmosphere
- Some sorption => slows down in groundwater
- Easily biodegraded under natural conditions => used by microbes in first 1000-3000 ft.
- Travels behind Benzene, so degraded after it

Fate and Transport: Isooctane

- Low Solubility => stays longer in gasoline spill
- Volatile => can evaporate from spills and can be removed from surface water reservoirs to atmosphere
- Higher sorption => slows down appreciably in groundwater
- Easily biodegraded under natural conditions => used by microbes in first 1000-3000 ft.
- Travels behind Benzene, so degraded after it

Cost of Water Treatment

- Cost of treating water with:
  - MTBE is about 40 to 100% higher than conventional gasoline
  - Ethanol should be similar to conventional gasoline **(RESEARCH NEEDED)**
  - Toluene similar to conventional gasoline
  - Iso-octane similar to conventional gasoline

Direct Costs

- Fuel Prices increase for MTBE, Ethanol and Iso-octane, relative to conventional gasoline (CEC, 1999)
- Fuel Prices increase initially for Toluene (first 1-3 years) then may drop in long-term
- Fuel Consumption increases for MTBE and Ethanol (get lower MPG)
- Fuel Consumption decreases for Toluene and Iso-octane

Cost/Benefit Analysis for California

Bren School of Environmental Science & Management, UCSB

	CaRFG2-MTBE	CaRFG2-Ethanol	Non-oxy CaRFG2
Air Quality Benefits	**$2 to $84 million**	**$2 to $84 million**	**$2 to $84 million**
Health Costs			
air quality damages	$0 to $27 million	$3 to $200 million	N.S.[1]
water treatment	$340 to $1480 million	N.S.[1]	$1 to$10 million
alternate water supplies	$1 to 30 million	N.S.[1]	N.S.[1]
Direct Costs			
fuel price increase	$135 to $675 million	$290 to $991 million	$141 to $1300 million
fuel efficiency decrease	$310 to $400 million	$290 to $580 million	($150) to ($230) million
Other Costs			
water monitoring	$2 to $4 million	N.S.[1]	N.S.[1]
recreational costs	$160 to $200 million	N.S.[1]	N.S.[1]
ecosystem damages	N.S.[1]	N.S.[1]	N.S.[1]
Costs Subtotal	**$0.9 to 2.8 billion**	**$0.6 to $1.8 billion**	**($0.09) to $1.2 billion**
Net Benefit or (Cost)	**($0.9) to ($2.7) billion**	**($0.5) to ($1.8) billion**	**$0 to ($1.2) billion**

[1]N.S. = not significant

Cost-Benefit Analysis

- RFG with MTBE: most expensive option to meet 1990 CAA objectives due to water treatment costs, higher fuel prices and higher fuel consumption
- RFG with Ethanol: intermediate option, with some air quality concerns (acetaldehyde) as well as need for ethanol subsidies to make it competitive
- Non-oxygenated RFG: least expensive option in long-term, and best considering the current average vehicle technology

Policy Recommendations

- Issues:
  - Need to evaluate risk of increasing toluene levels in gasoline
  - Premium grade probably needs oxygenate
- Flexibility in CAAA requirements, to find the least-cost option to achieve air quality objectives, considering the risks
- Study health and environmental impacts of any option **BEFORE** changing the law

Policy Recommendations

1) Promote accelerated removal of older, high emitting vehicles
2) Waive Federal requirement for oxygen content
3) Facilitate production of non-oxygenated gasoline
4) Assess groundwater contamination as soon as possible and avoid delays in clean-up: reduce risk and cost

Policy Recommendations

Bren School of Environmental Science & Management, UCSB

5) Provide incentives to adopt Best Management Practices for surface water reservoirs
6) Establish specific emissions requirements for motor boat engines
7) Fully assess environmental impacts of ethanol, toluene, alkylates as MTBE substitutes
8) Invest in long-term research program to determine toxicological effects of untested industrial products and fuel alternatives

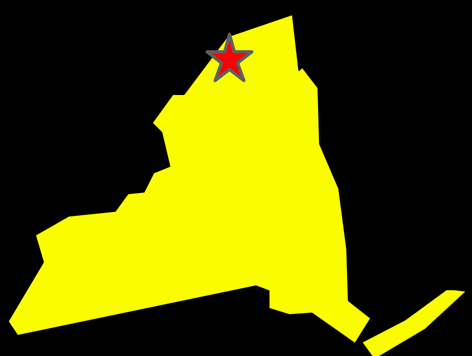
Acknowledgements

Bren School of Environmental Science & Management, UCSB

- Dr. Linda Fernandez, now at UC Riverside, was co-investigator in this study and provided the economic tools to analyze the various costs and benefits
- Research funded by UC Toxic Substances Research and Training Program under SB 521

Transport and dissolution of ethanol and ethanol-blended gasoline in the subsurface

Susan E. Powers, Ph.D., P.E.
Clarkson University
Potsdam NY



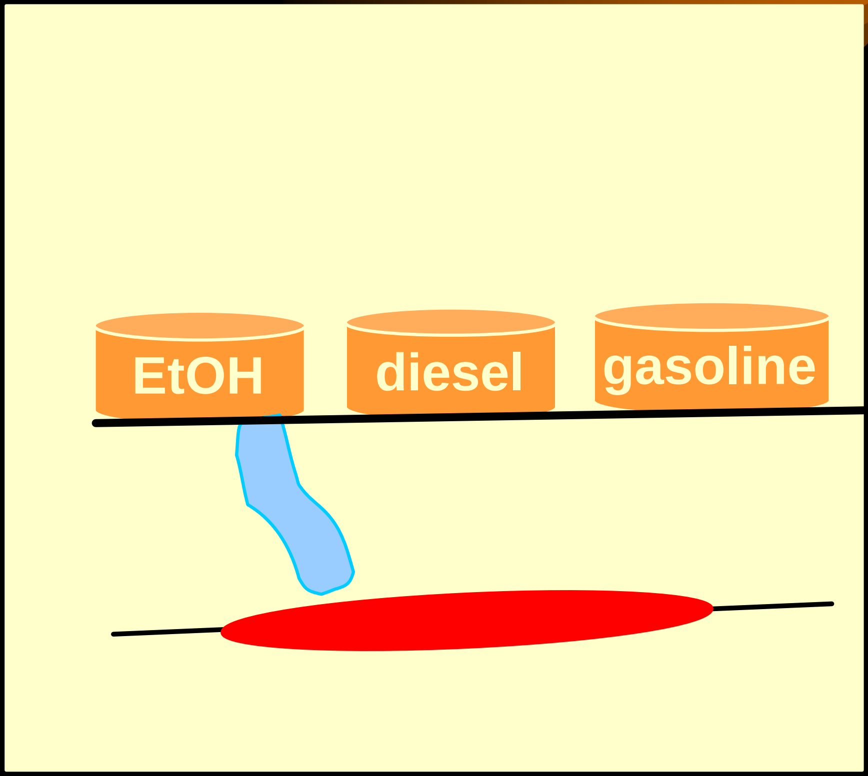
Workshop on Ethanol and Alkylates in California Automotive Fuels
April 11, 2001

Thank you!

- Financial support
  - US EPA, NCERQA – STAR program
  - LLNL / California
- Research collaboration – graduate students
  - Steven Heermann
  - Cory McDowell

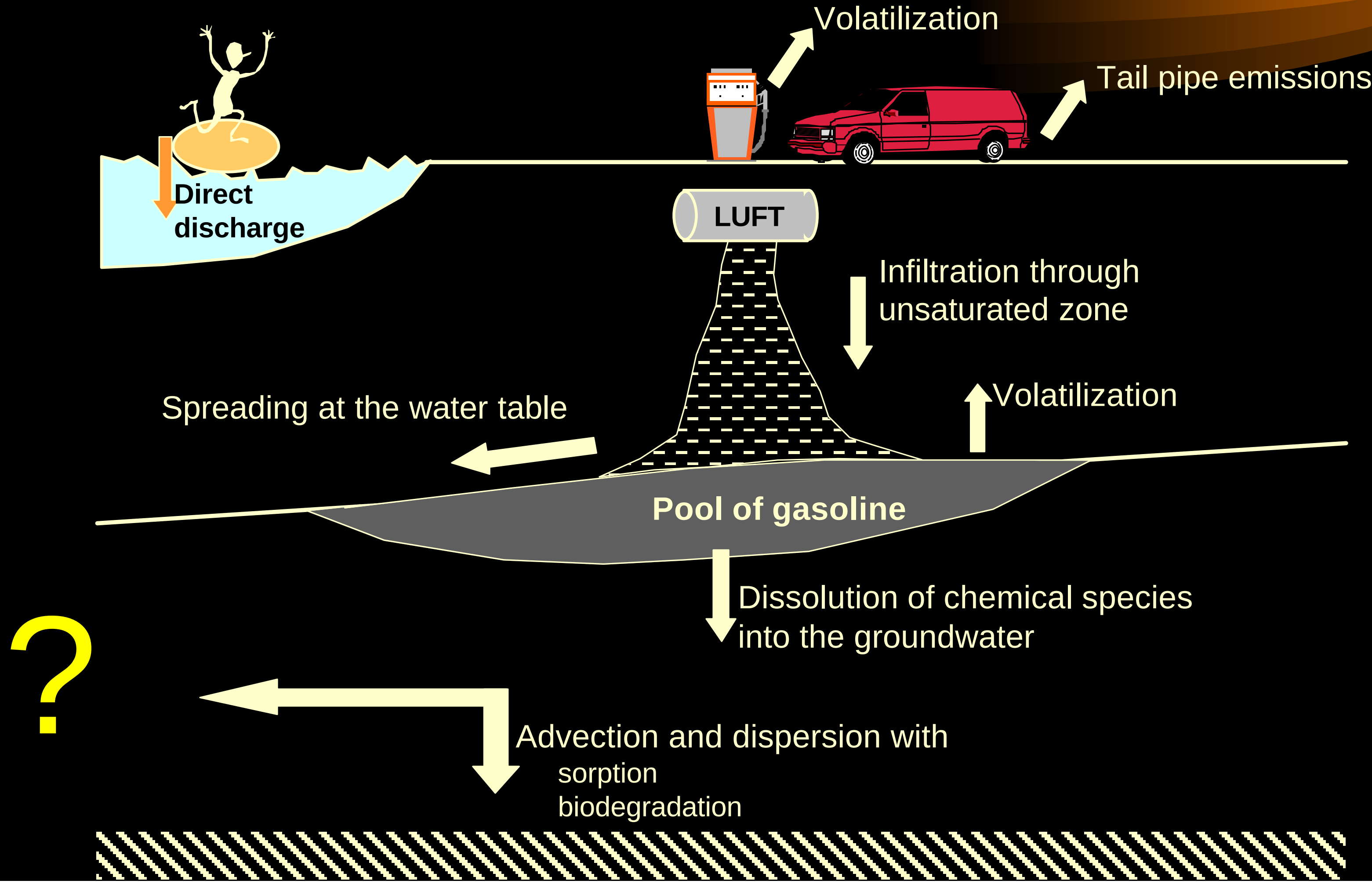
Potential Spill Scenarios

Gasohol from LUFT and trucks



Denatured ethanol at bulk storage terminals

Fate in the Environment



Molecular structure very revealing

Hexane | **MTBE** | **Ethanol**

$CH_3 - (CH_2)_4 - CH_3$

$$
\begin{array}{c}
\qquad\quad CH_3 \\
\qquad\quad | \\
CH_3\text{-}\ddot{\underset{\cdot\cdot}{O}}\text{-}C\text{-}CH_3 \\
\qquad\quad | \\
\qquad\quad CH_3
\end{array}
$$

$CH_3 - CH_2\text{-}\ddot{\underset{\cdot\cdot}{O}}H$

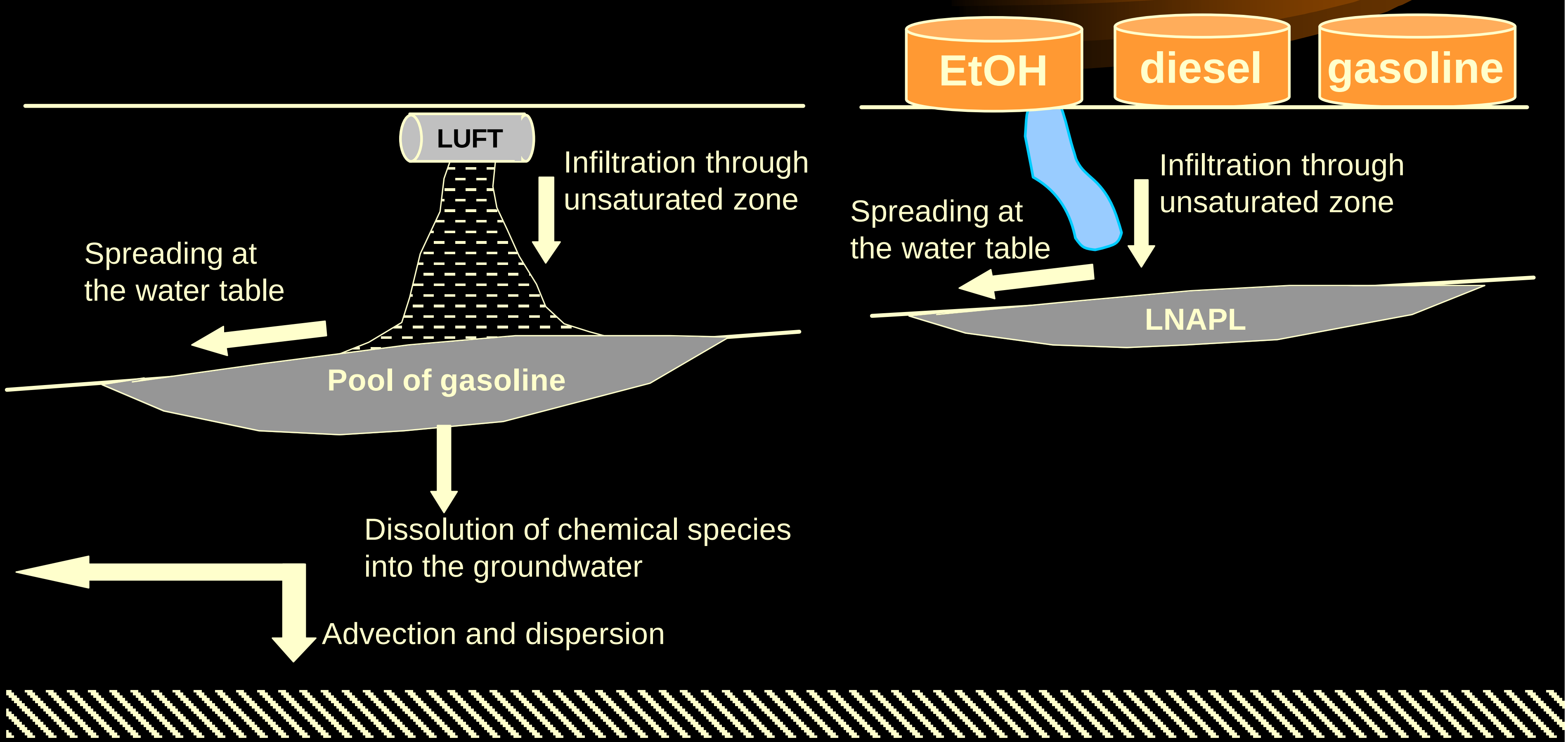
What are the difference in

solubility

volatility

biodegradation???

Focus of Our Work



Abiotic Properties

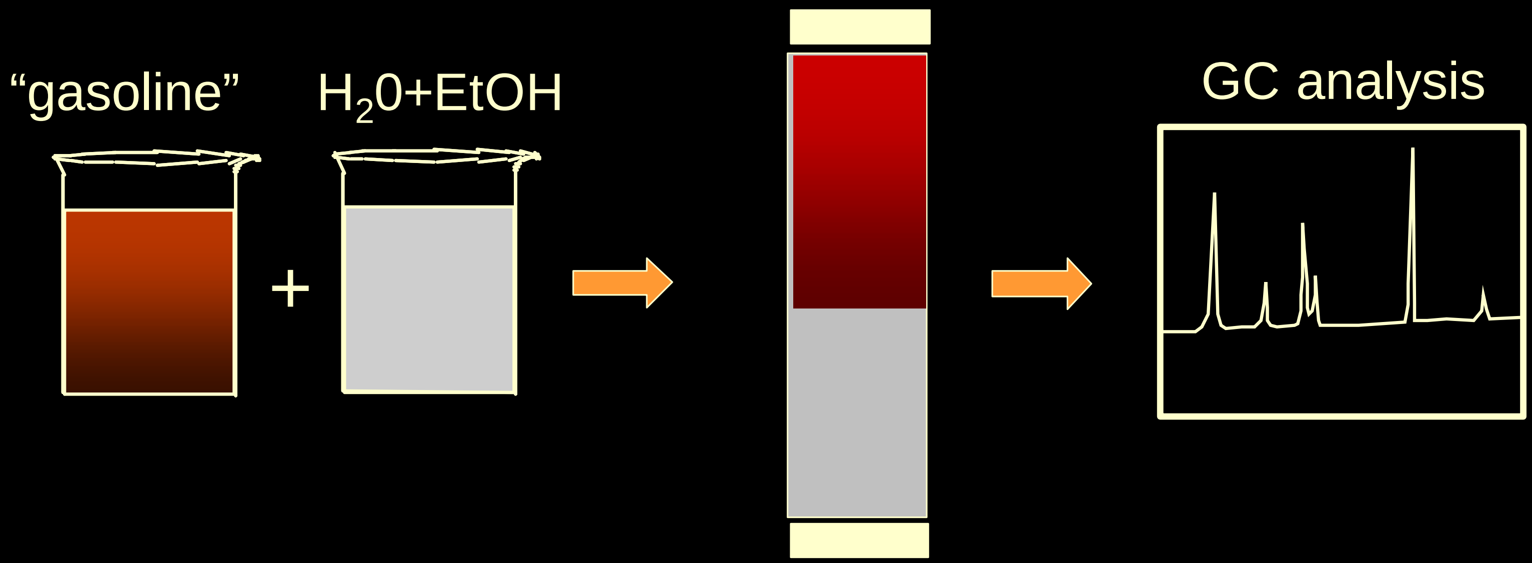
- Hydrophilic characteristics of ethanol affect two chemical properties
  - Interfacial tension
  - Cosolvency

Cosolvency

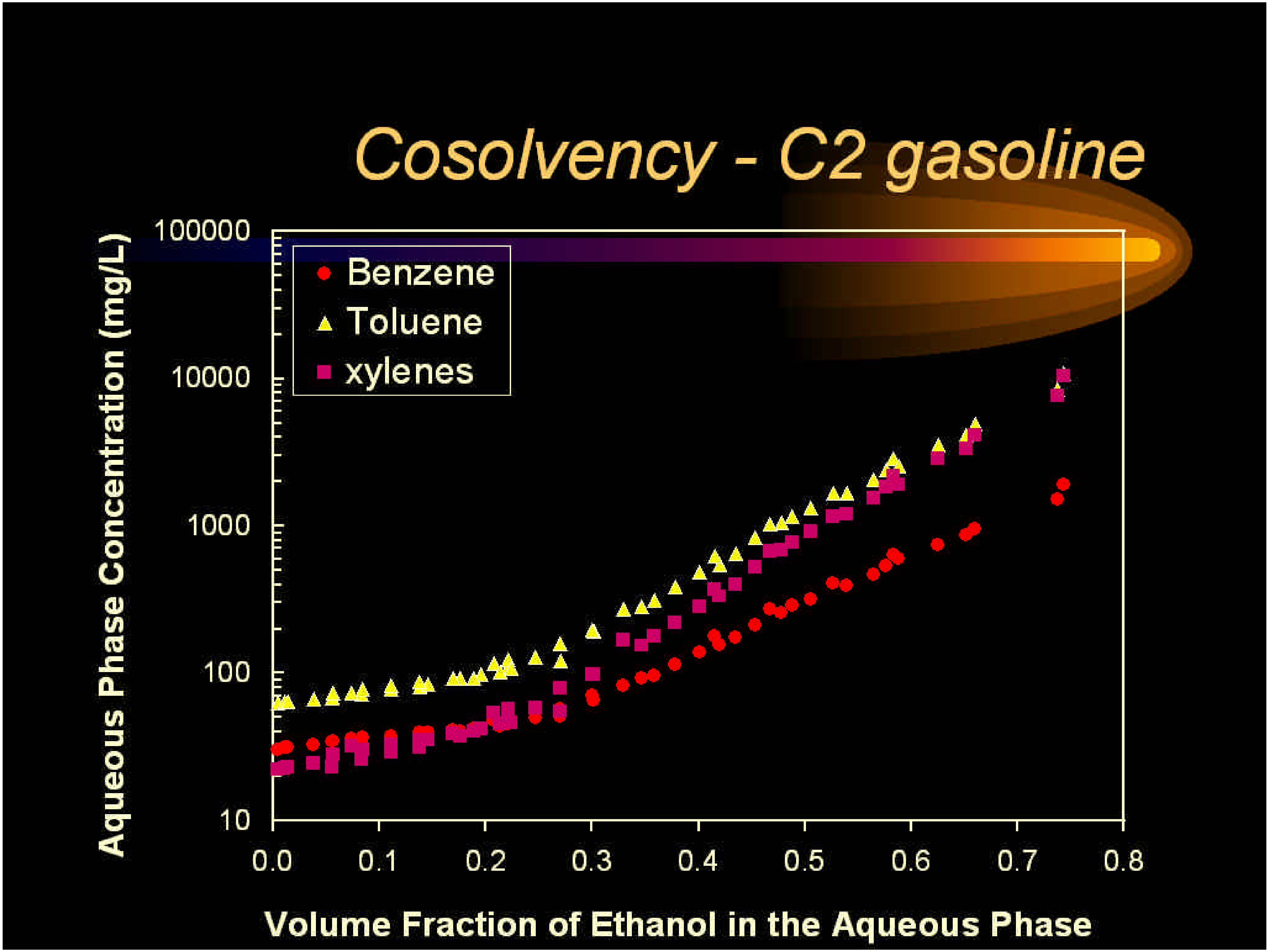
- Adding ethanol to water reduces the importance of hydrogen bonding in the aqueous phase making it less polar.
- Increased solubility of BTEX
  - Higher concentrations
  - Less retardation

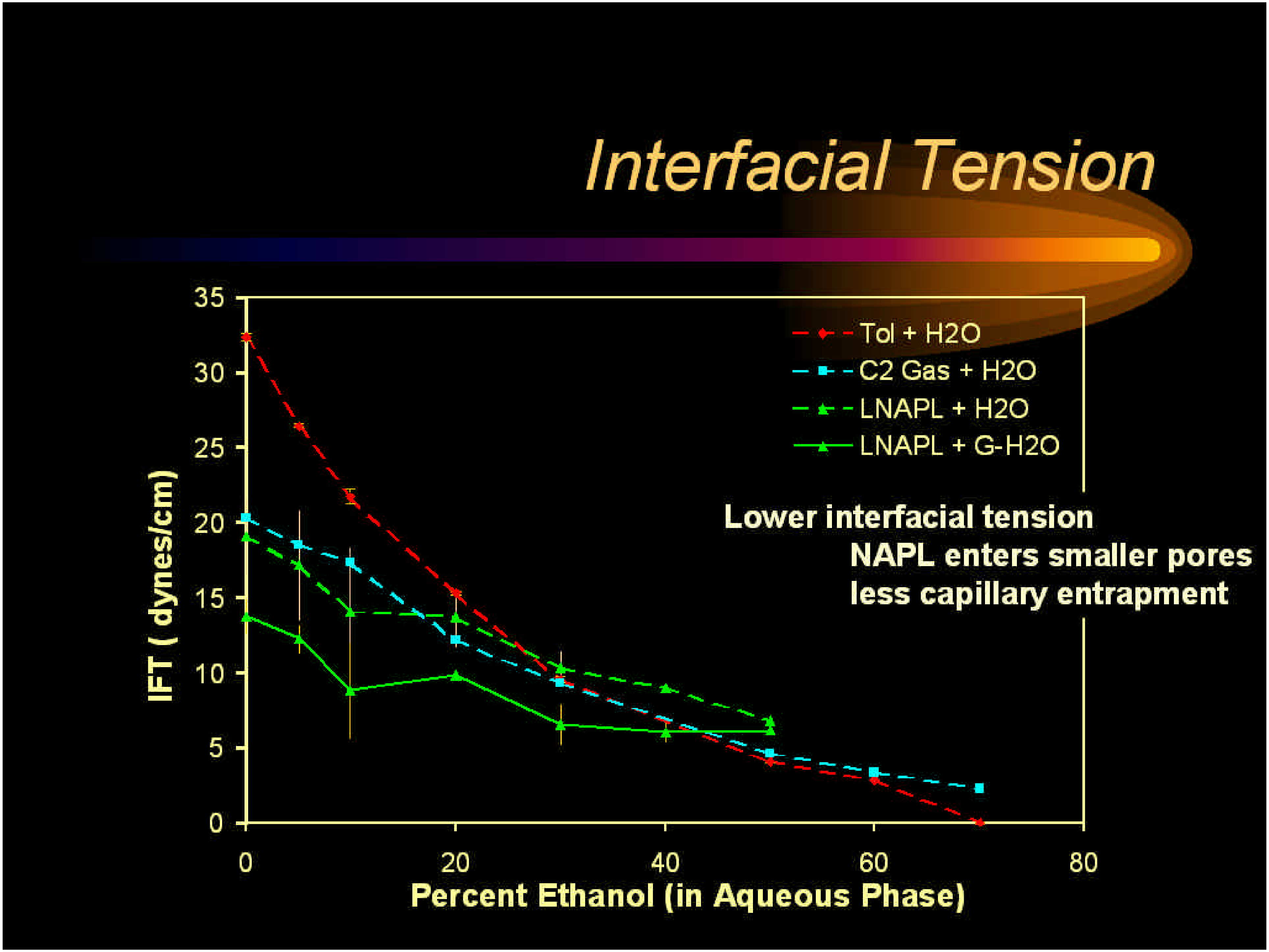
Experimental Methods

- Batch equilibrium experiments
  - surrogate gasolines (alkane + aromatic(s))
  - Philip's California Certified gasoline, "C2"



- Concentrations and densities measured

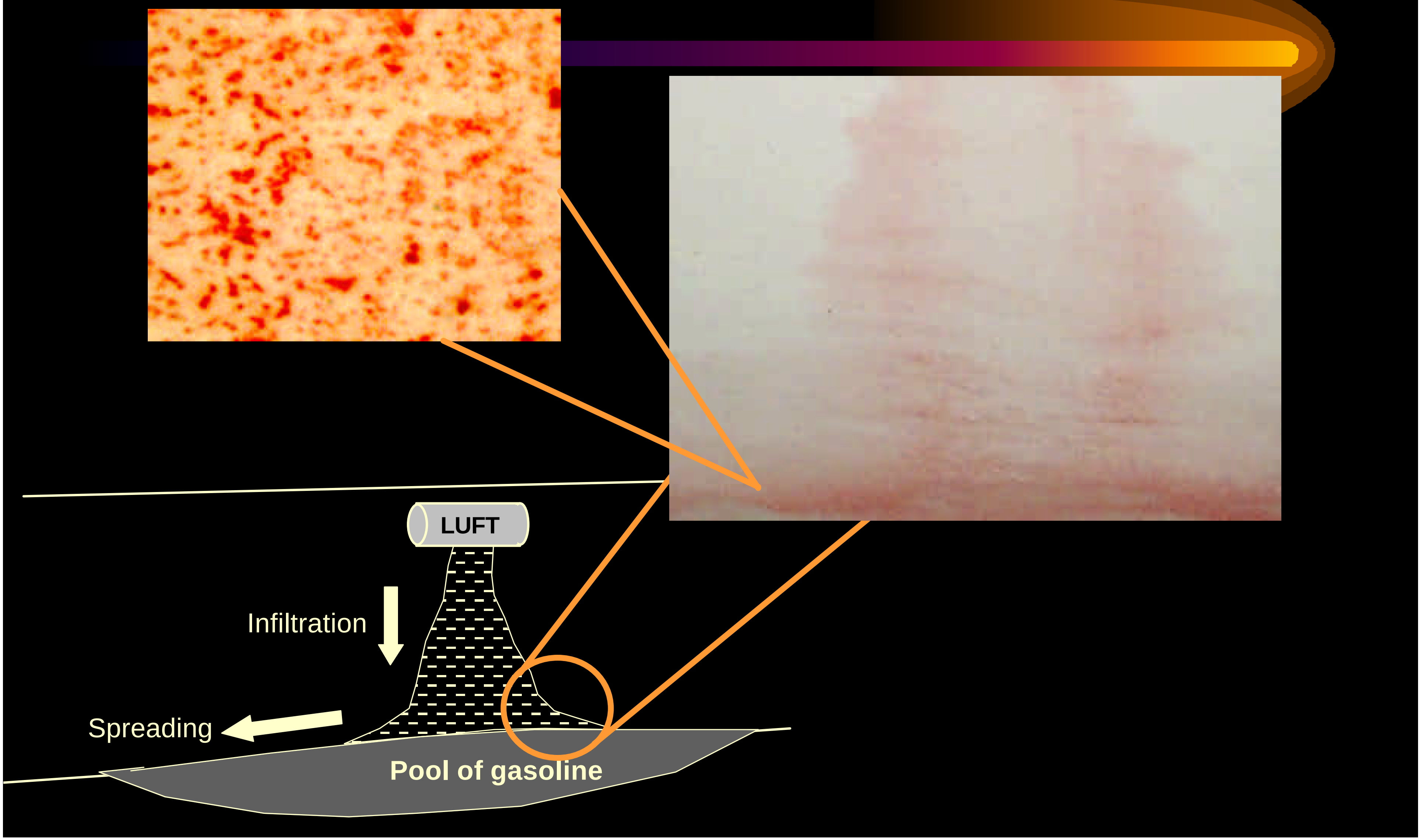

Cosolvency - C2 gasoline
Benzene
Toluene
xylenes
Aqueous Phase Concentration (mg/L)
100000
10000
1000
100
10
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Volume Fraction of Ethanol in the Aqueous Phase


Interfacial Tension
35
30
25
20
15
10
5
0
IFT (dynes/cm)
0
20
40
60
80
Percent Ethanol (in Aqueous Phase)
Tol + H2O
C2 Gas + H2O
LNAPL + H2O
LNAPL + G-H2O
Lower interfacial tension
NAPL enters smaller pores
less capillary entrapment

Focus of Our Work

- **Infiltration and spreading** of ethanol and ethanol-blended gasoline in vadose zone
- **Dissolution** of BTEX from the gasoline pool
  - Thermodynamic equilibrium - gasoline-ethanol-water
  - Rates of dissolution

Infiltration and spreading



Effects of added ethanol

Property Changes

Interfacial tension decreases

Increased solubility of NAPL

Potential Net Significance

Existing NAPL blobs dissolve and are mobilized

Reduction in capillary forces and capillary entrapment

Redistribution of NAPL

Example –

Ethanol spill into NAPL-contaminated soil

Observations – Gasoline Spill

Gasoline spill- spreading dominated by gravity and capillary action

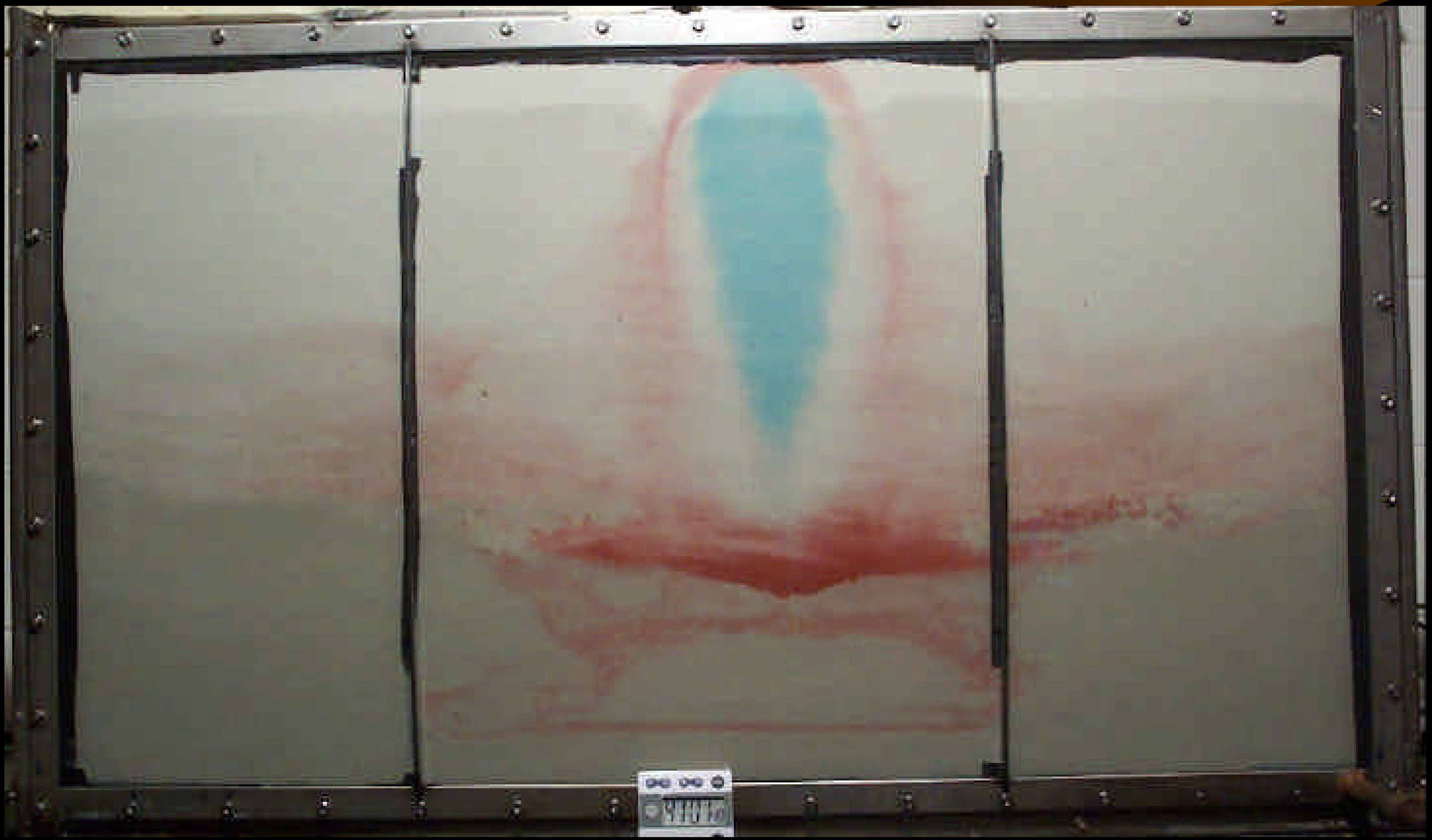
Observations – Subsequent EtOH Spill

Ethanol spill – gasoline dissolves and spreads ahead of ethanol front

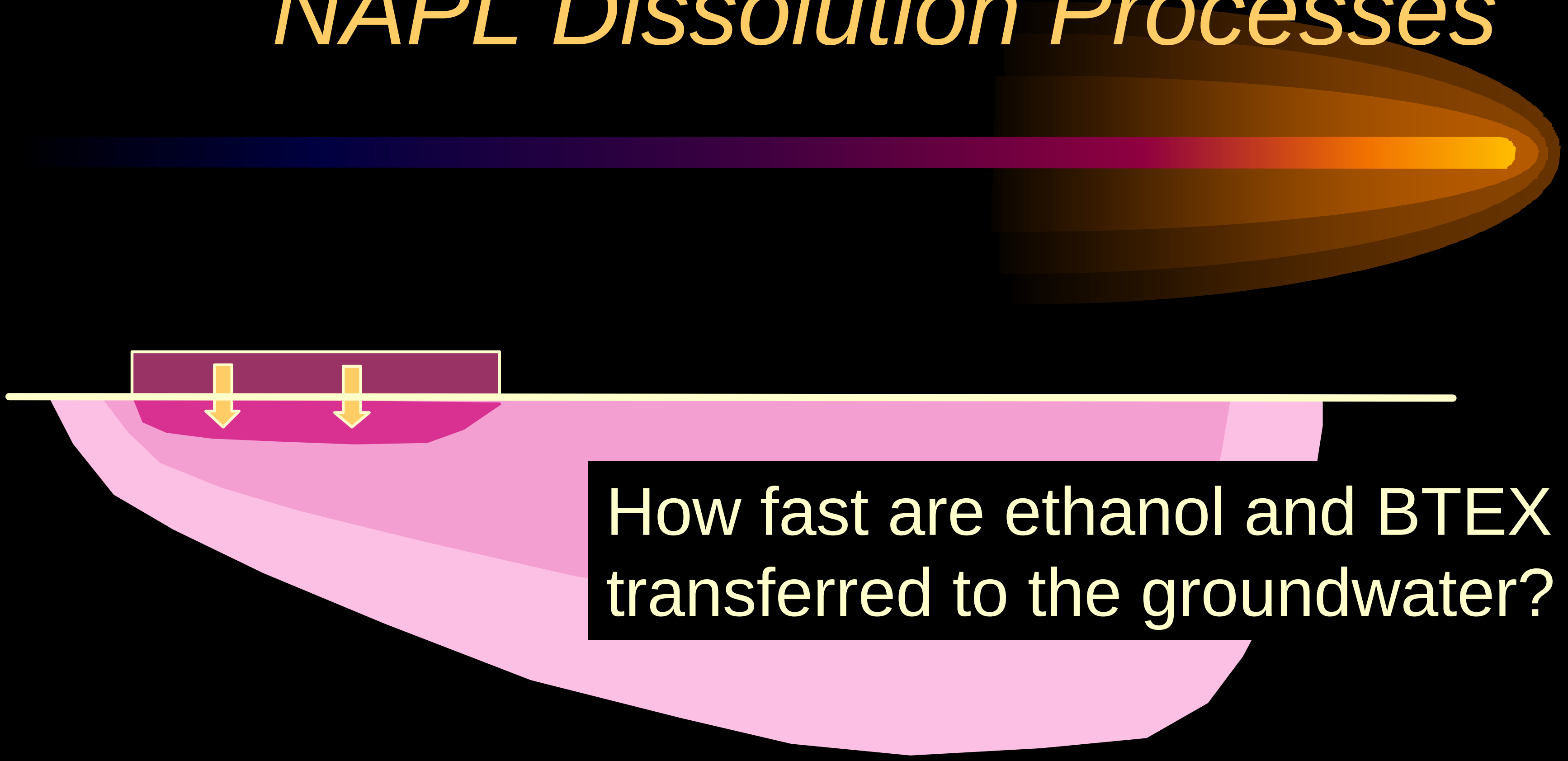
Ethanol does not spread by capillary action
Gasoline continues to move in advance of ethanol front
Capillary fringe is depressed

Significant reduction of gasoline in vadose zone
Spreading of gasoline into saturated zone

As ethanol concentration decreases,
Capillary fringe rebounds
Increase in LNAPL saturation at the capillary fringe
Smearing of residual saturation in the saturated zone

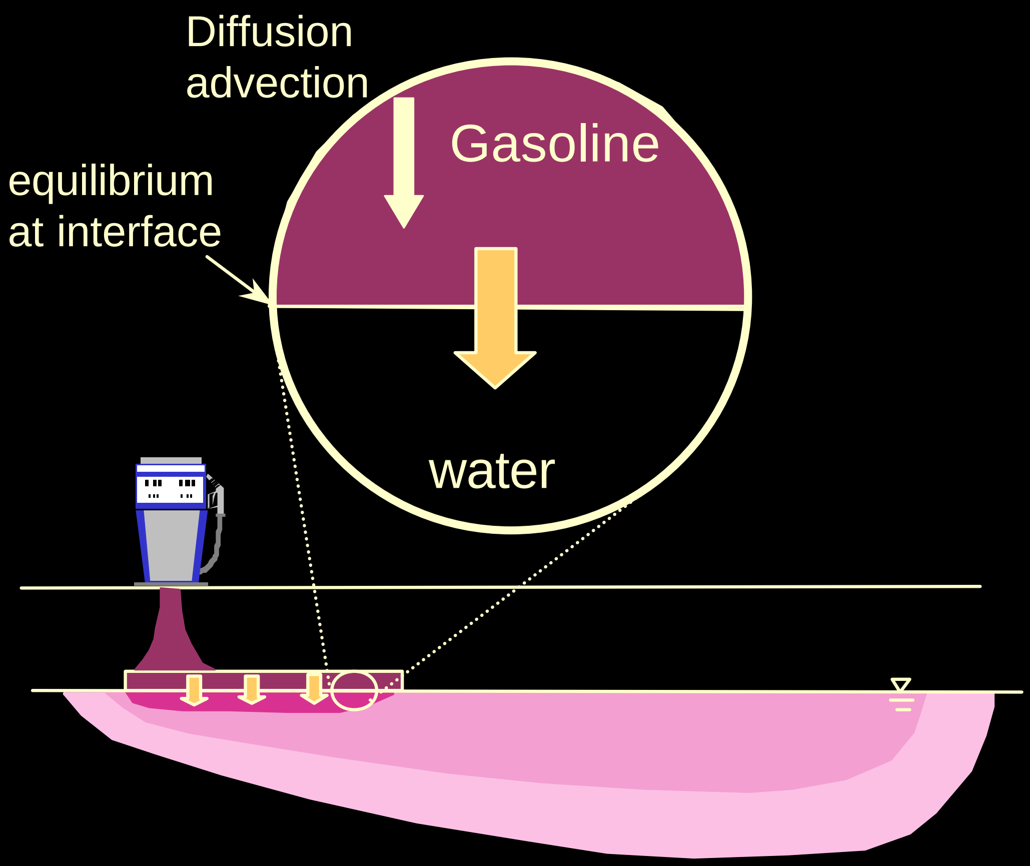


NAPL Dissolution Processes



How fast are ethanol and BTEX transferred to the groundwater?

Changes in the Gasoline Pool



Property Changes

Interfacial tension decreases

Composition of gasoline as ethanol leaches

Altered equilibrium condition

Potential Net Significance

Reduction in capillary forces

Concentration at source increased

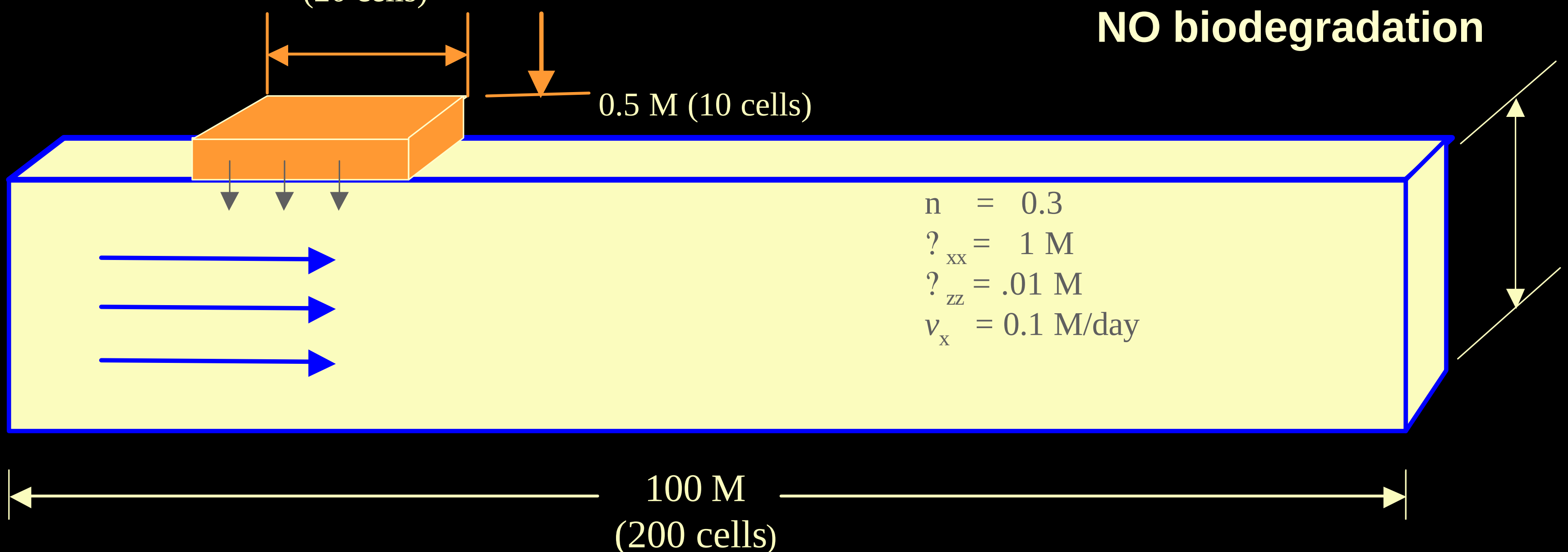
EtOH

BTEX

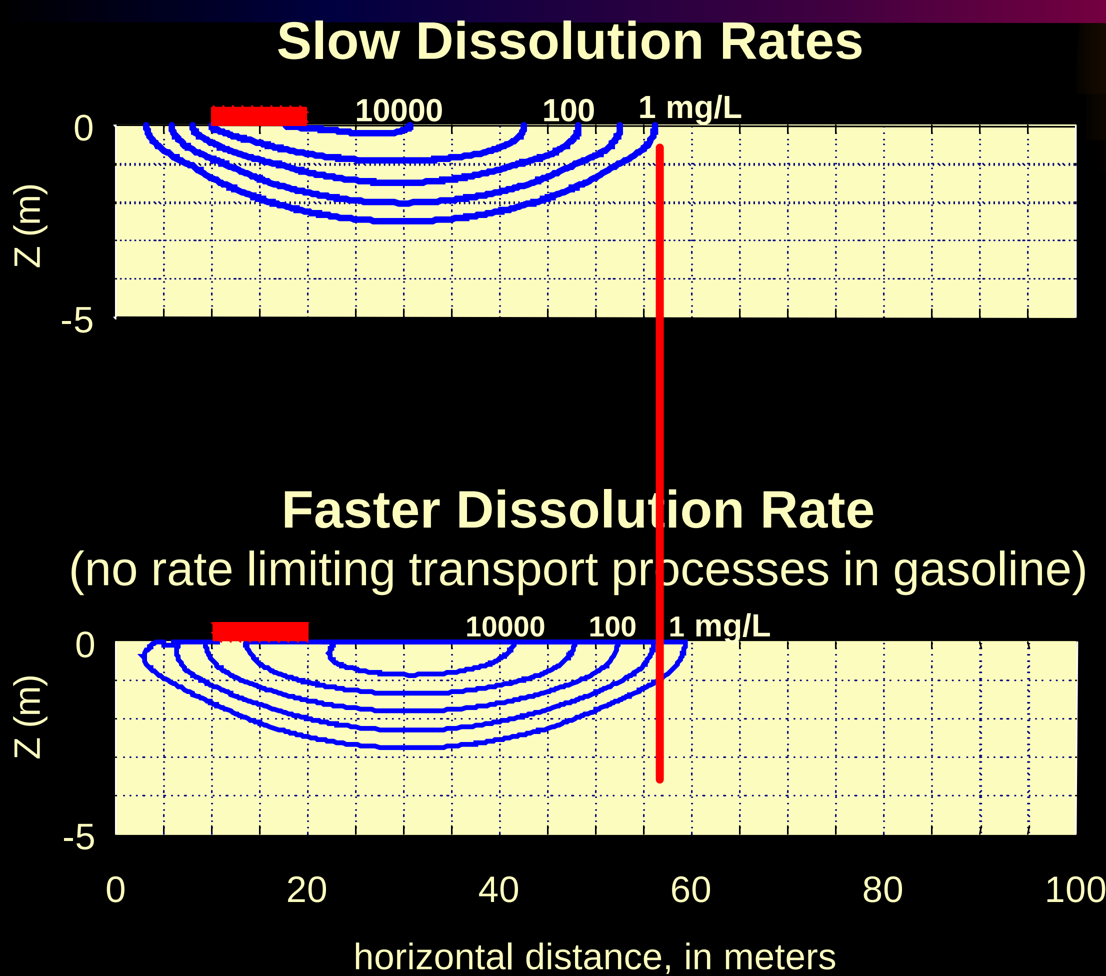
Modeling Efforts

Cosolvency
Dissolution rates
Reduced sorption

NO biodegradation



Modeling Results



Explanation

Gasoline pool:
20 wt% ethanol
16 wt% toluene
64 wt% *n*-heptane

Aqueous ethanol concentrations (mg/L)

Ethanol Concentrations (90 days)

Modeling Results

- no ethanol in gasoline

- 20 % etoh in gasoline;
- Slow mass transfer rates

- 20 % ethanol in gasoline;
- Fast mass transfer rates

Toluene Concentrations (90 days)

Modeling Predictions

- Slow mass transfer
  - –negligible increase in BTEX mass transfer due to ethanol
- Faster mass transport
  - –ethanol mass transfer rates are higher
  - –total travel distance is slightly longer
  - –cosolvency effect is sufficient to substantially increase BTEX concentrations in aquifer with 20% etoh in gasoline.

Summary

- LUFT spill events
  - Cosolvency and dissolution rates do not appear to have a significant impact on BTEX plumes
  - Uncertainty in rate of dissolution – but is it a significant issue?
  - Vadose zone issues still being investigated
- Ethanol spill events
  - Lowered interfacial tension greatly affects distribution of NAPL
  - Cosolvency effects result in significant increase in BTEX following ethanol spill

Research Needs

Individual processes studied in the laboratory have to get ***integrated*** to understand net impacts

- Computer modeling
- Field-scale spill study

Effect of Ethanol on BTEX Natural Attenuation:

Biodegradation Kinetics, Geochemistry, and Microbial Community Implications

Pedro J.J. Alvarez

The University of Iowa
Department of Civil & Environmental Engineering

Workshop on Ethanol & Alkykates in Fuels
April 11, 2001

Acknowledgments

Students

- Craig Hunt
- Nanh Lovanh
- Marcio da Silva
- Graciela Ruiz
- Jose Fernandez
- Jeff Pullen

Faculty/Scientists

- Sue Powers
- Henry Corseuil
- Dave Rice
- Harry Beller
- Tim Buscheck
- Microbial Insights, Inc.

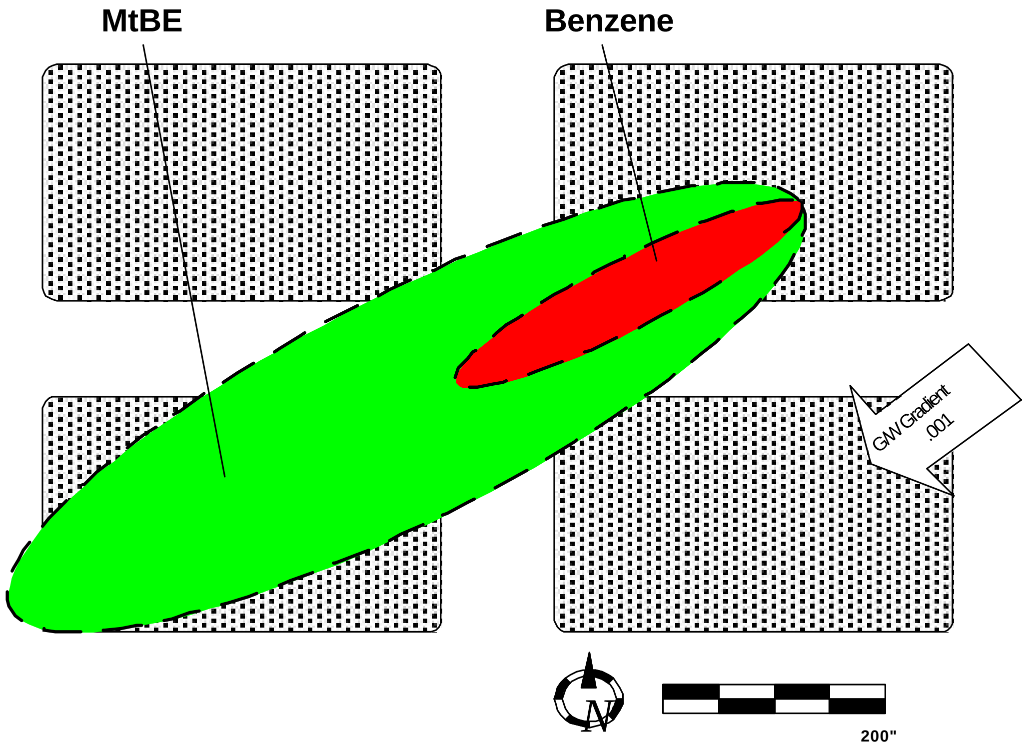
Funding

- California/LLNL
- EPA
- API

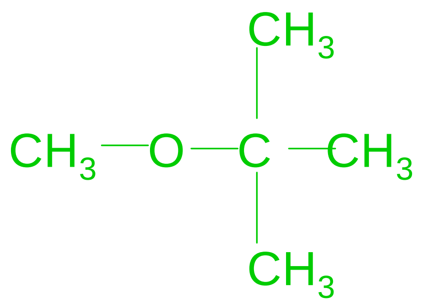
Emission control regulations and gasoline reformulation reduced air pollution

~15 years

Distribution of Key Constituents in Gasoline-Contaminated Groundwater



MTBE



Replace MTBE with Ethanol?

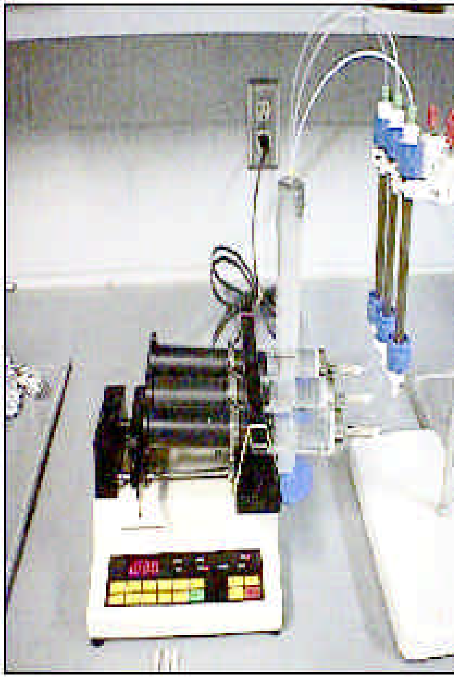
- Good oxygenate (reduces air pollution from combustion) renewable, biodegradable, non-toxic, and can serve as substitute fuel for imported oil. But...
- Can have adverse effects on migration and natural attenuation of priority pollutants such as benzene:
  - Increased hydrocarbon solubility in water (cosolvent effect) and enhanced transport
  - Inhibition of benzene biodegradation (preferential utilization, O_2 depletion, toxicity to bacteria if >4%)

Prospectus

- Do “typical” ethanol concentrations enhance BTEX migration by decreasing sorption-related retardation?
- How does ethanol affect BTEX biodegradation rates under different electron-acceptor conditions, and how do such effects differ from one site to another?
- Overall effect on BTEX natural attenuation and the resulting plume length?

Methods

Breakthrough studies
(Retardation)

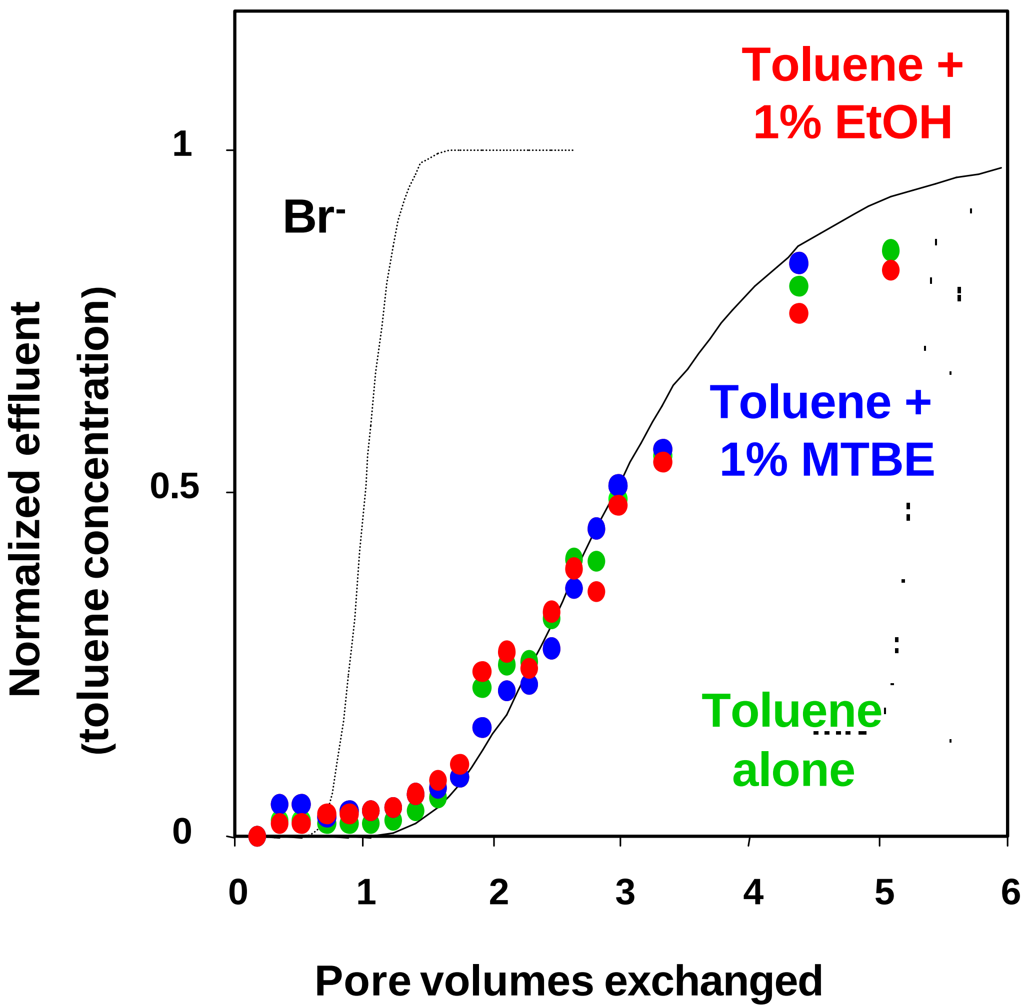


Chemostats
(Biodegradation)

Microcosms
(Variability)

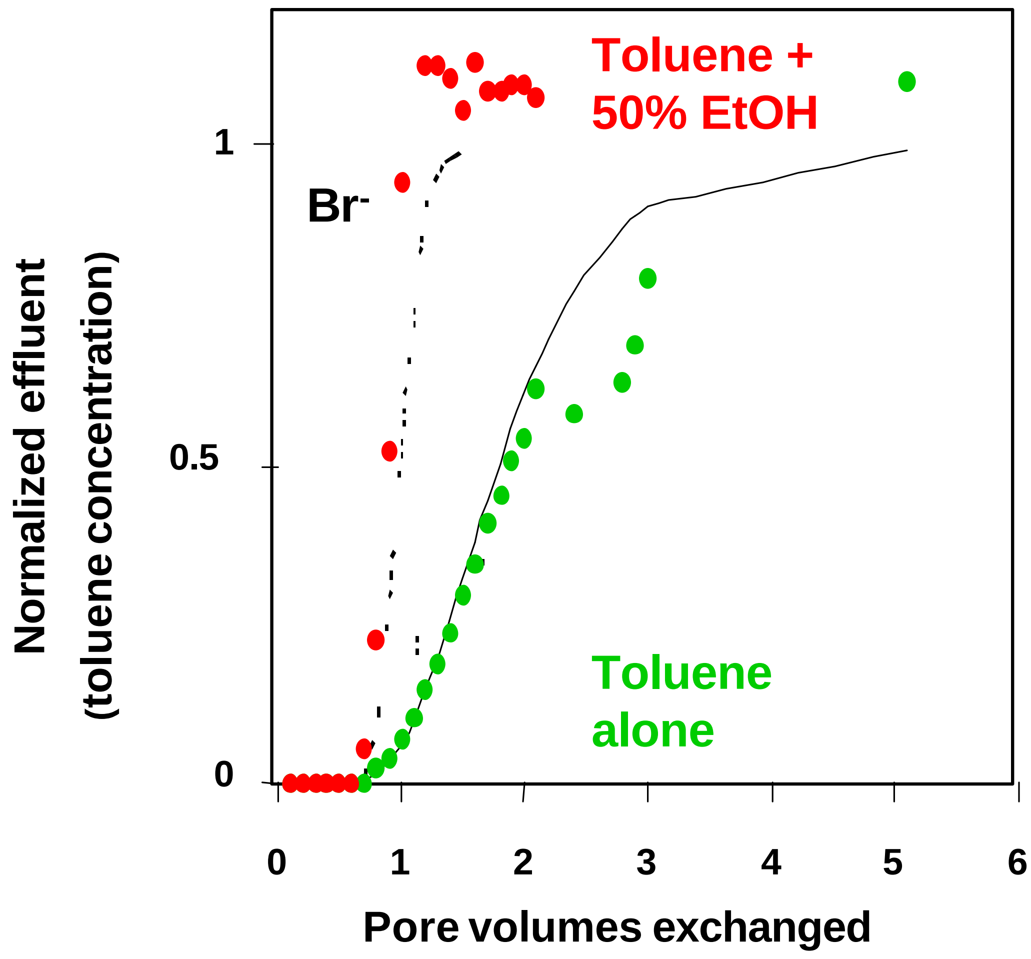
Column Profiles
(Natural attenuation)

No Effect of EtOH or MTBE on Sorption-Related BTX Retardation



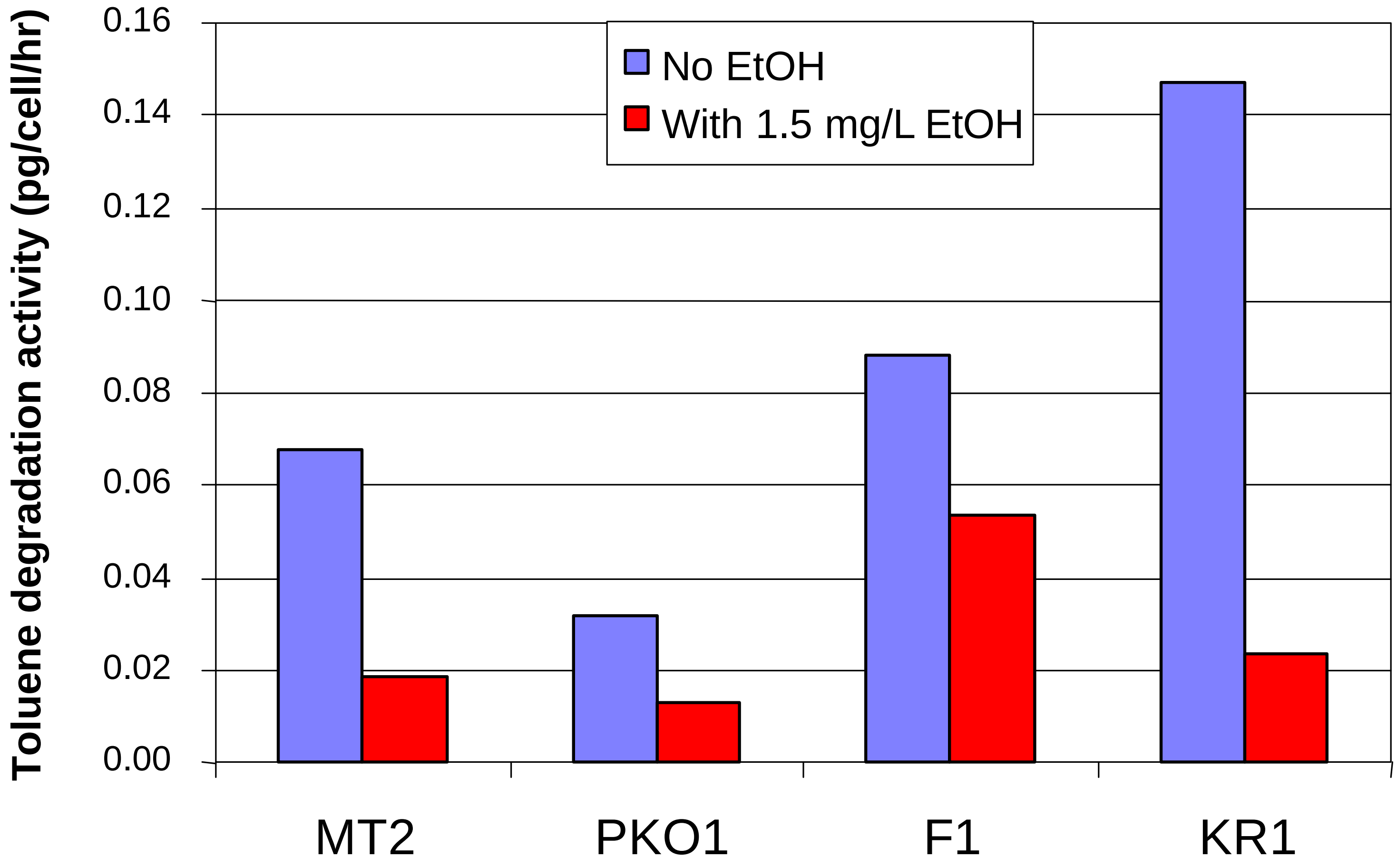
R_f = 3.4 for all cases

Effect of High EtOH Conc. on Sorption-Related BTX Retardation



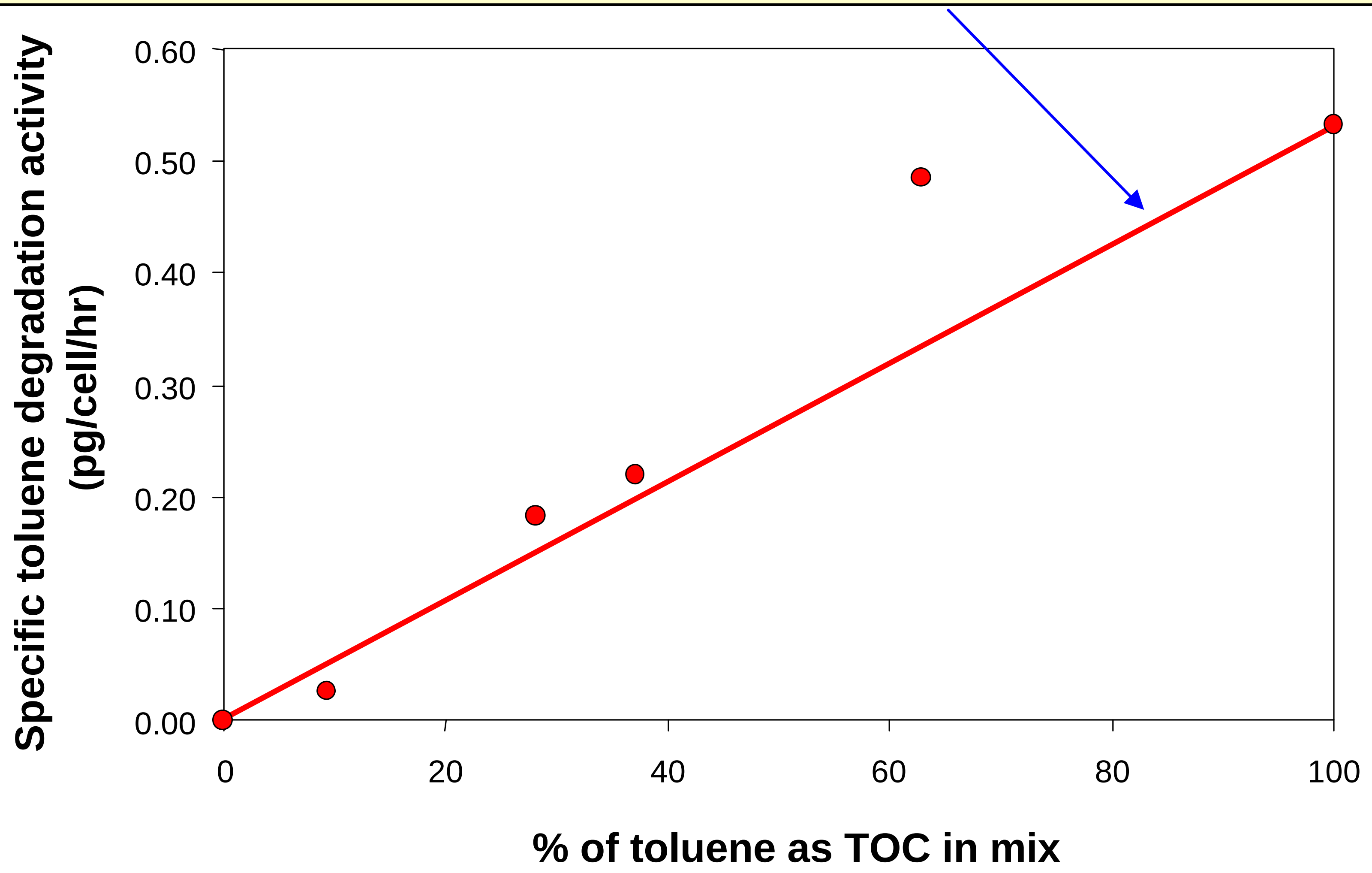
R_f = 1 with 50% EtOH

Effect of ethanol on aerobic toluene degradation activity in chemostats with different archetypes, fed 1 mg/L toluene



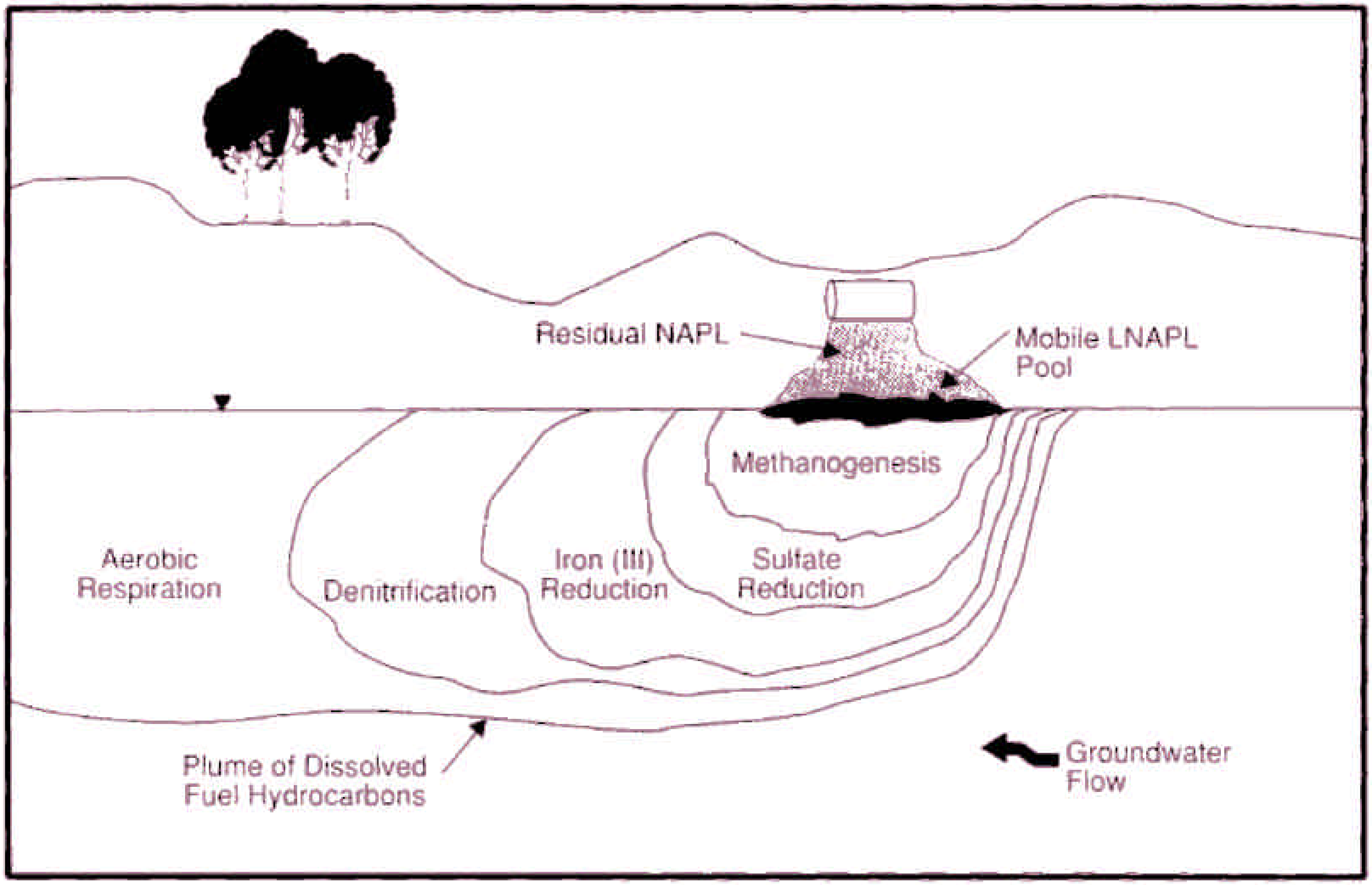
The specific degradation rate of toluene by *P. mendocina* KR1

Rate per cell (BTX)$_{mix}$= Rate per cell (BTX)$_{alone}$? (BTEX fraction in mix, as TOC)



Geochemical evolution of BTX-contaminated groundwater

(Source: Wiedemier et al., 1999)



Days to degrade 50 % of toluene (1-2 mg/L) in microcosms with aquifer material from different sites under different electron acceptor conditions

Site	Aerobic			Denitrifying			Iron-reducing			Sulfate-reducing			Methanogenic		
	BTEX Alone	With MTBE	With EtOH	BTEX Alone	With MTBE	With EtOH	BTEX Alone	With MTBE	With EtOH	BTEX Alone	With MTBE	With EtOH	BTEX Alone	With MTBE	With EtOH
A	7		6	32		30	29		***> 70***	> 70		> 70	57		**35**
B	1	1	***7***	4	4	4	5	5	***18***	11	11	**7**	5	5	***34***
C	11		14	> 48		**14**	13		**17**	24		**33**	> 54		> 56
D	3	**14**	**>13**	51	36	**30**				30	**8**	**11**	38	**16**	**26**

Site A = Tracy site, no known previous BTEX exposure.

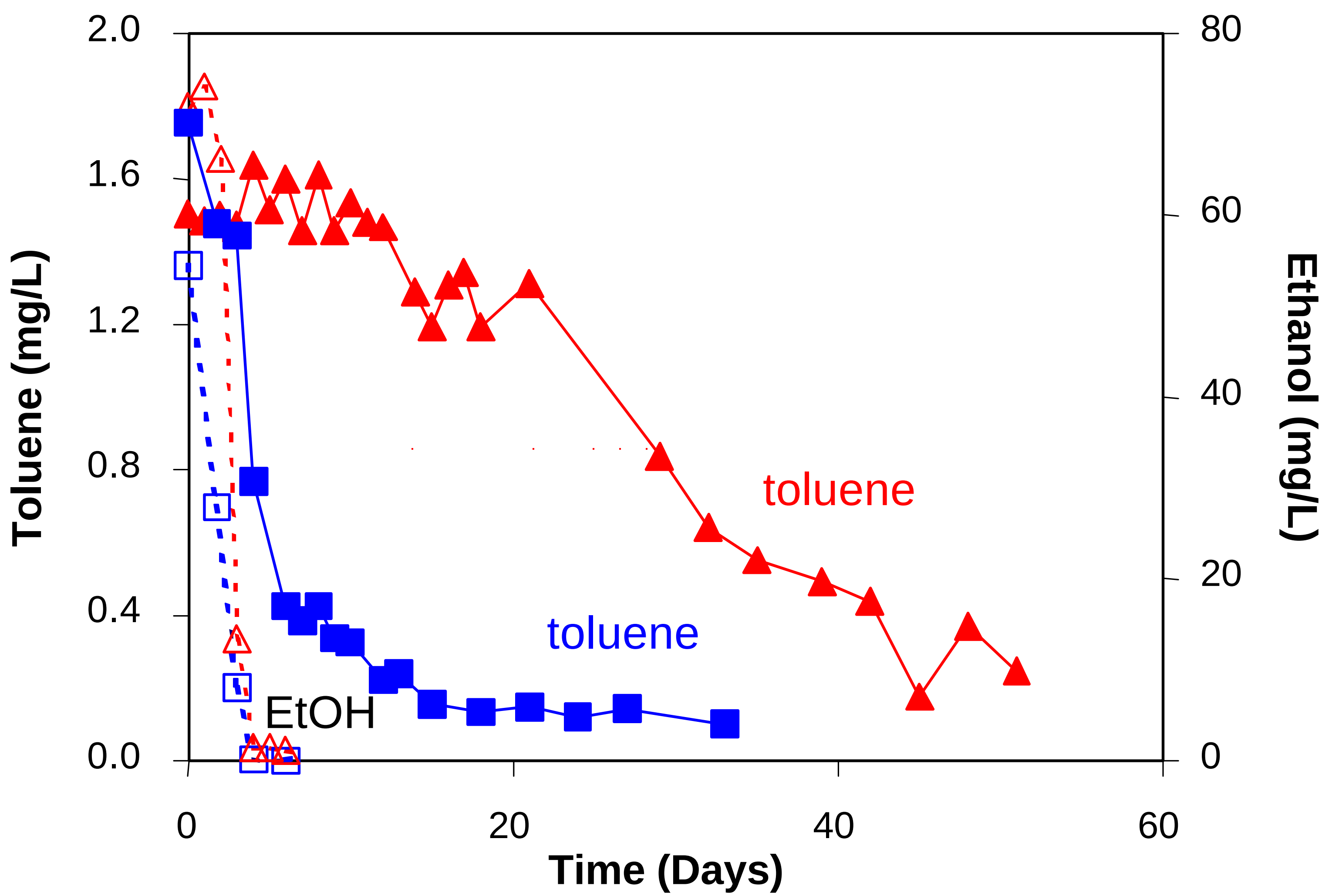
Site B = Travis AFB site, contaminated with BTEX and MTBE.

Site C = NW bulk terminal site, neat EtOH release over pre-existing BTEX contamination.

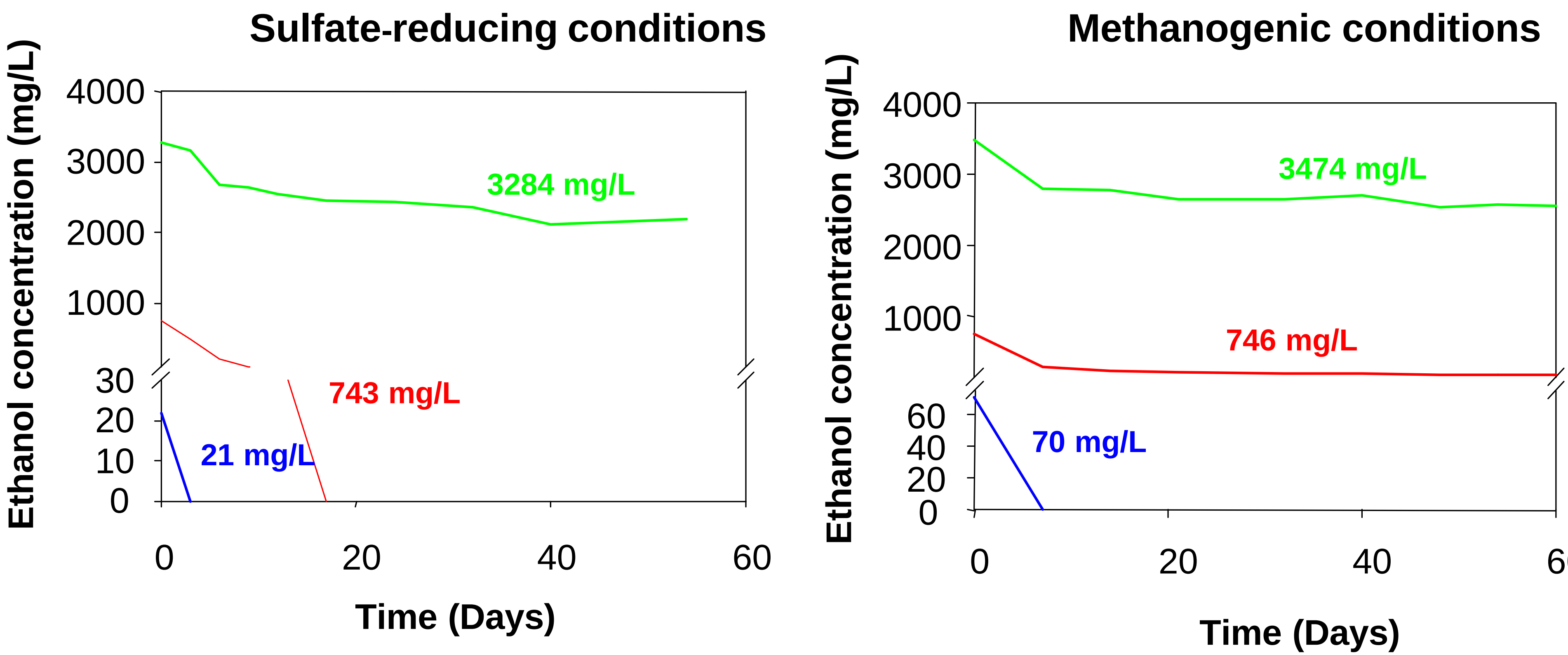
Site D = Sacramento site, contaminated with BTEX and MTBE.

EtOH or MTBE added at 100 mg/L

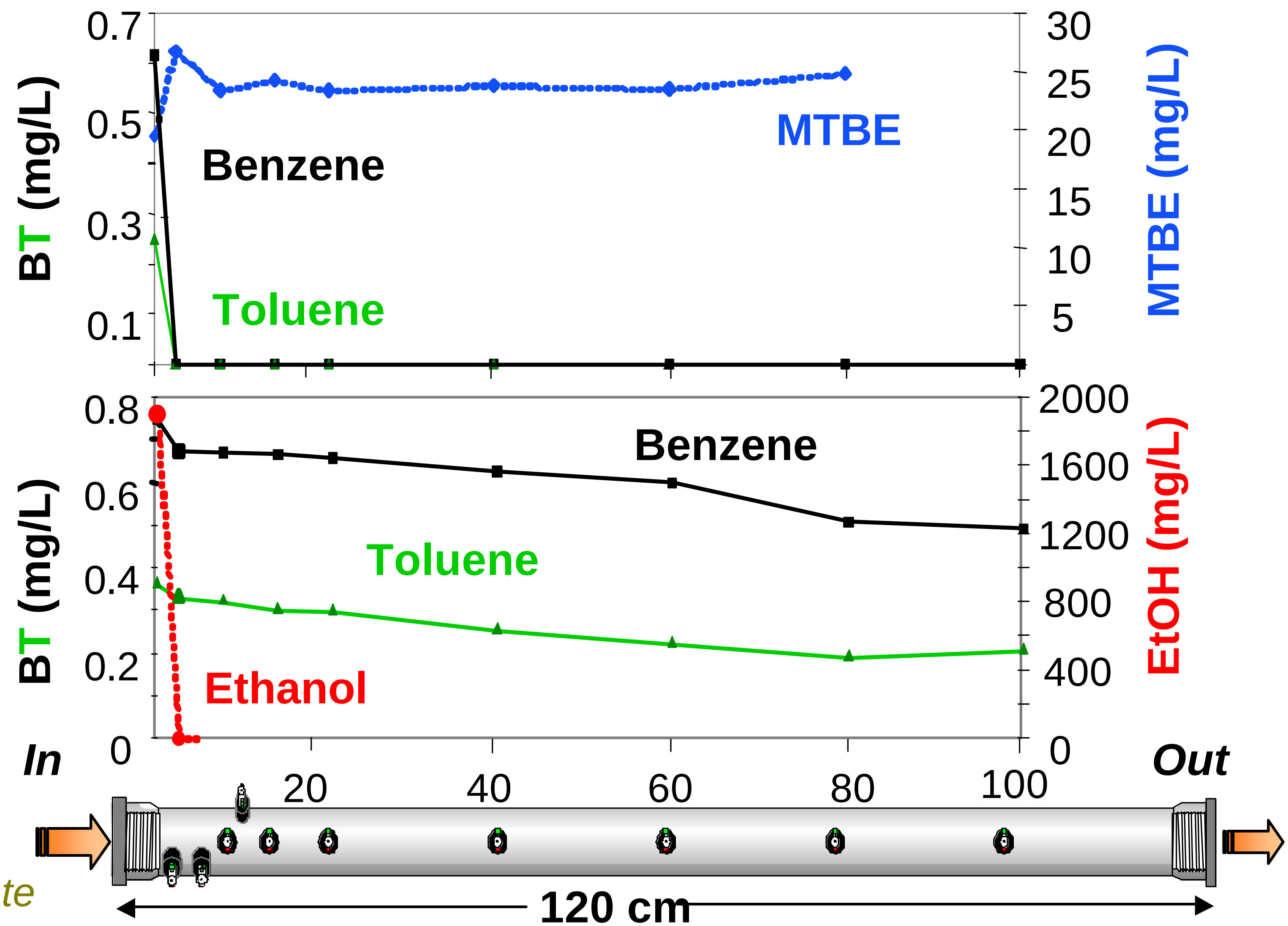
Toluene and ethanol degradation in denitrifying microcosms from contaminated and uncontaminated sites



Ethanol concentrations exceeding 3,000 mg/l were not degraded in anaerobic microcosms

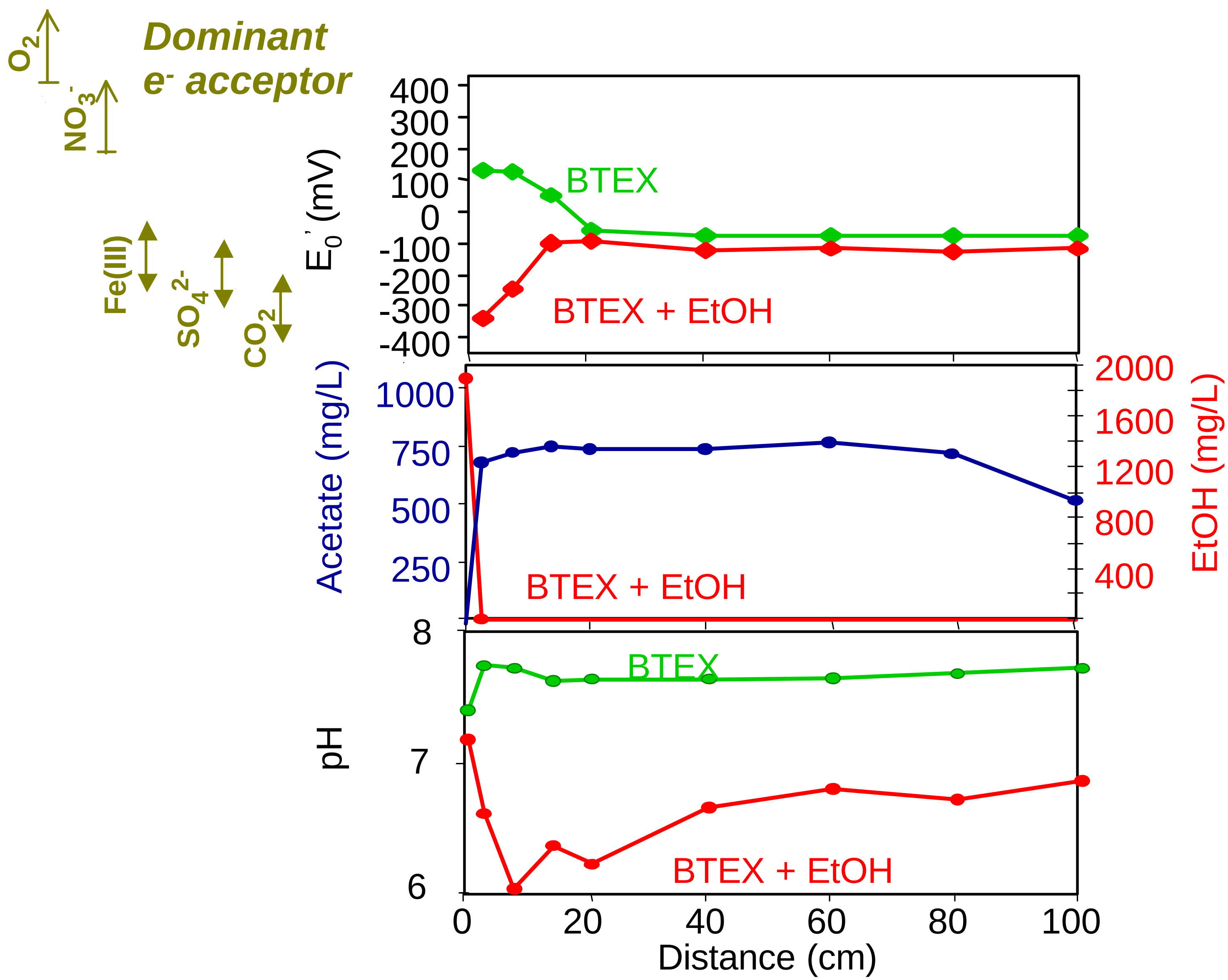


Effect of Ethanol and MTBE on BTX Natural Attenuation

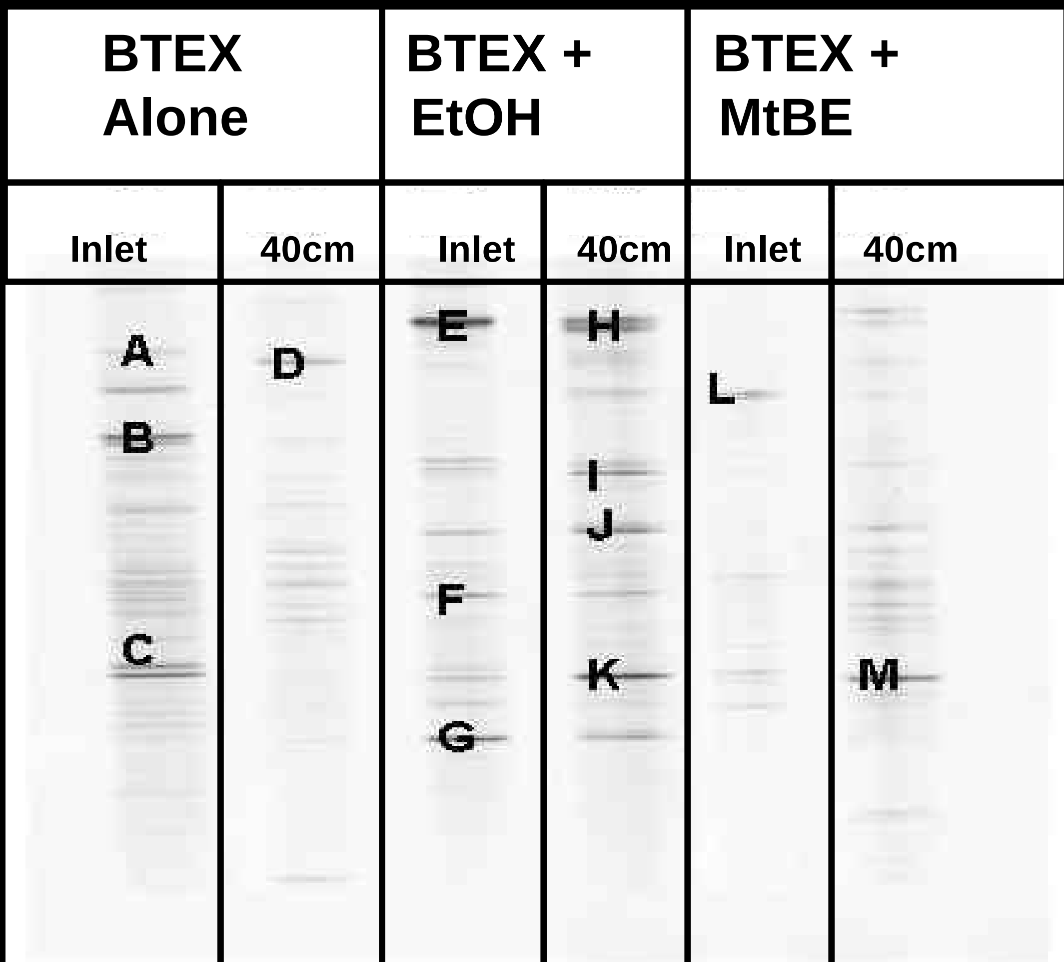


HRT = 5.5 days
8 ppm DO
30 ppm nitrate
100 ppm sulfate
1000 ppm bicarbonate

Effect of ethanol on redox potential, acetate production and pH



DGGE Analysis of the Effect of EtOH and MtBE on Microbial Community (by Microbial Insights, Inc.)



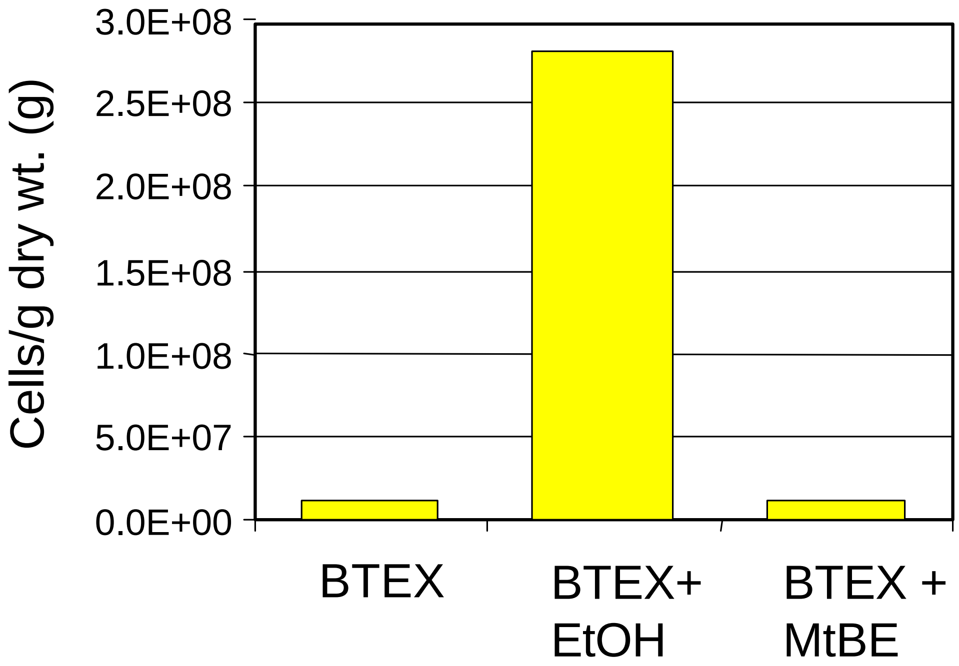
Dominant species

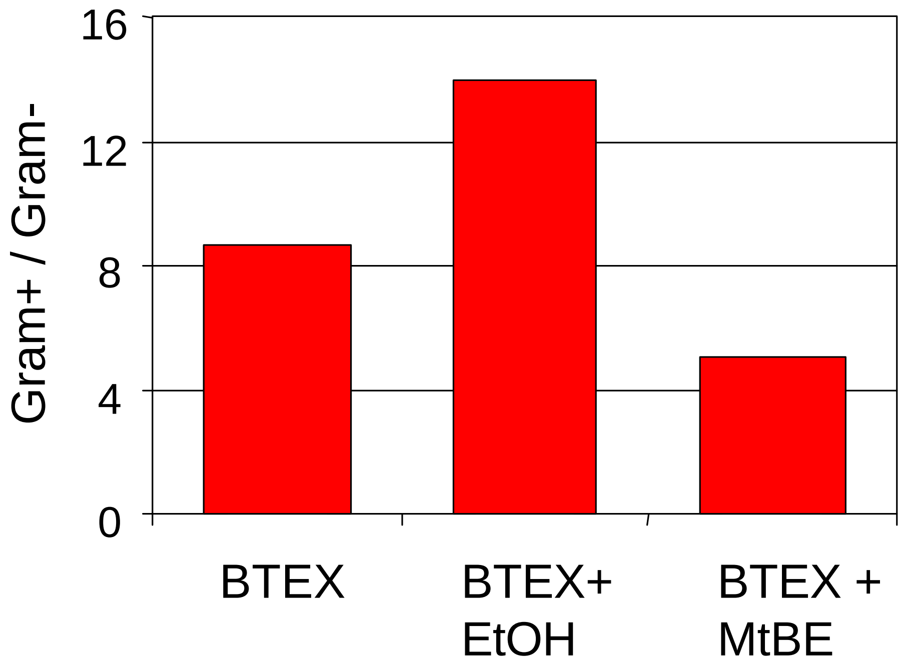
A - *Geobacter akaganeitreducens*
B - *Geobacter sp.*
C - *Clostridium sp.*
D - *Azoarcus sp.*

E - *Campylobacter sp.*
F - *Clostridium sp.*
G - *Desulfovibrio burkinensis*
H - *Sporomusa sp.*
I - *Clone WCHB1-71*
J - Failed
K - Clone SJA-181

L - *Geobacter akaganeitreducens*
M - *Slackia exigua*

PLFA Analysis of Microorganisms in the Inlet of the Columns





EtOH increased the biomass concentration (10X)

and the relative abundance of Gram+ bacteria

Conclusions

- Cosolvent effects are unlikely at gasohol-contaminated sites (i.e., [EtOH] < 10,000 mg/L) - ***but important for neat releases.***
- Ethanol itself is not a major groundwater quality problem, but it could ***increase BTEX plume lengths*** (preferential degradation and depletion of nutrients and electron acceptors that could otherwise be used for BTEX biodegradation).
- ***MTBE should not affect BTEX behavior***, but itself is a major concern in drinking water supplies.

Ethanol in Groundwater at a Northwest Terminal

Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California
April 10 & 11, 2001

Tim Buscheck
Senior Staff Hydrogeologist
Chevron Research and Technology Company

Kirk O'Reilly, Chevron Research and Technology Company
Gerard Koschal, PNG Environmental
Gerald O'Regan, Chevron Products Company

Groundwater Investigation

- In March, 1999 a 19,000-gallon release of neat ethanol occurred from an above ground storage tank
- Following the ethanol release, nine monitoring wells were installed in the fill and sampled six times between June 1999 and December 2000
- In May 2000 a sampling protocol was implemented to measure for indicators of in situ bioremediation
- In December 2000 eight additional monitoring wells were installed in the shallow fill and the deeper alluvium
- The objective of the groundwater sampling program is to delineate the ethanol plume and understand the impact of ethanol on the existing nonaqueous phase liquid (NAPL) and dissolved hydrocarbon plumes

Buscheck et al., 2001

The Cosolvent Effect

- With a sufficiently large amount of ethanol in a localized subsurface environment, gasoline and water become completely miscible with each other and merge into a single phase (Powers et al., 2001)
- Laboratory experiments demonstrate a logarithmic increase in BTEX with increasing ethanol concentrations (Heerman and Powers, 1998)
- Neat ethanol releases could result in an order of magnitude increase in BTEX concentrations (Powers et al., 2001)

Ethanol Biodegradation and the Impact on BTEX

- Ethanol can be degraded in both aerobic and anaerobic environments at a faster rate than other gasoline constituents

- Ethanol concentrations exceeding 40,000 mg/L in microcosm experiments were toxic to the microorganisms, as shown by a complete lack of oxygen consumption (Hunt et al., 1997)

- Ethanol will most likely be preferentially utilized over all the BTEX compounds under aerobic and anaerobic conditions

- Ethanol constitutes a significant demand on oxygen (and other electron acceptors) and is likely to cause the depletion of electron acceptors for BTEX degradation
  - this is particularly important for benzene because it degrades slowly under anaerobic conditions

Effect of Ethanol on BTEX Biodegradation

- da Silva et al. (2001) conducted microcosm experiments to study aerobic, denitrifying, iron-reducing, sulfate-reducing, and methanogenic conditions
- Aquifer materials from the Northwest Terminal were included in these experiments
  - ethanol retarded toluene degradation under aerobic, sulfate-reducing, and iron-reducing conditions
  - ethanol enhanced toluene degradation under denitrifying conditions

Northwest Terminal History and Setting

- The terminal began operations in 1911, distributing and blending a variety of petroleum products
- The area was once predominated by lakes and sloughs, filled with dredge materials from a nearby river
- Two other terminals border the site to the north and south; more than 100 borings and monitoring wells have been completed at the three terminals

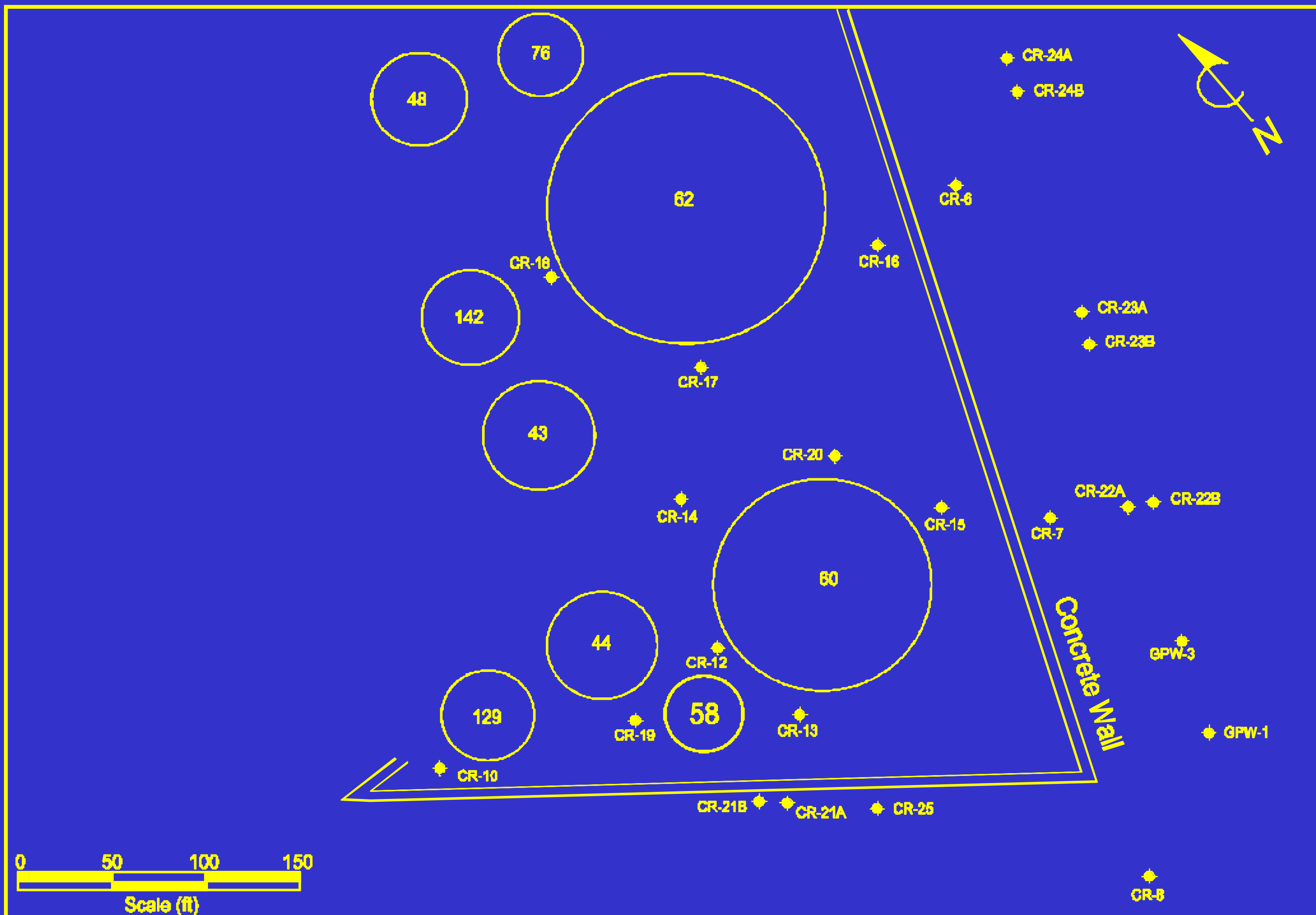
Site Geology

- Fill material of gravel, silt, and sand has been deposited over most of the site, varying in thickness from nonexistent to greater than 30 feet
- Fill is underlain by Holocene alluvial deposits of clay, silt, and sand
- In six borings at the terminal, the alluvium occurred to a depth of approximately 50 feet below grade; based on these borings, basaltic material is present at approximately 50 feet below grade

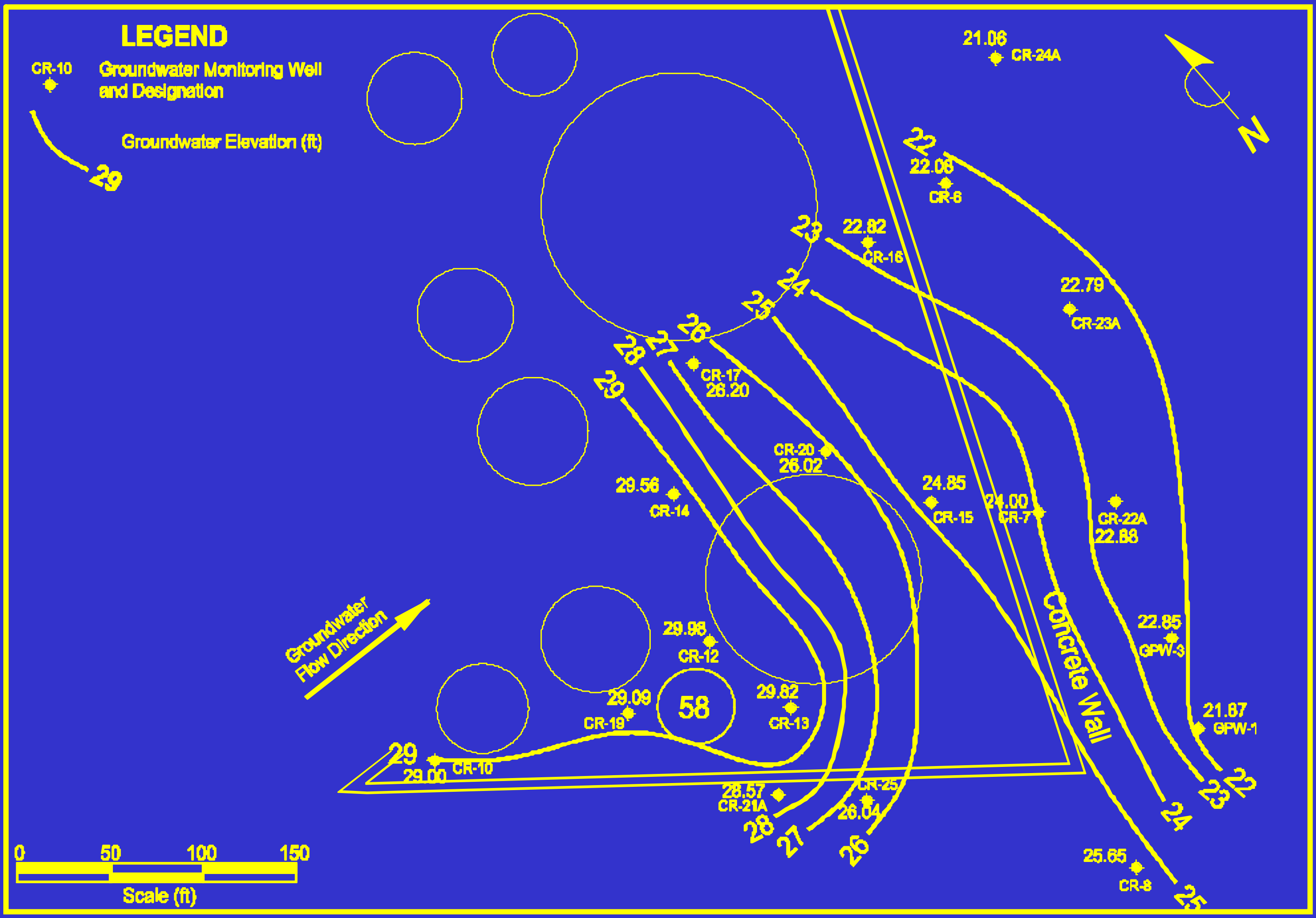
Site Hydrogeology

- The fill and alluvium are hydraulically connected; the units discharge to a river, approximately 1500 feet east of the ethanol release
- The fill is the primary zone for the occurrence of hydrocarbons
- Depth to groundwater varies from 2 to 15 feet below grade
- Groundwater velocity within the upper sandy fill is approximately 300 to 400 feet per year

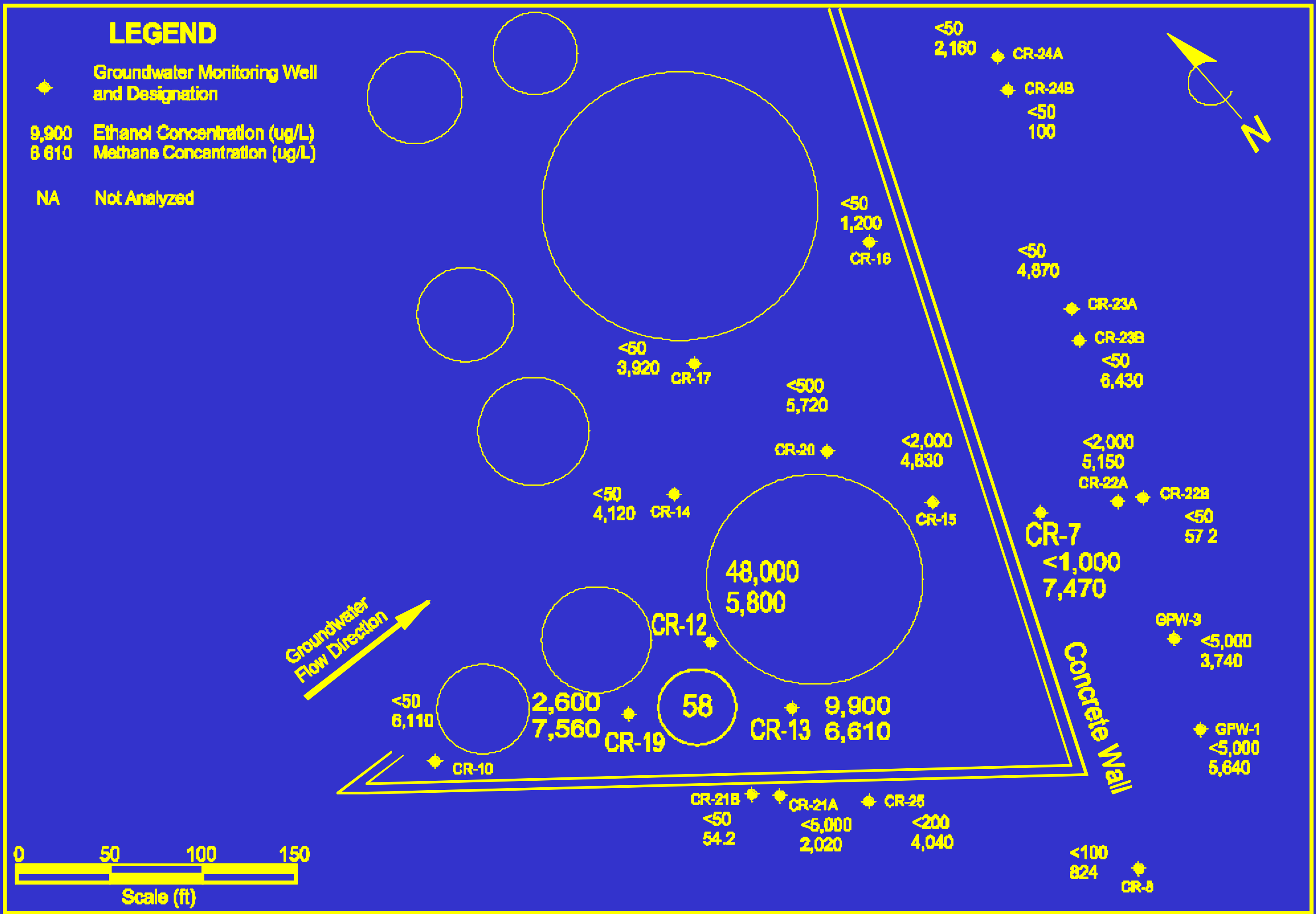
Monitoring Well Location Map



Groundwater Elevations
December, 2000



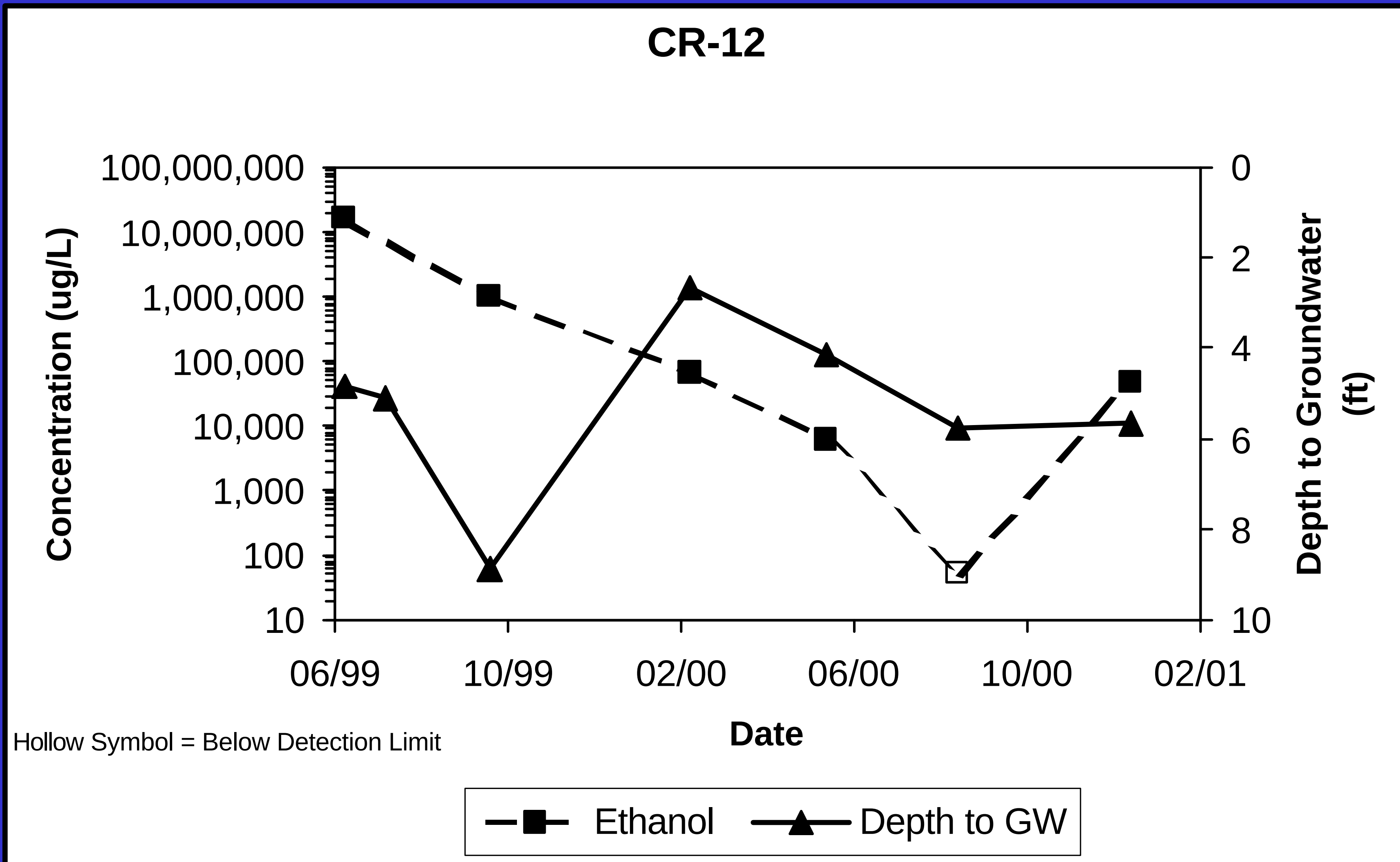
Ethanol and Methane Concentrations December, 2000



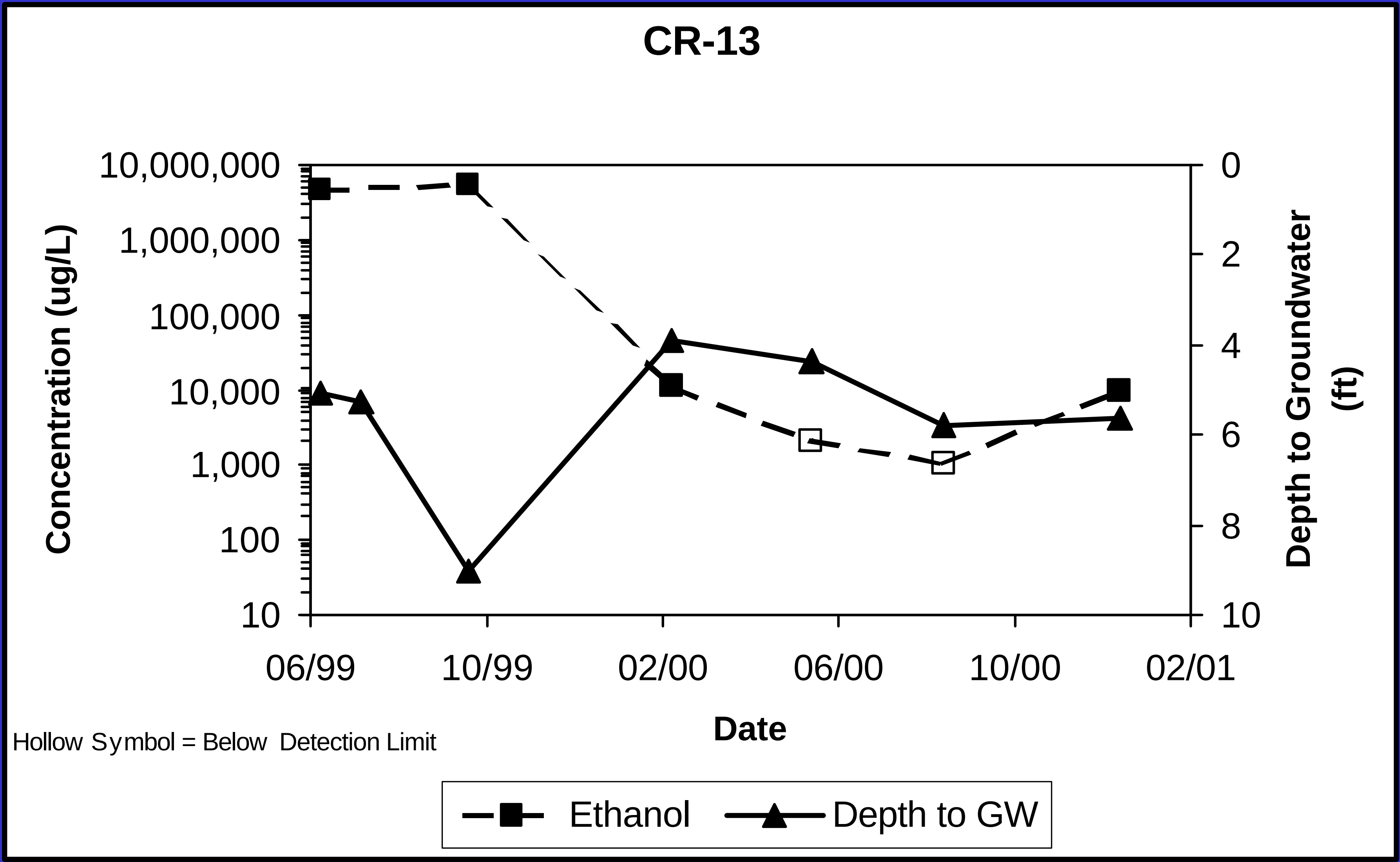
Groundwater Investigation Results

- Ethanol migrated approximately 250 feet (CR-16) between March and September 1999, consistent with groundwater velocity estimates
- Ethanol concentrations in two monitoring wells near the release have declined significantly over 18 months (CR-12 and CR-13)
- Ethanol appears to enhance the thickness of NAPL in two monitoring wells (CR-19 and CR-15)
- Cosolvent effects of ethanol are suggested by benzene concentrations increasing by a factor of 10 or more in one monitoring well (CR-7)
- The presence of ethanol has created a strongly anaerobic groundwater system, demonstrated by low dissolved oxygen, depleted nitrate and sulfate, and high methane concentrations

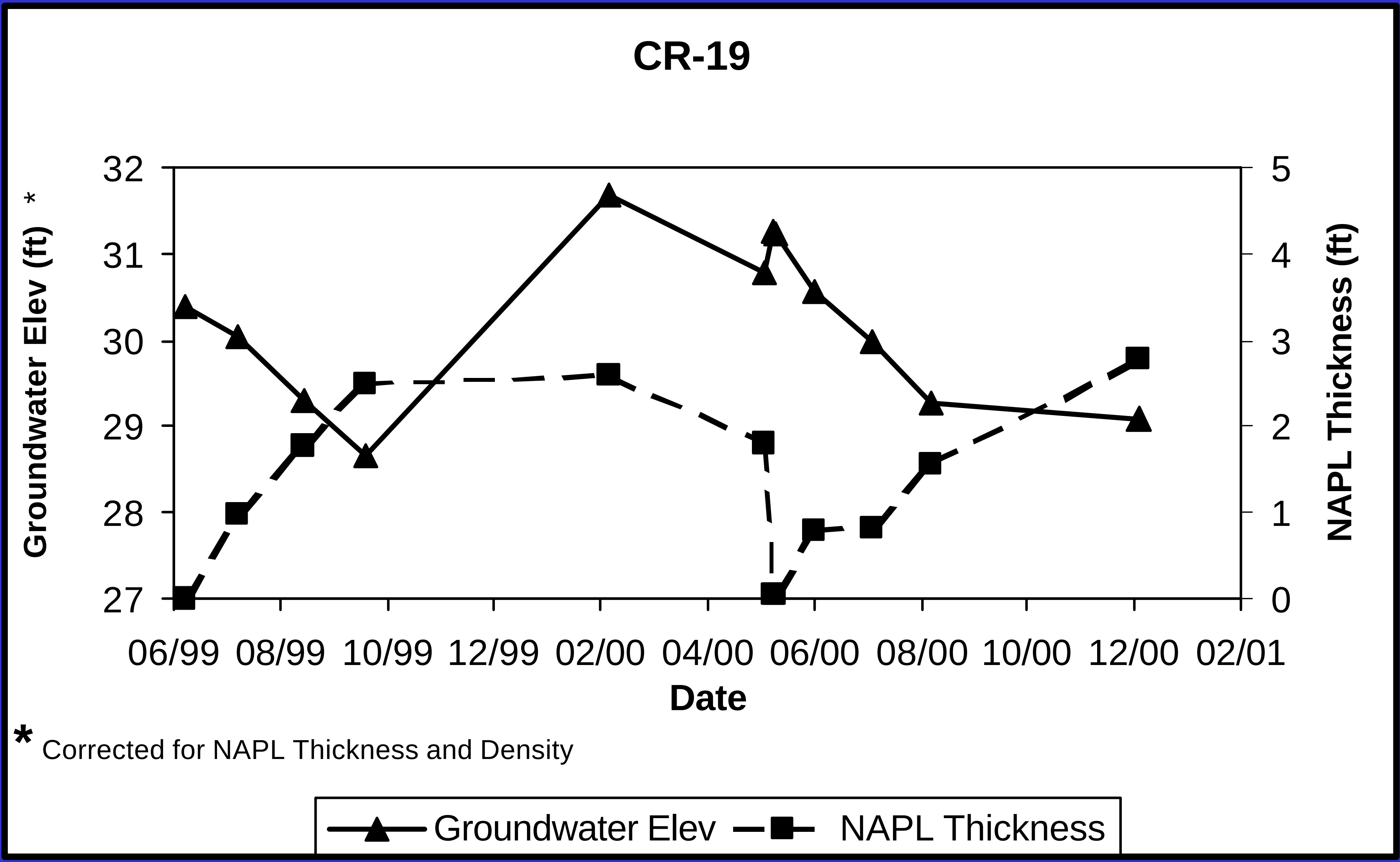
Ethanol and Depth to Groundwater versus Time



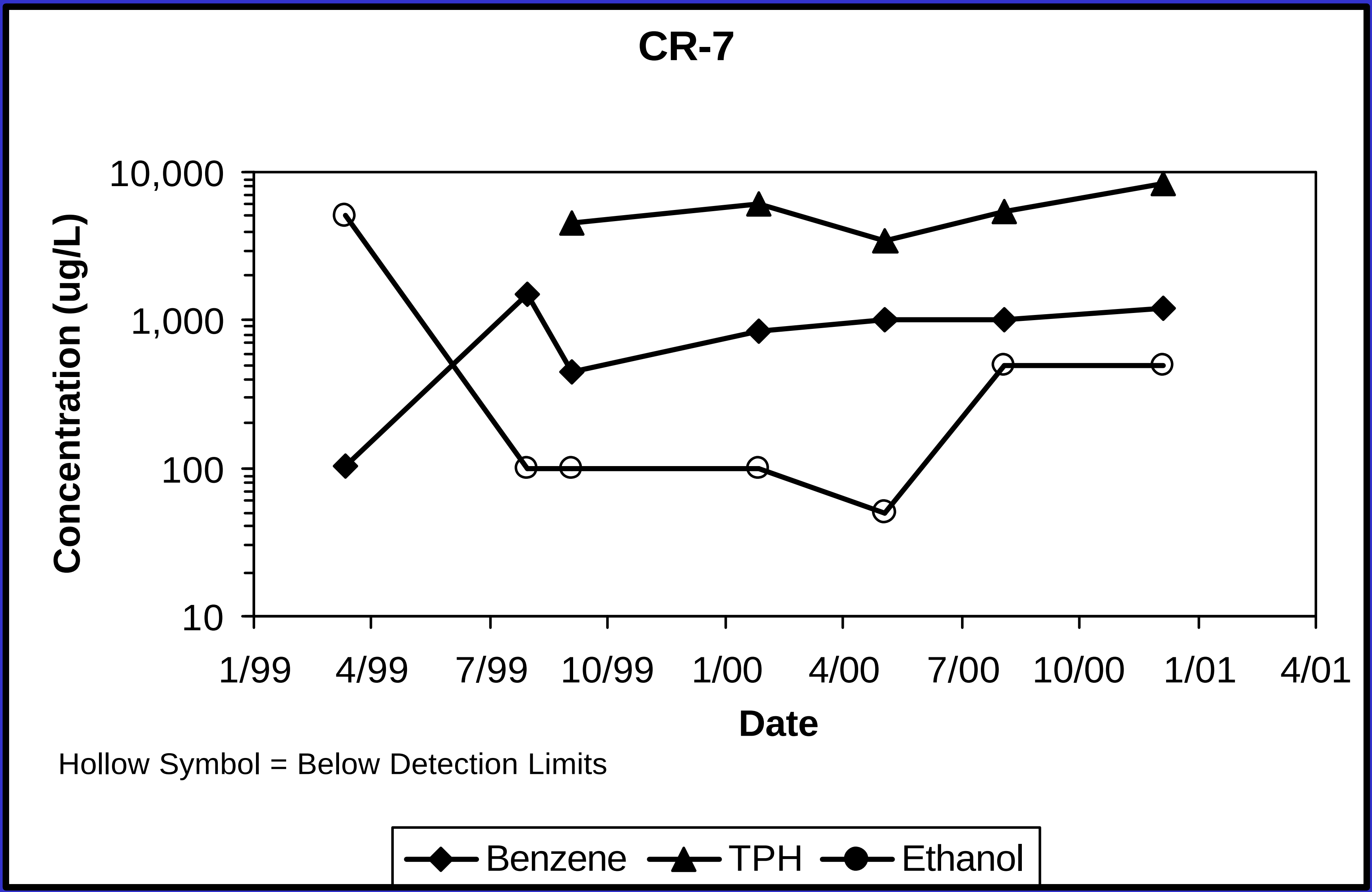
Ethanol and Depth to Groundwater versus Time



NAPL Thickness and Groundwater Elevation versus Time



Benzene, TPH & Ethanol Concentrations versus Time



Summary

- 17 new monitoring wells were installed over an 18-month period to delineate the ethanol plume that resulted from a 19,000-gallon release of neat ethanol
- The presence of ethanol in the subsurface has affected petroleum hydrocarbons in both the NAPL and dissolved phases
- There is evidence for ethanol biodegradation under methanogenic conditions, demonstrated by declining ethanol concentrations and high methane concentrations in the footprint of the ethanol plume
- Ethanol concentrations at UST release sites (10% ethanol) are not likely to be sufficiently high to cause cosolvent effects for BTEX

References

- Buscheck, T.E., K.T. O'Reilly, G. Koschal, and G. O'Regan. 2001. Ethanol in Groundwater at a Northwest Terminal. Sixth International Battelle Symposium on In Situ and On-Site Bioremediation, San Diego, CA, June 4-7, 2001.

- da Silva, M.L.B, G.M Ruiz, J.M. Fernandez, H.R. Beller, and P.J.J. Alvarez. 2001. Effect of Ethanol versus MTBE on BTEX Natural Attenuation. Sixth International Battelle Symposium on In Situ and On-Site Bioremediation. San Diego, CA, June 4-7, 2001.

- Heermann, S.E. and S.E. Powers. 1998. Modeling the Partitioning of BTEX in Water-Reformulated Gasoline Systems Containing Ethanol. *Journal of Contaminant Hydrogeology 34*(4): 315-341.

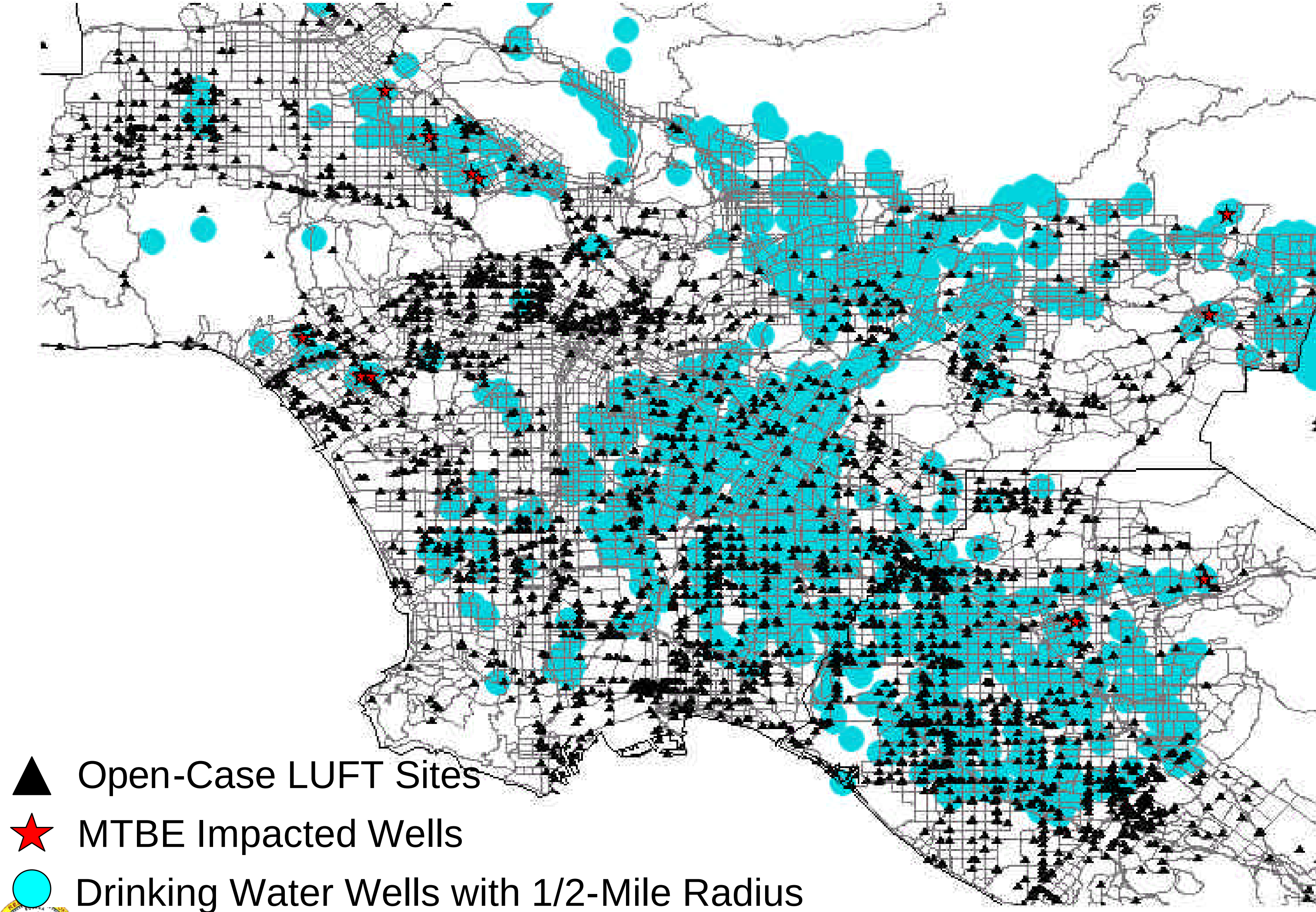
- Hunt, C., P.J.J. Alvarez, R. dos Santos Ferreira, and H. Corseuil. 1997. Effect of Ethanol on Aerobic BTEX Degradation. In: B.C. Alleman and A.L. Leeson (eds.) *In Situ and On-Site Bioremediation*, *4*(1). Battelle Press, Columbus, OH, pp. 49-54.

- Powers, S.E. and D.W. Rice, B. Dooher, and P.J.J. Alvarez. 2001. Will Ethanol-Blended Gasoline Affect Groundwater Quality? *Environmental Science & Technology 35*(1): 24A-30A.

Water Resource Vulnerability Issues Associated with the Increased Use of Ethanol and Alkylates in Fuels

Dr. Brendan P. Dooher
Lawrence Livermore National Laboratory
April 11, 2001

Los Angeles Basin

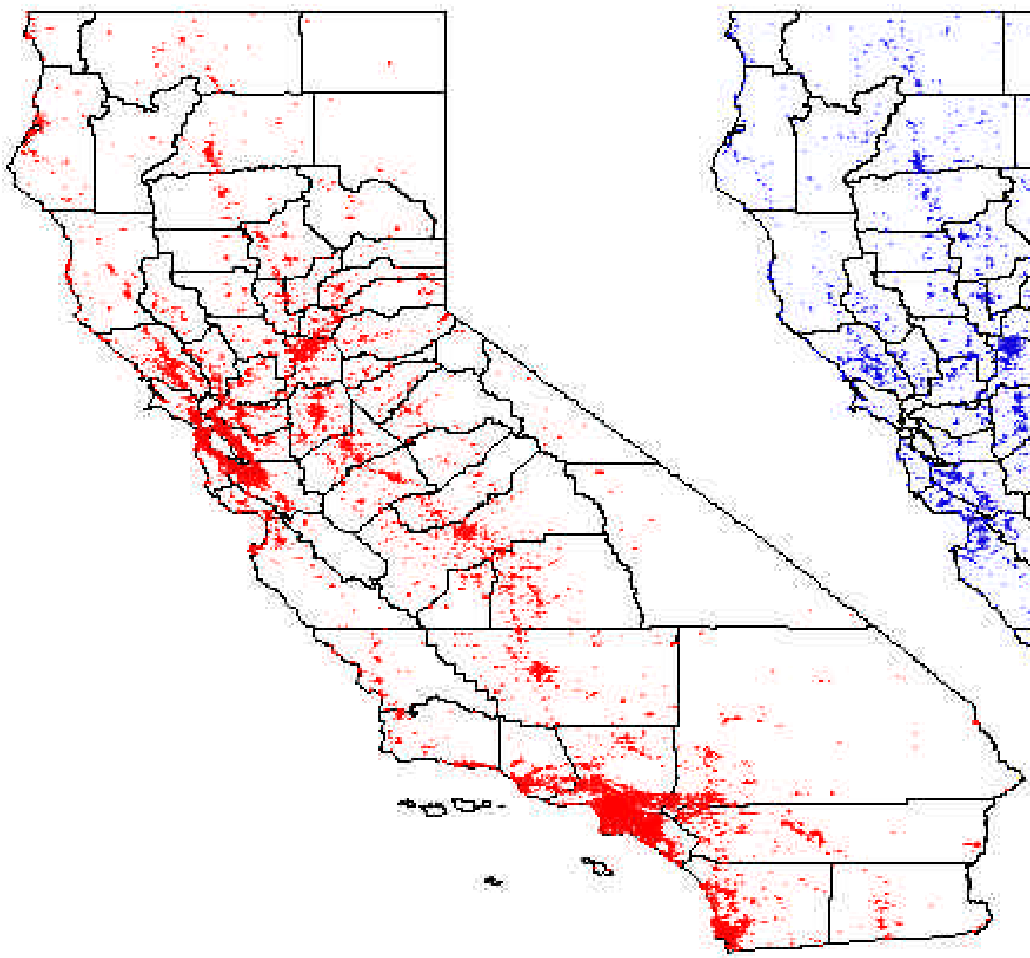


Constable, 1999: The World Atlas of Archeology

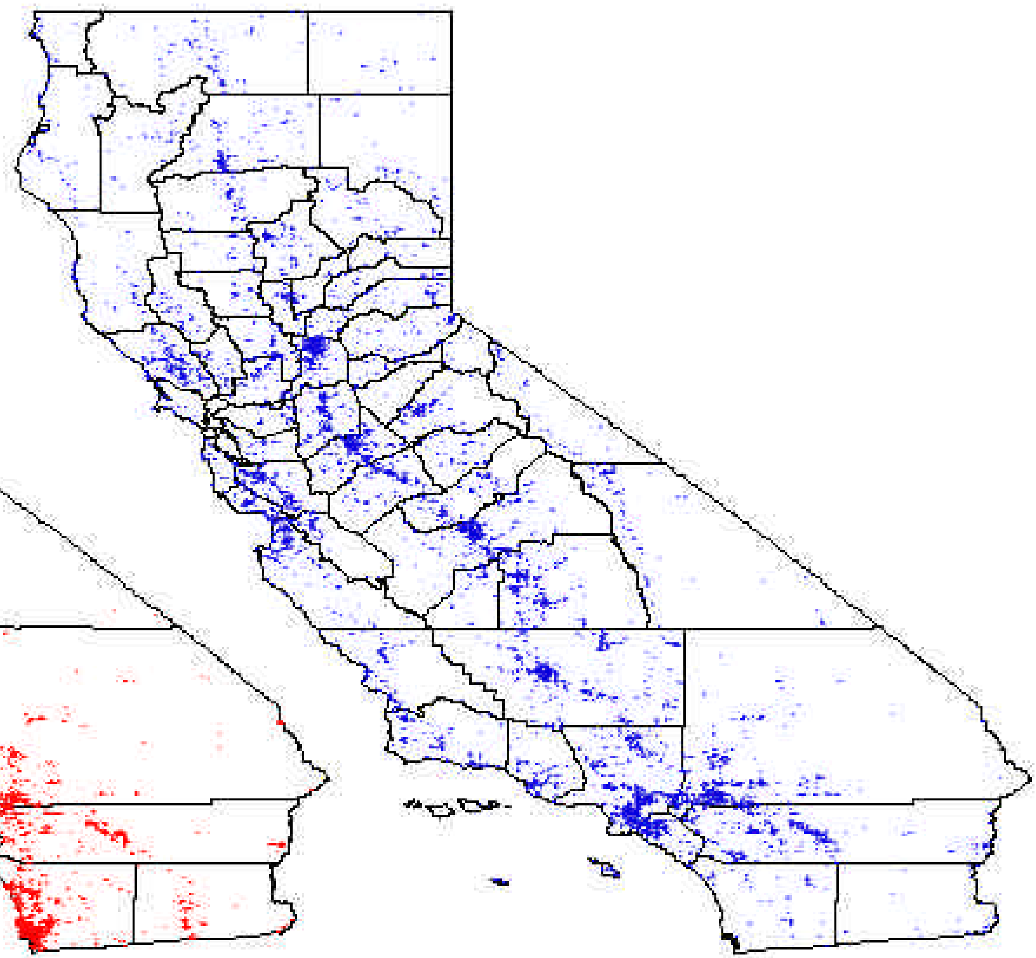
"Oldest archeological evidence of ethanol production (wine-making) in findings dated 5500 BC located 11 ft deep in sediments at the Mesopotamian City of Ur along the Euphrates river near the modern day City of Kuait.."

Locations of leaking underground fuel tanks (LUFTs) and public wells in California

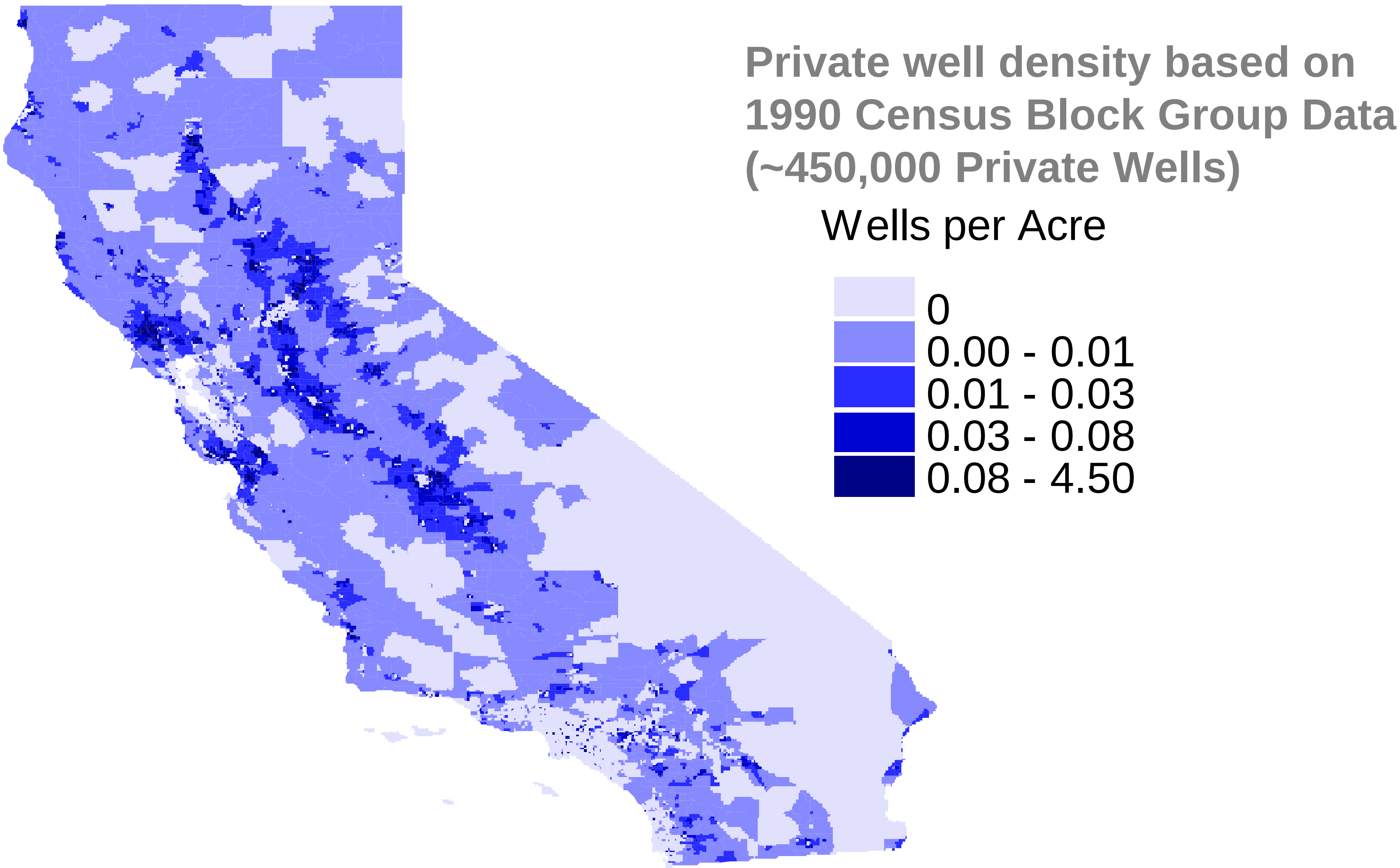
LUFT Sites



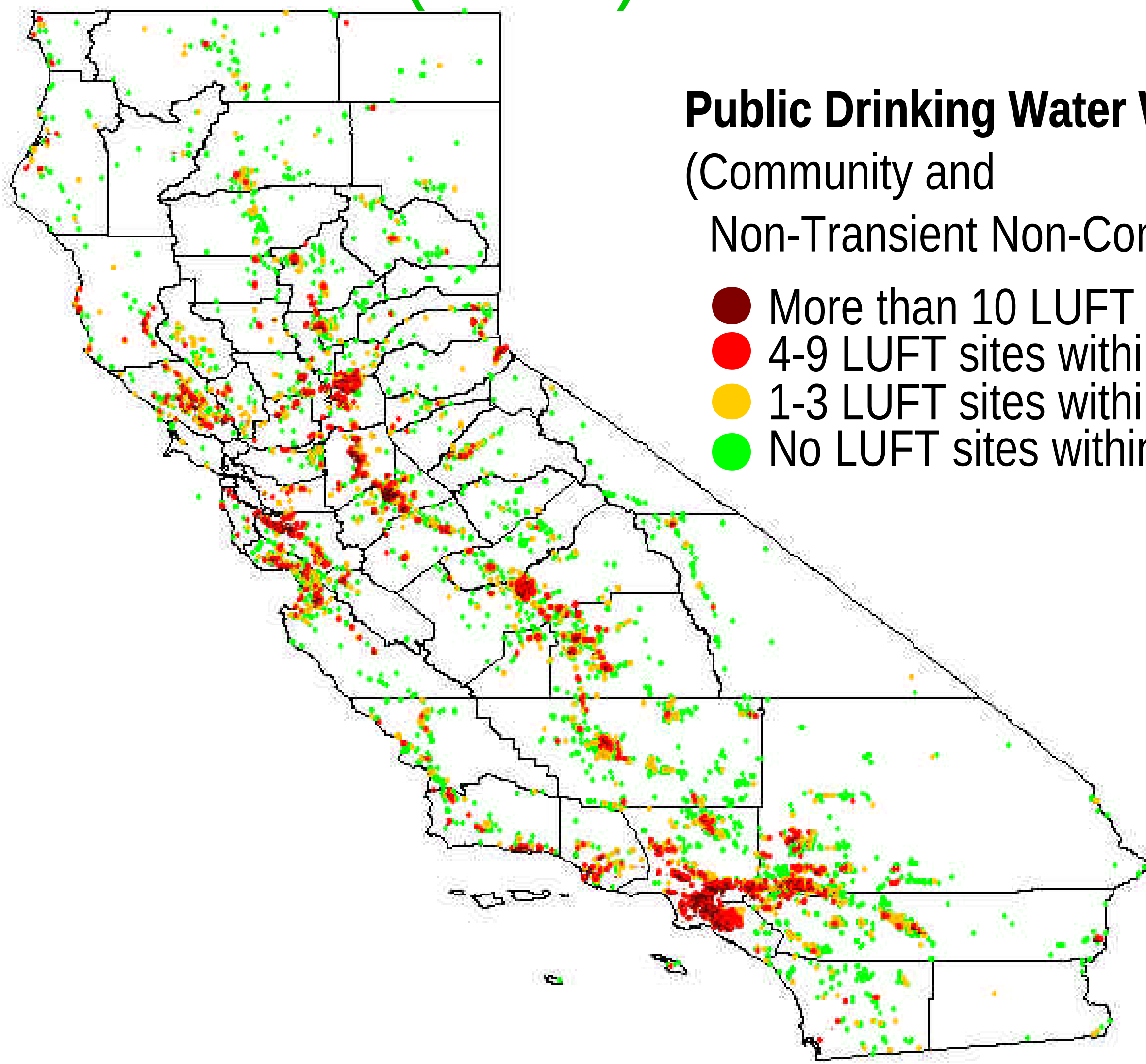
Public Groundwater Sources



Density of private wells in California



Public Drinking Water Wells in California: Estimated Number of Leaking Underground Fuel Tank (LUFT) Sites Within 1/2 Mile

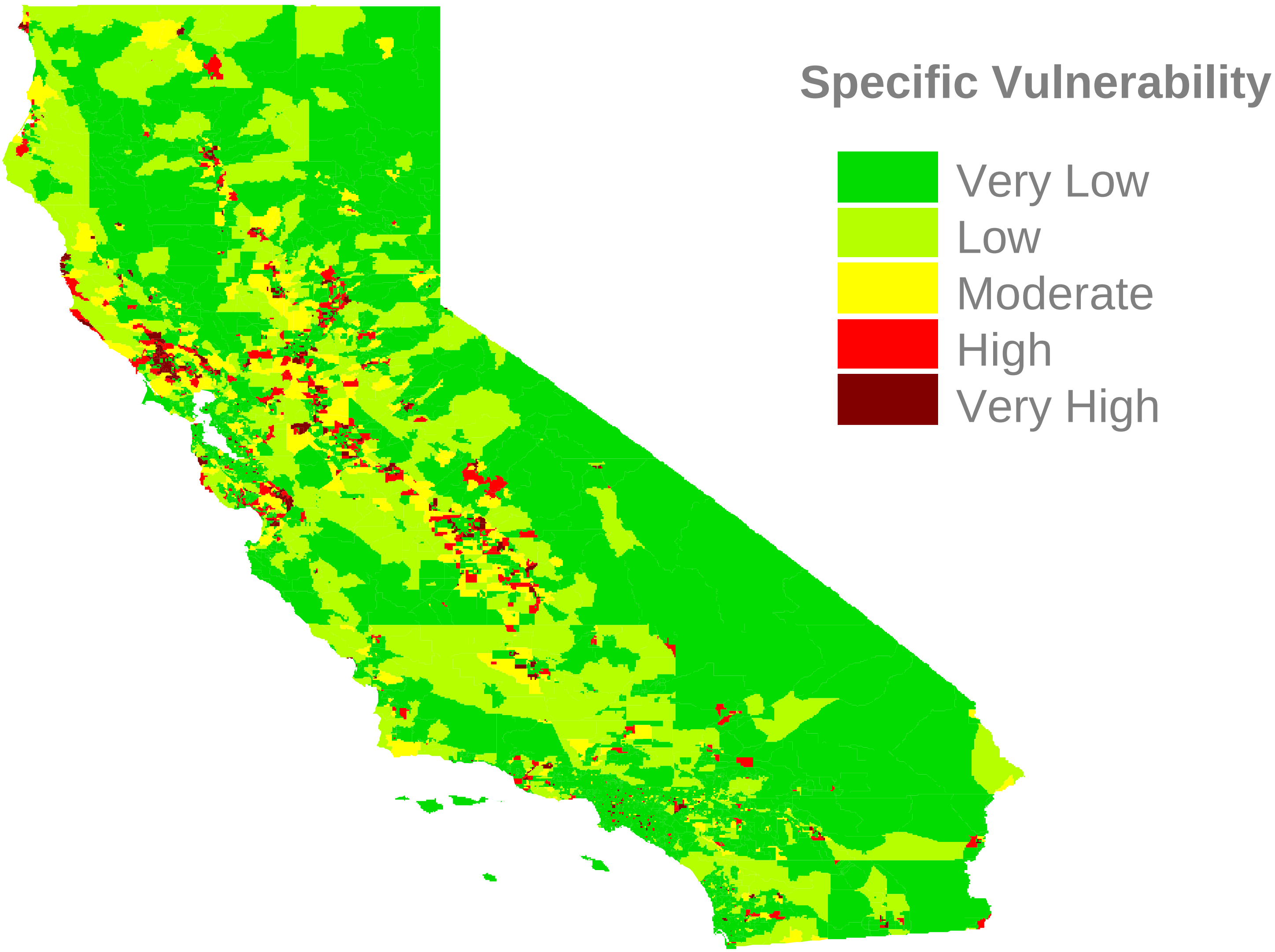


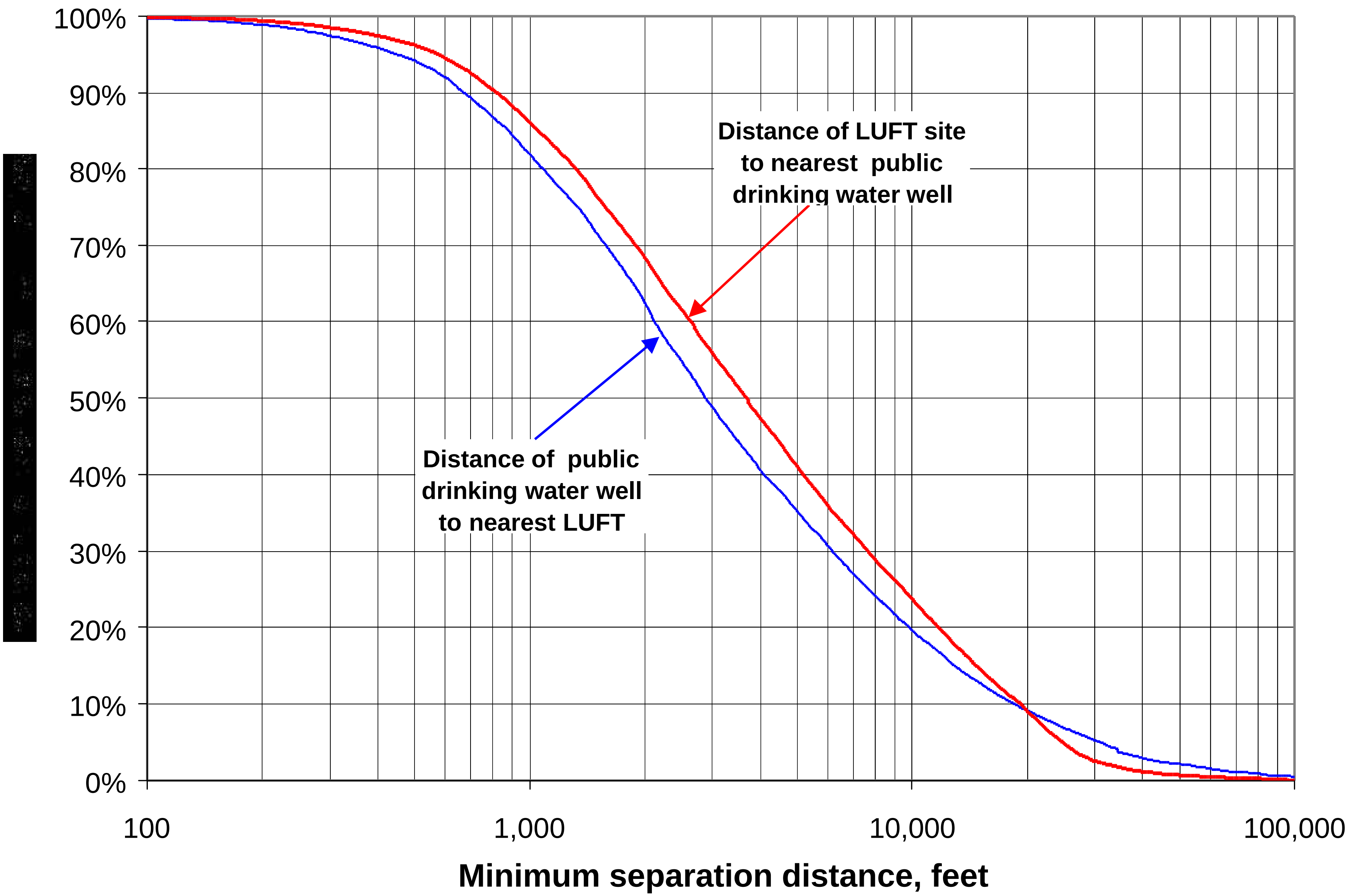
Public Drinking Water Wells

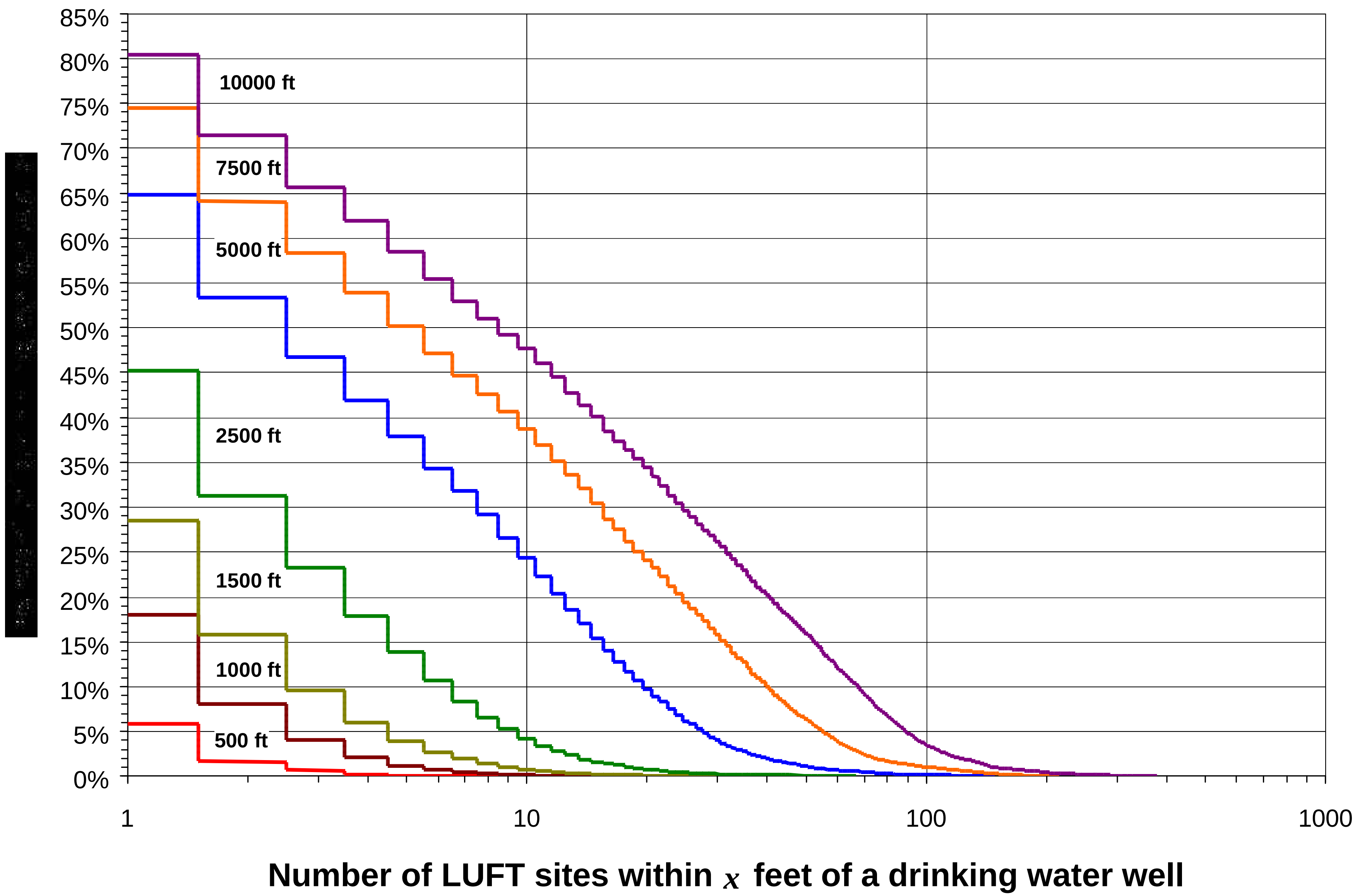
(Community and Non-Transient Non-Community)

- More than 10 LUFT sites within 1/2 mile
- 4-9 LUFT sites within 1/2 mile
- 1-3 LUFT sites within 1/2 mile
- No LUFT sites within 1/2 mile

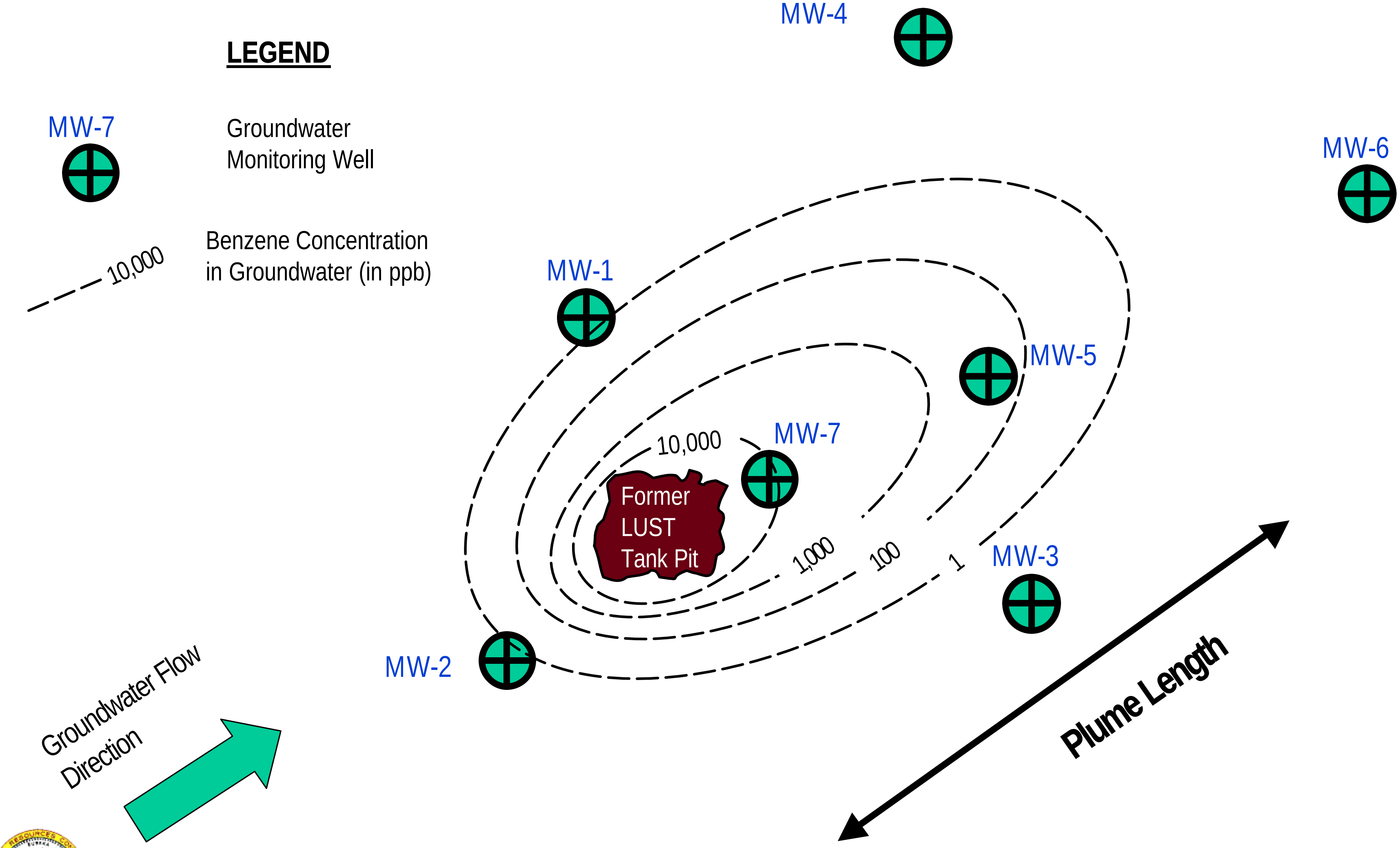
Co-locations of private water wells with leaking underground tanks



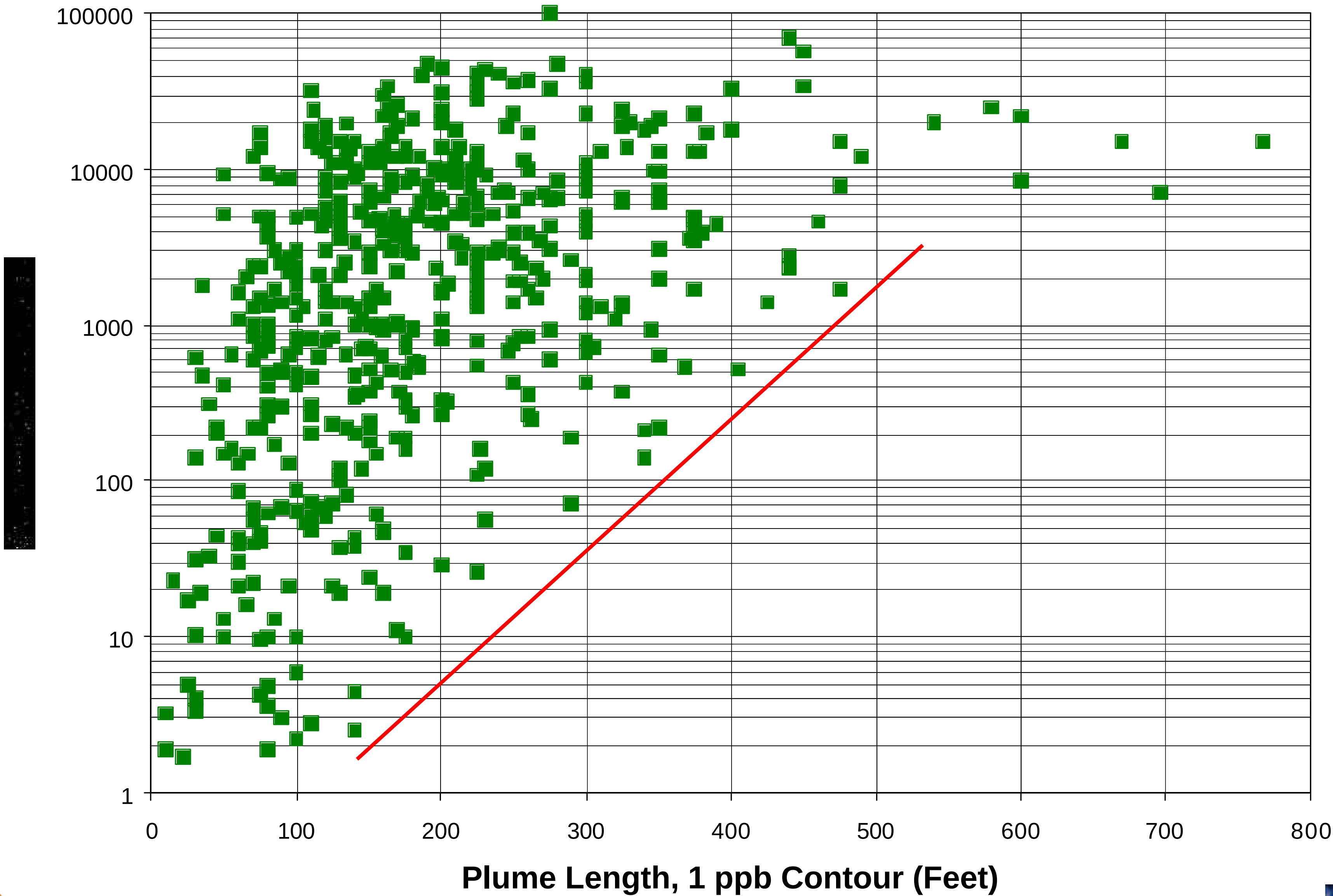

[redacted]
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Distance of LUFT site to nearest public drinking water well
Distance of public drinking water well to nearest LUFT
100
1,000
10,000
100,000
Minimum separation distance, feet


85%
80%
75%
70%
65%
60%
55%
50%
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
10000 ft
7500 ft
5000 ft
2500 ft
1500 ft
1000 ft
500 ft
1
10
100
1000
Number of LUFT sites within x feet of a drinking water well

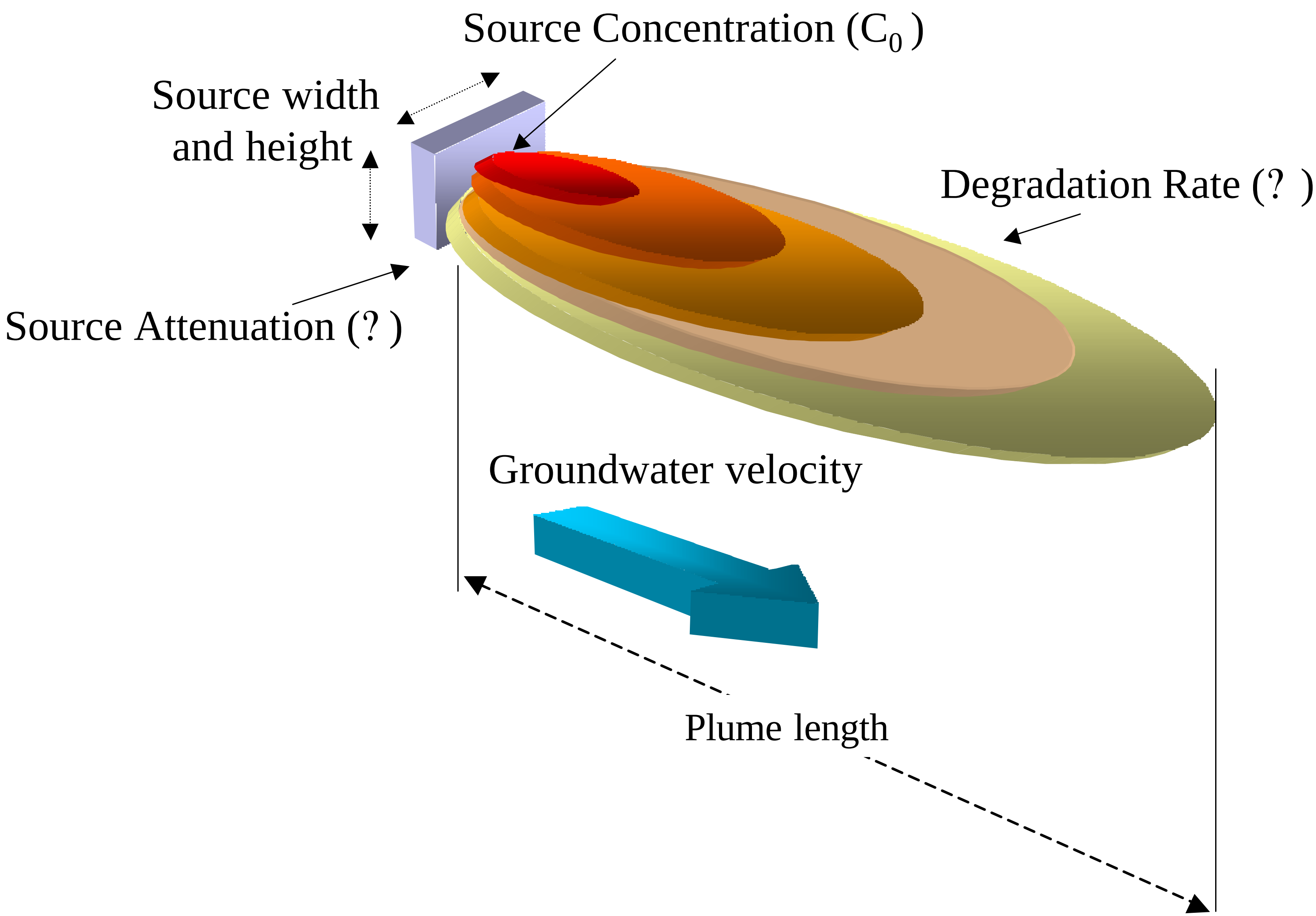
Determination of measured benzene plume lengths



Benzene plume lengths



Monte Carlo analysis with *Cleary and Ungs* (1978) model



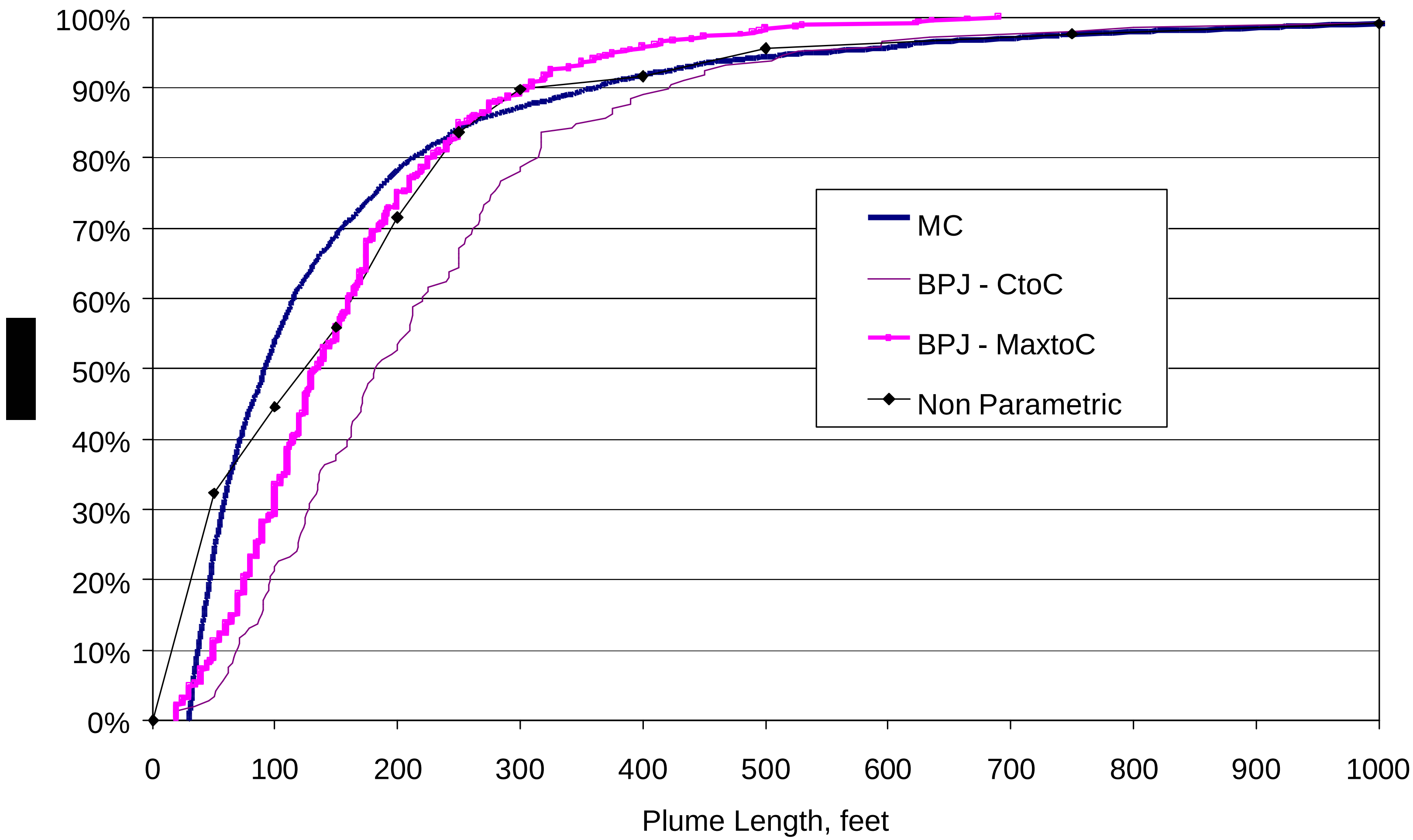
Monte Carlo analysis with *Cleary and Ungs* (1978) model
Model Inputs*:

- Source Concentration - 1999 Data from 4,300 LUFT sites
- Source Attenuation Half-life - Based on maximum benzene measurements from 1,000 LUFT sites from 1988 to 1994
- Source Width - Based on tank dimensions
- Source Height - Based on variations in groundwater depth
- Hydraulic Conductivity - Measured from 100 LUFT sites
- Hydraulic Gradient - Measured from 1,000 LUFT sites
- Dispersivity (based on Gelhar et al., 1992)
- Plume length taken at 5 ppb contour
- No degradation rate

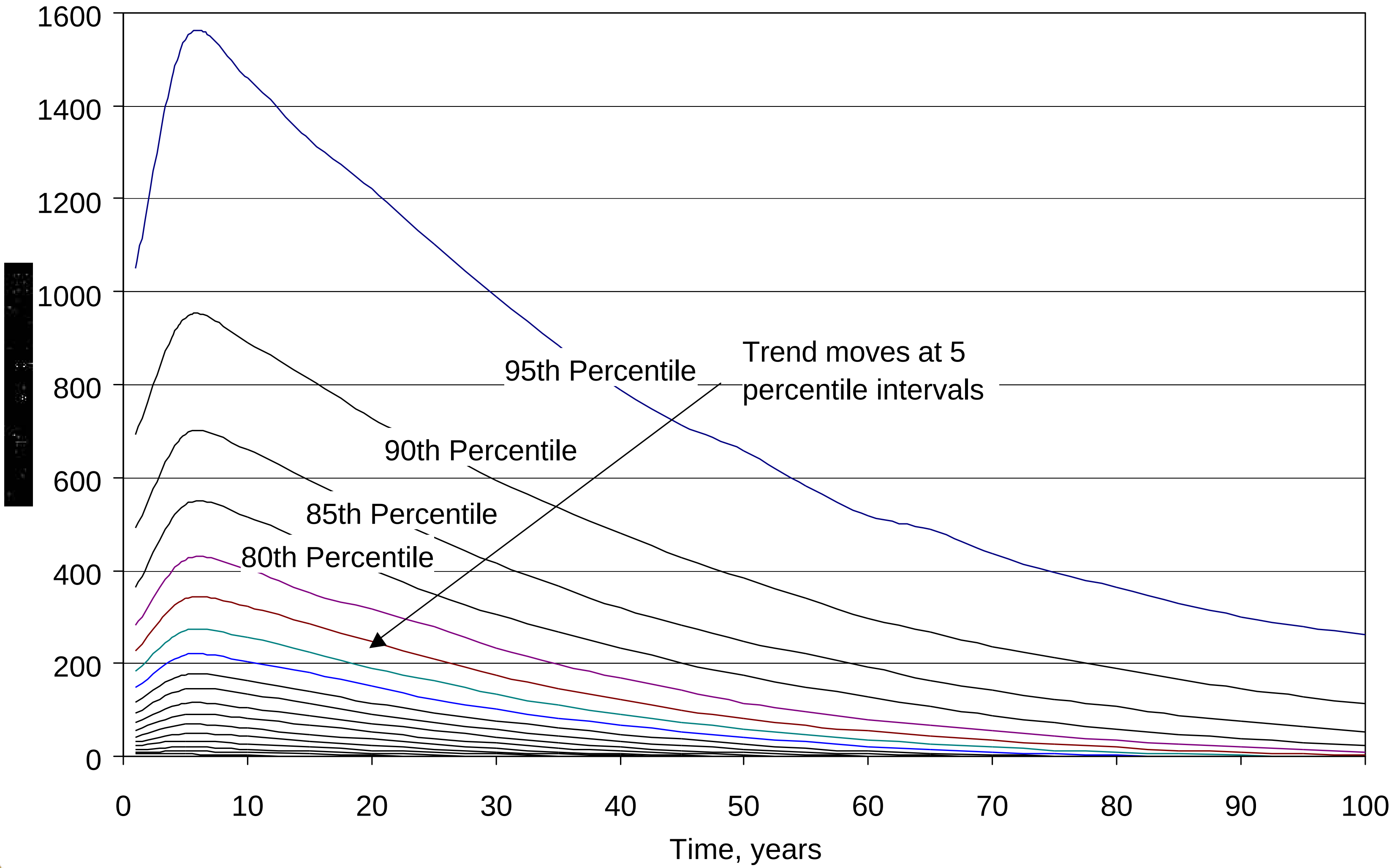
Data used as model inputs are derived from approximately 1,000 LUFT sites from throughout California

*Based on results measured at California LUFT sites, Dooher, March 1998

Simulated vs. measured plume lengths



Plume growth and decay for benzene



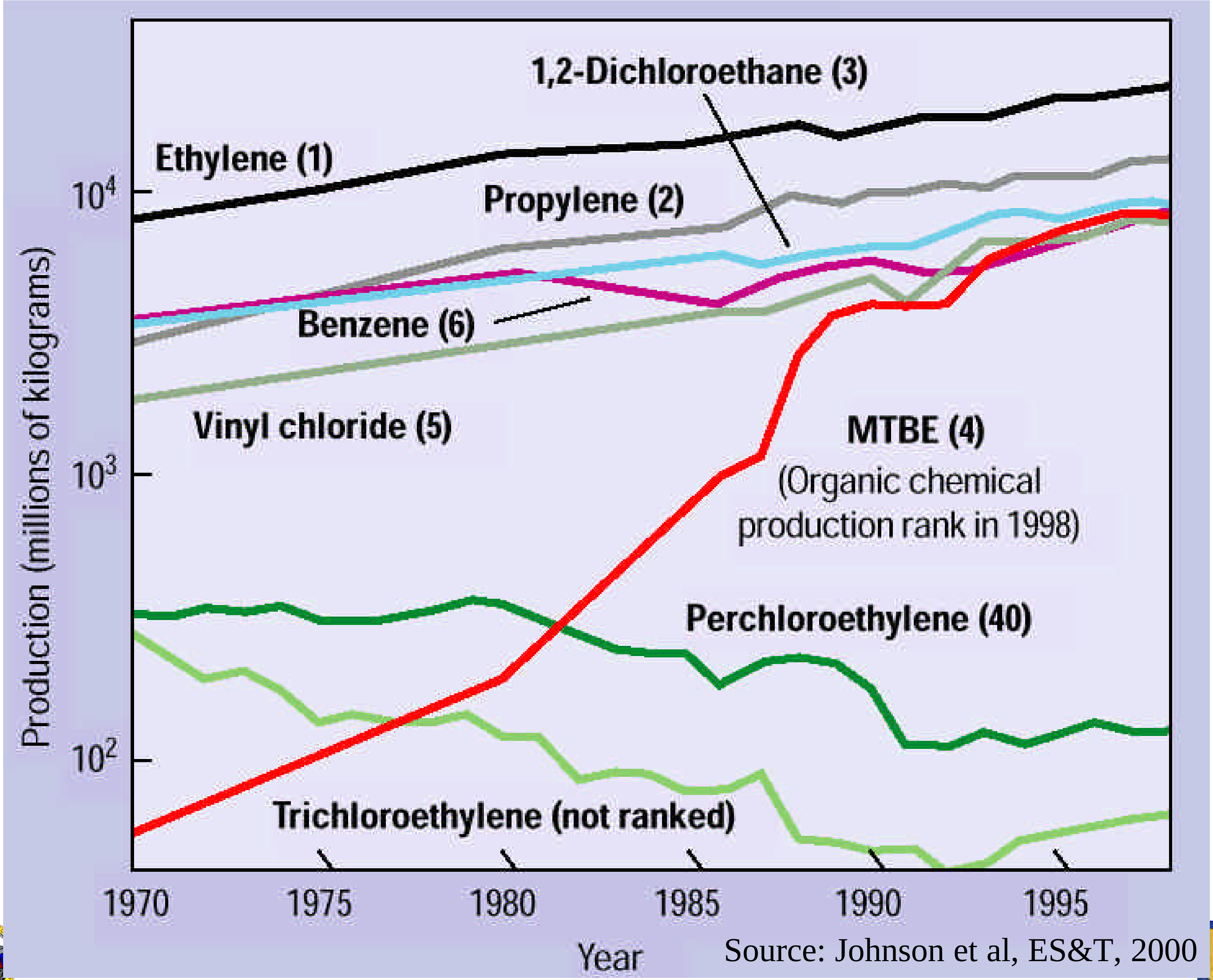
It Was a Dark and Stormy Night in Santa Monica

and MTBE was lurking...

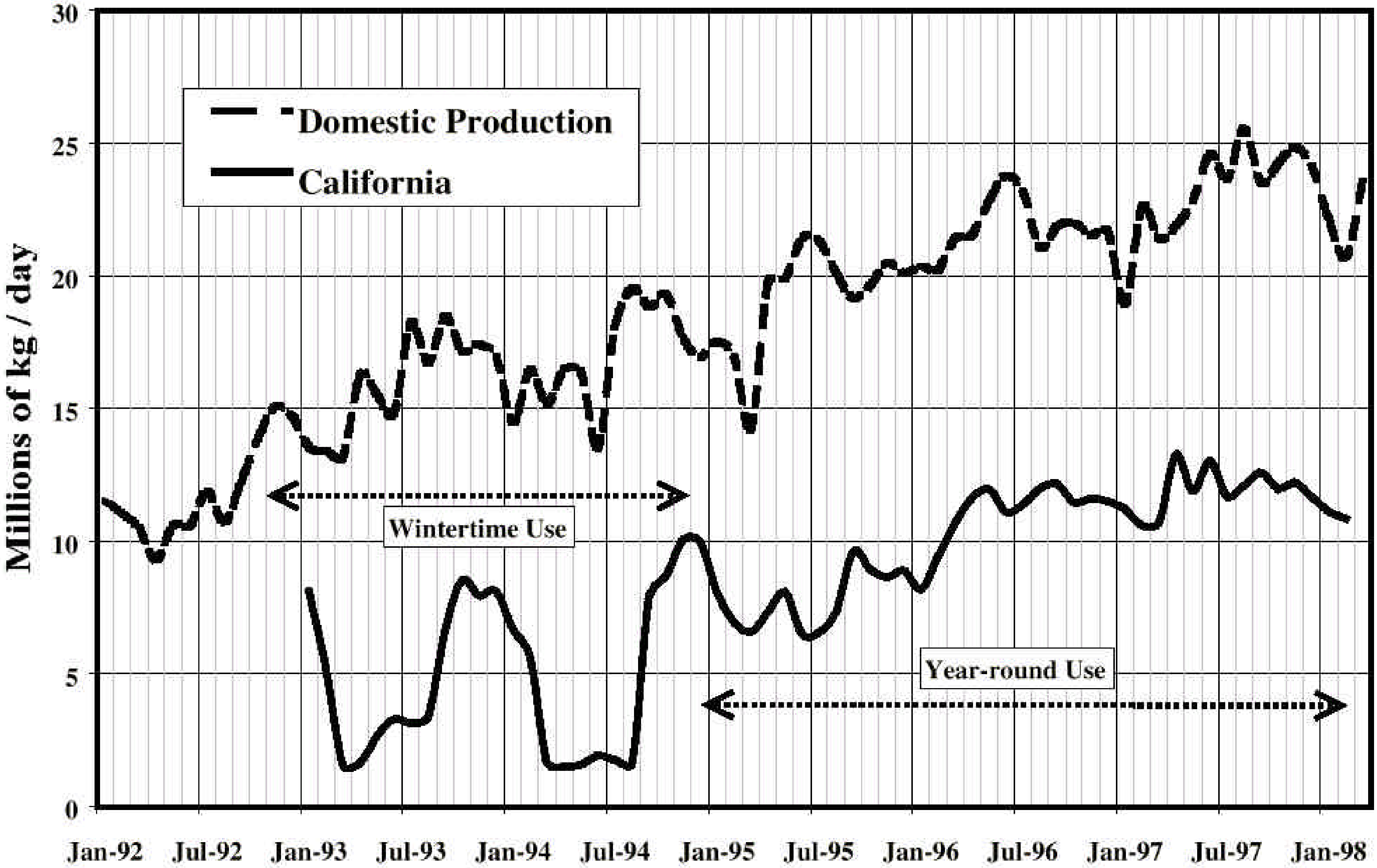
Dateline: January 1996

Comparison of maximum MTBE Concentrations detected at LUFT sites throughout California

ppb (parts per billion)	'95 - '96	January '99
	236 Sites	4300 Sites
<5	25%	23%
5-50	11%	12%
50-200	11%	11%
200-1000	18%	17%
1000-5000	16%	14%
5000-20000	13%	13%
20000-100000	4%	7%
>100000	1%	3%



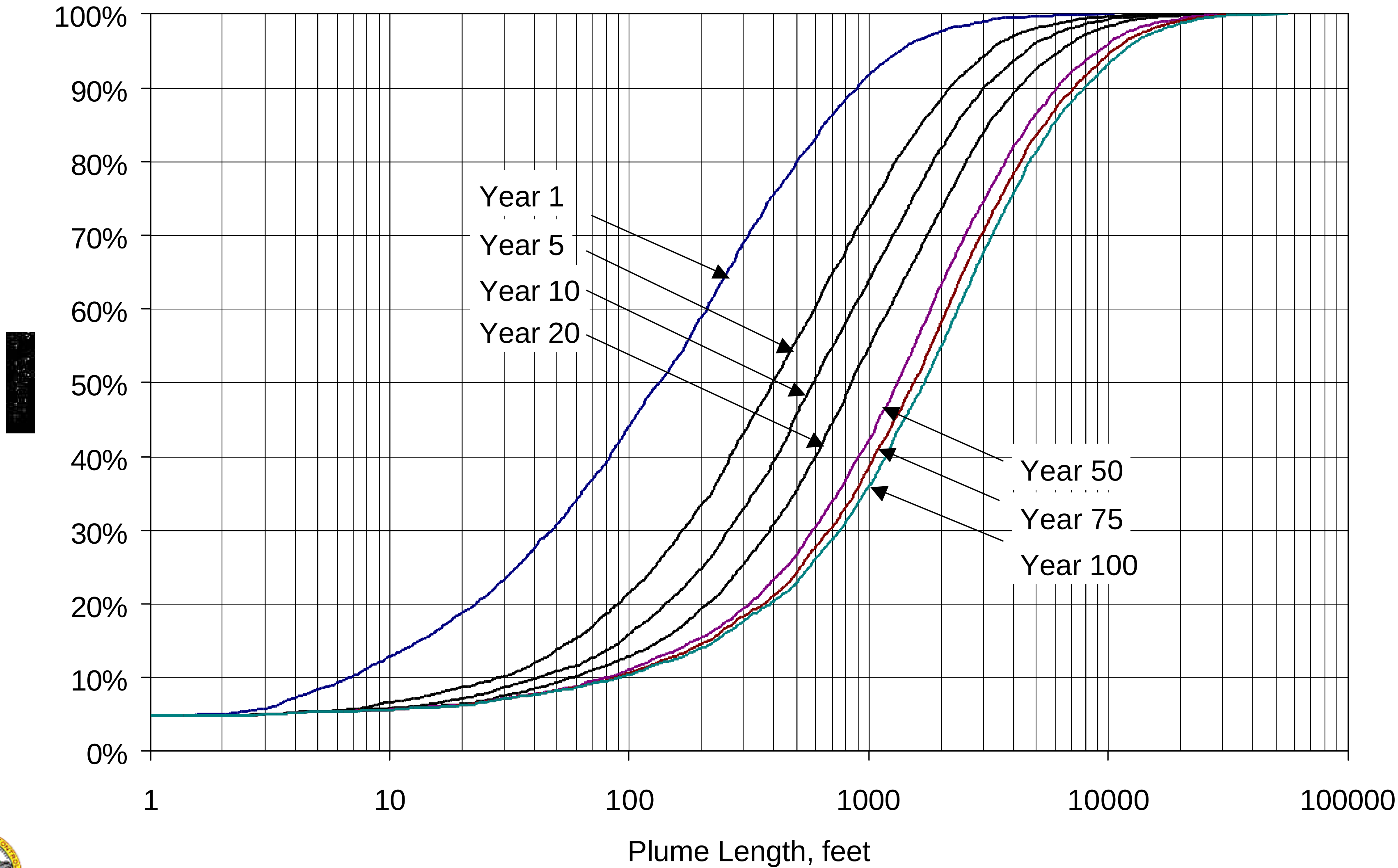
Source: Johnson et al, ES&T, 2000



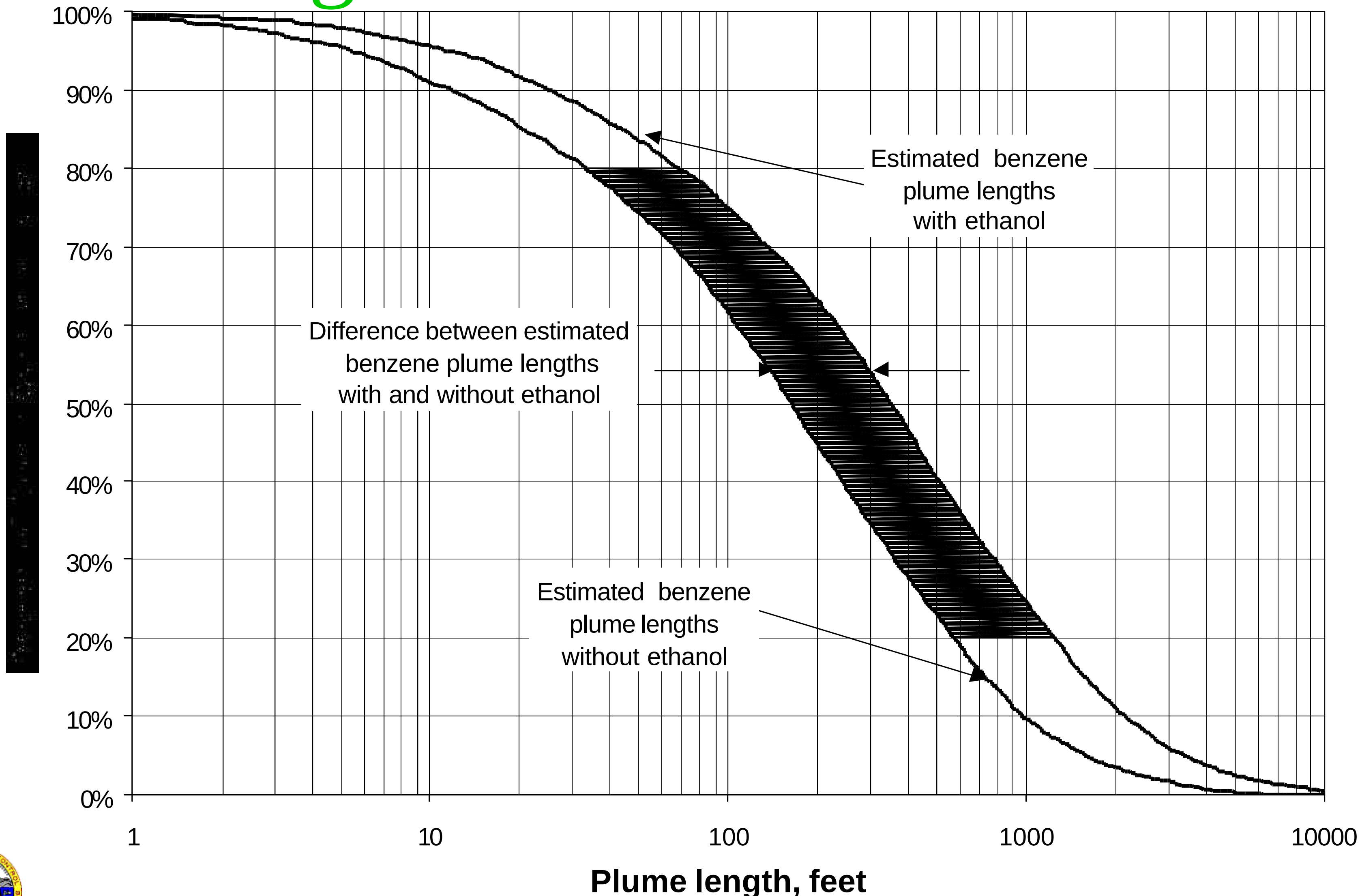
Domestic Production
California
Wintertime Use
Year-round Use
Millions of kg / day
30
25
20
15
10
5
0
Jan-92
Jul-92
Jan-93
Jul-93
Jan-94
Jul-94
Jan-95
Jul-95
Jan-96
Jul-96
Jan-97
Jul-97
Jan-98

MTBE plume length over time

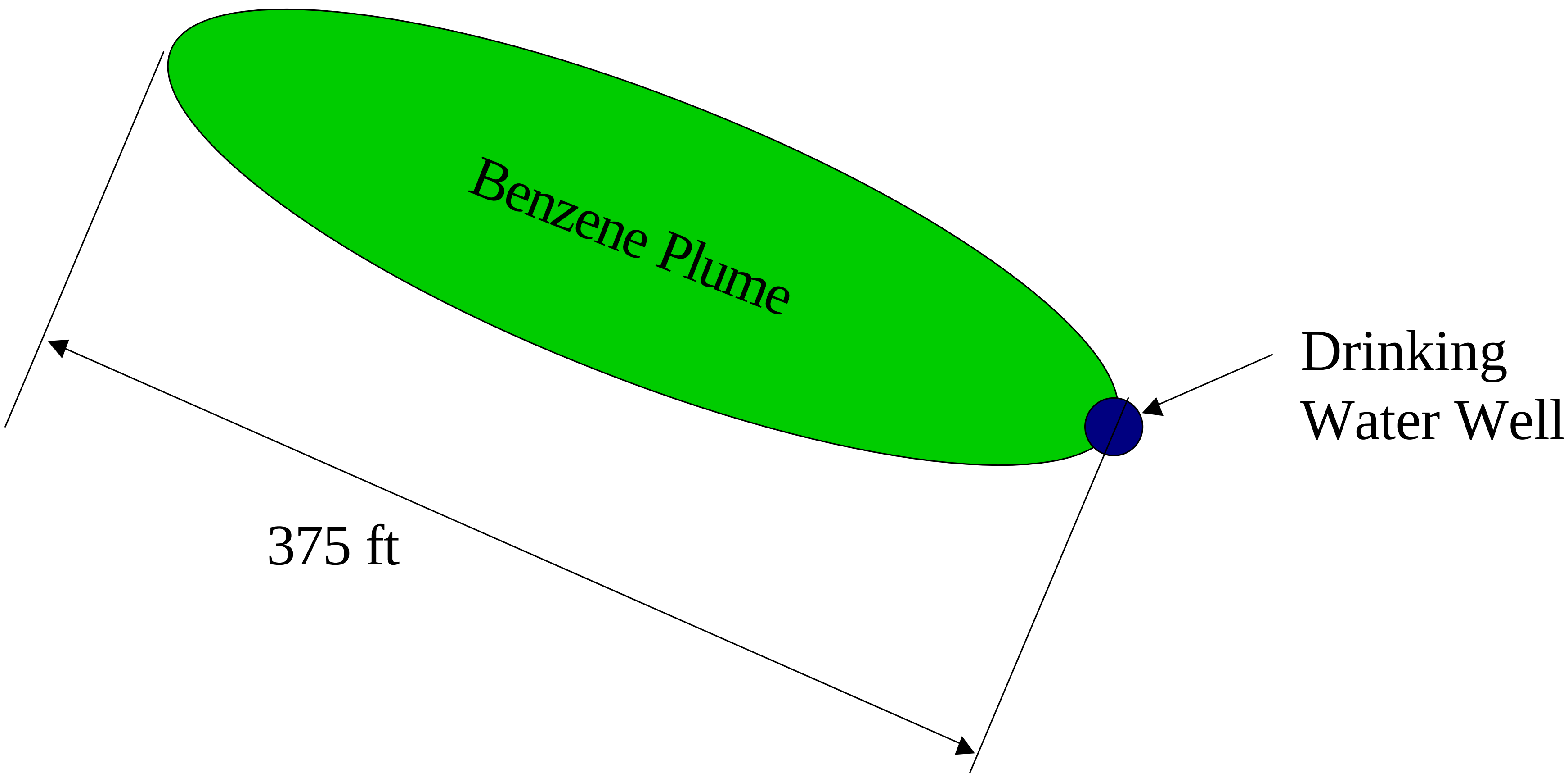
(non-degrading, constant source)



Difference in benzene plume lengths with ethanol added



Relation between well and LUFT site



Probabilities

Assumptions:

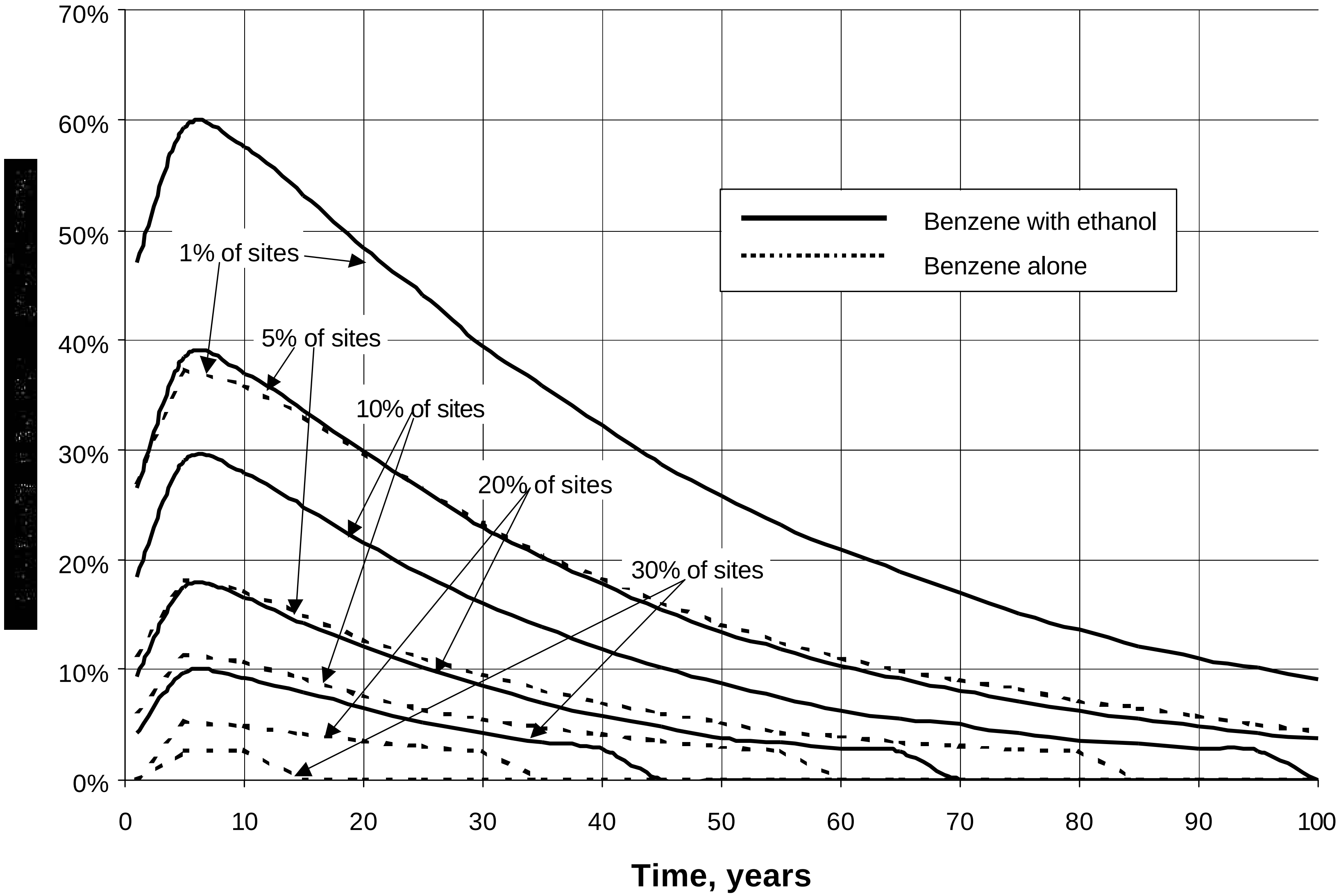
- Hydrogeologic features - unchanged.
- Well distributions - unchanged.
- LUFT site distributions - unchanged.

- The only factor that changes (significantly) is plume length.
  - Change in plume length becomes the metric for assessing the increased probability of threat...

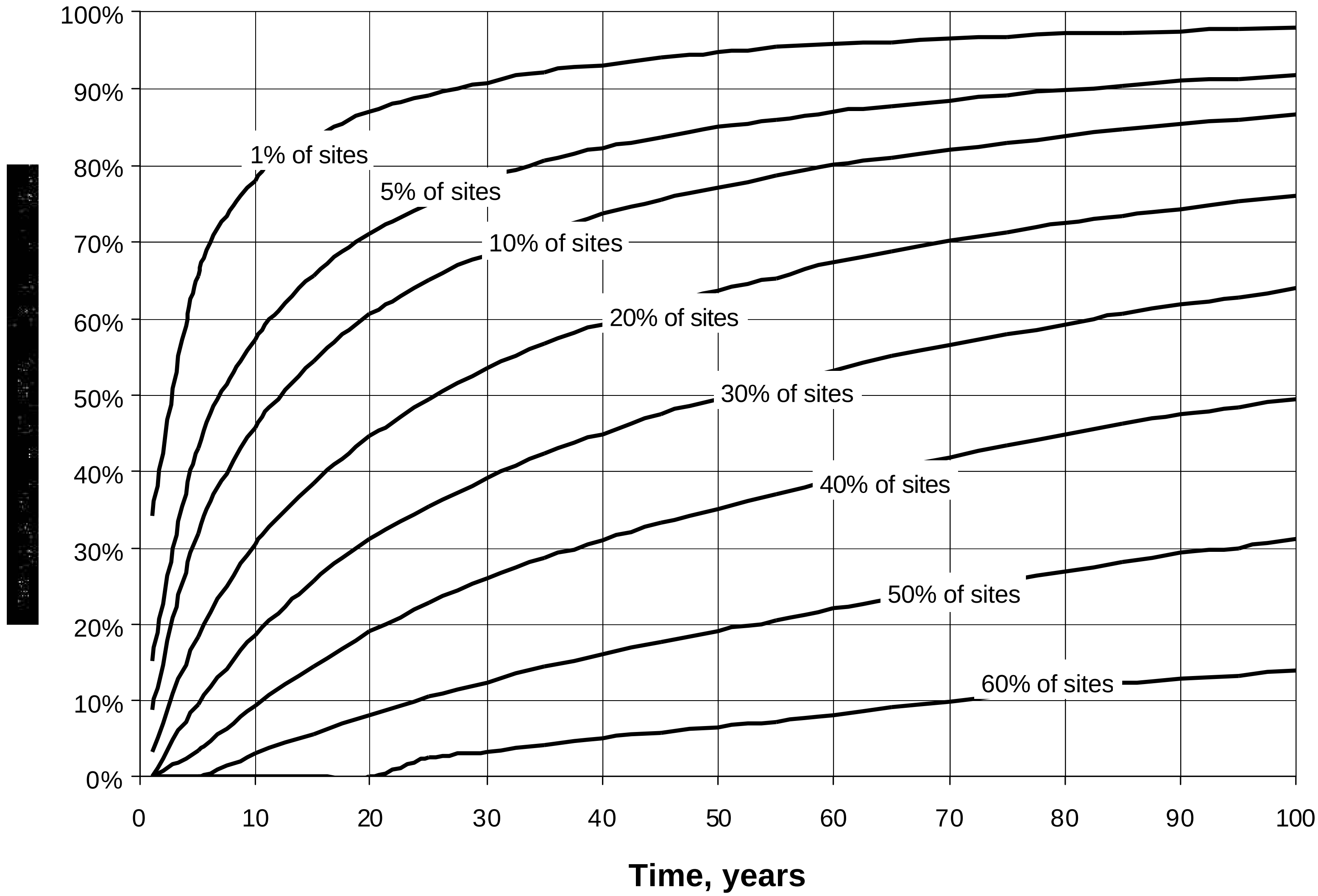
Probabilities

- Probability that plume travels 375 ft - 9%
  - Without ethanol
- Probability that plume travels 375 ft - 15%
  - With ethanol
- Change in probability - 67% increased chance of plume impacting well

Increased probability of threat: benzene alone and with ethanol

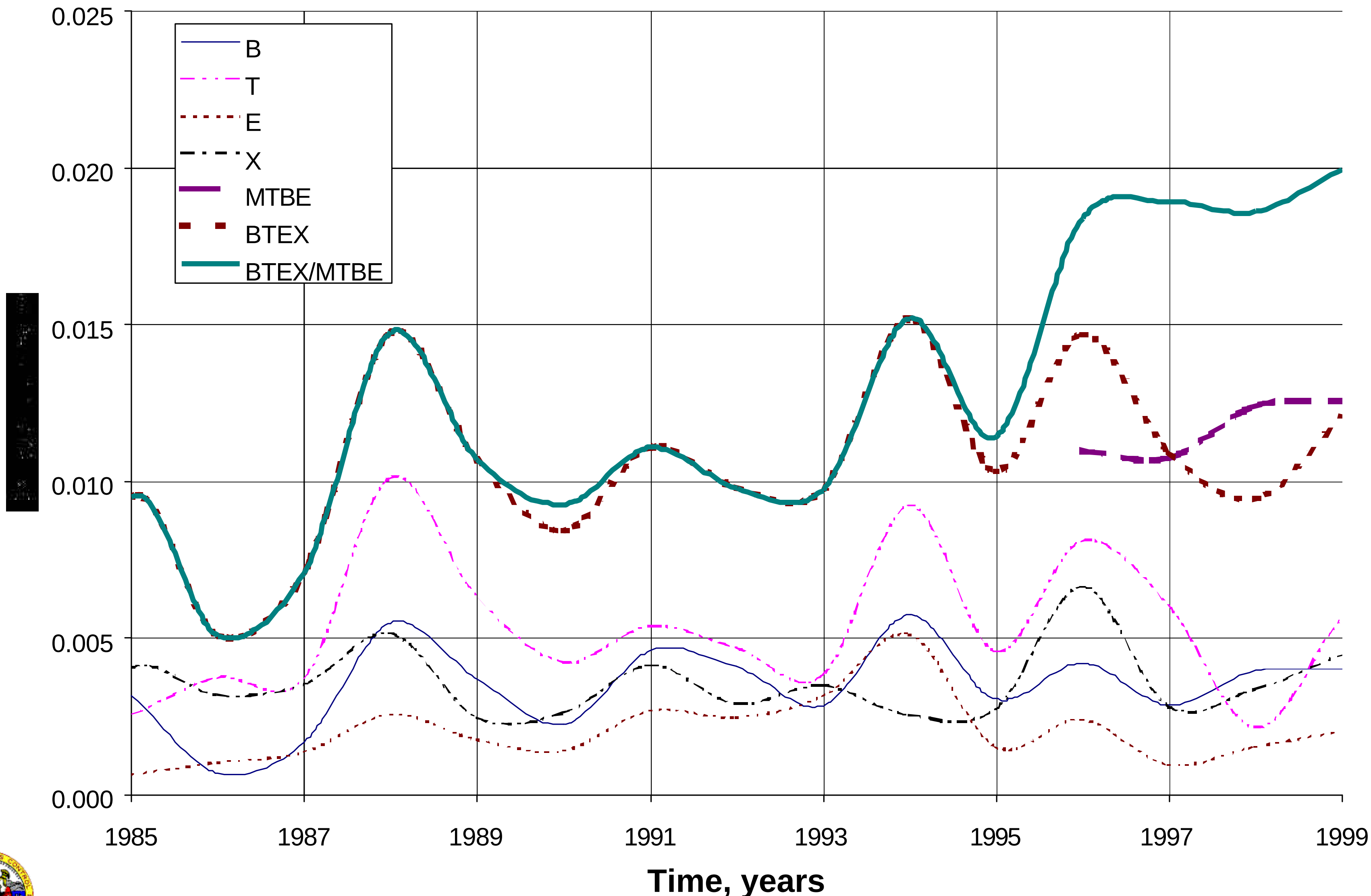


Increased probability of threat: MTBE

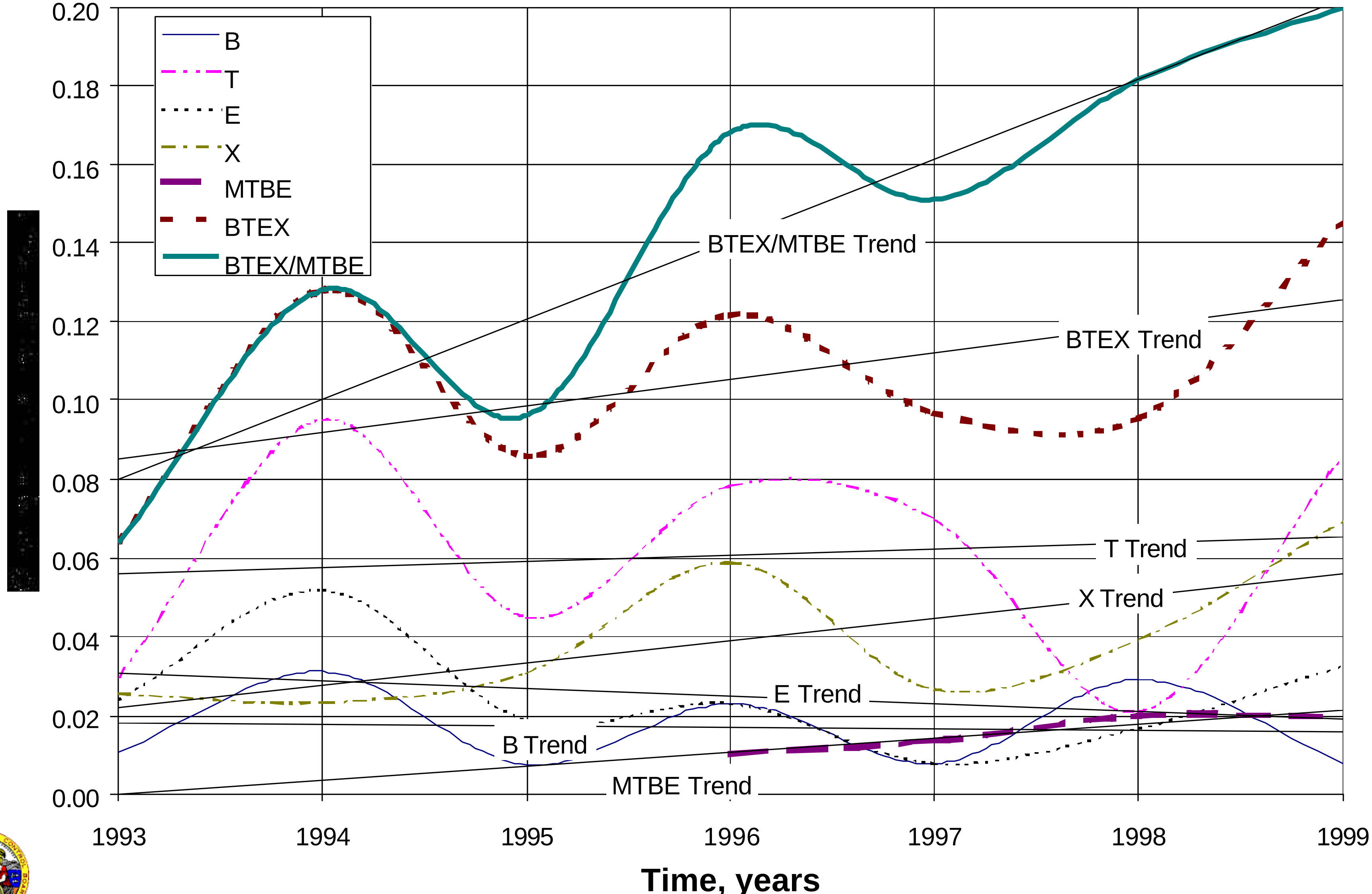


Drinking water wells

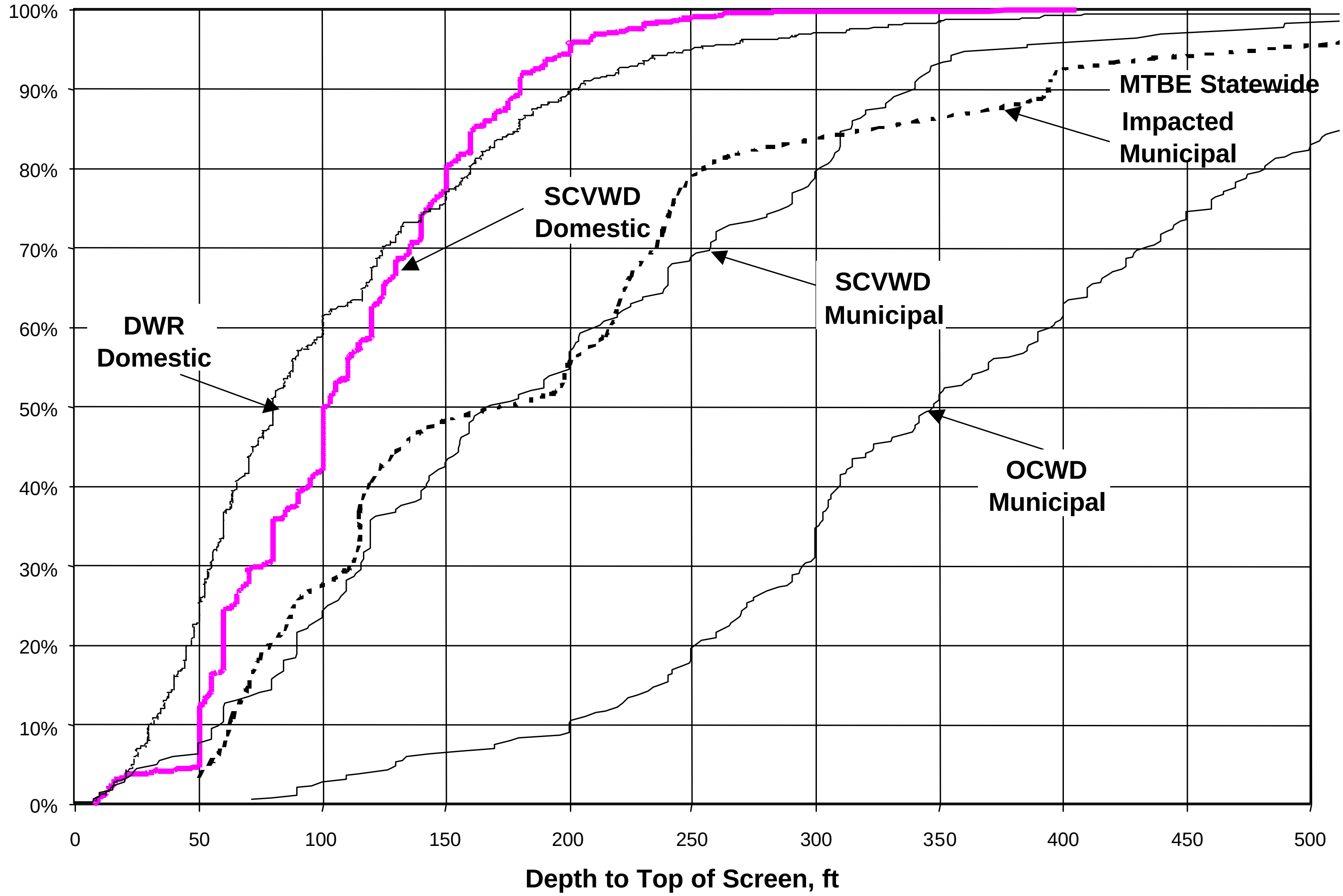
Detection rate of BTEX and MTBE in drinking water sources throughout California

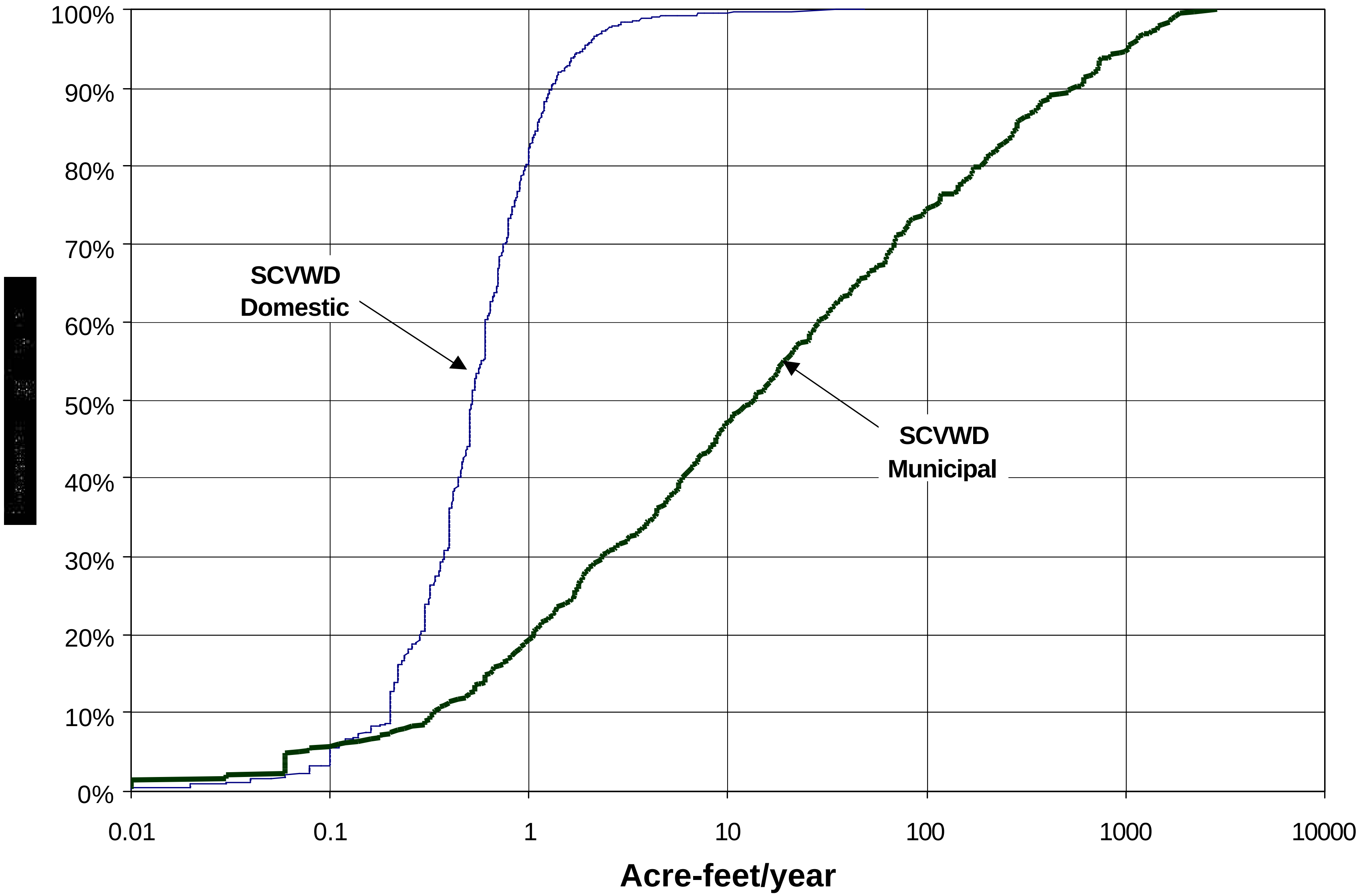


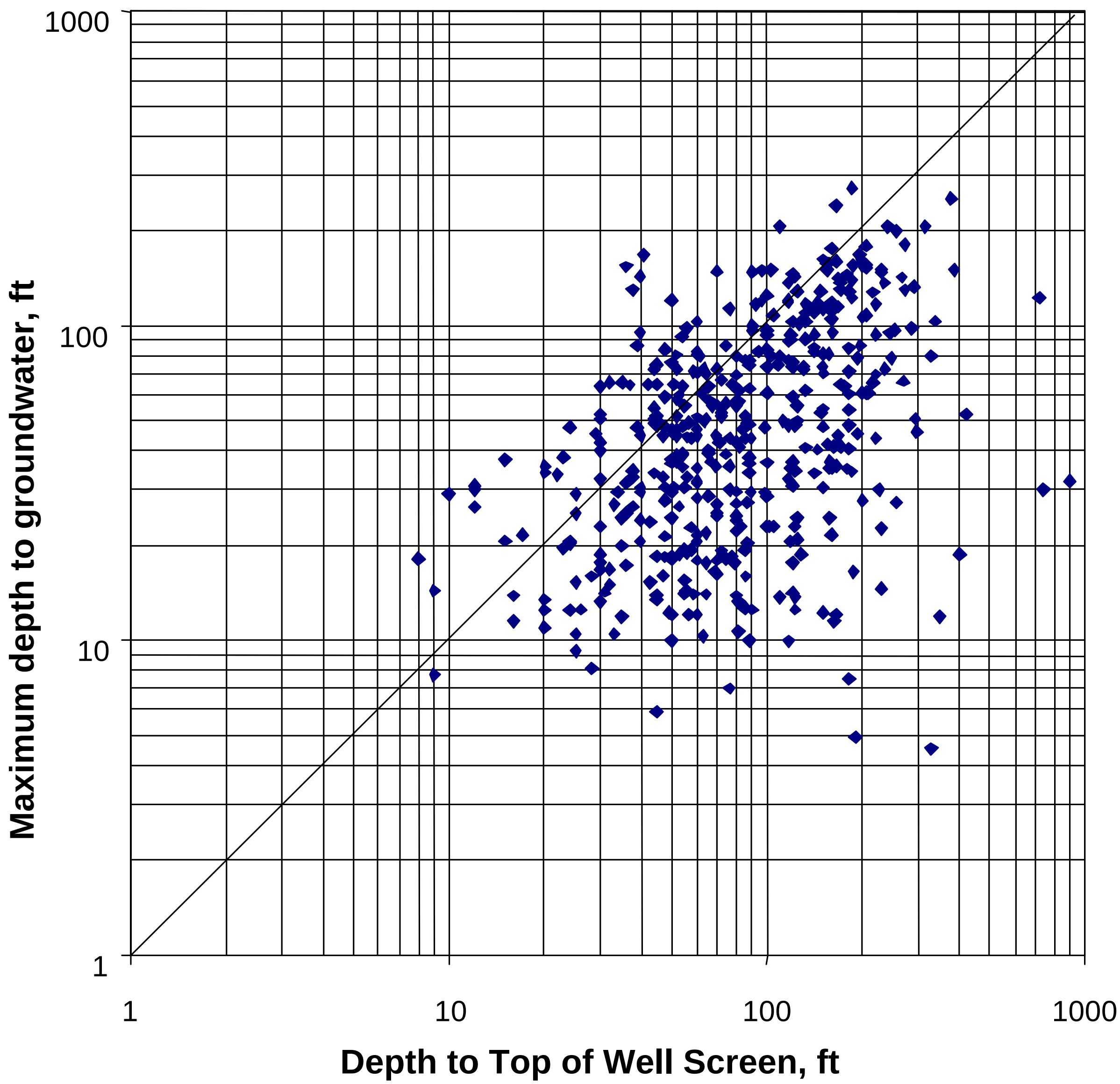
Change in detection rate of BTEX and MTBE in drinking water sources throughout California

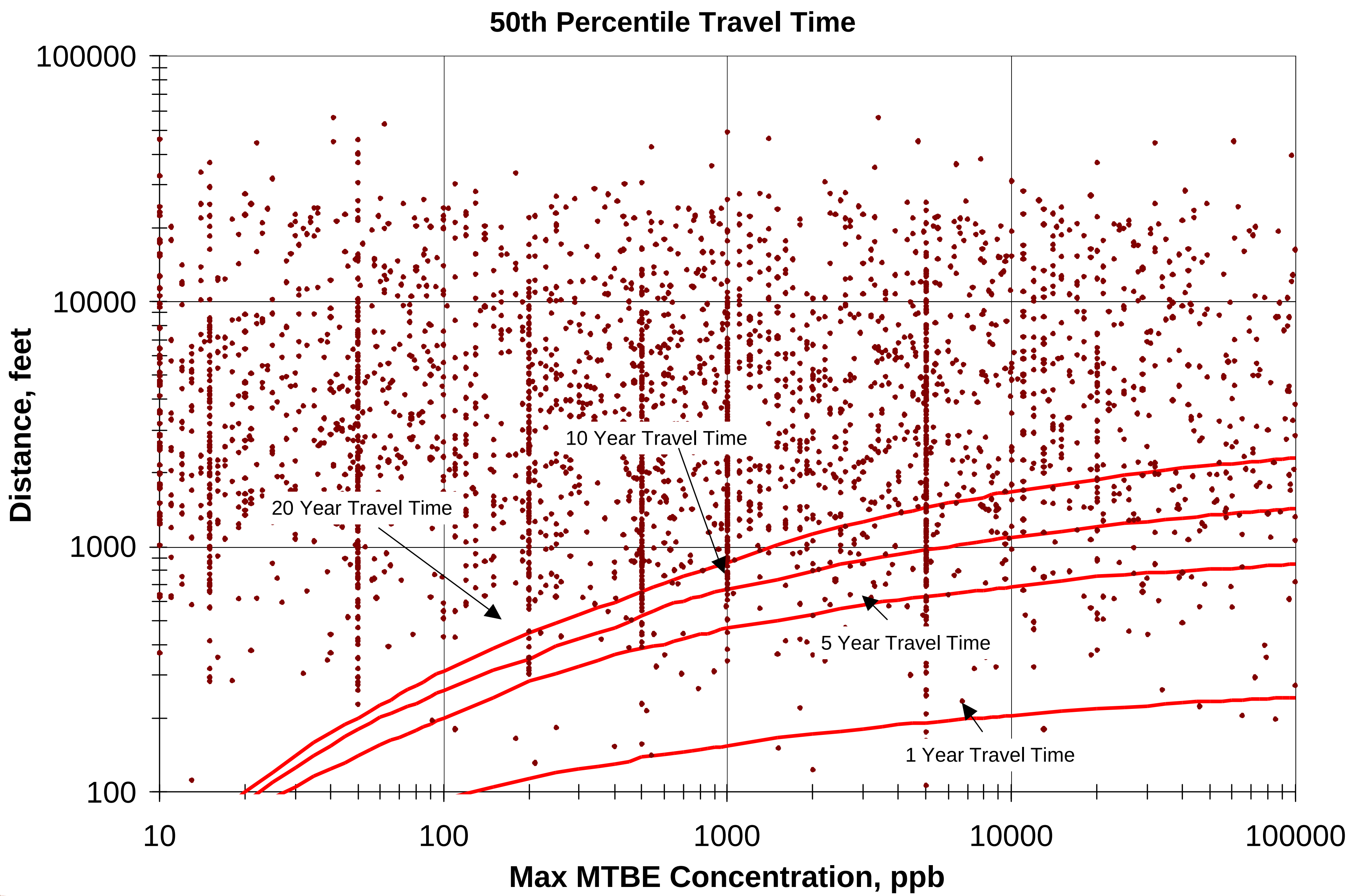


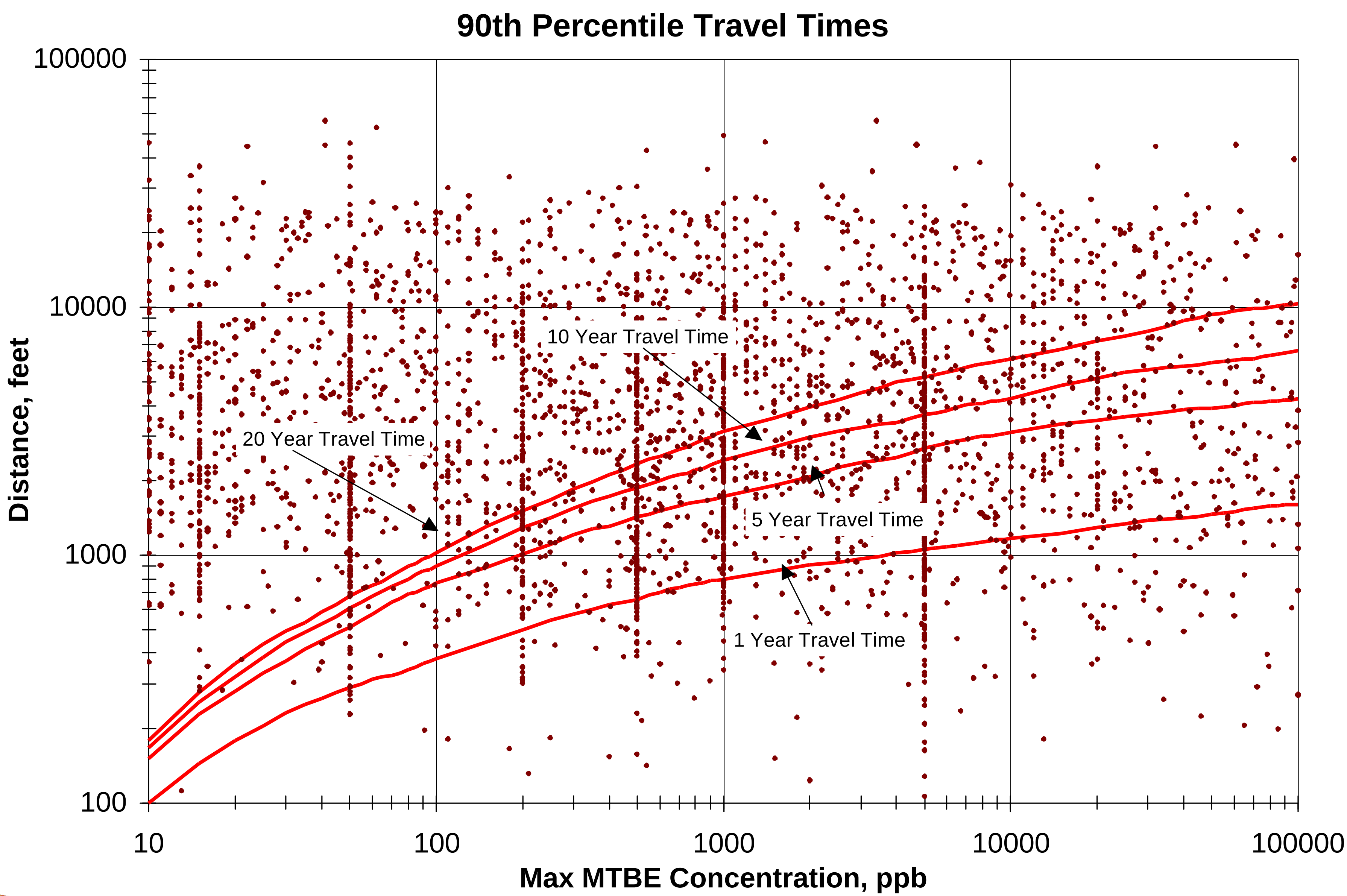
Depth to top of screen interval for different well types



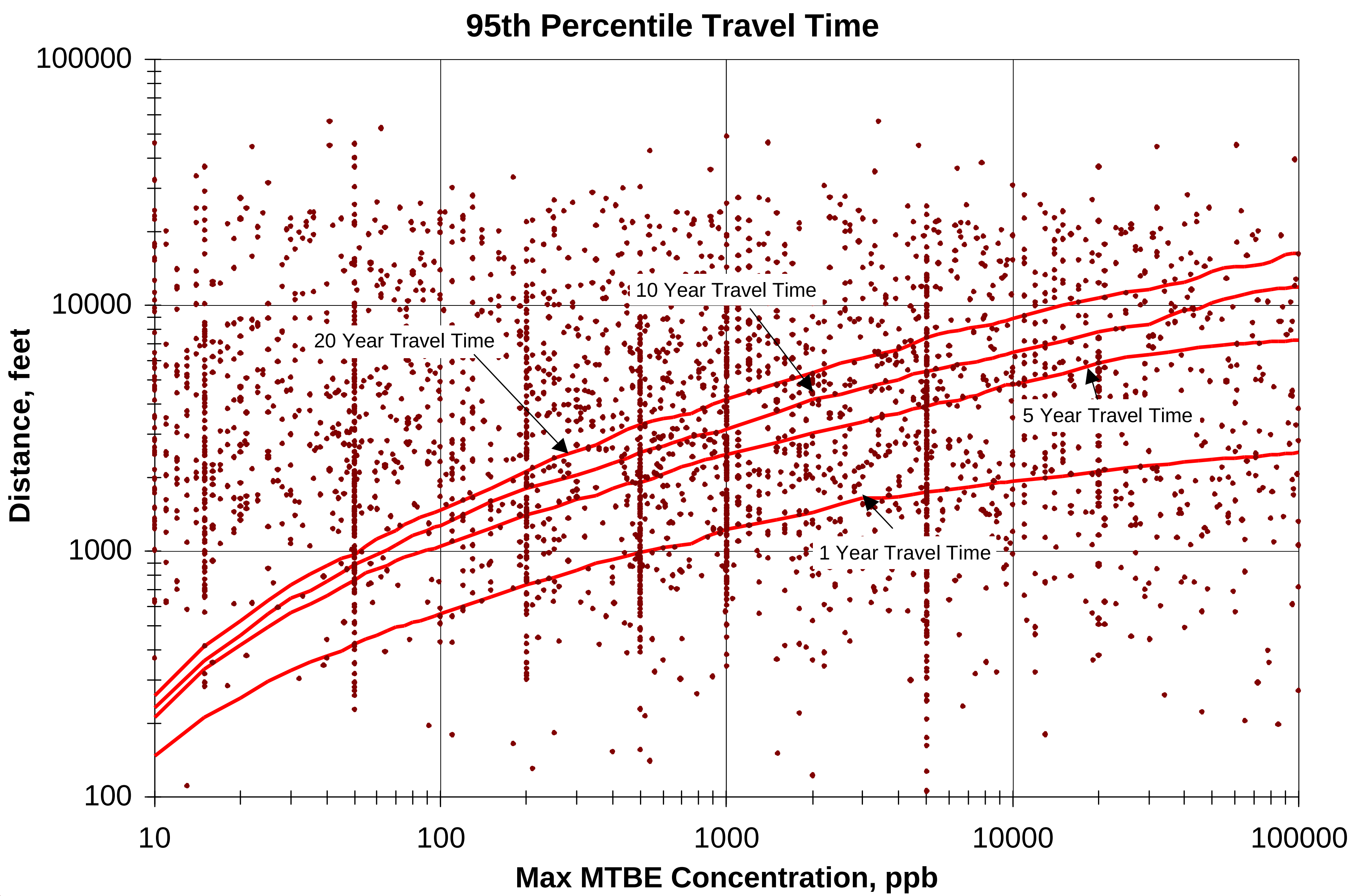

[redacted]
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
SCVWD
Domestic
SCVWD
Municipal
0.01
0.1
1
10
100
1000
10000
Acre-feet/year


1000
100
10
1
1
10
100
1000
Maximum depth to groundwater, ft
Depth to Top of Well Screen, ft


50th Percentile Travel Time
100000
10000
1000
100
Distance, feet
10 Year Travel Time
20 Year Travel Time
5 Year Travel Time
1 Year Travel Time
10
100
1000
10000
100000
Max MTBE Concentration, ppb



90th Percentile Travel Times
100000
10000
1000
100
Distance, feet
10 Year Travel Time
20 Year Travel Time
5 Year Travel Time
1 Year Travel Time
10
100
1000
10000
100000
Max MTBE Concentration, ppb


95th Percentile Travel Time
Distance, feet
100000
10000
1000
100
10
100
1000
10000
100000
Max MTBE Concentration, ppb
20 Year Travel Time
10 Year Travel Time
5 Year Travel Time
1 Year Travel Time

Senate Bill 1189 and Assembly Bill 592 (1997)

The State Water Resources Control Board shall...

Initiate a state-wide geographical information system (GIS) to manage the threat of MTBE contamination to public groundwater supplies.

- LLNL developed the database and GIS in consultation with the Mapping and Data Management Advisory Committee.

- This system must collect, store, retrieve, analyze, and display environmental geographic data in a database that is accessible to the public.

Senate Bill 989 (1999)

The State Water Resources Control Board shall…

- Identify areas of the state most vulnerable to contamination by MTBE…
  - Criteria including but not limited to
    - Hydrogeology
    - Soil composition
    - Density of USTs in relation to drinking water wells
    - The degree of dependence on groundwater for drinking water supplies
- Identify USTs within 1,000 feet of public drinking water wells
- Allows sites under investigative orders to access DWR well logs and construction for all wells within 2 miles of the site

Assembly Bill 2886
(2000)

The State Water Resources Control Board is authorized…

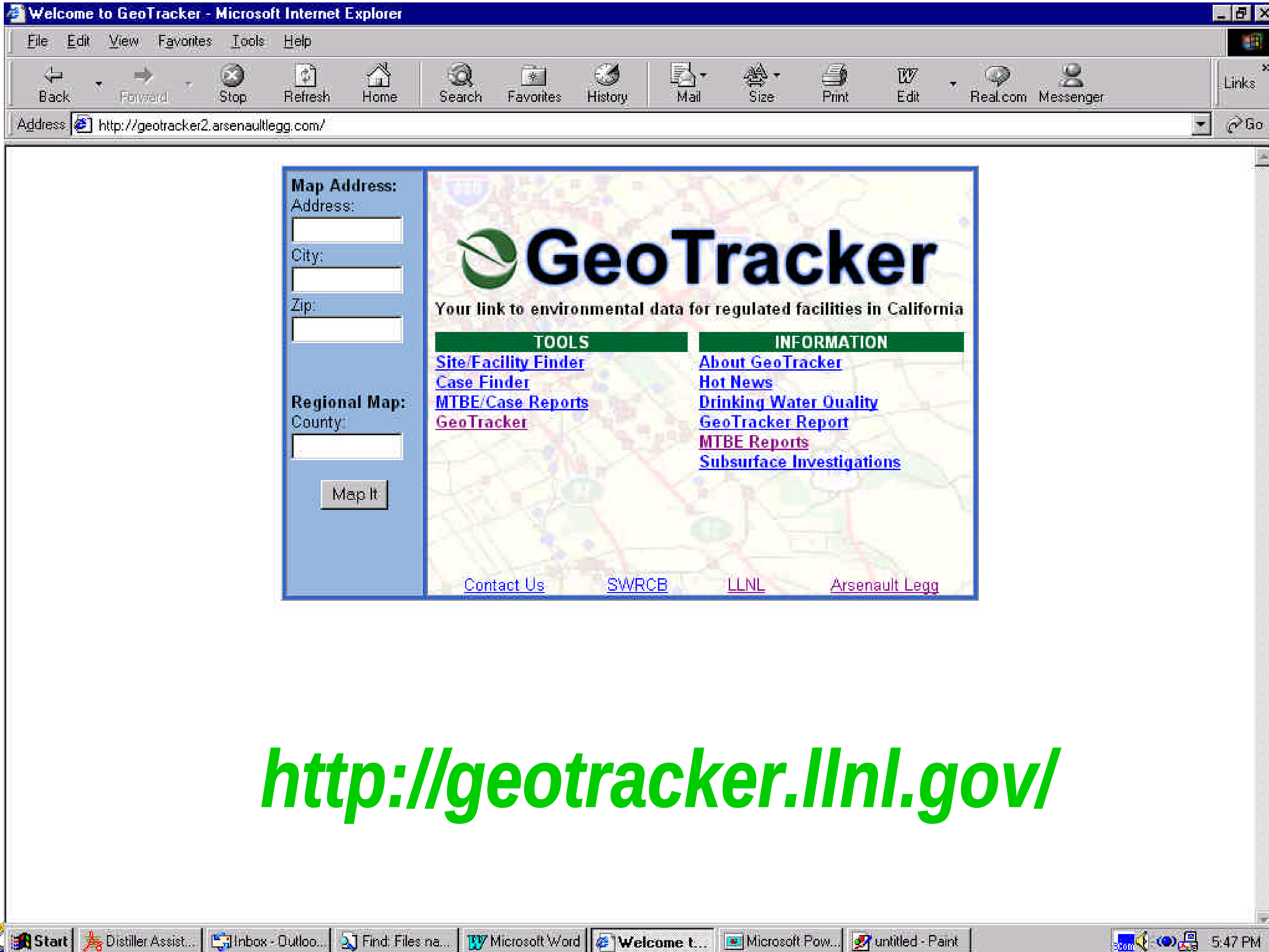
- To require a person who is submitting a report relating to a program administered by the board, to the board, a regional board, or a local agency, to submit the report in electronic format, as prescribed.

Managing the Risk of MTBE Contamination on a Regional Scale

- A key to preventing MTBE contamination is early identification of vulnerable drinking water supplies and critical MTBE sources.

- A risk assessment approach prioritizes contaminant sites and groundwater supplies for monitoring and remediation.

- Currently, risk management of groundwater supplies is not possible because neither the data nor the analytical tools are readily available to environmental managers.



http://geotracker.llnl.gov/

Information Integration Initiative Goals:

Build an information network that will establish a single integrated multi-media core of environmental data and tools:

- Improve environmental decision making by integrating facility information and ambient environmental data in a geographical format.
- Reduce burden and transaction costs for access to environmental data.
- Provide more reliable and transparent access for regulated businesses.
- Provide more accurate and reliable environmental data for better public access/understanding, improved compliance, and greater accountability.

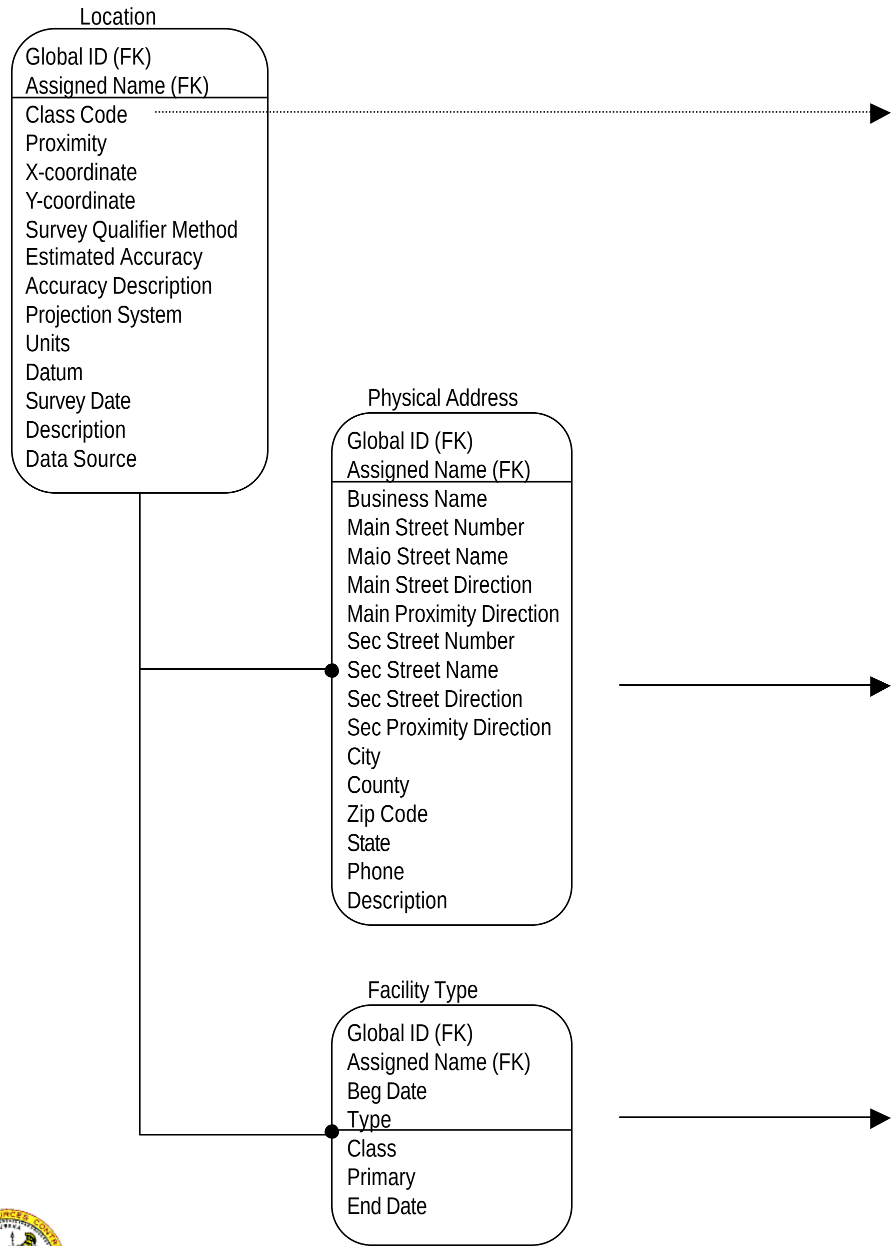
GeoTracker

- UST permit, LUFT, & drinking water program
- landfill, SLIC, NPDES, Water Rights, DOD, Beach closure, Ambient groundwater
- LTRM- Long term monitoring of residual contamination (land use planning)
- Watershed management

Soil, Water, & Vapor chemistry data from any point-source pollutant or non point-source (areal impact) and all types of groundwater resources

State-wide Base Maps….to meet case-worker daily needs for information

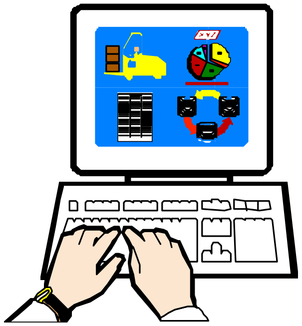
- **USGS Quads (changes projection "on-the-fly") ~40 GB**
- **ETAK street maps, ~10 GB**
- **Digital Ortho Quarter Quads, ~1 TB**
- **Groundwater Basins, 9 MB**
- **Watersheds, 5 MB**
- **DEM, slope & elevation contours**
- **Pipelines (under development, Office of the Fire Marshall)**



Drinking Well
Surface Water Intake...
UST Location
Dispenser
Borehole
Monitoring Well
Extraction Well...
Influent Monitoring Point
Effluent Monitoring Point…

Physical address

Water System
LUFT Site
Waste Water Treatment Plant
SLIC Site...
NPDS...
Standard Industrial Coding or
Regulatory Descriptions



Analytical Laboratory

EDF

Relational tables imported into GEIMS.

COELT

- Loads analytical data into EDF tables.

EDCC

Consistency checker for EDF format

- Generates hard copy reports directly from electronic data.

Hard copy reports

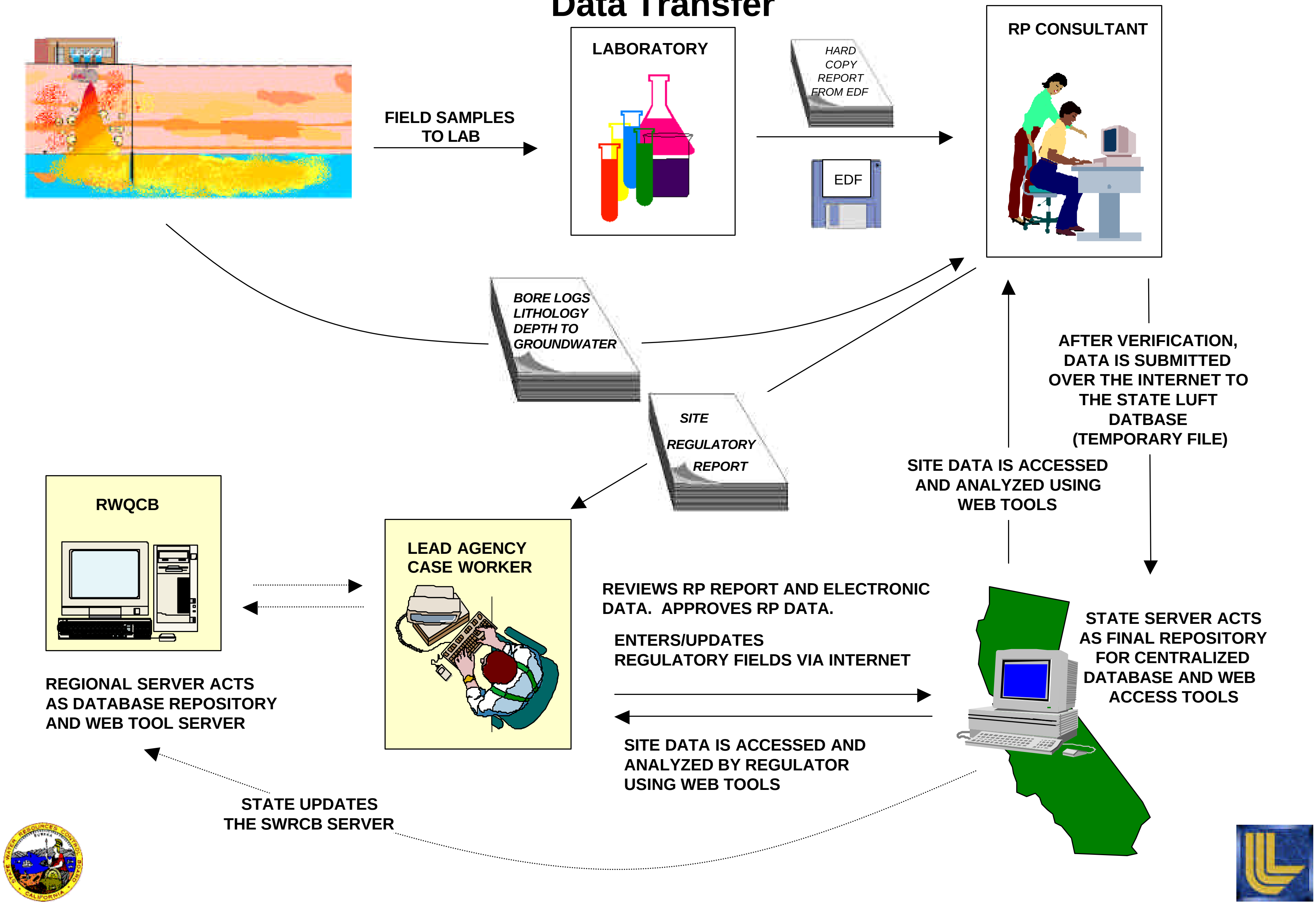
Electronic data

Environmental Contractor

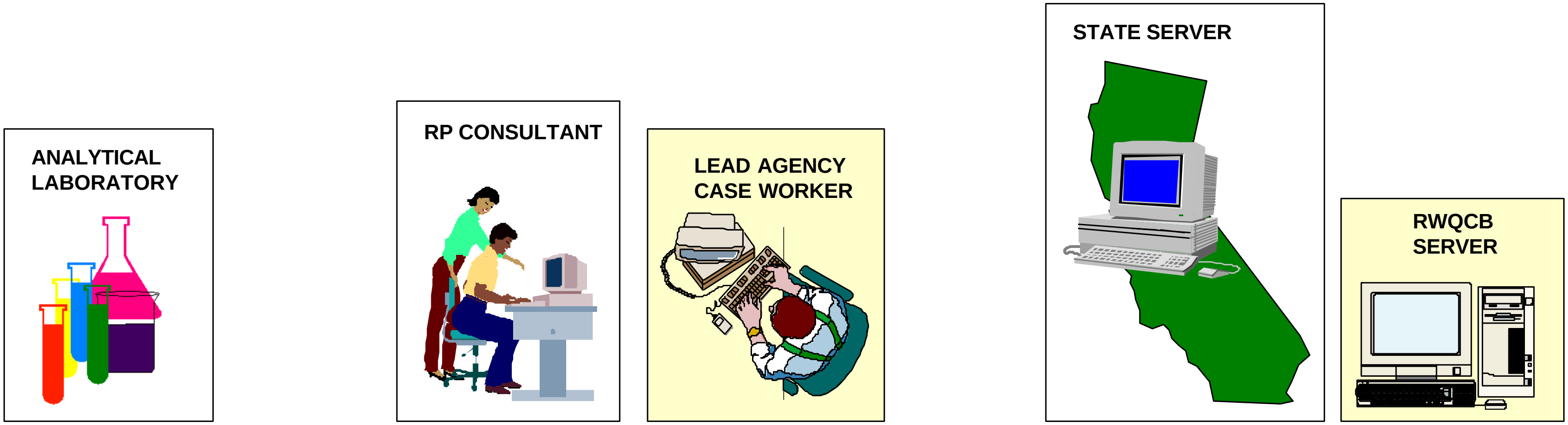
Where to get public domain EDF?

http://www.arsenaultlegg.com/

Geographical-Environmental Information Management System (GEIMS) Data Transfer



GEIMS and GeoTracker System Requirements



- COELT
- EDF
- EDCC

- Web Browser
- Datastream (optional)

- Oracle (LUFT database)
- Web server
- ESRI IMO Server
- GeoTracker

GeoTracker Benefits

- An integrated Internet site to manage data from unrelated regulatory groups
- Potential for cooperative usage among Cal-EPA agencies
  - Immediate: managing the MTBE problem
  - Long term: management of contaminant releases, water resources and environmental data
- Electronic permitting
  - Allows greater regulatory oversight
  - Reduces the paperwork burden on businesses

Introduction

We have been applying isotopes to hydrology issues in water resource management over the past 8 years. This effort began through LDRD support and has steadily grown into a program supported solely by local and state agencies. Most recently we have begun a large-scale program in conjunction with the U.S. Geologic Survey for the State of California (State Water Resources Control Board) to evaluate ambient groundwater quality throughout the entire state.

This poster covers three areas:

- Evaluation of California groundwater vulnerability
- Noble gas artificial groundwater tracers
- Tracking sources of uranium using isotope ratios

Tracer Studies in California Applied to Water Management

1 LLNL (Site 200, Site 300)

2 Alameda County Water District

3 Orange County Water District (OCWD)
L.A. County Sanitary District (LACSD)

4 West Basin Municipal Water District

5 El Toro Naval Air Station

CAS Project

- The CAS project (California Aquifer Susceptibility) is a large-scale investigation of California groundwater resources. It represents a major paradigm shift from previous efforts. Rather than perform detailed hydrogeologic investigations, we will use simple observational data measured in water samples and use a probabilistic approach to assess contamination vulnerability.

- **GOAL:** Sample the existing 16,000 public drinking water wells in California & estimate their susceptibility to contamination.

- **SCOPE:**

  1. FY01 pilot project ($1.1M LLNL, 0.5M USGS) will investigate 500 public water supply wells.

  - Tritium & dissolved noble gases: ^3H-^3He age dating
  - Ultra low-level VOCs: e.g. MTBE, TCE, PCE
  - $^{18}O/^{16}O$ in groundwater: water origin

  2. Full scale study expected to take 5 years & about $32M

  3. Public Outreach and education are an important part of this effort. We will be working with local High School teachers & students as part of the CAS project.

  - Science on Saturday (Feb 24, 2001): Presentation about groundwater in California for children and young adults.

The Team

Brendan Dooher, Dave Rice, Walt McNab, Anne Happel, Jean Moran, Gail Eaton, Lee Davisson, Bryant Hudson

Lawrence Livermore National Laboratory

Heidi Temko, Amy Tong, Steve Mizera, Angela Schroeter, Lisa Babcock, James Giannopoulos

State Water Resources Control Board

Neil M Dubrovsky, Karen R Burow, Jennifer L Shelton, Donna Knifong

USGS

Michael Legg

Arsenault-Legg Inc.

Conclusions

- Modeling based on detailed site-specific information is needed.
- Groundwater capture zones should be included in the analysis.
- More knowledge is required concerning the subsurface environment in California.
- A drinking water well sampling frequency policy that is based on proximity to LUFT sites may be more protective of public water supplies.
- Further comparative analysis of impacted public drinking water wells to gasoline continuing ethanol or MTBE and Well Impacted LUFT sites is needed.
- A voluntary sampling program for private wells should be established by the State.

Conclusions

- With the advent of the Internet, the once difficult-to-near-impossible task of accessing data from various agencies for thousands of contaminant sites or public wells can be made simple.
- GEIMS/GeoTracker can act as an important hub for integrating information from multiple agencies about contaminant sites and water resources.
- The GIS/database approach to information management allows for an integration of data, leading to a more complete understanding of the environmental problem.

Conclusions

With the advent of the Internet, the once difficult-to-near-impossible task of accessing data from various agencies for thousands of contaminant sites or public wells can be made simple.

GEIMS/GeoTracker can act as an important hub for integrating information from multiple agencies about contaminant sites and water resources.

The GIS/database approach to information management allows for an integration of data, leading to a more complete understanding of the environmental problem.

Conclusions

Based on results from LLNL's isotope hydrology studies, Water managers are making policy decisions that affect public health in California . Given that each public water supply well costs $1-2M, these decisions have a large economic impact.

- The CAS project takes a probabilistic approach to determine the susceptibility of a public water supply well to contamination. The results from CAS project will affect decisions regarding wellhead protection, land use, and requirements for artificial recharge.
- Artificial noble gas isotope tracers give detailed hydrogeologic information on a large scale. The properties of the tracers make them ideal for defining flowpaths in groundwater intended for potable use.
- Isotopic signatures provide fingerprints for water and contaminant sources. ANCD's state-of-the-art analytical facilities for measuring isotope ratios offers a powerful suite of tools for addressing emerging water resource issues.

Environmental Transport and Fate of Alkylates

Alfredo A. Marchetti

Lawrence Livermore National Laboratory
Energy and Environment Directorate

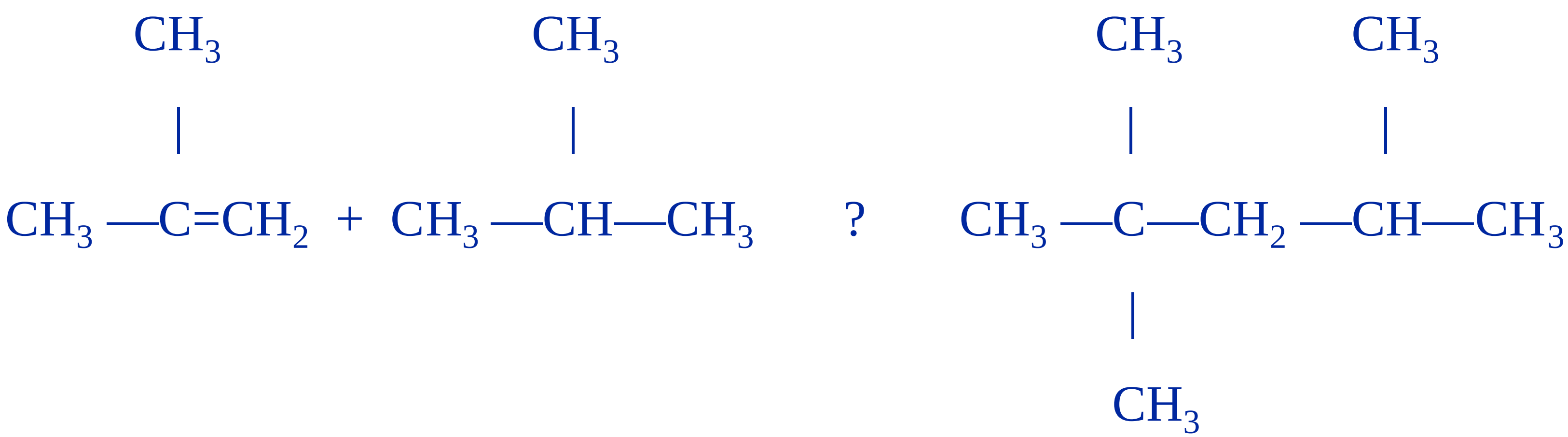
DOE Office of Fuel Development

Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California

April 10 & 11, 2001

Oakland, California

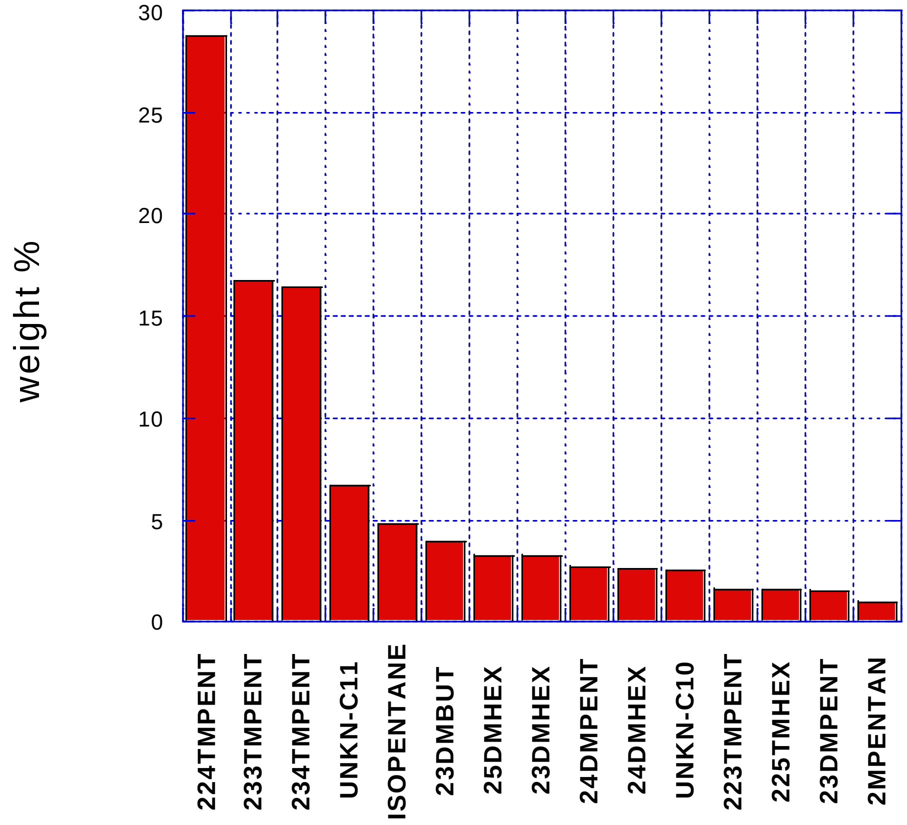
Alkylate synthesis: basic reaction



Isobutene	Isobutane	Isooctane
(2-Methylpropene)	(2-Methylpropane)	(2,2,4-Trimethylpentane)

The reaction is catalyzed with sulfuric acid at low temperature< 10°C.

Alkylate composition



Data from STRATCO

Percentages are in agreement with those presented by Durett *et al.* for a finished alkylate (*Anal. Chem.* **35** pp 637, 1963)

Physicochemical properties for MTBE, ethanol, benzene and isooctane

	Fuel Compound			
Property	**MTBE**	**Ethanol**	**Benzene**	**Isooctane**
MW (g/mol)	**88.15**	**46.07**	**78.11**	**114.23**
Boiling point(°C)	**55.2**	**78.2**	**80.1**	**99.2**
Density (g/mL)	**0.741**	**0.789**	**0.879**	**0.69**
K_{ow}	**8.71**	**0.50**	**135**	**12,200**
Vapor pressure† (kPa)	**33.3**	**7.9**	**12.6**	**6.49**
Solubility (mg/L)	**51,000**	**Miscible**	**1,800**	**2.44**
Henry's law† (Pa-m^3/mol)	**59.5**	**0.64**	**562**	**323,000**

†at 25°C

Air

- **Releases to the atmosphere**
  - **Incomplete combustion and evaporative emissions from vehicles and fuel delivery systems**
  - **Evaporation from direct spills on land and water**
- **Calculated rates of evaporation using two-film model for a pool of pure compound in mol/m^2-h** (Wind speed 1 m/s at 10 m from surface)

MTBE	**140**
Benzene	**57.6**
Ethanol	**43.2**
Isooctane	**25.2**
Water	**23.0**

Atmospheric reactions

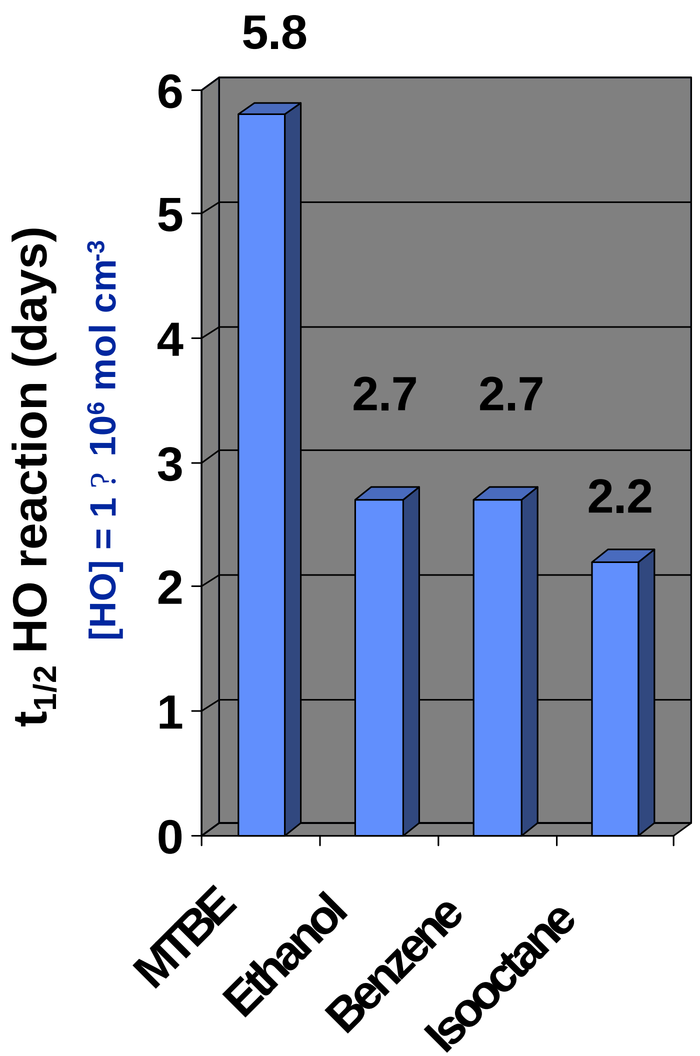
- **Main degradation reaction**

  HO + RH ✍ R· + H_2O

  - **For alkanes with 2 to 8 carbons, k_{HO}~ (0.3—9) ? 10^{-12} cm^3 mol^{-1} s^{-1}**
  - **Methane k_{HO}=0.0084 ? 10^{-12} cm^3 mol^{-1} s^{-1}, very long-lived, most abundant in atmosphere**

- **Ozone forming potential in the maximum incremental reactivity scale (Carter, 1994)**

	MIR [g O_3/g]
MTBE	0.62
Ethanol	1.34
Benzene	0.42
Isooctane	0.93
Olefins	up to ~10



Water

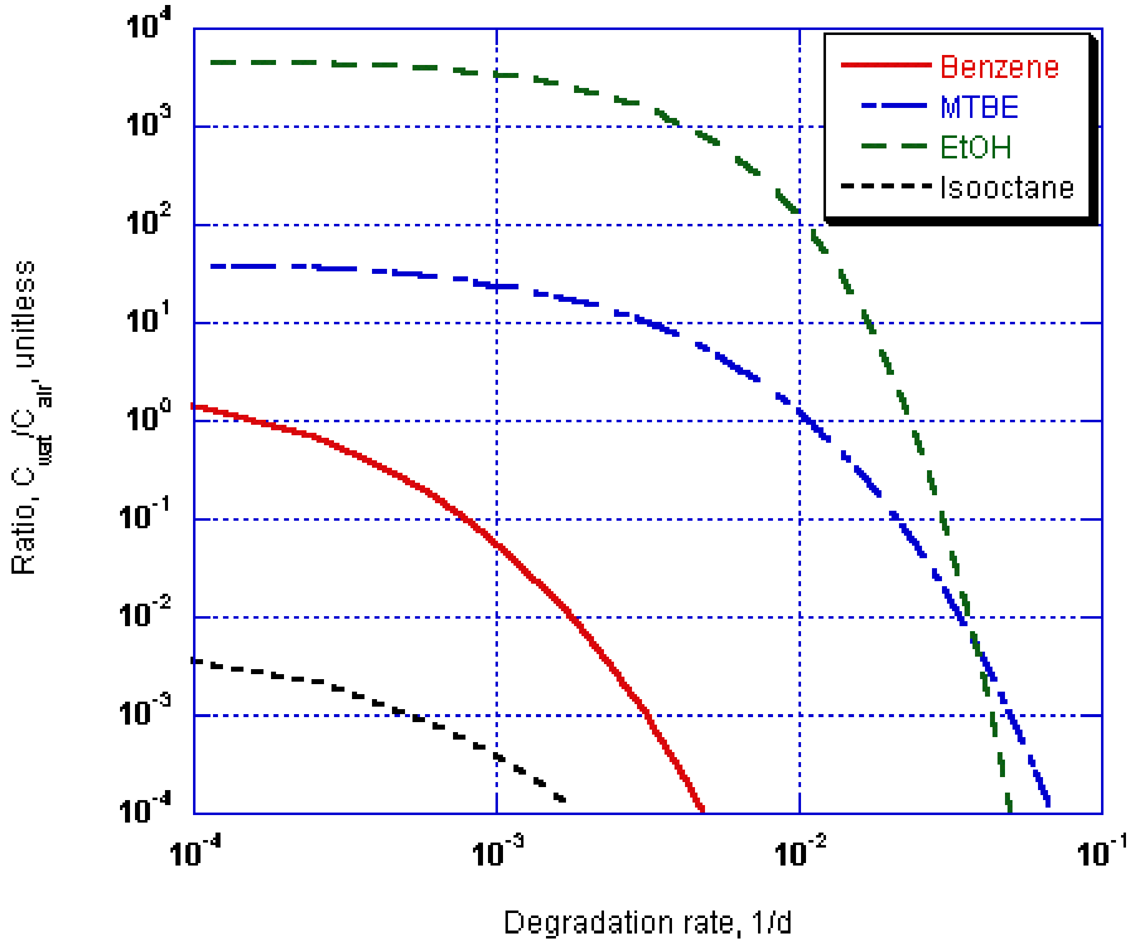
- Alkylates solubility in water is very low (10^{-4}—10^{-5} M)
  - Ethanol as cosolvent can increase the solubility of alkylates
    - E.g.: Calculations show that for an ethanol concentration in water of 10% [v] the solubility of isooctane would increase by ~1.5
- Alkylates have high Henry’s law constants ↴ in air-water systems they concentrate mainly in the air phase
  - The mass transfer velocity based on the two-film model for surface waters is ~0.3 m/day[‡], for isooctane, benzene, and MTBE; in contrast, for ethanol, it is ~0.05 m/day [‡]

    [‡]wind velocity at 10 m from surface = 1 m/s
  - Rainout calculation
    - Calculation of concentration in rain water using a concentration in air of 1 ppb [v] and assuming equilibrium
      - Ethanol 7.33 ? g/L
      - MTBE 0.17 ? g/L
      - Isooctane 0.000036 ? g/L

Relative impacts of atmospheric rainout of fuel compounds on shallow ground water

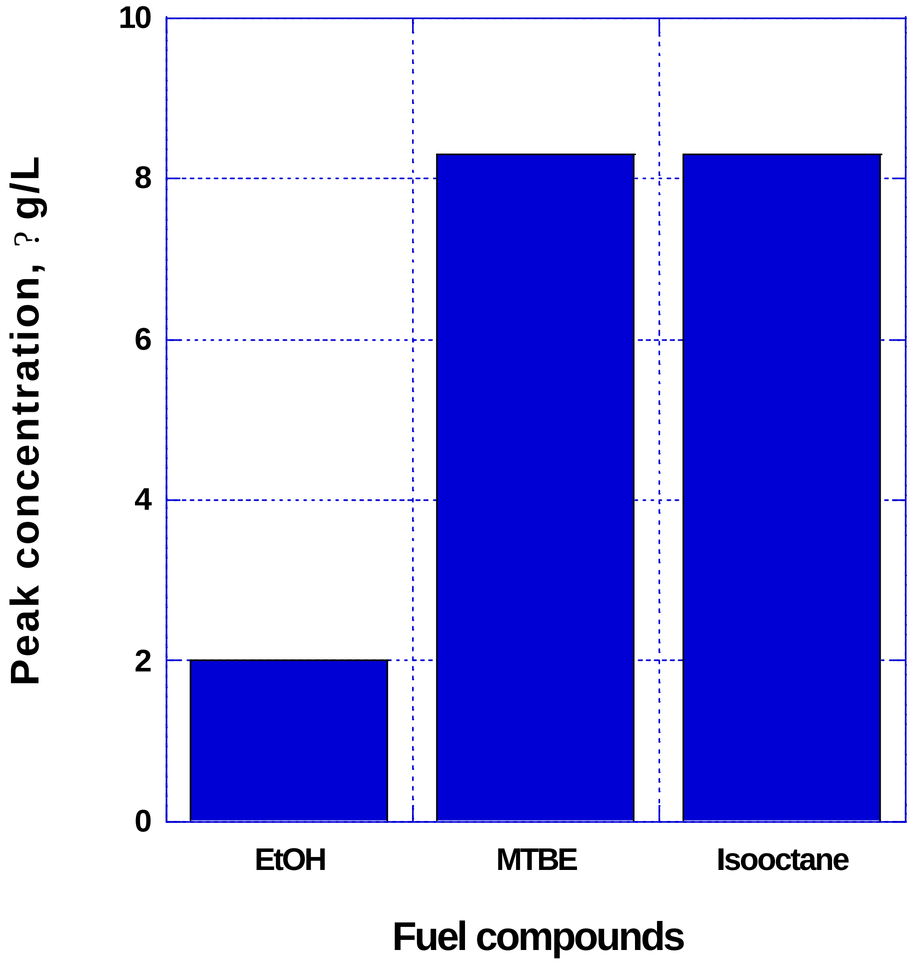
Baehr's model (1999) was used to simulate the impact of rainout onto a sandy soil with a depth of 5 m to the water table

The relative impacts on ground water are described by the ratio of the concentration of a fuel compound in ground water to its concentration in air



Impact to water or soil systems also depends on (bio)degradability, e.g., Predicted concentrations in a lake after a continuous, 7-day release of 40 kg/d

- **Reference conditions are an epilimnion of 8 m and an average wind speed of 3 m/s**
- **<u>With an assumed half-life of 24 hr, ethanol attains a substantially lower concentration in surface water than the other fuel compounds</u>**
- **The water-to-air mass transfer of both MTBE and isooctane are limited by resistance in the water phase**
- **The estimated volatilization half-lives for these two compounds are 15-16 days**



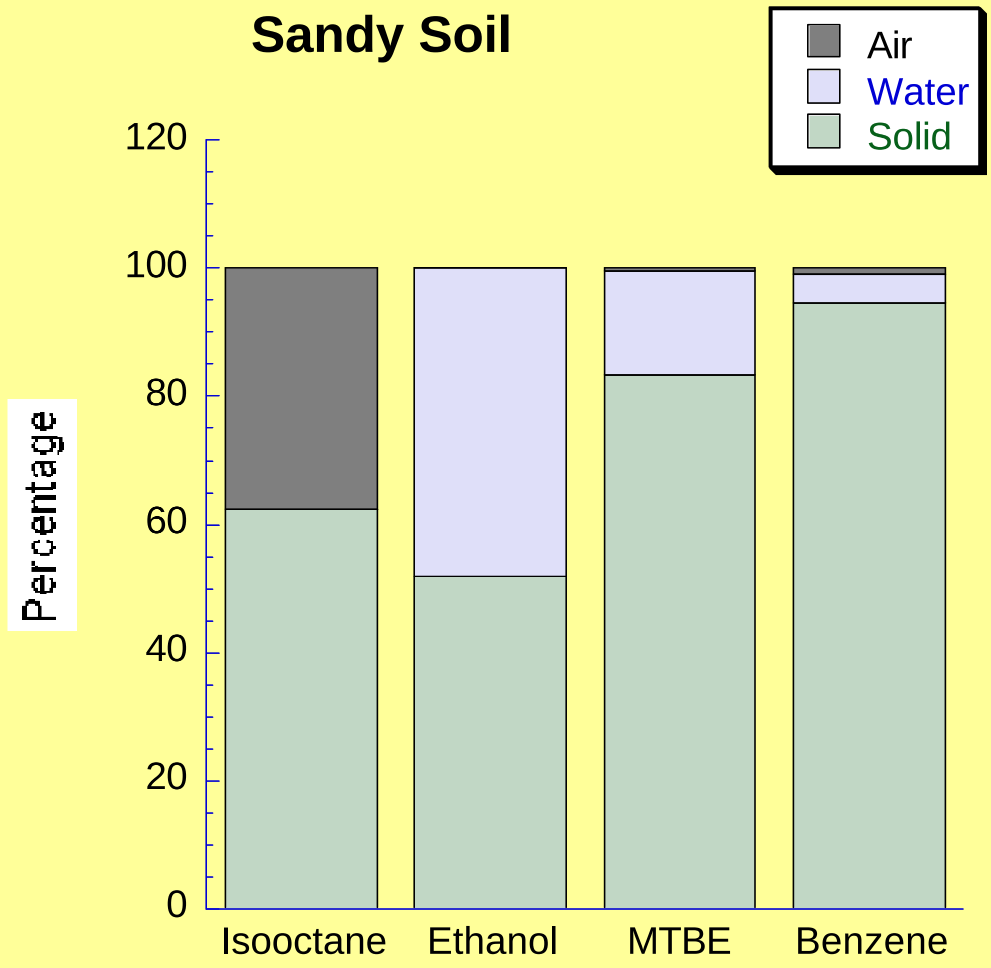
Soils: distribution among phases

Soil Characteristics

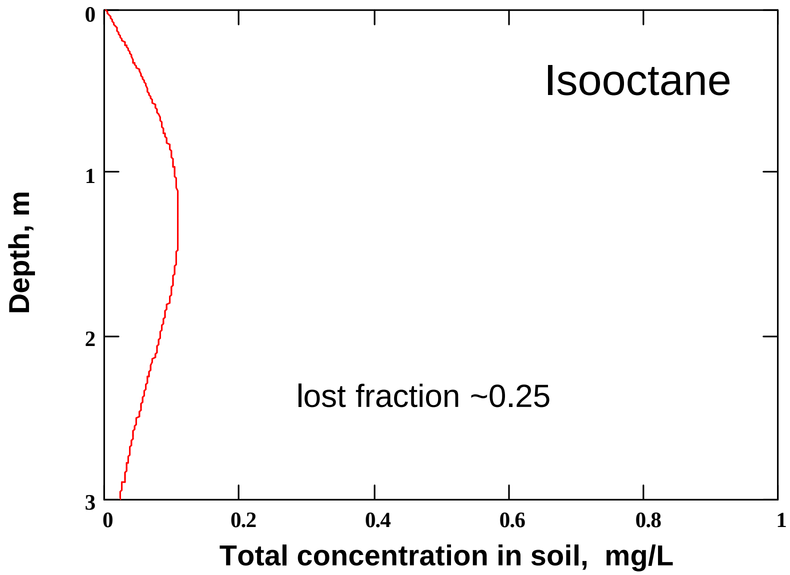
Density	**1.59**	**g/cm³**
Porosity	**0.4**	**L/L**
Water cont.	**0.18**	**L/L**
$f_{organic\text{-}carbon}$	**0.0075**	
Precipitation	**100**	**cm/y**
Infiltration rate	**18**	**cm/y**

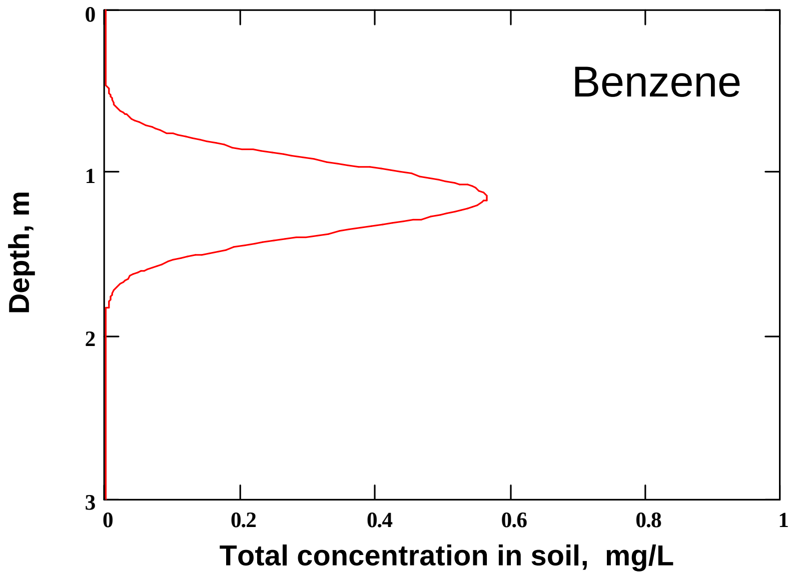
Tranport and losses in soil can be estimated using Jury's model (1990) with corrections by Robinson (2000)

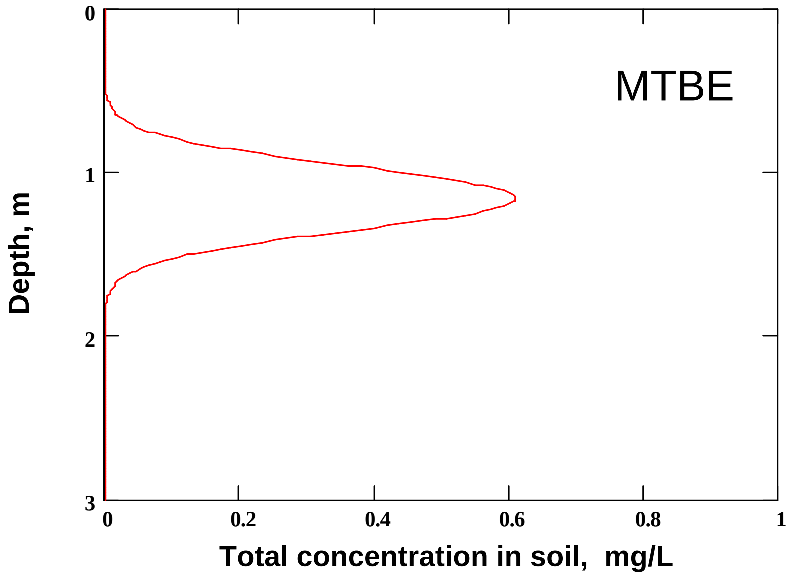
E.g.:
Sandy soil with a buried 1-m deep and 30-cm thick source; source concentration is 1 ppm and concentration in air is zero

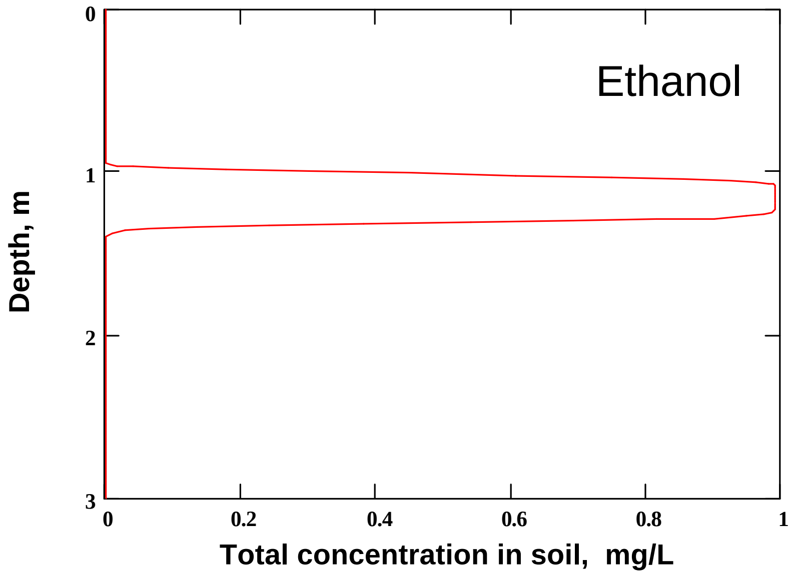


Concentration profiles in soil for a 1 ppm 30-cm wide 1-m deep input pulse after 5 days









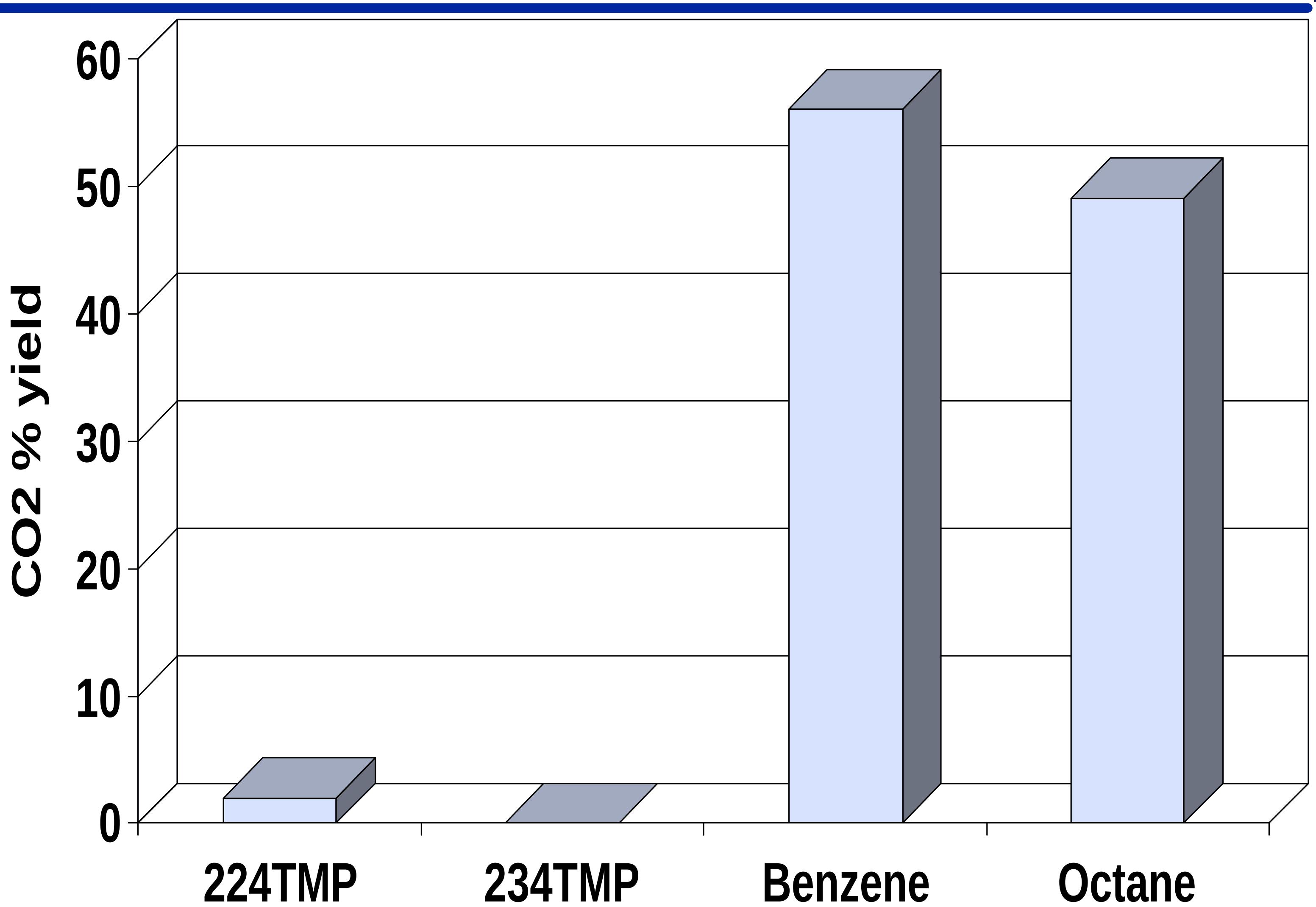
Biodegradation of isooctane

- A laboratory experiment conducted by Solano-Serena (1998) used an unpolluted forest soil to incubate a gasoline solution. After 28 days at 30^{o}C, 20 % of the isooctane was degraded. Benzene, in contrast, was completely degraded

- The corresponding degradation half-life is about 88 days for isooctane

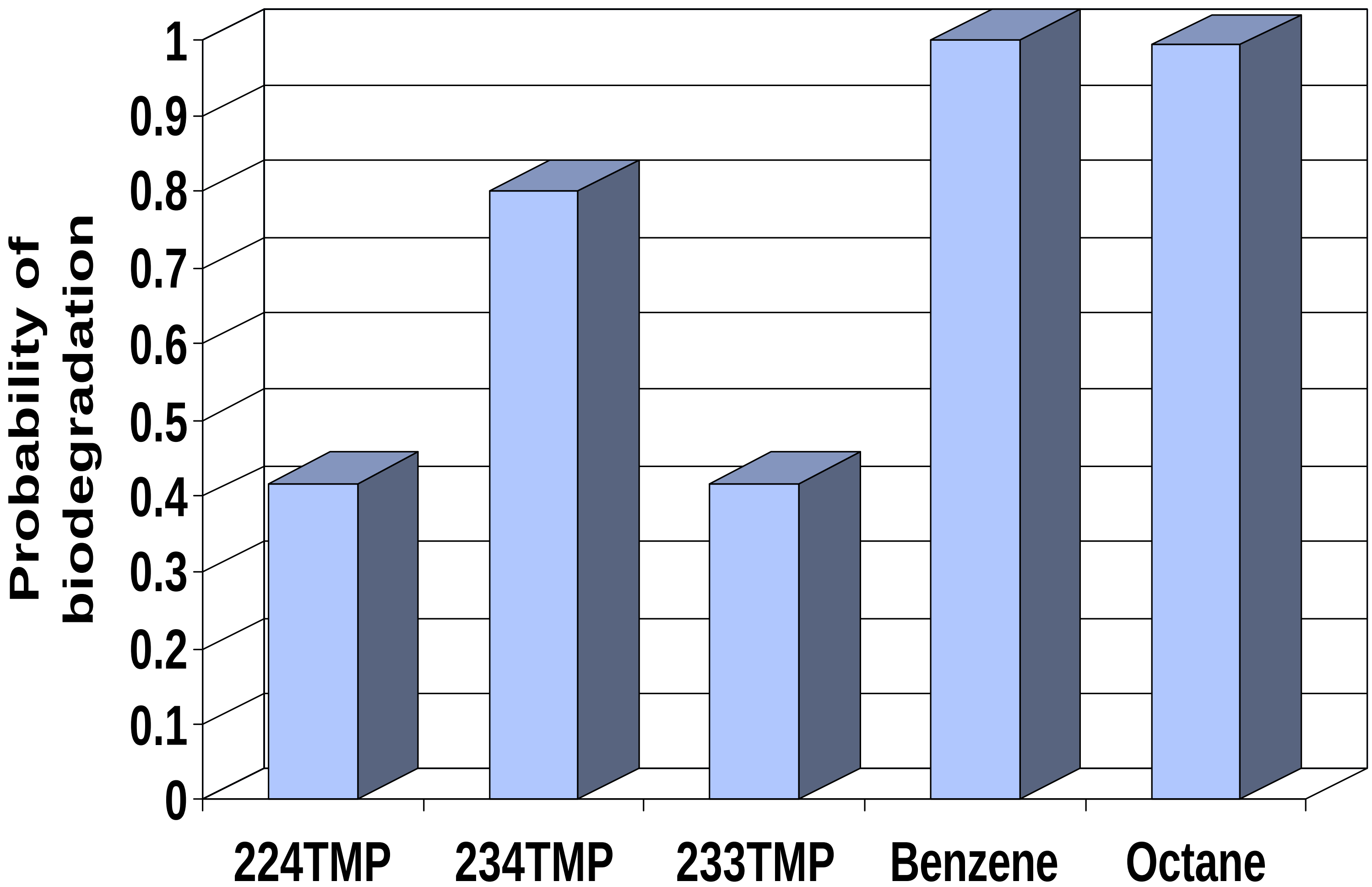
- Based on the results of a field study of a contaminated aquifer by Nielsen (1996), it is likely that the *in-situ* degradation of isooctane will be considerably longer and will depend in part on the occurrence of certain natural microorganisms capable of degrading fuel hydrocarbons

Biodegradation: mineralization yields in unpolluted soil



Mineralization of individual hyrdrocarbons by native soil microflora after 34 days of incubation at 30°C. From Solano-Serena *et al.* (1998)

Biodegradation prediction (BIOWIN)



Probability of biodegradation by group contribution method: program BIOWIN v4.0 from the Syracuse Research Corporation. **Probability > 0.5** implies readily biodegradable

Summary

- Alkylates—mostly branched C8-alkanes
  - Low solubility in water
  - High Henry's law constant
  - Less dense than water
  - High K_{ow}
- Transport and fate in the environment
  - Surface releases
    - Air is the major sink; HO-oxidation with 2-3 days halflife
    - Moderate ozone forming potential compared to other gasoline components
    - Possibly minimal impact on waters
  - Subsurface releases
    - Depending on soil characteristics and source location significant migration to the atmosphere is possible
    - There is also strong absorption in the soil organic phase (high K_{ow})
    - Branched alkanes tend to be recalcitrant—only few experimental biodegradation studies

Alkylate Measurements at Field Sites

M. Lee Davisson, **Alfredo Marchetti, Marina Chiarappa-Zucca, and David Layton**

Lawrence Livermore National Laboratory

Sponsor, DOE Office of Fuels Development

Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California

April 10-11, 2001

Oakland, CA

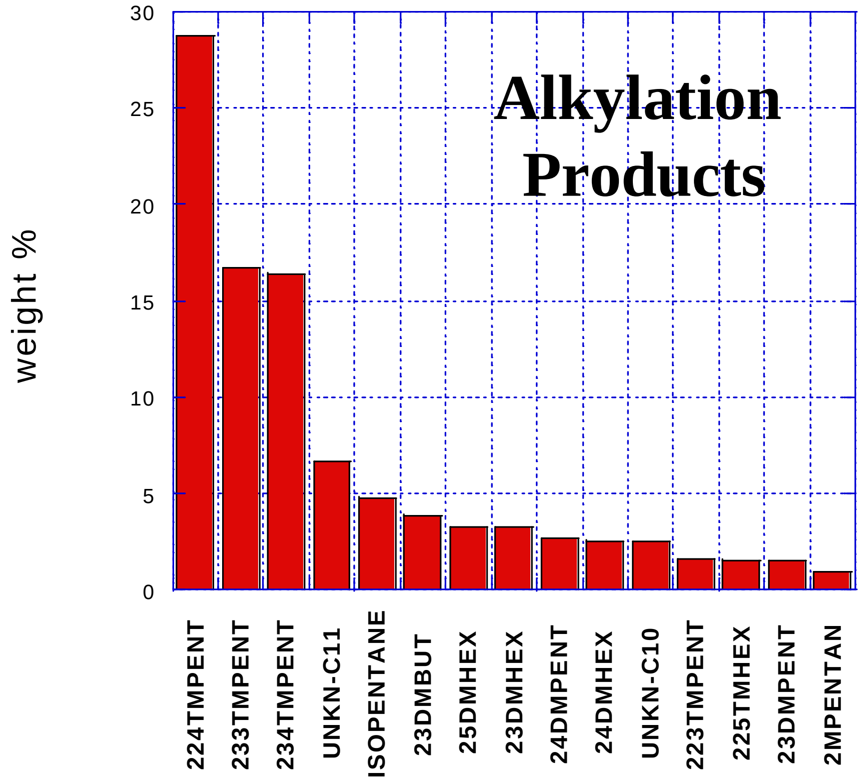
Presentation outline

- Alkylate compounds in current gasoline and their relationship to TPH-g and risk.
- Fate and transport issues in gasoline spills
- Analytical measurements, field sites, and experimental approach.
- Preliminary data

Estimated composition of California reformulated gasolines (from UCRL-AR-135949)

Fuel Component	MTBE-Blended	EtOH-Blended Volume %	No Oxygen
n-Butane	0.6	0.5	0.1
C_5 and C_6 alkanes	6.1	4.3	11.3
C_7 to C_9 branched alkanes	14.4	28.4	32.5
Benzene	0.67	0.80	0.80
Total aromatics	24.0	20.0	20
Total olefins	4.3	2.9	5.0
Oxygenate	11.4	7.8	0
Other	39	35	30
Total	100.47	99.7	100
Oxygen (wt%)	2.1	2.7	--

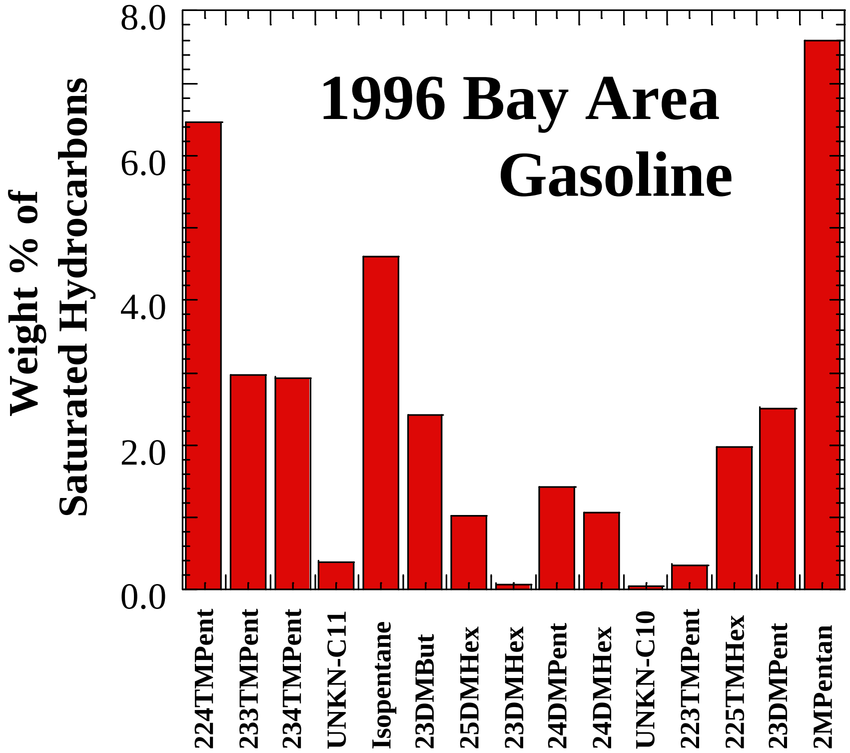
Alkylates already occur in gasoline



Data from STRATCO

Production Profile

Percentages are in agreement with those presented by Durett *et al.* for a finished alkylate (*Anal. Chem.* **35** pp 637, 1963)



Weight percent of total n-alkanes, isoalkanes, and cycloalkanes in 1996 Bay Area gasoline (Kirchstetter et al., 1999).

Physicochemical properties for MTBE, ethanol, and isooctane

		Fuel Compound		
Property	**Units**	**MTBE**	**Ethanol**	**Isooctane**
Molecular weight	g/mol	88.15	46.7	114.23
Weight % Oxygen		18.2	34.8	0
Octane rating		110	115	100
Density as liquid	g/mL	0.740	0.789	0.69
K_{ow}	dimensionless	8.71	0.50	12,200
Vapor pressure†	Pa	32,664	7,869	6,490
Solubility	mg/L	48,000	Miscible	2.4
Henry's law†	Pa-m^3/mol	53.5	0.64	323,000

Where's the data?

- Previous field studies on gasoline spills focused on fate and transport of BTEX and oxygenates.
- Regulatory mandate mostly requires quantification of carcinogens and TPH-g.
- TPH-g is not compound specific and often semi-quantitative.
- Biodegradation studies are limited for branched alkanes.

TPHCWG recommendations

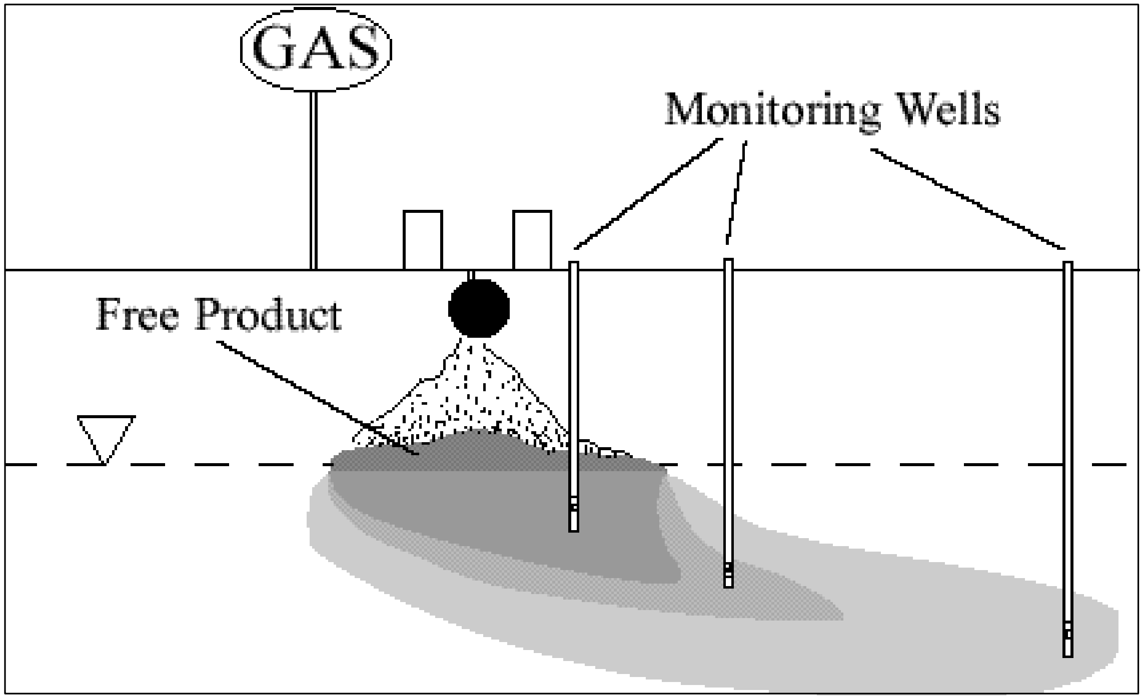
- Carcinogenic risk based on indicator compounds of benzene and PAHs.

- Non-carcinogenic risk based on fraction-specific toxicity criteria. Fractions determined by carbon number. e.g. RfDs: Benzene < C6-C9 < C10-C12

- Risk assessment based on exposure pathways and toxicity criteria.

- Update approach as data become available on fate, transport, and toxicity of TPH constituents.

Measurement approach



Data Collection
- Field Parameters
- BTEX and MTBE
- TPH-g
- Hydrocarbons
- Total non-volatile
- Carbon isotopes

Uncertainties
- Exact age and character of spill is typically not known.
- Sample reproducibility may be an issue for alkylates.
- Site-to-site variability may be large due to differences in environment, well construction, sampling method, etc.

Hydrocarbon measurements

Target compounds are alkanes greater than 1% by weight in commercial gasoline:

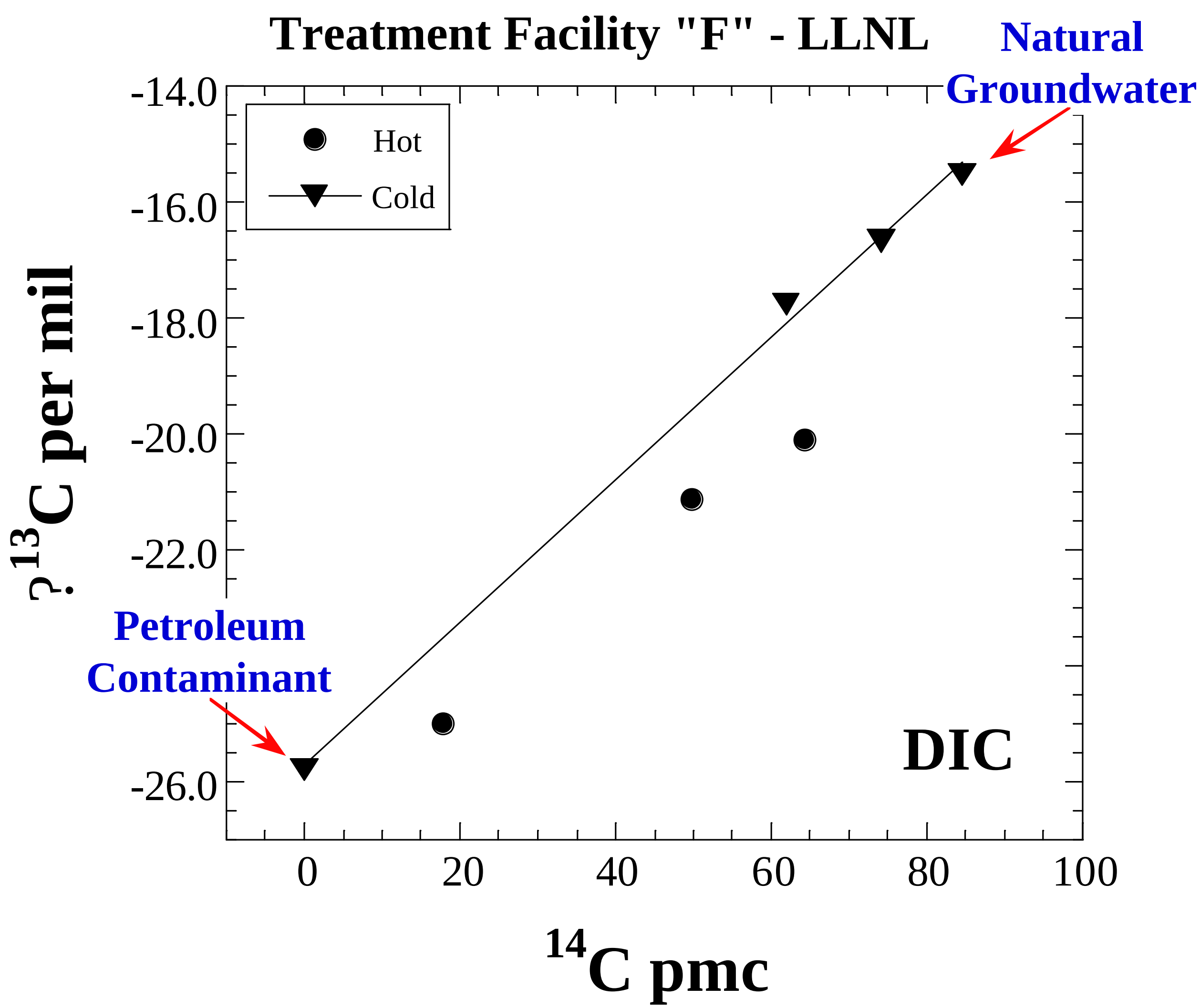
<u>n-alkanes</u>
n-pentane
n-hexane
n-heptane
n-octane

<u>isoalkanes</u>
2-methylbutane
2-methylpentane
3-methylpentane
2,2,4-trimethylpentane
2,3,3-trimethylpentane
2,3,4-trimethylpentane
2,2,5-trimethylhexane

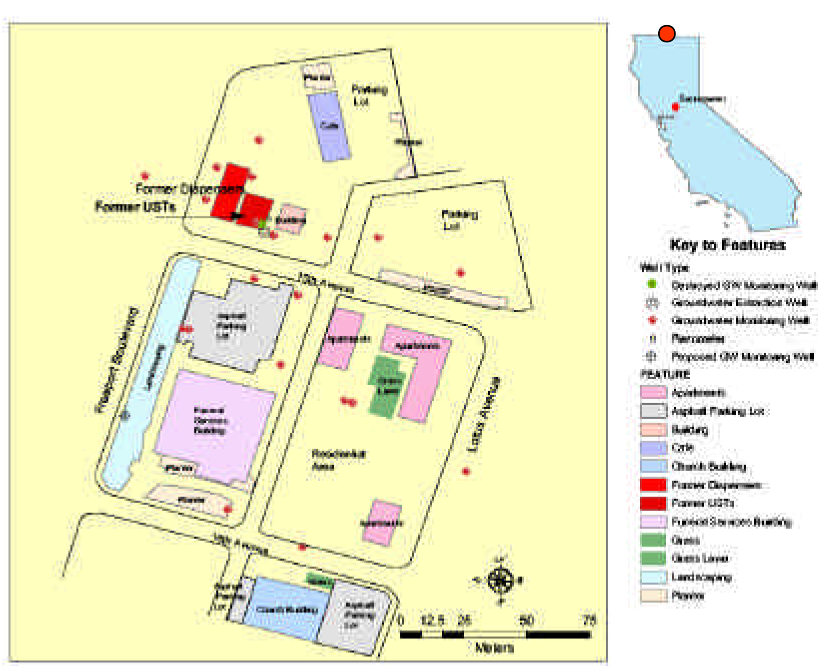
<u>cycloalkanes</u>
methylcyclopentane
cyclohexane
methylcyclohexane

Initial measurements were preformed by GC/FID using modified EPA 8015 and 8021 methods. Developing GC/MS method.

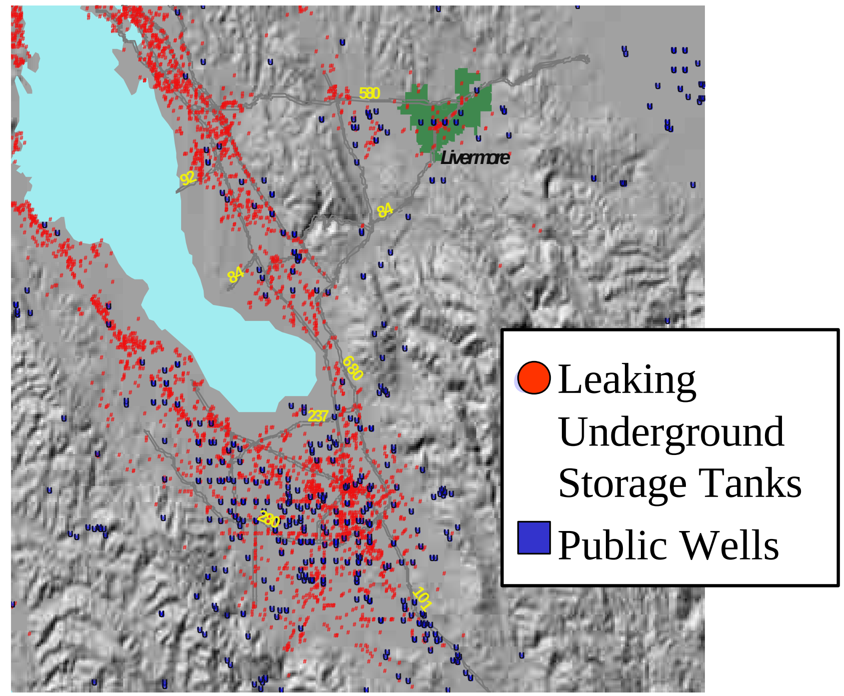
Isotope mass balance of biodegradation



Two UST sampling sites were selected



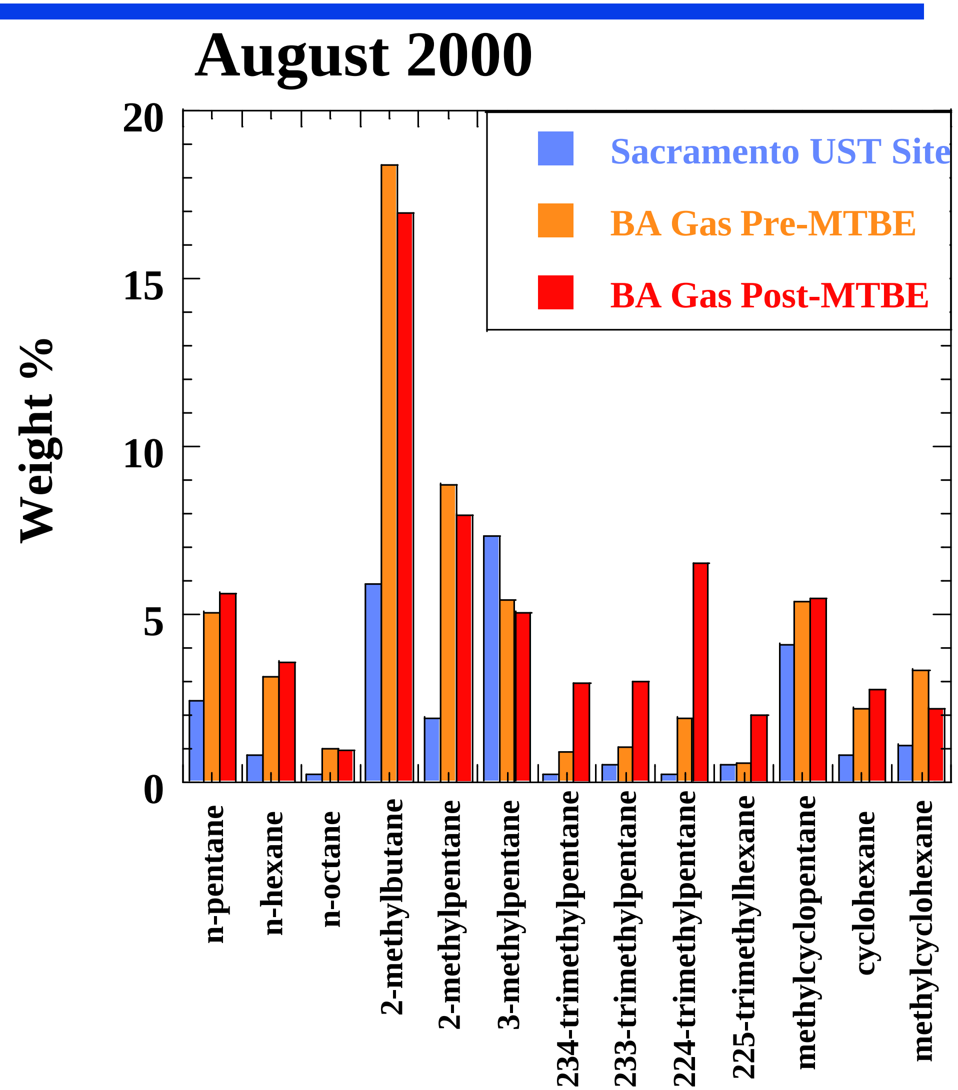
Sacramento
ETIC cooperation



San Jose
SCVWD cooperation

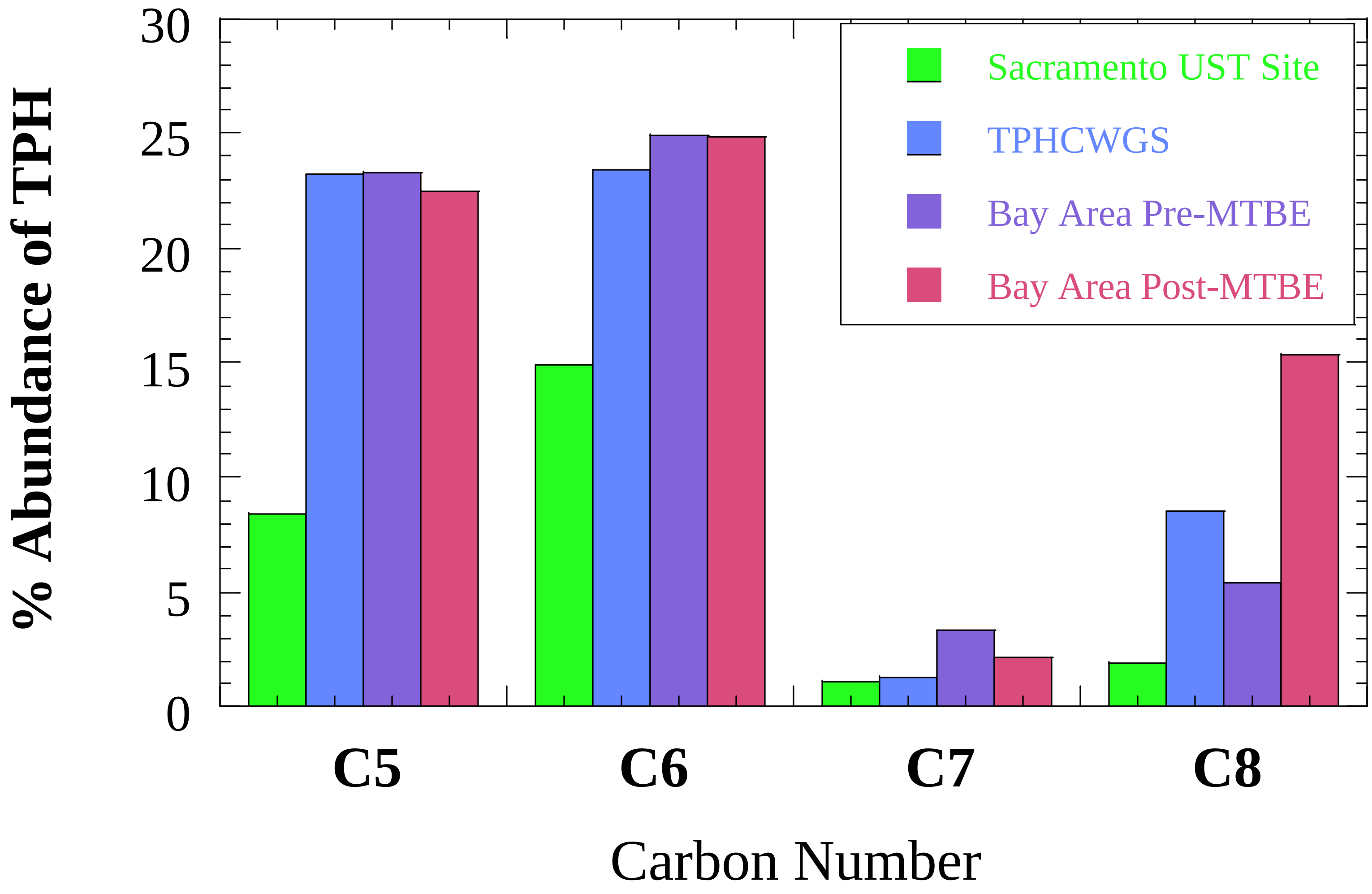
BTEX is 10X Greater than Branched Alkanes

	Avg. mg/L Sacramento
n-pentane	0.86
n-hexane	0.30
n-octane	0.10
2-methylbutane	2.18
2-methylpentane	0.73
3-methylpentane	2.73
234-trimethylpentane	0.12
233-trimethylpentane	0.22
224-trimethylpentane	0.10
225-trimethylhexane	0.23
methylcyclopentane	1.49
cyclohexane	0.33
methylcyclohexane	0.43
Benzene	27.0
Toluene	18.0
Ethyl-Benzene	3.9
Xylenes	23.0



Reportable detection limit is 0.1mg/L

TPH-g constituents roughly scale to parent gasoline



Summary statements

- Minor increases in alkylates probably will occur in subsurface spill sites.
- Persistence of isooctane and other branched alkanes in groundwater is poorly understood relative to BTEX.
- Even less understood for a gasohol spill
- Toxicological risk of these alkanes is 10X less than benzene.
- Any persistence of alkylates in groundwater would probably be more of a taste and odor issue.

KEY ENVIRONMENTAL CLEANUP CONSIDERATIONS FOR ETHANOL AND ALKYLATES

James M. Davidson

April 2001

Alpine Environmental, Inc.

Fort Collins, CO

Email: jdavidsonalpine@cs.com

Phone: 970-224-4608

OBJECTIVES

- REVIEW THE REMEDIATION AND TREATMENT OF ETHANOL
- REVIEW THE REMEDIATION AND TREATMENT OF ALKYLATES
- CONSIDER IMPACTS OF INCREASED USE OF ETHANOL AND ALKYLATES ON SUBSURFACE CLEANUPS

ETHANOL CHARACTERISTICS

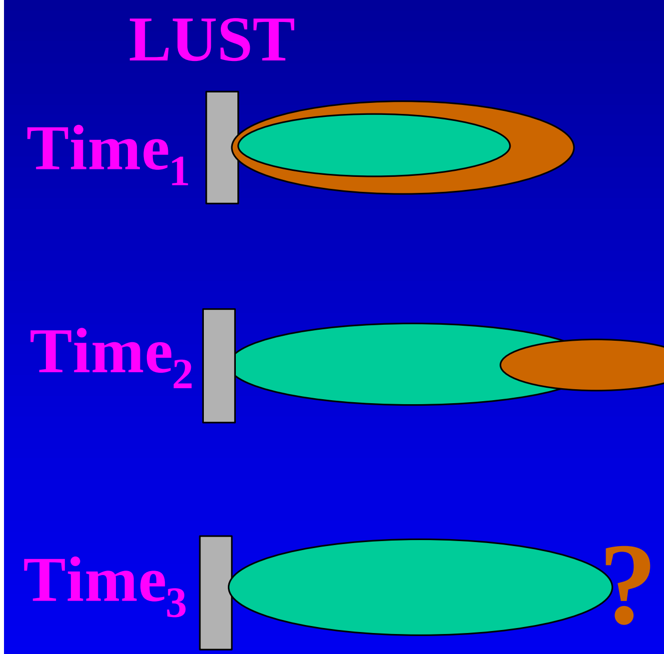
- INFINITELY SOLUBLE IN WATER (far more than benzene or MTBE)
- VERY LOW HENRY'S CONSTANT (far less volatile from water than benzene or MTBE)

✍ OVER TIME, ETHANOL WILL PRIMARILY OCCUR IN THE DISSOLVED PHASE, AND NOT IN THE NAPL OR VAPOR PHASES

ETHANOL CHARACTERISTICS

- ETHANOL ADSORPTION TO ORGANIC MATTER IS QUITE MINIMAL (far less than benzene, less than MTBE)
- HIGHLY BIODEGRADABLE, BOTH AEROBICALLY AND ANAEROBICALLY (more than benzene, much more than MTBE)
- ✍ETHANOL PREFERS DISSOLVED PHASE, BUT MAY BIODEGRADE QUICKLY IN SUBSURFACE

BTEX & ETHANOL PLUMES



BTEX & Ethanol plumes growing

BTEX plume now stable;
Ethanol readily degrading

Ethanol plume gone???

Based on modeling by Molson et al., 2000

ETHANOL BIODEGRADATION

- VARIOUS LABORATORY STUDIES SUGGEST AEROBIC HALF LIFE OF ETHANOL IN SOIL & GROUNDWATER OF 0.1 TO 5 DAYS => RAPID BIODEGRADATION (2-8 times faster than BTEX)
- BUT ARE LAB RATES REPRESENTATIVE OF FIELD CONDITIONS???
- FIELD VERIFICATION OF ETHANOL BIODEGRADATION RATES IS SEVERELY LACKING…

ETHANOL BIODEGRADATION IMPACTS ON BTEX PLUMES

- ETHANOL PREFFERRENTIALLY DEGRADED. RAPID AEROBIC BIODEGRADATION OF ETHANOL MAY UTILIZE MOST DISSOLVED OXYGEN (and/or nutrients)
- AEROBIC BTEX BIODEGRADATION SLOWED AND/OR DELAYED BY PRESENCE OF ETHANOL (various studies)
- BTEX PLUME LENGTHS MAY INCREASE BY:
  - 16-34% (Malcolm Pirnie, 1998)
  - 25% (Governor's Ethanol Coalition, 1999)
  - 20-100% (LLNL, 1999)
  - 20-100%, or more (Molson et al., 2000)

CO-SOLVENCY DUE TO ETHANOL'S PRESENCE

- LAB EXPERIMENTS SUGGEST THAT 10% ETHANOL (10,000 PPM in water) MAY INCREASE BTX LEVELS IN WATER 33%
- ETHANOL LEVELS OF 10,000 PPM ARE UNLIKELY TO EXIST FOR LONG AT ETHANOL-ENRICHED GASOLINE SPILL SITES
- ETHANOL LEVELS DO EXCEED 10,000 PPM AT NEAT ETHANOL SPILLS (data from 3 sites)
- THUS AT TERMINALS, STARTING BTEX LEVELS MAY BE ELEVATED, AND BTEX BIODEGRADATION RATES SLOWED - A NEGATIVE SYNERGISTIC EFFECT?

ENHANCED GASOLINE MOBILITY DUE TO ETHANOL'S PRESENCE

- NEAT ETHANOL IS USED AS SURFACTANT IN OIL E&P ACTIVITIES, TO INCREASE MOBILIZATION OF OIL FROM THE MATRIX
- ETHANOL LEVELS FROM SPILLS OF ETHANOL-ENRICHED GASOLINE LIKELY TOO LOW TO CREATE THIS EFFECT
- BUT, NEAT ETHANOL SPILLS AT BLENDING TERMINALS CAN CREATE THIS EFFECT ON PETROLEUM-IMPACTED SOILS

✍ THUS "IMMOBILIZED" RESIDUAL PRODUCT CAN BECOME MOBILIZED…

Maximum Measured Field Concentrations of Ethanol From Different Release Scenarios

Release Scenario	**Max. Measured Ethanol Conc. (mg/L)**
Spill of neat/denatured ethanol (97 - 100% EtOH)	81,000
Spill of ethanol-blended gas (24% EtOH – in Brazil)	2,503
Spill of ethanol-blended gas (10% EtOH)	0.65
Coated bentonite pellets	1,200

Field data are very limited; < 12 sites nationwide in USA

ETHANOL FATE & TRANSPORT SUMMARY

- ETHANOL ITSELF SHOULD READILY BIODEGRADE
- MAY DELAY BTEX BODEGRADATION AT GASOLINE SPILLS, THUS INCREASING BTEX PLUME LENGTHS
- AT NEAT ETHANOL SPILLS (terminals), CO-SOLVENCY MAY INCREASE BTEX LEVELS <u>AND</u> RESIDUAL GASOLINE NAPL MAY BECOME MOBILIZED
- VERY LITTLE FIELD DATA EXISTS

ETHANOL REMEDIATION

- CHARACTERISTICS THAT HURT:
  - High Solubility
  - Poor Adsorption To Carbon
  - Poor Volatility (low Henry's Constant)
- CHARACTERISTICS THAT HELP:
  - Very biodegradable

ETHANOL REMEDIATION

TECHNOLOGY	APPLICABILITY
GROUND-WATER EXTRACTION	As usual, good for plume control; fair for site remediation
SOIL VAPOR EXTRACTION	Ethanol’s low volatility makes extraction portion ineffective; added oxygen may be quite beneficial
AIR SPARGING	Ethanol’s low “stripability” makes aeration questionable, though added oxygen may be quite beneficial
ENHANCED BIODEGRADATION	Expected to be excellent; natural biodegradation rates may be so fast that enhancement rarely needed

ETHANOL REMEDIATION
MONITORED NATURAL ATTENUATION

- ETHANOL ITSELF EXPECTED TO NATURALY ATTENUATE QUITE WELL
- ETHANOL'S PRESENCE MAY NEGATIVELY IMPACT MNA OF OTHER GASOLINE COMPOUNDS AS:
  - BTEX PLUMES LONGER LIVED, AND GREATER LENGTH (16-100% longer? more?)
  - BTEX/TPH ELEVATED WHEN NEAT ETHANOL SPILLED (co-solvency)
  - FREE PRODUCT MORE MOBILE

TREATMENT OF ETHANOL-IMPACTED WATER

TECHNOLOGY	APPLICABILITY
AIR STRIPPING	Ethanol’s very high solubility and very low Henry’s Constant means air stripping quite ineffective
CARBON ADSORPTION	Ethanol’s poor adsorption to organic matter makes use of GAC likely to be quite poor
ADVANCED OXIDATION	Expected to be effective as ethanol readily oxidized; little data available
BIOTREATMENT	Expected to be excellent under a wide-variety of conditions

REMEDIATION IMPACTS OF USING MORE ETHANOL

- HARDLY ANY FIELD KNOWLEDGE EXISTS (or even ground-water concentration data!)
- UNSETTLING…NEED MORE FIELD INFORMATION!!!
- ETHANOL BIODEGRADES SO READILY THAT ETHANOL PLUMES THEMSELVES PROBABLY NOT A PROBLEM AT GASOLINE RELEASE SITES (needs verification)

REMEDIATION IMPACTS OF USING MORE ETHANOL

- ENLARGED BTEX PLUME COULD BE PROBLEMATIC AT SOME GAS SPILL SITES
- ENLARGED BTEX PLUME AND/OR REMOBILIZATION OF RESIDUAL NAPL LIKELY TO BE PROBLEM AT TERMINALS
- HIGH TASTE THRESHOLDS FOR ETHANOL COULD ALLOW FOR LONGER-TERM CONSUMPTION OF ETHANOL-IMPACTED DRINKING WATER (and possibly BTEX)

ALKYLATES CHARACTERISTICS

- BROAD SUITE OF $C_6 – C_9$ BRANCHED ALKANE COMPOUNDS
- COMPRISE ROUGHLY 14% OF GASOLINE (varies)
- HIGH OCTANE (92-94)

ALKYLATES CHARACTERISTICS

- LOW SOLUBILITY IN WATER (less than BTEX, far less than ethanol)
- ADSORB WELL TO SOIL ORGANIC MATTER (more retarded than BTEX, far more than ethanol)
- HIGH HENRY'S CONSTANT (more volatile from water than benzene, far more than ethanol)
- MODERATE BIODEGRADABILITY (less than BTEX, far less than ethanol)

ALKYLATES REMEDIATION

- USED IN GASOLINE FOR DECADES, THUS WE HAVE DONE LOTS OF ACTIVE REMEDIATION AND MNA PROJECTS ON ALKYLTAES (but, not much alkylate-specific data available)
- STANDARD GASOLINE REMEDIATION & TREATMENT METHODS HAVE WORKED ON ALYLATES IN THE PAST
- THEY SHOULD CONTINUE TO DO SO IN THE FUTURE

ALKYLATES REMEDIATION

- WITH HIGH RETARDATION & SLOW LEACHING, WILL INCREASED ALKYLATES USAGE MEAN EVEN MORE HYDROCARBON MASS TIED UP IN SOIL LONGER?
- DOES THIS MAKE RBCA OUTCOMES BETTER? WORSE?
- DOES THIS MAKE MNA BETTER? WORSE?

IN-SITU REMEDIATION

	BTEX	ALKYLATES	ETHANOL
MNA	Great	Good - great?	Great, but BTEX MNA worse?
PRODUCT RECOVERY	Good	Good?	Fair-good?
PUMP & TREAT	Good	Good?	Good?
AIR SPARGE	Good	Good – great?	Good?
SVE	Great	Good – great?	Good?
ENHANCED BIO.	Good	Good – great?	Great (if needed)

WATER TREATMENT

	BTEX	ALKYLATES	ETHANOL
AIR STRIPPING	Great	Good?	Poor?
GRANULATED ACTIVATED CARBON	Great	Good – great?	Poor?
BIOTREATMENT	Good	Good- great?	Great
ADVANCED OXIDATION PROCESS	Good	Good?	Good?

ETHANOL CONCLUSIONS

- FATE, TRANSPORT, REMEDIATION & TREATMENT KNOWLEDGE
  - THEORETICAL KNOWLEDGE = GOOD
  - FIELD BASED KNOWLEDGE = POOR TO NON-EXISTENT
- PHYSICAL & CHEMCIAL REMEDIATION & TREATMENT METHODS LIKELY BAD (air stripping, GAC)
- BIOLOGICAL REMEDIATION & TREATMENT METHODS LIKELY VERY GOOD (MNA, enhanced bioremediation, ex-situ biotreaters)
- BEWARE NEGATIVE IMPACTS ON BTEX PLUMES

Reference: Davidson, J.M., and Creek, D.N., 2000. "The Fate, Transport, and Remediation of the Gasoline Additive Ethanol". In Proceedings, *Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation*, National Ground Water Assoc., Westerville, OH, pp. 265-277.

ALKYLATES CONCLUSIONS

- FATE, TRANSPORT, REMEDIATION & TREATMENT KNOWLEDGE
  - THEORETICAL KNOWLEDGE = FAIR
  - FIELD BASED KNOWLEDGE = FAIR

  BUT NOT MUCH AYLKLATE-SPECIFIC INFO!
- PHYSICAL & CHEMICAL REMEDIATION & TREATMENT METHODS LIKELY GOOD
- BIOLOGICAL REMEDIATION & TREATMENT METHODS LIKELY GOOD (MNA, enhanced bioremediation, ex-situ biotreaters)
- LACK DIRECT DATA ON ALKYLATES (revise sampling & analyses approaches?)

UNCLEAR ISSUES

- WOULD CO-OCCURRENCE OF ETHANOL AND ALKYLATES HAVE SYNERGISTIC EFFECTS?
  - ETHANOL INCREASE SOLUBILITY & MOBILITY OF ALKYLATES?
  - WILL THEY LIMIT/DELAY ONE ANOTHER’S BIODEGRADATION?
  - LIMIT/DELAY BTEX BIODEGRADATION?
  - MANDATE ACTIVE REMEDIATION AND TREATMENT OF GASOLINE RELEASES MORE OFTEN THAN AT PRESENT?

Production, Distribution, Use, and Environmental Considerations of Alkylate 100SM

Glenn Giacobbe
Business Development Manager
Lyondell Chemical Company
Houston, Texas

LYONDELL

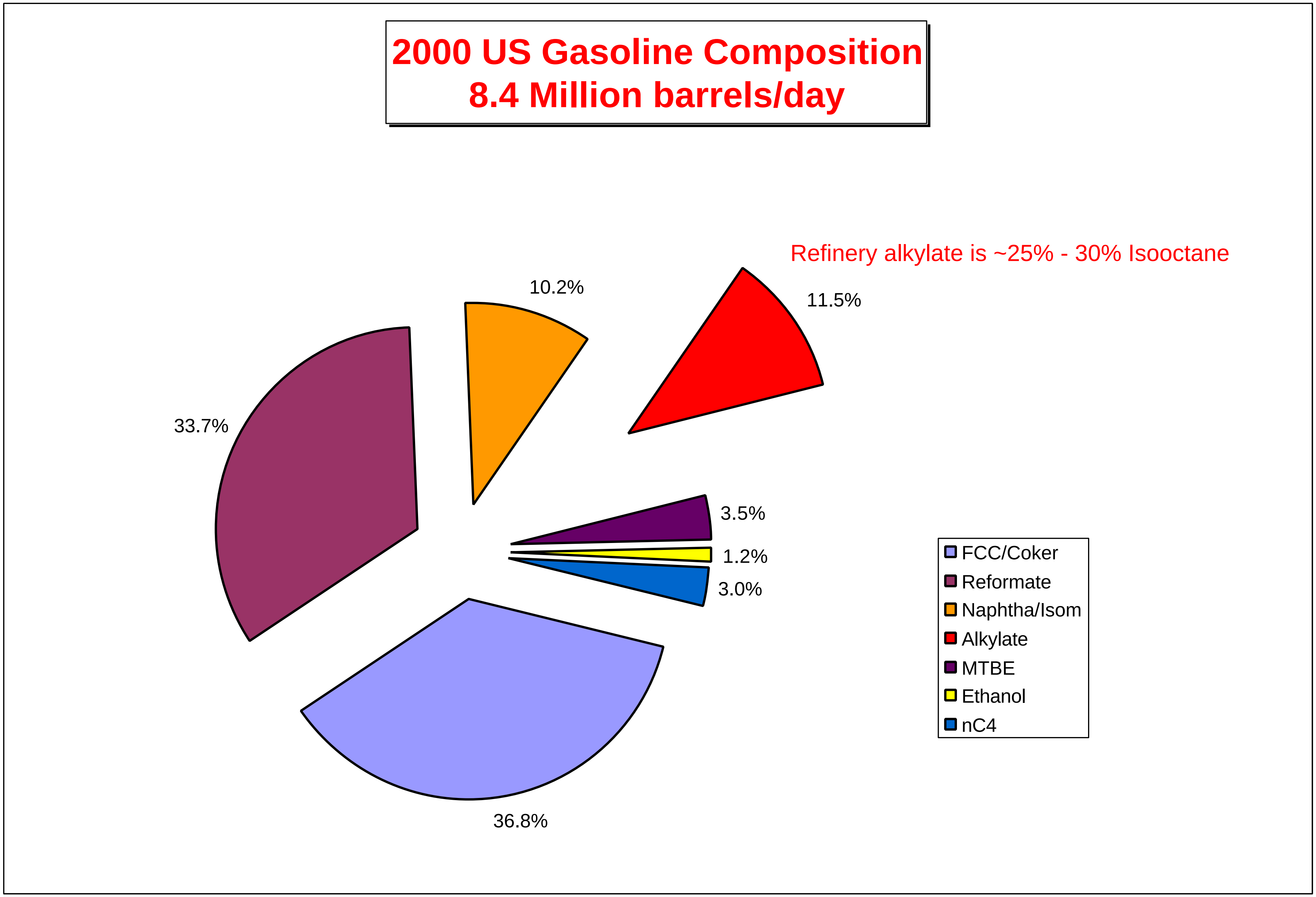
Presentation Overview

1) Alkylates have been in gasoline since 1938

2) Alkylate 100^{SM} (a.k.a isooctane) has many advantages to refinery grade alkylate

3) C8 alkylates are not conducive to California specifications

4) Alkylate 100^{SM} has favorable water properties


2000 US Gasoline Composition
8.4 Million barrels/day
Refinery alkylate is ~25% - 30% Isooctane
10.2%
11.5%
33.7%
3.5%
1.2%
3.0%
36.8%
FCC/Coker
Reformate
Naphtha/Isom
Alkylate
MTBE
Ethanol
nC4

LYONDELL

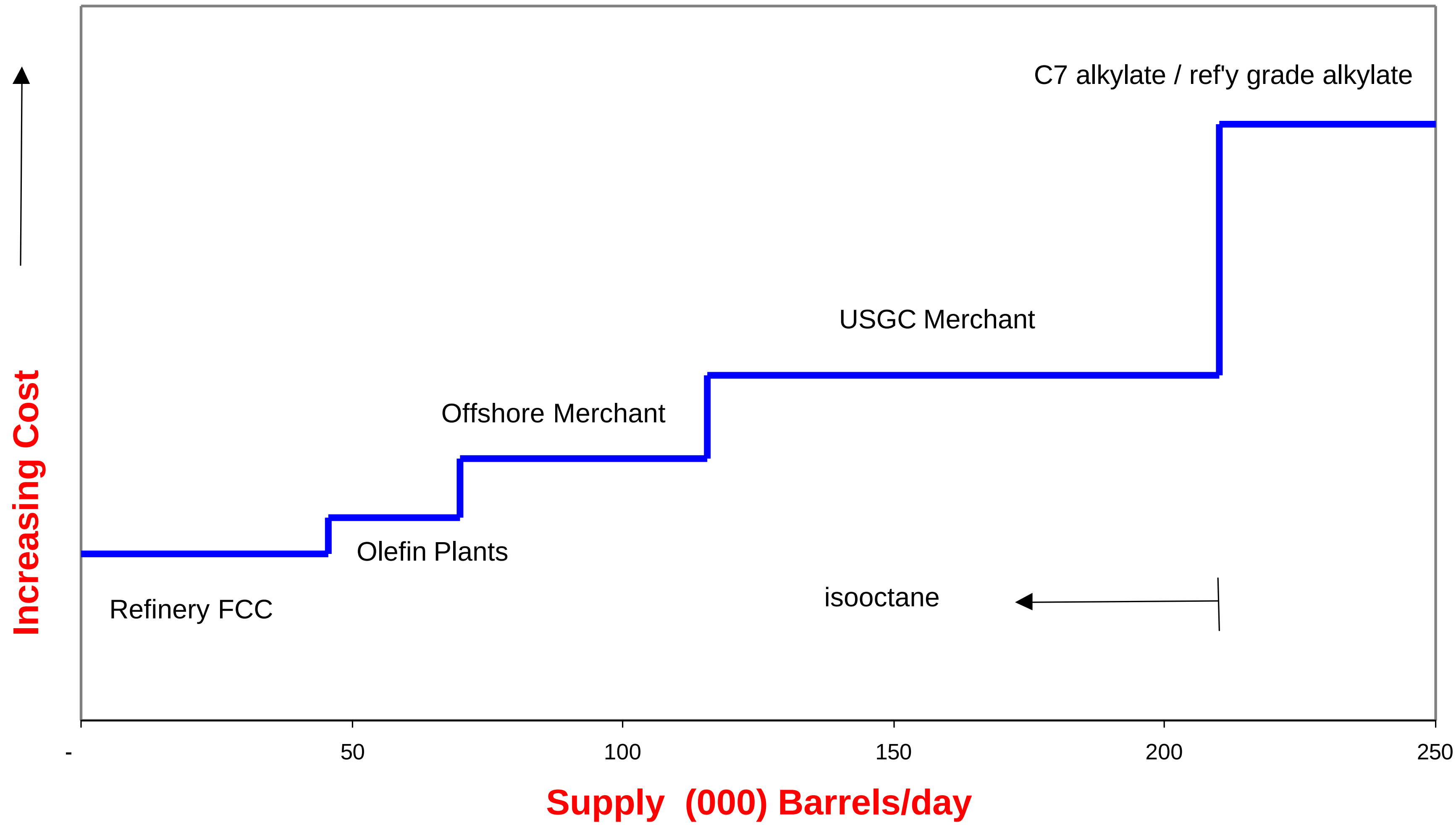
Alkylate 100^{SM} has many Advantages to refinery grade alkylate

- Higher Octane
  - 100 versus 92-94
- Lower volatility
  - 3 RVP versus 5-7
- Lower boiling point
  - 210 versus 230-240
- Merchant market potential
- Product flexibility (alkene or alkane)
- Different production processes

Alkylate 100SM is made differently than refinery grade alkylate

- Most MTBE facilities can be modified to produce Alkylate 100SM
- Low conversion costs (per MBD)
  - \$3 - \$6 million versus \$15 - \$30 million
- Production process requires no liquid acid step
  - Refinery processes subject to hydrofluoric and sulfuric acids

US Alkylate Supply Curve



LYONDELL

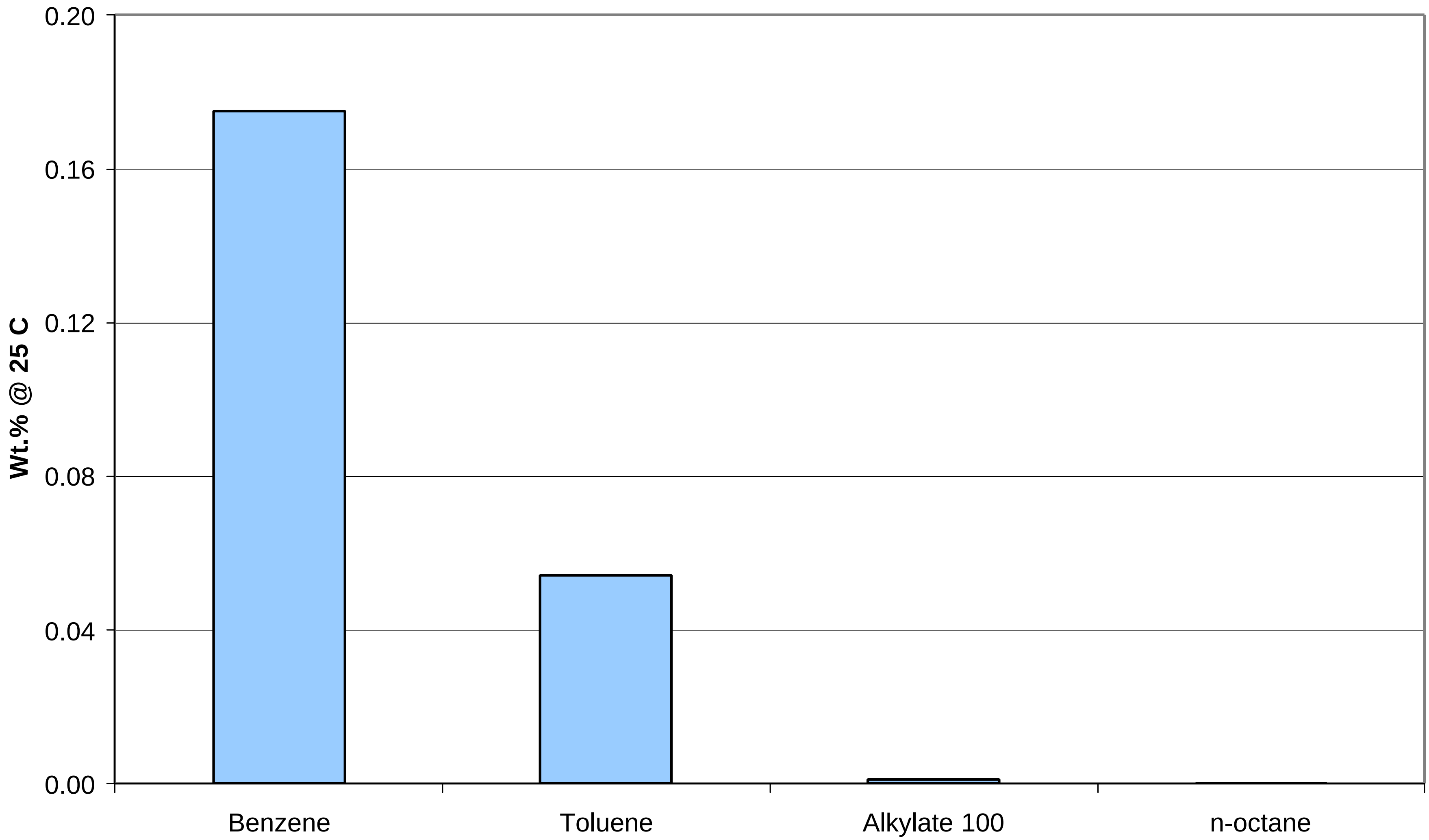
Alkylate 100SM is not conducive to CA RFG specifications

- T50 specification too tight @ 213 ^{o}F
  - 90% of all California gasoline falls in range of 182 to 210 ^{o}F
  - T50 will increase 10 ^{o}F with removal of MTBE
- Deminimus levels of oxygenates too restrictive and without basis
  - Prohibition calls for 0.05% max by 2004 for <u>all</u> oxygenates except ethanol
    - Would likely negate refinery based isooctane.
    - All ethers are not the same

Alkylate 100SM has favorable water properties

Physical Properties	*Alkylate 100 SM*	*Benzene*	*Ethanol*
Water Solubility (mg/l)	11	1,730	Infinity
Volatility RVP (psi)	3	5	18
Henry's Law constant	93	0.23	0.0002
Adsorption Coefficient (Log K_{oc})	2.5	1.7	0.7
Other			Net Energy Value <1

Water Solubility of Key Gasoline Components



Summary

1) Alkylates have been in gasoline since 1938

2) Alkylate 100^{SM} (a.k.a isooctane) has many advantages to refinery grade alkylate

3) C8 alkylates are not conducive to California specifications

4) Alkylate 100^{SM} has favorable water properties

Storage of Future California Automotive Fuels

Robert Wilkenfeld

Chevron Environmental Management Company

Product Risk Management

Product Stewardship:

Delivering safe and environmentally sound products to customers.

Product Integrity:

Delivering on-spec products all the time.

Product Stewardship Issues

Increasing Alkylate Use:

- No significant new concerns

Increasing Ethanol Use:

- Releases of neat ethanol during transportation & storage
  - Impacts to surface waters and existing subsurface releases of hydrocarbons
- Potential for increased corrosion
- Impacts to terminal wastewater systems (?)

Product Integrity Issues

Increasing Alkylate Use:

– No significant new concerns

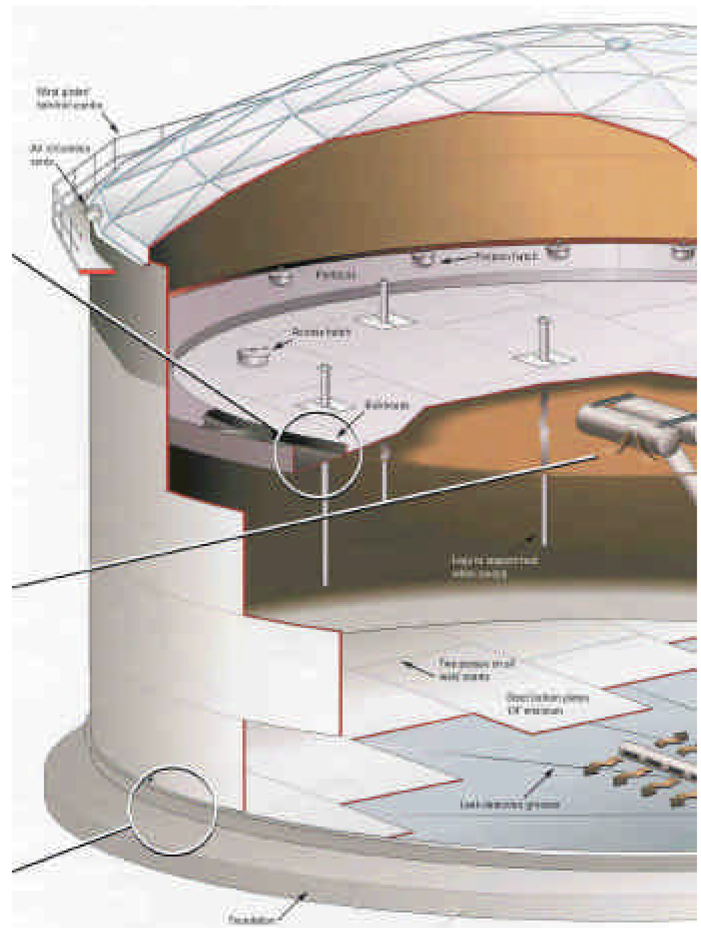
Increasing Ethanol Use:

– Water content, acidity and particulates
– Need for dedicated transportation and storage facilities
– Bacteria contamination

AST Release Prevention Measures

Chevron's Approach:

- Double bottoms & release prevention barriers
- Internal coatings, water monitoring & removal
- In-tank leak detection
- Automated overfill protection systems
- Tank inspection (API 653)
- Piping inspection (API 570)
- Behavior based safety program



UST Release Prevention Measures

Chevron's Nationwide Standards:

- Tank specification exceeds industry norm
- All components compatible with $\leq$15% ETOH
- Electronic tank, line & containment monitoring
  - Annual certification
- Positive pump shut-off
- Positive overfill prevention devices
- DW rigid fiberglass piping (vs. flexible hose)
- Dispenser containment
- Caulk drive slab joints
- Submersible pump containment at all CA facilities
- Behavior based safety program

UST Release Prevention Measures

Chevron's Evolving Standards:

- Liquid-filled interstitial space for improved leak detection (3Q01)
- Swivel fill connections (1Q01)
- Drainless spill buckets (1Q01)
- Vapor recovery and containment monitoring system (in development)

Panel 2 - Storage and Cleanup: Ethanol Fate and Transport

Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California

April 10 & 11, 2001

Tim Buscheck

Senior Staff Hydrogeologist

Chevron Research and Technology Company

Dissolution and Longevity of UST Source Zones - Conclusions & Implications

- In heterogeneous stratigraphic settings or fine textured soils, nonaqueous phase liquid (NAPL) source zones are subject to mass transfer limitations:
  - Source zones may be long lived, both for aromatics and MTBE
  - Source zones will be depleted of ethanol more rapidly than the aromatics and MTBE

Potential Vapor/Leachate Source: Key Points

- Ethanol vapor concentrations should be lower than MTBE vapor concentrations
- Ethanol will readily dissolve into soil moisture and be biodegraded
- Vapor/leachate sources should not result in persistent ethanol detections in groundwater as is observed with MTBE

Cost and Benefit Considerations for California's Automotive Fuel Needs

Diversify Vehicle Energy Sources

Emphasize Regional Flexibility of Fuel Rather than 100%

Air Quality Non-Attainment Areas can Use Oxygenated Fuel

Waiver on Oxygenate Requirement Elsewhere

Pursue Vehicle Technology Changes along with Fuel Blends

Economic Factors

Price of Supply and Demand will Reflect Timing and Scale of Use by Region

Environmental Health and Public Health Effects can be Measured on Regional Basis (Mortality and Morbidity Effects)

Vehicle Retirement and New Technology Promotion Costs and Reduced Pollution Benefits

Supply and Demand

Distinguish between Tax and Subsidy Portions of the Inputs to Produce, Transport, and Distribute Fuels

Consumer Price at Pump Could Include Environmental and Health Factors on Regional Basis (could be tied to federal and state taxes)

Valuation of Environmental Effects

Derive Mortality and Morbidity Impacts from Risk Assessment

Cost of Illness Approach for Morbidity

Survey Public for Morbidity and Mortality Values

The Net Energy Value Of Ethanol: Critical Issues.

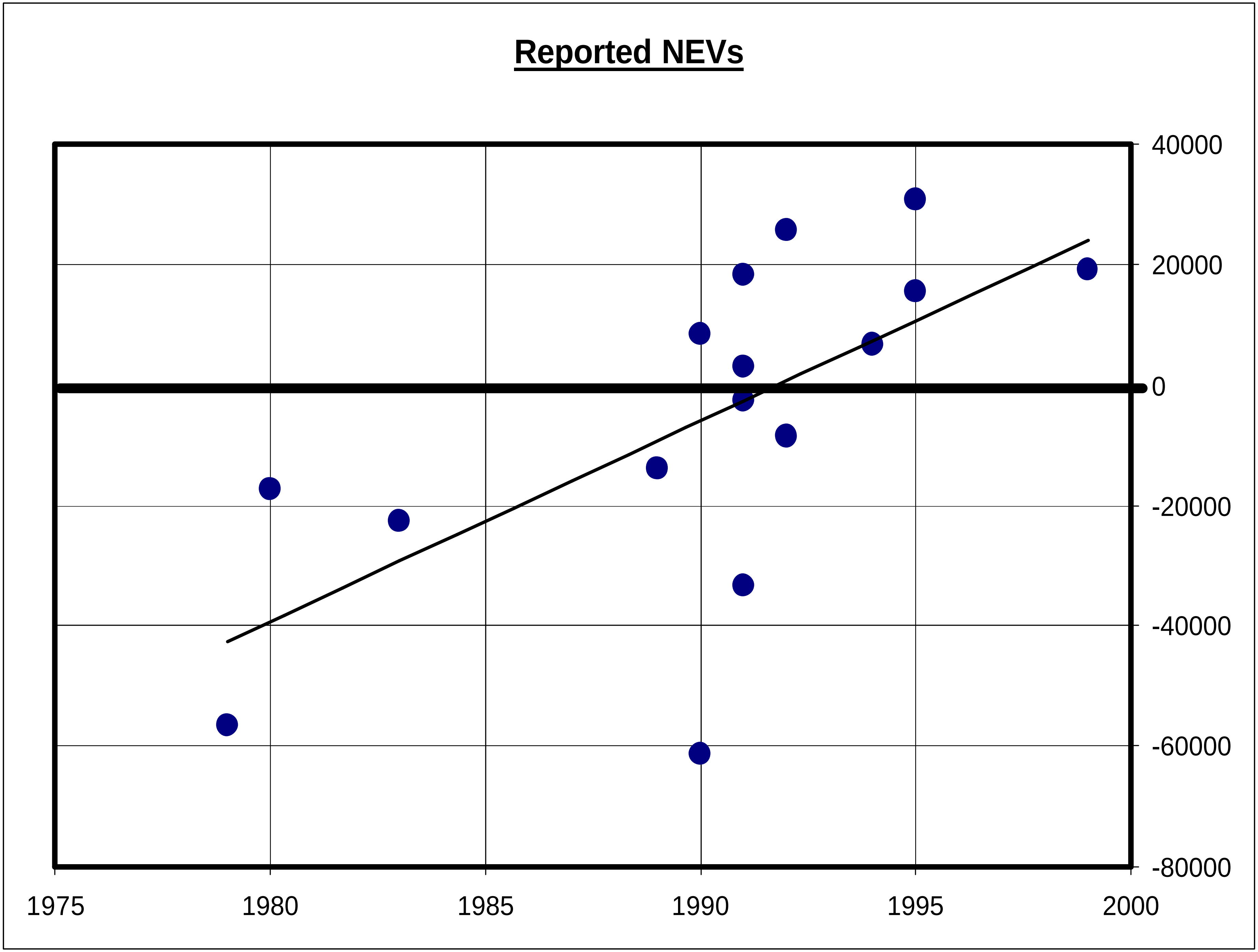
Amanda Lavigne

Dr. Susan E. Powers

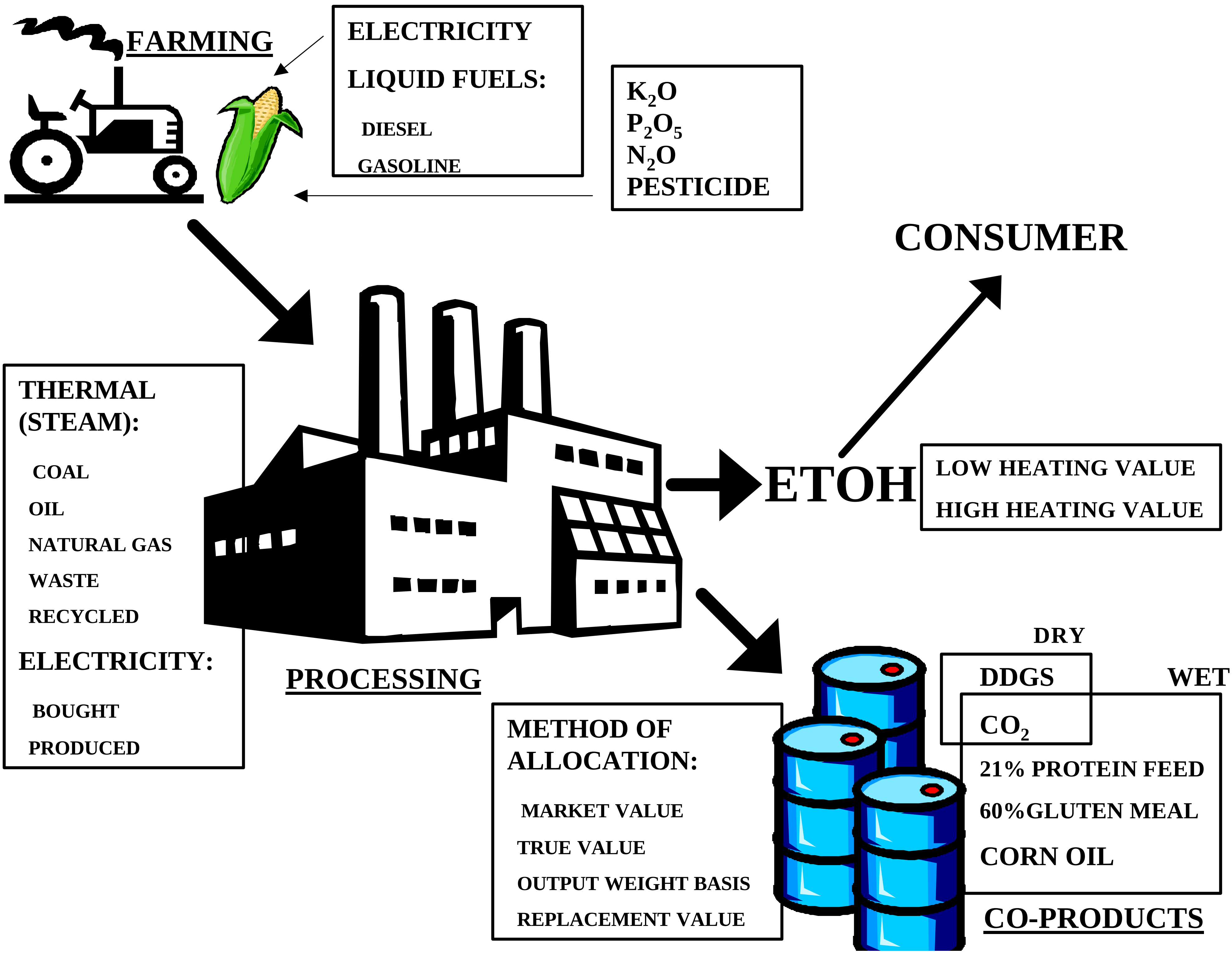
Clarkson University

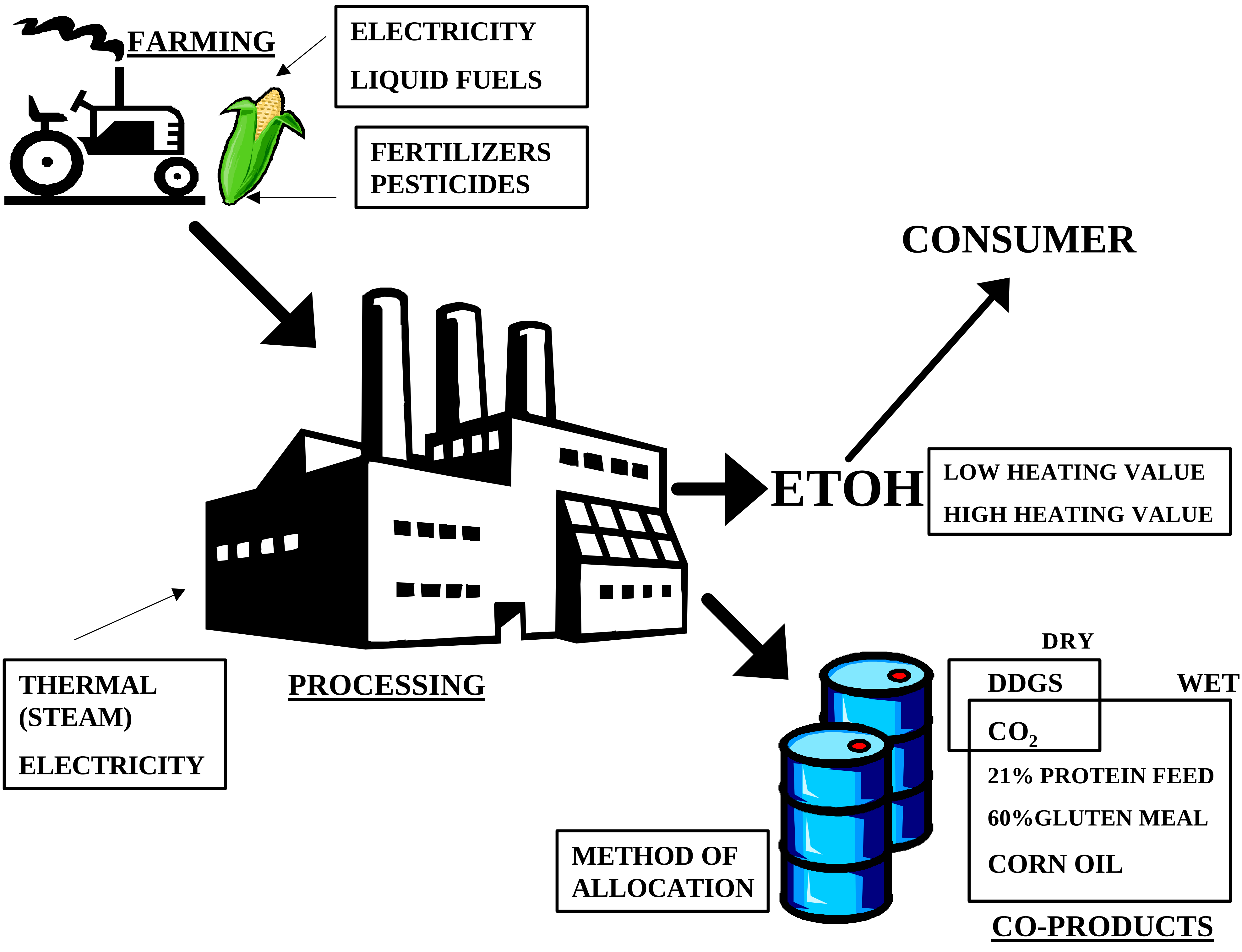
Critical Issues To Consider…

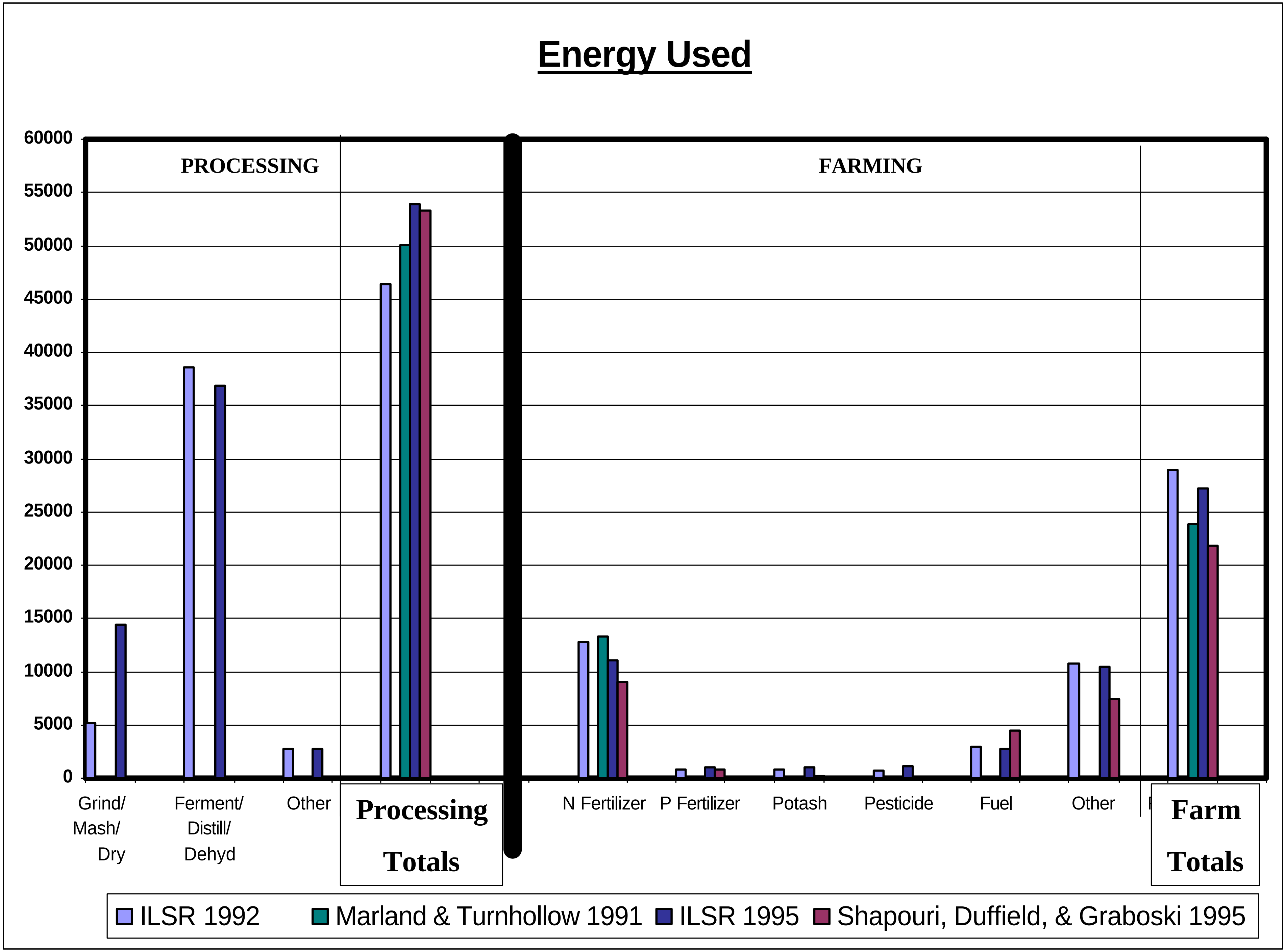
- Biases
- Data Origins
- Boundaries
- Heating Values (LHV vs. HHV)
- Co-Product Allocation Methods



Reported NEVs
40000
20000
0
-20000
-40000
-60000
-80000
1975
1980
1985
1990
1995
2000

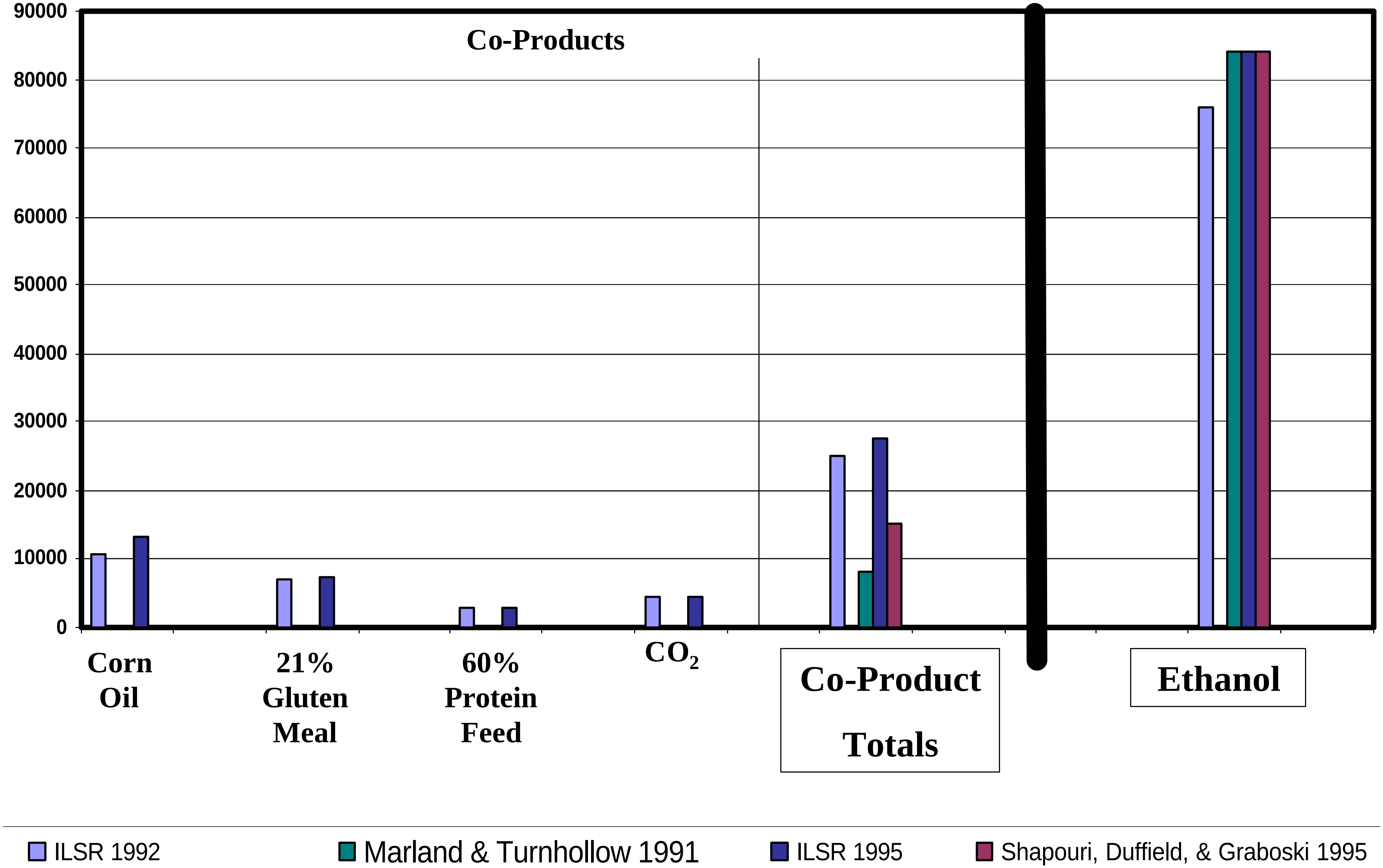

FARMING
ELECTRICITY
LIQUID FUELS:
DIESEL
GASOLINE
K_2O
P_2O_5
N_2O
PESTICIDE
CONSUMER
THERMAL (STEAM):
COAL
OIL
NATURAL GAS
WASTE
RECYCLED
ELECTRICITY:
BOUGHT
PRODUCED
PROCESSING
ETOH
LOW HEATING VALUE
HIGH HEATING VALUE
DRY
DDGS
WET
CO_2
21% PROTEIN FEED
60%GLUTEN MEAL
CORN OIL
METHOD OF ALLOCATION:
MARKET VALUE
TRUE VALUE
OUTPUT WEIGHT BASIS
REPLACEMENT VALUE
CO-PRODUCTS

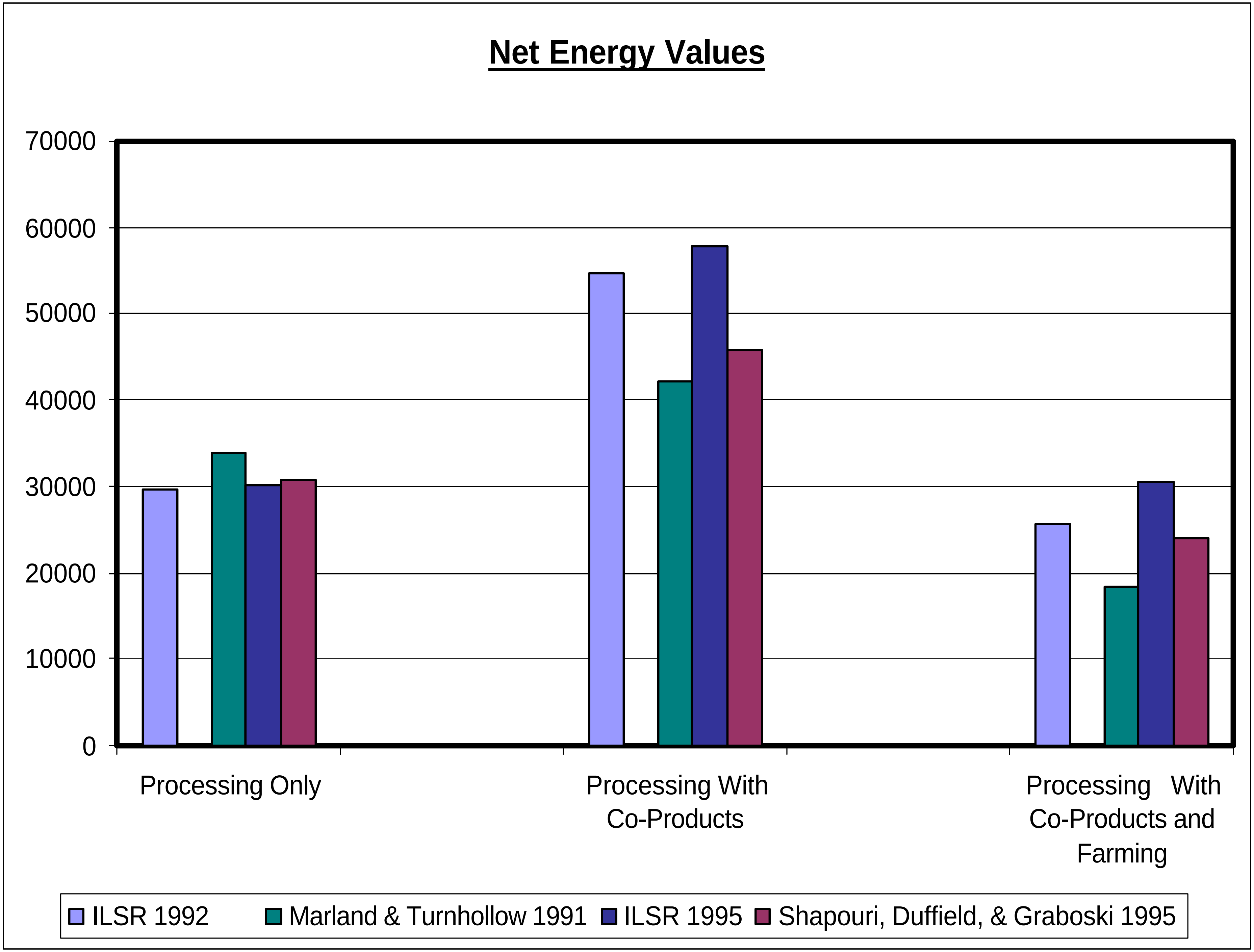

FARMING
ELECTRICITY
LIQUID FUELS
FERTILIZERS
PESTICIDES
CONSUMER
ETOH
LOW HEATING VALUE
HIGH HEATING VALUE
PROCESSING
THERMAL
(STEAM)
ELECTRICITY
DRY
DDGS
WET
CO_2
21% PROTEIN FEED
60%GLUTEN MEAL
CORN OIL
METHOD OF
ALLOCATION
CO-PRODUCTS



Energy Used
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
PROCESSING
FARMING
Grind/ Mash/ Dry
Ferment/ Distill/ Dehyd
Other
Processing Totals
N Fertilizer
P Fertilizer
Potash
Pesticide
Fuel
Other
Farm Totals
ILSR 1992
Marland & Turnhollow 1991
ILSR 1995
Shapouri, Duffield, & Graboski 1995

Energy Gained




Net Energy Values
70000
60000
50000
40000
30000
20000
10000
0
Processing Only
Processing With Co-Products
Processing With Co-Products and Farming
ILSR 1992
Marland & Turnhollow 1991
ILSR 1995
Shapouri, Duffield, & Graboski 1995

Focal Points For Additional Research:

- Improve technology for fermentation and distillation processes.

- Reduce need for nitrogen-based fertilizers.

- Explore impacts of bioengineered corn on farming methods/inputs and yields.

- Clarify co-product credit allocation methods and feasibility of markets.

Energy Issues Beyond The Balance (Additional Credit?)

- Accessible vs. Inaccessible
- Domestic vs. Foreign
- Renewable(?) vs. Non-Renewable
- Alternative Feedstocks

References

Congress of The United States, Office of Technical Assessment, *Gasohol – A Technical Memorandum*, September, 1979.

Ho, S.P., *Global Warming Impact of Ethanol Versus Gasoline*, Washington, DC, October, 1989.

International Energy Agency and the Organization for Economic Co-operation and Development, <u>Biofuels</u>, France, 1994.

Keeney, D.R., and T.H.DeLuca, *Biomass as an Energy Source for the Midwestern U.S.*, American Journal of Alternative Agriculture, Vol. 7 (1992), pp.137-143.

Lorenze, David, David Morris, *How Much Energy Does it Take to Make a Gallon of Ethanol*?, Institute for Local Self-Reliance, August, 1995.

Marland, G., and A.F. Turnhollow, *CO2 Emissions From the Production and Combustion of Fuel Ethanol From Corn*, U.S. Department of Energy, February, 1991.

Morris, David, Irshad Ahmed, *How Much Energy Does it Take to Make a Gallon of Ethanol*?, Institute for Local Self-Reliance, December, 1992.

Pimental, David, *Ethanol Fuels: Energy Security, Economics, and the Environment*, Journal of Agricultural and Environmental Ethics, Vol. 4 (1991), pp.1-13.

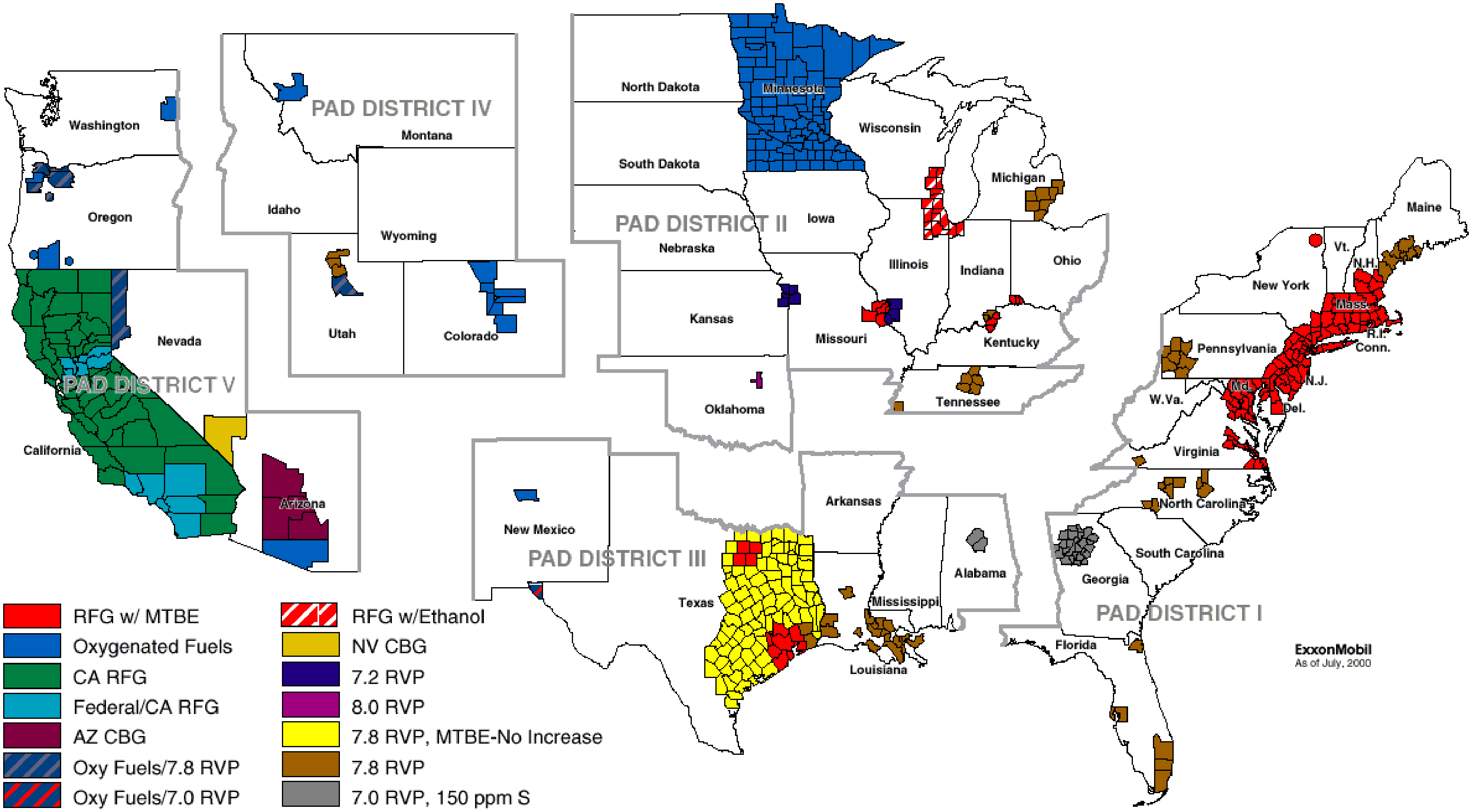
Shapouri, Hosein, James A. Duffield, Michael S. Graboski, *Estimating the Net Energy Balance of Corn Ethanol*, U.S. Department of Agriculture, Economic Research Service, Office of Energy, Agricultural Economic Report No. 721, July, 1995.

U.S. National Alcohol Fuels Commission, *Ethanol: Farm and Fuel Issues*, August, 1980.

U.S. National Alcohol Fuels Commission, *Energy Balances in the Production and End-Use of Alcohols Derived From Biomass, A Fuels-Specific Comparative Analysis of Alternate Ethanol Production Cycles*, U.S. Department of Energy, October, 1980..

Wayman, Morris, Sarad R. Parekh, Biotechnology Of Biomass Conversion, Fuel and Chemicals From Renewable Resources, Prentice Hall, New Jersey, 1990.

U.S. Fuel Requirements



This map is not intended to be used as guidance for oxy fuels or RFG compliance, nor is it legal advice.