TBA/MTBE/Ethanol Remediation Seminar

NATIONAL GROUND WATER ASSOCIATION

Petroleum Hydrocarbons and Organic Chemicals in Ground Water

Houston, Texas

November 2006

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TBA/MTBE/Ethanol Remediation Seminar Outline

Introduction

Properties of Gasoline Components

- Physical properties - solubility, vapor pressure, Henry's Law constant, adsorption
- Fate and transport

Site assessment and Analytical Issues

Applying Remedial Technologies

- Technology sequencing
- Importance and approach for rapid initial response to source zones
  - Receptor protection
  - Excavation
  - Hydraulic containment
  - Free product removal
  - Thermal mobilization

- Remediating residual and dissolved phase contamination
  - Soil vapor extraction (SVE)
  - Bioventing
  - Air sparging
  - Pump and treat (P&T, air stripping, carbon adsorption, oxidation)
  - In situ chemical oxidation (ISCO)
  - In situ bioremediation (ISB)
  - Ex situ bioremediation (ESB)
  - Phytoremediation
  - Monitored natural attenuation (MNA)

Case Studies - summarize site locations, initial concentrations, receptors, final concentrations, remediation technologies used, treatment times, lessons learned

- Long Beach, California, gas station – excavation, land farm, chemical oxidation, SVE
- Channelview, Texas, plant – source control, ISB
- Liberty County, Texas, petrochemical disposal site – thermal desorption, ISB, MNA
- Pacific Northwest Terminal – ethanol plume
- Philomath, Oregon, gas station – excavation, DPE, SVE, P&T, ISB
- North Texas, gas station – ISCO (Fenton's reagent)
- California, gas station – excavation, ISCO (ozone)
- Clifton, Colorado, fuel station – excavation, SVE, P&T
- Port Hueneme, California, gas station – source control, bioaugmentation with air/oxygen sparging in permeable reactive barrier
- Bedford, New Hampshire, gas station – ex situ bio
- Bayport, Texas, plant release – MNA of TBA using carbon isotope analysis
- Houston, Texas, gas station next to dry cleaner – excavation, chemical oxidation, SVE, P&T, ISB, MNA
- Omaha, Nebraska, gas station – excavation, SVE, P&T (ESB, GAC)

Summary and Conclusions

TBA/MTBE/Ethanol Remediation Seminar Abstract

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This seminar reviews physical, chemical, and biodegradation characteristics of the fuel oxygenates tert butyl alcohol (TBA), methyl tert butyl ether (MTBE), and ethanol. Consideration of these characteristics leading to the optimization of remedial technologies employed at affected groundwater sites is evaluated and illustrated through a number of case studies. Optimal remedial strategies take advantage of the characteristics of TBA, MTBE, ethanol, and gasoline hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes that may be present. Remedial strategies often consist of a sequence of actions starting with receptor protection and source control, followed by remediation of residual and dissolved contamination, and ending with natural attenuation.

TBA is often found in association with MTBE. Three potential sources of TBA are: 1) as a fuel oxygenate in its own right (although currently not in wide use); 2) as co-product present at low percent levels in commercial MTBE; and 3) as an intermediate product of MTBE biodegradation and chemical oxidation. In addition, it can be an artifact created during certain water sample preservation and analytical procedures.

TBA and MTBE differ from gasoline hydrocarbons in several physical characteristics, being relatively more soluble and less adsorptive. MTBE also has a higher vapor pressure, and TBA has a lower Henry's Law constant, than gasoline hydrocarbons. These physical attributes influence the selection and optimization of remedial options for residual and dissolved constituents.

Like TBA and MTBE, ethanol is more soluble and less adsorptive than gasoline hydrocarbons. In addition, it is more rapidly biodegraded than TBA, MTBE, and gasoline hydrocarbons, under both aerobic and anaerobic conditions. Preferential ethanol biodegradation can deplete electron acceptors in the subsurface, resulting in longer plumes of other gasoline constituents than would be the case if ethanol were not present.

Biodegradation of TBA and MTBE by naturally occurring bacteria has been demonstrated at many sites. Several pure cultures of microorganisms have been demonstrated to degrade these constituents aerobically to carbon dioxide and water. There is also evidence of TBA and MTBE mineralization by mixed cultures in aerobic/anaerobic environments. In the field, increasing the dissolved oxygen concentration increases aerobic biodegradation rates in a strong dose-response relationship. Biodegradation has also been demonstrated with other electron acceptors including nitrate, iron, sulfate and carbon dioxide. Biodegradation is an important mechanism for natural attenuation of TBA, MTBE, and ethanol.

The seminar will explore the selection and execution of current and emerging technologies for the remediation of gasoline components, including residual and dissolved TBA, MTBE, and ethanol. Commonly used technologies include: soil vapor extraction; bioventing; air sparging; in situ ground water bioremediation; ex situ groundwater bioremediation; pump and treat; in situ chemical oxidation; and monitored natural attenuation.

TBA and ethanol have moderate vapor pressures typical of other gasoline constituents, while MTBE has a higher vapor pressure. Consequently, soil vapor extraction is very effective for removing these chemicals from the unsaturated zone (soil conditions permitting), where catalytic oxidation or thermal oxidation can be used to treat

higher concentrations of these constituents aboveground (along with other gasoline constituents). Granular activated carbon (GAC) can be used for aboveground treatment of lower concentrations of MTBE. GAC is not typically the optimal technology for treating TBA or ethanol because of their low tendency to adsorb. Biofilters can be used to treat MTBE, TBA, and ethanol.

Air sparging is less effective at removing TBA, MTBE, and ethanol dissolved in water than it is for higher Henry's Law constant constituents, like benzene. However, when higher air to water ratios are used, sparging can be effective. TBA and ethanol are treated by biodegradation enhanced by the oxygenation that occurs as a result of air sparging, whereas MTBE is treated by both biodegradation and stripping processes.

High water solubility and low tendency to adsorb make these three constituents very amenable to groundwater extraction. Recovered groundwater can be treated aboveground by ex situ bioremediation or advanced oxidation processes. Additional options in the case of MTBE include carbon or resin adsorption, or air stripping followed by carbon adsorption or catalytic oxidation of the vapor phase. Air stripping of MTBE requires higher air to water ratios than for gasoline hydrocarbons.

A number of case studies will be presented that illustrate the effect of physical and biodegradation characteristics on remediation technology selection. Every site is different, with its own set of characteristics and challenges. Regardless of the composition of gasoline, rapid source control is critical to minimize environmental impact and to reduce overall remediation cost Optimal strategies take advantage of site characteristics as well as the specific characteristics of TBA, MTBE, and ethanol for cost-effective, timely, and environmentally sound remediation of these chemicals.

Biographies of Presenters

Ellen Moyer, Ph.D., P.E, Principal of Greenvironment, LLC, is a recognized expert in the assessment and remediation of fuel oxygenates contamination. She has an M.S. in Environmental Engineering and a Ph.D. in Civil Engineering. She has presented numerous seminars on assessment and remediation of fuel oxygenates and other VOCs and was the lead editor of an MTBE Remediation Handbook, now in its second printing. Dr. Moyer has managed all phases of assessment and remediation work, and her numerous projects have employed a wide range of in situ and ex situ remediation technologies at diverse sites with organic and inorganic contaminants.

Richard Sloan is President of Chickadee Remediation Co., whose primary business is to remediate contaminated soil and groundwater to the extent necessary to protect public health and the environment and acquire the long-term site environmental liability. Sloan has developed and implemented timely, cost-effective and environmentally-sound remediation plans for numerous Superfund, RCRA, and other sites with affected soils and groundwater. He has successfully established community/agency/company/contractor partnerships to focus the project efforts on common goals and apply a broad-based technical approach for each site. Sloan is also President of Chickadee Mining Co., which uses environmentally-sensitive procedures and equipment for precious metals mining.

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Objectives of the Workshop

Participants will understand:

- Process for addressing releases
- Fate and transport characteristics
- Current and emerging remedial technologies
- Selection and sequencing of remediation technologies
- The overall manageability of gasoline release impacts

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Outline of Workshop

- *Introduction*
- Physical properties, fate and transport
- Site assessment and analytical issues
- Applying remedial technologies
- Case studies of remediation
- Conclusion and summary

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Beyond the Scope

- Health effects and toxicology
- Benefits of oxygenates to air quality
- Gasoline formulation and performance
- Specific regulatory requirements
- Leak detection systems

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Gasoline Release Management Program

1. Status of potential pathways
2. Receptor protection
3. Source identification and control
4. Nature and extent of soil, groundwater, and vapor impacts
5. Physical characteristics of the subsurface
6. Properties of the chemicals present in the soils and groundwater
7. Develop/implement the appropriate technology sequence

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Gasoline Release Management Program

Design, Construction, and Operation

- Health, safety, and quality take priority
- Use standard sized pumps, meters, valves, controls, instruments, etc.
- Allow for "easy" changes and modifications in response to progress results
- Field fit most of mechanical and electrical
- Realistic cost and schedule
- Commit the necessary resources

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Bucks Co./Montgomery Co.

- Reviewed eight service stations in detail
- All had leaking underground storage tanks
- Operating issues: accurate inventory control, consistently negative inventory
- Shallow bedrock (varying depths)
- Groundwater in unconsolidated sediments is the critical zone
- MTBE and BTEX tended to co-exist in the impacted groundwater
- Numerous active water supply wells accelerated MTBE and BTEX migration

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Telford

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Pool’s Corner

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Bucks Co./ Montgomery Co.

- Slow response to evidence of gasoline spills or leaks
- Inadequate response action for 10 years or more allowed plumes to grow
- Private wells were impacted
- Groundwater is best protected by early detection and rapid response
- Groundwater monitoring next to UST systems may have detected plumes while still small and easy to remediate

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Bucks Co./ Montgomery Co.

- Receptors have been protected by point of entry treatment (POET) systems and bottled water
- Focused source control has been effective
- SVE and pump and treat have been effective
- MTBE and BTEX concentrations decreased

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tertiary-Butyl Alcohol ($C_4H_{10}O$)

- Fuel oxygenate
- Co-product (1-2%) in commercial MTBE
- Food-grade freeze drying additive
- Used as solvent for NAPL flushing
- Biodegradation product of MTBE
- Artifact of sample preservative and/or analysis
  - ❖Acid hydrolysis during preservation and analysis

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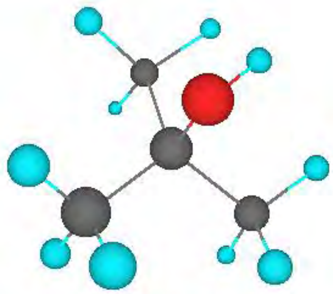
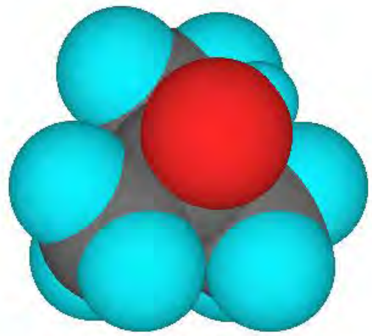
t-butanol molecule



(ball and stick)



(space - filling)

tert-butanol is a tertiary alcohol

Steric hindrance of molecule

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TBA Issues

- Fate and transport
- Effectiveness of traditional remediation technologies
- Biodegradability
- Production on GAC
- Ex-situ water treatment
  - Biological
  - Chemical oxidation

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Material Safety Data Sheet - TBA

- (Tertiary Butyl Alcohol)
- (Tert-Butanol)
- (2-methyl, 2-propanol)
  - Extremely volatile, flammable liquid
  - Camphor-like odor at >73 ppm in air
  - Alcohol-like taste at >5 ppm in water
  - Eye and skin irritation
  - Does not bioaccumulate
  - Avoid prolonged inhalation exposure
  - Avoid dermal contact and direct ingestion
  - Rat toxicology: LC_{50}>14,100 ppm, LD_{50}>2,700 mg/kg
  - Aquatic toxicity: LC_{50} and EC_{50} >5,500 ppm
  - Not a known human carcinogen or reproductive toxin

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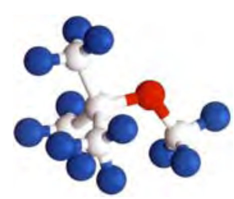
Methyl tertiary Butyl Ether ($C_5H_{12}O$)



1979	In gasoline at 2 - 4% to replace lead
1981	U.S. EPA allowed up to 7% MTBE
1990	Clean Air Act requires oxygenates
1992	Wintertime gasoline with 15% MTBE
1995	Year-round use of gasoline with 11% MTBE
2000	Groundwater concerns prompt decreased use in gasoline

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Material Safety Data Sheet - MTBE

- (Methyl Tertiary Butyl Ether)
- (Butyl Methyl Ether)
  - Extremely volatile, flammable liquid
  - Turpentine-like odor at >0.05 ppm in air
  - Turpentine-like taste at >0.05 ppm in water
  - Eye and skin irritation
  - Does not bioaccumulate
  - Avoid prolonged inhalation exposure
  - Avoid dermal contact and direct ingestion
  - Rat toxicology: LC_{50}>23,000 ppm, LD_{50}>4,000 mg/kg
  - Aquatic toxicity: LC_{50}>1,000 ppm
  - Not a known human carcinogen or reproductive toxin

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Ethanol (C_2H_6O)

- Fuel oxygenate
- Made from fermenting grains and other organic materials, or from natural gas
- Component of alcoholic beverages
- Extremely flammable and volatile
- Used as solvent for NAPL flushing
- Does not bioaccumulate

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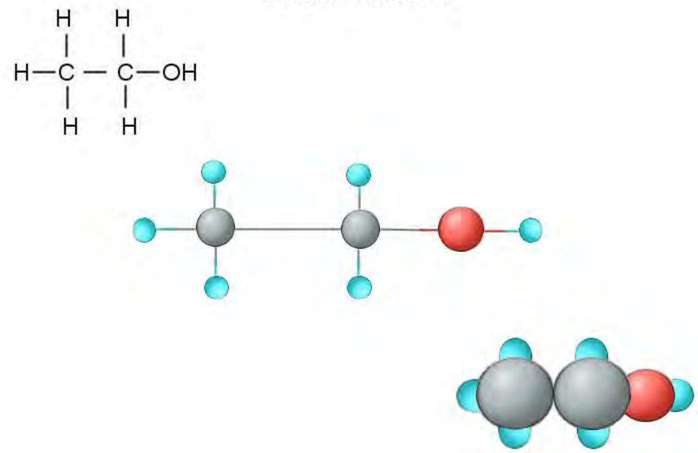
Ethanol molecule



little steric hindrance

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Material Safety Data Sheet - Ethanol

- (Ethyl Alcohol)
- (Ethyl Hydroxide)
- (Methyl Methanol)
  - ❖ Extremely volatile, flammable liquid
  - ❖ Alcohol-like odor at >90 ppm in air
  - ❖ Alcohol-like taste at >30 ppm in water
  - ❖ Eye irritation at elevated concentration
  - ❖ Not normally a skin irritant
  - ❖ Does not bioaccumulate
  - ❖ Avoid prolonged inhalation exposure
  - ❖ Rat toxicology: LC_{50}>100,000 ppm, LD_{50}>30,000 mg/kg
  - ❖ Aquatic toxicity: LC_{50}>50,000 ppm
  - ❖ Excessive, direct ingestion can cause cancer and birth defects

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History of USTs in the U.S.

1950s/60s Increasing UST installations

1988 2 million USTs at 700,000 facilities – U.S. EPA requires removal or upgrade in 10 years

1997 1.2 million USTs at 415,000 facilities

- 195,000 gas stations; 220,000 marinas, airports, hospitals, municipalities, etc.

2000 89% of USTs received required upgrades

- But 29% of USTs not being operated or maintained properly (U.S. GAO, 2001)

2006 592,000 active USTs

- 1.72 million USTs closed
- 553,000 confirmed releases
- 497,000 cleanups started / 462,000 cleanups completed

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Sources of UST System Failure

- Poor installation
- Seismic activity
- Surface deformation
- Mechanical damage
- Corrosion
- Inappropriate adhesive

Lust excavation reveals LNAPL source

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U.S. and European Differences

- Economic structure: taxed at wholesale
- Incentive for monitoring
  - ❖Urgency for action
- Distribution system installation, design and maintenance
  - ❖Pressure versus vacuum
- Proactive versus reactive response

AEHS Journal-2001 Special Oxygenated Fuels Issue (page 85)

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Gasoline Leaks, Spills, and Releases

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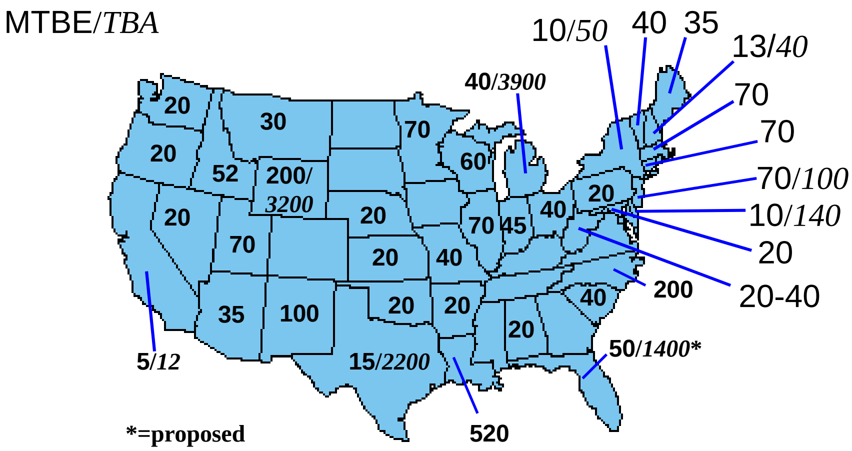
State Drinking Water Standards/Guidelines (υg/l) USEPA guideline for MTBE is 20-40



Note: Be sure to check for most up-to-date local standards/guidelines

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Physical Properties of MTBE, Benzene, TBA, Ethanol, and Isooctane

- All have:
  - Vapor density >1
  - Specific gravity <1

Gasoline = a mixture of several hundred compounds

- Differences:

	MTBE	Benzene	TBA	Ethanol	Isooctane
Water solubility (mg/l)	50,000	1,780	Infinite	Infinite	2.4
Vapor pressure (mmHg)	250	86	41	53	49
Henry's law constant	0.031	0.22	5E-4	2E-4	1E+4
Log K_{oc}	1.1	1.5	0.7	0.71	4.6

- Values are for pure compounds at 25°C

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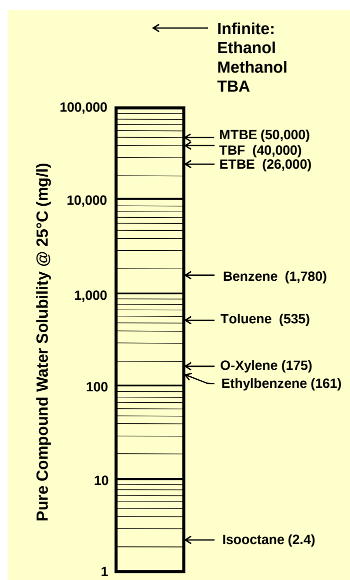
Solubility

- Degree to which a compound dissolves into water
- Solubility of each compound in a mixture like gasoline is a function of Raoult's Law

Gasoline Constituent	Approximate % by Volume	Solubility of Constituent (mg/l)
MTBE	11%	5, 500
Benzene	1%	18
Toluene	11%	59
Ethylbenzene	2%	3
Xylenes (mixed)	11%	19



Arulanantham et al., 1999

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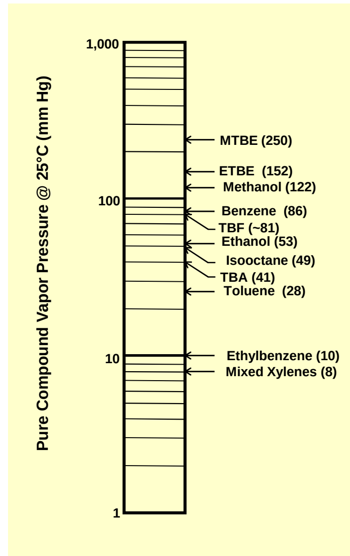
Vapor Pressure

- Volatilization from free phase (NAPL) to air
- Law of Partial Pressure
  - $P_{total} = P_{MtBE} + P_{\text{other gasoline constituents}}$
  - $P_{MtBE} = X_{MtBE}\, P^{o}_{MtBe}$

Gasoline Constituent	Approximate % by Volume	P_i (mm Hg)
MTBE	11%	28
Benzene	1%	0.9
Toluene	11%	3.1
Ethylbenzene	2%	0.2
Xylenes (mixed)	11%	0.9



Arulanantham et al., 1999

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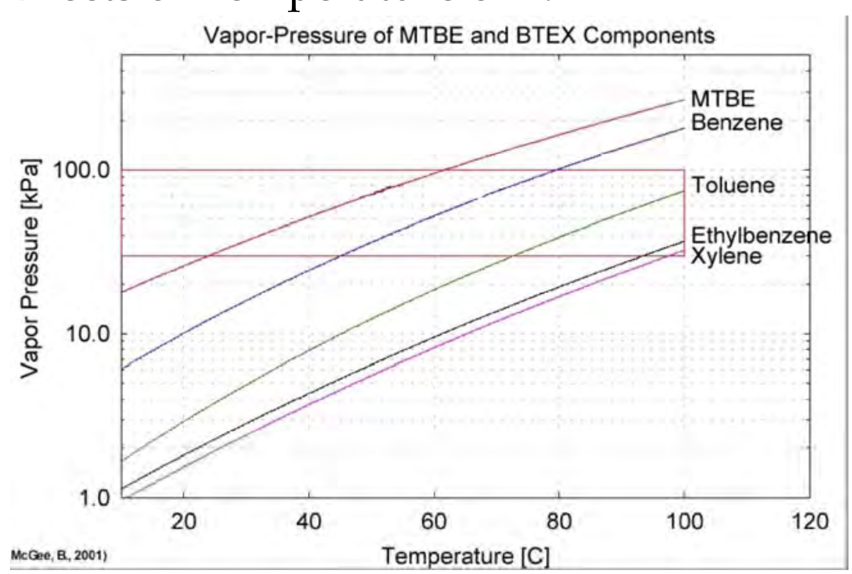
Effects of Temperature on VP



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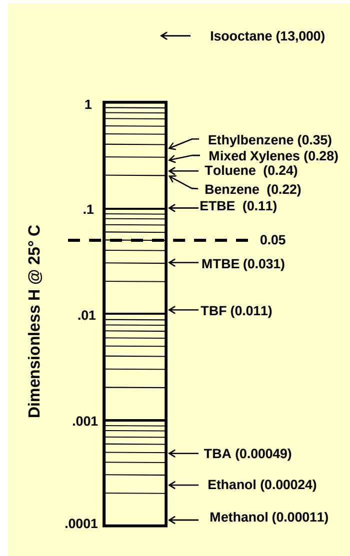
Henry's Law Constant

$$\mathbf{H} = \frac{\text{vapor conc.}}{\text{aqueous conc.}}$$

- Equilibrium partitioning between dissolved phase and air
- Henry's constant > 0.05
  - ❖Significant volatilization



Arulanantham et al., 1999

Adsorption

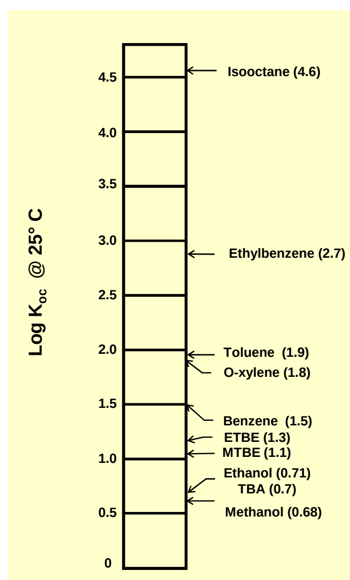
- Soil adsorption coefficient

$$K_d = \frac{\text{sorbed conc.}}{\text{solution conc.}}$$

$$K_d = f_{oc}\, K_{oc}$$

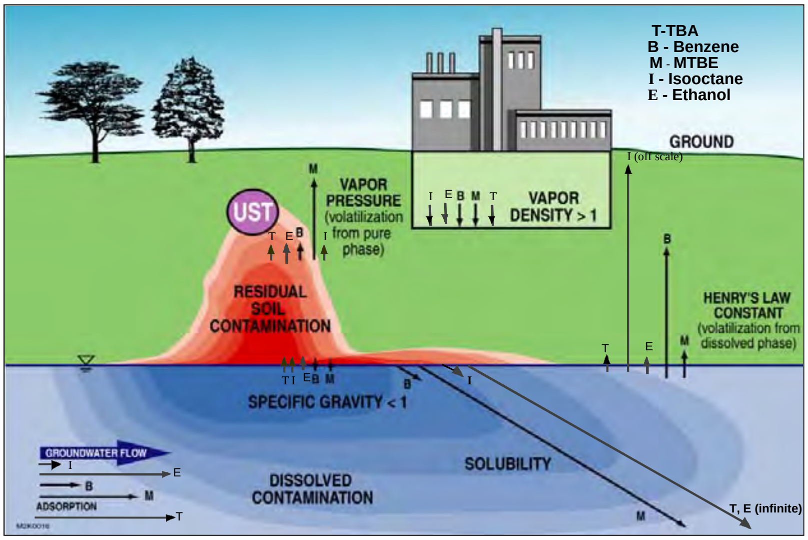
Fraction of soil organic carbon times organic carbon partitioning coefficient

- Adsorption retards advance of groundwater contamination front



Arulanantham et al., 1999

Physical Behavior of TBA, IsoOctane, MTBE, Ethanol and Benzene



Effects of Neat Ethanol

- Enhances the solubilization of BTEX from NAPL (cosolvency)
- Inhibits BTEX biodegradation
- Reduces interfacial and surface tensions
  - Increasing NAPL mobility
  - Height of capillary fringe is reduced
  - Gasoline pool at water table is thinner and larger in area
  - Gasoline can enter smaller pore spaces
- Creates anaerobic conditions, including methane generation

Solubility – Water, Hydrocarbons, Ethanol

- Standard gasoline and water are immiscible
- Ethanol is completely miscible with both gasoline and water at all concentrations
- When ethanol is present with both water and gasoline
  - Ethanol partitions into water
  - As a result, the water is more soluble in gasoline and gasoline hydrocarbons are more soluble in the water
    - » Can lead to longer BTEX plumes

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Solubility – Water, Hydrocarbons, Ethanol

- When a lot of ethanol is present (>70%)
  - Gasoline and water become completely miscible with each other and all 3 merge into a single phase
- When less ethanol – gasoline, and water+ethanol
  - Can happen with 0.5% water by mass and 10% ethanol by volume – separation to two phases
    - » Ethanol is added at terminals, not at refineries

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Site Assessments

- Surface and subsurface definition
  - Iterative process, data dependent
  - Hydrogeology controls transport
  - Evaluate all:
    - Media of concern
    - Relevant receptors
    - Contaminants
- Tools
  - Conventional
  - Emerging technologies

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Impact of Surface Features on Subsurface Distribution of LNAPL & Dissolved Phase

- Natural/man-made recharge barriers
  - ❖Tight clays, paving, buildings
- Natural/man-made recharge enhancements
  - ❖Losing streams and rivers
  - ❖Lakes and ponds
  - ❖Manmade surge basins, storm water basins
  - ❖Conduits connecting aquifer zones
    - » Buildings, foundations, basements
    - » Wells

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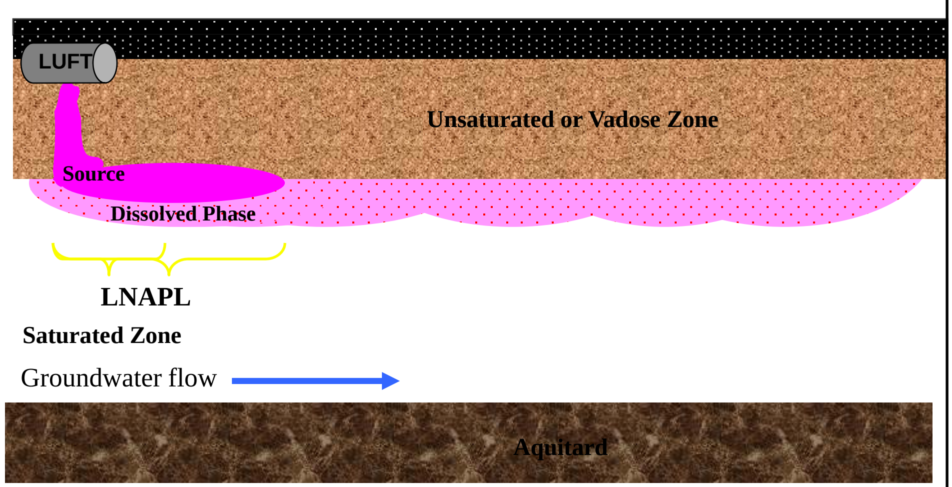
Natural or Man-made Barriers Limit Recharge



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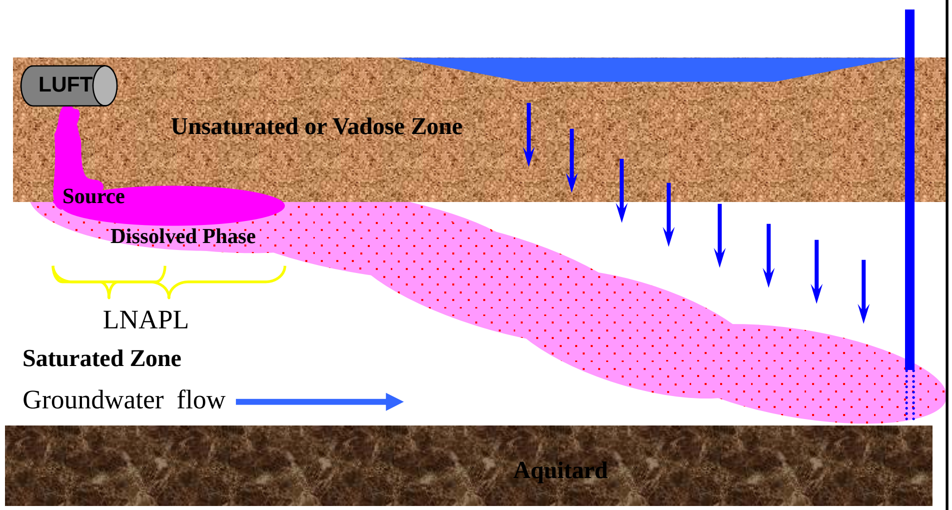
Natural or Man-made Enhanced Recharge



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Direct Push Rig

- Quick (samples/day)
- Cost-effective
- Access tight spaces
- Delineate stratigraphy
- Identify high/low K zones
- Depth limited

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Installation of 15 Port Sampling System

http://www.flut.com/sys_1.htm

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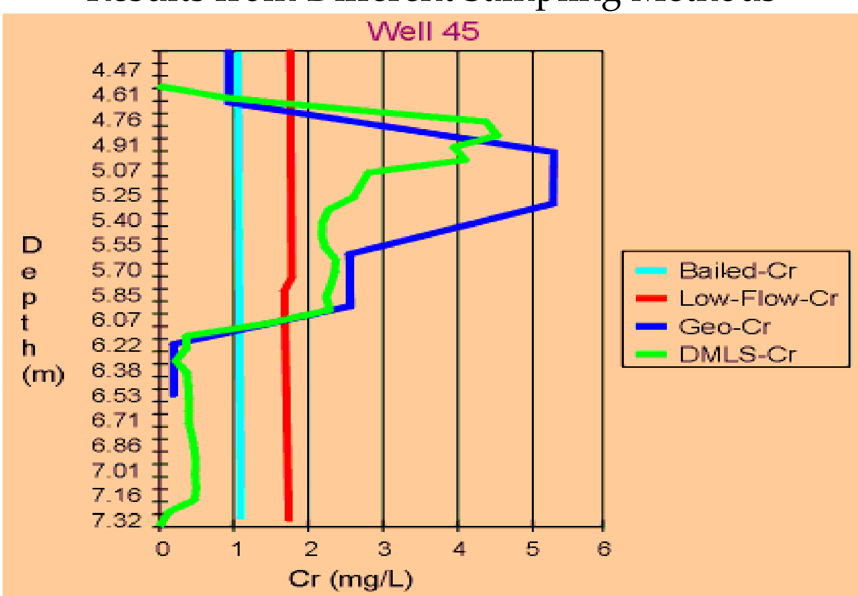
Results from Different Sampling Methods



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Site Assessments

- Subsurface Penetrations
  - Can generate contaminant pathway
  - CPT can be used to define subsurface stratigraphy
  - Immediately seal all penetrations not destined for future use
  - Do not screen monitoring wells across multiple water-bearing zones
  - Install "nests" of wells to define multiple water-bearing zones
  - Use isolation casing, separate well screens, grout seal, etc. to preserve aquitards

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Analytical Variability in Laboratory Prepared Performance Evaluation Samples

- 5-liter certified "clean" water
- Add

  42.8 ug/liter Benzene
  20.0 ug/liter Toluene
  185 ug/liter Xylene
  60.0 ug/liter 1,2 DCA
  197 ug/liter MIBK
  42.4 ug/liter PCE
  71.5 ug/liter TCE
- Six samples each of four "outside" laboratories
- Six samples analyzed by "in-house" laboratory

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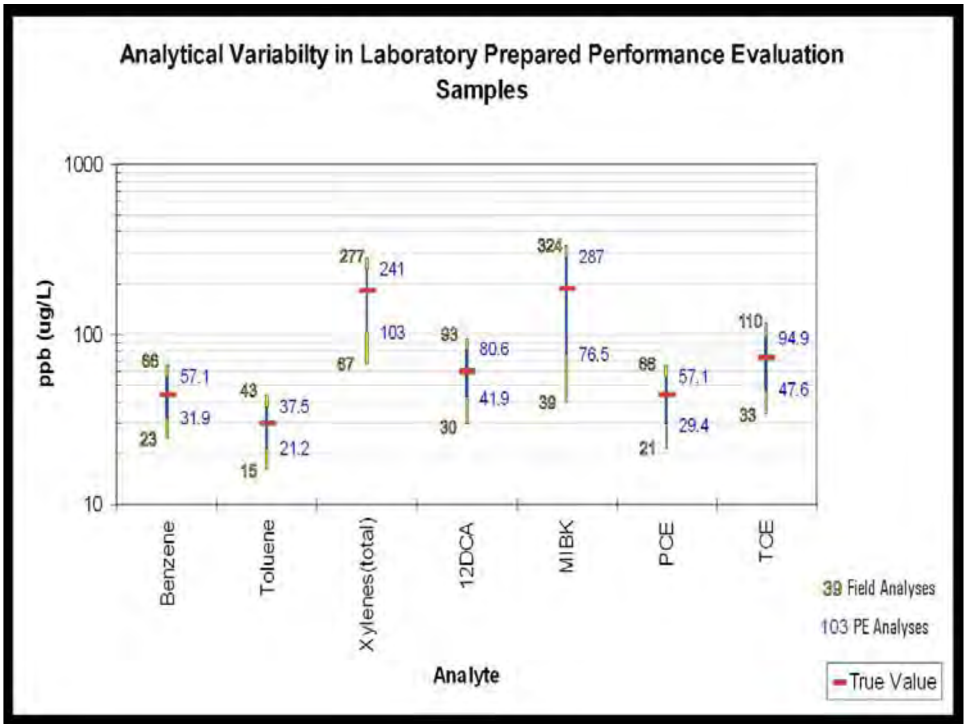
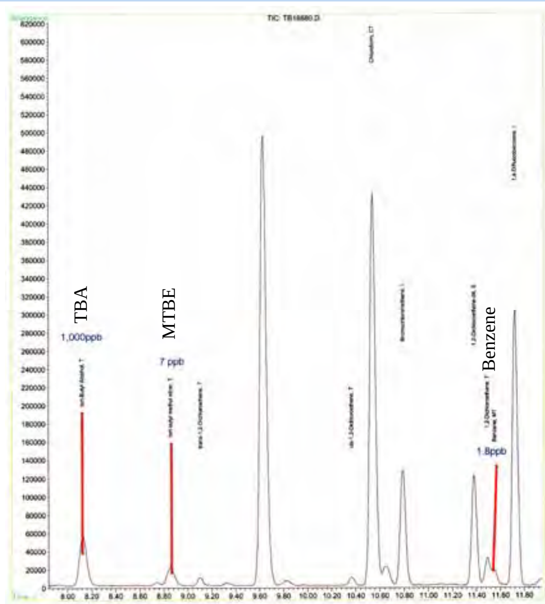


Compounds at lower concentrations are lost to dilution and reported at Below Detection Limit (<50 ppb)



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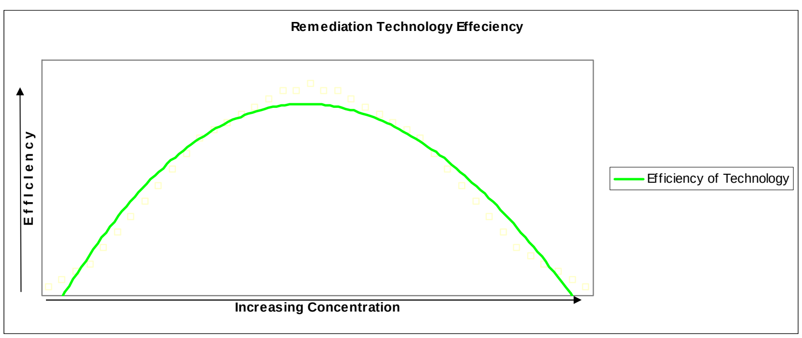
Remediation Phases

- Protect receptors
- Control sources
- Remediate residual and dissolved contamination
- Monitored natural attenuation



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Remediation Technology Sequencing

Technology & Typical Duration (months)	*Application range (ppb of VOCs in soil or groundwater)				
	≥100,000	10,000-100,000	1,000-10,000	500-1,000	<500
Excavation/Disposal/Treatment (2-3)	X				
In-Situ Thermal Desorption (3-5)	X				
Biopile Treatment (3-6)	X				
Soil Vapor Extraction/Thermal Oxidation (6-12)	X	X			
Pump and Treat (12-24)	X	X			
Chemical Oxidation (3-6)		X			
Air Sparging (10-15)		X			
Ex-Situ Groundwater Bioremediation (12-24)		X	X		
Bioventing (18-36)			X		
In-Situ Groundwater Bioremediation (18-36)			X	X	
Granular Activated Carbon (NA)					X
Monitored Natural Attenuation (5-15 yrs)					X

*** Approximate ranges based on cost and progress.**

Technology selection and sequence tends to be site-specific, depending on hydrogeology, receptors, chemicals present, etc.

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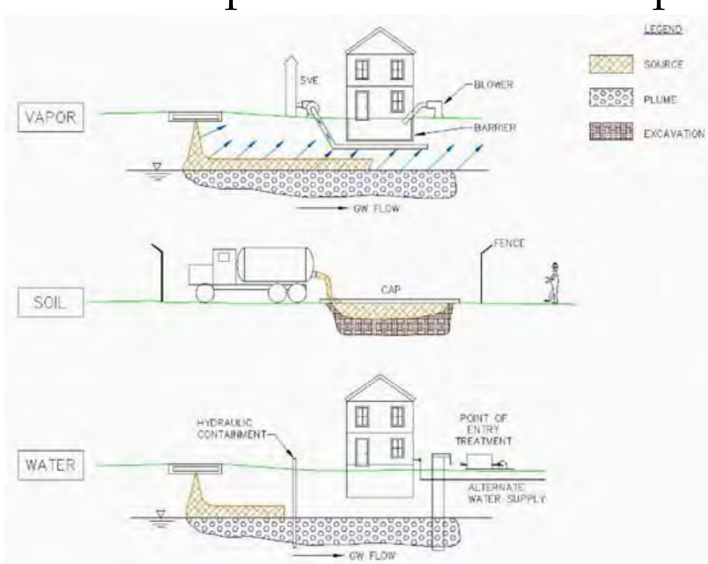
Immediate Response to Protect Receptors



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Point Of Entry Treatment (POET) Systems

- Granular Activated Carbon (GAC) for MTBE and BTEX
- UV/Hydrogen Peroxide or some other chemical oxidation would be required for TBA; or possibly bioreactor or vacuum distillation

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Source Control Technologies

- Essential to address source quickly
- Options
  - ❖ Excavation and treatment or disposal
  - ❖ Physical containment
  - ❖ Hydraulic containment
  - ❖ Free product removal
  - ❖ Thermal mobilization

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Physical and Hydraulic Containment

Protect downgradient receptors and prevent plume expansion

- Subsurface barriers (e.g., slurry or sheetpile walls)
- Pumping from wells or trenches
- Surface covers to limit infiltration
- Living caps to maximize evapotranspiration

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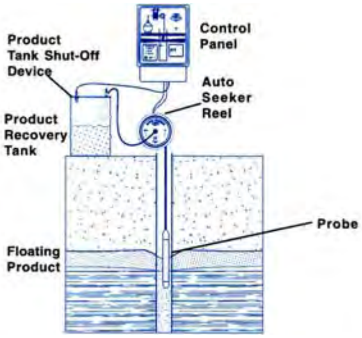
Free-Product Removal

Skimming Methods

- Continuous belt separation
- Spiral pump at the interface
- Smart pumps



Example of a smart pump

Multi-phase extraction

- Two-Phase Extraction (TPE)
  - ❖ Vapor and liquid extracted together
- Dual-Phase Extraction (DPE)
  - ❖ Gas and liquid extracted separately

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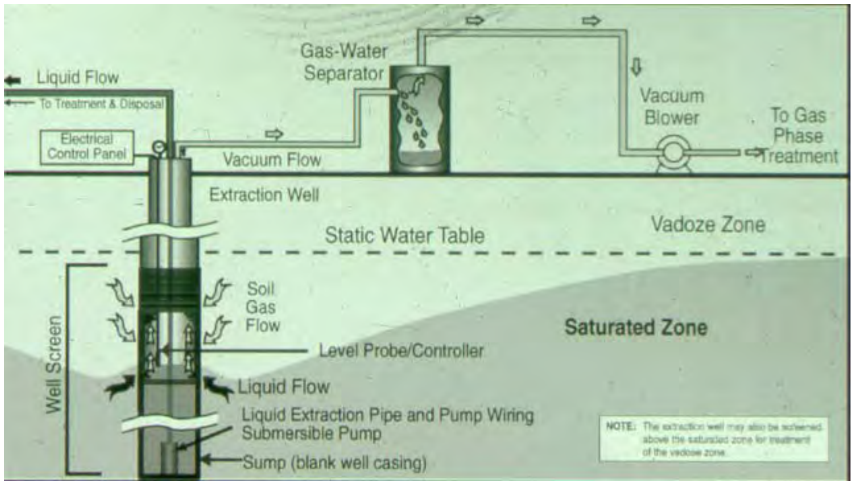
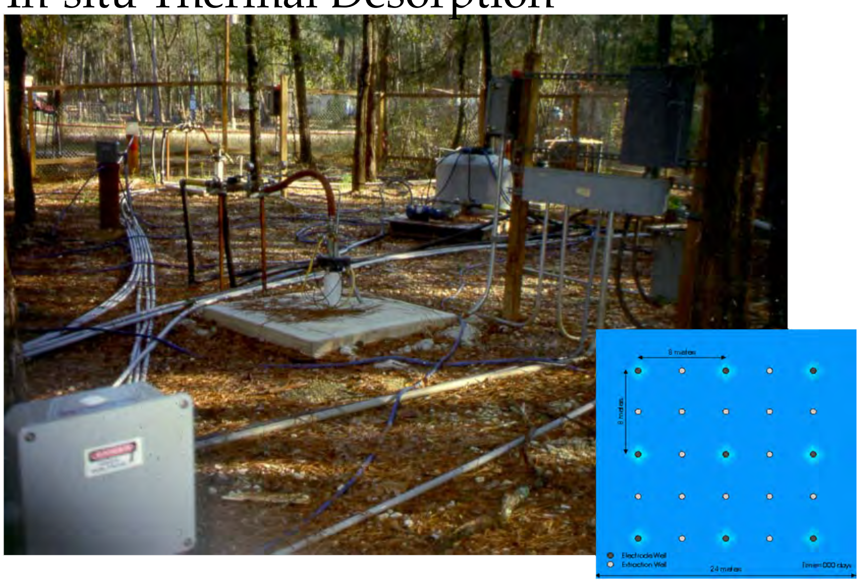
Dual Phase Extraction



Source: USCOE MPE Engineer Manual

In-situ Thermal Desorption



Courtesy Remedial Operations Group & McMillan-McGee

Thermal Oxidizer

Courtesy Remedial Operations Group

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Soil Vapor Extraction

	TBA/Ethanol	MTBE
■ SVE effective	✓	✓
■ High air flow rates to strip VOCs	✓	✓
■ Treats unsaturated zone	✓	✓
■ Expand vadose zone	✓	✓
■ Aboveground gas treatment by		
❖ Granular activated carbon	--	✓
❖ Catalytic oxidation	✓	✓
❖ Thermal oxidation	✓	✓
❖ Biofilters	✓	✓

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Bioventing

	TBA/Ethanol	MTBE
■ Low air flow rates	✓	✓
■ Aerates unsaturated zone	✓	✓
■ Treats unsaturated zone	✓	✓
■ Expand vadose zone	✓	✓

- Vapor treatment usually not required
- Passive systems - barometric pressure, wind turbine ventilation
- Active systems - blowers, compressors

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Subsurface ventilation

Courtesy Air Situ LLC, Houston, TX

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Air Sparging/Biosparging

	TBA/Ethanol	MTBE
■ Strips VOCs	--	✓
■ Oxygenates soil & groundwater		
❖ Vadose zone	✓	✓
❖ Saturated zone	✓	✓
■ SVE to manage vapors	✓	✓
■ Relatively inexpensive	✓	✓
■ Low adsorption is helpful	✓	✓

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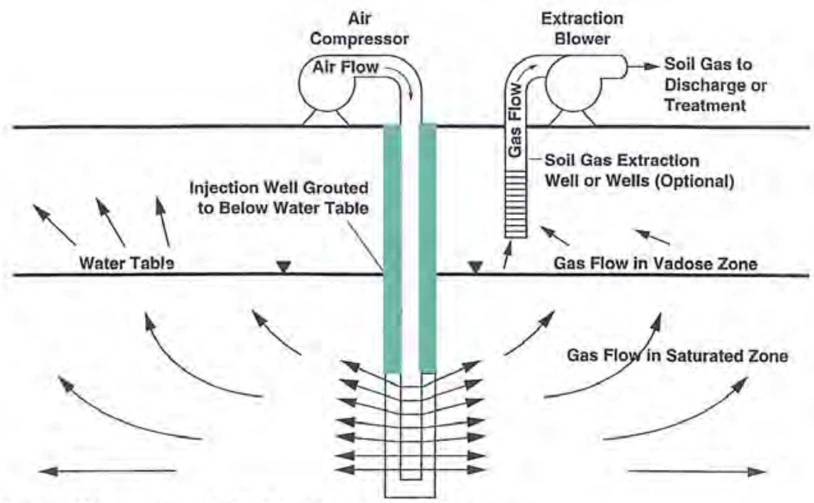
Air Sparging/SVE



Hinchee 1994. Air Sparging for Site Remediation - Lewis Publishers

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Groundwater Pump and Treat

	TBA/Ethanol	MTBE
❖Soluble	✓	✓
❖Non-adsorptive	✓	✓
❖Pump and treat very effective	✓	✓

Aboveground water treated by:

	TBA/Ethanol	MTBE
❖Granular activated carbon	--	✓
❖Air stripping » Vapor treatment required	--	✓
❖POTW - with pretreat if necessary	✓	✓
❖Bioreactor	✓	✓
❖Advanced oxidation processes » e.g. ozone, UV, UV/peroxide	✓	✓

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Relative Oxidizing Power of Chemical Oxidants

Reactive Species	Relative Oxidizing Power (Cl_2=1.0)
Fluorine	2.23
Hydroxyl Radical (Fenton's)	2.06
Sulfate Radical	1.91
Ozone	1.77
Persulfate Anion	1.72
Hydrogen Peroxide	1.31
Permanganate	1.24
Chlorine Dioxide	1.15
Chlorine	1.00
Bromine	0.80
Iodine	0.54

AEHS Journal-2002 Special Oxygenated Fuels Issue (page 71)

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In Situ Chemical Oxidation Treatment Considerations

	TBA/Ethanol	MTBE
■ Non-target organics/inorganics	✓	✓
■ Choice of oxidant is site-specific	✓	✓
■ Impact of treatment zone pH	✓	✓
■ Distribution of oxidant	✓	✓
■ Residual oxidation state	✓	✓
❖ In-situ bioremediation	✓	✓

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DRIS Oxidant Delivery

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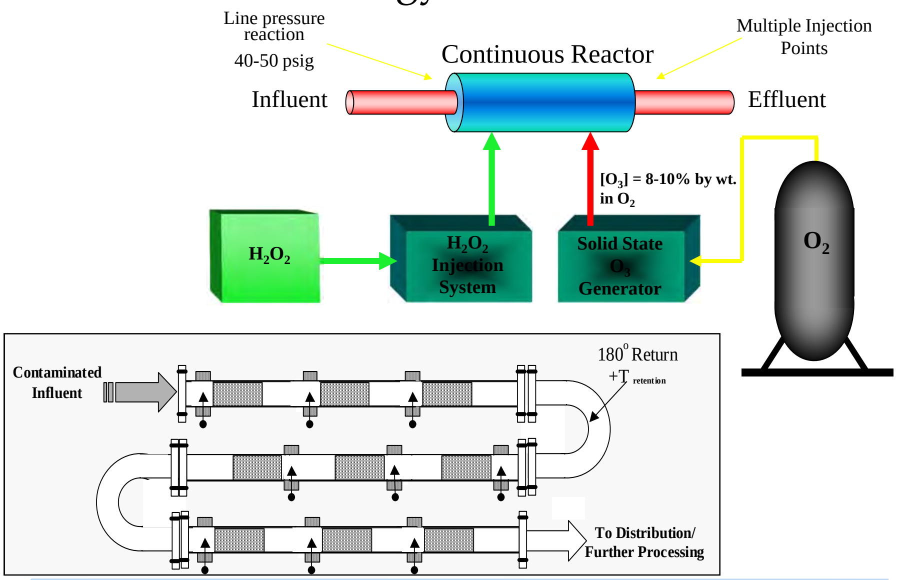
HiPOx^{TM} Technology



Courtesy Applied Process Technology, Inc. – Pleasant Hill, CA

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Bioremediation

	TBA	MTBE
■ Biodegradable	✓	✓
■ Indigenous organisms	✓	✓
■ Augment w/cultured organisms	✓	✓
■ Optimize		
❖ Electron acceptors	✓	✓
» O_2, NO_3, Mn^{+4}, Fe^{+3}, SO_4, CO_2		
❖ Supplemental carbon (e.g., propane)	✓	✓
❖ Nutrients (e.g., N, P, K)	✓	✓
❖ pH	✓	✓
❖ Reduce toxic factors	✓	✓

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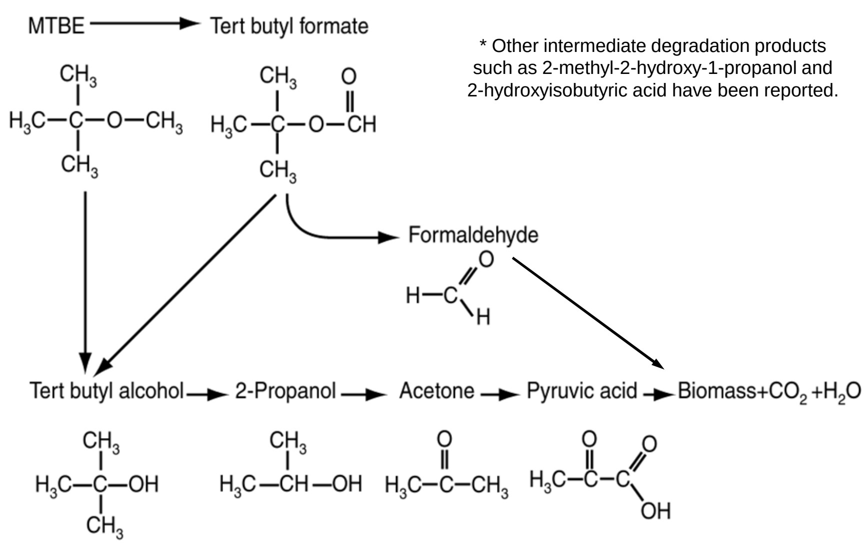
USGS Scientists Find Good Potential for Biodegradation at all 11 of 11 Sample Collection Sites

Bradley et al. 1999 ES&T 33(11):1877-1879

Aerobic Biodegradation of MTBE and TBA



* Other intermediate degradation products such as 2-methyl-2-hydroxy-1-propanol and 2-hydroxyisobutyric acid have been reported.

Courtesy http://umbbd.ahc.umn.edu/mtb/mtb_map.html and Steffan et al. 1997.

Microbial Metabolism of Organic Matter

Respiration Process	Electron Acceptor	Metabolic Products	Relative Potential Energy
Aerobic Respiration	O_2	CO_2, H_2O	High
Denitrification	NO_3^-	CO_2, N_2	
Iron reduction	Fe^{3+}	CO_2, Fe^{2+}	
Sulfate reduction	SO_4^{2-}	CO_2, H_2S	
Methanogenesis	CO_2	CH_4	Low

Suflita and Sewell (1991)

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MTBE/TBA Degrading Microbes

Bacteria	Aerobic	>15*	United States, Denmark, England, Mexico, France
Bacteria	Denitrification	Pending	United States, France
Bacteria	Iron reduction	Pending, Consortium?	United States
Bacteria	Sulfate Reduction	Pending, Consortium?	United States
Bacteria	Methanogenesis	Pending, Consortium?	United States
Fungi	Aerobic	Graphium, others pending	United States

*Gordonia (2), Hydrogenophaga, Nocardia, Rhodococcus, Sphingomonas, Xanthobacter, Methylobacterium, Arthrobacter, Burkholderia, Pseudomonas, Alcaligenes (2), Mycobacterium, Rubrivivax (Methylibium).

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In Situ GW Bioremediation Approaches

	TBA	MTBE
■ Directly inject amendments	✓	✓
■ Extract, amend, and re-inject	✓	✓
■ Diffuse amendments into GW	✓	✓

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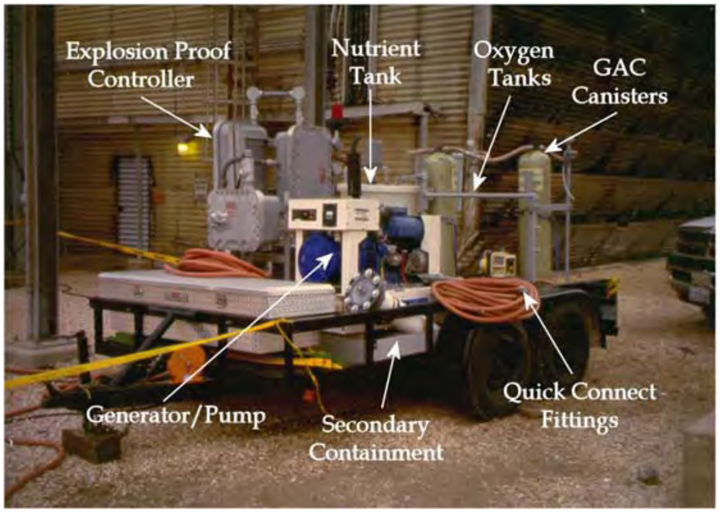
Mobile Well Service Unit



Courtesy Remedial Operations Group

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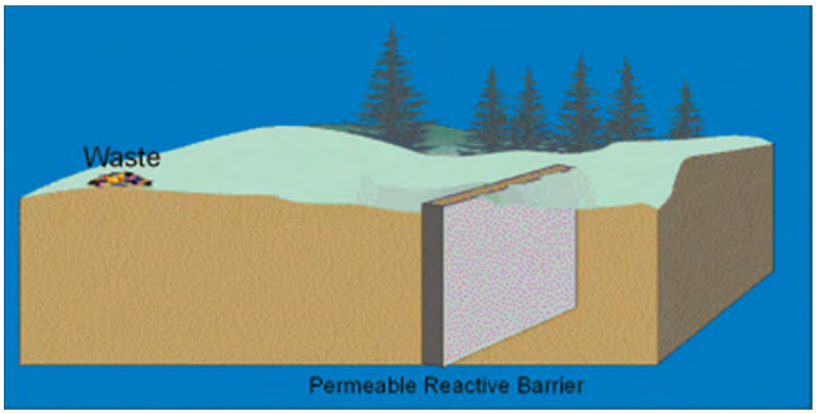
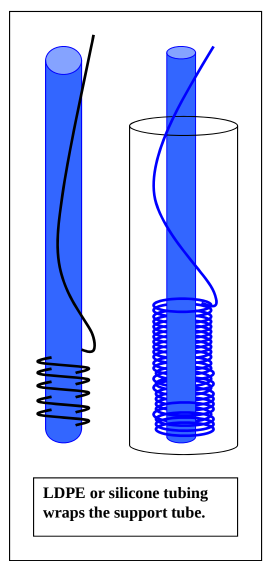
Permeable Reactive Barriers

- Biostimulation by oxygen release: Vandenberg AFB, CA
- Bioaugmentation & sparging: Port Hueneme, CA
- Chemical permeable reactive barrier: sulfated aluminum



Diffusive Oxygen Release Systems

- Rapid, inexpensive & effective delivery of dissolved oxygen to the saturated zone (Waterloo emitters)
- Cylindrical oxygen emitters →
- Permeable release panel pilot test
  - Emplace prefab permeable panel in trench containing oxygen or substrate release devices
  - Backfill around panel with sand/gravel
  - Initiate oxygen/substrate release from within panel



Installation of the Scaled up Cylindrical Oxygen Emitter Diffusive Barrier

Emitter arrays in a transect

Emitter array in a trench

Courtesy IT Corporation 2001

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Ex-Situ GW Bioremediation Approaches

- Used with GW pump and treat – treat in a tank – many configurations
- Activated Sludge (AS)– recirculating water and suspended microorganisms in a tank
- Fluidized Bed Bioreactor (FBBR)– organisms attached to particles are suspended by upflow in tank
- Fixed Film Bioreactor, Biotrickling Reactor (BTR)
- Bio-GAC – bioaugment GAC with organisms & amend influent water with oxygen and nutrients

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FBR Description

- Microorganisms attached to particles degrade contaminants in a water stream
- Ex-situ treatment applicable to GW pump-and-treat operations
- Particles are distributed in the reactor by an upflow of the water being treated
- Used in a variety of other applications including wastewater treatment and industrial waste treatment

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Bioreactor Design Considerations

- Flow rate of GW from site extraction wells
- Chemicals of concern and their influent concs.
- Required concs.
  - Site groundwater
  - Treated effluent
- Other chemicals
  - That could precipitate (e.g., Fe, Mn, hardness)
  - That could be biodegraded (e.g., BTEX)
  - That could be toxic (e.g., arsenic)
- Optimal population of microorganisms
- Dissolved oxygen
- Nutrients (N, P, K)
- Temperature
- pH

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Ex-Situ Bioreactor Treating MTBE & TBA

Courtesy Environmental Resolutions, Inc.

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Aerobic Biodegradation of Ethanol

- Most common aerobic bacteria can oxidize ethanol
- Intermediates include acetaldehyde and acetyl coenzyme A, and final product is CO_2
  - Non-toxic
  - Not likely to accumulate
- An exception
  - Acetic acid bacteria excrete acetate
  - Acetate will biodegrade under aerobic or anaerobic conditions
- Ethanol bio is faster than BTEX bio

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Anaerobic Biodegradation of Ethanol

- Most ethanol field sites will be anaerobic (having run out of oxygen by aerobic bio)
- Microorganisms that can ferment ethanol are ubiquitous
- Ethanol is a common intermediate between organic matter and non-toxic products such as acetate, CO_2, CH_4, H_2 gas
- Three stages of fermentation
  - 1 – produces organic acids, alcohols, H_2, CO_2
  - 2 – produces acetate, H_2, CO_2
  - 3 – produces CO_2, CH_4
- Ethanol bio is faster than BTEX bio

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Relative Biodegradation Rates

Chemical	Aerobic	Anaerobic
Ethanol	Very fast	Very fast
MTBE	Slow	Slow
TBA	Slow	Very slow
Benzene	Fast	Slow
Ethylbenzene	Fast	Fast
Toluene	Fast	Fast
Xylenes	Fast	Fast

Courtesy: Curt Stanley, Shell Global Solutions (US) Inc.

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Gasoline with 10% Ethanol

- Ethanol should not directly inhibit BTEX biodegradation
- Ethanol degraders depleting electron acceptors will reduce their availability to BTEX degraders
  - Can lead to longer BTEX plumes
    - Particularly benzene plumes
- Reportedly can cause dehydration of clays, producing microfractures within the clay
- Concern about ethanol degrader biomass possibly clogging aquifer and/or well screens?

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Relative Plume Lengths

- Modeling efforts – 10% ethanol predicted to increase benzene plume lengths by:
  - 17-34% (Malcolm Pirnie, 1998)
  - 100% (McNab et al., 1999)
  - 10-150% (Molson et al., 2002)
- Ruiz-Aguilar et al. (2003) study of:
  - 217 sites in Iowa (without ethanol)
  - 29 sites in Kansas (10% ethanol by volume)
  - Benzene plumes longer if ethanol present
    - Iowa mean 193′ Kansas mean 263′
    - Iowa median 156′ Kansas median 263′
  - Toluene plumes were not significantly longer

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Vandenberg AFB Field Experiment

- Side by side releases for ~9 months of GW amended with:
  - ❖ 1-3 mg/l each of benzene, toluene, and o-xylene
  - ❖ 1-3 mg/l each of benzene, toluene, and o-xylene, and 500 mg/l ethanol
- Into a sulfate-reducing aquifer
  - ❖ 20–160 mg/l sulfate; mean value 96 mg/l

Mackay et al., ES&T, 2006

Vandenberg Results

- Ethanol was rapidly degraded
  - ❖ Detected at only one well 0.5 m downgradient of injection wells
- Biodegradation of ethanol
  - ❖ Led to "plume" of sulfate-depleted water that was transported downgradient
  - ❖ Created methanogenic/acetogenic conditions
- Acetate and propionate
  - ❖ Apparent intermediates of ethanol biodegradation
  - ❖ Migrated further and were thus biodegraded more slowly than ethanol
- BTX degradation in No Ethanol Lane did not significantly alter sulfate concentrations

Mackay et al., ES&T, 2006

Vandenberg Results

- Initially, both BTX plumes extended same distance
- Later:
  - Plumes in No Ethanol Lane retracted significantly
  - Plumes in With Ethanol Lane retracted
    - More slowly
    - Not as far
- Conclusion: Biodegradation of ethanol can reduce rates of in situ biodegradation of aromatic fuel components in the subsurface
  - Under transient conditions
  - Under near steady-state conditions

Mackay et al., ES&T, 2006

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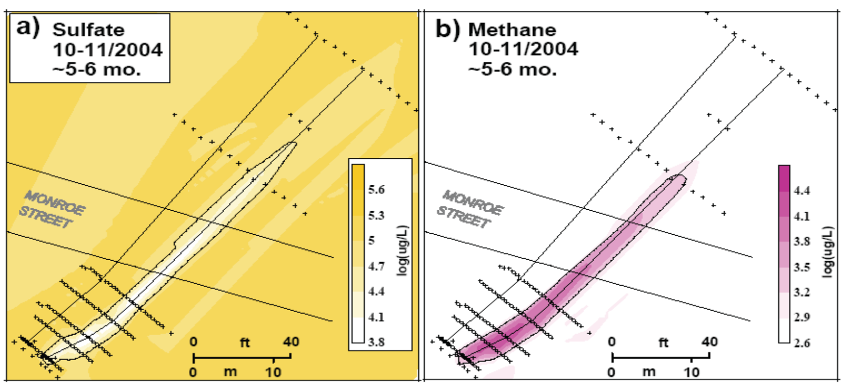
Vandenberg – Sulfate and Methane



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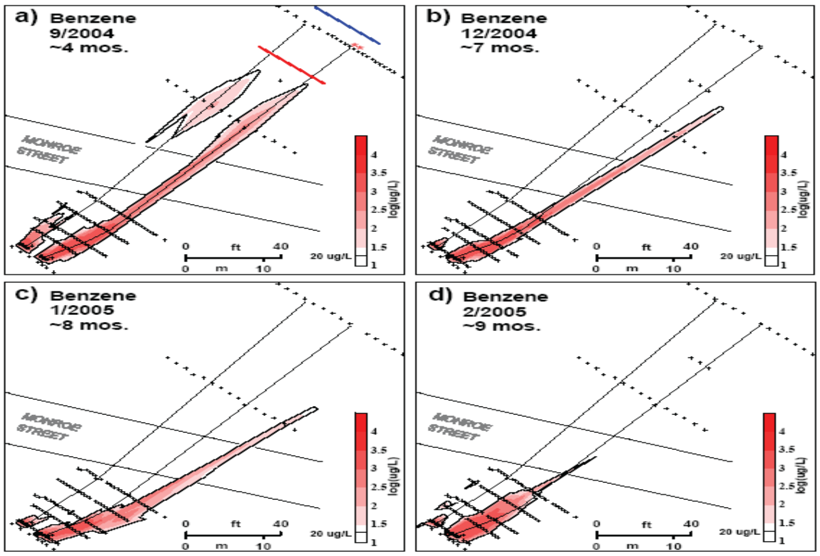
Vandenberg – Benzene Plumes



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Study of 7 Midwest States

- States were known to use ethanol in gasoline:
  - CO, IL, IN, KS, MN, NE, WI
- GW samples collected in 2000:
  - 75 samples from 28 vulnerable PWS systems
  - 221 samples from 70 LUST site MWs
  - 31 samples from between PWSs and LUSTs
- Samples analyzed for BTEX, MTBE, TBA, and ethanol

ENSR, 2001

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Study of 7 Midwest States

- PWS Results:
  - ❖ Only 2 samples exceeded regulatory criteria
    - » Well in NE: 19 ug/l benzene (no other compounds)
    - » Well in NE: 170 ug/l benzene (no other compounds)
  - ❖ Only several other detects
    - » 1 detect of benzene at 3 ug/l
    - » 5 detects of MTBE at 5 ug/l or less
  - ❖ No TBA, ethanol, TEX detected in any samples

ENSR, 2001

Study of 7 Midwest States

- LUST Site Results:
  - ❖ BTEX at 90% of sites
  - ❖ MTBE at 70% of sites
  - ❖ TBA at ~50% of sites
  - ❖ Ethanol only in 2 samples from 2 separate sites
    - » 650 and 130J ug/l
- Most releases were 5-10 years old, or more

ENSR, 2001

Study of 7 Midwest States

- Results for Samples between LUSTs and PWSs:
  - ❖Only BTEX detected; no MTBE, TBA, or ethanol
  - ❖Gasoline constituents generally not detected more than 100-200 feet from LUSTs
  - ❖Highest concentrations close to LUSTs
  - ❖Limited extent of impact from LUSTs

ENSR, 2001

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Number of samples containing Benzene (ug/L) or MTBE (ug/L) from LUST Sites in 7 States

Benzene	0.1-0.9	1.0-9.9	10-99.9	100-999.9	1,000-9,999.9	10,000-99,999.9
10,000-99,999.9	2			2	4	1
1,000-9,999.9	9	6	6	17	8	
100-999.9	18	2	8	7	6	
10-99.9	24	4	7	6	4	
1.0-9.9	51	2	9	14	4	
0.1-0.9						

MTBE

The number in each box denotes the groundwater sample concs. for the compound(s) that are within the two ranges specified.

ENSR, 2001

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Phytoremediation

	TBA/Ethanol	MTBE
■ Gradient control/evapotranspiration	✓	✓
■ Rhizosphere biodegradation	✓	✓
■ Native species perform best ❖ Low maintenance conditions	✓	✓
■ Plant selection influenced by water balance ❖ Model transpiration rate, stand density	✓	✓
■ Irrigation often required to establish stand ❖ Deep watering stimulates deep roots	✓	✓
■ Water/soil quality affects establishment ❖ Salt concentration, pH	✓	✓

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Phytoremediation of Shallow Hydrocarbons in Soil with Oleander

Courtesy Remedial Operations Group

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Plume Control Phreatophytes
Long Beach, California


Plume Control Phreatophytes
Long Beach, California

Monitored Natural Attenuation

- Begins when active treatment yields diminishing returns and monitoring efforts are reasonable
- Characterized by reduction of contaminant concentration, mass, toxicity or mobility
- Monitor/model:
  - Decreasing contaminant concentrations
  - Physical, chemical, biological processes

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Natural Attenuation Processes

	TBA	MTBE
■ Destructive (mass reduction)		
❖ Intrinsic biodegradation	✓	✓
❖ Abiotic chemical reactions	--	?
■ Non-destructive (mass conservative)		
❖ Adsorption	--	✓
❖ Dispersion	✓	✓
❖ Advection	✓	✓
❖ Diffusion	✓	✓
❖ Volatilization	--	✓
❖ Dilution	✓	✓

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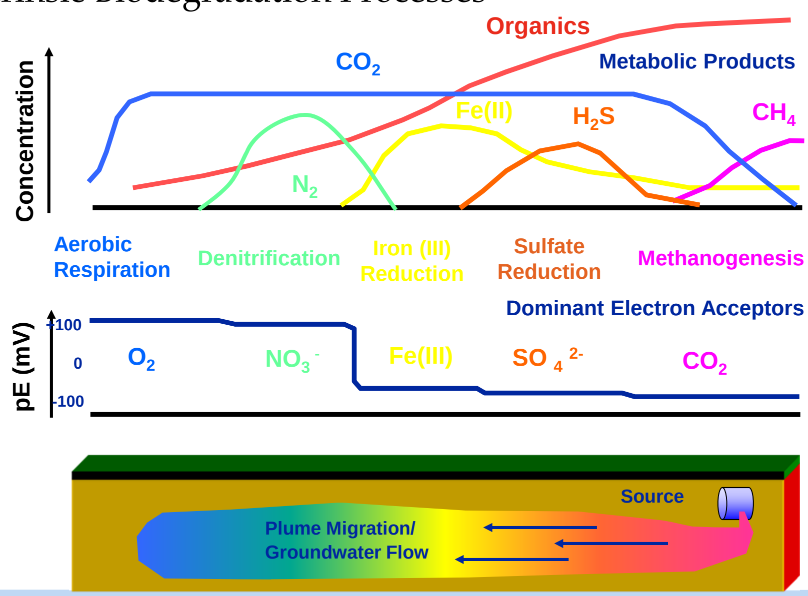
Intrinsic Biodegradation Processes



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Remediation Principles for Gasoline Contamination

- Complete site assessment and established cleanup goals are essential
- Technology sequencing to optimize remediation effectiveness and minimize costs
- Flexible design to accommodate changing conditions
- Take advantage of unique properties of chemicals and sites
- Expect surprises

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Outline of Workshop

- Introduction
- Properties, fate and transport
- Site assessment and analytical issues
- Applying remedial technologies
- *Case studies of remediation*
- Conclusion and summary

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Remediation Costs

- Highly site-specific and function of
  - ❖Time release has gone unremediated
  - ❖Size of release
  - ❖Hydrogeology
  - ❖Sensitive receptors and pathways to them
- Typical if only soil is impacted: $100K
- Typical if soil & GW are impacted: $250K

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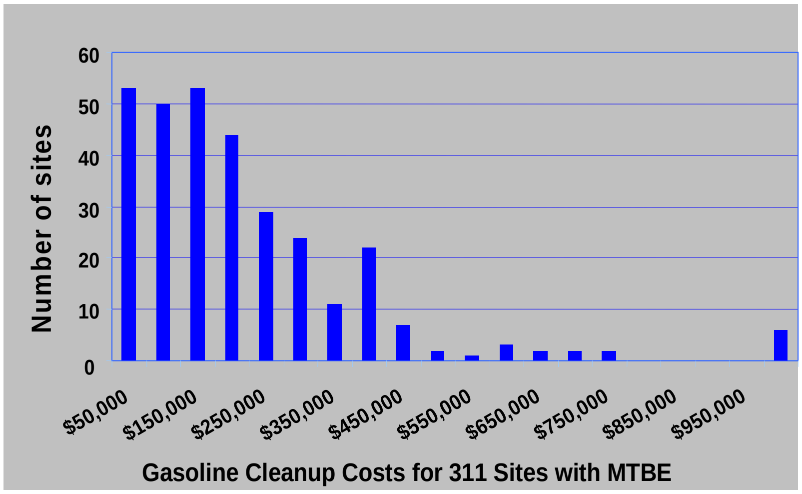
Gasoline Remediation Cost Histogram

(adapted from B.H.Wilson et al. 2001. Battelle Conf. San Diego, CA)



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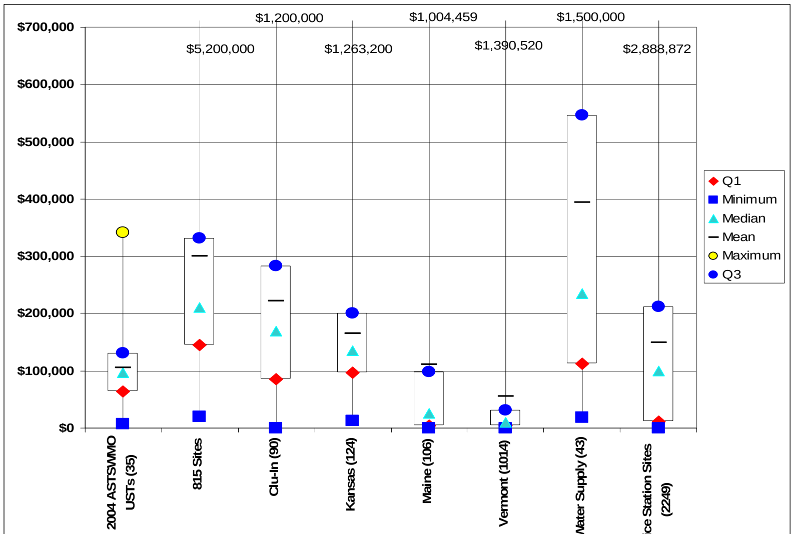
Summary of Remediation Costs



Barbara Wilson, Mike Martinson, Jim Davidson, Bruce Bauman.
11/7-8/2005 NGWA Conference, Houston TX

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Summary of Gas Station Remediation Costs

Study	Mean	Median
2249 SS Sites	$149,308	($99,495)
311 Sites	$200,827	($150,000)
815 Sites	$299,673	($210,374)
Maine (106 sites)	$110,589	($26,236)
Vermont (1,014)	$54,801	($10,619)
Kansas (124)	$165,183	($134,855)
ASTSWMO (35)	$105,757	($97,000)

Barbara Wilson, Mike Martinson, Jim Davidson, Bruce Bauman.
11/7-8/2005 NGWA Conference, Houston TX

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Remediation Costs – Wilson et al., 2005

- MTBE service station sites
  - $145,152 mean
  - $83,920 median

- BTEX and/or MTBE water supply sites
  - $393,720 mean
  - $235,000 median

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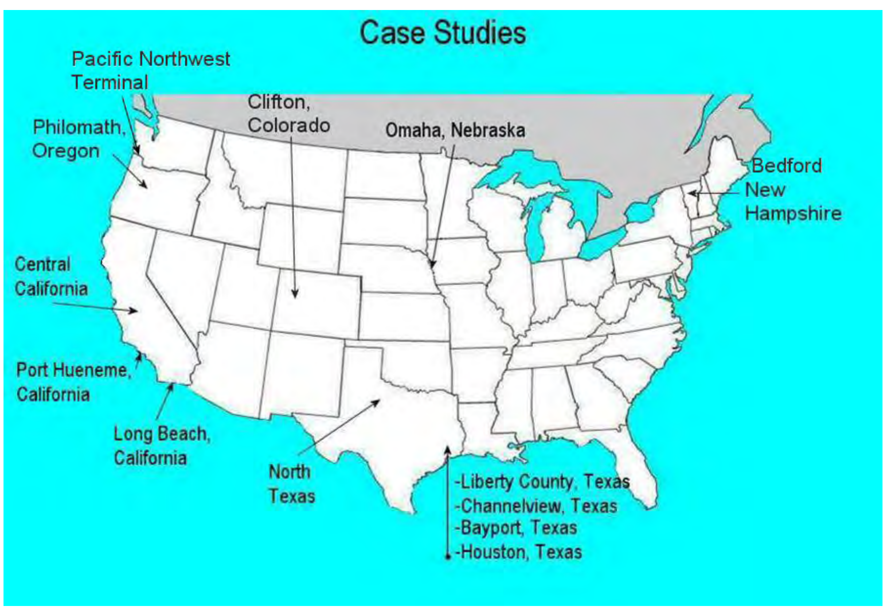

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Case Studies

Long Beach, CA
Gas station in developed area; plume well defined and responsive to source control

Channelview, TX
High concentrations of TBA and MTBE; evaluated in-situ technologies

Liberty County, TX
Complex plume (benzene, TBA, MTBE, chlorinateds) that was well-defined; responded to a sequence of technologies, starting with source control and thermal desorption

Pacific Northwest Terminal
Well defined ethanol plume

Philomath, OR
Gas station with significant free-phase; responded quickly to in-situ bio after effective source control

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Case Studies

North Texas ISCO
Large fuel spill and well defined BTEX/MTBE plume; responded rapidly to direct oxidation

CA ozonation
Typical LUST; source control was effective; used ozone injection to remediate the residual BTEX, MTBE, and TBA

Clifton, CO
Extensive leak of gasoline into ancient floodplain; physical limitations impacted source control; water main leak created local recharge mound

Port Hueneme, CA
Elongated BTEX, MTBE, TBA plumes; responded well to enhanced bioremediation; permeable reactive barrier worked well

Bedford, NH
Successful ex situ bioremediation of BTEX, MTBE, and TBA at cooler temperatures

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Case Studies

Bayport, TX
Elevated levels of TBA in shallow groundwater; source control was effective; confirm biological component of TBA natural attenuation

Westheimer and Shepherd, TX
Gas station and dry cleaner plumes co-mingled; effective source control was critical; pump and treat with in-situ bioremediation

Omaha, NE
Three LUSTs: BTEX, TBA, and MTBE plumes are well defined; responded rapidly to pump and treat and circulating in-situ bio

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Long Beach, CA: Description

- Abandoned gas station on 0.6 acre corner lot
- Tanks may have leaked 500 gallons of gasoline (1980-1995)
- Three leaking tanks removed
- 60 yd^3 soil with free-phase to landfarm
- Commercial use area being upgraded
- No at-risk receptors
- Groundwater plume well defined, 12 years of monitoring
- Groundwater impacted to about 30' bgs
- BTEX, MTBE, TBA are the chemicals of concern

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Long Beach, CA: Remediation

- Remove tanks and soils with free-phase
- Backfill tank area with clean soils amended with 5 lbs. $KMnO_4$ per ton
- Soil vapor extraction
  - Three 6" diameter wells
  - Screened from 5' to 20' bgs
  - Extract 10 CFM per well
  - Operate for 9 months
  - Treat vapor with GAC

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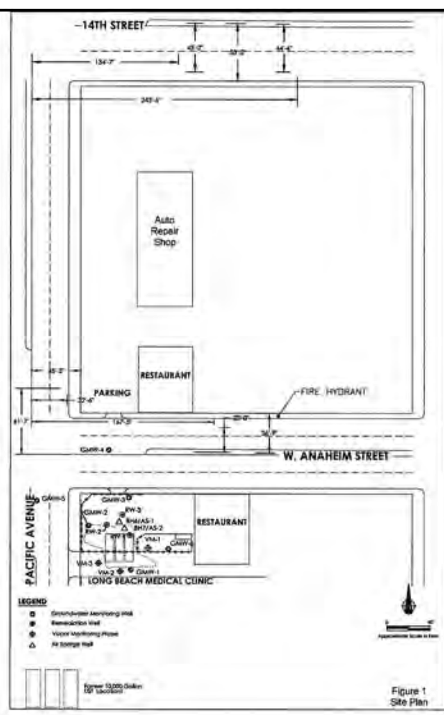
Long Beach, CA



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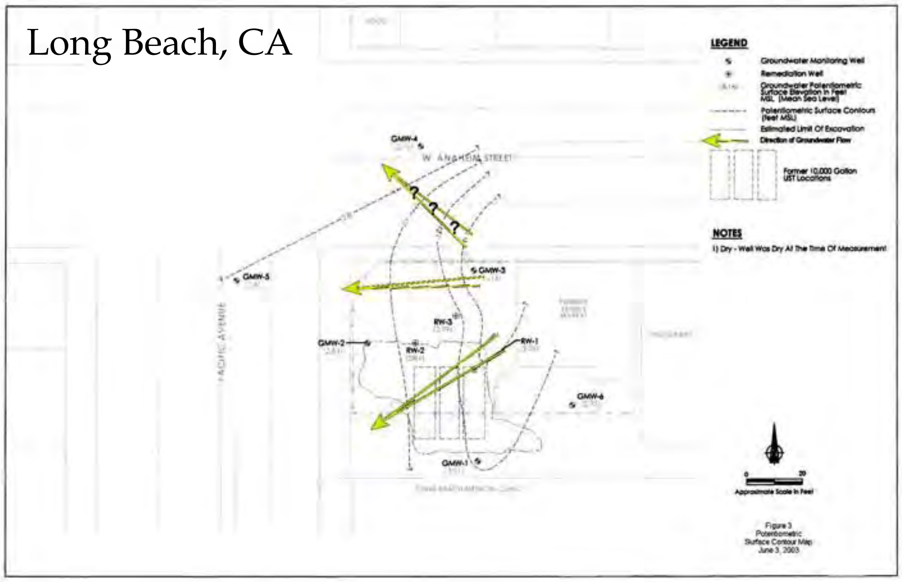
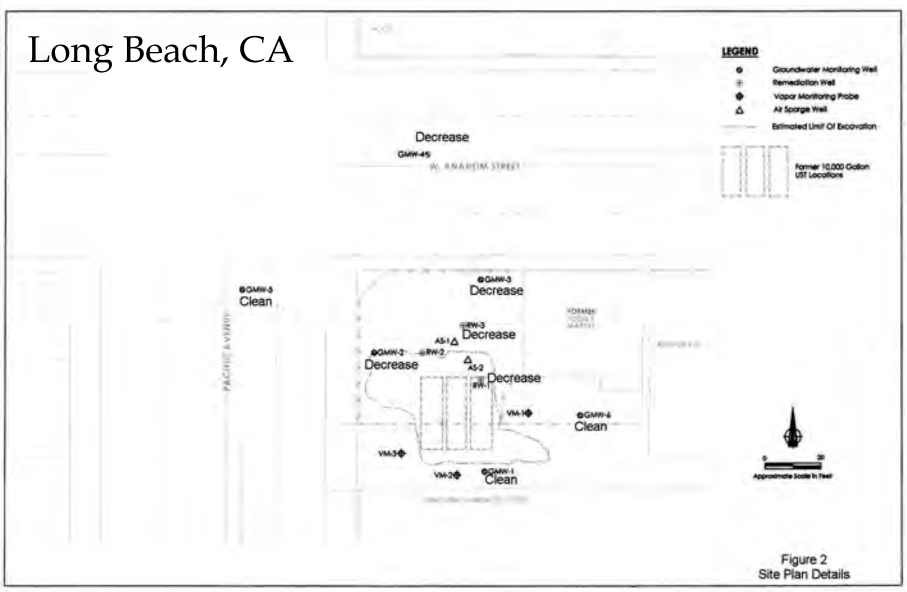
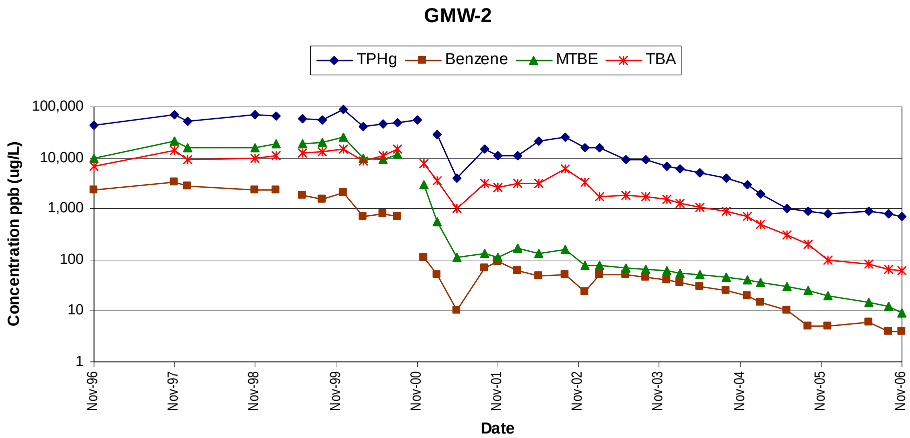
Long Beach, CA



Long Beach, CA



Long Beach, CA



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Channelview, TX: Active System

- Remedial Action
  - ❖Source control
  - ❖Pump and treat
  - ❖In-situ bioremediation
  - ❖Oxygen and nutrient addition
- Site
  - ❖Petrochemical plant setting
  - ❖Leaking process sump
- Source control completed by replacing sump
- Plume defined in detail:
  - ❖Natural attenuation on leading edge
  - ❖Dissolved plume remediation required

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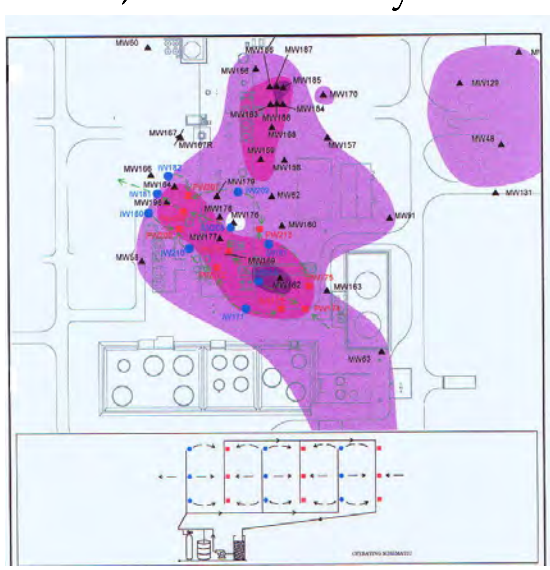
Channelview, TX: Active System

- Design for 12-18 month breakthrough
- Oxygen source and nutrients
- Supplemental food (corn syrup)
- Establish circulation
- Periodic microbe amendment
- Carbon adsorption testing

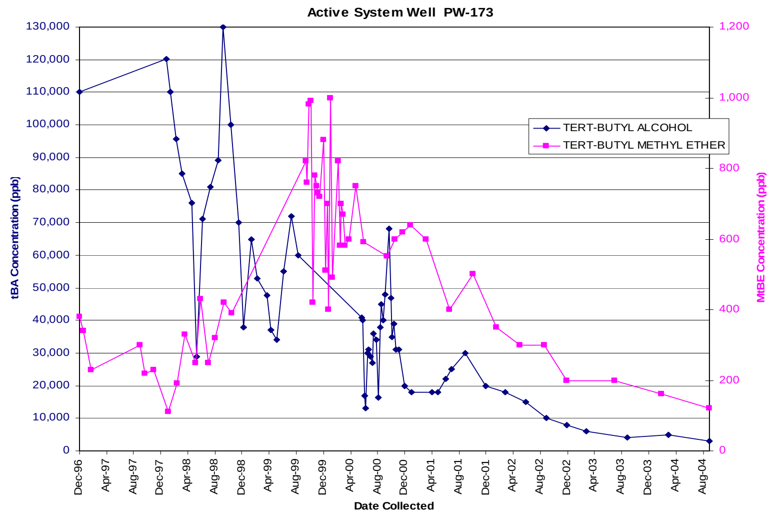
125

Channelview, TX: Well Layout



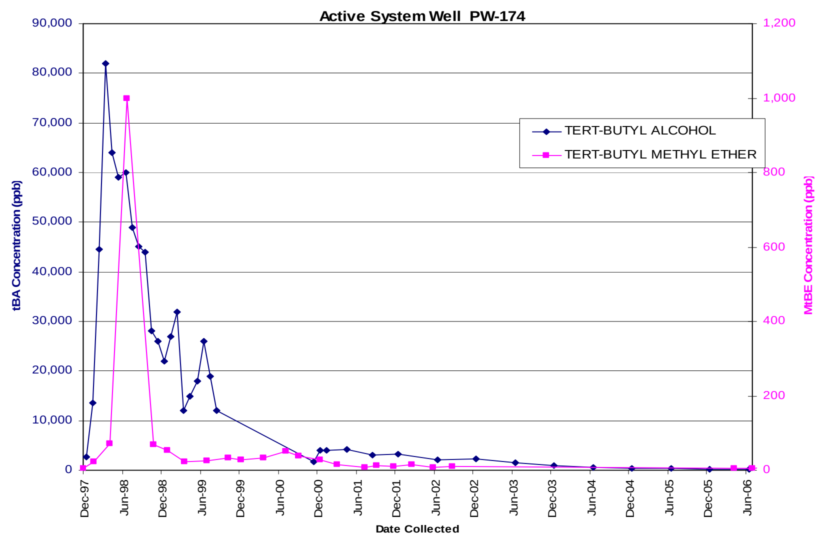
126

Channelview, TX: Progress Chart



127

Channelview, TX: Progress Chart



128

Liberty County Site

■Remedial action

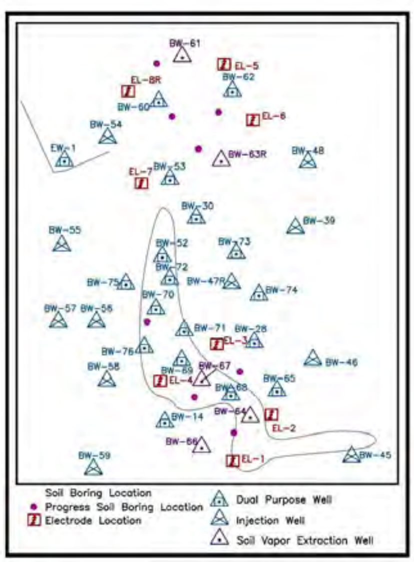
- ❖ Circulating pump and treat
- ❖ In-situ bioremediation
- ❖ Excavation/treatment of pit sludge and soils
- ❖ Thermal desorption and dual phase extraction
- ❖ Natural attenuation on plume fringes

■Site

- ❖ Disposal site for petrochemical waste
- ❖ Localized disposal pits with free phase organic chemicals
- ❖ Disposal pits were excavated 6'-8' deep in silty soil
- ❖ Chemicals of concern: aromatics, TBA
- ❖ Shallow alluvial zone aquifer affected to about 25' bgs

■Potential receptor exposure to free phase and vapors

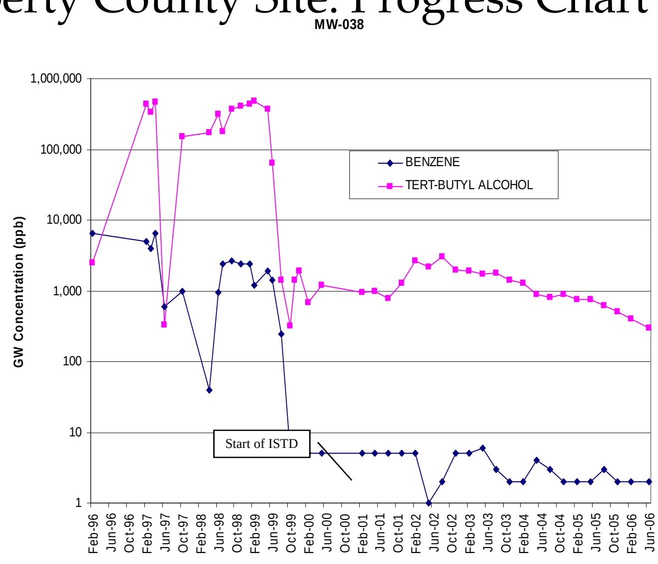
Liberty County Site: ISTD Area Well and Electrode Layout



Liberty County Site: Main Waste ISTD Area

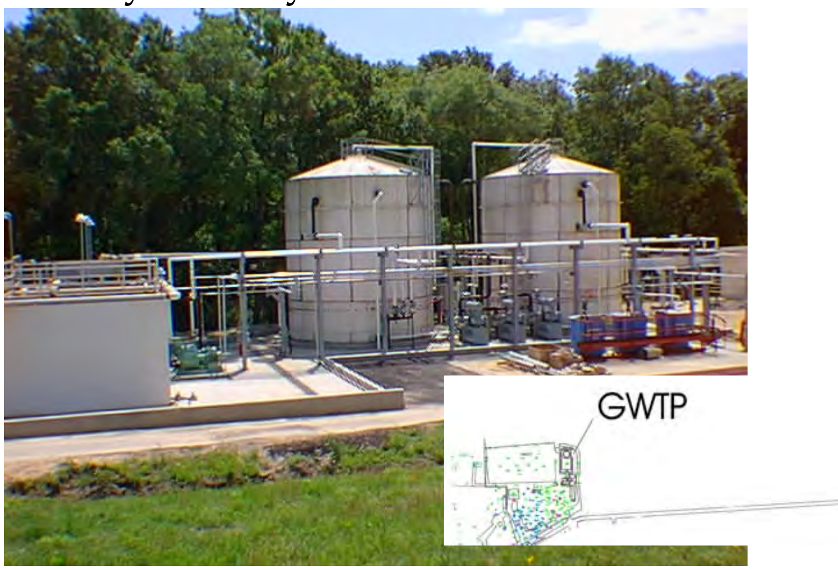
131

Liberty County Site: Progress Chart



132

Liberty County Site: Treatment Plant



133

Liberty County Site: Effluent Bioattenuation

134

Pacific NW Terminal – Ethanol

- 19,000 gallons of neat ethanol released 3/99 from an AST
- Release was in area of pre-existing dissolved hydrocarbon plume
- Ethanol affected both NAPL and dissolved hydrocarbons

Buscheck et al., 2001

135

Pacific NW Terminal – Site Setting

- Between 0 and 30 feet of fill (sand, silty sand) – primary zone for hydrocarbons
- Under fill to 50 feet bgs is alluvium (clayey silt with sand and organics)
- Basalt at 50 feet
- GW in fill and alluvium flows east
  - ❖DTW = 2-14 feet
  - ❖dh/dx = 0.01
  - ❖K_{fill} = 35 feet/day
  - ❖$V_{GWin\ fill}$ ~ 1 foot/day

Buscheck et al., 2001

136

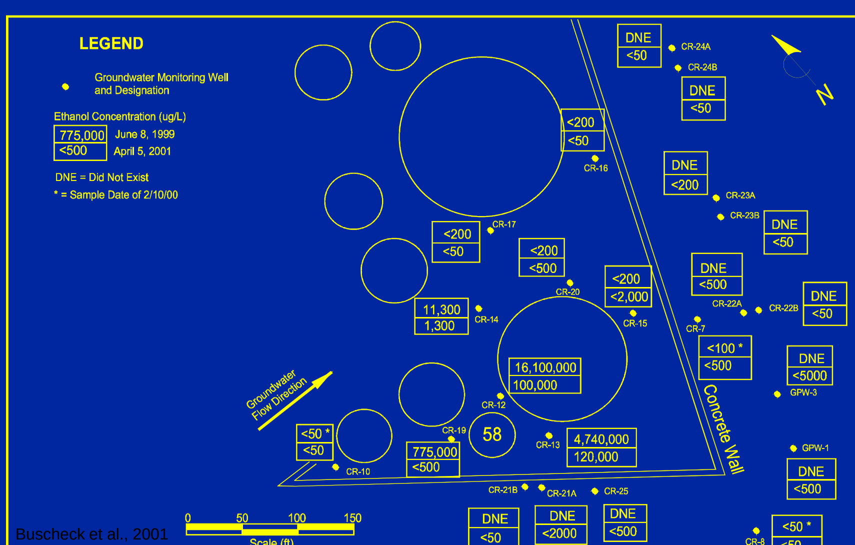
Pacific NW Terminal – Ethanol Bio

- Ethanol detected in 5 wells close to AST (most within 100′)
- Within 6 months, ethanol detected 250′ DG
- Within 6-12 months, attenuation terminated plume expansion
- Dramatic decrease in ethanol conc. from 6/99 to 4/01
  - ❖CR-12: 16,100,000 to <20 ug/l
  - ❖CR-13: 4,740,000 to <20 ug/l
- Strongly reducing conditions
  - ❖Oxygen, sulfate, nitrate depleted
  - ❖Methane generated

Buscheck et al., 2001

137

PNW Ethanol Concentrations 6/99 and 4/01



Buscheck et al., 2001

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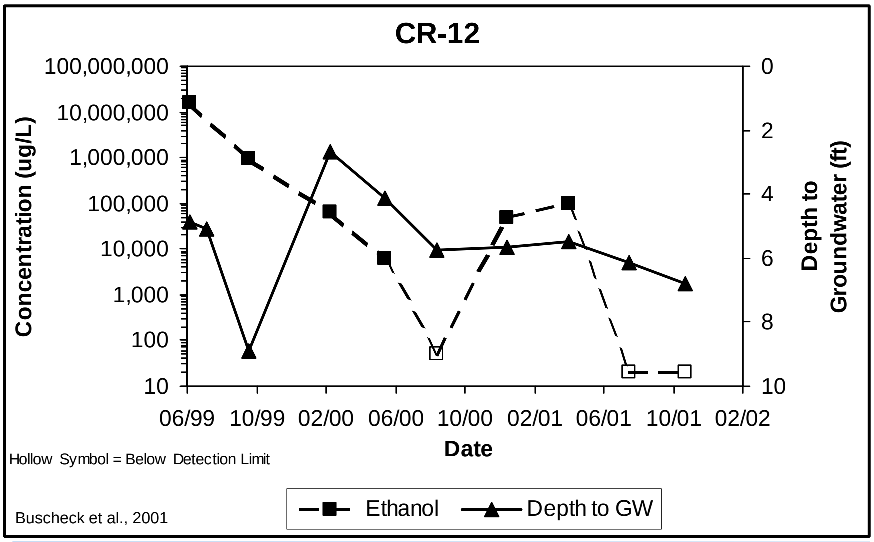
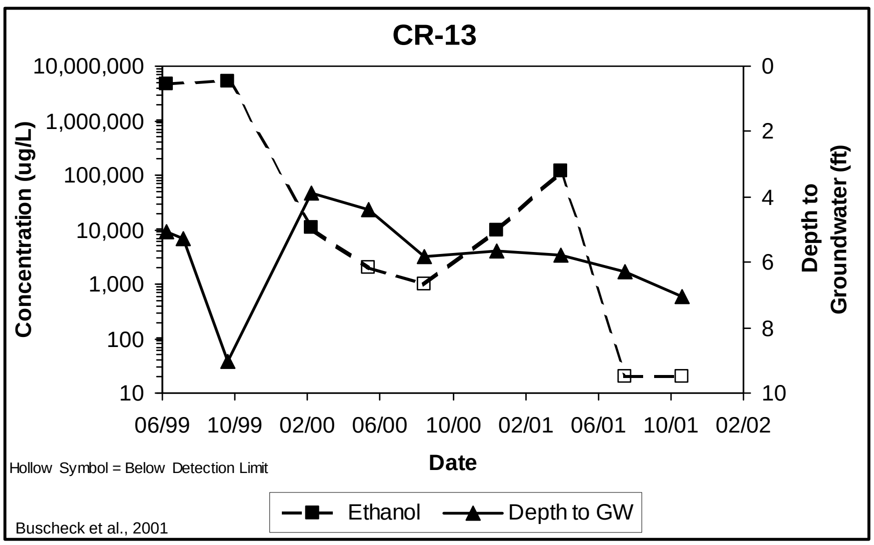
PNW Ethanol and DTW versus Time



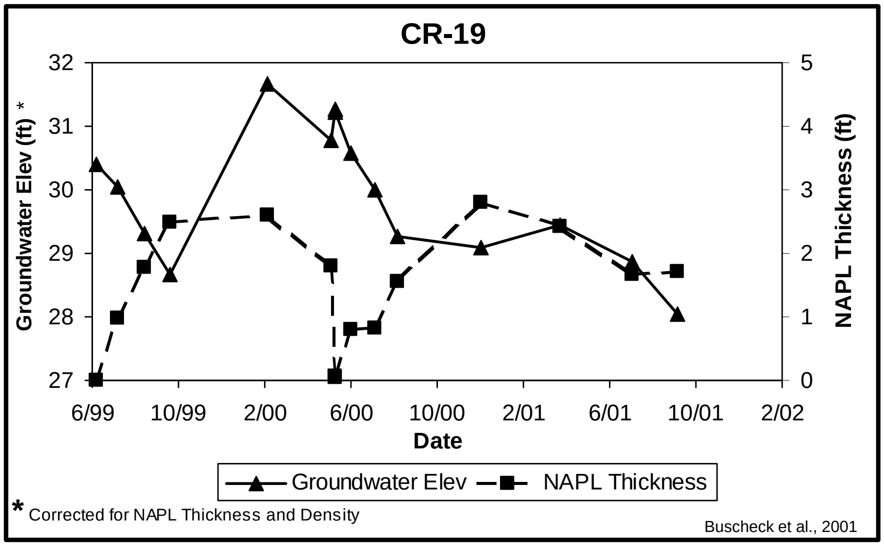
139

PNW Ethanol and DTW versus Time



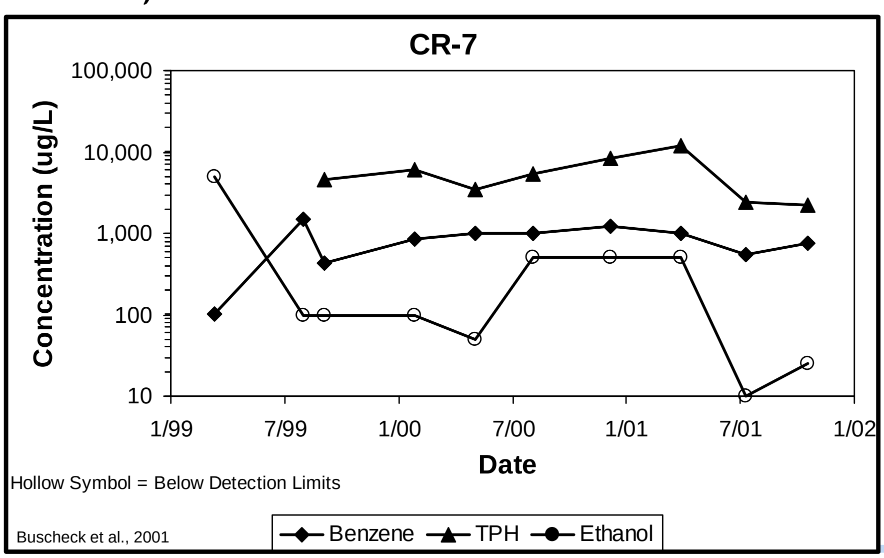
140

PNW Reduction in Interfacial Tension: NAPL Thickness and GW Elevation versus Time



141

Cosolvent Effect and Depletion of Electron Acceptors: Benzene, TPH & Ethanol Concentrations versus Time



142

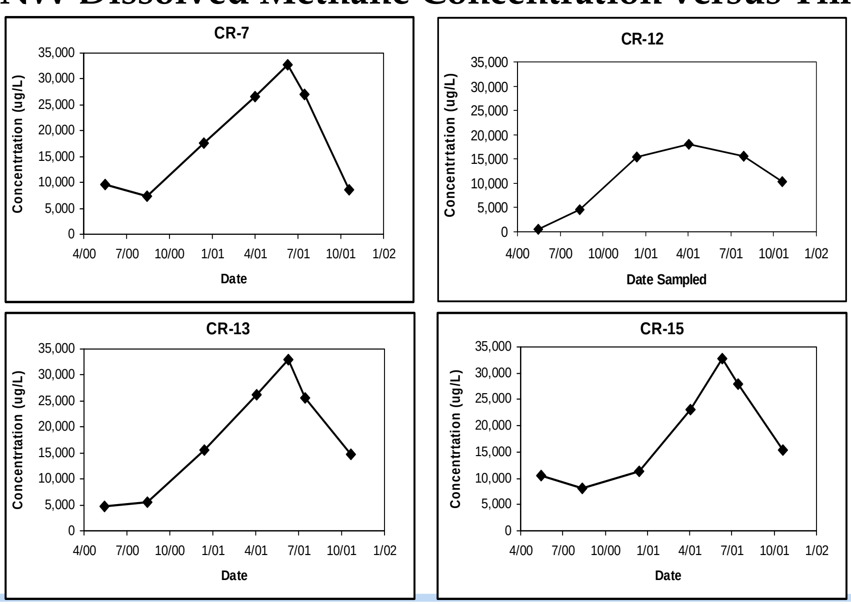
PNW Terminal – Methanogenesis

- Highest methane concs. were measured more than 2 years after the release
- Groundwater
  - ❖ Methane concs. generally increased from 6/00 to 6/01, then decreased a bit in final 7/01 round
  - ❖ Max. > 30,000 ug/l
  - ❖ Methane plume larger than ethanol plume
- Soil Gas
  - ❖ LEL = 50,000 ppmv (5% by volume)
  - ❖ UEL = 150,000 ppmv (15% by volume)
  - ❖ Methane concs. > UEL at 4′ bgs in area of highest dissolved methane

Buscheck et al., 2001

143

PNW Dissolved Methane Concentration versus Time



Buscheck et al., 2001

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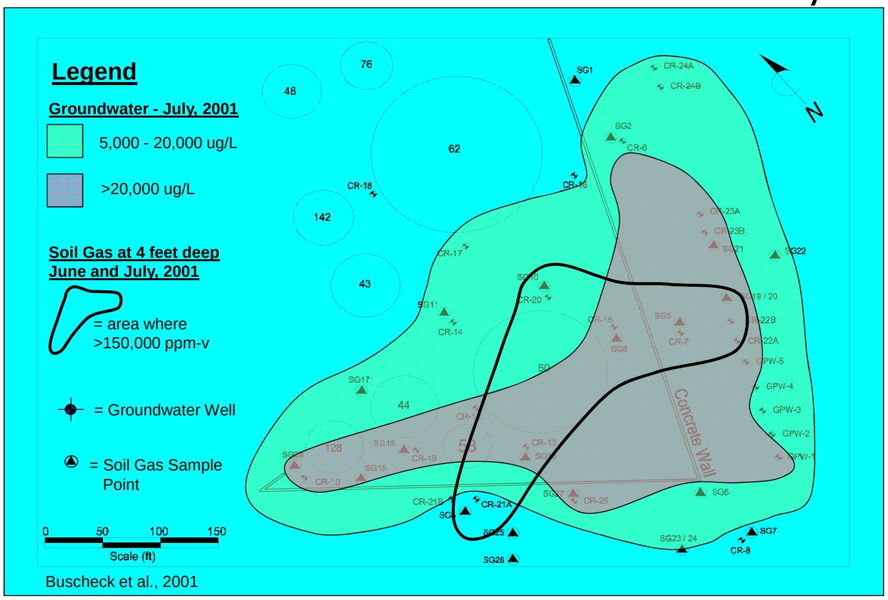
PNW Methane in Groundwater and Soil Gas 7/01



Buscheck et al., 2001

Philomath, OR

Background

- Operating gasoline station and auto repair for 40 years
- Residential and commercial urban location
- Major intersection
- Possible interaction with adjacent commercial activities
- Ten USTs (some "leakers") and some contaminated soils have been removed
- Focused response action over the last 10 years
- Subsurface stratigraphy and hydrogeology are well defined and consistent across the property
- Shallow groundwater at 20' bgs with competent aquitard at about 30' bgs
- No impact on local or regional potable water supplies

Philomath, OR

Environmental Issues

- Shallow soils have been contaminated at several locations
- Residual free-phase gasoline in soils acting as groundwater contamination sources
- BTEX and chlorinated solvents are the chemicals of concern
- December, 1999, DEQ "No Further Action" letter was premature and unrealistic
- Underground piping was source of leaks
- Casual storage/handling of degreasers for 20-30 years

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Philomath, OR

Remediation

- Expand soil/source definition
- Define extent of shallow groundwater plume(s)
- Remove, decontaminate, and salvage all buried piping
- Reopen the 10 former UST areas and remove contaminated soils:
  - Visible free-phase
  - Ship offsite
  - $KMnO_4$ with backfill
- Install 10 dual-phase remediation/monitoring wells:
  - 6" diameter x 25' deep
  - Screen 15' bgs to 25' bgs

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Philomath, OR

Remediation

- SVE at 5 CFM per well:
  - Cycle extraction and injection
  - Treat with carbon
  - Recycle carbon
- Pump and treat/in-situ bio:
  - Focus on BTEX plume
  - Sequence pumping wells
  - Treat with carbon
  - Anaerobic then aerobic
  - $(NH_4)PO_4$, K_2SO_4, KNO_3, O_2 amendments

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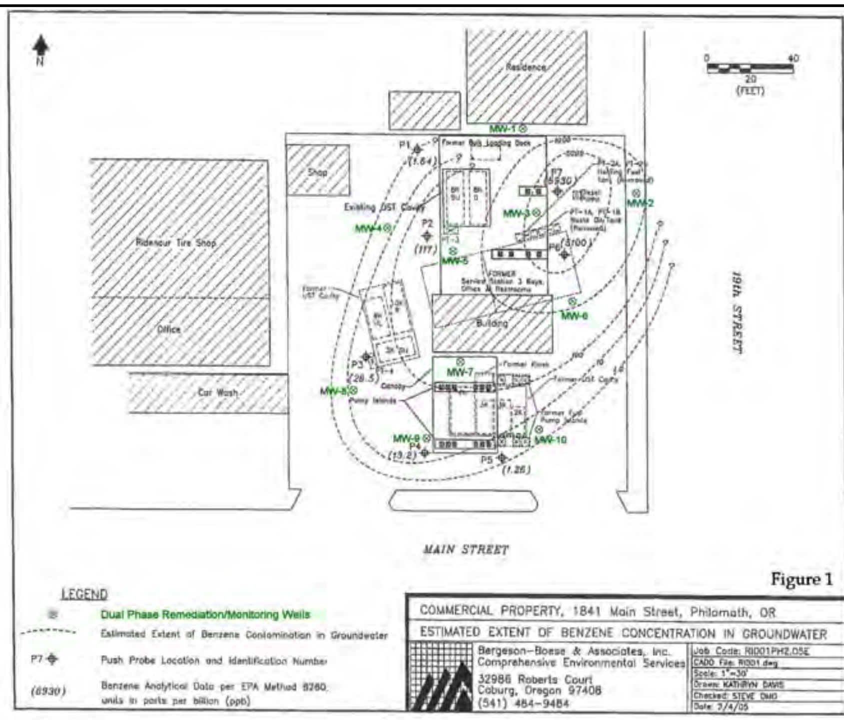

Figure 1

150

Philomath, OR

Costs

■ Soil borings	8,000
■ Trenches	6,000
■ Wells	36,000
■ Excavation, handling, backfill	12,000
■ Disposal (soil)	10,000
■ Piping removal	12,000
■ Concrete, blacktop repair	9,000
■ Chemicals	30,000
■ Supplies	15,000
■ Recycle (carbon)	12,000
■ Analytical	22,000
■ Technical support labor	18,000
■ Supervision	30,000
Total	220,000

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Philomath, OR

Schedule

■ Assessment	2 months
■ Source control	1 month
■ Construction	6 weeks
■ SVE	8 months
■ Pump and treat/in-situ bio	
❖ Anaerobic	12 months
❖ Aerobic	15 months
■ Monitor	10 years

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North Texas Gas Station

- Remedial action
  - ❖In-situ chemical oxidation
- Site
  - ❖Operating, urban, north Texas service station
  - ❖Low-permeability native soils, dry most of the year
  - ❖Tankhold area backfilled with sand/gravel
    - » Retains infiltrated rain at 3-6 ft bgs
- Release and response
  - ❖Product lines disconnected for construction
    - » During heavy rain, water displaced 7,052 gal of gasoline into tankhold area
  - ❖Recovered ~62,000 gal free & dissolved phase

Courtesy URS Corporation, Houston, TX **AEHS Journal-Special Oxygenated Fuels Issue, 2001(page 71); 2002(page 70)**

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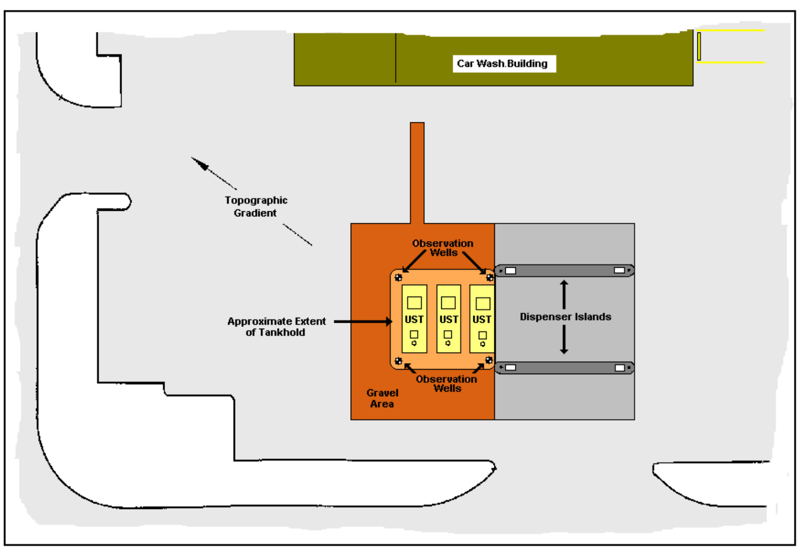
North Texas Gas Station: Site Plan View



Courtesy URS Corporation, Houston, TX

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North Texas Gas Station: Cost Comparison of Gasoline Remediation Technologies

Remediation Technology	Duration (months)	Approximate Costs (x 1,000)				
		Remediation	Sampling	Mgt. & Oversight	Reporting	Total
Pump & Treat[1]	48-120	$130-175[3]	$12 [4]	$8	$5	$155-200
ORC®[2]	36-48	$130-149[5]	$10	$10	$5	$155-174
Chemical Oxidation	14	140	$10	$15	$5	$170

[1] Pump & Treat would likely require a long-term effort and expenses. Overall costs are approximate due to unknown duration.

[2] Oxygen Release Compound mediated in situ biostimulation

[3] Pump and dispose of tankhold hydrocarbon-affected groundwater 20 times.

[4] Includes ten groundwater-monitoring events.

[5] Includes one injection per year for three years.

Courtesy URS Corporation, Houston, TX

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North Texas Gas Station: Remediation Process

Pretreatment Conc. (mg/L)		
	low	high
MTBE	411	475
Benzene	14.4	15.8
Toluene	27.9	28.0
Ethylbenzene	1.45	2.25
Xylene	1.45	2.25

Chemistry & Delivery	
2,700 gal	33% Hydrogen peroxide
600 gal	12% Ferrous sulfate
3,500 psi	Injection pressure

- Reactants' dose based on calculated hydrocarbon mass
- Iron preceded peroxide
- Four peroxide injections were made in an offset pattern
- USTs filled with water during chemical oxidation treatment
- H_2O_2 diluted to 8%-10% before injection

Courtesy URS Corporation, Houston, TX

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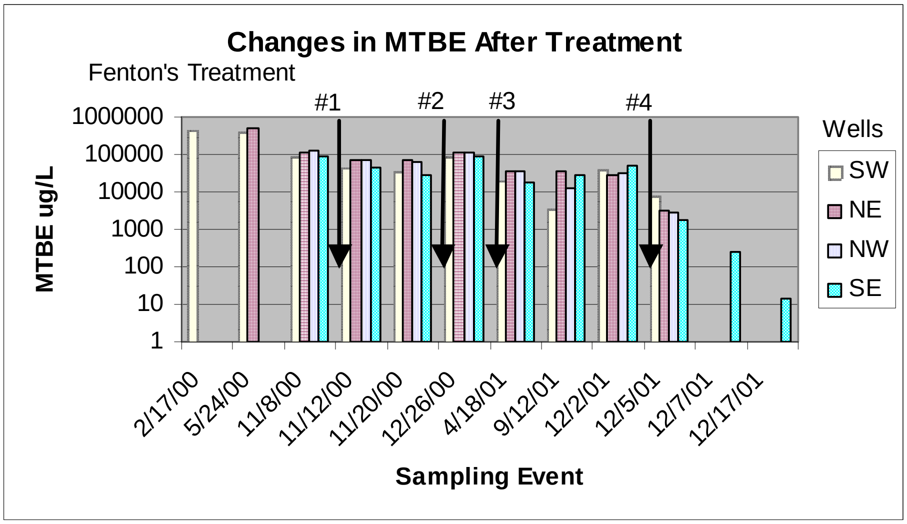
North Texas Gas Station: Two Week Separation Between Ferrous Sulfate and Hydrogen Peroxide Injection

Courtesy URS Corporation, Houston, TX

North Texas Gas Station: Fenton's Reaction Following Pressure Injection

Courtesy URS Corporation, Houston, TX

North Texas Gas Station



Courtesy URS Corporation, Houston, TX

159

North Texas Gas Station: Summary and Lessons Learned

- Chemical oxidation achieved rapid destruction of MTBE and BTEX
- Site was well suited for chemical oxidation
  - Small, well-defined hot spot
  - Highly-permeable treatment zone underlain by low permeability clay
  - Very little background, non-target organic material to consume oxidant
  - Rapid response = small impact area

Courtesy URS Corporation, Houston, TX

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CA Ozonation Site

- Remedial action:
  - Chemical oxidation
- Background
  - Store, service station, office & warehouse
  - Removed 7 USTs 1998
  - Excavated some impacted soil, also GW removed
  - Some inaccessible impacted soil left in place
  - UST pits backfilled with pea gravel & capped with asphalt
  - Now have ASTs & no USTs

Courtesy K-V Associates, Inc., Mashpee, MA

AEHS Journal-2001 Special Oxygenated Fuels Issue (page 77)

161

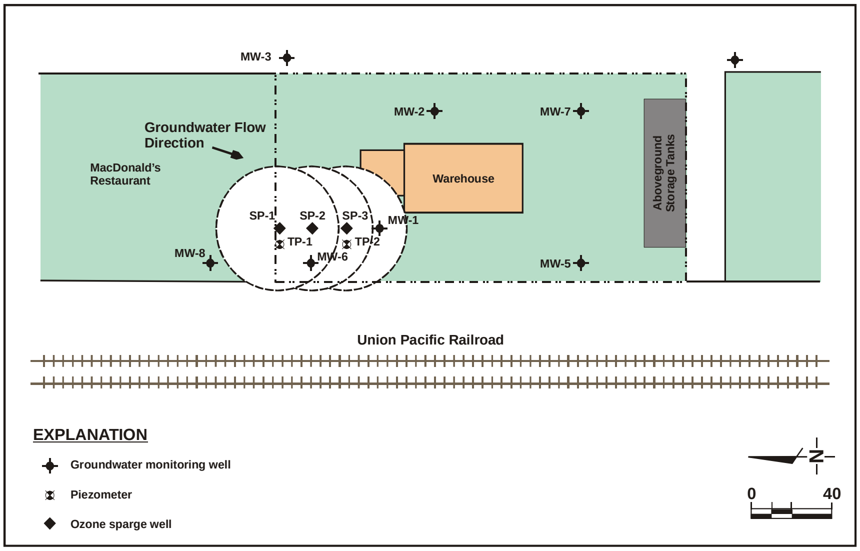
CA Ozonation Site: Hydrogeology and Well Installation

- GW at 6-7 feet bgs
- 3 MWs installed 1993
- 18 borings, 6 more MWs, 2 piezometers, 3 Spargepoints ® installed 2000 for pilot test
- 3 more MWs installed 2001
- 3.5 feet fill over 8.5 feet silty sand over silty sand with clay
- 5 more Spargepoints ® installed for full-scale system covering whole property

Courtesy K-V Associates, Inc., Mashpee, MA

162

CA Site: Pilot Test Wells and Radius of Influence



Courtesy K-V Associates, Inc., Mashpee, MA

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CA Ozonation Site: Pilot Test Plot

	Groundwater* (ug/L)			Soil (mg/kg)	
	Max	Average	Goal	Average	Goal
MTBE	12,000	6,000	5	500	
TBA	870	550	12	500	
TAME		10		10	
TPH	270		**		100
Benzene	<1		<0.5		
	* Contaminated thickness 26 feet				
	**Demonstration of no impact/risk to receptors				

Courtesy K-V Associates, Inc., Mashpee, MA

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CA Site: Total Ozone Demand (grams)

	MTBE	TBA	TAME	SUM
Total VOC Mass in Soil & GW	2,052	575	11	2,638
Stoichiometric Ozone Demand	6,162	2,243	33	8,438
Soil Oxidant Ozone Demand				179
Oxidizable Metals Ozone Demand				0
Other Organics Ozone Demand				20
TOTAL OZONE DEMAND				8,637

Courtesy K-V Associates, Inc., Mashpee, MA

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CA Ozonation Site: Installation

Courtesy K-V Associates, Inc., Mashpee, MA

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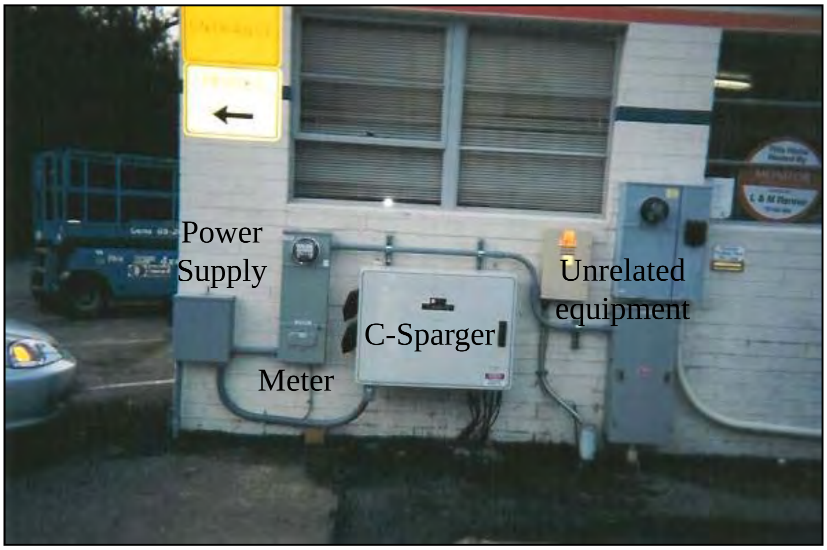
CA Site: KVA C-Sparger® Installation



Courtesy K-V Associates, Inc., Mashpee, MA

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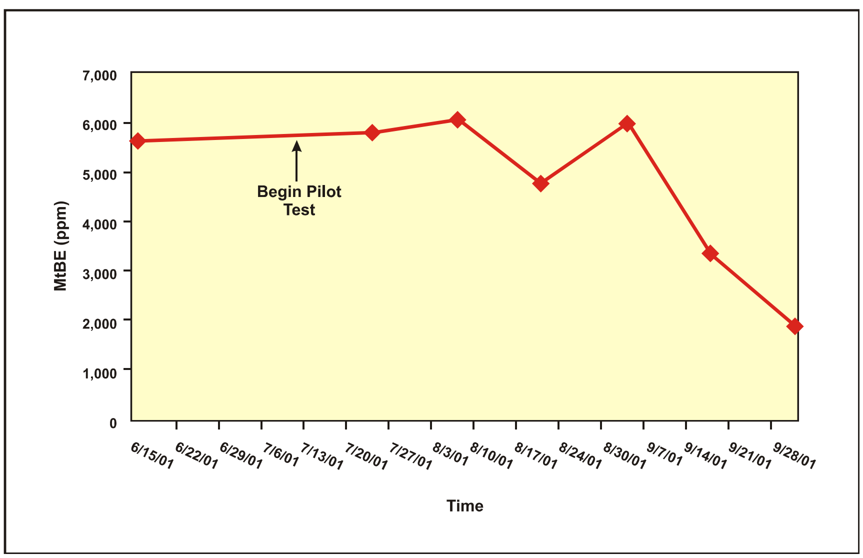
CA Ozonation Site: Removal of MTBE



Courtesy K-V Associates, Inc., Mashpee, MA

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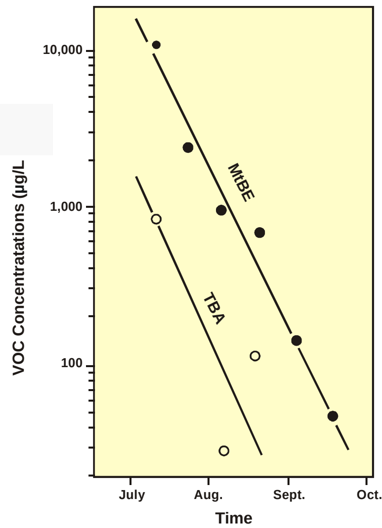
CA Ozonation Site: Removal of MTBE & TBA



MTBE and TBA half-lives:
~ 9 d 8' from inj.
~12 d 16' from inj.

(Doubling the O_3 inj. rate would halve the half-life)

Courtesy K-V Associates, Inc., Mashpee, MA

169

CA Site: Ozone Injection and Results

- O_3 is 12x more soluble than O_2
  - ❖Max. ozone injection conc. = 300 ppmv
  - ❖Typical ozone injection/well = 250 gram/day
  - ❖DO in MW-1, MW-6, TP-1, TP-2: 4.9 to 10.1 mg/l
  - ❖ROI ~ 35 feet
- Fe^{+2} decreased to non-detect (<0.05 mg/l)
  - ❖Oxidized to Fe^{+3}
- Mean GW concentrations after 1 year (ug/l, for pilot test area after, site-wide values are similar):
  - ❖MTBE 254 (4% of initial)
  - ❖TBA 18 (3% of initial)
  - ❖TAME <2.5 (<25% of initial)

Courtesy K-V Associates, Inc., Mashpee, MA

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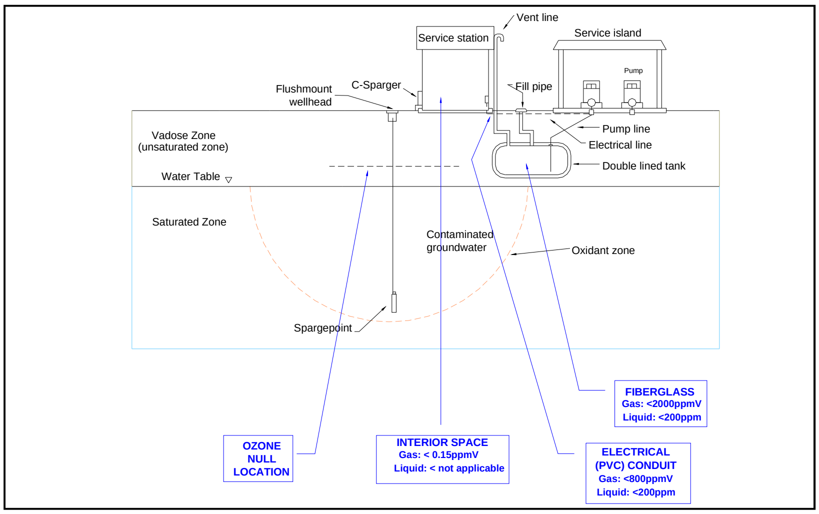
CA Ozonation Site: OSHA & Material Safety



Courtesy K-V Associates, Inc., Mashpee, MA

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Clifton, CO
Farm Co-op Fuel Station

- Background
  - ❖Farm co-op fuel station for 30 years
  - ❖Several USTs and several ASTs
  - ❖Numerous leaks and spills of gasoline
  - ❖Colorado River alluvial floodplain
  - ❖Impacted groundwater is brackish (+ 10,000 mg/l TDS) and near-potable
  - ❖Impacted aquifer is fine sand and silts at 30' to 50' bgs
  - ❖Proximity of major highway impacts excavation options

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Clifton, CO
Farm Co-op Fuel Station

- Remediation
  - ❖ Excavation of soils with free-phase
    - » Reasonable technical option
    - » Rapid response
    - » Highway and utilities would be impacted
    - » Not practical
  - ❖ Direct oxidation could impact utility corridor

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Clifton, CO
Farm Co-op Fuel Station

- ❖ Soil vapor extraction with groundwater pump and treat
  - » Expand the vadose zone
  - » Focused steam injection
  - » Focused free-phase removal
  - » 40 4" diameter x 40' deep vapor extraction wells with 20' screen
  - » 20 air bubbler lines to selected wells
  - » Free-phase removal via pump or bailer as required

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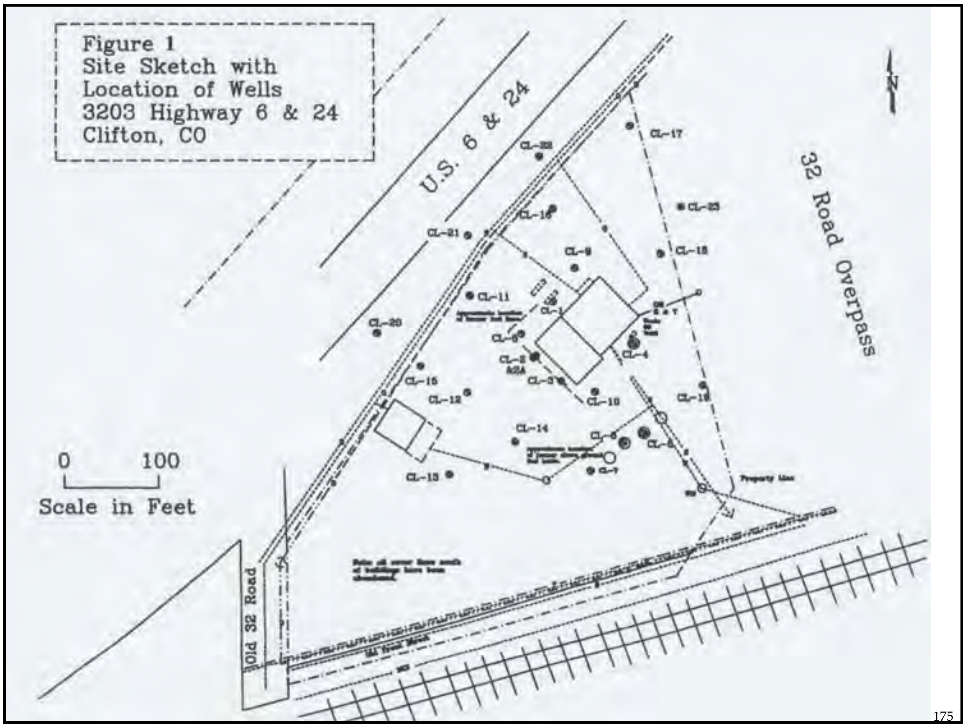


Figure 1
Site Sketch with
Location of Wells
3203 Highway 6 & 24
Clifton, CO
U.S. 6 & 24
32 Road Overpass
Old 32 Road
0 100
Scale in Feet
CL-17
CL-22
CL-23
CL-16
CL-18
CL-21
CL-9
CL-11
CL-20
CL-1
CL-4
CL-2
&2A
CL-3
CL-15
CL-12
CL-10
CL-19
CL-14
CL-6
CL-5
CL-7
CL-13
Property Line
175

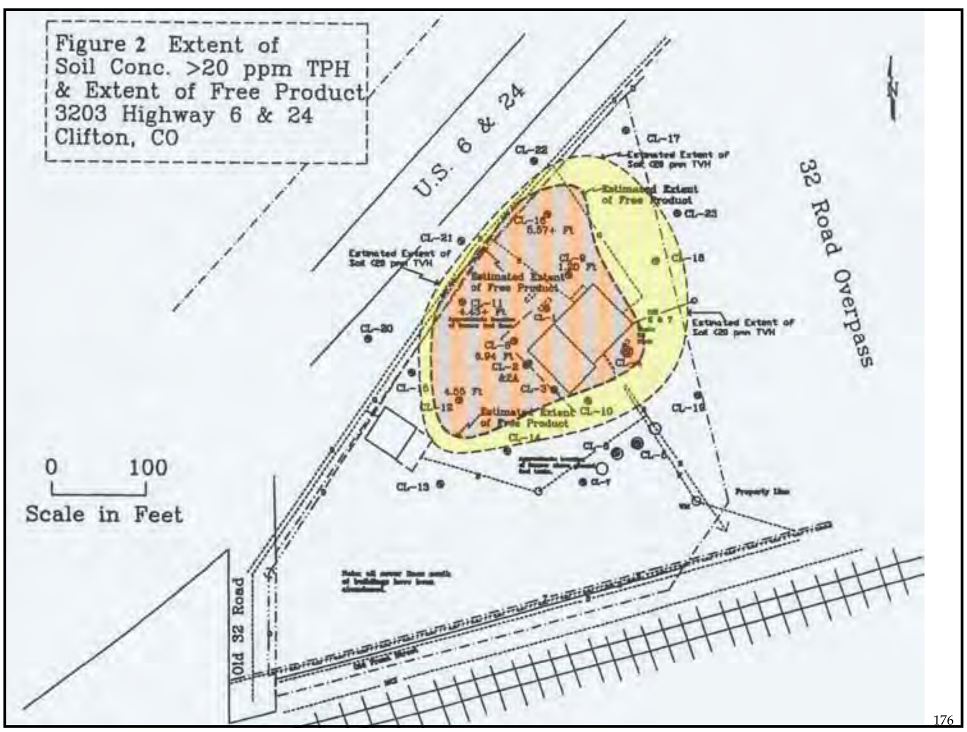


Figure 2 Extent of
Soil Conc. >20 ppm TPH
& Extent of Free Product
3203 Highway 6 & 24
Clifton, CO
U.S. 6 & 24
32 Road Overpass
Old 32 Road
0 100
Scale in Feet
Estimated Extent
of Free Product
6.57+ Ft
4.63+ Ft
5.94 Ft
4.55 Ft
CL-17
CL-22
CL-23
CL-16
CL-18
CL-21
CL-11
CL-20
CL-2
&2A
CL-3
CL-12
CL-10
CL-19
CL-14
CL-6
CL-5
CL-7
CL-13
Property Line
176

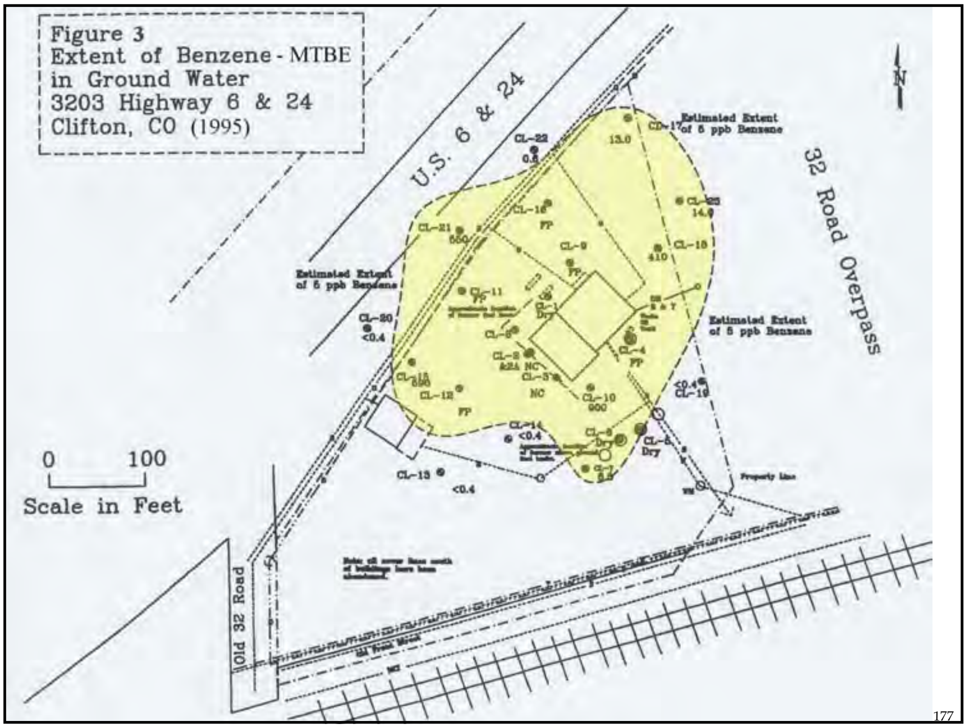


Figure 3
Extent of Benzene - MTBE
in Ground Water
3203 Highway 6 & 24
Clifton, CO (1995)
U.S. 6 & 24
32 Road Overpass
Old 32 Road
Estimated Extent of 5 ppb Benzene
0 100
Scale in Feet
177

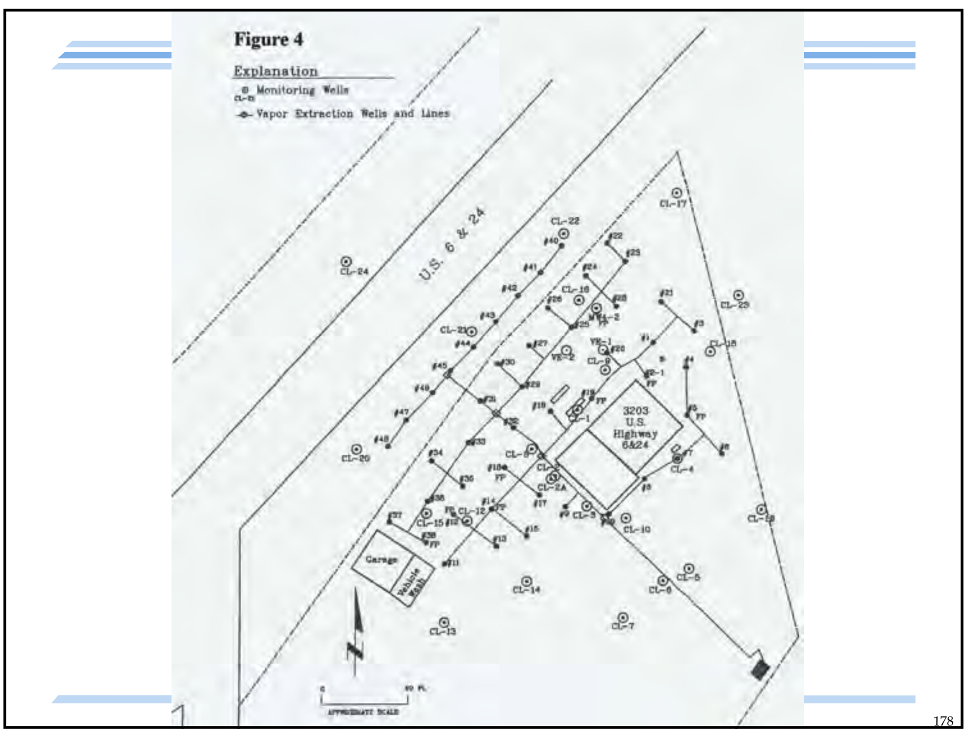
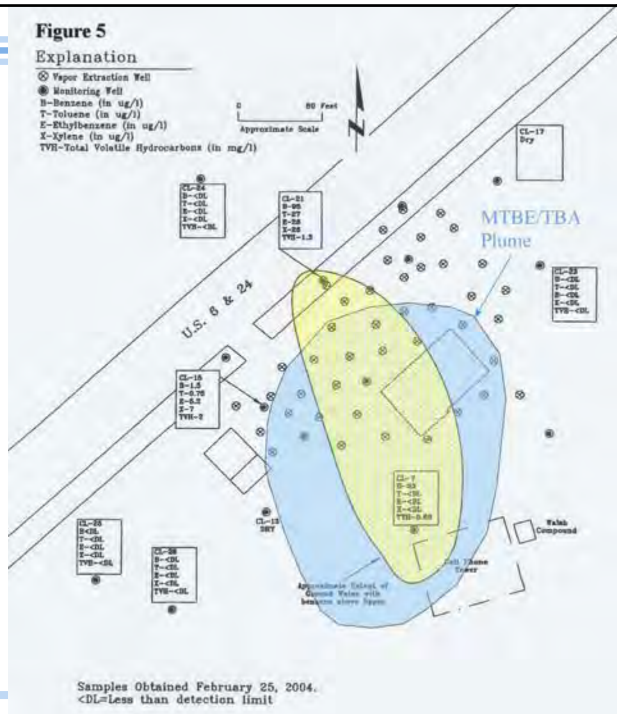


Figure 4
Explanation
Monitoring Wells
Vapor Extraction Wells and Lines
U.S. 6 & 24
3203 U.S. Highway 6&24
Garage
Vehicle Wash
178

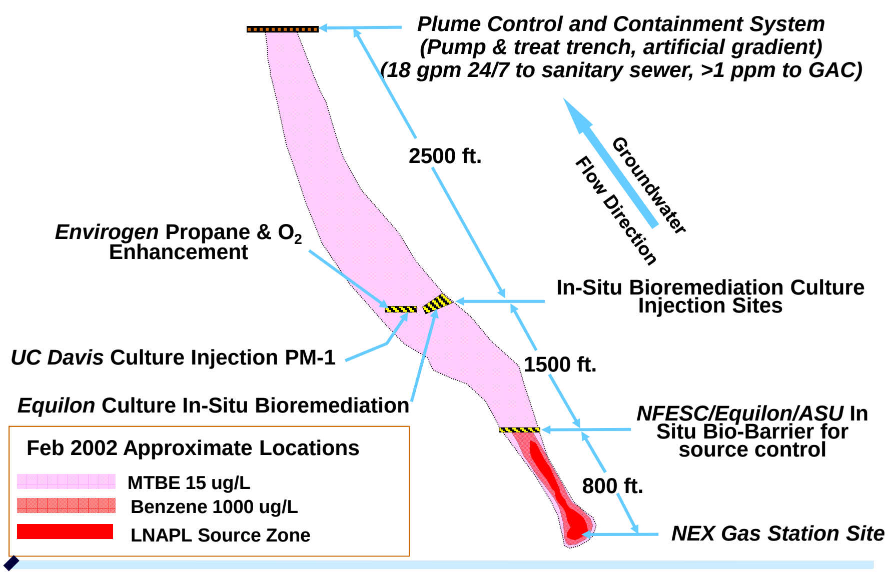


Port Hueneme Site, Ventura County, CA

- Remedial action
  - ❖ Permeable reactive biobarrier
  - ❖ Source control
    - » Excavation
    - » Pump and treat of free product
- Site
  - ❖ LUST at base service station released gasoline
  - ❖ Shallow aquifer, mixed alluvium (sand and gravel)
    - » 10 to 25 feet below ground surface
  - ❖ Gasoline plume following buried stream channel with groundwater flow (averaging 1/3-3/4 ft/d)
  - ❖ Entire aquifer anaerobic (<1 mg/L DO)

AEHS Journal-Special Oxygenated Fuels Issue, 2001(page 6); 2002(page 80)

Port Hueneme Benzene & MTBE Plume



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Scope of Port Hueneme In Situ Demonstrations

- Salinitro et al. *mixed culture* bioaugmentation (Equilon Enterprises, LLC)
  - ❖ Applied MTBE degrading consortium, at 10^9 CFU/gm in a solid matrix below water table
  - ❖ Grows on MTBE as sole carbon and energy source
  - ❖ Supplemental pure oxygen sparging
- Controls
  - ❖ Oxygen sparging alone, indigenous organisms
  - ❖ Intrinsic biodegradation, indigenous organisms

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Scope of Port Hueneme In Situ Demonstrations

- Scow et al. *pure culture* bioaugmentation (UC Davis)
  - Degrades MTBE as sole carbon and energy source
  - Rapid growth on toluene or ethanol
  - Intermittent oxygen sparging at two depths
  - Genetic markers track organism distribution
- Controls
  - Oxygen sparging alone
  - Air sparging alone

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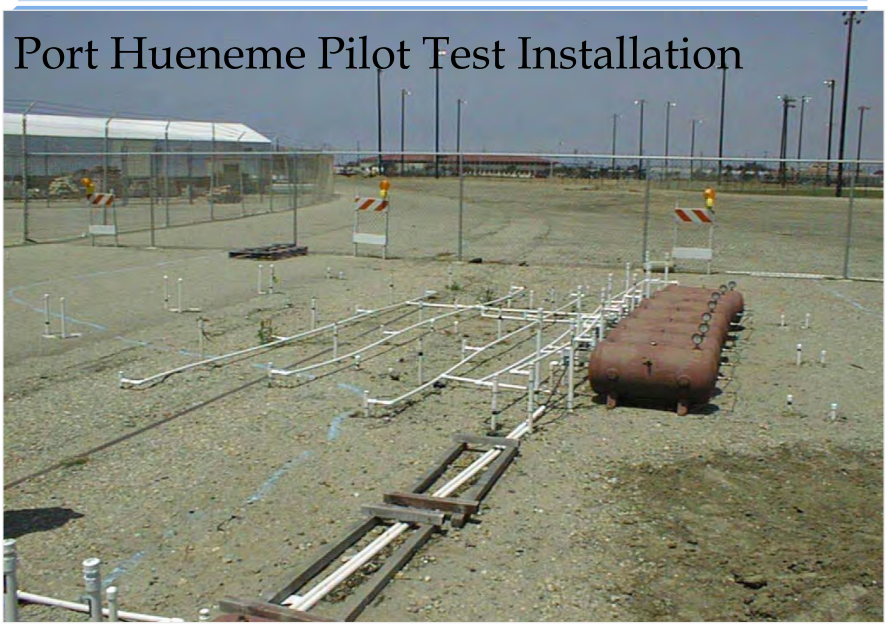
Port Hueneme Pilot Test Installation



Courtesy H20 R2 Consultants

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Port Hueneme: Bioaugmentation Results

- Salinitro (mixed culture)
  - ❖Natural attenuation rate ($t_{1/2}$ = 693 days)
  - ❖Oxygen sparging rate ($t_{1/2}$ = 99 days)
  - ❖Bioaugmentation rate ($t_{1/2}$ = 18 days)
- Scow (PM-1 pure culture)
  - ❖MTBE conc. reduced from 6 ppm to < 50 ppb
    - » bioaugmented test plot
    - » control (air/oxygen sparge) plots,
  - ❖TBA was not found

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Port Hueneme: Pilot Study Conclusions

- Indigenous microorganisms capable of degrading MTBE are stimulated by oxygen or aeration
  - ❖Microbes are more widespread than previously thought
- Bioaugmentation as a biobarrier transect
  - ❖Increases in situ degradation rate
  - ❖Decreases MTBE half-life in the field

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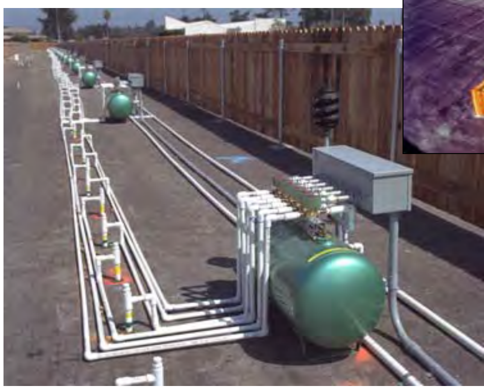
Port Hueneme: Scaled-up Biobarrier



Winner of 2001 NGWA Outstanding Project in Ground Water Remediation Award

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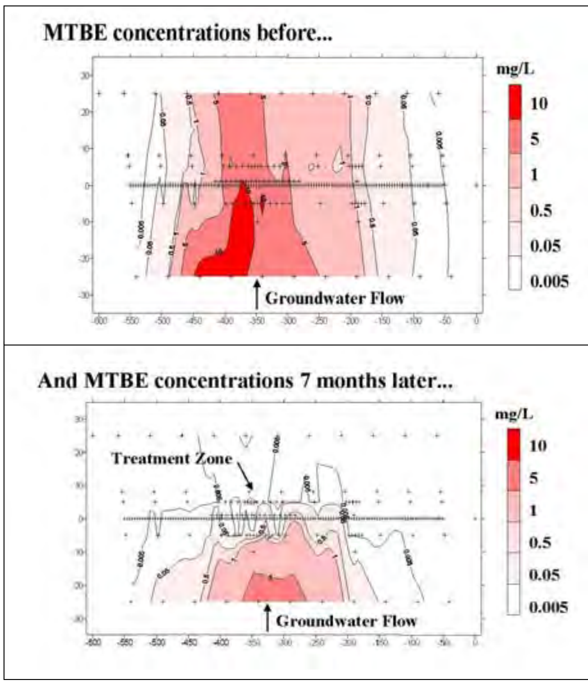
Port Hueneme MTBE Bio-Barrier



99.9% MTBE reduction

66% lower O&M Costs compared to conventional Pump &Treat systems

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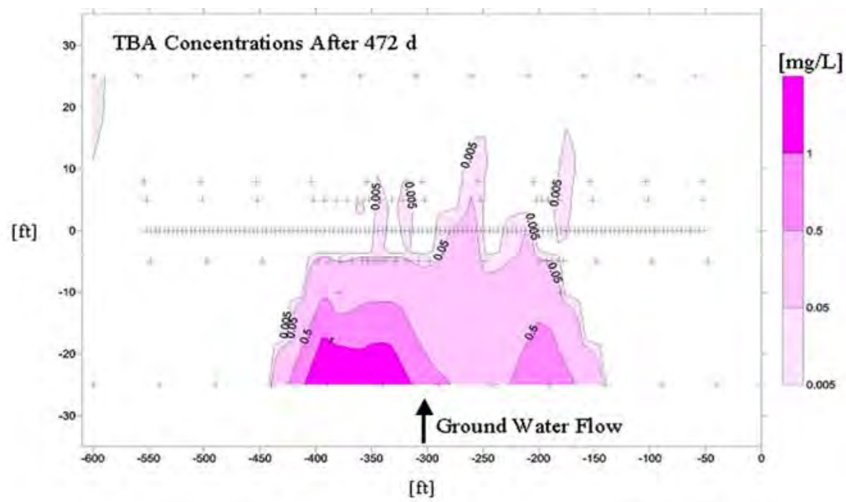
Port Hueneme Biobarrier Results: TBA



Bruce et al., 2002.

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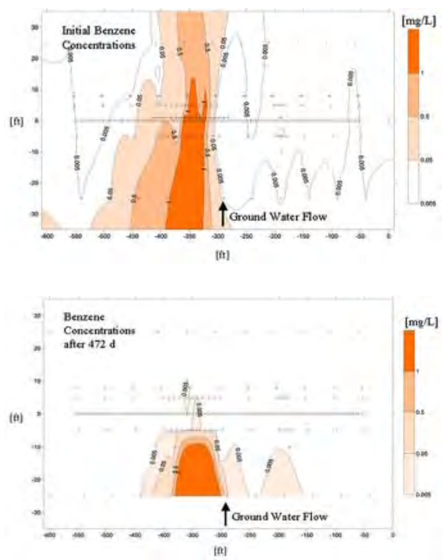
Port Hueneme Biobarrier Results: Benzene



- MWs at either end of biobarrier indicate GW is going through, not around, the bio-barrier
- Water Board approved biobarrier as final remedy for the plume

Bruce et al., 2002

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Bedford, New Hampshire, Bioreactor

Challenging System

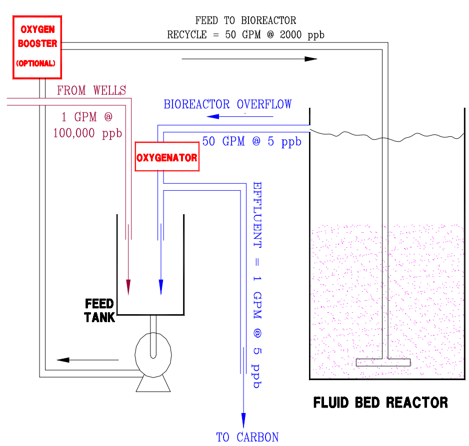
Weather proof enclosure

- Influent groundwater
  - BTEX (30,000 ppb)
  - MTBE (80,000 ppb)
  - TBA (8,000 ppb)
  - Iron (13 ppm)
  - Manganese (13 ppm)
- Suggest large bioreactor
- System includes:
  - Fe/Mn pretreatment
  - Air stripper
  - Small bioreactor
  - 500# carbon polishers
  - Discharge to on-site dry well

Courtesy: ERI

ERI Fluidized Bioreactor Operation

- Two-phase (solid-liquid)
- Re-oxygenation by air or O_2 in packed tower
- Recycle dilutes feed
- Recycle rate is fixed @ 50 gpm to fluidize the bed
- HRT ~ 20 minutes
- Feed adjusted for conc.
- Feed – 100,000 ppb-gpm, or 1.3 pounds/day

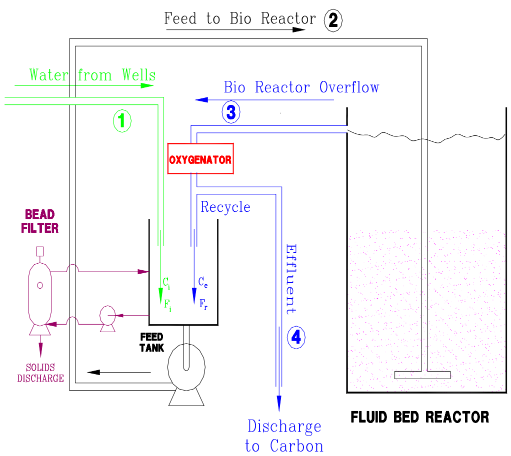


Environmental Resolutions, Inc.

ERI Bead Filter Operation

Bead filter handles the solids (Fe, Mn, hardness precipitates)

- Separate recycle loop
- Upflow until solids accumulate
- Isolate bead filter to backwash
- Beat the cake off the beads
- Allow beads to rise
- Filter cake will sink
- Take cake out as slurry
- Put filter back on line
- 1 drum/6 months typical
  - ❖ Non-hazardous



ERI FBR Placement in Treatment Train

- Upstream
  - ❖ Control source
  - ❖ Remove gross free product
  - ❖ Remove high BTEX (e.g., by air stripping or GAC)
  - ❖ Particulate filter
- Downstream
  - ❖ Particulate filter to remove bugs
  - ❖ GAC
    - » Polishing, and to handle upsets
    - » Very infrequent carbon changeouts

Air Stripper

4 trays
250-300 cfm
Up to 5 gpm

Courtesy: ERI 195

Carbon Vessels

Courtesy: ERI 196

- Bio-500 bioreactor – green
- Oxygenation tower - white
- Nutrient feed drum - blue
- Spa heater loop - gray
- Stripper effective for BTEX, MTBE, TAME
- TBA is removed in bioreactor
- Fe comes out in stripper and must be water blasted off
- Mn comes out in the Bio-500 - much can be siphoned off as a slurry
- Fe/Mn pretreatment added 8/05

Bedford, New Hampshire, Bioreactor

Courtesy: ERI

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ERI Bioreactor O&M

- Weekly:
  - ❖Measure DO, pH, temperature
  - ❖Record flow data
  - ❖Gauge depth to sand
  - ❖Backwash bead filter
  - ❖Fill nutrient drum
  - ❖Check pressures
- Periodically:
  - ❖Influent and effluent sampling for VOCs
  - ❖Field test for nitrogen
- Respond if recirculation stops

Environmental Resolutions, Inc.

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Bedford NH Bioreactor Data

Date	Flow (gpm)	Temperature (degrees F)	Bioreactor TBA (ug/l) Influent	Effluent	Notes
2/15/05	1.4	65	6,440	<20	
2/22/05	1.5	63	4,930	27	
2/28/05	1.4	65	5,820	<20	
3/7/05	1.4	80	6,320	<20	
3/14/05	0.5	77	3,570	<20	
4/5/05	0.9	72	2,770	<20	
5/2/05	0.8	67	4,230	<20	
6/28/05	1.5	81	1,230	<20	
7/19/05	2.0	86	608	<20	
7/20/05	1.0	79	574	<20	
8/12/05	2.0	76	<20	<20	
8/22/05	1.8	73	890	<20	
9/20/05	0.9	75	374	<20	

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Bedford NH Bioreactor Data

Date	Flow (gpm)	Temperature (degrees F)	Bioreactor TBA (ug/l) Influent	Effluent	Notes
10/22/05	1.7	60	3,930	<20	Record rainfall; new well
11/4/05	4.9	54	7,210	4,030	on line; increase loading
11/5/05	4.9	54	4,590	1,820	5-fold; decreased temp.
11/28/05	4.9	56	1,940	540	
12/31/05	2.7	57	490	<20	
1/20/06	3.9	56	1,600	34	
2/13/06	3.3	51	1,480	<20	
3/13/06	4.3	55	245	<20	
4/14/06	4.4	57	276	<20	
5/19/06	2.2	65	70	<20	
6/5/06	4.6	59	185	<20	
6/26/06	5.8	64	912	<20	25% stripper bypass
7/10/06	5.1	64	417	<20	50% stripper bypass
7/21/06	4.5	65	258	<20	75% stripper bypass
8/4/06	4.2	61	<160	<20	100% stripper bypass
9/8/06	4.3	64	NA	<20	100% stripper bypass

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Bedford NH – Recent MTBE and BTEX Data

	Bioreactor MTBE (ug/l)		Bioreactor BTEX (ug/l)		
Date	Influent	Effluent	Influent	Effluent	Notes
6/5/06	51	19	ND	ND	0% stripper bypass
6/26/06	530	46	663	ND	25% stripper bypass
7/10/06	>1,900	16	707	ND	50% stripper bypass
7/21/06	2,990	29	579	ND	75% stripper bypass
8/4/06	2,410	42	562	ND	100% stripper bypass
9/8/06	NA	104	NA	ND	100% stripper bypass

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Bedford NH

- Bioreactor destroyed TBA to below standard (40 ug/l) except in 11/05 during period of:
  - Drastically increased TBA mass loading to bioreactor
  - Decreased temperature
  - Malfunctioning iron/manganese pretreatment system
- Dissolved oxygen concentrations up to 38 mg/l have been achieved by oxygen booster
- Air stripper is now bypassed - bioreactor treats all BTEX, TAME, MTBE, as well as TBA
- GAC is now bypassed – oxygenated water with bugs discharged to GW, promoting ISB
- Possible future changes:
  - Allow bioreactor to acclimate to gradually decreasing water temperatures
  - Increase groundwater flow rate as appropriate

Courtesy: ERI

202

Bayport, TX Surface Spills

- Remedial action
  - ❖Source control
    - » Leaks/spills stopped
  - ❖Pump and treat
  - ❖Permeable reactive barrier
  - ❖Monitor source and plume to confirm stability
  - ❖Proof of natural attenuation by carbon isotope study
- Site
  - ❖Petrochemical plant setting
  - ❖Leaking TBA process lines and valves
  - ❖Shallow groundwater in interbedded alluvium

Day and Gulliver, 2003

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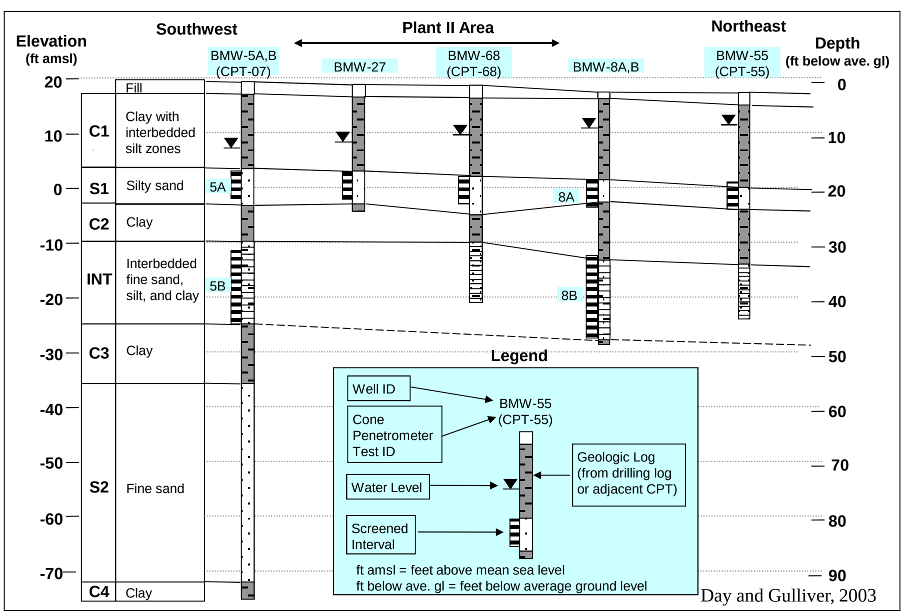

Day and Gulliver, 2003

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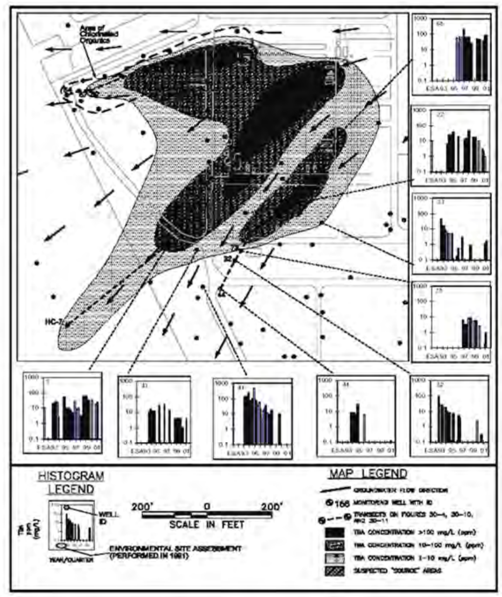
Bayport, Texas TBA MNA Case Study - Plume

- Bifurcated plume
- Northern lobe has CVOCs and TBA
- Southern part of plume – TBA the only significant compound
- Concs. decreasing over time on fringes suggest NA is occurring



Day and Gulliver, 2003

Bayport, Texas: Carbon Isotope Analysis to Document Biodegradation

- Biodegradation is slightly faster for TBA with ^{12}C than ^{13}C
  - ❖ Easier for bugs to eat lighter isotopes because of weaker bonds
- Carbon isotope results reported as delta C
  - ❖ Delta $^{13}C = (R_s/R_r - 1) \times 1{,}000$
    - » where:
    - » R_s = $^{13}C/^{12}C$ ratio of the sample
    - » R_r = $^{13}C/^{12}C$ ratio of an international standard

Day and Gulliver, 2003

Bayport, Texas: Carbon Isotope Analysis

- Atmospheric carbon has delta C of -7 (background)
- Fossil hydrocarbons (including the raw material for TBA) are depleted in ^{13}C
  - ❖Delta C of original TBA product is -29 in this study
- ^{13}C enrichment (i.e., biodegradation) corresponds to less negative delta C values
- Delta C values
  - ❖ -22 near the plume fringe
  - ❖ -28 in high conc. areas (TBA > 10 mg/l)
  - ❖ These results indicate that substantial biodegradation occurs at the edges of the plume

Day and Gulliver, 2003

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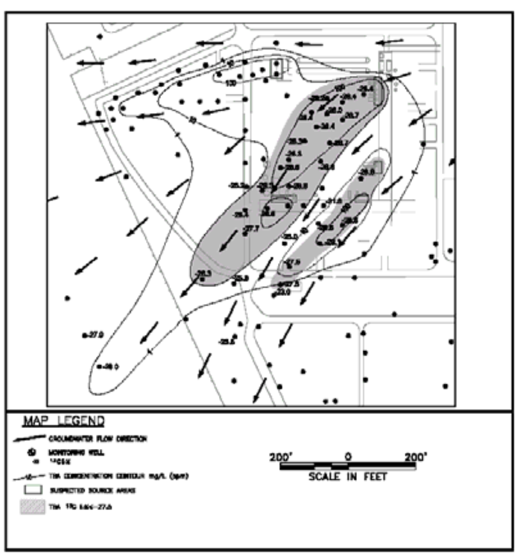
Bayport, Texas: Delta C Values



Day and Gulliver, 2003

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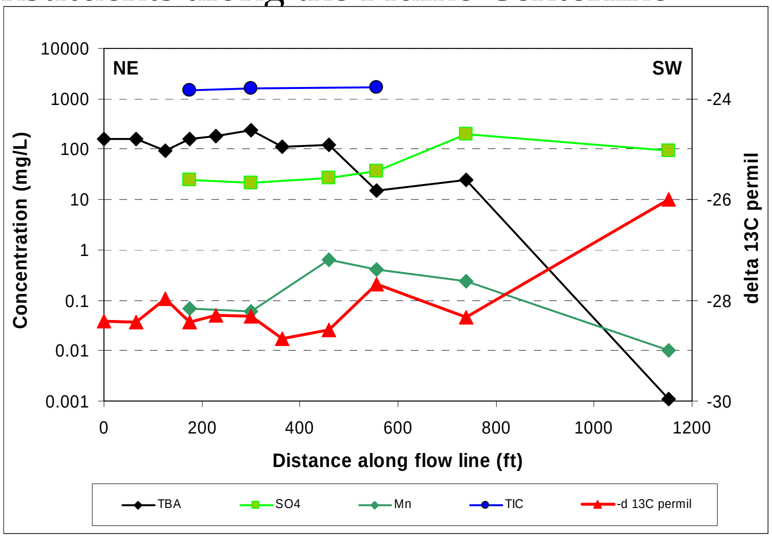
Bayport, Texas: Variation of Selected Constituents along the Plume Centerline



Day and Gulliver, 2003

Westheimer & Shepherd (Houston, TX)

- Description
  - ❖Operating, independent gas station
  - ❖Adjacent to "old" dry cleaner
  - ❖Leaking gasoline tanks replaced
  - ❖BTEX, MTBE, TBA, TCE, DCE, and VC are the chemicals of concern
  - ❖Groundwater impacted to about 40' bgs
  - ❖Plume has impacted adjacent properties

Westheimer & Shepherd (Houston, TX)

- Remediation
  - ❖ Remove tanks and soils with free-phase
  - ❖ Replace boiler and dry cleaning machine
  - ❖ Secondary containment for "new" dry cleaning machine
  - ❖ Backfill tank area with clean soils and 5 lbs $KMnO_4$ per ton
  - ❖ Soil vapor extraction
    - » Six 6" diameter dual-phase extraction wells
    - » Screened from 15' bgs to 35' bgs
    - » Extract 20 CFM per well
    - » Incinerate vapor for 1st 4 months, then GAC for 8 months

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Westheimer & Shepherd (Houston, TX)

- Remediation (continued)
  - ❖ Groundwater pump and treat
    - » Six 6" diameter dual-phase extraction wells
    - » Pump 0.5 to 1.0 gpm per well
    - » Treat groundwater with UV/ozone (1st 6 months)
    - » Treat groundwater with GAC (months 7-18)
    - » Discharge to POTW

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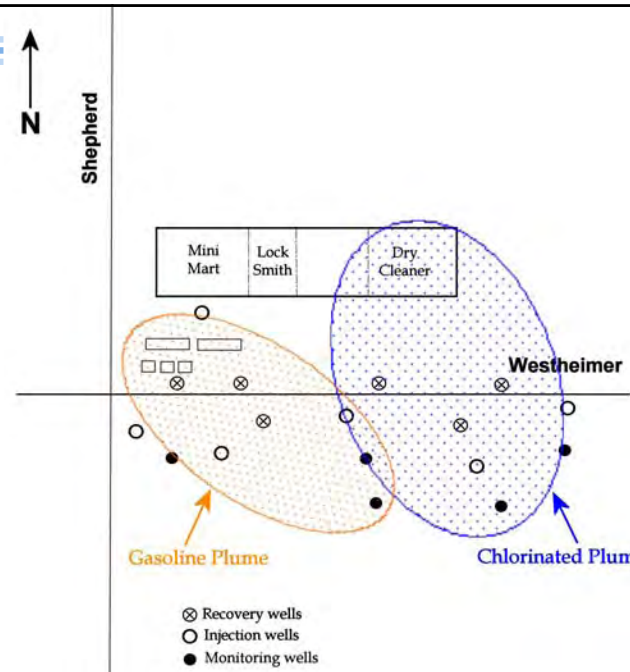

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Westheimer & Shepherd (Houston, TX)

- Remediation (continued)
  - ❖In-situ bioremediation
    - » Six extraction wells
    - » Six 6" diameter injection wells; screened from 20' bgs to 35' bgs
    - » Pump 0.5 to 1.0 gpm per well
    - » Start in-situ bio after 9 months of pump and treat
    - » Treat groundwater with GAC
    - » Add K_2SO_4 (10 ppm) and NH_3NO_3 (5 ppm) and inject
    - » Add 40 ppm O_2 after TCE reaches 1,000 ppb

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Westheimer & Shepherd (Houston, TX)

- Remediation (continued)
  - Monitored natural attenuation
    - 10-year data base
    - 4-year MNA
    - Steady decrease
    - No at-risk receptors

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Westheimer & Shepherd (Houston, TX)

- Results/Comments
  - Significant impact on adjacent properties
  - Construction excavation the only risk
  - Cooperation/access required from adjacent property owners
  - Presence of TCE delayed use of aerobic bioremediation
  - Chlorinated with the BTEX, TBA, and MTBE in the plumes complicated the remediation sequence
  - TBA "stalled" until converted to aerobic in-situ bioremediation

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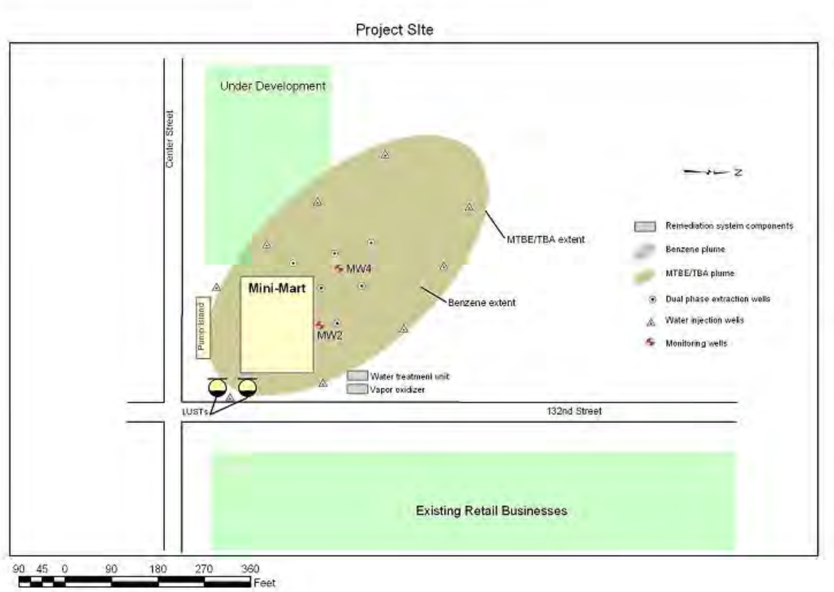
Gas Station/Mini Mart (Omaha, NE)

- Description
  - ❖Two USTs leaked for over 10 years
  - ❖Soil and groundwater impacted to 30' bgs
  - ❖Potable wells ~600' downgradient have been impacted
  - ❖POET systems have been installed at 28 residences
  - ❖Removed LUSTs and 300 yd^3 of contaminated soil
  - ❖Property is prime commercial real estate



Omaha, Nebraska

Gas Station/Mini Mart (Omaha, NE)

- Assessment
  - Two phases of soil borings and monitoring wells
  - Free-phase gasoline in vadose zone soils and in groundwater
  - 100' x 700' dissolved plume in 1st water-bearing zone (20' bgs to 30' bgs)
  - Uniform hydrogeology across the affected area
  - Source control has been effective

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Gas Station/Mini Mart (Omaha, NE)

- Remediation
  - Soil vapor extraction, thermal oxidation, and pump and treat
    - » Free-phase zones
    - » High concentration dissolved zones
  - 200 scfm from six 6" diameter extraction wells
  - Treat vapor with thermal oxidizer for 4 months; then treat with GAC

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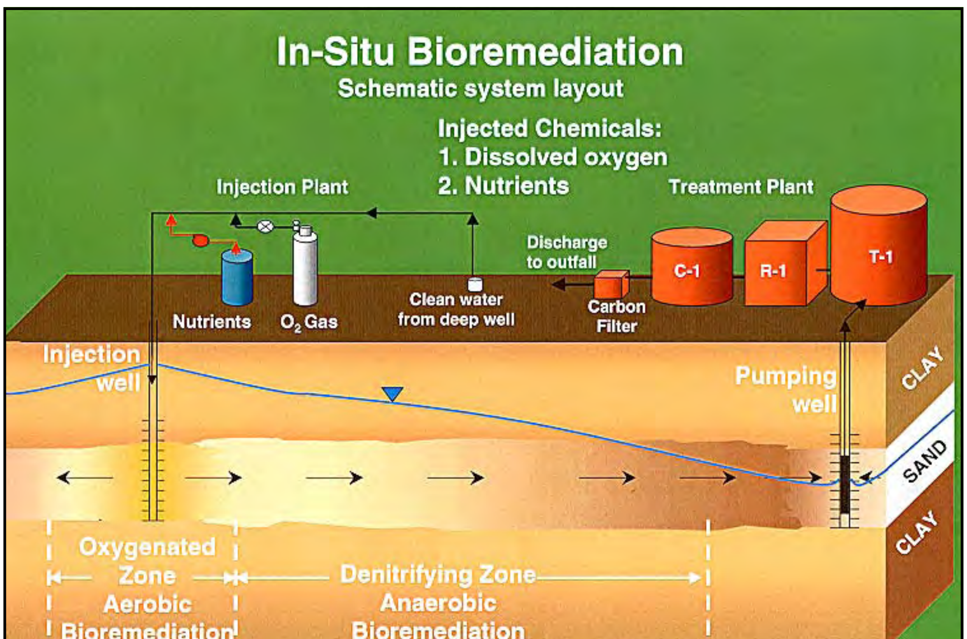
Gas Station/Mini Mart (Omaha, NE)

- Remediation (continued)
  - ❖ Pump and treat 4.5 gpm via activated sludge unit for 9 months; then treat with GAC
  - ❖ Discharge treated water to POTW for 9 months
  - ❖ Convert to circulating in-situ anaerobic bioremediation during month 9
    - » K_2SO_4 – 5 ppm as SO_4
    - » NH_4NO_3 – 10 ppm as NO_3
  - ❖ Convert to monitored natural attenuation
    - » Benzene < 120 ppb
    - » MTBE < 150 ppb
    - » TBA < 200 ppb

221



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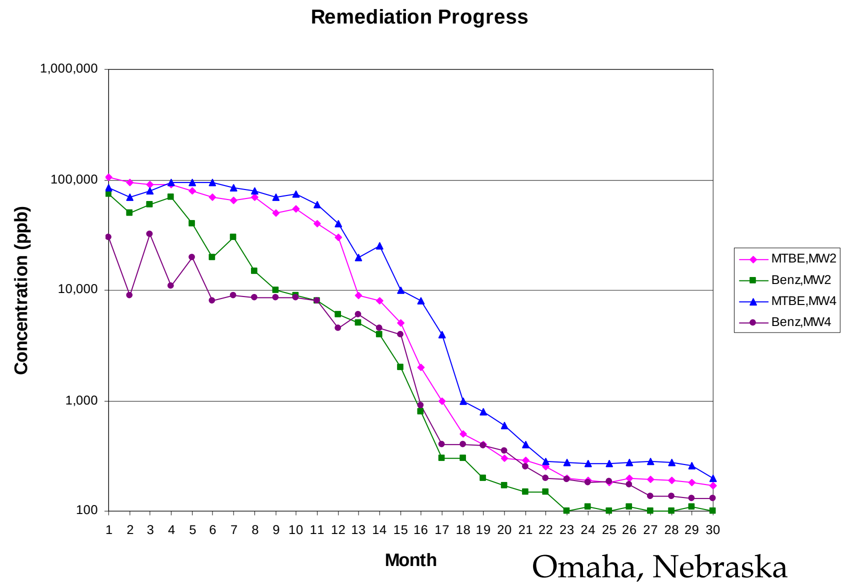

Omaha, Nebraska

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Outline of Workshop

- Introduction
- Properties, fate and transport
- Site assessment and analytical issues
- Applying remedial technologies
- Case studies of remediation
- *Conclusion and summary*

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TBA/MTBE/Ethanol Remediation Summary

- ❖ MTBE and TBA impacted groundwater has been successfully remediated using proven technology
- ❖ Active remediation of ethanol is rare – biodegrades quickly
- ❖ The presence of TBA with MTBE and BTEX can complicate the response
- ❖ The presence of ethanol can result in longer plumes of other constituents
- ❖ Many plume length studies indicate TBA, MTBE, ethanol, and BTEX plume dimensions are very site-specific
- ❖ TBA and MTBE, due to higher solubility and lower adsorption, will tend to be on the leading edge of plumes

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TBA/MTBE/Ethanol Remediation Summary

- ❖ Ethanol, due to fast biodegradation, will tend to have smaller plume (even though soluble and non-adsorptive)
- ❖ All chemicals dissolved in groundwater move with groundwater flow and respond to recharge and drawdown
- ❖ Spilled or leaked gasoline - with or without TBA, MTBE, or ethanol - is a threat to groundwater
- ❖ Cost-effective technologies have been developed that focus on TBA and MTBE
- ❖ Microorganisms at many sites regularly degrade MTBE and TBA, but not as readily as ethanol

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TBA/MTBE/Ethanol Remediation Summary

- ❖Field experience confirms the widespread existence of natural MTBE, TBA, and ethanol degraders
- ❖Natural attenuation has been demonstrated for TBA, MTBE, and ethanol
- ❖TBA and MTBE in spilled gasoline often increase the remediation duration and cost; few data exist for ethanol impacts
- ❖Remediation costs are site-specific and are largely determined by the duration of the gasoline leak, the adequacy of source control, local groundwater use, and hydrogeological conditions

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Design Issues that Drive the Process

- Receptor protection
- Physical characteristics influence remediation of gasoline constituents:
  - ❖Solubility
  - ❖Vapor pressure
  - ❖Henry's Law constant
  - ❖Adsorption
- Site specific conditions
  - ❖Hydrogeology
  - ❖Migration pathways
  - ❖Utilities, access and other features

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TBA/MTBE/Ethanol Remediation Seminar

Thank you for joining us!

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