

**Bioremediation and Monitored Natural
Attenuation of Volatile Organic Compounds
Seminar**

**NATIONAL GROUND WATER
ASSOCIATION
Petroleum Hydrocarbons and Organic
Chemicals in Ground Water
Houston, Texas
November 2006**

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Bioremediation and Monitored Natural Attenuation of Volatile Organic Compounds Seminar Outline

Introduction

Properties of Gasoline Components

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

Biological Processes

Applying Biological Processes

Technology sequencing
In situ bioremediation
Air sparging
Bioventing
Bioslurping
Permeable reactive barriers
Ex situ bioremediation
Phytoremediation

Natural Attenuation Processes

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

Edinger Dry Cleaner CA – in situ bioremediation of CVOCs
Bedford NH Gas Station – ex situ bioremediation of TBA and other gasoline VOCs
Hainepoint NJ – in situ bioremediation and MNA as part of a remediation sequence for aromatics and CVOCs
Turtle Bayou TX – in situ bioremediation of aromatics, alcohols, and CVOCs
Port Hueneme CA – sparge bio-barrier with bioaugmentation to treat gasoline oxygenates and aromatics
Norge Valley Cleaners CA – anaerobic to aerobic to MNA sequencing for CVOCs remediation
Bayport TX – confirmation of TBA MNA through carbon isotope studies
CEN Electronics – in situ bioremediation of CVOCs and BTEX
Pacific NW Terminal – MNA of ethanol
Pasadena TX Industrial Site – in situ bioremediation of CVOCs
Jacinto Port TX – in situ bioremediation of CVOCs using mobile unit
Vandenberg AFB CA – diffusive oxygen emitter bio-barrier for fuel oxygenates remediation
Fuller Martel Apartments CA – source removal and MNA of CVOCs and gasoline VOCs

Summary and Conclusions

Bioremediation and Monitored Natural Attenuation of VOCs

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This workshop describes aerobic and anaerobic respiration processes that can be exploited in bioremediation and MNA of VOCs. In situ and ex situ bioremediation technologies are explored through case studies that cover a wide range of site conditions and engineered solutions. Methods of demonstrating the types and rates of biodegradation are discussed.

Biographies of Presenters

Ellen Moyer, Ph.D., P.E. is a recognized expert in the assessment and remediation of VOC contamination. She has an M.S. in Environmental Engineering, a Ph.D. in Civil Engineering, and over 20 years of professional experience. 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. She was the lead editor of an *MTBE Remediation Handbook*, now in its second printing. Her Ph.D. research investigated soil vapor extraction, air sparging, and bioventing of gasoline VOCs.

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.

Aerobic and Anaerobic Bioremediation and Monitored Natural Attenuation of VOCs

**Ellen Moyer, Ph.D., P.E.
Greenviroment, LLC**

**Richard Sloan
Chickadee Remediation Co., Houston, TX**

**Petroleum Hydrocarbons and Organic
Chemicals in Groundwater**

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Objectives of the Workshop

Participants will understand:

- Fate and transport characteristics of volatile organic chemicals (VOC)
 - Engineered and natural biological processes
 - Current and emerging bioremediation technologies
 - Overall remediation management
-

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Outline of Workshop

■ *Introduction*

- Physical properties
- Biological processes
- Applying biological technologies
- Natural attenuation processes
- Case studies
- Conclusion and summary

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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) Timely, cost-effective, and environmentally-sound remedial action
- 8) Develop/implement the appropriate technology sequence

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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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Technology Selection and Sequence

- Properties of the chemicals present in the soils and groundwater
- Status of potential pathways and receptors
- Site facilities, utilities, and support systems
- Project specific remediation criteria
- Cost and schedule considerations
- Progress monitoring and response

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Outline of Workshop

- Introduction
- *Physical properties*
- Biological processes
- Applying biological technologies
- Natural attenuation processes
- *Case studies*
- Conclusion and summary

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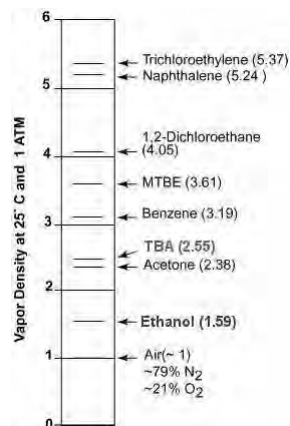
Summary of Physical Property Values

Chemical	Vapor Density (g/l)	Specific Gravity (unitless)	Solubility (mg/l)	Vapor Pressure (mm Hg)	Henry's Constant (unitless)	Log K _{oc} (unitless)
Trichloroethylene	5.37	1.46	1,100	77	0.422	2.2
Naphthalene	5.24	1.12	30	0.082	0.020	3.3
1,2-Dichloroethane	4.05	1.24	8,718	79	0.040	1.2
Methyl tert butyl ether	3.61	0.741	49,000	250	0.055	1.1
Benzene	3.19	0.879	1,780	86	0.22	1.8
Acetone	2.38	0.790	Infinite	266	0.0016	0.024
Tert butyl alcohol	2.55	0.786	Infinite	41	0.00049	0
Ethanol	1.59	0.789	Infinite	53	0.00024	0.71

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Vapor Density

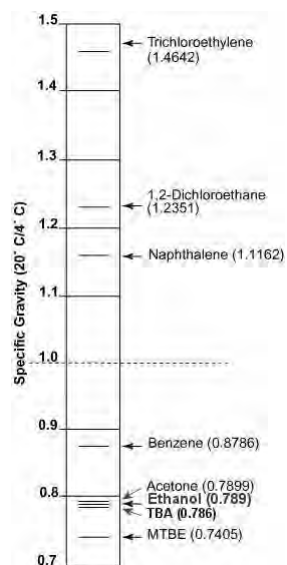
- Mass per volume of air
(gram/liter)
- Vapor density of air
~ 1 g/l
- If vapor density > 1 g/l
vapor will sink
- Can calculate from Ideal
Gas Law



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Specific Gravity

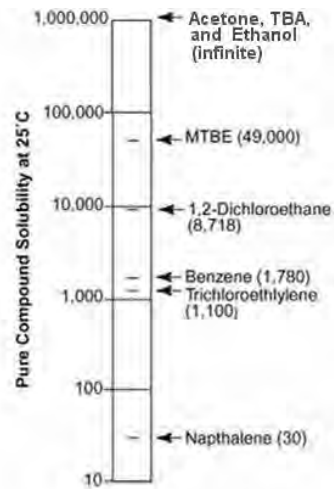
- Mass of a given volume to
that of the mass of the same
volume of water
- If S.G. >~1, pure product will
sink in water
- If S.G. <~1, pure product will
float on water



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Solubility

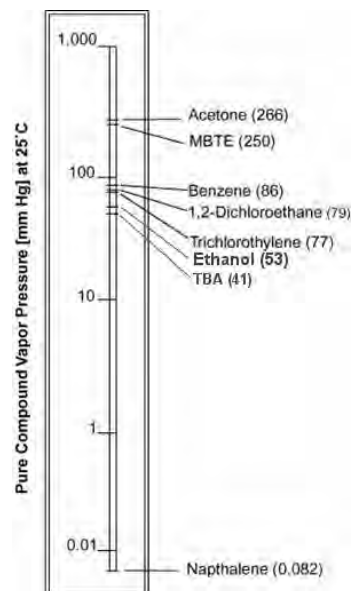
- Solubility: degree to which a contaminant dissolves in groundwater and unsaturated zone pore water
- Solubility of each compound in a mixture like gasoline is a function of Raoult's Law



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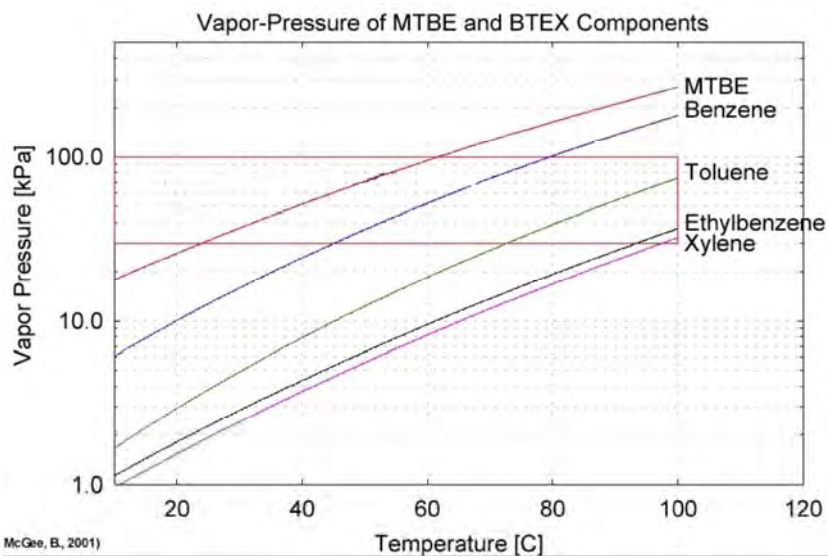
Vapor Pressure (mm Hg)

- If vapor pressure
 - > 100 mm Hg
 - ❖ Significant NAPL volatilization
 - ❖ Vaporization of residual product from dry soil
- Law of Partial Pressure
 - ❖ $P_{\text{benzene}} = X_{\text{benzene}} P^{\circ}_{\text{benzene}}$



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Effects of Temperature on VP



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Henry's Law Constant (H)

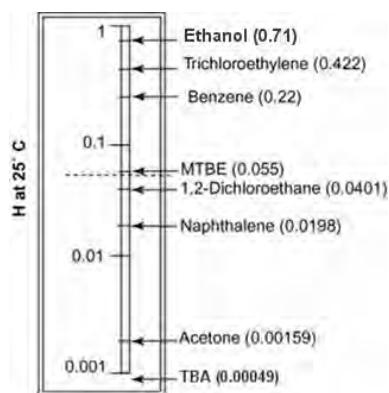
$$H = \frac{C_G \text{ vapor concentration}}{C_W \text{ aqueous concentration}}$$

■ Henry's constant > 0.05

- ❖ Volatilization likely
- ❖ Off-gassing likely

■ Henry's constant < 0.05

- ❖ Volatilization unlikely



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Adsorption

■ Soil adsorption coefficient

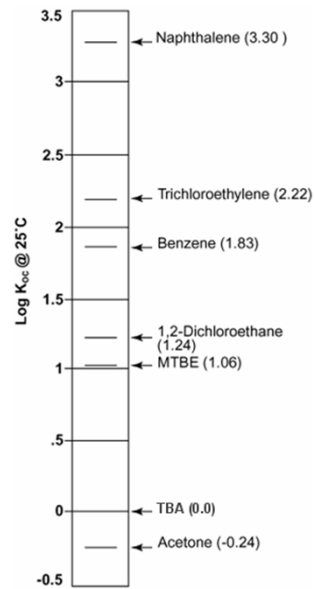
$$K_d = \frac{C_s}{C_w}$$

sorbed concentration
solution concentration

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

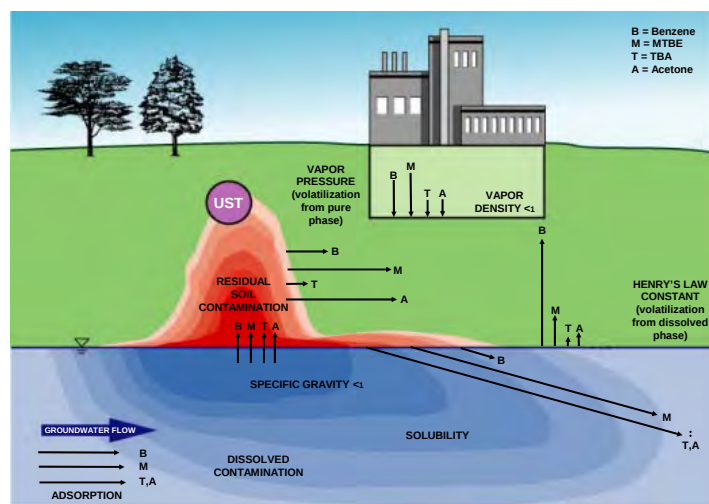
fraction of organic content in soil
times amount of adsorption on a
unit carbon content basis

■ Adsorption retards contaminant migration in groundwater



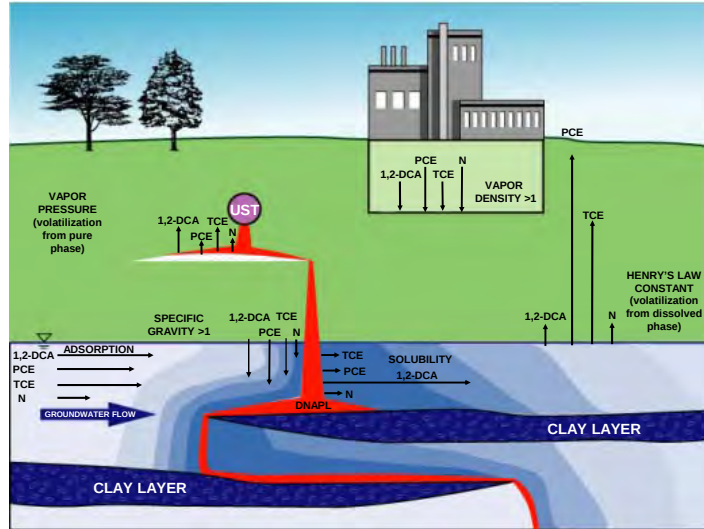
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Physical Behavior of LNAPL Constituents



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Physical Behavior of DNAPL Constituents



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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

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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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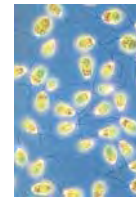
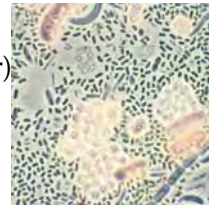
In Situ Bioremediation

- Most VOCs are biodegradable
- Optimize electron acceptors/donors, nutrients, pH and other factors
- Several approaches:
 - ❖ Direct injection of amendments to subsurface
 - ❖ Extraction/reinjection of water with amendments
 - ❖ Membrane diffusion of amendments into groundwater
- Optimize as part of technology sequence

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Subsurface Microorganisms

- Bacteria (*Pseudomonas*, *Arthrobacter*, *Acinetobacter*)
 - ❖ 0.1 to >5 micron in diameter
 - ❖ Variety of shapes (e.g., cocci, rods, spirilla)
 - ❖ Many can move via flagella
 - ❖ Some produce endospores
 - » Resistant to heat, drying, etc.
 - » May be dormant and inactive for many years
 - » Germinate with chemical or thermal stimulus
- Fungi
 - ❖ Molds (filamentous), *Phanerochaeta*
 - ❖ Yeasts (unicellular), *Rototurula*
 - ❖ Mushrooms (form large complicated structures)
 - » Shitake, *Agaricus*
- Protozoa (unicellular)
 - ❖ Predators
 - ❖ Flagella, cilia, or amoeboid locomotion



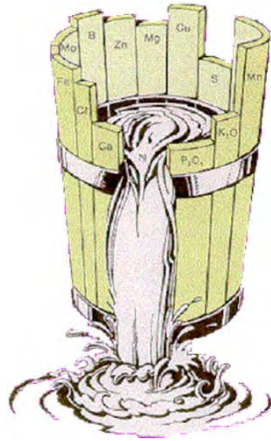
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Classifications of Microorganisms

- Prokaryotes vs Eukaryotes
- Aerobic vs anaerobic
- Chemotrophs vs. phototrophs
 - ❖ Autotrophs vs. heterotrophs
- Electron donor vs electron acceptor
 - ❖ OIL RIG (of electrons)
- Indigenous vs bioaugmentation
 - ❖ Capable organisms
 - ❖ Population density

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Justin von Liebig's Law of the Minimum



- Potential biomass yield
- Limited by growth limiting factors

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Bioremediation - Optimizing Conditions for Microorganisms

- Electron acceptors (oxygen, nitrate, etc.)
- Alternate carbon sources sometimes desired - many options - often used to kick start the process
 - ❖ Citric acid, orange juice
 - ❖ Diesel
 - ❖ Karo syrup, molasses
 - ❖ Propane, butane
 - ❖ Lactate (e.g., HRC)
- Nutrients (esp. nitrogen, phosphorus, potassium)
- pH
- Temperature
- Bioaugmentation (option for potentially higher rates)

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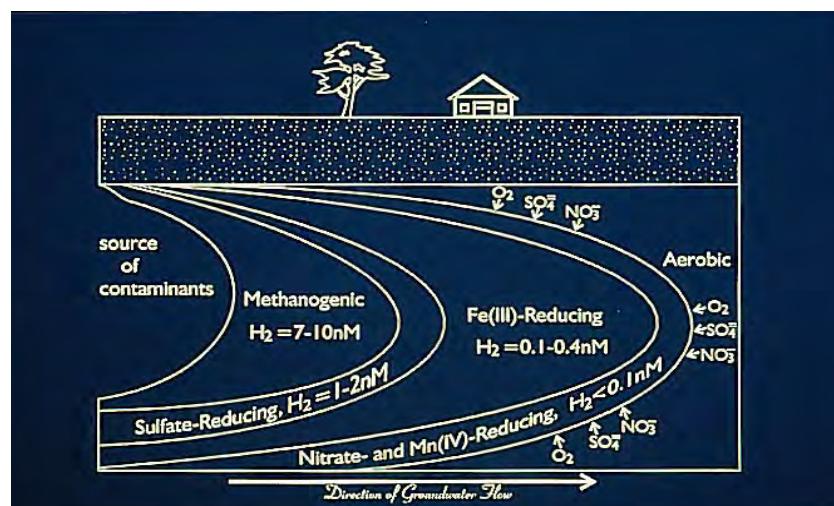
Microbial Metabolism of Organic Matter

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	

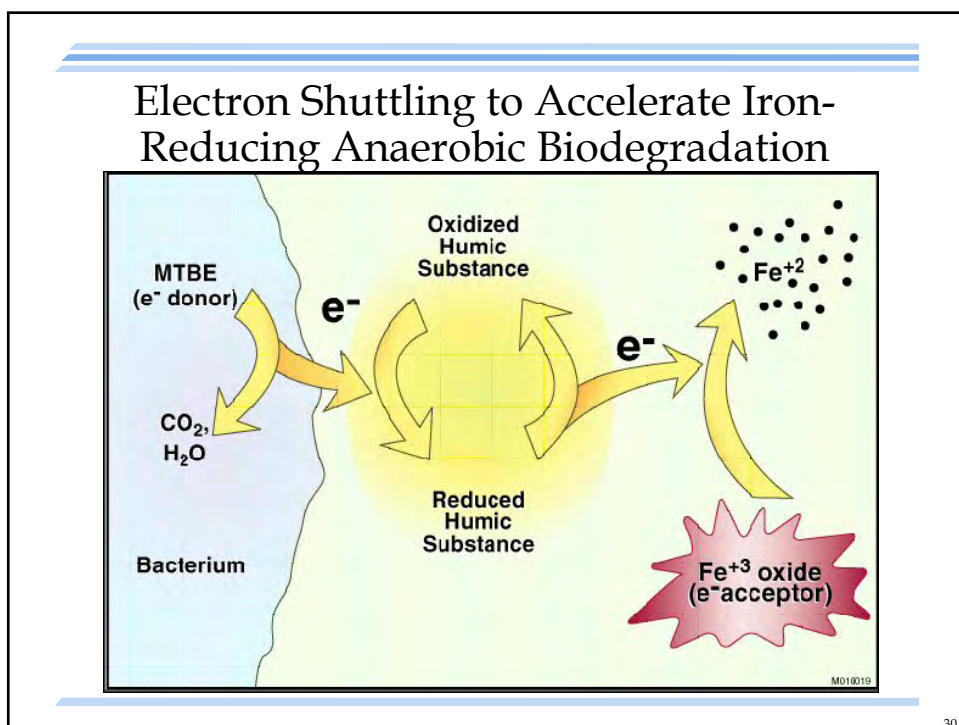
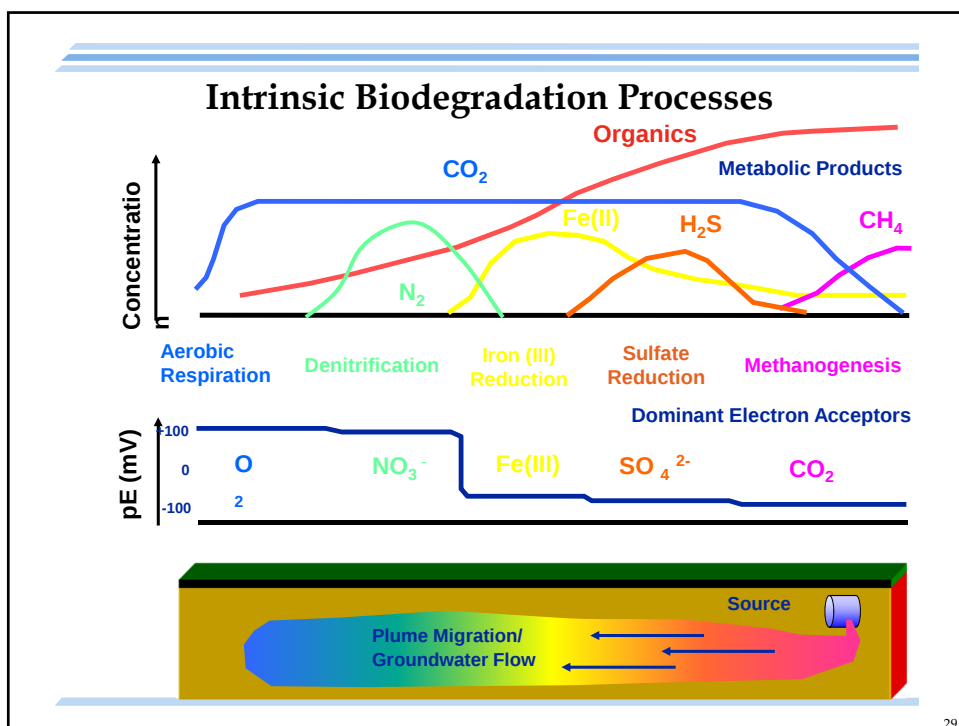
Sufliita and Sewell (1991)

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Terminal Electron Acceptor Process (TEAP) Zones and Associated Dissolved Hydrogen Concentrations



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Biocatalysis/Biodegradation Database

<http://umbbd.ahc.umn.edu/>

- 131 Pathways
- 831 Reactions
- 785 Compounds
- 530 Enzymes
- 326 Microorganisms
- 110 Biotransformation rules
- 50 Organic functional groups

Predict microbial catabolic reactions

Biochemical periodic table

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Metapathway Trunk

Aerobically

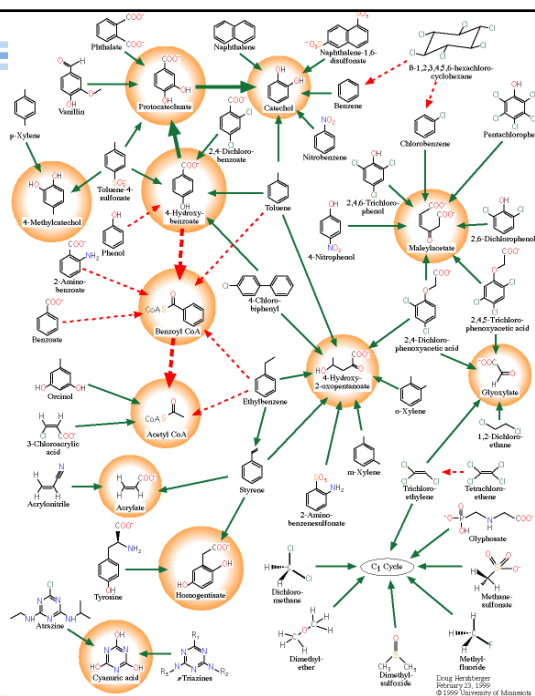
Anaerobically

Starting compound to intermediate cpd

Intermediate compound to intermediate cpd

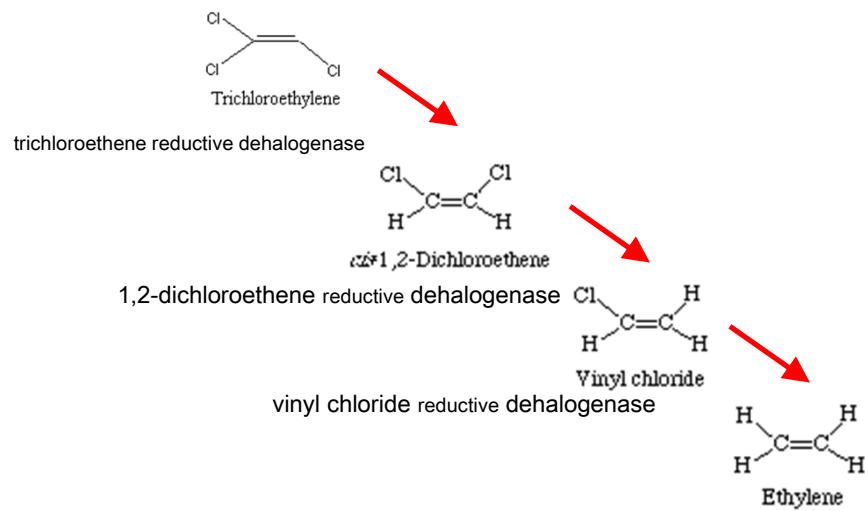
Starting compound to intermediate cpd

Intermediate compound to intermediate cpd



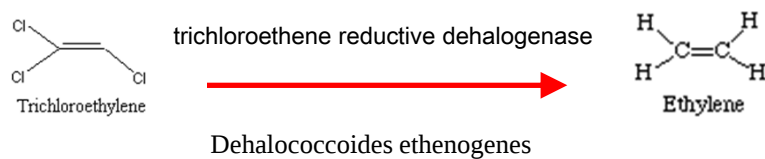
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Anaerobic/Aerobic Biodegradation of TCE



Courtesy University Minnesota Bio Database: <http://umbbd.ahc.umn.edu/> 33

Halo-respiring Microbes Convert TCE Directly to Ethylene



Courtesy University Minnesota Bio Database: <http://umbbd.ahc.umn.edu/> 34

In Situ Delivery Systems

- Pump, treat, and inject
- Intermittent sparging/injection
- Gaseous diffusion
 - ❖ Triethyl phosphate
 - ❖ Ammonia
 - ❖ Carbon cometabolites (e.g., propane)

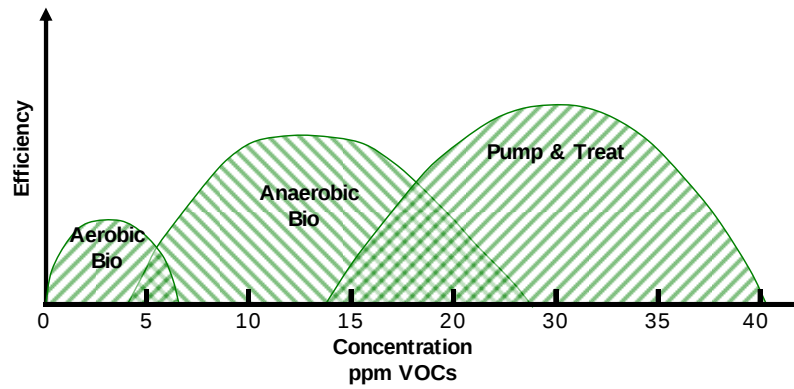
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Three Phase Approach for Some CVOCs

- Sweep dissolved phase with pump and treat
- In situ reductive dehalogenation stimulated with nitrate
- In situ aerobic degradation stimulated by dissolved oxygen
- Optimum concentration range for each phase

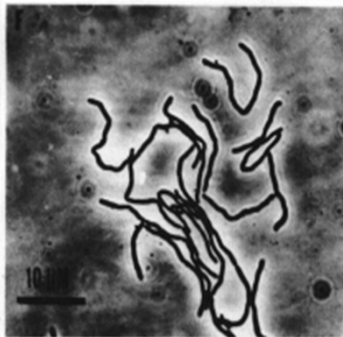
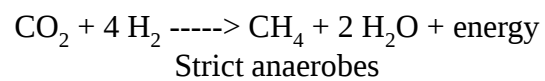
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Phase Sequencing



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Methanogens: Methane Generators



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Methanotrophs: Methane Eaters



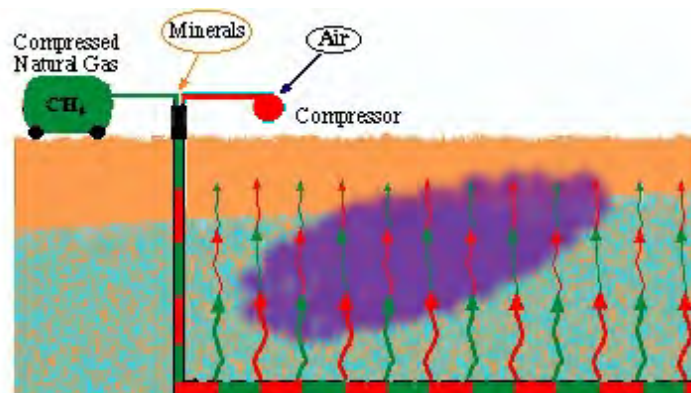
Aerobic organisms capable of transforming chlorinated aliphatics, including TCE by co-metabolism. They can be stimulated to degrade TCE and CO but need methane as a carbon and energy source.



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Bioremediation System for TCE

- Methane builds population and stimulates enzyme production; gratuitous degradation of TCE



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Chloro Respirers

- *Dehalococcoides ethenogenes*
 - ❖ Anaerobic respiration of PCE and TCE to ethene
 - ❖ Hydrogen as electron donor

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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 CO₂
 - ❖ 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, CO₂, CH₄, H₂ gas
- Three stages of fermentation
 - ❖ 1 - produces organic acids, alcohols, H₂, CO₂
 - ❖ 2 - produces acetate, H₂, CO₂
 - ❖ 3 - produces CO₂, CH₄
- 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

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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

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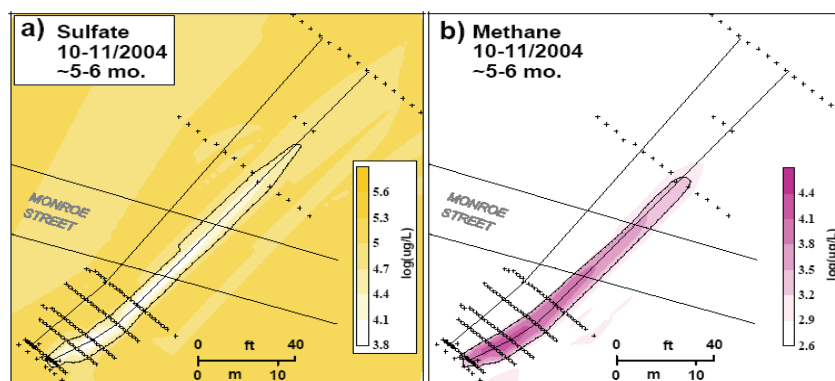
Vandenberg Results

- 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

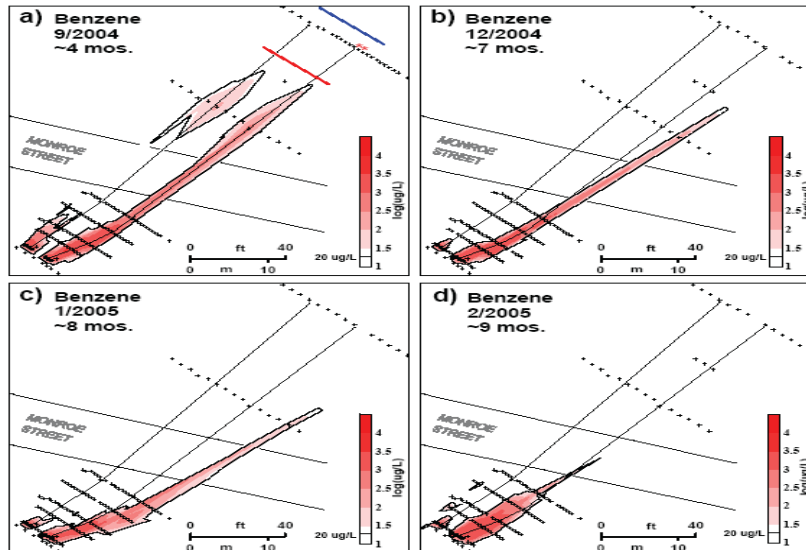
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Vandenberg - Sulfate and Methane



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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

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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

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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	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						
		0.1-0.9	1.0-9.9	10-99.9	100-999.9	1,000-9,999.9	10,000-99,999.9
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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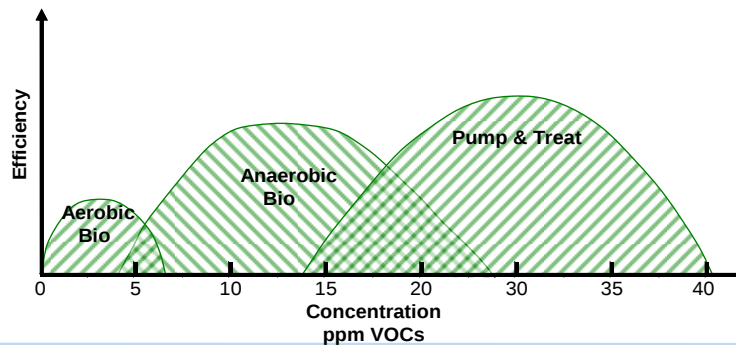
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Remediation Phases

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



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Ways to Deliver Oxygen to the Subsurface

<u>Method</u>	<u>O₂ Demand</u>
Hydrogen peroxide injection	High
Air/oxygen sparging, pulsed	Med.
Diffusive oxygen emitters	Med.
Eductors, supersaturate, P & T	Med.
In-well oxygenation (course/fine bubble, gas membranes)	Med.
Electrolysis ($\text{H}_2\text{O} \rightarrow \text{H}_2$ and O)	Low
Solid forms (oxygen/magnesium)	Low

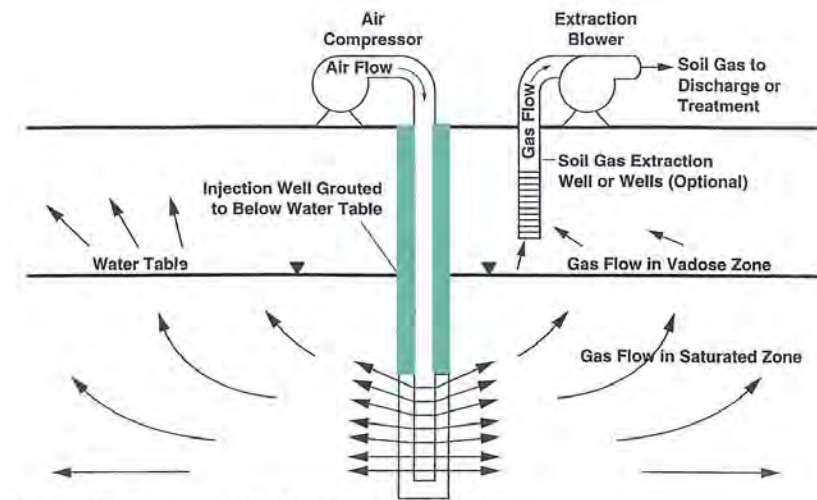
59

Air Sparging/Bio-sparging

- 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



Hinchee, 1994. Airsparging for Site Remediation - Lewis Publishers.

61

Bioventing

- Low air flow rates in injection or extraction mode
- Aerates unsaturated zone to enhance bioremediation in situ
- Treats upper portion of unsaturated zone
- Helpful to lower water level (expand vadose zone)
- Aboveground vapor treatment usually not required
- Active systems – use compressors or blowers
- Passive systems - barometric pressure, wind turbine ventilation

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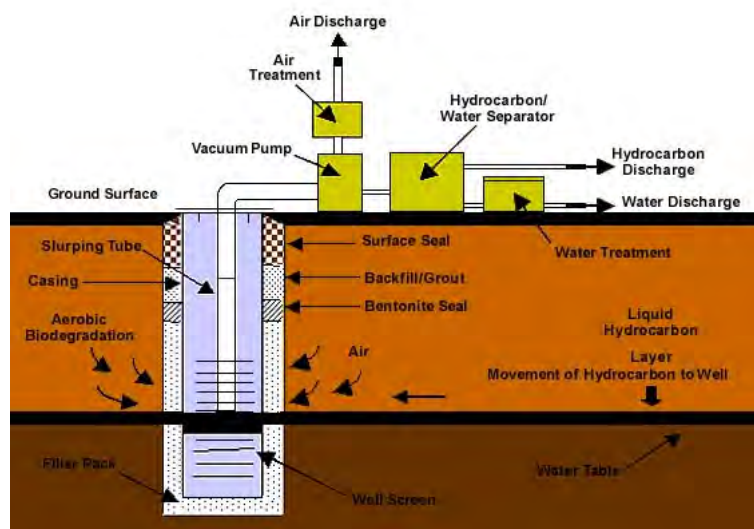
Subsurface ventilation



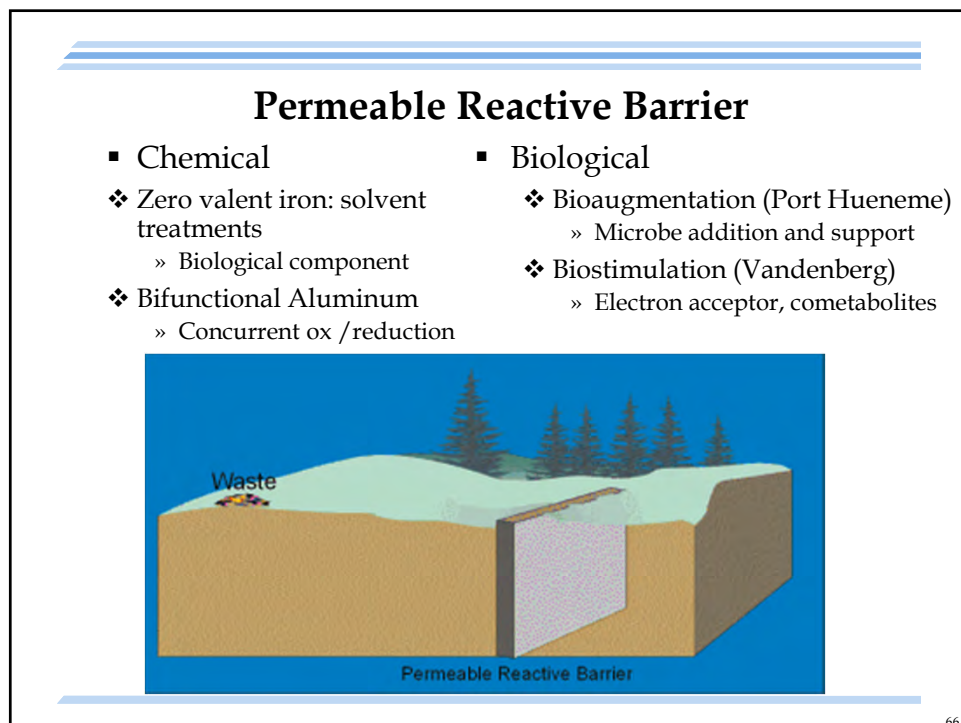
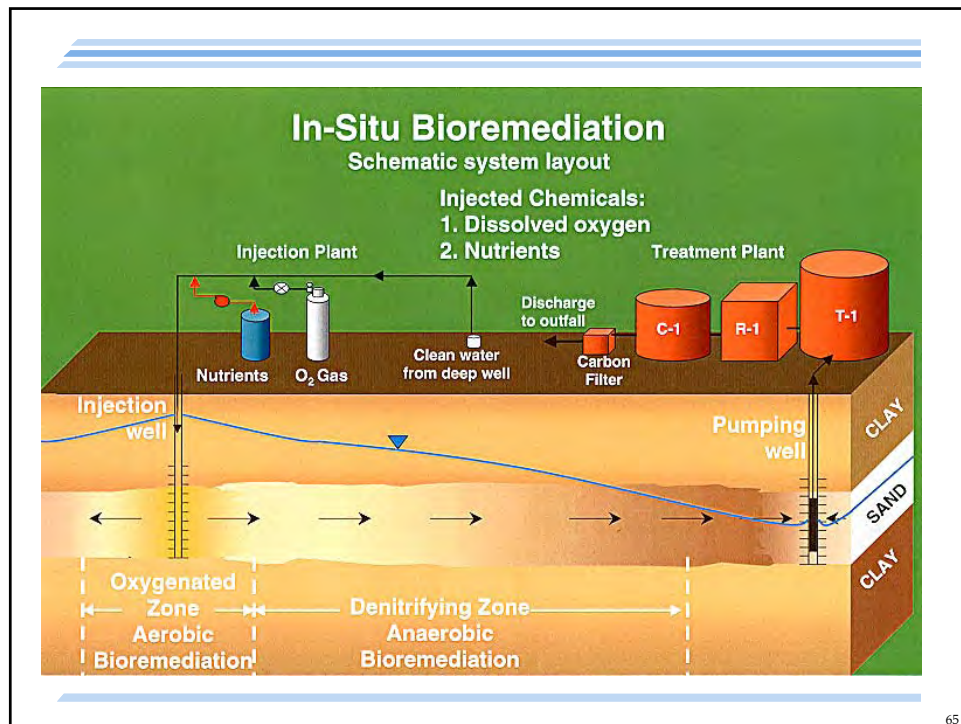
Courtesy Air Situ LLC, Houston, TX

63

Bioslurping System



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Ex-Situ GW Bioremediation Approaches

A form of GW pump and treat – treat in a tank – many configurations

- Activated sludge – recirculating water and suspended microorganisms in a tank
- Fluidized bed bioreactor – organisms attached to particles are suspended by upflow in tank
- Rotating biological contactor – organisms fixed on vertical disks that rotate into and out of water
- Fixed film bioreactor
- BioGAC – can amend influent water with oxygen and nutrients; possibly seed GAC with organisms

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ERI Bioreactor Treating MTBE & TBA



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Phytoremediation

- Gradient control/evapotranspiration
- Rhizosphere biodegradation
- Native species perform best
 - ❖ Low maintenance conditions
- Plant selection influenced by water balance
 - ❖ Model transpiration rate, stand density
- Irrigation required to establish stand
 - ❖ Deep watering stimulates root growth
- Water/soil quality affects establishment
 - ❖ Salt concentration, pH

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Phytoremediation of Shallow Hydrocarbons in Soil with Oleander



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Plume Control Phreatophytes
Long Beach, California



Plume Control Phreatophytes
Long Beach, California





Outline of Workshop

- Introduction
- Physical properties
- Biological processes
- Applying biological technologies
- *Natural attenuation processes*
- Case studies
- Conclusion and summary

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

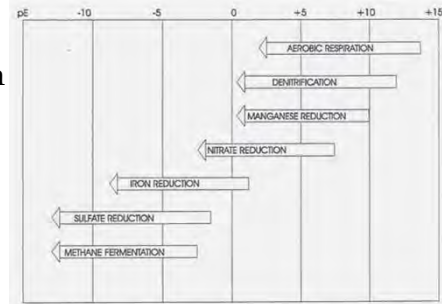
- Destructive (mass reduction)
 - ❖ Intrinsic biodegradation
 - ❖ Abiotic chemical reactions
- Non-destructive (mass conservative)
 - ❖ Adsorption to organic fraction
 - ❖ Dispersion
 - ❖ Advection
 - ❖ Diffusion
 - ❖ Volatilization
 - ❖ Dilution

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NA Processes – Intrinsic Biodegradation

- Any or all Terminal Electron Acceptor Processes (TEAPs)

- ❖ Aerobic ($O_2 \rightarrow CO_2$)
- ❖ Denitrification ($NO_3^- \rightarrow N_2$)
- ❖ Nitrate reduction ($NO_3^- \rightarrow NH_4^+$)
- ❖ Iron reduction ($Fe^{+3} \rightarrow Fe^{+2}$)
- ❖ Sulfate reduction ($SO_4^{-2} \rightarrow H_2S$)
- ❖ Methanogenesis ($C_5H_{12}O \rightarrow CH_4$)



- Demonstrate by measuring concentration changes over time and/or distance
- Dissolved hydrogen concentrations can provide confirmatory evidence of the TEAP(s)

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NA Processes– Abiotic Chemical Reactions

- Typically not significant for VOCs

- Many types

- ❖ Acid-base reactions (transfer of hydrogen ions)
- ❖ Redox reactions (transfer of electrons)
- ❖ Complexation (anions and cations)
- ❖ Chemical absorption (dissolved chemicals enter the lattice of the solid)
- ❖ Hydrolysis (typically extremely slow)
- ❖ Radioactive decay (radionuclides)

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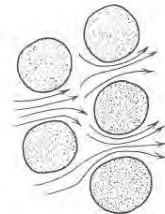
NA Processes – Adsorption

- Retards the advance of a dissolved contamination front
- Occurs when the surfaces of mineral and organic materials contain functional groups with electric charges
- Functional groups react with dissolved chemicals by complexation or ion exchange
- Potentially reversible – adsorbed chemicals can desorb

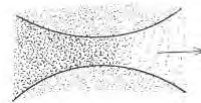
79

NA Processes – Dispersion/Advection

- Contaminant transport by groundwater flow (Darcy's law)
- Mixing of dissolved substances as GW moves
- Includes molecular diffusion
- Dispersion increases with increasing GW flow
- Longitudinal (in the direction of GW flow) and transverse (perpendicular to the direction of GW flow)

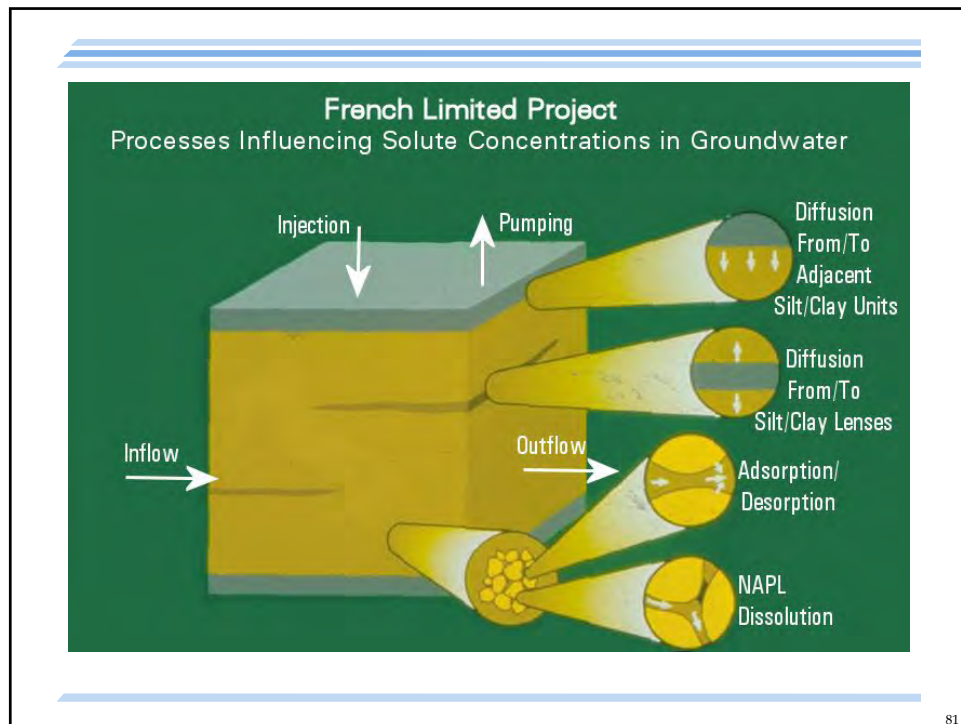


Mixing of pore channels



Mixing by molecular diffusion

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NA Processes – Volatilization / Dilution

- Volatilization is a function of Henry's law
 - ❖ H constant predicts extent of volatilization from dissolved phase to vapor
 - ❖ H quantifies the competition between vapor pressure and solubility
 - ❖ Typically not significant with mature plumes
- Dilution
 - ❖ Recharge adds new water to the system and dilutes contaminant concentrations
 - ❖ Most pronounced under pervious conditions with minimal runoff and maximum recharge
 - ❖ Optimize physical conditions

Transition to Natural Attenuation

■ Sequence

- ❖ Active remediation
- ❖ Transition : subsurface conditioning
- ❖ Monitored natural attenuation
- ❖ Evaluate progress
- ❖ Rebound response
- ❖ Institutional controls

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Transition to Natural Attenuation

■ Active remediation end point

- ❖ Analytical basis
 - » COCs
 - » Electron acceptors, nutrients, other
- ❖ Physical basis (e.g., pumping rate low)
- ❖ Modeling

■ Cost/benefit analysis

■ Human health and environmental risk assessment

- ❖ Attenuation action levels
- ❖ Concentration reduction factors
- ❖ Final compliance goals
- ❖ Protect nearest receptors

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Transition to Natural Attenuation

- Monitoring network adequate to track progress
- Expect some rebound : equilibration
- Evaluate rebound and overall database
- Periodically reevaluate risk to nearest receptors
- Allow time for natural attenuation to work
- Develop rebound response plan
- Everything is site-specific

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Case Studies

1. Edinger CA Dry Cleaner: In situ bioremediation of CVOCs
2. Bedford NH Gas Station: Ex situ bioremediation of TBA and other gasoline constituents
3. Hainesport NJ: In situ bioremediation and MNA as part of a remediation sequence for aromatics and CVOCs
4. Turtle Bayou TX: In situ bioremediation of aromatics, alcohols, and CVOCs
5. Port Hueneme, CA: Sparge bio-barrier with bioaugmentation to treat gasoline oxygenates and aromatics
6. Norge Valley Cleaners CA: Anaerobic to aerobic to MNA sequencing for chlorinated volatile plumes

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Case Studies

7. Bayport TX: Confirmation of TBA MNA through carbon isotope studies
8. CEN Electronics: In situ bioremediation of CVOCs and BTEX
9. Pacific NW Terminal: MNA of ethanol
10. Pasadena TX Industrial Site: In situ bioremediation of CVOCs
11. Jacinto Port TX: In situ bioremediation of CVOCs using mobile unit
12. Vandenberg AFB CA: Diffusive oxygen emitter bio-barrier for fuel oxygenates remediation
13. Fuller Martel Apartments CA: Source removal and MNA of CVOCs and gasoline VOCs

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Edinger Dry Cleaner, CA

Background

- Former dry cleaner in 10-unit shopping mall in retail area
- No current threat to human health or the environment
- Operating dry cleaner from 1965 to 2000
- Above-ground dry cleaning equipment has been removed
- Entire area covered with concrete or blacktop; no vertical infiltration
- Property is free of trash and debris
- Shallow groundwater at 10' bgs to 30' bgs slow migration (2' per year) toward SW

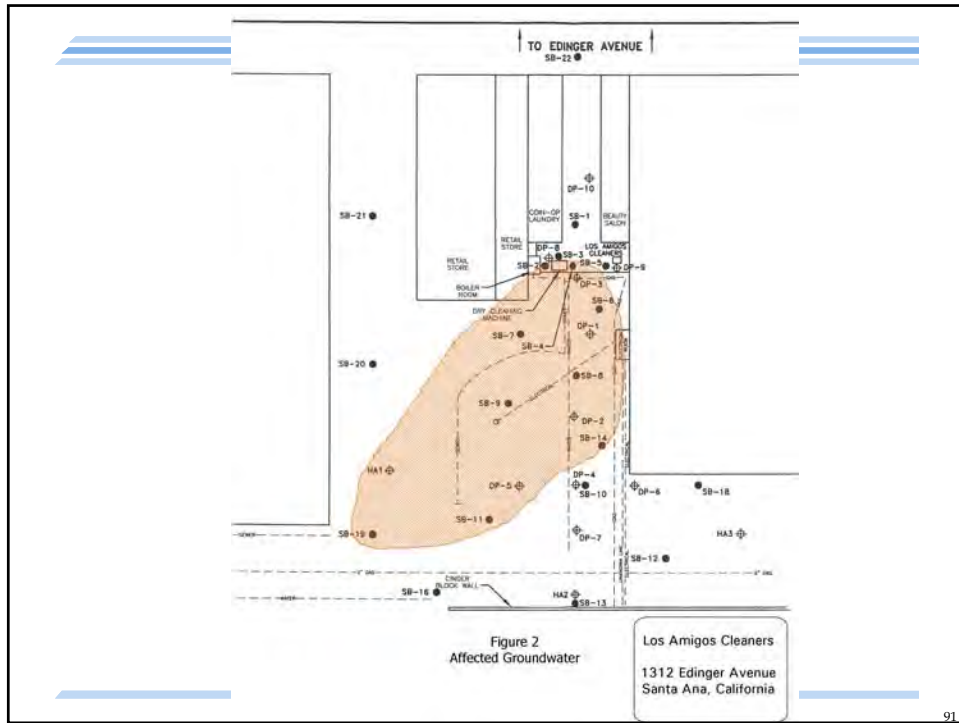
89

Edinger Dry Cleaner, CA

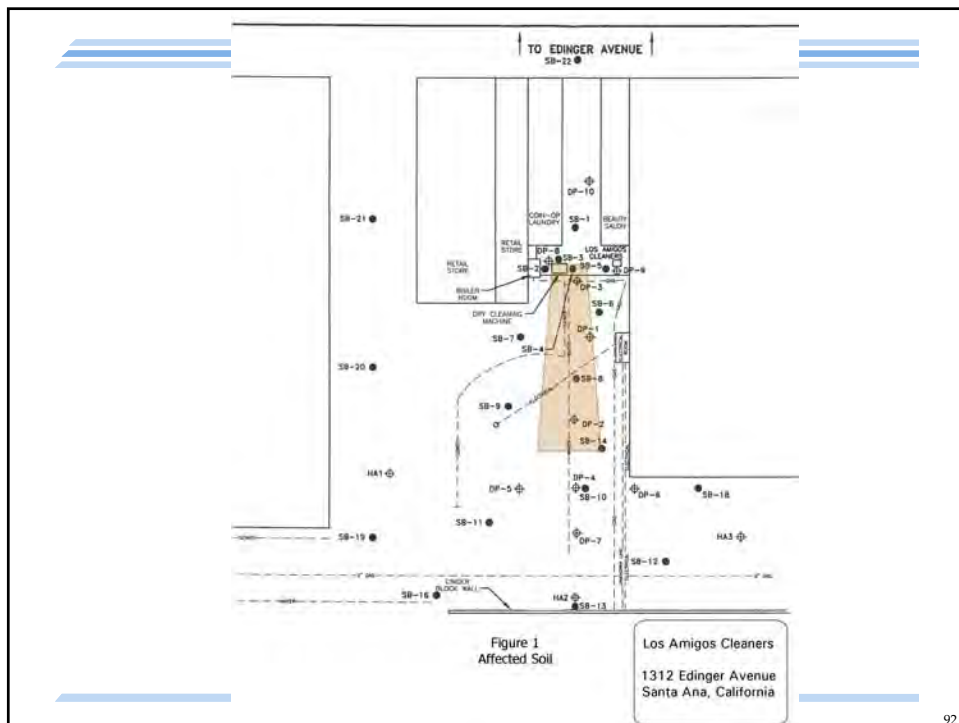
Environmental Issues

- PCE, TCE, and chlorinated degradation products are the chemicals of concern
 - ❖ Initial total CVOCs up to 400,000 ug/l
- The nature and extent of the contaminated soil and groundwater have been defined
- Some DNAPL may exist just south of the building
- PCE in soil and groundwater drives the remedial action
- No regulatory reporting or involvement to-date
- There are no at-risk potable water sources

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Edinger Dry Cleaner, CA

Remediation

- SVE and circulating aerobic in-situ bio
- Focused soil excavation under south side of dry cleaner site:
 - ❖ Remove 60 yd³ soil
 - ❖ Temporary structural support
 - ❖ Backfill with structural fill and compact
 - ❖ Add K₂MnO₄ to backfill
 - ❖ Analyze, profile, dispose of soil
- Install 8 dual-phase remediation/monitoring wells:
 - ❖ 6" diameter x 25' deep
 - ❖ Screen 5' bgs to 25' bgs
 - ❖ Extraction or injection

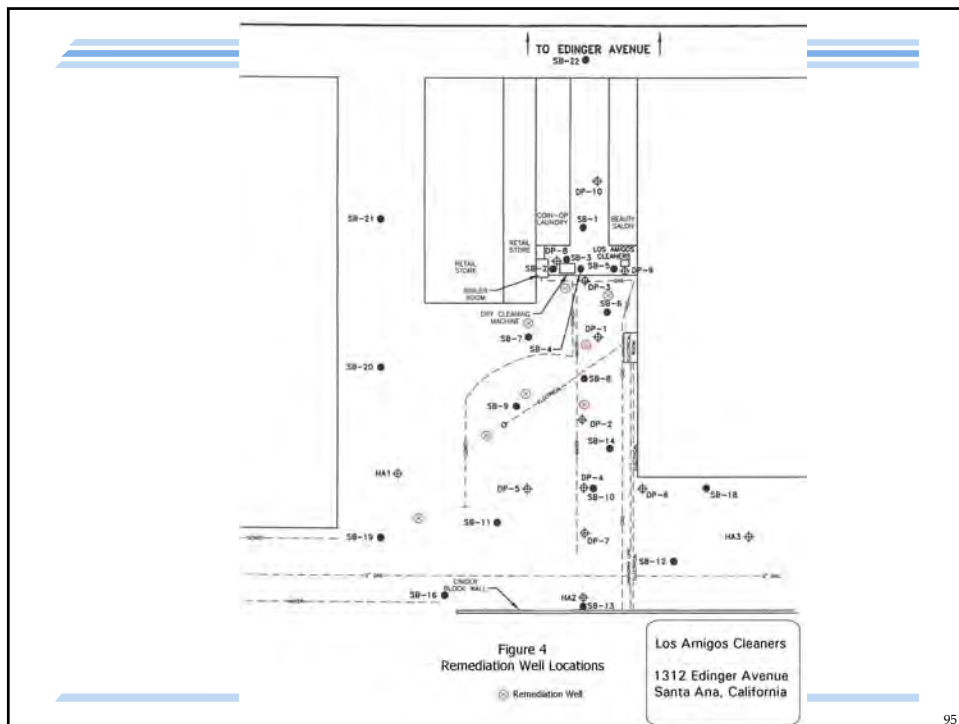
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Edinger Dry Cleaner, CA

Remediation

- Soil vapor extraction:
 - ❖ 5 CFM per well
 - ❖ Cycle 7 days on/7 days off
 - ❖ Treat with carbon
- Pump and treat, in-situ bio:
 - ❖ Cycle/rotate well function
 - ❖ Reverse the plume gradient
 - ❖ Carbon treatment
 - ❖ (NH₄)P₂O₄, KNO₃, K₂SO₄, O₂ amendments

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Figure 3



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Edinger Dry Cleaner, CA

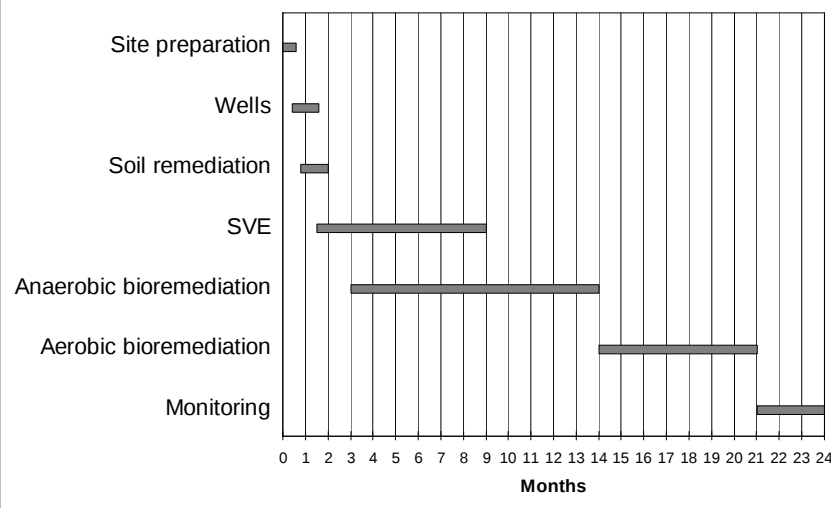
Costs

■ Wells	26,000
■ Excavation, handling, backfill	14,000
■ Disposal (soil)	12,000
■ Piping removal	6,000
■ SVE system	24,000
■ Pump and treat system	32,000
■ In-situ bio system	14,000
■ Power	4,000
■ Chemicals	8,000
■ Supplies	5,000
■ Analytical	30,000
■ Concrete, blacktop repair	9,000
■ Field labor	38,000
■ Technical support labor	18,000
■ Supervision	<u>20,000</u>
Total	260,000

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Edinger Dry Cleaner, CA

Schedule



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Bedford, New Hampshire, Bioreactor

Challenging System

Weather proof enclosure

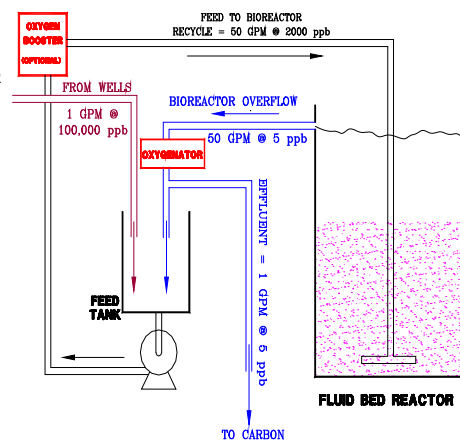
- Influent groundwater
 - ❖ BTEX (30,000 ppb)
 - ❖ MTBE (80,000 ppb)
 - ❖ TBA (8,000 ppb)
 - ❖ Iron (13 ppm)
 - ❖ Manganese (13 ppm)
- Suggest large bioreactor
- System includes:
 - ❖ Fe/Mn pretreatment
 - ❖ Air stripper
 - ❖ Small bioreactor
 - ❖ 500# carbon polishers
 - ❖ Discharge to on-site dry well



Courtesy: ERI 99

ERI Fluidized Bioreactor Operation

- Two-phase (solid-liquid)
- Re-oxygenation by air or O₂ 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

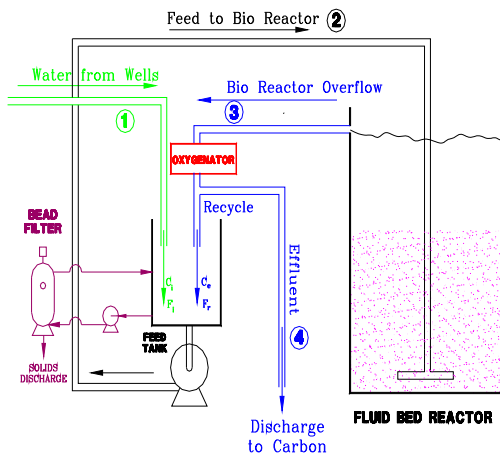


Environmental Resolutions, Inc. 100

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



Environmental Resolutions, Inc.

101

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

Environmental Resolutions, Inc.

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Air Stripper

4 trays
250-300 cfm
Up to 5 gpm



Courtesy: ERI 103

Carbon Vessels



Courtesy: ERI 104

- 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 105

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. 106

Bedford NH Bioreactor Data

<u>Date</u>	<u>Flow (gpm)</u>	<u>Temperature (degrees F)</u>	<u>Bioreactor TBA (ug/l)</u>		<u>Notes</u>
			<u>Influent</u>	<u>Effluent</u>	
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

<u>Date</u>	<u>Flow (gpm)</u>	<u>Temperature (degrees F)</u>	<u>Bioreactor TBA (ug/l)</u>		<u>Notes</u>
			<u>Influent</u>	<u>Effluent</u>	
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

Date	<u>Bioreactor MTBE (ug/l)</u>		<u>Bioreactor BTEX (ug/l)</u>		Notes
	Influent	Effluent	Influent	Effluent	
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 110

Hainesport - NJ

Background

- Relatively flat, 8-acre property
- Gas station, auto service, light industry for 70-80 years
- Four USTs have been removed
- Discharged liquid wastes onsite; several onsite disposal/dumping areas
- No current direct risk to the public health or the environment
- Normal shallow groundwater gradient is toward the east; a major river drainage about one mile to the east is the controlling hydrogeological feature

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Hainesport - NJ

Environmental Issues

- Detailed definition of the contaminated soils and groundwater was required
- 18 areas of concern were evaluated
- TCE, BTEX, TPH have been detected in soils and groundwater
- Numerous affected areas:
 - ❖ Require remedial action
 - ❖ Stabilize and isolate
- Shallow groundwater at 15'-20' bgs has been impacted
- Potable water wells within one mile east of the property could be at risk long-term
- Heavy rains could cause contaminant migration offsite

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Hainesport - NJ

Remediation

- Remove trash, scrap, debris from the property
- Identify and remove all abandoned process piping
- Soil borings in former UST areas to determine the effectiveness of source removal
- Detailed site assessment:
 - ❖ CTP
 - ❖ Trenches
 - ❖ Analytical
- Excavate contaminated soils:
 - ❖ Add 10 lbs KMnO_4 per ton
 - ❖ Place in onsite landfarm
 - ❖ Till in 12" lifts

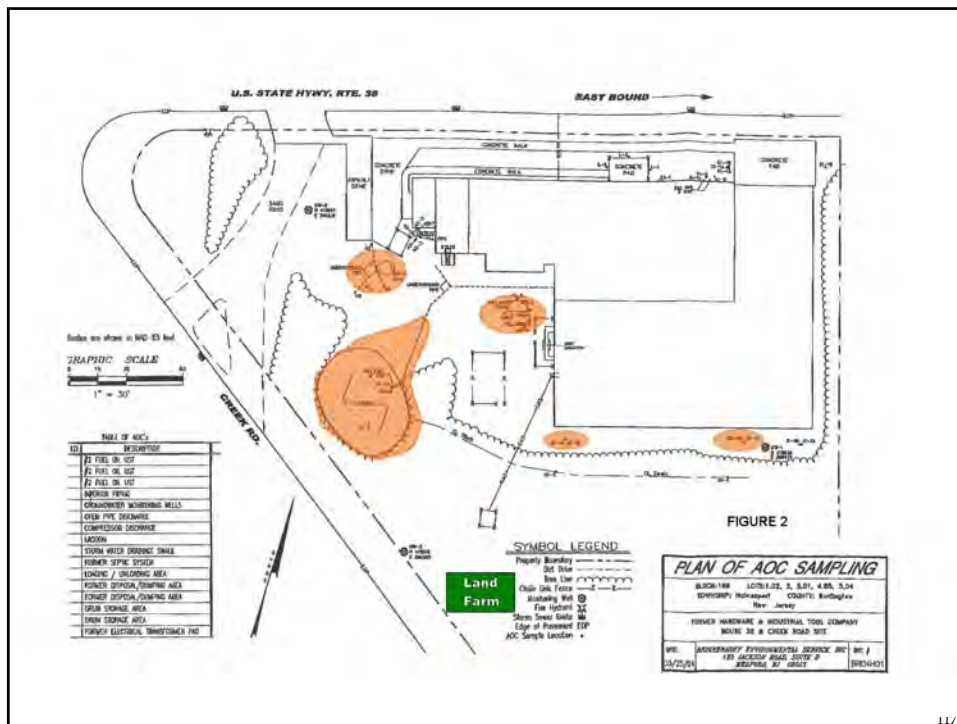
115

Hainesport - NJ

Remediation

- Groundwater and vadose zone remediation:
 - ❖ Install 10 dual-phase (vapor and water) remediation/monitoring wells
 - ❖ 6" diameter x 30' bgs
 - ❖ 15' screen from 12' bgs to 28' bgs
 - ❖ Treat vapor and groundwater with granulated activated carbon
 - ❖ Anaerobic, then aerobic in-situ bioremediation when TCE concentration reached 200 ug/l

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Hainesport - NJ

Costs

CPT	20,000
Trenches	35,000
Wells	15,000
Pumps, piping	30,000
Water treatment	25,000
Vapor treatment	15,000
Carbon recycle	20,000
Disposal	25,000
Soil handling/treatment	30,000
Supplies	30,000
Chemical	20,000
Analytical	30,000
Technical support	25,000
Supervision	40,000
Admin. support	10,000
Total	370,000

Hainesport - NJ

Schedule

■ Assessment	8 weeks
■ Design	3 weeks
■ Site clean-up	3 weeks
■ Demolish and dispose	5 weeks
■ Soil remediation	3 weeks + 6 months
■ Construct remedial systems	5 weeks
■ Operate remediation systems	15 months
■ Monitor	10 years

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Turtle Bayou Easement Area

- COCs: benzene, ethylbenzene, toluene, 1,2-DCA, MTBE, TBA, naphthalene
- Soil hot spot remediation
 - ❖ In situ thermal desorption/SVE/thermal oxidation
 - ❖ Excavation
 - ❖ Chemical oxidation
- Reduce VOC concentrations into the effective in situ bioremediation range

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Turtle Bayou Easement Area

■ Groundwater in situ bioremediation

❖ 30 extraction wells to WWTP

❖ 30 injection wells

» Potable water amended with oxygen / nutrients

● 40-50 ppm dissolved O_2

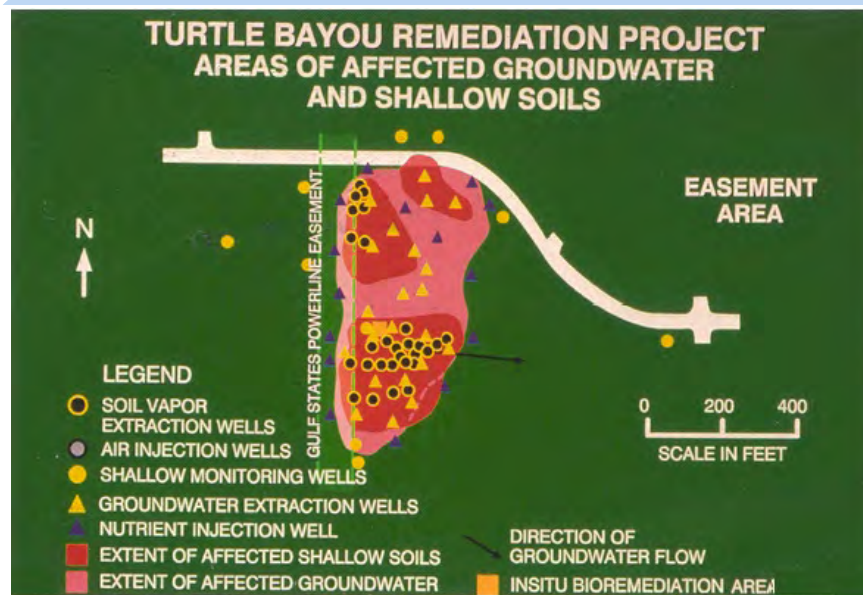
● 5-10 ppm NO_3 (from potassium nitrate)

● ~10 ppm SO_4 (from potassium sulfate)

● ~2 ppm phosphate (from diammonium phosphate)

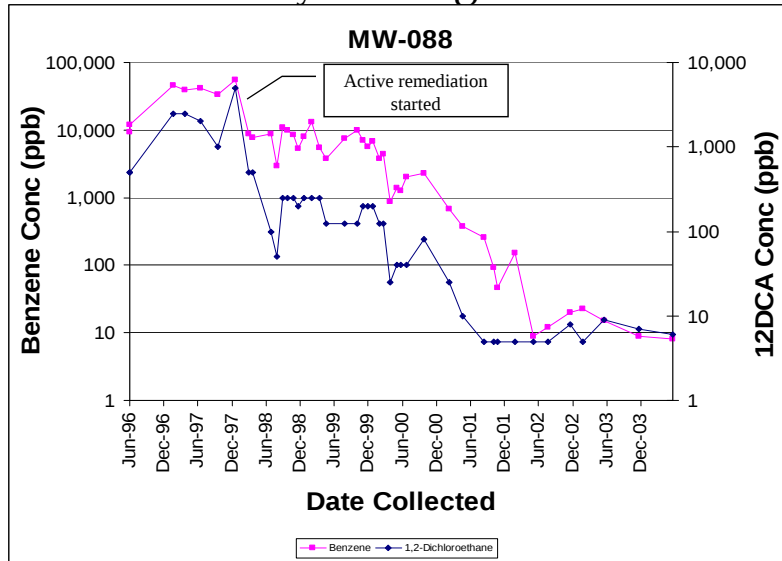
■ Monitored natural attenuation (focused areas)

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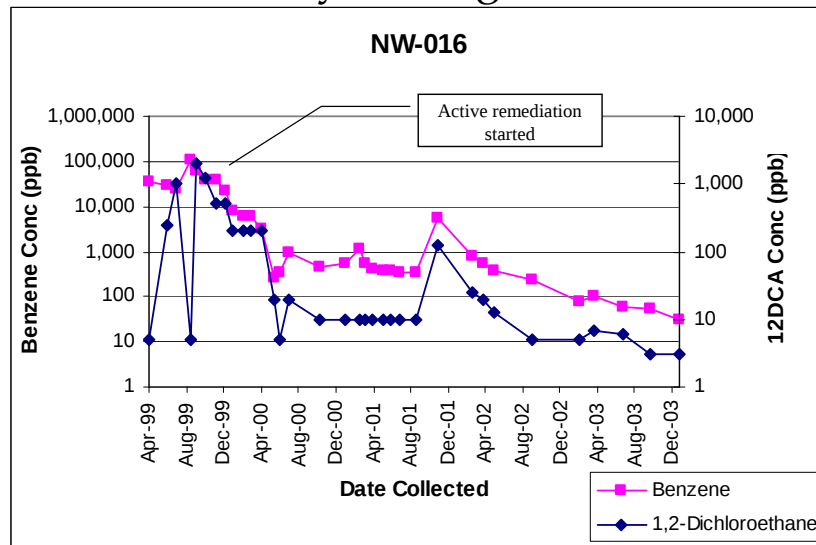
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Turtle Bayou Progress Curve



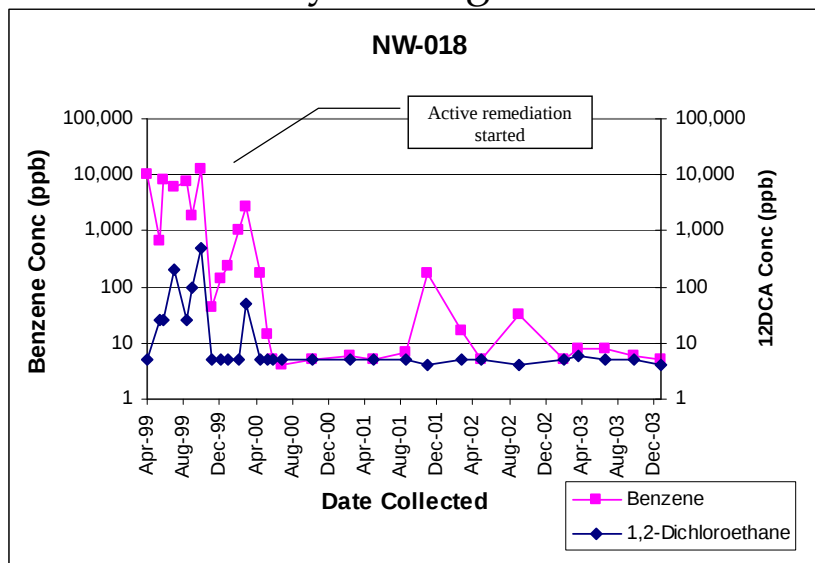
123

Turtle Bayou Progress Curve



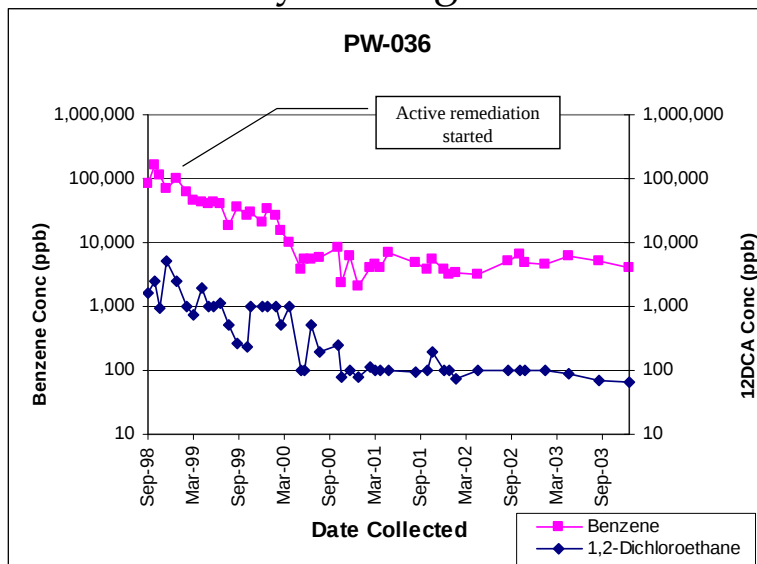
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Turtle Bayou Progress Curve



125

Turtle Bayou Progress Curve



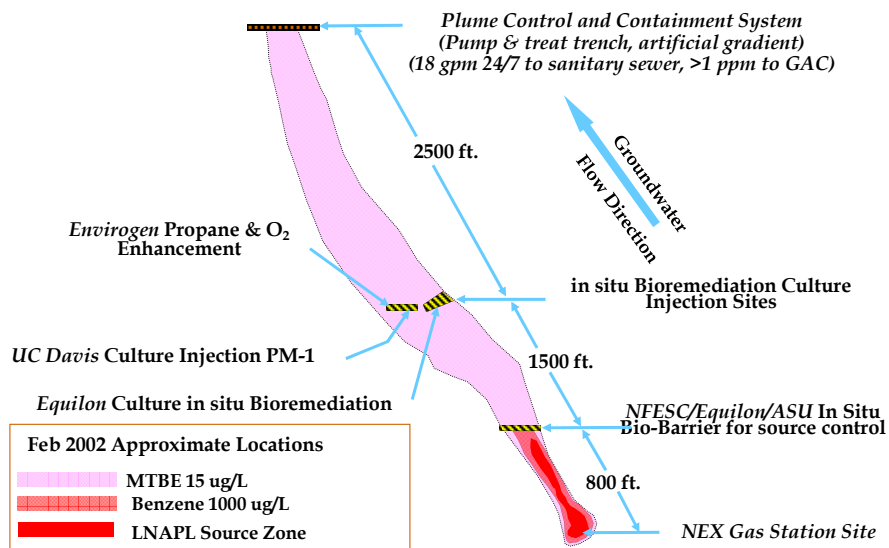
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Port Hueneme Site, Ventura County, CA

- LUST at base service station
 - ❖ Released gasoline
- Source control by excavation and limited pump and treat of free product material
- Shallow aquifer, mixed alluvium (sand and gravel)
 - ❖ 10 to 25 ft below ground surface
- Gasoline plume following buried stream channel with groundwater flow (averaging 1/3-3/4 ft/d)
- Entire aquifer anaerobic (D.O. <1 mg/L)

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Port Hueneme Benzene & MTBE Plume



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Scope of 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 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, indigenous organisms
 - ❖ Air sparging, intrinsic biodegradation, indigenous organisms

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Courtesy H2O R2 Consultants

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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 in all plots, 6 ppm to < 50 ppb
 - » Biodegradation occurred in both test and control plots
 - » Intermittent oxygen sparging → biostimulation/biodegradation
 - » Intermittent air sparging → biostimulation/biodegradation
 - » TBA was not found

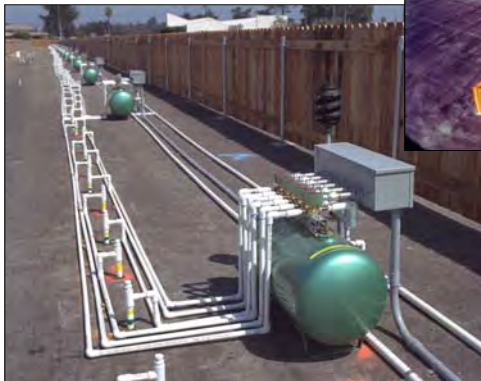
132

Port Hueneme Research & 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 bio-barrier transect
 - ❖ Increases in situ degradation rate
 - ❖ Decreases MTBE half-life in the field

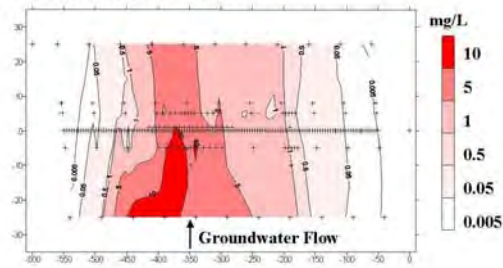
133

Port Hueneme Scaled-up Bio Barrier

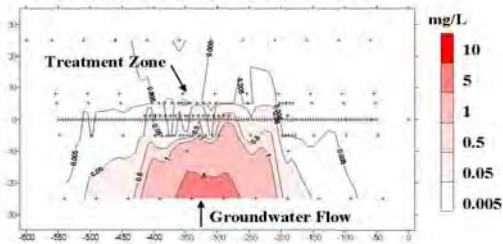


134

MTBE concentrations before...



And MTBE concentrations 7 months later...



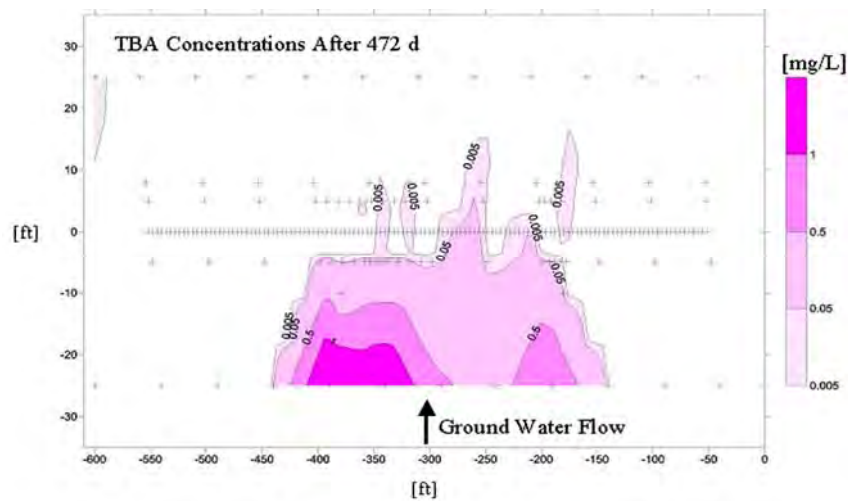
Port Hueneme MTBE Bio-Barrier

99.9% MTBE reduction

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

135

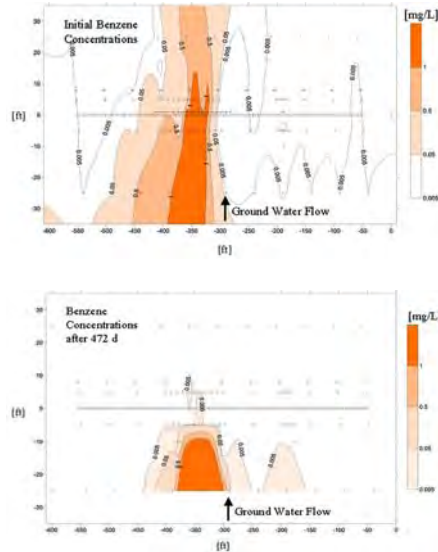
Port Hueneme Biobarrier Results: TBA



Bruce et al., 2002.

136

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

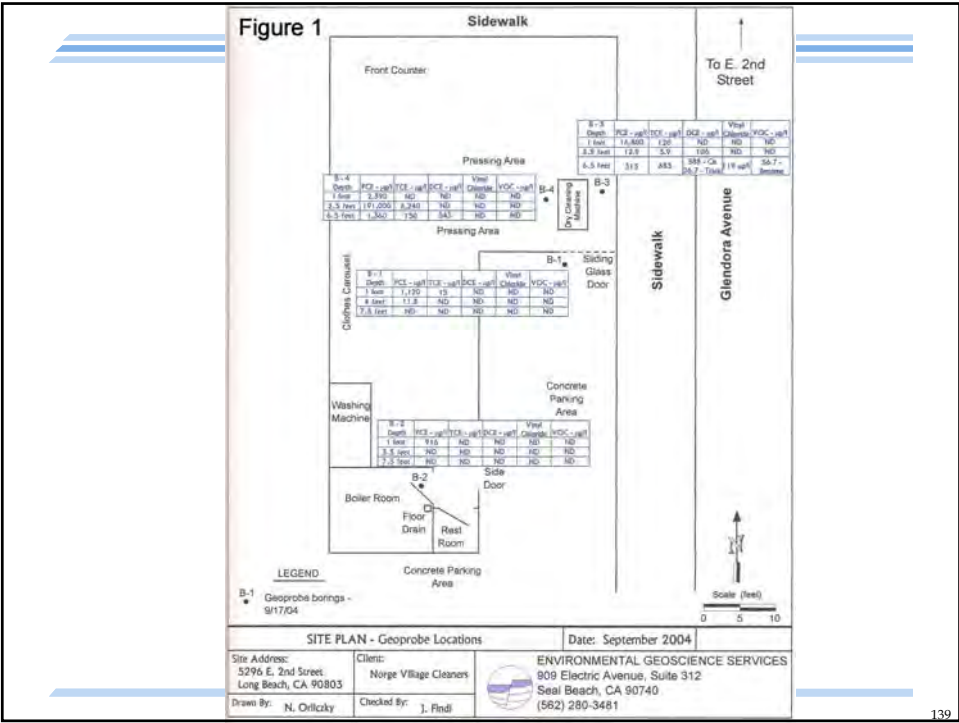
137

Norge Village Cleaners

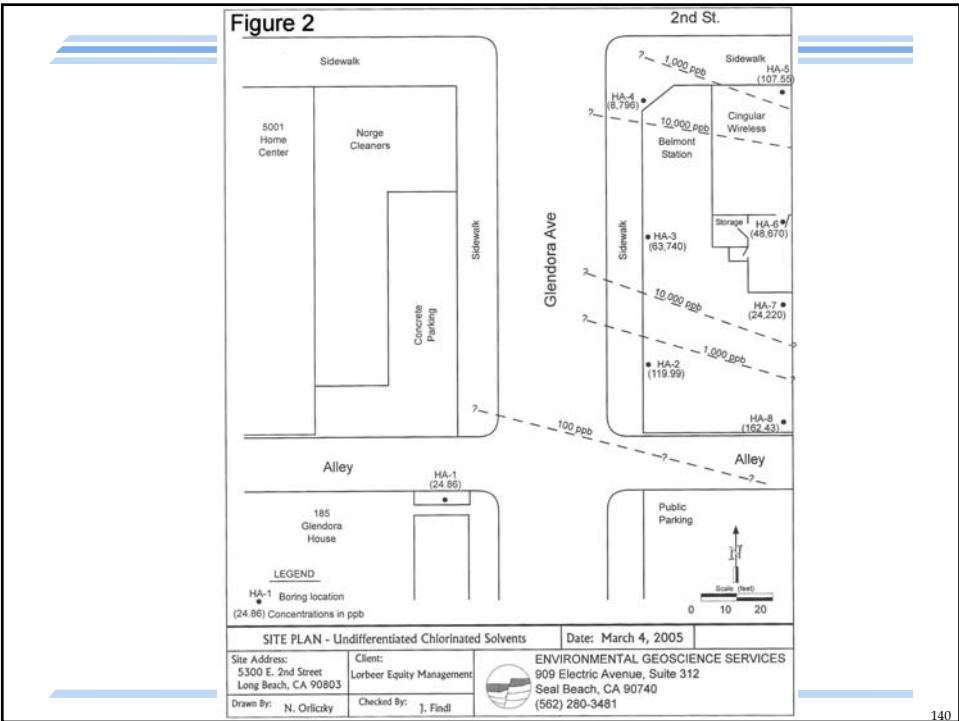
Background

- Operating dry cleaner since 1960, Long Beach, CA
- PCE leaks and spills, 1960-1990
- Replaced dry cleaning machine and piping in 1994; no soil removal
- No assessment or response action, 1994-2003
- No direct threat to human health or the environment
- Covered with blacktop and concrete
- Property sale is driving response action

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Norge Village Cleaners , CA

Environmental Issues

- Shallow soils and groundwater have been contaminated
- PCE, TCE, and degradation products are the chemicals of concern
- Shallow groundwater at 2' bgs to 20' bgs; slow migration to ESE
- High impact residential/commercial area
- Low profile remedial response action

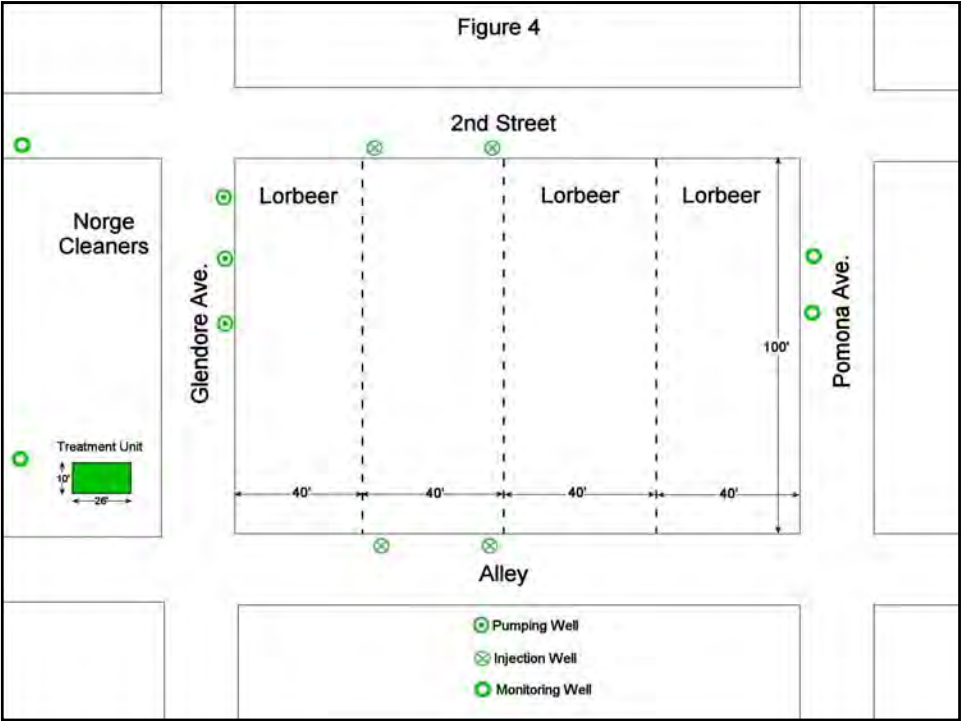
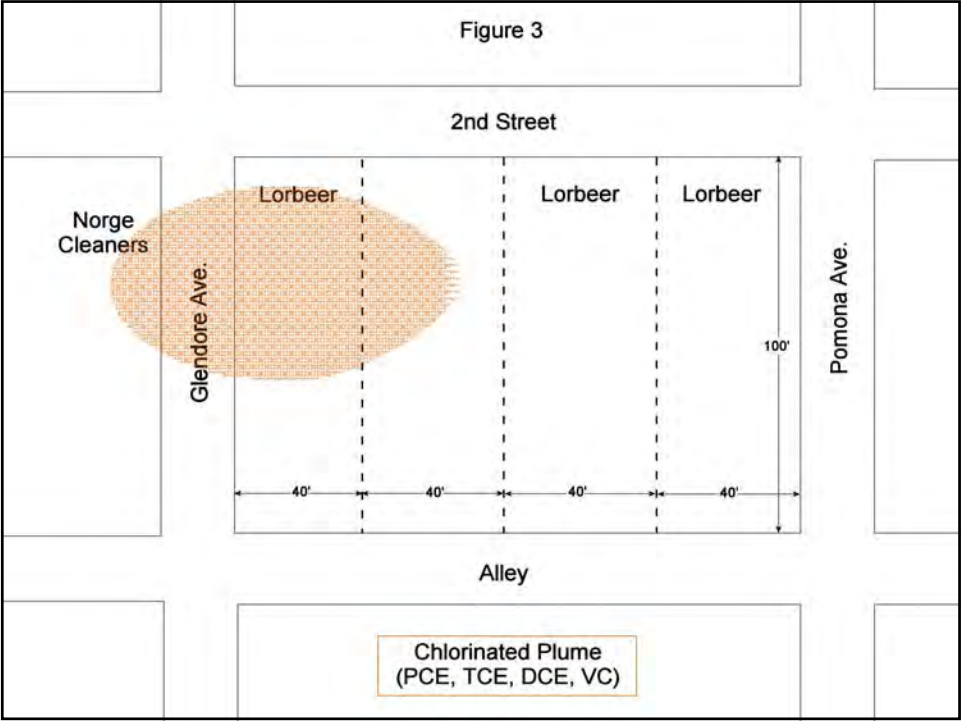
141

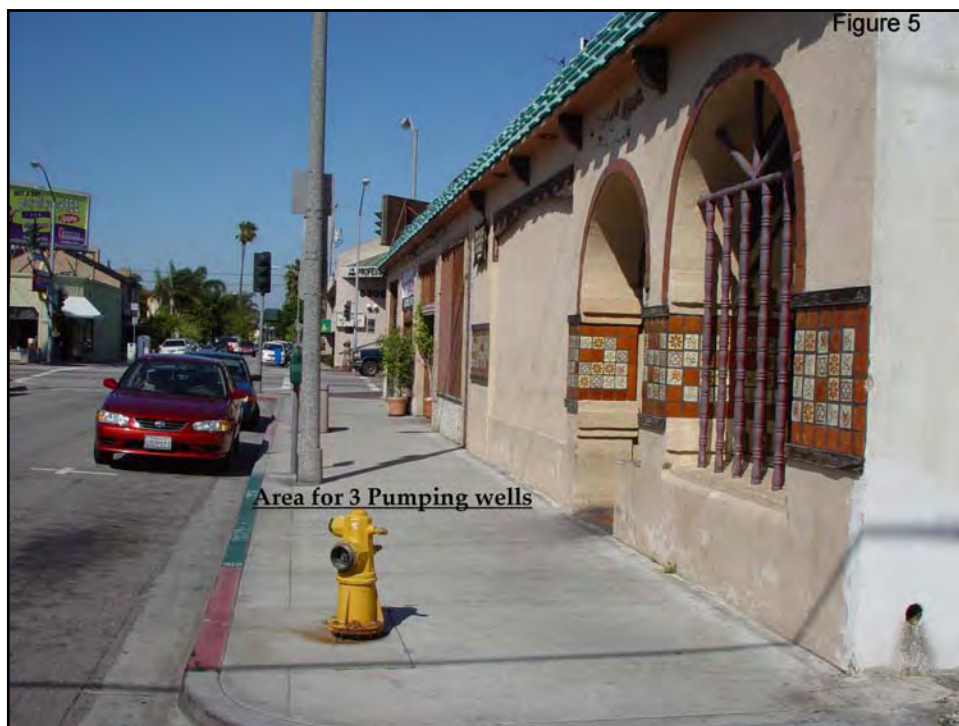
Norge Village Cleaners, CA

Remediation

- Seven 6" diameter by 20' deep dual phase extraction and injection wells; screen 5' bgs to 20' bgs
- Four 4" diameter by 20' deep monitoring wells; screen 5' bgs to 20' bgs
- Accommodate local commercial activity
- Treat extracted vapor (~20 cfm) with granulated activated carbon and vent
- Treat extracted water (2 gpm) with granulated activated carbon, add amendments, and inject at the fringes of the plume
- Add K_2SO_4 (4 ppm), $(NH_3)_2PO_4$ (3-4 ppm) as nutrients

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Norge Village Cleaners, CA

Costs

■ Wells	30,000
■ Pumps, piping	12,000
■ Electrical	10,000
■ Road, sidewalk repair	14,000
■ Chemicals	18,000
■ Disposal (carbon)	15,000
■ Supplies	18,000
■ Labor	
❖ Field	105,000
❖ Technical support	34,000
❖ Supervision	38,000
❖ Admin. support	16,000
■ Analytical	32,000
Total	342,000

147

Norge Village Cleaners, CA

Schedule

■ Assessment, design, build	3 months
■ Operate	12 months
■ Monitor	10 years

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TBA MNA Case Study – Bayport, Texas

■ Tert butyl alcohol and MNA

- ❖ Low K_{oc} , so adsorption negligible
- ❖ Low H , so volatilization negligible
- ❖ Chemical reactions negligible
- ❖ Advection, dispersion, dilution dictated by hydrogeology
- ❖ Biodegradation a significant NA mechanism

Day and Gulliver, 2003

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TBA MNA Case Study – Release

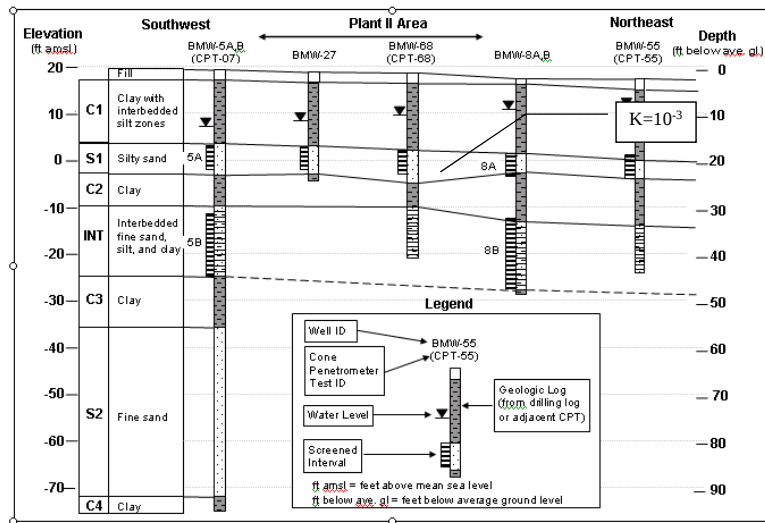
- Surficial clay is partially penetrated by chemical plant sumps, underdrains, and subsurface utilities
- Plant has operated for ~28 years
- Historic operational spills and leaks over the years have impacted GW in S1 unit
 - ❖ Source effectively controlled
- GW flow to the southwest

Day and Gulliver, 2003

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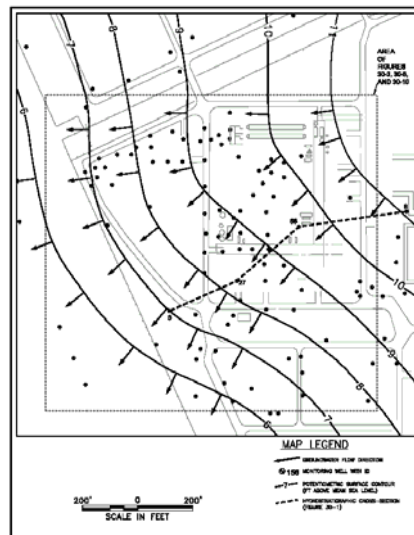
TBA MNA Case Study – Cross-Section

Day and Gulliver, 2003



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TBA MNA Case Study – GW Flow in S1 Unit



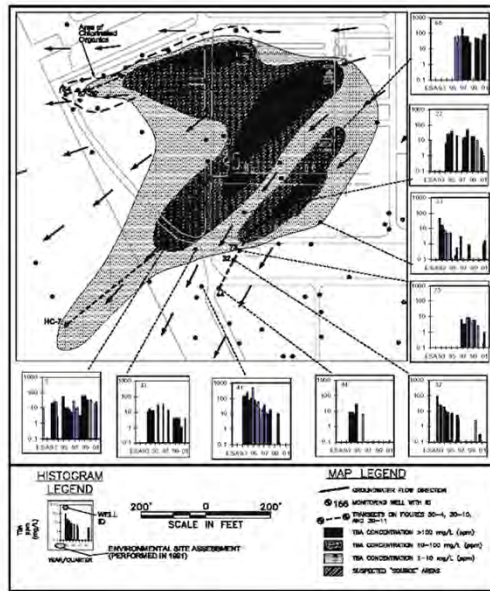
Day and Gulliver, 2003

152

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

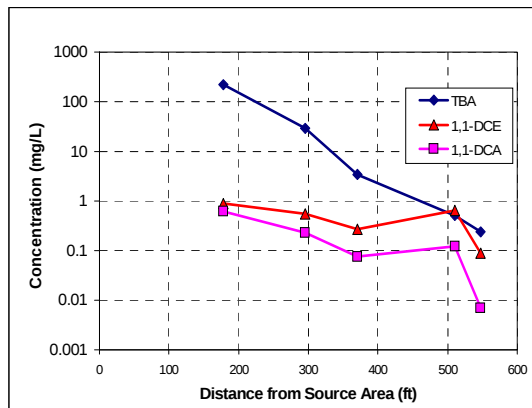
Day and Gulliver, 2003



153

TBA MNA Case Study - CVOC vs. TBA Attenuation in Northern Lobe of Plume

- Sequestering of TBA in clay was ruled out by data - and confirmed by modeling
- TBA attenuating more than DCE and DCA
 - ❖ Reverse would be expected if diffusion or adsorption were significant



Day and Gulliver, 2003

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TBA MNA Case Study – Carbon Isotope Analysis to Document Biodegradation

- Biodegradation is 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
 - ❖ $\Delta^{13}\text{C} = (R_s/R_r - 1) \times 1,000$
 - » where:
 - » $R_s = ^{13}\text{C}/^{12}\text{C}$ ratio of the sample
 - » $R_r = ^{13}\text{C}/^{12}\text{C}$ ratio of an international standard

Day and Gulliver, 2003

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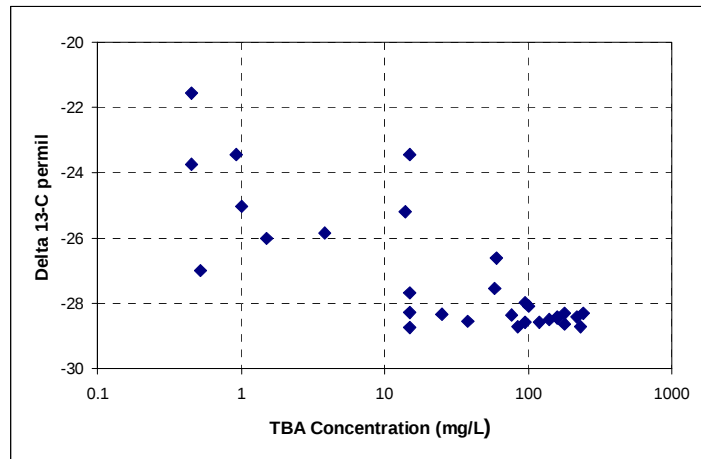
TBA MNA Case Study – Carbon Isotope Analysis

- 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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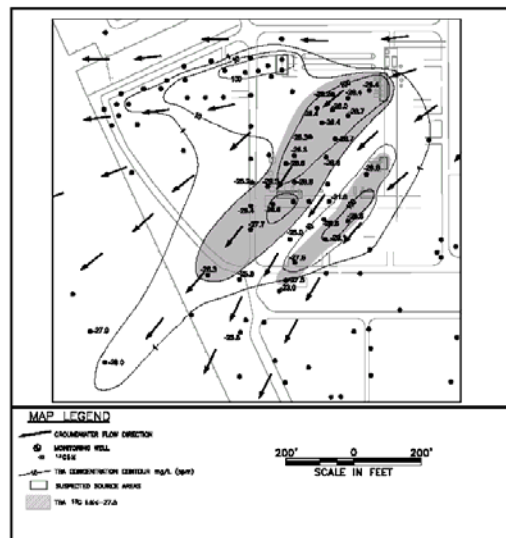
TBA MNA Case Study – TBA Conc. and Delta C



Day and Gulliver, 2003

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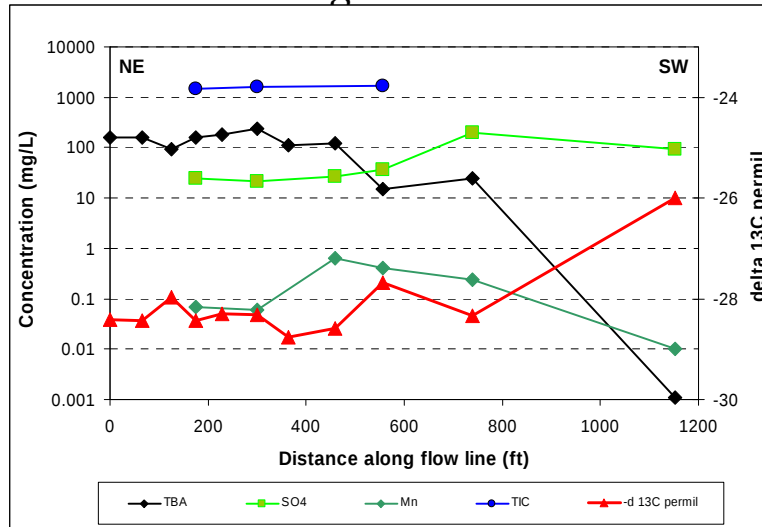
TBA MNA Case Study – Delta C Values



Day and Gulliver, 2003

158

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



Day and Gulliver, 2003

159

TBA MNA Case Study – Other Indicators of Biodegradation

- Anaerobic conditions
 - ❖ DO in plume is depleted (0.8 mg/l) relative to background wells (2 mg/l)
- Dissolved hydrogen gas (average 0.9 nM) indicates iron-reducing to sulfate-reducing conditions
 - ❖ Also, sulfate is depleted in plume core ~55 mg/l (vs. 128 mg/l in background wells)
- Further evidence of biodegradation + mineralization
 - ❖ Elevated total inorganic carbon (= CO₂ + bicarbonate) up to 2,100 mg/l (vs. 1,300 mg/l background)
 - ❖ Elevated CO₂ up to 66 mg/l (vs. 32 mg/l background)
 - ❖ Absence of other organics like methane, ethane, acetone
- Manganese elevated in the plume core (0.3 mg/l vs. 0.1 mg/l background)
 - ❖ Manganese reduction may also be occurring

Day and Gulliver, 2003

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TBA MNA Case Study – Biodegradation Rates

- Bio rates estimated from TBA concs. over distance and Buscheck and Alcantar (1995) equation
- Biodegradation half-life for TBA at this site estimated at 0.63-2.7 years

Day and Gulliver, 2003

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TBA MNA Case Study - Conclusions

- The TBA plume is stationary or shrinking, indicating attenuation at its leading edge
- Significant biodegradation is occurring
 - ❖ Aerobic (fringes)
 - ❖ Anaerobic (core)
 - » Iron-reducing
 - » Sulfate-reducing
- Bio is more active downgradient of source areas (indicated by carbon isotope data)

Day and Gulliver, 2003

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CEN Electronics - Caledonia, NY

Background

- 20 acres used for manufacturing and industrial, 1960 to present
- Generally flat surface with slight surface slope to the north
- No current threat to the public health or the environment
- Typical coastal plain hydrogeology along southern shore of the Great Lakes
- The first water-bearing zone is at 20'-30' deep; shallow gradient to the north

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CEN Electronics - Caledonia, NY

Background

- Several assessments over a 20-year period have identified contaminated soils and groundwater
- Septic systems, floor drains, and dry chemical wells are likely sources of TPH and chlorinated solvents to the shallow groundwater
- Potable water supply wells 1/2 mile downgradient from the property could be at risk

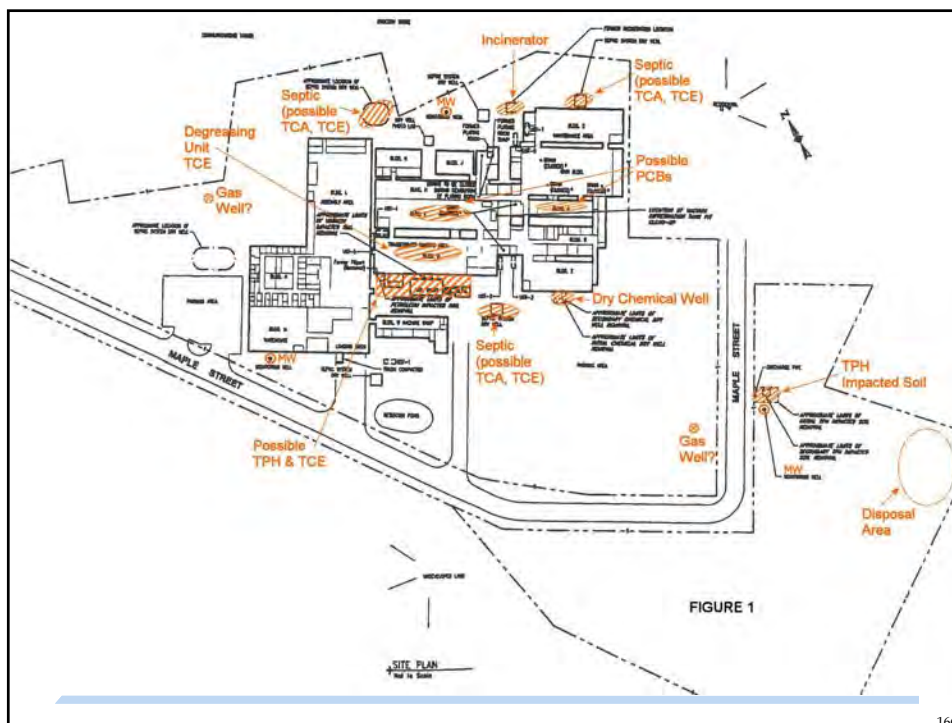
164

CEN Electronics - Caledonia, NY

Environmental Issues

- Natural springs and shallow subsurface spring channels in the area
- Onsite disposal, spills, leaks of chlorinated solvents and fuels
- Chlorinated solvents in degreasing area
- Soils in dry chemical well area contain BTEX, PCBs, and chlorinated solvents
- Metals and TPH in former incinerator area
- Comprehensive site assessment required to develop remediation plan

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CEN Electronics - Caledonia, NY

Costs

CPT	15,000
Trenches, borings	32,000
Wells	40,000
Pumps, piping	36,000
Water treatment	62,000
Vapor treatment	30,000
Supplies	50,000
Chemicals	40,000
Carbon recycle	20,000
Soil handling/treatment	45,000
Analytical	100,000
Disposal	40,000
Technical support	50,000
Supervision	80,000
Admin. support	<u>30,000</u>
Total	670,000

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CEN Electronics - Caledonia, NY

Remediation

- Remove trash, debris, scrap from the property
- Salvage/demolish the structures on the property
- Define local subsurface lithology with CPT
- Trenches to define the extent of the contaminated soils
- Excavate contaminated soils to 8' bgs and landfarm onsite
 - ❖ Add 10 lbs KMnO_4 per ton
 - ❖ Till in 1-foot lifts
 - ❖ Maintain 10-12% moisture

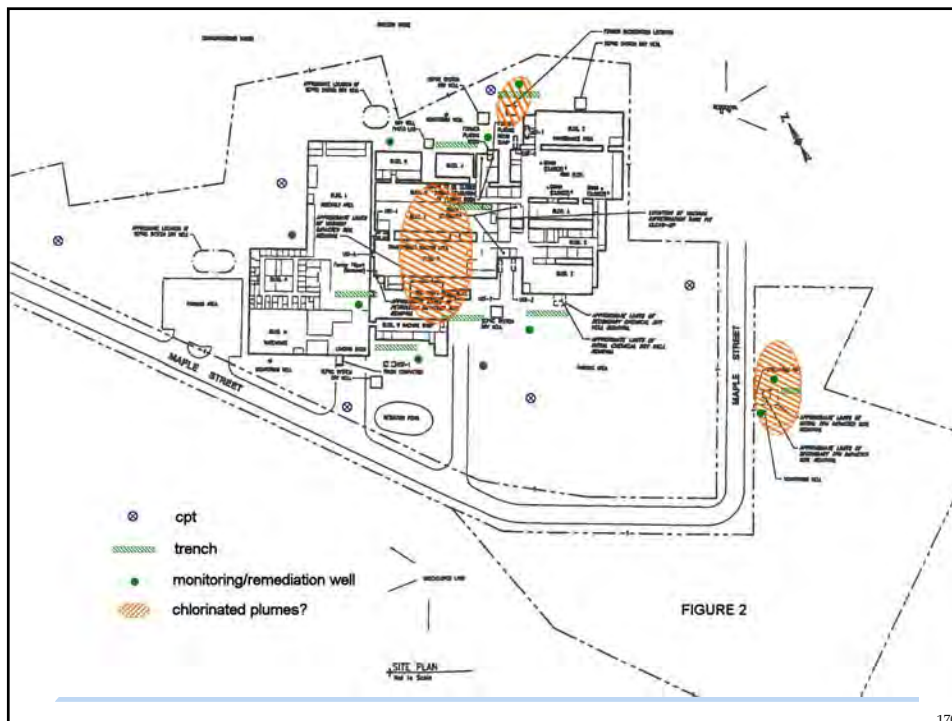
168

CEN Electronics - Caledonia, NY

Remediation

- 10 dual-phase (vapor and water) remediation/monitoring wells
 - ❖ 6" diameter x 35' bgs
 - ❖ Screen from 20' bgs to 35' bgs
- Soil vapor extraction at 10 cfm per well
- Treat soil vapor with granulated activated carbon
- Circulating in-situ groundwater bioremediation
 - ❖ Anaerobic (NH_3PO_4 , K_2SO_4)
 - ❖ Aerobic (O_2 , NH_3 , PO_4)
 - » West plume - switchover at 300 ug/l TCE
 - » East plume - switchover at 1,000 ug/l TCE
 - ❖ Treat with carbon

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CEN Electronics - Caledonia, NY

Schedule

■ Assessment	2 months
■ Design remediation	1 month
■ General site clean-up	1 month
■ Demolish and dispose	2 months
■ Soil remediation	5 months
■ Construct SVE, pump and treat, in-situ bio systems	2 months
■ Operate remediation systems	13 months
■ Monitor	10 years

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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

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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
 - ❖ $dh/dx = 0.01$
 - ❖ $K_{\text{fill}} = 35 \text{ feet/day}$
 - ❖ $V_{\text{GW in fill}} \sim 1 \text{ foot/day}$

Buscheck et al., 2001

173

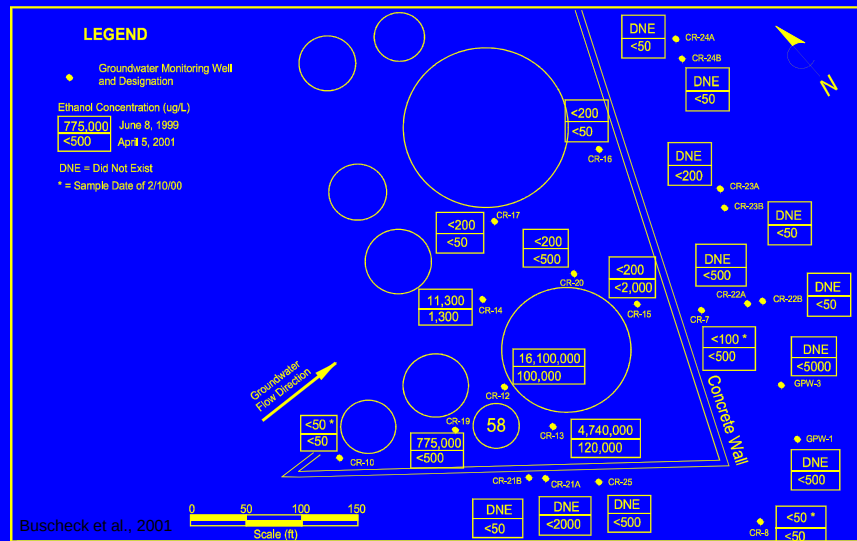
Pacific NW Terminal – Ethanol Bio

- 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

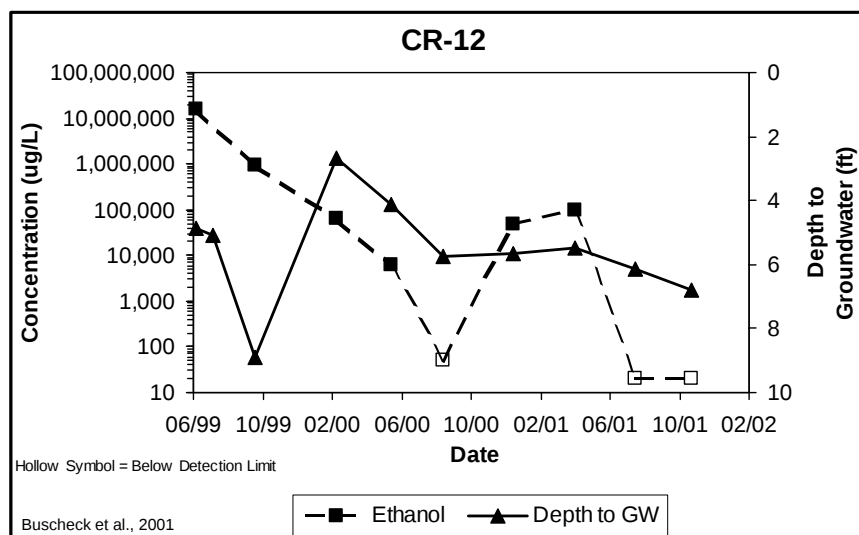
174

PNW Ethanol Concentrations 6/99 and 4/01



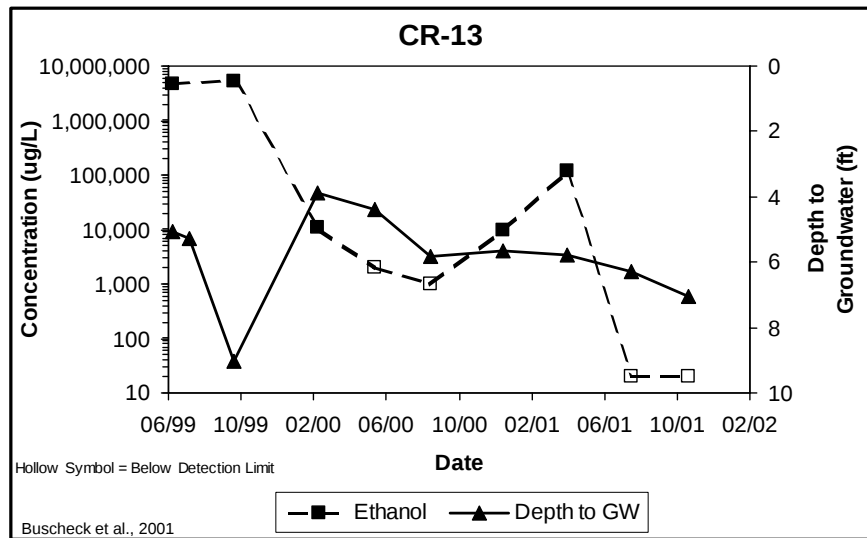
175

PNW Ethanol and DTW versus Time



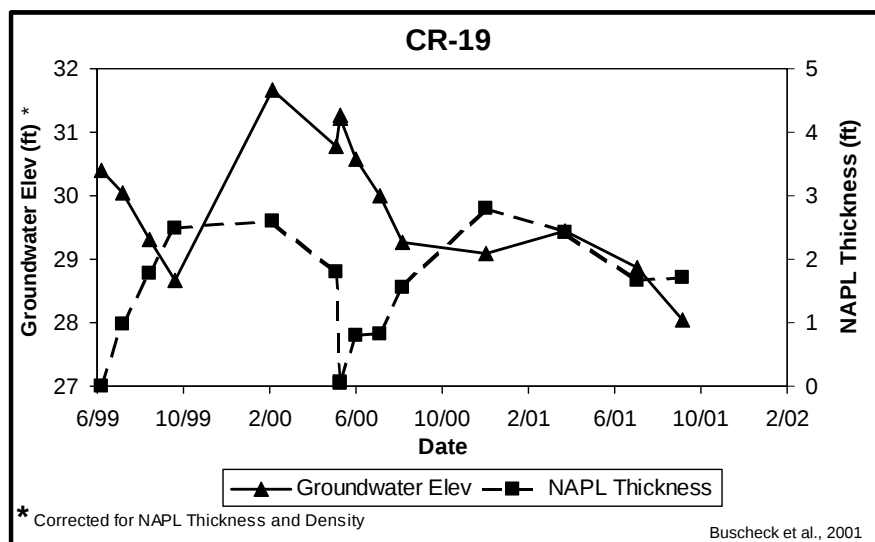
176

PNW Ethanol and DTW versus Time



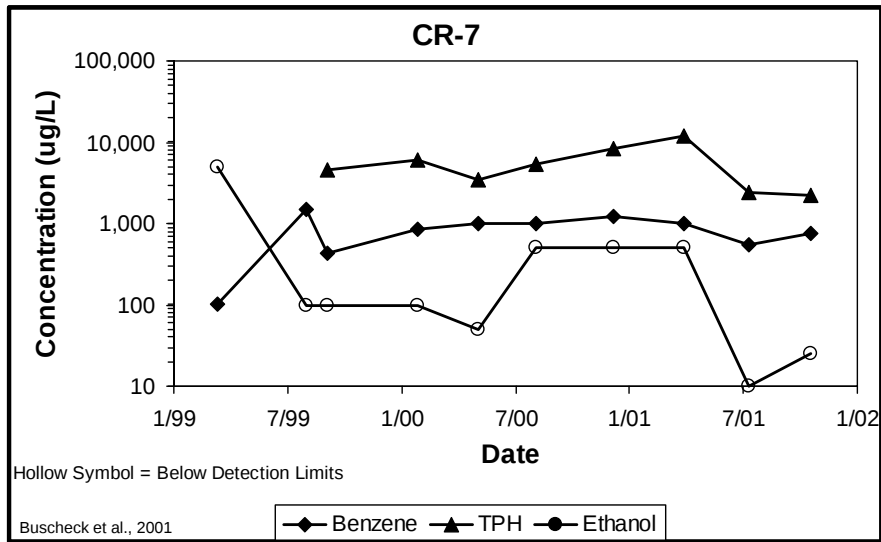
177

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



178

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



179

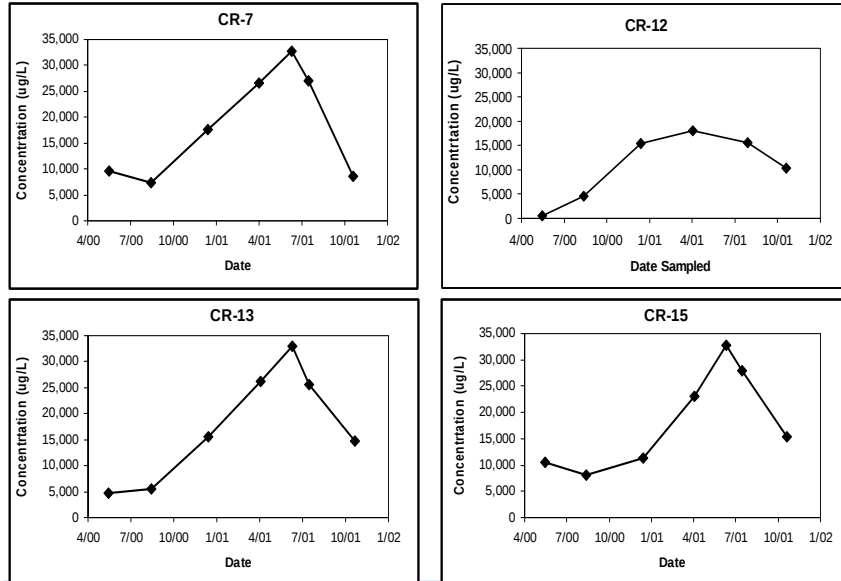
PNW Terminal - Methanogenesis

- 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

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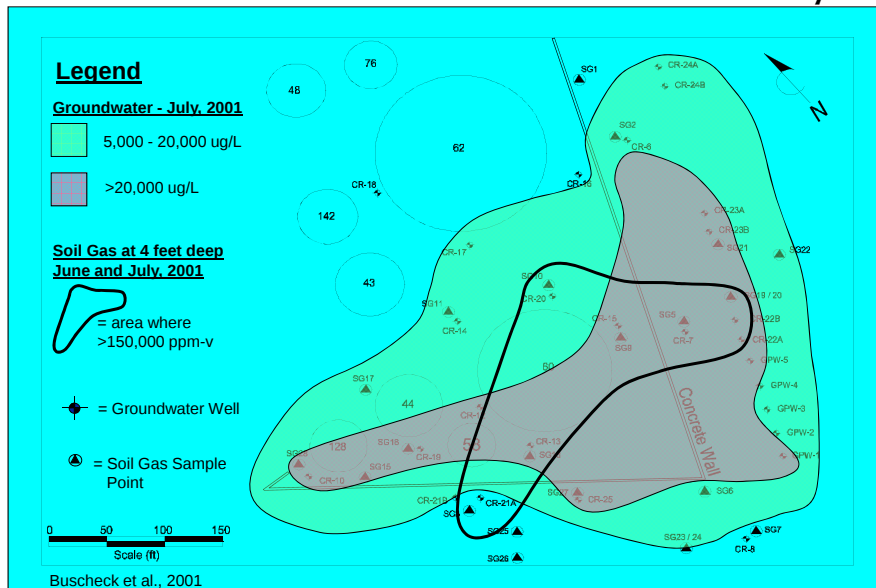
PNW Dissolved Methane Concentration versus Time



Buscheck et al., 2001

181

PNW Methane in Groundwater and Soil Gas 7/01



Buscheck et al., 2001

182

Pasadena, TX, Industrial Site

- Area A: Anaerobic to MNA
 - ❖ Schedule issues
 - ❖ Low receptor risk
- Area B: Anaerobic to aerobic
 - ❖ Continue active
 - ❖ Nearby receptors
- Areas C, D, E: Anaerobic to MNA
 - ❖ Low receptor risk
 - ❖ Continued MNA trends
- Area Fn: Anaerobic to aerobic
 - ❖ Steady progress
 - ❖ Active circulation
- Area Fs: Anaerobic to aerobic
 - ❖ Steady progress
 - ❖ Active circulation
 - ❖ Nearby receptors

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Pasadena, TX – Area A

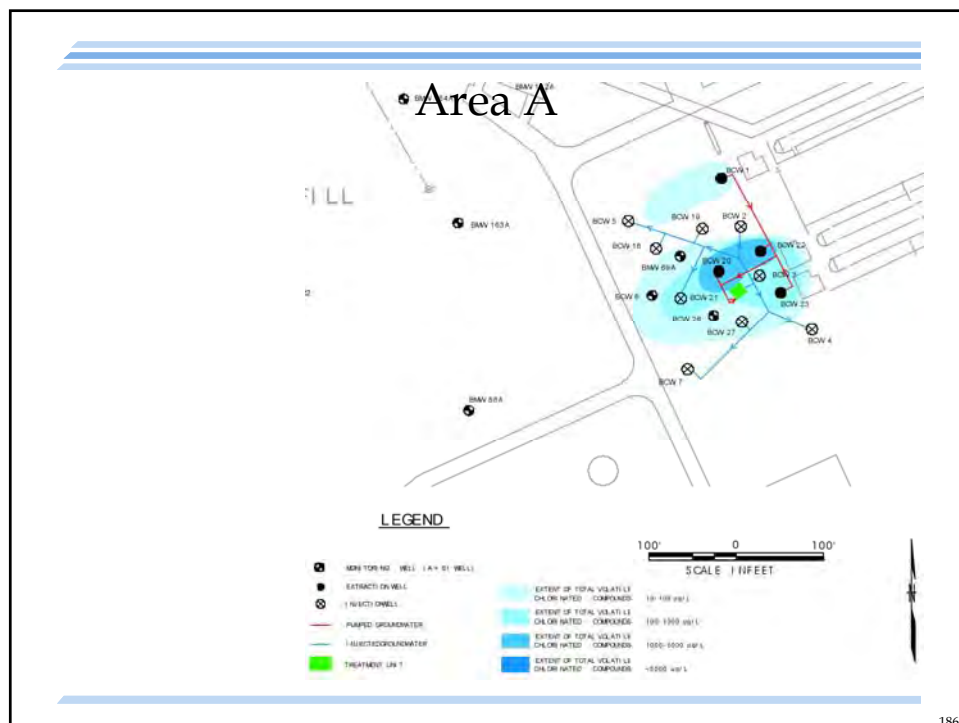
- Spills, leaks of maintenance chemicals, not process chemicals
- VOC impacted shallow groundwater beneath periodic maintenance yard
 - ❖ Chlorinated chemicals no longer used for maintenance
- Chemicals of concern are 1,1-DCE and 1,1-DCA
- Plume is well defined
 - ❖ Only the shallow (10'-20' bgs) water bearing zone is affected

184

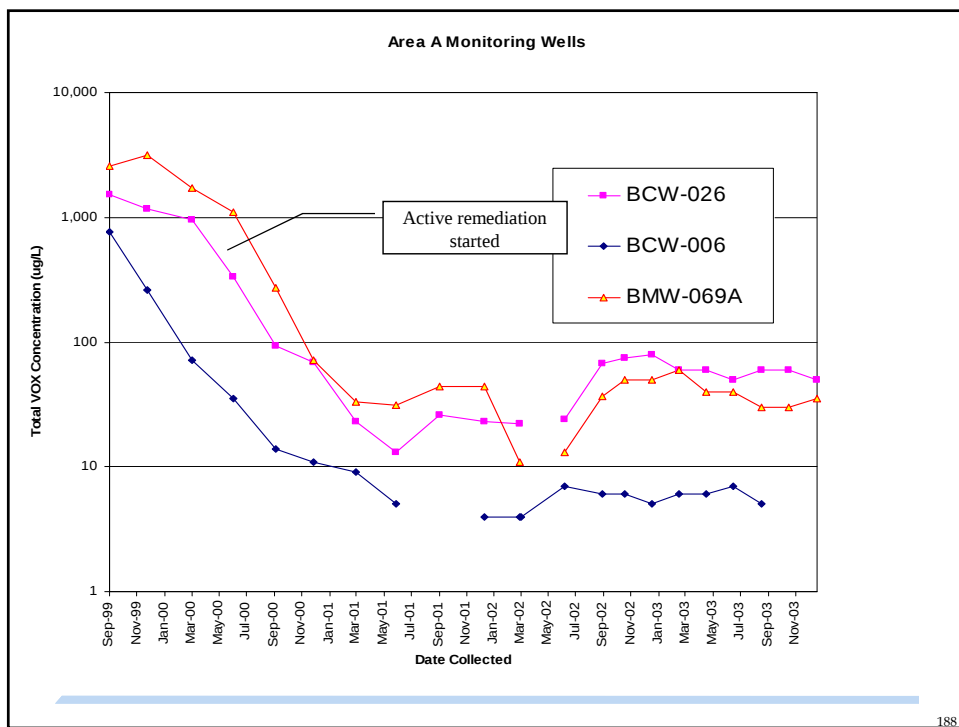
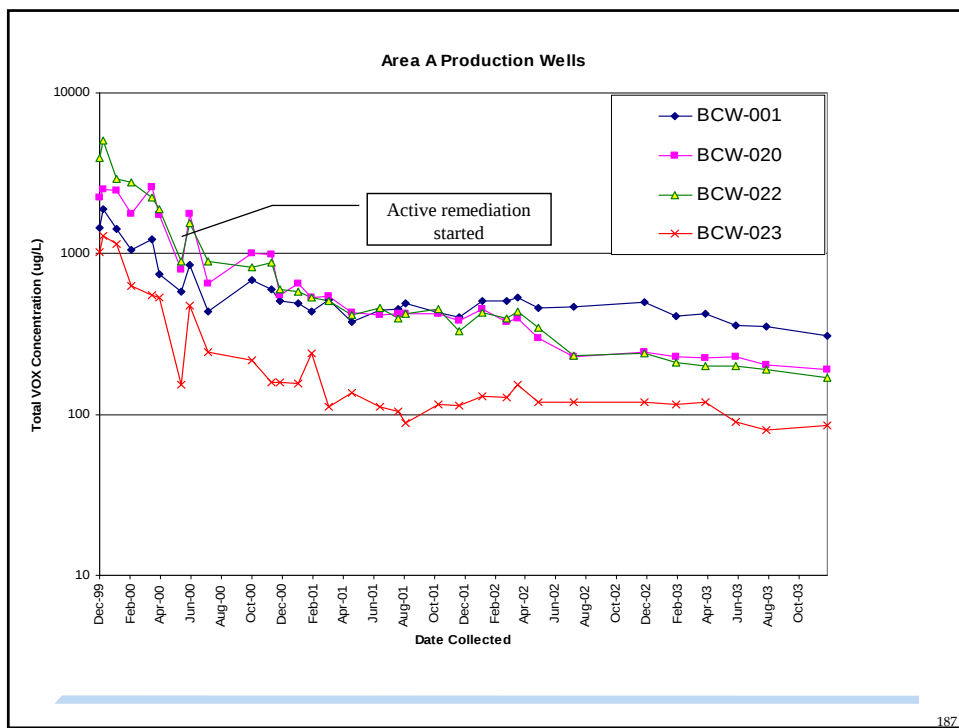
Pasadena, TX – Area A

- Use groundwater pump and treat and anaerobic in situ bioremediation
 - ❖ Extract 1.6 gpm from 4 extraction wells (6" dia. with 10' screens in the affected zone)
 - ❖ Treat water with GAC and inject into 9 wells
 - » 5 ppm nitrate (from KNO_3)
 - » 5-10 ppm sulfate (from K_2SO_4)
 - » 2-3 ppm phosphate (from $(\text{NH}_3)_2 \text{PO}_4$)
- Converted to MNA in Sept. 2002

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Pasadena, TX – Area B and B(West)

- Chemicals of concern are 1,1-DCE and 1,1-DCA
- On-going plume definition and response
- Two separate sources
 - ❖ Both related to intermittent use as a maintenance area
- Address as two separate plumes and develop two remediation systems
- Concentrations and risk levels are different
 - ❖ Both will respond to the anaerobic-aerobic-MNA sequence

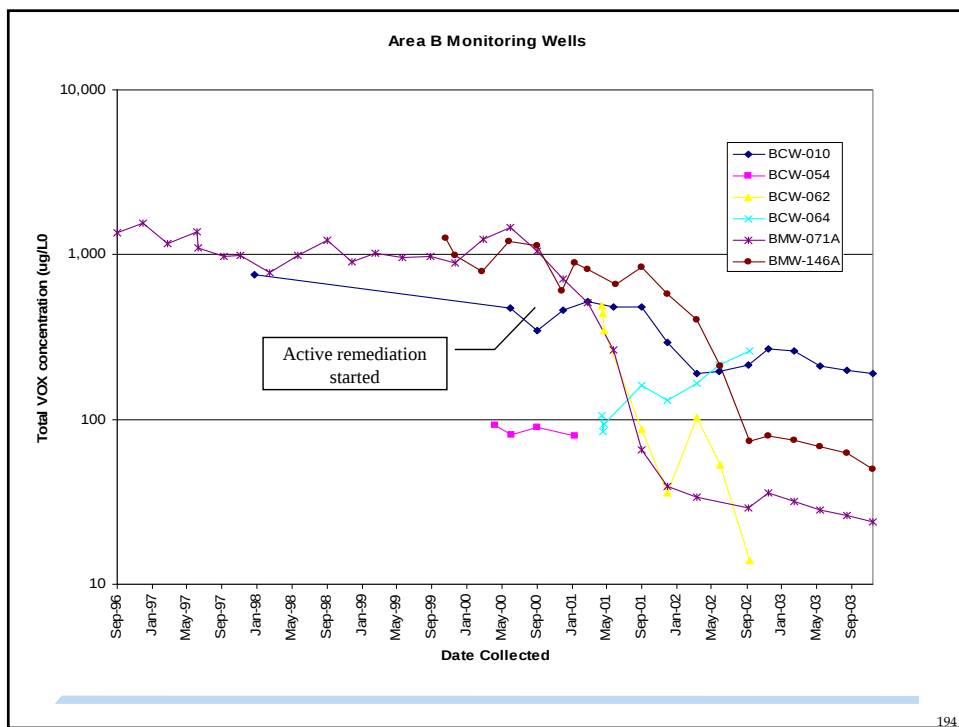
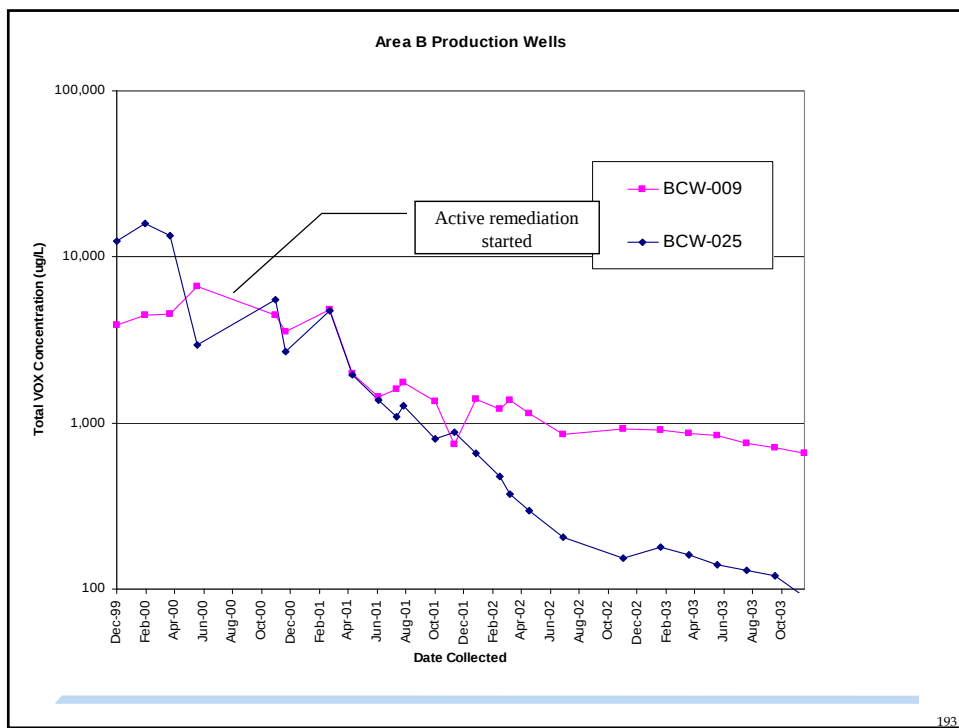
189

Pasadena, TX – Area B

- Use groundwater pump and treat and anaerobic in situ bioremediation
 - ❖ Extract 2 gpm from 5 extraction wells
 - ❖ Treat water with GAC and inject into 9 wells
 - » 10-20 ppm O₂ (from peroxide)
 - » 5-10 ppm nitrate (from KNO₃)
 - » 2-3 ppm phosphate (from (NH₃)₂ PO₄)

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- » 5-10 ppm nitrate (from KNO_3)
- » 2-3 ppm phosphate (from $(\text{NH}_3)_2 \text{PO}_4$)



Pasadena, TX – Area Fn and Fs

- Source area was former electronics repair area where chlorinated solvents were used
 - ❖ Source area has been removed
 - ❖ Plume is well defined
- Installed separate systems to address the hot-spots in the plume (Fn) and to protect the nearest receptors (Fs)
- Installed anaerobic-aerobic-MNA sequence, but at different transition concentrations

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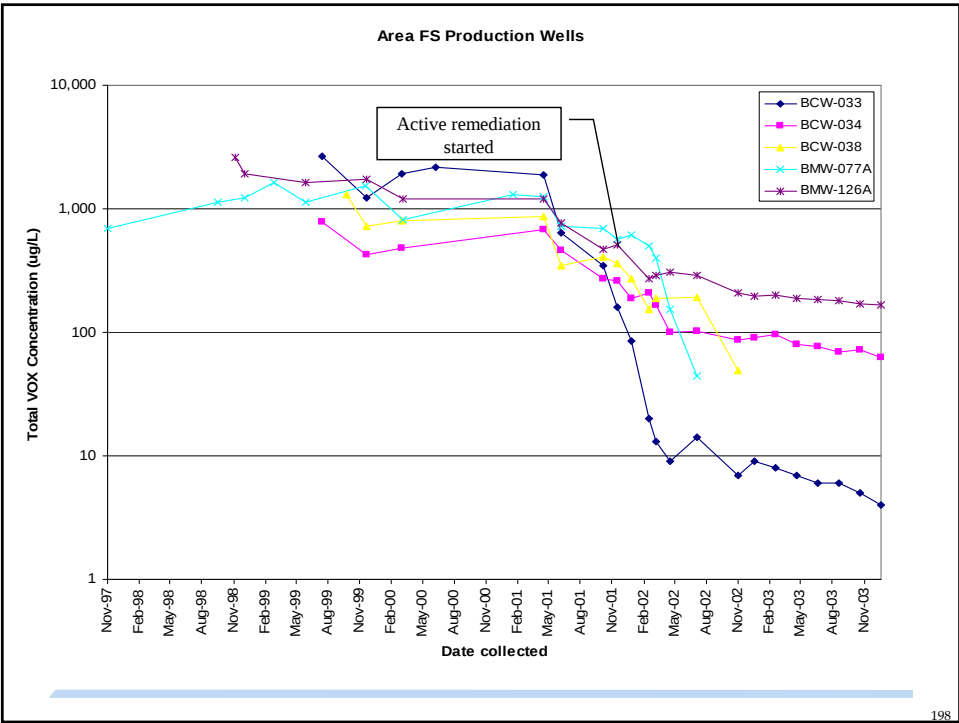
Pasadena, TX – Areas Fn and Fs

- May be able to skip the aerobic step in Fn
 - ❖ Lower risk – higher transition concentrations
- Use pump and treat and in situ bioremediation in Fn and Fs
 - ❖ Extract 7 gpm from 10 extraction wells
 - ❖ Treat water with GAC and inject into 17 wells
 - » 5-10 ppm nitrate (from KNO_3)
 - » 2-3 ppm phosphate (from $(\text{NH}_3)_2 \text{PO}_4$)

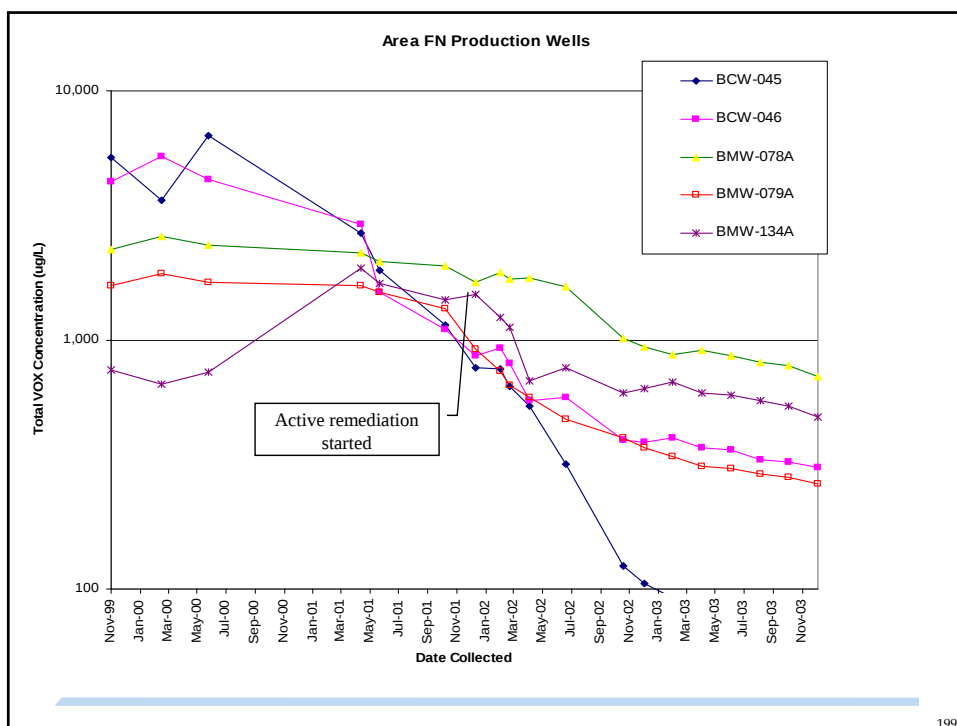
196



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Jacinto Port, Texas

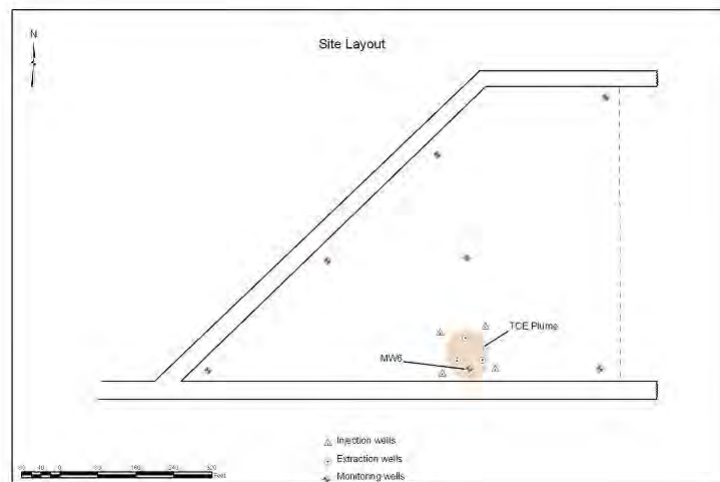
- TCE spill on vacant property
 - Groundwater impacts discovered as part of property transfer evaluation
 - Defined source and groundwater plume with soil borings and monitoring wells
 - Anaerobic in situ bioremediation for 6 months
 - Monitored natural attenuation
- 200

Jacinto Port, Texas

■ In situ bioremediation

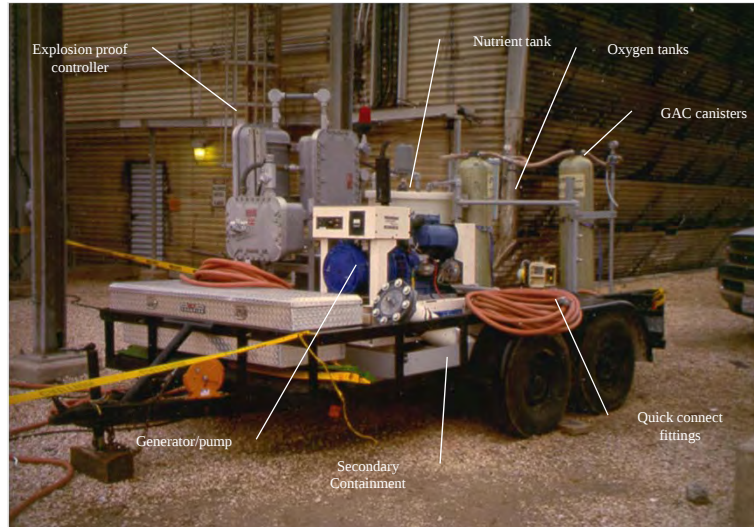
- ❖ Pump, treat, add nutrients and inject
- ❖ Pump in center of plume; inject on perimeter of plume
- ❖ Inject KNO_3 , $(\text{NH}_3)_2\text{PO}_4$, and K_2SO_4
- ❖ Circulate until TCE converted to DCE and DCE had started to convert to vinyl chloride
- ❖ Total cost \$40,000

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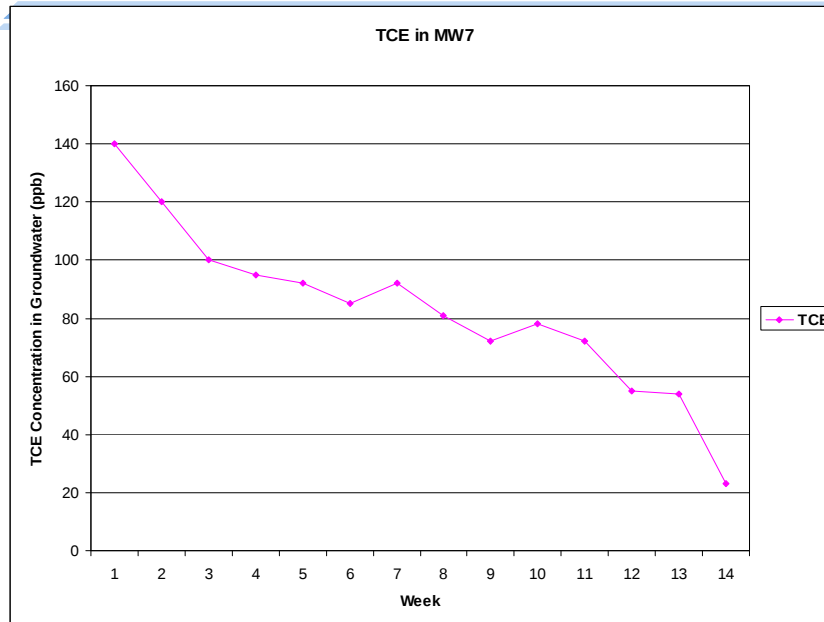


202

Jacinto Port, Texas-Mobile Treatment Unit



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Biostimulation of Native Aerobic Microorganisms at Vandenberg Air Force Base, Lompoc, CA

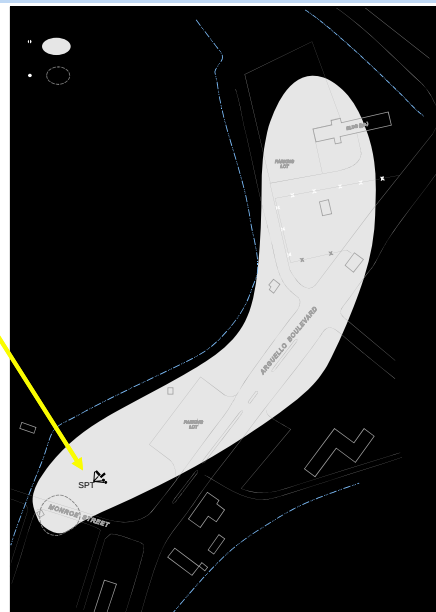
- UST site at base service station
 - ❖ Inventory reconciliation revealed release of 572 gallons unleaded gasoline 1994
- Source control by excavation in 1995
 - ❖ Sand & pea gravel backfill became recharge area
 - ❖ Shallow sand/gravel alluvial aquifer 5-8' bgs
 - ❖ 1.1ft/d
- Research Project: Biostimulation by O₂ injection
 - ❖ D. Mackay, R. Wilson, G. Durrant, K. Scow, A. Smith, M. Einarson, and B. Fowler

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Small-scale Pilot Tests Started Fall 1999

Goal: Stimulate and sustain *in situ* degradation of MtBE by native aerobic microbes within or down-gradient of diffusive oxygen release system

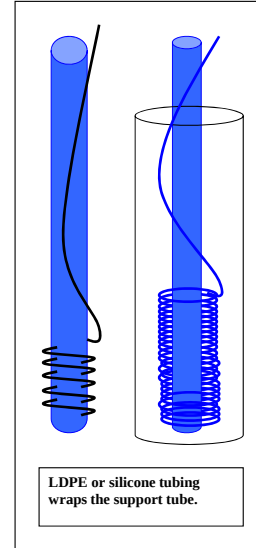


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Diffusive Oxygen Release Systems

- Rapid, inexpensive & effective delivery of dissolved oxygen to the saturated zone.
- 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



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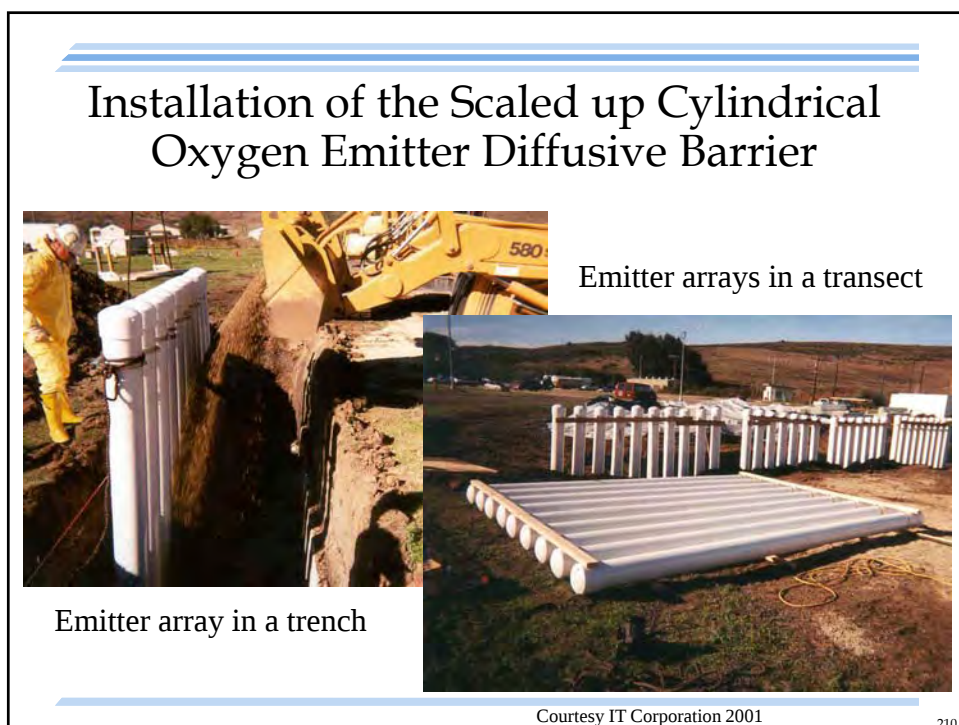
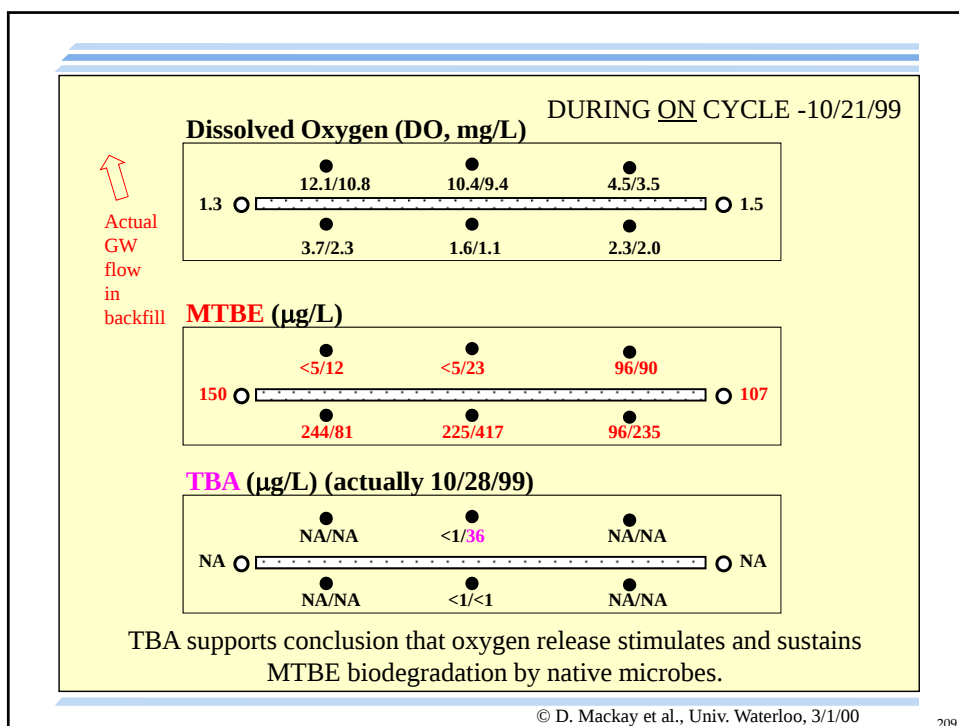
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Permeable Release Panel Pilot Test



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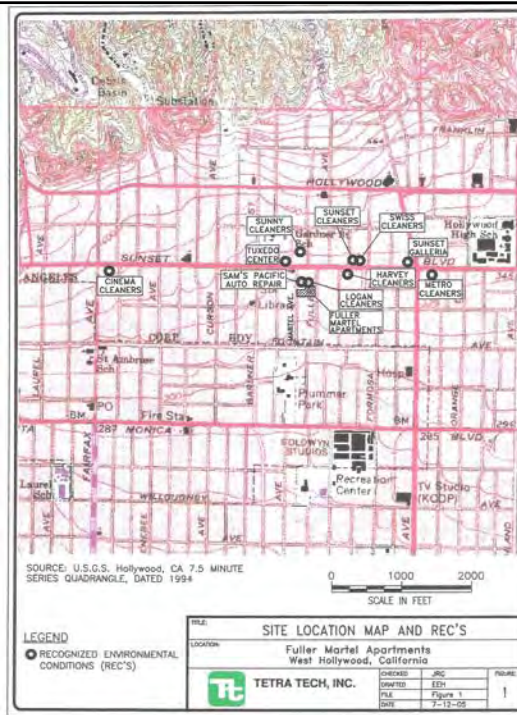


Fuller Martel Apartments, CA

Background

- Apartment building adjacent to gasoline station and dry cleaners
- Property sale is driving response action
- PCE and gasoline leaks and spills from 1960 to 2000 from multiple sources
- Some source control over last 5-8 years
- No risk to potable water supplies
- Potential ambient air risk in common areas on north side
- Nature and extent of the contaminated soil and groundwater are defined

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Fuller Martel Apartments, CA

Environmental Issues

- PCE drives the remediation
- TCE, DCE, DCA, VC, and BTEX, TBA, and MTBE are present
- Soils are contaminated to 35' bgs along the north side of the property
- BTEX and chlorinated concentrations are stable; no additional free-phase is indicated
- Shallow contaminated soils are source of BTEX and chlorinateds to the deeper groundwater
- Low levels of PCE and BTEX in groundwater at 110' bgs
- Shallow groundwater gradient at 110' bgs; no risk to potable water supplies

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Fuller Martel Apartments, CA

Contaminant Levels

Groundwater:	<u>UG/Liter</u>
TCE	5,000 – 9,000
DCE	6,000 – 10,000
DCA	3,500 – 6,000
VC	1,000 – 1,600
BTEX	3,000 – 8,500
TBA	4,500 – 6,000
MTBE	1,800 – 3,600

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Fuller Martel Apartments, CA

Remediation

- Conduct indoor ambient air quality study in apartments and common areas
- Confirm status of all potential sources
- Excavate shallow soils to 15' deep:
 - ❖ North side opposite Logan Cleaners
 - ❖ Excavate 400 yd³, classify and dispose
 - ❖ Provide temporary structural support
 - ❖ Backfill/compact with structural fill
 - ❖ Add K₂MnO₄ to fill

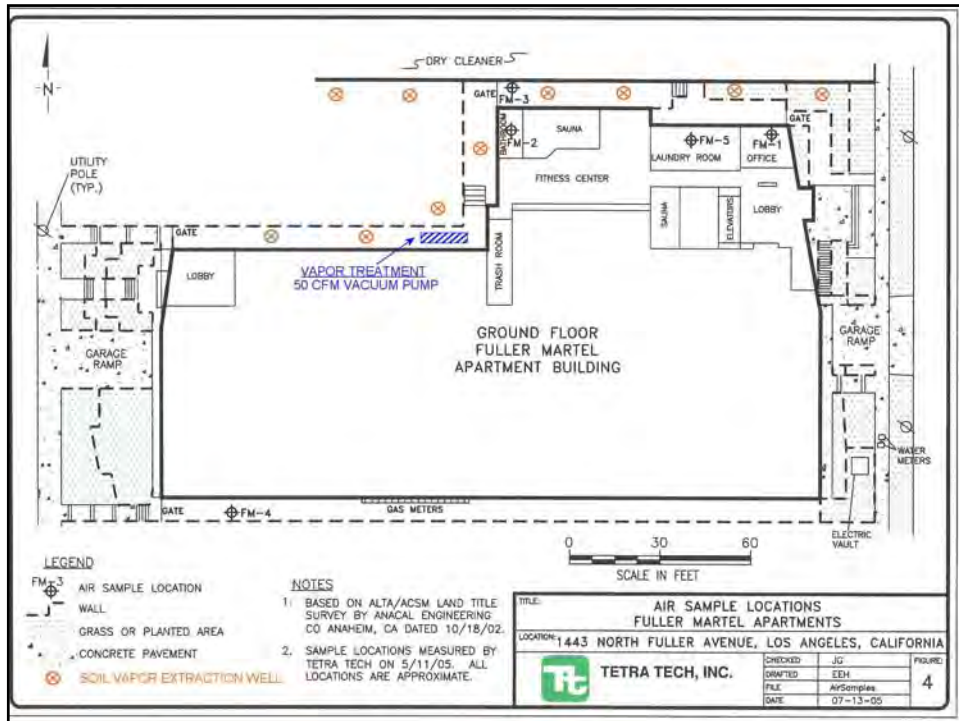
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Fuller Martel Apartments, CA

Remediation

- Soil vapor extraction:
 - ❖ Install ten 6" diameter x 35' deep vapor extraction wells
 - ❖ 20' screens, 15' bgs to 35' bgs
 - ❖ Extract 3 CFM per well
 - ❖ Treat vapor with carbon
- Natural attenuation:
 - ❖ BTEX, TBA, MTBE
 - ❖ Deeper groundwater

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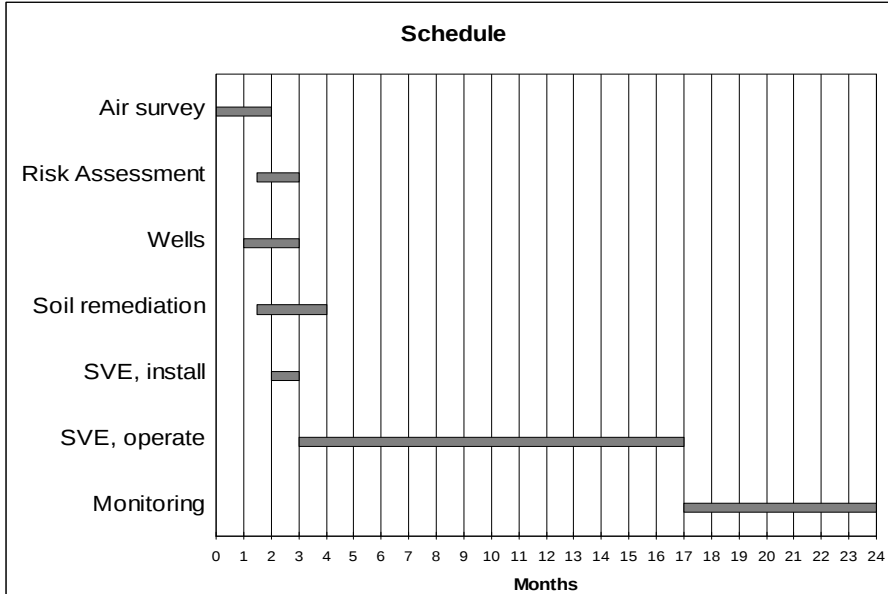


Fuller Martel Apartments, CA

Costs

■ Indoor air survey	15,000
■ Risk assessment	16,000
■ Excavate shallow soils	55,000
■ Disposal (soil)	25,000
■ Structural backfill	26,000
■ Chemicals	20,000
■ Wells	46,000
■ SVE system	235,000
■ Recycle (carbon)	12,000
■ Supplies	42,000
■ Analytical	35,000
■ Technical support	45,000
■ Supervision	48,000
■ Field labor	80,000
Total	700,000

Fuller Martel Apartments, CA



Outline of Workshop

- Introduction
- Physical properties
- Biological processes
- Applying biological technologies
- Natural attenuation processes
- Case studies
- *Conclusion and summary*

Bioremediation of VOCs

- VOCs are biodegradable under many conditions
- Anaerobic, aerobic, and alternating cycles
- Enhance/stimulate the biological processes
 - ❖ Carbon sources
 - ❖ Electron acceptors
 - ❖ Focused nutrients
 - ❖ Heat
- Bioaugmentation
- Manage the biological support systems
 - ❖ Circulation
 - ❖ Basic chemistry (pH, TDS, TOC, etc.)
 - ❖ Biomass
- Monitor

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Bioremediation of VOCs

- Each site/project is unique
- Optimize use of bioremediation
 - ❖ Generally low cost
 - ❖ Destroys contaminants
- Analytical, QA/QC and data management
- Refine remediation plan based on progress data
- Set up for successful MNA

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Natural Attenuation of VOCs

- Natural attenuation occurs at all sites
- Realistic expectations (time, concentrations) for MNA
- Adequate monitoring plan for MNA
 - ❖ Location, number and screen interval of wells
 - ❖ Chemicals of concern (COCs)
 - ❖ QA/QC and data management
 - ❖ Challenge COC list periodically
- Protect public health and the environment

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Aerobic and Anaerobic Bioremediation and Monitored Natural Attenuation of VOCs

Thank you for joining us!

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