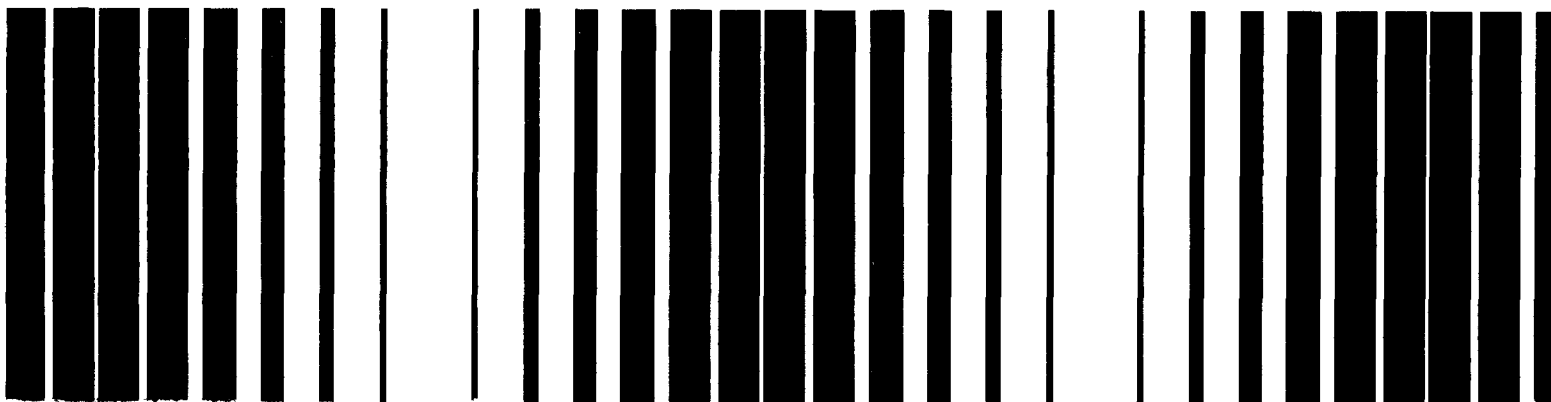




Seminar on Characterizing and Remediating Dense Nonaqueous Phase Liquids at Hazardous Sites

Presentation Outlines and Slide Copy

U.S. Environmental Protection Agency
Region 5, Library (PL-12J)
77 West Jackson Boulevard, 12th Floor
Chicago, IL 60604-3590



Disclaimer

Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

.

Table of Contents

Speaker Biographies A-1

Dense Nonaqueous Phase Liquid (DNAPL)
Contamination and Transport 1-1
David K. Kreamer

DNAPL Site Characterization 2-1
Robert M. Cohen
James W. Mercer

Options for DNAPL Remediation 3-1
Charles J. Newell

Speaker Biographies

Robert M. Cohen

Principal Hydrogeologist, GeoTrans, Inc., Sterling, VA

Robert M. Cohen is a principal hydrogeologist with GeoTrans, Inc. He received a B.S. from Dickinson College and an M.S. from Pennsylvania State University, with degrees in geology. Since 1982, Mr. Cohen has been with GeoTrans, Inc. where he has directed numerous environmental contamination and ground water resource development projects.

Mr. Cohen has been involved in the evaluation of various nonaqueous phase liquid (NAPL) contamination sites, including several chemical waste landfills in the Niagara Falls, New York area (Love Canal and 102nd Street hazardous waste landfills, among others) as well as the Fairfax, Virginia, Tank Farm petroleum release site, PCB sites in Florida, and several sites contaminated with chlorinated solvents. In 1987, Mr. Cohen co-authored a paper on the investigation and hydraulic containment of four NAPL contaminated chemical waste landfills in Niagara Falls, New York. In 1990, he co-authored a review paper on NAPL contamination and in 1992 he co-authored the U.S. Environmental Protection Agency's (EPA's) Dense Nonaqueous Phase Liquids (DNAPLs) Workshop Summary document. Also in 1992, Mr. Cohen co-authored a paper on evaluating visual methods to detect NAPLs in soil and water. Along with Dr. James W. Mercer, Mr. Cohen recently completed an EPA guidance document entitled "DNAPL Site Evaluation."

David K. Kreamer

**Director, Water Resources Management Graduate Program
University of Nevada—Las Vegas, Las Vegas, NV**

David K. Kreamer is presently the Director of the interdisciplinary Water Resources Management Graduate Program at the University of Nevada—Las Vegas. He also is an associate professor of geoscience and a member of the Graduate Faculty in Civil and Environmental Engineering. Prior to joining the faculty of University of Nevada—Las Vegas, he was an assistant professor of civil engineering at Arizona State University. Dr. Kreamer's undergraduate work was in microbiology and chemistry; he holds a M.S. and a Ph.D. in hydrology, with a minor in geosciences, from the University of Arizona.

Dr. Kreamer's present responsibilities include teaching, research, service, and program administration. He has researched many water-related topics, particularly the fate and transport of environmental contaminants, NAPLs, vadose zone hydrology, radioactive waste disposal, ground water hydrology, landfills, monitoring well design, and water resources management. He has been an invited lecturer at many conferences including a presentation in Brazil for the American Participant Program administered through the Executive Branch of the U.S. Government. He has given national lectures and training for EPA, the U.S. Bureau of Land Management, and the National Ground Water Association. In addition, he has presented workshops at the Hanford Nuclear Site and for the states of Alaska, Arizona, and Idaho.

Dr. Kreamer has been an external peer reviewer for risk assessment methodologies at the Rocky Flats Plant as part of the Rocky Mountain Consortium and for the Early Site Suitability documentation for the hydrology of Yucca Mountain. He served as a member of EPA's Science Advisory Board subcommittee on carbon-14 migration as carbon dioxide gas from high level nuclear waste repositories. He has worked at many CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) and RCRA (Resource Conservation and Recovery Act) sites, including Johnston Atoll in the Pacific Ocean. Dr. Kreamer has authored over 40 professional publications.

James W. Mercer

President, GeoTrans, Inc., Sterling, VA

James W. Mercer received a B.S. from Florida State University, and a M.S. and a Ph.D. from the University of Illinois, with degrees in geology. Dr. Mercer began working at the U.S. Geological Survey in 1971, where his research involved geothermal reservoir simulation and engineering. He worked on the simulation of isothermal two-phase flow (light nonaqueous phase liquids [LNAPLs] and water) and subsequently worked on the simulation of two-phase heat transport (steam and water). His work was published in the 1970s. In 1979, Dr. Mercer co-founded GeoTrans, Inc. and in 1980 he began simulation analysis of the Love Canal hazardous waste site in Niagara Falls, New York. In 1985, Dr. Mercer received the Wesley W. Horner Award of the American Society of Civil Engineers for the work that he performed at the Love Canal site.

Dr. Mercer became involved at other sites in Niagara Falls, New York, including the Hyde Park and 102nd Street landfills. He continued to study the physics of DNAPL flow and co-authored a paper on SWANFLOW, a three-dimensional multiphase flow code. He also became involved in characterizing DNAPL sites. In 1987, Dr. Mercer lectured on NAPLs for the National Water Well Association's Distinguished Seminar Series and in 1989 he lectured on characterizing oily wastes for EPA. In 1990, Dr. Mercer published a paper entitled "A Review of Immiscible Fluids in the Subsurface: Properties, Models, Characterization and Remediation." In 1991, he participated in the DNAPL Workshop sponsored by EPA's Robert S. Kerr Environmental Research Laboratory. Along with Mr. Robert M. Cohen, Dr. Mercer recently completed an EPA guidance document entitled "DNAPL Site Evaluation." Throughout the 1980s, Dr. Mercer continued to work on numerous sites and projects involving NAPLs, with work ranging from site characterization to evaluation of various types of remediation.

Charles J. Newell

Vice President, Groundwater Services, Inc., Houston, TX

Charles J. Newell has a B.S. in chemical engineering and a M.S. and a Ph.D. in environmental engineering from Rice University. He has ten years of experience working as an environmental consultant on surface water, ground water, and NAPLs issues. Dr. Newell currently serves as a vice president and environmental engineer at Groundwater Services, Inc. His project experience includes ground water flow modeling, solute transport modeling, design and construction of ground water and NAPL remediation systems, and field evaluation of emerging remediation technologies.

Dr. Newell directed the development of the OASIS ground water modeling software system under a two-year contract from EPA's Center for Groundwater Research. He has applied this software to solute transport studies and risk assessments at several industrial sites. He participated in the DNAPL Workshop sponsored by EPA's Robert S. Kerr Environmental Research Laboratory. Dr. Newell has co-authored EPA publications that address both DNAPLs and LNAPLs issues. Dr. Newell served as an instructor on ground water modeling for the Graduate Environmental Engineering Program at the University of Houston and is a contributing author to the Standard Handbook of Environmental Engineering.

Dense Nonaqueous Phase Liquid (DNAPL) Contamination and Transport

David K. Kreamer

Director, Water Resources Management Graduate Program, University of Nevada—Las Vegas

I. Introduction

A. Schedule for the Day

B. Definitions and Introduction

II. DNAPL Properties

A. Chemical Composition

1. General DNAPL Classification

a. Halogenated versus Non-Halogenated

b. Volatile versus Semi Volatile

c. Other DNAPLs

2. Organic Chemistry Review

3. Types of Problem Compounds

a. Solvents/Degreasers

b. Selected Pesticides

c. Polychlorinated Biphenyl Oils

d. Creosote and Coal Tar

B. Physical Properties of DNAPLs

1. Density

2. Viscosity

3. Solubility

a. Aqueous Solubility and Preferential Dissolution

b. Solubility in the Oil Phase

c. Cosolvency

4. Vapor Pressure, Henry's Law, and Volatilization

5. Partitioning Into Organic Liquids/ K_{ow}

6. Surface Tension and Interfacial Tension

7. Wettability and Wetting Angle
 - a. Capillary Force
 - b. Hydrophobicity
8. Electrical Properties
9. Photo (Light) Related Properties
 - a. Fluorescence
 - b. Photochemical Sensitivity
 - c. Photo-enhanced Degradation
10. Immunological Response

C. Microbial Transformation

1. The Subsurface Microbial Environment
2. Processes Affecting the Rate of Biodegradation
3. Typical DNAPL Biodegradation
 - a. Solvent Dehalogenation
 - b. Aromatic Dehalogenation
 - c. PCB Degradation
4. Cometabolism
5. Rules of Thumb for Biodegradation
6. Critical Evaluation of Bioremediation Claims

III. Vadose Zone Movement of DNAPLS

A. Nonaqueous Phase Movement

1. Wetting Front Instabilities (Fingering)
2. Blockage by Water and Stratigraphic Layers
 - a. Porous Media
 - b. Fractured Media
3. Perched Layers, Slanted Layers, and Well Construction Challenges

B. Leaching and Aqueous Phase Movement

1. Unsaturated Zone Aqueous Phase Movement
2. Unsaturated Zone Hydraulic Conductivity

C. Vapor Movement

1. Leaching of Vapors
2. Advective Gaseous Flux
 - a. Pressure Induced Flow
 - b. Density Driven Flow
3. Diffusion

IV. DNAPL Movement in Groundwater

A. Nonaqueous Phase Movement

1. Non-Geological Considerations
 - a. Spill Size
 - b. Types of DNAPL Spilled
2. Considerations in Movement
 - a. Initial Penetration of Groundwater
 - b. Effect of Pore Size
 - c. Downward Migration
 - d. Mobilization
3. Porous Media
4. Fractured Rock

B. Aqueous Phase Movement

1. Dissolution - Process and Rates
2. Preferential Dissolution
3. Advection and Dispersion
4. Retardation

SEMINAR SERIES

Characterizing and Remediating Dense Nonaqueous Phase Liquids at Hazardous Sites

- DNAPL Contamination and Transport
- DNAPL Site Characterization
- Options for DNAPL Remediation

DNAPLs

DNAPL Contamination and Transport

David K. Kreamer, Ph.D.
Director
Water Resources Management Graduate Program
University of Nevada, Las Vegas

DNAPLs

DNAPL Contamination and Transport

Talk Outline

- DNAPL Properties
- Vadose Zone Movement
- Groundwater Movement

Terminology

NAPL : Nonaqueous Phase Liquid

DNAPL : Dense Nonaqueous Phase Liquid

LNAPL : Light Nonaqueous Phase Liquid

Terminology (Cont.)

LNAPLs	Floaters
	Sp. Gravity < 1.0
WATER	Sp. Gravity = 1.0
DNAPLs	Sinkers
	Sp. Gravity > 1.0

DNAPLs

Classification

Halogenated Vs. Non-Halogenated

Volatiles Vs. Semi-Volatiles

Miscellaneous

DNAPLs**Examples****Halogenated Semi-Volatiles**

	Rank *
Chlordane	11
Aroclor 1260	13
Dieldrin	30
Pentachlorophenol	31

* ATSDR (Agency for Toxic Substances and Disease Registry)
List of Hazardous Substances

DNAPLs**Examples****Halogenated Volatiles**

	Rank *
Chloroform	8
Trichloroethylene (TCE)	10
Tetrachloroethylene (PCE)	22
Carbon Tetrachloride	33

* ATSDR List of Hazardous Substances

DNAPLs**Examples****Non-Halogenated Semi-Volatiles**

	Rank *
Benzo(a)Anthracene	40
Naphthalene	60
Phenol	85
Chrysene	95

* ATSDR List of Hazardous Substances

DNAPLs

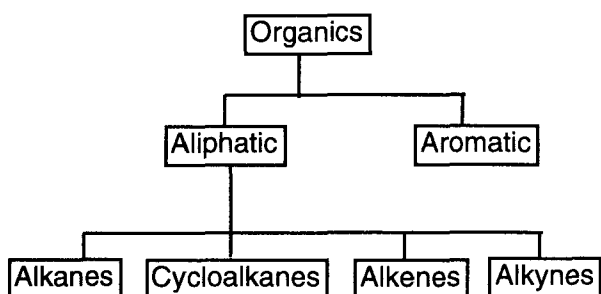
Examples

Miscellaneous

	Rank *
Mercury	3
Creosote	16

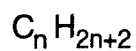
* ATSDR List of Hazardous Substances

Organic Chemistry

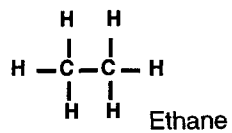
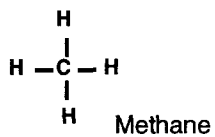


Organic Chemistry

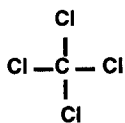
Alkanes (Paraffins)



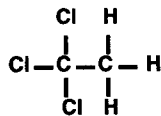
- Saturates
- Single Bonds



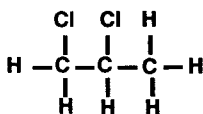
DNAPLs



Carbon Tetrachloride



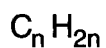
1,1,1-Trichloroethane



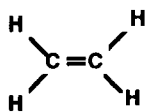
1,2-Dichloropropane

Organic Chemistry

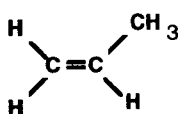
Alkenes (Olefins)



- Unsaturates
- At least one C=C (double) Bond

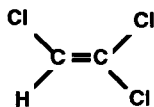


Ethene

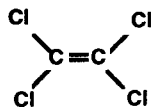


Propene

DNAPLs



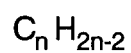
Trichloroethylene
(TCE)



Tetra(per)chloroethylene
(PCE)

Organic Chemistry

Alkynes



- Unsaturation
- At least one $C \equiv C$ (Triple) Bond



Acetylene

Organic Chemistry

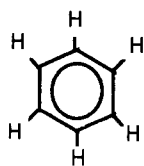
Aromatics

- Carbon atoms connected in a planar ring structure with bonds in "resonance"
- Different from Cycloalkanes

Organic Chemistry

Aromatics

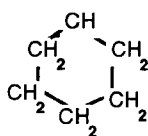
- Corner represents carbon atom



Benzene

Cycloalkanes

- Corner represents CH_2



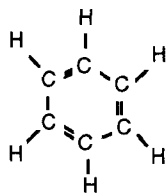
Cyclohexane

Organic Chemistry

Aromatics

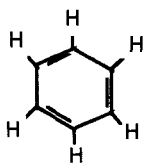


Benzene



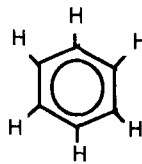
Benzene

or



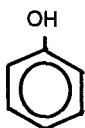
Benzene

or

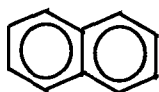


Benzene

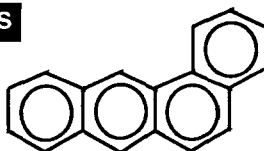
DNAPLs



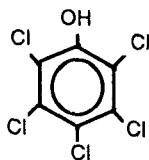
Phenol



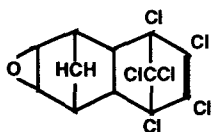
Naphthalene



Benzo(a)Anthracene



Pentachlorophenol



Dieldrin

Why is it difficult to figure out Pesticides ?

Example : Co-ral (livestock insecticide)

Aliases : Muscatox, Resistox, Coumaphos,
Bay 21/199, Asuntol, Baymix, Meldane.

Chemical Name :

O,O-diethyl-O-(3-chloro-4-methyl-
1-2-oxo(2H)-1-benzopyran-7-yl)-
phosphorothionate.

or 3-chloro-4-methyl-7-coumarinyl
diethyl phosphorothionate

Specific Gravity : 1.47

(Verschueren, 1983)

Selected Pesticide Names

Name	Other Name or Ingredient	Purpose
Ambush	Aldicarb, Temik	Systemic Insecticide
Compound 497	Dieldrin	Insecticide
Seedrin Liquid	Aldrin	Insecticide Fumigant

(Verschuieren, 1983)

Selected Pesticide Names

Name	Other Name or Ingredient	Purpose
Grisetin	Griseofulvin	Fungicide
Co-op Brushkiller 112	Iso-Octyl esters of 2,4-D and 2,4,5-T	Herbicide
Warf-12	Warfarin	Rodenticide

(Verschuieren, 1983)

DNAPLs

Interesting Names/Abbreviations

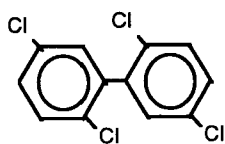
- **TCA** = Trichloroacetic acid S.G. 1.63
 = 1,1,1 Trichloroethane S.G. 1.35
 = Tucson Commission
 on the Arts S.G. ?
- **ABS** = Teepol 715 = AAS
- **TDE** = DDD

DNAPLs

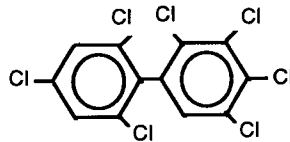
Poly Chlorinated Biphenyls (PCBs)

- Mixtures of poly chlorinated biphenyls
- Relatively non-flammable, useful heat-exchange and dielectric properties
- Electrical Industry : Capacitors & Transformers
- Also used in Lubricating and Cutting Oils, Pesticides, Adhesives, Plastics, Inks, Paints, and Sealants

PCBs - Examples



2,2',5,5' - Tetrachloro biphenyl



2,2',3',4,4',5',6-Heptachloro biphenyl

DNAPLs

PCBs (Cont.)

- Generally, more Chlorine => more Water Soluble
- Degree of chlorination often indicated by trade name
 - Aroclor 1242 - 42 % Chlorine (S.G. 1.42)
Aroclor 1260 - 60 % Chlorine (S.G. 1.44)
 - Phenoclor DP6 and Clophen A60 have approximately 6 Chlorine atoms/molecule.

Creosote

- A mixture of phenols and phenol derivatives.
- Obtained by the destructive distillation of wood tar, or from the fractional distillation of coal tar.
- Most common wood preservative

Composition of Creosote

	Aqueous Solubility (mg/l)	Log K_{ow}	K_{oc}
Naphthalene	31.700	3.37	1,300
Acenaphthalene	3.930	4.33	----
Fluorene	1.980	4.18	----
Phenanthrene	1.290	4.46	23,000
Fluoranthene	0.260	5.33	----
Pyrene	0.135	5.32	84,000

(J.M.Henson, 1989)

DNAPLs

Physical Characteristics

- Density
- Viscosity
- Solubility
- Octanol - Water Partition Coeff. (K_{ow})
- Vapor Pressure and Henry's Coeff.

DNAPLs

Physical Characteristics (Cont.)

- Interfacial Tension
- Wettability
- Dielectric Constant
- Light (Photo) Related Reactions

DNAPLs

Density

- Mass (of fluid) per unit volume (g/mL)
- Similar expressions include
 - Specific Weight
 - Specific Gravity

DNAPLs

Density (Cont.)

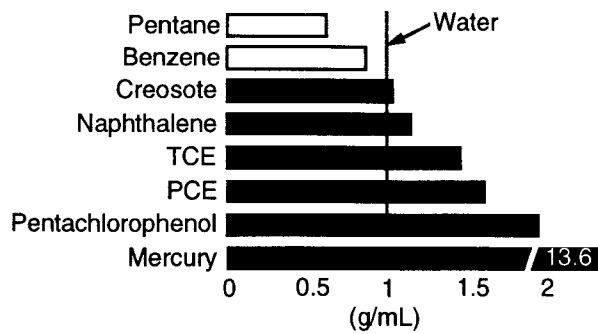
Specific Weight

- Weight per unit volume (lbs/ft³)

Specific Gravity

- Density Relative to Water
- $$\frac{\text{Wt. of given vol. of Liquid}}{\text{Wt. of same vol. of Water}}$$

Density - Examples



DNAPLs

Viscosity

- Measure of a fluid's resistance to flow
- Main Cause : Molecular Cohesion
- Absolute (Dynamic) Vs. Kinematic
- Typical Units : Centipoise (cp)
- $1\text{cp} = 0.01\text{poise} = 0.01\text{g/s.cm}$

DNAPLs

Viscosity (Cont.)

- "Mobility" Increases with Increasing Temp.

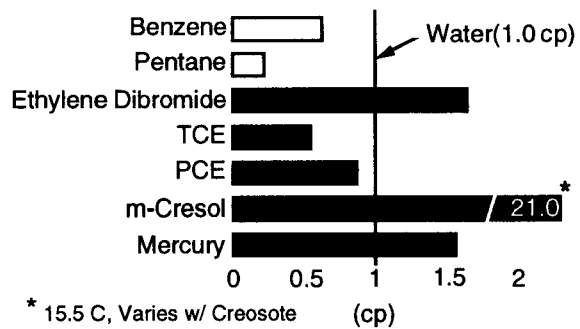
As Temperature Increases, the Cohesive forces Decreases, and the Absolute Viscosity Decreases, thus Increasing its "mobility"

DNAPLs Viscosity (Cont.)

- May change with time

Crude Oil, after losing lighter Volatile compounds due to evaporation, may become heavier and more viscous

Viscosity - Examples



DNAPLs Hydraulic Conductivity (K)

- $K = \text{fn} [\text{Fluid density } (\rho) \text{ \& Viscosity } (\mu)]$

- $$K = \frac{k \rho g}{\mu}$$

- In Saturated Porous Media, Fluids with

$$\rho > \rho_w \quad \text{or} \quad \mu < \mu_w$$

will move faster relative to Water.

DNAPLs Aqueous Solubility

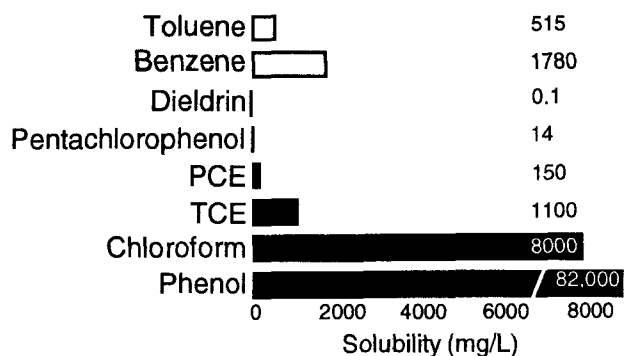
- Equilibrium Concentration of a Chemical or Compound in Water.
- mg/L
- Influencing Variables
 - Molecular Weight & Structural Complexity
 - Dissolved Salts or Minerals
 - Cosolvency in mixed solvent system
 - pH

DNAPLs Aqueous Solubility (cont.)

Factors affecting rate of dissolution

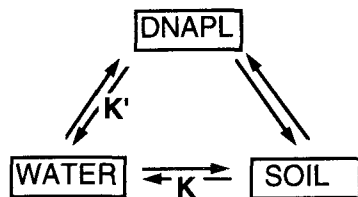
- Solubility of the Compound
- Groundwater Flow Conditions
- Contact Area
- Contact Time

Aqueous Solubility - Examples



DNAPLs

Three Phase System



Partition Coeffs.

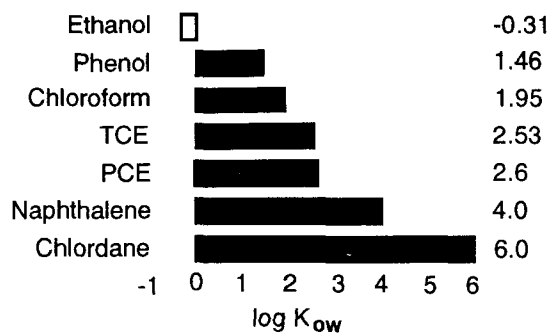
K = Soil-Water

K' = DNAPL-Water

Octanol-Water Partition Coeff. (K_{ow})

- Tendency of a chemical to partition between Organic and Aqueous phase
- $K_{ow} = \frac{\text{Con. in Octanol phase}}{\text{Con. in Aqueous phase}}$
- Low K_{ow} => Hydrophilic
- High K_{ow} => Hydrophobic

K_{ow} - Examples



Cosolvency

- Addition of a second solvent to a mixture, changes the original solubility of a chemical.
- Two solvents change other properties as well

Vapor Pressure

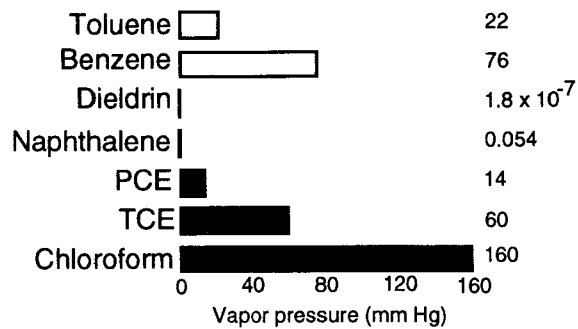
- Determines how readily vapors volatilize from pure liquid phase
- Partial pressure exerted at the surface of the liquid phase by the free molecules
- Directly dependent upon temperature
- atm, mm Hg

Vapor Pressure (Cont.)

- Migration Controlled by Diffusion
- Soil-Vapor Monitoring
- Soil Venting

(Mercer, 1989)

Vapor Pressure - Examples



Henry's Law Constant (K_H)

- $$K_H = \frac{\text{Con. of a compd. in the vapor phase}}{\text{Con. in the aqueous phase}}$$

Also

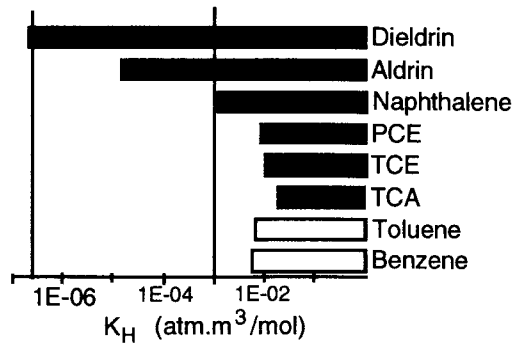
- $$K_H = \frac{\text{Vapor Pressure (atm)}}{\text{Solubility (mol/m}^3\text{)}} \left[\frac{\text{atm-m}^3}{\text{mol}} \right]$$

Henry's Law Constant (Cont.)

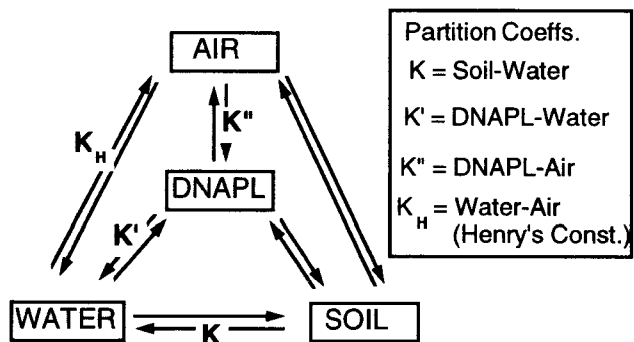
- Soil-Gas Monitoring Implications

Higher the K_H for a compound, the more readily it will partition into the vapor phase, and will be more amenable to Soil-Gas monitoring.

Henry's Law Const. - Examples



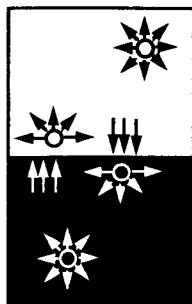
DNAPLs Four Phase System



Interfacial Tension

Interfacial Tension

Force exerted on the interface between two liquids



Interfacial Tension (Cont.)

- Measured as the force required to draw a thin platinum wire ring through the interface between two liquids.
- Typical Unit : dynes/cm
- Magnitude of Interfacial Tension is lesser than the larger of Surface Tension for pure liquids

Interfacial Tension (Cont.)

- Higher the I.T., less likely emulsions will form, and better the phase separation after mixing.
- Lower the I.T. between a DNAPL and water, higher the instability of the interface, and more likely the immiscible fingering.

The Blender Test

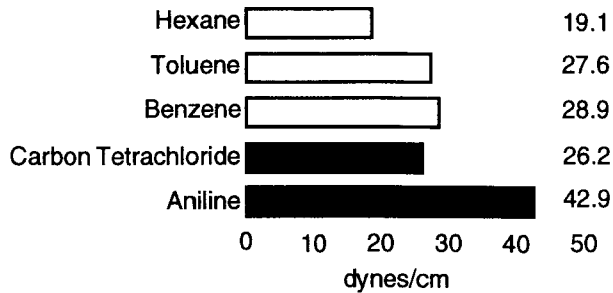
Put a drop of DNAPL in a small vial of water and blend the contents using a blender apparatus.

The effect of shear on the hydro-carbon-water mixture can be examined.

Indicates whether emulsions can form under certain pumping conditions

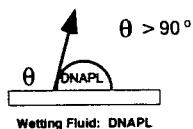
(Mercer, 1989)

Interfacial Tension- Examples



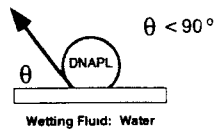
Wettability

- Describes the preferential spreading of one fluid over solid surfaces in a two fluid system.
(S.G.Huling et al., 1991)
- Inferred from the Contact (Wetting) angle [θ]
(USEPA, 1990)
- The wetting angle is typically measured against a clean, polished mineral surface (usually calcite and quartz).
(Mercer, 1989)



Wetting Fluid: DNAPL

Water



Wetting Fluid: Water

Water

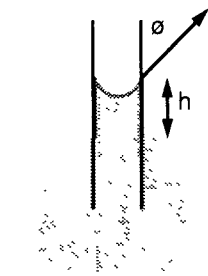
Fluid Relationships:

System	Wetting Fluid	Non-Wetting Fluid
air:water	water	air
air: DNAPL	DNAPL	air
water:DNAPL	water	DNAPL
air:DNAPL:water	water>organic>air ⁽¹⁾	

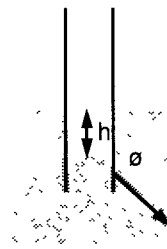
(1) Wetting fluid order

After, Waterloo Centre for Groundwater Research, 1989
RSKRL 101-015

Capillary Rise Theory

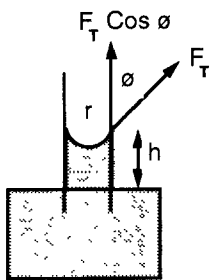


Adhesive dominant



Cohesive dominant

Capillary Rise Theory



Upward Force :
 $F_T \cos \theta (2 \pi r)$

Downward Force :
 $(\pi r^2 h) (\rho g)$

$$h = \frac{2 F_T \cos \theta}{\rho g r}$$

Electrical Properties

- Dielectric Constant
- Other Electrical Properties

Light (photo) Related Reactions

- Fluorescence
- Light-Induced Reactions
- Photoassisted Degradation

Fluorescence

- Spontaneous emission of visible light resulting from a concomitant movement of electrons to higher and lower orbital states when excited by UV radiation.
- NAPLs can be identified by visual examination of soil or water samples using this property.

(R.M.Cohen et al., 1992)

Fluorescence (Cont.)

- The examination is made in a dark room by scanning the sample in a clear plastic bag with the UV light.
- The sample fluoresce depending upon the contaminants.
- Nearly all crude Oils, petroleum products, aromatics, and many Unsaturated Aliphatics fluoresce.

(R.M.Cohen et al., 1992)

Light (Photo) -Induced Reactions

- DNAPL is sorbed onto Solid-Phase Extraction Membranes (SPE) from the aqueous phase
- Silver Nitrate reagent is sprayed on the SPE tabs and exposed to UV light.

(E.J.Poziomek et al., 1993)

Light (Photo) -Induced Reactions (Cont.)

- DNAPL presence indicated by the development of gray coloration on the tabs.
- Proven effective for PCBs

(E.J.Poziomek et al., 1993)

DNAPLs

Photoassisted Catalytic Degradation

- Isothermal, parallel plate, fluidized bed reactor
- Titanium dioxide (TiO_2) illuminated with near ultraviolet light.
- Cr-doped TiO_2 tested under visible light excitation.

(Dibble, 1989)

DNAPLs

Photoassisted Catalytic Degradation

(Cont.)

- Reactor effluents analyzed by Gas Chromatography
- Gaseous TCE tested, 100 % conversion to carbon dioxide and hydrogen chloride
- High flowrates possible over long periods of time

(Dibble, 1989)

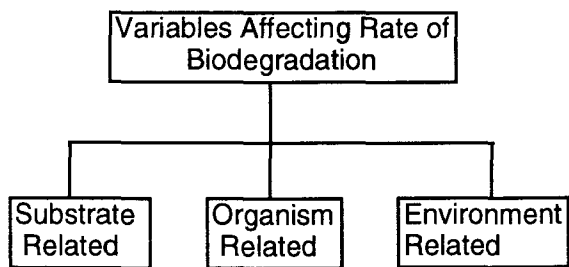
Immunological Response

- Immunoassays use polyclonal antibodies
- Semi quantitative
- Available tests for PCBs in soil and other NAPLs

Microbial Ecology of Subsurface

- 1×10^6 to 1×10^8 microbes/gm soil (more in pristine environments)
- > 90% of microbes attached to soil
- Metabolically active
- Metabolically versatile
- Oxidic and anoxic conditions

Microbial Transformation



(Lyman et al., 1990)

Substrate Related

- Physico - Chemical Properties
- Concentration

(Lyman et al., 1990)

Organism Related

- Species Composition of Population
- Spatial Distribution
- Population Density
- Inter & Intra Species Reactions
- Enzymatic Makeup and Activity

(Lyman et al., 1990)

Environment Related

- Temperature
- pH
- Moisture
- Oxygen Availability
- Salinity
- Other Nutrient Availability
- Soil Toxicity

(Lyman et al., 1990)

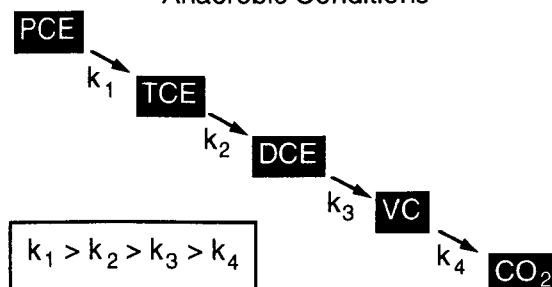
Selected Types of Aerobic & Anaerobic Respiration - Microbial Metabolism of Organics

Process	Electron Acceptor	Metabolic Products	Relative Potential Energy
Aerobic Heterotrophic Respiration	O ₂	CO ₂ , H ₂ O	↑ HIGH
Denitrification	NO ₃ ⁻	CO ₂ , N ₂	
Iron Reduction	Fe ³⁺	CO ₂ , Fe ²⁺	
Sulfate Reduction	SO ₄ ²⁻	CO ₂ , H ₂ S	
Fermentation	Glucose	EtOH	↓ LOW
Methanogenesis	CO ₂	CO ₂ , CH ₄	

(Adapted from Suffita et al., 1991)

Halogenated Aliphatic Compounds

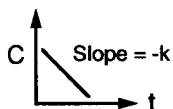
Anaerobic Conditions



Rate Reactions

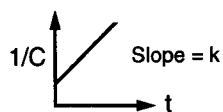
Zero-Order

- $C_t = C_0 - kt$
- $t_{1/2} = C_0 / 2k$



First Order

- $C_t = C_0 e^{-kt}$
- $t_{1/2} = 0.693/k$



Rate Reactions (Cont.)

Hyperbolic Reactions

$$\mu = \mu_m \frac{S}{K_s + S} \quad \text{Monod Equation}$$

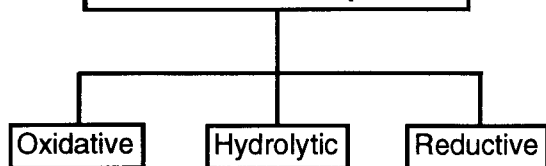
μ = Specific growth rate (1/t)

μ_m = Max specific growth rate (1/t)

K_s = Saturation Coeff. (mg/L)

S = Growth limiting substrate concentration (mg/L)

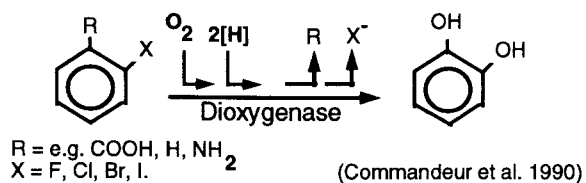
Dehalogenation of Aromatic Compounds



(Commandeur et al. 1990)

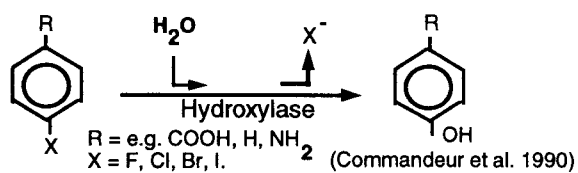
Oxidative Dehalogenation

- Halogen is lost fortuitously during oxygenation of the ring
- Only in aerobic conditions



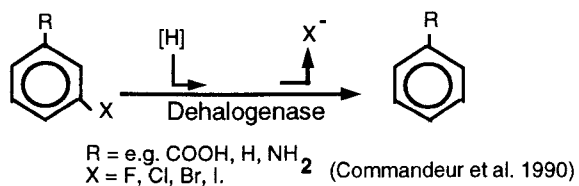
Hydrolytic Dehalogenation

- Hydrogen is specifically replaced by a 'OH' group
- O₂ atom in the hydroxyl group is derived from water instead of oxygen
- Aerobic and Denitrifying conditions



Reductive Dehalogenation

- Halogen is replaced by a Hydrogen
- Halogenated aromatic compound acts as the terminal electron acceptor
- Sulfogenic and Methanogenic conditions



PCB Degradation

Anaerobic Conditions

- Reductive Dechlorination
(Chlorines replaced by H's)
- Reduces Toxicity
- Enhances Aerobic Degradability

(J.M.Henson, 1989)

PCB Degradation (Cont.)

Anaerobic Conditions

- Soils previously exposed to PCB's showed activity.
- Added 700 ppm Aroclor 1242

Time 0 - 1% mono chlorinated biphenyls

Time 16 wks - 76% mono chlorinated biphenyls

- Penta-chlorinated biphenyls gone
- Most activity in first 4 weeks

(J.M.Henson, 1989)

PCB Degradation (Cont.)

Aerobic Conditions

- Lower Chlorinated Compounds more Susceptible
- Treatment Evaluations should Perform Mass Balance
- GC/MS to Detect Preferential Degradation

(J.M.Henson, 1989)

PCB Structure and Biodegradability

- The less chlorinated the biphenyl, the faster aerobic degradation takes place.
(Biphenyls with more than 5 chlorines substituted are resistant to degradation)
- Dioxygenation takes place on the ring with the least chlorine atoms.

(Furukawa, 1982)

PCB Structure and Biodegradability (Cont.)

- Nonchlorinated vincinal *ortho* and *meta* positions favor dioxygenation
- PCBs with chlorine substituents on both rings are more recalcitrant than isomers containing an unchlorinated ring.
- Congeners with substituted *ortho* positions are recalcitrant.

(Furukawa, 1982)

Cometabolism

Definition

The degradation of a compound that does not provide a nutrient or energy source for the degrading organisms but is broken down during the degradation of other substances.

(Alexander M., 1979)

Cometabolism (Cont.)

- Does not provide a growth substrate
 - => The Population increase characteristic of metabolic degradation reaction does not take place.
- Rate of degradation is often slower

(Alexander M., 1979)

Rules of Thumb for Biodegradability

Rules of Thumb for Biodegradability

Branching

Highly branched Compounds are more resistant.

Chain Length

Short chains are more resistant

Oxidation

Highly oxidized compounds, like halogenated compounds, may resist further oxidation under aerobic conditions but may be more rapidly degraded under anaerobic conditions.

(Lyman et al., 1990)

Rules of Thumb for Biodegradability

Substituents (Number of)

- Increased substitution hinders oxidation responsible for breakdown of alkyl chains
- No significant oxidation of PAH's with more than three rings
- On aromatic ring, the more the chlorines the more resistant the compound.

(Lyman et al., 1990)

Rules of Thumb for Biodegradability

Substituents (Position of)

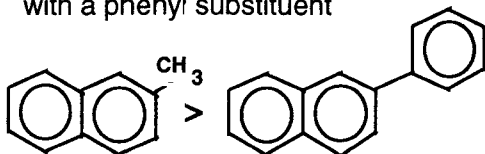
- Ortho and meta substituted aromatics with methyl, chloro, nitro or amino are more resistant than corresponding para substituted.
- Meta-disubstituted phenols and phenoxyls are more resistant than ortho or para isomers.

(Lyman et al., 1990)

Rules of Thumb for Biodegradability

Substituents (Type of)

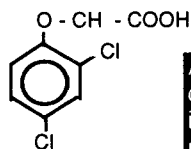
For Naphthalene compounds, nuclei bearing single small alkyl groups (methyl, ethyl, or vinyl) oxidize faster than those with a phenyl substituent



Rules of Thumb for Biodegradability

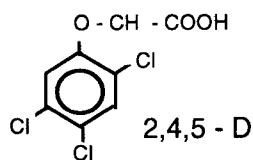
Some Examples

Biodegradable



2,4,-dichlorophenoxy
acetic acid
(2,4 - D)

Recalcitrant



2,4,5-trichlorophenoxy
acetic acid

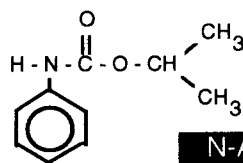
(Atlas and Bartha, 1987)

Additional
chlorine
in *meta*
position

Rules of Thumb for Biodegradability

Some Examples

Biodegradable

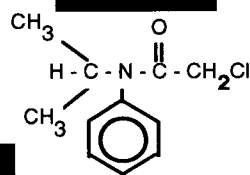


Protham
(Isopropyl-N-phenyl-
carbamate)

N-Alkyl
substitution

(Atlas and Bartha, 1987)

Recalcitrant



Propachlor
(N-isopropyl-1-2-
chloroacetanilide)

Critical Evaluation of Bioremediation Claims

- Reduction in Subsurface Concentration
-Mass Balances
- Increase in Biomass/Activity
- Production of Catabolites
- Consumption of Terminal Electron Acceptor

Critical Evaluation of Bioremediation Claims (Cont.)

- Adaptation/Acclimation Phenomena
- Biodegradation Kinetics
- All factors relative to appropriate Abiotic Controls

DNAPLs

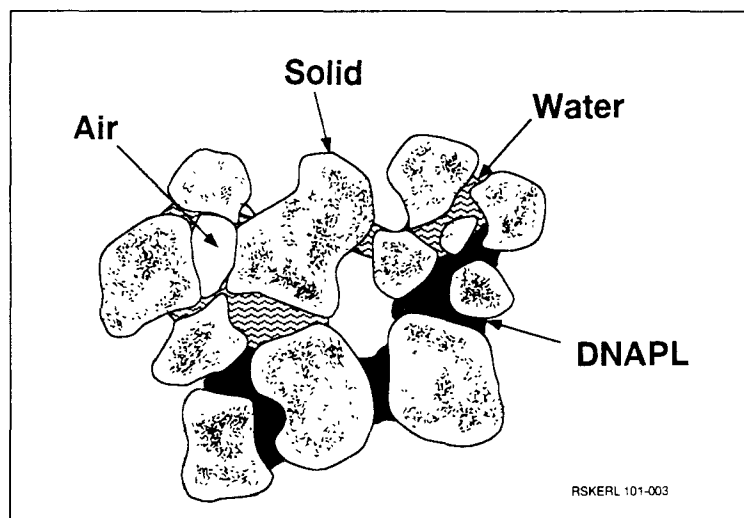
Vadose Zone Movement

- Nonaqueous Phase Movement
- Aqueous Phase Movement
- Vapor Movement

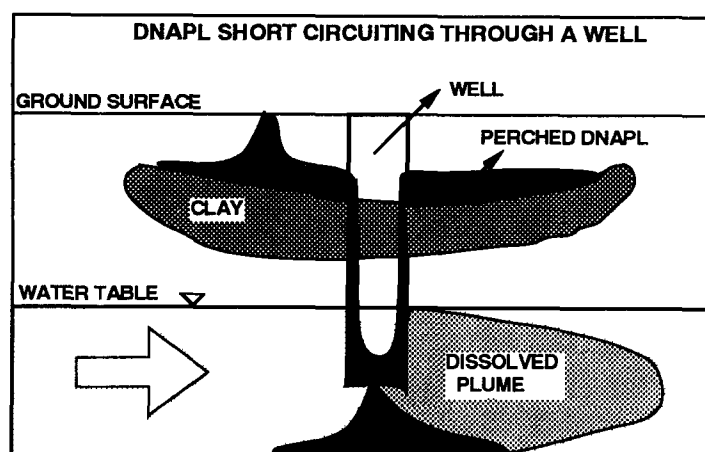
VADOSE ZONE

Nonaqueous Phase Movement

- Wetting Front Instabilities
- Blockage by Water and Stratigraphic Layers
- Perched Layers



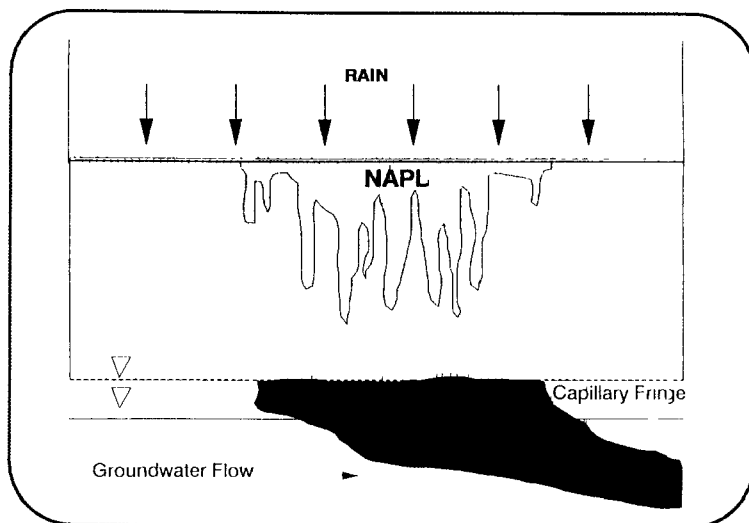
DNAPL, WATER, AND AIR IN POROUS MEDIA



VADOSE ZONE

Aqueous Phase Movement and Leaching

- Leaching and Water Movement
- Unsaturated Zone Hydraulic Conductivity



Sample Numbers Required to Estimate Various
Soil, Water, and Chemical Transport Properties
to Within 10, 20, 50% of the Mean Value at
95% Confidence Interval

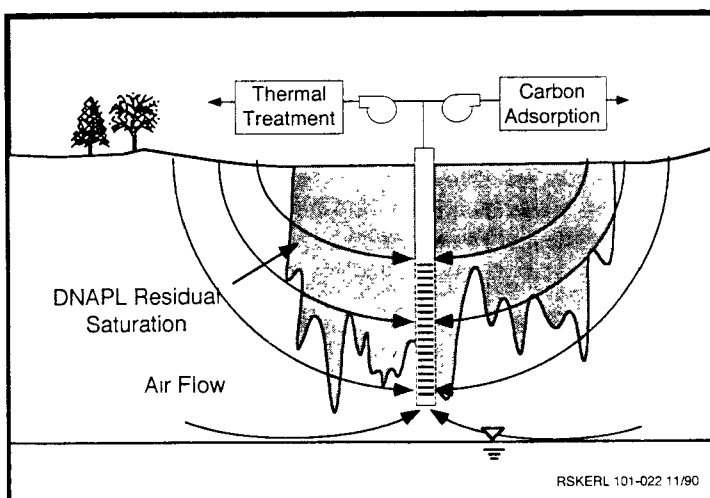
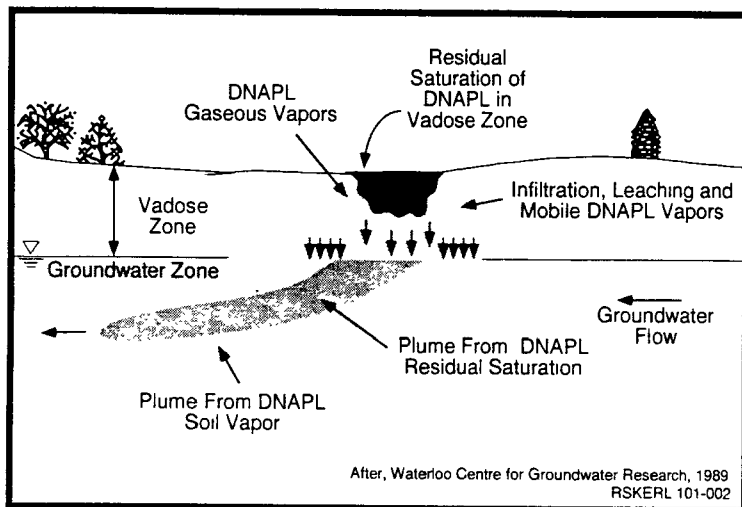
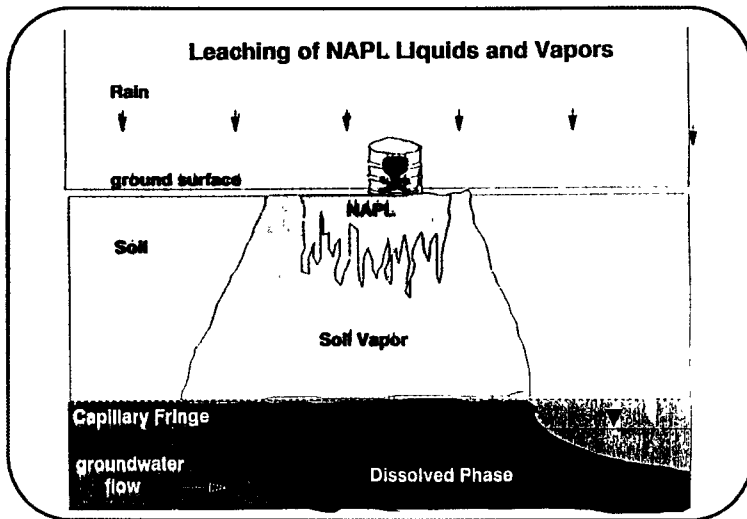
Parameter	10%	20%	50%	Comments
Porosity	4	1	1	4 Studies
Bulk Density	4	1	1	8 Studies
Soil pH	3	1	1	4 Studies
Saturated "K"	576	144	23	12 Studies
K (Θ)	4225	1057	169	1 Study (4 methods)

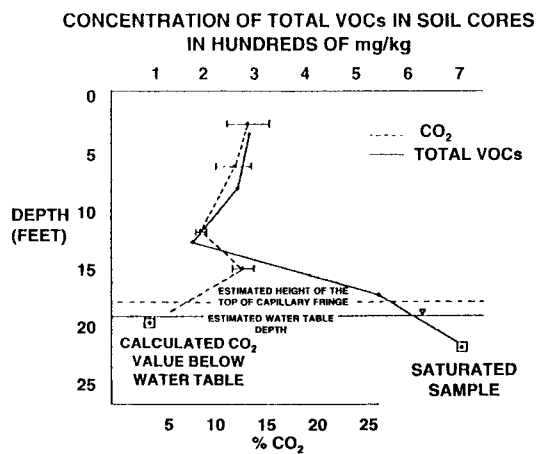
(Jury)

VADOSE ZONE

Vapor Movement of DNAPLs

- Leaching of Vapors
- Advective Gaseous Flux
- Diffusion





Comparison of measured gaseous carbon dioxide concentrations versus total organic compounds in soil cores from a vadose zone in a region of known contamination.

DNAPL Movement in Groundwater

- Nonaqueous Phase
- Aqueous Phase

GROUNDWATER

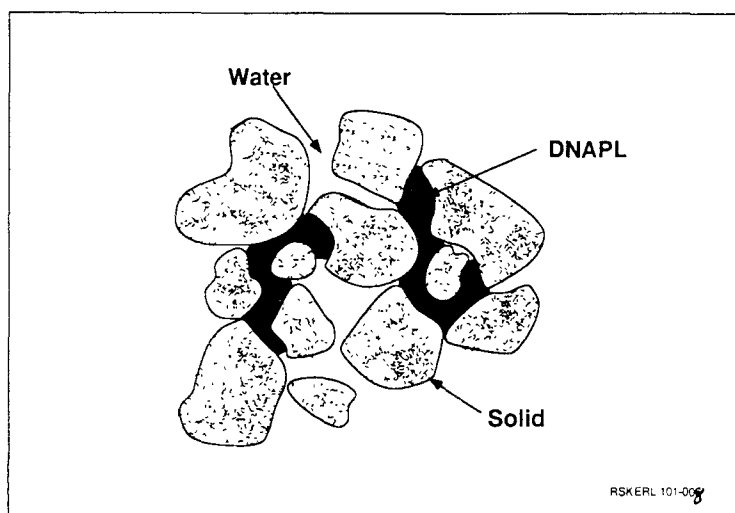
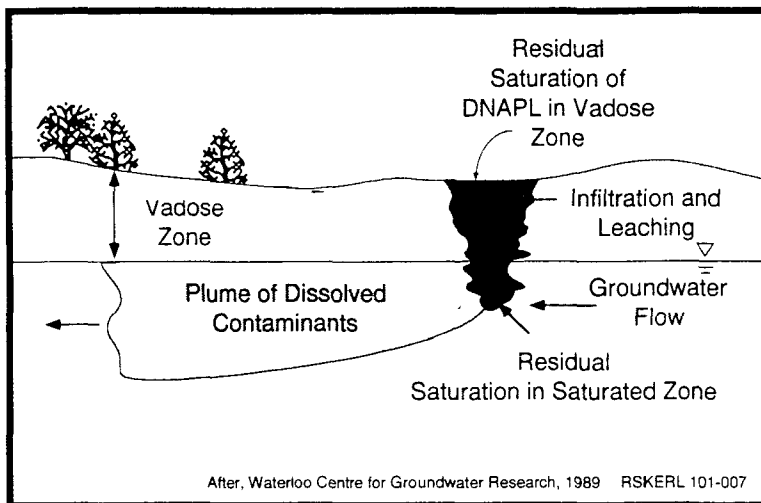
Nonaqueous Phase Movement

- Non-Geological Considerations
- Movement
- Porous Vs. Fractured Rock

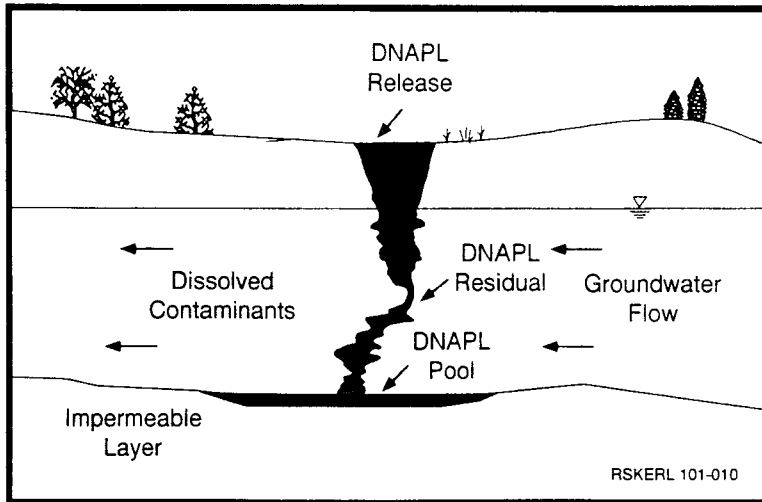
GROUNDWATER

Non-Geological Considerations

- Spill Size
- Types of DNAPL Spilled



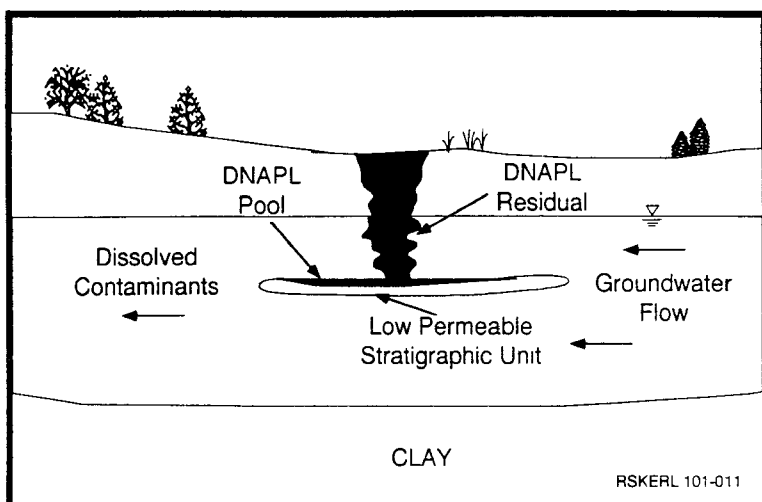
DNAPL & WATER IN A POROUS MEDIA

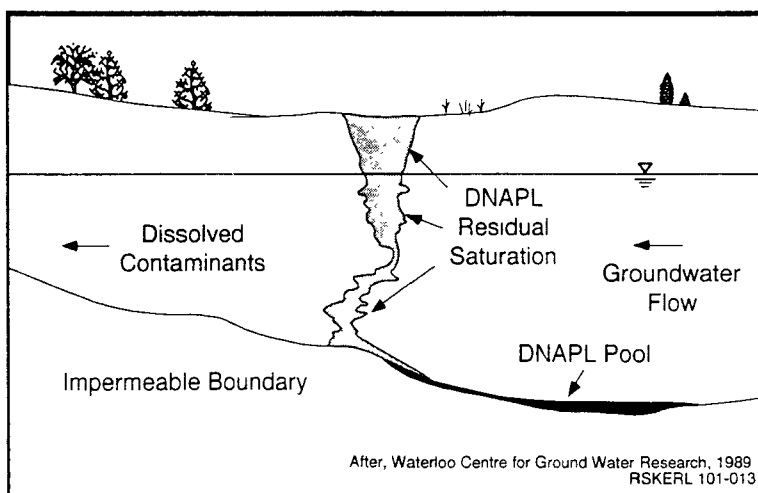
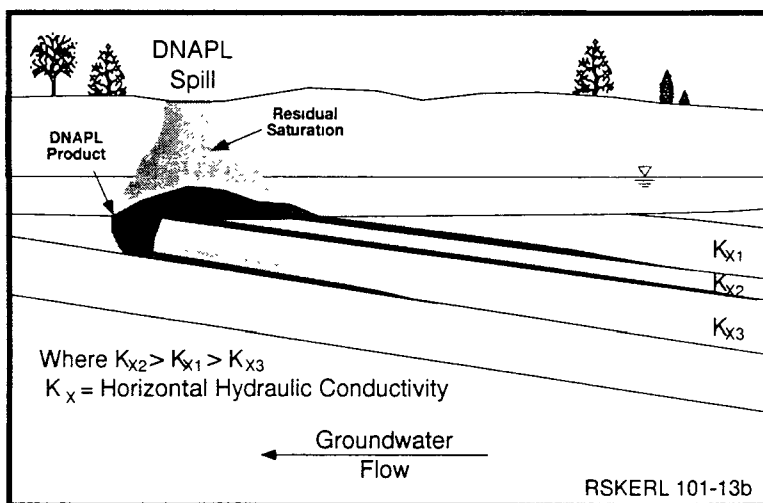
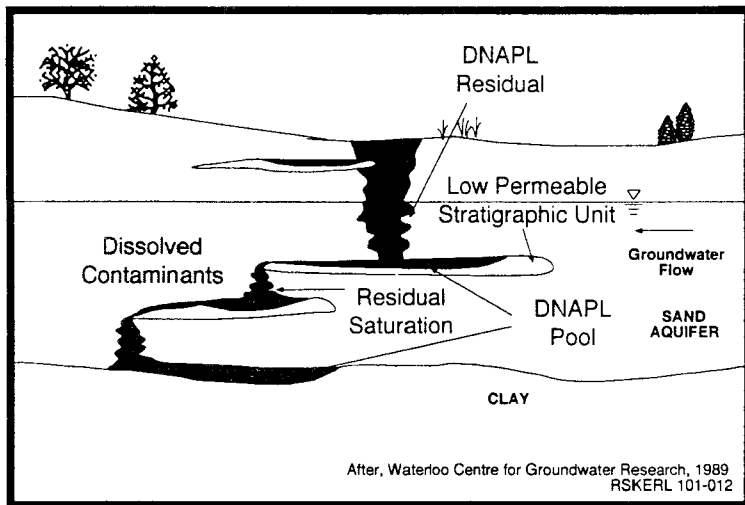


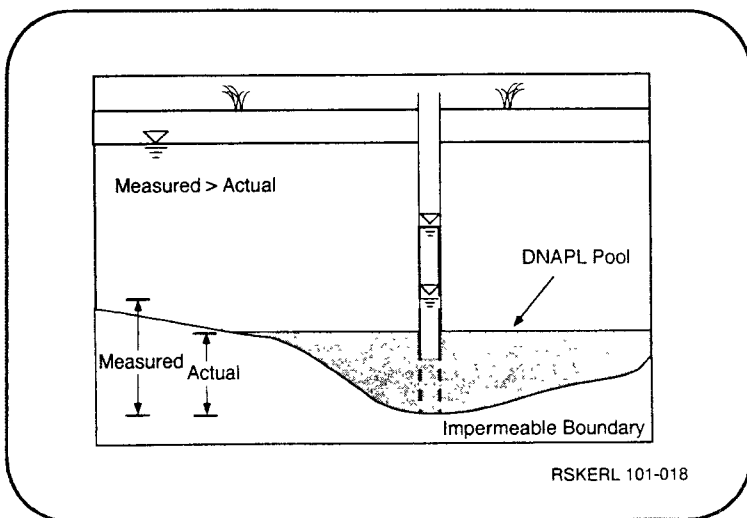
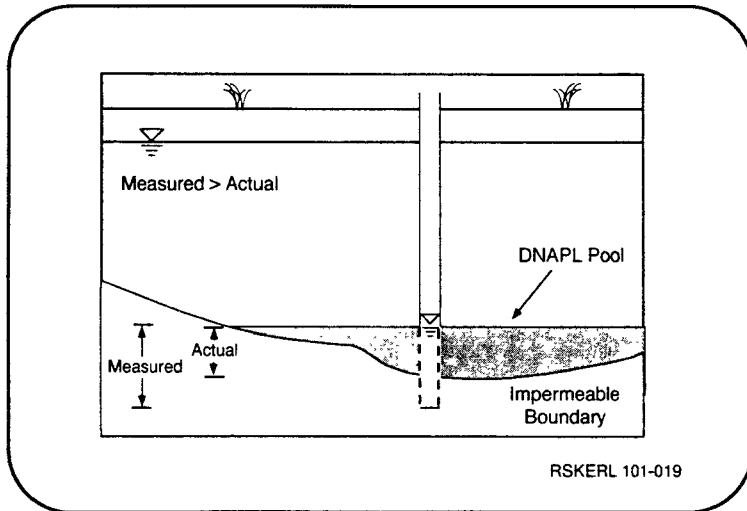
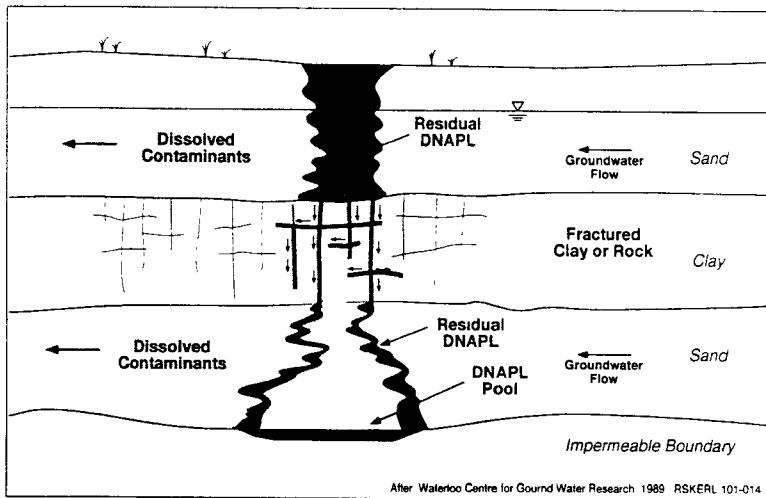
GROUNDWATER

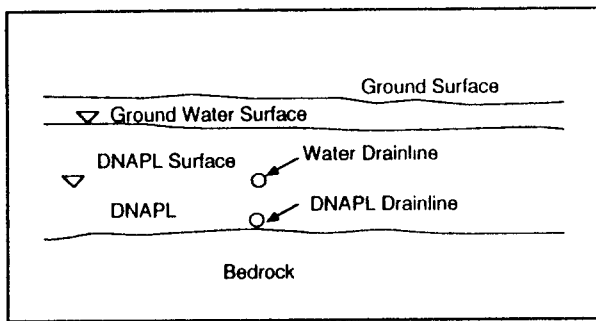
Considerations in Movement

- Initial Penetration of Groundwater
- Effect of Pore Size
- Downward Migration
- Mobilization

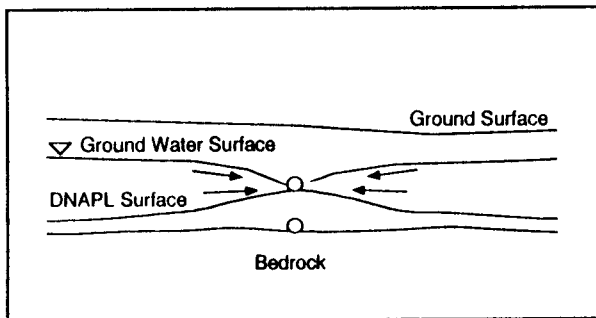




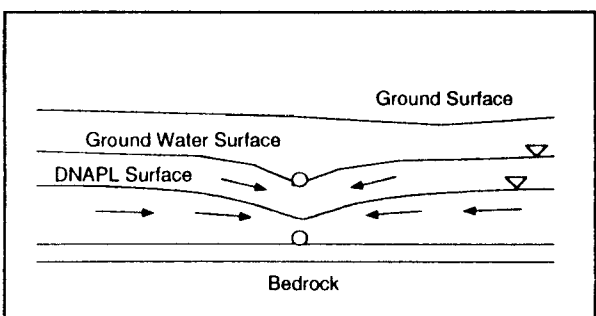




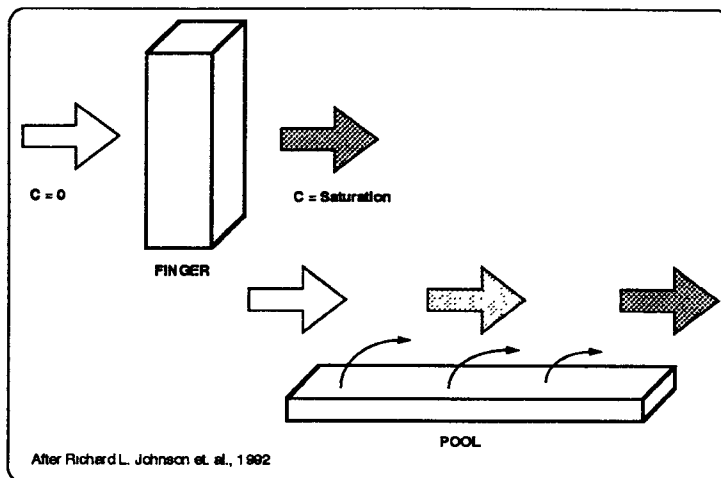
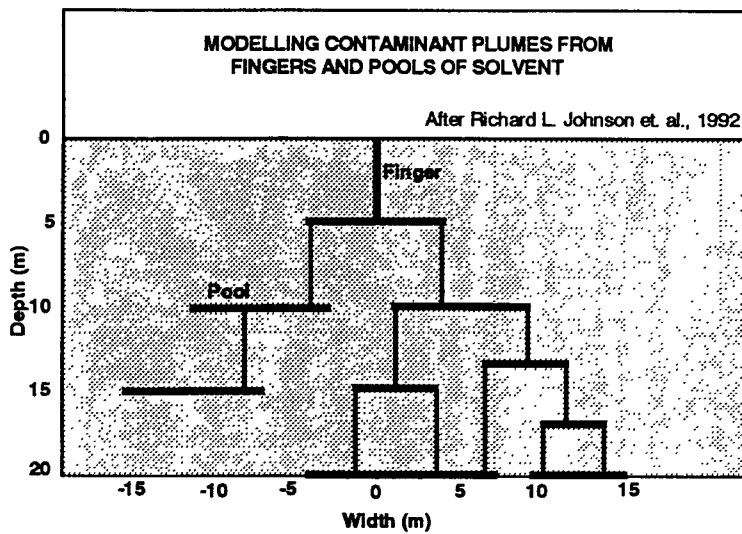
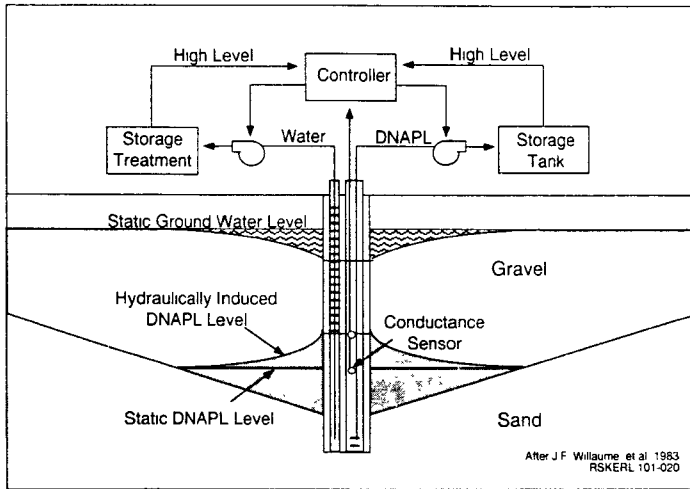
Oil Distribution

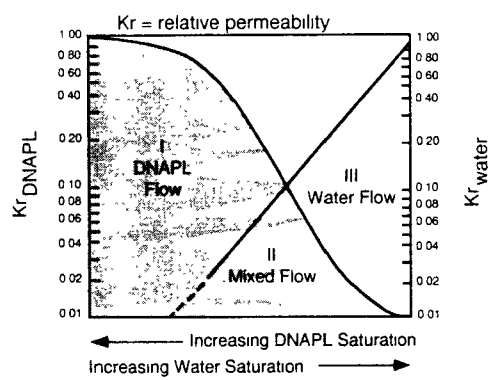


DNAPL Mounding

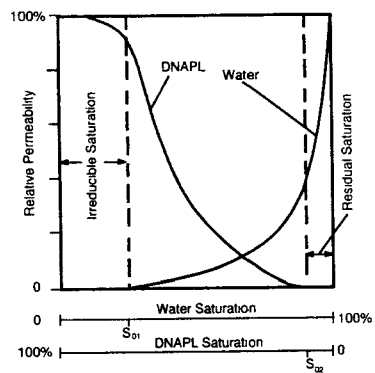


DNAPL Recovery

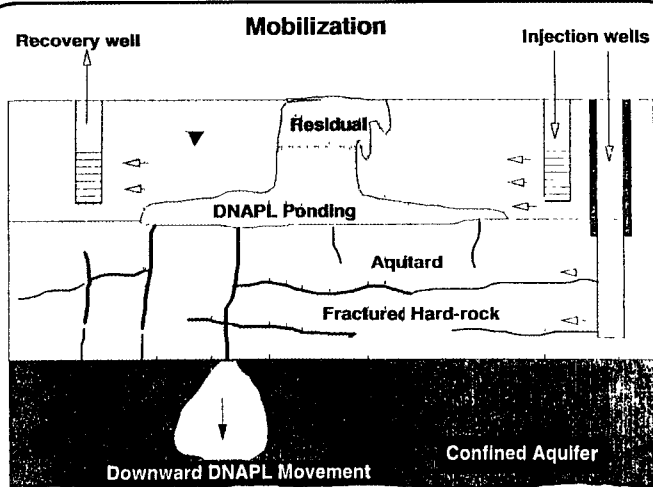


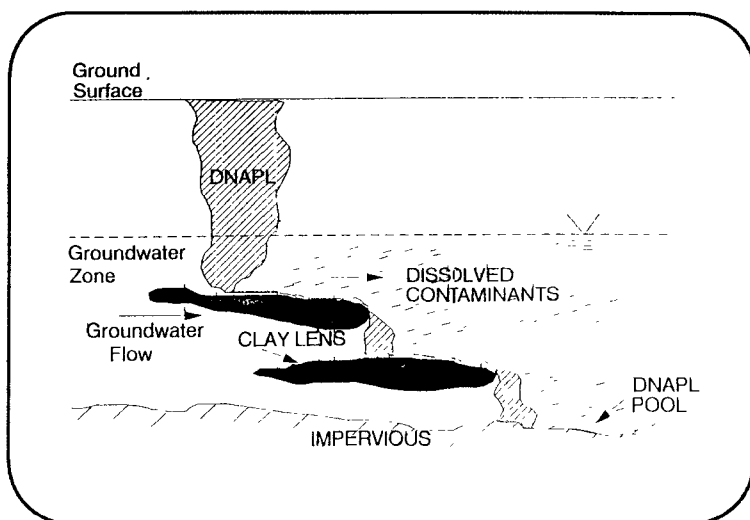
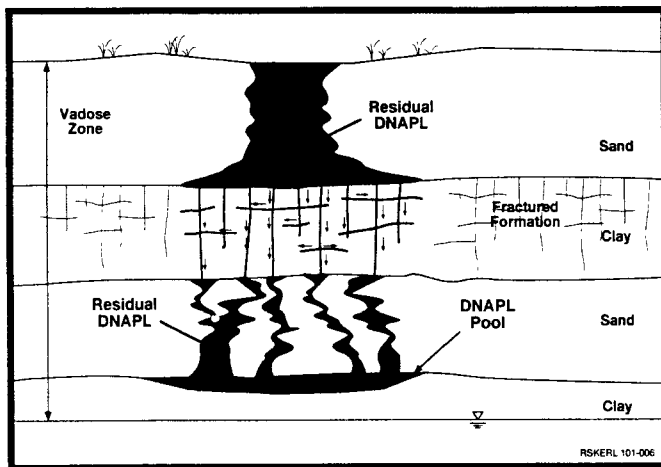
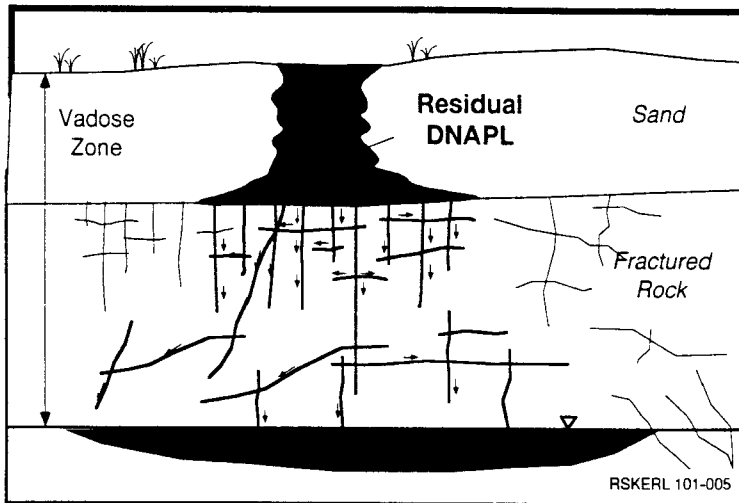


After Williams and Wilder, 1971
RSKERL 101-016

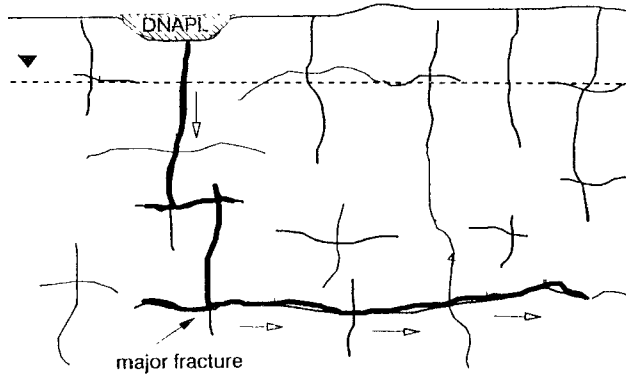


After Schwille, 1988
RSKERL 101-017





HORIZONTAL DNAPL MIGRATION IN FRACTURED ROCK



GROUNDWATER

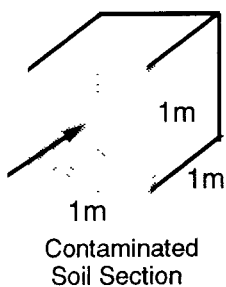
Aqueous Phase Movement

- Dissolution - Process and Rates
- Preferential Dissolution
- Advection and Dispersion
- Retardation
- Facilitated Transport

DNAPLs

Dissolution

Example



Hydraulic Conditions

$$K = 10^{-3} \text{ cm/sec}$$

$$i = 1\%, n = 30\%$$

$$\Rightarrow V = 0.03 \text{ m/day}$$

$$Q = 1\text{m}^2 \times 0.03 \text{ m/day}$$

$$= 0.03 \text{ m}^3/\text{day}$$

$$= 30 \text{ L/day}$$

DNAPLs Dissolution (Cont.)

Example (Cont.)

Case 1 30 L/m³ of TCE

s.g. = 1.46 => (43.8 kg)

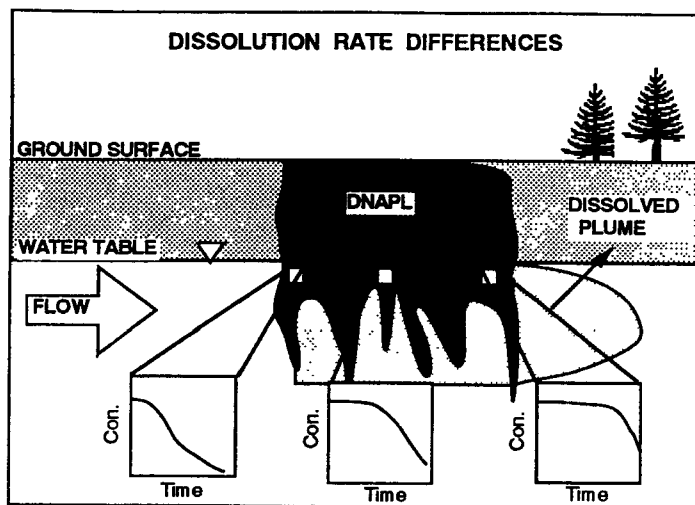
Solub. = 1100 mg/L

10% Solub = 110mg/L = 1.1×10^{-4} kg/L

Time to dissolve = 37 Years

Case 2 30 L/m³ of Dieldrin (s.g. 1.74), S=0.1mg/l

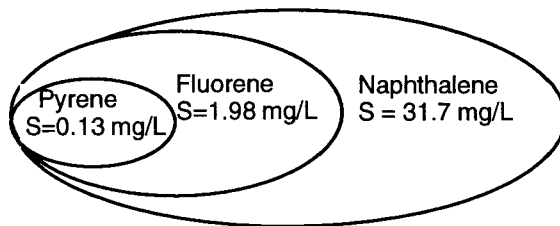
Time to dissolve = 479,452 Years



Preferential Dissolution

- In a mixture, such as creosote, certain compounds dissolve more readily than others.
- The mixture "ages"
(Changes composition with time).

Preferential Dissolution



Advection and Dispersion

Advection

Transport of solutes along streamlines at average groundwater velocity.

Dispersion

Transport of solutes by hydraulic mixing process due to local variations in groundwater velocity.

Advection and Dispersion

Instantaneous Point Source



Dispersion at time 0



Dispersion at time 1



Dispersion at time 2



Retardation

$$\text{Retardation Factor (R)} = \frac{\text{Groundwater Velocity}}{\text{Solute Velocity}}$$

$$R = 1 + \frac{k_p \rho_d}{n}$$

$k_p = f_{oc} \times k_{oc}$
 ρ_d = bulk density
 n = effective porosity

Facilitated Transport

- Cosolvent effect
- Particle Transport
 - Organic
 - Inorganic
 - Biological

References

Atlas, R.M., and Bartha, K., Microbial Ecology - Fundamentals and Applications, Benjamin/Cummings Publishing Company, 1987, 553 pp.

Cohen, Robert M., et al., Evaluation of Visual Methods to Detect NAPL in Soil and Water: Ground Water Monitoring Review, Fall 1992, pp 132-139.

Commandeur, L.C.M. and Parsons, J.R., Degradation of Halogenated Aromatic Compounds: Physiology of Biodegradative Microorganisms, Kluwer Academic Publishers, 1991, pp 207-220.

References (Cont.)

Huling, Scott G., Facilitated Transport : EPA Superfund Ground Water Issue, EPA/540/4-89/003, 1989.

Huling, Scott G., et al., Dense Nonaqueous Phase Liquids: EPA Ground Water Issue, EPA/540/4-91-002, 1991.

Lyman, W.J., et al., Handbook of Chemical Properties Estimation Methods, McGraw Hill Book Company, 1990.

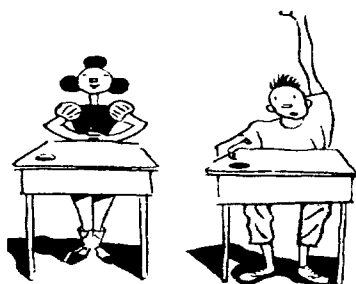
Poziomek, E.J., et al., A Field Screening Method for PCBs in Water : Publication from the Third International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Las Vegas, February 1993.

References (Cont.)

Suflita, J.M. and Sewell, Guy W., Anaerobic Biotransformation of Contaminants in the Subsurface, USEPA Environmental Research Brief, EPA/600/M-90/024 February 1991.

Verschueren, K., Handbook of Environmental Data on Organic Chemicals, Van Nostrand Reinhold Company, 1983, 1310 pp.

Questions ?



DNAPL Site Characterization

Robert M. Cohen, Principal Hydrogeologist, GeoTrans, Inc.
James W. Mercer, President, GeoTrans, Inc.

I. DNAPL Investigation Motivation

II. Characterization Objectives and Conceptual Model Development

III. DNAPL Site Identification

- A. Historical Information**
- B. Site Data Interpretation**
- C. NAPL Detection Methods**

IV. Noninvasive Methods

- A. Aerial Photograph Interpretation**
- B. Soil Gas Surveys**
- C. Surface Geophysics**

V. Invasive Methods

- A. Concerns and Risks**
- B. Risk Minimization**
- C. Drilling**
- D. Monitor Wells**
- E. Fluid Measurement Data**

DNAPL SITE CHARACTERIZATION

Robert M. Cohen and James W. Mercer

GeoTrans, Inc.
Sterling, Virginia

REFERENCES

- *DNAPL Site Evaluation*, USEPA guidance document (1993)
- *Estimating Potential for Occurrence of DNAPL at Superfund Sites*, USEPA Quick Reference Fact Sheet (1992)
- *Dense Nonaqueous Phase Liquids – A Workshop Summary*, USEPA (1992), EPA/600/R-92/030
- Waterloo Centre for Groundwater Research, University of Waterloo, DNAPL short course



TOPICS



WHY INVESTIGATE DNAPL

DNAPL SITE CHARACTERIZATION OBJECTIVES

METHODS FOR DIRECT DETECTION OF
NAPL IN SOIL AND WATER

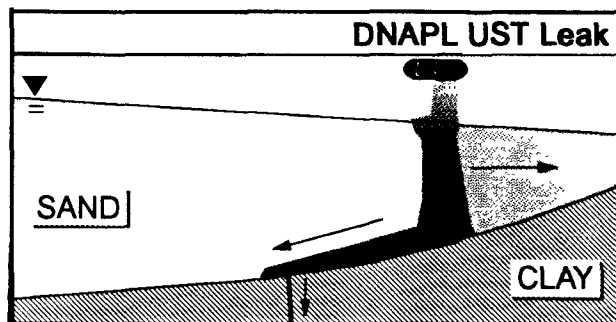
DNAPL SITE IDENTIFICATION

WHY CHARACTERIZE DNAPL?

- Subsurface DNAPL cannot be adequately characterized by investigating miscible contamination due to differences in transport principles and properties

(1 of 5)

DIFFERENT TRANSPORT MECHANISMS DNAPL v. Dissolved Contaminants

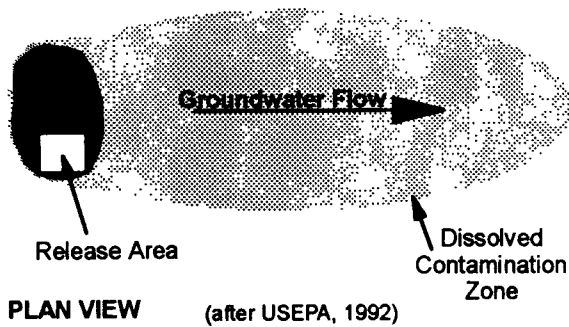


WHY CHARACTERIZE DNAPL?

- DNAPL movement extends the source of groundwater contamination from the release area to the limits of DNAPL migration ("the moving landfill" analogy)

(2 of 5)

DEFINED AREAS AT A DNAPL SITE



WHY CHARACTERIZE DNAPL?

- DNAPL migration dominates contaminant mass loadings to offsite areas, streams, wells, etc.

(3 of 5)

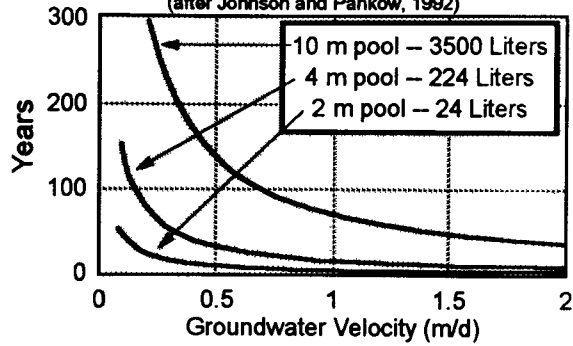
WHY CHARACTERIZE DNAPL?

- DNAPL can persist for decades as a significant source of groundwater and soil gas contamination

(4 of 5)

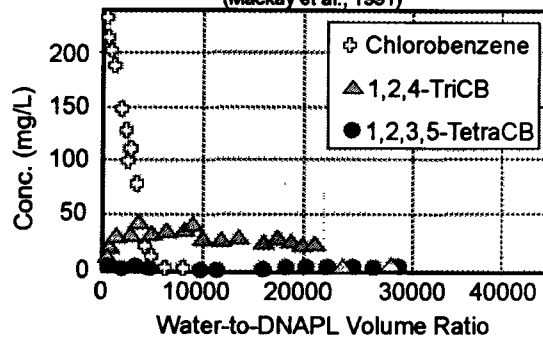
DISSOLUTION TIMES FOR TCE POOLS (POOL DEPTH=0.01 LENGTH)

(after Johnson and Pankow, 1992)



WEATHERING/DISSOLUTION OF CHLOROBENZENE MIXTURE

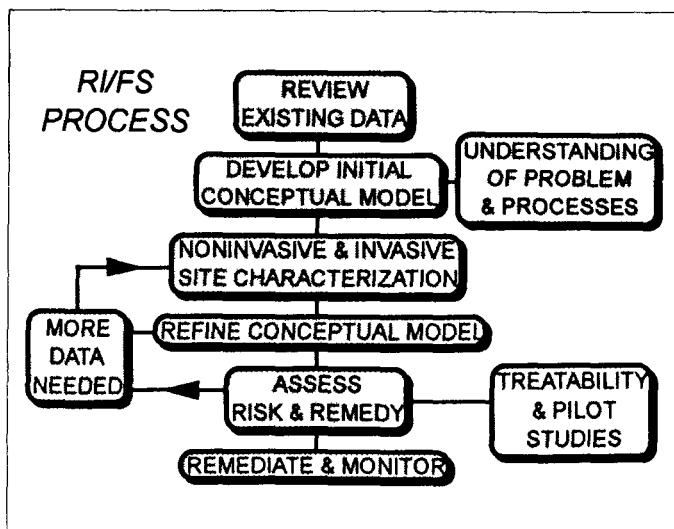
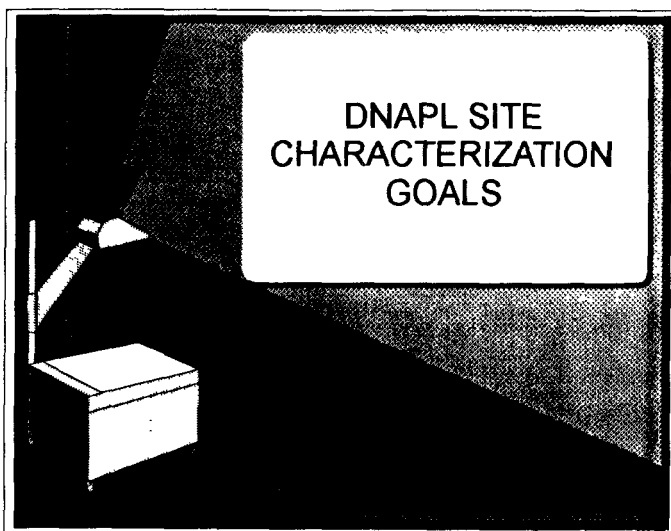
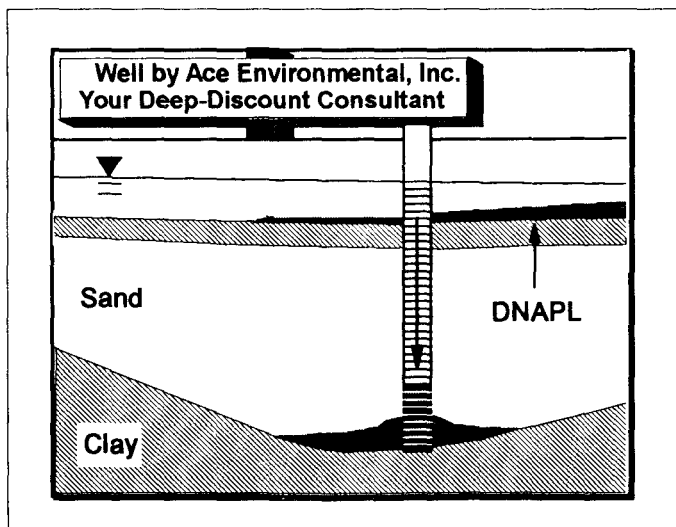
(Mackay et al., 1991)



WHY CHARACTERIZE DNAPL?

- To avoid selecting an inappropriate remedy or exacerbating the contamination problem by remedial activities

(5 of 5)



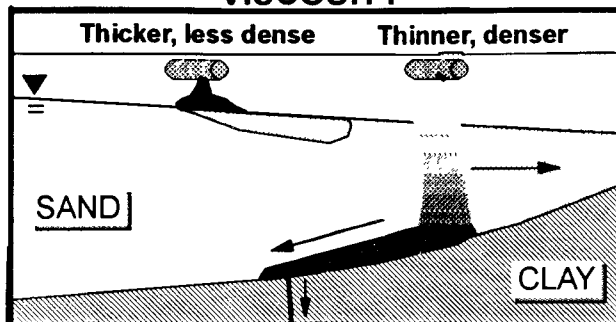
KEY OBJECTIVES OF DNAPL SITE CHARACTERIZATION

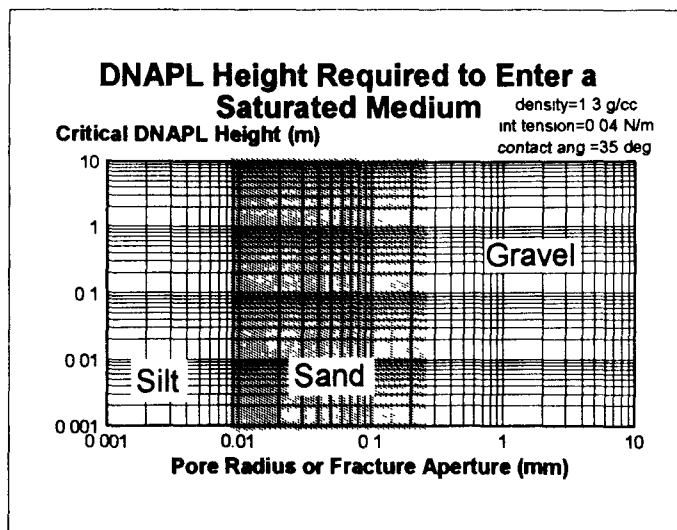
- Determine DNAPL properties
- Identify DNAPL release/source areas
- Define stratigraphy
- Delineate DNAPL distribution
- Minimize investigation risk

DNAPL PROPERTIES

- Composition (yields information on solubility, volatility, toxicity, etc.)
- Density
- Viscosity
- Wettability
- Interfacial tension

DNAPL PROPERTIES: SIGNIFICANCE OF DENSITY AND VISCOSITY

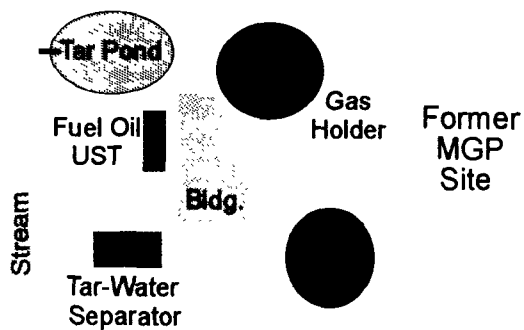




IDENTIFY DNAPL RELEASE AREAS AND VOLUMES

- Site history information
- Air photos and maps
- Knowledge of industrial practices
- Field investigations and data interpretation

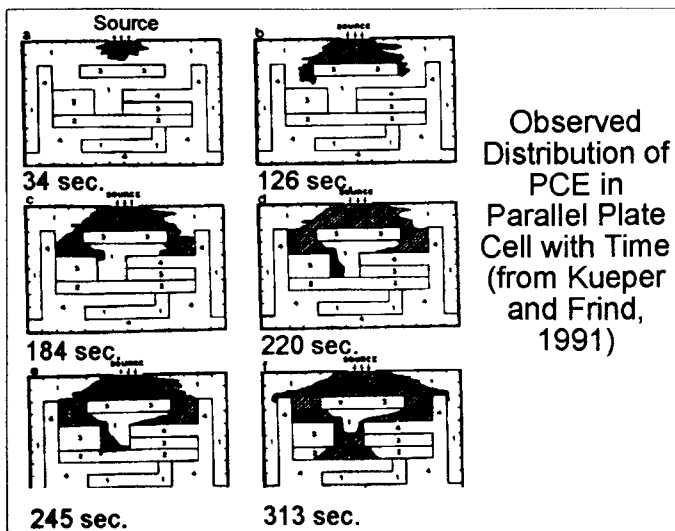
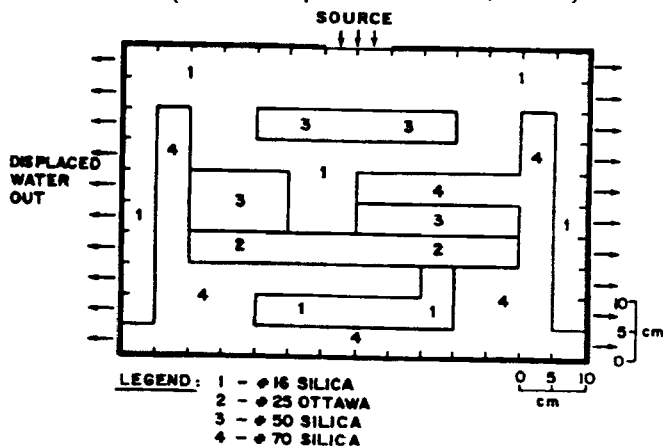
USE KNOWLEDGE OF SOURCE AREAS TO GUIDE INVESTIGATION



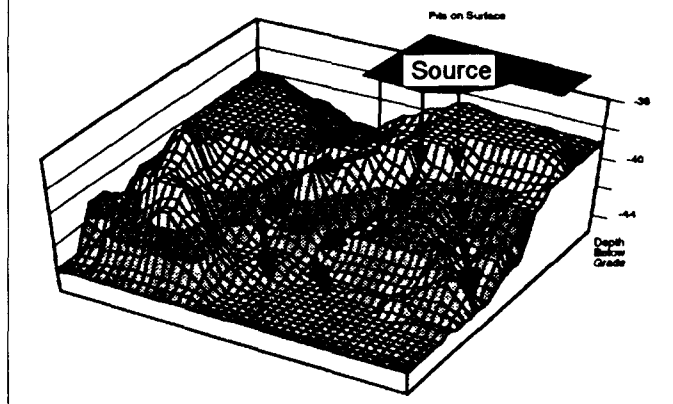
DEFINE STRATIGRAPHY

- Stratigraphic barriers and traps
- Migration pathways
 - Fractures in rock or cohesive soil
 - Coarse lenses and layers
 - Rootholes, burrow holes
 - Manmade structures (sewers, foundations, wells) and backfill
 - Heterogeneity and anisotropy

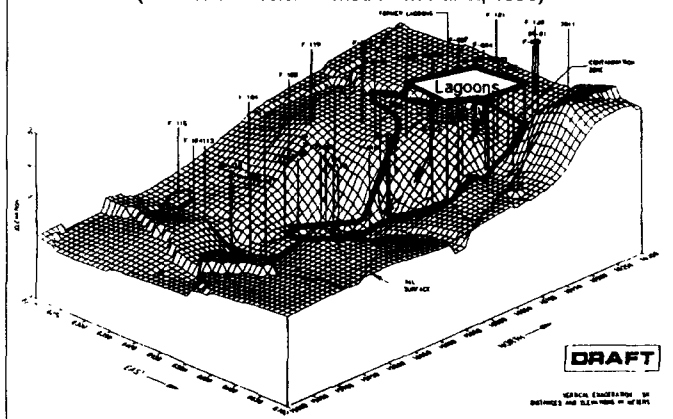
Distribution of Sand Lenses in Parallel-Plate Cell (from Kueper and Frind, 1991)



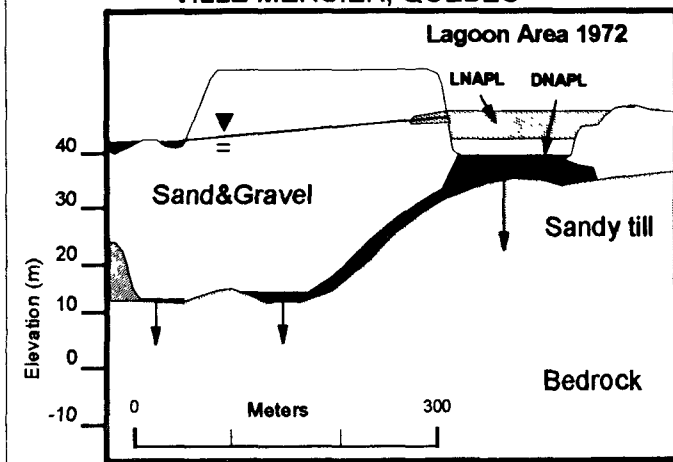
**Surface of Unfractured Clay Unit Showing
DNAPL Movement Down Topographic
Valleys (from Newell and Connor, 1992)**



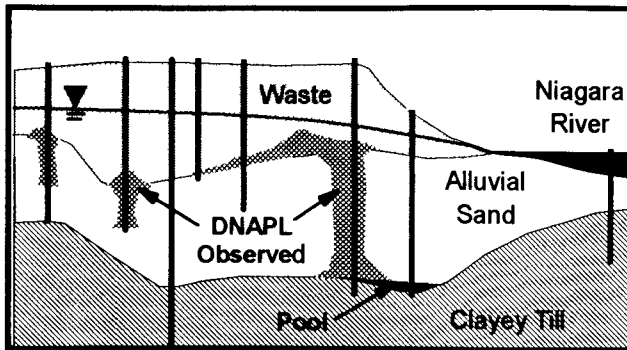
**DNAPL Movement Along Top of Sandy Till
from the Former Ville Mercier Lagoons
(from The Mercier Remediation Panel, 1993)**



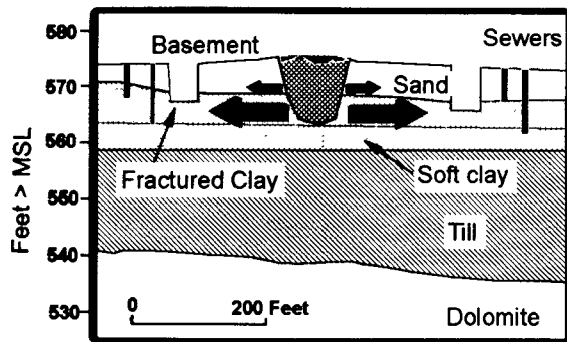
**STRATIGRAPHIC CONTROL ON DNAPL FLOW
VILLE MERCIER, QUEBEC**



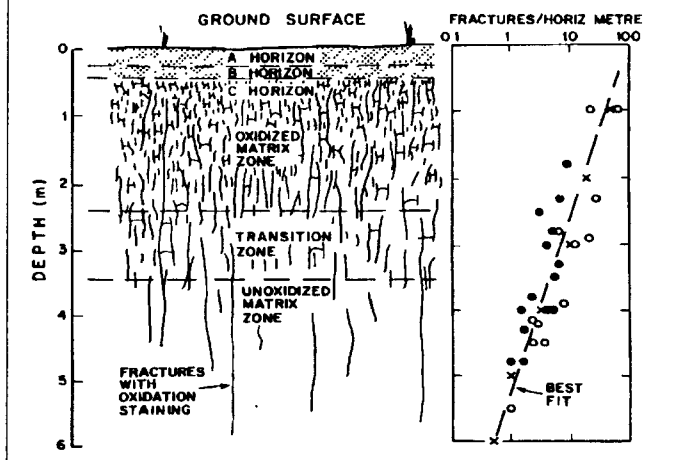
STRATIGRAPHIC TRAP AT THE 102nd ST.
LANDFILL, NIAGARA FALLS, NY
after OCC/Olin (1990)

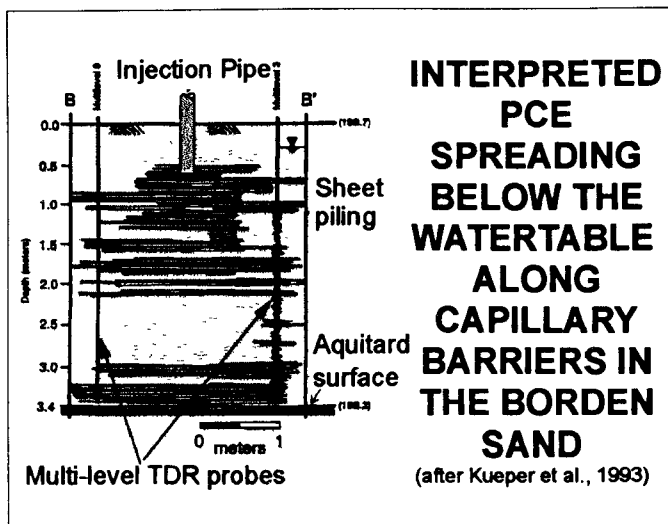
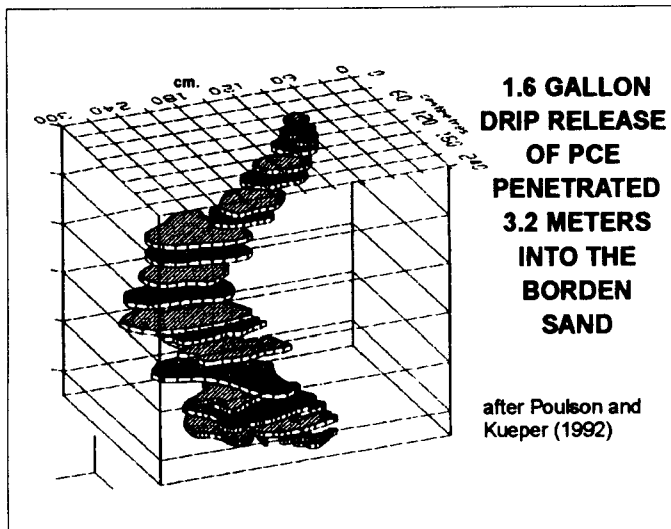
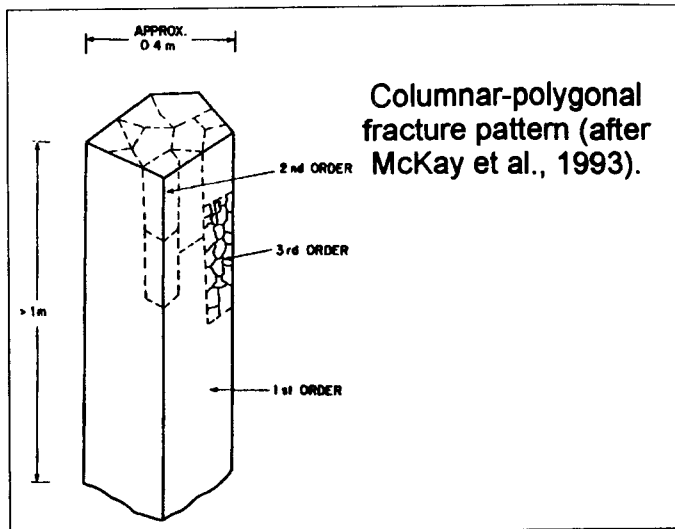


E-W CROSS SECTION, LOVE CANAL
NIAGARA FALLS, NY



Typical Weathering Sequence in Fine-Grained
Media (from McKay et al., 1993)



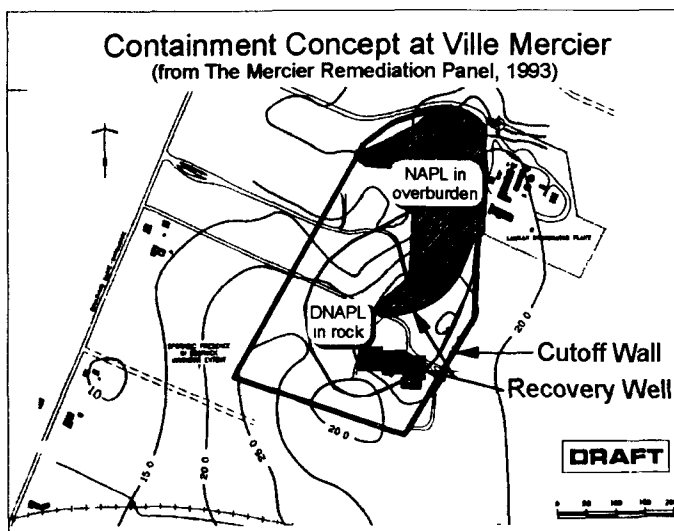


GEOLOGIC VARIABILITY

- Results in complex contaminant distribution
- Limits effectiveness of remedies which rely on fluid delivery systems to flush and/or contact contaminants
- External agents (injected air, cosolvents, waterflood, etc.) will follow high K zones
- Favors containment strategy

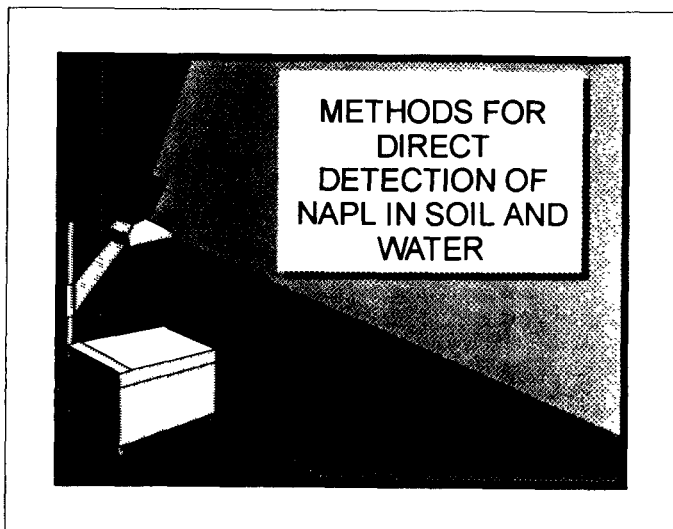
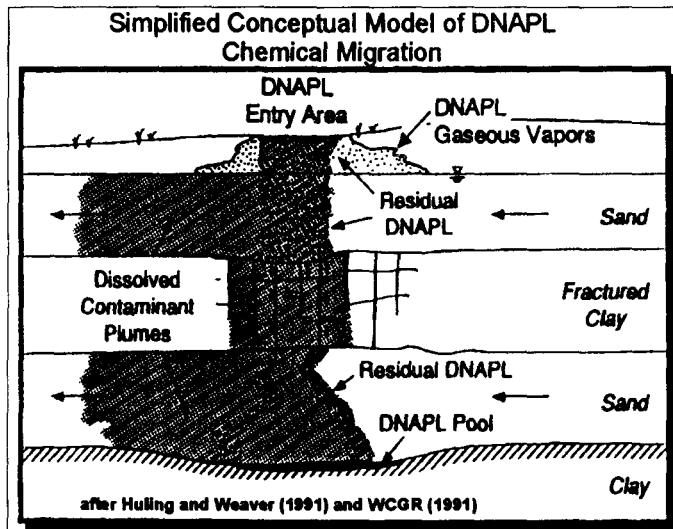
DELINEATE DNAPL DISTRIBUTION: Mobile and Residual

- Review site history and data
- Noninvasive methods
- Invasive methods
- Data synthesis



MINIMIZE RISK ASSOCIATED WITH INVESTIGATION

- Worker health and safety concerns
- Risk of inducing unwanted DNAPL movement by invasive field activities
 - Outside-in approach
 - Noninvasive methods
 - Optimize invasive methods and materials
 - Phased characterization



DNAPL DETECTION

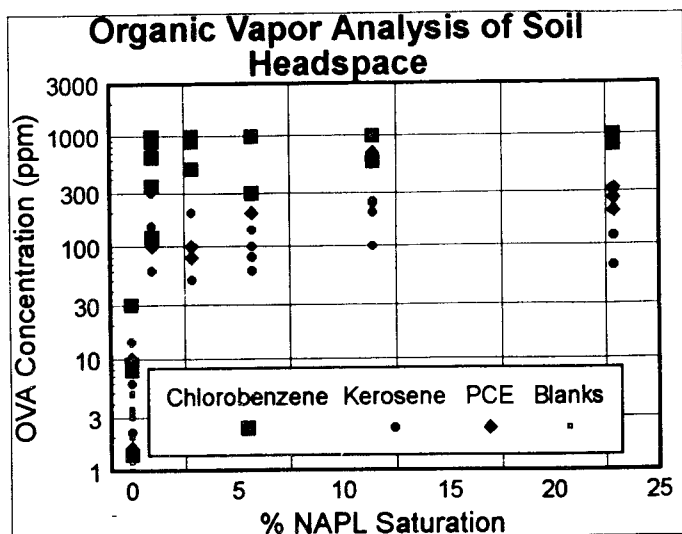
- To minimize risk of causing DNAPL migration during drilling
- To delineate DNAPL zone for remedy design

DIRECT VISUAL DETECTION OF NAPL IN SOIL AND WATER

- Inexpensive
- Immediate
- Difficult where NAPL is clear and colorless, at low saturation, or distributed heterogeneously

SAMPLE SCREENING

- Organic Vapor Analysis (OVA)



DIRECT DETECTION METHODS

- Unaided
- UV fluorescence
- Hydrophobic dye shake test
- Centrifugation
- Use syringe needle to extract and place suspect globules into a water column
- Use hydrophilic filters or hydrophobic materials for phase separation

HYDROPHOBIC DYE SHAKE TEST

Add water and hydrophobic dye powder to soil in container



Cap and shake



Examine for presence of dyed NAPL



HYDROPHOBIC DYE

- Sudan IV powder dyes organic fluids red upon contact but does not partition into water or air
- Few mg powder used per sample
- 100 grams costs about \$19.
- Irritant and potential mutagen
- Other color hydrophobic dyes available

UV FLUORESCENCE DETECTION OF NAPL

- Fluorescent NAPLs include nearly all petroleum products, all aromatic compounds, and many unsaturated aliphatic hydrocarbons (e.g., TCE & PCE)
- Saturated aliphatic hydrocarbons such as dichloromethane generally do not fluoresce unless mixed with fluorescent impurities

(1 of 2)

UV FLUORESCENCE DETECTION OF NAPL

- SW-LW blacklight cheap and simple to use
- Can examine soil-water slurry in polybag; squeeze sample to bring fluid to surface
- UV analysis used for decades by oil industry to identify petroleum in well cuttings

(2 of 2)

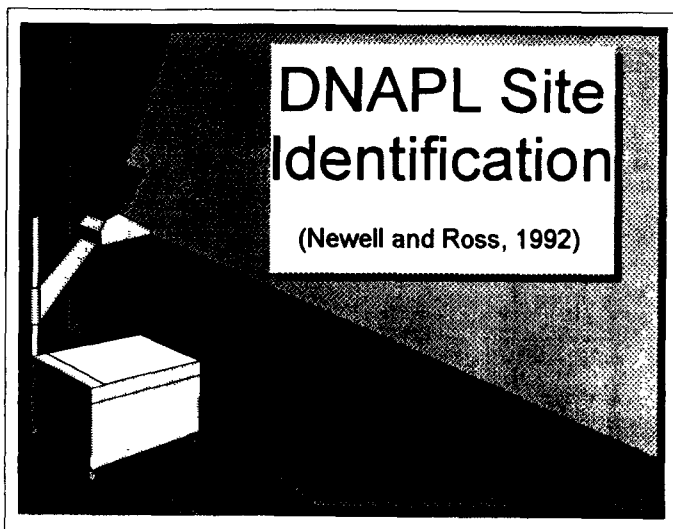
VISUAL METHOD CONCLUSIONS

- The hydrophobic dye shake test, followed by UV fluorescence, are simple, practical, and inexpensive means for direct NAPL detection



VISUAL METHOD CONCLUSIONS

- For volatile NAPLs, organic vapor analysis can be used to screen samples for further examination, and possibly to infer NAPL presence



IS IT A DNAPL SITE???

INDUSTRY
TYPE

DNAPL DETECTED IN
WELLS, GROUNDWATER,
SOIL OR ROCK SAMPLES

PROCESS
OR WASTE
PRACTICE

DNAPL INDICATED
BY CHEMICAL ANALYSIS

DNAPL
USE

DNAPL SUGGESTED
BY CHEMICAL ANALYSIS

DATA ADEQUATE?

SITE HISTORY INFORMATION

- Corporate owner/operator records
- Government records
- Universities, libraries, historic societies
- Personnel interviews or depositions
- Aerial photographs and maps

INDUSTRIES USING DNAPLS

- | | |
|-------------------------|----------------------|
| ▶ Chemical | ▶ Dry cleaning |
| ▶ Solvents&refrigerants | ▶ Textile processing |
| ▶ Electronic/computer | ▶ Metal degreasing |
| ▶ Metal parts/products | ▶ Metal machining |
| ▶ Music instruments | ▶ Storage/transfer |
| ▶ Aircraft/automotive | ▶ Paint removal |
| ▶ Office machinery | ▶ Wood preserving |
| ▶ Plastics | ▶ Steel coking |
| ▶ Pharmaceuticals | ▶ Waste disposal |
| ▶ MGPs (1850-1950) | |

COMMON SUSPECT AREAS

- Floordrains/sumps
- Pits, ponds, lagoons
- Sewer systems
- Septic tanks
- Leach fields
- Disposal areas
- Pipelines
- Disturbed areas
- Process tanks
- Wastewater tanks
- UST areas
- AST areas
- Chemical storage and transfer areas
- Loading docks
- Drainage paths

DETECTING NAPL IN WELLS

- Survey fluid column with interface probe
- Pump or bail samples from top and bottom of fluid column
- Use other discrete-depth sampler
- Inspect fluid on weighted cotton string, bailer cord, probe wire, etc.

INFERRING NAPL PRESENCE FROM CHEMICAL ANALYSES

- Chemical concentration in groundwater >1% of pure phase or effective solubility limit
- Chemical concentration in soil >10,000 mg/kg (1% of soil mass)

INFERRING NAPL PRESENCE FROM CHEMICAL ANALYSES

- Chemical concentration in groundwater calculated from soil-water partitioning relationship and soil analysis > effective solubility (Feenstra et al., 1991)
- Extremely high OVA concentrations

2 of 2

SUSPECTING NAPL BASED ON FIELD CONDITIONS

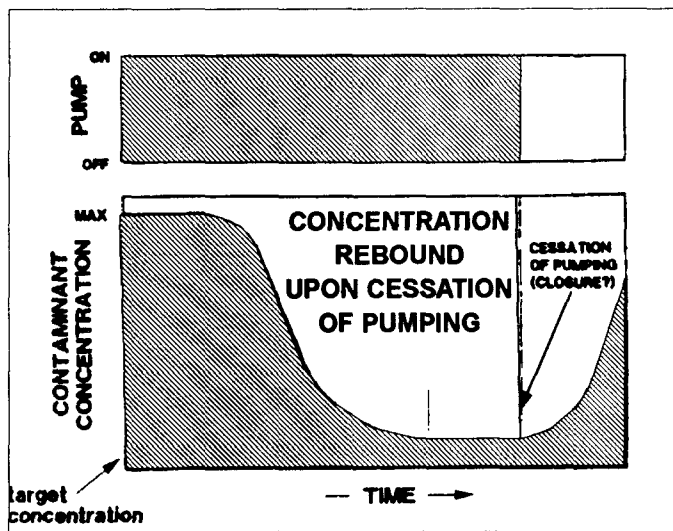
- DNAPL chemical concentrations increase with depth in a pattern that is inconsistent with advective transport
- DNAPL chemical concentrations increase counter to the hydraulic gradient from a release area presumably due to DNAPL spreading

1 of 3

SUSPECTING NAPL BASED ON FIELD CONDITIONS

- Erratic concentrations of NAPL chemicals in groundwater, soil and soil gas
- Dissolved NAPL chemical concentrations rebound after turning off a pumping system

2 of 3



SUSPECTING NAPL BASED ON FIELD CONDITIONS

- Presence of DNAPL chemicals in groundwater that is older than potential release dates (using tritium for age dating)
- Deterioration of wells and pumps

3 of 3

IS IT A DNAPL SITE???

INDUSTRY
TYPE

PROCESS
OR WASTE
PRACTICE

DNAPL
USE

DNAPL DETECTED IN
WELLS, GROUNDWATER,
SOIL OR ROCK SAMPLES

DNAPL INDICATED
BY CHEMICAL ANALYSIS

DNAPL SUGGESTED
BY CHEMICAL ANALYSIS

DATA ADEQUATE?

DATA AND CONDITIONS THAT CAN HELP INDICATE NAPL PRESENCE OR ABSENCE

- Many wells with screens across the water table and in stratigraphic traps
- Multi-level fluid sampling capability
- Extensive chemical analysis
- Defined stratigraphy & release history

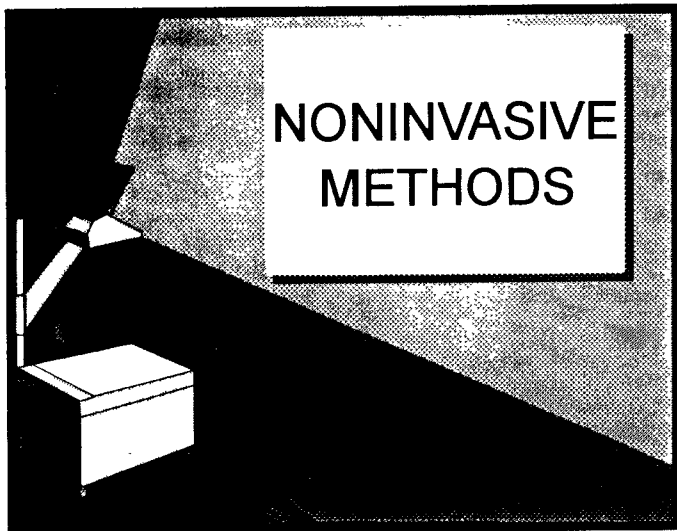


TOPICS

- Noninvasive methods
- Invasive methods and concerns

STRATEGY

- Phased study
- Site-specific application of methods
- Outside-in approach
- Noninvasive methods
- Optimize invasive methods



NONINVASIVE METHODS

- Air photo interpretation
- Soil gas analysis
- Surface geophysics

NONINVASIVE METHODS

- Can often be used during the early phases of field work to optimize the cost-effectiveness of a site study.
- Conceptual model refinements derived using these methods reduce the risk of spreading contaminants during later invasive field work.

AIR PHOTO INTERPRETATION

- Historic conditions (i.e., waste disposal practices and areas, ponded fluids, disturbed soils, vegetative stress, etc.)
- Photogeology (to interpret geologic and hydrologic conditions)
- Fracture trace analysis (to identify surface expressions of fracture zones)

AIR PHOTO INVENTORY Earth Science Information Center U.S.G.S. in Reston, VA

- Provides free listing of available images from government and private vendors
- Source, date, scale, film type, etc.

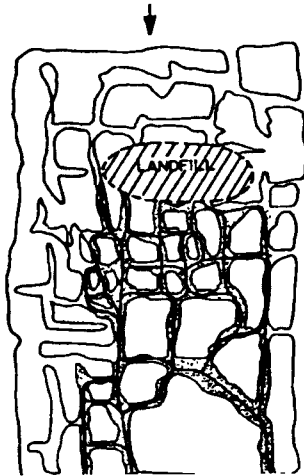
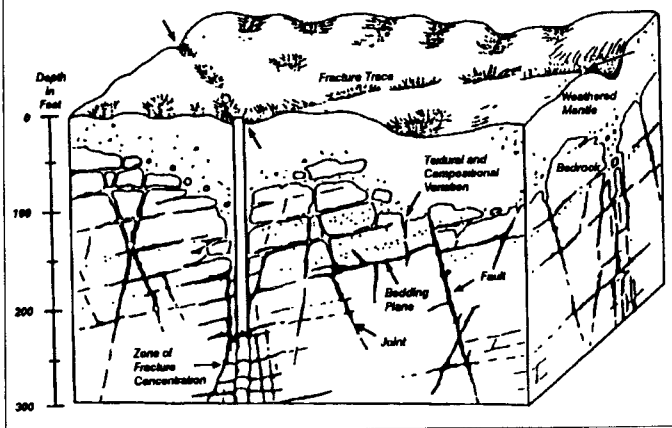
FRACTURE TRACES

- Linear surface expressions of subsurface zones of fracture concentration, typically 5-60 ft wide and near vertical, that are mapped by stereo-interpretation of air photos
- Surface features used to map fracture traces include: straight valley segments; aligned sags, depressions, soil tone anomalies, etc.

Groundwater flow and chemical migration are concentrated in bedrock fractures, particularly where permeability is enhanced by dissolution.

FRACTURE TRACE DIAGRAM

(from Lattman and Parizek, 1964)



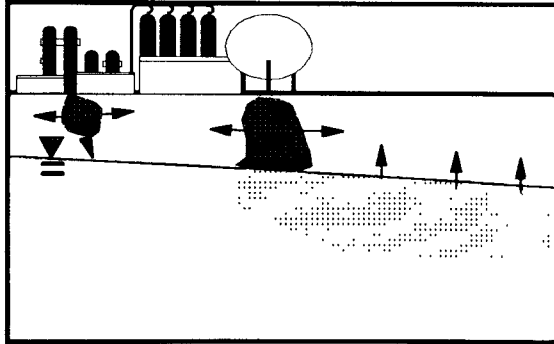
Contaminant
detection
and
recovery are
enhanced by
locating
wells in
fracture
zones

Plan view

FRACTURE TRACE APPLICATIONS

- To identify preferential zones of fluid flow and chemical migration
- To site monitor and recovery wells

VOCs IN GROUNDWATER AND NAPL VOLATILIZE INTO SOIL GAS



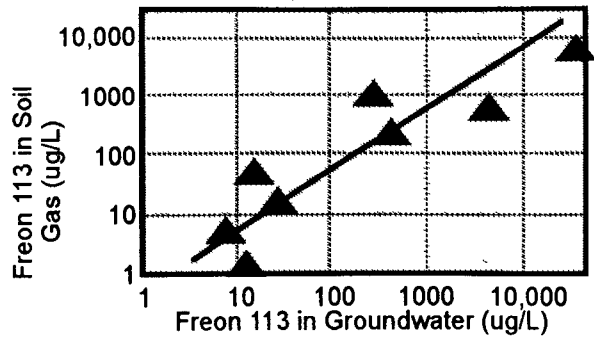
SOIL GAS SURVEYS

- Delineate volatile NAPL in vadose zone
- Delineate shallow groundwater contamination
- Very limited capacity to delineate deep groundwater contamination
- Results can be misleading if subsurface conditions are misunderstood
- Requires confirmation by analysis of soil and fluid samples

SOIL GAS GRAB SAMPLING

- Typical procedure:
 - Drive hollow probe to 3-10 ft
 - Pump and purge soil gas from probe
 - Collect sample from gas stream in glass or stainless steel container
- Can collect and analyze 20-50 samples/day @ \$110-\$190 each
- Onsite analysis facilitates direction of survey
- With introduction of volatile tracers into tanks or pipelines, can be used for leak detection

CORRELATION BETWEEN FREON 113 IN SHALLOW SOIL GAS AND GROUNDWATER (after Thompson and Marrin, 1987)

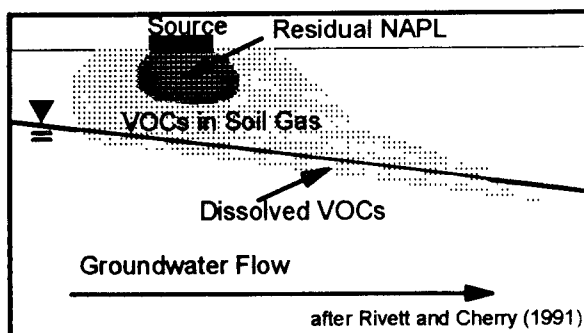


TYPICAL NAPL ANALYTES AND PRODUCTS DETECTABLE BY SOIL GAS ANALYSIS

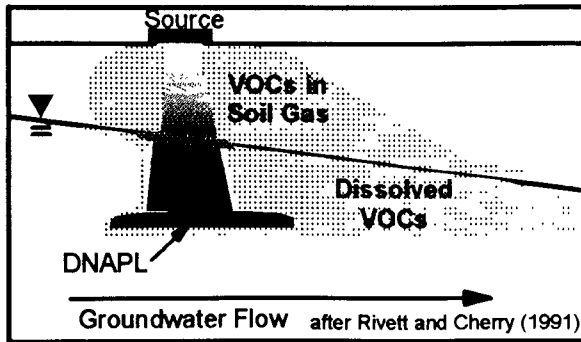
- | | |
|-------------------------|------------------------------|
| • BTEX compounds | • Gasoline |
| • Carbon Tetrachloride | • Jet Fuel |
| • Chloroform | • Diesel Fuel |
| • 1,1-Dichloroethane | • Heating Oil |
| • 1,1,-Dichloroethene | • Coal Tar |
| • 1,2-Dichloroethene | • Solvents & Cleaning Fluids |
| • Methylene Chloride | • Refrigerants |
| • Tetrachloroethene | • Paint Thinners |
| • 1,1,1-Trichloroethane | |
| • 1,1,2-Trichloroethane | |
| • Trichloroethene | |

modified from
Tillman et al
(1989)

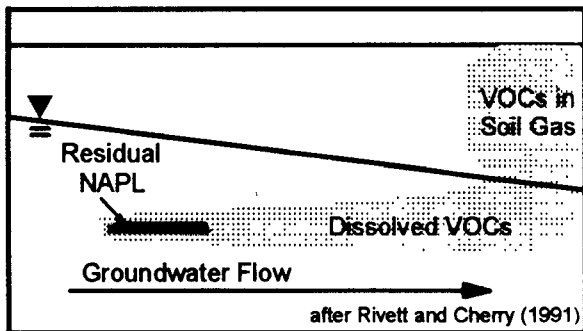
VOCs DIFFUSE FROM RESIDUAL NAPL CONTAMINATE SHALLOW GROUNDWATER REPARTITION TO SOIL GAS



VOC TRANSPORT IN SOIL GAS AND GROUNDWATER

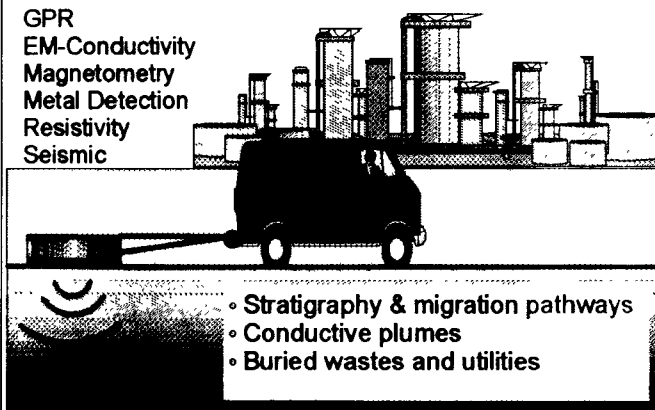


LIMITED DIFFUSION OF VOCs FROM GROUNDWATER TO SOIL GAS REDUCES SOIL GAS SURVEY EFFECTIVENESS



SURFACE GEOPHYSICS

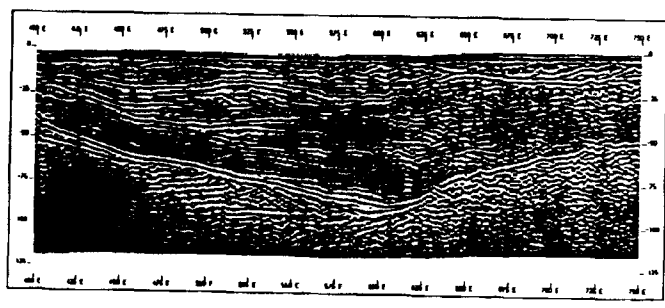
GPR
EM-Conductivity
Magnetometry
Metal Detection
Resistivity
Seismic



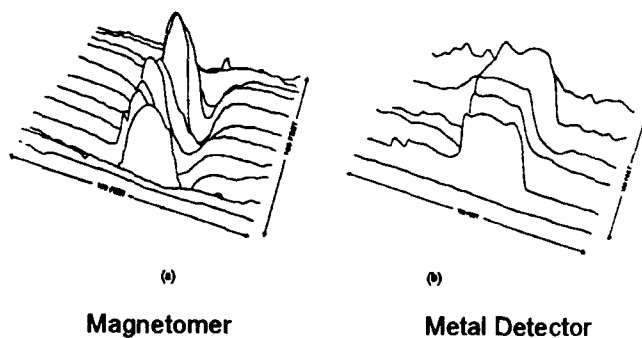
Geologic Interpretation Using Ground Penetrating Radar (GPR) (after Benson, 1991)

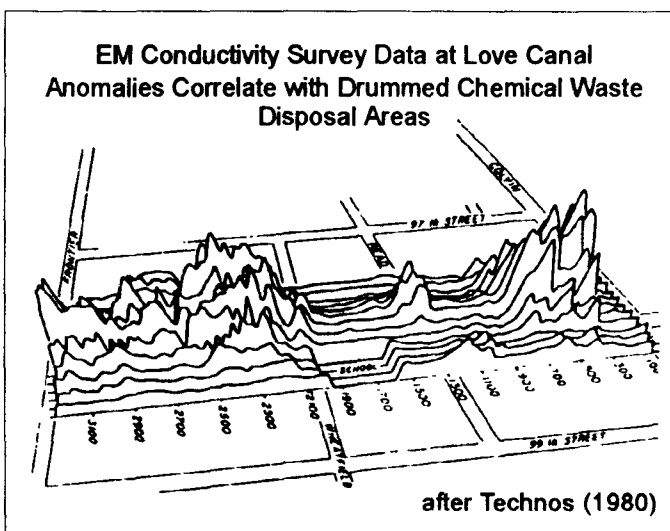
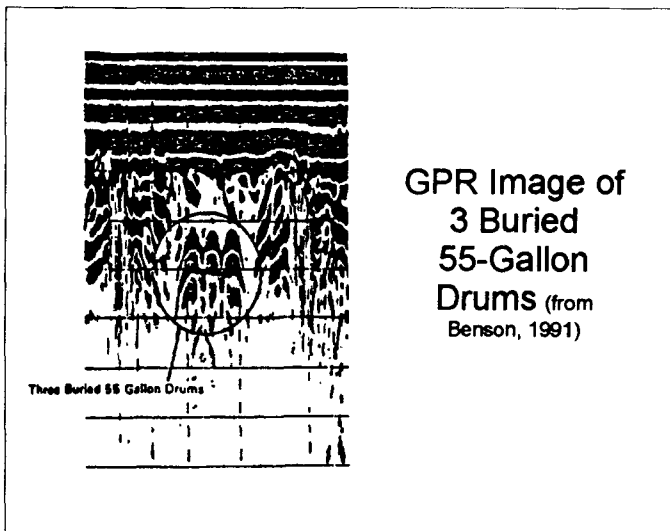


GPR Image of a Buried River Channel Deposit (from MacLeod and Dobush, 1991)



Detecting Buried Metal Drums in a Trench 20' x 100' x 6' Deep (after Benson, 1991)





DIRECT DETECTION OF DNAPL USING SURFACE GEOPHYSICS

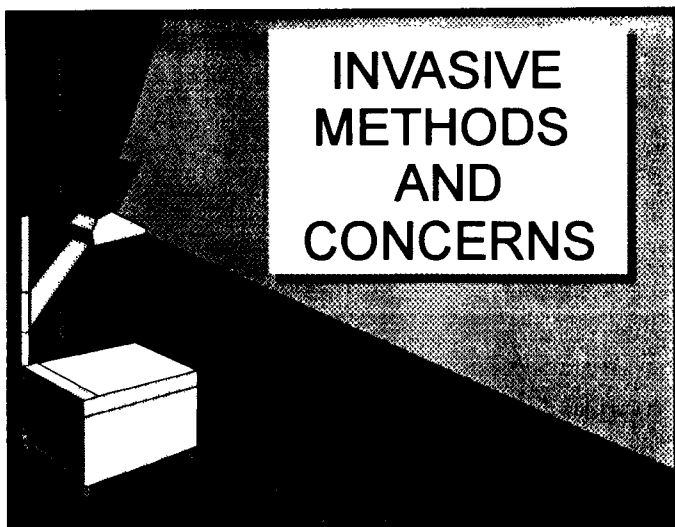
- GPR to provide detailed stratigraphic images and detect anomalous dielectric properties due to NAPL presence
- EM Conductivity or Electrical Resistivity to monitor reductions in electrical conductivity due to NAPL presence

FAVORABLE CONDITIONS FOR DIRECT DETECTION OF DNAPL

- Simple stratigraphy
- Large quantities
- Baseline pre-release survey
- Expert investigators

SURFACE GEOPHYSICAL SURVEYS

- Enhance delineation of release areas, stratigraphy, and migration routes
- Direct detection of NAPL is limited by lack of cost-effective methods and geophysicists trained in methods potentially applicable at NAPL sites



TEST PIT AND TRENCHES

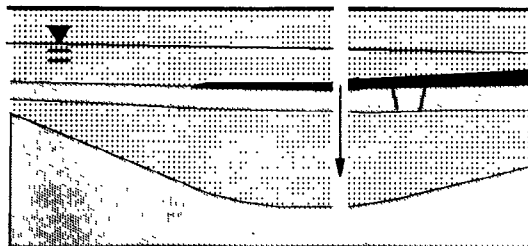
- Delineate
 - Stratigraphy
 - Waste disposal areas
 - Grossly contaminated areas
 - Buried pipelines, USTs, etc.
- Sampling
- Large, continuous exposure
- Limited risk of vertical migration

INVASIVE METHOD CONCERNS AT DNAPL SITES

- Increased health and safety risk
- Material compatability
- Cross-contamination potential
(DNAPL >> dissolved)
- Data acquisition and interpretation

INVASIVE METHOD RISKS

- Drilling and well installations may create vertical pathways for DNAPL movement
- Pumping may induce DNAPL migration



INVASIVE METHOD RISKS

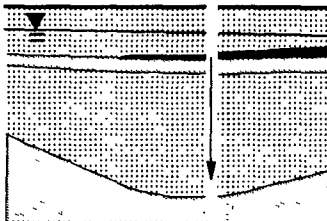
- Induced NAPL transport may:
 - Heighten the risk to receptors
 - Increase remedial difficulty and cost
 - Generate misleading data leading to development of a flawed conceptual model and a flawed remedy

INVASIVE METHODS RISKS INCREASE WHERE THERE ARE

- Fractured and/or heterogeneous media
- Subtle NAPL barrier layers
- Multiple NAPL release locations
- Large NAPL release volumes
- Mobile NAPL (low viscosity, high density)

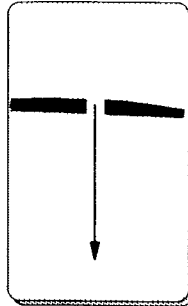
RISK MINIMIZATION 13 suggestions

- Use knowledge of stratigraphy and DNAPL distribution to guide drilling
- Characterize DNAPL zone from top down
- Avoid unnecessary drilling in the DNAPL zone



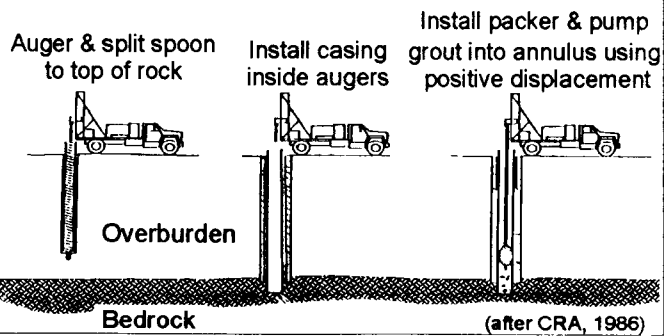
RISK MINIMIZATION

- Minimize time during which boring is open
- Minimize length of hole open to formation

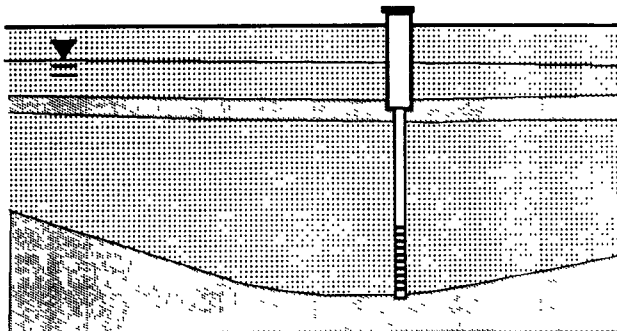


RISK MINIMIZATION

- Maintain hydrostatic head in borehole; consider using a dense drilling fluid
- Use telescoped-casing drilling techniques to isolate contaminated zones

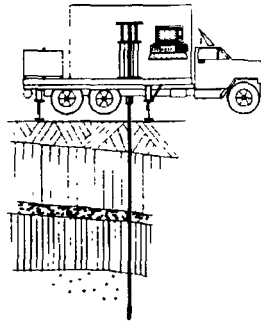


TELESCOPED WELL CASING TO ISOLATE SHALLOW ZONE



RISK MINIMIZATION

- Use less invasive "Direct-Push" sampling methods (i.e., Cone Penetrometer, Geo-Probe, HydroPunch) to examine stratigraphy, soil gas, and fluids with depth



CONE PENETROMETER

Advantages

- + Efficient for stratigraphic logging of soft soils
- + Continuous measurement
- + Sensors measure penetration resistance, pore pressure, radiation, fluorescence . . .
- + Soil gas and fluid sampling
- + No cuttings
- + Less intrusive; can grout hole

Limitations

- Unable to penetrate dense formations
- Limited depth capability
- Limited soil and fluid sampling capability
- Limited well construction capability
- Needs confirmation
- Limited availability

RISK MINIMIZATION

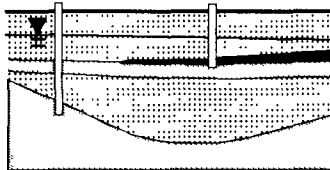
- Carefully examine samples as drilling progresses to avoid drilling through a barrier layer below DNAPL
 - Visual evidence (sheens, staining, globules, etc.)
 - Organic vapor analysis
 - Hydrophobic dye test and/or UV examination
 - Examine fractures, soil ped faces, macropores, coarser lenses
 - Dissect samples to reveal inner surfaces

RISK MINIMIZATION

- Consider chemical compatibility of well materials
 - PVC & ABS -- degraded by aromatics and organic solvents
 - Carbon steel -- corrodes
 - Fluoropolymers -- good resistance except to fluorinated solvents; very expensive
 - Stainless steel -- generally recommended due to good resistance (however, DNAPL may wet steel)
- DNAPL may shrink bentonite; however, bentonite-cement grout may be appropriate

RISK MINIMIZATION

- Outside-in approach
- Noninvasive methods
- At many sites, the DNAPL zone can be characterized by limiting drilling to shallow depth; deeper units can be characterized by drilling beyond the DNAPL zone



BEDROCK DRILLING/TESTING PROTOCOL

- Pressure grout surface casing to top of rock
- Core 15' rock interval
- Packer-pump test, collect sample
- Pressure grout test interval
- Ream grout to 6", pressure test, regrout if needed
- Continue coring, testing and grouting to base of aquifer

DNAPL SITE DRILLING RISKS

- Some potential for causing downward DNAPL migration occurs with all drilling methods
- "Safe" methods for drilling and constructing wells through DNAPL zones have not been adequately demonstrated

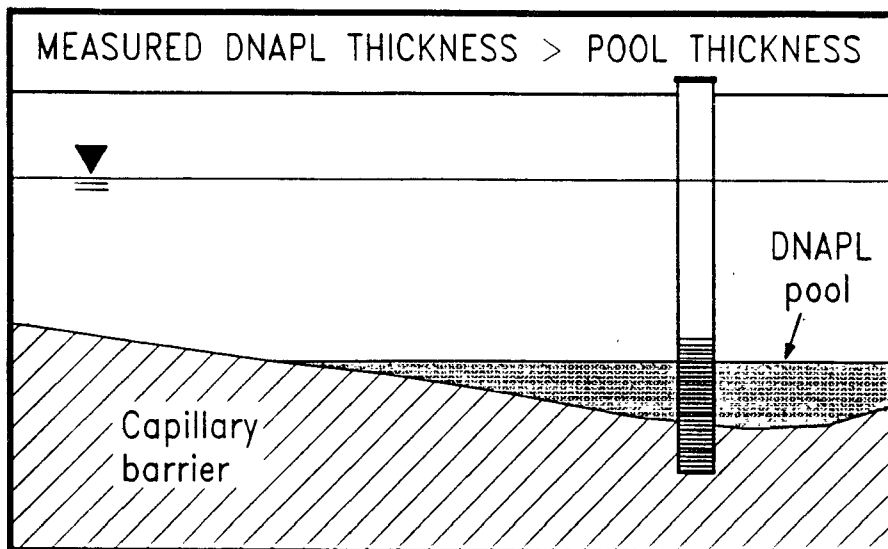
MONITOR WELL USE

- Characterize immiscible fluid distribution, flow directions and rates, groundwater quality, and hydraulic properties
- Well design and location influence DNAPL fluid movement and distribution in the well environment
- Qualitative nature of DNAPL distribution data

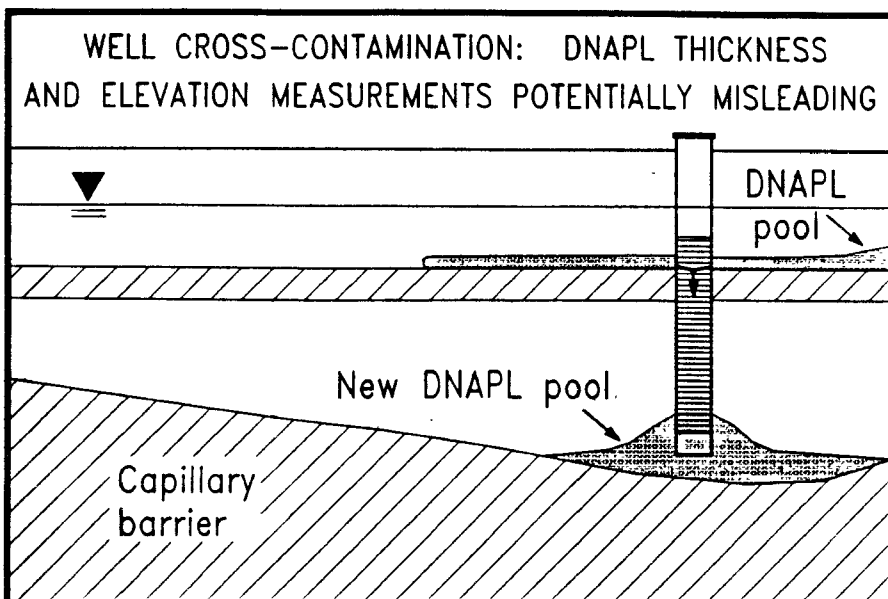
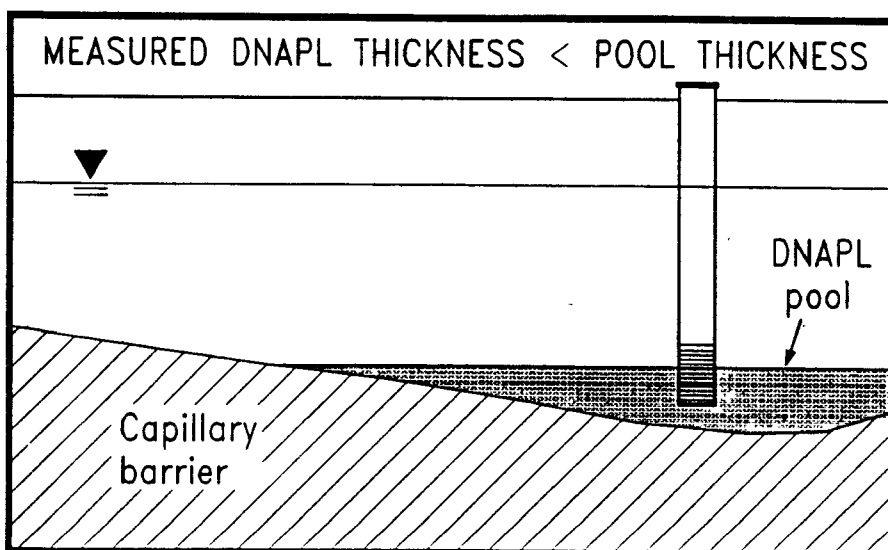
FLUID MEASUREMENT METHODS

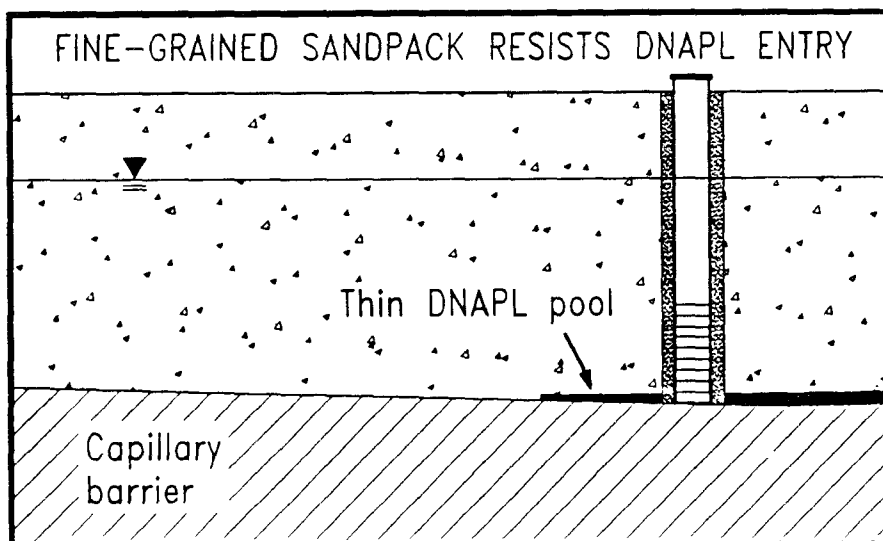
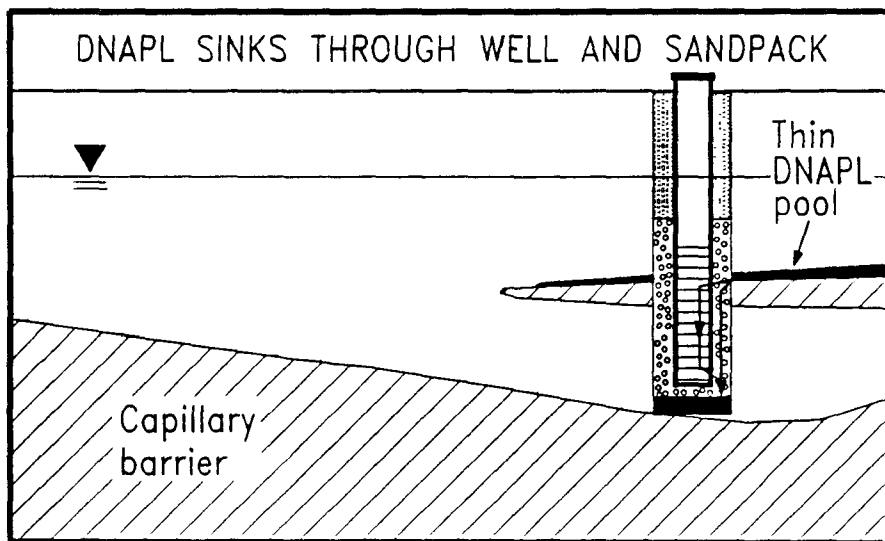
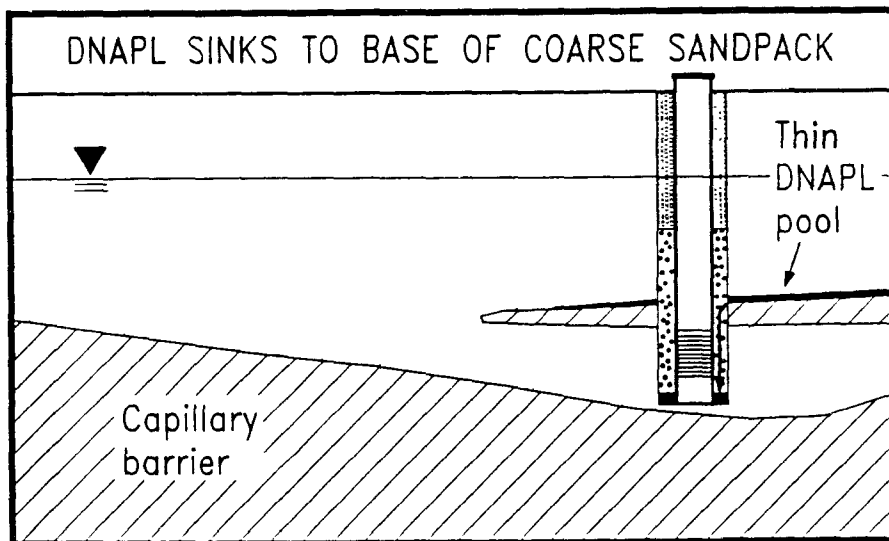
- Interface probe
- Hydrocarbon and water detection pastes
- Transparent bailers
- Other depth-discrete bailers
- Weighted string

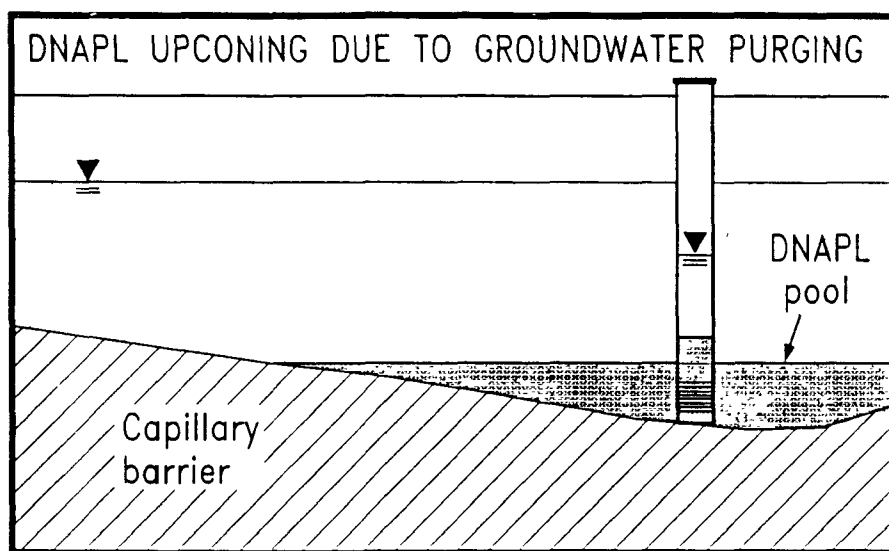
Consider the potential for cross-contamination and the cost to decontaminate equipment.



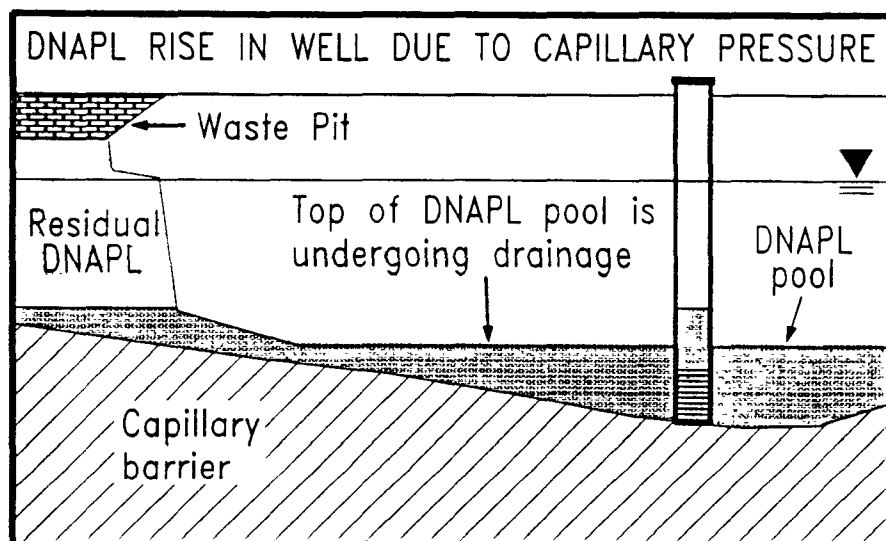
(after Huling and Weaver, 1991)







(after Huling and Weaver, 1991)



(after WCGR, 1991)

DNAPL WELL DESIGN SUGGESTIONS

- Complete to top of capillary barrier beneath DNAPL
- Screen across entire continuous DNAPL thickness
- Sandpack coarser than media (consider hydrophobic sandpack)
- Competent materials

FLUID MEASUREMENT DATA

- Interpret with caution
- Compare well fluid distribution measurements to boring data

INTEGRATED INVESTIGATION AND DATA ANALYSIS

- No practical cookbook approach
- Site-specific conditions and issues
- Phased characterization to meet risk and remedy assessment needs
- Apply standard and special methods to deal with DNAPL site concerns and data needs

References

DNAPL Site Characterization **Robert M. Cohen and James W. Mercer**

- Benson, R.C. "Remote Sensing and Geophysical Methods for Evaluation of Subsurface Conditions." Practical Handbook of Ground-Water Monitoring. D.M. Nielsen, ed. Chelsea, MI: Lewis Publishers, 1991: 143-194.
- Cohen, R.M. and J.W. Mercer. DNAPL Site Evaluation. Chelsea, MI: Lewis Publishers, 1993.
- Huling, S.G. and J.W. Weaver. "Dense Nonaqueous Phase Liquids." USEPA Groundwater Issue Paper, EPA/540/4-91, 1991: 21.
- Johnson, R.L. and J.F. Pankow. "Dissolution of Dense Immiscible Solvents in Groundwater: 2. Dissolution from Pools of Solvent and Implications for the Remediation of Solvent-Contaminated Sites." Environmental Science & Technology, Vol. 26, No. 5, 1992: 896-901.
- Kueper, B.H., D. Redman, R.C. Starr, S. Reitsma, and M. Mah. "A Field Experiment to Study the Behaviour of Tetrachloroethylene Below the Watertable: Spatial Distribution of Residual and Pooled DNAPL." Submitted to Ground Water.
- Kueper, B.H. and E.O. Frind. "Two-Phase Flow in Heterogeneous Porous Media: 1. Model Development." Water Resources Research, Vol. 27, No. 6, 1991a: 1049-1058.
- Kueper, B.H. and E.O. Frind. "Two-Phase Flow in Heterogeneous Porous Media: 1. Model Application." Water Resources Research, Vol. 27, No. 6, 1991b: 1059-1070.
- Lattman, L.H. and R.R. Parizek. "Relationship Between Fracture Traces and the Occurrence of Ground-water in Carbonate Rocks." Journal of Hydrology, Vol. 2, 1964: 73-91.
- Mackay, D., W.Y. Shiu, A. Maijanen and S. Feenstra. "Dissolution of Non-Aqueous Phase Liquids in Groundwater." Journal of Contaminant Hydrology, Vol. 8, No. 1, 1991: 23-42.
- MacLeod, I.N. and T.M. Dobush. "Geophysics—More Than Numbers." National Water Well Association Outdoor Action Conference Proceedings. Las Vegas, NV, 1990.
- McKay, L.D., J.A. Cherry, and R.W. Gillham. "Field Experiments in Fractured Clay Till: 1. Hydraulic Conductivity and Fracture Aperture." Water Resources Research, Vol. 29, No. 4, 1993: 1149-1162.
- Mercier Remediation Panel. "Evaluation of Long-Term Remedial Measures for the Subsurface Contamination Associated with the Former Mercier Lagoons." Preliminary draft report submitted to Laidlaw Environment Services, 1993.

References—Continued

- Newell, C.J. and R.R. Ross. "Estimating Potential for Occurrence of DNAPL at Superfund Sites." USEPA Quick Reference Fact Sheet, Ada, OK: Robert S. Kerr Environmental Research Laboratory, 1992.
- Poulsen, M.M. and B.H. Kueper. "A Field Experiment to Study the Behavior of Tetrachloroethylene in Unsaturated Porous Media." Environmental Science and Technology, Vol. 26, No. 5, 1992: 889-895.
- Rivett, M.O. and J.A. Cherry. "The Effectiveness of Soil Gas Surveys in Delineation of Groundwater Contamination: Controlled Experiments at the Borden Field Site." Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration, National Water Well Association/American Petroleum Institute. Houston, TX, 1991: 107-124.
- Technos, Inc. Geophysical Investigation Results, Love Canal, New York. Report to GCA Corporation and USEPA, Miami, FL: Technos, Inc., 1980.
- Thompson, G.M. and D.L. Marrin. "Soil Gas Contaminant Investigations: A Dynamic Approach." Ground Water Monitoring Review, Vol. 7, No. 3, 1987: 88-93.
- Tillman, N., K. Ranlet and T.J. Meyer. "Soil Gas Surveys: Part I." Pollution Engineering, Vol. 21, No. 7, 1989a: 86-89.
- Tillman, N., K. Ranlet and T.J. Meyer. "Soil Gas Surveys: Part II, Procedures." Pollution Engineering, Vol. 21, No. 8, 1989b: 79-84.
- U.S. Environmental Protection Agency. "Dense Nonaqueous Phase Liquids—A Workshop Summary." Dallas, TX, April 17-18, 1991: EPA/600-R-92/030. Robert S. Kerr Environmental Research Laboratory, Ada, OK.
- WCGR. "Dense, Immiscible Phase Liquid Contaminants (DNAPLs) in Porous and Fractured Media, A Short Course." Notes from the DNAPL Short Course, October 7-10, 1991, Waterloo Center for Groundwater Research, University of Waterloo, Kitchner Ontario, Canada.

Options for DNAPL Remediation

Charles J. Newell
Vice President, Groundwater Services, Inc.

I. Introduction

- A. Design Process
- B. Can We Clean Up DNAPL Sites?
- C. How Remediation Technology Evolves

II. Proven DNAPL Remediation Options

A. Remediating DNAPLs in the Unsaturated Zone

- 1. Excavation
 - a. Applicability
 - b. Design Basis Information
 - c. Design Process
 - d. Case Study
- 2. Soil Vapor Extraction (SVE)
 - a. Applicability
 - b. Design Basis Information
 - c. Design Process
 - d. Case Study

B. Remediating DNAPLs in the Saturated Zone

- 1. Pumping DNAPL
 - a. Applicability
 - b. Design Basis Information
 - c. Design Process
 - d. Case Study
- 2. Pump-and-Treat (DNAPL Dissolution)
 - a. Applicability
 - b. Design Basis Information
 - c. Design Process
 - d. Case Study

3. In-Situ Biodegradation

- a. Applicability
- b. Design Basis Information
- c. Design Process
- d. Case Study

C. Other DNAPL Remediation/Control Approaches

- 1. Treatment Train
- 2. Containment
 - a. Hydraulic Containment
 - b. Physical Barriers
 - c. Natural Dilution/Attenuation
 - d. Case Study

III. Emerging DNAPL Remediation Technologies

A. Implementing Emerging Remediation Technologies

B. Selected Emerging Technologies

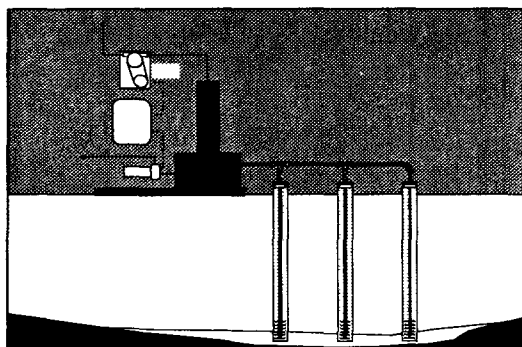
- 1. Air Sparging in the Saturated Zone
- 2. Dewatering/Soil Venting
- 3. Surfactants and Other Mobility-Increasing Agents
- 4. Chemically-Enhanced Dissolution
- 5. Bioventing
- 6. Steam Injection
- 7. Pumping Systems: Horizontal Wells and Wellpoint Pumps
- 8. Permeable Reaction Walls (Magic Sand)

OPTIONS FOR DNAPL REMEDIATION



Charles J. Newell, Ph.D., P.E.

*Groundwater Services, Inc.
Houston, Texas*



Roadmap

- Introduction

- Design Process

- Can We Clean Up DNAPL Sites?

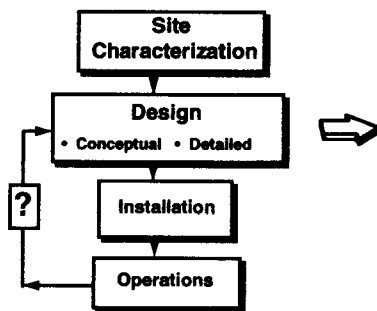
- How Remediation Technology Evolves

- Five Proven Remediation Technologies

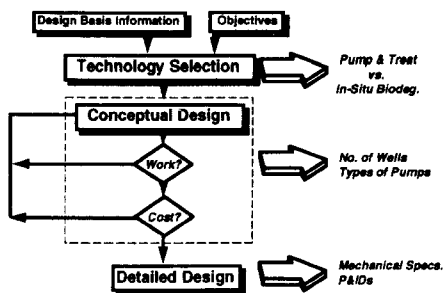
- Emerging Technologies



Typical Remediation Work Program



Design Process and Products



Can We Clean Up DNAPL Sites?

- No Proven Technologies to:

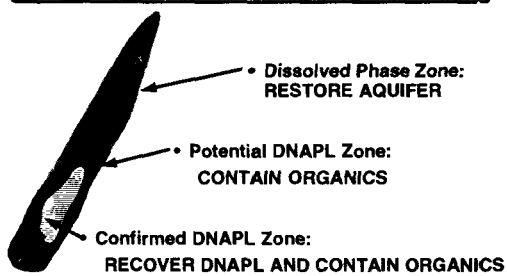
- Remove All DNAPL



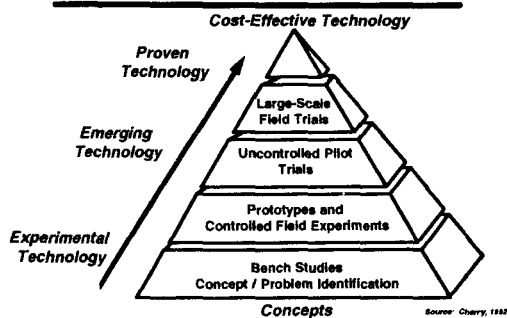
- Reach Drinking Water Standards



GENERAL DNAPL MANAGEMENT STRATEGY



How Remediation Technology Evolves



Roadmap

- Introduction
- • Five Proven Remediation Technologies

- Emerging Technologies



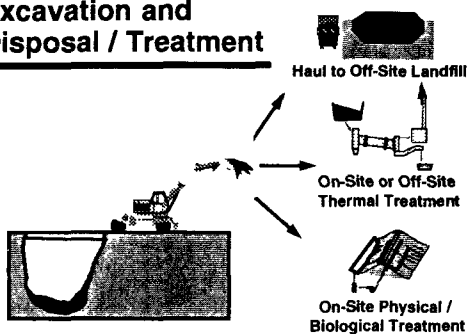
Five Proven Remediation Technologies

- • EXCAVATION AND DISPOSAL / TREATMENT

- Soil Vapor Extraction (SVE)
- Pumping DNAPL
- Pump & Treat (Dissolution)
- In-Situ Biodegradation



Excavation and Disposal / Treatment



Applicability of Excavation

- **Standard Construction Practice to 25 Feet Depth**
- **Dewatering Required if Below Water Table**
- **Unconsolidated Material**
- **Best Technology for Small Volumes**



Design Basis Information: Excavation

- **Excavation: Depth, Volume**
- **Disposal: Type of Waste, Distance**
- **Thermal Treatment: BTU Content, Type of Soil**
- **On-Site Treatment**
 - Soil Vapor Extraction
 - Biodegradation

Design Process: Excavation/Disposal

- **Excavation Cost: \$ 20 - \$ 50 per cubic yard**
 - Depth of Excavation?
 - Area of Excavation?
 - Need to Control Fugitive Dust, Vapors?
 - Safety Issues?
- **Off-Site Disposal**
 - Need for On-Site Pretreatment?
 - Distance to Landfill?
 - Hazardous Waste Landfill: \$ 100 - \$ 500 per cubic yard

Design Process: Treatment

• Thermal Treatment

- High Vs. Low BTU?
- Presence of PCBs, Dioxin?
- Low Temperature Treatment \$ 100 - \$ 200 / ton
- Thermal Destruction \$ 300 - \$ 1,000 / ton

• On-Site Treatment

- Site Available for Treatment?
- Volatile or Biodegradable?
- Soil Vapor Extraction (SVE)
- Biodegradation



Five Proven Remediation Technologies

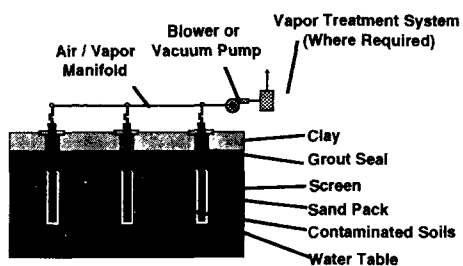
• Excavation and Disposal / Treatment

➔ • SOIL VAPOR EXTRACTION (SVE)

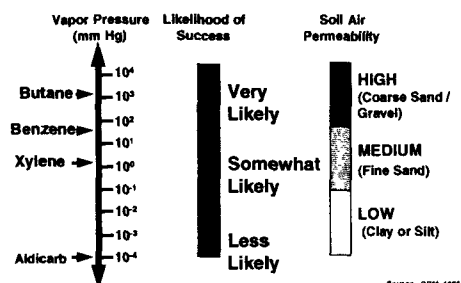
- Pumping DNAPL
- Pump & Treat (Dissolution)
- In-Situ Biodegradation



Soil Vapor Extraction



Applicability of SVE



Design Basis Information: SVE

- **Air Permeability**
 - Estimated from Soil Properties
 - Measured With Test in Field
- **Contaminant Characteristics**
 - DNAPL Composition
 - Volatility (Vapor Pressure, Henry's Law Coefficient)
- **Air Flow**
 - Stratigraphy
 - Need for Impermeable Cap
 - Water Table and Need for Pumping



SVE Design Process

- Choose Number of Vapor Extraction Wells
- Choose Well Spacing, Inlet Wells, Seals
- Design Well Screens and Construction
- Remember Vapor Treatment
- Check for Groundwater Upwelling



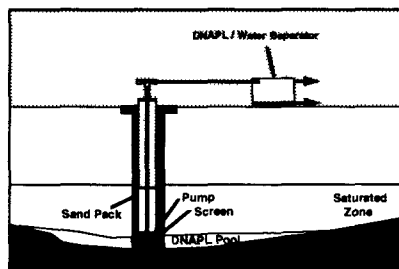
Source: Johnson 1996

Five Proven Remediation Technologies

- Excavation and Disposal / Treatment
- Soil Vapor Extraction (SVE)
- ➔ • **PUMPING DNAPL**
- Pump & Treat (Dissolution)
- In-Situ Biodegradation



Pumping DNAPL



Applicability of DNAPL Pumping

- Sites With Large Amounts of DNAPL
- Look for Wells With Free-Phase DNAPL
- Easier to Remove Chlorinated Solvents
- Potentially Higher Gradient Under Confined Conditions

Design Basis Information: DNAPL Pumping

- **General**
 - Types of Chemicals, Viscosity, Interfacial Tension
 - Stratigraphy
 - Hydraulic Conductivity
- **Free-Phase DNAPL**
 - Thickness of DNAPL Pool
 - Relative Permeability of DNAPL
- **Residual DNAPL**
 - Maximum Hydraulic Gradient
 - Capillary Number



DNAPL Pumping Design Process

- **Choose Location of DNAPL Wells**
- **Select Pumps and Materials**
- **Assess EOR Technologies**
 - Vacuum-Enhanced Pumping
 - Waterflooding
 - Surfactants
 - Steam
- **Design Treatment System**

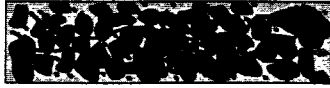


Five Proven Remediation Technologies

- **Excavation and Disposal / Treatment**
- **Soil Vapor Extraction (SVE)**
- **Pumping DNAPL**
- ➔ • **PUMP & TREAT (DISSOLUTION)**
- **In-Situ Biodegradation**



Pump-and-Treat (Dissolution)



- Dissolve Residual DNAPL
- Based on Number of Pore Volumes
- Key Concept: Effective Solubility

Applicability of Dissolution

- DNAPLs in Saturated Zone
- DNAPL with Very Soluble Components
- Sites With Low Amounts of DNAPL
- Highly Permeable Aquifers

Design Basis Information: Dissolution

- Mass of Residual DNAPL in Subsurface
- Effective Solubility of Key Contaminants
- Maximum Potential Groundwater Velocity
- Remediation Period



Dissolution Design Process

- Estimate Total DNAPL Mass
- Make Concentration Assumptions
 - Constant Solubility
 - Effective Solubility
- Divide to Get Number of Pore Volumes
- Size Recovery Well System

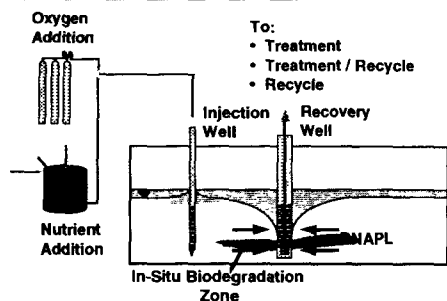


Five Proven Remediation Technologies

- Excavation and Disposal / Treatment
- Soil Vapor Extraction (SVE)
- Pumping DNAPL
- Pump-and-Treat (Dissolution)
- • IN-SITU BIODEGRADATION



In-Situ Biodegradation



Applicability of In-Situ Biodeg.

- Sites With Non-Chlorinated Compounds
 - BTEX
 - Creosote Sites (Naphthalene, PAHs)
 - Coal Tar
- Sites With Depressed Oxygen in Plume Area
- Aquifers With High Permeability

Design Basis Information: In-Situ Biodeg.

- Biodegradability of Contaminants
 - Chlorinated Compounds: No
 - Non-Chlorinated Aromatics: Yes
- Presence of Indigenous Aerobic Microorganisms
 - Bugs Almost Always Present
 - NEVER ADD BUGS
- Water Chemistry
 - Iron
 - Calcium Carbonate



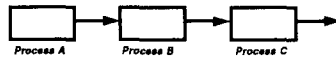
In-Situ Biodeg. Design Process

- Estimate Total DNAPL Mass
- Calculate Required Mass of Oxygen to Be Injected
 - Yield: 2 gm Oxygen for 1 gm Hydrocarbon
- Select Method to Add Oxygen to Injection Water
 - Bubble Air in Injection Water – 10 mg/l
 - Pure Oxygen – 25 mg/l
 - Hydrogen Peroxide – 100 mg/l (?)
- Calculate Water Needed
- Size Recovery Well System



Other DNAPL Remediation Approaches

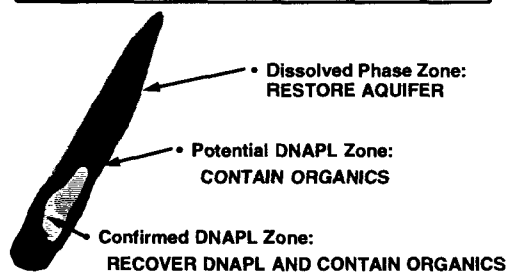
- Treatment Train



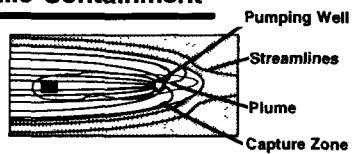
- Long-Term Containment



GENERAL DNAPL MANAGEMENT STRATEGY



Hydraulic Containment



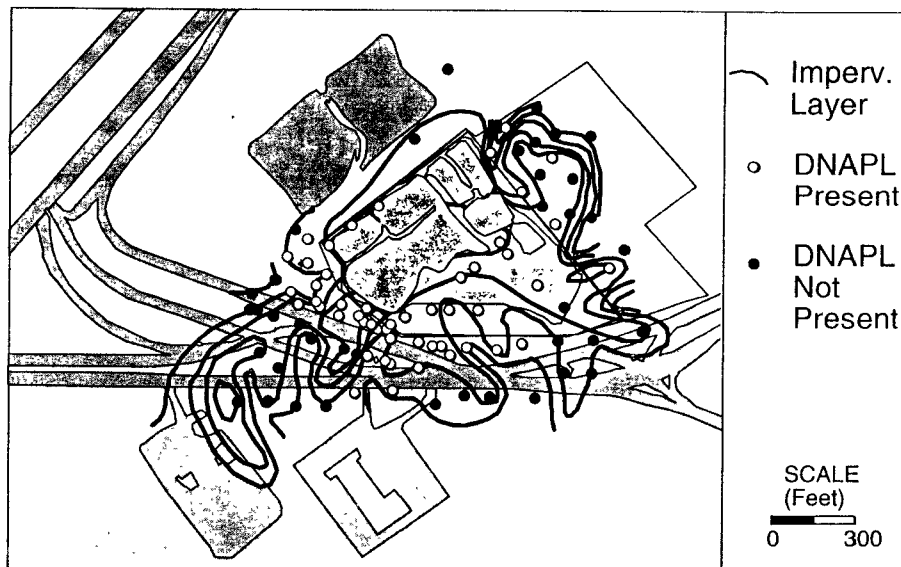
- Design Methods
 - Javendahl Capture Zone Curves
 - Computer Models

- Operational Factors
 - Well Efficiency
 - Seasonal / Annual Effects

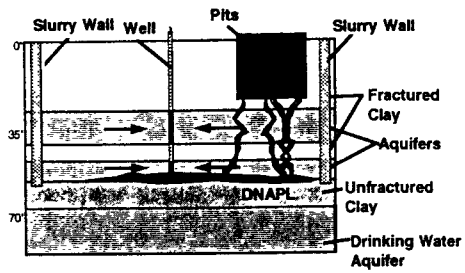
Physical Barriers

- **Purpose**
 - Prevent Outward Migration of Organics
 - Reduce Inflow of Ground Water
- **Design**
 - Type of Barriers
 - Configuration
- **Construction**
 - Routinely Installed Down to 50 Feet
 - Cost: ~ \$ 10 - \$ 20 per square foot for Slurry Wall

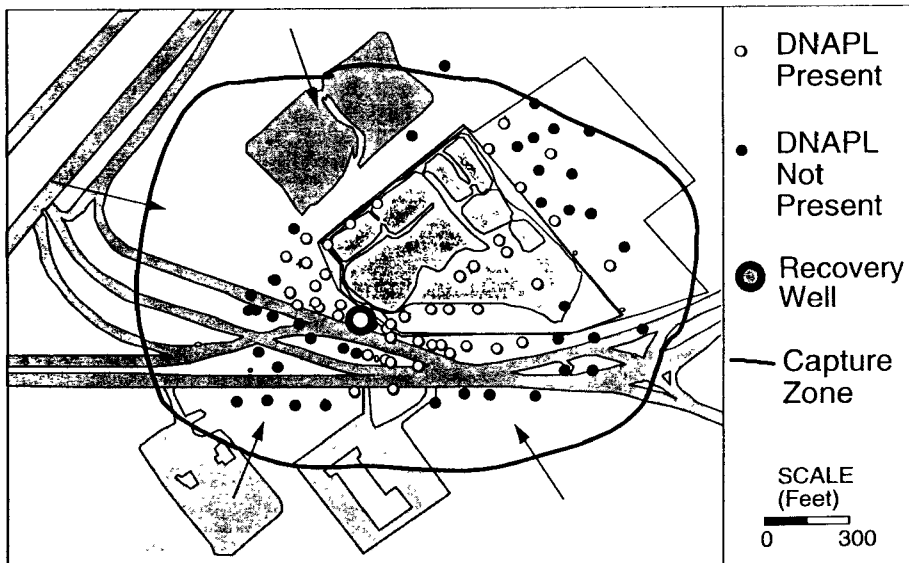
DNAPL Occurrence at Superfund Site



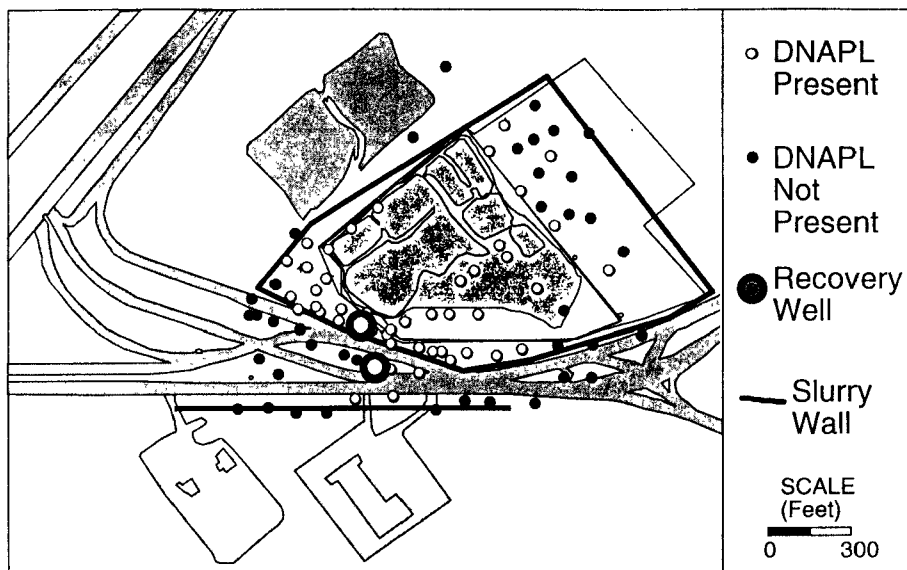
Hydraulic Containment With Slurry Wall



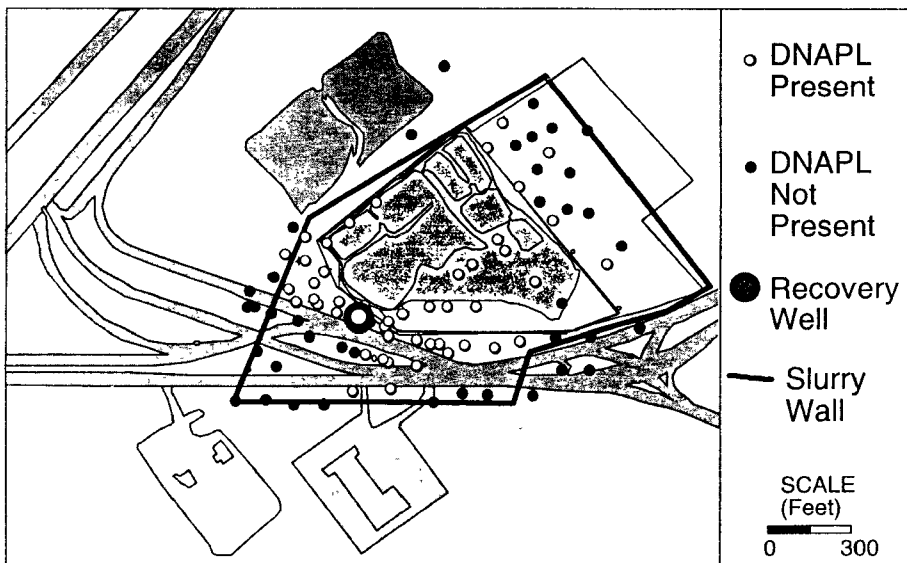
Capture Zone With No Slurry Wall Pumping Rate: 2 GPM



Capture Zone With Slurry Wall "A" Pumping Rate: 1 GPM



Capture Zone With Slurry Wall "B" Pumping Rate: 0.3 GPM



Natural Dilution / Attenuation

• Key Processes

- Hydrolysis
- Natural In-Situ Biodegradation
- Recharge
- Discharge to Surface Water

• Assessment Techniques

- Monitoring
- Computer Modeling

Roadmap

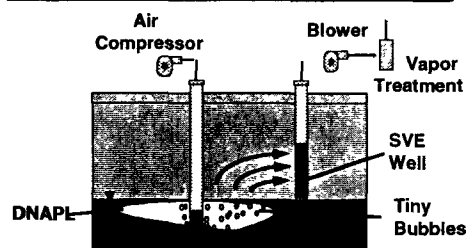
• Introduction

• Five Proven Remediation Technologies

→ • Emerging Technologies

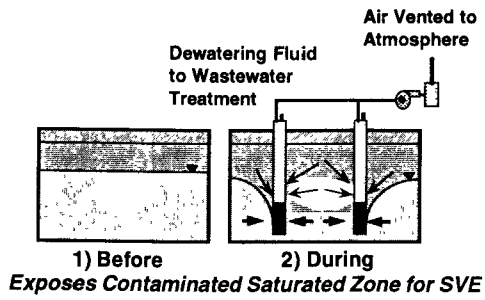


Air Sparging

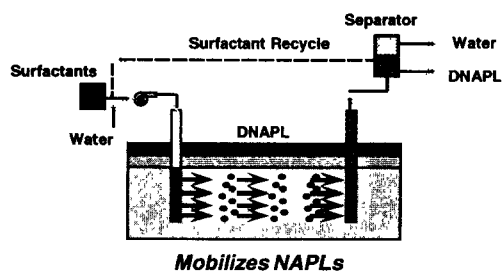


Volatilizes Organics and Promotes In-Situ Biodeg.

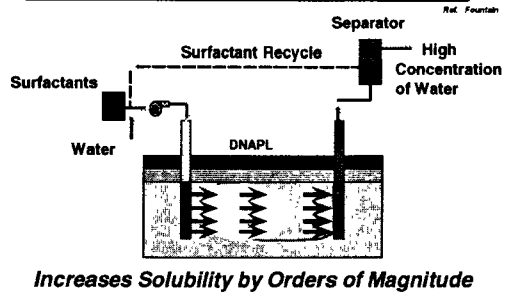
Dewatering / Soil Venting



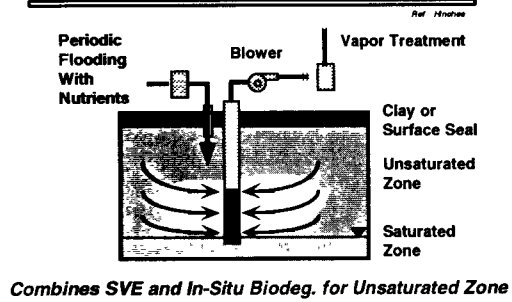
Mobility-Increasing Agents



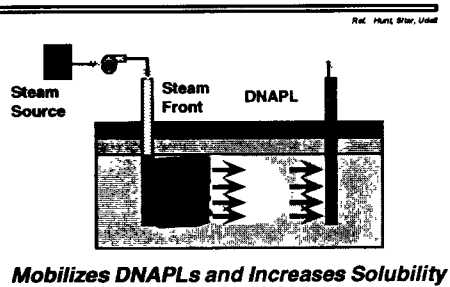
Chemically-Enhanced Dissolution



Bioventing

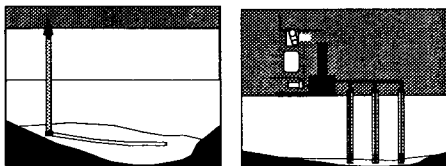


Steam Injection



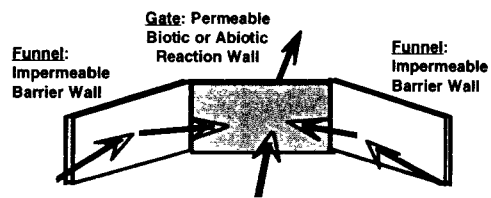
Pumping Systems

- Horizontal Wells
- Wellpoint Pumps



Permeable Reaction Walls

Ref: 02900



Funnels Dissolved Organics Through Reaction Wall

References

Options for DNAPL Remediation Charles J. Newell

- Hinchee, R.E., D.C. Downey, and E.J. Coleman. "Enhanced Bioreclamation, Soil Venting, and Groundwater Extraction: A Cost-Effectiveness and Feasibility Comparison." Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, National Water Well Association/American Petroleum Institute, Nov. 17, 1987: 147.
- Hunt, J.R., N. Sitar, and K.D. Udell. "Nonaqueous Phase Liquid Transport and Cleanup." Water Resources Research, Vol. 24, No. 8, 1991.
- Johnson, P.C., et al. "A Practical Approach to the Design, Operation, and Monitoring of In-Situ Soil-Venting Systems." Groundwater Monitoring Review, Spring 1990.
- Lee, M.D., R.L. Jamison, and R.L. Raymond. "Applicability of In-Situ Bioreclamation as a Remedial Action Alternative." Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, National Water Well Association/American Petroleum Institute. Nov. 17, 1987: 167-185.
- Mackay, D.M. and J.A. Cherry. "Ground-Water Contamination: Pump and Treat Remediation." Environmental Science & Technology, Vol. 23, No. 6, 1989.
- Mercer, J.W., and R.M. Cohen. "A Review of Immiscible Fluids in the Subsurface: Properties, Models, Characterization and Remediation." Journal of Contaminant Hydrology, Vol. 6, 1990.
- Miller, C.T., M.M. Poirier-McNeill, and A.S. Mayer. "Dissolution of Trapped Nonaqueous Phase Liquids: Mass Transfer Characteristics." Water Resources Research, Vol. 26, No. 11, 1990: 2783-2796.
- Schwille, F. Dense Chlorinated Solvents in Porous and Fractured Media: Model Experiments (English Translation). Ann Arbor, MI: Lewis Publishers, 1988.
- U.S. Environmental Protection Agency. "Dense Nonaqueous Phase Liquids." EPA Ground Water Issue Paper, EPA/540/4-91-002, 1991a.
- U.S. Environmental Protection Agency. "Dense Nonaqueous Phase Liquids—A Workshop Summary." EPA Ground Water Issue Paper, EPA/600-R-92/030, 1992b.
- U.S. Environmental Protection Agency. In Situ Treatment of Contaminated Ground Water: An Inventory of Research and Field Demonstrations: Strategies for Improving Ground Water Remediation. EPA/500/K-93/001, January 1993.
- U.S. Environmental Protection Agency. Soil Vapor Extraction Technology Reference Handbook. EPA/540/2-91/003, February 1991. (CDM Reference)

References—Continued

- Waterloo Centre for Ground Water Research, University of Waterloo Short Course. Dense Immiscible Phase Liquid Contaminants in Porous and Fractured Media. Kitchener, Ontario: University of Waterloo, October 1991.
- Wilson, J.L. and S.H. Conrad. "Is Physical Displacement of Residual Hydrocarbons a Realistic Possibility in Aquifer Restoration?" Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, National Water Well Association. Houston, TX, Nov. 5-7, 1984.
- Wilson, J.L., et al. Laboratory Investigation of Residual Liquid Organics from Spills, Leaks, and the Disposal of Hazardous Wastes in Groundwater. EPA/600/6-90/004, April 1990.
- Wilson, J.T. and C.H. Ward. "Opportunities for Bioreclamation of Aquifers Contaminated with Petroleum Hydrocarbons." Developments in Industrial Microbiology (Journal of Industrial Microbiology Suppl. No. 1), Volume 27, 1987.

References—Case Studies

- Connor, J.A., C.J. Newell, and D.K. Wilson. "Assessment, Field Testing, and Conceptual Design for Managing DNAPL at a Superfund Site." Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, National Water Well Association. Houston, TX, 1989.
- Newell, C.J., J.A. Connor, D. Wilson, and T.E. McHugh. "Impact of Dissolution of Dense Non-Aqueous Phase Liquids (DNAPLs) on Groundwater Remediation." Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, National Water Well Association. Houston, TX, November 1991.
- Sale, T. and K. Pionteck. "A Decade of Remedial Action at a Former Wood-Treating Facility." Pre-Conference Seminar, Water Environment Federation 65th Annual Conference. New Orleans, LA, Sept. 19, 1992.