United States
Environmental Protection
Agency

Robert S. Kerr Environmental
Research Laboratory
Ada, OK 74820

Center for Environmental
Research Information
Cincinnati OH 45268

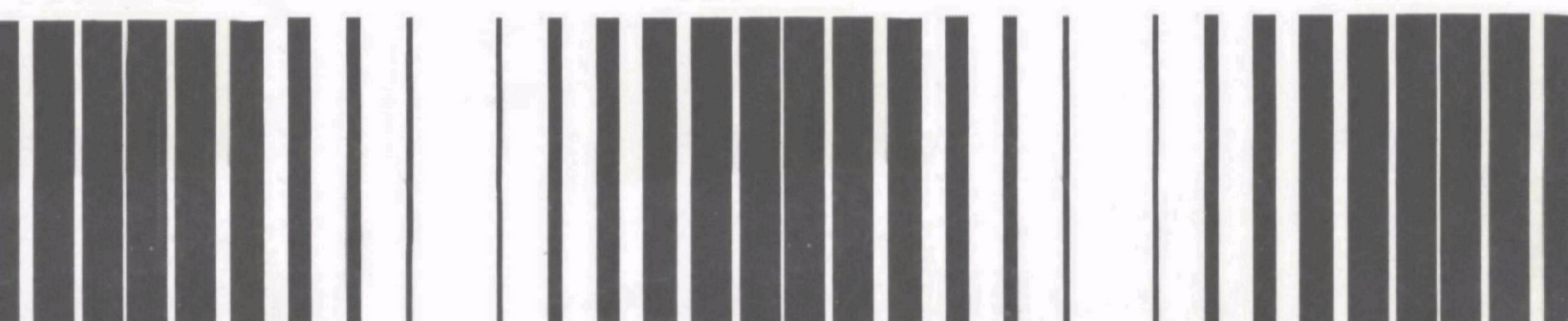
Technology Transfer

CERI-87-45

EPA

Seminar on Transport and Fate of Contaminants in the Subsurface

Slide Copies



FATE AND TRANSPORT	INSTRUCTORS
Physical Processes	Carl D. Palmer
Chemical Processes	Richard L. Johnson
Biological Processes	Joseph M. Suflita
Simulation and Prediction	Joseph F. Keely

OBJECTIVE:

To transfer results from scientific research concerning natural processes that govern the transport and fate of ground-water contaminants from the research community to the regulatory community.

PHYSICAL PROCESSES

- Advection-Dispersion Theory
- Transport in Fractured Media
- Non-Aqueous Phase Liquids
- Particle Transport & Filtration
- Estimation of Transport Parameters

CHEMICAL PROCESSES

- Inorganic Contaminants
- Behavior of Organics
- Laboratory Methods
- Field Experiments
- Case Histories

BIOTRANSFORMATION PROCESSES

- Microbial Ecology
- Metabolism of Contaminants
- Bioremediation Strategies
- Field and Laboratory Methods
- Case Histories

SIMULATION AND PREDICTION

- Types of Models
- Data Requirements
- Quality Control
- Agency Uses and Needs
- Management Considerations

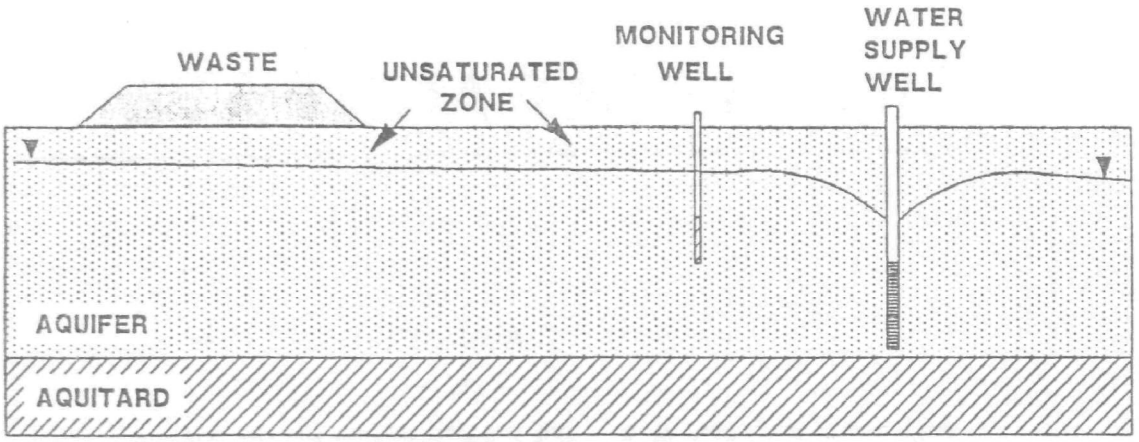
TRANSPORT AND FATE

PHYSICAL PROCESSES

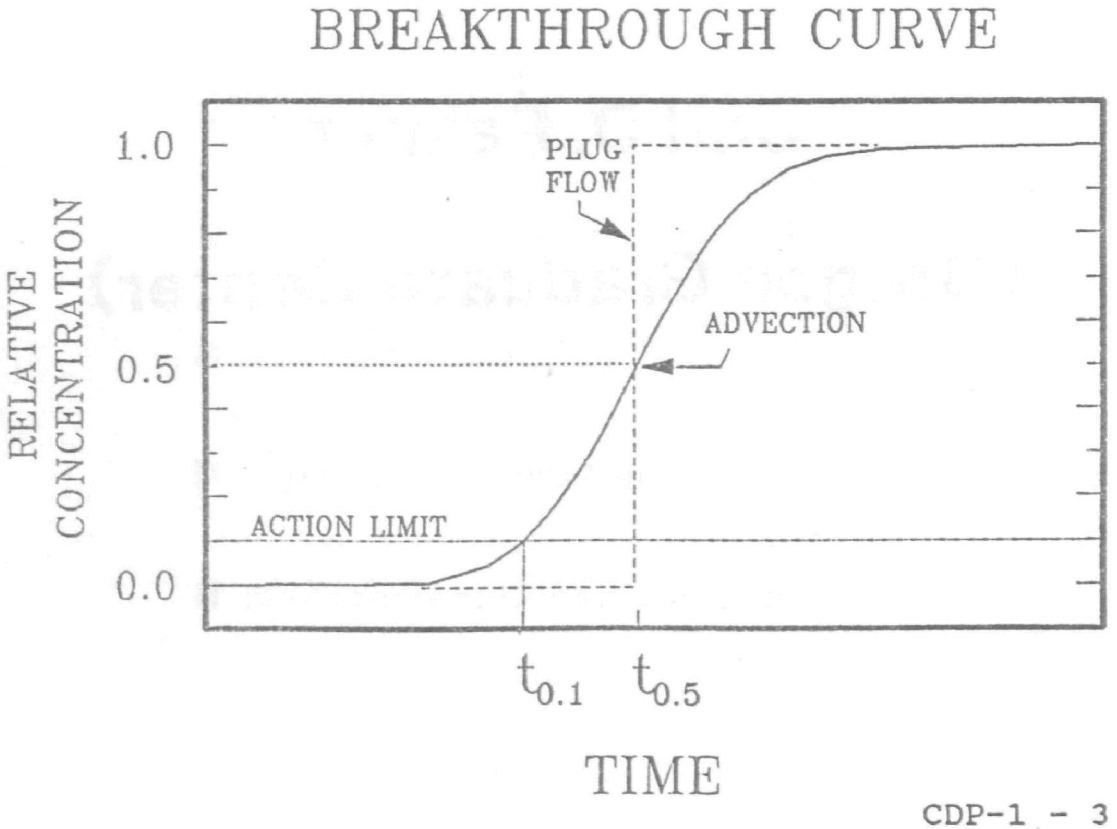
Session 1

Carl D. Palmer

(Oregon Graduate Center)


WASTE
UNSATURATED ZONE
MONITORING WELL
WATER SUPPLY WELL
AQUIFER
AQUITARD

CDP-1 - 2

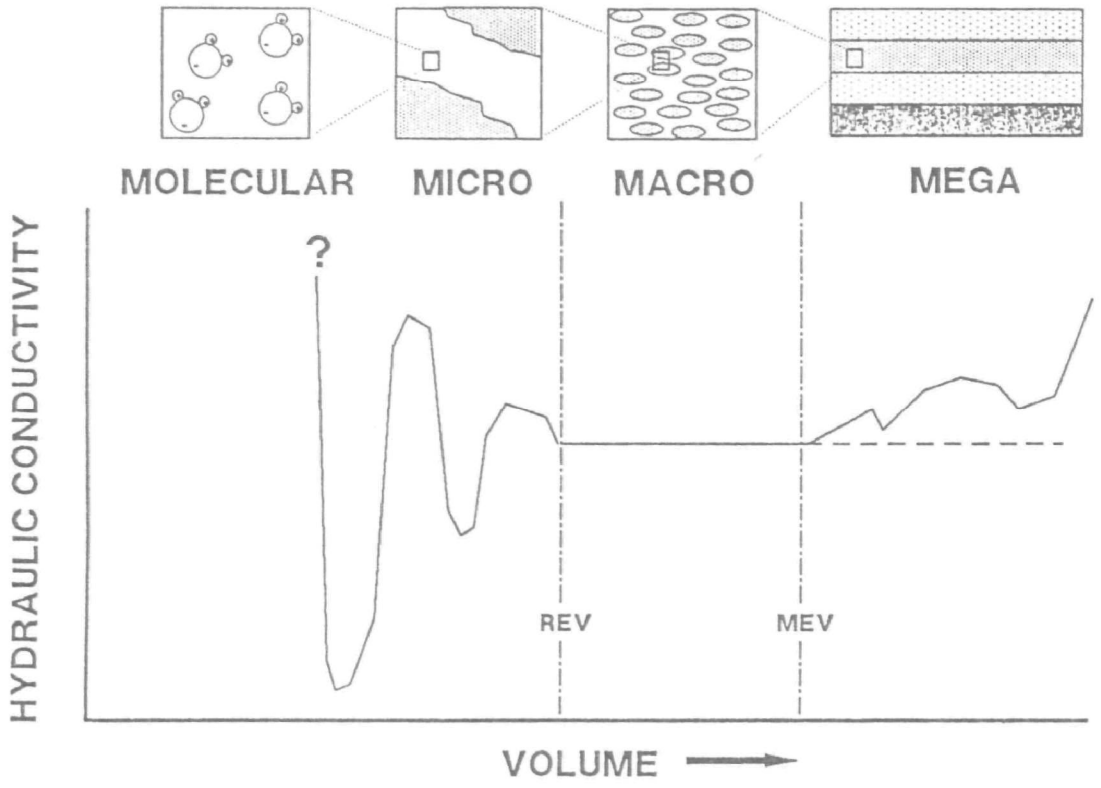

BREAKTHROUGH CURVE
RELATIVE CONCENTRATION
1.0
0.5
0.0
PLUG FLOW
ADVECTION
ACTION LIMIT
$t_{0.1}$
$t_{0.5}$
TIME

CDP-1 - 3

WHY SHOULD WE BE INTERESTED IN DISPERSION?

- Prediction of arrival of an action limit for a contaminant
- Estimation of the costs for aquifer remediation
- Development of aquifer remediation strategies

CDP-1 - 4



After Gillham and Cherry (1982).

CDP-1 - 5

ADVECTION–DISPERSION EQUATION

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

Dispersive Term	Advective Term	Change in Mass per Unit Time

CDP-1 - 6

DISPERSION COEFFICIENT

$$D = D_d + D_m$$

Dispersion Coefficient	Moleculuar Diffusion Coefficient	Mechanical Diffusion Coefficient

CDP-1 - 7

MECHANICAL DISPERSION COEFFICIENT

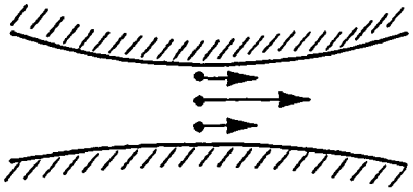
$$D_m = \alpha v$$

Mechanical Dispersion Coefficient	Dispersivity Parameter	Groundwater Velocity

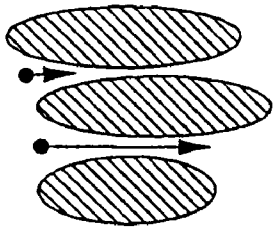
CDP-1 - 8

MECHANICAL DISPERSION

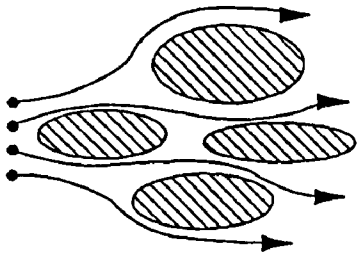
A



B



C

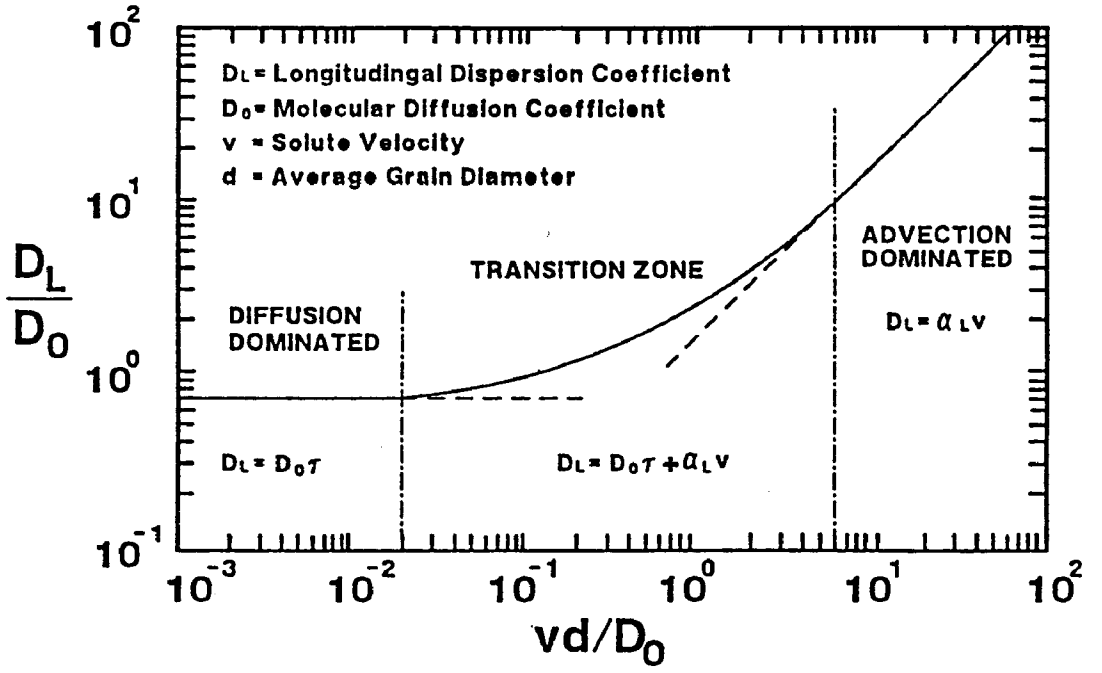


After Gillham and Cherry (1982).

MOLECULAR DIFFUSION COEFFICIENT

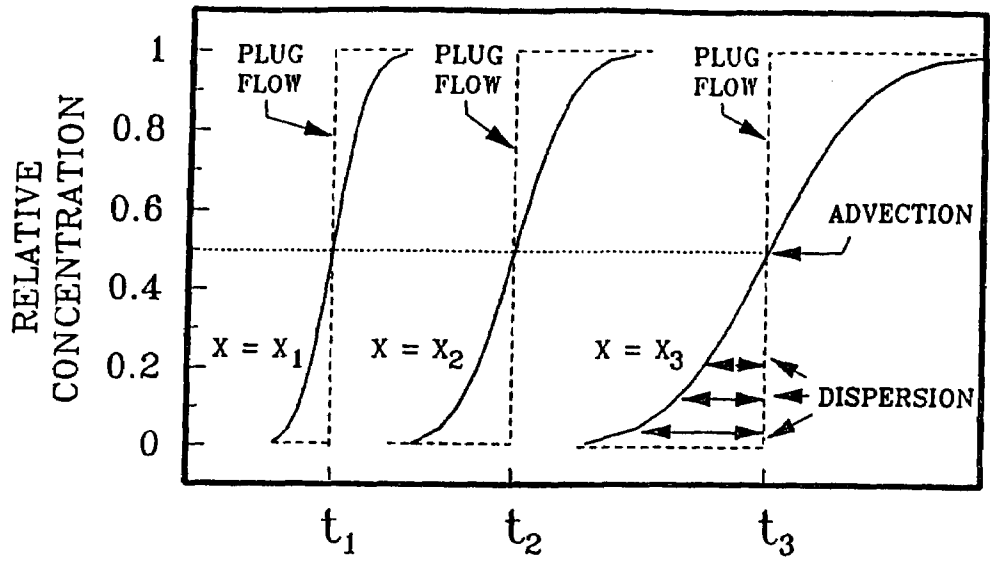
$$D_d = D_0 \tau$$

- D_d: Molecular Diffusion Coefficient
- D_0: Free Solution Diffusion Coefficient
- τ: Tortuosity Factor



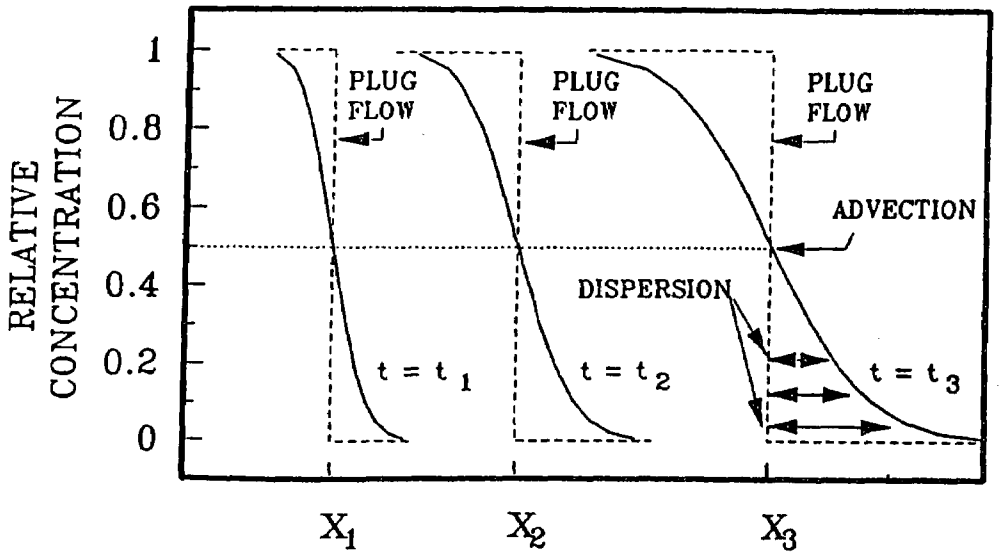
After Perkins and Johnston, 1963.

BREAKTHROUGH CURVE



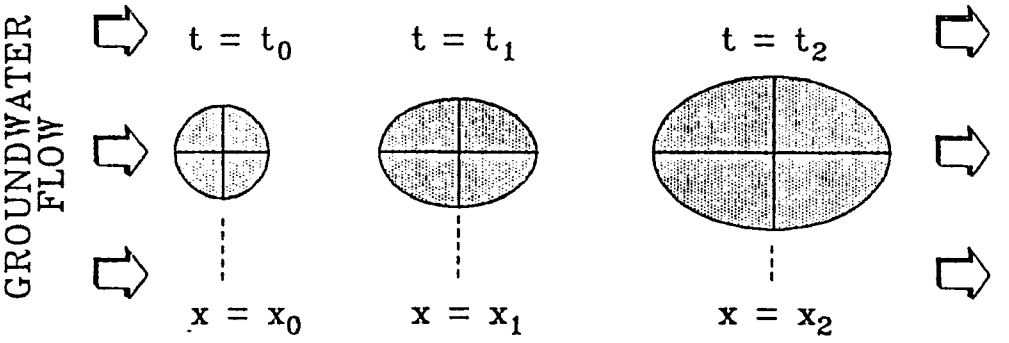
CDP-1 -12

CONCENTRATION DISTRIBUTION



CDP-1 -13

ADVECTION AND DISPERSION OF A CONTAMINANT SLUG



ADVECTION–DISPERSION EQUATION

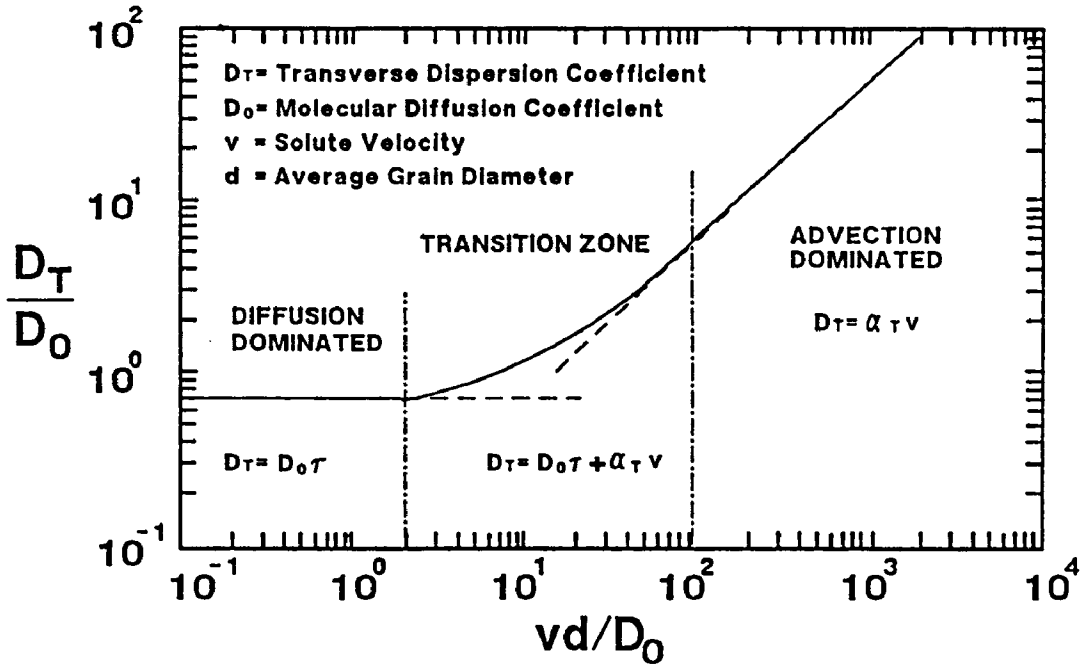
$$\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial (Cv_i)}{\partial x_i} = \frac{\partial C}{\partial t}$$

Dispersive Term	Advective Term	Change in Mass per Unit Time

$$D_{ii} = \alpha_L \frac{V_i^2}{\bar{V}} + \alpha_T \frac{V_j^2}{\bar{V}} + D_d$$

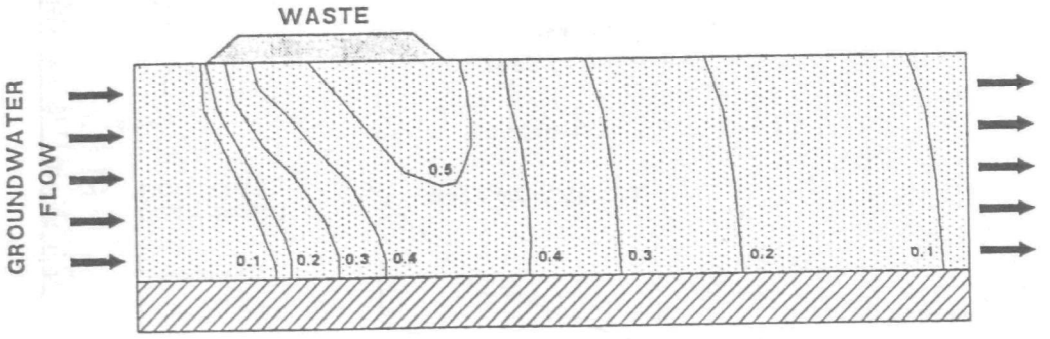
$$D_{ij} = D_{ji} = (\alpha_L - \alpha_T)\frac{V_i V_j}{\bar{V}}$$

$$\bar{V} = \sum_i (v_i^2)^{1/2}$$



After Perkins and Johnston (1963).

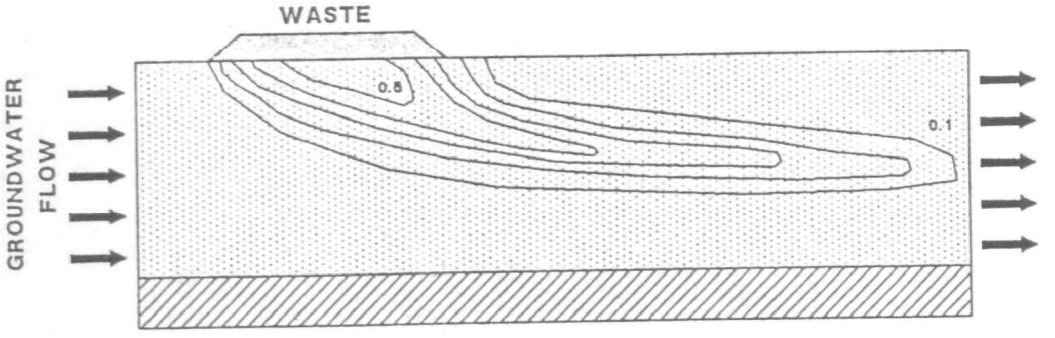
HYPOTHETICAL CONTAMINANT PLUME WITH A LARGE TRANSVERSE DISPERSIVITY



After Frind and Palmer (1980).

CDP-1 -17

HYPOTHETICAL CONTAMINANT PLUME WITH A SMALL TRANSVERSE DISPERSIVITY



CDP-1 -18

DISCREPANCIES BETWEEN THEORY AND EXPERIMENTAL RESULTS FROM LABORATORY EXPERIMENTS ARE THE RESULT OF:

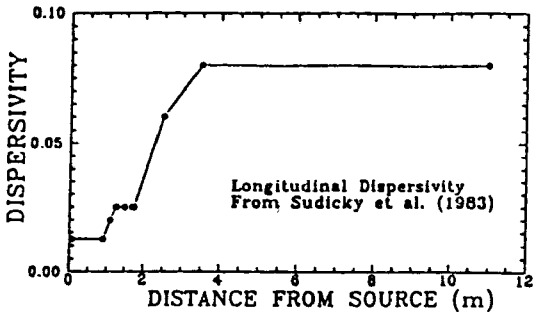
- Immobile Zones of Water
- Solution-Solid Interface Processes
- Anion Exclusion
- Diffusion in or out of Aggregates

LONGITUDINAL DISPERSITY VALUES

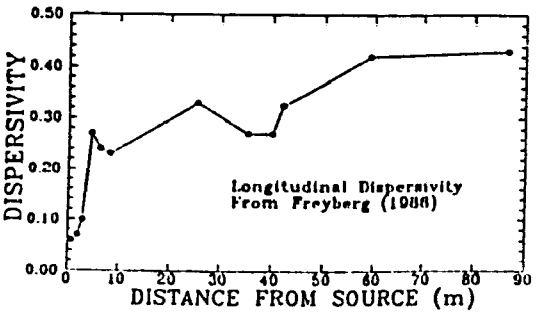
LABORATORY TESTS	0.0001 to 0.01 M
NATURAL GRADIENT TRACER TESTS	0.01 to 2 m
SINGLE WELL TESTS	0.03 to 0.3 m
RADIAL AND TWO-WELL TESTS	0.5 to 15 m
MODEL CALIBRATION TO CONTAMINANT PLUMES	3 to 61 m

After Gillham and Cherry (1982).

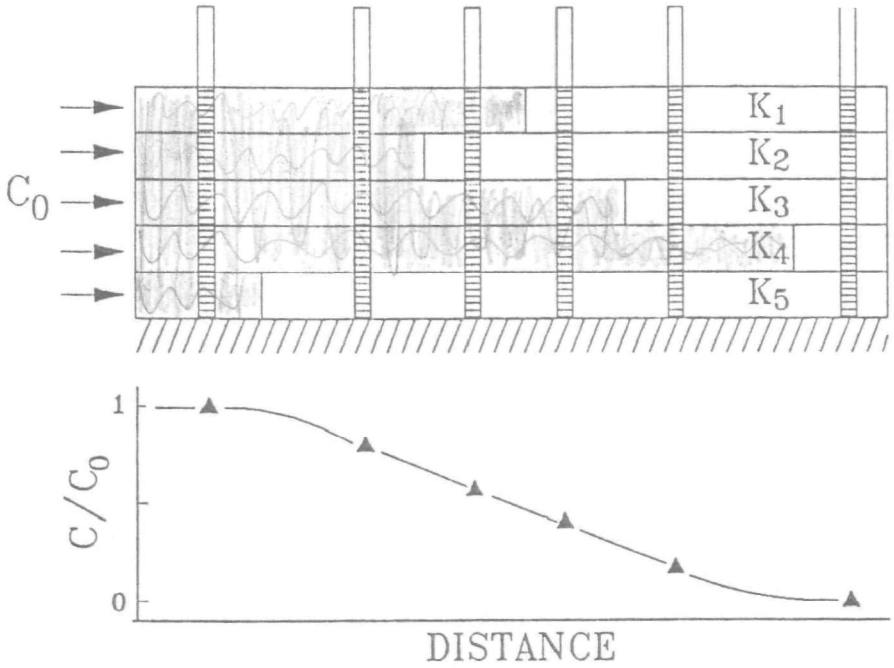
CDP-1 -20



CDP-1 -21

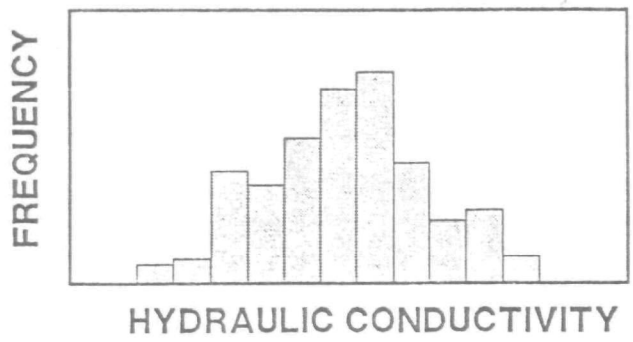


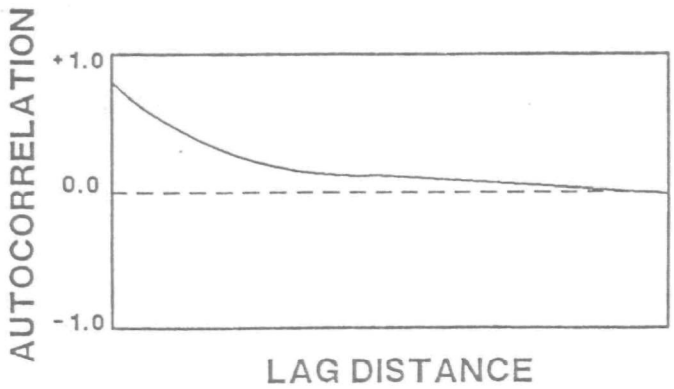
CDP-1 -22



After Gillham and Cherry (1982).

STATISTICAL INFORMATION THAT CAN BE OBTAINED





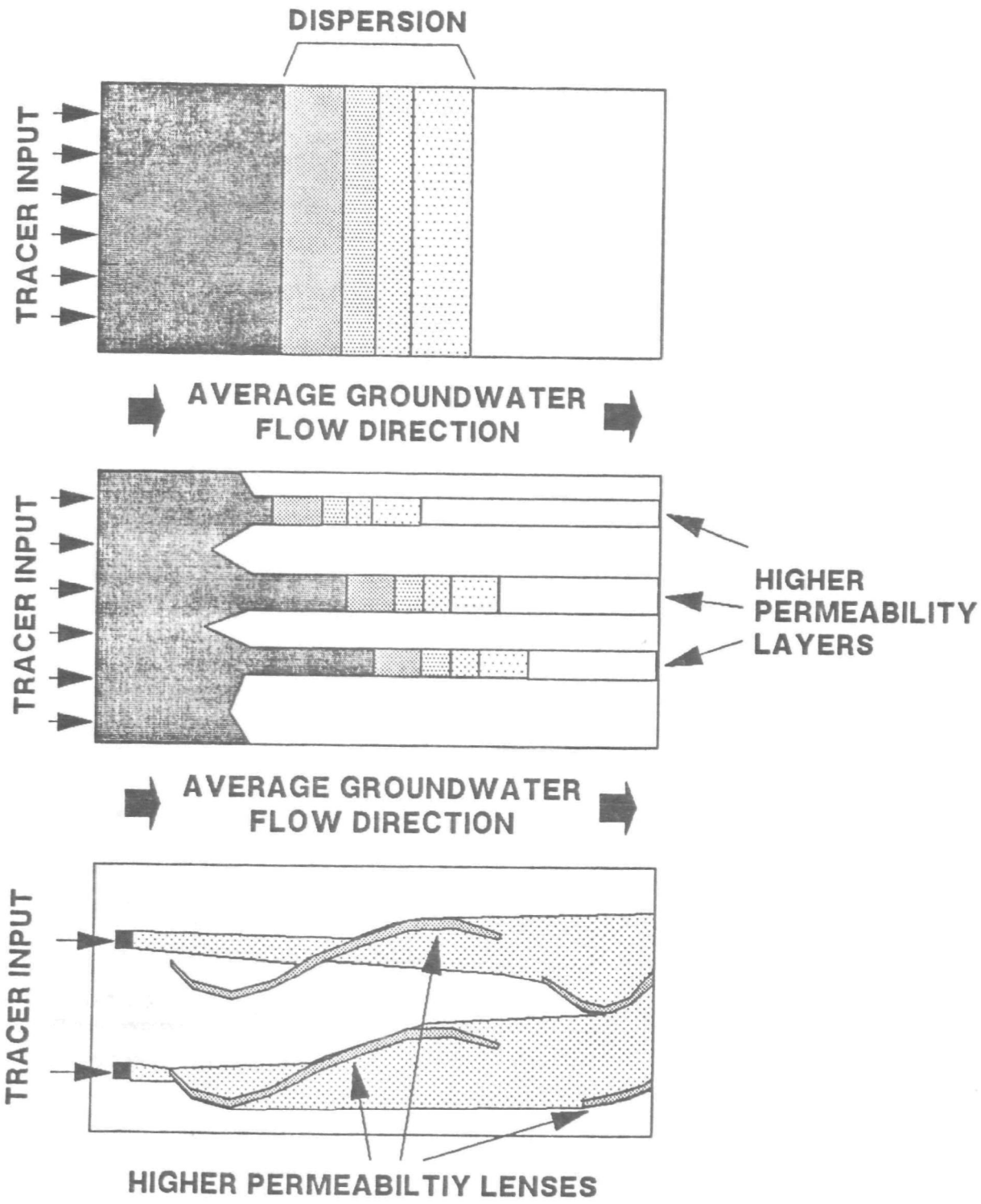
ASYMPTOTIC DISPERSIVITY TENSOR

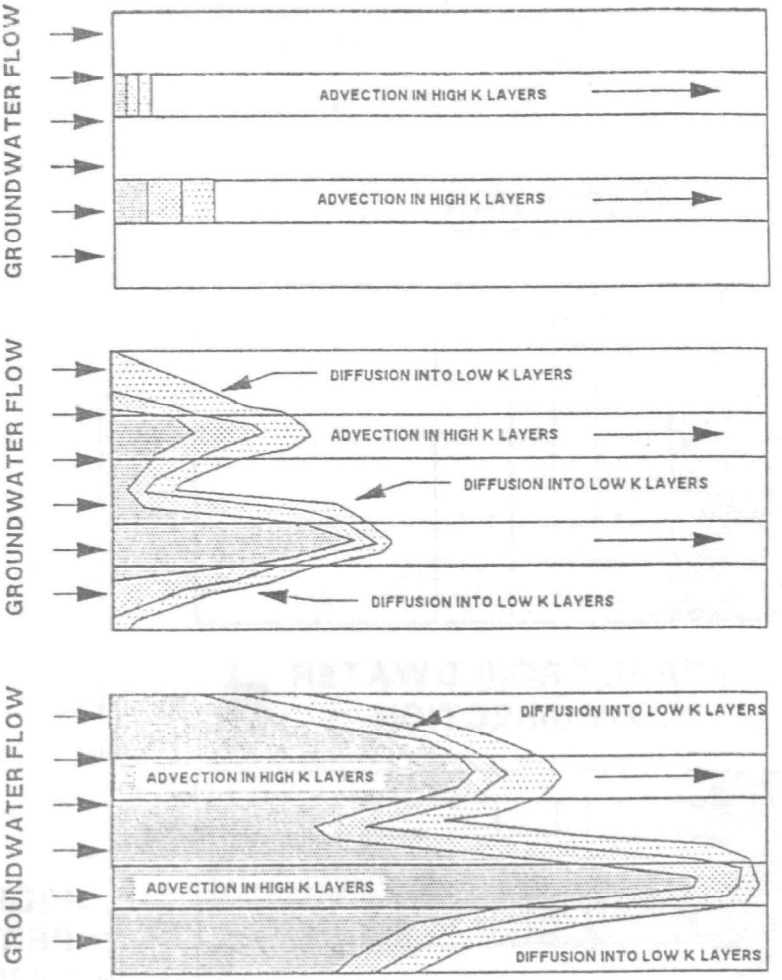
$$\begin{bmatrix} 0.61\ \text{m} & & \sim 0 \\ & \sim 0 & \\ \sim 0 & & \sim 0 \end{bmatrix}$$

BORDEN AQUIFER
SUDICKY (1986)

TRANSPORT CONCEPTS

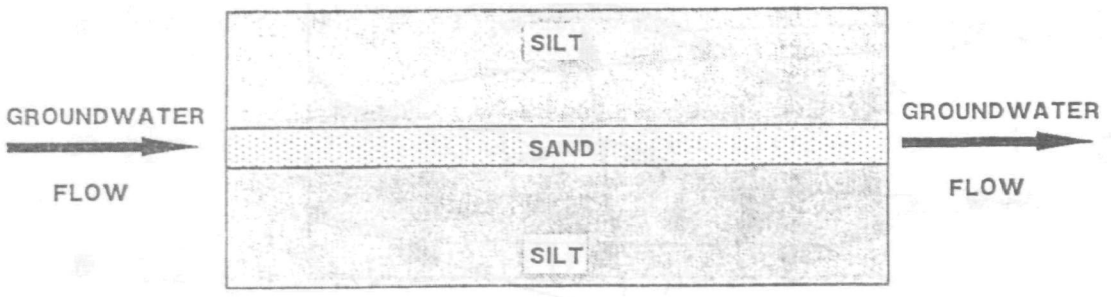
- Homogeneous Media
- Heterogeneous Advection
- Advection–Diffusion


DISPERSION
TRACER INPUT
AVERAGE GROUNDWATER FLOW DIRECTION
TRACER INPUT
HIGHER PERMEABILITY LAYERS
AVERAGE GROUNDWATER FLOW DIRECTION
TRACER INPUT
HIGHER PERMEABILTIY LENSES



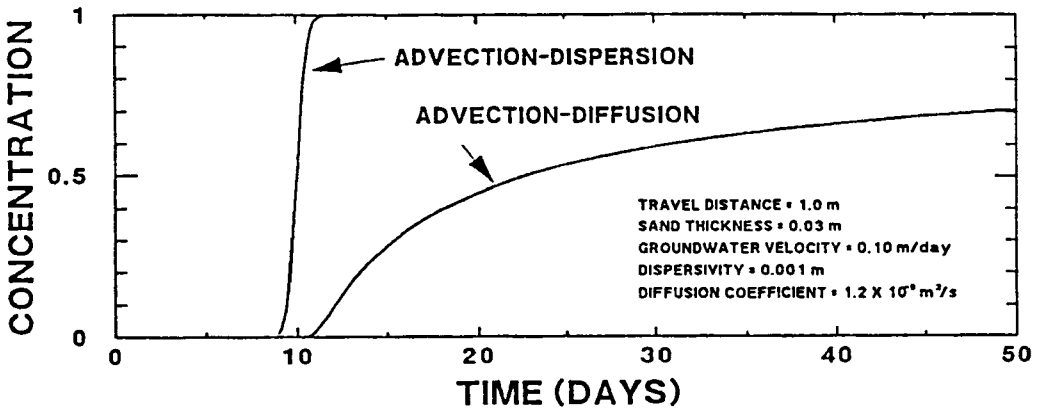
After Gillham et al. (1984).

CDP-1 -28



CDP-1 -29

BREAKTHROUGH CURVES SHOWING EFFECT OF TRANSVERSE DIFFUSION



FACTORS CONTRIBUTING TO THE SPREADING OF CONTAMINANTS

- Diverging Flow Lines
- Three Dimensional Flow
- Variable Source Function
- Temporal Variations in Watertable
- Heterogeneity

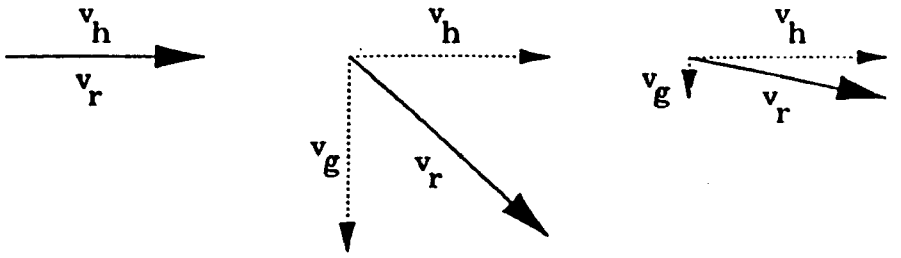
DENSITY COMPONENT OF FLOW

$$v_g = -K_{zz}\left[(\rho/\rho_0)-1\right]/n$$

Velocity Component Due to Gravity	Vertical Hydraulic Conductiviity	Density	Back-Ground Density	Porosity

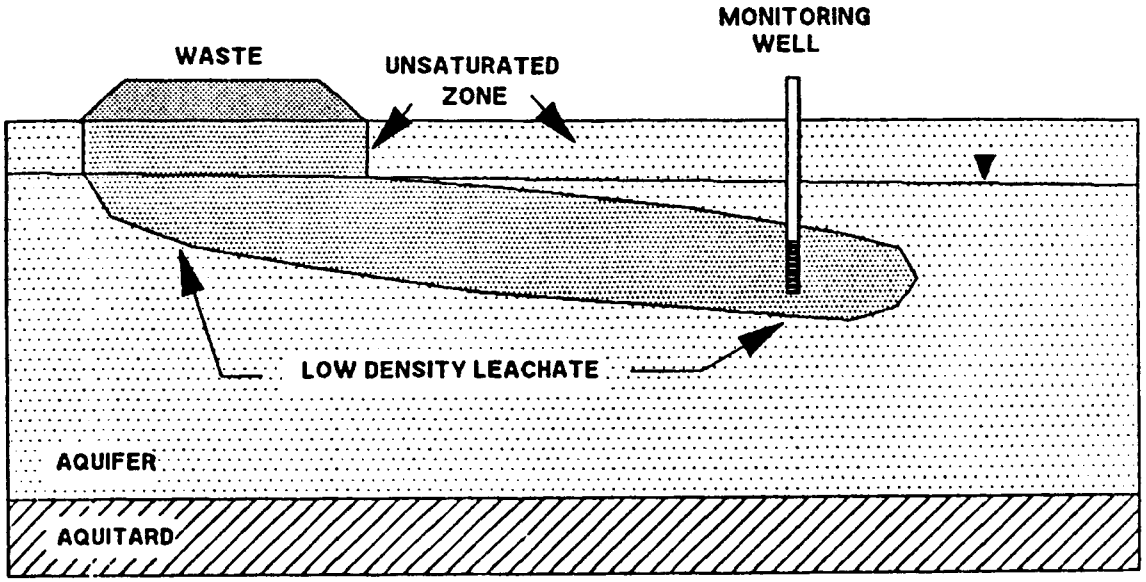
EFFECT OF DENSITY

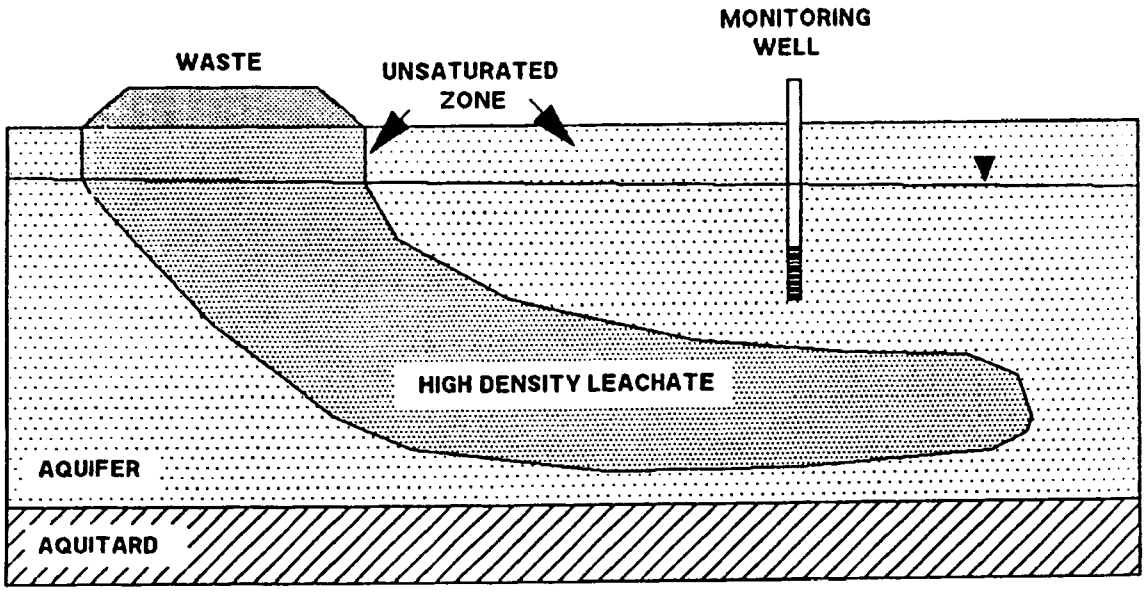
DENSITY OF UNCONTAMINATED WATER = 1.000
NATURAL HOIZONTAL GRADIENT = 0.005
NATURAL VERTICAL GRADIENT = 0.000



DENSITY = 1.000	DENSITY = 1.005	DENSITY = 1.005
$K_h/K_v = 1$	$K_h/K_v = 1$	$K_h/K_v = 5$

DENSITY DEPENDENT TRANSPORT AND MONITORING



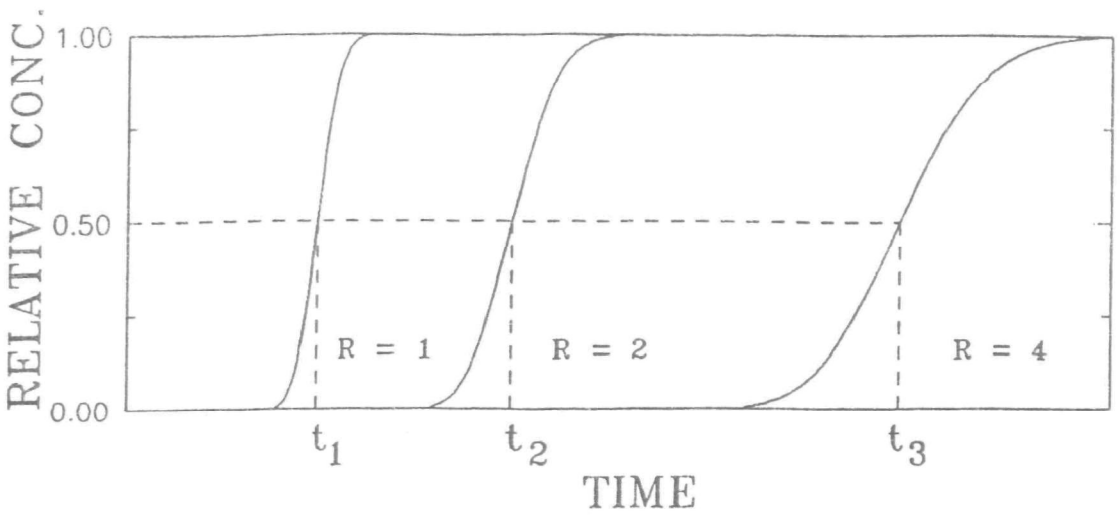


ADVECTION–DISPERSION EQUATION WITH RETARDATION

$$\frac{D}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v}{R}\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$

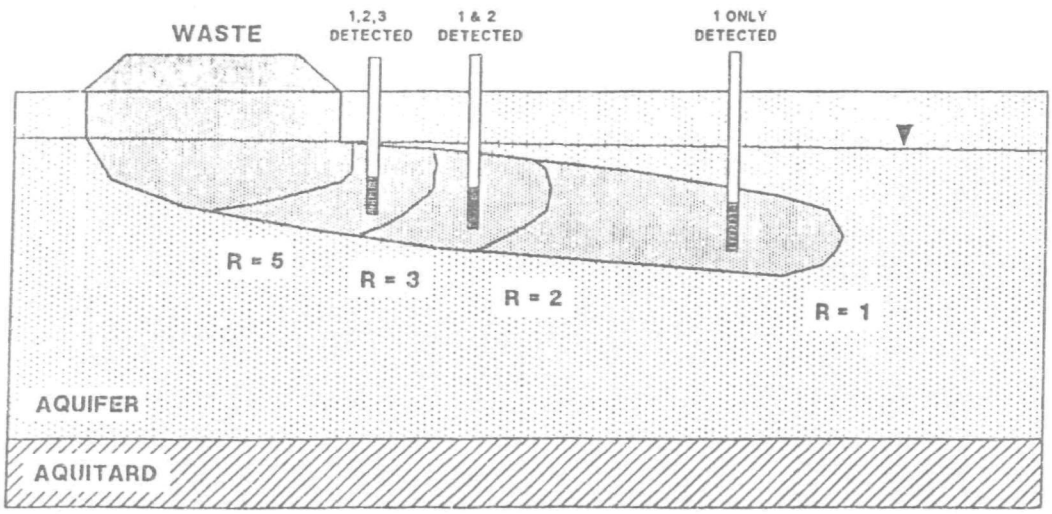
Dispersive Term	Advective Term	Change in Mass per Unit Time

R = RETARDATION FACTOR



CDP-1 -36

RETARDATION AND MONITORING



CDP-1 -37

IMPORTANCE OF THE UNSATURATED ZONE

- Increases overall length of flow path
- Can have greater sorption capacity than saturated zone and can thus act as a source of contamination even after site surface is cleaned
- Can be an zone of significant biodegradation
- Can be a source of metal ions
- It is a pathway for the transport of gases and volatile organics

UNSATURATED FLOW

$$C(\psi)\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial z}\left[K(\psi)\frac{\partial \psi}{\partial z} \right] + \frac{\partial}{\partial z}[K(\psi)]$$

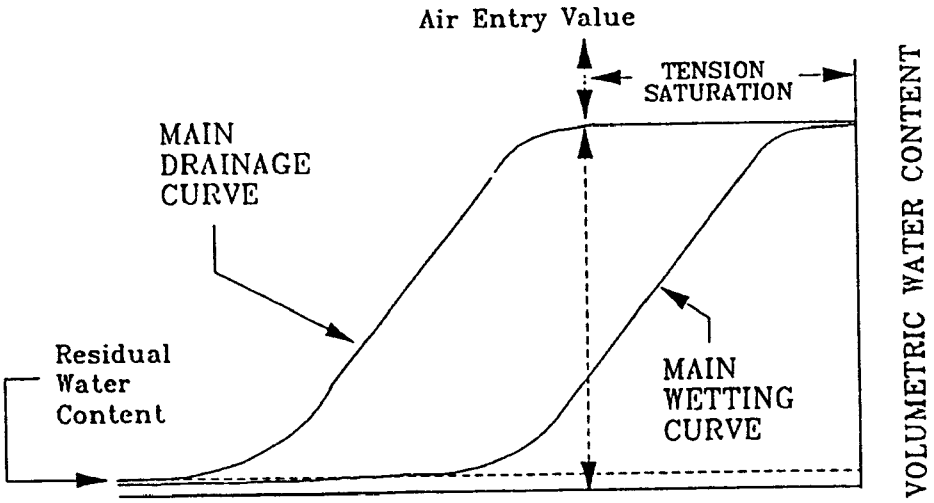
$c(\psi) = \frac{\partial \theta}{\partial \psi}$ = Specific Water Capacity

θ = Volumetric Water Content

ψ = Soil Water Pressure Head

$K(\psi)$ = Hydraulic Conductivity

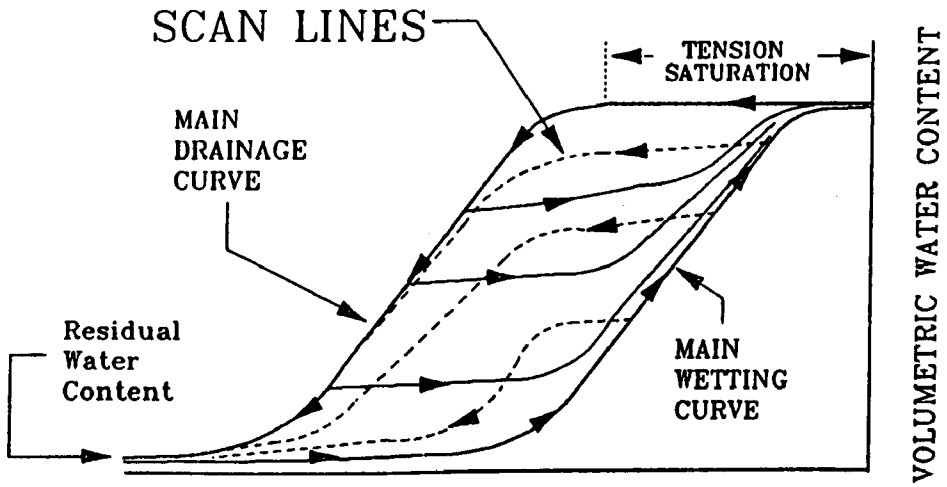
CHARACTERISTIC CURVE

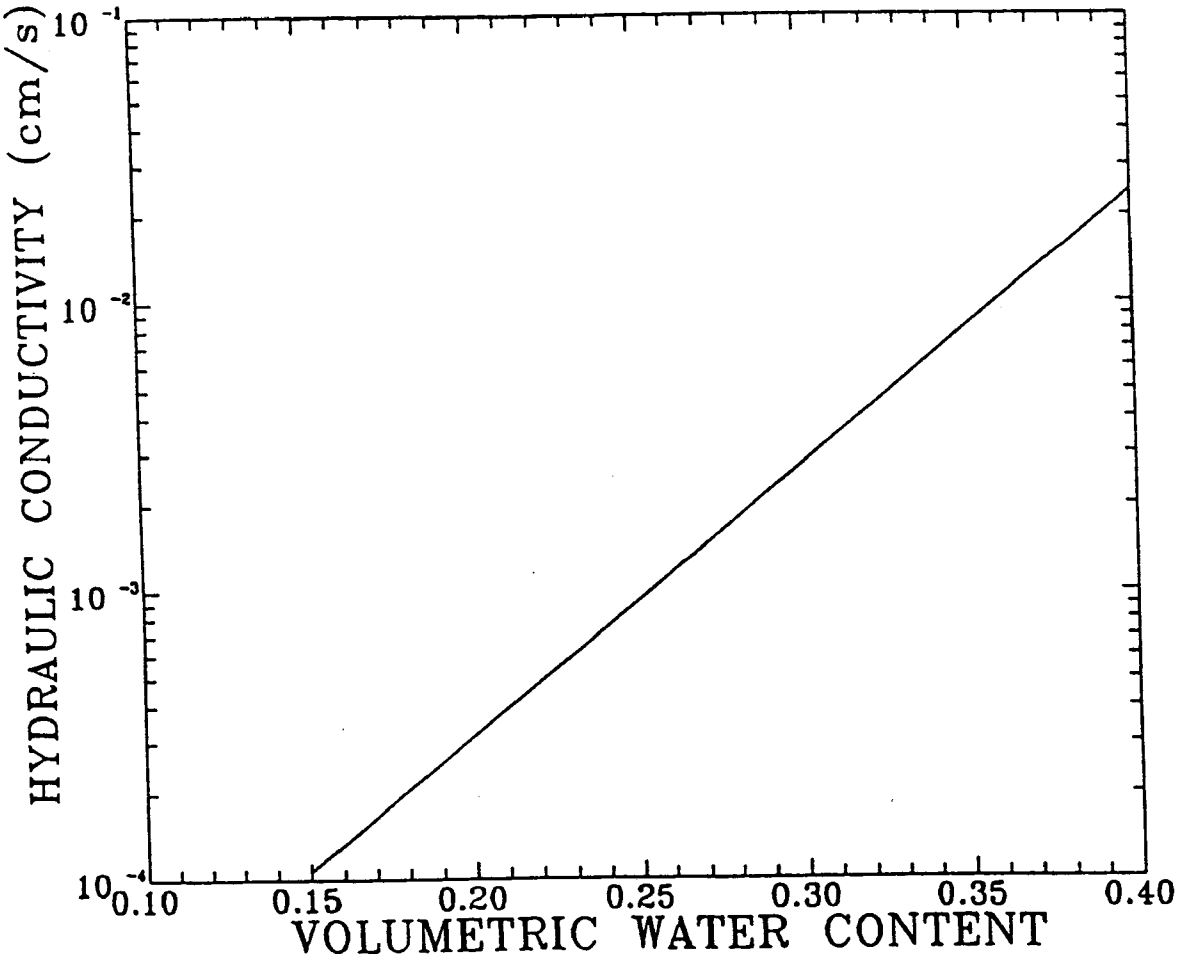


HYSTERESIS

Refers to the observation that the soil water pressure head is not a unique function of volumetric water content but depends on the moisture history of the soil.

CHARACTERISTIC CURVE




HYDRAULIC CONDUCTIVITY (cm/s)
10 -1
10 -2
10 -3
10 -4
0.10
0.15
0.20
0.25
0.30
0.35
0.40
VOLUMETRIC WATER CONTENT

UNSATURATED ZONE TRANSPORT EQUATION

$$\frac{\partial(\theta c)}{\partial t} = \frac{\partial}{\partial z}\left[\theta D \frac{\partial c}{\partial z}\right] - \frac{\partial(qc)}{\partial z}$$

θ = Volumetric Water Content

c = Solute Concentration

D = Dispersion Coefficient

q = Volumetric Water Flux

UNSATURATED ZONE DISPERSION COEFFICIENT

$$D = D_0 \tau + \alpha v(\theta)$$

D = Dispersion Coefficient

D_0 = Free Solution Diffusion Coefficient

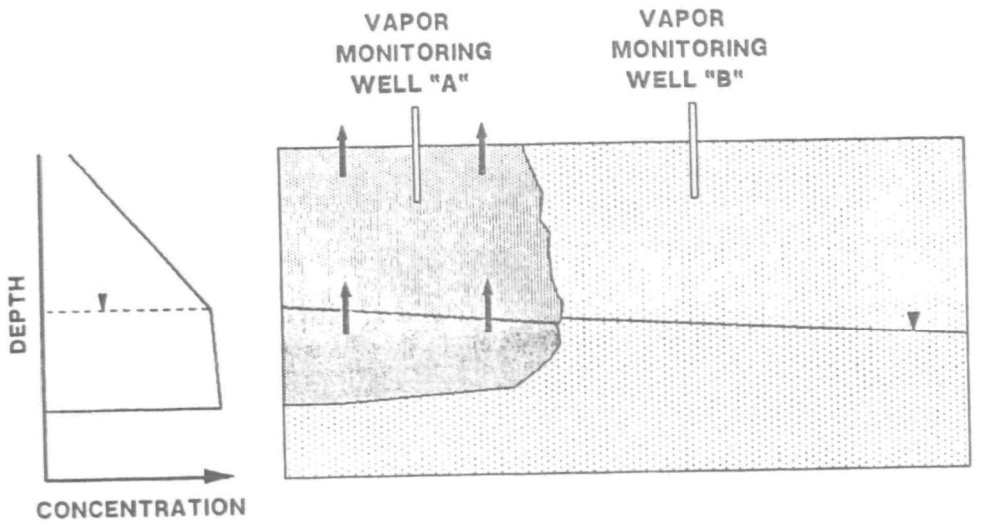
τ = Tortuosity Factor

α = Dispersivity

$v(\theta) = q/\theta$ = solute velocity

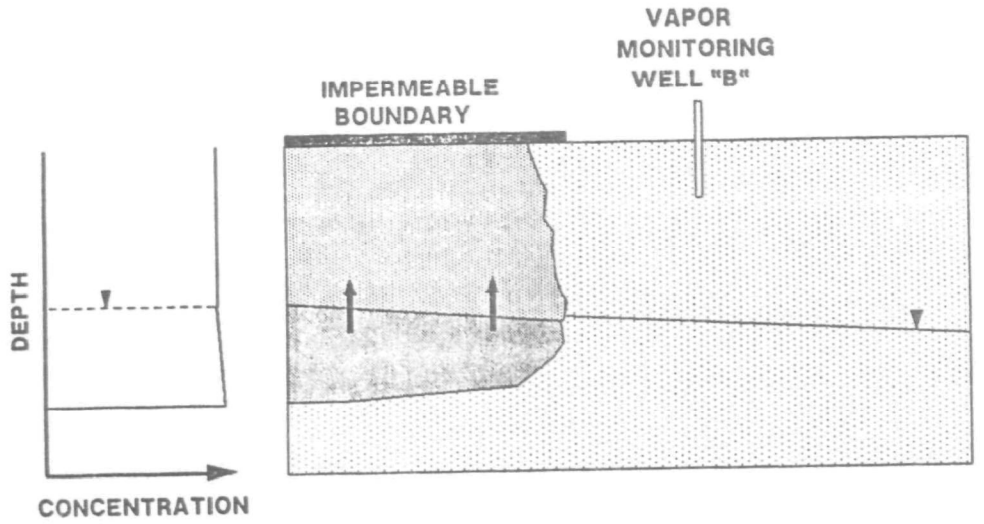
θ = Volumetric Water Content

VAPOR TRANSPORT



CDP-1 -46

VAPOR TRANSPORT

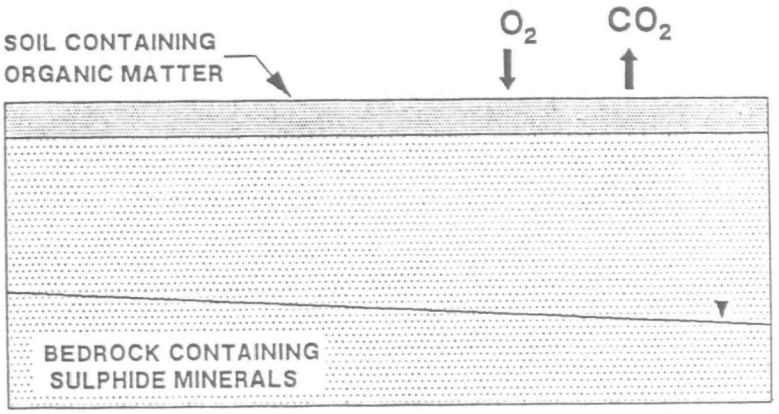


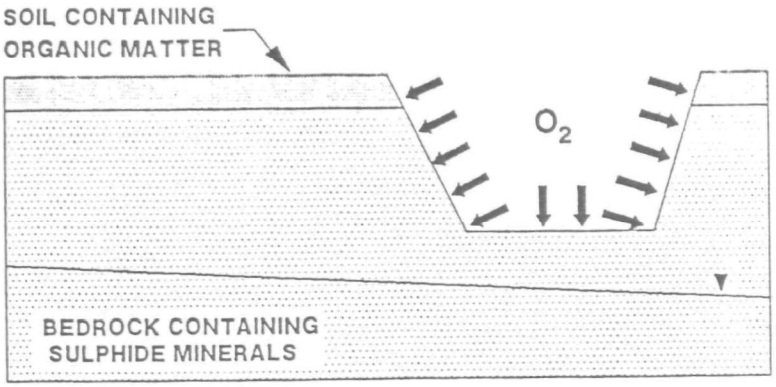
CDP-1 -47

FACTORS AFFECTING VAPOR TRANSPORT

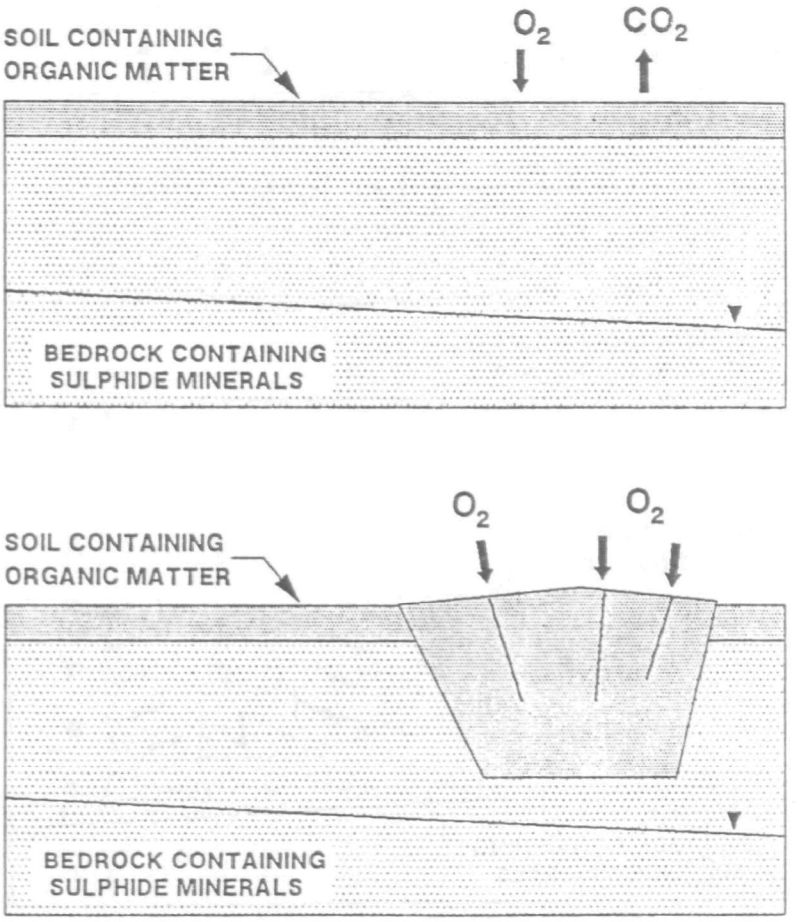
- Diffusion
- Advection
- Density
- Cultural Features
- Partitioning into Soil Water
- Thermal Effects
- Chemical Reactions

TRANSPORT OF GASES





TRANSPORT OF GASES

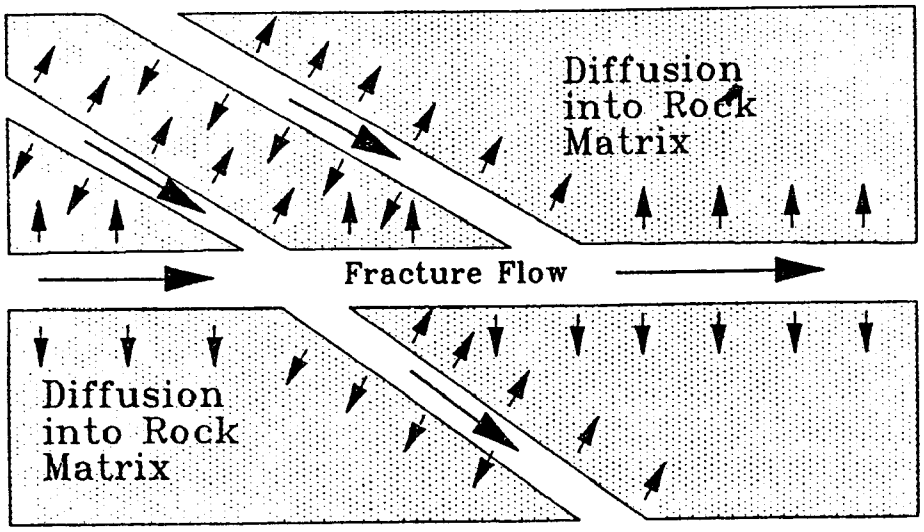


TRANSPORT PROCESSES IN FRACTURED GEOLOGIC MEDIA

- Advection
- Diffusion
- Dispersion

CDP-1 -51

FRACTURED POROUS ROCK



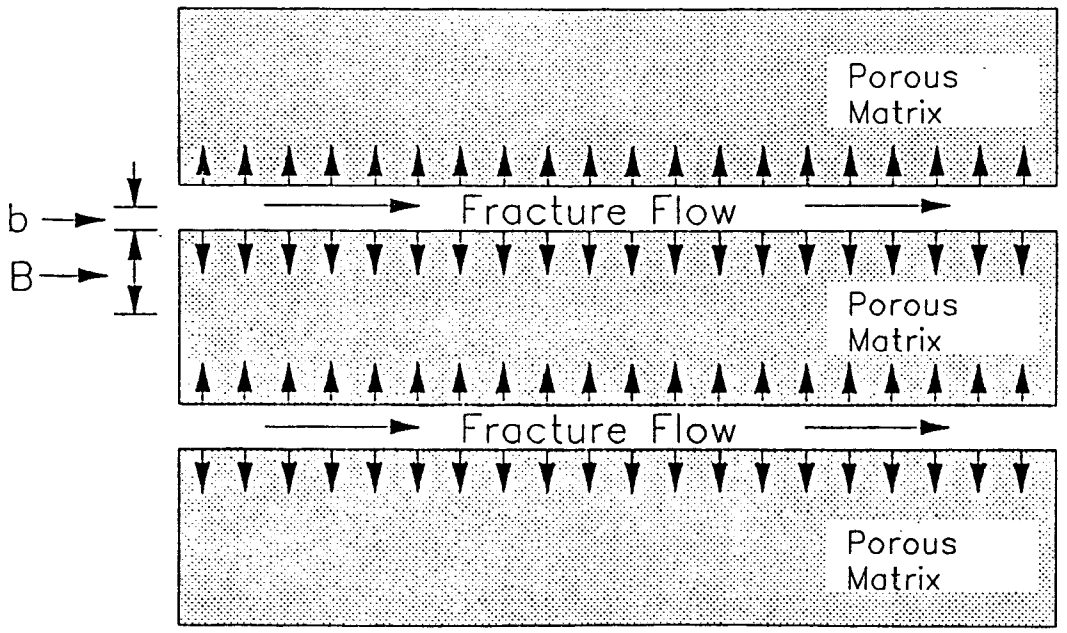
CDP-1 -52

DISPERSION PROCESSES IN FRACTURED GEOLOGIC MEDIA

- Velocity Distributions
- Mixing at Fracture Intersections
- Variation in Aperature Width along Stream Line
- Distribution in Aperature Width across Flow Path
- Diffusion

MODELS FOR TRANSPORT IN FRACTURED ROCK

- **CONTINUUM MODELS**
  - Single Porosity
  - Double Porosity
- **DISCREET FRACTURE MODELS**
  - Deterministic
  - Stochastic
- **HYBRID MODELS**
- **CHANNEL MODELS**



CUBIC LAW

FRACTURE:

$$K = (2b)^3 \rho g/(12\mu)$$

EQUIVALENT POROUS MEDIA

$$K = (2b)^3 \rho gN/(12B\mu)$$

N = number of fractures over B
K = hydraulic conductivity
B = thickness of formation
b = half-width of fracture
μ = fluid viscosity
ρ = fluid density

EQUIVALENT POROUS MEDIA

$$v_{EPM} = v_f/R_f$$

$$R_f = 1 + nB/b$$

FRACTURE NETWORKS BEHAVE LIKE CONTINUA WHEN:

- FRACTURE DENSITY IS INCREASED
- APERTURES ARE CONSTANT RATHER THAN DISTRIBUTED
- ORIENTATIONS ARE DISTRIBUTED RATHER THAN CONSTANT
- LARGER SAMPLE SIZES ARE TESTED

(J. LONG, 1982)

DIFFUSION

Fick's Law:

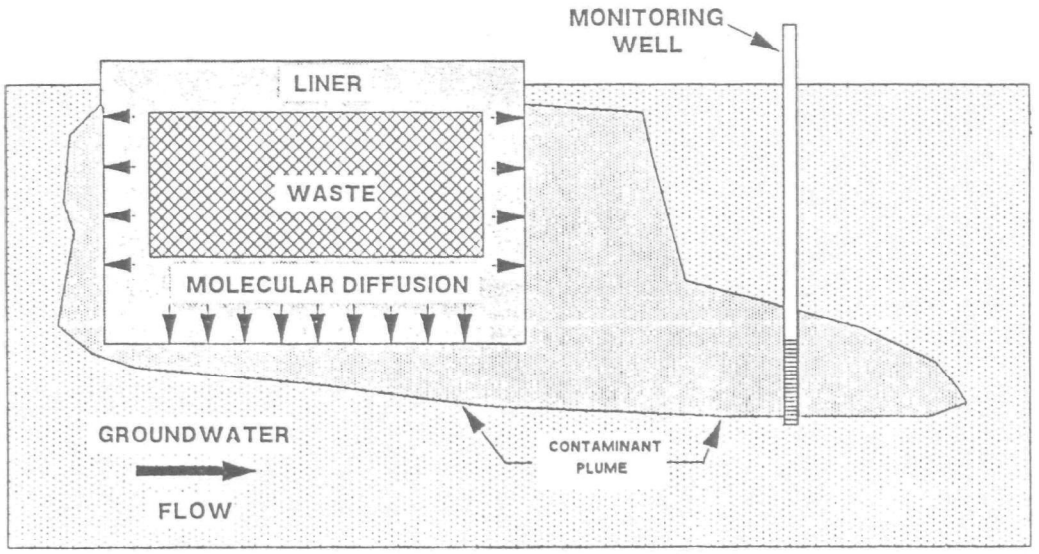
$$J_d = -nD_d \frac{\partial C}{\partial x}$$

$$\frac{\partial C}{\partial t} = nD_d \frac{\partial^2 C}{\partial x^2}$$

IMPORTANCE OF MOLECULAR DIFFUSION

- Heterogeneous Porous Media
- Fractured Media
- Vapor Phase Transport
- Low Permeability Formations
- Barriers and Liners
- Residual NAPLs

DOES DETECTION OF CONTAMINANTS INDICATE "FAILURE" OF LINER?



NON-AQUEOUS PHASE LIQUIDS

(NAPLs)

- Light NAPLs (LNAPLs)
- Dense NAPLs (DNAPLs)

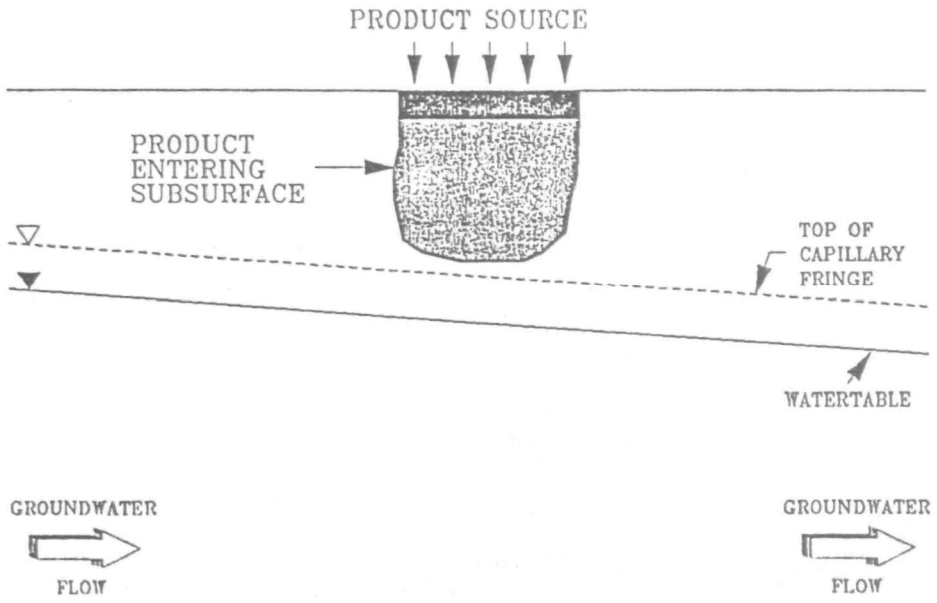
CDP-1 -62

LNAPLs

- Gasoline
- Heating Oil
- Kerosene
- Jet Fuel
- Aviation Gas

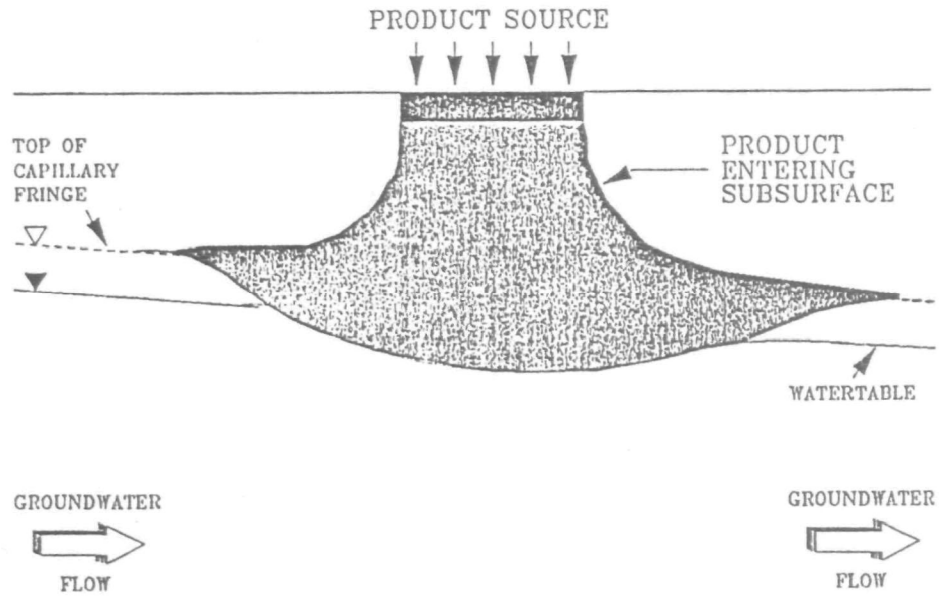
CDP-1 -63

LNAPLs



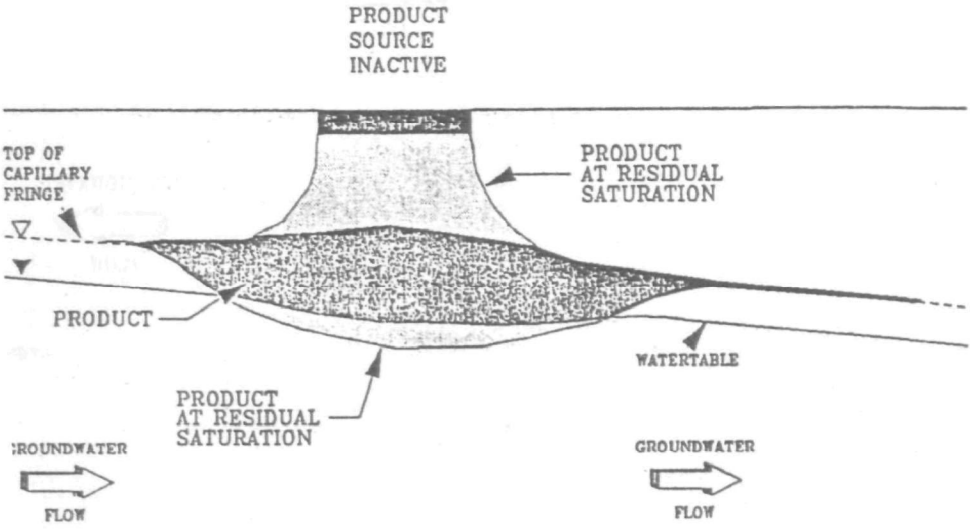
CDP-1 -64

LNAPLs



CDP-1 -65

LNAPLs



CDP-1 -66

DNAPLs

- 1,1,1 – Trichloroethane
- Carbon Tetrachloride
- Pentachlorophenols
- Dichlorobenzes
- Tetrachloroethylene
- Creosote

DNAPLs

Identified at

4 of top 5

and

10 of top 20

Hazardous Waste Sites

(Plumb and Pitchford, 1985)

DNAPLs

MAGNITUDE OF PROBLEM

7 L (10 kg) of TCE can contaminate 10^8 L of groundwater at 100 pbb

CDP-1 -69

DNAPLs

MOBILITY CAN BE GREAT

- Low Solubility
- High Density
- Low Viscosity

CDP-1 -70

DNAPLs

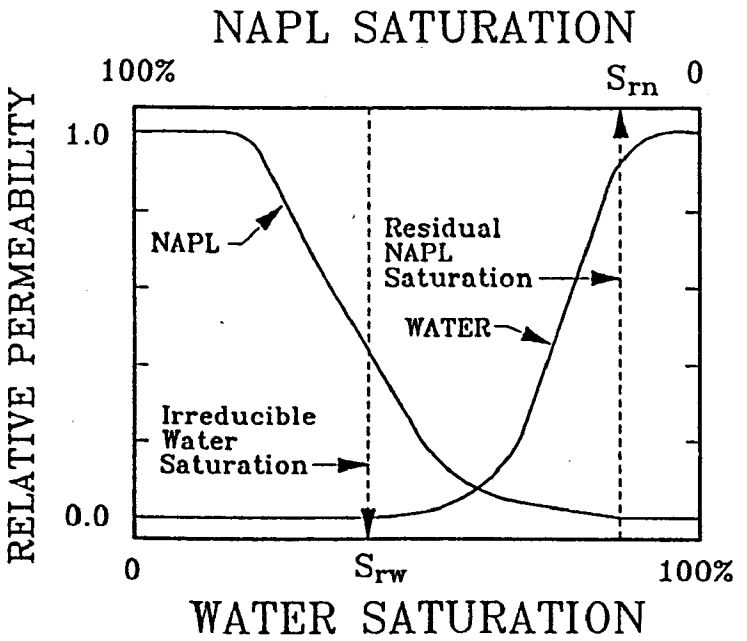
PRIMARY FACTORS THAT CONTROL MIGRATION

- Type of Solvent
- Volume Released
- Rate of Release
- Area of Infiltration

RELATIVE PERMEABILITY

$$k_r = k(S_n)/k_s$$

k_r = relative permeability
$k(S_n)$ = permeability at S_n
S_n = NAPL saturation
k_s = permeability at 100% saturation



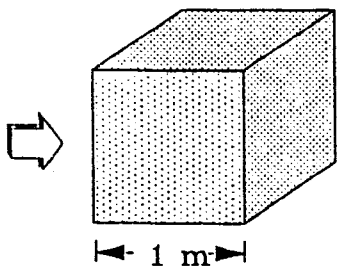
DNAPLs

DNAPLs will not be Mobile when DNAPL content is less than the Residual Saturation

CDP-1 -74

Natural Groundwater Flux Rate = 10 cm/day

Effective Groundwater Flux Rate = 1.7 cm/day



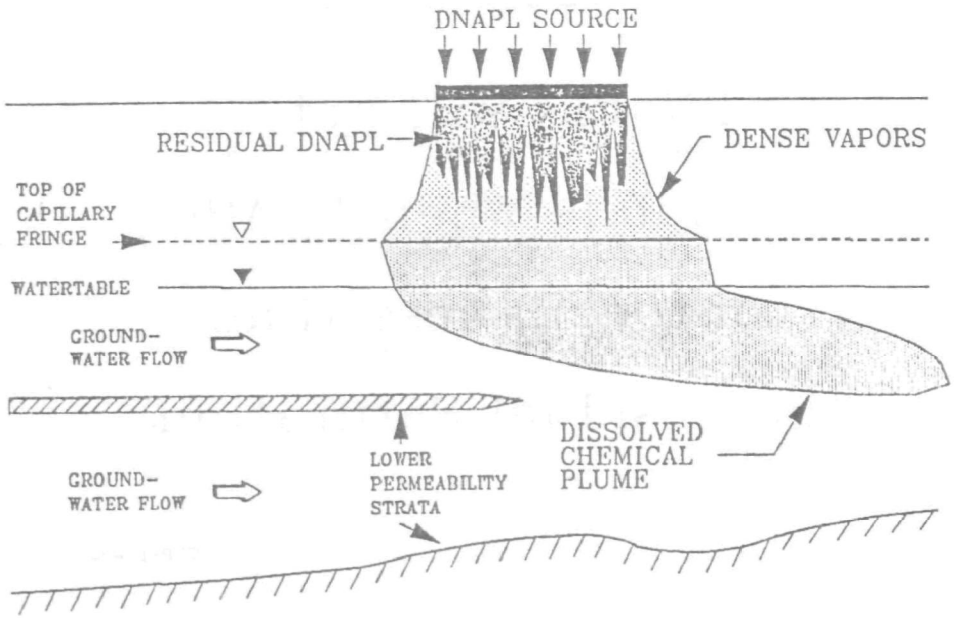
Groundwater Saturated with TCE

Residual Saturation = 20%
Porosity = 0.35
Volume of TCE = 0.07 cubic meters
Mass of TCE = 103 kg
Solubility of TCE = 1100 mg/l

TIME REQUIRED TO REMOVE TCE BY DISSOLUTION	=	15.4 YEARS/m

CDP-1 -75

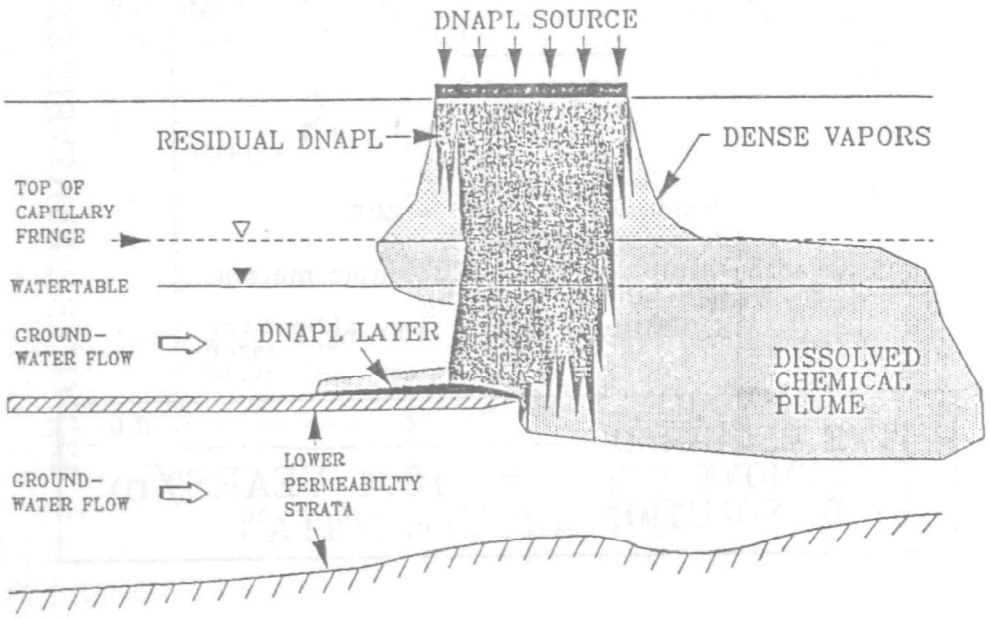
DNAPLs



CDP-1 -76

After Feenstra and Cherry, (1987).

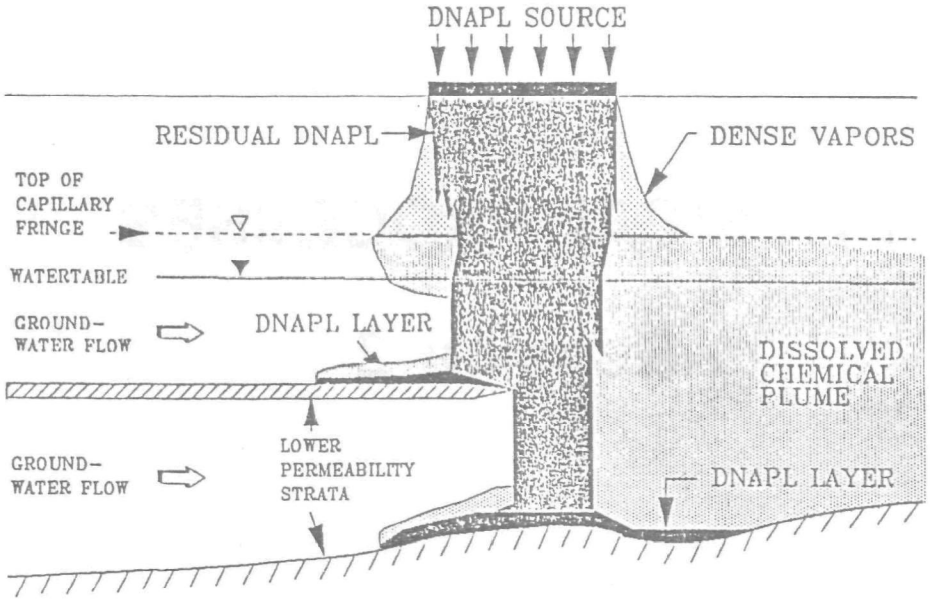
DNAPLs



CDP-1 -77

After Feenstra and Cherry (1987).

DNAPLs



CDP-1 -78

After Feenstra and Cherry (1987).

TRANSPORT AND FATE

PHYSICAL PROCESSES

Session 2

Carl D. Palmer

(Oregon Graduate Center)

PARTICLE TRANSPORT THROUGH POROUS MEDIA

A potential mechanism for the rapid movement of contaminants in the subsurface.

"Facilitated Transport"

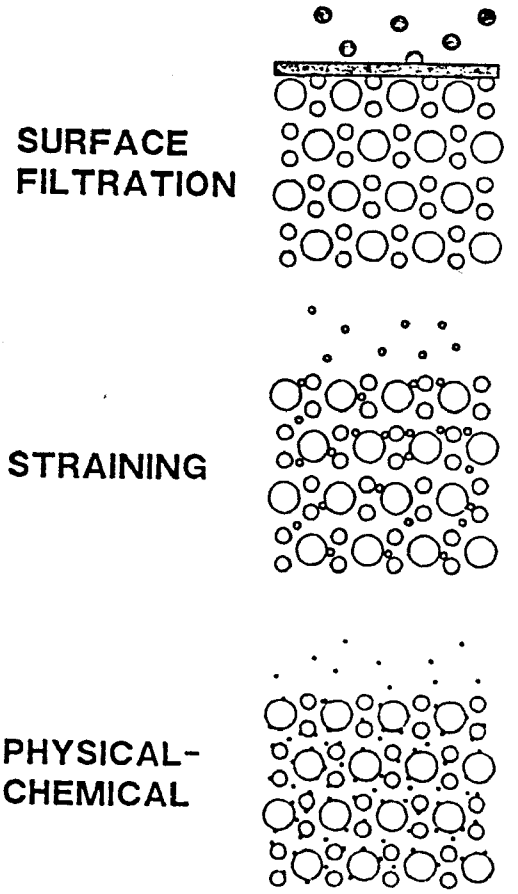
TYPES OF PARTICLES

- Bacteria and Viruses
- Natural Organic Matter
- Inorganic Precipitates
- Asbestos Fibers
- Clay

FILTRATION MECHANISMS

- Surface Filtration
- Straining
- Physical–Chemical

FILTRATION MECHANISMS



After McDowell-Boyer et al. (1986).

MECHANISMS CONTROLLING THE TRANSPORT OF MICROORGANISMS

- Straining
- Adsorption
- Sedimentation
- Interception
- Diffusion
- Chemotaxis
- Die–Off
- Growth

LABORATORY METHODS

- Grain–Size Analysis
- Permeameter
- Consolidation Tests
- Triaxial Cells
- Porosity
- Bulk Density
- Water Content
- Mineralogy

GRAIN-SIZE ANALYSIS

1. METHODS

- Seive
- Hydrometer
- Settling Tube
- Light Scattering Techniques

GRAIN-SIZE ANALYSIS

2. RESULTS

- Estimate of Local Hydraulic Conductivity
  - Masch and Denny (1966)
  - Hazen
  - Grain-Size/Porosity Methods
- Estimate Proper Monitoring Well Slot-Size

PERMEAMETER TESTS

1. METHODS

- Steady Flow
- Transient Flow

2. Results

- Hydraulic Conductivity

TRIAXIAL CELL TESTS
CONSOLIDATION TESTS

RESULTS

- Hydraulic Conductivity
- Specific Storage
- Coefficient of Compressibility

SOILS TESTS

- Porosity
- Bulk Density
- Water Content

FIELD METHODS

- Slug Tests
- Aquifer Tests
- Interference Pumping Tests
- Time-Series Sampling Tests
- Borehole Dilution
- Seepage Meters
- Fracture Mapping
- Geophysical Techniques
- Tracer Tests

SLUG TESTS

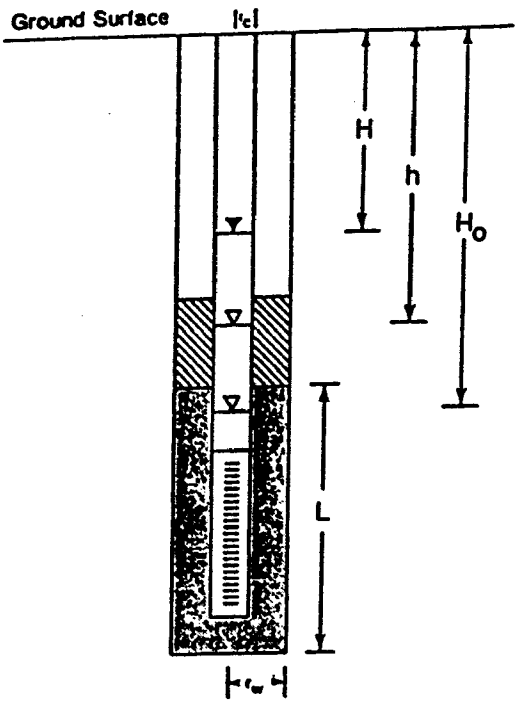
TYPES

- Falling Head Test
- Rising Head Test
- Bail Test
- Pressure/Packer Test

SLUG TESTS

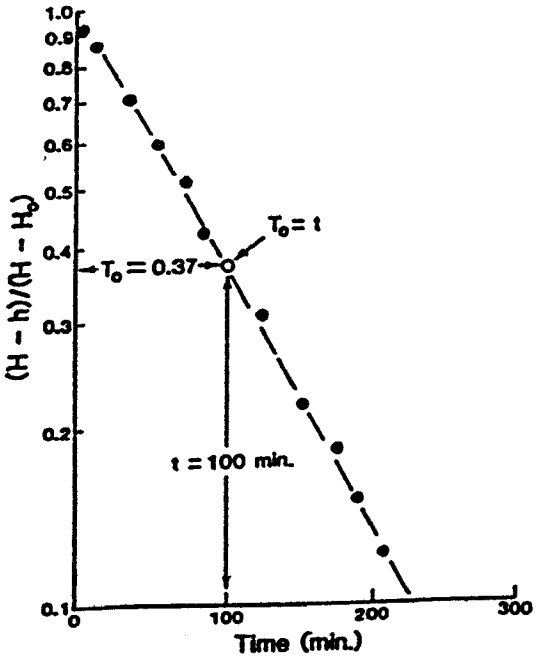
METHODS OF ANALYSIS

- Hvorslev (1961)
- Bouwer and Rice (1976)
- Cooper et al. (1967)
- Nguyen and Pinder (1984)



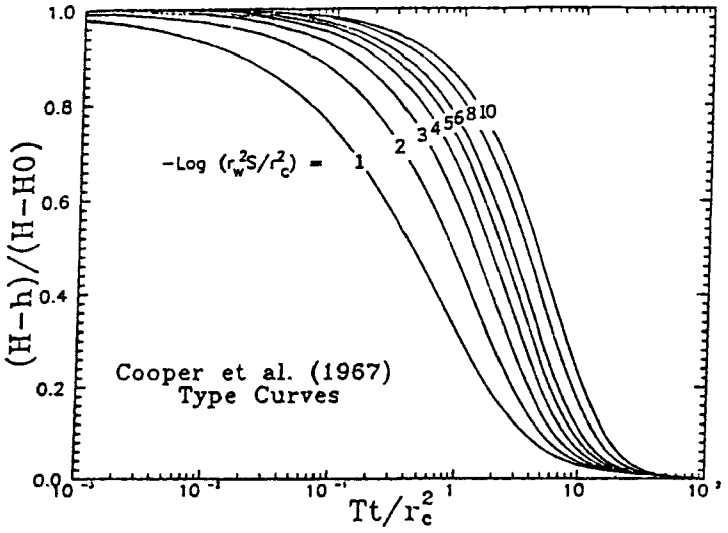
CDP-2 -16

Palmer and Paul (1987).



CDP-2 -17

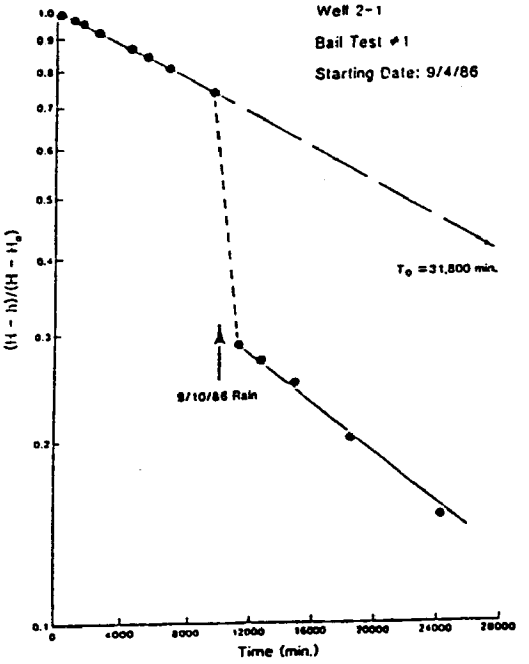
Palmer and Paul (1987).



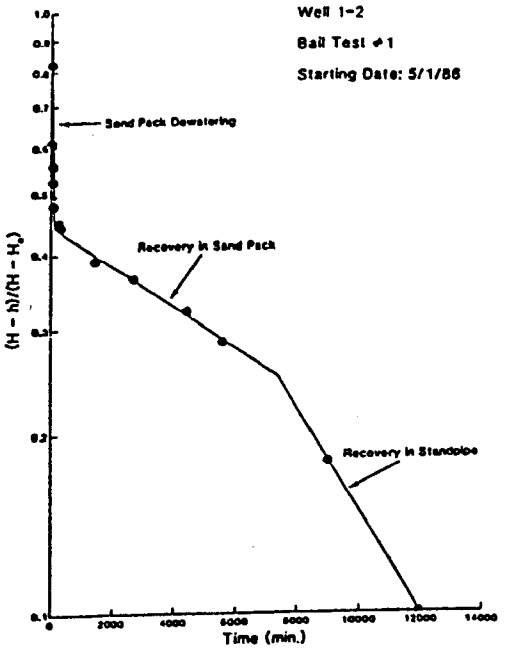
SLUG TESTS

POTENTIAL SOURCES OF ERROR

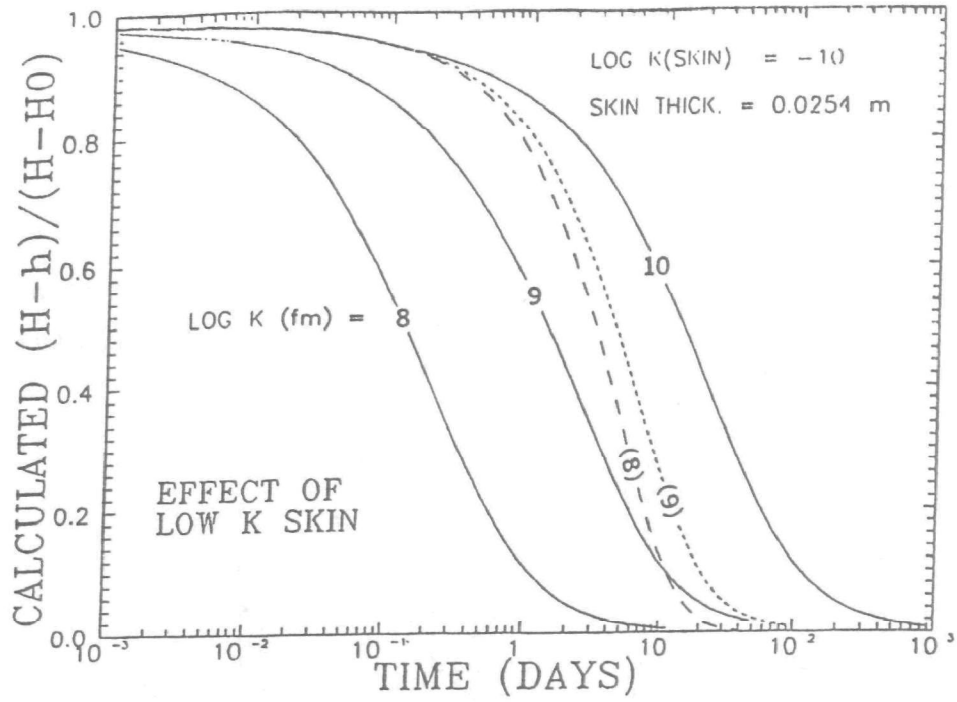
- Bridging of Seals
- Leaky Joints
- Formation of Low Permeability Skin
- Entrapped Air
- Presence of Fractures
- Stress Release Around Borehole
- Partial Penetration of Well
- Anisotropy of Formation
- Varying Regional Piezometric Surface
- Boundary Conditions
- Sand Pack Effects
- Uncertainty in Initial Head
- Radius of Influence of Test
- Thermal Expansion



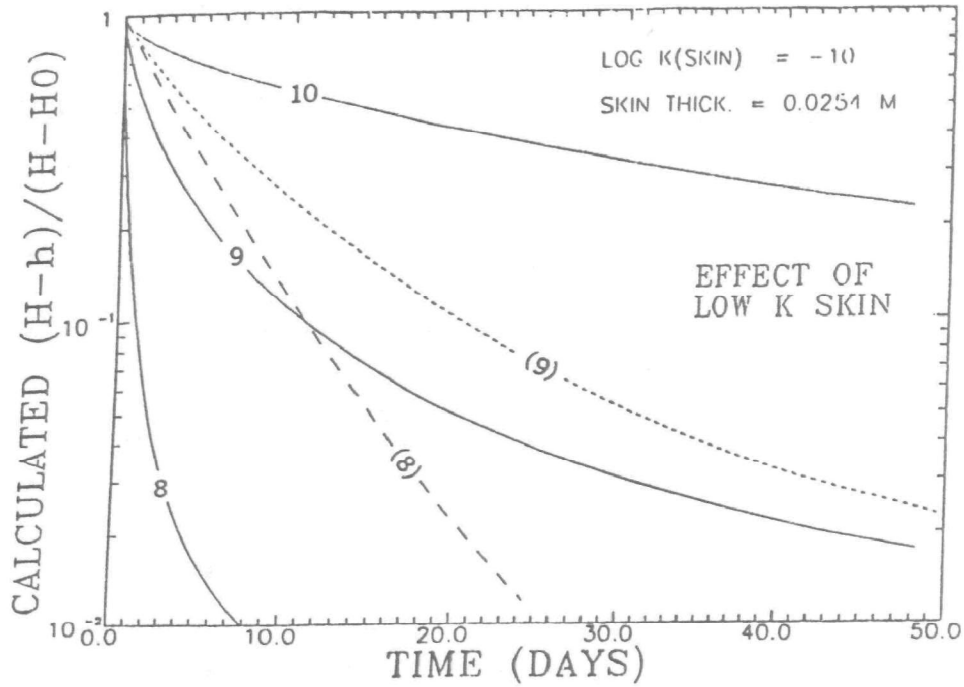
Palmer and Paul (1987).



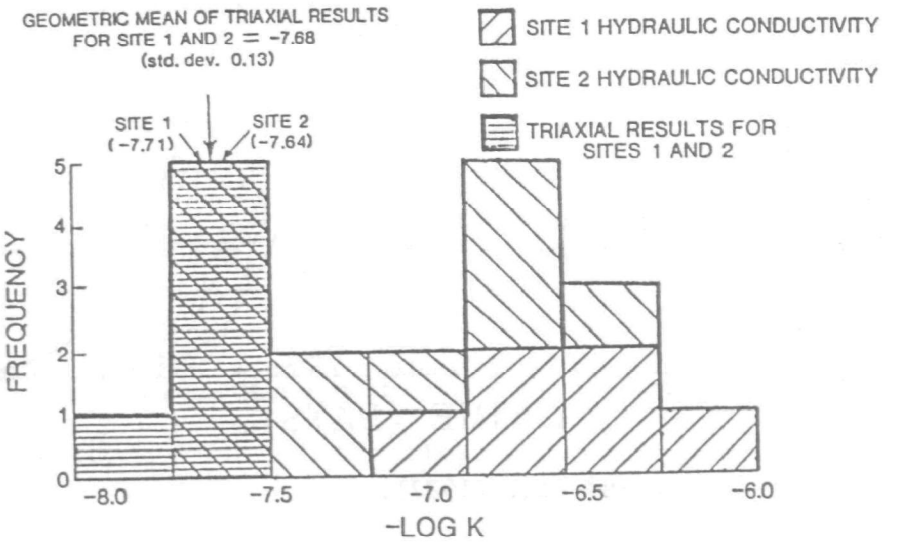
Palmer and Paul (1987).



From Palmer and Paul (1987).



Palmer and Paul (1987).



From Paul (1987).

AQUIFER TESTS

PARAMETERS DETERMINED

- Hydraulic Conductivity
- Specific Storage
- Leakance
- Anisotropy
- Boundaries
- Aquitard Diffusivity

AQUIFER TESTS

TYPES OF TESTS

- Constant Rate
- Constant Head
- Variable Rate

AQUIFER TESTS

TYPES OF FLOW EQUATIONS

- Steady–State Flow
- Non–Steady State Flow

AQUIFER TESTS

TYPES OF AQUIFERS

- Confined
- Unconfined
- Semi–Confined (Leaky)
- Semi–Unconfined

AQUIFER TESTS IN FRACTURED ROCK

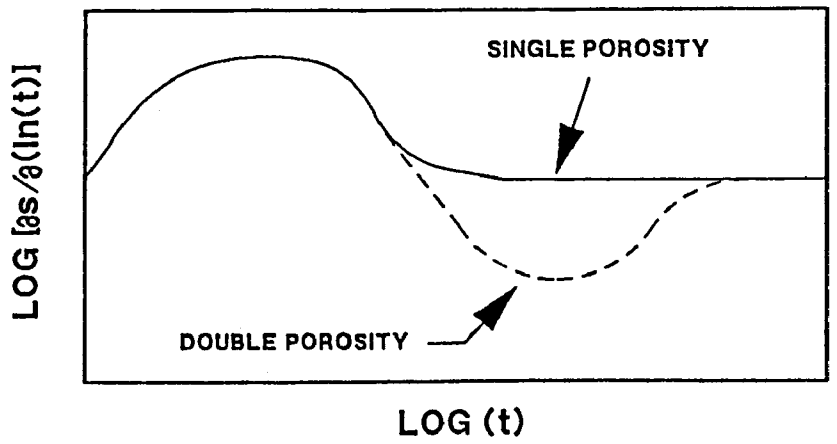
- **SINGLE POROSITY**
  - Same Methods as used for porous media
  - Anisotropy will be important

    Weeks (1969)

    Way and McKee (1982)
- **DOUBLE POROSITY**
  - Barenblatt (1960)
  - Boulton and Streltsova (1977)

DIFFERENTIATING DOUBLE POROSITY MEDIA FROM SINGLE POROSITY MEDIA

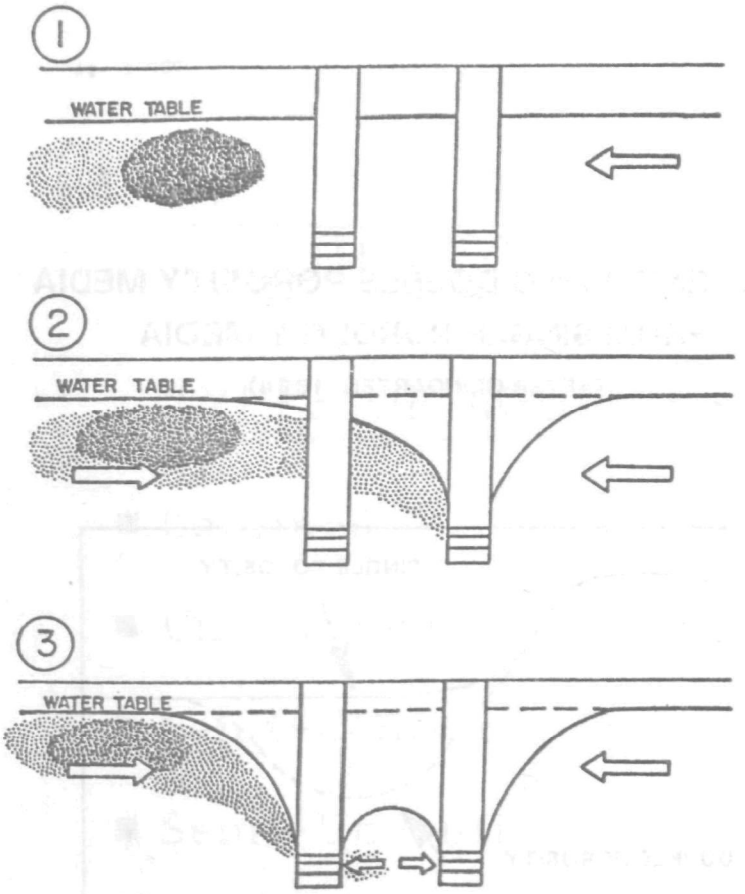
(AFTER GRINGARTEN, 1984)



TIME SERIES SAMPLING

Can be used in evaluation
of source of contamination.

CDP-2 -31



CDP-2 -32

Keely, J.F., 1982. Chemical Time-Series Sampling.
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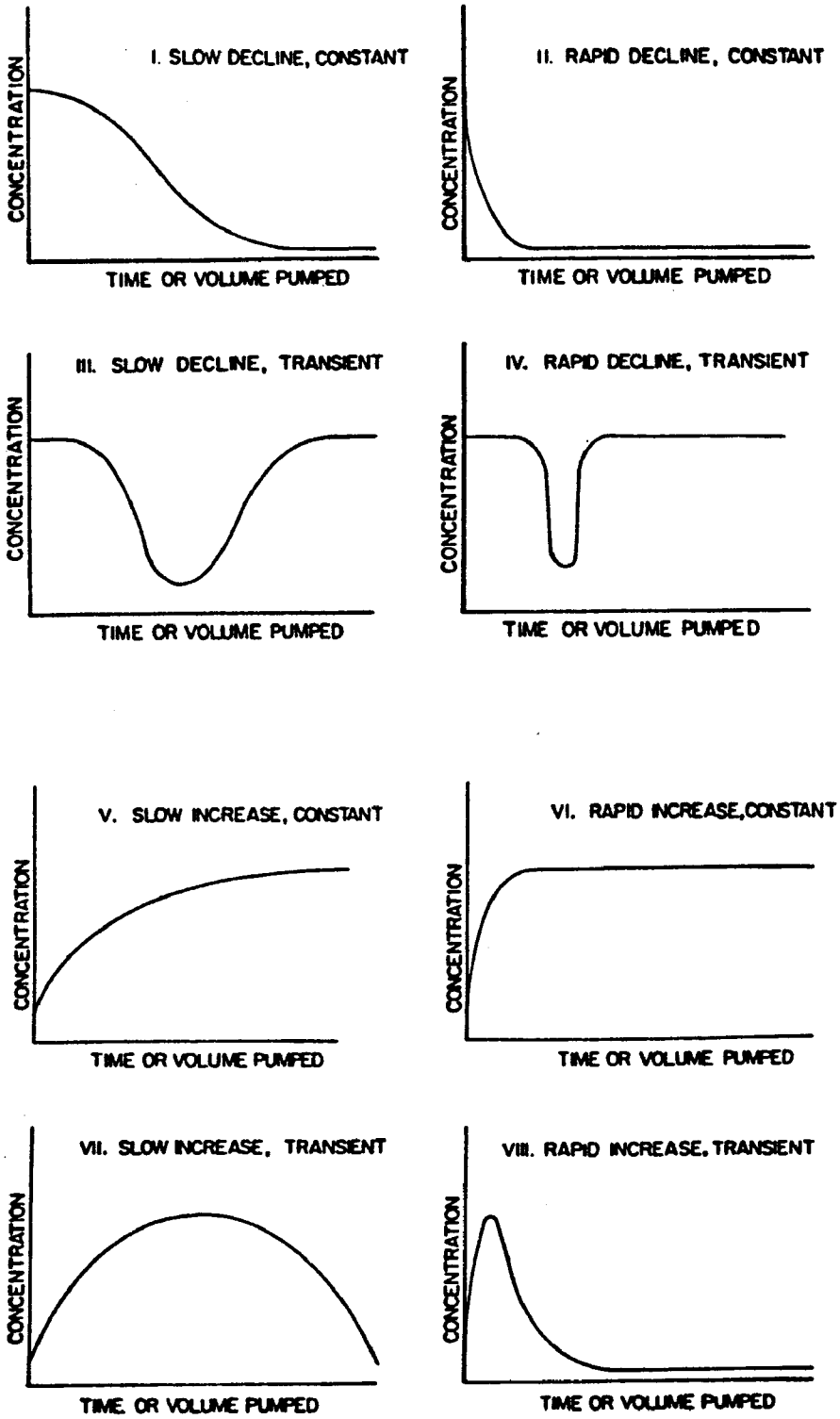
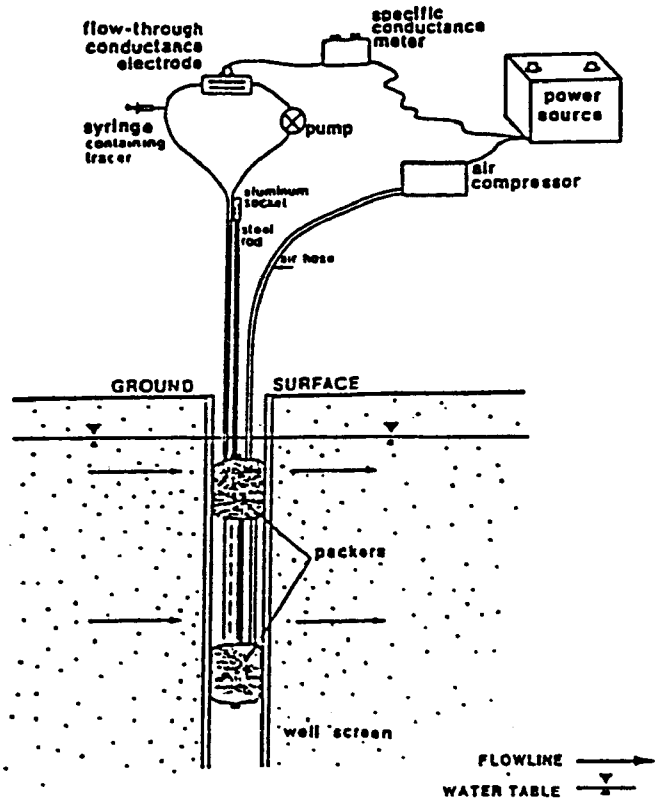


From: Keely, J.F., 1982. Chemical Time-Series Sampling. Ground Water Monitoring Review, Fall, 1982, p.29-38.

BOREHOLE DILUTION

PARAMETERS OBTAINED

- Magnitude of Groundwater Flux
- Direction of Groundwater Flow



From: McLinn, 1987.

BOREHOLE DILUTION

$$\ln\left[\frac{(c-c')}{(c_0-c')}\right] = -\frac{A\alpha q}{W}(t-t_0)$$

where

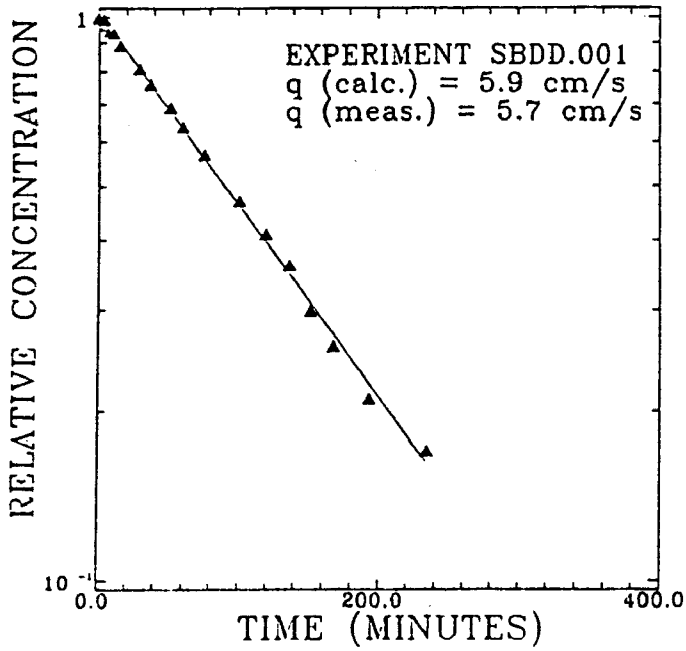
c' = background concentration

c_0 = concentration in injected slug

A = cross-sectional area of borehole

W = volume in borehole section

q = groundwater flux

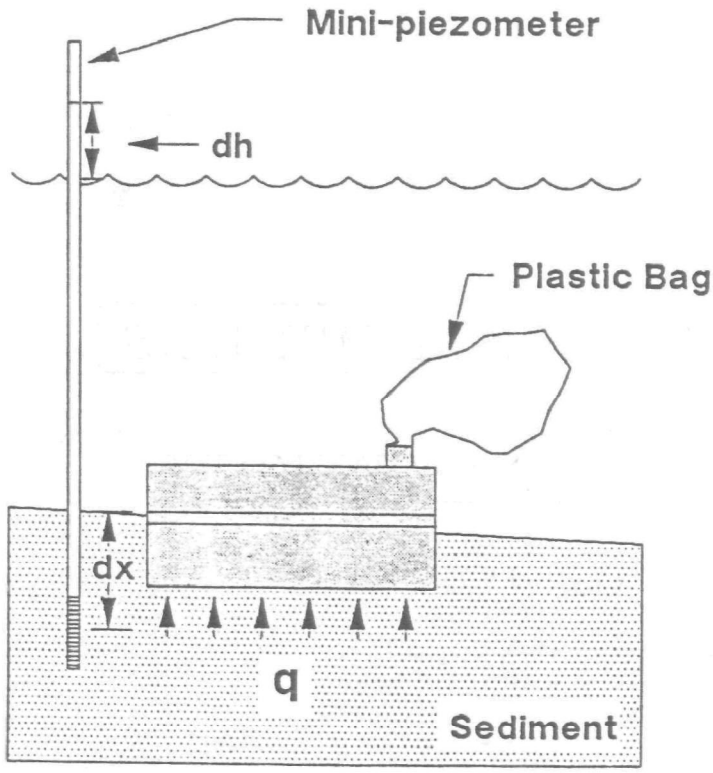


BOREHOLE DILUTION

TYPES OF DEVICES

- Radioisotope Devices
- Specific Ion Electrode Devices
- Specific Conductance Devices
- Thermal Devices
- Resistivity Devices

Seepage Meter



FRACTURE MAPPING

- Orientation
- Aperature
- Spacing

GEOPHYSICAL METHODS

SURFACE TECHNIQUES

- Gravity Survey
- Infrared Imagery
- Ground Penetrating Radar
- Induced Electrical Polarization
- Resistivity
- Metal Detection
- Magnetometer
- Reflection Seismics
- Electromagnetic Surveys

GEOPHYSICAL METHODS

BOREHOLE METHODS

- Geothermetry
- Electrical
- Acoustic
- Nuclear

GEOPHYSICAL METHODS

BOREHOLE METHODS

- Electrical
  - Resistance
  - Normal
  - Lateral
  - Induction
  - Self Potential
  - Sidewall
  - Induced Polarization

GEOPHYSICAL METHODS

BOREHOLE METHODS

- Nuclear
  - Natural Gamma
  - Gamma-Gamma
  - Neutron
  - Spectronic Gamma

TRACER TESTS

INFORMATION GAINED

- Dispersion
- Heterogeneity
- Porosity

TRACER TESTS

TYPE OF TESTS

- Natural Gradient
- Forced Gradient
  - Single Well Tests
  - Two-Well Tests
- Push-Pull

IMPROVED UNDERSTANDING OF THE FATE AND TRANSPORT OF CONTAMINANTS IN HYDROGEOLOGIC SYSTEMS WILL REQUIRE BETTER CHARACTERIZATION OF THE PHYSICAL NATURE OF THE SUBSURFACE

- Three-Dimensional Monitoring
- Hydraulic Tests
- Tracer Tests
- Use of Geophysical Tools

RESEARCH FRONTIERS

- Spatial Variability
- Chemical/Physical Interactions
- Multiphase Transport
- Multicomponent Transport
- Tool Development
- Particle Transport
- Transport in Fractured Rock
- Source Identification
- Modelling Techniques
- Aquifer Remediation

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TRANSPORT AND FATE

CHEMICAL PROCESSES

Session 3

Richard L. Johnson

(Oregon Graduate Center)

MAJOR IONS (NATURAL)

ANIONS	CATIONS
chloride	sodium
sulfate	calcium
bicarbonate	magnesium
carbonate	potassium

RLJ3A1-2

RADIOISOTOPES (NATURAL)

- Uranium
- Radium
- Radon

$^{238}U \rightarrow \rightarrow ^{226}Ra \rightarrow \rightarrow ^{222}Rn$

RLJ3A1-3

TRACE METALS (NATURAL)

- Arsenic
- Selenium
- Lead
- Barium
- Cadmium

RLJ3A1-1

WATER QUALITY PARAMETERS

- TOTAL DISSOLVED SOLIDS
- SPECIFIC CONDUCTANCE
- DISSOLVED OXYGEN
- AKLAKINITY
- ACIDITY
- pH
- pE (Eh)
- ODOR
- TURBIDITY
- COLOR

RLJ3A1-5

MAJOR IONS (Anthropogenic)

ANIONS	CATIONS
Cyanide	Hydrogen
Nitrate	
Phosphate	

RLJ3A2-2

RADIOISOTOPES (Anthropogenic)

- Uranium
- Cesium
- Strontium
- Ruthenium
- Tritium

RLJ3A2-3

TRACE METALS
(ANTHROPOGENIC)

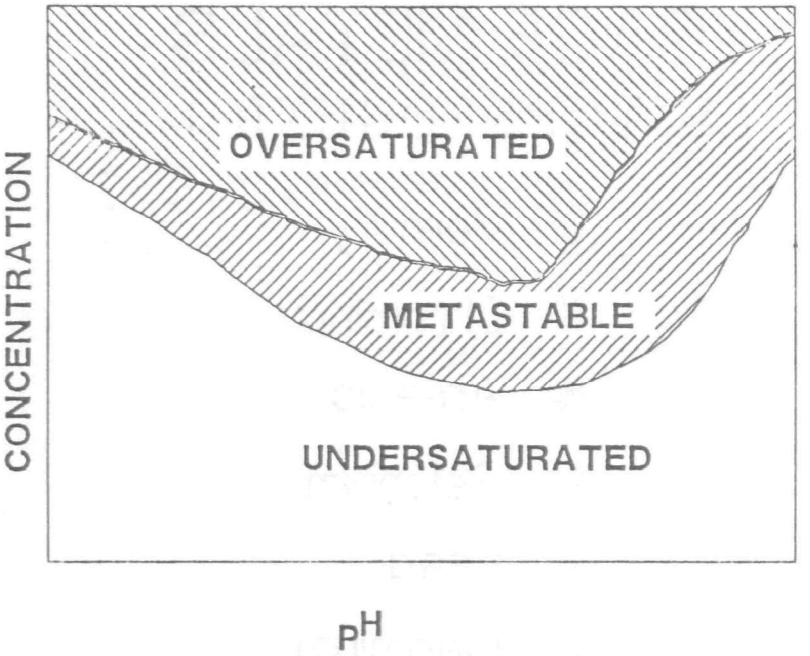
- Mercury
- Chromium
- Arsenic
- Selenium
- Lead
- Cadmium

RLJ3A2-4

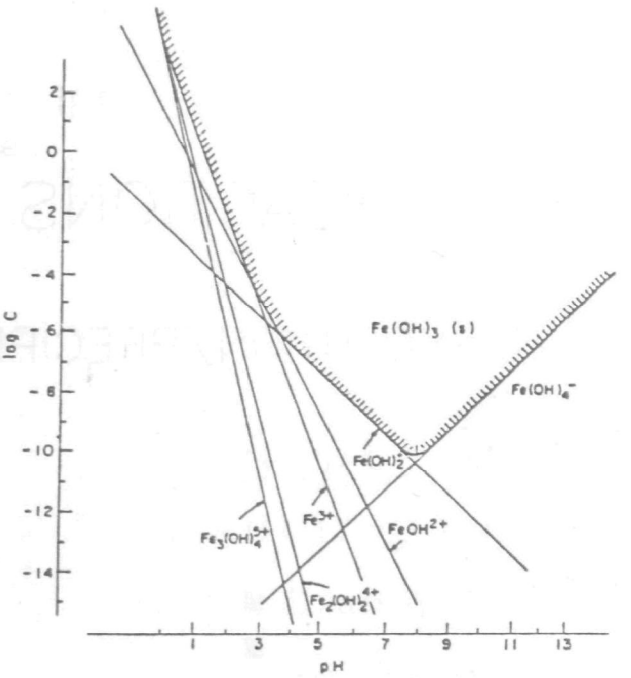
INORGANIC REACTIONS

- SOLUBILITY/DISSOLUTION/PRECIPITATION
- COMPLEXATION
- ION EXCHANGE
- OXIDATION/REDUCTION
- RADIODECAY

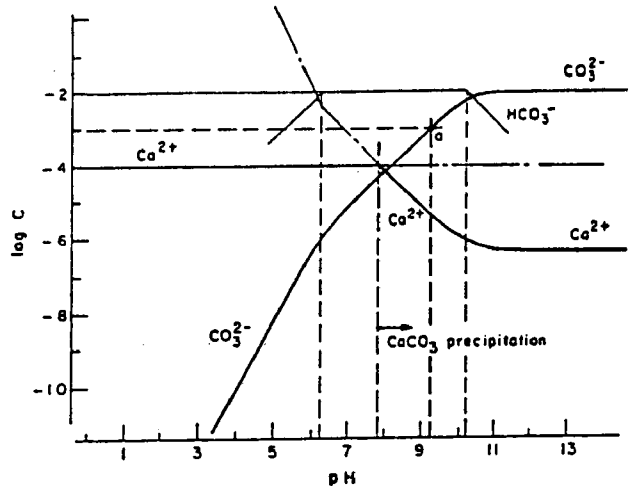
RLJ3A4-1



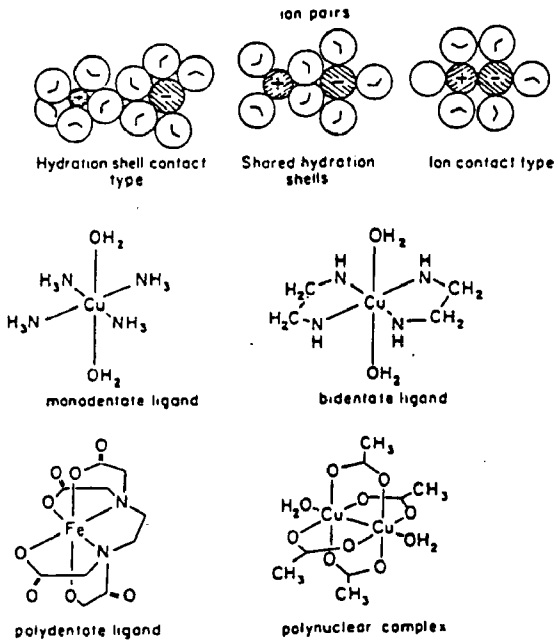
RLJ3A4-2



RLJ3A4-3



RLJ3A4-4



Source: Morel, 1983 (Used with permission)

RLJ3A4-5

Mononuclear Complexes
Addition of ligand

$$M \xrightarrow[K_1]{L} ML \xrightarrow[K_2]{L} ML_2 \cdots \xrightarrow[K_i]{L} ML_i \cdots \xrightarrow[K_n]{L} ML_n$$

$$\beta_2 \longrightarrow$$
$$\beta_i \longrightarrow$$
$$\beta_n \longrightarrow$$

$$K_i = \frac{[ML_i]}{[ML_{(i-1)}][L]}$$

$$\beta_i = \frac{[ML_i]}{[M][L]^i}$$

Addition of protonated ligands

$$M \xrightarrow[{}^*K_1]{HL} ML \xrightarrow[{}^*K_2]{HL} ML_2 \cdots \xrightarrow[{}^*K_i]{HL} ML_i \cdots \xrightarrow{HL} ML_n$$

$${}^*\beta_2 \longrightarrow$$
$${}^*\beta_i \longrightarrow$$
$${}^*\beta_n \longrightarrow$$

$${}^*K_i = \frac{[ML_i][H^+]}{[ML_{(i-1)}][HL]}$$

$${}^*\beta_i = \frac{[ML_i][H^+]^i}{[M][HL]^i}$$

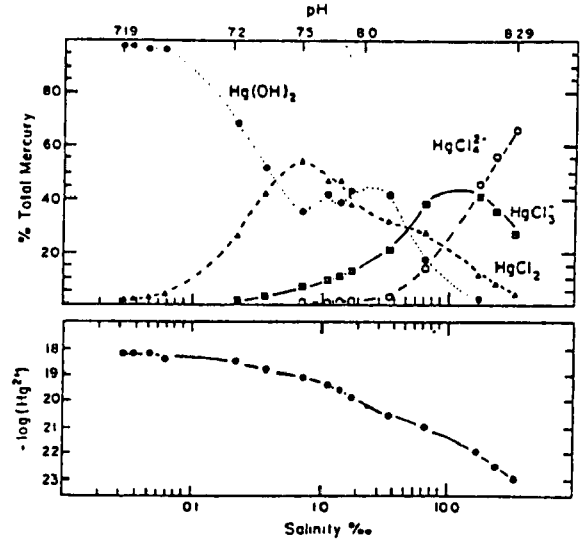
Polynuclear Complexes
In β_{nm} and ${}^*\beta_{nm}$ the subscripts n and m denote the composition of the complex M_nL_n formed. [If $m = 1$, the second subscript (= 1) is omitted.]

$$\beta_{nm} = \frac{[M_nL_n]}{[M]^n[L]^n}$$

$${}^*\beta_{nm} = \frac{[M_nL_n][H^+]^n}{[M]^n[HL]^n}$$

Source: Morel, 1983 (Used with permission)

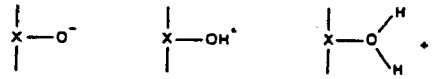
RLJ3A4-6



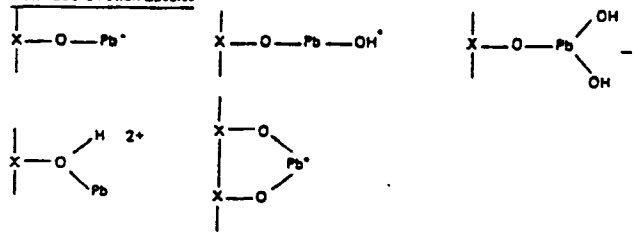
Source: Morel, 1983 (Used with permission)

RLJ3A4-7

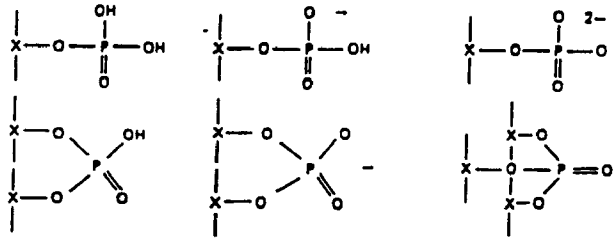
Acid–Base Species



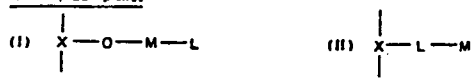
Metal Coordination Species



Ligand Coordination Species



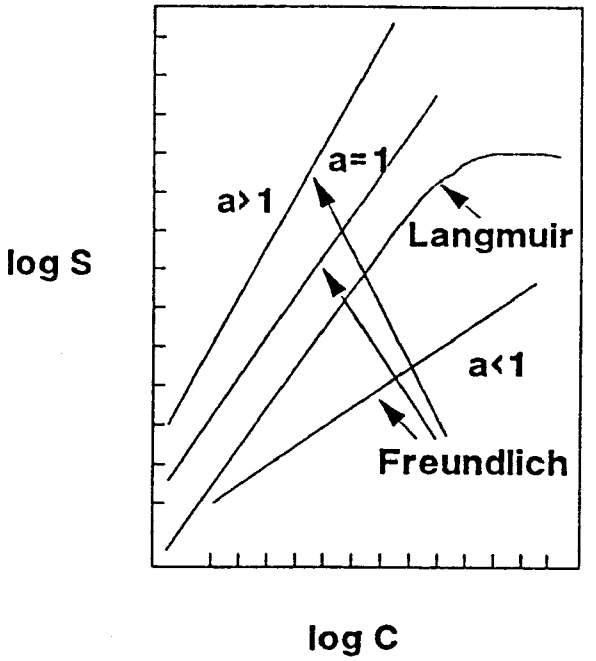
Ternary Complexes



Ion Pairs

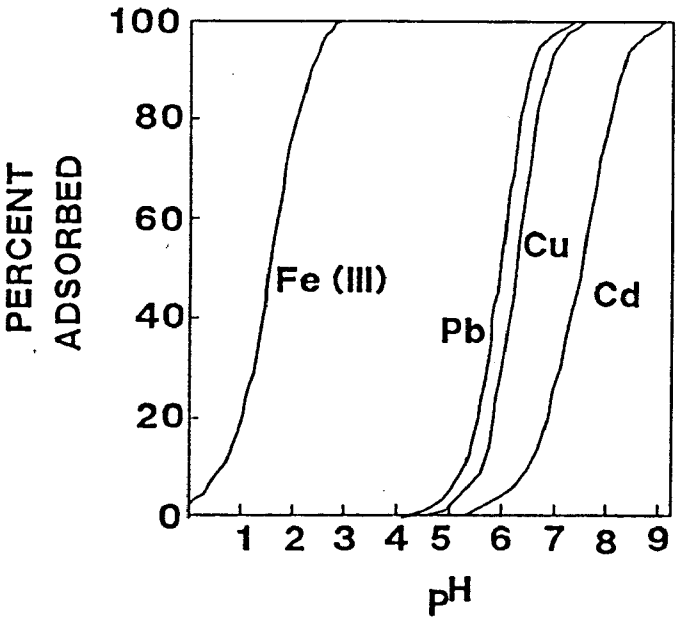
Source: Morel, 1983 (Used with permission)

RLJ3A4-8



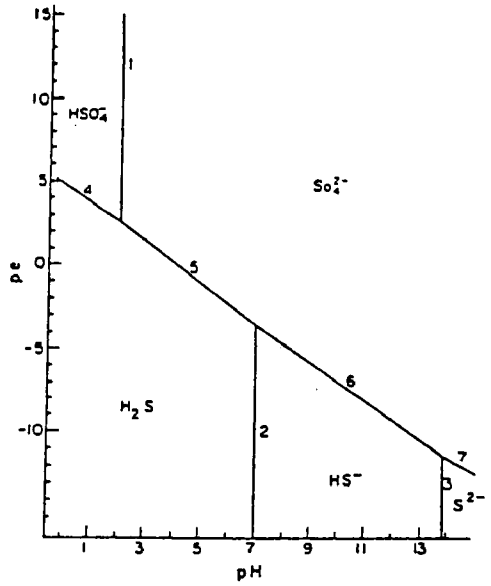
RLJ3A4-9

METAL ION BINDING TO OXIDE SURFACES

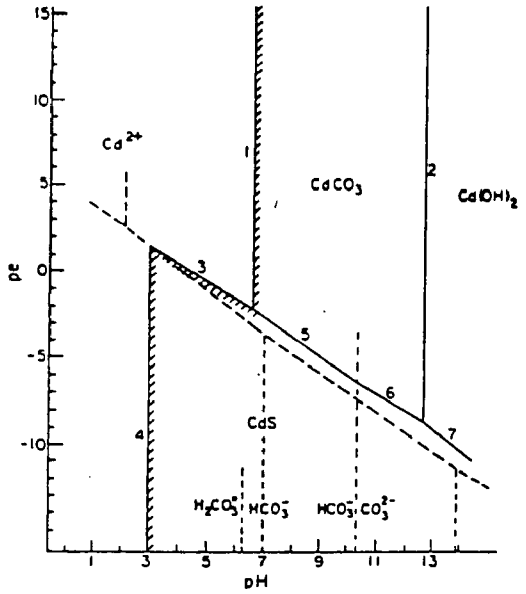


Adapted from Hohl and Stumm, 1976

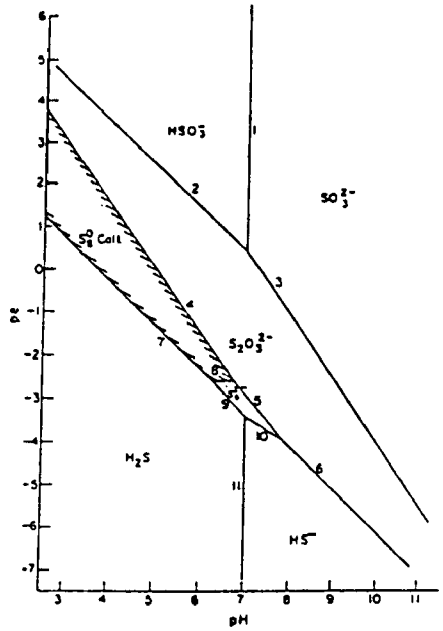
RLJ3A4-14



RLJ3A4-17



RLJ3A4-18

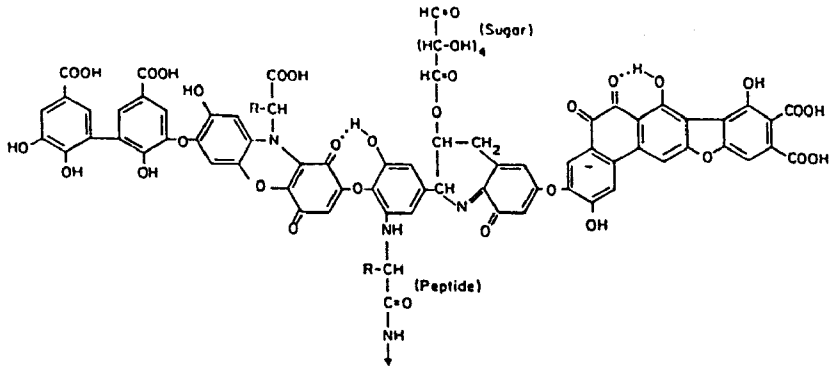


RLJ3A4-19

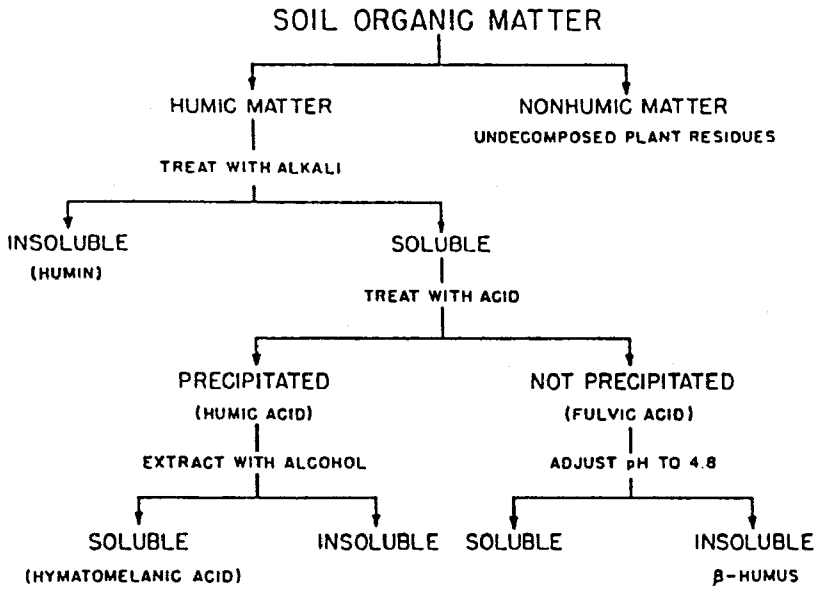
ORGANICS (NATURAL)

- HUMICS, FULVICS
- COAL, PEAT, LIGNITE
- PETRO-ORGANICS

RLJ3B1-1



RLJ3B1-2



RLJ3B1-3

ORGANICS (ANTHROPOGENIC)

- EPA PRIORITY POLLUTANTS
- RCRA APPENDIX IX
- POLAR ORGANICS
- IONIZABLE ORGANICS
- EVERYTHING ELSE

RLJ3B2-1

POLAR AND IONIZABLE COMPOUNDS

ALCOHOLS (ISOPROPANOL)
ANALINES (NITROANALINES)
ACETATES (VINYLACETATE)
AMINES (DIPHENYLAMINE)
THIOLS (TRICHLOROMETHANETHIOL)
FURANS (DIBENZOFURAN)
NITRILES (ACRYLONITRILE)
PHENOLS (CHLORO- AND NITROPHENOLS)
ALDEHYDES AND KETONES (ACETONE)
ACIDS

RLJ3B2-4

ORGANIC REACTIONS

- HYDROLYSIS
- SORPTION
- COSOLVATION
- IONIZATION
- BIODEGRADATION

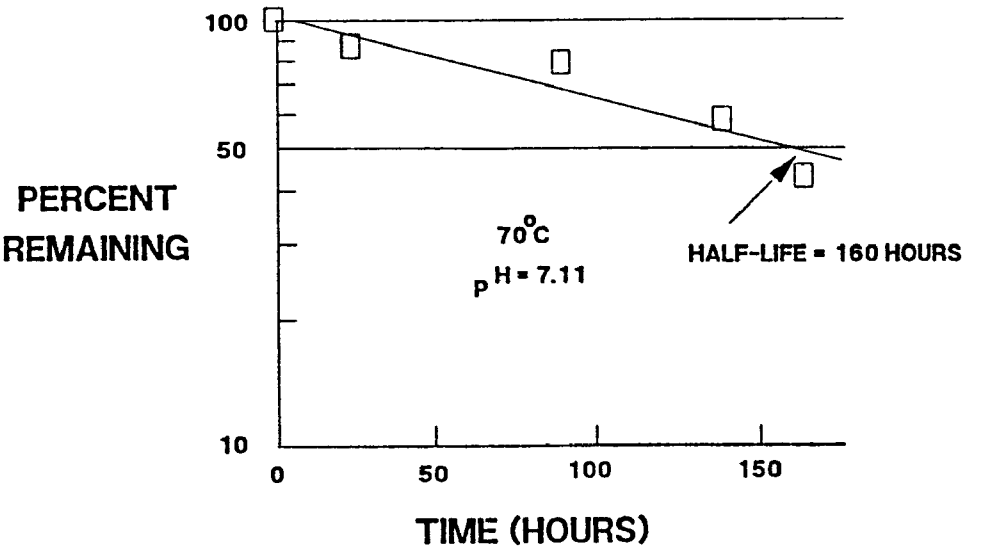
RLJ3B4-1

$$RX + HOH \longrightarrow ROH + HX$$

$$\begin{array}{l} H\ \ X \\ |\ \ \ | \\ C-C \end{array} \xrightarrow[OH^-]{H^+ \text{ or}} C=C + HX$$

RLJ3B4-2

HYDROLYSIS OF 1,2,4-TRICHLOROBENZENE



Adapted from Ellington et al. 1986.

RLJ3B4-9

$$\frac{dC}{dt} = -KC$$

$$\ln\left[\frac{C}{C(0)}\right] = -Kt$$

at the half-life: $\left[\frac{C}{C(0)}\right] = 0.5$

$t = 160$ hours

thus, $K = 0.69/160$

$$\boxed{K = 4.3 \times 10^{-3}\ hr^{-1}}$$

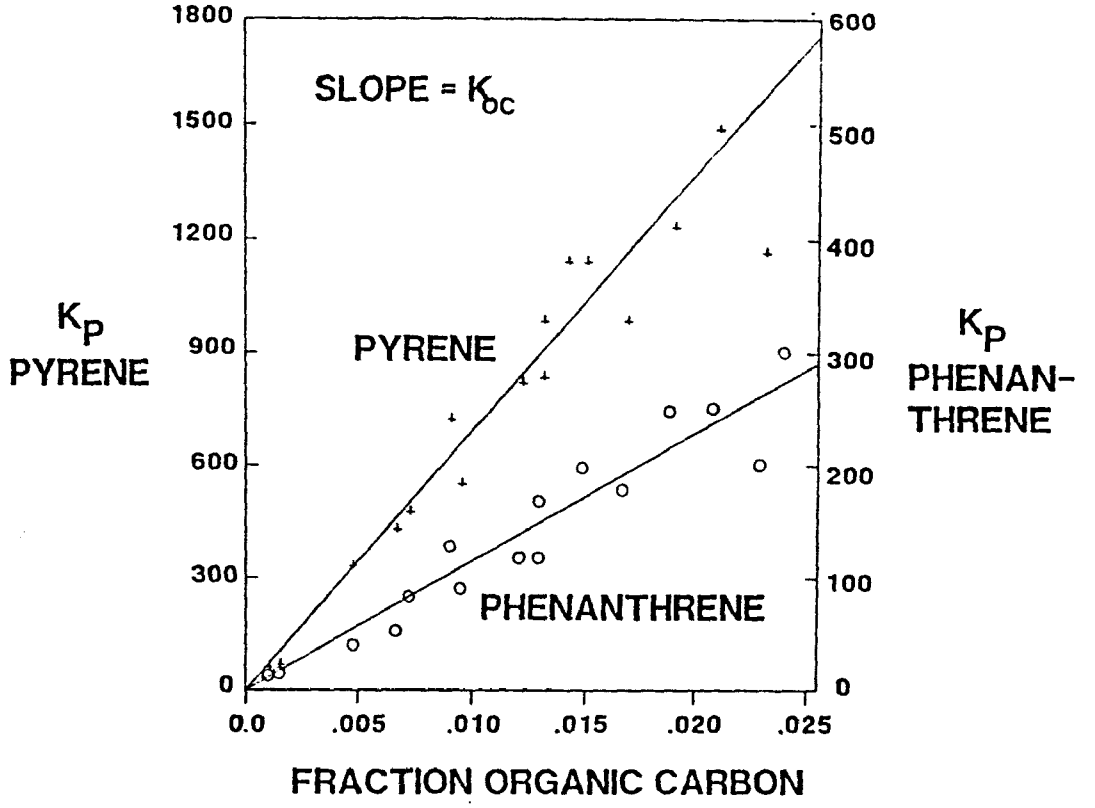
RLJ3B4-10

ADVECTION–DISPERSION EQUATION

WITH FIRST-ORDER DEGRADATION (IRREVERSIBLE)

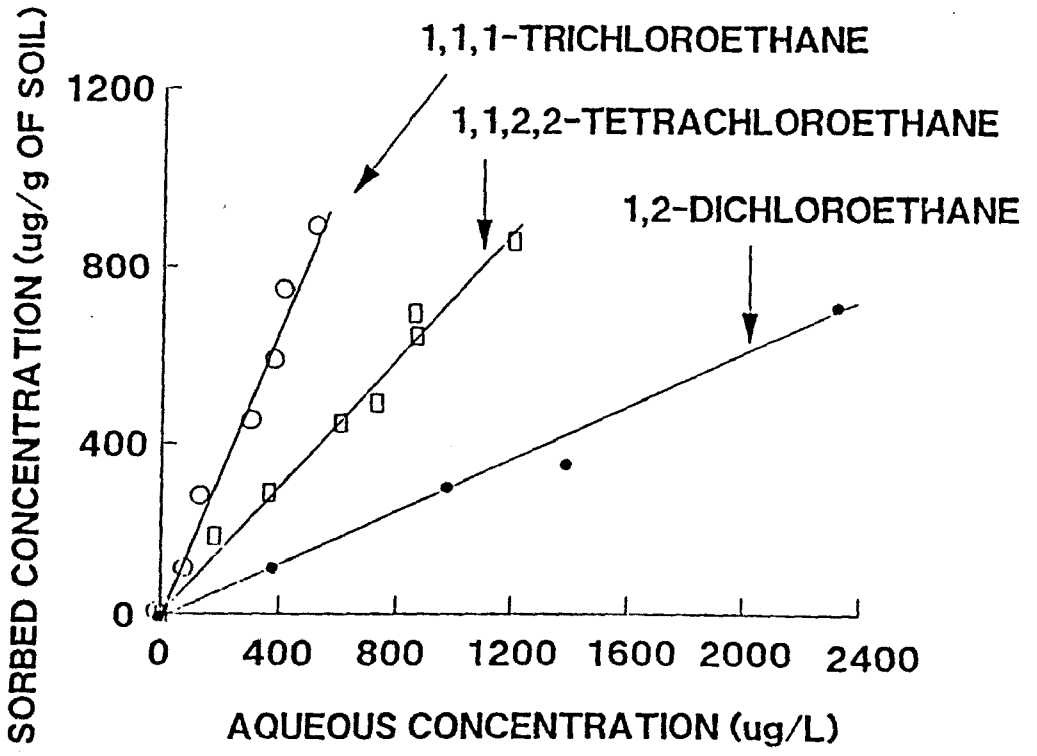
$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} - KC$$

RLJ3B4-11



RLJ3B4-12

Adapted from Karickhoff, 1981



RLJ3B4-13

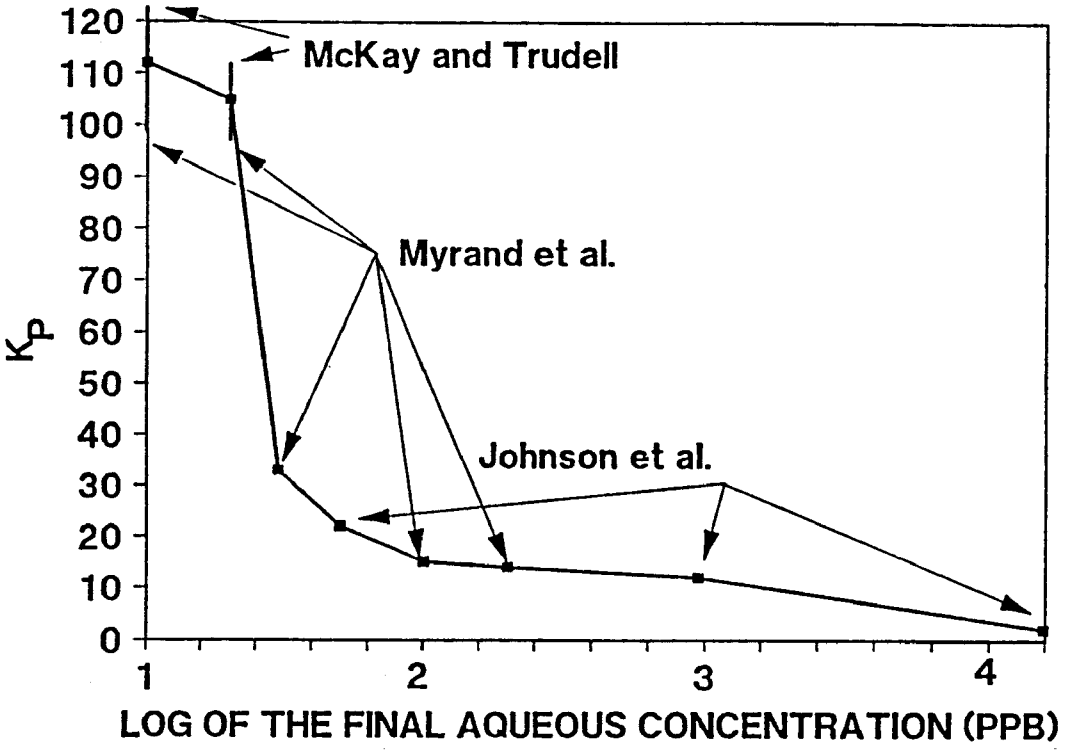
Adapted from Chiou et al.,1981.

ADVECTION–DISPERSION EQUATION

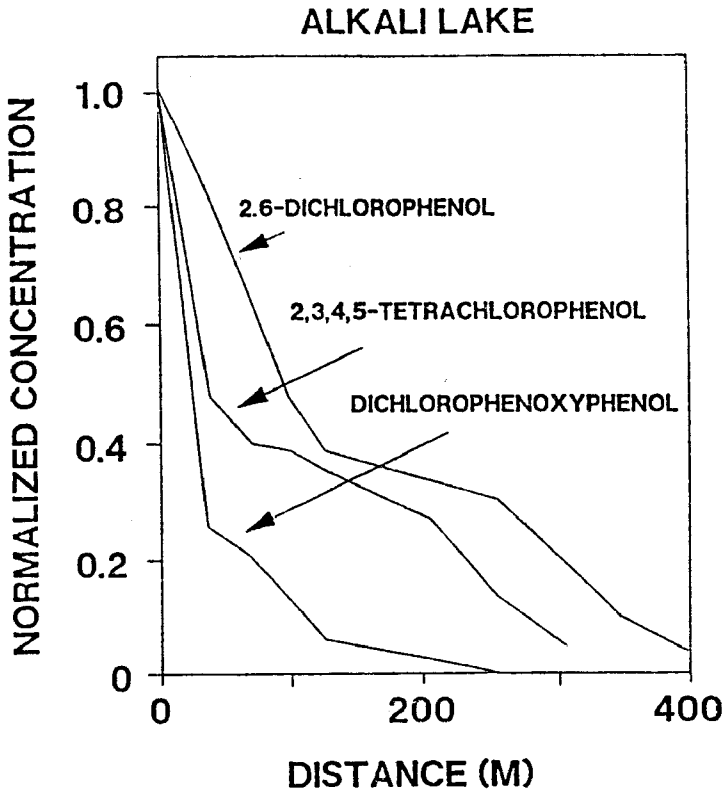
WITH LINEAR EQUILIBRIUM PARTITIONING

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = R \frac{\partial C}{\partial t}$$

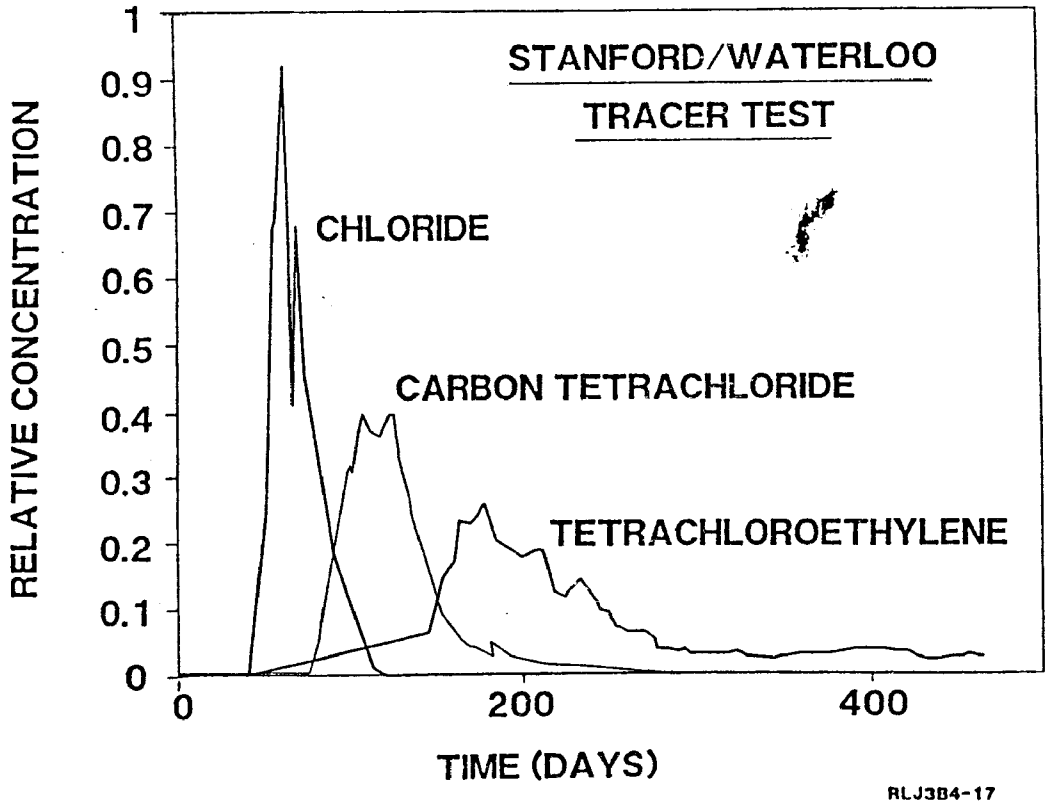
RIJ3B4-14


120
110
100
90
80
70
60
50
40
30
20
10
0
K_P
McKay and Trudell
Myrand et al.
Johnson et al.
1
2
3
4
LOG OF THE FINAL AQUEOUS CONCENTRATION (PPB)

RLJ3B4-15

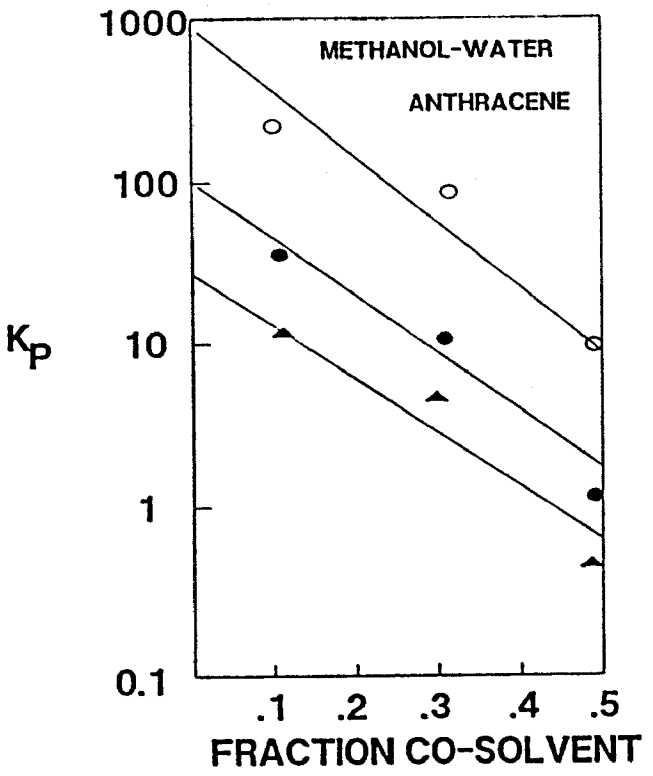


RLJ3B4-16



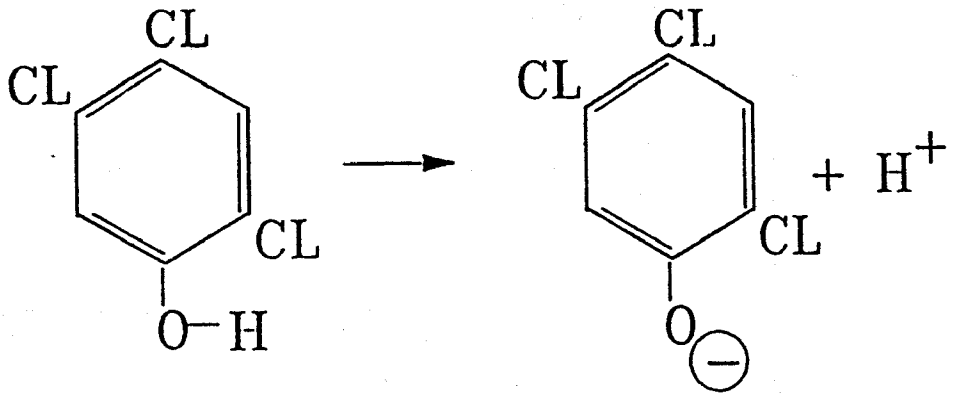
RLJ3B4-17

Adapted from Roberts et al., 1986.



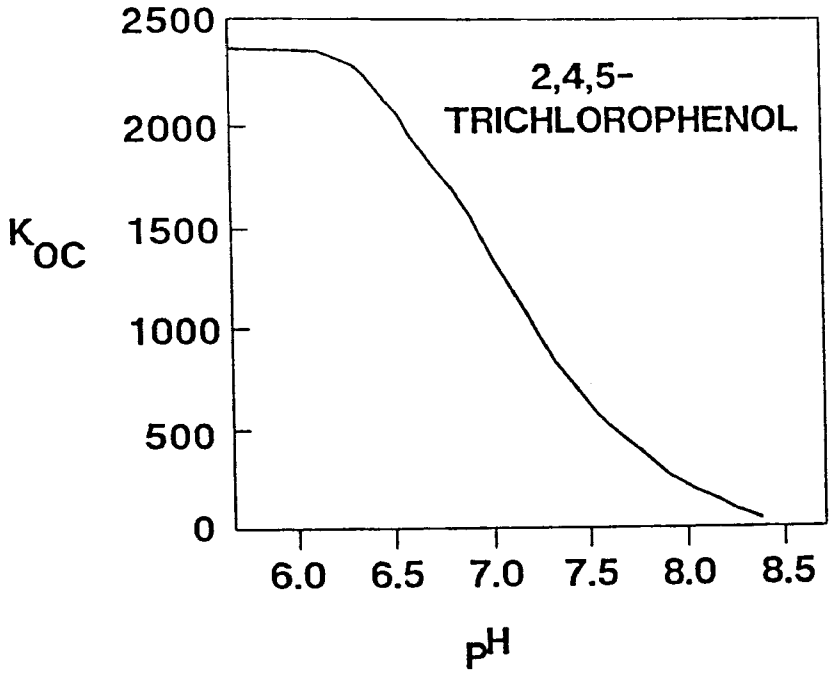
Adapted from Nkedi-Kizza et al., 1985.

RLJ3B4-18

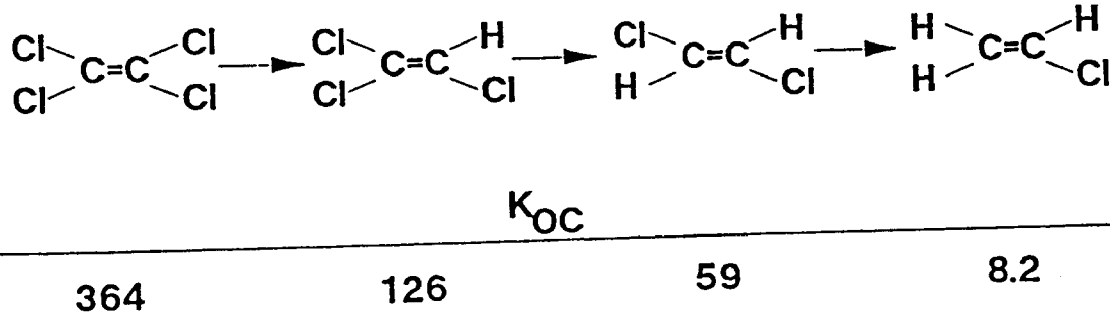


$K_{oc}=2330$ $K_{oc}\sim 0$

RLJ3B4-5

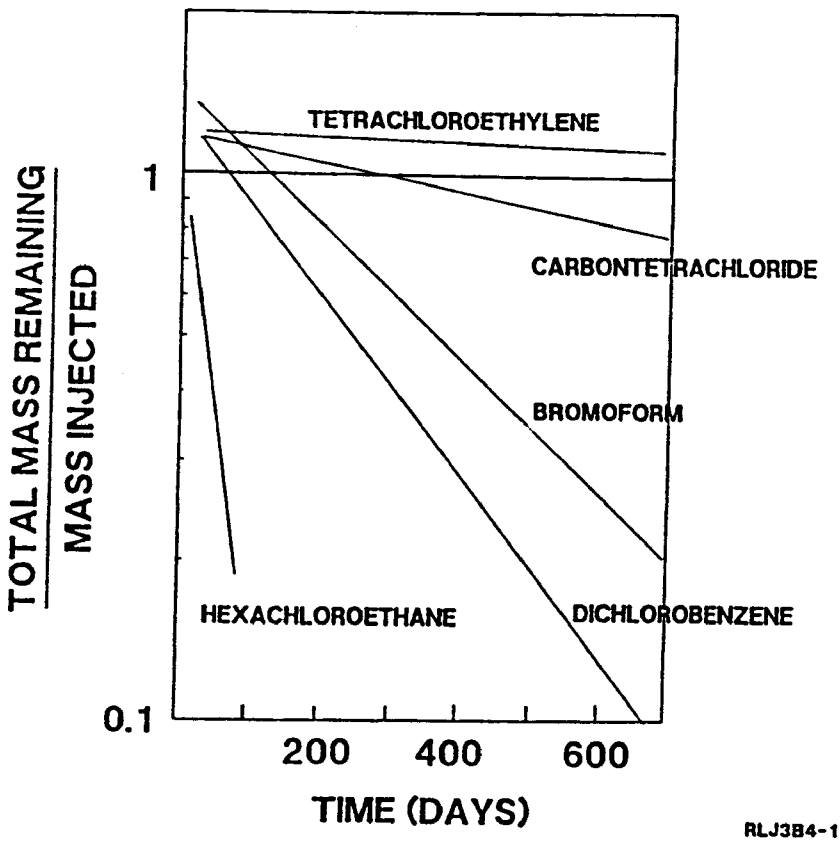


RLJ4D2-5



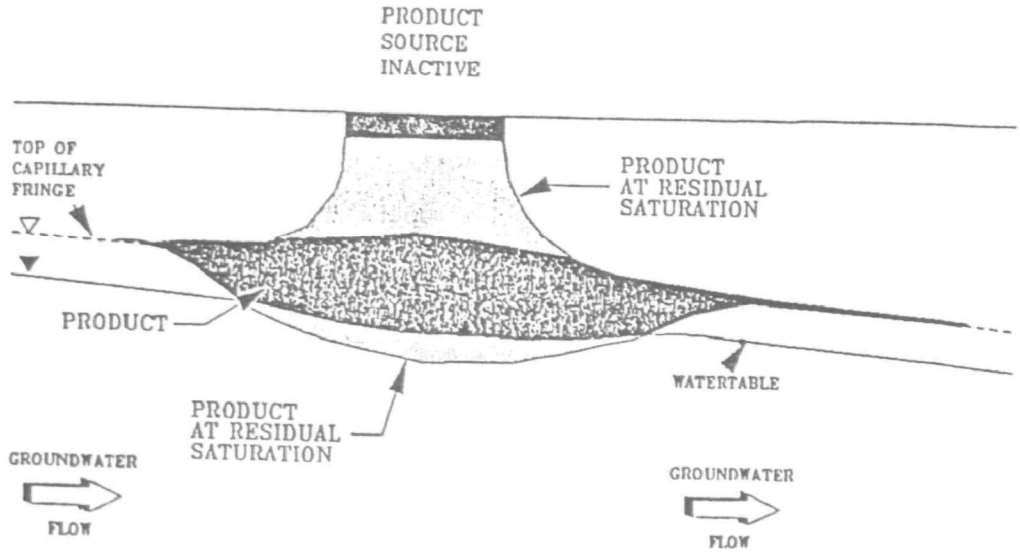
K_{OC}			
364	126	59	8.2

RLJ3B4-20



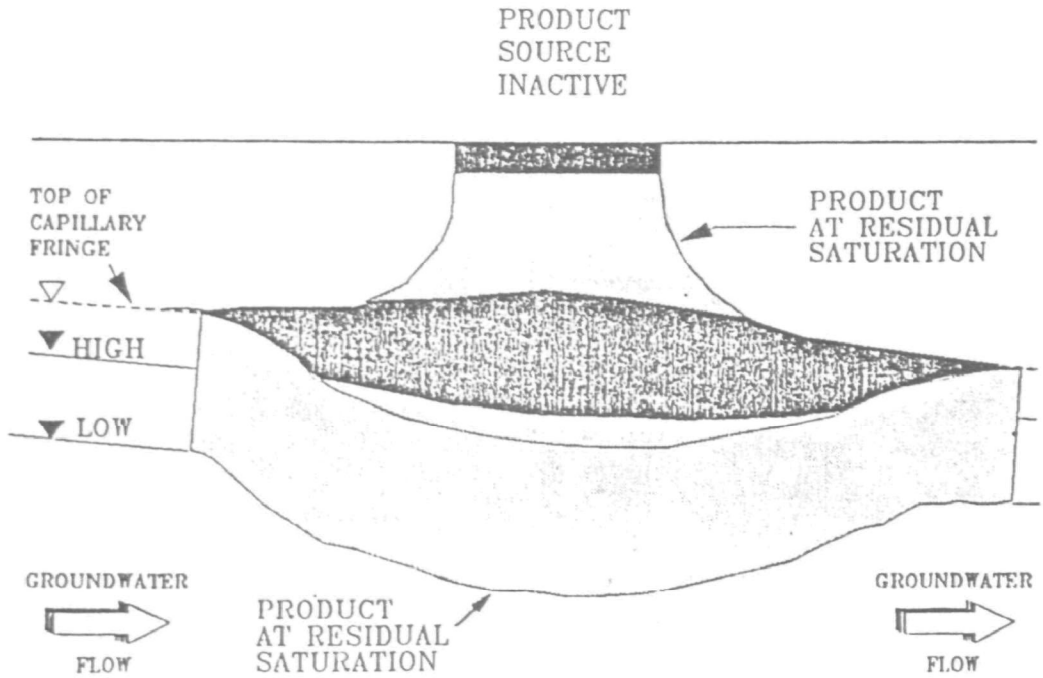
Adapted from Roberts et al. 1986.

LNAPLs

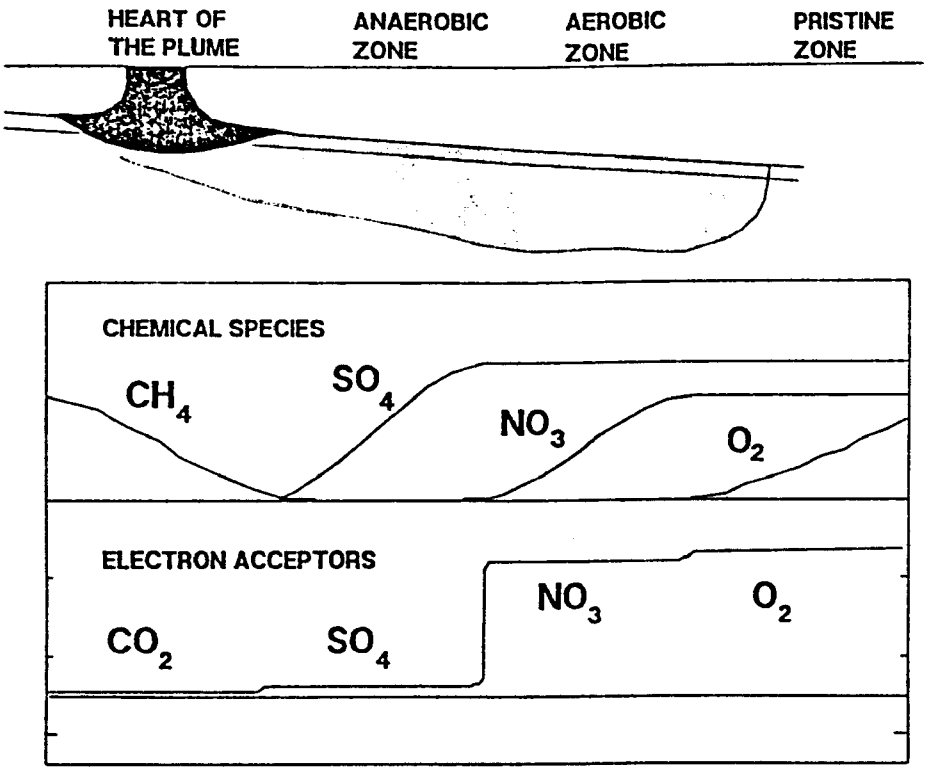


RLJ3D1-1

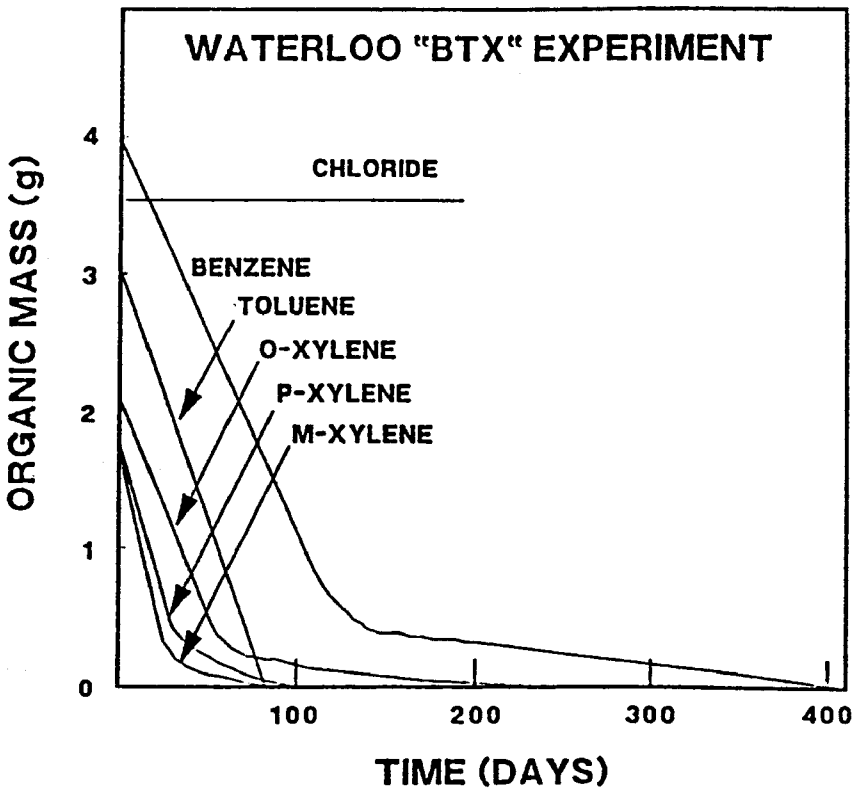
LNAPLs



RLJ3D1-2

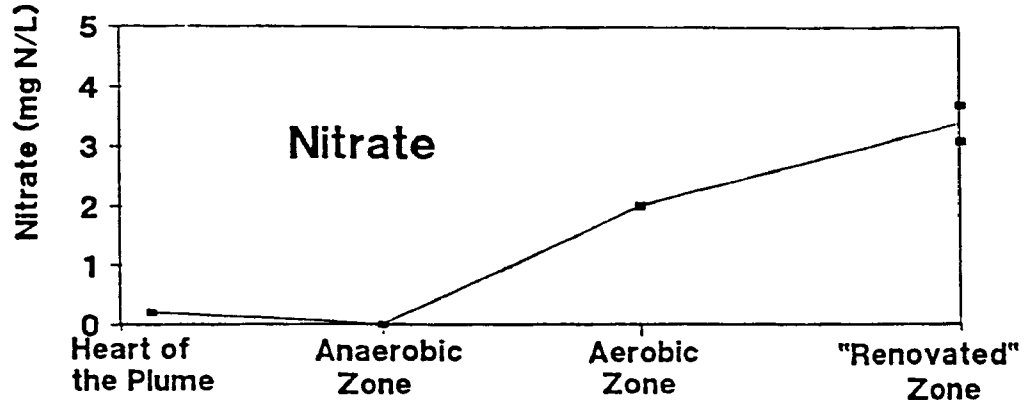


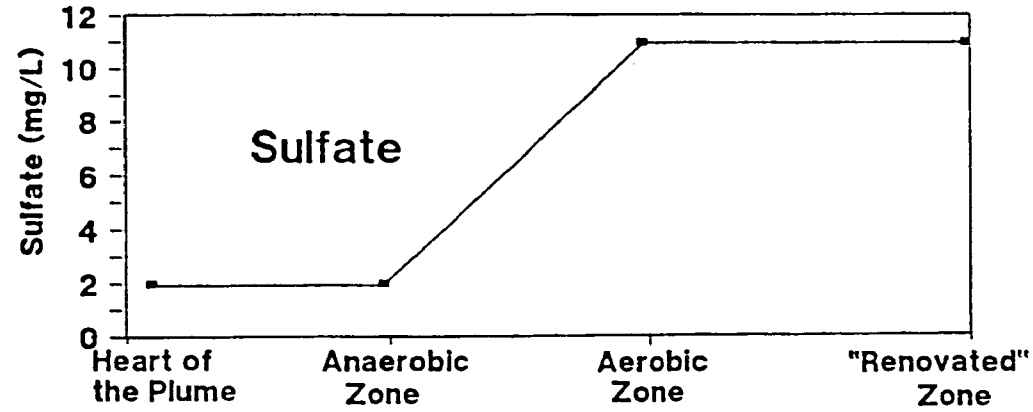
RLJ3D1-8

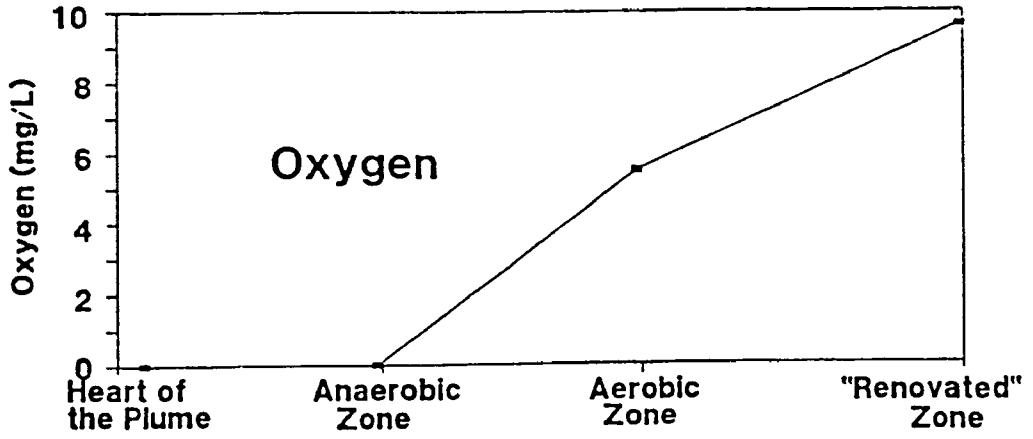


Adapted from Patrick and Barker, 1987.

RLJ3D1-7

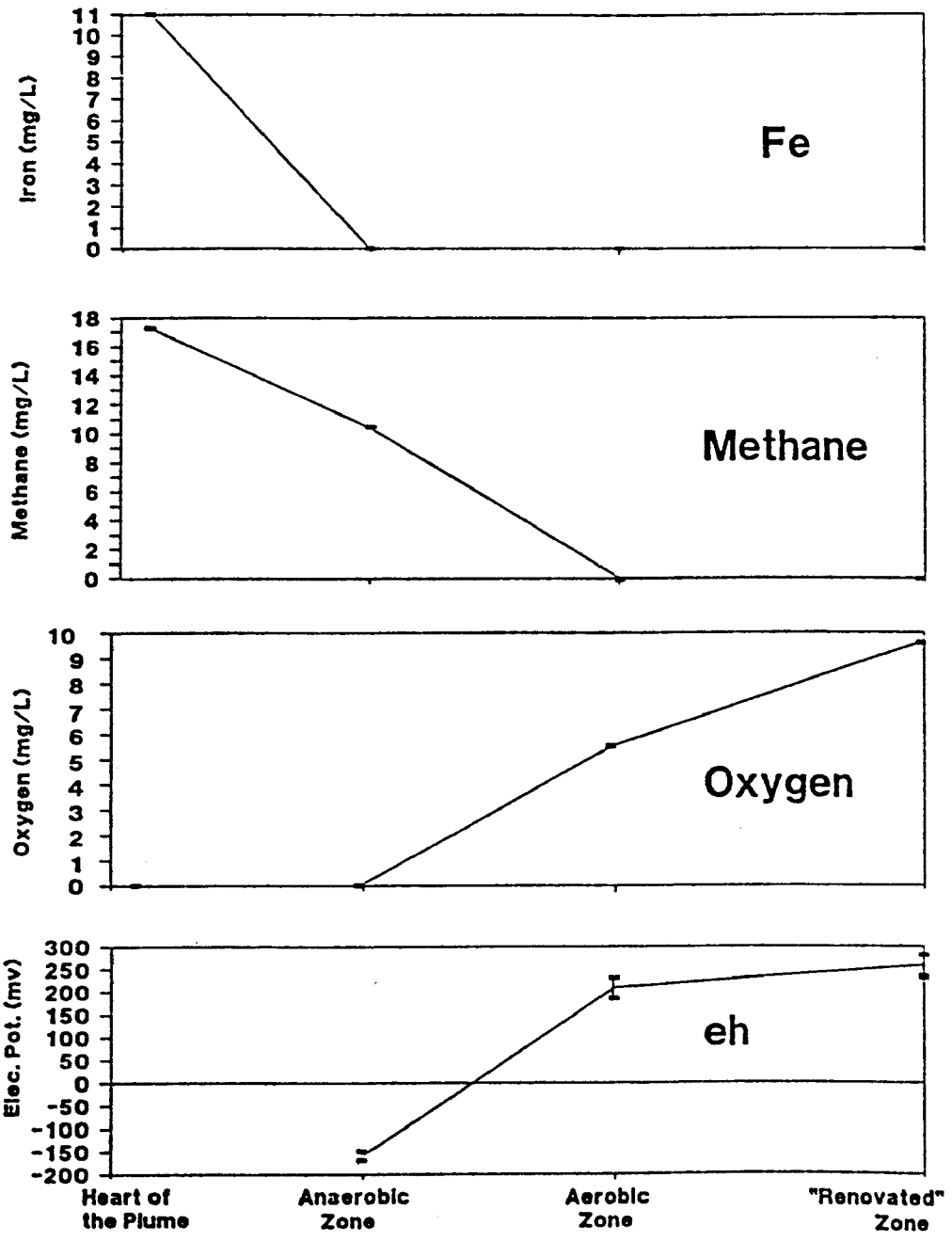






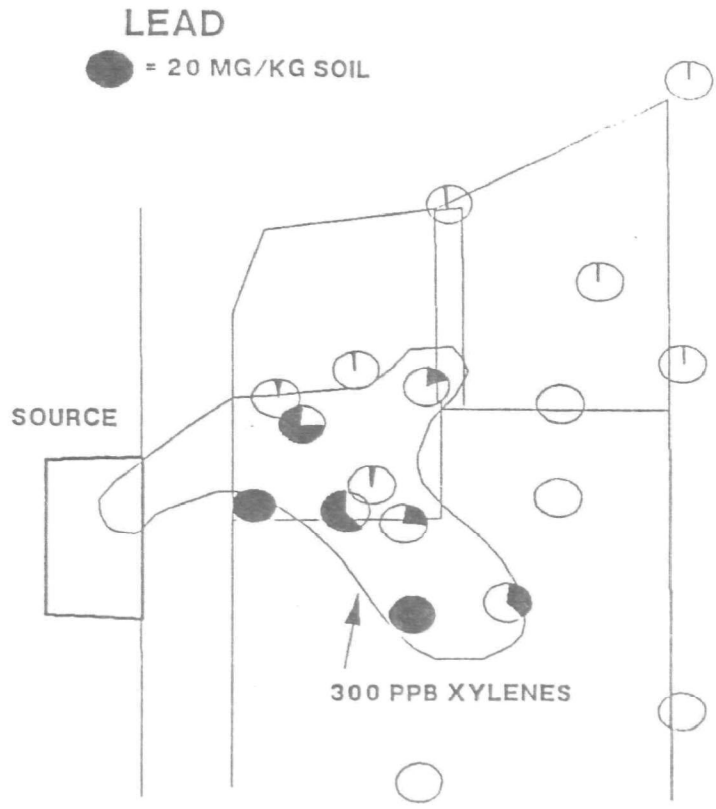
Adapted from Wilson et al., 1986.

RLJ3D1-9



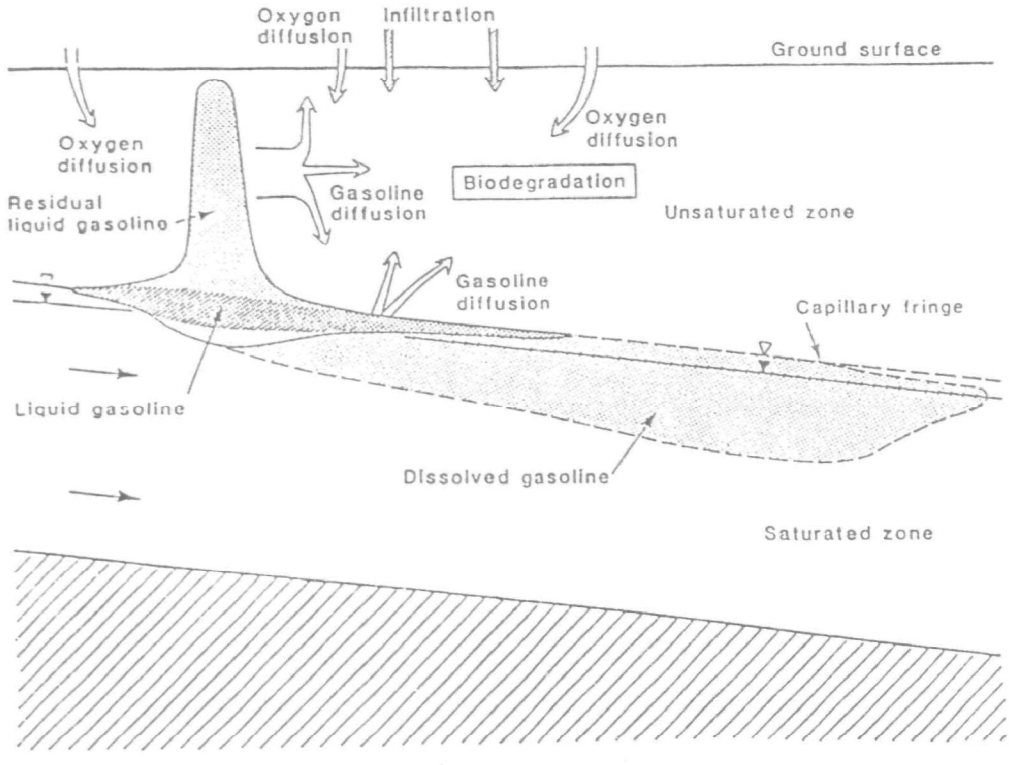
Adapted from Wilson et al. 1986.

RLJ3D1-10

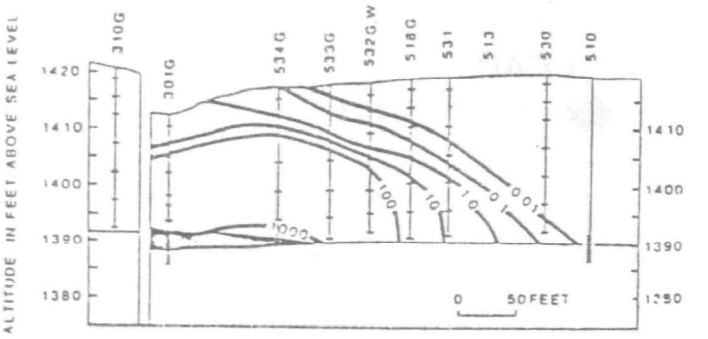


RLJ3D1-11

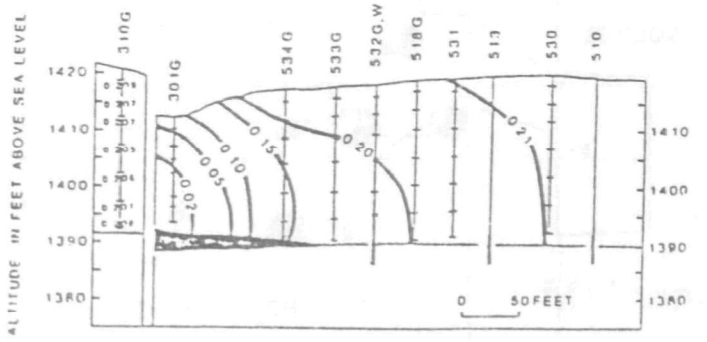
B)



RLJ3D1-12



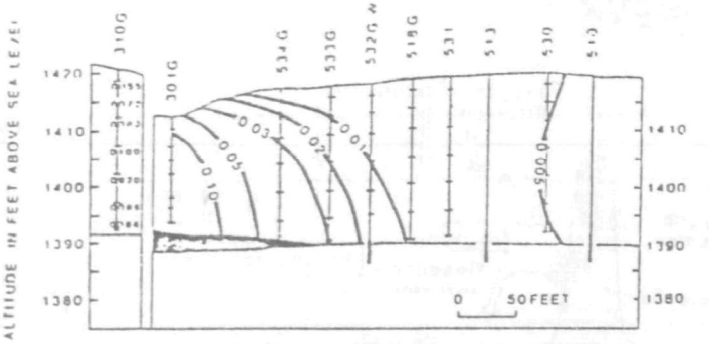
TOTAL VOLATILE HYDROCARBONS, g/m³



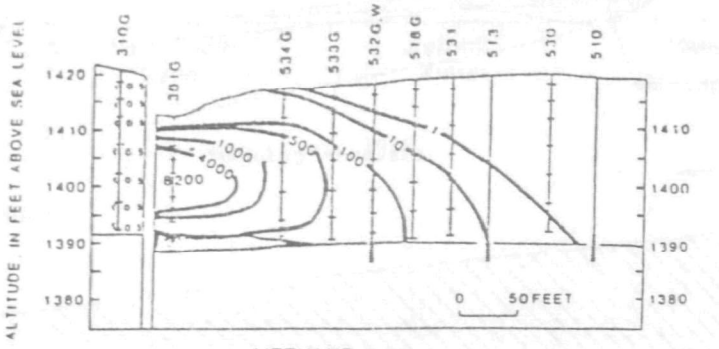
PARTIAL PRESSURE OXYGEN

Source: Hult et al., 1985.

RLJ3D1-13



PARTIAL PRESSURE CARBON DIOXIDE

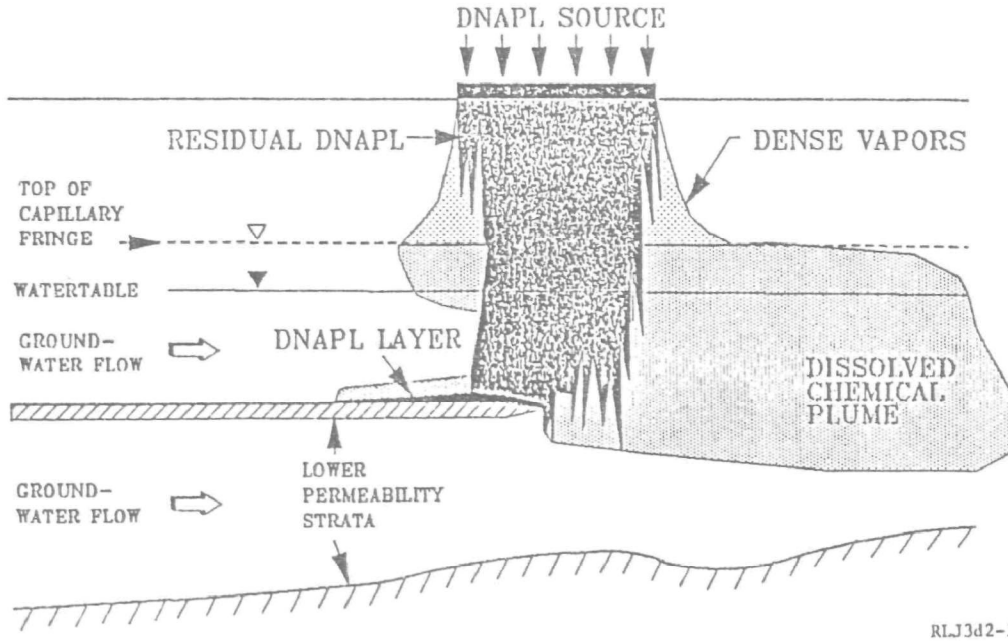


METHANE, ppm

Source: Hult et al., 1985.

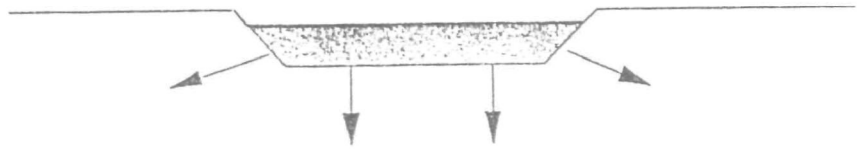
RLJ3D1-14

DNAPLs

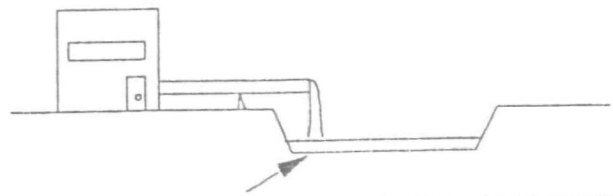


RLJ3d2-3

UNLINED CREOSOTE POND

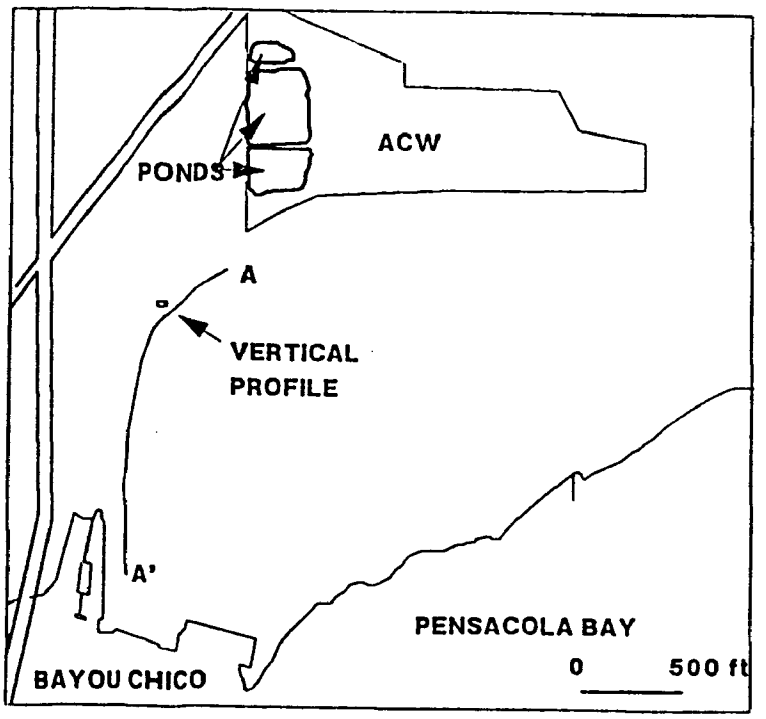


PRESSURE-TREATING FACILITY



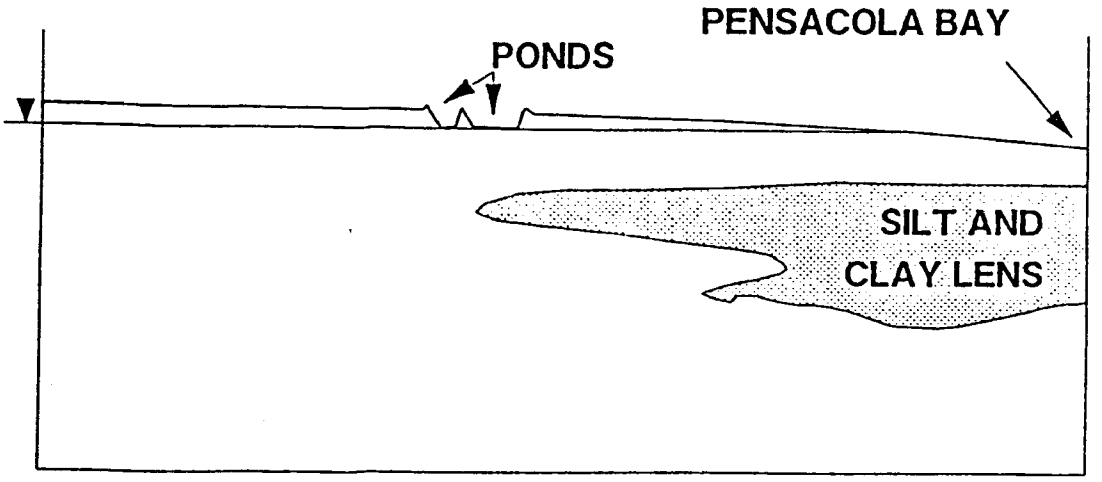
CREOSOTE, PENTA, WATER, AND DIESEL

RLJ3D3-1



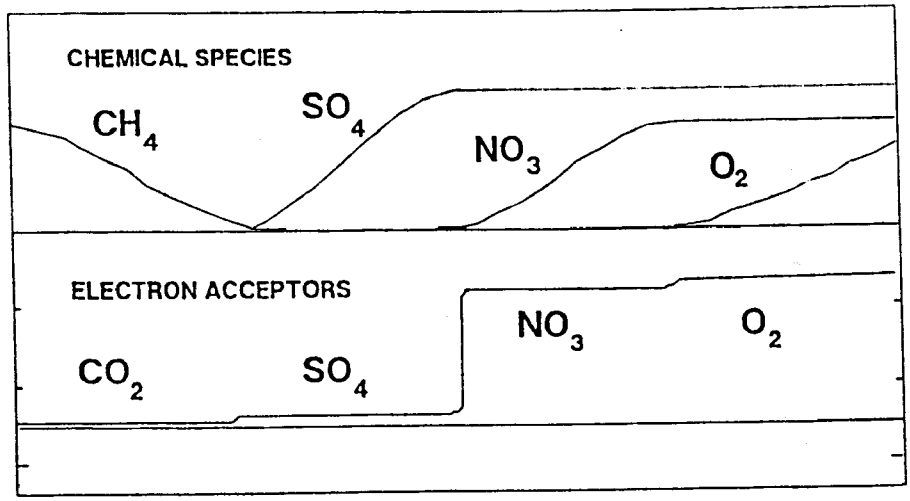
After Franks et al., 1984.

RLJ3D3-2

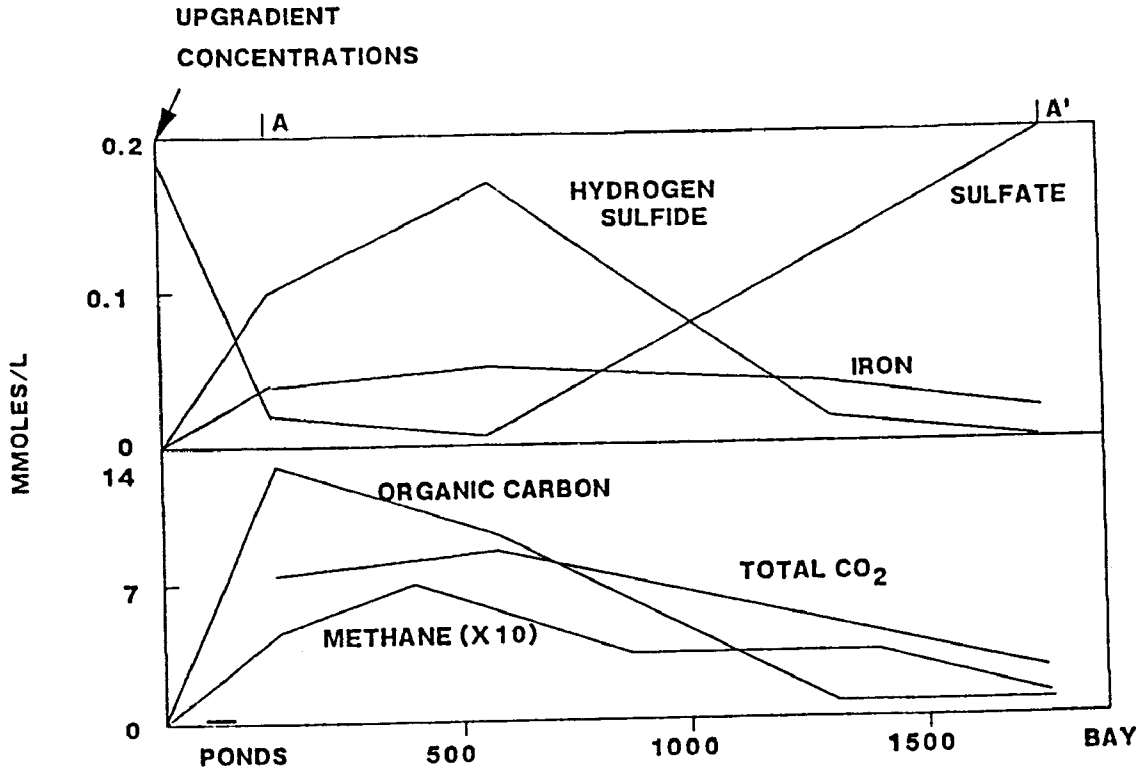


After Baedecker et al. 1985.

RLJ3D3-3

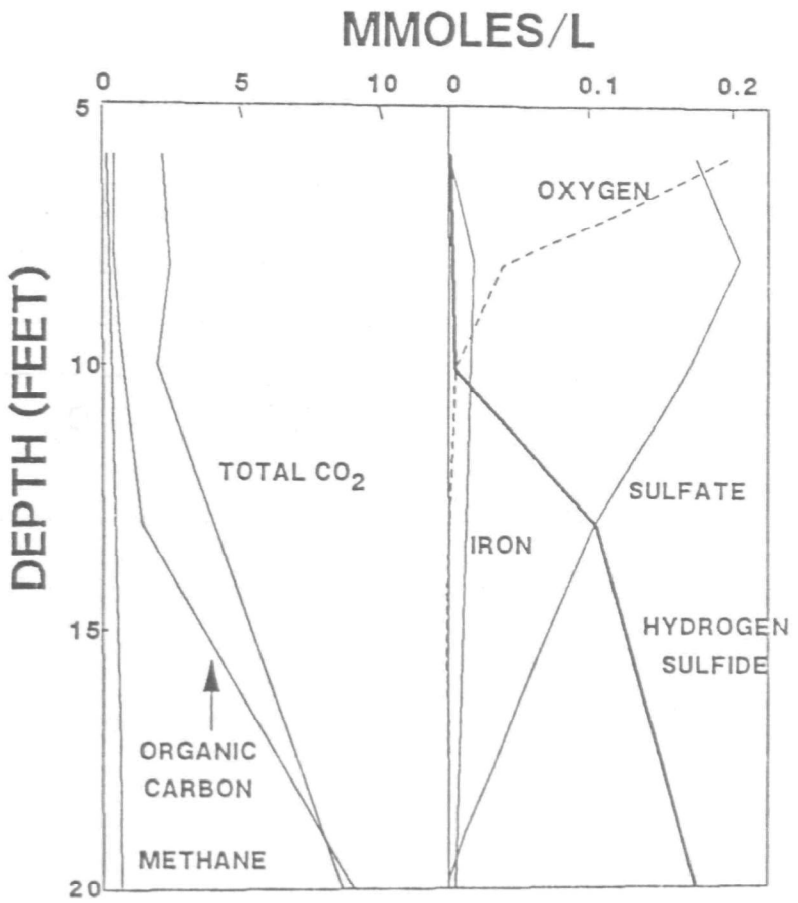


RLJ3D3-4



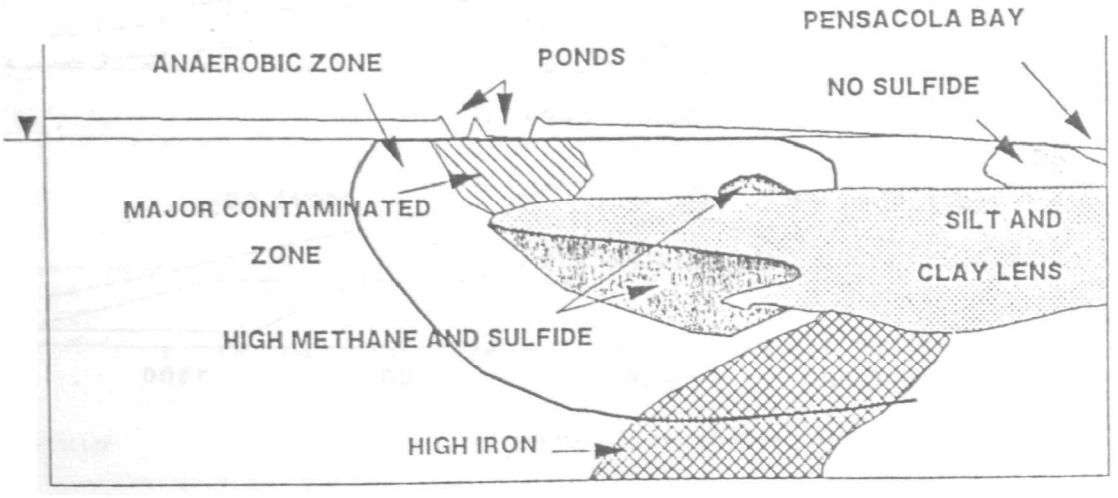
After Baedecker et al., 1985.

RLJ3D3-5



After Baedecker et al., 1985.

RLJ3D3-6



After Baedecker et al., 1985.

RLJ3D3-7

TRANSPORT AND FATE

CHEMICAL PROCESSES

Session 4

Richard L. Johnson

(Oregon Graduate Center)

GROUNDWATER SAMPLING

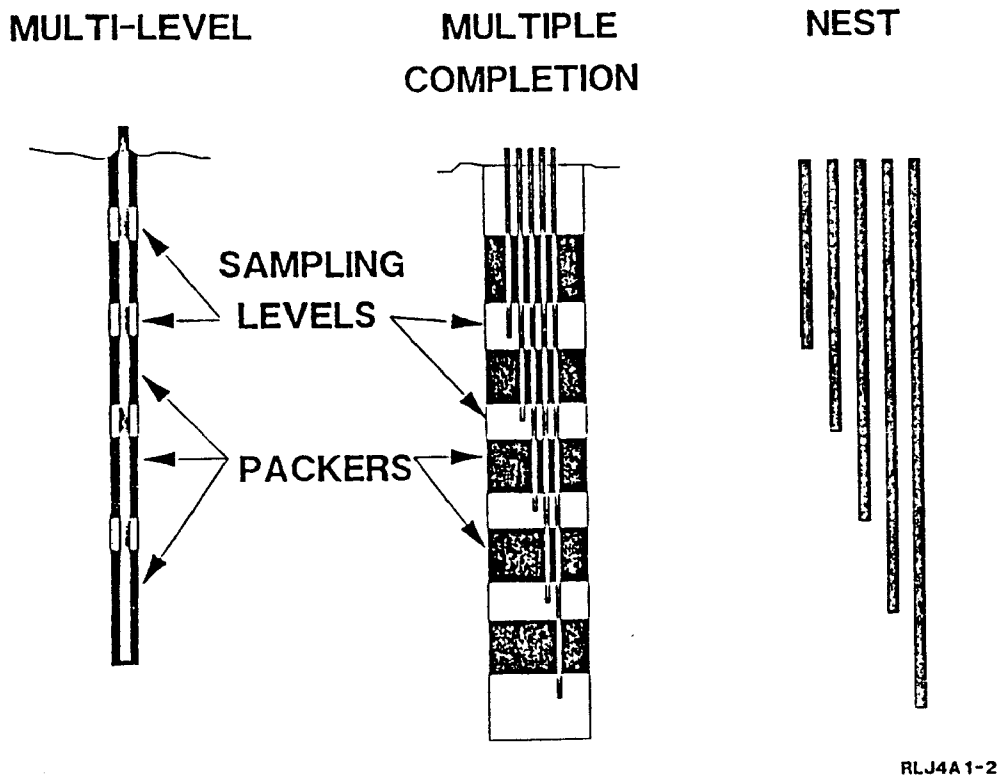
- SAMPLING USING MONITORING WELLS
- SAMPLING USING CORING TECHNIQUES
- SAMPLING IN THE UNSATURATED ZONE

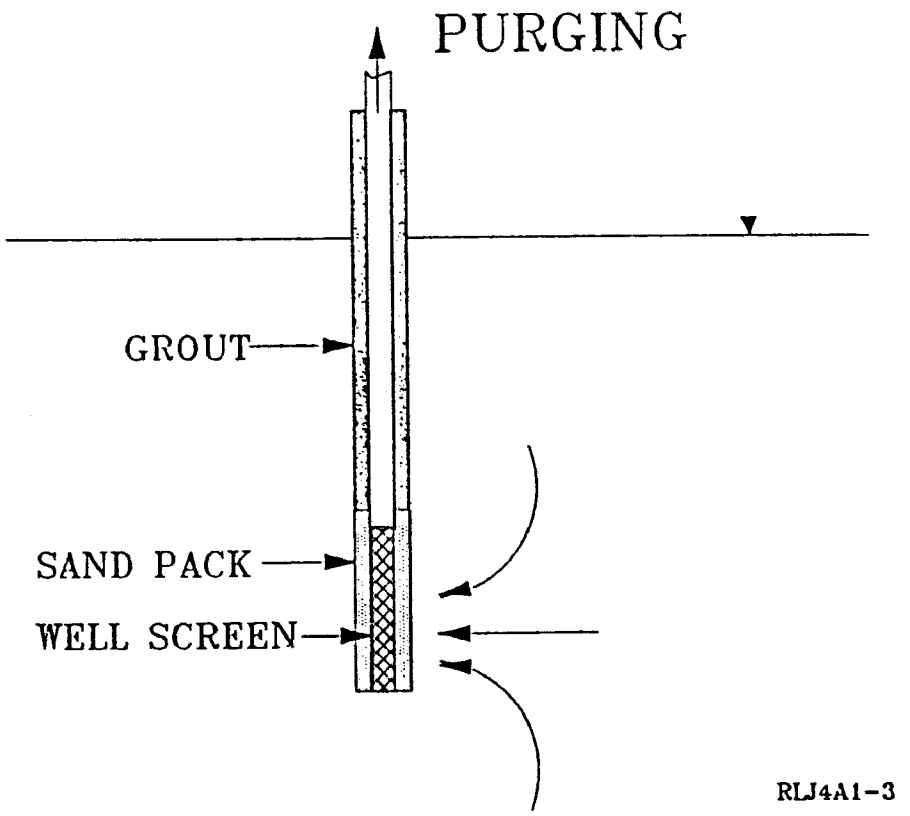
RLJ4A-1

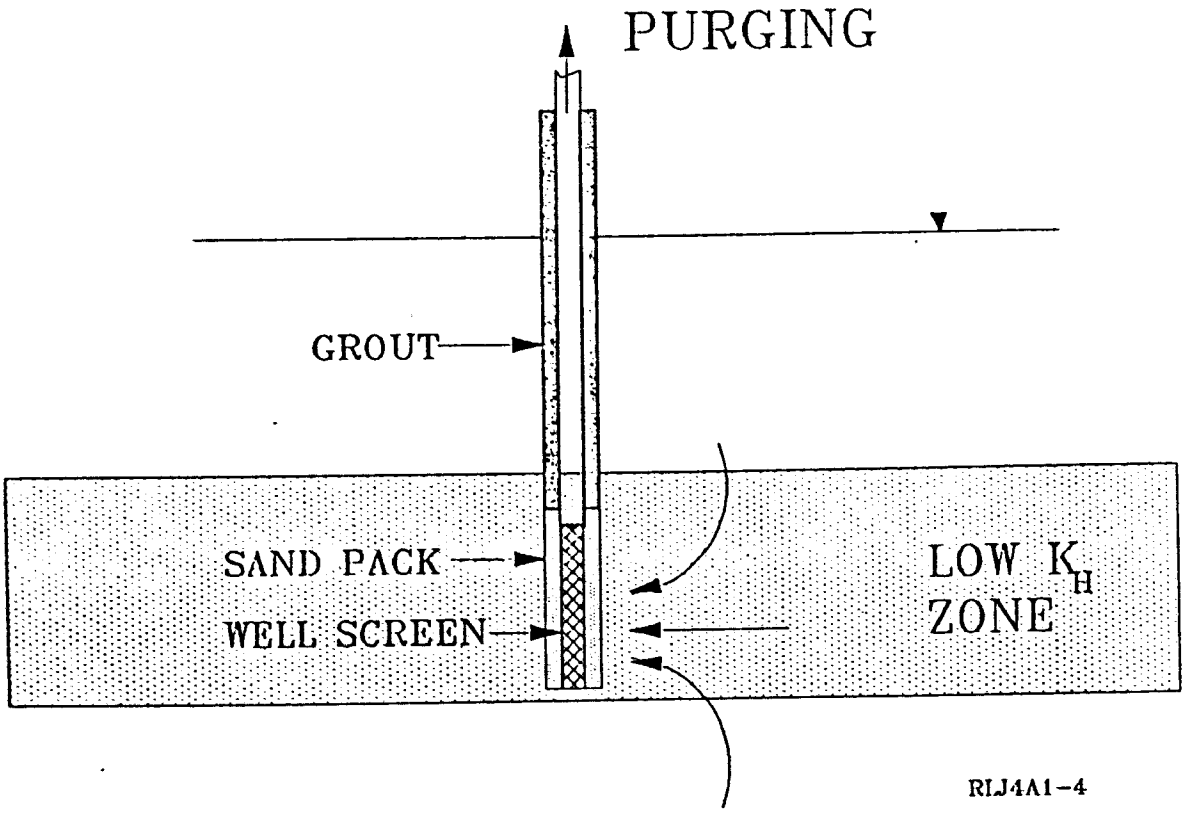
SAMPLING USING MONITORING WELLS

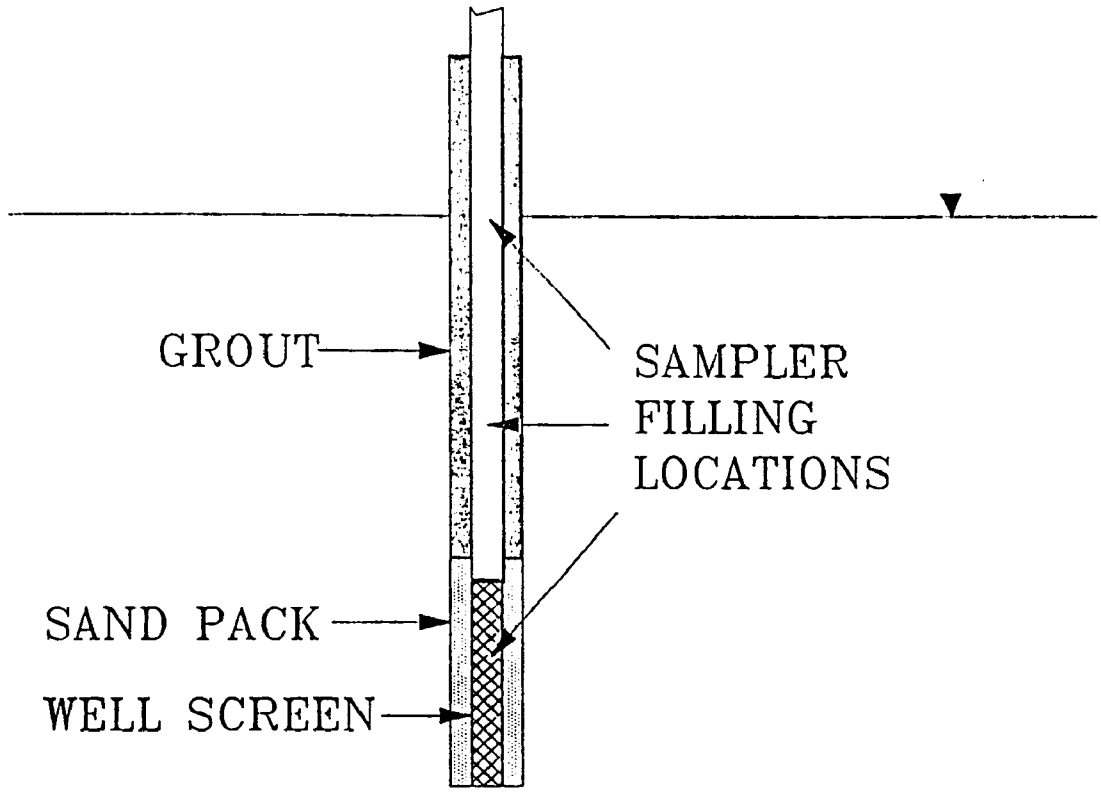
- WELL PLACEMENT
- WELL DESIGN
- WELL PURGING
- SAMPLING AND STORAGE

RLJ4A1-1

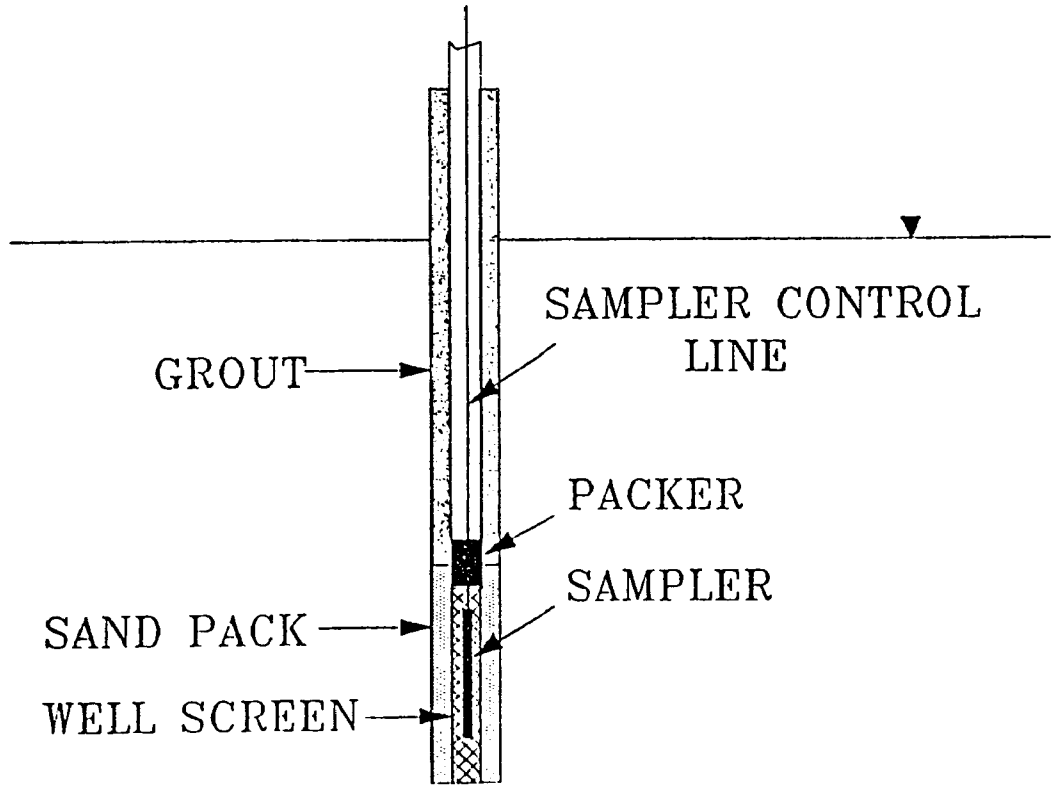

MULTI-LEVEL
MULTIPLE COMPLETION
NEST
SAMPLING LEVELS
PACKERS
RLJ4A1-2


PURGING
GROUT
SAND PACK
WELL SCREEN
RLJ4A1-3

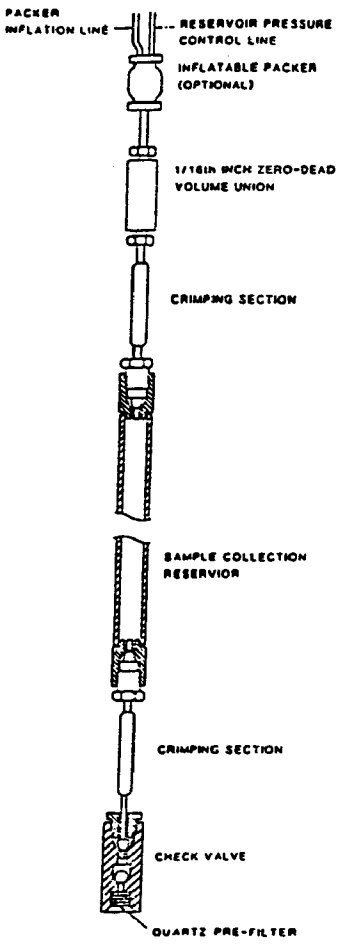

PURGING
GROUT
SAND PACK
WELL SCREEN
LOW K_H
ZONE
RLJ4A1-4



RLJ4A1-5



RLJ4A1-6



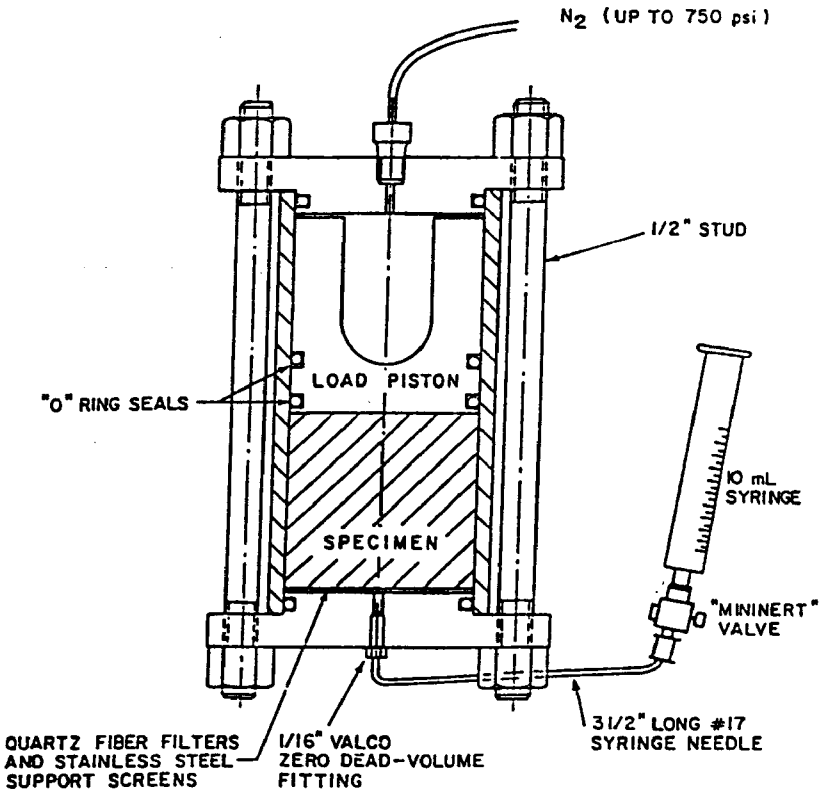
Example of a small-diameter reservoir sampler (Johnson et al. 1987)

RLJ4A1-7

SAMPLING USING CORING TECHNIQUES

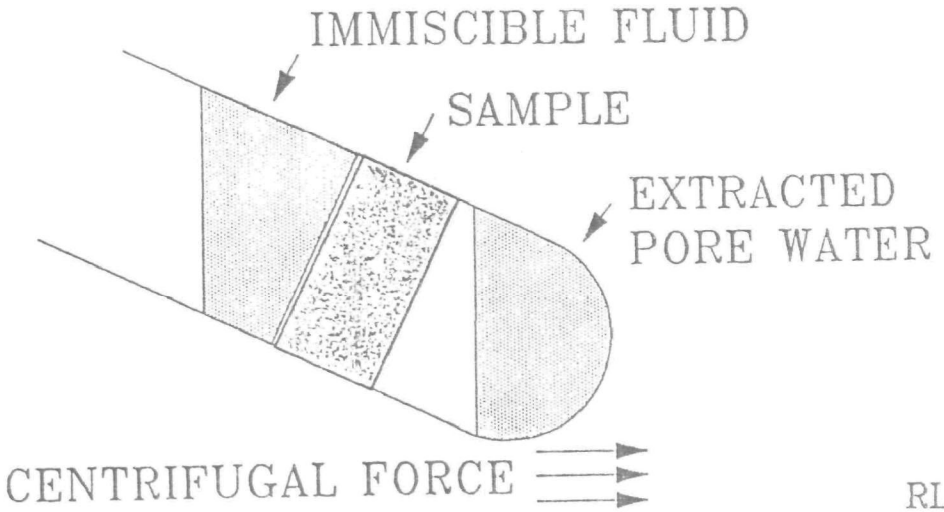
- CORING AND SQUEEZING
- CORING AND DISPLACEMENT
- CORING AND EXTRACTION
- CORING FOR MICROBIOLOGY
- FREEZE–CORING

RLJ4A2-1

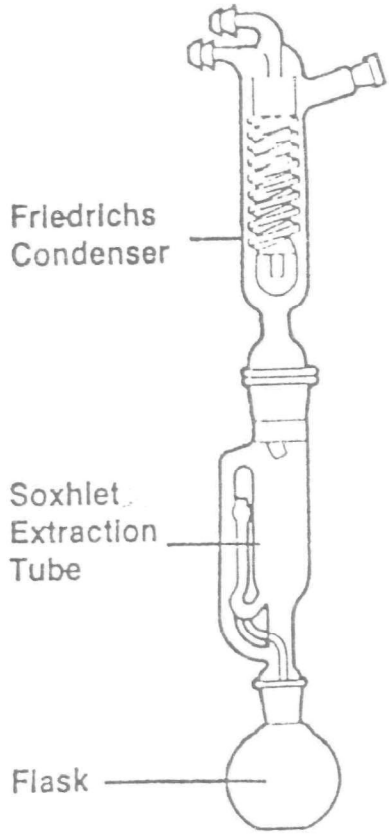

N_2 (UP TO 750 psi)
1/2" STUD
LOAD PISTON
"O" RING SEALS
SPECIMEN
10 mL SYRINGE
"MININERT" VALVE
3 1/2" LONG #17 SYRINGE NEEDLE
QUARTZ FIBER FILTERS AND STAINLESS STEEL SUPPORT SCREENS
1/16" VALCO ZERO DEAD-VOLUME FITTING

RLJ4A2-2

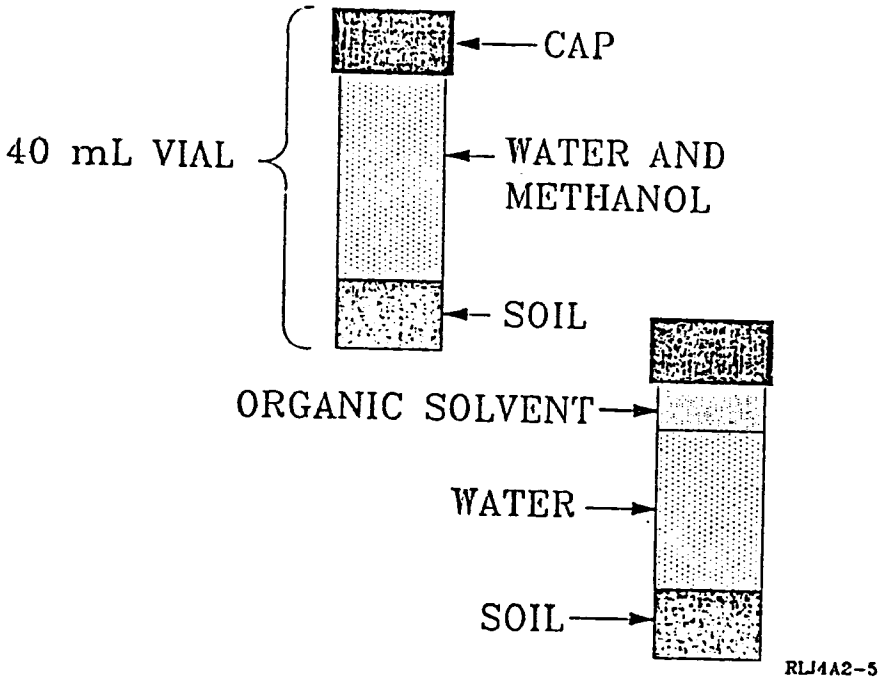
PORE-WATER EXTRACTION BY DISPLACEMENT



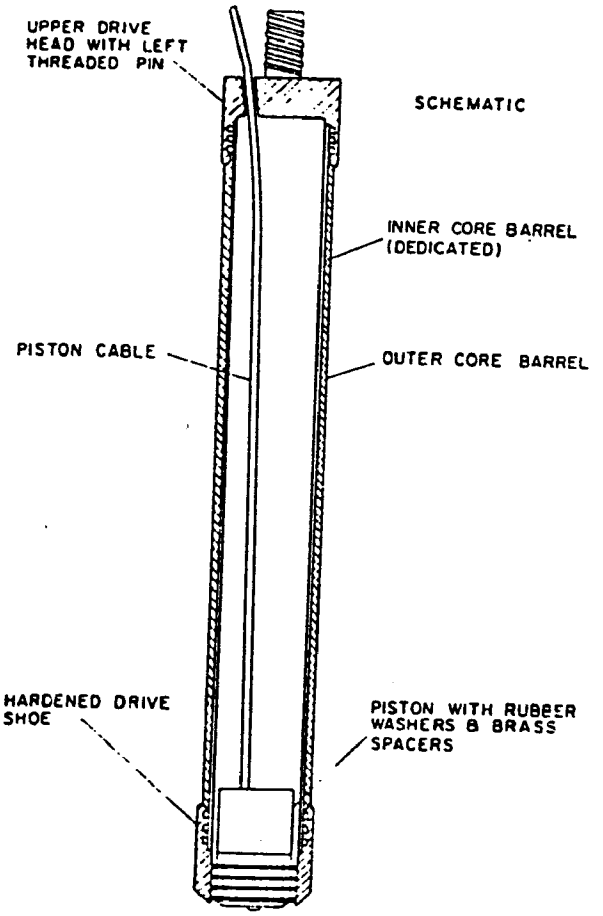
RLJ4A2-3



RLJ4A2-4

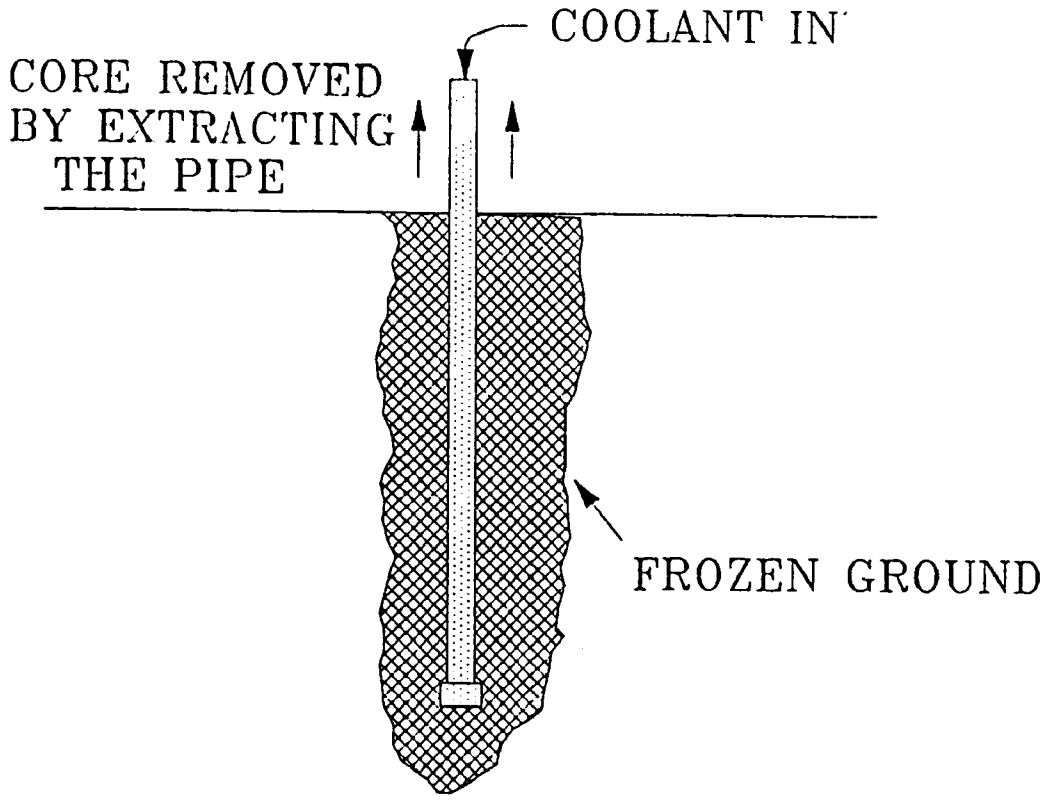


RLJ4A2-5



Source: Zapeco et al., 1987.

RLJ4A2-6



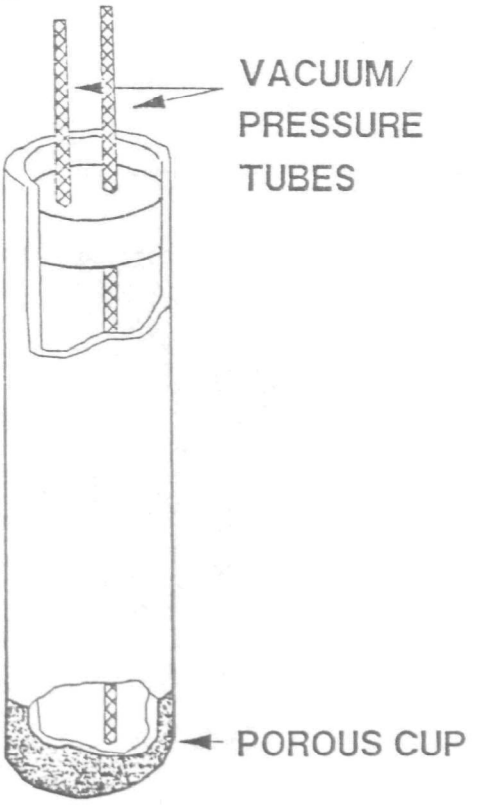
RLJ4A2-7

SAMPLING IN THE UNSATURATED ZONE

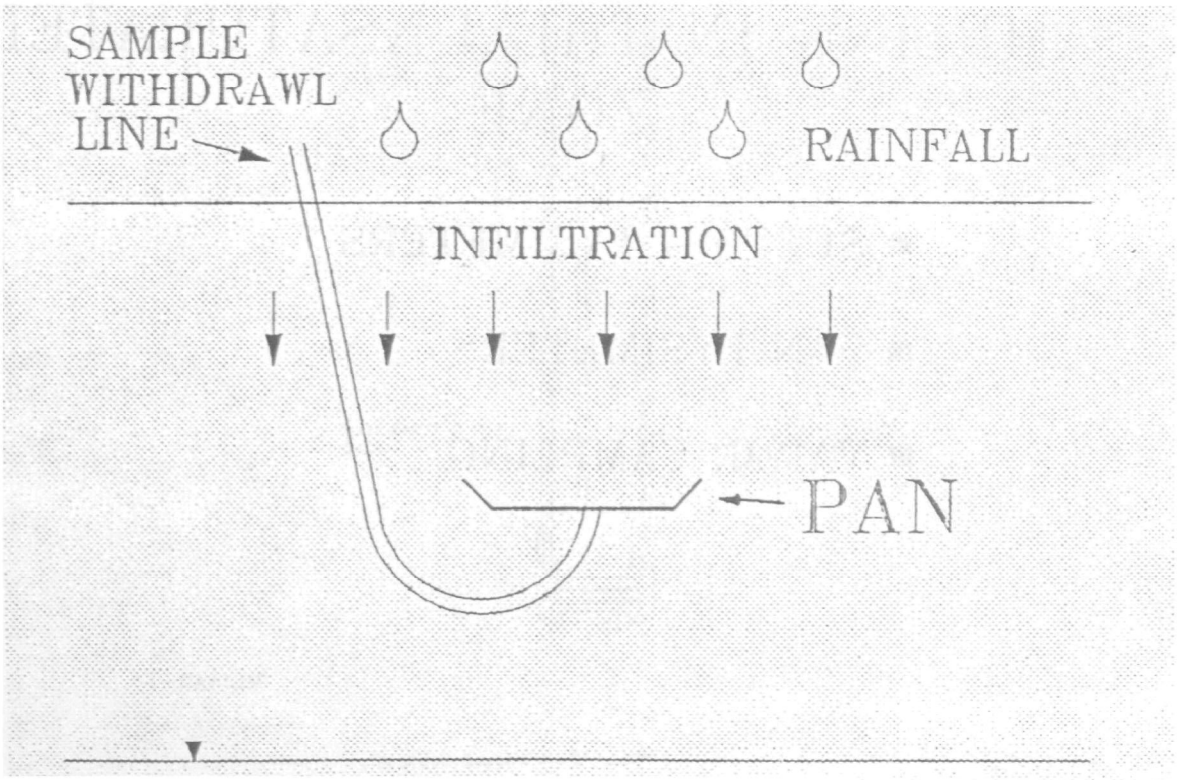
- SUCTION LYSIMETERS
- PAN LYSIMETERS
- VAPOR SAMPLING

RLJ4A3-1

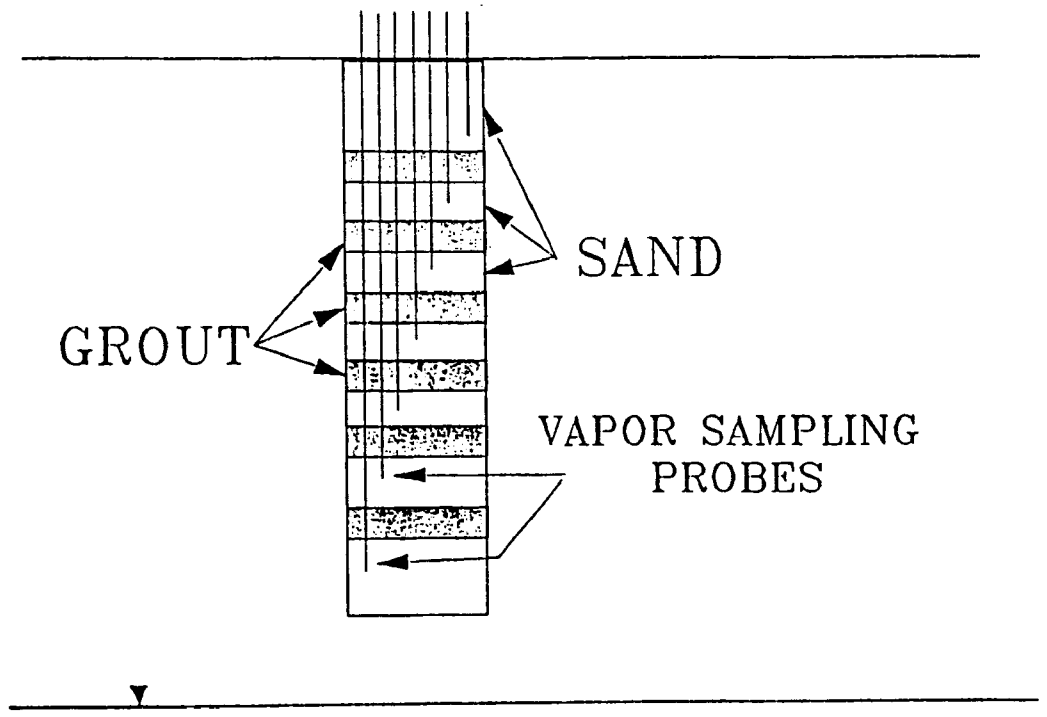
SUCTION LYSIMETER



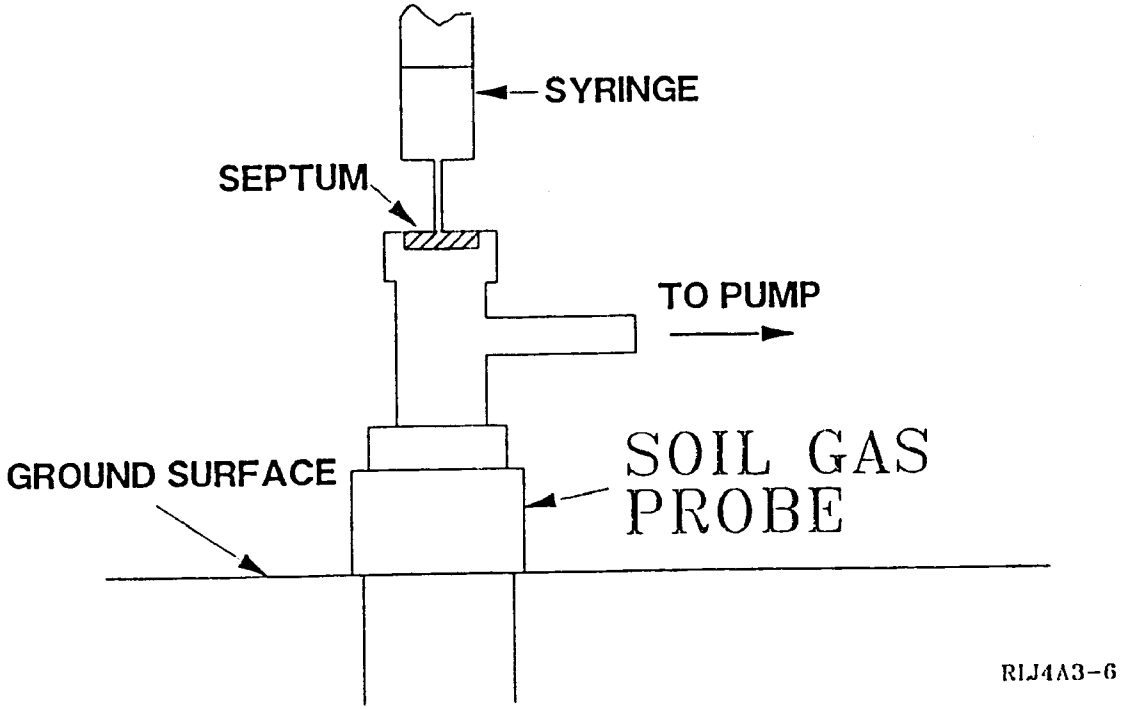
RLJ4A3-2



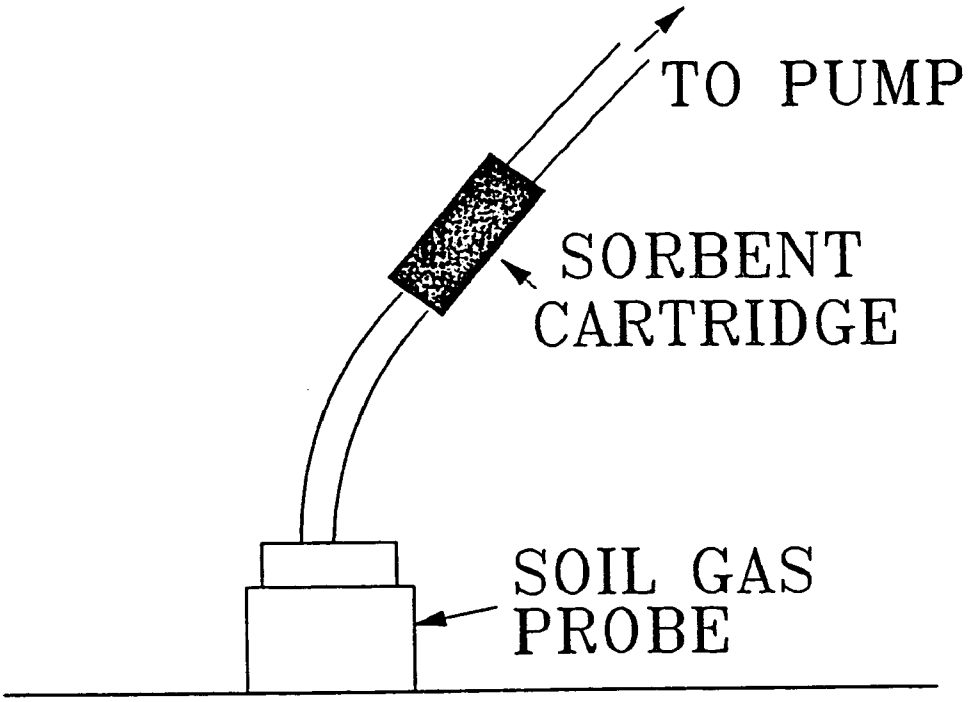
RLJ4A3-3



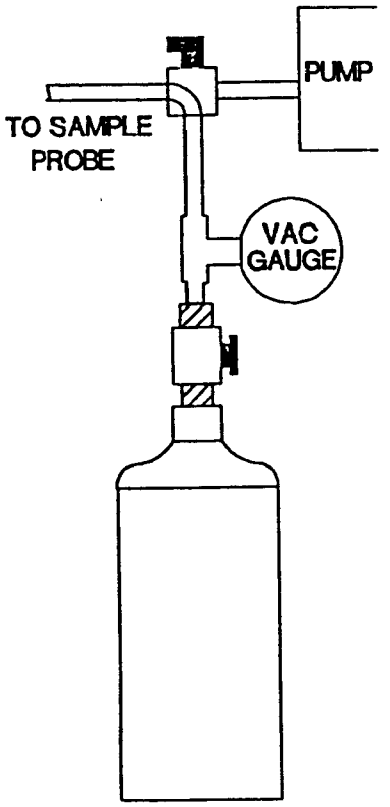
RLJ4A3-4



RLJ4A3-6



RLJ4A3-7



RLJ4A3-8

EXPERIMENTAL METHODS -CHEMICAL

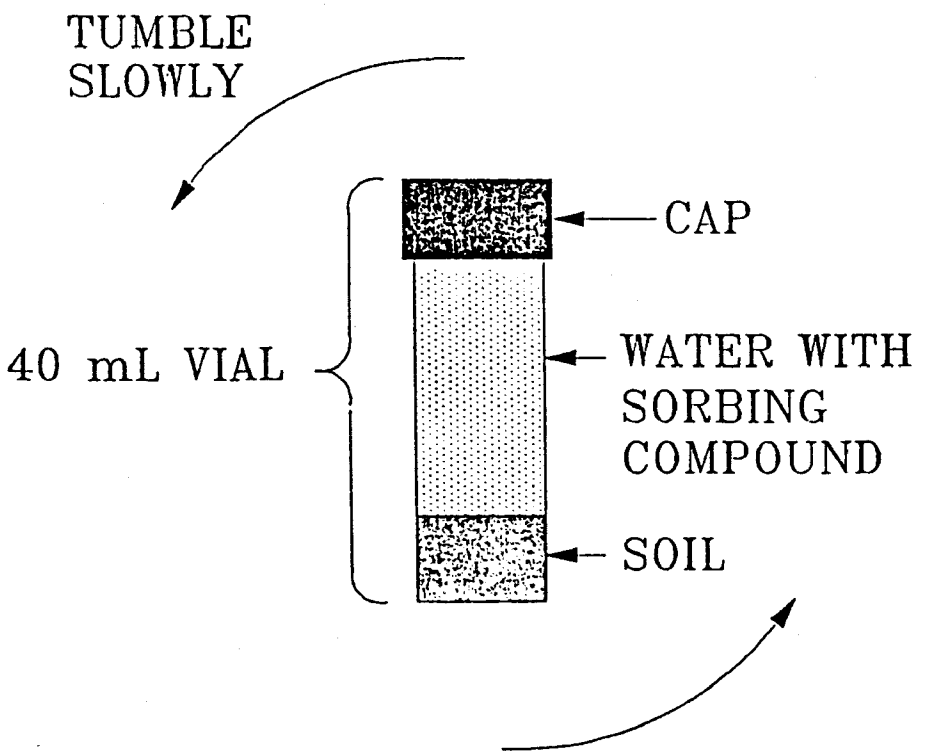
- LABORATORY METHODS
- FIELD METHODS

RLJ4C-1

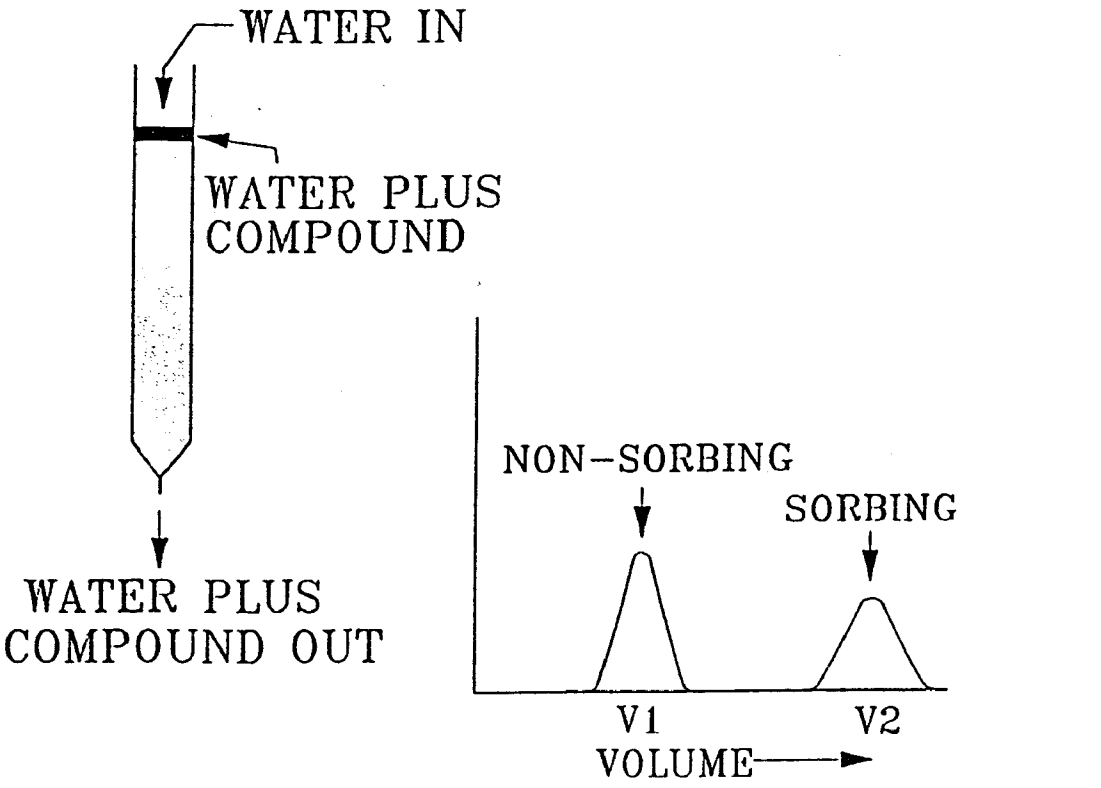
EXPERIMENTAL METHODS - LABORATORY

- SORPTION
- VOLATILIZATION
- DIFFUSION
- ION EXCHANGE
- HYDROLYSIS
- DIAGENESIS
- COMPLEXATION
- DEGRADATION
- DISSOLUTION/PRECIPITATION

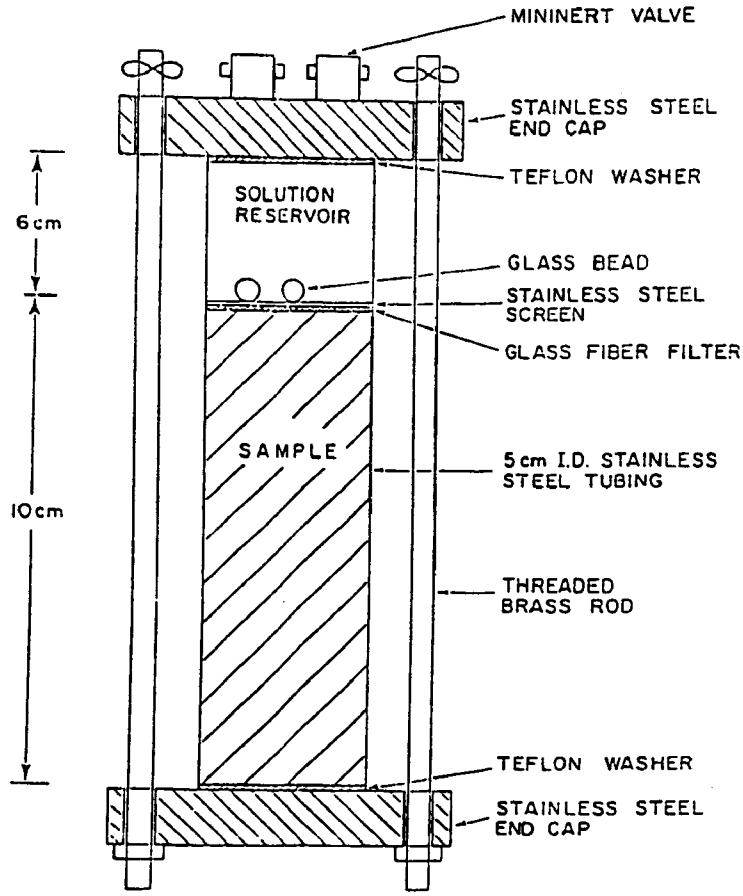
RLJ4C1-1



RLJ4C1-2



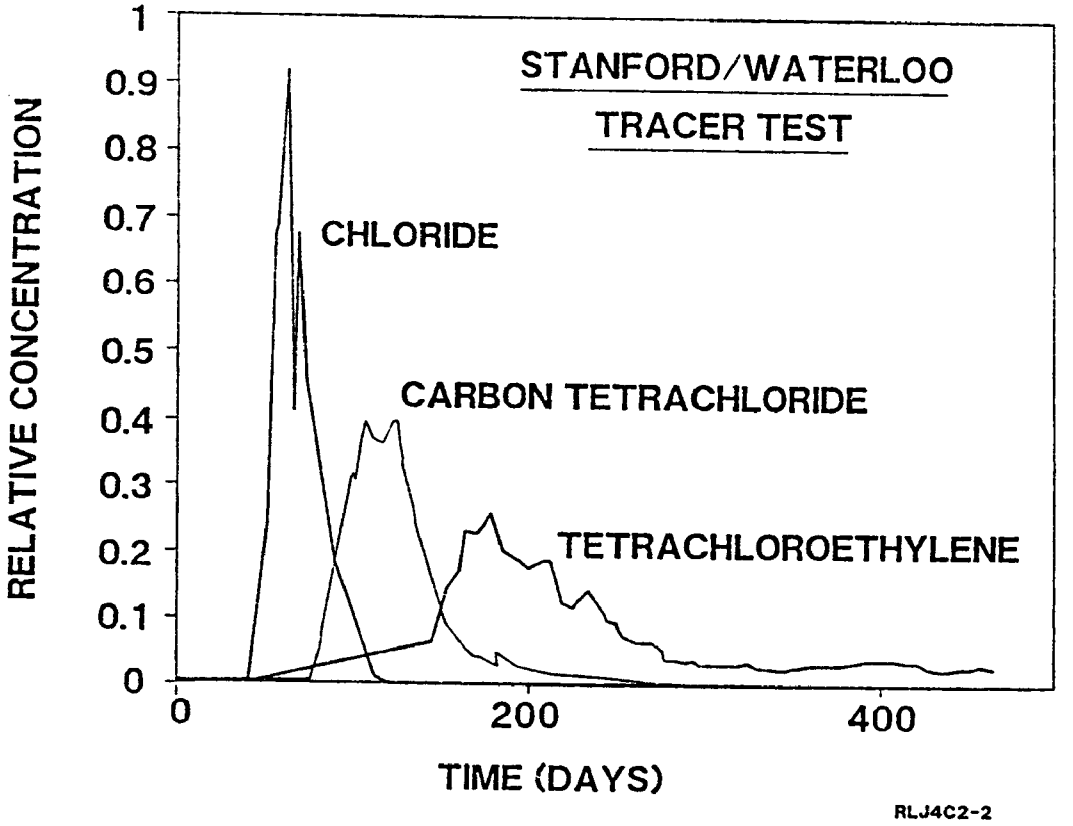
RLJ4C1-3



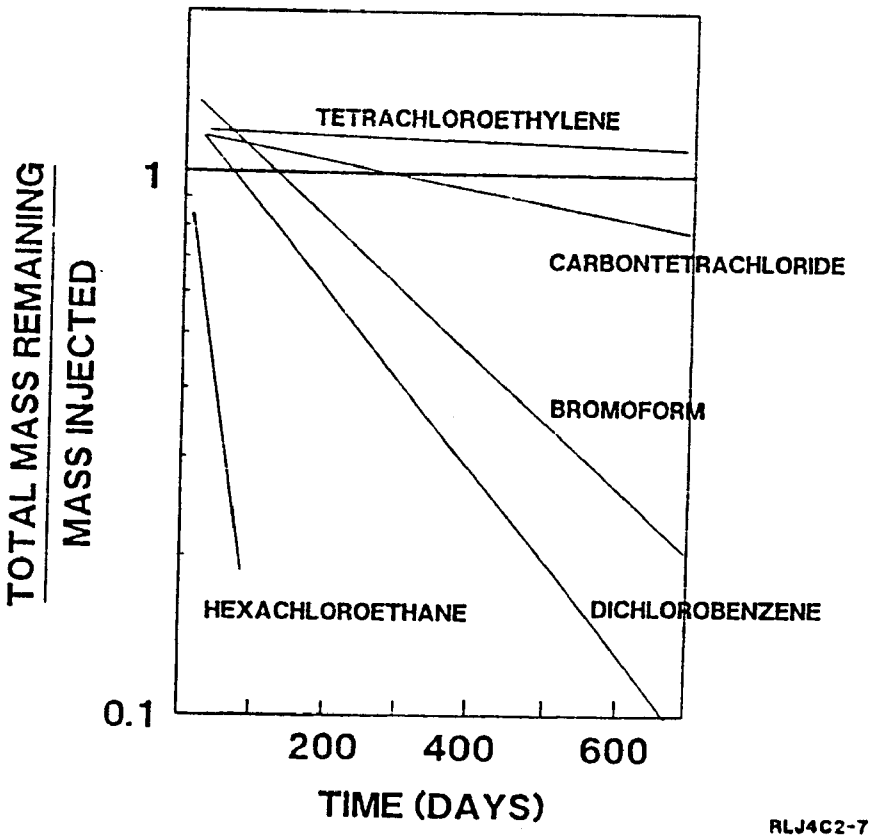
RLJ4C1-4

EXPERIMENTAL METHODS – FIELD

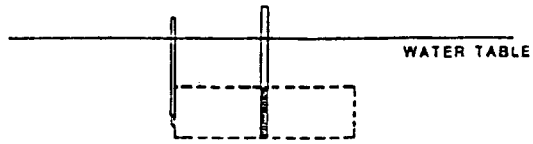
- SORPTION
- DEGRADATION
- DIFFUSION
- OTHER REACTIONS



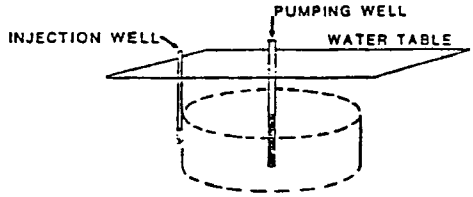
After Roberts et al., 1986.

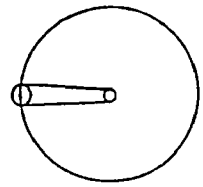


After Roberts et al., 1986.



Cross-Section

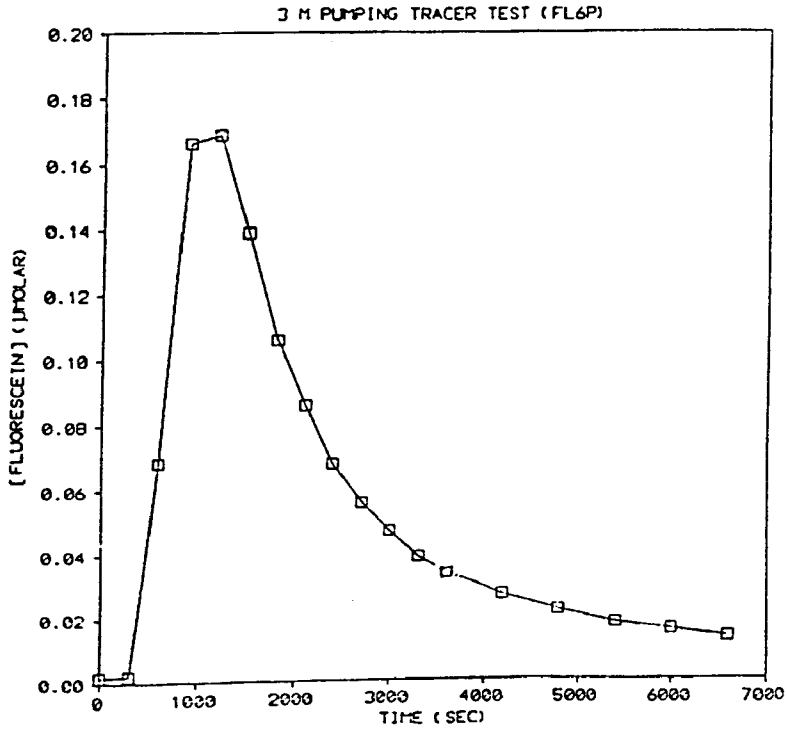




Plan View

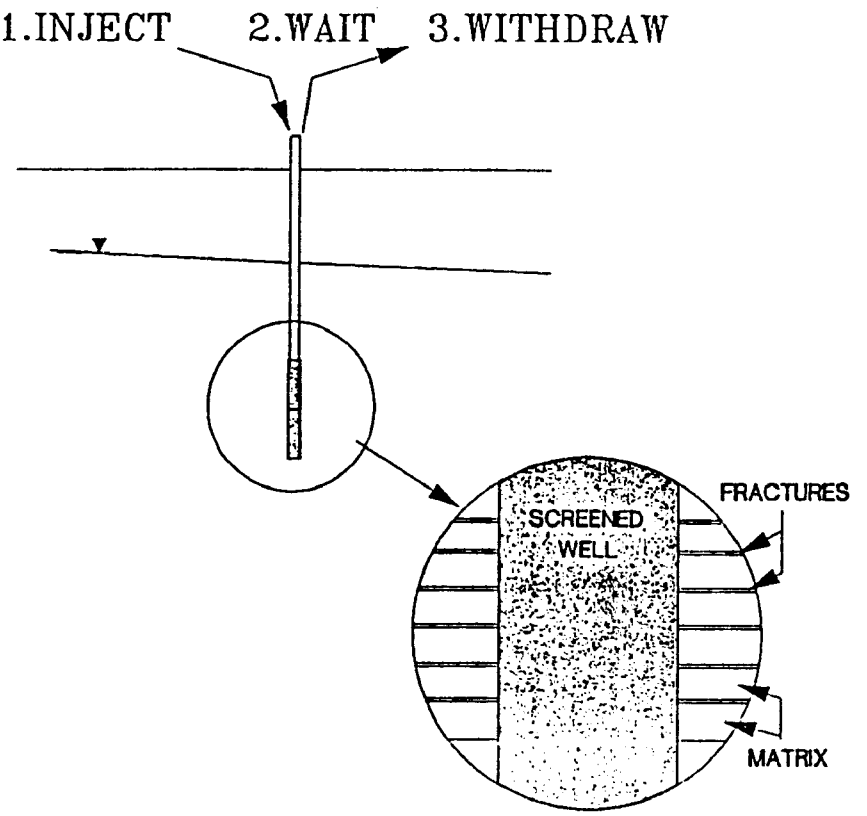
Source Johnson, 1984.

RLJ4C2-3

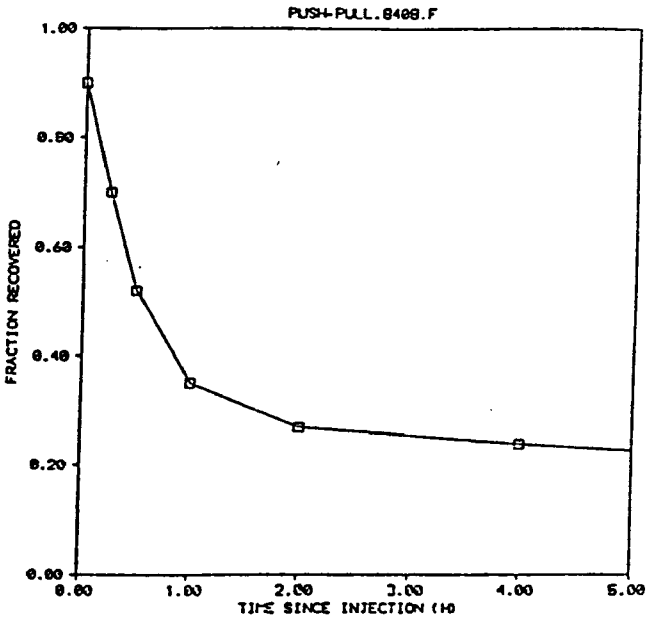


RLJ4C2-4

Source: Johnson, 1984.



RLJ4C2-5



Fraction of mass recovered during pumping versus residence time of the tracer in the ground prior to beginning of pumping for the "push-pull" tests using fluorescein.

Source: Johnson, 1984.

RLJ5C2-6

RESEARCH FRONTIERS

- INDICATOR COMPOUNDS
- SORPTION EXPERIMENTS
- PARTICLE TRANSPORT
- SOLVENT/CLAY INTERACTIONS
- DIFFUSION IN CLAY
- UNSATURATED ZONE VAPOR MOVEMENT
- ANALYTICAL METHODS DEVELOPMENT

RIJ4D-1

INDICATOR COMPOUNDS FOR COMPLIANCE MONITORING

- CONSERVATIVE AND NON-REACTIVE
- UNIQUE TO THE WASTE MATERIALS
- REPRESENTATIVE OF THE WASTE MATERIALS

RIJ4D1-1

COMMON INDICATOR COMPOUNDS

- Chloride
- Bromide
- TOC
- TOX
- Halogenated Aliphatic Hydrocarbons

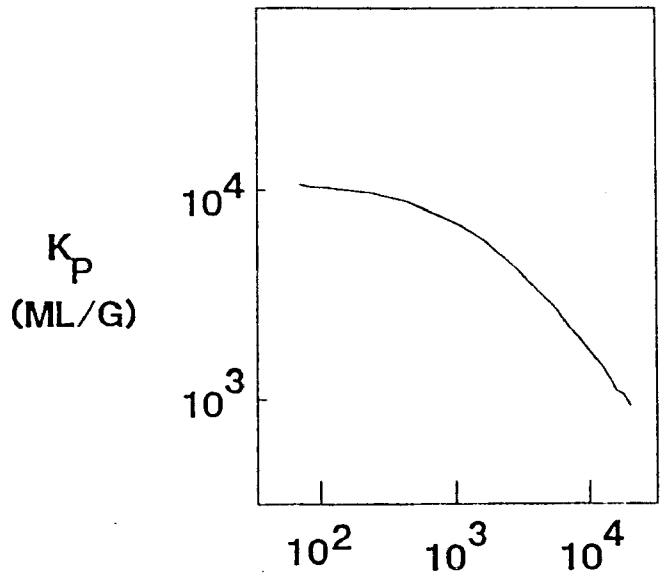
RLJ4D1-2

SORPTION EXPERIMENTS

- K_p = F(SOIL/WATER)?
- NON-SETTLING PARTICLES
- IRREVERSIBLE SORPTION
- SORPTION OF NON-HYDROPHOBIC COMPOUNDS

RLJ4D2-1

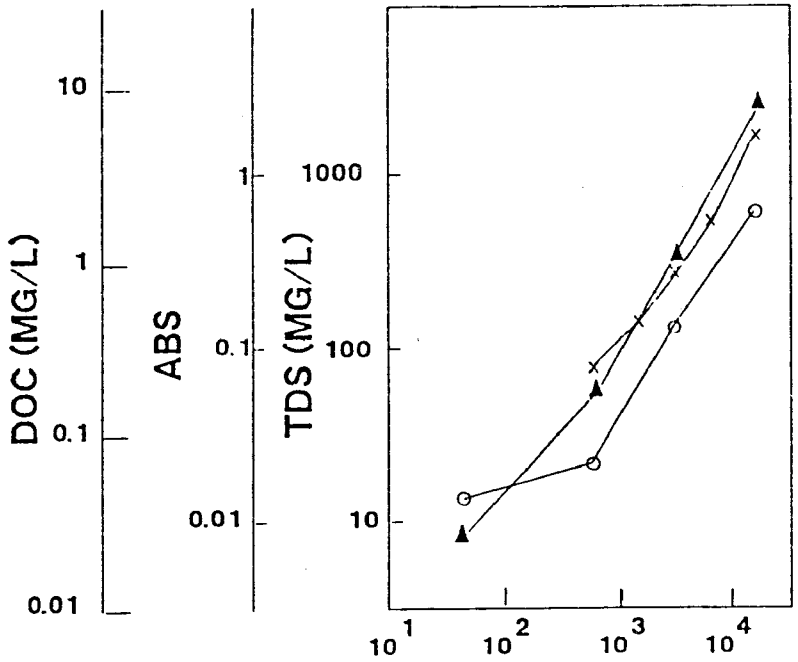
2,3,4,5,6,2',5'-HEPTACHLOROBIPYENYL



SEDIMENT CONCENTRATION
(MG/L)

After Gschwend and Wu, 1985.

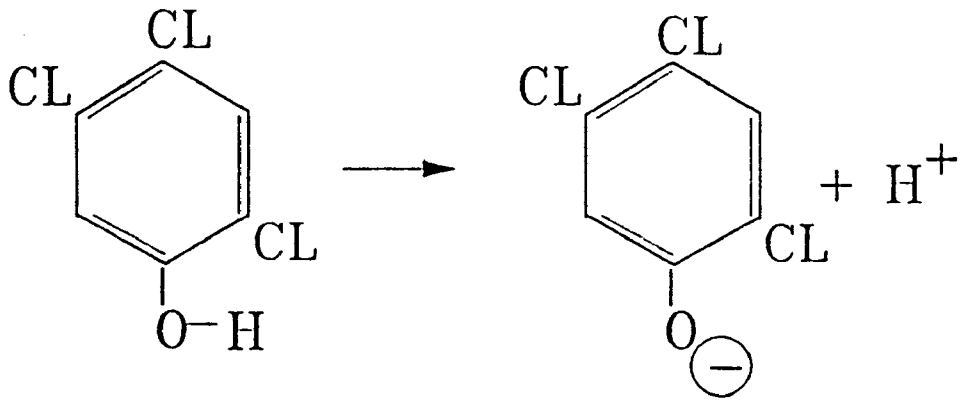
RLJ4D2-2



SEDIMENT CONCENTRATION
(MG/L)

RLJ4D2-3

After Gschwend and Wu, 1985.



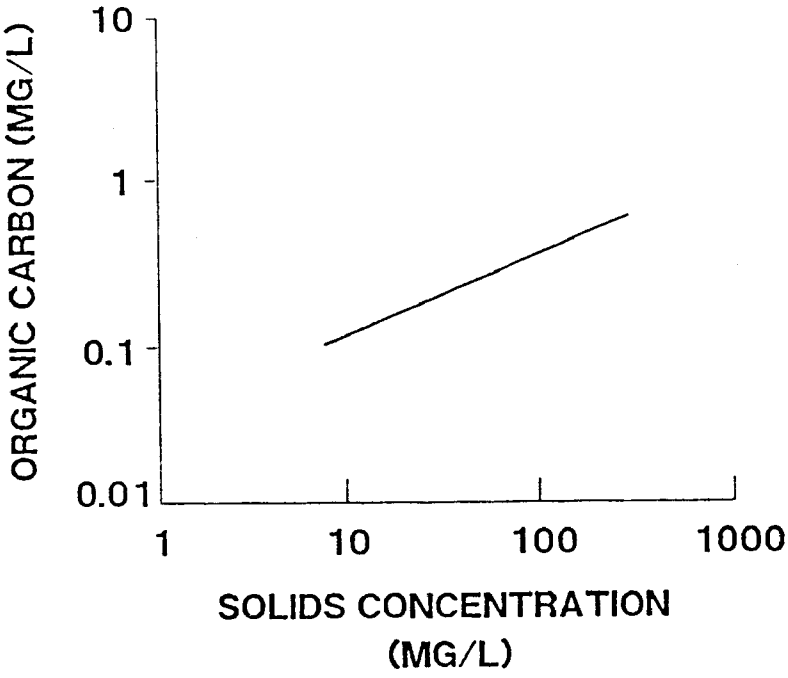
$K_{oc}=2330$ $K_{oc}\sim 0$

RLT4D2-4

PARTICLE TRANSPORT

- MICROPARTICLES, COLLOIDS, AND MACROMOLECULES
- TRANSPORT OF INORGANICS
- TRANSPORT OF ORGANICS

RLJ4D3-1



RLJ4D3-2

WHEN IS PARTICLE TRANSPORT OF ORGANICS IMPORTANT?

EXAMPLE:

1. Mass of NSP = 100 mg/L
2. foc of NSP = 0.01
3. therefore, mass of C = 1 mg/L
4. if Koc = 10^6, then
   mass on NSP = mass in water
5 if Koc = 10^5, then
   mass on NSP = $\frac{\text{mass in water}}{10}$

PRIORITY POLLUTANTS WITH K_{oc} VALUES GREATER THAN 10^6

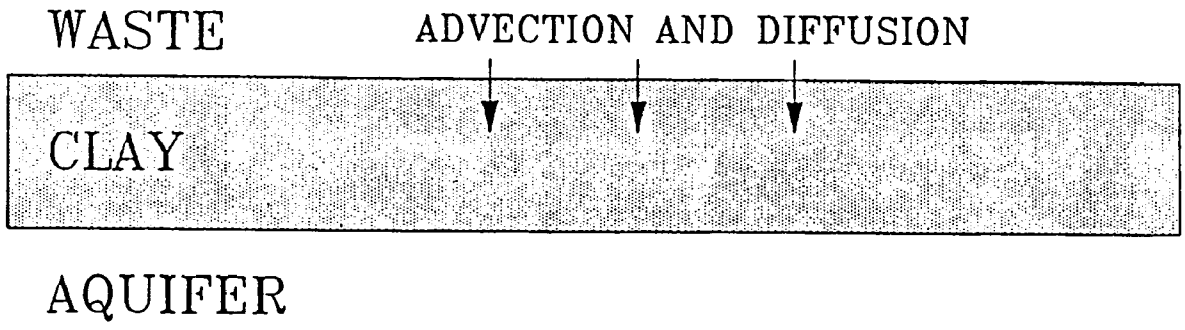
DDE	PAHs
DDT	TCDD
Aroclor 1260	
Toxaphene	
hexachlorobenzene	
Dioctyl phthalate	

RLJ4D3-4

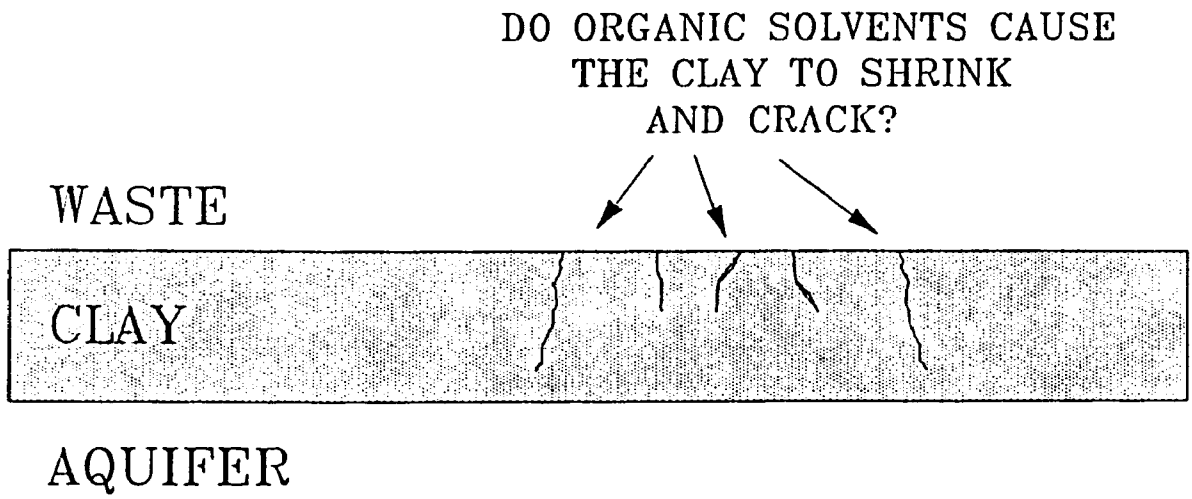
SOLVENT/CLAY INTERACTIONS

- PERMEABILITY CHANGES
- DIFFUSION

RLJ4D4-1



RLJ4D4-2

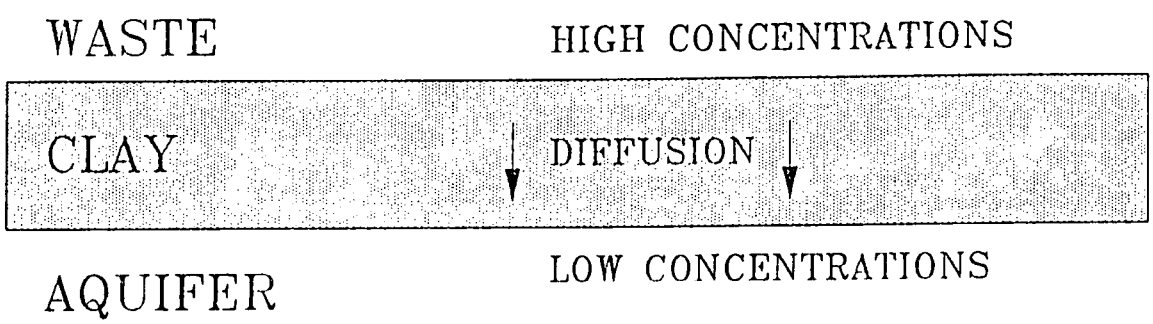


RLJ4D4-3

DIFFUSION IN CLAY

- DIFFUSION THROUGH LINERS
- RETARDATION
- SOLVENT/CLAY INTERACTIONS
- STEADY-STATE DIFFUSION
- DIFFUSION THROUGH AQUITARDS

RLJ4D5-1



RLJ4D5-2

DIFFUSION

FICKS SECOND LAW:

$$\frac{\partial C}{\partial t} = -\mathcal{T}\, n D_d \frac{\partial^2 C}{\partial x^2}$$

RLJ4D5-3

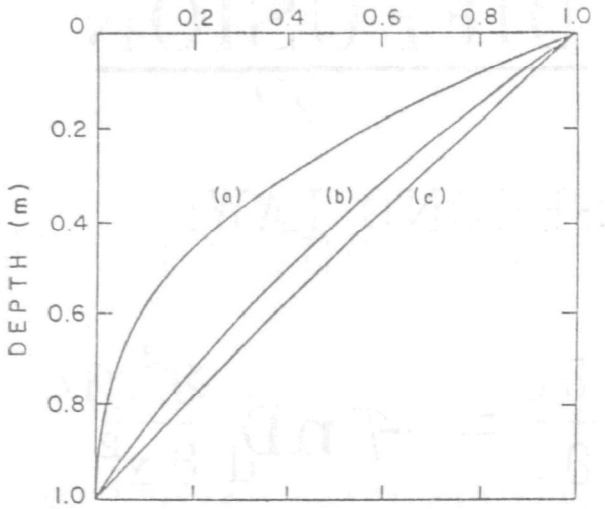
DIFFUSION

WITH SORPTION

FICKS SECOND LAW:

$$\frac{\partial C}{\partial t} = \frac{-\mathcal{T}\, n D_d}{R} \frac{\partial^2 C}{\partial x^2}$$

RLJ4D5-4

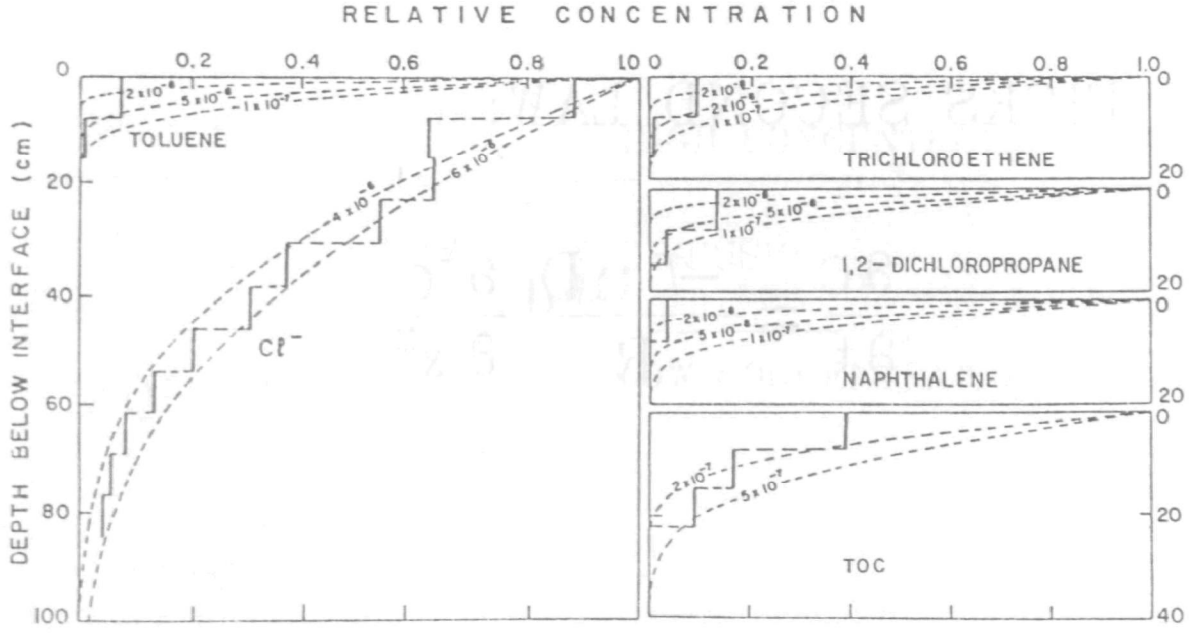


(a) D-4x10^{-6} cm^2/s; or D-2x10^{-7}; or D-2x10^{-8}
T-5 years T-100 T-1,000

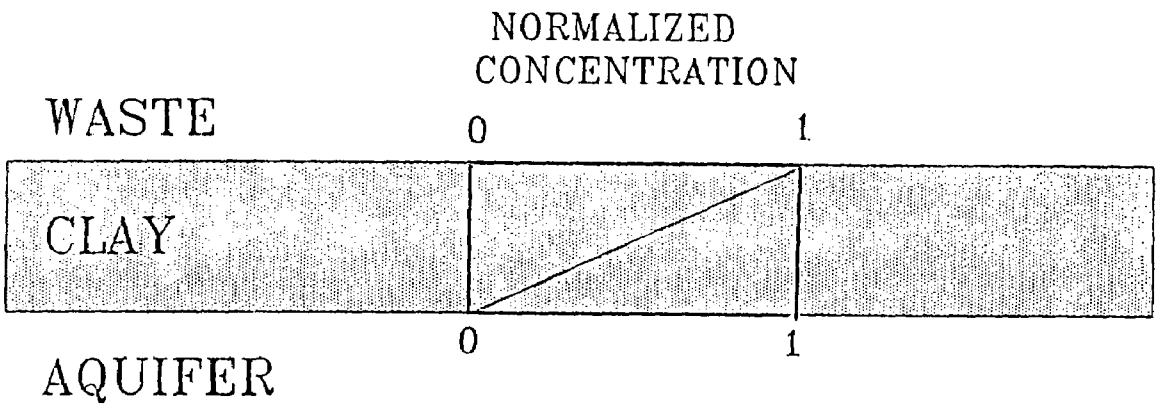
(b) D-4x10^{-6} cm^2/s; or D-2x10^{-7}; or D-2x10^{-8}
T-15 years T-300 T-3,000

(c) D-4x10^{-6} cm^2/s; or D-2x10^{-7}; or D-2x10^{-8}
T-25 years T-500 T-5,000

Source: Johnson et al., 1987b. RLJ 4D5-5



Source: Johnson et al., 1987. RLJ4D5-8



RLJ4D5-10

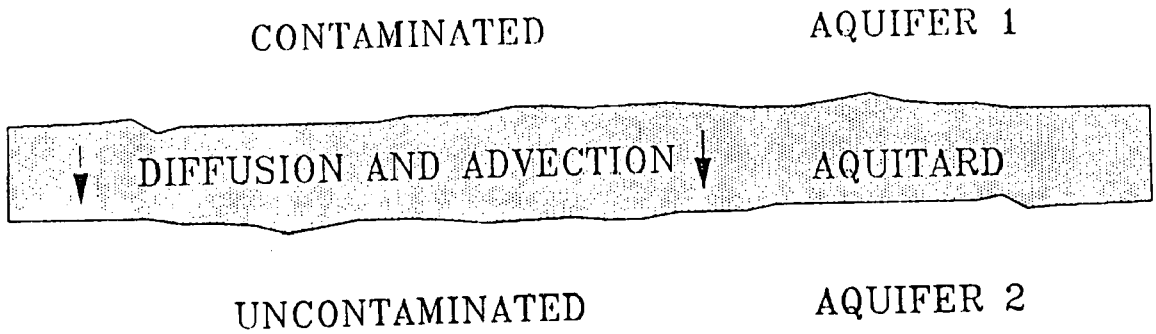
DIFFUSION

STEADY-STATE

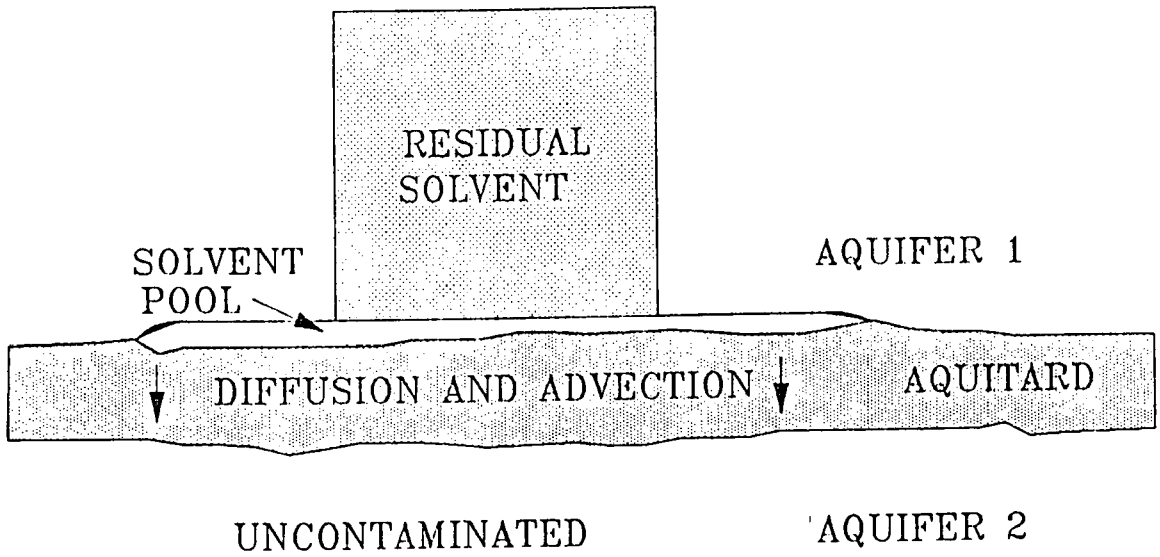
FICK'S FIRST LAW:

$$J_d = -\tau n D_d \frac{\partial C}{\partial x}$$

RLJD45-11



RLJ4D5-12



RLJ4D5-13

ANALYTICAL METHODS DEVELOPMENT

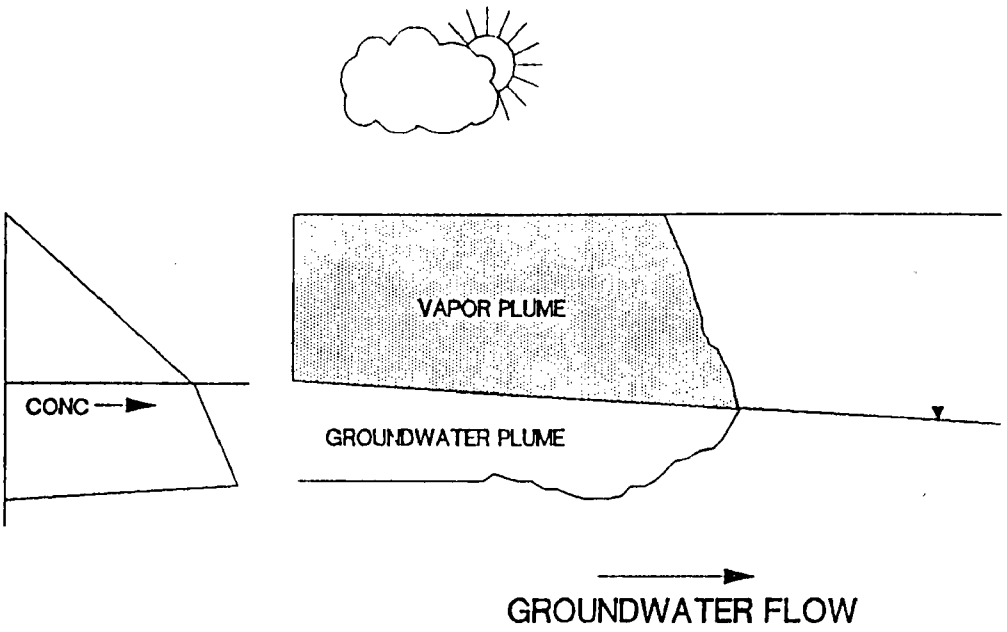
- ION CHROMATOGRAPHY
- IMPROVED VOLATILES ANALYSIS
- SUPERCRITICAL FLUID CHROMATOGRAPHY
- MS/MS/MS
- GC/MS/MS .....

RLJ4D6-1

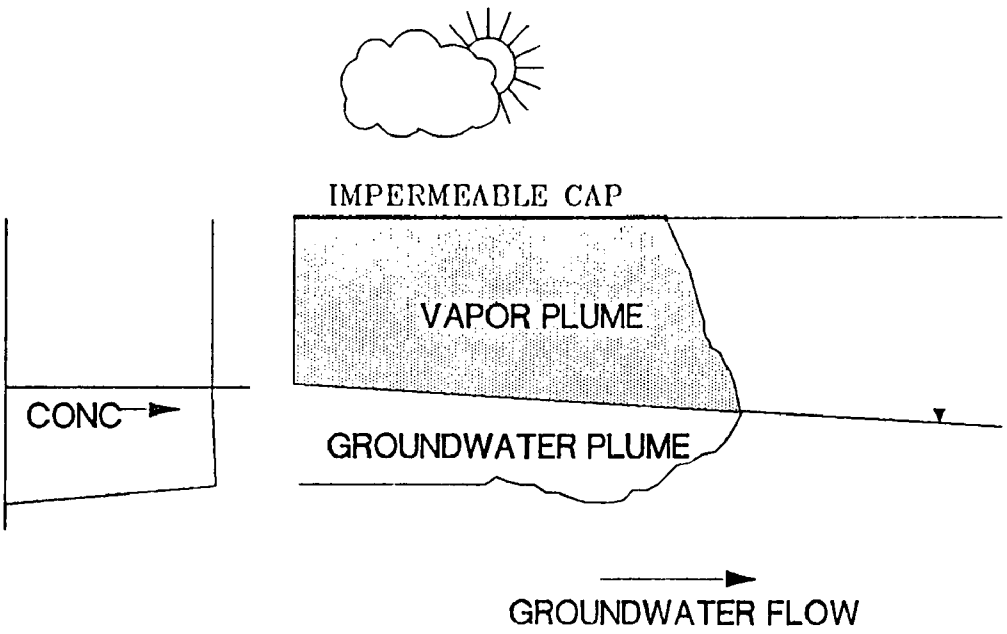
UNSATURATED ZONE VAPOR MOVEMENT

- "PLUME SNIFFING"
- PHYSICAL/CHEMICAL PROCESSES
- MICROBIOLOGICAL PROCESSES
- FLUX TO THE ATMOSPHERE

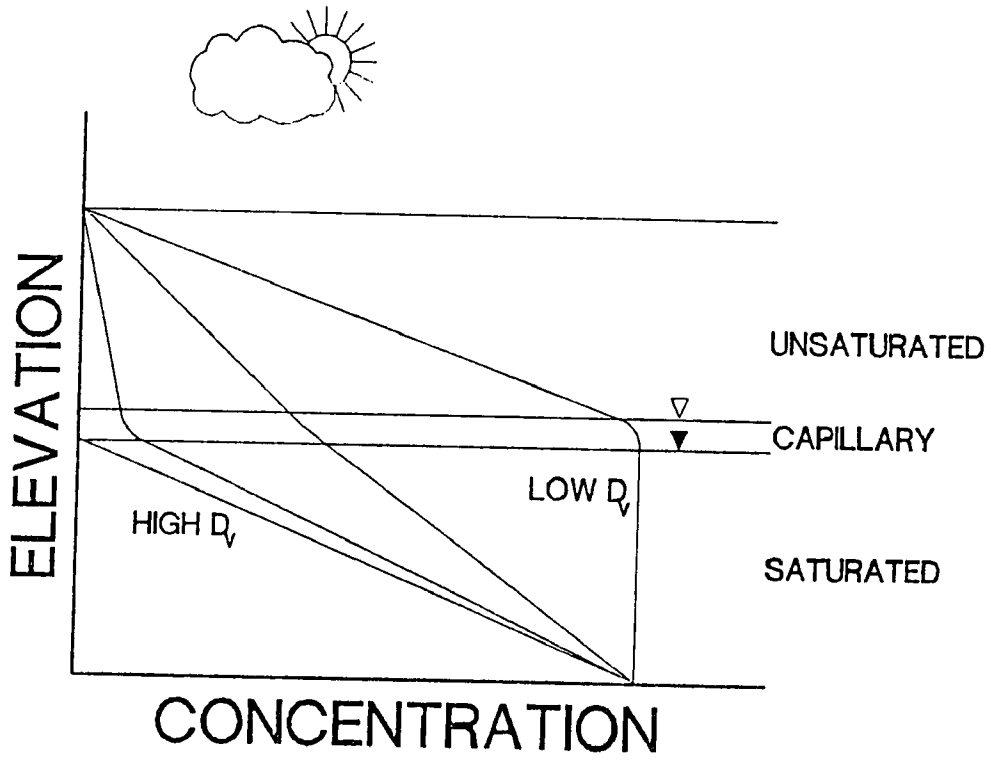
RLJ4D7-1



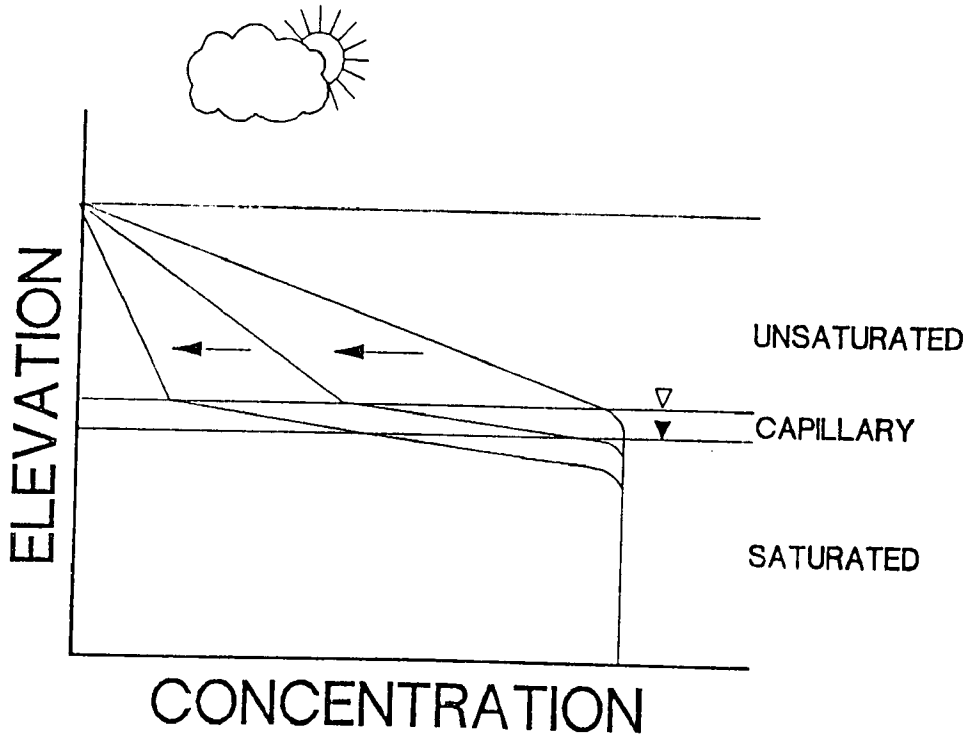
RLJ4D7-2



RLJ4D7-3



RLJ4D7-4



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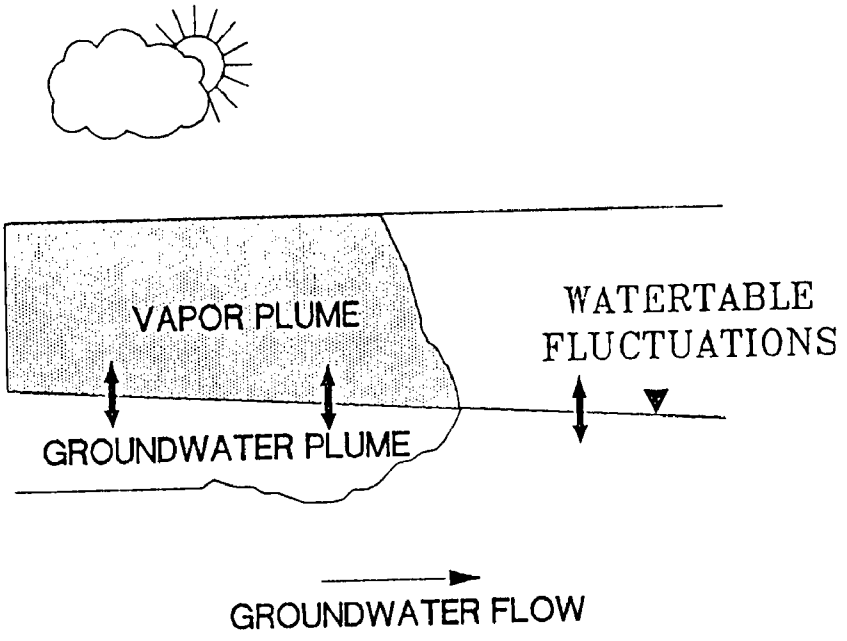
VAPOR PLUME
WATERTABLE
FLUCTUATIONS
GROUNDWATER PLUME
GROUNDWATER FLOW

RIJ4D7-6

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TRANSPORT AND FATE

BIOTRANSFORMATION PROCESSES

Session 5

Joseph M. Suflita

(University of Oklahoma, Norman)

THE MICROBIAL ECOLOGY GOVERNING POLLUTANT BIODEGRADATION IN TERRESTRIAL SUBSURFACE ECOSYSTEMS

BY

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Department of Botany and Microbiology
The University of Oklahoma
Norman, Oklahoma 73019

Summary: The first seminar is an introduction to the historical and current scientific perspectives regarding the microbial ecology of the terrestrial subsurface. Careful attention is paid to how these perceptions evolved. Examples are given of the diverse types of subsurface microorganisms and microbial communities and their associated metabolic activities are emphasized. The metabolic principles that govern pollutant biodegradation in other habitats are extrapolated to subterranian aquifers. The limits of pollutant biodegradation in aquifers are considered in the context of the existing environmental conditions, the physiology of the indigenous microflora and the chemical structure of the offending materials. Lastly, it is shown how these principles might apply to a bioreclamation/bioremediation approach to the clean-up of contaminated aquifers in either an *in situ* or above ground treatment process.

MICROBIAL ECOLOGY

Microbial ecology has sometimes appeared to be the art of talking about what nobody really knows about in a language that everyone pretends to understand

----Francis E. Clark, USDA-ARS

The Truth About Ground Water Pollution:

Surface	Misconceptions:
Unsaturated Zone	• "Living Filter" degrades pollutants before ground water contamination occurs • No microorganisms below surface soil layers
Saturated Zone	Facts:
	• Pollutants do contaminate aquifers • Microorganisms do exist in subsurface

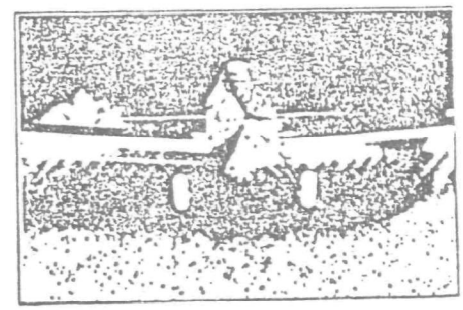
Groundwater contamination

The environmental issue of the 1980's

- **50% of population depends on groundwater**
- **256% growth in demand from 1950-1980**
- **1/3 of the large public water systems have man-made contamination**
- **7,741 private, public and industrial wells have been closed or seriously affected by contamination**

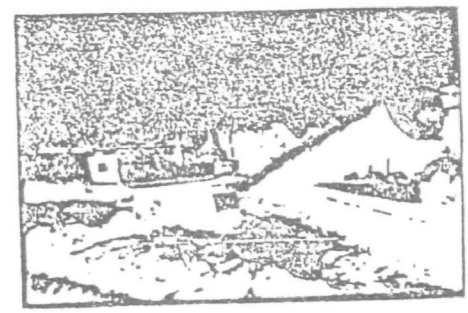
Non-point sources

Agriculture
Road salt

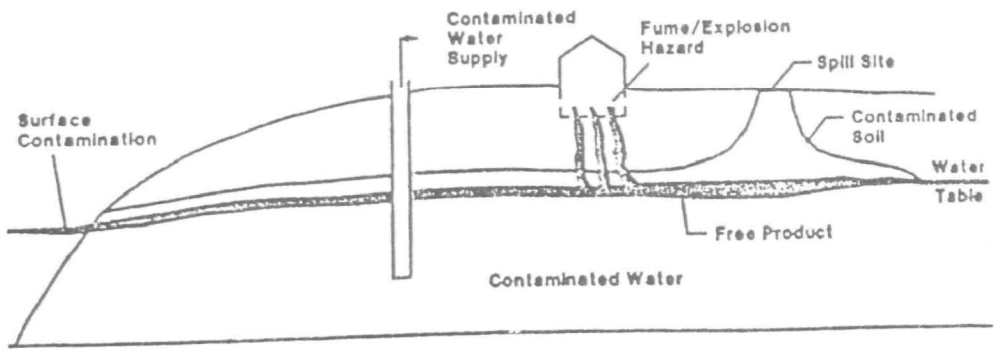


Point sources

Residential septic systems
Leaking underground storage tanks
Surface impoundments
Landfills
Transportation losses



Groundwater pollution



Types of groundwater pollution

Free product

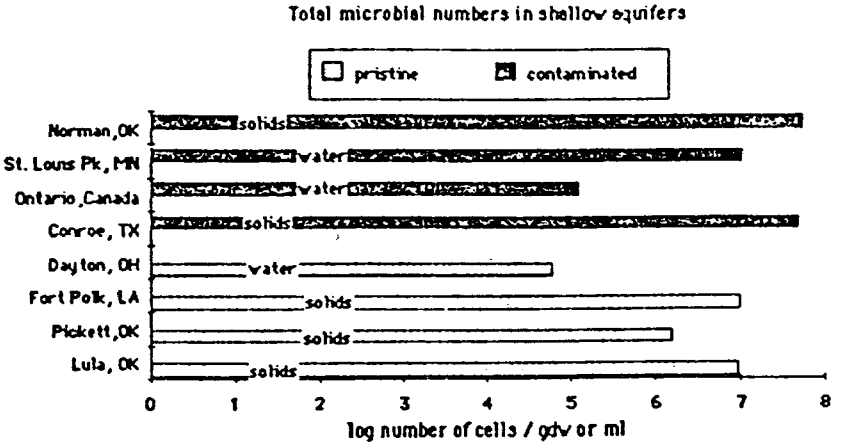
- **Most severe**
- **Limited area**
- **Source of soil & water contamination**

Contaminated soil

- **Severity is soil dependent**
- **Follows free product movement**
- **Source of water contamination & fumes**

Contaminated water

- **Lower concentration**
- **Greatest area**
- **High public exposure**



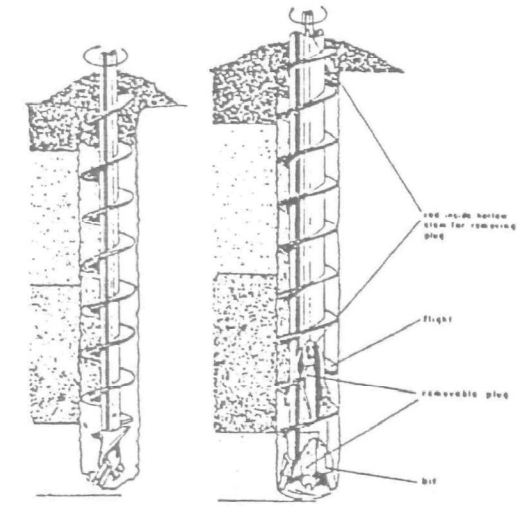


Figure 11.3. Auger drilling. The continuous-flight auger bores into the soil and rotates the cuttings upward along the flights. In order to core, the auger must be removed when the desired depth is reached. The hollow-stem, continuous-flight auger bores into soft soils and carries the cuttings upward along the flights. When the desired depth is reached, the plug is removed from the bit and withdrawn from inside the hollow stem. A core barrel can then be inserted to the bottom of the hollow stem.

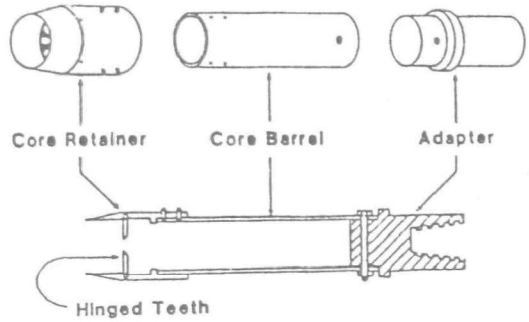


FIG. 1. Coring device.

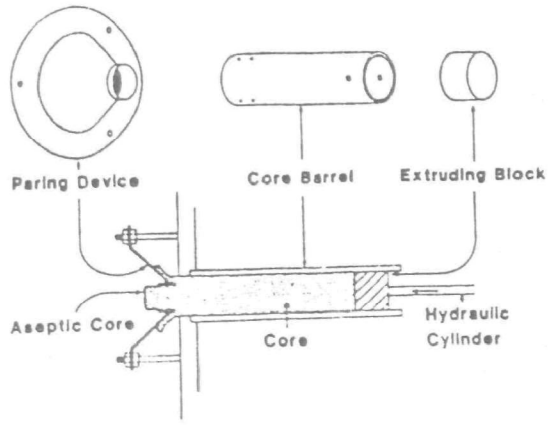
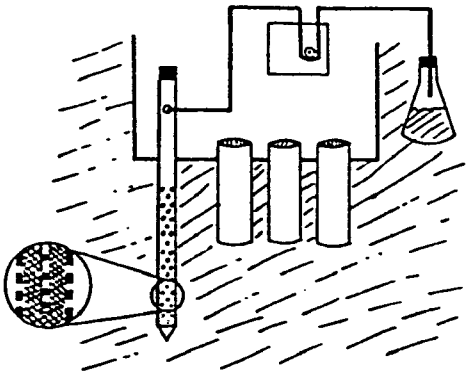
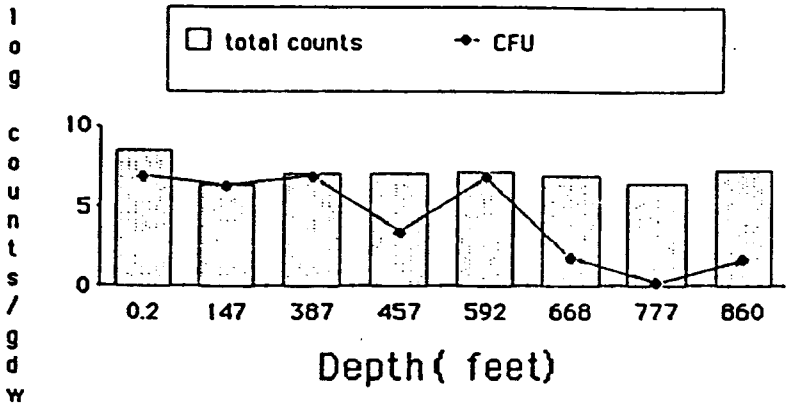


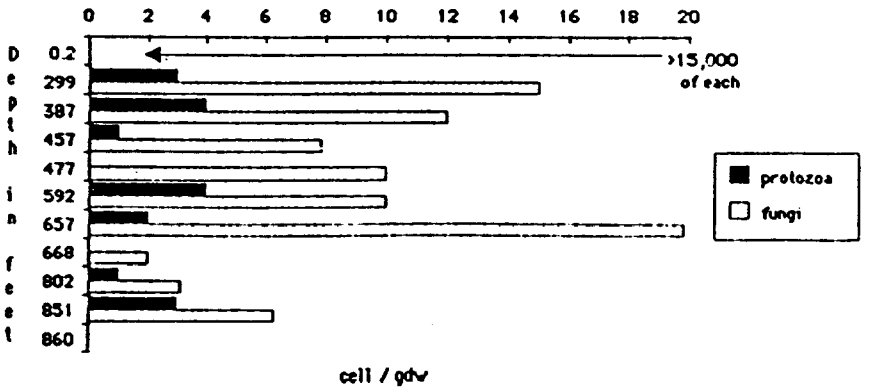
FIG. 2. Device to recover cored material aseptically



Total and viable bacteria with depth



Eucaryotes in the subsurface



Questions About Subsurface Microorganisms

- Are they metabolically active?
- How diverse is their metabolism?
- What factors serve to stimulate and/or limit their growth and activity?
- Can we take advantage of their metabolism for aquifer remediation?

Metabolic Processes Detected in the Subsurface and Oxygen Requirements

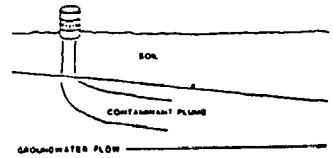
Metabolic Process	Oxygen Requirement	Reference
I BIODEGRADATION OF ORGANIC POLLUTANTS		
A) Petroleum Hydrocarbons	Aerobic	21,46,58,59,60,61,62
B) Alkylpyridines	Aerobic/Anaerobic	63
C) Creosote Chemicals	Aerobic/Anaerobic	26,55
D) Coal Gasification Products	Aerobic	52
E) Sewage Effluent	Aerobic	53,64,65
F) Halogenated Organic Compounds	Aerobic/Anaerobic	21,24,25,46,66,67
G) Nitrilotriacetate (NTA)	Aerobic/Anaerobic	67,68
H) Pesticides	Aerobic/Anaerobic	25,67,68

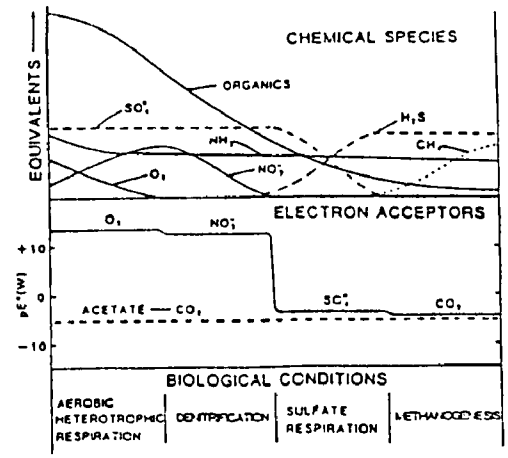
Metabolic Processes Detected in the Subsurface and Oxygen Requirements - Continued

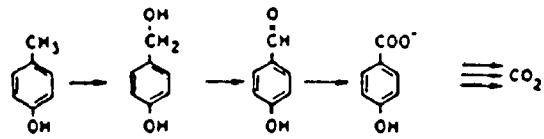
Metabolic Process	Oxygen Requirement	Reference
II Nitrification	Aerobic	69,70,71
III. Denitrification	Anaerobic	55,67,72
IV. Sulfur oxidation	Aerobic	73
V. Sulfur reduction	Anaerobic	74,75,76,77,78
VI. Iron Oxidation	Aerobic	73,79
VII Iron Reduction	Anaerobic	53,55
VIII. Manganese Oxidation	Aerobic	79
IX Methanogenesis	Anaerobic	24,25,53,76,80,81

Redox conditions and biotransformations in a polluted aquifer

(Bouwer, 1984)







Redox Conditions	Biodegradability	Lag Time	Relative Rate	Ref.
Aerobic	+			1
Denitrifying	+			2
Sulfate Reducing	+			3,4
Methanogenic	+			4,5,6

(1) Hopper, 1976, 1978; (2) Bossert & Young, 1986; (3) Bak & Widdel, 1986; (4) Smolenski & Suflita, 1987; (5) Godsy et al., 1983; (6) Senior & Balba, 1984.

Degradation of pollutants in an aerobic and in a methanogenic biofilm column (Bouwer, 1984)

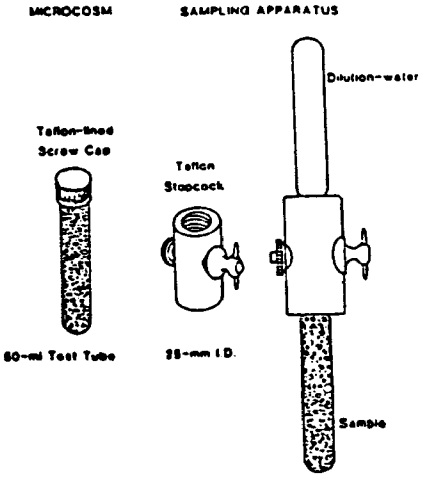
Substrate[1]	Aerobic degradation[2]	Methanogenic degradation[3]
Acetate	++	++
Chlorobenzene	++	-
1,2-Dichlorobenzene	++	-
1,3-Dichlorobenzene	+	-
1,4-Dichlorobenzene	++	-
1,2,4-Trichlorobenzene	++	-
Ethylbenzene	++	-
Naphthalene	++	-
Chloroform	-	++
1,1,1-Trichloroethane	-	++
Tetrachloroethylene	-	++
Carbontetrachloride	-	++
Bromoform	-	++

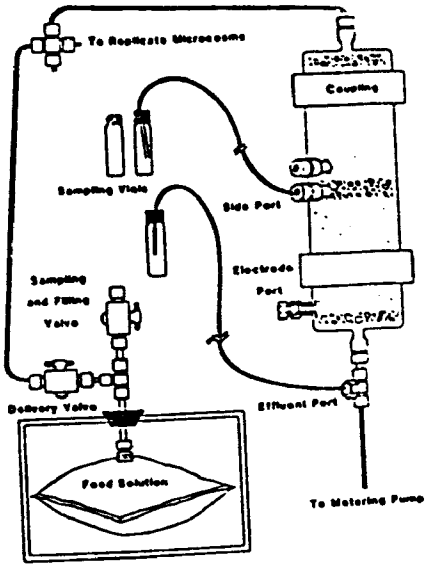
1) Fed as secondary substrate (1 - 30 µg/lit)
2) Detention time: 20 min.
3) Detention time: 2 days

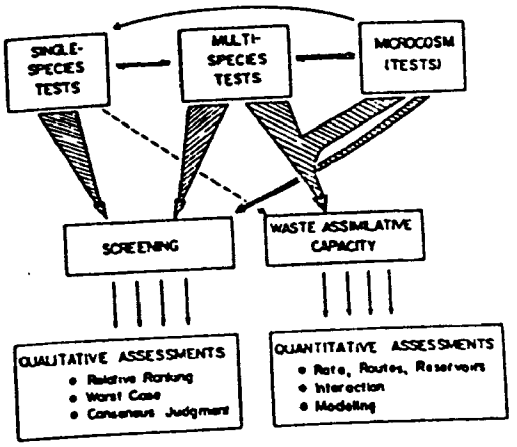
MICROCOSM

....a calibrated laboratory simulation of a portion of a natural environment in which environmental components, in as undisturbed a condition as possible, are enclosed within definable physical and chemical boundaries and studied under a standard set of laboratory conditions.

--P.H. Pritchard, U.S. EPA


MICROCOSM
SAMPLING APPARATUS
Teflon-lined
Screw Cap
Teflon
Stopcock
Dilution-water
60-ml Test Tube
25-mm I.D.
Sample


To Replicate Microcosms
Sampling Vials
Side Port
Electrode
Port
Sampling
and Filling
Valve
Effluent Port
Food Solution
To Metering Pump


SINGLE-
SPECIES
TESTS
MULTI-
SPECIES
TESTS
MICROCOSM
(TESTS)
SCREENING
WASTE ASSIMILATIVE
CAPACITY
QUALITATIVE ASSESSMENTS
• Relative Ranking
• Worst Case
• Consensus Judgment
QUANTITATIVE ASSESSMENTS
• Rate, Routes, Reservoirs
• Interaction
• Modeling

UTILITY OF MICROCOSMS

Risk Assessment

Waste Assimilatory Capacity of an Environment

Transport of a Contaminant

Fate of a Contaminant

A) identify biodegradable pollutants

B) examine the effects of substate concentration on biodegradation

C) determine biodegradation pathways

D) estimate rates of biotransformation

ADVANTAGES OF MICROCOSMS

Replicable

Vary chemical and physical parameters

Perturbable

Manipulate trophic structure

Control of inports and exports

Can be time efficient

Avoid field pollution

Accessible and Containable

LIMITATIONS OF MICROCOSMS

Containerization

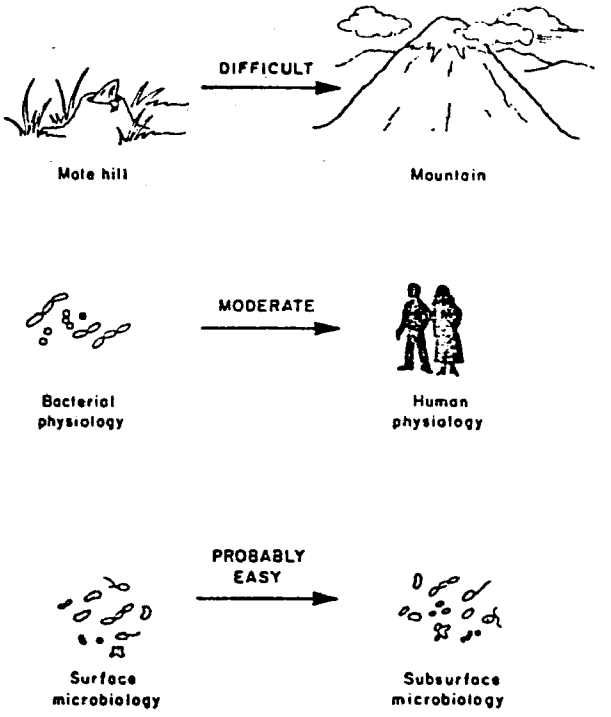
Structural and functional disturbance

high initial costs

high operating costs

high surface to volume ratios

EASE OF EXTRAPOLATION



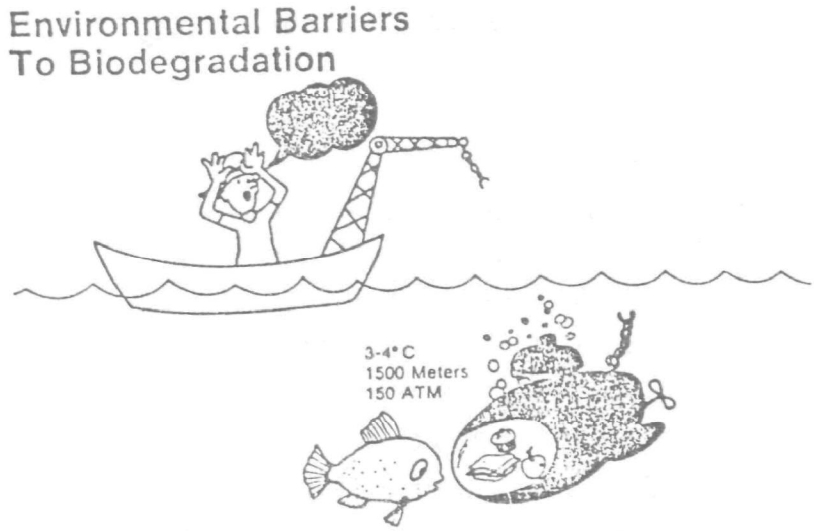
Factors Influencing Pollutant Biodegradation

- Existing Environmental Conditions
- Physiology of the Requisite Microorganisms
- Chemical Structure of the Contaminant

Organic Materials That Persist in Various Habitats

Organic Material	Source	Age (Yrs.)
Human Hair	Desert Cemetery	$> 5 \times 10^3$
Protolytic Enzymes	Permafrost Soils	$> 5 \times 10^3$
Wood	Soil/Lagoons/ Peats	$2\text{-}20 \times 10^3$
Microbiol Spores	Fresh Water Sediments	3×10^4
Oil Deposits	Subsurface	4×10^8

Environmental Barriers To Biodegradation



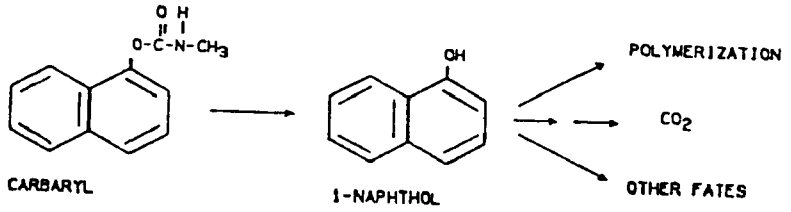
Potentially Limiting Environmental Factors

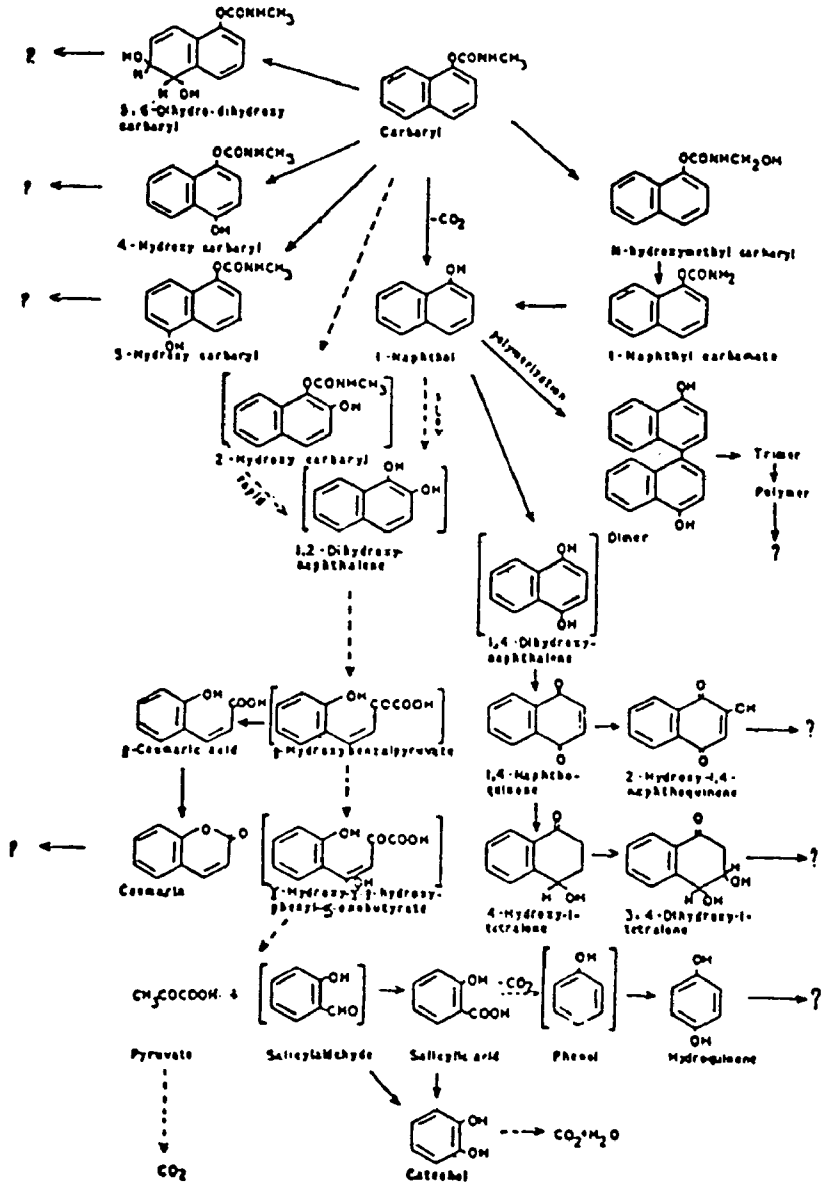
- pH
- Salinity
- Other Synthetic Chemicals
- Heavy Metals
- Osmotic Pressure
- Hydrostatic Pressure
- Free Water Limitations
- Radiation

Physiological Barriers To Biodegradation

A contaminant will be a poor substrate if:

- No active microorganism is present, therefore, no available enzymatic machinery
- Microorganisms present, but ...
  - — Substrate is a poor inducer
  - — Substrate concentration is too low
  - — Substrate fails to enter cells
  - — Cell lacks other essential nutrients
  - — Inhibition/toxicity of enzymes by substrate or products
  - — Other necessary microbes are absent

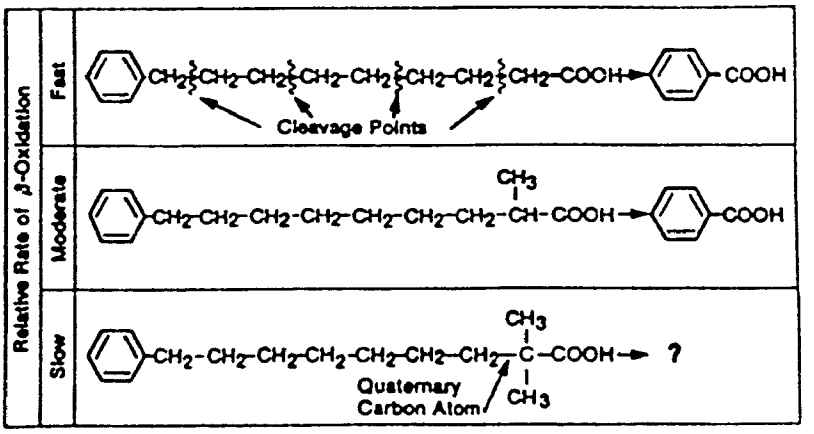




From J. E. Baynard et al. 1974 Effect of pesticides on bacterial enzymes

Chemical Barriers To Biodegradation

Effect of Branching



Microbe	1-Phenyldecane	1-Phenyl-4-methyldecane	1-Phenyl-4,4-dimethyldecane
Micrococcus cerificans HOI-N	2	0	0
Micrococcus cerificans HO 3	2	0	0
Micrococcus cerificans HO. 4	2	0	0
Micrococcus cerificans S-18.2	2	0	0
Micrococcus cerificans S-14.1	2	0	0
Pseudomonas aeruginosa 119 JWF	2	0	0
Pseudomonas aeruginosa 191 JWF	2	0	0
Pseudomonas aeruginosa Sol 20 JS	2	0	0
Mycobacterium phlei No. 451	2	2	0
Mycobacterium fortuitum No. 389	2	2	0
Mycobacterium rhodochrous No. 382	2	2	0
Mycobacterium smegmatis No. 422	2	2	1
Nocardia opaca	2	2	1
Nocardia rubra	2	2	1
Nocardia erythropolis	2	2	1
Nocardia polychromogenes	2	2	1
Nocardia corallina	2	2	1

The rate of anaerobic monohalobenzoate metabolism exhibited by an enrichment of dehalogenating bacteria

POSITION	------DEHALOGENATION RATE (μmoles / l / hr)-----			
	F	Cl	Br	I
ORTHO	n.d.	0	1.20	0.50
META	0	4.63	3.70	0.89
PARA	0	0	0.05	0.66

Ease of Biodegradation

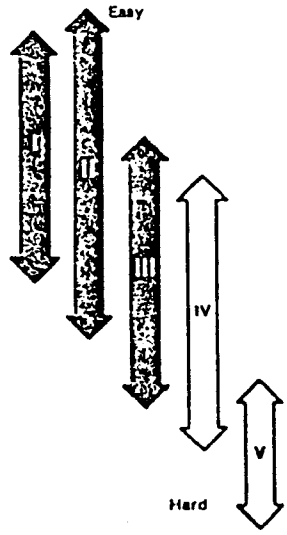
Labile

Structural Analogs of Natural Materials

Recalcitrant

Chemicals With No Natural Counterpart

Biodegradability



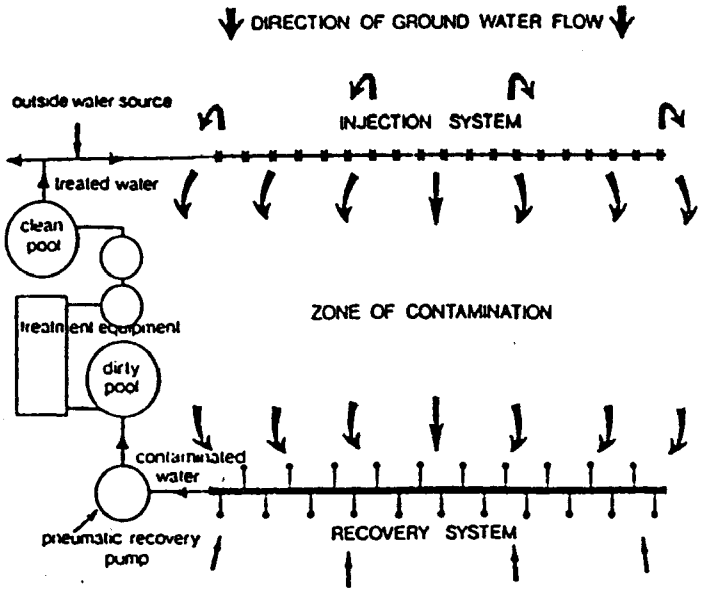
I. Hydrocarbons
II Substituted Hydrocarbons, Phenols, Esters, Alcohols, Nitriles, Partially Chlorinated
III Pesticides
IV Highly Chlorinated Compounds
V "Monster" Molecules
— Kepone
— PCB

It's Not Whether, It's How Easy!

Enhanced bioreclamation is the use of common soil bacteria to degrade organic contaminants

Biodegradation of organic contaminants

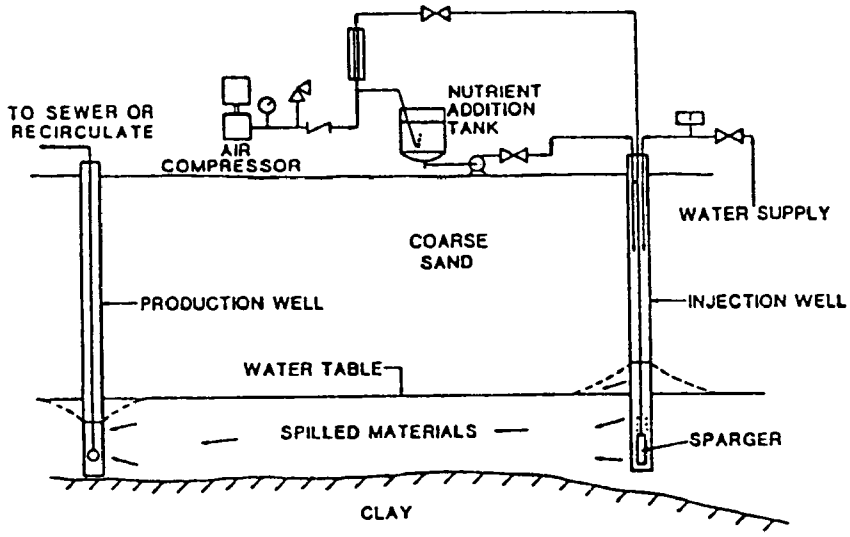
Bioreclamation stimulates this natural process

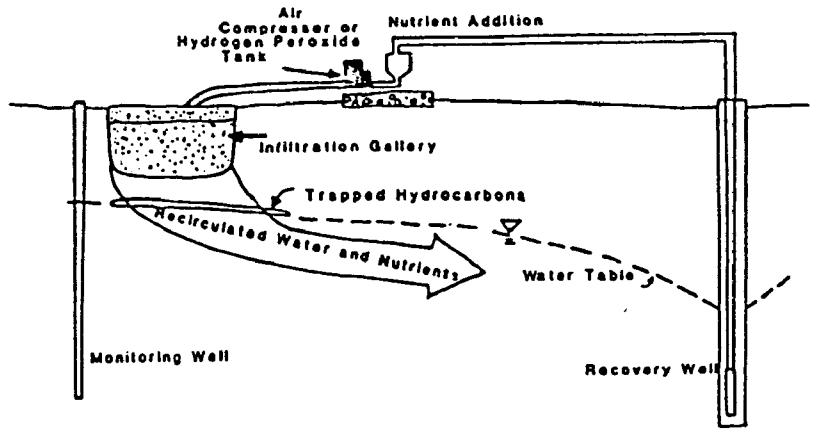


What Is In Situ Remediation?

In Situ:	"In the natural or original position"
Remediation:	"A process of correcting or counteracting an evil"

∴ In Situ Remediation is the process of correcting a contamination problem in the environment in which it occurs





Advantages of bioresteration

Can be used to treat some common aquifer pollutants
Environmentally sound - complete destruction of contaminant
Utilizes indigenous microorganisms
Treatment moves with the water
Economical

Disadvantages of bioresteration

Bacteria are subject to inhibitors
Bacteria can potentially plug formations
Incomplete degradation can lead to taste and odor problems
Maintenance intensive
Limited to aquifers of high permeability
Long term effects unknown

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TRANSPORT AND FATE

BIOTRANSFORMATION PROCESSES

Session 6

Joseph M. Suflita
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MICROBIOLOGICAL PRINCIPLES INFLUENCING THE BIORESTORATION OF AQUIFERS

BY

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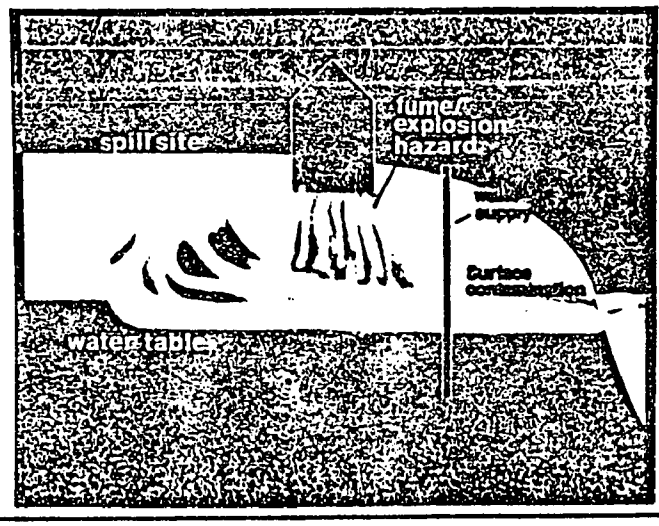
Summary: The second seminar briefly considers various treatment options for the clean-up of contaminated aquifers and shows how and why biorestoration techniques fit into the myraid of pollution mitigation tools. Attention is given to the types of considerations that must be made before an aquifer biorestoration strategy is implemented in the field. The example of spilled gasoline in an aquifer is chosen to help illustrate specifically how chemical, physical and microbiological principles meld into an overall aquifer treatment strategy. Guidelines for the critical evaluation of the claims for aquifer restoration are also given with specific suggestions for the types of information that might be collected to bolster such claims. Particular attention is also paid to *in situ* biorestoration attempts that rely on the inoculation of desirable microorganisms. Lastly, a perspective on biorelamation techniques is provided through a consideration of the pratical limitations of the technology. This then leads to the realization that properly considered, bioreclamation is not a panacea for the many different types of subsurface pollution problems but should prove valuable under specific sets of circumstances.



Subsurface contamination

Symptoms of groundwater pollution

- Contaminated water well
  - Odor, taste, free product
  - Potential health risk
- Fumes
  - Explosion risk
  - Potential health risk
- Surface water contamination
  - Oil seeps, color/odor, fish kills

Fate of a Contaminant

	Environment	Contaminant
Movement	Rate Ground Water Flow Permeability	Amount of Material Physical State Solubility Viscosity Surface Tension
Retention	Soil Type Organic Content	Solubility (Lack of) Ionic Character
Reaction	pH Redox Conditions Microbial Communities	Chemical Reactivity Biodegradability

Mechanisms Affecting Fate

- Movement
  - — Gravity
  - — Ground water motion (vertical and horizontal)
  - — Dissolution
- Retention
  - — Sorption
  - — Properties of contaminant
- Reaction
  - — Hydrolysis
  - — Precipitation
  - — Oxidation/reduction
  - — Biological transformation

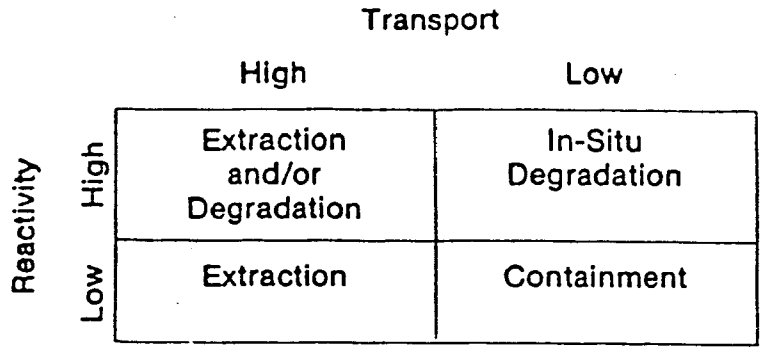
These mechanisms controlled by chemical properties of contaminant and subsurface environment

The fate of a contaminant is determined by its

- Transport
- Reaction with the environment

Remediation is governed by the same factors

Treatment Options



Treatment options

- **Containment - physical & hydrological**
  - **Costly**
  - **Can't guarantee longterm effectiveness**
  - **Doesn't address problem**
- **Excavation**
  - **Costly**
  - **Transfers the problem**
  - **Removes only limited material (physical constraints)**

Treatment options

- **Pump & treat**
  - **Low yearly cost**
  - **Long term commitment/maintenance**
  - **Effectiveness limited to dissolved**
- **Bioreclamation**
  - **Short term/high cost**
  - **Addresses total groundwater problem (adsorbed and dissolved)**
  - **Definite end point/short treatment**

Containment

- If it moves slow, it can be contained
- But, the contaminant persists
- Methods
  - Slurry walls
  - Clay caps
  - Interceptor trenches
  - Hydraulic barriers

Extraction

- Easily transported substances
- But, requires surface treatment
  - Air stripping
  - Carbon
  - Reaction
  - Discharge
- Methods
  - Water
  - Venting

Reaction

- Reactive species can be treated in situ
  - Chemically - Oxidation, Reduction, Hydrolysis, Polymerization
  - Biologically - Degradation, Mineralization
- Treatment chemicals/nutrients must be transported
- Methods
  - Chemical reclamation
  - Enhanced bioreclamation

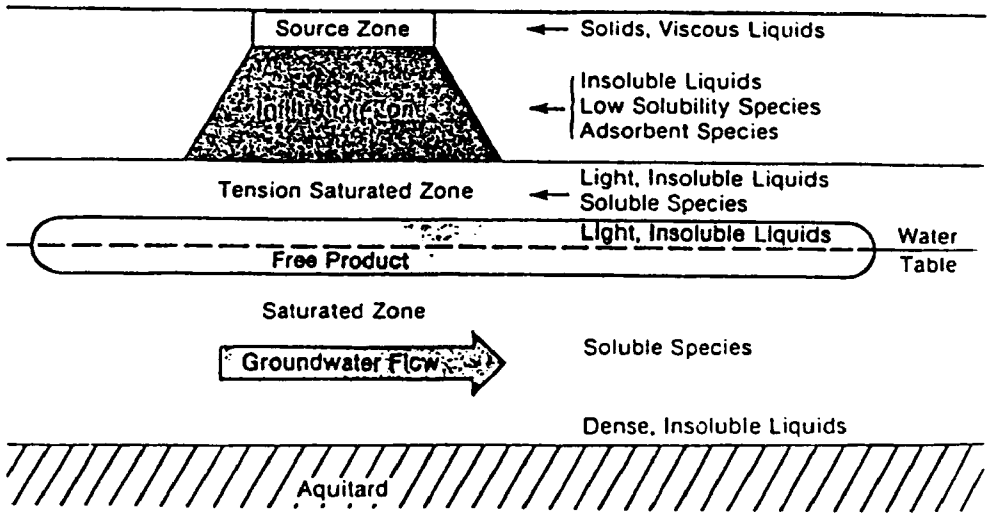
AQUIFER REMEDIATION CONSIDERATIONS

A. Type of Contaminant
   phases, solubility, susceptibility to biodegradation
B. Pathways of Biodegradation
C. Site Characteristics
   hydrology, geology, depth to water table
D. Removal of Free Product
E. System Design
   above or below ground
F. Laboratory Investigation
   evaluation of biodegradation
G. Operation of Biostimulation
   lab effort to design stimulation, extrapolate to field
H. Monitor Progress

The Ideal Site

- Homogeneous, Permeable Soil
- Single Point Source
- Low Groundwater Gradient
- No Free Product
- No Soil Contamination
- Easily Degraded, Extracted or Immobilized Contaminant

The Real Site



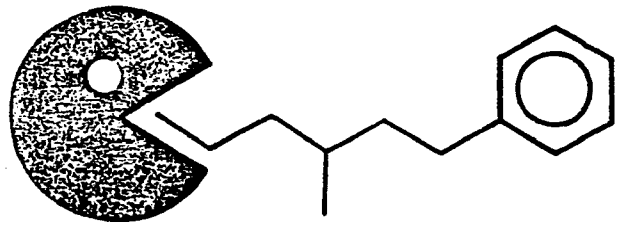
Hydrogeologic Variables That Impact In-Situ Remediation

- Vadose Zone
  - — Thickness
  - — Permeability (Horizontal + Vertical)
  - — Geologic Complexity
  - — Organic Content
- Saturated Zone
  - — Type of Aquifer (Composition)
  - — Thickness of Shallow Aquifer
  - — Interconnection of Aquifers
  - — Location of Discharge Area
  - — Water Table Fluctuations
  - — Ground Water Flow Rate

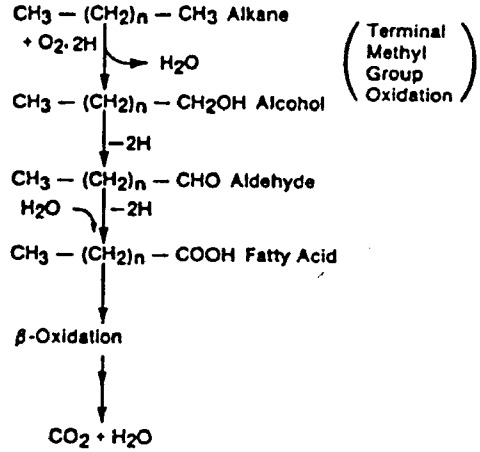
Major Classes of Gasoline Components

Hydrocarbon Class	Conroe, Texas	Colinga, California	Jennings, Louisiana
Alkanes	16.8	18.0	24.5
Cycloalkane	47.1	55.5	38.4
Aromatic	19.5	10.2	15.6

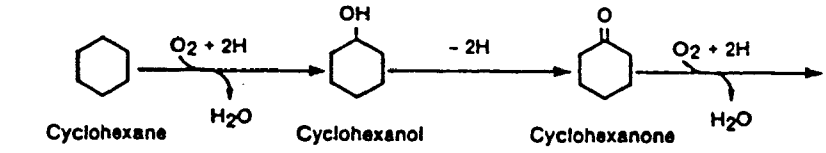
Metabolic Pathways

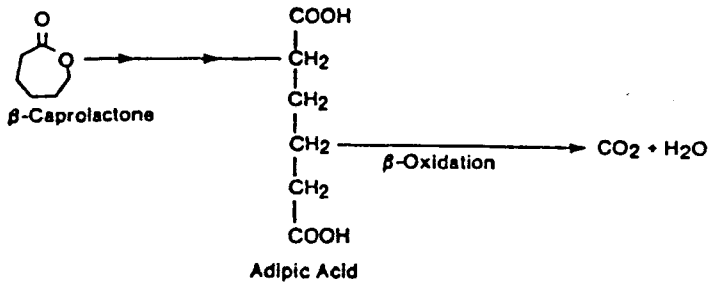


Alkane Degradation Path

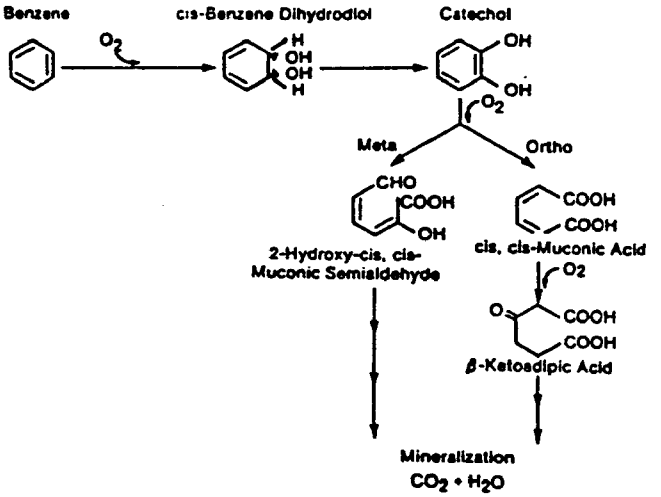


Alicyclic Hydrocarbons

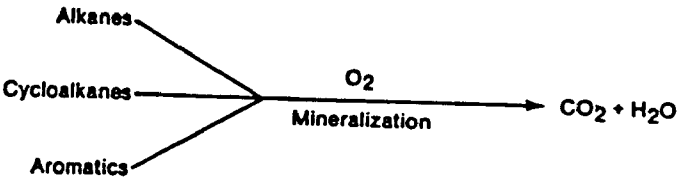




Aromatic Hydrocarbons

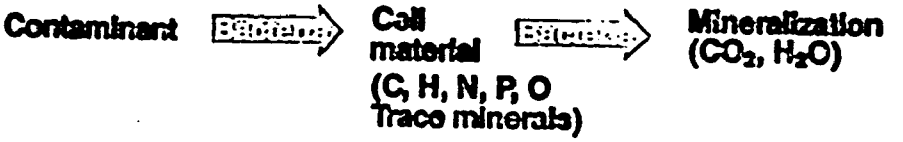


Hydrocarbon Remediation Requirements



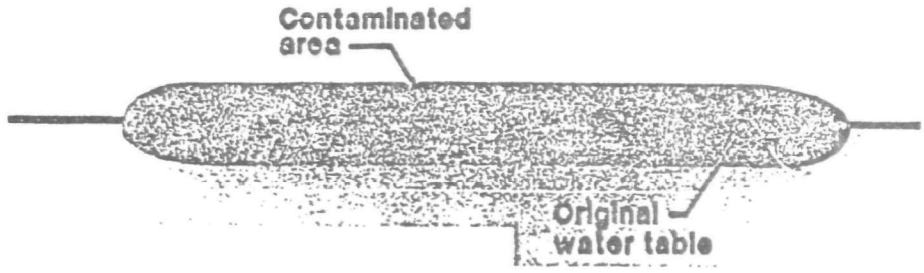
Microorganisms Need

- Nitrogen
- Phosphorus
- Sulfur
- Trace elements
- Suitable environment

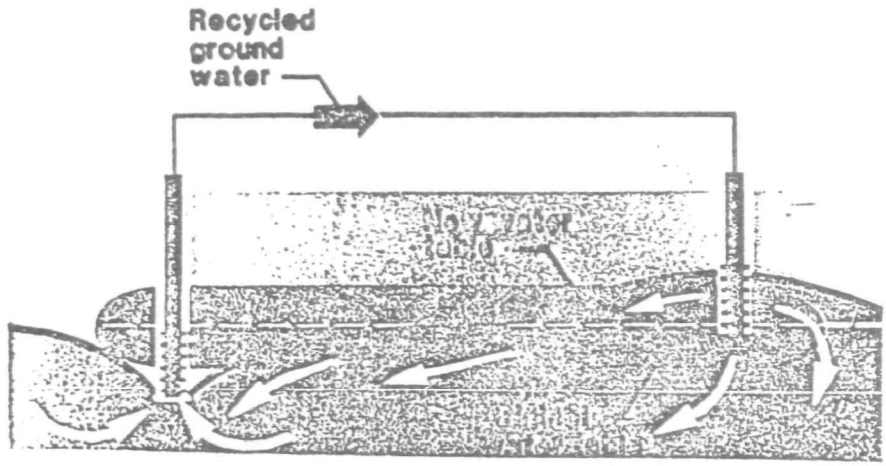


How does bioreclamation work?

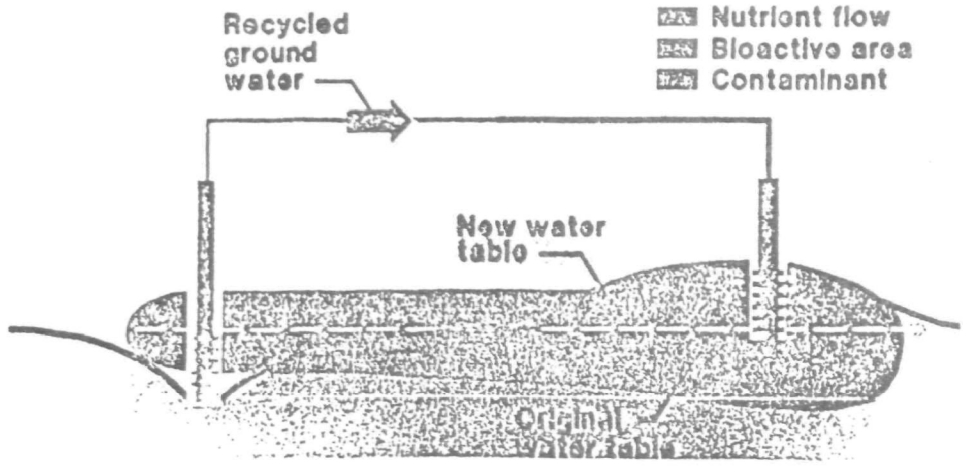
Enhanced bioreclamation
Contaminated aquifer



Enhanced bioreclamation
Creating a reaction vessel

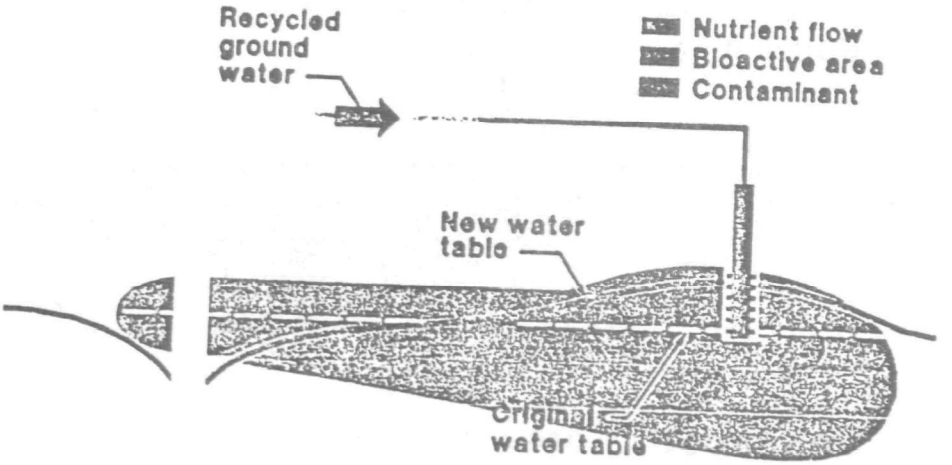


Enhanced bioreclamation
Creating a chemical environment



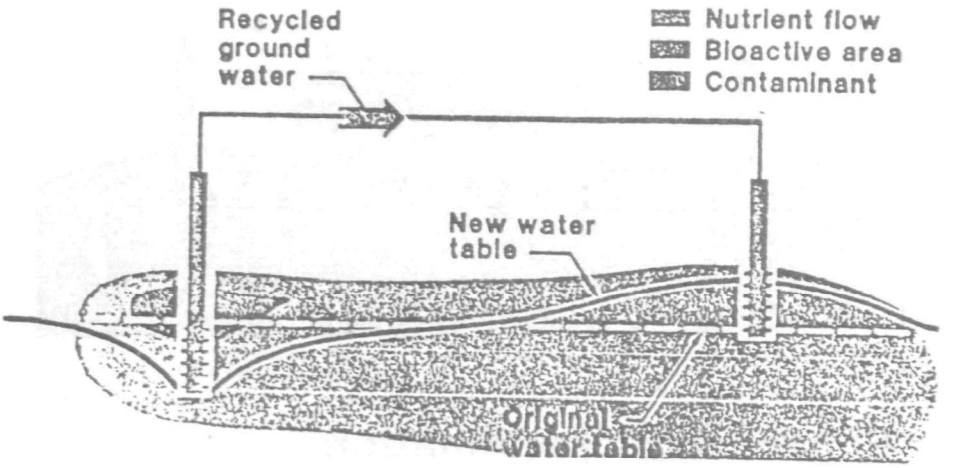
Enhanced bioreclamation

Managing in situ biodegradation



Enhanced bioreclamation

Site remediation



Bioreclamation Works Because:

- Hydrocarbon degrading microorganisms are widely distributed
- Hydrocarbons are essentially natural substrates
- Over 30 years of basic scientific information
- Nutrient requirements for metabolism are well understood

Carbon Adsorption

Circulation Rate	50 gpm	100 gpm
Influent Conc. (Initial)	80 ppm	40 ppm
Project Timing	10-20 yrs.	10-20 yrs.
Project Costs ($K)	420-800	600-1000
Construction (Inc. Elect.)	90	200
Carbon Replac. (Annual)	15	15
Operator (Annual)	18	25

Enhanced Bioreclamation

Circulation Rate	50 gpm	100 gpm
Project Timing	8-10 Months	4-5 Months
Project Costs ($K)	220-290	180-241
Design & Startup	50-75	50-75
Nutrients	90-112	90-112
Service & Equipment	70-88	35-44
Operator	10-15	6-10

Contaminants treated by *In situ* Bioremediation

A. Hydrocarbons
- gasoline
- mineral oil
- aliphatic plasticizers

B. Solvents
- methyl chloride
- n-butanol
- acetone
- ethylene glycol
- isopropanol
- tetrahydrofuran
- chloroform

C. Other compounds
- dimethyl aniline

Flow Characteristics Of Aquifers Where Bioremediation Has Been Tried

Pumping Rate
25-380 (L/min)

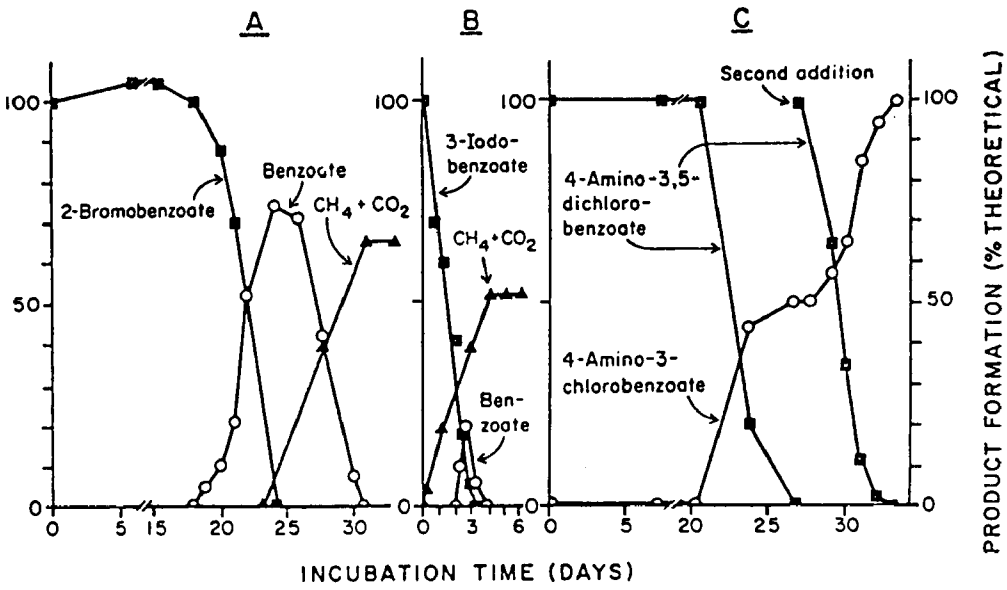
Flow Rate
0.6 - 800 (m/y)

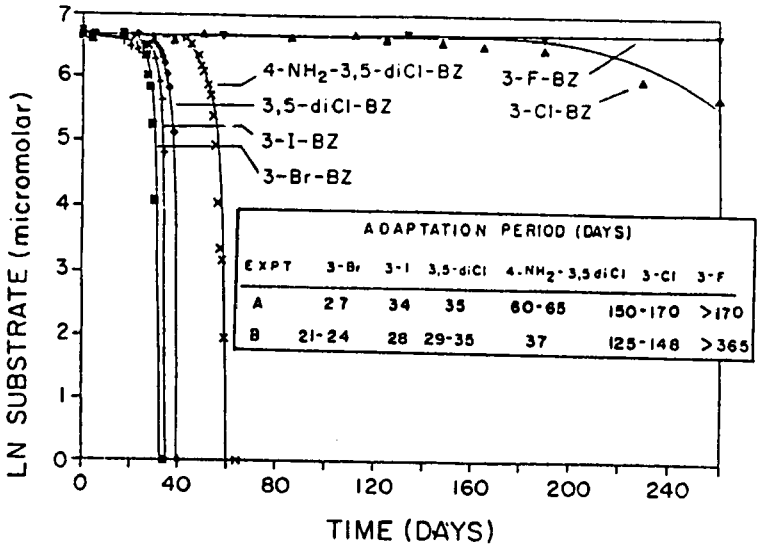
Hydraulic Conductivity
10^{-5} - 10^{-3} (cm/sec)

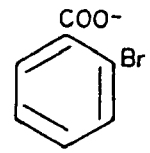
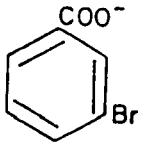
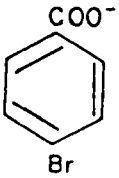
CRITICAL EVALUATION OF BIORESTORATION CLAIMS

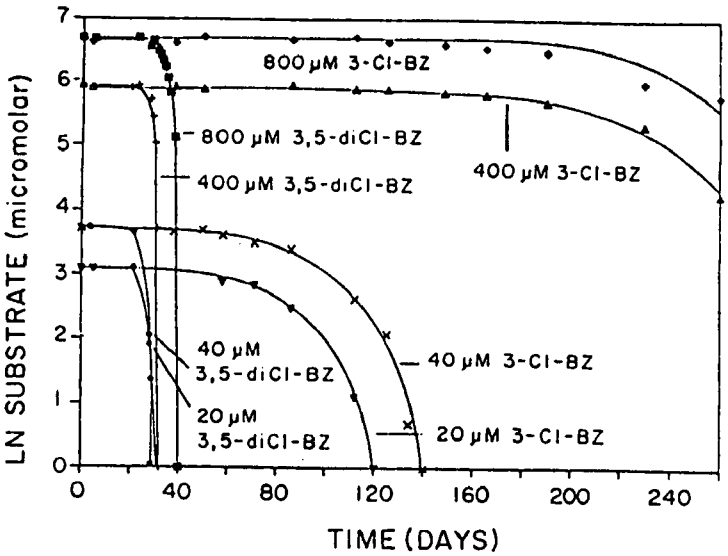
Reduction in Substrate Concentration - Mass Balances
Increase in Biomass/Activity
Production of Catabolites
Consumption of Terminal Electron Acceptors
Adaptation / Acclimation Phenomena
Biodegradation Kinetics

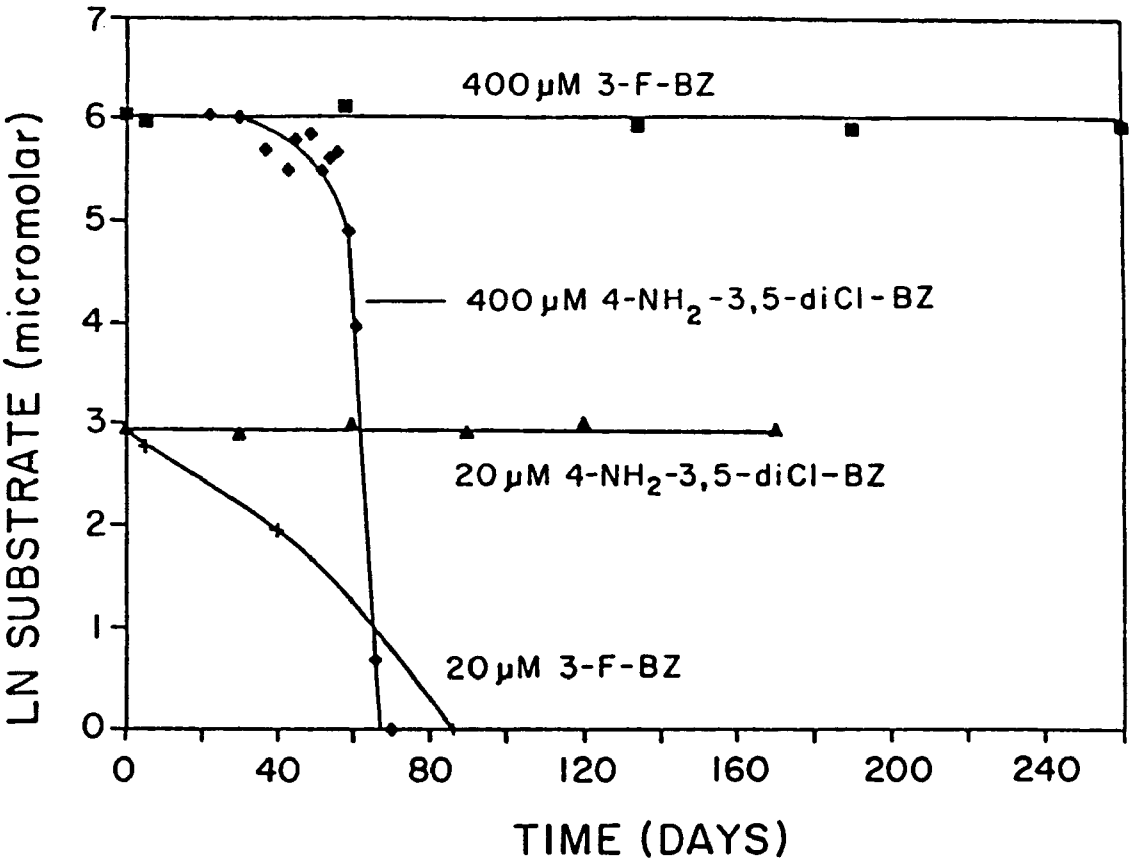
ALL FACTORS RELATIVE TO APPROPRIATE ABIOTIC CONTROLS





SUBSTRATE	ADAPTATION TIME
	20 days
	23-35 days
	39 days





REASONS FOR LAG PERIOD PRIOR TO BIODEGRADATION

Requirement for bacterial growth
Specific substrate concentration
Need to deplete competing substrates
Nutrient limitations
Need to exchange genetic material
Laboratory artifacts ????

SITE	ADAPTATION PERIOD[a]
1	5 WKS
2	4-5 WKS
3	4-5 WKS
4[b]	4-6 WKS

[a] average of 10 replicates

[b] stored sample (2 yr); site 2

CAN BIODEGRADATION BE STIMULATED ????

YES -- BUT.....

REQUIRES AN UNDERSTANDING OF THE FACTORS CONTROLLING THE LAG AND ADAPTATION PERIODS

POSSIBLE STIMULATION APPROACHES

CROSS ACCLIMATION

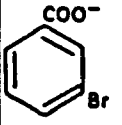
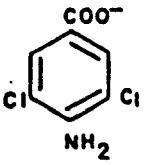
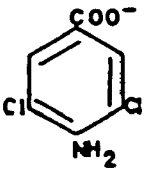
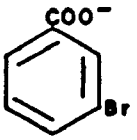
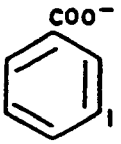
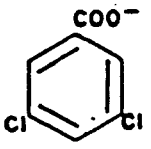
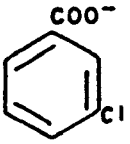
ANALOG "ENRICHMENT"

OVERCOMING NUTRIENT LIMITATIONS

BIOMASS ENRICHMENT

OVERCOMING ENVIRONMENTAL FACTORS

OTHERS...

SUBSTRATE TESTED for CROSS-ADAPTATION	ADAPTATION TIME (WK)	TIME(wk) for COMPLETE DEGRADATION In SEDIMENT ADAPTED TO: 	
	3 - 8	2-3	2-3
	0.5-4	<1	<1
	2- 3	2-3	2-3
	2 - 3	<1	<1
	32-40	LAG	LAG

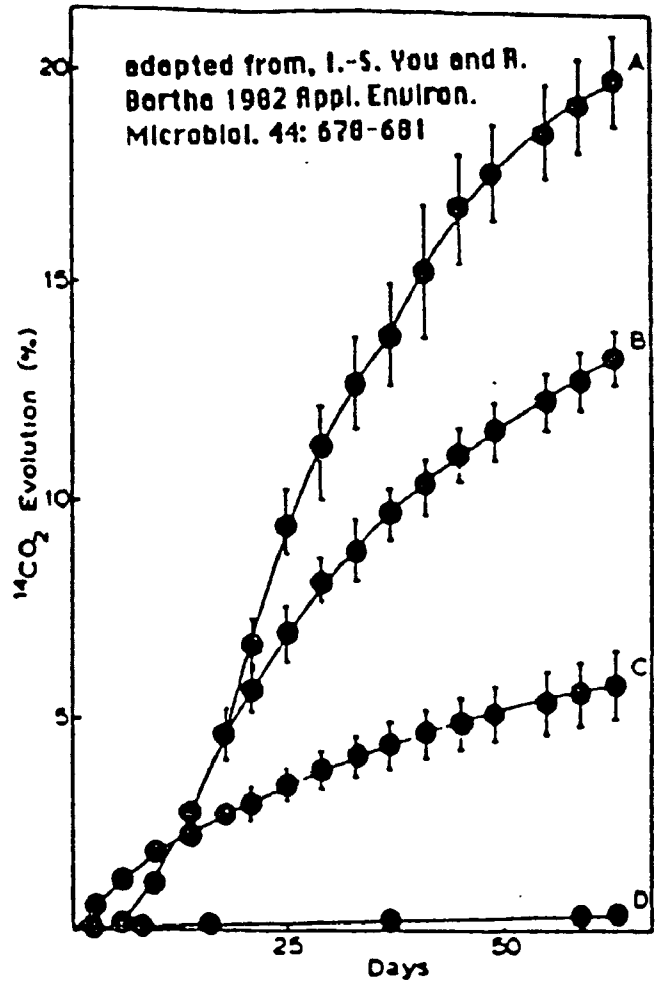


FIG. 1. Effect of aniline on the mineralization of DCA (5 μg/g) in soil. (A) 1.8 mg of aniline added per g; (B) 0.4 mg of aniline added per g; (C) no aniline added; (D) poisoned by $HgCl_2$. Aniline additions to (A) were made in three increments on days 0, 18, and 37, up to the total specified above.

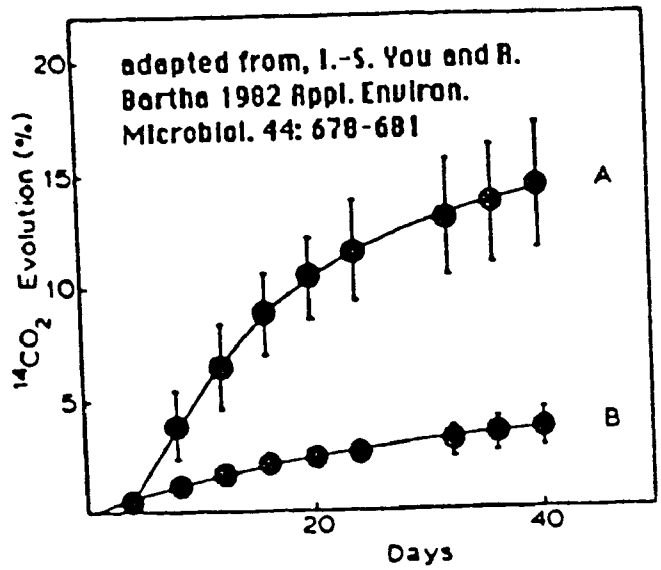


FIG. 2. Effect of aniline on the mineralization of humus-bound DCA in soil. HA-DCA complex (0.5 mg/g) containing 2.5 μg of bound DCA per g was incubated with (A) and without (B) 1.4 mg of aniline per g. Aniline was added in two increments on days 0 (0.4 mg) and 12 (1 mg).

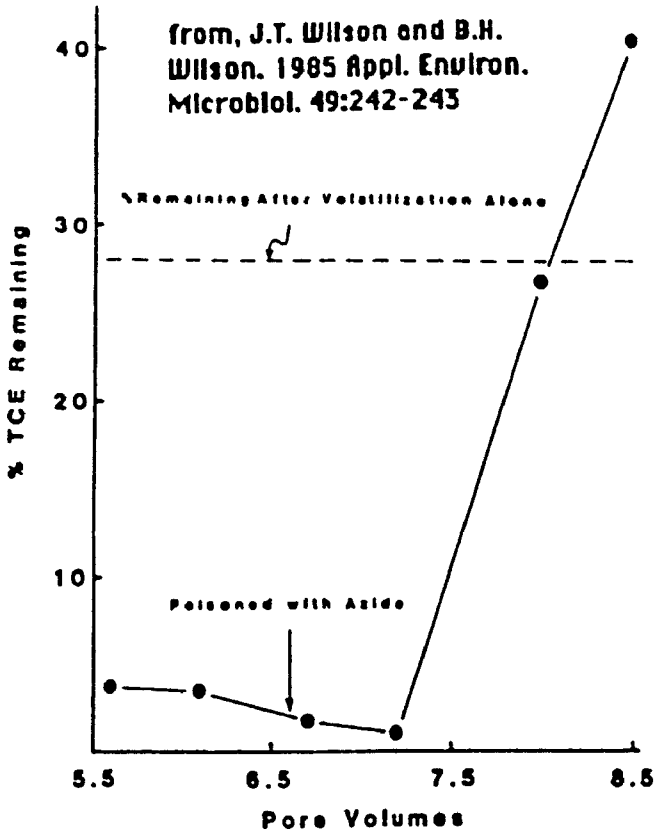


FIG. 1. Removal of TCE during passage through unsaturated soil exposed to an atmosphere of 0.6% methane (vol/vol) in air.

Selected List Of Organic Substances Subject To Co-Metabolism

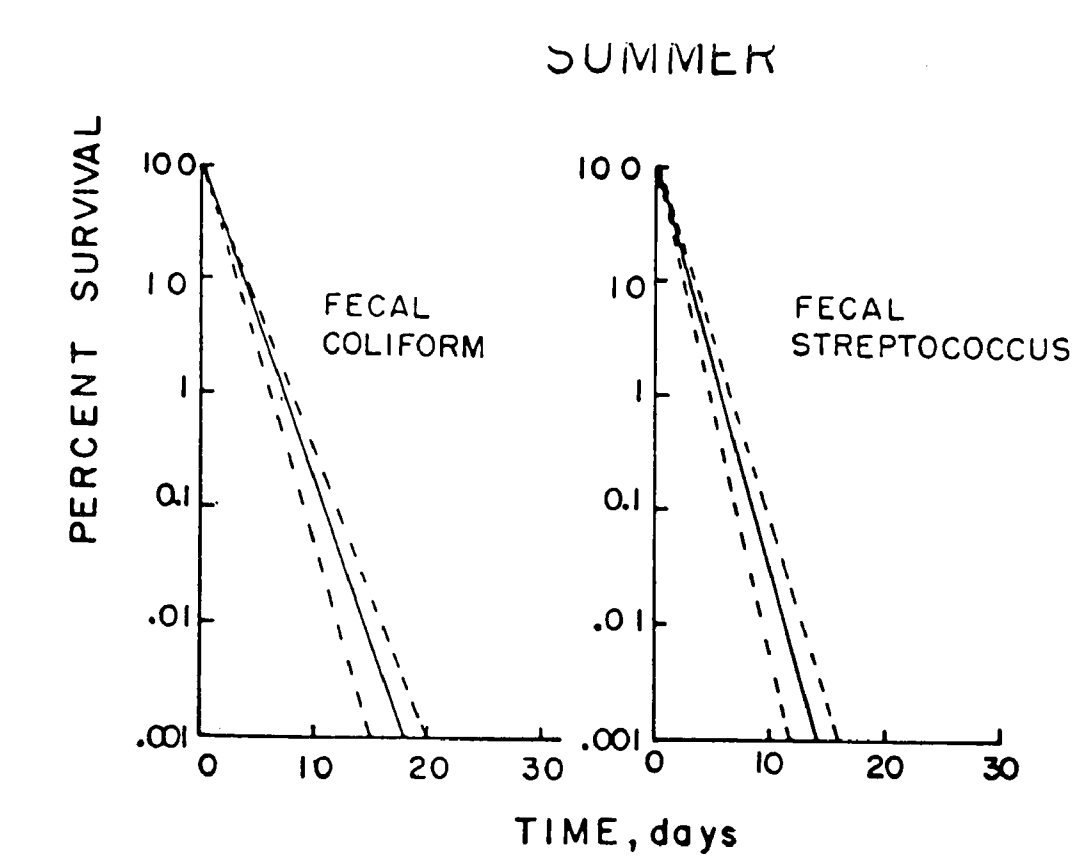
ETHANE
PROPANE
3-CHLOROBENZOATE
2-FLUORO-4-NITROBENZOATE
o- or p-XYLENE
PYRROLIDONE
2,3,6-TRICHLOROBENZOATE
2,4,5-T
DDT

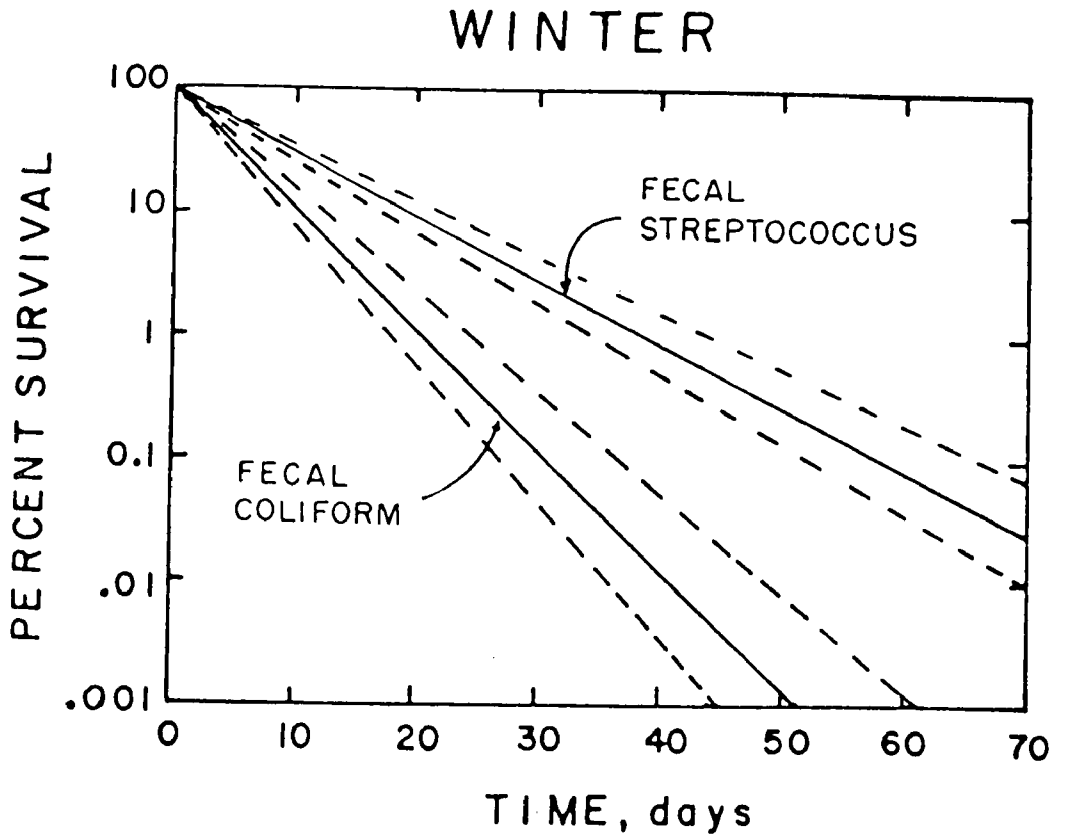
WOULDN'T **YOU** WANT A PRODUCT THAT:
SUBSTITUTES FOR FERTILIZER AND LIME
GET RID OF EXCESS HERBICIDE RESIDUES
GIVES HIGHER GROWTH YIELDS
MAKES DEPLETED SOILS COME ALIVE
GIVES PLANTS AN UNEXPLAINED PROTECTION FROM DISEASES
GIVES LUSTER TO GRAIN

SURVIVAL OF MICROORGANISMS INOCULATED INTO SOIL
from Katznelson, H. 1940a,b Soil Sci 49: 21-31, 283-293

ORGANISM	Manured Soil			Manured and Limed Soil		
	INCUBATION (DAYS)					
	0	45	100	0	45	100
	NUMBERS PER GRAM DRY SOIL • 10^5					
Penillillium sp.	24.7	7.7	7.1	33.9	2.7	2.2
Actinocycetes cellulosae	8.4	0.1	0	7.6	0.04	0
Bacillus cereus	23.2	57.4	49.3	86.9	8.6	12.3
Pseudomonas fluorescens	142.8	0	0	175	1.1	0
Azotobacter chroococcum	200	0,300*	0	360	120	0

* reinoculated


SUMMER
PERCENT SURVIVAL
100
10
1
0.1
.01
.001
FECAL
COLIFORM
FECAL
STREPTOCOCCUS
0
10
20
30
TIME, days


WINTER
PERCENT SURVIVAL
100
10
1
0.1
.01
.001
FECAL
STREPTOCOCCUS
FECAL
COLIFORM
0
10
20
30
40
50
60
70
TIME, days

SELECTED ABIOTIC FACTORS LIMITING THE SURVIVAL OF MICROORGANISMS

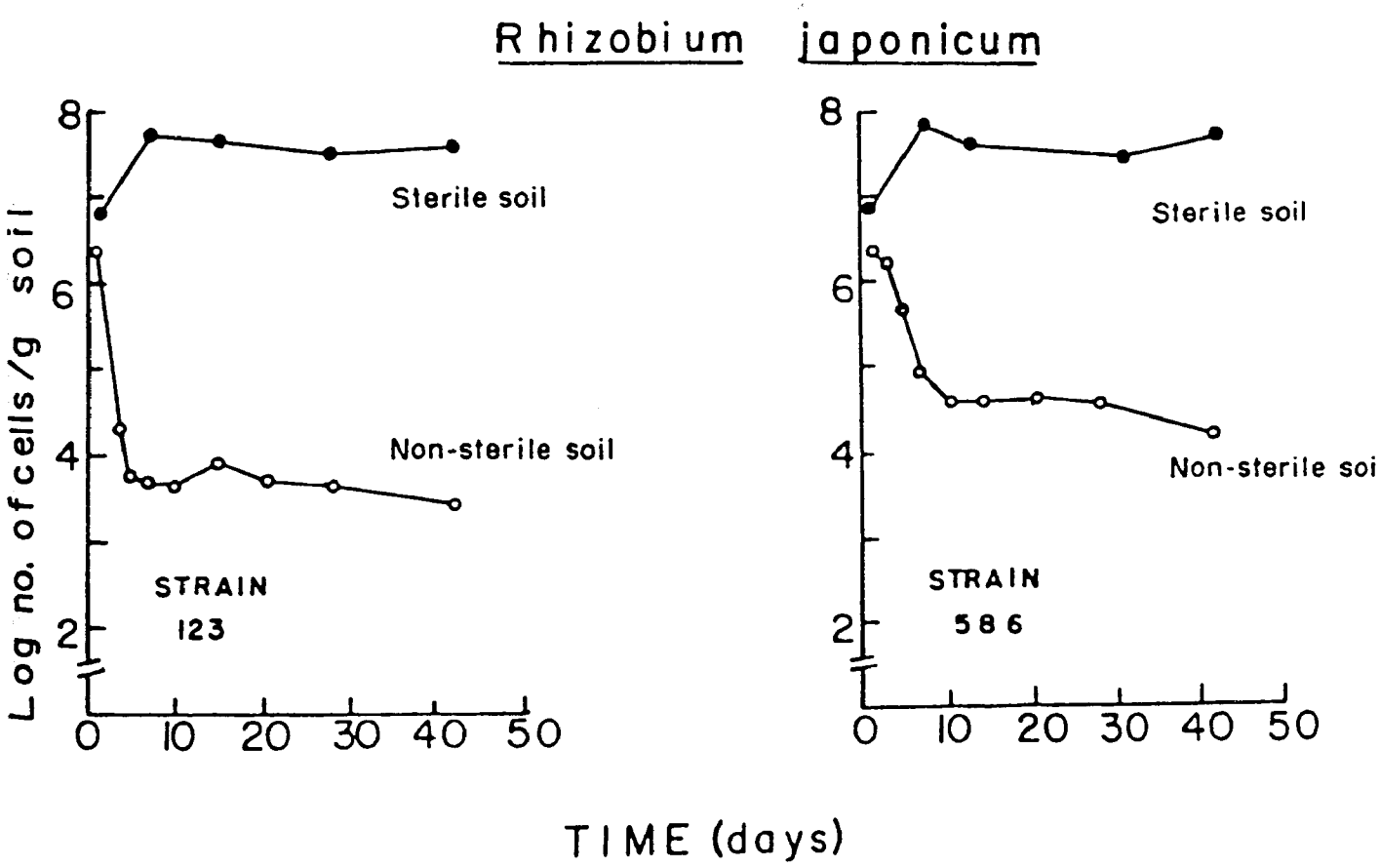
A) pH

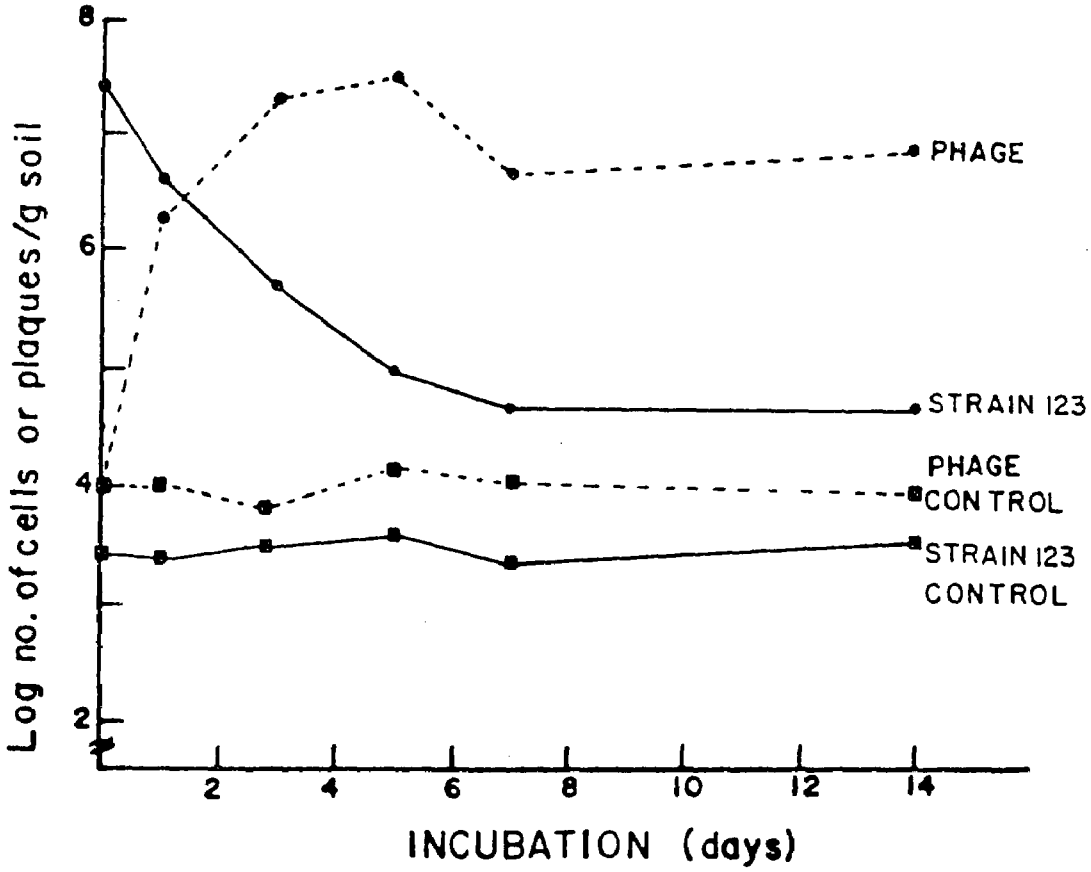
B) Temperature

C) Salinity

D) Water

E) Pressure





Microbial Populations in Inoculants

PRODUCT	Microorganism Type	Cells / ml Product	Cells / g Soil *
MEDINA	ALGAE	650	0.005
	BACTERIA	870	0.007
	FUNGI	0	0
SUPERNATE	ALGAE	0	0
	BACTERIA	6200	0.052
	FUNGI	870	0.007

*calculation based on maximum recommended application rate

Microbiological Profile of a Soil Treated with Inoculants

Treatment	Bacteria		Actinomycetes		Fungi	
	CK	Litter	CK	Litter	CK	Litter
	----------1 • 10^5 / g Soil----------					
Untreated	31	60	46	100	4	16
Medina	37	32	32	119	6	12
Supernate	39	39	40	100	4	10

EFFECT OF MICROBIAL INOCULANTS ON SOIL RESPIRATION

SOIL TREATMENT	CHECK	PINE LITTER
	------mg CO_2 evolved------	
Untreated	36	94
Medina	25	94
Supernate	27	97

HABITAT

AN AREA OF UNDEFINED SIZE WITH A DEGREE OF UNIFORMITY IN CHARACTERISTICS OF ECOLOGICAL SIGNIFICANCE FOR AN ORGANISM. THE *"ADDRESS"* OF AN ORGANISM

NICHE

A TERM USED TO DESIGNATE THE UNIQUE FUNCTIONS OF AN ORGANISM IN ITS HABITAT. THE *"OCCUPATION"* OF AN ORGANISM

COMMUNITY

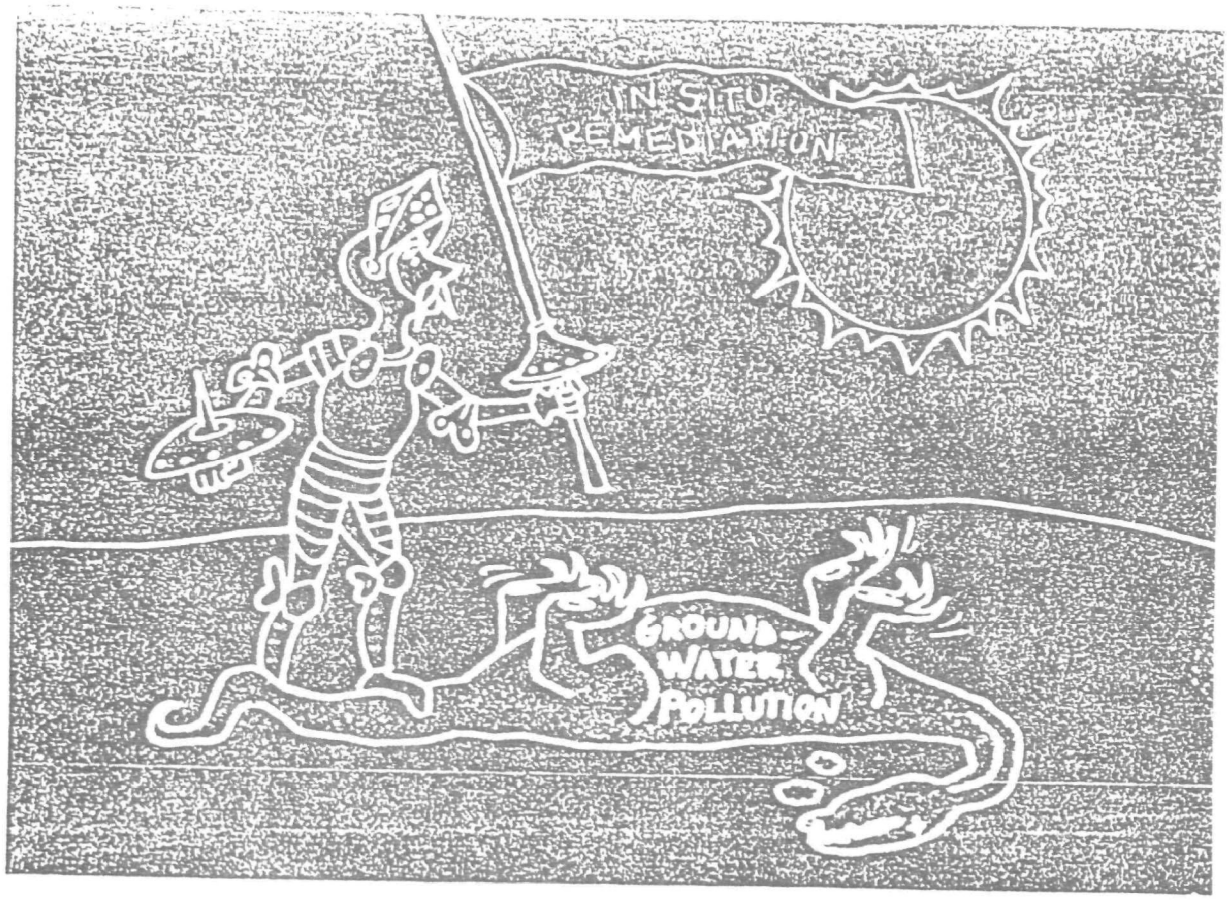
THE ORGANISMS INHABITING A GIVEN HABITAT

ECOSYSTEM

THE COMMUNITY OF ORGANISMS IN A SPECIFIC ENVIRONMENT AND THE ABIOTIC SURROUNDINGS WITH WHICH THE ORGANISMS ARE ASSOCIATED

HOMEOSTASIS

THE CAPACITY FOR A COMMUNITY OF MICROORGANISMS TO REMAIN QUALITATIVELY AND QUANTITATIVELY STABLE UNDER A VARIETY OF BIOLOGICAL AND NONBIOLOGICAL STRESSES



BIORESTORATION

IS NOT A PANACEA FOR ALL TYPES OF POLLUTANTS

NEEDS TO BE CONSIDERED AS ANOTHER PART OF THE
POLLUTION MITIGATION ARSENAL

References

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Miller, R. H. 1979. Ecological factors which influence the success of microbial fertilizers or activators. [redacted]. Dev. Ind. Microbiol. 20: 335-342

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EPA/600/2-87/008
January 1987

LEAKING UNDERGROUND STORAGE TANKS: REMEDIATION WITH EMPHASIS ON IN SITU BIORESTORATION

by

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L. W. Canter and C. H. Ward

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OFFICE OF RESEARCH AND DEVELOPMENT
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ADA, OKLAHOMA 74820

CONTENTS

E. IN SITU BIOLOGICAL TREATMENT

1. Microbial Activity In Aquifers

Microbial processes may be used to degrade contaminants in situ by stimulating the native microbial population. Another in situ biostimulation

technique which is not yet demonstrated is the inoculation of the subsurface with a microbial population that has specialized metabolic capabilities. Even in the presence of an indigeneous population which is acclimated to the organic contaminants, degradation may be limited at high contaminant concentrations or by some environmental factor. Addition of electron acceptors, such as oxygen, and inorganic nutrients, typically nitrogen, phosphorus, and trace metals, may provide the microflora with essential nutrients that are limiting in the presence of high concentrations of pollutants. Inoculation of a specialized microbial population may reduce the time required for acclimation to the contaminants and/or allow the removal of recalcitrant contaminants. Related processes such as the addition of bioemulsifiers or surfactants to increase the availability of subsurface contaminants to the microflora can also be used. When applicable, biological processes may offer the advantage of partial or complete destruction of the contaminants rather than simply transferring the pollution to another phase of the environment.

Technologies for biorestoration of polluted aquifers have resulted from recent research indicating that subsurface microorganisms exist, are metabolically active and often nutritionally diverse. A review, published by Dunlap and McNabb (1973) of the Robert S. Kerr Environmental Research Laboratory, addressed subsurface biological activity in relation to ground water pollution and initiated most of the research in this area . Before publication of the review, the concept of biological activity below the rhizosphere had not been widely received. Microbiologists were skeptical about biological activity in the subsurface because of oligotrophic conditions below the rhizosphere (Leenheer et al., 1974) and an early study which had indicated that microbial numbers decreased precipitously with depth (Waksman, 1916).

Sampling Methods for Subsurface Microbes--

A document that described sampling methods for subsurface microorganisms was published in 1977, by the Environmental Protection Agency (Dunlap et al., 1977). The method for procuring a representative sample of unconsolidated subsurface soil has since been modified (Wilson et al., 1983). A soil sample is collected by first drilling a borehole to a desired depth with an auger and then taking the sample with a core barrel. After sample procurement, the core is extruded through a sterile paring device that removes the outer layer of soil that has come in contact with the core barrel. The remaining soil core is thus uncontaminated by the sampling procedure and representative of the subsurface.

Investigations of microbial activity in the subsurface conducted prior to the development of the sampling techniques were equivocal because of the potential for contamination during sample procurement. In addition, many of the investigations were conducted using well water instead of core material. Recent evidence suggests that the majority of subsurface microorganisms are associated with soil particles (Harvey et al., 1984). In addition, well water may contain microorganisms that are artifacts of the well because of subsurface contamination during well installation and changes in water quality around the well.

Microbial Numbers in the Subsurface--

Methods to enumerate the subsurface microflora also have been developed. Electron microscopy, viable counts, epifluorescence microscopy, and measurements of biochemical components have been used to estimate microbial biomass (Ghiorse and Balkwill, 1985; Ghiorse and Balkwill, 1983; Wilson et al., 1983; Smith et al., 1986; Stetzenbach et al., 1986; Smith et al., 1985; Balkwill and Ghiorse, 1985; Bone and Balkwill, 1986; Webster et al., 1985; White et al., 1983; Hoos and Schweisfurth, 1982; Ehrlich et al., 1983; Federle et al., 1986). In contrast to Waksman's study (1916) which reported that microbial numbers declined with depth, uniform population levels around 10^6-10^7 cells/g dry soil, measured by epifluorescence microscopy, were reported for profiles of uncontaminated shallow aquifers (Ghiorse and Balkwill, 1985; Webster et al., 1985; Wilson et al., 1983; Ghiorse and Balkwill, 1983; Balkwill and Ghiorse, 1985; Bone and Balkwill, 1986). However, bacteria in a chalk aquifer (consolidated) were sporadically distributed with depth (Fowler et al., 1985). Close examination of the subsurface strata indicates patchiness of bacterial populations; samples from the top of the unsaturated zone of an artesian aquifer yielded the highest counts whereas those from bedrock and confining layers yielded the lowest total counts (Beloin et al., 1986).

Microbial Ecology of the Subsurface--

Bacteria are the predominant form of microorganism observed in the subsurface although a few higher life forms have been detected (Wilson et al., 1983; Ghiorse and Balkwill, 1985; White et al., 1983). Some eucaryotic forms which may be fungal spores or yeast cells have been observed in the upper 10 m of a soil profile (Ghiorse and Balkwill, 1983; Hoos and Schweisfurth, 1982; Federle et al., 1986). Bacteria, protozoa, and fungi have been detected in samples of ground water collected from one-year-old wells (Hirsch and Rades-Rohkohl, 1983). In addition, a slow-growing amoeba has been isolated and cultured from the ground water interface of an uncontaminated soil (Balkwill and Ghiorse, 1985; Beloin et al., 1986).

Metabolic Activity of the Subsurface Microbial Community--

Organic matter that enters the uncontaminated subsurface is usually the more refractory humic substances which resist degradation while percolating through the biologically active soil zone. The organic material available for metabolism by the subsurface microflora is likely to be in low concentration and difficult to degrade. The majority of microorganisms present in such nutrient-poor environments are generally oligotrophic. Characterization of the subsurface microflora indicates that the bacteria are usually smaller (<1.0 μm in size) than those in eutrophic environments and both Gram positive and negative cell types are present (Ghiorse and Balkwill, 1983; Wilson et al., 1983; Ghiorse and Balkwill 1985). Gram positive forms predominate in many uncontaminated soils. The predominance of small, coccoid cells and hence a large surface to volume ratio for enhanced nutrient uptake, is a likely mechanism for survival in an oligotrophic environment such as the uncontaminated subsurface (Wilson et al., 1983). In contrast, subsurface soil contaminated with creosote waste was found to contain more biomass and a greater proportion of Gram negative to Gram positive microbes when compared to uncontaminated soil from the same site (Smith et al., 1985; Smith et al., 1986).

Studies have also indicated that many subsurface microorganisms are metabolically active. Of the total cell count, about 0.01 to 50 percent can be recovered by plating on solid media and about 1 to 10 percent exhibit respiratory activity measured by the reduction of 2-(p-iodophenyl) -3-p-nitrophenyl)-5-phenyl tetrazolium chloride by cytochromes (Balkwill and Ghiorse, 1985; Webster et al., 1985). Microbial activity, measured by the hydrolysis of fluorescein diacetate, declined with depth in the unsaturated zone of Ultisols and Alfisols (Federle et al., 1986); however, 2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyl tetrazolium chloride reduction varied greatly between strata of a soil profile obtained from a shallow aquifer (Beloin et al., 1986).

Many subsurface microorganisms are nutritionally diverse (Table 2-3). Simple substrates such as glucose, glutamic acid, arginine, a mixture of amino acids, and a synthetic compound, nitrilotriacetic acid, were mineralized in samples of uncontaminated ground water (Larson and Ventullo, 1983). Polar solvents such as acetone, isopropanol, methanol, ethanol, and tert-butanol also have been reported to degrade aerobically by subsurface microorganisms (Novak et al., 1984; Jhaveri and Mazzacca, 1983). More challenging contaminants that are aerobically degraded by subsurface microorganisms include the methylated benzenes, chlorinated benzenes (Kuhn et al., 1985), chlorinated phenols (Suflita and Miller, 1985), and methylene chloride (Jhaveri and Mazzacca, 1983). Highly lipophilic compounds such as naphthalene, methylnaphthalenes, dibenzofuran, fluorene, and phenanthrene are also biotransformed in the subsurface (Wilson et al., 1985; Lee and Ward, 1985).

The microflora in some uncontaminated soils require little or no acclimation period to degrade many xenobiotics. For example, toluene, chlorobenzene, and bromodichloromethane were biotransformed in uncontaminated soil, but not 1,2 dichloroethane, 1,1,2-trichloroethane, trichloroethylene, and tetrachloroethylene (Wilson et al., 1983). Benzene, toluene and the xylene isomers were found to degrade in uncontaminated subsurface soils (Barker and Patrick, 1986). In addition, methanol (80-100 ppm) was degraded completely after two months, whereas tert-butanol degraded much slower in two uncontaminated anaerobic aquifers (White et al., 1986).

In contrast to reports of degradation of xenobiotics in uncontaminated soil, long periods of acclimation to subsurface pollutants may be required before biodegradation can occur. Wilson et al. (1985) reported degradation of naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, dibenzofuran and fluorene at 100-1000 μg/l in subsurface soil in the plume of contamination from a creosote waste pit; however, degradation of these compounds was not observed in uncontaminated soil from the same site. The time and concentration required for acclimation of the microflora to subsurface pollutants are unknown. Spain and Van Veld (1983) reported a threshold concentration of 10 ppb for adaptation to p-nitrophenol in samples of sediment and natural water. A better understanding of acclimation processes may explain why some chemicals persist in the subsurface even though they have been reported to degrade in laboratory cultures and samples of water and soil.

TABLE 2-3. ORGANIC COMPOUNDS THAT HAVE BEEN SHOWN TO BE BIODEGRADABLE IN THE SUBSURFACE

Compound	Soil from Contaminated Area	Aerobic	Reference
Natural Compounds			
glucose glutamic acid arginine	no	yes	Larson and Ventullo, 1983
Solvents			
acetone ethanol isopropanol	yes	yes	Jhaveri and Mazzacca, 1983
tert-butanol methanol	yes	yes	Novak et al., 1984
bromodichloromethane	no	yes	Wilson et al., 1983
Aromatics			
benzene xylene	no	yes	Barker and Patrick, 1983
methylated benzenes chlorinated benzenes	yes	yes	Kuhn et al., 1985
chlorinated phenols	yes	yes	Suflita and Miller, 1985
naphthalene dibenzofuran fluorene phenanthrene	yes	yes	Wilson et al., 1985; Lee and Ward, 1985
toluene chlorobenzene	no	yes	Wilson et al., 1983

Environmental Factors Which May Limit Biodegradation--

Environmental factors may limit or preclude the biodegradation of subsurface organic pollutants, even in the presence of adapted organisms. Recalcitrance of compounds thought to be biodegradable may result from lack of an essential nutrient, substrate concentration, substrate inaccessibility, and the presence of toxicants (Alexander, 1975). Transport of contaminants

in the subsurface also affects biodegradation. Transport is discussed in detail in Section II.F.

Biodegradation of many organic pollutants in the subsurface may be limited by insufficient oxygen. Alexander (1980) reported that even the metabolism of carbohydrates may be inhibited in oxygen-depleted environments. Lee and Ward (1985) found that the rate and extent of biotransformation of naphthalene, 2-methyl naphthalene, dibenzofuran, fluorene, and phenanthrene were greater in oxygenated ground water than in oxygen-depleted water. Contrary to general theory that complete degradation (mineralization) of hydrocarbons requires molecular oxygen, more recent research suggests that alternate pathways exist under anaerobic conditions. Kuhn et al. (1985) reported mineralization of xylenes in samples of river alluvium under denitrifying conditions. In addition, benzene, toluene, the xylenes, and other alkylbenzenes were metabolized in methanogenic river alluvium that had been contaminated with landfill leachate (Wilson and Rees, 1985); mineralization of toluene was confirmed by adding ^{14}C-labelled toluene and measuring the amount of $^{14}CO_2$ produced. Grbic-Galic and Vogel (1986) also reported mineralization of toluene and benzene under anaerobic conditions by a methanogenic consortium acclimated to ferulate. Further tests indicated that water supplied the oxygen that is first incorporated into the toluene and benzene ring (Vogel and Grbic-Galic, 1986).

The presence of oxygen may inhibit the biodegradation of many halogenated aliphatic compounds in the subsurface. Degradation of trihalomethanes, trichloroethylene, and tetrachloroethylene did not occur in aerobic cultures of sewage bacteria; however, the trihalomethanes were degraded anaerobically by mixed cultures of methanogens (Bouwer et al., 1981). In addition, Bouwer and McCarty (1983b) reported that chloroform, carbon tetrachloride and brominated trihalomethanes, but not chlorinated benzenes, ethylbenzene, or naphthalene were biotransformed under denitrifying conditions.

In addition to oxygen, other nutrients may limit the biodegradation of organic pollutants in the subsurface. Inorganic nutrients, such as nitrogen and phosphorous, may be limiting when the ratios of carbon to nitrogen or phosphorous exceed that necessary for microbial processes. On the other hand, the presence of sulfate may inhibit methanogenic consortia that have been reported to dehalogenate and mineralize many chlorinated aromatic compounds (Suflita and Gibson, 1985; Suflita and Miller, 1985).

The effect of substrate concentration on biodegradation of organic compounds in surface soils and waters has been documented (Alexander, 1985). Thresholds below which degradation is slow or does not occur may exist for compounds that are readily biodegradable at higher concentrations. Boethling and Alexander (1979) reported that less than 10 percent of 2,4-dichlorophenoxyacetate at concentrations of 22 pg/ml and 2.2 ng/ml was mineralized in stream water whereas about 80 percent was mineralized at higher concentrations of 0.22 and 22 µg/ml. On the other hand, microorganisms may be inhibited or killed by high concentrations of organic pollutants that result from injection wells and hazardous waste sites. Lee (1986) reported that glucose mineralization was inhibited in

subsurface soil heavily contaminated with creosote; however, glucose was mineralized in uncontaminated and slightly contaminated core material from the same site.

Other factors such as sorption, pH and temperature may also affect biodegradation of pollutants in the subsurface. Many of the organic compounds contaminating the subsurface are highly lipophilic. These compounds are sorbed by soil more strongly than the more hydrophilic compounds (Hutchins et al., 1985). Sorption may enhance degradation by concentrating nutrients or conversely, prevent degradation by rendering the substrate unavailable to the microorganism. Zobell (1943) reported that sorption of organic material to solid surfaces in dilute nutrient solutions increased microbial respiration. In contrast, Ogram et al. (1985) observed that 2-4 dichlorophenoxy acetic acid sorbed to soil was completely protected from microbial degradation. Therefore, sorption may be important in nutrient scavenging in uncontaminated aquifers which are generally oligotrophic; however, sorption may compete with the microflora for subsurface pollutants that are relatively hydrophobic.

The soil pH may affect sorption of ionizable compounds in addition to limiting the types of microorganisms in the subsurface. Methanogens, which have been implicated in mineralization of some aromatic hydrocarbons, are inhibited at pH values less than 6.0 (Alexander, 1977). Nitrification, the microbial conversion of ammonia to nitrate, is also limited at pH values below 6.0 and is negligible below 5.0. Hambrick et al. (1980) also reported that mineralization of octadecane and naphthalene in sediment was faster at a pH of 8.0 than 5.0.

Temperature also influences microbial metabolism of subsurface pollutants. The temperature of the upper 10 m of the subsurface may vary seasonably; however, that between 9-18 m approximates the mean air temperature (between 3 and 25°C in the United States) of a particular region (McNabb and Dunlap, 1975). Biodegradation of subsurface pollutants in the more northern climates may therefore be limited by cooler temperatures. Bartholomew and Pfaender (1983) reported that the microbial metabolism of m-cresol, nitrilotriacetic acid, and chlorinated benzenes in fresh water and estuarine areas decreased as temperature decreased. Atlas (1975) and Mulkins-Phillips and Stewart (1974b) also reported a direct relationship between petroleum hydrocarbon degradation and temperature.

In summary, the subsurface environment contains microbes that degrade many of the organic compounds that contaminate ground water. The subsurface microorganisms in uncontaminated aquifers are likely to be oligotrophic. The majority of the microorganisms are associated with soil particles. Even in the presence of adapted populations, environmental factors such as temperature, pH, dissolved oxygen levels, inorganic nutrient concentrations, and the availability and concentration of the organic contaminants may limit biodegradation of subsurface pollutants.

2. Biostimulation by Addition of Limiting Nutrients

Development of the In Situ Biostimulation Process with Oxygen Supplied by Air Sparging

Application of the degradative activity of subsurface microbes--The potential for biodegradation of organic compounds in contaminated aquifers was first reported in 1971. Bacteria capable of degrading hydrocarbons were observed in an area contaminated with gasoline; however, biodegradation of the gasoline was limited by the availability of oxygen, mineral nutrients, and hydrocarbon surface area (Williams and Wilder, 1971). Williams and Wilder (1971) suggested that these hydrocarbon-degrading bacteria could be used to clean the aquifer of residual gasoline; however, concern was expressed that bacterial growth would plug the well and formation. Davis et al. (1972) recommended supplying the indigenous microflora with nutrients, oxygen, and moisture rather than inoculating the subsurface with commerical biological products such as dried bacterial cultures. Oxygen-limited degradation of hydrocarbons was reported by McKee et al. (1972) in studies designed to investigate the fate of gasoline trapped in the pore space of sand columns. Several species of Pseudomonas and Arthrobacter were isolated from ground waters associated with a gasoline spill and used in the column experiments. The total number of gasoline-degrading bacteria in the ground water numbered over 50,000 cells/ml in the contaminated zone, but less than 200 cells/ml had been found in the uncontaminated wells and in wells where gasoline had not been detected for a year. The presence of high numbers of gasoline-degrading bacteria was suggested as an indicator of cleanup progress. In the column study, the bacteria rapidly degraded the gasoline in the zone of aeration but slowly degraded that in the saturated zone. In a similar study, Litchfield and Clark (1973) enumerated hydrocarbon-degrading bacteria in ground waters from 12 sites which were contaminated with petroleum. The numbers of hydrocarbon-degrading bacteria ranged from 10^3 to 10^6 cells/ml, with similar numbers of both aerobic and microaerophilic organisms, in ground waters containing more than 10 ppm hydrocarbon. Hydrocarbon-degrading bacteria were found in ground water from all 12 sites; however, on a site by site basis, there were no relationships between the types of organisms, the type of petroleum contamination, the geological characteristics, or the geographical location of the site.

Application of the degradative capacity of subsurface microorganisms to restore gasoline-contaminated ground water was first demonstrated by Raymond, Jamison, Hudson and coworkers at Suntech (Lee and Ward, 1985). In 1974, Raymond (1974) received a patent on a process designed to remove hydrocarbon contaminants from ground waters by stimulating the indigenous microbial population with nutrients and oxygen. Oxygen and nutrients are introduced into the formation through injection wells and production wells were used to circulate them through the aquifer. Placement of the wells was dependent on the area of contamination and the porosity of the formation, but usually no closer than 100 ft apart. The nutrient amendment consists of nitrogen, phosphorus, and other inorganic salts, as required, at concentrations of 0.005 to 0.02 percent by weight; oxygen was supplied by sparging air into the ground water. The process was projected to require about six months to achieve degradation of 90 percent of the hydrocarbons if the growth rate of the microorganisms was 0.02 g/L per day. The numbers of

bacterial cells were expected to return to ambient levels once the addition of nutrients was terminated. The process was expected to be more efficient in treating ground water contaminated with less than 40 ppm of gasoline.

First application of the biostimulation process--A pipe line leak in Ambler, Pennsylvania was the first site where Raymond's patent on biorestoration was demonstrated. An estimated 380,000 L of high octane gasoline had leaked into a highly fractured dolomite outcrop underlaid by quartzite (Raymond et al., 1975). Depth to the water table ranged from 9.2 to 30.5 m in the 46 monitoring wells installed at the site. Before biorestoration was attempted, conventional pump and treat technologies were used as remedial action. Containment of the gasoline was achieved by continuously pumping water from wells located in the spill area. About 238,000 L of the gasoline was recovered by physical methods; however, the recovery program was incomplete and approximately 119,000 L of residual gasoline remained. The concentration of dissolved gasoline in the withdrawn ground water averaged less than 5 ppm. The time required for restoration of the aquifer using this pump and treat technique was estimated to be more than 100 years.

Problems in analyzing the concentration of residual hydrocarbons during the pump and treat phase were later attributed to the presence of hydrocarbon-degrading bacteria (Raymond et al., 1975). A program designed to investigate the potential for biodegradation of the gasoline by these organisms was then initiated. A laboratory study indicated that supplements of air, inorganic nitrogen, and phosphate salts could increase the numbers of hydrocarbon-degrading bacteria by one thousand-fold (Raymond et al., 1976). Small scale field studies also indicated that nutrient additions would enhance the growth of bacteria that degrade hydrocarbons (Jamison et al., 1975). A full scale program to stimulate the biodegradation of the gasoline in the aquifer was then initiated (Raymond et al., 1976). The nutrient amendment, which contained ammonium sulfate, disodium phosphate, and monosodium phosphate, was injected into the aquifer as a 30 percent concentrate by batch addition. Either ammonium or nitrate could serve as the nitrogen source. Magnesium, calcium, and iron were not included in the concentrate because the small scale field study indicted that these inorganic nutrients were not limiting (Jamison et al., 1975). Biodegradation of 1 liter of gasoline was estimated to require 44 g of nitrogen, 22 g of phosphorus, and 730 g of oxygen. However, Baehr and Corpcioglu (1985) estimated that degradation of a pound (0.63 liter) of gasoline requires 3.5 g of oxygen. Batch addition of the nutrients worked as well as continuous addition and was more cost-effective; however, high concentrations of nutrients may osmotically shock the microorganisms (Raymond et al., 1976). Oxygen was supplied by sparging air into the wells using paint sprayer-type compressors and Carboundum diffusers with a flow rate of 0.06 m^3/min. As a result, the bacterial population increased from about 10^3 to 10^7 cells/ml. High bacterial counts mirrored locations of high gasoline concentrations at the site (Raymond et al., 1975).

During the biostimulation program at the Ambler, Pennsylvania site, 32 cultures of bacteria that actively metabolized gasoline were isolated and characterized; the isolates included species of the genera Nocardia,

Micrococcus, Acinetobacter, Flavobacterium, and Pseudomonas; some cultures could not be identified. Studies were conducted to determine the metabolic capabilities of these isolates (Jamison et al., 1976). The data suggested that the Nocardia cultures were largely responsible for the degradation of the aliphatic hydrocarbons whereas those from the genus, Pseudomonas, degraded the aromatics. Branched paraffins, olefins, or cyclic alkanes did not support the growth of any isolate. Co-oxidation may have played a major role in the biodegradation of these organics. An alternative hypothesis is that the bacteria capable of degrading these compounds were not isolated. The lack of microbial growth on some types of hydrocarbons may result from the toxicity or structure of the substrate. Straight chain aliphatics which are less than 10 carbons in length can be toxic whereas longer chains and branched alkanes are often resistant to microbial attack (Suflita, 1985). Substitutions on aromatics that are biodegradable may render them recalcitrant. Huddleston et al. (1986) gave the following order for petroleum hydrocarbon constituents, in order of decreasing biodegradability: linear alkanes C_{10-19}, gases C_{2-4}, alkenes C_{5-9}, branched alkenes C_{12}, alkenes C_{3-11}, branched alkenes, aromatics, and cycloalkanes.

The bioreclamation program conducted by Suntech at Ambler, Pennsylvania, was reasonably successful. During the period of nutrient addition, the concentration of gasoline in the ground water did not decline; however gasoline could not be detected in ground water 10 months later (Raymond et al., 1976). A thousand-fold increase in the numbers of total and hydrocarbon-degrading bacteria was observed in ground water from many wells (Raymond et al., 1975). The waters from some wells exhibited foaming because of high microbial numbers and associated exopolysaccharides. Counts of microorganisms determined one year after nutrient addition was terminated indicated that the microbial population had declined. Estimates based on the amount of nitrogen and phosphorus removed from the nutrient solution suggested that between 88,600 and 112,400 L of gasoline were degraded. However, this estimate was not particularly accurate because some of the nutrients may have been adsorbed by soil or lost from the biostimulation area by dilution. In addition, the estimates were based on discrete samples rather than composited samples. Large quantities of nutrients were used in this project; approximately 79 metric tons of food grade reagents were purchased.

Steps in the biostimulation process--The Ambler, Pennsylvania site case history is an example of the biostimulation process. The basic steps involved in an in situ biorestoration program are the following: 1) site investigation; 2) free product recovery; 3) microbial degradation enhancement study; 4) system design; 5) operation; and 6) monitoring (Lee and Ward, 1986). The first step in the process is to define the hydrogeology and the extent of contamination of the site. Important hydrogeologic characteristics include the direction and rate of ground water flow, the depths to the water table and to the contaminated zone, the specific yield of the aquifer, and the heterogeneity of the soil. In addition, hydraulic connections between aquifers, potential recharge and discharge areas, and fluctuations in the water table must be considered. The sustainable pumping rate must also be determined (Roux, 1985; Brown et al., 1985a). These parameters can be determined by surveying the existing

data for that site and region, reconnaissance by experienced hydrogeologists, geophysical surveys, excavation of test pits, and installation of boreholes and monitoring wells (Josephson, 1983). Low dissolved oxygen concentrations may indicate an active zone of hydrocarbon biodegradation (Chaffee and Welmer, 1983). The types and concentrations of contaminants is also important (Brown et al., 1985a). The type of remedial action chosen depends on the time elapsed since the spill, the areal extent of contamination, the nature of contaminants and whether the contamination is acute, chronic, or periodic. The urgency for action and the treatment level that must be achieved will depend on the potential for contamination of drinking water or agricultural water wells.

After defining the site hydrogeology, the next step is recovery of free product. Depending on the characteristics of the aquifer and contaminants, free product can account for as much as 91 percent of the spilled hydrocarbon (Brown et al., 1985a). The remaining hydrocarbon, which is sorbed to the soil and dissolved in the ground water, may account for 9 to 40 percent of the total hydrocarbon spilled; the majority is usually sorbed, however, the dissolved phase is the most difficult to treat. The pure product can be removed using techniques described in sections II B.2. an D. Physical recovery often accounts for only 30 to 60 percent of the spilled hydrocarbon before yields decline (Yaniga and Mulry, 1985).

Prior to <u>in situ</u> treatment, a laboratory study is conducted to determine the nutrient requirements that will enable the indigenous microorganisms to efficiently degrade the contaminants (Lee and Ward, 1985b). Kaufman (1986) suggested that these laboratory studies can provide a reliable basis for field trials; however, the studies must be performed under conditions that simulate the field. For example, Kuhlmeier and Sunderland (1986) conducted a laboratory investigation of the unsaturated zone using samples saturated with ground water. Clearly, the results of their study do not represent the fate of the organics in the unsaturated zone. A chemical analysis of the ground water provides little information about the nutrient requirements of the microflora (Raymond et al., 1978). However, the chemistry of the site will affect the nutrient formulation. For example, large quantities of oxygen may be consumed to oxidize reduced iron (Hallberg and Martinell, 1976). In addition, nutrients may sorb onto soils, especially silts and clays and be unavailable to the microflora (Brubaker and Crockett, 1986). Limestone and high mineral content soils and ground waters will also affect nutrient availability by reacting with the phosphorus.

Nutrient requirements are usually site specific. Nitrogen and phosphorus were required at the Ambler site (Raymond et al., 1976a); however, the addition of ammonium sulfate, mono-and disodium phosphate, magnesium sulfate, sodium carbonate, calcium chloride, manganese sulfate, and ferrous sulfate was required at other sites (Raymond et al., 1978; Minugh et al., 1983). The form of the nutrient may also be important; ammonium nitrate was less efficient than ammonium sulfate in one aquifer system.

Laboratory studies conducted to determine appropriate nutrient formulations can be performed using a number of techniques. An increase in

the number of total and hydrocarbon degrading bacteria has been used to identify limiting nutrients in a factorial experimental design (Raymond et al., 1976, 1978). However, an increase in microbial numbers does not demonstrate that the substrate of interest is being used. Batch culture techniques designed to measure the disappearance of the contaminant (Flathman and Githens, 1985) and electrolytic respirometer studies designed to measure the uptake of oxygen also have been used (Flathman et al., 1985). The results of another laboratory investigation indicated that dissolved oxygen was the primary factor limiting biodegradation of aromatic contaminants at a wood creosoting site rather than inorganic nutrients (Lee, 1986). Biotransformation studies which measure the disappearance of the contaminants or mineralization studies which indicate the complete destruction of the compound to carbon dioxide and water will confirm that the contaminants are being degraded. Controls to detect abiotic transformation of the pollutants and tests to detect toxic effects of the contaminants on the microflora should be included (Flathman et al., 1984).

A system for injection of nutrients into the formation and circulation through the contaminated portion of the aquifer must be designed and constructed (Lee and Ward, 1985b). The system usually includes injection and production wells and equipment for the addition and mixing of the nutrient solution (Raymond, 1978). A typical system is shown in Figure 2-1. Placement of injection and production wells may be restricted by the presence of physical structures. Wells should be screened to accommodate seasonal fluctuations in the level of the water table. Air can be supplied with carborundum diffusers (Raymond et al., 1975), by smaller diffusers constructed from a short piece of DuPont Viaflo tubing (Raymond et al., 1978), or by diffusers spaced along air lines buried in the injection lines (Minugh et al., 1983). The size of the compressor and the number of diffusers are determined by the extent of contamination and the time allowed for treatment (Raymond, 1978). Nutrients also can be circulated using an infiltration gallery (Figure 2-2); this method provides an additional advantage of treating the residual gasoline that may be trapped in the pore spaces of the unsaturated zone (Brenoel and Brown, 1985). Oxygen also can be supplied using hydrogen peroxide, ozone, or soil venting (see section on alternative oxygen sources). Well installation should be performed under the direction of a hydrogeologist to ensure adequate circulation of the ground water (Lee and Ward, 1985b). Produced water can be recycled to recirculate unused nutrients, avoid disposal of potentially contaminated ground water, and avoid the need for makeup water.

Inorganic nutrients can be added to the subsurface once the system is constructed. Continuous injection of the nutrient solution is labor intensive but provides a more constant nutrient supply than a discontinuous process. Continuous addition of oxygen is recommended because the oxygen is likely to be a limiting factor in hydrocarbon degradation.

The performance of the system and proper distribution of the nutrients can be monitored by measuring the organic, inorganic, and bacterial levels (Lee and Ward, 1985b). Carbon dioxide levels are also an indicator of microbial activity in the formation (Jhaveri and Mazzacca, 1985). Depending on the charcteristics of the nutrients and soil, nutrients can be removed

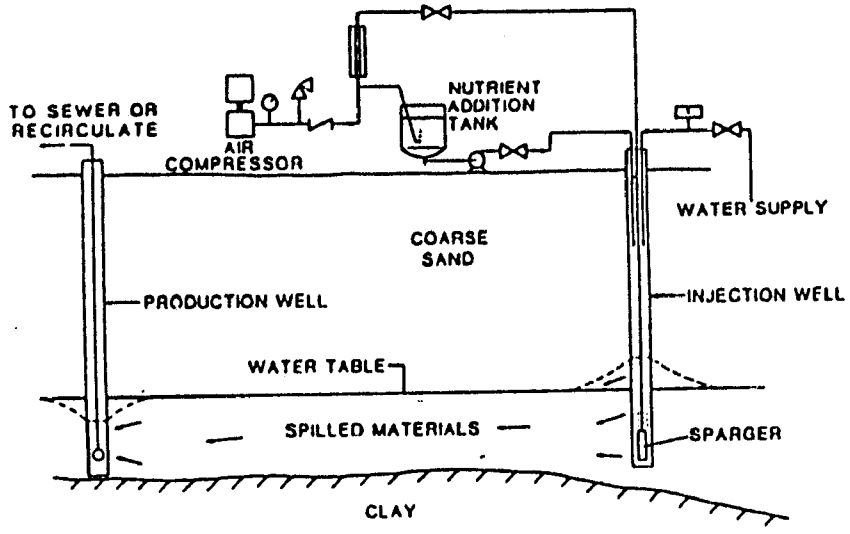

Figure 2-1. Typical schematic for aerobic subsurface biorestoration.

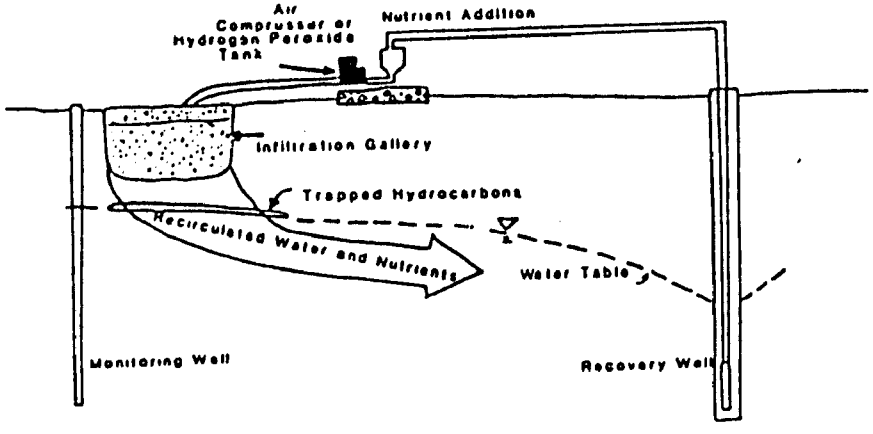

Figure 2-2. Use of infiltration gallery for recirculation of water and nutrients in <u>in situ</u> biorestoration.

from solution by sorption onto soil (Brubaker and Crockett, 1986). About 90 percent of the ammonium and phosphate and 70 percent of the hydrogen peroxide added to a sandy soil with low calcium, magnesium, and iron was recovered. After passage of a nutrient solution through a column packed with a clay soil that had high calcium and magnesium but low iron and chloride levels, 100, 66 and 25 percent of the ammonium, phosphate, and hydrogen peroxide were recovered, respectively. However, after passage of a nutrient solution through a column packed with a clay soil high in calcium, magnesium, and chloride, but low in iron, 75, 100; and 15 percent of the ammonium, phosphate, and hydrogen peroxide, respectively, were recovered. Both soil and ground water samples should be collected and analyzed to fully evaluate the treatment effectiveness (Roux, 1985). Raymond et al. (1975) reported that the most difficult problem in optimizing microbial growth in the Ambler reservoir was the distribution of nutrients, which was made difficult by the heterogeneity of the dolomite formation.

<u>Additional case histories in which oxygen was supplied by air sparging</u>--<u>In situ</u> biorestoration has been largely used to treat gasoline spills and with reasonably good success. However, many of the reports on <u>in situ</u> biorestoration lack sufficient data to fully judge the overall effectiveness and costs associated with the process.

In a high permeability sand aquifer contaminated with hydrocarbons in Millville, New Jersey, the <u>in situ</u> biorestoration program was successful in removing free product, but residual hydrocarbon was found at the last sampling period (Raymond et al., 1978). The nutrient solution was moved through the formation at rates of 8 to 14 ft/day, but dissolved oxygen was rapidly consumed and did not increase in some of the main wells at all. However, analysis of core material collected from the aquifer indicated that the concentration of gasoline had not changed substantially during the biostimulation program. During the initial treatment process, inadequate dissolved oxygen levels led to the microbial formation of phenol, but the phenol levels declined as more aerobic conditions were achieved. A ten to one thousand-fold increase in the number of gasoline-utilizing bacteria was noted in the area with the highest gasoline levels. The cleanup met the state requirement of removal of the free gasoline and was subsequently stopped.

At a gasoline spill in La Grange, Oregon, nine months of treatment by <u>in situ</u> biorestoration and a vapor elimination program succeeded in removing the free product and mitigating the vapor problems at two restaurants (Minugh et al., 1983); however, the concentration of gasoline in the pits in the biorestoration treatment area still ranged from 100 to 500 ppm in the majority of the samples. After an additional three months of treatment, the dissolved organic levels in the ground water had decreased from an average of 20 ppm to less than 5 ppm in the majority of the samples.

Fumes released from a pipeline spill of gasoline temporarily closed an elementary school (Suntech, 1978). A pumping well was used to maintain the water table below the school's foundation and physical recovery was used to remove two-thirds of the gasoline. An enhanced biodegradation program was initiated by circulating nutrients and oxygen through the formation for six

months. After the cleanup, hydrocarbons could not be detected and the fumes that had threatened the school had been eliminated.

Minimum hydrocarbon concentrations achievable by in situ biostimulation- The minimum concentration of hydrocarbon that can be achieved by in situ biorestoration is unknown and is most likely site specific. A natural gradient field test in a sandy Canadian aquifer required 434 days to reduce 1,000 to 2,400 ppb of benzene, toluene, and the xylene isomers to below the detection limits (1 to 2 ppb) in the absence of added nutrients and oxygen (Barker and Patrick, 1986). The distribution of dissolved oxygen in the plume was heterogeneous and probably controlled biodegradation of the aromatics.

Jensen et al. (1986) suggested that the indigenous microflora should be able to reduce the concentration of hydrocarbons below 1 µg/L when the initial hydrocarbon concentration is less than 10 mg/L and adequate quantities of nutrients and oxygen are supplied. The results of batch experiments using ground water from hydrocarbon-contaminated aquifers showed that the native microflora could generally reduce the concentrations of toluene, benzene, xylene, trimethyl benzene, naphthalene, methyl naphthalene, biphenyl, ethyl naphthalene, and dimethyl naphthalene from a range of 400 to 1,100 µg/L to less than 1 µg/L within a week in the presence of oxygen and nutrients, however, phenanthrene and toluene persisted at higher concentrations in two of the ground waters after incubation for six days.

The concentration of trace level organics in an aquifer may be reduced by providing a primary substrate that supports microbial growth and allows the organisms to act upon the trace level organics as secondary substrates (Bouwer, 1984). The concentration of the trace organic or secondary substrate is thought to be below the minimum substrate concentration (S_{min}) required to support microbial growth (Rittman and Kobayashi, 1982). The S_{min} concept was developed to describe limitations related to transport of organics into a biofilm and the subsequent kinetics of reaction. There are several examples of S_{min}. A reactor fed laboratory grade water containing 0.59 mg/L TOC was able to reduce acetate below the S_{min} value (0.03 mg/L) for acetate. Shimp and Pfaender (1985) demonstrated that addition of fatty acids, carbohydrates and amino acids enhanced the ability of mixed microbial populations to degrade substituted phenols. These data suggest that the addition of naturally occurring substrates may enhance the biodegradation potential of some xenobiotics. However, the addition of a primary substrate may not support the removal of some compounds. A biofilm supported by thymine could utilize alanine and acetate, both common metabolites, but not phenol and galactose (Rittman and Kobayashi, 1982).

Treatment trains--In many hydrogeologic systems which become contaminated from leaking underground storage tanks, a remediation process may be so complex in terms of contaminant behavior and site characteristics that no one system or unit will meet all requirements. Very often, it is necessary to combine several unit operations, in series and sometimes in parallel, into one treatment process train in order to effectively restore

ground water quality to a required level (Wilson et al., 1986). Examples of treatment trains include:

(1) physical containment with product removal and surface treatment;
(2) product removal with unsaturated zone flushing followed by in situ chemical treatment;
(3) physical containment with in situ physical/chemical treatment; and
(4) product removal followed by in situ biological treatment.

Physical containment through barriers and hydrodynamic controls alone merely act as temporary plume control measures. However, hydrodynamic processes must also be integral parts of any withdrawal and treatment or in situ treatment measures. Most remediation projects where enhanced biorestoration has been applied have started by removing heavily contaminated soils. This was usually followed by installing pumping systems to remove free product floating on the ground water, before biorestoration enhancement measures were initiated to degrade the more diluted portions of the plume.

There are numerous proven surface treatment processes available for treating a variety of organic and inorganic wastewaters. However, regardless of the source of ground water contamination and the remediation measures anticipated, the limiting factor is getting the contaminated subsurface material to the treatment unit or units, or in the case of in situ processes, getting the treatment process to the contaminated material. The key to success is a thorough understanding of the hydrogeologic and geochemical characteristics of the area. Such an understanding will permit full optimization of all possible remedial actions, maximum predictability of remediation effectiveness, minimal remediation costs, and more reliable cost estimates (Wilson et al., 1986).

The role of biorestoration in combination treatment schemes is often difficult to assess. Yaniga et al. (1985a) described the cleanup of a gasoline spill in which an air stripper was used to reduce the contaminants in the withdrawn ground water and to supply oxygen before the water was recirculated to the aquifer via an infiltration gallery. Before recirculation, ammonium chloride, sodium monophosphate, sodium diphosphate, iron sulfate, and manganese sulfate were added in slug batches to the treated water. Additional oxygen was supplied by sparging air into the wells. As a result, the dissolved oxygen increased from a range of 0-5 to 5-10 ppm; the hydrocarbon degrading bacteria increased from 10^2-10^3 to 10^3-10^4 cells/ml with just oxygen addition by air stripping and sparging and then increased to 10^6 cells/ml with nutrient addition and additional oxygen. Brown et al. (1985b) identified another gasoline contaminated aquifer which was treated using air sparging. An estimated 25,000 to 30,000 gallons of gasoline entered a 20 ft thick coarse grain sand and fine gravel aquifer. Recovery of free product accounted for 18,500 gallons of the spilled gasoline; however, an estimated 10,000 gallons was sorbed to the soil at concentrations of 2,000 to 3,000 ppm and 30 to 40 ppm was dissolved in the ground water. The concentration of gasoline was reduced to less than 50 ppm in the soil and less than 1 ppm in the ground water by air sparging.

Only 1 to 2 ppm of dissolved oxygen could be achieved in the wells by air sparging.

A spill of four solvents--methylene chloride, n-butanol, acetone, and dimethyl aniline--into a glacial till aquifer was withdrawn and treated by an activated sludge process, allowed to settle, and then recharged into the subsurface through injection trenches after being aerated and amended with nutrients (Jhaveri and Mazzacca, 1983). The recharge water contained organisms acclimated to the solvents in addition to a nutrient amendment containing nitrogen, phosphate, magnesium, sulfate, carbonate, manganese, and iron. Additional oxygen was supplied to the aquifer using a series of injection wells. Removal efficiencies of methylene chloride, n-butanol, and acetone were greater than 97 percent and the dimethyl aniline levels were reduced by greater than 93 percent in the above ground treatment. The concentrations of the solvents in the resulting effluent decreased to 0.04 mg/L for n-butanol, 0.92 mg/L for methylene chloride, 0.18 mg/L for dimethyl aniline, and 1.12 mg/L for acetone from initial concentrations of 19.1, 58.5, 2.9, and 38.8 µg/L, respectively. Based upon COD and gas chromatography analysis, the plume was reduced in size by 90 percent after three years of operation (Jhaveri and Mazzacca, 1985). The COD was reduced from 300 to 20 mg/L in one monitoring well. Based on the rate of ground water flow, this reduction in COD coincided with the expected arrival time of the treated ground water at that well. Elevated levels of carbon dioxide in ground water collected from the treatment zones, in comparison to those observed in uncontaminated and decontaminated wells, suggested that in situ biorestoration was occurring. However, the solvents were detected in the ground water beyond the projected date for completion of the project and the New Jersey Department of Environmental Protection standards had not been achieved after three years of operation.

Flathman et al. (1985) and Quince et al. (1985) discussed cleanup of a methylene chloride spill using physical and biological above-ground treatment processes and in situ biological treatment. Following sand filtration to remove particulates, air stripping, combined with a heat exchanger to improve stripping efficiency, was initially used to treat the withdrawn ground water and the water was used to flush the soil (Quince et al., 1985). Air stripping removed about 98 to 99.9 percent of the methylene chloride in the withdrawn water. The concentration of methylene chloride in the ground water was reduced by 97 percent in one downstream monitoring well. Biological treatment was used to further reduce the concentration of the methylene chloride after addition of ammonia and phosphate. An activated sludge unit was seeded with acclimated organisms from a wastewater treatment plant receiving methylene chloride and these organisms were used to inoculate the soil (Flathman et al. 1985). After 43 days of in situ biological treatment, the concentration of methylene chloride in ground water from a monitoring well 20 ft from the spill declined from 192 to 6 ppm and 156 ppm chloride was released; however, it could not be determined whether the added bacteria or indigenous microflora or both were involved in methylene chloride degradation. Both air stripping and biological treatment removed 99.9 percent of the initial amount of methylene chloride present during the four months of field operation. The concentration of methylene

chloride was reduced from 20,000 to less than 1 ppm in the source wells (Quince et al., 1985).

The subsurface at the Naval Air Engineering Center in Lakehurst, New Jersey, was contaminated with ethylene glycol resulting from the loss of about 4,000 gallons of cooling water from a lined surface storage lagoon (Flathman et al., 1984). The unsaturated zone was contaminated with concentrations of ethylene glycol as high as 4,900 mg/kg soil whereas ethylene glycol in the ground water was 2,100 mg/L. The highly contaminated soils were treated using injection and recovery wells whereas the ground water contaminated with ethylene glycol was treated by an above ground activated sludge unit and by adding ethylene glycol degrading bacteria and nutrients to the subsurface (Flathman et al., 1985). A biofeasibility study using an electolytic respirometer had demonstrated that the concentration of ethylene glycol could be reduced to less than 50 ppm within ten days by the natural microflora in the ground water and that the concentration of ethylene glycol at 1,300 ppm was not toxic. The initial operational phase was designed to degrade as much of the ethylene glycol as possible by treatment above ground with an activated sludge unit. The effluent from the activated sludge unit was amended with oxygen, nitrogen, and phosphorus, adjusted to neutral pH, and then reinjected into the subsurface to create a closed-loop system. The amended effluent was used to flush the contaminated soil and inoculate the ground water with nutrients and acclimated bacteria. The concentration of ethylene glycol in ground water collected from the plume recovery wells was reduced from 420-690 ppm to less than 50 ppm within 26 days (Flathman and Caplan, 1985); however, the unsaturated zone still contained pockets of ethylene glycol. A passive treatment system which involved adding lime and diammonium phosphate to the soil surface continued after termination of the active biorestoration phase. By the end of the treatment program, ethylene glycol could not be detected (detection limit, 50 ppm) in ground water collected from the production wells.

A shallow basin comprised of sand and pea gravel was contaminated with isopropanol and tetrahydrofuran (Flathman and Githens, 1985). In addition to isopropanol and tetrahydrofuran, acetone was also detected in the ground water and believed to be a byproduct of isopropanol degradation. Remedial action consisted of a recovery system, an above ground biological reactor, and recharging the aquifer with the effluent from the reactor which created a closed-loop system. The effluent, which contained acclimated bacteria, was also amended with nutrients before reinjection into the subsurface. The soils were flushed with the treated ground water to remove sorbed organics and introduce acclimated organisms into the aquifer. Maximum concentrations of isopropanol (950 ppm) and acetone (190 ppm) were detected in ground water from a centrally located well as a result of flushing pockets of contamination from the subsurface. The pattern of change in isopropanol and acetone concentrations was similar. The concentration of acetone in the ground water increased initially until the majority of the isopropanol had been degraded, and then declined to less than 0.2 ppm. Extrapolations from the data indicated that 99 percent of the contaminants would be removed within 33 days. Estimated cost for removal and disposal of 200,000 ft^3 of contaminated soil was $550,000 whereas the biological treatment program was estimated to cost one-fifth as much.

Winegardner and Quince (1984) documented two additional case histories of *in situ* biorestoration that involved addition of acclimated bacteria. The first case history described the cleanup of a train derailment which released a semi-soluble aliphatic hydrocarbon plasticizer. Recovery wells were used to collect the plasticizer from the subsurface. Later, surface recharge and shallow injection were used to flush the plasticizer out of the soil; this treatment reduced the peak concentration of greater than 2,000 ppm in a widespread area to a much smaller zone after 70 days, in addition to reducing the concentration of the plasticizer throughout the contaminated area. Air stripping and carbon adsorption were used initially; however, these techniques were replaced by biological treatment using activated sludge. The water treated by activated sludge was used as an inoculant to introduce the acclimated bacteria into the subsurface to enhance *in situ* biorestoration. The concentration of the plasticizer in the recovered water was reduced from approximately 1,700 to 400 ppm after clarification; however, the importance of each component in the treatment process could not be determined.

The second case history involved contamination of a glacial kame deposit of sand, gravel, silt, and clay with chloroform from a leaking pipeline. Ground water was withdrawn and treated with a mixed media prefilter, an activated sludge bioreactor and settling vessel, and a heated air stripper. The effluent from the activated sludge bioreactor was used as an inoculant for biorestoration. The effluent from the air stripper was discharged into a process sewer or into the subsurface. A forced flushing/recovery system was used to enhance the recovery of the chloroform. Biological treatment followed the physical recovery; however, treatment effectiveness was not discussed.

Summary of Aerobic *In Situ* Biostimulation Processes--

There are a number of advantages and disadvantages in using *in situ* biorestoration (Table 2-4). Compounds ranging from petroleum hydrocarbons to solvents have been treated by *in situ* biorestoration (Table 2-5). Unlike many aquifer remediation techniques, *in situ* bioreclamation can often treat contaminants that are sorbed to soil or trapped in pore spaces. In addition to treatment of the saturated zone, organics held in the unsaturated and capillary zone can be treated when an infiltration gallery or soil flushing is used. Biodegradation in the subsurface can be enhanced by increasing the concentration of dissolved oxygen, through the use of hydrogen peroxide, ozone, or a colloidal dispersion of air (colloidal gas asphrons). Complete biodegradation (mineralization) of organic compounds usually produces carbon dioxide, water, and an increase in cell mass. However, incomplete degradation (biotransformation) of organic materials can produce byproducts that are more toxic than the parent molecule. An example of biotransformation is the degradation of isopropanol to acetone at a hazardous waste site described by Flathman and Githens (1985). The levels of acetone increased initially, but declined after most of the isopropanol was removed. *In situ* biorestoration may rely on the biodegradation potential of the indigenous

TABLE 2-4. ADVANTAGES AND DISADVANTAGES OF BIORESTORATION (J. R. B. Associates, 1982; Yang and Bye, 1979)

Advantages

- Can be used to treat hydrocarbons and certain organic compounds, especially water-soluble pollutants and low levels of other compounds that would be difficult to remove by other methods
- Environmentally sound because it does not usually generate waste products and typically results in complete degradation of the contaminants
- Utilizes the indigenous microbial flora and does not introduce potentially harmful organisms
- Fast, safe and generally economical
- Treatment moves with the ground water
- Good for short-term treatment of organic contaminated ground water

Disadvantages

- Can be inhibited by heavy metals and some organics
- Bacteria can plug the soil and reduce circulation
- Introduction of nutrients could adversely affect nearby surface waters
- Residues may cause taste and odor problems
- Labor and maintenance requirements may be high, especially for long term treatment
- Long term effects are unknown
- May not work for aquifers with low permeabilities that do not permit adequate circulation of nutrients

TABLE 2-5. CONTAMINANTS TREATED BY IN SITU BIOSTIMULATION

Contaminants	Treatment Description	References
high octane gasoline	air sparging with nitrogen and phosphorus addition	Raymond et al., 1975 Raymond et al., 1975 Jamison et al., 1975 Jamison et al., 1976
gasoline	air sparging with complete mix of inorganics	Raymond et al., 1978
gasoline	air sparging with addition of complete inorganic nutrient solution	Minugh et al., 1983
gasoline	air sparging and addition of nutrients	Suntech, 1978
gasoline	dissolved oxygen supplied by an air stripper and sparging; nutrients also added	Yaniga et al., 1985a Yaniga et al., 1985b
gasoline	dissolved oxygen supplied by an air stripper	Brown et al., 1985b
gasoline	hydrogen peroxide plus nutrients	Yaniga and Mulry, 1984
gasoline	initial treatment utilized air stripping; hydrogen peroxide used later with the nutrient formulation	Yaniga, 1982 Brown et al., 1985b Yaniga et al., 1985b
unleaded gasoline	hydrogen peroxide supplied the oxygen	Brown and Norris, 1986
mineral oil hydrocarbons	withdrawn water treated with ozone and reinfiltrated	Nagel et al., 1982
gasoline	soil venting used to supply oxygen to unsaturated zone	Kuhlmeier and Sunderland, 1986

(Continued)

TABLE 2-5. (Continued)

Contaminants	Treatment Description	References
waste solvents and alkanes	nutrients plus hydrogen peroxide	Brown et al., 1985b Westray el al., 1985 Brenoel and Brown, 1985 Brown et al., 1986
methyl chloride, n-butanol, dimethyl aniline, acetone	withdrawal and treatment by an activated sludge process and recharge of aerated nutrient-laden water.	Jhaveri and Mazzacca, 1983 Jhaveri and and Mazzacca, 1985
methylene chloride	withdrawal and treatment with air stripping followed later by treatment in an activated sludge unit and recharge	Quince, et al., 1985 Flathman et al., 1985
ethylene glycol	treatment following withdrawal with ethylene-degrading bacteria and nutrients and then recharge	Flathman et al., 1985 Flathman and Caplan, 1985
isopropanol and tetrahydrofuran	treatment in an above ground reactor with addition of acclimated microbes to the aquifer along with nutrients	Flathman and Githens, 1985
aliphatic hydrocarbon plasticizer	activated sludge and recharge of acclimated bacteria and nutrients	Winegardner and Quince, 1984
chloroform	activated sludge bioreactor with the bacteria innoculated into the subsurface	Winegardner and Quince, 1984

subsurface microflora which usually contains few pathogenic organisms unless the aquifer has been contaminated with wastewaters (Keswick, 1984). The time required to treat subsurface pollution using in situ biorestoration can often be faster than some withdrawal and treatment procedures. A gasoline spill in Ambler, Pennsylvania, was remediated in 18 months using in situ biorestoration whereas pump and treat techniques were estimated to require 100 years to reduce the concentrations of gasoline to potable levels (Raymond et al., 1976). In situ biorestoration can also cost less than

other remedial options. Flathman and Githens (1985) estimated that the cost of in situ biorestoration would be one-fifth of that for excavation and disposal of soil contaminated with isopropanol and tetrahydrofuran and in addition would provide an ultimate disposal solution. The areal zone of treatment using biorestoration can be larger than other remedial technologies because the treatment moves with the plume and can reach areas which are otherwise inaccessible.

There are also disadvantages to in situ biorestoration programs. Many organic compounds in the subsurface are resistant to degradation. In situ biorestoration requires an acclimated population; however, adapted populations may not develop for recent spills or recalcitrant compounds. Heavy metals and toxic concentrations of organics may inhibit microbial activity and preclude the use of the indigenous microflora for in situ biorestoration at some sites. One option in this instance would be to remove the inhibitory substances and then seed the subsurface with appropriately adapted microorganisms; however, the benefits to adding microorganisms to the subsurface are still undemonstrated. The formation and injection wells may clog from profuse microbial growth which results from the addition of oxygen and nutrients. In one biostimulation project, microbial growth produced foaming in the well casings (Raymond et al., 1976a). In addition, the hydrodynamics of the restoration program must be properly managed. The nutrients added must be contained within the treatment zone because the profusion of inorganics into untargeted areas can result in eutrophication. High concentrations of nitrate can render ground water unpotable. Metabolites of partial degradation of organic compounds may impart objectionable tastes and odors. For example, the incomplete degradation of gasoline under low dissolved oxygen conditions resulted in phenol production; phenol was then degraded when more aerobic conditions were achieved (Raymond et al., 1976). Biostimulation projects require continuous monitoring and maintenance for successful treatment; whether these requirements are greater than those for other remedial actions is debatable. The process results in increased microbial biomass which could decompose and release undesirable metabolites. In addition, microbial growth can exert an oxygen demand that may drive the system anaerobic and result in the production of hydrogen sulfide or other objectionable byproducts. The long term effects of biorestoration are unknown. In situ biorestoration is difficult to implement in low permeability aquifers in which perfusion of nutrients and oxygen is slow or negligible; however, many in situ physical and chemical remediation processes are subject to the same restrictions. The success of in situ treatment schemes in low permeability aquifers depends on transporting the nutrients to the microflora or the active agent to the contaminants. The process has been used in different hydrogeological formations (Table 2-6).

Potential problems for any aquifer restoration program include reversible adsorption of the contaminants, poor delineation of the plume, inadequate sizing of the recovery system, pollution at depth, high costs, treating and disposing of large amounts of pollutants, constraints on ground water pumping, access to the contaminated area, and substantial quantities of pollutants in the vadose zone (Schmidt, 1983). To decrease the expense of an aquifer cleanup, Myer (1985) advocated a policy of life cycle design

TABLE 2-6. TYPES OF AQUIFERS WHERE IN SITU BIOSTIMULATION HAS BEEN UTILIZED

Aquifer Description	Flow Characteristics	Reference
high permeability dolomite	pumping rate of 265 to 378 L/min	Raymond et al., 1976 Raymond et al., 1975 Jamison et al., 1975 Jamison et al., 1976
medium to coarse sand	pumping rate of 65 to 151 L/min	Raymond et al., 1986
alluvial fan deposit of sand, gravel, and cobbles with some clay and silt	flow of 2.4 m/day	Minugh et al., 1983
poorly sorted mixture of boulders, pebbles, cobbles, sand, silt and clay	hydraulic conductivity of 9.4×10^{-5} to 1.7×10^{-3} cm/sec	Jhaveri and Mazzacca, 1983 Jhaveri and Mazzacca, 1985
perched water table in unstratified, unsorted layer of clay, silts, sands, gravels, and cobbles above a clay layer	pumping rate of 38 to to 57 L/min	Quince et al., 1985 Flathman et al., 1985
tank vault filled with pea gravel surrounded by sand and sandy clay strata	flow rate in excess 100 m/yr pumping rate of 151 L/min	Westray et al., 1985 Brown et al., 1985b Brenoel and Brown, 1985
glacial outwash composed of silt, sand, and gravel	hydraulic conductivity of 8.8×10^{-4} to 1.5×10^{-3} cm/sec	Brown and Norris, 1986
coarse sands and gravel	hydraulic conductivity of 2.1 cm/sec	Nagel et al., 1982
shale and siltstone	pumping rate of 68 L/min	Brown et al., 1985b Yaniga et al., 1982 Yaniga et al., 1985b
coarse sand with greater than 5% gravel	gradient of 0.015 to 0.02 m/m; flow of 0.61 to 0.91 m/yr	Yaniga and Mulry, 1984
glacial till composed of sand, gravel, and boulders in a silty clay matrix connected to a fractured sandstone		Yaniga et al., 1985b
shallow basin containing sand and pea gravel	flow of 27 to 38 L/min	Flathman and Githens, 1985

for remedial actions in which some of the equipment could be recycled and used at other sites. An example of this system was proposed to remediate contaminated ground water from a Gulf Coast hazardous waste site. The ground water contained high concentrations of phenol and enough dissolved solids (15,000 mg/L) to be considered a brine. The treatment system consisted of two activated sludge units, a fixed film-activated sludge unit, a dual media filter, and a carbon adsorption column. The components of the treatment system could be easily changed to accomodate the change in concentration of the contaminants during the clean up process.

Potential for Anaerobic Processes--

Anaerobic degradation pathways in the subsurface--Anaerobic processes are important in the subsurface environment because oxygen may be depleted in contaminated aquifers as a result of aerobic microbial activity. However, low levels of oxygen will support some microbial activity. Once the dissolved oxygen content in ground water declines as a result of microbial activity, replacement depends on recharge, reaeration from soil gases, and mixture with oxygenated waters surrounding the organic plume (Borden and Bedient, 1986; Borden et al., 1986).

Degradation of a variety of compounds under anaerobic conditions has been demonstrated to occur in aquifers and laboratory experiments using subsurface materials. However, anaerobiosis may retard the degradation of many compounds (Hutchins et al., 1985). The sequence of microbial processes that occur as environmental conditions change from aerobic to anaerobic in the subsurface usually follows the pattern of aerobic respiration, denitrification, manganese and iron reduction, sulfate reduction, and finally methane formation (Bouwer, 1985; Downes, 1985). Net energy production decreases as the redox potential decreases (Downes, 1985). Bouwer and McCarty (1983a;1983b) demonstrated differences in the degradation of organic compounds under different redox potentials; chloroform and 1,1,1-trichloroethylene were degraded by methanogenic, but not denitrifying bacteria. Ehrlich et al. (1982; 1983) reported the degradation of phenolics, but not polynuclear aromatics such as naphthalene, under methanogenic conditions. Recently Kuhn et al. (1985) documented removal of tetrachloroethylene, the xylene isomers, and dichlorobenzene isomers under denitrifying conditions. Wilson and Rees (1985) showed that degradation of benzene, ethylbenzene, toluene, and o-xylene occurred in methanogenic aquifer material from a landfill, although the process was slow compared to aerobic pathways. The concentration of toluene had been reduced by 87 percent after six weeks, however, more than 20 percent of the benzene, ethylbenzene, and o-xylene added to the microcosms persisted beyond 40 weeks. In the same study, trichloroethylene and styrene degraded under anaerobic conditions, whereas chlorobenzene persisted. Suflita and Gibson (1985) reported that 13 of 19 halogenated isomers of benzoate, phenol, and phenoxyacetate persisted at concentrations greater than 90 percent of that initially added to subsurface materials collected from a sulfate-reducing zone; however, only 3,4-dichlorobenzene remained at concentrations greater than 5 percent of that originally added to methanogenic samples collected downgradient of the sulfate reducing zone. Maximal numbers of sulfate-reducing and methanogenic bacteria are found at redox potentials of -100 to -150 and -250 to -350 mV, respectively (Van Engers, 1978). Halogenated aliphatics such as trichloroethylene, tetrachloroethylene, carbon tetrachloride, and 1,1,1-trichloroethane can be mineralized or dehalogenated under reducing conditions (Parsons et al., 1985) to potentially more toxic compounds such as vinyl chloride (Vogel and McCarty, 1985; Wood et al., 1985).

Anaerobic processes in in situ biostimulation--Anaerobic processes may be of potential use in in situ biorestoration processes. The redox potential would be selectively adjusted to favor the degradation of a particular contaminant. In addition to adjusting the redox potential, the pH of the ground water could be adjusted to the neutral or alkaline conditions required for sulfate reduction, methanogenesis, and usually denitrification. Anaerobic degradation of organic compounds would probably require less inorganic nutrient supplementation because less energy and therefore biomass is produced (Rittman and Kobayshi, 1982). Batterman (1983) added nitrate to ground water contaminated with hydrocarbons in an attempt to promote denitrification. The contaminated aquifer consisted of an 8 to 10 meter thick layer of sand which contained some silt and clay beds and a ground water flow of 4 m/day. The water was withdrawn from a deeper uncontaminated aquifer, aerated, passed through a sand filter, and amended with nitrate at 300 mg/L before being recharged to the shallow aquifer. Phosphate was not added because it was not limiting. The authors suggested that anaerobic degradation accounted for the removal of 7.5 tons of hydrocarbon within a period of 120 days. Removal of 1 mg of the hydrocarbon required 3.3 mg of nitrate (Batterman and Werner, 1984). The concentration of aliphatics declined slowly from 1.5 to about 0.7 mg/L whereas the total aromatics declined from 5.5 mg/L down to about 1.5 mg/L in approximately one year. The rate of decline in the concentration of xylene was much slower than that of benzene and toluene. Water was injected during the test which resulted in a rise in the level of the hydrocarbons as well as the water table into the unsaturated zone. There was an overall 40 percent reduction in the concentration of hydrocarbon as a result of the treatment process. Insufficient information was provided to determine if anaerobic degradation was responsible for the removal of the contaminants or if the removal was due to the oxygen introduced when the injection water was aerated before it was recharged into the shallow aquifer.

Degradation of low concentrations of organic compounds under methanogenic conditions, with acetate added at higher concentrations as a primary substrate, has been demonstrated (Bouwer, 1985). McCarty (1985) proposed a scheme to treat contaminated ground water anaerobically using the primary substrate concept. The system consists of an above ground reactor to which substrate and nutrients are added, a well casing bioreactor which operates anaerobically like a trickling filter, and the aquifer. The above ground reactor is used to develop an acclimated population. The effluent from the above ground reactor is injected into the well casing bioreactor to introduce acclimated microbes into the aquifer or enhance adaptation of the indigenous population to the contaminants. Once the acclimated population has developed, use of the above ground reactor can be discontinued.

A method that utilizes sequential aerobic and anaerobic conditions to degrade hazardous wastes has been studied in soils and may be applicable to subsurface cleanup. An insecticide, methyoxychlor, was slightly degraded in soil under either aerobic or anaerobic conditions after three months of incubation. When the samples were converted from an anaerobic to an aerobic status, mineralization of the methoxychlor increased 10 to 70 times of that observed in soils maintained aerobically throughout the incubation period (Fogel et al., 1982). The enhancement in methoxychlor degradation in soils

exposed to anaerobic and then aerobic conditions may be a result of dechlorination of the insecticide under anaerobic conditions and degradation of the dechlorinated products under aerobic conditions. This anaerobic-aerobic treatment scheme may be useful in biorestoration of aquifers contaminated with halogenated compounds. The aquifer could be managed like a sequencing batch reactor in which an acclimated population is exposed to deoxygenated water, then to aerobic conditions and then the treated water is withdrawn. The hydraulically managed system is then allowed to sit idle until the next cycle is initiated.

Rates of degradation under anaerobic conditions are typically slower than those under aerobic conditions; in addition, organic compounds may not be mineralized under anaerobic conditions even after long periods of incubation (Wilson and Rees, 1986). However, anaerobic treatment may be required to degrade pollutants that are recalcitrant under aerobic conditions; also, anaerobic treatment may require less management. The application of anaerobic conditions to biorestoration is still in the development stage and more research is required to demonstrate its usefulness in the field.

3. Addition of Specialized Microbial Populations to the Subsurface

In addition to stimulating the indigenous microbial population to degrade organic compounds, another innovative but not yet demonstrated technique is to add microorganisms with specific metabolic capabilities (Lee and Ward, 1985b). Specialized organisms may be inoculated into the subsurface environment or the environment may be altered to favor growth of a population with specific metabolic capacities. Populations that are specialized in degrading target compounds are selected by enrichment culturing or genetic manipulation. Enrichment culturing involves exposure of microorganisms to increasing concentrations of a contaminant or mixture of contaminants. The type of microorganisms that is selected or in essence, acclimates to the contaminant, depends on the source of the inoculum, the conditions used for the enrichment, and the substrate (Atlas, 1977). Acclimation can result from an increase in the number of organisms that can degrade the contaminant, new metabolic capabilities that result from genetic changes, or an increase in the quantity of the enzymes necessary for the transformation (Spain et al., 1980). The genetic changes include overproduction of enzymes, inactivation or alteration of regulatory gene control, or production of enzymes with altered specificities (Ghosal et al., 1985).

Genetic manipulation of microorganisms to produce specialized populations that can degrade target contaminants is a relatively recent development. According to Kilbane (1986), genetic engineering may accelerate and focus the process of evolution. Genetic manipulation can be accomplished by two different methods. In the first method, the organisms are exposed to a mutagen such as ultraviolet light, nitrous oxide, or 8-azaquinonone and then a population with specialized degradative capabilities is isolated by enrichment culturing (Zitrides, 1978; Kopecky, 1982); however, this may produce weakened strains because the process is non-specific and affects the entire genome (Zitrides, 1978). In the second

method, recombinant DNA technology is used to change the genetic structure of the microorganism (Kilbane, 1986). The genetic structure is changed by inserting a DNA fragment, often a plasmid that codes for a specific degradative pathway, into another organism. A plasmid is a piece of DNA that exists independently from the cell's chromosomes (Birge, 1981). The extra-chromosomal DNA can be transformed from one bacterium to another by conjugation, transduction, or transformation. Multiple degradative capabilities can be placed on a single plasmid that will allow the organism to degrade an array of compounds or complete the degradation of a nonbiodegradable molecule. Genetic engineering can be used to stabilize the degradative traits coded by the plasmid, increase the number of plasmids in a cell, amplify enzyme production and activity, invoke multiple degradative traits, or produce a novel degradative pathway (Pierce, 1982). In addition, organisms with different substrate affinities, pH optima, or degradation rates can be fashioned (Johnston and Robinson, 1982a).

Genetic Engineering to Enhance Degradative Activity--

Genetic engineering has been used to enhance the degradation of the recalcitrant pesticide, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). Biodegradation of the pesticide is usually very slow (Kilbane et al., 1982). A mixed culture of microorganisms that uses 2,4,5-T as a sole carbon and energy source was obtained by a technique called plasmid-assisted molecular breeding (Kellog et al., 1981). The technique involves inoculating a chemostat with microorganisms from a variety of hazardous waste sites and organisms that carry an array of plasmids that code for degradation of specific xenobiotics. A pure culture that could use 2,4,5-T as a sole carbon and energy source was isolated from the mixed population and tentatively identified as Pseudomonas cepacia (Kilbane et al., 1983). In addition, the culture, designated P. cepacia AC1100, was reported to oxidize many chlorophenols. Degradation of both 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-T was expressed in another strain of P. cepacia after conjugal transfer of two plasmid from an Alcaligenes entrophs sp. that degraded some chlorinated phenoxy herbicides (Ghosal et al., 1985). An inoculum of 2×10^7 cells/g of P. cepacia AC1100 degraded 95 percent of the 1,000 mg/L 2,4,5-T added to soil at 25 percent moisture and incubated at 30°C (Chatterjee et al., 1982). Less 2,4,5-T was removed with a smaller inoculum size and different temperatures and moisture contents. In addition, the 2,4,5-T degrading bacteria did not survive in soil without 2,4,5-T or when the concentration of the compound had been depleted (Kilbane et al., 1983). Field trials to determine the effectiveness of the 2,4,5-T-degrading bacteria have not been conducted.

Colsruotolo et al. (1985a) received a patent for "microbial degradation of obnoxious organic wastes into innocuous materials." The process involves isolation of microbial cultures from samples of soil and leachate from a hazardous waste site by enrichment culturing and then application of the purified strains in the field to remove the contaminants. Microorganisms capable of degrading selected isomers of chlorotoluene, dichlorotoluene, and dichlorobenzoate were isolated. Conjugation and transformation experiments were conducted to transfer the plasmid DNA, which conferred the ability to degrade some chloroaromatics, from the original isolates to another organism. The patent claimed that the organisms could be used to

decontaminate soil, remove contaminants in the air, mineralize toxic organics in the leachate from a chemical landfill and thereby reduce the concentrations of noxious chemicals.

Issues in Genetic Engineering of Microbes--

Organisms that can not easily exchange their genetic information with other organisms and are restricted to growth under defined environmental conditions are preferred candidates for genetic manipulation (Pierce, 1982). Issues concerning the use of genetically engineered organisms in the environment include: 1) adverse effects on human health, 2) how to effectively monitor their dispersal, 3) survival of the engineered organism in the environment, 4) regulation of activity in nontarget areas; and 5) determination of set risk levels acceptable to the public (Joyce, 1983). Many scientists argue that the engineered organism is not radically different from that which is genetically unaltered. The release of genetically engineered organisms into the environment is of great concern and some time may elapse before these organisms are used (Fox, 1985). The survivability of genetically altered organisms in the environment is also of concern. Surrogates of genetically engineered organisms which carried antibiotic resistance were added to samples of sewage, lake water, and soil and survived at rates that varied with the strain and environment tested (Liang et al., 1982). Some of the antibotic-resistant strains reached steady-state concentrations in lake water and sewage; however, all strains declined in the soil after a period of one month. Pseudomonas strains that degrade 2,4-dichlorophenol and p-nitrophenol were isolated from soil by enrichment culturing techniques. The ability of the isolates to degrade the phenol derivations was variable when inoculated into lake water, sewage, and soil (Goldstein et al., 1985).

Inoculation of a specialized microbial population into the environment may not produce the desired results for many reasons (Table 2-8). The concentration of the target compound required to support activity of a specific degrader may be limiting. Toxic or antimicrobial substances such as antibiotics may be found in many environments. High density inocula may be grazed by predators and the degradative capacity severely decreased if the growth rate of the introduced organisms is slow. In addition, adequate mixing to ensure contact of the organism with the pollutant will be difficult to achieve in the subsurface.

Most hazardous waste sites involve contamination of the environment with more than one compound. Therefore a mixture of organisms may be necessary to degrade all of the compounds in the waste (Atlas, 1977). Populations that have adapted to degrade many organic contaminants may be isolated from biological treatment processes such as sewage treatment, which receive pollutants. The efficacy of an inoculated population of specific degraders will depend on environmental constraints such as temperature, pH, and the concentrations of substrate, nutrients, and oxygen (Atlas, 1977; Zajic and Daugulis, 1975). Successful results from inoculation of foreign organisms are more likely in simple environments because the environment can be controlled more easily. An example of inoculation into a simple environment would be the introduction of bacteria into a biological reactor, oil tanker ballast tanks, or fermentator; these also provide the benefit of

TABLE 2-8. REASONS WHY INTRODUCED ORGANISMS FAIL TO FUNCTION IN THE ENVIRONMENT (Goldstein et al., 1985)

1.	The concentration of the compound is too low
2.	The environment contains some substance or organisms that inhibit growth or activity, including predators
3.	The inoculated organism uses some other organic other than the one it was selected to metabolize
4.	The organic is not accessible to the organism

containing the microorganisms. To avoid problems encountered with inoculation of foreign organisms into the environment, samples from the contaminated environment can be collected, microorganisms that can degrade the pollutants can be cultured by enrichment techniques or genetically engineered, and finally the specialized population can be reintroduced into the environment from which they came (Omenn, 1986). In addition, genetic manipulation of oligotrophic bacteria with high affinity enzyme systems may be advantageous because these enzyme systems will allow the organism to attack low concentrations of organic pollutants (Johnston and Robinson, 1982b).

Seeding Aqueous Environments with Microorganisms--

Inoculants of specialized microorganisms have been used in treatment of contaminated water. Atlas and Bartha (1973) tested several commercial bacterial preparations and found that the inocula were ineffective in treating oil spills in the marine environment. However, the addition of fertilizer and a bacterial seed isolated from an estuarine environment increased petroleum degradation in a saline but not in a freshwater pond (Atlas and Busdosh, 1975). After six weeks, 50 percent of the oil remained in the saline pond. The lack of activity in the freshwater pond suggests that the inoculum should be cultured from an environment similar to that being treated. Colwell and Walker (1977) suggested that seeding would be unsuccessful in environments such as the ocean; however, contained spills and lagoons may be amenable to such treatment. Gutnick and Rosenberg (1977) stated that "there is no evidence to support the claim that "seeding" oil slicks with microorganisms reduces oil pollution by stimulating petroleum biodegradation."

Seeding Soil Environments with Microorganisms--

The efficacy of inoculating soil with acclimated bacteria to remove selected contaminants was tested in a series of experiments (Watzel et al., 1981) using experimental chambers set up in greenhouses. The contaminants,

aniline and formaldehyde, were added to three types of soils (clay, sandy loam, and organic-rich) and plants were seeded in the chambers. Removal of the contaminants by a mixed microbial population from primary sewage effluent and an acclimated population was investigated. Formaldehyde was not removed in organic soils amended with sewage and acclimated bacteria; however, this treatment was successful in the upper and middle zones of the sand and clay soils. Aniline was removed in the organic and sandy soils after a second application of sewage microorganisms, nutrients, and yeast extract. Chemical oxidation of the organics using hydrogen peroxide was effective in reducing aniline concentrations. None of the treatments were successful in removing aniline from the clay soil. The removal of chlordane and 2,4-dinitrophenol by mutant adapted microbial cultures was also investigated. The inoculum was successful in degrading 2,4-dinitrophenol from the upper layer of the clay soil only. The authors suggested that the sewage inoculum was a low cost, effective method for removal of aniline and formaldehyde in most soil types; however, addition of the adapted population was not successful in these tests.

Inoculation of soils to remove chlorinated organics and pesticides has been attempted. Daughton and Hsieh (1977) reported that inoculation of sterilized soils with a parathion-acclimated culture reduced the concentration of the insecticide by 85 percent; however, the efficiency of the inoculum in non-sterile soil was greatly reduced. Focht and Brunner (1985) used an Acinetobacter strain as an inoculum to degrade biphenyl and polychlorinated biphenyls in soils. The inoculum increased the initial and maximum mineralization rates and the disappearance of the more heavily chlorinated biphenyls, but the overall extent of mineralization of polychlorinated biphenyls was not greater than that in inoculated soil to which biphenyl had been added. The process was thought to be a cometabolic-commensal metabolism of the PCBs.

Remediation of soil contaminated with hydrocarbons by inoculating with hydrocarbon degrading organisms has been met with varying success. Schwendinger (1968) demonstrated that inoculation of a hydrocarbon-degrading strain of Cellumonas in soil contaminated with petroleum increased the rate of reclamation in comparison to soils amended with only nutrients. Jobson et al. (1974) reported that the application of 10^6 cells of oil-degrading bacteria per cubic cm of soil slightly increased the degradation of the C_{20}- to C_{25}- group of n-alkanes in comparison to soils amended with fertilizer only. However, Lehtomaki and Niemela (1975) reported that brewer's yeast added to soils served primarily as a fertilizer rather than as an inoculum to actively degrade the oil. Seeding boreal soil with an oil-degrading inoculum increased microbial activity (Hunt et al., 1973). In laboratory studies, the addition of 300 ppm nitrogen and 100 ppm phosphorus, inoculation, and adjusting the pH to 7, increased microbial activity by at least a factor of four in comparison to unamended samples after 40 days of incubation. An increase in plant growth in an oil contaminated area in response to fertilizer addition was shown in field studies; however, the increased growth could have resulted from the addition of fertilizer or enhanced removal of the petroleum. In contrast, Westlake et al. (1978) reported no beneficial effects from the addition of oil-degrading bacteria to boreal soils. The lack of enhancement may be a

result of inadequate application of the inoculum. The type of organisms isolated from enrichment culturing depends on conditions used during the isolation procedure. For example, enrichments made at 4 and 20°C contained different organisms, and cultures enriched on a low quality crude were better adapted to utilize a lower quality crude than cultures enriched on a high quality crude (Jobson et al., 1972). These data suggest that enrichments for specialized populations should be conducted using the environmental conditions and contaminants that are unique to the site under investigation.

An inoculum of pentachlorophenol-degrading organisms has been used to decontaminate soil, river water, ground water and other freshwaters (Martinson et al., 1984). A Flavobacterium sp. that could mineralize pentachlorophenol (PCP) was isolated from a man-made channel which was exposed to the compound for several weeks (Crawford and Mohn, 1985). In addition to mineralizing PCP, the microorganism could attack a number of other chlorinated phenols but not all isomers (Stelert and Crawford, 1985). The Flavobacterium sp. at a cell density of 10^6 cells/ml removed over 90 percent of the PCP added to river water, ground water and other fresh waters, usually within 48 hours (Martinson et al., 1984). The organisms ability to degrade PCP was best between 15 and 35°C, and at pH values between 7.5 and 9.0. Inoculum densities as low as 10^4 cells/ml resulted in efficient removal of PCP. The time required to remove the PCP increased with increasing concentrations of PCP. When added to uncontaminated soil, the PCP was rapidly mineralized (Crawford and Mohn, 1985). The highest extent of mineralization occurred in soils with moisture contents between 15 to 20 pecent.

Mineralization of PCP was observed at inoculum densities as low as 3.1 x 10^3 cells/g; however, a slightly higher extent of mineralization was observed at a cell density of 3.1 x 10^6 cells/g (Crawford and Mohn, 1985). Mineralization of PCP in one uninoculated soil began after seven days of incubation and mineralization proceeded to the same point as the sample inoculated with 10^7 cells/g. Concentrations of PCP in soil contaminated from a wood treating landfill were reduced from 298 to 58 ppm after four applications of the inoculum in a period of 100 days. In another contaminated soil, PCP levels were reduced from 321 to 41 ppm after one application of seed, but similar levels of removal were observed in the uninoculated control. The seed could not remove PCP from a third soil in which the concentration of PCP had been diluted 10 fold to 553 ppm and the pH adjusted to neutrality. Addition of 10^6 cells/g soil of a culture of PCP-degrading Arthrobacter sp. reduced the half-life of PCP from two weeks to 15 hours (Finn, 1982). Edgehill and Finn (1983) reported that the rate of PCP disappearance was proportional to inoculum size that ranged from 10^4 to 10^6 cells/g soil. Up to 85 percent of the PCP was removed within 12 days in soil in which the seed had been thoroughly mixed; however, only 50 percent was removed in the unmixed soil. Brown et al. (1986) suggested that fixed film reactors with a PCP-adapted population may be used to treat waters contaminated with PCP at concentrations below the threshold of toxicity. A consortium that was attached to rocks from an artificial stream amended with PCP was generally able to degrade PCP as fast as the Flavobacterium sp. described by Crawford and Mohn (1985). A treatment

system using two fixed film reactors in series was then proposed; the first reactor would reduce high concentrations of PCP and the second reactor would contain organisms that could remove PCP to low levels. The consortium was able to remove PCP to less than 1 µg/L when the initial concentrations were less than 1 mg/L.

Seeding the Subsurface with Microorganisms--

Inoculation of bacteria into the subsurface for biorestoration has been met with some success, but the contribution of the introduced bacteria to the overall cleanup can not be readily determined. In most cases, the role of the introduced bacteria in degradation of the contaminants can not be determined because appropriate control plots were not incorporated into the experimental design and the results were not quantitatively measured throughout the course of the project. The biggest concern of inoculation into the subsurface is ensuring contact between the specialized cells and the target contaminants. The cells may be filtered out of the perfusing solution or sorbed onto soil before reaching the contaminants (Bouwer, 1984). In addition, normal die-off may control the movement and spread of bacteria in well-sorted sand, gravels, fractured rock, and karstic limestone.

Microbial movement through the subsurface depends on the characteristics of the soil and microorganisms. Only 1 percent of an inoculum of a Pseudomonas strain passed through a 2-inch sandstone core after washing with 123 pore volumes (Jenneman et al., 1984). Penetration of bacteria into sandstone cores with hydraulic conductivities greater than 100 millidarcies was rapid; however, penetration in cores with hydraulic conductivities below 100 millidarcies was slow (Jenneman et al., 1985). Motile bacteria moved three to eight times faster than nonmotile bacteria. Hagedorn (1984) summarized the results of selected studies on the maximum distance that microorganisms moved in various soils: 19.8 m in 27 weeks in a fine sand; 10.7 m in a sand and sandy clay in eight weeks; 24.4 m in a fine and coarse sand (time of travel not reported); 30.5 m in a sand and pea gravel aquifer in 35 hours; 0.6 to 4 m in a fine sandy loam (time of travel not reported); 457.2 m in a coarse gravel aquifer in 15 days; 28.7 m in 24 to 30 hours in a crystalline bedrock. Bacteria have moved as far as 920 meters in the subsurface at rates up to 350 m/day (Gerba, 1984). Microbial movement through soil macropores is an important mechanism of transport in all subsurface soils except sandy soils and those that are disturbed (Smith et al., 1983).

Transport of microorganisms in the subsurface can occur. However, in situ biorestoration programs using inoculation techniques will be affected by adverse conditions that decrease the survivability of microorganisms in the environment. Several factors must be considered before an in situ biorestoration program utilizing acclimated bacteria is implemented. The source, quantity, nature and biodegradability of the contaminants, and the environmental conditions of the site must be determined (McDowell et al., 1980). In addition, laboratory tests to determine the kinetics of degradation, the potential for inhibition under various conditions, requirements for oxygen and nutrients, and the effects of temperature should be conducted. The formation must be permeable enough to perfuse nutrients and the inoculum through the zone of contamination.

Aquifer Remediation Using Inoculation Techniques--

Inoculation of microorganisms into the subsurface has been used in aquifer remediation in conjunction with wastewater treatment processes. These cases are summarized in Table 2-9. A representative system is shown in Figure 2-3. In one case study, 7,000 gallons of acrylonitrile was spilled in a metropolitan area from a leaking rail car (Walton and Dobbs, 1980). The receiving aquifer contained significant amounts of silt and clay and hence was rather impermeable. Initial treatment involved withdrawal and treatment of the ground water by air stripping. After the concentration of acrylonitrile had declined to nontoxic levels, mutant bacteria were seeded into the soil. The concentration of acrylonitrile declined from 1,000 ppm to nondetectable levels (limit of detection 200 ppb) within one month; however, the role of the bacterial seed in acrylonitrile degradation could not be determined.

Quince and Gardner (1982a; 1982b) documented the cleanup of 100,000 gallons of various organic compounds, including ethylene glycol and propyl acetate, over a 250,000 square foot area. The soil consisted of a thick silty clay that extended to a depth of more than 50 feet; migration of the organics into the main aquifer was prevented by the structure of the formation. Containment and recovery of the organics were limited to the perched water table located in the upper clay layer. The contaminated ground water was withdrawn and treated by clarification, aeration, and granular activated carbon. A biostimulation program with specialized bacteria, nutrients, and air was initiated after the levels of the contaminants had decreased from 2,000-10,000 ppm to less than 200 ppm. During treatment, the concentration of ethylene glycol was reduced from 1,200 to less than 50 mg/L, propyl acetate was reduced from 500 mg/L to less than 50 mg/L, and the total concentration of spilled compounds declined from 36,000 to less than 100 mg/L. The resulting concentrations of contaminants were acceptable to the regulatory agencies.

Quince and Gardner (1982a; 1982b) documented the cleanup of a number of organic chemicals including dichlorobenzene, methylene chloride, and trichloroethane that contaminated the subsurface as a result of a spill from leaking tankers. The treatment scheme included recovery of product with a vacuum system, soil flushing, air stripping, and then inoculation of commercial hydrocarbon-degrading bacteria into an above ground reactor followed by recharge of the effluent into the subsurface. A commercial microbial inoculum seeded into the above ground reactor significantly decreased the concentrations of the organic contaminants after 36 hours of exposure. The operation was terminated after a 95 percent reduction in the organic levels was achieved. The injected hydrocarbon degraders were expected to complete the biodegradation in situ; however, the role of the added bacteria was not demonstrated.

An accidental spill of 130,000 gallons of organic chemicals entered a 15 foot thick shallow unconfined aquifer and resulted in total contaminant levels as high as 10,000 ppm (Ohneck and Gardner, 1982). A drinking water aquifer was separated from the contaminated zone by 50 to 60 feet of silty clay. The contaminated ground water was withdrawn and treated by clarification, granular activated carbon adsorption, and air stripping. A

TABLE 2-9. SUMMARY OF AQUIFER REMEDIATION CASE HISTORIES UTILIZING INTRODUCED ORGANISMS

Compound	Treatment Description	Reference
acrylonitrile	mutant bacteria added after concentrations had been reduced by air-stripping	Walton and Dobbs, 1980
phenol and chlorophenol	initial treatment by adsorption onto GAC followed by innoculation with mutant bacteria	Walton and Dobbs, 1980
ethylene glycol and propyl acetate	treatment above ground and later with specialized bacteria	Quince and Gardner 1982a and b
dichlorobenzene, dichloromethane, and trichloroethane	initial treatment with air stripping and then innoculation with a hydrocarbon-degrading bacteria	Quince and Gardner, 1982a and b
unidentified organic compounds	hydrocarbon-degrading bacteria added after levels reduced by GAC and air stripping	Ohneck and Gardner, 1982
formaldehyde	commercial degrader added to above ground treatment system formed from rail ballast	Sikes et al., 1984

program to enhance in situ biological degradation was initiated after the concentration of the organics had declined from as high as 10,000 ppm to 1,000 ppm. The results of laboratory tests indicated that the indigenous bacteria could degrade the contaminants when supplied with nutrients. Application of a commercial bacterial inoculum did not increase the biodegradation rates of the organics; in fact, one compound (unidentified) was degraded slower by the commercial hydrocarbon-degrading inoculum than the indigenous population. Effluent from the treatment system was amended with hydrocarbon degrading bacteria, air, and nutrients, and injected into the vadose zone. As a result, the concentrations of the contaminants in one soil core were reduced from 800 to 150 mg/L in two months. In another area, the concentration of the chemicals in composited soil samples declined from 24,000 to 2,000 mg/L. The concentrations of the organics in the ground water were reduced to less than 1 ppm, which met regulatory approval.

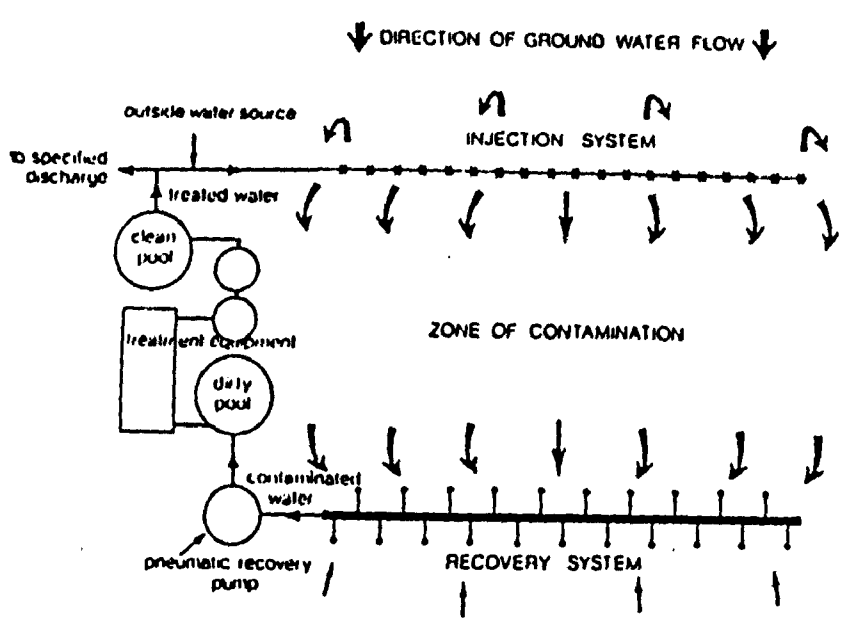

Figure 2-3. Combination of above ground treatment with in situ bioreotoration.

Incorporation of biological treatment into the restoration program decreased the cost of operation and maintenance. The role of the commercial inoculum in the removal of the contaminants could not be determined; in addition, laboratory studies indicated that the inoculum did not enhance biodegradation.

A spill of 20,000 gallons of a 50 percent solution of formaldehyde from a railroad tank car contaminated the soil and railroad bed in Ukiah, California (Sikes et al., 1984). Contaminated surface and ground waters were removed by a vacuum truck and 250 cubic yards of soil were excavated. Approximately 13 million gallons of water was collected. The water was initially treated with hydrogen peroxide to reduce the concentration of formaldehyde from 10,000-50,000 to 500-1,000 ppm by oxidation. See Section II.D. for more details of the use of hydrogen peroxide in this case study. The feasibility of in situ biological degradation of the remaining formaldehyde using a commercial bacterial inoculum was then investigated. A commercial inoculum that contained specially cultured microorganisms was chosen for the project. The biological treatment system consisted of a portable aeration tank, a spray system, and a trickling filter. The ground water was heated to increase the destruction rate and the pH was adjusted as necessary with sulfuric acid or soda ash; nitrogen and phosphorus were added as needed. The inoculum was rehydrated with chlorine-free water and added to the system at a rate of 3 lbs per day. The concentration of formaldehyde in the treatment tank fell from greater than 700 to about 10 mg/L after 24 days. The oxygen uptake rate in the sump ranged from 12 to 82 mg/L hr^{-1} and from 29-51 mg/L hr^{-1} in the ballast gravel. The treatment program was temporarily suspended for a day and the system was flushed. During this period, the concentration of formaldehyde increased greatly; however, a rapid reduction in formaldehyde levels followed. The authors suggest that the removal of the formaldehyde was a result of biological activity, however, they concede that proving the role of microorganisms in formaldehyde degradation would be difficult. In addition, the role of indigeneous and inoculated bacteria in formaldehyde degradation could not be separated.

TRANSPORT AND FATE

SIMULATION AND PREDICTION

Session 7

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MODELING APPROACHES

- Conceptual
- Physical
- Analog
- Mathematical

TYPES OF MODELS

- Flow models
- Transport models
- Multi-phase models
- Chemical reaction models
- Parameter identification models
- Data manipulation models
- Resource management models

MODEL DIMENSIONALITY

- 1,2,3-D spatially
- Steady-state or transient
- Non-dimensional

CONCEPTUAL MODELS

Definition:

An organizational framework for observations and ideas, that conveys an impression of causes and effects of the observations.

Example:

Integration of the natural processes that affect the movement of a specific contaminant in a particular setting, for assessment or prediction purposes.

CONCEPTUAL FLOW MODELS

- Confined (artesian) flow
- Unconfined (water-table) flow
- Fractured rock flow
- Multi-phase flow
- Unsaturated (vadose) zone flow

CONCEPTUAL TRANSPORT MODELS

- Advection–dispersion
- Diffusion dominated
- Advection dominated
- Advection–diffusion
- Discrete fracture
- Dual porosity, MINC
- Multi–phase

CONCEPTUAL MULTI-PHASE MODELS

- Unsaturated (vadose) zone
- Salt-water intrusion
- Immiscible phases (NAPL's)
- Compositional simulators

CONCEPTUAL CHEMICAL MODELS

- Equilibrium speciation
- Mass transfer
- Mass balance
- Kinetic rate
- Graphical relationships

INTEGRATED CONCEPTUAL MODELS

- Transport and speciation
- Transport and kinetics
- Well-mixed reactor cells
- Density dependent transport

OTHER CONCEPTUAL MODELS

- Inverse parameter i.d.
- Data input & output
- Statistical methods
- Resource management
- Economics

PHYSICAL MODELS

Definition:

A scaled replica of a real-world system, simplified and idealized for practical considerations.

Examples:

"Sand-tank" artificial aquifers, laboratory column experiments, and biological microcosms.

ANALOG MODELS

Definition:

A contrivance that imparts insights regarding cause & effect relationships within one physically distinct system to those of another physically distinct system.

Example:

Electric-analog model for water-supply wellfield management, using resistors for permeability, capacitors for storage effects, etc.

MATHEMATICAL MODELS

Definition:

A collection of equations that relate input parameters and variables to quantified outputs, based on specific assumptions and simplifications of the real-world system being modeled.

Example:

The Konikow-Bredehoeft contaminant transport model that employs a finite difference formulation for the flow field and a method-of-characteristics formulation for transport predictions.

FORMS OF MATHEMATICAL MODELS

- Analytical - closed form solutions
- Numerical - iterative solutions
- Semi-analytical - mixed form
- Computer - any form, codified

STATISTICAL BASES OF MATHEMATICAL MODELS

- Deterministic (spatially & temporally fixed inputs and outputs)
- Stochastic (probabilistic inputs and/or outputs)
- Geostatistical (spatial interpolation)
- Statistical (regression, correlation)

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PERFORMANCE AND ANALYSIS OF AQUIFER TRACER TESTS WITH IMPLICATIONS FOR CONTAMINANT TRANSPORT MODELING

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FOREWORD

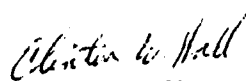
The U.S. Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of the facilities, the Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated zone and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

This report contributes to that knowledge which is essential in order for EPA to establish and enforce pollution control standards which are reasonable, cost effective and provide adequate environmental protection for the American public.



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Research Laboratory

Abstract

Due to worsening national problems, hydrologists are being asked to identify, assess or even anticipate situations involving groundwater contamination, and a large fraction of the regulation activities of the U.S. Environmental Protection Agency is in the groundwater area. In both regulation and assessment, increasing use is being made of complex mathematical models that are solved with the aid of a digital computer. Typically, such models are collections of partial differential equations that contain a number of parameters which represent aquifer physical properties and must be measured in the field. Of the various parameters involved, the hydraulic conductivity distribution is of major importance. Other parameters such as those relating to sorption, hydrodynamic dispersioon, and chemical/biological transformation are important also, but hydraulic conductivity is more fundamental because combined with head gradient and porosity it relates to where the water is moving and how fast. Therefore, this communication is devoted mainly to the conceptualization and measurement of hydraulic conductivity distributions and the relationship of such measurements to dispersion (spreading) of contaminants in aquifers.

For the most part, contemporary modeling technology is built around two-dimensional models having physical properties, such as transmissivity, that are averaged over the vertical thickness of the aquifer. In such a formulation, the major aquifer property related to contaminant spreading is forced to be longitudinal dispersivity. This is not due to any fundamental theoretical limitation. The major limitation is that dependable and economical field approaches for measuring vertically-variable hydraulic

conductivity distributions are not available. In the absence of such data, one has no choice in a modeling sense but to use some type of vertically-averaged advection-dispersion approach built around full aquifer longitudinal dispersivities.

In order to begin to overcome this limitation, a series of single-well and two-well tracer tests were performed at a field site near Mobile, Alabama, and a major objective of this communication is to describe these tracer tests and discuss some practical implications of the results with regard to modeling of contaminant dispersion in aquifers. The tests utilize multilevel sampling wells which have to be designed and installed carefully. Tracer test results along with theoretical studies suggest that the following working conclusions are warranted.

I. Local longitudinal hydrodynamic dispersion plays a relatively unimportant role in the transport of contaminants in aquifers. Differential advection (shear flow) in the horizontal direction is much more important.

II. The concept of full-aquifer dispersivity used in vertically-averaged (areal) models will not be applicable over distances of interest in most contamination problems. If one has no choice but to apply a full-aquifer dispersion concept, the resulting dispersivity will not represent a physical property of the aquifer. Instead, it will be an ill-defined quantity that will depend on the size and type of experiment used for its supposed measurement.

III. Because of conclusion II, it makes no sense to perform tracer tests aimed at measuring full-aquifer dispersivity. If an areal

model is used, the modeler will end up adjusting the dispersivity during the calibration process anyway, independent of the measured value.

IV. When tracer tests are performed, they should be aimed at determining the hydraulic conductivity distribution. Both our theoretical and experimental work have indicated that the variation of horizontal hydraulic conductivity with respect to vertical position is a key aquifer property related to spreading of contaminants.

V. Two- and three-dimensional modeling approaches should be utilized which emphasize variable advection rates in the horizontal direction and hydrodynamic dispersion in the transverse directions along with sorption and microbial/chemical degradation.

VI. In order to handle the more advection-dominated flow systems described in conclusion V, one will have to utilize or develop numerical algorithms that are more resistant to numerical dispersion than those utilized in the standard dispersion-dominated models.

Much of contemporary modeling technology related to contaminant transport may be viewed as an attempt to apply vertically homogeneous aquifer concepts to real aquifers. Real aquifers are not homogeneous, but they are not perfectly stratified either. What is being suggested, therefore, is that the time may have arrived to begin changing from a homogeneous to a vertically-stratified concept when dealing with contaminant transport, realizing fully that such an approach will be interim in nature and not

totally correct. Field calibration will still be required. However, the performance and simulation of several single- and two-well tracer tests suggests that the stratified approach is much more compatible with valid physical concepts, and at least in some cases results in a mathematical model that has a degree of true predictive ability.

An obvious implication of the study reported herein is that any type of groundwater contamination analysis and reclamation plan will be difficult, expensive and probably unable to meet all of the desired objectives in a reasonable time frame. Therefore, one can not overemphasize the advantages of preventing such pollution whenever it is feasible.

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Introduction

Due to worsening national problems and potential problems relating to industrial waste disposal, municipal waste disposal, radioactive waste disposal and others, there is increasing pressure on hydrologists to identify, assess or even anticipate situations involving groundwater contamination. In order to meet these demands, subsurface hydrologists have turned increasingly to the use of complex mathematical models that are solved with the aid of a digital computer. Some of the principal areas where mathematical models can now be used to assist in the management of EPA's groundwater protection programs are:

(1) appraising the physical extent, and chemical and biological quality, of groundwater reservoirs (e.g., for planning purposes),

(2) assessing the potential impact of domestic, agricultural, and industrial practices (e.g., for permit issuance, EIS's, etc.),

(3) evaluating the probable outcome of remedial actions at hazardous waste sites, and of aquifer restoration techniques generally,

(4) providing exposure estimates and risk assessments for health-effects studies, and

(5) policy formulation (e.g., banning decisions, performance standards).

These activities can be broadly categorized as being either site-specific or generic modeling efforts, and both categories can be further subdivided into point-source or nonpoint-source problems. The success of these efforts depends on the accuracy and efficiency with which the natural processes controlling the behavior of groundwater, and the chemical and biological species it transports, are simulated. The accuracy and efficiency of the simulations, in turn, are heavily dependent on the applicability of the

assumptions and simplifications adopted in the model(s), and on subjective judgments made by the modeler and management.

EPA's Site-Specific Modeling Efforts

Whether for permit issuance, investigation of potential problems, or remediation of proven contamination, site-specific models are necessary for the Agency to fulfill its mandate under a number of major environmental statutes. The National Environmental Policy Act (1970) stipulates a need to show the impact of major construction activities in Environmental Impact Statements and potential impacts are often projected by the use of mathematical models. The Underground Injection Control (UIC) program, which originated in the Safe Drinking Water Act (1974) (SDWA) and is now subject to provisions of the Resource Conservation and Recovery Act (1984 Amendments) (RCRA), requires an evaluation of the potential for excessive pressure build-up and contaminant movement out of the injection zone. Mathematical models are the primary mechanism for the required evaluation, due in part to the difficulty of installing monitoring wells several thousand feet deep.

UIC also calls for determinations of which aquifers serve, or could serve, as underground sources of drinking water (USDW's), based on a lower quality limit of 10,000 ppm total dissolved solids. Here, modeling has been found to be a useful adjunct to gathering and interpreting field data, such as in the U.S. Geological Survey's efforts to assist EPA in determining USDW's (e.g., the RASA program). Another SDWA program, for the designation of Sole Source Aquifers (SSA), has frequently employed the use of models for establishing and managing water-quality goals. Designation of the Spokane

Valley - Rathdrum Prairie SSA, for instance, included an evaluation of nonpoint-sources of nitrates with a groundwater model developed for EPA by the USGS.

Some of the most difficult site-specific problems facing the Agency involve hazardous waste sites falling under the purviews of RCRA and CERCLA/Superfund. Associated with most of these sites is a complex array of chemical wastes and the potential for groundwater contamination. Their hydrogeologic settings usually appear quite complicated when examined at the scale appropriate for technical assessments and remediation efforts (e.g., 100's to 1000's of feet). Groundwater models are used to assist in the organization and interpretation of data gathered during remedial investigations, the prediction of potential contaminant transport pathways and rates of migration, the setting of Alternate Concentration Limits, the design and comparison of remedial alternatives, and the evaluation of the performance of final ('as built') designs at hazardous waste sites. They are also used to help determine the adequacy of monitoring and compliance networks, and to determine the feasibility of meeting clean-up targets.

EPA's Generic Modeling Efforts

There are a number of instances where the Agency has limited data or other constraints, such that site-specific modeling is not feasible. As a result, many decisions are made with the assistance of generic modeling efforts. Generic efforts utilize analytical models, as opposed to numerical models, to a much greater degree than occurs in site-specific efforts. This is a logical consequence of the simplified mathematics of analytical models,

the significantly greater data requirements of numerical models, and the higher costs of numerical simulations.

The Agency has many statutory responsibilities which benefit from generic modeling, including the estimation of potential environmental exposures, and their integration with dose-response models to yield health-based risk assessments. These are necessary, for example, in issuing compound-specific rulings on products subject to pre-registration requirements under the Toxic Substances Control Act and the Federal Insecticide, Fungicide, and Rodenticide Act. More generalized policy formulation activities also benefit from generic modeling efforts. Examples include making policy decisions about land disposal 'banning,' preparing Technical Enforcement Guidance Documents (i.e., for monitoring network designs), and 'delisting' under RCRA.

Subsurface Transport Models

The most common types of modern groundwater transport models are a collection of partial differential equations and other mathematical/physical relationships that embody our best understanding of the system of interest, which in the present context is an aquifer. Virtually all groundwater models contain a number of parameters, which are simply numbers or functions that represent the physical and chemical properties of an aquifer and the aqueous solution that it contains. In order to apply a model to a particular problem situation, one must specify all the parameters (length, width, thickness, hydraulic conductivity, dispersivity, retardation coefficient, etc.) that pertain to that particular system. This is what

distinguishes one system from another in the application of a mathematical model.

In the actual process of using a mathematical model, the user puts all necessary information into the model (geometry, physical properties, initial and boundary conditions), and a computer is employed to rapidly solve the resulting equations which generates the model output. Output, for example, might include a predicted contaminant concentration distribution 10 years in the future. Presently, this predictive process is far from satisfactory (Konikow, 1986). Our understanding of all the physical and chemical phenomena involved is imperfect, and there are immense difficulties in measuring and specifying all of the required input data. If accurate information is not put into a mathematical model, one cannot expect accurate information to come out.

Over the past decade, a significant number of scientists have concluded that the single most important barrier to developing an improved ability to simulate groundwater contamination problems is our inability to measure, specify and, therefore, understand the type of hydraulic conductivity distribution that occurs in natural aquifers (Smith and Schwartz, 1981). This is not to say that other parameters such as those relating to sorption, hydrodynamic dispersion and chemical/biological transformations are not important. It is simply that the hydraulic conductivity is more fundamental, because together with the hydraulic head distribution and porosity, it is the physical property that relates to where and how fast the groundwater is moving. If one does not have the ability to specify the location of a parcel of water at a given time, one can hardly specify what

is going on chemically and biologically in that water. Therefore, this communication is devoted mainly to the conceptualization and measurement of hydraulic conductivity distributions and the relationship of such measurements to dispersion (spreading) of contaminants in aquifers.

The Hydraulic Conductivity Distribution

Measurement of hydraulic conductivity is difficult because of aquifer location (i.e., below the ground surface) and the nonhomogeneity of most natural aquifers. (It is not uncommon for hydraulic conductivity to vary by a factor of 10^8 or more within a given subsurface hydrologic system (Freeze and Cherry, 1979).) As discussed by Schwartz (1977), almost a continuously increasing scale of heterogeneity can be visualized in most aquifers. The heterogeneities arise due to variations in grain sizes and pore sizes, permeability trends due to stratification and variations in the original depositional environment, anisotropy, fractures, overall stratigraphic framework and more (Alpay, 1972). Because of the range of many of these variations and the unique physical, chemical and biological environments found in the subsurface, it is difficult or impossible to study spatial variability in a definitive way with laboratory experiments.

According to Philip (1980) field heterogeneity can be classified as either deterministic or stochastic. Deterministic heterogeneity refers to hydraulic conductivity variations that are sufficiently ordered to be characterized by a set number of measurements, although in practice the measurements may be difficult to make. Stochastic heterogeneity refers to hydraulic conductivity changes that are essentially random, making it pointless to try to measure them all. However, even these categories depend

on scale of observation (problem size), because variations that can be viewed collectively as stochastic on a sufficiently large scale (regional scale) may have to be treated as deterministic on a smaller scale such as a site-specific scale. In addition, stochastic variations are often embedded in systematic trends (i.e., random variations within discrete strata).

Since a complete characterization of the spatial distribution of hydraulic conductivity and hence a complete description of all the details of the flow field in an aquifer are practically impossible, various stochastic convection-dispersion models for solute transport have been proposed in recent years (e.g., Gelhar and Axness, 1983; Winter, 1982). While these models may be useful under certain conditions, they also have various limitations. Detailed discussions of the capabilities and limitations of these models may be found in Gelhar et al. (1979), Matheron and deMarsily (1980), Gelhar and Axness (1983), Dagan (1984), and Sposito, Jury and Gupta (1986). As reviewed in detail in the recent paper by Sposito, Jury and Gupta (1986), all such models involve a conceptual collection (ensemble) of statistically similar aquifers rather than a specific real aquifer. Consequently, these stochastic models provide results which are averages over the collection and, therefore, not directly applicable to a single aquifer. In addition, only under very limited conditions can measurements in a single real aquifer be related even conceptually to the statistics of a collection of aquifers that contains the real aquifer as one of its members. Essentially, the real aquifer must be statistically homogeneous on the average and ergodic (Neuman, 1982; Sposito, Jury and Gupta, 1986). Without going into details here, it is sufficient to

say that such a condition is very restrictive and does not allow an aquifer to have the type of general variability and persistent hydraulic conductivity trends that we believe are essential to understanding contaminant transport, particularly in site-specific situations involving relatively short travel distances. For these reasons and others, Sposito, Jury and Gupta (1986) concluded that "much more theoretical research is required and the stochastic convection-dispersion model does not yet warrant unqualified use as a tool for physically based, quantitative applications of solute transport theory to the management of solute movement at field scales."

In order to circumvent the fundamental difficulties of the stochastic convection-dispersion approach discussed in the previous paragraph and to deal at the same time with the problem of prediction uncertainty caused by data limitations, Smith and Schwartz (1981) (see also Dagan, 1984) have suggested the use of conditional simulations, a technique originally developed in the field of geostatistics (see, e.g., Journel and Huijbregts, 1978). Recent developments in the application of geostatistical estimation methodology in the groundwater field (Kitanidis and Vomvoris, 1983; Hoeksema and Kitanidis, 1984) make this approach promising. The geostatistical conditional simulations approach allows one to make direct use of all the available field data in solute transport predictions for a given aquifer, and also to provide estimates of the uncertainty in these predictions. Using this technique, the known features of the aquifer and the flow are taken into account in a deterministic manner while the unknown features are approximated and dealt with in a probabilistic manner. A major difference between this approach and the stochastic convection-dispersion model is that

the geostatistical methodology takes into account the actual spatial variations of aquifer properties by conditioning the simulations on the available measurements while the aforementioned stochastic models make use of the available data only to estimate the statistical structure of the assumed aquifer collection (ensemble). In fact, the results provided by the stochastic models referred may be viewed as being equivalent to the averages of the results which would be provided by unconditional simulations of the geostatistical approach. Due to the lack of conditioning, considerable uncertainty may exist in the predictions of the stochastic models when compared with the predictions of conditional simulations as indicated by the results of Smith and Schwartz (1981) and Güven (1986). While the geostatistical approach does appear promising in dealing with problems of solute transport, it is presently at an early stage of development and considerable theoretical work, improved numerical procedures, improved field measurement techniques and field verification studies are needed before any routine application of this approach in the field would be practical. In the meantime, interim approaches are required to advance our capability of modeling solute transport. More will be said about one such interim approach later.

The Mechanisms of Dispersion

In order to improve our capability of modeling solute transport, it is very important to understand the major physical mechanisms which affect the evolution and probable future of an existing groundwater contamination plume or the future course of an anticipated plume. The catch-all name given to the spreading of a contaminant in groundwater is dispersion, a term which is

familiar to almost everyone. However, as illustrated in Figure 1, many different phenomena contribute to the dispersion process in aquifers. The horizontal extent of the hypothetical tracer plume in Figure 1 is determined mainly by the elapsed travel time and the difference between the maximum and minimum values of the horizontal advective velocities. These velocity variations result primarily from the variations of hydraulic conductivity. Dilution within the plume and along the plume boundaries is caused by pore-scale mixing (local hydrodynamic dispersion) due in part to molecular diffusion, velocity variations within each pore, and the overall tortuosity of the flow path. In the hypothetical situation depicted in Figure 1, there is an overall trend of hydraulic conductivity increase from the top towards the bottom of the aquifer. Four minor trends, resulting in hydraulic conductivity peaks in both the upper third and bottom third of the aquifer, are evident also, with the lower peak being more pronounced. The plume concentration distribution is determined to a large extent by these trends. In addition, there are "wobbles" in the concentration distribution caused by seepage velocity components in all directions at a scale smaller than the scale of the minor trends noted above. Thus the actual concentration distribution of the plume is determined by a combination of strata-scale advective effects arising from the nonuniform velocity distribution and pore-scale mixing effects caused by the concentration differences within the plume and the basic nature of pore-scale flow. This pore-scale effect is most pronounced at the plume boundaries because the concentration gradients are largest there. In addition, wobbles in the concentration distribution at an intra-stratum scale could, after a sufficient travel time, result in a type of semi-local mixing, which some researchers have called macro-dispersion (Gelhar and Axness, 1983). As the plume travels further

downstream, the concentration gradients in the transverse direction would be gradually smoothed out due to both hydrodynamic dispersion and seepage velocity components in the transverse direction and a somewhat well-mixed condition would develop at each streamwise station over the whole depth of the aquifer after a sufficiently long travel time. However, the time required for this behavior could be very large (see, e.g., Gelhar et al., 1979; Matheron and deMarsily, 1980; Molz et al. 1983; Güven et al., 1984). In many site-specific situations, such large travel times are usually not involved, and variations of concentration over the depth of the aquifer are expected to be an important consideration when dealing with particular site-specific problems.

Simulation of Advection-Dispersion Processes

Historically, the field of subsurface hydrology developed mainly in response to groundwater supply problems. To solve such problems there was often little need to develop detailed information concerning the spatial variability of hydraulic conductivity within a given aquifer. Knowledge of the average transmissivity and storativity of the aquifer was adequate along with specification of the vertical aquifer boundaries (water table or confining layers) and in some cases the lateral boundaries. For these conditions, one-dimensional, horizontal, transient flow in a confined homogeneous aquifer may be written as (Freeze and Cherry, 1979)

$$\frac{\partial^2 h}{\partial x^2} = \frac{S}{T}\frac{\partial h}{\partial t} \qquad (1)$$

where x = length in the direction of flow, t = time, h = hydraulic head, S = storativity and T = transmissivity. Typically, the average S and T values would be determined by a pumping test utilizing fully-screened, fully-penetrating pumping and observation wells (Freeze and Cherry, 1979).

More recently, when societal trends shifted from groundwater supply to groundwater contamination problems, it seemed logical to work with the contaminant transport version of equation (1). For steady horizontal flow but transient (time changing) dispersion of a conservative solute in a confined aquifer, this equation is given by (Freeze and Cherry, 1979)

$$\frac{\partial c}{\partial t} + V\frac{\partial c}{\partial x} = D_L\frac{\partial^2 c}{\partial x^2} \qquad (2)$$

where c = solute concentration, V = uniform seepage velocity and D_L = longitudinal dispersion coefficient. D_L is given by the product $\alpha_L V$, where α_L is the longitudinal dispersivity, which represents the random local mixing properties of the aquifer. But what happens if one attempts to blindly apply equation (2) to the situation depicted in Figure 1? First of all, one would have to work with some average horizontal velocity, $\bar{V}$, an average concentration, $\bar{c}$, and some type of apparent or effective dispersion coefficient, D_L^*, which we will call the "full aquifer" dispersion coefficient. With these assumptions, solutions of equation (2) would predict tracer distributions similar to those shown in Figure 2. Comparison of the predicted distributions (which, as a result of the assumptions are uniform in the vertical direction) with the more realistic distribution (Figure 1B) shows this approach to be generally unsatisfactory. A lot of useful information has been lost by not incorporating the vertical distribution of hydraulic conductivity. This example highlights the problem that results when attempting to solve groundwater contamination problems with approaches found to be useful in water supply problems. Two-dimensional versions of equation (2) are the so-called areal advection-dispersion models; they are based on the same vertically-averaged approach and thus suffer from the same limitations.

If one considers explicitly the vertical variation of hydraulic conductivity for the transport problem illustrated in Figure 1 with flow, V(z), parallel to the stratification in a horizontal stratified aquifer, the governing equation becomes (Molz, Güven and Melville, 1983)

$$\frac{\partial c}{\partial t} + V(z)\frac{\partial c}{\partial x} = D_L(z)\frac{\partial^2 c}{\partial x^2} + \frac{\partial}{\partial z}\left(D_T(z)\frac{\partial c}{\partial z}\right) \qquad (3)$$

where c = c(x,z,t) = concentration distribution, z = vertical coordinate, $D_T = \alpha_T V(z)$ = transverse (vertical) dispersion coefficient, $D_L = \alpha_L V(z)$ = longitudinal dispersion coefficient, α_T = local transverse (vertical) dispersivity and α_L = local longitudinal dispersivity. If D_L is small, as is often the case (Pickens and Grisak, 1981), one can neglect, without much error, the local longitudinal mixing term in equation (3) which leaves (Güven et al., 1984)

$$\frac{\partial c}{\partial t} + V(z)\frac{\partial c}{\partial x} = \frac{\partial}{\partial z}\left(D_T(z)\frac{\partial c}{\partial z}\right) \qquad (4)$$

While the local longitudinal mixing term may be neglected, the local transverse mixing term has a very important influence on the solute spreading, particularly at intermediate and large times (Molz et al., 1983; Güven et al, 1984). Noting that by identity $V(z) = \bar{V} + (V(z) - \bar{V})$, one can write equation (4) as

$$\frac{\partial c}{\partial t} + \bar{V}\frac{\partial c}{\partial x} = \frac{\partial}{\partial z}\left(D_T(z)\frac{\partial c}{\partial z}\right) - (V(z)-\bar{V})\frac{\partial c}{\partial x} = \frac{\partial}{\partial z}\left(D_T(z)\frac{\partial c}{\partial z}\right) - \frac{\partial}{\partial x}\left((V(z)-\bar{V})c\right) \qquad (5)$$

In this form it is particularly illuminating to compare equations (2) and (5), because one can see in mathematical/physical terms an implication of the discrepancy illustrated graphically in Figures 1 and 2. If one forces equation (2) to fit a dispersion process properly described by equation (5), then the full aquifer dispersion term will have to model solute spreading

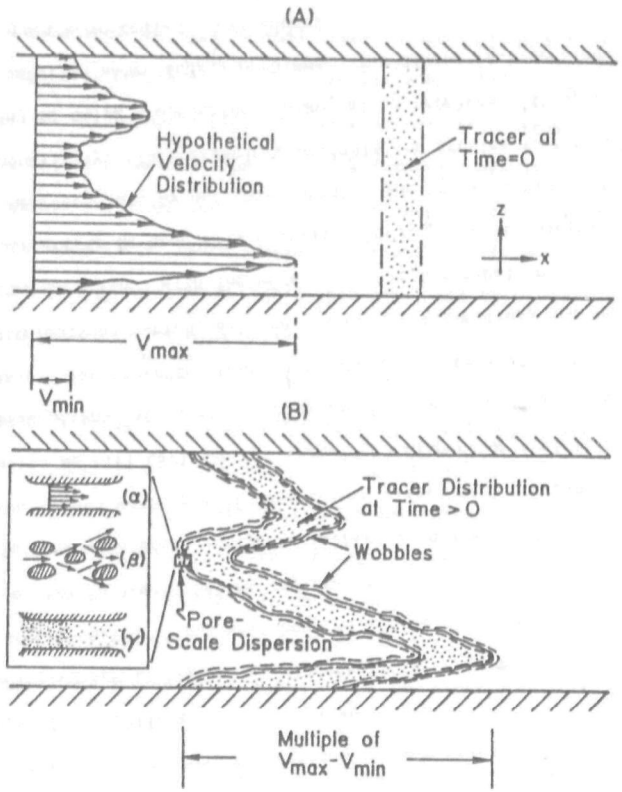

Figure 1. Part (A) shows a hypothetical velocity distribution and an initial distribution of tracer while part (B) shows how the tracer would be dispersed by the moving groundwater at several different scales. Three common mechanisms of pore scale dispersion (velocity variation within a pore (α); flow path tortuosity (β), and molecular diffusion due to concentration differences (γ)) are illustrated also.

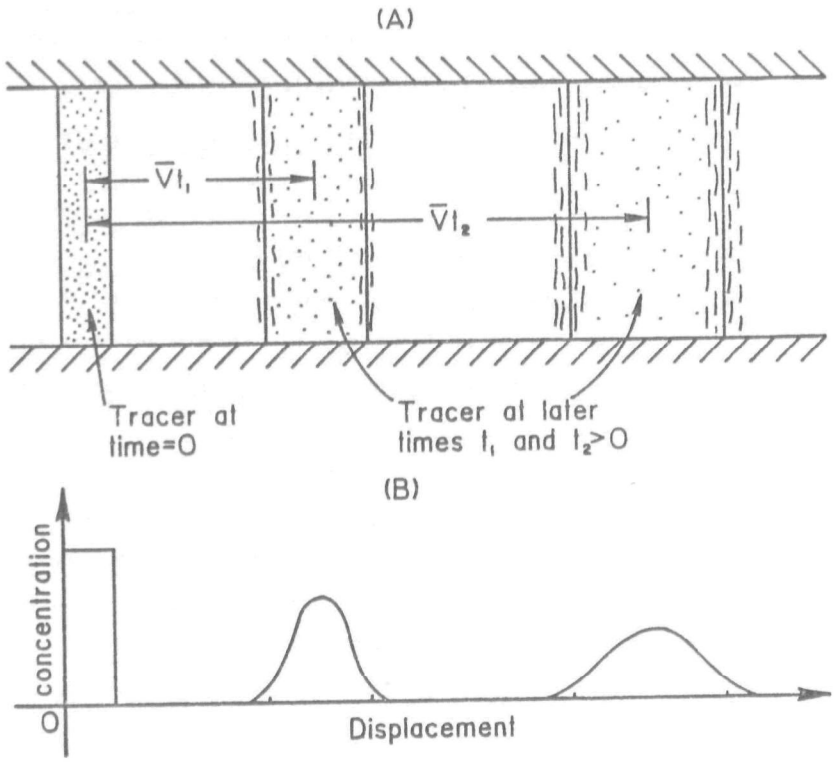

Figure 2. Schematic diagram showing the inherent lack of vertical contaminant concentration structure resulting from vertically-averaged transport models (part A) and the resulting plots of concentration versus distance (part B).

due to a combination of local mixing, $D_T(z)\partial c/\partial z$, and differential advection, $(V(z)-\bar{V})c$. Combining local mixing and differential advection within a single dispersion term is not reasonable physically and not strictly possible mathematically, as discussed by Molz, Güven and Melville (1983) and elaborated in more detail by Güven, Molz and Melville (1984). The overall approach makes the full-aquifer dispersivity, α_L^*, scale-dependent, which means that it is not a unique property of the aquifer or of anything else in particular. The full-aquifer dispersivity simply becomes a parameter used to fit equation (2)-type solutions to vertically-averaged concentration distributions when the desirable information concerning hydraulic conductivity profiles is not available. Not only is the fit often poor, but the numerical size of such "fitted" dispersivity values is usually several orders of magnitude larger than laboratory measurements of true hydrodynamic dispersivities (Pickens and Grisak, 1981; Anderson, 1983). This suggests that the differential advection arising from the overall hydraulic conductivity distribution plays a major role in the dispersion process.

These remarks are not provided simply to discredit areal advection-dispersion models because such models have been applied productively. However, the fitting process associated with the identification of full-aquifer dispersivity values means that the use of such models as truly predictive tools is highly questionable. Their success to date has been severely limited by the non-unique and ill-defined nature of the full-aquifer dispersivity. Partly because of this, examination of down-gradient impacts of a contaminant plume usually requires major re-calibration of a full-aquifer model developed for the local site. Despite these limitations, areal advection-dispersion models continue to serve a useful purpose because of the lack of adequate and practical field

techniques for determining the hydraulic conductivity distribution. Only recently have experiments with the objective of measuring vertical distributions of horizontal hydraulic conductivity been performed (Pickens and Grisak, 1981; Molz et al., 1985, 1986). Thus the required instrumentation and testing techniques are neither fully developed nor widely available. In the absence of vertically-distributed data, one has no choice in a modeling sense but to use some type of vertically-averaged advection-dispersion approach built around full aquifer dispersivities. However, we believe that much more can be done with existing instrumentation and techniques than is typically done during field investigations of groundwater contamination incidents.

As supported by the previous arguments, it is likely that any real advance in our ability to simulate the contaminant dispersion process in aquifers will have to be built upon more detailed measurements of hydraulic conductivity and head distributions so that the advection field is defined in more detail. It is particularly important to move away from the exclusive use of vertically-averaged aquifer properties and flow variables. Recently, we have performed single-well and two-well tracer tests at a site near Mobile, Alabama with the objective of measuring relative travel time distributions across the vertical dimension of an aquifer, assuming horizontal flow on the average. We conducted those experiments because tracer tests provide the most definitive data with which to infer hydraulic conductivity distributions. A major purpose of this communication is to describe these tracer tests and testing procedures and to discuss some practical implications of the results with regard to modeling of contaminant dispersion in aquifers.

Types of Tracer Tests

It is generally agreed that tracer tests are currently the most reliable field methods for obtaining data to describe dispersion in groundwater. Most tracer tests can be placed in two major categories--natural gradient and forced gradient. As the name implies, natural gradient tests involve various means of placing an inert, non-adsorbing chemical (tracer) in an aquifer and allowing it to move with the natural groundwater flow (Sudicky, Cherry and Frind, 1983). Stanford University, in cooperation with the University of Waterloo, has recently completed a detailed natural gradient test soon to be reported in Water Resources Research. Herein we are concerned mainly with forced gradient tests which employ pumping wells (injection and/or withdrawal) to move a tracer through the test aquifer. Normally, the selected pumping rates are such that the resulting hydraulic gradients are much larger than the natural gradient. For this reason, forced gradient tests are much shorter in duration than natural gradient tests. The most common types of forced gradient tracer tests are single-well tests and two-well tests. Over the past two years, both types have been performed at the Mobile site (Molz et al., 1985, 1986), and both types have been studied in some theoretical detail relative to their analysis and interpretation in stratified aquifers (Güven et al., 1985, 1986). The stratified aquifer assumption represents the simplest aquifer idealization having a horizontal hydraulic conductivity distribution that depends on the vertical coordinate (Güven, Molz and Melville, 1984).

Shown in Figure 3 is a typical configuration for a single-well test. The term "single-well" represents the fact that only one pumping well is required in order to perform the test. As detailed in Güven et al. (1985), an observation well with multilevel samplers is required in order to obtain

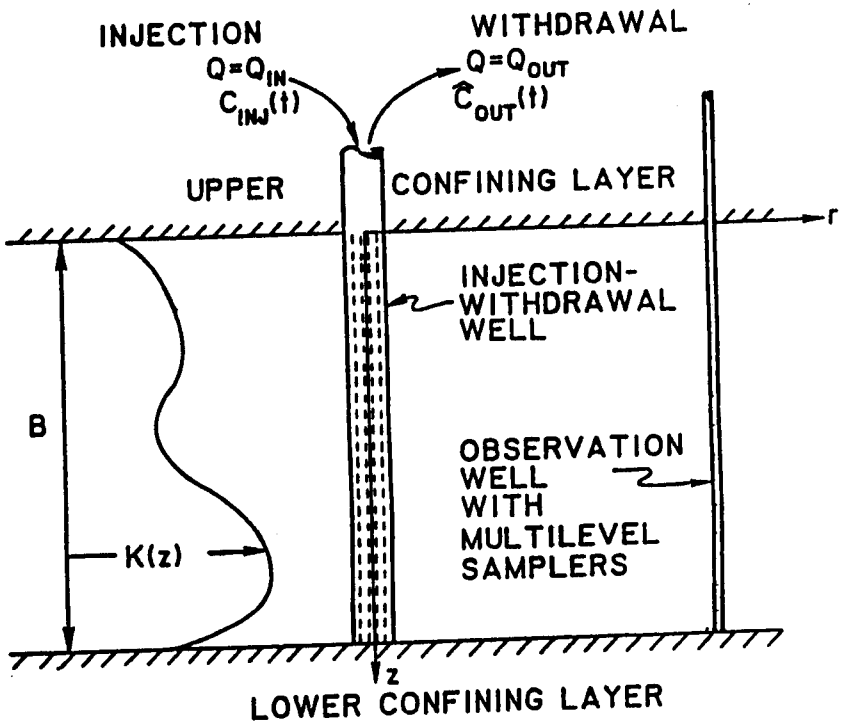

Figure 3. Vertical cross-sectional diagram showing single-well test geometry.

tracer travel time data at several vertical positions in the aquifer. One or more such observation/sampling wells may be used in any particular tracer test. Actual test performance involves the injection of water having a known concentration of tracer, $C_{inj}(t)$, in a well which is fully penetrating and fully screened over the entire thickness of the aquifer (Figure 3). After some time, the flow may be reversed and the tracer-labeled water removed from the same well, although this withdrawal phase is not strictly necessary. If there is a withdrawal phase in the experiment, the tracer concentration in the water leaving the well, $\hat{C}_{out}(t)$, may be measured and recorded as a function of time to produce a concentration versus time breakthrough curve. Certain other useful information may be obtained also such as the percent of injected tracer that is recovered.

In a laterally isotropic, homogeneous confined aquifer or in a perfectly stratified confined aquifer, the flow during the single-well test is horizontal, radially diverging during injection, and radially converging during withdrawal. In the past, data analysis was accomplished by assuming an equivalent homogeneous aquifer of constant thickness B (Fig. 3 with K(z) constant). In such analyses, a withdrawal phase was necessary and the concentration versus time data from the injection-withdrawal well were used to estimate an effective longitudinal full-aquifer dispersivity (see, e.g., Fried, 1975; Pickens and Grisak, 1981). As mentioned previously, we believe that an approach which does not rely on the vertically homogeneous aquifer assumption is more reliable for predictive purposes.

In the single-well tests to be discussed, one or more observation wells containing isolated multilevel sampling devices are installed around the injection-withdrawal well (Fig. 3). Concentration versus time measurements are then made at the different isolated points in each observation well

during the experiment. The resulting tracer travel time information may be used to infer vertical profiles of horizontal hydraulic conductivity. When a single-well test is performed in this manner, the data from the multilevel observation well(s) is what one is after. Therefore, a withdrawal phase is not strictly necessary but is recommended, if for no other reason than to remove tracer from the study aquifer.

A typical configuration and flow pattern for a two-well tracer test is illustrated in Figure 4. Here there are two pumping wells because the experiment involves the simultaneous operation of an injection well and a withdrawal well, both of which are fully screened and fully penetrating over the entire thickness of the aquifer. Water is pumped into the injection well at a steady flow rate, Q, and is removed from the withdrawal well, usually at the same rate, although two-well tests have been performed in which the flow rates in the two pumping wells were not equal (e.g., Gelhar, 1982). A conservative tracer of known concentration, $C_{in}(t)$, is added at the injection well for a period of time, t_{in}, and the concentration of tracer in the water leaving the withdrawal well, $\hat{C}_{out}(t)$, is measured and recorded as a function of time to give a concentration versus time breakthrough curve. The tracer injection period is usually short compared to the total time of the experiment.

Two-well tests may be carried out in either a recirculating or non-recirculating mode. In the recirculating mode, the water pumped from the withdrawal well is piped to the injection well, where it is injected back into the aquifer. The concentration of tracer entering the injection well during a two-well test with recirculation, $C_{inj}(t)$, will be equal to $C_{inj}(t) = C_{in}(t) + \hat{C}_{out}(t)$, approximately, assuming that the travel time in the pipe joining the two wells is negligible. In the non-recirculating

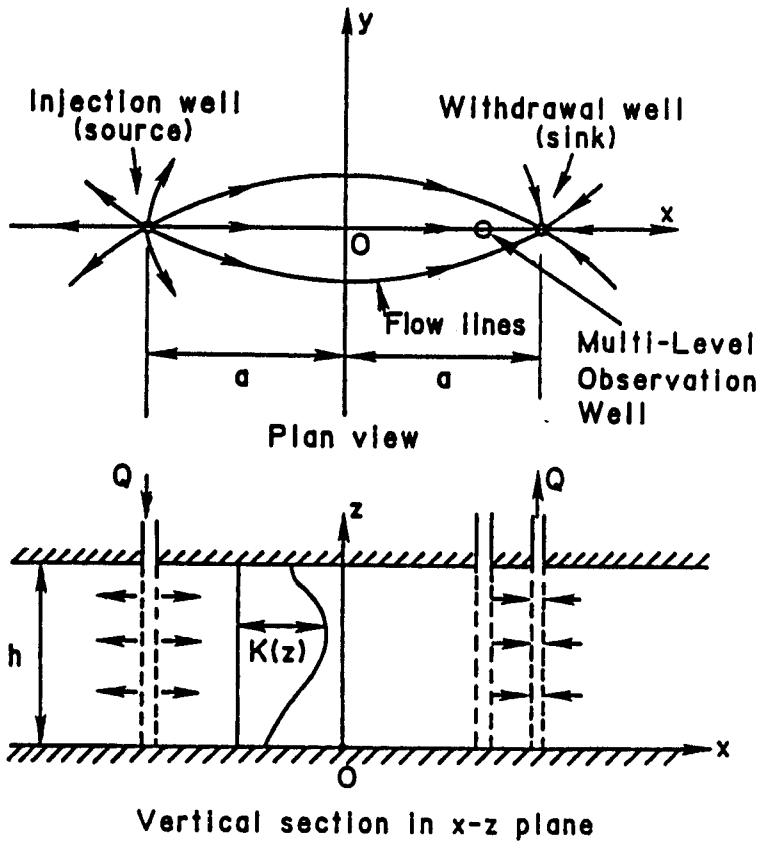

Figure 4. Two-well test geometry in a stratified aquifer.

mode, the water produced from the withdrawal well is wasted at a safe distance from the test area. A separate water supply, usually a well in the same aquifer but sufficiently far from the two test wells, so that negligible hydraulic interference occurs, provides the injection water. The injection tracer concentration in this case is $C_{inj}(t) = C_{in}(t)$.

For the two-well tests discussed herein, observation wells containing isolated multilevel samplers are installed between the injection well and the withdrawal well in order to sample the tracer concentration at different elevations in the aquifer during the experiment. From the tracer arrival times at several isolated sampling points in a multilevel sampling observation well, the variation of horizontal hydraulic conductivity in the vertical may be inferred (Pickens and Grisak, 1981). As will be described in more detail later, the inference assumes that the aquifer is perfectly stratified and of constant thickness and porosity in the vicinity of the test wells.

Design and Construction of Multilevel Sampling Wells

As explained in the previous section, the most unique aspect of the single- and two-well tests that we are discussing is the use of one or more multilevel sampling wells to obtain tracer travel time data at different elevations in the study aquifer. This changes the objective of the tests from attempting to determine a number for the so-called full aquifer longitudinal dispersivity α_L^* (which we believe is rather meaningless at the scale of practical tracer tests) to one of gathering information about the advection pattern in the aquifer, which in most situations will dominate the early tracer dispersion process as illustrated in Figure 1. (Field evidence in support of this statement will be presented later.) Because of the emphasis on obtaining accurate tracer travel times at isolated elevations in

the study aquifer, it is vital that multilevel sampling wells be constructed so that dependable data are obtained. Unfortunately, a satisfactory solution to the multilevel sampling well construction problem is not yet available.

Shown in Figure 5 are three multilevel sampling well types. In recent tracer tests with which the authors are concerned, various versions of type I have been attempted. Type I and related types have appeal because of the convenient vertical location of the sampling zones, and the potential economy of installation. Illustrated in Figure 6 is the multilevel sampling system described by Pickens et al. (1978) and later used in single- and two-well tracer tests (Pickens and Grisak, 1981). The system was designed for shallow water table applications and was usually forced into position using a high pressure water jet (Pickens et al., 1978). Identical or similar systems have been utilized or tested by other research groups (Stanford University, Tennessee Valley Authority, personal communications). For the Pickens et al. (1978) system to perform acceptably, the study aquifer must collapse around the sampler and make good contact so that spurious high vertical permeability pathways are not created along or near the aquifer-sampler boundary (Fig. 14). Apparently, this was not a problem in the clean sandy aquifer studied by Pickens and Grisak (1981). However, in more cohesive aquifers with lower vertical hydraulic conductivities and higher vertical head gradients, problems have been observed (Tennessee Valley Authority, personal communication).

Moltyaner and Killey (1986) have developed an automated multilevel sampling system designed for use with radioactive tracers. This system, which uses a dry access well monitoring technique, is illustrated in Figure 7. With this arrangement Moltyaner and Killey (1986) made the equivalent of

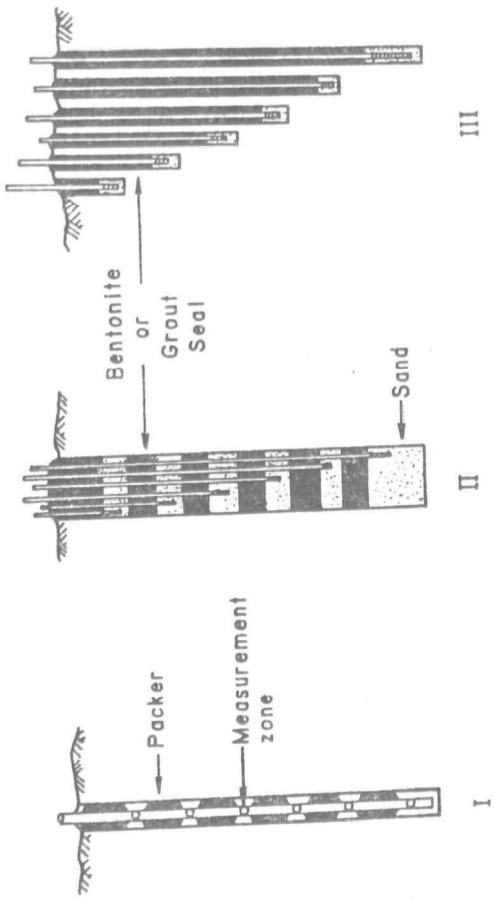

Figure 5. Various types of multilevel sampling systems.

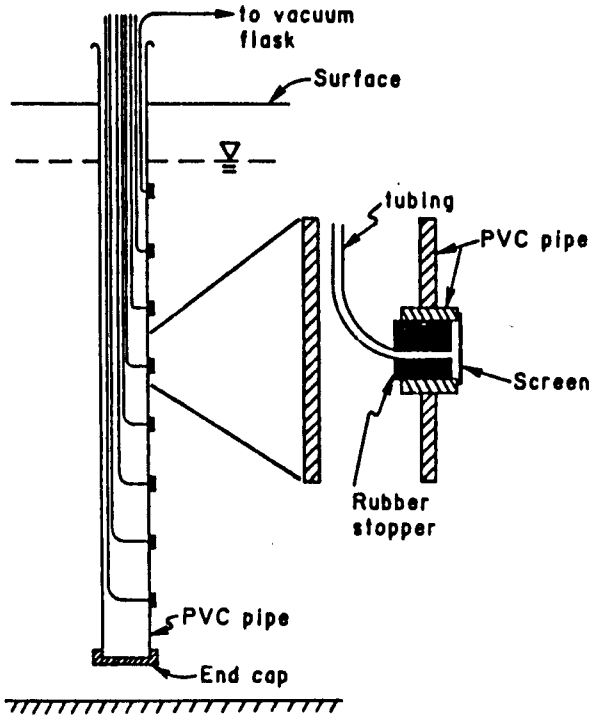

Figure 6. Pickens et al. multi-level sampling/observation well.

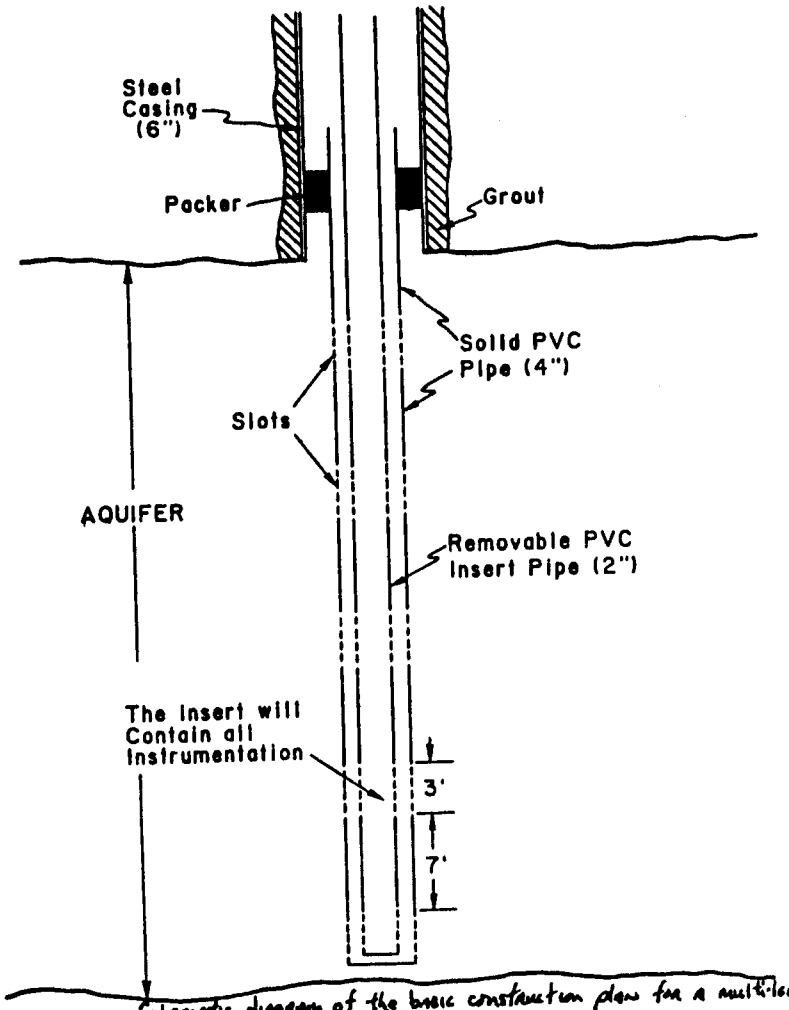

Figure 8. Schematic diagram of the basic construction plan for a multi-level sampling well with removable insert.

Figure 7 NOT SHOWN

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750,000 point measurements using computer-controlled probe placement and data aquisition, which illustrates one of the tremendous labor-saving advantages associated with the use of radioactive tracers.

Presumably, the dry access tube(s) could be implaced using a variety of drilling techniques, each of which would have a different effect on the tube-aquifer boundary. If the tubes were jetted into the study aquifer or placed in auger holes with the idea of having the formation collapse around them, then the same potential vertical leakage problem discussed previously would seem to exist. If thick drilling mud were used, however, and the access tube placed in a mud-lined hole, it would seem that the potential for spurious vertical leakage would be diminished greatly.

Molz et al. (1985) describe the design and construction of a multilevel sampling well system for use with chemical tracers in a variety of confined and unconfined aquifers. The actual sampling system is not perfected and should be viewed as a prototype. However, it appeared to work in a satisfactory manner at the Mobile site.

As shown in Figure 8, the screened portions of the multilevel observation wells are not of a standard design. The screens themselves are composed of 91 cm (3') slotted sections alternating with 213 cm (7') solid sections. Although 5 slotted sections are shown in Figure 8 for purposes of illustration, the actual screens contained 7 slotted sections.

As also shown in Figure 8, a 5.1 cm (2") diameter PVC insert was constructed with slotted and solid portions that matched with those of the observation well screen. The insert was designed to hold any wires, tubing, or instrumentation that ultimately would be placed in an observation well. Composed of threaded 3.05 m (10') sections, the inserts extended all the way to the land surface. In order to isolate the various sampling zones, the

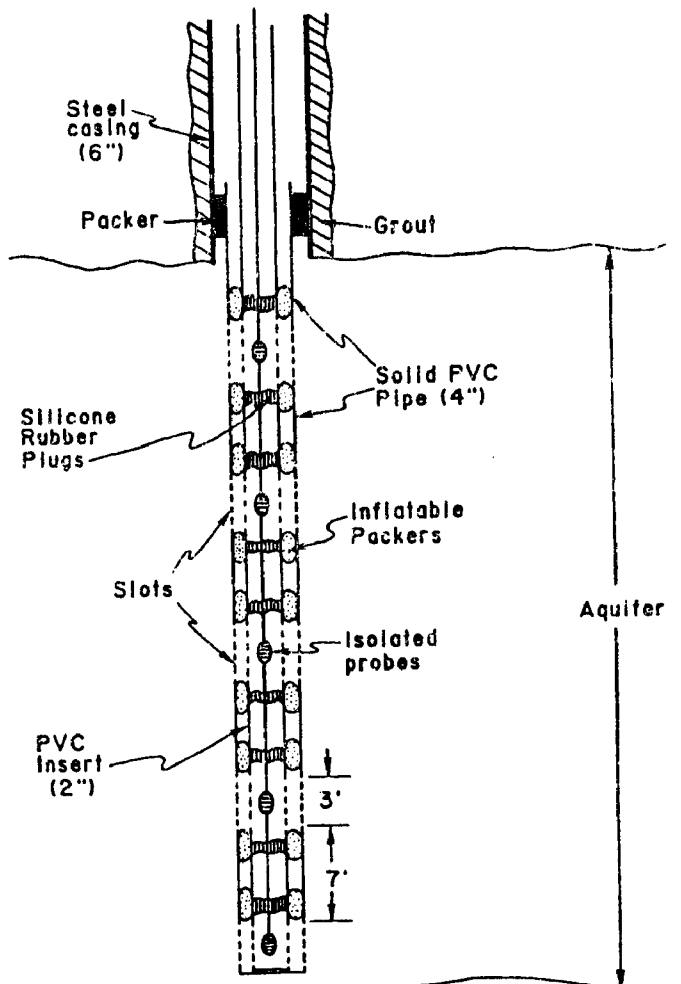

Figure 8. See title on original illustration, p. 31.
~~Schematic diagram of the basic construction plan for a multilevel sampling well with a removable insert.~~
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inserts were fitted externally with cylindrical annular inflatable packers as illustrated in Figures 9 and 10. After the required probes, tubing and wires were placed within the inserts, the sampling sections were isolated internally with silicone rubber plugs. The complete insert was constructed on the surface, then placed in the well, using a crane, positioned and the packers inflated. After installation, each isolated 91 cm (3') sampling zone appeared as shown in Figure 11. A conductivity probe was placed near the zone center, and two lengths of vacuum tubing connected the sampling zone to the surface. This tubing could be used with peristaltic pumps to mix the contents of the sampling zone and to obtain groundwater samples for analysis as illustrated in Figure 12.

In designing the multilevel sampling wells for use at the Mobile site, the drilling and well development process illustrated in Figure 13a,b was visualized. After removal of the drilling equipment, the drilling mud and disturbed aquifer material are mixed significantly as shown in Figure 13a. The cleaning and development procedure then was to pump and surge the wells until the water was clear and devoid of drilling mud and fine material. As shown in case (b), Figure 13, this procedure probably left some drilling mud adjacent to the solid casing segments and a disturbed (perhaps more permeable) aquifer material near the slotted segments where samples were to be collected. Such mud remnants would not be left behind (see Figure 13c) if a fully slotted screen had been used. The potentially beneficial effects of a partially slotted (segmented) screen with respect to a fully slotted screen, and a vertical leakage path possible in the fully slotted case, are illustrated further in Figure 14. The drilling mud remnant adjacent to the solid portion of the screen may result in a barrier to vertical flow that is very desirable. For the fully slotted screen, very little mud remains after

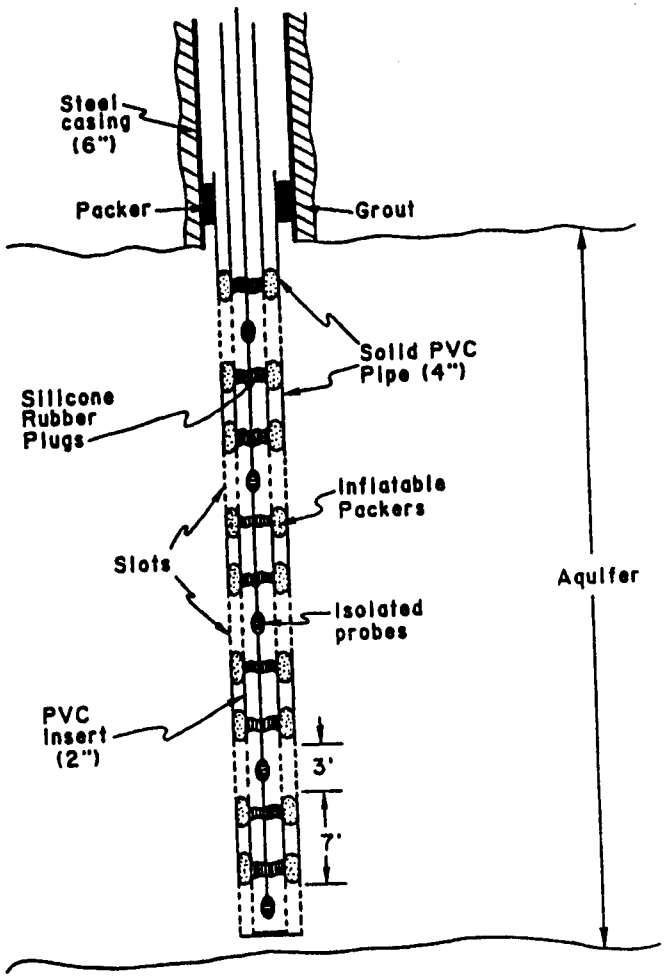

Figure 9. Multilevel sampling well with sampling zones isolated with inflatable packers and silicone rubber plugs.

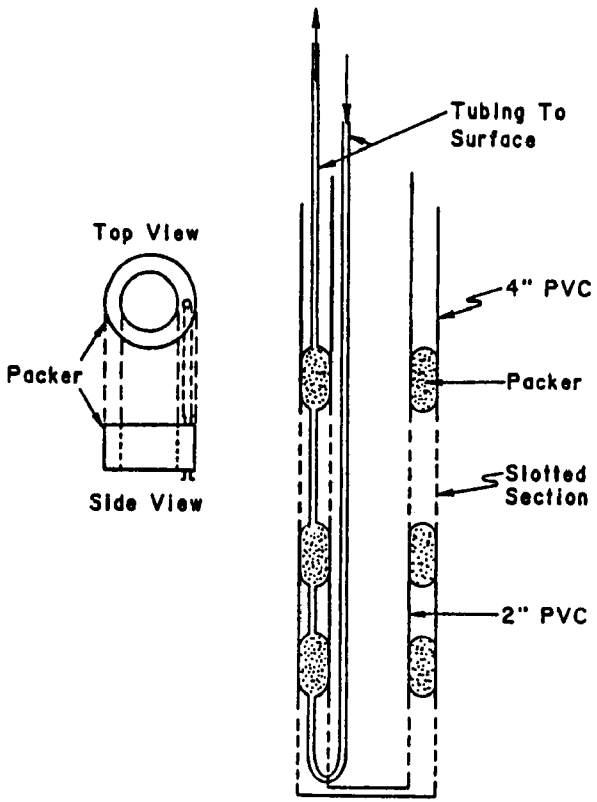

Figure 10. Details concerning the geometry and installation of inflatable packers. The packers were inflated with water.

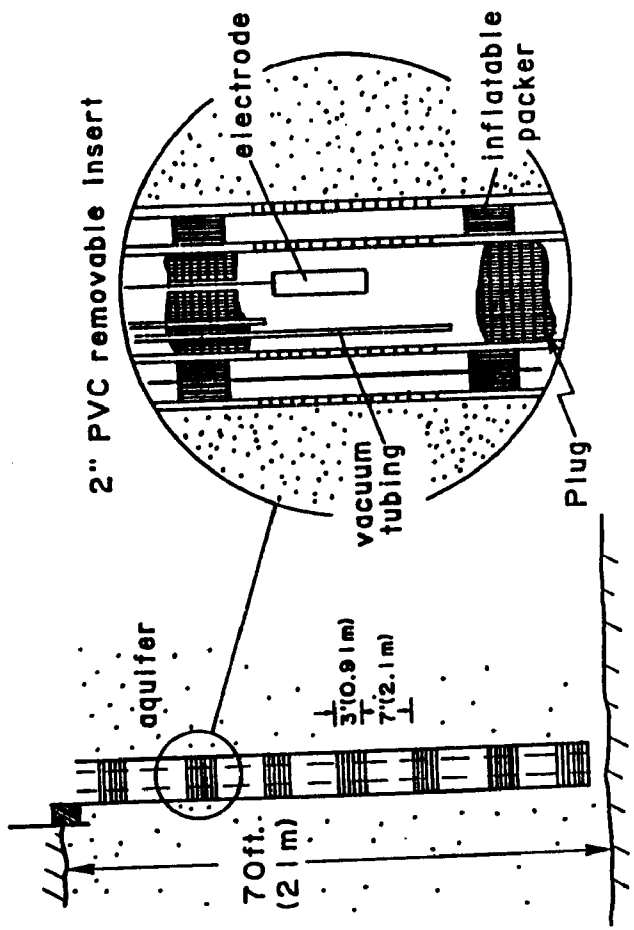

Figure 11. Diagram of a completed multilevel sampling well. This and similar systems were used at the Mobile site.

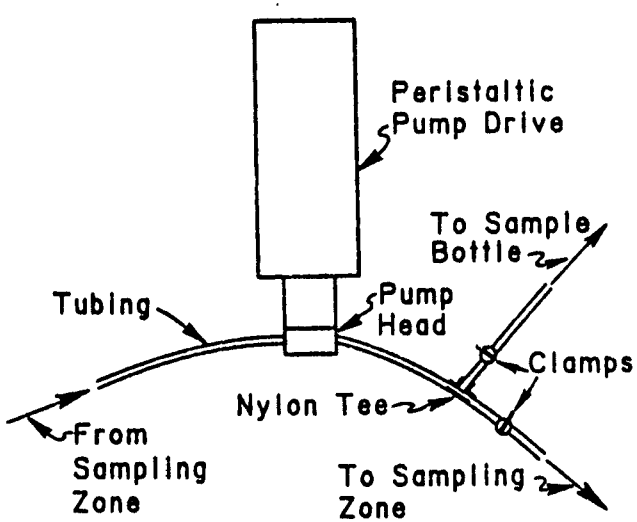

Figure 12. Diagram illustrating the scheme for causing mixing in the various isolated sampling zones and obtaining samples for laboratory analysis.

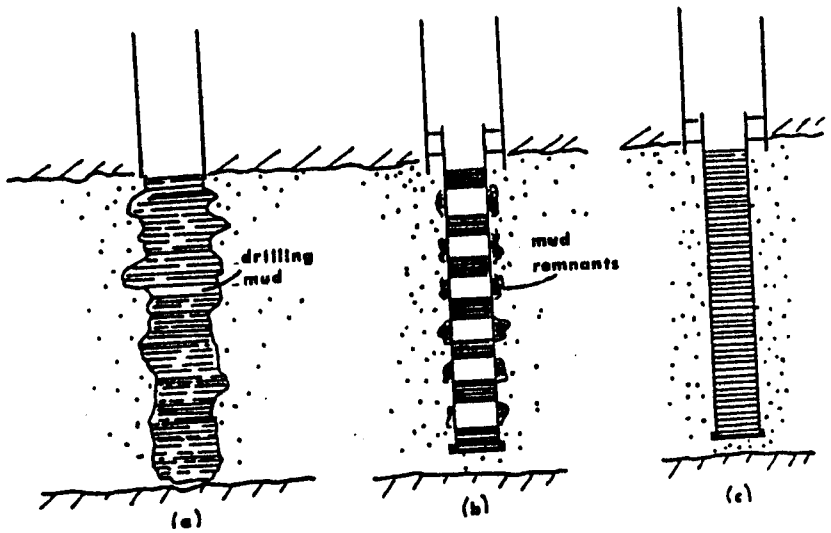

Figure 13. Diagram illustrating what may happen during drilling and installation of various types of screens.

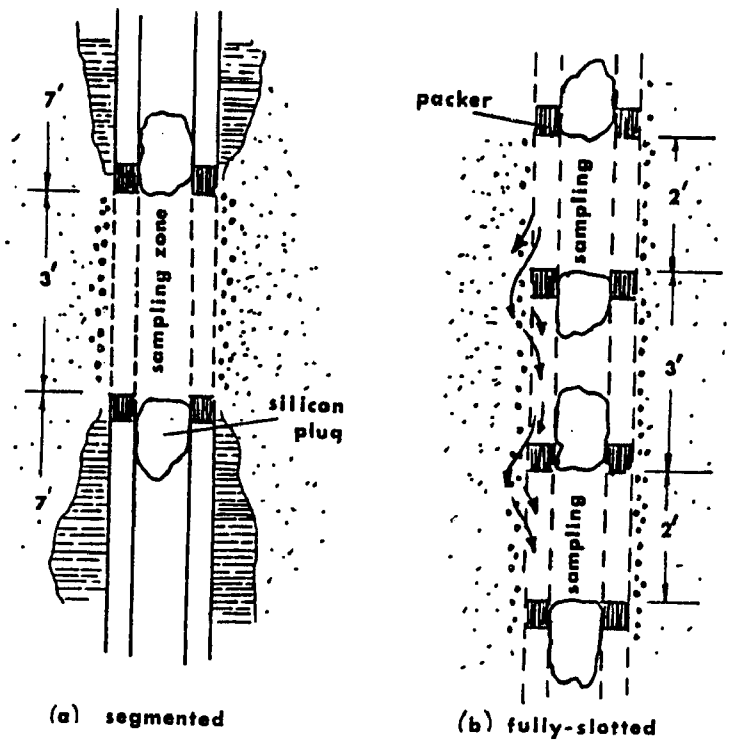

Figure 14. Details concerning the possible beneficial effects of drilling mud left behind in the formation (a) and possible leakage paths associated with fully-slotted screen (b).

development and a disturbed aquifer material of possibly higher permeability would result along the entire length of screen.

The most thought out and best designed multilevel sampling system from a vertical integrity viewpoint of which the authors are aware appears to be the multiple port system manufactured by Westbay Instruments, Ltd. of Vancouver, B.C. In its present configuration, however, the system is suited for groundwater monitoring but not tracer testing which requires the ability to sample rapidly and simultaneously from a number of elevations. Lack of a solution to the vertical integrity problem valid in a broad range of aquifer types coupled with the unavailability of economic, dependable and flexible commercial equipment is a major impediment to the practical application of most types of multilevel tracer testing.

Performance and Results of Single-Well and Two-Well Tracer Tests at the Mobile Site

Using the multilevel sampling wells described in the previous section, a series of single-well and two-well tracer tests were performed at the Mobile site over the past two years. The major purpose of these tests was to measure the tracer travel times between an injection well and one or more multilevel sampling wells. Subject to several assumptions to be discussed later in this section, the resulting travel time data allows one to infer a vertical distribution of horizontal hydraulic conductivity. We view the experiments to be described as the simplest and most convenient tracer tests which yield some information about the variation of aquifer hydraulic properties with respect to the vertical position in the aquifer. The basic experimental plan was to conduct a series of single-well and two-well tests at different locations in an attempt to build up a three-dimensional picture of the hydraulic conductivity distribution. We did not attempt to make point measurements or nearly point measurements as was done by Pickens and

Grisak (1981). Our objective was to average tracer travel times over a suitable aquifer thickness. Thus the inferred hydraulic conductivity distribution that results may be viewed as being based on a type of spatial average.

The project site is located in a soil borrow area at the Barry Steam Plant of the Alabama Power Company, about 32 km (20 mi) north of Mobile, Alabama. The surface zone is composed of a low-terrace deposit of Quaternary age consisting of interbedded sands and clays that have, in geologic time, been recently deposited along the western edge of the Mobile River. These sand and clay deposits extend to a depth of approximately 61 m (200 ft) where the contact between the Tertiary and Quaternary geologic eras is located. Below the contact, deposits of the Miocene series are found that consist of undifferentiated sands, silty clays and thin-bedded limestones extending to an approximate depth of 305 m (1000 ft). The study formation is a confined aquifer approximately 21 m (69 ft) thick which rests on the Tertiary-Quaternarty contact.

Except for the well diameters, Figure 15 is a vertical section scale drawing of the subsurface hydrologic system at the Mobile site. Included in the drawing are 3 pumping wells (E1, I2 and E10) and 4 multilevel observation wells (E5, E3, E7 and E9) all situated at approximately the same vertical plane. (A schematic plan view showing the wells E1 and I2 and the supply well S2 is given in Figure 17). The study aquifer is well confined above and below by clay-bearing strata that probably extend laterally for several thousand feet or more, and the natural piezometric surface of the confined aquifer at the test site is at a depth of 2 to 3 m (6 to 10 ft) below the ground surface. In experiments performed to date, vertical hydraulic gradients within the aquifer have been small. A medium to fine

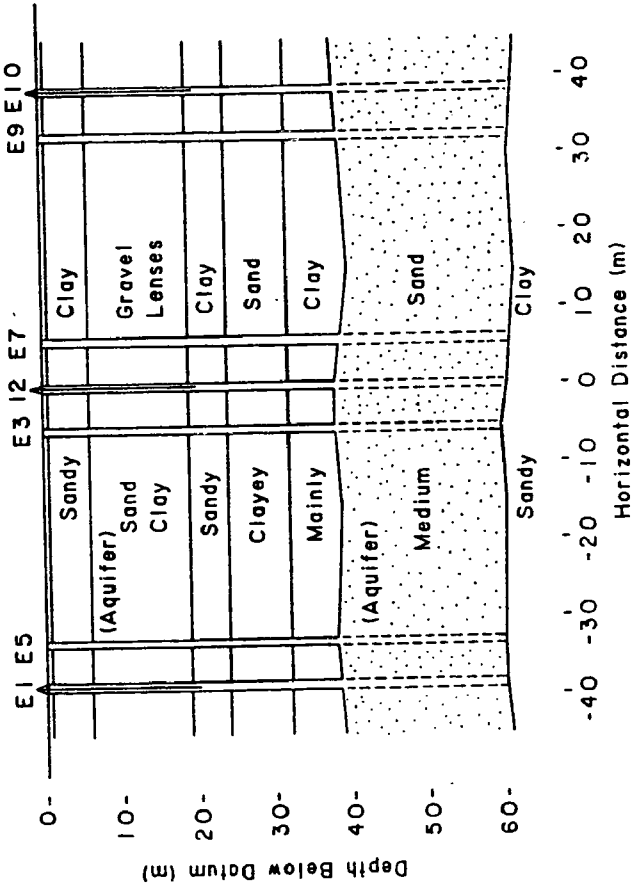

Figure 15. Diagram of the subsurface hydrologic system at the Mobile site where tracer tests were performed. Wells E1, I2 and E10 are pumping wells, while E5, E3, E7 and E9 are multilevel sampling wells. All wells shown are situated at approximately the same vertical plane. See Figure 17 for a schematic plan view showing wells E1 and I2.

sand containing approximately 3 percent silt and clay by weight composes the main aquifer matrix at well E3. (At other locations in the aquifer the fines vary from 1% to 15% by weight.) When E3 was constructed, moderately disturbed cores were obtained at 7 locations throughout the depth of the study aquifer using a Shelby tube. The resulting particle size and distribution data, which we believe are accurate despite the moderate disturbance, are presented in Table 1. Further details concerning aquifer/aquitard hydraulic and other physical properties may be found in Parr et al. (1983).

The pumping wells are constructed of 20.3 cm (8") steel casings with 15.2 cm (6") stainless steel, wire wrapped screens and are grouted from the top of the study aquifer to the land surface. As illustrated in Figure 16, the piping and valve system associated with each pumping well is designed so that the well can be used for injection or withdrawal of tracer solution. In the single-well test to be reported in detail herein, tracer solution was injected through well I2. As illustrated in Figure 17, supply water was obtained from a well (S2) screened in the study aquifer about 244 m (800 ft) east of I2. This separation was sufficiently large so that the hydraulic effects of S2 pumping did not affect the tracer experiments in the vicinity of I2. Concentrated tracer solution was mixed in a 4800 liter (1270 gal) tank and added to the 10.2 cm (4 in) pipeline connecting S2 and I2 using a metering pump. The pipeline travel distance from the metering pump to the study aquifer was at least 160 m (525 ft) which was more than sufficient to insure complete mixing of the tracer. It was assumed that the piezometric head distribution in the injection well screen was uniform with depth since the screen diameter was 15.2 cm (6 in) which resulted in a maximum average vertical fluid velocity in the screen of 0.84 m/s (2.75 ft/s) (during

Table 1. Particle size distribution data for the seven disturbed cores obtained during construction of well E3.

Depth of Core (m)	D_{60} (mm)	D_{30} (mm)	D_{10} (mm)	Percent Passing #200 Sieve (%)
40.2	0.46	0.35	0.21	1.8
43.3	0.36	0.26	0.13	1.4
46.6	0.58	0.45	0.21	3.0
49.7	0.46	0.27	0.12	5.6
52.7	0.49	0.28	0.15	3.5
56.1	0.59	0.44	0.26	1.2
59.1	0.94	0.56	0.19	3.8

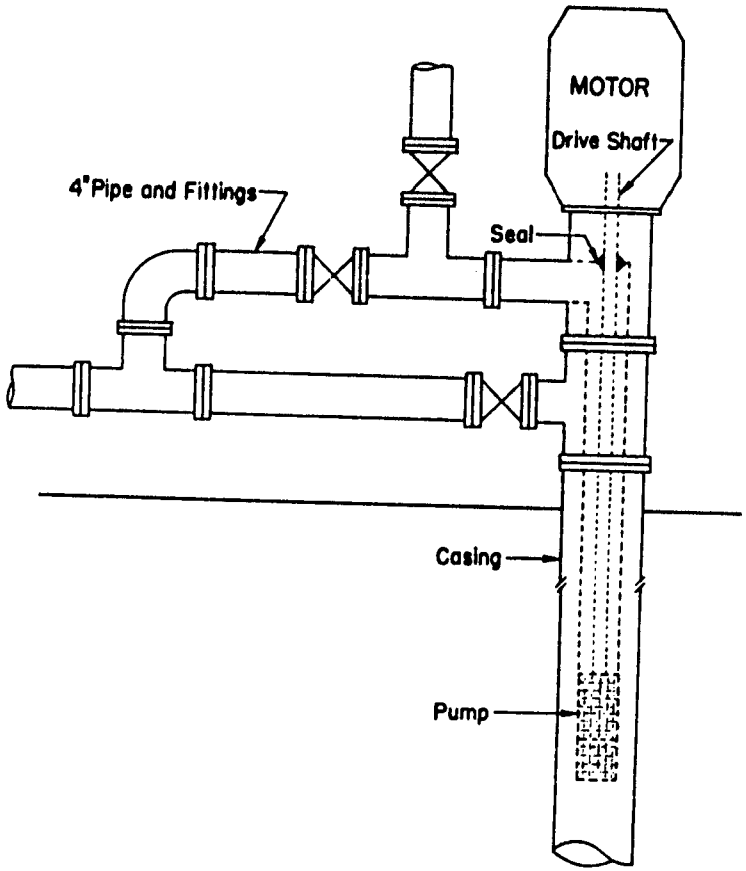

Figure 16. Piping and valving scheme associated with pumping wells at the Mobile site.

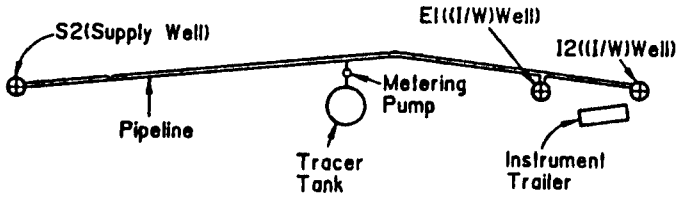

Figure 17. Diagram showing the main features of the surface hydraulic system used in the single- and two-well tracer tests at the Mobile site.

experiment #4). Thus the maximum velocity head was only 0.037 m (0.12 ft) and the head losses due to friction along the 21 m (69 ft) length of screen would be less than 0.10 m (0.33 ft). These totals when compared to the injection head of approximately 3 m (9.8 ft) are consistent with the assumption of constant head in the well screen interior.

As discussed in detail by Molz et al. (1985), several preliminary tests were conducted with the objective of assessing the vertical integrity of the multilevel sampling wells and the effect of mixing the water within each sampling zone which was approximately 0.91 m (3 ft) high. It was concluded that sample zone isolation was adequate for tests which were to follow. There was a significant difference between breakthrough curves at the seven sampling zones depending on whether sample zone mixing was induced. Therefore, it was concluded that mixing within each isolated sampling zone is desirable. For a sampling zone of finite length it is possible for the tracer to enter the zone anywhere along the slotted length and then be recorded depending on unknown natural mixing and probe position. Imposed mixing forces an integration effect causing tracer concentration to be more representative of the entire length of the sampling zone. (This relates back to the moving average concept discussed previously.) Without imposed mixing, the effective sampling length in the vertical direction is unknown.

Single-Well Test

The first complete single-well tracer test conducted at the Mobile site was labeled "experiment #4" and utilized the multilevel sampling well E3 (Figure 15). To start the experiment, supply groundwater without tracer was injected into I2 until the initial transients disappeared and a steady injection rate resulted (approximately 2 hours). Then at time zero tracer was added to the injection water, and the actual test initiated. Shown in

Figure 18 are the bromide concentrations measured in I2 (injection/withdrawal well), while the concentration breakthrough curves measured in E3 (multilevel sampling well) are shown in Figure 19. (Water samples were obtained from the injection/withdrawal well using a faucet in the pipeline.) During the experiment tracer solution at an average concentration of 242 mg/l was injected at the rate of 0.915 m^3/min (242 gpm) for the first 32 hours. This injection rate, without tracer added to the water, was maintained for the next 22 hours at which time injection was halted. One hour and 15 minutes later withdrawal pumping was initiated at the rate of 1.19 m^3/min (314 gpm) and continued for two weeks so that virtually all tracer was removed from the system. Note that Figure 18 contains both injection and withdrawal data while Figure 19 contains only injection breakthrough data.

Table 2 contains the time for 50% of breakthrough for each level based on the electrical conductivity measurements for experiment #4 shown in Figure 20 and the concentration data shown in Figure 19. With the probable exception of level 1, the concentration data look quite good. On the average, the arrival times based on electrical conductivity lag those based on concentration by about 2 hours. (We will refer to this as the "two-hour rule" later on.) This is largely due to the fact that the electrical conductivity of the supply water, which is ultimately mixed with tracer, is lower than that of the native groundwater in the vicinity of I2 by about 16%, caused in part by water chemistry changes induced by previous aquifer thermal energy storage experiments at the same site (Molz et al., 1983). Thus as the tracer solution approaches a conductivity probe, the reading will decrease initially even though the bromide concentration is increasing. The net effect of this interaction is to cause the electrical conductivity

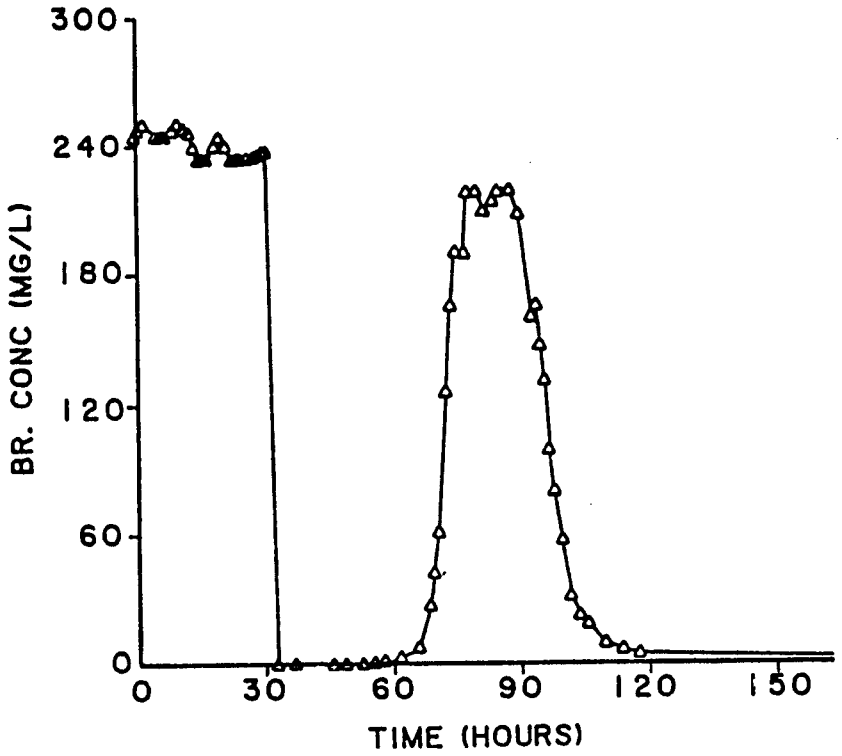

Figure 18. Bromide concentration in the injection/withdrawal well (I2) during experiment #4. Tracer injection ended at t=32 hours; injection ended at t=54 hours. Withdrawal began at t=55.25 hours.

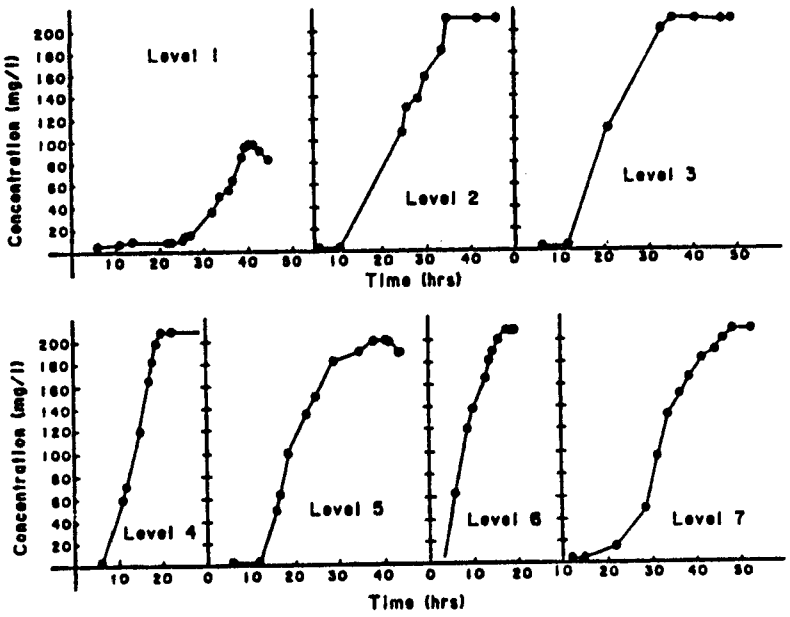

Figure 19. Bromide concentration breakthrough curves at the seven levels of well E3 during experiment #4.

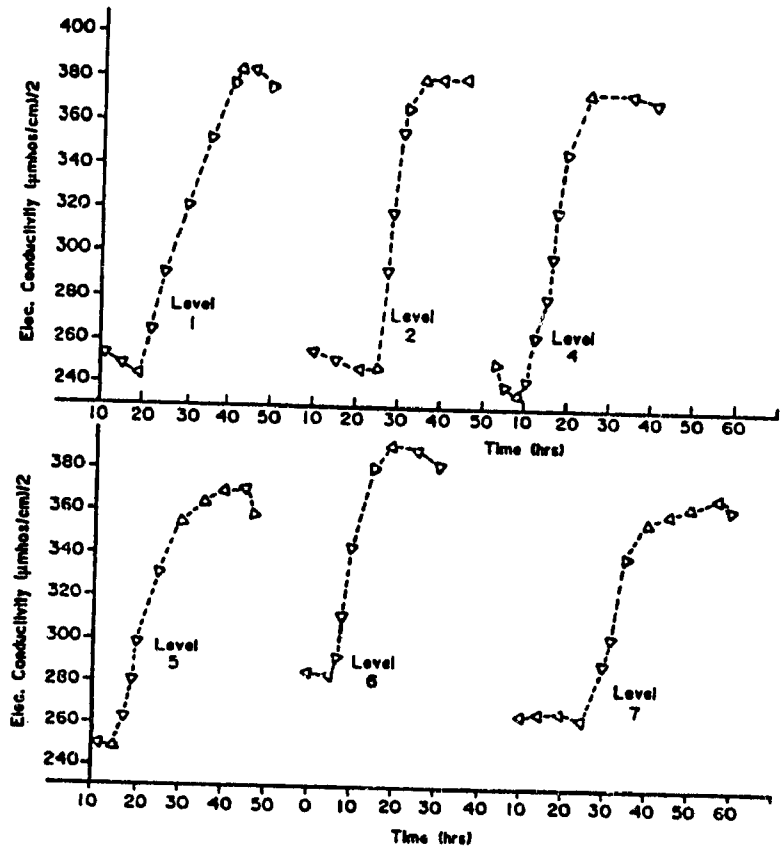

Figure 20. Electrical conductivity breakthrough curves at various levels of well E3 during experiment #4.

Table 2. Sampling zone elevations, arrival times for fifty percent breakthrough, apparent dispersivity values and inferred normalized hydraulic conductivity values for experiment #4.

Level #	Mid-Zone Elevation	Arrival Times from Concentration Measurements	Normalized Hydraulic Conductivity	Apparent Dispersivity	Arrival times from Electrical Conductivity Measurements	Normalized Hydraulic Conductivity
1	-40.7 m	33.4 hr?	0.24	0.07±0.01 m	29.0 hr	0.34
2	-43.8 m	24.3 hr	0.33	0.18±0.02 m	27.3 hr	0.37
3	-46.8 m	20.5 hr	0.39	0.17±0.06 m	--	--
4	-49.9 m	14.0 hr	0.57	0.12±0.04 m	16.0 hr	0.63
5	-52.9 m	19.0 hr	0.44	0.32±0.08 m	21.8 hr	0.46
6	-56.0 m	8.0 hr	1.00	0.50±0.03 m	10.0 hr	1.00
7	-59.0 m	32.4 hr	0.25	0.04±0.01 m	33.2 hr	0.30

data to overestimate the actual mid-rise arrival time. Presumably, this could be corrected by adding additional ions, other than bromide, to the supply water. However, we did not attempt this because the probe recordings were used mainly to orient ourselves qualitatively as to what was happening in the subsurface. Ultimately, calculations of normalized hydraulic conductivity were based mainly on arrival times deduced from concentration data measured in the laboratory. The results of both are shown in Table 2 mainly for comparison and information purposes.

Tracer travel time data alone does not enable one to calculate an absolute value of hydraulic conductivity. To calculate such a value for the general nonhomogeneous case, one must know the flow path, porosity and hydraulic head distribution along the flow path in addition to the travel time. It was not feasible to measure all these quantities during our tracer tests. However, if one approximates the real aquifer in the test vicinity with a perfectly stratified aquifer of constant porosity and horizontal layering, then for a fully penetrating injection well the Darcy velocity at the elevation of each sampling zone will be horizontal and proportional to the hydraulic conductivity at that level. Thus the following equations can be written

$$K_i = B(R)v_i(R) = \frac{1}{2}B(R)R/t_i = \frac{\pi\theta TR^2}{Qt_i} \qquad (6)$$

where K_i = horizontal hydraulic conductivity at the ith level, $B(R) = \theta/(dh/dr)$ where θ is the porosity and dh/dr is the hydraulic gradient at radius R, v_i = seepage velocity at the ith level, R = constant radial distance between the injection well and a particular multilevel sampling well, t_i = tracer travel time between the two wells at the ith level, T =

aquifer transmissivity, and Q = injection flowrate. At any particular level, t_i is taken as the time between the start of tracer injection and when 50% of breakthrough occurs. In any given experiment there will be a minimum arrival time, t_{min}, which corresponds to the layer with the largest hydraulic conductivity, K_{max}, and from equation (6)

$$K_{max} = \frac{1}{2}B(R)R/t_{min} \qquad (7)$$

Forming the ratio of equations (6) and (7), one arrives at what can be called the normalized hydraulic conductivity

$$\frac{K_i}{K_{max}} = \frac{t_{min}}{t_i} \qquad (8)$$

It is also possible to calculate the ratio $K_i/\bar{K} = \bar{t}/t_i$, where the "bar" notation indicates average values (Pickens and Grisak, 1981). $\bar{K}$ could then be equated, as a first approximation, to the hydraulic conductivity obtained from a fully penetrating pumping test, as $\bar{K} = T/B$ where T is the transmissivity and B is the aquifer thickness. This would enable explicit values to be calculated for each K_i.

We would like to re-emphasize that the simple equations (6) through (8) all result from the "stratified aquifer" approximation which many hydrologists may consider too idealized to represent a real aquifer. There is certainly some merit to this viewpoint. However, the only other practical alternative that we see at the present time is to make the usual assumption of a homogeneous or statistically homogeneous aquifer and go after a full-aquifer dispersivity which, as discussed in the introduction, is a much worse approximation. More will be said about this later.

Based on equation (8), Figure 21 resulted which is a plot of normalized hydraulic conductivity (K/K_{max}) as determined from the concentration data of experiment #4. Since the concentration data for level 1 are not consistent with that from the other levels (perhaps a tubing leak?), we used the electrical conductivity data and the 2-hour rule (see page 22) to provide an improved estimate of the level 1 relative permeability. At this level the electrical conductivity data were normal in appearance and resulted in the level 1 value on the curve shown in Figure 21. The results displayed indicate the presence of a high permeability zone in the bottom third of the aquifer, along the line connecting E3 and I2. This result is consistent with the findings from previous thermal energy storage experiments at the Mobile site which indicated the presence of a high permeability zone, although at a slightly higher elevation in the aquifer (Molz et al., 1983; Buscheck et al., 1983).

In displaying the data of Figure 21, it was decided to simply draw straight lines between the points where hydraulic conductivity was known or measured. In doing this use was made of nine points--the top and bottom of the aquifer, where the clay confining layers force the permeability to essentially zero, and the seven sampling points where tracer travel times were recorded.

Two-Well Test

As described previously, a two-well test may be used with one or more multilevel sampling wells to obtain tracer travel time information similar to that obtained with a single-well test. However, the two-well test is generally performed on a larger scale and, therefore, is more time consuming. At the Mobile site our single-well tests lasted about 5 days, while the two-well tests required 30 to 35 days followed by a month or more

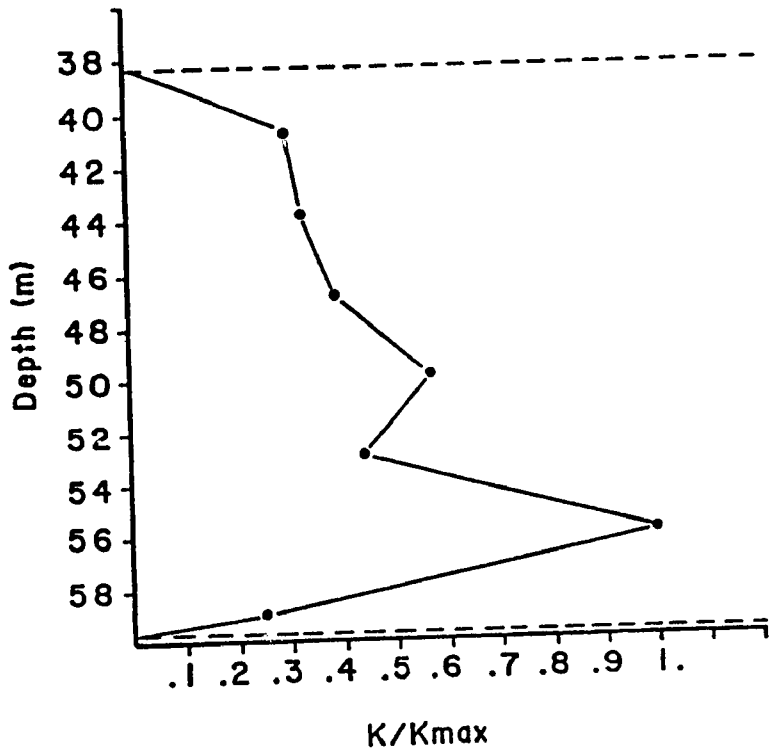

Figure 21. Inferred normalized hydraulic conductivity distribution based on the results of experiment #4 and the stratified aquifer assumption.

of withdrawal to remove all remnants of tracer. Generally speaking, single-well tests are suited for relatively low cost but small scale hydraulic conductivity measurements because only a single pumping well is required. A two-well test in the non-recirculating mode requires at least 2 pumping wells but provides the advantage of being able to move water relatively rapidly over larger travel distances.

Another aspect of a two-well test which was exploited in the present study is that it offers a convenient vehicle for testing tracer transport prediction capability. In several of our experiments at the Mobile site we chose to employ the single-well test as a means for inferring the hydraulic conductivity distribution in a relatively small aquifer region between an injection well and a multilevel observation well (maximum tracer travel distance of 5.5 m (18 ft)). The two-well test was then used to test predictions over a relatively large aquifer region (minimum tracer travel distance of 38.3 m (126 ft)) based on the vertical distribution of horizontal hydraulic conductivity inferred from the single-well test. This procedure helps to define what is actually being measured during a single-well test and over what travel distances such a measurement might have meaning. It also provides valuable insight concerning fundamental properties of the flow field which was established during the experiments. Predictions of two-well test outcomes based on single-well test results are discussed in the next section entitled "Computer Simulation of Single-Well and Two-Well Test Results."

At this time in the project, 2 two-well tests have been performed at the Mobile site. The pairs of pumping wells used in the first and second tests, respectively, were E1-I2 and I2-E10. Both tests were done in the non-recirculating mode with E1 and I2 used as injection wells in the first

test and second test, respectively. Herein, only the E1-I2 test will be described in detail.

Preparation for the execution of a two-well test is similar in philosophy to that for a single-well test. The first step is to establish the flow field between the injection and withdrawal wells using groundwater without tracer. As illustrated in Figure 17, the piping between E1 and I2 was valved off, and a pump in well S2 was used to inject water into E1. Simultaneously, a pump in I2 withdrew water which was then wasted. Discharges were measured with standard turbine-type water meters and only minor valve adjustments were required in order to get the injection and withdrawal rates essentially equal and to maintain equality throughout the test. Following flow field establishment, tracer injection was initiated simply by turning on the metering pump in the line connecting the tracer tank to the S2-E1 pipeline (Fig. 17). The E1-I2 test was performed within the geometry illustrated previously in Figure 15. Both the injection well (E1) and withdrawal well (I2) have 15.2 cm (6") diameter stainless steel screens that fully penetrate the study aquifer. The observation wells (E5 and E3) are constructed of PVC pipe as described in the discussion of multilevel sampling well design and construction.

The test began (tracer injection initiated) at 9:50 AM on August 31, 1984 and continued until 8:00 AM on October 2, 1984. Injection and withdrawal rates averaged 0.946 m^3/min (250 gpm) and, typically, were equal to within less than 1%. Tracer was added to the injection water during the first 76.6 hours of the experiment which resulted in the injection concentration versus time function shown in Figure 22. After approximately 70 hours, tracer began to appear in the withdrawal well. As shown in Figure 23, the withdrawal concentration versus time function was complex, and

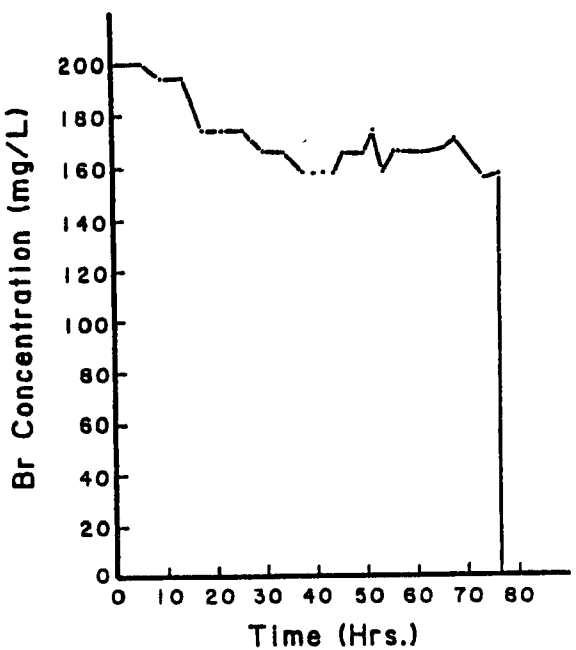

Figure 22. Injection well tracer concentration versus time during the first 80 hours of the two-well test.

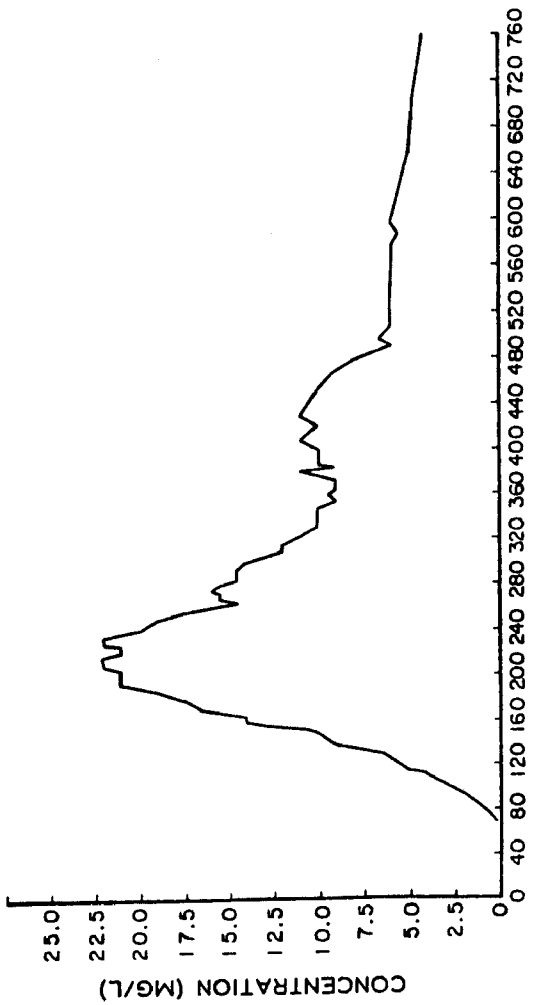

Figure 23. Measured tracer concentration versus time in the withdrawal well during the two-well test.

measurable tracer concentrations persisted throughout the 32.5 day experiment. The peak concentration occurred rather early in the experiment (~210 hours), and the curve had a well-defined "tail" that was still 15% of the peak value (~40 times the background value of 0.1 mg/l) when the experiment was terminated. Computer simulations (see below) indicated that the tailing was due to the late arrival of tracer being brought to the withdrawal well along the flow lines which follow the longer and larger arcs between the injection well and the withdrawal well shown in Figure 4.

Throughout the experiment, data were collected at the two multilevel observation wells shown in Figure 15. There were seven 0.9 m (3 ft) long isolated sampling zones in each well that were kept continuously mixed using peristaltic pumps on the surface, just as in the previously described single-well test. The peristaltic pumps were used also to obtain samples for analysis. Shown in Figure 24 (lines connecting dots) are breakthrough curves for the seven isolated levels in well E3. The data for well E5 is not shown because it was invalidated by the presence of drilling mud that was inadvertently left in the formation during the well construction process (Molz et al., 1985).

A tracer travel time analysis similar to that described for the single-well test and embodied in equations (6), (7), and (8) can be applied to the two-well test (Pickens and Grisak, 1981). When this is done, using the experimental data in Figure 24, the normalized hydraulic conductivity distribution shown in Figure 25 results. Although there are some differences, this distribution is quite similar to that shown in Figure 21 which resulted from the single-well test.

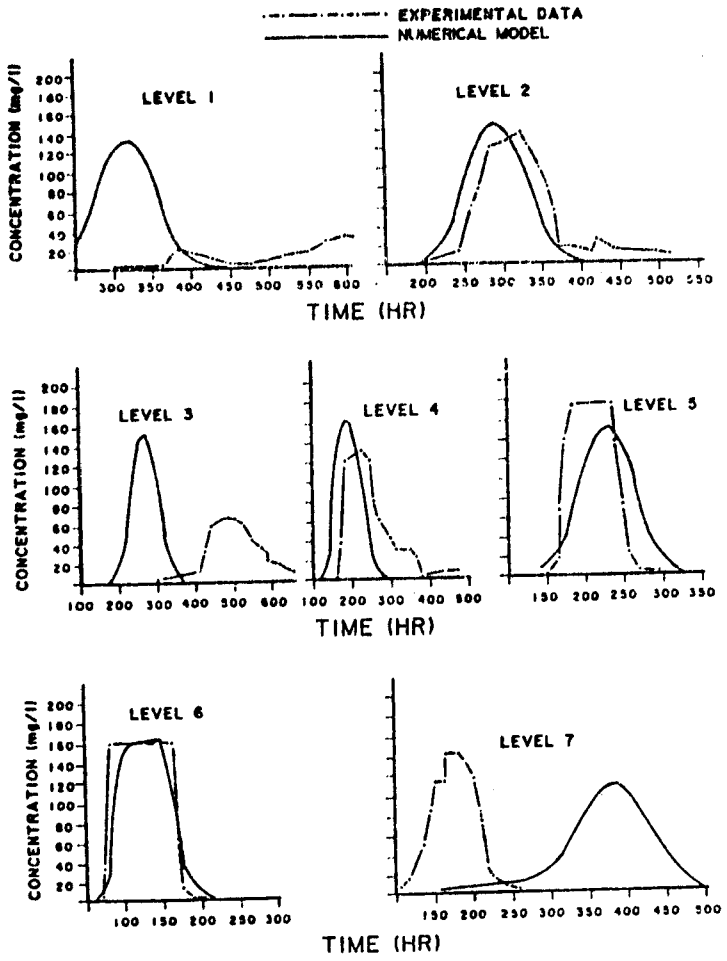

Figure 24. Measured (lines connecting dots) and predicted (full lines) breakthrough curves at the 7 levels of observation well E3.

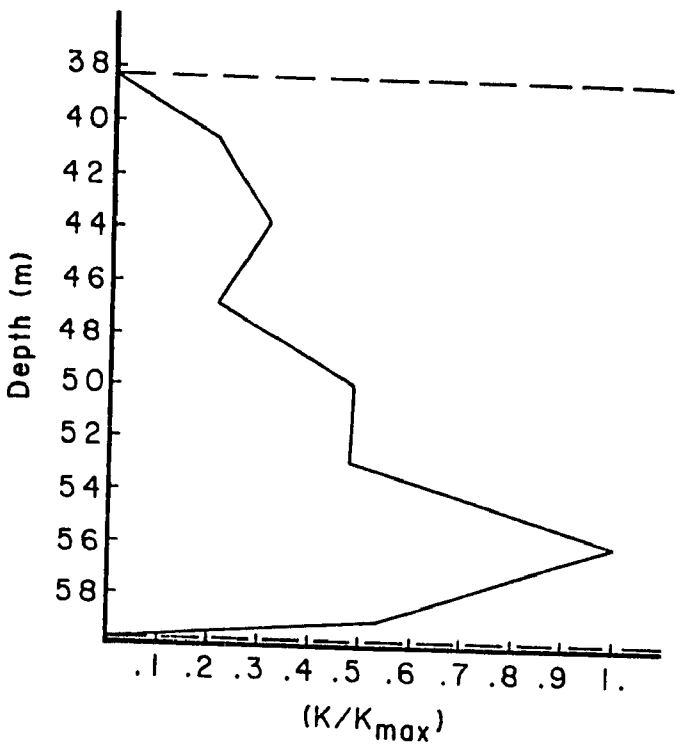

Figure 25. Normalized hydraulic conductivity distribution inferred from travel times measured during the two-well test.

Computer Simulation of Single-Well and Two-Well Test Results

The schematic diagram of tracer dispersion drawn in Figure 1 represents an advection-dominated process. One of the objectives of the research reported in this communication is to develop some indication of how much information concerning tracer dispersion is actually contained in normalized hydraulic conductivity distributions similar to the type determined in single-well and two-well tracer tests subject to the stratified aquifer approximation. Moreover, when such information is put into a mathematical model, how much of the dispersion process due to true hydrodynamic dispersion and other factors, such as spatial variations of hydraulic conductivity not allowed in the stratified aquifer assumption, is left unaccounted for? To begin to answer this question for aquifers where the required information is available, computer simulations for various experiments were developed which explicitly considered the vertical variation of horizontal hydraulic conductivity as determined by single-well or two-well tracer tests. Predictions of the computer models, which were made without "calibration" of any model parameters, were then compared with actual field results.

Simulation of Single-Well Tests

The first field tracer tests studied in this manner were the single-well tests performed by Pickens and Grisak (1981). This particular test was chosen for analysis because of the availability of very detailed data on hydraulic conductivity, local dispersivity and concentration distributions from the test. The computer model that was developed is called SWADM (Falta, 1984; Güven et al., 1985). It takes into account depth-dependent advection in the radial direction and local hydrodynamic dispersion in the

vertical and radial directions (Güven et al., 1985). The model is based on the equation given by

$$\frac{\partial C}{\partial t} + U_r \frac{\partial C}{\partial r} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_r \frac{\partial C}{\partial r}\right) + \frac{\partial}{\partial z}\left(D_z \frac{\partial C}{\partial z}\right) \qquad (9)$$

where r is the radial coordinate, $C = C(r,z,t)$ is the tracer concentration, $U_r = U_r(r,z)$ is the radial seepage velocity, $D_r = D_o + \alpha_r|U_R|$ is the radial dispersion coefficient, $D_v = D_o + \alpha_v|U_r|$ is the vertical dispersion coefficient, D_o is the effective molecular diffusion coefficient, and α_r and α_v are the radial and vertical local dispersivities.

The very detailed single-well tracer dispersion experiment of interest was performed in a shallow unconfined aquifer. A volume of 95.6 cubic meters of tracer-labeled water was injected into an 8.2 m thick aquifer at a rate of 3.2 m^3/hr for a period of 30 hours and then withdrawn at the same rate. Withdrawal began immediately at the end of injection. The previously-described samplers were located in the aquifer at observation stations 1, 2, 3, 4 and 6 m from the injection-withdrawal well. From the relative tracer arrival times at different elevations in the observation wells, a radial hydraulic conductivity distribution in the vertical (expressed as $K_i/\bar{K}$) was calculated. Additionally, Pickens and Grisak (1981) estimated the local longitudinal dispersivity at each sampling point and found the values to be fairly constant with an average magnitude of about 0.007 m. The $K/\bar{K}$ distribution inferred from the breakthrough data at the observation well at a distance of 1 m from the injection-withdrawal well in test SW1 was used in the SWADM simulation. This profile is shown in Figure 26. The actual unsteady injection concentration, shown in Figure 27, was used in the simulation (Pickens, 1983, personal communication), along with local radial and vertical dispersivities of 0.007 m. The value used for the

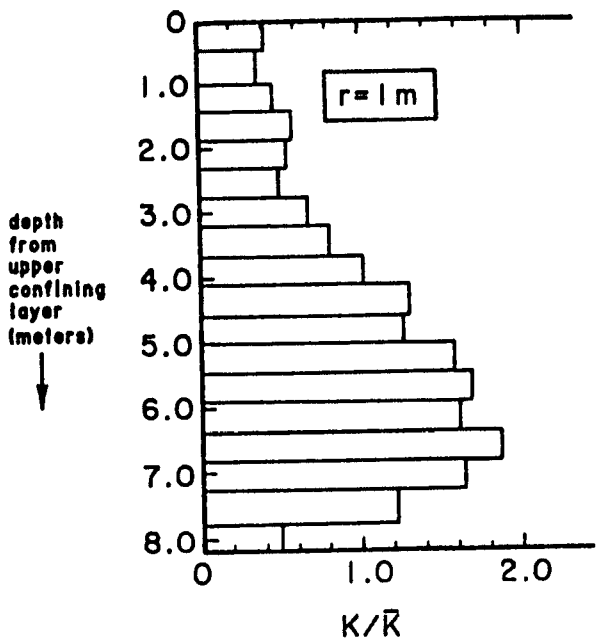

Figure 26. Hydraulic conductivity profile measured by Pickens and Grisak (1981) and used in the present calculations.

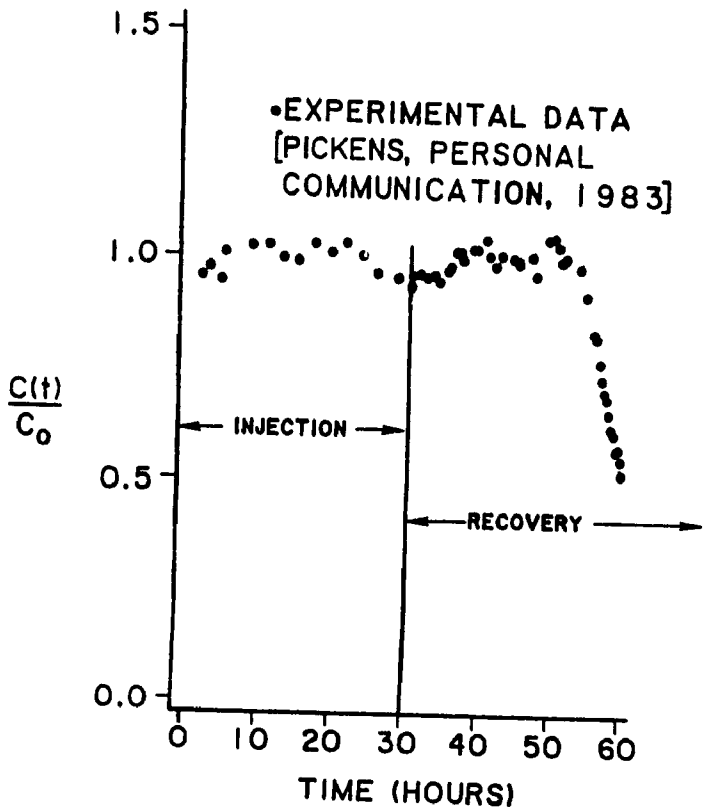

Figure 27. Unsteady injection concentration during the Pickens and Grisak (1981) single-well field experiment.

radial dispersivity is based on the observations, but the value used for the vertical dispersivity is arbitrary and it was chosen simply as a possible upper limit for this quantity in this case as discussed in more detail by Güven et al. (1985). The effects of the well radius and molecular diffusion were neglected. The porosity value used in the calculations was 0.38 as given by Pickens and Grisak (1981, page 1197).

In Figures 28 and 29, the actual flow-weighted breakthrough curves from observation wells located 1 and 2 m from the injection-withdrawal well respectively (Pickens and Grisak, 1981b) are shown along with the flow-weighted breakthrough curves calculated by SWADM. (The flow-weighted concentration, $\hat{C}$ is defined as $\hat{C} = \int_0^B (K(z)/\bar{K})Cdz/B$, where B is the aquifer thickness.) In Figure 29, the wavy appearance of the computed curve for a time greater than about 10 hours is due to the unsteady injection concentration used in the simulation. The experimental concentration versus time data measured at the injection-withdrawal well is shown in Figure 30 along with the results of the SWADM simulation using the unsteady input concentrations. The early part of the experimental data seems to show a large amount of scatter; however, this part of the curve is closely modeled by SWADM using the actual unsteady injection concentration. The later part of the breakthrough curve is underestimated by SWADM. The reasons for this are not clear. One possible contributing factor could be the presence of small-scale, three-dimensional, very-low-permeability lenses embedded in the aquifer, which the present model does not take into account. These lenses could act as temporary storage zones for the tracer which may diffuse into these zones during injection and then move out slowly during withdrawal, leading to larger concentrations during withdrawal than predicted by SWADM. Another possible contributing factor for the behavior noted above is that

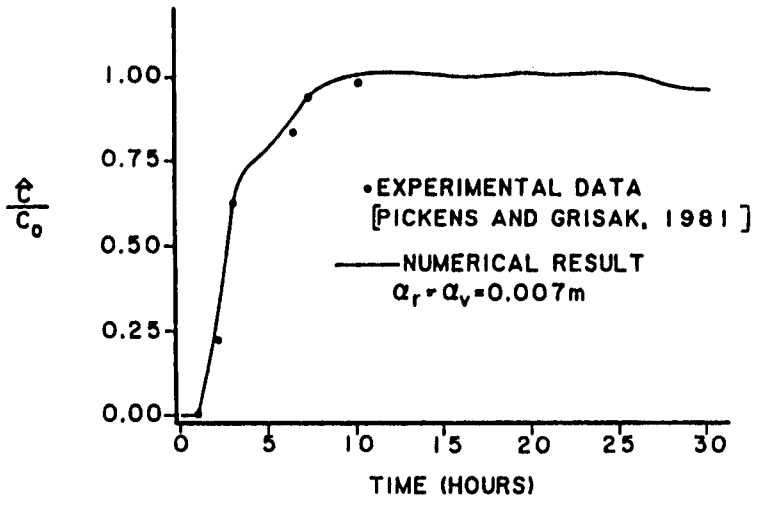

Figure 28. Comparison of SWADM results with field data for the flow-weighted concentration from an observation well one meter from the injection-withdrawal well.

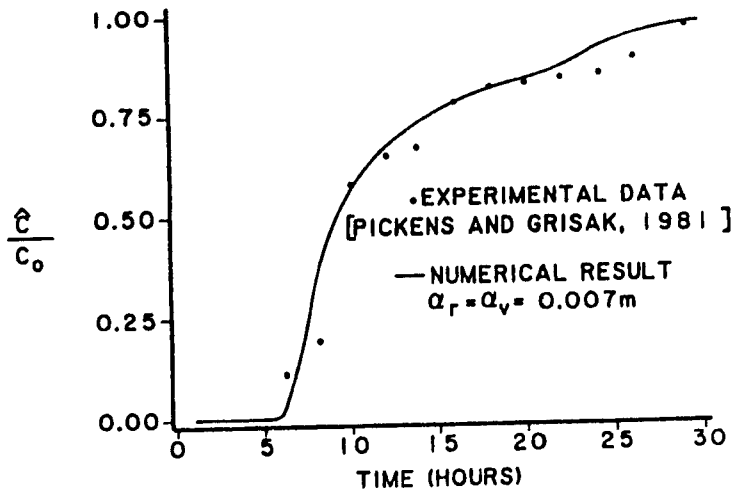

Figure 29. Comparison of SWADM results with field data for the flow-weighted concentration from an observation well two meters from the injection-withdrawal well.

according to the measured data, approximately 2.5 percent more tracer was shown to have been withdrawn than was injected. While this is certainly not a large experimental error for a field experiment (in fact it is quite small), it is enough to have significantly changed the slope of the later part of the curve if that is where the error occurred. Since a mass balance was not satisfied perfectly during this experiment, the net area under the experimental curve is greater than the area under the calculated curve. However, in obtaining the results shown in Figures 28, 29, and 30, no "model calibration" of any type was performed. Only parameter values measured by Pickens and Grisak (1981) were utilized. The resulting curves represent very accurate simulations which indicate an advection-dominated dispersion process with local dispersivities approaching those measured in the laboratory. As also discussed in more detail by Molz et al. (1983) and Güven et al. (1984), it is clear that if a full-aquifer dispersivity were calculated from these data it would not represent a physical property of the aquifer.

Simulation of Two-Well Tests

To date, simulations have been performed for two separate two-well tests, the Pickens and Grisak (1981) test and the Mobile test described in a previous section. Only the Mobile two-well test simulation will be presented in detail because the conclusions are similar to those that result from simulation of the Pickens and Grisak (1981) test but are somewhat more significant because of the larger scale of the experiment.

In our simulation of the E1-I2 two-well test we chose to employ the single-well test as a means for inferring the hydraulic conductivity distribution in a relatively small aquifer region between the injection well and a multilevel observation well. The two-well experiment was then used to

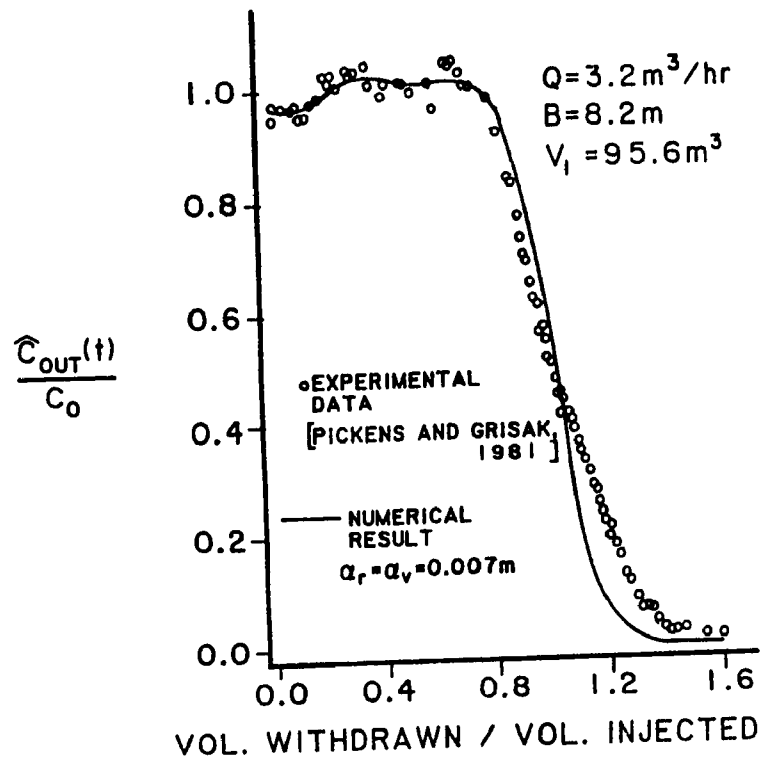

Figure 30. Comparison of SWADM results with field data for the concentration leaving the injection-withdrawal well.

test the prediction capability over a relatively large aquifer region, based on the vertical distribution of hydraulic conductivity inferred from the single-well test shown in Figure 21. This procedure helps to define what is actually being measured during a single-well test and over what travel distances such a measurement might retain some meaning. It also provides insight concerning fundamental properties of the flow fields which were established at the Mobile site during the various tests.

Two separate and independent models were used to simulate the results of the two-well test. Under contract to Auburn University, GeoTrans, Inc., developed a three-dimensional advection-dispersion model that took advantage of our particular geometry (Huyakorn et al., 1986a, 1986b). The aquifer was divided vertically into 12 layers of varying thicknesses (Table 3), depending on the rate of change of the relative hydraulic conductivity distribution, and flow between the injection and production wells was assumed to be stratified, steady and horizontal within each layer. The advection pattern for such a situation is well known (Davis and DeWiest, 1966, p. 209), so the Darcy velocity, U, could be calculated at any particular point within the 12-layer system (Huyakorn et al., 1986a, 1986b). Given the known velocity distribution, the advection-dispersion equation was solved using a finite element approach (Huyakorn et al., 1986b) with the governing equation written in three-dimensional curvilinear coordinates (s,n,z), where s and n are the coordinates along and normal to a local streamline, and z is the vertical coordinate. In this system the transformed advection-dispersion equation is given by

$$\frac{1}{h_2}\frac{\partial}{\partial s}\left(h_2 D_s \frac{\partial c}{\partial s}\right) + \frac{1}{h_1}\frac{\partial}{\partial n}\left(h_1 D_n \frac{\partial c}{\partial n}\right) + \frac{\partial}{\partial z}\left(D_z \frac{\partial c}{\partial z}\right) - \frac{U}{\theta}\frac{\partial c}{\partial s} - \frac{\partial c}{\partial t} = 0 \qquad (10)$$

Table 3. Two-well test parameters supplied to GeoTrans, Inc. for their 3-dimensional simulations based on the advection-dispersion equation.

(Normalized Hydraulic Conductivity Distribution)

Layer # (i)	Layer Center (z_i)	Layer Thickness	Normalized Cond. ($K(z_i)/K_{max}$)
12	20.4 m	2.40 m	0.15
11	17.97	2.46	0.31
10	15.62	2.24	0.34
9	13.37	2.25	0.38
8	11.50	1.50	0.48
7	10.00	1.50	0.57
6	8.50	1.50	0.51
5	7.00	1.50	0.44
4	5.50	1.50	0.72
3	4.00	1.50	1.00
2	2.50	1.50	0.65
1	0.87	1.75	0.25

(Additional Parameters)

Longitudinal dispersivity	0.15 m
Transverse (horizontal) dispersivity	0.05 m
Transverse (vertical) dispersivity	0.01 m
Tracer injection time	3.19 days
Total injection time	32.5 days
One-half well spacing	19.14 m
Radius of injection and production wells	0.08 m
Injection and production rates	0.9464 m^3/min
Porosity	0.35
Aquifer thickness	21.6 m
Molecular diffusion coefficient	1×10^{-9} m^2/s
Screen location (Injection well)	Fully penetrating
Screen location (Withdrawal well)	Fully penetrating
E3 observation well coordinates	(x=13.56 m, y = 0)

where D_s, D_n and D_z are principal components of the hydrodynamic dispersion tensor in the longitudinal, transverse and vertical directions, respectively, and h_1 and h_2 are the scale factors of the curvilinear coordinate system (Huyakorn et al., 1986a). The dispersion coefficients are defined as

$$D_s = \alpha_L \, U/\theta + D_o \tag{11a}$$

$$D_n = \alpha_T \, U/\theta \tag{11b}$$

$$D_z = \alpha_z \, U/\theta + D_o \tag{11c}$$

where α_z is the vertical dispersivity, and U is a function of s, n and z. Solution of equation (10) enables one to predict the tracer concentration in the production well as a function of time and also the tracer concentrations as functions of time at each level in the multilevel observation well E3. The actual information supplied to GeoTrans is listed in Table 3. The Cartesian coordinates listed are based on Figure 4.

The second model used to simulate the two-well test is called the two-well advection model (TWAM) and was developed at Auburn University (Falta, 1984; Güven et al., 1986). A Lagrangian solution method is used in this model based on the travel times of tracer along various flow lines from one well to the other. In this model, it is assumed that the aquifer is horizontal, confined, of constant thickness and porosity, and perfectly stratified in the vicinity of the test wells. TWAM takes into account the depth-dependent advection in the horizontal planes, but neglects completely any local hydrodynamic dispersion. Thus any simulations resulting from application of TWAM will yield dispersed concentration distributions based solely on differential advection, which is also called shear flow (Fischer et al., 1979).

Shown in Figure 31 are the results of the 3-dimensional dispersion simulation and the advection simulation using the model called TWAM (Güven et al., 1986). Both models do a remarkably good job of predicting the

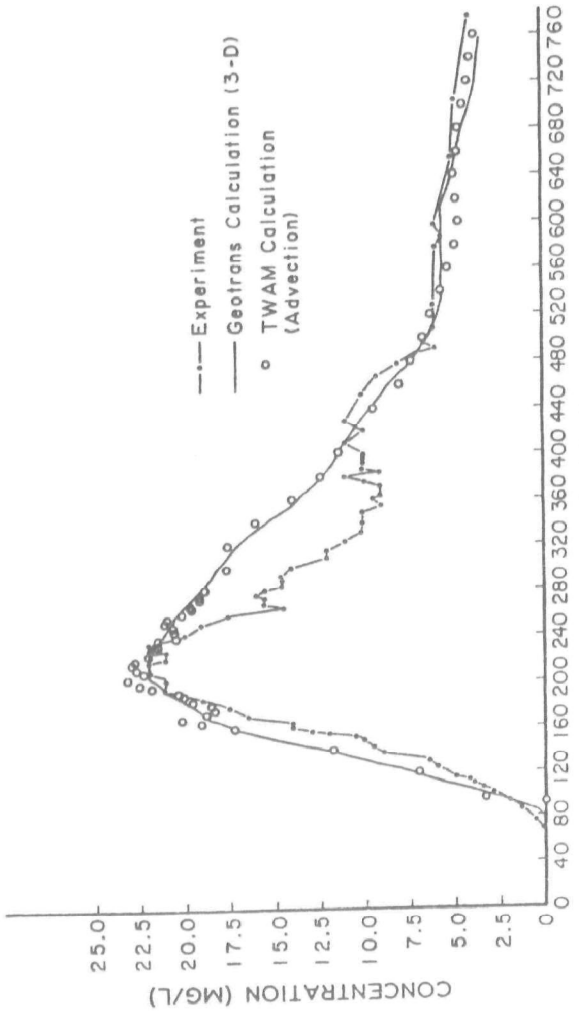

Figure 31. Results of various simulations of the two-well test. No "calibration" or curve-fitting of any type was used.

recovery concentrations during the two-well test. Since the two independent predictions agreed quite well, one can conclude that local hydrodynamic dispersion played a very minor role in determining the time distribution of tracer concentration in the withdrawal well. The entire experiment, which involved estimated travel distances over individual flow paths ranging from 38.3 m to about 90 m in the most permeable layer, was highly advection-dominated. The dominant role of advection in the two-well test was also noted earlier by Hoopes and Harleman (1967) for the case of a homogeneous aquifer.

We would like to emphasize that no prior calibration was done in order to arrive at the results shown in Figure 31. All of the information supplied to our subcontractor is listed in Table 3. They did not know the result of the experiment they were attempting to simulate. With the exception of the dispersivity values and the porosity, all of the information contained in Table 3 was measured directly in the field or calculated from field measurements. The dispersivity values were chosen arbitrarily to have relatively small finite values because the 3-D model would develop numerical dispersion and/or excessive CPU time problems if the dispersivity got too close to zero. Porosity was measured in the laboratory on disturbed core samples obtained from well E3 during drilling operations. The seven samples were compacted lightly and the porosity measured based on the determination of solids specific gravity and saturated water content. The average for well E3 was 0.41. It was reasoned that this value would likely be higher than the undisturbed in-situ values, so an effective porosity of 0.35 was chosen prior to any simulations. The 3-D model result in Figure 31, based on the 0.35 porosity value, was obtained from a single computer run which

required 8.5 hours of CPU time on a Prime 550-2 minicomputer (Huyakorn et al., 1986b). Runs at Auburn University based on identical data using TWAM (Falta, 1984; Güven et al., 1986) were performed independently of the GeoTrans run.

The calculated withdrawal concentration functions in Figure 31 were obtained from a flow-weighted average of the concentrations along the withdrawal well screen and thus is a vertically integrated quantity. A comparison between concentration breakthrough curves measured at the 7 discrete levels of observation well E3 and those predicted by the 3-D model are shown in Figure 24. At levels 2, 4, 5, and 6, the agreement is good, while at levels 3 and 7 it is poor. A valid comparison cannot be made at level 1 because of an apparent leak in the tubing used to obtain the level 1 samples (Molz et al., 1985). The mixed results of Figure 24 are not unexpected because one would not expect the normalized hydraulic conductivity distribution shown in Figure 21 to remain completely invariant in a fluvial aquifer over the 38.3 m separation between the injection and production wells. However, it is significant that the integrated prediction (Figure 31) remains quite good.

The prediction of concentration versus time in the withdrawal well is sensitive to the normalized hydraulic conductivity distribution. Shown in Figure 32 is the withdrawal concentration breakthrough that would result if one assumed a homogeneous aquifer with a normalized hydraulic conductivity of unity throughout. In such a situation, one would observe a longer travel time for the first arrival of the tracer at the withdrawal well and a much higher peak concentration than was realized during the actual experiment. However, the general behavior of the tail of the curve does not appear sensitive to the details of the normalized hydraulic conductivity distribution.

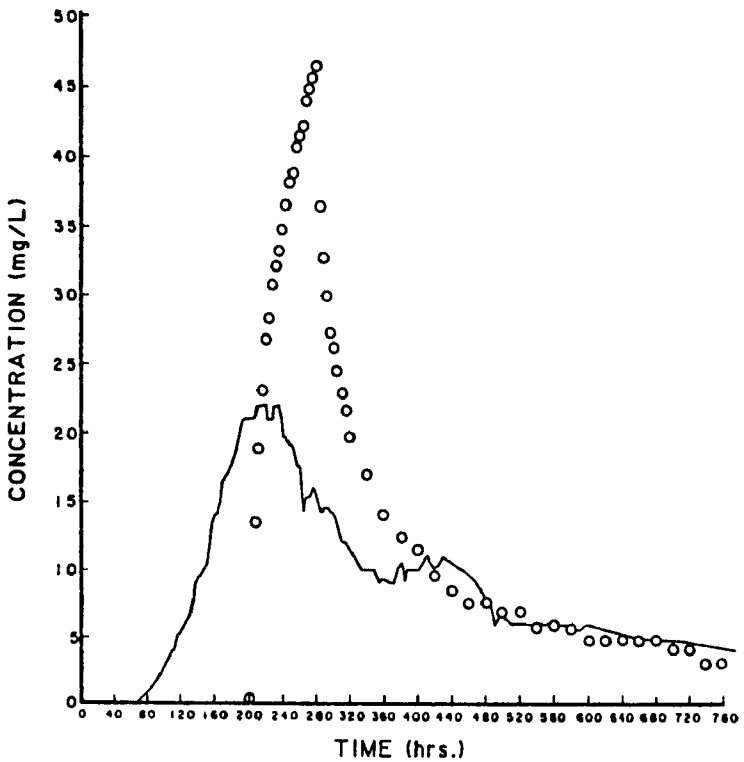

Figure 32. Calculated tracer concentration versus time in the withdrawal well based on an assumed homogeneous, isotropic aquifer with no local dispersion (circles) shown together with the results of the present two-well test (full line).

A good fit to the data results if one assumes a full-aquifer longitudinal dispersivity of 4 m (Huyakorn et al., 1986b).

Further understanding of the implications of the data and computations contained in Figures 24 and 31 can be obtained by selecting a normalized hydraulic conductivity distribution so that the computed and measured breakthrough curves of Figure 24 are made to agree with each other as far as peak arrival times are concerned. (Essentially, this is equivalent to using the two-well test itself to estimate the normalized hydraulic conductivity distribution.) This was discussed previously, and the distribution shown in Figure 25 was obtained. There is not a tremendous difference between the normalized hydraulic conductivity distributions shown in Figures 21 and 25, but the Figure 25 conductivity values in the upper half of the aquifer are smaller. A TWAM simulation of the withdrawal well concentrations based on the Figure 25 distribution is shown in Figure 33. While the rising limb of the breakthrough curve is not simulated as well, there is closer agreement between the data and computations for the falling limb than was obtained previously (Figure 31) using the normalized hydraulic conductivity distribution shown in Figure 21. Overall, the simulations shown in Figures 31 and 33 are of comparable quality.

The single-well and two-well test simulations discussed in this section pertained to different aquifers in widely separated locations. The single-well test was performed in a clean, sandy, glaciofluvial aquifer in Canada, while the two-well test was performed in a fluvial, low-terrace deposit containing sand with appreciable amounts of clay. Both simulations were quite accurate in an integrated sense and consistent with an advection-dominated (shear flow) dispersion process. When advection was considered

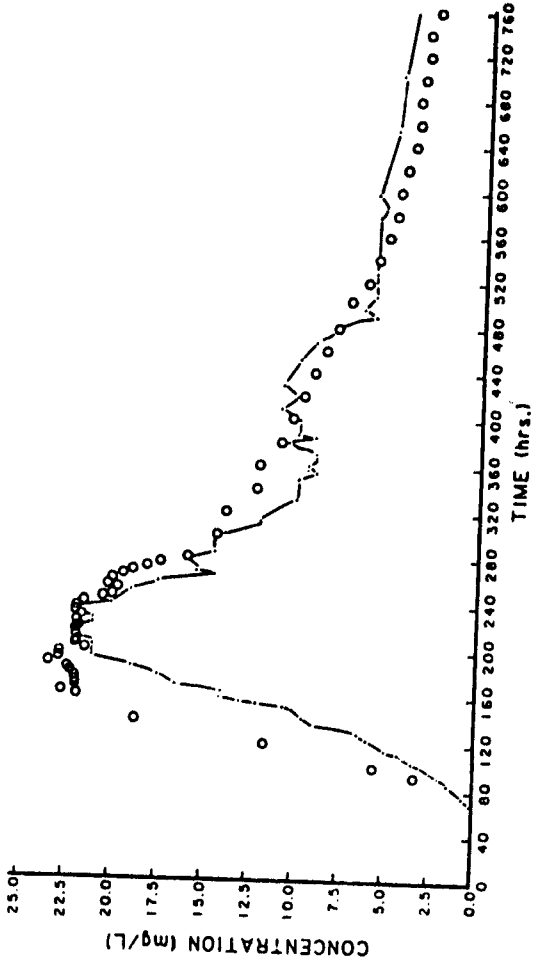

Figure 33. Comparison of measured and calculated tracer concentration versus time in the withdrawal well based on the normalized hydraulic conductivity distribution shown in Figure 25.

explicitly, large, scale-dependent, full-aquifer dispersivities were not required.

Discussion and Conclusions

In the recent past, some hydrologists advocated the use of single-well or two-well tracer dispersion tests as a means for measuring full-aquifer longitudinal dispersivity. However, our analyses of single- and two-well tests in stratified aquifers indicate that if this is done, the resulting number will have little physical meaning. In the case of single-well tests, the full-aquifer breakthrough curves measured in observation wells are determined mainly by the hydraulic conductivity profile in the region between the injection-withdrawal well and an observation well if the travel distance between the injection-withdrawal well and the observation well is typical of most test geometries. Thus, information about the conductivity profile is necessary for meaningful test interpretation. The relative concentration versus time data recorded at the injection-withdrawal well itself is primarily a measure of the combined local and (perhaps?) semi-local dispersion which has taken place during the experiment. Of course, the effects of such dispersion will depend in part on the hydraulic conductivity distribution in the aquifer, and in part on the size of the experiment. As the size of the experiment increases, the effects of local vertical dispersion will become larger compared to the effects of local radial dispersion (Güven et al., 1985).

The two-well test simulations show that the concentration versus time breakthrough curve measured at the withdrawal well would be very sensitive to variations of the hydraulic conductivity in the vertical. Without the use of multilevel observation wells, the test would give little useful information about the hydraulic or dispersive characteristics of the

aquifer, such as aquifer stratification or values of local dispersivities. Factors such as the length of the injection period, the use of recirculation, and the physical size of the experiment all have a strong effect on the breakthrough curve measured at the withdrawal well, making the interpretation of field results difficult, unless aquifer stratification is measured and properly taken into account (Güven et al., 1986).

Based on the above observations and the large values for full-aquifer dispersivities that consistently result from calibrated areal groundwater transport models, we believe that the following working conclusions are warranted.

I. Local longitudinal hydrodynamic dispersion plays a relatively unimportant role in the transport of contaminants in aquifers. Differential advection (shear flow) in the horizontal direction is much more important.

II. The concept of full-aquifer dispersivity used in vertically-averaged (areal) models will not be applicable over distances of interest in most contamination problems. If one has no choice but to apply a full-aquifer dispersion concept, the resulting dispersivity will not represent a physical property of the aquifer. Instead, it will be an ill-defined quantity that will depend on the size and type of experiment used for its supposed measurement.

III. Because of conclusion II, it makes no sense to perform tracer tests aimed at measuring full-aquifer dispersivity. If an areal model is used, the modeler will end up adjusting the dispersivity during the calibration process anyway, independent of the measured value.

IV. When tracer tests are performed, they should be aimed at determining the hydraulic conductivity distribution. Both our theoretical and experimental work have indicated that the variation of horizontal hydraulic conductivity with respect to vertical position is a key aquifer property related to spreading of contaminants.

V. Two- and three-dimensional modeling approaches should be utilized which emphasize variable advection rates in the horizontal direction and hydrodynamic dispersion in the transverse directions along with sorption and microbial/chemical degradation.

VI. In order to handle the more advection-dominated flow systems described in conclusion V, one will have to utilize or develop numerical algorithms that are more resistant to numerical dispersion than those utilized in the standard dispersion-dominated models.

As discussed in the introduction, much of our contemporary modeling technology related to contaminant transport may be viewed as an attempt to apply vertically homogeneous aquifer concepts to real aquifers. Real aquifers are not homogeneous, but they are not perfectly stratified either. What we are suggesting, therefore, is that the time may have arrived to begin changing from a homogeneous to a vertically-stratified concept when dealing with contaminant transport, realizing fully that such an approach will be interim in nature and not totally correct. However, our performance and simulation of several single- and double-well tracer tests suggests that the stratified approach is much more compatible with valid physical concepts, and at least in some cases, results in a mathematical model that has a degree of true predictive ability. Nevertheless, real-world applications will undoubtedly require calibration, which in the stratified approach would

involve varying the hydraulic conductivity distribution rather than the longitudinal dispersivity. The benefit is that when calibrating the K distribution, one is dealing with the physical property that probably dominates the dispersion process.

The change from a vertically-homogeneous to a vertically-stratified approach will not be easy from a field measurement viewpoint nor will it be inexpensive. The work of Pickens and Grisak (1981) and the work described herein has developed some prototype technology and methodology for obtaining the type of information shown in Figure 34. This figure presents the results of a preliminary analysis of all single-well tests to date that have been performed at the Mobile site and analyzed in the vertical plane shown in Figures 15 and 34. The mean locations in the aquifer where the tests took place are indicated in the bottom half of the figure.

Examination of the K/K_{max} plots in Figure 34 reveal some interesting trends. A high hydraulic conductivity zone in the bottom third of the aquifer is evident in all four of the tests. A similar high hydraulic conductivity zone appeared in the top third of the aquifer during the E5-E1 test and the E10-E9 test, but not in the two tests conducted in the vicinity of I2. If one attempted to "fit" a stratified mathematical model to the situation illustrated in Figure 34, the strict definition of a stratified aquifer could not be maintained. As a practical necessity, one would have to postulate a "local" or "quasistratified concept" wherein flow was generally horizontal on the average with the vertical distribution of horizontal hydraulic conductivity gradually shifting from one distribution to the other. There are, however, other considerations that may make the "approximately stratified" idealization work better than expected. While the imposed flow was observed to be locally stratified in the present

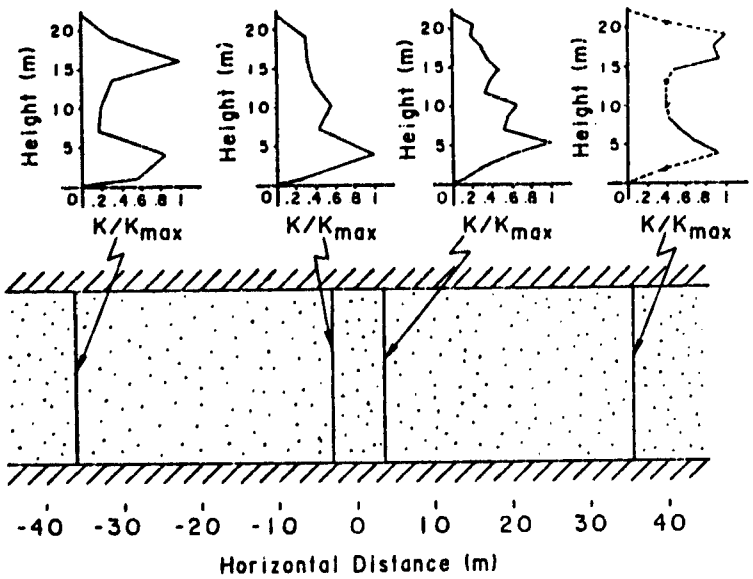

Figure 34. Preliminary results of four single well tests performed at the Mobile site. All stations shown are situated at approximately the same vertical plane.

experiments and in the experiments of Pickens and Grisak (1981), this does not necessarily mean that the aquifer hydraulic conductivity distribution is also stratified around the localities where the tests were performed; areal variations of hydraulic conductivity could still be present at each level of the aquifer around a test well. However, an overall stratified flow pattern could still develop in a confined aquifer even if the hydraulic conductivity distribution is not perfectly stratified. This is because the flow is forced to be horizontal on the average in a confined aquifer, and a quasi-stratified flow may develop along various flow paths in response to the effective average value of the hydraulic conductivity at each level of the aquifer along the flow path, as observed in the field experiments discussed above. This behavior seems to be supported also by the results of some ongoing numerical solute transport experiments presently being performed at Auburn University. In a three-dimensional numerical experiment in a confined aquifer with a completely random computer-generated synthetic hydraulic conductivity distribution, it was observed, somewhat surprisingly, that a quasistratified flow field developed along the entire travel path of a contaminant slug introduced numerically into the aquifer, which resulted in considerable longitudinal spreading (shear flow dispersion) of the contaminant plume.

A question that should be considered further relates to the practical feasibility of performing the tracer tests required by the stratified approach. In most situations we view tracer tests as feasible technically but only marginally feasible in a routine practical sense. As discussed in the section on multilevel sampling wells, the unavailability of widely accepted commercial equipment is a major practical impediment. However, that problem may disappear in the near future, and the need to consider

vertical aquifer property variations is very real. As illustrated by the field work of Osiensky, Winter and Williams (1984), the use of full-aquifer dispersion concepts to model what is essentially a shear flow dispersion process does not result in a conservative estimate of contaminant concentrations. Instead, the model induces a large amount of artificial mixing which often leads to an unrealistically-rapid dilution of a contaminant plume. Such an analysis at a site in central Wyoming concluded that the 1000 mg/l sulfate contour line was located at a maximum distance of about 450 m downgradient from the source. However, further study by Osiensky et al. (1984) which considered the structure of the fluvial aquifer in more detail showed that there were portions of the aquifer 1020 m downgradient that contained sulfate concentrations in excess of 5000 mg/l. Occurrence of this kind of potential mistake can be minimized only by including more information about the actual geometry and hydraulic conductivity distribution regardless of whether a mathematical model is part of the analysis. The interim stratified aquifer approach to tracer test analysis and modeling discussed herein is meant to be a step in that direction.

One obvious implication of our study is that any type of groundwater contamination analysis and reclamation plan will be difficult, expensive and probably unable to meet all of the desired objectives in a reasonable time frame. This reinforces the time-honored saying that 0.0283 kg (1 oz) of prevention is worth 0.454 kg (1 lb) of cure, which in the case of groundwater pollution is probably an understatement. One can not over-emphasize the advantages of preventing such pollution whenever it is feasible.

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TRANSPORT AND FATE

MANAGEMENT CONSIDERATIONS

Session 8

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