&EPA

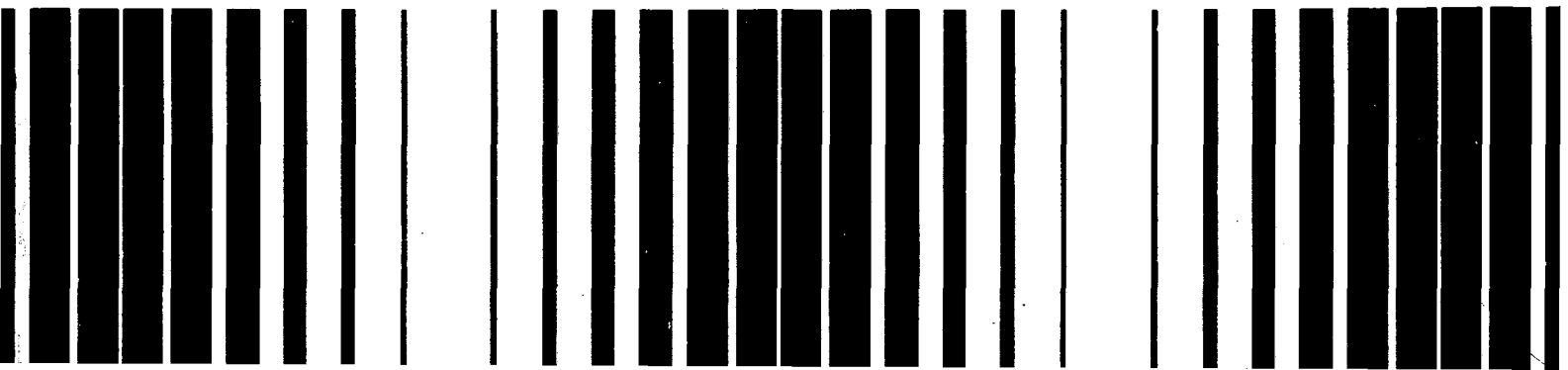# Seminar on Site Characterization for Subsurface Remediations

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Dr. James W. Mercer

Dr. James W. Mercer received a bachelor's degree in Geology from Florida State University in 1969 and an M.S. and Ph.D. in geology from the University of Illinois in 1971 and 1973, respectively. For eight years, he was a research hydrologist with the U.S. Geological Survey. Since 1979, he has been President of GeoTrans, Inc. In 1985, Dr. Mercer received the Wesley W. Horner Award of the American Society of Civil Engineers for work performed at the Love Canal hazardous waste site. He is a former secretary of the hydrology section of the American Geophysical Union and a former member of the National Research Council's Water Science and Technology Board. He is a Fellow of the Geological Survey of America and is an associate editor of the Journal of Contaminant Hydrology.

SEMINAR OVERVIEW

- Transport Processes

- Data Sources

- Geology

- Impacts on Remediation

I.   INTRODUCTION

     A.   Purpose and Scope of Seminar

     B.   Speakers

     C.   Seminar Format

II. DATA COLLECTION GOALS

     A.   Determine Nature and Extent of Contamination
          1.   Important processes
               a.   advection
               b.   dispersion
               c.   sorption
               d.   degradation
               e.   volatilization
          2.   Data requirements
               a.   flow conditions
               b.   chemistry

     B.   Determine Remedial Option
          1.   Type of contaminant
               a.   nonaqueous phase liquid
               b.   dissolved compounds
               c.   natural chemistry
          2.   Contaminant distribution
               a.   vadose zone
               b.   saturated zone
          3.   Type of media
               a.   porous
               b.   fractured

III. SOURCES OF DATA

     A.   Existing Site-Specific Data
          1.   Source type and history
          2.   Previous studies
          3.   Regulatory reporting

     B.   General Data
          1.   Regional
               a.   U.S. Geological Survey
               b.   state reports
               c.   other government agencies
          2.   Chemical specific
               a.   chemical handbooks
               b.   research papers

     C.   Collection of Site-Specific Data
          1.   Stratigraphy
          2.   Lithology
          3.   Structural geology
          4.   Water-level data
          5.   Hydraulic conductivity
          6.   Chemical distribution
          7.   Source(s)/receptor(s)

IV. DATA COLLECTION TECHNIQUES

     A.   Indirect Methods
          1.   Geophysical techniques
          2.   Soil gas survey

     B.   Direct Methods
          1.   Soil borings
          2.   Piezometers
          3.   Monitoring wells

V.   DATA COLLECTION STRATEGIES

     A.   Network Design
          1.   Source(s)
          2.   Pathway
          3.   Receptor

     B.   Phased Approach
          1.   Spatial variability
          2.   Temporal variability
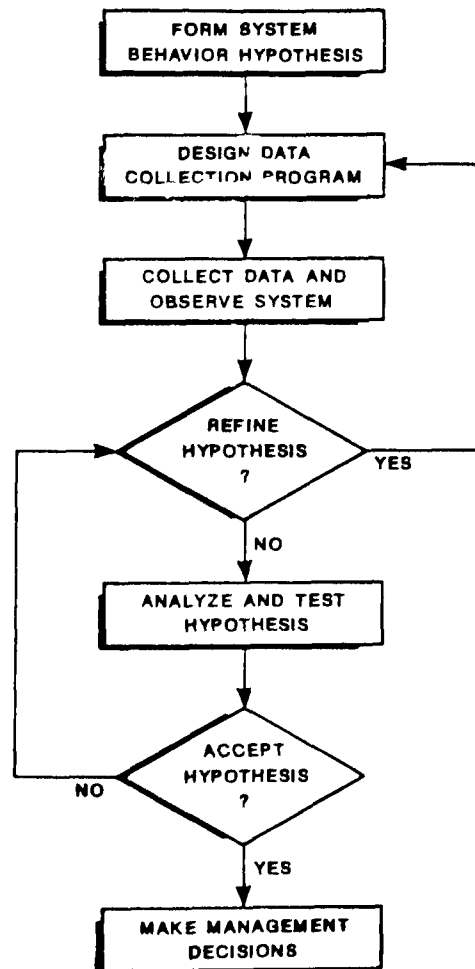
VI. DATA ANALYSIS

     A.   Graphical Analysis

     B.   Scoping Calculations

     C.   Statistical Analysis

     D.   Modeling
          1.   Analytical
          2.   Numerical

VII. CASE HISTORY

     A.   Site Characterization

     B.   Analysis

     C.   Remediation

CONTAMINANT TRANSPORT PROCESSES

```
FORM SYSTEM
BEHAVIOR HYPOTHESIS
        |
        v
DESIGN DATA
COLLECTION PROGRAM  <---------+
        |                     |
        v                     |
COLLECT DATA AND              |
OBSERVE SYSTEM               |
        |                     |
        v                     |
     REFINE                   |
    HYPOTHESIS  ---- YES ------+
        ?
        |
        NO
        v
ANALYZE AND TEST
HYPOTHESIS
        |
        v
     ACCEPT
NO  HYPOTHESIS
        ?
        |
       YES
        v
MAKE MANAGEMENT
DECISIONS
```

- **MASS TRANSPORT**

  - advection

  - diffusion

  - dispersion

- **CHEMICAL MASS TRANSFER**

  - radioactive decay

  - sorption

  - dissolution/precipitation

  - acid-base reactions

  - complexation

  - hydrolysis/substitution

  - redox reactions (biodegradation)

- **BIOLOGICALLY MEDIATED MASS TRANSFER**

  - biological transformations

Bouwer et al. (1988)

A Summary of the Processes Important in Dissolved
Contaminant Transport and Their Impact on Contaminant Spreading

Process	Definition	Impact on Transport
MASS TRANSPORT		
1 Advection	Movement of mass as a consequence of ground water flow	Most important way of transporting mass away from source
2. Diffusion	Mass spreading due to molecular diffusion in response to concentration gradients.	An attenuation mechanism of second order in most flow systems where advection and dispersion dominate.
3. Dispersion	Fluid mixing due to effects of unresolved heterogeneities in the permeability distribution.	An attenuation mechanism that reduces contaminant concentration in the plume. However, it spreads to a greater extent than predicted by advection alone.
CHEMICAL MASS TRANSFER		
4. Radioactive decay	Irreversible decline in the activity of a radionuclide through a nuclear reaction.	An important mechanism for contaminant attenuation when the half-life for decay is comparable to or less than the residence time of the flow system. Also adds complexity in production of daughter products.
5. Sorption	Partitioning of a contaminant between the ground water and mineral or organic solids in the aquifer.	An important mechanism that reduces the rate at which the contaminants are apparently moving. Makes it more difficult to remove contamination at a site.

NRC (1989)

Process	Definition	Impact on Transport
6. Dissolution/ precipitation	The process of adding contaminants to or removing them from solution by reactions dissolving or creating various solids.	Contaminant precipitation is an important attenuation mechanism that can control the concentration of contaminant in solution. Solution concentration is mainly controlled either at the source or at a reaction front
7 Acid-base reactions	Reactions involving a transfer of protons (H^+).	Mainly an indirect control on contaminant transport by controlling the pH of ground water
8. Complexation	Combination of cations and anions to form a more complex ion.	An important mechanism resulting in increased solubility of metals in ground water, if adsorption is not enhanced. Major ion complexation will increase the quantity of a solid dissolved in solution.
9. Hydrolysis/ substitution	Reaction of a halogenated organic compound with water or a component ion of water (hydrolysis) or with another anion (substitution).	Often hydrolysis/ substitution reactions make an organic compound more susceptible to biodegradation and more soluble.
10. Redox reactions (biodegradation)	Reactions that involve a transfer of electrons and include elements with more than one oxidation state.	An extremely important family of reactions in retarding contaminant spread through the precipitation of metals.
BIOLOGICALLY MEDIATED MASS TRANSFER		
11. Biological transformations	Reactions involving the degradation of organic compounds and whose rate is controlled by the abundance of the microorganisms, and redox conditions.	Important mechanism for contaminant reduction, but can lead to undesirable daughter products.

Relative Concentration ↑

A — A Advection
D — Dispersion
S — Sorption
B — Biotransformation

A + D + S

A + D

A + D + S + B

Distance from Continuous Contaminant Source

Relative Concentration ↑

A + D + S

A

A + D + S + B
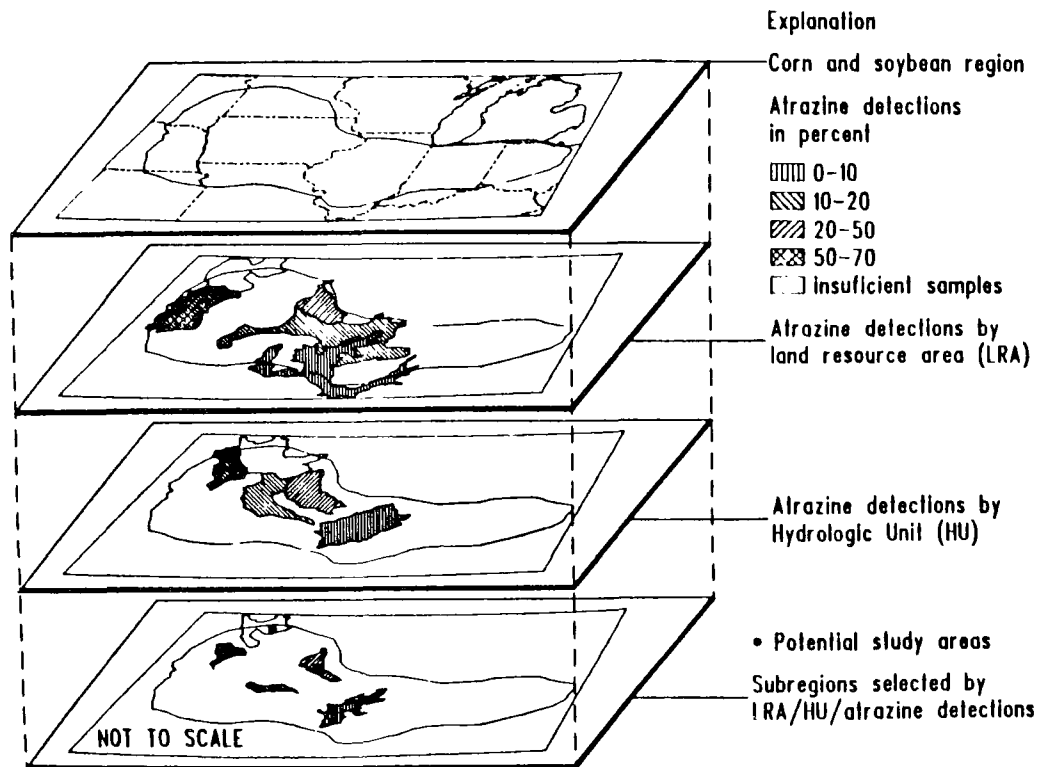
A + D

Distance from Slug-Release Contaminant Source
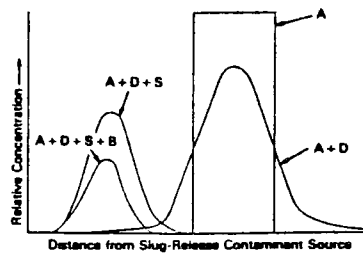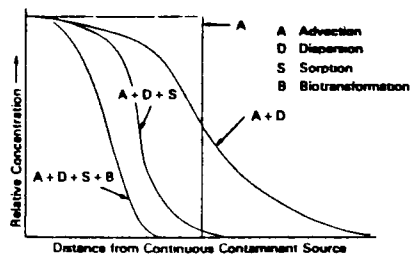
The influence of natural processes on levels of contaminants downgradient from continuous and slug-release sources.

Keely et al. (1986)

HYDROLOGIC SYSTEM COMPONENTS

MASS BALANCE ELEMENTS PROCESSES	ATMOSPHERE	SOIL/ ROOT ZONE	UNSATURATED ZONE	SATURATED ZONE	SURFACE WATER
TRANSPORT					
VOLATILIZATION					
PLANT UPTAKE					
DIFFUSION					
SOLUTION					
CAPILLARY FLOW					
MACROPORE FLOW					
TRANSFORMATION					
BIOLOGICAL					
CHEMICAL					
PHOTO					
STORAGE					
SOLUTION					
SORPTION (MINERALS)					
SORPTION (ORGANICS)					
BIOACCUMULATION					

Matrix of physical compartments and processes affecting atrazine.

Explanation

Corn and soybean region

Atrazine detections
in percent

▦ 0-10
▧ 10-20
▨ 20-50
▨ 50-70
▢ insuficient samples

Atrazine detections by
land resource area (LRA)

Atrazine detections by
Hydrologic Unit (HU)

• Potential study areas

Subregions selected by
LRA/HU/atrazine detections

NOT TO SCALE

Regional, subregional and area delineations for factor verification
or further study by a geographic information system.

SOURCES OF INFORMATION

- EPA AND STATE ENVIRONMENTAL OFFICE FILES

- COUNTY OR REGIONAL PLANNING OFFICES

- CITY OFFICES

- COMPANY FILES AND RECORDS

- UTILITY COMPANIES

- U.S. GEOLOGICAL SURVEY

- U.S. DEPARTMENT OF AGRICULTURE

- STATE GEOLOGICAL SURVEYS

SOURCES	TYPES/COMMENTS
1. EPA and State Environmental Office files for: RCRA permits and applications	
Waste Generators and Transporters	EPA Identification numbers Generator annual reports
TOSCA	May require special clearance for reviewer
NPDES permits and applications	Liquid waste types Treatment processes Production information
Uncontrolled waste disposal sites	
Spills of oil and hazardous materials	
Water supplies	Nearest water supply
Enforcement actions	
Surveillance reports	Problem history Previous findings
2. County or Regional Planning Agencies for Areawide Waste Treatment Mgmt. (CWA - Section 208 Agency)	Plans, concerns, and past problems
3. Other County offices Health Department	Problems, complaints, analytical results
Planning and zoning	Land use restrictions
Assessor	Plat maps and land owners
4. City offices Chamber of Commerce	Information and local industries incl. number of employees, principal products, and facility addresses
Clerk	
Engineer	Foundation and inspection reports Survey benchmark locations
Fire Department	History of fires and/or explosions at facility
Law Enforcement	Complaints and violations of local ordinances
Water and Sewer	Location of buried mains and lines
5. Company files and records	Confidential records require special handling and storage
6. Contractors Building	Local soils, geology, and shallow water levels
Soil exploration and foundation Water well drillers	Local soils, geology, hydrogeology, water levels, regulations, and equipment availability

7. Utility Companies
   Gas
   Electric
   Water
   Petroleum or Natural Gas Pipelines
	Location of buried lines

8. U.S. Geological Survey	Technical geologic and hydrologic reports, maps, aerial photographs, and water monitoring data
9. Remote Sensing Imagery	Drainage patterns, land use, vegetation stress, historical land development, and geologic structure
10. Computer Data Bases	Wide variety of reference data and bibliographies
11. U.S. Department of Agriculture	Soil maps, types, physical characteristics, depths association, and uses
12. State Geological Surveys	Technical geologic and hydrologic reports, State geologic maps, and monitoring data
13. U.S. Department of Labor Occupational Safety and Health Administration (OSHA)	Processes Hazards Protective equipment needs
14. National Oceanic and Atmospheric Administration (NOAA)	Climatic data
15. National Ocean Survey	Tidal data; historic, recent, and projected

ACTIONS TYPICALLY TAKEN

- install a few dozen shallow monitoring wells

- sample ground-water numerous times for 129+ priority pollutants

- define geology primarily by driller's logs and drill cuttings

- evaluate local hydrology with water level contour maps of shallow wells

- possibly obtain soil and core samples for chemical analyses

Benefits

- Rapid screening of the site problems
- Costs of investigation are moderate to low
- Field and laboratory techniques used are standard
- Data analysis/interpretation is straightforward
- Tentative identification of remedial alternatives is possible

Shortcomings

- True extent of site problems may be misunderstood
- Selected remedial alternatives may not be appropriate
- Optimization of final remediation design may not be possible
- Clean-up costs remain unpredictable, tend to excessive levels
- Verification of compliance is uncertain and difficult

RECOMMENDED ACTIONS

- install depth-specific clusters of monitoring wells

- initially sample for 129+ priority pollutants, be selective subsequently

- define geology by extensive coring/sediment samplings

- evaluate local hydrology with well clusters and geohydraulic tests

- perform limited tests on sediment samples (grain size, clay content, etc.)

- conduct surface geophysical surveys (resistivity, EM, ground-penetrating radar)

Recommended Actions

* Install depth-specific clusters of monitoring wells
* Initially sample for 129+ priority pollutants, be selective subsequently
* Define geology by extensive coring/sediment samplings
* Evaluate local hydrology with well clusters and geohydraulic tests
* Perform limited tests on sediment samples (grain size, clay content, etc.)
* Conduct surface geophysical surveys (resistivity, EM, ground-penetrating radar)

Benefits

* Conceptual understandings of site problems are more complete
* Prospects are improved for optimization of remedial actions
* Predictability of remediation effectiveness is increased
* Clean-up costs are lowered, estimates are more reliable
* Verification of compliance is more soundly based

Shortcomings

* Characterization costs are somewhat higher
* Detailed understandings of site problems are still difficult
* Full optimization of remediation is still not likely
* Field tests may create secondary problems (disposal of pumped waters)
* Demand for specialists is increased, shortage is a key limiting factor

IDEALIZED APPROACH

- assume state-of-the-art as starting point

- conduct soil vapor surveys for volatiles, fuels

- conduct tracer tests and borehole geophysical surveys (neutron and gamma)

- conduct karst stream tracing and recharge studies, if appropriate to the setting

- conduct bedrock fracture orientation and interconnectivity studies, if appropriate

- determine the percent organic carbon and cation exchange capacity of solids

- measure redox potential, pH, and dissolved oxygen levels of subsurface

- evaluate sorption-desorption behavior by laboratory column and batch studies

- assess the potential for biotransformation of specific compounds

Idealized Approach

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- Determine the percent organic carbon and cation exchange capacity of solids
- Measure redox potential, pH, and dissolved oxygen levels of subsurface
- Evaluate sorption-desorption behavior by laboratory column and batch studies
- Assess the potential for biotransformation of specific compounds

Benefits

- Thorough conceptual understandings of site problems are obtained
- Full optimization of the remediation is possible
- Predictability of the effectiveness of remediation is maximized
- Clean-up costs may be lowered significantly, estimates are reliable
- Verification of compliance is assured

Shortcomings

- Characterization costs may be much higher
- Few previous applications of advanced theories and methods have been completed
- Field and laboratory techniques are specialized and are not easily mastered
- Availability of specialized equipment is low
- Need for specialists is greatly increased (it may be the key limitation overall)

GEOLOGICAL ASPECTS
OF
SITE REMEDIATION

```
┌─────────────┐           ┌─────────────┐
│             │           │    SITE     │
│   GEOLOGY   │  ◄─ ? ─►  │ REMEDIATION │
│             │           │             │
└─────────────┘           └─────────────┘
```
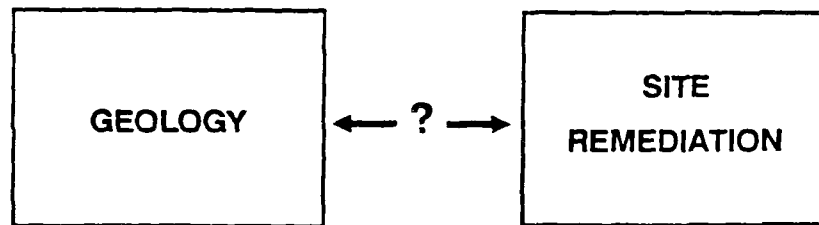
GEOLOGICAL FACTORS

- STRATIGRAPHY

- LITHOLOGY

- STRUCTURAL GEOLOGY

- HYDROGEOLOGY

QUESTIONS

- WHAT GEOLOGIC FACTORS ARE SIGNIFICANT TO REMEDIATION?

- HOW ARE GEOLOGIC DATA COLLECTED?

- HOW ARE GEOLOGIC DATA INTERPRETED?

STRATIGRAPHY

- Formation, composition, sequence and correlation of stratified rocks and unconsolidated surficial materials (clays, sands, silts, gravels).

- Necessary to identify pathways of migration, estimate extent, and to define hydrogeologic frame work.
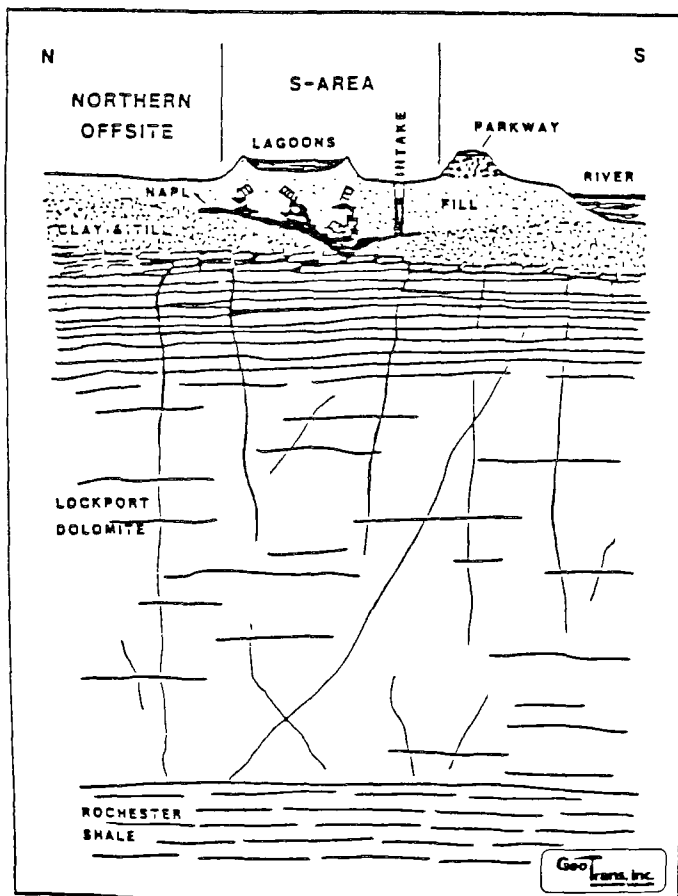
Section from north to south through S-Area showing generalized geological conditions: thickness of fractures and bedding planes exaggerated to illustrate concepts.

STRATIGRAPHIC CONSIDERATIONS . REMEDY
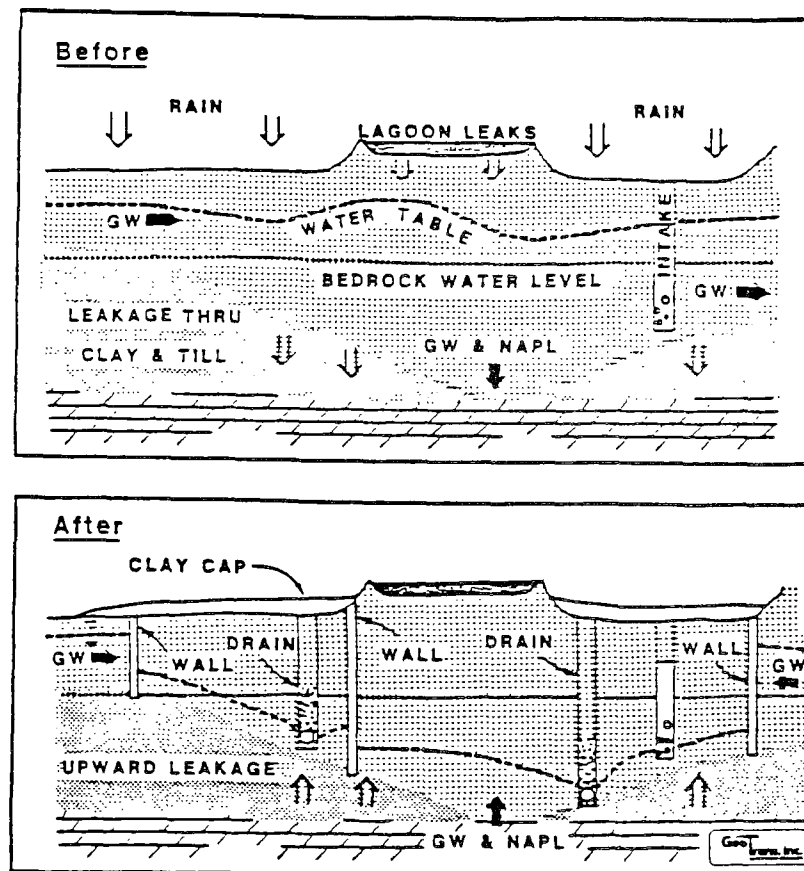
Generalized north-south section through Northern Offsite and S-Area showing the impact of remedies on water levels and ground-water and NAPL flow directions.

STRUCTURAL GEOLOGY

- Features produced by movement after deposition-faults, folds, fractures

- Fractures or faults may provide preferential pathways for contaminants to move and require special attention during remediation

- Important where surficial deposits are thin or very permeable

LITHOLOGY

- COMPOSITION OF UNCONSOLIDATED DEPOSITS OR ROCKS

  - MINERALOGY

  - GRAIN SIZE

  - GRAIN SHAPE

  - PACKING

Major mechanisms of liquid waste transport from the Keyser borehole to the water table.
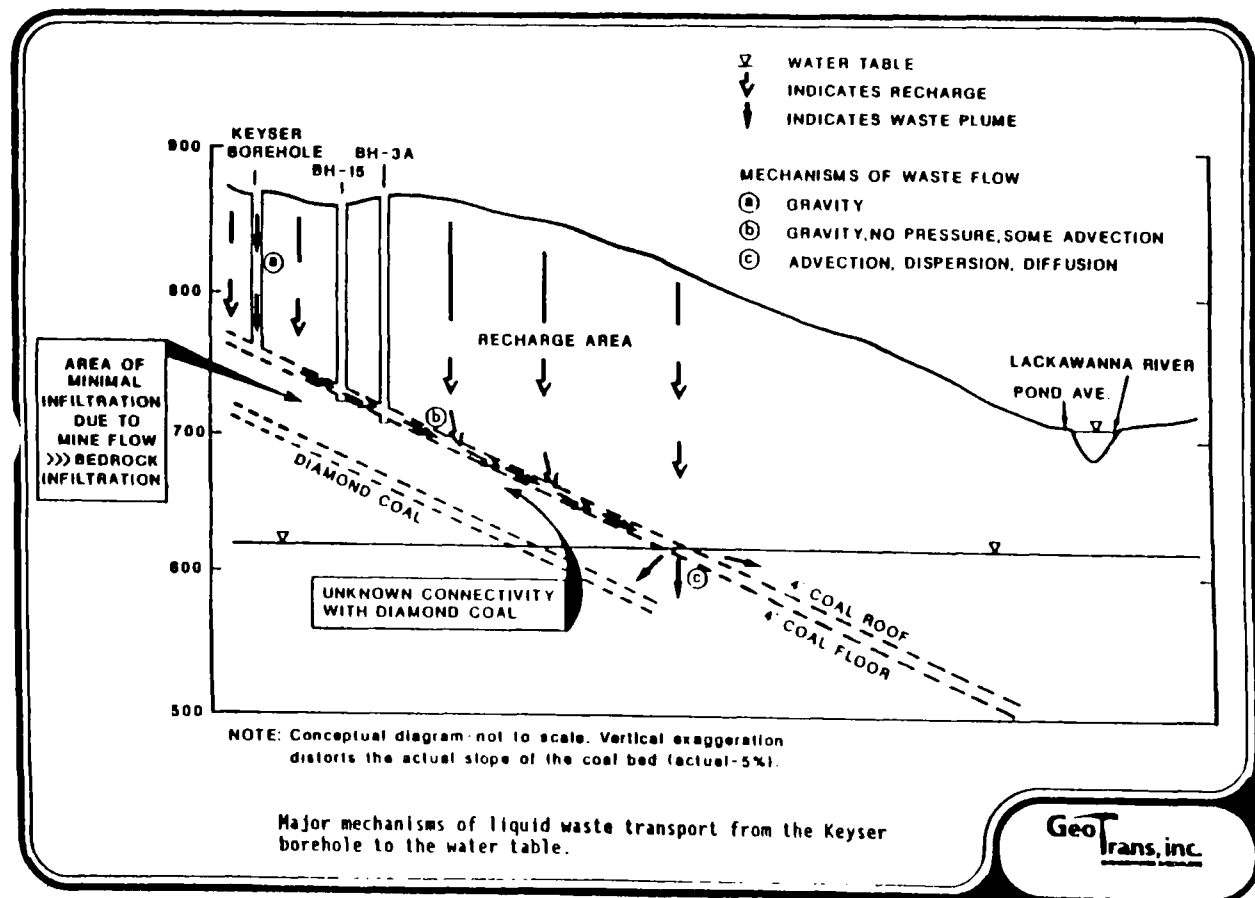
- RELATIONSHIP OF MOVEMENT OF SUB-SURFACE WATERS TO GEOLOGY

- DIRECTIONS AND RATES OF GROUNDWATER FLOW

- TIES STRATIGRAPHY, LITHOLOGY, STRUCTURAL GEOLOGY TO THEORY OF GROUNDWATER HYDRAULICS

- ESSENTIAL TO ANY GROUNDWATER REMEDIATION, GROUNDWATER MONITOR-ING OF SURFACE CLEANUP (I.E., EXCAVA-TION, VACUUM EXTRACTION)

Hydrologic cycle.

GeoTrans (1989)
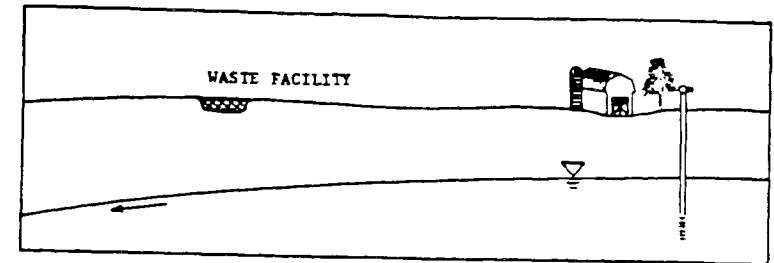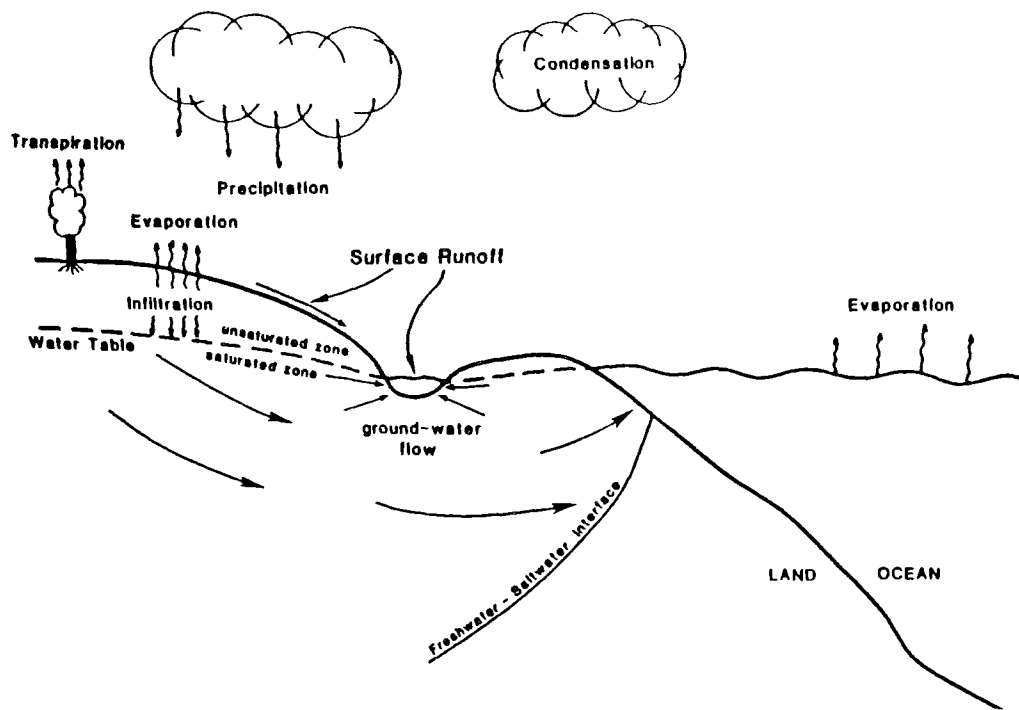
(a)
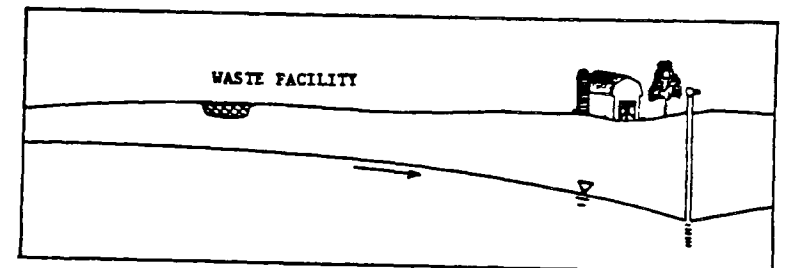
(b)

Seasonal variations in recharge and pumping can reverse flow directions during the year (a) late fall water-table with no significant pumping and low recharge (b) early summer after spring recharge and significant pumping for agriculture

HYDROGEOLOGIC INVESTIGATIONS

- DELINEATE EXTENT OF CONTAMINATION IN SUBSURFACE

- DETERMINE FLOW DIRECTIONS PATHWAYS AND RATES FOR GROUNDWATER AND POTENTIAL CONTAMINANTS

- PROVIDE FRAMEWORK FOR DESIGN OF GROUNDWATER REMEDIAL PROGRAM

  - wells – where and how many
  - pumping rates
  - treatment facility influent

- PROVIDE BASIS FOR SELECTING FROM ALTERNATIVE REMEDIAL STRATEGIES AND NO ACTION

  - concentrations of contaminants at point of use or property boundary

EXPLANATION

—8360— Equipotential Line

● Pumping Well

O Observation Well

⌒ Flow Line

SCALE

0   1000   2000

Feet

Datum - Mean Sea Level
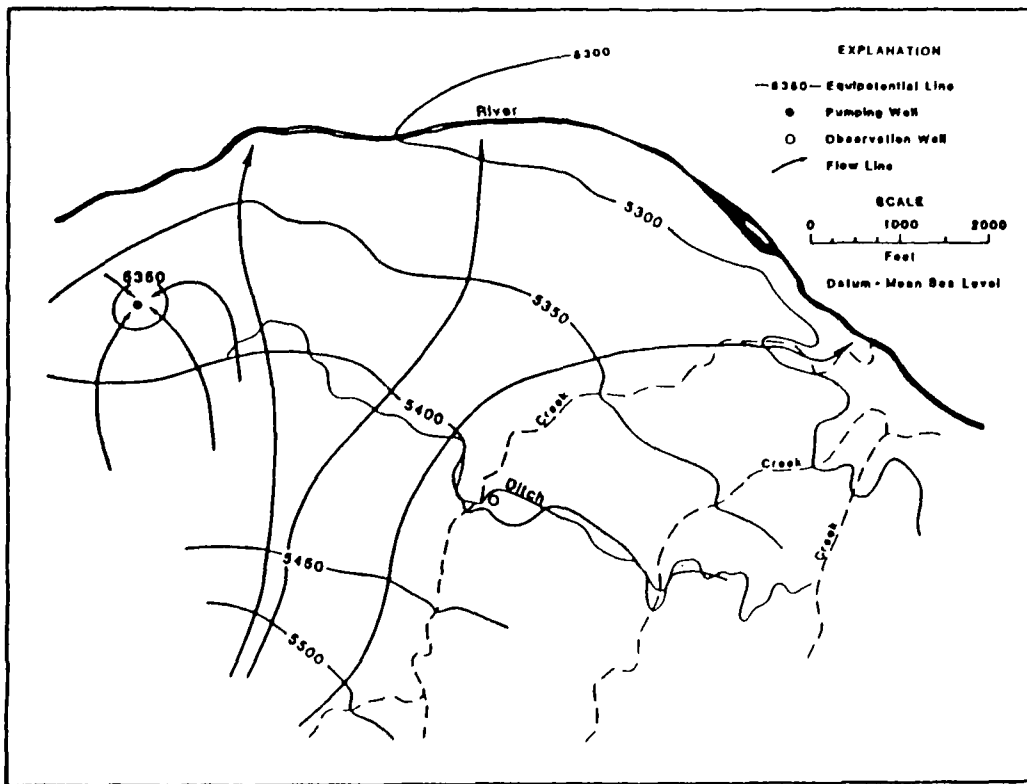
Potentiometric surface and flow lines.

GeoTrans (1989)

FIELD METHODS

- GEOLOGICAL INFORMATION

  - borehole exploration

  - mapping surface features

  - geophysical methods
    - surface
    - downhole

- GROUNDWATER FLOW INFORMATION

  - monitor water elevations in wells, adjacent surface waters

  - aquifer test
    - pump tests
    - slug tests

  - special methods
    - laboratory properties
    - flow meters

- GROUNDWATER CONTAMINATION INFORMATION

  - sample wells/analyze

  - measure/pump free product

  - soil sample analysis

GEOPHYSICAL METHODS

- SURFACE TECHNIQUES

  - gravity survey

  - infrared imagery

  - ground penetrating radar

  - induced electrical polarization

  - resistivity

  - metal detection

  - magnetometer

  - reflection seismics

  - electromagnetic surveys

- BOREHOLE METHODS

  - geothermetry

  - electrical

  - acoustic

  - nuclear

Gas Vent Tube

Well Cap

1/4" Gas Vent

Steel Protector Cap with Locks

Surveyor's Pin (flush mount)

Concrete Well Apron

Frost Zone

Continuous Pour Concrete Cap and Well Apron (expanding cement)

Vadose Zone

Non-shrinking Cement

Borehole Wall

Potentiometric surface

Saturated Zone

Annular Sealant

Filter Pack (2 feet or less above screen)

Screened Interval

Sump/Sediment Trap

Bottom Cap

A typical monitoring-well design.

GeoTrans (1989)

METHODS OF ANALYSIS

● **DESCRIPTIVE**

● **GRAPHICAL**

● **QUANTITATIVE**

    – **statistical**

    – **analytical solutions or calculations**

    – **numerical models**
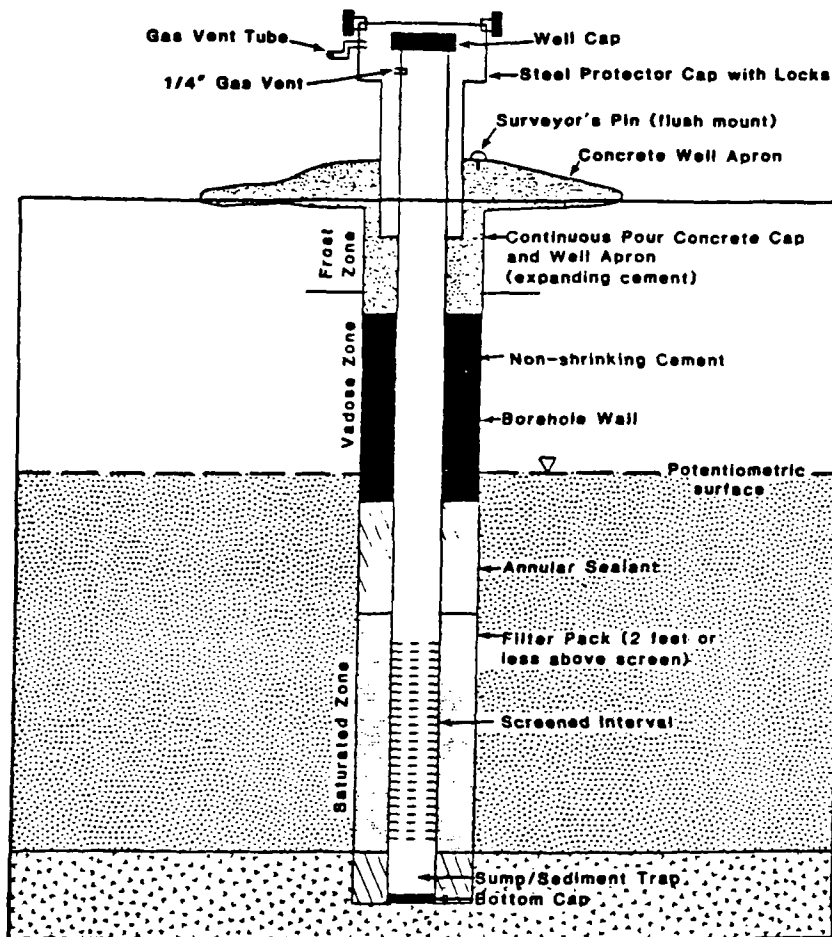
HYDE PARK LANDFILL

● **PROBLEMS:**   **Extensive contamination of bedrock by immiscible dense contaminants**

● **GEOLOGY:**   **Glacial deposits ~ 30 feet thick above flat lying sedimentary bedrock**

● **REMEDY:**   **Groundwater pump and treat with reinjection**

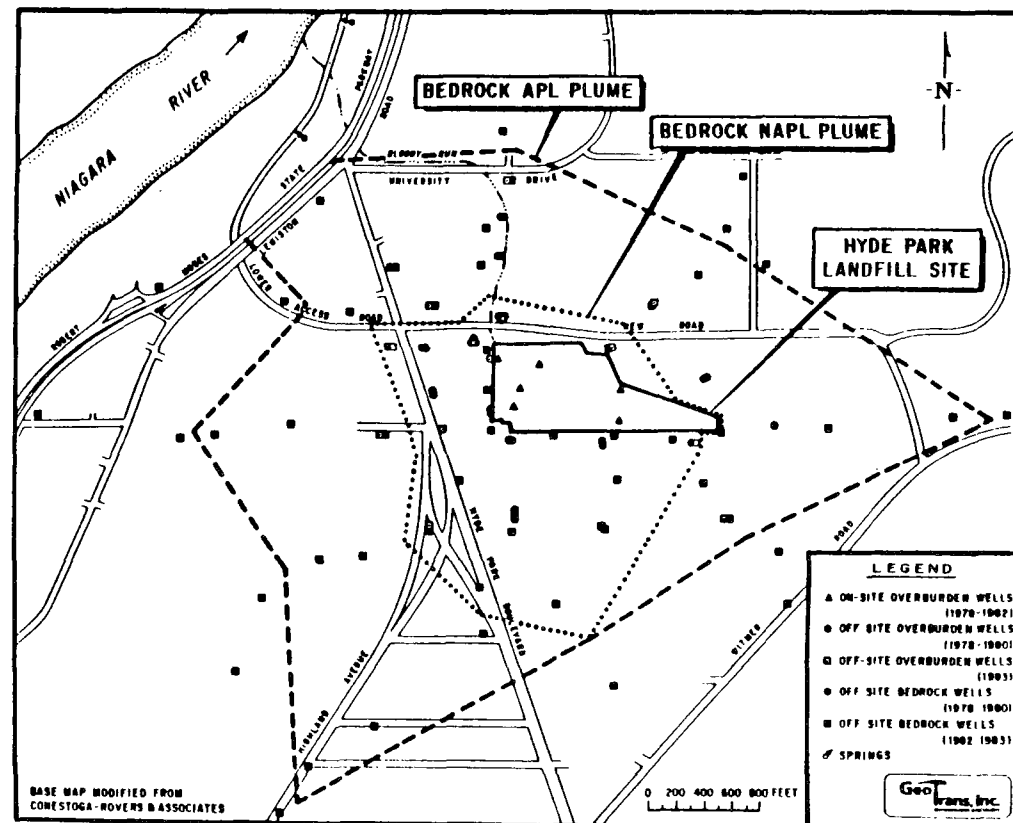● **METHODS:**   **Groundwater modeling to design prototype program and help set ACL s**

HYDE PARK LANDFILL

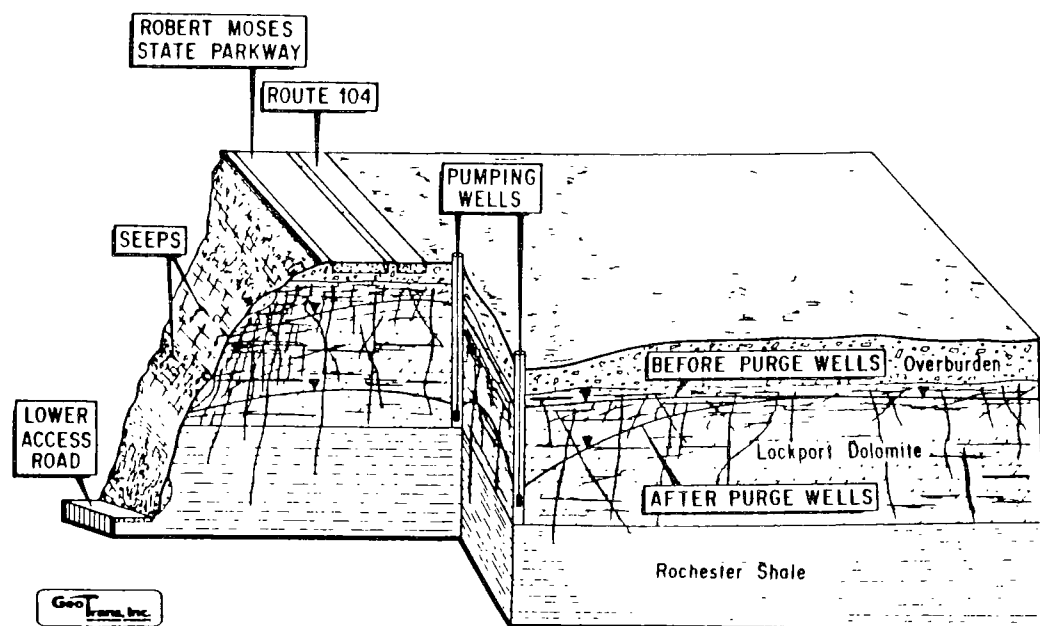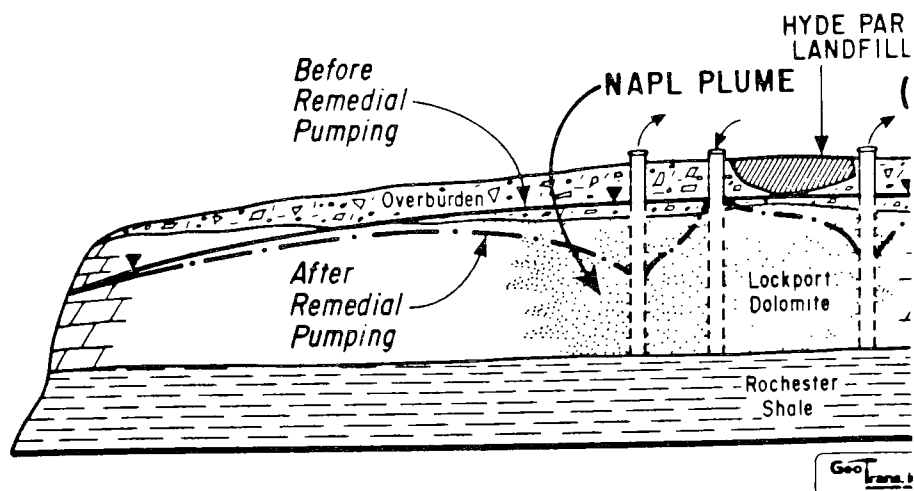PUMPED-STORAGE RESERVOIR

BURIED CONDUITS

POWER CANAL

ROBERT MOSES STATE PARKWAY

HYDE PARK BOULEVARD

ROBERT MOSES NIAGARA POWER PLANT

600 FEET
500
400
300
200
100

Lockport Dolomite

Rochester Shale

Sandstone and Shale

Irondequoit and Reynales Limestones

Whirlpool Sandstone

Queenston Shale

NIAGARA RIVER

7000 FEET
6000
5000
4000
3000
2000
1000

GeoTrans, Inc.

GEOTRANS, INC

Generalized diagram showing the geologic formations and topographic features in the

N

ESCARPMENT

NIAGARA

RESERVOIR PUMP-GENERATING PLANT

ROBERT MOSES NIAGARA POWER PLANT

PUMPED-STORAGE RESERVOIR

OPEN CANAL

THE WHIRLPOOL

CANADA

UNITED STATES

HYDE PARK LANDFILL

TWIN CONDUITS (COVERED)

CITY OF NIAGARA FALLS

NEW YORK

NIAGARA COUNTY

AMERICAN FALLS

INTAKES

HORSESHOE FALLS

RAPIDS

NIAGARA RIVER

SCALE

0   1 MILE

NAVY ISLAND

GRAND ISLAND
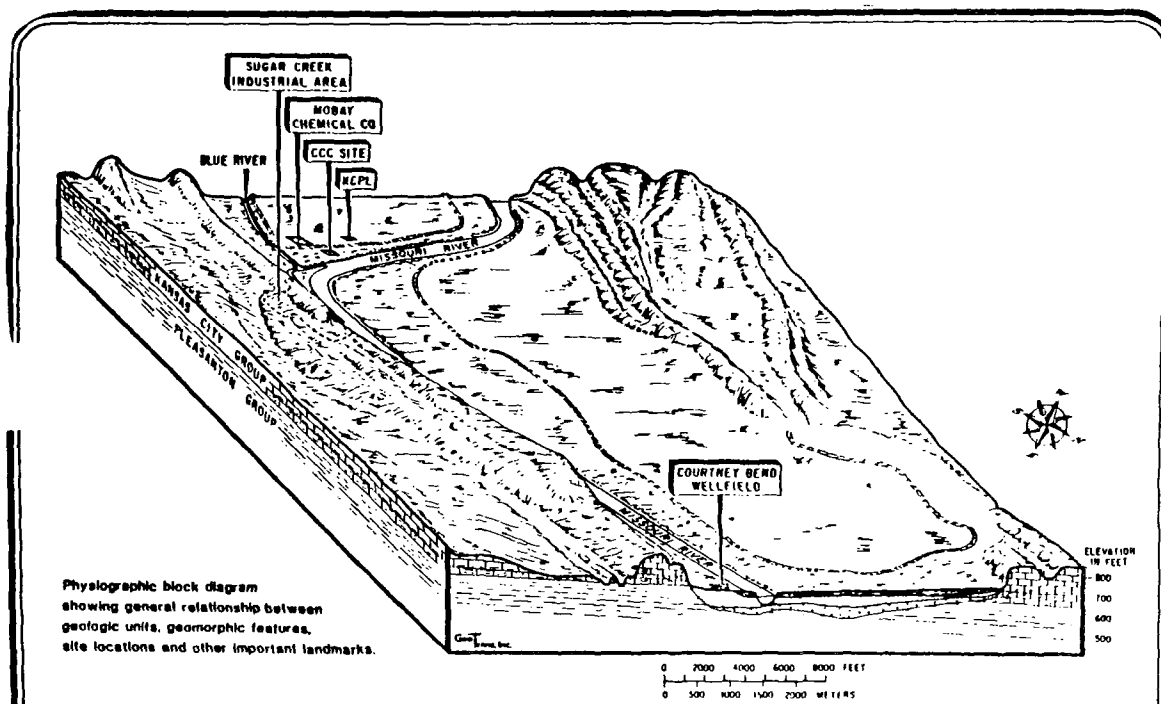
GeoTrans, Inc.

Map showing location of the Hyde Park Landfill.

Lockport Dolomite plumes as defined by the Hyde Park surveys in accordance with the Settlement Agreement (December 1982 – May 1983).
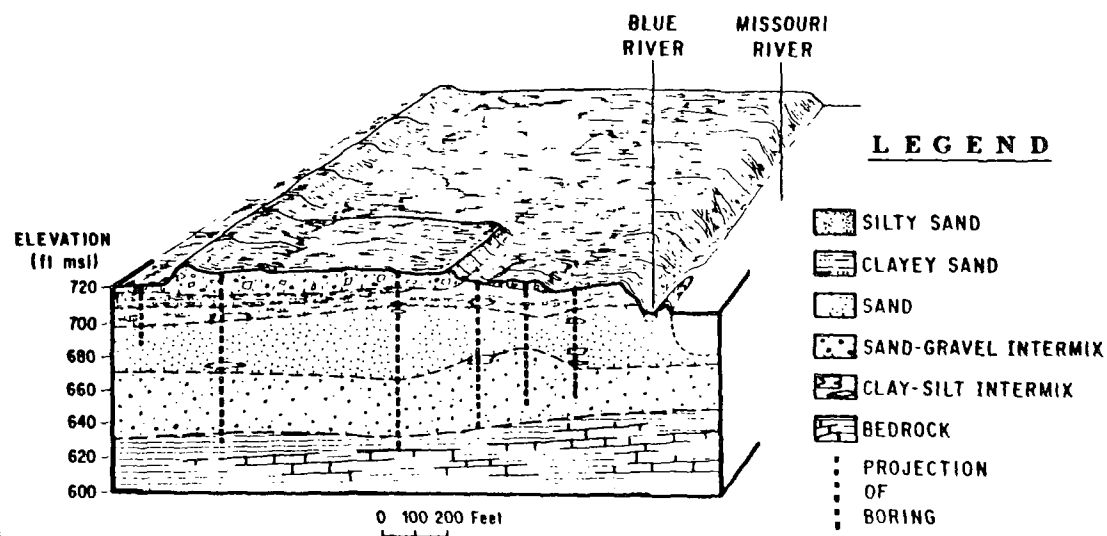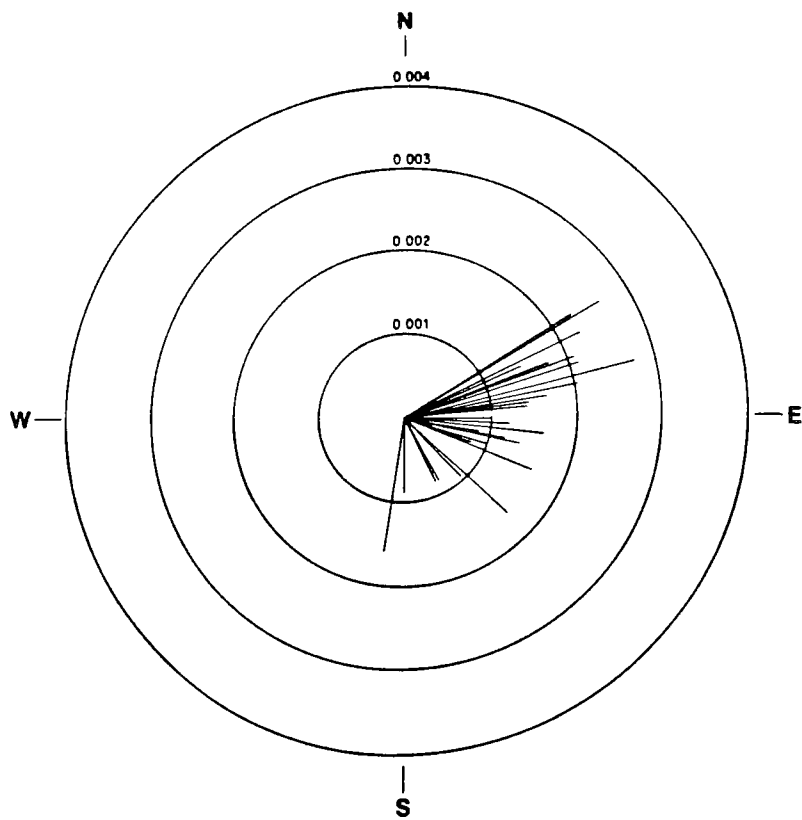

Overburden plumes as defined by the Hyde Park surveys in accordance with the Settlement Agreement (December 1982 – June 1983).

Before Remedial Pumping

NAPL PLUME

HYDE PAR LANDFILL

Overburden

After Remedial Pumping

Lockport Dolomite

Rochester Shale

-N-

0   500   1000 1500 FEET

POWER CANAL

NIAGARA RIVER

ROBERT MOSES STATE PARKWAY

HYDE PARK BOULEVARD

BURIED CONDUITS

GeoTrans, Inc.

Before Remedial Pumping

NAPL PLUME

HYDE PAR LANDFILL

Overburden

After Remedial Pumping

Lockport Dolomite

Rochester Shale

GeoTrans, Inc.

ROBERT MOSES STATE PARKWAY

ROUTE 104

PUMPING WELLS

SEEPS

LOWER ACCESS ROAD

BEFORE PURGE WELLS   Overburden

AFTER PURGE WELLS

Lockport Dolomite

Rochester Shale

GeoTrans, Inc.

CONSERVATION CHEMICAL SITE

Physiographic block diagram showing general relationship between geologic units, geomorphic features, site locations and other important landmarks.

- **PROBLEM:** Contamination of a valley fill aquifer near the Missouri River

- **GEOLOGY:** Alluvial aquifer ~ 100 feet thick

- **REMEDY:** Groundwater pump and treat

- **METHODS:** – Statistical analysis of groundwater flow directions
  – Computer modeling to design initial pump and treat system

GENERALIZED GEOLOGIC SECTION

LEGEND

SILTY SAND
CLAYEY SAND
SAND
SAND-GRAVEL INTERMIX
CLAY-SILT INTERMIX
BEDROCK
PROJECTION OF BORING

Groundwater flow directions and gradients observed
in piezometers 1C, 4C, 11C [from Larson (1986)].

GeoTrans, inc.

SLURRY WALL WITH INTERIOR PUMPING
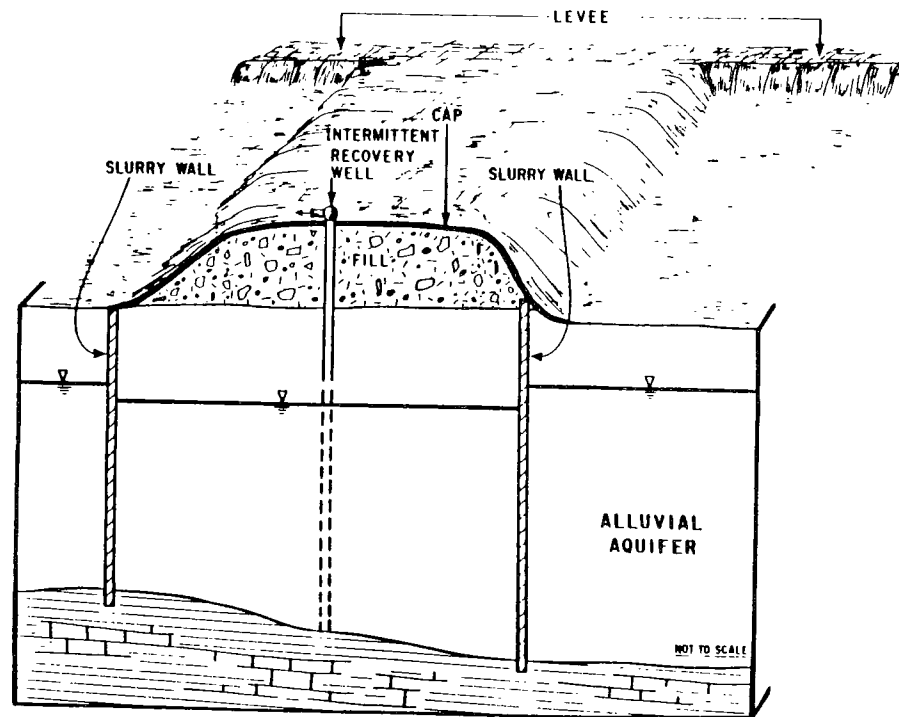
CONCEPT OF HYDRAULIC CONTROL

LEVEE

PIEZOMETER
RECOVERY WELL
CAP
PIEZOMETER

FILL

WATER TABLE BEFORE PUMPING

DIVIDE

WATER TABLE AFTER PUMPING

ALLUVIAL AQUIFER

NOT TO SCALE
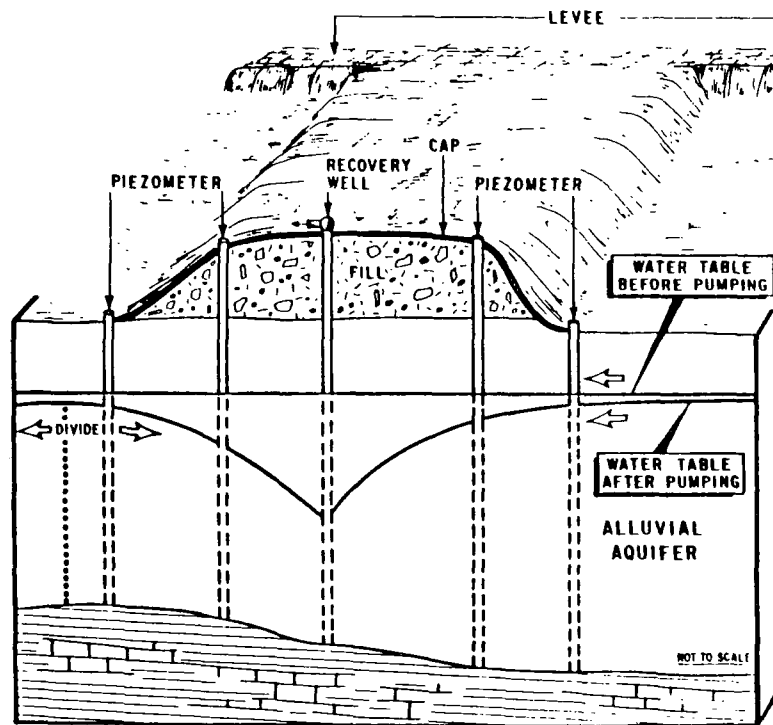
PLAN B1

$T \approx 15,500 \ ft^2/d$

Gradient 090°
    at 0.0012

Q each well
    = 200 gpm

Q Mobay well
    = 500,000 gpd

RUN # C1S6G2

KCPL

MOBAY

LEVEE

BLUE RIVER

BIG SOU RIVER

| 500 | 0 | 500 | 1000 |

SCALE IN FEET

Steady-state simulation results for remedy based on site pumping; Run #C1S6G2.

GeoTrans, Inc.

CONCLUSIONS

Three hazardous waste sites involving groundwater contamination have been reviewed in an effort to summarize effectiveness and costs of remedial actions. Several conclusions are made based on this review:

(1) Hazardous waste sites involving groundwater contamination generally require more time and effort to characterize and remediate than sites not involving groundwater contamination.

(2) Good pre-remedial site characterization is critical to both selection and implementation of remediation. Because of seasonal changes in groundwater. a minimum of one year should be devoted to monitoring and characterization before a remedy is selected. As the site complexity increases, this time will increase proportionately.

(3) In order to minimize costs, both site characterization and remediation should be performed in phases, such that later phases may be modified based on knowledge gained from earlier phases.

(4) As the scale of the observation increases, properties, such as permeability, tend to increase because more heterogeneities are encountered. Therefore, remediations based on core-scale observations, may underestimate groundwater flow rates.

(5) Site characterization and remediation tend to be costly at sites involving groundwater contamination, with clean up costs difficult to estimate accurately.

(6) Monitoring is critical for both site characterization and remediation. Long-term monitoring should be an integral part of any remedial action plan. In addition, it is important to monitor before, during and after remediation in

order to evaluate effectiveness. Groundwater elevation data, which is relatively inexpensive to obtain, can be particularly useful in the evaluation of remedial effectiveness.

(7) The effectiveness of various remediations varies from site to site, and depends in large part on the site characterization and analysis. Of particular importance at hazardous waste sites is the lack of good bedrock characterization prior to remediation. Apparent containment can be lost because of unexpected flow through the bedrock (in addition to some cases presented in this paper, for example, see Ozbilgin and Powers, 1984, concerning the site in Nashua, New Hampshire).

Mercer et al. (1987)

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Keely, J.F., M.D. Piwoni, and J.T. Wilson, 1986. Evolving concepts of subsurface contaminant transport, Jour. Water Pollution Control Federation (May), pp 349-357.

Mercer, J.W., C.R. Faust, A.D. Truschel, and R.M. Cohen, 1987. Control of groundwater contamination: Case studies, Proceedings of Detection, Control, and Renovation of Contaminated Ground Water, EE Div/ASCE, pp 121-133.

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CHARACTERIZATION OF WATER MOVEMENT IN THE SUBSURFACE

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Herndon, Virginia

I.   DETERMINATION OF WATER MOVEMENT IN SATURATED POROUS MEDIA

A.   Data Pertinent to the Prediction of Groundwater Flow
1.   Physical framework
2.   Stresses on system
3.   Observable responses
4.   Other factors

B.   Review of Terminology
1.   Hydrologic cycle
2.   Water balance
3.   Aquifer
4.   Hydraulic head
5.   Hydraulic gradient
6.   Potentiometric surface
7.   Surface water features
8.   Flow net
9.   Groundwater flow
a.   recharge effects
b.   hydraulic conductivity effects
c.   advective transport
d.   surface water - groundwater interaction
e.   multiple aquifers
f.   pumping effects

C.   Monitoring Well Construction
1.   Well casing and screen material
2.   Multi-level monitoring well design
3.   Well development techniques

D.   Drilling Methods
1.   Auger
2.   Rotary
3.   Cable tool

E.   Measurement of Hydraulic Head
1.   Steel tape
2.   Electric probe
3.   Air line
4.   Pressure transducer
5.   Acoustic sounder
6.   Tensiometry
7.   Electrical resistivity
8.   Thermocouple psychrometry
9.   Thermal diffusivity
10. Well placement
11. Frequency of measurement

F   Measurement of Storage Properties
1.   Pumping test
2.   Slug test
3.   Water balance
4.   Laboratory

G.   Measurement of Hydraulic Conductivity
1.   Slug test
2.   Permeameter
3.   Pumping test
a.   Theis solution
b.   Jacob method
c.   recovery
d.   Hantush solution
e.   boundaries

Dr. James W. Mercer

H.   Measurement of Spatial Variability
1.   Piezometer slug tests
2.   Hydraulic conductivity from grain size
3.   Surface geophysics
a.   direct current resistivity
b.   electromagnetic induction
4.   Borehole geophysics
5.   Pumping tests
6.   Facies mapping
7.   Continuous core
8.   Borehole flowmeter
9.   Geo flowmeter

I.   Analysis of Data
1.   Mathematical modeling
2.   Geostatistical methods
3.   Time-series techniques
4.   Graphical methods
5.   Filtering/synthesizing techniques

J.   Groundwater Remediation
1.   Hydraulic containment
2.   Physical containment
3.   Innovative technologies

II. DETERMINATION OF WATER MOVEMENT IN THE VADOSE ZONE

A.   Data Pertinent to the Prediction of Vadose Zone Flow
1.   Soil characteristics
2.   Soil chemistry characteristics
3.   Vadose zone characteristics

B.   Soil Characteristics
1.   Soil particle sizes
a.   mechanical-analysis method (sieve)
b.   hydrometer
c.   settling tube
2.   Soil texture
a.   soil cores
b.   test pits
3.   Mineralogical composition
4.   Organic matter
5.   Density
a.   particle density
b.   bulk density
6.   Soil-water consistency (Atterberg limits)
a.   liquid limit
b.   plastic limit
c.   plasticity index
7.   Shrinkage and expansion of soils
8.   Soil compaction
9.   Elasticity and compressibility
10. Temperature

C.   Review of Terminology
1.   Capillary rise
2.   Capillary fringe
3.   Pressure head
4.   Moisture content
5.   Water table
6.   Perched water
7.   Infiltration
8.   Recharge
9.   Porosity
10. Relative permeability
11. Runoff
12. Evaporation

D. Measurement of Moisture Content
    1. Gravimetric
    2. Neutron scattering
    3. Gamma ray attenuation
    4. Electromagnetic
    5. Tensiometric
    6. Porous plate
    7. Vapor equilibration
    8. Osmotic
    9. Thermocouple psychrometer

E. Measurement of Unsaturated Hydraulic Conductivity
    1. Constant-head borehole infiltration
    2. Guelph permeameter
    3. Air-entry permeameter
    4. Instantaneous profile

    5. Crust-imposed steady flux
    6. Sprinkler-imposed steady flux
    7. Parameter identification
    8. Empirical equation
    9. Vertical permeability to air

F. Measurement of Moisture Movement
    1. Infiltration
    2. Vadose zone flux
    3. Vadose zone velocity

G. Vadose Zone Remediation
    1. Soil venting
    2. Fixation
    3. Excavation

III. DETERMINATION OF WATER MOVEMENT IN SATURATED FRACTURED MEDIA

A. Geometry
    1. Fracture trace analysis
    2. Surface geophysics
    3. Tracer (dye) tests

B. Flow Parameters
    1. Aquifer tests
    2. Slug tests
    3. Spatial variability

C. Discrete Fracture vs. Dual Porosity Concepts
    1. Matrix diffusion

D. Data Analysis

DETERMINATION OF WATER MOVEMENT IN SATURATED POROUS MEDIA

● Water Storage

● Water Movement

● Contaminant Storage

● Contaminant Movement

● Impacts on Remediation

DATA PERTINENT TO THE PREDICTION
OF GROUNDWATER FLOW

- **PHYSICAL FRAMEWORK**
  - Hydrogeologic map showing areal extent and boundaries of aquifer
  - Topographic map showing surface-water bodies
  - Water-table, bedrock-configuration, and saturated-thickness maps
  - Hydraulic conductivity map showing aquifer and boundaries
  - Hydraulic conductivity and specific storage map of confining bed
  - Map showing variation in storage coefficient of aquifer
  - Relation of stream and aquifer (hydraulic connection)

- **STRESSES ON SYSTEM**
  - Type and extent of recharge areas (irrigated areas, recharge basins, recharge wells, impoundments, spills, tank leaks, etc.)
  - Surface-water diversions
  - Groundwater pumpage (distributed in time and space)
  - Stream flow (distributed in time and space)
  - Precipitation and evapotranspiration

- **OBSERVABLE RESPONSES**
  - Water levels as a function of time and position

- **OTHER FACTORS**
  - Economic information about water supply
  - Legal and administrative rules
  - Environmental factors
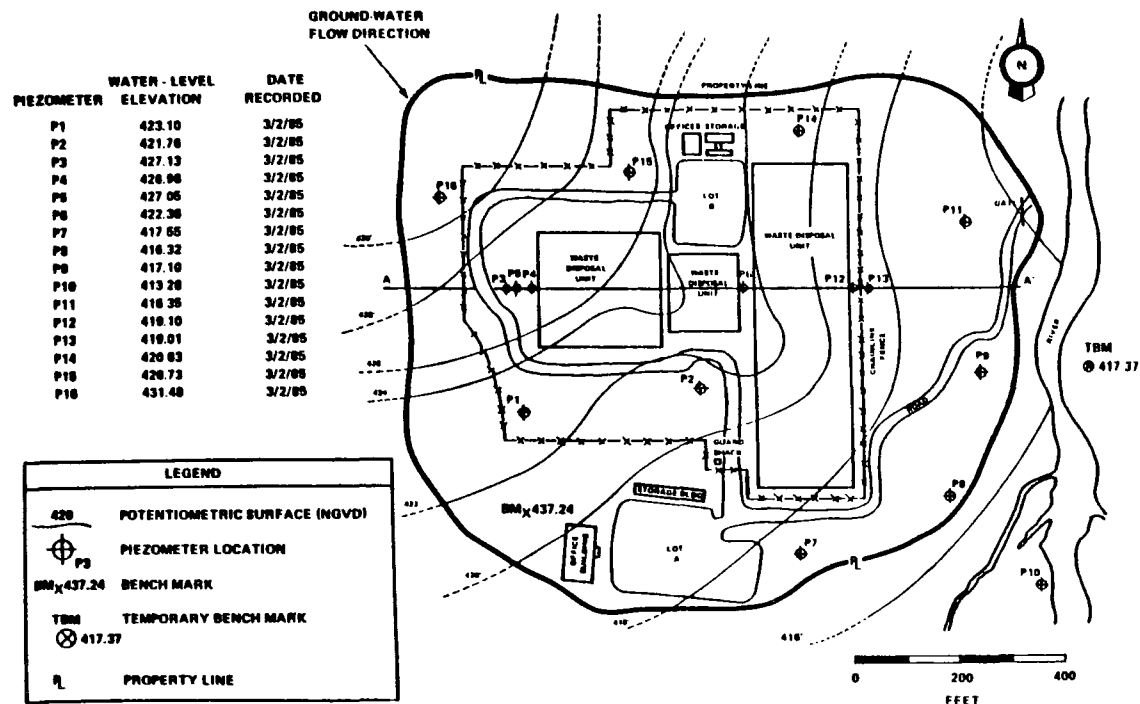 - Planned changes in water and land use
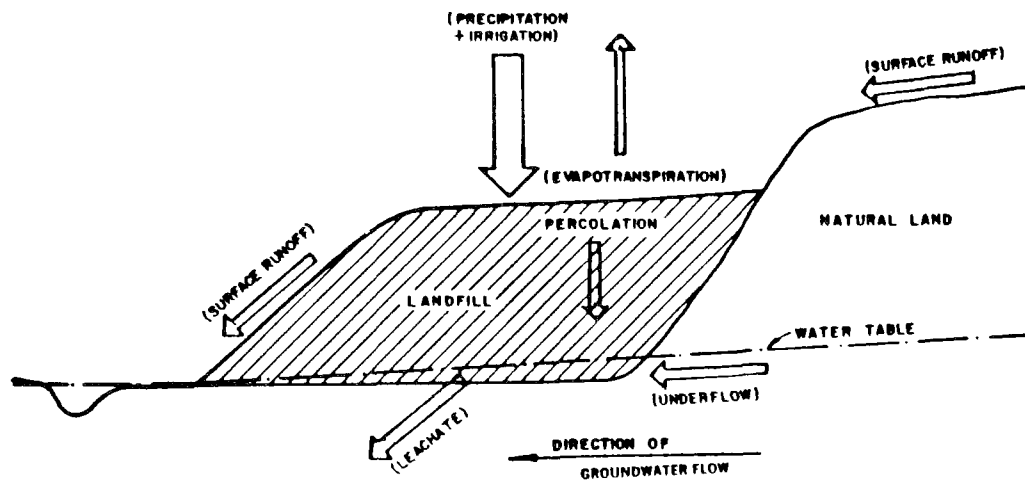
Simplified Landfill Water Balance
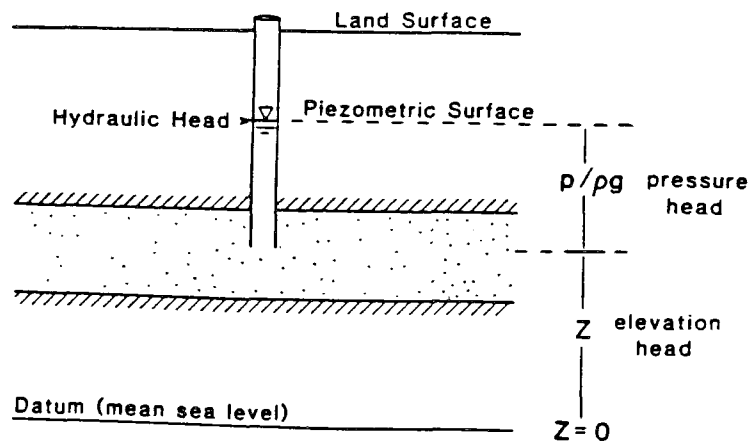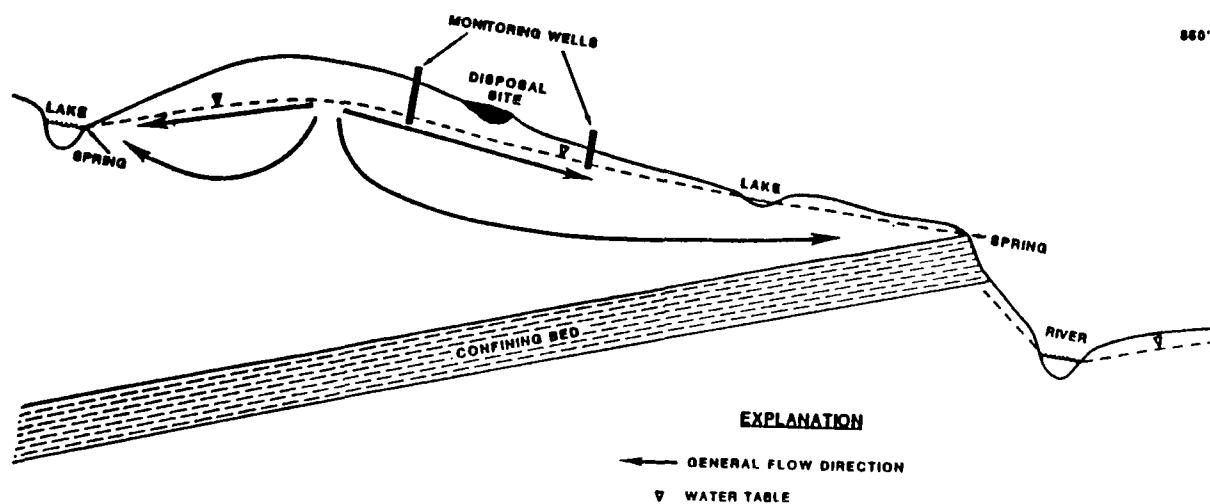

Components of hydraulic head (modified from Freeze and Cherry, GROUNDWATER, (c)1979, pp. 22. Englewood Cliffs, New Jersey.)

(A)

(B)

$$\frac{dh}{dl} = \frac{20}{200} = 0.10$$

(C)

(D)
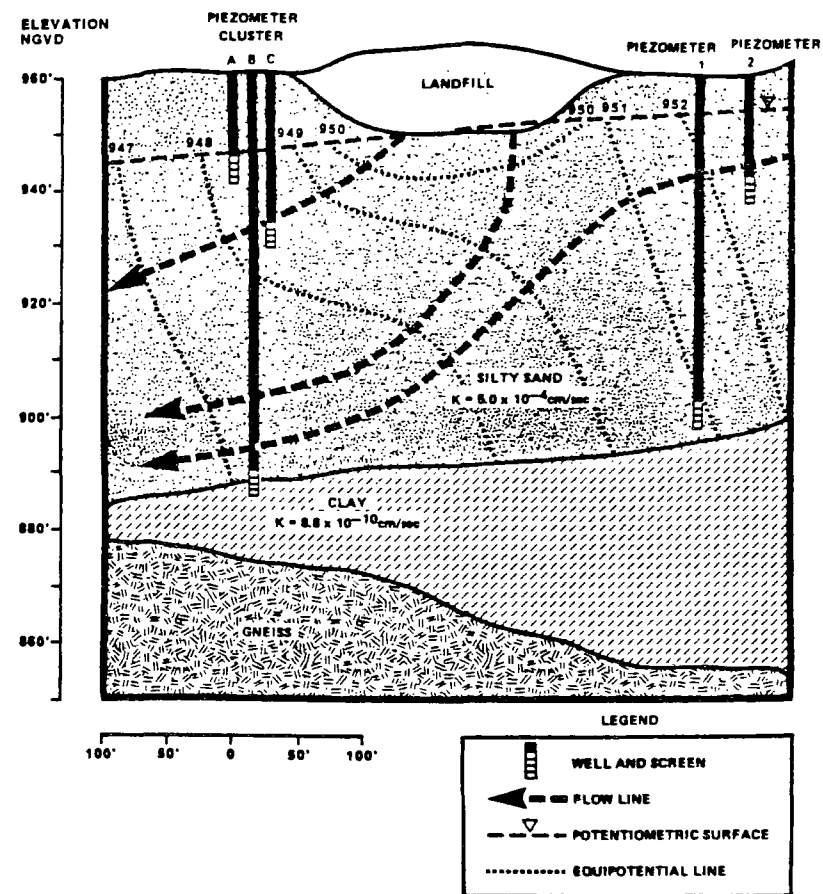
$$\frac{dh}{dl} = \frac{20}{50} = 0.40$$
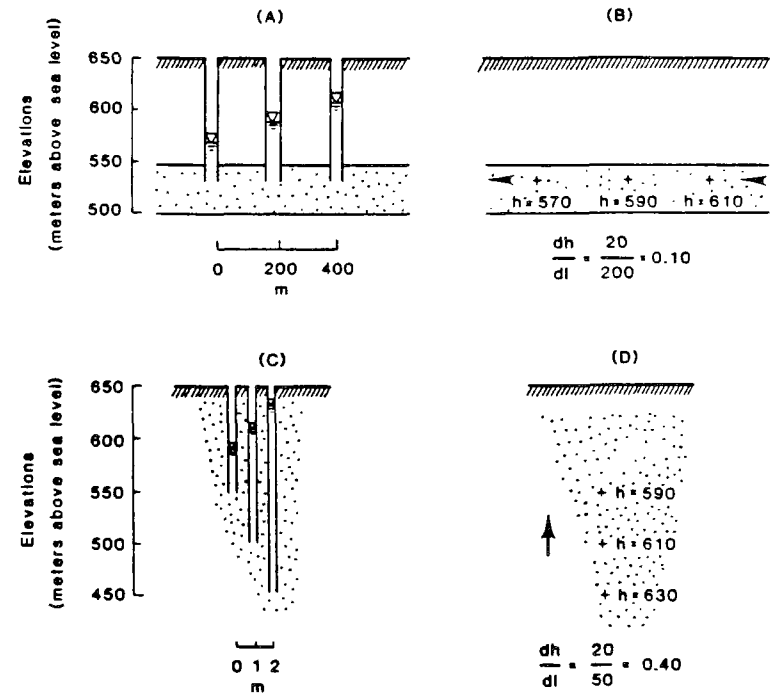
Determination of flow directions and hydraulic gradients from nested piezometers (from Freeze and Cherry, GROUNDWATER, (c)1979, pp. 24. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, New Jersey.)
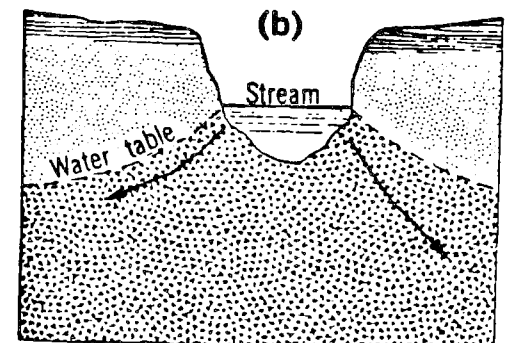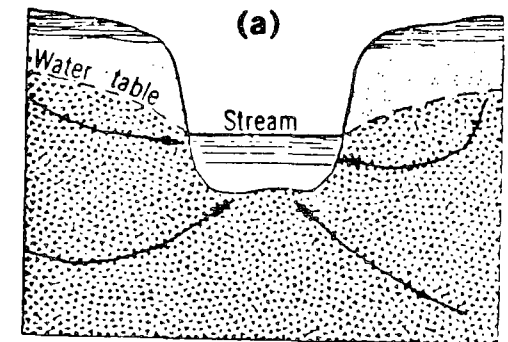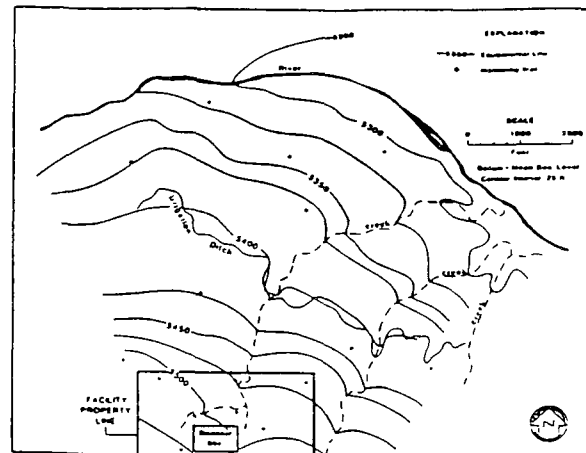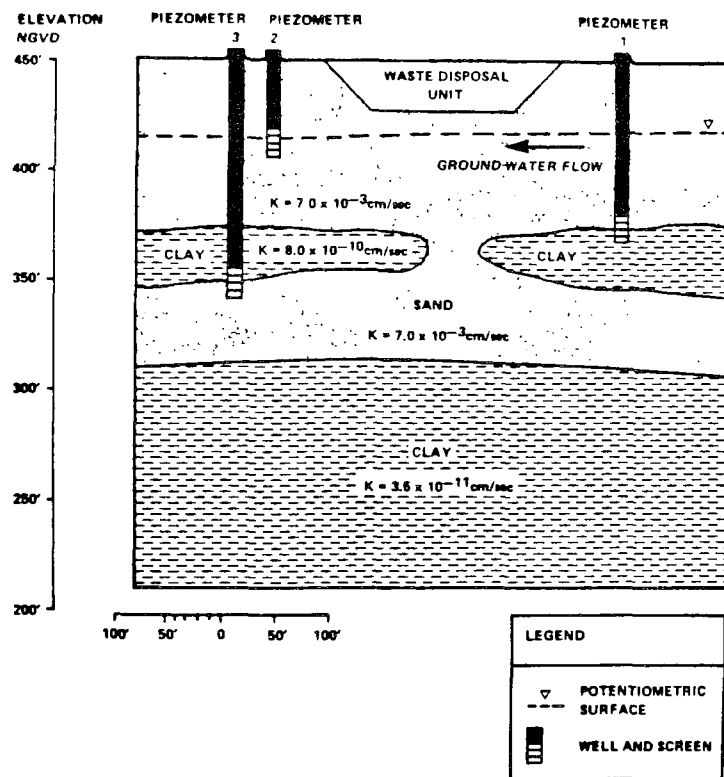
PIEZOMETER	WATER - LEVEL ELEVATION	DATE RECORDED
P1	423.10	3/2/85
P2	421.76	3/2/85
P3	427.13	3/2/85
P4	426.96	3/2/85
P5	427.05	3/2/85
P6	422.36	3/2/85
P7	417.55	3/2/85
P8	416.32	3/2/85
P9	417.10	3/2/85
P10	413.26	3/2/85
P11	416.35	3/2/85
P12	419.10	3/2/85
P13	419.01	3/2/85
P14	420.63	3/2/85
P15	420.73	3/2/85
P16	431.48	3/2/85

LEGEND

420 POTENTIOMETRIC SURFACE (NGVD)

⊕ P5 PIEZOMETER LOCATION

BM X 437.24 BENCH MARK

TBM ⊗ 417.37 TEMPORARY BENCH MARK

PL PROPERTY LINE

POTENTIOMETRIC SURFACE MAP

0   200   400

FEET

MONITORING WELLS

DISPOSAL SITE

LAKE

SPRING

LAKE

SPRING

RIVER

CONFINING BED

EXPLANATION

GENERAL FLOW DIRECTION

▽ WATER TABLE

ELEVATION NGVD

PIEZOMETER CLUSTER

A B C

LANDFILL

PIEZOMETER 1

PIEZOMETER 2

960'

940'

920'

900'

880'

860'

SILTY SAND
$K = 8.0 \times 10^{-4}$ cm/sec

CLAY
$K = 8.8 \times 10^{-10}$ cm/sec

GNEISS

LEGEND

100' 50' 0 50' 100'

WELL AND SCREEN

FLOW LINE

POTENTIOMETRIC SURFACE

EQUIPOTENTIAL LINE

AN EXAMPLE OF A FLOW NET DERIVED FROM PIEZOMETER DATA

Use of surface-water features to supplement hydraulic-head data from monitoring wells.

ELEVATION
NGVD

PIEZOMETER 3   PIEZOMETER 2   PIEZOMETER 1

WASTE DISPOSAL UNIT

GROUND-WATER FLOW

$K = 7.0 \times 10^{-3}$ cm/sec

CLAY $K = 8.0 \times 10^{-10}$ cm/sec   CLAY

SAND

$K = 7.0 \times 10^{-3}$ cm/sec

CLAY

$K = 3.6 \times 10^{-11}$ cm/sec

100' 50' 0 50' 100'

LEGEND

▽ POTENTIOMETRIC SURFACE

▨ WELL AND SCREEN

EXAMPLE OF HYDRAULIC COMMUNICATION BETWEEN WATER - BEARING UNITS

Water-table (piezometric) map and associated contaminant isocons.

(a)

Water table

Stream

Effluent streams gain water because the water table is above the stream level

(b)

Water table

Stream

Influent streams lose water to the aquifer because the stream level is higher than the water table.

Effluent and Influent Streams
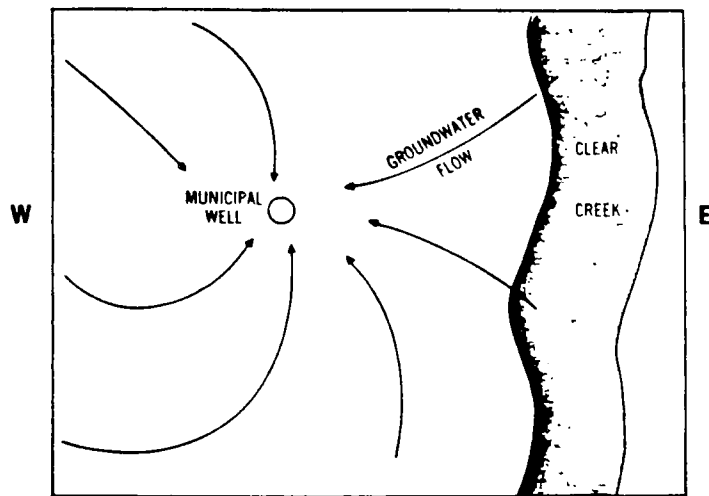
MAP VIEW
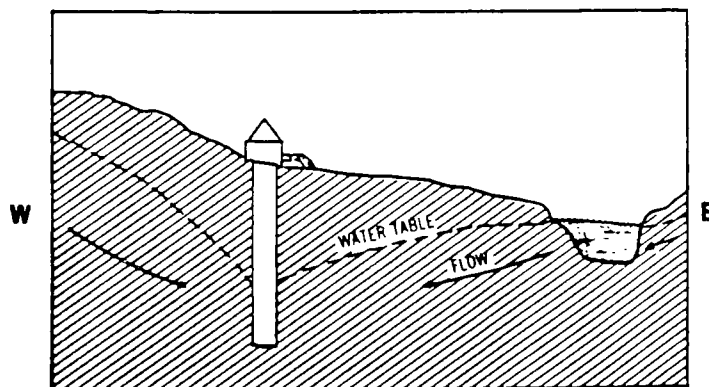
VERTICAL CROSS SECTION

Groundwater Flow Affected by a Pumped Well
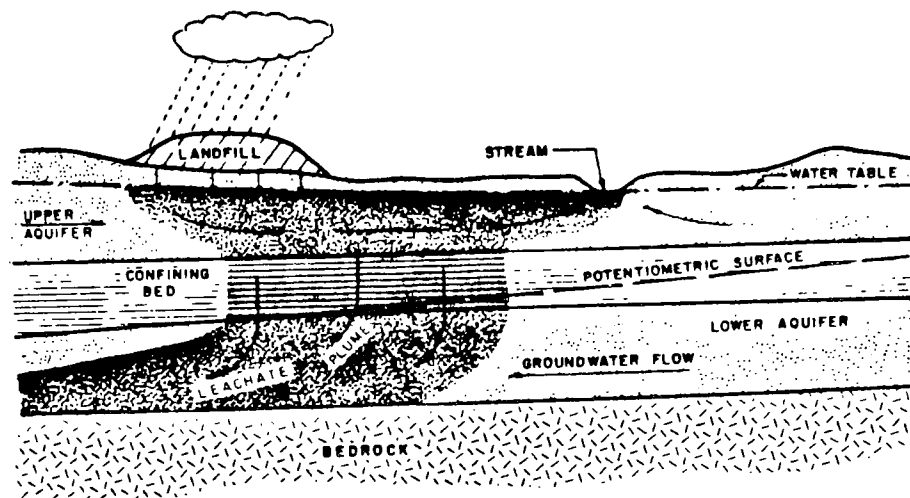
Two-Aquifer System With Opposite Flow Directions
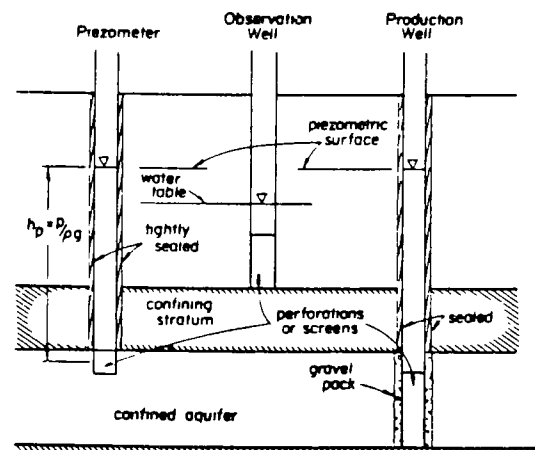
Common facilities for observing water levels in aquifers (from McWhorten and Sunada, 1977).

A typical monitoring-well design.

WELL CASING AND SCREEN MATERIAL
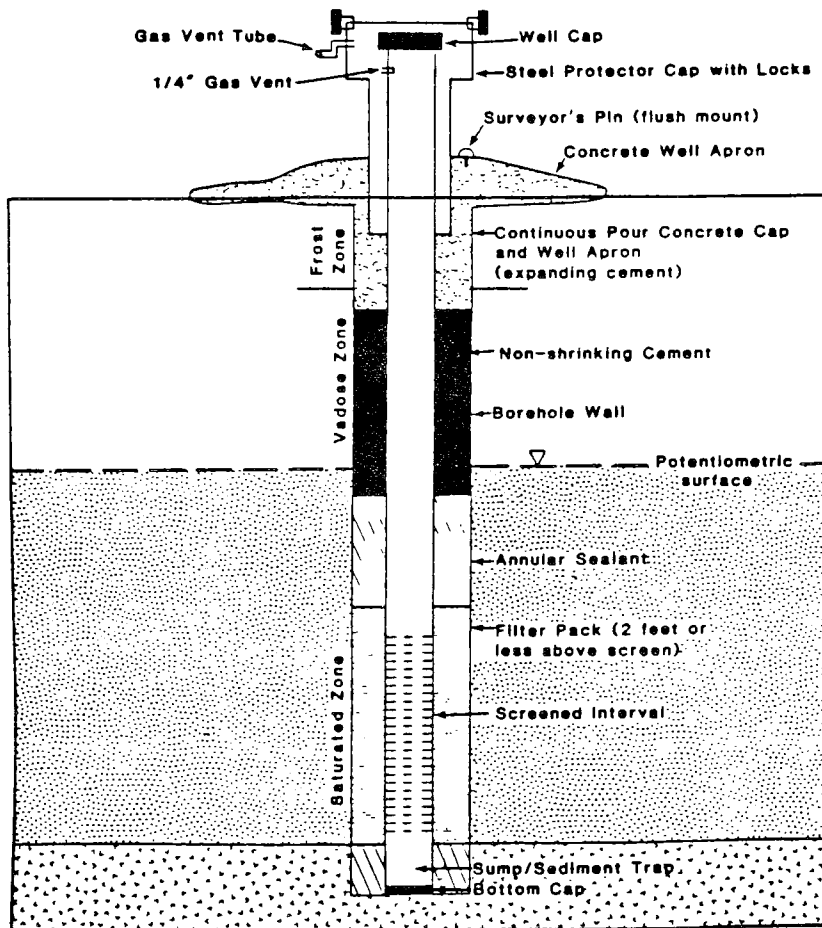
- FLUORINATED ETHYLENE PROPYLENE (FEP)

- POLYTETRAFLUORETHYLENE (PTFE) OR TEFLON

- POLYVINYLCHLORIDE (PVC)

- ACRYLONITRILE BUTADIENE STYRENE (ABS)

- POLYETHYLENE

- POLYPROPYLENE

- KYNAR

- STAINLESS STEEL

- CAST IRON & LOW-CARBON STEEL

- GALVANIZED STEEL

Well casing and screen material   advantages and disadvantages in monitoring wells.

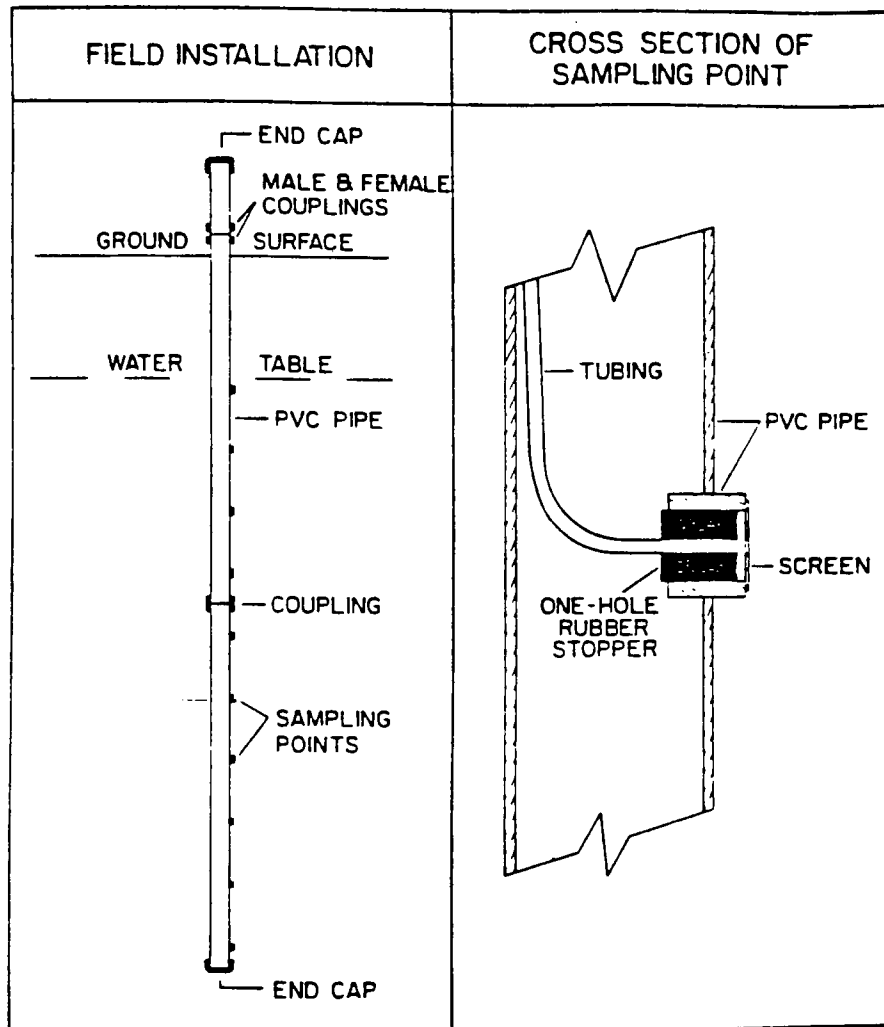| Type	Advantages	Disadvantages
Fluorinated Ethylene Propylene (FEP)	• Good chemical resistance to volatile organics • Good chemical resistance to corrosive environments	• Lower strength than steel and iron
Polytetrafluoroethylene (PTFE) or Teflon	• Lightweight • High-impact strength • Resistant to most chemicals	• Weaker than most plastic material
Polyvinylchloride (PVC)	• Lightweight • Resistant to weak alkalis, alcohols, aliphatic hydro-carbons and oils • Moderately resistant to strong acids and alkalis	• Weaker than steel and iron • More reactive than PTFE • Deteriorates when in contact with ketones, esters, and aromatic hydrocarbons
Acrylonitrile Butadiene Styrene (ABS)	• Lightweight	• Low strength • Less heat resistant than PVC • Lower strength than steel and iron • Not commonly available
Polyethylene	• Lightweight	• Low strength • More reactive than PTFE, but less reactive than PVC • Not commonly available
Polypropylene	• Lightweight • Resistant to mineral acids • Moderately resistant to alkalis, alcohols, ketones and esters	• Low strength • Deteriorates when in contact with oxidizing acids, aliphatic hydro-carbons, and aromatic hydrocarbons • More reactive than PTFE, but less reactive than PVC • Not commonly available
Kynar	• High strength • Resistant to most chemicals and solvents	• Poor chemical resistance to ketones, acetone • Not commonly available
Stainless Steel	• High strength • Good chemical resistance to volatile organics	• May be a source of chromium in low pH environments • May catalyze some organic reactions
Cast Iron & Low-Carbon Steel	• High strength	• Rusts easily, providing highly sorptive surface for many metals • Deteriorates in corrosive environments
Galvanized Steel	• High strength	• May be a source of zinc • If coating is scratched, will rust, providing a highly sorptive surface for many metals

MULTI-LEVEL MONITOR WELL DESIGN

- **MULTIPLE-PORT SAMPLER**

- **NESTED SAMPLER/SINGLE BOREHOLE**

- **NESTED SAMPLER/MULTIPLE BOREHOLES**
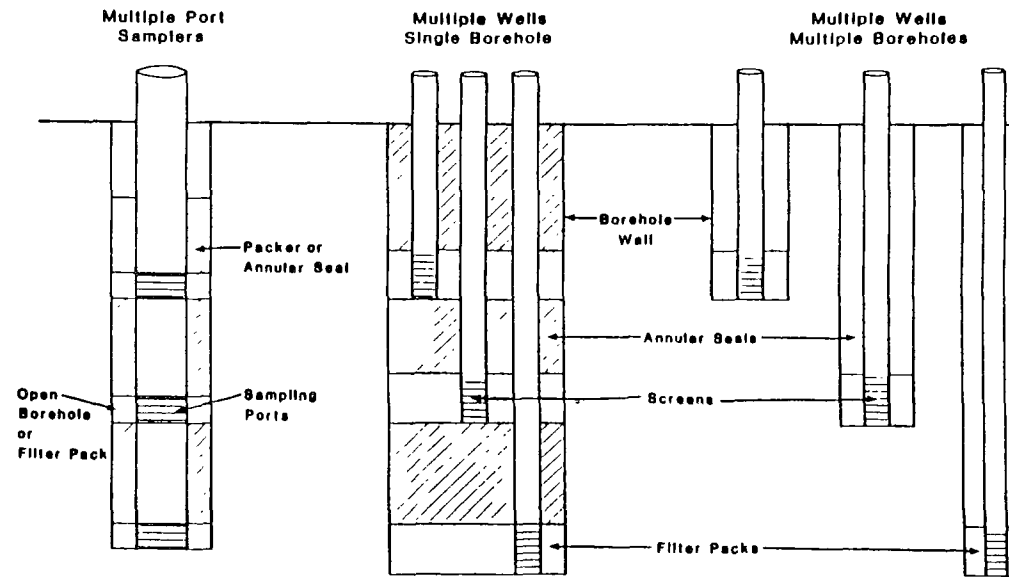
A conceptual comparison of three multi-level sampling designs.

Multi-level monitoring well design - advantages and disadvantages.

Type	Advantages	Disadvantages
Multiple-Port Sampler	• Large number of sampling zones per borehole	• Potential for cross contamination among ports
	• Smaller volume of water required for purging than #2 and #3	• Potential for sampling ports becoming plugged
	• Lower drilling costs than #3	• Special sampling tools required
Nested Sampler/ Single Borehole	• Lower drilling costs than #3	• Potential for cross contamination among screen intervals
	• Low potential for screens becoming plugged	• Number of sampling intervals limited to three or four
		• Larger volume of water required for purging than #1 or #3
		• Higher installation costs
Nested Sampler/ Multiple Boreholes	• Potential for cross-contamination minimized	• Higher drilling costs
	• Volume of water required for purging smaller than #2	
	• Low installation costs	
	• Low potential for screens becoming plugged	

FIELD INSTALLATION	CROSS SECTION OF SAMPLING POINT

END CAP

MALE & FEMALE COUPLINGS

GROUND SURFACE

WATER TABLE

PVC PIPE

COUPLING

SAMPLING POINTS

END CAP

TUBING

PVC PIPE

SCREEN

ONE-HOLE RUBBER STOPPER

Multi-level sampler (Cherry et al., 1981).

WELL DEVELOPMENT TECHNIQUES

- OVERPUMPING

- BACKWASHING

- MECHANICAL SURGING

- HIGH VELOCITY JETTING

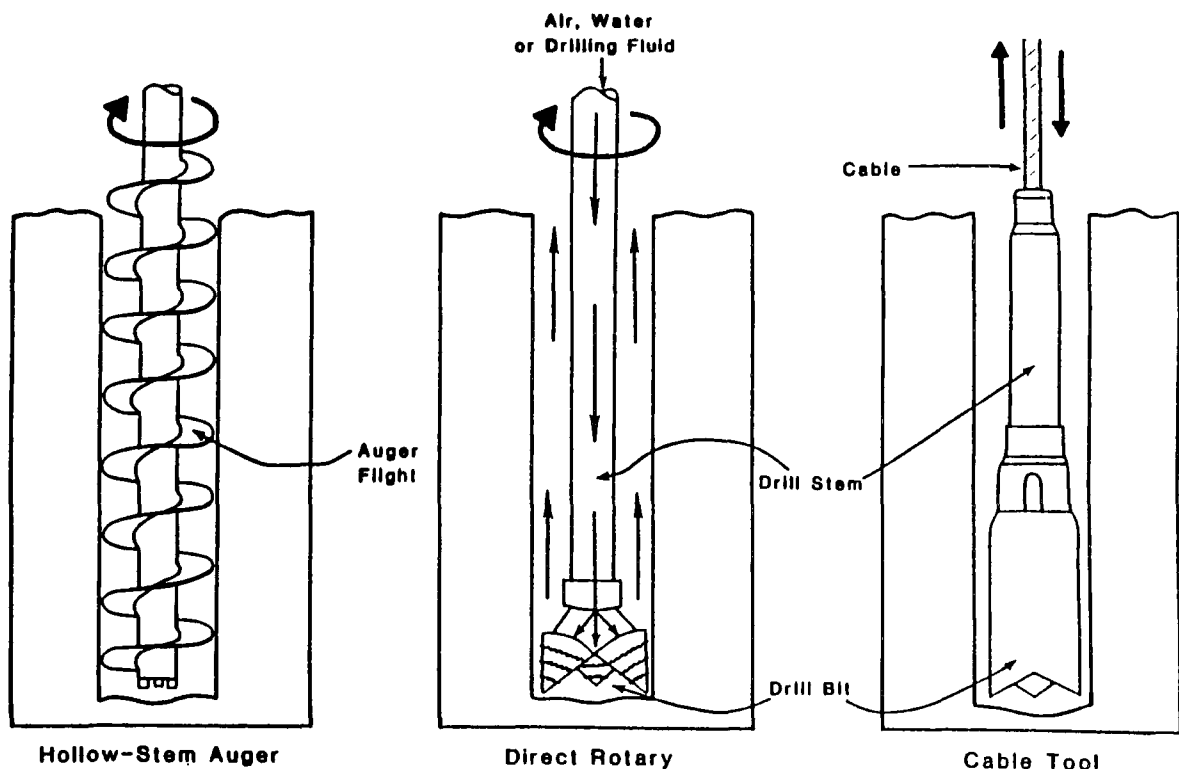Well development techniques - advantages and disadvantages.

Type	Advantages	Disadvantages
Overpumping	• Minimal time and effort required	• Does not effectively remove fine-grained sediments
	• No new fluids introduced	• Can leave the lower portion of large screen intervals undeveloped
	• Remove fluids introduced during drilling	• Can result in a large volume of water to be contained and disposed
Backwashing	• Effectively rearranges filter pack	• Tends to push fine-grained sediments into filter pack
	• Breaks down bridging in filter pack	• Potential for air entrapment if air is used
	• No new fluids introduced	• Unless combined with pumping or bailing, does not remove drilling fluids
Mechanical Surging	• Effectively rearranges filter pack	• Tends to push fine-grained sediments into filter pack
	• Greater suction action and surging than backwashing	• Unless combined with pumping or bailing, does not remove drilling fluids
	• Breaks down bridging in filter pack	
	• No new fluids introduced	
High Velocity Jetting	• Effectively rearranges filter pack	• Foreign water and contaminants introduced
	• Breaks down bridging in filter pack	• Air blockage can develop with air jetting
	• Effectively removes the mud cake around screen	• Air can change water chemistry and biology (iron bacteria) near well
		• Unless combined with pumping or bailing, does not remove drilling fluids

DRILLING TECHNIQUES

- AUGER

- ROTARY

- CABLE TOOL

Auger, rotary and cable-tool drilling techniques   advantages and disadvantages for construction of monitoring wells.

| Type	Advantages	Disadvantages
Auger	• Minimal damage to aquifer • No drilling fluids required • Auger flights act as temporary casing, stabilizing hole for well construction • Good technique for unconsolidated deposits • Continuous core can be collected by wire-line method	• Cannot be used in consolidated deposits • Limited to wells less than 150 feet in depth • May have to abandon holes if boulders are encountered
Rotary	• Quick and efficient method • Excellent for large and small diameter holes • No depth limitations • Can be used in consolidated and unconsolidated deposits • Continuous core can be collected by wire-line method	• Requires drilling fluids which alter water chemistry • Results in a mud cake on the borehole wall, requiring additional well development, and potentially causing changes in chemistry • Loss of circulation can develop in fractured and high-permeability material • May have to abandon holes if boulders are encountered
Cable Tool	• No limitation on well depth • Limited amount of drilling fluid required • Can be used in both consolidated and unconsolidated deposits • Can be used in areas where lost circulation is a problem • Good lithologic control • Effective technique in boulder environments	• Limited rigs and experienced personnel available • Slow and inefficient • Difficult to collect core

Air, Water or Drilling Fluid

Cable

Auger Flight

Drill Stem

Drill Bit

Hollow-Stem Auger   Direct Rotary   Cable Tool

A conceptual comparison of the hollow-stem auger, the direct-rotary, and the cable-tool drilling methods.

METHODS TO MEASURE HYDRAULIC HEAD

- **STEEL TAPE**

- **ELECTRIC PROBE**

- **AIR LINE**

- **PRESSURE TRANSDUCER**

- **ACOUSTIC SOUNDER**

- **TENSIOMETRY**

- **ELECTRICAL RESISTIVITY**

- **THERMOCOUPLE PSYCHROMETRY**

- **THERMAL DIFFUSIVITY**

Method	Application	Reference
Steel Tape	Saturated zone. Most precise method. Noncontinuous measurements. Slow.	Garber and Koopman (1968)
Electric Probe	Saturated zone. Frequent measurements possible. Simple to use. Adequate precision.	Driscoll (1986)
Air Line	Saturated zone. Continuous measurements. Useful for pumping tests. Limited accuracy.	Driscoll (1986)
Pressure Transducer	Saturated or unsaturated zone. Continuous or frequent measurements. Rapid response to changing pressure. Permanent record. Expensive.	Garbar and Koopman (1968)
Acoustic Sounder	Saturated zone. Fast; permanent record. Imprecise.	Davis and DeWiest (1966)
Tensiometry	Saturated or unsaturated zone. Laboratory or field method. Useful range is 0 to 0.85 bars capillary pressure. Direct measurement. A widely used method.	Cassel and Klute (1986); Stannard (1986)
Electrical Resistivity	Unsaturated zone. Laboratory or field method. Useful range is 0 to 15 bars capillary pressure. Indirect measurement. Prone to variable and erratic readings.	Campbell and Gee (1986); Rehm et al. (1987)
Thermocouple Psychrometry	Unsaturated zone. Laboratory or field method. Useful range 10 to 70 bars capillary pressure. Interference from dissolved solutes likely in calcium-rich waste.	Rawlins and Campbell (1986)
Thermal Diffusivity	Unsaturated zone. Laboratory or field method. Useful range 0 to 2.0 bars capillary pressure. Indirect measurement.	Phene and Beale (1976)
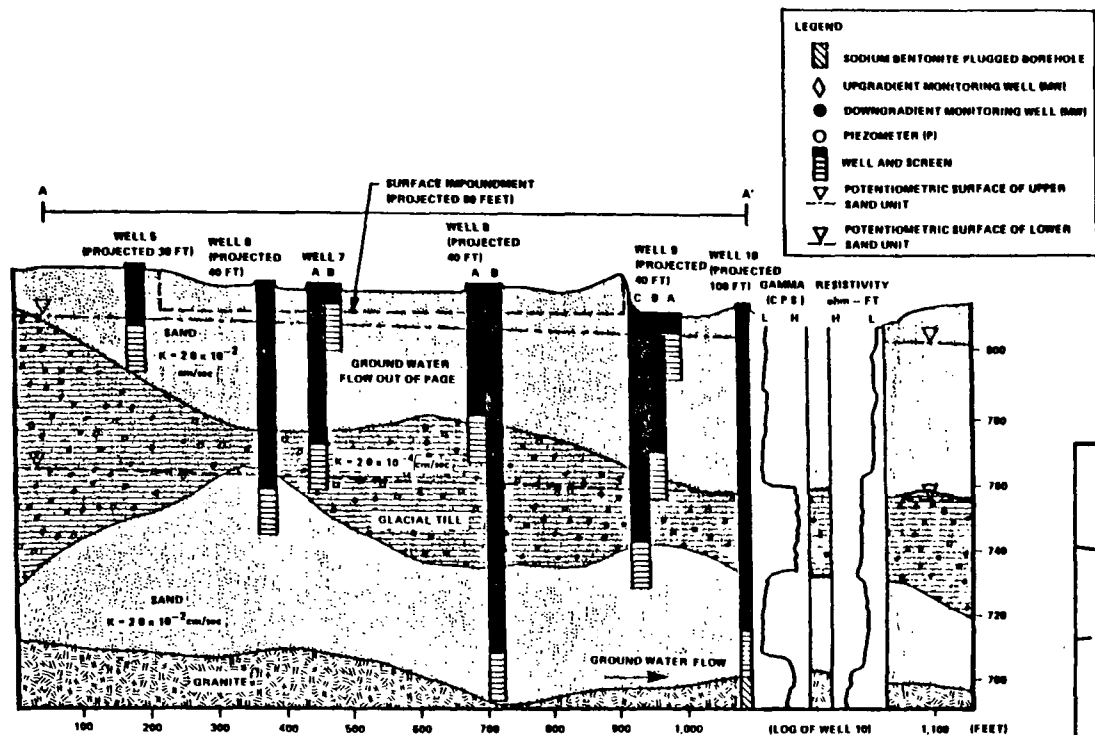
MONITORING WELL PLACEMENT AND SCREEN LENGTHS IN A GLACIAL TERRAIN
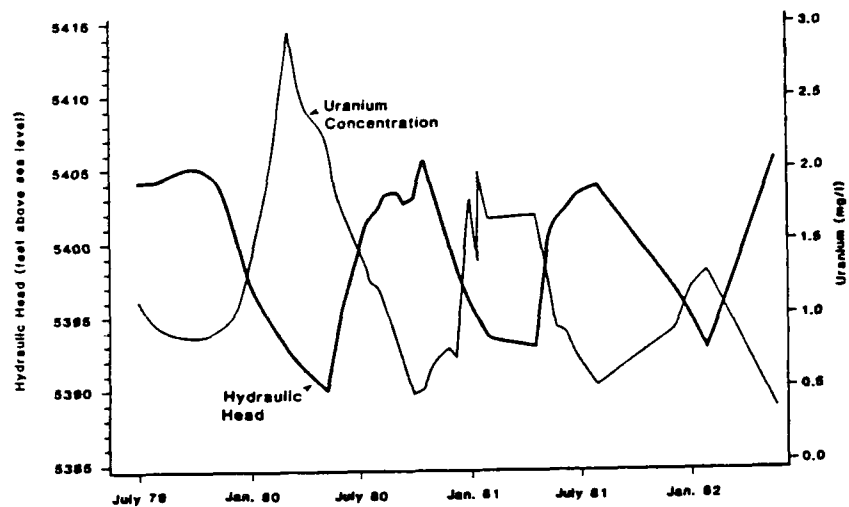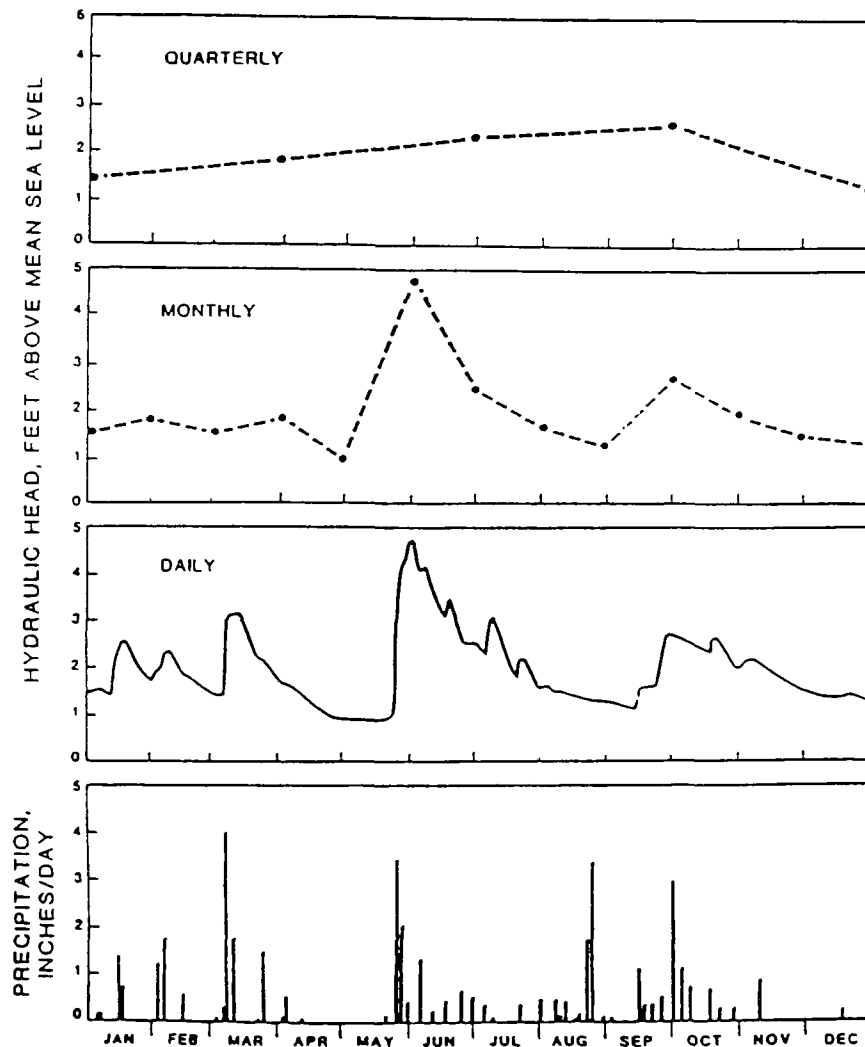

Hydrograph versus uranium concentrations (modified from Goode, et al., 1987).
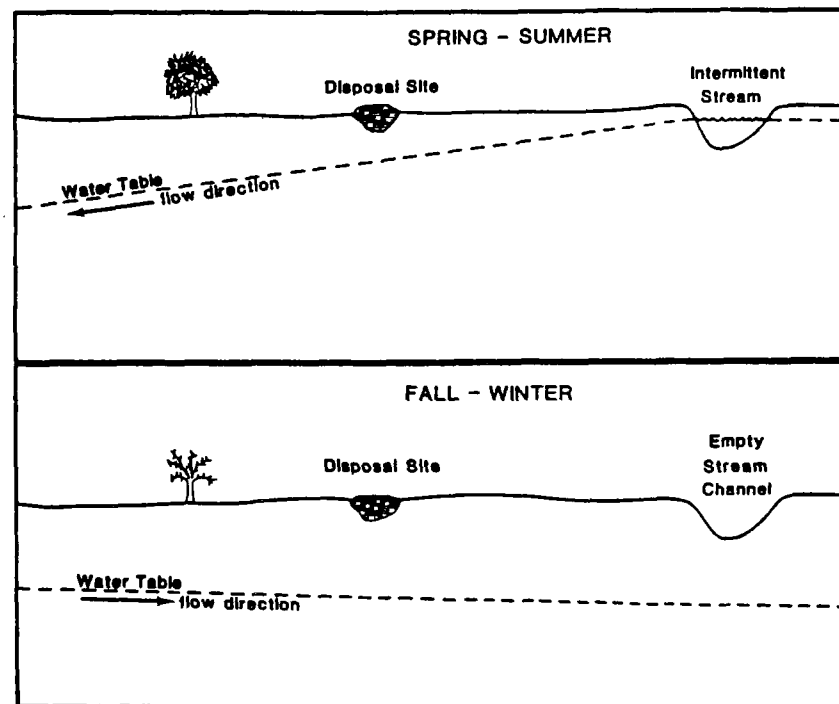
Effect of seasonal fluctuations in surface-water flow on groundwater-flow directions.

Daily measurements of precipitation versus daily, monthly, and quarterly measurements of hydraulic head (modified from Bearden, 1974).

METHODS TO MEASURE STORAGE PROPERTIES

- **PUMPING TEST**

- **SLUG TEST**

- **WATER BALANCE**

- **LABORATORY**

SUMMARY OF METHODS TO MEASURE STORAGE PROPERTIES

Method	Application	Reference
Pumping Test	Can be used to measure storage values for unconfined or confined aquifers. Multiple-well tests are more accurate than single-well tests. Tests a relatively large volume of the aquifer	Bureau of Reclamation (1977); Stallman (1971); Driscoll (1986); Lohman (1979)
Slug Test	Single-well tests for confined or unconfined aquifers. Test highly influenced by well construction and borehole conditions.	Hvorslev (1951); Bouwer and Rice (1976); Lohman (1972); Cooper et al. (1967)
Water-Balance	Measures specific yield only. Requires several observation wells around pumping well to accurately determine the cone of depression. Tests a relatively large volume of the aquifer.	Nwankwor et al. (1984); Neuman (1987)
Laboratory	Obtain a maximum long-term value. Fractures, macropores, and heterogeneities of geologic material may not be represented. Only specific yield can be determined.	Nwankwor et al. (1984)

METHODS TO MEASURE SATURATED HYDRAULIC-CONDUCTIVITY

- **SLUG TEST**

- **PUMPING TEST**

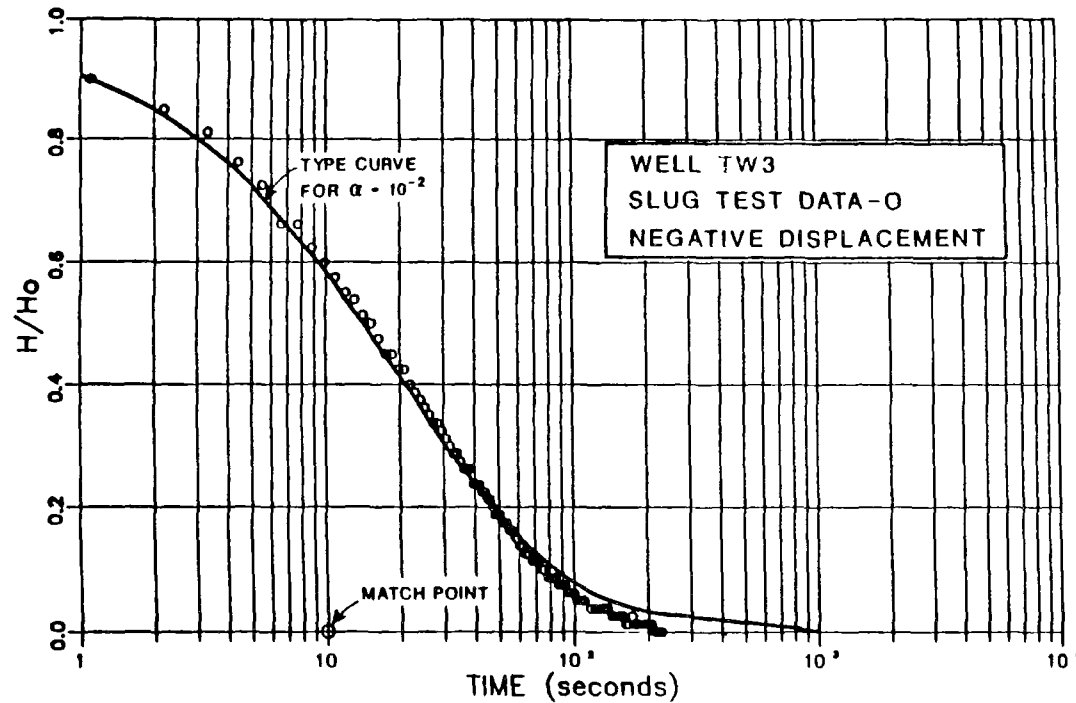- **STEADY-STATE PERMEAMETER**

- **FALLING-HEAD PERMEAMETER**

SUMMARY OF METHODS TO MEASURE SATURATED HYDRAULIC-CONDUCTIVITY
VALUES IN THE FIELD AND LABORATORY

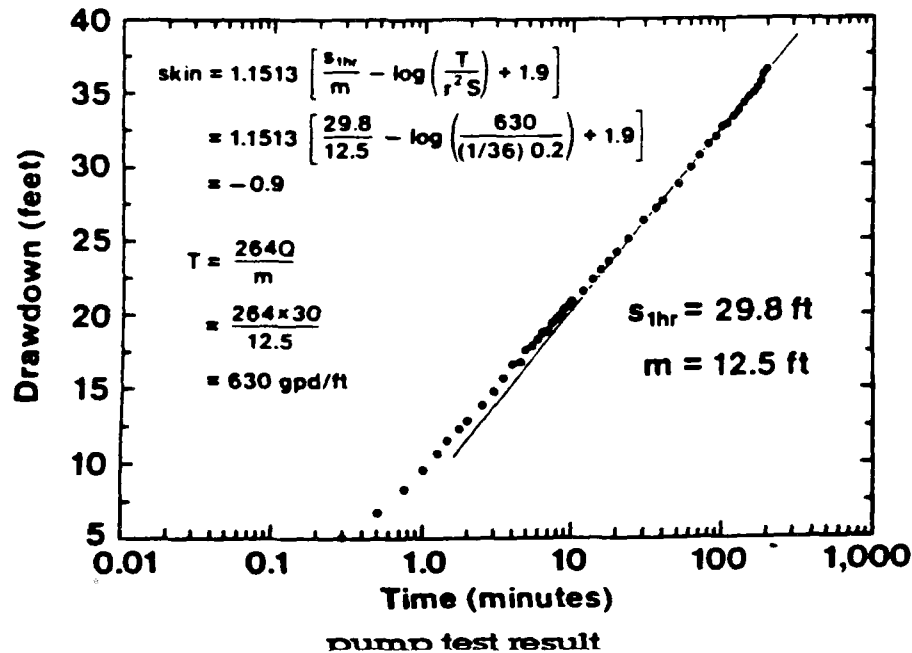| Method	Application	Reference
Slug Test	Confined aquifers with fully-penetrating wells screened along the entire aquifer thickness. Single-well test for wells not intended for sampling.	Hvorslev (1951); Bouwer and Rice (1976); Lohman (1972)
Pumping Test	Complex multiple-well test for confined or unconfined aquifers with fully pr partially penetrating wells. Used for wide range of aquifer permeabilities. Test wells can be used for sampling. Tests a relatively large volume of the aquifer.	Bureau of Reclamation (1977); Stallman (1971); Driscoll (1986); Lohman (1972)
Steady-State Permeameter	Laboratory method to determine sample hydraulic conductivity within a range from 1.0 cm/sec to 10^{-5} cm/sec.	Klute and Dirksen (1986)
Falling-Head Permeameter	Laboratory method to determine sample hydraulic conductivity within a range from 10^{-3} cm/sec to 10^{-9}	Klute and Dirksen (1986)
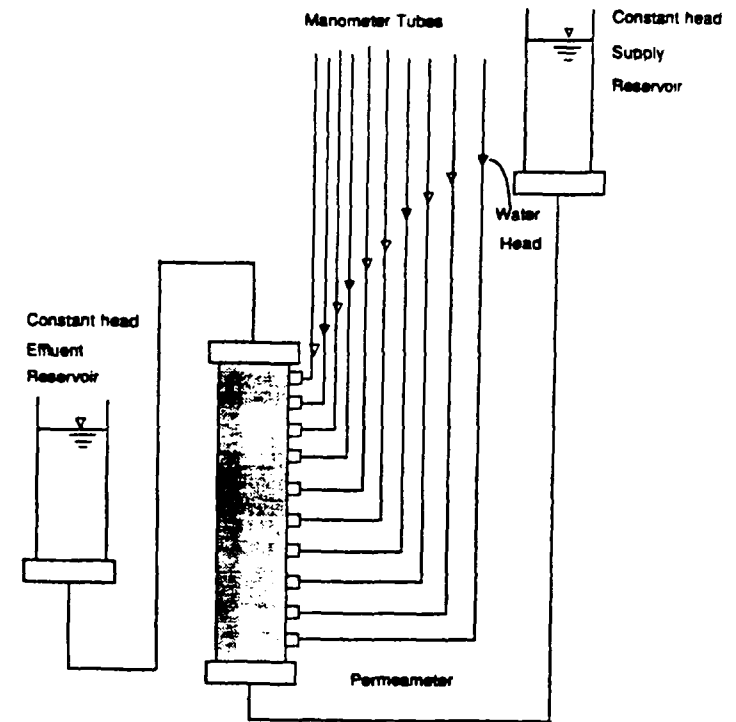
Schematic Diagram of Core Sampler Permeameter System

Source: Boggs et al., 1988

Graph 1 (top):

WELL TW3
SLUG TEST DATA-O
NEGATIVE DISPLACEMENT

TYPE CURVE FOR $\alpha = 10^{-2}$

MATCH POINT

Y-axis: H/H_o (1.0, 0.8, 0.6, 0.4, 0.2, 0.0)

X-axis: TIME (seconds) (1, 10, 10^2, 10^3, 10^4)

Theoretical type curve and observed data for the negative displacement slug test conducted in well TW3.

Graph 2 (bottom):

$$\text{skin} = 1.1513 \left[\frac{s_{1hr}}{m} - \log\left(\frac{T}{r^2 S}\right) + 1.9 \right]$$

$$= 1.1513 \left[\frac{29.8}{12.5} - \log\left(\frac{630}{(1/36)\,0.2}\right) + 1.9 \right]$$

$$= -0.9$$

$$T = \frac{264Q}{m}$$

$$= \frac{264 \times 30}{12.5}$$

$$= 630 \text{ gpd/ft}$$

$s_{1hr} = 29.8$ ft

$m = 12.5$ ft

Y-axis: Drawdown (feet) (5, 10, 15, 20, 25, 30, 35, 40)

X-axis: Time (minutes) (0.01, 0.1, 1.0, 10, 100, 1,000)

pump test result

METHODS TO MEASURE SPATIAL VARIABILITY

- PIEZOMETER SLUG TESTS

- HYDRAULIC CONDUCTIVITY FROM GRAIN SIZE

- SURFACE GEOPHYSICS

- BOREHOLE GEOPHYSICS

- LARGE-SCALE AQUIFER TESTS (PUMPING TESTS)

- GEOLOGICAL MAPPING OF SEDIMENTOLOGICAL FACIES

- CONTINUOUS CORE

- BOREHOLE FLOWMETER

Method	Application	Reference
Piezometer Slug Tests	Localized measurement, influenced by well disturbed zone. Efficient and easy to conduct.	Hvorslev (1951); Bouwer and Rice (1976); Lohman (1979)
Hydraulic Conductivity from Grain Size	Samples of aquifer material required. Empirical and poor accuracy, especially for silt and clay fractions.	Hazen (1892); Krumbein and Monk (1942); Masch and Denny (1966); Seiler (1973)
Surface Geophysics	Direct current resistivity, electromagnetic induction, streaming potential. Difficult to interpret and poor accuracy.	Zohdy et al. (1974); Sendlein and Yazicigal (1981); Yazicigal and Sendlein (1982)
Borehole Geophysics	Natural gamma, gamma-gamma density, single-point resistance, neutron. $K=f(\phi)$, accuracy?	Serra (1984); Wheatcraft et al. (1986); Wyllie (1963); Patten and Bennett (1963)
Large-Scale Aquifer Tests (Pumping Tests)	Provides bulk parameters over relatively large region.	Bureau of Reclamation (1977); Stallman (1971); Driscoll (1986); Lohman (1972)
Geological Mapping of Sedimentological Facies	Problems with extrapolation--geological sections above water table and away from site.	
Continuous Core	Split-spoon sampler, samples are disturbed. Grain size analysis, laboratory K.	Wolf (1988)
Borehole Flowmeter	Most promising. Equipment difficult to obtain.	Rehfeldt et al. (1988); Hufschmied (1983, 1986)

HYDRAULIC CONDUCTIVITY FROM GRAIN SIZE

$$K = \chi d^2$$

K = hydraulic conductivity (cm/sec)

d = representative grain diameter (cm or mm)

χ = proportionality factor (a function of the uniformity coefficient, U)

$$U = d_{60}/d_{10}$$

d_{60} = diameter such that 60% of the sample (by weight) is of diameter less than d_{60}

d_{10} = diameter such that 10% of the sample (by weight) is of diameter less than d_{10}
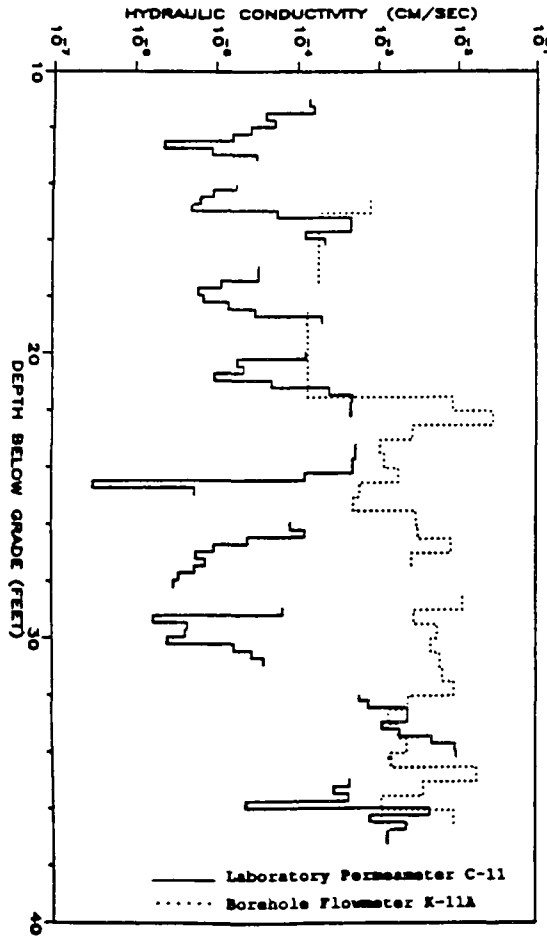
Seiler (1973):

$$K = \chi(U)\, d_{10}^2 \quad (cm) \quad 5 \le U \le 17$$
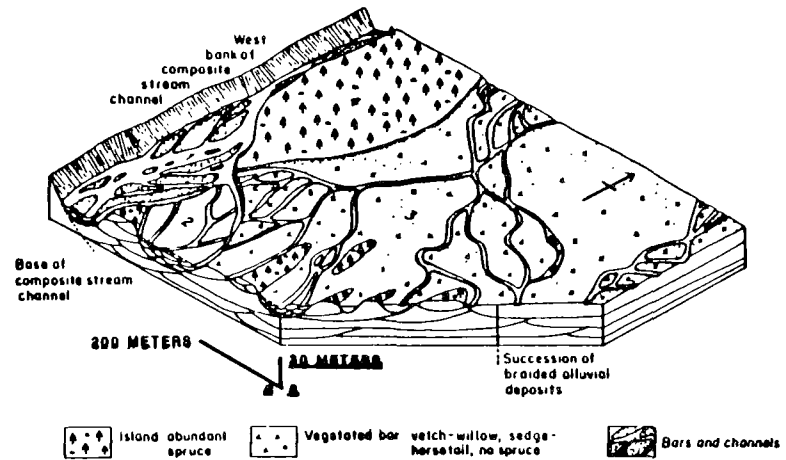
$$K = \chi(U)\, d_{25}^2 \quad (cm) \quad U \ge 17$$
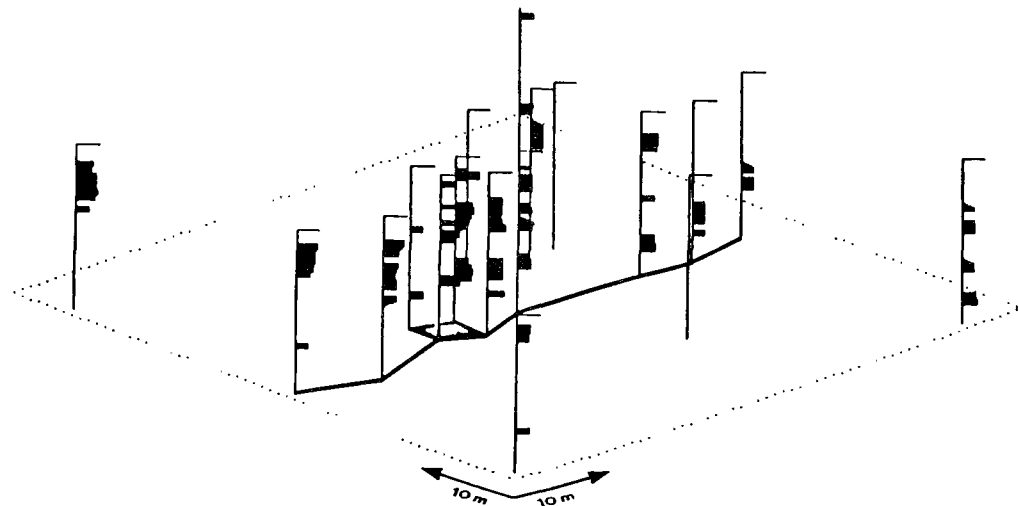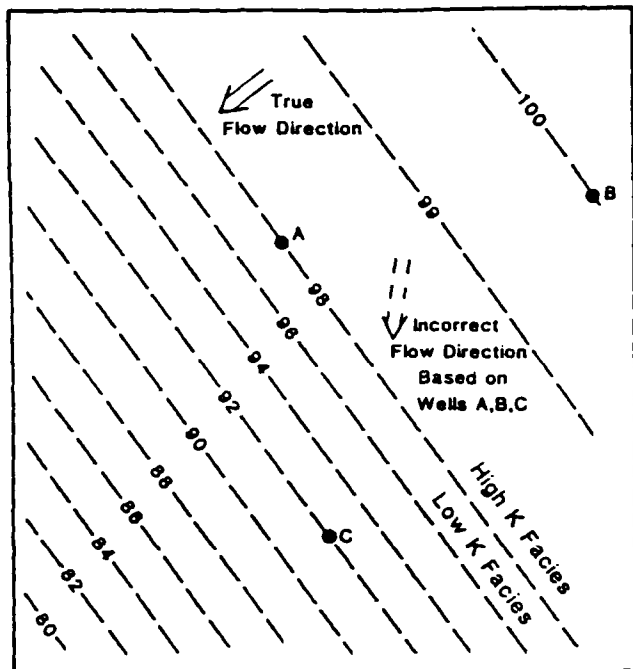
Hazen (1892):

$$K = d_{10}^2 \quad (mm) \quad U < 5$$

Comparison of the Hydraulic Conductivity Profiles from
Laboratory Measurements in Core Hole C-11 and Borehole
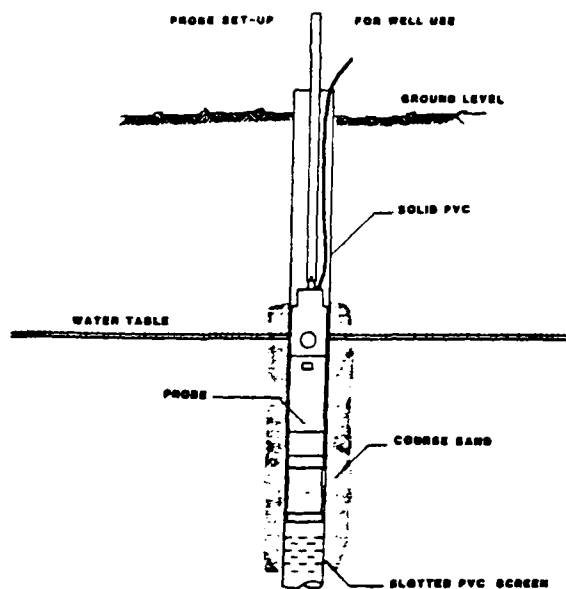Flowmeter Measurements in Well K-11A.

Three-dimensional geometry of braided stream deposits.

High hydraulic conductivity (>10⁻² cm/s) zones in borehole flowmeter test wells.

Miscalculation of groundwater-flow directions caused
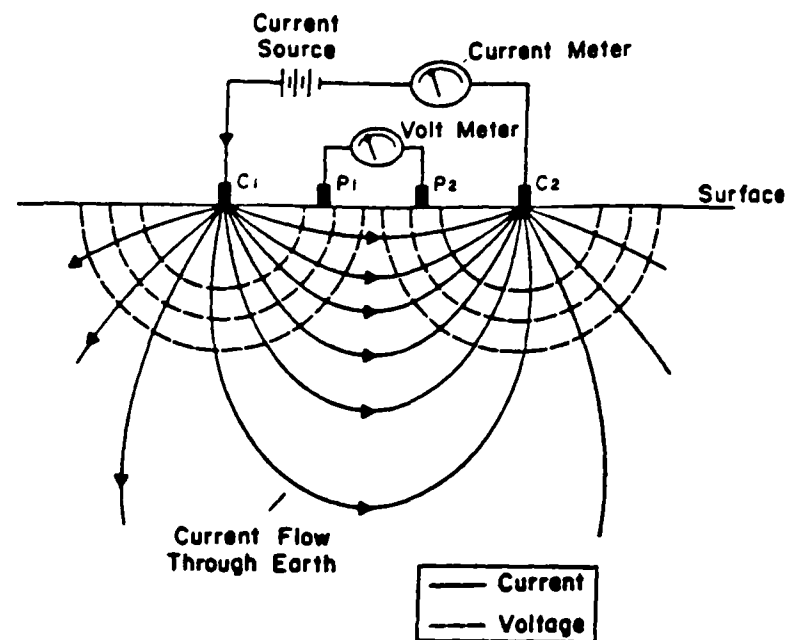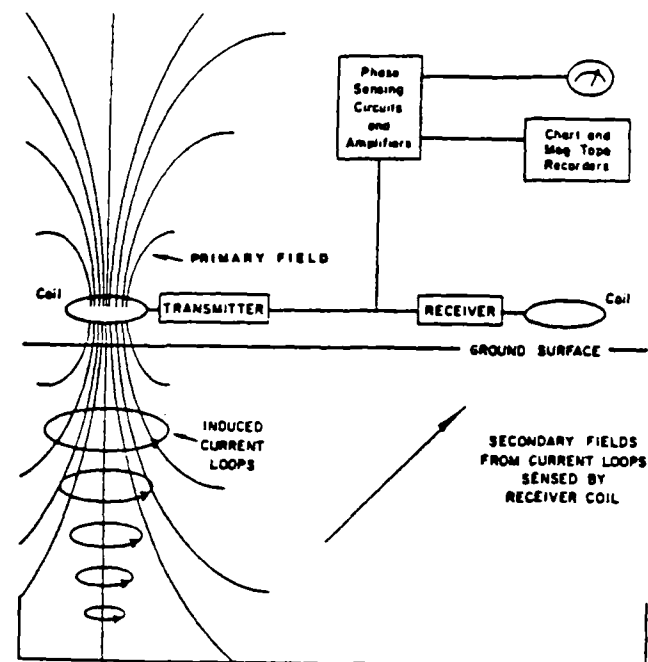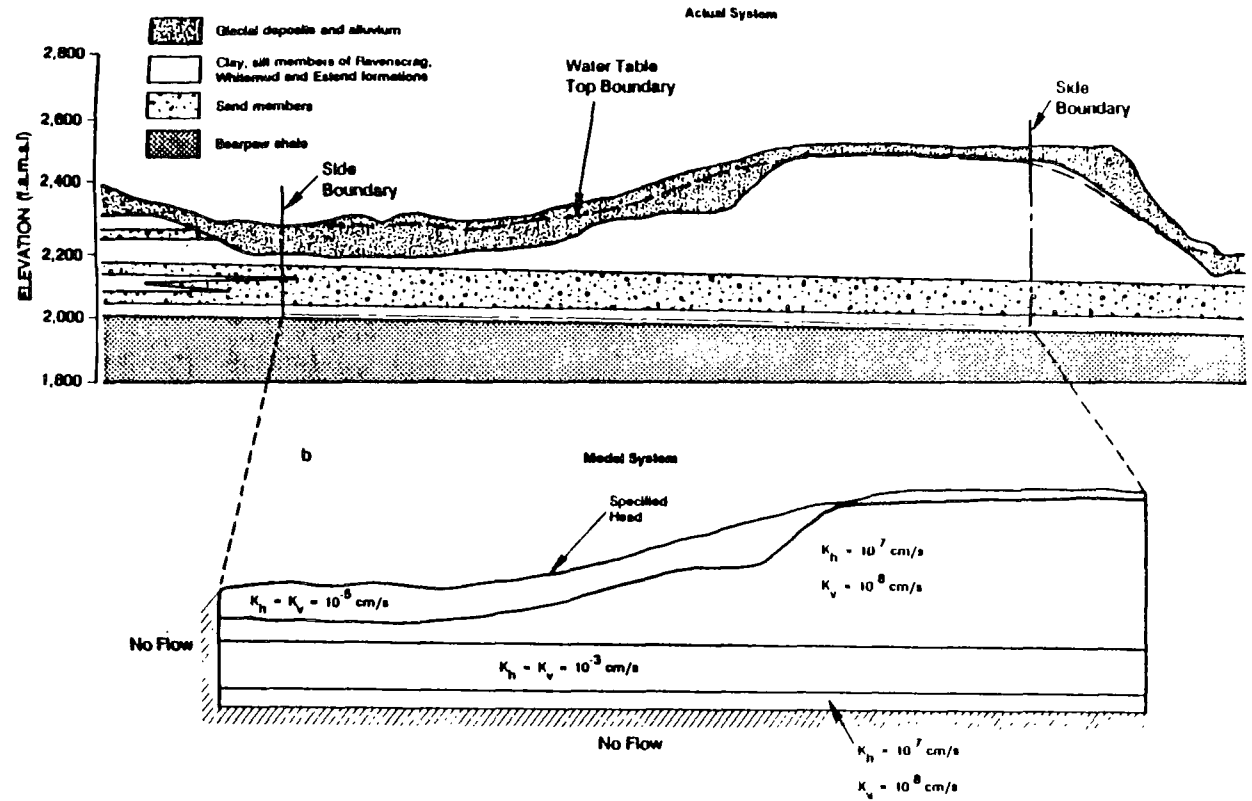by unrecognized heterogeneity

DIAGRAM SHOWING BASIC CONCEPT OF RESISTIVITY MEASUREMENT
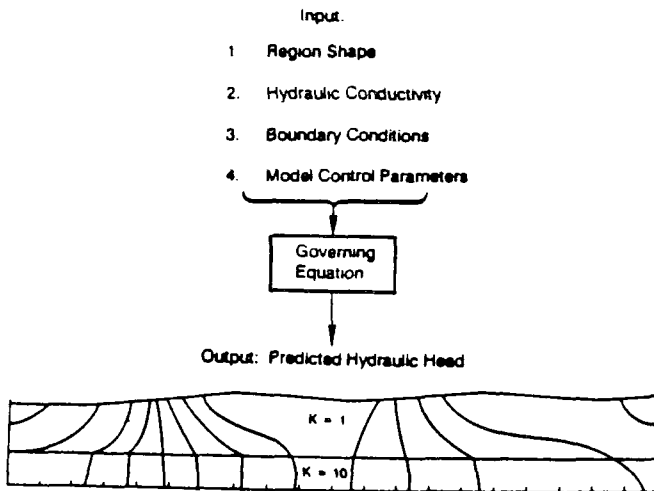

Downwell setup for the Geo Flowmeter

BLOCK DIAGRAM SHOWING EM PRINCIPLE OF OPERATIONS

ANALYSIS OF DATA

- **MATHEMATICAL MODELING**
- **GEOSTATISTICAL METHODS**
- **TIME-SERIES TECHNIQUES**
- **GRAPHICAL METHODS**
- **FILTERING/SYNTHESIZING TECHNIQUES**

Input.

1. Region Shape
2. Hydraulic Conductivity
3. Boundary Conditions
4. Model Control Parameters

Governing Equation

Output: Predicted Hydraulic Head

K = 1

K = 10

The components of a model: input data, a governing equation solved in the code, and the predicted distribution, which for this example is hydraulic head.

Actual System

2,800
2,600
2,400
2,200
2,000
1,800

ELEVATION (f.a.m.s.l.)

Glacial deposits and alluvium

Clay, silt members of Ravenscrag, Whitemud and Eatend formations

Sand members

Bearpaw shale

Water Table
Top Boundary

Side Boundary

Side Boundary

b   Model System

Specified Head

$K_h = 10^{-7}$ cm/s

$K_v = 10^{-8}$ cm/s

$K_h = K_v = 10^{-8}$ cm/s

No Flow

$K_h = K_v = 10^{-3}$ cm/s

No Flow

$K_h = 10^{-7}$ cm/s
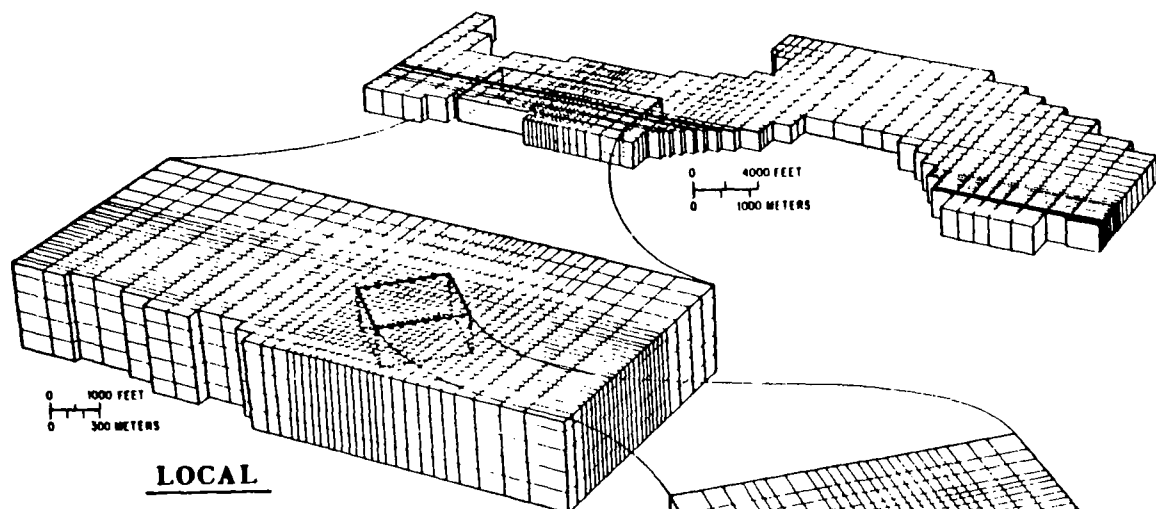
$K_v = 10^{-8}$ cm/s

An example of how (a) a "real" system is represented by (b) a model system, which is defined by a region shape, boundary conditions, and hydraulic parameters. The example section comes from Freeze (1969a).
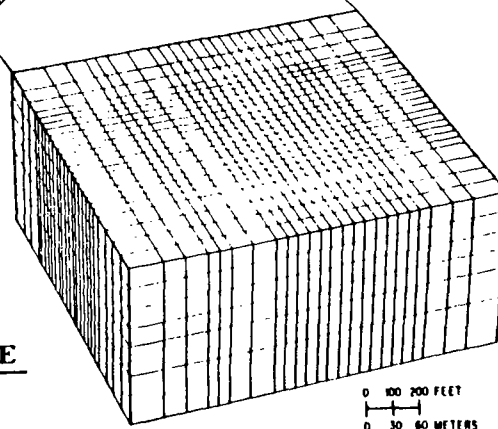
REGIONAL

REGIONAL

0   4000 FEET
0   1000 METERS

LOCAL

0   1000 FEET
0   300 METERS

SITE

0   100   200 FEET
0   30   60 METERS

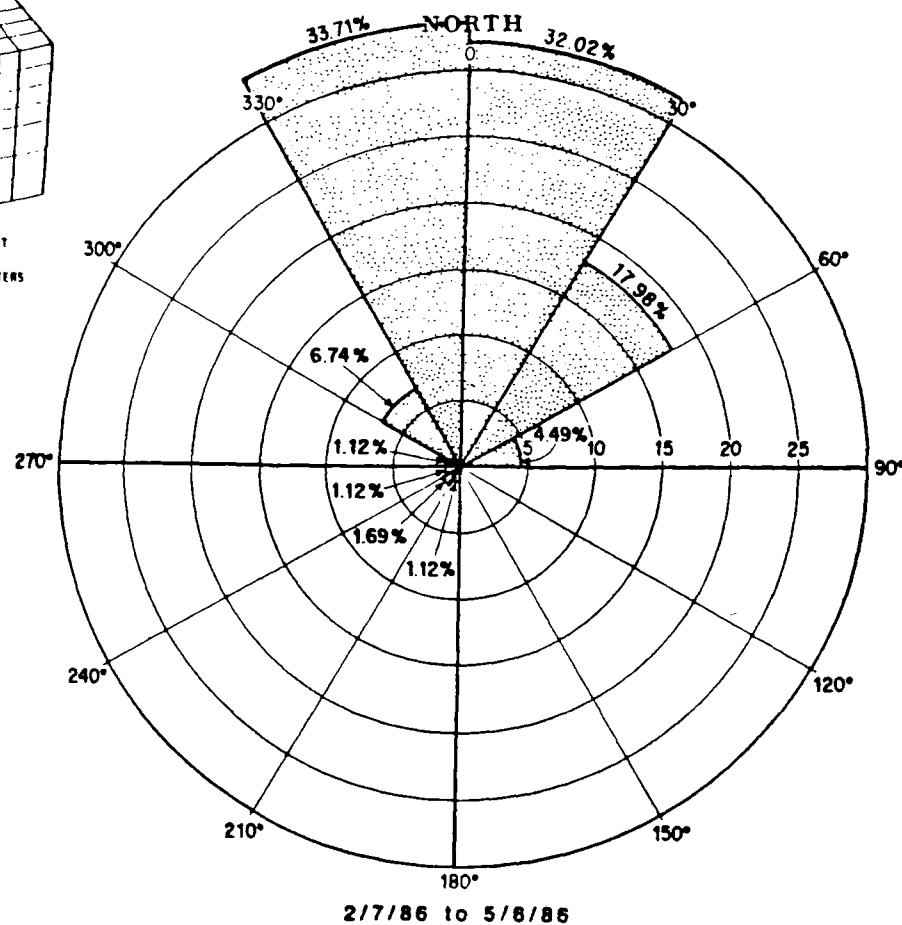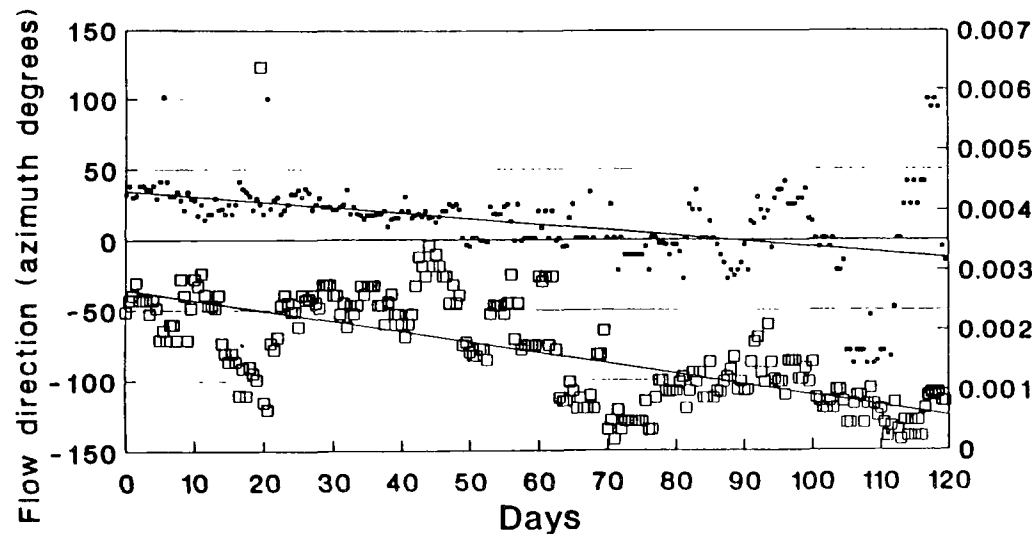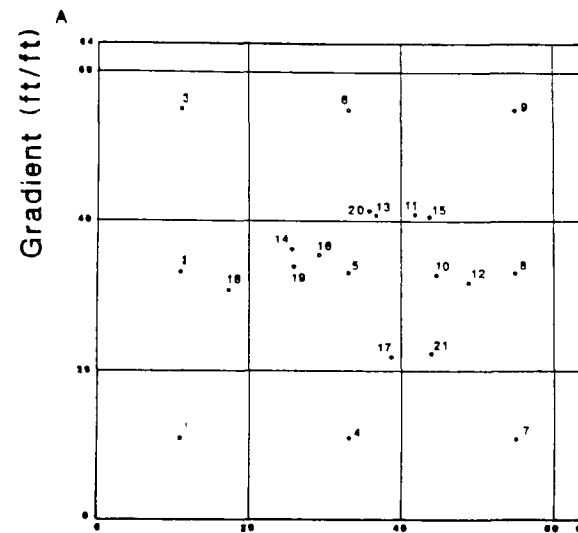## igwwc

International Ground Water Modeling Center
Holcomb Research Institute
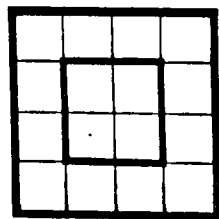Butler University
Indianapolis, Indiana 46208

NORTH

33.71%   32.02%

330°   0°   30°

17.98%

6.74%   60°

300°   1.12%   4.49%

270°   1.12%   5   10   15   20   25   90°

1.69%

1.12%

240°   120°

210°   150°

180°

2/7/86 to 5/6/86

FLOW DIRECTION FLUCTUATIONS

Flow direction (azimuth degrees) / Gradient (ft/ft) vs Days

Legend: —•— Azimuth   —□— Gradient

OPTIONS FOR NETWORK DESIGN

REGULAR WELLS
ON A 4X4
RECTANGULAR GRID
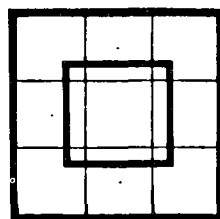
REGULAR WELLS
ON A 3X3
RECTANGULAR GRID
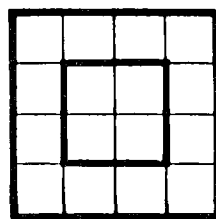
REGULAR WELLS
ON A 4X4
HEXAGONAL GRID

REGULAR WELLS	4X4 RECTANGULAR	16	R41	R42	R43
	3X3 RECTANGULAR	9	R31	R32	R33
	4X4 HEXAGONAL	14	H41	H42	H43
			OVER WHOLE AREA	STRATIFIED	ONLY IN MIDDLE 25% OF AREA

RANDOM WELLS

□ middle 25% of area

A

	x_i	y_i
1	11	11
	11	33
3	11	55
	33	11
5	33	33
	33	55
7	55	11
	55	33
9	55	55
	44.5	32.5
11	41.9	40.7
	48.8	31.6
13	36.5	40.5
	25.5	36.1
15	43.8	40.5
	29.0	35.3
17	38.6	21.8
	17.2	30.6
19	25.8	33.5
	35.8	41.0
21	43.8	22.4

B

C

D
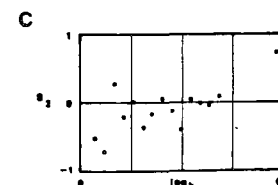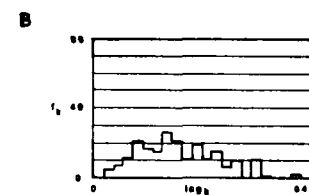
Final results of well planning
on 1-acre test site.

A: Map showing optimal sites at 21 wells.

B: Histogram showing no. of observations for 3 m lag intervals (lag_k).

C: Difference between average distance between well pairs and required lag for all intervals.

D: Standard deviation of distance between well pairs.
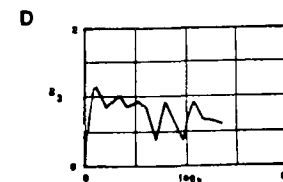
GROUNDWATER REMEDIATION

- **HYDRAULIC CONTAINMENT**
  - **Pump-and-treat technology**

- **PHYSICAL CONTAINMENT**
  - **Slurry walls**

- **INNOVATIVE TECHNOLOGIES**
  - **Soil venting**
  - **In situ heating**
  - **Bioreclamation**
  - **Fixation**

PROBLEMS WITH PUMP-AND-TREAT TECHNOLOGIES

- **MATRIX DIFFUSION**
- **DESORPTION**
- **RESIDUAL SATURATION (IMMISCIBLE FLUID)**

LEADS TO LONG CLEAN UP TIME FRAMES

NOTE: Conversion Factor
1 ppb = 1 $\mu g L^{-1}$
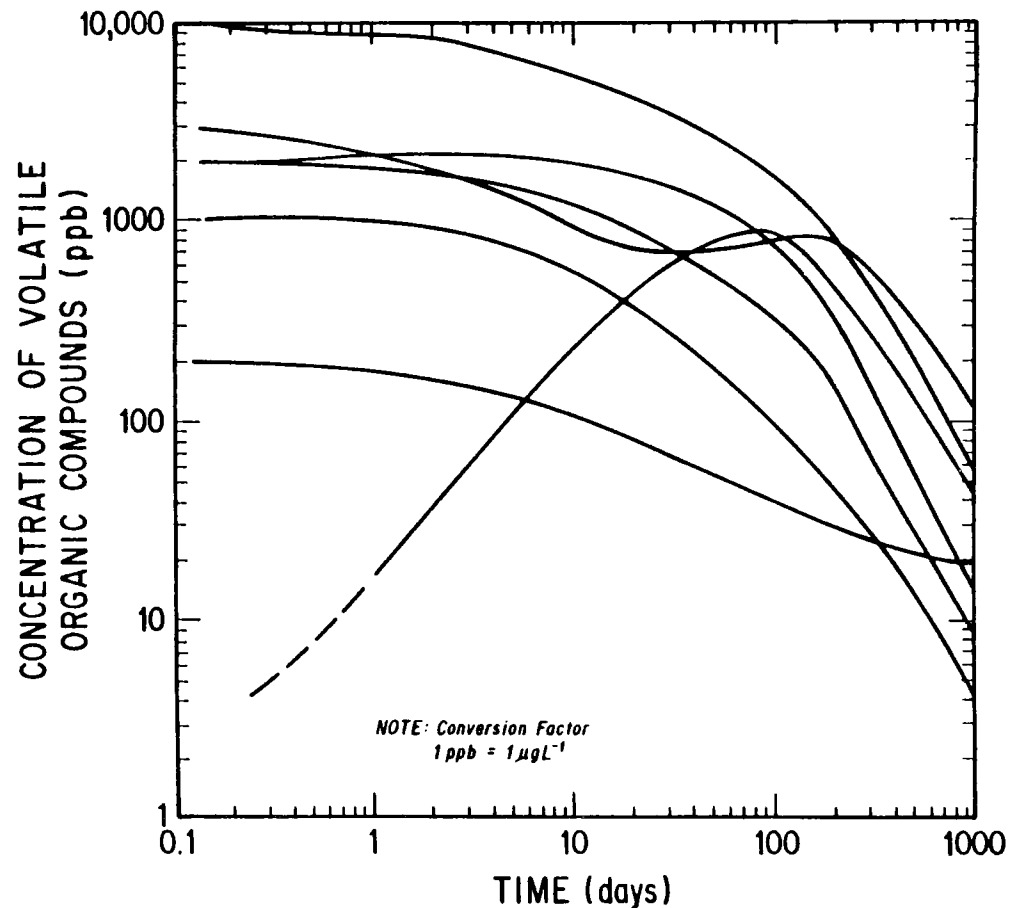
PROBLEMS WITH SLURRY WALLS

- **DIFFICULT TO ACHIEVE DESIGN PERMEABILITY**
- **DIFFICULT TO PREVENT UNDER FLOW**

LEADS TO LOSS OF CONTAINMENT

BIORECLAMATION

- CONSISTS OF INJECTING OXYGEN INTO A CONTAMINATED ZONE TO ENHANCE NATURAL BIODEGRADATION
  - Hydraulics (delivery) problem

IN SITU BIOREACTION
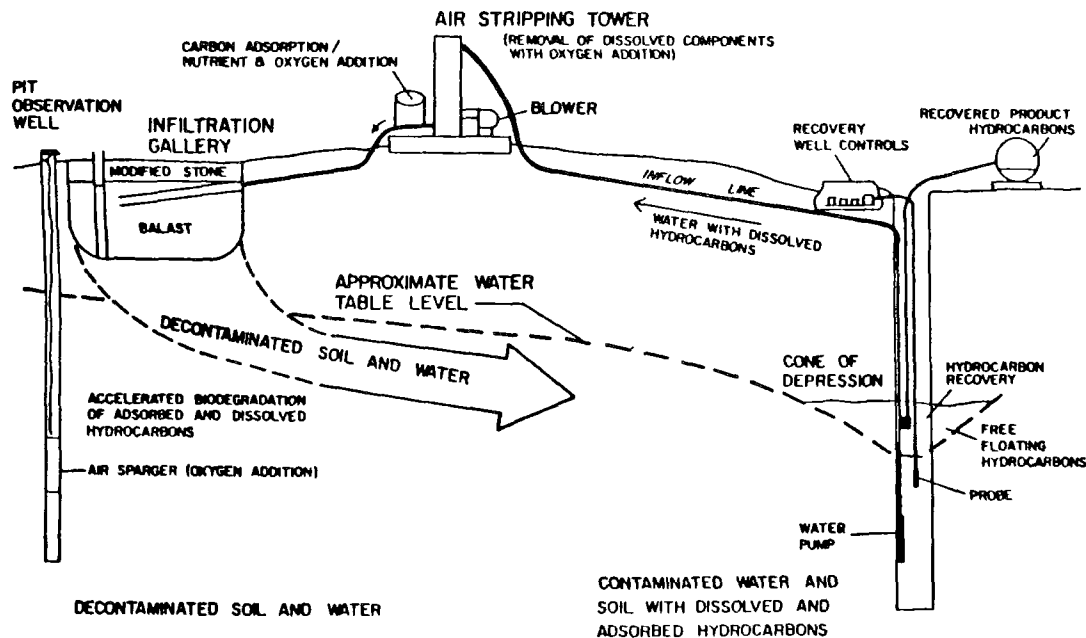
SATURATED ZONE SUMMARY

- no subsurface characterization technique provides perfect information; use several techniques in combination

- determine data thresholds (phased approach) for remedial decisions; decisions will have uncertainty; importance of monitoring

- presented general data requirements and characterization techniques; each application of techniques is unique and site specific

- data interpretation is just as importnat as data collection; need to understand data analysis and why data are collected

AIR STRIPPING TOWER (REMOVAL OF DISSOLVED COMPONENTS WITH OXYGEN ADDITION)

CARBON ADSORPTION / NUTRIENT & OXYGEN ADDITION

PIT OBSERVATION WELL

INFILTRATION GALLERY

MODIFIED STONE

BALAST

BLOWER

RECOVERY WELL CONTROLS

RECOVERED PRODUCT HYDROCARBONS

INFLOW LINE

WATER WITH DISSOLVED HYDROCARBONS

APPROXIMATE WATER TABLE LEVEL

DECONTAMINATED SOIL AND WATER

ACCELERATED BIODEGRADATION OF ADSORBED AND DISSOLVED HYDROCARBONS

AIR SPARGER (OXYGEN ADDITION)

CONE OF DEPRESSION

HYDROCARBON RECOVERY

FREE FLOATING HYDROCARBONS

PROBE

WATER PUMP

DECONTAMINATED SOIL AND WATER

CONTAMINATED WATER AND SOIL WITH DISSOLVED AND ADSORBED HYDROCARBONS

DETERMINATION OF WATER MOVEMENT IN SATURATED POROUS MEDIA

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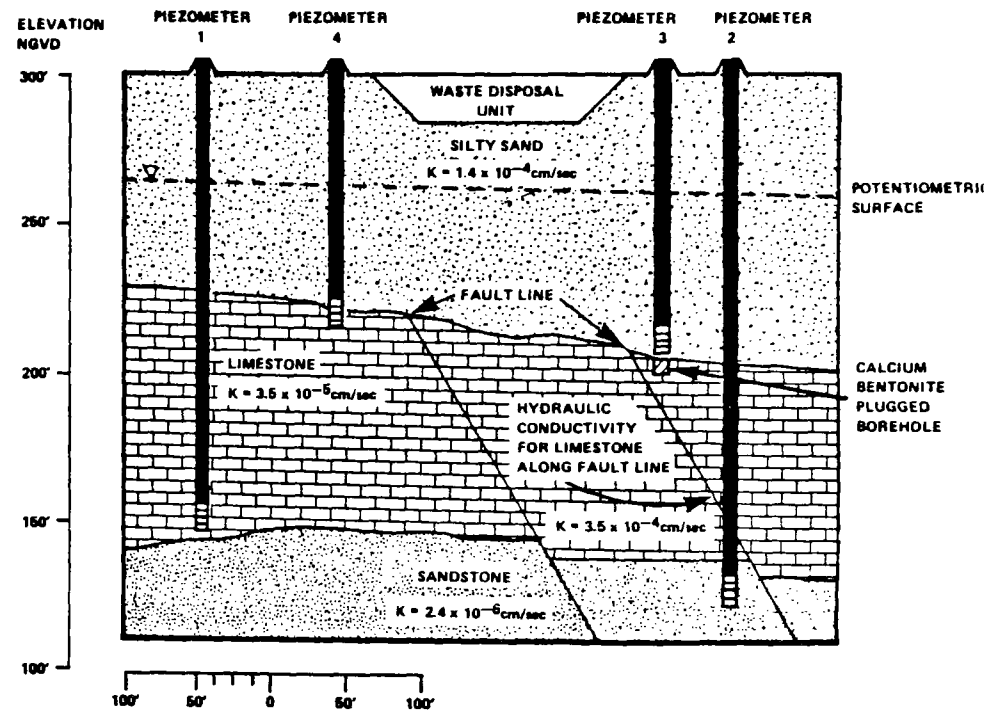
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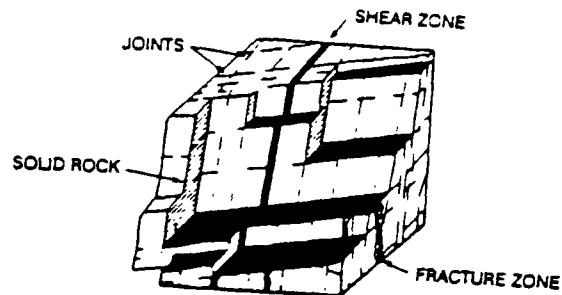
DETERMINATION OF WATER MOVEMENT IN SATURATED FRACTURED MEDIA

- ● Water Storage

- ● Water Movement

- ● Contaminant Storage

- ● Contaminant Movement

- ● Impacts on Remediation

ELEVATION NGVD

PIEZOMETER 1   PIEZOMETER 4   PIEZOMETER 3   PIEZOMETER 2

WASTE DISPOSAL UNIT

SILTY SAND
$K = 1.4 \times 10^{-4}$ cm/sec

POTENTIOMETRIC SURFACE

FAULT LINE

LIMESTONE
$K = 3.5 \times 10^{-5}$ cm/sec

HYDRAULIC CONDUCTIVITY FOR LIMESTONE ALONG FAULT LINE
$K = 3.5 \times 10^{-4}$ cm/sec

CALCIUM BENTONITE PLUGGED BOREHOLE

SANDSTONE
$K = 2.4 \times 10^{-6}$ cm/sec

100' 50' 0 50' 100'

AN EXAMPLE OF HYDRAULIC COMMUNICATION CAUSED BY FAULTING

SHEAR ZONE
JOINTS
SOLID ROCK
FRACTURE ZONE

Conceptualization of discontinuities in a fractured medium.

FRACTURE FLOW
DIFFUSION
POROUS ROCK MATRIX
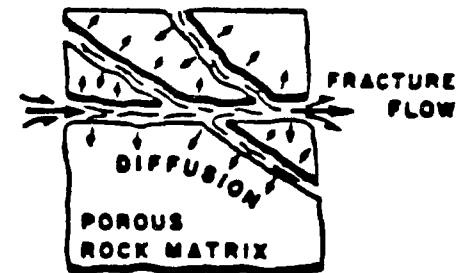
Flow through fractures and diffusion of contaminants from fractures into the rock matrix of a dual-porosity medium.

DEPTH IN FEET
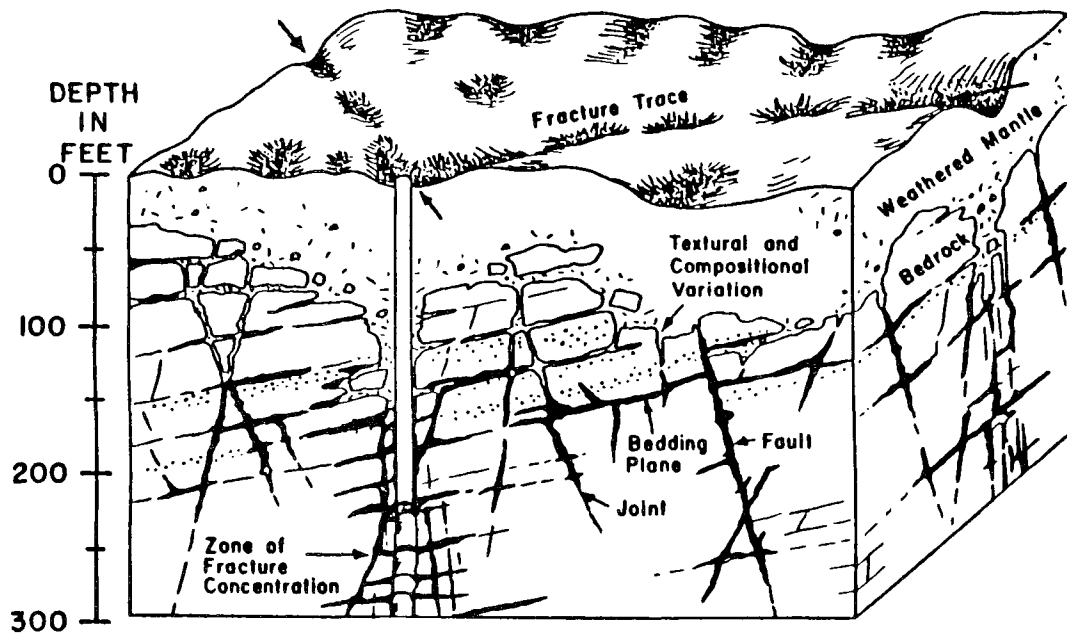
(After Lattman and Parizek 1964)

Localization of water-yielding openings along bedrock fractures in carbonate aquifers.

FRACTURE MAPPING

- ORIENTATION

- APERATURE

- SPACING
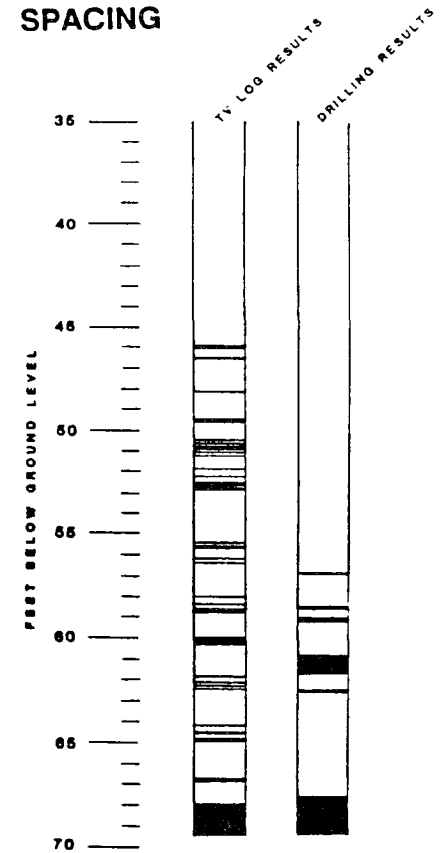
DARKENED AREAS INDICATE
BROKEN ROCK AND VOID SPACE
OR ZONES THAT DRILL RODS
DROPPED THROUGH

DARKENENED AREAS INDICATE
APPROXIMATELY FOUR FEET
OF VOID SPACE

Various zones of broken rock are compared
to the television log

- - - - MAPPED BY GEOTRANS

===== MAPPED BY LEAVY (1985)

SCALE 1 24000

CONTOUR INTERVAL 10 FEET
NATIONAL GEODETIC VERTICAL DATUM OF 1929

WELL A GEOLOGIC LOG

ELEVATION IN FEET (USGS DATUM)

PORTLAND CEMENT SEAL

STEEL PROTECTIVE CASING W/ LOCKING CAP

PORTLAND CEMENT GROUT

BORE HOLE

CLAY
CLAY & LIMESTONE PCS
LIMESTONE W/ SHALE
LIMESTONE W/ SHALE
LIMESTONE

CALIPER DIAMETER INCHES   GAMMA RAY COUNT MINUTE

SOLUTION DEVELOPMENT ALONG MORE RESISTANT BED CONTACTS

CLAY LINED VOID OR WASHED OUT CLAY OR SHALE HORIZON

WELL B GEOLOGIC LOG

ELEVATION IN FEET (USGS DATUM)

PORTLAND CEMENT SEAL

STEEL PROTECTIVE CASING W/ LOCKING CAP

PORTLAND CEMENT GROUT

BORE HOLE

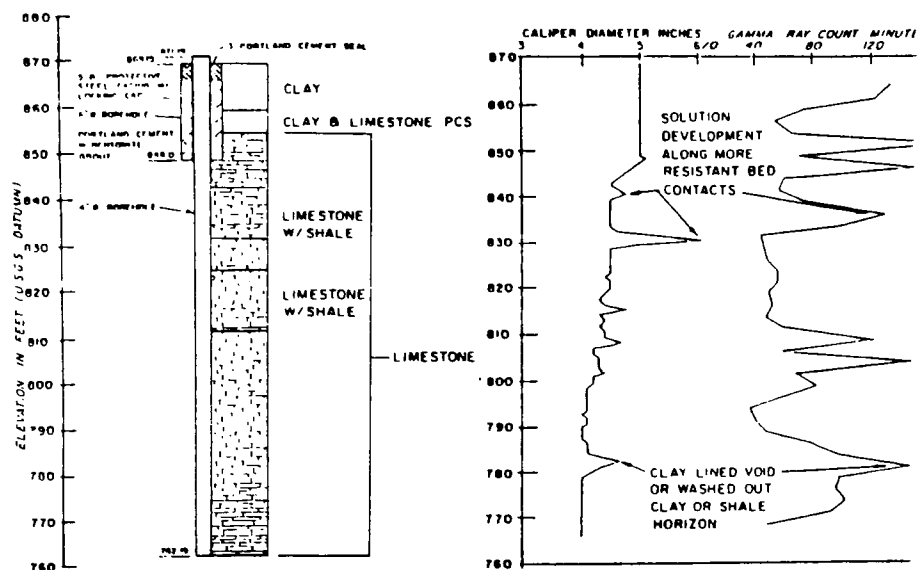CLAY
CLAY
LIMESTONE W/ SOME CHERT
LIMESTONE W/ SOME CHERT
LIMESTONE
SHALEY LIMESTONE

CALIPER DIAMETER IN INCHES   GAMMA RAY COUNTS

OPEN FRACTURE OR SOLUTION CHANNEL

HYDRATED SHALE

PACKER

PACKER AND SAMPLING PORT

PVC PIPE
O-RING
RUBBER MEMBRANE
DOWELL SEAL
NYLON-MESH SCREEN CLOTH
HOLES DRILLED IN PVC PIPE
PVC COUPLING

POLYETHYLENE TUBING
90° POLYETHYLENE ELBOW WITH 1/8" NPT
O-RING
NYLON THREADED ROD
PVC PIPE

Schematic diagram of a six-port multilevel assembly and detailed views of a packer and sampling port systems.
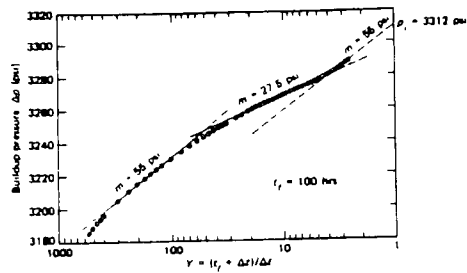
Pressure buildup data exhibiting a three-segment pattern
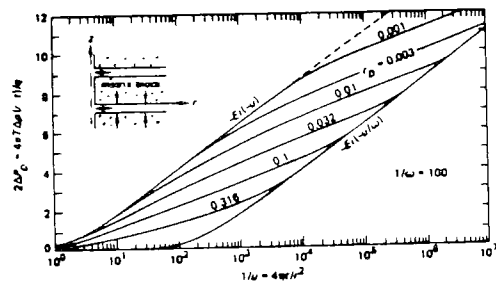
Dimensionless pressure drawdown versus dimensionless time for a
distributed-parameter model of a naturally fractured formation
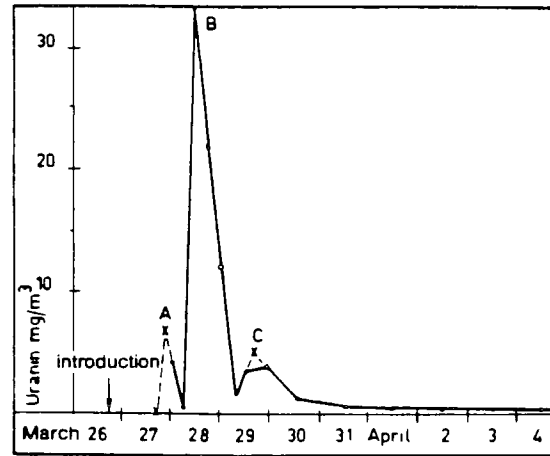
Tracer-diagram
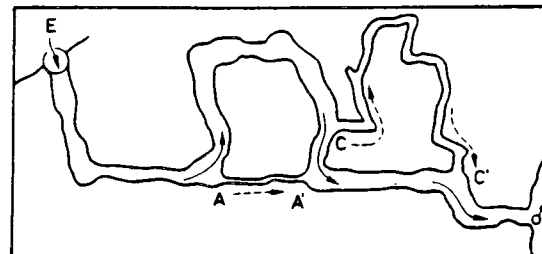
Model of a network of passages

Va: vadose zone
Vo: Base level
Pi: Piezometric surface
Ph: Phreatic zone
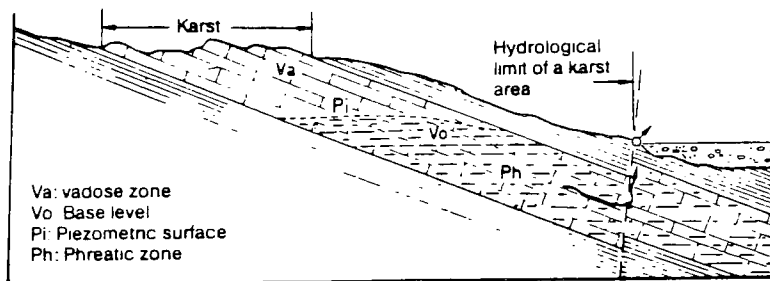
Hydrological limit of a karst area.
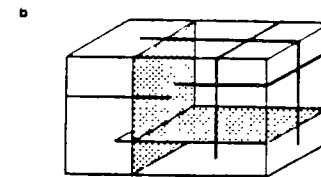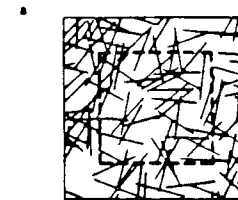
Three different conceptualizations of fracture networks

porous media

fractured

REV

ψ_{pm}

porous media

REV
REGION (Pores)

(a)

L

ψ_f

fractured media

REV
REGION
(Fractures)

(b)

L

(c)
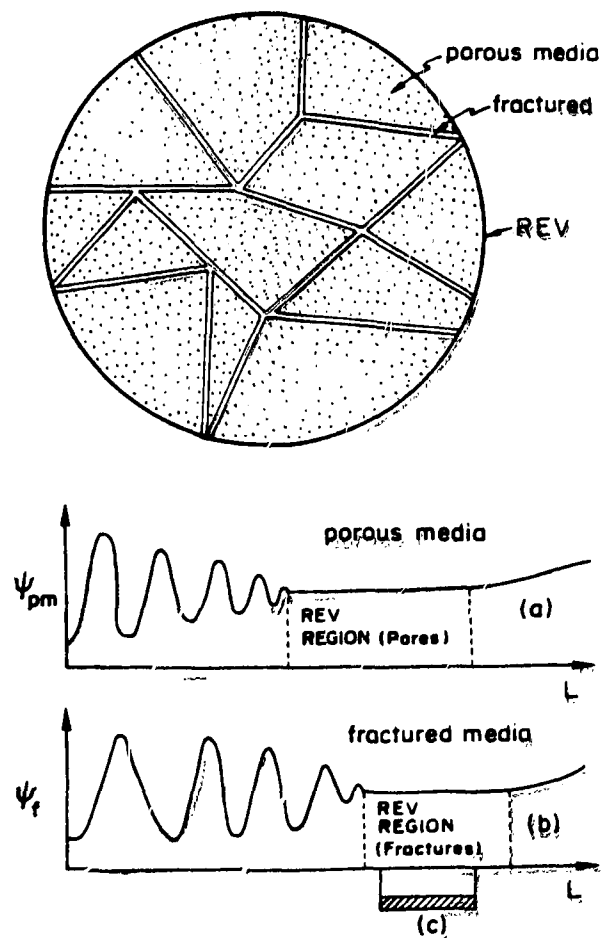
XBL 795-9557

Conceptual model for overlapping continua, curve (a) is the plot of a property ψ measured for different volume (REV) L^5 of porous media; curve (b) is the plot of a property ψ measured for different volumes (REV) L^5 of fractured porous media. The region (c) is the common region where both the porous medium and fracture medium physics can be represented as though each were a continuum.
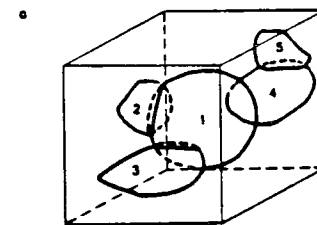
LEGEND

BACKGROUND/UPGRADIENT WELL

DOWNGRADIENT MONITORING WELL

WELL SCREEN

POTENTIOMETRIC SURFACE

FRACTURED TRACE

OUTLINE OF CAVERN (PLAN VIEW)

PLUGGED BOREHOLE

SINKHOLE

LANDFILL

200 FEET

WELL 2
(PROJECTED 100 FEET)

WELL 4 WELL 5
(PROJECTED 100 FEET) (PROJECTED 50 FEET)

LANDFILL
(PROJECTED 0 - 50 FEET)

A

A'

WELL 1

WELL 3

WELL 6

REGOLITH
$K = 1.0 \times 10^{-3}$ cm/sec

1,120

1,100

1,080

1,060

1,040

1,020

(FEET)

100   150   200   250   300   350   400   450   500   550   600

LIMESTONE MATRIX
$K = 2.0 \times 10^{-3}$ cm/sec

SOLUTION CHANNEL
LIMESTONE
$K = 5.0 \times 10^{-1}$ cm/sec

GROUND WATER FLOW
OUT OF PAGE

FOSSIL HASH
$K = 4.5 \times 10^{-1}$ cm/sec

MONITORING WELL PLACEMENT AND SCREEN LENGTHS IN A MATURE KARST TERRAIN/FRACTURED BEDROCK SETTING
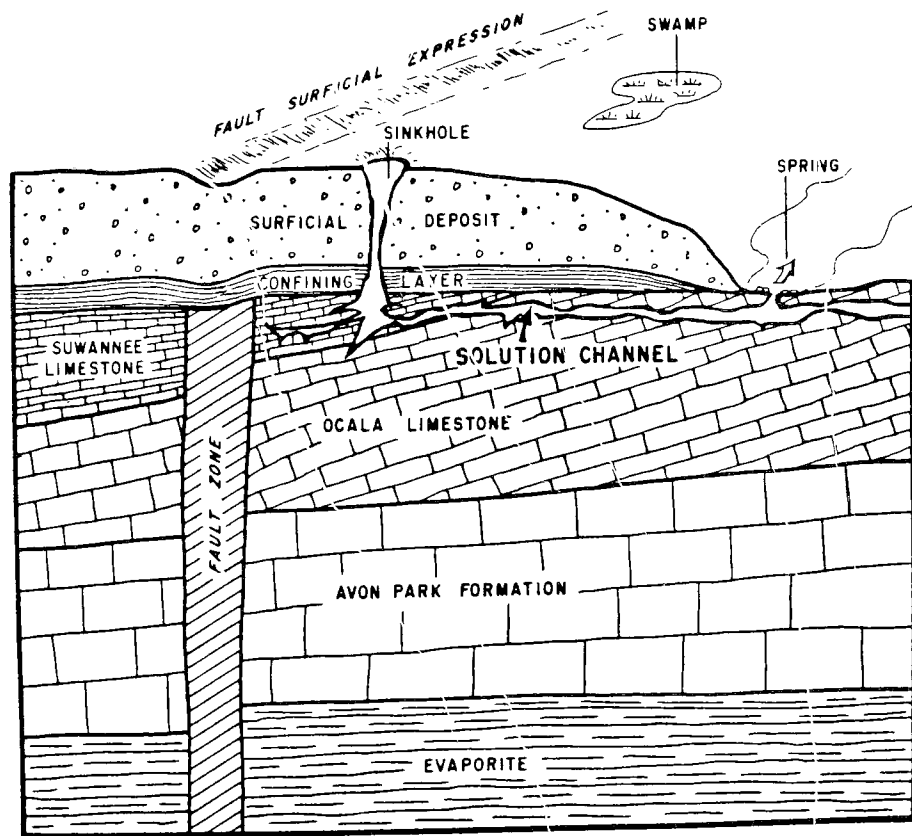
LOCATION OF GEOPHYSICAL SURVEY LINES
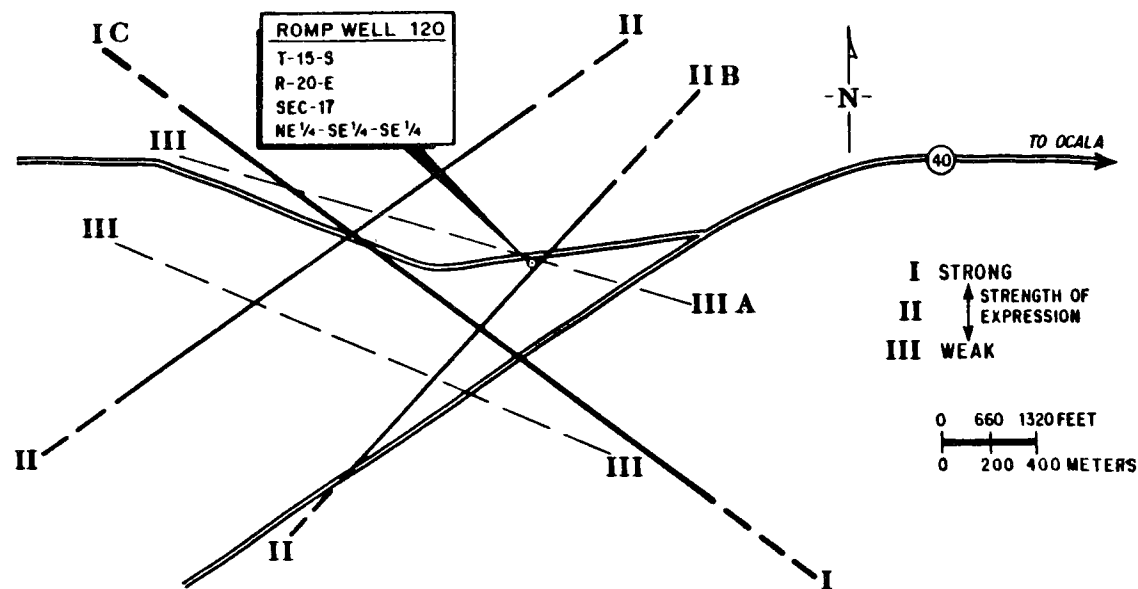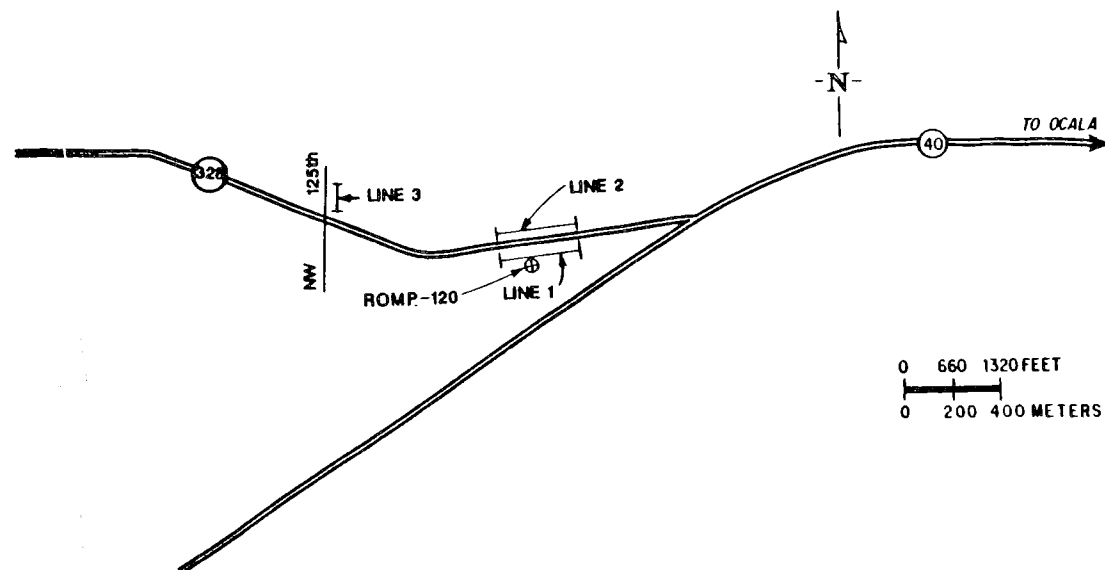
FRACTURE TRACES NEAR ROMP WELL 120

ROMP WELL 120
T-15-S
R-20-E
SEC-17
NE¼-SE¼-SE¼

I STRONG
II STRENGTH OF EXPRESSION
III WEAK

CONDUCTIVE:

□ CPPC
+ CCPP
◇ CPCP

CONDUCTIVE SHEET

RESISTIVE:

□ CPPC
+ CCPP
◇ CPCP

RESISTIVE SHEET

TRI-POTENTIAL DATA
LINE 1: SOUTH SIDE 328

ANOMALY 'A'   ANOMALY 'B'

□ CPPC   + CCPP   ● CPCP

COUNTY ROAD 328

OW2 (PROPOSED)   OW3   LINE 2
OW4   OW2 (ACTUAL) LINE 1
ROMP 120   OW1 (ACTUAL)
OW1 (PROPOSED)

45°

25N
0
25S

25W   0   25E   50   75   100   125   150E

DISTANCE IN METERS

-N-

INTERSECTION LOCATION

75M   SOUTH
EDGE OF ROAD
17M
X

Location of four observation wells in the vicinity
of ROMP 120.

Geophysical log interpretation of observation wells.

OW1 (deep) Drawdown
Jacob Approximation

PERIODIC MEASUREMENT

$\Delta s = .30$

Q = 180 gpm
t_0 = 0.0045
r = 136 ft

DRAWDOWN (ft)

TIME (min)

OW1 (deep) Drawdown
Theis Analysis

PERIODIC MEASUREMENT

*W (u) = 1
1/u = 3.5
S = .11 ft
t = .42 min

Q = 180 gpm
r = 136 ft

DRAWDOWN (ft)

TIME (min)

HEAD (feet)

OW1 SLUG TEST DATA

NEGATIVE DISPLACEMENT

POSITIVE DISPLACEMENT

TIME (sec)

HEAD (feet)

OW2 SLUG TEST DATA

POSITIVE DISPLACEMENT

NEGATIVE DISPLACEMENT

TIME (sec)

FRACTURED MEDIA SUMMARY

● heterogeneity is important to characterize, but is especially important in karst and fractured media

● characterization techniques are somewhat limited: coring, aquifer tests, tracer tests, geophysical tools, and fracture trace analysis

● difficult to characterize and predict behavior: equivalent porous media, discrete fractures, dual porosity, and stochastic approach

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DETERMINATION OF WATER MOVEMENT IN THE VADOSE ZONE

- ● Water Storage

- ● Water Movement

- ● Contaminant Storage

- ● Contaminant Movement

- ● Vapor Movement

- ● Impacts on Remediation

American Society for Testing and Materials: Colloids* | Clay | Silt | Fine sand | Medium sand | Coarse sand | Gravel

American Association of State Highway Officials: Colloids* | Clay | Silt | Fine sand | Coarse sand | Fine gravel | Medium gravel | Coarse gravel | Boulders

U.S. Department of Agriculture: Clay | Silt | Very fine sand | Fine sand | Medium sand | Coarse sand | Very coarse sand | Fine gravel | Coarse sand | Cobbles

Federal Aviation Administration: Clay | Silt | Fine sand | Coarse sand | Gravel

Corps of Engineers, Bureau of Reclamation: Fines (silt or clay)** | Fine sand | Medium sand | Coarse sand | Fine gravel | Coarse gravel | Cobbles

Sieve sizes: 270 | 200 | 140 | 60 | 40 | 20 | 10 | 4 | ½" | ¾" | 3"

Particle size, mm: .001 .002 .003 .004 .006 .008 .01 .02 .03 .04 .06 .08 .1 .2 .3 .4 .6 .8 1.0 2.0 3.0 4.0 6.0 8.0 10 20 30 40 60 80

*Colloids included in clay fraction in test reports.
**The LL and PI of "Silt" plot below the "A" line on the plasticity chart, Table 4, and the LL and PI for "Clay" plot above the "A" line.

Soil-separate size limits of ASTM, AASHO, USDA, FAA, Corps of Engineers, and USBR.
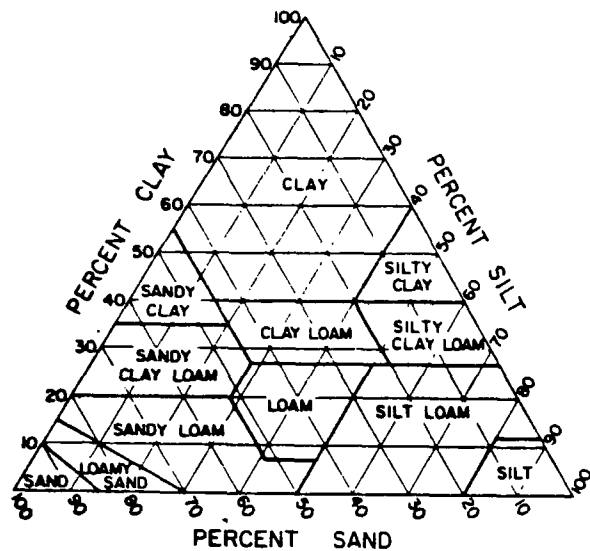
Triangular chart showing the percentages of sand, silt, and clay in the basic soil textural classes.

Bouwer (1978)

Particle-size distribution for a uniform sand and a well-graded soil.

Bouwer (1978)

DIVISIONS OF SUBSUR-
FACE WATER.

$r_1 < r_2 < r_3$

$h_1 > h_2 > h_3$

Capillary Rise Equation

$$h = \frac{0.15}{r}$$
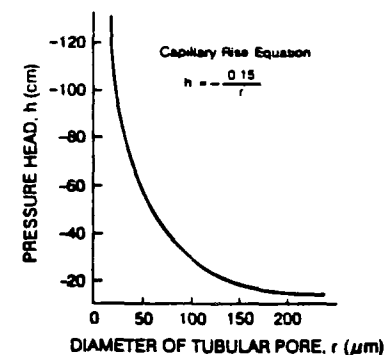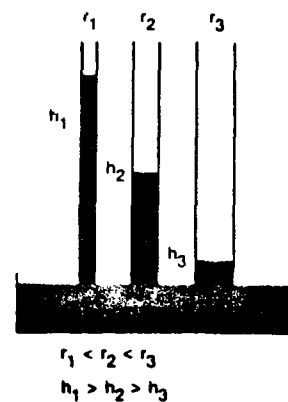
Relationship between pore size (r) on capillary rise and pressure head (h).

NEGATIVE PRESSURE POTENTIAL

POSITIVE PRESSURE POTENTIAL
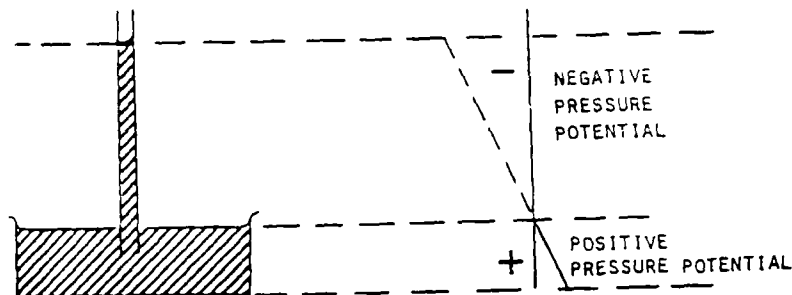
Illustration of pressure potential and matric potential below and above a free water surface. The capillary tube represents an idealized soil void.

METHODS TO MEASURE PRECIPITATION

- SACRAMENTO GAGE

- WEIGHING GAGE

- TIPPING-BUCKET GAGE

PRECIPITATION

↓ ↓ ↓ ↓ ↓

EVAPOTRANSPIRATION

EXPLANATION

Low   High
RELATIVE DISSOLVED SOLID CONCENTRATION

▷ DIRECTION OF WATER MOVEMENT
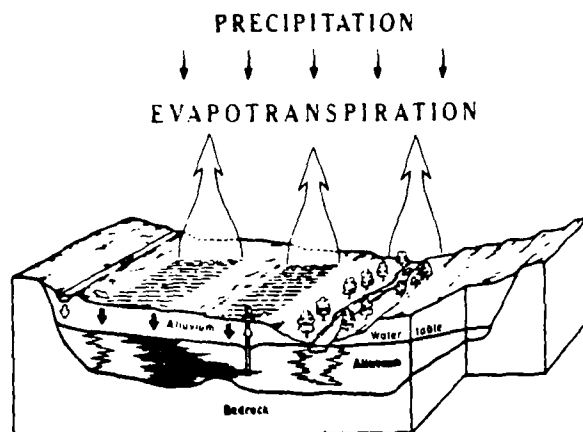
Idealized block diagram illustrating typical geometry of the stream-aquifer system and the relation between water movement and water quality.

SUMMARY OF METHODS TO MEASURE PRECIPITATION

Method	Application	Reference
Sacramento Gage	Accumulated precipitation. Manual recording.	Finkelstein et al. (1983); National Weather Service (1972)
Weighing Gage	Continuous measurement of precipitation. Mechanical recording.	Finkelstein et al. (1983); Kite (1979)
Tipping-bucket Gage	Continuous measurement of precipitation. Electronic recording. Recommended.	Finkelstein et al. (1983); Kite (1979)

METHODS TO MEASURE EVAPORATION

● **CLASS-A PAN**

SUMMARY OF METHODS TO MEASURE EVAPORATION

Method	• Application	Reference
Class-A Pan	Evaporation from surface of free liquid.	Veihmeyer (1964); National Weather Service (1972)

METHODS TO MEASURE OR ESTIMATE EVAPOTRANSPIRATION

● **WATER BALANCE METHODS**

- pan lysimeter
- soil moisture sampling
- potential evapotranspirometers
- cl⁻ tracer
- water-budget analysis
- groundwater fluctuation

● **MICROMETEOROLOGIC METHODS**

- profile method
- energy budget/Bowen ratio
- Eddy covariance method
- Penman equation
- Thornwaite equation
- Blaney-Criddle equation

SUMMARY OF METHODS TO MEASURE OR ESTIMATE EVAPOTRANSPIRATION

Method	Application	Reference
WATER BALANCE METHODS		
Pan Lysimeter	Direct field method; accurate; moderate to low cost.	Veihmeyer (1964); Sharma (1985)
Soil Moisture Sampling	Direct field method; accurate; moderate to low cost.	Veihmeyer (1964)
Potential Evapotrans-pirometers	Direct field method of PET. Moderately accurate and low cost.	Thornthwaite and Mather (1955)
Cl⁻ Tracer	Indirect combined field and laboratory method; moderate to high cost.	Sharma (1985)
Water-Budget Analysis	Indirect field estimate of ET; manageable to difficult; moderate to low cost.	Davis & Dewiest (1966)
Ground-water Fluctuation	Indirect field method; moderate to low cost.	Davis & Dewiest (1966)
MICROMETEORO-LOGIC METHODS		
Profile Method	Indirect field method.	Sharma (1985)
Energy Budget/ Bowen Ratio	Indirect field method; difficult; costly; requires data which is often unobtainable; research oriented.	Veihmeyer (1964); Sharma (1985)
Eddy Covariance Method	Indirect field method; costly; measures water-vapor flux directly; highly accurate; well accepted; research oriented.	Veihmeyer (1964); Sharma (1985)
Penman Equation	Indirect field method; difficult; costly; very accurate; eliminates need for surface temperature measurements; research oriented.	Veihmeyer (1964); Sharma (1985)
Thornwaite Equation	Empirical equation; most accepted for calculating PET; uses average monthly sunlight; moderate to low cost.	Veihmeyer (1964); Sharma (1985)
Blaney-Criddle Equation	Empirical equation; widely used; moderate to high accuracy; low cost; adjusts for certain crops and vegetation.	Stephens & Stewart (1964)

METHODS TO MEASURE OR ESTIMATE INFILTRATION RATES

- INFILTROMETERS

- SPRINKLER INFILTROMETER

- AVERAGE INFILTRATION METHOD

- EMPIRICAL RELATIONS

- INFILTRATION EQUATIONS

SUMMARY OF METHODS TO MEASURE OR ESTIMATE INFILTRATION RATES

Method	Application	Reference
Infiltrometers	Measures the maximum infiltration rate of surface soils. Useful for determining relative infiltration rates of different soil types; however, infiltration rates determined by this method tend to overestimate actual rates.	Dunne and Leopold (1978); Bouwer (1986)
Sprinkler Infiltrometer	Measures the potential range of infiltration rates under various precipitation conditions. Tends to be expensive and non-portable. Sprinkler infiltrometers have typically been used for long duration research studies.	Dunne and Leopold (1978); Peterson and Bubenzer (1986)
Average Infiltration Method	Method for estimating the average infiltration rate for small water sheds. Provides an approximate estimate of infiltration for specific precipitation events and antecedent moisture conditions.	Dunne and Leopold (1978)
Empirical Relations	Methods to approximate the infiltration for large watersheds. These methods can be useful when combined with limited infiltrometer measurements to obtain a gross approximation of infiltration.	Musgrave and Holtan (1964)
Infiltration Equations	Analytical equations for calculating infiltration rates. Parameters required in the equations can be readily measured in the field or obtained from the literature. Probably the least expensive and most efficient method for estimating infiltration.	Bouwer (1986); Green and Ampt (1911); Philip (1957)
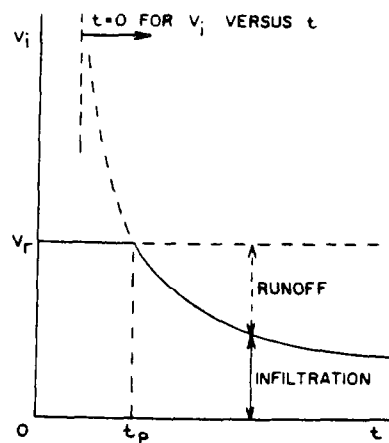
Infiltration and runoff for rain of uniform intensity.

Bouwer (1978)

Cross section of hypothetical cover design
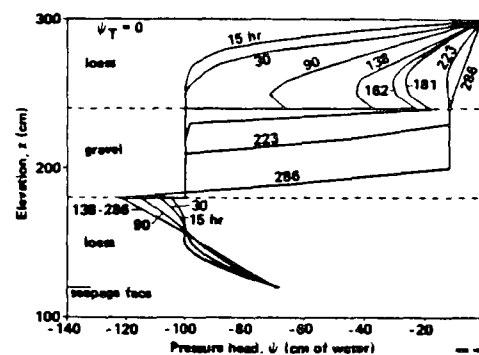
Predicted distribution of pressure head

water utilization from various depth layers
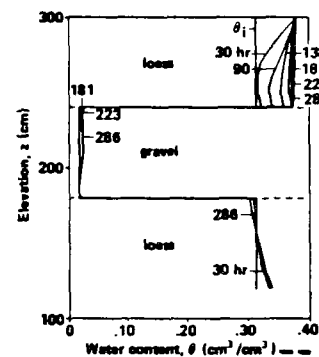
Predicted distribution of soil water content

METHODS FOR MEASURING MOISTURE CONTENT

- ● GRAVIMETRIC

- ● NEUTRON SCATTERING

- ● GAMMA RAY ATTENUATION

- ● ELECTROMAGNETIC

- ● TENSIOMETRY
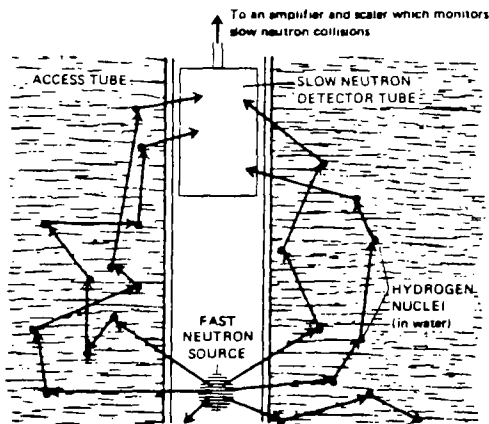
How a neutron moisture meter operates. The probe, containing a source of fast neutrons and a slow neutron detector, is lowered into the soil through an access tube. Neutrons are emitted by the source (for example, radium or americium–beryllium) at a very high speed. When these neutrons collide with a small atom such as hydrogen contained in soil water, their direction of movement is changed and they lose part of their energy. These "slowed" neutrons are measured by a detector tube and a scaler. The reading is related to the soil moisture content.

SUMMARY OF METHOD FOR MEASURING MOISTURE CONTENT

Method	Application	Reference
Gravimetric	Laboratory measurements of soils which should be dried at 110°C. The standard method for moisture content determina-tion. Recommended.	Gardner (1986); EPRI (1984)
Neutron Scattering	In situ measurements via installed access tubes. Widely used. Requires calibration curves. Recommended.	van Bavel (1963)
Gamma Ray Attenuation	In situ measurements via installed access tubes. Difficult to use. Not recommended for routine use.	Gardner (1986)
Electromagnetic	In situ measurements from implanted sensors. Not widely used. Not recommended for routine use.	Schmugge et al. (1980)
Tensiometry	In situ measurements inferred from moisture-matric potential relationship. Prone to error resulting from uncertainty of moisture-matric potential relationship. Not recommended.	Gardner (1986)
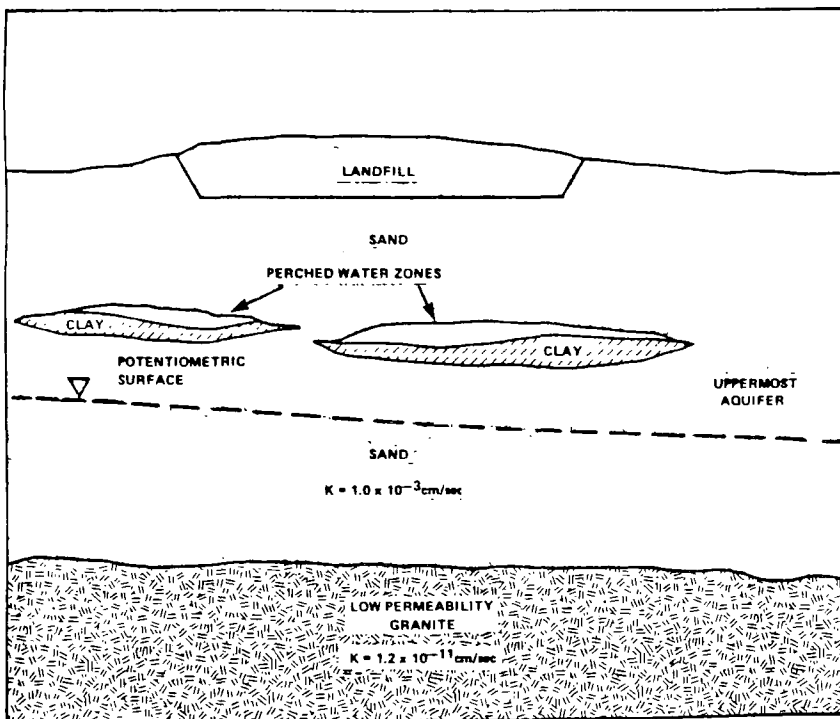
PERCHED WATER ZONES AS PART OF THE UPPERMOST AQUIFER

SOIL-WATER SYSTEMS
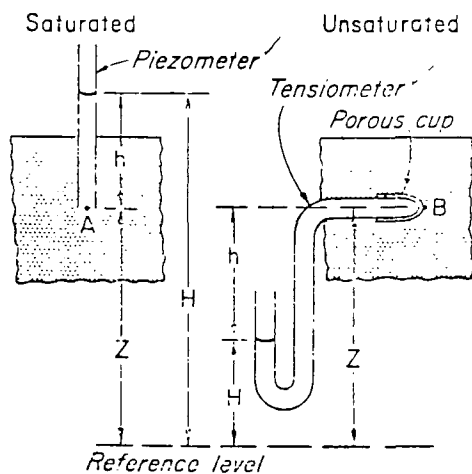
A diagram of the relationships between hydraulic
head, H, pressure head, h, and gravitational head,
Z. The pressure head is measured from the level of
termination of the piezometer or tensiometer in the
soil to the water level in the manometer and is
negative in the unsaturated soil.
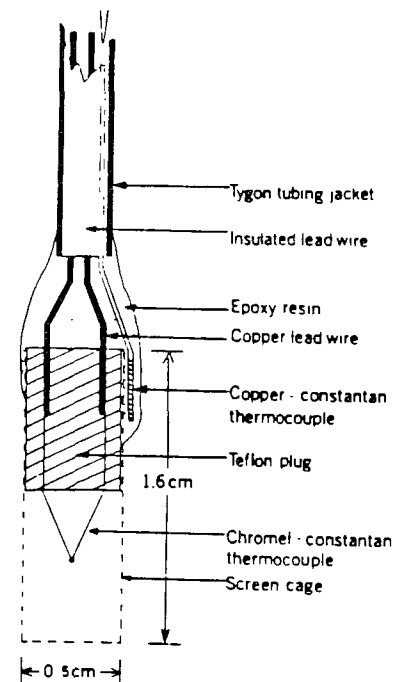
Median longitudinal section of a screen-enclosed
thermocouple psychrometer (after Meyn and White,
1972).

METHODS FOR DETERMINING MOISTURE CHARACTERISTIC CURVES

- ● **POROUS PLATE**

- ● **VAPOR EQUILIBRATION**

- ● **OSMOTIC**

SUMMARY OF METHODS FOR DETERMINING MOISTURE CHARACTERISTIC CURVES

Method	Application	Reference
Porous Plate	Standard laboratory method for measurement of soils. Can be used to characterize both wetting and drying behavior.	Klute (1986)
Vapor Equilibration	Best suited for matric potentials less than -15 bars.	Klute (1986)
Osmotic	Similar to porous plate method. Requires long equilibration times. Not recommended.	Klute (1986)
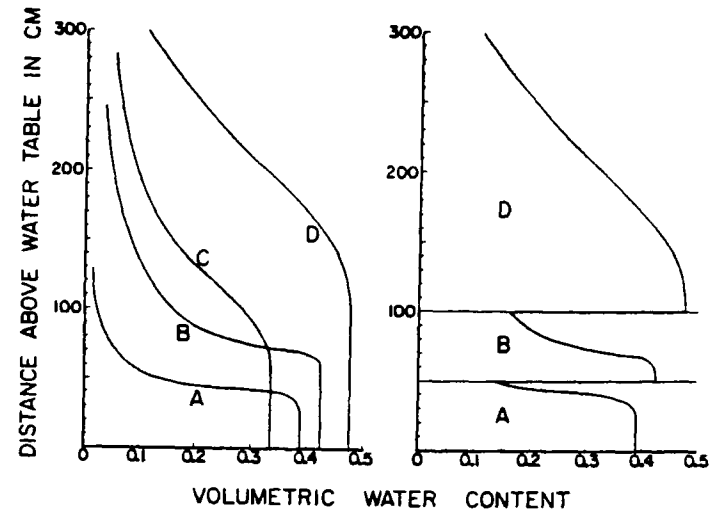
Schematic equilibrium water-content distribution above a water table (left) for a coarse uniform sand (A), a fine uniform sand (B), a well-graded fine sand (C), and a clay soil (D). The right plot shows the corresponding equilibrium water-content distribution in a soil profile consisting of layers of materials A, B, and D.

Bouwer (1978)
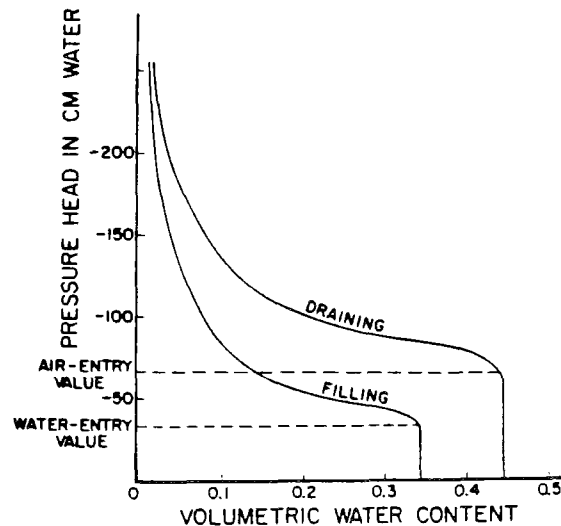
Schematic of water-content distribution above a water table
after the water table was falling (soil pores drained) and rising
(soil pores filled).

Bouwer (1978)
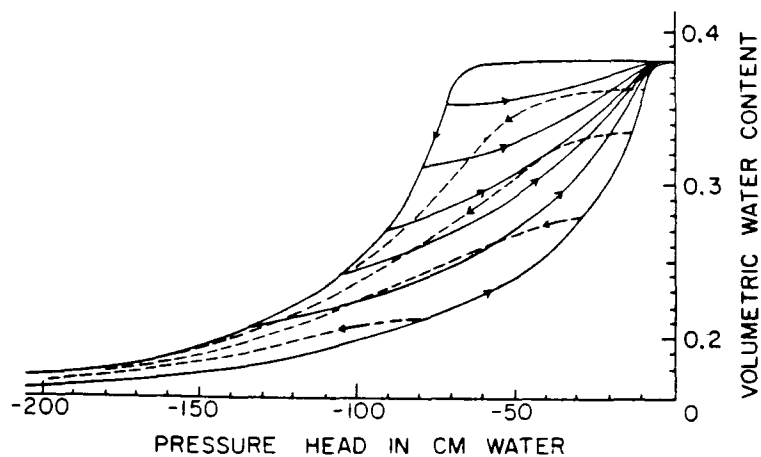
Hysteretic relations between h and θ for Rubicon sandy loam.

METHODS TO MEASURE UNSATURATED HYDRAULIC - CONDUCTIVITY VALUES

- CONSTANT-HEAD BOREHOLE INFILTRATION

- GUELPH PERMEAMETER

- AIR-ENTRY PERMEAMETER

- INSTANTANEOUS PROFILE

- CRUST-IMPOSED STEADY FLUX

- SPRINKLER-IMPOSED STEADY FLUX

- PARAMETER IDENTIFICATION

- EMPIRICAL EQUATIONS

Method	Application	Reference
Constant-Head Borehole Infiltration	Field method in open or partially cased borehole. Most commonly used method. Includes a relatively large volume of porous media in test.	Bouwer (1978); Stephens and Neuman (1982a,b,c); Amoozegar and Warrick (1986)
Guelph Permeameter	Field method in open, small-diameter borehole (>5 cm). Relatively fast method (5 to 60 minutes) requiring small volume of water. K_s, $K(\psi)$ and sorptivity are measured simultaneously. Many boreholes and tests may be required to fully represent heterogeneities of porous media.	Reynolds and Elrick (1986)
Air-Entry Permeameter	Field method. Test performed in cylinder which is driven into porous media. Small volume of material tested; hence, many tests may be needed. Fast, simple method requiring little water (-10 L).	Bouwer (1966)
Instantaneous Profile	Field or lab method. Field method measures vertical $K(\theta,\psi)$ during drainage. Measurement of moisture content and hydraulic head needs to be rapid and non-destructive to sample. Commonly used method, reasonably accurate.	Bouma, Baker, and Veneman (1974); Klute and Dirksen, (1986)
Crust-Imposed Steady Flux	Field method. Measures vertical $K(\psi)$ during wetting portion of hysteresis loop. Labor and time intensive.	Green, Ahuja, and Chong (1986)
Sprinkler-Imposed Steady Flux	Field method. Larger sample area than for crust method. Useful only for relatively high moisture contents.	Green, Ahuja, and Chong (1986)
Parameter Identification	Results of one field or lab test are used by a numerical approximation method to develop $K(\theta)$, $K(\psi)$, and $\psi(\theta)$ over a wide range of θ and ψ. Relatively fast method; however, unique solutions are not usually attained.	Zachmann et al. (1981a,b, 1982); Kool et al. (1985)
Empirical Equations	Each empirical equation has its own application based upon the assumptions of the equation. Relatively fast technique.	Brooks-Corey (1964); van Genuchten (1980); Mualem (1986)
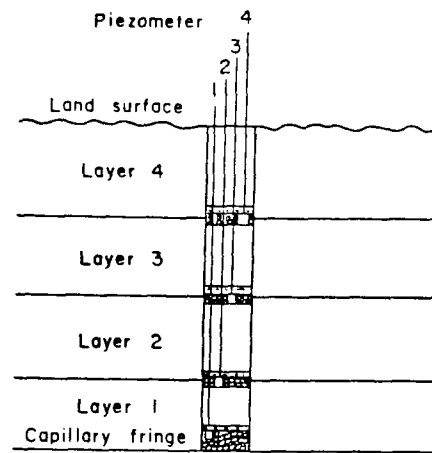
Piezometer nest used to determine pneumatic head differences in the unsaturated zone
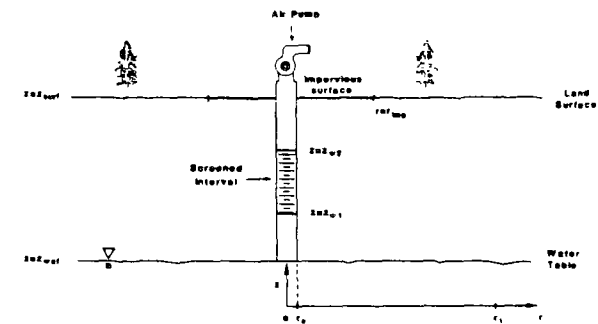
Radially symmetric region for single-well air flow model

NOTE: All pipe fittings, valves, and hoses are standard 1/4-inch items

NOTE: Connection shown is that used when the downhole pressure is greater than that at land surface, and the valve settings are those for reading piezometer 1.
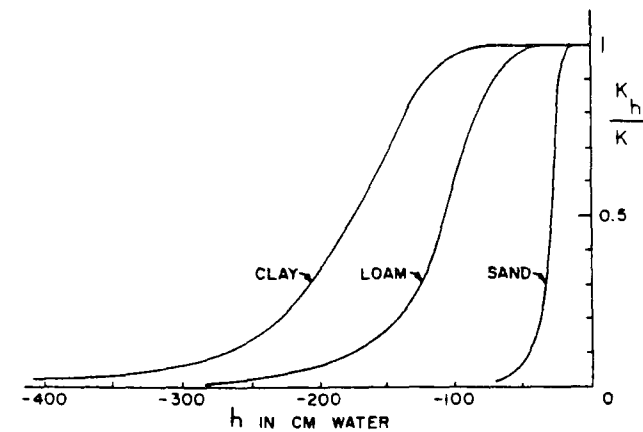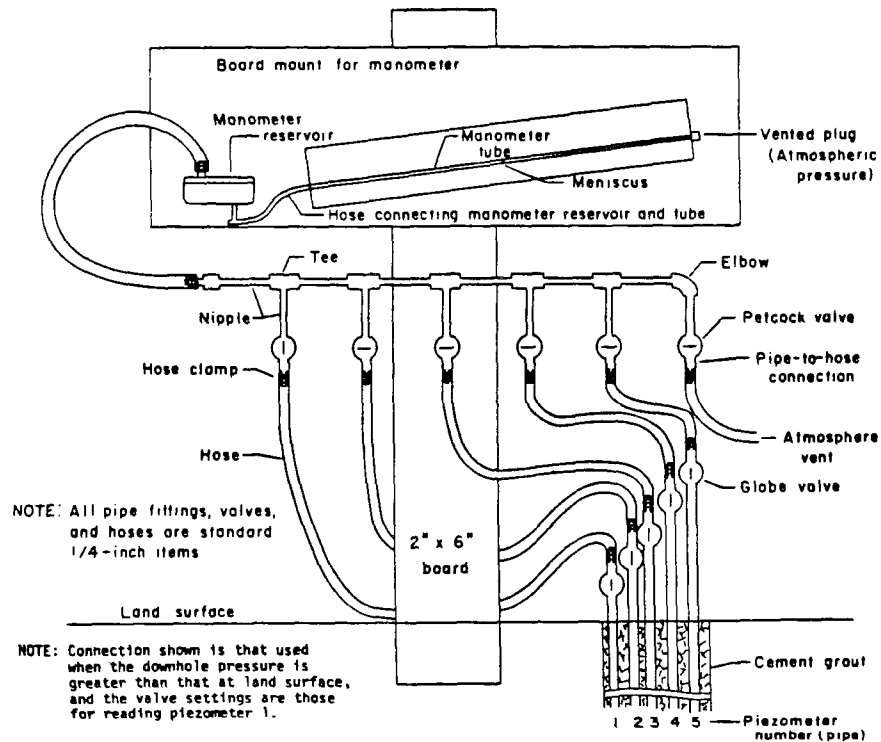
Schematic relations between K_h (expressed as K_h/K) and h for sand, loam, and clay.

Legend

Clay	⊕ – – – ⊕
Clay Loam	▲ – – – ▲
Loam	+ – – – +
Loamy Sand	× – – – ×
Silt Loam	✳ – – – ✳
Silty Clay Loam	▣ – – – ▣
Sand	◆ – – – ◆
Sandy Clay	+ – – – +
Sandy Clay Loam	Y – – – Y
Sandy Loam	+ – – – +

Geometry and symbols for piston-flow infiltration system.
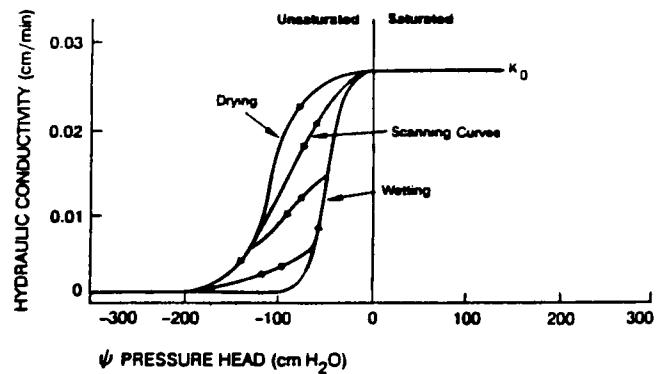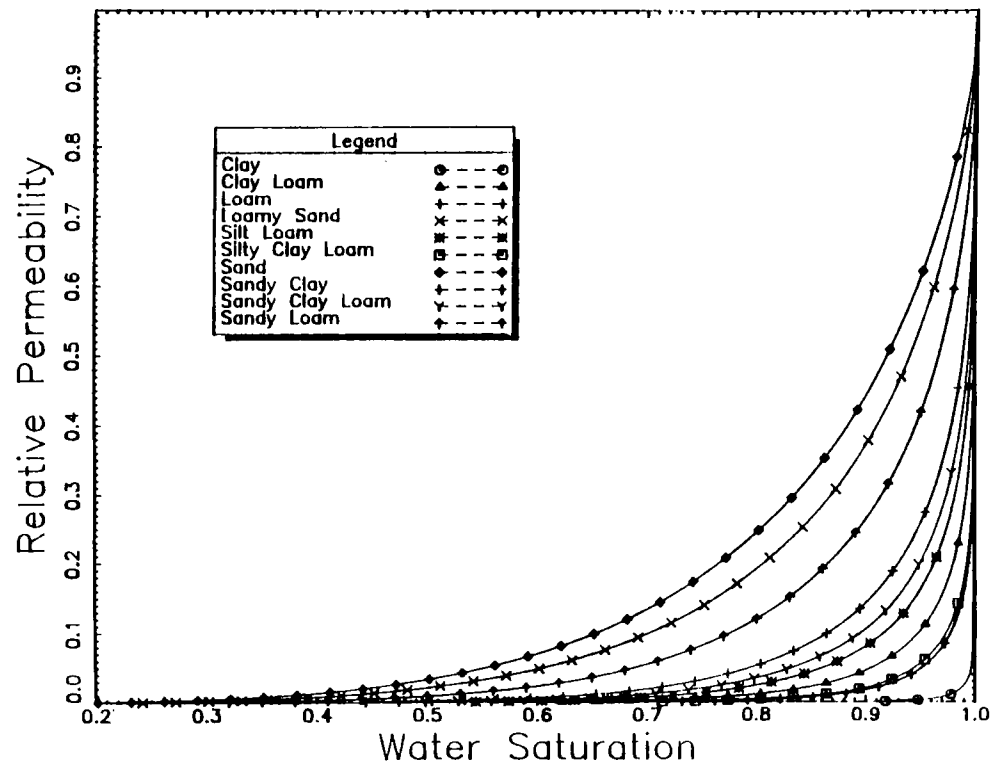
Bouwer (1978)

Example of the relationships between pressure head and hydraulic conductivity for an unsaturated soil
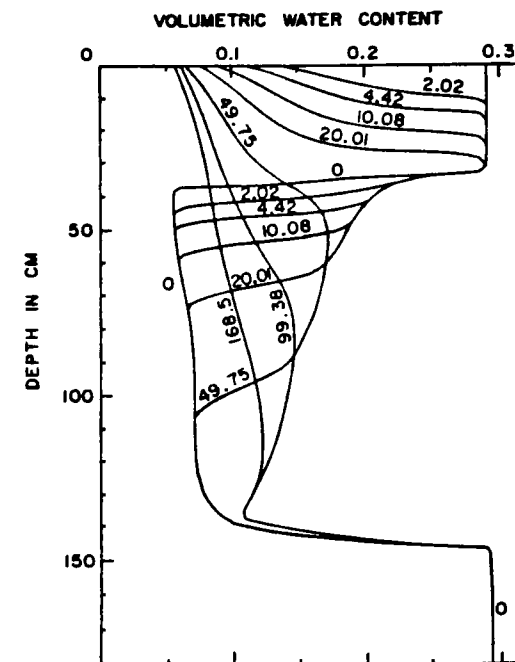
Calculated water-content profiles in sand at various times (in minutes on the curves) after cessation of infiltration.

Bouwer (1978)

SOIL VENTING

- OR STRIPPING INVOLVES THE FORCED MOVEMENT OF AIR THROUGH SOILS CONTAMINATED WITH VOLATILE ORGANIC COMPOUNDS
  - Increases volatilization of residuals

PILOT STUDY APPARATUS

Soil Contamination
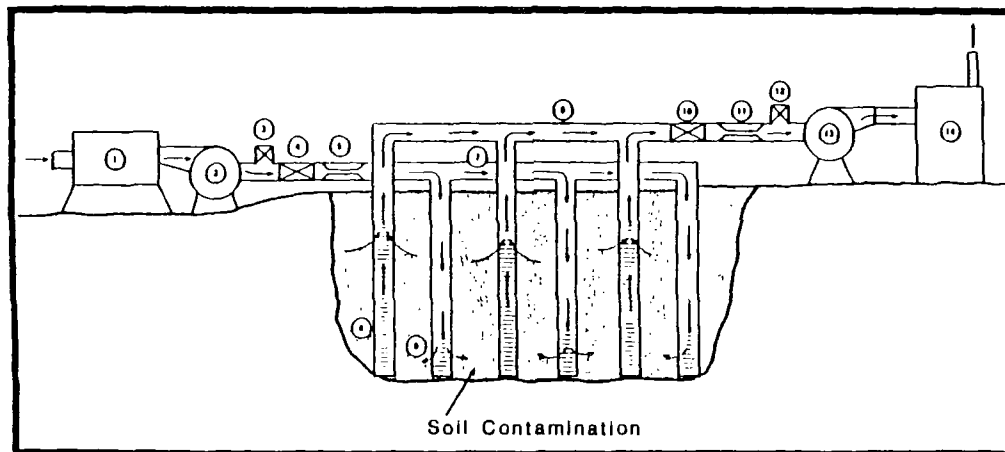
1 Electric Air Flow Heater	8 Slotted Vertical Extraction Vent Pipe (typ)
2 Forced Draft Injection Fan	9 Slotted Vertical Injection Vent Pipe (typ)
3 Injection Air Bypass Valve	10 Extraction Air Sampling Port
4 Injection Air Sampling Port	11 Extraction Air Flow Meter
5 Injection Air Flow Meter	12 Extraction Air Bypass Valve
6 Extraction Manifold	13 Induced Draft Extraction Fan
7 Injection Manifold	14 Vapor Carbon Package Treatment Unit

PRE-TREATMENT SHALLOW SOIL GAS CONCENTRATION

POST-TREATMENT SHALLOW GAS CONCENTRATION

WELLHEAD TCE CONCENTRATION VS TIME

EXTRACTION WELL #1
(SHALLOW)

$Y = 159.33 * EXP(-0.05X)$
Curve Coefficient $R2 = 0.62$

RF HEATING SYSTEM

Transition section
RF power feed point
Vapor barrier
Concrete pad
Pea gravel
Vapor collection manifold
Electrodes
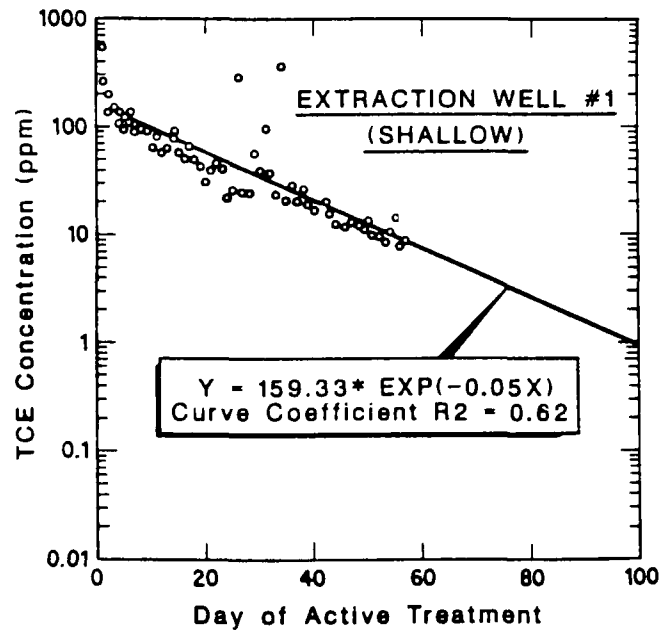
IN SITU HEATING

- **INVOLVES HEATING CONTAMINATED SOILS TO VAPORIZE HYDROCARBONS**
  - *For example using radio-frequency electromagnetic energy*
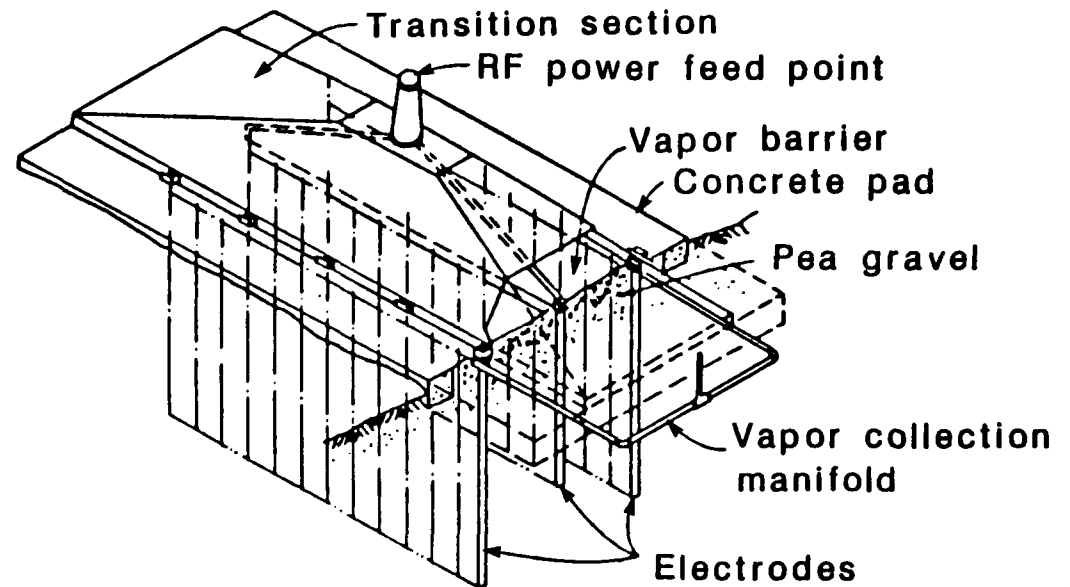
FIXATION

- **CHANGES PHYSICAL CHARACTERISTICS OF WASTE (BECOMES LESS WATER SOLUBLE AND TOXIC) AND DECREASES SURFACE AREA OF POLLUTANTS AVAILABLE FOR LEACHING**

PEPPER'S STEEL AND ALLOY SITE
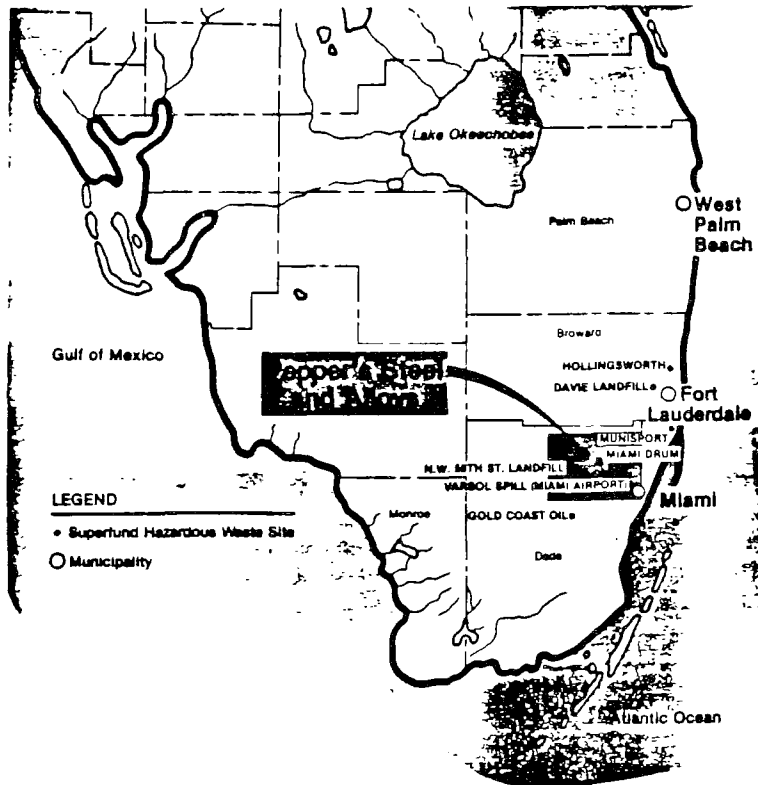
- PROBLEM – PCB S IN A SHALLOW SOIL

- GEOLOGY

  - Surficial sands ~ 5 feet thick

  - Limestone bedrock

- REMEDY

  - Fixation of oil soaked fill

  - Monitor bedrock groundwater quality

- METHODS

  - Kriging (statistical) – determine cleanup areas

  - Groundwater modeling – set ACL s

SCHEMATIC SW-NE SECTION THROUGH SITE

FILL

OIL

PEAT

SAND

MARL & SAND

LIMESTONE
PINNACLES

BEDROCK

PCB — KRIGED MAP IN UPPER FILL LAYER (WITHOUT TOP .5 FT)
PLOT NO. 1   DATE 01/27/88   TIME 12:19:48

SITE WATER
DRAINAGE
PEPPERS STEEL AND ALLOYS SITE
MEDLEY, FLORIDA
PREPARED FOR
FLORIDA POWER AND LIGHT
Canonie Environmental
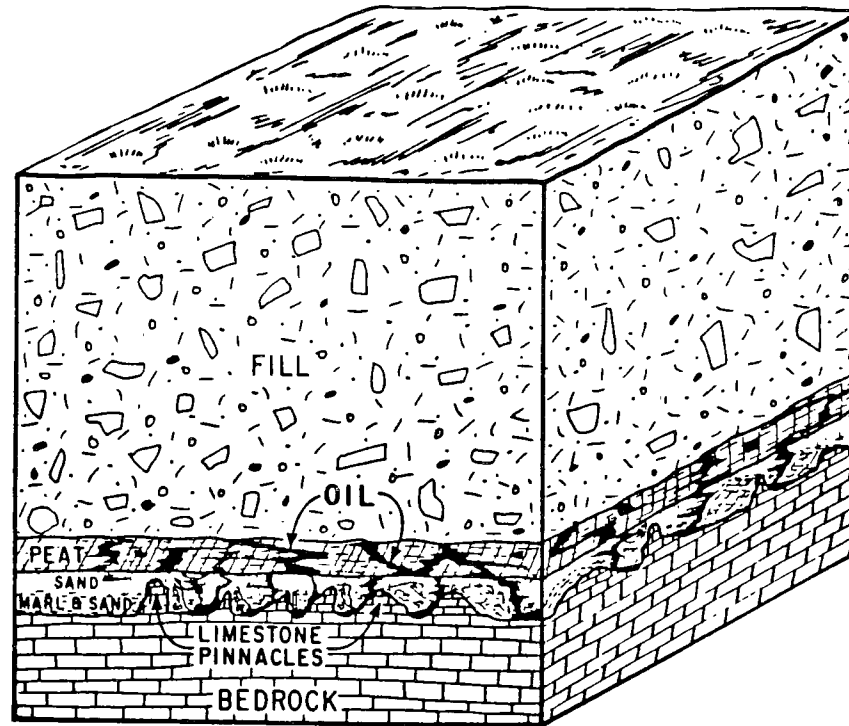
TREATMENT OF CONTAMINATED SOILS
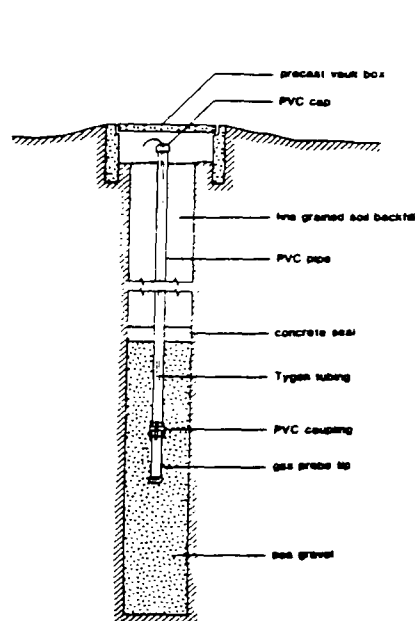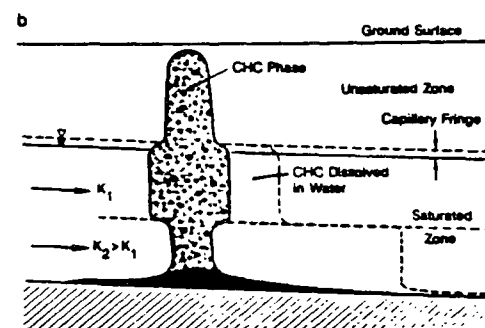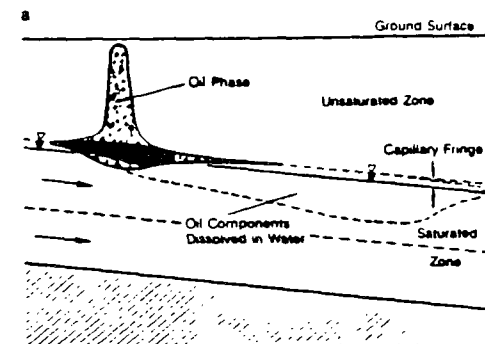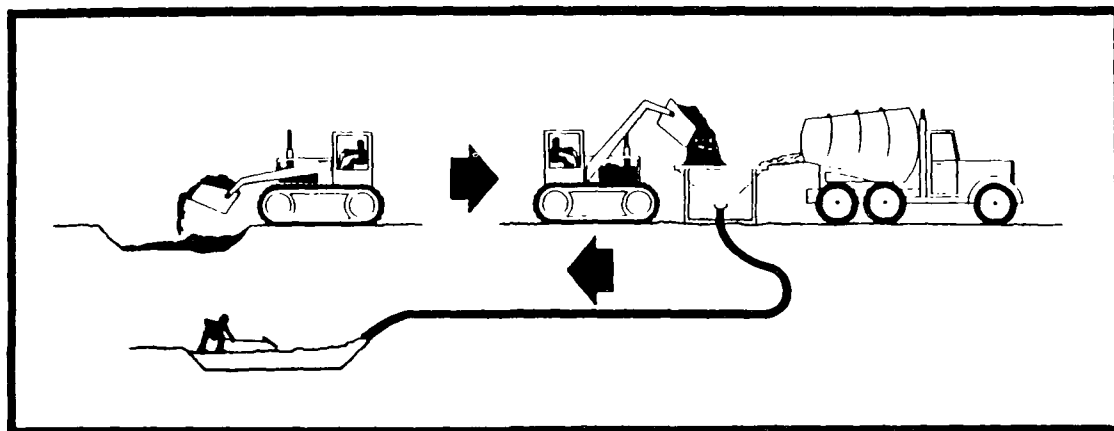
Landfill gas sampling probe
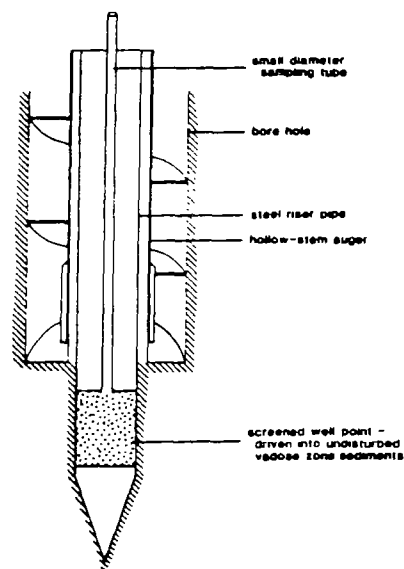
Vadose-zone sampling probe

The flow of a nonaqueous phase liquid that is (a) less dense than water (oil), and (b) more dense than water (chlorohydrocarbon) in the unsaturated and saturated zones. In both cases the contaminants are also transported as dissolved compounds in the ground water (from Schwille, 1984).

CENTER FOR

EXPOSURE ASSESSMENT MODELING

Robert B. Ambrose, Jr., P.E.
Manager

Center for Exposure Assessment Modeling
Office of Research and Development
U.S. Environmental Protection Agency
Athens, GA   30613

Distribution of Model Codes and Manuals	Training in Model Applications	Expert Advice on Solving a Problem	In-depth Participation in Planning and Conducting Priority Projects

Exposure Evaluation Division (EED) of OPTS

Graphical Exposure Modeling System (GEMS)

SESOIL   SEasonal SOIL compartment model

AT123D

PRZM
(1-D Flow and Transport)

VADOSE ZONE MODEL

VADOFT
(1-D Flow and Transport)

SATURATED ZONE MODEL
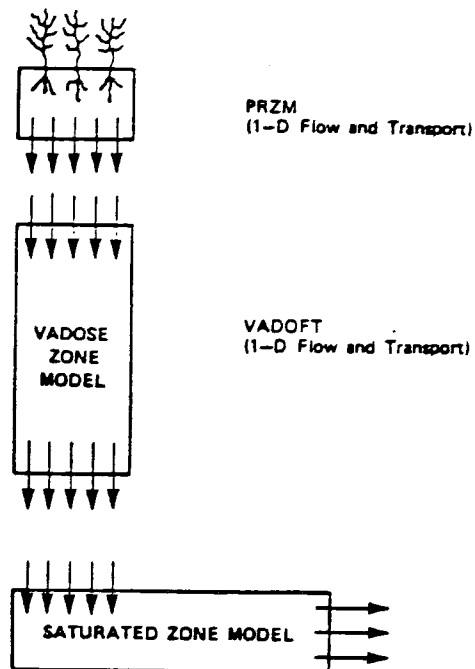
SAFTMOD
(2-D Flow and Transport)

JOE WILLIAMS

KERR ENVIRONMENTAL RESEARCH LABORATORY

ADA, OKLAHOMA

MODELS:

RITZ

PESTAN

BIOPLUME II

CHEMFLO

VADOSE ZONE SUMMARY

- more difficult to characterize than the saturated zone

- vadose and saturated zones are part of a continuous subsurface system; remediation decisions must address both zones

  — treatment trains

- 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 a zone of significant biodegradation

- it is a pathway for the transport of gases and volatile organics

Catalog of Methods for Monitoring Water Content in the Vadose Zone

Method	Principle	Advantages	Disadvantages	References
1. Gravimetric a. Oven drying	Core samples are obtained from the vadose zone using tube samplers for shallow depths and hollow stem auger plus core sampling for greater depths. A core sample is weighed, oven dried at 105 C for 24 hours, and reweighed. The water content is determined by difference in weight. Results expressed on a dry weight or volume basis. The difference in water content values of successive samples represents change in storage.	1. A direct method. 2. The most accurate of available methods. 3. Simple.	1. A large number of replicate samples are required for each depth increment (necessitating several holes) to account for spatial variability of water holding properties. 2. Expensive if large numbers of samples are required. 3. A destructive method—i.e., additional measurements cannot be obtained at the same sites.	Gardner (1965), Hillel (1971), Schmugge, Jackson and McKim (1980), Reynolds (1970a, 1970b), Brakensiek, Osborn and Rawls (1979).
b. Carbide method	A field method. Solids samples are placed in a container with calcium carbide. The calcium carbide reacts with water, releasing a gas. The gas pressure, registered on a gage, is converted into water content on a dry weight basis.	1. More rapid than oven drying. 2. Initial capital investment is lower than for oven drying.	1. May not be as accurate as oven drying. 2. Other disadvantages are the same as for oven drying.	
2. Neutron moisture logging (neutron scatter method)	A source of high energy neutrons (e.g., amerecium-beryllium) in a down-hole tool is lowered into an access well. Water in the vadose zone slows down the fast neutrons, which are captured by a detector in the tool. Counts are measured by a surface scaler, ratemeter, or recorder. Counts are converted into volumetric water content by an appropriate calibration relationship. Successive readings show temporal changes in water storage at successive depths.	1. Rapid. 2. An in-situ method. 3. Can be conducted in cased or uncased holes (for safety in unstable material should install casing). 4. Can be interfaced with portable data collection system. 5. Successive readings are obtained in the same profile at the same field location. 6. Can be used to locate perched ground-water zones. i.e., valuable for positioning monitoring wells for sampling perched ground water.	1. Expensive, requiring the purchase or lease of equipment. 2. Water content is measured in a sphere. Cannot relate results exactly to a specific depth. 3. Fast neutrons are moderated by other constituents besides hydrogen in water, e.g., chlorine or boron. Accuracy may be affected. 4. During installing of access wells, cracks or cavities may be formed causing leakage along the casing wall. 5. An indirect method requiring calibration. Calibration is a difficult procedure. 6. Accurate readings are not possible within 6 in. of soil surface. 7. Cannot be used to infer water movement in regions where storage changes do not occur.	Holmes, Taylor and Richards (1967), van Bavel (1963), Keys and MacCary (1971), McGowan and Williams (1980), Schmugge, Jackson and McKim (1980), Wilson (1980), Hillel (1971), Brakensiek, Osborn and Rawls (1979), Visvalingum and Tandy (1972).

Method	Principle	Advantages	Disadvantages	References
3. Gamma ray attenuation. a. Transmission method.	Two parallel wells installed at precise distances apart are required. A probe with a gamma photon source (e.g. cesium 137) is lowered in one well. A second probe with a detector (e.g. sodium iodide scintillation crystal) is lowered at the same rate in the second well. Accessories include a high-voltage supply. amplifier. scaler. timer. spectrum analyzer. pulse height analyzer and photomultiplier tube. The degree to which a beam of monoenergetic gamma rays is attenuated depends on the bulk density and water content. Assuming that the bulk density remains constant. changes between readings reflects changes in water content.	1. A rapid. in-situ method. 2. Water content is obtained in a narrow beam—depth-wise measurement can be obtained as close as one inch apart. 3. Measurements can be obtained within one inch of surface. 4. Nondestructive and successive measurements are obtained at same locations. 5. Can be interfaced with portable data collection system.	1. Limited to shallow depths because of difficulties in installing precisely parallel wells. particularly in rocky material. 2. Instabilities in count rate may occur. 3. Expensive. 4. Changes in bulk density in shrinking-swelling material affects accuracy of water content readings. 5. Variations in water content and bulk density occur in stratified soils. 6. Care must be taken in handling radioactive source.	Brakensiek. Osborn and Rawls (1979). Gardner (1965). Bouwer and Jackson (1974). Reginato and van Bavel (1964). Reginato and Jackson (1971). Schmugge. Jackson and McKim (1980).
b. Scattering method.	A single probe is used, containing a gamma source and a detector. separated by a lead shield. Gamma rays beamed into the surrounding media are absorbed by the solid media and water. Back-scattered rays are detected and measured. Knowing the dry bulk density of the media. the water content can be calculated. Requires empirical calibration curves.	1. Rapid. 2. Nondestructive. with successive measurements obtained at same depth. 3. In contrast to the transmission method only one access well is required. Readings can be obtained at great depth in vadose zone.	1. Requires a source of higher strength than transmission method. 2. Not as accurate as transmission method because water content measured in sphere and not a beam. 3. Expensive. 4. Changes in bulk density in shrinking. swelling material changes calibrations.	Keys and MacCary (1971). Brakensiek. Osborn and Rawls (1979). Paetzold (1979).
4. Tensiometers	A tensiometer consists of a porous ceramic cup cemented to rigid plastic tube. containing small diameter tubing leading to a surface reservoir of mercury. Alternate version uses strain gage transducer in lieu of mercury manometer. The body tubing is filled with water. Pores in cup form continuum with pores in exterior medium. Water moves into or out of body tube until equilibrium is reached. Measured water pressure reflects corresponding water pressure in medium. By using appropriate soil water characteristic curve. pressure can be related to water content.	1. Provide continuous. in place measurements of water content. 2. Successive measurements are obtained. 3. Inexpensive and simple. 4. Transducer units respond fairly rapidly to water content changes.	1. Units fail at the air entry value of the ceramic cup. generally about -0.8 atmospheres. 2. Results are subject to hysteresis. that is. different results are obtained for wetting vs. drying media. 3. If proper contact is not made between cup and media units will not operate properly. 4. Sensitive to temperature changes. 5. Difficult to install at great depth in vadose zone.	Brakensiek. Osborn and Rawls (1979). Holmes. Taylor and Richards (1967). Bianchi (1967). Galron and Hadas (1973). Schmugge. Jackson and McKim (1980). Wilson (1980). Oaksford (1978).

Method	Principle	Advantages	Disadvantages	References
5. Electrical resistance blocks	Blocks consist of electrodes embedded in porous material (plaster of paris, nylon, cloth, fiberglass). Water content of blocks change with water content of soil. Electrical properties of blocks change with changing water content. Electrical properties are measured using a meter. Calibration curves must be obtained.	1. Can be interfaced with portable data collection system. 2. Can be used at soil water pressures less than -0.8 atmospheres. 3. Gypsum blocks are inexpensive. 4. Precision is good.	1. Subject to hysteresis. 2. May be difficult to install at great depth in vadose zone and maintain good contact. 3. Requires calibration for each textural type in profile. 4. Lack of insensitivity in wet range. 5. Sensitivity to soil salinity (except gypsum blocks). 6. Gypsum blocks deteriorate badly in certain media. 7. Calibration curves of some units shift with time. 8. Time lag in response.	Brakensiek, Osborn and Rawls (1979). Holmes, Taylor and Richards (1967). Phene, Hoffman and Rawlins (1971). Schmugge, Jackson and McKim (1980). Galron and Hadas (1973).
6. Thermocouple psychrometers/hygrometers	A psychrometer unit consists of a porous bulb with a chamber in which the relative humidity of the exterior media is sampled: a sensitive thermocouple, a heat sink, reference electrode, and electrical circuitry. The unit operates on the principle that a relationship exists between soil water potential and relative humidity. Two types are available, the wet bulb type and the dew point type. Both types rely on cooling of the thermocouple junction by the Peltier effect. In the wet bulb type, when the temperature of the junction is reduced below the dew point, cooling is discontinued. As condensed water evaporates, the temperature increases to ambient. Signal from the junction at the temperature plateau is proportional to relative humidity. In the dew point type, the temperature at junction is held constant at dew point. The thermocouple signal corresponds to dew point depression, and thus to the relative humidity. Different methods are required for the two types. The dew point method is more accurate. Calibration curves relating relative humidity to water potential are required. Water potential and water content are related through a characteristic curve for each material.	1. In-situ pressure measurements are possible down to -50 atmospheres, permitting the determination of water contents in the very dry range. 2. Permits continuous recording of pressures (and water contents) at the same depth. 3. Can be interfaced with portable or remote data collection systems. 4. Some units have been installed to great depth (down to 300 feet).	1. Results are subject to hysteresis. 2. Good contact between bulb and surrounding media may be difficult to obtain. 3. Provide point measurements only. 4. May be difficult to obtain accurate calibration curves for deep regions of the vadose zone. 5. Fragile, requiring great care in installation.	Rawlins and Dalton (1967). Merrill and Rawlins (1972). Enfield, Hsieh and Warrick (1973). Schmugge, Jackson and McKim (1980). Hanks and Ashcroft (1980). Briscoe (1979). Campbell, Campbell and Barlow (1973).

| 7. Heat dissipation sensor | Heat dissipation sensors operate on the principle that the temperature gradient to dissipate a given amount of heat in a porous medium of low conductivity is related to water content. In practice, the water content of a soil can be measured by applying a heat source at a central point within the sensor and measuring the temperature rise at that point. Calibration curves of matric potential vs. temperature difference are obtained using a pressure plate apparatus with soils from the site. The matric potential is related to water content by preparing a water characteristic curve. Commercial sensors consist of a miniature heater, temperature sensors and circuitry, embedded in a cylindrical porous ceramic block within a small-diameter PVC tube, and a lead cable. | 1. Simple. 2. May be interfaced with a data acquisition system for remote collection of data. 3. Measurements are independent of salt content of soil. 4. Calibration appears to remain constant. 5. Can be used to measure soil temperature as well as matric potential. 6. Useful for measuring water contents in the dry range. | 1. Subject to hysteresis in the water characteristic. 2. Calibration is required for each change in texture. 3. May be difficult to install at depth in the vadose zone and maintain good contact between the sensor and medium. | Phene, Hoffman and Rawlins (1971a). Phene, Rawlins and Hoffman (1971b). Schmugge, Jackson and McKim (1980). |

Catalog of Methods for Monitoring or Estimating Flux of Wastewater in the Vadose Zone

Method	Principles	Advantages	Disadvantages	References
1. Infiltration at land surface				
a. Impoundments				
(i) Water budget method	Entails solving for the seepage component of the water budget equation. That is: Inflow − Outflow = ± ΔS. $S_L = (I + P) − (D + E) ± ΔS.$ Where S_L = seepage loss I = inflow from all sources P = precipitation D = discharge E = evaporation S = storage Measurements of I, P, D, E. ΔS are required: requiring flumes, raingages, evaporation pan, and staff gages or water stage recorders. Calibration curve or table of head vs. surface area is required.	1. Averages intake rate for the entire surface area of the pond (sides and bottom). 2. Measurements do not interfere with normal pit operation.	1. Time consuming and expensive. 2. Errors in measurements of auxiliary parameters affect accuracy in estimating seepage. 1. May cause inconvenience to pond operator. 2. The measured instantaneous rate does not account for rate fluctuations caused by fluctuations in inflow and outflow components.	Bouwer (1978).
(ii) Instantaneous rate method	By shutting down all inflows to a pond and all discharges from a pond, the water level will recede primarily as a result of infiltration. That is, all the components of the water budget equation are set equal to zero except for infiltration, evaporation and change in storage. Measuring ΔS for a short time provides a value for infiltration rate (neglecting evaporation).	1. Simple and inexpensive. 2. Errors in measuring auxiliary components do not enter into calculations. 3. Estimates average intake rate for entire surface area of pond.		
(iii) Seepage meters	Seepage meters are cylinders, capped at one end and open at the other end. The open end of the cylinder is forced into the pond surface and seepage is equated to the outflow from the cylinder when pressure heads inside and outside the cylinder are equal. Types include: the SCS seepage meter, the USBR seepage meter and the Bouwer-Rice seepage meter.	1. Inexpensive. 2. Simple to operate. 3. Uses only one piece of equipment. i.e., reduces the overall error compared to using several measuring devices as with water budget.	1. Measures seepage at discrete points and a large number of measurements are required to obtain "average" intake rates (including both sides and bottom points). 2. Operator will need to swim underwater to install units in bottom of pond.	Bouwer (1978). Bouwer and Rice (1963). Kraatz (1977).
b. Land treatment areas and irrigated fields				
(i) Water budget method	See impoundments: Water budget method. Inflow and outflow from fields are measured by flumes, weirs, etc. Evaporation equated to that from a free surface.	See impoundments: water budget method.	See impoundments: water budget method.	

Method	Principles	Advantages	Disadvantages	References
(ii) Infiltrometers	An infiltrometer is an open ended cylinder driven into the ground. The amount of water added to maintain a constant head in the cylinder is equated to infiltration rate. Types include single-ring and double-ring infiltrometers. In double-ring type both the outer and inner annular areas are flooded, ostensibly to minimize divergence in flow from inner area. Intake measurements are taken in the inner area.	1. Simple 2. Inexpensive 3. Portable	1. Provides point measurements only. 2. Because of spatial variability in soil properties a large number of readings required to estimate "average" infiltration. 3. Shallow, flow impeding layers affect results. 4. Divergence in subsurface flow occurs because of unsaturated flow (Bouwer recommends using single, large cylinder to minimize this problem). 5. Leakage along side walls may cause anomalously high rates.	Bouwer (1978), Dunne and Leopold (1978), Burgey and Luthin (1956), U.S. Environmental Protection Agency, U.S. Army Corps of Engineers and U.S. Department of Agriculture (1977).
(iii) Test basins	Large basins (e.g. 20 feet by 20 feet) are constructed at several locations in a field. The basins are flooded and intake rates are measured. Results are related to "average" intake rate for the field. (The water source to be used for field-sized operations should be used during testing.)	1. Provides more representative intake rates than infiltrometers-results can be used to design full-scale projects. 2. Simple.	1. Expensive. 2. Time consuming. 3. May be difficult to transport water to sites. 4. Shallow lenses of fine material will affect results by causing divergence of flow. 5. Spatial variability in soil properties affects results.	U.S. Environmental Protection Agency, U.S. Corps of Engineers and U.S. Department of Agriculture (1977).
2. Flux in the vadose zone. a. Water budget with soil moisture accounting.	The water budget method of Thornthwaite and Mather (1957) is applied to a given soil depth (e.g. root zone of an irrigated field; final soil cover on a landfill). Inflow components include rainfall and irrigation. Outflow components include runoff, evapotranspiration, drainage, and deep percolation (flux). Change in storage equals water content change in depth of interest. Flux equated to known inflow and outflow components and ΔS. Evapotranspiration may be most difficult component to measure (see Jensen, 1973 for alternative methods).	1. Estimates flux for entire area and not only points. 2. Computer programs are available to simplify calculations (e.g. WATBUG, Willmott, 1977).	1. Errors in measurement or estimation of components accumulate in estimates of flux.	Thornthwaite and Mather (1957), Willmott (1977), Mather and Rodriguez (1978), Fenn, Hanley and DeGeare (1975), Jensen (1973).

Method	Principles	Advantages	Disadvantages	References
b. Methods relying on water content measurements (e.g., draining profile methods).	Flux is related to water content changes in a given depth of the vadose zone. The relationship between flux and water content is expressed as follows: $$J = -\int_{o}^{z} \frac{\partial \theta}{\partial t}\, dz$$ Where J = flux, θ = water content, z = depth, and t = time. (This method is actually a profile-specific water budget with all terms except flux and storage change set equal to zero). Water content changes are measured by neutron logging, tensiometers, resistance blocks and psychrometers.	1. Simple. 2. Compared to methods relying on data for hydraulic gradients, a large number of measurements can be obtained with minimal cost and labor needs. 3. A large number of measurements using simple methods is more amenable to statistical analyses.	1. Errors in measuring devices affect results. 2. Spatial variability in soil hydraulic properties requires that a large number of measurements be obtained to obtain an "average" value. 3. Costly. 4. May not be suitable for measuring flux below impoundments of landfills because of difficulties in installing measuring units.	Libardi et al. (1980). Nielsen, Biggar and Erh (1973). Warrick and Amoozegar-Fard (1980). Bouwer and Jackson (1974). Wilson (1980).
c. Method requiring measurements of hydraulic gradients.	The method is based on solving Darcy's equation for unsaturated flow. $$J = K(\theta)\, i$$ where K(θ) designates that hydraulic conductivity is a function of water content θ; i = hydraulic gradient. Hydraulic gradients are measured by installing tensiometers, blocks or psychrometers. Calibration curves are required to relate negative pressure measurements to water content and water content to unsaturated hydraulic conductivity. Separate curves are required for each textural change.	1. A very precise method.	1. More complex than methods using water content values. 2. Results are subject to hysteresis in the calibration curves. 3. Expensive to install the requisite number of units for statistical analyses. 4. May not be suitable for ponds or landfills. 5. Generally restricted to shallow depths in the vadose zone.	LaRue, Nielsen and Hagan (1968). Bouwer and Jackson (1974). Wilson (1980).
d. Method based on assumption that hydraulic gradients are unity.	Same as above except that unit hydraulic gradient is assumed so that $J = K(\theta)$. Only one pressure measuring unit is required at each depth of interest to permit estimating θ from a pressure vs. water content curve. K(θ) is estimated from a separate curve. (For a more complex version of this method see Nielsen, Biggar and Erh, 1973.) An alternative approach is to use the relationship $J = K(\psi_m)$, which requires a curve showing the changes in hydraulic conductivity with metric potential (ψ_m). Bouma, Baker and Veneman (1974) described the so-called "crust test" for preparing a K(θ) vs. ψ_m curve. This field procedure is carried out on cylindrical columns.	1. Simpler and less expensive than methods requiring gradients.	1. Assumption of unit hydraulic gradients may fail, particularly in layered media. 2. Results are subject to hysteresis in calibration curves. 3. May not be suitable for ponds or landfills. 4. More complex than methods requiring soil moisture evaluation. 5. Large number of units required to offset spatial variability in soil properties.	Nielsen, Biggar and Erh (1973). Bouwer and Jackson (1974). Warrick and Amoozegar-Fard (1980) and Bouma, Baker and Veneman (1974).

Method	Principles	Advantages	Disadvantages	References
	constructed in a test pit. Each column is instrument-ed with a tensiometer, a ring infiltrometer, and gypsum-sand crusts. A series of crusts are used during different runs to impose varying resistances to flow. During each run, infiltration rates and ten-siometer values are mon-itored.			
e. Flowmeters	Flux is measured directly using flowmeters. Princi-ples of two available types are as follows: (1) direct flow measurement using a sensitive flow transducer, and (2) flow is related to movement of a heat pulse in water moving in a por-ous cup buried in the soil. Calibration curves are re-quired for second type.	1. Do not require in-formation on hy-draulic conductivity or hydraulic gradi-ents.	1. Disturbance of soil dur-ing installation may af-fect results. 2. Convergence/divergence problems arise in the flow field. 3. Limited range of soil types and fluxes. 4. Calibration procedures are tedious. 5. Applicability to deeper regions of the vadose zone is questionable.	Cary (1973), Dirksen (1974a), Dirksen (1974b).
f. Methods based on estimating or measuring hy-draulic conductiv-ity, K (I) Laboratory methods.	The premise of these methods is that if K values are available the flux can be estimated by assuming hydraulic gradients are unity, and that Darcy's law is valid.			
(aa) Permea-meters	Cylindrical cores of vadose zone sediments are placed in tight fitting metal or plastic cylinders. Water is applied to the cores and outflow is metered. The head of water applied to cores may be either con-stant head or falling. Appropriate equations are solved to determine K, knowing head values, ap-plication rates and dimen-sions of the container. Primarily for saturated K.	1. Simple 2. May be used to deter-mine variations in K values because of stratifications.	1. Expensive if a large number of samples are required. 2. Accuracy of method is questionable because of wall effects. 3. Not an in-situ method—results will be affected by spatial variability of hydraulic properties in vadose zone.	Bouwer (1978), Freeze and Cherry (1979).
(bb) Relation-ships be-tween hydraulic conduct-ivity and grain-size.	Grain-size distribution curves are obtained for samples of vadose zone material. The hydraulic conductivity is calculated from equations which ac-count for a representative grain-size diameter or from the spread in the gradation curve. Primarily for satur-ated K.	1. A "first cut" method if other data are un-available. 2. May be used to esti-mate relative varia-tions in K because of stratification.	1. Accuracy is question-able. 2. A disturbed method—results may not be repre-sentative of in-situ values. 3. Expensive if grain-size values are unavailable. 4. Requires trained per-sonnel.	Freeze and Cherry (1979) and references therein.
(cc) Cata-log of hydraulic proper-ties.	A catalog of hydraulic pro-perties of soils, prepared by Mualem (1976) is con-sulted for soil types sim-ilar to vadose zone sedi-ments. Both saturated and unsaturated K values are reported.	1. Simple. 2. A quick method. 3. May be used to estim-ate relative varia-tions in K because of stratification. 4. Inexpensive—provi-ded that grain-size data are available.	1. Problems arise because of hysteresis in unsatu-rated K. 2. Because of errors in measuring K (θ), values for a particular soil type may not be transferable to similar types. To ob-tain a closer estimate K(θ) must be evaluated for each soil (Evans and Warrick, 1970).	Mualem (1976).

Method	Principles	Advantages	Disadvantages	References
(II) Field methods. (aa) Shallow methods. (aa1) Methods for measuring saturated K in the absence of a water table.	A portion of the soil zone is brought to saturation and saturated K is estimated for the flow system thus created. Appropriate measurements and equations are used to solve for K. Alternative methods include: (1) pump-in method. (2) air-entry permeameters. (3) infiltration gradient method. and (4) double tube method.	1. Each method has its own advantages—see Bouwer and Jackson (1974).	1. Each method has its own disadvantages—see Bouwer and Jackson (1974). 2. Because of air entrapment during tests complete saturation is not possible. Measured K values may be 1/2 actual values (Bouwer. 1978). 3. Several of the methods are based on the assumption that flow is entirely vertical—a false premise.	Bouwer and Jackson (1974).
(aa2) Instantaneous profile method.	The basis of this method is the Richards equation. rewritten as follows: $$K(\theta) = \dfrac{\partial\theta/\partial t}{\partial\psi_h/\partial z} z$$ In practice. a soil plot in the region of interest is instrumented with a battery of tensiometers. with individual units terminating at depths of interest for measuring water pressures; and with an access tube for moisture logging. The soil is wetted to saturation throughout the study depth. Wetting is stopped and the surface is covered to prevent evaporation. Water pressure and water content measurements are obtained during drainage. Curves of ψ_h vs. z and θ vs. t are prepared. Slopes of the curves at the depths of interest are used to solve for $K(\theta)$. Values of $K(\theta)$ at varying times can be used to prepare $K(\theta)$ vs. θ and $K(\psi_m)$ vs. ψ_m curves: (for a detailed description of the method. including step by step procedures. see Bauma. Baker and Veneman. 1974)	1. Method can be used in stratified soils. 2. Simple. 3. Reasonably accurate. at least at each measuring site.	1. Provides hydraulic conductivity values only for draining profiles. Because of hysteresis. these values are not representative of the hydraulic conductivity during wetting cycles. 2. Because of spatial variabilities in soil hydraulic properties. a large number of sites must be used to obtain mean values of hydraulic conductivity. 3. Time consuming and relatively expensive.	Bouma. Baker and Veneman (1974).
(bb) Deeper methods. (bb1) USBR single well method.	Water is pumped into a borehole at a steady rate such that a uniform water level is maintained in a basal test section. Saturated K is estimated from appropriate curves and equations. knowing dimensions of the hole and inlet pipes. length in contact with formation. height of water above base of borehole. depth to water table. and intake rate at steady state. Two types of tests: (1) open-end casing tests. in which water flows only out of the end of the casing, and (2) open-hole tests. in which water flows out of sides and bottom.	1. May be used to estimate K at great depths in vadose zone. 2. A profile of K values may be obtained.	1. Solution methods are based on assumption that flow region is entirely saturated (free surface theory)—this is not true. 2. As a consequence of 1. K is underestimated. 3. Expensive and time consuming. 4. Requires skilled personnel to conduct tests.	U.S. Bureau of Reclamation (1977).

Method	Principles	Advantages	Disadvantages	References
(bb2) USBR multiple well method.	Used to estimate K in vicinity of widespread lenses of slowly permeable material. An intake well and series of piezometers are installed. Water is pumped into well at a steady rate and water levels are measured in piezometers. Appropriate curves and equations are used to determine K.	1. Results can be used to estimate lateral flow rates in perched ground-water regions.	1. Expensive and time consuming. 2. Requires trained personnel.	U.S. Bureau of Reclamation (1977).
(bb3) Stephens-Neuman single well method.	Stephens and Neuman (1980) developed an empirical formula based on numerical simulations using the unsaturated characteristics of four soils. That is, this approach accounts for unsaturated flow.	1. The formula can be used to estimate the saturated hydraulic conductivity of an unsaturated soil with improved accuracy. 2. No need to wait for steady state conditions—the final flow rate can be estimated from data during transient stage.	1. Needs field testing.	Stephens and Neuman (1980).
(bb4) Air permeability method.	Air pressure changes are measured in specially constructed piezometers during barometric changes at the land surface. Pressure response data are coupled with information on air-filled porosity to solve equations leading to air permeability. If the Klinkenberg effect is small, air permeability is converted to hydraulic conductivity.	1. Can be used to estimate hydraulic conductivity values of layered materials in the vadose zone.	1. An indirect method. 2. Presence of excessive water limits the utility of the method. 3. Expensive. 4. Time consuming. 5. Complex—requires trained personnel.	Weeks (1978).
3. Velocity in the vadose zone. a. Tracers	A suitable tracer (e.g. tritium, iodide, bromide, fluorocarbons) is introduced into the liquid source. (Alternatively, a tracer such as chloride already present in the source could be used.) Samples are obtained from suction cups at successive depths and tracer break-through curves are prepared.	1. A direct method. 2. Simple. 3. Accounts for flow in actual pores—a closer measure of the true velocity. 4. More accurate than methods requiring knowledge of components of Darcy's equation.	1. Analyses of tracers may be expensive. 2. Operation of suction samplers may affect natural flow field, leading to incorrect values. 3. In structured media the actual velocity may be higher than measured because of flow in cracks. 4. If velocities are slow, excessively long time periods will be required for tests.	Freeze and Cherry (1979). Frissel et al. (1974).
b. Calculation using flux values. $$v = \frac{J}{\theta}$$	Flux values obtained by methods described above are used, together with estimated or measured water content values, in the following relationship: where v = velocity, J = flux and θ = water content. Assumes that (1) hydraulic gradients are unity, (2) an average water content can be determined, (3) flow is vertical and (4) homogeneous media.	1. Inexpensive when coupled with other methods. 2. Simple. 3. A "quick and dirty" method for estimating the travel time of pollutants in the vadose zone.	1. Velocity will be higher in structured media than that calculated. 2. Method assumes vertical flow only—perching layers cause lateral flow. 3. For multilayered media an average θ and v value may be difficult to obtain.	Bouwer (1980). Wilson (1980).

Method	Principles	Advantages	Disadvantages	References
c. Calculation using long-term infiltration data.	The long-term infiltration rate. I. of the facility is assumed to equal the steady state flux J in the vadose zone. Consequently. $$v = \frac{I}{\theta} = \frac{J}{\theta}$$ Also assumes the (1) hydraulic gradients are unity. (2) average water content $= \theta$. (3) flow is vertical. and (4) homogeneous media.	1. Simple. 2. Probably satisfactory as first estimate of velocity. 3. Inexpensive.	1. Velocity will be higher in structured media than calculated. 2. Method assumes vertical flow only. Perching layers cause lateral flow. 3. For multilayered media an average θ and v may be difficult to obtain.	Bouwer (1980). Warrick (1981).

Catalog of Methods for Monitoring Pollutant Movement in the Vadose Zone

Method	Principles	Advantages	Disadvantages	References
1. Indirect methods a. Four probe electrical method	Used for measuring soil salinity in situ. Basically the method consists of measuring soil electrical conductivity using the Wenner four probe array. The apparent bulk soil conductivity is related to the conductivity of the saturated extract using calibration relationships.	1. An in-place method. 2. Readings are obtained quickly and inexpensively. 3. Can be used to detect the presence of shallow saline ground water. 4. Can be used to determine lateral transects of salinity. 5. By varying electrode spacing can be used to determine vertical changes in salinity. 6. The salinity in larger volumes of soil are measured compared to other methods.	1. Obtaining calibration relationships may be tedious. 2. Accuracy decreases in layered soils. 3. Chronological in situ changes cannot be measured except by taking sequential traverses. 4. Primarily used for shallow depths of the vadose zone. 5. Does not provide data on specific pollutants.	Rhoades and Halvorson (1977), Rhoades (1979a), Rhoades (1979b).
b. EC probe.	The EC (electrical conductivity) probe consists of a cylindrical probe containing electrodes at fixed spacing apart. The probe is positioned in a cavity and resistivity is measured at successive depths. Calibration required. Primarily used for land treatment areas and irrigated fields. An alternative version consists of inexpensive probes which can be permanently implanted for periodic measurements.	1. Changes in salinity are measured at discrete depths in stratified soils. 2. Measurements are obtained at greater depth than four electrode method. 3. The in-place units permit determining changes in salinity with time.	1. Individual calibration relationships are required for each strata—time consuming and expensive. 2. Variations in water content may affect results. 3. Primarily used for shallow depths of the vadose zone. 4. Does not provide data on specific pollutants.	Rhoades and Halvorson (1977), Rhoades and van Schilfgaarde (1976), Rhoades (1979a), Rhoades (1979c).
c. Salinity sensors.	Sensors consist of electrodes embedded in porous ceramic. When placed in soil the ceramic comes in hydraulic equilibrium with soil water. Electrodes measure the specific conductance of the soil solution. This method is most suitable for land treatment areas and irrigated fields, although sensors could be installed below ponds before ponds are put in operation. Calibration curves are required.	1. Simple, easily read and sufficiently accurate for salinity monitoring. 2. Readings are taken at same depths each time. 3. By installing units at different depths chronological salinity profiles can be determined. 4. Output can be interfaced with data acquisition systems.	1. More subject to calibration changes than four electrode method. 2. More expensive and less durable than four electrode method. 3. Time lag in response to changing salinity. 4. Cannot be used at soil water pressures less than -2 atmospheres. 5. Soil disturbance during installation may affect results. 6. Does not provide data on specific pollutants.	Rhoades (1979a), Oster and Ingvalson (1967), Richards (1966), Oster and Willardson (1971).
2. Direct methods. a. Solids sampling followed by laboratory extraction of pore water. Inorganic constituents.	Solids samples are obtained by hand or power auger and transported to a laboratory. Normally samples are taken in depth-wise increments. Samples are used to prepare saturated extracts (see Rhoades, 1979a, for method). Extracts are analyzed to determine the concentrations of specific constituents.	1. Depth-wise profiles of specific pollutants can be prepared. 2. Variations in ionic concentrations with changes in layering are possible. 3. Solids samples can be used for additional analyses such as grain size, cation exchange capacity, etc.	1. Because of the spatial variability of soil properties an inordinate number of samples are required to ensure representativeness. 2. Expensive, if deep sampling is undertaken. 3. Changes in soil water composition occur during preparation and extraction. 4. Samples should be extracted at prevailing water content, i.e., ionic composition changes during saturation. 5. A destructive method—samples cannot be retaken in exactly the same location. spatial variability in sediments precludes comparing successive results.	Rhoades (1979a), Rible et al. (1976), Pratt, Warneke and Nash (1976).

Method	Principles	Advantages	Disadvantages	References
b. Solids sampling for organic and microbial constituents—dry tube coring procedure.	A hole is augered to above the desired sampling depth. A dry-tube core sampler of special design is forced into the sampling region. Separate sub-samples are obtained for analyses of organics and microorganisms. Extreme care must be exercised to avoid contamination.	1. Contamination of samples is minimized c.f. other core sampling methods. 2. Additional sub-samples could be taken for chemical analyses.	1. Expensive and time consuming. 2. Difficult to obtain samples at great depth in vadose zone. 3. Samples cannot be obtained directly below impoundments. 4. A destructive method. 5. Results are affected by spatial variabilities in properties of the vadose zone.	Dunlap et al. (1977)
c. Ceramic type samplers (suction lysimeters). (i) Vacuum operated type.	A ceramic cup is mounted on the end of a small diameter PVC tube. A one-hole rubber stopper is pushed into opening in tube. A small diameter tube is forced through stopper, terminating at base of ceramic cup. Unit is placed in shallow soil depth. A vacuum is applied to the small tube and soil water moves through the ceramic cup. Sample is sucked out the small tubing into a collection flask. Samples are analyzed in the laboratory. When using such samplers extreme care must be exercised to prepare cups to remove sorbed ions. An acid treatment is recommended for this purpose. A variation of this type uses a filter candle in lieu of a suction cup.	1. A direct method for determining the chemical characteristics of soil water. 2. Samples can be obtained repeatedly at the same depths. 3. Inexpensive and simple. 4. Can be installed below shallow impoundments and landfills prior to construction, for later monitoring of seepage.	1. Generally limited to soil depths less than 6 feet. 2. Limited to soil water pressures less than air entry value of the cups (-1 atmosphere). 3. Point samplers—because of the small volume of sample obtained representativeness of results is questionable. 4. Pore water in the soil blocks is sampled. In structured soils, water moving through cracks may have different ionic composition than water in blocks. 5. Suction may affect soil-water flow patterns. Tensiometers must be installed to ensure that the proper vacuum is applied. 6. Samples may not be representative of pore water because technique does not account for relationships between pore sequences, water quality and drainage rates (Hansen and Harris, 1975).	Rhoades (1979a). England (1974). Hoffman et al. (1978).
(ii) Vacuum-pressure type.	A ceramic body tube contains a two hole rubber stopper. A small diameter tube is pushed into one opening, terminating at the base of the cup. A second tube pushed into the other opening terminates below the rubber stopper. The long line is connected to a sample bottle. The short line is connected to a pressure-vacuum source. When the unit is in place, a vacuum is applied to draw in exterior solution. Pressure is then applied to blow the sample into a flask.	1. Can be used at depths below the suction lift of water. 2. Several units can be installed in a common borehole to determine depth-wise changes in quality. Also: See advantages for vacuum operated type.	1. When air pressure is applied some of the solution is forced through the walls of the cup. Also: See disadvantages 2 through 6, vacuum operated type.	Rhoades (1979a). England (1974). Parizek and Lane (1970). Apgar and Langmuir (1971). Johnson and Cartwright (1980).

Method	Principles	Advantages	Disadvantages	References
(iii) High pressure-vacuum type.	The sampler is divided into two chambers. The lower chamber is a ceramic cup. Upper and lower chambers are connected via tubing with one-way valve. A plug in the upper chamber has two openings. One opening is connected by tubing to a pressure-vacuum source. The second opening is connected to a line within the upper chamber. This line contains a one-way valve. The line also extends to the surface, terminating in a collection flask. When vacuum is applied to one tube, solution is drawn into the upper chamber. When pressure is applied the one-way valve in base prevents sample from being forced out of cup. Sample is forced up the outlet line into collection flask.	1. Prevents air pressure from blowing sample out of cup. 2. Can be used at great depths. 3. Several units can be installed in a common borehole. Also: See advantages for vacuum operated type.	1. Same as for vacuum-pressure type except for disadvantage No. 1.	Wood (1973). Wood and Signor (1975).
d. Sampling perched ground water.	Perched ground-water regions frequently are observed in vadose zones, for example, in alluvial valleys in the west. Water samples may be extracted from perched ground-water regions for analyses. For shallow perched ground water, samples can be obtained by installing wells, piezometer nests or multilevel samplers. For deeper perched ground water, two possibilities exist: (1) sampling cascading water in existing wells, or (2) constructing special wells.	1. Large sample volumes are obtainable particularly desirable when sampling for organics and viruses. 2. Samples reflect the integrated quality of water draining from an extensive portion of overlying vadose zone—more representative than point samples. 3. Cheaper than installing deep wells with batteries of suction samplers. 4. Can be located near ponds and landfills without concern about causing leaks. 5. Nested piezometers and multilevel samplers can be used to delineate vertical and lateral extent of plumes and hydraulic gradients.	1. Perched zones may not be present in source area. 2. Detection of perched ground water may be expensive, requiring test wells or geophysical methods. 3. Some perched ground water regions are ephemeral and may dry up. 4. The method is most suitable for diffuse sources, such as land spreading areas or irrigated fields. 5. Multilevel sampling is restricted to regions with shallow water tables permitting vacuum pumping.	Wilson and Schmidt (1979). Schmidt (1980). Graf (1980). Pickens et al. (1981). Hansen and Harris (1974, 1980).

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SESSION II

Determination of Extent and Magnitude of Contamination in the Subsurface

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Dr. Michael J. Barcelona

Michael J. Barcelona received the B.A. and M.S. degrees in Chemistry from St. Mary's College (Winona, MN) and Northeastern University (Boston, MA) in 1971 and 1973, respectively. He received the Ph.D. degree in Marine Chemistry from the University of Puerto Rico (Mayaguez, P.R.) in 1976. He served as an instructor of marine chemistry and chemical oceanography while he completed his thesis on the interactions of natural organic compounds with gypsum in seawater. Following nearly three years as a research postdoctoral fellow in Environmental Engineering Sciences at Caltech (Pasadena, Ca) with Dr. James J. Morgan, Dr. Barcelona joined the Water Survey Division of the Illinois Department of Energy and Natural Resources in 1979.

Since 1980 he has been head of the Survey's Aquatic Chemistry Section, building form a group of 5 to the current 21 chemists and engineers. The Section provides research and services to State, Federal and industrial sponsors. As a Principal Scientist, Dr. Barcelona is involved in environmental research on a wide range of topics, including sampling, organic compound analysis, ground-water geochemistry and monitoring network design. He has authored more than 25 peer-reviewed publications and over 50 technical reports, many of which are in wide use in ground-water sciences.

PART 1. SUBSURFACE GEOCHEMICAL CONDITIONS: VARIABILITY, CONTROLLING FACTORS AND SAMPLING CONSIDERATIONS

 A. Nature of Variability in General
  1. Discussion of error; systematic vs. random
  2. Sources of error (sampling, analysis, siting, design, etc.)
 B. Subsurface Variability (Aquifer Properties, Water Quality, Geochemistry)
  1. Spatial (physical, chemical, biological)
  2. Temporal (physical, chemical, biological)
  3. Equilibrium versus kinetic controls on subsurface
   geochemistry - redox processes
  4. Summary
 C. Sampling Considerations
  1. Environmental sampling in general
  2. Sampling protocols for site characterization work
   a. scope and magnitude of the problem/Relation to
    sampling intervals and representativeness
   b. interactions between contaminated and uncontaminated sub-areas within the site
   c. choice of diagnostic parameters, analytes
   d. sampling protocols based on hydrogeologic data
   e. sampling experiments
   f. refined sampling protocol
   g. transition from characterization work to monitoring remediation efforts

A. Nature of Variability in General

B. Subsurface Variability (Aquifer Properties,

   Water Quality, Geochemistry)

C. Sampling Considerations

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┌──────────────────┐     ┌──────────────────┐     ┌──────────────────┐     ┌──────────────────┐
│       SITE       │     │     SAMPLING     │     │   MEASUREMENT    │     │       DATA       │
│    SELECTION     │     │                  │     │     METHODS      │     │     HANDLING     │
│                  │────▶│                  │────▶│                  │────▶│                  │
│      S²g         │     │      S²s         │     │      S²m         │     │      S²d         │
│                  │     │                  │     │                  │     │                  │
│ S²g = S²VERT. +  │     │ S²s = S²SYSTEMATIC + │  │                  │     │                  │
│   S²HORIZ.       │     │  S²RANDOM + S²NAT'L. │  │                  │     │                  │
└──────────────────┘     └──────────────────┘     └──────────────────┘     └──────────────────┘
                                                            ▲
                                                   ┌──────────────────┐
                                                   │    REFERENCE     │
                                                   │     SAMPLES      │
                                                   │                  │
                                                   │      S²r         │
                                                   │                  │
                                                   └──────────────────┘
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$S_g^2 = S_{VERT.}^2 + S_{HORIZ.}^2$

$S_s^2 = S_{SYSTEMATIC}^2 + S_{RANDOM}^2 + S_{NAT'L.}^2$
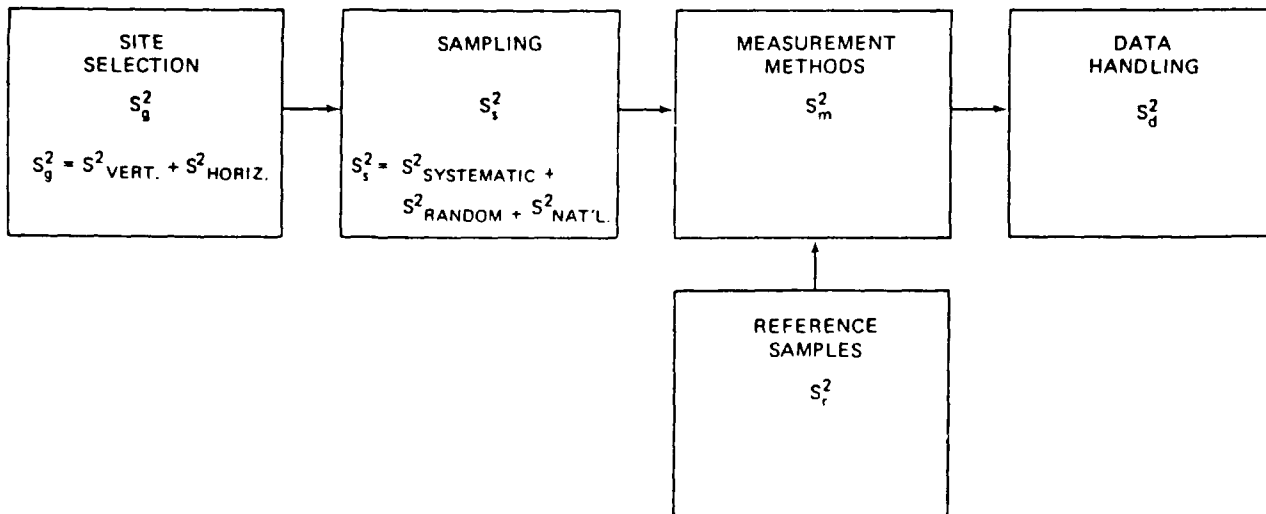
Thus the overall variance $= S^2 = S_g^2 + S_s^2 + S_m^2 + S_r^2 + S_d^2$

Sources of error involved in ground-water monitoring programs contributing to total variance

<u>PURPOSE</u>

- OUTLINE BASIC INFORMATION NECESSARY TO MAKE INFORMED DECISIONS ON: NATURE AND EXTENT OF CONTAMINATION, REMEDIATION SCHEMES, LIFE CYCLE COSTS, ETC.

- PROVIDE REFERENCES ON SAMPLING (THE EYE OF THE NEEDLE!)

- RECOGNIZING THAT WE NEVER HAVE ENOUGH DATA

<u>MONITORING SCALES</u>

(DEGREE OF HOMOGENEITY AND BASIS FOR INTERPRETATION)

REGIONAL	(10's to 100's of kilometers)
LOCAL	(kilometer)
SITE	(meters)

<u>ASSUMPTIONS</u>

- WHAT YOU DON'T OBSERVE CANNOT BE REMEDIATED

- ALL OBSERVATIONS ARE TIME DEPENDENT

- HYDROGEOLOGY PROVIDES THE BASIS FOR JUDGING REPRESENTATIVENESS <u>AND</u> THE BASIS FOR <u>ANY</u> CHEMICAL INTERPRETATION

- OBJECTIVES INCLUDE A <u>CONTROLLED</u> DATA COLLECTION EFFORT

<u>CHEMICAL DATA RESOLUTION</u>

REGIONAL	(CARBONATE EQUILIBRIA IN LIMESTONE AQUIFERS)
LOCAL	(RECHARGE OF OXYGENATED WATER)
SITE	(POLLUTANT OF THE MONTH IN THE BACKYARD)

<u>MONITORING SYSTEMS/PURPOSES</u>

(EVOLVE TOWARDS INCREASING COMPLEXITY)

DETECTION (SOURCE?)

ASSESSMENT (APPROXIMATE MAGNITUDE)

EVALUATION (SEVERITY, EXTENT, AND VARIABILITY)

SCOPE (LIFE-CYCLE COST ANALYSIS)

REMEDIATION (FINAL WASH)

<u>MAJOR MESSAGES</u>

- INCREASED VERTICAL RESOLUTION AND DETAIL OF BOTH SUBSURFACE GEOCHEMISTRY AND CONTAMINANT DISTRIBUTIONS

- QUARTERLY SAMPLING AS A STARTING POINT, AND HIGHER FREQUENCIES FOR REACTIVE CHEMICAL CONSTITUENTS

- RECOGNITION OF MAJOR SOURCES OF UNCERTAINTY IN PROBLEM ASSESSMENT AND THE <u>PROBABILITY</u> OF SUCCESS IN REMEDIATION (WE NEVER HAVE ENOUGH INFORMATION)

1. Discussion of error; systematic vs. random

2. Sources of error (sampling, analysis, siting, design, etc.)

FIGURE 1
Water Research Centre interpretation of the bull's-eye analogy
for describing analytical error

(a) Large random errors,
   no systematic errors
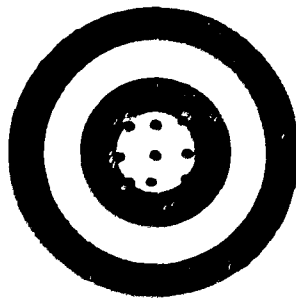
(b) Small random errors,
   no systematic errors

(c) Small random errors,
   large systematic errors

(d) Large random errors,
   large systematic errors

$(R.B. MURPHY)$
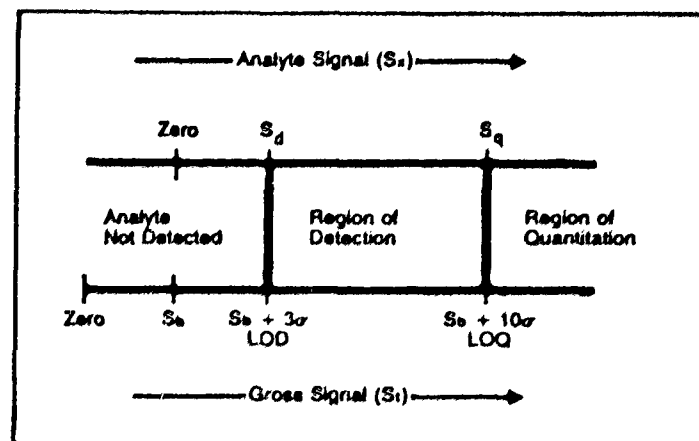
Figure 1. The limit of detection (LOD) is located 3σ above the measured average blank. The limit of quantitation is 10σ above the blank. These are the minimal criteria recommended by these guidelines.

Table I. Regions of Analyte Measurement

analyte signal (S_x)	recommended inference
$<3\sigma$	analyte not detected
3σ to 10σ	region of detection
$>10\sigma$	region of quantitation

NATURE OF UNCERTAINTY

— SUBSURFACE ENVIRONMENTAL CONDITIONS

o LACK OF KNOWN "TRUE" VALUES

IDENTIFICATION OF THE SAMPLE POPULATION

-- HYDROGEOLOGIC INHOMOGENEITY

-- HYDROGEOLOGY AND SAMPLING WELL DESIGN

NATURE OF UNCERTAINTY IN GROUND-WATER CHEMISTRY

-- ENVIRONMENTAL CONDITIONS

o LACK OF KNOWN "TRUE" VALUES

o COMPLEX, LIVING, DYNAMIC SYSTEMS

o SPATIAL AND TEMPORAL VARIABILITY

o ANTHROPOGENIC DISTURBANCE

o EQUILIBRIUM VS. KINETIC CONTROL

-- SAMPLING AS A SELECTION PROCESS:
PROTOCOL DEVELOPMENT

-- ERROR IDENTIFICATION AND CONTROL MEASURES

-- SUMMARY

CERTAINTY IN GROUND-WATER CHEMICAL MEASUREMENTS

WELL DESIGN -- DRILLING

CONSTRUCTION/SCREEN DESIGN/
DEVELOPMENT

MATERIALS

PURGING PROCEDURES

SAMPLING DEVICES

SAMPLING HANDLING/ON-SITE ANALYSIS

SAMPLING STORAGE/PRESENTATION

RECOGNITION OF UNCERTAINTY

B. Subsurface Variability (Aquifer Properties, Water Quality, Geochemistry)

1. Spatial (physical, chemical, biological)

2. Temporal (physical, chemical, biological)

3. Equilibrium versus kinetic controls on subsurface geochemistry - redox processes

4. Summary

-- SUBSURFACE ENVIRONMENTAL CONDITIONS

o PHYSICAL VARIABLES: TEMPERATURE AND PRESSURE

	EFFECTS	NATURAL	DISTURBED
T	MIXING, REACTION PATHS AND RATES	3°-20°C	3°-35°C
	SOLUBILITY CONSIDERATIONS	(Δ 10-15 C°)	(Δ 10-25 C°)
	(DEPTH VARIATIONS)		
	(SOURCE VARIATIONS)		
P	GAS SOLUBILITY	1-10 bar	1-1000 bar
	PERMEABILITY AND POROSITY		

-- SUBSURFACE ENVIRONMENTAL CONDITIONS

o PHYSICAL VARIABLES (cont'd.): FLOW VELOCITY

	HYDRAULIC EFFECTS	NATURAL	DISTURBED
	HEAD DIFFERENCES/GRADIENTS		
V ($m \cdot d^{-1}$)	PUMPING	<1-10	<1-100
	MIXING	<1-1000	<1-1000

-- SUBSURFACE ENVIRONMENTAL CONDITIONS

o BIOLOGICAL VARIABLES

		NATURAL	DISTURBED
BIOMASS	CATALYTIC OR TRANSFORMATION POTENTIAL	10^1-10^8 (cells·g^{-1})	10^4-10^8 (cells·g^{-1})
ACTIVITY	TURNOVER RATES	0.1 µg·L^{-1}·hr^{-1}	?
V_{MAX} Glucose (Specific activity)	METABOLIC STATUS	(0.03-0.06 x 10^{-9} glucose·h^{-1}· $cell^{-1}$)	

-- SUBSURFACE ENVIRONMENTAL CONDITIONS

o CHEMICAL VARIABLES: RANGES

	NATURAL	DISTURBED
pH	5.5-9.5	3-12
Conductance (µS·cm^{-1})	+5,000 to 100	>10,000 to 100
Eh (mv)	+600 to -100	+600 to -250
Dissolved Oxygen (mg·L^{-1})	-10 to <0.3	>10 to <0.3
Alkalinity (mg·L^{-1} $CaCO_3$)	1,000 to 100	>1,000 to <100

-- SUBSURFACE ENVIRONMENTAL CONDITIONS

   o CHEMICAL VARIABILITY: SPATIAL

	SITE SCALE	LARGE SCALE
HORIZONTAL		
O_2	-0.01 to +0.5 $(mg \cdot L^{-1}/m^{-1})$	0.3 to 1 $(mg \cdot L^{-1} \cdot km^{-2})$
Fe^{2+}		
Eh	-3 to 1 (mv/m^{-1})	-0.5 to -180 $(mv \cdot km^{-1})$
VERTICAL		
O_2	-0.2 to +0.77	--
Fe^{2+}		
Eh	-2 to -40 $(mg \cdot m^{-2})$	--
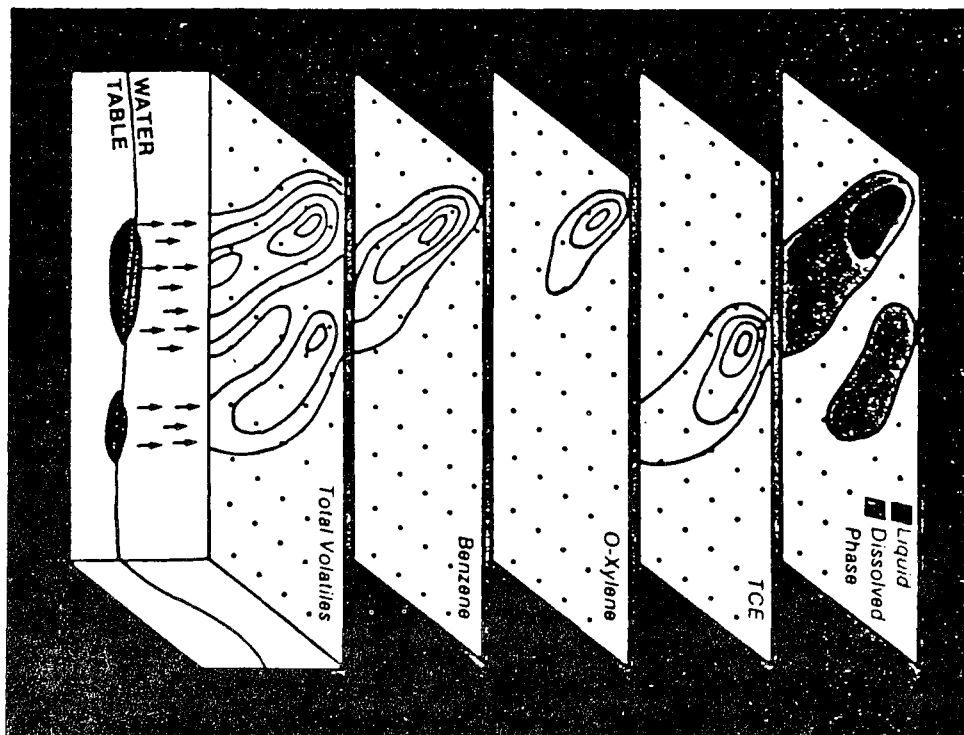
Changes In Plumes and Factors Causing the Changes

Source: U.S. EPA, 1977

- - - - Former boundary
───── Present boundary
● Waste site

Direction of Ground-water flow →

ENLARGING PLUME

1. Increase in rate of discharged wastes

2. Sorption activity used up

3. Effects of changes in water table

REDUCING PLUME

1. Reduction in wastes

2. Effects of changes in water table

3. More effective sorption

4. More effective dilution

5. Slower movement and more time for decay

NEARLY STABLE PLUME

1. Essentially same waste input

2. Sorption capacity not fully utilized

3. Dilution effect fairly stable

4. Slight water-table fluctuation or effects of water-table fluctuation not important

SHRUNKEN PLUME

1. Waste no longer disposed and no longer leached at abandoned waste site

SERIES OF PLUMES

1. Intermittent or seasonal source

DATA REQUIREMENTS FOR WATER SOURCE DEFINITION AND AQUIFER REPRESENTATION

A. Drilling History

B. Well-Completion Data

C. Well-Pumping History

D. Effects of Well Construction, Completion and Development of Water Quality

E. Effects of Sampling Mechanisms and Materials on Water Quality Measurements

SAMPLING FREQUENCY

- NATURAL (OR SOURCE) VARIABILITY MAY EXCEED CONTROLLED SAMPLING AND ANALYTICAL ERRORS

- GROUND-WATER QUALITY DATA ARE NON-NORMAL, HIGHLY AUTOCORRELATED, AND USUALLY OF VERY SHORT DURATION

- QUARTERLY SAMPLING FREQUENCY IS A GOOD STARTING POINT FOR MANY CONSTITUENTS

- REACTIVE CONSTITUENTS OR HIGHLY VARIABLE HYDROGEOLOGIC SETTINGS MAY REQUIRE MORE FREQUENT SAMPLING (i.e., MONTHLY OR BIMONTHLY)

Temperature
(a)

Total Organic Carbon
(b)

Ferrous Iron
(c)
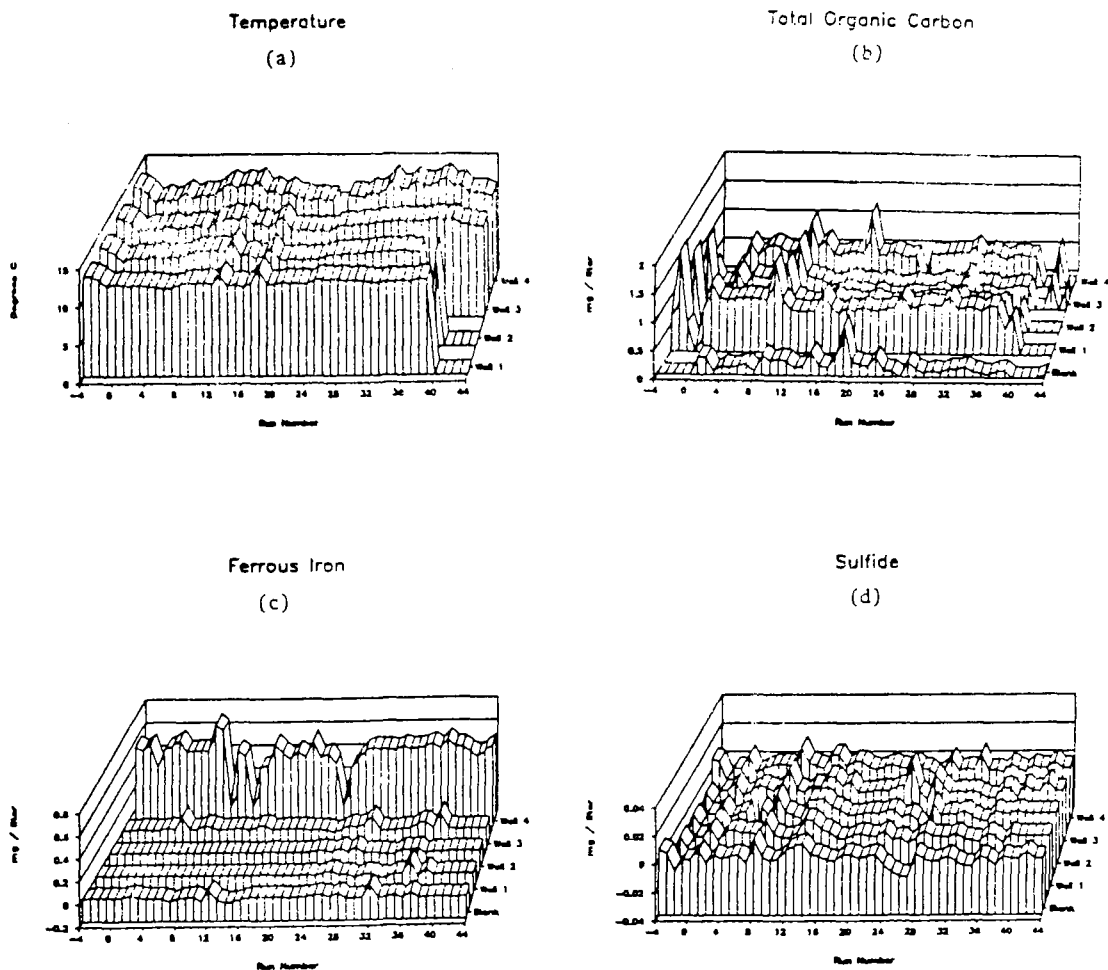
Sulfide
(d)

Fig. 2. Time series of flow cell temperature (2a), total organic carbon (2b), ferrous iron (2c), and sulfide (2d) for the wells at the Sand Ridge site.

Temperature
(a)

Total Organic Carbon
(b)

Ferrous Iron
(c)

Sulfide
(d)

-- SUBSURFACE ENVIRONMENTAL CONDITIONS

o CHEMICAL VARIABILITY: TEMPORAL CONCENTRATION VARIATIONS

SHORT-TERM (MINUTES TO DAYS)

NO_3^-	13X	Fe^{2+}	110X
SO_4^-	7X	HS^-	15X
NH_3	3X		

LONG-TERM (WEEKS TO YEARS)
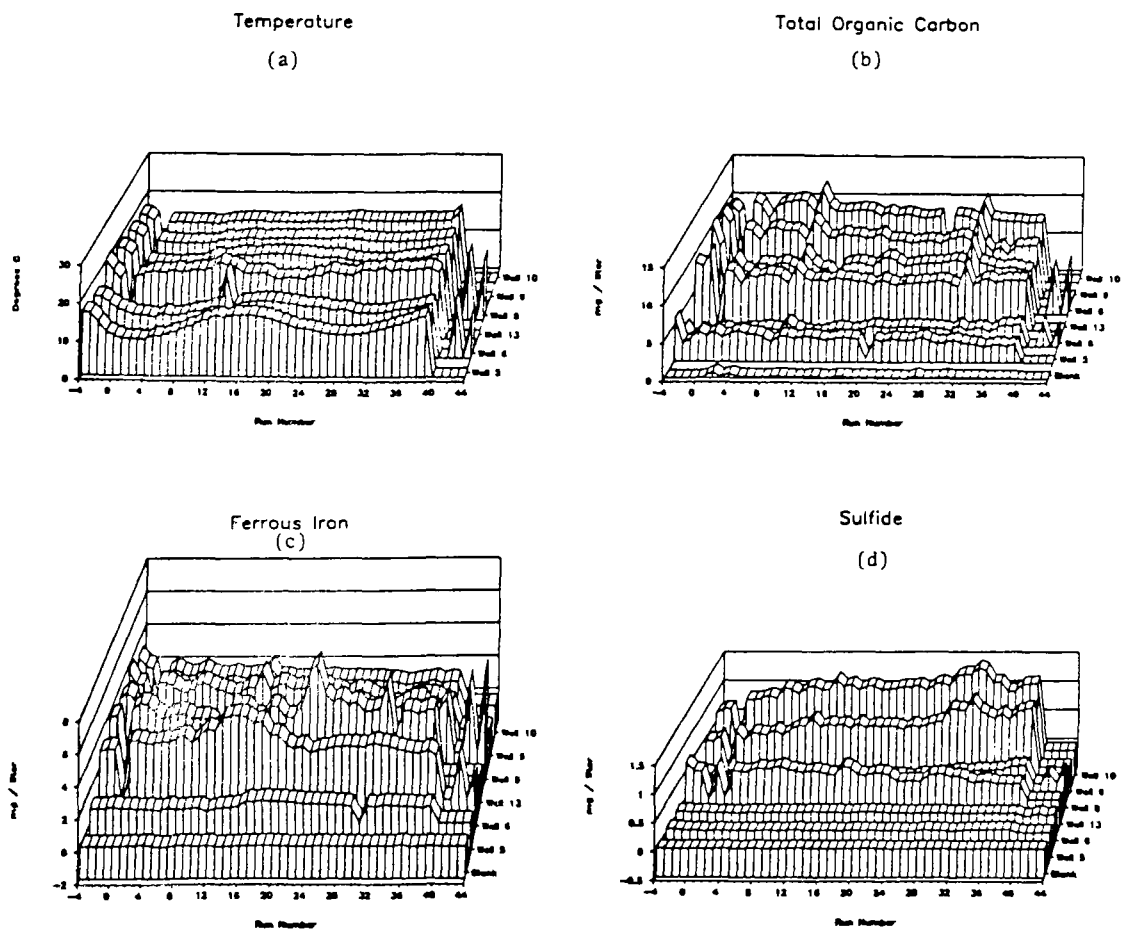
NO_3^-	6X	Fe^{2+}	3X
SO_4^-	7X		
Cl^-	3X		

Observations of temporal variations in ground-water quality: short-term variations

	Constituents (concentration variation)	Nature of variability		Reference
		Period	Probable cause	
Agricultural sources	Se (± 2 mg·L^{-1})	Monthly	Irrigation/return/indeterminate	Crist (1974)[*]
	NO_3^- (1-3X) SO_4^- (3-7X)	Minutes	Pumpage/head changes and leaching from unsaturates zone	Schmidt (1977)[*]
	NO_3^- (1-4X)	Minutes	Pumpage/vertical stratification	Eccles et al. (1977)[*]
	NO_3^- (1-10X) SO_4^- (1-1.5X)	Monthly	Irrigation/fertilizer applications/ leaching; locational differences apparent	Spalding and Exner (1980)
	NO_3^- (0.5-2X) Atrazine (1-5X)	Hours to weeks	Surface runoff recharge	Libra et al. (1986)
Non-Agricultural or mixed sources	H_2S (1-5X) SO_4^- (1-1.2X) NH_3 (1-3X)	Minutes to hours	Pumping rate and well drilling	Colchin et al. (1978)[*]
	NO_3^- (1-13X) SO_4^- (1-2X)	Minutes to hours	Pumping rate and purging	Humenick et al. (1980)[*]
	Fe (1-3X) Mn (1-1.5X)	Minutes	Purging	Wilson and Rouse (1983)
	PCE, TCE, 1,2-t-DCE (1-10X)	Minutes	Pumping rate and purging	Keely and Wolf (1983)[*]
	TCE (2-10X) Fe^{2+} (1-110X) S^- (1-15X)	Monthly to weekly	Pumping rate and development of cone of depression	McReynolds (1986)[*]
	Volatile halocarbons (1-8X)	Minutes	Purging	Barcelona and Helfrich (1986)

[*] Denotes variations observed in water supply production wells, PCE = perchloroethylene, TCE = trichloroethylene, 1,2-t-DCE = 1,2 trans-dichloroethylene.

Observations of temporal variations in ground-water quality: long-term variations

	Constituents (concentration variation)	Nature of variability		Reference
		Period	Probable cause	
Agricultural sources	Cl^- (+1.5X) SO_4^- (2-4X)	Decades	Irrigation/recharge	Evenson (1965)[*]
	NO_3^- (3-6X) SO_4^- (3-7X)	Seasonal	Irrigation/precipitation	Tenorio et al. (1969)[*]
	NO_3^- (±48 $mg \cdot L^{-1}$ yr^{-1})	Seasonal	Leaching/recharge	Tryon (1976)
	NO_3^- (1-12X) SO_4^- (1-1.5X)	Seasonal	Irrigation/fertilizer applications	Spalding and Exner (1980)
	NO_3^- (1-5X)	Seasonal	Recharge/fertilizer applications	Rajagopal and Talcott (1983)
	NO_3^- (1-1.5X) Pesticides (1-1.5X)	Years-seasonal	Infiltration/recharge	Libra et al. (1986)
Non-Agricultural or mixed sources	Conductance (2-3X) SO_4^- (1-3.5X) Hardness (2-6X)	Seasonal	H_2O level fluctuations freezing/thawing recharge	Feulner and Shupp (1963)
	Conductance (+2,000 $\mu S \cdot cm^{-1}$)	Decades	Irrigation/upconing of saline water	Handy et al. (1969)[*]
	NO_3^- (±55 $mg \cdot L^{-1}$ yr^{-1})	Seasonal	Sewage/fertilizer recharge and applications	Perlmutter and Koch (1972)
	Cl^- (1-3X)	Seasonal	Oil field brine/recharge	Pettyjohn (1976), (1982)
	PCE (±1-20X)	Seasonal	Infiltrated surface water quality variations	Schwarzenbach et al. (1983)
	TCE (±1-3X)	Seasonal	Pumping rate and patterns in well field	McReynolds (1986)[*]

[*] Denotes variations observed in water supply production wells, PCE = perchloroethylene, TCE = trichloroethlylene.

Subjective estimate of strength of seasonality or trend in variables by location

	Sand Ridge (1-4)	Beardstown (upgradient)	Beardstown (downgradient)	Number of violations
pH				0
Cond	•	+	+	2
Temp C	+	+	+	6
Temp W	+	+	+	4
Eh				1
Probe O_2				0
Wink O_2				0
Alk	•	+	•	1
NH_3				3
NO_3 N				1
NO_3NO_2 N				0
HS^-			•	0
SO_4		•	•	0
SiO_2		•		0
o-PO_4			•	1
T-PO_4			•	1
Cl^-		•	+	2
Fe^2			•	3
Ca	•	•	+	1
Mg	•	•		2
Na		•	•	3
K		•	•	3
Fe_T				0
Mn_T		•	+	0
TOX				2
VOC				6
NVOC			•	4
TOC			•	3

+ Indicates strongly seasonal.
• Indicates apparent trend or possible seasonality.
TOC = VOC + NVOC; Total Organic Carbon = Volatile Organic Carbon + Nonvolatile Organic Carbon.

ESTIMATED RANGES OF SAMPLING FREQUENCY (IN MONTHS) TO
MAINTAIN INFORMATION LOSS AT <10% FOR SELECTED TYPES OF
CHEMICAL PARAMETERS

Type of parameter	Pristine background conditions	Contaminated	
		Upgradient	Downgradient
Water Quality			
Trace constituents (<1.0 mg·L^{-1})	2 to 7	1 to 2	2 to 10
Major constituents	2 to 7	2 to 38	2 to 10
Geochemical			
Trace constituents (<1.0 mg·L^{-1})	1 to 2	~2	1 to 5
Major constituents	1 to 2	7 to 14	1 to 5
Contaminant Indicator			
TOC	2	3	3
TOX	6 to 7	24	7
Conductivity	6 to 7	24	7
pH	2	2	1

Average overall accuracy and precision for the chemical constituents determined in the study

Param.	Overall		Sand Ridge		Beardstown	
	Acc.	Prec.	Acc.	Prec.	Acc.	Prec.
NH$_3$	95.90	23.49	91.99	29.80	100.09	12.54
T-PO$_4$	99.64	8.60	100.95	9.28	98.24	7.56
Fe^{+2}	96.07	18.80	NA*	NA	96.07	18.80
NO$_2^-$	82.17	36.29	81.07	35.00	83.27	37.50
S$^-$	NA	NA	NA	NA	NA	NA
NO$_3$	100.35	10.27	98.85	7.82	101.97	12.17
SiO$_2$	99.47	5.03	100.21	2.97	98.71	6.41
o-PO$_4$	103.44	15.38	106.54	20.77	100.12	2.32
Cl$^-$	105.78	32.59	112.01	46.55	100.18	1.52
SO$_4^-$	95.77	21.85	94.73	6.58	97.24	33.07
Ca	98.36	3.88	98.65	3.76	98.07	3.98
Mg	99.15	8.70	99.90	10.72	98.42	6.03
Na	101.69	12.17	103.51	16.16	99.95	5.87
K	97.85	5.17	99.10	5.15	96.63	4.89
Fe	99.22	5.80	100.34	7.20	98.04	3.46
Mn	101.04	6.46	101.28	8.17	100.79	3.92

* NA indicates that the number of observations for which accuracy and precision could be determined was less than five, principally due to a larger number of below detection limit results.

Percentage of variance attributable to laboratory error, field error, and natural variability by chemical and site

Type of parameter	Sand Ridge			Beardstown (upgradient)			Beardstown (downgradient)		
	lab	field	nat	lab	field	nat	lab	field	nat
Water quality									
NO$_3^-$	0.0	00.0	100.0	0.1	NA*	99.9	0.2	NA	99.8
SO$_4^-$	0.0	0.0	100.0	0.2	NA	99.8	1.4	0.1	98.6
SiO$_2$	0.0	NA	100.0	0.0	20.0	80.0	0.0	6.8	93.2
o-PO$_4^-$	1.2	1.2	97.6	0.0	0.0	100.0	0.0	0.0	100.0
T-PO$_4^-$	0.0	NA	100.0	2.8	NA	97.8	0.9	NA	99.1
Cl$^-$	7.2	NA	92.8	0.0	3.3	96.7	0.0	17.2	82.8
Ca	0.0	45.7	54.3	0.0	2.3	97.7	0.0	3.6	96.4
Mg	0.0	20.0	80.0	0.0	2.2	97.8	0.0	2.8	97.2
Na	0.0	NA	100.0	0.0	0.3	99.7	0.0	7.1	92.9
K	0.0	NA	100.0	33.9	NA	66.1	87.1	NA	12.9
Geochmical									
NH$_3$	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0	100.0
NO$_2^-$	NA	NA	NA	0.1	NA	99.9	0.3	NA	99.7
S$^-$	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fe^{+2}	NA	NA	NA	0.0	0.1	99.9	0.0	5.9	94.1
Fe$_T$	0.0	NA	100.0	0.0	0.0	100.0	0.0	NA	100.0
Mn$_T$	0.0	NA	100.0	0.0	40.1	59.9	0.0	73.6	26.4
Contaminant indicator	lab + field**			lab + field			lab + field		
TOC	15.4		84.6	29.9		70.1	40.6		59.5
TOX	0.0		100.0	12.5		87.5	24.6		75.4

* NA indicated that the number of observations on which the estimated variance was based was less than 5, or the estimated variance was negative.
** True field spiked standards no available for these constituents demanding combined estimates of laboratory and field variability.

TABLE 1. Physical Characteristics of the Study Sites and Well Installations

| Condition of Groundwater | Well No. | Depth | | Hydraulic Conductivity* | | Bulk Flow Velocity, cm/day |
		Meters Below Land Surface	Screen Elevation msl, m	gpd/ft^{-2}	cm/s	
Site 1, Sand Ridge noncontaminated	1	11	142†	200–500	0.01–0.024	10–30
	2	15	137†	700–7000	0.033–0.33	30–50
	3	21	133†			
	4	32	120†			
Site 2, Beardstown contaminated	5	5.5	131	600–900	0.03–0.042	20–30
	6	7.0	129			
	8	7.5	131	500–800	0.02–0.038	40–55
	9	10	129.5			40–55
	10	10.5	128			40–55
	11†	10	129.5			40–55
	12‡	10	129.5			40–55
	13	10	129.0			40–55

Land surface 152 m above msl.
*Modified slug test results [Hvorslev, 1951].
†Stainless steel well finished at 10 m depth along a perpendicular to the flow direction downgradient from the treatment impoundment.
‡Polyvinyl chloride well finished at 10 m depth along a perpendicular to the flow direction downgradient from the treatment impoundment.

TABLE 2. Average Results for Groundwater Chemical Analyses

| Parameter | Well 1 | | Well 4 | | Well 5 | | Well 8 | |
	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
Eh, mV*	456	91	110	50	226	33	102	27
Ω^{-1}, μS/cm*	359	11	225	11	375	97	1607	173
pH*	7.75	0.53	7.80	0.37	6.48	0.35	6.87	0.20
T, °C	12.0	0.9	12.2	0.3	12.5	2.7	15.6	1.6
TOC	0.85	0.26	0.57	0.2	3.08	0.75	6.78	1.17
TOX, μg/L	3.65	5.0	3.07	4.0	6.26	4.6	10.9	7.6
CH_4	−0.12†	0.8	0.01	0.08	0.00	0.036	1.33	0.71
NO_2^--N	0.00	0.002	0.00	0.001	0.00	0.002	0.01	0.004
NH_3	−0.01	0.014	0.06	0.04	0.26	0.15	174	51.3
Fe (II)	0.01	0.04	0.50	0.08	1.04	0.18	2.21	0.82
Fe_T	0.01	0.03	0.44	0.10	1.02	0.23	2.15	0.78
Mn_T	0.00	0.009	0.15	0.03	0.09	0.02	0.63	0.10
S^-	0.00	0.03	0.00	0.005	0.04	0.01	0.14	0.07
O_2 (probe)*	9.00	0.50	0.61	0.27	0.36	0.13	0.36	0.18
O_2 (Winkler)*	8.82	0.86	0.46	0.06	N.D.	N.D.	N.D.	N.D.
Alkalinity (as $CaCO_3$)*	216	12	132	5.4	65.5	5.7	690	81
Cl^-	2.19	0.71	1.67	0.72	66.6	38.9	141	10.1
$(NO_3^- + NO_2^-)$-N	0.95	0.2	−0.01	0.07	−0.02	0.023	1.89	2.07
SO_4^-	36.2	5.8	22.1	4.49	76.7	13.1	35.6	5.59
o-PO_4^-	0.02	0.02	0.11	0.023	0.06	0.03	14.6	7.7
T-PO_4^-	0.04	0.074	0.13	0.05	0.10	0.05	14.7	7.6
Silica	15.5	0.4	15.7	0.62	13.3	1.08	19.0	4.95
Ca^{2+}	65.9	3.3	38.4	2.36	38.5	8.6	44.1	7.1
Mg^{2+}	22.6	1.25	12.3	0.62	14.7	3.1	17.5	2.2
Na^{2+}	3.11	0.49	3.53	0.54	33.9	11.9	117	14.6
K^+	0.71	0.08	0.73	0.09	2.85	0.82	22.7	2.47
Depth	35 feet (11 m)		105 feet (32 m)		upgradient 18 feet (5.5 m)		downgradient 25 feet (7.5 m)	

S.d., standard deviation in concentration or similar units; N.D., not detected. Values represent the results are given in milligrams per liter unless otherwise specified for duplicate determinations on each of 39 sampling dates over the study period.
*Determined in the field.
†Negative mean values result from the reporting of actual sample results above and below the limit of detection as recommended by ASTM [1987].
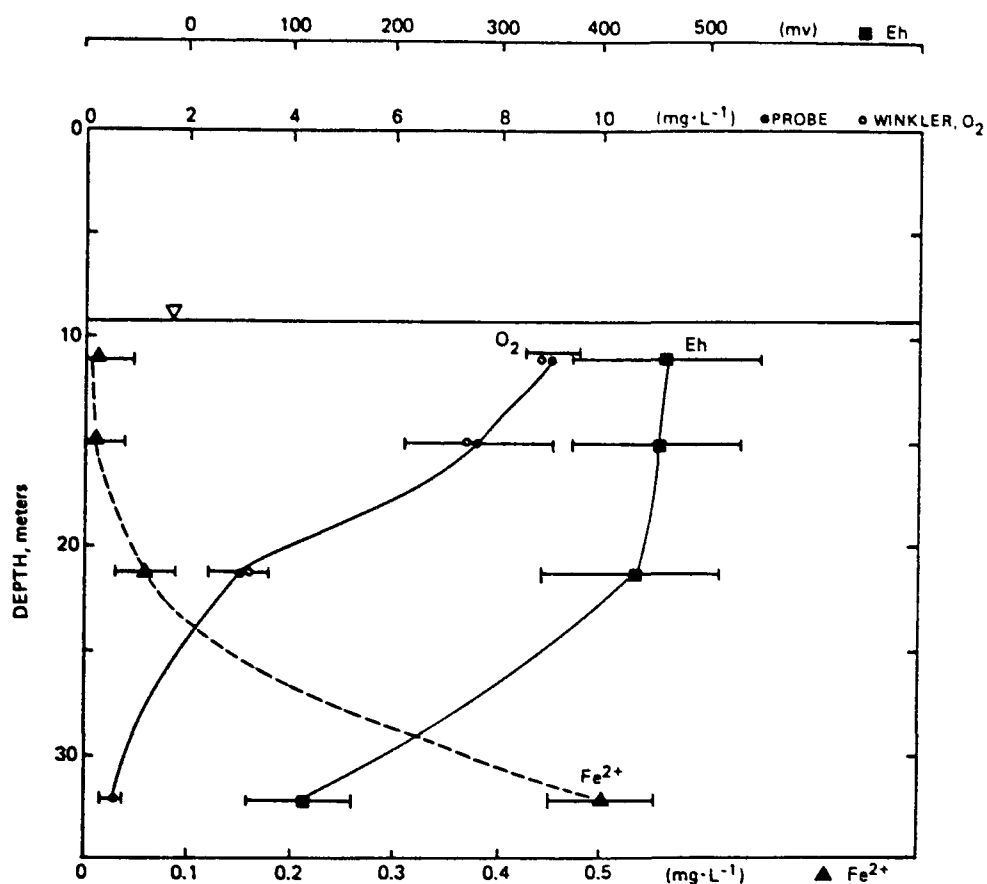
Fig. 2. Average profiles of Eh (solid squares), dissolved oxygen (solid circles, probe; open circles, Winkler) and ferrous iron (solid triangle) gradients with depth at the uncontaminated site, Sand Ridge State Forest.
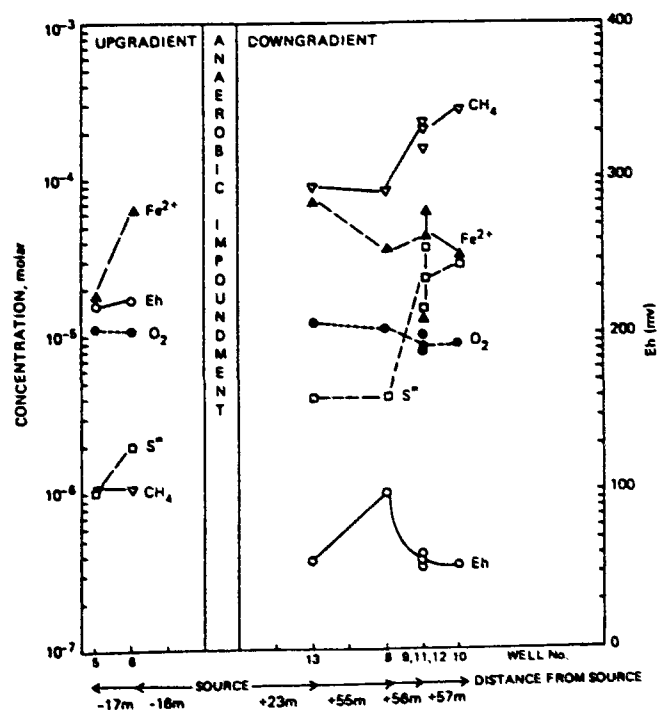

Fig. 3. Average concentrations of redox-active chemical species with distance from the contaminant source (concentration in logarithmic scale with reference tick marks on each margin, Eh scale linear).
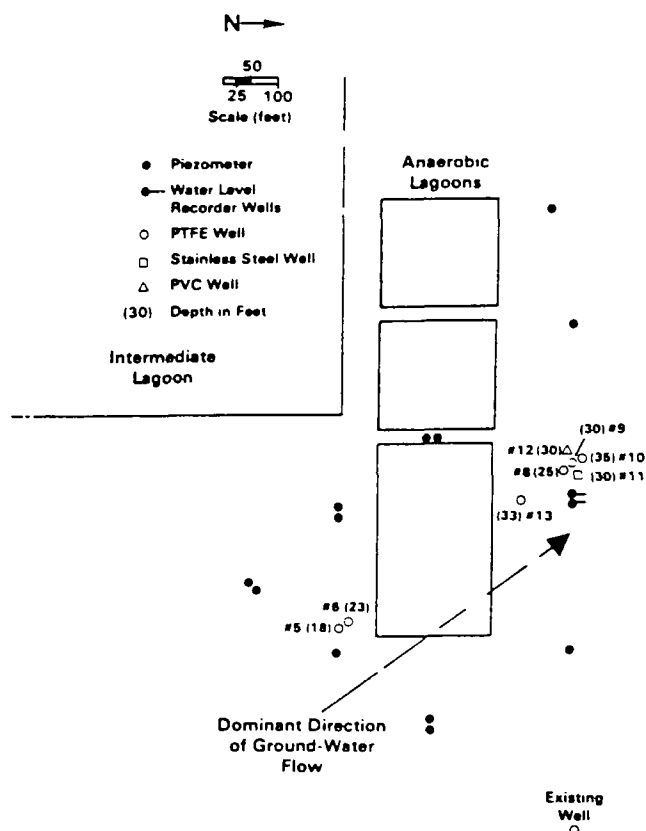
Fig. 1. Plan diagram of the monitoring well locations at the contaminated groundwater site at Beardstown, Illinois.
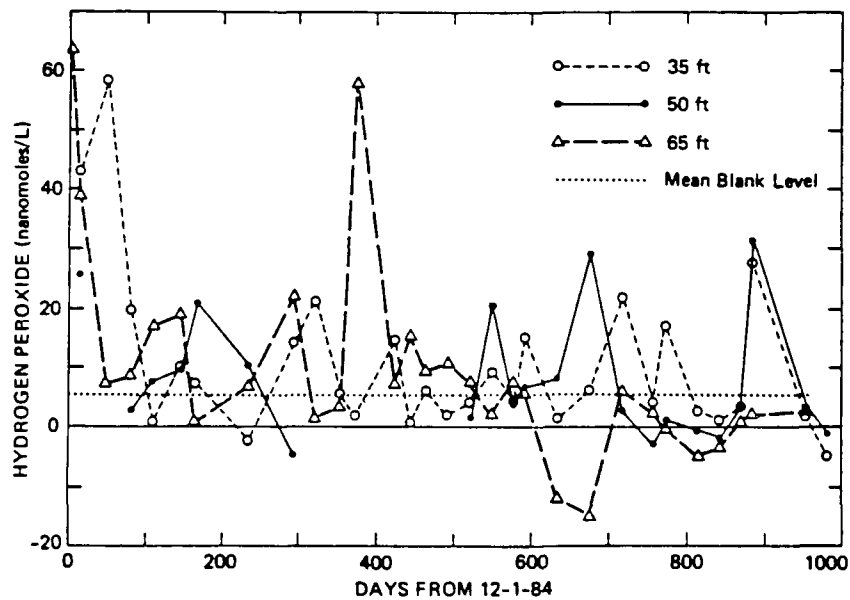

Fig. 6. Time series plot of H_2O_2 concentration from December 1, 1984, for oxic groundwater samples from depths of 35 (11 m) (open circles), 50 (15 m) (solid circles), and 65 feet (21 m) (open triangles). Mean field blank level is shown on the dotted line.
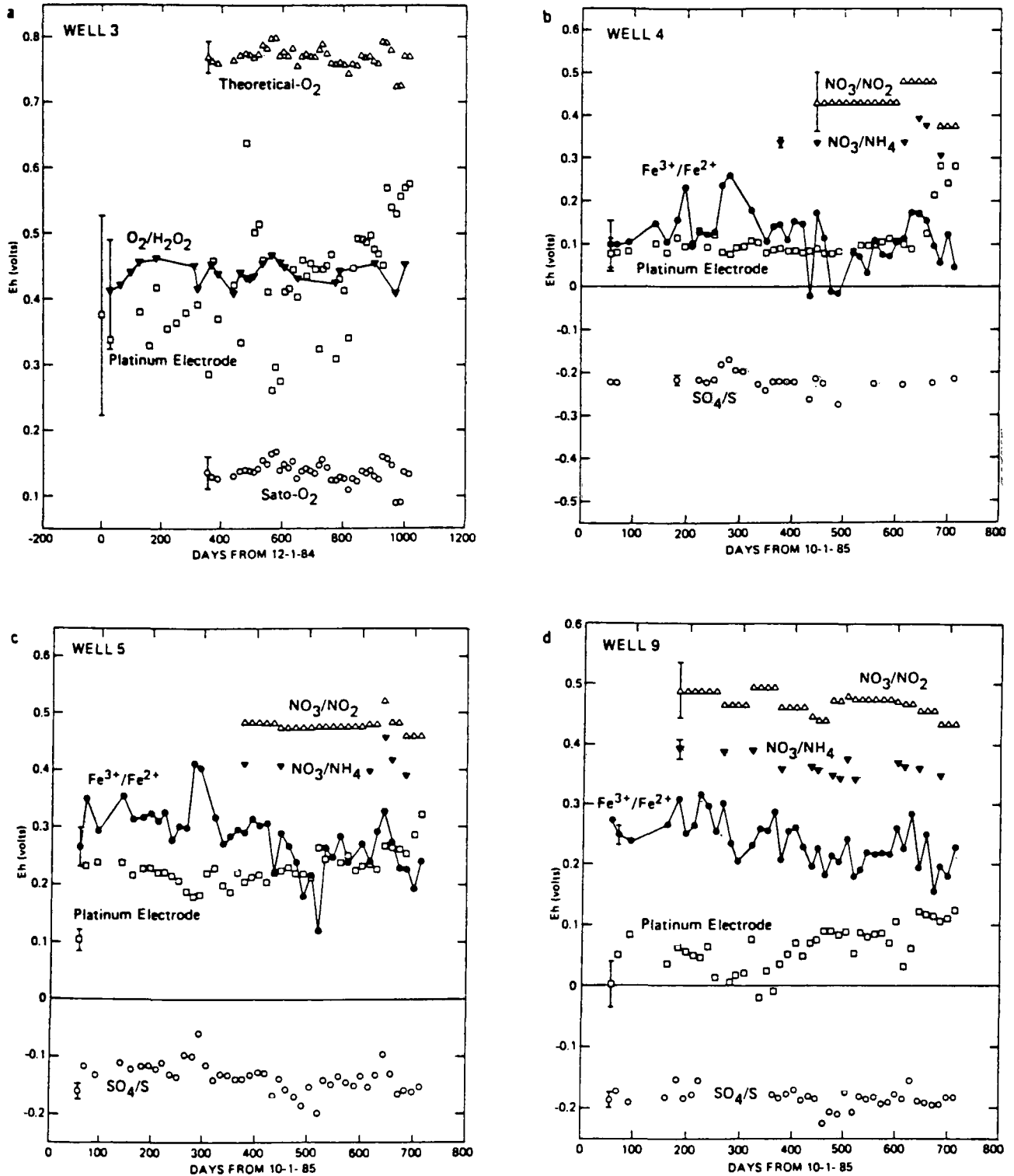
Fig. 5. Comparison of Eh potential measurement results with calculated Eh values during the study period for (a) well 3, (b) 4, (c) 5, and (d) 9.

TABLE 4a. Spatial Gradients in Subsurface Oxidation- Reduction Conditions, Site Scale

Type of Environment	Redox Gradient		Contaminant?	Reference
	ΔO_2, mg L^{-1} m^{-1}	ΔEh, mV/m		
Horizontal (Along General Groundwater Flow Path)				
Unconfined sand		+1	landfill leachate	*Nicholson et al.* [1983]
Unconfined sand	−0.04	−2	high organic carbon recharge	*Jackson and Patterson* [1982]
Unconfined sand/gravel	+0.1		landfill leachate	*Baedecker and Back* [1979b]
Unconfined sand/gravel		−3	inorganic fertilizer plume	*Barcelona and Naymik* [1984]
Unconfined sand		−1.5*	anaerobic treatment leachate	this study (Beardstown)
Confined sand/gravel	−0.01	−2.5	high organic carbon recharge water	*Jackson and Patterson* [1982]
Confined sand/gravel	+0.5		artificial recharge	*Van Beek and Van Puffelen* [1987]
Vertical (Increasing Depth)				
Unconfined sand		−10 to −15	background	*Jackson et al.* [1985]
Unconfined sand	−0.34†	−2 to −40†	landfill leachate	*Jackson et al.* [1985]
Unconfined sand/gravel	−0.7	−30	high organic carbon recharge water	*Jackson and Patterson* [1982]
Unconfined sand/gravel	−0.2 to 0.77*	−2 to −30‡	background	this study (Sand Ridge)
Unconfined sand		−8 to −27*	anaerobic treatment leachate	this study (Beardstown)

*Eighteen month average between wells 8 and 10.
†Values available from two separate sampling periods.
‡Thirty month average range between wells 1 and 3 and 3 and 4, respectively.

TABLE 4b. Spatial Gradients in Subsurface Oxidation-Reduction Conditions, Large Scale

Type of Gradient	Type of Environment	Redox Gradient		Reference
		ΔO_2, mg L^{-1} km^{-1}	ΔEh, mV/km	
Horizontal (Along general groundwater flow path)	confined sandy clay/gravel (Patuxent)		−34	*Back and Barnes* [1965]
	confined sand/clay, lignite (Raritan-Magothy)		−57	*Back and Barnes* [1965]
	confined carbonate chalk (Berkshire)	−0.30	−30	*Edmunds et al.* [1984]
	confined limestone (Lincolnshire)	−0.34	−180	*Edmunds et al.* [1984]
	confined sandstone/siltstone (Foxhills-Basal Hell Creek)	none	−0.4 to +5	*Thorstenson et al.* [1979]
	unconfined sand/gravel (Tucson Basin)	+1	+23	*Rose and Long* [1988]

-- SUBSURFACE ENVIRONMENTAL CONDITIONS

o EQUILIBRIUM VS. KINETIC CONTROL OF SPECIES CONCENTRATIONS

Is the reaction fast w.r.t. rates of flow/mixing?

Do equilibrium assumptions apply?

Can we use stepwise-equilibrium calculations within the
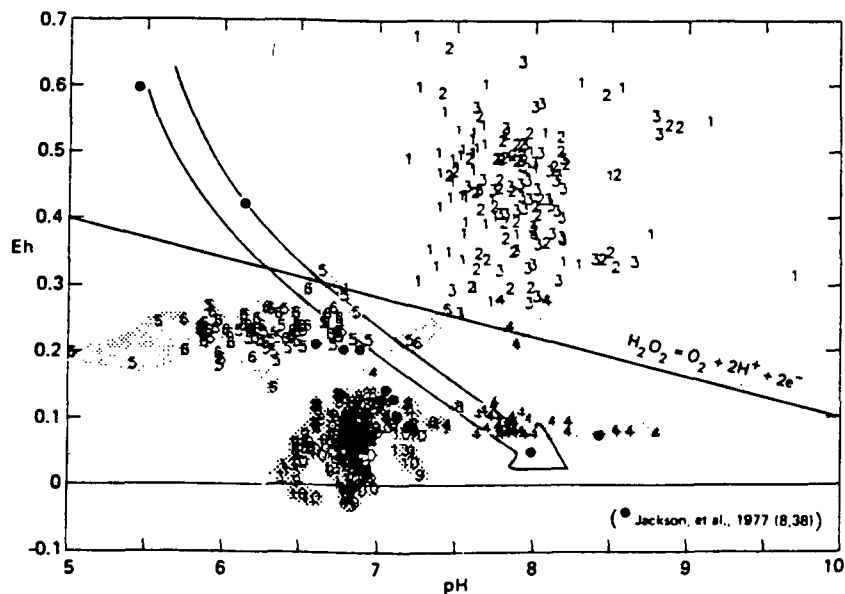limits of solute-transport models?

Fig. 4. Grouping of Eh-pH measurement results for the monitoring wells used in this study. The H_2O_2/O_2 standard potential line from *Sato* [1960] is shown on the diagram. Solid symbols are for data from *Jackson and Patterson* [1982].

OXIDATION AND REDUCTION

INTENSITY --   Eh POTENTIAL MEASUREMENTS,
              RATIOS OF OXIDIZED AND REDUCED
              SPECIES

              Fe(III), Fe(II)
              O_2, H_2O_2
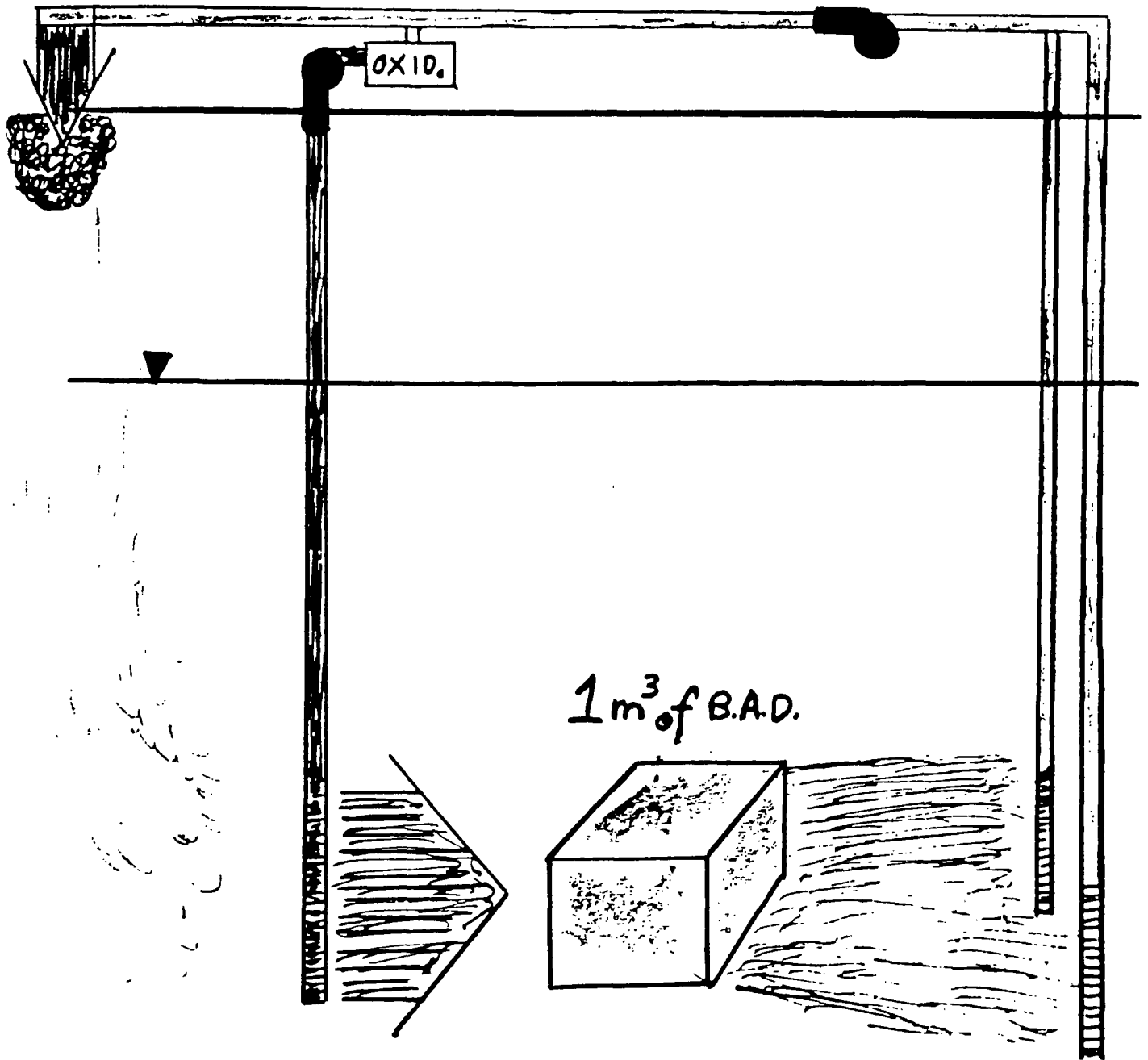   [As(V), As(III)]

   ■   IDENTIFICATION OF IMPORTANT SPECIES,
       BIOGEOCHEMICAL POSSIBILITIES

CAPACITY --   REDUCTION OR OXIDATION CAPACITIES

   ■   BEAR DIRECTLY ON THE POTENTIAL FOR IN
       SITU OXIDATION OR REDUCTION OF
       CONTAMINANTS

PERFECT (HYPOTHETICAL) IN-SITU OXIDATIVE REMEDIATION SCHEME

OXID.

$1 m^3$ of B.A.D.

HYPOTHETICAL IN SITU OXIDATIVE REMEDIATION (100% EFFECTIVE)

ESTIMATED CHEMICAL COST (per m^3 of Aquifer)

HYDROGEN PEROXIDE (H_2O_2)	$25 to $1,000
POTASSIUM PERMANGANATE ($KMnO_4$)	$50 to $2,000
POTASSIUM PERSULFATE ($K_2S_2O_8$)	$1,100 to $42,000

C. Sampling Considerations

1. Environmental sampling in general

2. Sampling protocols for site characterization work

   a. scope and magnitude of the problem/relation to sampling intervals and representativeness

   b. interactions between contaminated and uncontaminated sub-areas within the site

   c. choice of diagnostic parameters, analytes

   d. sampling protocols based on hydrogeologic data

   e. sampling experiments

   f. refined sampling protocol

   g. transition from characterization work to monitoring remediation efforts

ENVIRONMENTAL SAMPLING

-- A SELECTION PROCESS

o Objects within populations of increasing complexity

o Evolutionary approach and sampling experiments

o Isolate variables of importance in specific situations

o Ambient, contaminated, and exposure conditions must be weighed in network design and sampling protocol development

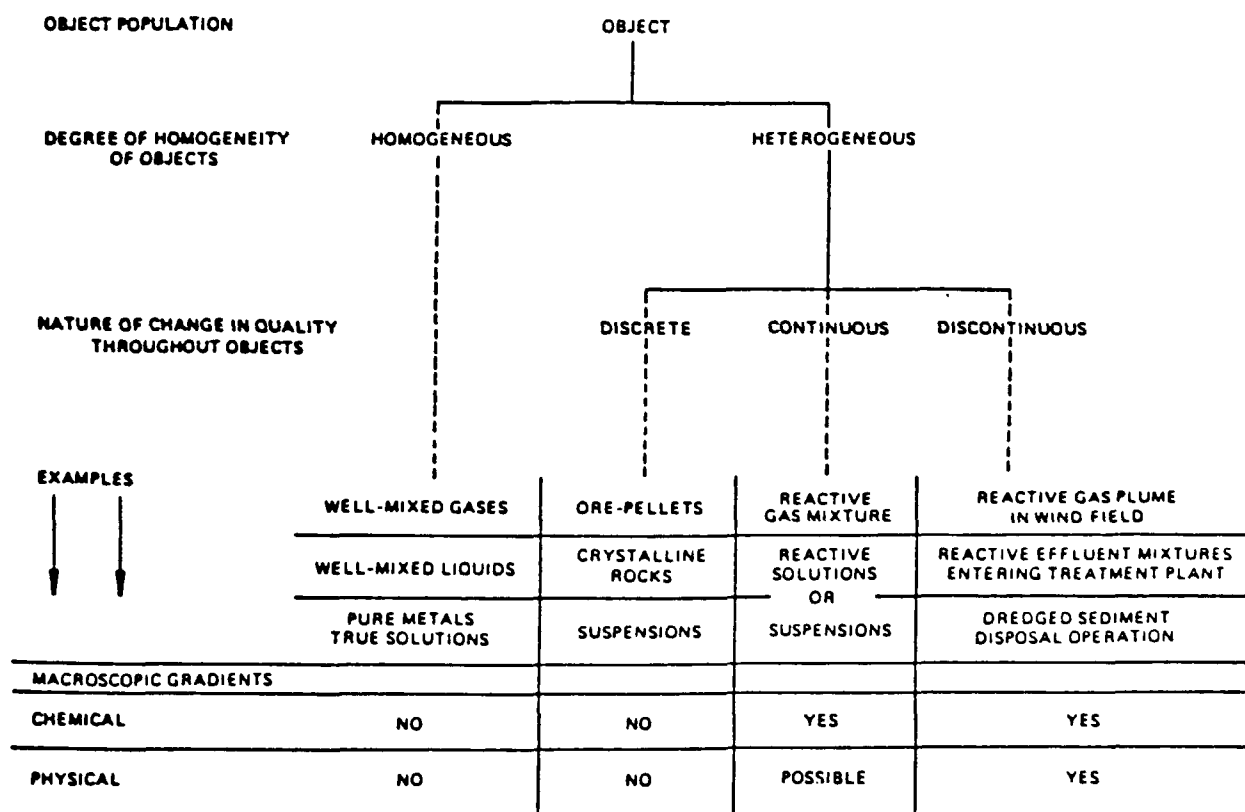|				
OBJECT POPULATION		OBJECT		
DEGREE OF HOMOGENEITY OF OBJECTS	HOMOGENEOUS		HETEROGENEOUS	
NATURE OF CHANGE IN QUALITY THROUGHOUT OBJECTS		DISCRETE	CONTINUOUS	DISCONTINUOUS
EXAMPLES	WELL-MIXED GASES	ORE-PELLETS	REACTIVE GAS MIXTURE	REACTIVE GAS PLUME IN WIND FIELD
	WELL-MIXED LIQUIDS	CRYSTALLINE ROCKS	REACTIVE SOLUTIONS OR	REACTIVE EFFLUENT MIXTURES ENTERING TREATMENT PLANT
	PURE METALS TRUE SOLUTIONS	SUSPENSIONS	SUSPENSIONS	DREDGED SEDIMENT DISPOSAL OPERATION
MACROSCOPIC GRADIENTS				
CHEMICAL	NO	NO	YES	YES
PHYSICAL	NO	NO	POSSIBLE	YES

Figure 1. Types of macroscopic objects or sample origins.

-- SUBSURFACE ENVIRONMENTAL CONDITIONS

    o CHEMICAL CONCENTRATION VARIABILITY

        SHORT-TERM; PUMPING, RECHARGE EFFECTS

        LONG-TERM; SEASONALITY, TREND ANALYSIS

-- CALL FOR

    ● INTEGRATION OF HYDROLOGIC AND CHEMICAL DATA INTERPRETATION

    ● CAREFUL SELECTION OF SAMPLING FREQUENCY
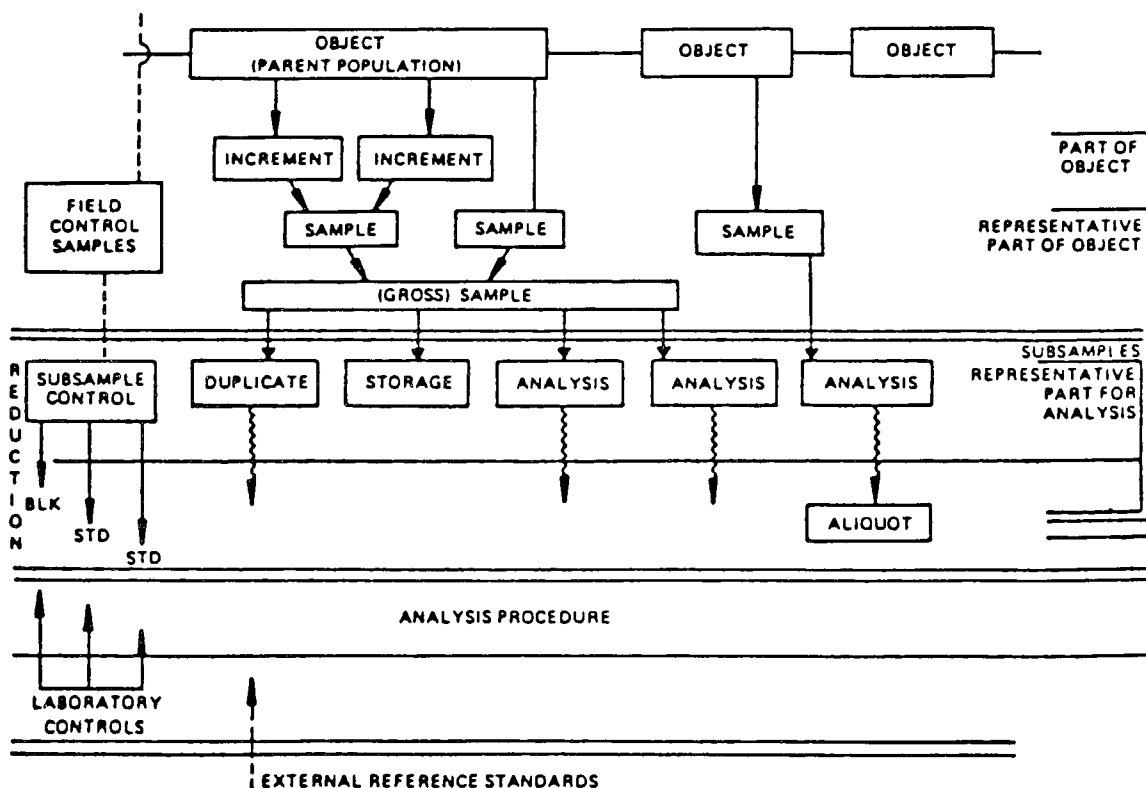
        (HOW OFTEN IN THE FLOW PATH ....)
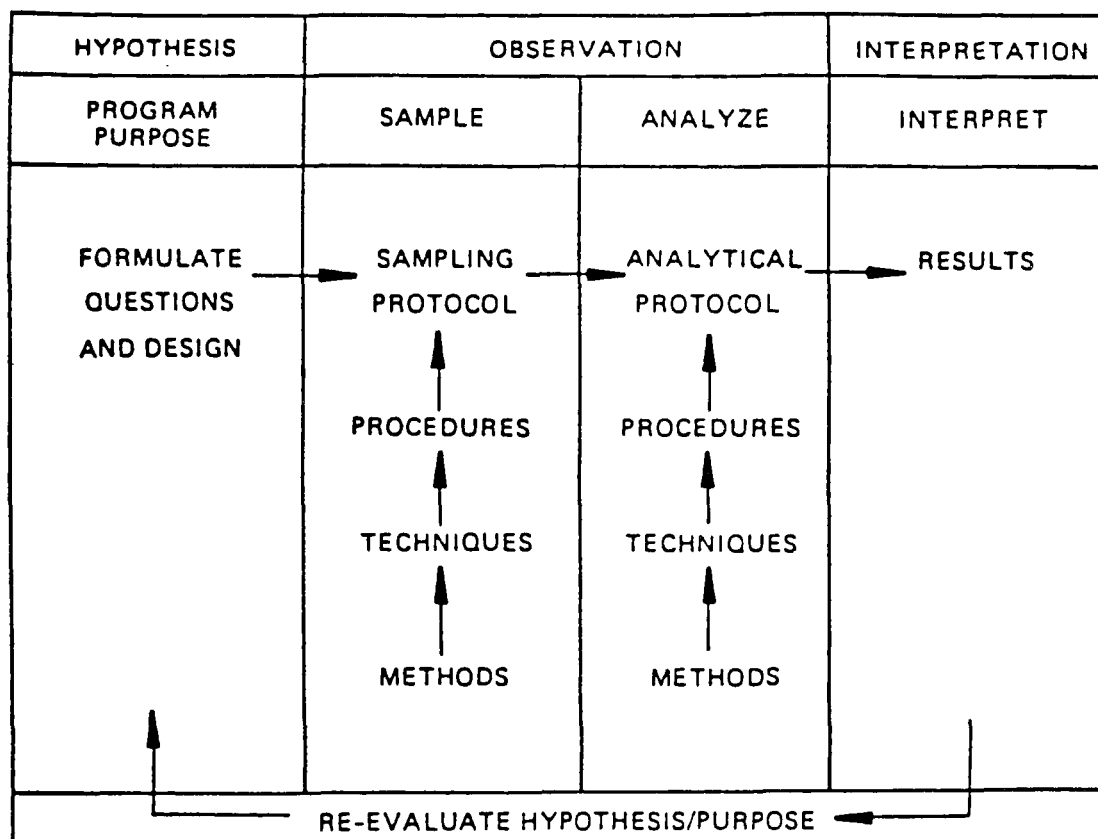

Figure 2. Sample nomenclature overview.

HYPOTHESIS	OBSERVATION		INTERPRETATION
PROGRAM PURPOSE	SAMPLE	ANALYZE	INTERPRET
FORMULATE QUESTIONS AND DESIGN	SAMPLING PROTOCOL ↑ PROCEDURES ↑ TECHNIQUES ↑ METHODS	ANALYTICAL PROTOCOL ↑ PROCEDURES ↑ TECHNIQUES ↑ METHODS	RESULTS
RE-EVALUATE HYPOTHESIS/PURPOSE			

Figure 3. Relationship of program purpose and protocols to the scientific method.

Table 1.1. Data Requirements for Water-Source Definition and Aquifer Representation of Ground-Water Samples (Modified after Claassen, reference 31)

A. Drilling history
   1. Well depth and diameter
   2. Drill-bit type and circulating fluid
   3. Lithologic data from cores or cuttings
   4. Well-development before casing
   5. Geophysical logs obtained

B. Well-completion data
   1. Casing sizes, depths and leveling information relative to both land surface and top of casing
   2. Casing material(s)
   3. Cemented or grouted intervals and materials used
   4. Plugs, stabilizers, and so forth, left in hole and materials used
   5. Gravel packing: volume, sizes, and type of material
   6. Screened, perforated, or milled casing or other intervals which allow water to enter the borehole
   7. Pump type, setting, intake location, construction materials, and pump-column type and diameter
   8. Well maintenance record detailing type of treatment and efficiency

C. Well pumping history
   1. Rate
   2. Frequency
   3. Static and pumping water levels

D. Estimation of effect of contaminants introduced into aquifer during well drilling and completion on native water quality

E. Effect of sampling mechanism and materials on the composition of ground-water sample
   1. Addition of contaminants
   2. Removal of constituents
      a. Sorption
      b. Precipitation
      c. Degassing

PART 1

SAMPLING IN GENERAL

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GENERAL STATISTICAL CONSIDERATIONS

U.S. Environmental Protection Agency, 1989. "Guidance Document on the Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities -- Interim Final Guidance." Office of Solid Waste Management Division, April 1989 (VERY USEFUL LIST OF REFERENCES in Appendix C).

SESSION 2. DETERMINATION OF EXTENT AND MAGNITUDE OF CONTAMINATION
IN THE SUBSURFACE

PART 2. SOIL AND AQUIFER SEDIMENT SAMPLE COLLECTION

PART 2. SOIL AND AQUIFER SEDIMENT SAMPLE COLLECTION

A.   Solid Sample Collection

### B.   Solid Sampling in Practice

C.   New Methods for Solid-Associated

Contaminant Investigations

A. Solid Sample Collection

   1. Sampling strategies/recognizing major sources of error

   2. Hydrogeologic and source considerations

   3. Statistical considerations

      a. general

      b. case studies

Figure 3-2. Major Hydrochemical Processes In the Soil Zone of Recharge Areas
Source: R. Allan Freeze and John A. Cherry, *Groundwater*
(Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1979), p. 204
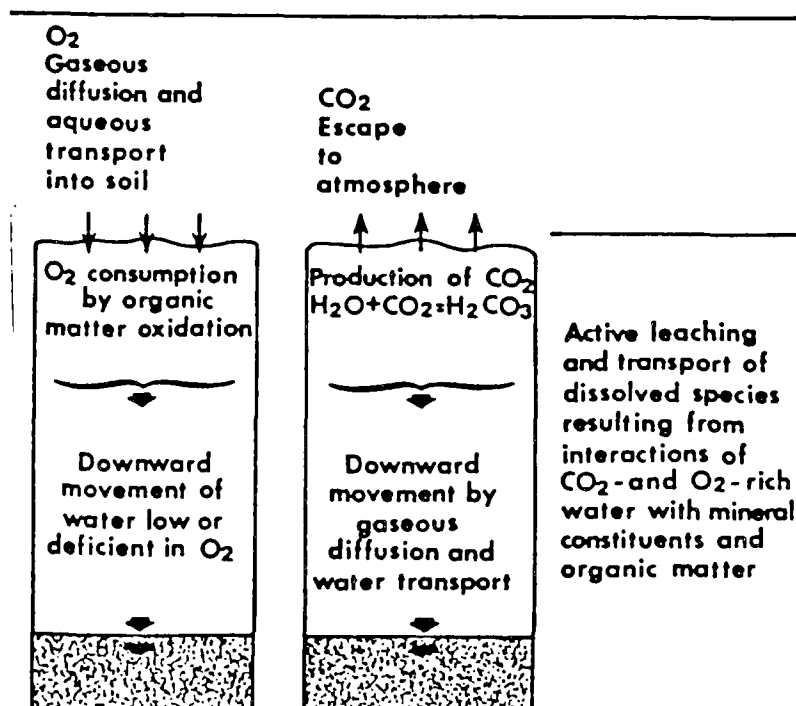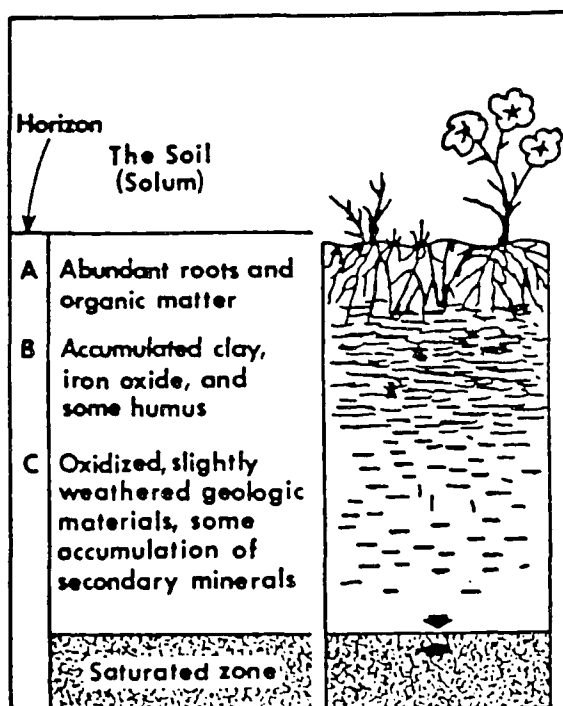
SOIL AND AQUIFER SEDIMENT SAMPLING

SAMPLING STRATEGIES:

- **PURPOSES**
  - DETECTION
  - ASSESSMENT
  - EVALUATION

- **STRATEGY QUESTIONS**
  - Is area/volume contaminated?
  - Is contamination widespread?
  - Are H_2O and solids contaminated? What is the spatial distribution of contamination?

SOLID SAMPLING

- **DEVELOPMENT OF A SOLID'S MONITORING PROGRAM**

  - NECESSITY OF A SAMPLING EXPERIMENT AS A BASIS FOR MORE FOCUSSED OBSERVATION, ANALYSIS, DECISION-MAKING

  - MONITORING DATA ALONE WILL NOT ESTABLISH UNEQUIVOCALLY "CLEAN" OF CONTAMINATED" AREAS

  - "WHAT IS THE PROBABILITY THAT THE AREA TO BE TREATED HAS A CONTAMINANT CONCENTRATION LESS THAN THE ACTION LEVEL?"

SAMPLING STRATEGIES

- SCOPE (EXAMPLES) ZONES OF INFLUENCE

  - SMELTERS
    - Pb (Dallas, TX) ~400 m "radius"
    - Zn, Cd, Pb, Cu (Palmerton, PA) ~5,000 m "radius"

  - UST's
    - Solvents, Hydrocarbons (various sites) ~50 to 2,000 m "radius"

  - NAPL's
    - R-Cl$_x$ (various sites) ~50 to 2,000 m; depths to 500 m

SOLID SAMPLING

PROTOCOL DEVELOPMENT

- Preliminary Sampling Experiment

  - Preliminary Sampling Array (i.e., grid size, spacing and number of samples)

  - Sample type and device (i.e., grab, composite, etc.)

  - Statistical analysis of Data (i.e., geostatistics, Kriging)

  - Refined network design/hypothesis

SOLID SAMPLING PROTOCOL

- Determine Spatial Distribution of Contaminants at known precision

  - Intensity of sampling depends on non-sampling variance and spatial structure of the concentration data.

    (ALWAYS EASIER TO COLLECT SOLIDS THAN TO ANALYZE THEM -- ARCHIVE)

- Preliminary Sampling Experiment provides these values.

SOLID SAMPLING PROTOCOL -- SAMPLING ARRAY

- GRIDS   --   ALLOW PRECISE ESTIMATION OF SHORT RANGE CORRELATIONS

- TRANSECTS --   ALLOW PRECISE ESTIMATION OF LONG RANGE CORRELATIONS

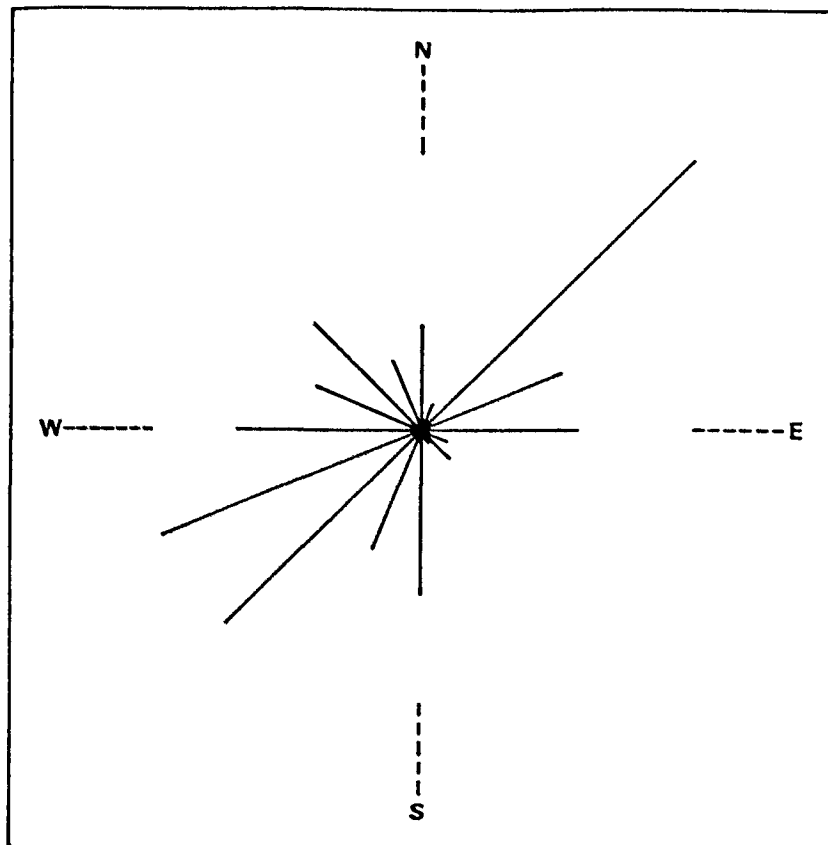- COMBINATIONS OF THE ABOVE ARRAYS SHOULD PROVIDE THE BASIS FOR MORE REFINED HYPOTHESES.
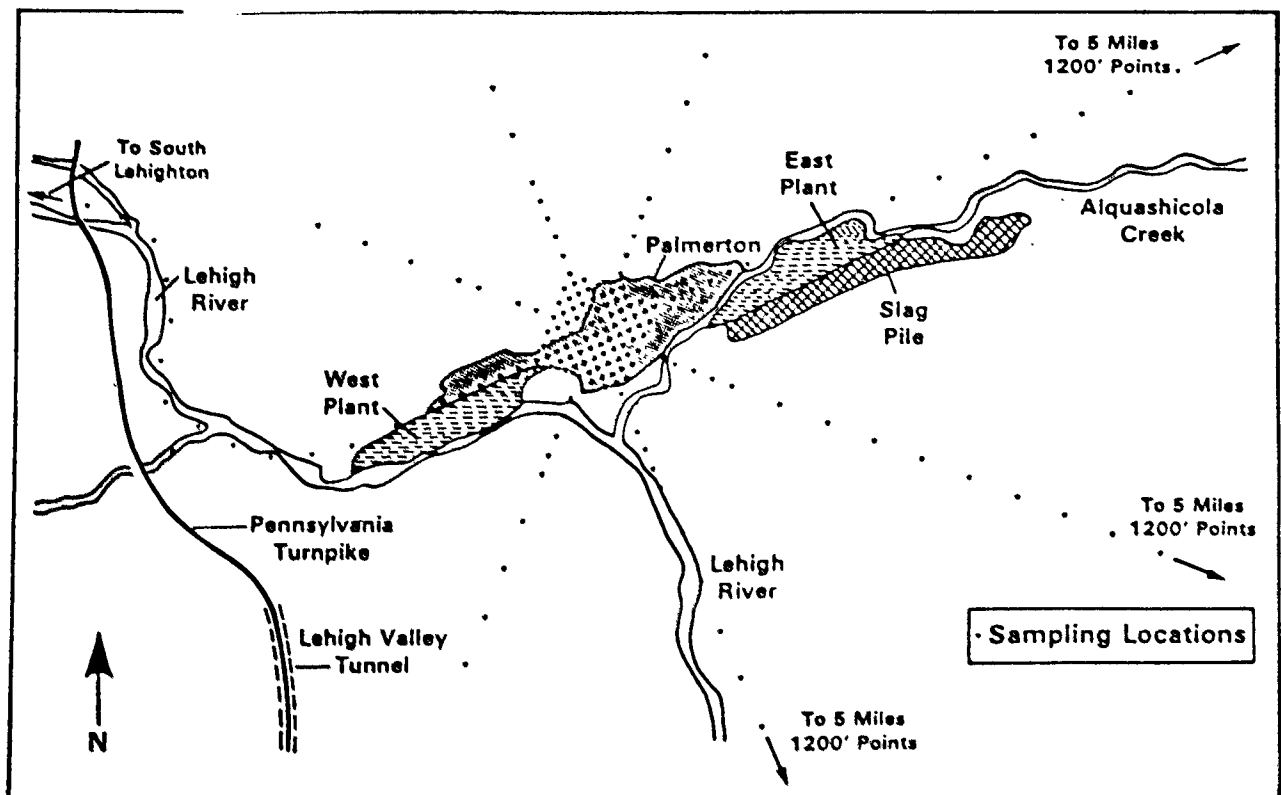
FIG. 1—Palmerton Wind Rose 1978-1979 data.

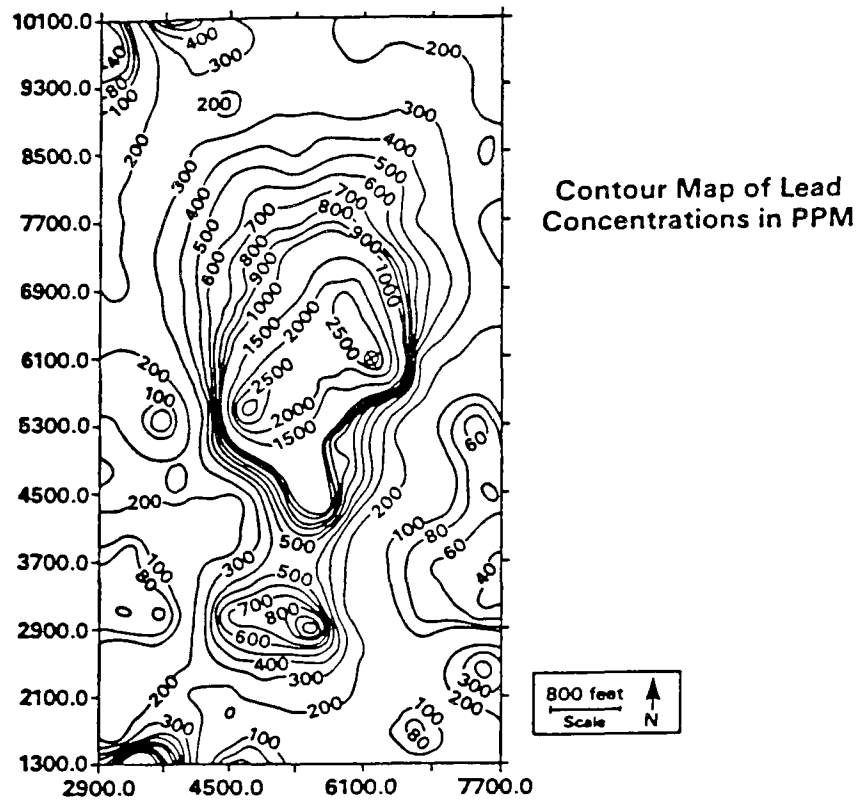FIG. 2—Sample pattern for the initial Palmerton Survey (1" = 4250').

Contour Map of Lead
Concentrations in PPM

FIG. 2—Contour map of the lead concentrations in ppm around
the smelter.

Gamma (the variance of differences between sample values)

Tickmark = 167 m (500 feet)

Lag. (the distance between sample locations)
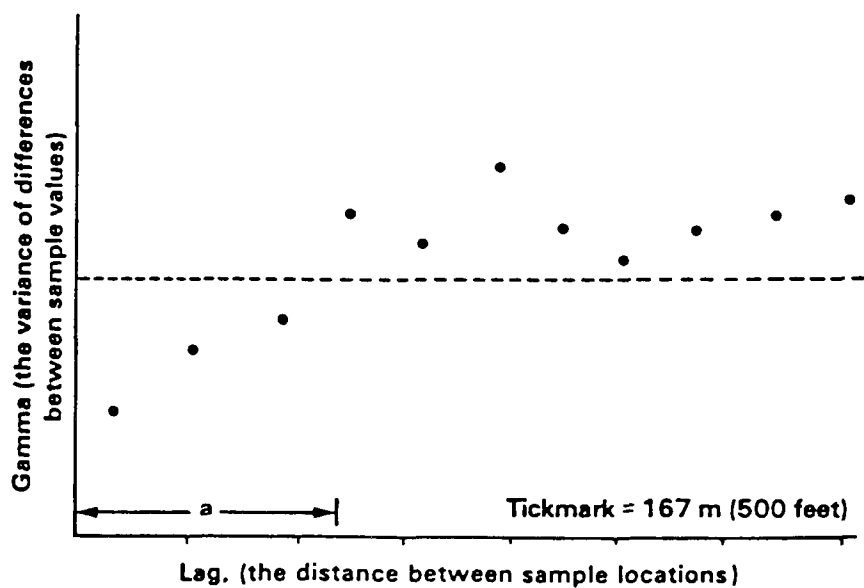
FIG. 1—A semivariogram of lead samples taken systematically
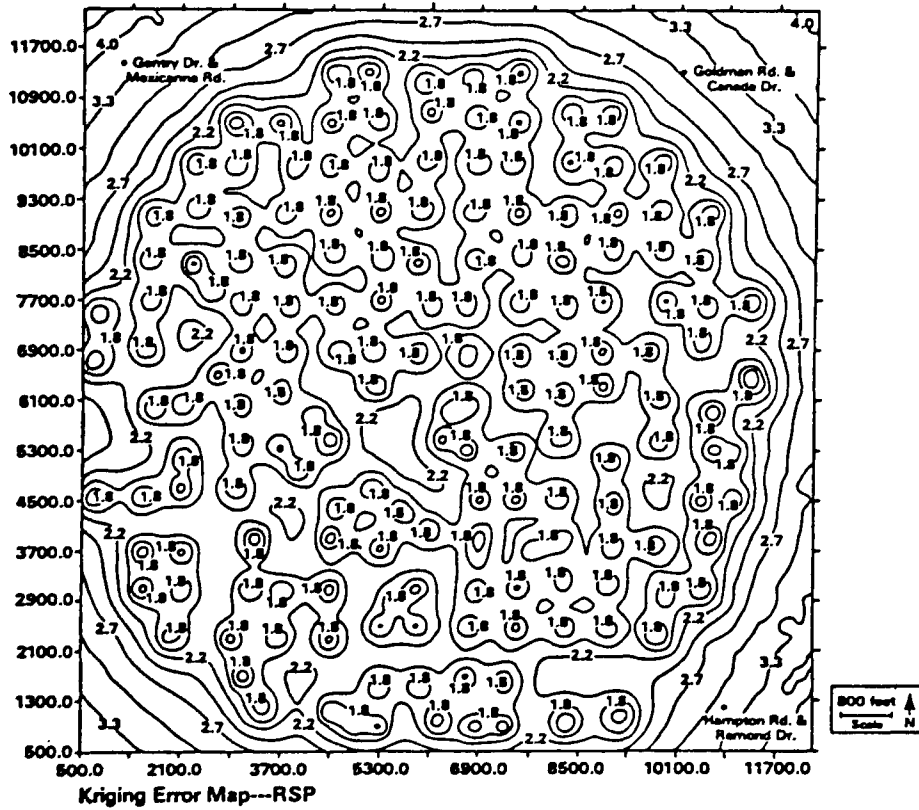on a 230m (750 foot) grid. (FLATMAN, 1986)

FIG. 3—Contour map of standard deviations of the lead
concentrations in ppm.

SOLID SAMPLING PROTOCOL -- ERRORS

- AUTOCORRELATION (in space or time) POSITIVE OR NEGATIVE

  - SYSTEMATIC SAMPLING RATHER THAN RANDOM

  - CONTOURING RATHER THAN "t" TESTING

SOLID SAMPLING PROTOCOL -- SAMPLE TYPE

(AT LEAST)

- FOUR SPACED SAMPLING SITES ON TRANSECTS/GRIDS AT DISTANCES BELOW THE EXPECTED RADIUS OF INFLUENCE

- DUPLICATE SAMPLES AT 5% OF THE SAMPLING POINTS (HELP SORT OUT SHORT-RANGE VARIABILITY)

- SPLIT-SAMPLES AT 5% OF THE SAMPLING POINTS (PROVIDES COMBINED SUBSAMPLING AND ANALYTICAL ERROR VARIANCE)

PLUS

- COMPOSITING LARGER SAMPLES OFTEN IMPROVES VARIANCE ESTIMATES (TRY TO AVOID SAMPLES LESS THAN 100 g)

SOLID SAMPLING – ERROR

- AUTOCORRELATION (HIGH FOLLOWS HIGH AND V.V.)

- SUBSAMPLING ERROR (REPRESENTATIVENESS OF "SMALL" SAMPLES)

- ANALYTICAL ERROR (INTERFERENCES, INCOMPLETE RECOVERIES, ETC.

  - Detection Limit Values (Built-in Bias)

- SPATIAL "REPRESENTATIVENESS"

  - The Geographic Area defined by a radius centered at the sample site and of a length (L) equal to that of the range of correlation

SOLID SAMPLING – REPRESENTATIVENESS

- SPATIAL VARIABLES (TIME OR SPACE)

  - The range of correlation of the spatial correlation structure of the contaminant distribution can be estimated by semivariograms

  - The range of correlation

    = MAX. L between sampling sites at which samples are correlated.

    = MIN. L at which samples are independent

  - Semivariograms can provide this information.

B. Solid Sampling in Practice

    1. Program objectives and the preliminary sampling protocol

    2. Analyte selection (i.e., contaminants, soil or aquifer properties)

    3. Sampling points and devices

    4. Sampling experiment

    5. Refined sampling protocol/refined hypotheses and objectives

SOLID SAMPLING PROTOCOL – ANALYTES

- INORGANIC — "CRUSTAL" – Fe, Mn, Al, Si

  — "CONTAMINANTS" – Zn, Cd, Pb, As, Se, Cu, Ni, Co

- ORGANIC — TIC, TOC

  VOLATILE ORGANIC COMPOUNDS
  SEMI-VOLATILE ORGANIC
  COMPOUNDS

- MICROBIOLOGICAL
  PARAMETERS

- HYDROGEOLOGIC
  PARAMETERS

  — GRAIN SIZE DISTRIBUTION,

  PERMEABILITY

SOLID SAMPLING PROTOCOL – SAMPLING DEVICE

- SOIL — HAND AUGER, BRACE AND BIT,

  POST-HOLE, CORING DEVICES

- AQUIFER SOLIDS — SPLIT SPOON, SHELBY TUBE

  — CONTINUOUS CORER

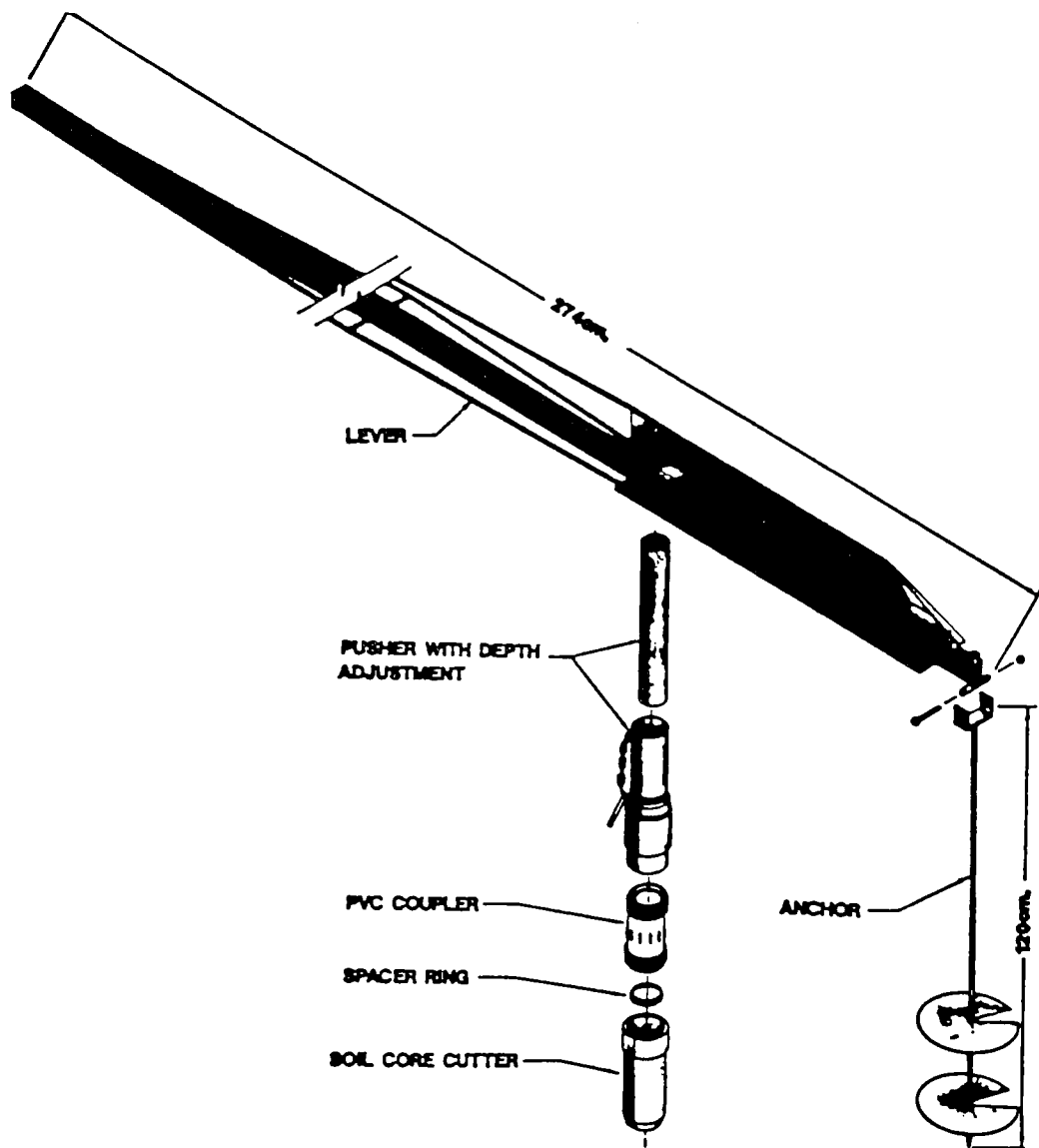 — DRIVEN OR PUSHED CORER

  — DIAMOND CORE

  — BAIL (CABLE TOOL METHOD)

Fig. 1. Undisturbed soil core sampling apparatus. (MYERS et al. 1987)

LEVER

PUSHER WITH DEPTH ADJUSTMENT

PVC COUPLER

SPACER RING

SOIL CORE CUTTER

ANCHOR

1	Teflon Wiper Disc.
2	Brass Bushings
3	Neoprene Seals
4	Swivel
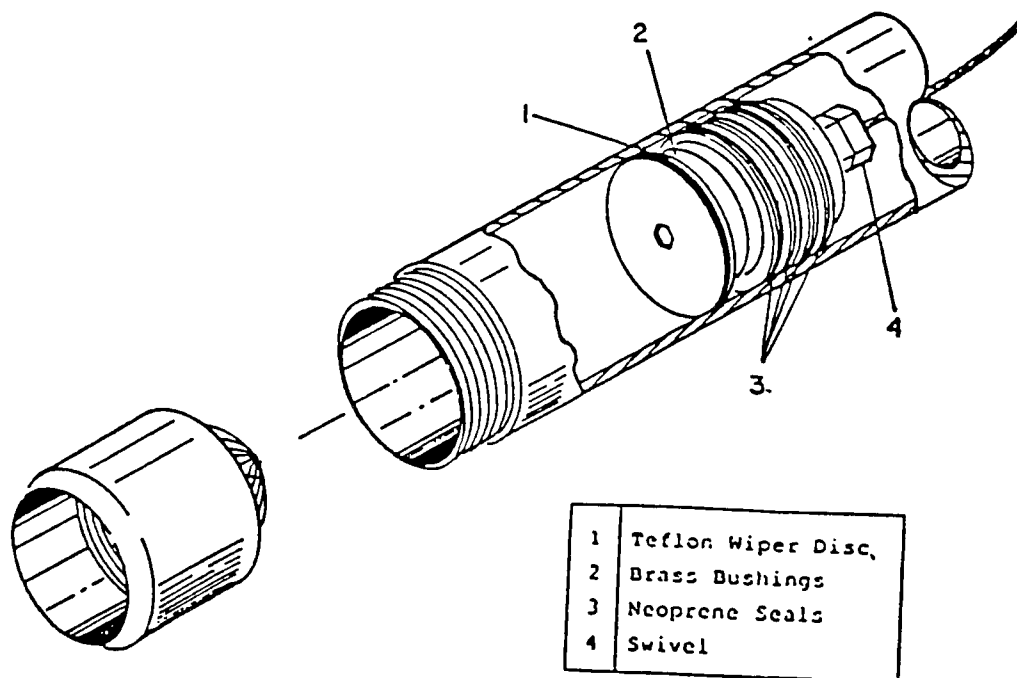
MODIFIED WIRELINE PISTON DESIGN

AUGER HEAD

BIT
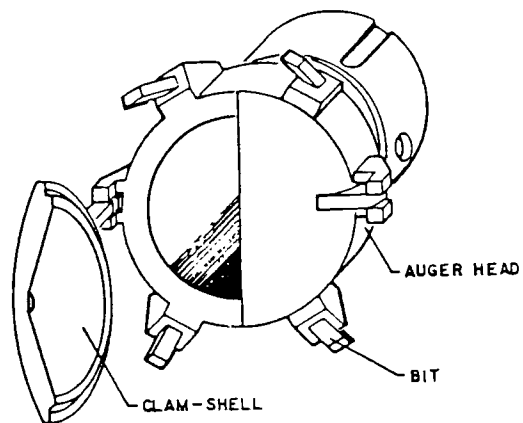
CLAM-SHELL

CLAM-SHELL FITTED AUGER HEAD

① PLACEMENT

② ADVANCEMENT (SAMPLING)

DRILL RODS
WIRELINE
BOREHOLE
DRILLING MUD
FILTER CAKE

HOLLOW-STEM AUGER
CORE BARREL
LINER
PISTON
DRILL BIT
AQUIFER
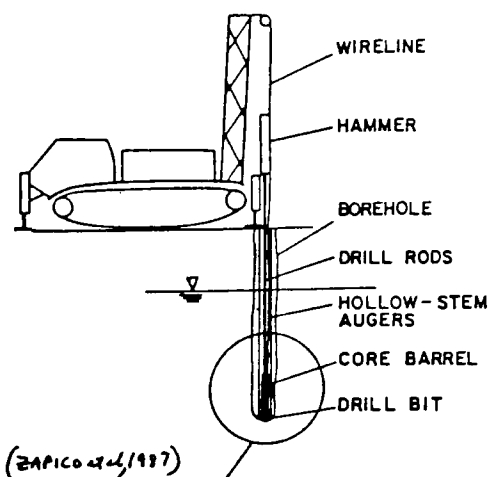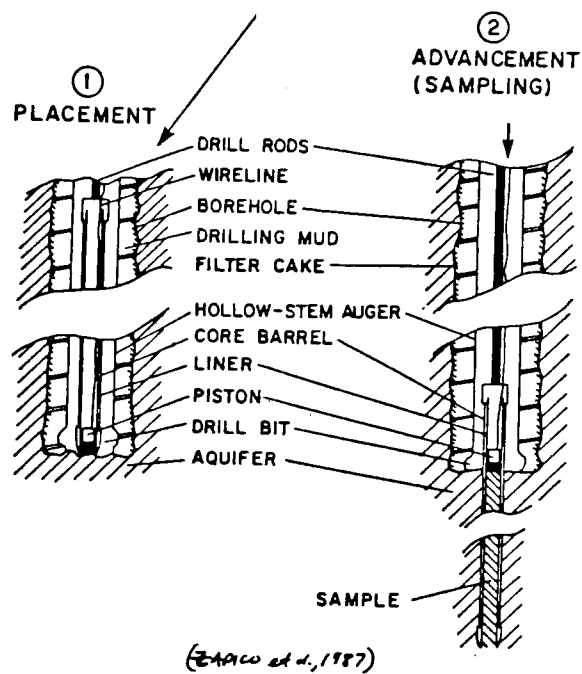
SAMPLE

(Zapico et al., 1987)

③ WIRELINE RECOVERY

DRILL BIT

DRILLING MUD

SAMPLE HOLE

(Zapico et al., 1987)

WIRELINE

HAMMER

BOREHOLE

DRILL RODS

HOLLOW-STEM AUGERS

CORE BARREL

DRILL BIT
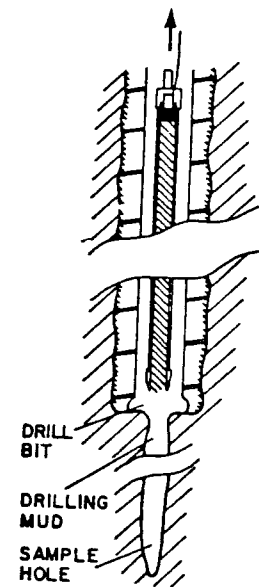
(Zapico et al., 1987)
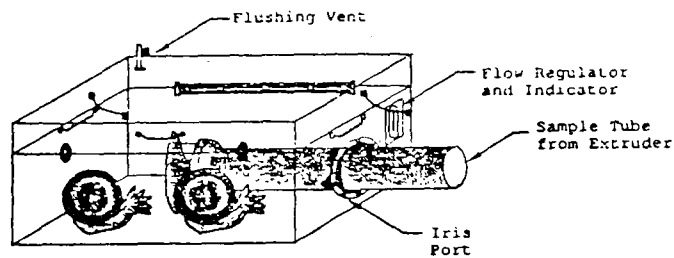
Field Sampling Glove Box
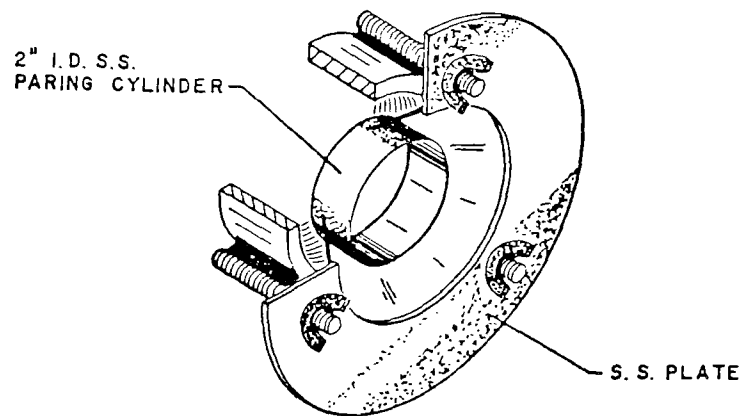
SOIL SAMPLING -- CASE STUDY (Williams et al., 1989)

^{226}Ra CONCENTRATIONS IN SOIL -- URANIUM MILL TAILINGS

STANDARD -- ^{226}Ra < 5 pCi/gram above background in top 15 cm
               <15 pCi/gram above background in deeper
               15 cm layers, both over 100 m^2 area

BACKGROUND -- 1 to 2 pCi/gram

CORE PARING TOOL

CASE STUDY -- ^{226}Ra

SAMPLING STRATEGY

    10 -- (50 g) composite
    20 -- (25 g) composite
    1 -- (500 g) grab

DATA ANALYSIS APPROACHES

    ■   Single 20 composite
    ■   Single 10 composite
    ■   5 to 20 random grabs
    ■   5 to 20 uniformly-spaced grabs

CASE STUDY – ^{226}Ra

APPROACH	RANKED PRECISION	RANKED ACCURACY
Single 20 composite	1	1
Single 10 composite	2	1*
Random grabs	2	2
Uniform grabs	2	2

* larger composites better

CASE STUDY – ^{226}Ra

SUMMARY

- 80-90% confidence is achievable with a reasonable number of samples if accuracy of 70 to 130% is satisfactory.

- Single 10-composite samples would be within 30% of true mean about 75% of the time.

- TWO 10-composite ≈30% of true mean ~90% of the time.

- THREE 10-composite ≈30% of true mean ~95% of the time.

- GROSS GAMMA MEASUREMENTS ARE USEFUL IN SAMPLING DESIGN AND EVALUATION; NOT NECESSARILY AS PREDICTORS OF ^{226}Ra.
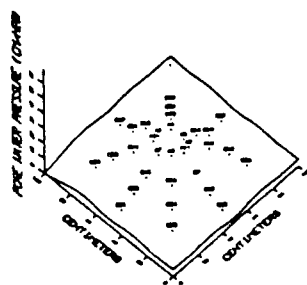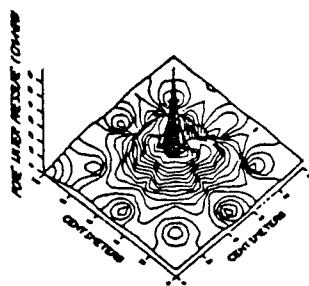
Monitoring Points   time=1000 min.
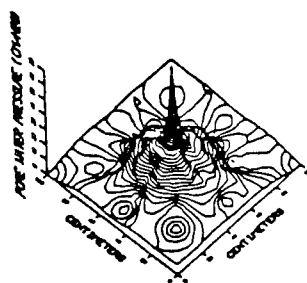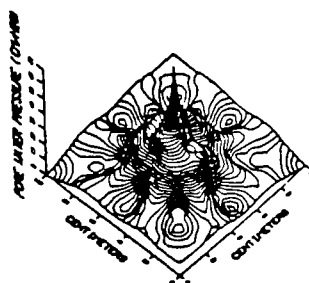
time=2000 min.   time=3000 min.

Change in Matric Potential with Time Adjacent to a
Porous Cup Sampler Evacuated with a Constant Vacuum of
70 kPa. (IN uNiFoRM SAND); MoRRiCoN/1981.

C. New Methods for Solid-Associated Contaminant Investigations

1. Soil-Gas techniques

2. Hybrid samplers (i.e., H₂O and soil)

NEW METHODS FOR SOLID-ASSOCIATED CONTAMINANT MONITORING

- **EMPHASIZE DETECTION** (May be difficult to reproduce)

- **SOIL GAS**

  - DYNAMIC (Pumped grab sample)
  - STATIC (Act. Carbon, Curie Point Method for "integrated" sampling)

- **HYDROPUNCH**[®]

  - DRIVEN SAMPLER (to collect H_2O in saturated zone)

FIGURE 1
Soil-gas concentrations under a variety of conditions

(A) Homogeneous porous material with sufficient air-filled porosity
(B) Impermeable subsurface layer (e.g., clay or perched water)
(C) Impermeable surface layer (e.g., pavement)
(D) Zone of high microbiological activity (circles and wavy lines indicate different compounds)
(E) VOC source in the vadose zone
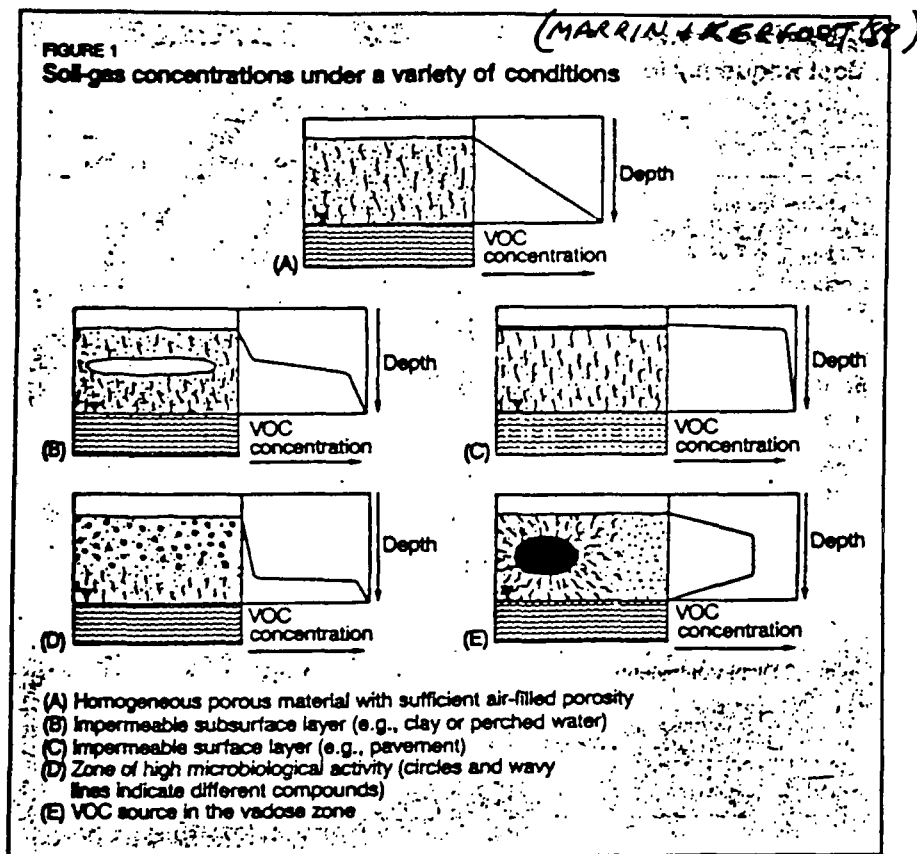
SOIL GAS-MEASUREMENTS

- **AMENABLE TO VOLATILE ORGANIC COMPOUNDS AND GASES**

SOLVENTS	–	TCA, TCE, PER, DCE, CLF, CH_2Cl_2, FREONS
FUELS	–	TOLUENE, BENZENE, ETHYLBENZENE, XYLENES
FIXED GASES	–	CO_2, CH_4, O_2, N_2

- **NOT DIRECTLY APPLICABLE TO SEMIVOLATILE ORGANICS OR INORGANICS**

SEMIVOLATILES	–	NAPHTHALENE, PHENOLS, AMINES, ETC.
NONVOLATILE	–	PCB's, BAP, "WEATHERED" FUELS, ETC.
INORGANICS	–	METALS, SALTS, ETC.

SOIL GAS-ANALYTES

- **PORTABLE (NONSPECIFIC) SENSORS: PID, FID**

- **MOBILE LABORATORY: GC-PID, GC-FID, GC-ECD, ETC.**

- **ANALYTICAL LABORATORY: GC-PID, GC-FID, GC-ECD, ETC.**
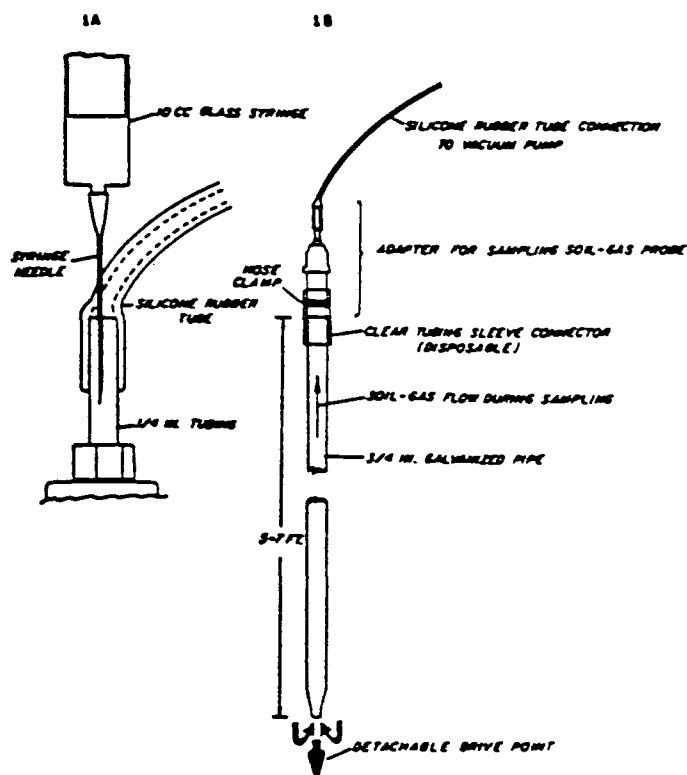
Figure 1. Soil gas sampling apparatus: (a) Close-up view of syringe sampling through the evacuation line. (b) gas flow through a soil gas probe *(THOMPSON AND MARRIN, 1987)*

TABLE 3
Profiles of F-113 (1,1,2-Trichlorotrifluoroethane) and TCE (Trichloroethylene) in Soil Gas

| Case #1 | | | Case #2 | |
| (A) | | | (B) | |
Depth (m)	F-113 (μg/L)		Depth (m)	TCE (μg/L)
0.6	0.004		3.0	0.006
1.1	0.3	Soil	7.6	0.02
3.4	33	Gas	15.2	0.03
6.1	1800		27.4	9
8.0	81	Water	32.0	140

Ground water concentrations of the two halocarbons analyzed at the water table are shown. All concentrations are presented in units of μg/L.

(THOMPSON AND MARRIN, 1987)

⊙ VERTICAL PROFILE BORINGS
● GROUNDWATER MONITORING WELLS
245 ● SOIL-GAS SAMPLING POINTS ·
—0.5— TCE CONCENTRATION CONTOURS IN
SOIL GAS (µg/L)
(30) TCE CONCENTRATIONS IN GROUNDWATER
MONITORING WELLS (ppb)

RAILROAD

EPA-3
(13)

930   330

55

420   320   0.05   60

EPA-2   0.001

795   785   775   310   740   70

300   510 515 520

● EPA-1   140   585 580 575 570   305   0.5   530   80

(30)   175   165 160 155 150 145   135 130 125 120 115 110 105 100   90   WASH

170   140

PAVED ROAD

● CU (2800)

● M-7 (4100)

Figure 4. Concentration contours of trichloroethylene (TCE) in soil gas for Case #2   (THOMPSON AND MARRIN, 1987)
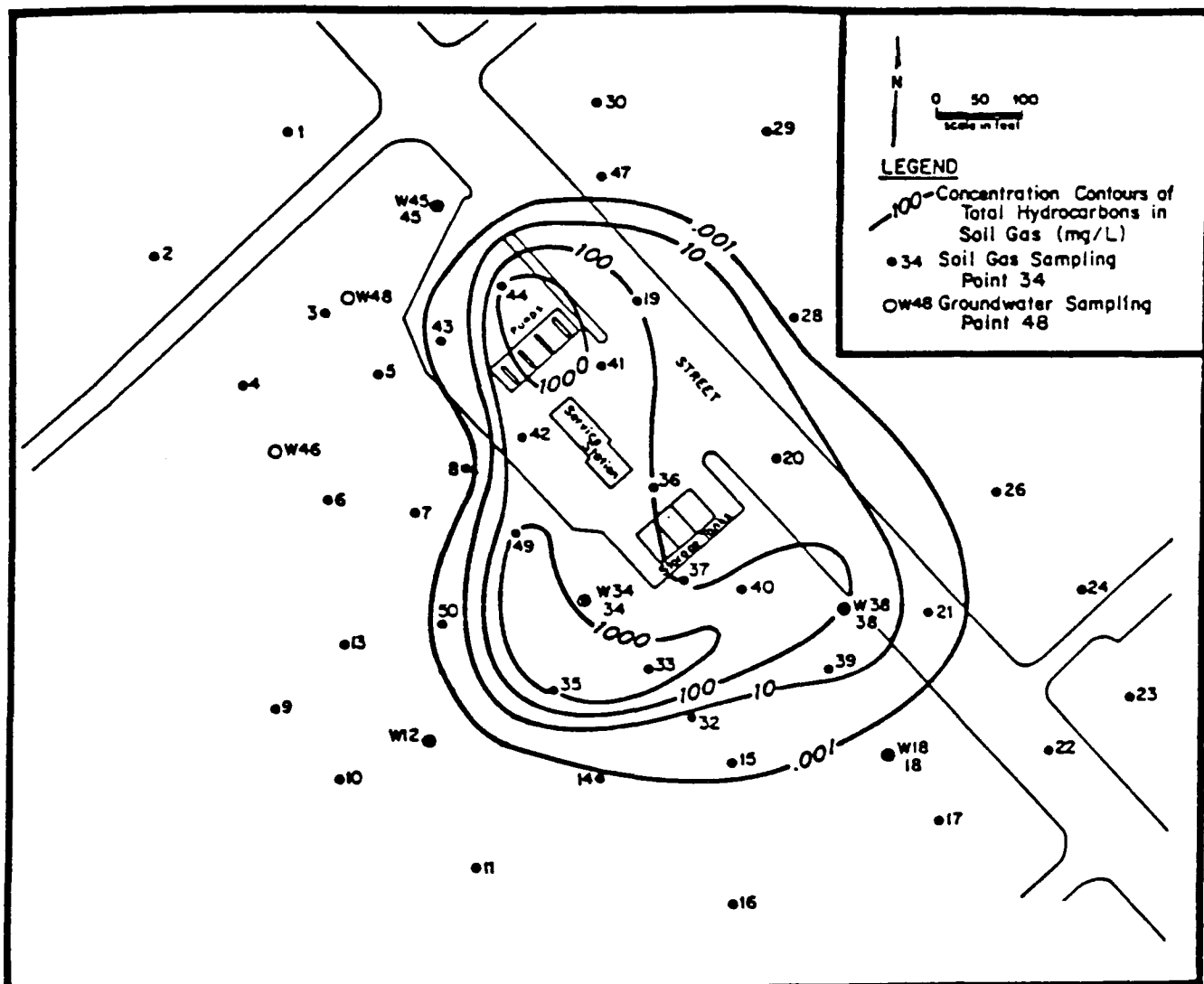
Figure 5. Concentration contours of total hydrocarbons in soil gas for Case #4 *(THOMPSON AND MARLIN, 1987)*

FIGURE 2
1,1,1-Trichloroethane concentrations in soil gas

Source

Groundwater flow

W-10
W-4
W-9
W-1
W-3
W-6
W-5
W-8   W-7
W-2
W-11

Legend
•   Wells
⌐1.0   1,1,1,-Trichloroethane
        contours in soil gas (µg/L)

North

Scale
0   25
Meters
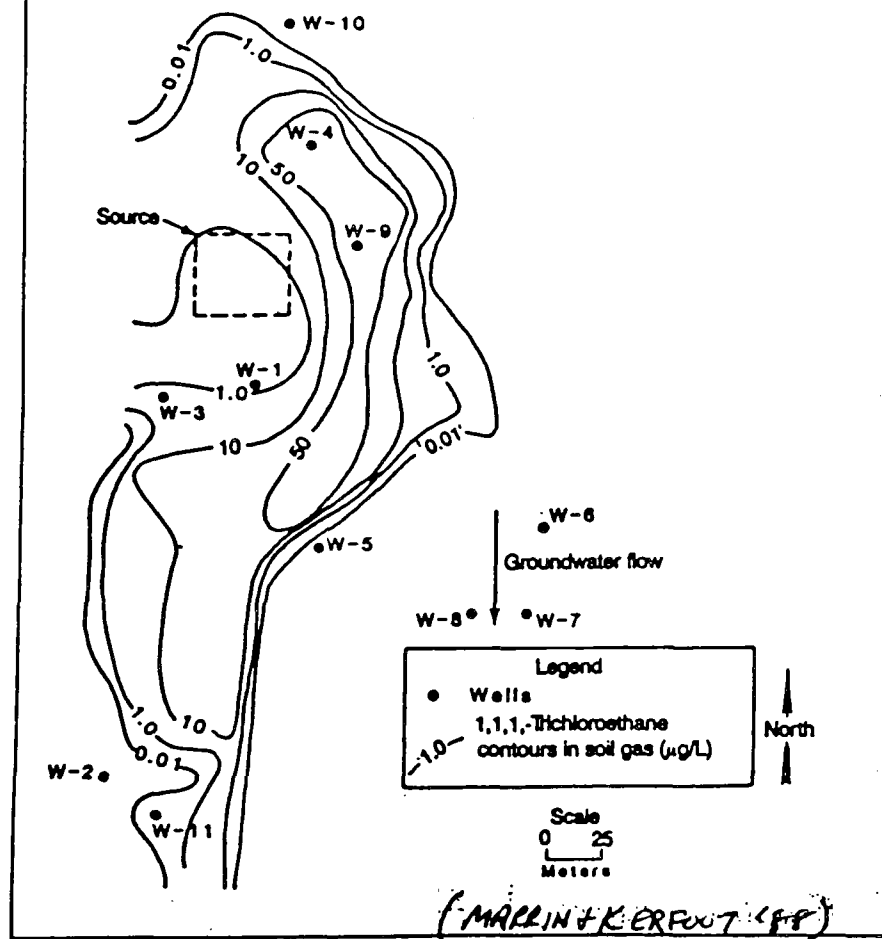
(MARRIN + KERFOOT '88)

FIGURE 3
Correlation between 1,1,1,-trichloroethane concentrations in soil gas and in groundwater samples from 11 wells

R = 0.88

TCA concentration in soil gas (µg/L)

W-4
W-9
W-3
W-1
W-11
W-5
W-10
W-6
W-2
W-8
W-7

TCA concentration in groundwater (µg/L)
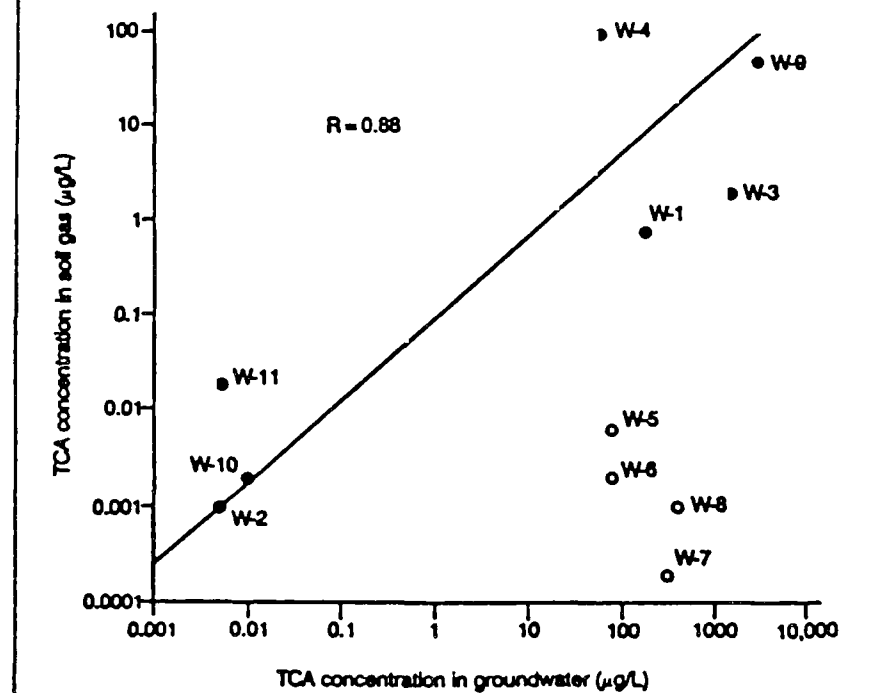
(MARRIN + KERFOOT '88)

FIGURE 4
Subsurface contamination from a leaking gasoline tank

Source
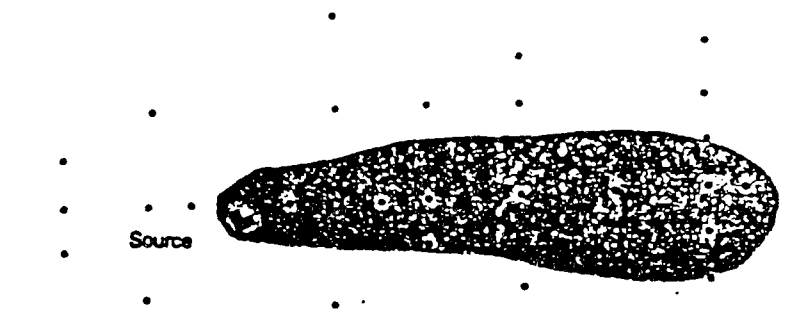
(a) Product plume according to confirmatory borehole results
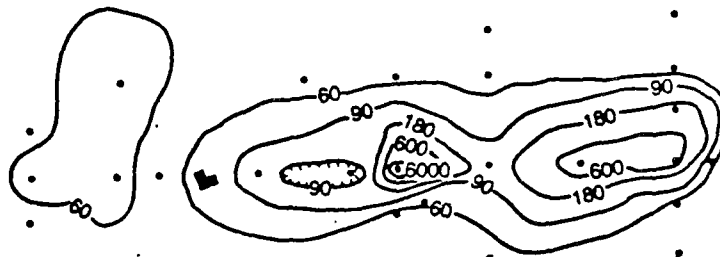
(b) Isooctane concentrations (ppb by volume) in soil gas at 2.2 meters
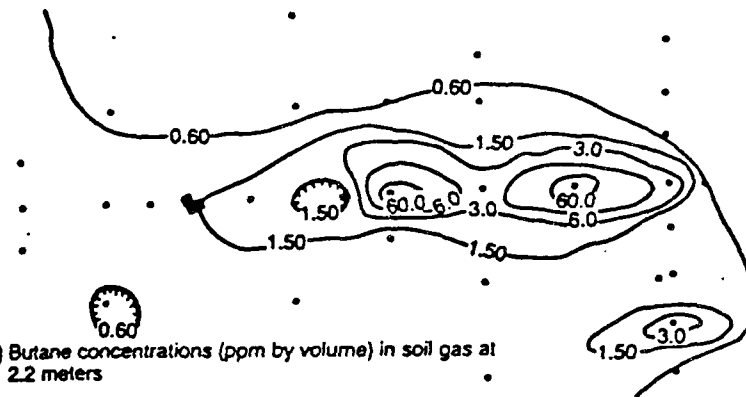
(c) Butane concentrations (ppm by volume) in soil gas at 2.2 meters

Legend
〰 Contour line
• Sampling point

Scale
0   50   100
(meters)
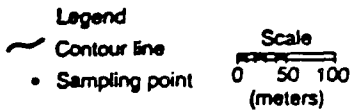
▬ Contamination from well and exploratory borehole data
Contaminated groundwater prediction
◯ Enclosed low-concentration zone

(MARLIN & KERFOOT '88)

SOIL GAS SAMPLING

■ RESULTS OF PRELIMINARY SAMPLING NEEDED?:

- AIR FILLED POROSITY >5%

- VOLATILE CONTAMINANTS PRESENT AT SIGNIFICANT LEVELS

- SELECT OPTIMAL SAMPLING DEPTH

- INITIAL SAMPLING LOCATIONS, GRID/TRANSECT

■ CO_2, O_2, CH_4 SHOULD NOT BE IGNORED IN FAVOR OF POLLUTANTS OF THE MONTH.

SOIL GAS AND HYDROPUNCH(R) SAMPLING

ADVANTAGES:

■ USED TOGETHER THEY CAN SUBSTANTIALLY IMPROVE THE DESIGN OF MONITORING NETWORKS BEYOND THE DETECTION STAGE

■ COMPLEMENT EACH OTHER IN ESTABLISHING CONTAMINANT MOVEMENT, PERSISTENCE AND RECOVERABILITY

■ MAY GIVE THE BEST PICTURE OF SHORT-RANGE VARIABILITY IN SPACE

SOIL GAS AND HYDROPUNCH(R) SAMPLING

DISADVANTAGES:

- SOIL GAS – Difficult to reference directly to pore water or ground-water contaminant concentrations

- MAY BE DIFFICULT TO REPRODUCE AND PROBABLY NOT VERY USEFUL IN REMEDIATION EVALUATIONS

- CAREFUL DECONTAMINATION AND QUALITY CONTROL MUST BE DONE IN THE FIELD – DIFFICULT CONDITIONS TO CONTROL

Figure 1. A logarithmic time scale for all possible events and durations.

PART 2

SOILS AND AQUIFER SOLIDS

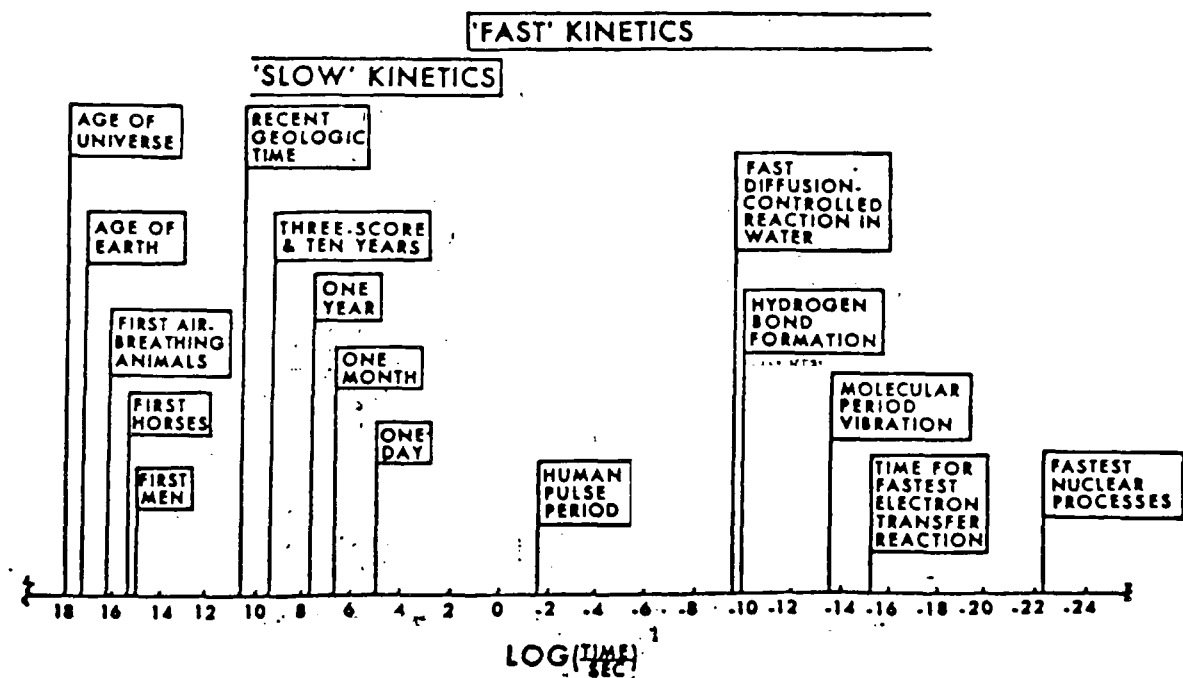Andreini, M., and T. Steenhuis, 1988. Preferential flow under conservation and conventional tillage. American Society of Agricultural Engineers. International Winter Meeting of the ASCE, Dec. 13-16, 1988. Paper No. 88-2633. pg. 22.

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PART 3. GROUND-WATER SAMPLE COLLECTION AND DATA INTERPRETATION

A. General Considerations
    1. Sampling strategies/evolving a network design
    2. Hydrogeologic and statistical considerations
    3. Development of a preliminary sampling protocol, QA/QC
B. Ground-Water Sampling in Practice
    1. Objectives and the preliminary sampling protocol
    2. Analyte selection (i.e., contaminants, major ionic
        constituents)
    3. Sampling points and devices
    4. Sampling experiment
    5. Refined sampling protocol/refined hypotheses
C. Interpretation of Geochemical and Water Chemistry Data
    1. Analytical performance, QA/QC, consistency checks
    2. Major ion, trace constituents and background conditions
    3. Contamination problems and comparisons with background
    4. Recognition of interferences, gross errors, etc.
    5. Dealing with snapshot data in a dynamic environment
    6. Case studies

TABLE II

Chemical constituents of interest in ground-water monitoring

Type of analyte	Analyte	Laboratory/Field determination L or F	Information applications				
			Water quality	Drinking H$_2$O suitability	Contamination indicators	Possible source impacts	Geochemical evaluation of data
Geochemical	pH, Eh	F	X	X	X	X	X
	Conductivity						
	Temperature						
	Dissolved oxygen		X				X
	Alkalinity	F (Field Filtered, FF)			X	X	X
	Ca^{++}, Mg^{++}	L (Field Filtered, FF)					X
	Na$^+$, K$^+$	L (Field Filtered, FF)	X	X			
	Cl$^-$, SO$_4^-$, PO$_4^-$	F (Field Filtered, FF)	X	X	X	X	X
	Silicate	L (Field Filtered, FF)					X
Water Quality	Trace Metals (Fe, Mn	L					
	Cr, Cd	(FF)	X	X	X	X	X
	Pb, Cu)						
	NO$_3^-$, NH$_4^+$	L(FF)	X	X	X	X	X
	F$^-$	L(FF)	X	X		X	
	TOC	L	X	X	X	X	
	TOX		X	X	X	X	
	TDS	L					
		(FF)	X	X	X	X	X
	Organic Compounds	L	X	X	X	X	

GROUND WATER SAMPLING (FOR ANALYSIS)

o Sampling in the "dark" given significant unknowns

o Most efforts are regulatory, legal or assessment for remedial action

o Trace organic and inorganic overemphasized

o Little or no treatment of "master" variables, major ionic constituents

o Solids, colloids, hydrogeochemical effects virtually ignored

-- GROUND-WATER SAMPLING AS A SELECTION PROCESS: PROTOCOL DEVELOPMENT

o Preliminary-Establish Hydrogeologic Basis

(hydraulic gradient, velocity-magnitude and direction)

o Location of Sampling Points

o Well Design, Drilling, Construction/Development

o Purging of Stagnant Water

● Sampling

● Sample Handling/Field Analysis

● Sample Storage

----

o Refine Protocol on the Basis of New Information

-- level of detail, time/resources, certainty required

TABLE 1—Ground-water quality monitoring network design activities.

Stage	Activity
Detective work	Study site characterization facility operations/land use hydrogeologic geochemical
Preliminary network design	Scope of network purpose and parameter selection quality assurance/quality control detection assessment
	Sampling points well placement and construction well development and performance evaluation
Working network design	Preliminary sampling protocol sampling mechanism and material selections water level measurements well purging sample collection sample filtration/preservation field determinations, blanks, standards sample storage/transport
Refine network design and sampling protocol	Analytical operations
	Interpret chemical and hydrologic results

Table 1.1. Data Requirements for Water-Source Definition and
Aquifer Representation of Ground-Water Samples
(Modified after Claassen, reference 31)

A. Drilling history

1. Well depth and diameter
2. Drill-bit type and circulating fluid
3. Lithologic data from cores or cuttings
4. Well-development before casing
5. Geophysical logs obtained

B. Well-completion data

1. Casing sizes, depths and leveling information relative to
   both land surface and top of casing
2. Casing material(s)
3. Cemented or grouted intervals and materials used
4. Plugs, stabilizers, and so forth, left in hole and
   materials used
5. Gravel packing: volume, sizes, and type of material
6. Screened, perforated, or milled casing or other intervals
   which allow water to enter the borehole
7. Pump type, setting, intake location, construction
   materials, and pump-column type and diameter
8. Well maintenance record detailing type of treatment and
   efficiency

C. Well pumping history

1. Rate
2. Frequency
3. Static and pumping water levels

D. Estimation of effect of contaminants introduced into aquifer
   during well drilling and completion on native water quality

E. Effect of sampling mechanism and materials on the composi-
   tion of ground-water sample

1. Addition of contaminants
2. Removal of constituents

   a. Sorption
   b. Precipitation
   c. Degassing

-- GROUND WATER SAMPLING: TOPICS OF SPECIAL INTEREST
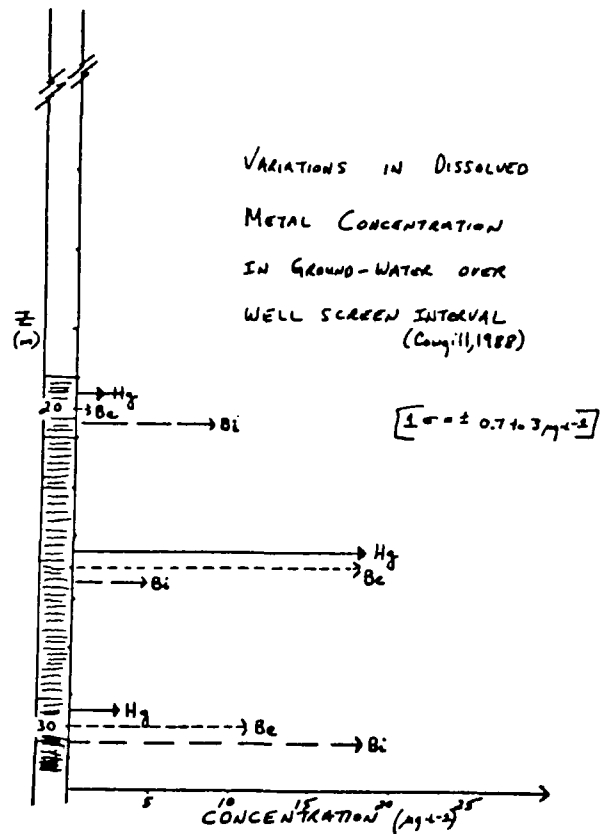
     Well Casing: Geochemical Disturbance, long-term Fe^{2+} trends

     Well Purging: Making the Hydrologic Connection, Gross Errors

     Sampling Devices: Reproducibility and Minimizing Systematic Error

     Tubing: Gas Permeability and Oxidation

     Filtration: Truly Dissolved Constituents, Colloids, Artefacts

     Storage: Keep it on ice!

WELL CASING:

o SCREEN DESIGN AND DURABILITY MOST IMPORTANT.

o INEVITABLE DISTURBANCE DURING DRILLING.

o AVOID MUDS OR DRILLING FLUIDS.

o PLACE GROUTS AND SEALS CAREFULLY.

o LONG-TERM GEOCHEMICAL EFFECTS POSSIBLE.

o ALL MATERIALS SORB TO SOME EXTENT.

WELL PURGING:

o CALCULATED PURGE REQUIREMENTS; VERIFY BY MEASUREMENTS OF pH, Ω^{-1}, T, (O_2, Eh).

o ESTABLISH HYDRAULIC CONNECTION BETWEEN SYSTEM AND SAMPLING POINT.

o BE CONSISTENT AND DOCUMENT RESULTS.

VARIATIONS IN DISSOLVED

METAL CONCENTRATION

IN GROUND-WATER OVER

WELL SCREEN INTERVAL
(Cowgill, 1988)

$\boxed{1\,\sigma = \pm\,0.7\,to\,3\,\mu g\,L^{-1}}$

CONCENTRATION ($\mu g L^{-1}$)

TRICHLOROETHYLENE CONCENTRATION VARIATIONS
WITH PURGING (Smith et al., 1988)
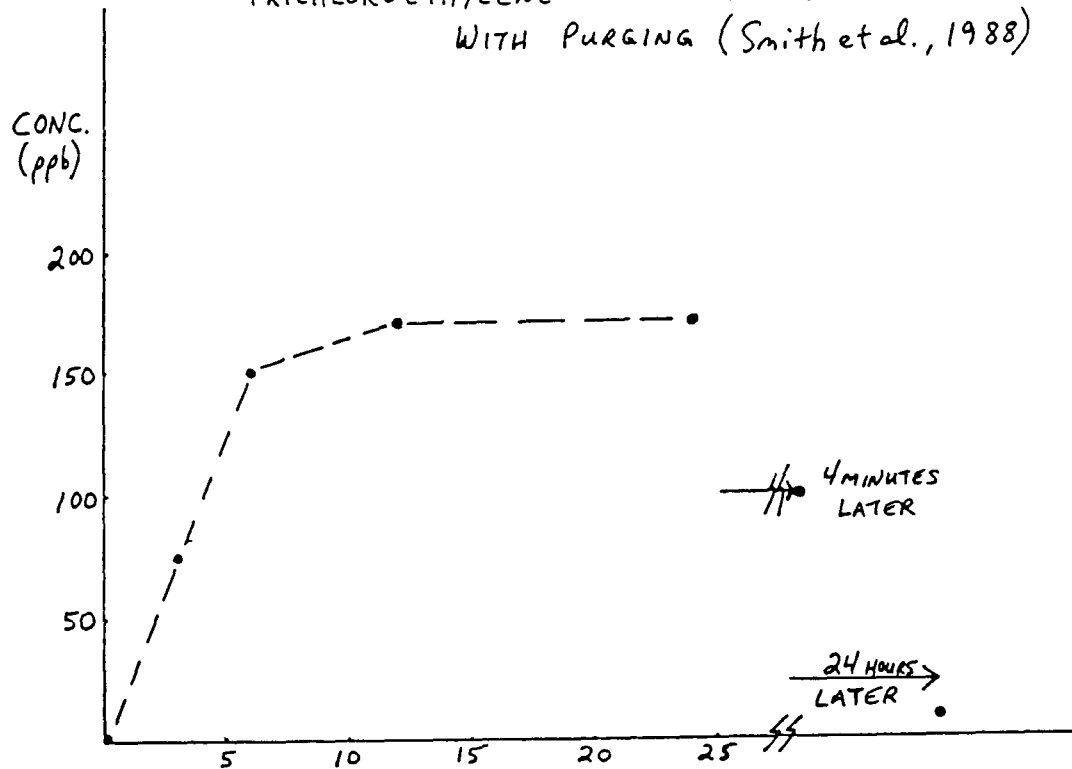
TABLE 3

METALS DETECTION LIMITS (PPM)

Cadmium(0.01) Magnesium(0.10)
Calcium(0.10) Nickel(0.05)
Chromium(0.10) Sodium(0.10)
Copper(0.10)   Zinc(0.10)
Lead(0.50)   Uranium(0.5)
Iron(0.50)

Monitor Well MSB 3A
Metals Data in ppm

Well Volumes	Ca	Fe	Mg	N_2	Zn
0	6.70	0.22	1.91	18.80	0.12
2	8.57	0.30	2.68	10.20	0.15
4	8.37	1.08	2.67	10.50	0.16
6	8.27	0.24	2.59	9.76	0.15
8	8.09	0.35	2.58	9.88	0.13
10	8.47	0.50	2.60	10.10	0.13

LORENZ + PRICE (1988)

620.0 m^2/day

62

6.2

0.62

PERCENT AQUIFER WATER

Transmissivity 0.062 m^2/day
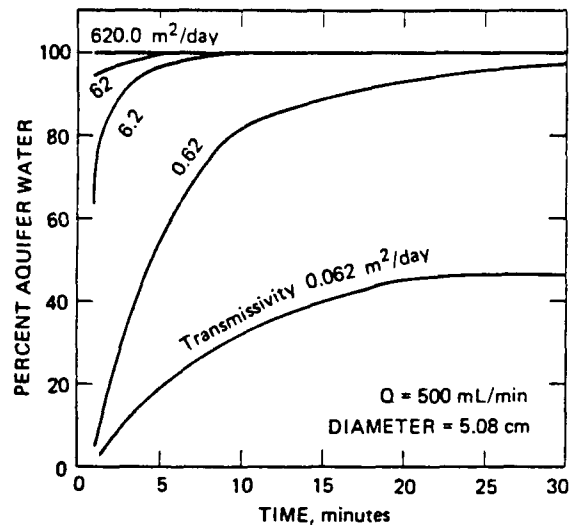
Q = 500 mL/min
DIAMETER = 5.08 cm

TIME, minutes

Figure 2.15. Percentage of aquifer water versus
time for different transmissivities

Example 2.4. Well purging strategy based
on hydraulic conductivity data

Given:
    48-foot-deep, 2-inch-diameter well
    2-foot-long screen
    3-foot-thick aquifer
    Static water level about 15 feet below land surface
    Hydraulic conductivity = 10^{-2} cm/sec

Assumptions:
    A desired purge rate of 500 mL/min and sampling rate of 100 mL/
    min will be used.

Calculations:
    One well volume = (48 ft − 15 ft) x 613 mL/ft (2-inch-diameter well)
                 = 20.2 liters

    Aquifer transmissivity = hydraulic conductivity x aquifer thickness
                       = 10^{-4} m/sec x 1 meter
                       = 10^{-4} m^2/sec or 8.64 m^2/day

From Figure 2.15:
    at 5 minutes ~95% aquifer water and
                    (5 min x 0.5 L/min)/20.2 L
                    = 0.12 well volumes
    at 10 minutes ~100% aquifer water and
                    (10 min x 0.5 L/min)/20.2 L
                    = 0.24 well volumes

RIGID MATERIAL RECOMMENDATION

PURPOSE OF PROGRAM

DETECTIVE   ASSESSMENT

SUBSURFACE
CONTAMINATION
CONDITIONS

UNKNOWN   HIGH   HIGH ORGANIC   HIGH ORGANIC   HIGH ORGANIC
           INORGANIC   OR INORGANIC   NO ORGANIC   AND/OR INORGANIC
           SUSPECTED   SUSPECTED   KNOWN   KNOWN

PTFE   PTFE   PTFE   PTFE
SS   SS   PVC   SS
PVC   PVC   SS

IMPORTANCE OF   COULD PPB LEVEL
TRACE LEVEL   ORGANICS BE IMPORTANT?   PTFE - polytetrafluoroethylene
ORGANICS   SS - stainless steel (316 or 304)
                                                              PVC - polyvinyl chloride

                      YES   NO

                      |PTFE| PTFE
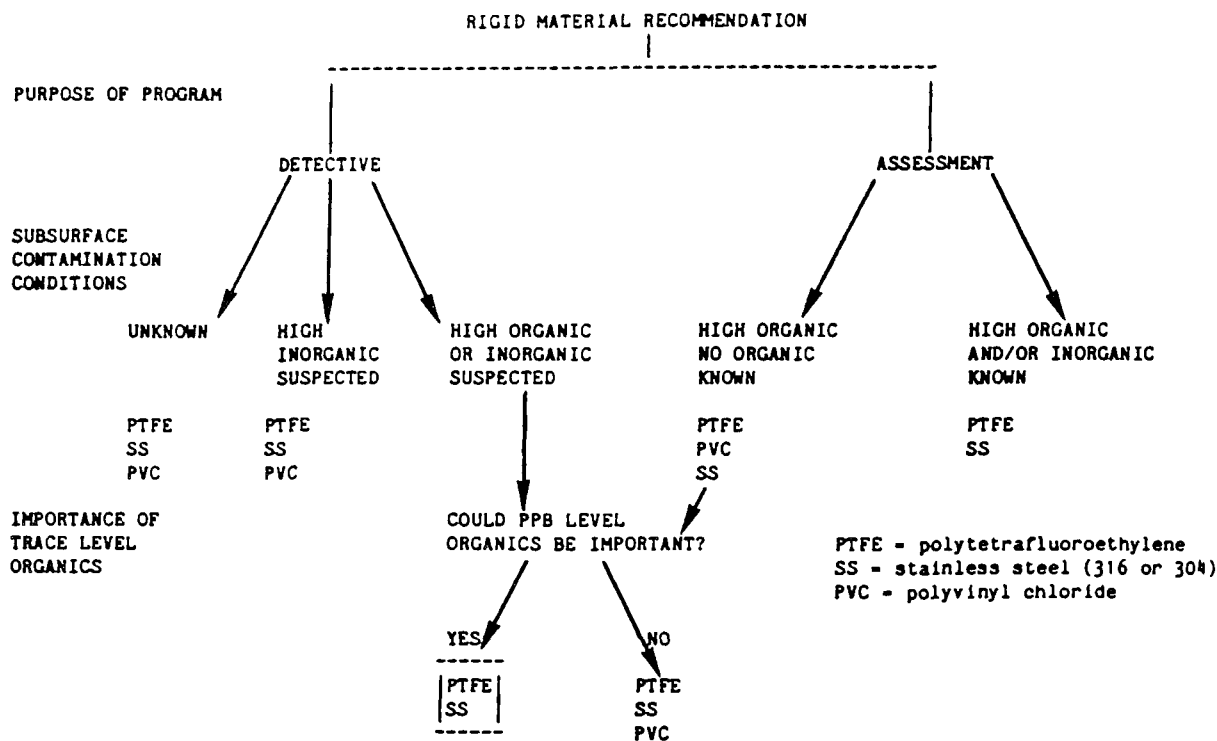 |SS | SS
                                         PVC

FIG. 1b—*Example decision tree for recommended well-casing/screen materials (adapted from Ref 13).*

SAMPLING MECHANISM RECOMMENDATION

LIFT REQUIREMENTS

                      <140 m (450')   >140 m

FLOW RATE
VARIABILITY OF MECHANISM
(PURGING AND SAMPLING)

              YES   LIMITED   YES   LIMITED

              PUMPS   GRAB OR   PUMPS   GRAB OR
                           GAS LIFT   GAS LIFT

        YES   NO   NO   YES   YES   NO   NO   YES

ARE |NO GAS CONTACT| NO GAS CONTACT: BAILER   THIEF   - INCOMPLETE -
PARAMETERS OF |P-D BLADDER | P-D BLADDER   THIEF
INTEREST |P-D MECHANICAL| P-D MECHANICAL
VOLATILE,   OR
OR pH SENSITIVE?   GAS-DRIVE
                                    CENTRIFUGAL
                                    PERISTALTIC
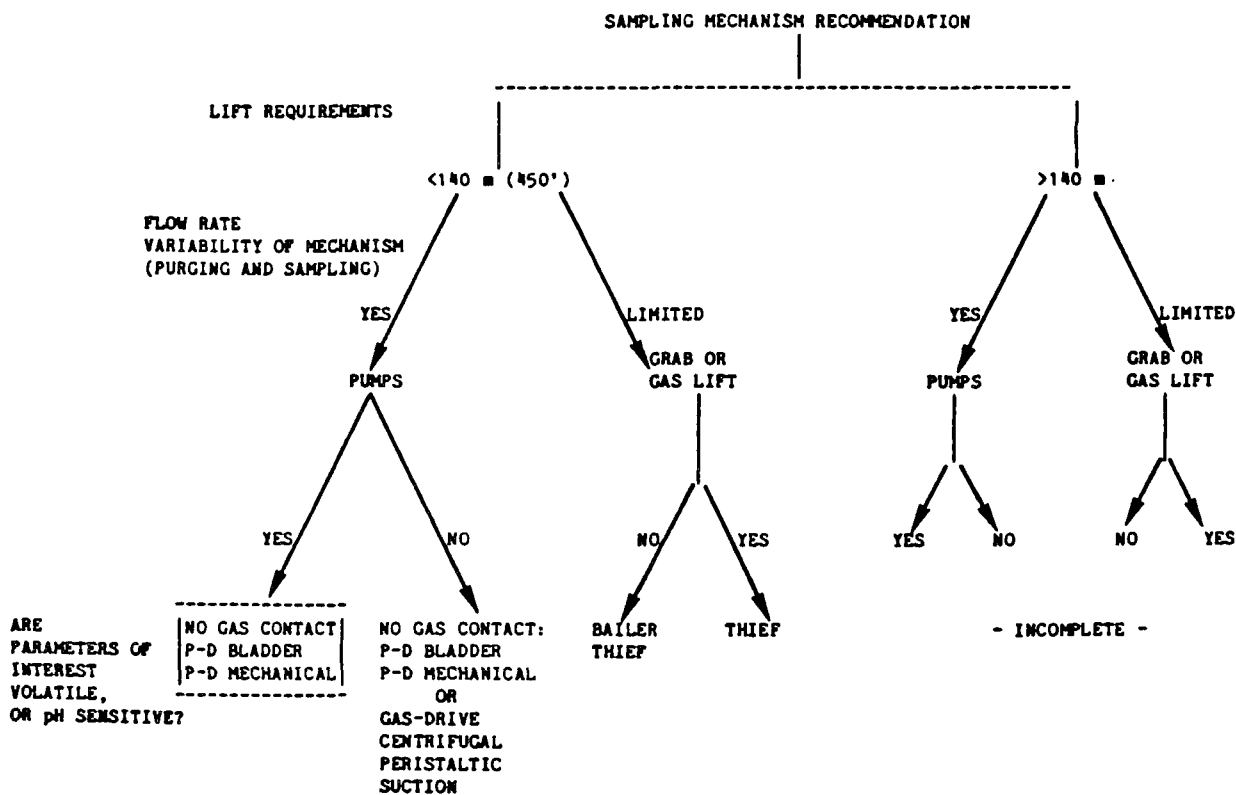   SUCTION

FIG. 3—*Example decision tree for recommended purge and sampling mechanism (adapted from Ref 13).*

Type of constituent	Example of constituent	Positive-displacement bladder pumps	Thief, in situ or dual check valve bailers	Mechanical positive-displacement pumps	Gas-drive devices	Suction mechanisms
			INCREASING RELIABILITY OF SAMPLING MECHANISMS →			
Volatile Organic Compounds Organometallics	Chloroform TOX CH_3Hg	Superior performance for most applications	May be adequate if well purging is assured	May be adequate if design and operation are controlled	Not recommended	Not recommended
Dissolved Gases Well-Purging Parameters	O_2, CO_2 pH, Ω^{-1} Eh	Superior performance for most applications	May be adequate if well purging is assured	May be adequate if design and operation are controlled	Not recommended	Not recommended
Trace Inorganic Metal Species Reduced Species	Fe, Cu NO_2^-, S^-	Superior performance for most applications	May be adequate if well purging is assured	Adequate	May be adequate	May be adequate if materials are appropriate
Major Cations & Anions	Na^+, K^+, Ca^{++} Mg^{++} Cl^-, SO_4^-	Superior performance for most applications	Adequate May be adequate if well purging is assured	Adequate	Adequate	Adequate

TABLE 2—*Matrix of sensitive chemical constituents and various sampling mechanisms (from Ref 3).*

SAMPLING DEVICES:

o MOST ACCURATE AND REPRODUCIBLE; <u>BLADDER PUMPS</u>

o MOST RELIABLE AND EASY TO DIAGNOSE MALFUNCTION

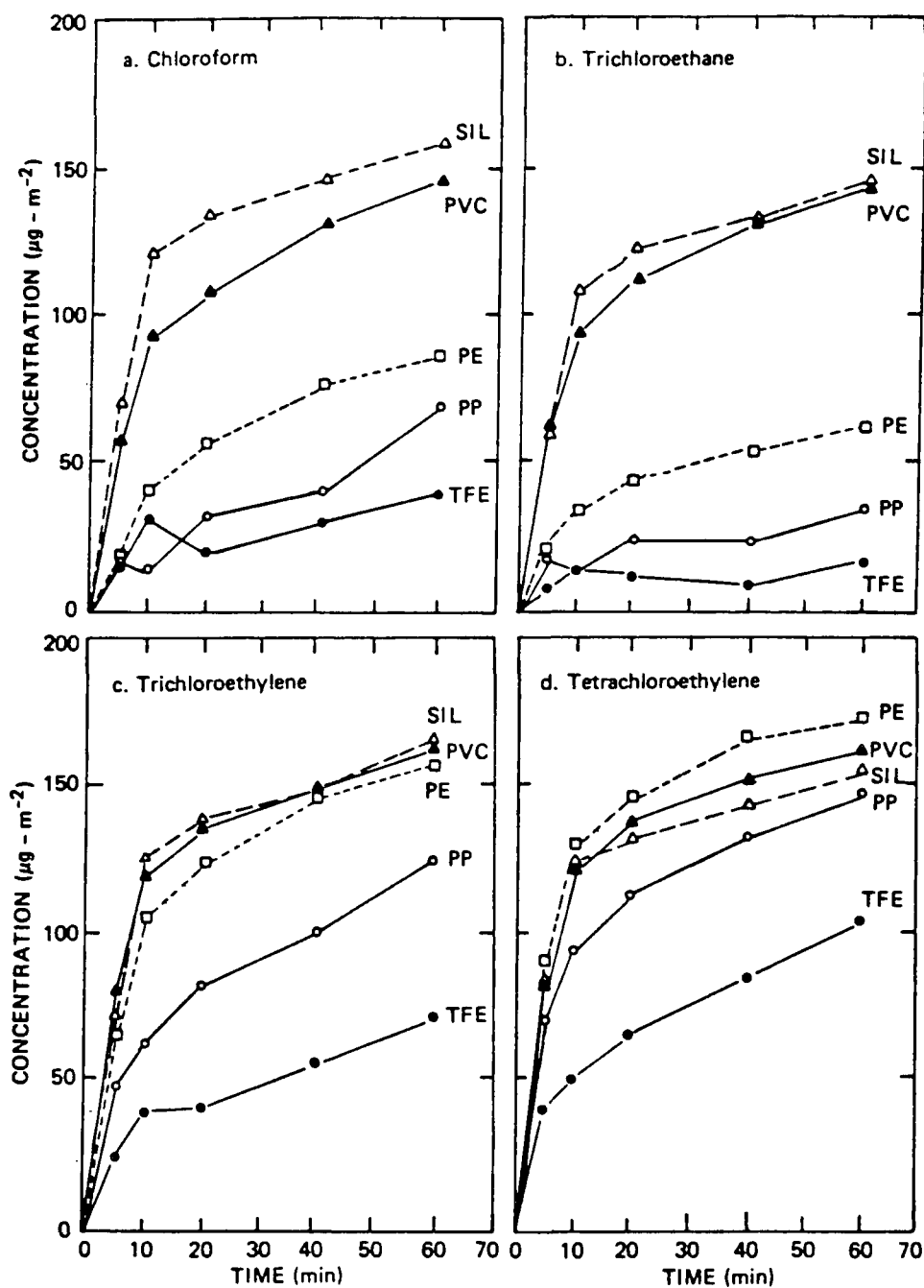o DEDICATION TO THE WELL AVOIDS CROSS-CONTAMINATION AND FIELD DECONTAMINATION

FIG. 1—*Concentration of sorbed chlorinated organics. The sorbed concentration ($\mu g \cdot m^{-2}$ of the four test compounds from distilled water solutions is shown as a function of time in exposure to tubing materials: (a) chloroform, (b) trichloroethane, (c) trichloroethylene, (d) tetrachloroethylene. Dissolved concentrations were initially between 90 and 120 ppb of each compound (from Ref 22).*

SAMPLING TUBING:

o OXYGEN PERMEABILITY MAY GIVE RISE TO BIASED RESULTS FROM DEEP INSTALLATIONS.

o RAPID SORPTION OF ORGANIC COMPOUNDS A CONCERN.

Table 7-9. Frequency of Occurrence of Phthalate Esters
in Wastewater and Ground-Water Samples

Phthalates	Industrial wastewaters	N.Y. state public water supply wells	"Superfund" monitoring samples
bis-(2-ethylhexyl) phthalate	42%	98%	0%
Dibutyl phthalate	19	72	4.8
Diethyl phthalate	8	35	1.9
Butylbenzyl phthalate	8	26	<1
Dioctyl phthalate	6	11	1.1
Number of Samples	2532-2998 (avg. 2617)	56	1150
Reference	112	39	113

SAMPLE FILTRATION:

o SUB-MICROMETER PARTICLES ARE MOBILE.

o OPERATIONALLY DISSOLVED CONSTITUENTS VS. COLLOIDAL.

o DRILLING, WELL DESIGN AND CONSTRUCTION DECISIONS MAY BIAS ALL SUBSEQUENT RESULTS.
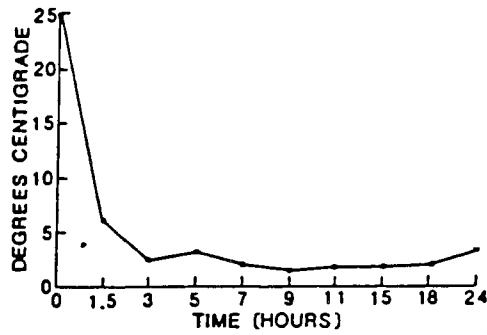
Figure 4. Field refrigeration of samples with water ice.
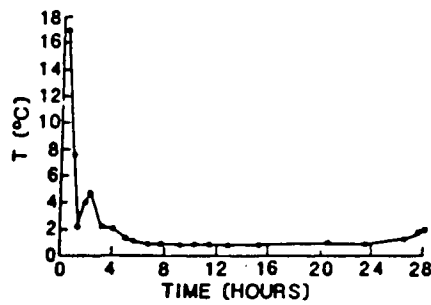
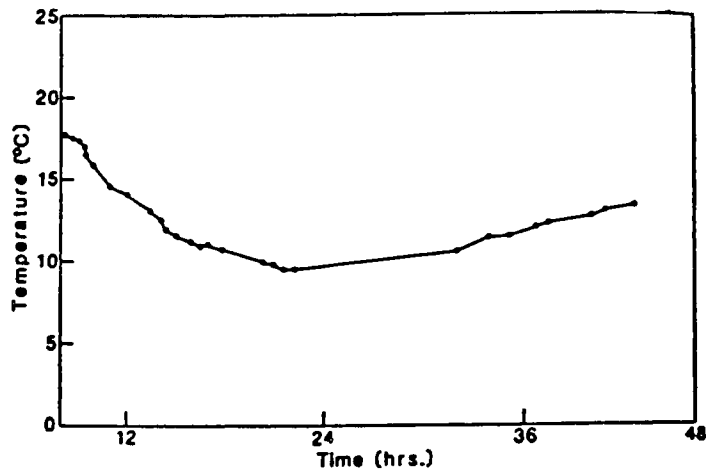Figure 5. Bottles placed in crushed ice chilled to 4 °C and transferred to an ice chest prechilled with blue ice.

Figure 6. Field refrigeration of samples with blue ice.

SAMPLE STORAGE:

Kent & Payne, 1988

o CHILL WITH WATER, ICE OR MECHANICAL REFRIGERATION
   IMMEDIATELY.

o TRANSPORT RAPIDLY AND OBSERVE CHAIN OF CUSTODY PROCEDURES.

o ARTIFICIAL ICE-PACKS ALONE DON'T WORK.

TABLE 4—*Potential contributions of sampling methods and materials to error* in ground-water chemical results.*

ameter	Concentration, units	Drilling Muds	Grouts, Seals	Well Purging	Well Casing	Sampling Mechanism	Sampling Tubing	References
	5-9 pH units	. . .	+, 4 to 5 units cement	±, 0.1 to 4 units	.	gas lift +. 0.1 to 3 units	.	*10, 11, 14*
C	0.5-25 mg·C·L⁻¹	+, 300%	. . .	±, 500%	±, 200%	bailer +, 150%	. .	Table 1, *10*
II)	0.01-10 mg·L⁻¹	. .	-,* 500% cement	-,* 1000%	+. 1000% iron, galvanized steel	gas lift -,* 500%	. .	*2, 10, 11, 14*
latile	0.5-15 µg·L⁻¹	. .	. . .	±, 10 to 100%	±, 200%	. . .	. . .	*10*
ganic :ompounds	80-8000 µg·L⁻¹	. . .	. . .	. . .	. .	suction -,* 1 to 15%	-10 to 75%	*20, 21*

¹ Bias values exceeding > ± 100% denoted as gross errors (+ or -); other values expressed as percent of reported mean.
² No data available on the type and extent of error for this parameter.

CONCLUSIONS:

o SAMPLING ERRORS CAN BE CONTROLLED IF LOCATION, SAMPLING-POINT DESIGN AND CONSTRUCTION ARE DONE PROPERLY.

o PURGING IS THE SINGLE-MOST IMPORTANT STEP IN SAMPLING.

o SAMPLING AND ANALYTICAL PROTOCOL DEVELOPMENT SHOULD BE PHASED AND REFINED AS DETAIL REQUIRES.

o ANALYTICAL ERRORS CAN BE CONTROLLED WITH PROPER QA/QC.

o "NATURAL" VARIABILITY CAN BE ESTIMATED WITH QUARTERLY SAMPLING; SEASONAL VARIATIONS MAY TAKE YEARS OF SUCH SAMPLING TO RESOLVE.

TABLE 3—*Generalized ground-water sampling protocol.*

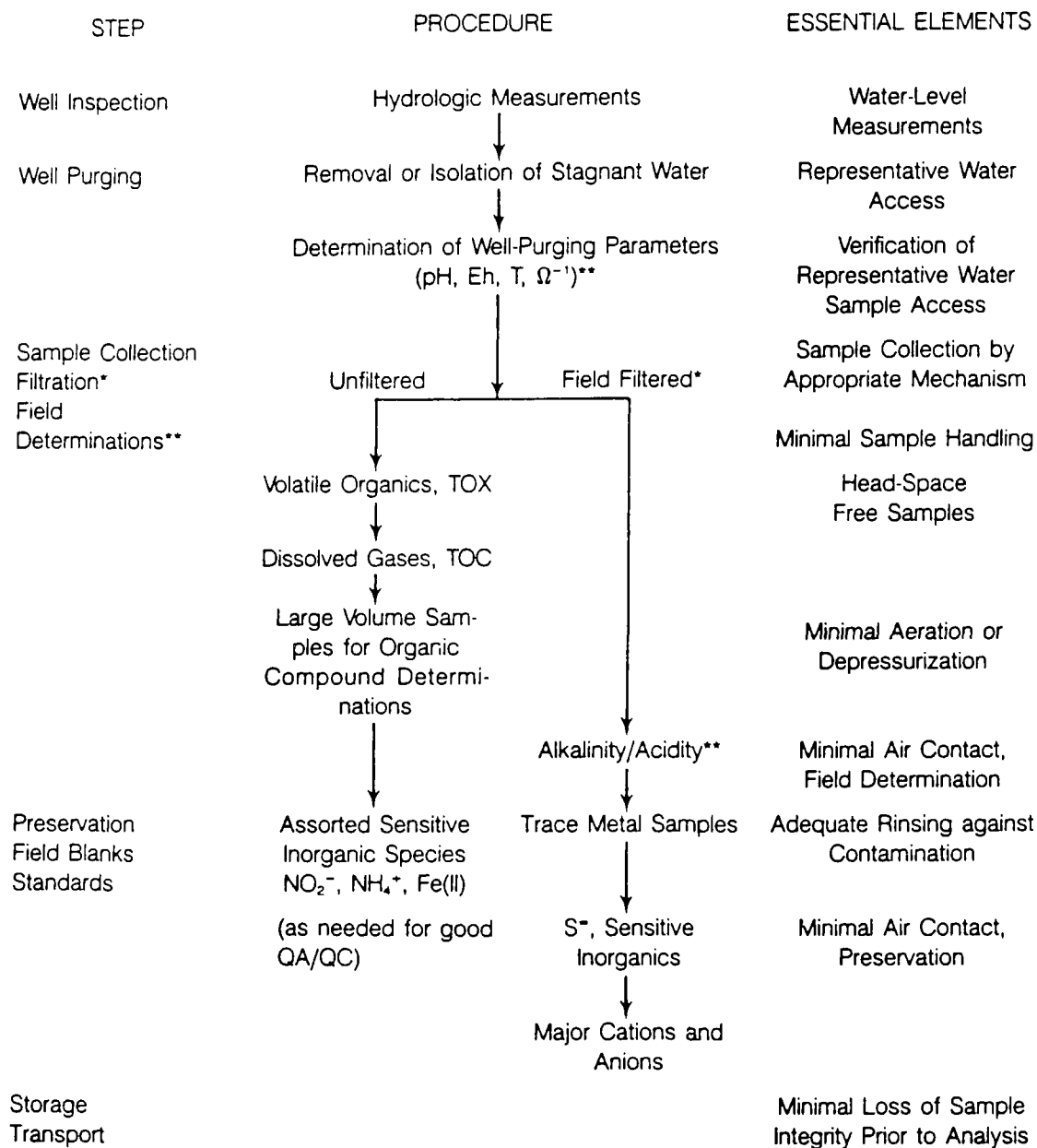| Step	Goal	Recommendations
Hydrologic measurements	establish nonpumping water level	measure the water level to ±0.3 cm (±0.01 ft*)
Well purging	removal or isolation of stagnant H_2O which would otherwise bias representative sample	pump water until well purging parameters (such as pH, T, Ω^{-1}, Eh) stabilize to ±10% over at least two successive well volumes pumped
Sample collection	collection of samples at land surface or in well-bore with minimal disturbance of sample chemistry	pumping rates should be limited to ~100 mL/min for volatile organics and gas-sensitive parameters
Filtration/preservation	filtration permits determination of soluble constituents and is a form of preservation. It should be done in the field as soon as possible after collection	*filter:* trace metals, inorganic anions/cations, alkalinity *do not filter:* TOC, TOX, volatile organic compound samples; other organic compound samples only when required
Field determinations	field analyses of samples will effectively avoid bias in determinations of parameters/constituents which do not store well: for example, gases, alkalinity, pH	samples for determinations of gases, alkalinity and pH should be analyzed in the field if at all possible
Field blanks/standards	these blanks and standards will permit the correction of analytical results for changes which may occur after sample collection: preservation, storage, and transport	at least one blank and one standard for each sensitive parameter should be made up in the field on each day of sampling. Spiked samples are also recommended for good QA/QC
Sampling storage/transport	refrigeration and protection of samples should minimize the chemical alteration of samples prior to analysis	observe maximum sample holding or storage periods recommended by the Agency. Documentation of actual holding periods should be carefully performed

* 1 ft = 0.3048 m.

B. Ground-Water Sampling in Practice

1. Objectives and the preliminary sampling protocol

2. Analyte selection (i.e., contaminants, major ionic constituents)

3. Sampling points and devices

4. Sampling experiment

5. Refined sampling protocol/refined hypotheses

STEP	GOAL	RECOMMENDATIONS
Hydrologic Measurements	Establishment of nonpumping water level.	Measure the water level to ± 0.3 cm (± 0.01 ft).
Well Purging	Removal or isolation of stagnant H_2O which would otherwise bias representative sample.	Pump water until well purging parameters (e.g., pH, T, Ω^{-1}, Eh) stabilize to $\pm 10\%$ over at least two successive well volumes pumped.
Sample Collection	Collection of samples at land surface or in well-bore with minimal disturbance of sample chemistry.	Pumping rates should be limited to ~ 100 mL/min for volatile organics and gas-sensitive parameters.
Filtration/ Preservation	Filtration permits determination of soluble constituents and is a form of preservation. It should be done in the field as soon as possible after collection.	*Filter:* Trace metals, inorganic anions/cations, alkalinity. *Do not filter:* TOC, TOX, volatile organic compound samples. Filter other organic compound samples only when required.
Field Determinations	Field analyses of samples will effectively avoid bias in determinations of parameters/ constituents which do not store well: e.g., gases, alkalinity, pH.	Samples for determinations of gases, alkalinity and pH should be analyzed in the field if at all possible.
Field Blanks/ Standards	These blanks and standards will permit the correction of analytical results for changes which may occur after sample collection: preservation, storage, and transport.	At least one blank and one standard for each sensitive parameter should be made up in the field on each day of sampling. Spiked samples are also recommended for good QA/ QC.
Sampling Storage/ Transport	Refrigeration and protection of samples should minimize the chemical alteration of samples prior to analysis.	Observe maximum sample holding or storage periods recommended by the Agency. Documentation of actual holding periods should be carefully performed.

Figure 2.16. Generalized ground-water sampling protocol

STEP	PROCEDURE	ESSENTIAL ELEMENTS
Well Inspection	Hydrologic Measurements	Water-Level Measurements
Well Purging	Removal or Isolation of Stagnant Water	Representative Water Access
	Determination of Well-Purging Parameters (pH, Eh, T, Ω^{-1})**	Verification of Representative Water Sample Access
Sample Collection Filtration* Field Determinations**	Unfiltered Field Filtered*	Sample Collection by Appropriate Mechanism
		Minimal Sample Handling
	Volatile Organics, TOX	Head-Space Free Samples
	Dissolved Gases, TOC	
	Large Volume Samples for Organic Compound Determinations	Minimal Aeration or Depressurization
	Alkalinity/Acidity**	Minimal Air Contact, Field Determination
Preservation Field Blanks Standards	Assorted Sensitive Inorganic Species NO_2^-, NH_4^+, Fe(II) Trace Metal Samples	Adequate Rinsing against Contamination
	(as needed for good QA/QC) S^-, Sensitive Inorganics	Minimal Air Contact, Preservation
	Major Cations and Anions	
Storage Transport		Minimal Loss of Sample Integrity Prior to Analysis

* Denotes samples which should be filtered in order to determine dissolved constituents. Filtration should be accomplished preferably with in-line filters and pump pressure or by N_2 pressure methods. Samples for dissolved gases or volatile organics should not be filtered. In instances where well development procedures do not allow for turbidity-free samples and may bias analytical results, split samples should be spiked with standards before filtration. Both spiked samples and regular samples should be analyzed to determine recoveries from both types of handling.

** Denotes analytical determinations which should be made in the field.

Figure 3.1. Generalized flow diagram of ground-water sampling steps

Table 3.1. Recommended Analytical Parameters for Detective Monitoring

Type of parameter	Type of determination Lab. (L), Field (F)	Analytes	
		Required by regulation	Suggested for completeness
Well-purging	F	pH, conductivity (Ω^{-1})	Temperature (T) Redox potential (Eh)
Contamination indicators	F	pH, Ω^{-1}	
	L	Total organic carbon (TOC)	
	L	Total organic halogen (TOX)	
Water quality*	L	Cl⁻, Fe, Mn, Na⁺, SO₄⁻	Alkalinity (F) or acidity (F)
	L	Phenols	Ca⁺⁺, Mg⁺⁺, K⁺, NO₃⁻, PO₄⁻, silicate, ammonium
Drinking water suitability**	L	As, Ba, Cd, Cr, F⁻, Pb, Hg, NO₃⁻, Se, Ag	
	L	Endrin, lindane, methoxychlor, toxaphene 2,4-D, 2,4,5-TP (Silvex)	
	L	Radium, gross alpha/beta coliform bacteria	
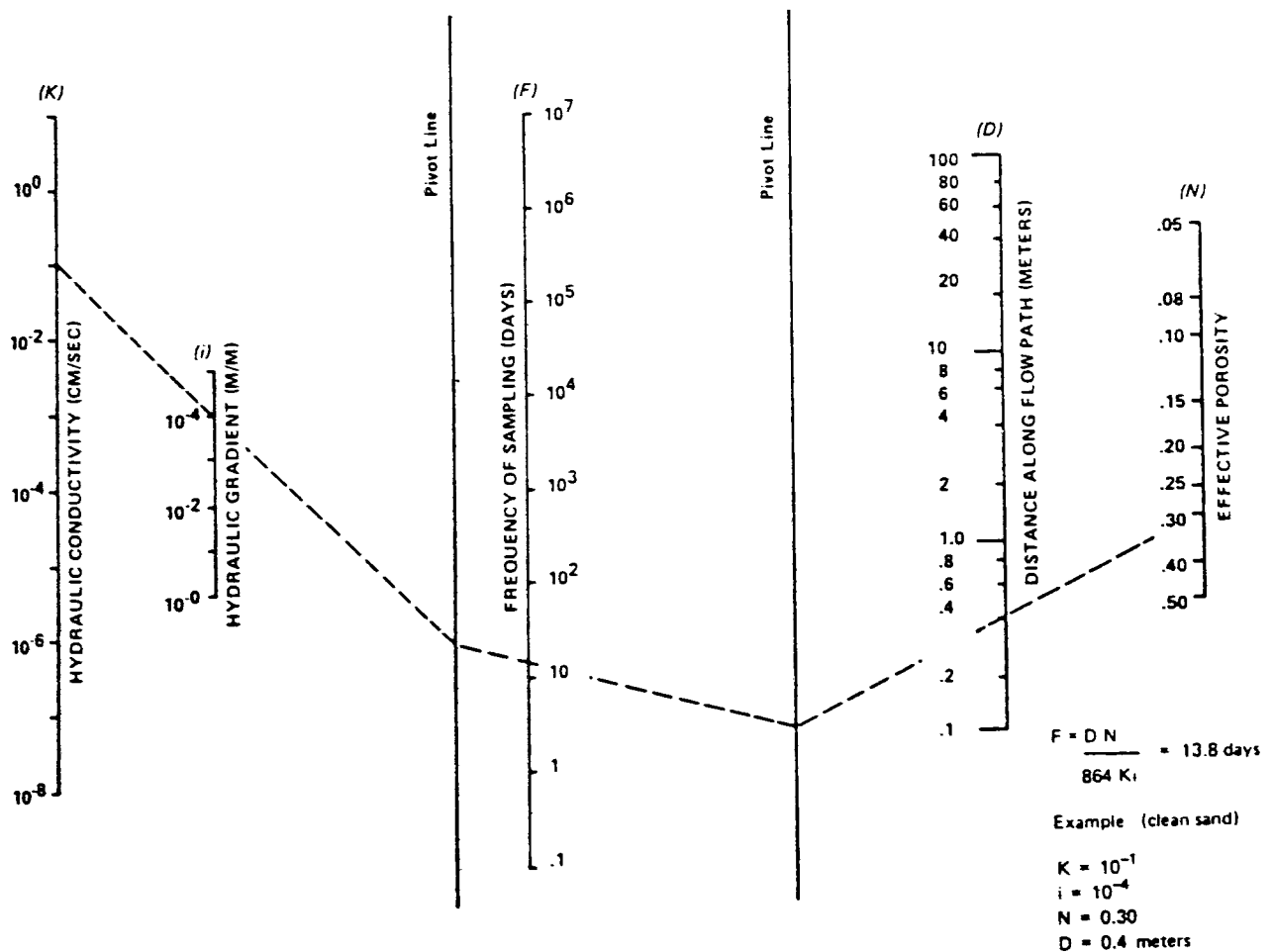
Figure 2.8. Sampling frequency nomograph

C. Interpretation of Geochemical and Water Chemistry Data

1. **Analytical performance, QA/QC, consistency checks**

2. **Major ion, trace constituents and background conditions**

3. **Contamination problems and comparisons with background**

4. **Recognition of interferences, gross errors, etc.**

5. **Dealing with snapshot data in a dynamic environment**

6. **Case studies**

Table 2.10. Field Standard and Sample Spiking Solutions

| | | | | Stock solution for field spike of split samples | | |
Sample type	Volume	Composition	Field standard (concentration)	Solvent	Concentration of components	Field spike volume
Alkalinity	50 mL	Na⁺, HCO₃⁻	10.0; 25 (ppm)	H₂O	10,000; 25,000 (ppm)	(50 μL)
Anions	1 L	K⁺, Na⁺, Cl⁻, SO₄⁻ F⁻, NO₃⁻, PO₄⁻, SI	25, 50 (ppm)	H₂O	25,000; 50,000 (ppm)	(1 mL)
Cations	1 L	Na⁺, K⁺ Ca⁺⁺, Mg⁺⁺, Cl⁻, NO₃⁻	5.0; 10.0 (ppm)	H₂O, H⁺ (acid)	5,000; 10,000 (ppm)	(1 mL)
Trace metals	1 L	Cd⁺⁺, Cu⁺⁺, Pb⁺⁺ Cr⁺⁺⁺, Ni²⁺, Ag⁺ Fe⁺⁺⁺, Mn⁺⁺	10.0; 25.0 (ppm)	H₂O, H⁺ (acid)	10,000; 25,000 (ppm)	(1 mL)
TOC	40 mL	Acetone KHP	0.2; 0.5 (ppm-C) 1.8; 4.5 (ppm-C)	H₂O	200; 500 (ppm-C) 1,800; 4,500 (ppm-C)	(40 μL)
TOX	500 mL	Chloroform 2,4,6 Trichlorophenol	12.5; 25 (ppb) 12.5; 25 (ppb)	H₂O/poly* (ethylene glycol)	12.5; 25.0 (ppm) 12.5; 25.0 (ppm)	(500 μL)
Volatiles	40 mL	Dichlorobutane, Toluene Dibromopropane, Xylene	25; 50 (ppb)	H₂O/poly* (ethylene glycol)	25; 50 (ppm)	(40 μL)
Extractables A	1 L	Phenol Standards	25; 50 (ppb)	Methanol**	25; 50 (ppm)	(1 mL)
Extractables B	1 L	Polynuclear Aromatic Standards	25; 50 (ppb)	Methanol	25; 50 (ppm)	(1 mL)
Extractables C	1 L	Standards as required	25; 50 (ppb)	Methanol	25; 50 (ppm)	(1 mL)

* = 75.25 Water/Polyethylene Glycol (400 amu) Mixture
** = Glass Distilled Methanol

STEP

SOURCES OF ERROR

Samples, from Storage
Field Blanks and Standards

"Aged" samples; loss of analytes;
contamination

↓

Subsampling

Sample aging/contamination in lab; cross-
contamination; mishandling/labeling

↓

Procedural Standards

"Aged" standards; analyst error

↓

Analytical Separation

Matrix interferences; inappropriate/
invalid methodology; instrumental
malfunction/analyst error

↓

Analysis

Matrix interference; inappropriate/
invalid methodology; instrumental
malfunction/analyst error

↓

Reference Standards

"Aged" standards

↓

Calculations

Transcription/machine errors; sample loss in
tracking system; improper extrapolation/
interpolation; over-reporting/
under-reporting errors

↓

Results

Figure 1.2. Steps in water sample analysis and sources of error

STEP

SOURCES OF ERROR

In-Situ Condition

↓

Establishing a Sampling Point

Improper well construction/placement;
inappropriate materials selection

↓

Field Measurements

Instrument malfunction; operator error

↓

Sample Collection

Sampling mechanism bias; operator error

↓

Sample Delivery/Transfer

Sampling mechanism bias; sample exposure,
degassing, oxygenation; field conditions

↓

Field Blanks, Standards

Operator error; matrix interferences

↓

Field Determinations

Instrument malfunction; operator error;
field conditions

↓

Preservation/Storage

Matrix interferences;
handling/labeling errors

↓

Transportation

Delay; sample loss

Figure 1.1. Steps in ground-water sampling and sources of error

CASE STUDY -- WOOD PRESERVING SITE (Franks et al., 1985)

- CREOSOTING FACILITY OPERATED BETWEEN 1902 AND 1981

- SURFICIAL SAND/GRAVEL AQUIFER -- PENSACOLA BAY

- PRIMARY CONTAMINANTS

--	PHENOLS	0.00 to 116 mg/L
--	ORG. N COMPOUNDS	0.00 to 88 mg/L
--	PAH's	0.00 to 19 mg/L
		(naphthalene, indene)
--	CH_4	0.0 to 14 mg/L

- BOTH UPPER WATER TABLE ZONE AND DEEPER CONFINED ZONE AFFECTED TO DEPTHS OF 25 M
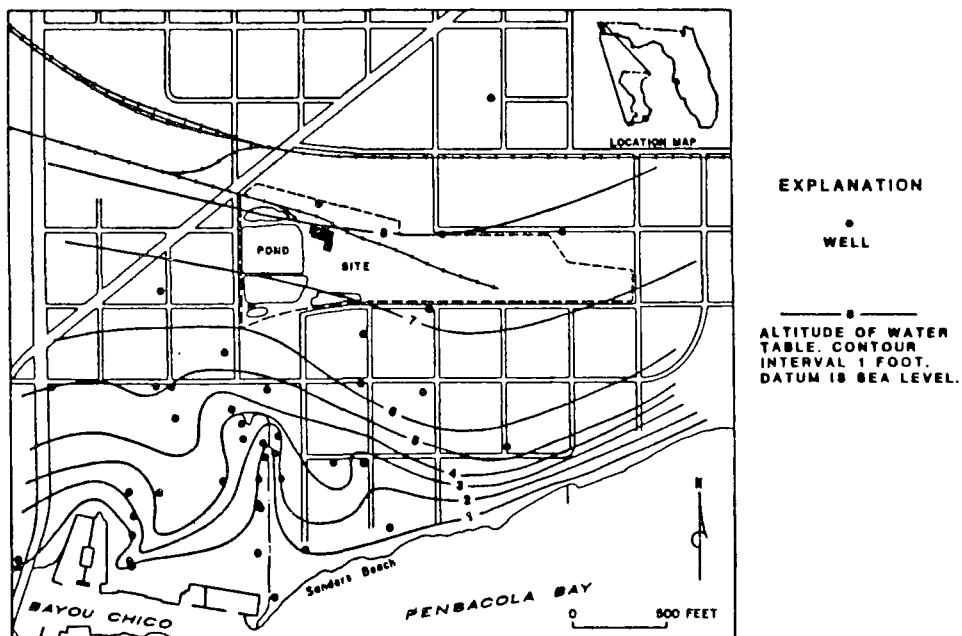
CASE STUDY – WOOD PRESERVING SITE

- 1983 monitoring results, from up to 45 sampling points, emphasized shallow water table aquifer contamination (at levels in excess of 1 mg/L)

- "Affected" Volume:

Naphthalene	4.1×10^5 m^3
Phenols	3.5×10^5 m^3
CH$_4$	7.1×10^5 m^3

- Other "plume" effects: pH ~5.4
  TDS ~350
  Dissolved Oxygen ~0

- H$_2$S, NH$_3$, Fe, DOC variable

CASE STUDY – WOOD PRESERVING SITE

- 1985 monitoring results, from up to 75 sampling points disclosed extensive contamination of the lower confined zone as well.

- On-site analyses identified organic nitrogen compounds and much more "rapid" migration of naphthalene and CH$_4$ than predicted.

- The "affected volume" of water table aquifer contamination increased by 49% (naphthalene), 66% (phenols) and 100% (CH$_4$) over previous levels.

- Nearly 1.4×10^6 m^3 of contaminated material and H$_2$O

WATER TABLE ZONE *(1983)*   WATER TABLE ZONE *(1985)*

NAPHTHALENE

.01 - 1

1 - 5

> 5

TOTAL PHENOLS

.01 - 1

1 - 10

> 10

METHANE

.01 - 1

1 - 5

> 5
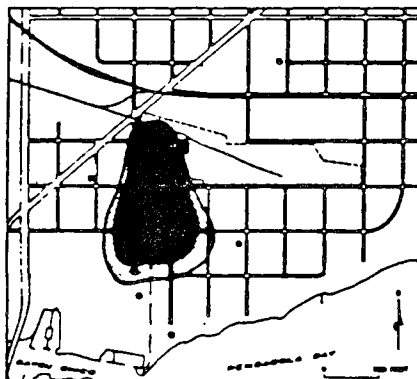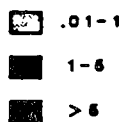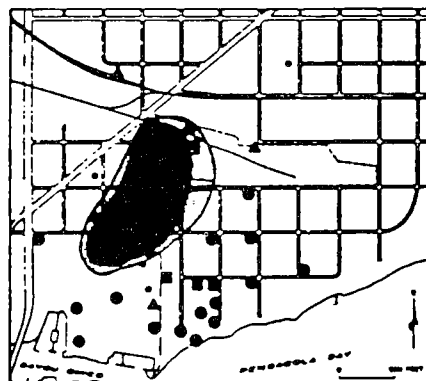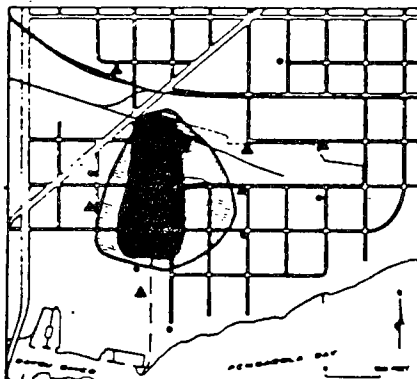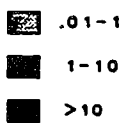
EXPLANATION

WELL
▲ TROUTMAN ET. AL. 1984
• WATTAND AND FRANKS 1984

(WELLS OUTSIDE CONTOURS IMPLY ANALYZED VALUES BELOW DETECTION LIMIT)
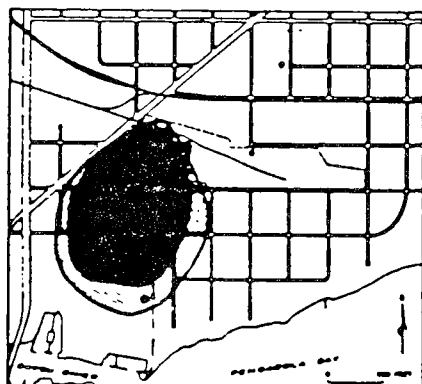
MONITORING – CASE STUDY

WISCONSIN – DNR

- 25 LANDFILLS (19 MUNICIPAL, 6 INDUSTRIAL)

GOALS
- EXTENT OF VOC CONTAMINATION
- OCCURRENCE OF INDIVIDUAL VOC'S
- SITE CONDITIONS AND CONTAMINATION EXTENT
- USEFULNESS OF INORGANIC PARAMETERS AS CONTAMINANT INDICATORS
- PRACTICES IN OTHER STATES

WDNR STUDY

CONDITIONS

1. "UPGRADIENT" WELL, A NUMBER OF DOWNGRADIENT WELLS AT EACH SITE

~90% OF THE WELLS AT WATER TABLE WITH 10 TO 15' SCREENS

~10% SEALED BELOW THE WATER TABLE

~95% OF THE WELLS WITHIN 150' DISTANCE FROM LANDFILL CELLS

PROTOCOL

- BAILER SAMPLING AFTER PURGING 4 WELL VOLUMES
- FOUR VOC SAMPLES FROM EACH BAILER
- EXPANDED ANALYTES (COD, Cl^-, Ω^{-1}, ALK, HARDNESS)
- CAREFUL, CONSISTENT PROCEDURES

WDNR STUDY

RESULTS

- ~2.5 WELLS/LANDFILL ON THE AVERAGE

- 15/19 SITES HAD CONTAMINATED GROUND WATER

- 32/79 SAMPLES HAD DETECTABLE VOC'S

- DCA, DCE, VCM, BZ, PER, TCE, TOC MAJOR CONTAMINANTS

- RELIABLE SAMPLES COULD BE TAKEN AT LEVEL OF ~1 μg/L

- NAP, FREONS, ACETONE, DIMETHYLSULFIDE COMMONLY OBSERVED

- INORGANIC CONSTITUENTS COINCIDE WITH VOC DETECTS IN 41% OF SAMPLES

WDNR STUDY

RESULTS

MOST LIKELY CONTAMINATED SITUATION

- MUNICIPAL, UNLINED, NO CONTAMINANT OR LEACHATE COLLECTION IN COARSE OR "MIXED" SURFICIAL RATHER THAN FINE DEPOSITS (NO CORRELATION WITH AGE OF FILL, DEPTH, DEPTH TO BEDROCK OR BEDROCK TYPE)

OTHER STATES? (MORE THAN 3,000 LANDFILLS)

- ~2/3 REQUIRE SOME SAMPLING (~25% ON A ROUTINE BASIS)

  ~1/3 HAVE BEEN SAMPLED FOR VOC'S

  FEW REQUIRE MORE THAN ANNUAL FREQUENCY

FIGURE 8. VOC MONITORING STRATEGIES NATIONWIDE (BY STATES).
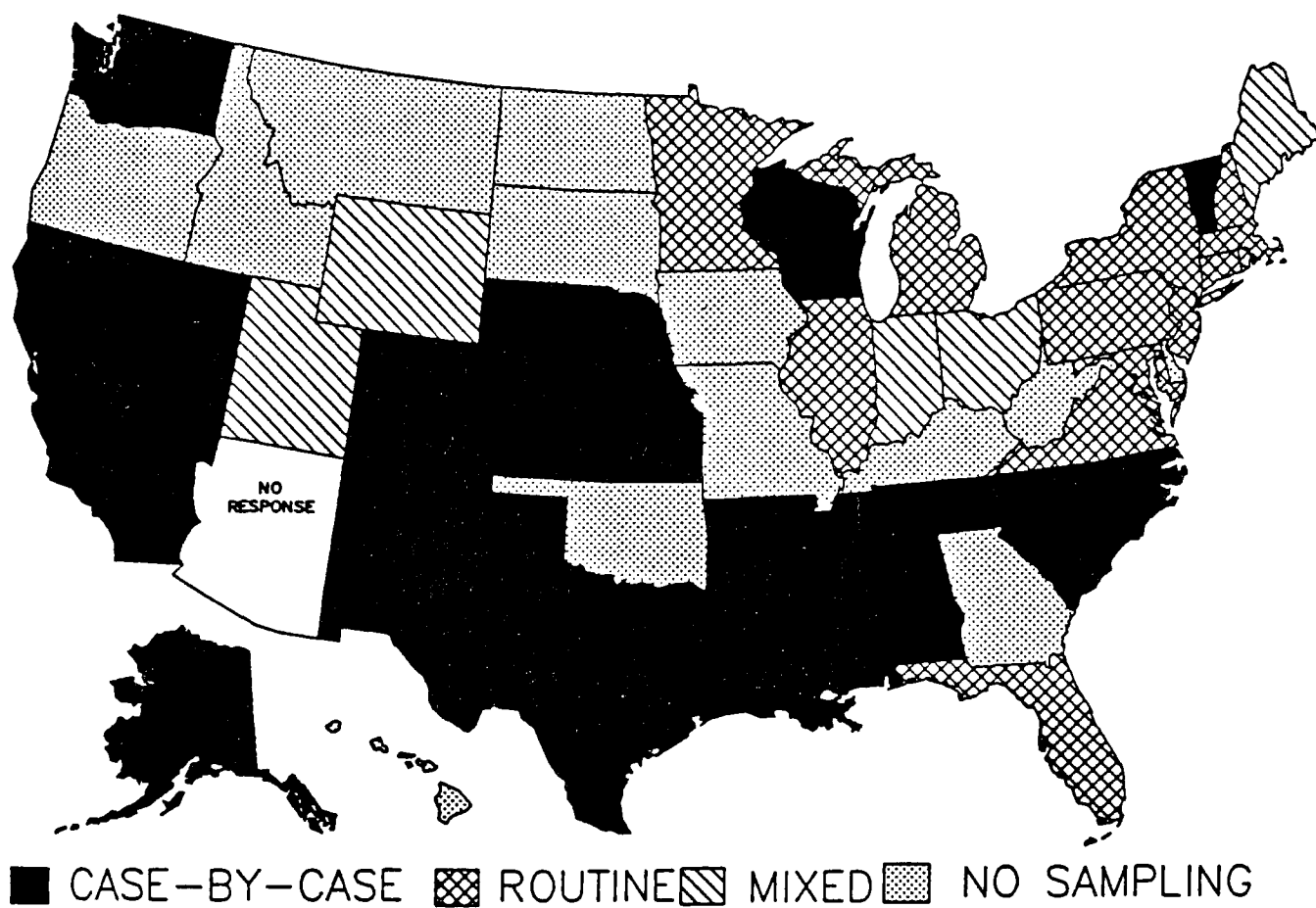
CASE STUDY NO. 1
Dominant VOC Distribution at Well Locations

GW FLOW

LEGEND
Unique Well Types

- ⊕ 1,1,2-Trichloroethane
- ● Trichloroethylene
- ■ Trichloromethane
- □ Dichloromethane
- ▲ Tetrachloroethylene
- △ Tetrachloromethane
- ● 1,2 - Transdichloroethene
- ○ No Organics
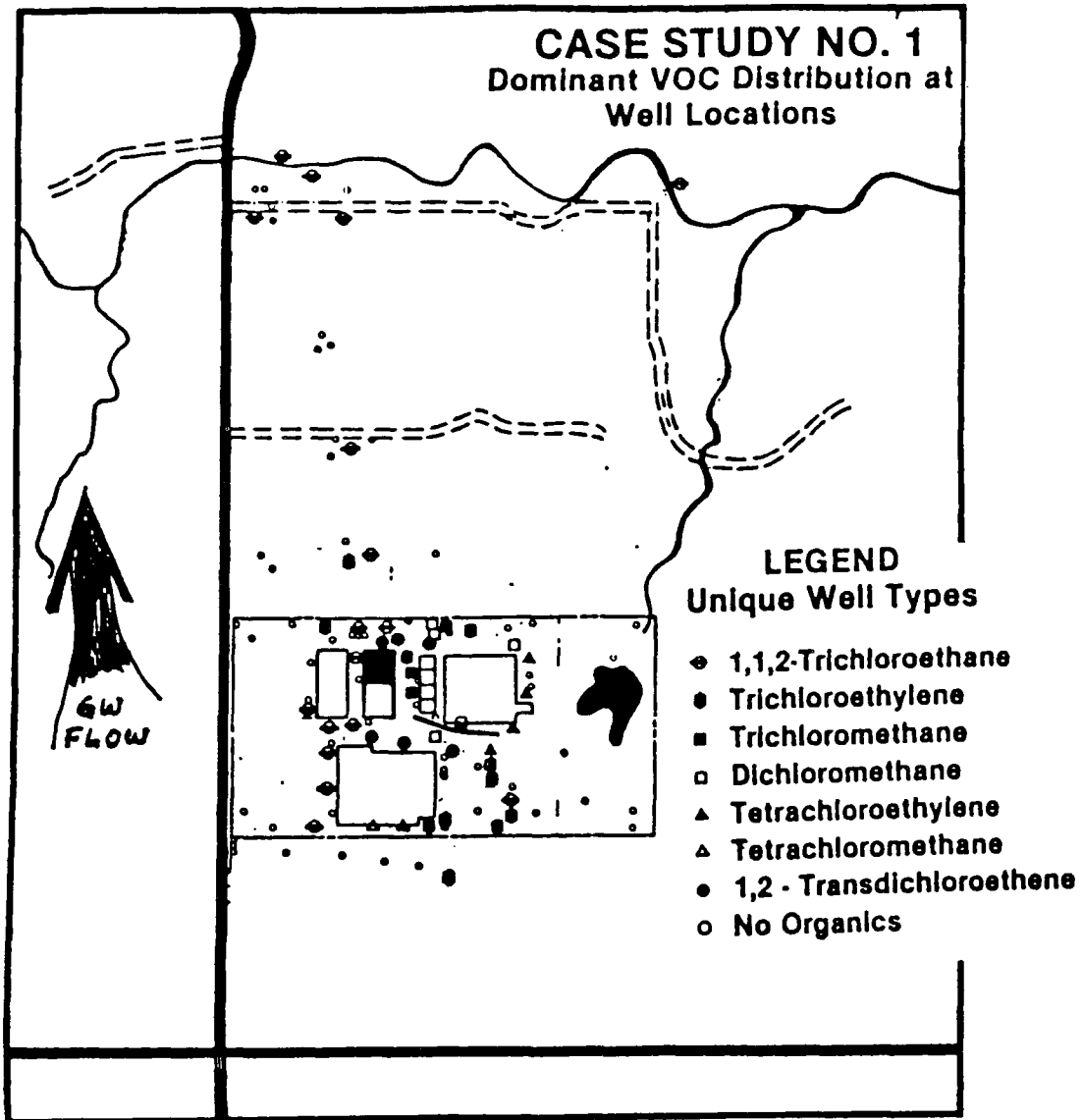
<u>WMI CASE STUDY 1984</u>

- ■ LARGE LANDFILL, EVAPORATION/ACID NEUTRALIZATION PONDS SITE

- ■ FORTY-FOUR WELLS OVER AREA OF 3.6×10^5 M^2

- ■ REASONABLY CONTROLLED SAMPLING/ANALYSIS PROTOCOLS

- ■ ARE VOC'S GOOD TRACERS, CONTAMINATION INDICATORS

WMI CASE STUDY

RESULTS

- ~20% OF "UPGRADIENT" WELLS CONTAMINATED
  (TCA, TCE)

- ~50% OF "DOWNGRADIENT" WELLS CONTAMINATED
  (TCA, TCE, CLF, PER, DCE)

- ~30% OF "DOWNGRADIENT", OFFSITE WELLS
  CONTAMINATED (TCA, TCE)

- ISOLATED DETECTS FOR NONVOLATILES (PHENOLS)

- VOC'S REASONABLE TRACERS FOR "DETECTION"
  (RARELY ONE OR TWO COMPOUNDS)

WMI CASE STUDY

"REMEDIATION" MEASURES

- LOWER GROUND-WATER MOUND

- POND DRAINAGE, SLUDGE REMOVAL, BACKFILLED
  AND CLAY COVERED

"REMEDIATION" SUCCESS

- VOC'S NOT MEASURABLY REDUCED
  (MOST CONCENTRATIONS >1000 PPB VOC'S)

- Cr REDUCED SOMEWHAT NEAR ACID PONDS

- IMPROPERLY PLUGGED EXPLORATORY BOREHOLES
  A LIABILITY

DETECTION LIMITS (ASTM Recommendations)

THREE TREATMENTS

- HEAVILY CENSORED   #1

- NEGATIVELY CENSORED   #2

- ACTUAL RESULTS   #3

DETECTION LIMITS (ASTM) – EXAMPLE

HEAVY	NEGATIVE	UNCENSORED
<3 μg	2 μg	2 μg
<3	0	-2
<3	0	-1
4	4	4
3	3	3
<3	0	-3
<3	1	1
<3	0	-1
<3	0	0
<3	2	2

DETECTION LIMITS (ASTM) – EXAMPLE

#1   Average   – 3.5 μg
     (ARE CONSTITUENTS PRESENT OR NOT?)

#2   Average   – 1.2 μg
     95% Confidence 0.14 to 2.26 μg
     (CONTAMINATED!)

#3   Average   – 0.5 μg
     95% Confidence -1.13 to 2.13 μg
     (DATA EQUIVOCAL!)

- PRUDENT TO REPORT LESS THAN ZERO VALUES AS TRACE

PART 3

QA/QC EVALUATION

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Characterization of Subsurface Physiochemical Processes

Dr. Carl D. Palmer

Dr. Carl D. Palmer is an assistant professor in the Department of Environmental Science and Engineering at the Oregon Graduate Center. He received his Ph.D. in Hydrogeology in 1983 from the Department of Earth Science at the University of Waterloo, Waterloo, Ontario. Dr. Palmer's research activities has involved modeling of aqueous geochemical systems, the use of tracer tests, heat transport in the subsurface, ground-water monitoring, and modeling. He is currently developing innovative methods for enhancing remedial activity at hazardous waste sites, studying geochemical controls on the transport and fate of chromium, developing methods for aquifer characterization, and addressing groundwater monitoring issues. Dr. Palmer was a speaker at the U.S. EPA workshop on the "Transport and Fate of Contaminants in the Subsurface" that was held in each of the EPA regions during 1987/88. He is coauthor of five chapters in an EPA document of the same title. Dr. Palmer is editor and author of a book entitled, The Chemistry of Groundwater that is to be published next year by Lewis Publishers.

I. INTRODUCTION/OVERVIEW

II. ORGANIC CONTAMINANTS
    A. Processes
        1. Abiotic degradation
        2. Biotic degradation
        3. Dissolution
        4. Sorption of neutral, nonpolar, hydrophobic compounds
            a. Isotherms
            b. Definition of K_p
            c. Role of Soil Organic Carbon
            d. Linear Retardation
    B. Method for Determining K_p
        1. Correlation Equations
            a. K_{oc} versus solubility
            b. K_{oc} versus octanol/water partition coefficient
            c. Organic Carbon
        2. Batch Tests
            a. General Methodology
            b. Soil Preparation
            c. Non-settling Particles
        3. Column Tests
        4. Field Data
        5. Comparison
    C. Other Considerations
        1. Nonlinear Isotherms
        2. Ionization
        3. Cosolvent Effects
        4. Kinetics

CHARACTERIZATION OF SUBSURFACE
PHYSICOCHEMICAL PROCESSES

ORGANIC
CONTAMINANTS

CHEMICAL PROCESSES AFFECTING
ORGANIC CONTAMINANTS

- ABIOTIC DEGRADATION
- BIOTIC DEGRADATION
- DISSOLUTION
- SORPTION
- IONIZATION

DNAPL SPILL

DNAPL SOURCE

RESIDUAL DNAPL
DENSE VAPORS

TOP OF
CAPILLARY
FRINGE

WATERTABLE

GROUND-
WATER FLOW → DNAPL LAYER

DISSOLVED
CHEMICAL
PLUME

GROUND-
WATER FLOW → LOWER
PERMEABILITY
STRATA
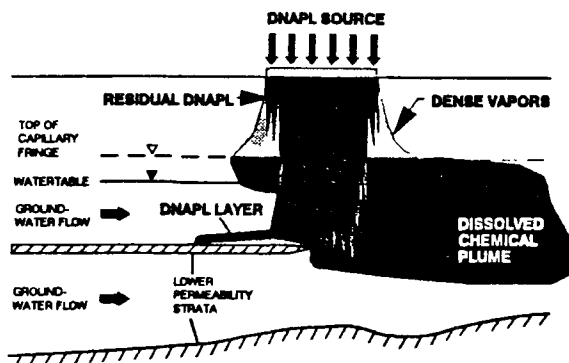
After Feenstra and Cherry,
1988.

TRANSPORT OF REACTIVE SOLUTES

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

Dispersive   Advective   Change in   Reaction
Term   Term   Mass per   Term
                     Unit Time

SORPTION ISOTHERMS

- **■ LANGMUIR**

- **■ FREUNDLICH**

- **■ LINEAR**

FREUNDLICH ISOTHERM

$$S = KC^a$$

LANGMUIR ISOTHERM

$$S = S_{MAX}\frac{K*C}{1 + K*C}$$

1,1,1-TRICHLOROETHANE

1,1,2,2-TETRACHLOROETHANE

1,2-DICHLOROETHANE

(After Chiou et al, 1979)
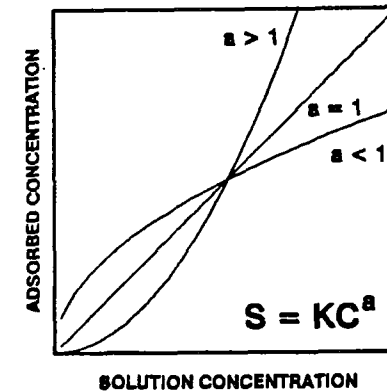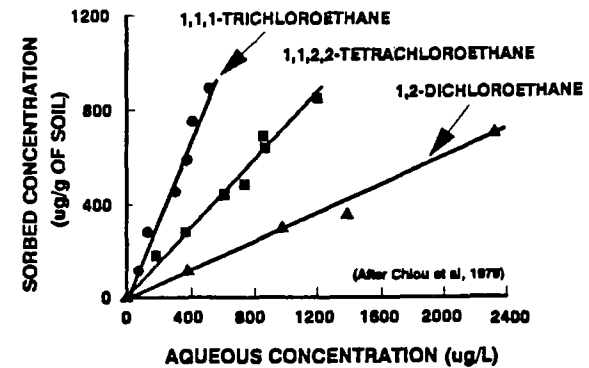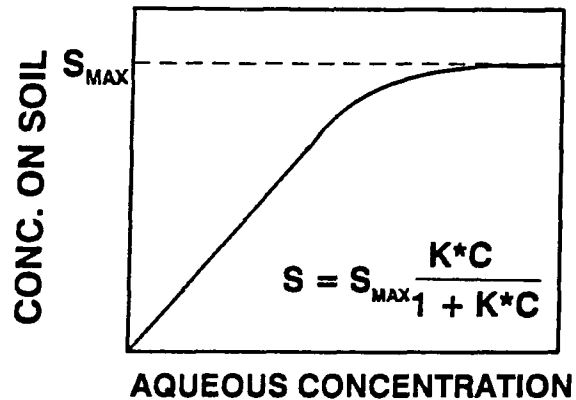
ADSORPTION ISOTHERMS FOR NONPOLAR ORGANICS ARE LINEAR IF

$$C < 10^{-5} M$$

OR

$$C < 0.5 * SOLUBILITY$$
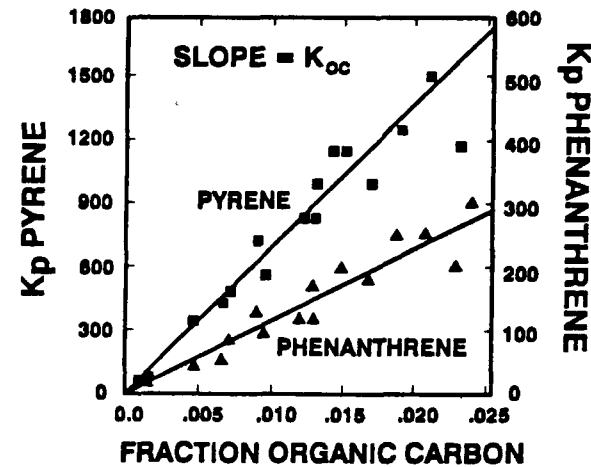
PARTITION COEFFICIENT

$$K_p = \frac{CONCENTRATION\ ON\ SOIL}{CONCENTRATION\ IN\ WATER}$$

$$= SLOPE\ OF\ ISOTHERM$$

$$K_p = f_{oc} K_{oc}$$

K_p = Soil Partition Coefficient

f_{oc} = fraction of organic carbon in the soil

K_{oc} = Partition Coefficient between aqueous phase and some some hypothetical, pure organic carbon

SORPTION OF ORGANICS

SORPTION OF NONPOLAR,
HYDROPHOBIC COMPOUNDS IS
PRIMARILY BY PARTITIONING TO
ORGANIC MATTER IN THE SOIL.

LINEAR RETARDATION

$$R = 1 + K_p \rho_b / n$$

$K_p =$ Partition Coefficient
$\rho_b =$ Dry Bulk Density of Medium
$n =$ Porosity of Medium

TRANSPORT WITH LINEAR RETARDATION
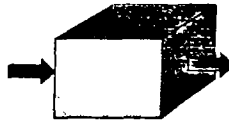
$$D \frac{\partial^2 c}{\partial x^2} - V \frac{\partial c}{\partial x} = R \frac{\partial c}{\partial t}$$

Dispersive   Advective   Change In
Term   Term   Mass per
                         Unit Time

METHODS FOR OBTAINING K_p

- CORRELATION EQUATIONS
- BATCH TESTS
- COLUMN TESTS
- FIELD DATA
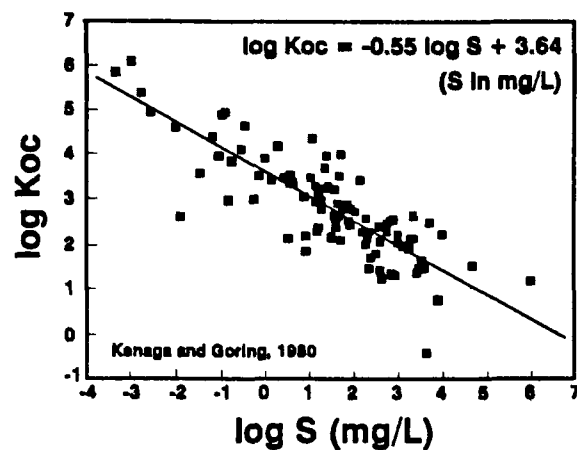
REGRESSION EQUATIONS

$$\text{Log } K_{oc} = -0.55 \text{ Log } S + 3.64$$

$$\text{Log } K_{oc} = 0.544 \text{ Log } K_{ow} + 1.377$$
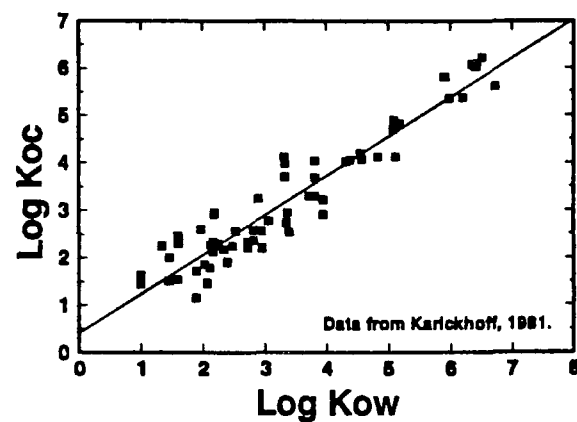
ORGANIC CARBON

$$K_p = f_{oc} K_{oc}$$

■ WET COMBUSTION

■ DRY COMBUSTION

ORGANIC CARBON
WET COMBUSTION

Oxidation of Soil Carbon by Dichromate:

$$2Cr_2O_7^{2-} + 3C^0 + 16H^+ \Rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O$$
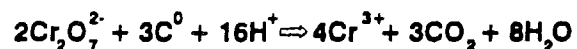
WET COMBUSTION METHODS

- **WALKLEY-BLACK**
  Dichromate oxidation <u>without</u> external heat

- **MODIFIED MEBIUS PROCEDURE**
  Dichromate oxidation <u>with</u> external heat

WET COMBUSTION
PROBLEMS

- Reduction of Cr(VI) by Fe(II) and Chloride

- Oxidation of Cr(III) by MnO_2

- Incomplete Oxidation of Carbon (Walkley-Black)

ORGANIC CARBON
DRY COMBUSTION

$$C_6H_{12}O_6(s) + 6O_2(g) \xrightarrow{HEAT} 6CO_2(g) + 6H_2O$$
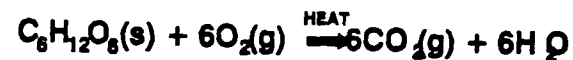
ORGANIC CARBON

DRY COMBUSTION

- Drive off Carbonates with Acid

- Pass Oxygen over Sample at 600° to 1000° C

- Measure CO_2 Generated

ORGANIC CARBON / DRY COMBUSTION

QUANTITATION OF CO_2

- Gravimetric Determination of CO_2 on Absorbent (e.g. Ascarite)

- Catalytic Conversion of CO_2 to Methane and Measurement with Flame Ionization Detector

BATCH TESTS

SOLUTION WITH CONTAMINANT + SOIL WITH ORGANIC MATTER → SHAKE AND EQUILIBRATE

BATCH TESTS

SAMPLE AND MEASURE CONTAMINANT CONCENTRATION IN SOLUTION
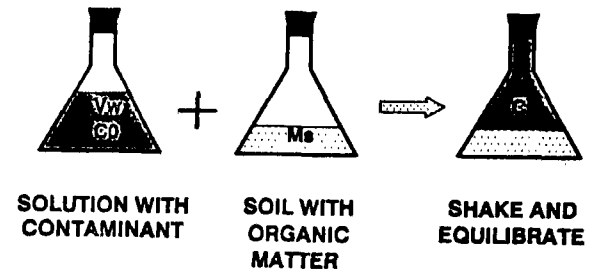
$$S = V_w(C_0 - C)/M_s$$
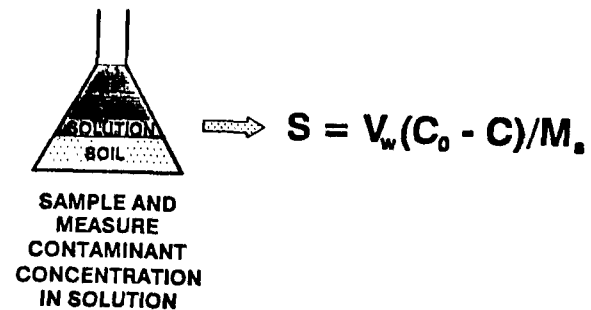
BATCH TESTS
SOIL PREPARATION

- Dry Soil
- Sieve (<2 mm)
- Estimate K_p

DESORPTION OF HEXACHLOROBENZENE

BATCH TESTS
NEED ESTIMATE OF K_p

- If K_p is large and too much soil added then concentration in solution cannot be accurately determined

- If K_p is small and too little soil added then concentration on the solid cannot be accurately determined

After Pankow, 1984.

WATER IN

WATER PLUS COMPOUND

WATER PLUS COMPOUND OUT

CONCENTRATION

NON-SORBING

SORBING

V1 V2

VOLUME
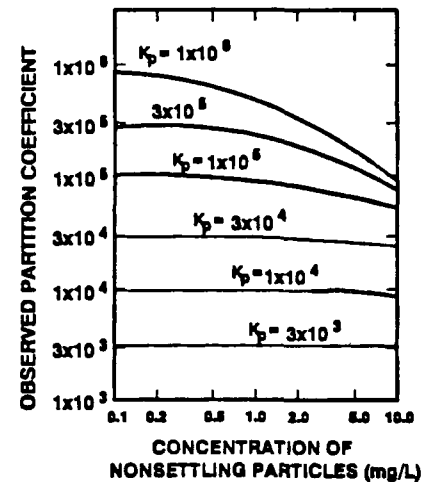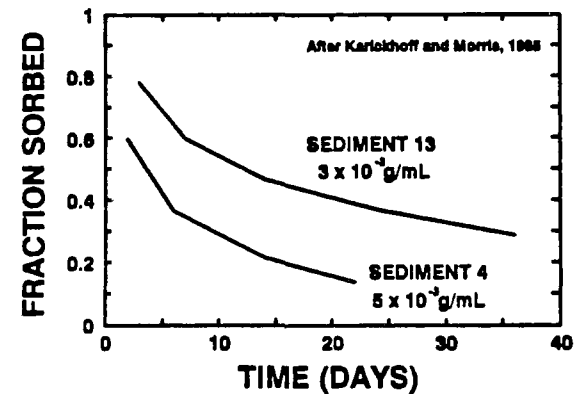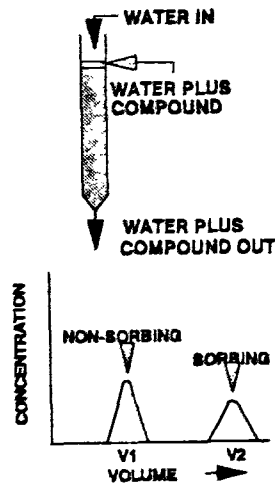
RETARDATION FACTORS

FIELD METHODS

- BREAKTHROUGH CURVES
- SPATIAL DISTRIBUTION

RELATIVE CONCENTRATION

STANFORD/WATERLOO TRACER TEST

CHLORIDE

CARBON TETRACHLORIDE

TETRACHLOROETHYLENE

TIME (DAYS)
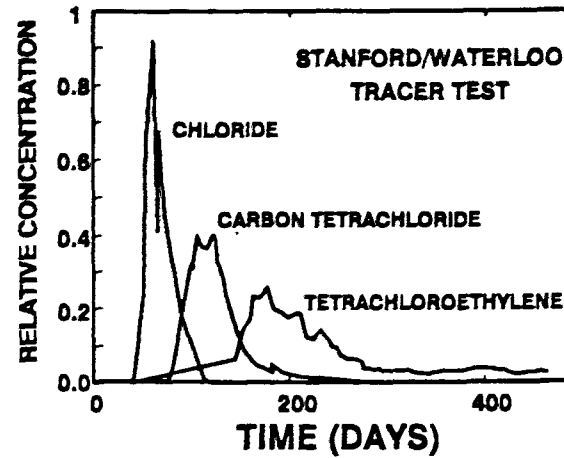
COMPARISON OF METHODS
FOR RETARDATION FACTORS

	OFFICE	LAB	FIELD	
SOLUTE	ESTIMATED	BATCH	TEMPORAL	SPATIAL
CTET	1.3	1.9	2.7	2.1
BROMO	1.2	2.0	1.7	2.2
TeCE	1.3	3.6	3.3	4.3
DCB	2.3	6.9	2.7	6.2
HCB	2.3	5.4	4.0	6.5

SORPTION OF TCE ON GLACIAL TILL

McKay and Trudell (1988)

Myrand et al. (1989)

Johnson et al. (1989)

K_p

LOG AQUEOUS CONCENTRATION (PPB)

COSOLVENTS

K_p

ANTHRACENE

FRACTION CO-SOLVENT
(METHANOL)

IONIZATION

$+ H^+$

$K_{oc} = 2330$ $K_{oc} \sim 0$
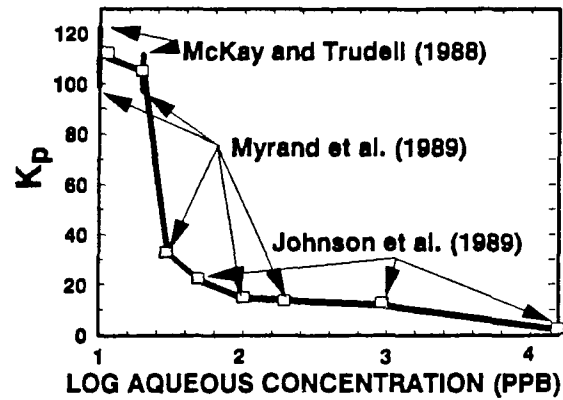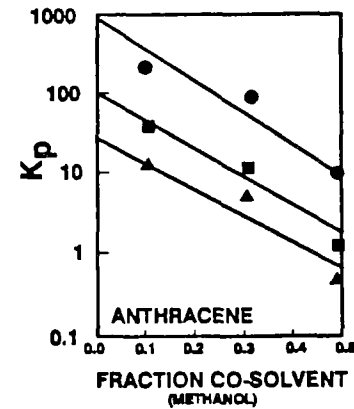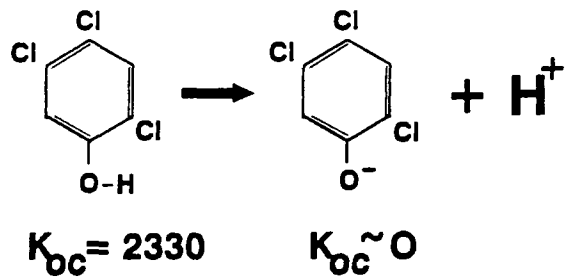
ADVECTION-DISPERSION EQUATION

WITH FIRST-ORDER DECAY

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

CHARACTERIZATION OF SUBSURFACE PHYSICOCHEMICAL PROCESSES

VOLATILIZATION AND VAPOR TRANSPORT

II. VOLATILIZATION
- A. Four Phase System
- B. Gas Phase Concentration
- C. Processes
- D. Theory of Vapor Phase Diffusion
    - 1. Transport Equation
    - 2. Tortuosity
    - 3. Retardation
- E. Methods for Obtaining Vapor Diffusion Coefficients
- F. Examples of Vapor Transport
- G. Additional Factors
    - 1. Cultural Features
    - 2. Temperature
- H. Summary

■ RESIDUAL-PRODUCT
☐ VAPOR
■ DISSOLVED

□ FREE-PRODUCT
■ RESIDUAL-PRODUCT
□ VAPOR
■ DISSOLVED
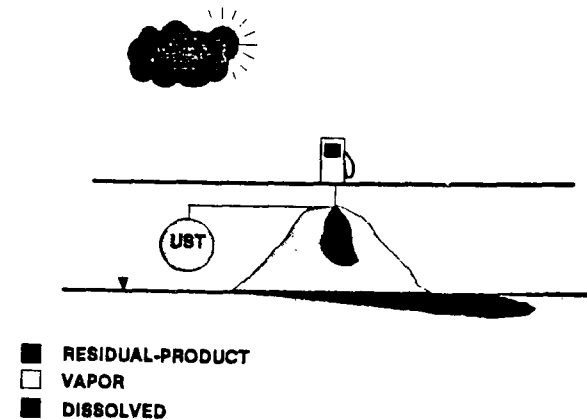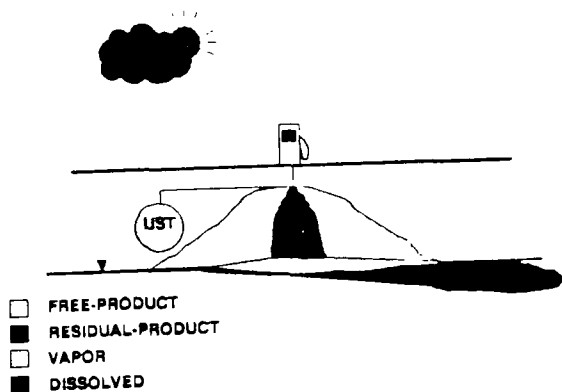
FOUR PHASE SYSTEM
(After Schwille, 1988)

▨ WATER ☐ NAPL ☐ AIR
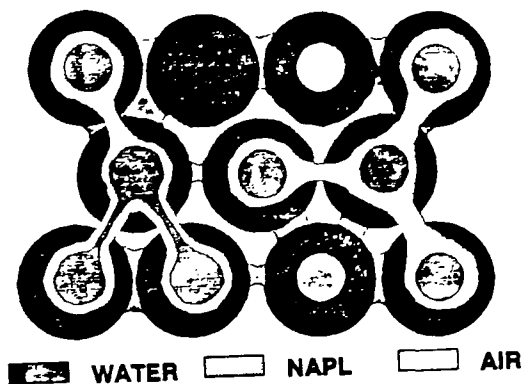
VOLATILIZATION

$$P_k = X_k P_k^o$$

P_k = partial pressure of component k in soil air

X_k = mole fraction of kth component in NAPL

P_k^o = vapor pressure of pure component

EQUATION OF STATE FOR AN IDEAL GAS

$$n/V = P/(RT)$$

n = Number of Moles
V = Volume of Gas
P = Partial Pressure
R = Gas Constant
T = Temperature (kelvins)

FACTORS AFFECTING SUBSURFACE VAPOR CONCENTRATIONS

■ DIFFUSION
■ ADVECTION
■ DENSITY
■ CULTURAL FEATURES
■ PARTITIONING TO SOIL
■ PARTITIONING TO PORE WATER
■ THERMAL EFFECTS
■ DEGRADATION REACTIONS
■ GROUND WATER CONCENTRATIONS
■ WATERLEVEL FLUCTUATIONS
■ RECHARGE

PARTIALLY SATURATED POROUS MEDIA

DIFFUSION

FICKS SECOND LAW:

$$\frac{\partial \Theta_A G}{\partial t} = \tau_A \Theta_A D \frac{\partial^2 G}{\partial x^2}$$

AIR PHASE TORTUOSITY
MILLINGTON-QUIRK
(MILLINGTON, 1959)

$$\tau_A = \frac{\Theta_A^{2.333}}{(\Theta_A + \Theta_W)^2}$$

$(\Theta_a + \Theta_w) = 0.2$ 0.3 0.4 0.5

τ_A vs Θ_A
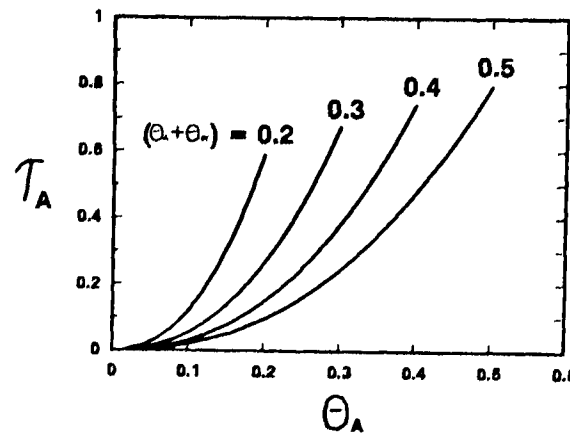
VAPOR PHASE
LINEAR RETARDATION FACTOR

$$R = 1 + \frac{\rho_b K_P}{\Theta_A K_H} + \frac{\Theta_W}{\Theta_A K_H}$$

PARTITIONING INTO
SOIL ORGANIC MATTER

PARTITIONING INTO
RESIDUAL SOIL WATER

VAPOR DIFFUSION
WITH LINEAR RETARDATION

$$\frac{\partial \Theta_A G}{\partial t} = \frac{\tau_A \Theta_A D}{R} \frac{\partial^2 G}{\partial x^2}$$


BENZENE   TOLUENE   HEXANE

RETARDATION FACTOR vs HENRY'S CONSTANT (dimensionless)

TOTAL POROSITY = 0.35

RETARDATION FACTOR vs WATER CONTENT: BENZENE, PENTANE

RELATIVE CONCENTRATION vs TIME (MIN): CE, DRY, CHLOROBENZENE, METHANE, DAMP
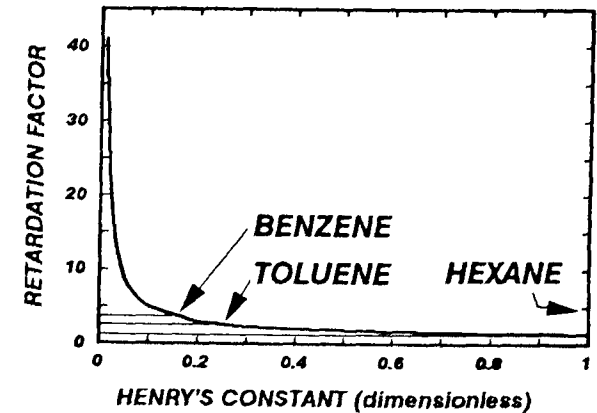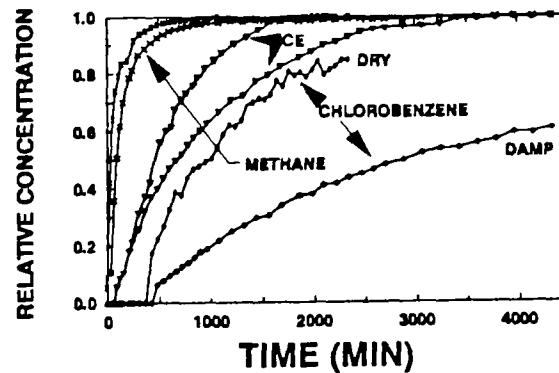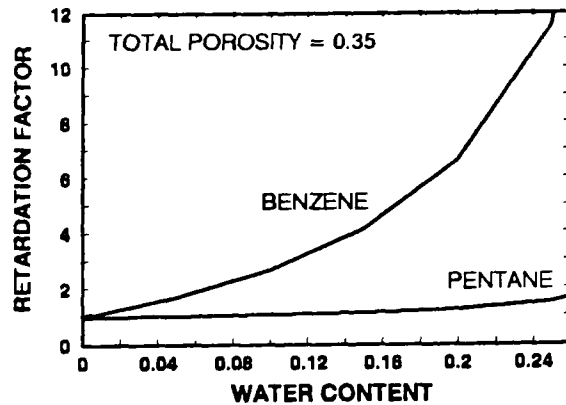
From Johnson et al., 1987.

10% WATER CONTENT, 1% SOC

C/C(0) vs PORE VOLUMES: METHANE, OCTANE, BENZENE
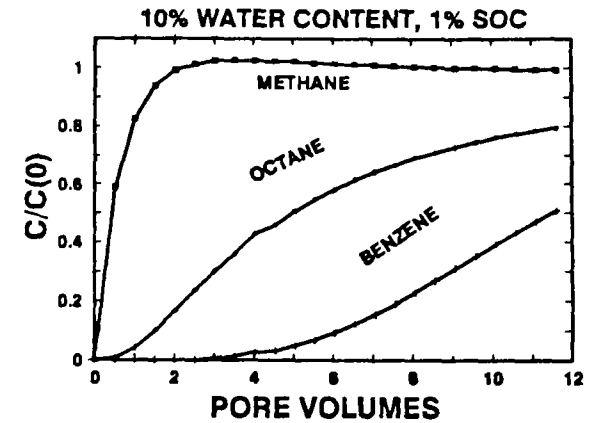
VAPOR DIFFUSION IS IMPORTANT WHEN

- THE HENRY'S CONSTANT IS LARGE
- THE SOIL WATER CONTENT IS LOW

10% WATER CONTENT

C/C(0) vs PORE VOLUMES: OCTANE, BENZENE, METHANE
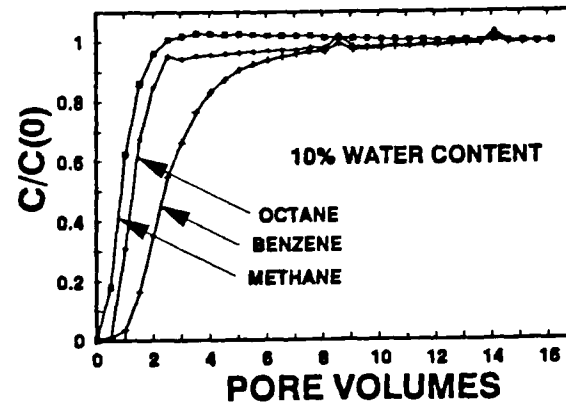
METHODS FOR OBTAINING VAPOR DIFFUSION COEFFICIENTS

- ESTIMATION METHOD
- COLUMN TESTS
- FIELD DATA

Sample Line to GC

Nitrogen + organics in

Cap

Nitrogen + organics out
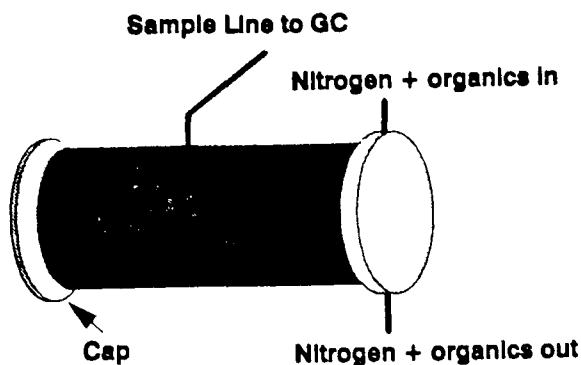
After Johnson et al., 1987

VAPOR DIFFUSION COEFFICIENTS

EFFECT OF TEMPERATURE

(Hamaker, 1972)

$$D_1 / D_2 = (T_2 / T_1)^m$$

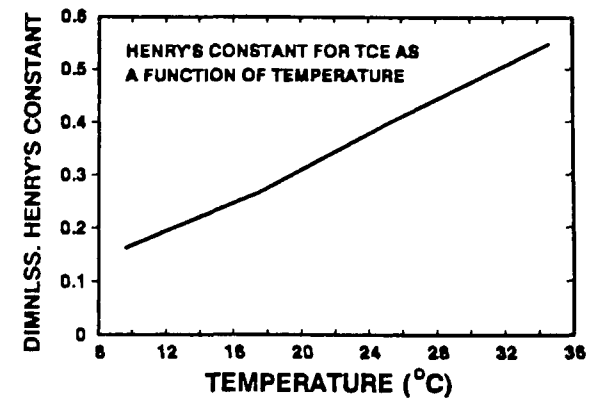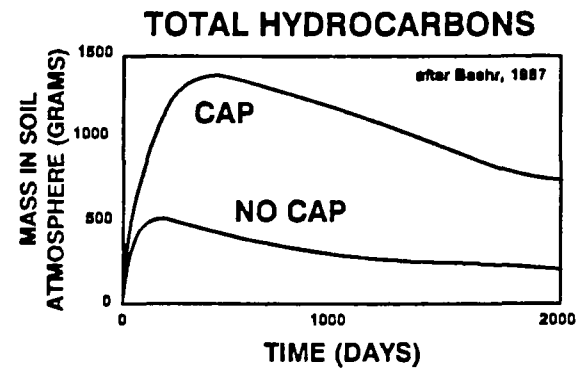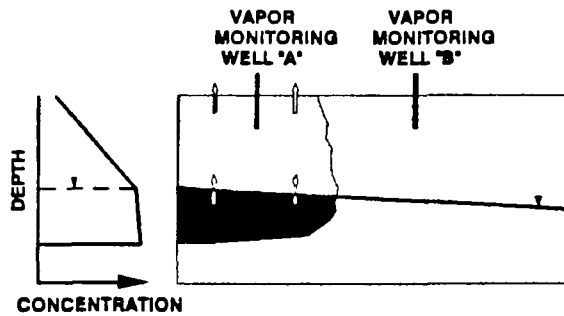$$m = \begin{cases} 1.5 \text{ (THEORETICAL)} \\ 1.75\text{-}2.0 \text{ (EXPERIMENTAL)} \end{cases}$$

ADVECTIVE FLOW

- ATMOSPHERIC PUMPING
- WATER-LEVEL FLUCTUATIONS
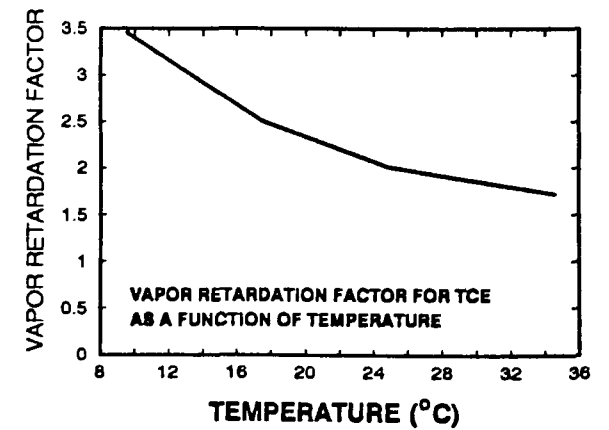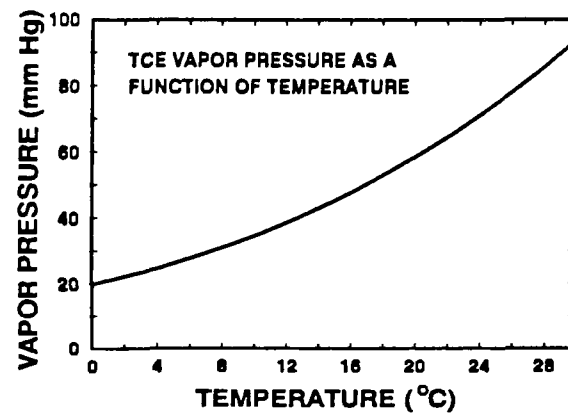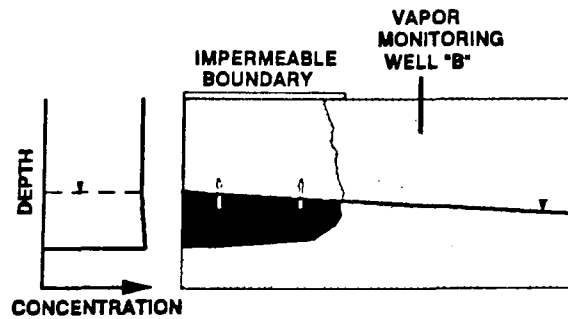- GRAVITY-DRIVEN FLOW
- VAPOR EXTRACTION WELLS

**FACTORS CONTROLLING
GRAVITY-DRIVEN FLOW**

- PERMEABILITY
- VAPOR PRESSURE
- MOLECULAR WEIGHT
- DIFFUSION COEFFICIENT
- RETARDATION
- WATER CONTENT
- SOURCE SIZE
- SURFACE COVER

**VAPOR DIFFUSION COEFFICIENTS
EFFECT OF MOLECULAR WEIGHT**

$$D_1 / D_2 = \sqrt{M_2 / M_1}$$

OREGON GRADUATE CENTER

**LARGE EXPERIMENTAL
AQUIFER PROGRAM**

OGC/LEAP

**Richard L. Johnson
Director**

VAPOR TRANSPORT

DEPTH

VAPOR MONITORING WELL "A"

VAPOR MONITORING WELL "B"

CONCENTRATION

TOTAL HYDROCARBONS

MASS IN SOIL ATMOSPHERE (GRAMS)

after Baehr, 1987

CAP

NO CAP

TIME (DAYS)

DIMNLSS. HENRY'S CONSTANT

HENRY'S CONSTANT FOR TCE AS A FUNCTION OF TEMPERATURE

TEMPERATURE (^{o}C)

VAPOR TRANSPORT

DEPTH

IMPERMEABLE BOUNDARY

VAPOR MONITORING WELL "B"

CONCENTRATION

VAPOR PRESSURE (mm Hg)

TCE VAPOR PRESSURE AS A FUNCTION OF TEMPERATURE

TEMPERATURE (^{o}C)

VAPOR RETARDATION FACTOR

VAPOR RETARDATION FACTOR FOR TCE AS A FUNCTION OF TEMPERATURE
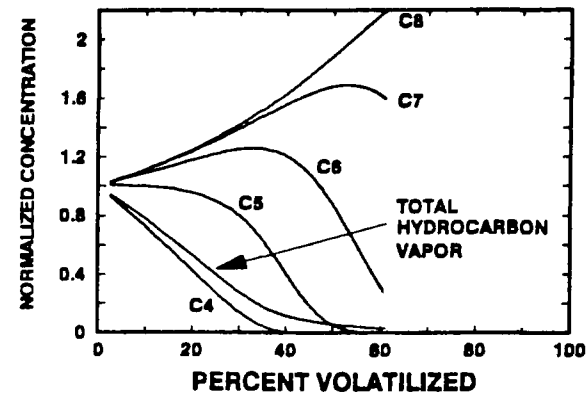
TEMPERATURE (^{o}C)

FACTORS AFFECTING DIFFUSION

- ☐ MOLECULAR SIZE
- ☐ TEMPERATURE
- ☐ HENRY'S GAS CONSTANT
- ☐ GRAIN SIZE
- ☐ AIR-FILLED POROSITY
- ☐ WATER-FILLED POROSITY
- ☐ SOIL CARBON CONTENT

ENVIRONMENTAL EFFECTS

- ☐ THE BACKFILL
- ☐ THE TANKS
- ☐ BACKFILL/SOIL INTERFACE
- ☐ PIPES AND CONDUITS
- ☐ TRENCHES, ETC.
- ☐ WATER LEVEL
- ☐ ATMOSPHERIC PUMPING
- ☐ INFILTRATION

INORGANIC CONTAMINANTS

III. INORGANIC CONTAMINANTS
    A. Processes
        1. Speciation
        2. Oxidation/Reduction
        3. Dissolution/Precipitation
        4. Adsorption/surface chemistry
            a. Oxide-water interface
            b. Adsorption of ions onto oxide surfaces
            c. Surface complexation models
            d. Comparison and validity of models
    B. Chemical Models
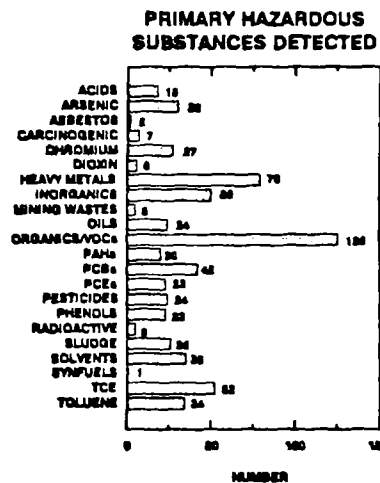   1. Mass balance
        2. Speciation
        3. Mass Transfer
    C. Organic/Inorganic Interactions
    D. Example: Chromium

13 PRIORITY METALS

- SILVER
- ARSENIC
- BARIUM
- CADMIUM
- CHROMIUM
- NICKEL
- MERCURY
- LEAD
- SELENIUM
- THALLIUM
- ANTIMONY
- COPPER
- ZINC

**PRIMARY HAZARDOUS
SUBSTANCES DETECTED**

After Palmer et al., 1988.

OTHER IMPORTANT METALS

- **IRON**

- **MANGANESE**

- **ALUMINUM**

CHEM-DYNE HAZARDOUS WASTE SITE

HAMILTON, OH

AIR STRIPPING OF VOLATILE ORGANICS

REMEDIATION BROUGHT TO A HALT
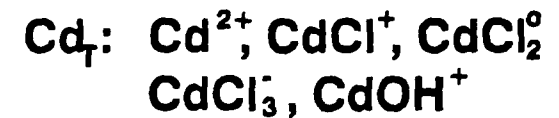WHEN AIR STRIPPER BECOMES
CLOGGED WITH IRON PRECIPITATES

INORGANIC CONTAMINANTS
PROCESSES

- SPECIATION

- OXIDATION/REDUCTION

- DISSOLUTION/PRECIPITATION

- ADSORPTION/ION EXCHANGE

INORGANIC CONTAMINANTS
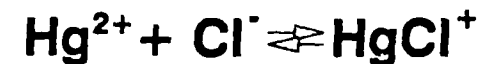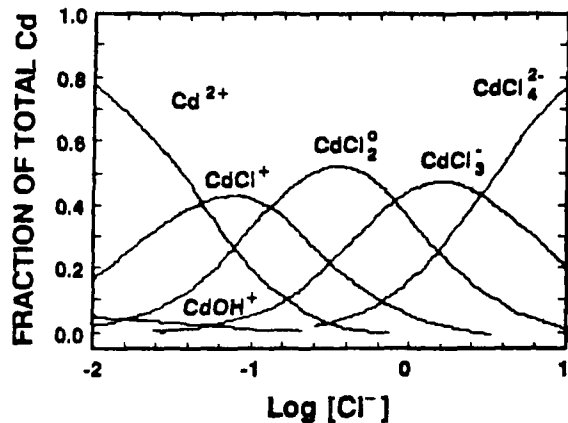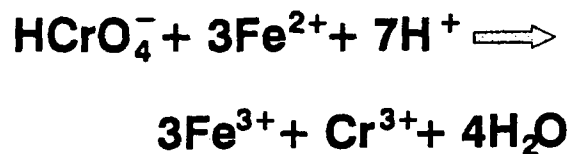## SPECIATION

Cd_T: Cd^{2+}, $CdCl^+$, $CdCl_2^0$
$CdCl_3^-$, $CdOH^+$

Zn_T: Zn^{2+}, $ZnCl^+$, $ZnSO_4^0$

Cu_T: Cu^{2+}, $CuCO_3^0$, $CuOH^+$

INORGANIC CONTAMINANTS
SPECIATION

$$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+$$

$$K_a = \frac{[HgCl^+]}{[Hg^{2+}][Cl^-]}$$

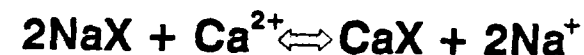After Moore and Ramamoorthy, (1984).

OXIDATION/REDUCTION

■ REDOX CAN GREATLY AFFECT CONTAMINANT TRANSPORT

■ REDOX REACTIONS ARE OFTEN MICROBIALLY MEDIATED

■ REDOX CONDITIONS ARE NOT EASILY PREDICTED

ION EXCHANGE

$$2NaX + Ca^{2+} \Longleftrightarrow CaX + 2Na^+$$

$$K_{ex} = \frac{[CaX][Na^+]^2}{[NaX]^2[Ca^{2+}]}$$

ISOTHERMS

■ ANIONS HAVE LANGMUIR ISOTHERMS

■ CATIONS HAVE FREUNDLICH ISOTHERMS

OXIDATION/REDUCTION

$$HCrO_4^- + 3Fe^{2+} + 7H^+ \Longrightarrow$$

$$3Fe^{3+} + Cr^{3+} + 4H_2O$$

DISSOLUTION/PRECIPITATION

$$BaCrO_4(s) \Longleftrightarrow Ba^{2+} + CrO_4^{2-}$$

$$K = [Ba^{2+}][CrO_4^{2-}]$$

METAL CATION BINDING TO OXIDE SURFACES
"pH EDGE"
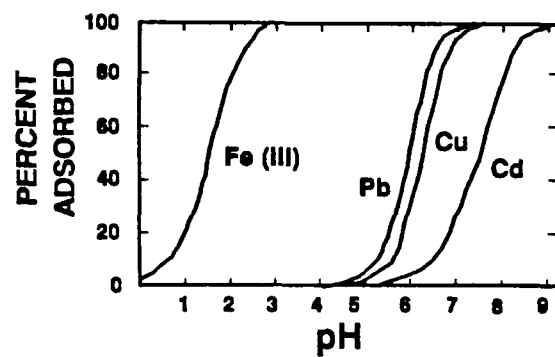
After Schindler et al., 1976.

pH EDGES
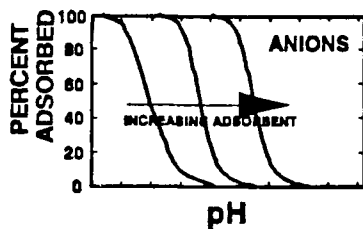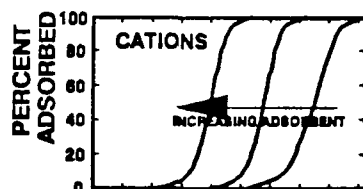
After Dzombak, 1986.

After Benjamin and Leckie (1982)

- 0.7 M NO_3
- 0.5 M Cl
- 0.2 M SO_4

30 g/L SiO_2
5×10^{-7} M Cd
I = 0.7 M

A

B

C

After Schindler, 1981.

$+ M^{++} = \qquad M^{+} + H^{+}$

$+ L^{-} = \qquad L + OH^{-}$

TWO-LAYER MODEL
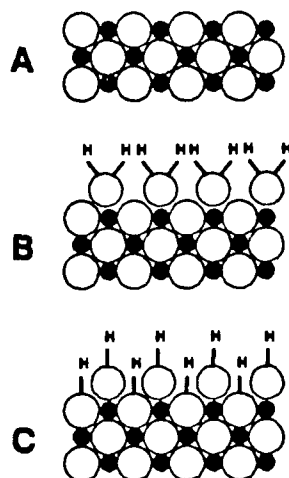
GOOD FOR:

- ANION ADSORPTION

- CATION ADSORPTION AT LOW ADSORBATE CONCENTRATION
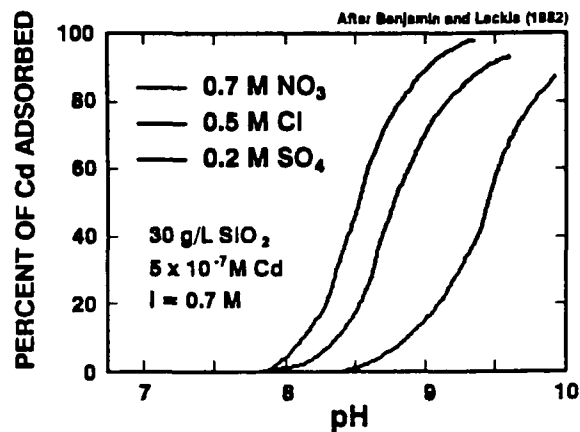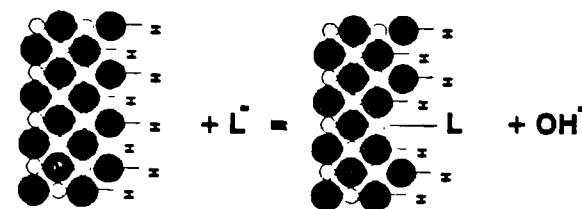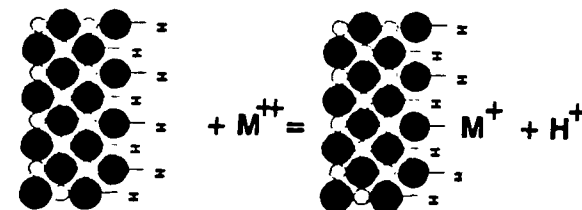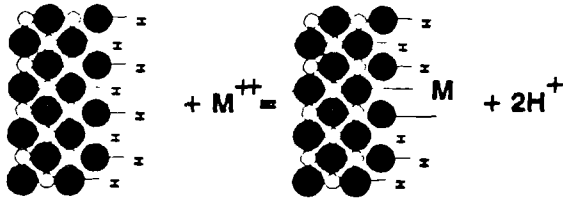
SURFACE COMPLEXATION MODELS

$$K_1 = \frac{[XOM^+][H^+]}{[XOH][M^{2+}]} \exp\{F(2\psi_1 - \psi_{H^+})/RT\}$$

$$K_2 = \frac{[XL][OH^-]}{[XOH][L^-]} \exp\{F(\psi_2 - \psi_{OH^-})/RT\}$$

HIGH CATION CONCENTRATION

SURFACE COMPLEXATION MODELS

$$XOH + M^{2+} \rightleftharpoons XOM^+ + H^+ \quad ; K_1$$

$$XOH + L^- \rightleftharpoons XL + OH^- \quad ; K_2$$

SURFACE COMPLEXATION MODELS

- TWO-LAYER MODELS

- STERN-LAYER MODELS

- TRIPLE-LAYER MODELS

- MULTIPLE SITE MODELS

- SURFACE PRECIPITATION MODELS
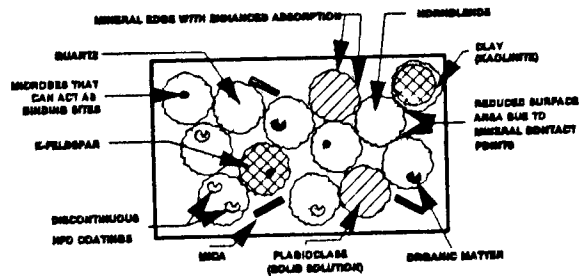
NATURAL POROUS MEDIUM

COMPUTATIONAL TOOLS

- MASS BALANCE
- CHEMICAL SPECIATION
- MASS TRANSFER
- MULTICOMPONENT TRANSPORT

COMPUTATIONAL TOOLS

- BALANCE
- WATEQ4F
- PHREEQE
- SOLMNEQ88
- MINTEQ
- EQ6

DATA REQUIREMENTS
FOR COMPUTATIONAL TOOLS

- FIELD
  - pH
  - Temperature
  - Alkalinity/Acidity
  - Redox Conditions

- LABORATORY
  - "Complete" Analysis

ACTIVTIY OF Cd^{109} ON MINERALS

	ACTIVITY (CPS/g)
UNFRACTIONATED SAND	62
QUARTZ (NO COATINGS)	15
FELDSPAR (NO COATINGS)	65
HEAVY MINERALS	49
QTZ + FELD + OXIDES	92
FELD + CALCITE	110
CARBONATE GRAINS	330

Data from Fuller and Davis (1987)

MASS BALANCE

WELL A   WELL B

$A + B \rightleftharpoons (AB)$

$A + C \rightleftharpoons (AC)$

$D_a \rightleftharpoons D_g$

GROUNDWATER
FLOW

| PRODUCT AT RESIDUAL SATURATION | BIODEGRADATION
CONSUMPTION OF OXYGEN
CONSUMPTION OF ORGANIC MATTER
PRODUCTION OF CO_2 |

DECREASED pe
DECREASED pH

GROUNDWATER
FLOW

| NATURAL HFO
HIGH ADSORPTION CAPACITY
ADSORBED METAL IONS | DISSOLUTION OF HFO
DESORPTION OF NATURAL METALS
REDUCED SORPTIVE CAPACITY
COMPETITION FOR ADSORPTION SITES |

ORGANIC/INORGANIC
INTERACTIONS

■ INDIRECT

  − REDOX CONDITIONS

  − pH CHANGES

■ DIRECT

  − CHELATION

  − COMPETITION FOR

  − OXIDATION/REDUCTION

CHARACTERIZATION OF SUBSURFACE PHYSICOCHEMICAL PROCESSES

IV FACILITATED TRANSPORT
    A. Mechanisms
    B. Particle Transport
         1. Types of particles
         2. Particle removal mechanisms
         3. Mechanisms controlling the transport of microorganisms
    C. Suspect environments
    D. Examples
    E. Importance to Transport of Organic Contaminants

FACILITATED TRANSPORT

FACILITATED TRANSPORT

- COSOLVENT EFFECTS
- PARTICLE TRANSPORT
  - ORGANIC
  - INORGANIC
  - BIOLOGICAL

FILTRATION MECHANISMS

SURFACE FILTRATION

STRAINING

PHYSICAL-CHEMICAL
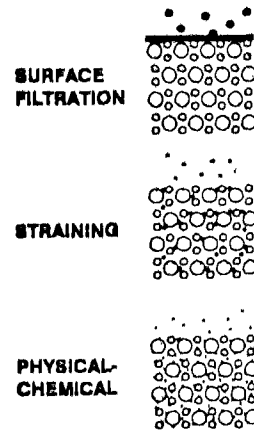
TYPES OF PARTICLES

- BACTERIA
- VIRUSES
- NATURAL ORGANIC MATTER
- INORGANIC PRECIPITATES
- ASBESTOS FIBERS
- CLAY

MECHANISMS CONTROLLING THE TRANSPORT OF MICROORGANISMS

- STRAINING
- ADSORPTION
- SEDIMENTATION
- INTERCEPTION
- DIFFUSION
- CHEMOTAXIS
- DEATH
- GROWTH

FACILITATED TRANSPORT SUSPECT ENVIRONMENTS

- HIGH CONCENTRATIONS OF
  - ORGANIC CARBON
  - DISSOLVED SOLIDS
  - SUSPENDED SOLIDS
- HIGH FLOW RATES
- ABRUPT TRANSITIONS IN pH
- ABRUPT TRANSITIONS IN REDOX CONDITIONS
- SUPERSATURATION WITH MINERAL PHASES

METHODS FOR PARTICLE DETECTION

- FILTRATION
  - Membrane Filters
  - Ultrafiltration
- MICROSCOPY
- ELECTROPHORESIS
- LIGHT SCATTERING

PARTICLE FORMATION IN OTIS AFB PLUME
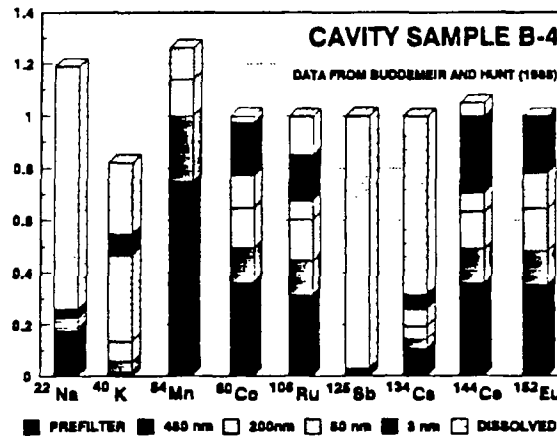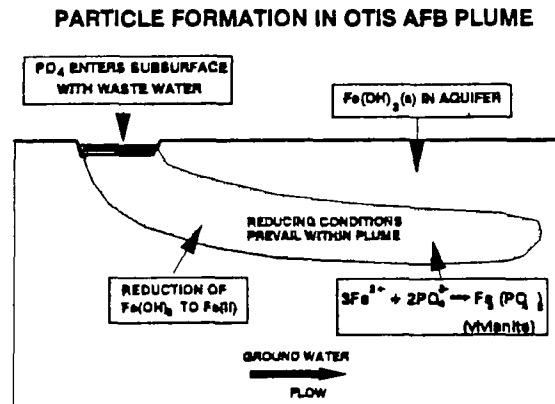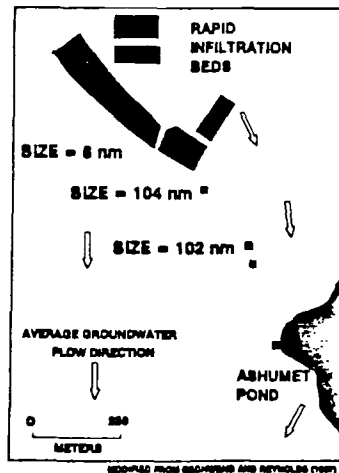
WHEN IS PARTICLE TRANSPORT OF ORGANICS IMPORTANT?

EXAMPLE:

Mass of NSP = 10 mg/L

$f_{oc} = 0.1$

$$M_s = \frac{n\, f_{oc}\, K_{ow}\, M_w}{1000\, \rho_b}$$

$$M_s = 2 \times 10^{-6}\, K_{ow}\, M_w$$

WHEN IS PARTICLE TRANSPORT OF ORGANICS IMPORTANT?

EXAMPLE:

Mass of NSP = 10 mg/L

$f_{oc} = 0.1$

THEREFORE:

IMPORTANT IF

$$K_{ow} > 10^6$$

CAVITY SAMPLE B-4

PRIORITY POLLUTANTS WITH

K$_{oc}$ VALUES GREATER THAN 10^6

DDE   PAHs

DDT   TCDD

Aroclor 1260   Toxaphene

hexachlorobenzene

Dioctyl phthalate

FACILITATED TRANSPORT
AND REMEDIATION

- ■ PLUGGING OF INJECTION WELLS

- ■ EASY REMOVAL FROM SUBSURFACE

- ■ AGGREGATION IN THE SUBSURFACE

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Characterization of Subsurface Degradation Processes

Dr. J. Michael Henson

Dr. Henson joined RMT's staff in February 1988. He directs biological remediation investigations and is responsible for identifying the potential for biological degradation of solid and hazardous wastes. Just prior to joining RMT, he was a research microbiologist with the U.S. EPA's Robert S. Kerr Environmental Research Laboratory where he conducted research on the microbiological transformation of pollutants in subsurface environments. Specific research activities were directed at metabolism of pollutants by enhancing the growth and activity of aerobic and anaerobic bacteria. Remediation projects included sites that were contaminated with fuel hydrocarbons and halogenated hydrocarbons.

Other research projects Mike has directed include quantitation of bacterial lipids in environmental samples to assess the status of the microbial community within those environments. Some of these environments include bioreactors enhanced to degrade pollutants, methane-producing digestors, and undisturbed soils. He has utilized Fourier transform-infrared spectroscopy to analyze bacterial polymers and bacterial biofilms involved in microbially-facilitated corrosion in the marine environment.

He earned his Ph.D. in 1983 from the University of Florida where he investigated the role that fatty-acid intermediates played in the anaerobic conversion of biomass to methane. These studies were augmented by studying the effects that various supplements had on anaerobic conversion processes. Dr. Henson also participated in the design and construction of various anaerobic digestions systems. At Clemson University, he earned a MS while performing research to determine the potential for microbial degradation of petroleum products in the marine environment. The effects of the results of microbial degradations processes might have on the marine environment were also investigated.

I.   INTRODUCTION TO SESSION

    A.   Objectives

    B.   Relationship of abiotic and microbiological transformations

II.   ABIOTIC TRANSFORMATIONS

    A.   Introductions

    B.   Abiotic reactions that organic chemicals may undergo
        1. Hydrolysis
        2. Substitution
        3. Elimination
        4. Oxidation
        5. Reduction

    C.   Rates of abiotic reactions

    D.   Examples of compounds susceptible to abiotic reactions

KNOWLEDGE of:

(1) transport processes and

(2) non-biological or biological reactions

that a contaminant may undergo in the subsurface

will provide an understanding of the fate of that

contaminant.

This knowledge should guide site investigation remediation

efforts.

OBJECTIVES

- Discuss abiotic and biotic degradation
  processes

- Provide information for site evaluation
  related to biological remediation

- Build the foundation for Biorestoration
  discussion topic

ABIOTIC VS BIOTIC TRANSFORMATIONS

- Abiotic transformations are much slower than
  biotic transformations (generally)

- Abiotic transformations receive little attention
  as a potential remediation mechanism

- Abiotic transformations may not provide a
  permanent treatment technology

ABIOTIC TRANSFORMATIONS

Definitions:

1) "not biotic" - Webster's Ninth New Collegiate
    Dictionary

2) "those reactions that do not involve (a) metabolically
    active organisms, (b) extracellular enzymes, or
    (c) metabolic intermediates such as NADH, NADPH,
    flavins, flavoproteins, hemoprotein, iron porphyrins,
    chlorophyll, cytochromes, and glutathiones" -
    Dragun, 1988

ABIOTIC REACTIONS - ORGANIC CHEMICALS

- Hydrolysis

- Substitution

- Elimination

- Oxidation

- Reduction

<u>Compound</u>

Compound	Half-Life (in H_2O, pH = 7)
Atrazine	2.5h
Chloroethane	38d
Chloromethane	339d
Dichloromethane	704y
Malathion	8.1d (pH = 6.0)
Parathion	17d (pH = 6.0)
Methyl Parathion	10.9d (pH = 6.0)
Tetrachloromethane	700y (1 ppm)
	7y (1000 ppm)
Trichloromethane	3500y

ORGANIC CHEMICALS NOT SUSCEPTIBLE TO HYDROLYSIS

- Aldehydes

- Alkanes, Alkenes, Alkynes

- Aliphatic amides

- Amines

- Carboxy groups

- Nitro-groups

YDROLYSIS

- A chemical reaction in which an organic chemical reacts with either water or a hydroxide ion:

  $R - X + H_2O \longrightarrow R-OH + H^+ + X^-$

  $R - X + OH^- \longrightarrow R-OH + X^-$
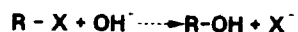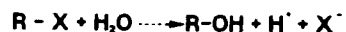
- Nucleophilic displacement reaction

  Sn1 - requires two separate reactions

  Sn2 - one-step reaction

- First order with respect to concentration of organic chemical

$$k = \left[\frac{2.303}{t}\right] \log \left[\frac{C_0}{C_0 - C_1}\right]$$

$$t_{1/2} = \frac{0.693}{k}$$

ORGANIC CHEMICALS SUSCEPTIBLE TO HYDROLYSIS

- Alkyl halides

- Chlorinated amides

- Carbamates

- Esters

- Epoxides

- Sulfones

- Phosphonic - and Phosporic - acid esters

EFFECTS OF SOILS ON HYDROLYSIS

Soil can have great affect on hydrolysis half-lives

- pH at soil particle surfaces

- presence of metals

- sorption

- soil water content

- soil type

SUBSTITUTION

- Hydrolysis is a Sn1 or Sn2 nucleophilic substitution reaction

- HS or RS⁻ will react with alkyl halides

- Results in sulfur-containing intermediates

ELIMINATION

- Involves the loss of two leaving groups

- Forms a double (or triple) bond

$$R - \underset{\underset{X_1}{|}}{CH} - \underset{\underset{X_2}{|}}{CH_2} \longrightarrow R - CH = CH_2$$

- Reaction mechanisms: E1, two-step process

  E2, one-step process

- Examples: 1,2-dibromoethane

  1,2-dibromoprobane

- Rates; First-order

ABIOTIC DEGRADATION OF 1,1,1-TRICHLOROETHANE

[Cline, et al, 1988]

1,1,1-TCA → 1,1-Dichloroethylene — Elimination pathway

1,1,1-TCA → Acetic Acid — Substitution pathway
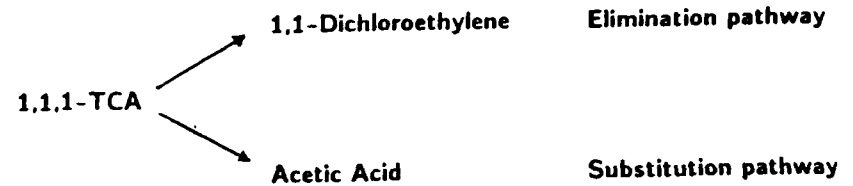
- ≈25% 1,1-DCE, ≈75% Acetic Acid

- May produce more 1,1-DCE in southern aquifers

- 1,1-DCE more soluble

OXIDATION/REDUCTION

- Coupled reactions

- Oxidation is the net loss of electrons

- Reduction is the net gain of electrons

- Can be very complex in soil systems with multiple redox couples

CHARACTERIZATION OF SUBSURFACE DEGRADATION PROCESSES

III.   MICROBIOLOGICAL TRANSFORMATIONS

    A.   Introduction
        1. Principles of microbial ecology
        2. Degradation vs mineralization
        3. Environmental factors controlling bioremediation
        4. Microbial adaptation/acclimation

    B.   Metabolic diversity of microbes and possibilities for biological remediation
        1. Oxygen respiration
        2. Denitrification
        3. Sulfate respiration
        4. Nitrate respiration
        5. Fermentation
        6. Iron respiration
        7. Carbonate respiration

    C.   Rates of biodegradation

    D.   Classes of compounds amenable to bioremediation
        1. Hydrocarbon fuels
        2. Creosote wastes
        3. Phenols and halogenated phenols
        4. Halogenated aliphatic hydrocarbons
        5. Halogenated aromatic compounds
        6. Polychlorinated biphenyls
        7. Pesticides
        8. Other organic compounds

IV   EVALUATION OF A SITE FOR BIOLOGICAL REMEDIATION

    A.   Collection of samples for microbiological analysis
        1. Collection of soil/aquifer samples
        2. Preservation and holding of samples

    B.   Enumeration of microorganisms present
        1. Necesssity for enumeration
        2. Viable/Plate counts
        3. Acridine orange direct counts
        4. Most Probable Number counts
        5. Other techniques

    C.   Evaluation of biodegradation potential
        1. Presence of substrates toxic to microorganisms
        2. Establishing proper controls
        3. Microcosm evaluation

V.   SUMMARY

    A.   Abiotic degradation

    B.   Biotic degradation

BIOREMEDIATION

Utilization of microbial processes in a controlled
environment to remove a variety of compounds from
a location where they are unwanted.

BIOREMEDIATION

Requires integrated approaches from several disciplines:

- Microbiology

- Hydrogeology

- Engineering

MICROBIAL ECOLOGY OF SUBSURFACE

- 1×10^6 to 1×10^8 microbes/gm soil
  (lower in pristine environments)

- >90% of microbes attached to solids

- metabolically active

- metabolically versatile

- oxic and anoxic conditions

MINERALIZATION

Conversion of organic chemicals to CO_2 [CH_4], water,
and inorganic minerals.

1,2-dichlorophenol ----> CO_2 + H_2O + Cl + Biomass
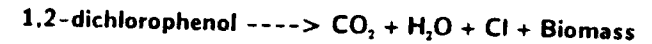
BIODEGRADATION

Biological transformation of an organic chemical to
another form, without regard to extent.

POTENTIALLY LIMITING ENVIRONMENTAL FACTORS

- pH

- salinity – osmotic pressure

- available water

- temperature

- hydrogeologic conditions

ADAPTION/ACCLIMATION

An observed increase in the rate of biodegradation after some period of exposure of the microbial community to a chemical.

A - ADAPTATION TIME
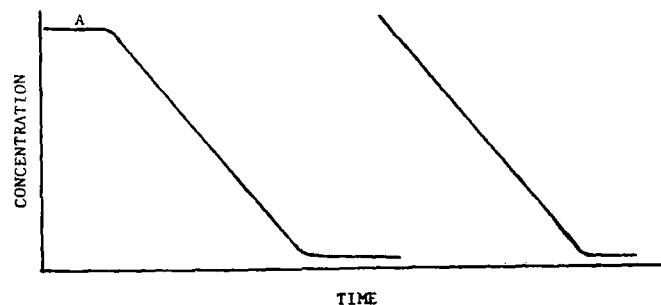
MICROBIAL ADAPTATION

- When adaptation occurs, the rate of removal is not governed by an intrinsic property of the microbes, but is governed by the physical processes controlling the availability of nutrients - principally oxygen.

- Allows for mathematical models

NON-GROWTH METABOLISM

Gratuitous metabolism:

enzyme has low substitute specificity

Ex: methane mono-oxygenase

Cometabolism or Co-oxidation:

a substance that can not be used for growth is transformed in the presence of a growth substitute
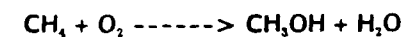
Ex: some PAH's

AEROBIC METABOLISM

RESPIRATION

- Oxygen is the terminal electron acceptor

- Water is the product

- Energy is released, which is partially captured

DEGRADATION

- Oxygen is a co-substrate

    - Mono-oxygenase

    $CH_4 + O_2 ------> CH_3OH + H_2O$

    - Di-oxygenase

ANAEROBIC METABOLISM

Anaerobic respiration: terminal electron acceptor is an
inorganic compound such as nitrate,
sulfate, nitrate, carbonate

Anaerobic fermentation: terminal electron acceptor is an
organic compound such as pyruvic
acid to lactic acid or acetaldehyde to
ethanol

DENITRIFICATION

- Nitrate is electron acceptor
- N_2 is product of nitrate metabolism
- Facultative organisms are involved
- Wide variety of biochemistry
- Energetics similar to oxygen

SULFATE RESPIRATION

- Hydrogen sulfate is produced
- Occurs under reducing conditions
- Energy transfer much less than oxygen
- Area of much research
- Some compounds are amenable to degradation under
  sulfate-reducing conditions

NITRATE RESPIRATION

- Ammonia is the product
- Occurs under reducing conditions
- Energy transfer much less than oxygen

CARBONATE RESPIRATION

- Methane is the product
- Highly specialized group of bacteria - methanogens
- Occurs under highly reducing conditions
- Energy transfer much less than oxygen

IRON RESPIRATION

- Fe^{3+} is electron acceptor
- Fe^{3+} is the product
- Area of research - learn from environment
- Energetics similar to oxygen
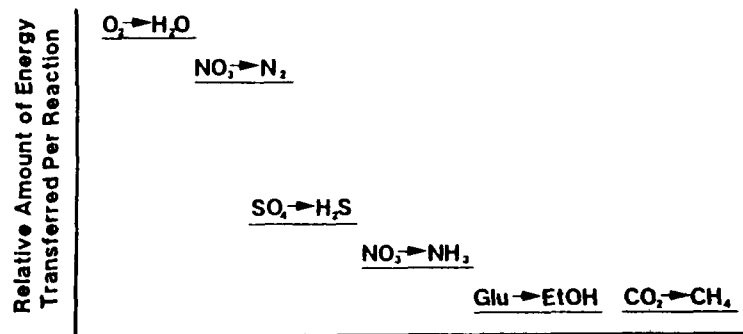
BIOLOGICAL REACTION KINETICS

FERMENTATION

- Organic compound is electron acceptor
- Products vary: alcohols, organic acids,
- Occurs under reducing conditions
- Energy transfer much less than oxygen
- Primarily carbohydrates; role in mixed consortia

- First order with respect to concentration of organic chemical.

$$k = \left[\frac{2.303}{t}\right] \log \left[\frac{C_0}{C_0 - C_1}\right]$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

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

- Monod kinetics (hyperbolic) may apply with higher concentrations where degradation rate becomes independent of concentration.

- Second order rate expression is derived from Monod equation. Dependent on concentration of organic chemical and microbial biomass.

SEQUENCE FOR CONSUMPTION OF ELECTRON ACCEPTORS

Relative Amount of Energy Transferred Per Reaction

$O_2 \rightarrow H_2O$

$NO_3^- \rightarrow N_2$

$SO_4 \rightarrow H_2S$

$NO_3^- \rightarrow NH_3$

$Glu \rightarrow EtOH$ $CO_2 \rightarrow CH_4$

RELATIVE EASE OF BIODEGRADATION;
i.e., COMPOUNDS APPROPRIATE FOR CONSIDERATION

- Hydrocarbons; fuels, BTEX, PNA's lower molecular weight, normal paraffins

- Organics in general; THF, MEK, IPA, EG, Phenols, Chlorinated Phenols, other alcohols, esters, aldelydes

- N-, S-, O- containing organics

- Creosote; PNA's and PCP

- Halogenated compounds; not always straight forward, may require other biological reactions - Co-Metabolism.

- Key considerations: solubility and

CREOSOTE

- By-product from the production of coke from coal, i.e., it is a coal tar

- Complex mixture of organic compounds with over 200 compounds identified

- Composition varies with the source of coal, equipment, and process

- Primarily composed of neutral fraction

- Most common wood preservative

PENTACHLOROPHENOL (PCP)

- Dissolved in No. 2 Fuel Oil as carrier

- Technical grade PCP is about 85 to 90 % pure PCP
    tetrachlorophenol
    chlorinated phenoxyphenols
    chlorinated dibenzofurans
    chlorinated dibenzodioxins

- K_{ow} = 1760

- Solubility = 14 mg/L (20 C)

- Protonated form insoluble, pK_a = 4.7 - 4.8

COMPOSITION OF CREOSOTE

	Aqueous Solubility (μg/l)	Log Kow	Koc
Naphthalene	31,700	3.37	1,300
Acenaphthalene	3,930	4.33	-----
Fluorene	1,980	4.18	-----
Phenanthrene	1,290	4.46	23,000
Fluoranthene	260	5.33	------
Pyrene	135	5.32	84,000
			(62,700)

DEGRADABILITY

- PCP — moderately persistent
    half-life 30 to 60 day range
    acclimated population
    aerobic and anaerobic conditions
    mineralized - partial products are possible

- Creosote — complex mixture of PAH's
    half-life increases with molecular weight
    PAH's with 3 rings or less quicker
    Co-metabolism may be important
    Aerobic [anoxic - denitrification, less
        known about other anoxic processes]

HALOGENATED ALIPHATIC COMPOUNDS

Anaerobic Conditions

PCE

k_1 ↓

TCE

k_2 ↓

DCE

k_3 ↓

VC

k_4 ↓

CO_2

$k_1 > k_2 > k_3 > k_4$
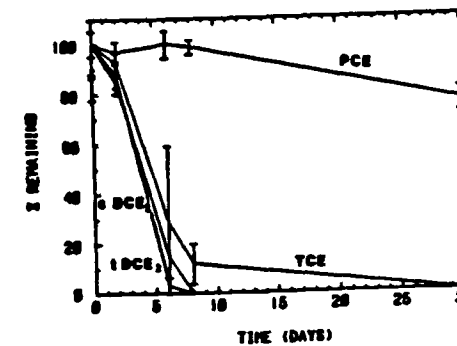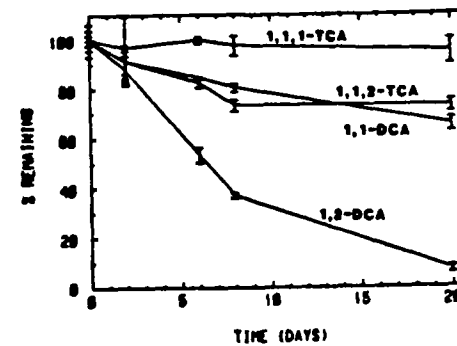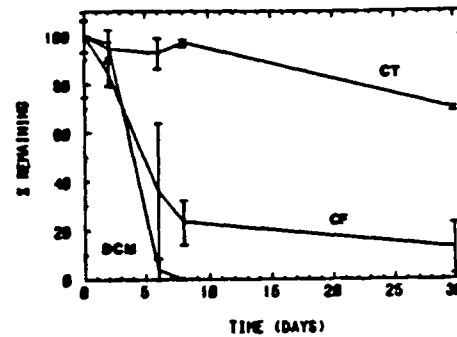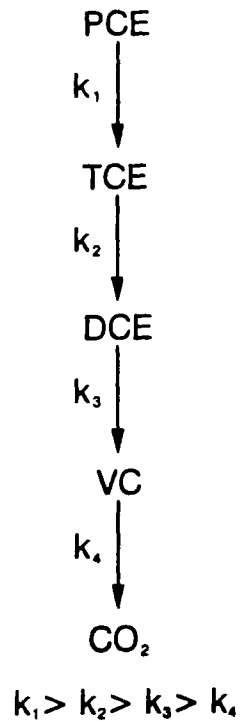
METHANE MONO-OXYGENASE

- $CH_4 + O_2 ----> CH_3OH$ (used by bacteria)
- Also reacts with many other hydrocarbons to produce alcohols
- Reacts with ethylene to produce epoxide
- TCE degradation by methane addition –
  Wilson and Wilson, 1985

(From Henson et al., 198?)

PCB DEGRADATION

- Anaerobic conditions

    - Reductive dechlorination; i.e., chlorines are replaced by H's

    - Reduces toxicity

    - Enhances aerobic degradability

Soils previously exposed to PCB's showed activity.

Added 700 ppm Arochlor 1242
Time 0   - 1% mono-chlorinated biphenyls
Time 16 wks.- 76% mono-chlorinated biphenyls, Penta chlorinated biphenyls gone.
          - Most activity took place within first 4 weeks.

- Aerobic conditions

    - lower chlorinated compounds more susceptible

    - treatment evaluations should perform mass balance

    - GC/MS to detect preferential degradation

GENERAL CONCLUSIONS

Soil conditions very important.

Bioavailability of PCB's very important, hydrophobic compound.

Previous exposure results in adapted bacteria.

Not the cure yet, but new organisms, tricks, and GEM's may make cost effective quickly.

Anaerobic pretreatment followed by aerobic treatment.

BASIC PREMISES OF BIODEGRADATION AS THEY RELATE TO BIOREMEDIATION

- Provides carbon and energy requirements

- Take advantage of carbon cycle

- Environmental factors may be determinate

- Biodegradation can occur in many environments

- Utilize enzymes evolved to degrade biogenic compounds to degrade man-made compounds

INFORMATION REQUIREMENTS FOR REMEDIAL DESIGN

- Thorough assessment of site
  site history
  geology
  hydrology

- Regulatory requirements

- Thorough assessment of microbiology
  presence of requisite microorganisms
  assessment of toxicity to microorganisms
  nutrient requirements to enhance degradation
  compatibility of geochemistry with enhancement

REQUISITE MICROORGANISMS

- Detected in many samples of subsurface materials

- Do not assume ubiquity, however

- Must be able to metabolize compounds of concern

- Examine for toxicity

EVALUATION PHASE

- Toxicity

- Limiting nutrients or electron acceptor

- Analogue addition

- Numbers of microbes present

GROWTH CONDITIONS

- Microorganisms require carbon, nitrogen, phosphorous, and other inorganics

- Also require a Terminal Electron Acceptor
  oxygen, nitrate, (denitrification)
  sulfate, nitrate (nitrate reduction),
  carbonate, organics (fermentation)

- Naturally-occurring microorganisms

ꞁORATORY EVALUATIONS

- Based of collection of subsurface core materials

- Number of heterotrophic and specific compound-degrading bacteria present

- Disappearance of parent compound

- Nutrient mixture that best supports removal nitrogen, phosphorous, potassium, other nutrients geochemistry may support without additions

- Electron acceptor evaluation and consumption

- GC/MS of daughter products

- Determination of removal rates and final enumeration

METHODS FOR MICROBIAL ENUMERATION

PURPOSE: To ensure system is not toxic; requisite organisms are present; show subsequent increase. Not to predict activity or rates

- Plate Counts:

  Standard microbiological technique: habitat-simulating

- Most Probable Number (MPN):

  Statistical counting technique in liquid medium

- Acridine Orange Direct Count (AODC):

  Stain microorganisms – count via microscopy. Not a viable count

- Cell components:

  Fatty acids
  Total Lipid Phosphate
  DNA

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

SUMMARY

Abiotic

- Rates not as fast as microbiological transformation rates

- In subsurface, observe abiotic transformations

- Explains some constituents that were not originally present

Biotic

- Diversity of metabolic activities resulting in many possible remediation schemes

- Explains the presence of some constituents

- Explains alteration of ecosystem

- Provides potential technology for site remediation if applied correctly in appropriate environments

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Dragun, J. 1988. The Soil Chemistry of Hazardous Waste. Hazardous Materials Control Research Institute, Silver Spring, MD.

Gibson, D. T. 1984. Microbial Degradation of Organic Compounds. Marcel Dekker, Inc., New York.

Parr, J. F., P. B. Marsh, and J. M. Kla. 1983. Land Treatment of Hazardous Wastes. Noyes Data Corporation, Park Ridge, NJ.

Loehr, R. C. and J. F. Malina, Jr. 1986. Land Treatment: A Hazardous Waste Management Alternative. Center for Research in Water Resources. The University of Texas at Austin, Austin, TX.

Vogel, T. M., C. S. Criddle, and P. L. McCarty. 1987. Transformations of halogenated aliphatic compounds. Environ. Sci. Technol. 21:722-736.

Tiedje, J. M., S. A. Boyd, and B. Z. Fathepure. 1987. Anaerobic degradation of chlorinated aromatic hydrocarbons. Dev. Indust. Microbiol. 27:117-127.

Nyer, E. K. and G. J. Skladany. 1989. Relating the physical and chemical properties of petroleum hydrocarbons to soil and aquifer remediation. Ground Water Monitoring Review. 9:54-60.

Henson, J. M., M. V. Yates, and J. W. Cochran. 1989. Metabolism of chlorinated methanes, ethanes, and ethylenes by a mixed bacterial culture growing on methane. J. Indust. Microbiol. 4:29-35.

Wilson, J. T. and C. H. Ward. 1987. Opportunities for bioreclamation of aquifers contaminated with petroleum hydrocarbons. Dev. Indust. Microbiol. 27:109-116.

Wilson, J. T., L. E. Leach, M. Henson, and J. N. Jones. 1986. In situ biorestoration as a ground water remediation technique. Ground Water Monitoring Review 6:56-64.

Lee, M. D., J. M. Thomas, R. C. Borden, P. B. Bedient, J. T. Wilson, C. H. Ward. 1988. Biorestoration of aquifers contaminated with organic compounds. CRC Critical Reviews in Environmental Control 18:29-89.

Schwarzenbach, R. P., W. Giger, C. Schaffner, and O. Warner. 1985. Groundwater contamination of volatile halogenated alkanes: Abiotic formation of volatile sulfer compounds under anaerobic conditions. Environ. Sci. Technol. 19:322-327.

Cooper, W. J., M. Mehran, D. J. Riusech, and J. A. Jones. 1987. Abiotic transformation of halogenated organics. 1. Elimination reaction of 1,1,2,2-tetrachloroethane and formation of 1,1,2-trichloroethene. Environ. Sci. Technol. 21:1112-1114.

Cline, P. V., J. J. Delfino, T. Potter. 1988. Degradation and advection of 1,1,1-trichloroethane in the saturated zone containing residual solvent. Proc. Superfund '88, Washington, DC. Hazardous Materials Control Research Institute, Silver Spring, MD.

Thomas, J. M. and C. H. Ward. 1989. In situ biorestoration of organic contaminants in the subsurface. Environ. Sci. Technol. 23:760-766.

SESSION V

Applications and Limitations of In-Situ Soils Remediation

Dr. Ronald C. Sims

Dr. Sims has advanced degrees in environmental microbiology (University of North Carolina at Chapel Hill, School of Public Health) and environmental engineering (Washington State University) at the M.S. level, and has Ph.D. minors in toxicology, soil science and mathematics in addition to his Ph.D. major in biological engineering (North Carolina State University). After receiving his Ph.D. degree, Dr. Sims joined the faculty of the Division of Environmental Engineering at Utah State University, Logan, Utah, in 1982. Dr. Sims served as principal investigator foe the U.S. EPA project to develop guidance concerning in-situ treatment technologies applicable to contaminated surface soils (Review of In-Place Treatment Techniques for Contaminated Surface Soils, 1984).

In addition to his academic position at Utah State University, Dr. Sims has also worked for the University of North Carolina at Chapel Hill, North Carolina, as Director of the International Program in Environmental Aspects of Industrial Development, for Mobay Chemical Corporation, Charleston, South Carolina, as Environmental Control Laboratory Supervisor, and as an environmental engineer for Research Triangle Institute (RTI), Research Triangle Park, North Carolina. Dr. Sims spent the 1989-1990 academic year on sabbatical leave with the U.S. Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, where he assisted EPA in the area of subsurface bioremediation investigations.

APPLICATIONS & LIMITATION OF IN-SITU SOILS REMEDIATION -
SOIL VACUUM EXTRACTION

Ronald C. Sims, Professor and Head, Environmental Engineering Division
Utah State University, Logan, Utah

I.   DESCRIPTION OF PROCESS

        A.   Characterization
                1. Site characterization requirements
                   a. location
                   b. permeability
                2. Waste/soil information requirements
                   a. volatility
                   b. water solubility
                   c. partitioning into oil
                   d. soil texture
                   e. soil organic carbon
                   f. soil moisture

        B.   Components and operating characteristics
                1. Components
                2. Operating characteristics
                3. Passive systems
                4. Active systems
                5. Soil gas monitoring probes

II.   APPLICATIONS OF SOIL VACUUM EXTRACTION

        A.   Approach
                1. Timing
                2. Iterative design
                3. Target treatment level
                4. Treatment train

        B.   Removal of volatile light non-aqueous phase liquids

        C.   Control of explosive vapors or harmful gases

        D.   Removal of non-volatile organic chemicals in soil

III.   LIMITATIONS OF SOIL VACUUM EXTRACTION

        A.   Contaminants

        B.   Site/soil factors
                1. Location
                2. Permeability

SOIL REMEDIATION

      Soil Vacuum Extraction

      Bioreclamation

      Contaminant Immobilization

      Contaminant Mobilization

APPROACH

      Description of Process

      Applications

      Limitations

Summary Matrix of Treatment Technologies

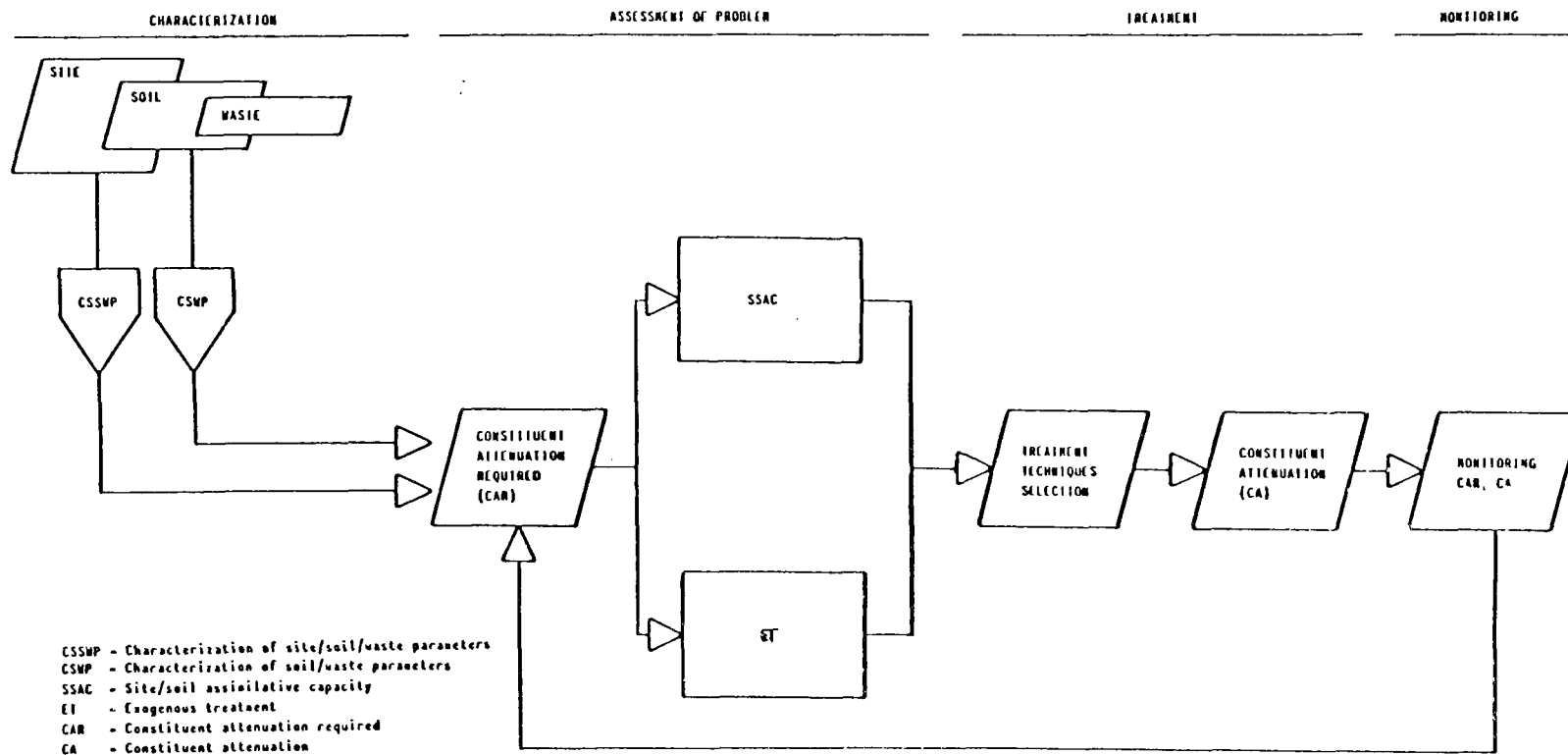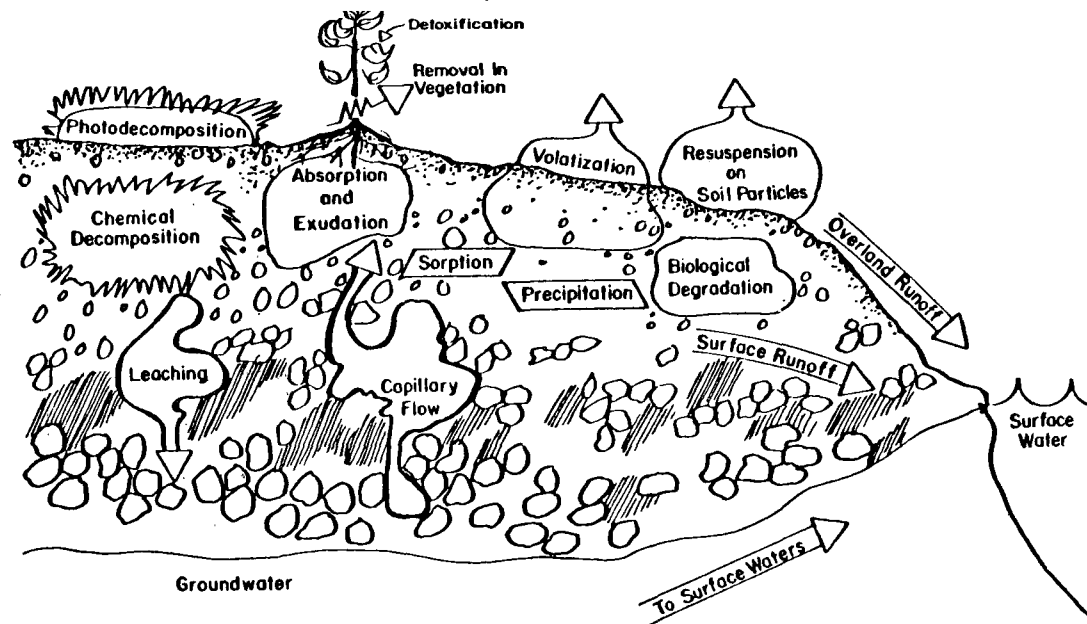| Technology	Wastes amenable to treatment	Status	Ease of application	Potential level of treatment	Reliability
Soil Flushing	Soluble organics and inorganics	Laboratory Pilot scale	Easy - difficult	Variable	Good
Immobilization					
Sorption (heavy metals)					
Agri. products	Heavy metals	Field	Easy - difficult	High	Retreatment required
Activated carbon	Heavy metals	Conceptual	Easy - difficult	Unknown	Unknown
Tetren	Heavy metals	Laboratory	Easy - difficult	High	Unknown
Sorption (organics)					
Soil mositure	Organics, nonvolatile, Kd<10	Conceptual	Easy - difficult	High	Retreatment required
Agri products	Organics	Laboratory	Easy - difficult	High	Retreatment required
Activated carbon	Organics, low water solubility	Field	Easy - difficult	Low - high	Unknown
Ion exchange					
Clay	Cationic components	Laboratory	Easy - difficult	High	Good
Synthetic resins	Certain cationic and anionic compounds	Laboratory	Easy - difficult	Variable	Unknown
Zeolites	Heavy metals	Conceptual	Easy - difficult	Unknown	Unknown
Precipitation					
Sulfides	Heavy metals	Conceptual	Difficult	High	Fair
Carbonates, phosphates and hydroxides	Heavy metals	Laboratory	Easy - difficult	Unknown	Retreatment required
Degradation					
Oxidation					
Soil catalyzed reactions	Aliphatic organics, other organics	Limited field	Easy - difficult	Variable	Good
Oxidizing agents	Various organics	Limited field	Moderate - difficult	High	Good
Reduction					
Organics	Chlorinated organics, unsaturated aromatics, aliphatics	Limited field	Easy - difficult	High	Retreatment required
Chromium	Hexavalent chromium	Limited field	Easy - difficult	High	Retreatment required
Selenium	Hexavalent selenium	Limited field	Easy - difficult	High	Retreatment required
Sodium	PCB, dioxin, halogenated compounds	Conceptual	Moderate	High	Good
Polymerization	Aliphatics, aromatics, oxygenated organic compounds	Expt. field	Moderate - difficult	Variable	Unknown
Biodegradation					
Soil moisture	Organics	Field	Easy - difficult	Low - high	Retreatment required
Soil oxygen - aerobic	Organics	Field	Easy - difficult	Low - high	Retreatment required
Soil oxygen - anaerobic	Halogenated organics	Conceptual	Moderate - difficult	Low - high	Retreatment required
Soil pH	Organics	Field	Easy - difficult	High	Retreatment required
Nutrients	Organics	Field	Easy - difficult	High	Retreatment required

(continued)

(continued)

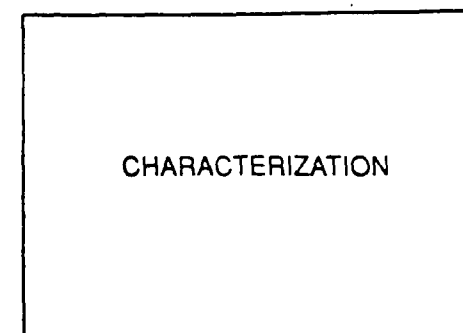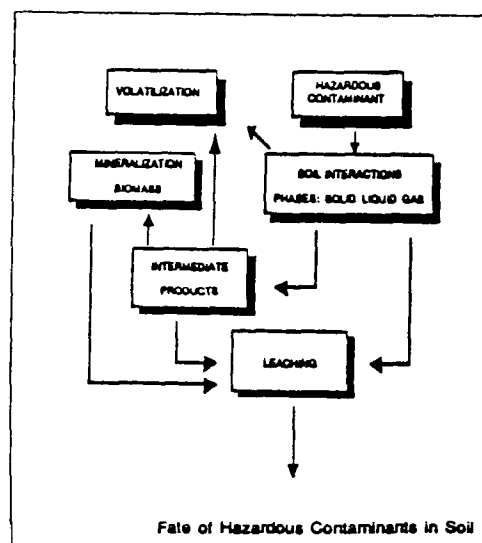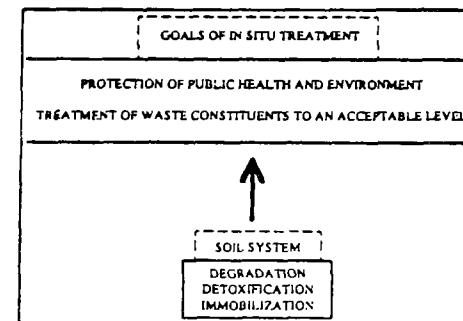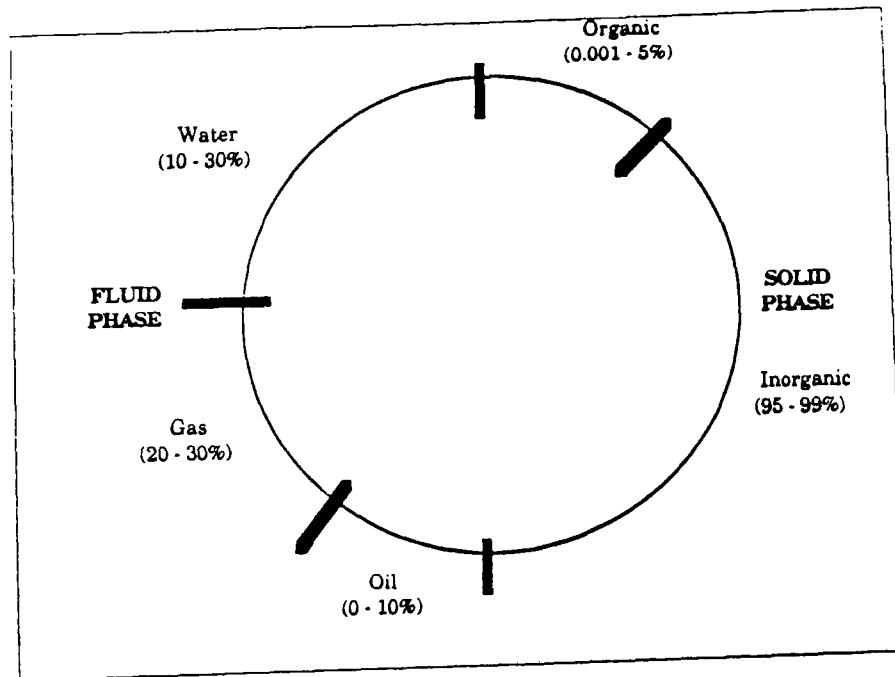| Technology	Wastes amenable to treatment	Status	Ease of application	Potential level of treatment	Reliability
Nonspecific organic amendments	Organics, arsenite wastes	Laboratory	Easy - difficult	Low - high	Retreatment required
Analog enrichment for cometabolism	Some organics with analogs	Laboratory	Easy - difficult	Low - high	Unknown
Exogenous acclimated or mutant micro-organisms	Various organics	Field	Easy - difficult	High	Retreatment required
Cell-free enzymes	Organics	Laboratory	Difficult	High	Unknown
Photolysis					
Proton donors	Some organics, including TCDD, Kepone, PCB	Field	Easy - difficult	High	Unknown
Enhance volatilization	Specific organics	Laboratory	Easy - difficult	High	Good
Reduction of Volatile Materials					
Soil vapor extract	Volatile organics and inorganics	Field	Easy - difficult	Low - medium	Good
Soil cooling	Volatile organics	Expt., limited field	Difficult	Low - medium	Retreatment required

Adapted from EPA 1984.

PEI Associates, Inc. and University of Cincinnati. 1989 Handbook on In Situ Treatment of Hazardous Waste. Draft. U.S. Environmental Protection Agency, Office of Research and Development, Risk Reduction Research Laboratory, Cincinnati, Ohio.

Sims, R.C., et al. 1986. Contaminated Surface Soils In-Place Treatment Techniques. Noyes Publications, Park Ridge, NJ

Sims, R.C., D.L. Sorensen, J.L. Sims, J.E. McLean, R.H. Mahmood, and R.R. Dupont. 1984. Review of In-Place Treatment Techniques for Contaminated Surface Soils. Volumes 1 and 2. EPA-540/2-84-003a,b. U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio.

Detoxification

Removal In Vegetation

Photodecomposition

Chemical Decomposition

Absorption and Exudation

Volatization

Resuspension on Soil Particles

Sorption

Precipitation

Biological Degradation

Overland Runoff

Leaching

Capillary Flow

Surface Runoff

Surface Water

To Surface Waters

Groundwater

CHARACTERIZATION

ASSESSMENT OF PROBLEM

TREATMENT

MONITORING

SITE

SOIL

WASTE

CSSWP

CSWP

CONSTITUENT ATTENUATION REQUIRED (CAR)

SSAC

ST

TREATMENT TECHNIQUES SELECTION

CONSTITUENT ATTENUATION (CA)

MONITORING CAR, CA

CSSWP - Characterization of site/soil/waste parameters
CSWP   - Characterization of soil/waste parameters
SSAC   - Site/soil assimilative capacity
ET   - Exogenous treatment
CAR   - Constituent attenuation required
CA   - Constituent attenuation

Organic
(0.001 - 5%)

Water
(10 - 30%)

FLUID
PHASE

SOLID
PHASE

Inorganic
(95 - 99%)

Gas
(20 - 30%)

Oil
(0 - 10%)

GOALS OF IN SITU TREATMENT

PROTECTION OF PUBLIC HEALTH AND ENVIRONMENT

TREATMENT OF WASTE CONSTITUENTS TO AN ACCEPTABLE LEVEL

SOIL SYSTEM

DEGRADATION
DETOXIFICATION
IMMOBILIZATION

VOLATILIZATION

HAZARDOUS
CONTAMINANT

MINERALIZATION

BIOMASS

SOIL INTERACTIONS

PHASES: SOLID LIQUID GAS

INTERMEDIATE

PRODUCTS

LEACHING

Fate of Hazardous Contaminants in Soil

CHARACTERIZATION

INTERPHASE TRANSFER
POTENTIAL

DEGRADATION

Biotic

Abiotic

VOLATILIZATION

Partitioning Information

Ko = partitioning of constituent between water and oil phase

Kd = partitioning of constituent between water and soil phase

Kh = partitioning of constituent between water and air phase
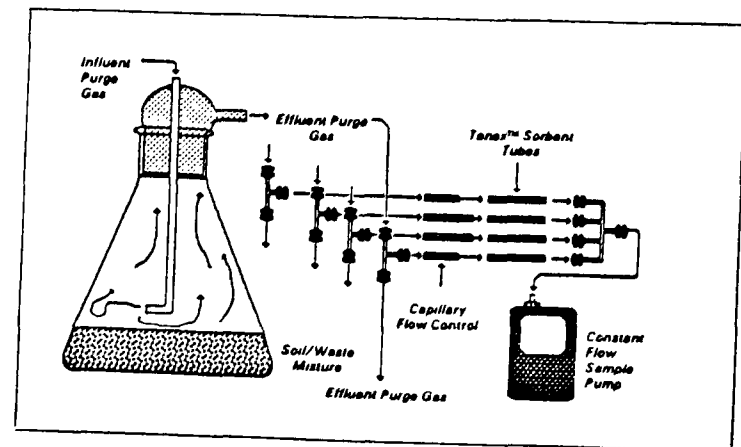
VOLATILIZATION

        Naphthalene   - 30% loss from soil

        1-Methylnaphthalene - 20% loss from soil

ABIOTIC DEGRADATION

        Naphthalene   - 12% loss from soil

        1-Methylnaphthalene - 12% loss from soil

        Anthracene   -   9% loss from soil

        Phenanthrene   - 17% loss from soil

Park et al. Environmental Toxicology and Chemistry. 1990. Vol. 9(2).

RETARDATION or IMMOBILIZATION

$R = Vw/Vp$

    R = Retardation

    Vw = velocity of water

    Vp = velocity of pollutant

BIOLOGICAL DEGRADATION

Half-life of a PAH Compound:

$$t_{1/2} = \frac{0.693}{k}$$

Where

$t_{1/2}$ = half-life of PAH compound in soil (time)

k = first-order rate constant (time^{-1}) for microbial degradation

---

IMMOBILIZATION

$$R = 1 + \frac{\rho K_d}{\theta}$$

ρ = soil bulk density

K_d = partition coefficient

θ = volumetric moisture content

SOIL-BASED WASTE CHARACTERIZATION

Chemical Class	Soil Sorption Parameters	Soil Degradation Parameters	Chemical Properties
Acid Base Polar Neutral Nonpolar Neutral Inorganic	Freundlich Sorption Constants (K,N) Sorption based on Organic Content (K_{oc}) Octanol water partition Coefficient (K_{ow})	Half-life ($t_{1/2}$) Rate Constant Relative bio-degradability	Molecular Weight Melting point Specific Gravity Structure Water Solubility

DETERMINATION OF CONTAINMENT REQUIREMENTS

SOIL-BASED WASTE CHARACTERIZATION

Volatilization Parameters	Chemical Reactivity	Soil Contamination Parameters
Air:water partition coefficient (K_w) Vapor pressure Henry's law constant ($1/K_w$) Sorption based on organic carbon content (Koc) Water solubility	Oxidation Reduction Hydrolysis Precipitation Polymerization	Concentration in soil Depth of Contamination

PROBLEM FOR ASSESSMENT

If the rate of transport (leaching) is significant compared with the rate of biodegration, both factors must be considered (degradation and leaching)

The constituent(s) may reach a "critical depth" in the soil before being degraded

MOBILITY AND DEGRADATION INDEX (MDI)

$MDI = T/t_{1/2}$

T = time required for chemical to travel through a critical depth

$t_{1/2}$ = chemical half-life in soil or time required for chemical to be degraded to one-half of the original concentration

SOIL TEXTURE

— — — Clay
——— Sandy Loam
—·—— Sand

$\rho = 1.6$

$V_d = 0.004$ in/hr (0.01 cm/hr)

$d_c = 2$ ft (60 cm)

MATHEMATICAL MODELS

Ratios of Concentration of Pesticides Between Water/Soil and Air/Soil at 15 cm After 81 Days (Ranked in Order from Greatest Potential for Leaching and Volatilization to Least Potential)

Pesticide (1)	Leaching potential (concentration in soil water/concentration in soil) (2)	Pesticide (3)	Volatilization potential (concentration in soil air/concentration in soil) (4)
Disulfoton	330	Toxaphene	7.4
Phorate	23	Disulfoton	3.6×10^{-2}
Methylparathion	4.8	Phorate	5.2×10^{-3}
Toxaphene	0.5	Heptachlor	5.5×10^{-3}
Endosulfan	0.12	Endosulfan	4.0×10^{-4}
Parathion	0.06	Aldrin	2.0×10^{-5}
Heptachlor	0.06	Methylparathion	1.2×10^{-5}
Aldrin	0.0009	Parathion	1.6×10^{-6}

McLean et al. 1988. Evaluation of Mobility of Pesticides in Soil Using U.S. EPA Methodology. Journal of Environmental Engineering. Vo. 114(3): 689-703.
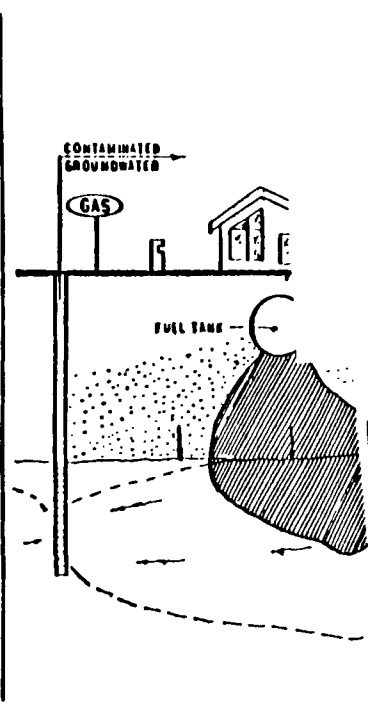
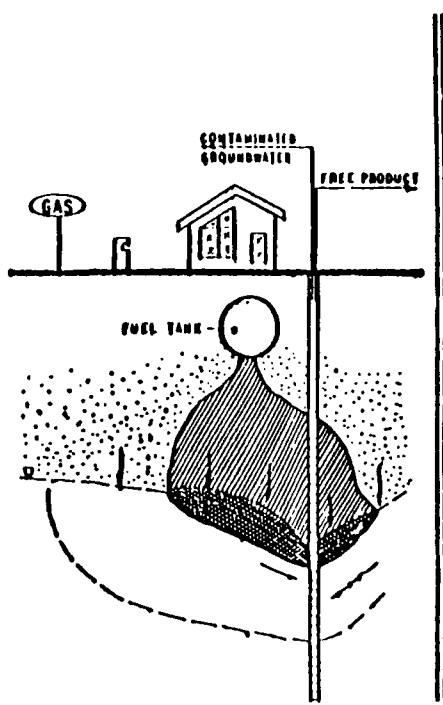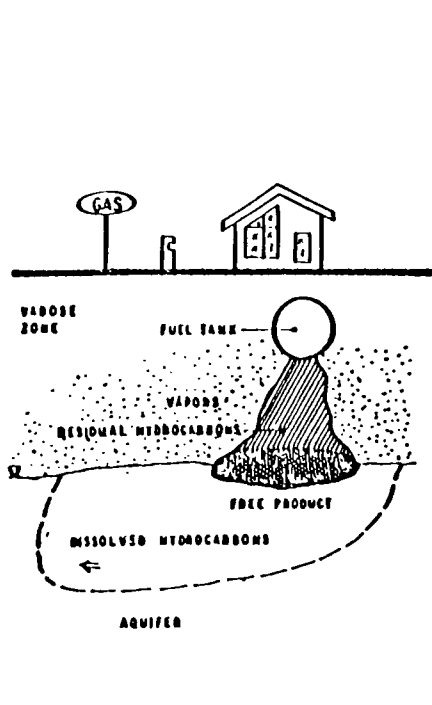## SOIL VACUUM EXTRACTION

Characterization

Components

INFORMATION

Performance Standards

3-D Contamination

Vapor Monitoring Probes

Pathways of Vacuum Propagation
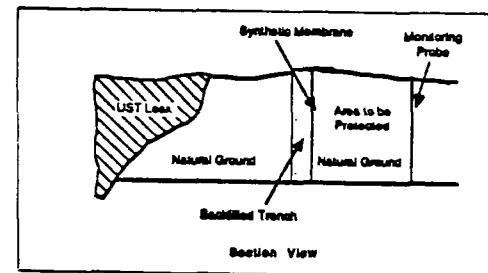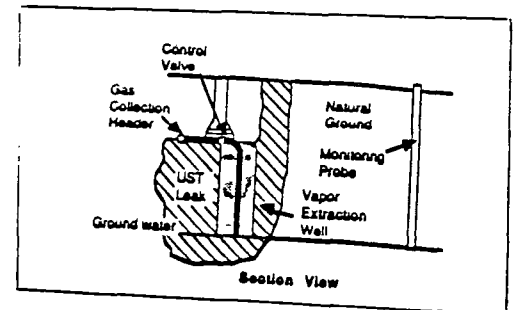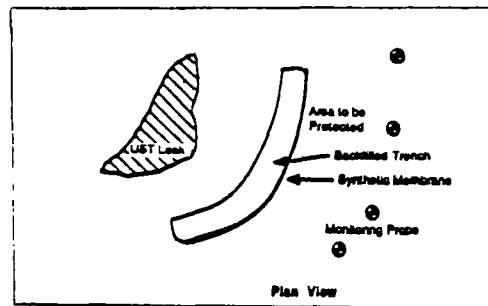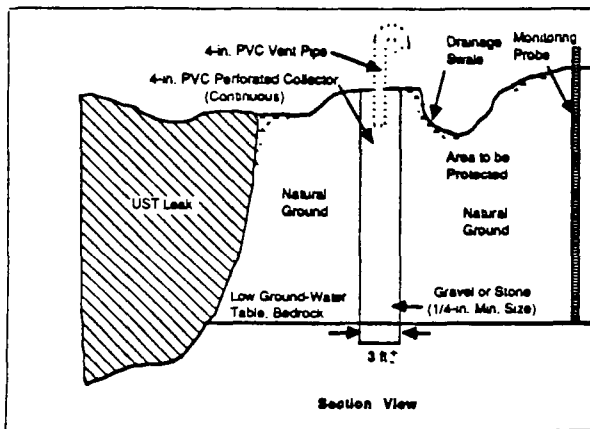
GAS

CONTAMINATED GROUNDWATER

FREE PRODUCT

CONTAMINATED GROUNDWATER

VADOSE ZONE

FUEL TANK

VAPORS

RESIDUAL HYDROCARBONS

FREE PRODUCT

DISSOLVED HYDROCARBONS

AQUIFER

FUEL TANK

FUEL TANK

GAS

GAS

VADOSE ZONE HYDROCARBONS

DISSOLVED HYDROCARBONS

VADOSE ZONE

FUEL TANK

VAPORS

RESIDUAL HYDROCARBONS

FREE PRODUCT

5-22

DISSOLVED HYDROCARBONS

AQUIFER

FUEL TANK

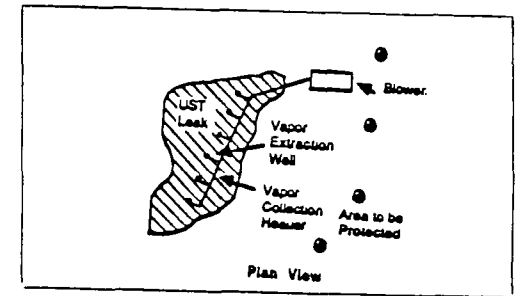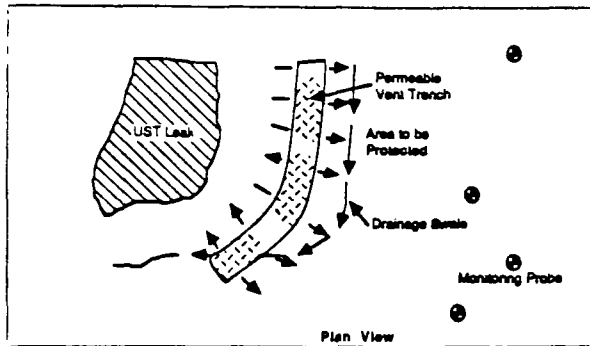DISSOLVED HYDROCARBONS

FUEL TANK

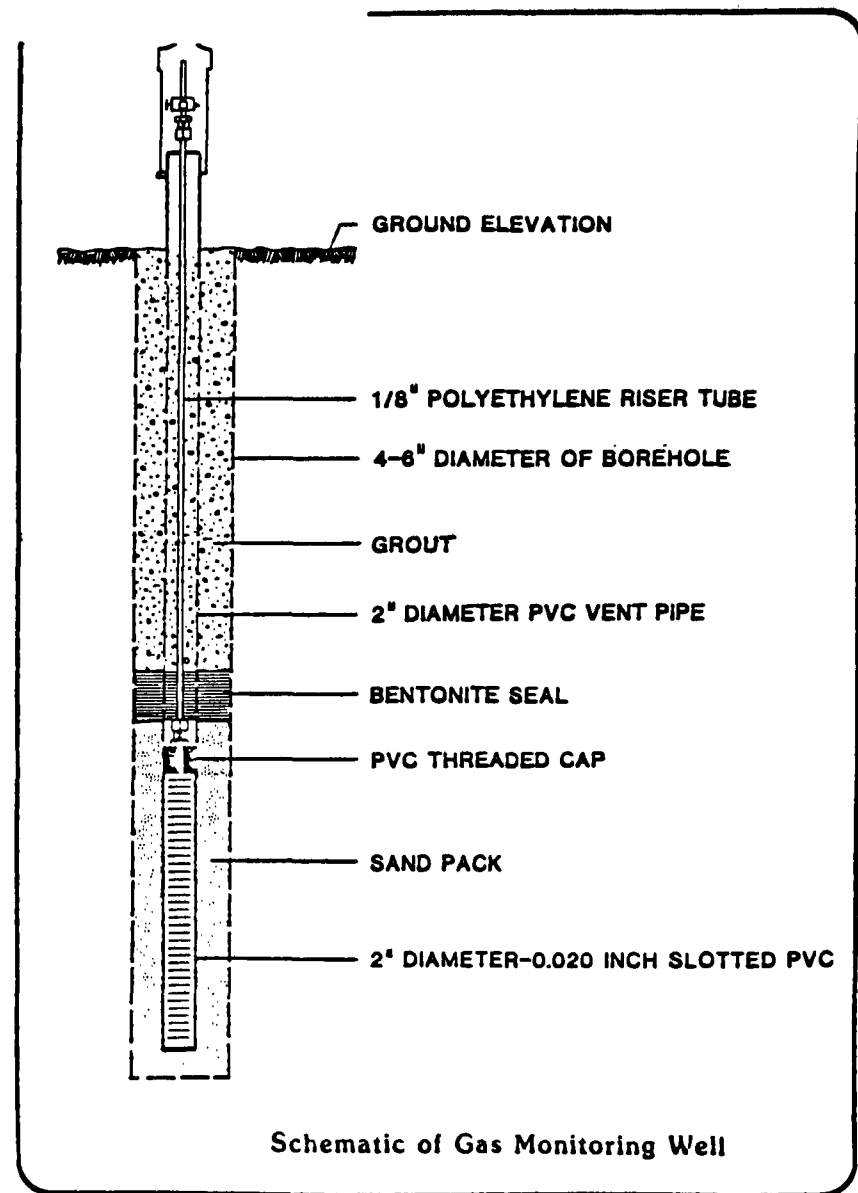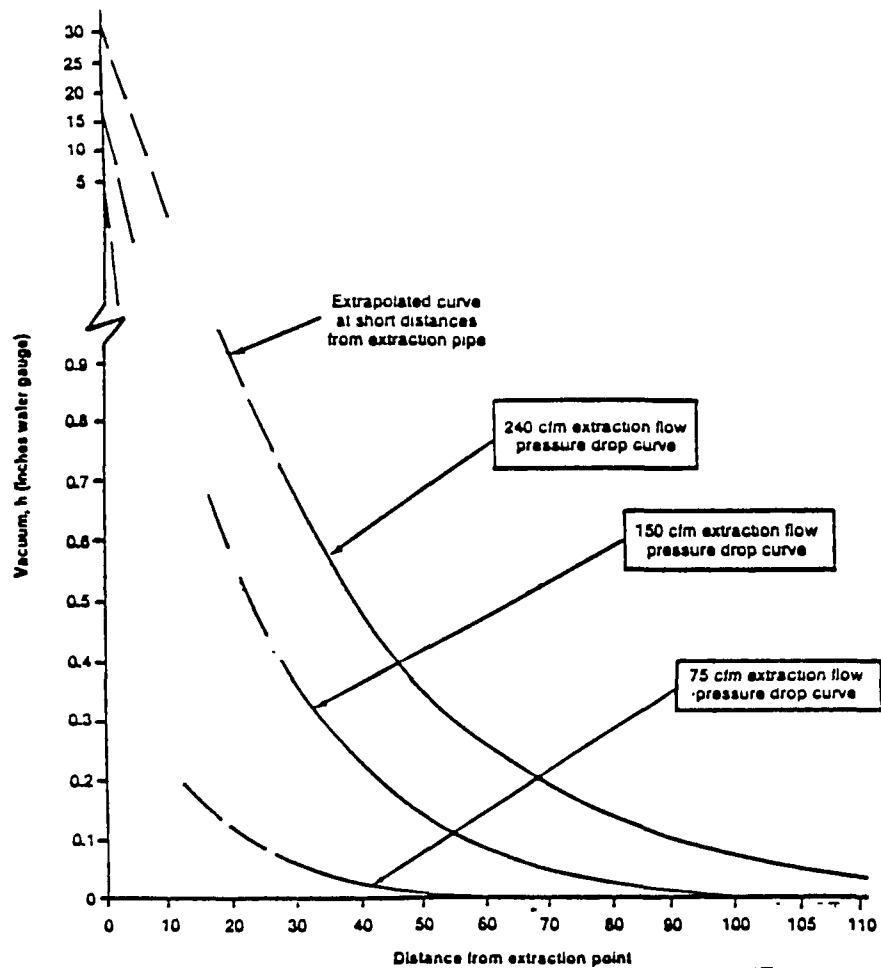## VAPOR PRESSURES OF SOME COMMONLY DETECTED COMPOUNDS EXCEEDING 10.0 mm Hg

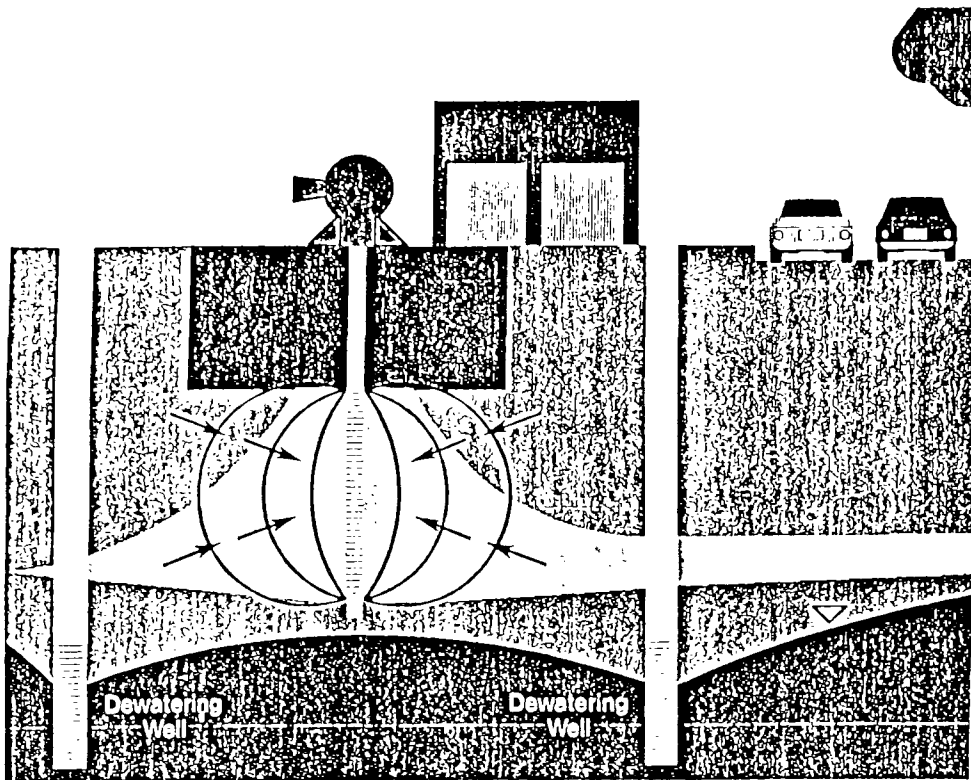| Compound	Vapor Pressure (mm Hg) at 20°C
Vinyl Chloride*	2660
Chloroethane	1000
1,1-dichlorothylene (1,1-DCE)*	591
Methylene Chloride*	362.4
Hydrogen Cyanide (pKa=9)	360 (7°C)
1,2-trans Dichloroethylene	200
1,1-Dichloroethane	180
Chloroform*	150.5
Methyl Ethyl Ketone	100
1,1,1-Trichloroethane (1,1,1-TCA)	96
Benzene*	95.2
Carbon Tetrachloride (CCl₄)*	90
1,2-Dichloroethane*	61
Trichloroethylene (TCE)*	57.9
1,2-Dichloropropane	42
Bis(chloromethyl)ether	30
Toluene	28.4
2-Chloroethyl vinyl ether	26.75
1,3-dichlorpropene	25
1,1,2-Trichloroethane (1,1,2-TCA)	19
Perchloroethylene (PCE)*	14.3
Chlorobenzene	11.8
Dibromoethylene	11.6

* Known or suspected carcinogen

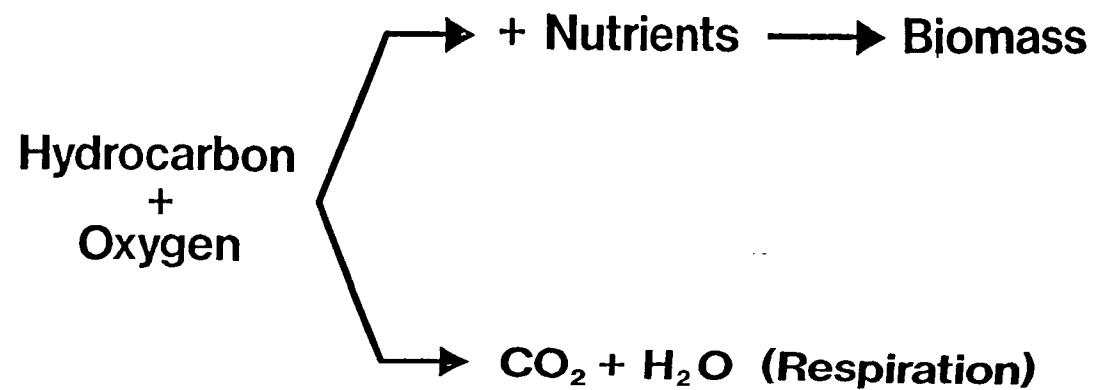## VAPOR PRESSURES OF SOME COMMONLY DETECTED COMPOUNDS LESS THAN 10.0 mm Hg

Compound	Vapor Pressure (mm Hg) at 20°C
Ethylbenzene	7
Triethylamine	7
o-xylene	6.6
1,1,2,2-Tetrachloroethane	5
Styrene	4.5
2-Chlorophenol	2.2
4-Nitrophenol	2.2
1,3-Dichlorobenzene	2.2
1,4-Dichlorobenzene	1.8
1,2-Dichlorobenzene	1.5
2,4,6-Trichlorophenol	1.0
2-Nitrophenol	1.0
Bis(2chloroisopropyl)ether	0.85
Bis(2-chloroethyl)ether	0.71
Phenol	0.53
1,2,4-Trichlorobenzene	0.42
Hexachloroethane	0.4
Hexachlorobutadiene	0.15
Nitrobenzene	0.15
2,4-Dichlorophenol	0.12

Plan View

Permeable Vent Trench

UST Leak

Area to be Protected

Drainage Swale

Monitoring Probe

Section View

4-in. PVC Vent Pipe

4-in. PVC Perforated Collector (Continuous)

Drainage Swale

Monitoring Probe

UST Leak

Natural Ground

Area to be Protected

Natural Ground

Low Ground-Water Table. Bedrock

Gravel or Stone (1/4-in. Min. Size)

3 ft.

Plan View

UST Leak

Area to be Protected

Backfilled Trench

Synthetic Membrane

Monitoring Probe

Section View

Synthetic Membrane

Monitoring Probe

UST Leak

Area to be Protected

Natural Ground

Natural Ground

Backfilled Trench

Plan View

Blower

UST Leak

Vapor Extraction Well

Vapor Collection Header

Area to be Protected

Section View

Control Valve

Gas Collection Header

Natural Ground

UST Leak

Monitoring Probe

Ground water

Vapor Extraction Well

Vacuum, h (inches water gauge) (vertical axis)

30
25
20
15
10
5

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

Extrapolated curve
at short distances
from extraction pipe

240 cfm extraction flow
pressure drop curve

150 cfm extraction flow
pressure drop curve

75 cfm extraction flow
pressure drop curve

0 10 20 30 40 50 60 70 80 90 100 105 110

Distance from extraction point

GROUND ELEVATION

1/8" POLYETHYLENE RISER TUBE

4-6" DIAMETER OF BOREHOLE

GROUT

2" DIAMETER PVC VENT PIPE

BENTONITE SEAL

PVC THREADED CAP

SAND PACK

2" DIAMETER-0.020 INCH SLOTTED PVC

Schematic of Gas Monitoring Well

Aerobic Biodegradation

$$\text{Hydrocarbon} + \text{Oxygen} \longrightarrow \begin{cases} + \text{ Nutrients} \longrightarrow \text{Biomass} \\ \\ CO_2 + H_2O \text{ (Respiration)} \end{cases}$$

Aerobic Biodegradation – Respiration

$$C_6 H_6 + 7\tfrac{1}{2} O_2 \longrightarrow 6\ CO_2 + 3\ H_2O$$

$$3.1\ lb\ O_2 / lb\ C_6 H_6$$

$$C_6 H_{14} + 9\tfrac{1}{2} O_2 \longrightarrow 6\ CO_2 + 7\ H_2O$$
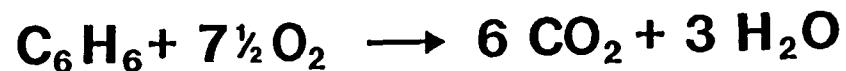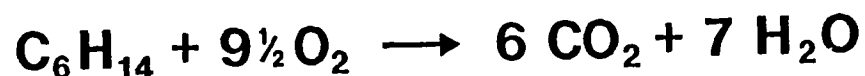
$$3.5_2\ lb\ O_2 / lb\ C_6 H_{14}$$

OXYGEN SUPPLY

	Oxygen Supply
Water	lb Carrier/lb Oxygen
Air Saturated	100,000
Pure Oxygen Saturated	25,000
500 mg/ l Hydrogen Peroxide	5,000
Air	4

Monitoring Point Y In-Situ Respiration Test
December 19, 1988

X Oxygen, k = −.00059/min
O Carbon Dioxide
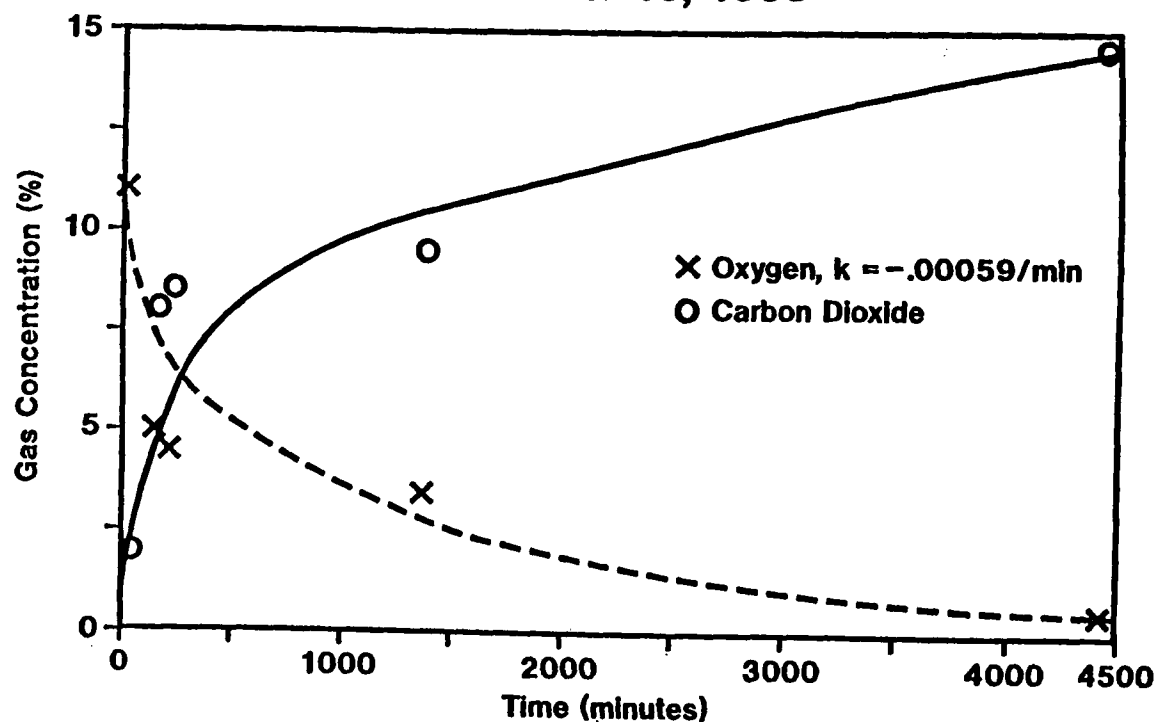
With Nutrients
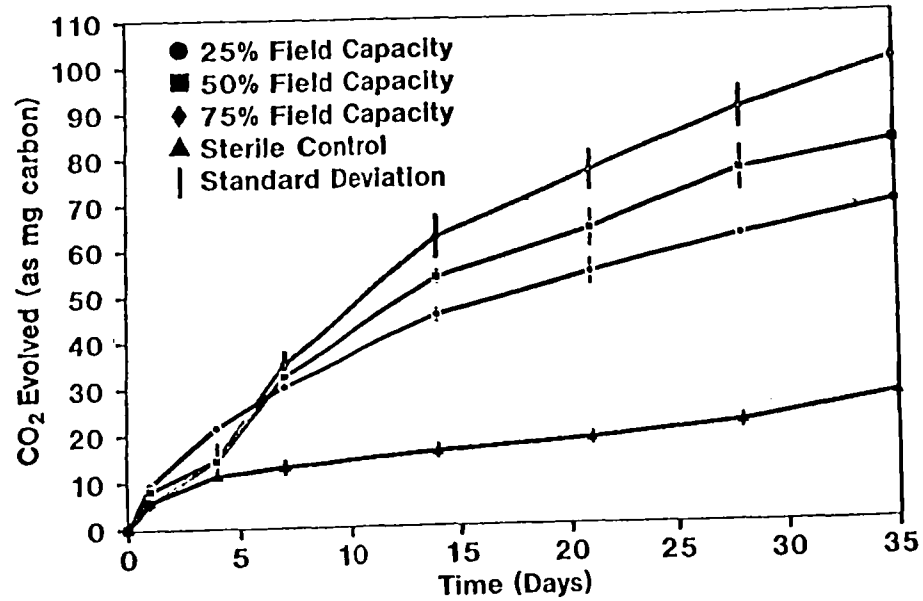
Cumulative Hydrogen Removal
Hill AFB Soil Venting Site
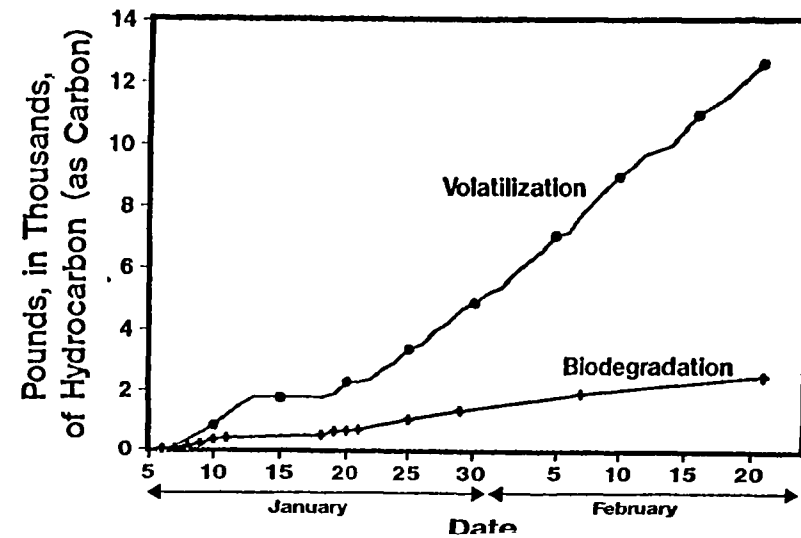
APPLICATIONS & LIMITATIONS OF IN-SITU SOILS REMEDIATION -
BIORECLAMATION

Ronald C. Sims, Professor and Head, Environmental Engineering Division
Utah State University, Logan, Utah

I.   DESCRIPTION OF THE PROCESS

        A.   Bioreclamation systems
                1. Information requirements
                2. Approaches

        B.   Characterization
                1. Waste/site/soil characterization
                2. Determination of containment requirements
                3. Enhancement of microbial processes

II.   APPLICATION OF BIORECLAMATION

        A.   Waste types
                1. Non-halogenated chemicals
                2. Halogenated chemicals

        B.   Treatability studies
                1. Environmental factors
                2. Rate and extent evaluation
                3. Detoxification evaluation

        C.   Full-scale sites
                1. Wood-preserving waste contamination
                2. Petroleum waste contamination
                3. Pesticide contamination
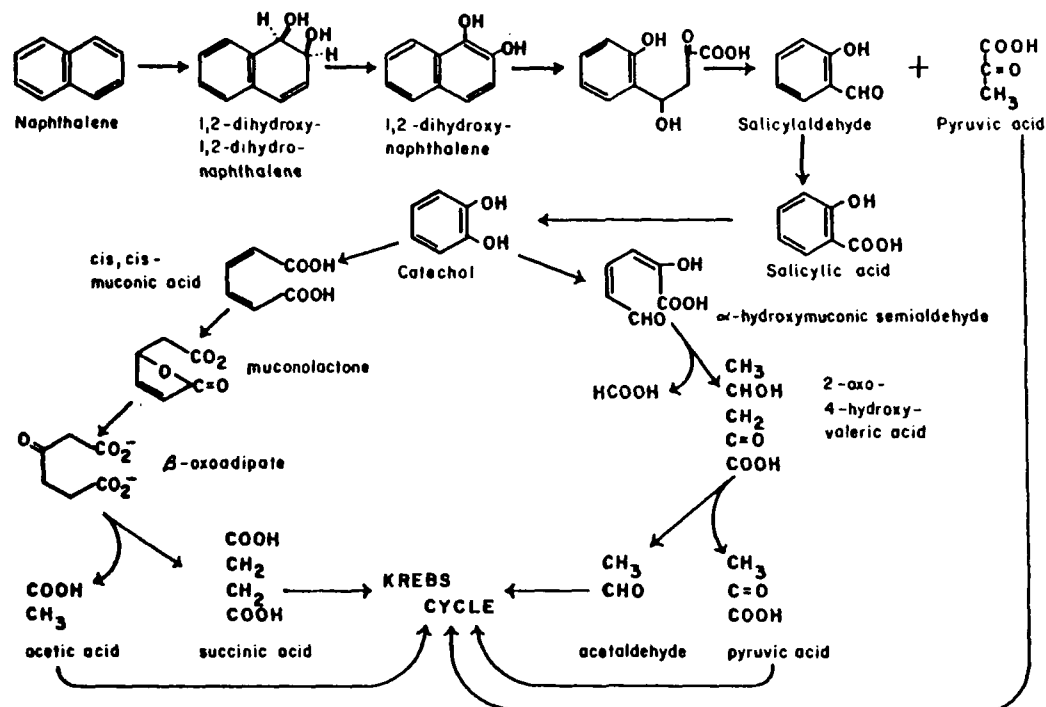   4. PCB contamination

III.   LIMITATIONS OF BIORECLAMATION

        A.   Site-specific aspects
                1. Unsuitable site/waste characteristics
                2. Time required for clean-up
                3. Level of clean-up attainable
                4. Cost of clean-up

        B.   Additional factors
                1. Production of biochemical by-products or intermediates
                2. Mixtures of metals and organic chemicals
                3. Microorganism seeding

BIORECLAMATION

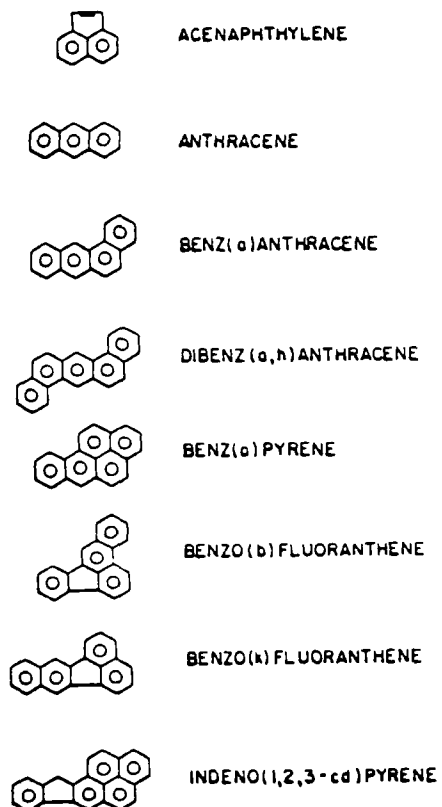Characterization

Containment

Microbial Activity Enhancement

Naphthalene → 1,2-dihydroxy-1,2-dihydro-naphthalene → 1,2-dihydroxy-naphthalene → ... → Salicylaldehyde + Pyruvic acid

Salicylic acid

Catechol

cis,cis-muconic acid

muconolactone

β-oxoadipate

acetic acid   succinic acid   KREBS CYCLE   acetaldehyde   pyruvic acid

α-hydroxymuconic semialdehyde

2-oxo-4-hydroxy-valeric acid

HCOOH

Metabolism of naphthalene by soil bacteria (DEAN-RAYMOND and BARTHA 1975, GIBSON 1976 and GIBSON 1968).

	Site Name	Region	Contaminant
1.	L.A. Clark & Sons	3	1*
2.	American Creosote	4	1
3.	Brown Wood Preserving	4	1
4.	Crosby	4	1
5.	Wilmington	4	1
6.	Burlington Northern	5	1
7.	North Cavalcade Street	6	1
8.	Old Inger	6	2**
9.	Brio Refining	6	2
10.	Joplin	7	1*
11.	Baxter/Union Pacific	8	1
12.	Burlington Northern	8	1
13.	Libby	8	1
14.	ARCO	8	3***
15.	Koppers Company	9	1
16.	J.H. Baxter	9	1

PROPOSED/ACTIVE BIOREMEDIATION SITES

*   Wood Preserving
*** Coal Gasification

POLYNUCLEAR AROMATICS

ACENAPHTHYLENE

ANTHRACENE

BENZ(a)ANTHRACENE

DIBENZ(a,h)ANTHRACENE

BENZ(a)PYRENE

BENZO(b)FLUORANTHENE

BENZO(k)FLUORANTHENE

INDENO(1,2,3-cd)PYRENE

Polynuclear aromatic hydrocarbon compounds

Mean t1/2, days

1000

800

600

400

200

0

■ Synth. mix
■ Oil ref. waste
▨ Creosote waste

3   4   5

Number of rings
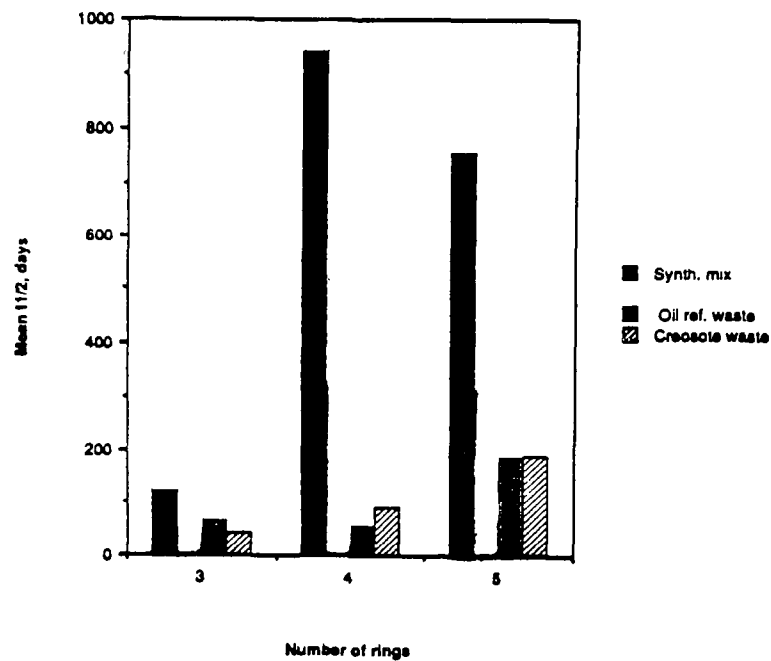
ENHANCEMENT OF
MICROBIAL ACTIVITY

SOIL/SITE ASSIMILATIVE CAPACITY (SSAC)

Techniques

(1) Soil incorporation or mixing
(2) Aeration of the soil
(3) Addition of nutrients
(4) Addition of microbial carbon and
    energy sources
(5) Water addition (irrigation)
(6) Drainage
(7) Runon and Runoff Controls
(8) pH adjustment
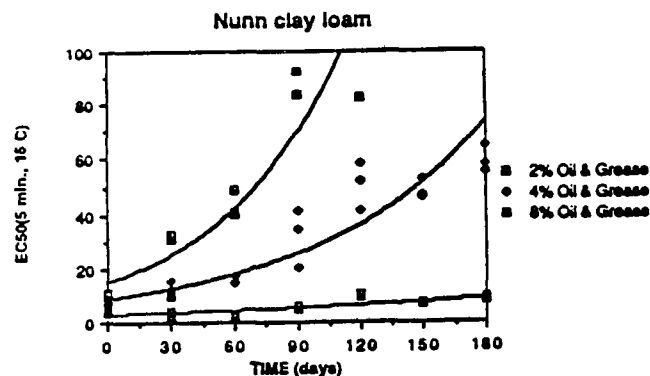
Nunn clay loam

EC50(5 mln., 15 C)

TIME (days)

■ 2% Oil & Grease
♦ 4% Oil & Grease
■ 8% Oil & Grease

Symons, B.D., and R.C. Sims. 1988. Assessing Detoxification of a Complex Hazardous Waste Using the Microtox Bioassay. Arch. Environ. Contam. Toxicol. 17:497-505.

Kidman sandy loam

EC50(5 mln, 15 C)

TIME (days)

▢ 2% Oil & Grease
♦ 4% Oil & Grease
■ 8% Oil & Grease
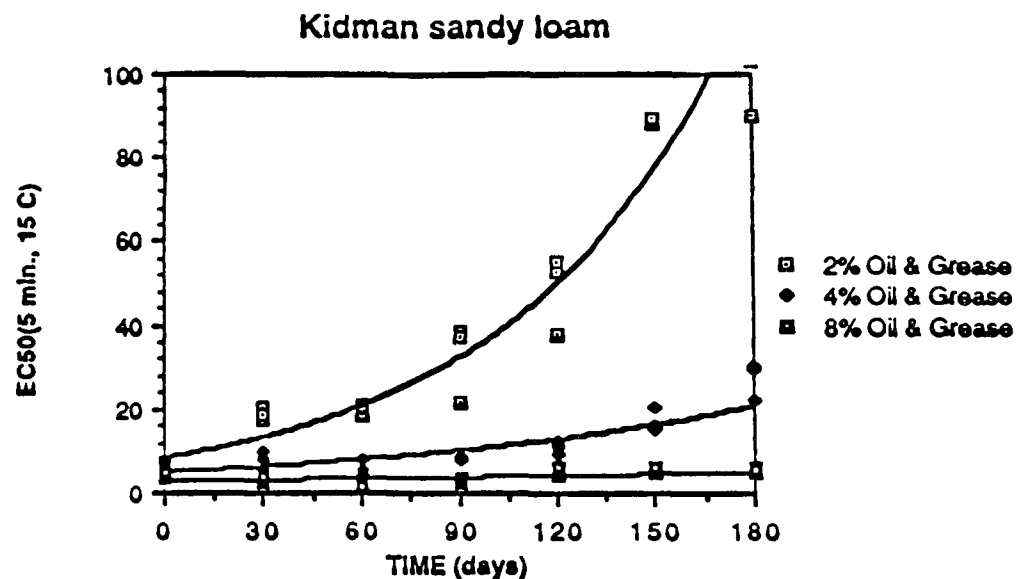
Symons, B.D., and R.C. Sims. 1988. Assessing Detoxification of a Complex Hazardous Waste Using the Microtox Bioassay. Arch. Environ. Contam. Toxicol. 17:497-505.

DEGRADATION IN CLAY LOAM SOIL

2 % Oil and Grease

Compound	C_o µg/g	$T_{1/2}$ days	R^2	95% Confidence Interval ($T_{1/2}$) (days)	
				Lower	Upper
Fluoranthene	351	15	0.966	13	18
Pyrene	283	32	0.884	26	41
Benzo(a)anthracene	86	139	0.397	87	347
Benzo(g,h,i)perylene	8	1661	0.006	139	ND
Indenopyrene	5	69	0.559	43	139

C_o = Initial Concentration

$T_{1/2}$ = Half-Life (first order kinetics)

ACCLIMATION OF SOIL TO COMPLEX FOSSIL FUEL WASTE

PNA Constituent	Unacclimated Soil Reduction in 40 days (%)	Acclimated Soil Reduction in 22 days (5)
Naphthalene	90	100
Phenanthrene	70	83
Anthracene	58	99
Fluoranthene	51	82
Pyrene	47	86
Benz(a)anthracene	42	70
Chrysene	25	61
Benz(a)pyrene	40	50

WAYS TO MAXIMIZE AVAILABLE SOIL OXYGEN

- Prevent Water Saturation
- Presence of Sand, Loam (Not Hvy Clay)
- Moderate Tilling
- Avoid Compaction
- Controlled Waste Loading

EFFECT OF SOIL MOISTURE ON PAH DEGRADATION

Moisture (Field Capacity)	Half-Life (Days)		
	Anthracene	Phenanthrene	Fluoranthene
20 - 40	43	61	559
60 - 80	37	54	231

EFFECT OF MANURE AND pH AMENDMENTS ON PAH DEGRADATION IN A COMPLEX WASTE INCORPORATED INTO SOIL

PAH Compound	Half-Life In Waste:Soil Mixture (Days)	
	Without Amendments	With Amendments
Acenaphthylene	78	14
Anthracene	28	17
Phenanthrene	69	23
Fluoranthene	104	29
Benz(a)antrhacene	123	52
Benz(a)pyrene	91	69
Dibenz(a,h)anthracene	179	70
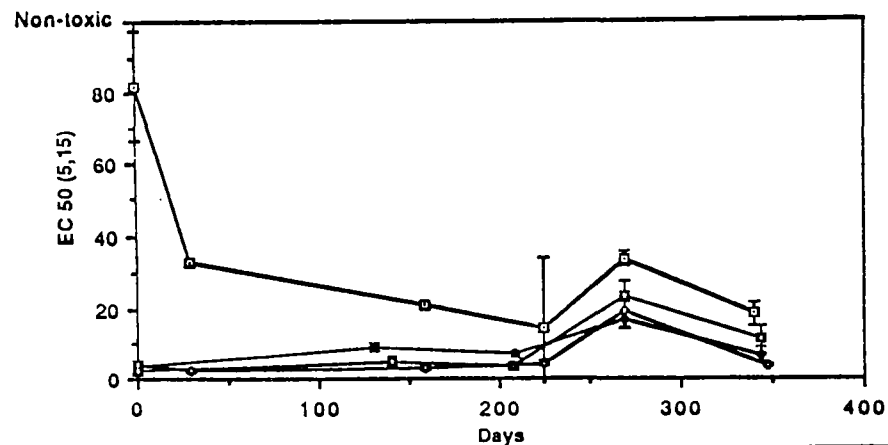
Aprill,W. et al. 1989. Assessing Detoxification and Degradation of Wood Preserving and Petroleum Wastes in Contaminated Soils. Waste Management & Research (In Press).

TEMPERATURE EFFECT ON DEGRADATION RATE

Compound	Half-Life (days)[a]		
	10 C	20 C	30 C
Fluorene	60 (50-71)	47 (42-53)	32 (29 37)
Phenanthrene	200 (160-240)	<60	<60
Anthracene	460 (320-770)	260 (190-420)	200 (170-290)
Pyrene	[f]	1900 (1100-8100)	210 (150-370)
Benzo(a)pyrene	530 (300-2230)	290 (170-660)	220 (160-380)

a Half-life (95% confidence interval)
f Least squares slopes = zero with 95% confidence

Coover, M.P., and R.C. Sims. 1987. The Effect of Temperature on Polycyclic Aromatic Hydrocarbon Persistence in an Unacclimated Agricultural Soil. Haz. Waste & Haz. Mat. Vo. 4(1):69-82.

(^{14}C) 7,12-DIMETHYLBENZ(a)ANTHRACENE AND TRANSFORMATION PRODUCTS IN A SANDY LOAM SOIL

Time (days)	^{14}C in each fraction (%)				
	Soil Extract		Residue	CO_2	Total
	Parent Compound	Transformation Products			
0	62 (69)	4 (6)	12 (13)	0 (0)	78 (88)
14	26	43	16	0	85
28	20 (60)	53 (11)	17 (16)	0 (0)	90 (87)

Poisoned (control) data in parentheses

Park, K.S., et al. 1988. Biological Transformation and Detoxification of 7,12-Dimethylbenz(a)anthracene in Soil Systems. J. Wat. Pollut. Control Fed. Vol. 60(10):1822-1825.

FIELD STUDY SITE PROFILE
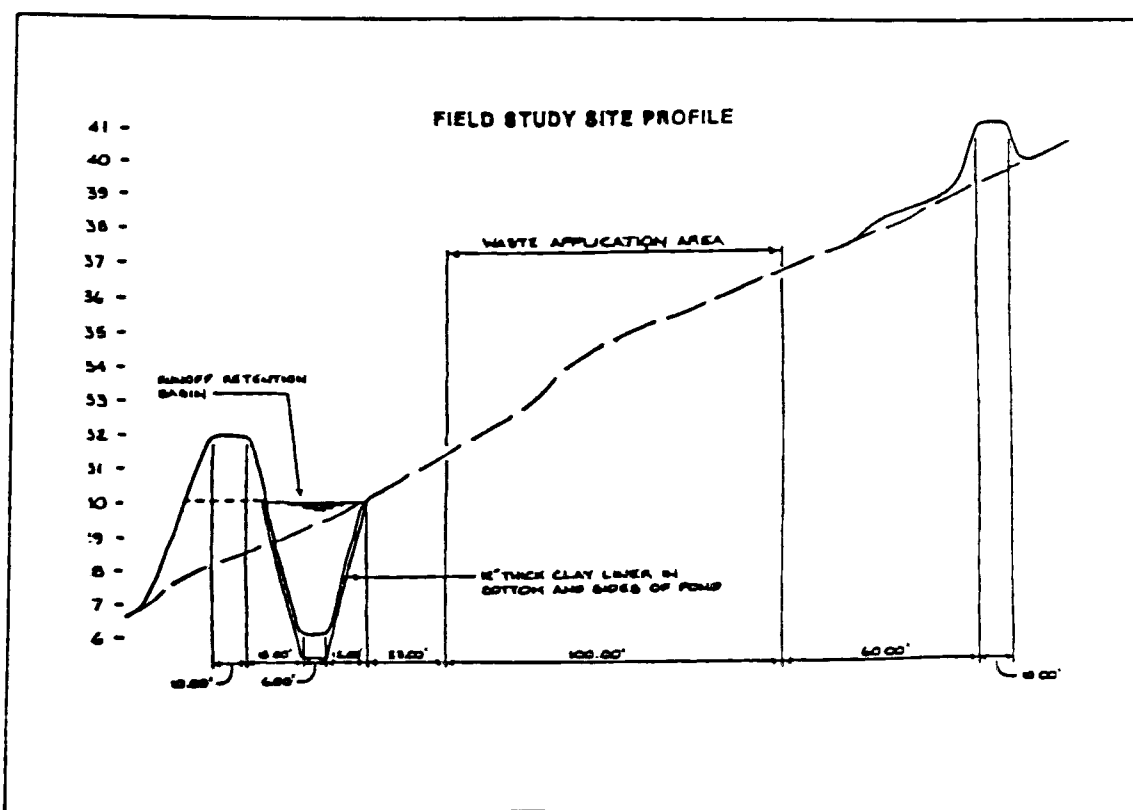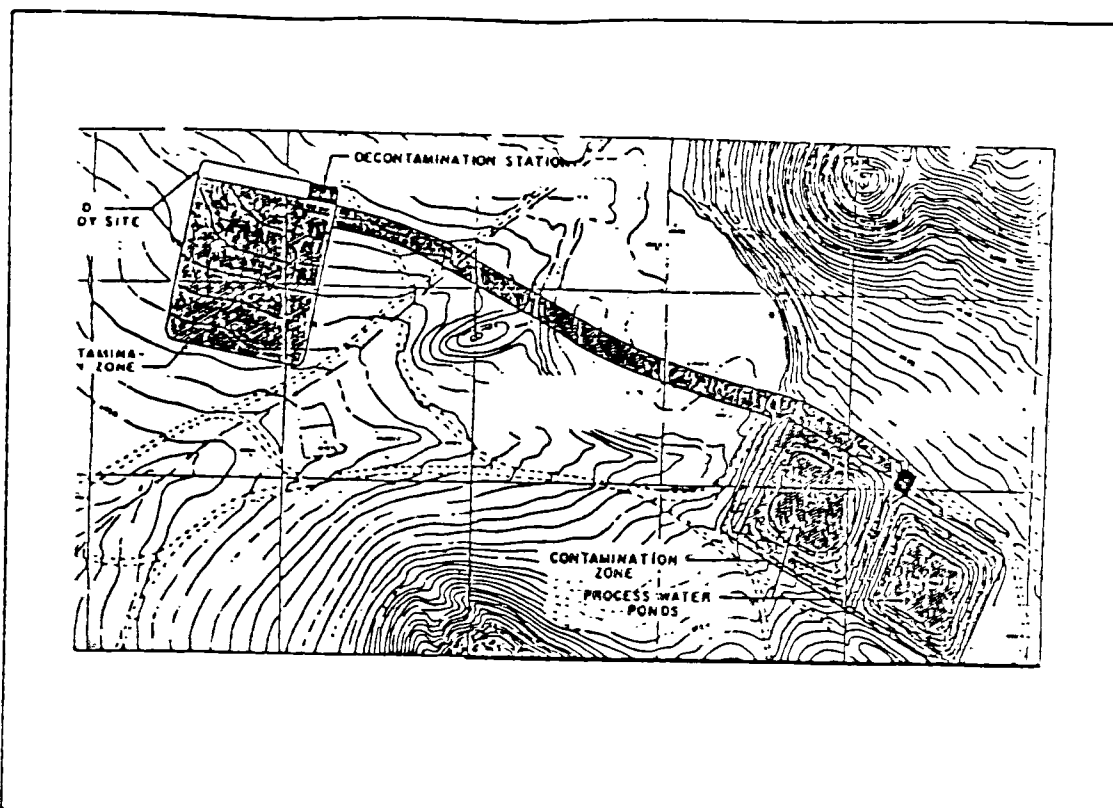
FIELD RESULTS FOR SOIL SAMPLES

Compound	C_o (µg/g)			91 days (µg/g)		
	AVG	SD	CV (%)	AVG	SD	CV(%)
Naphthalene	186	68	37	3	1.8	61
Acenaphthene	729	276	38	1	1.8	157
Phenanthrene	78	28	36	2.6	0.6	23
Benz(a) anthracene	86	42	49	2	0.8	38
Dibenz(a,h) anthracene	52	36	69	ND	--	--

C_o = Initial Soil Concentration

PERFORMANCE EVALUATION-- MONITORING

● Soil Cores

● Soil-Pore Liquid

● Ground Water

● Runoff Water

● Air

MONITORING TECHNIQUES

Waste Analyses

VOLATILIZATION/
PHOTODEGRADATION

APPLIED WASTE

Soil
Cores

Lysimeters

Wells

DEGRADATION/
TRANSFORMATION/
IMMOBILIZATION

Soil Pore
Liquid

LEACHATE

Groundwater

a. API Separator Sludge

b. Slop Oil Emulsion Solids

c. Creosote Sludge

d. PCP-Creosote Mixed Sludge

Mutagenic Ratio

mg soil/plate
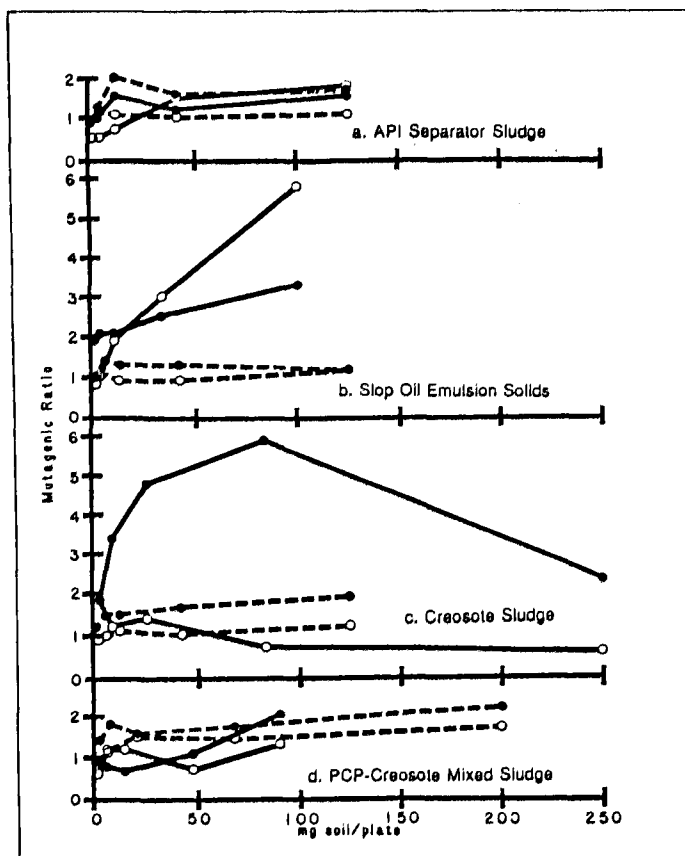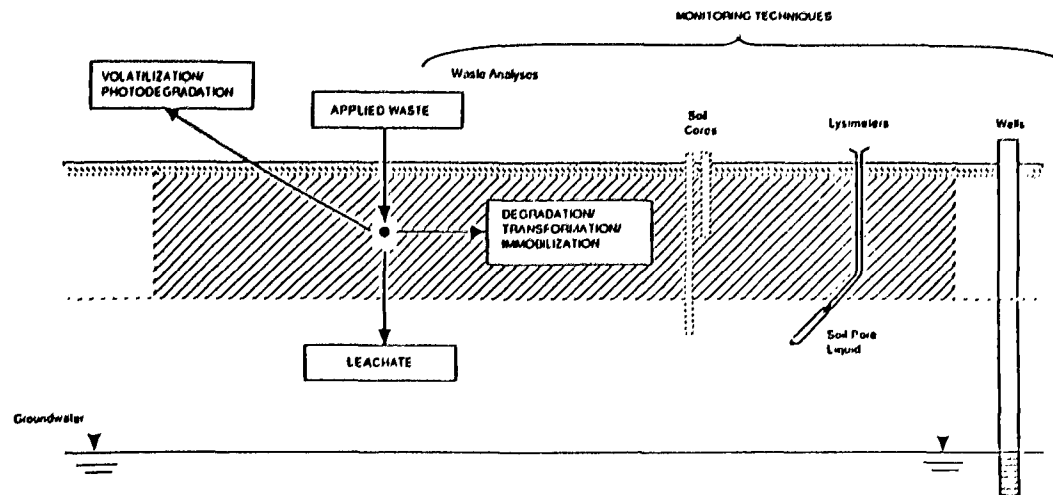
COSTS

Scope	Current Dollars
● Laboratory Treatability Study	-- 50,000-100,000
● *Pilot Scale Study*	-- 150,000-200,000
● Full Scale Study	-- 400,000 +

APPLICATION AND LIMITATIONS OF IN-SITU SOILS REMEDIATION - CONTAMINANT IMMOBILIZATION

Ronald C. Sims, Professor and Head, Environmental Engineering Division
Utah State University, Logan, Utah

I. DESCRIPTION OF PROCESS

    A. Characterization
        1. Sorption
        2. Ion exchange
        3. Precipitation

    B. Site characteristics
        1. Waste properties
        2. Soil properties
        3. Climate

II. APPLICATIONS OF IMMOBILIZATION

    A. Sorption
        1. Control of soil moisture
        2. Addition of agricultural byproducts
        3. Addition of activated carbon
        4. Chelation

    B. Ion exchange
        1. Addition of clays
        2. Addition of synthetic resins
        3. Addition of zeolites

    C. Precipitation
        1. Precipitation as sulfides
        2. Precipitation as carbonates, phosphates, and hydroxides

III. LIMITATIONS OF IMMOBILIZATION

    A. Characteristics limiting processes
        1. Site factors
        2. Soil factors
        3. Waste factors

    B. Potential reversibility of reactions
        1. Environmental factors
        2. Chemical factors
        3. Microbiological factors

CONTAMINANT IMMOBILIZATION

Sorption

Ion Exchange

Precipitation

SORPTION

$S = KC^N$

S = Amount of constituent sorbed per unit dry
weight of soil
K, N = Constants
C = Solution phase equilibrium concentration

IMMOBILIZATION TECHNIQUES

REVIEW OF IN-PLACE TREATMENT TECHNIQUES FOR
CONTAMINATED SURFACE SOILS. 1984
EPA-540/2-84-003a,b. Vols. 1 and 2.
R.S. Sims, D.L. Sorensen, J.L. Sims, J.E. McLean,
R.H. Mahmood, and R.R. Dupont.

IMMOBILIZATION TECHNIQUES

HANDBOOK ON IN SITU TREATMENT OF HAZARDOUS
WASTES. 1989. DRAFT. U.S. EPA (PEI Associates,
Inc. and Univ. of Cincinnati). To Be Published
Fall, 1989.
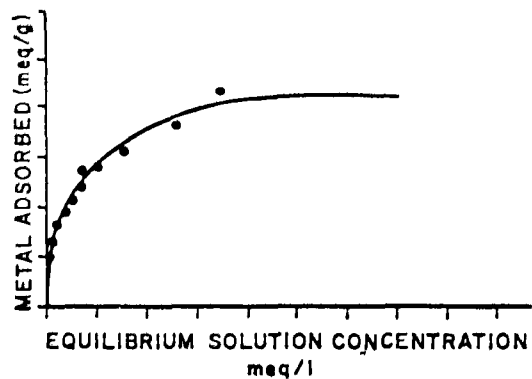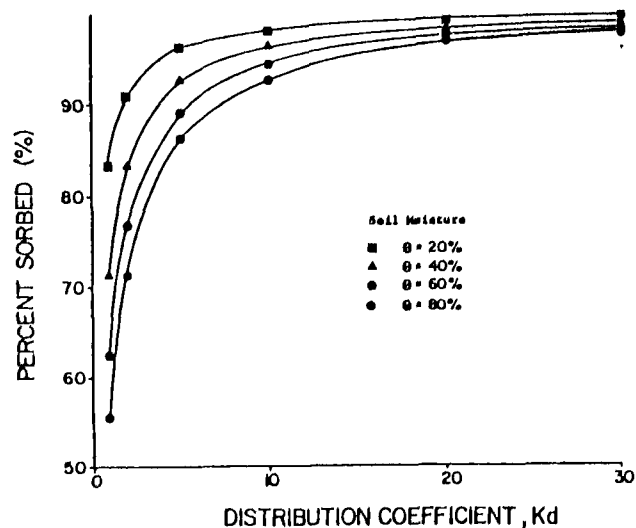
Typical adsorption isotherm for metals and soil.

IMMOBILIZATION TECHNIQUES

Sorption

    Soil moisture control

    Agricultural product

    Activated carbon

IMMOBILIZATION TECHNIQUES

Ion Exchange

    Metal + Clay-Calcium ----- Calcium + Clay-Metal

IMMOBILIZATION TECHNIQUES

Ion Exchange

    Clay

    Synthetic Resins

    Zeolites

IMMOBILIZATION TECHNIQUES

Precipitation

    Sulfides

    Phosphates

    Hydroxides

    Carbonates

IMMOBILIZATION OF METALS

pH Effect

    As pH decreases, the number of negatively
    charged sites decreases due to competition
    from H^+ and Al^{+3} ions

IMMOBILIZATION OF METALS

Iron and Manganese Oxides

    Play a prinicple role in metal retention in soil

    Below pH 6 oxides dissolve releasing sorbed metal
    ions into solution
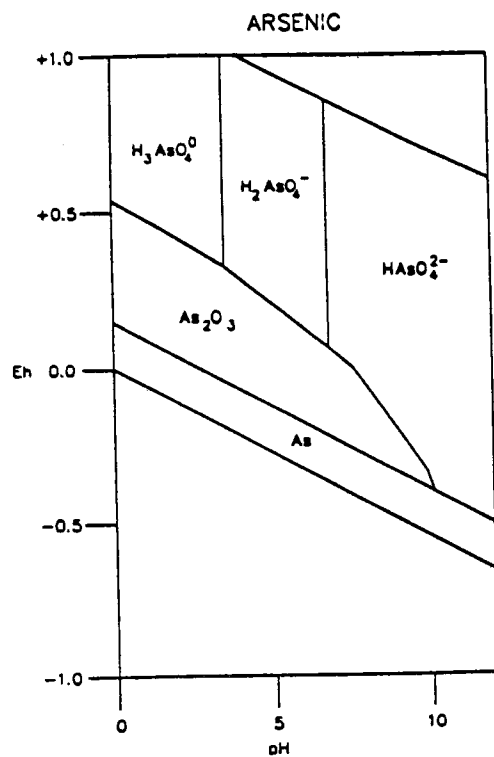
ARSENIC

Eh, pH diagram with species: $H_3AsO_4^0$, $H_2AsO_4^-$, $HAsO_4^{2-}$, As_2O_3, As

CHROMIUM

Eh, pH diagram with species: $HCrO_4^-$, CrO_4^{2-}, Cr^{3+}, Cr_2O_3 $(Cr(OH)_3)$

SELENIUM

Eh, pH diagram with species: $HSeO_4^-$, H_2SeO_3, SeO_4^{2-}, $HSeO_3^-$, SeO_3^{2-}, Se

Dragun, J. 1988. The Soil Chemistry of Hazardous Materials.
Hazardous Materials Control Research Institute, Silv er Spring,
MD
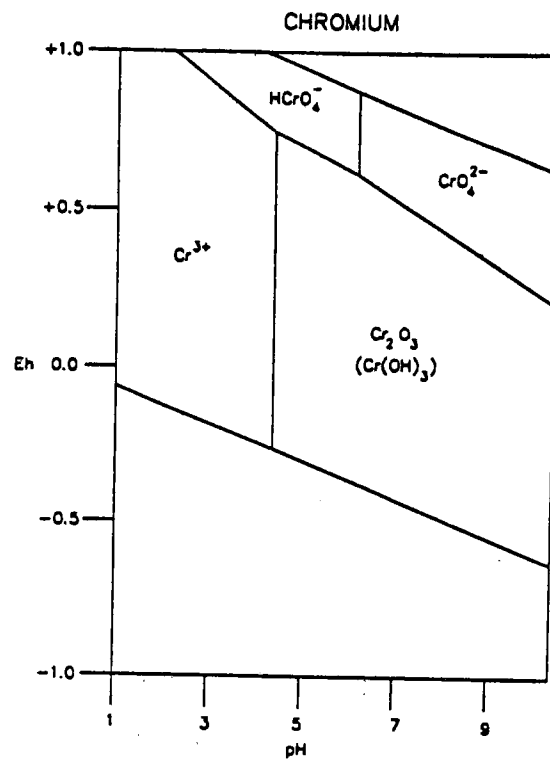
Dragun, J. 1988. The Soil Chemistry of Hazardous Materials.
Hazardous Materials Control Research Institute, Silv er Spring,
MD
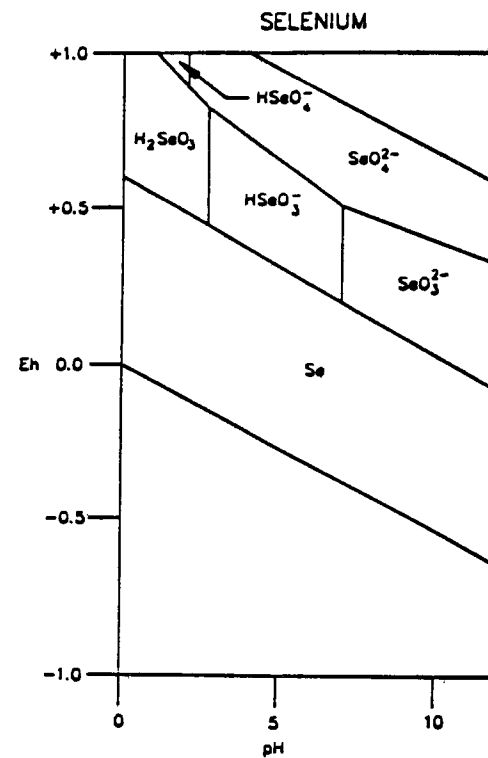
Dragun, J. 1988. The Soil Chemistry of Hazardous Materials.
Hazardous Materials Control Research Institute, Silv er Spring,
MD

APPLICATIONS & LIMITATION OF IN-SITU SOILS REMEDIATION - CONTAMINANT MOBILIZATION (SOILS FLUSHING)

Ronald C. Sims, Professor and Head, Environmental Engineering Division
Utah State University, Logan, Utah

I.   DESCRIPTION OF THE PROCESS

    A.   Types of flushing solutions
        1. Aqueous solutions
        2. Petroluem recovery solutions

    B.   Properties of bulk fluids that hinder soil flushing
        1. Low water solubility
        2. High interfacial tension
        3. High mobility ratio

II.   APPLICATIONS OF SOILS FLUSHING

    A.   Treatment train concept
        1. Product removal
        2. In situ soil flushing
        3. In situ bioreclamation of residual contamination

    B.   Applications for bulk fluids
        1. Surfactants
        2. Alkaline/polymer flooding

III. LIMITATIONS OF SOILS FLUSHING

    A.   Potential impact on soils and the environment
        1. Soil permeability
        2. Toxicity to aquatic organisms

    B.   Limitations of methods for bulk liquids
        1. Aqueous solutions
        2. Petroleum recovery methods

    C.   Treatment of fluids withdrawn from subsurface
        1. Adverse effects on reuse
        2. Above-ground treatment processes required

CONTAMINANT MOBILIZATION - SOIL FLUSHING

Water

Acidic Solutions

Basic Solutions

Surfactants

Chelation Solutions

APPLICATIONS FOR BULK SOLUTIONS

In-Situ Solvent Flushing

Hot Water or Steam

Carbon Dioxide

Surfactants

Alkaline Solutions

Polymer Solutions

Schematics of an electrode recycle system.
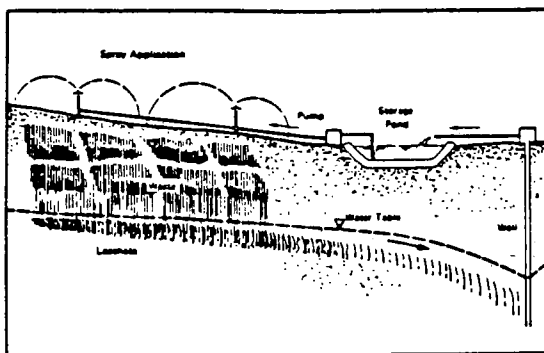
Sims, et al. 1984. Review of In-Place Treatment
Techniques for Surface Contaminated Soils. EPA-540/2-
84-003a,b. Vols. 1 and 2.

BULK FLUIDS

Low Water Solubility

High Interfacial Tension

Poor Relative Permeability

RELATIVE PERMEABILITY

M = [Kd/Ud] / [Ko/Uo]

M = Mobility Ratio

Kd = Fluid Permeability

Ko = Oil Permeability

Ud = Viscosity of Fluid

Uo = Viscosity of Oil

PNA adsorption isotherm in methanol and Ada, Oklahoma soil.

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Sims, R.C., J.L. Sims, D.K. Sorensen, J.E. McLean, R.J. Mahmood, and J.J. Jurinak. 1986. Contaminated Surface Soils In-Place Treatment Techniques. Noyes Publications, Park Ridge, New Jersey. 536pp.

Woodward, R.E. 1988. Bioremediation Feasibility Studies for Hazardous Waste. Pollution Engineering 20(7): 102-103.

U.S. EPA. 1986. Permit Guidance Manual for Hazardous Waste Land Treatment Demonstrations. Office of Solid Waste, Washington, D.C. EPA-530/SW-86-032. February.

Martin, J.P., R.C. Sims, and J.E. Matthews. 1986. Review and Evaluation of Current Design and Management Practices for Land Treatment Units Receiving Petroleum Wastes. Hazardous Wastes and Hazardous Materials, 3(3):261-280.

U.S. EPA. 1981. A Survey of Existing Hazardous Waste Land Treatment Facilities in the United States. U.S. EPA, Contract No. 68-03-2943.

Sims, R.C. 1986. Loading Rates and Frequencies for Land Treatment Systems. In: Land Treatment: A Hazardous Waste Management Alternative (R.C. Loehr and J.F. Malina, Eds. Water Resources Symposium Number Thirteen, Center for Research in Water Resources, College of Engineering, The University of Texas at Austin.

Loehr, R.C., J.H. Martin, and E.F. Neuhauser. 1983. Disposal of Oily Wastes by Land Treatment. Report to 38th Annual Purdue Industrial Waste Conference, Purdue University, West Lafayette, Indiana, May.

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K.W. Brown and L.E. Duel. 1982. An Evaluation of Subsurface Conditions at Refinery Landfarm Sites. Prepared for the American Petroleum Institute and the U.S. EPA, Grant No. CR-807868.

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Mahmood, R.J., and R.C. Sims. 1986. Mobility of Organics in Land Treatment Systems. Journal of Environmental Engineering 112(2):236-245.

Overcash, M.R., K.W. Brown, and G.B. Evans. 1987. Hazardous Waste Land Treatment: A Technology and Regulatory Assessment. Prepared for the U.S. Department of Energy by Argonne National Laboratory, September 22.

U.S. EPA. 1983. Hazardous Waste Land Treatment. Revised Edition. SW-874. Office of Solid Waste and Emergency Response, U.S. EPA, Washington, D.C.

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APPLICATIONS & LIMITATION OF AQUIFER RESTORATION-PRODUCT REMOVAL

Ronald C. Sims, Professor and Head, Environmental Engineering Division
Utah State University, Logan, Utah

I.   DESCRIPTION OF THE PROCESS

   A   Characterization of product
       1. Location
       2. Distribution

   B.   Product pumping systems
       1. Light NAPLs
           a. dual-pump systems
           b. floating-filter pumps
           c. collector trenches
           d. surface oil/water separators
       2. Dense NAPLs
           a. single wells
           b. subsurface drainlines

II.   APPLICATIONS OF PRODUCT REMOVAL

   A   Site characteristics
       1. Location
       2. Distribution

   B.   Product pumping systems
       1. Light NAPLs
           a. dual-pumping systems
           b. floating-filter pumps
           c. collector trenches
           d. surface oil/water separators
       2. Dense NAPLs
           a. single wells
           b. subsurface drainlines

III.   LIMITATIONS OF PRODUCT REMOVAL

   A   Site characteristics
       1. Three dimensional distribution
       2. Complex geological structure

   B.   NAPL contamination of clean areas
       1. LNAPL residual saturation
       2. DNAPL residual saturation

AQUIFER RESTORATION

Product Removal

Pump and Treat

Biorestoration

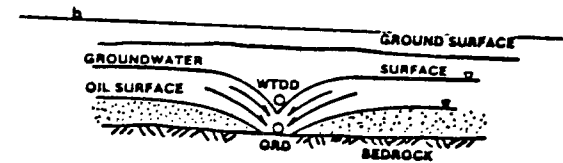Non-Aqueous Phase Liquid (NAPL)
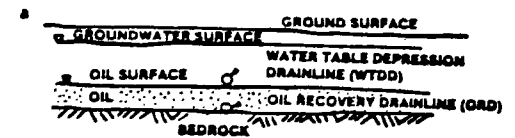
Light Non-Aqueous Phase Liquid (LNAPL)

Oil

Pentachlorophenol

Dense Non-Aqueous Phase Liquid (DNAPL)

Creosote

Methylene Chloride

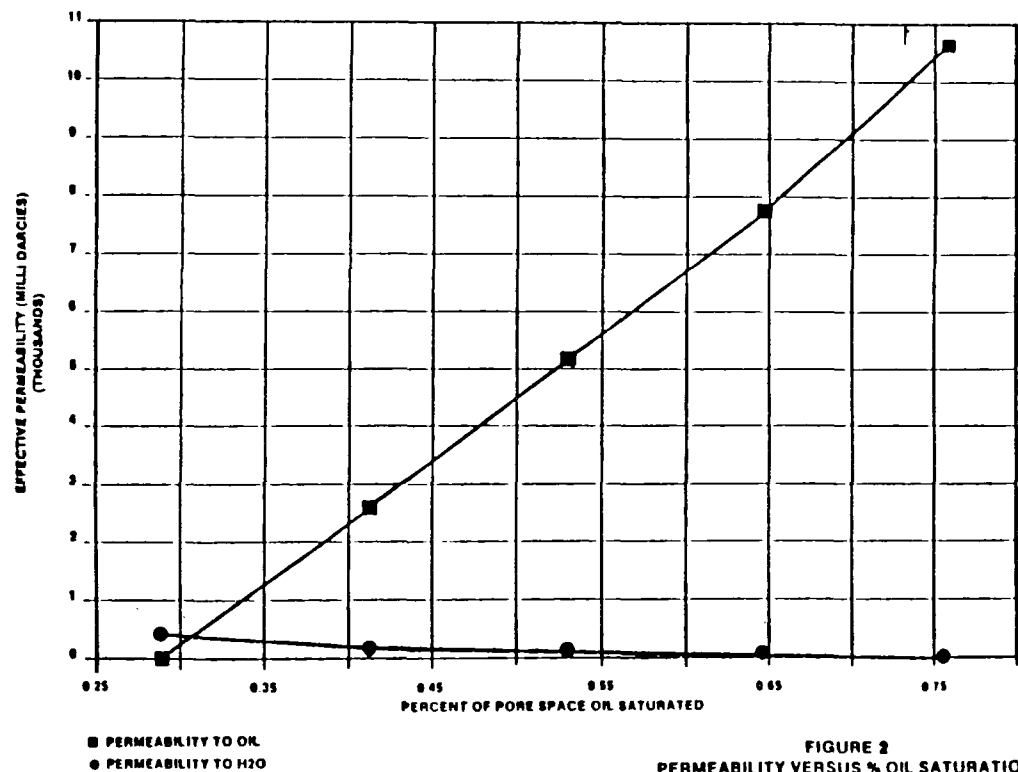PRODUCT REMOVAL

Product Characterization

Product Location

Pumping Systems

Water Table
Depression

Water Table
Depression
Pump Controls

Clean
Water
Output

Oil-Contaminated Soil

Perforated
Well Casing

Floating
Oil/Water
Filter

Probe

Water Table
Depression Pump

Oil/Water
Separation

Scavenger
Control and
Pump Assembly

Oil-Recovery
Tank

Oil Layer

Water Table

Siphon Breaker of
1/4-in. Pipe

Vent

2-in.-diameter Pipe

250-Gallon or Larger Tank

2-in.-diameter Nipple

Separated Gasoline

Separated Water

Spigot for Product Removal
(Closed During Operation)

Separated Water Exit

Pipe 2 to 4 in. from
Bottom of Tank

Spigot for Tank Drainage or for
Pump Cooling Water

a

GROUND SURFACE
GROUNDWATER SURFACE
WATER TABLE DEPRESSION
DRAINLINE (WTDD)
OIL SURFACE
OIL
OIL RECOVERY DRAINLINE (ORD)
BEDROCK

b

GROUND SURFACE
GROUNDWATER
SURFACE
OIL SURFACE
WTDD
ORD
BEDROCK

c

GROUND SURFACE
GROUNDWATER
SURFACE
WTDD
OIL SURFACE
ORD
BEDROCK

d

GROUND SURFACE
GROUNDWATER
SURFACE
WTDD
OIL SURFACE
ORD
BEDROCK

FIGURE 2
PERMEABILITY VERSUS % OIL SATURATION

■ PERMEABILITY TO OIL
● PERMEABILITY TO H2O

Session 6: Ronald C. Sims
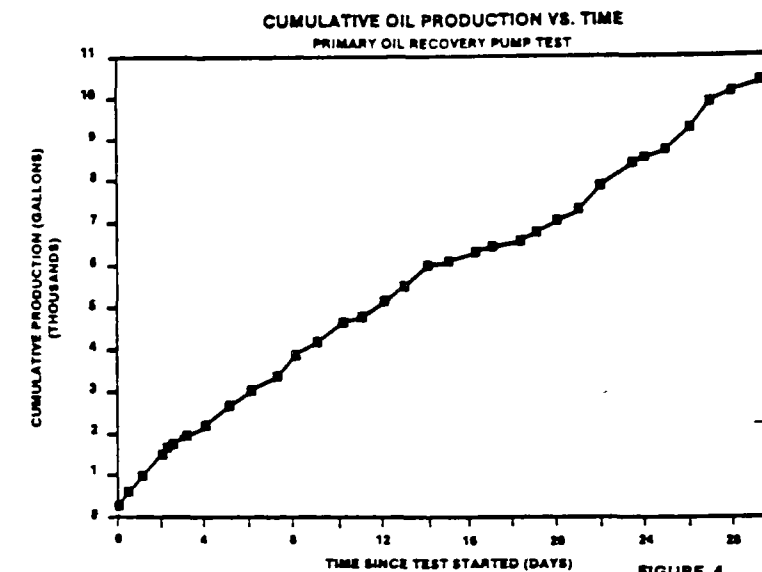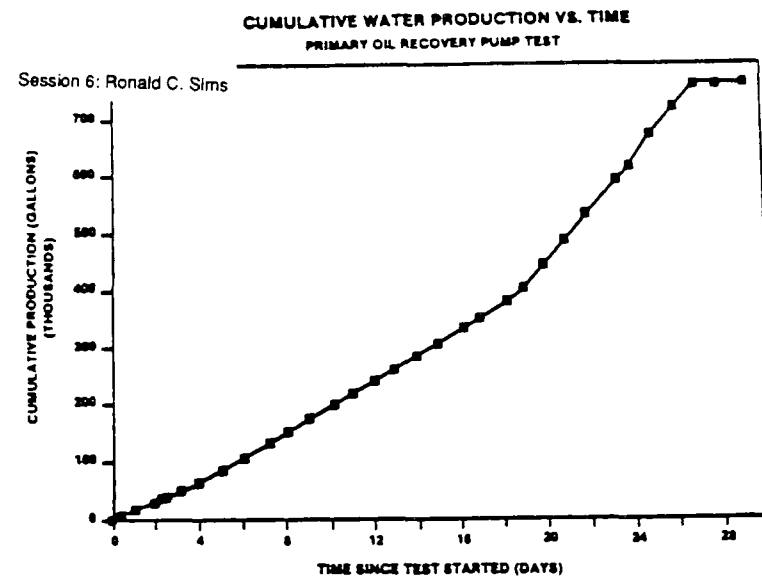
FIGURE 4
CUMULATIVE OIL
AND WATER PRODUCTION

APPLICATIONS & LIMITATIONS OF AQUIFER RESTORATION-PUMP AND TREAT

Ronald C. Sims, Professor and Head, Environmental Engineering Division
Utah State University, Logan, Utah

I.   DESCRIPTION OF THE PROCESS

    A.   Characterization of pumping systems
        1. Extraction wells
        2. Extraction and injection wells

    B.   Characterization of treatment systems
        1. Physical processes
        2. Biological processes
        3. Chemical processes

II. APPLICATIONS OF PUMP AND TREAT TECHNOLOGY

    A.   Applications of pumping systems
        1. Site characteristics
        2. Waste location and pumping system
           a. wellpoint systems and suction wells
           b. deep wells and ejector wells
        3. Pulsed pumping
        4. Well repositioning

    B.   Application of treatment systems
        1. Gasoline and volatile organics
        2. Non-volatile organics
        3. Inorganics

III. LIMITATIONS OF PUMP AND TREAT TECHNOLOGY

    A.   Transport processes in the subsurface
        1. Diffusion
        2. Hydrodynamic isolation
        3. Sorption-desorption
        4. Liquid-liquid partitioning

    B.   Geologically complex aquifers

PUMP AND TREAT

Pumping Systems

Treatment Systems

HYDRAULIC CONTAINMENT

The migration of a plume away from its source area can often be prevented by capturing the plume with a purge well. The well must pump hard enough to overcome regional flow in the aquifer. The flow from purge wells that is necessary to capture a plume depends on the hydraulic permeability of the aquifer, the regional hydraulic gradient, and the size of the source area.

CONTROL OF HYDROLOGY ON THE RATE OF REMEDIATION

Seepage Velocity α Hydraulic Permeability x Hydraulic Gradient

Hydraulic permeability is an intrinsic property of the subsurface. It is difficult or impossible to improve it, but it is easily degraded.

The hydraulic gradient is controlled by the amount of water available for pumping, and by the difference in elevation between the source area and the land surface.

HYDRAULIC CONTAINMENT OF SUBSURFACE REMEDIATION

Hydraulic containment of a source area can be achieved if more water is extracted than injected. If water is recirculated through the source area, a portion of the extracted water can be discharged to a sewer of surface drainage, resulting in a net extraction of water across the entire system.
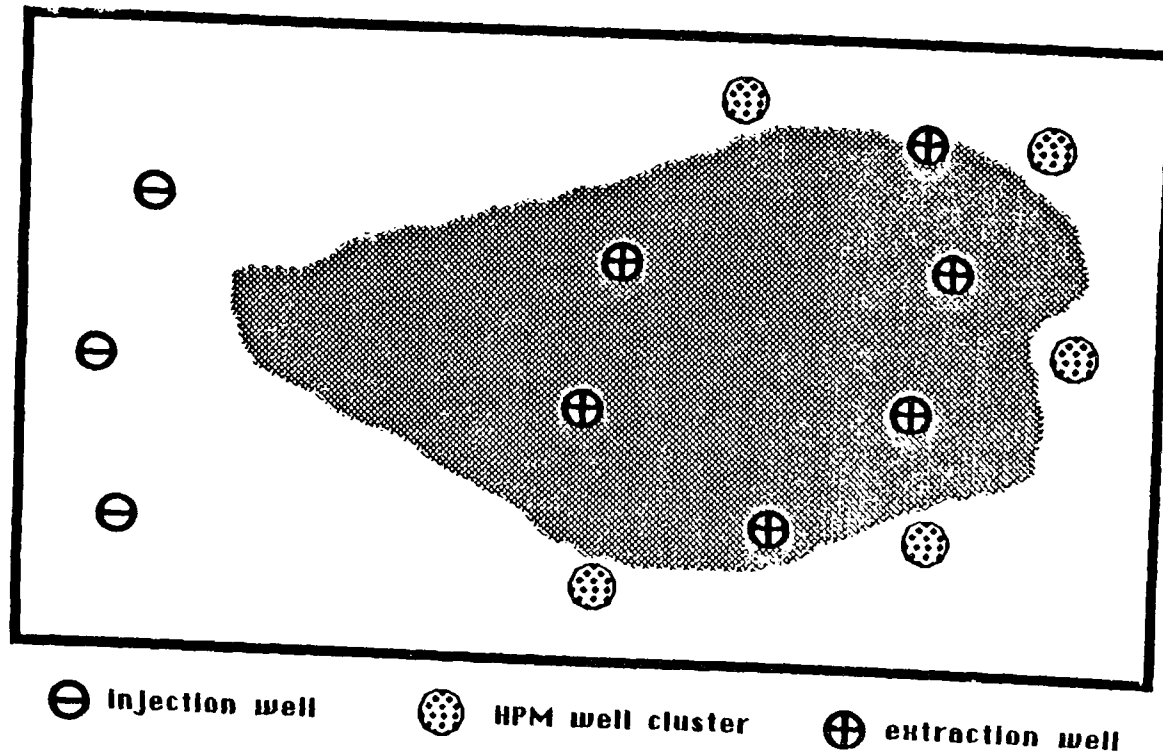
Cross-Sectional View

Static Piezometric Surface

Upper Confining Bed

Drawdown Cone

Artesian Aquifer

Lower Confining Bed

- - - Flow Lines
—— Equipotential Lines
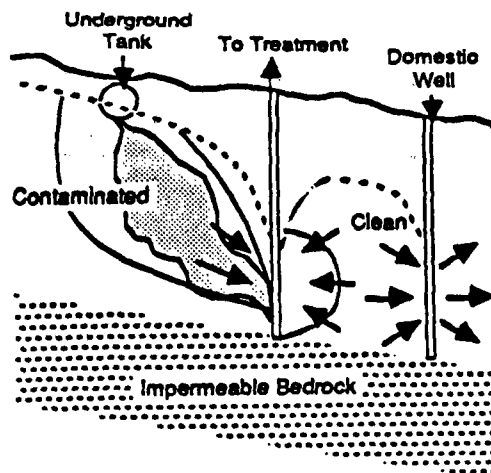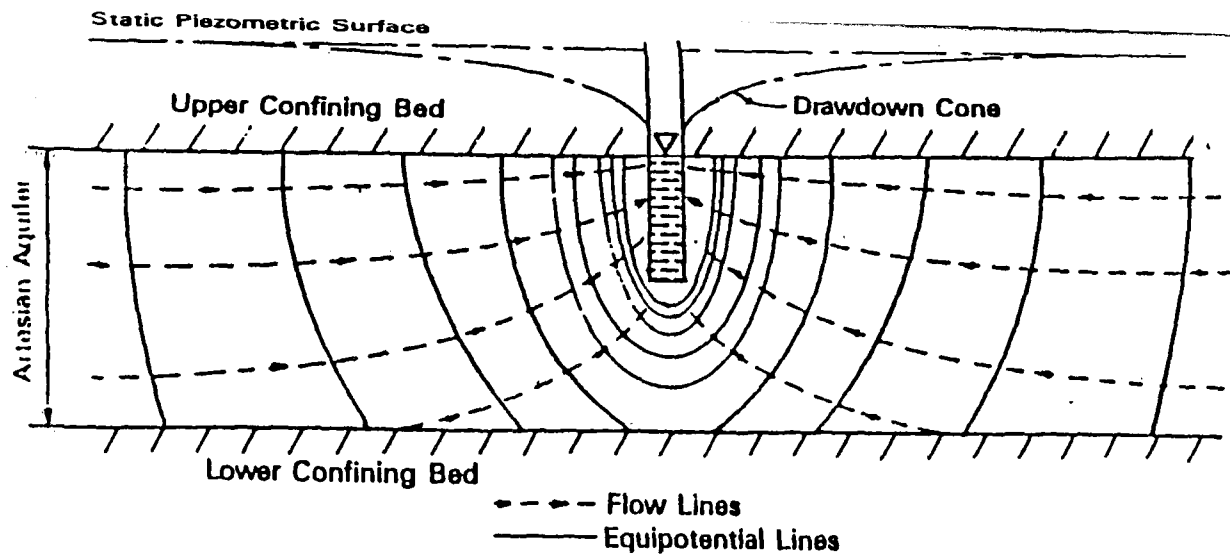
Hydrodynamic Performance Monitoring

Underground Tank

Domestic Well

Extraction Wells with Radius of Influences

Plan View

⊖ Injection well   ⊗ HPM well cluster   ⊕ extraction well
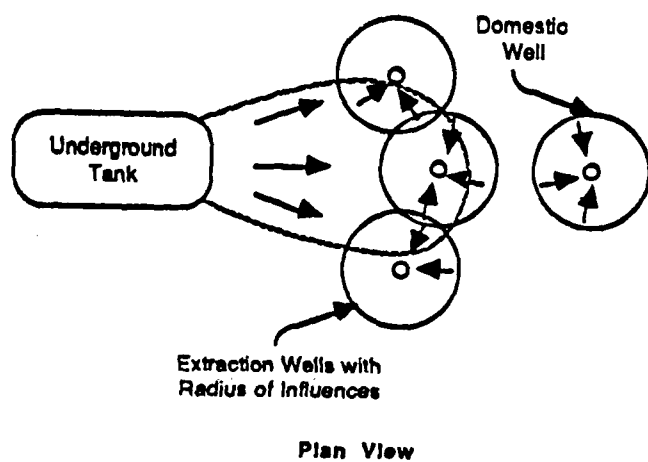
AQUIFERS AND NATURAL CONFINING LAYERS

Frequently, geological structures that readily yield water are layered above or between geological materials that do not readily transmit water. These non-transmissive layers can act as natural containment for subsurface bioremediation. Don't assume the bed rock is a confining layer; it is often fractured.
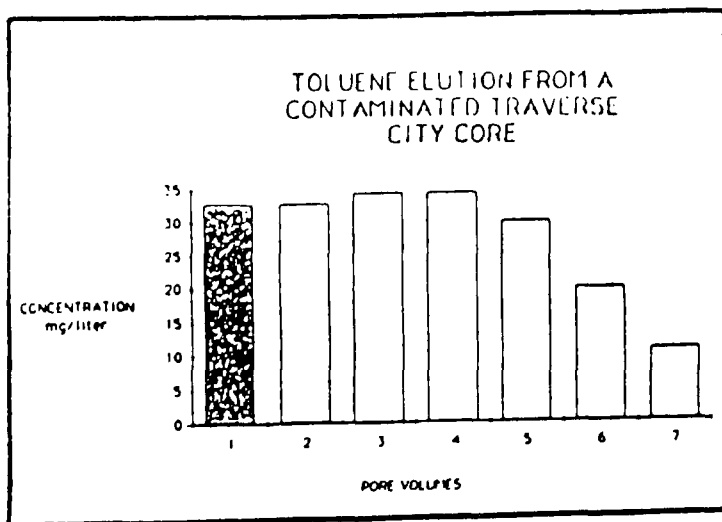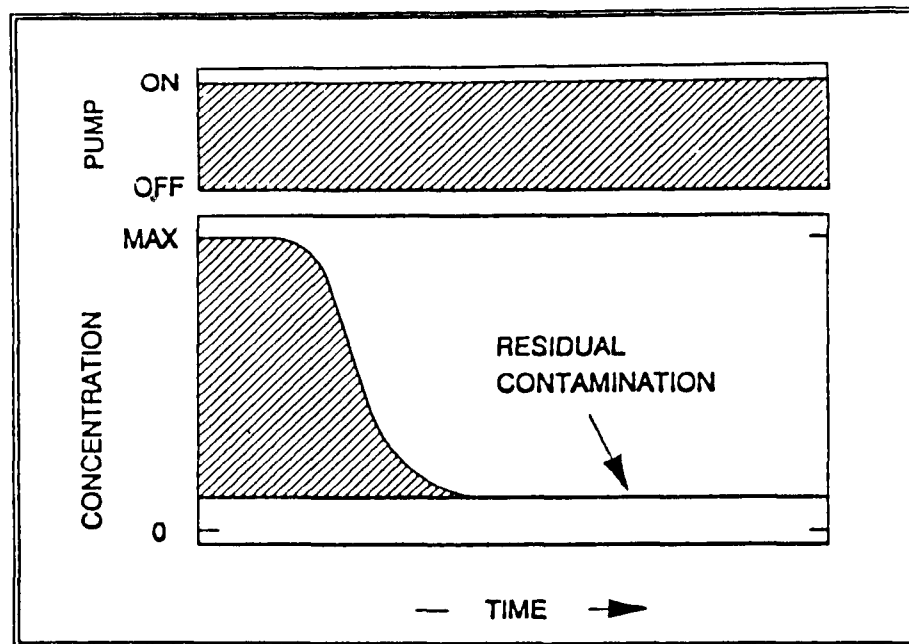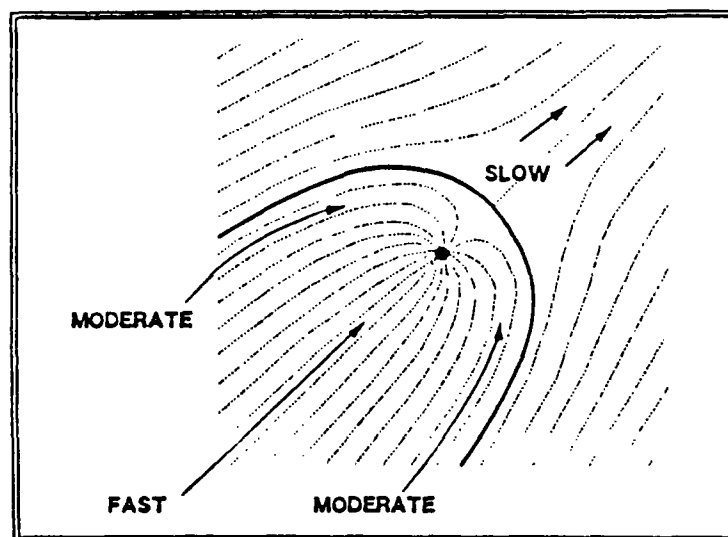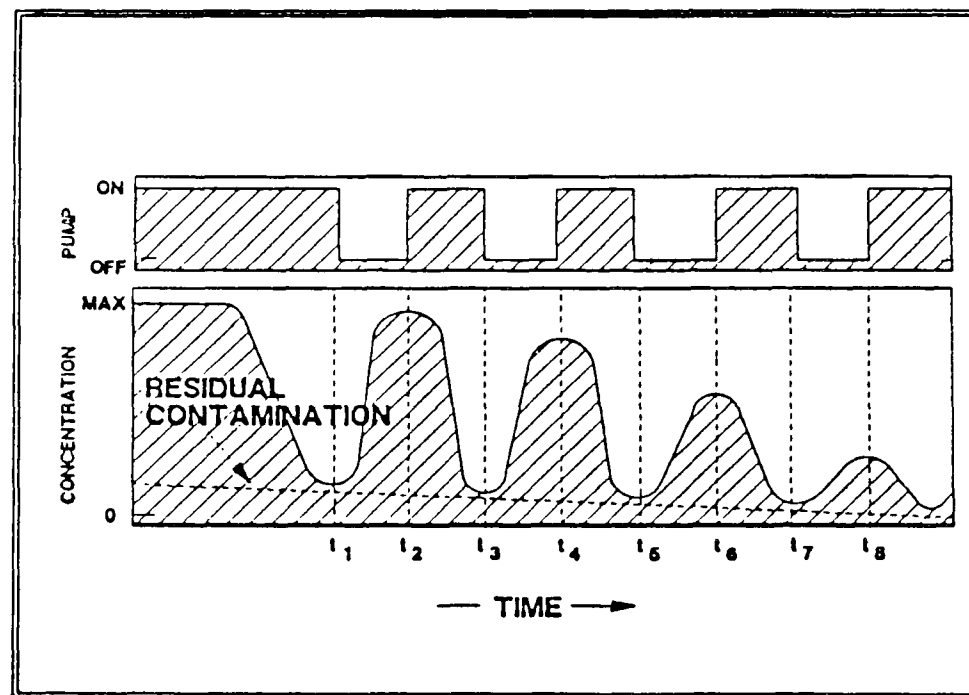

LIFE-CYCLE DESIGN

Time Effect on Concentrations

Capital Costs

Operator Expenses

Nyer, E.K. 1985. Groundwater Treatment Technology. Van Nostrand Reinhold Co., New York

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BACKHOE KEYS TRENCH INTO BEDROCK

BACKFILL PLACED HERE

SLURRY LEVEL

GROUND WATER LEVEL

BENTONITE SLURRY

BACKFILL SLOUGHS FORWARD

BEDROCK

LEACHATE

CONCENTRATION — INCREASING

WELL AT BEGINNING OF PLUME

WELL AT END OF PLUME

INCREASING

TIME

LEACHING COLUMN CONFIGURATION

Column with contaminated aquifer sample

Supply flask (10⁻³ M CaCl₂)

60 ml syringe

Valve

Valve

Syringe pump

PUMP

ON

OFF

CONCENTRATION

MAX

RESIDUAL CONTAMINATION

0

— TIME →

TOLUENE ELUTION FROM A CONTAMINATED TRAVERSE CITY CORE

CONCENTRATION mg/liter

35
30
25
20
15
10
5
0

1   2   3   4   5   6   7

PORE VOLUMES

PUMP

ON

OFF

CONCENTRATION

MAX

APPARENT RESIDUAL CONTAMINATION

3 yrs RCRA window

CESSATION OF PUMPING (CLOSURE?)

?

0

TIME → t_1 t_2

APPLICATION & LIMITATIONS OF AQUIFER RESTORATION - BIORESTORATION

Ronald C. Sims, Professor and Head, Environmental Engineering Division
Utah State University, Logan, Utah

I.   DESCRIPTION OF THE PROCESS

      A.   Characterization
             1. Pump and treat aqueous phase
             2. In situ treat residual contamination

      B.   Phases of in-situ aquifer biorestoration
             1. Site investigation and characterization
             2. Determination of containment requirements
             3. Performance of treatability studies
             4. Bioremediation design, implementation, monitoring

II.   APPLICATIONS OF BIORESTORATION

      A.   Types of environments
             1. Dissolved phase
             2. Sorbed phase
             3. Residual saturation

      B.   Biorestoration systems
             1. Subsurface injection of nutrients and electron acceptor
               a. wells
               b. injection galleries
             2. Pulsed pumping of nutrients and electron acceptor
             3. Hydraulic containment of biorestoration
             4. Physical containment of biorestoration

III.   LIMITATION OF BIORESTORATION

      A.   Biological factors limiting biorestoration
             1. Waste type resistent to biodegradation
             2. Microorganism population
             3. Toxicity
             4. Biochemical by-products

      B.   Environmental factors limiting biorestoration
             1. Low-permeability of aquifer
             2. Problems with adequate containment
             3. Costs for bioremediation
             4. Time requirements

AQUIFER BIORESTORATION

Pump and Treat Aqueous Phase

In Situ Treatment of Residual Saturation
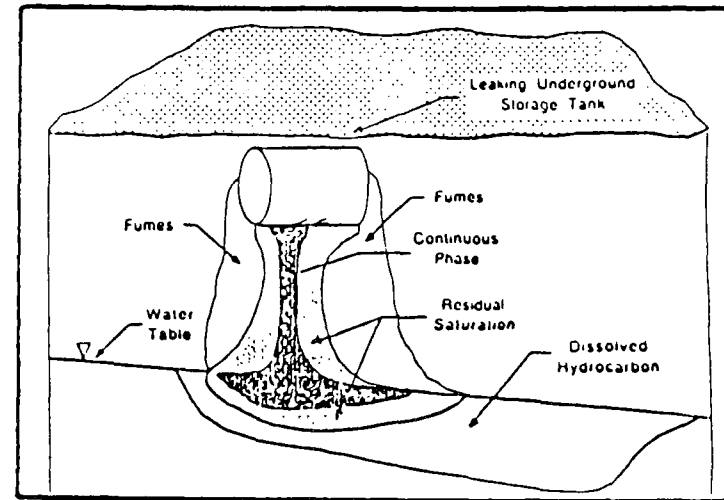
PRIMARY EMPHASIS IN
SUBSURFACE REMEDIATION

Hazardous wastes that occur as a discrete oily-phase act as source areas for plumes of contamination in ground water. They also contaminate the soil air with hazardous fumes. The primary emphasis in subsurface bioremediation has been the source areas. Subsurface bioremediation of the plumes is often technically feasible, but it is usually easier to pump them out and treat them on the surface.

IDENTIFY THE MOST
CONTAMINATED FLOW PATH

Some regions of the source area will clean up faster than others. One flow path will be the last to clean up. If this flow path can be identified, then its properties can be used to determine how much effort is required to remediate the entire source area, and how long it will take.

INJECTION WELL · EXTRACTION WELL · LAND SURFACE
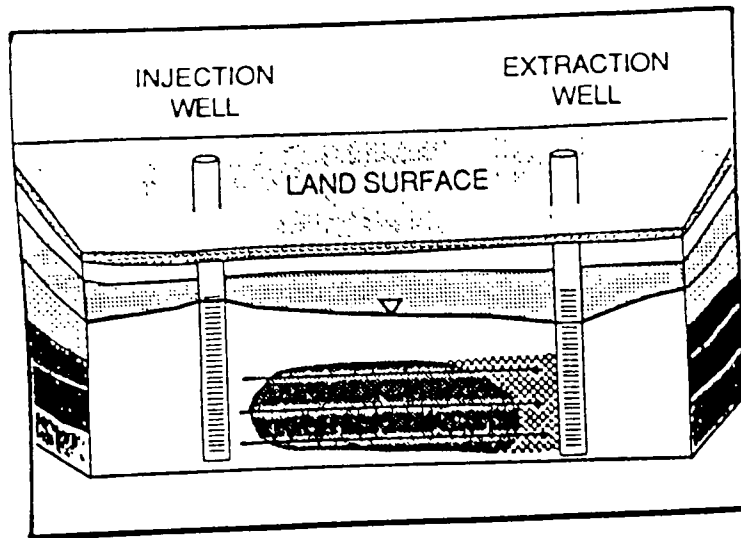
CHARACTERIZATION OF THE MOST CONTAMINATED INTERVAL

$$\text{Time required to clean most contaminated flow path} \quad \alpha \quad \frac{\text{Length of path through source area} \quad \times \quad \text{Concentration of contaminant along flow path}}{\text{Seepage velocity along the most contaminated flow path}}$$
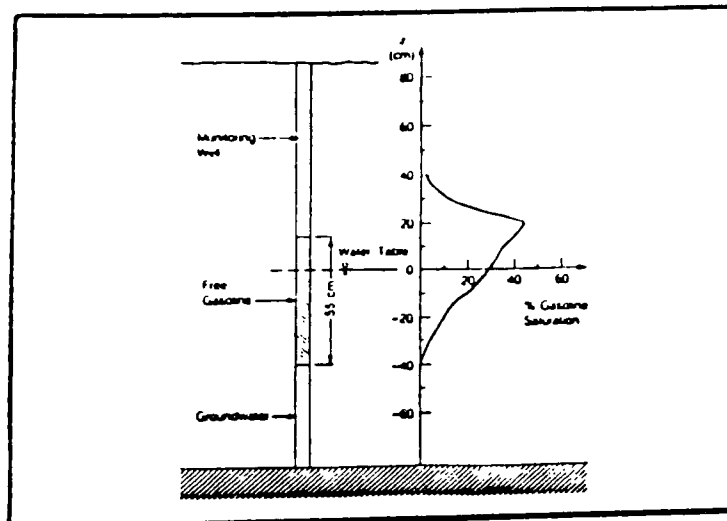
If the supply of mineral nutrients is adequate, the rate of bioremediation is the rate of supply of electron acceptor. As a result, the rate of remediation is directly proportional to the concentration of electron acceptor in the injected water, and directly proportional to the flow velocity of water through the source area.

PROBLEMS WITH WELLS AS MONITORING TOOLS

Treatment can occur in the well itself. The water in the well may not be representative of the water in the aquifer.

A conventional monitoring well produces a composited water sample. Water from the most contaminated flow path is diluted by water from many other flow paths that are less contaminated.

A water sample from a well tells nothing about the amount of hazardous material that is absorbed to aquifer solids or is trapped as an oily phase.

HOW TO PLUG UP AN INJECTION WELL

Add oxygen or hydrogen peroxide to water with Fe^{+2}

$\rightarrow$ get $Fe(OH)_3$

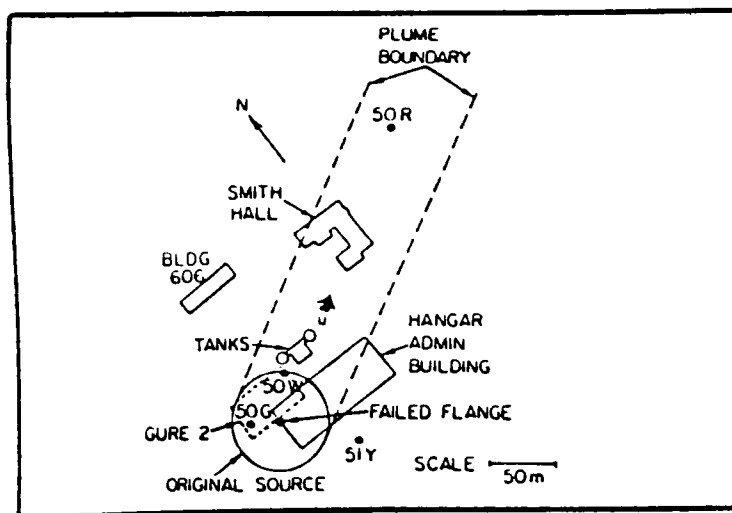Add oxygen or hydrogen peroxide to water with Mg/l of organics

$\rightarrow$ get biofouling

Add phosphate to aquifer with $Ca(Mg)CO_3$ matrix
$\rightarrow$ $Ca(Mg)PO_4$

Nutrients

In-line Oxygen Source

In-situ Aeration

Soil Flushing

Contaminated Soil

Groundwater

Aeration Well Bank

Injection Well

Leachate Plume

Simplified View of Bioreclamation of Soil and Groundwater

Aeration Zone

Direction of Groundwater Flow

Extraction Well
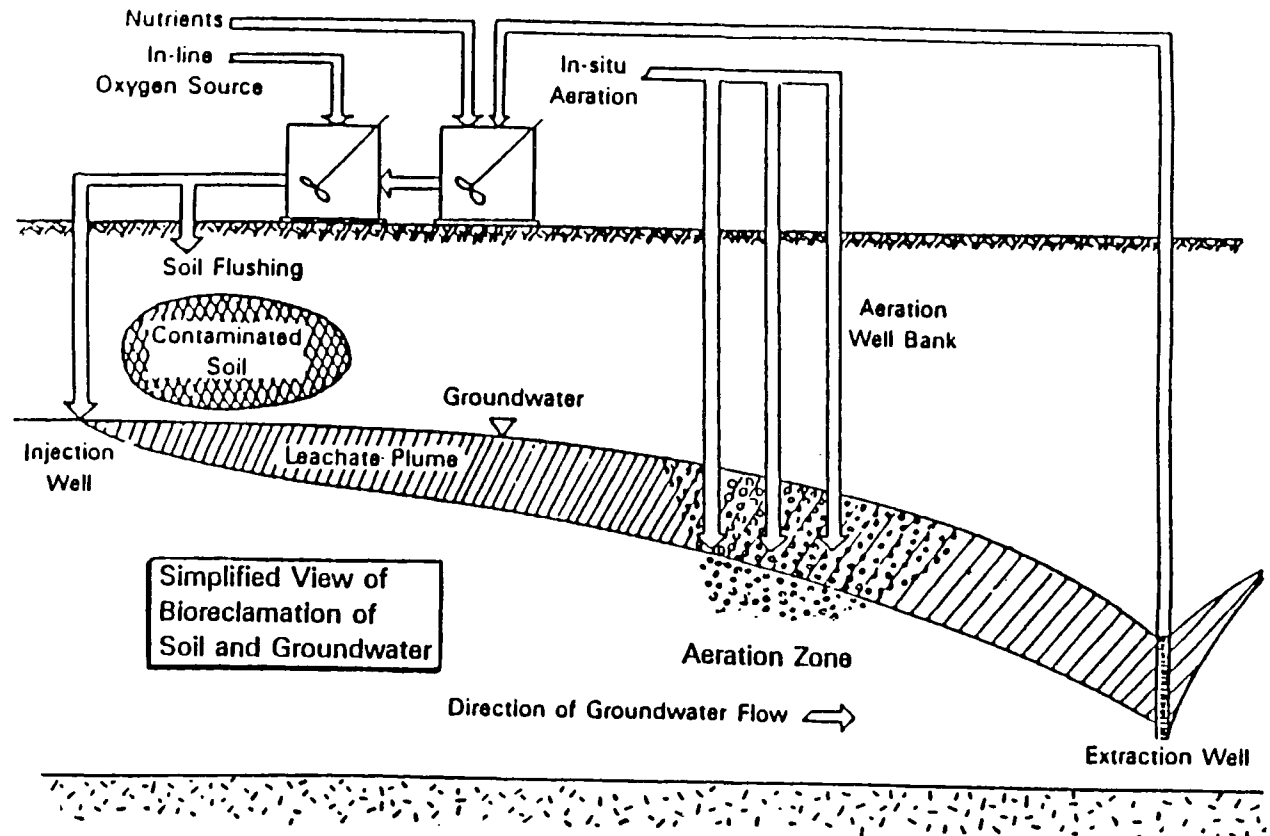
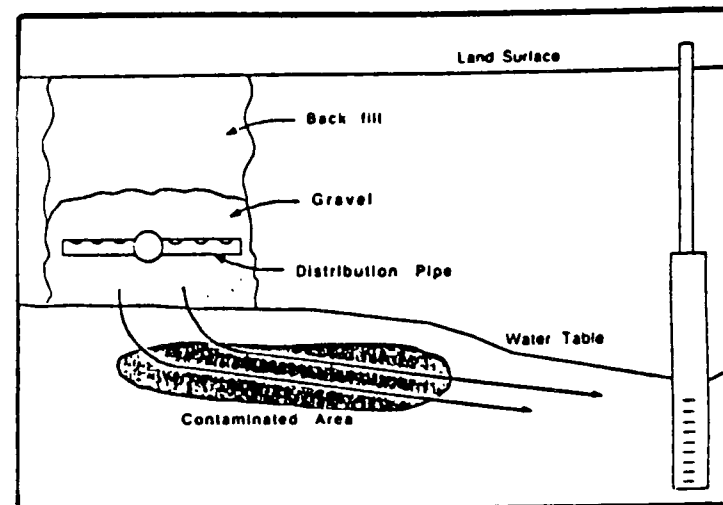In the most contaminated interval at Traverse City

The concentration of fuel hydrocarbons averages 7,500 mg/kg aquifer material, the porosity is 0.4, and the bulk density is 2.0 kg/dm³.

Each kilogram of aquifer contains 0.2 liter of water, and each liter of pore water is exposed to 37,500 mg of fuel hydrocarbons.

The oxygen demand of the hydrocarbons is 128,000 mg O_2 per liter pore water.

CO-DISTRIBUTION OF CONTAMINATION AND HYDRAULIC PERMEABILITY IN AN AQUIFER CONTAMINATED BY A FUEL SPILL

Depth Interval (feet below surface) Interval Cored or Screened Interval	Fuel Hydrocarbons (mg/kg aquifer)	Seepage Velocity (feet per day)
15.1 - 15.5	< 11	
15.5 - 15.8	39	
15.8 - 16.2	2370	
16.2 - 16.5	8400	7.2
16.5 - 17.2	624	
17.2 - 17.5	< 13	9.0
18.0 - 18.3	< 13	
19.4 - 19.6		15.6
20.9 - 21.4		19.7

FORMULATION OF
NUTRIENT MIX

- ◆ Usually determined empirically

- ◆ Not related to C.N.P.S ratios

- ◆ Use high concentrations to project significant concentrations into the aquifer

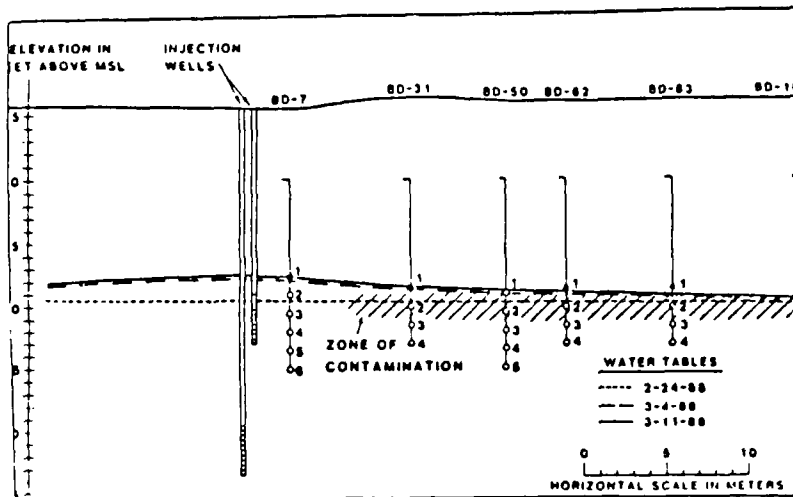- ◆ Should formulations be related to O.N.P.S ratios?

PROPERTIES OF
MOLECULAR OXYGEN

ADVANTAGES

- ◆ Low toxicity to acclimated organisms
- ◆ Supports removal of many organic compounds
- ◆ Inexpensive

DISADVANTAGES

- ◆ Low solubility in water
- ◆ Will precipitate iron hydroxide

PROPERTIES OF
HYDROGEN PEROXIDE

ADVANTAGES

- ◆ Miscible in water
- ◆ Supports bioremediation of many organic compounds
- ◆ Chemically oxidizes many organic and inorganic contaminants
- ◆ Removes biofouling

DISADVANTAGES

- ◆ Toxic at concentrations much above 500 mg/liter
- ◆ Will precipitate iron hydroxide
- ◆ Relatively expensive

COST COMPARISON OF ELECTRON ACCEPTORS

Electron Acceptors	Bulk Cost (per kg)	Electrons Accepted (moles / kg)	Real Cost (per moles of electrons accepted)
Sodium Nitrate	$0.66	58.8	$1.12
Liquid Oxygen	$1.46	125.0	$1.17
Hydrogen Peroxide	$1.54	58.8	$2.62

MONITOR THE OPERATION OF THE SYSTEM AS WELL AS ITS PERFORMANCE

◆ Delivery of mineral nutrients

◆ Delivery of electron acceptor

◆ Position in the water table

◆ Effectiveness of containment


ADVANTAGES OF PULSING AMENDMENTS

If more than one amendment is required to promote subsurface bioremediation, they can be injected in alternating pulses. This prevents undue production of biomass near the injection system, which would otherwise plug the system.

High concentrations of hydrogen peroxide (>100,000 mg/liter) can remove biofouling and restore the efficiency in injection wells or injection galleries.
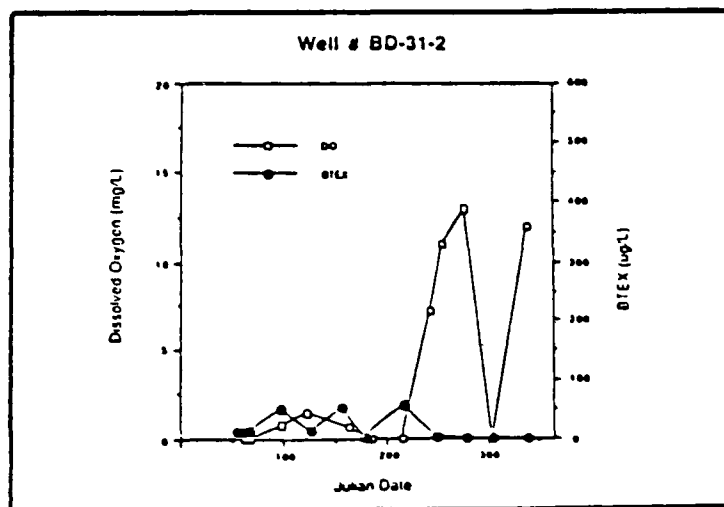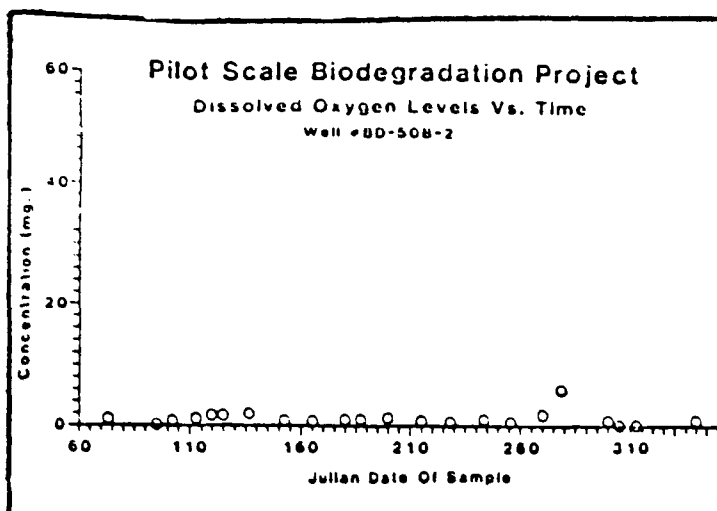
Pulses of hydrogen peroxide at high concentration can sterilize the aquifer and destroy catalase activity, preventing premature decomposition of the peroxide.

Pilot Scale Biodegradation Project
Dissolved Oxygen Levels Vs. Time
Well #BD-508-2

Well # BD-31-2
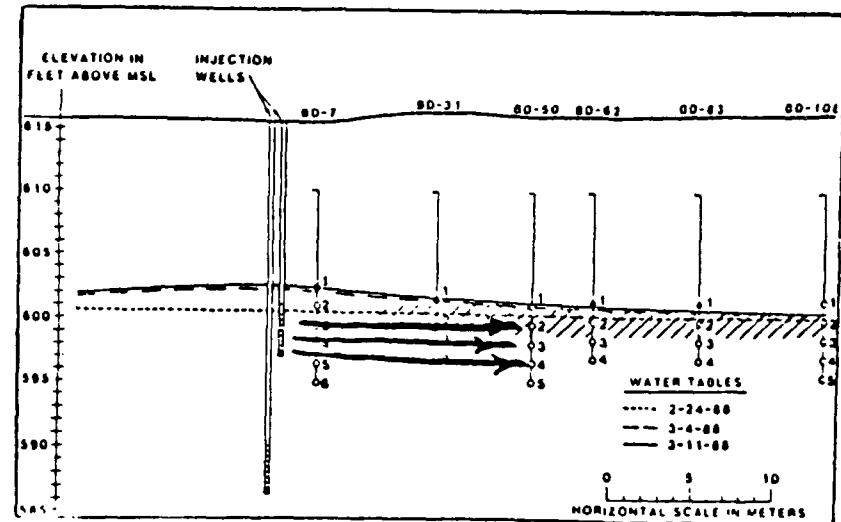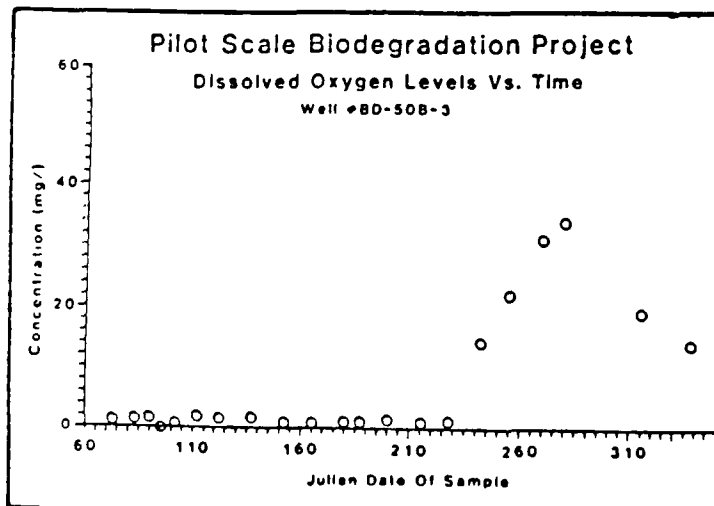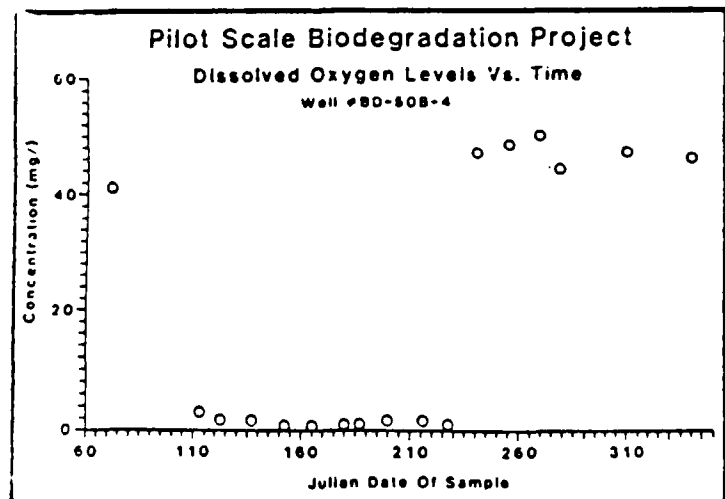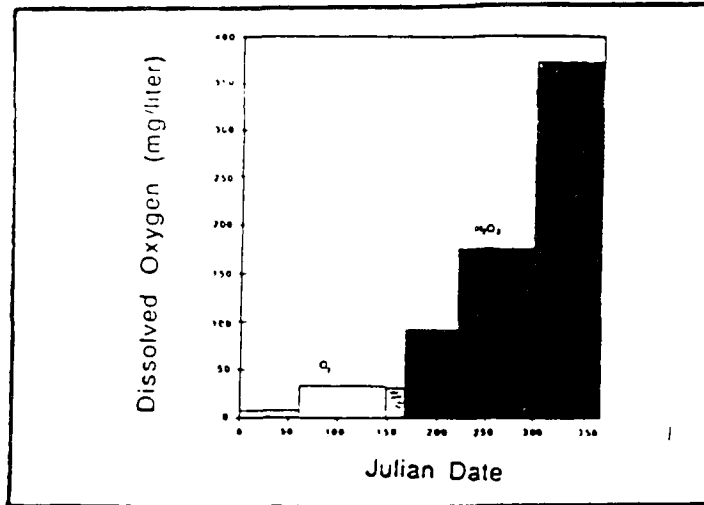
PERFORMANCE OF BIORESTORATION NEAR BD 31

Parameter (mg/kg aquifer)	Before 8/87	Just Before 8/88	After 10/88
Total Fuel Hydrocarbon	6,500	1,220*	8,400
Toluene	544	37	<0.3
m + p Xylene	58	<1	<0.3
o - Xylene	42	8.4	<0.3
Benzene	0.3	0.6	<0.3

* Sample diluted with uncontaminated material

STOICHIOMETRY OF AEROBIC BIORESTORATION

Oxygen required	BD 31-2	BD 50B-2
	......mg O_2 / liter pore water--	
Estimated based on:		
Total Fuel Hydrocarbons	62,212	90,000
BTX only (8/87)	8,710	12,000
BTX only (3/88)	2,364	3,420
Actually required	2,989	2,952

HOW OFTEN SHOULD A MONITORING WELL BE SAMPLED?

The frequency of sampling should be related to the time expected for significant changes to occur along the most contaminated flow path.

IMPORTANT CONSIDERATIONS

◆ Time required for water to move from injection wells to the monitoring wells

◆ Seasonal variations in water-table elevation or hydraulic gradient.

◆ Changes in the concentration of electron acceptor.

◆ Cost of monitoring compared to day-to-day cost of operation.

FACTORS CONTROLLING THE RATE AND EXTENT OF BIOREMEDIATION AT FIELD SCALE

◆ Rate of supply of essential nutrients, usually the electron acceptor

◆ Spatial variability in flow velocity

◆ Seclusion of the waste from the microorganisms

Rates and extent of treatment at field scale should be

estimated with a comprehensive mathematical model

that incorporates

- biological reaction rates

- stoichiometry of waste transformation

- mass-transport considerations

- spatial variability in treatment efficiency

MORE COSTS
ASSOCIATED WITH
SUBSURFACE REMEDIATION

SYSTEM INSTALLATION

Wells, infiltration galleries, pumps, pipelines, tanks,
control devices, treatment systems

MATERIALS AND OPERATING EXPENSES

Water, electron acceptor, fertilizer, inoculant,
maintenance, power, sewer charges

MONITORING

Monitoring wells and pumps, cores and their analysis

SITE SECURITY AND OPERATIONAL OVERSIGHT

COSTS ASSOCIATED WITH
SUBSURFACE REMEDIATION

SITE CHARACTERIZATION

Wells, Soil Gas Survey, Coring and Core Analysis,
Geological Section, Aquifer Tests, Tracer Tests

REMEDIAL DESIGN

Treatability Tests, Mathematical Modeling

SYSTEM DESIGN

Permits, Negotiating trade-offs between cost and time
required

REFERENCES: SESSION 6

Goldstein, R.M., L.M. Mallory, and M. Alexander. 1985. Reasons for possible failure of inoculation to enhance biodegradation. Applied and Environmental Microbiology 50:977.

Lee, M.D., Thomas, J.M., Borden, R.C., Bedient, P.B., Wilson, J.T., and Ward, C.H. 1988. Biorestoration of aquifers contaminated with organic compounds. CRC Critical Reviews in Environmental Control. 18(1):29-89.

Nyer, E.K. 1985. Groundwater Treatment Technology. Van Nostrand Reinhold Company, Inc. ISBN: 0-442-26706-1. 188 pp.

Wilson, J.T., and D.H. Kampbell. 1989. Challenges to the practical application of biotechnology for the biodegradation of chemicals in ground water. Preprint Extended Abstract, American Chemical Society, Division of Environmental Chemistry, April 9-14, Dallas, Texas.

Wilson, J.T., L.E. Leach, M. Henson, and J.N. Jones. 1986. *In situ* biorestoration as ground water remediation technique. Ground Water Monitoring Review, pp. 56-64 (Fall).