United States
Environmental Protection
Agency

Office of Research and
Development
Washington, DC 20460

EPA/625/K-98/001
September 1998

EPA

Seminars

Monitored Natural Attenuation for Ground Water

September 2–3, 1998—Philadelphia, PA

September 14–15, 1998—Denver, CO

September 16–17, 1998—Chicago, IL

October 14–15, 1998—Kansas City, MO

November 2–3, 1998—Dallas, TX

November 16–17, 1998—Atlanta, GA

December 2–3, 1998—Seattle, WA

December 8–9, 1998—Boston, MA

December 14–15, 1998—San Francisco, CA

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Seminars on Monitored Natural Attenuation for Ground Water

Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC

Notice

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Acknowledgements

This seminar series was funded by the Office of Solid Waste and Emergency Response (OSWER). The seminar was developed by Drs. Francis Chapelle (U.S. Geological Survey), Kelly Hurt (National Research Council), Fran Kremer (USEPA, ORD) and John Wilson (USEPA, ORD). Input on the seminar was received from OSWER and the Regional Offices, including the CERCLA, RCRA and UST programs. Special thanks to Ken Lovelace, Guy Tomassoni, Hal White and the Ground Water Forum for their contributions. The series presentations were a collaborative effort between the USEPA and the U.S. Geological Survey (USGS). Special thanks to Herb Buxton of the USGS for supporting this effort.

Sources of Information

Recent EPA Bioremediation Publications
http://www.epa.gov/ORD/WebPubs/biorem/

Bioremediation in the Field Search System: Database on national and some international field applications
Version 2.1 **EPA/540/R-95/508b** (Revised)
Also on the Internet

Request to be on EPA's bioremediation mailing list or to request specific bioremediation documents
513-569-7562

NRMRL/SPRD Home Page
http://www.epa.gov/ada/kerrlab.html

OUST Home Page with links to OSWER Policy Directives
http://www.epa.gov/swerust1/directiv/index.htm

Background on Monitored Natural Attenuation

EPA Policy On Use of Monitored Natural Attenuation For Site Remediation

Background on Directive

EPA's Office of Solid Waste and Emergency Response (OSWER) developed Policy Directive: Use *of Monitored Natural Attenuation at **Superfund,** RCRA Corrective Action, and Underground Storage Tank **Sites,** Directive 9299.447,* **December 1, 1997.**

- **Clarifies EPA's position on use of monitored natural attenuation (MNA) for remediating contaminated sites.**
- **Not intended to be a detailed technical guidance.**
- **Does not deal with legal or administrative issues (e.g., property transfer, NPL deletion).**

How To Obtain Directive

- RCRA, **Superfund** Hotline: I-600-424-9346
- OUST Home Page
  - ▶**More Information**
  - ▶**Policy Directive**
  - ▶**http://www.epa.gov/swerust1/directiv/9200_417.htm**

EPA Definition

- **Monitored Natural Attenuation (MNA):**

... *the* use *of* ***natural*** attenuation ***processes*** *within the* ***context*** of 8 carefully *controlled and monitored* ***site cleanup approach that will*** *reduce contaminant concentrations* to levels that ***are*** *protective of* ***human*** *health and the environment* within 8 ***reasonable time frame.***

MNA Processes

- **Physical, chemical, or biological processes that act without human intervention** to reduce the **mass,** toxicity, mobility, volume, or concentration of contaminants.
- **Includes biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization or destruction of contaminants.**

MNA Processes *(cont'd)*

- **EPA prefers those processes that degrade contaminants and expects that MNA will be most appropriate where plumes are stable.**
- **Some processes have undesirable results, such as:**
  - ▶**Creation** of toxic daughter products, or
  - *Transfer of contaminants to other media.

Role of MNA in OSWER Remediation Programs

- ALL remedies must protect human health and the environment.
- NOT a "walk away" or "do nothing" option.
- NOT a "default" or presumptive remedy.

Role of MNA in OSWER Remediation Programs *(cont'd)*

- Site-specific, risk-based decisions are essential. MNA is an active choice although it is a passive remediation technology.
- Proponent must demonstrate that MNA is the appropriate option, not the implementing agency.

Demonstrating the Efficacy of MNA

- Three types of site-specific information may be required:
  1. Historical ground water and/or soil chemistry data demonstrates trend of declining **contaminant** concentration.
  2. Hydrogeologic and **geochemical** data that demonstrate NA processes and rates.
  3. Field or microcosm studies.
- Unless #1 is of sufficient quality and duration, #2 is generally required (regulatory decision).

Sites Where MNA May Be Appropriate

- MNA is appropriate as remedial approach only where it:
  - ▶ Can be demonstrated to achieve remedial objectives within reasonable time frame, **and**
  - ▶ Meets the applicable remedy selection **criteria** for the particular OSWER program.

Sites Where MNA May Be Appropriate *(cont'd)*

- MNA will typically be used in conjunction with active remediation measures (e.g., source control) or as follow-up to such measures.
- MNA should not be used where such an approach would result in significant contaminant migration or unacceptable impacts to receptors.

Reasonable Time Frame

- Time frame should not be excessive compared to that required for other remedies.
- Reasonable time frame is a site-specific decision.

Reasonable Time Frame *(cont'd)*

- Some factors that impact "reasonableness" of time frame include:
    - Current and potential future uses of affected ground water,
    - Relative time frame in which aquifer may be needed,
    - Public acceptance of extended time for remediation,
    - Reliability of monitoring and institutional controls, adequate funding over time required to reach cleanup objectives.
    - Regional resource issues

Remediation of Sources

- EPA expects that source control measures will be evaluated for all sites and implemented at most sites where practicable.
- Measures include removal, treatment or containment of sources.
- Source control is especially important where MNA is part of the remedy.
- Appropriate source control actions are high priority and should be implemented sooner rather than later in site response.

Performance Monitoring

- Required to gauge effectiveness and protect human health and the environment.
- Of even greater importance for MNA remedies because longer cleanup time frames are generally involved.
- Must demonstrate that NA is occurring as expected, identify transformation products, detect plume migration, and verify no impact to receptors.
- Required for as long as contamination levels remain above cleanup goals.

Contingency Remedies

- A cleanup technology or approach that will function as a "backup" in the event that MNA fails to perform as anticipated.
- Contingency measures are especially important when MNA is selected based primarily on predictive analysis (i.e., uncertainty is greater than when based on historical data).
- "Triggers" should be established which signal unacceptable performance of the MNA remedy.

Summary

- MNA is appropriate at many but NOT **all** sites.
- NOT a "no action," "default" or "presumptive" remedy.
- Should NOT result in significant contaminant migration or unacceptable impacts to receptors.

Summary *(cont'd)*

- Progress should be carefully monitored.
- Contingency measures should be included when selection of MNA was based mostly on predictive analysis.
- A cleanup is NOT completed until cleanup objectives, set by the implementing Agency, have been met.

Where to Find the OSWER MNA Directive and Technical Updates

- http://www.epa.gov/swerust1/directiv/9200_417.htm
- http://www.epa.gov/ORD/WebPubs/biorem
  (case sensitive)

Trends in the Use of Monitored Natural Attenuation

Trends in the Use of MNA

Fran **Kremer**
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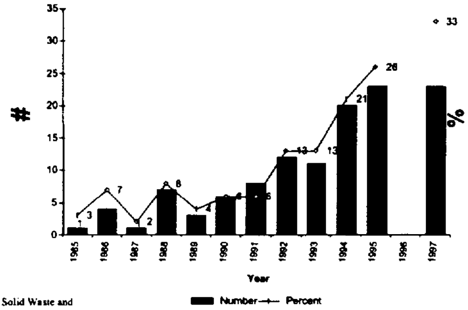
Programs that May Look at Natural Attenuation in Cleanup

- **UST**
- **CERCLA**
- **RCRA**
- **State Voluntary Cleanup Programs**
- **Brownfields Sites**

How Has Natural Attenuation Been Used?

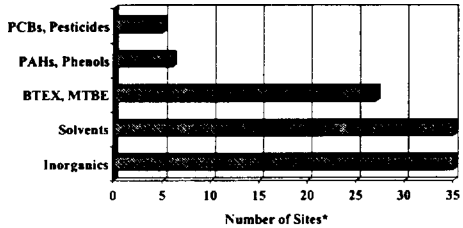
- **Variety of sites, including MLFs, industrial LFs, refineries, recyclers, etc.**
- **At all but six sites, natural attenuation used in combination with active remedy components**
- **Often have** low **exceedences of cleanup levels**
- **Contingencies for active measures**

MNA Groundwater RODs



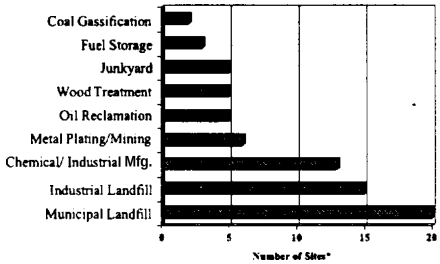
Office of Solid Waste and
Emergency Response

Contaminants Present at Sites for which Natural Attenuation was Specified



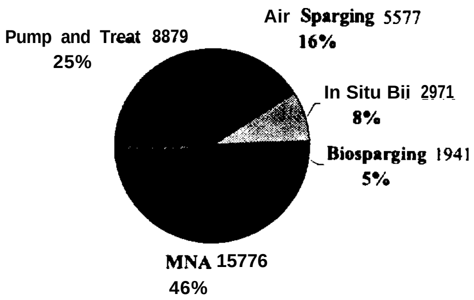
*Some sites have more than one contaminant

Contaminants Present at Sites for which Natural Attenuation was Specified

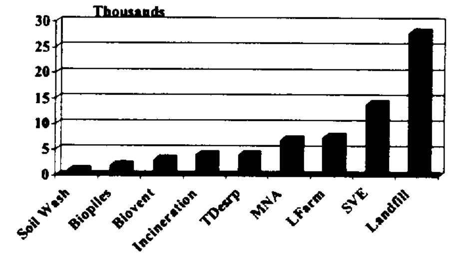


*Some sites have more than one contaminant

LUST Groundwater Remediation Technologies, FY97



Soil Remediation Technologies at UST Sites, FY97



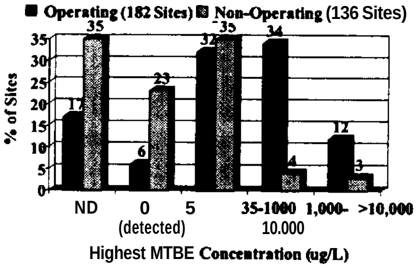
Office of Underground Storage Tanks, 1998

Occurrence of MTBE by Geographical Area

- Maximum MTBE Concentrations Exceed 1 mg/L at:
  - – 47% of 251 California sites
  - – 63% of 153 Texas sites
  - – 81% of 41 Maryland sites

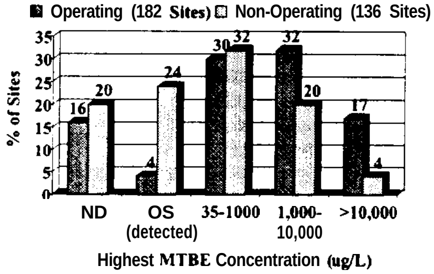
T. Buscheck, et al

MTBE Occurrence at Northern California Sites



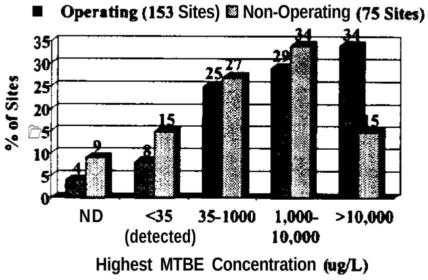
T Buscheck, et al.

MTBE Occurrence at Southern California Sites



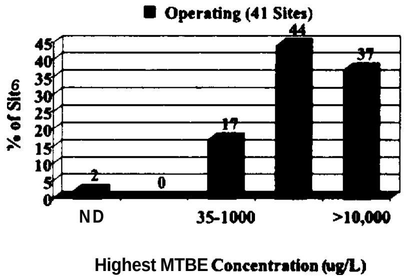
T. Buscheck, et al

MTBE Occurrence at Texas Sites



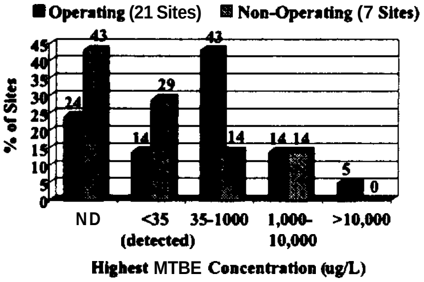
T. Buscheck, et al.

MTBE Occurrence at Maryland Operating Sites



T. Buscheck, et al.

MTBE Occurrence at Florida Sites



T. Buscheck, et al.

Framework for Use of Monitored Natural Attenuation

Framework for Use of MNA

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National Risk Management Research Lab
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Potential Advantages of MNA

- Generation of lesser volume of remediation wastes, reduced potential for cross-media transfer of contaminants, & reduced risk of human exposure to contaminated media
- Less intrusion
- Potential for application to all or part of given site

Potential Advantages of MNA

- Use in conjunction with, or as a follow up to, other (active) remedial measures
- Lower overall remediation costs than those associated with active remediation

Potential Disadvantages of MNA

- Longer time frame may be required to achieve remediation objectives
- Site characterization may be more complex and costly
- Toxicity of transformation products may exceed that of the parent compound
- Long term monitoring

Potential Disadvantages of MNA

- Institutional controls may be necessary to ensure long-term productiveness
- Potential for contaminant migration
- Possible renewed mobility of previously stabilized contaminants
- More extensive education and outreach efforts

Two Basic Questions for Bioremediation

- **When to start?**
- **When to stop?**

When to Stop Active Remedial Processes

- When active treatment no longer doing any good
- When active treatment is no faster than MNA

Contaminant Releases

- Migrate from source area
- Area of contamination expands until equilibrium reached
- MNA equals source output

When/Where is Equilibrium Reached?

- Site factors- soil type, precipitation influx
- Contaminant factors- solubility, concentration, carrier...

Equilibrium

- Eventually, MNA exceeds rate of source output, and concentration of contaminant(s) stabilizes or decreases
- Importance of source control as the primary remedial alternative

Source Control

- "Source control actions should use treatment to address "principal threat" wastes (or products) wherever practicable, and engineering controls such as containment for waste (or products) that pose a relatively low long-term threat or where treatment is impracticable"

Monitoring Strategies

- Three kinds of monitoring
  - 1. Site characterization to describe disposition of contamination and forecast its future behavior.
  - 2. Validation monitoring to determine whether the predictions of site characterization are accurate.
  - 3. Long-term monitoring to ensure that the behavior of the contaminant plume does not change

Developing Conceptual Model

- Determine nature and 3-D extent of contamination
- Determine site processes mobilizing contaminants
- Determine factors influencing contaminant movement pathways
- Determine changes in contaminant location and concentration with time
- Determine the point(s) of attainment

Determine Nature and 3-D Extent of Contamination

- Contaminants
- Contaminant properties
  - P/C-solubility, volatility, Henry's Law, sorption coefficients, pH
  - Bio-degradation potential, required redox, electron acceptors/donors, by products

Determine Nature and 3D...(cont)

- Contaminant location- where are they, how far have they moved, define in 3-D
- Contaminant concentration
- Contaminant form/phase-solid, NAPL, vapor, adsorbed, dissolved

Determine Processes Mobilizing Contaminants

- Volatilization
- Leaching
- Mobile NAPL-gravity, water table fluctuations, GW flow
- Dissolution in GW

Determine Factors Influencing Contaminant Movement Pathways

- Lithology
- Hydrogeology-flow rates, flow paths, gradients

Determine Changes in Contaminant Location and Concentration with Time

- Soil concentrations
- NAPL movement
- Changes in dissolved fraction
- Seasonal fluctuations

Points of Attainment

- Given 3-D extent of contamination, will natural attenuation be protective?
- Develop model

Predictive Models

- Use of site specific data to predict the fate and transport of solutes, given the controlling physical, chemical and biological processes
- Results of the modeling only as good as the data input
- Several solute fate and transport models available

How to Improve Understanding & Implementation of MNA

- Control/treat/remove sources
- Thoroughly monitor plume and downgradient areas
- Include contingencies for other measures if MNA fails to meet desired goals
- Involve regulatory agencies early in process

How to Improve Understanding & Implementation of MNA

- Communicate that MNA is a responsible, managed remediation **approach(not** a walk **away)**
- Present site-specific data and analysis that demonstrate occurrence
- Develop defensible conceptual model supporting MNA
- Build defensible predictive models, where appropriate

Natural Attenuation

- Burden of proof is on the proponent, not the regulator
- Not a default technology or presumptive remedy
- Not complete until goals of the regulatory agency have been reached to their satisfaction

Biological and Geochemical Context for Monitored Natural Attenuation

Biological Processes

Natural Attenuation of Petroleum Hydrocarbons in Ground Water

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National Risk Management Research Laboratory
U.S.Environmental Protection Agency
Cincinnati, Ohio

Patterns of Natural Bioremediation

- Limited by supply of a soluble electron acceptor
  - Aerobic respiration
  - Nitrate reduction
  - Sulfate reduction
- Controlled by mixing processes (biopiume)

Patterns of Natural Attenuation

- Limited by biological activity
  - Iron reduction
  - Methanogenesls
  - Sulfate reduction
- First-order kinetics

Patterns of Natural Attenuation

- Limited by supply of electron donor
- Reductive dechlorination
- Controlled by supply of electron donor

Lines of Evidence

- Documented loss of contaminants at the field scale
- Geochemical indicators
- Laboratory microcosm studies, accumulation of metabolic end-products, volatile fatty acids, FAME

Documented Occurrence of Natural Attenuation

- Use geochemical data to support natural attenuation
- Tmnds during biodegradation (plume interior vs. background concentrations)
  - **Dissolved** oxygen **concentrations** below beckground
  - **Nitrate** conwntretions below beckground
  - Iron **(II)** conwntretions **above** beckground
  - Sulfete conwntntions below beckground
  - Yethene **concentrations** ebove beckground

Total Assimilative Capacity

Calculation of BTEX destroyed from changes in the concentrations of :

- Oxygen
- Nitrate
- iron ii
- Sulfate
- Methane

Total Assimilative Capacity

Calculations are most appropriately used to rationalize degradation of BTEX that appears to have already happened in the field

Calculations am usually not appropriate to predict future degradation of BTEX in existing contamination

Total Assimilative Capacity

Calculations reveal:

Assimilative Capacity that was used

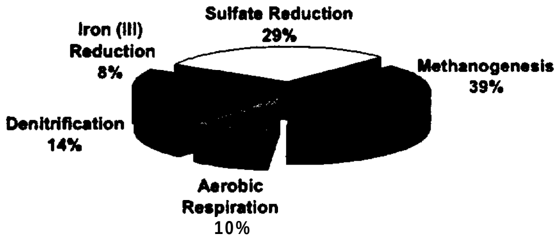
Not Assimilative Capacity remaining

Total Assimilative Capacity

Oxygen = 1,920 µg/L
Denitrification = 1,660 µg/L
Iron Reduction = 2,550 µg/L
Sulfate reduction = 21,000 µg/L
Methanogenesis = 2,560 µg/L

Total Assimilative Capacity = 29,710 µg/L

Relative importance of Biodegradation Mechanisms at 25 Fuel Spill Sites



Total Assimilative Capacity

Greatest sources of error:

Under-estimates contribution of iron reduction.

Assumes all the electron acceptor demand is BTEX.

Native organic matter (TOC) may have an important electron acceptor demand.

Natural Attenuation of Oxygenates in Ground Water

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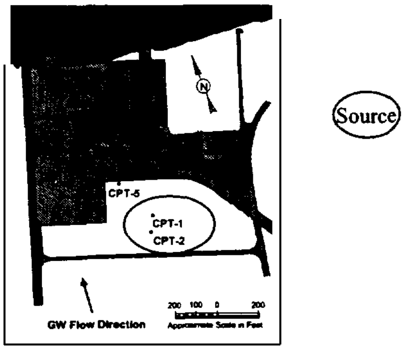
Cincinnati, Ohio

Natural Attenuation of MTBE in Ground Water

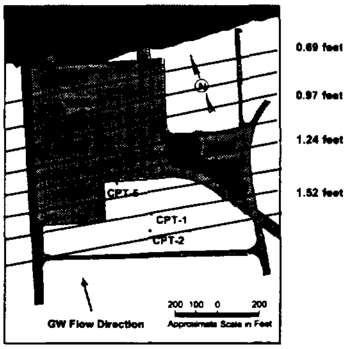
Natural Attenuation of MTBE in Ground Water under methanogenic conditions

Depletion of MTBE and Benzene down gradient of the source area at the U.S. Coast Guard Support Center at Elizabeth City, N.C.

The source is a spill of JP-4 jet fuel from an old fuel farm in the flood plain of the Pasquotank River. The source area is located on the following map



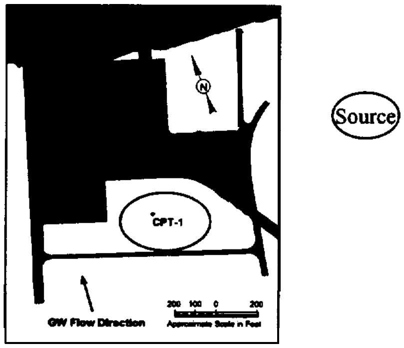
Elizabeth City, North Carolina



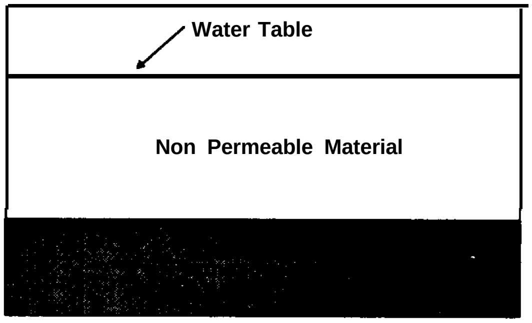
Elizabeth City, North Carolina

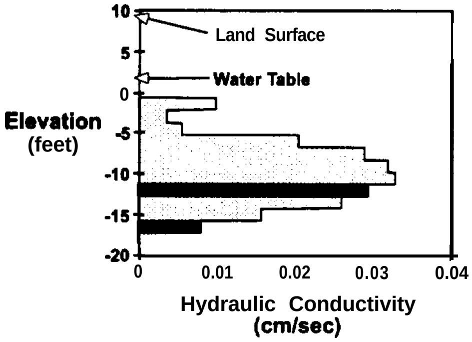
Natural Attenuation of MTBE in Ground Water under methanogenic conditions

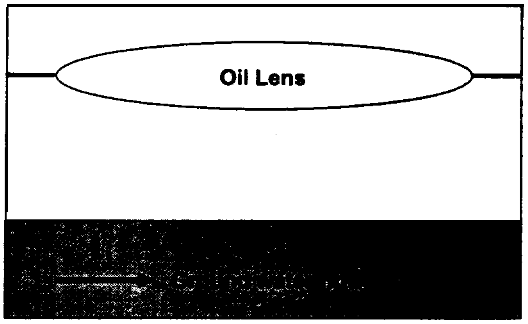
Conditions in the source area (CPT-1)

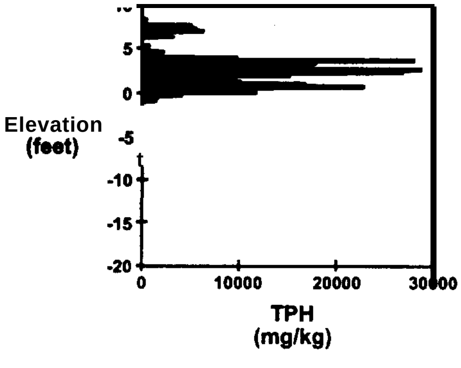


Elizabeth City, North Carolina



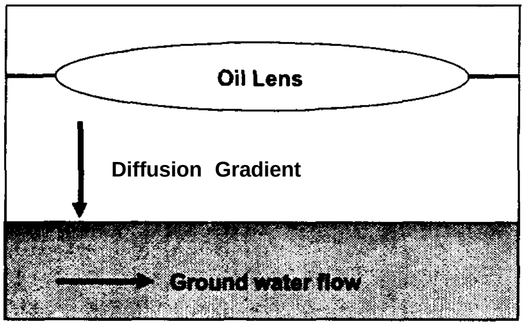


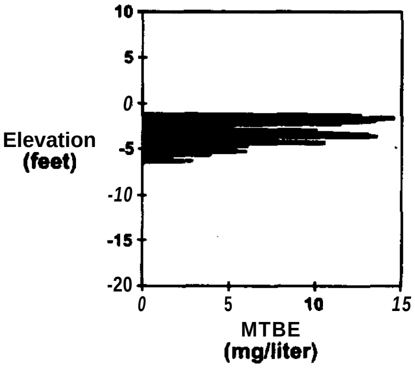


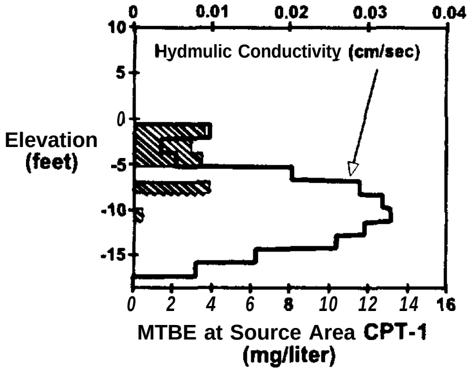


In many floodplain landscapes, the most important transfer of contaminants from LNAPL to ground water is through diffusion from the LNAPL to transmissive layers in the aquifer, rather than through dissolution and direct advection.

This suggests an approach to estimate the impact of spills of petroleum hydrocarbons on ground water.

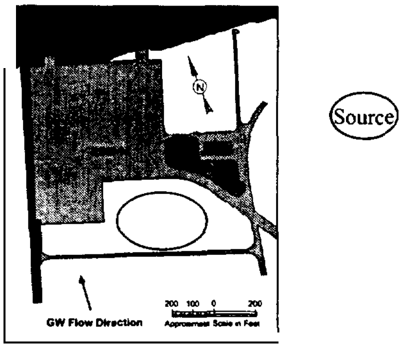




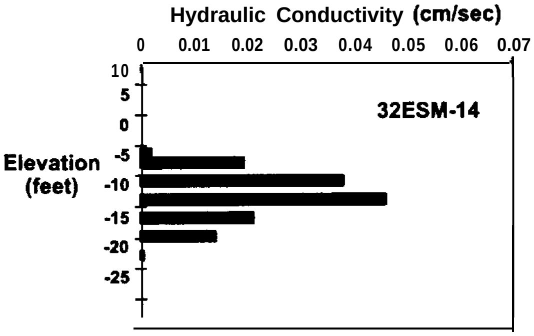


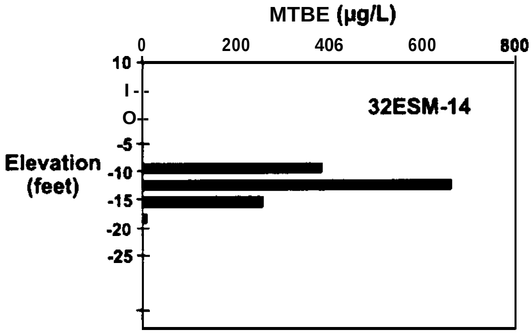
Natural Attenuation of MTBE in Ground Water under methanogenic conditions

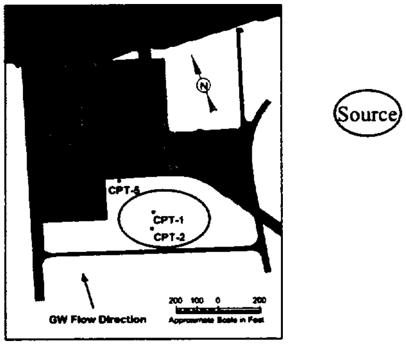
Conditions down gradient of the source area, beyond the edge of the LNAPL at ESM-14



Elizabeth City, North Caroline



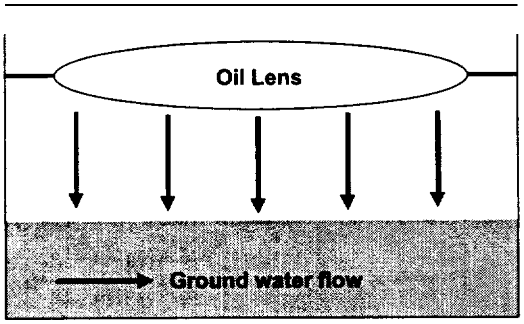


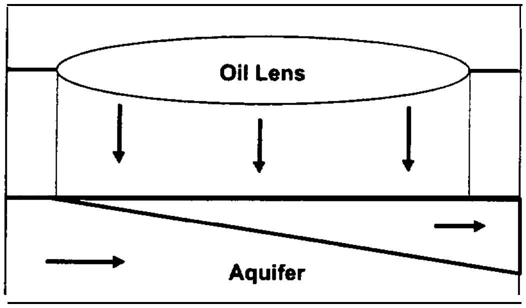


Elizabeth City, North Carolina

Location	MTBE	Benzene	Methane
	----------(mg/liter)------- - -		
CPT-2	0.47	0.033	0.57
CPT-1	3.9	2.3	6.1
CPT-5	0.71	1.6	10.6
ESM-14	0.38	0.39	9.2
ESM-10	0.024	0.47	8.5
GP-1	0.001	0.015	2.3

Location	DO	Sulfate	Nitrate	Iron II
	-----------(mg/liter)-----------			
CPT-2	1.3	35.3	co.1	2.6
CPT-1	0.0	10.9	co.1	22.8
CPT-5	0.0	co.1	<0.1	47.3
ESM-14	0.1	<0.1	co.1	91.3
ESM-10	1.1	<0.1	co.1	68.8
GP-1	0.1	co.1	<0.1	91.5





Natural Attenuation of MTBE in Ground Water under methanogenic conditions

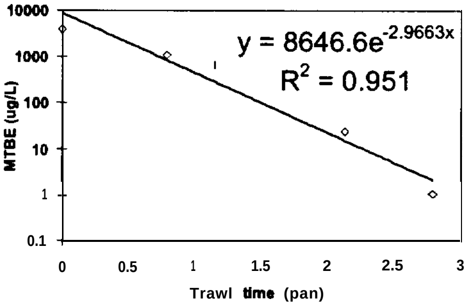
By the time ground water had moved entirely underneath the LNAPL, soluble electron acceptors were depleted, Methane and Iron II were accumulating, and the ground water contained high concentrations of MTBE and BTEX.

Natural Attenuation of MTBE in Ground Water under methanogenic conditions

The highest hydraulic conductivity and the hydraulic gradient were used to estimate travel time between monitoring locations along the flow path.

A linear regression of the Natural Logarithm of MTBE concentration against time of travel predicts a first order rate in the field of

-3.0 per year.



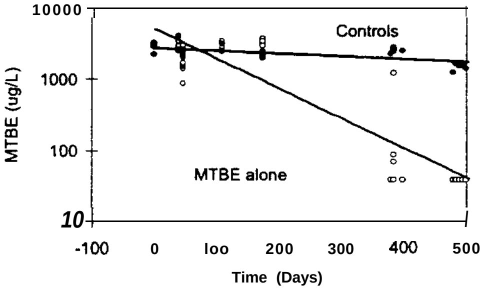
Natural Attenuation of MTBE in Ground Water under methanogenic conditions

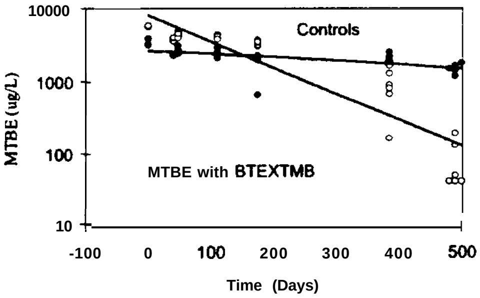
Core material was acquired from the more conductive depth intervals at location MW-14.

Microcosms were constructed with:

MTBE alone, and an autoclaved control

MTBE plus BTEX, and an autoclaved control





Rate of Natural Biodegradation of MTBE under methanogenic conditions in microcosms

Treatment	Rate	Upper 95%	Lower 95%
	--- per year ---		
MTBE alone	-3.21	-3.72	-2.70
MTBE plus BTEXXXTMB	-2.62	-2.95	-2.30

Rates of removal in controls subtracted

Natural Attenuation of MTBE in Ground Water under methanogenic conditions

The rate of attenuation in the field is in good agreement with the rate in laboratory.

At this site, the rate of attenuation was rapid.

Elizabeth City, N.C., Old Fuel Farm

Exposure: Decades

Geochemistry Strongly Methanogenic

MTBE Degradation rate 2 to 3 per year

Elizabeth City, N.C. Fire Station Spill

A leak from a buried pipeline, about 1/2 mile from the fuel farm site.

Exposure < 10 years

Geochemistry is Sulfate Reducing, no Methane

MTBE Degradation in Field 0.47 per year

East Patchhogue, NY

Glacial Sands on Long Island

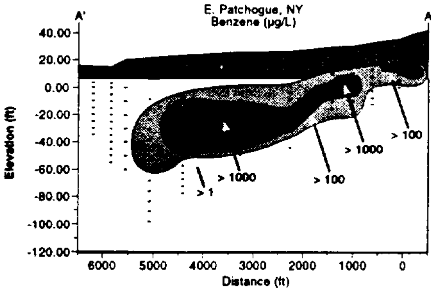
Hydraulic Conductivity 0.05 to 0.10 cm/sec, or

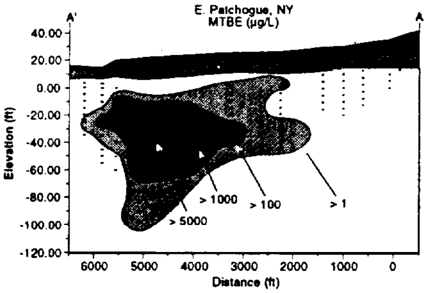
40 to 80 feet/day

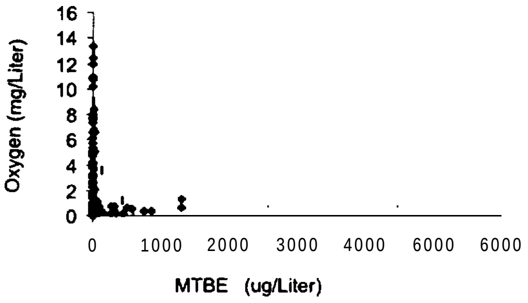
Release after 1979, tanks removed 1988

Geochemistry No Oxygen where MTBE is present, little Methane

MTBE is persistent







East Patchhogue, NY

Glacial Sands on Long Island

Where oxygen is present in the ground water **(>1**.O **mg/L),** MTBE is absent **(<20 ug/Liter)**

MTBE exists in a "shadow" of depleted oxygen, down gradient from the spill.

No Oxygen, No Methane, No MTBE degradation

Location CFB, Ontario

Exposure A few years

Geochemistry No Oxygen
No Nitrate

MTBE Degradation None apparent

Location **CFB,** Ontario

Exposure A few more years

Geochemistry Mixed in Oxygen

MTBE Degradation Gone?

Location CFB, Ontario

Exposure A few more years

MTBE Degradation at Field Scale

0.44 per year

MTBE Degradation in Aerobic Microcosms

2.4 per year

Location Sampson Co, N.C.

Exposure Many years

Geochemistry Iron Reducing

No Methane

MTBE Degradation in Field

0.0, 0.3 and 0.4 per year

MTBE Degradation in Aerobic Microcosms

2.4 per year

Aerobic Degradation of MTBE in Microcosms is much more Rapid than at Field Scale

Aerobic Degradation may be controlled by the Kinetics of Re-oxygenation, not the Kinetics of Biodegradation.

Kinetics of Aerobic Biodegradation may be Specific to the Geochemistry and Geometry of the MTBE plume.

Location Sampson Co, N.C.

Exposure Many years

Geochemistry Iron Reducing

No Methane

MTBE Degradation in Field

0.0, 0.3 and 0.4 per year

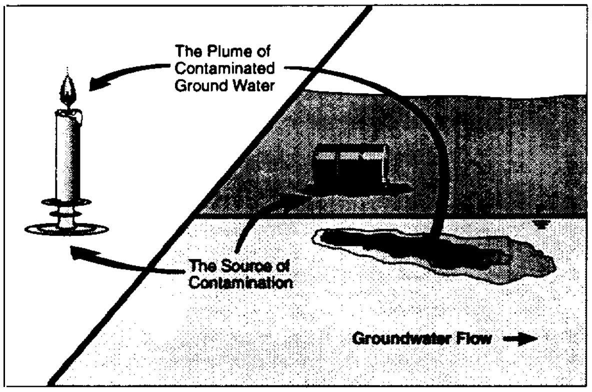
MTBE Degradation in Aerobic Microcosms

2.4 per year

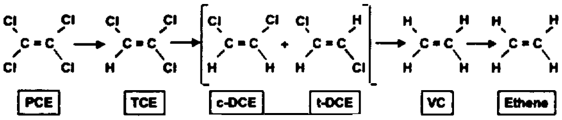
Natural Attenuation of Chlorinated Solvents in Ground Water

John T. Wilson

Office of Research and Development
National Risk Management Research Laboratory
U.S.Environmental Protection Agency
Cincinnati, Ohio



Mechanism of Chloroethene Biotransformation

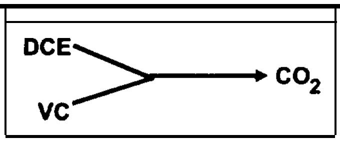


Reductive dehalogenation:
- Oxidation/n **duction** reaction where electrons are transferred from donor to chlorinated hydrocarbon acceptor

Co-metabolic process:
- Organisms growing on alternate carbon **sources**

Primary substrates:
- **Potential** for natural (soil organic matter) and anthropogenic sources

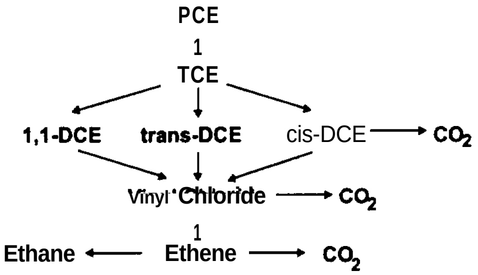
Alternate Pathways for Chloroethene Biotransformation



Oxidative biodegradation:
- Vinyl **chloride** shown to biodegrada under aerobic conditions
- Fe reducers may also oxidize vinyl chloride

Supporting ***evidence:***
- **Transport** properties (migration) of DCE and VC relative to **TCE**
- Aerobic biode**gradation** of **vinyl** chloride to CO_2 dsmonstratsd in microcosms

Native **Biotransformations** for Chloroethenes



Requirements for Reductive Dechlorination

- Primary substrate
  - Native organic carbon, BTEX, landfill leachate, etc.
- Strongly reducing conditions
  - Generally need methanogenic conditions

Behavior of Chlorinated Solvent Plumes

- Type 1 Behavior
  - Primary substrate is anthropogenic organic carbon
  - Solvent plume degrades
- Type 2 Behavior
  - Primary substrate is native organic carbon
  - Solvent plume degrades
- Type 3 Behavior
  - Low native organic carbon concentrations
  - Low anthropogenic organic carbon concentrations
  - PCE. TCE and DCE? do not degrade

Type 1 Behavior

- Primary substrate is anthropogenic organic carbon
  - BTEX, landfill leachate, etc.
- Anthropogenic organic carbon drives dechlorination
- Questions
  - Does electron acceptor supply exceed demand? (i.e., is electron acceptor supply adequate?)
  - Will plume strangle before it starves?
  - What is role of competing electron acceptors?
  - Do PCE, TCE and DCE dechlorinate?
  - Is vinyl chloride oxidized?
  - Is biodegradation rate adequate?

Type 2 Behavior

- Primary substrate is native organic carbon
- Native organic carbon drives dechlorination
- Questions
  - Does electron acceptor supply exceed demand? (i.e., is electron acceptor supply adequate?)
  - Will plume strangle before it starves?
  - What is role of competing electron acceptors?
  - Do PCE, TCE and DCE dechlorinate?
  - Is vinyl chloride oxidized?
  - Is biodegradation rate adequate?

Type 3 Behavior

- Low native organic carbon concentrations
- Low anthropogenic organic carbon concentrations
- Dissolved oxyen (and nitrate) concentration(s) greater than 1.0 mg/L (oxygenated system)
- Reductive dechlorination will not occur
  - Highly halogenated compounds such as PCE and TCE will not degrade
- DCE (?) and VC may be oxidized

Natural Attenuation of Metals in Ground Water

John T. **Wilson**

Office of Research and Development
National Risk Management Research Laboratory
U.S.Environmental Protection **Agency**
Cincinnati, **Ohio**

Factors Affecting the Concentration of Metals in Solution

ion exchange and adsorption

oxidation or reduction reactions

precipitation and dissolution of solids

acid-base reactions

complex formation

Factors Affecting the Concentration of Metals in Solution

ion exchange and adsorption

Cadmium	**Copper**
Lead	**Mercury I and II**
Nickel	**Zinc**

Factors Affecting the Concentration of Metals in Solution

ion exchange and adsorption

relative order of sorption, in general

Lead > Coppers Zinc > Cadmium *Nickel

Sandy Aquifers are particularly vulnerable to Cadmium and Nickel

---

Concentration of Metal in Solution

In the most simple form, described by

Distribution Coefficient

$$K_d = \frac{\text{Concentration on Solids}}{\text{Concentration in water}}$$

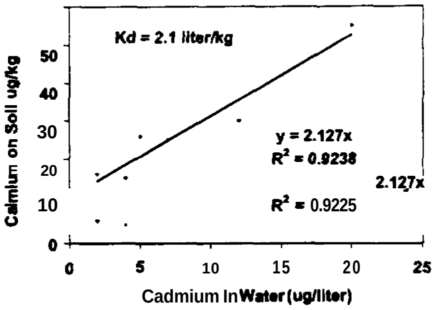
Cadmium and Nickel Distribution Coefficients for Sandy Aquifer Materials

Christensen et al, Journal of Contaminant Hydrology 24(1996):75-84

Sorption isotherms for Cadmium and Nickel in 18 samples of sandy aquifer material from 12 locations in Denmark, at pH ranging from 4.9 to 8.9

Concentration of Metals in Solution

Example sorption isotherm for Cadmium in Sandy aquifer material from Denmark, pH 4.9

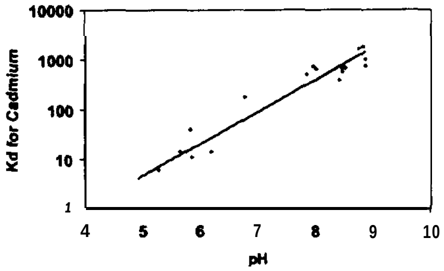


Factors Affecting the Concentration of Metals in Solution

ion exchange and adsorption

Kd is sensitive to the pH of the Ground Water

Effect of pH on Kd for Cadmium in core material from 28 sandy aquifers in Denmark



Concentration of Metal in Solution

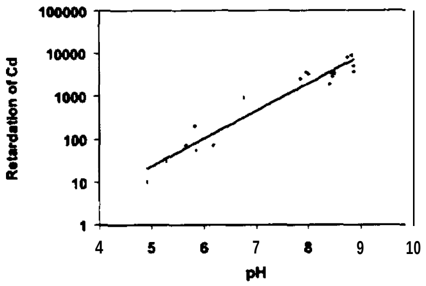
Kd = <u>Concentration on Solids</u>

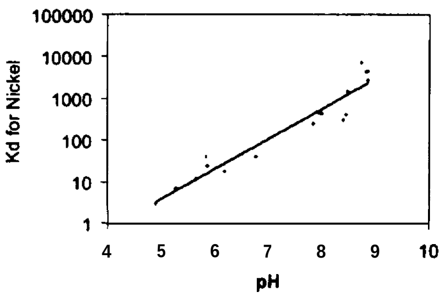
Concentration in water

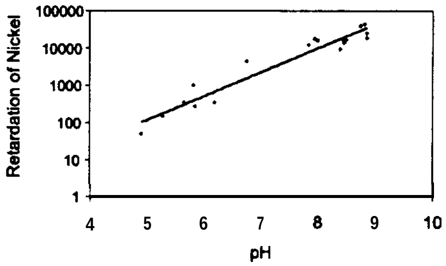
If bulk density = 1.6 kg/liter

and water-filled porosity = 0.32

and Kd >> 1.0 liter/kg;







Factors Affecting the Concentration of Metals in Solution

ion exchange and adsorption

In neutral or alkaline ground water, simple sorption makes a substantial contribution to natural attenuation of metals that are multivalent cations, even in sandy aquifers

Factors Affecting the Concentration of Metals In Solution

oxidation or reduction reactions

Particularly important for Arsenic, Chromium and Manganese

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

Under anaerobic conditions, Arsenic V (AsO_4^{-3} or Arsenate) may serve as an alternate electron acceptor and be reduced to Arsenic III (AsO_2^{-1} or Arsenite) by natural biological activity.

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

Manganese salts of Manganese IV may also be reduced to Manganese II (Mn^{+2}).

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

Arsenite and Mn^{+2} are more toxic than Arsenate or Mn^{+4}, are move soluble, and more mobile in ground water.

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

Under aerobic conditions, Arsenic III (AsO_2^{-1} or Arsenite) and Manganese II (Mn^{+2}) may be oxidized back to Arsenic V (AsO_4^{-3} or Arsenate) and Manganese IV by natural biological activity.

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

Chromium VI exists as an oxyanion, as

bichromate $HCrO_4^-$ below pH 6.5

chromate CrO_4^{-2} near pH 6.5

and dichromate $Cr_2O_7^{-2}$ at concentrations

greater than 10 mM.

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

Chromium VI is mobile in ground water, and is a greater health hazard than Chromium III

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

Chromium III is a cation, that tends to bind strongly to aquifer material

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

Dissolved Organic Matter in the ground water will reduce Chromium VI to Chromium III, making it effectively immobile.

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

Oxidized forms of Manganese in the aquifer matrix material will oxidize Chromium III back to Chromium VI

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

The equilibrium concentration of Chromium VI, and therefore the natural attenuation of chromium, is controlled by the competition between the oxidation and reduction reactions.

Factors Affecting the Concentration of Metals in Solution

oxidation or reduction reactions

The natural attenuation of chromium, is site specific, and must be confirmed by monitoring

Geochemical Processes

Geochemical Processes and Natural Attenuation

U.S. Geological Survey

Why is *Geochemistry Important to Natural Attenuation?*

- Ground-water geochemistry is a record of ongoing chemical, physical, and microbial processes.
- Ergo: The efficiency of natural attenuation can often be determined from ground-water chemistry information (redox conditions).

*What is a **redox** process?*

- Electrons are transferred in chemical or biochemical reactions.
- Benzene + 0, ⟶ CO, + e^-

*In a **redox** reaction, one compound <u>donates</u> an electron and another compound <u>accepts</u> an electron:*

- Benzene + 0, ⟶ CO, + e^- (Benzene is electron donor)
- e^- +TCE ⟶ DCE + Cl^- (TCE is electron acceptor)

***The flow** of **electrons from** donors to acceptors is capable of doing* work.

- Microorganisms (and everybody else) uses the work done by flowing electrons to sustain life functions.

*Biodegradation of Petroleum Hydrocarbons are **electron-donating** processes.*

- Benzene ⟶ CO, + e- (benzene donates e^-)
- $2e^- + \underbrace{0,}_{\text{Electron Acceptor}} \longrightarrow 2H_2O$ (Oxygen accepts e^-)

Because the biodegradation of petroleum hydrocarbons are electron donating processes:

- The availability of electron acceptors determines the rate and extent of biodegradation.
  - Oxygen
  - Fe(III)
  - sulfate
  - CO_2
  - Chlorinated solvents

Benzene Oxidation Aerobic Respiration

$$7.5\ O_2 + C_6H_6 \longrightarrow 6\ CO_{2(g)} + 3\ H_2O$$

$^2G^\circ_r$ = - 3566 **kJ/mole** benzene

Mass Ratio of 0, to C_6H_6 = **3.1:1**

0.32 **mg/L** C_6H_6 degraded per **mg/L** O_2 consumed

Biodegradation of Benzene Consumes Dissolved Oxygen

- Low concentrations of dissolved oxygen are associated with benzene biodegradation coupled to oxygen reduction.

Benzene Oxidation Iron Reduction

$$60H^+ + 30Fe(OH)_{3(a)} + C_6H_6 \rightarrow 6CO_{2(g)} + 30Fe^{2+} + 78H_2O$$

$^2G^\circ_r$ = - 2343 **kJ/mole** benzene

Mass Ratio of $Fe(OH)_3$ to C_6H_6 = 41:1

Mass Ratio of Fe^{2+} produced to C_6H_6degraded = 15.7:1

0.06 **mg/L** C_6H_6 degraded per **mg/L** Fe^{2+} produced

Biodegradation of Benzene Produces Dissolved Iron

- High concentrations of dissolved iron are associated with benzene biodegradation coupled to iron reduction.

Benzene Oxidation Sulfate Reduction

$$7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \longrightarrow 6CO_{2(g)} + 3.75H_2S + 3H_20$$

$^2G^\circ_r$ = - 340 **kJ/mole** benzene

Mass Ratio of SO_4^2 to C_6H_6 = **4.6:1**

0.22 **mg/L** C_6H_6 degraded per **mg/L** SO_4^{2-} **consumed**

Biodegradation *of Benzene Consumes Sulfate*

- Low concentrations of dissolved sulfate are associated with benzene biodegradation coupled to sulfate reduction.
- High concentrations of H_2S

Benzene Oxidation Methanogenesis

$4.5\ H_2O + C_6H_6 \longrightarrow$ 2.25 CO,,,, + 3.75 CH,

$^2G^\circ_r$ = - 135.6 kJ/mole benzene

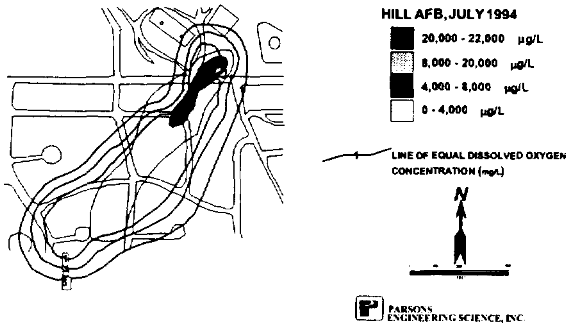
Mass Ratio of CH, produced to C_6H_6 = 0.8:1

1.25 mg/L C_6H_6 degraded per mg/L CH, produced

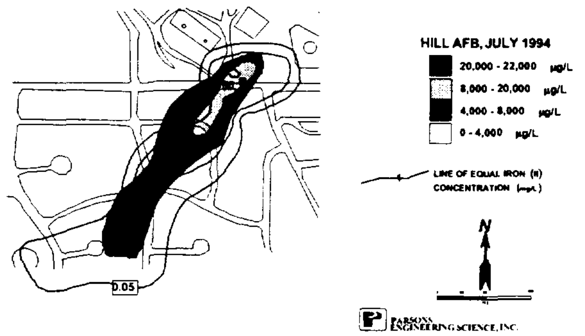
Biodegradation of Benzene Produces Methane

- High concentrations of methane are associated with benzene biodegradation coupled to methanogenesis.

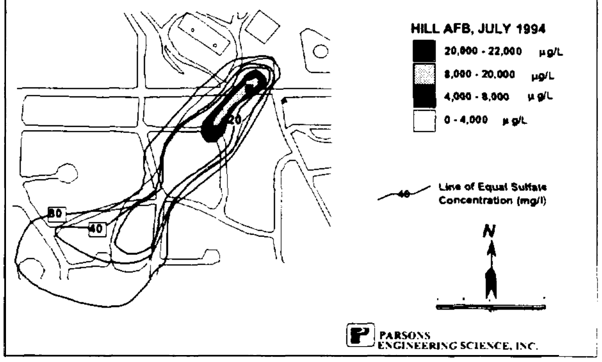
Total BTEX and Dissolved Oxygen

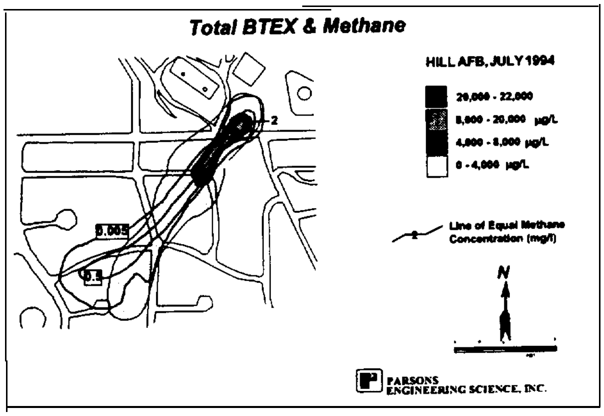


Total BTEX and Iron (II)



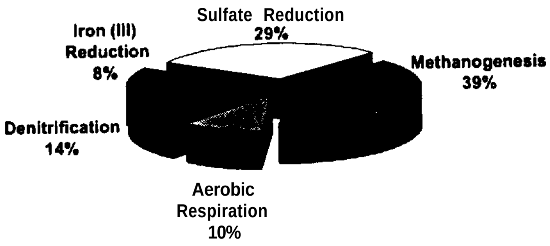
Total BTEX & Sulfate





Total BTEX & Methane

Relative Importance of Biodegradation Mechanisms at 25 Sites



Geochemical Data Can Indicate:

- If biodegradation is occurring.
- If biodegradation has occurred in the past.
- If electron acceptors are available to support biodegradation in the future!

Redox Zonation and Biodegradation Efficiency

U.S. Geological Survey

---

*In a **redox** reaction, one compound <u>donates</u> an electron and another compound <u>accepts</u> an electron:*

- Benzene + O_2 $\longrightarrow$ CO_2 + e^- (Benzene is electron donor)
- e^- +TCE $\longrightarrow$ DCE + Cl- (TCE is electron acceptor)

***The flow of electrons from donors** to acceptors is capable of doing work.*

- Microorganisms (and everybody else) uses the work done by flowing electrons to sustain life functions.

---

*Biodegradation of Chlorinated ethenes **can** be electron-accepting processes (ie., reductive dechlorination).*

- TCE + e^- $\longrightarrow$ cis-DCE + Cl^-

---

*Biodegradation of **chlorinated** ethenes can also be **electron-**donating processes (oxidation).*

- Vinyl Chloride $\longrightarrow$ CO_2 + Cl + e-

+ $2e^-$ + O_2 $\longrightarrow$ $2H_2O$

Because of this complexity, chlorinated ethenes do not behave uniformly in ground-water systems

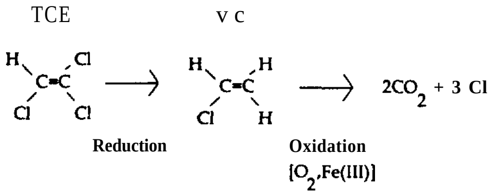
- **Poly-Chlorinated** ethenes will reduce under reducing conditions.
- DCE and VC will oxidize under oxidizing conditions.

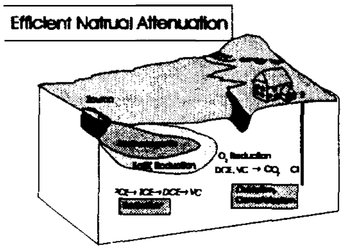
The Rate and Extent of Biodegradation Processes at any Given Site Depends Upon:

- ❖ Ambient **Redox** Conditions
- ❖ The <u>Succession</u> of **Redox** Conditions

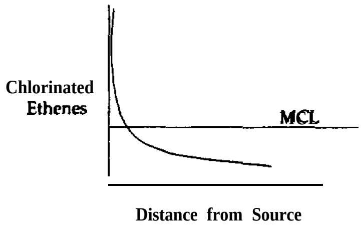
EXAMPLE

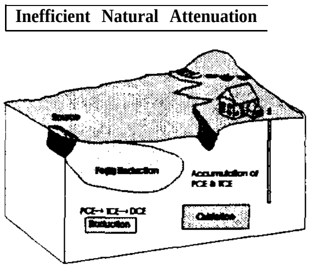
Sequential Reduction/Oxidation



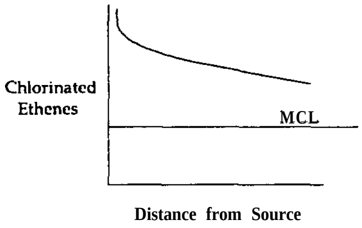


Efficient NA leads to rapid decrease of contaminants away from source area.





Inefficient NA leads to gradual decrease of contaminants away from source area.



How can we quickly screen water chemistry data from a site in order to determine if chlorinated solvent biodegradation is possible?

Initial Screening Process

The screening process is designed to recognize reductive dechlorination of chlorinated solvents.

It presupposes that natural attenuation of chlorinated solvents in most plumes will be not be important unless the solvents are initially dechlorinated.

Analytical Parameters and Their Weighting for Preliminary Screening

Analysis	Condition	Value
Oxygen	< 0.5 mg/L	3
Oxygen	> 1.0 mg/L	-3
Nitrate	< 1 mg/L	2
Iron II	> 1 mg/L	3

Analytical Parameters and Their Weighting for Preliminary Screening

Oxygen is toxic to the organisms that carry out reductive dechlorination.

If it is present reductive dechlorination cannot occur.

Analytical Parameters and Their Weighting for Preliminary Screening

Analysis	Condition	Value
Sulfate	< 20 mg/L	2
Sulfide	> 1 mg/L	3
Methane	> 0.1 mg/L	2
	> 1.0 mg/L	3
Redox(Eh)	< +50 millivolts	1
	< -100 millivolts	2

Analytical Parameters and Their Weighting for Preliminary Screening

Analysis	Condition	Value
DOC	>20 mg/L	2
Temp	> 20°C	1
CO_2	> 2x background	1
Alkalinity	> 2x background	1

Analytical Parameters and Their Weighting for Preliminary Screening

Analysis	Condition	Value
Chloride	> 2x background	2
Hydrogen	> 1 nanomolar	3
VFA	> 0.1 mg/L	2
BTEX	> 0.1 mg/L	2

Analytical Parameters and Their Weighting for Preliminary Screening

Analysis	Condition	Value
Reduced daughter products TCE, DCE, vinyl chloride, chloroethane, chlorobenzene		2
Ethene	> 0.01 mg/L > 0.1 mg/L	2 3

Hypothetical Site #1

Analysis	Condition	Score
DO	0.1 mg/L	3
Nitrate	0.3 mg/L	2
Iron II	10 mg/L	3
Sulfate	2 mg/L	2

Hypothetical Site #1

Analysis	Condition	Score
Methane	5 mg/L	3
Redox	-190 millivolts	2
Chloride	45 mg/L	
Background	10 mg/L	2

Hypothetical Site #1

Analysis	Condition	Score
PCE (spilled)	1,000 µg/L	0
TCE (not spilled)	1,200 µg/L	2
cis-DCE	500 µg/L	2
Vinyl chloride	50 µg/L	2

Hypothetical Site #2

Analysis	Condition	Score
DO	3.0 mg/L	0
Nitrate	0.3 mg/L	2
Iron II	Not Detected	0
Sulfate	10 mg/L	2

Hypothetical Site #2

Analysis	Condition	Score
Methane	Not Detected	0
Redox	+100 millivolts	0
Chloride Background	15 mg/L 10 mg/L	0

Hypothetical Site #2

Analysis	Condition	Score
TCE (spilled)	1,200 µg/L	0
cis-DCE	< 1 µg/L	0
Vinyl chloride	< 1 µg/L	0

Interpretation of Results from Preliminary Screening

Total Score	Interpretation
0 to 5	Inadequate evidence
6 to 15	Limited evidence
16 to 20	Adequate evidence
over 20	Strong evidence

Interpretation of Results from Preliminary Screening

Hypothetical Site #1

23 total points - strong evidence

Hypothetical Site #2

4 total points - inadequate evidence

The Rate and Extent of Chlorinated Ethene Biodegradation Processes Depends Upon:

- Ambient Redox Conditions
- The Succession of Redox Conditions

How Hydrogeology Affects the Efficiency of Natural Attenuation

How Hydrogeology Affects the Efficiency of Natural Attenuation

U.S. Geological Survey

OSWER recognizes that Natural Attenuation Processes include physical, biological, and chemical processes . These are:

- ❖ Physical (Dispersion, advection).
- ❖ Chemical transformations (sorption).
- ❖ Biological processes (reduction, oxidation).

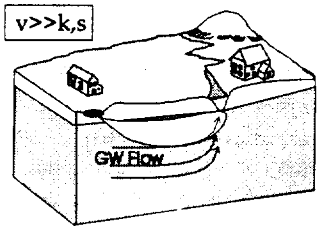
How can we take all of these processes into account?

- ❖ To illustrate, let s do a mental experiment.

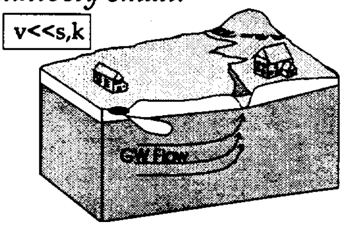
Consider a contaminant spill that reaches the water table. The size of the contaminant plume that develops is controlled by:

- ❖ Size of the spill.
- ❖ velocity of G.W. flow (v).
- ❖ Sorptive capacity of aquifer solids (s).
- ❖ Biodegradation (k).

***If** v is large compared to s and **k,** the plume will be relatively large.*



*Conversely, ifv is small relative to s and **k,** the plume will be **relatively small.***



*Postulate: The **efficiency** of natural attenuation is inversely proportional to the distance of contaminant migration*

$$E \sim l/d$$

Therefore: The efficiency of natural attenuation depends on:

- Velocity of ground water
- Sorptive capacity of aquifer
- Rates of biodegradation

***This** reasoning is useful because it can be quantified:*

$$\frac{\partial C}{\partial t} = \underbrace{D\frac{\partial^2 C}{\partial x^2}}_{\text{dispersion}} - \underbrace{v\frac{\partial C}{\partial x}}_{\text{advection}} - \underbrace{SC^n}_{\text{sorption}} - \underbrace{kC}_{\text{biodegradation}} \tag{1}$$

OSWER recognizes that Natural Attenuation Processes include physical, biological, and chemical processes . These are:

- Physical (Dispersion, advection).
- Chemical transformations (sorption).
- Biological processes (reduction, oxidation).

This is saying *mathematically, what the OSWER Directive says in English.*

$$\frac{\partial C}{\partial t} = \underbrace{D\frac{\partial^2 C}{\partial x^2}}_{\text{dispersion}} - \underbrace{v\frac{\partial C}{\partial x}}_{\text{advection}} - \underbrace{SC^n}_{\text{sorption}} - \underbrace{kC}_{\text{biodegradation}} \tag{1}$$

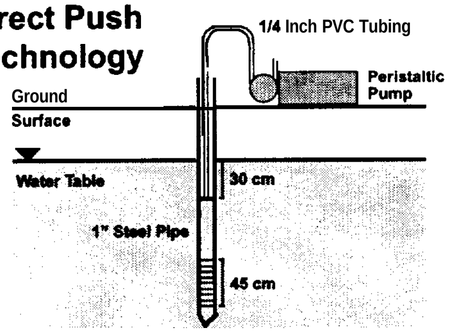
The key to assessing natural *attenuation is to have:*

- Hydrologic information (directions and rates of GW flow).
- Geochemical information (sorptive capacity of aquifer sediments).
- Microbiologic information (rates of biodegradation).

How do you get this information ?

- Hydrologic testing (hydraulic conductivity, water-level maps)
- Geochemical testing (redox conditions, sorptive capacity).
- Microbiologic testing (field and/or lab).

Direct Push Technology

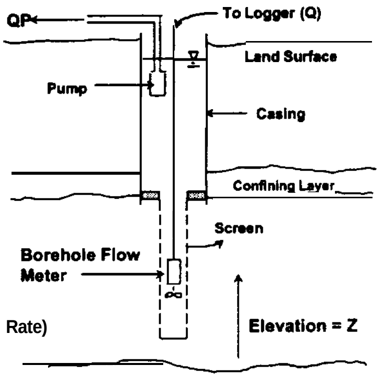


Application of the Electromagnetic Borehole Flowmeter

Steven C. Young, Hank E. Julian,
Hubert S. Pearson, Fred J. Molz, and
Gerald K. Boman

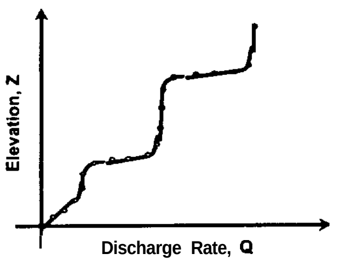
EPA/600/SR-98/058

Apparatus and Geometry Associated with a Borehole Flowmeter Test

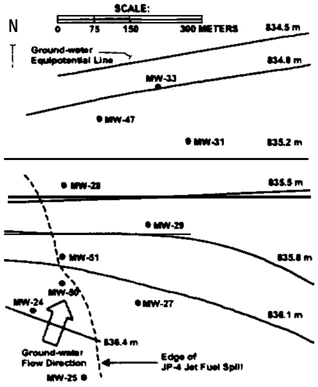


(Q = Discharge Rate)

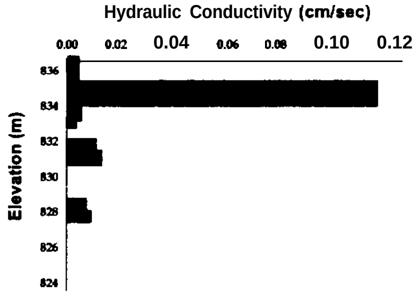
Data from a Borehole Flowmeter Test



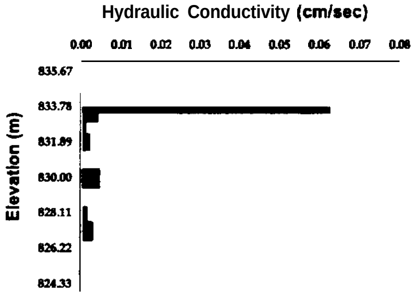
George Air Force Base, California



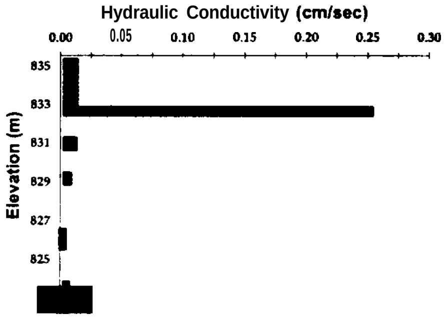
Hydraulic Conductivity - MW 27



Hydraulic Conductivity - MW 29



Hydraulic Conductivity - MW 31

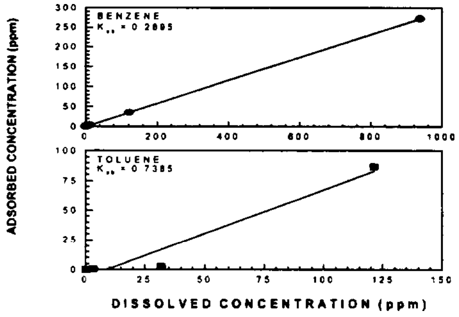


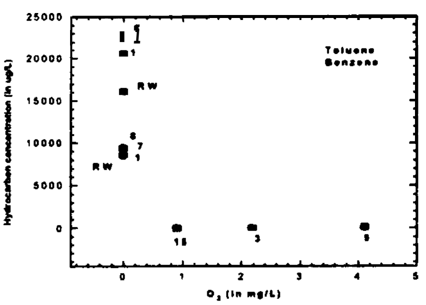
George AFB

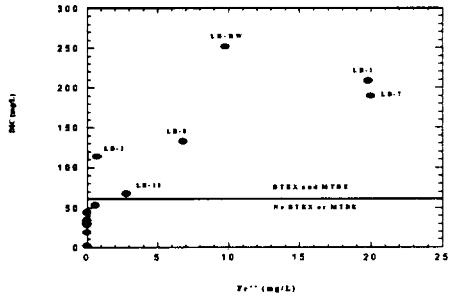
Monitoring Well	Average Hydraulic Conductivity **(cm/sec)**	Hydraulic Conductivity of Most Transmissive Interval (cm/sac)
MW-27	0.0074	0.11
MW-26	0.0046	0.022
MW-29	0.0026	0.062
MW-31	0.013	0.26
MW-45	0.0032	0.0066
MW-46	0.016	0.40

How do you get this information?

- Hydrologic testing (hydraulic conductivity, water-level maps)
- Geochemical testing (redox conditions, sorptive capacity).
- Microbiologic testing (field and/or lab).



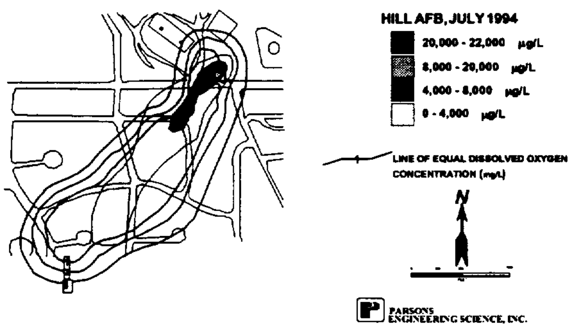




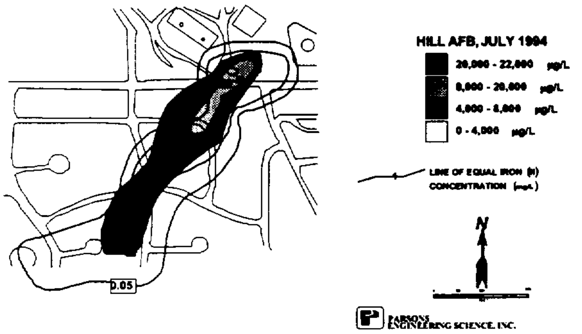
How do you get this information?

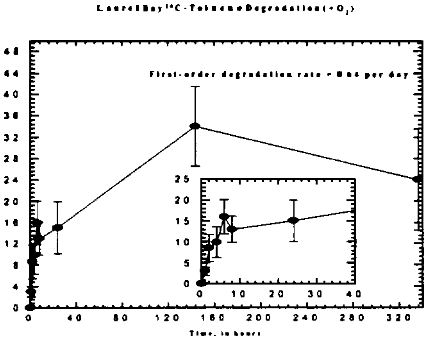
- Hydrologic testing (hydraulic conductivity, water-level maps)
- Geochemical testing (redox conditions, sorptive capacity).
- Microbiologic testing (field and/or lab).

Total BTEX and Dissolved Oxygen



Total BTEX and Iron (II)

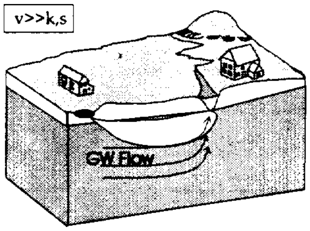




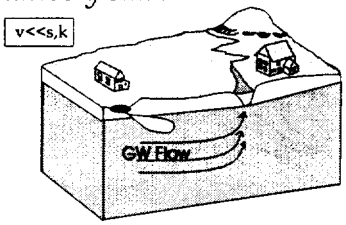
Analytic or Digital Soulutions can then be used to assess Natural Attenuation:

$$\frac{\partial C}{\partial t} = \underbrace{D\frac{\partial^2 C}{\partial x^2}}_{\text{dispersion}} - \underbrace{v\frac{\partial C}{\partial x}}_{\text{advection}} - \underbrace{SC^{n}}_{\text{sorption}} - \underbrace{kC}_{\text{biodegradation}} \qquad (1)$$

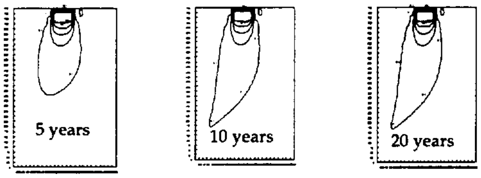
If v is large compared to s and k, the plume will be relatively large.



Conversely, ifv is small relative to s and k, the plume will be relatively small.



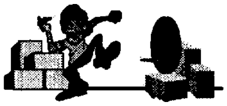
Example 1: Source Remains in Place:Plume becomes stable.



Example 2: Source Removed: Plume dissipates.

Even with sophisticated models, there is still uncertainty!

- Predictive models must be tested against historical data.
- Modeling must be verified with monitoring data.



Site Characterization and Data Interpretation for Evaluation of Natural Attenuation at Hazardous Waste Sites

Site Characterization and Data Interpretation for Evaluation of Natural Attenuation at Hazardous Waste Sites

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The most common site characterization question.

How many wells are enough?

The Two Most Common Answers

- As many as you can get.
- It's site specific.

Review of the current state of practice for site characterization.

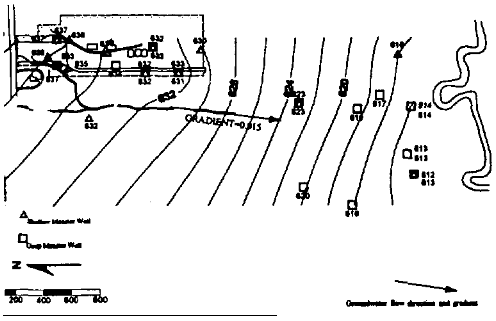
"State of the Practice"

- Install monitoring wells to determine ground-water flow direction.
- Install additional monitoring wells downgradient of the source area to define the extent of contamination.

“State of the Practice”

- Determine whether the plume is expanding, steady-state or shrinking.
- Determine whether the plume has impacted or will impact receptors.

A Typical Site



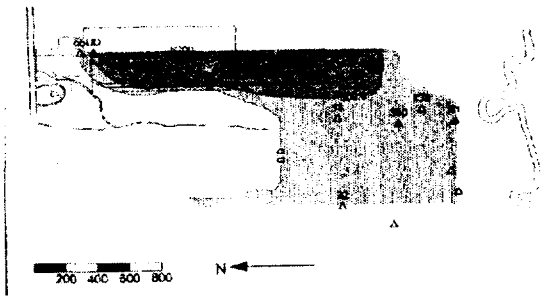
- * Upgradient monitoring wells were used to define background conditions in the aquifer.
- Additional wells were installed along the inferred centerline of the plume.
- Wells were placed on the lateral and terminal edges of the plume.

Typical Data Presentation

- Contour maps depict concentration profiles of a variety of parameters.
- These maps show the *size* and *shape* of the contaminant plume and distribution of geochemical parameters.
- Data are presented in terms of surface area impacted.

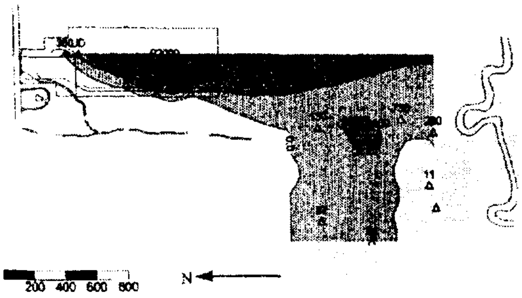
PCE (ppb)

Deep PCE (µg/L)

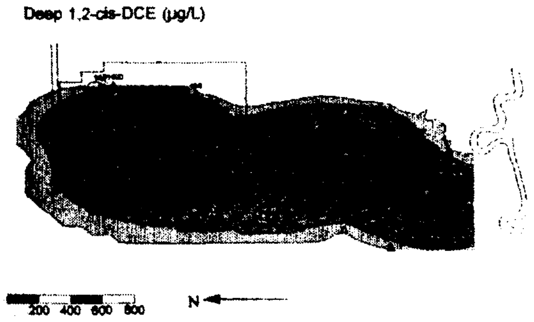


TCE (ppb)

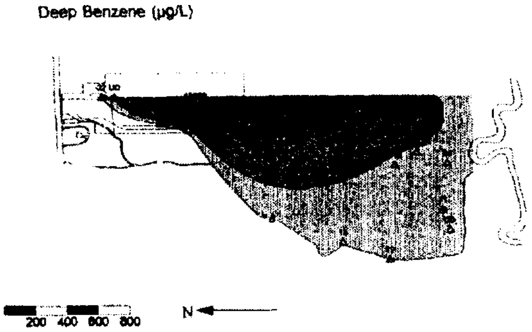
Deep TCE (µg/L)



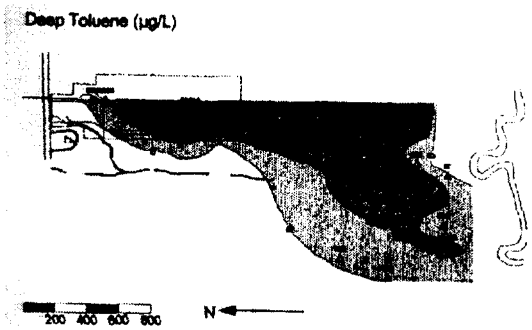
cis-DCE (ppb)



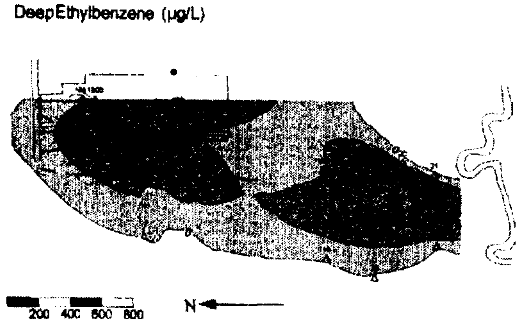
Benzene (ppb)



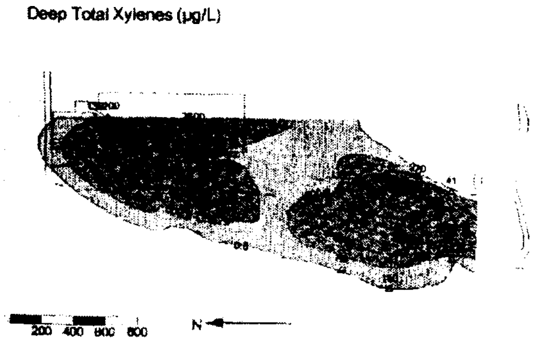
Toluene (ppb)



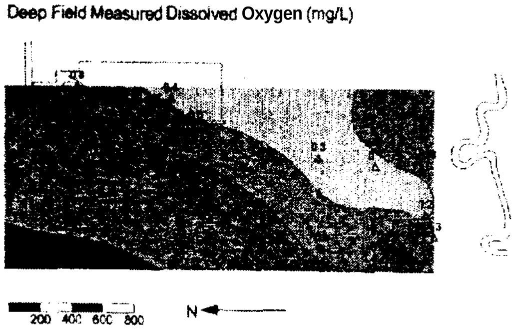
Ethylbenzene (ppb)



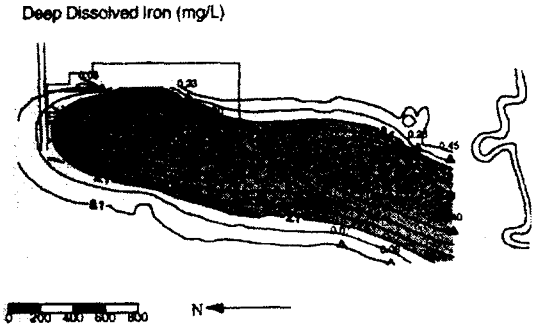
Xylene (ppb)



Oxygen (mg/L)



Iron (II) (mg/L)



Rules of Thumb for Site Investigations

- Dissolved oxygen is directly proportional to redox potential.
- Dissolved oxygen concentrations are inversely proportional to iron II and alkalinity concentrations.

Rules of Thumb for Site Investigations

- Alkalinity concentrations are directly proportional to iron II, but iron II is not necesarrily directly proportional to alkalinity.

Typical Site Characterization

- Designed to determine absence or presence of contamination.
- Not designed to describe how the plume is behaving.

Typical Site Characterization

- Typically uses permanent monitoring wells to map the contaminant plume.
- Emphasizes concentrations of contaminants of concern.

Typical Site Characterization

- Does not emphasize hydrogeologic characterization of the site. At best, it uses slug testing to estimate the transmissivity of the screened interval.

Typical Site Characterization

- Conceptualizes the plume as a static object in 2-D space

- There is a fundamental difference in the requirements for site characterization if natural attenuation is to be evaluated as a remedy.

Selection of natural attenuation as a remedy demands a higher level of understanding of mechanisms acting on the contaminant plume than needed for other remediation techniques. Therefore, more importance is given to collecting data from within the plume.

Contour maps do not provide information on the rate of ground-water flow, the flux of contamination being released from the source area, the quantity of contaminant in the plume, or the flux of contaminant to surface waters or other receptor.

An Iterative Approach to Fate and Transport

- Typically uses push technology to map the contaminant plume.
- Emphasizes the concentrations of geochemical indicators, as well as contaminants.

An Iterative Approach to Fate and Transport

- Concentration data are also organized to determine the flux of contaminant in the entire plume from the source, along the flow path and to the receptor.

Calculation of Contaminant Flux Along the Flowpath

- The reduction in the flux along the flowpath is the best estimate of natural attenuation of the plume *as a whole.*

Calculation of Contaminant Flux Along the Flowpath

- The flux is the best estimate of the amount of contaminant leaving the source area. This information would be needed to scale active remedy if necessary.

Calculation of Contaminant Flux Along the Flowpath

- Flux estimate across the boundary to a receptor is the best estimate of loading to a receptor.

An Iterative Approach to Fate and Transport

- Has a greater investment in hydrogeological characterization.
- More conservative estimates of transmissivity are produced by conducting pumping tests.

Benefits of an Iterative Approach to Fate and Transport

- Higher resolution site characterization.
- Optimization of well placement.
- More representative data.
- Better understanding of the fate and transport of contaminants.

Thermo Chem Case Study

Purpose of the Case Study

- Compares three levels of. characterization; (1) Conventional wells widely spaced, (2) Dense array of conventional wells in transects, (3) GeoProbe transects.

Purpose of the Case Study

- The dense array of conventional wells arranged in transects are assumed to yield correct data.

Purpose of the Case Study

- Results from the dense array of conventional wells are compared to a dense array of GeoProbe samples to evaluate the performance of push techniques.

Purpose of the Case Study

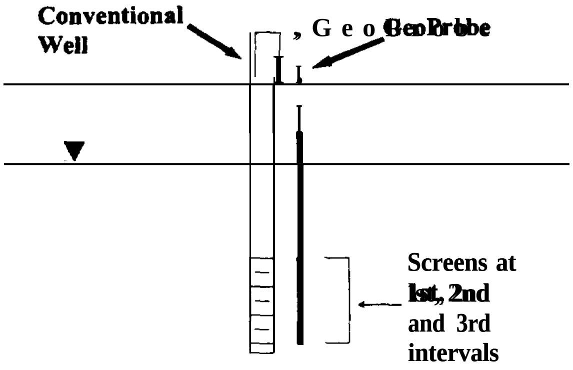
- Results from the dense array of conventional wells are compared to a conventional array of monitoring wells to determine the resolution of conventional monitoring strategies.

Benchmarking Direct-Push Technology Against Permanent Wells

- Hydraulic Conductivity Tests
- Contaminant Data
- Geochemical Data

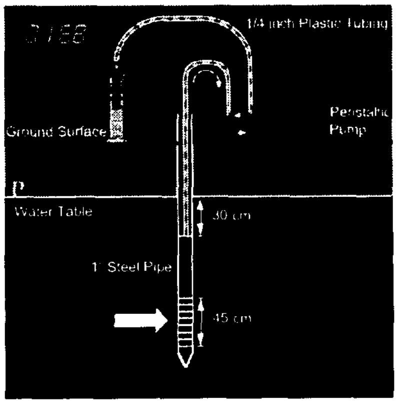
Hydraulic Conductivity Tests

- A GeoProbe unit was used to estimate hydraulic conductivity values at the same depth intervals as existing conventional monitoring wells.



K Tests

- Single well pumping test (Specific Capacity)
- Measure discharge and drawdown



K Tests

- 1.5' GeoProbe screens
- Permanent monitoring well screens ranged from 4 to 9 ft.
- Comparison was conducted over the same interval.
- Distance between the push probe and monitoring well varied from 3 to 10 feet.

Data Analysis

- Jacob's solution to the Theis equation was used to estimate transmissivity .

Jacob's Solution (1946) to the Theis Equation

$$\frac{Q}{\Delta s} = \frac{T}{264 \log\left(\frac{0.3Tt}{r^2 S}\right)}$$

- Q = pumping rate, gpm
- s = drawdown in the well, ft
- T = transmissivity, gpd/ft (assume 30,000 gpd/ft initially, then revise with first estimate from calculations)
- t = time since pumping started, days

- r = radius of the well, ft
- S = storativity, dimensionless (.001 for a confined aquifer, .075 for unconfined aquifers)

The known parameters can be substituted into the equation and simplified for easier use.

For example, when using a direct push well

- T = 30,000 gpd/ft
- t = 0.01 days
- r = 0.04 ft
- s = .075

The equation can be simplified to

$$T = 1550\left(\frac{Q}{\Delta s}\right)$$

For example, when using a direct push well

- T = 30,000 gpd/ft
- t = 0.01 days
- r = 0.16 ft
- s = .075

The equation can be simplified to

$$T = 1230\left(\frac{Q}{\Delta s}\right)$$

Then substitute the measured Q and drawdown to get an estimate of T.

Divide T by screen length to get a relative estimate of K for the interval tested.

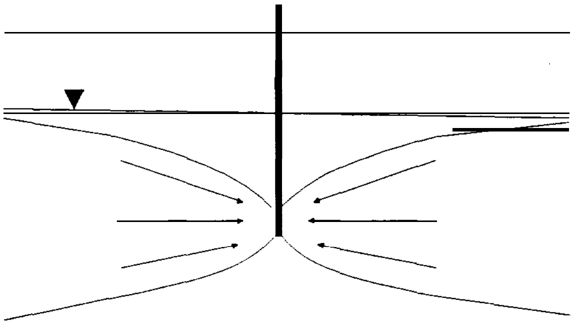
Assumptions

- Borehole storage is negligible
- Horizontal flow.
- Late-time conditions are reached quickly.
- 100% efficient wells.
- Laminar flow exists throughout the well and aquifer.

Partial Penetration

- Since the GeoProbe screens are only partially penetrating, estimates of K average conductivities from above and below the interval being tested due to radial flow.

Partial Penetration of an Aquifer by a GeoProbe Screen



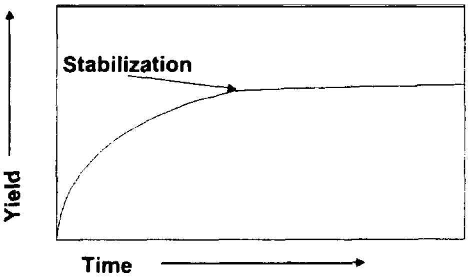
Late Time Conditions

- Early time data may be invalid for use with the Jacob Solution to the Theis equation.

Late Time Conditions

- The Jacob equation largely ignores the effect of time on pumping yield. The calculation of u, an evaluation parameter, is necessary to ensure that the asymptote has been reached.

Late Time Conditions



Late Time Conditions

- If the calculated u is less than 0.05, then the assumption of late time conditions is justified.

Late Time Conditions

$$u = \frac{1.87\, r^2\, S}{Tt}$$

Late Time Conditions

- For example, when r = 0.5 in. (0.04 ft), S = 0.075, T = 5000 gpd/ft, and t = 20 min (0.01 days):

P-f

Late Time Conditions

$$\frac{1.87(0.04)^2\,0.075}{(5000)(0.01)}$$

Late Time Conditions

$$u = 0.000004$$

Laminar Flow

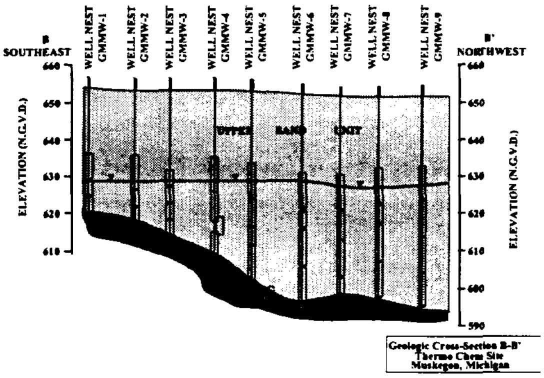
- Q=VA
- Q = maximum pumping rate at which laminar flow exists
- V = entrance velocity (can not exceed 0.1 ft/sec (0.03 m/sec)}
- A = open screen area

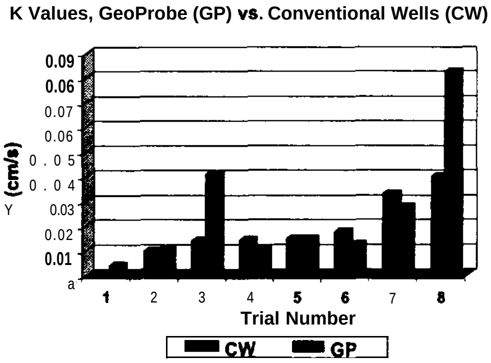
Laminar Flow

- For example, when A = 0.0042 ft^2
- Q = 0.1 ft/sec (0.0042 ft^2)
- Q = 0.00042 ft^3/sec or approximately 700 mL/min

- This calculation is necessary because of the limited open screen area in the GeoProbe point. Exceeding the maximum discharge will result in well efficiency concerns and invalid estimates of K.

Results





In the glacial-outwash sands at this site, the GeoProbe test and permanent monitoring wells produced comparable estimates of hydraulic conductivity.

Range of Values

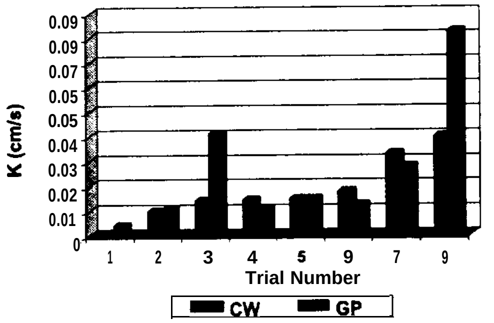
- K values ranged from 0.00005 cm/s to 0.1 cm/s.
- Certainly both methods had enough sensitivity to differentiate between low and high flow zones during site characterization.

- However, some of the assumptions associated with this method of data analysis are not met. Thus, the GeoProbe method of approximating K was used for preliminary site analysis.

Comparing Push Technology to Permanent Wells

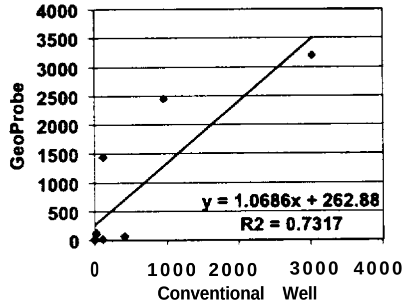
- When the two estimates of K differed, the estimate acquired using the GeoProbe was larger.

K Values, GeoProbe (GP) vs. Conventional Wells (CW)

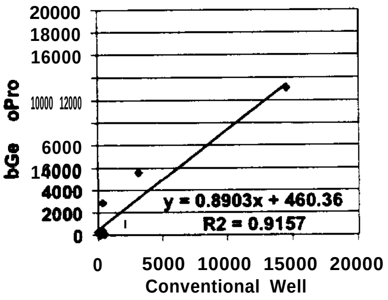


Contaminant Data

Correlation Between PCE Concentrations Obtained from Conventional Wells and GeoProbe Points

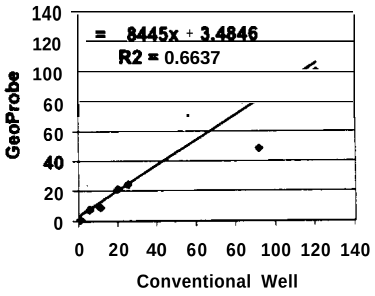


Correlation Between TCE Concentrations Obtained from Conventlonal Wells and GeoProbe Points

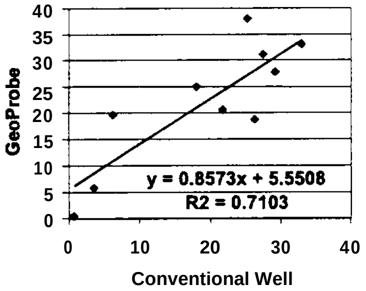


Geochemical Data

Correlation Between Chloride Concentrations Obtained from Conventional Wells and GeoProbe Points



Correlation Between Sulfate Concentrations Obtained from Conventional Wells and GeoProbe Points

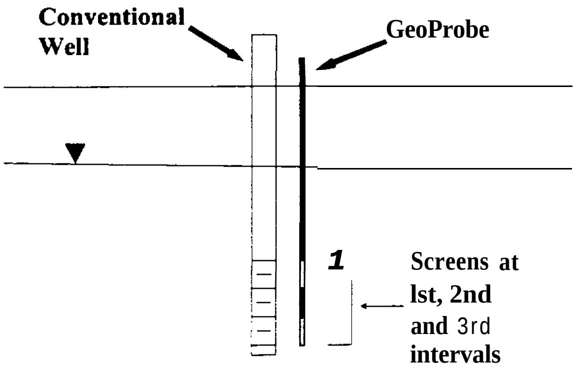


Calculation of Contaminant Flux Along the Flowpath

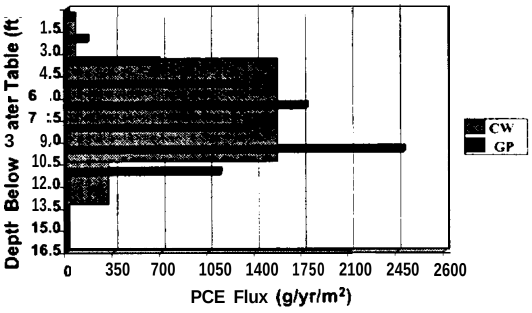
Contaminant Flux Calculations

- Flux = VAC
- V = interstitial seepage velocity
- A = cross-sectional area represented by the sample
- C = concentration

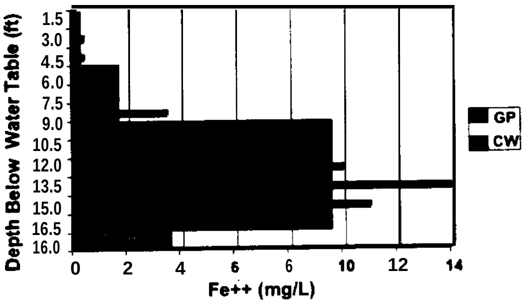
Using push-technology it is possible to see contaminant flux and geochemical distribution with greater resolution.



PCE Flux (g/yr/m²), GeoProbe (GP) vs. Conventional Wells (CW)



Fe ++ (mg/L), GeoProbe (GP) vs. Conventional Wells (CW)



Flux Estimates

- Flux estimates from permanent transect wells, GeoProbe transect wells, and a conventional array of wells (located in same area as the transect) were calculated.

Estimates of Flux Across Transect (kg/yr)

	Permanent Transect	GeoProbe Transect	Conventional Well Array
PCE	55.1	45.9	1.5
TCE	182.5	224.2	8.9
cis-DCE	311.7	918.0	19.0
v c	26.7	53.0	0.05

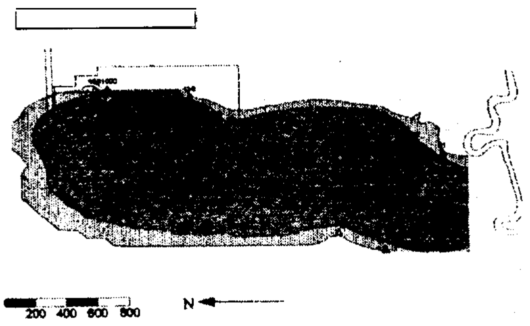
Flux Estimates

- Due to the wide spacing, the conventional array of wells fails to adequately characterize contaminant flux. The more densely sampled transects yield much more conservative estimates.

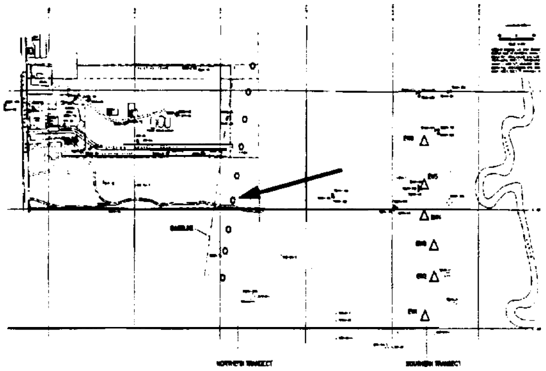
Data Use

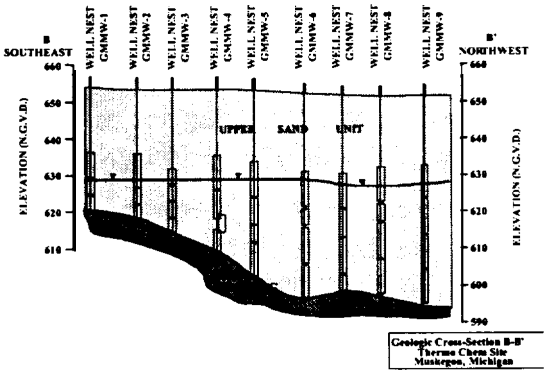
- By examining preliminary contaminant flux and geochemical data, judgements can be made about the heterogeneity of natural attenuation before proceeding further.

Location of the Plume

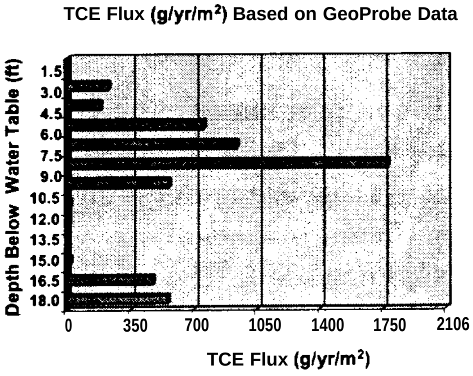


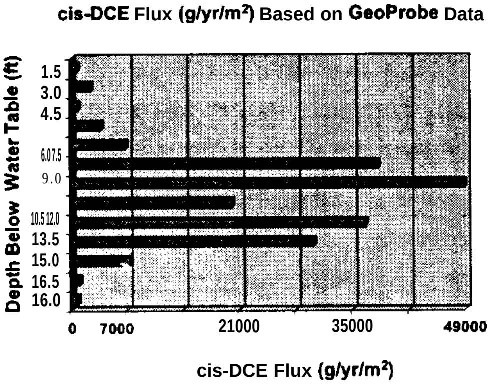
Transect Location



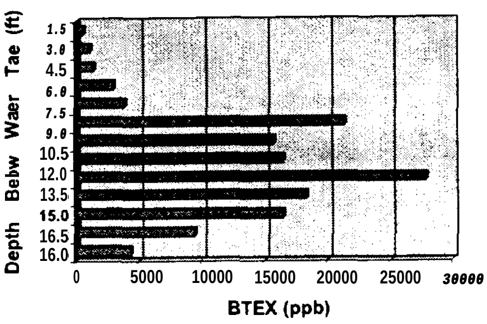


- Data presented are from GeoProbes near well cluster 6. This is the most heavily impacted location along the transect.

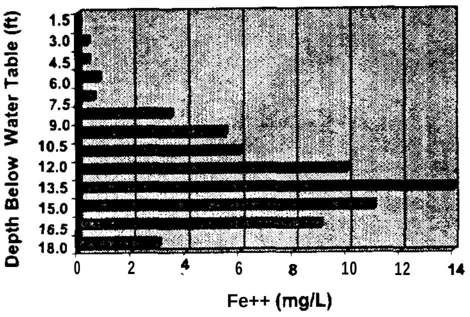




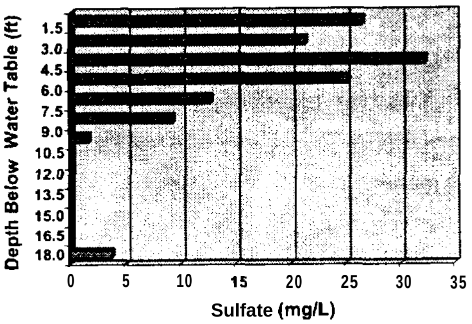
BTEX Concentrations (ppb) Based on GeoProbe Data



Fe ++ Concentrations (mg/L) Based on GeoProbe Data



Sulfate Concentrations (mg/L) Based on GeoProbe Data



Lines of Evidence

- Disappearance of contaminants - Less flux of TCE is apparent in some of the intervals (9 - 16.5 ft).
- Appearance of byproducts - At this site, intervals that yield small amounts of TCE yield large amounts of cis-DCE.

Lines of Evidence

- BTEX is present at the appropriate interval to drive reductive dechlorination.
- Fe++ is being produced, and sulfate is being removed in the interval containing a higher cis-DCE flux.

Interpretation

- The contaminants in the interval 9 - 16.5 feet below the water table are undergoing significant biological transformation.

Temporary Transects

- **The majority of the intervals along the transect produce evidence that biological attenuation is occurring.**

Temporary Transects

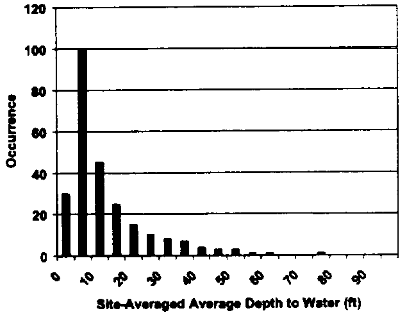
- **Natural attenuation may or may not be protective of potential receptors.**
- **The preliminary data justifies carrying out a complete assessment of natural attenuation.**

Extent, Mass, and Duration of Hydrocarbon Plumes from Leaking Petroleum Storage Tank Sites in Texas

Robert E. Mace, R. Stephen Fisher, David M. Welch, and Sandra P. Parra

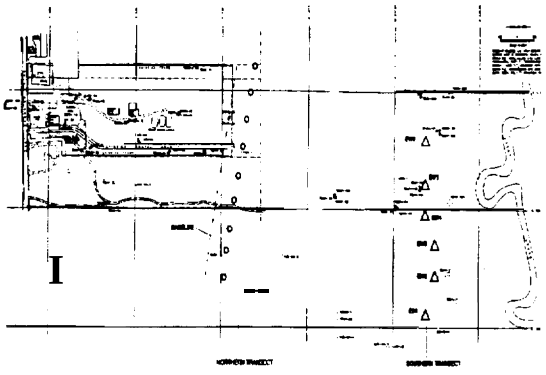
Bureau of Economic Geology
University of Texas at Austin
Austin, Texas 787 13-8924

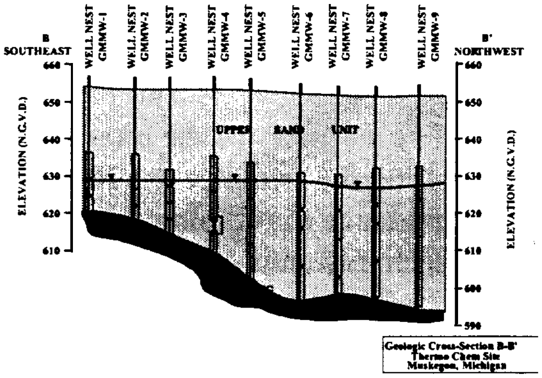
Average Depth to Water at 246 Sites



Construction of Permanent Transects

A permanent transect (designated by the circles) was constructed at the site to conduct long term monitoring of temporal trends in flux and geochemical parameters.





Benefits of Constructing Transects

- Reveals the characteristics of a cross section of the contaminant plume.
- Temporal comparisons can be made on the same water with the aid of a downgradient transect.

- More accurate flux and degradation rate estimates due to a more comprehensive sampling of the plume.

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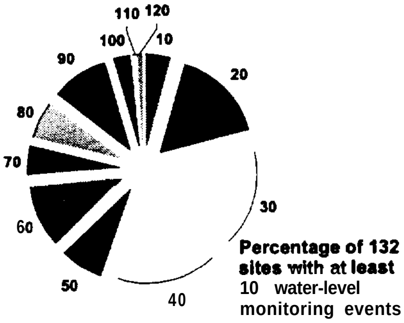
Standard Deviation of the Direction of Hydraulic Gradient (degrees)



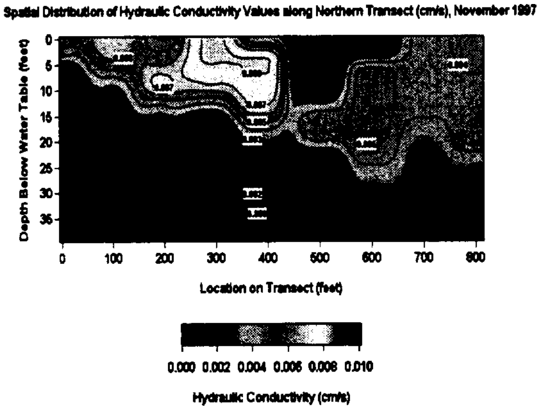
The previous cross section reveals the vertical placement of the well screens within each cluster along the transect.

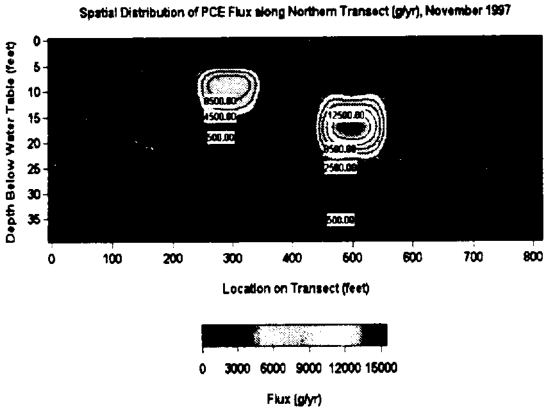
Monitoring of the Permanent Transect

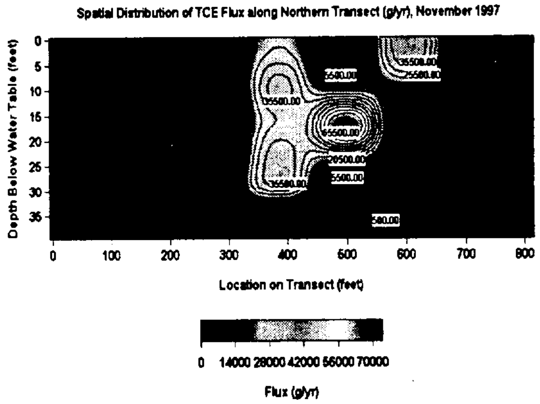
- Using the same methods as with the site characterization, flux and geochemical data can be collected at any time.

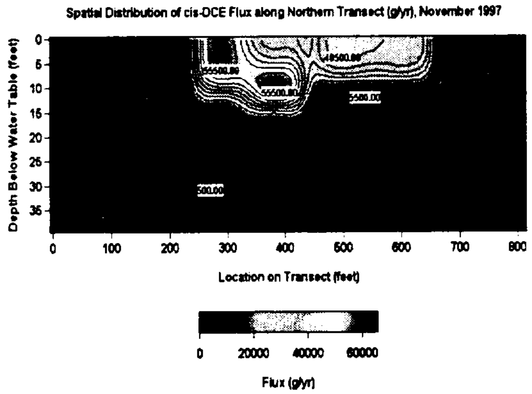
Also, the spatial relationships between contaminants, electron acceptors, and carbon sources can be demonstrated by mapping the transect.

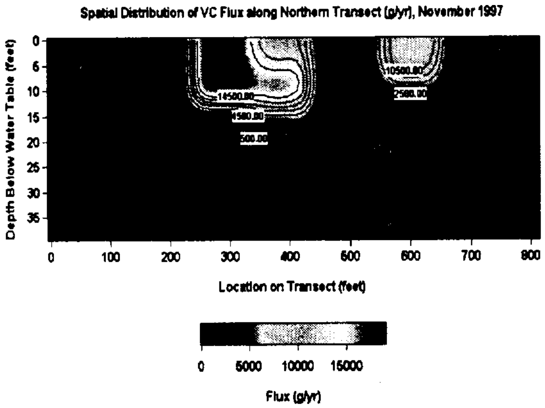
When viewing transect maps remember that ground-water flow is from the viewer into the screen.

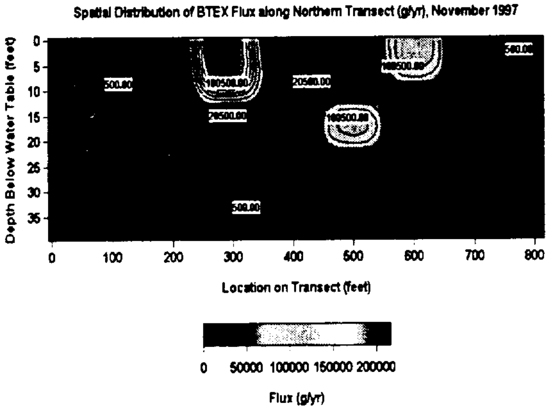



Spatial Distribution of PCE Flux along Northern Transect (g/yr), November 1997


Spatial Distribution of TCE Flux along Northern Transect (g/yr), November 1997


Spatial Distribution of cis-DCE Flux along Northern Transect (g/yr), November 1997

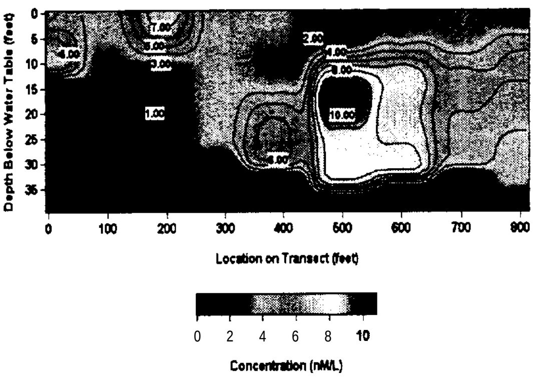

Spatial Distribution of VC Flux along Northern Transect (g/yr), November 1997

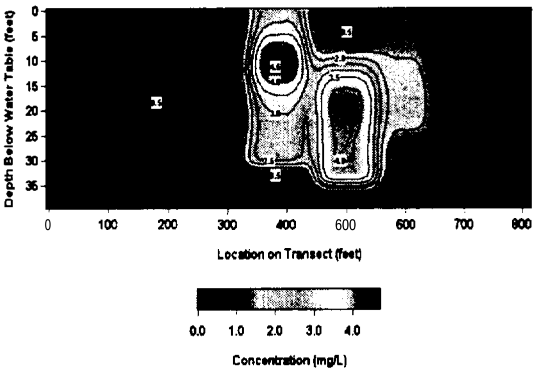

Spatial Distribution of BTEX Flux along Northern Transect (g/yr), November 1997

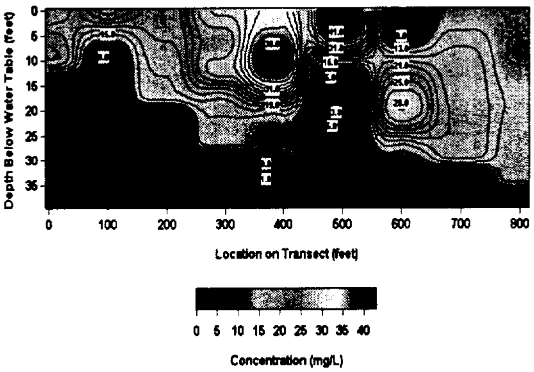
Hydrogen Data

- Hydrogen data is an important piece of evidence used to demonstrate that intrinsic bioremediation is occurring at a significant rate.

Due to hydrogen production during installation, direct-push wells can not be used to monitor dissolved hydrogen gas concentrations. Thus, the need for permanent wells.


Spatial Distribution of Hydrogen along Northern Transect (nM/L), November 1997


Spatial Distribution of Fe++ along Northern Transect (mg/L), November 1997


Spatial Distribution of Sulfate along Northern Transect (mg/L), November 1997

Interpretation

- **Interpretation is the same as with the temporary transect. Use the transect maps to differentiate between areas that behave as is expected when natural attenuation is occurring and those that don’t.**

Examples of Heterogeneity

- **At the 500 ft interval, PCE is surrounded by TCE and both are an in area that has high hydrogen concentrations, relatively high Fe++ concentrations, and low sulfate concentrations. Natural attenuation processes are at work.**

Examples of Heterogeneity

- The upper portion of the aquifer is transmitting most of the cis-DCE and VC. Therefore, this area has undergone more reductive dechlorination.

Examples of Heterogeneity

- A less complete sampling regime would fail to demonstrate the complex nature of fate and transport mechanisms in the aquifer.

What About the Geology?

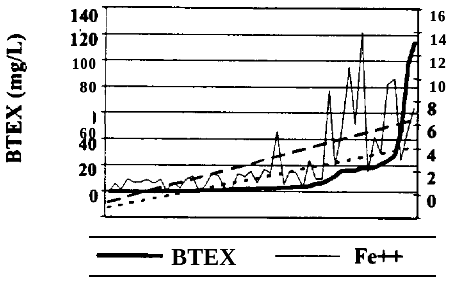
- Push technology can also be used to take core samples of aquifer material.
- Core samples can be used to verify trends seen in K estimates.

Field Techniques to Evaluate Sampling Locations in Real Time

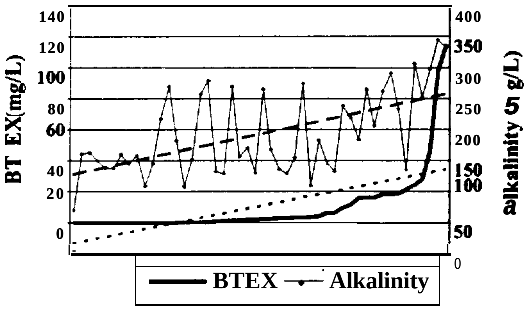
Field Test Kits

- Test kits for Fe(II), alkalinity, and in some cases contaminants, can be used in the field to map the plume both laterally and vertically. This allows the field scientist to take the majority of samples from contaminated areas.

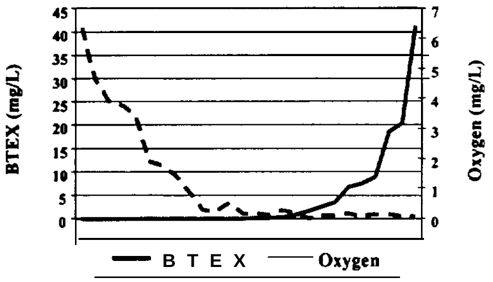
Trend Agreement Between BTEX and FE++



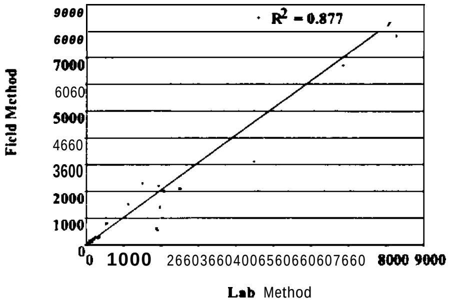
Trend Agreement Between BTEX and Alkalinity



Relationship Between BTEX and Oxygen Measurements



Correlation Between Field and Lab Determination of TCE Concentration in Water



Site Characterization Recommendations

- **Use direct-push technology to conduct site characterization, preferably by constructing temporary transects**
- **Install monitoring well transects based on the information provided by the site characterization.**

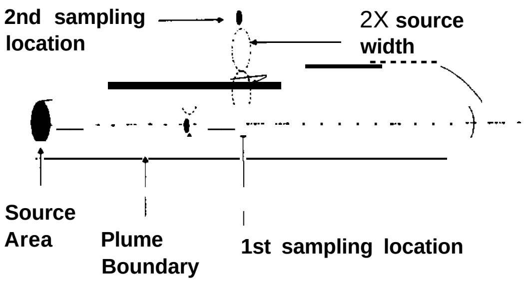
Site Characterization Recommendations

- **Use monitoring well transects to *monitor temporal trends*.**

GeoProbe Spacing on Temporary Transect

- **Probe locations are determined by starting at the inferred center of the plume and moving out in a stepwise fashion at intervals of two times the source area width.**

Spacing on Temporary Transect



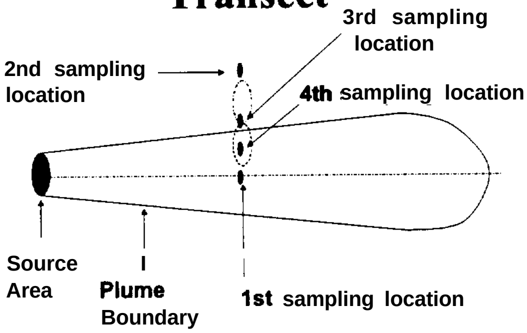
GeoProbe Spacing on Temporary Transect

- If the 2nd sampling location is contaminated, then sample 2x the source area width further along the transect.

GeoProbe Spacing on Temporary Transect

- If the 2nd sampling location is not contaminated, then double the sampling location density between the 1st and 2nd location until the plume is delineated.

Spacing on Temporary Transect



Vertical Profiling

- Follow the same logic as used with lateral well placement. Start at the water table, especially if the contaminant is a LNAPL, and proceed at an interval appropriate for the site.

Vertical Profiling

- Aquifer thickness, contaminant properties and distance from the source area must be considered when determining the initial sampling interval.

Vertical Profiling

- The goal of vertical profiling is to ensure that variations in physical and biological systems are adequately characterized.

Vertical Profiling

- As site characterization proceeds, then the sampling intervals can be refined. Typically, this will involve increasing sampling density until distinct patterns in physical and geochemical parameters are obvious.

Vertical Profiling

- One of the most important physical characteristics is hydraulic conductivity. Use the specific capacity test to estimate relative differences in flow of different intervals.

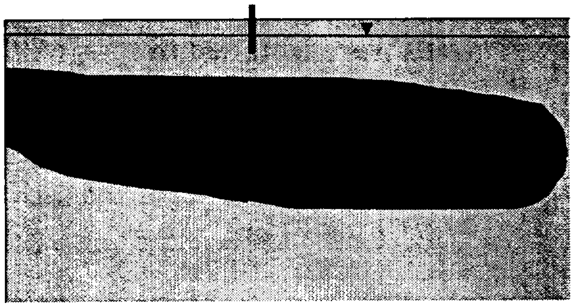
Vertical Profiling

- Use field test kits such as alkalinity, Fe II, sulfide, and dissolved oxygen to detect variations in biological processes in the aquifer.

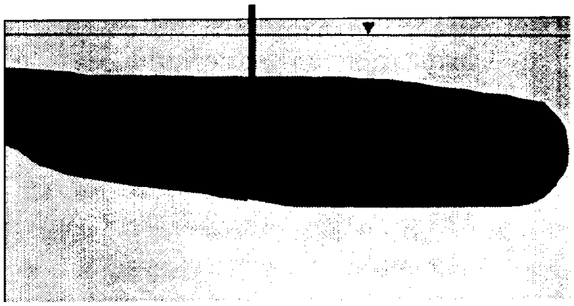
Vertical Profiling

- If possible, conduct continuous vertical profiling. This will reduce the amount of uncertainty in site characterization.

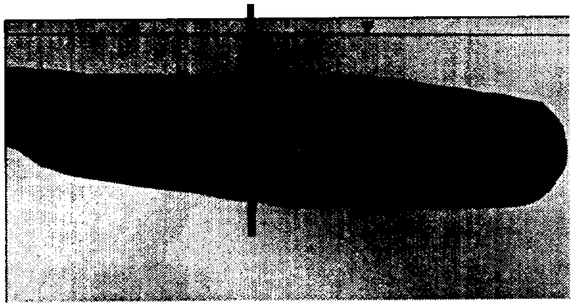
Vertical Profiling



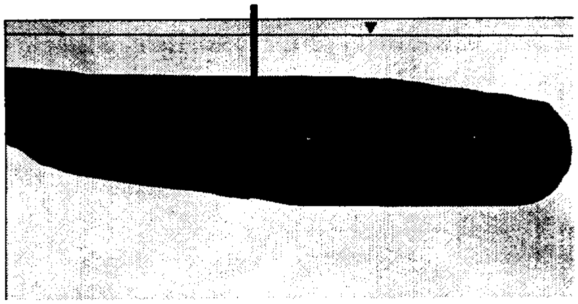
Vertical Profiling



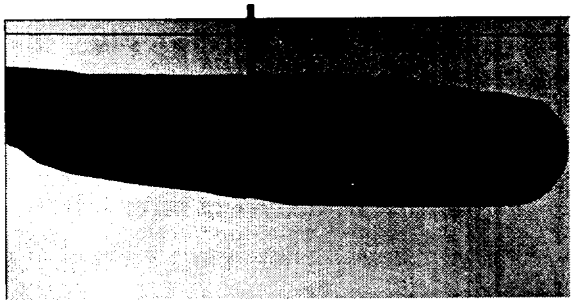
Vertical Profiling



Vertical Profiling



Vertical Profiling



Resource Allocation

- At this site, 80 monitoring wells were installed to characterize and monitor the site.
- Twenty of the wells do not contribute to the interpretation of the site.

- One conventional well cost as much as three complete temporary push locations.
- That includes installation, well development, and sampling.

- So, 60 temporary push locations (continuous vertical sampling) could have been completed for the same cost as the 20 wells that didn't yield any additional information.

At this site, as with many sites, a more thorough site characterization and permanent transect installation could have been achieved for the same cost as a conventional site characterization and monitoring network.

Take Home Points

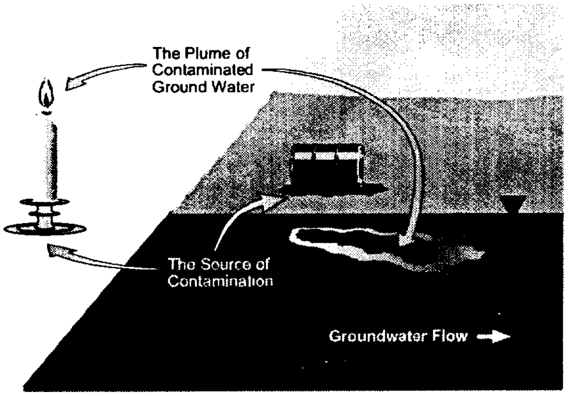
- It doesn't cost the PRP's more.
- Consultants don't lose money.
- Regulators can make their decisions easier.

Estimating Biodegradation and Attenuation Rate Constants

Estimating Biodegradation and Attenuation Rate Constants

John T. Wilson

Office of Research and Development
National Risk Management Research Laboratory
U.S.Environmental Protection Agency
Cincinnati, Ohio



Why Calculate Rate Constants?

1) Calculate concentrations at the point of attainment of standards
2) Compare rates at the site to literature to determine if the site is behaving like other sites
3) Predict changes caused by changes in flow velocity

Why Calculate Rate Constants?,

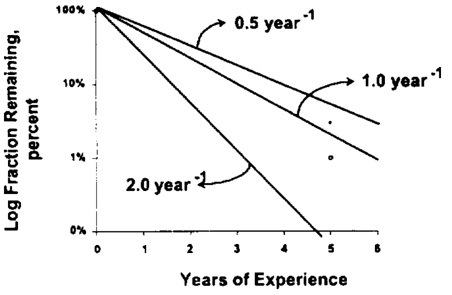
4) To determine how rapidly the ground water plume will clean up after the source is controlled.

Attenuation

First order rate constants?

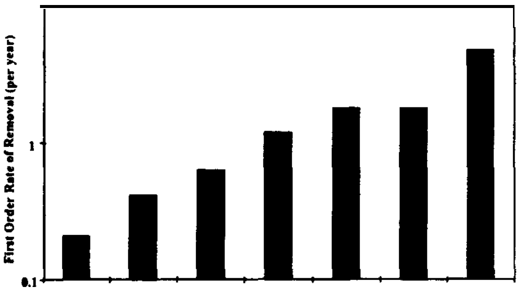
A first order rate of 1.0 per year equivalent to 2% a week or a half life of 8.3 months

First Order Rate Constants

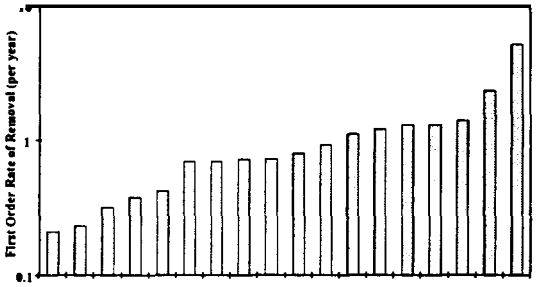


Literature Values for Natural Attenuation in Ground Water

TCE Attenuation in Microcosms



TCE Attenuation in Field



Literature Values for Natural Attenuation in Ground Water

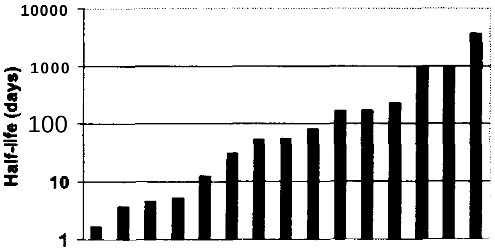
Anaerobic Biodegradation of Organic Chemicals in Groundwater: A Summary of Field and Laboratory Studies (SRC TR-97-0223F)

Dallas Aronson

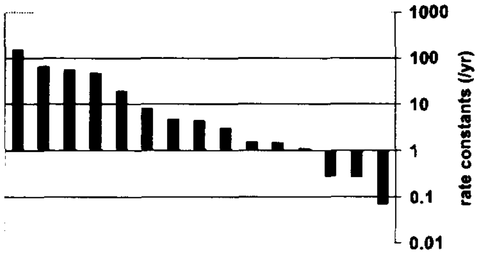
Philip Howard

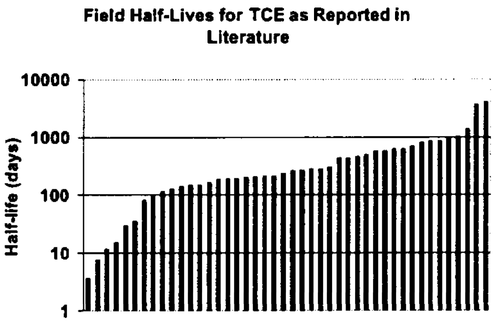
Environmental Science Center, Syracuse Research Corporation, 6225 Running Ridge Road, North Syracuse, NY 13212-2509

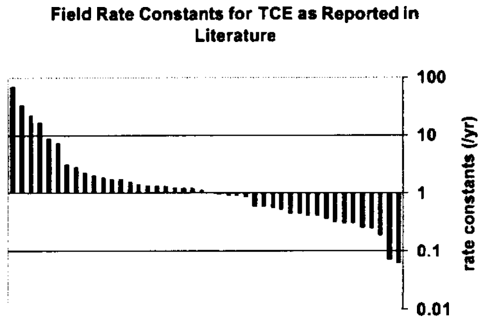
Field Half-Lives for PCE as Reported in Literature

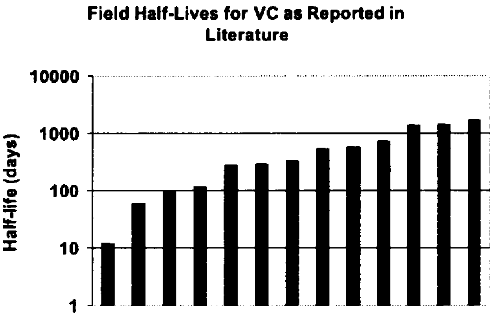


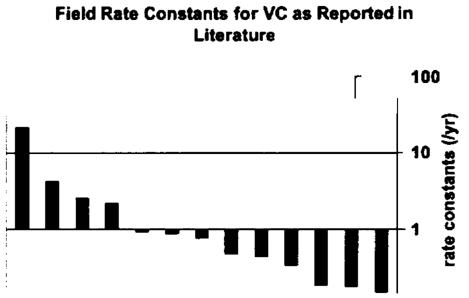
Field Rate Constants for PCE as Reported in Literature




Field Half-Lives for TCE as Reported in Literature


Field Rate Constants for TCE as Reported in Literature


Field Half-Lives for VC as Reported in Literature


Field Rate Constants for VC as Reported in Literature

Field Data

Analyte	Number	Rate (per year)
PCE	4	4.0
TCE	18	1.1
cis-DCE	13	1.6
Vinyl chloride	6	1.3

Microcosm Studies

Analyte	Number	Rate (per year)
TCE	7	1.6
cis-DCE	3	4.3
Vinyl chloride	FO 2I	4.0 4.2
1,1,1-TCA	3	2.0

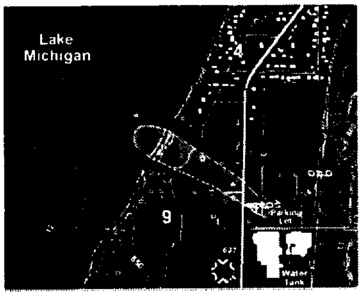
St. Joseph, Michigan

Case Study

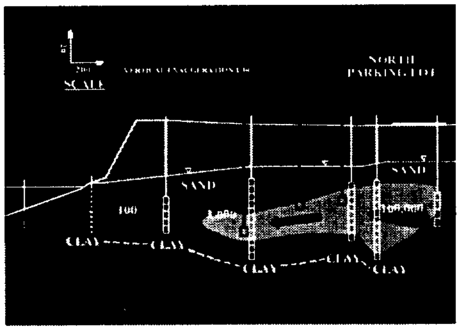
Natural Attenuation of TCE

Extracting Rate Constants

St. Joseph Site



St. Joseph Site



Vertical Transects
(TRANSECTOR)

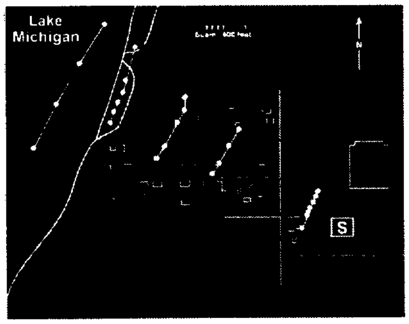
- Transects form logical units for studying sites
- Data in this form can be displayed in two-dimensions:

  By representing the data as rectangles around each measurement point

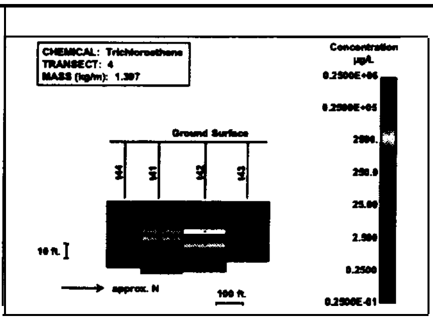
  (chemical mass per unit thickness = porosity x concentration x length x width)

The transects provide much more spatial resolution than is usually available. They will be taken as ground truth to evaluate other approaches.

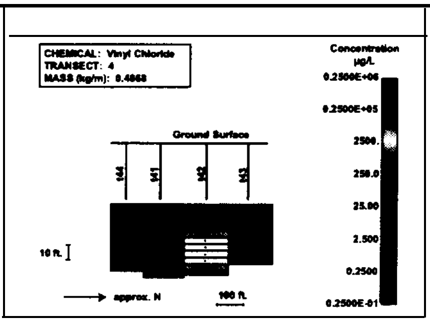
St. Joseph Site



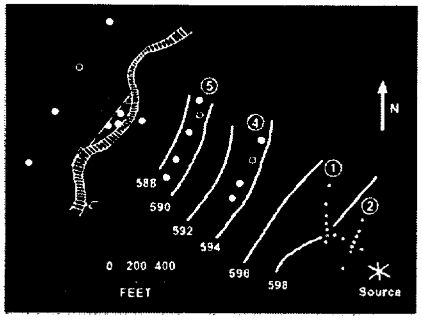
St. Joseph Site



St. Joseph Site



St. Joseph Site



Transect-Averaged Concentrations (µg/L) Dissolved Oxygen below 2.0 mg/L

Chemical	Transect 2	Transect 4	Transect 5	Lake Transect
TCE	7411	864	30.1	1.4
c-DCE	9117	1453	281	(0.80)
t-DCE	716	34.4	5.39	1.1
1,1-DCE	339	24.3	2.99	nd

Transect-Averaged Concentrations (µg/L) Dissolved Oxygen below 2.0 mg/L

Chemical	Transect 2	Transect 4	Transect 5	Lake Transect
TCE	7411	864	30.1	1.4
c-DCE	9117	1453	281	(0.80)
Vinyl Chloride	998	473	97.7	(0.16)

Transect-Averaged Concentrations (µg/L) Dissolved Oxygen below 2.0 mg/L

Chemical	Transect 2	Transect 4	Transect 5	Lake Transect
Ethene	480	297	24.2	no data
Sum of the Ethenes	19100	3150	442	3.5
Chloride	65073	78505	92023	44418

Apparent Loss Coefficients

$$\ln\left(\frac{c_{j+1}}{c_j}\right) = \lambda\ {}^{2}t$$

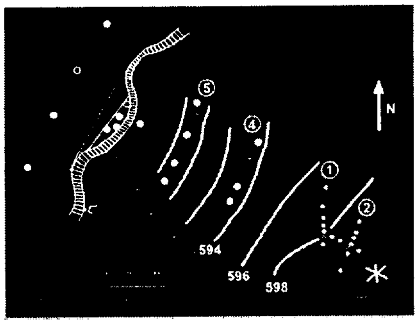
c_{j+1} = average concentration at the down gradient transect

c_j = average concentration at the up gradient transect

λ = apparent loss coefficient from transect j to j+1

${}^{2}t$ = travel time, determined from the seepage velocity, retardation factor and the distance

St. Joseph Site



For TCE from transect 2 to 4

${}^{2}t$ = 340 weeks

$c_{j+1} = 5.04 \times 10^{-4}$ kg/m^3

$c_j = 6.70 \times 10^{-3}$ kg/m^3

λ = -0.38 / year

For TCE from transect 4 to 5

${}^{2}t$ = 145 weeks

$c_{j+1} = 1.44 \times 10^{-5}$ kg/m^3

$c_j = 5.04 \times 10^{-4}$ kg/m^3

λ = -1.3 / year

Transect Pair	TCE	c-DCE	Vinyl Chloride
	Apparent change (per year)		
2 to 4	- 0.38	- 0.50	- 0.18
4 to 5	- 1.3	- 0.83	- 0.88
5 to Lake	**- 0.94**	- 3.1	- 2.2

Calculate Rate Constants

The next slides are a comparison of reconstructed hypothetical wells using data from the **Keck** Slotted Hollow Stem Auger technique to concentrations in real monitoring wells with short screens.

The whole approach requires properly constructed, properly installed, and properly maintained monitoring wells.

Transect 2

Compound	Reconstructed from slotted auger samples	RI Permanent Monitoring Well
	T-2-5	OW-19
	(mg/L)	
TCE	12.1	1.64
cis-DCE	33.7	4.63
Vinyl Chloride	2.3	2.4
Chloride	89.7	84.6

Transect 1

Compound	Reconstructed from slotted auger samples	RI Permanent Monitoring Well
	T-1-4	OW-18
	(mg/L)	
TCE	3.4	0.201
cis-DCE	11.2	0.413
Vinyl Chloride	3.7	0.922
Chloride	78.6	84.6

Transect 4

Compound	Reconstructed from slotted auger samples	RI Permanent Monitoring Well	RI Permanent Monitoring Well
	T-4-2	OW-29	OW-31
		(mg/L)	
TCE	1.3	<0.001	<0.001
cis-DCE	2.3	0.312	0.255
Vinyl Chloride	0.51	0.423	0.120
Chloride	98.9	31.1	81.1

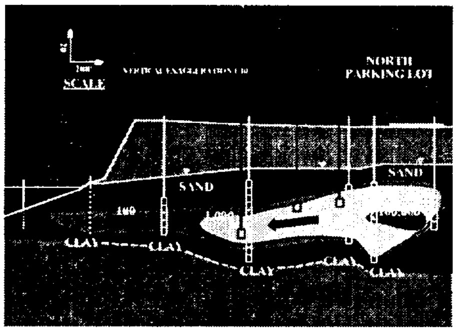
Transect 5

Compound	Reconstructed from slotted auger samples	RI Permanent Monitoring Well	RI Permanent Monitoring Well
	T-5-3	OW-32	OW-31
		(mg/L)	
TCE	0.035	0.0024	<0.001
cis-DCE	0.22	<0.001	0.255
Vinyl Chloride	0.063	<0.001	0.120
Chloride	63.6	16.2	81.1

Calculate Rate Constants

The next figure compares the screened intervals of the permanent monitoring wells to the intervals sampled by the Keck Slotted Auger technique.

St. Joseph Site



Calculate Rate Constants

The permanent wells may have been screened above or below the centerline "hot spot".

The permanent wells would have overestimated natural attenuation

We will use reconstructed concentrations from the **Keck** survey instead of the permanent monitoring wells.

Methods to Calculate Rate Constants

1) Method of **Buscheck** and Alcantar (1995)
2) Normalize to a conservative tracer
3) Calibrate a mathematical model

First-Order Decay Rate for a Steady State Plume

$$\lambda = \frac{v_c}{4\alpha_x}\left(\left[1 + 2\alpha_x\left(\frac{k}{v_x}\right)\right]^2 - 1\right)$$

where:

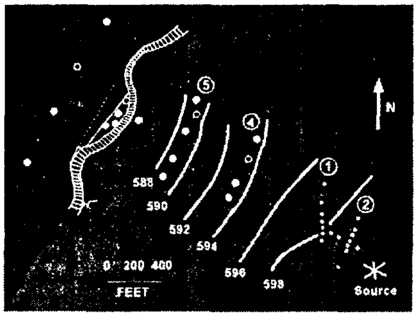
λ = first order biodegradation rate constant (approximate)

v_c = retarded contaminant velocity in the **x-direcion**

a, = dispersivity

k/V,= slope of line formed by making a lop-linear plot of contaminant concentration vs. **distance** downgrsdient along flow path

St. Joseph Site



Sampling Locations Along Centerline of Plume - St. Joseph

	T-26 on	T-14 200 n	**T-4-2** iooon	T-5-3 **1500 ft**	55AE **2000 ft**
			mg/L		
TCE	12.1	3.4	1.3	0.035	0.022
cis-DCE	33.7	11.2	2.3	0.22	0.42
Vinyl chloride	2.3	3.7	0.51	0.063	0.070
Organic chlorine	35.6	11.2	3.0	0.23	0.37

Method of Buscheck and Alcantar (1995)

Linear Regression of Ln **conc.** TCE against distance along the flow path

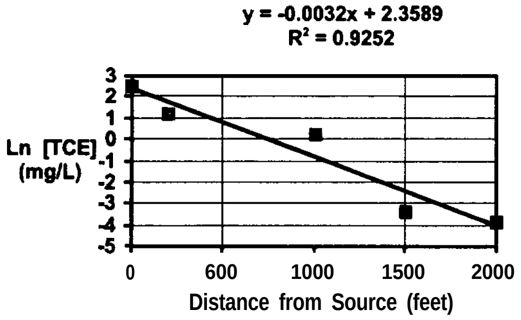
Slope of the regression is **k/Vx**

I-f

Method of Buscheck and Alcantar (1995)

Distance (ft)	TCE (mg/L)	Ln conc. TCE
0	12.1	2.49
200	3.4	1.22
1000	1.3	0.262
1500	0.035	- 3.35
2000	0.022	- 3.62

St. Joseph Site



Method of Buscheck and Alcantar (1995)

$R = 1 + Koc\ foc\ \rho / \theta$

Koc = 120 mL/g
foc = 0.001
Porosity = 0.3
Bulk Density = 1.7 g/cm^3

Retardation = 1.7

Method of Buscheck and Alcantar (1995)

Contaminant velocity (V,) equals seepage velocity divided by the retardation factor

V_c = 1.3 ft per day / 1.7
= 0.76 ft per day
= 277 ft per year

Method of Buscheck and Alcantar (1995)

When
V_c = 277 ft per year
a_x = 100 feet

$k / V_x = -0.0032$

Then
$\lambda = -0.00165$ per day
$= -0.602$ per year

Normalize to a Conservative Tracer

Will use the sum of chloride ion and organic chlorine as a tracer

Normalize to a Conservative Tracer

Multiply the concentration of chlorinated organic analytes by their mass fraction of chlorine

Sum the concentrations of chloride ion and organic chlorine in each chlorinated analyte

Mass Fraction Chlorine

Compound	Daltons	Daltons Chlorine	Mass Fraction Chlorine
PCE	166	142	0.855
TCE	137.5	106.5	0.810
DCE	97	71	0.732
Vinyl chloride	62.5	35.5	0.568

Sampling Locations Along Centerline of Plume - St. Joseph

	T-2-5 **0 ft**	T-14 200 n	T-4-2 iooon	T-5-3 **1500 ft**	**55AE** **2000 ft**
	-	-	-	mg/L	
Chloride	69.7	76.6	96.9	63.6	54.7
Organic Chlorine	35.6	11.2	3.0	0.23	0.37
Total Chlorine & Chloride	125.5	69.6	101.9	63.6	**55.1**

Normalize to a Conservative Tracer

Multiply the concentration of analyte down gradient by the dilution of the tracer to estimate the concentration expected in the absence of dilution

Calculation of Corrected Concentration

Where flow of ground water is from point A to **point B:**

$$C_{B, Cm} = C_B \text{ (Chloride A /Chloride B)}$$

$C_{B, Corr}$ = **corrected concentration** of contaminant at pdnt **B**

C_B = **measured concentration** of **contaminant at** point **B**

Chloride A = **measured concentration** of **tracer at point** A

Chloride B = **measured** concentration of **tracer** at **point B**

Normalize to a Conservative Tracer

From T-2-5 to **55AE,** for TCE

$$\text{Corrected Concentration} = \frac{0.022 \text{ mg/L } (125.5 \text{ mg/L})}{(55.1 \text{ mg/L})}$$

= 0.050 **mg/L**

First-Order Decay

$$C = C_0 \, e^{kt}$$

where:

C = contaminant concentration at time t

C_0 = initial contaminant concentration

k = first-order rate constant

Normalize to a Conservative Tracer

From T-2-5 to **55AE**, for TCE

$$C_{(55AE)} = C_{(T-2-5)} \, e^{kt}$$

$$(0.050/12.1) = e^{kt}$$

Normalize to a Conservative Tracer

$$\ln(0.050 \,/\, 12.1) = kt$$

$$-\,5.49 = kt$$

$$k = -\,5.491\ t$$

Normalize to a Conservative Tracer

The locations are 2,000 feet apart.

if the seepage velocity is 1.3 feet per day,

the retarded TCE velocity = 1.3 / 1.7 feet per day
= 0.76 **feet per day**

Normalize to a Conservative Tracer

The travel time □ 2,000 feet IO.76 feet per day
= 2,631 days

Normalize to a Conservative Tracer

k = - 5.49 / **2,631** days
= - 0.00208 **I day**
= - 0.76 **/ year**

Comparison of Rate Constants

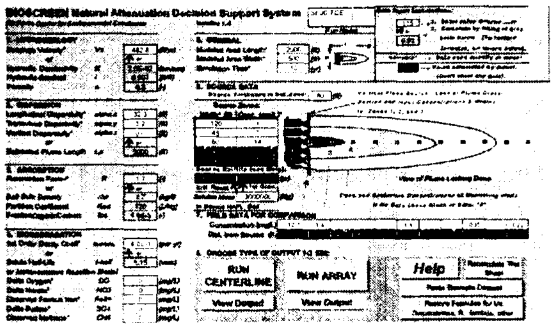
Normalize to a conservative tracer
= *-0.76* per year

Method of Buscheck and Alcantar
= *-0.602* per year

Transect comparisons
= -0.94 per year
= -1.3 per year
= *-0.38* per year

Calibrate BIOSCREEN

West Plume at St. Joseph, Michigan

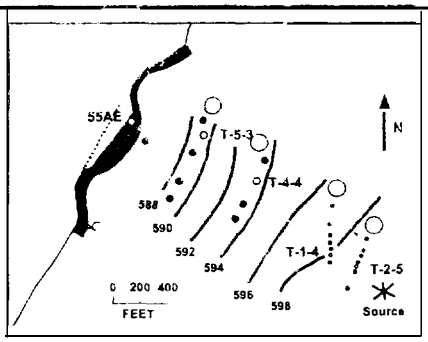


See following page for a full-size version of the slide

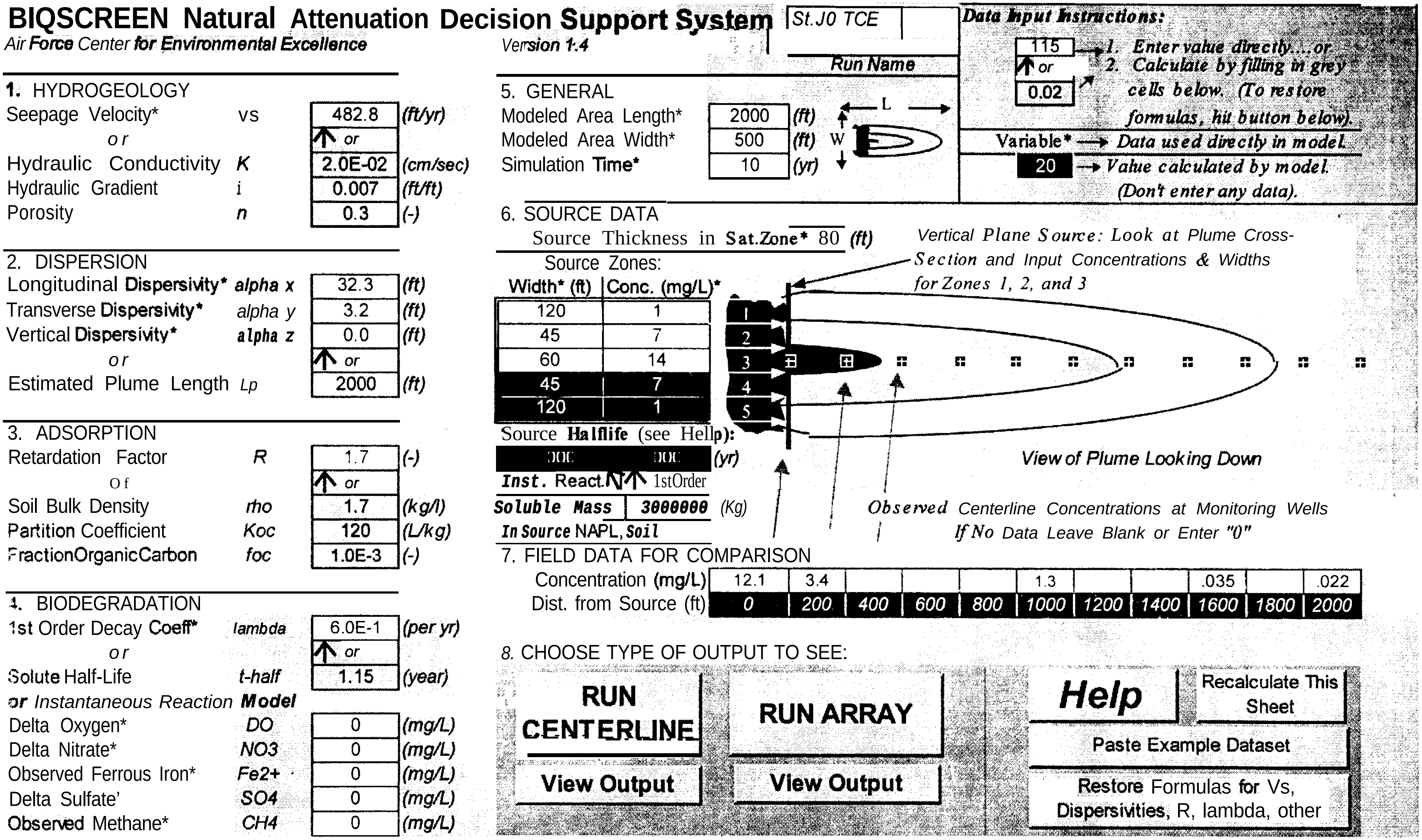
Calibrate BIOSCREEN

Use the next figure to estimate the hydraulic gradient

St. Joseph Site



The average hydraulic conductivity is 50 feet per day or 0.02 cm per sec.



BIOSCREEN Natural Attenuation Decision Support System

Air Force Center for Environmental Excellence

Version 1.4

St.J0 TCE

Run Name

Data Input Instructions:

115	*1. Enter value directly....or*
or	*2. Calculate by filling in grey cells below. (To restore formulas, hit button below).*
0.02	
Variable*	→ *Data used directly in model.*
20	→ *Value calculated by model. (Don't enter any data).*

1. HYDROGEOLOGY

Seepage Velocity*	Vs	482.8	*(ft/yr)*
or		or	
Hydraulic Conductivity	*K*	2.0E-02	*(cm/sec)*
Hydraulic Gradient	*i*	0.007	*(ft/ft)*
Porosity	*n*	0.3	*(-)*

2. DISPERSION

Longitudinal Dispersivity*	*alpha x*	32.3	*(ft)*
Transverse Dispersivity*	*alpha y*	3.2	*(ft)*
Vertical Dispersivity*	*alpha z*	0.0	*(ft)*
or		or	
Estimated Plume Length	*Lp*	2000	*(ft)*

3. ADSORPTION

Retardation Factor	*R*	1.7	*(-)*
or		or	
Soil Bulk Density	*rho*	1.7	*(kg/l)*
Partition Coefficient	*Koc*	120	*(L/kg)*
FractionOrganicCarbon	*foc*	1.0E-3	*(-)*

4. BIODEGRADATION

1st Order Decay Coeff*	*lambda*	6.0E-1	*(per yr)*
or		or	
Solute Half-Life	*t-half*	1.15	*(year)*
or Instantaneous Reaction ***Model***			
Delta Oxygen*	*DO*	0	*(mg/L)*
Delta Nitrate*	*NO3*	0	*(mg/L)*
Observed Ferrous Iron*	*Fe2+*	0	*(mg/L)*
Delta Sulfate'	*SO4*	0	*(mg/L)*
Observed Methane*	*CH4*	0	*(mg/L)*

5. GENERAL

Modeled Area Length*	2000	*(ft)*
Modeled Area Width*	500	*(ft)*
Simulation Time*	10	*(yr)*

6. SOURCE DATA

Source Thickness in Sat.Zone* 80 *(ft)*

Source Zones:

Width* (ft)	Conc. (mg/L)*
120	1
45	7
60	14
45	7
120	1

Source Halflife (see Help):

[illegible]	[illegible]	*(yr)*
Inst. React.	1stOrder	
Soluble Mass	***3000000***	*(Kg)*

In Source NAPL, ***Soil***

Vertical Plane Source: Look at Plume Cross-Section and Input Concentrations & Widths for Zones 1, 2, and 3

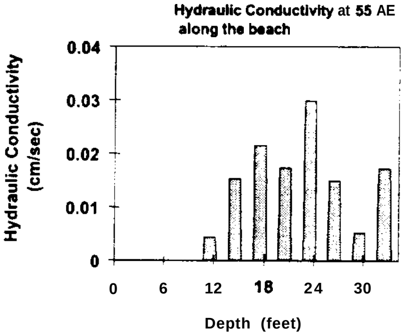
View of Plume Looking Down

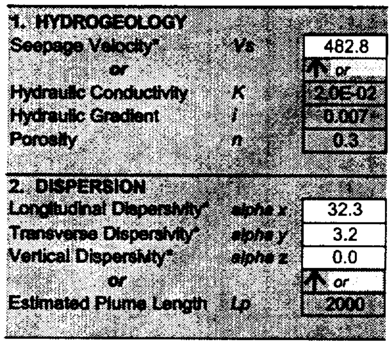
Observed Centerline Concentrations at Monitoring Wells If No Data Leave Blank or Enter "0"

7. FIELD DATA FOR COMPARISON

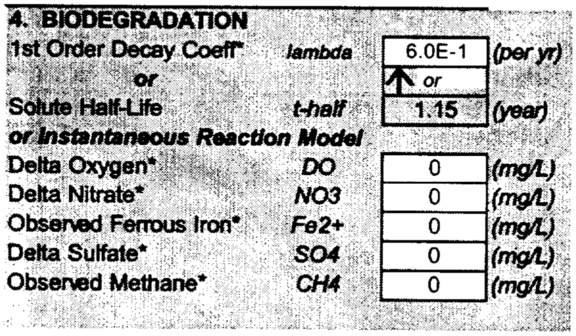
Concentration (mg/L)	12.1	3.4				1.3			.035		.022
Dist. from Source (ft)	0	200	400	600	800	1000	1200	1400	1600	1800	2000

8. CHOOSE TYPE OF OUTPUT TO SEE:





1. HYDROGEOLOGY		
Seepage Velocity*	*Vs*	482.8
or		↑ or
Hydraulic Conductivity	*K*	2.0E-02
Hydraulic Gradient	*i*	0.007
Porosity	*n*	0.3
2. DISPERSION		
Longitudinal Dispersivity*	*alpha x*	32.3
Transverse Dispersivity*	*alpha y*	3.2
Vertical Dispersivity*	*alpha z*	0.0
or		↑ or
Estimated Plume Length	*Lp*	2000



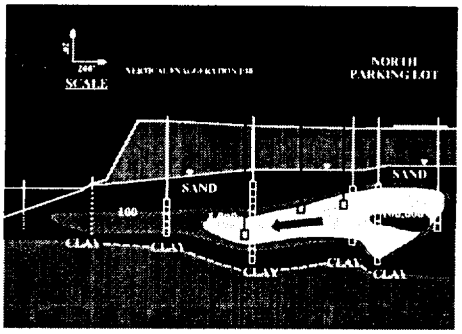
4. BIODEGRADATION			
1st Order Decay Coeff*	*lambda*	6.0E-1	*(per yr)*
or		↑ or	
Solute Half-Life	*t-half*	1.15	*(year)*
or Instantaneous Reaction Model			
Delta Oxygen*	*DO*	0	*(mg/L)*
Delta Nitrate*	*NO3*	0	*(mg/L)*
Observed Ferrous Iron*	*Fe2+*	0	*(mg/L)*
Delta Sulfate*	*SO4*	0	*(mg/L)*
Observed Methane*	*CH4*	0	*(mg/L)*

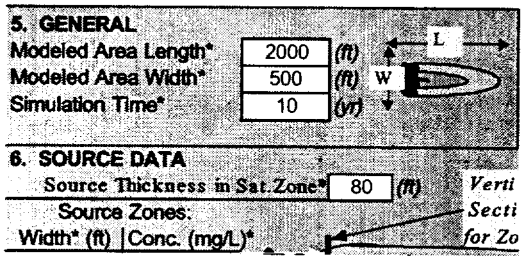
Calibrate BIOSCREEN

Use the next figure to estimate the geometry of the plume.

The vertical scale bar in the upper left corner represents 20 feet.

St. Joseph Site



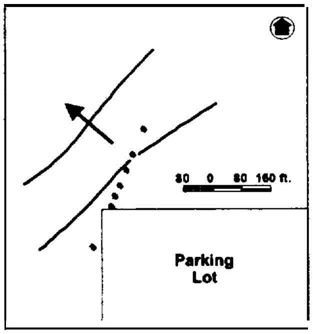


5. GENERAL			
Modeled Area Length*	2000	*(ft)*	
Modeled Area Width*	500	*(ft)*	
Simulation Time*	10	*(yr)*	
6. SOURCE DATA			
Source Thickness in Sat.Zone*	80	*(ft)*	*Verti*
Source Zones:			*Secti*
Width* (ft) | Conc. (mg/L)*			*for Zo*

Calibrate BIOSCREEN

Use the next figure to set up the lanes in BIOSCREEN for TCE attenuation.

St. Joseph Site



Sampling locations along upstream transect

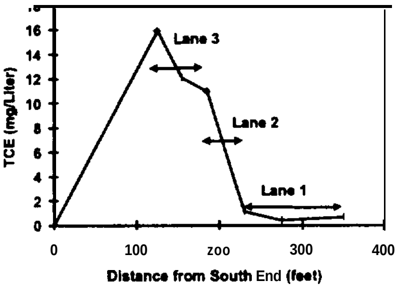
T2-7	T2-2	T2-5	T2-1	T2-6	T24	T2-2

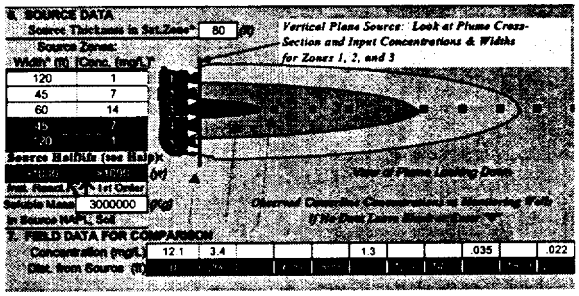
Distance from south end of transect, feet

0	125	155	185	230	275	350

Average conc. TCE, mg/liter

0.02	15.9	12.1	11.0	1.1	0.39	0.68





6. SOURCE DATA

Source Thickness in Sat.Zone* 80 (ft)

Source Zones:

Width* (ft)	Conc. (mg/L)*
120	1
45	7
60	14
45	7
120	1

Source Halflife (see Help): >1000 >1000 (yr)

Inst. React. 1st Order

Soluble Mass 3000000 (Kg) in Source NAPL, Soil

Vertical Plane Source: Look at Plume Cross-Section and Input Concentrations & Widths for Zones 1, 2, and 3

7. FIELD DATA FOR COMPARISON

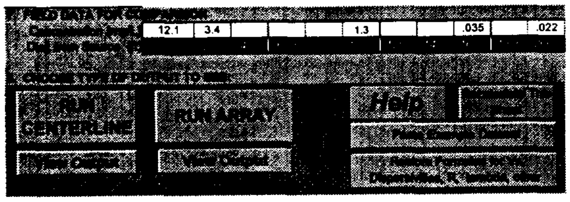
Concentration (mg/L)	12.1	3.4				1.3			.035		.022
Dist. from Source (ft)	[illegible]	[illegible]		[illegible]	[illegible]		[illegible]	[illegible]		[illegible]	[illegible]

Calibrate BIOSCREEN

Use the next table to set up field. data in BIOSCREEN for attenuation of TCE

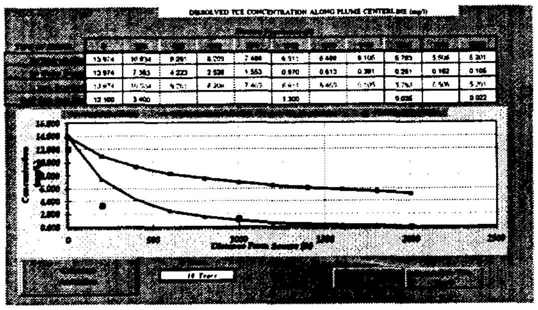
Sampling Locations Along Centerline of Plume - St. Joseph

	T-2-5 0 ft	T-1-4 200 ft	T-4-2 1000 ft	T-5-3 1500 ft	55AE 2000 ft
			mg/L		
TCE	12.1	3.4	1.3	0.035	0.022
cis-DCE	33.7	11.2	2.3	0.22	0.42
Vinyl chloride	2.3	3.7	0.51	0.063	0.070



Calibrate BIOSCREEN

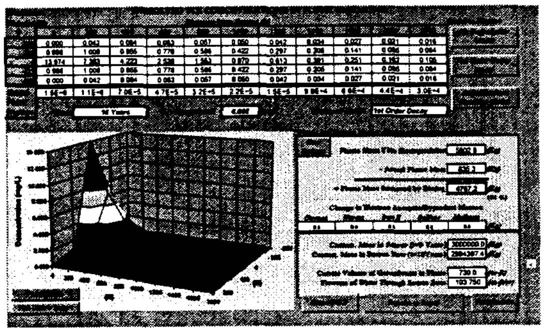
Results from RUN CENTERLINE



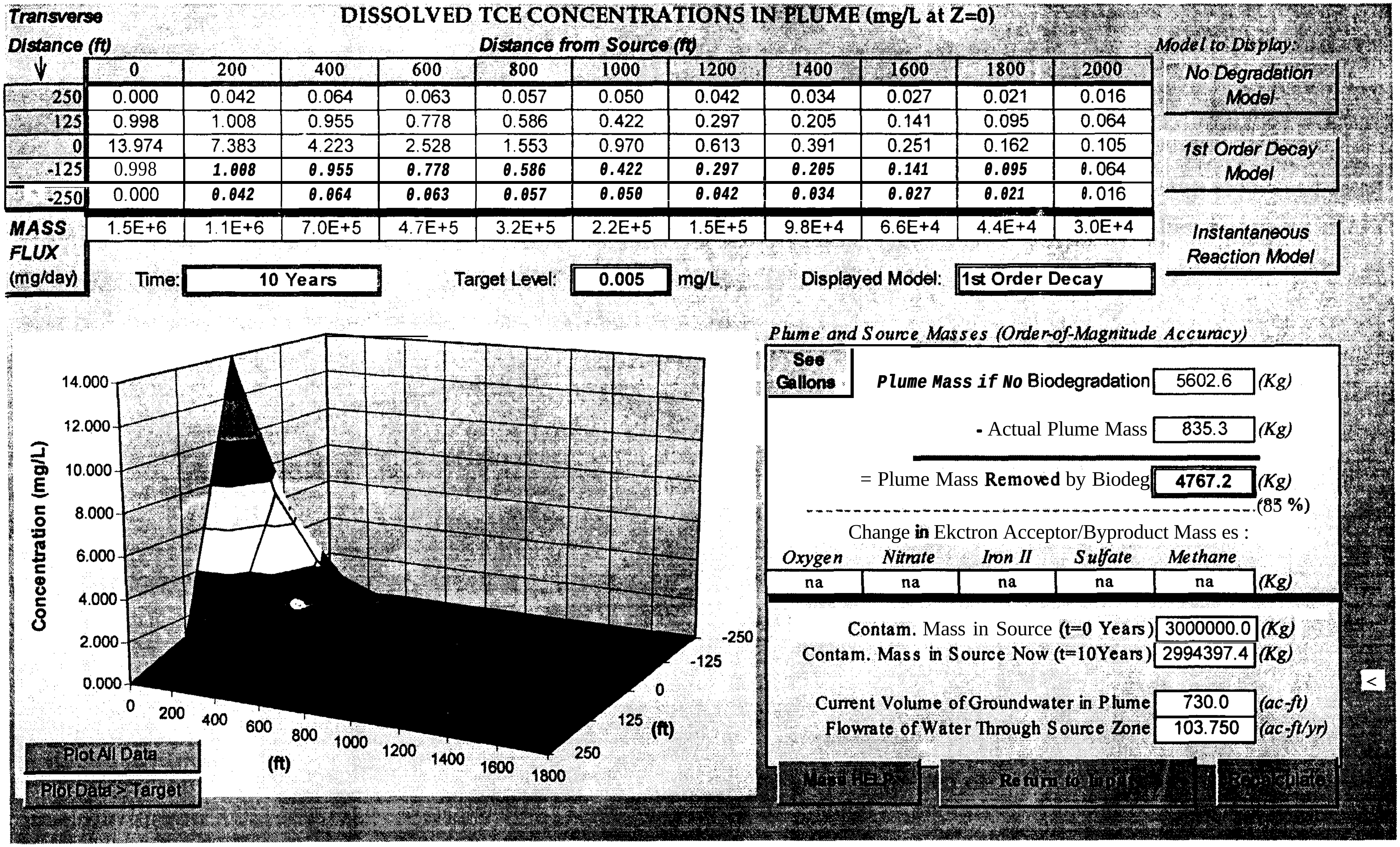
See following page(s) for a full-size version of the slide.

Calibrate BIOSCREEN

Results from RUN ARRAY



See following page(s) for a full-size version of the slide.



DISSOLVED TCE CONCENTRATIONS IN PLUME (mg/L at Z=0)

Transverse Distance (ft) ↓	Distance from Source (ft) 0	200	400	600	800	1000	1200	1400	1600	1800	2000
250	0.000	0.042	0.064	0.063	0.057	0.050	0.042	0.034	0.027	0.021	0.016
125	0.998	1.008	0.955	0.778	0.586	0.422	0.297	0.205	0.141	0.095	0.064
0	13.974	7.383	4.223	2.528	1.553	0.970	0.613	0.391	0.251	0.162	0.105
-125	0.998	1.008	0.955	0.778	0.586	0.422	0.297	0.205	0.141	0.095	0.064
-250	0.000	0.042	0.064	0.063	0.057	0.050	0.042	0.034	0.027	0.021	0.016
MASS FLUX (mg/day)	1.5E+6	1.1E+6	7.0E+5	4.7E+5	3.2E+5	2.2E+5	1.5E+5	9.8E+4	6.6E+4	4.4E+4	3.0E+4

Time: 10 Years

Target Level: 0.005 mg/L

Displayed Model: 1st Order Decay

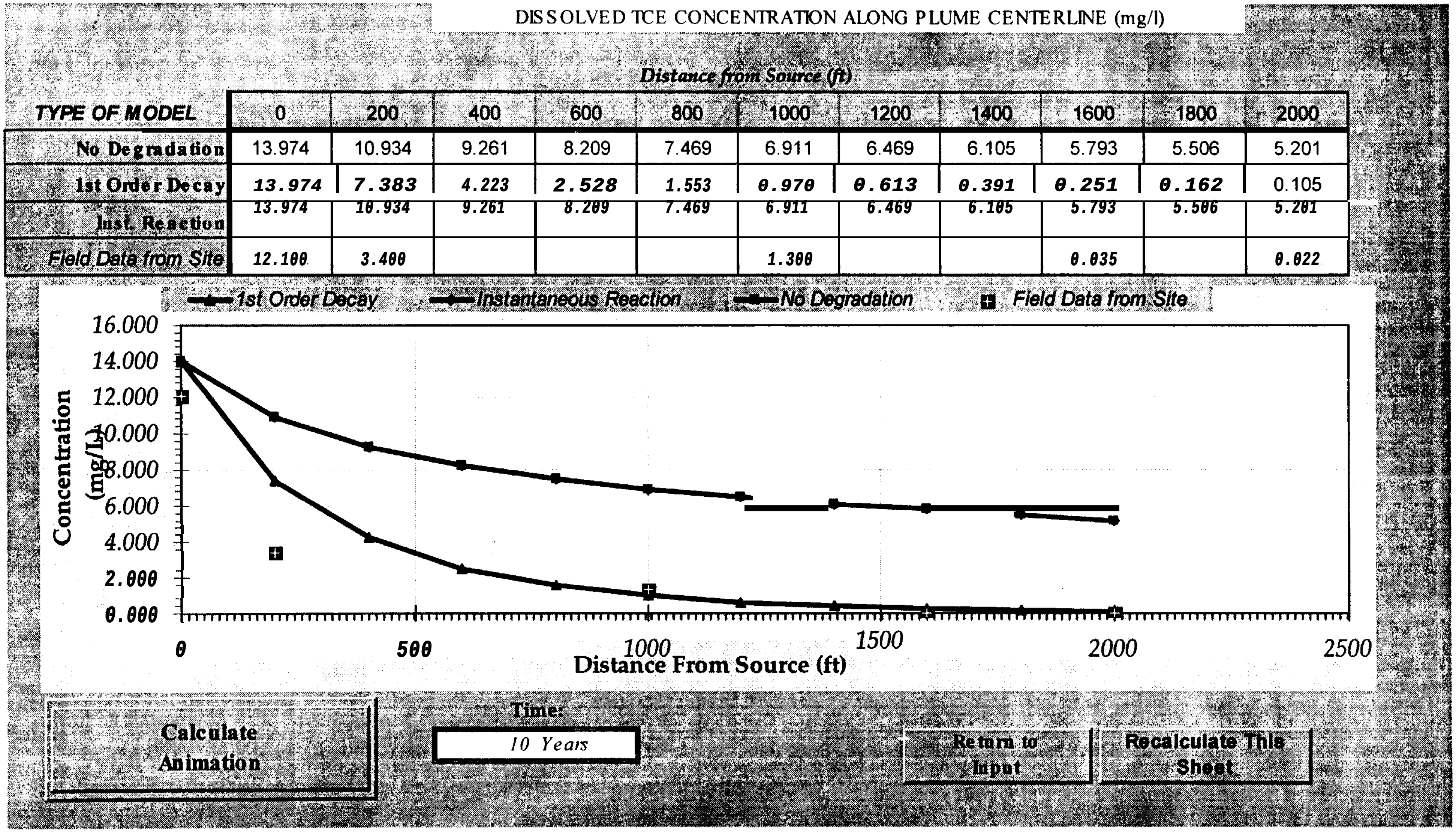
Plume and Source Masses (Order-of-Magnitude Accuracy)

Plume Mass if No Biodegradation	5602.6	(Kg)
- Actual Plume Mass	835.3	(Kg)
= Plume Mass Removed by Biodeg	4767.2	(Kg) (85 %)

Change in Ekctron Acceptor/Byproduct Mass es :

Oxygen	Nitrate	Iron II	Sulfate	Methane	
na	na	na	na	na	(Kg)

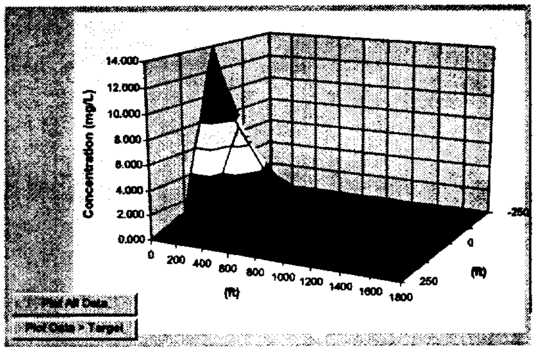
Contam. Mass in Source (t=0 Years)	3000000.0	(Kg)
Contam. Mass in Source Now (t=10Years)	2994397.4	(Kg)
Current Volume of Groundwater in Plume	730.0	(ac-ft)
Flowrate of Water Through Source Zone	103.750	(ac-ft/yr)

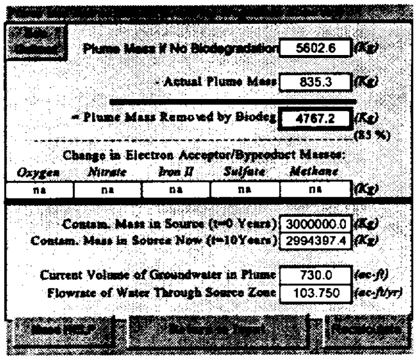


DISSOLVED TCE CONCENTRATION ALONG PLUME CENTERLINE (mg/l)

Distance from Source (ft)

TYPE OF MODEL	0	200	400	600	800	1000	1200	1400	1600	1800	2000
No Degradation	13.974	10.934	9.261	8.209	7.469	6.911	6.469	6.105	5.793	5.506	5.201
1st Order Decay	13.974	7.383	4.223	2.528	1.553	0.970	0.613	0.391	0.251	0.162	0.105
Inst. Reaction	13.974	10.934	9.261	8.209	7.469	6.911	6.469	6.105	5.793	5.506	5.201
Field Data from Site	12.100	3.400				1.300			0.035		0.022





Plume Mass if No Biodegradation	5602.6	(Kg)
- Actual Plume Mass	835.3	(Kg)
= Plume Mass Removed by Biodeg	4767.2	(Kg)
		(85 %)

Change in Electron Acceptor/Byproduct Masses:

Oxygen	Nitrate	Iron II	Sulfate	Methane	
na	na	na	na	na	(Kg)

Contam. Mass in Source (t=0 Years)	3000000.0	(Kg)
Contam. Mass in Source Now (t=10Years)	2994397.4	(Kg)
Current Volume of Groundwater in Plume	730.0	(ac-ft)
Flowrate of Water Through Source Zone	103.750	(ac-ft/yr)

Calibrate BIOSCREEN

1 .O acre foot per year =

3.4 cubic meters per day

0.62 gallons per minute

100 acre feet per year =

0.09 million gallons per day

Sources of information

BIOSCREEN

BIOSCREEN and BIOPLUME III are available on the NRMRL/SPRD Web page:

http://www.epa.gov/ada/kerrlab.html

Information by Phone, FAX, or Mail

- NCEPI
  - Order documents and databases with “EPA” document numbers free of charge
  - FAX requests to 5134696695
  - Mail requests to NCEPI, PO Box 42419, Cincinnati, OH 45242
- ☠❄✋🌢
  - Purchase products with **“PB”** document numbers
  - Order **by** phone **at 7034674650 or 800-553-NTIS** **(for** rush service)

TIO Information Online

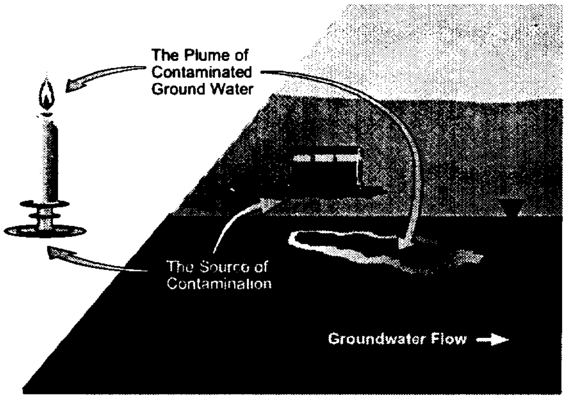
- Clean-up Information (CLU-IN) System
  - WWW site
    - http://clu-in.com
    - Go to "Publications and Software" area to download publications and databases

Risk Management of Monitored Natural Attenuation

Risk Management of Monitored Natural Attenuation

John T. Wilson

Office of Research and Development
National Risk Management Research Laboratory
U.S.Environmental Protection Agency
Cincinnati, Ohio



Benefits of Source Control

Case study:

Characterization and Monitoring Before and After Source Removal at a Former Manufactured Gas Plant (MGP) Disposal Site

EPRI TR-105921 Final Report Jan 1996

Benefits of Source Control

Source Area- 114 acre

Depth of Contamination- 0 to 20 feet

Volume of Contamination- 96,000 cubic yards

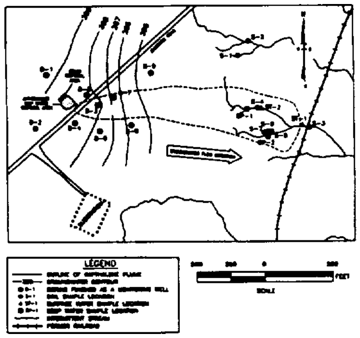
Water Table- 7 feet

Geology- 20 feet of sand over silty clay

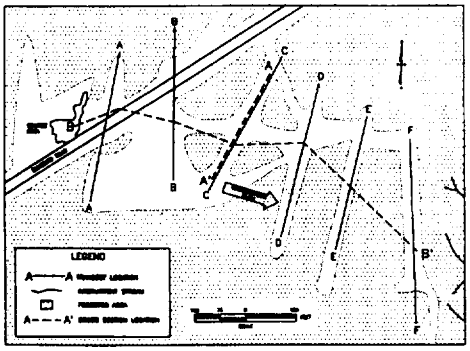
Benefits of Source Control

Costs for remedy **$3,087,000**	
site work	37%
soil transportation	34%
soil treatment	24%
waste water disposal	5%

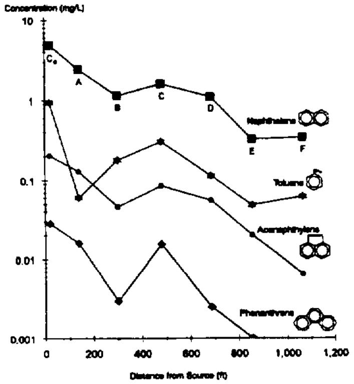
Estimated Groundwater Naphthrlene Plume and Groundwater **Contours** Based on the 1983 Investigation



Location of Downgndient Geological Cross Sections

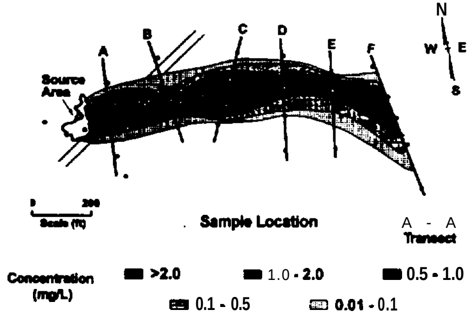


Centerline Groundwater Concentrations



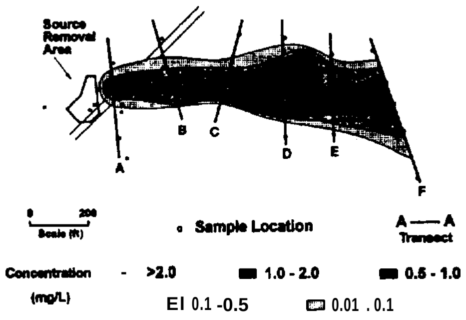
Naphthalene Groundwater Plume In 1990 and 1991
Areal View

Pre - Source Removal - June 1990



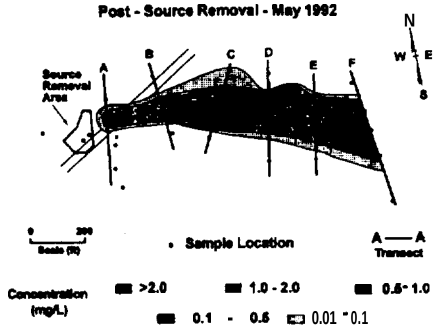
Naphthalena Groundwater Plume in 1990 and 1991
Areal View (Cont'd)

Post - Source Removal - **November 1991**



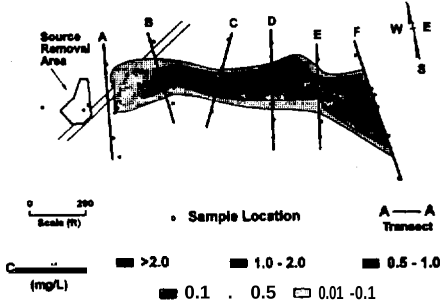
Naphthalena Groundwater Plume in 1992
Areal View

Post - Source Removal - May 1992

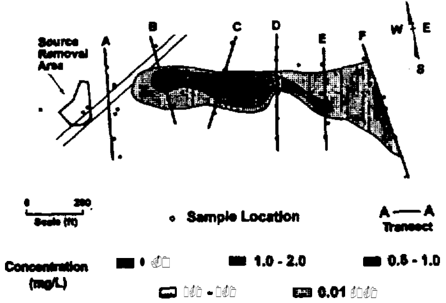


Naphthalena Groundwater Plume in 1993
Areal View

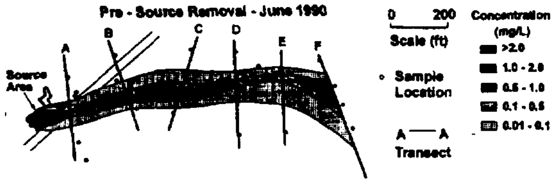
Post - Source Removal - April 1993



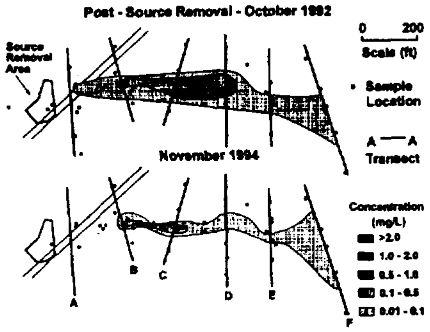
Naphthalena Groundwater Plume in 1994
Areal View
Post **- Source Removal - April** 1994



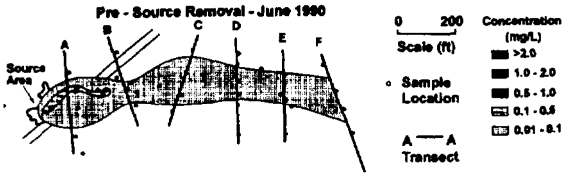
Toluene Groundwater Plume
Areal View



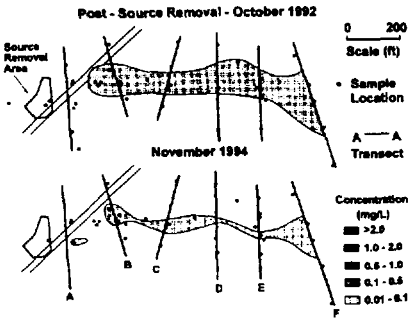
Toluene Groundwater Plume
Areal View (Cont'd)



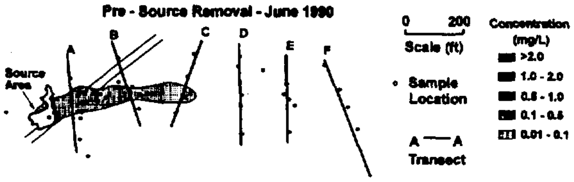
Acenaphthylene Groundwater Plume
Areal View



Acenaphthylene Groundwater Plume
Areal View (Cont'd)

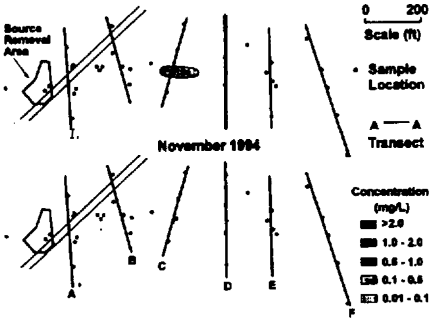


Phenanthrene Groundwater Plume
Areal View



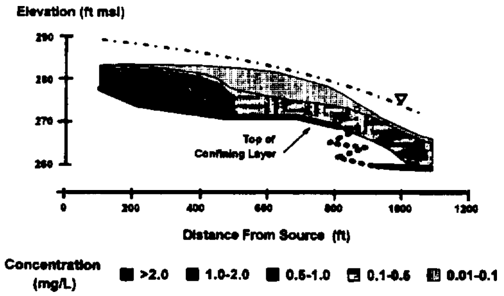
Phenanthrene Groundwater Plume Anal View (Cont'd)

Post - Source Removal - October 1992



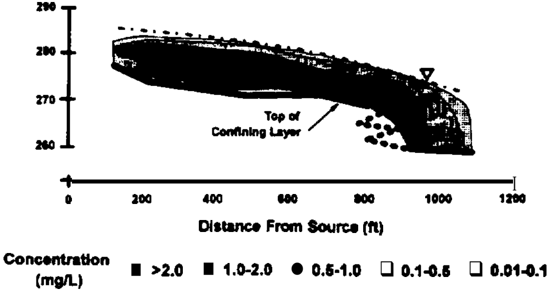
Naphthalene Groundwater Concentrations in 1990 and 1991 Cross-Sectional View

Pre - Source Removal - June 1999



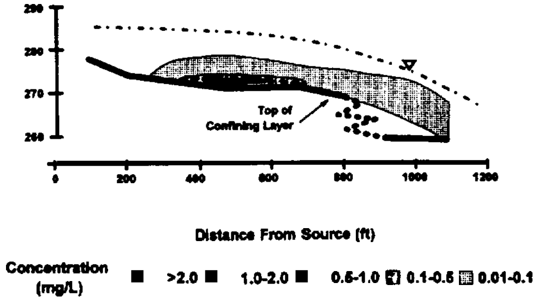
Naphthalene Groundwater **Concentrations** in 1990 and 1991 Cross-Sectional View (Cont'd)

Post-Source **Removal** - Novsmber 1991

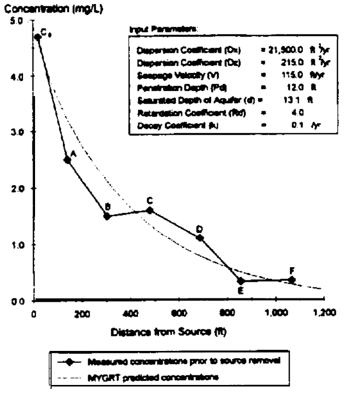


Naphthalene Groundwster **Concentrations** in **1994** **Cross-Sectional** View

Novsmber **1994**



Measuredand MYGRT-Predicted Naphthalene Concentrations in Groundwater



Input Parameters:

Dispersion Coefficient (Dx) = 21,500.0 ft ^{2}/yr

Dispersion Coefficient (Dz) = 215.0 ft ^{2}/yr

Seepage Velocity (V) = 115.0 ft/yr

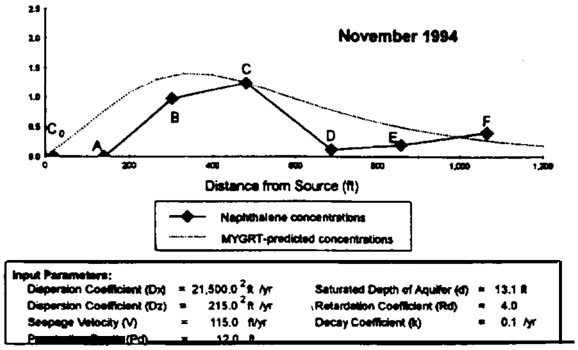
Penetration Depth (Pd) = 12.0 ft

Saturated Depth of Aquifer (d) = 13.1 ft

Retardation Coefficient (Rd) = 4.0

Decay Coefficient (k) = 0.1 /yr

Measured and Pmdicted Naphthalene **Concentrations**



Input Parameters:

Dispersion Coefficient (Dx) = 21,500.0 ^{2}ft /yr

Dispersion Coefficient (Dz) = 215.0 ^{2}ft /yr

Seepage Velocity (V) = 115.0 ft/yr

P[illegible] (Pd) = 12.0 ft

Saturated Depth of Aquifer (d) = 13.1 ft

Retardation Coefficient (Rd) = 4.0

Decay Coefficient (k) = 0.1 /yr

Benefits of Source Control

After source removal, the aquifer cleaned up from the front end to the tail end.

The benefit moved faster than the average seepage velocity. The whole plume cleaned up, not just the front end.

Plume projected to reach NYDEC Drinking Water Standard for Naphthalene by 2030.

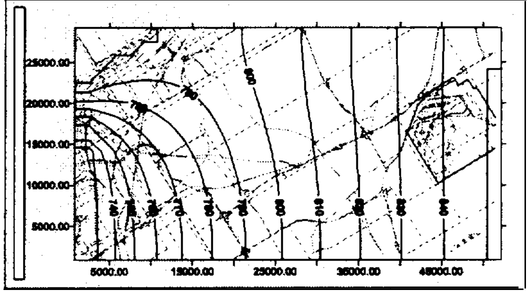
Large Chlorinated Solvent Plume

Natural Attenuation Model Study
Calibrated to Long Term Monitoring
Data

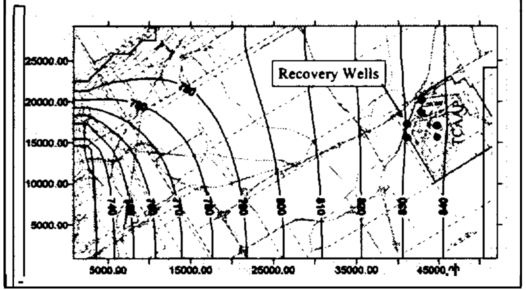
Basic Model Input Parameters

- Hydraulic Conductivity = 280 **ft/day**
- **Thickness** = 190 **feet** including unconsolidated sand **and fractured bedrock aquifers**
- **Effective** porosity = 0.20
- **Retardation** factor = I .O
- Start **time** for model approximately **1940**
- **Model domain x = 53,000 feet y = 30,000 feet**
- Pumping **from recovery wells** active for all **simulations according to published** rates. **Pump and treat began** in 1989

Simulated Static Water Level



Simulated Water Level With
Active Recovery Wells



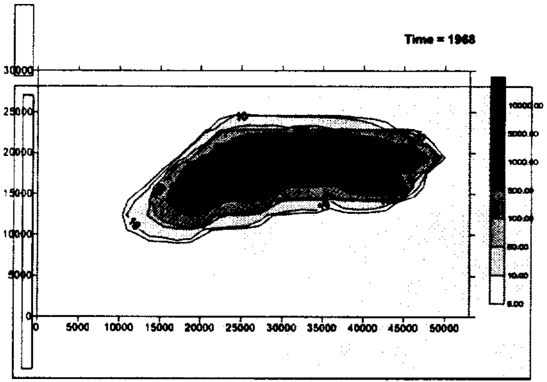
Flow Model Conclusion:

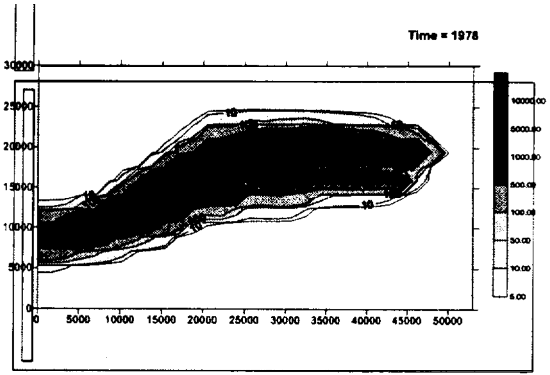
- **Regional flow appears to be strongly influenced by river navigation system causing flow to converge southeast**
- **Recovery wells do no appear to modify flow patterns significantly on a regional scale**

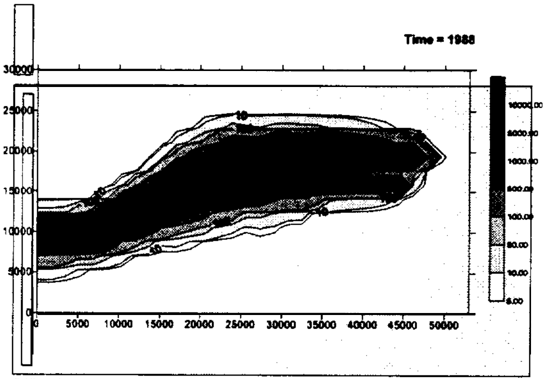
Initial Simulation:
No Source or Dissolved Decay

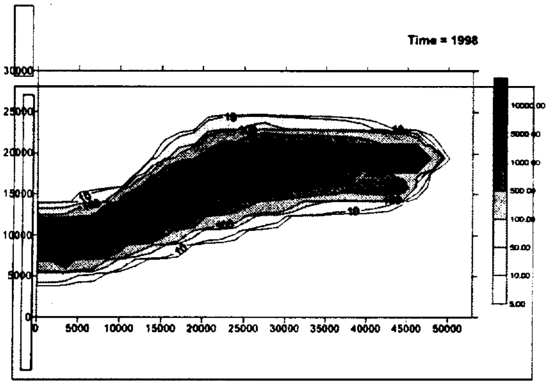
- **Source 1:**
  - Located: North **half of site**
  - Active **from** beginning of model
- **Source2:**
  - **Located:** South half of site
  - Active from **1960**

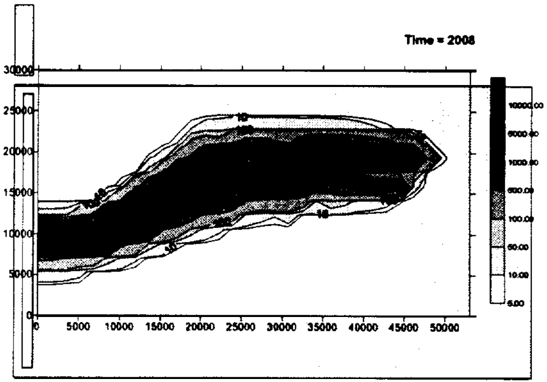
No Decay Simulation







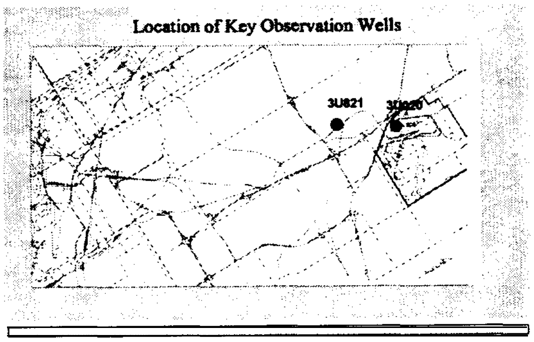


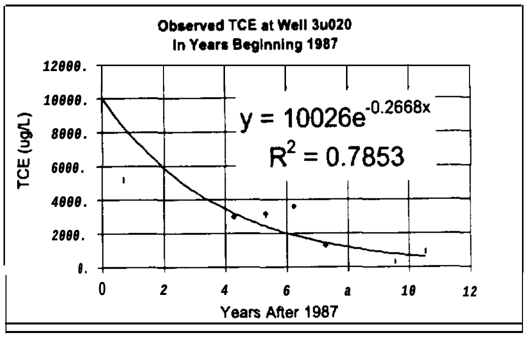


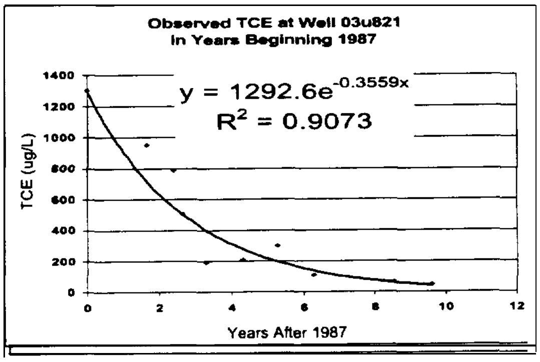
No Decay Simulation Conclusions

- Contaminants are predicted to reach the river with no natural degradation or source removal
- Time to reach river ~34 years
- Steady state reached in ~46 years

Addition of Source Decay


Location of Key Observation Wells

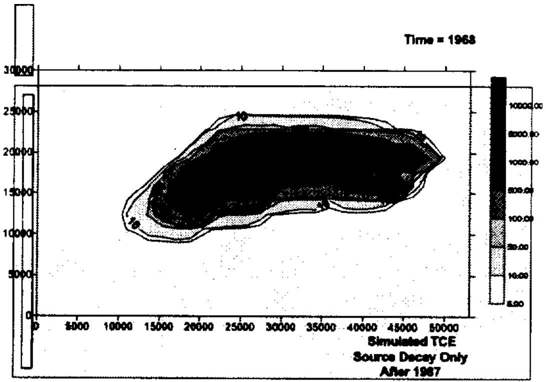

Observed TCE at Well 3u020 In Years Beginning 1987


Observed TCE at Well 03u821 In Years Beginning 1987

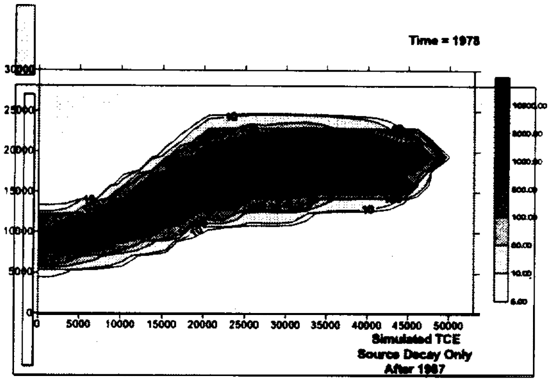
Second Simulation:
Addition of Source Decay

- Source decay fit to actual decline in concentrations in monitoring wells over time
- Source decay added according to first order kinetics with k = 0.25 per year
- Sources held constant till 1988 after which decay was allowed

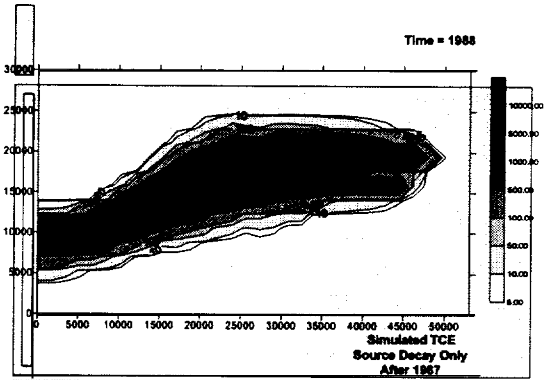
Source Decay Simulation



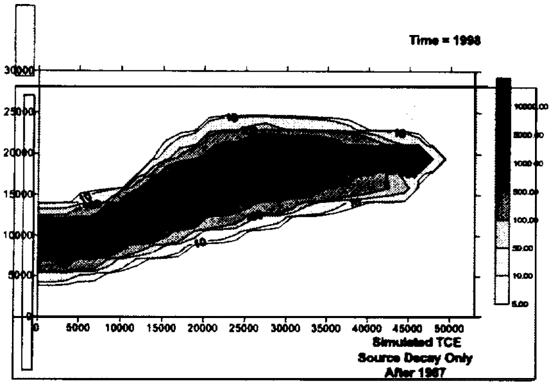
Simulated TCE
Source Decay Only
After 1967



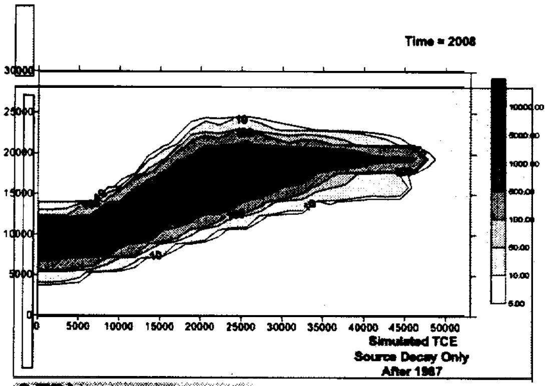
Simulated TCE
Source Decay Only
After 1967



Simulated TCE
Source Decay Only
After 1967



Simulated TCE
Source Decay Only
After 1967



Simulated TCE
Source Decay Only
After 1967

Source Decay Simulation Conclusion:

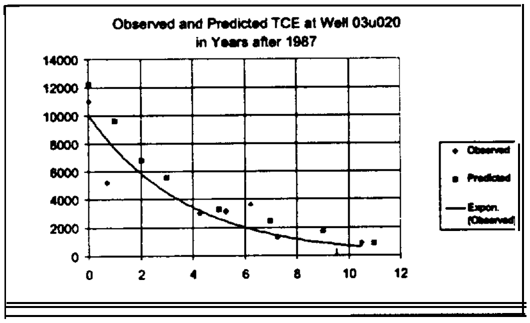
- **Without** dissolved phase natural attenuation, **TCE still would be predicted** to reach the **river even though pumping and source decay/removal are active**
- **Plume** duration is **ultimately controlled** by **source** discharge **of TCE to the aquifer from the source area**

Third Simulation:

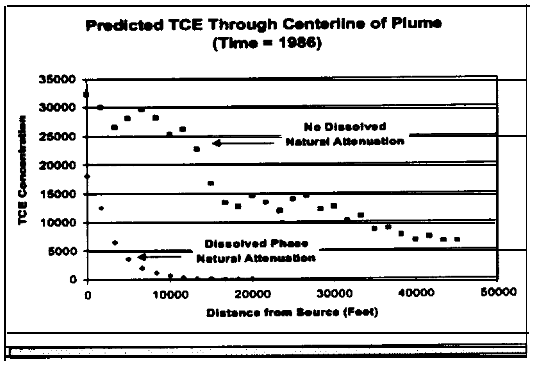
Addition of Intrinsic Bioremediation

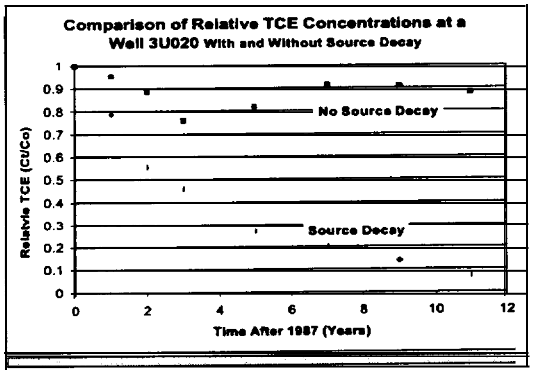
- Bioremediation added at k = 0.35 per year or **half** life = 2 years
- Rates applied throughout the time domain of the simulation
- Pumping and source decay still active

Comparison of Simulation Results



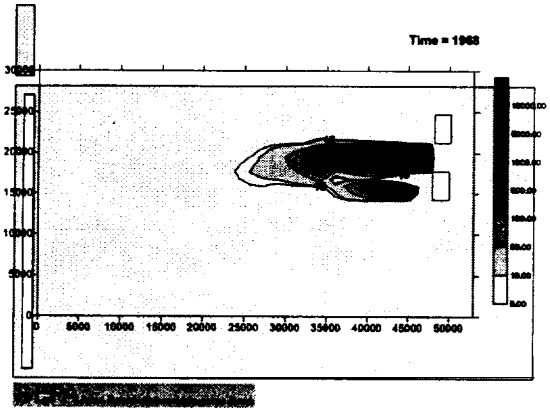
Go to Location Map





Go to Location Map

Source and Dissolved Phase Decay Simulation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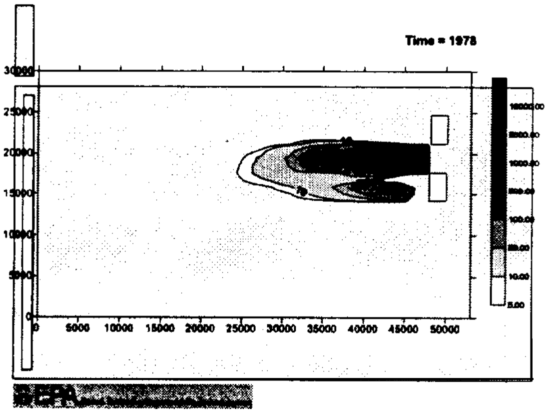
EPA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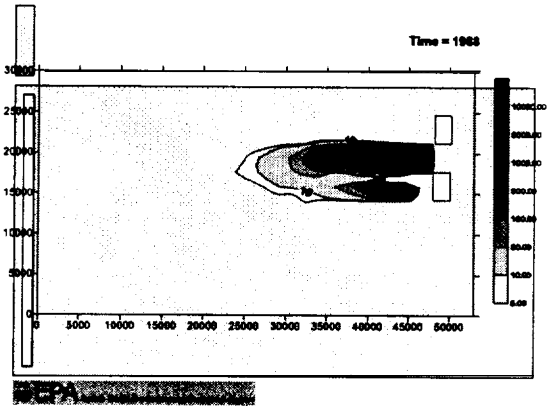
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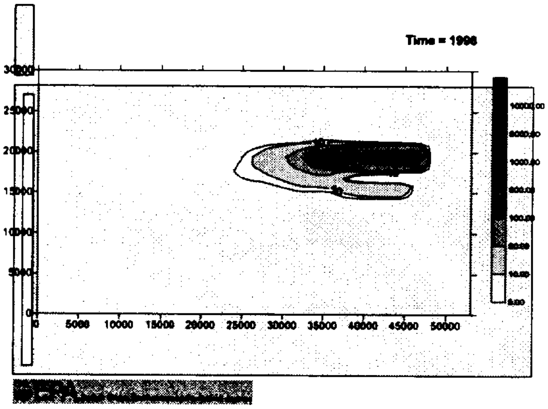
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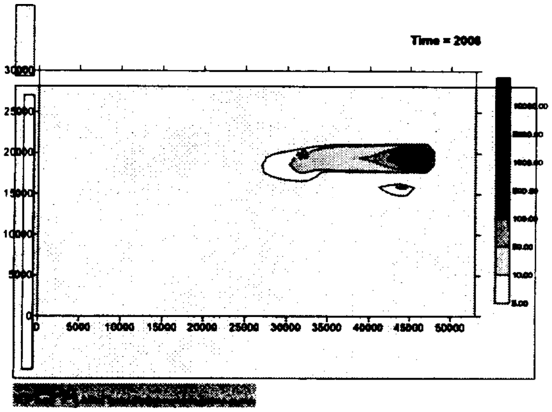
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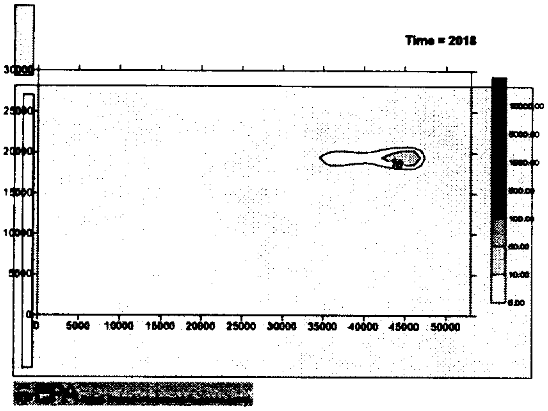
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30000
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45000
50000
10000.00
5000.00
1000.00
500.00
100.00
50.00
10.00
5.00
EPA

Source and Dissolved Phase Decay Simulation Conclusions:

- Plume length and width reduced
- TCE is predicted to not reach the river at concentrations greater than 5 ug/L
- Plume reaches steady state in ~20 years after release
- Concentrations of < 5 ug/L are reached everywhere in the plume approximately year 2022

Effect of Source Control

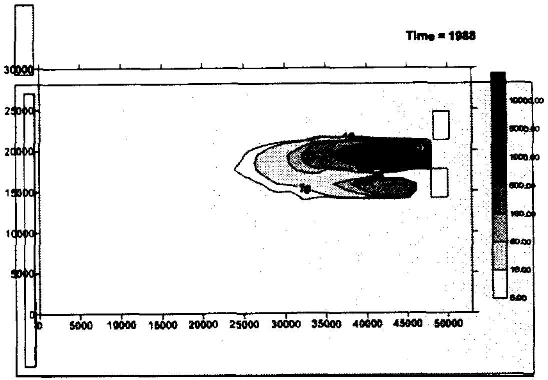
Pumping Assumptions

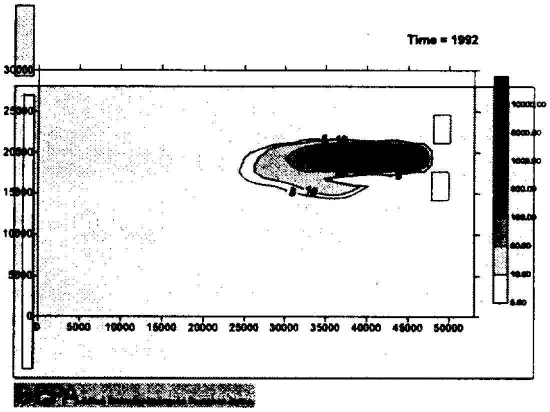
- Model assumes fully penetrating recovery wells with completely mixed TCE solute across the aquifer's saturated thickness
- Actual pumping may or may not recover TCE as predicted due to the vertical position of the well screen relative to contaminant distribution

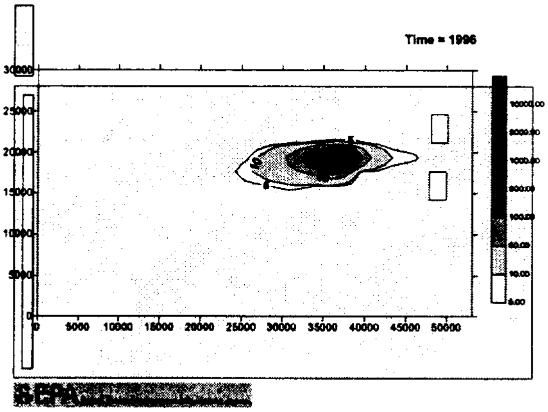
Simulated Total Control of TCE by Pumping

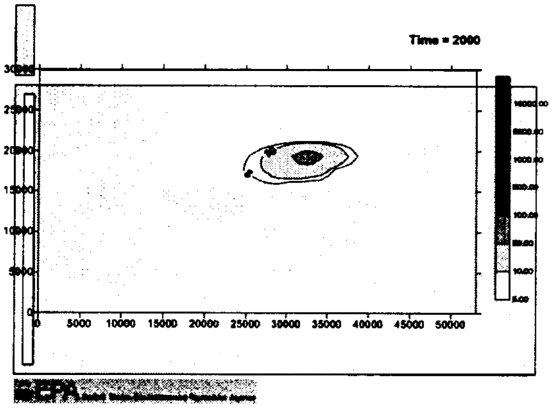
- Total control of release of TCE was simulated by eliminating the sources after 1988.
- Recovery well pumping rates were maintained at the same level as all prior simulations to simulate capture of the existing plume.

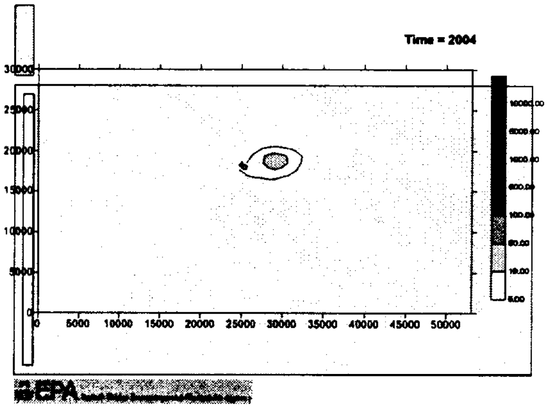
Theoretical TCE Control by Pumping

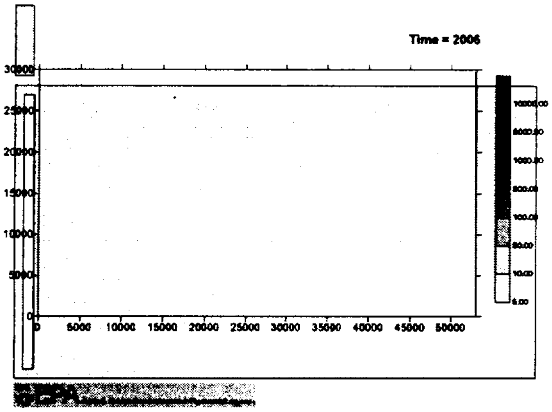


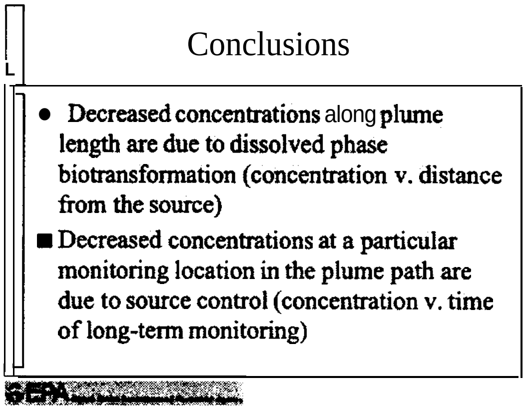












Conclusions

- Decreased concentrations along plume length are due to dissolved phase biotransformation (concentration v. distance from the source)
- Decreased concentrations at a particular monitoring location in the plume path are due to source control (concentration v. time of long-term monitoring)

Calculating Confidence Intervals on Rate Constants

John T. Wilson

Back-of-the-Envelope Prediction of the Rate of Remediation, using Simple Regression Techniques

assume:

Stable **contaminant** plume

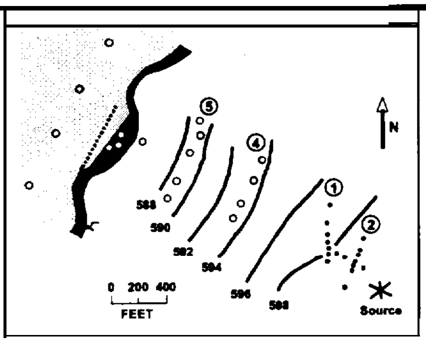
Contaminant plume contained within the foot **print** of **geochemical** tracers

Contaminant attenuation follows **a first-order rate** law

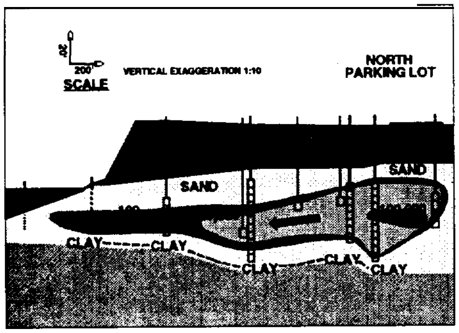
Core of the Plume has **been identified**

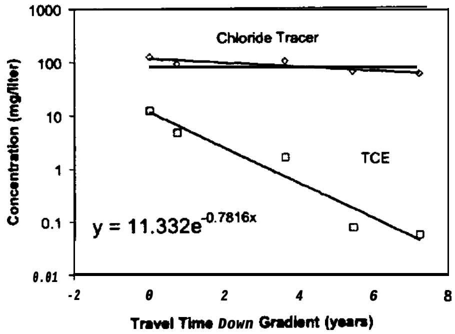
Monitoring wells **available** along the **core** center-line

St. Joseph Site

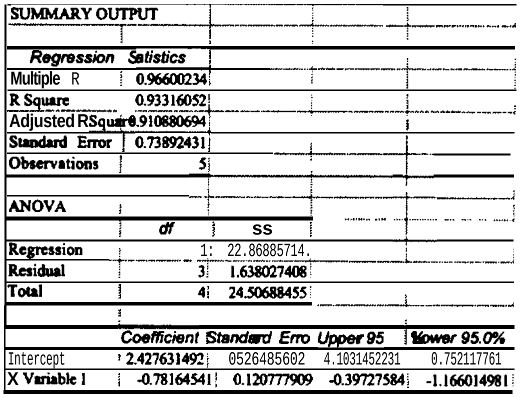


St. Joseph Site

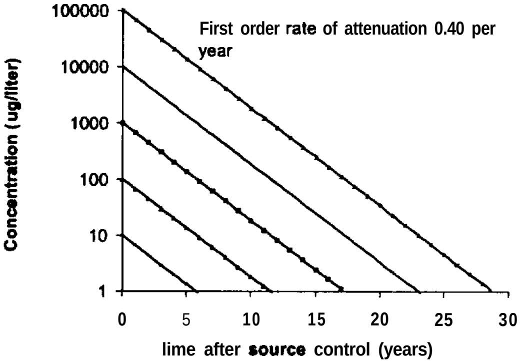




Distance	‘Years	TCE ug/L	LN TCE Conc.
0	0	12.11	2.493205453
200	**0.722022'**	4.7	**1.5475625091**
1000	3.610108	1.6	0.470003629
1500	5.415162	0.07	-2.659260037
2000	**7.220217**	0.051	-2.9759296461



SUMMARY OUTPUT				
Regression Satistics				
Multiple R	0.96600234			
R Square	0.93316052			
Adjusted R Square	0.910880694			
Standard Error	0.73892431			
Observations	5			
ANOVA				
	df	SS		
Regression	1	22.86885714		
Residual	3	1.638027408		
Total	4	24.50688455		
	Coefficient	*Standard Erro*	*Upper 95*	*Lower 95.0%*
Intercept	2.427631492	0526485602	4.1031452231	0.752117761
X Variable 1	-0.78164541	0.120777909	-0.39727584	-1.166014981



Sampling, Analysis, and Monitoring to Evaluate Monitored Natural Attenuation

Site Characterization

Monitoring the Effectiveness of Natural Attenuation

U.S. Geological Survey
and
Barbara H. Wilson

Methods for Monitoring Contaminants

Analysis	Method/Reference	Comments
Aromatic and chlorinated hydrocarbons (BTEX, trimethylbenzene isomers, chlorinated compounds)	SW8020 (sites with petroleum hydrocarbons only) SW8260A (sites with chlorinated solvents or mixed solvents/petroleum hydrocarbons)	Handbook method; analysis may be extended to higher molecular weight alkyl benzenes

Monitoring for Geochemical Conditions

Analytical Parameter	Field or laboratory parameter	Method of analysis
Dissolved oxygen (DO)	field	meter, field kit titration
Nitrate (NO_3)	laboratory	Ion Chromatography
Nitrite (NO_2)	laboratory	Ion Chromatography
Dissolved ferrous iron (Fe^{2+})	field	Field kit spectrophotometer
Sulfate (SO_4)	laboratory	Ion Chromatography
Hydrogen sulfide (H_2S)	field	Field kit spectrophotometer
Dissolved Methane (CH_4)	laboratory	GC FID[1]
pH (units)	field	meter
Eh (redox potential)	field	meter
Dissolved Hydrogen (H_2)	field	gas chromatography[2]

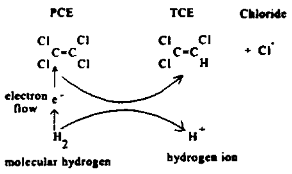
When Hydrogen Analyses are Useful

Some chlorinated solvents plumes exhibit attenuation of solvents without significant accumulation of transformation products.

If hydrogen concentrations range from 1 nannomolar to 4 nannomolar, reductive dechlorination will occur.

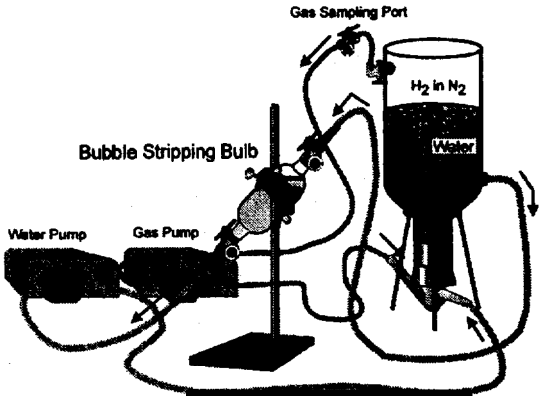
Molecular Hydrogen (H_2) drives Reductive Dechlorination

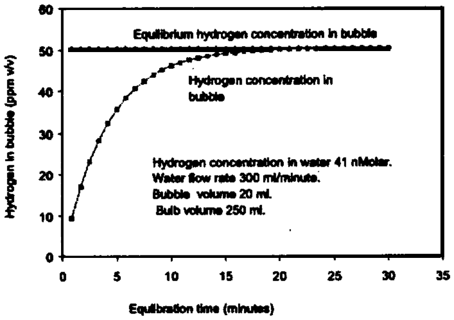
(Gosset and Zinder, 1996)



Steady-State Hydrogen Concentrations Reflect Redox Processes

Terminal Electron-Accepting Process	Characteristic Hydrogen Concentration (nM)
Denitrification	0.1
Fe(III) Reduction	0.2-0.8
Sulfate Reduction	1.0-4.0
Methanogenesis	>5.0





Monitoring Strategies

There are three kinds of monitoring.

1) **Site characterization to describe disposition of contamination and forecast its future behavior.**
2) **Validation monitoring to determine whether the predictions of site characterizations are accurate.**
3) **Long-term monitoring to ensure that the behavior of the contaminant plume does not change.**

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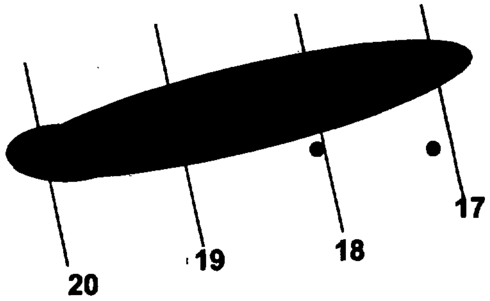
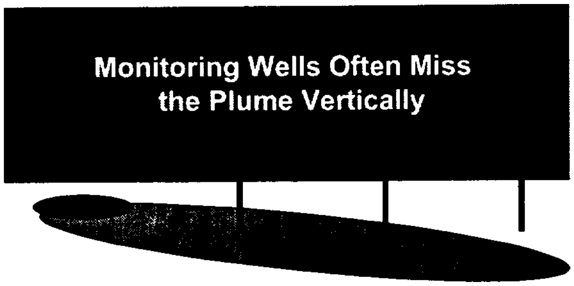
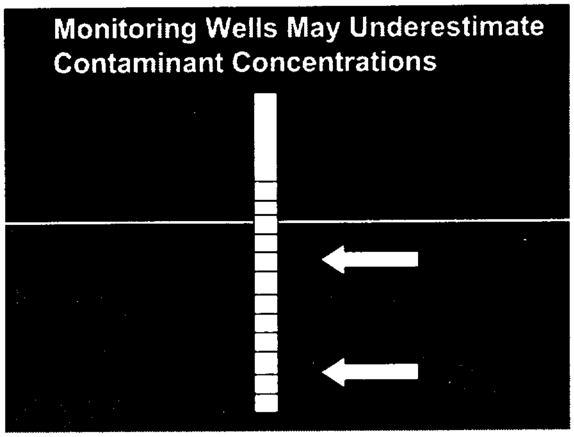
Monitoring Wells Often Miss the Plume (Plan View)

Until you have wells, you don't know the direction of ground-water flow





Monitoring Wells Often Miss the Plume Vertically



Monitoring Wells May Underestimate Contaminant Concentrations

Example of Characterization Monitoring

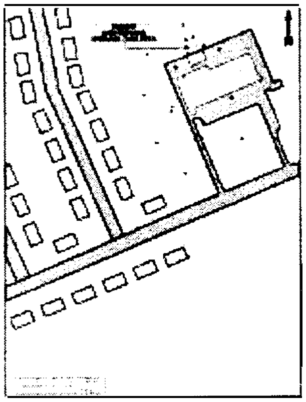
It's not nice to fool Mother Nature,
but she doesn't mind fooling you

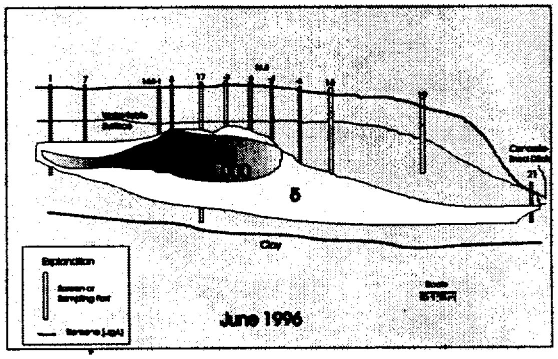
Fate of MTBE relative to benzene at a gasoline spill site (1993-98)

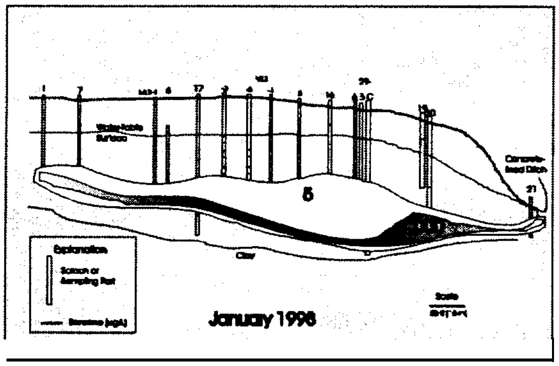
By

James E. Landmeyer
U.S. Geological Survey

Battelle Conference, May 1998







Monitoring Wells Often Miss the Plume Vertically

Site Characterization

- Distribution of contamination can be mapped using:
- Geoprobe samples
- The Waterloo sampler
- Hydropunch samples
- other water sampling through a cone penetrometer
- extraction of core samples
- soil gas sampling

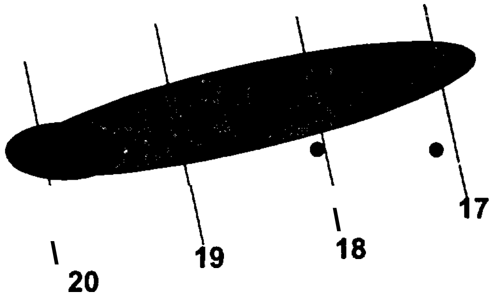
Example: Characterization Monitoring: Kings Bay, GA

- Monitoring Wells
- Geoprobe Source area delineation
- Redox parameters
- Chlorinated ethenes

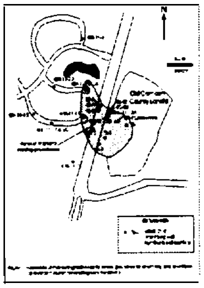
Site Characterization

- **Each potentially transmissive interval should be sampled**
- YOU OUGHT TO KNOW WHERE THE WATER'S GOING TO GO <u>BEFORE</u> YOU PUT IN YOUR WELLS!!

Until you have wells, you don't know the direction of ground-water flow



Old Camden County Landfill, Kings Bay, GA

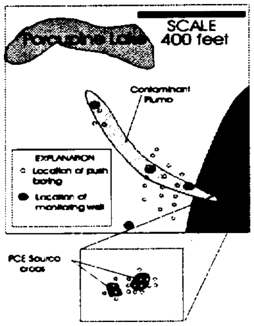


Site Characterization

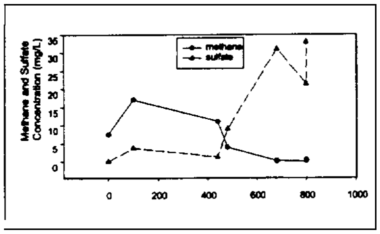
- **The density of sampling during the site characterization must be related to:**

  The geological complexity of the site

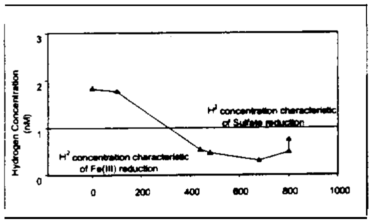
Location of Source Areas and Contamination Plume



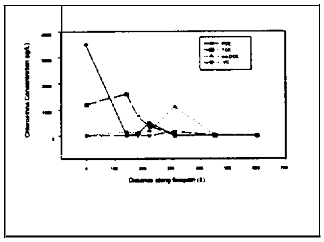
Redox Zonation of Kings Bay Site



Redox Zonation of Kings Bay Site (Cont'd)



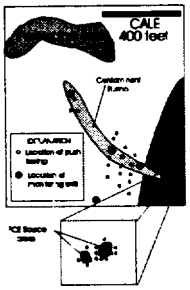
Concentrations of Changes of Chlorinated Ethenes



Natural Attenuation of Chlorinated Solvents, Old Camden County Landfill

- Is relatively efficient.
- Nevertheless, it is not efficient enough to meet remediation goal.
- NA was combined with source removal.

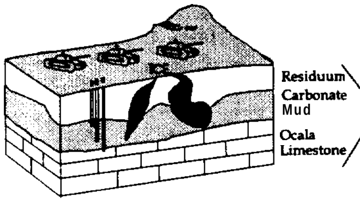
CAP Specifies Source Area removal, Plume is treated with Natural Attenuation.



Example: Characterization Monitoring: Albany, GA

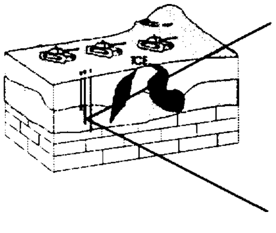
- Monitoring Wells
- Redox parameters
- **Chlorinated** ethenes

Marine Corps Logistics Base, Albany, Georgia



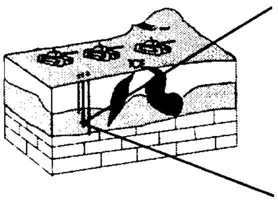
Virtually no organic carbon

Well ALB 12- 1 B--Redox Conditions not favorable for Reductive Dehalogenation



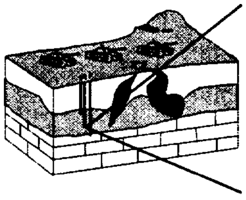
- DO = 7.5 mg/L
- H_2 = 0.05nM
- CH_4 < 0.02 mg/L
- Benzene < 0.2 µg/L
- TCE = 2 202 µg/L
- cis DCE < 0.2 µg/L
- VC < 0.2 µg/L

Well 22 18-MW2--Presence of BTEX drives Reductive Dehalogenation



- DO = 2.0 mg/L
- H_2 = 7.3 mg/L
- CH_4 = 0.7 mg/L
- Benzene = 151 µg/L
- TCE = 168 µg/L
- cis DCE = 568 µg/L
- VC = 236 µg/L

Well 2218-MW-1 -- Water Chemistry Records Past Reductive Dehalogenation



- DO = 5.0 mg/L
- H_2 = 0.59 nM
- CH_4 < 0.02 mg/L
- Benzene < 0.2 µg/L
- TCE = 201 µg/L
- cis DCE = 71 µg/L
- VC = 2.7 µg/L

Redox Chemistry gives a Snapshot in Time.

- **It may not reflect the historical behavior of the contamination.**
- **It may not predict future behavior of the contamination.**

Kings Bay is an Example of Efficient NA--Albany is an example of Inefficient NA

- **This illustrates why characterization monitoring is so important for assessing natural attenuation.**
- **EVERY SITE IS DIFFERENT!!!**

Site Characterization Monitoring Should Consider Multiple Lines of Evidence

- **Redox Conditions**
  - **Presently observed conditions**
- **Distribution of Daughter Products**
  - Record of past conditions
- **Hydrologic Framework**
  - Prediction of **future** conditions

Verification and Long-term Monitoring

Monitoring the Effectiveness of Natural Attenuation

U.S. Geological Survey
and
Barbara H. Wilson

Monitoring Strategies

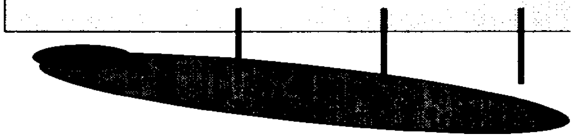
There are three kinds of monitoring.

1) Site characterization to describe disposition of contamination and forecast its future behavior.
2) Validation monitoring to determine whether the predictions of site characterizations are accurate.
3) Long-term monitoring to ensure that the behavior of the contaminant plume does not change.

Validation Monitoring

- Once a conceptual model has been accepted, a period of monitoring is required to verify that the forecast of the conceptual model is adequate

Monitoring Wells Often Miss the Plume Vertically



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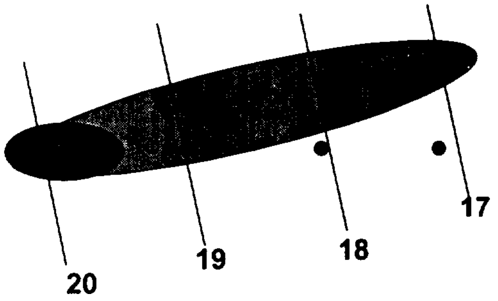
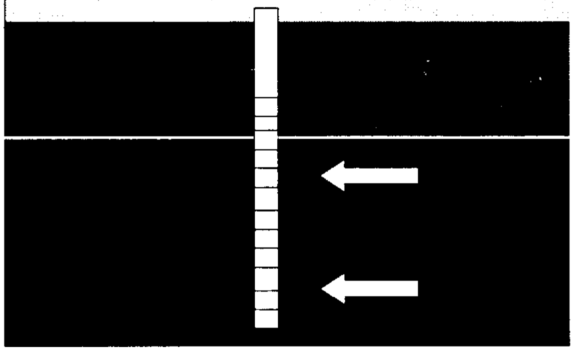


Monitoring Wells May Underestimate Contaminant Concentrations



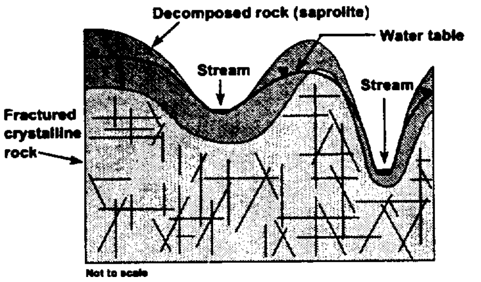
The frequency of validation monitoring should be related to:

- **The natural variability in contaminant concentrations**
- **The distance and time of travel from the source to the location where the acceptance criteria are applied**
- **The reduction in contaminant concentration required to meet the acceptance criteria**

Example: Woodlawn NPL Site
Cecil County, Maryland

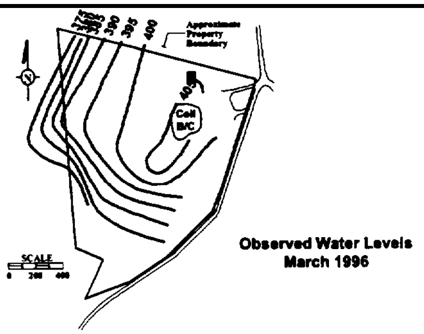
Vinyl Chloride Plume in
Decomposed Rock (Saprolite)
and Fractured Bedrock.
VC at this site is from an industrial
source.

Woodlawn NPL Site
Cecil County, Maryland



Occurrence of ground water in the Piedmont

Woodlawn NPL Site
Cecil County, Maryland



Woodlawn NPL Site
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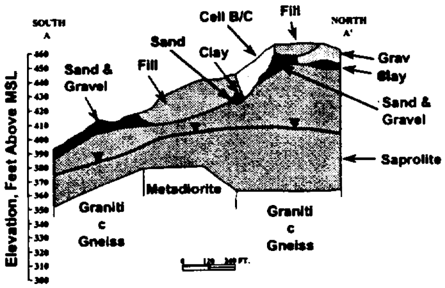
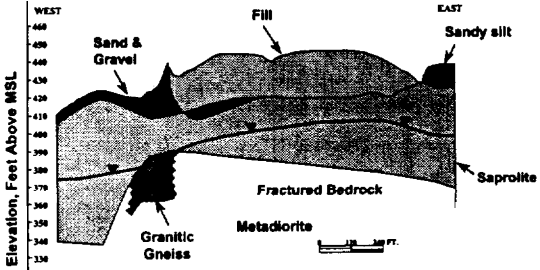


Generalized North/South Geologic Cross-Section

Woodlawn NPL Site
Cecil County, Maryland



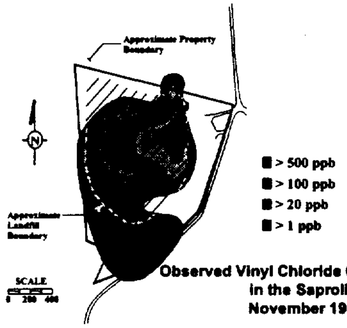
Generalized **East/West** Geologic Cross-Section

Woodlawn NPL Site
Cecil County, Maryland

Saprolite

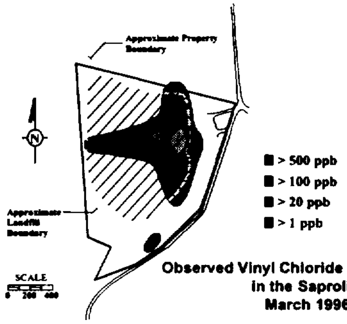
Hydraulic Conductivity	0.24 to 0.79 ft/d
Hydraulic Gradient	0.06
Seepage Velocity	67 ft/year
Plume Length	1,000 feet
Half Life total plume	-0.3 years

Woodlawn NPL Site
Cecil County, Maryland



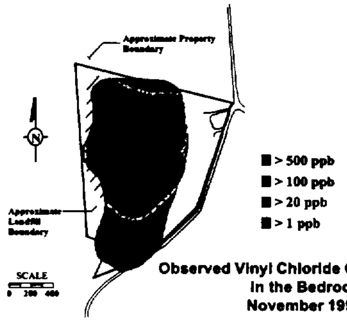
Observed Vinyl Chloride Concentration
In the Saprolite
November 1987

Woodlawn NPL Site
Cecil County, Maryland



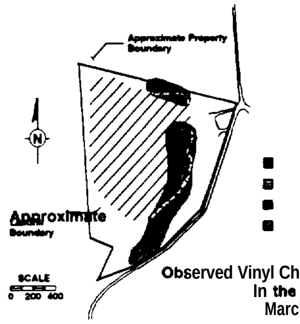
Observed Vinyl Chloride Concentration
In the Saprolite
March 1996

Woodlawn NPL Site
Cecil County, Maryland



Observed Vinyl Chloride Concentration
In the Bedrock
November 1990

Woodlawn NPL Site
Cecil County, Maryland



Observed Vinyl Chloride Concentration
In the Bedrock
March 1996

Contaminant Transport

- Contaminant plume appears to be moving through fractured portions of the bedrock.

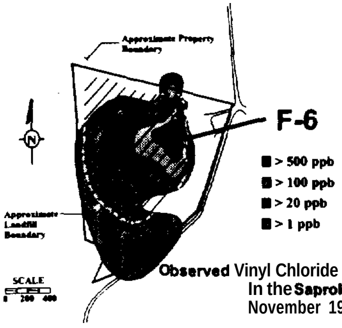
Woodlawn NPL Site
Cecil County, Maryland

VC degradation:
WHY IS IT HAPPENING?

- **Aerobic Oxidation (most rapid)**
  » $2O_2 + CH_2 = CHCl >> 2CO_2 + 3H^+ + Cl$
- **Anoxic Oxidation**
  $10Fe_3^+ + CH_2 = CHCl + 4H_2O \dashrightarrow 2CO_2 + 11H^+ + Cl + 10Fe_2^+$
- **Volatilization**
- **Sorption (very low for vinyl chloride)**

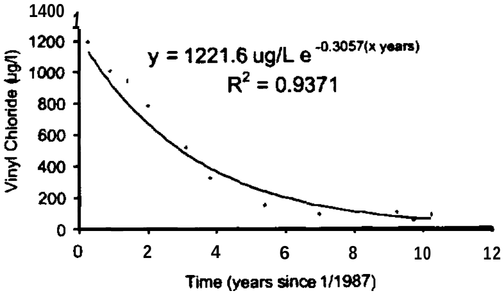
Location of Well F-6

Woodlawn NPL Site
Cecil County, Maryland



Observed Vinyl Chloride **Concentration**
In the **Saprolite**
November 1967

Monitoring Well F-6 at Woodlawn Landfill



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3) **Long-term monitoring to ensure that the behavior of the contaminant plume does not change.**

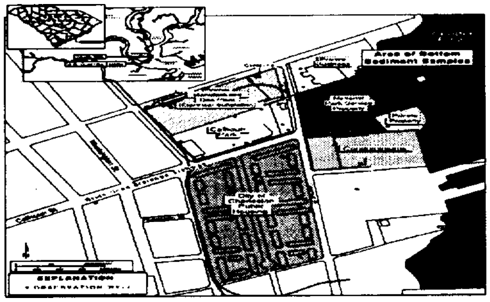
Long-term Monitoring

- **If validation monitoring documents that natural attenuation will meet the acceptance criteria, then a program of long-term monitoring should be implemented.**

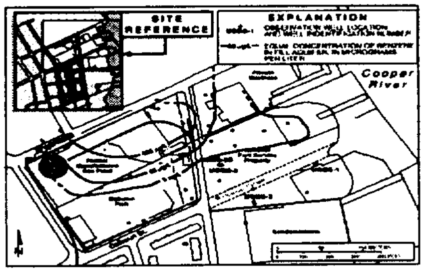
Long-term Monitoring

- The interval of sampling should be related to the expected time of travel of the contaminant along the flow path from one monitoring well to the next.

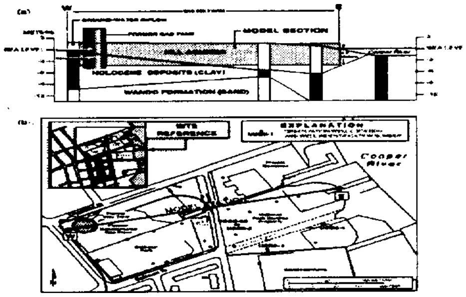
Example of Validation & Long-Term Monitoring:Charleston MGP Site



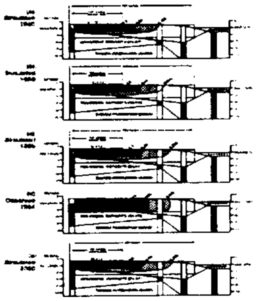
Contaminants in Ground Water



Hydrogeology of MGP Site



Simulation of Plume Migration

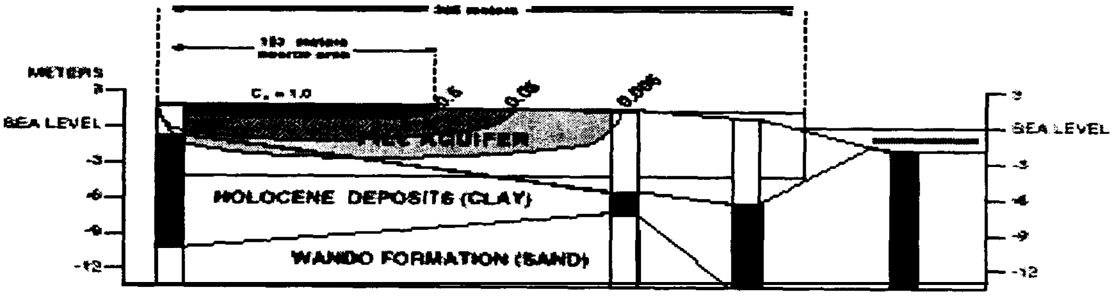


See following page for an enlarged version of this slide.

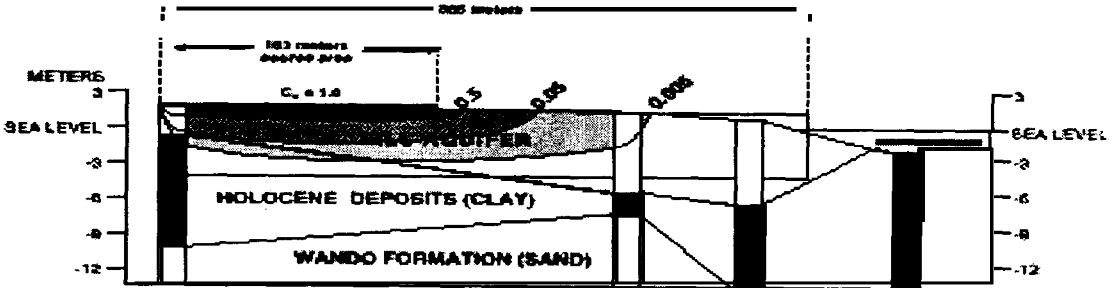
Long-Term Monitoring Plan for the MGP Site

- Model indicates plume is stationary. Long Term Monitoring designed to evaluate changes in plume size.
- GW time of travel is relatively slow (~40 ft/yr). Quarterly sampling is probably too frequent; annual or biannual sampling is more appropriate.

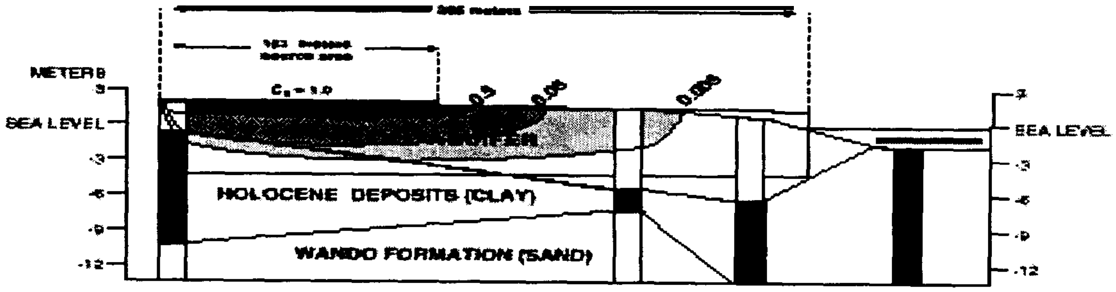
Simulation of Plume Migration



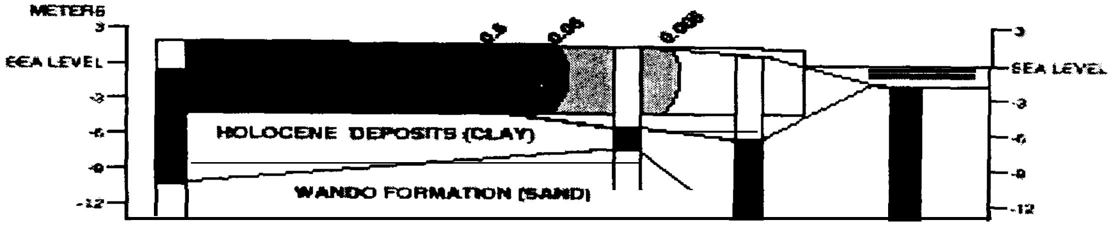
(a). Simulated 1900



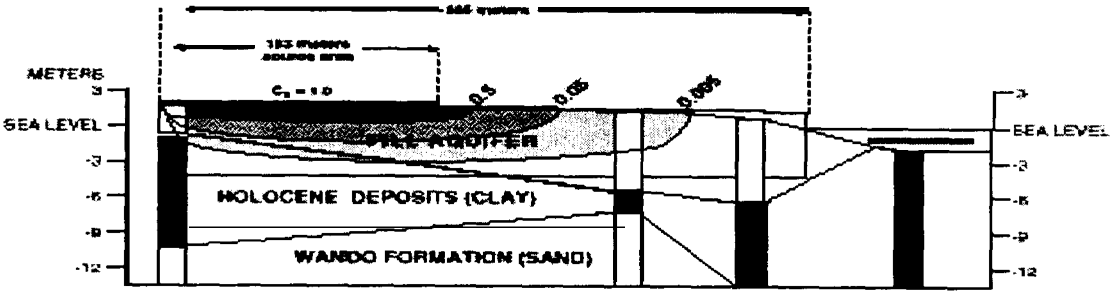
(b). Simulated 1950



(c). Simulated 1995



(d). Observed 1994



(e). Simulated 2050

Criteria for Success

Criteria for Sucess

Francis Chapelle
John T. Wilson
Fran Kremer
Kelly Hurt

Criteria for Success

- Understand how the plume is formed in the first place

*Understand the rate of transport and the rate of attenuation

*Understand the persistence of the contaminant mass

Criteria for Success

- Understand how the plume was formed in the first place

Understand the **3-dimensional** distribution of the original source of contamination

Understand the movement of water and vapor through and from the original source

Criteria for Success

- Understand how the plume was formed in the first place

Does existing ground water contamination make sense based on what is known about the original source material and the hydrogeology of the site?

Criteria for Success

'Understand the rate of transport and the rate of attenuation

What is the natural variation in ground water flow velocity and flow direction?

What is the seepage velocity of the lithology that actually carries the plume?

Criteria for Success

'Understand the rate of transport and the rate of attenuation

What is the mass flux of contaminants?

Is it decreasing along the flow path?

Criteria for Success

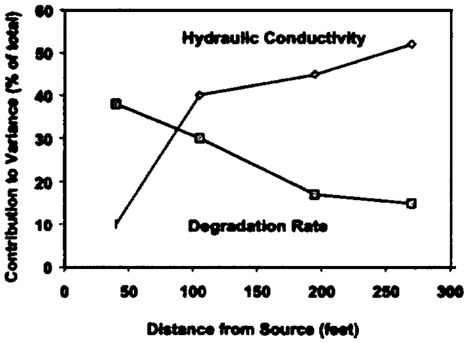
What is the relative importance in understanding?

hydraulic **conductivity**

hydraulk **gradient**

dispersivity

rate of biodegradation

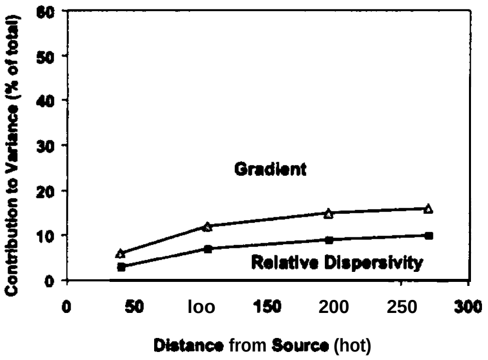


Criteria for Success

Uncertainty Analyaaa of Fuel Hydrocarbon Biodegmdation Signatures in Ground **Water** by **Probabilistic** Modeling

W.W. **McNab** and B.P. Doohar

Ground Wahr **36(4):691-698** July August 1999



Criteria for Success

***Understand the rate of transport and the rate of attenuation**

What la **the confidence** In **the** method uaad to **estimate** hydmulk conductivity?

la **the resolution** of tha monltorlng **well ●** yatam **defined and documented?**

Criteria for Success

***Understand** tha rata of **transport** and tha rata of attenuation

Will tha currant rata of attanuation ba maintained?

Will an accaptabla mta of attenuation ba maintainad?

Criteria for Success

*Understand the **rate** of transport and the **rate** of attenuation

Is there a sufficient supply of electron acceptors or donors to complete attenuation of the contaminants in ground **water?**

Criteria for Success

The resolution of each well in the monitoring well system is the product of:

Lateral distance between adjacent monitoring wells in a transect

Vertical screen interval

Darcy velocity of ground water

lime between samples

Criteria for Success

The resolution of each well in the monitoring well system has the units of volume.

Acre feet

Million gallons

Cubic feet.

Criteria for Success

When the resolution of the permanent monitoring wells is predetermined, then the monitoring system can designed and scaled to meet that predetermined resolution.

Criteria for Success

Evaluate the resolution of monitoring wells along with the concentrations of contaminants and geochemical indicators.

Criteria for Success

*Understand the persistence of the contaminant mass

Evaluate the effectiveness of source control measures

- Is a new plume forming?
- Is the hot spot moving down gmdient of the former source area?

Criteria for Success

- Understand the persistence of the contaminant mass

Statistical estimate of the rate of attenuation of the hot spot, after source control

  - How fast is the old plume going away?
  - How fast will other remedies approach cleanup goals?

Criteria for Success

- Understand the persistence of the contaminant mass

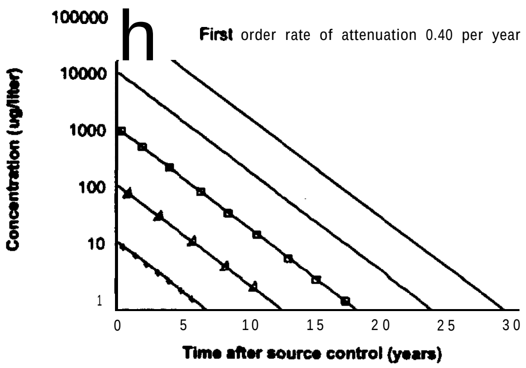
Required are a statistical comparison of two rates of remediation, the **rate** of natural attenuation, and the rate of active remedy.

Criteria for Success

- **Understand** the **persistence** of the contaminant mass

The confidence in the **comparison** is limited by the confidence in the estimate of the two **rates**.

If the comparison is not expressed **with** an estimate of confidence, it is worthless.



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