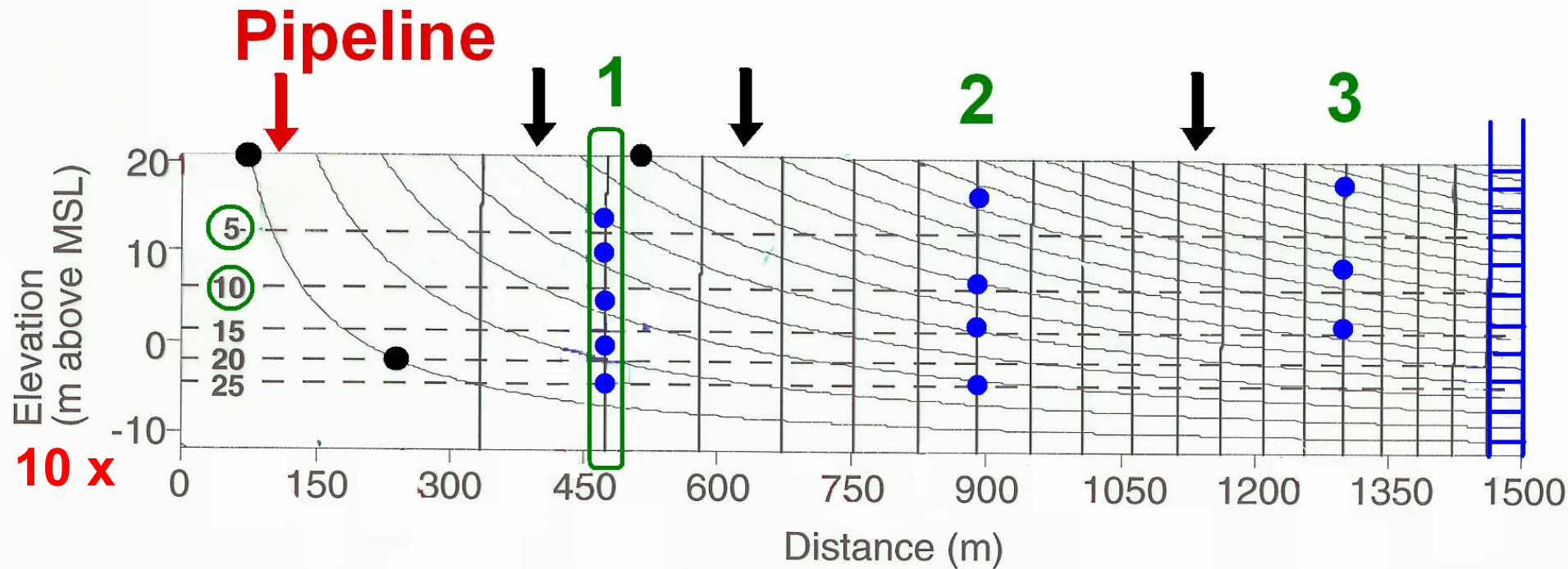


Fig. 5. Simulated stream functions, hydraulic potentials, and the configuration of the water table (note expanded scale). Also shown is the simulated location of water recharged in 1975 beneath Greenway Road at various points in time along the flow system. The shaded region highlights a flow line and does not represent a simulated contaminant plume.

Model Simulation

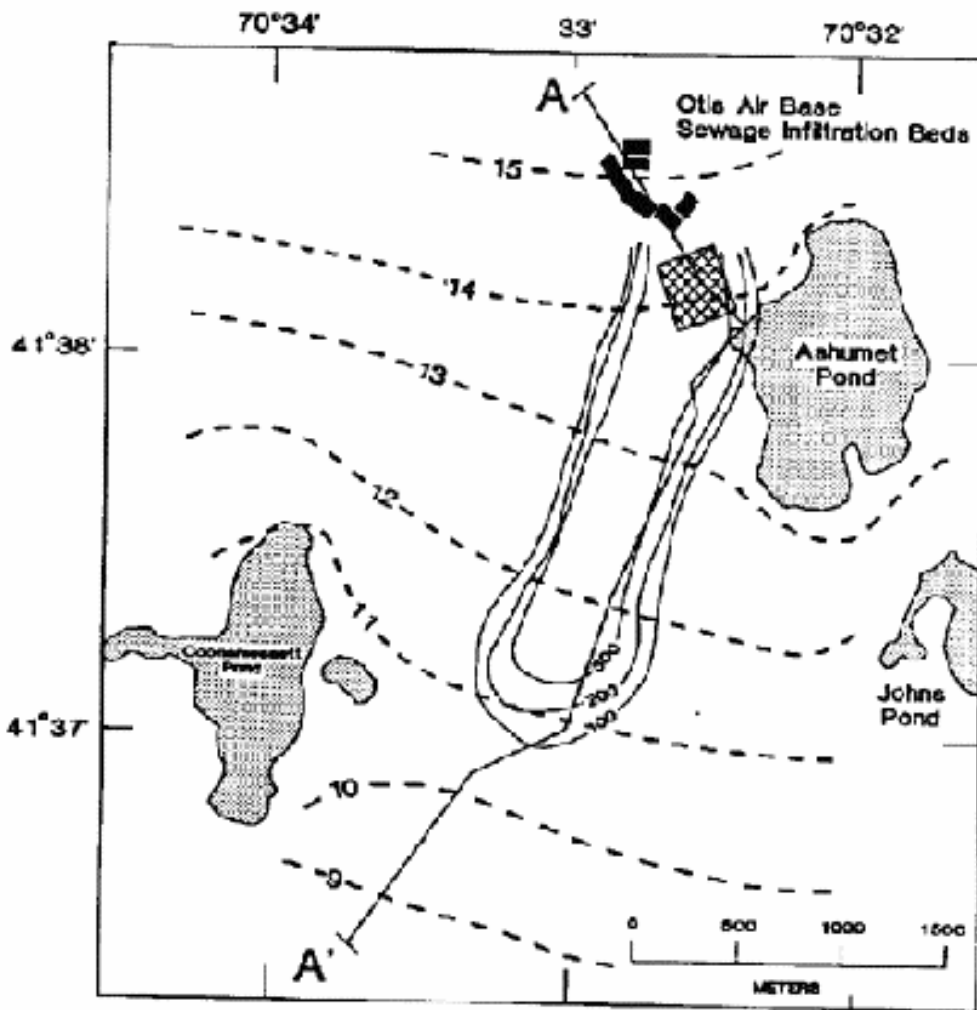
Uniform Recharge – 60 cm/yr






-5- Travel Time (year)
Stream Function
Potential

Potential Interval 0.0028 m
Stream Function Interval 0.12 m² /d

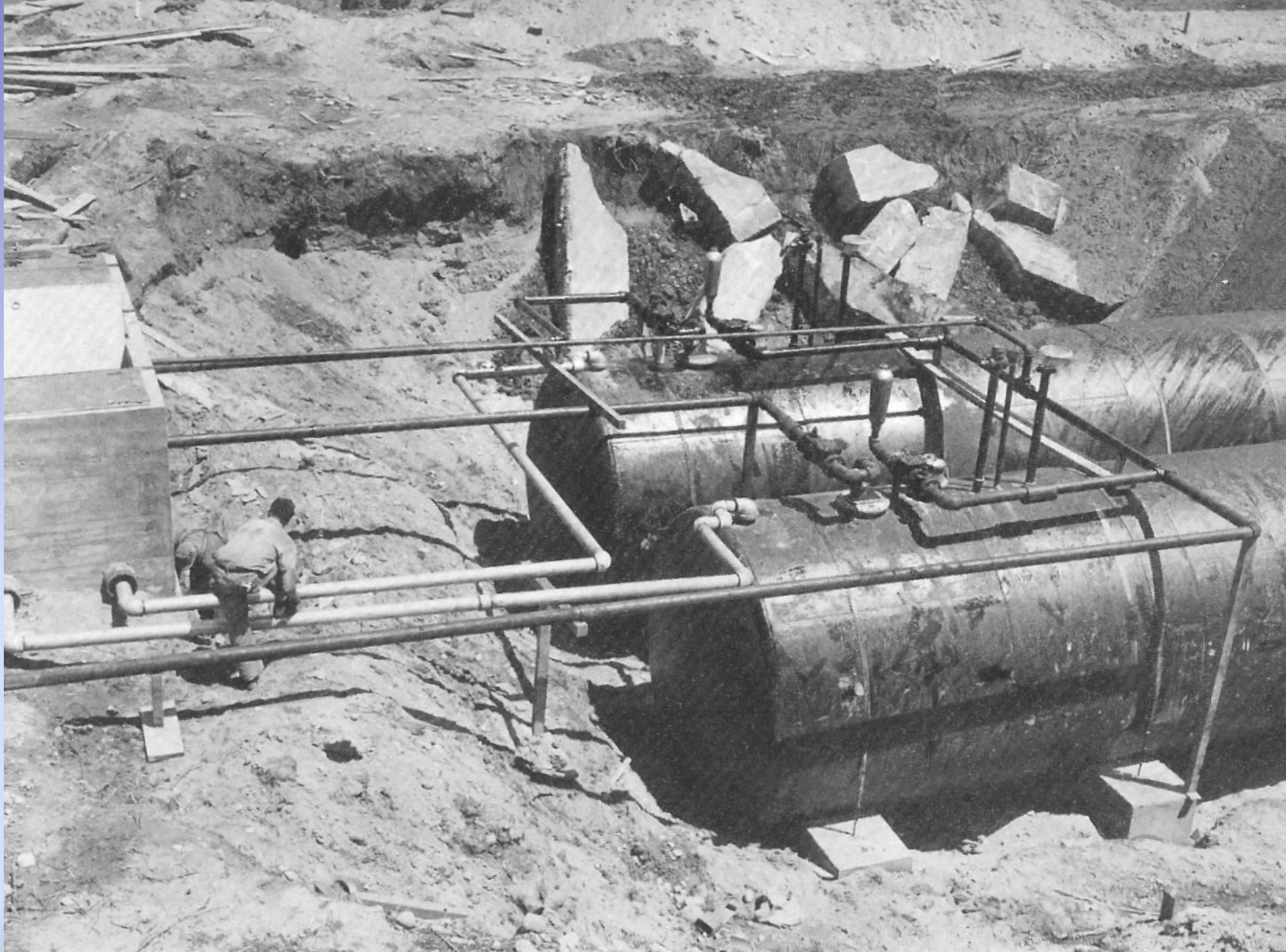
High degree of vertical stratification



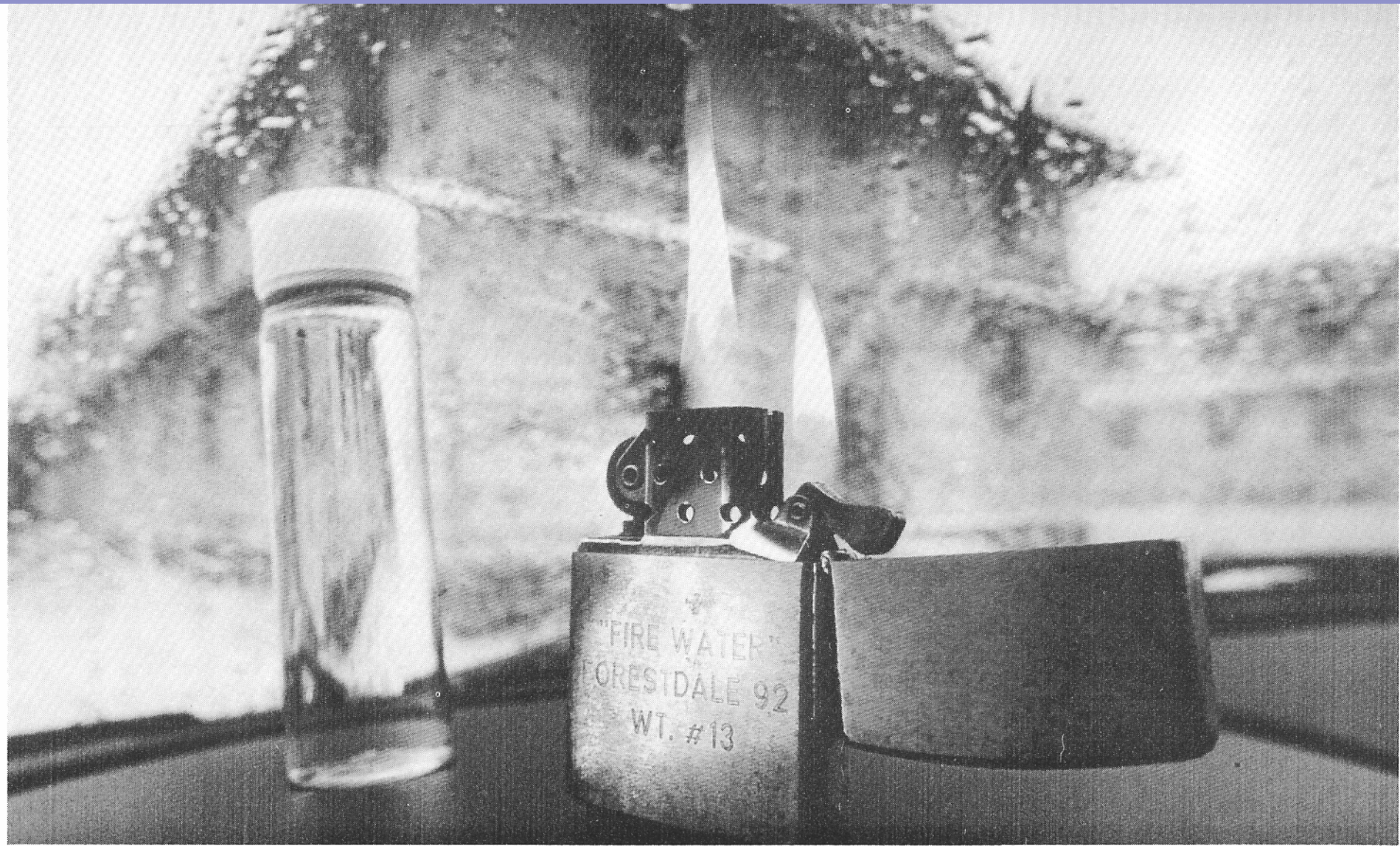
EXPLANATION

-  **TRACER-TEST SITE** — Shows area in figure 4.
-  **LINE OF EQUAL BORON CONCENTRATION, 1978-79**—
Concentrations in micrograms per liter.
-  **WATER-TABLE CONTOUR, NOVEMBER 1978**—
Altitude of water table in meters. Datum is sea level.
- A—A'** **LINE OF SECTION SHOWN IN FIGURES 2 AND 14.**

LeBlanc et al. (1991) WRR, 27, 895



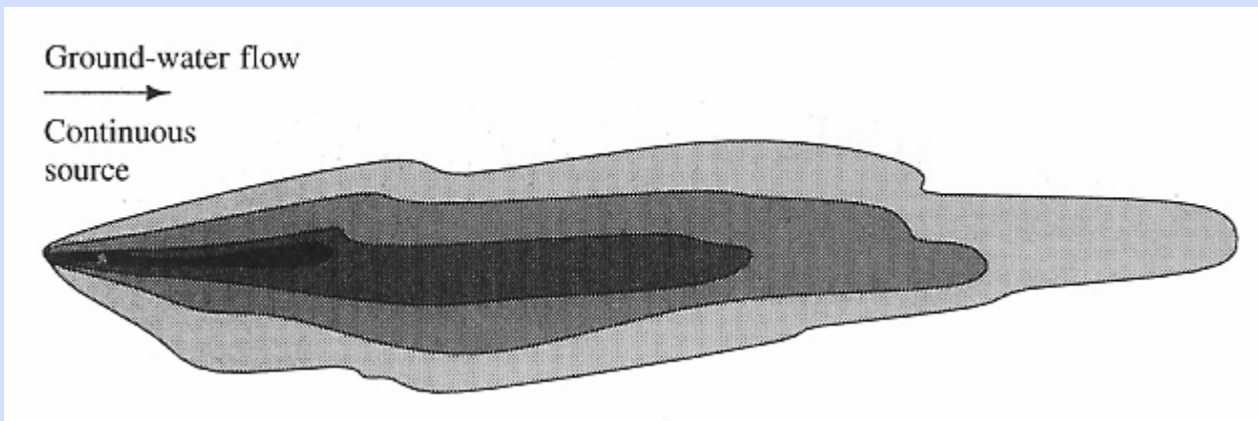
Underground fuel storage: out of sight, out of mind. June, 1941.



Firewater: A groundwater sample, taken from the area of the Sandwich pipeline, contained enough jet fuel to burn.

Other Conservative Groundwater tracers

- tracer moves at the same rate as the water
 - not impeded by methods such as chemical reactions or degradation. Influenced only by physical processes such as mixing, diffusion, etc.
- * See page from book: John Cherry, Camp Borden, Ontario.



Plume resulting from the continuous injection of a tracer into a two-dimensional flow field.

Injection of a slug tracer into a two-dimensional flow field shown at 3 time increments.

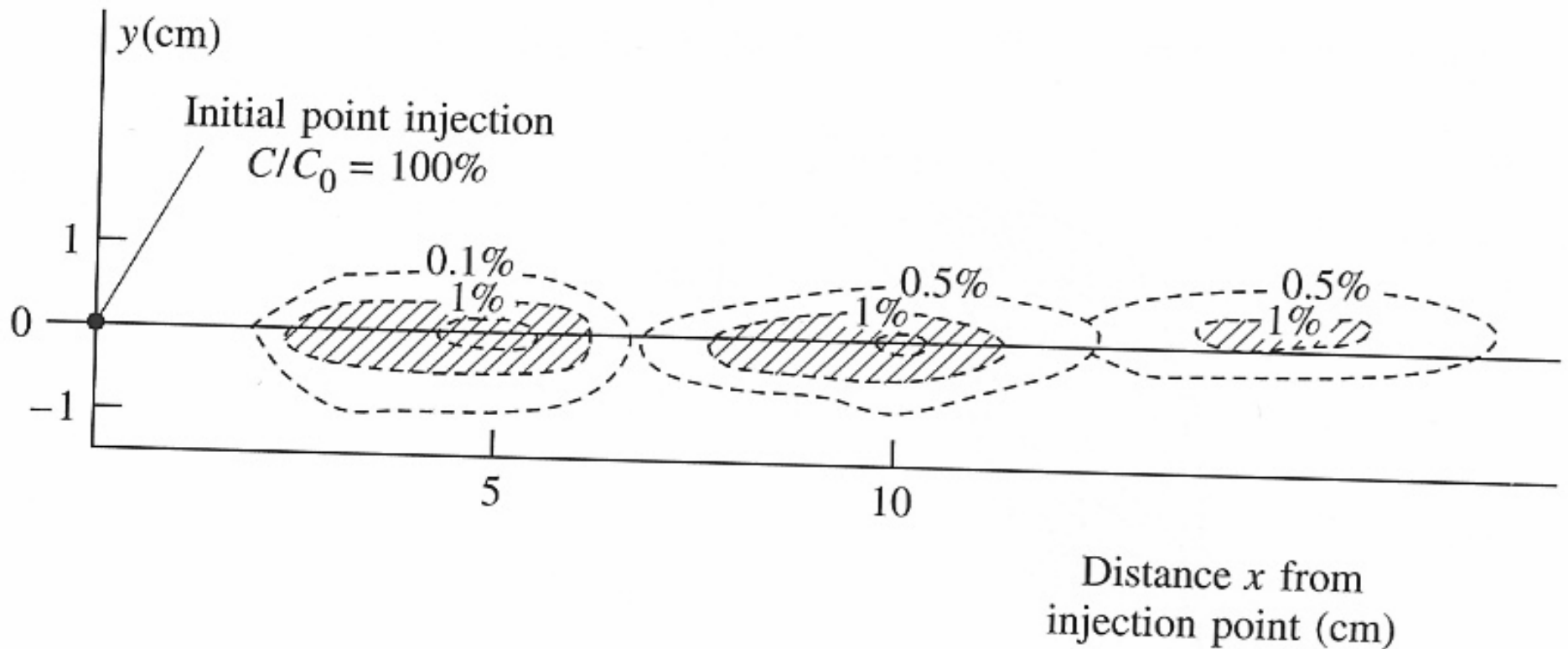


Figure 2.12. Fetter, Contaminant Hydrogeology 3rd Edition

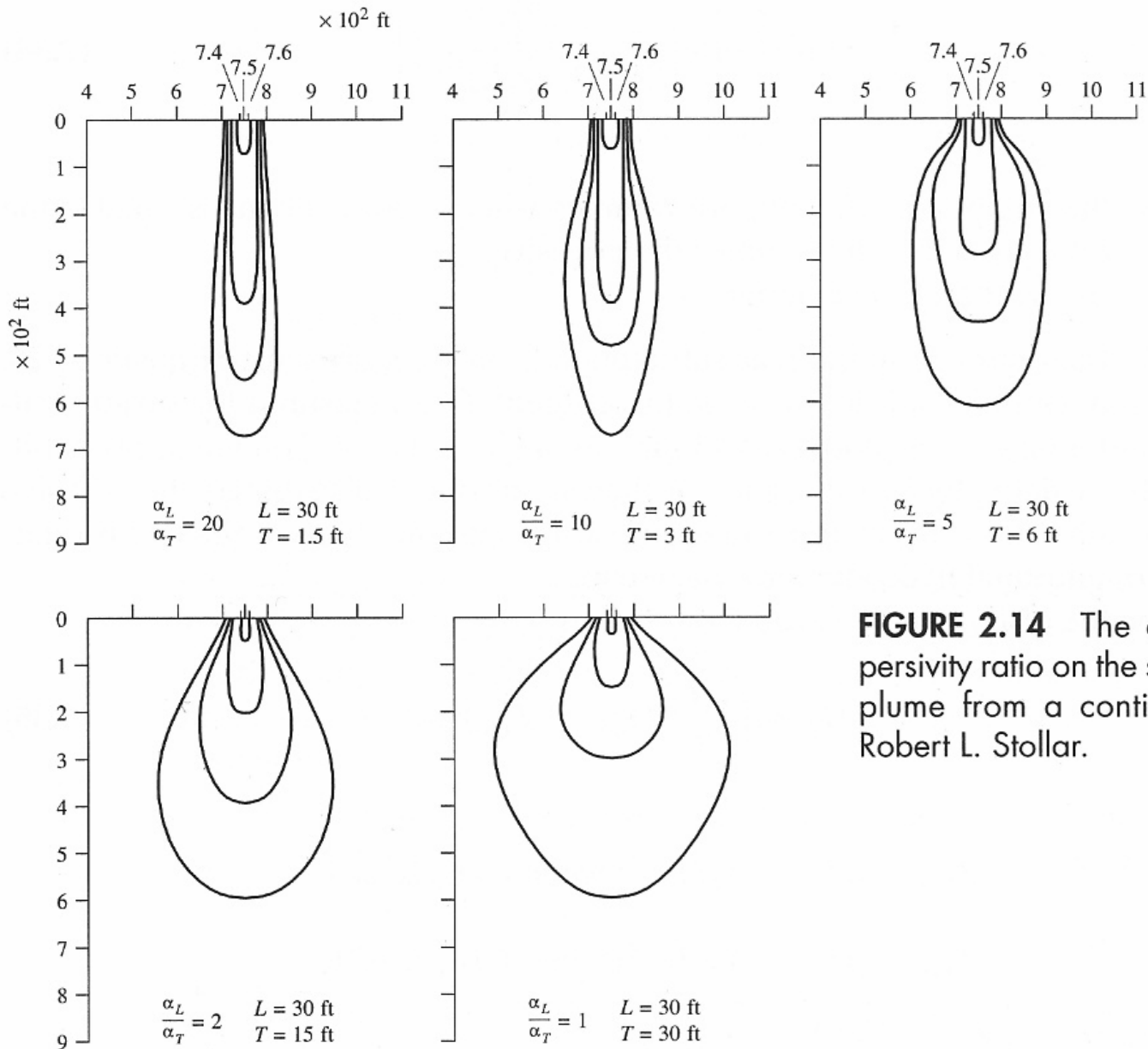


FIGURE 2.14 The effect of changing dispersivity ratio on the spread of a contaminant plume from a continuous source. *Source:* Robert L. Stollar.

Behaviors of contaminants

I. Movement:

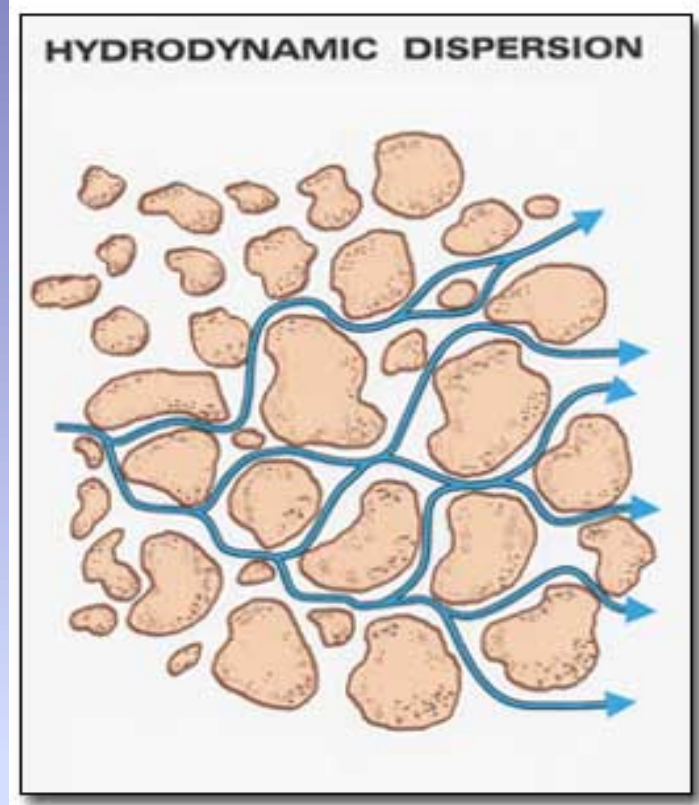
- the release (plume) will not spread at a constant rate because there are different paths that it could take- it moves with the water- will take short or long paths around grains.

A. Dispersion: spreading of plumes

*water flowing through a porous medium takes different routes

*important components:
longitudinal & transverse dispersion

→ velocity dependent, so
equivalent only for very slow flow



<http://www.theshop.net/xibits/litigation/diagrams9.htm>

- $D^* = 10^{-5} \text{ m}^2/\text{day}$. (D^* = diffusion constant)
- $\alpha_L = .1 \text{ m/day}$ (dispersion constant, longitudinal).
- $\alpha_r = .001 \text{ m/day}$ (dispersion constant, transverse).
- $(\alpha_L)(V_x) + D^* = D_L$ ---> longitudinal
- $(\alpha_T)(V_z) + D^* = D_T$ ---> transverse

Factors causing pore-scale longitudinal dispersion

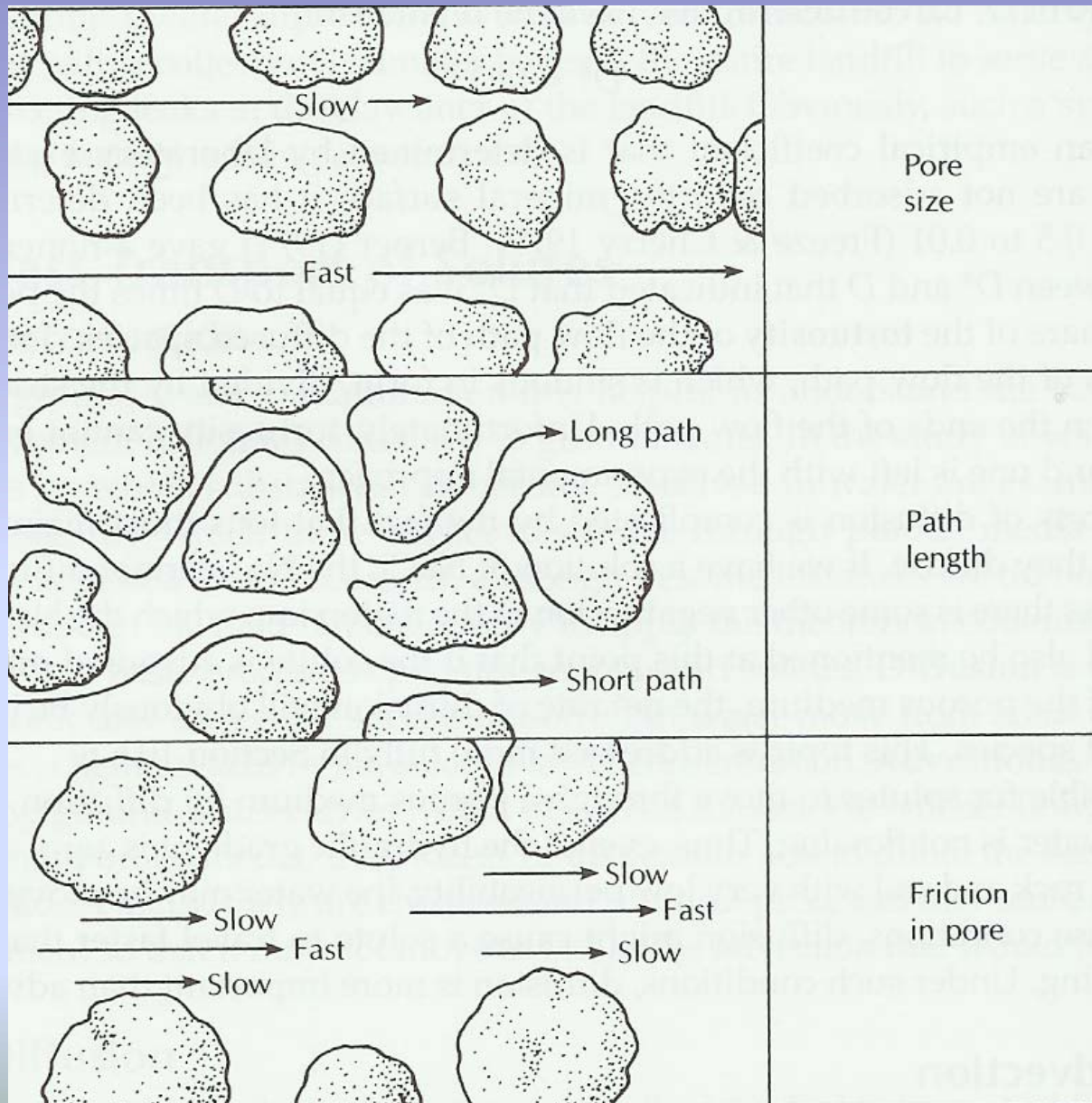


Figure 10.8 Fetter, *Applied Hydrogeology 4th Edition*

B. Advection: horizontal velocity

Advective transport and the influence of dispersion and diffusion on “breakthrough” of a solute

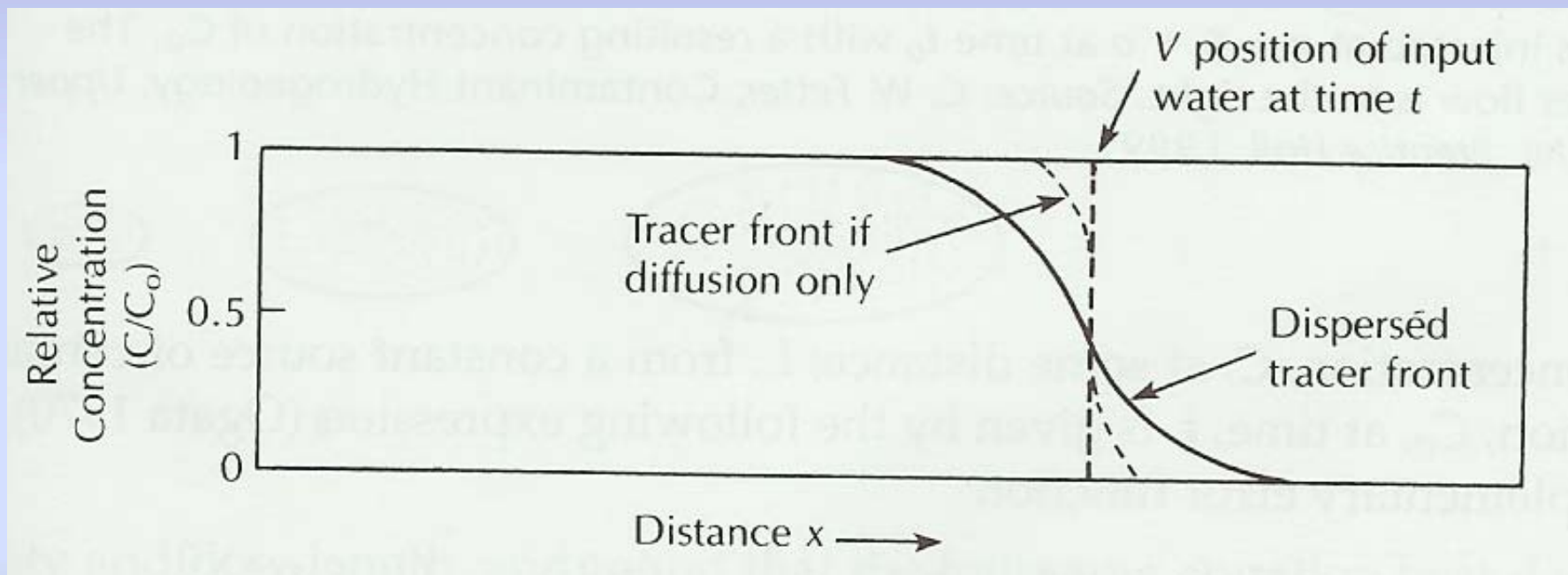


Figure 10.10 Fetter, *Applied Hydrogeology 4th Edition*

Transport and spreading of a solute slug with time due to advection and dispersion. A slug of solute was injected at $x = 0 + \alpha$ at time t_0 with a resulting concentration of C_0 . The ground-water flow is to the right.

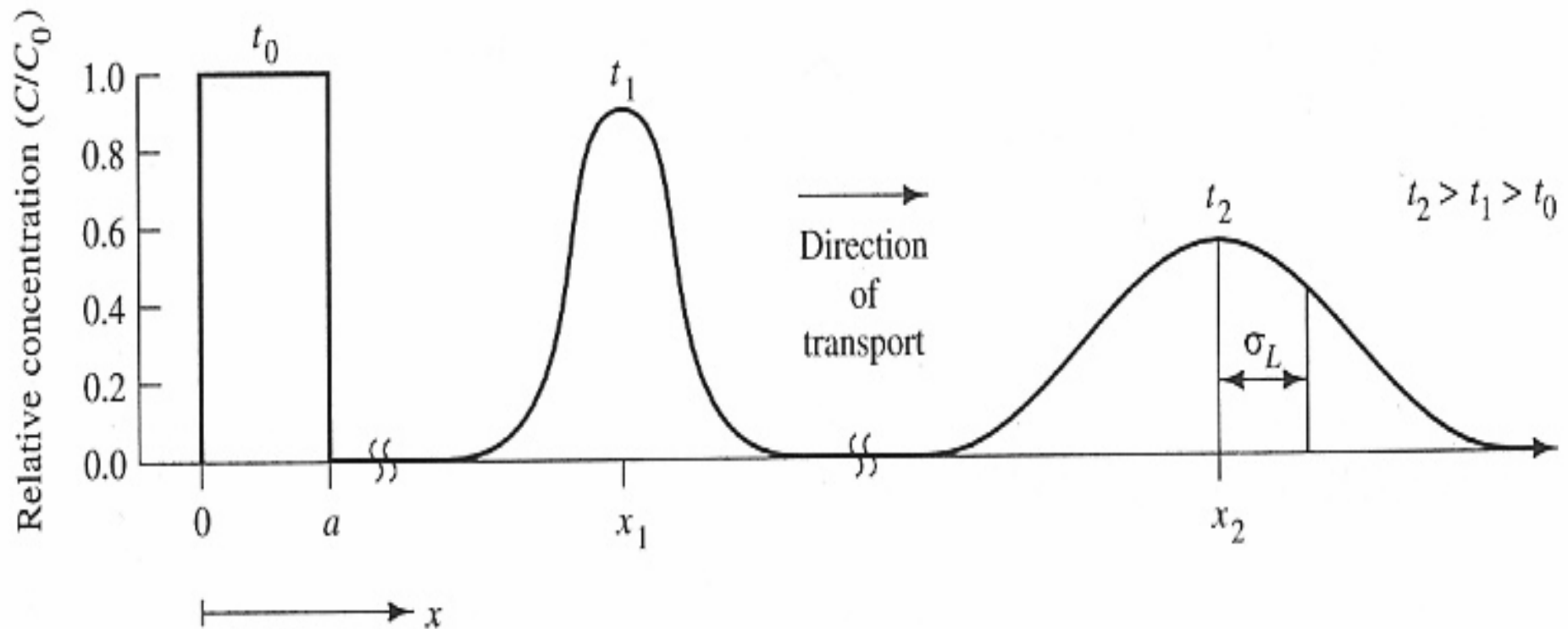


Figure 2.6. Fetter, *Contaminant Hydrogeology 3rd Edition*

C. Diffusion: function of concentration & diffusion coefficient

Spreading of a solute slug with time due to diffusion. A slug of solute was injected into the aquifer at time t_0 with a resulting initial concentration of C_0 .

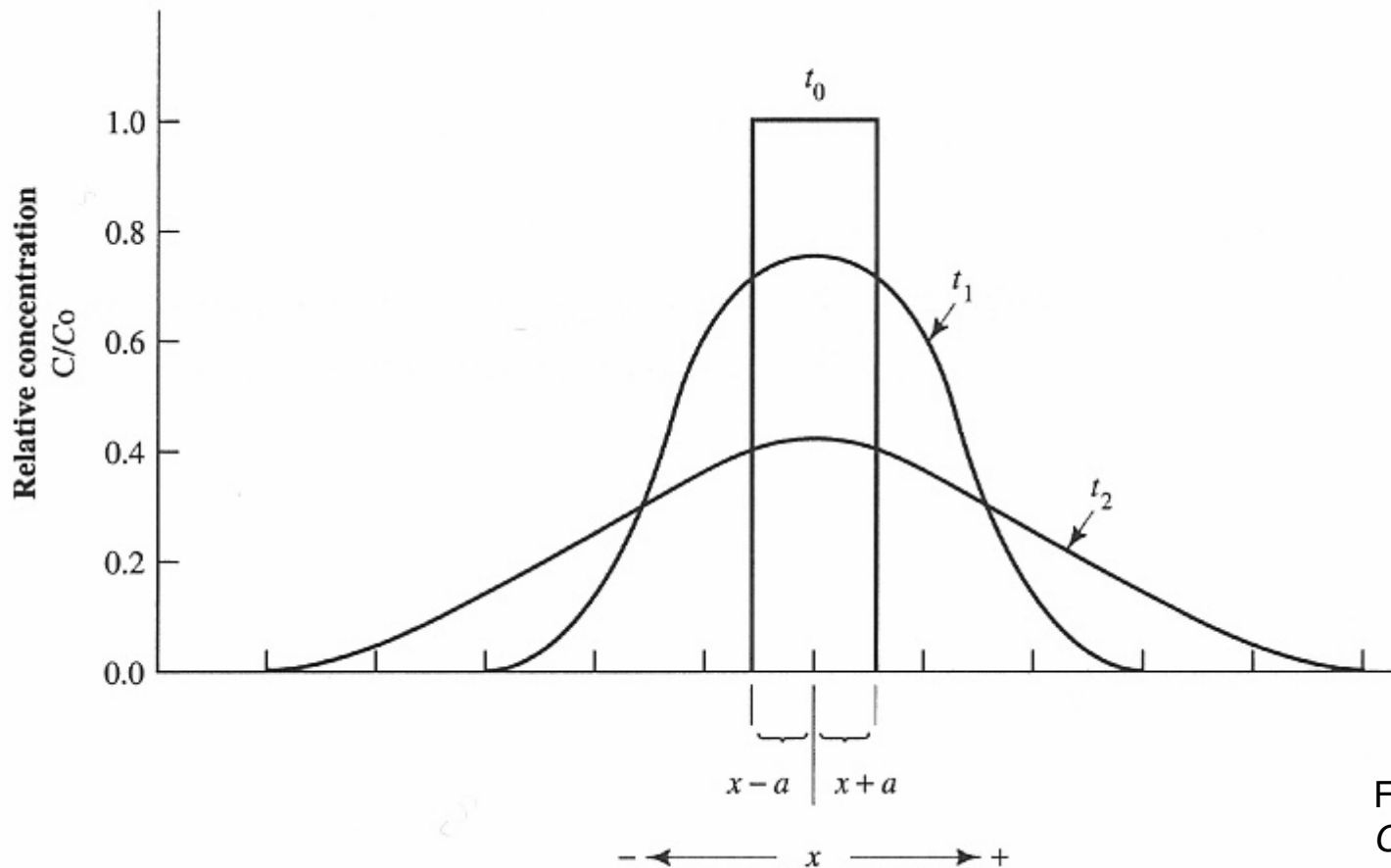
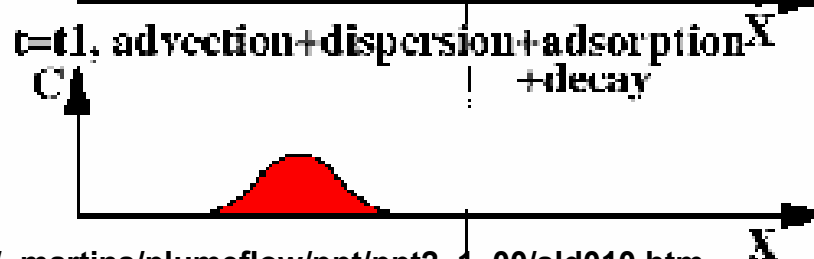
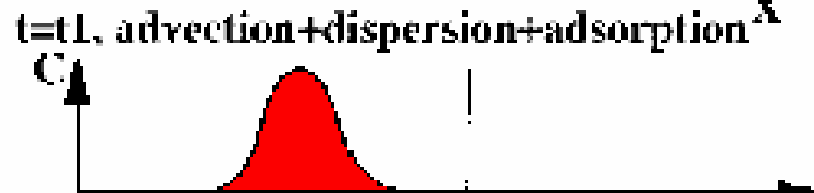
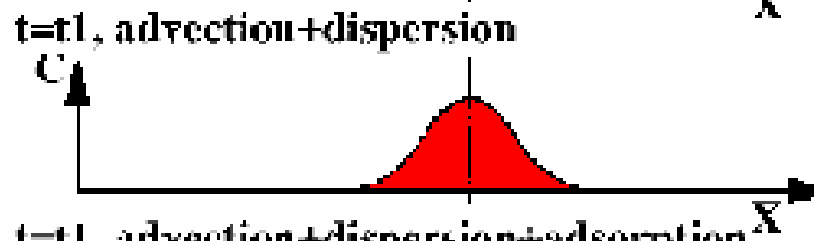
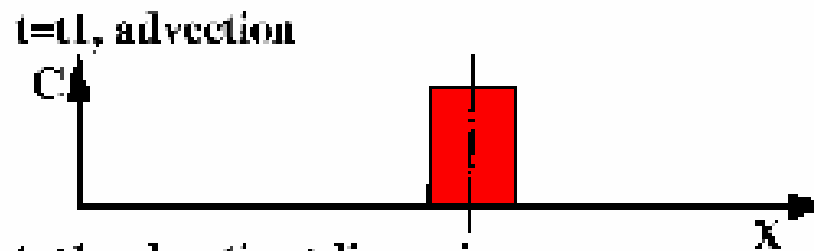
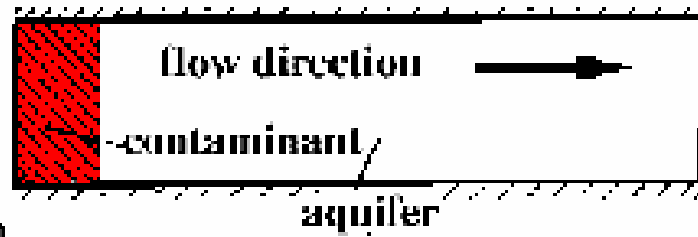


Figure 2.1. Fetter, *Contaminant Hydrogeology* 3rd Edition



D. Retardation:

$K_D = \text{concentration absorbed} / \text{concentration dissolved in water} = \text{ml/g}$

- metals attach onto clays.
- contaminants attach onto organic carbons.
- the higher the K_D , the slower things will move in water.

$$\rightarrow V_x = V(\text{H}_2\text{O}) / [1 + K_D (\rho/\eta)]$$

Influence of retardation on movement of a solute front in a one-dimensional column 1

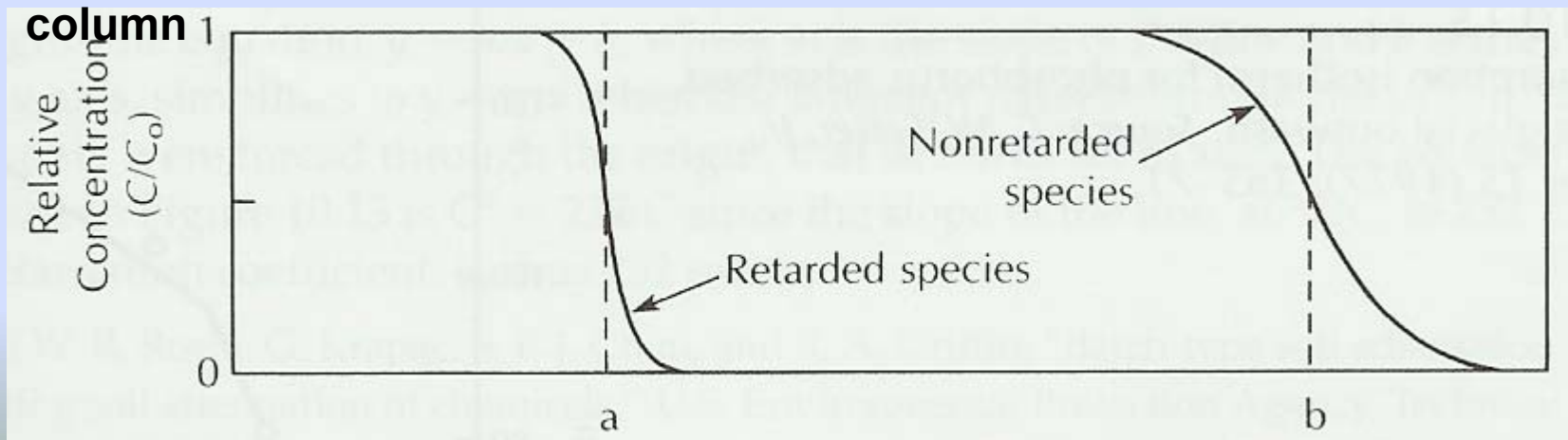


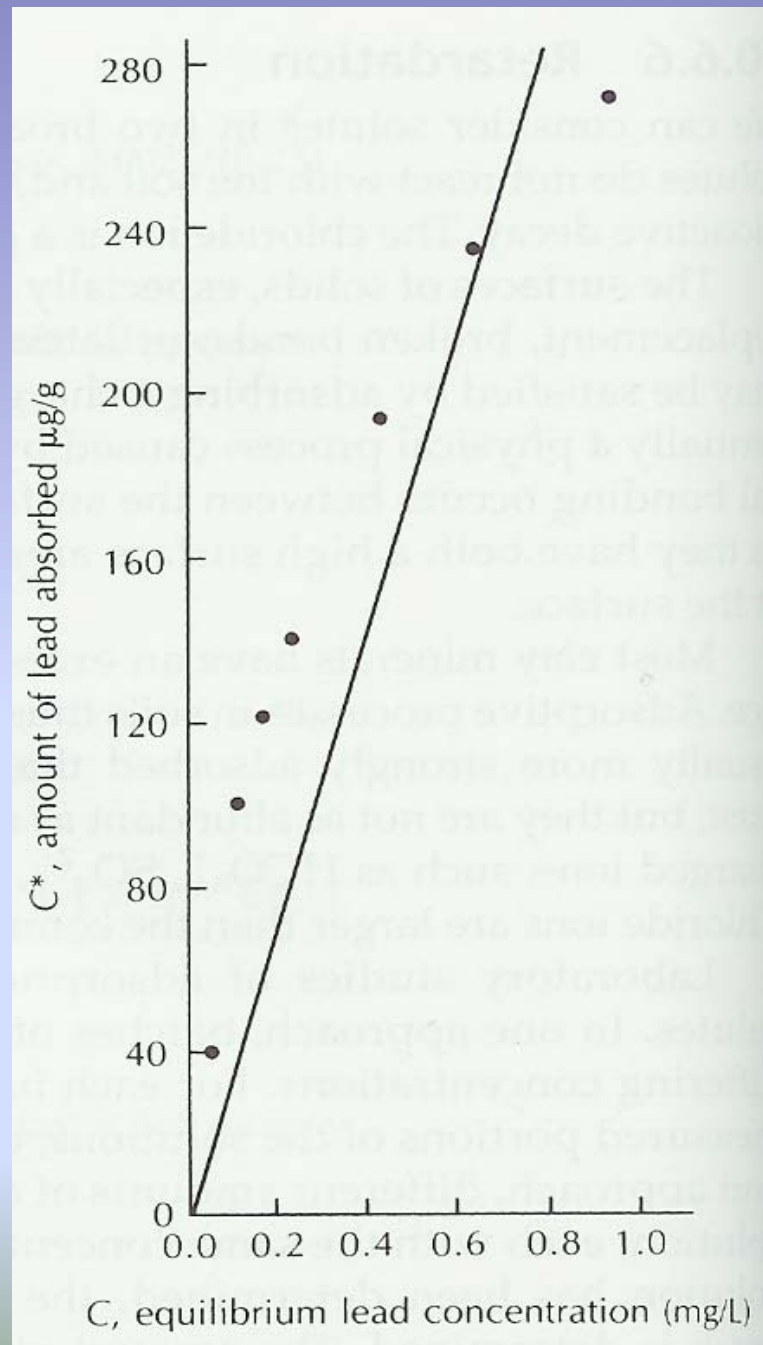
Figure 10.14 Fetter, *Applied Hydrogeology 4th Edition*

Lead adsorption by Cecil clay loam at pH 4.5 and at 25°C described by a linear Freundlich equation through the origin.

Figure 10.13 Fetter, *Applied Hydrogeology 4th Edition*

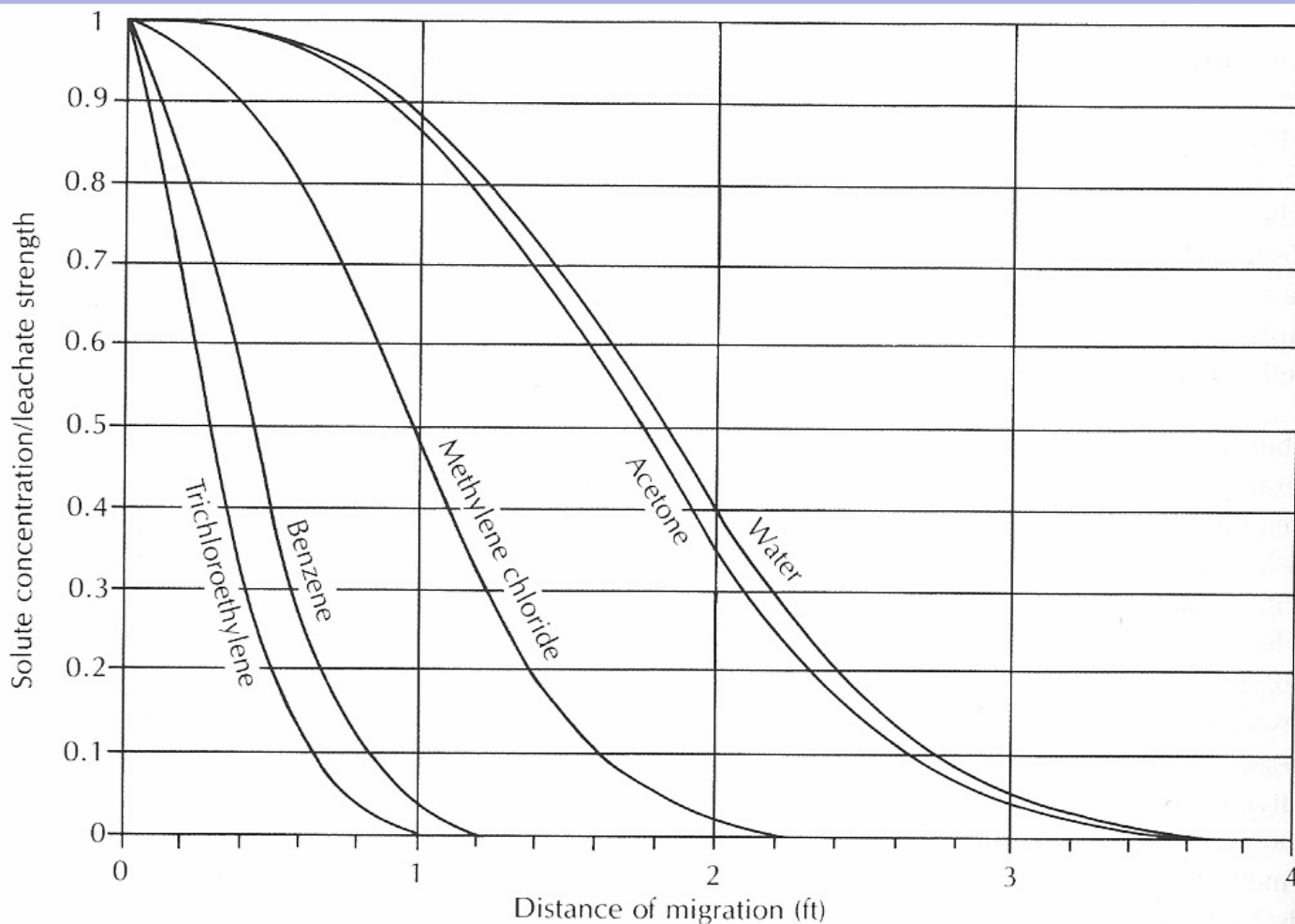
$$\log C(\text{ads}) = j \cdot \log C(\text{diss}) + \log K_f$$

$$C(\text{ads}) = K_f \cdot C^j$$



$V_x = V_{H_2O} / [1 + K_D (\rho/\eta)]$ Solubility of organics in H_2O

- K_D is proportional to K_{oc} (octonal and water). $K_D = K_{OC} * \%C$
- K_D is proportional to the organic carbon content -- the higher the K_D , the more things attach onto organic carbon, and it moves slower.



Vertical migration, in feet per 100 y, of various synthetic organic compounds through a soil with hydraulic conductivity of 1.6×10^{-8} cm/s, hydraulic gradient of 0.222, bulk density of 2.00 g/cm³, particle density of 2.65, effective porosity of 0.22, and soil organic carbon content of 0.5%. Figure 10.16. Fetter, *Applied Hydrogeology 4th Edition*

Solubilities and Octanol- Water Partition Coefficients for Some Common Organic Pollutants

Table 6-5. Drever *The Geochemistry of Natural Waters 3rd Edition*

<i>Compound</i>	<i>Specific gravity</i>	<i>Solubility in water at 25°C (mg/l)</i>	<i>log K_{OW}</i>
<i>Aliphatic hydrocarbons</i>			
<i>n</i> -heptane	0.68	3	4.50
<i>n</i> -octane	0.70	0.7	5.15
<i>Aromatic hydrocarbons</i>			
Benzene	0.88	1800	2.13
Toluene	0.87	500	2.73
<i>o</i> -Xylene (1,2-dimethylbenzene)	0.88	180	3.12
Ethylbenzene	0.87	170	3.15
<i>Chlorinated hydrocarbons</i>			
Chloroform (trichloromethane)	1.48	8000	1.97
Carbon tetrachloride (tetrachloromethane)	1.59	800	2.83
1, 2 Dichloroethane	1.25	8500	1.48
1,1,2 Trichloroethane	1.44	4500	2.1
1,1,2,2 Tetrachloroethane	1.59	3000	2.4
Vinyl chloride	gas		1
Trichloroethylene (trichloroethene)	1.46	1200	2.4
Perchloroethylene (tetrachloroethene)	1.62	200	3
Chlorobenzene	1.11	450	2.84
1,3 Dichlorobenzene	1.29	120	3.5
<i>p,p'</i> -DDT		0.003	6.19
2,4,2',4'-Tetrachlorobiphenyl (PCB-47)	1.20	0.1	6.0
<i>Polynuclear aromatic hydrocarbons (PAH)</i>			
Naphthalene	1.15	32	3.35
Anthracene	1.3	0.07	4.50
Phenanthrene	1.2	1.2	4.52
Pyrene	1.3	0.13	5.00

*There is considerable uncertainty associated with some of the solubility and log K_{OW} numbers.

II. Two ways organics migrate

- 1) **Dissolved**: solubility is proportional to mobility (high solubility, then high mobility).
- 2) **NAPL**: non-aqueous phase liquid

III. Two types of contaminants

(Very broad classes)

A. DNAPL (Dense Non-Aqueous Phase Liquid)

* TCE (density = 1.46) $K_{oc} = 150$

Solubility in water: 1100ppm

* TCA (density = 1.33)

1180ppm

* PERC (perchloroethylene, density = 1.6)

* Methylene Chloride (density = 1.33)

Solubility = 13000ppm $K_{oc} = 25$

→ These are extremely dense.

B. LNAPL (Light Non-Aqueous Phase Liquid)

- * Benzene 1800ppm $K_{OC} = 100$
- * Toluene 500ppm $K_{OC} = 240$
- * Vinyl Chloride (density less than water and highly volatile)

***NOTE: solubilities given by weight (1 ppm = mg/L).

➔ The drinking water standard for benzene is 5 ppb (parts per BILLION)

C. Characteristics:

1. Densities of NAPL's range from .8x water to 1.6x water
2. Density is a function of the chloride.
3. Higher density contaminants can sink quickly through a water table aquifer.
4. Porous vs Fractured Systems exhibit very different behavior.
5. Pure phase vs. dissolved phase → different problems associated with each.

NAPL: non-aqueous phase liquid

A) * **L-NAPL's**: less dense than water.

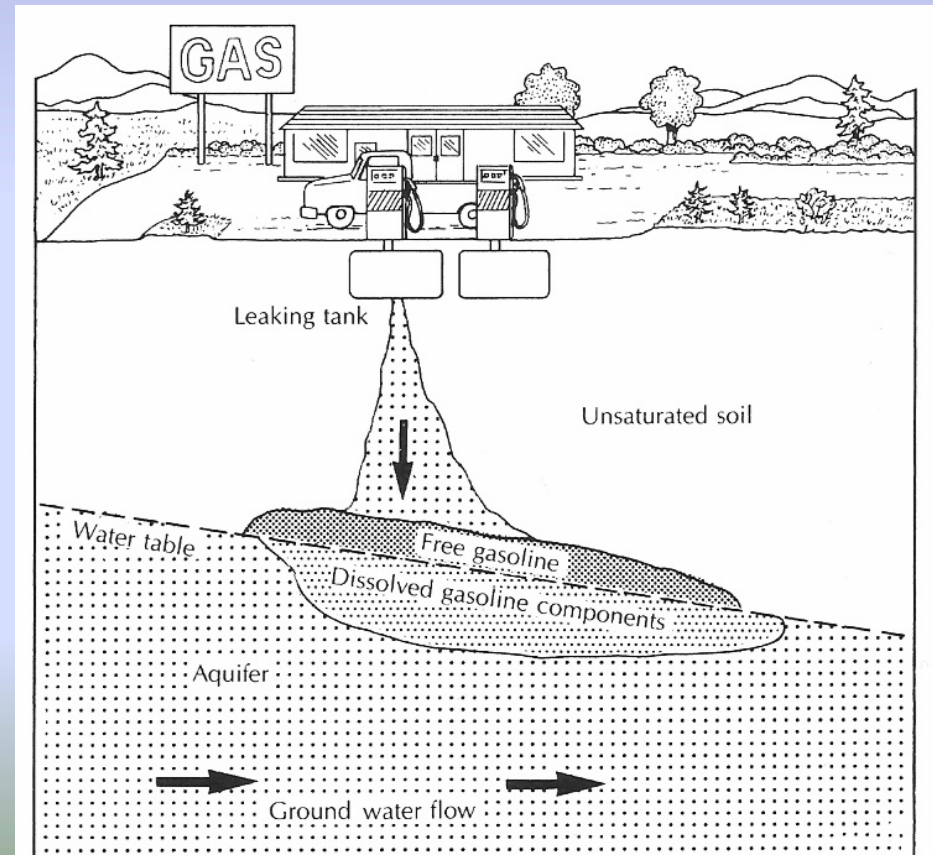
–ex. *Gasoline* - forms a pocket which floats on the water table

–soluble material e.g. *benzene, toluene, xylene* (aromatic –6C ring) dissolves in the water

→ the gasoline (straight chain- octane C_8H_{18}) evaporates.

Organic liquids such as gasoline, which are only slightly soluble in water and are less dense than water, tend to float on the water table when a spill

occurs. Figure 10.19. Fetter,
Applied Hydrogeology 4th Edition



NAPL: non-aqueous phase liquid

B) * D-NAPL's: denser than

water

–ex. *methylene chloride* - when its spilled, it is gone and not seen again.

–*trichloroethylene* – can break down to vinyl chloride.

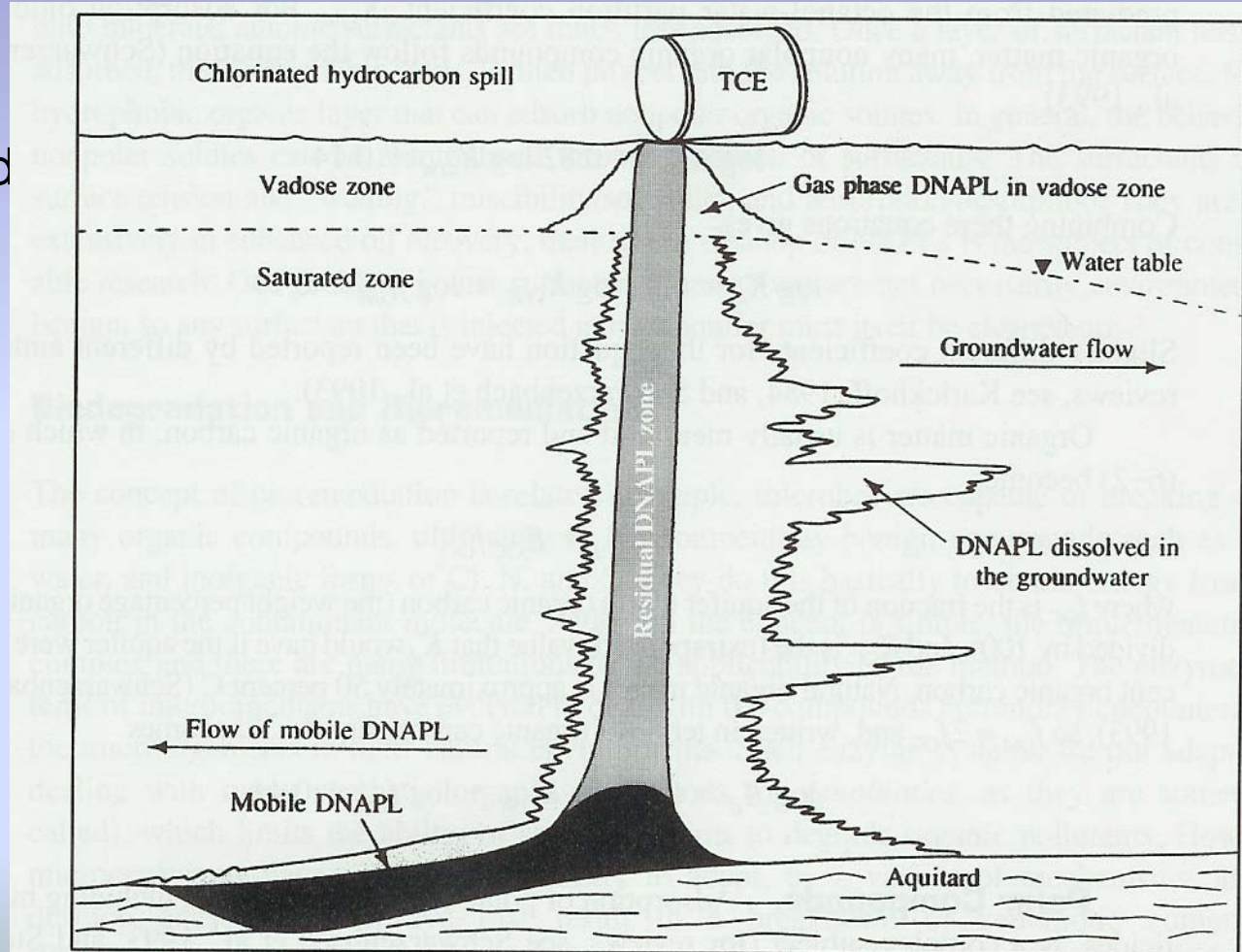


FIGURE 6-7 General distribution of a DNAPL in the subsurface following a spill. CONTAMINANT HYDROGEOLOGY by Fetter, C. W., ©1993. Reprinted by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

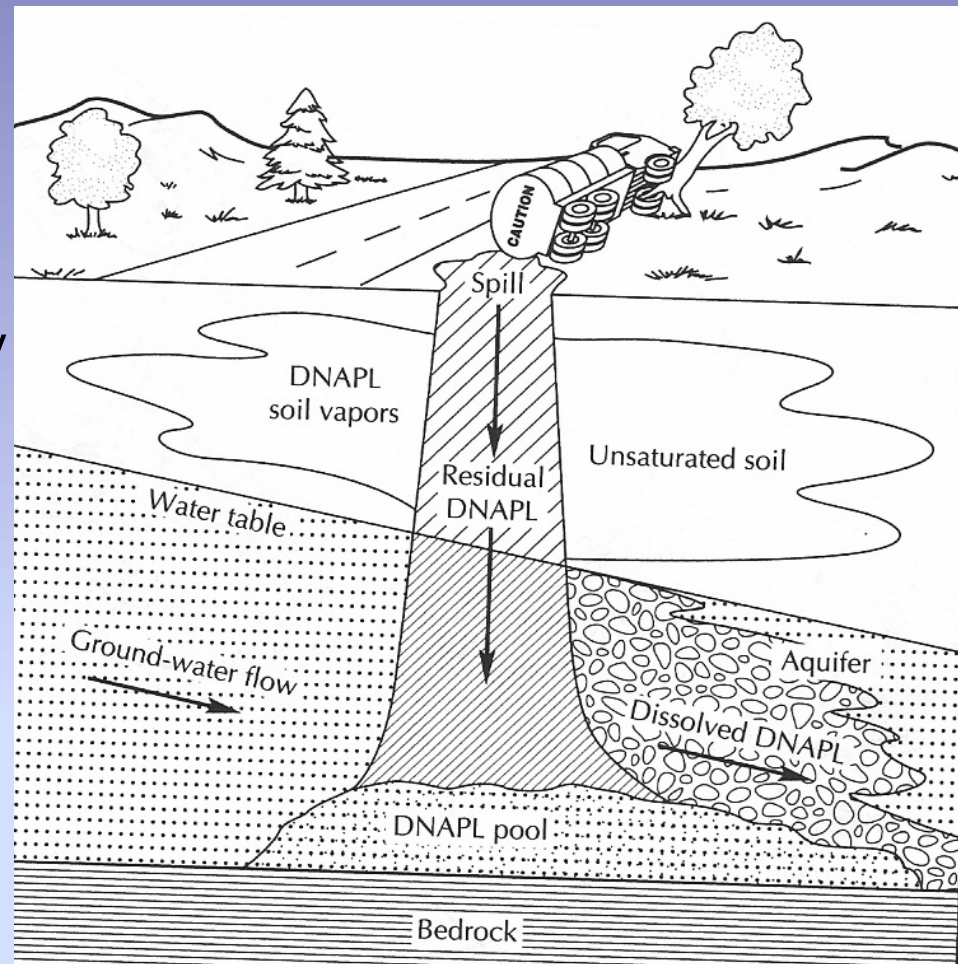
IV. Example: Spill of trichloroethylene (density = 1.33 g/cc).

- not that soluble.

→ What happens: migrates down to bedrock and pools there & slowly dissolves as water flows past.

-- OR --

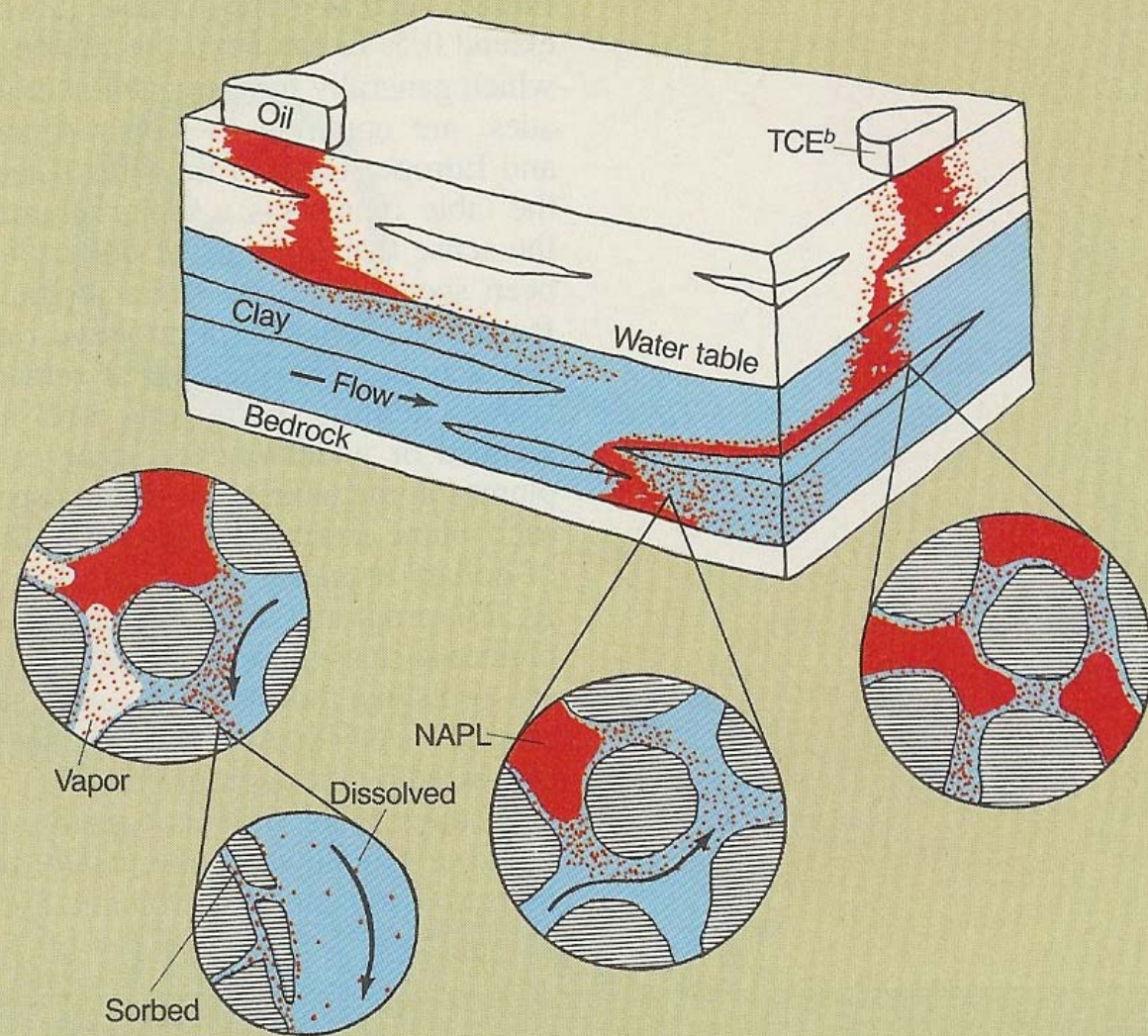
- if there are lenses of clay, it will pool on them.
- distributed over a wide area, it is impossible to find it and get it out!
- try to pump it out → only end up removing a small amount of the dissolved phase.
- if spill is 100,000 L at 5 ppm, you have to pump 2×10^9 L of water.
- concentration decrease overtime as water in shorter contact with NAPL when pumping stops- water flow slows and the concentration goes up.



Organic liquids such as trichloroethylene, which are only slightly soluble in water and are more dense than water, may sink to the bottom of an aquifer when a spill occurs.

Figure 10.20. Fetter, *Applied Hydrogeology 4th Edition*

FIGURE 1
Schematic of granular subsurface environment^a



^aIllustrates phases in which organic contaminants may be present or migrate. Note deflection of NAPLs by large clay strata and fine lenses of less permeable material such as clay or silt within the predominantly sand-gravel aquifer. Note that sorbed phase may be associated with the exterior of the particles or with interior sites.

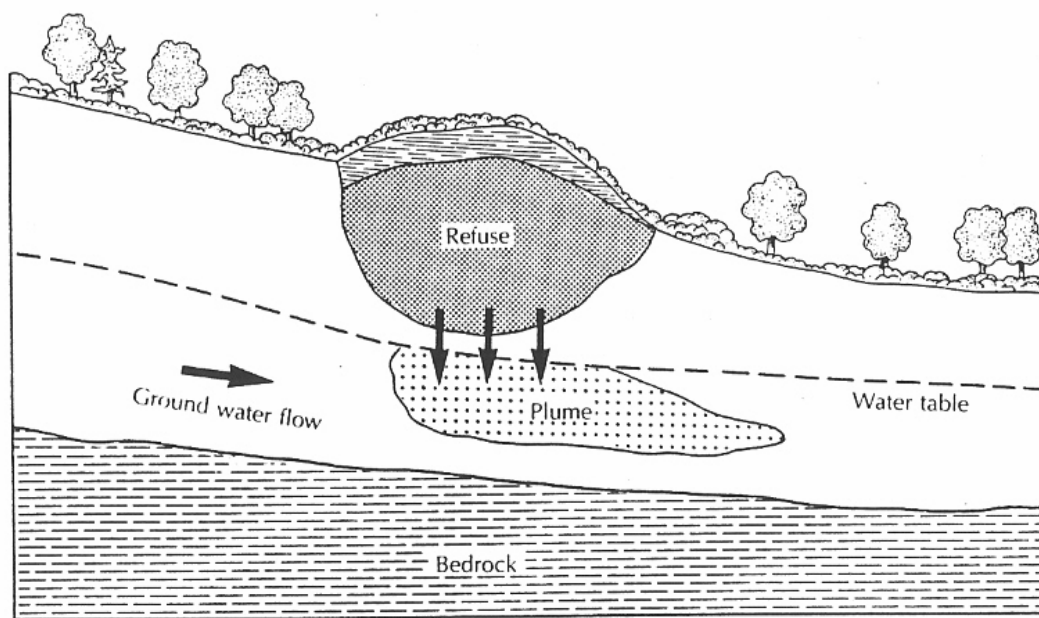
^bTrichloroethylene.

V. Remediating systems

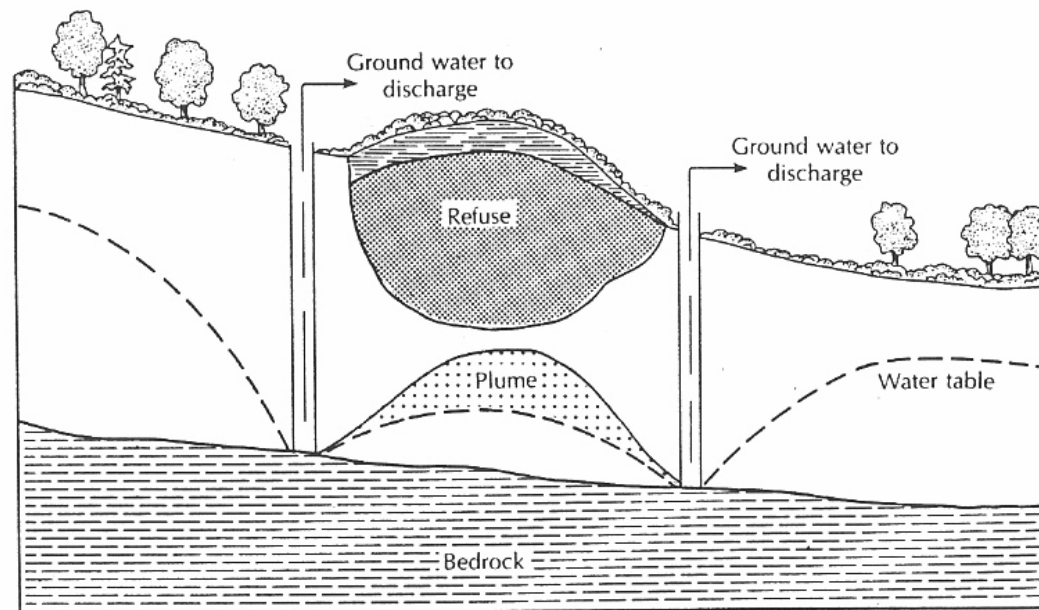
→ Is there really the possibility of remediating organically contaminated systems or are funds better spent elsewhere?

A. Questions:

1. size of the spill in terms of 1000's of liters of pure contaminant - need to remediate to a few ppb or less??
2. mobility. How fast will this move?
3. degradation → rate at which organic material will degrade is dependent on the medium through which it travels. i.e. Small amounts of organic carbon is enough to slow this down.



Before pumping



After pumping

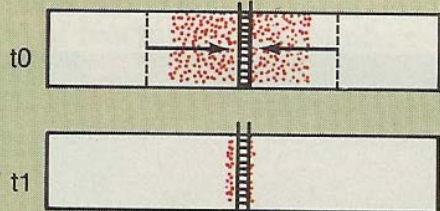
Use of Extraction Wells to Remove Contaminated Ground Waters

FIGURE 10.27 Use of extraction wells to remove contaminated ground water. Source: U.S. Environmental Protection Agency.

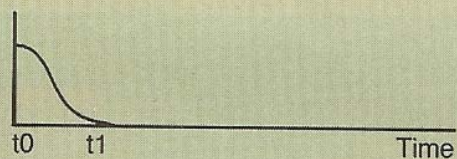
FIGURE 2

Hypothetical examples of contaminant removal from aquifers^a

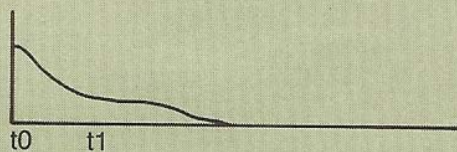
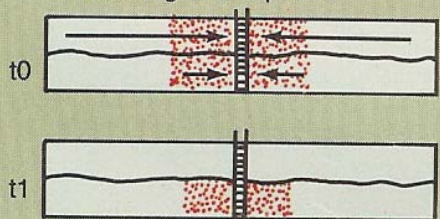
(a) Uniform sand-gravel aquifer^b



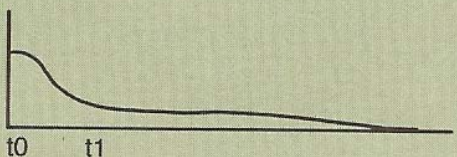
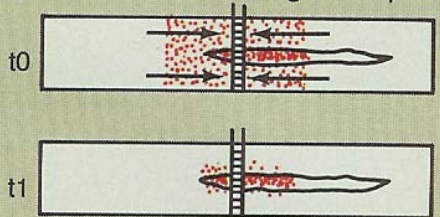
Contaminant concentration in extracted water



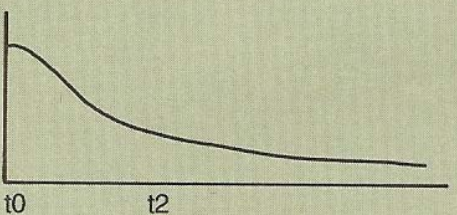
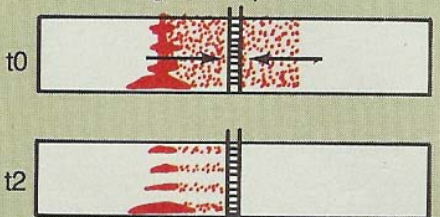
(b) Stratified sand-gravel aquifer



(c) Clay lens in uniform sand-gravel aquifer



(d) Uniform sand-gravel aquifer



^aDense color indicates NAPL contaminant, stippling indicates contaminant in dissolved and sorbed phases (assumed uniformly distributed initially), and arrows indicate relative velocity of groundwater flow. The groundwater is assumed to be extracted from the well at the same rate in the four cases.

^bDotted lines enclose total volume of water that would be pumped to remove contaminant with retardation factor of 2.

Remediating systems

B. Problems:

Volume calculations:

- 10,000 liters of contaminant dissolves to affect 6,000,000,000 liters of plume!!
- 15,000 liters of contaminant dissolves to affect 40,000,000,000 liters of plume!

(This takes less than a tanker to contain)

How much pure product is there and how can we get to it?








–This ends up causing a lot of problems especially since water wells are close.

How hard will it be to remove
ie 5 billion liters of water?
EXTREMELY hard!



TABLE 1

Relatively well-documented organic contaminant plumes in sand-gravel aquifers^a

Site location and plume map	Presumed sources	Predominant contaminants ^b	Plume volume (liters) ^c	Contaminant mass dissolved in plume (as equivalent NAPL volume in liters or 55-gal drums) ^c
 Ocean City, NJ	chemical plant	TCE TCA PER	5,700,000,000	15,000 (72 drums)
 Mountain View, CA	electronics plants	TCE TCA	6,000,000,000	9800 (47 drums)
 Cape Cod, MA	sewage infiltration beds	TCE PER Detergents	40,000,000,000	1500 (7 drums) ^d
 Traverse City, MI	aviation fuel storage	Toluene Xylene Benzene	400,000,000	1000 (5 drums)
 Gloucester, ON Canada	special waste landfill	1, 4 Dioxane Freon 113 DEE, THF	102,000,000	190 (0.9 drum)
 San Jose, CA	electronics plant	TCA Freon 113 1, 1 DCE	5,000,000,000	130 (0.6 drum)
 Denver, CO	trainyard, airport	TCE TCA DBCP	4,500,000,000	80 (0.4 drum)

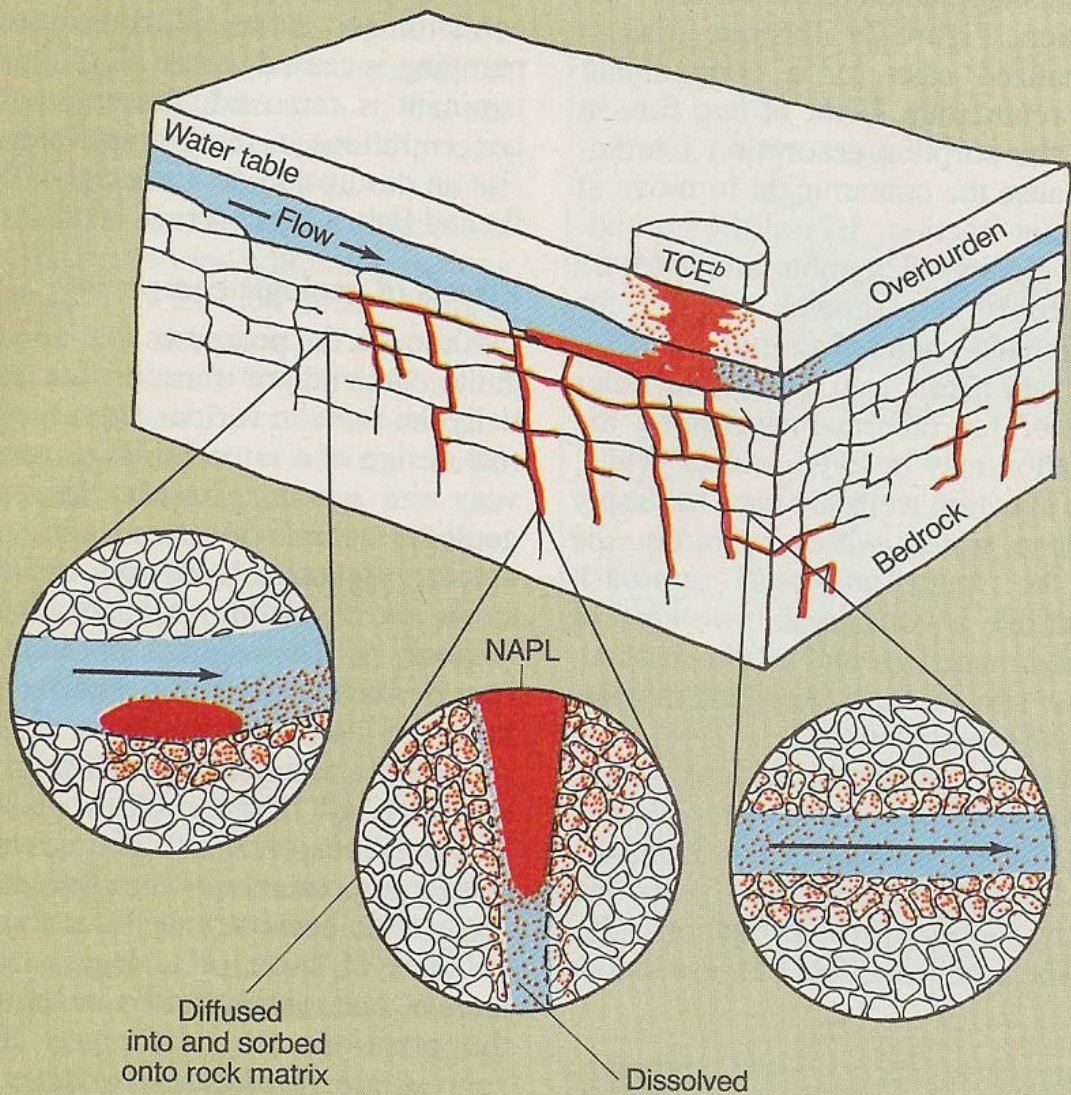
^a Readers aware of other well-documented cases for which reliable estimates of contaminant mass distribution and organic carbon content (f_{oc}) of the aquifer solids are available are encouraged to contact the authors, who plan to expand this compendium.

^b TCE = trichloroethylene; TCA = 1, 1, 1 trichloroethane; PER = per-, i.e., tetrachloroethylene; 1, 1DCE = 1, 1 dichloroethylene; CHCL₃ = chloroform; DEE = diethyl ether; THF = tetrahydrofuran; DBCP = dibromochloropropane.

^c Approximate estimates derived from plume length, groundwater velocity, contaminant concentration distributions, etc., provided for illustrative purposes only. Estimated contaminant mass accounts only for the dissolved phase (i.e., does not account for contaminant sorbed to the aquifer media throughout the plume or for NAPL contaminant, if any, from the sources). Most of basic data is from unpublished sources; data on three plumes are published (13, 27, 28, 29).

^d This mass estimate is for the halogenated contaminants only (i.e., detergents are excluded).

FIGURE 3
Schematic of subsurface environment composed of fractured rock under the overburden^a



^aThe fracture system may lead to the appearance of NAPL or dissolved contaminant in unpredictable locations. Dense color indicates NAPL contaminant; stippling indicates contaminant in the dissolved phase, either in water in the fractures or diffused into water held in the porous rock matrix.

^bTrichloroethylene.

Remediating systems

D. Why won't it work?

- * No aquifer is perfectly homogenous -- Even the simplest aquifer is heterogeneous (i.e. grain size).
- * Conductivity varies by at least an order of magnitude ie about 1 log unit.
 - What does this do to the system?
 - → Small lenses form whose conductivity is 1 or 2 orders of magnitude less than the rest of the system. The NAPL will congregate on the low permeability area. Therefore it doesn't fall neatly straight down, but will cascade down and form a complex distribution.

Remediating systems

D. Why won't it work?

- * Water will not be seeing NAPL and therefore may take a long or infinite amount of time to pump out. More time is needed for higher heterogeneity ---> These stringers of low conductivities hold NAPL and don't allow solubility and movement of it ---> never attack the material in fine-grained, low conductivity sediments.
- * L NAPL is easier to extract by vapor extraction if not too much is dissolved in the plume.

Permeable Reactive Barriers –Partial Solution

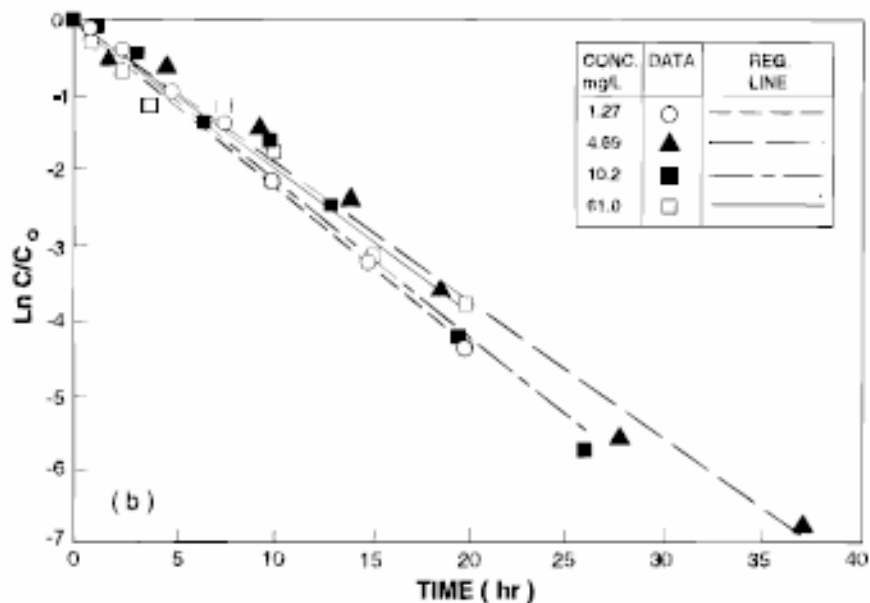
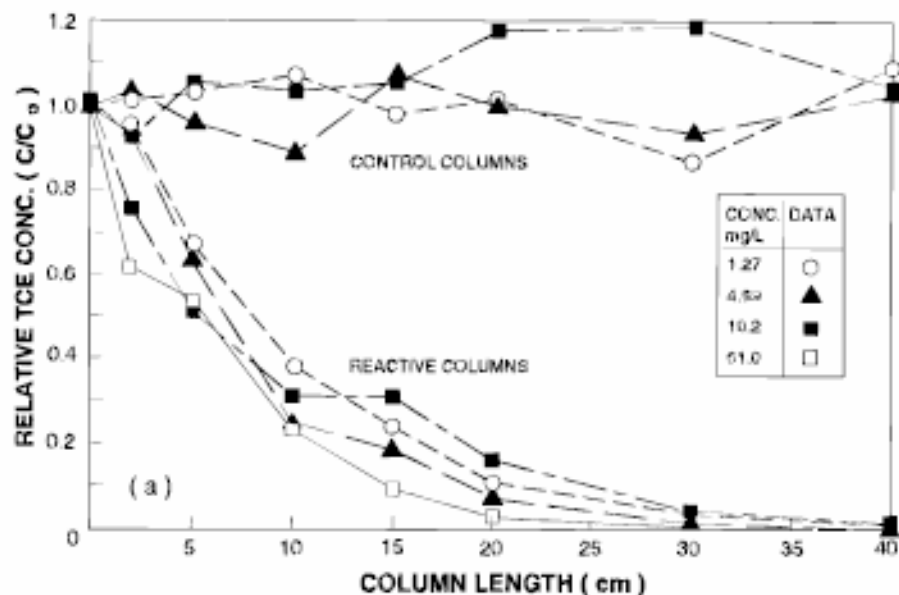


FIGURE 1. Steady-state concentration for TCE (a) relative concentration (C/C_0) versus distance along the column (b) natural log of the relative concentration versus residence time.

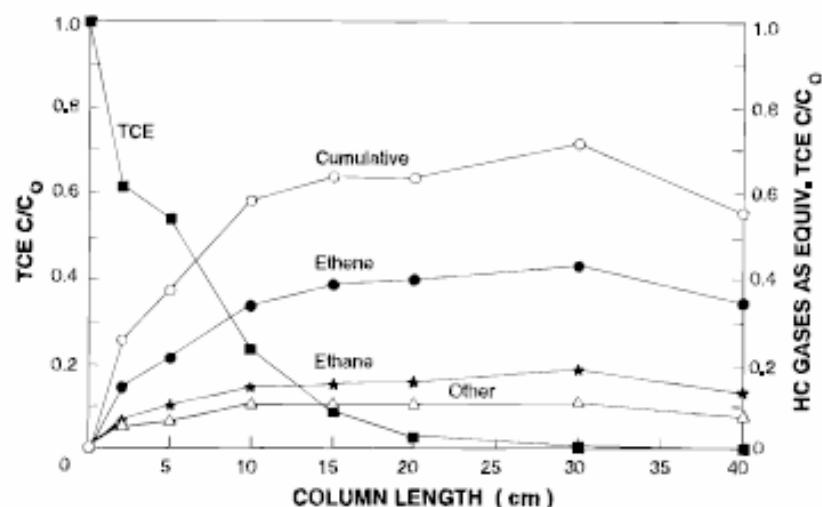
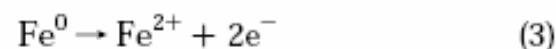


FIGURE 2. Concentration of non-chlorinated hydrocarbons, expressed as equivalent TCE, versus distance along the column. The increasing concentrations are in response to dechlorination of TCE at an initial concentration of 4.69 mg/L.

Following Matheson and Tratnyek (10), it is proposed that the degradation process is a consequence of direct oxidative corrosion of the iron by TCE. The primary products of TCE degradation were ethene and ethane in the ratio of about 2:1 (Figure 2). Assuming ethene to be the primary product, the redox couple can be written as



Thus, the complete degradation of 1 mol of TCE would add 1 mol of ethene and 3 mol each of Cl^- and Fe^{2+} to the solution phase.

As a result of the simultaneous reactions (oxidation of iron by water and by TCE) with Fe^{2+} as a common product, as well as secondary reactions, stoichiometry is of limited value in confirming the applicability of the above equations.

Moffett Field, CA Test Site TCE contours in ppb

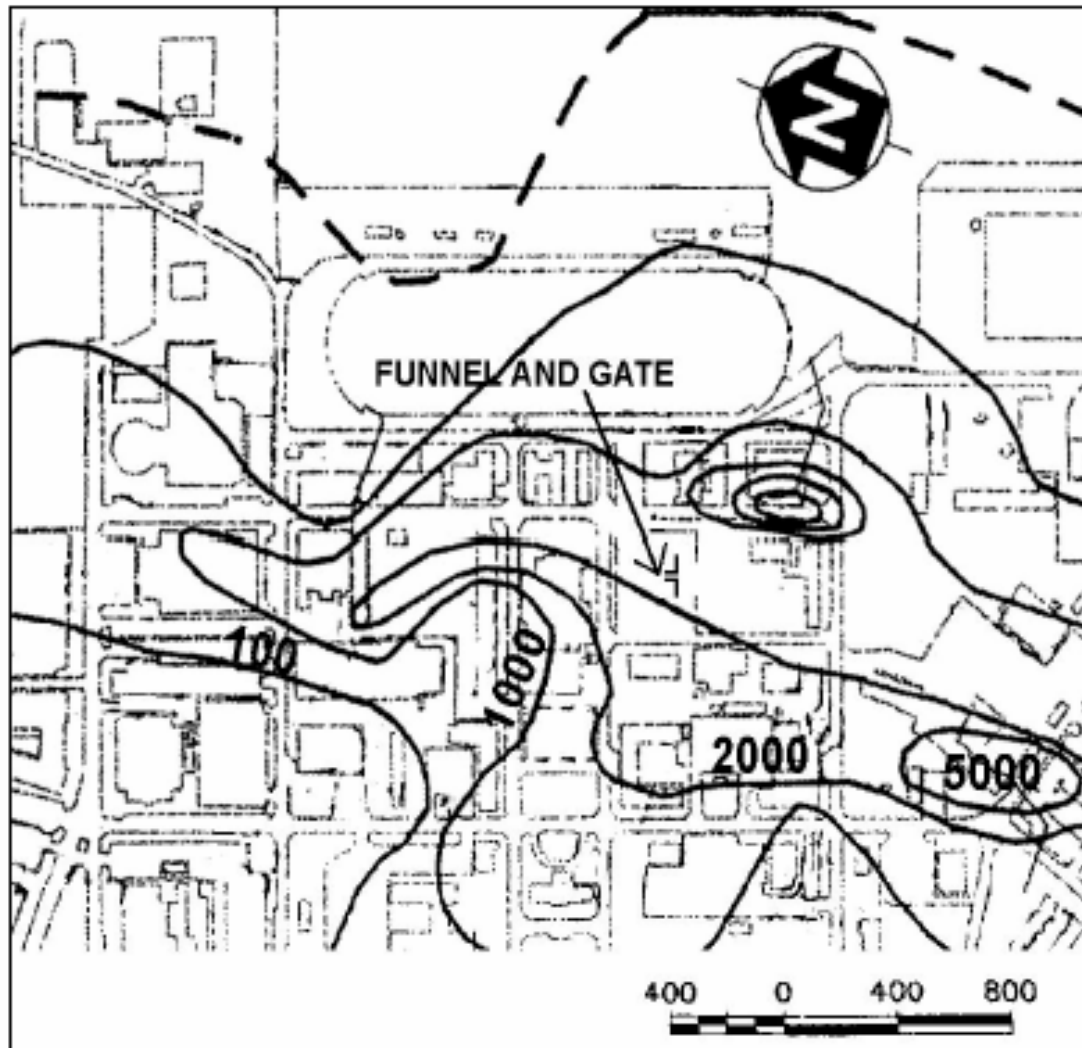


Figure 1. TCE Concentration ($\mu\text{g/L}$) (February/March 1995) [2]

Moffett Field, CA Test Site

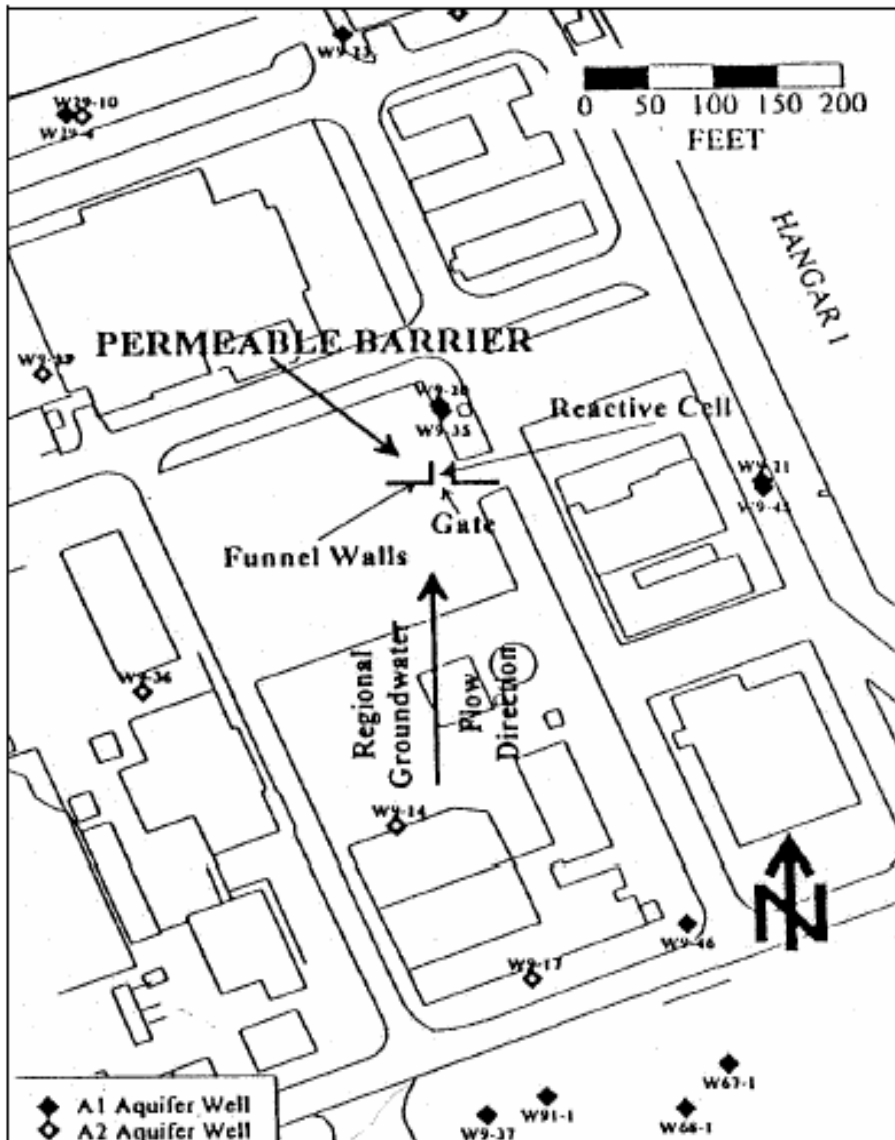


Figure 3. Site Plan [2]

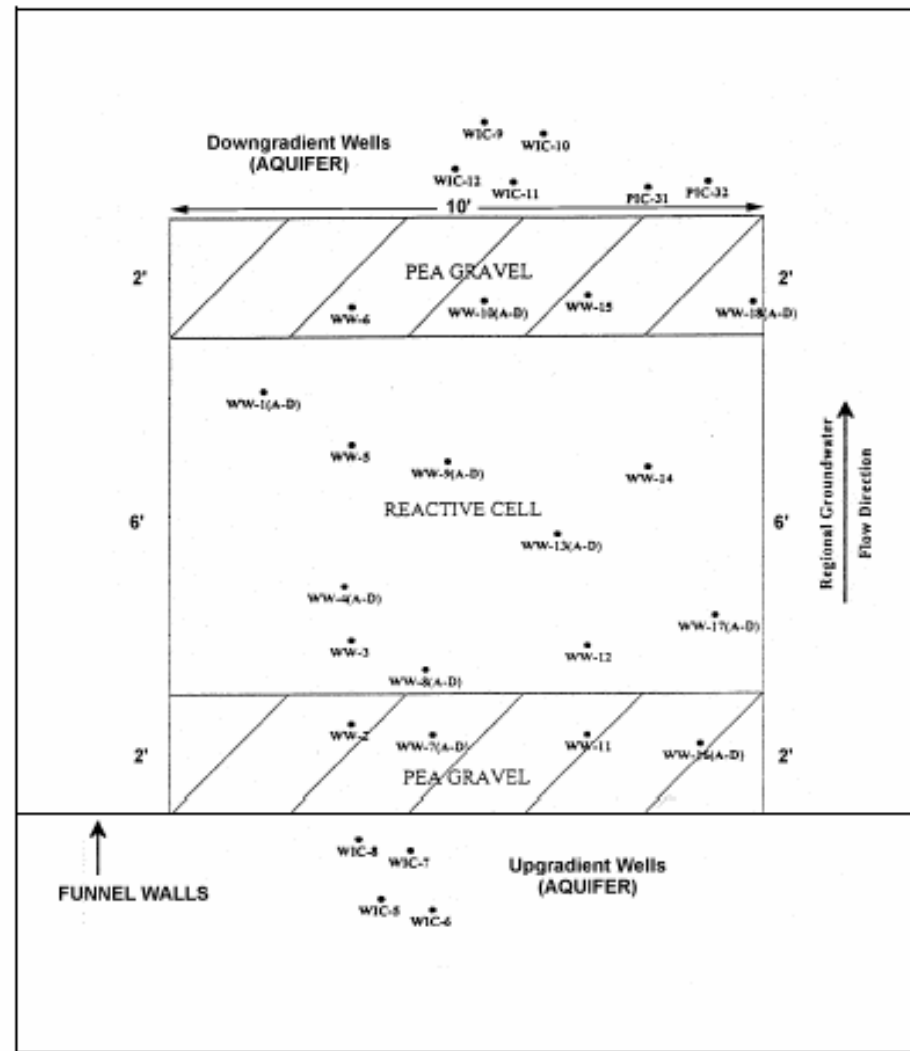


Figure 2. Funnel and Gate Plan View [3]

Reduction of TCE concentrations at Moffett Field: note increase in DCE concentration (breakdown product of TCE) TCE reduction ~ 3 grams/day

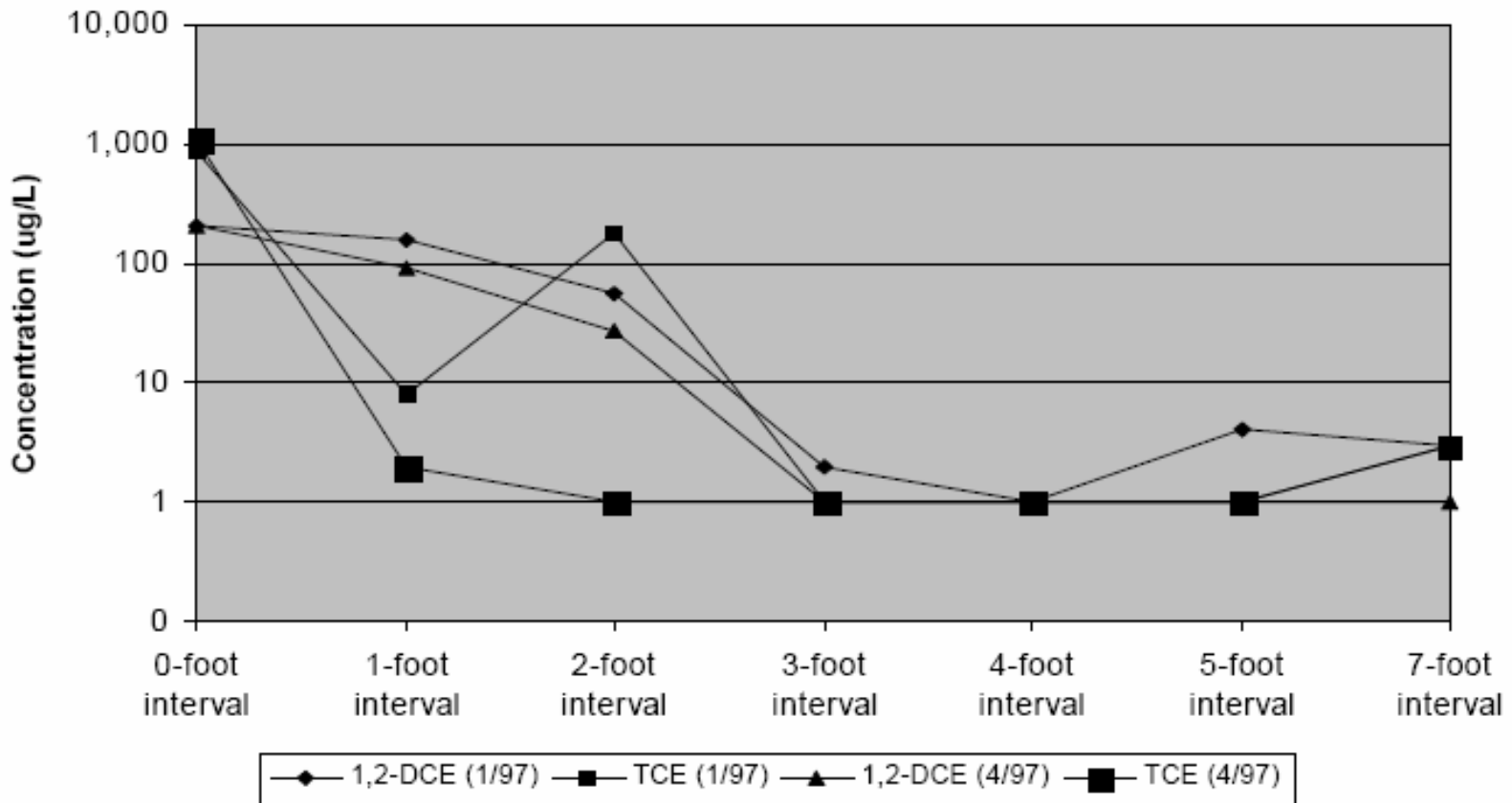


Figure 4. Concentration Reduction Through the PRB [3]

Summary of Moffett Field, CA – TCE removal field study

The cost for groundwater remediation at this site over one year was approximately \$405,000 (\$373,000 in capital costs and \$32,000 in operating costs), corresponding to a unit cost of \$1,400 per 1,000 gallons of groundwater treated.

Based on sampling data from the January, April, and July sampling events, concentrations of PCE, TCE, and 1,2-DCE are being reduced as groundwater passes through the reactive zone.

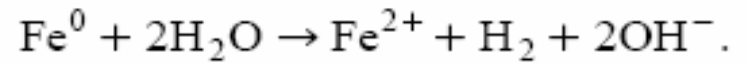
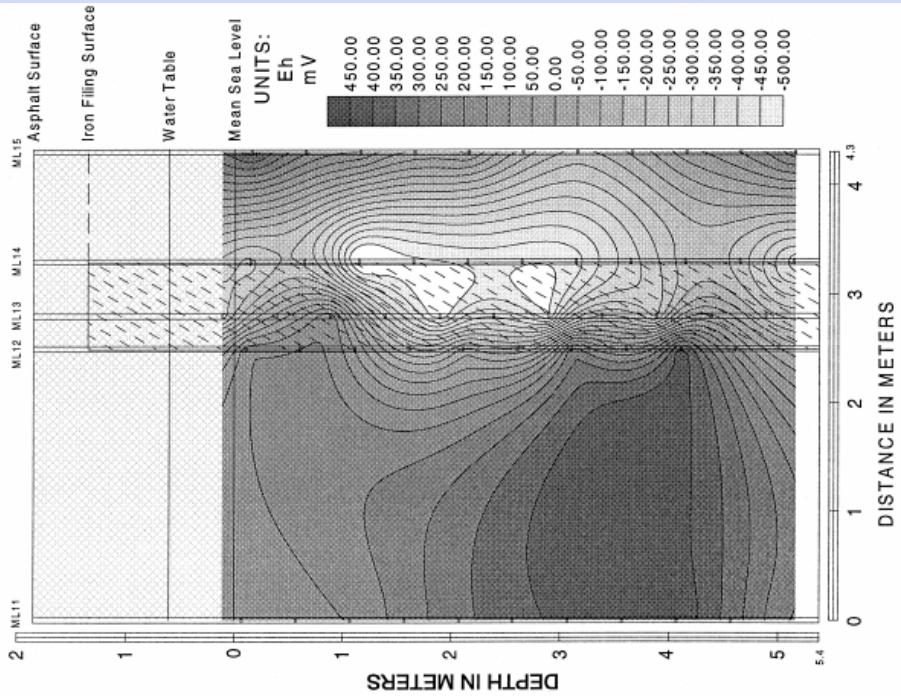
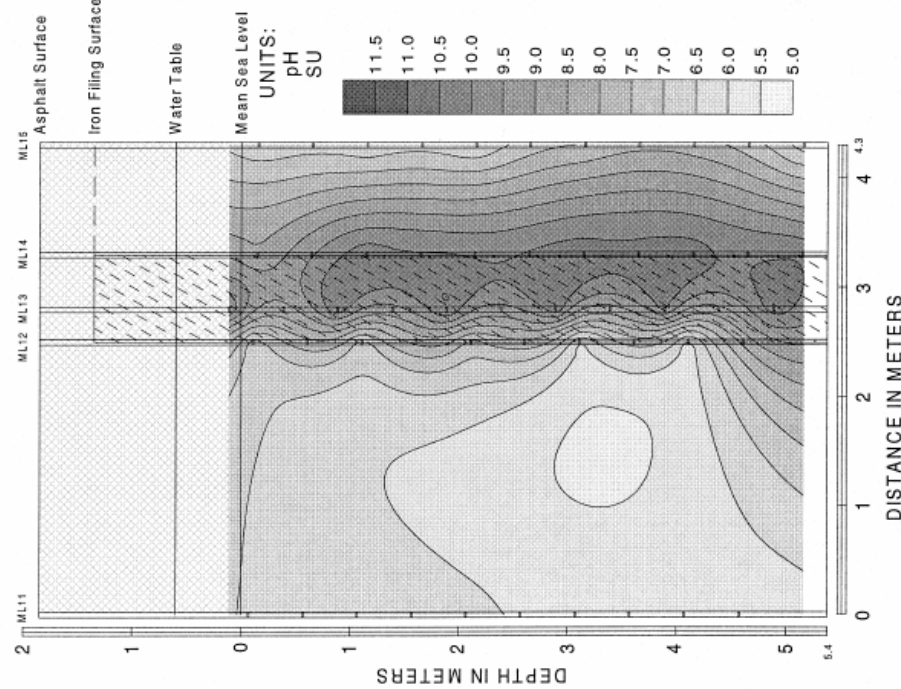
Data from monitoring points within the iron show that, by the fourth foot of iron, contaminant concentrations were reduced below detection limits.

- Mass flux was calculated from the quarterly data and an estimate of groundwater velocity from the tracer test conducted in July. Mass flux data have increased over the three sampling events indicating an increase in influent concentrations, while treatment goals continue to be met.
- ESTCP is sponsoring performance monitoring and cost data collection for technology certification and validation. Performance sampling is scheduled to continue on an annual basis for at least two more years. The final technology evaluation report is planned to be completed by August 1998. Proposals are being presented to continue the sampling process annually or semiannually.

**Permeable Reactive Barriers Using Continuous Walls to Treat Chlorinated Solvents
Summary of Project Performance**

Project	Contaminant	Influent Concentration (µg/L)	Effluent Concentration (µg/L)	Cleanup Goal (µg/L)	Reported % Reduction	Calculated % Reduction
Full-Scale Projects						
Copenhagen Freight Yard	cis-DCE	3,000	NP	NP	NP	NP
	trans-DCE	700	NP	NP	NP	NP
	TCE	NP	NP	NP	NP	NP
	PCE	NP	NP	NP	NP	NP
	VC	NP	NP	NP	NP	NP
Former Manufacturing Site	1,1,1-TCA	1,200	ND*	30	NP	NP
	PCE	19	ND*	1	NP	NP
	TCE	110	ND*	1	NP	NP
Industrial Site	TCE	25,000	NP	5	NP	NP

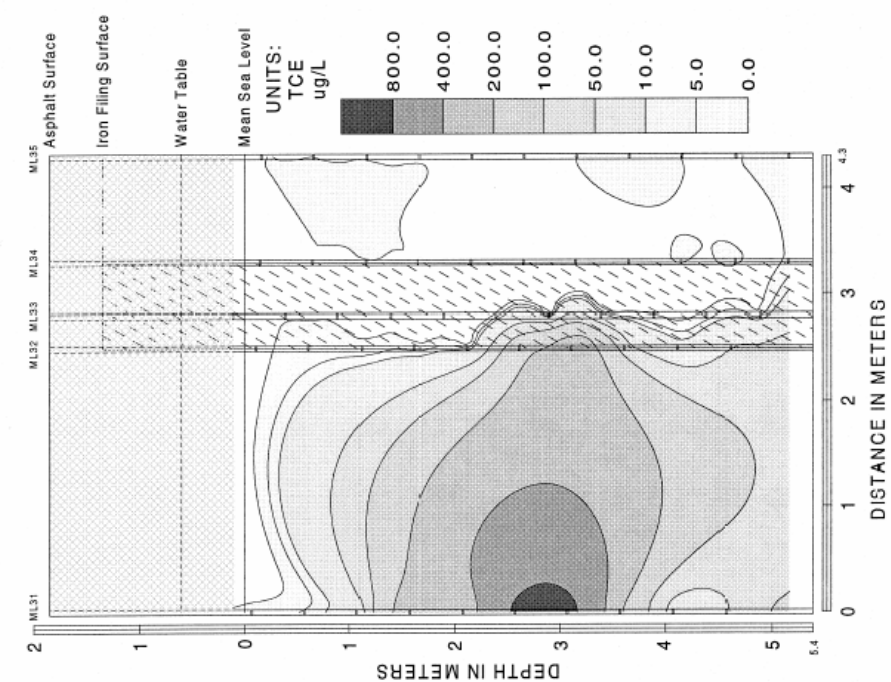
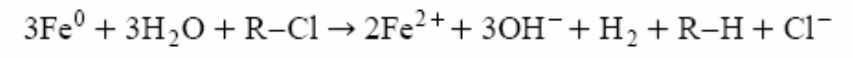
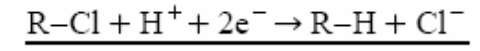
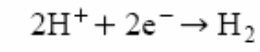
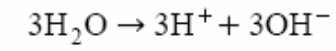
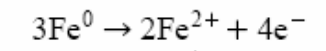
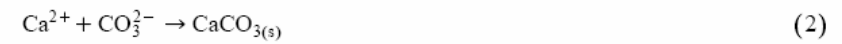
Project	Contaminant	Influent Concentration (µg/L)	Effluent Concentration (µg/L)	Cleanup Goal (µg/L)	Reported % Reduction	Calculated % Reduction
	cis-DCE	3,500	NP	70	NP	NP
	VC	900	NP	2	NP	NP
Kansas City Plant	1,2-DCE	1,377	NP	70	97	NP
	VC	291	NP	2	97	NP
Shaw AFB	TCA	18,100	1	NP	NP	>99%
	DCA	4,554	340	NP	NP	93%
	DCE	2,500	40	NP	NP	98%
	VC	180	290	NP	NP	Increase
Pilot Scale Study						
Borden Aquifer	TCE	250,000	NP	NP	90%	NP
	PCE	43,000	NP	NP	86%	NP



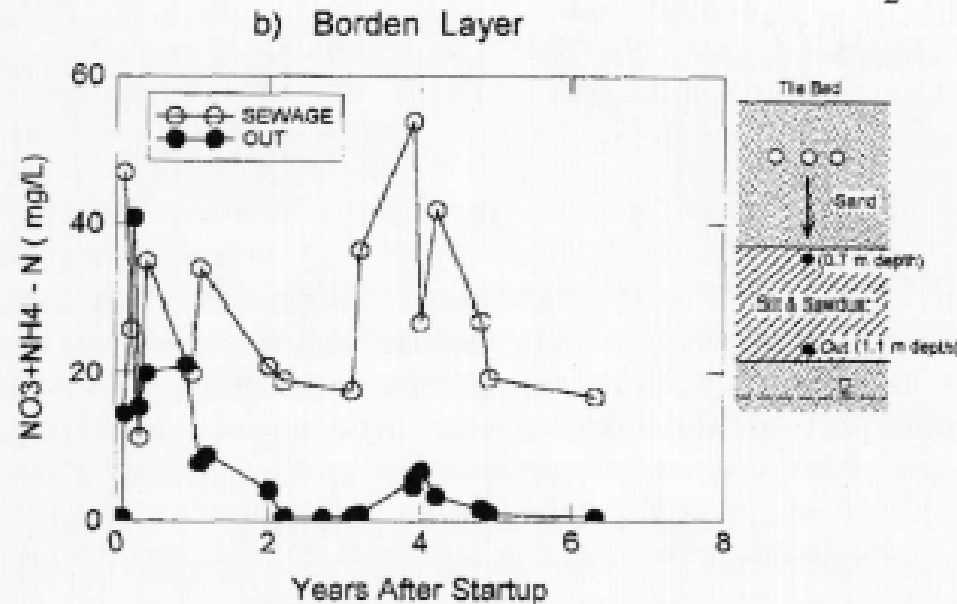
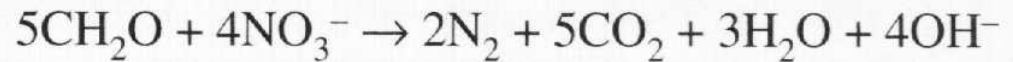
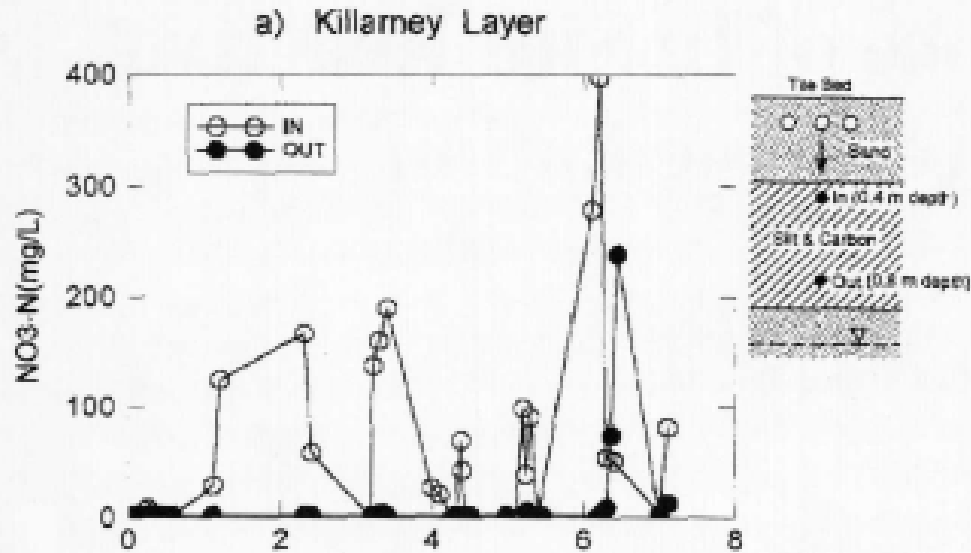
As groundwater moves through granular iron, the pH of the groundwater increases and the E_h decreases as a consequence of iron corrosion. As the pH increases, bicarbonate (HCO_3^-) in solution converts to carbonate (CO_3^{2-}) to buffer the pH increase:



The carbonate then combines with cations (Ca^{2+} , Fe^{2+} , Mg^{2+} , etc.) in solution to form mineral precipitates:



PRB installed beneath infiltration beds ; note reduction of nitrate and ammonia by more than 90%



Denitrification by "PRB" –Vertical Wall

Denitrification by "PRB" – Output from drainage tile

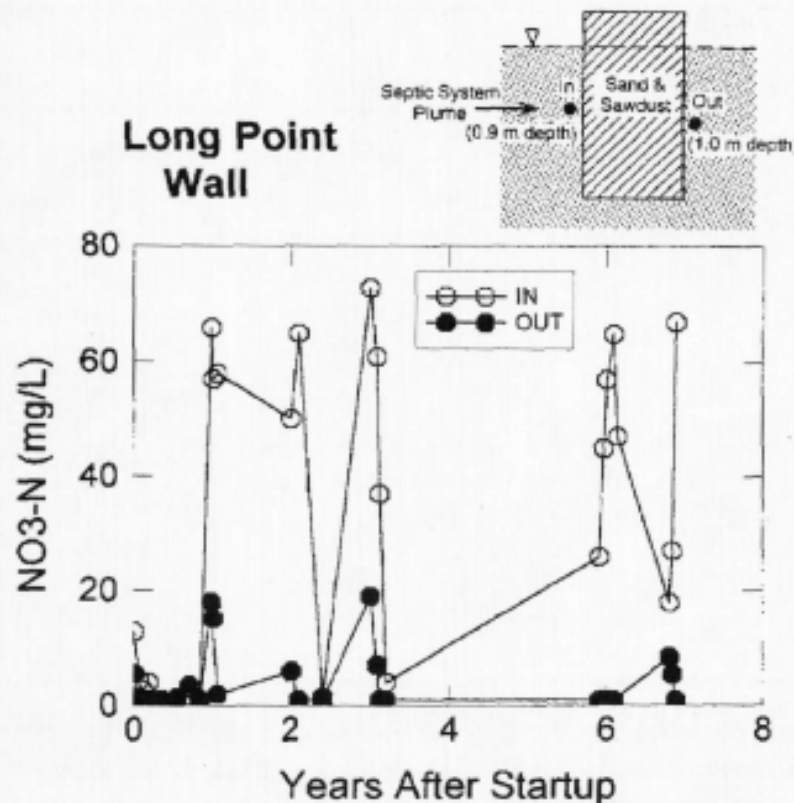
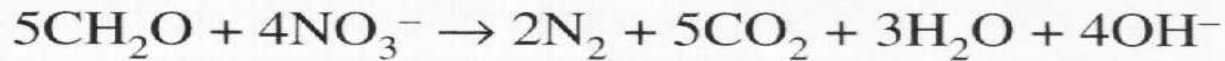


Figure 2. NO₃⁻ removal trend at a site where a reactive barrier is installed as a vertical wall intercepting a horizontally migrating septic system plume. Low "in" values indicate dilution from background ground water during nonuse periods.

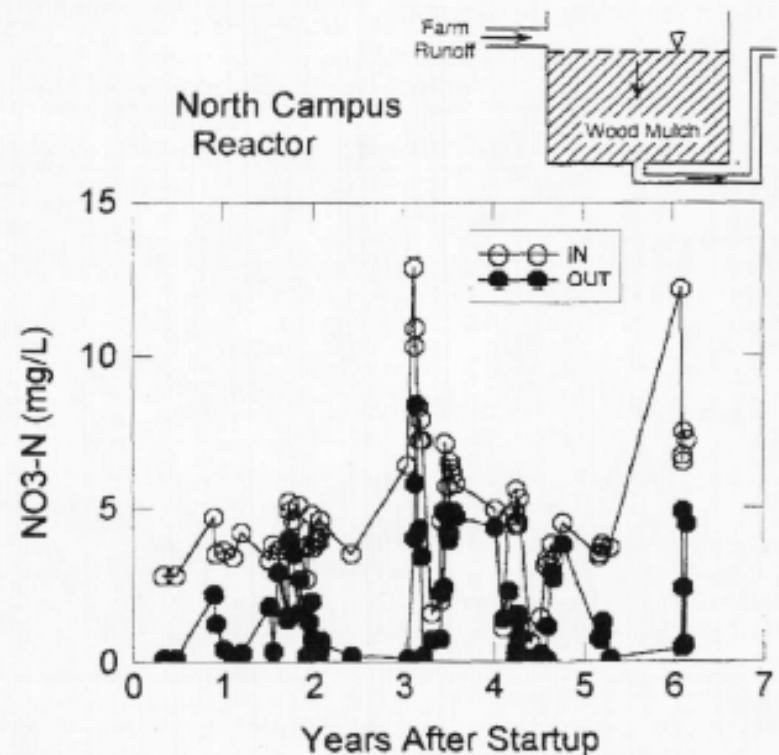


Figure 3. NO₃⁻ removal trend at a site where a reactive barrier is installed as a containerized reactor treating water from a farm field drainage tile.