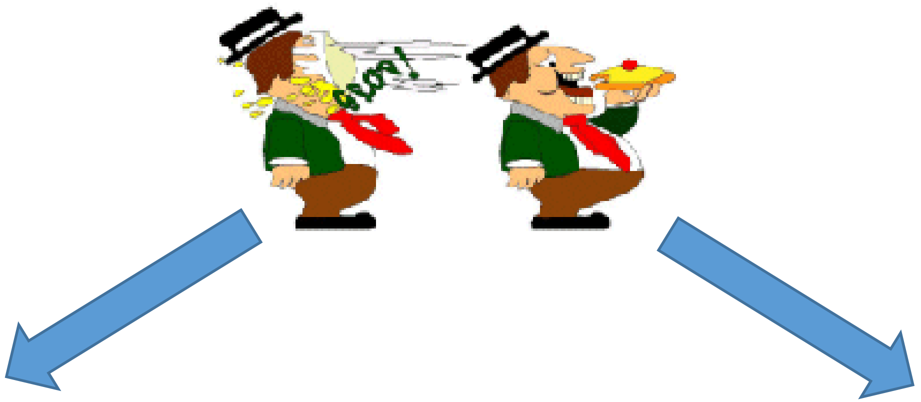
Contaminant Transport

Today's agenda

- Sorption
- Case Study
- Modeling solute transport
- Calculating solute fluxes

Sorption…

is a combination of: *adsorption* and *absorption*



Adsorption means to attach to a surface

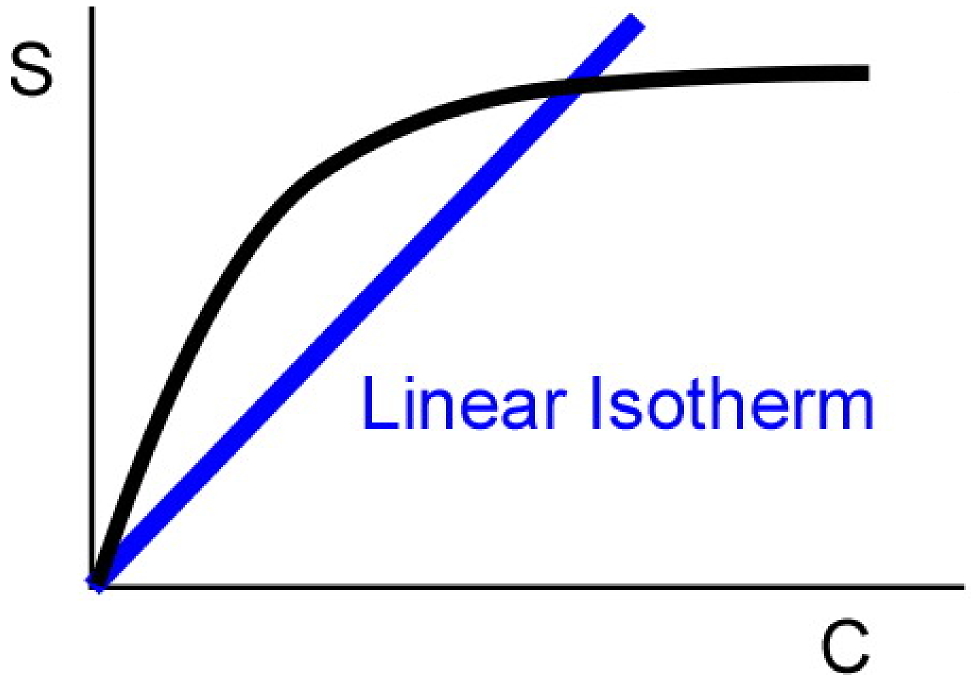
Absorption means to be incorporated into something

With sorption, the solute spends some of its time stuck to solid surfaces, thereby delaying its arrival in a process known as ***retardation***.

Chemical Reaction During Transport

Equilibrium Isotherm: a relationship that is not a function of time showing
C - the concentration in solution versus
S - that adsorbed on the solid surface, (solute mass/ solid dry mass)

Linear Isotherm says: $S = K_d C$



Chemical Reaction During Transport

Retardation factor (R): the factor by which the non-reactive (nonsorbing) solute migrates compared to the sorbing solute which is delayed

$$R = \frac{Velocity_{nonreactive}}{Velocity_{sorbing}} = \left(1 + \frac{\rho_b}{\eta} K_d\right)$$

ρ_b is dry bulk mass density of the soil [M/L3] (e.g., g/cm3)
η Is volumetric moisture content of the soil [-]
K_d is distribution coefficient for solute with soil [L3/M] (e.g., L/g)
…this is the amount of ion adsorbed per unit weight of soil, C* [mg/g] divided by the concentration of the ion in solution, C [mg/L]

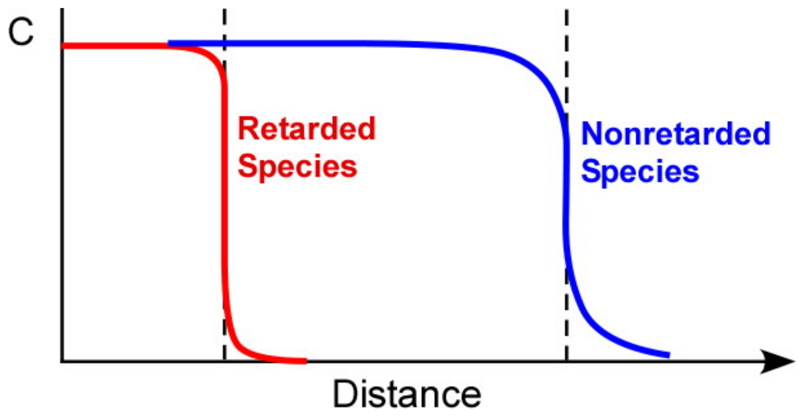
A retarded species will travel at a slower rate than ambient groundwater. The advective velocity is:

$$v_c = \frac{v_x}{\left(1 + \frac{\rho_b}{\eta} K_d\right)}$$

v_x is average linear velocity
v_c is velocity of the center of mass of the plume

For example, if the retardation factor is 2, then the plume will move at ½ the velocity of the ambient groundwater

Chemical Reaction During Transport



One good thing about sorption

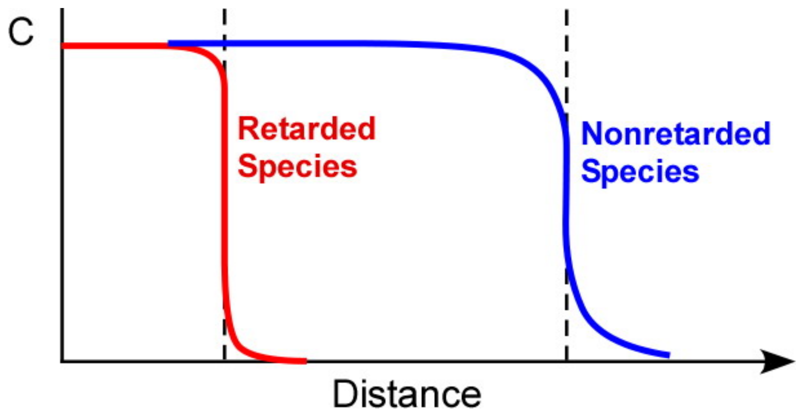
- Some hazardous species haven't migrated far

Some spills involving plutonium (!) indicate that it has migrated only a few meters at most (in unsaturated zone)

One bad thing about sorption

- Even if you pump out a contaminant plume, there will still be stuff stuck to the solids that will make its way back to the liquid (eventually). Therefore, it takes a long time to clean up a contaminant plume if there is sorbed solute.

Chemical Reaction During Transport



Hot topics in transport:

- Complex chemical reaction modeling (reactive transport)
- Coupled process models (temperature, chemistry, high concentrations, density)
- Dispersion Theory
- Rate-limited mass transfer
- Microbial activity to degrade VOCs
- Optimal design of remedial systems

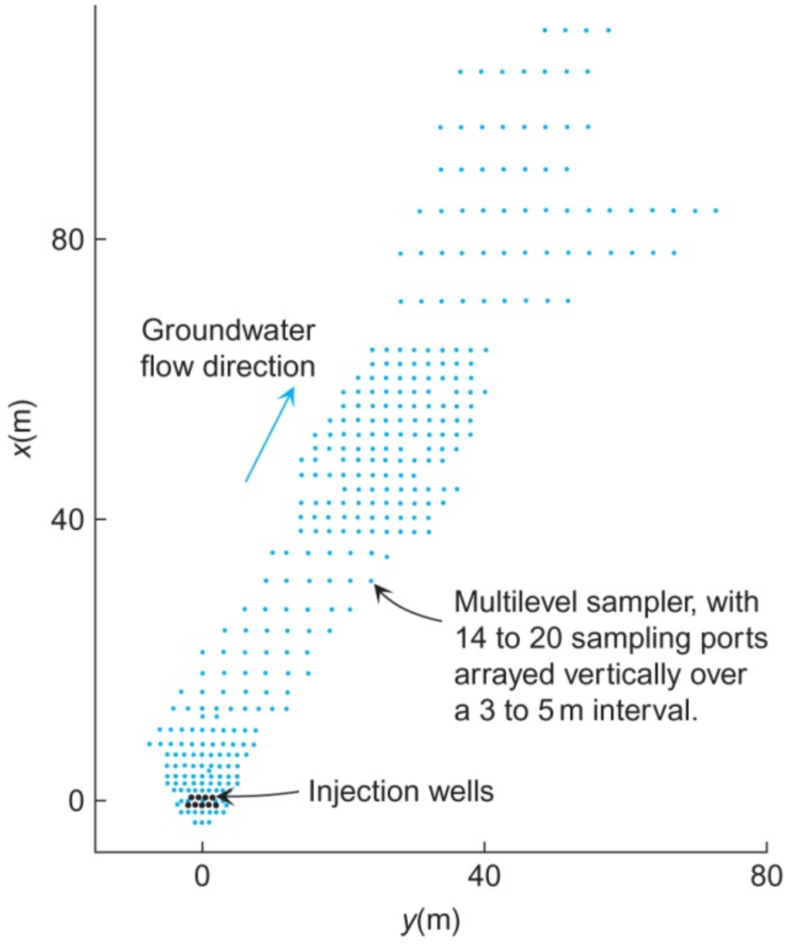
Case study: Borden CFB

Borden CFB

Borden Airforce Base,
Ontario Canada

This is a famous groundwater site, where a range of experiments were performed in the 1980s

100s of measurements of *K*, and a number of tracer injection experiments



Borden CFB

12 m^3 of groundwater with 7 chemicals was injected, and monitored for 3 years:

Inorganic, non-reactive:

Chloride (Cl^-)

Bromide (Br^-)

Organic, reactive:

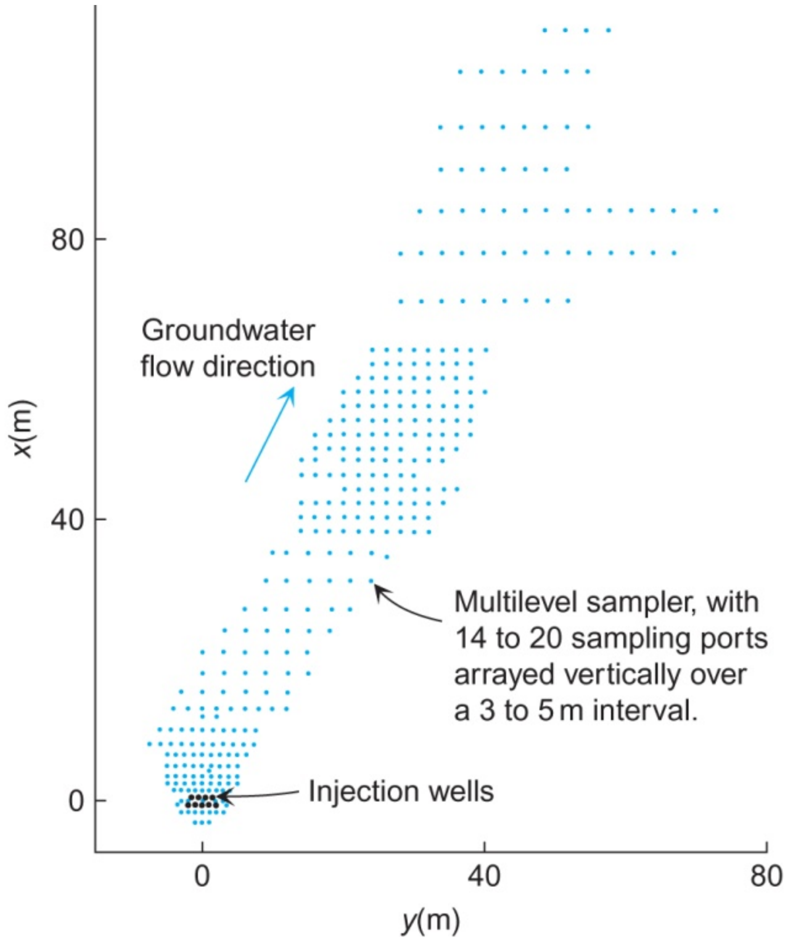
Boroform ($CHBr_3$)

Carbon tetrachloride (CCl_4)

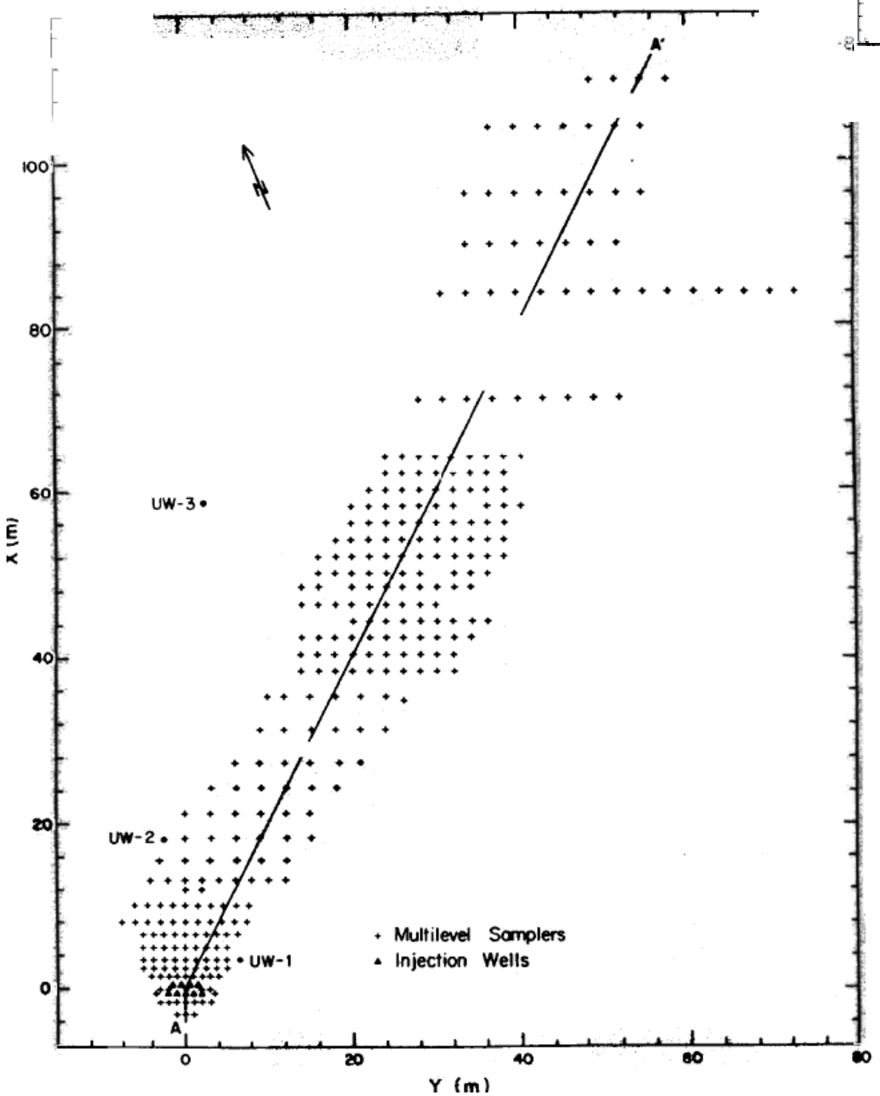
Tetrachloroethylene (PCE, C_2Cl_4)

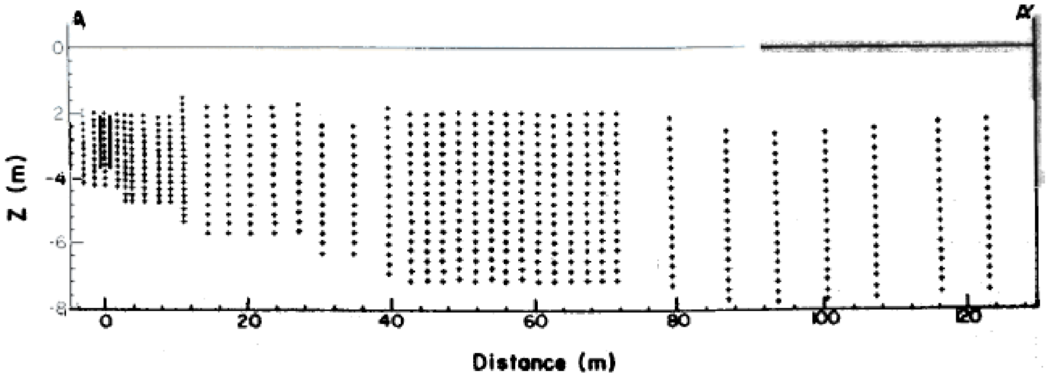
1,2-dichlorobenzene ($C_6H_4Cl_2$)

Hexachloroethane (C_2Cl_6)



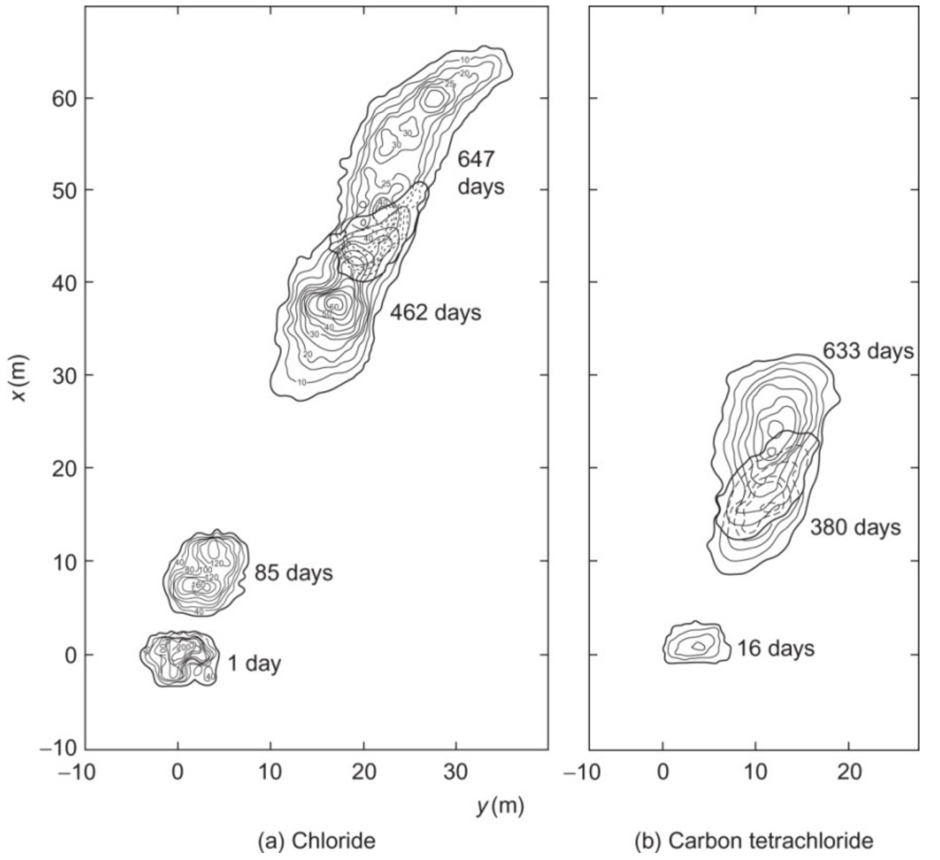
Borden Site (Canada)





Source: MacKay et al., 1986

Borden CFB

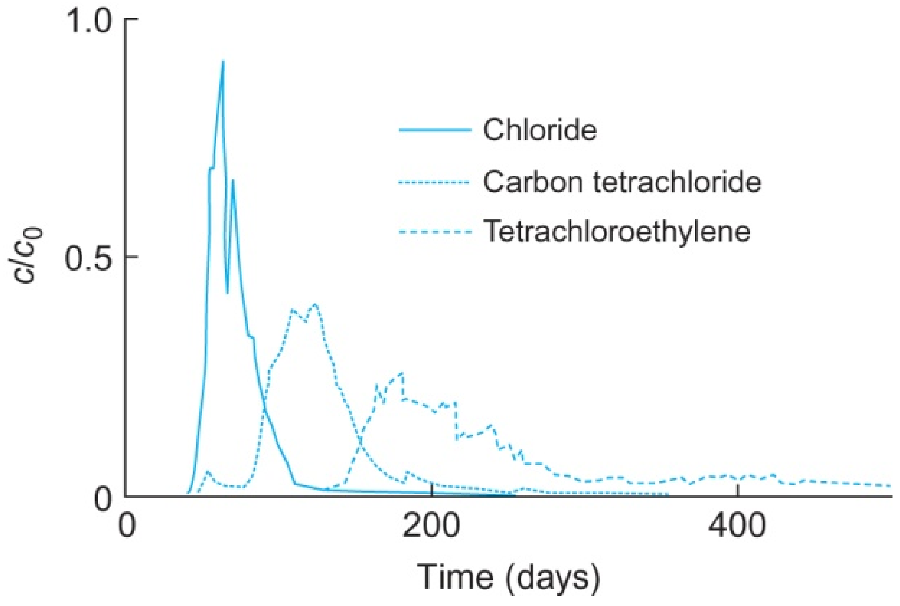


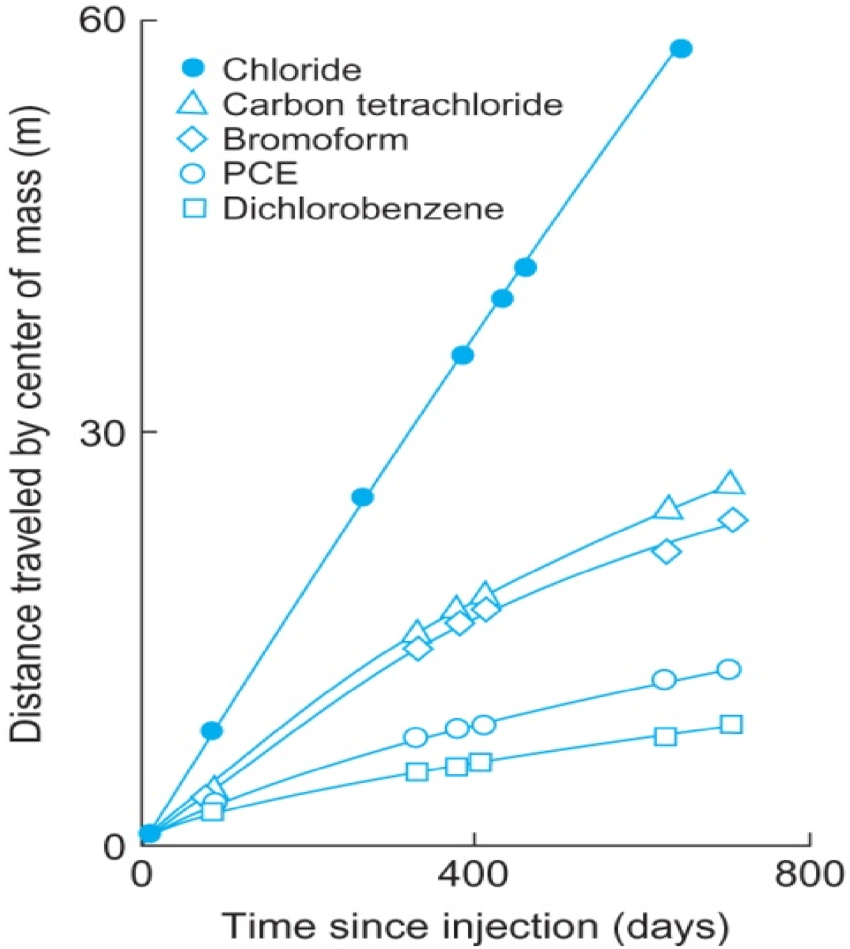
Site had multilevel piezometers, with 5000(!) sampling points.

Depth averaged concentrations of non-reactive chloride, and reactive carbon tetra chloride

This plot shows influences of retardation and dispersion.

Borden CFB


1.0
0.5
0
c/c_0
Chloride
Carbon tetrachloride
Tetrachloroethylene
0
200
400
Time (days)


60
30
0
Distance traveled by center of mass (m)
Chloride
Carbon tetrachloride
Bromoform
PCE
Dichlorobenzene
0
400
800
Time since injection (days)

USGS Cape Cod Toxic Substances Hydrology Research Site

Cape Cod Toxic Substances Hydrology Research Site

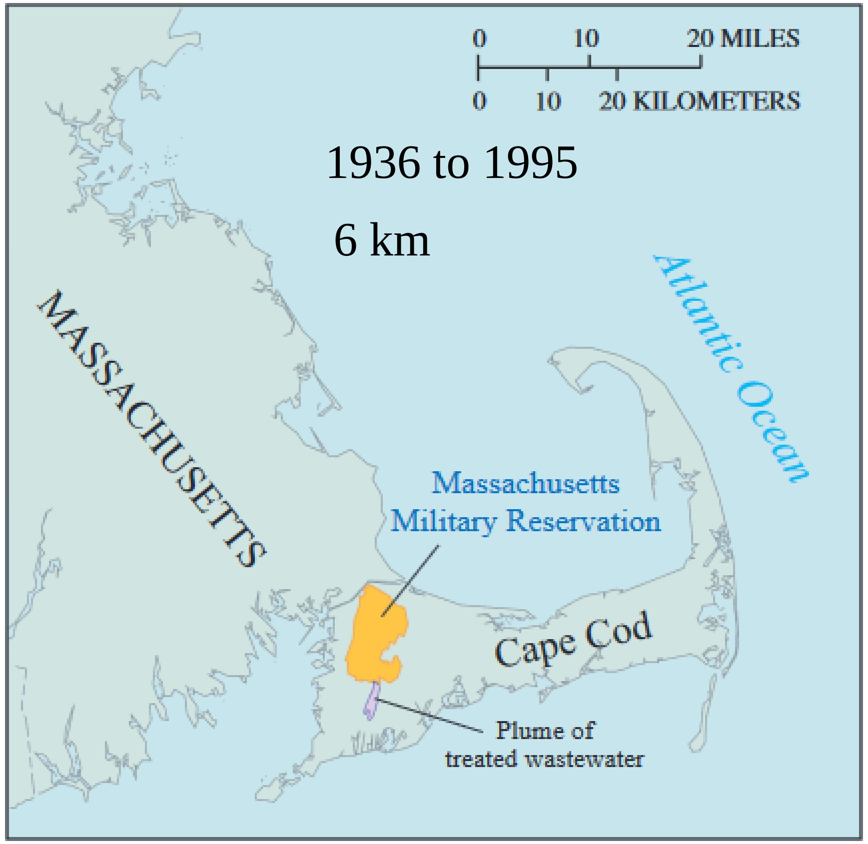
Physical, Chemical, and Biological Processes that Control the Fate of Contaminants in Ground Water

Groundwater contaminants from:

- Fuel and industrial-chemical use
- hard-rock mining
- fertilizer application
- land disposal of solid waste and wastewater

- Phosphate
- nitrate
- metal ions
- Detergents
- organic chemicals
- microbes

- Hydrologists
- Chemists
- Microbiologists
- computer modelers
- geophysicists



Location map showing MMR and plume of treated wastewater

https://pubs.usgs.gov/fs/2006/3096/pdf/fs2006_3096.pdf

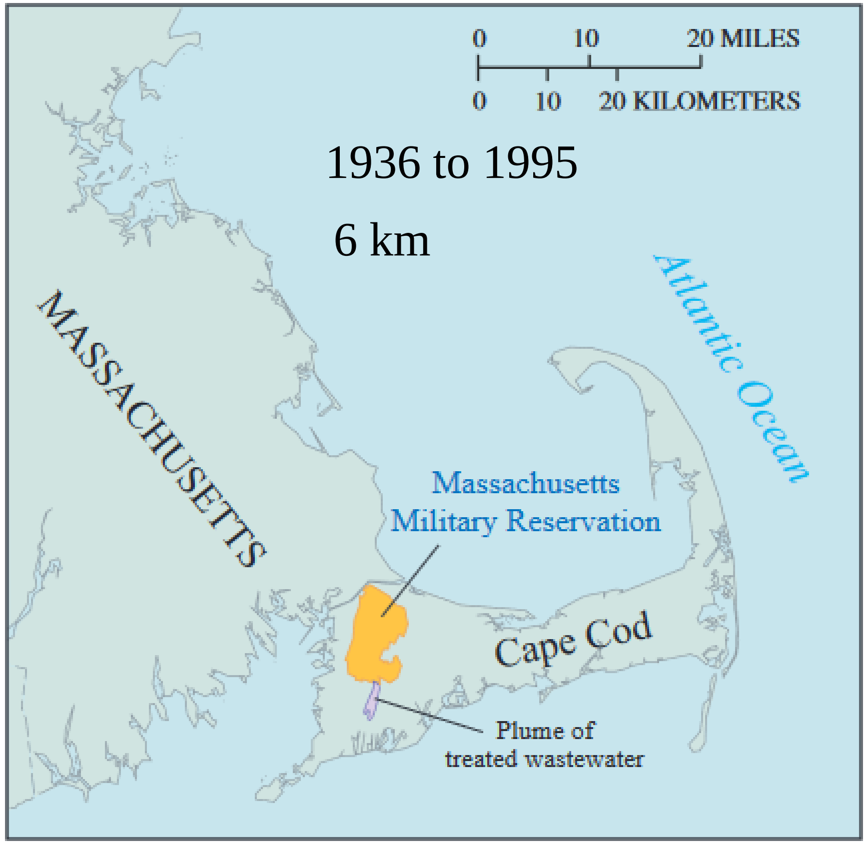
Cape Cod Toxic Substances Hydrology Research Site

Physical, Chemical, and Biological Processes that Control the Fate of Contaminants in Ground Water

Groundwater contaminants from:

- Fuel and industrial-chemical use
- hard-rock mining
- fertilizer application
- land disposal of solid waste and wastewater

Nonbiodegradable detergents in wastewater plume cause foaming on water from monitoring well



Location map showing MMR and plume of treated wastewater

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Cape Cod Toxic Substances Hydrology Research Site

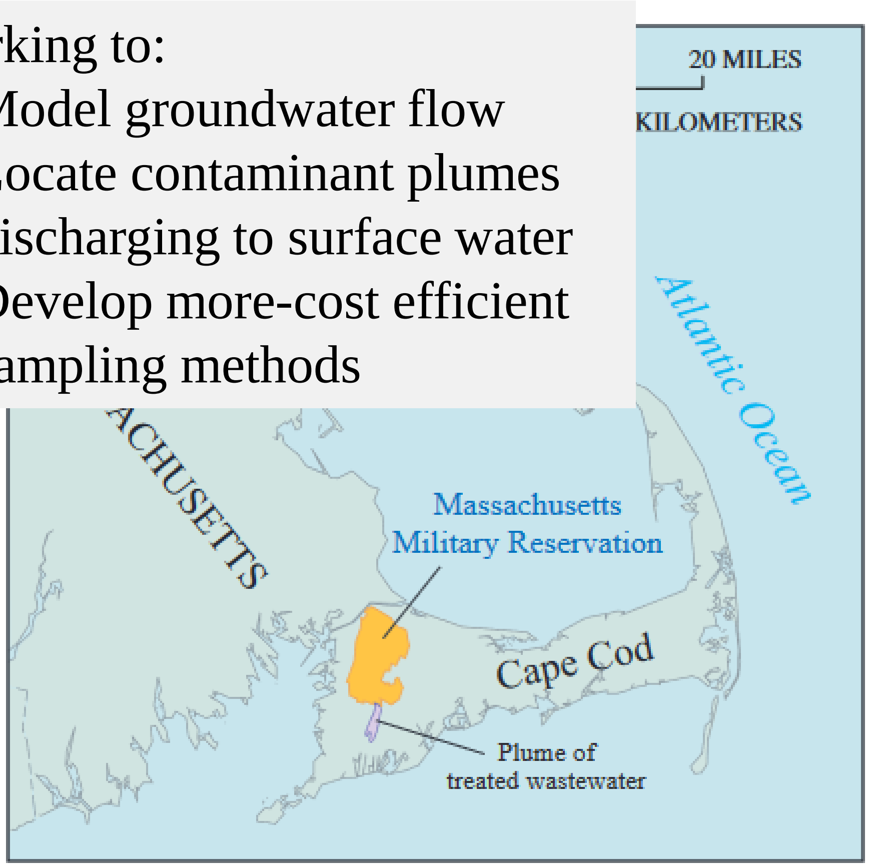
Physical, Chemical, and Biological Processes that Control the Fate of Contaminants in Ground Water

1500 wells!

12,000 sampling ports!!

Working to:

- Model groundwater flow
- Locate contaminant plumes discharging to surface water
- Develop more-cost efficient sampling methods



Location map showing MMR and plume of treated wastewater

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When simulating solute transport…

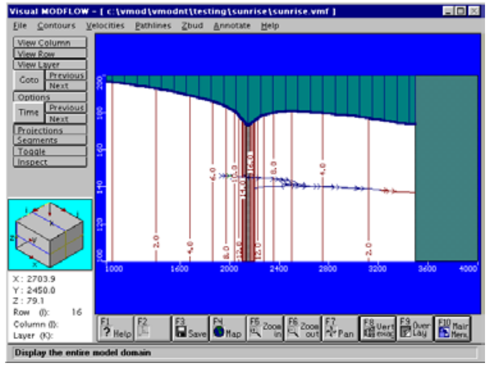
Bare bones basics of modeling

Groundwater modeling software (e.g. MODFLOW, FEFLOW, Hydrus, etc.) solve equations relating to flow (and sometimes transport too)

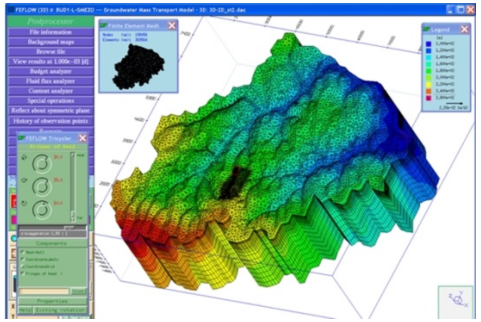
Basically we 'discretize' space and time, and calculations are made for each grid cell and timestep

We can (try to) predict potential behavior (influence of pumping, fate of a pollutant spill)

Screenshot from Visual MODFLOW



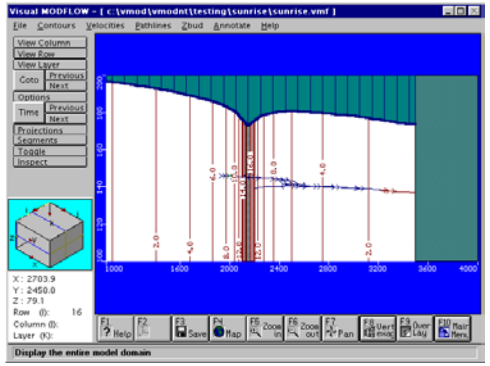
Screenshot from FEFLOW



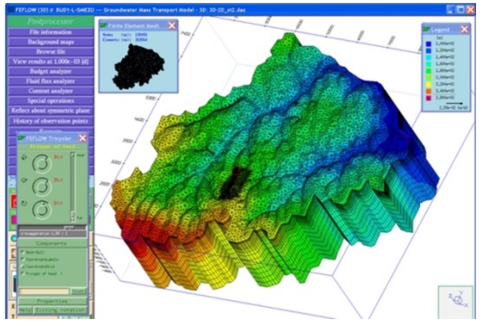
Why use a groundwater model?

It is important to remember...

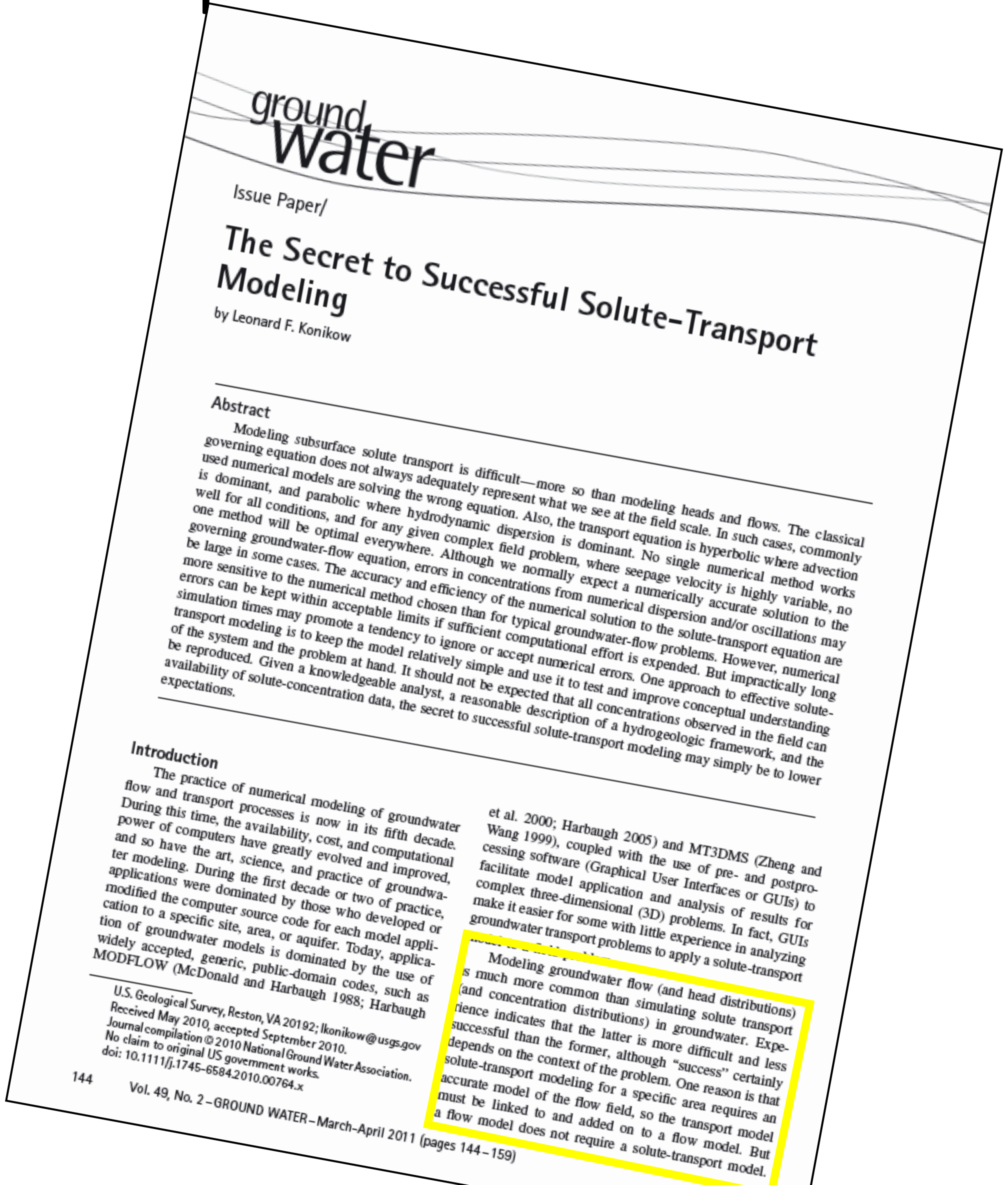
Screenshot from Visual MODFLOW



Screenshot from FEFLOW



Using models to predict solute transport



ground water

Issue Paper/

The Secret to Successful Solute-Transport Modeling

by Leonard F. Konikow

Abstract

Modeling subsurface solute transport is difficult—more so than modeling heads and flows. The classical governing equation does not always adequately represent what we see at the field scale. In such cases, commonly used numerical models are solving the wrong equation. Also, the transport equation is hyperbolic where advection is dominant, and parabolic where hydrodynamic dispersion is dominant. No single numerical method works well for all conditions, and for any given complex field problem, where seepage velocity is highly variable, no one method will be optimal everywhere. Although we normally expect a numerically accurate solution to the governing groundwater-flow equation, errors in concentrations from numerical dispersion and/or oscillations may be large in some cases. The accuracy and efficiency of the numerical solution to the solute-transport equation are more sensitive to the numerical method chosen than for typical groundwater-flow problems. However, numerical errors can be kept within acceptable limits if sufficient computational effort is expended. But impractically long simulation times may promote a tendency to ignore or accept numerical errors. One approach to effective solute-transport modeling is to keep the model relatively simple and use it to test and improve conceptual understanding of the system and the problem at hand. It should not be expected that all concentrations observed in the field can be reproduced. Given a knowledgeable analyst, a reasonable description of a hydrogeologic framework, and the availability of solute-concentration data, the secret to successful solute-transport modeling may simply be to lower expectations.

Introduction

The practice of numerical modeling of groundwater flow and transport processes is now in its fifth decade. During this time, the availability, cost, and computational power of computers have greatly evolved and improved, and so have the art, science, and practice of groundwater modeling. During the first decade or two of practice, applications were dominated by those who developed or modified the computer source code for each model application to a specific site, area, or aquifer. Today, application of groundwater models is dominated by the use of widely accepted, generic, public-domain codes, such as MODFLOW (McDonald and Harbaugh 1988; Harbaugh et al. 2000; Harbaugh 2005) and MT3DMS (Zheng and Wang 1999), coupled with the use of pre- and postprocessing software (Graphical User Interfaces or GUIs) to facilitate model application and analysis of results for complex three-dimensional (3D) problems. In fact, GUIs make it easier for some with little experience in analyzing groundwater transport problems to apply a solute-transport model to a field problem.

Modeling groundwater flow (and head distributions) is much more common than simulating solute transport (and concentration distributions) in groundwater. Experience indicates that the latter is more difficult and less successful than the former, although "success" certainly depends on the context of the problem. One reason is that solute-transport modeling for a specific area requires an accurate model of the flow field, so the transport model must be linked to and added on to a flow model. But a flow model does not require a solute-transport model.

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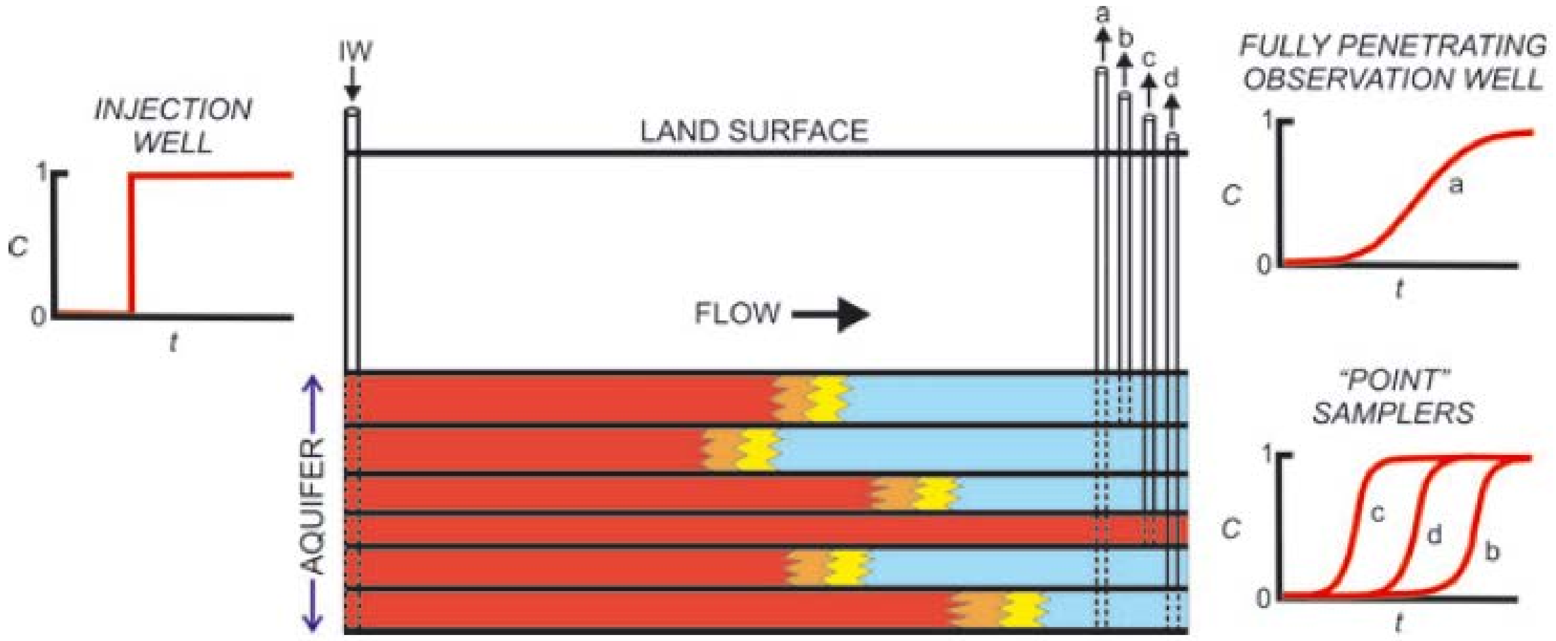
Do we know what we are measuring?

Typically, when a model is being set up, we test to see whether it can reproduce field measurements (e.g. heads, or concentrations)

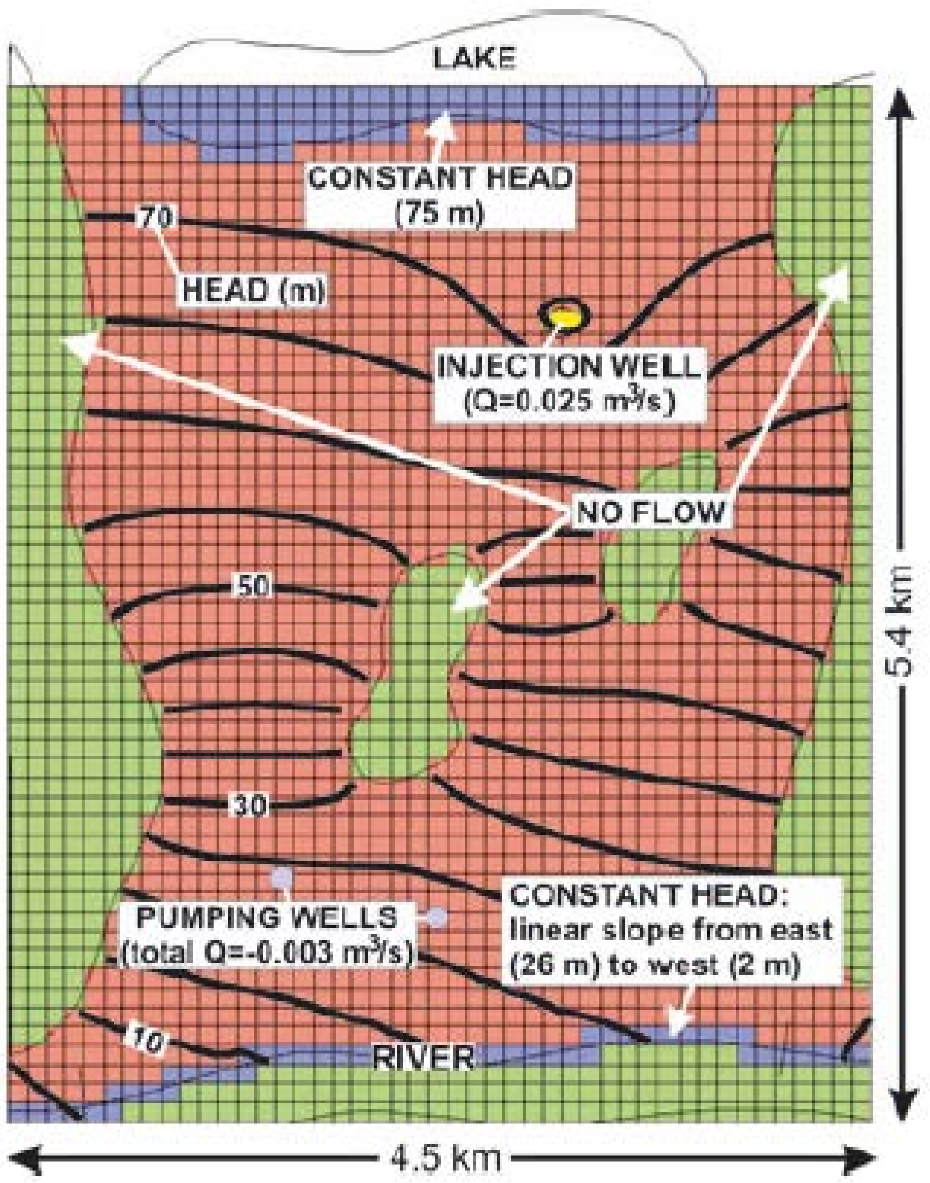


Test case

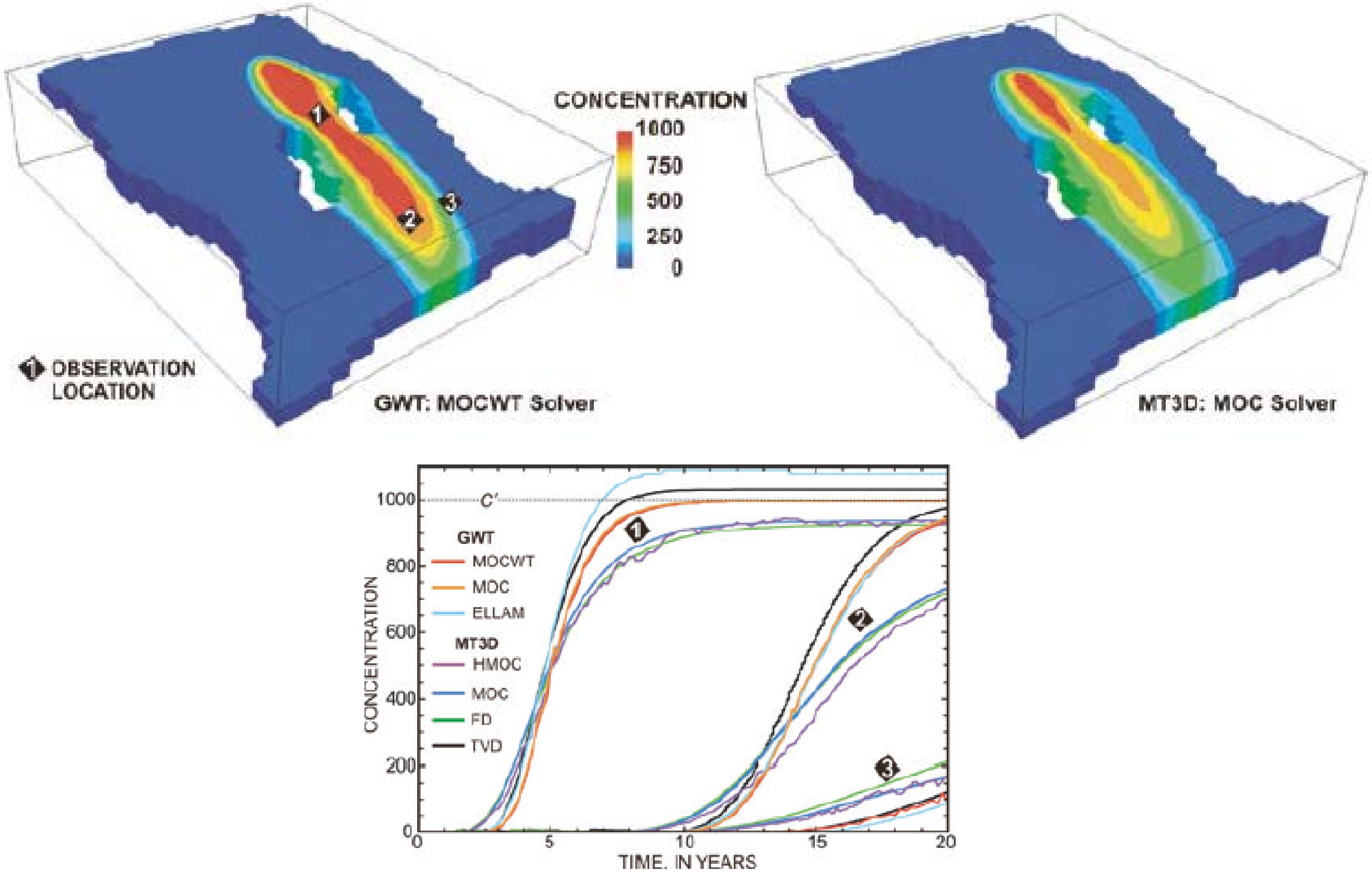
The benefits of a model to explore processes... We can set up a case where everything is known.

In this example:

- Constant head (e.g. water bodies)
- No flow (e.g. low K regions)
- Aquifer
- Constant head lines
- Pollution source



Which mathematical approach to solve equations?



How to represent heterogeneity

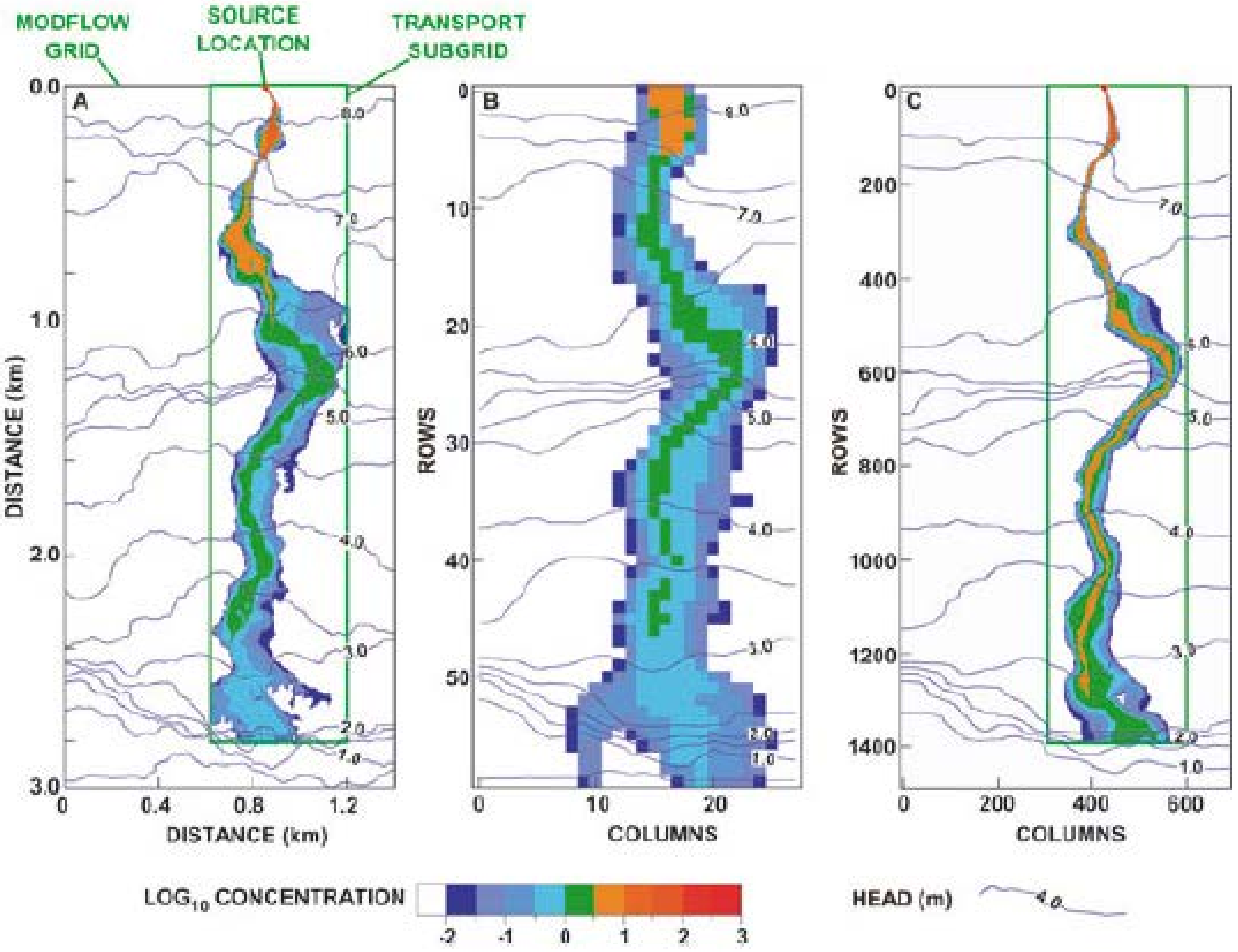
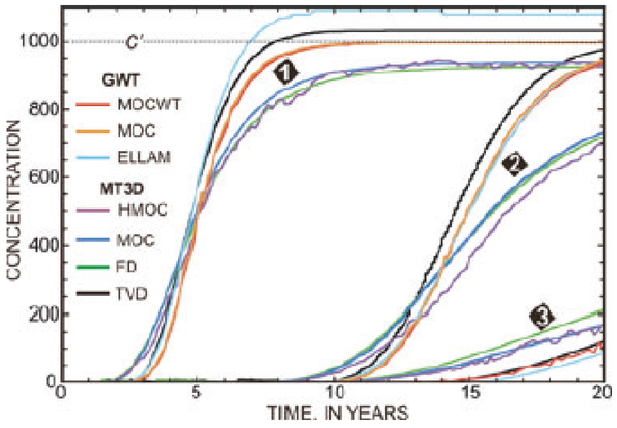
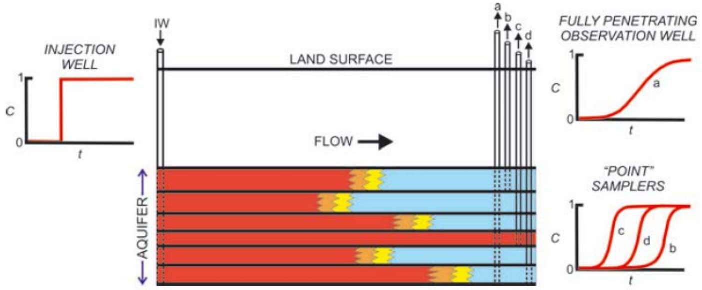
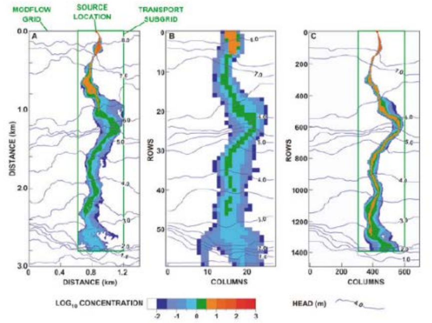


Figure 8. Effect of scale of discretization and resolution of heterogeneity on calculated heads and concentrations for case of hypothetical contaminant release from a leaky borehole in a regional aquifer: (A) grid spacing = 2 m; (B) grid spacing = 50 m; and (C) T defined on 50-m spacing from B, but numerical solution obtained using grid spacing = 2 m.

…the secret to successful solute-transport modeling may simply be to lower expectations.







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