EPA United States Environmental Protection Agency

CLEMSON UNIVERSITY

UF UNIVERSITY of FLORIDA

AIR FORCE INSTITUTE OF TECHNOLOGY

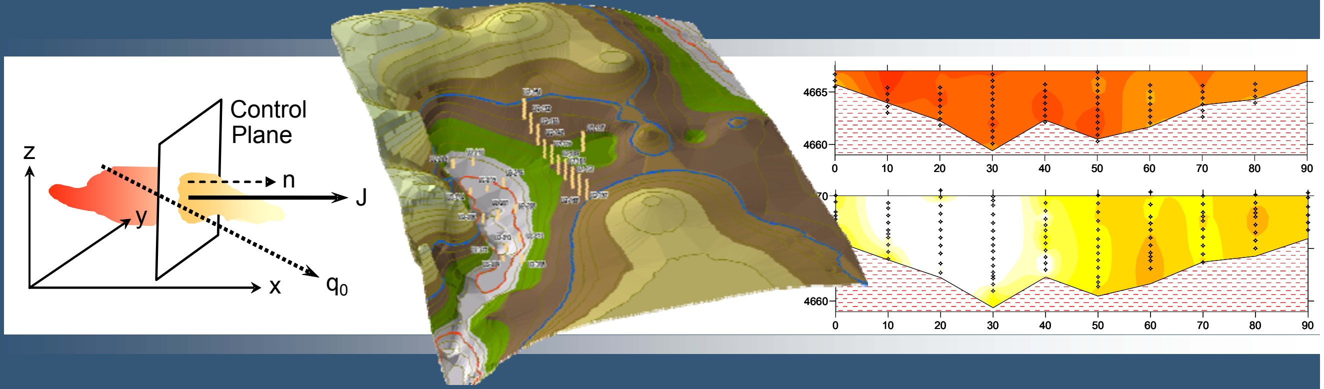
PURDUE

DoD EPA DOE SERDP Strategic Environmental Research and Development Program

Triad Conference – June 10, 2008

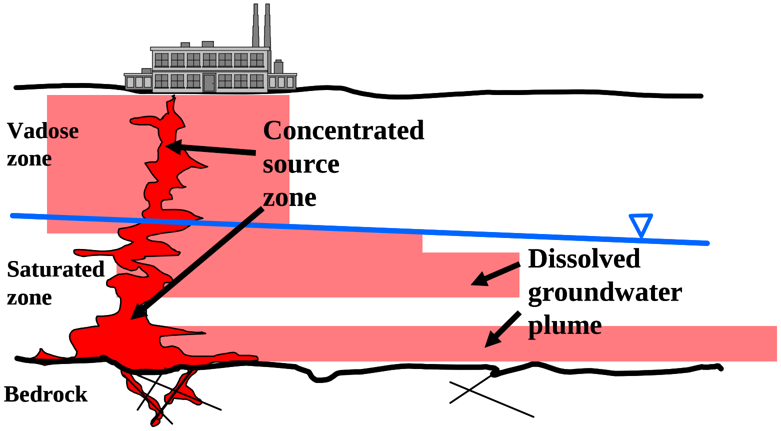
# Flux-Based Remedial Design and Assessment Tools

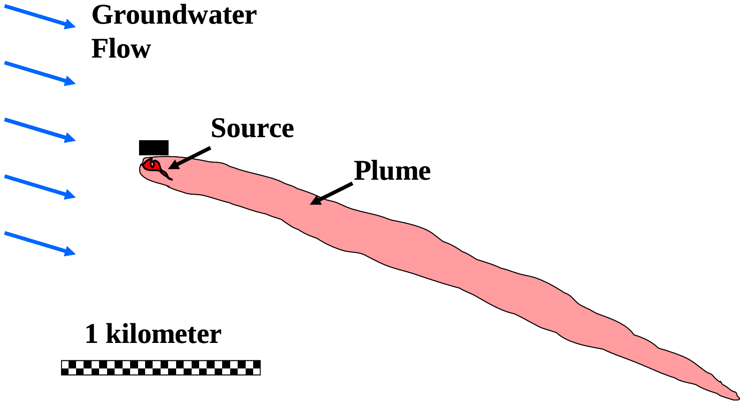
*Ronald W. Falta, Clemson University, South Carolina*



**Office of Research and Development**
National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division, Ada, Oklahoma

# The Site Managers Dilemma



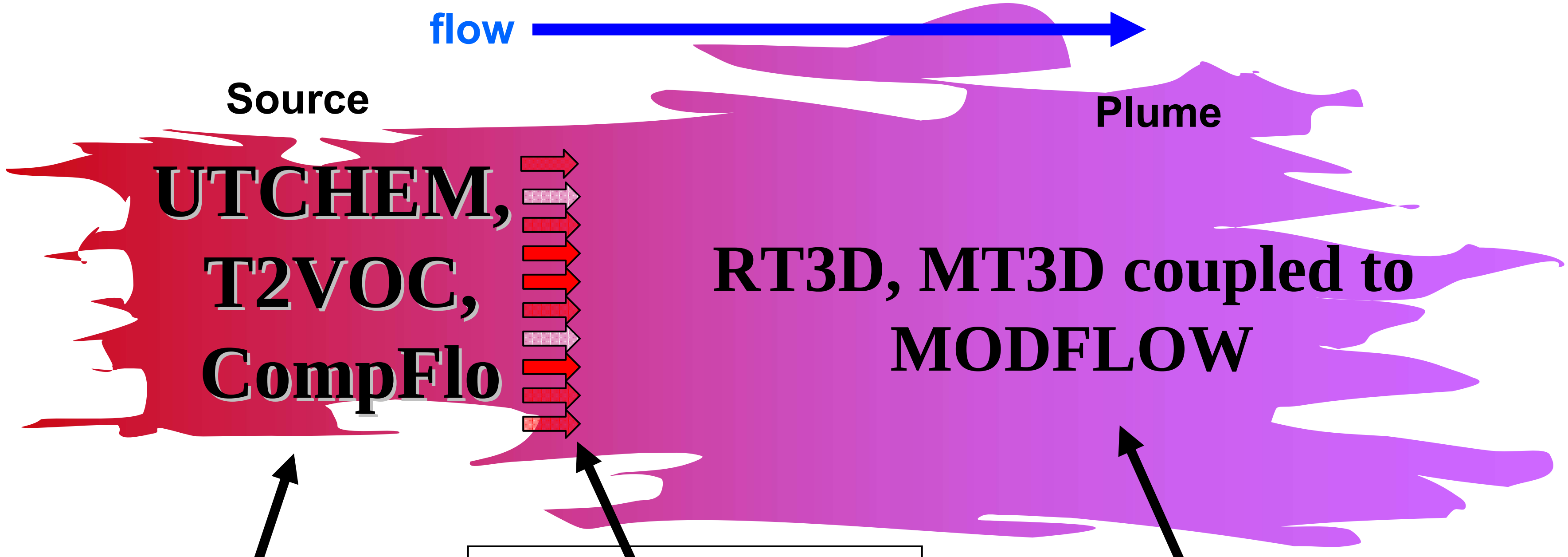


“Should we spend our money and effort on cleaning up the source zone? That’s where most of the contaminant mass is”

“Or should we focus on controlling the plume using pump and treat, a reactive barrier, or enhanced plume degradation?”

**“Is there some kind of quantitative model to guide these decisions?”**

# One approach: use complex 3-D numerical models to represent the source and plume



flow

**Source**

**Plume**

**UTCHEM, T2VOC, CompFlo**

**RT3D, MT3D coupled to MODFLOW**

**Simulate multiphase flow and remediation process in the source zone with full heterogeneity**

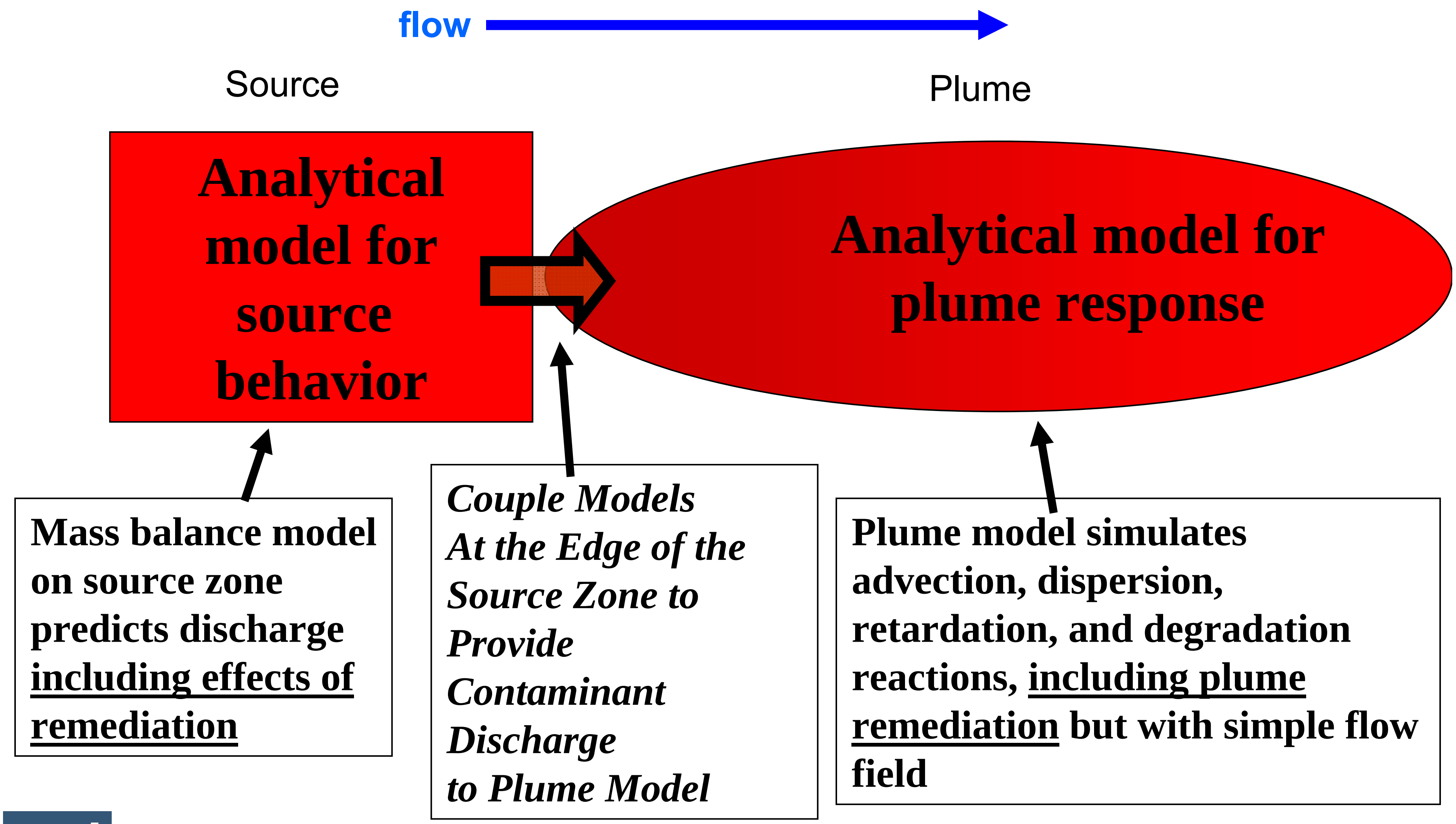
***Couple Models At the Edge of the Source Zone to Provide Contaminant Flux Distribution to Plume Models***

**Simulate dissolved groundwater plume transport with various biological and geochemical reactions with full heterogeneity**

# Observation

- If we had large amounts of field data, lots of time, and lots of money, we would probably select the full rigorous 3-D numerical modeling approach
- Many sites do not fit this description – these sites could benefit from a more practical and simpler modeling approach
- **Such a "screening-level" model should still conserve mass in the source and plume zones, and it should still represent the dominant processes**

# A much simpler model



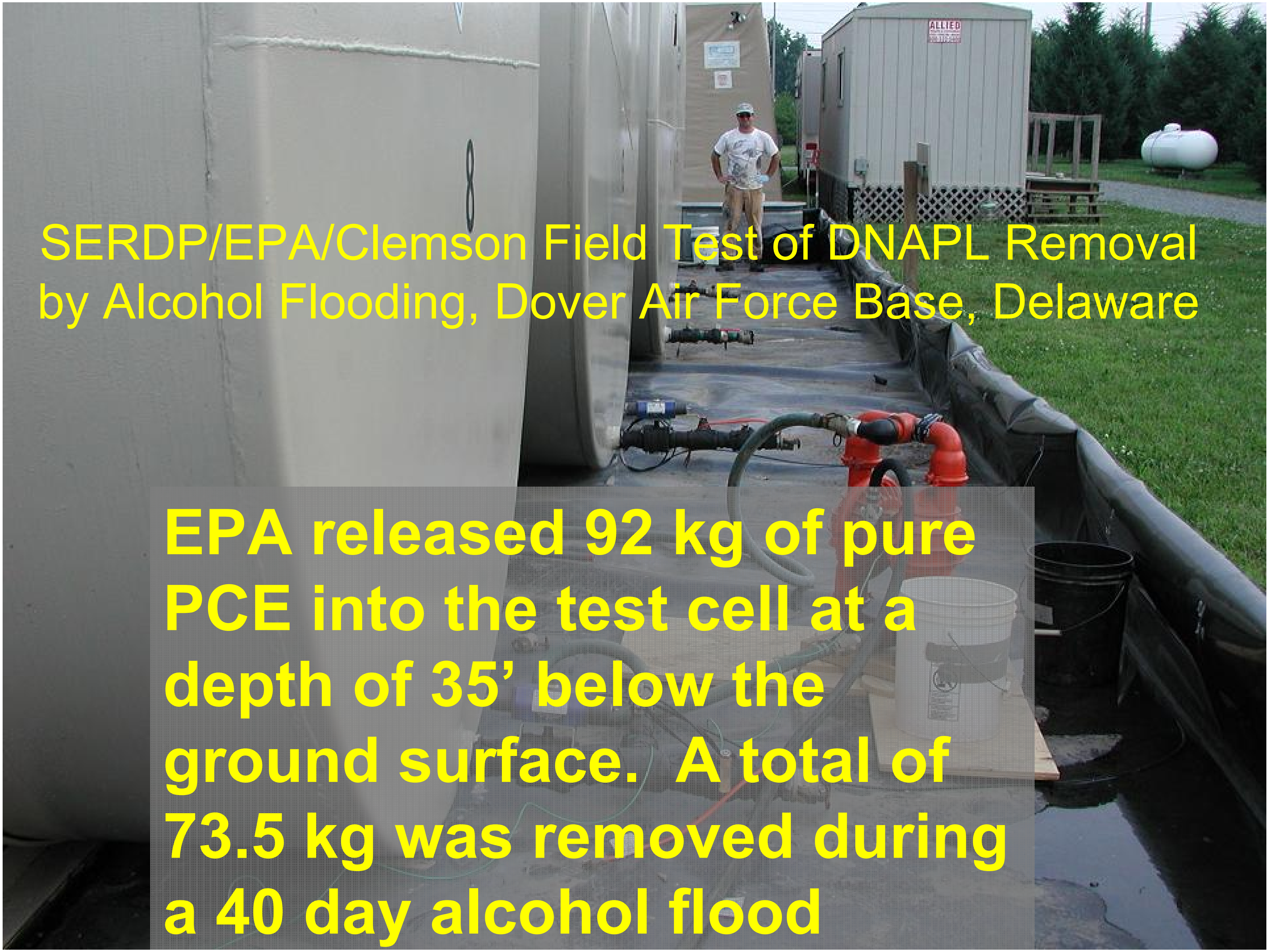
**Analytical model for source behavior**

**Analytical model for plume response**

**Mass balance model on source zone predicts discharge <u>including effects of remediation</u>**

***Couple Models At the Edge of the Source Zone to Provide Contaminant Discharge to Plume Model***

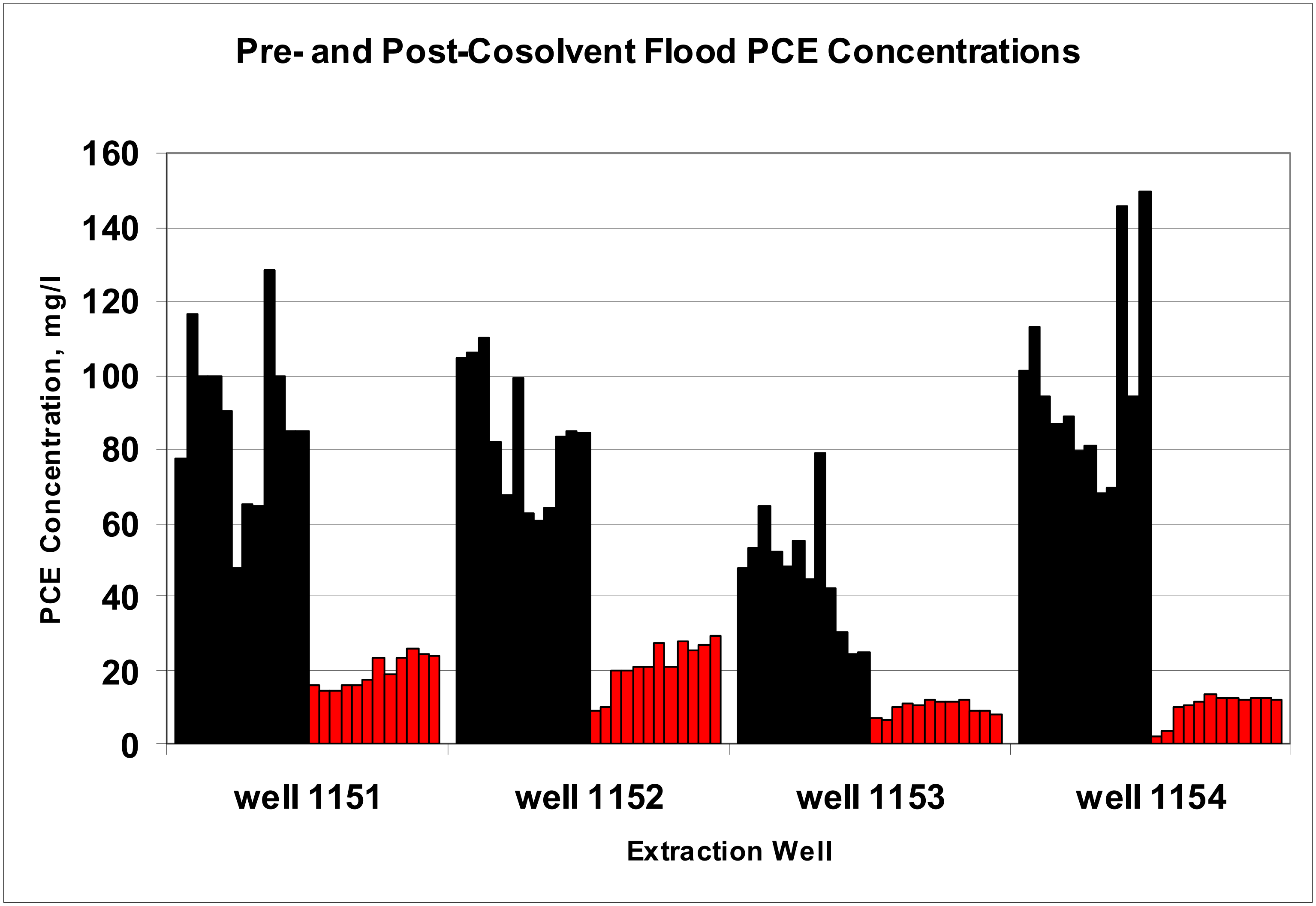
**Plume model simulates advection, dispersion, retardation, and degradation reactions, <u>including plume remediation</u> but with simple flow field**



SERDP/EPA/Clemson Field Test of DNAPL Removal by Alcohol Flooding, Dover Air Force Base, Delaware

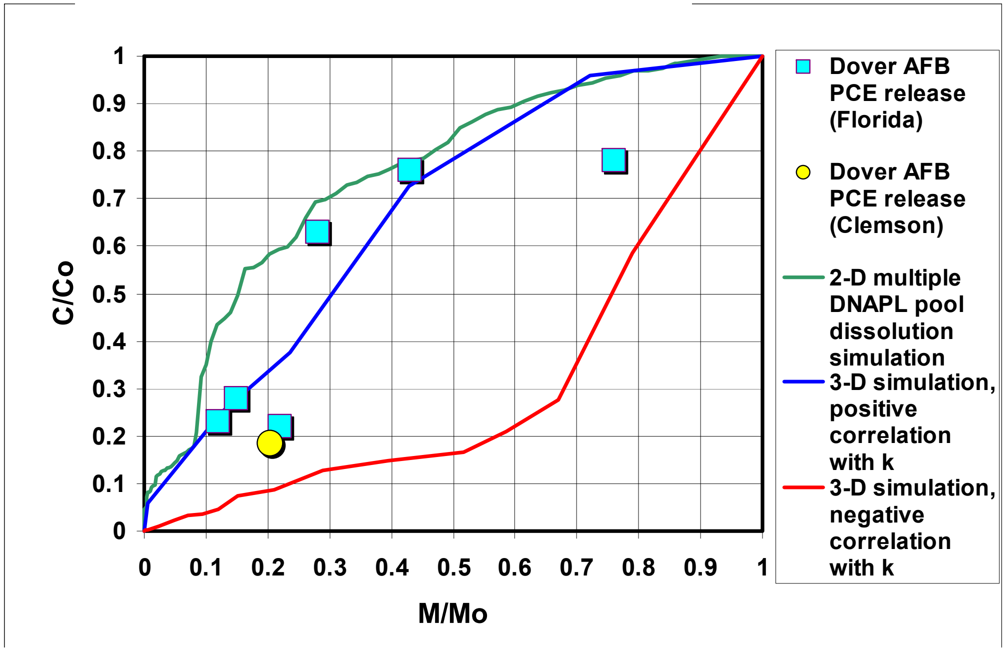
**EPA released 92 kg of pure PCE into the test cell at a depth of 35’ below the ground surface. A total of 73.5 kg was removed during a 40 day alcohol flood**

# 80% source removal resulted in 81% reduction in groundwater concentration

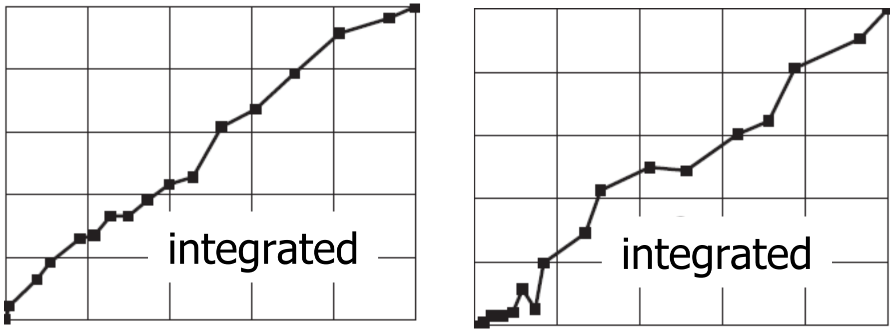


# Source mass reduction leads to discharge reduction

Field and Modeling Data



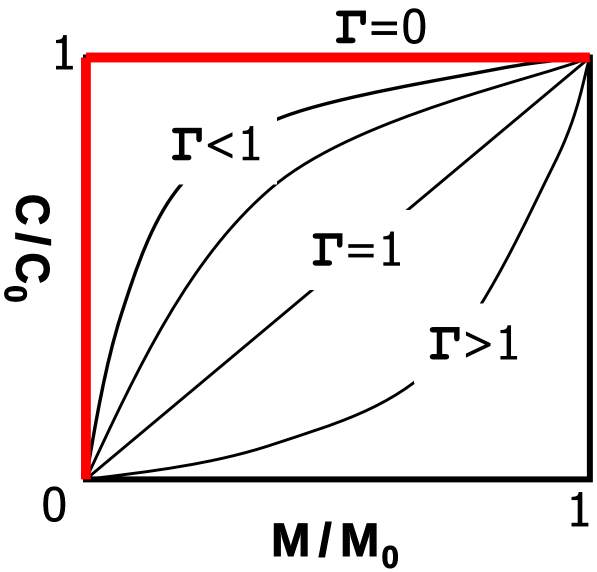
Laboratory dissolution experiments (Jawitz et al.)



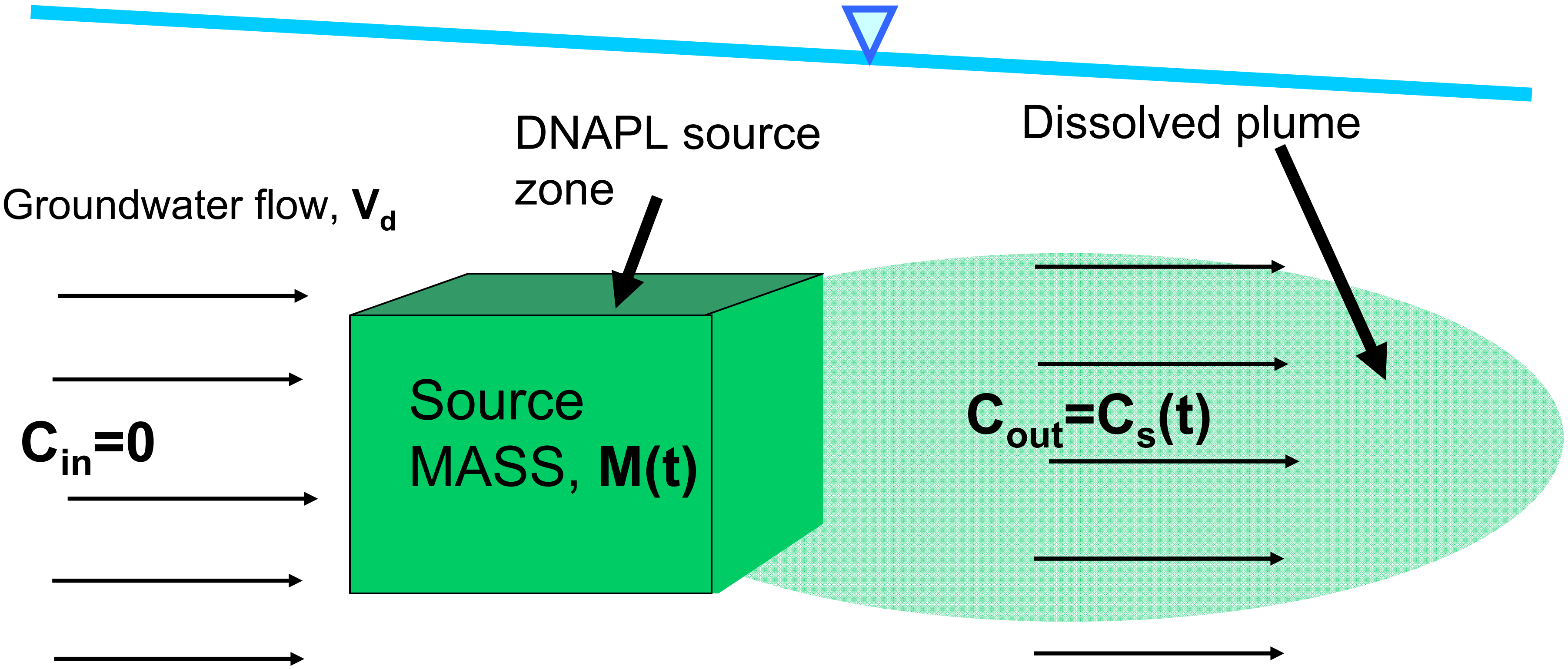
## Power function model

[Rao et al., 2001; Parker and Park, 2004; Zhu and Sykes, 2004]

$$\frac{C}{C_0} = \left(\frac{M}{M_0}\right)^{\Gamma}$$



**Source conceptual model**: Mass is mainly removed by flushing. Remediation is simulated by removing a fraction of the source mass at the time of remediation



Groundwater flow, $\mathbf{V_d}$

DNAPL source zone

Dissolved plume

$\mathbf{C_{in}=0}$

Source MASS, **M(t)**

$\mathbf{C_{out}=C_s(t)}$

$$\frac{dM}{dt} = -Q(t)C_s(t) - \lambda_s M \qquad\qquad C_s(t) = C_0\left(\frac{M(t)}{M_0}\right)^{\Gamma}$$

# Source Zone Solutions

Falta et al., 2005

General Solution before remediation occurs

$$M(t) = \left\{ -\frac{V_d A C_0}{\lambda_s M_0^{\Gamma}} + \left( M_0^{1-\Gamma} + \frac{V_d A C_0}{\lambda_s M_0^{\Gamma}} \right) e^{(\Gamma-1)\lambda_s t} \right\}^{\frac{1}{1-\Gamma}}$$

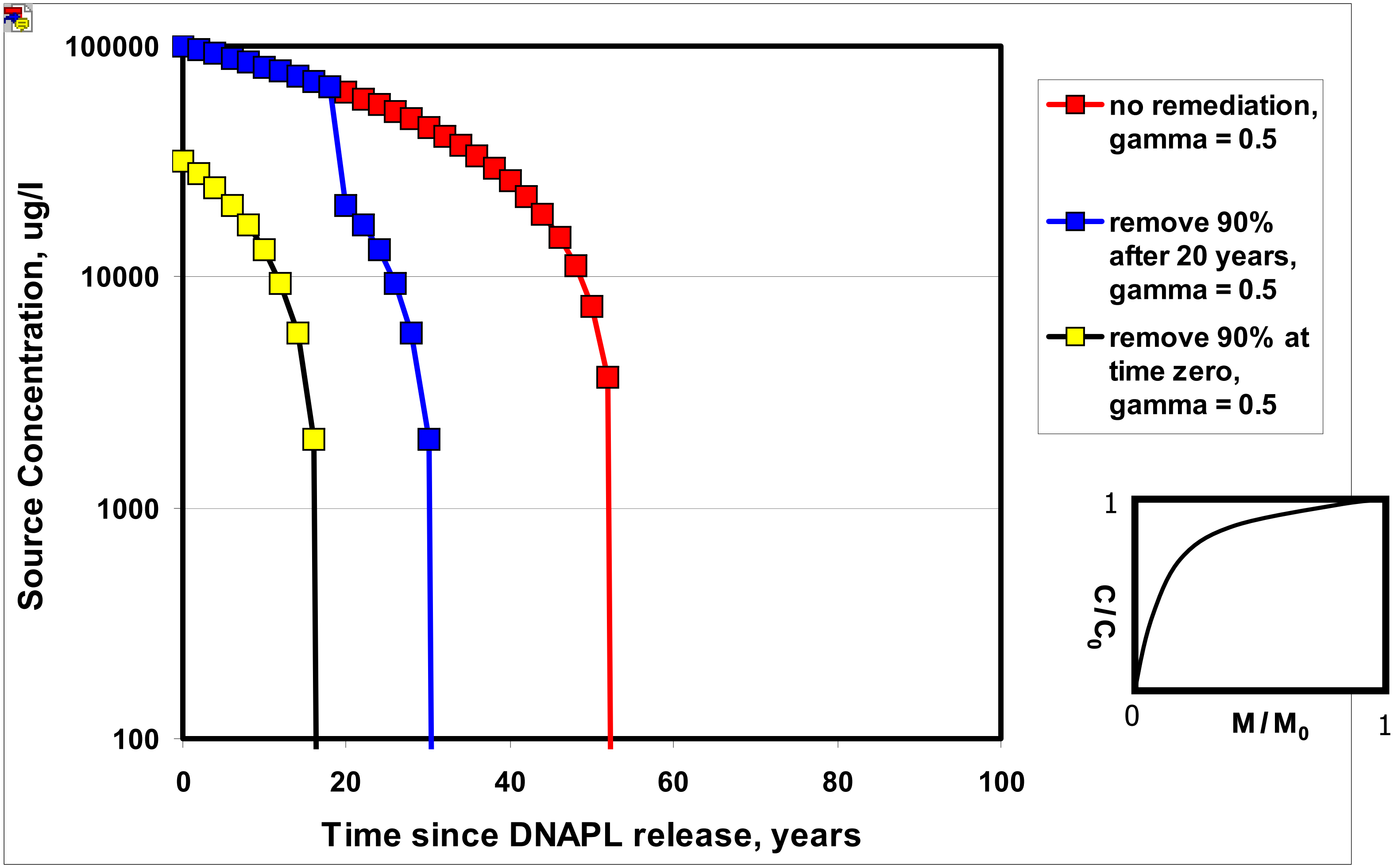
If we remove a fraction, **X**, of the DNAPL mass by remediation at time *TR*, then

$$M(t) = \left\{ \frac{-V_d A C_{TR}(1-X)^{\Gamma}}{\lambda_s \left[(1-X)M_{TR}\right]^{\Gamma}} + \left( \left[(1-X)M_{TR}\right]^{1-\Gamma} + \frac{V_d A C_{TR}(1-X)^{\Gamma}}{\lambda_s \left[(1-X)M_{TR}\right]^{\Gamma}} \right) \exp\left[(\Gamma-1)\lambda_s t\right] \right\}^{\frac{1}{1-\Gamma}}$$

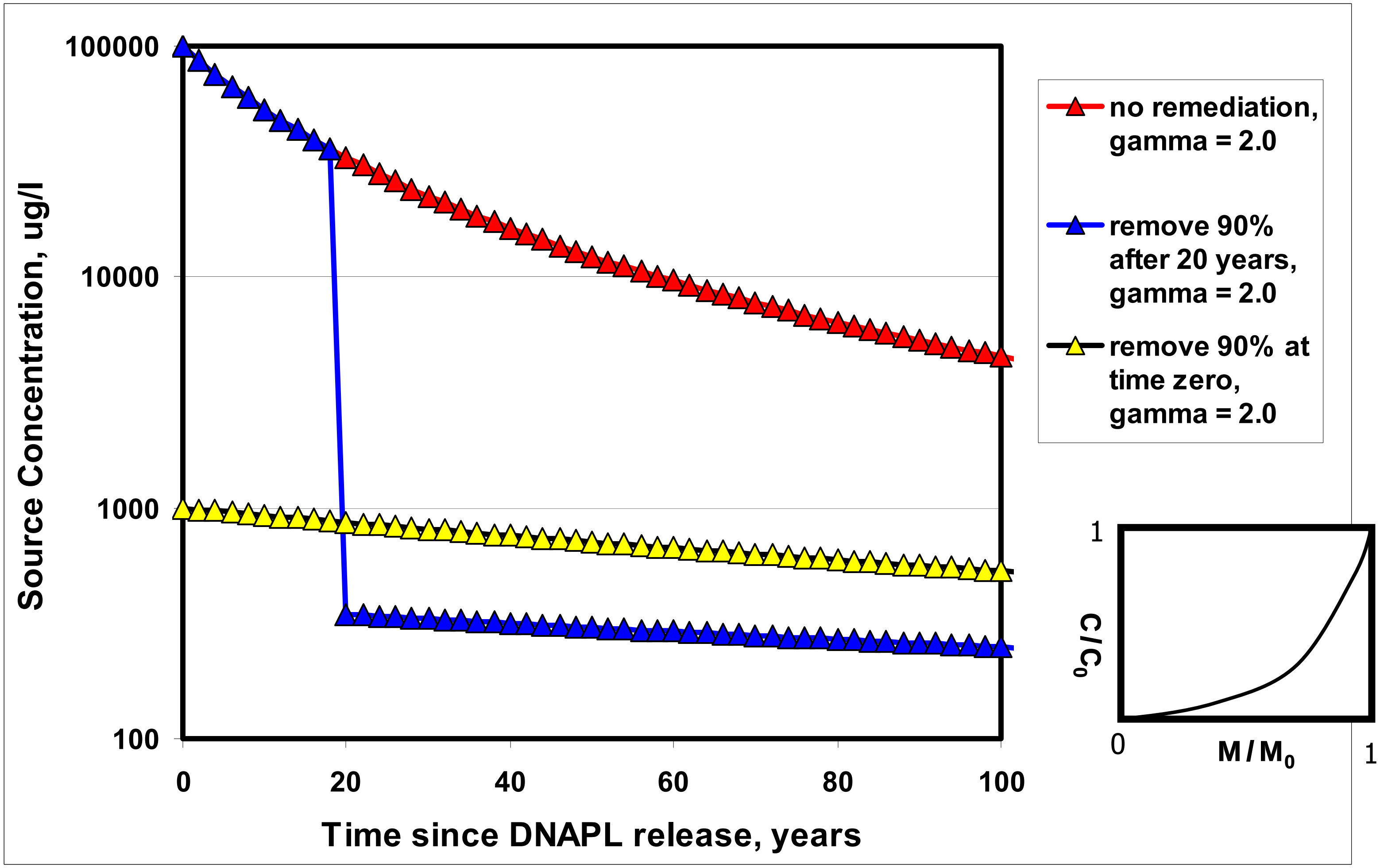
and the source discharge is computed from

$$C_s(t) = C_{TR}\left(\frac{M(t)}{M_{TR}}\right)^{\Gamma}$$

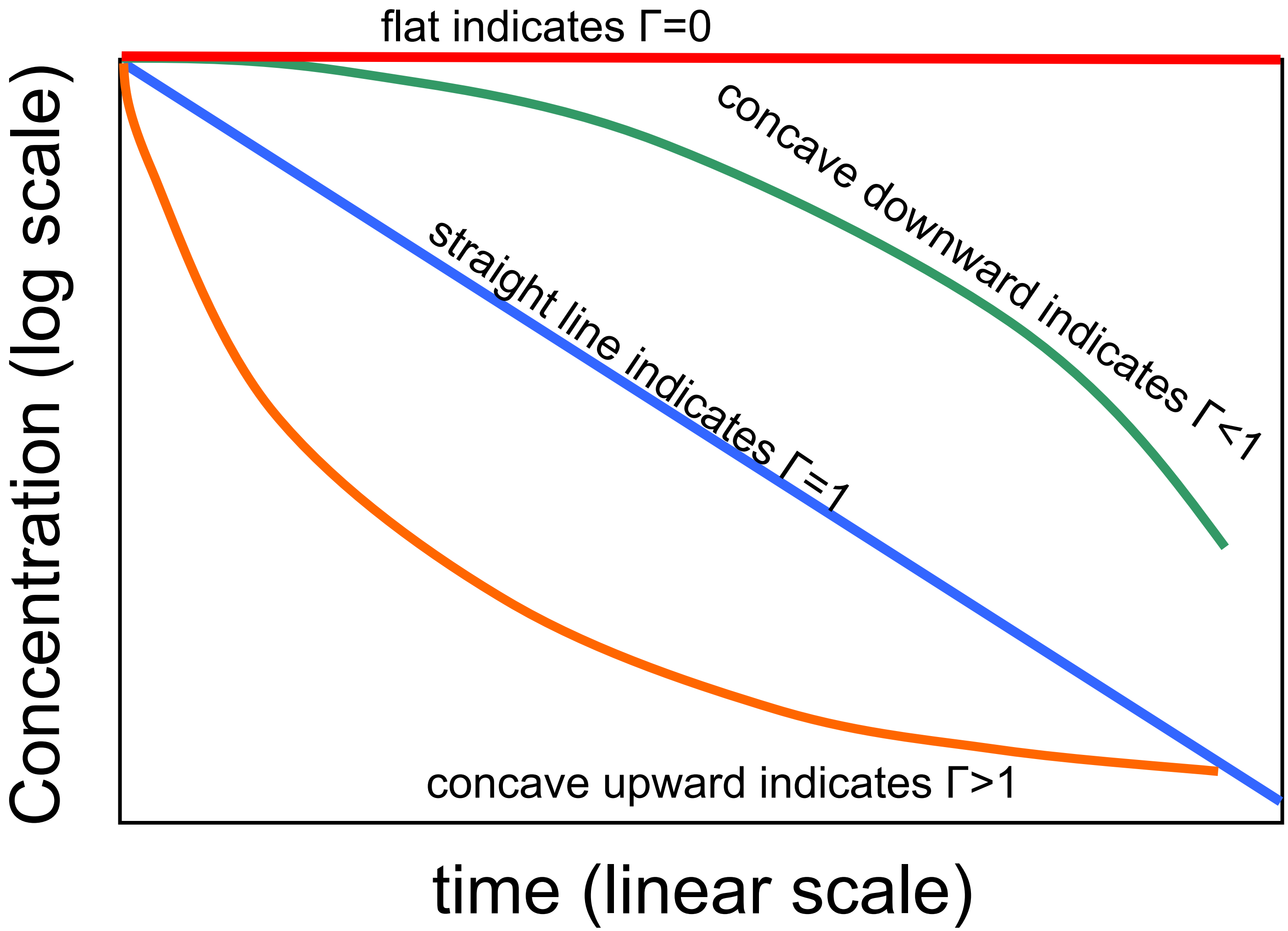
# Source Behavior: $\Gamma$=0.5, $M_0$= 1620 kg, V=20 m/yr, A=10m x 3m, $C_0$=100 mg/l



# Source Behavior: $\Gamma$ =2.0, $M_0$= 1620 kg, V=20 m/yr, A=10m x 3m, $C_0$=100 mg/l



# How to estimate Γ from field data using concentration versus time curves



# Couple the source function to the plume in an analytical model:

Use the source function as the boundary condition in a 3-D advection dispersion differential equation:

$$R\frac{\partial C_i}{\partial t} = -v\frac{\partial C_i}{\partial x} + \alpha_x v\frac{\partial^2 C_i}{\partial x^2} + \alpha_y v\frac{\partial^2 C_i}{\partial y^2} + \alpha_z v\frac{\partial^2 C_i}{\partial z^2} + rxn_i$$

Use a flux-based, mixed boundary condition at x=0:

$$mass\ \ flux\,of = V_d C_s(t) = \left[ V_d C - \phi\alpha_x v\frac{\partial C}{\partial x} \right]_{x=0}$$

Where

$$C_s(t) = \frac{(C_{TR}(1-X)^{\Gamma})}{\left[(1-X)M_{TR}\right]^{\Gamma}}\left\{\frac{-V_d A C_{TR}(1-X)^{\Gamma}}{\lambda_s\left[(1-X)M_{TR}\right]^{\Gamma}} + \left(\left[(1-X)M_{TR}\right]^{1-\Gamma} + \frac{V_d A C_{TR}(1-X)^{\Gamma}}{\lambda_s\left[(1-X)M_{TR}\right]^{\Gamma}}\right)\exp\left[(\Gamma-1)\lambda_s t\right]\right\}^{\frac{\Gamma}{1-\Gamma}}$$

# Consider coupled parent-daughter reactions in the plume

For example, we could include reductive dechlorination of PCE to TCE to DCE to vinyl chloride:

$$rxn_{PCE} = -\lambda_{PCE} C_{PCE}$$

$$rxn_{TCE} = y_{TCE/PCE} \lambda_{PCE} C_{PCE} - \lambda_{TCE} C_{TCE}$$

$$rxn_{DCE} = y_{DCE/TCE} \lambda_{TCE} C_{TCE} - \lambda_{DCE} C_{DCE}$$

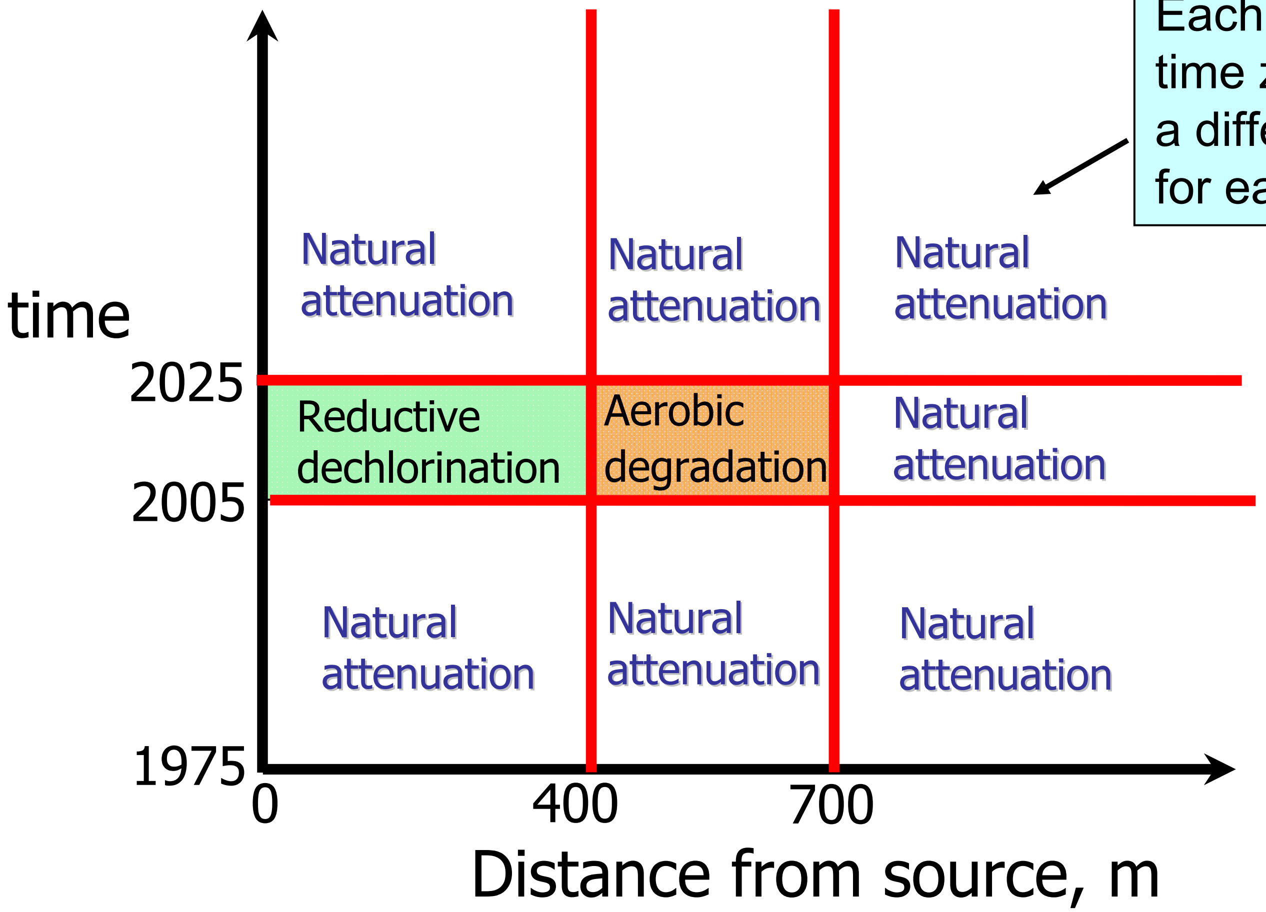
$$rxn_{VC} = y_{VC/DCE} \lambda_{DCE} C_{DCE} - \lambda_{VC} C_{VC}$$

We would like for all of these decay rate constants to be functions of distance and time.

**This lets us simulate enhanced plume remediation downgradient from the source**

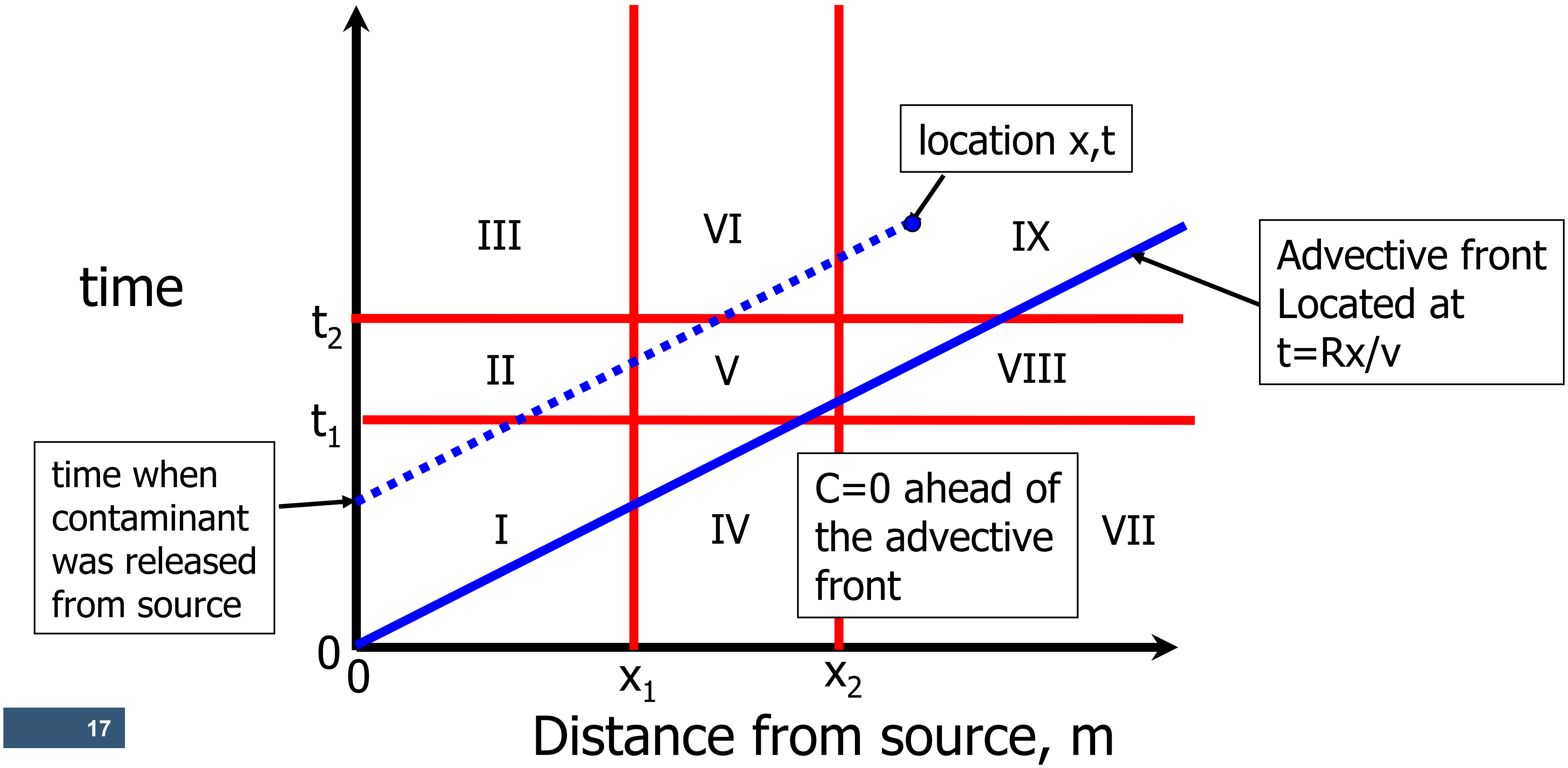
# Plume Remediation Model – divide space and time into "reaction zones", solve the coupled parent-daughter reactions for chlorinated solvent degradation in each zone

Example:



Each of these space-time zones can have a different decay rate for each chemical species

# **Solution:** method of characteristics with reactions. The residence time in each "reaction zone" is easily calculated. These are treated as batch reactions in each zone.



location x,t

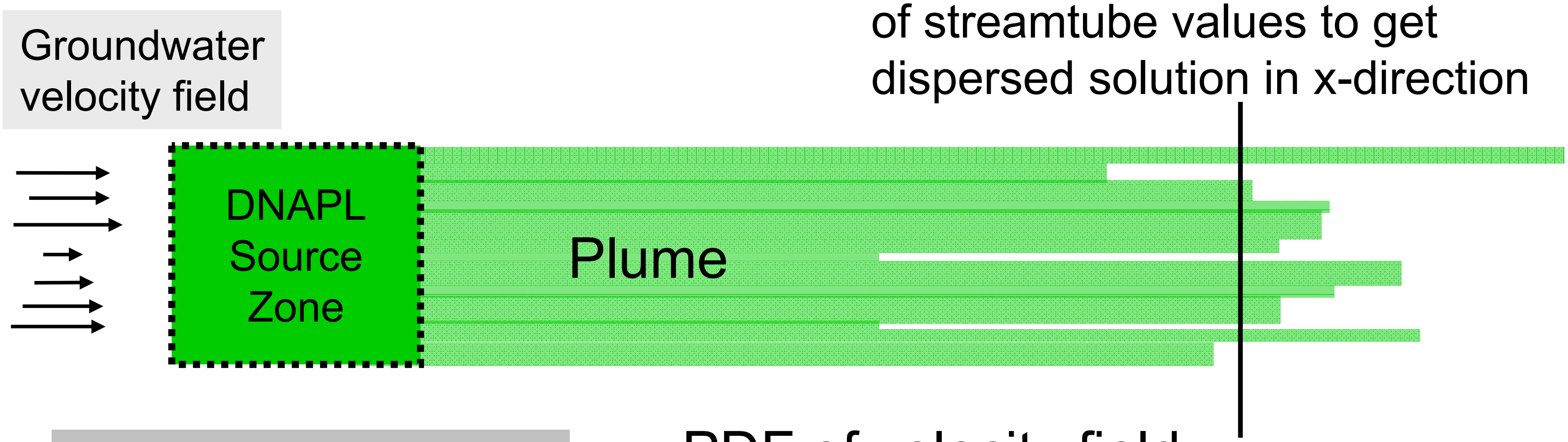
Advective front Located at t=Rx/v

C=0 ahead of the advective front

time when contaminant was released from source

# Scale-dependent longitudinal dispersion is included by assuming that a bundle of streamtubes pass through the source zone

Use probability-weighted average of streamtube values to get dispersed solution in x-direction



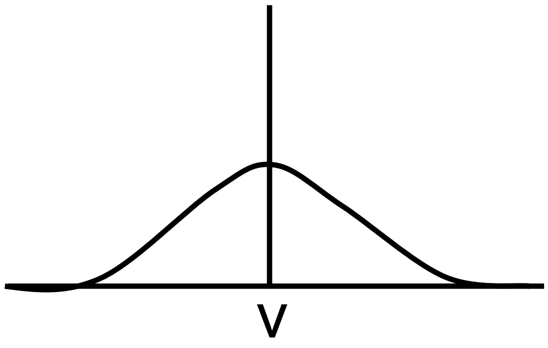
Groundwater velocity field

DNAPL Source Zone

Plume

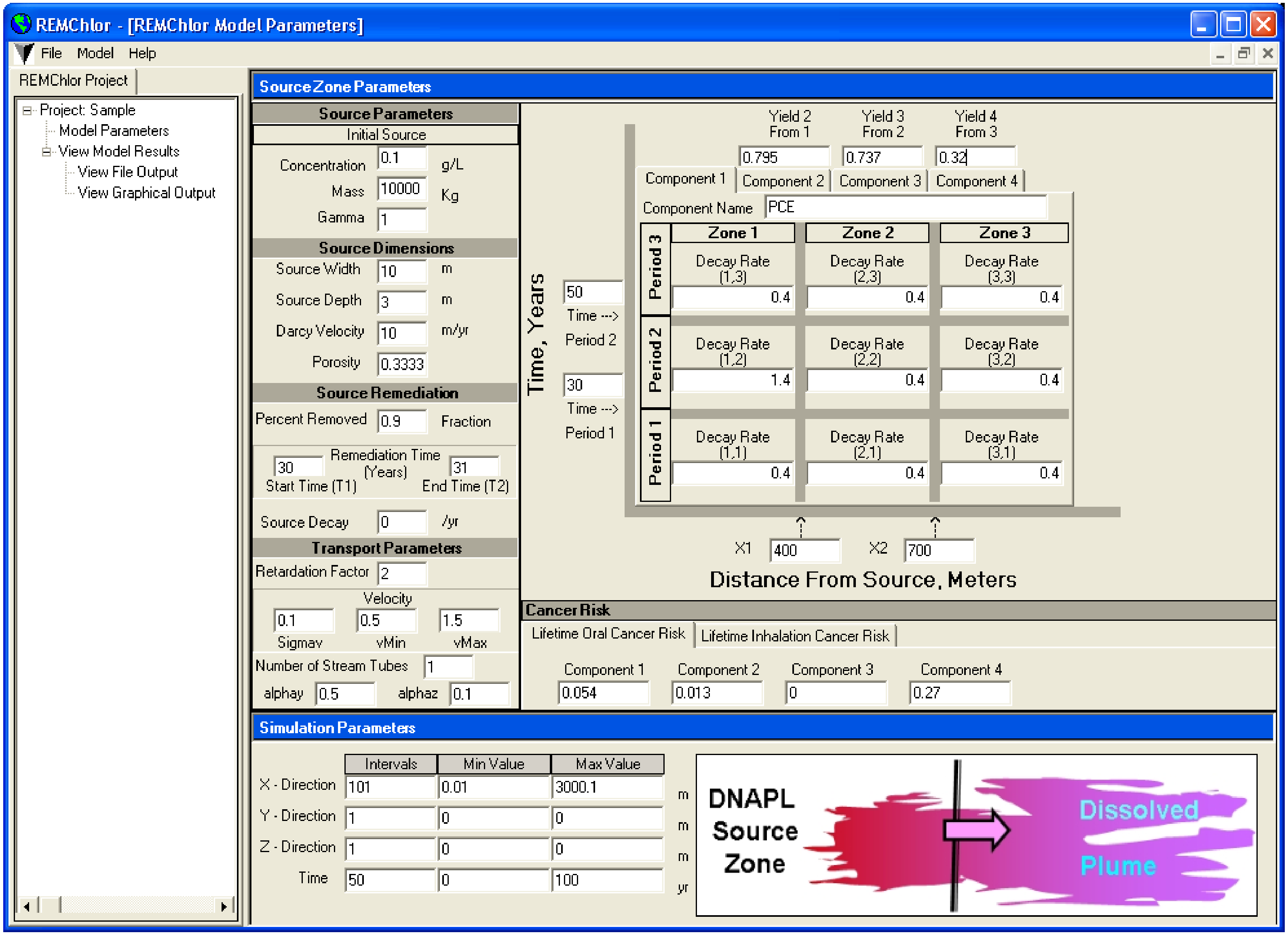
Assume a normally distributed velocity field, with a mean of v and a standard deviation of σ

PDF of velocity field



$$\alpha_x = \frac{1}{2}\left(\frac{\sigma}{v}\right)^2 x$$

# This source/plume remediation model is called REMChlor, and it is available for free from the US EPA: http://www.epa.gov/ada/csmos/models/remchlor.html



**Source Zone Parameters**

**Source Parameters**

Initial Source

Concentration 0.1 g/L
Mass 10000 Kg
Gamma 1

**Source Dimensions**

Source Width 10 m
Source Depth 3 m
Darcy Velocity 10 m/yr
Porosity 0.3333

**Source Remediation**

Percent Removed 0.9 Fraction

Remediation Time (Years): Start Time (T1) 30; End Time (T2) 31

Source Decay 0 /yr

**Transport Parameters**

Retardation Factor 2

Velocity: Sigmav 0.1; vMin 0.5; vMax 1.5

Number of Stream Tubes 1

alphay 0.5
alphaz 0.1

| Yield 2 From 1 | Yield 3 From 2 | Yield 4 From 3 |
|---|---|---|
| 0.795 | 0.737 | 0.32 |

Component 1 | Component 2 | Component 3 | Component 4

Component Name PCE

Time, Years

| | Zone 1 | Zone 2 | Zone 3 |
|---|---|---|---|
| Period 3 | Decay Rate (1,3) 0.4 | Decay Rate (2,3) 0.4 | Decay Rate (3,3) 0.4 |
| 50 Time --> Period 2 | | | |
| Period 2 | Decay Rate (1,2) 1.4 | Decay Rate (2,2) 0.4 | Decay Rate (3,2) 0.4 |
| 30 Time --> Period 1 | | | |
| Period 1 | Decay Rate (1,1) 0.4 | Decay Rate (2,1) 0.4 | Decay Rate (3,1) 0.4 |

X1 400
X2 700

Distance From Source, Meters

**Cancer Risk**

Lifetime Oral Cancer Risk | Lifetime Inhalation Cancer Risk

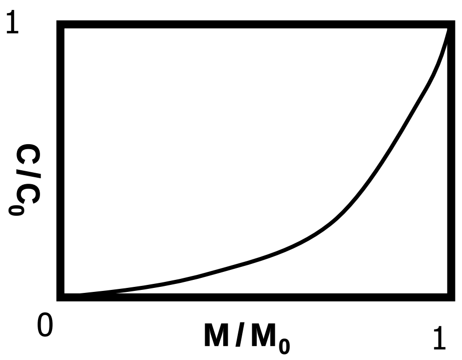
| Component 1 | Component 2 | Component 3 | Component 4 |
|---|---|---|---|
| 0.054 | 0.013 | 0 | 0.27 |

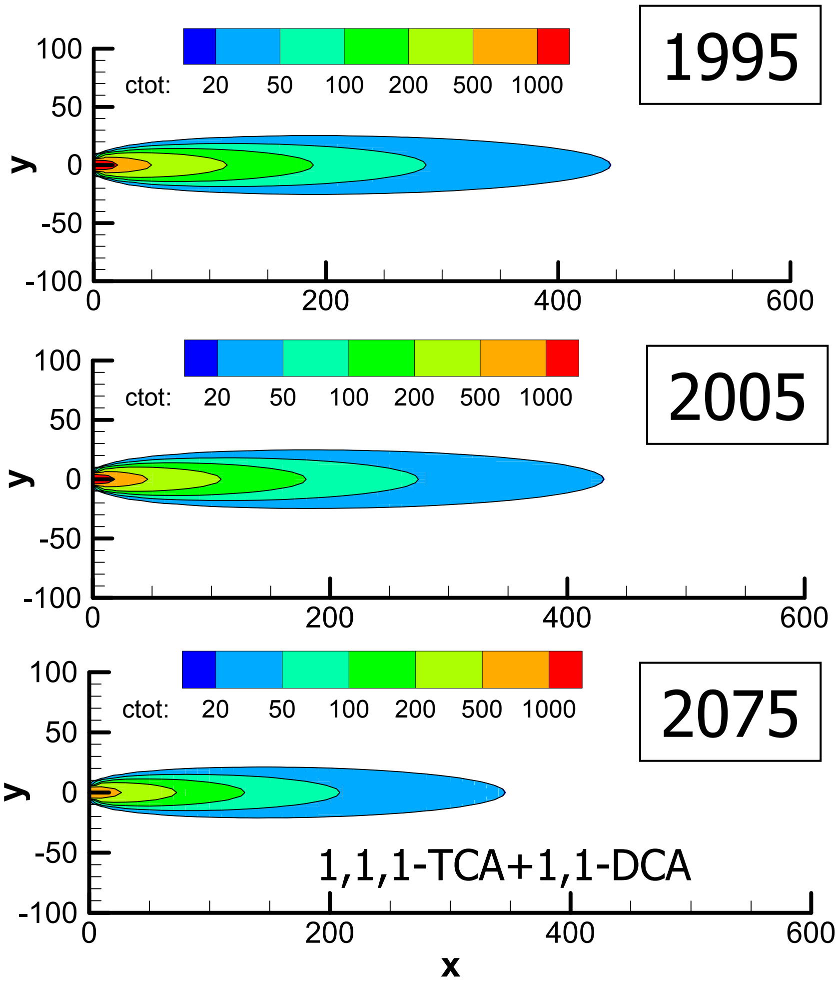
**Simulation Parameters**

| | Intervals | Min Value | Max Value | |
|---|---|---|---|---|
| X - Direction | 101 | 0.01 | 3000.1 | m |
| Y - Direction | 1 | 0 | 0 | m |
| Z - Direction | 1 | 0 | 0 | m |
| Time | 50 | 0 | 100 | yr |

# REMChlor example: 300 kg release of 1,1,1-TCA in 1975

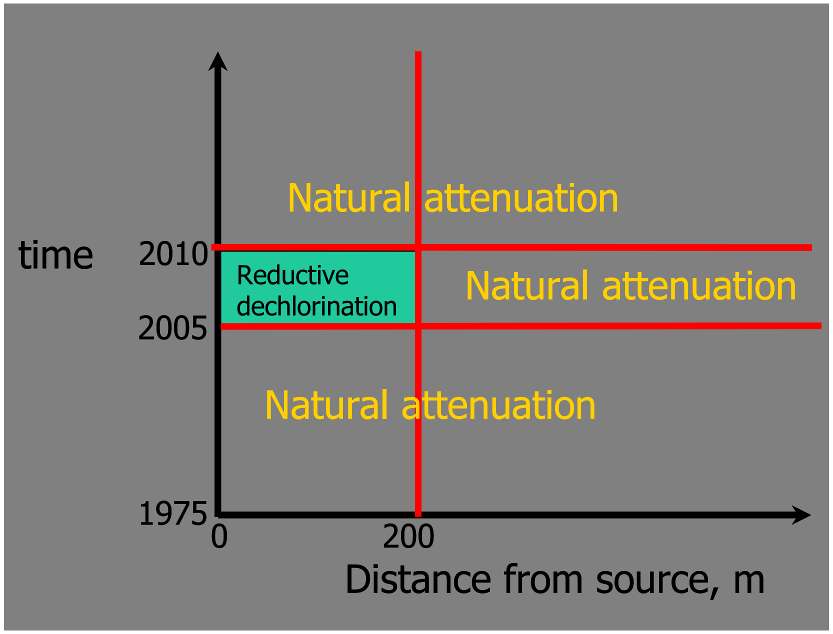
- DNAPL source has $\Gamma=2.0$, $C_0=2$ mg/l; water flow through source zone is 600 $m^3$ per year
- The TCA is assumed to undergo reductive dechlorination in the plume to 1,1-DCA with a first order rate of 0.8/yr (very low).
- 1,1-DCA degrades to chloroethane with a first order rate of 0.2/yr (very low)

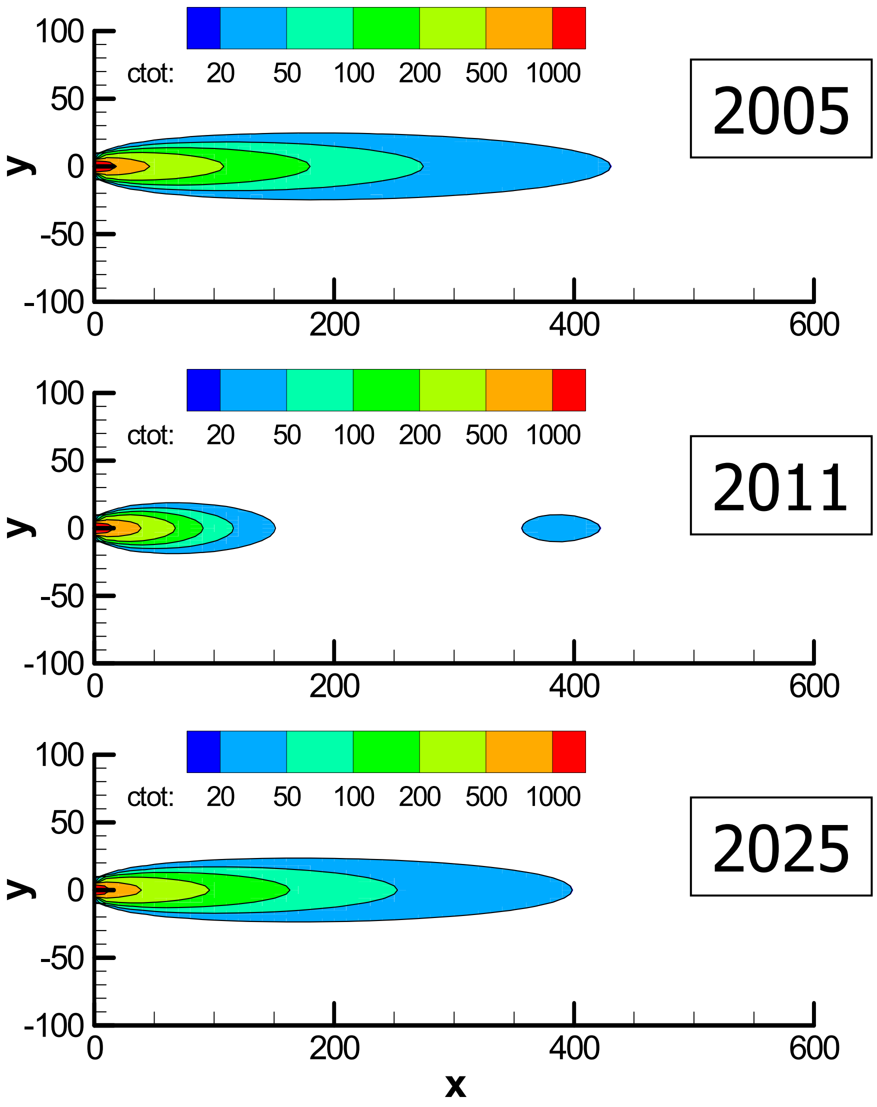




# REMChlor simulation of plume remediation

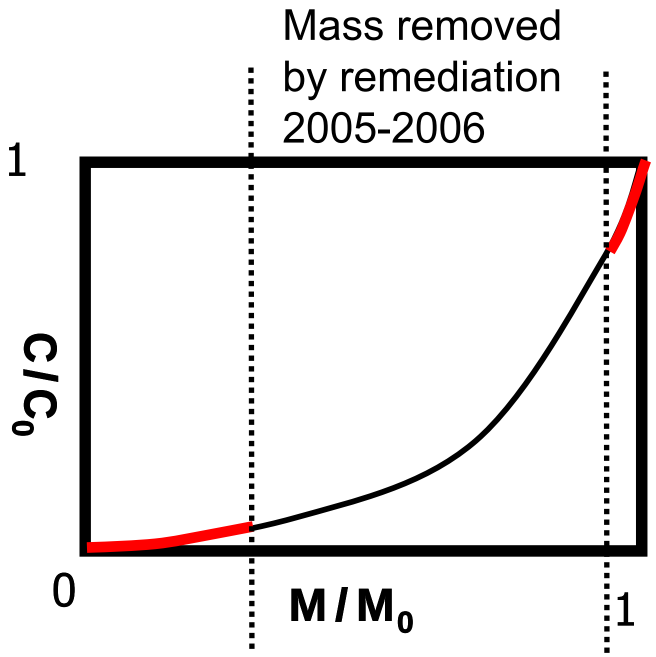
Enhance reductive dechlorination in the plume from 0-200 m, during the period of 2005 to 2010

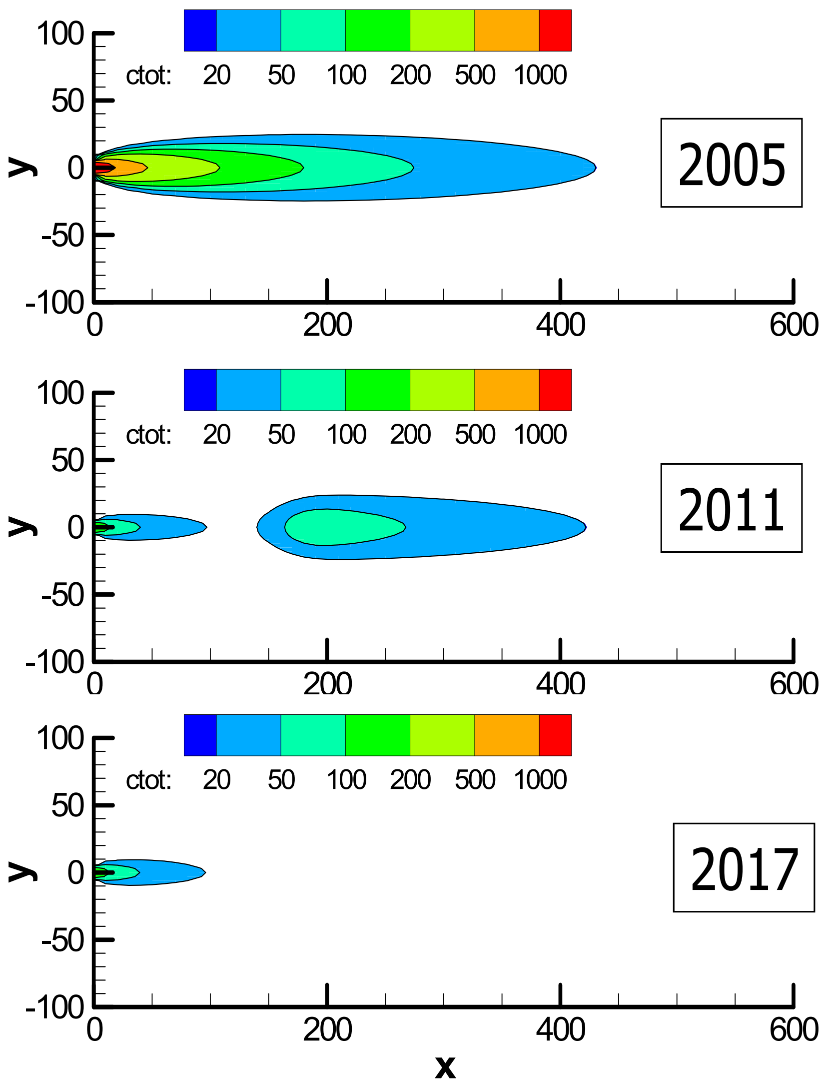




# REMChlor simulation of source remediation

Remove 70% of source mass between 2005 and 2006


Mass removed by remediation 2005-2006

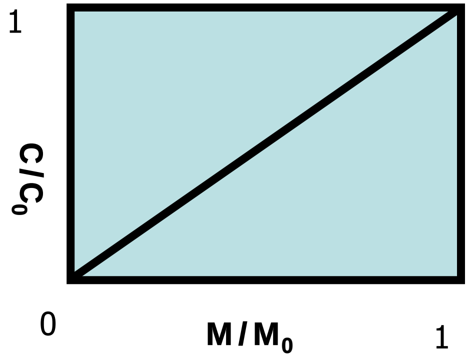


# More Complex Example Model Application

- Difficult case where natural attenuation will not work
- Long-lived PCE source, high discharge to groundwater
- Low rates of PCE-TCE-DCE-VC decay
- Plume is defined by 1 ppb

# Hypothetical 1620 kg Release of PCE in 1975

- DNAPL source has $\Gamma$=1.0, $C_0$=100 mg/l; water flow through source zone is 300 $m^3$ per year
- Assume reductive dechlorination from PCE→TCE →DCE →VC
- Assume that only ½ of DCE is converted to vinyl chloride (VC) by reductive dechlorination, the other ½ is destroyed
- Ground water pore velocity is 30 m/yr, R=2, decay rates are low: PCE, 0.4/yr; TCE, 0.15/yr; DCE, 0.1/yr; VC, 0.2/yr



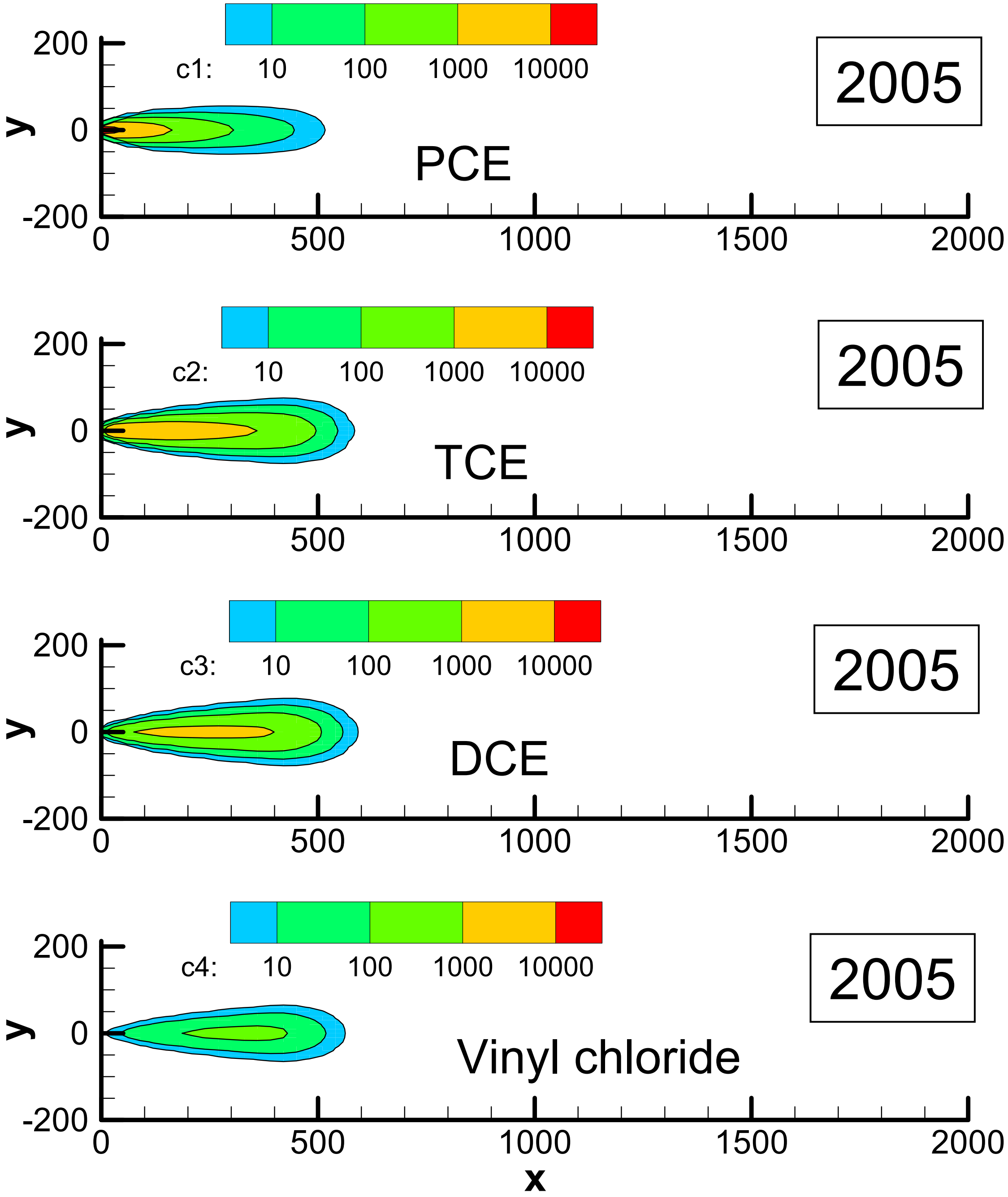
Initial mass discharge to plume is 30 kg/year

Plumes are contoured down to 1 ug/l

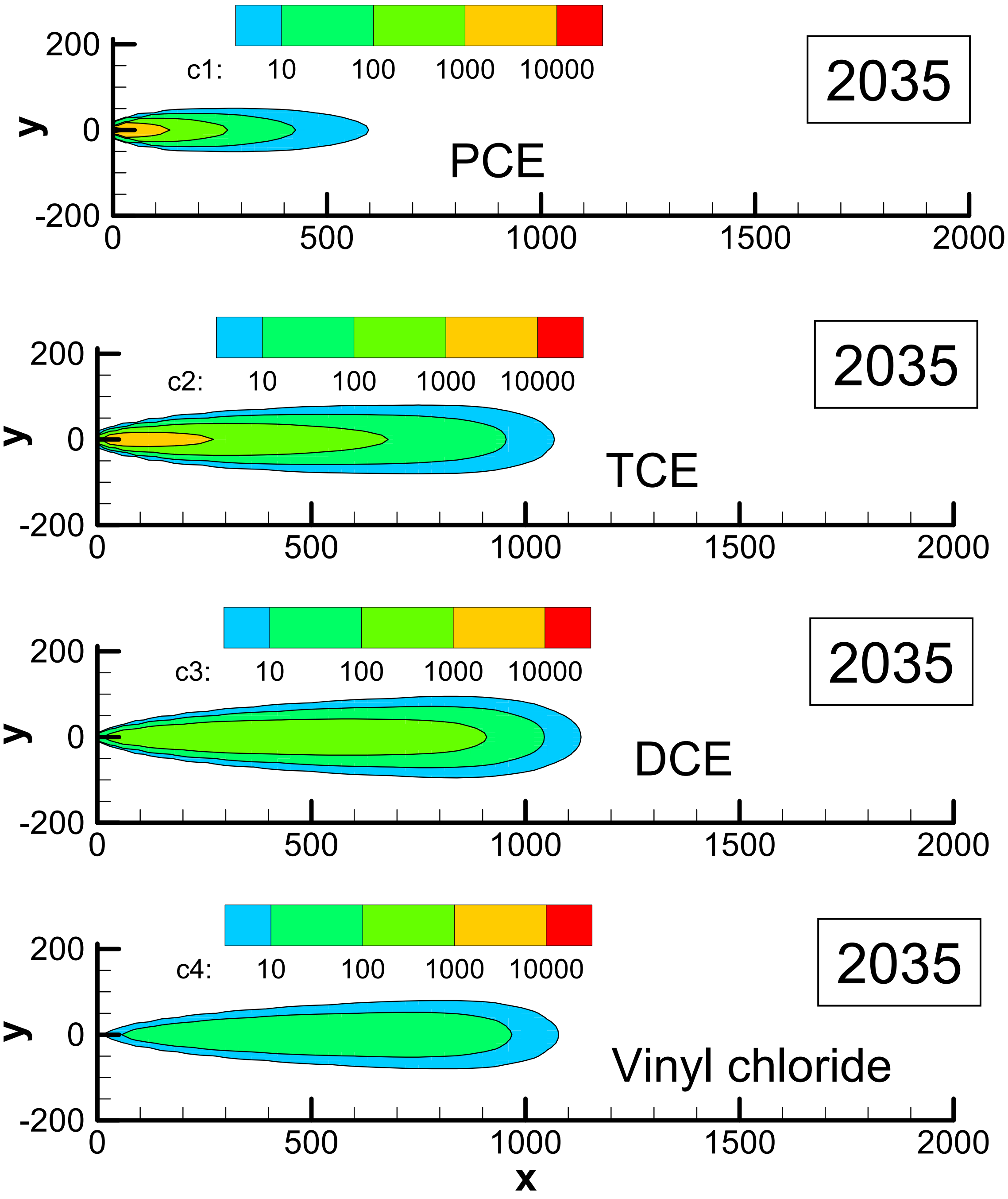
Hypothetical release 1620 kg PCE in 1975.

Plume reactions PCE →TCE →DCE →VC

57% of the PCE DNAPL remains in the source zone In 2005

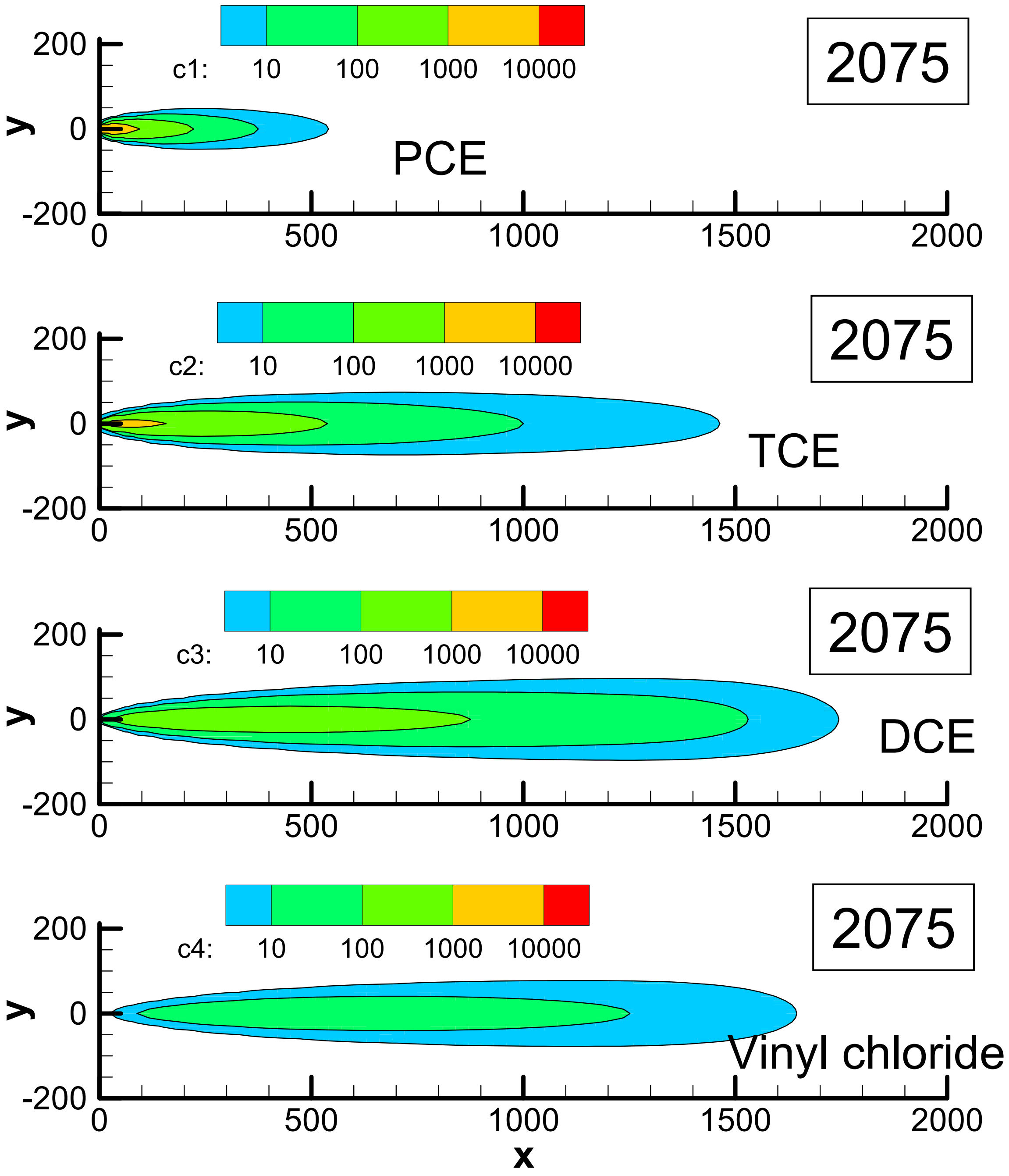


Distribution of PCE, TCE, DCE, and VC 60 years after spill, with no remediation of the source or plume



33% of the PCE DNAPL remains in the source zone

Distribution of PCE,TCE, DCE, and VC 100 years after spill, with no remediation
of the source or plume



15% of the PCE DNAPL remains in the source zone

# Cancer Risk From Drinking Water at a Given Location Over Time (REMChlor also includes the inhalation risk)

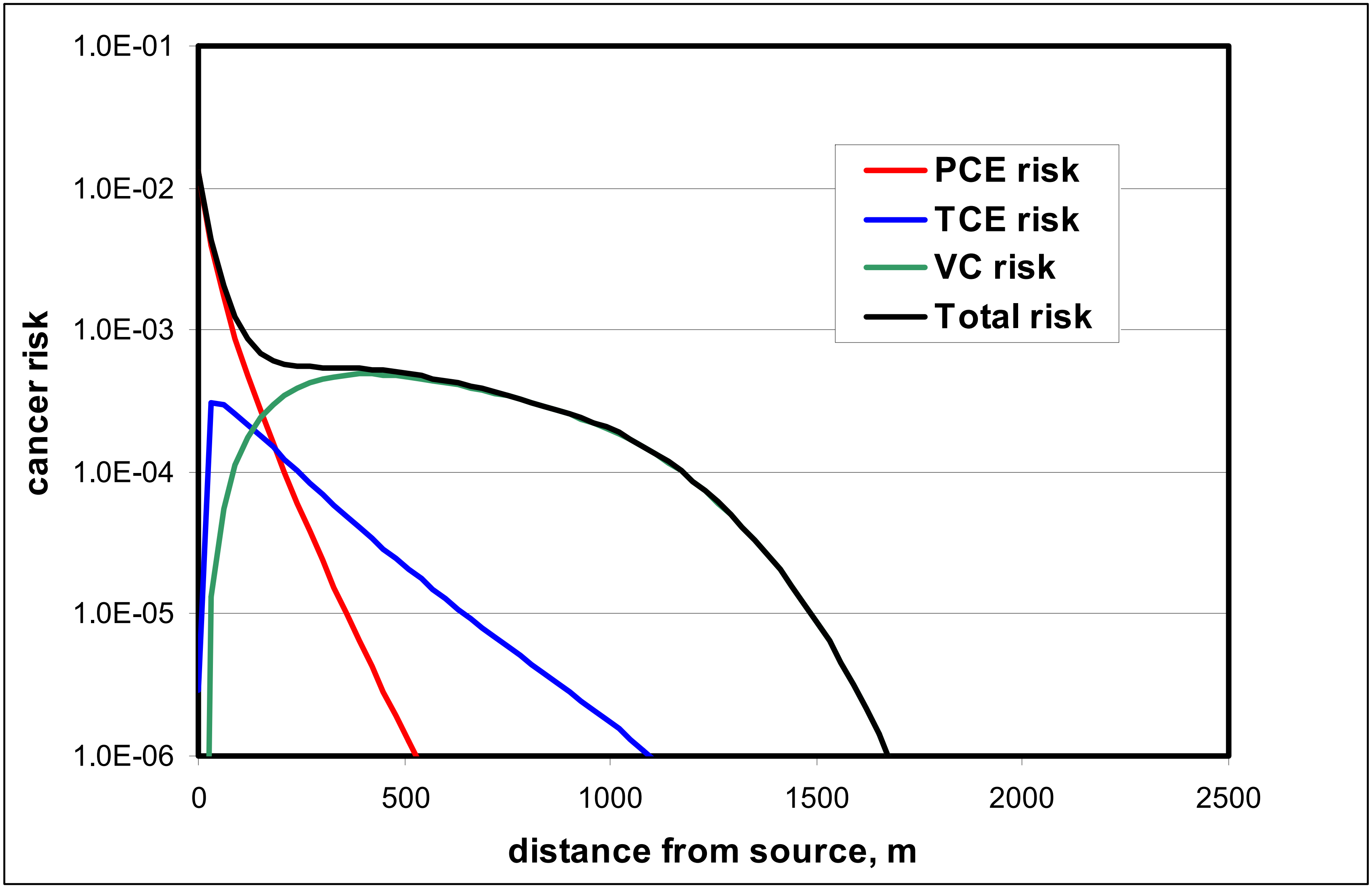
Compute chronic daily intake (CDI) of each carcinogen:

$$CDI_i = \frac{q_w}{mT_{life}} \int_{\max(0,t-T_{ex})}^{t} C_w^i(t)\,dt$$

Where $q_w$ is the daily water intake (2 l/d), m is the body mass (70 kg), $T_{life}$ is the 70 year lifetime averaging period, t is the Time, $T_{ex}$ is the length of the exposure period (30 years), and $C_w$ is the concentration of the carcinogen in the well. The CDI is essentially the cumulative dose of carcinogen. With a cancer risk slope factor, SF, the cancer risk is then:

$$Risk_i = CDI_i \; x \, SF_i \qquad Risk_T = \sum Risk_i$$

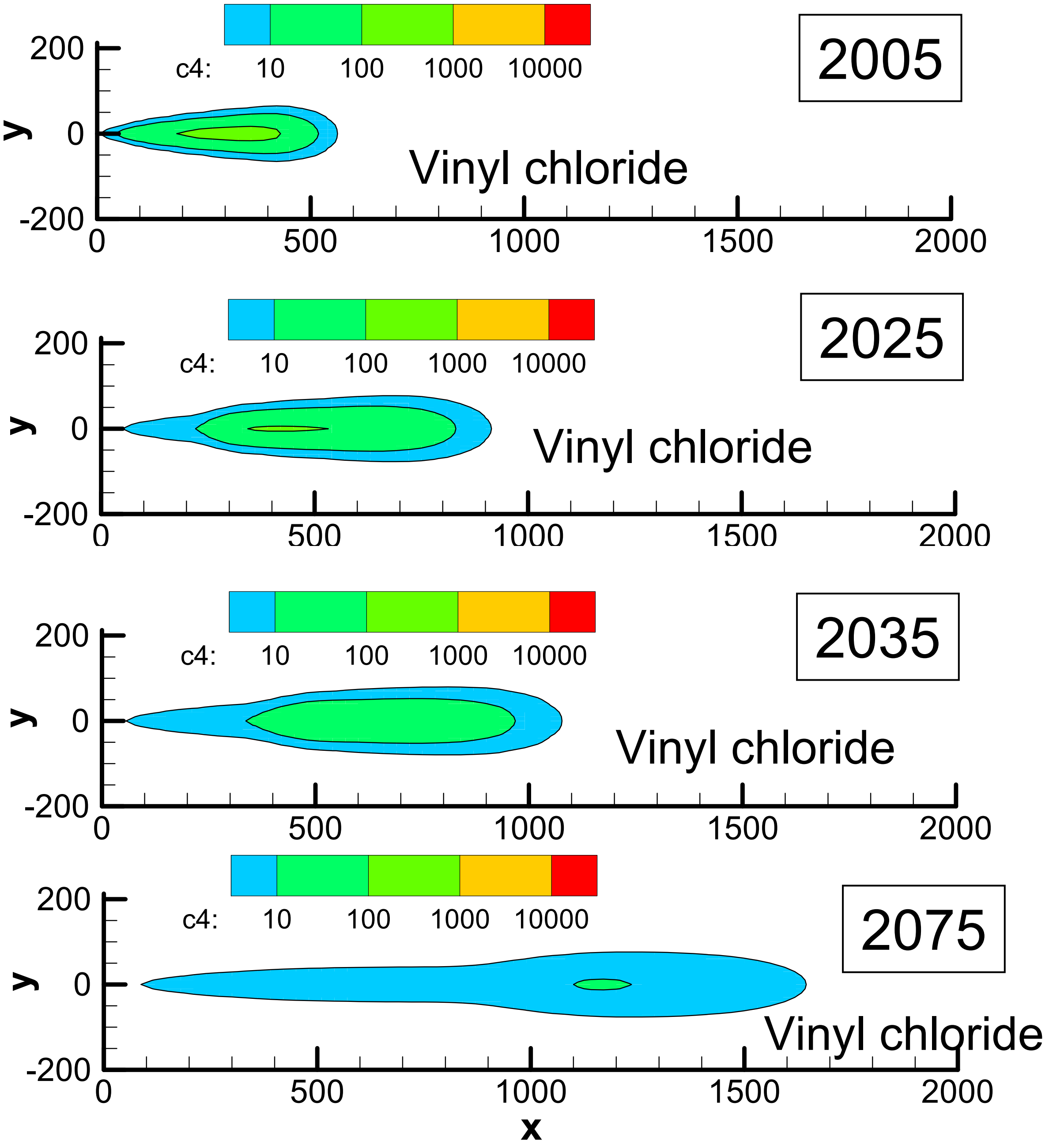
# Lifetime cancer risks in 2075 (exposure from 2045-2075)



# Try 2 Different Remediation Schemes, Focusing on Managing the Vinyl Chloride Plume

- 1) Try DNAPL source remediation alone: remove 90% of PCE DNAPL in 2005
- 2) Also include plume remediation: set up an enhanced reductive dechlorination zone from 0 to 400 meters, and an enhance aerobic degradation zone from 400 to 700 meters, in years 2005 to 2025

Source Remediation: Remove 90% of the remaining PCE DNAPL in 2005

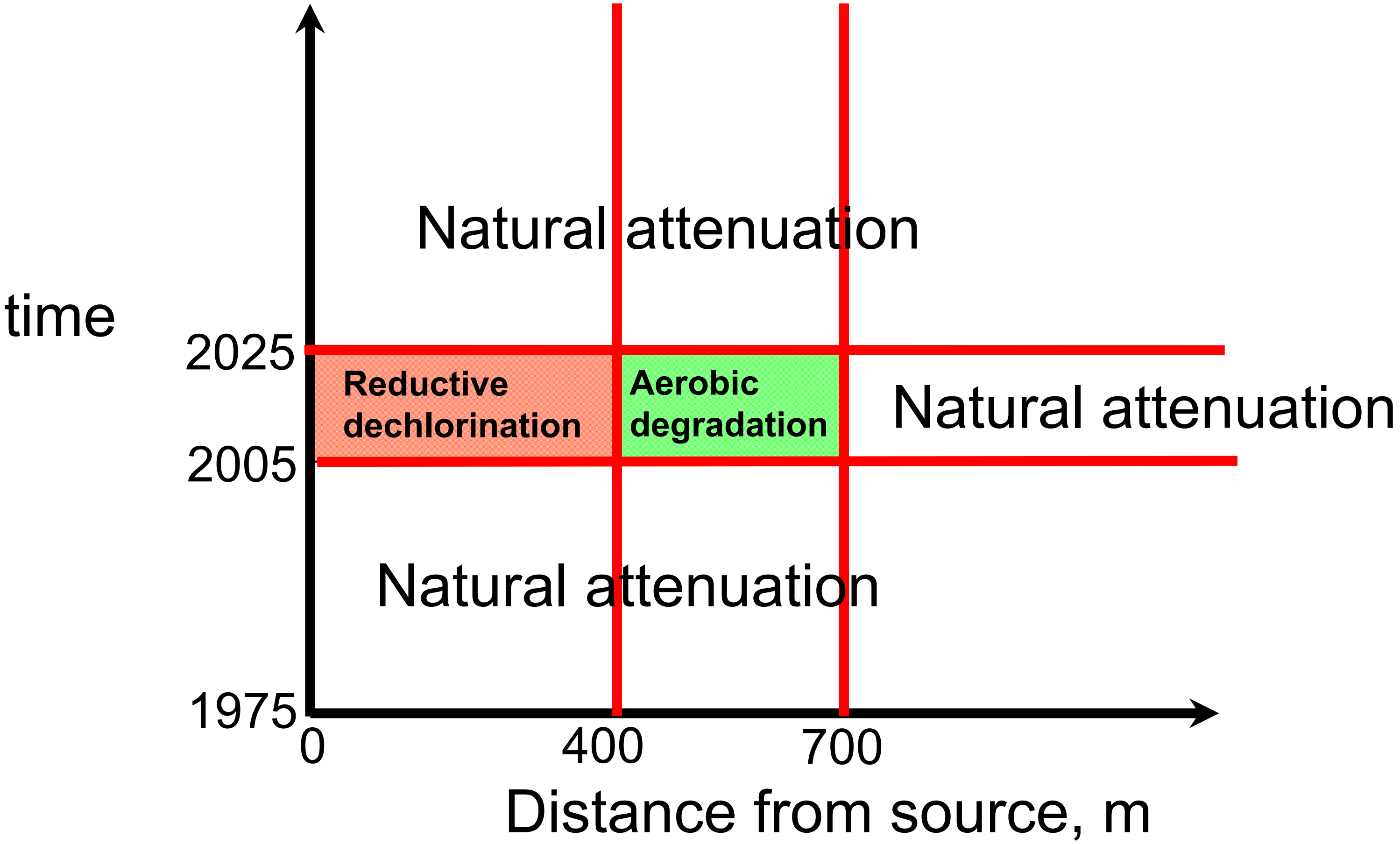


Only the vinyl chloride plume is shown

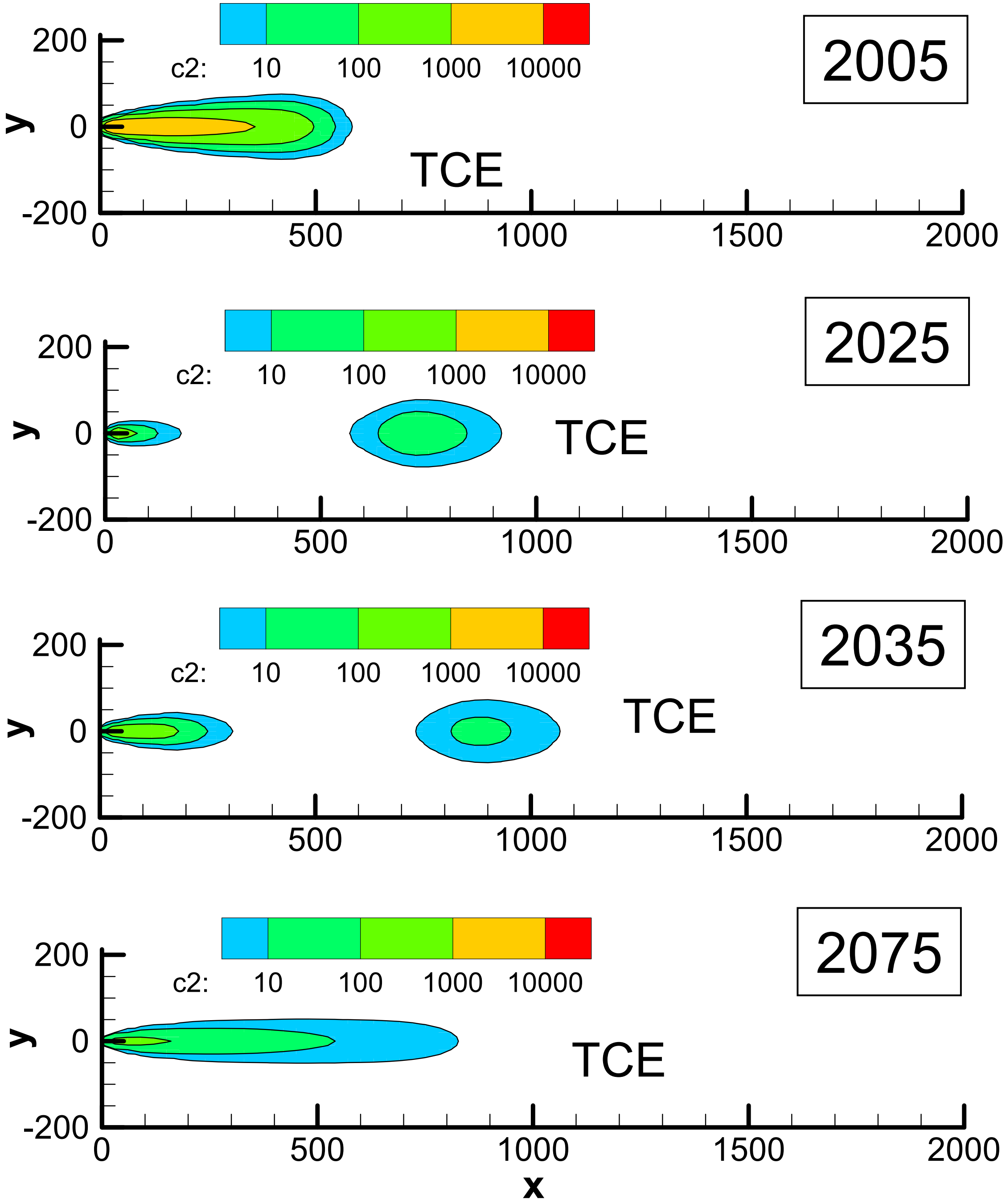
# Add Plume Remediation

- A) Set up an enhanced reductive dechlorination zone 0-400 meters from 2005 to 2025
- Increase PCE decay rate from 0.4 to 1.4/yr, TCE from 0.15 to 1.5/yr, and DCE from 0.1 to 0.2/yr. No change in VC decay
- B) Set up an enhanced aerobic degradation zone from 400-700 meters, from 2005 to 2025
- Increase DCE decay rate from 0.1 to 3.5/yr, and VC decay rate from 0.2 to 3.6/yr. PCE and TCE decay rates remain at background levels

# Plume Remediation

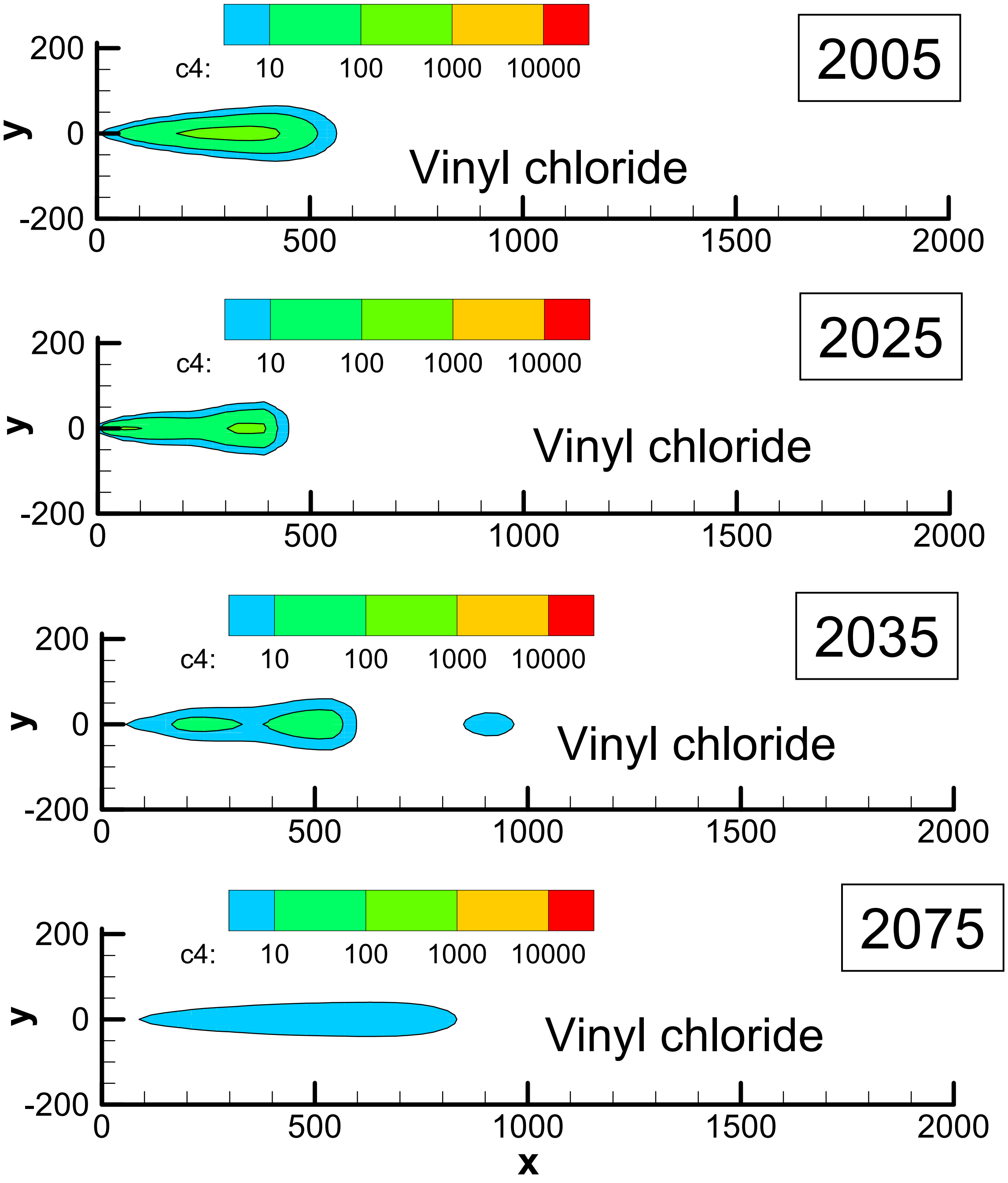


Source and plume remediation



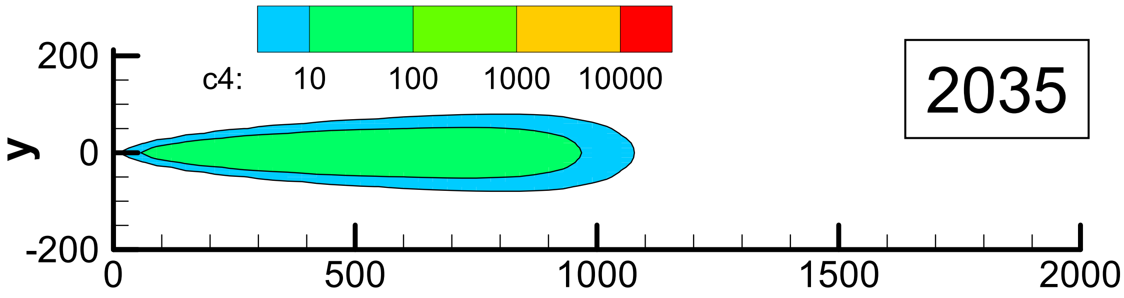
Only the TCE plume is shown here

Source and plume remediation

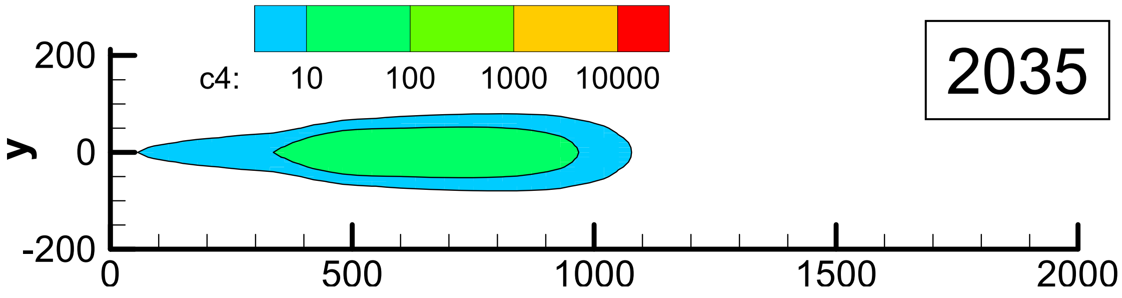


Only the vinyl chloride plume is shown

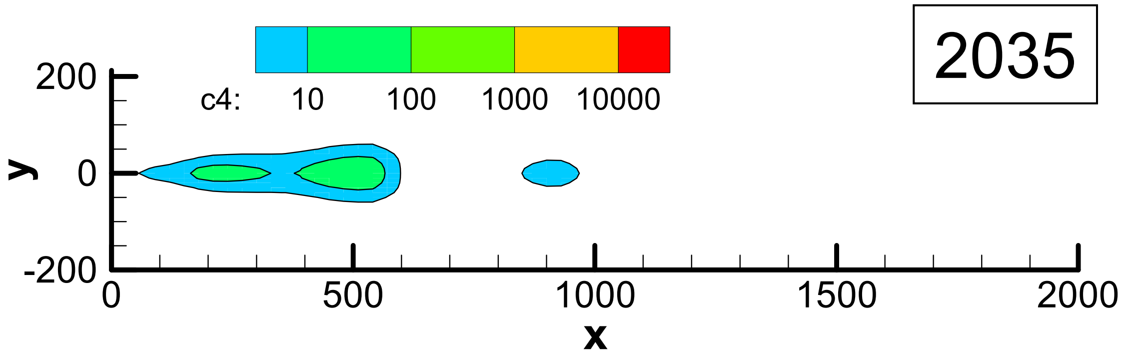
# Compare Remediation Effects on Vinyl Chloride Plume



No remediation

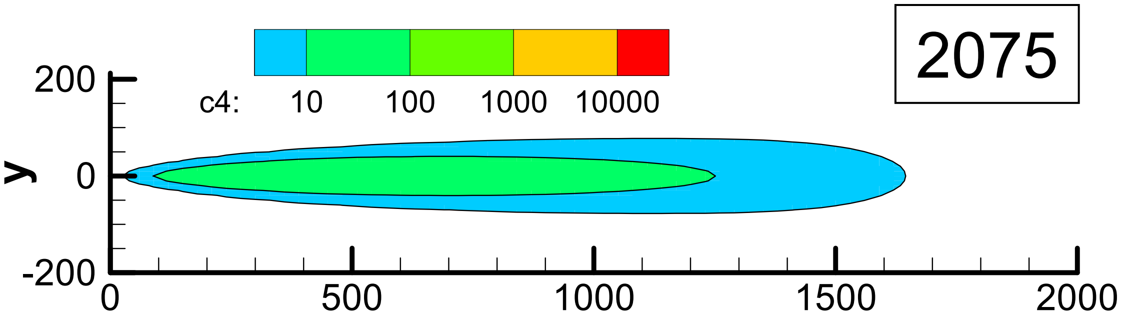


DNAPL source remediation

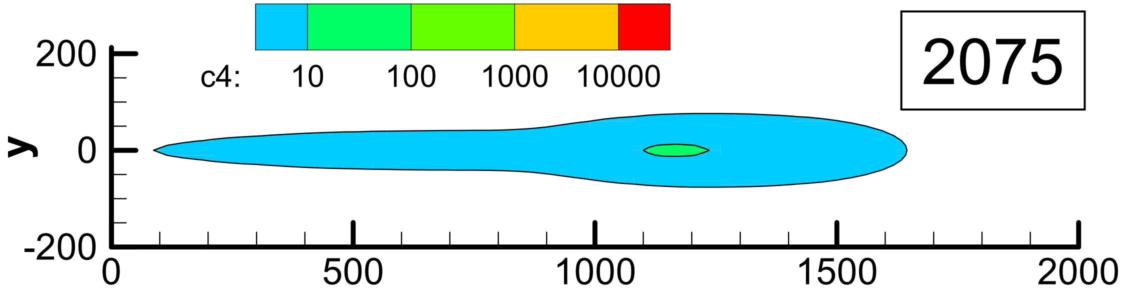


Source and plume remediation

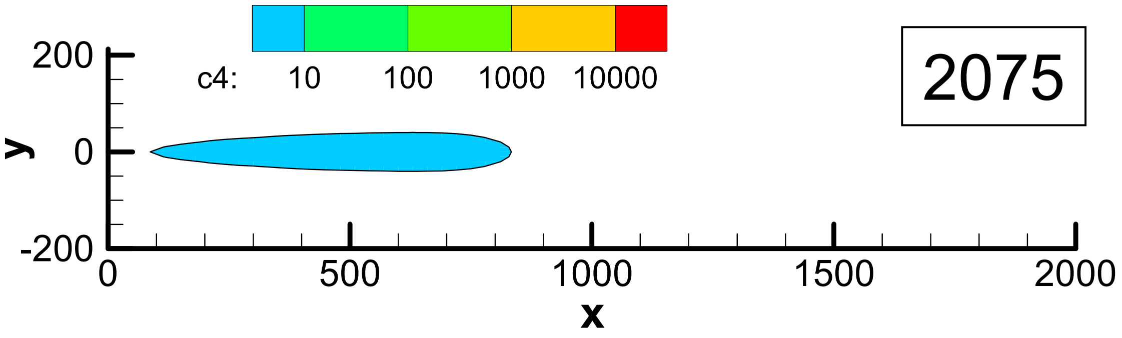
# Compare Remediation Effects on Vinyl Chloride Plume



No remediation

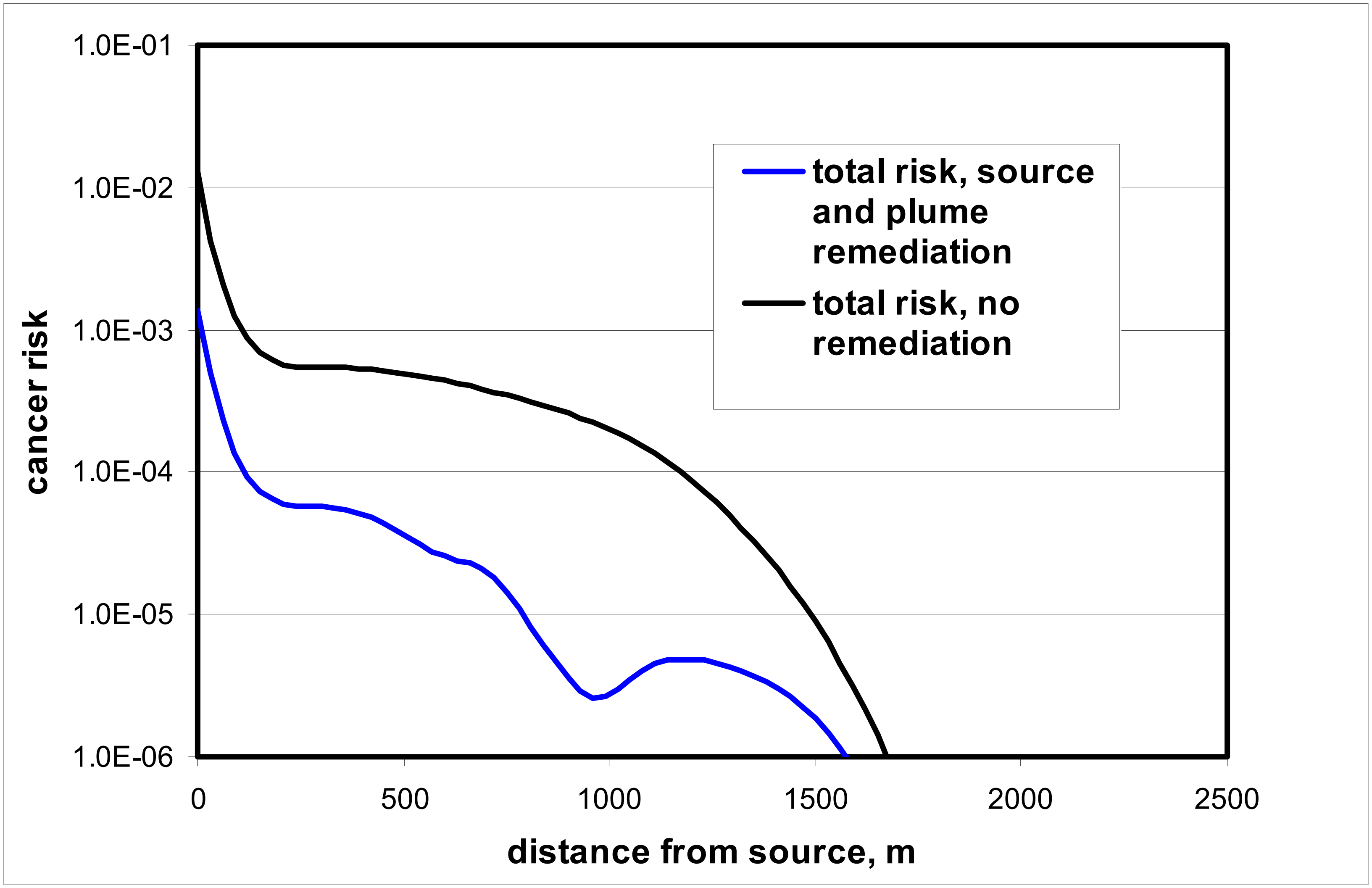


DNAPL source remediation



Source and plume remediation

# Lifetime Cancer Risks in 2075 (exposure from 2045-2075)



# Observations on PCE Example

- This case was very difficult because of a) the persistent DNAPL source, b) the generation of hazardous daughter products in the plume, and c) the high source concentrations compared to MCLs
- Source remediation alone may not be capable of reducing plume extent, although it greatly reduces plume mass
- A combination of source and plume remediation appears to be capable of reducing the plume extent and longevity

# Alternative Source Models

## Numerical Source Remediation Models

- ► Advanced 3-D multiphase flow models such as UTCHEM, T2VOC, STOMP, NUFT
- ► Models include advanced process simulation capability (surfactants, thermal processes, gravity effects)
- ► Can handle complex geological heterogeneity
- ► Can include the DNAPL “architecture”, but how well is this really known?

# Lagrangian Models of Source Zone

(Enfield et al., 2005; Wood et al., 2005; Jawitz et al., 2005; Basu et al., 2007)

- Based on the concept of streamtubes that pass through the source zone
- Streamtube velocities (travel times) are characterized by a log-normal distribution
- Where NAPL is present, it is distributed in the streamtubes, and can be correlated to travel time
- Mass discharge from individual streamtubes are added to get overall discharge
- NAPL removal from each streamtube depends on water velocity, and initial NAPL mass in streamtube

# Comments on Lagrangian Models

- Ideally suited for flushing processes with a flow field that does not change with time.
- Much more practical to parameterize than full 3-D numerical models
- They do not consider buoyancy effects or diffusion into low permeability zones
- They do not model thermal conduction or multiple domain heat and mass transfer processes

# Other Useful Tools for Flux-Based Remedial Design

- Mass Flux Toolkit (Farhat, et al., 2006) http://www.gsi-net.com/Software/massfluxtoolkit.asp)
- SourceDK (Farhat, et al., 2004) http://www.gsi-net.com/Software/SourceDK.asp
- Natural Attenuation Software (NAS), (Chapelle et al., 2003 ) http://www.nas.cee.vt.edu/index.php