Arthur T. Ippen Lecture
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Dealing with complex transport problems in groundwater: when one is expected to provide exact solutions with little to none information

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“Hydraulic engineering was at the forefront of science for centuries. The end of the 20th century marked a **change of perception** in our society, especially in developed countries, with a focus on **environmental sustainability and management**.” Hubert CHANSON, 13th Ippen Award Lecture, 2003

Engineers are **problem solvers**. We are expected to come up with solutions. For this purpose we have or ask for information.

We ALWAYS claim we need more information, but here I want to highlight some significant differences between surface and subsurface hydrology

First,

Surface hydrologists consider a nice water cycle where they include runoff, evapotranspiration and something called losses

We hydrogeologists have a hard time trying to tell students that you do not lose these losses, but rather they are our input and we call them AQUIFER RECHARGE (eventually you can drink it!)

Second,

You do see things!

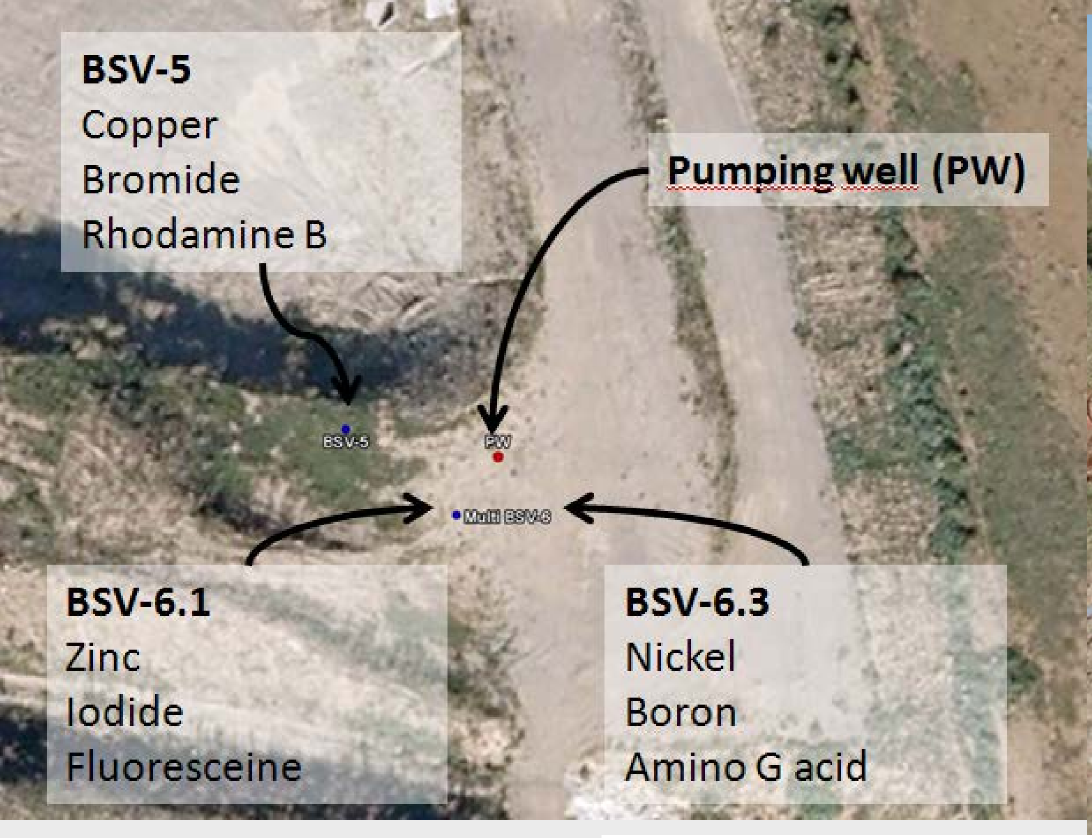
… and then act accordingly

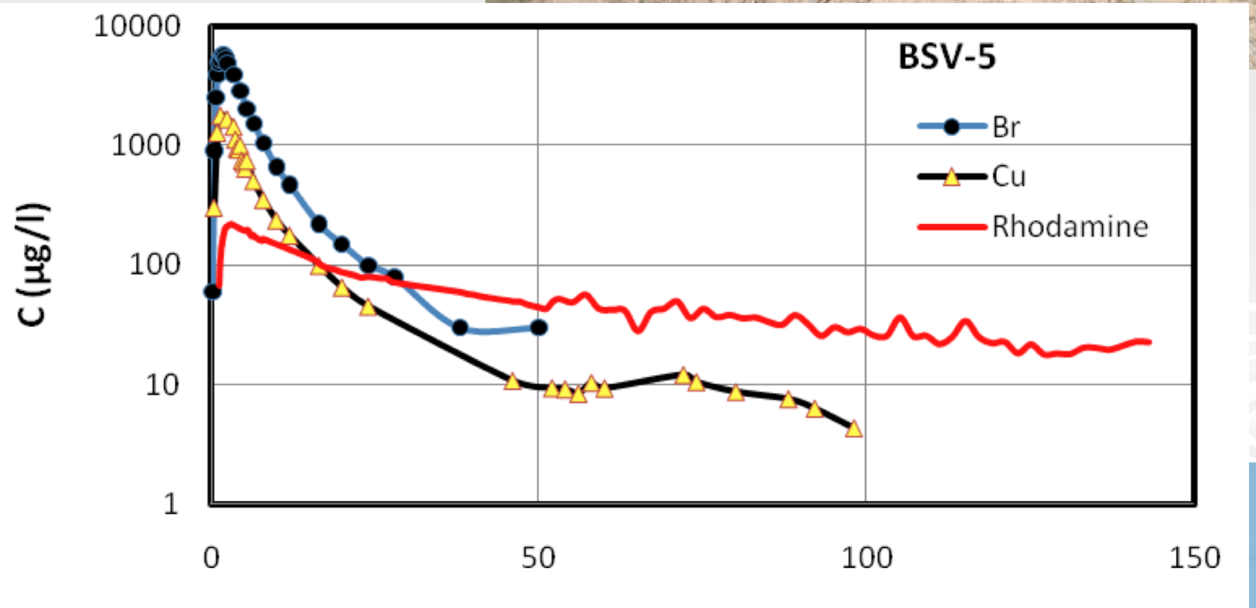
- We just do not see anything … so just guessing?

Third,

You can control things

A tracer test in a river. You place a dye and watch it as it moves. You can take pictures!


BSV-5
Copper
Bromide
Rhodamine B
Pumping well (PW)
BSV-5
PW
Multi BSV-6
BSV-6.1
Zinc
Iodide
Fluoresceine
BSV-6.3
Nickel
Boron
Amino G acid

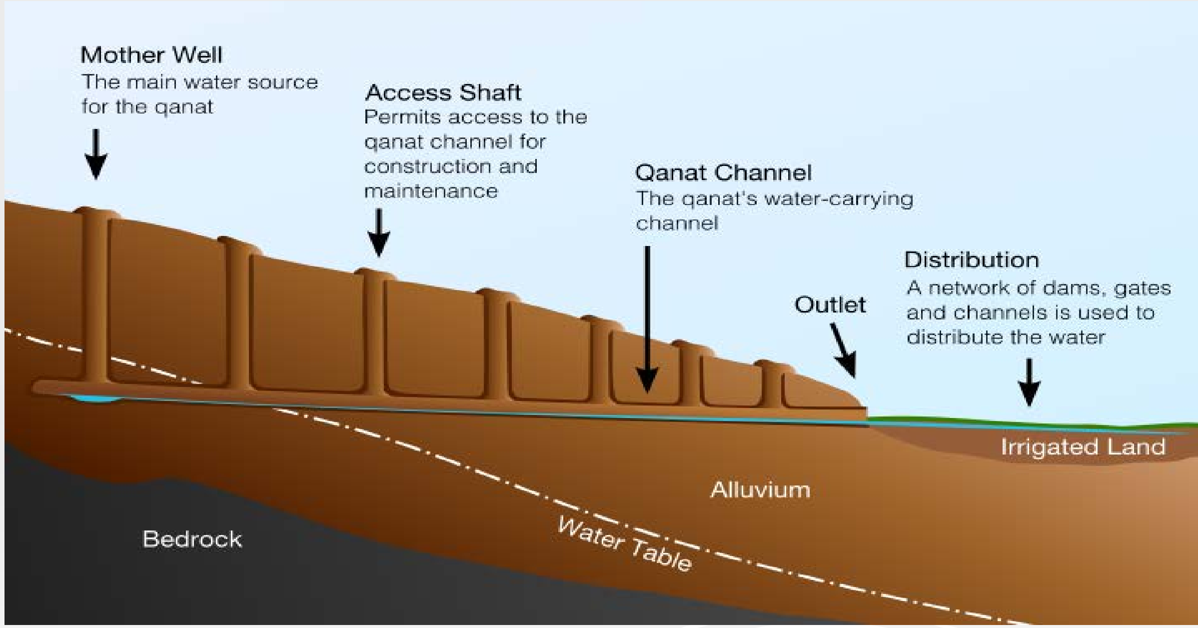

BSV-5
Br
Cu
Rhodamine
C (µg/l)
10000
1000
100
10
1
0
50
100
150

Hydraulic engineering for centuries: Is hydro-geo engineer the oldest job in history?

- The qanat technology is known to have developed in middle-East 3000 years ago.

- Iran has the oldest qanat (circa 1000 BC) and longest (71 km). From there extensions to several locations in middle-east

- Also, a qanat-like system called the Turpan Water System originated in China during the Han Dinasty (around 206 BC).



Change of perception: Hitting the news?

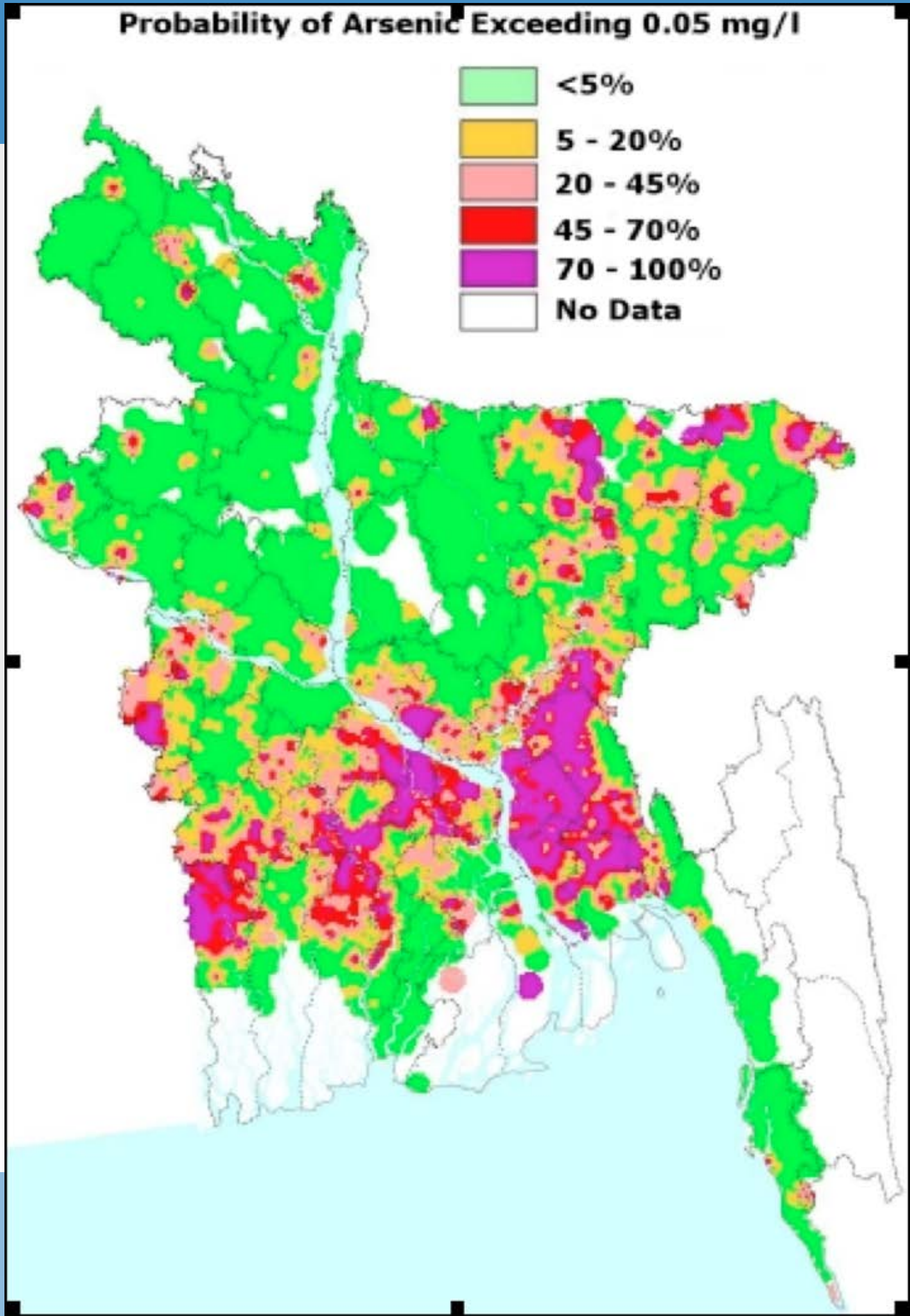
Media most likely would cover a new dam put in service than placing a pump in a borehole to get some water

But some problems in hydrogeology are really affecting millions of people:

-in terms of quantity: refugee camps

-in terms of quality: Bangladesh

- In Bangladesh nearly 90% of the population uses groundwater as its primary source of fresh water.
- **Up to 77 million people in Bangladesh have been exposed to toxic levels of arsenic (naturally occurring) from drinking water.**
- WHO said the exposure was "the largest mass poisoning of a population in history".
- Death counting is in the tens of thousands



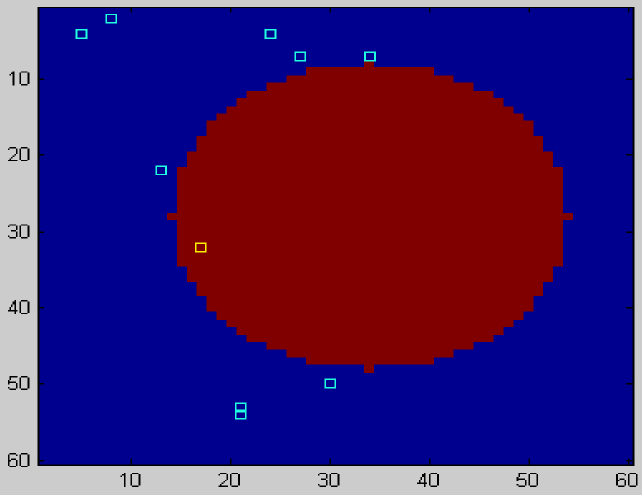
We DO face complex/difficult problems

- Early XXth Century: Flow in porous media/well hydraulics. Emphasis: QUANTITY
- Second part of the century: Geochemistry, transport of conservative solutes: Emphasis: QUALITY
- 80's on: Stochastic hydrogeology, modelling
- New stuff every decade: surface/subsurface interactions, coastal aquifer dynamics, geothermal, vadose zone infiltration,…
- **multispecies reactive transport**, CO2 sequestration, climate change & **alternative resources** related to integrated water management, **risk evaluation**, …

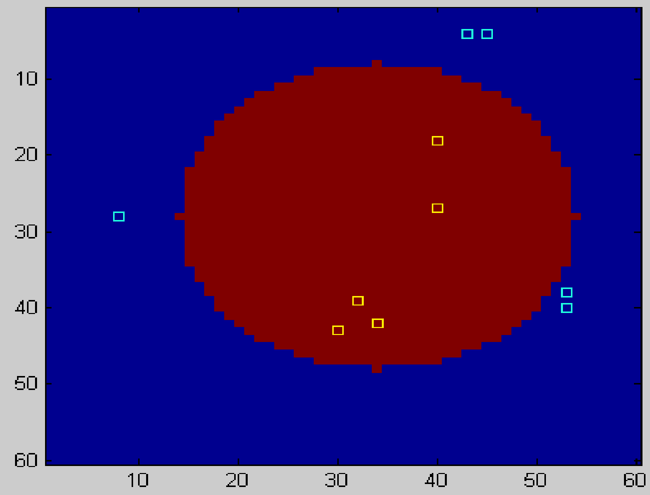
And WE CANNOT SEE ANYTHING! So, treating geological complexity

- We need kind of geological reconstruction

- Very similar to CSI
- With little (to no) information, reconstruct as best as possible the undersampled formation



Realization 1



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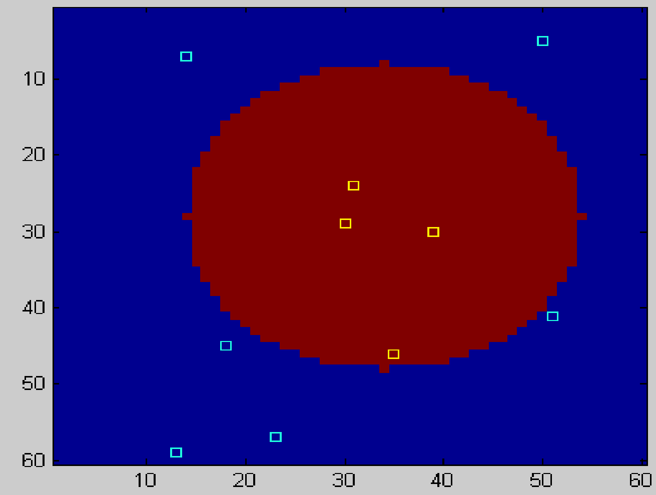

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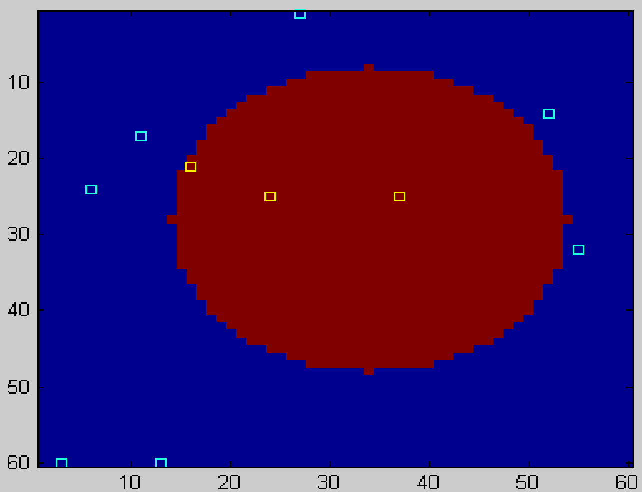

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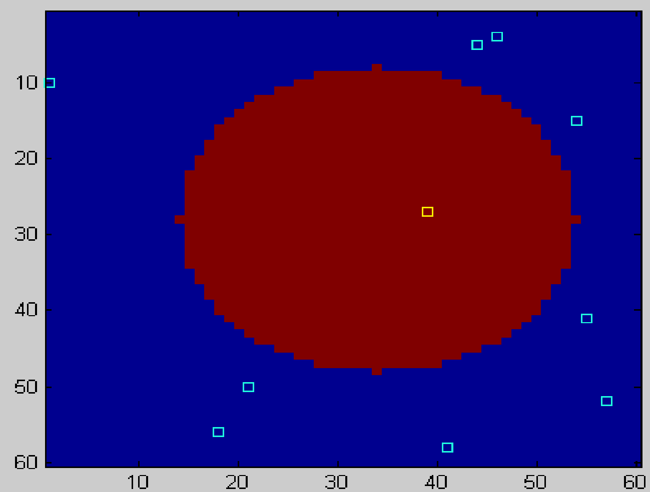
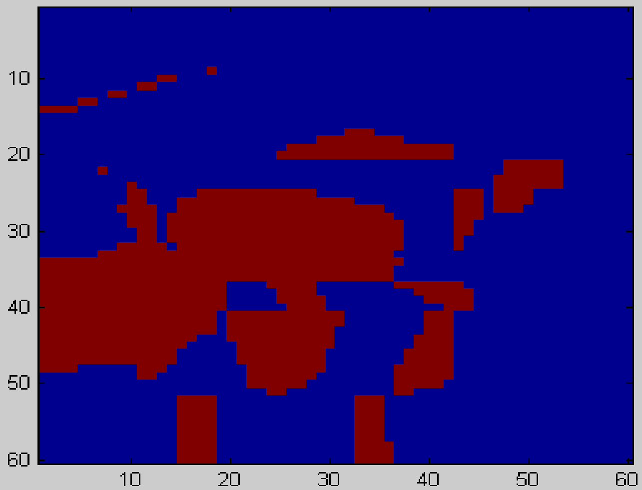
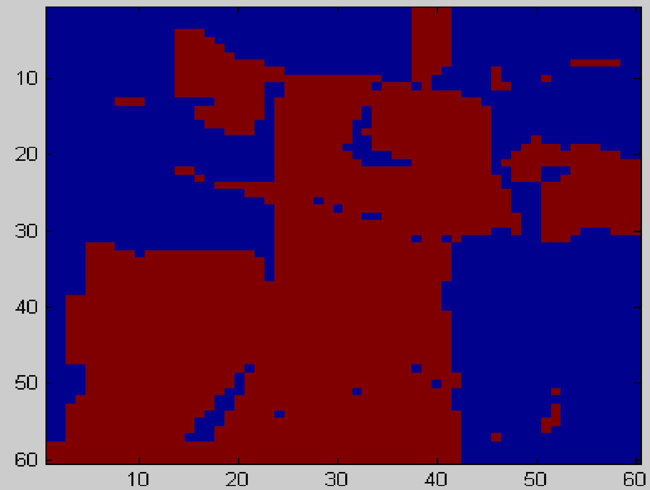


100

Original figure. Selection of 10 random samples



Realization 1



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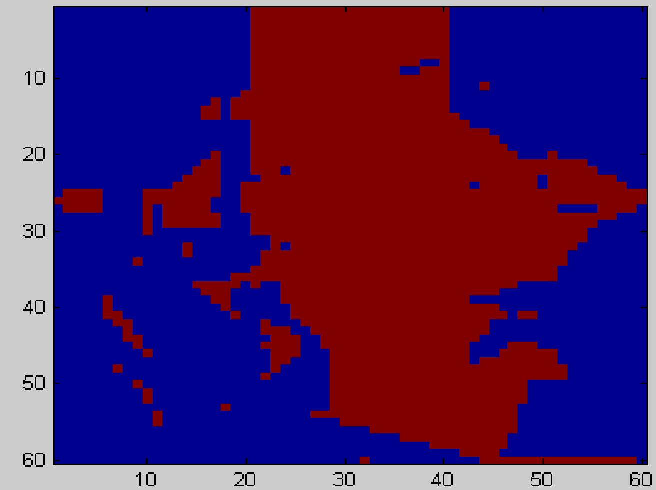

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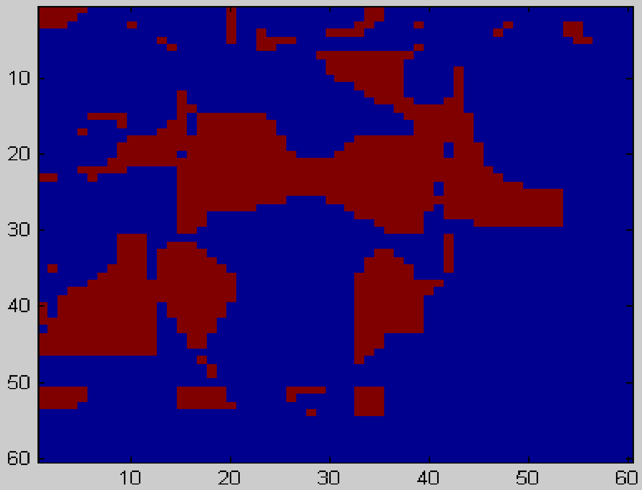

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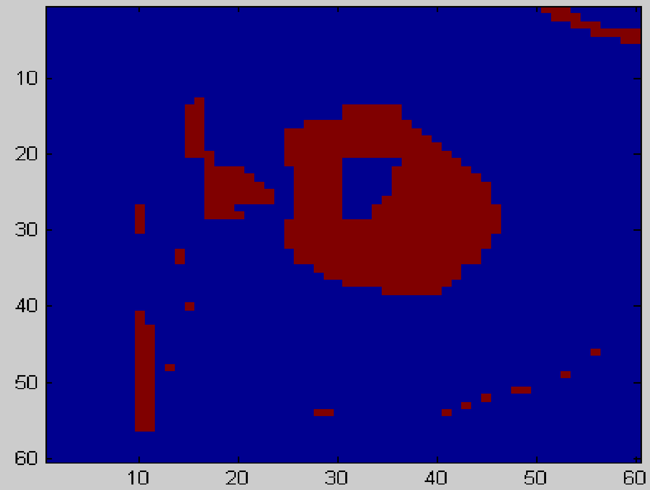

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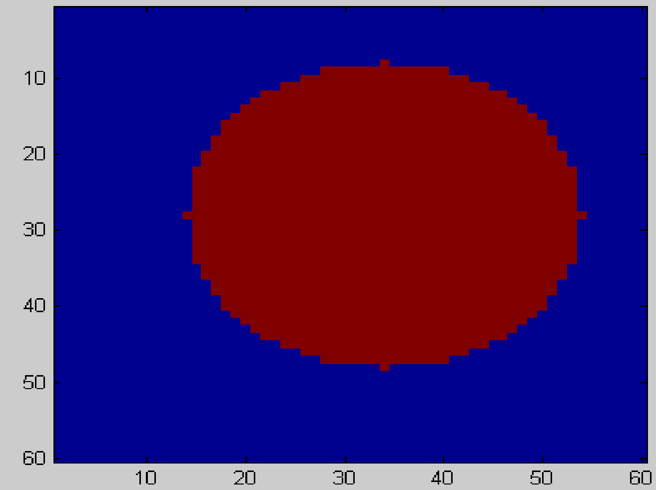
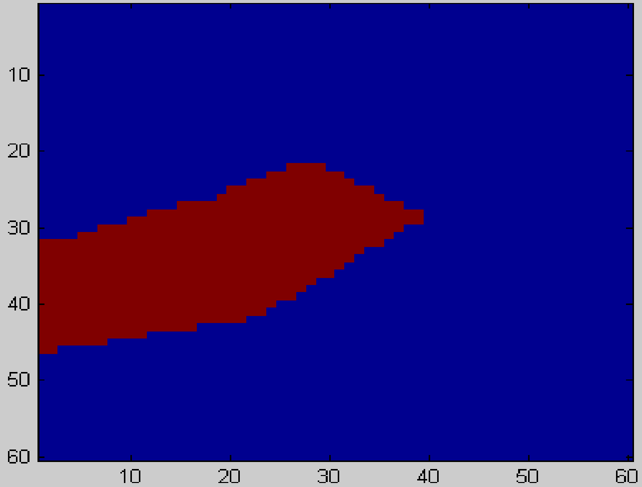
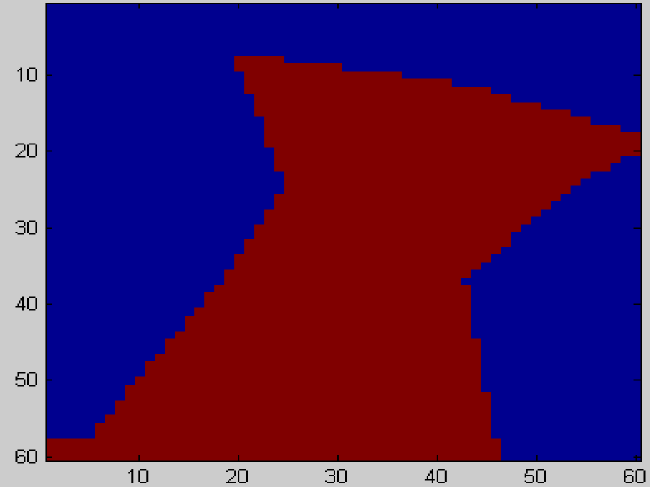


Original Figure

Classsical Kernel Regression



Realization 1



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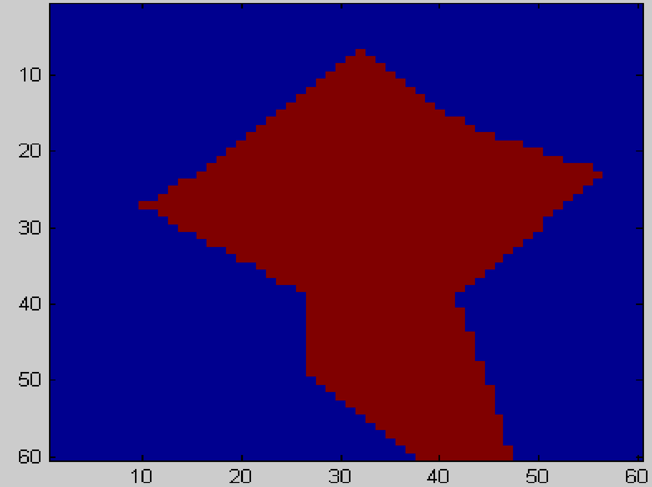

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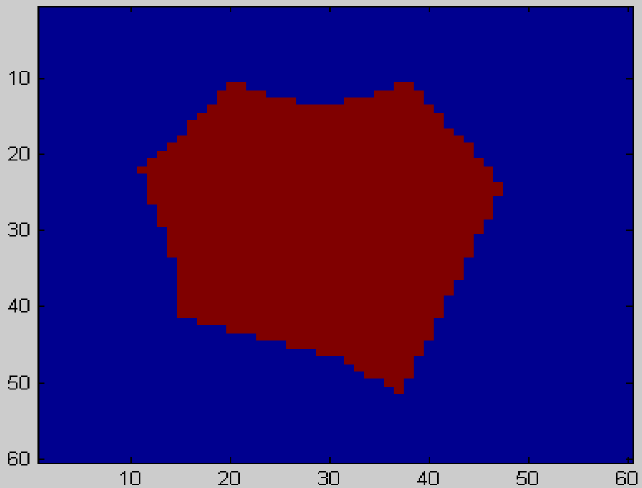

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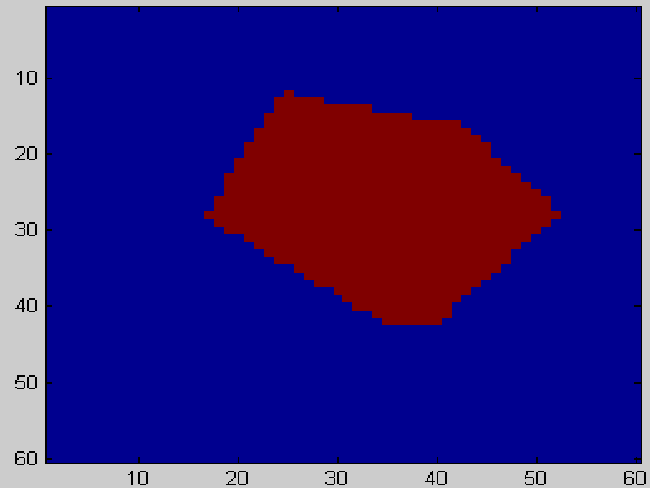

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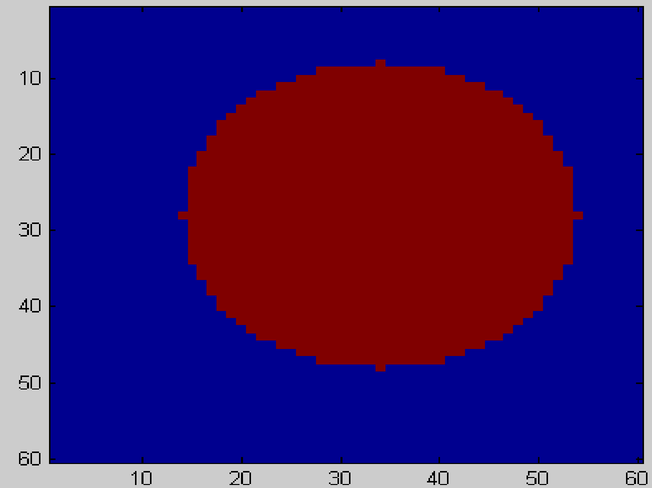
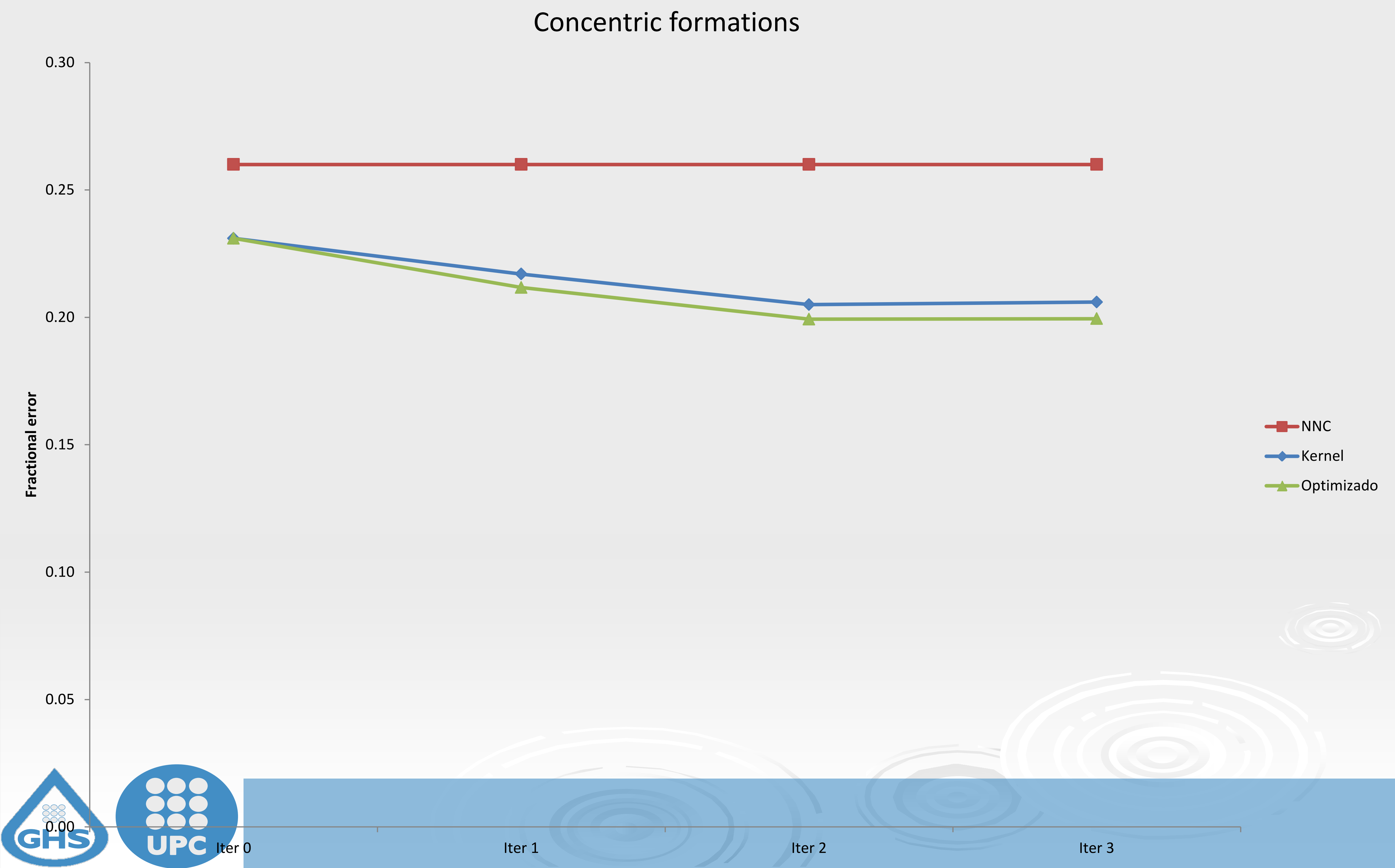


Original Figure

Steering Kernel Regression Second Order
(after 2 iterations)



Concentric formations
Fractional error
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Iter 0
Iter 1
Iter 2
Iter 3
NNC
Kernel
Optimizado
GHS
UPC

Complexity in processes adds to that in geology; e.g, multispecies reactive transport

- Goal: Providing “simple”, understandable solutions for evaluating the fate of reacting plumes (complex multispecies reactive transport problems).

- Is it really possible?

YES!!!!

The idea of pollution

Pollution starts at one point and moves. Along the movement several processes occur to change direction and to spread the problem so that the neighbours are ”not-happy”

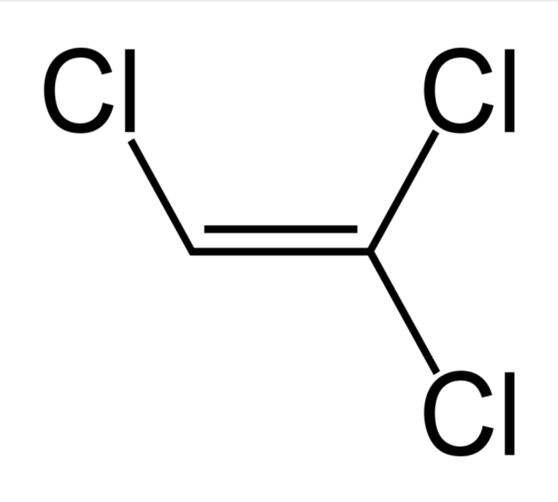
The idea of groundwater pollution

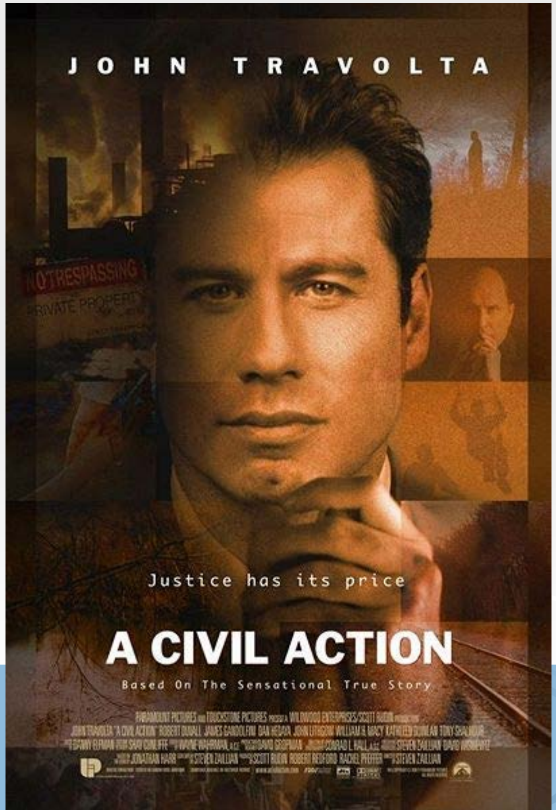
- You do not see anything until it is too late, PERFECT FOR LAW SUES
- Famous cases:

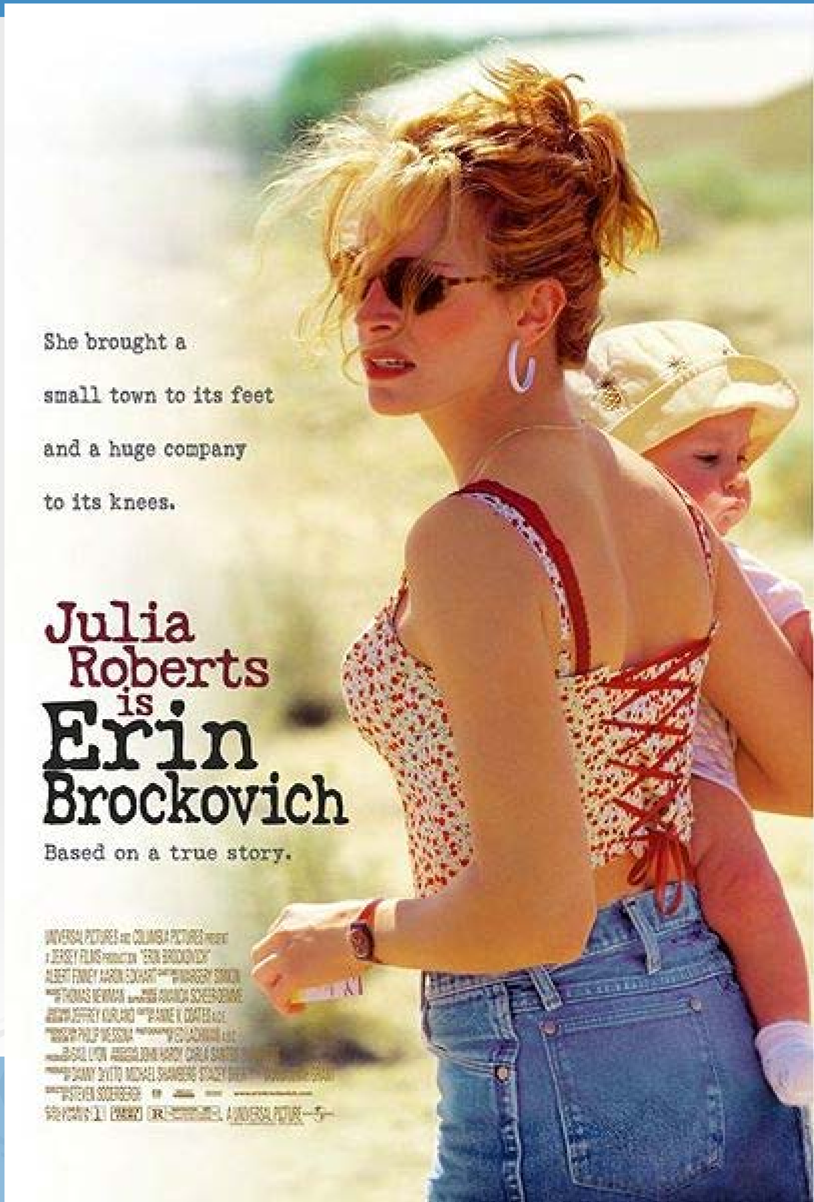
Hinkley, CA: Cr (VI)

Woburn, MA:

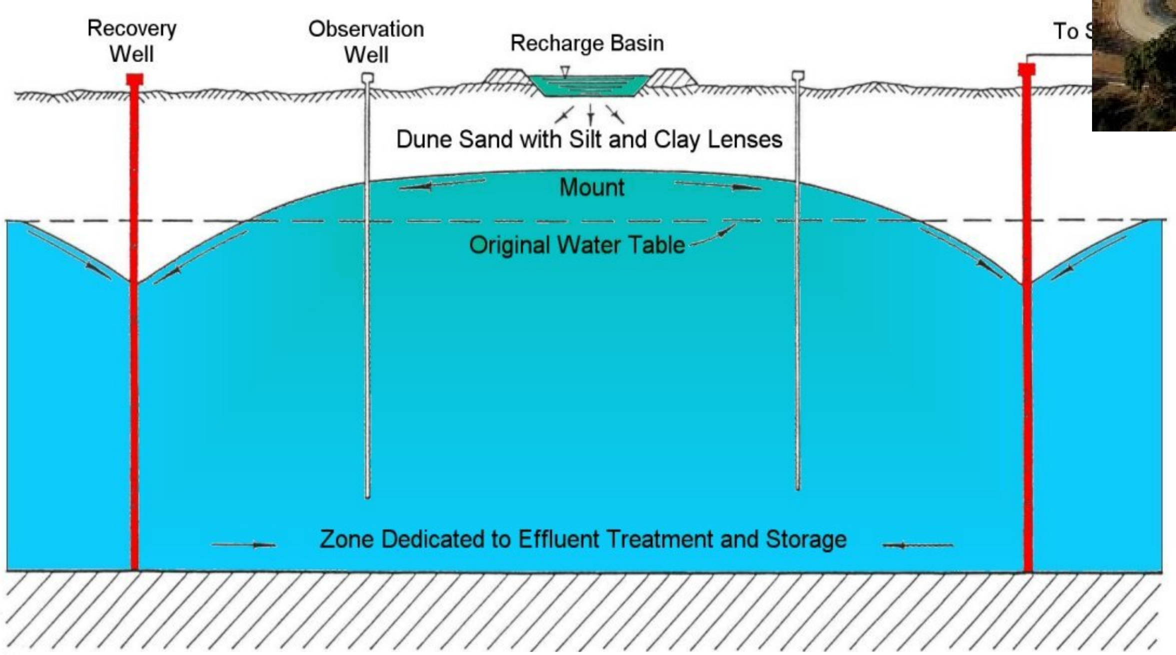
Trichloroethylene





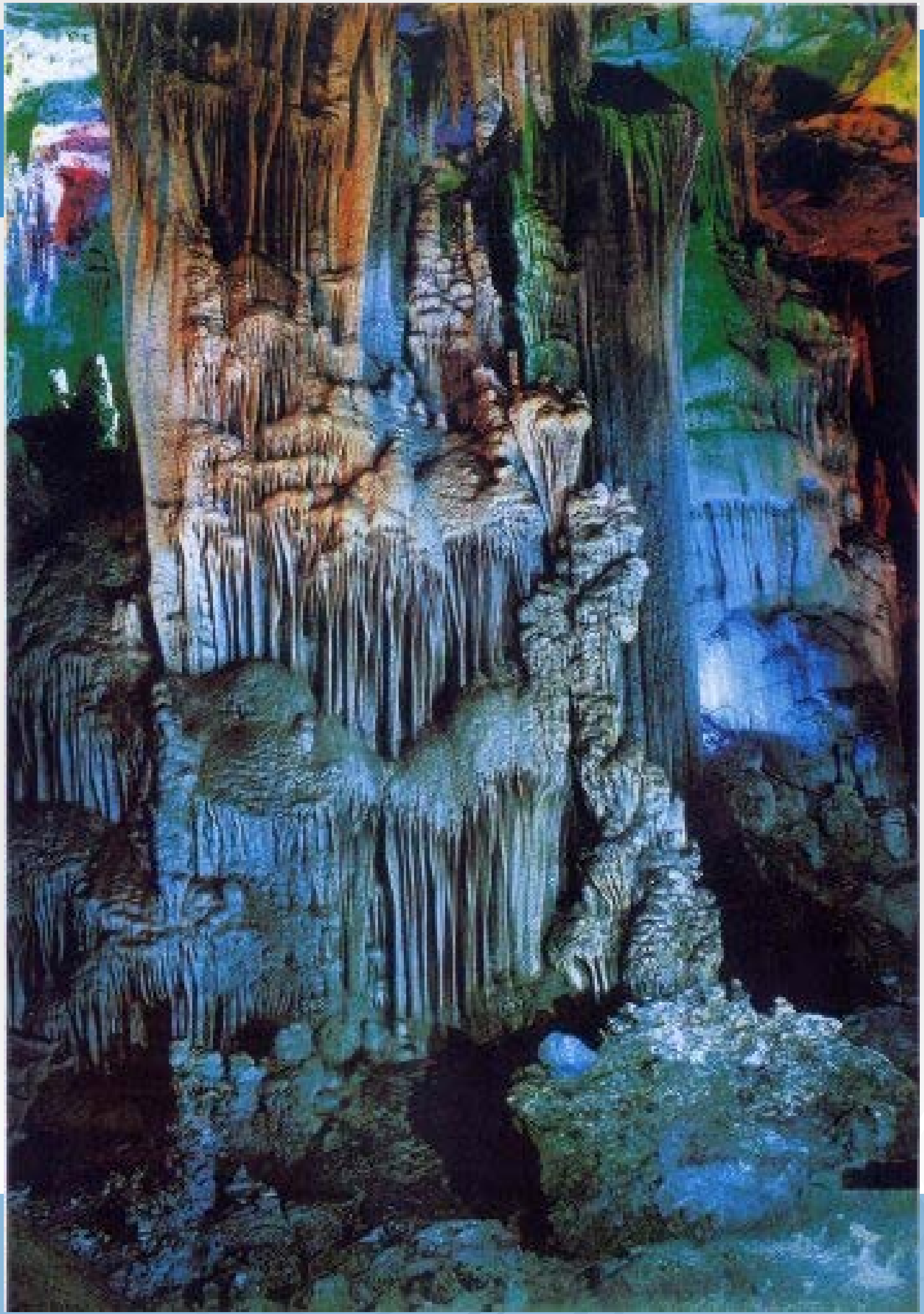


Fortunately not everything GW carries is a pollutant. Still GW solute transport can be relevant in other biogeochemical problems



ARTIFICIAL RECHARGE (different waters mix, and then react)

CAVE FORMATION (limestone dissolution and reprecipitation)



Multispecies Reactive Transport

Mixing of two (or more) waters in perfect geochemical equilibrium (regarding aqueous species, biological species and minerals) produces **local disequilibrium**. Reactions will then take place to re-equilibrate the system (acid/base, redox, precip./dissol., adsorption/desorption, biological growth)

Example not so rare: 19 chemical species and 13 reactions THIS MEANS SOLVING A SYSTEM OF 32 NON-LINEAR PDE's

Coupled flow and reactive transport problem is modeled with **numerical codes**

Reaction	**log *K***
$CaCl^{+} = Ca^{2+} + Cl^{-}$	0.6938
$CaCl_{2(aq)} = Ca^{2+} + 2Cl^{-}$	0.6283
$CaHCO_3^{+} = Ca^{2+} + HCO_3^{-}$	-1.0606
$CaOH^{+} + H^{+} = Ca^{2+} + H_2O$	12.9321
$CO_{2(aq)} + H_2O = HCO_3^{-} + H^{+}$	-6.3636
$CO_3^{2-} + H^{+} = HCO_3^{-}$	10.3524
$OH^{-} + H^{+} = H_2O$	14.0707
$HCl_{(aq)} = H^{+} + Cl^{-}$	0.6693
$NaCl_{(aq)} = Na^{+} + Cl^{-}$	0.7811
$NaCO_3^{-} + H^{+} = Na^{+} + HCO_3^{-}$	9.8145
$NaHCO_{3(aq)} = Na^{+} + HCO_3^{-}$	-0.1715
$NaOH_{(aq)} + H^{+} = Na^{+} + H_2O$	14.2479
$CaCO_{3(s)} + H^{+} = Ca^{2+} + HCO_3^{-}$	1.8789

Reactions

- Best place to occur: reactors

THE CONCEPT OF MIXING

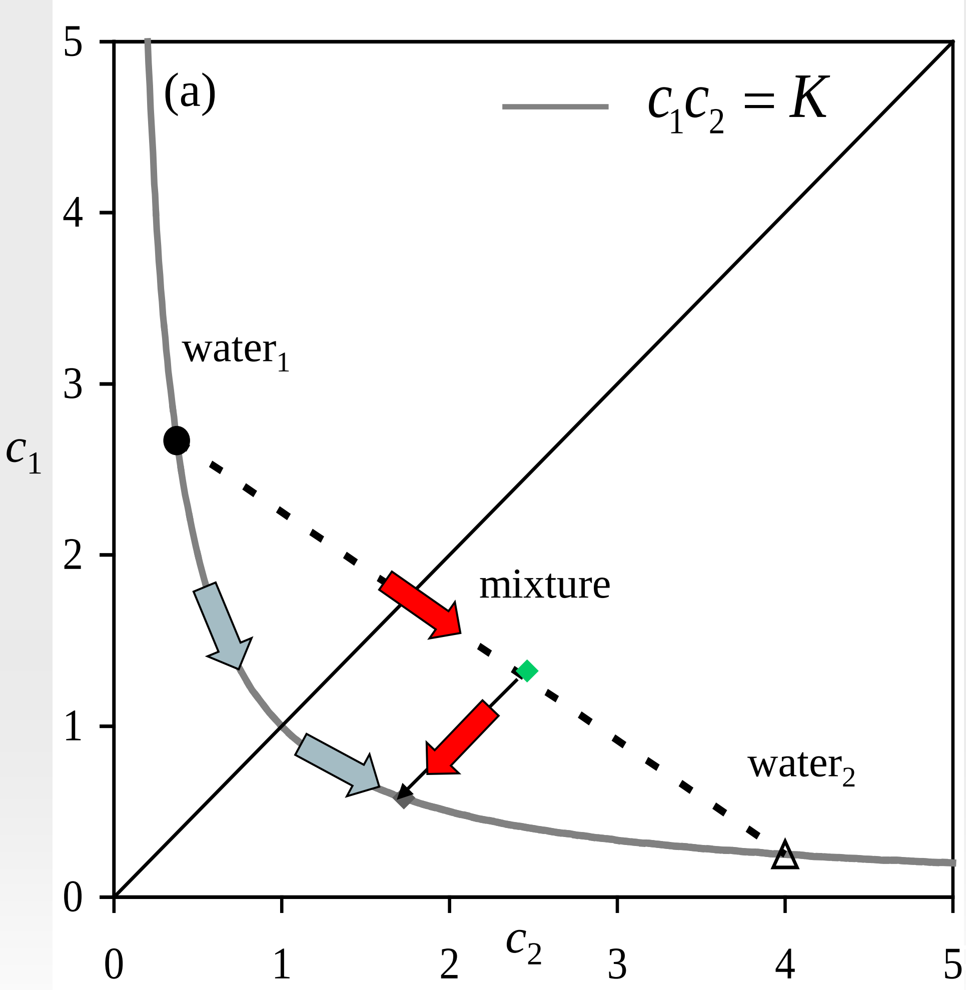
Confluence Amazon – Rio Negro

Mixing without reactors?

THE CONCEPT OF MIXING

Mixed, not stirred! (Connery, 1964)

FIRST, WE GO LOCAL



Reactions driven by mixing

Alternatives: reactions in permanent equilibrium (instantaneous eq) or not. Depends on the Damköhler number, i.e. ratio of two characteristic times

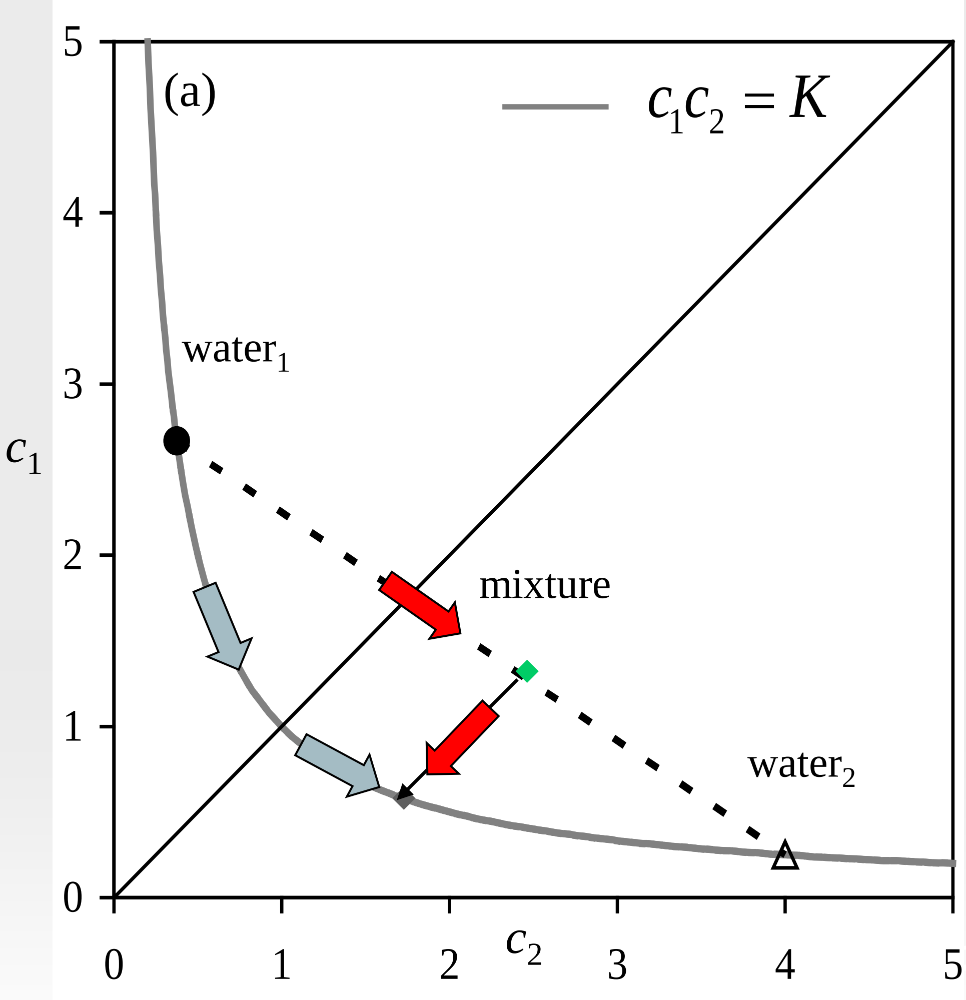
$$Da = \frac{\tau_D}{\tau_r}$$

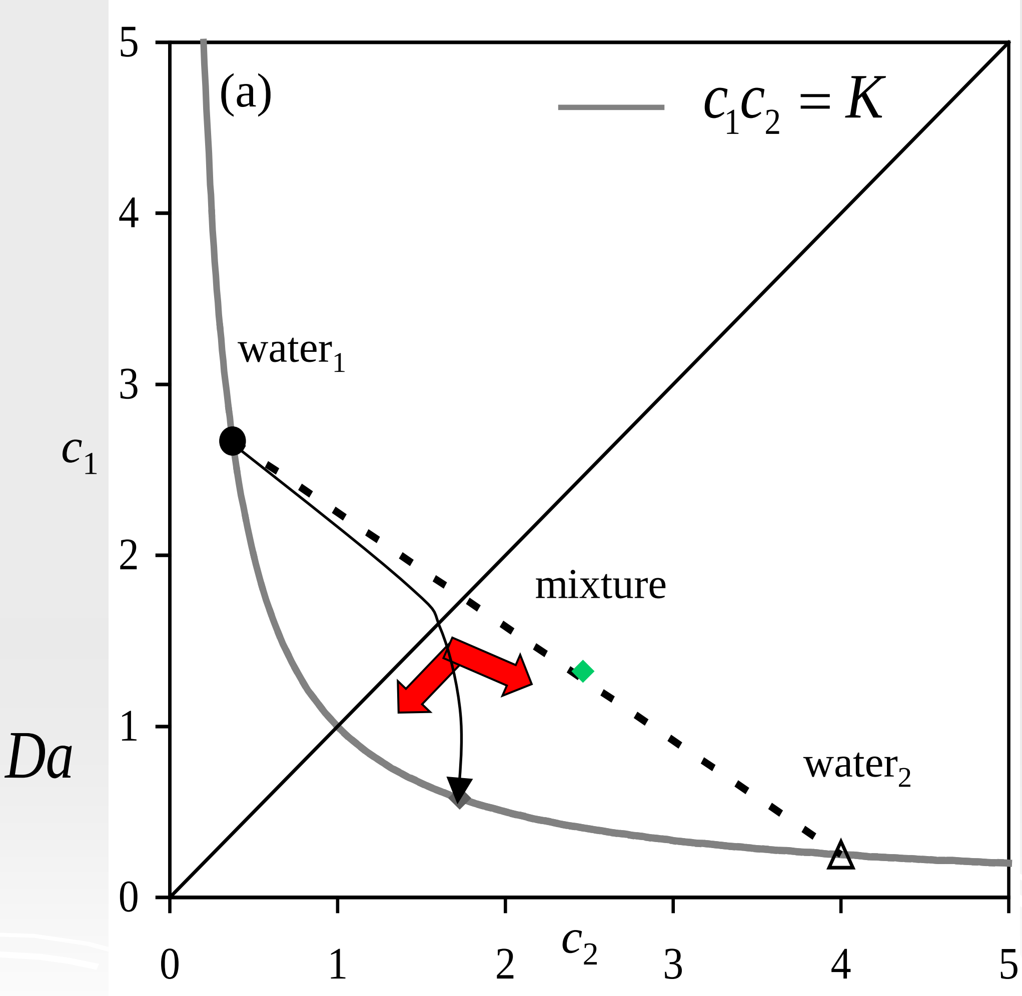
Equilibrium means $Da \to \infty$ and trajectory is the grey line (and arrow)

$Da \to 0$ means slow mixing (in relative terms), and r follows red arrows.

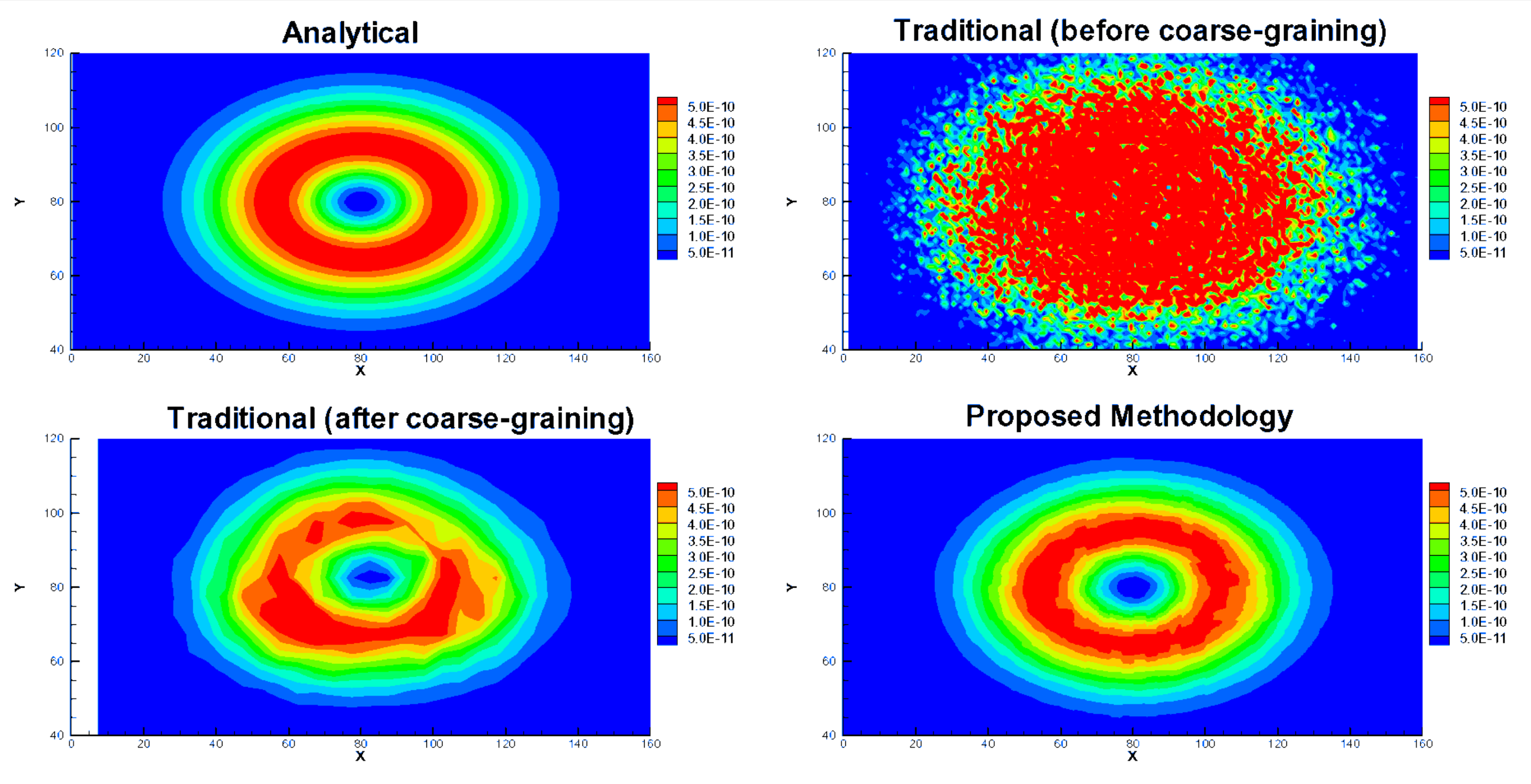
Reality could be something in between

WHAT IF NON-EQUILIBRIUM?





MAPPING REACTIONS



Not an easy task indeed!

So a new methodology has recently been proposed

Problem 1: Fast, "easy" reaction (local scale)

Assume 2 species (e.g. SO_4^{2-} and Ca^{2+}) in eq. with gypsum

Step 1: Chemical system

Reaction
$$Ca^{2+} + SO_4^{2-} \rightleftarrows CaSO_{4s} \Rightarrow \left[Ca^{2+}\right]\cdot\left[SO_4^{2-}\right] = K$$

Components:
$$u = \left[Ca^{2+}\right] - \left[SO_4^{2-}\right]$$
is conservative!

Step 2: Solve transport of u

$$\left.\begin{aligned}
&(1)\quad \frac{\partial(\phi C_1)}{\partial t} + \mathbf{q}\cdot\nabla C_1 - \nabla\cdot(\mathbf{D}\nabla C_1) = -r \\
&(2)\quad \frac{\partial(\phi C_2)}{\partial t} - \mathbf{q}\cdot\nabla C_2 + \nabla\cdot(\mathbf{D}\nabla C_2) = -r
\end{aligned}\right\}$$

3 eqs
3 unknowns

(1)-(2) yields:
$$\frac{\partial(\phi u)}{\partial t} = L(u)$$
CONSERVATIVE!!!

1 eqs
1 unknown

Analytical solution for 2 species

Step 3: Speciation

Solve $u = c_1 - c_2$

Together with $c_1 \cdot c_2 = K$

$$\left.\begin{array}{l} u = c_1 - c_2 \\ c_1 \cdot c_2 = K \end{array}\right\} \Rightarrow \begin{array}{l} c_1 = \dfrac{u + \sqrt{u^2 + 4K}}{2} \\ c_2 = \dfrac{-u + \sqrt{u^2 + 4K}}{2} = c_2(u) \end{array}$$

Step 4: Compute r

$$\boxed{r = \frac{\partial^2 c_2}{\partial u^2}\left[\nabla u^T \cdot \mathbf{D} \cdot \nabla u\right]}$$

Transport

Chemistry

$$\boxed{\frac{\partial^2 c_2}{\partial u^2} = \frac{2K}{\left(u^2 + 4K\right)^{3/2}}}$$

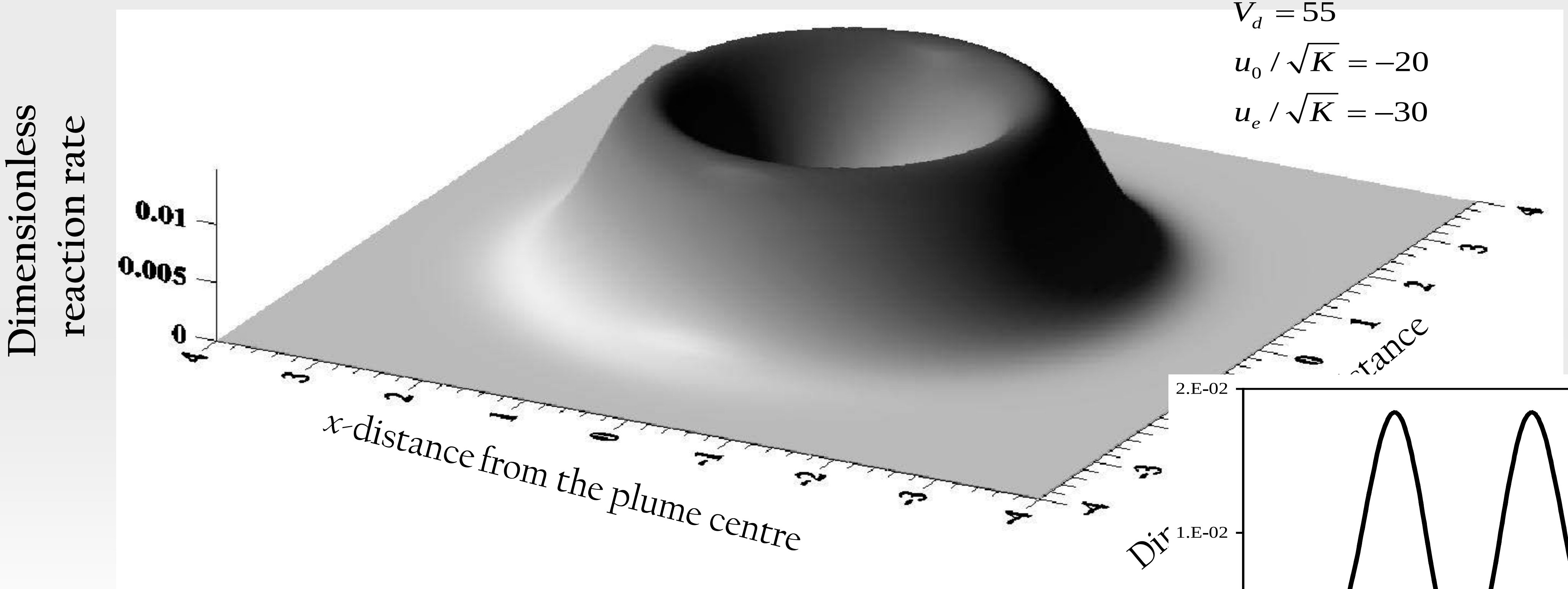
Solution of binary system for pulse input

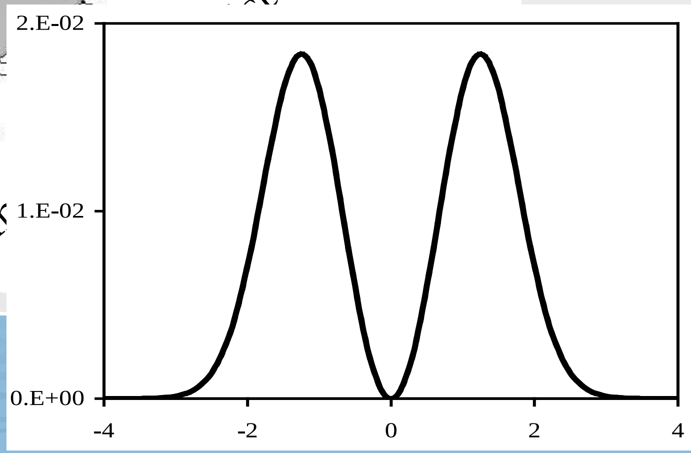
$$u(x,t) = u_0 + \frac{18}{(2\pi)^{1/2}} \frac{u_e}{\tilde{V}_d} \exp\left[-\frac{1}{2} \left(\frac{(x - Vt)^2}{2tD_L} + \frac{y^2 + z^2}{2tD_T} \right) \right]$$

$\tilde{V}_d = 55$

$u_0 / \sqrt{K} = -20$

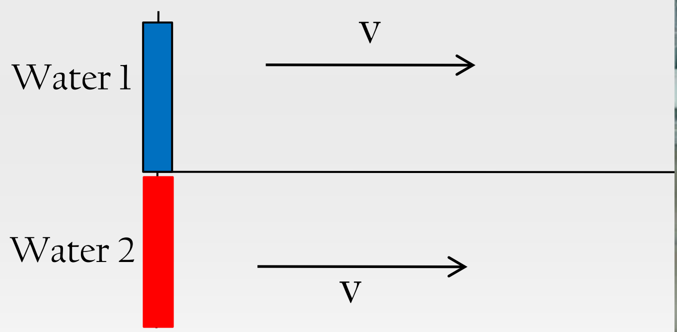
$u_e / \sqrt{K} = -30$

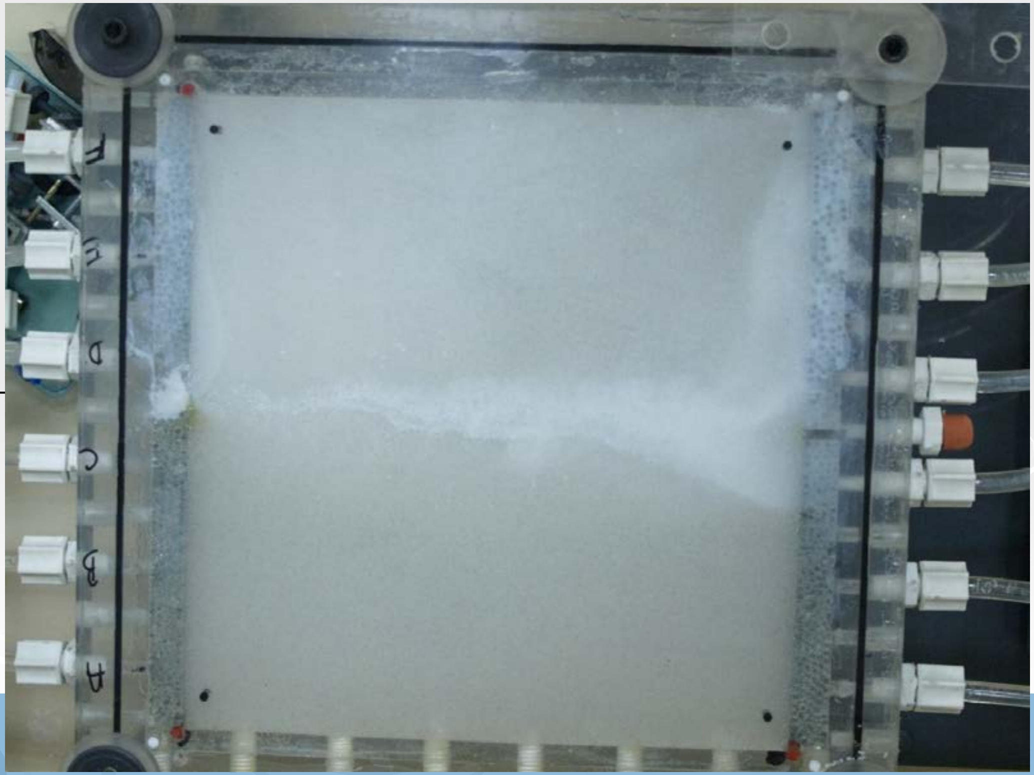




Problem 2: mixing of two waters

- Water 1 in proportion α ; water 2, 1- α (α is a conservative quantity)
- Mixing takes place BECAUSE of dispersion: NO DISPERSION, NO MIXING!!!





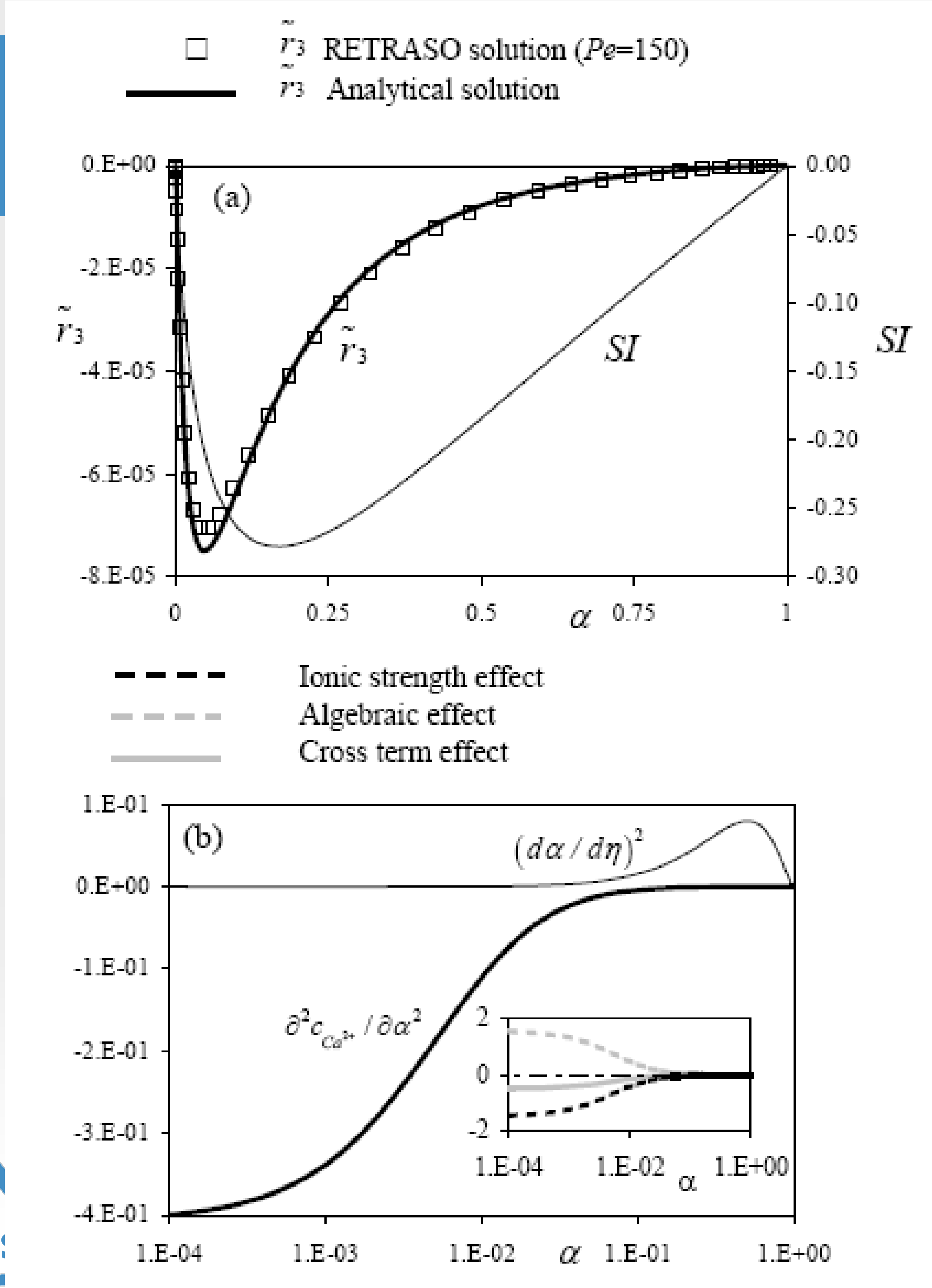
Problem 2: mixing of two waters (ii)

- With a geochemical problem involving 8 species (6 aq., 2 ct activity)

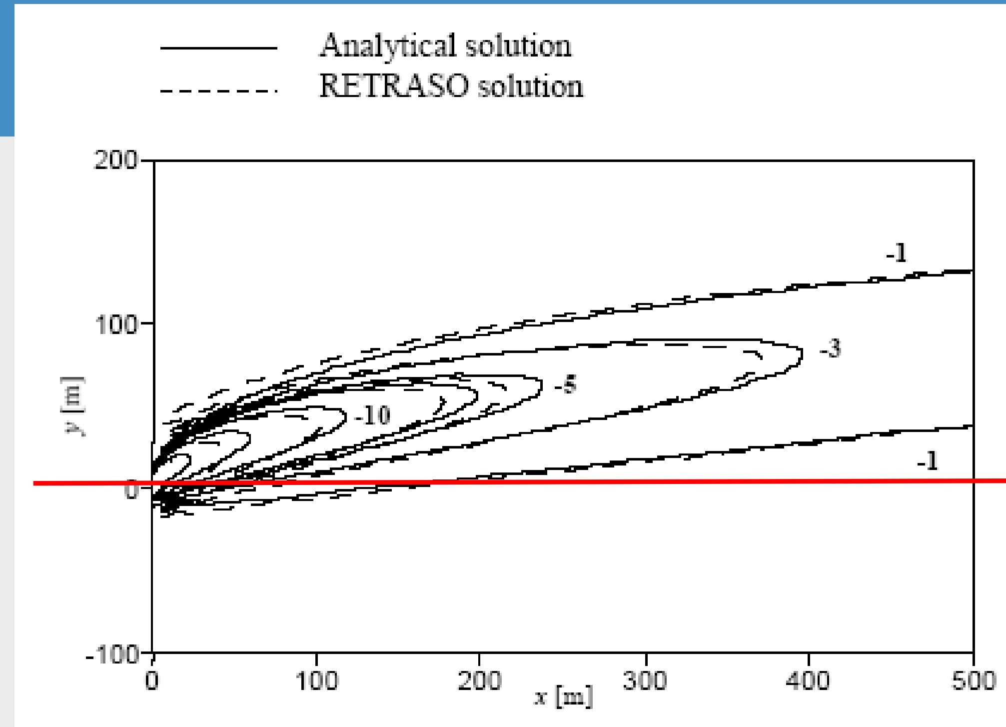
R1	$HCO_3^- = CO_{2(aq)} + H_2O - H^+$
R2	$CO_3^{2-} = CO_{2(aq)} + H_2O - 2H^+$
R3	$Ca^{2+} = CaCO_3 - CO_{2(aq)} - H_2O + 2H^+$
R4	$OH^- = H_2O - H^+$

- The full approach would be solving 6 coupled PDE's simultaneously with 4 non-linear identities (huge supercomputer)

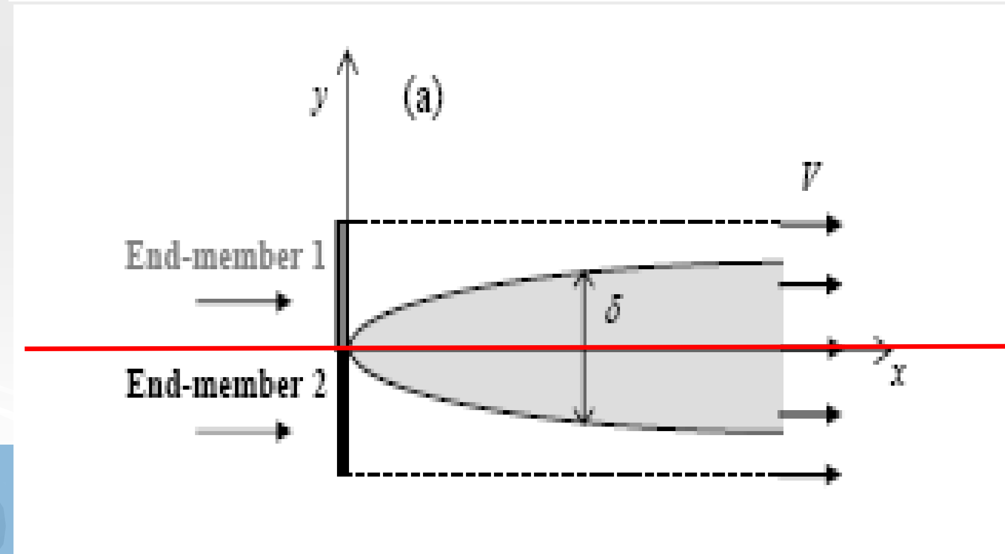
- SOLUTION: Solving for mixing proportions based e.g. on Cl content (freshwater – saline water problem). Solve ONE LINEAR PDE
- Then do speciation, which in this case is solving a "simple" 6th order polynomial (pocket calculator/Spread sheet).



$\tilde{r}_3$ RETRASO solution (Pe=150)
$\tilde{r}_3$ Analytical solution
(a)
$\tilde{r}_3$
SI
0.E+00
-2.E-05
-4.E-05
-6.E-05
-8.E-05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
0
0.25
0.5
α
0.75
1
Ionic strength effect
Algebraic effect
Cross term effect
(b)
$(d\alpha / d\eta)^2$
$\partial^2 c_{Ca^{2+}} / \partial \alpha^2$
1.E-01
0.E+00
-1.E-01
-2.E-01
-3.E-01
-4.E-01
1.E-04
1.E-03
1.E-02
1.E-01
1.E+00
2
0
-2
1.E-04
1.E-02
1.E+00



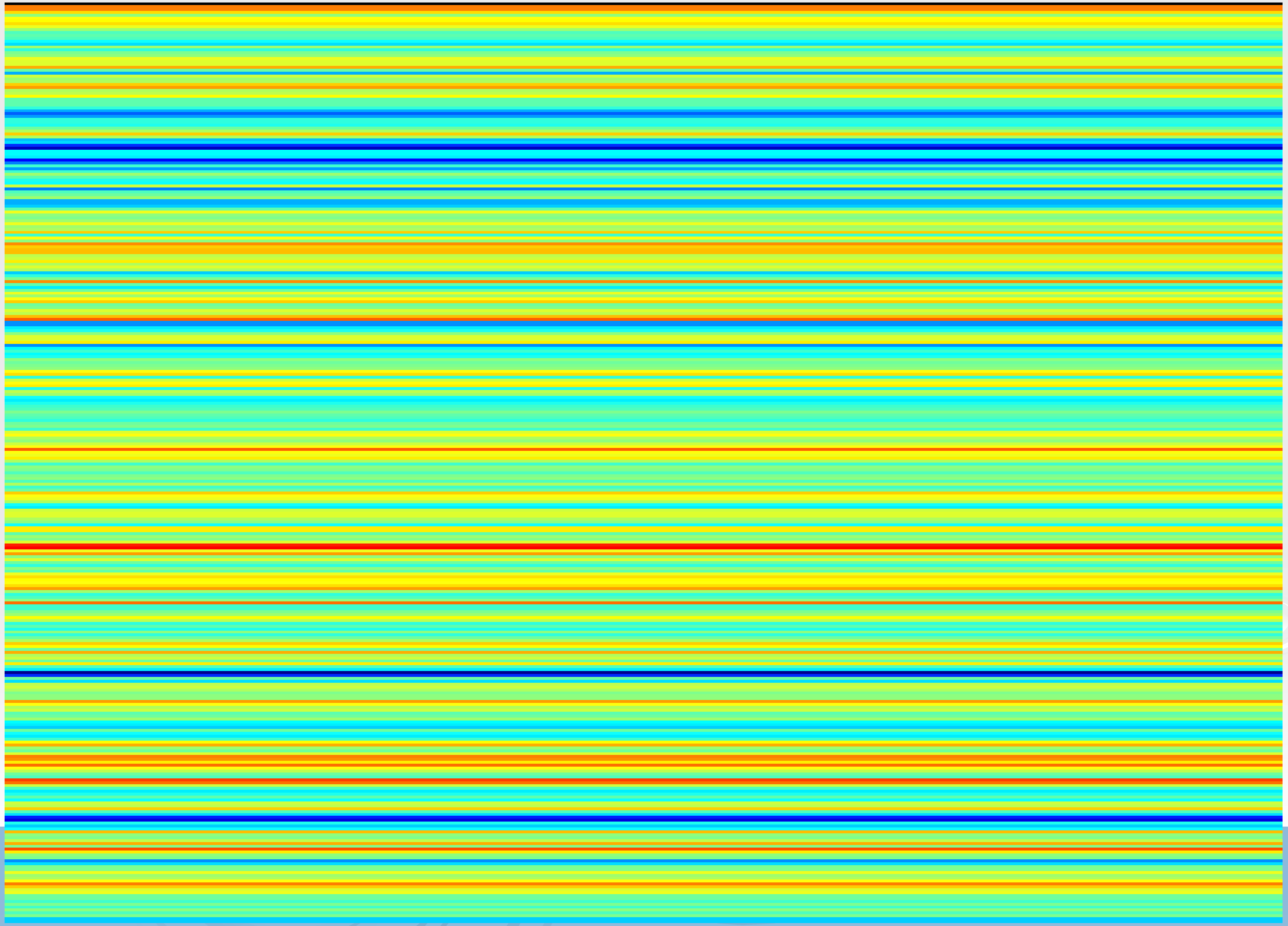
Analytical solution
RETRASO solution
200
100
0
-100
y [m]
0
100
200
300
400
500
x [m]
-1
-3
-5
-10
-1

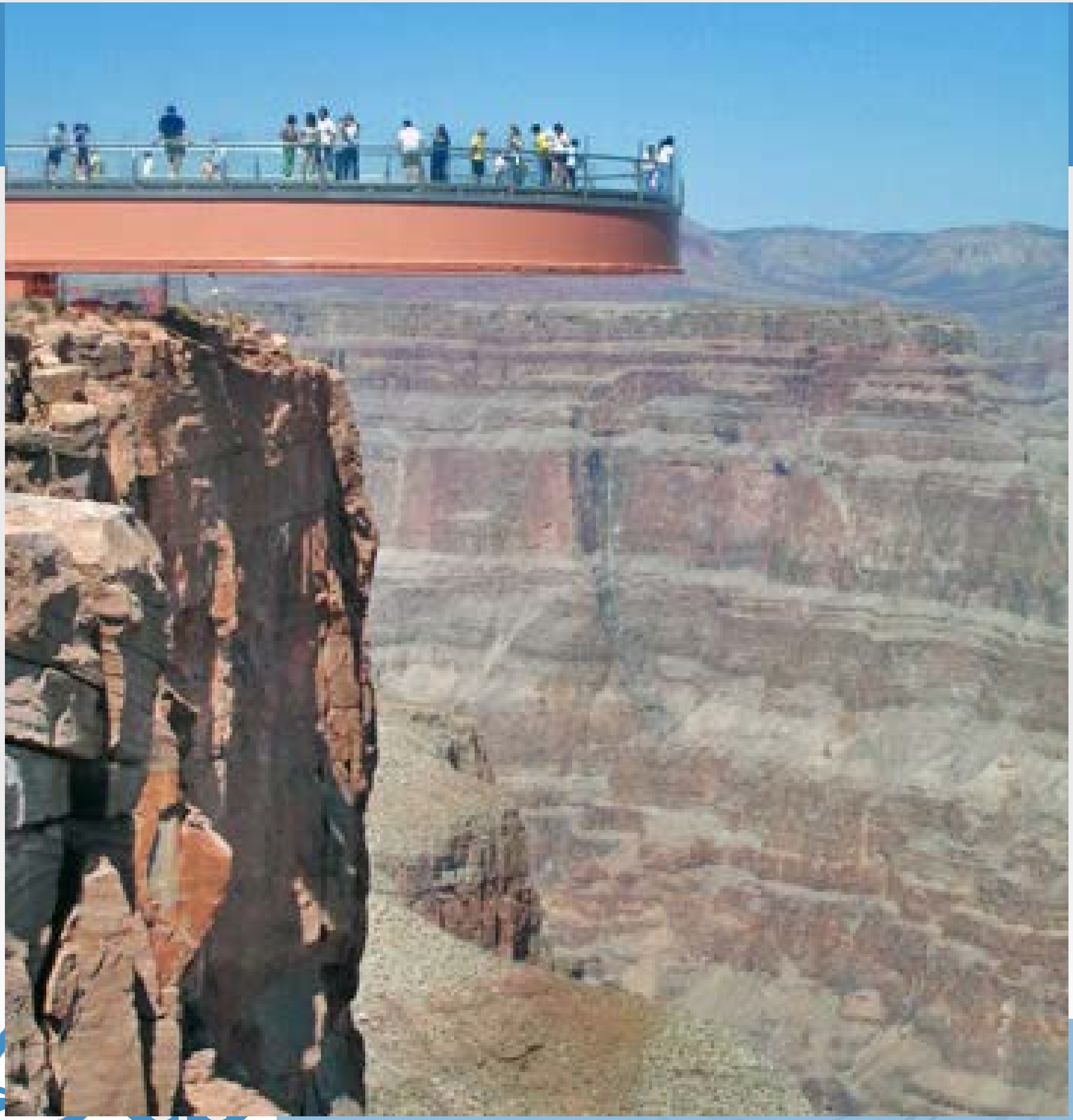


y
(a)
V
End-member 1
End-member 2
δ
x

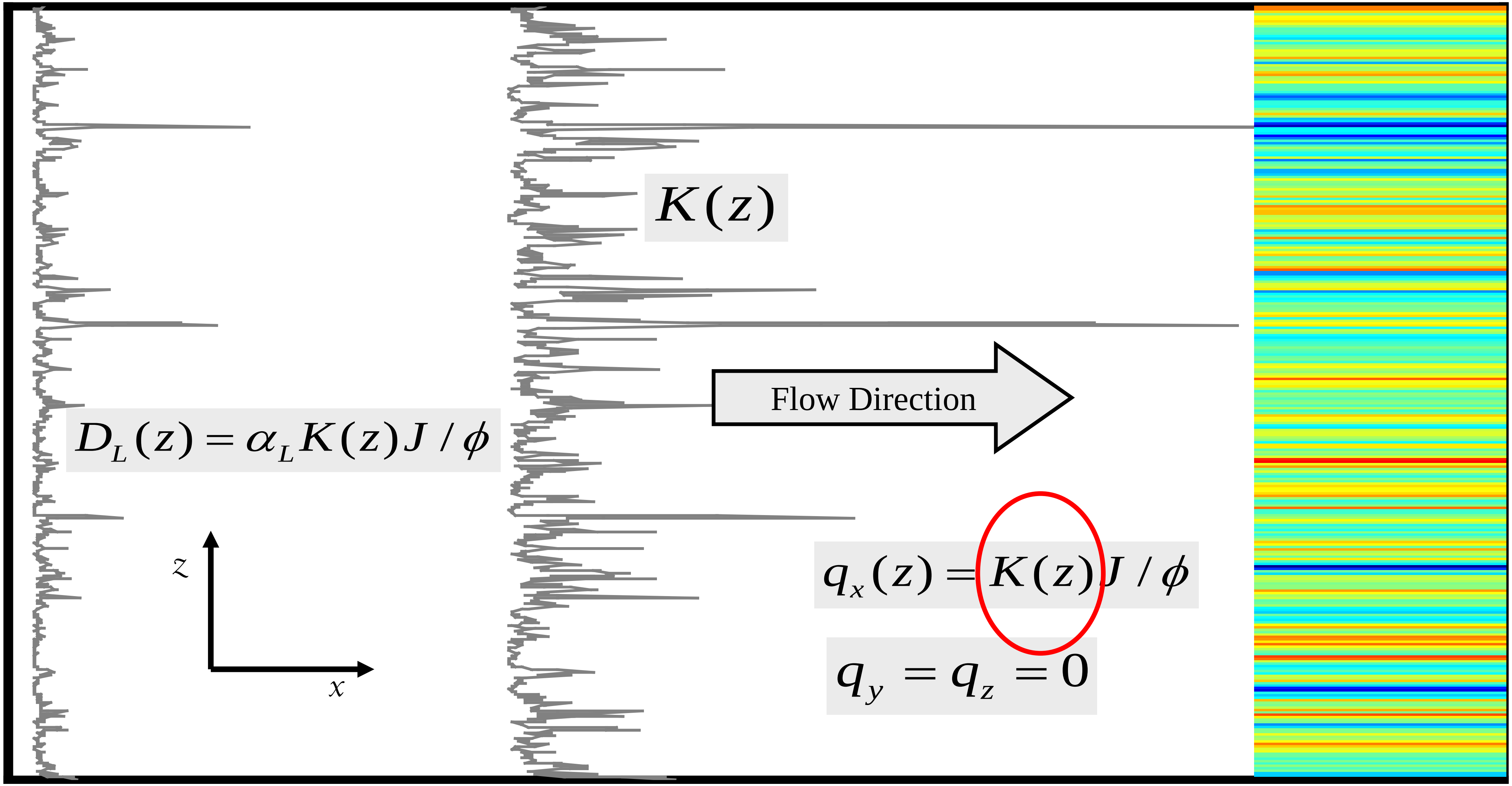
Problem 3: NOW UPSCALING

Why heterogeneous?

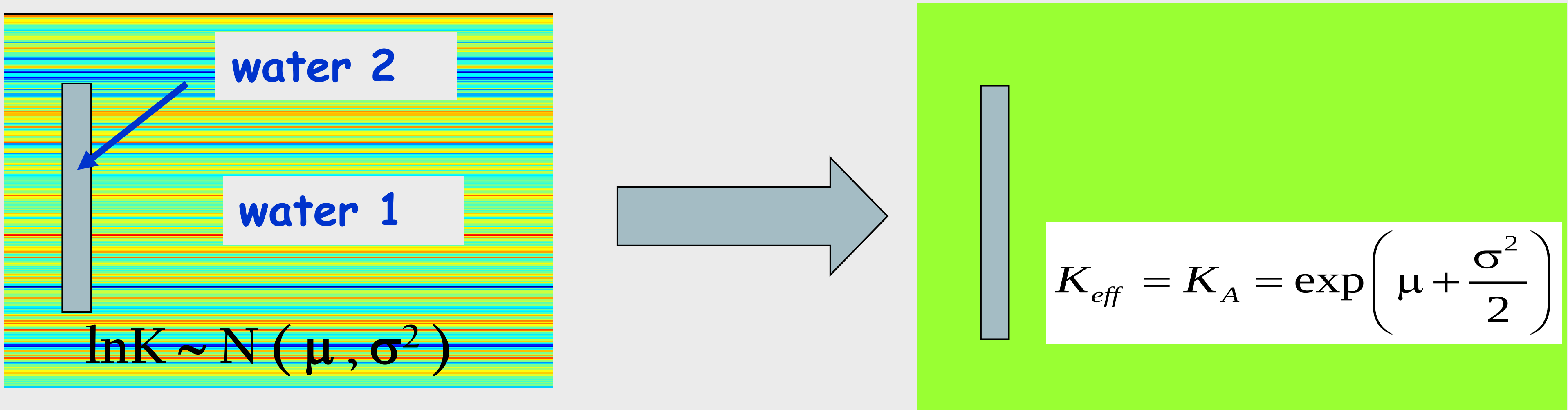




Well, nature
IS HETEROGENEOUS!


$K(z)$
$D_L(z) = \alpha_L K(z) J / \phi$
Flow Direction
$q_x(z) = K(z) J / \phi$
$q_y = q_z = 0$
z
x

ANY HOPE FOR UPSCALING?



$$u^2 + 4K_e \approx u_0^2 + 4K_e$$

$$D_T = 0$$

Heterogeneous medium:

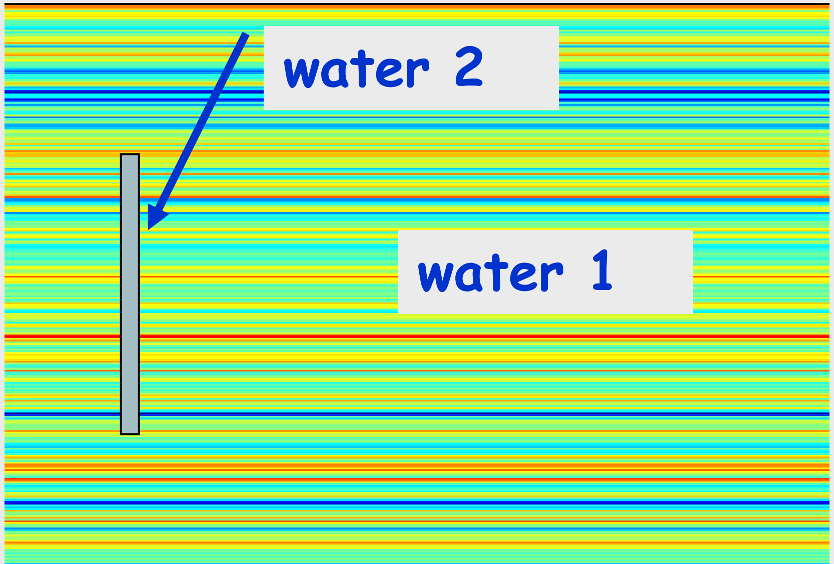
$$\boxed{R(t) \approx \Delta u_0^2 \frac{K_e}{4(u_0^2 + 4K_e)^{3/2}} \left(2\alpha_L \frac{J}{\phi}\right)^{-1/2} \exp\left(-\frac{\mu}{2} + \frac{\sigma^2}{8}\right) t^{-3/2}}$$

Homogenized medium:

$$\boxed{R(t) \approx \Delta u_0^2 \frac{K_e}{4(u_0^2 + 4K_e)^{3/2}} \left(2\alpha_L \frac{J}{\phi}\right)^{-1/2} \exp\left(-\frac{\mu}{2} - \frac{\sigma^2}{4}\right) t^{-3/2}}$$

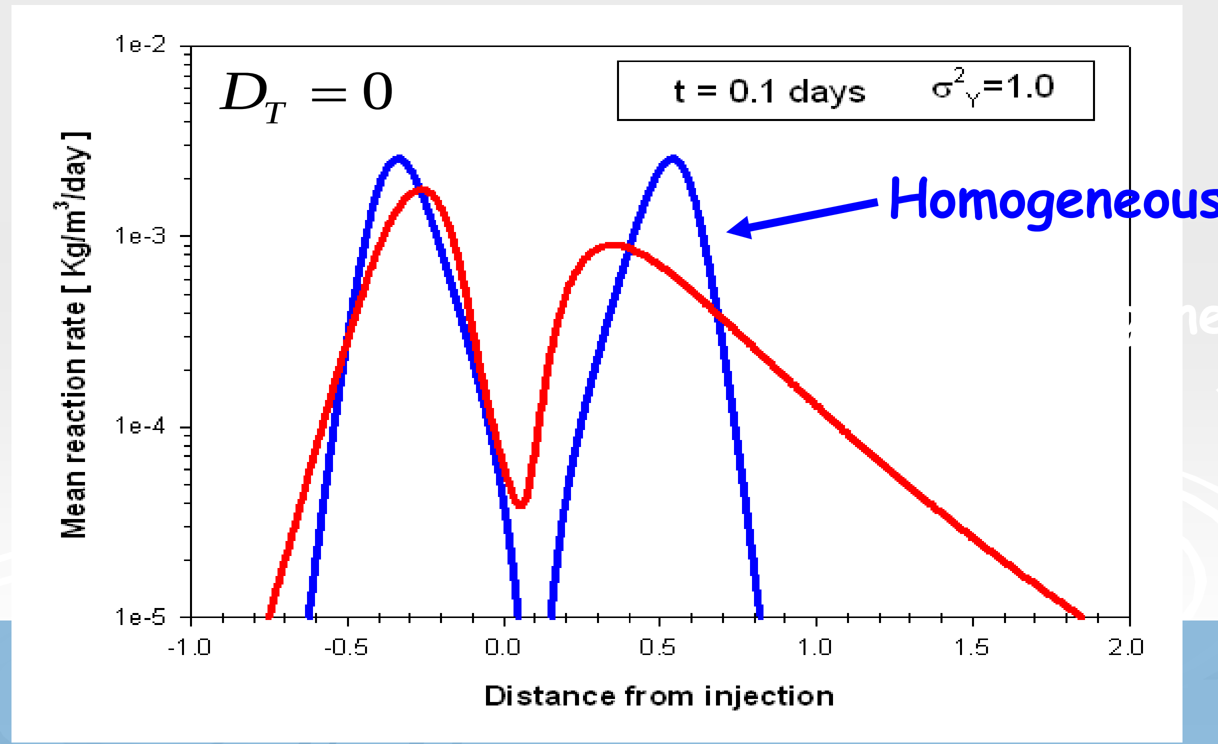
Discrepancy !!!

Heterogeneous Solution (stratified system)



Log-normal K distribution

Mean Reaction Rates

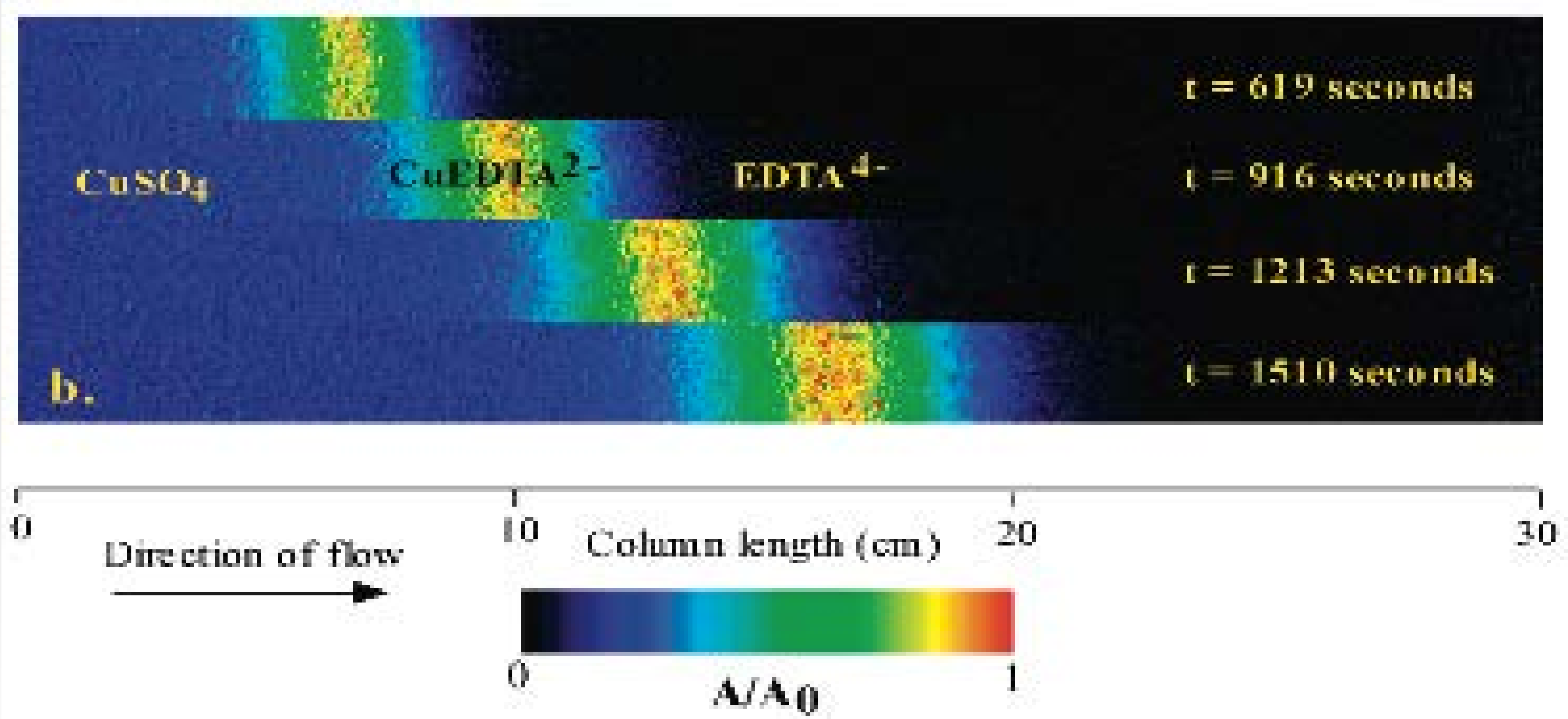


Reaction is also controlled by imperfect mixing at the local scale transmitting to the global scale

The experiment (*Gramling et al.*, ES&T, 2002)

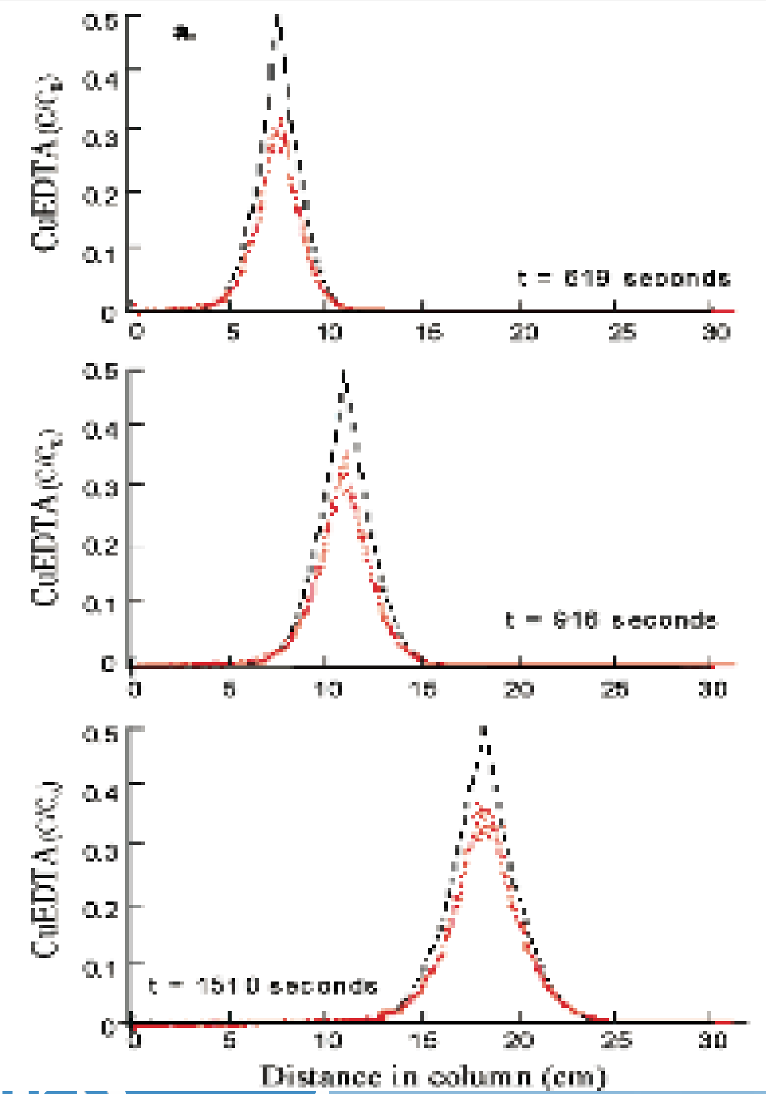
1-D sand-filled column, constant $EDTA^{4-}$ initial concentration, flow from left to right (controlled), $CuSO_4$ injected continuously at the left boundary.

Homogeneous irreversible reaction



At the time-scale of the experiment, reaction can be considered instantaneous: $A + B \rightarrow C$ (meaning A, B cannot coexist at the same point)

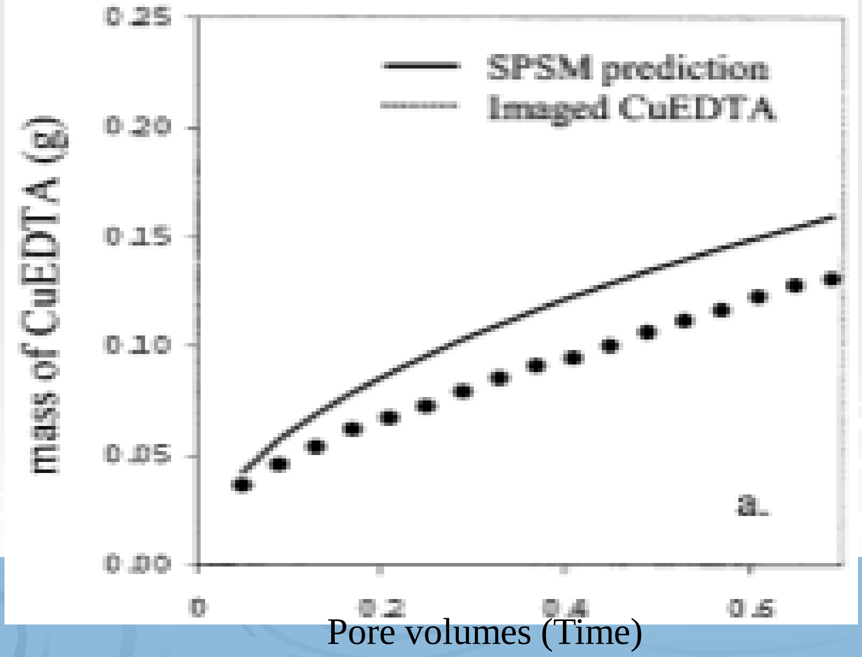
1st modeling approach: ADE + Instantaneous equilibrium

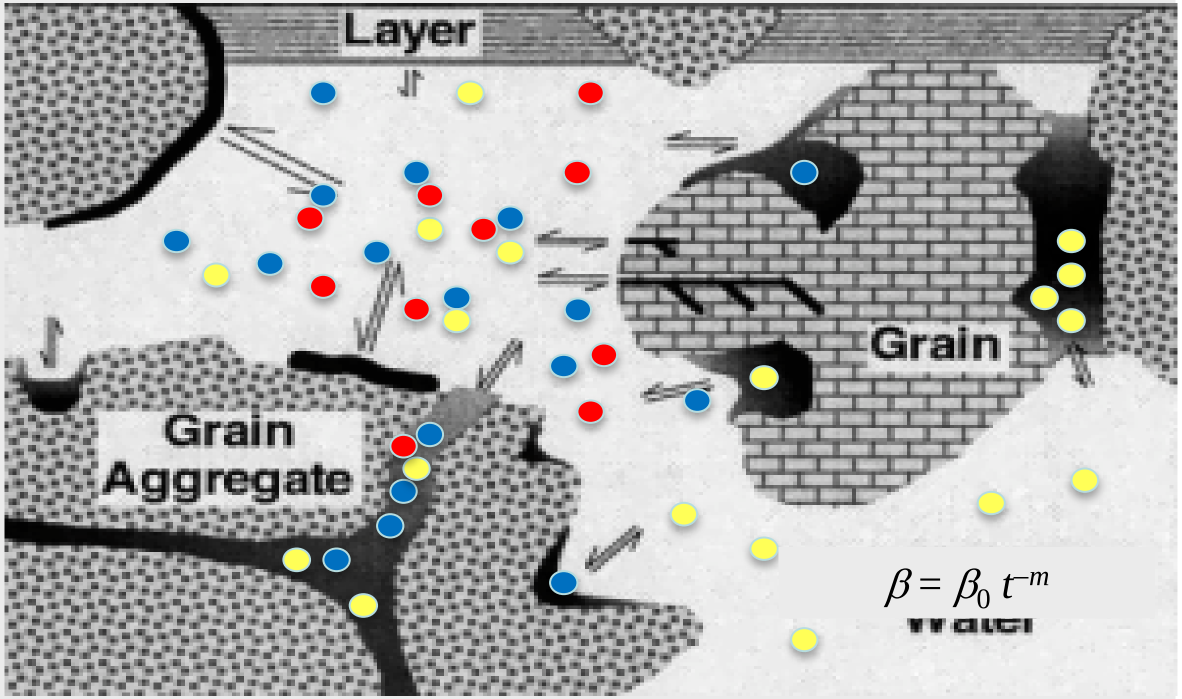


ADE + instantaneous equilibrium does not reproduce the observations properly:

(a) It predicts a normalized concentration peak (C/C_0) which DOES NOT CHANGE with time

(b) It over-predicts the total produced mass



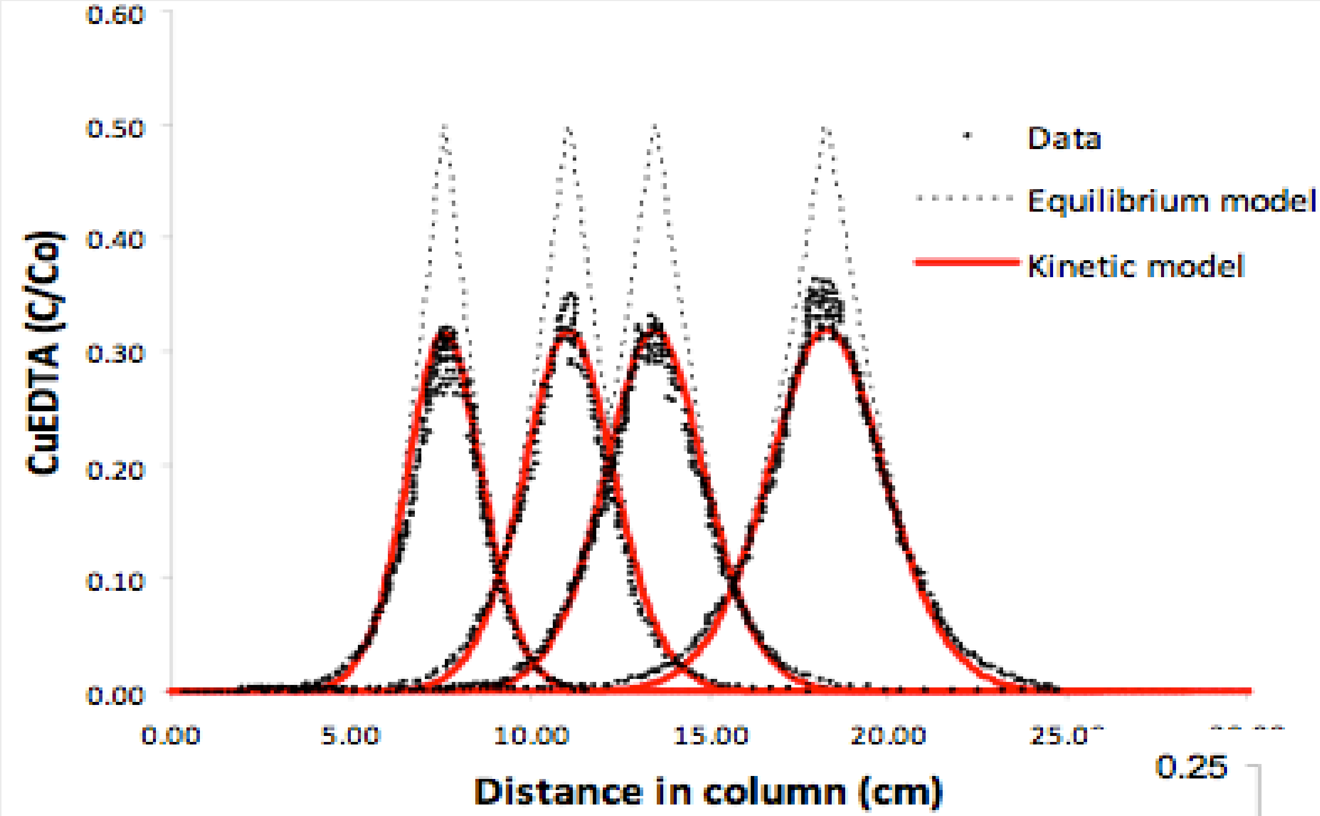


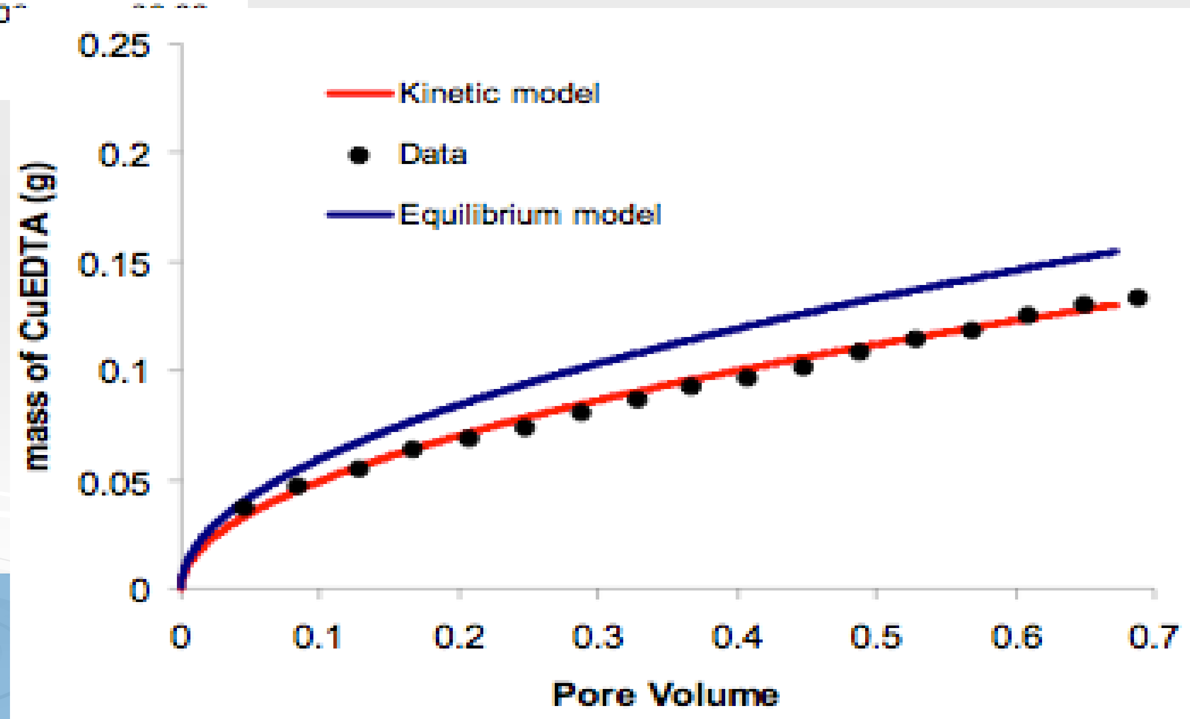
Adapted from *Haggerty and Gorelick* [1995]

Key idea: incomplete mixing can be modeled at a continuum-scale by adding a kinetic (non-instantaneous) reactive term to the driving equation

Species *A* does not completely and instantaneously react with an already existing species *B*, as part of the pore water is not instantaneously accessible. This results in slow and incomplete mixing at a macroscale.

$$\frac{\partial c_i}{\partial t} = -v\frac{\partial c_i}{\partial x} + D\frac{\partial^2 c_i}{\partial x^2} - \beta c_A c_B; \qquad i = A, B$$


CuEDTA (C/Co)
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.00
5.00
10.00
15.00
20.00
Distance in column (cm)
Data
Equilibrium model
Kinetic model

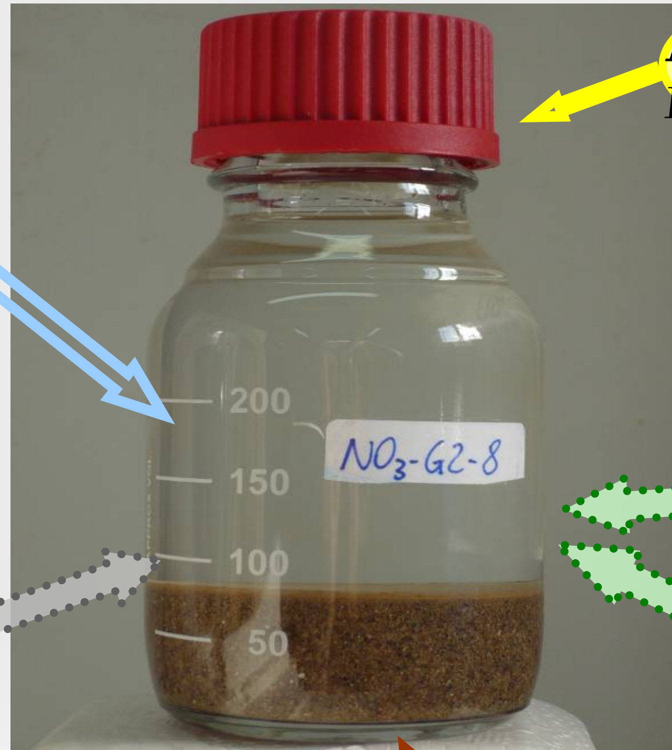

mass of CuEDTA (g)
0.25
0.2
0.15
0.1
0.05
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Pore Volume
Kinetic model
Data
Equilibrium model

But we should also worry about organic chemistry

Suite of batch experiments under controlled redox conditions

WATER:
240mL
(SYNTHETIC,
similar to recharge
water at Test Site)

Headspace:
10mL



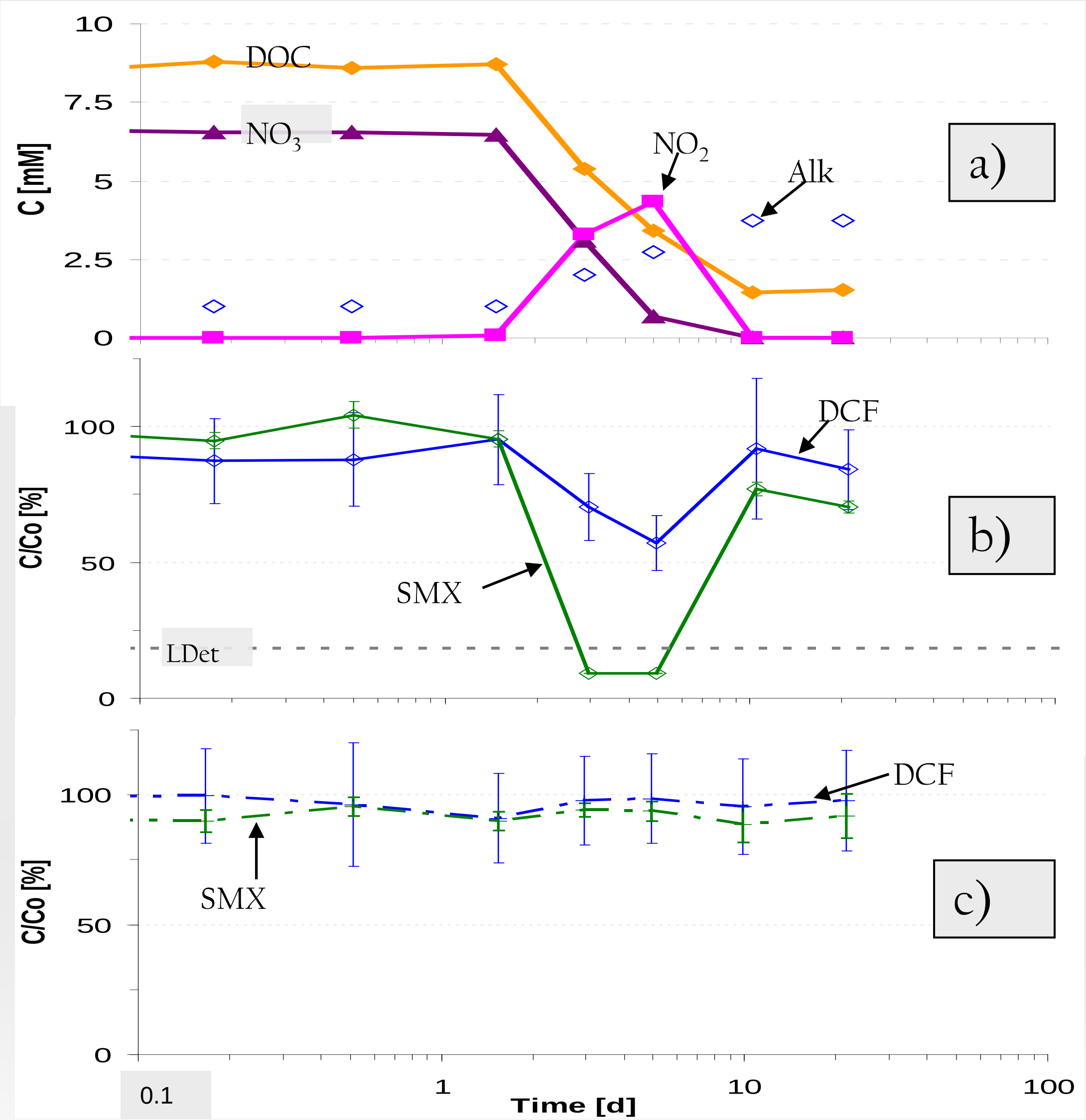
additional
e^- acceptor:
O_2 or
NO_3 or
Mn oxides or
Fe oxides or
SO_4^{2-}

e^- donor:

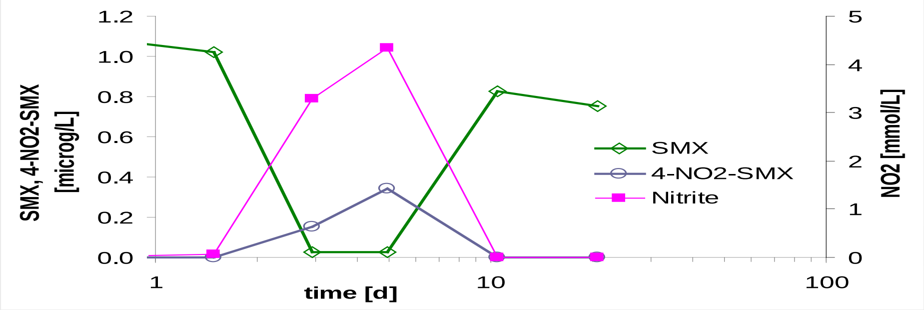
Na-acetate & MeOH
as ***easily degradable***
organic substrate

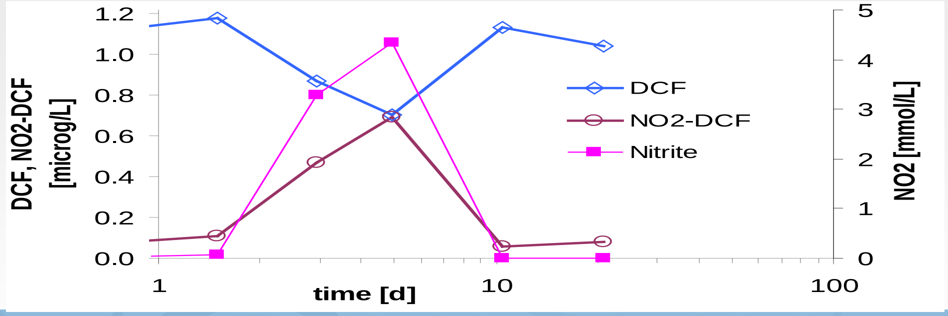
MICROPOLLUTANTS

SOIL:
120g of d < 1mm
(from Test Site)

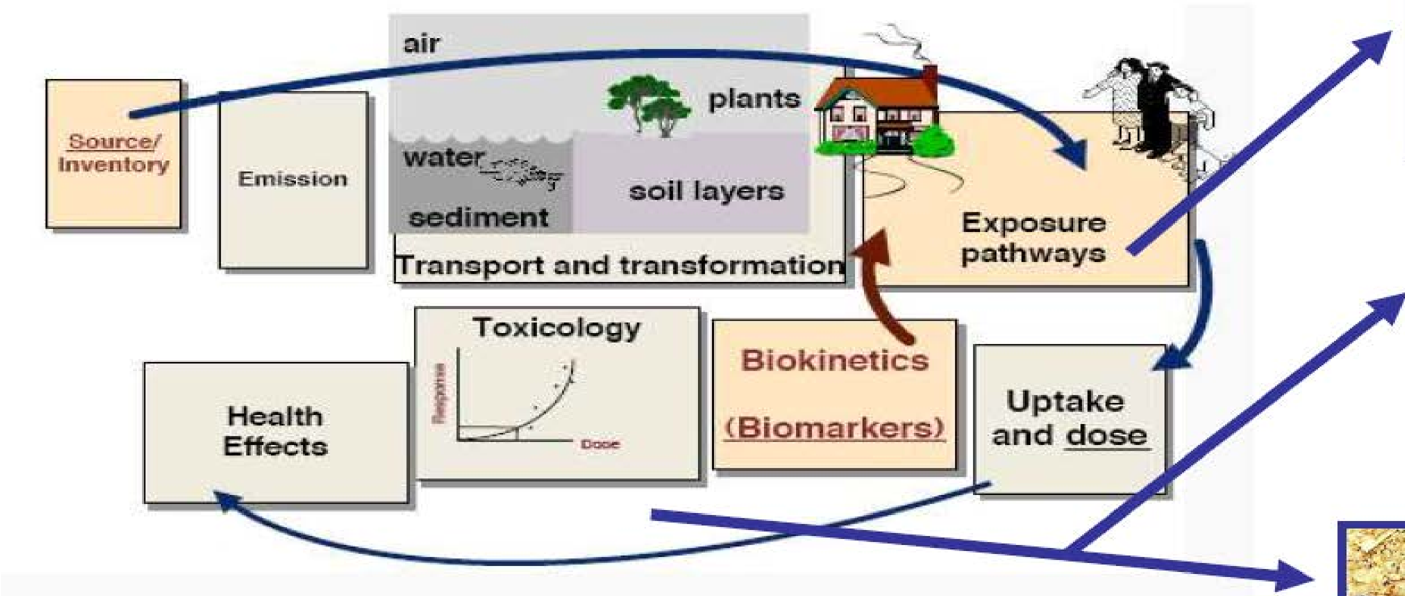


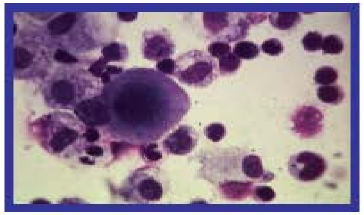
Extremely relevant for water quality purposes





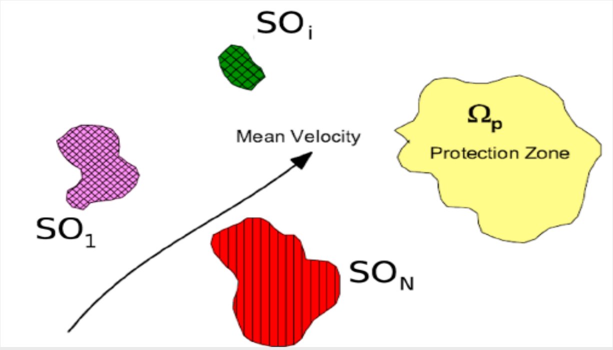
Risk Assessment: Overview and Challenges



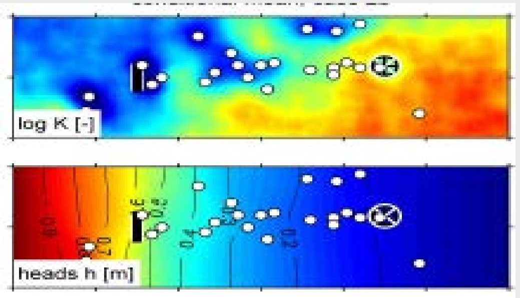


Source: T. McKone's Risk Lecture, UC Berkeley

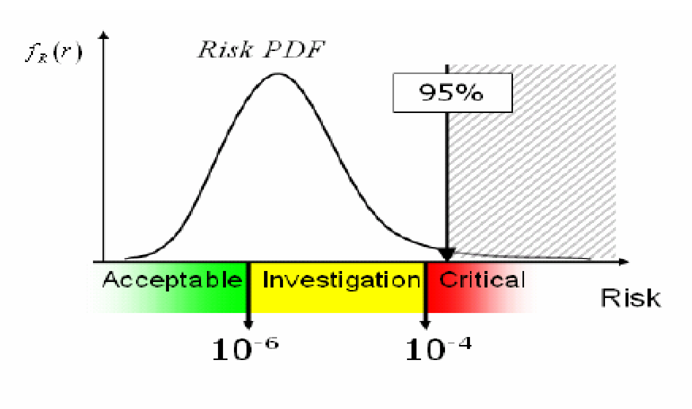
Need Probabilistic Concepts!



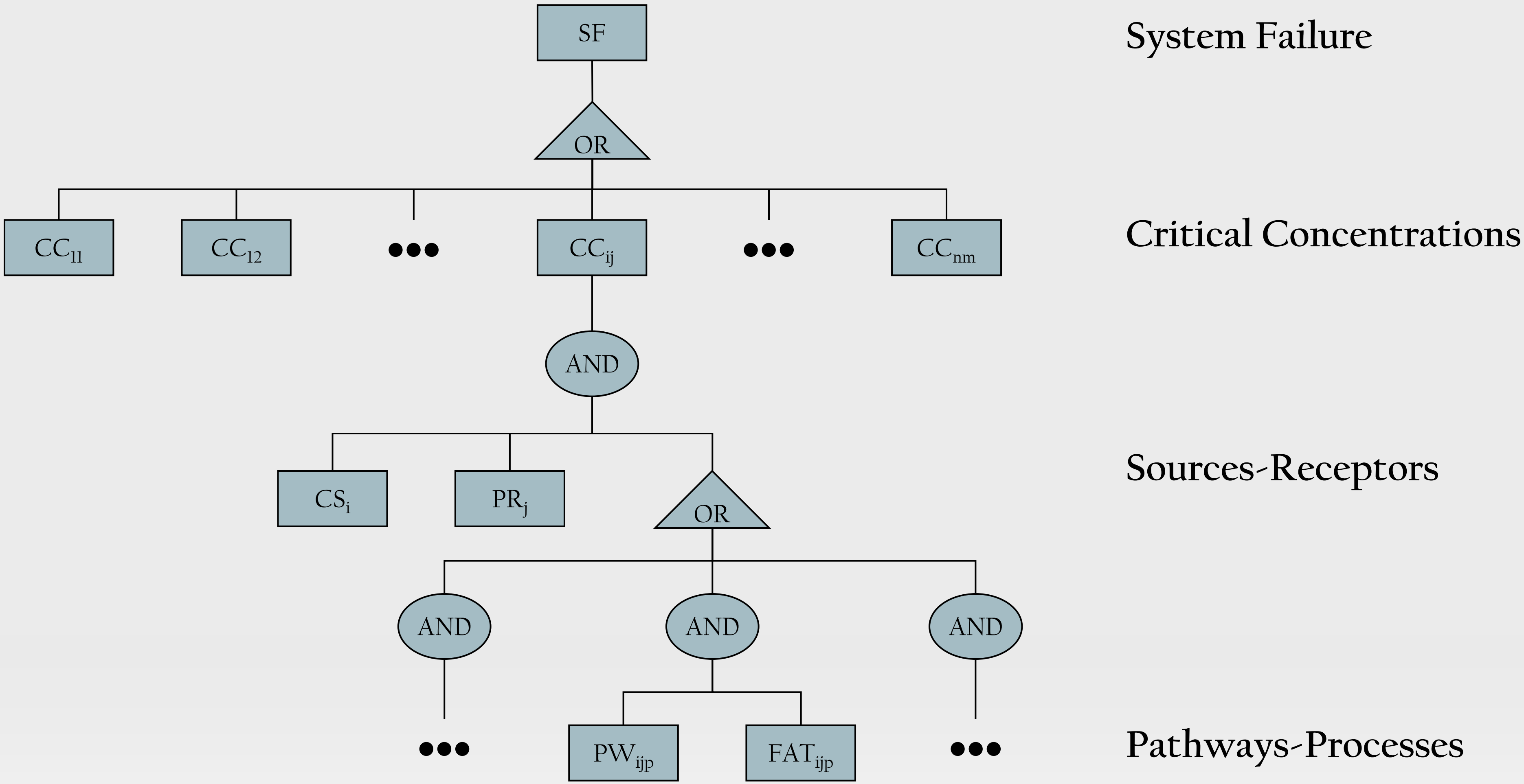
1) Identifying contaminant source releases & environmentally sensitive targets.

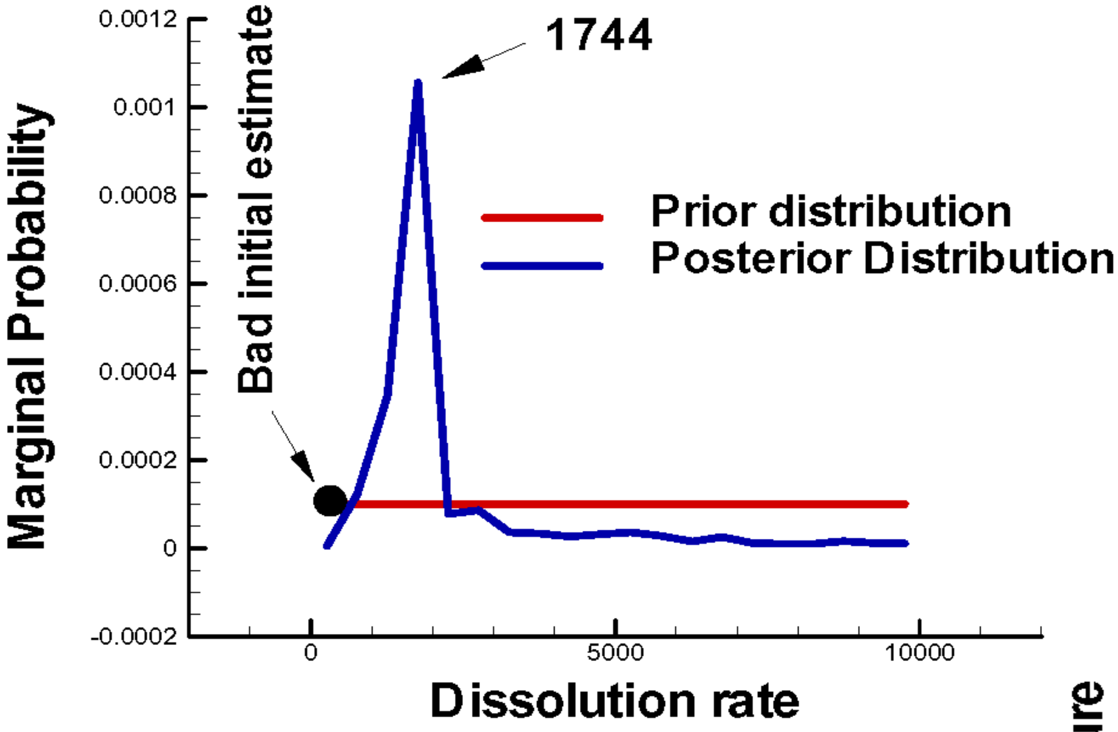


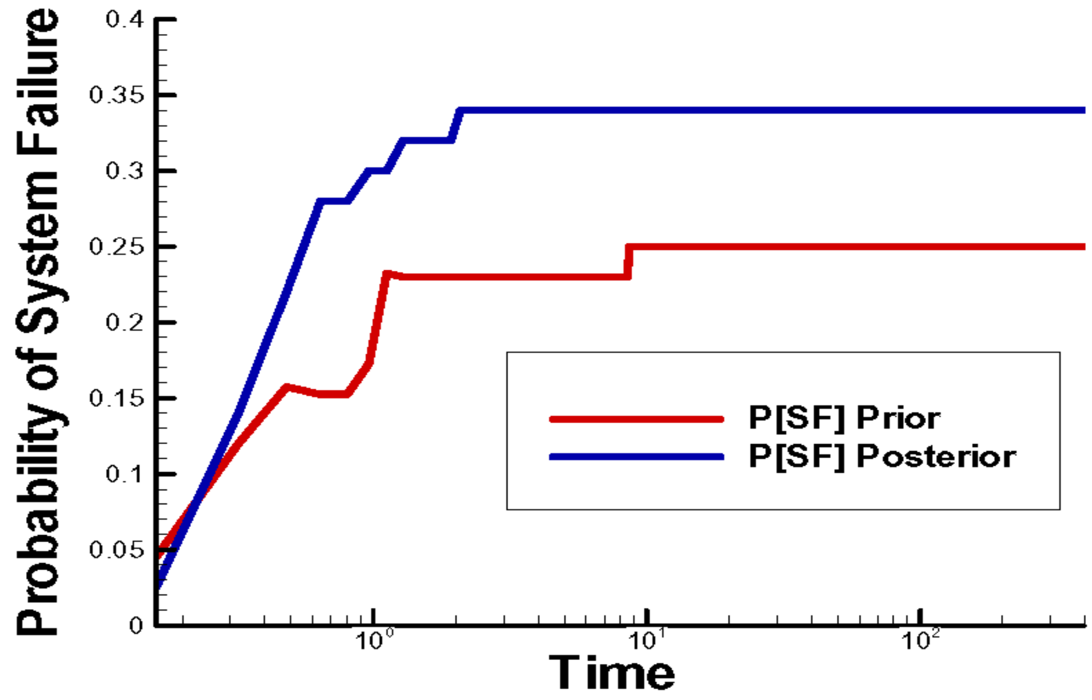
2) Data acquisition used to infer modeling parameters! Site characterization.



3) Final task: Estimate human health risk toward decision making! Should a site be remediated or not? Is the exposed population at risk?


SF
OR
CC11
CC12
CCij
CCnm
AND
CSi
PRj
OR
AND
AND
AND
PWijp
FATijp
System Failure
Critical Concentrations
Sources-Receptors
Pathways-Processes


1744
Bad initial estimate
Prior distribution
Posterior Distribution
Marginal Probability
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
-0.0002
0
5000
10000
Dissolution rate


Probability of System Failure
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
P[SF] Prior
P[SF] Posterior
10^0
10^1
10^2
Time

Final remarks

- Arthur T. Ippen (1970) advocated for the inclusion of complex environmental and social factors when dealing with engineering problems
- As engineers we face a daily challenge of solving complex problems, a lot of information is needed
- As scientists/researchers we deal with the advancement of science, uncertainty should be treated in a rigurous manner, starting at the small scale, then upscaling, then providing estimates in terms of probabilities
- As professionals living in a real world we need to get **the best of both worlds** (Hanna Montana dixit). We have to make an effort to convey our clients the problems associated to our job and the impossibility to produce exact results when data is never extensive
- More research; i.e., more money is needed!

In memoriam

Gerhard H. Jirka
1944 – 2010
Arthur T. Ippen Award recipient (1989)

GHS UPC