MAR SOL MANAGED AQUIFER RECHARGE SOLUTIONS

THE FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION HORIZON 2020 FREEWAT

European Commission

EIP Water Online Market Place
Matchmaking for water Innovation
MAR Solutions - Managed Aquifer Recharge Strategies and Actions (AG128)

Modeling reactive transport with Lagrangian approaches: implications to human health risk

Daniel Fernàndez-Garcia

X. Sanchez-Vila, C. Henri, E. Siirila, D. Pedretti, M. Rahbaralam, J. Carrera, E. Castro-Alcalá

UPC Escola de Camins
Escola Tècnica Superior d'Enginyeria de Camins, Canals i Ports
UPC BARCELONATECH

Grup d'hidrologia subterrània
UPC CSIC

Joint International Workshop

EU FP7 MARSOL and EU HORIZON 2020 FREEWAT projects and EU EIP MAR Solutions - Managed Aquifer Recharge Strategies and Actions (AG128)

Pisa - April 21st 2015

INSTITUTE OF LIFE SCIENCES
Scuola Superiore Sant'Anna

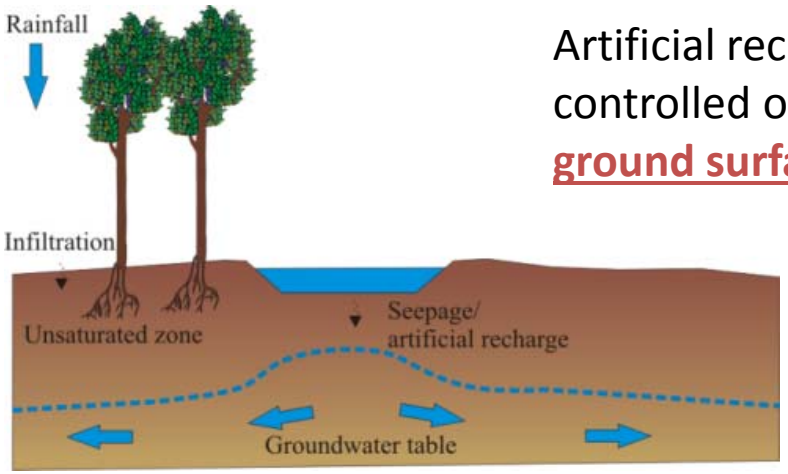
TEASISTEMI
ENERGY AND ENVIRONMENT TECHNOLOGIES

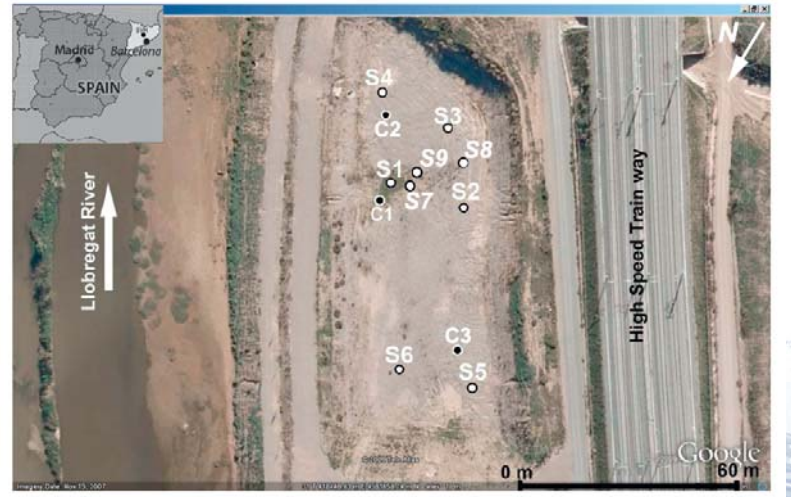
PROVINCIA di Lucca

Content

- Introduction to numerical modeling and artificial recharge
- Lagrangian versus Eulerian approaches
- Can we really simulate reactions with Eulerian methods
- Advances in Lagrangian methods
    - Avoid reconstruction problems with kernels
    - Simulate reactions with transition probabilities:
        - Pseudo-first-order Network reactions
        - Non-linear reactions → interaction of nearby particles
- Implications to human health risk
    - Chemical mixtures
    - Characterization of hot spots and the role of preferential channels

Artificial recharge and numerical modeling





Artificial recharge may be defined as man-made controlled operations aimed at **transferring water from ground surface into underlying aquifers**.

Two objectives are achieved:

Storage (say if water in the river is available in winter and is needed for irrigation in summer), and

Improvement of water quality, at least by the removal of fines in the settling basins and also the removal and destruction of microorganisms and toxic contaminants as the recharge water percolates through the unsaturated zone.

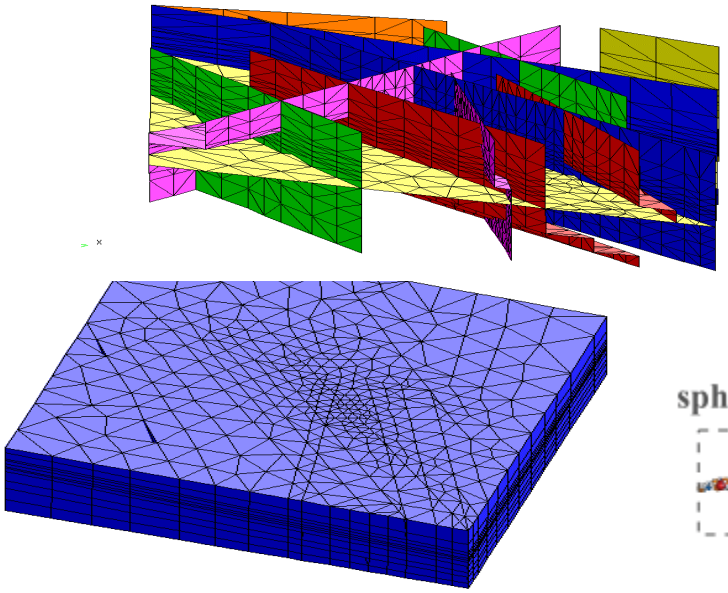
But in order to assess water quality we need to model complex reactive transport systems. For example,

- Redox reactions catalyzed by microorganisms
- Special case: organic matter **degradation**, the electron donor is organic matter (generically, CH_2O). The **natural sequence** is:
  - $CH_2O + O_2 \rightarrow CO_2 + H_2O$ **$\Delta G=120$** kcal/mol C
  - $CH_2O + 0.8NO_3^- + 0.8H^+ \rightarrow CO_2 + 0.4N_2 + 1.4H_2O$ **$\Delta G=114$**
  - $CH_2O + 2MnO_2 + 4H^+ \rightarrow CO_2 + 2Mn^{2+} + 3H_2O$ **$\Delta G=81$**
  - $CH_2O + 4Fe(OH)_3 + 8H^+ \rightarrow CO_2 + 4Fe^{2+} + 11H_2O$ **$\Delta G=28$**
  - $CH_2O + 0.5SO_4^{2-} + H^+ \rightarrow CO_2 + 0.5H_2S + H_2O$ **$\Delta G=25$**
  - CH_2O ($0.5\ CH_2O + 0.5\ CH_2O$) $\rightarrow 0.5CO_2 + 0.5CH_4$ **$\Delta G=22$**

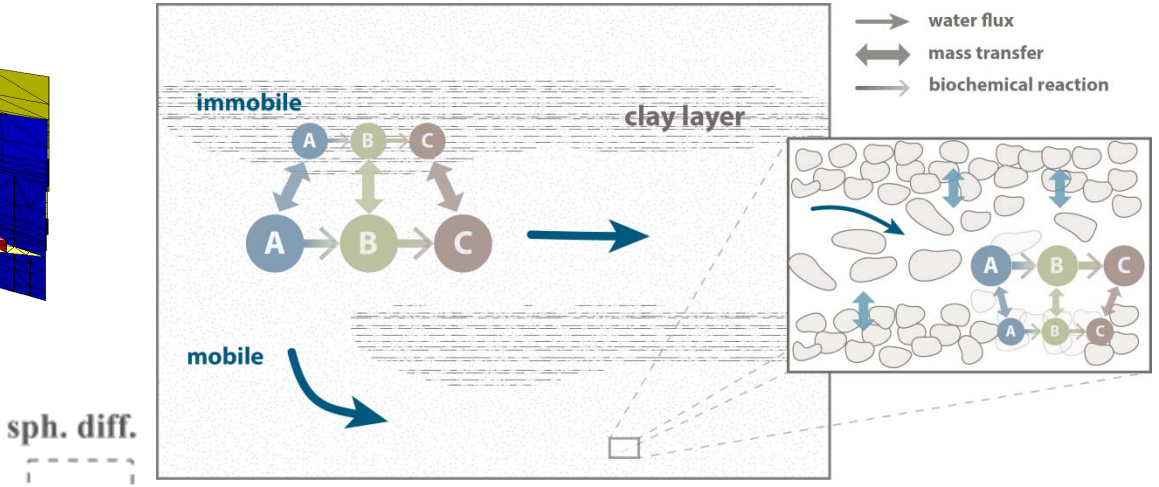
The most **efficient organisms dominate each stage**, inhibiting the development of the ones below. Yet, their success is their nemesis, as they **exhaust their electron acceptor**. This opens the path for the **next organism down the ladder**, which dominates the next stage.

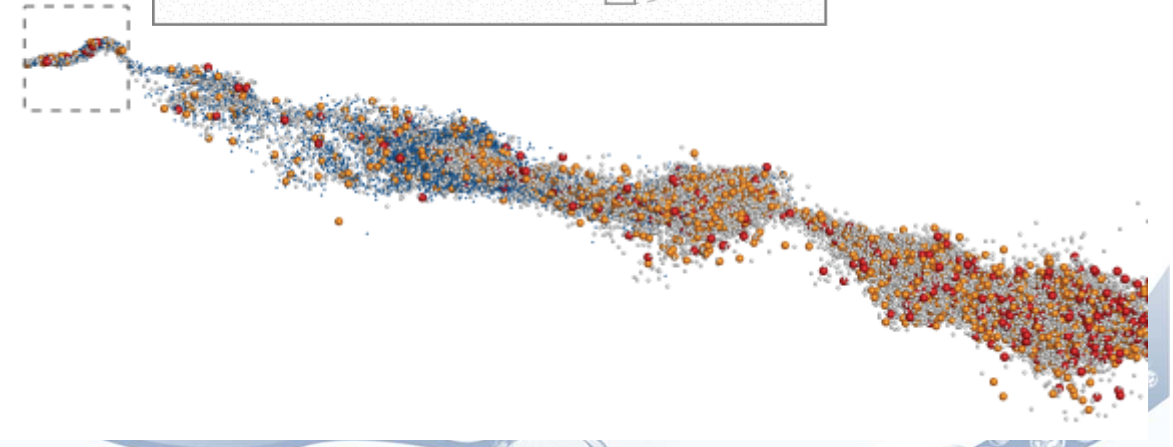
Reactive transport modeling approaches

Eulerian



Lagrangian



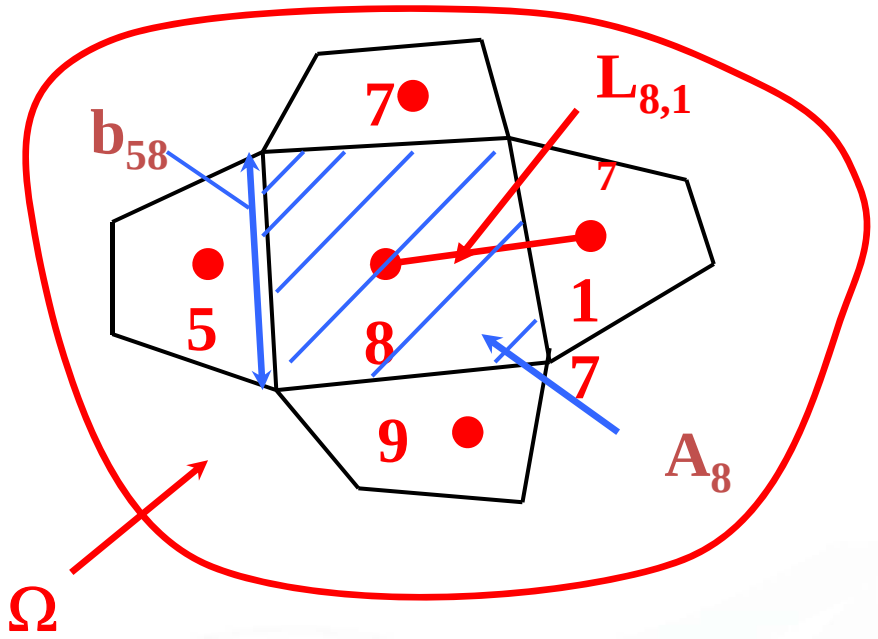


Eulerian numerical modeling

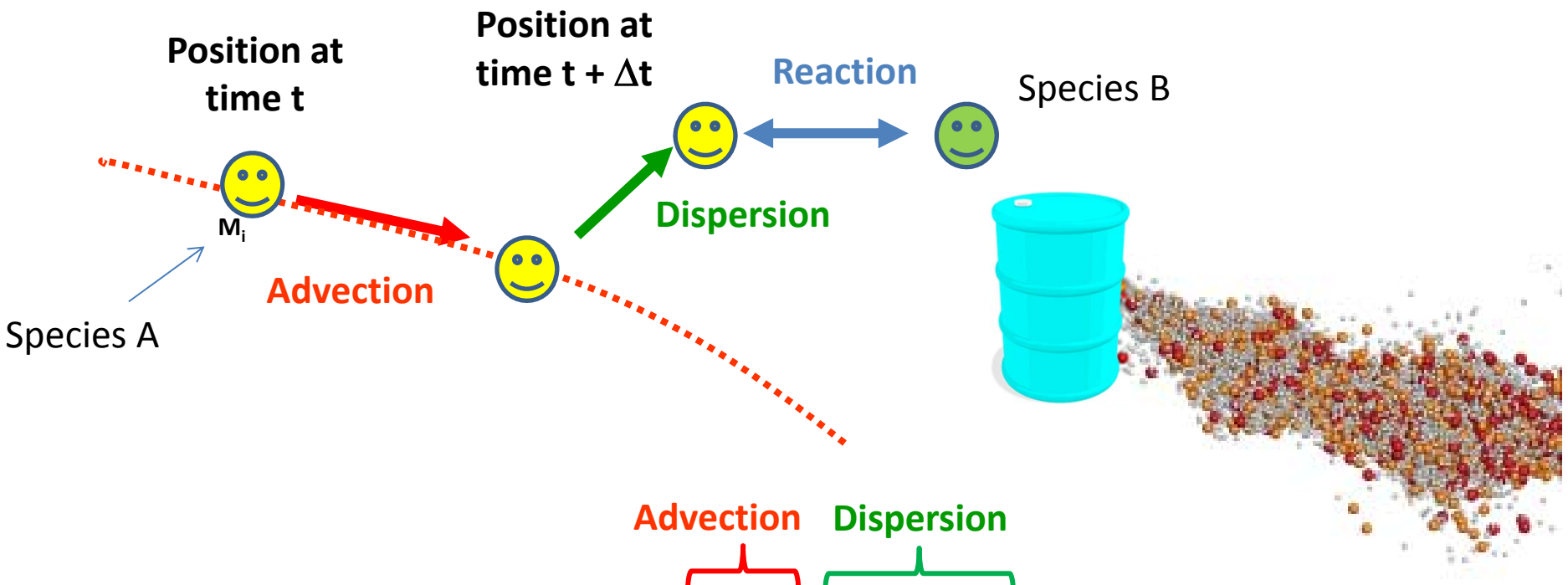
- Domain discretization
- The problem is reduced to solve a system of equations

$$\boldsymbol{E}\,\boldsymbol{c} + \boldsymbol{F}\frac{d\boldsymbol{c}}{dt} = \boldsymbol{G}$$

- Time discretization
- Calculate state variables in time t^k and nodes or grid-cells



Lagrangian numerical modeling

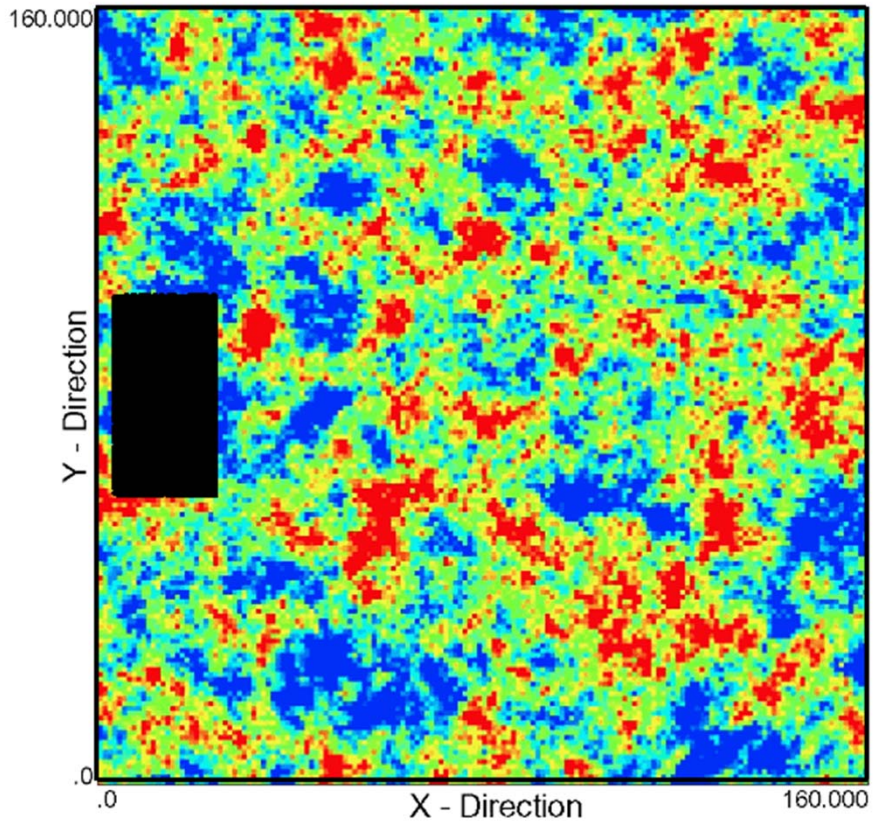


Advection Dispersion

Movement $$x_p(t + \Delta t) = x_p(t) + v\,\Delta t + \xi\sqrt{2D\,\Delta t}$$

Reactions $$s_p(t) \xrightarrow[\text{Reaction}]{\text{change of species}} s_p(t + \Delta t)$$

An example



Advantages and disadvantages

	Eulerian (mesh-based)	Lagrangian (meshless)
Advantages	• Well established and documented • Can be used with a wide range of chemical reactions and conditions • Comercial codes and softwares available	• Absence of numerical dispersion • Easy to incorporate anomolous transport and multiple porosity systems • Absence of artificial mixing • Computationally efficient
Limitations	• Susceptible to numerical dispersion and oscillations • Overestimation of reaction rates and mixing • Computationally demanding	• Not yet well established and doc • Limited number of chemical reactions available • Statistical fluctuations from the reconstruction of concentrations based on limited number of particles

Can we really simulate chemical reactions with an Eulerain?

A simple example

$A + B \rightarrow M$

$$\phi \frac{\partial A}{\partial t} = -\boldsymbol{q}\nabla A + \nabla \cdot (\phi \boldsymbol{D} \nabla A) + \phi\, r \quad \text{Species A}$$

$$\phi \frac{\partial B}{\partial t} = -\boldsymbol{q}\nabla B + \nabla \cdot (\phi \boldsymbol{D} \nabla B) + \phi\, r \quad \text{Species B}$$

$$A\,B = K_{sp} \quad \text{Equilibrium}$$

Three coupled equations 2 of them PDE (non-linear system)

De Simoni et al. (2005)

$$r(\boldsymbol{x}, t) = f_{ch}\, \nabla u^t\, \boldsymbol{D}\, \nabla u \qquad \text{where} \quad u = A - B$$

chemistry mixing

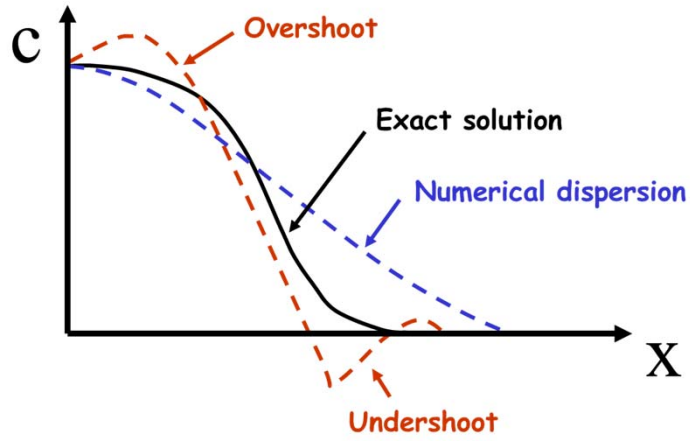
Implications to Eulerian Approaches

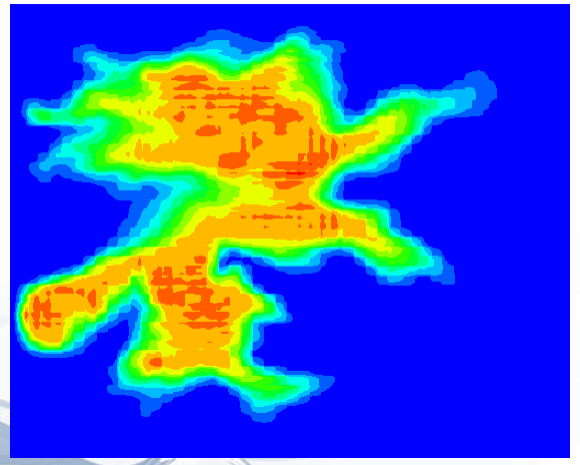
Affected by numerical dispersion

$$r(\boldsymbol{x}, t) = f_{ch}\, \nabla u^t\, \boldsymbol{D}\, \nabla u$$

Affected by truncation errors

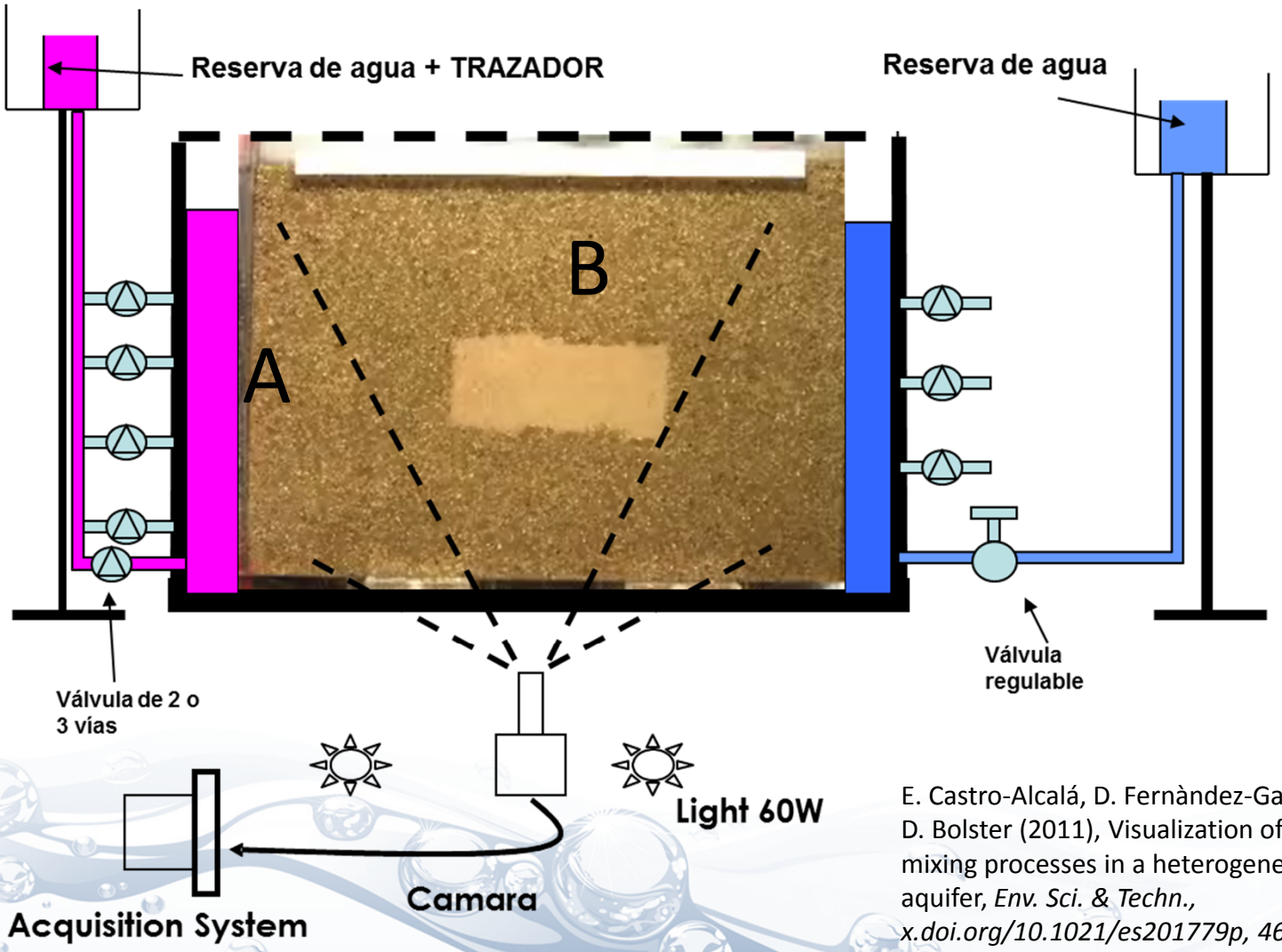
The role of heterogeneity





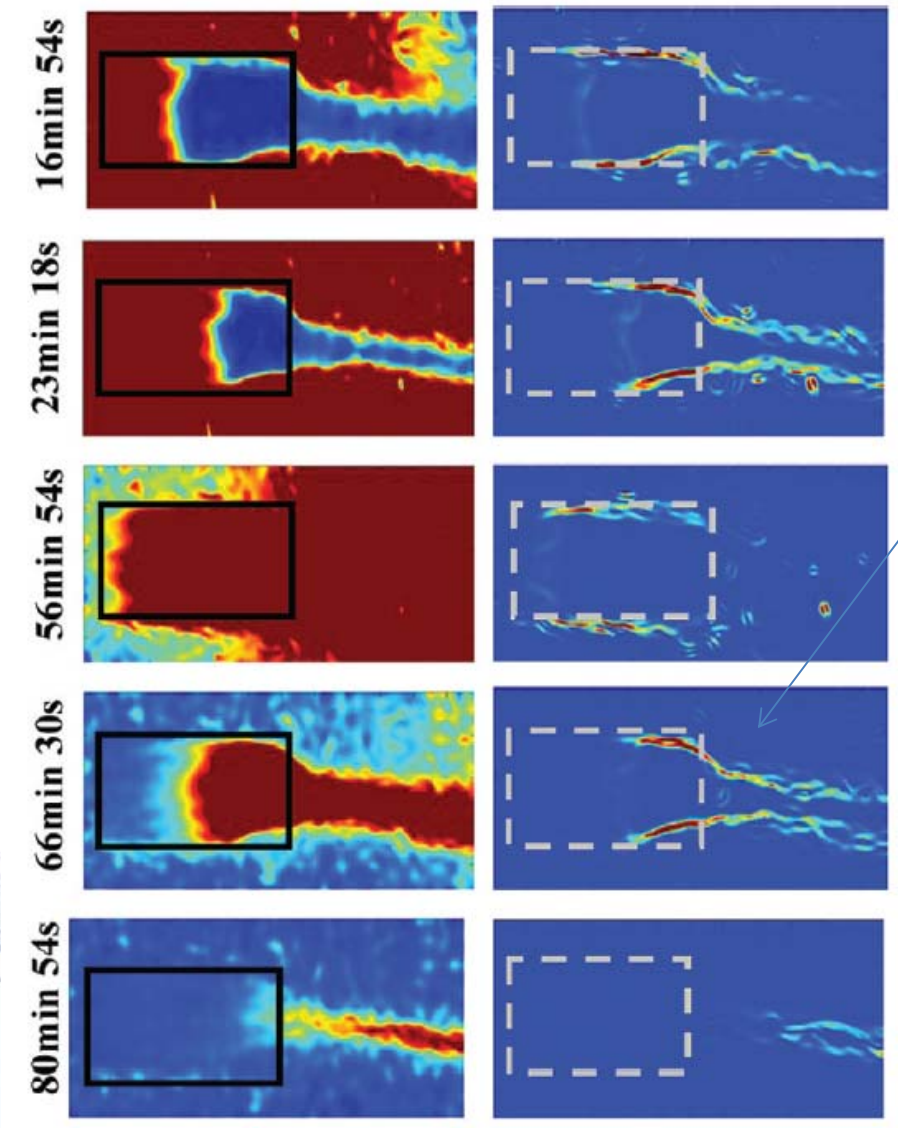
An experimental example

$$A + B \rightarrow M$$



E. Castro-Alcalá, D. Fernàndez-Garcia, J. Carrera, D. Bolster (2011), Visualization of pore-scale mixing processes in a heterogeneous sand box aquifer, *Env. Sci. & Techn., x.doi.org/10.1021/es201779p, 46, 3228−3235*

$$u = A - B \qquad r(\boldsymbol{x}, t) = f_{ch}\, \nabla u^t\, \boldsymbol{D}\, \nabla u \qquad A + B \rightarrow M$$



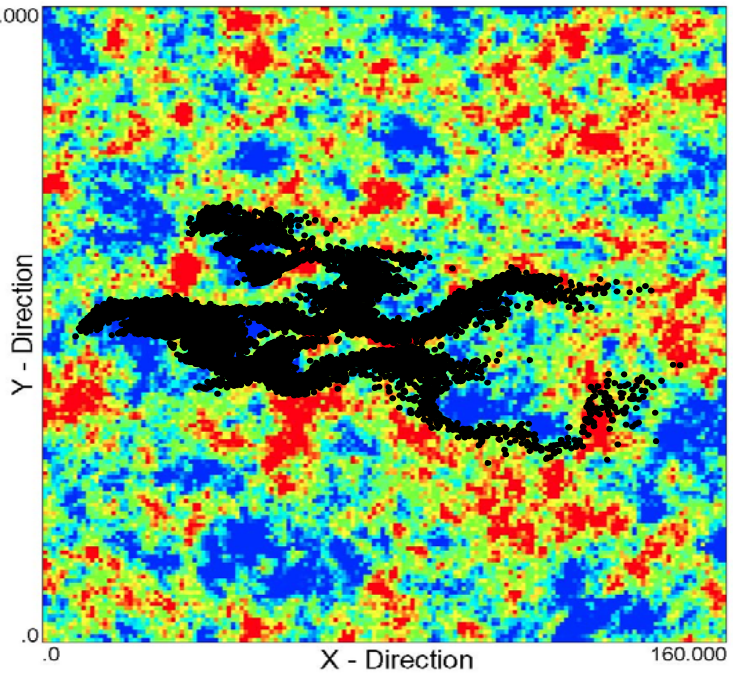
Reactions occur at a very small scale

Can we really simulate this with Eulerian Approaches ????

E. Castro-Alcalá, D. Fernàndez-Garcia, J. Carrera, D. Bolster (2011), Visualization of pore-scale mixing processes in a heterogeneous sand box aquifer, *Env. Sci. & Techn., x.doi.org/10.1021/es201779p, 46, 3228–3235*

Lagrangian techniques are attractive then

- Abscence of numerical dispersion
- Computationally efficient
- Well suited for heterogeneities
- Easy to incorporate:
  - Non-Fickian transport (FADE, CTRW..)
  - Multi-rate mass transfer processes
  - Incomplete mixing
- Chemical reactions with simple probabilistic rules



But still suffers from…

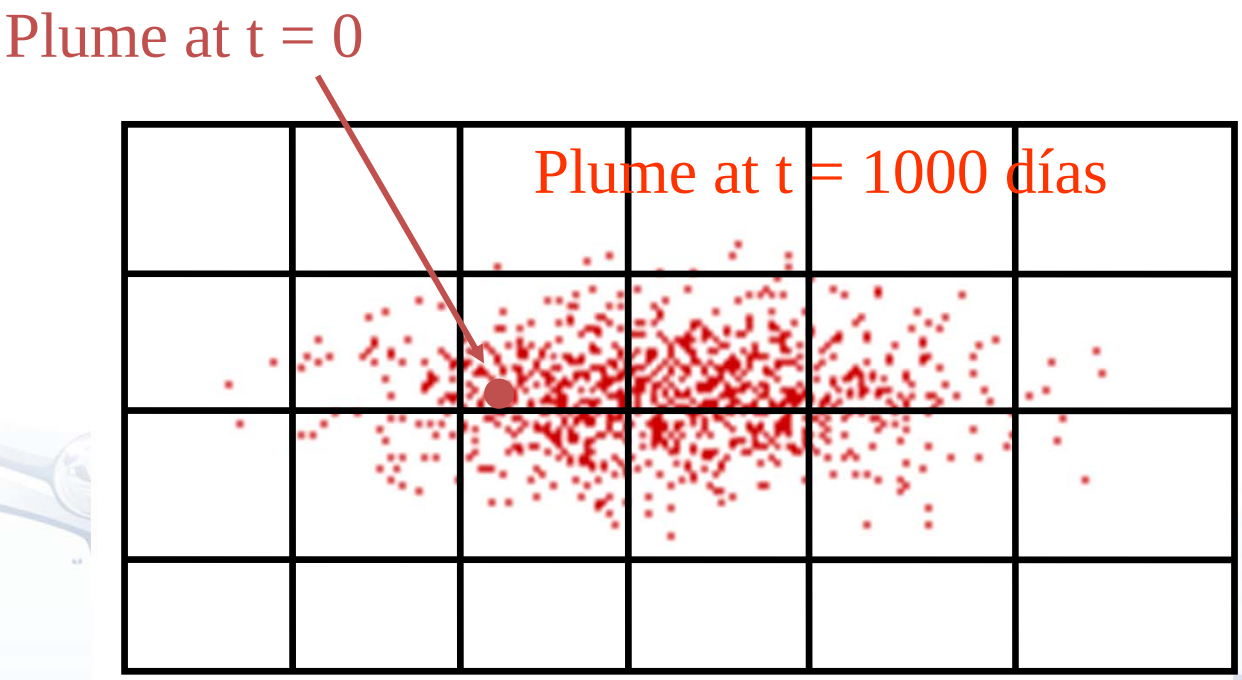
- Sometimes we need many particles to obtain accurate estimates of concentrations and their functionals (reaction rates)
  - **Kernel density estimates** reduces the number of particles maintaining accuracy

- Multispecies reactive transport is challenging but we can use:
  - conservative components when reactions are in equilibrium
  - **State Transition Probabilities** when kinetic reactions
  - **Interaction between nearby particles**

Problems stemming from the reconstruction of c(x,t) from particle distributions have prevented its use in reactive transport problems

Counting particles in bins

$$c \approx \sum_{p} \frac{m_p I\{\mathbf{x} \in B_j\}}{\phi \Delta V_j}$$



$\alpha_T = 10$ m

$\alpha_L = 100$ m

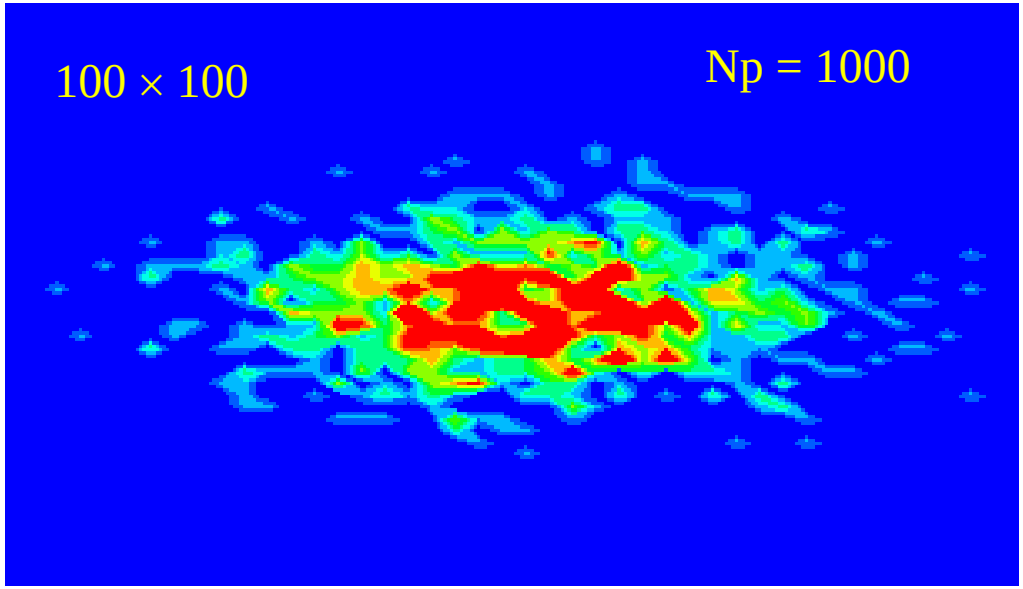
$v = 1$ m/dia

$\phi = 0.17$

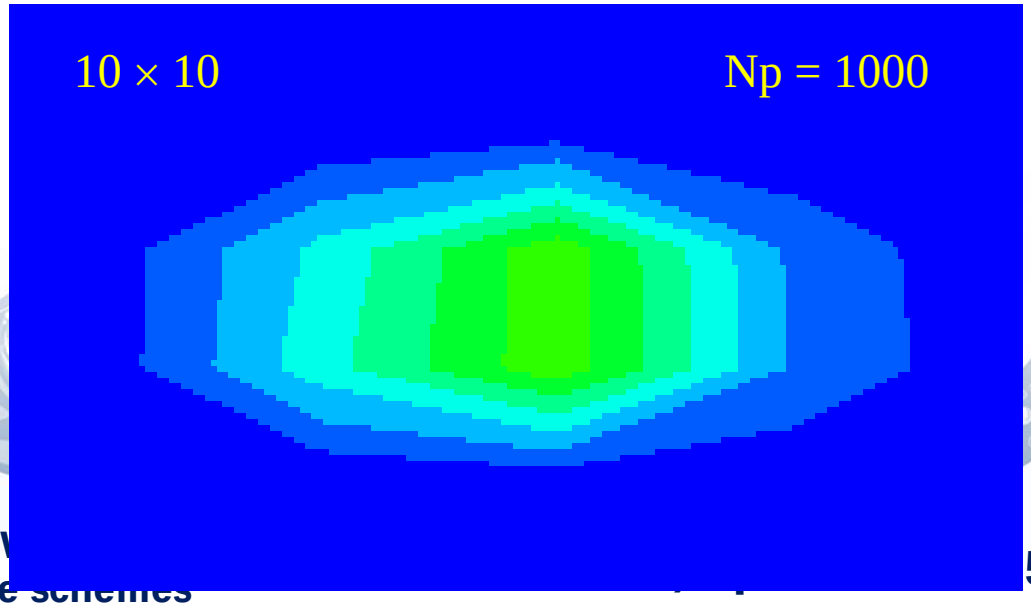
$N_p = 1000$

Fluctuations + Smoothing

- Undersmoothing → fluctuations



- Oversmooting → bias



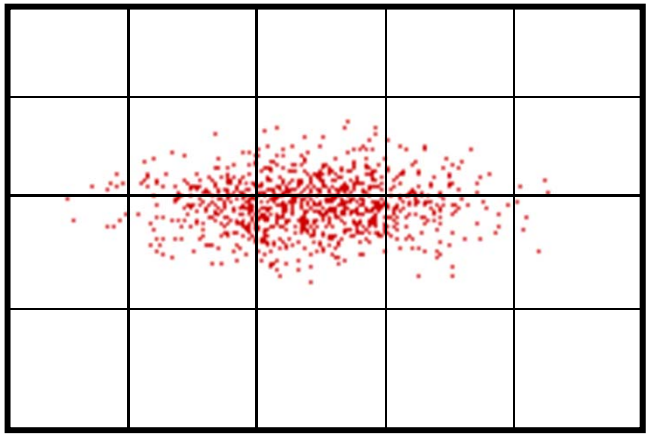
Fundamentals

Normalized concentrations

$$u \approx \hat{u} = \frac{1}{M_t} \sum_p m_p \frac{I(\mathbf{X}_p \in B_j)}{\Delta V_j}$$

Count particle mass in bins

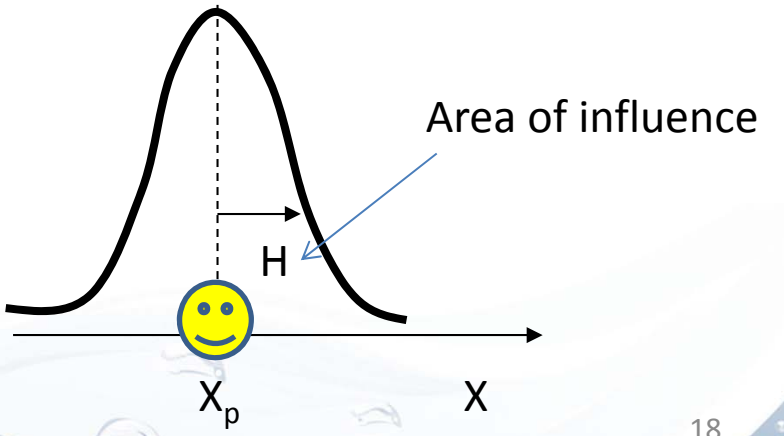
Traditional PDF estimation



Kernel PDF estimation

$$u \approx \hat{u} = \frac{1}{M_t} \sum_p m_p K_H(\mathbf{x} - \mathbf{X}_p)$$

K_H is the weight assigned to a particle



Advantages of Kernel estimation

- Since it is non-parametric, it allows identification of multimodal distributions and non-Fickian transport features
- It provides not only good estimates of concentrations but also of their functionals (gradients, mixing, reaction rates…)
- It can be used to directly estiate the optimal area of influence H !!!! → key for the interaction between nearby particles in modeling nonlinear chemical reactions

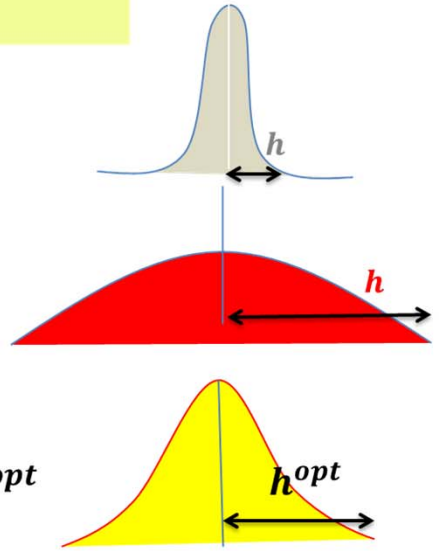
Optimal estimates of H exist !!!

h : **Smoothing parameter** defines how the particle attributes can influence the concentrations

Small support combined with a finite number of particles leads to very **noisy estimates** $h \downarrow$

whereas an increase in the support tends to **over smooth** the estimated concentration distribution $h \uparrow$

optimum choice of the support size h^{opt}



Kernel Density Estimators (KDE) provide a convenient mathematical framework to obtain this optimal support

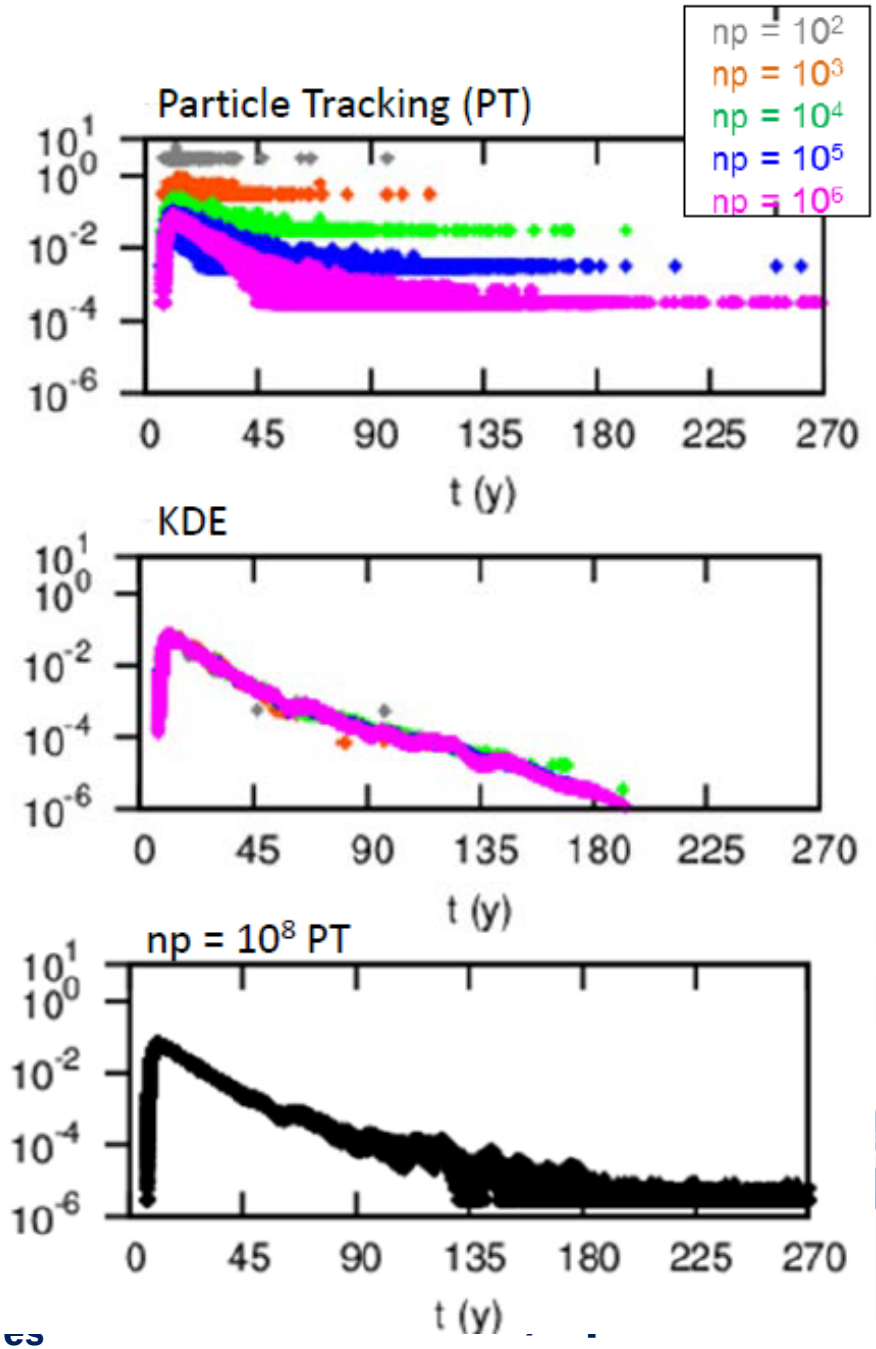
The same can be done for mixing, risk metrics,…

D. Fernàndez-Garcia, X. Sanchez-vila, Optimal reconstruction of concentrations, gradients and reaction rates from particle distributions, *Journal Contam. Hydrol.*, 120-21 (2011) 99–114, doi: 10.1016 / j.jconhyd. 2010.05.001.

Reconstructing concentrations…

- If the number of particles (*np*) is too low, raw particle tracking (PT) BTCs will not produce local peaks, nor will the environmental concentration (input into risk equation) be represented correctly

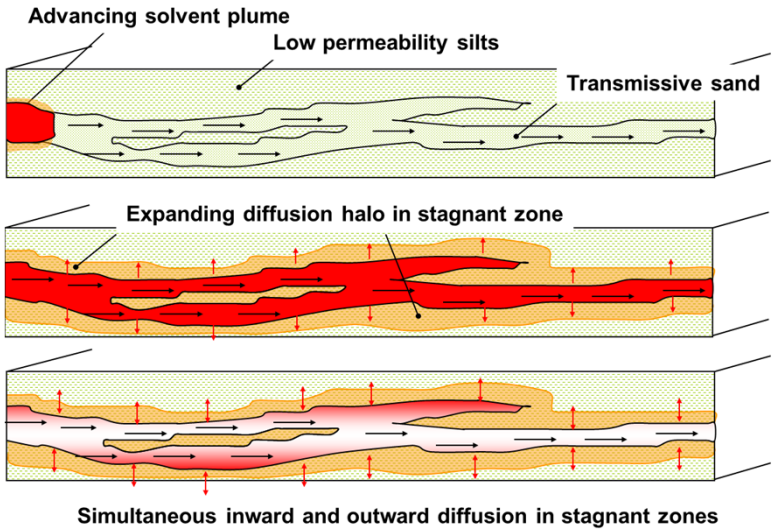
- Remarkably, even simulations with $np=10^2$ (gray points), KDEs can reproduce the main features of BTCs

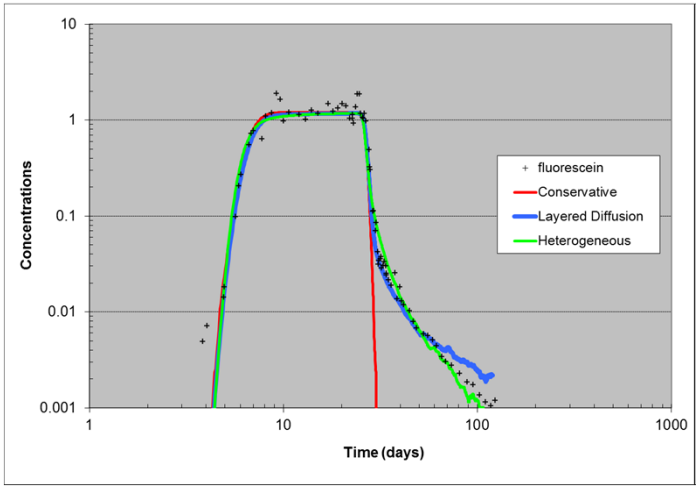


Siirila-Woodburn, E. R., D. Fernàndez-Garcia, and X. Sanchez-Vila (2015), Improving risk metrics with the use of kernel density estimators in breakthrough curve reconstruction from particle distributions, Water Resour. Res., In review.

What about tailing…

D. Pedretti and D. Fernàndez-Garcia (2013), An automatic locally-adaptive method to estimate heavily-tailed breakthrough curves from particle distributions, *Advances in Water Resources,* 59, 52–65.

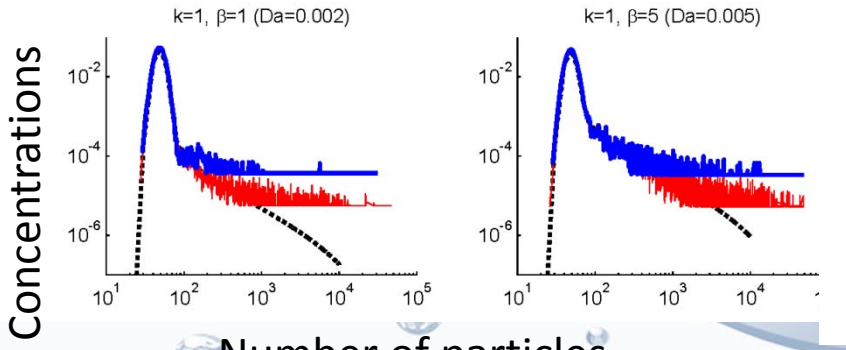


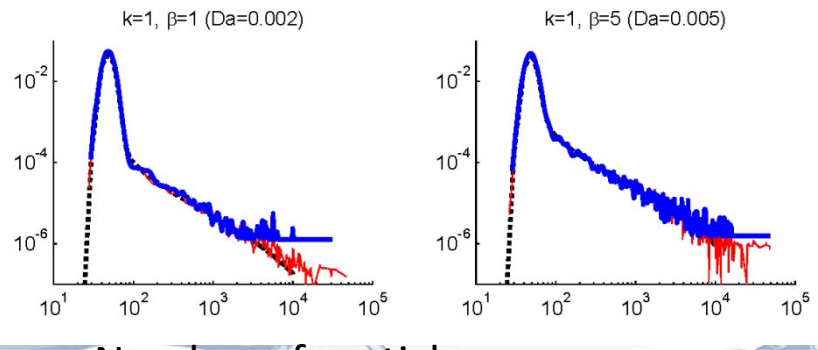


$$c(t) \approx \frac{1}{Q} \sum_{i=1}^{n} \frac{m_i}{h} K\left(\frac{t - t_i}{h}\right)$$

$$c(t) \approx \frac{1}{Q} \sum_{i=1}^{n} \frac{m_i}{h_i} K\left(\frac{t - t_i}{h_i}\right)$$

Locally adaptive h

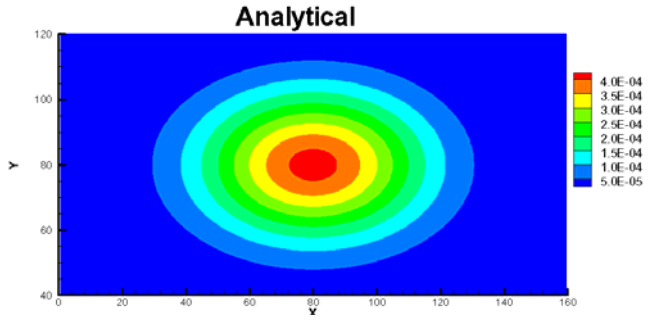




What about reaction rates…

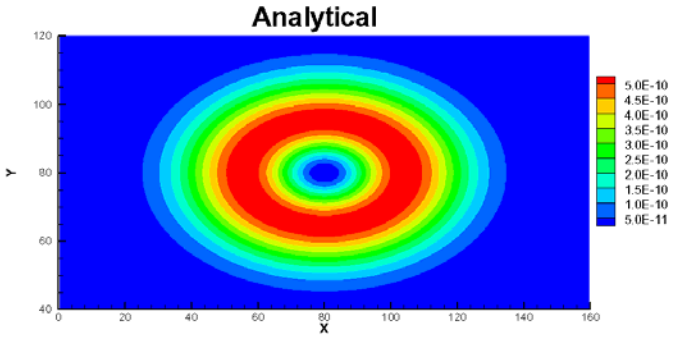
$A + B \rightarrow M$

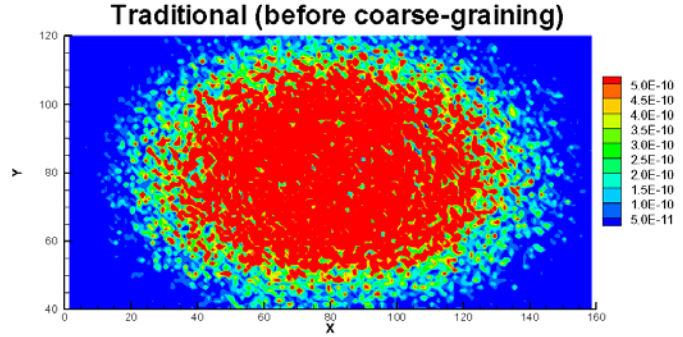
Concentrations

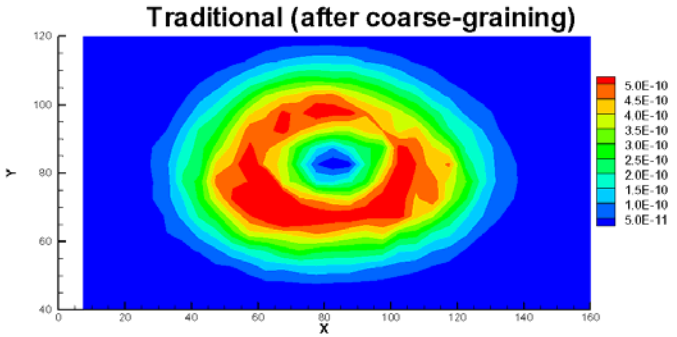


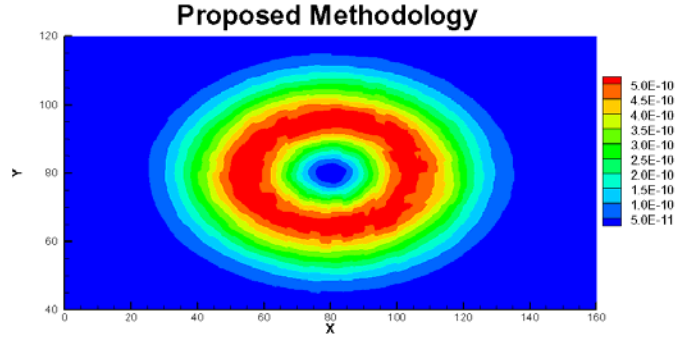
$$\mathbf{r} = \phi \mathbf{H} \nabla \mathbf{u}^t \mathbf{D}_d \nabla \mathbf{u}$$

Reaction rates



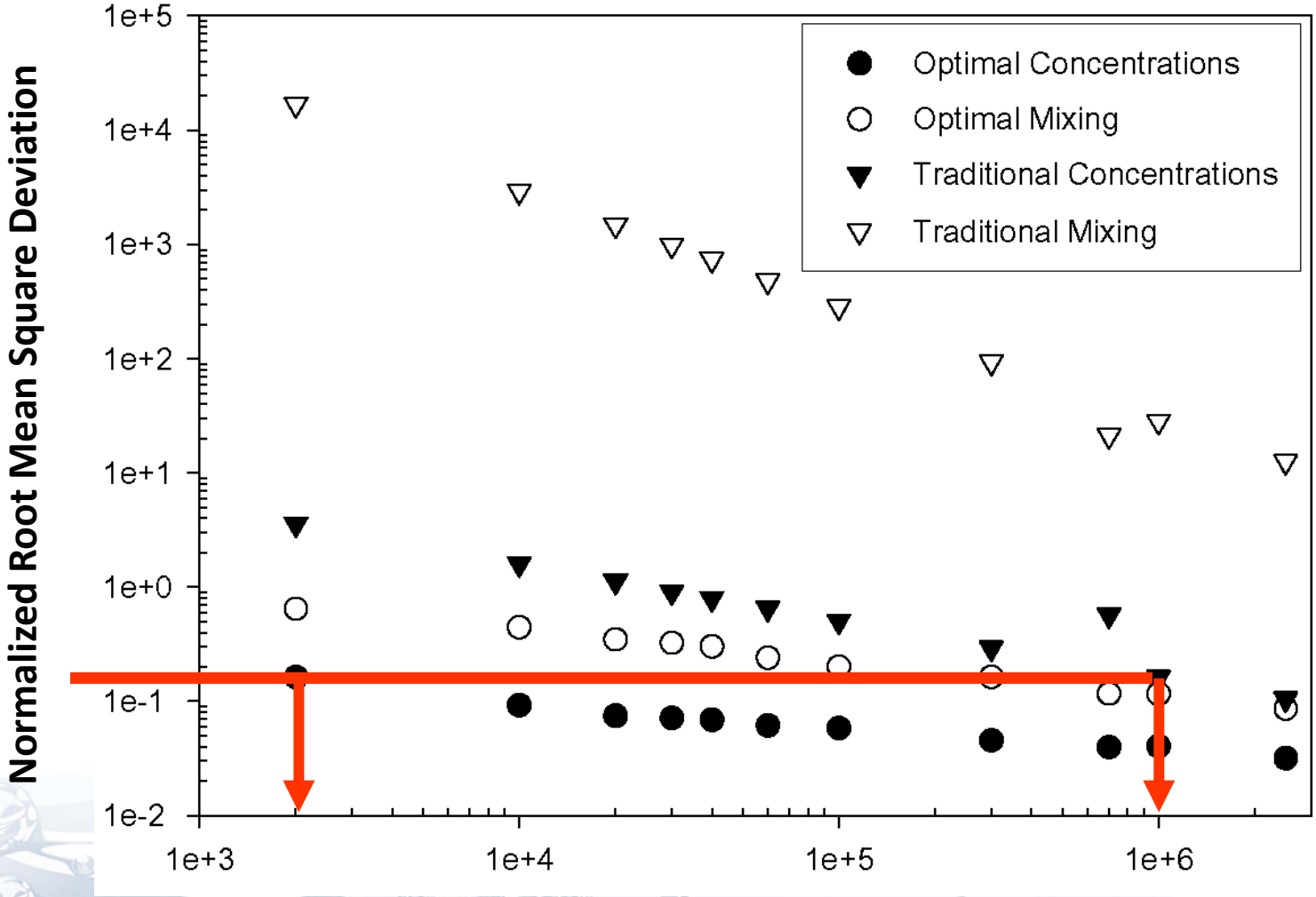






D. Fernàndez-Garcia, X. Sanchez-vila, Optimal reconstruction of concentrations, gradients and reaction rates from particle distributions, *Journal Contam. Hydrol.,* 120-21 (2011) 99–114, doi: 10.1016 / j.jconhyd. 2010.05.001.

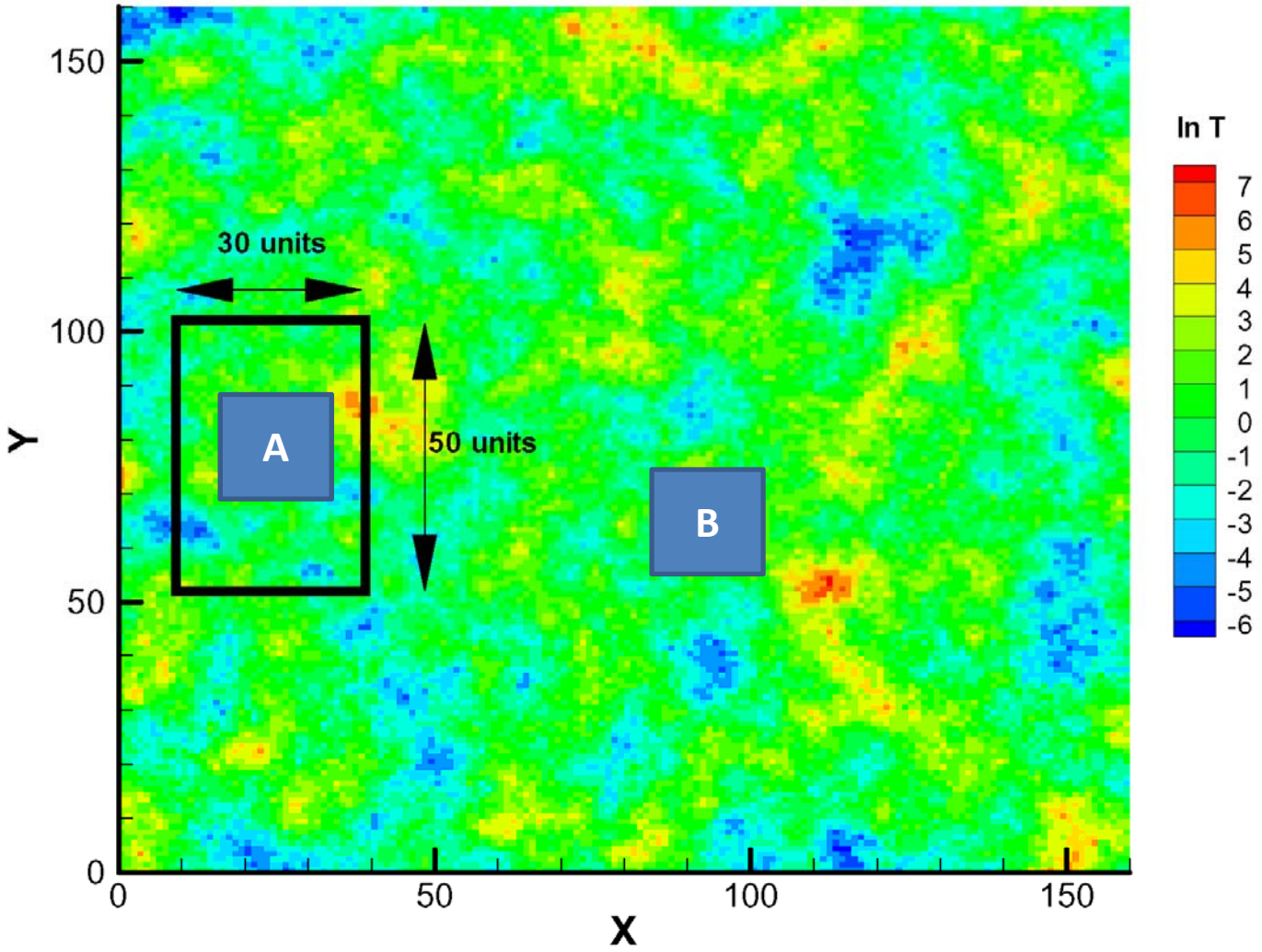
Performance



D. Fernàndez-Garcia, X. Sanchez-vila, Optimal reconstruction of concentrations, gradients and reaction rates from particle distributions, *Journal Contam. Hydrol.,* 120-21 (2011) 99–114, doi: 10.1016 / j.jconhyd. 2010.05.001.

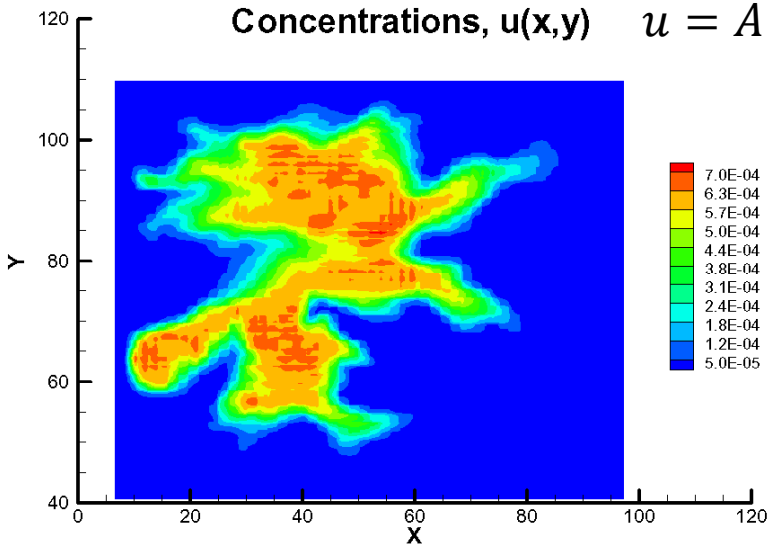
What happens in heterogeneous media ??

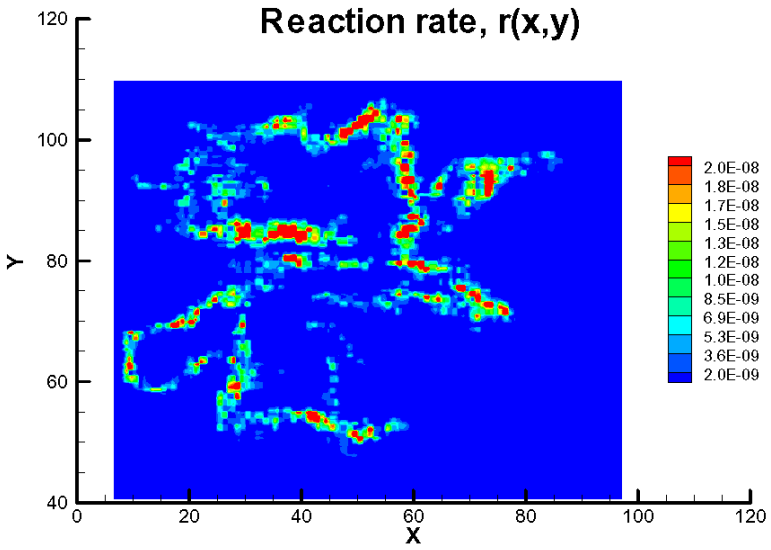
$$A + B \rightarrow M$$



Heterogeneous media

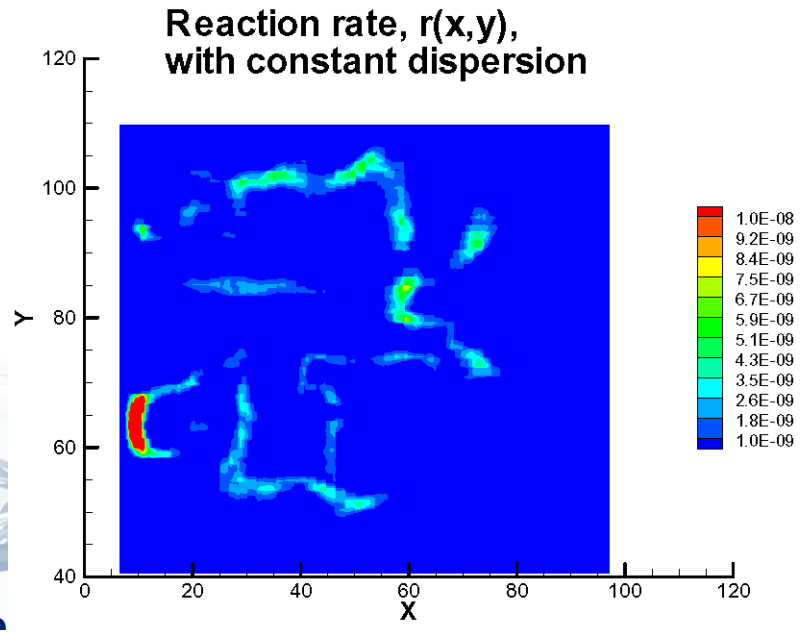
$A + B \rightarrow M$





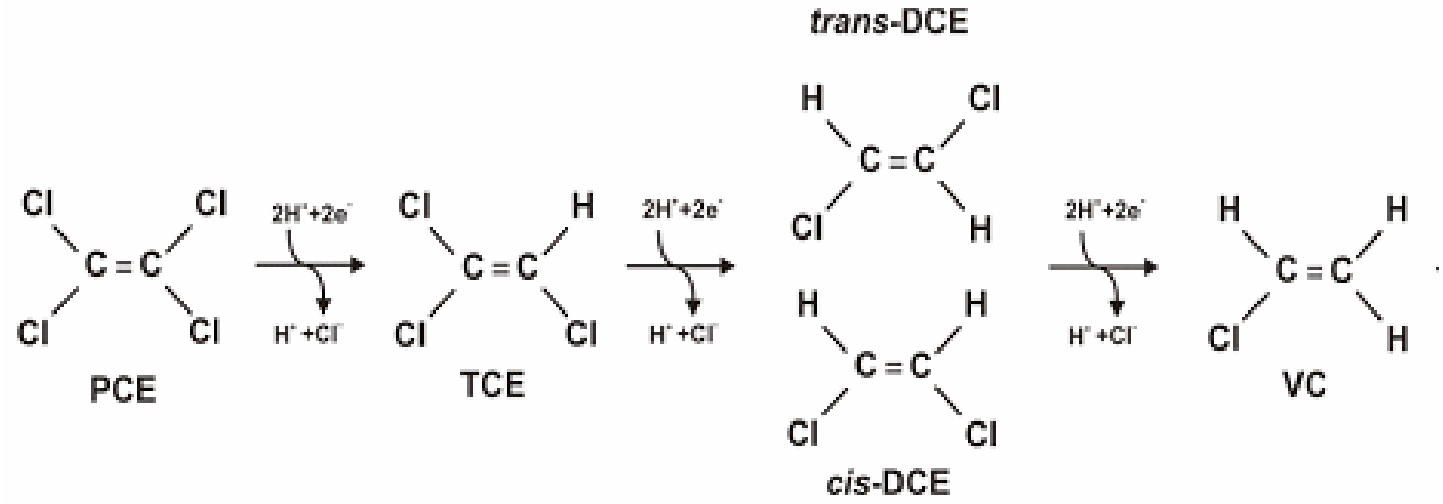
Reaction rate:

$$\mathbf{r} = \phi \mathbf{H} \nabla \mathbf{u}^t \mathbf{D}_d \nabla \mathbf{u}$$



Use of state transition probabilities (kinetic)

Let us consider network reactions, for instance



$$\phi R_i \frac{\partial c_i}{\partial t} - \nabla \cdot (\phi D \nabla c_i) + \nabla \cdot (\phi v c_i) = y_i k_{i-1} \phi c_{i-1} - k_i \phi c_i$$

Radioactive species, pesticides, organic phosphates, and nitrogen species transformations have been also typically modeled through first-order network reactions [e.g., van Genuchten, 1985; Mishra and Mishra, 1991; Vishwanathan et al., 1998].

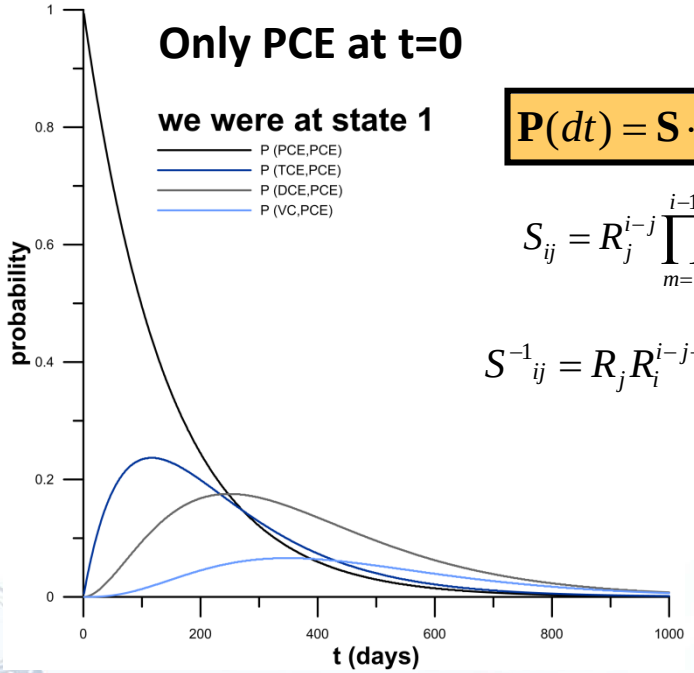
State Transition Probabilities

Definition: A state transition probability denotes the probability that a particle being presently **species *j*** will be **species *i*** a time *dt* later.

Henri, C. V., and D. Fernàndez-Garcia (2014), Toward efficiency in heterogeneous multispecies reactive transport modeling: A particle-tracking solution for first-order network reactions, *Water Resour. Res.*, 50, doi:10.1002/2013WR014956.

$$\mathbf{P}(dt) = \begin{bmatrix} P_{11} & P_{12} & \cdots & P_{1n} \\ P_{21} & P_{22} & \cdots & P_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ P_{n1} & P_{n2} & \cdots & P_{nn} \end{bmatrix}$$

prob. species 2 will turn into species n after a time dt



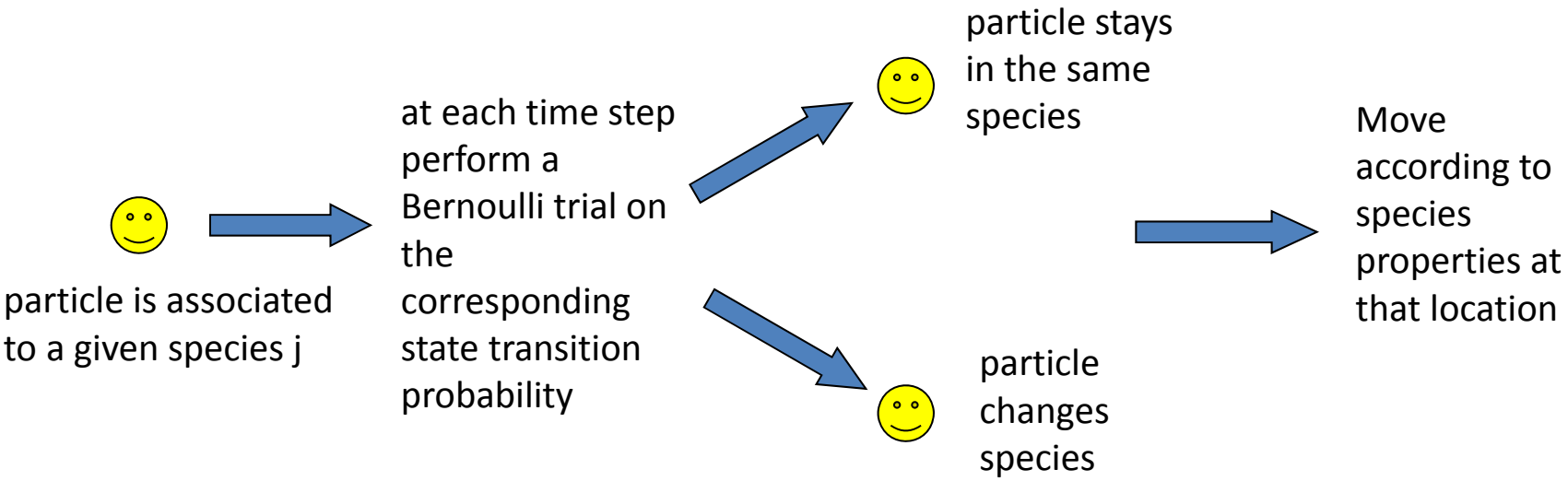
$$\mathbf{P}(dt) = \mathbf{S} \cdot \exp\left(\mathbf{K}' dt\right) \cdot \mathbf{S}^{-1}$$

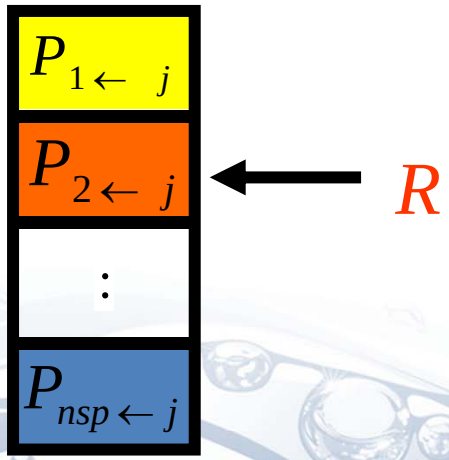
$$S_{ij} = R_j^{i-j} \prod_{m=j}^{i-1} \frac{k_m y_{m+1}}{R_j k_{m+1} - R_{m+1} k_j}$$

$$S^{-1}{}_{ij} = R_j R_i^{i-j-1} \prod_{m=j}^{i-1} \frac{-k_m y_{m+1}}{R_m k_i - R_i k_m}$$

$$K'_{ii} = -\frac{k_i}{R_i}$$

Application of state transition probabilities



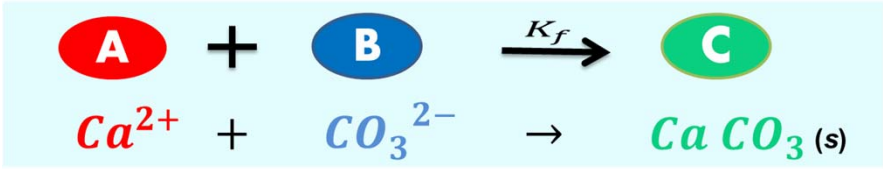


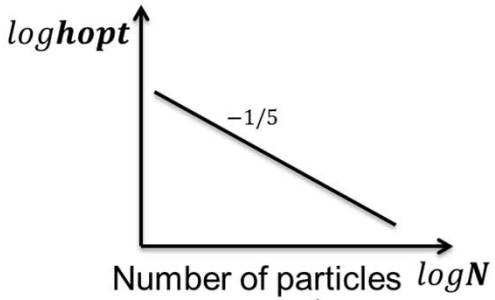
Find the new species after a time dt by generating a random number *R*

Henri, C. V., and D. Fernàndez-Garcia (2014), Toward efficiency in heterogeneous multispecies reactive transport modeling: A particle-tracking solution for first-order network reactions, *Water Resour. Res.*, 50, doi:10.1002/2013WR014956.

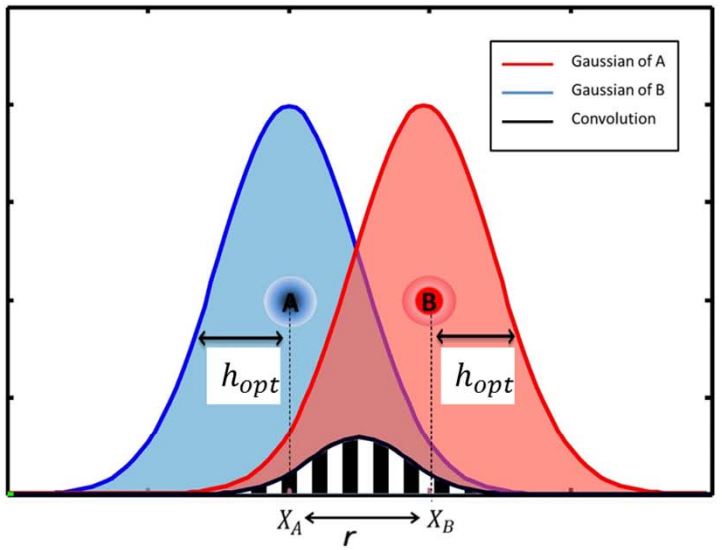
Interactions between nearby particles

Non-linear reactions





$$h_{opt} = c \,.\, N^{-\frac{1}{5}}$$



Broader range for lower number of particles

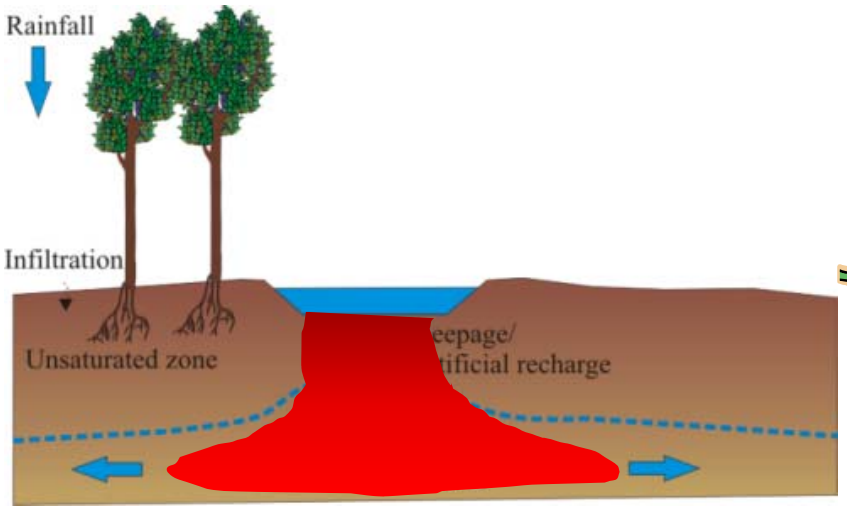
More particles come into contact with the decay of particles

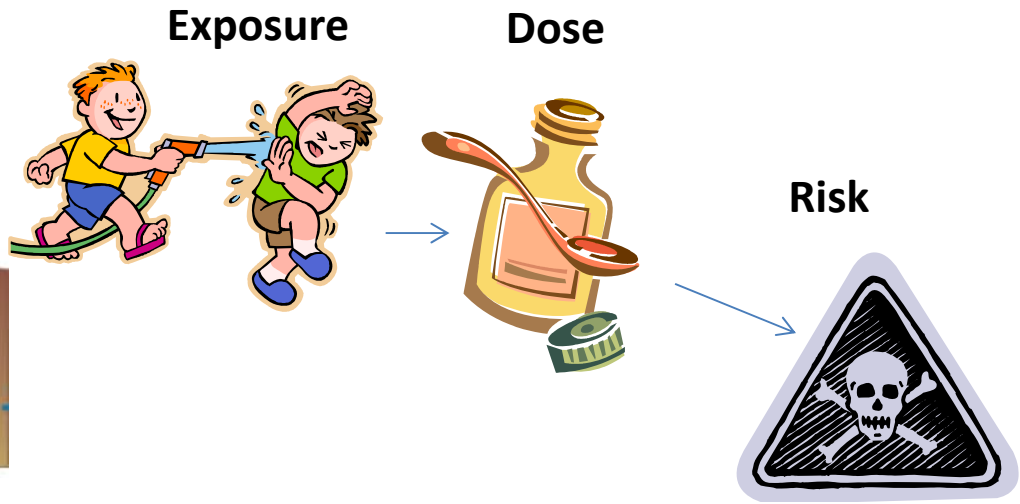
More probability of chemical reactions

$$P_{KDE}(r) = \frac{1}{2h_{opt}\sqrt{\pi}} \exp\left(\frac{-r^2}{4{h_{opt}}^2}\right)$$

M. Rahbaralam, D. Fernàndez-Garcia, X. Sanchez-Vila (2015), Modeling non-linear reactive transport with kernel density functions

Human health risk assessment





However, one should carefully examine the danger of damaging an aquifer's water quality by recharging it with water containing toxic pollutants → we need to assess the risk to sensitive locations (humans and ecosystems)

Recycled water can suppose a major health risk associated to microbial pathogens and emerging contaminants

Carcinogenic risk is defined by a **toxicity** parameter, exposure **time** parameters, and by the environmental **concentration**

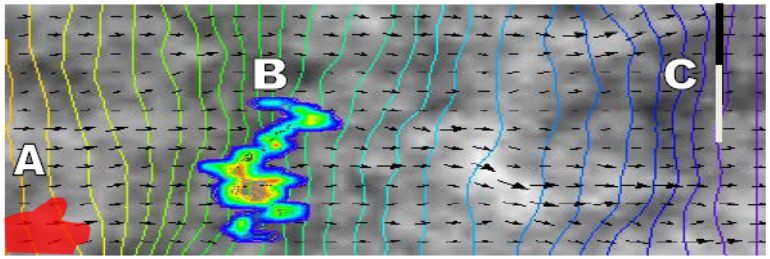
$$Risk = 1 - e^{CPF_{metal,i} \times ADD_{metal,i}}$$

Toxicity Value: Cancer Potency Factor *(CPF)*

Exposure Time : Average Daily Dose (*ADD*)

$$ADD_{metal,i} = \langle C \rangle \left[\frac{IN_i}{BW} \right] \frac{ED \times EF}{AT}$$

Environmental Concentration: $\langle C \rangle$



from ***Erica R. Siirila et al. (2014)***

There is considerable uncertainty in each of these categories

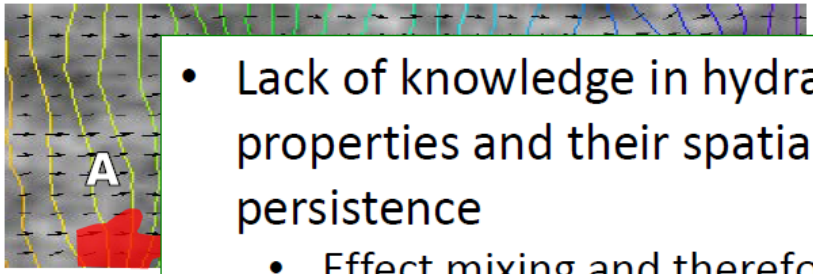
Toxicity Value:

- Dose-response variation in tested populations
- Extrapolations from animals to humans
- Extrapolation from sub-chronic to chronic studies

Exposure Time:

- Natural physiological variation in individuals
- Variation in exposure durations and frequencies

Environmental concentration:

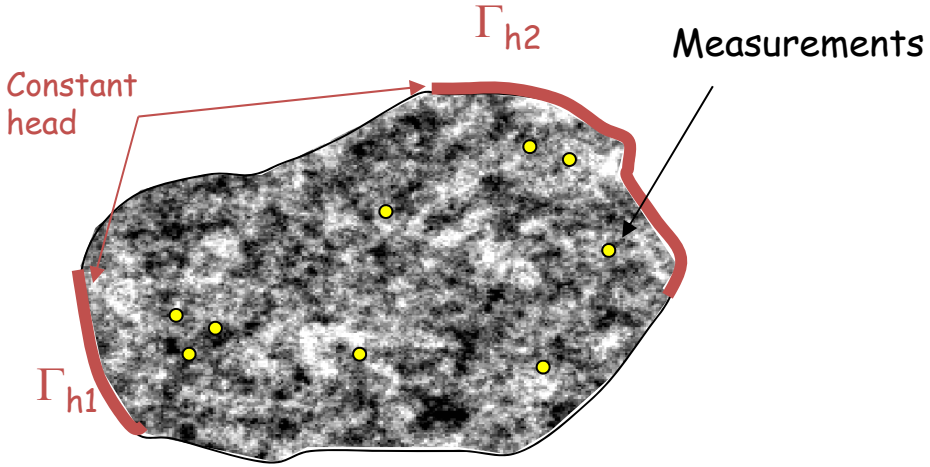


- Lack of knowledge in hydraulic properties and their spatial persistence
  - Effect mixing and therefore concentration dilution
- Uncertainty in geochemical processes, well capture, etc.

from ***Erica R. Siirila et al. (2014)***

Uncertainty & Lagrangian methods

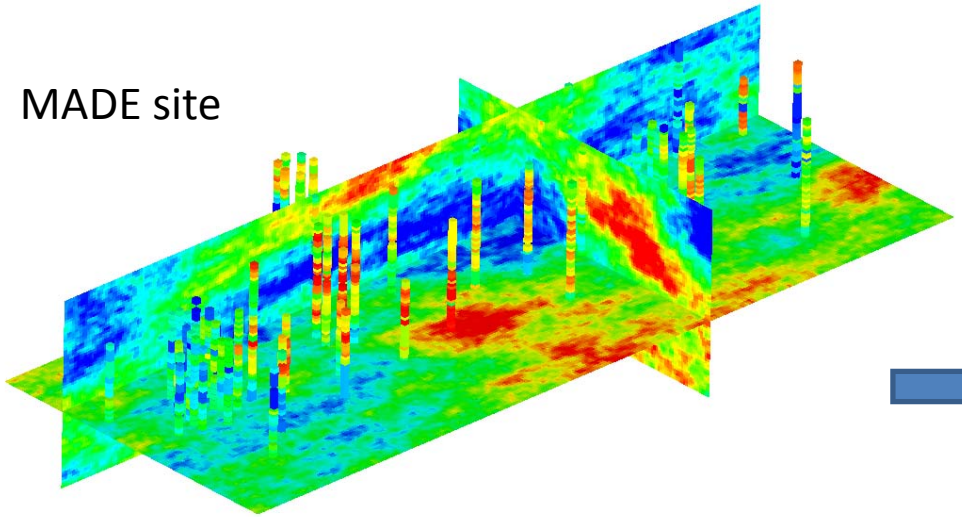
Subsurface properties largely unknown (K)



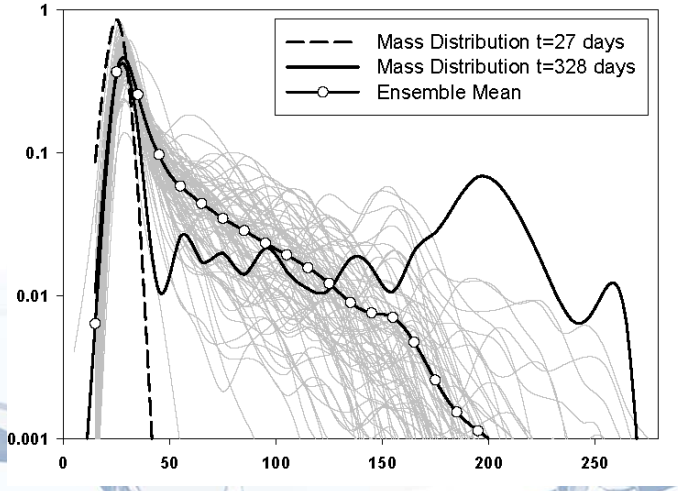
Determine preferential pathways, travel times and concentrations

Lagrangian methods are well suited for Monte Carlo Simulations

MADE site



Ensemble of concentrations



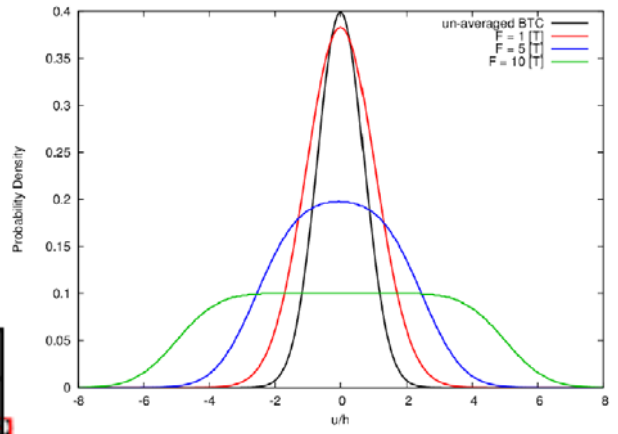
Salamon, P., Fernàndez-Garcia, D., J. J. Gómez-Hernández (2007), Modeling tracer transport at the MADE site: The importance of heterogeneity, *Water Resour. Res.*, 43, W08404, doi:10.1029/ 2006WR005522.

Kernels permit to estimate risk metrics directly from particles

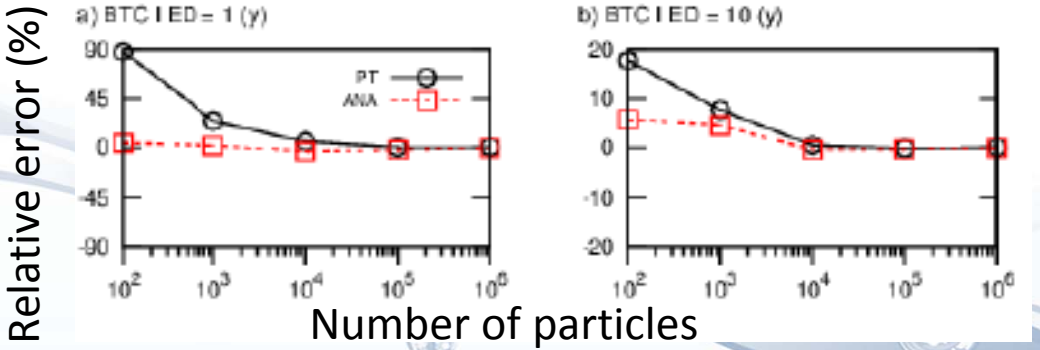
without an explicit calculation of concentrations, thus removing the propagation of statistical errors. Just need to modify the kernel according to exposure duration (ED)

$$K^*(t - t_i; h; ED) = \frac{1}{2\,ED}\left[\mathrm{erf}\left(\frac{u + ED/2}{\sqrt{2}\,h}\right) - \mathrm{erf}\left(\frac{u - ED/2}{\sqrt{2}\,h}\right)\right]$$

$$\langle C(t; ED)\rangle \approx \frac{1}{Q}\sum_{i=1}^{n} m_i K^*(t - t_i; h; ED)$$

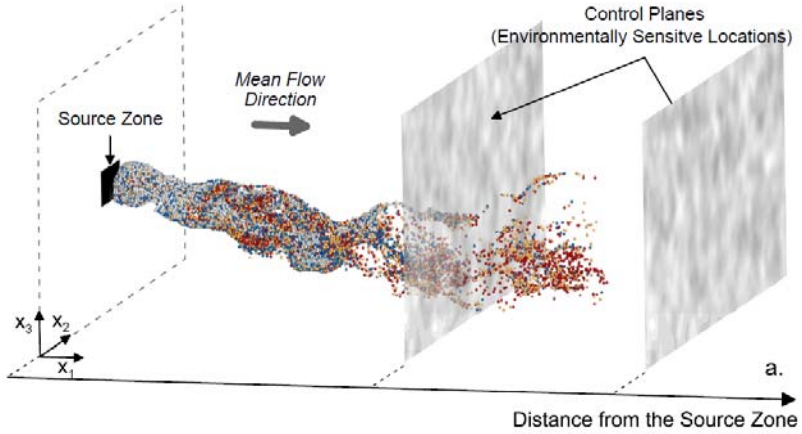


Performance



Siirila-Woodburn, E. R., D. Fernàndez-Garcia, and X. Sanchez-Vila (2015), Improving risk metrics with the use of kernel density estimators in breakthrough curve reconstruction from particle distributions, Water Resour. Res., In review.

Chemical mixtures and human health risk

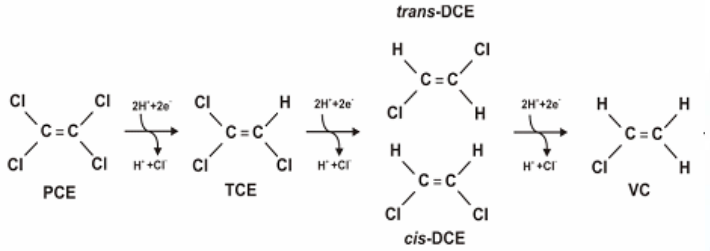


Before reaching a harmless chemical form, intermediate degradation products can constitute **new noxious chemical compounds not necessarily less toxic** than their parent product. In this situation, we have a hazardous **chemical mixture composed of products of different toxicity**.

We have a chemical cocktel

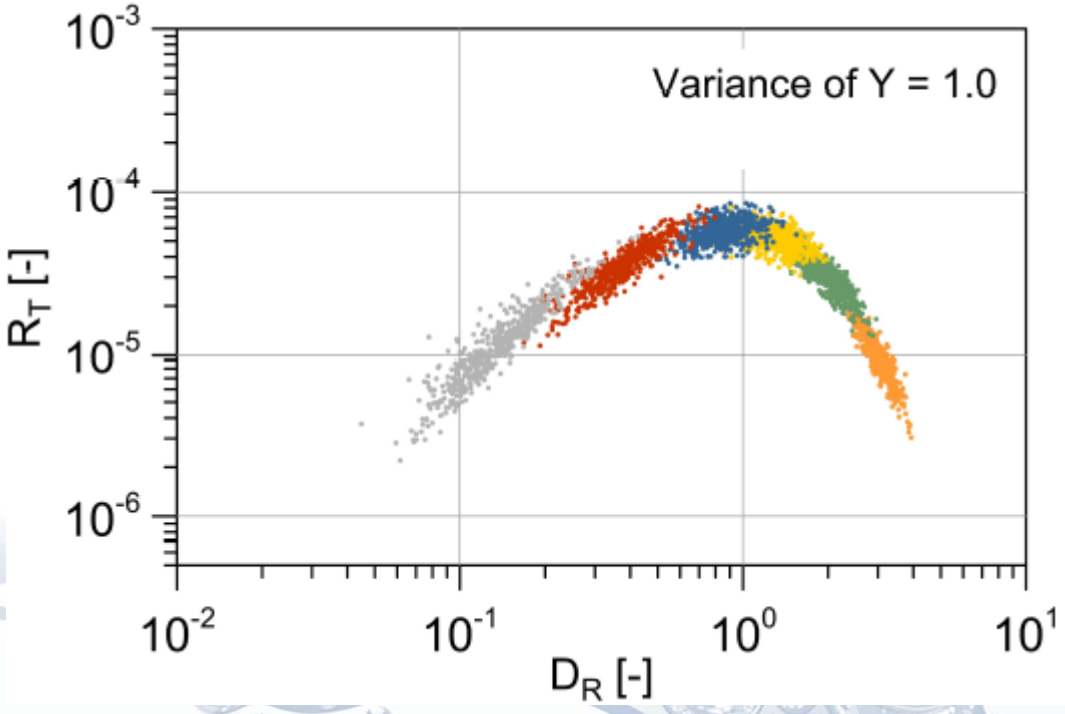
Additive human health risk model:

$$R_T(x) = R_{PCE} + R_{TCE} + R_{DCE} + R_{VC}$$



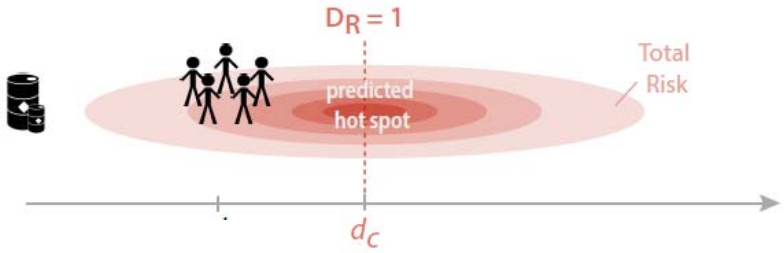
Hot spots: Areas of elevated risk in chemical mixtures

When the toxicity of intermediate products is larger than that of the parent species, the total risk can increase to a maximum (R_c) at a critical position (d_c) far from the source.



The critical position (d_c) is characterized by a toxicological-based Damkohler number

$$D_R = \frac{d}{d_c} = \frac{d}{v_a\, t_c}$$

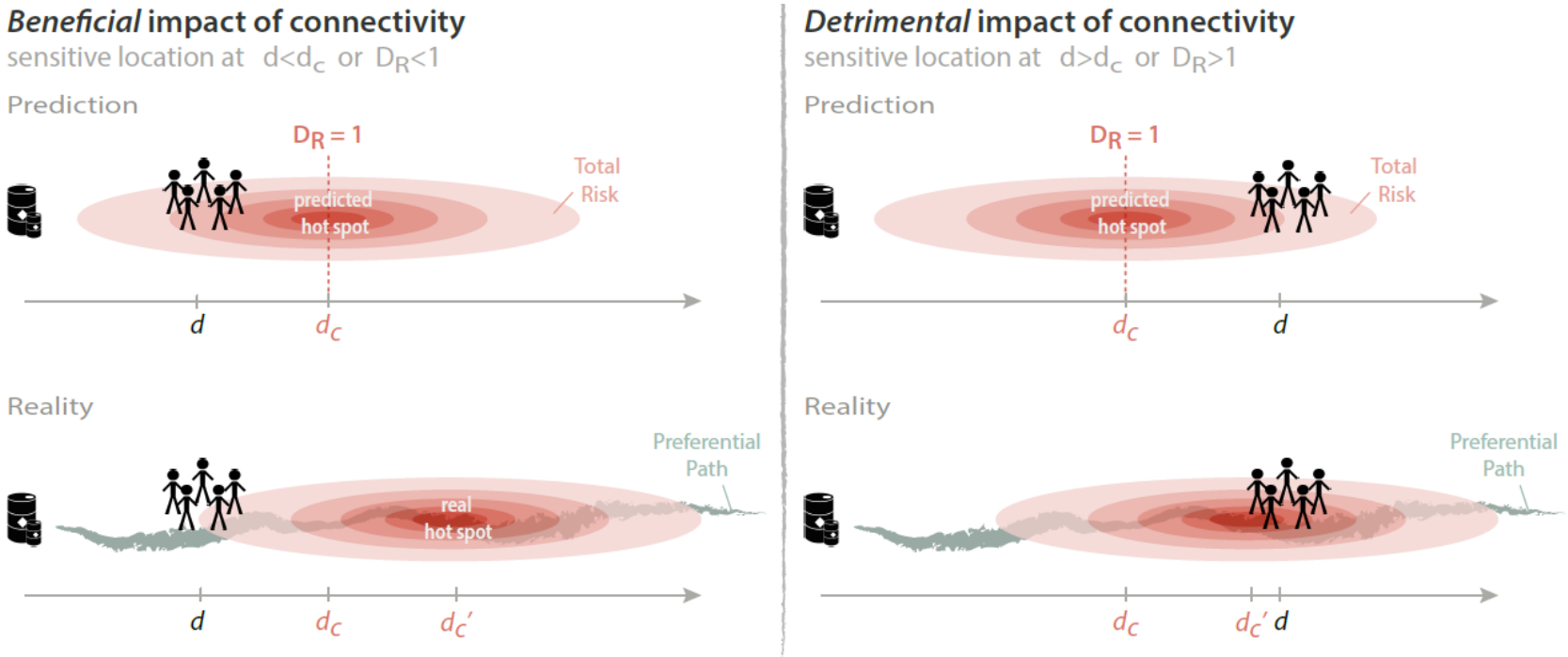


$$t_c = F(k_i, R_i, toxicology)$$

Derived analytically

Henri, C. V., D. Fernàndez-Garcia, F. P. J. deBarros (2015), Probabilistic Human Health Risk Assessment of Degradation-related Chemical Mixtures in Heterogeneous Aquifers: Risk Statistics, Hot Spots and Preferential Channels, *Water Resour. Res.*, In review.

Can preferential channels be beneficial ??? YES



$$d_c = v_a\, t_c \qquad t_c = F(k_i, R_i, toxicology)$$

Affected by heterogeneity and preferential channels → Uncertain

Henri, C. V., D. Fernàndez-Garcia, F. P. J. deBarros (2015), Probabilistic Human Health Risk Assessment of Degradation-related Chemical Mixtures in Heterogeneous Aquifers: Risk Statistics, Hot Spots and Preferential Channels, *Water Resour. Res.*, In review.

Escola de Camins
Escola Tècnica Superior d'Enginyeria de Camins, Canals i Ports
UPC BARCELONATECH

Grup d'hidrologia subterrània
UPC
CSIC

Thank you

- D. Fernàndez-Garcia, X. Sanchez-vila (2011), Optimal reconstruction of concentrations, gradients and reaction rates from particle distributions, *Journal Contam. Hydrol.,* 120-21, 99–114, doi: 10.1016 / j.jconhyd. 2010.05.001.
- Henri, C. V., and D. Fernàndez-Garcia (2014), Toward efficiency in heterogeneous multispecies reactive transport modeling: A particle-tracking solution for first-order network reactions*, Water Resour. Res.*, 50, doi:10.1002/2013WR014956.
- Henri, C. V., D. Fernàndez-Garcia, F. P. J. deBarros (2015), Probabilistic Human Health Risk Assessment of
- Degradation-related Chemical Mixtures in Heterogeneous Aquifers: Risk Statistics, Hot Spots and Preferential Channels*, Water Resour. Res.*, In review.
- M. Rahbaralam, D. Fernàndez-Garcia, X. Sanchez-Vila (2015), Modeling non-linear reactive transport with kernel density functions, To be submitted.
- Siirila-Woodburn, E. R., D. Fernàndez-Garcia, and X. Sanchez-Vila (2015), Improving risk metrics with the use of kernel density estimators in breakthrough curve reconstruction from particle distributions, Water Resour. Res., In review.
- D. Pedretti and D. Fernàndez-Garcia (2013), An automatic locally-adaptive method to estimate heavily-tailed breakthrough curves from particle distributions, *Advances in Water Resources,* 59, 52–65.
- E. Castro-Alcalá, D. Fernàndez-Garcia, J. Carrera, D. Bolster (2011), Visualization of pore-scale mixing processes in a heterogeneous sand box aquifer, Env. Sci. & Techn., x.doi.org/10.1021/es201779p, 46, 3228−3235