UNIVERSITAT POLITÈCNICA DE CATALUNYA
Department of Civil and Environmental Engineering
Hydrogeology Group GHS (UPC-CSIC)

WE-NEED

LAGRANGIAN METHODS FOR REACTIVE TRANSPORT IN HETEROGENEOUS POROUS MEDIA

Milan, Italy, June 12th, 2019

Presenting Author: Guillem SOLE-MARI (UPC)

Co-Authors: Daniel FERNÀNDEZ-GARCIA (UPC)

Diogo BOLSTER (Notre Dame)

Xavier SANCHEZ-VILA (UPC)

UNIVERSITAT POLITÈCNICA DE CATALUNYA
Department of Civil and Environmental Engineering
Hydrogeology Group GHS (UPC-CSIC)

TABLE OF CONTENTS

1. Introduction: Lagrangian models of transport & RWPT.

2. Kernel Density Estimation for reactive transport simulations.

3. Mixing-limited reactive transport.

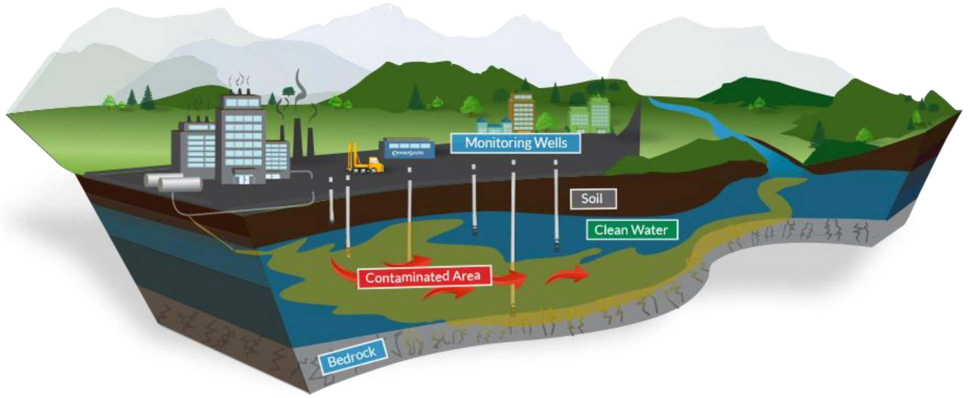
UNIVERSITAT POLITÈCNICA DE CATALUNYA
Department of Civil and Environmental Engineering
Hydrogeology Group GHS (UPC-CSIC)

WE-NEED

PART 1: LAGRANGIAN MODELS OF TRANSPORT AND RANDOM WALK PARTICLE TRACKING

LAGRANGIAN MODELS AND RWPT

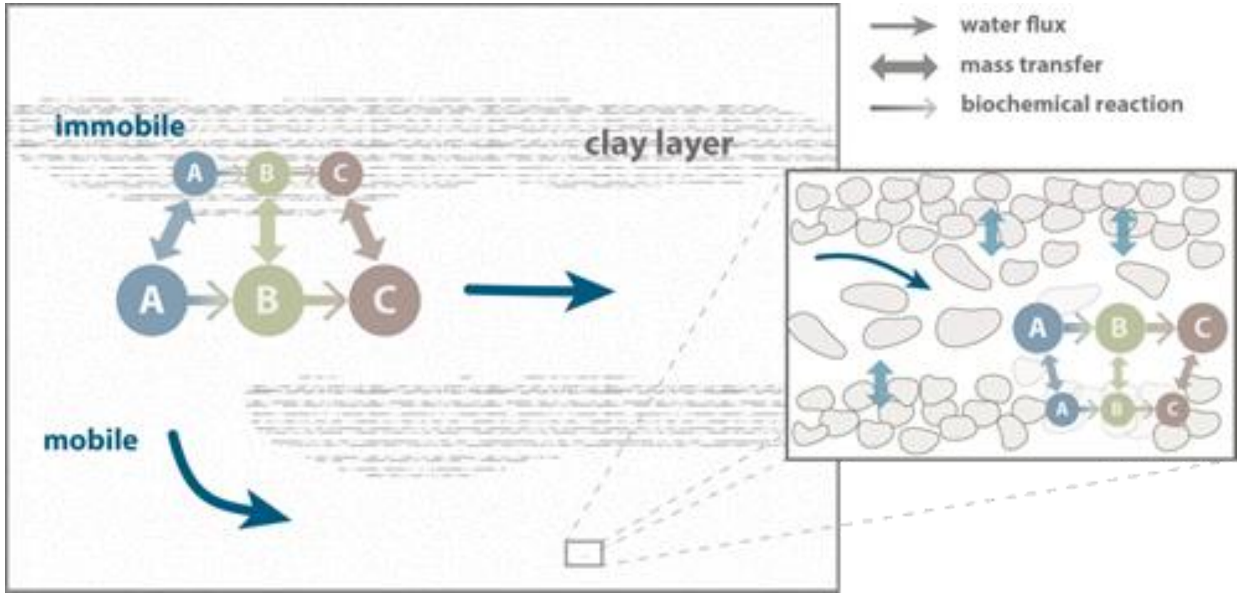
- Modeling of contaminant transport in aquifers is **important** for:
  - **Risk** assessment
  - Evaluation of **remediation** strategies
  - **Delimitation** of protection perimeters near recovery wells
  - **Characterization** of the hydraulic properties of the aquifer
  - (…)

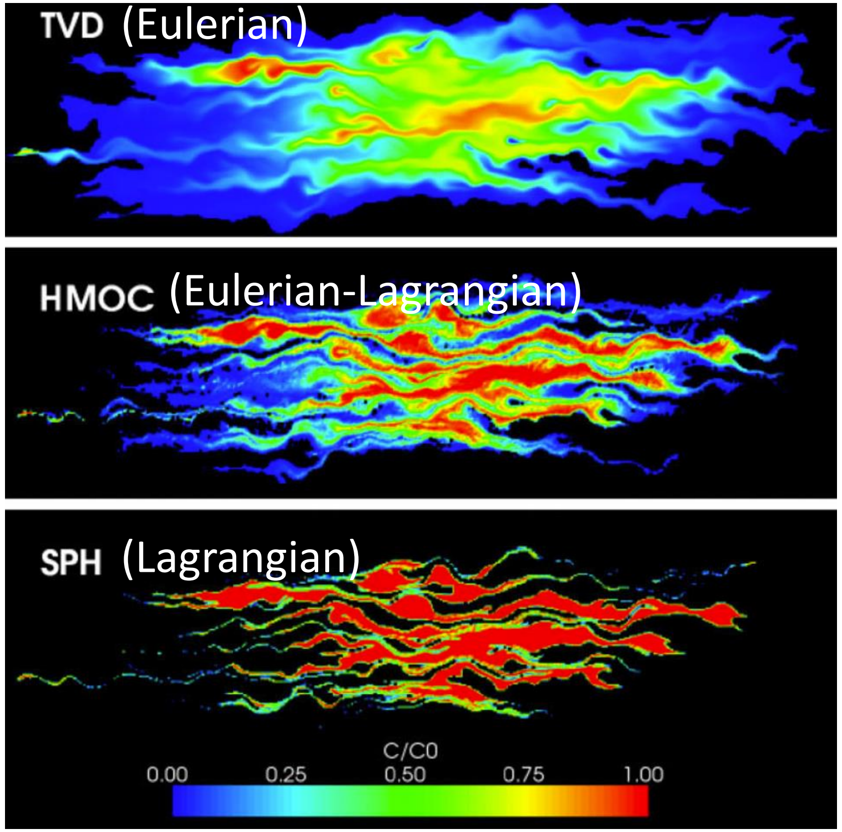


- Subsurface is complexly **heterogeneous** and observations are scarce.
- For these reasons, we need models to be **stochastic**.
- Two main groups of methods for numerical modeling of transport:
  - **Eulerian**
  - **Lagrangian**

LAGRANGIAN MODELS AND RWPT

- **Lagrangian** methods: Advect the numerical element (**particle**) and "remove" the advection term from the transport equation.
- Particularly good for **advection-dominated** problems. ($Pe \gg 1$)
- **Random-Walk Particle Tracking** (RWPT): Dispersion is modeled as random fluctuations of the particle displacement in a time step.
- Random variables in RWPT models can simulate processes and fluctuations occurring at the **sub-grid** scale.





Herrera et al., 2009

LAGRANGIAN MODELS AND RWPT

LAGRANGIAN MODELS ARE:

- Efficient
- Versatile
- Mass conservative
- No numerical dispersion
- No instabilities
- Well suited for stoch. modeling
- RWPT: “Multiscale modeling”

BUT…

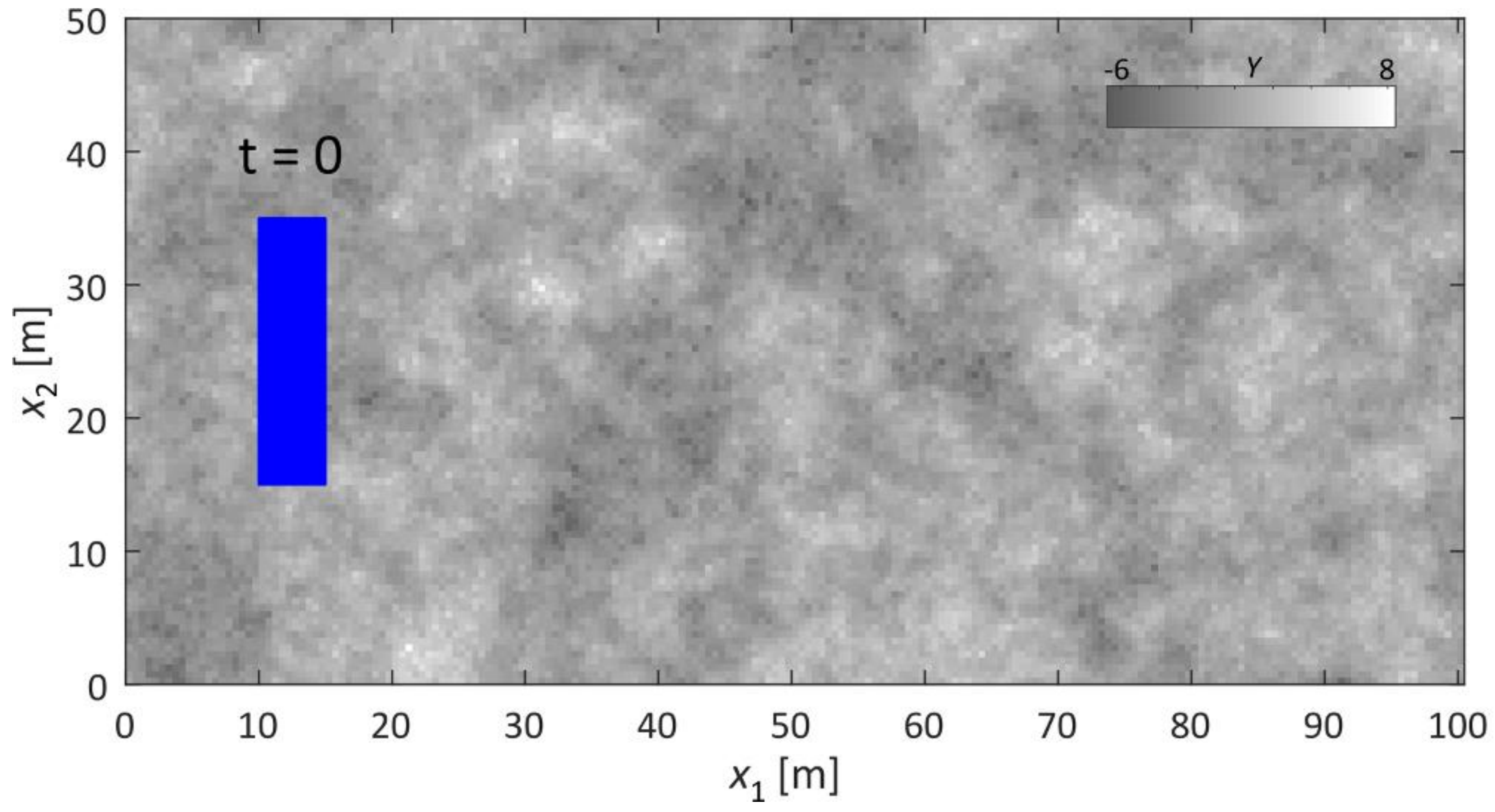
- Simulation of nonlinear reactive processes require interaction between particles

UNIVERSITAT POLITÈCNICA DE CATALUNYA
Department of Civil and Environmental Engineering
Hydrogeology Group GHS (UPC-CSIC)

WE-NEED

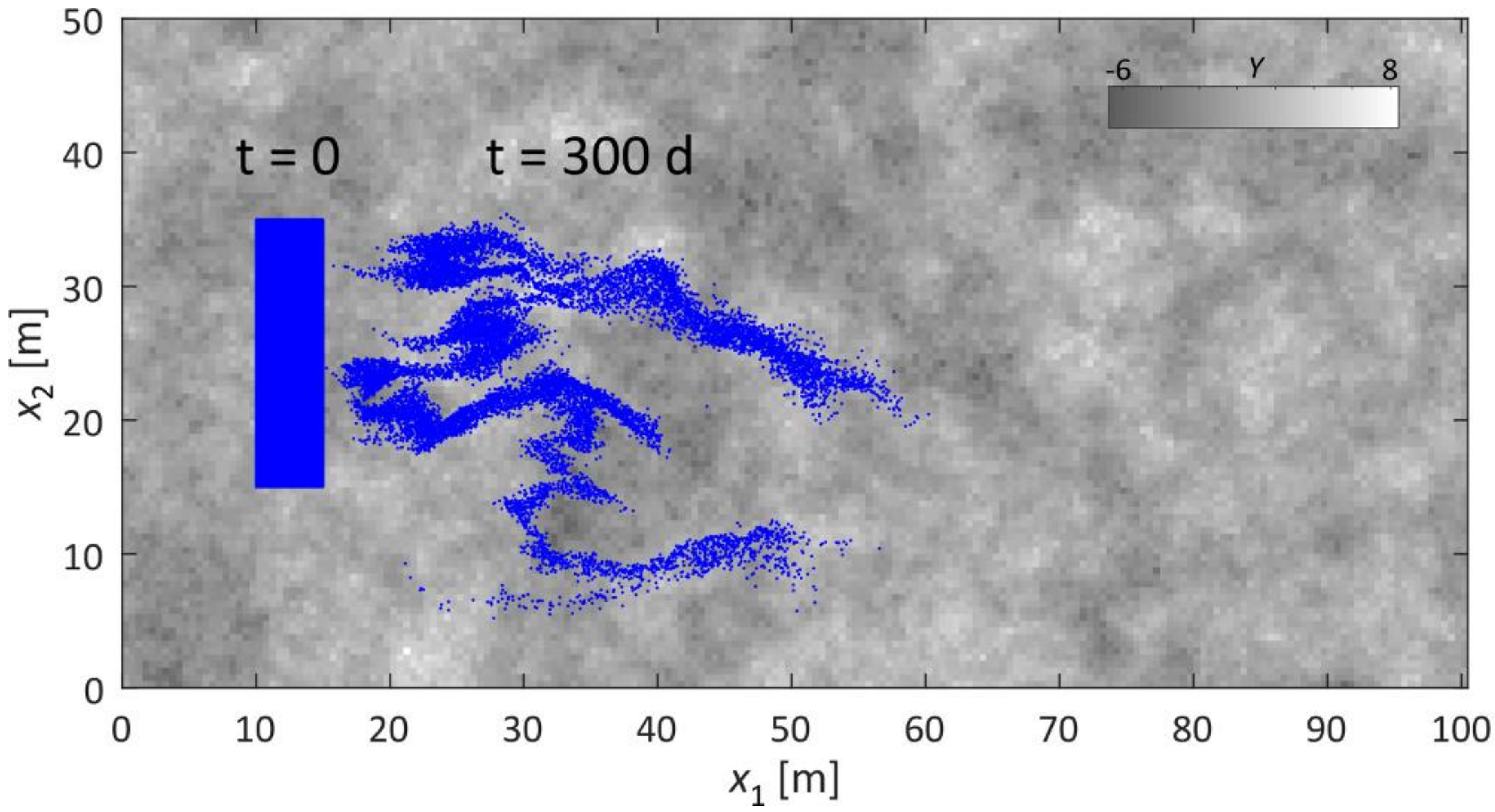
PART 2: KERNEL DENSITY ESTIMATION FOR REACTIVE TRANSPORT SIMULATION WITH RWPT

1.1. The need for a density estimator in particle methods

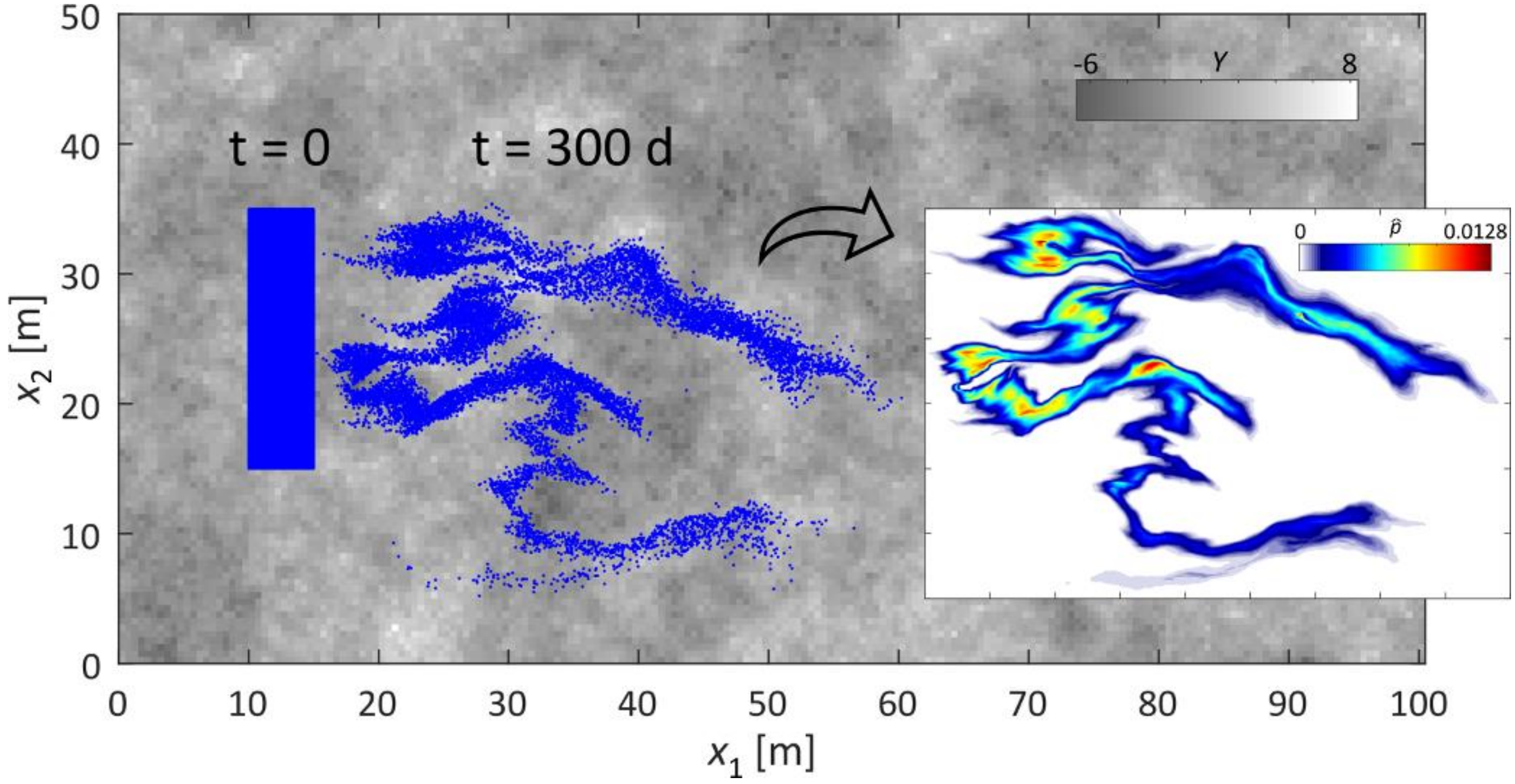


1. INTRODUCTION

1.1. The need for a density estimator in particle methods

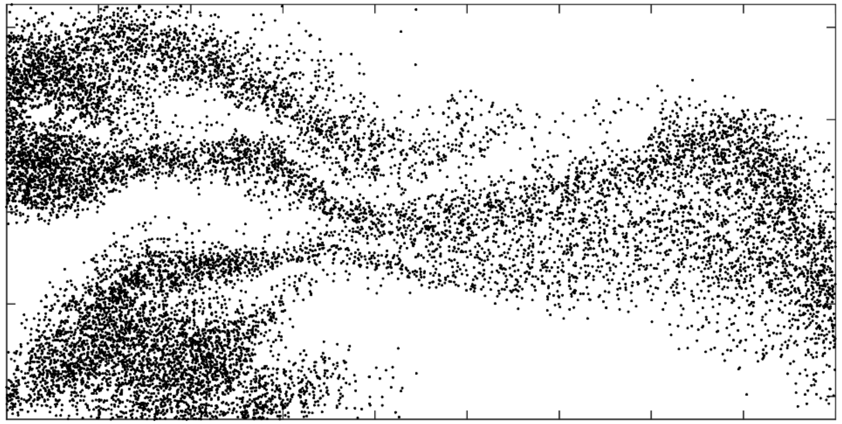


1.1. The need for a density estimator in particle methods



1.2. Two possible density estimators

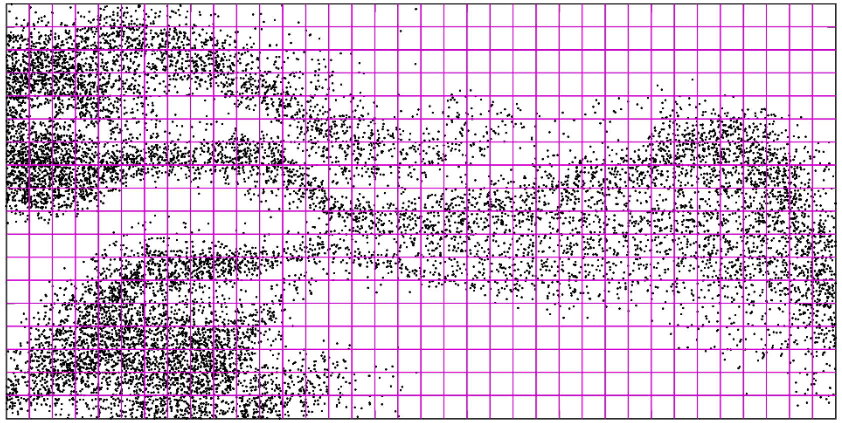
Binning



1. INTRODUCTION

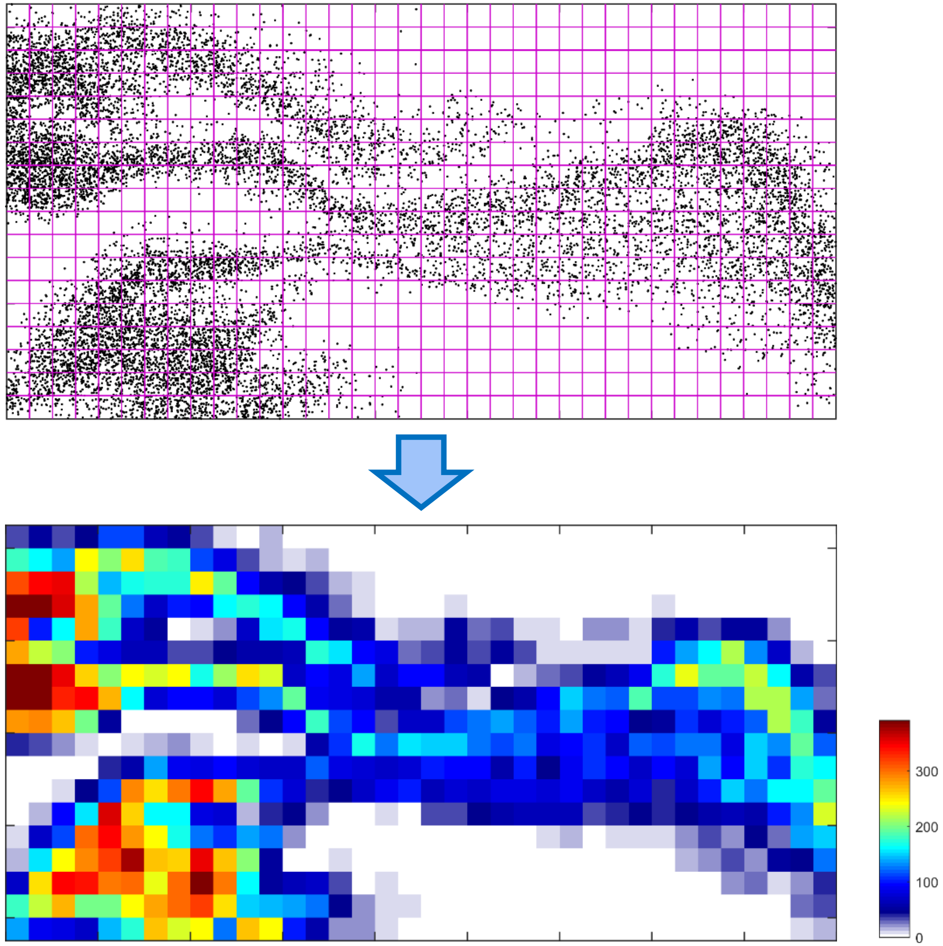
1.2. Two possible density estimators

Binning



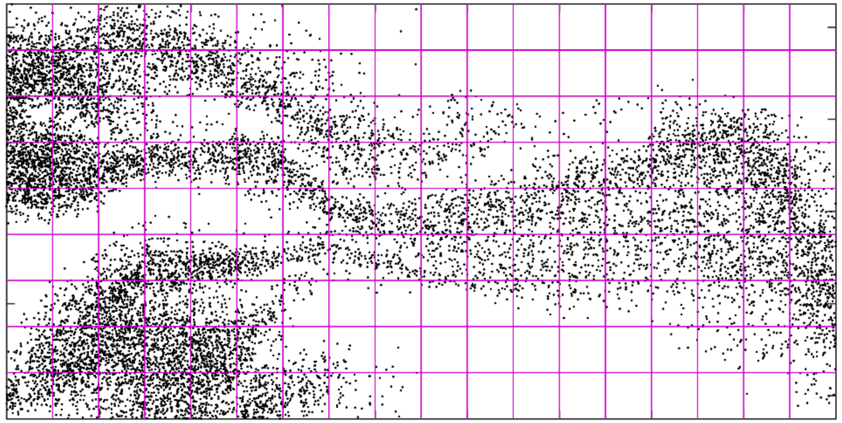
1.2. Two possible density estimators

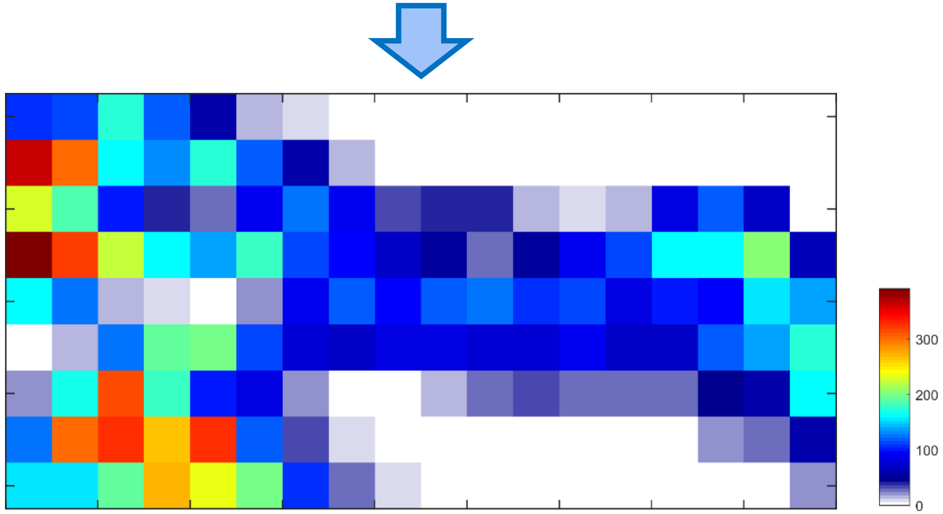
Binning



1.2. Two possible density estimators

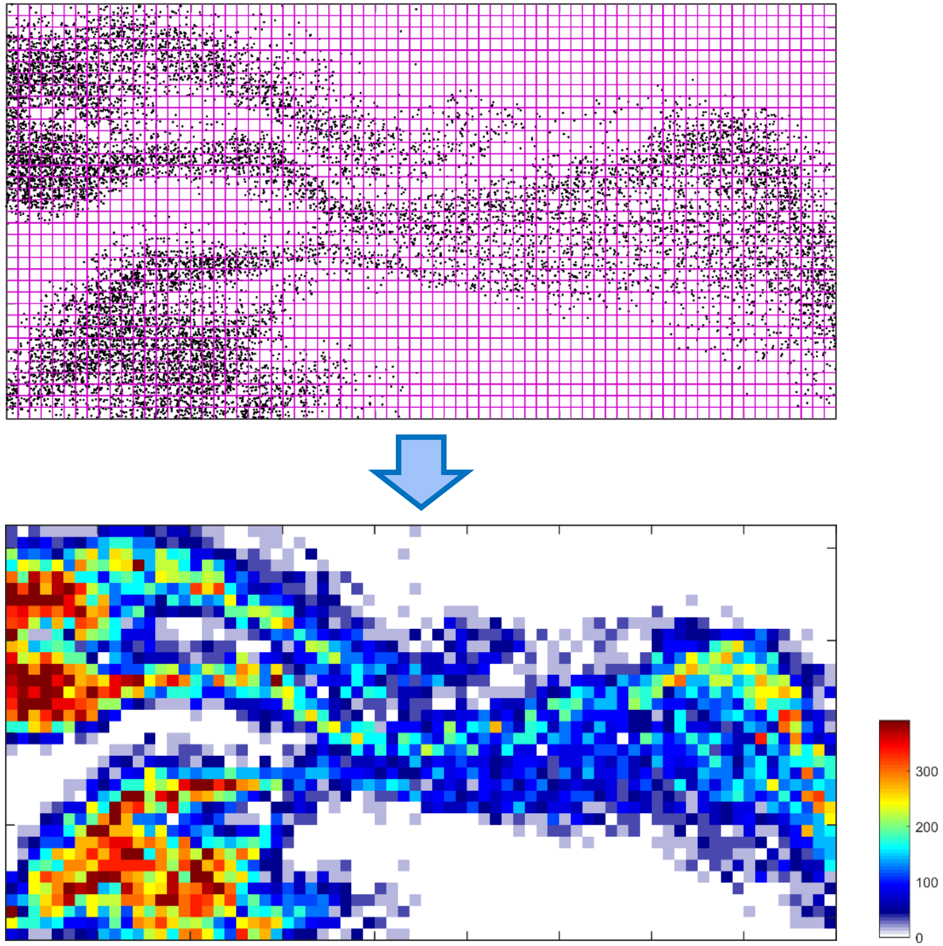
Binning





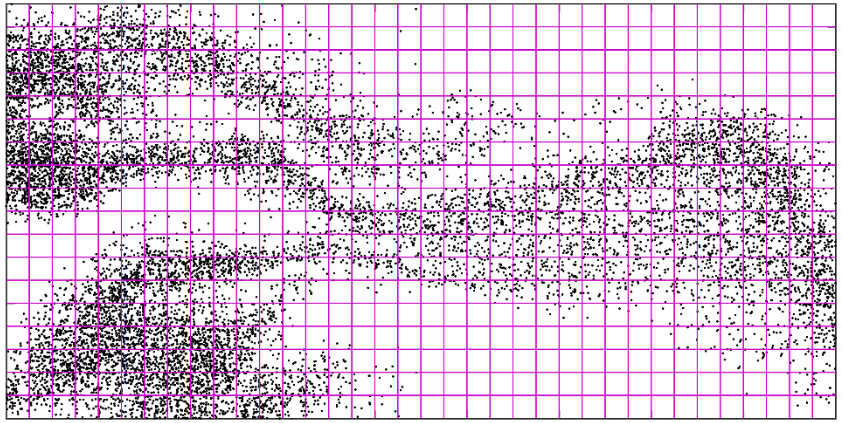
1.2. Two possible density estimators

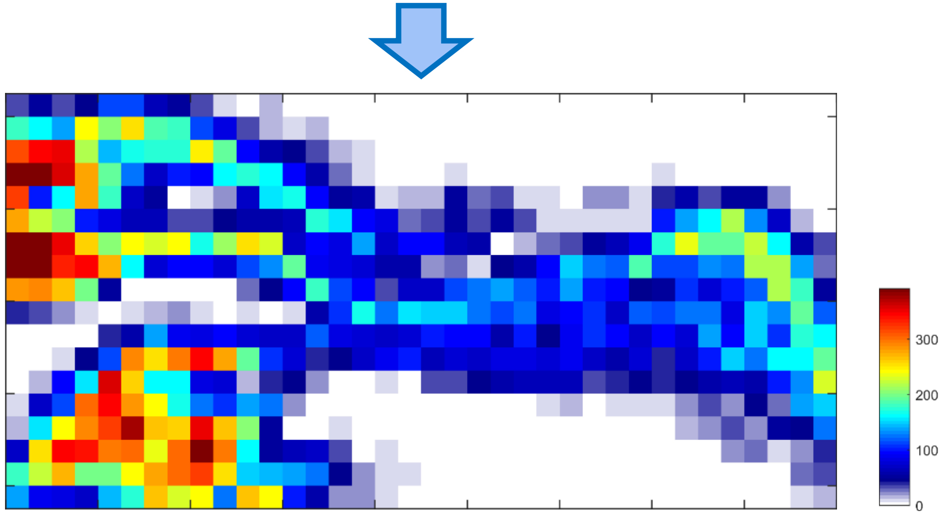
Binning



1.2. Two possible density estimators

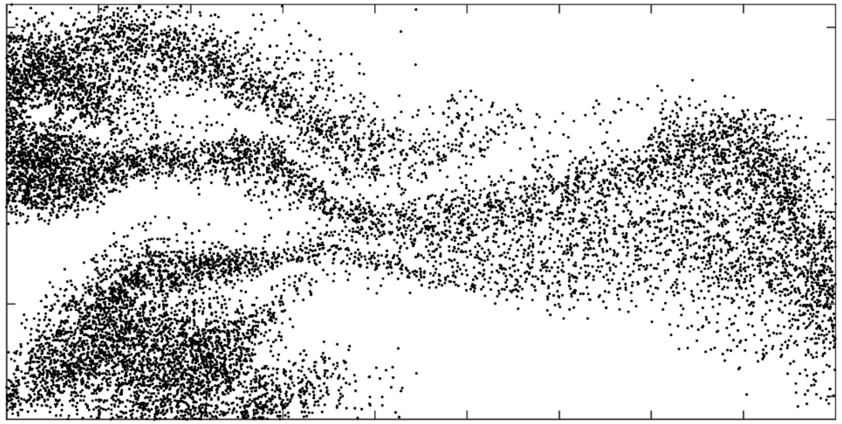
Binning





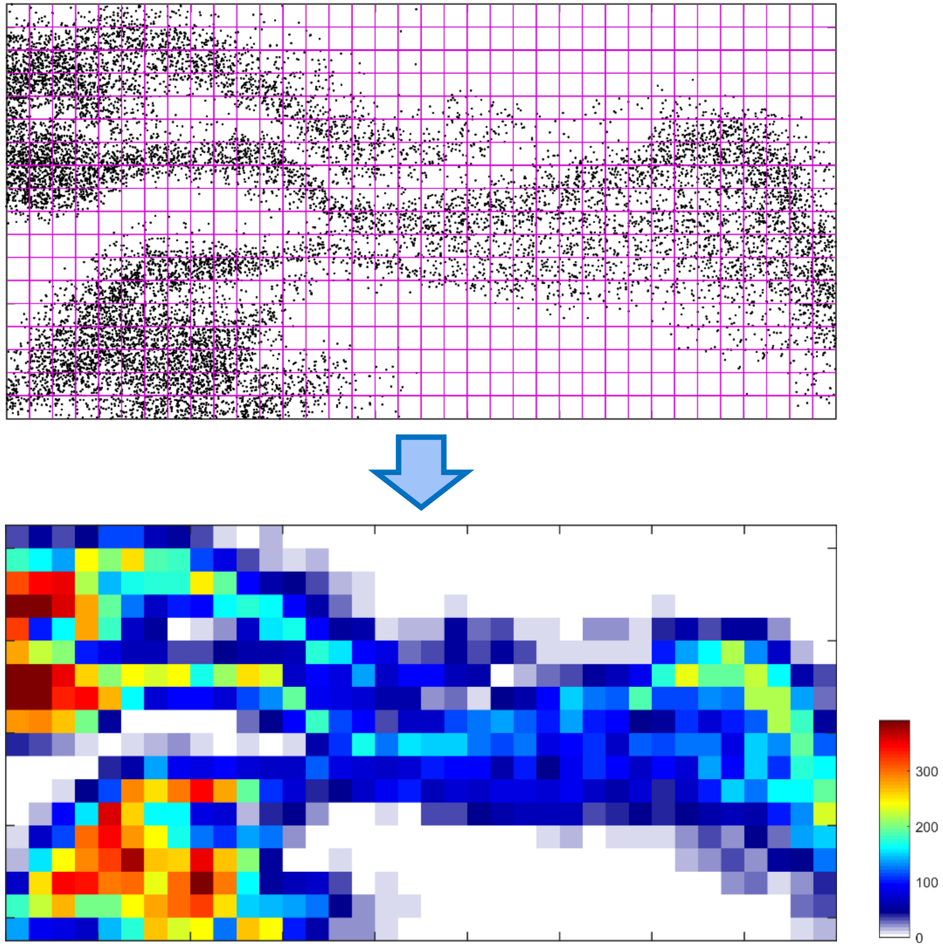
vs

Kernel Density Estimation (KDE)



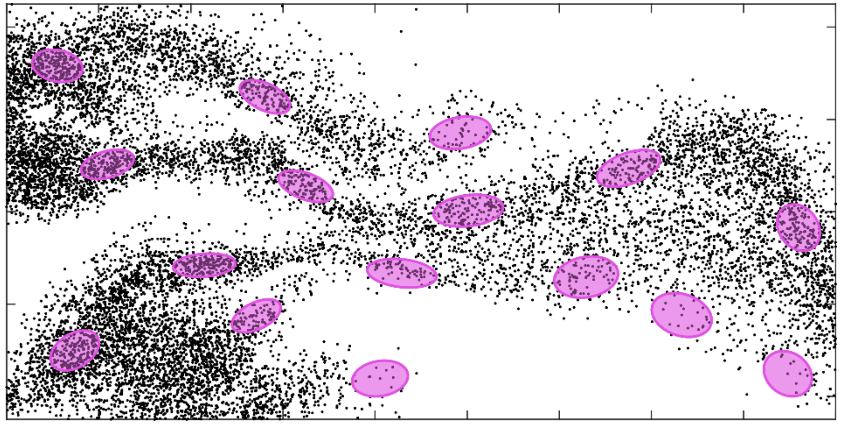
1.2. Two possible density estimators

Binning



VS

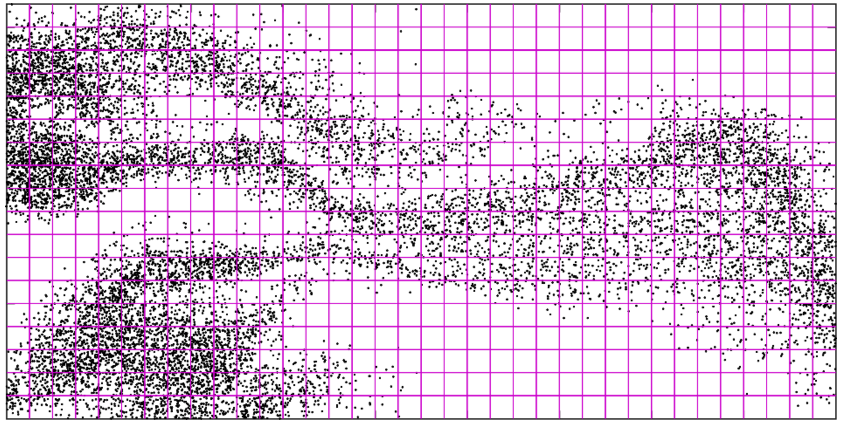
Kernel Density Estimation (KDE)

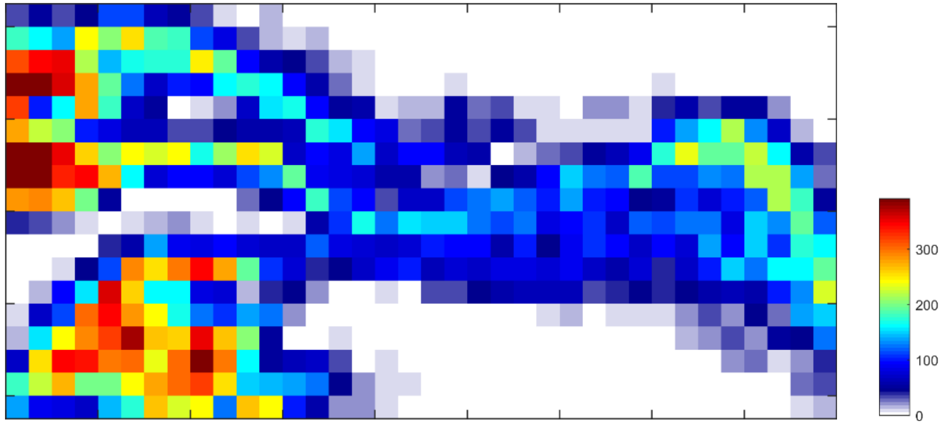


1. INTRODUCTION

1.2. Two possible density estimators

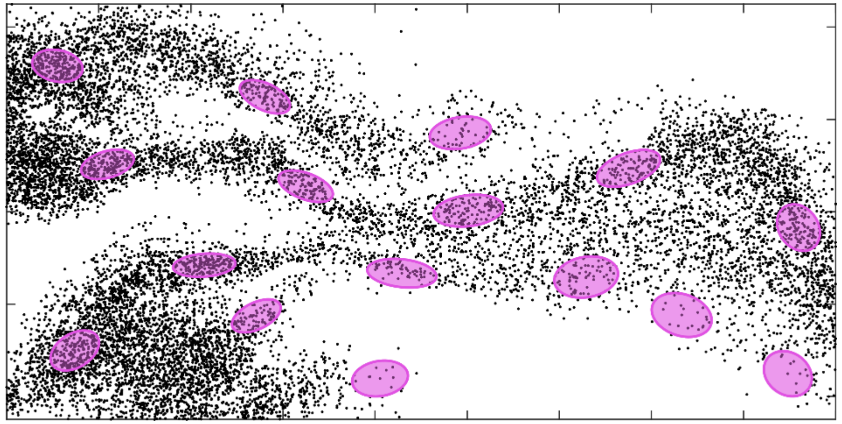
Binning

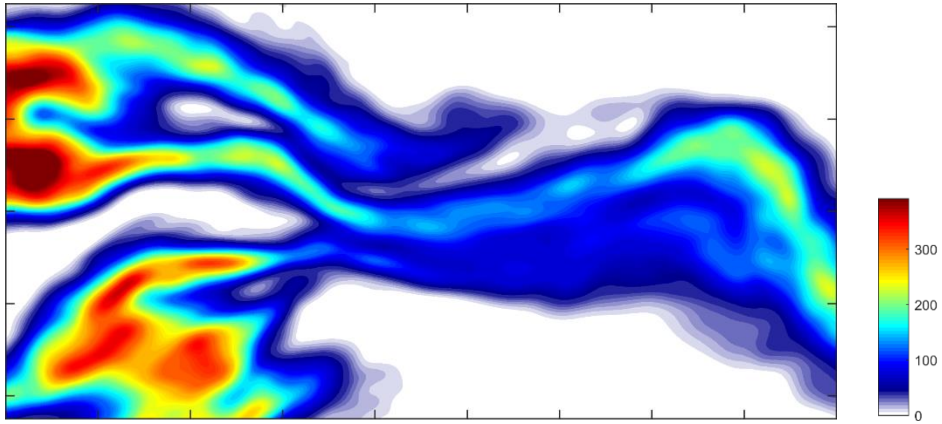




VS

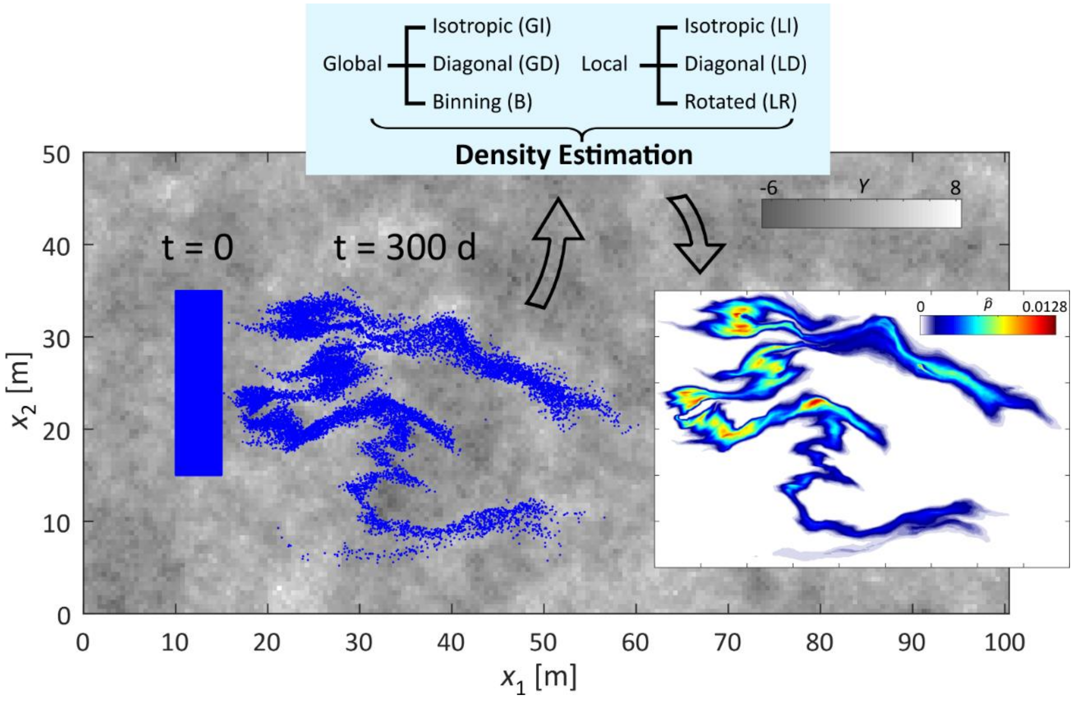
Kernel Density Estimation (KDE)

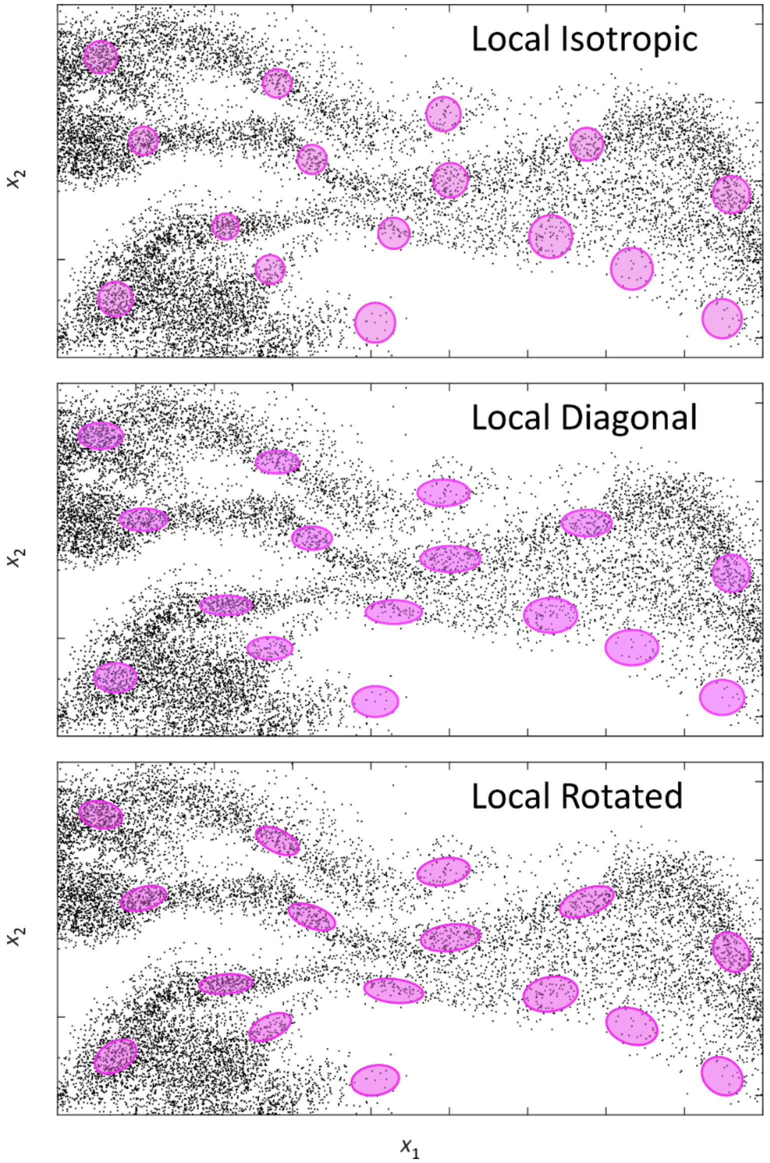




1.3. Local vs Global optimal KDE

- We developed a **locally optimized KDE** method and compared it to existing global (constant) KDE approaches.

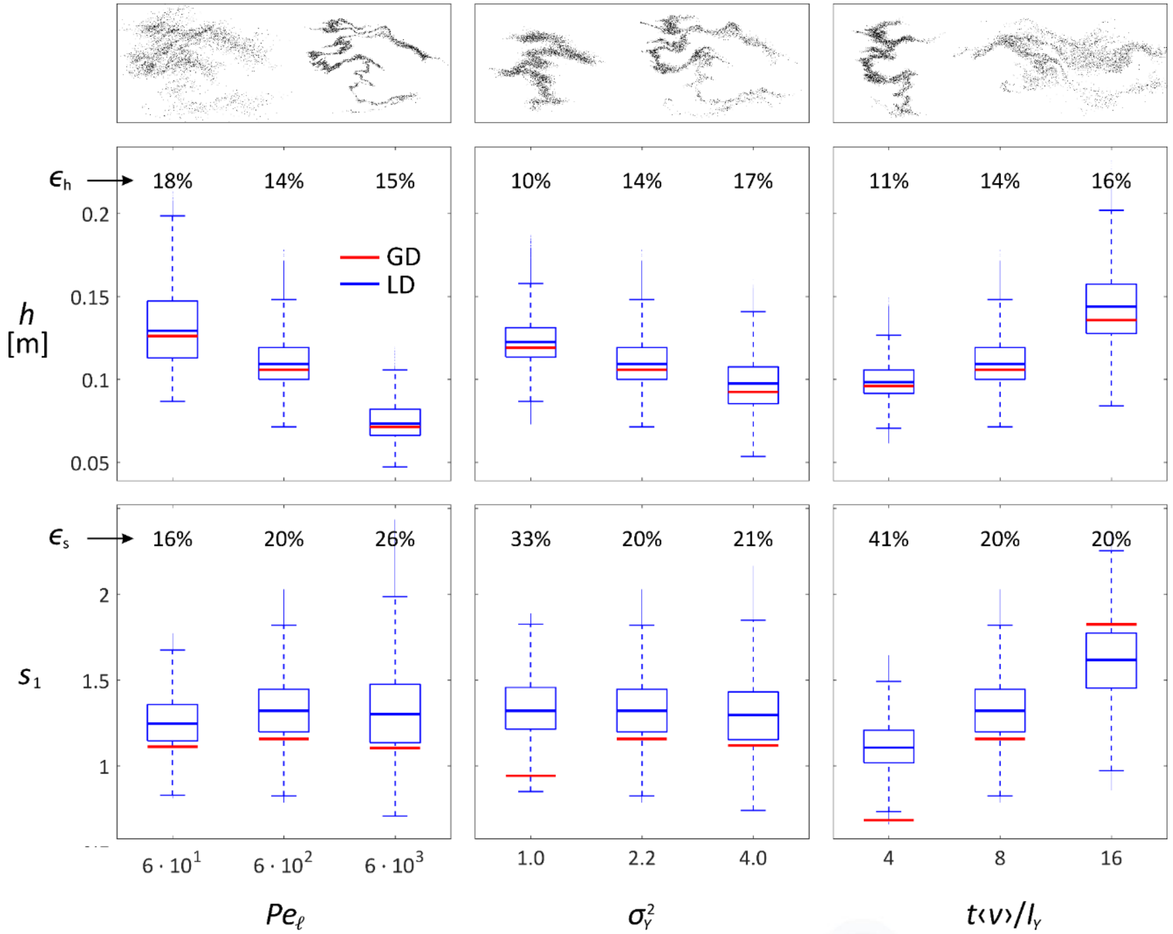




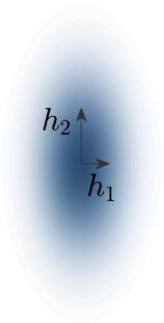
1.3. Local vs Global optimal KDE

- We developed a **locally optimized KDE** method and compared it to existing global (constant) KDE approaches.

- The local method is able to **mimic** the wide variety of local states of the particle plume.

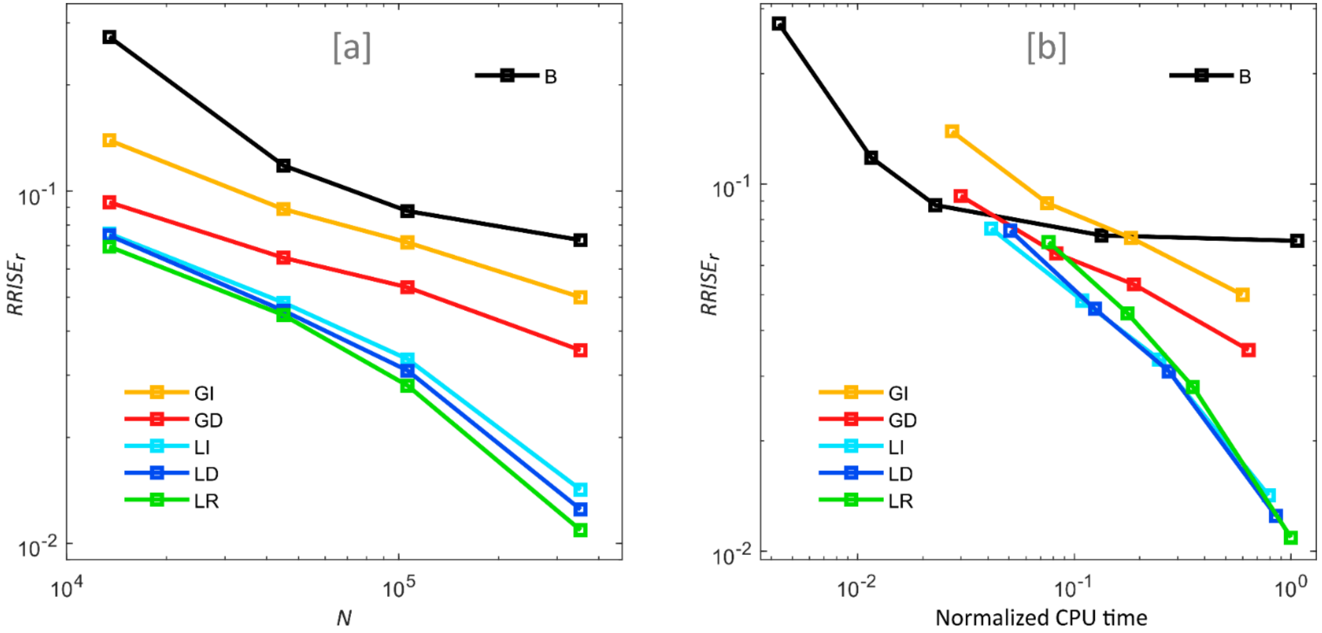


*
$$h := \sqrt{h_1 h_2}$$
$$s_1 = h_1/h_2$$



1.3. Local vs Global optimal KDE

- We developed a **locally optimized KDE** method and compared it to existing global (constant) KDE approaches.
- The local method is able to **mimic** the wide variety of local states of the particle plume.
- As a consequence, it is **more accurate** and hence, also more efficient than existing methods.



1.4. Bounded Grid-Projected Adaptive Kernel Smoothing

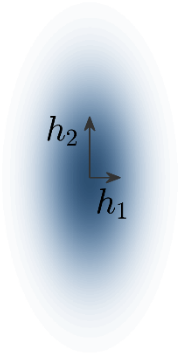
- Recently [1] we developed a **locally adaptive KDE method** for implementation in RWPT.
- However, the kernel approach can be **computationally expensive** for high particle numbers.
- Besides, the issue of **boundary conditions** has (or had) not been addressed.

- We present a "hybrid" approach [2] that combines the **low computational costs of binning** & the **accuracy of KDE**, while accounting for the effect of **boundary conditions** on the kernel.

[1] Sole-Mari & Fernàndez-Garcia (2018). *Lagrangian Modeling of Reactive Transport (…)*, WRR.
[2] Sole-Mari et al. (2019). *Particle Density Estimation with Grid-Projected (…)* , Preprint submitted to AWR.

2.1. General idea: A "hybrid" density estimation method

DENSITY KERNEL



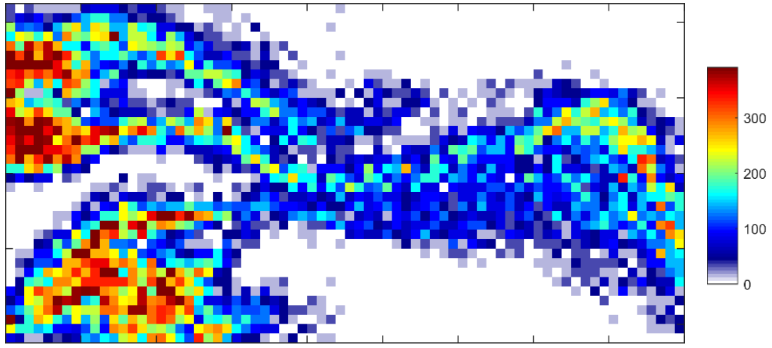
$\approx$

λ_1, λ_2

0.01	0.04	0.01
0.04	0.17	0.04
0.06	0.27	0.06
0.04	0.17	0.04
0.01	0.04	0.01

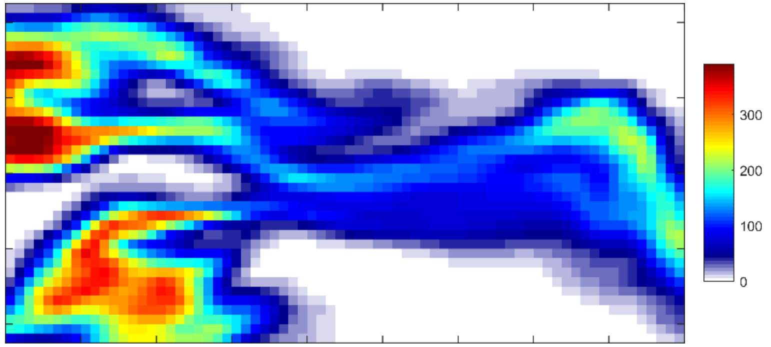
$+$

PILOT BINNING



DENSITY

ρ



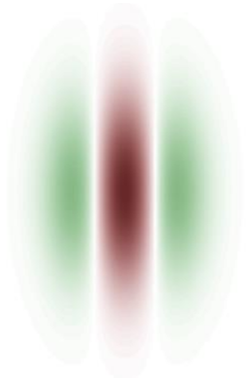
CONCENTRATIONS

$$c = \rho m / \phi$$

CHEMICAL REACTIONS

2.2. The locally optimal density kernel

CURVATURE KERNEL

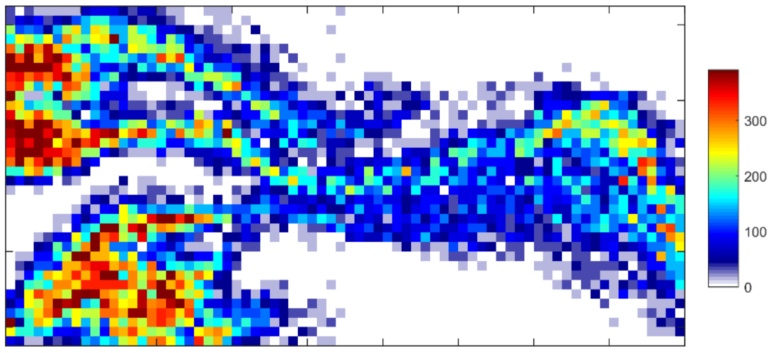


≈

0.07	−0.13	0.07
0.26	−0.52	0.26
0.42	−0.83	0.42
0.26	−0.52	0.26
0.07	−0.13	0.07

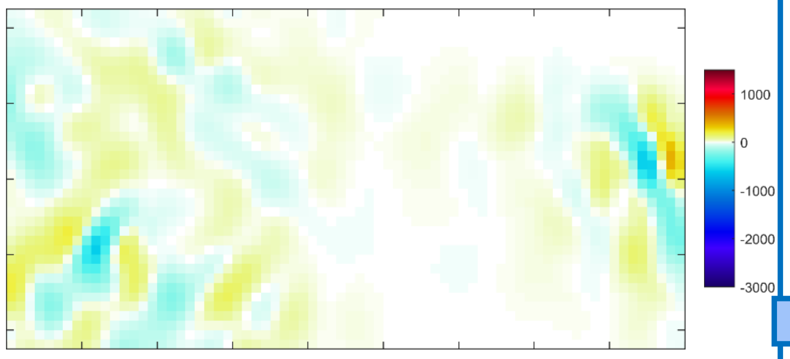
+

PILOT BINNING

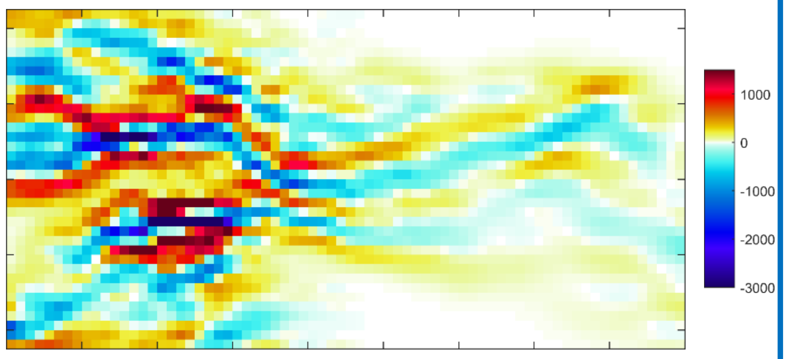


CURVATURES

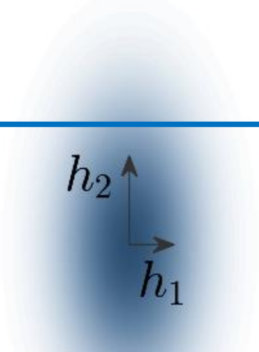
$\kappa^{(1)}$



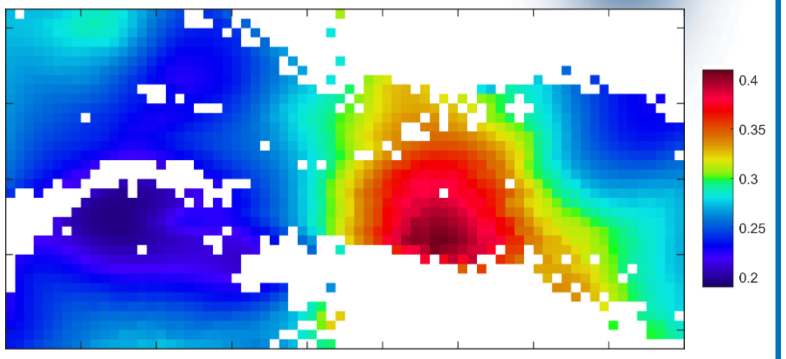
$\kappa^{(2)}$



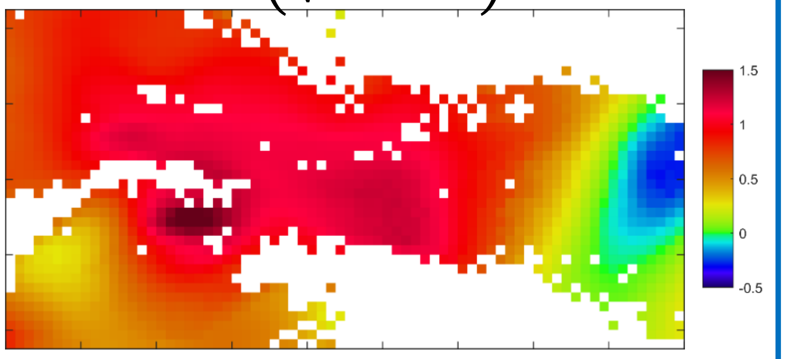
(OPTIMAL) DENSITY KERNEL



$\sqrt{h_1 h_2}$



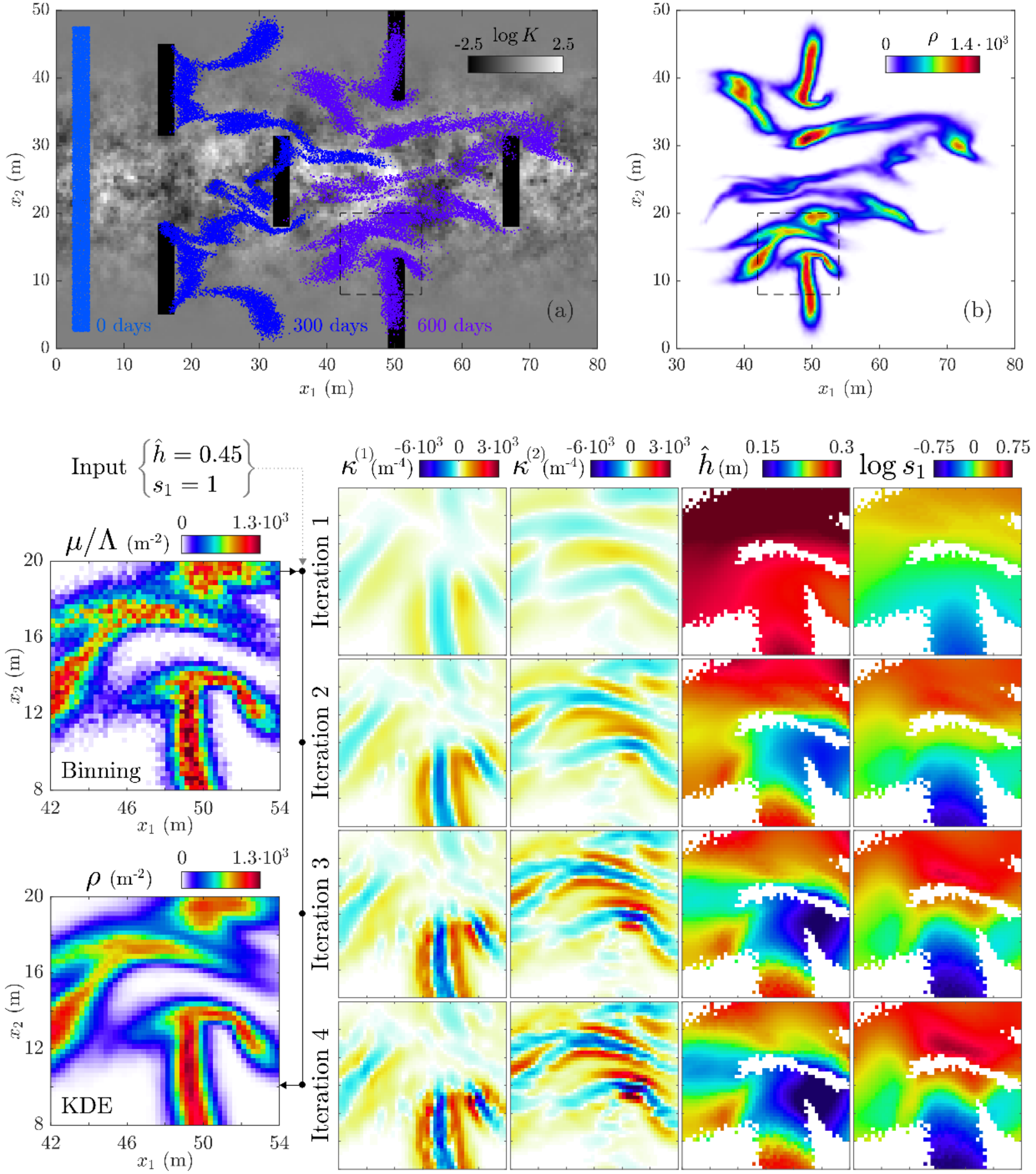
$\log\left(\sqrt{h_1/h_2}\right)$



2. THE ADAPTIVE KERNEL METHOD

2.3. Fixed-point iteration

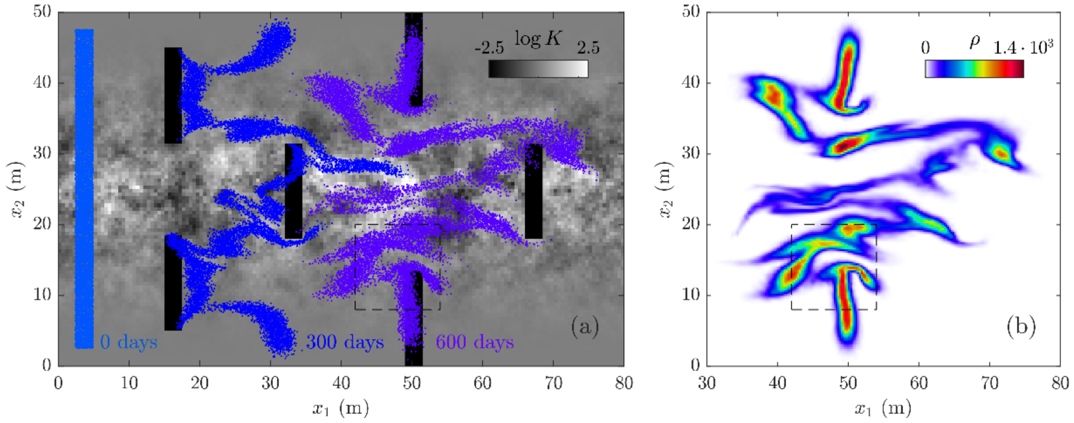
- The kernel **evolves** recursively.

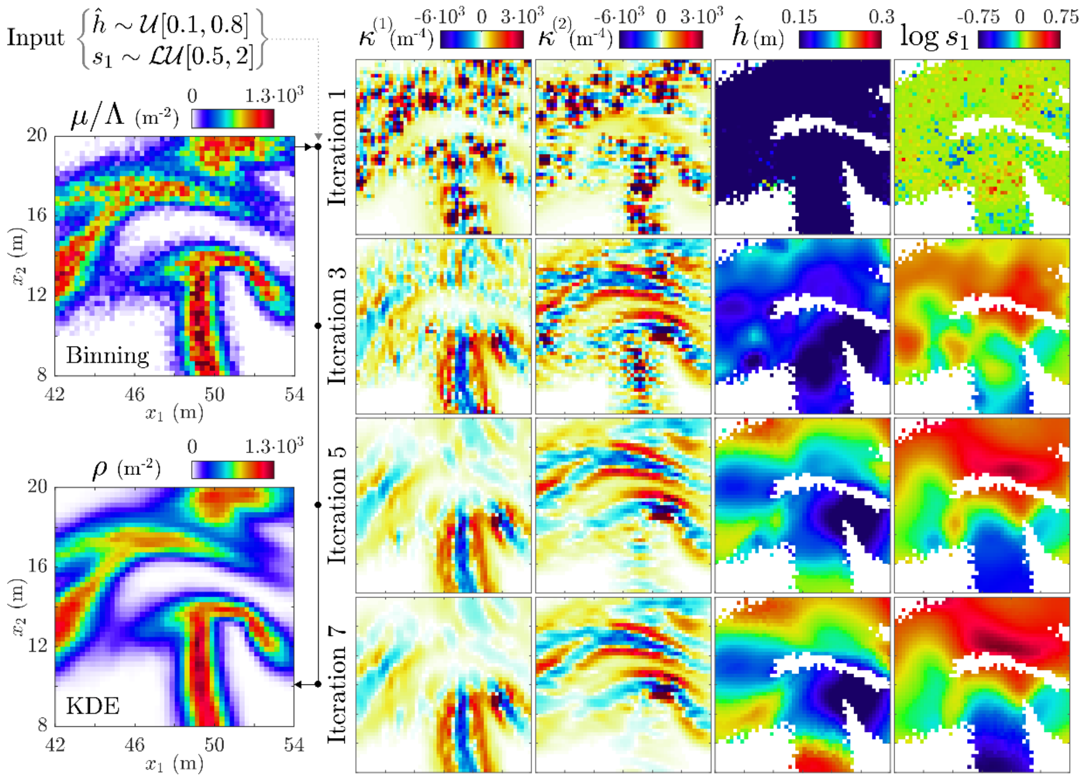


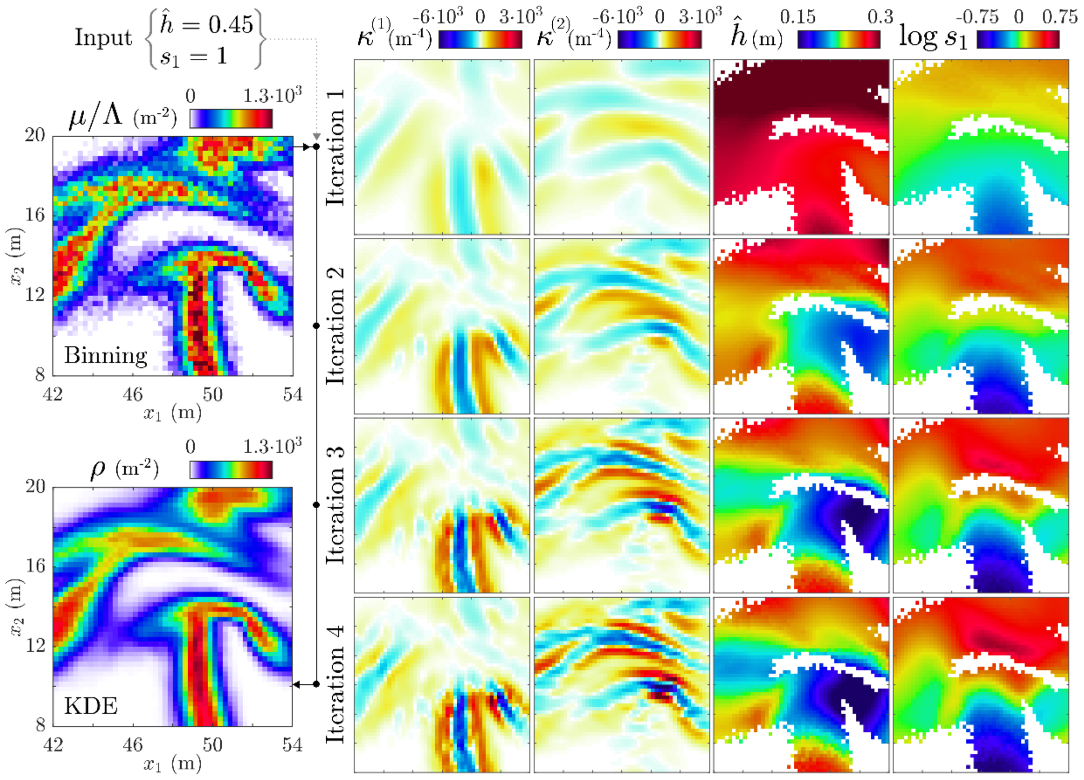
2. THE ADAPTIVE KERNEL METHOD

2.3. Fixed-point iteration

- The kernel **evolves** recursively.
- **Robust** convergence even for "bad" input.



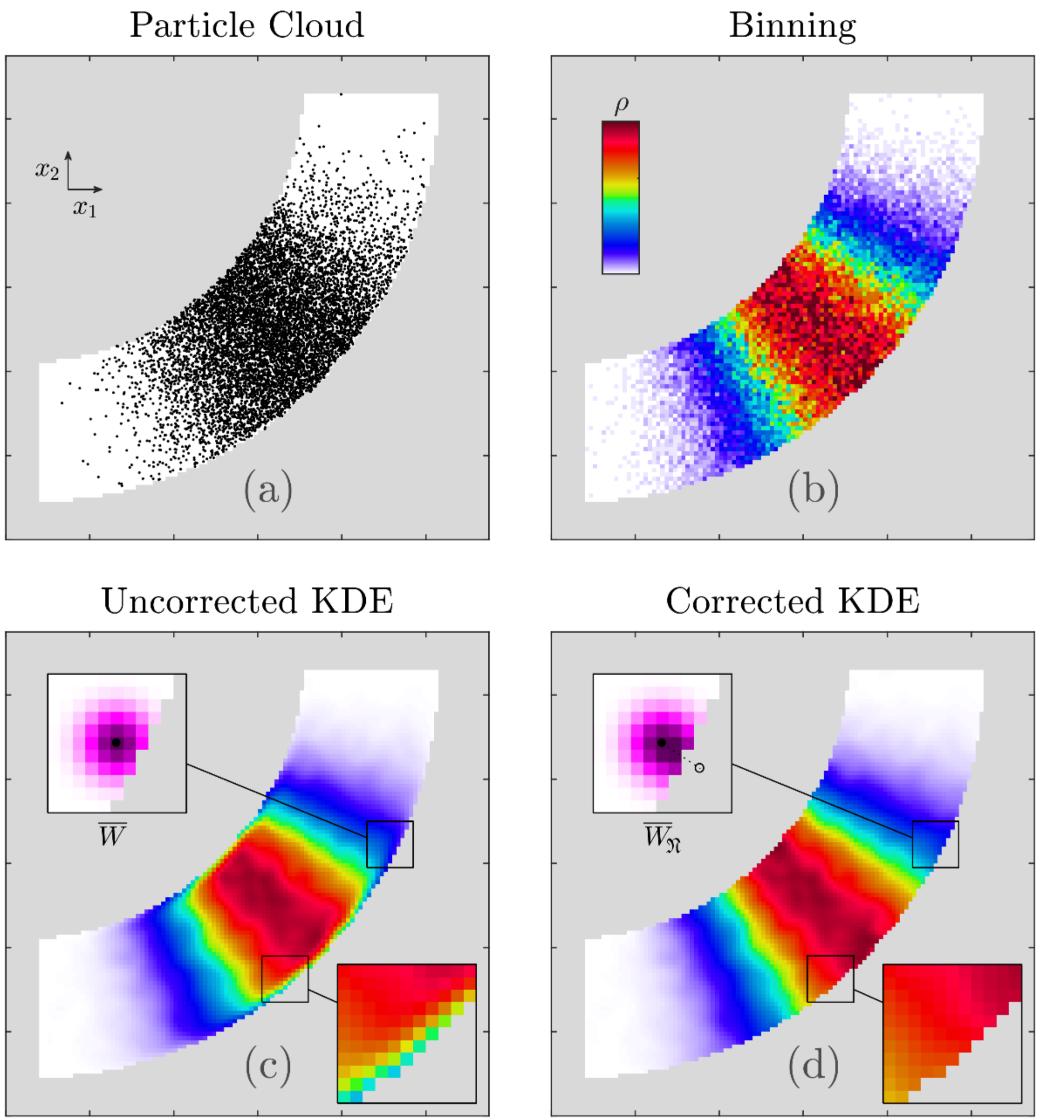




2. THE ADAPTIVE KERNEL METHOD

2.4. The former trouble with boundaries

- Conventional KDE **fails near boundaries**
- Correction to account for boundaries: **Impermeable**, **Dirichlet** or **Robin.**
- Based on treating the kernel as a diffusive process: (pseudo)-**reflection** principles.
- Applicable to **irregular** boundaries.

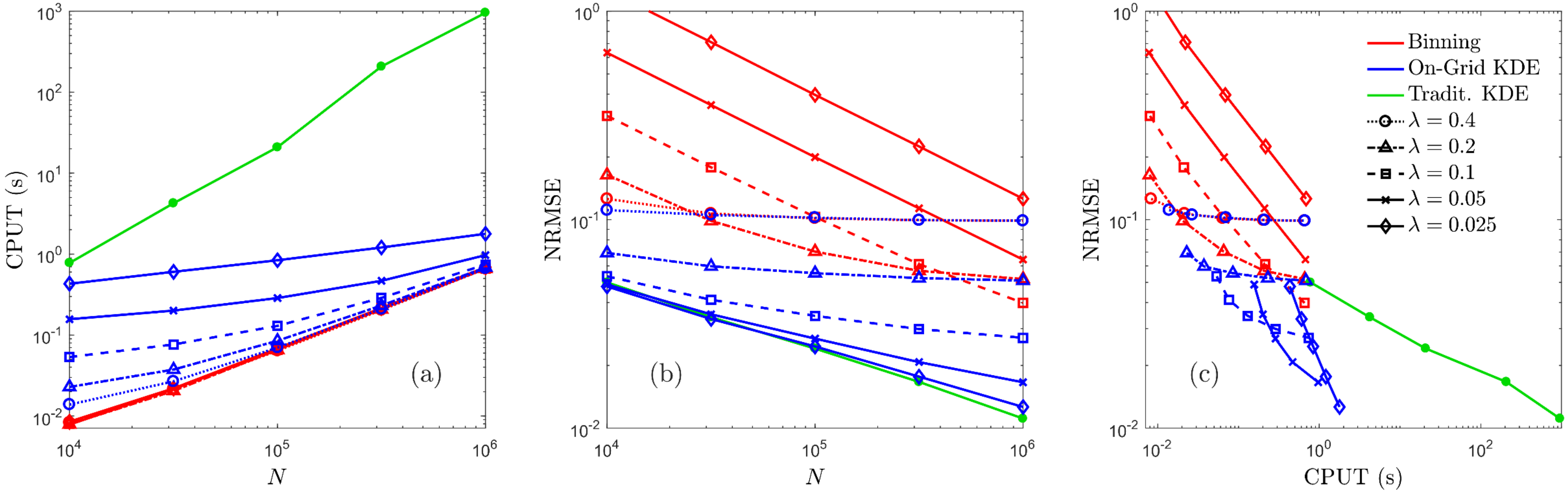


2.5. Computational efficiency

CPU Time ~ Binning

Error ~ KDE

Optimal CPU-Error Ratio



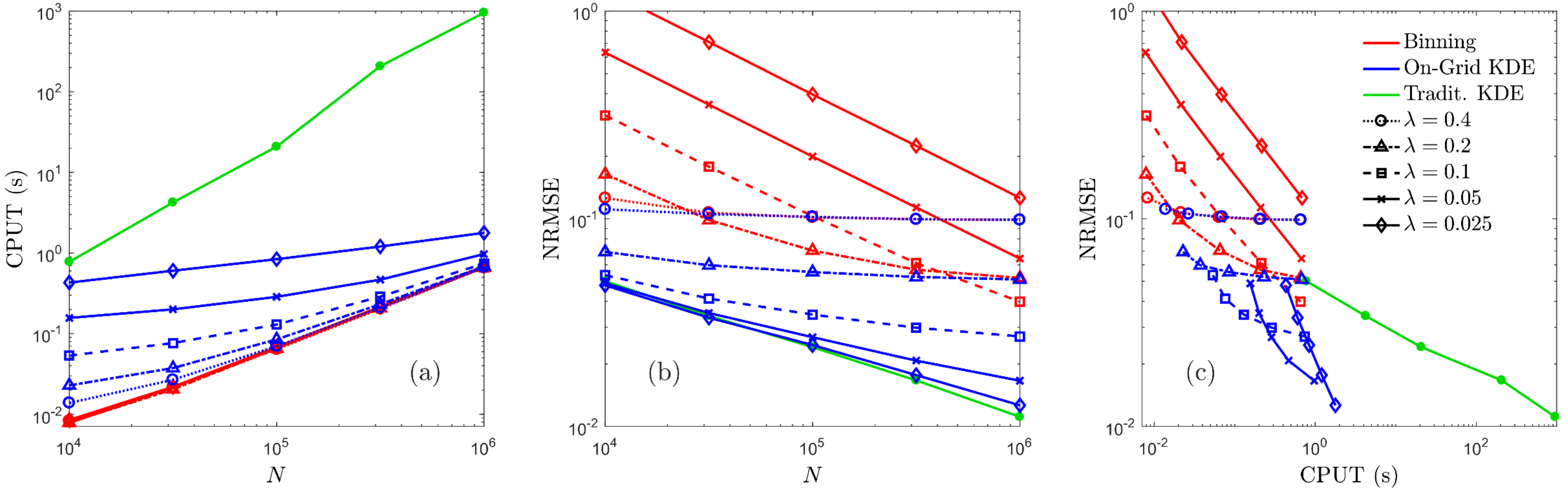
2. THE ADAPTIVE KERNEL METHOD

2.5. Computational efficiency

CPU Time ~ Binning

Error ~ KDE

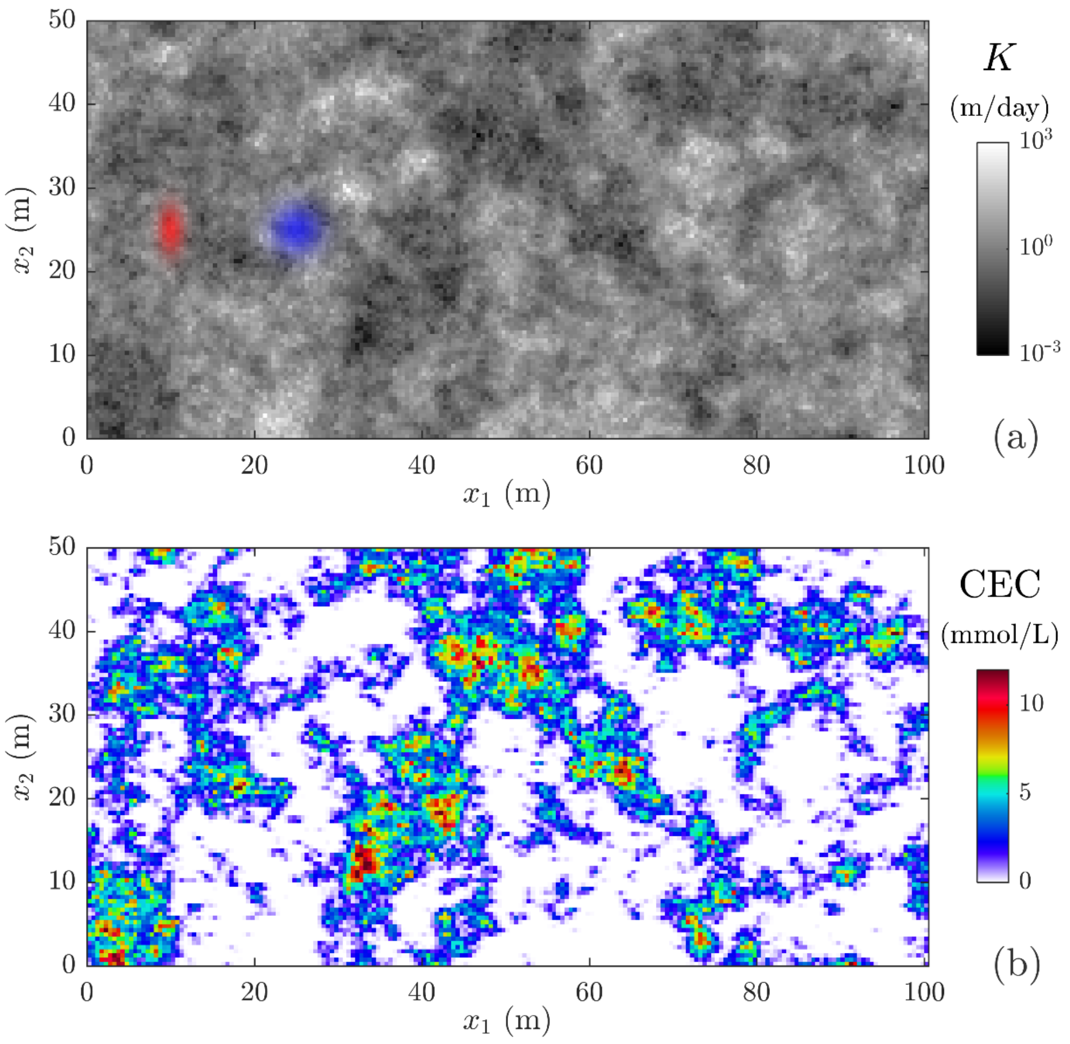
Optimal CPU-Error Ratio



≪No excuse for using binning!!≫

3. IMPLEMENTATION EXAMPLE

3.1. Example reactive simulation



- Days 0-500: Release of Cd^{2+} into the aquifer.
- Days 2000-2050: Release of disolved CO_2.
- CEC present in lower conductivity areas.

$$Ca^{2+} + X_2Cd \rightleftharpoons Cd^{2+} + X_2Ca$$

$$H^+ + OH^- \rightleftharpoons \cancel{H_2O}$$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons \cancel{CaCO_3}$$

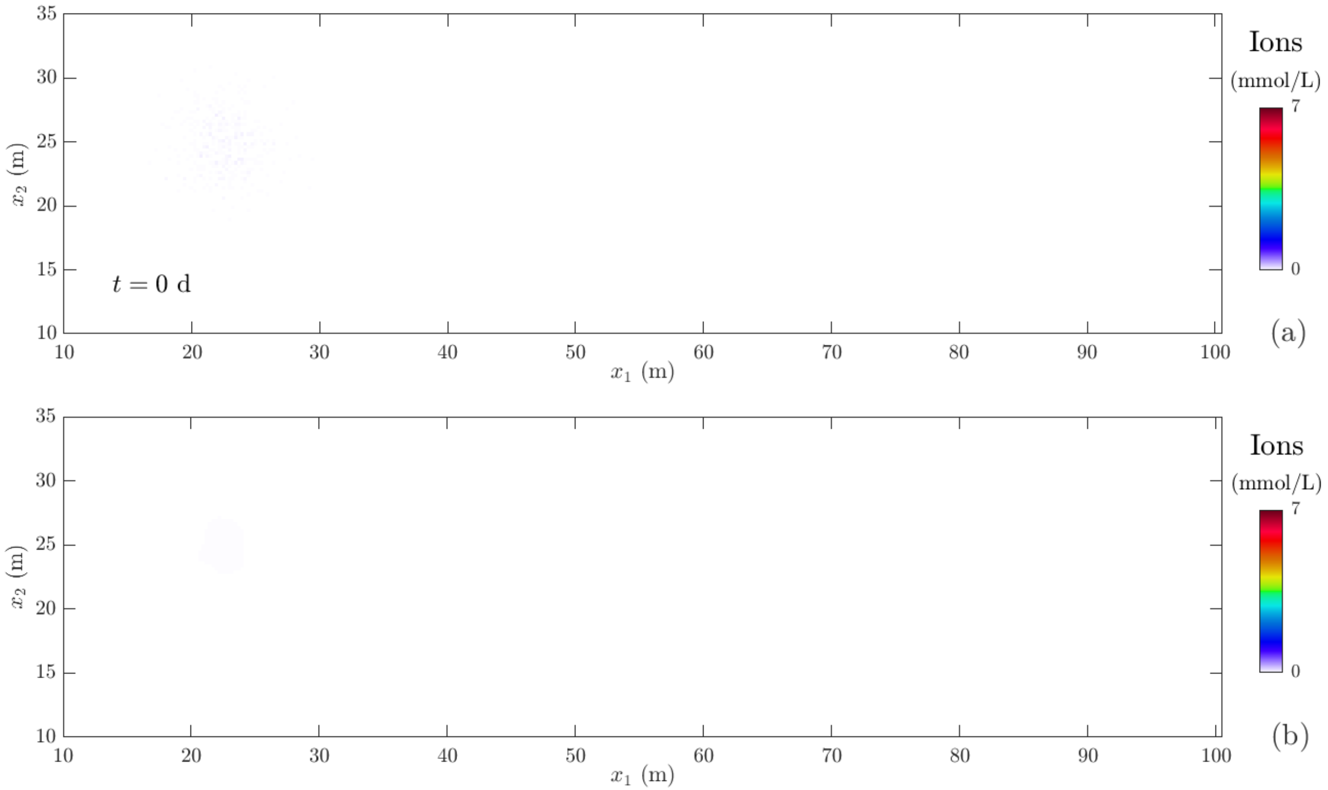
$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

$$CO_3^{2-} + 2H^+ \rightleftharpoons H_2O + CO_2$$

$$\begin{array}{r|ccccccccc|}
 & Ca^{2+} & Cd^{2+} & CO_2 & X_2Ca & CO_3^{2-} & HCO_3^- & H^+ & OH^- & X_2Cd \\
\text{Ions} & 1 & 1 & 0 & 0 & -1 & -0.5 & 0.5 & -0.5 & 0 \\
\text{Tot. Cd} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
\text{Acidity} & 0 & 0 & 1 & 0 & 0 & 0.5 & 0.5 & -0.5 & 0 \\
\text{CEC} & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1
\end{array}$$

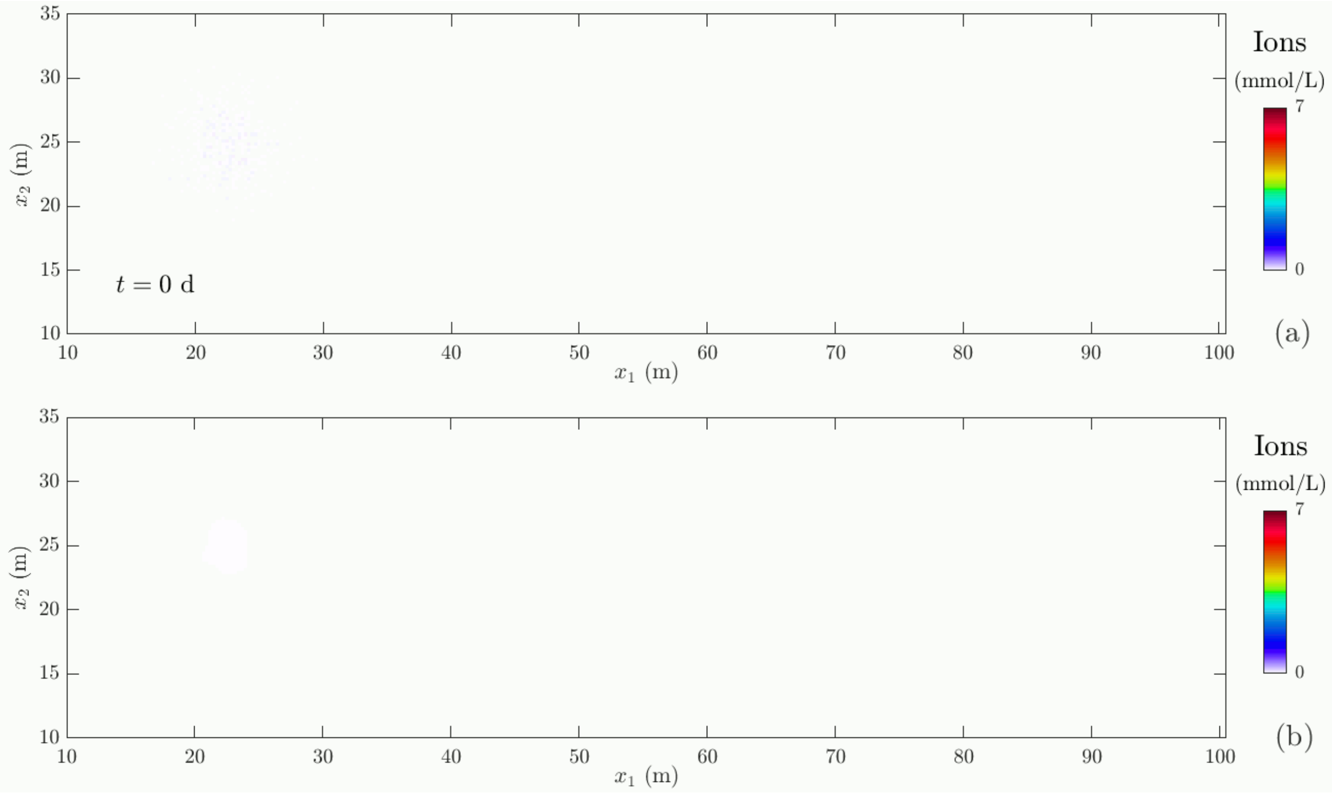
3.2. Binning-KDE comparison (Ions)

- **Binning**: Artificial fluctuations, especially for areas/times of low particle density.
- **KDE**: Eliminate fluctuations with optimal time-space adaptive smoothing.



3.2. Binning-KDE comparison (Ions)

- **Binning**: Artificial fluctuations, especially for areas/times of low particle density.
- **KDE**: Eliminate fluctuations with optimal time-space adaptive smoothing.

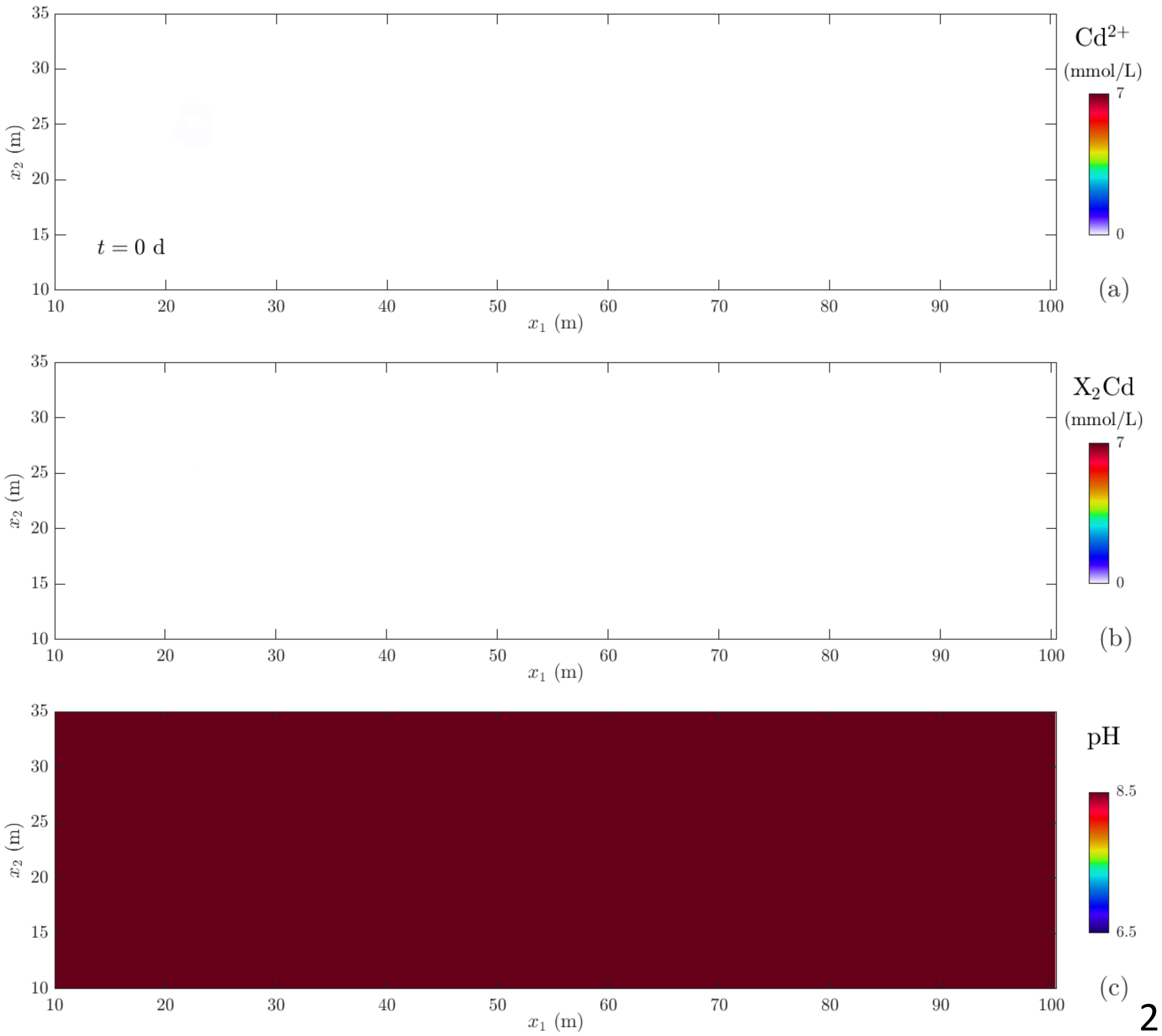


3. IMPLEMENTATION EXAMPLE

3.3. Concentrations overview

- $\mathbf{Cd^{2+}}$ **is trapped** by cation exchange, **mobilizing** $\mathbf{Ca^{2+}}$ and **reducing** $\mathbf{pH}$ by carbonate precipitation.

- With CO_2 injection, $\mathbf{pH}$ **decreases** causing $\mathbf{Ca^{2+}}$ **dissolution**, hence **remobilizing trapped** $\mathbf{Cd^{2+}}$ by cation exchange.

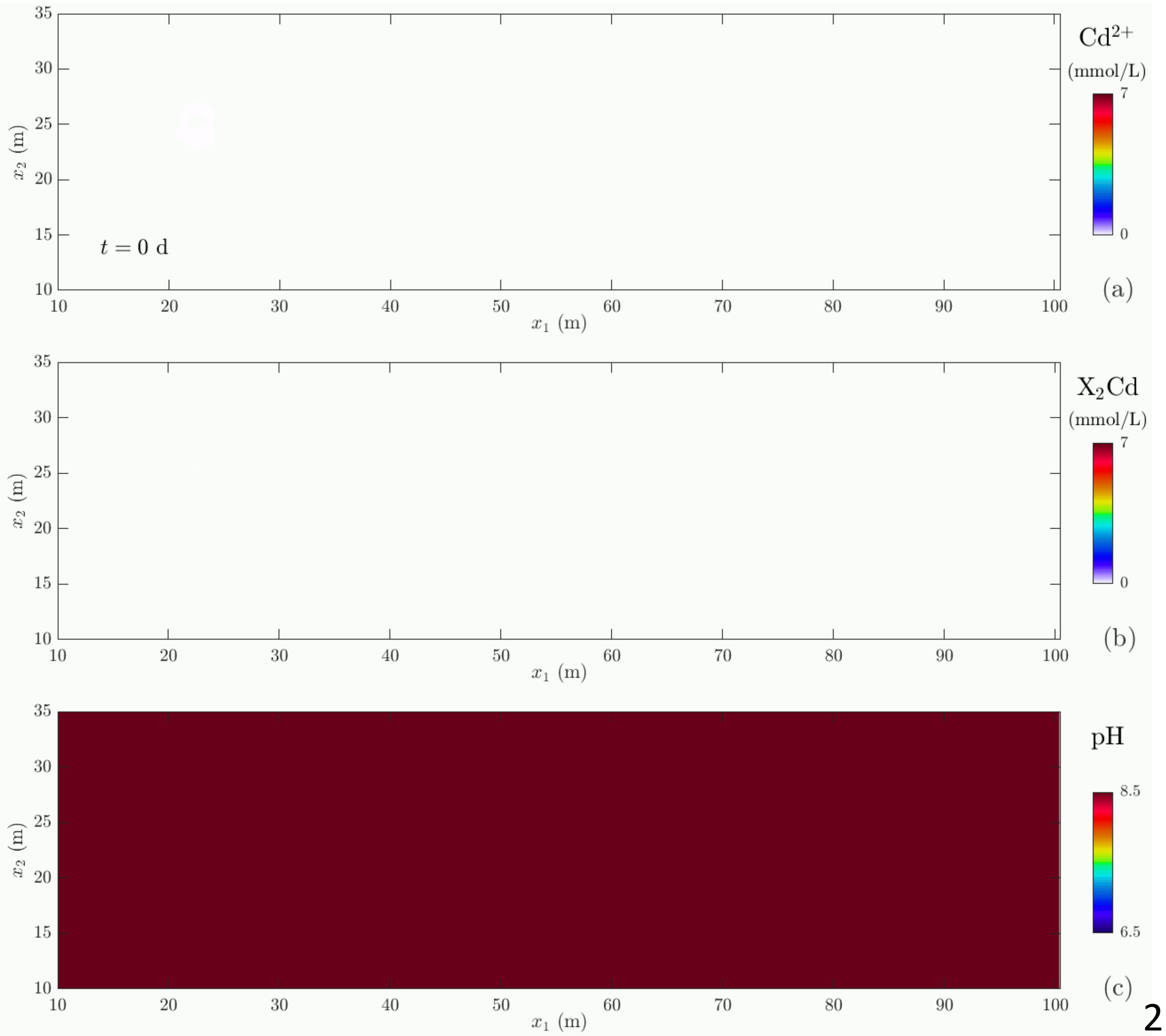


3. IMPLEMENTATION EXAMPLE

3.3. Concentrations overview

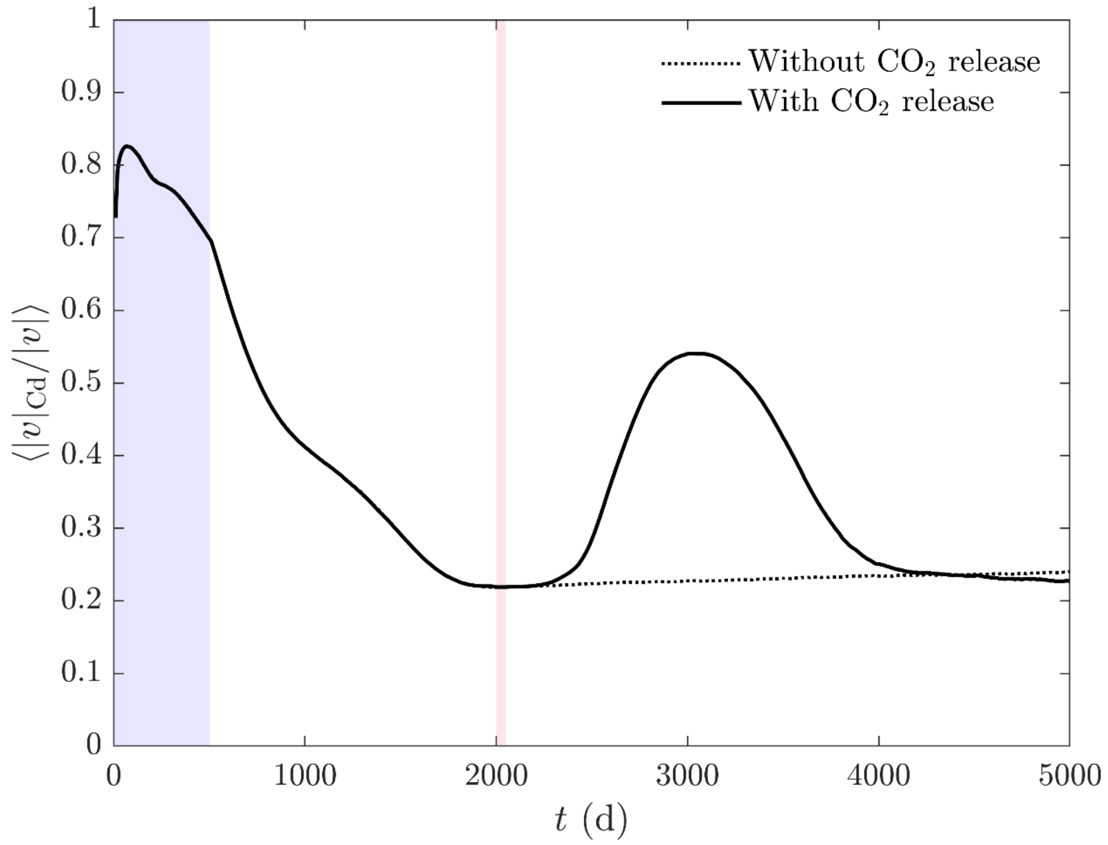
- $\mathbf{Cd^{2+}}$ **is trapped** by cation exchange, **mobilizing** $\mathbf{Ca^{2+}}$ and **reducing pH** by carbonate precipitation.

- With CO_2 injection, **pH decreases** causing $\mathbf{Ca^{2+}}$ **dissolution**, hence **remobilizing trapped** $\mathbf{Cd^{2+}}$ by cation exchange.

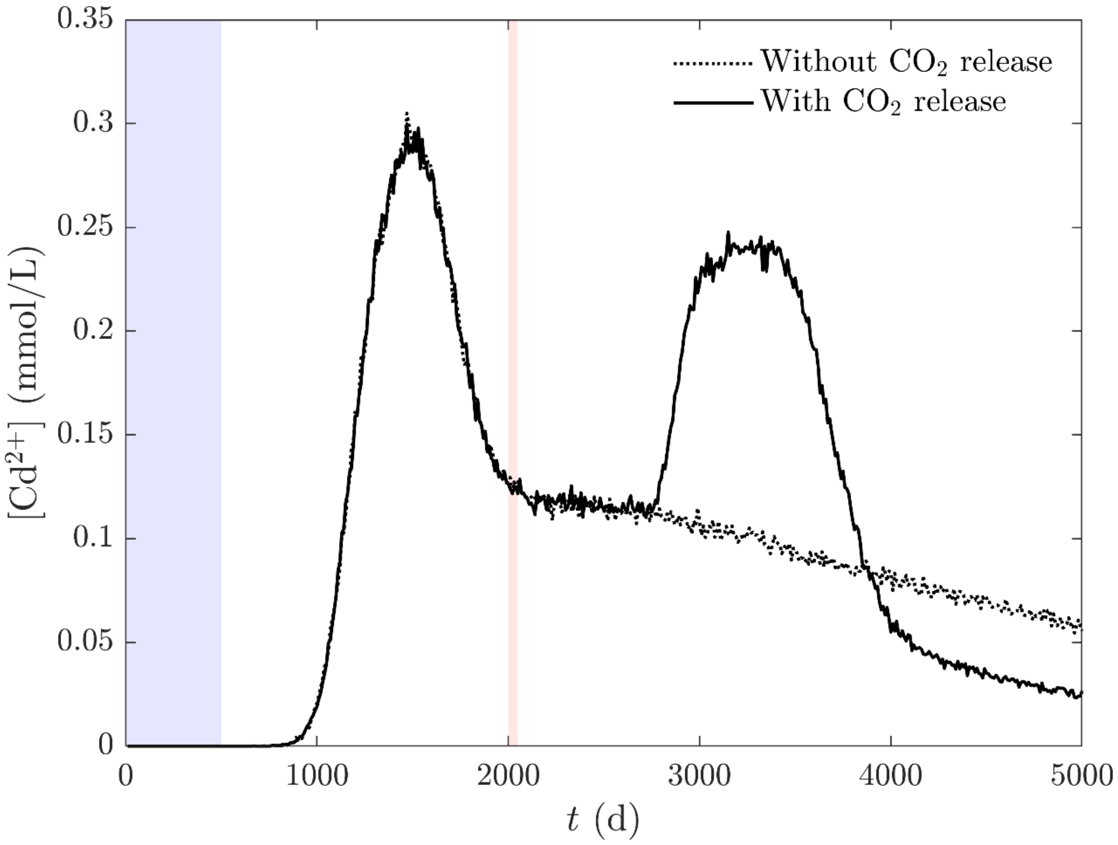


3.4. Cadmium particle velocities and Break-Through Curve

Mean mobility of Cadmium

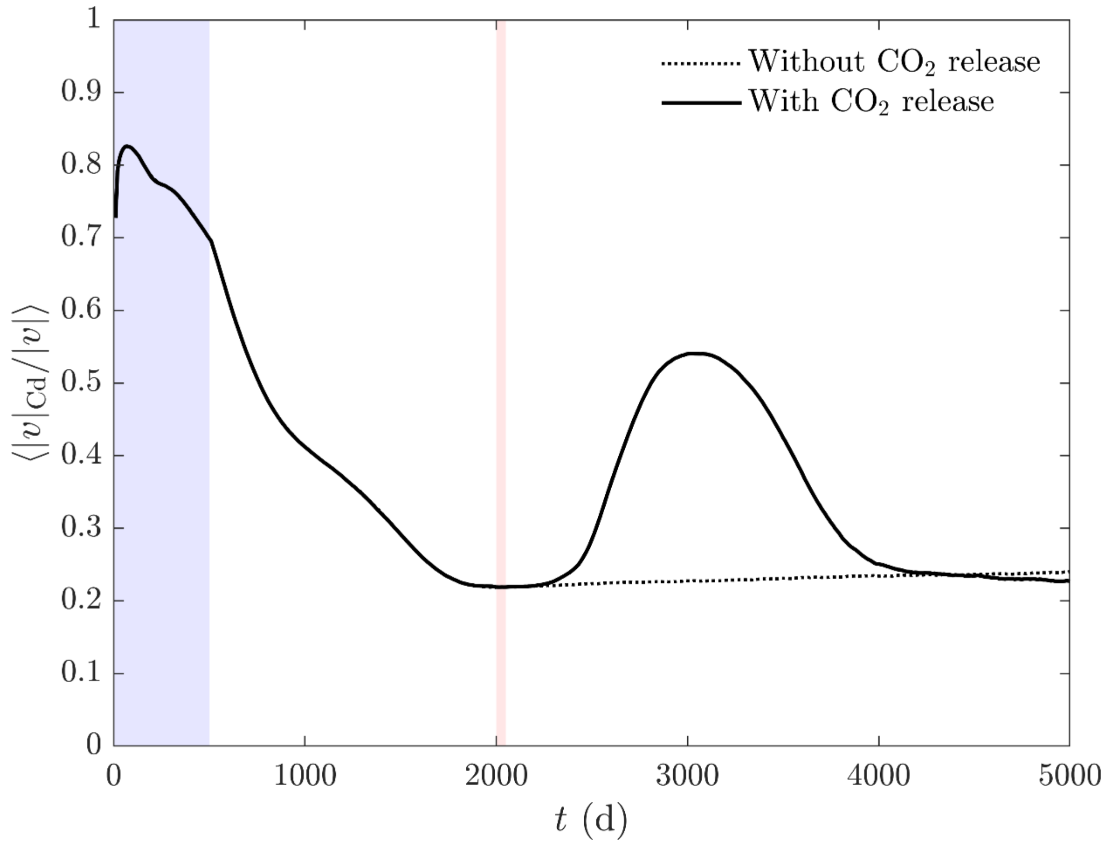


Cadmium Break-Through at Outlet

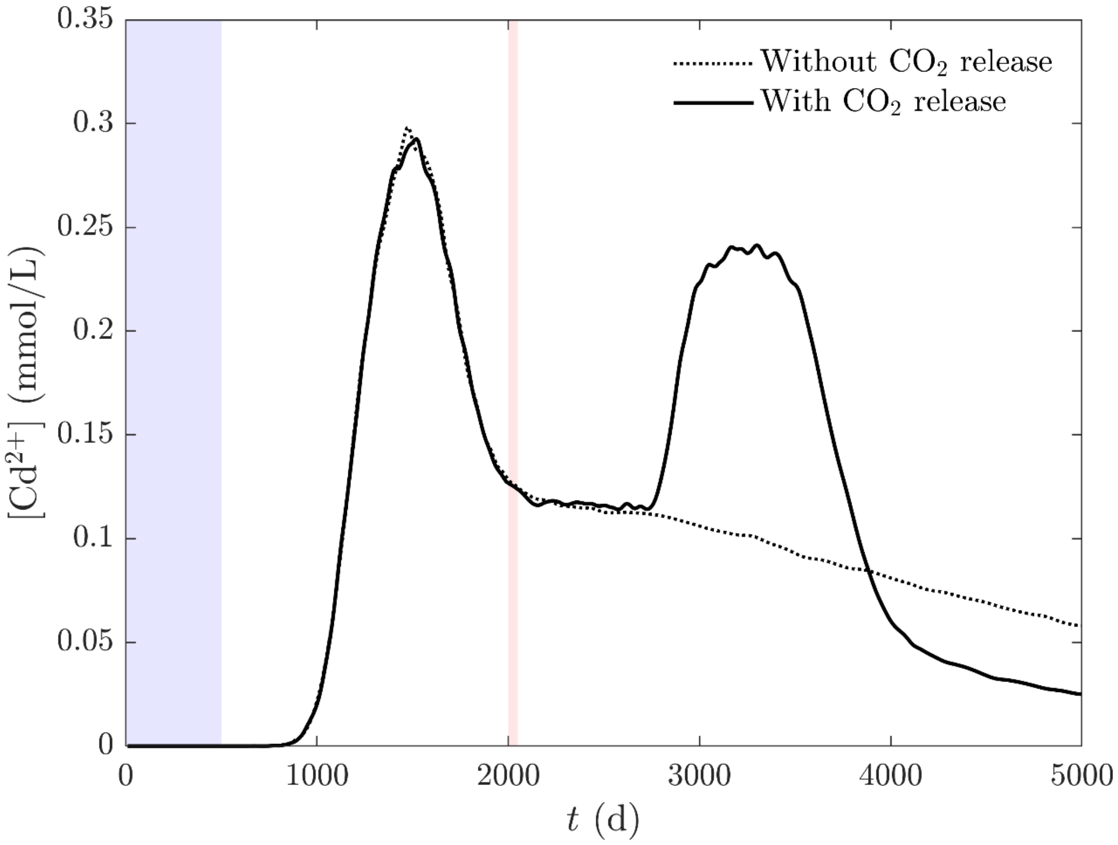


3.4. Cadmium particle velocities and Break-Through Curve

Mean mobility of Cadmium



Cadmium Break-Through at Outlet



4. SUMMARY AND CONCLUSIONS

- The presented technique deals with the problem of **density reconstruction** in particle methods.
- We see evidence of an ideal **accuracy** vs **computational effort** ratio.
- Bounded domains with physical **boundary conditions** are supported.
- It allows us, for instance, to conduct RWPT simulations with **geochemical equilibrium reactions**.
- A versatile MATLAB code called "**bounded adaptive kernel smoothing**" (baks.m) has been developed and published.

5. TO-DO LIST

- **Other applications**? E.g., reconstruction of noisy experimental observations?

- Link optimal kernel evolution to **physical properties** in order to skip optimization phase.

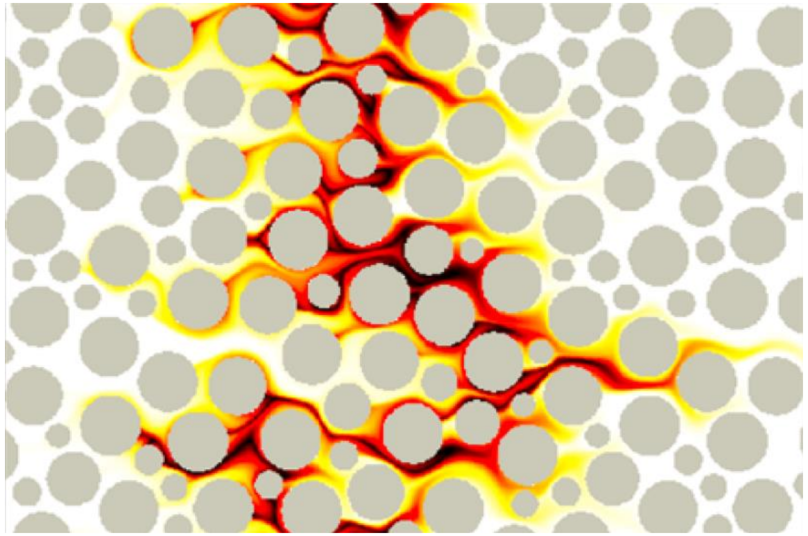
UNIVERSITAT POLITÈCNICA DE CATALUNYA
Department of Civil and Environmental Engineering
Hydrogeology Group GHS (UPC-CSIC)

WE-NEED

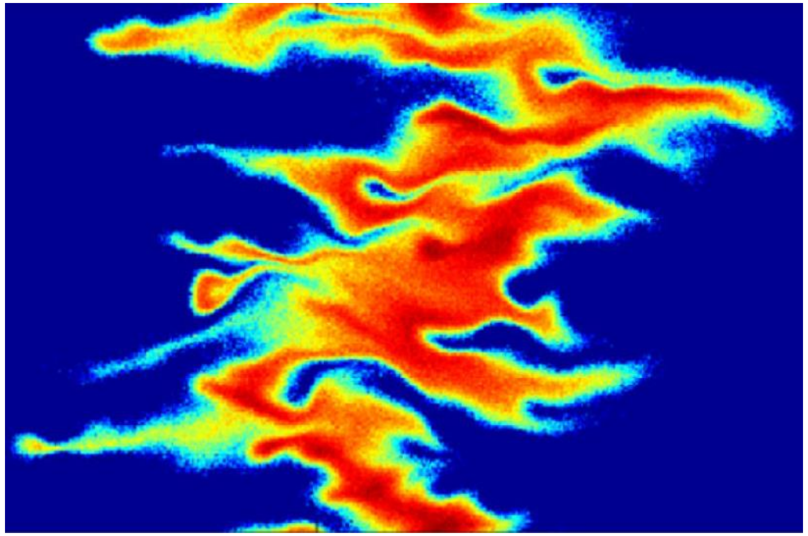
PART 3: A LAGRANGIAN MODEL OF MIXING-LIMITED REACTIVE TRANSPORT

1.1. The upscaled ADE: Spreading vs Mixing

- The **spreading of solutes** in Porous media may be represented by the Advection Dispersion Equation
- However, **spreading ≠ mixing**, and **local fluctuations** are important for chemical reactions.
- Development of **particle-based model** to simultaneously account for the **model-scale dispersion** and the **sub-scale mixing** and reaction.



De Anna et al., 2014



De Dreuzy et al., 2012

2. PROPOSED FORMULATION

2.1. Core idea: The particle as a sub-scale

- At the **model scale**, particles represent the solute spreading as Advection-Dispersion (RWPT):

$$\mathrm{d}X_p = v\mathrm{d}t + \sqrt{2D\mathrm{d}t}\,\xi, \qquad \overline{c}_\mathrm{A}(x) = \phi^{-1}\sum_{p=1}^{N} m_{\mathrm{A},p}\, W(x - X_p)$$

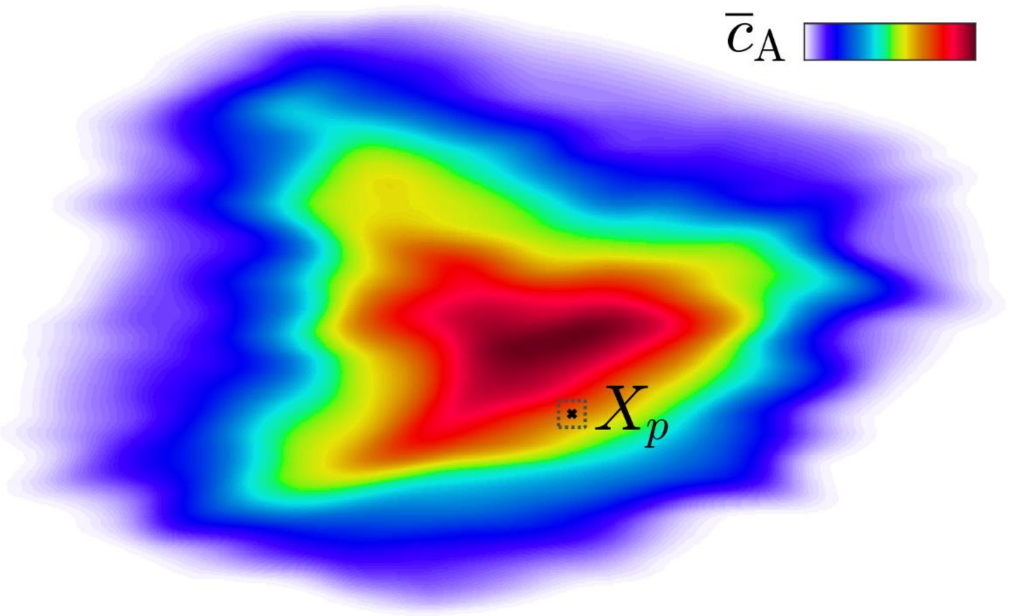
- At the **local scale**, particles are at disequilbrium:

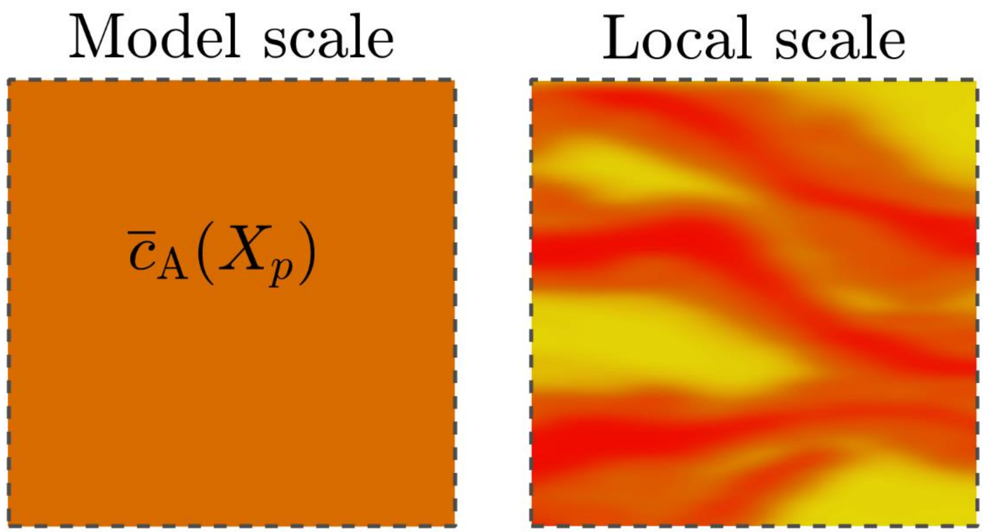
$$C'_{\mathrm{A},p} = C_{\mathrm{A},p} - \overline{c}_\mathrm{A}(X_p)$$

- Hence, a **Eulerian** and a **Lagrangian** conc. coexist.
- The disequilibrium evolves on particles as:

$$\boxed{\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = -\eta\frac{\mathrm{d}\overline{c}_{\mathrm{A},p}}{\mathrm{d}t} - \chi C'_{\mathrm{A},p}}$$

$$0 < \eta < 1, \;\; \chi > 0$$





2.1. Core idea: The particle as a sub-scale

- At the **model scale**, particles represent the solute spreading as Advection-Dispersion (RWPT):

$$\mathrm{d}X_p = v\mathrm{d}t + \sqrt{2D\mathrm{d}t}\,\xi, \qquad \overline{c}_\mathrm{A}(x) = \phi^{-1}\sum_{p=1}^{N} m_{\mathrm{A},p}\, W(x - X_p)$$

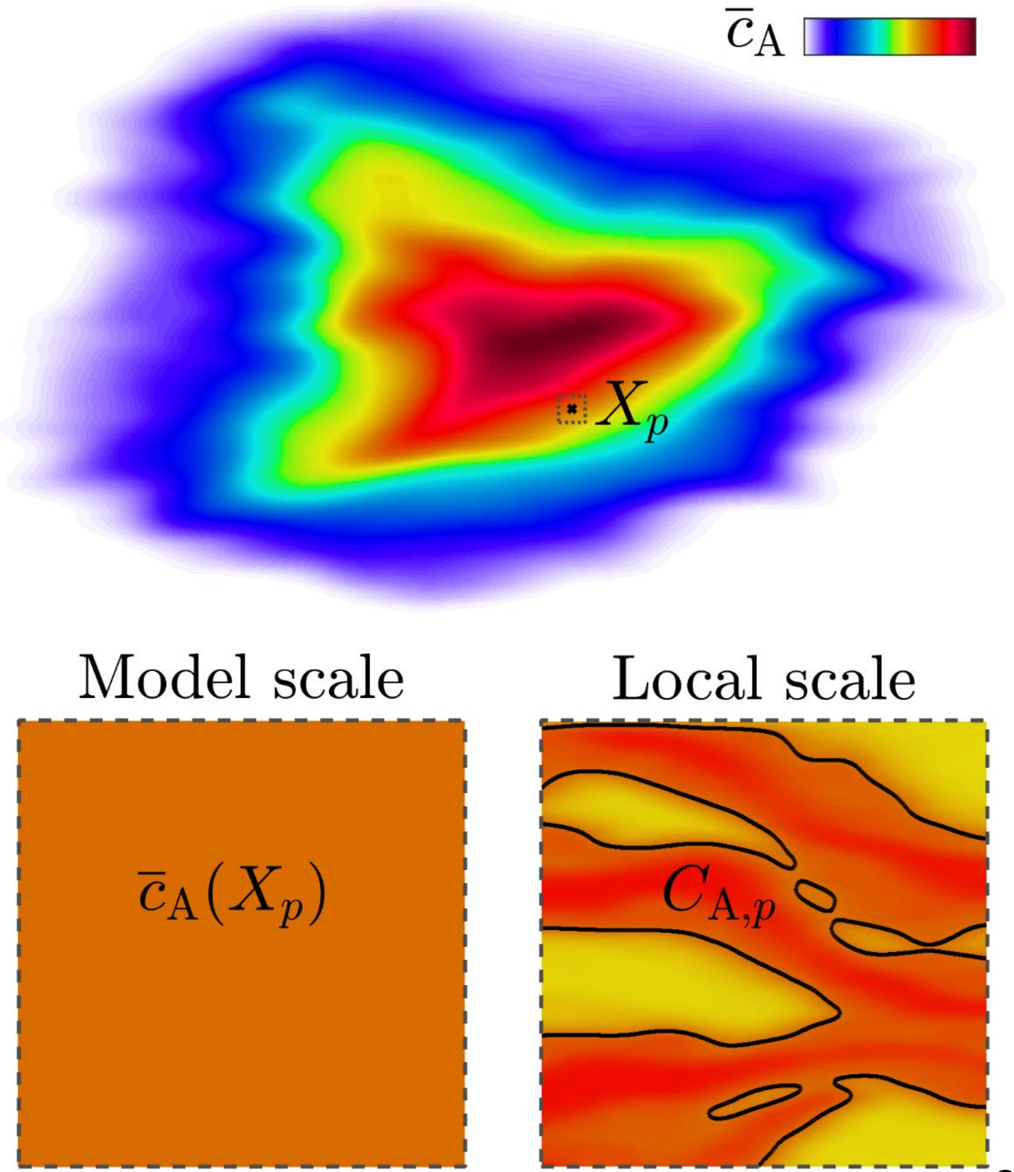
- At the **local scale**, particles are at disequilbrium:

$$C'_{\mathrm{A},p} = C_{\mathrm{A},p} - \overline{c}_\mathrm{A}(X_p)$$

- Hence, a **Eulerian** and a **Lagrangian** conc. coexist.
- The disequilibrium evolves on particles as:

$$\boxed{\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = -\eta\frac{\mathrm{d}\overline{c}_{\mathrm{A},p}}{\mathrm{d}t} - \chi C'_{\mathrm{A},p}}$$

$$0 < \eta < 1, \quad \chi > 0$$



2. PROPOSED FORMULATION

WE-NEED

2.2. The simplified local mixing process

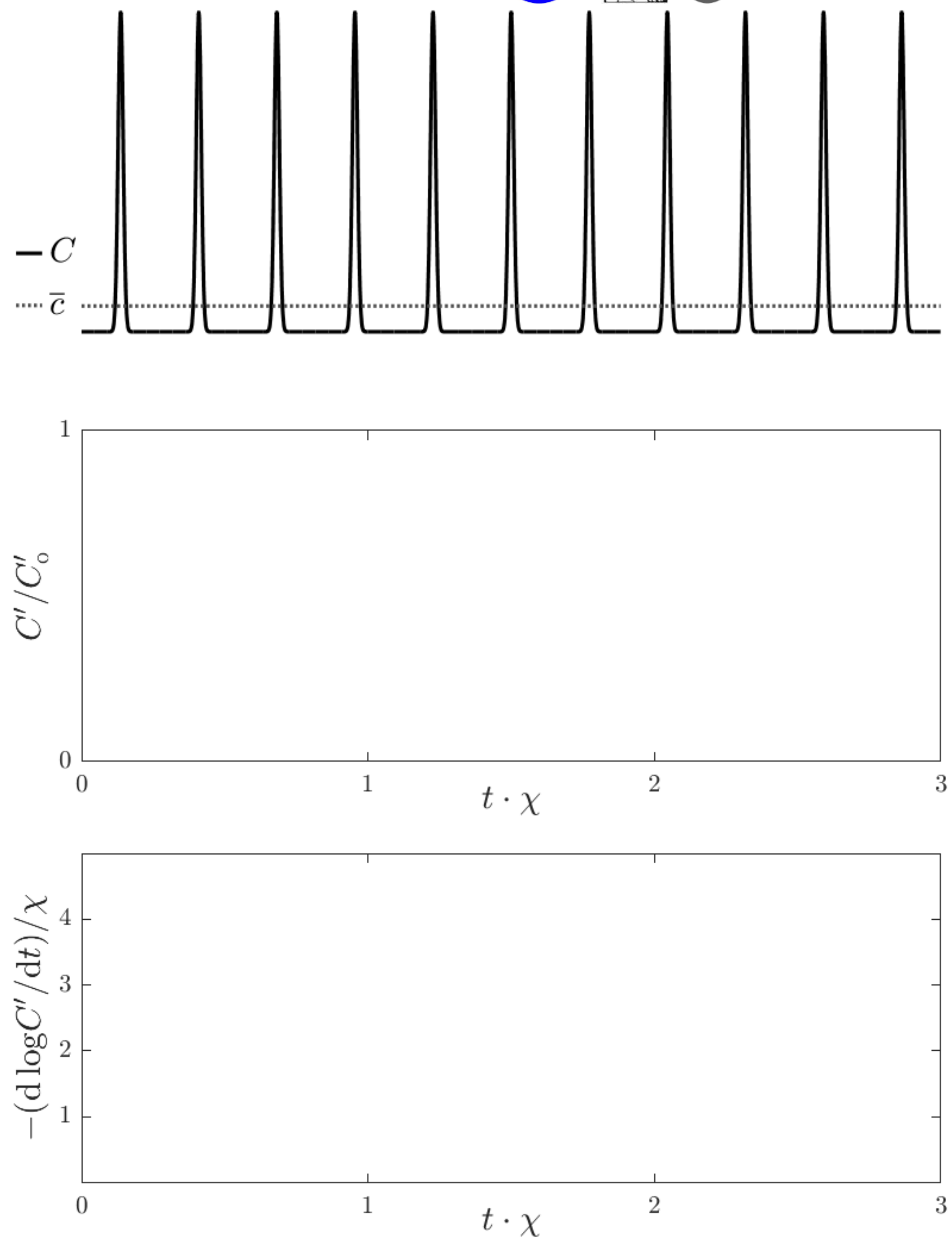
$$\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = \overbrace{-\eta \frac{\mathrm{d}\bar{c}_{\mathrm{A},p}}{\mathrm{d}t}}^{\text{Disequilibrium } \textbf{Generation}} \overbrace{- \chi C'_{\mathrm{A},p}}^{\text{Disequilibrium } \textbf{Destruction}}$$

Fraction of “linear mixing”

Rate of “linear mixing”

Every change in “ambient” concentration experienced by the particle is the result of **hydrodynamic spreading**. Hence, it triggers a **mixing event**, in which:

- The “instantaneous” mixing $(1-\eta)$ represents the initial process of **stretching**-enhanced mixing.
- The mixing rate χ accounts for the first-order mixing in a **stationary** (coalescent) regime, $\chi = D_\mu / s^2$.



2. PROPOSED FORMULATION

WE-NEED

2.2. The simplified local mixing process

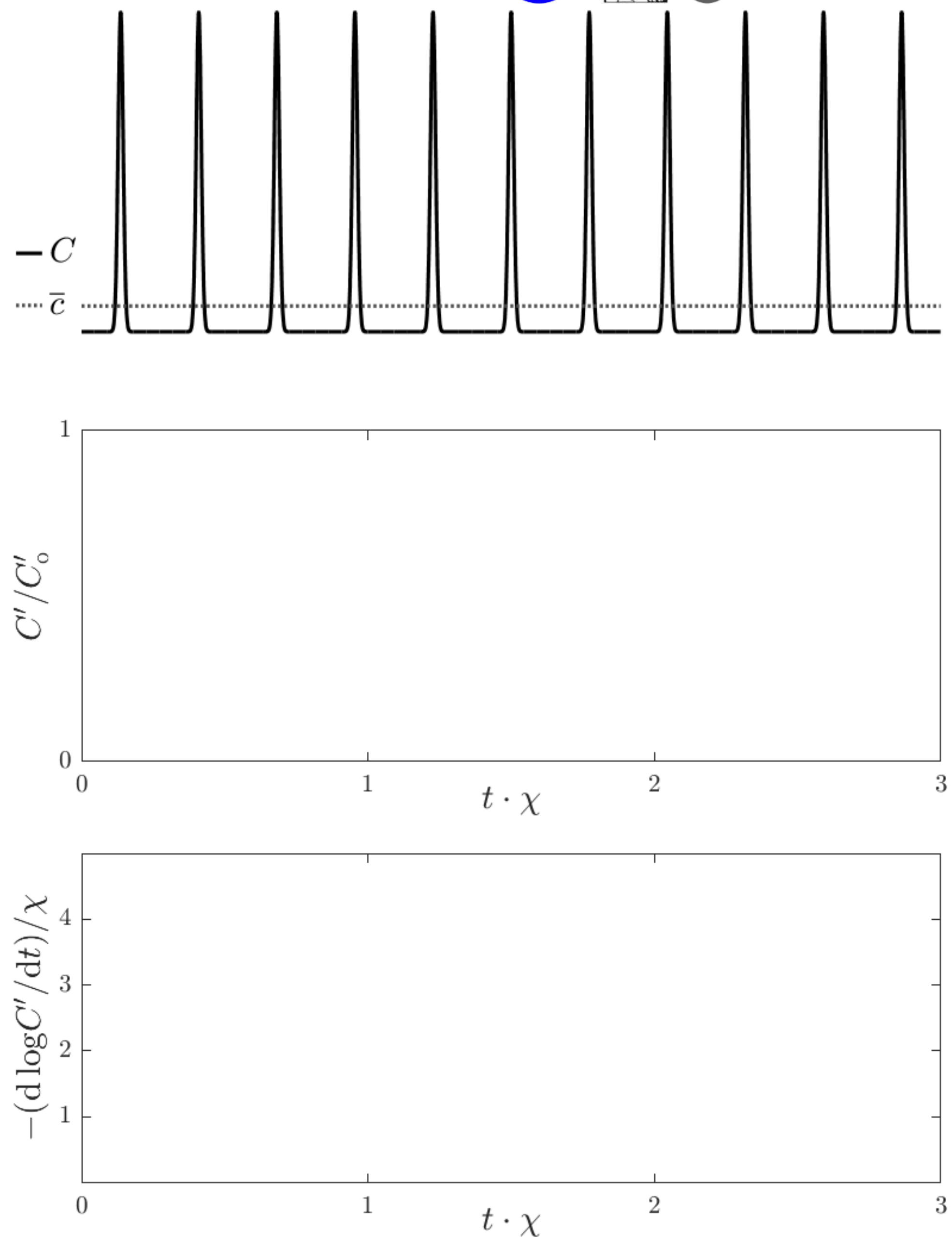
$$\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = \overbrace{-\eta \frac{\mathrm{d}\overline{c}_{\mathrm{A},p}}{\mathrm{d}t}}^{\text{Disequilibrium Generation}} \overbrace{- \chi C'_{\mathrm{A},p}}^{\text{Disequilibrium Destruction}}$$

Fraction of "linear mixing"

Rate of "linear mixing"

Every change in "ambient" concentration experienced by the particle is the result of **hydrodynamic spreading**. Hence, it triggers a **mixing event**, in which:

- The "instantaneous" mixing $(1-\eta)$ represents the initial process of **stretching**-enhanced mixing.
- The mixing rate χ accounts for the first-order mixing in a **stationary** (coalescent) regime, $\chi = D_\mu / s^2$.



2.2. The simplified local mixing process

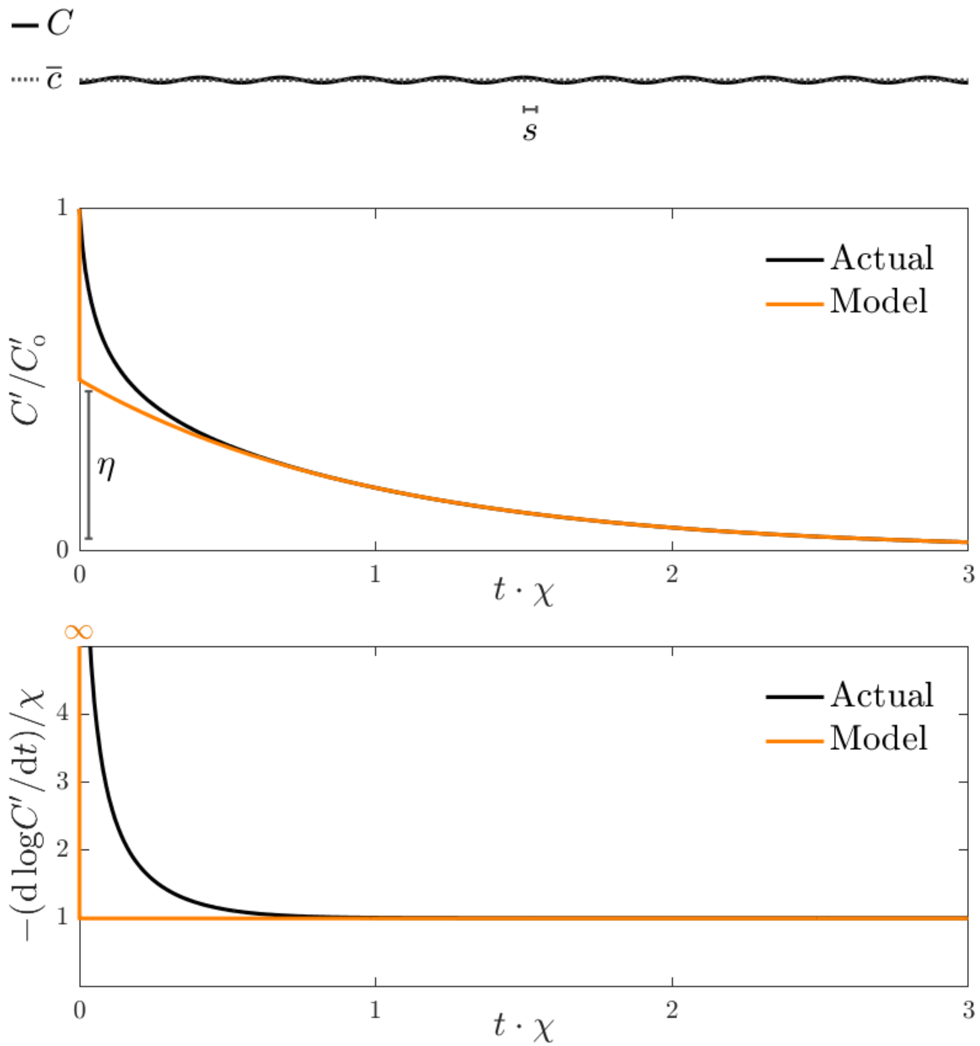
$$\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = \underbrace{-\eta\frac{\mathrm{d}\bar{c}_{\mathrm{A},p}}{\mathrm{d}t}}_{\text{Disequilibrium Generation}} \underbrace{- \chi C'_{\mathrm{A},p}}_{\text{Disequilibrium Destruction}}$$

η: **Fraction** of "linear mixing"

χ: **Rate** of "linear mixing"

Every change in "ambient" concentration experienced by the particle is the result of **hydrodynamic spreading**. Hence, it triggers a **mixing event**, in which:

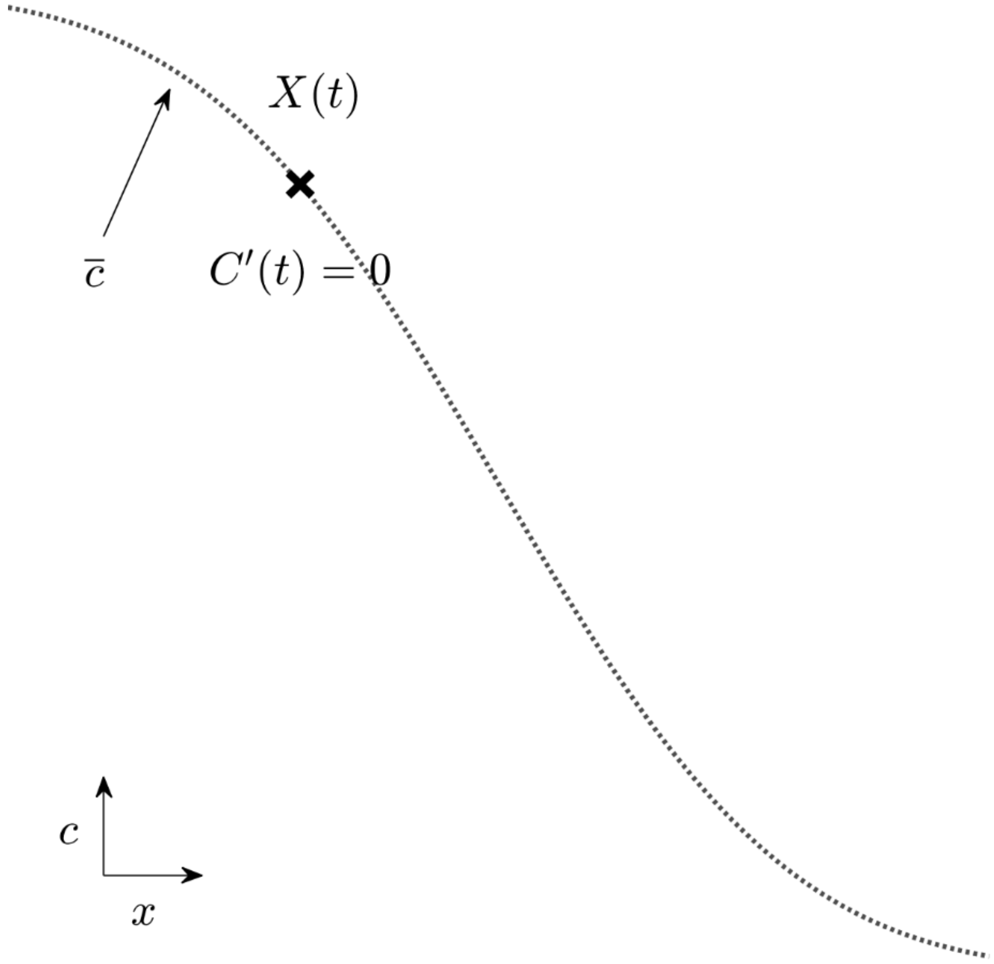
- The "instantaneous" mixing $(1-\eta)$ represents the initial process of **stretching**-enhanced mixing.
- The mixing rate χ accounts for the first-order mixing in a **stationary** (coalescent) regime, $\chi = D_\mu/s^2$.



2.2. The simplified local mixing process

$$\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = \underbrace{-\eta \frac{\mathrm{d}\overline{c}_{\mathrm{A},p}}{\mathrm{d}t}}_{\text{Disequilibrium Generation}} \underbrace{- \chi C'_{\mathrm{A},p}}_{\text{Disequilibrium Destruction}}$$

Fraction of "linear mixing" (η); **Rate** of "linear mixing" (χ)



Every change in "ambient" concentration experienced by the particle is the result of **hydrodynamic spreading**. Hence, it triggers a **mixing event**, in which:

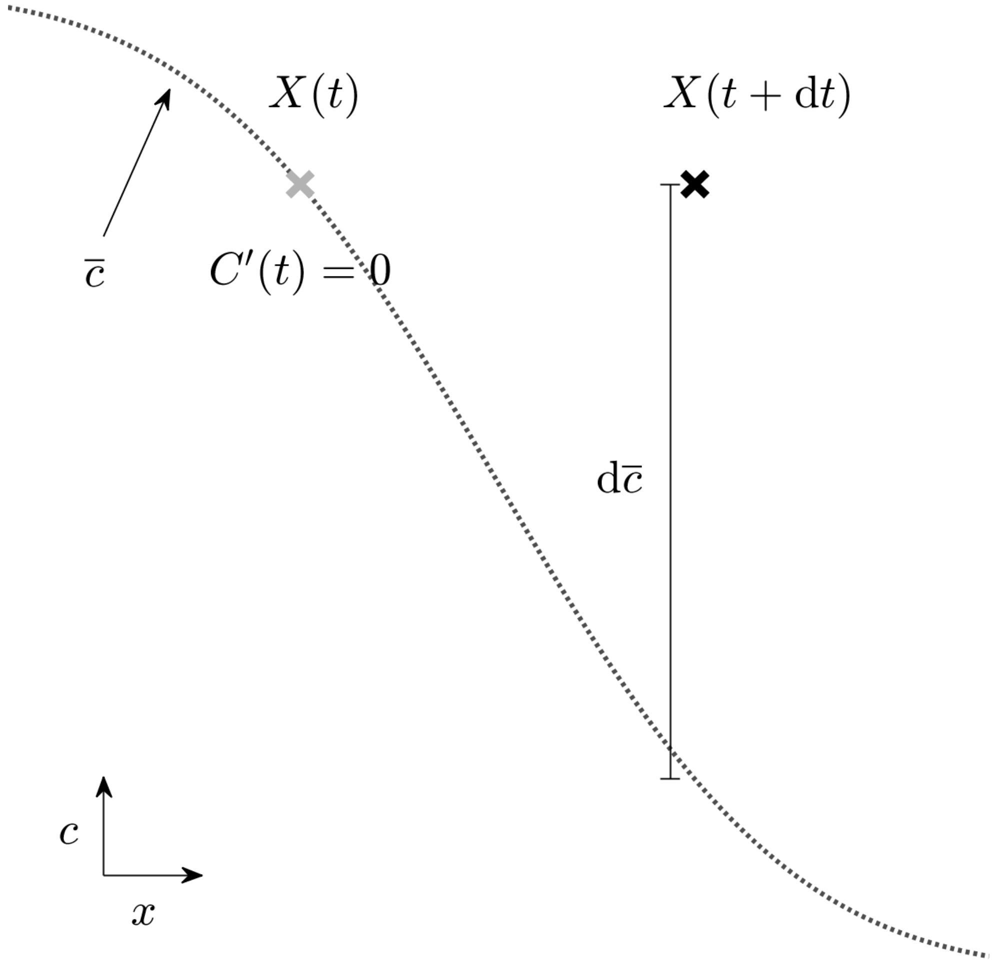
- The "instantaneous" mixing $(1-\eta)$ represents the initial process of **stretching**-enhanced mixing.
- The mixing rate χ accounts for the first-order mixing in a **stationary** (coalescent) regime, $\chi = D_\mu / s^2$.

2.2. The simplified local mixing process

$$\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = -\overbrace{\eta\,\frac{\mathrm{d}\bar{c}_{\mathrm{A},p}}{\mathrm{d}t}}^{\text{Disequilibrium } \textbf{Generation}} - \overbrace{\chi C'_{\mathrm{A},p}}^{\text{Disequilibrium } \textbf{Destruction}}$$

Fraction of "linear mixing" (η)

Rate of "linear mixing" (χ)



Every change in "ambient" concentration experienced by the particle is the result of **hydrodynamic spreading**. Hence, it triggers a **mixing event**, in which:

- The "instantaneous" mixing $(1-\eta)$ represents the initial process of **stretching**-enhanced mixing.
- The mixing rate χ accounts for the first-order mixing in a **stationary** (coalescent) regime, $\chi = D_\mu / s^2$.

2.2. The simplified local mixing process

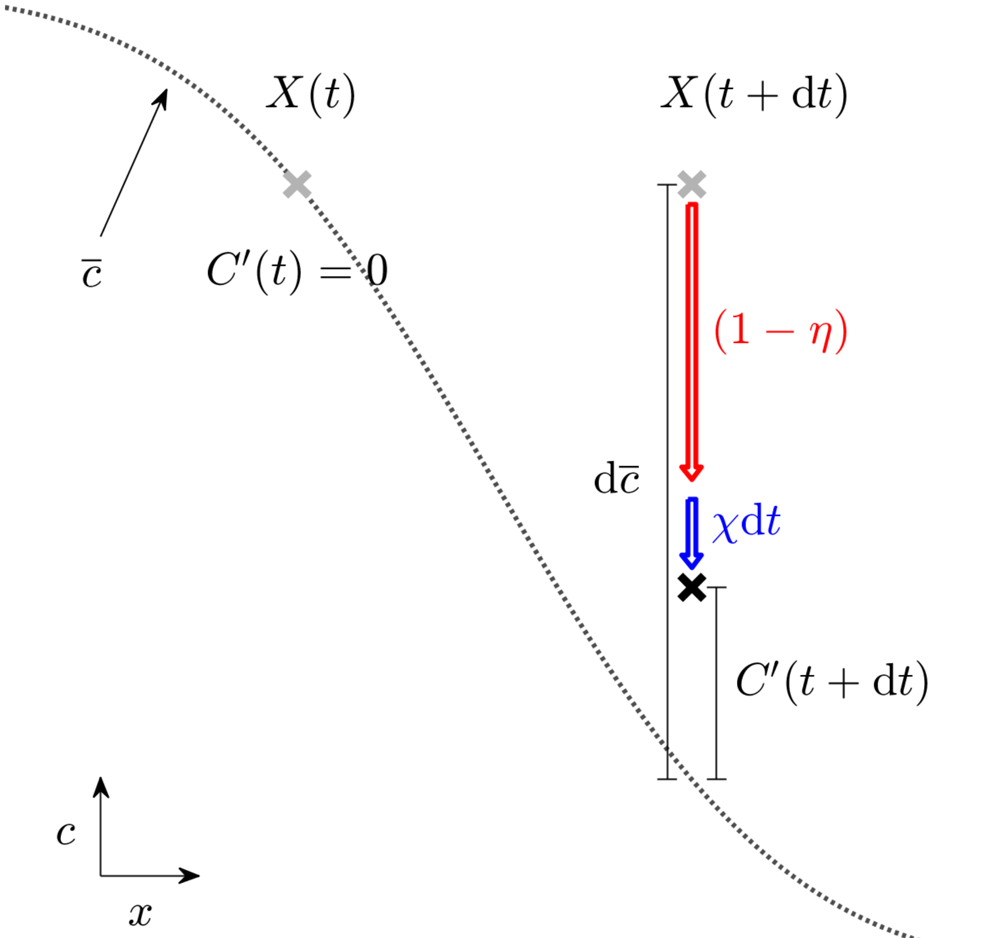
$$\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = \underbrace{-\eta \frac{\mathrm{d}\bar{c}_{\mathrm{A},p}}{\mathrm{d}t}}_{\substack{\text{Disequilibrium} \\ \textbf{Generation}}} \underbrace{- \chi C'_{\mathrm{A},p}}_{\substack{\text{Disequilibrium} \\ \textbf{Destruction}}}$$

η: **Fraction** of "linear mixing"

χ: **Rate** of "linear mixing"

Every change in "ambient" concentration experienced by the particle is the result of **hydrodynamic spreading**. Hence, it triggers a **mixing event**, in which:

- The "instantaneous" mixing $(1-\eta)$ represents the initial process of **stretching**-enhanced mixing.
- The mixing rate χ accounts for the first-order mixing in a **stationary** (coalescent) regime, $\chi = D_\mu / s^2$.

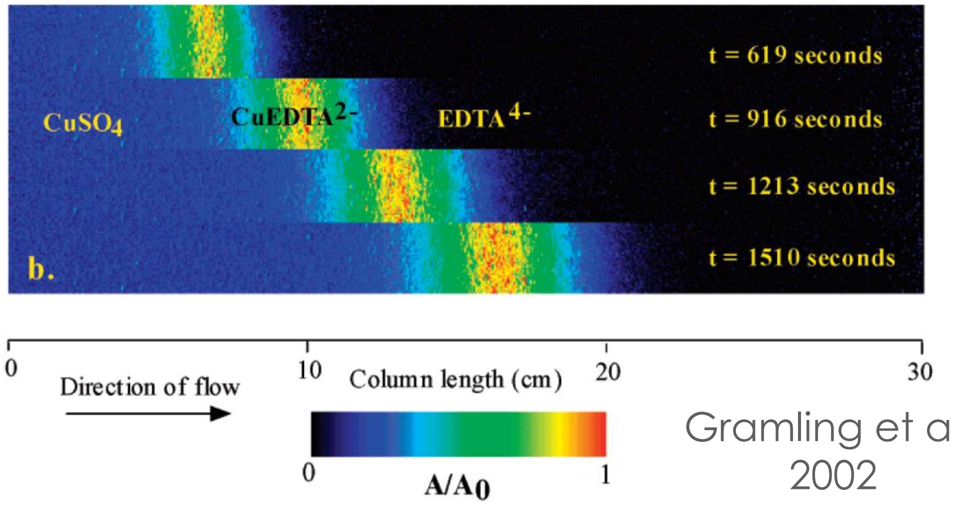


3. IMPLEMENTATION

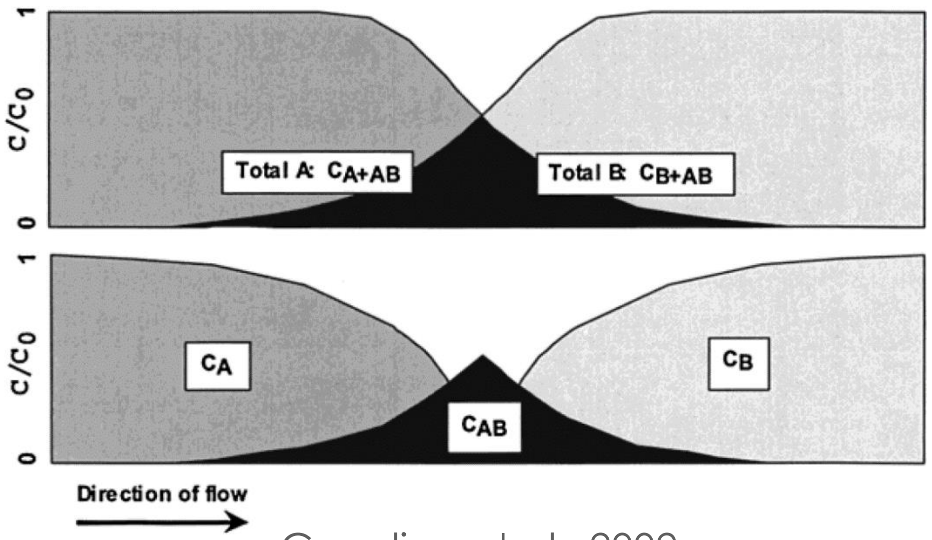
3.1. Gramling et al.'s experiment (2002)

A B

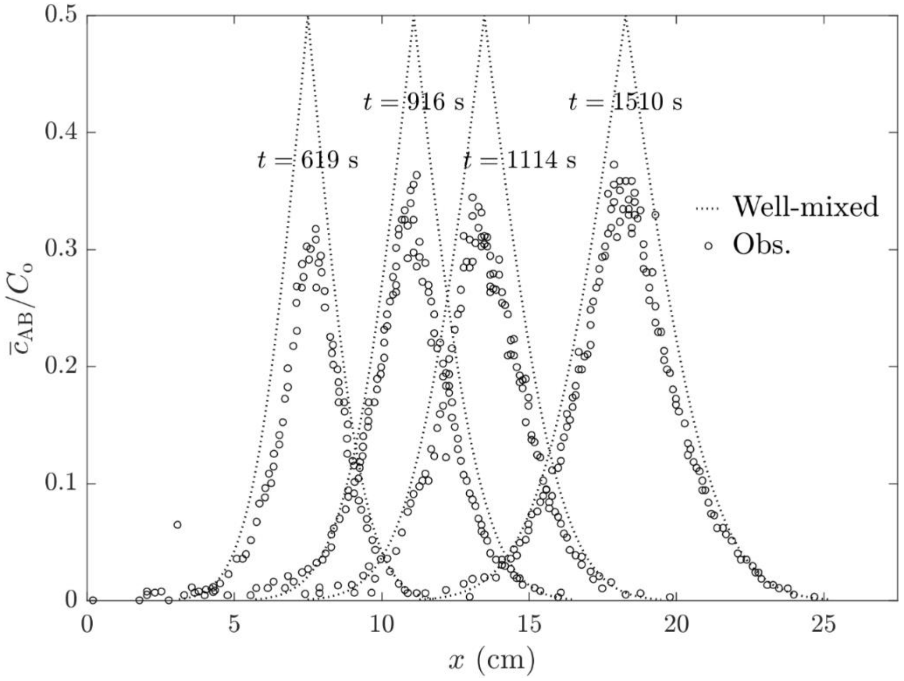
- "Instantaneous" reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}$.
- "Conservative" trnsp. of $\mathrm{A_{tot}} = \mathrm{A} + \mathrm{AB}$, $\mathrm{B_{tot}} = \mathrm{B} + \mathrm{AB}$.
- "Homogeneous" porous medium.
- Reaction did not match well-mixed prediction.



Gramling et al., 2002



Gramling et al., 2002

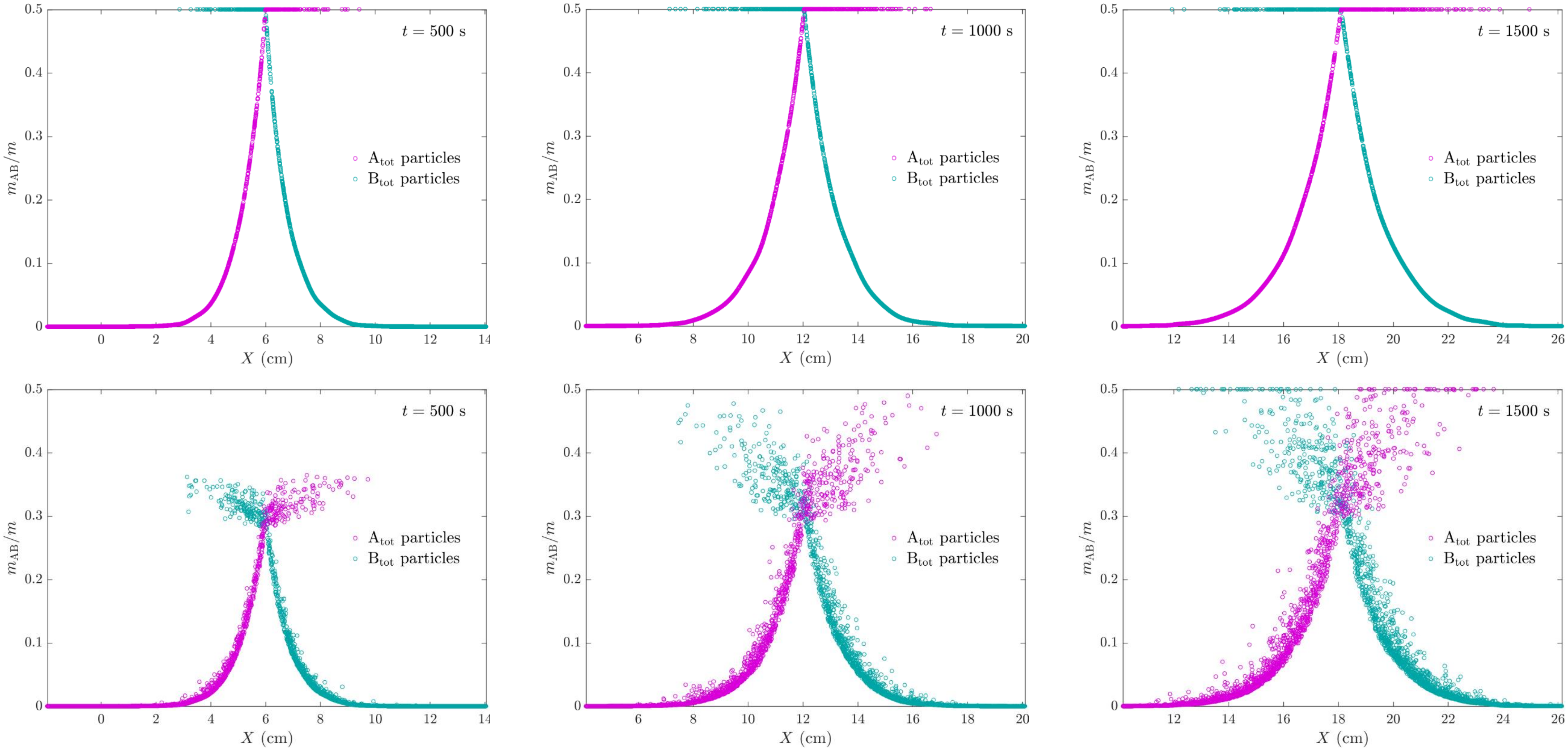


3. IMPLEMENTATION

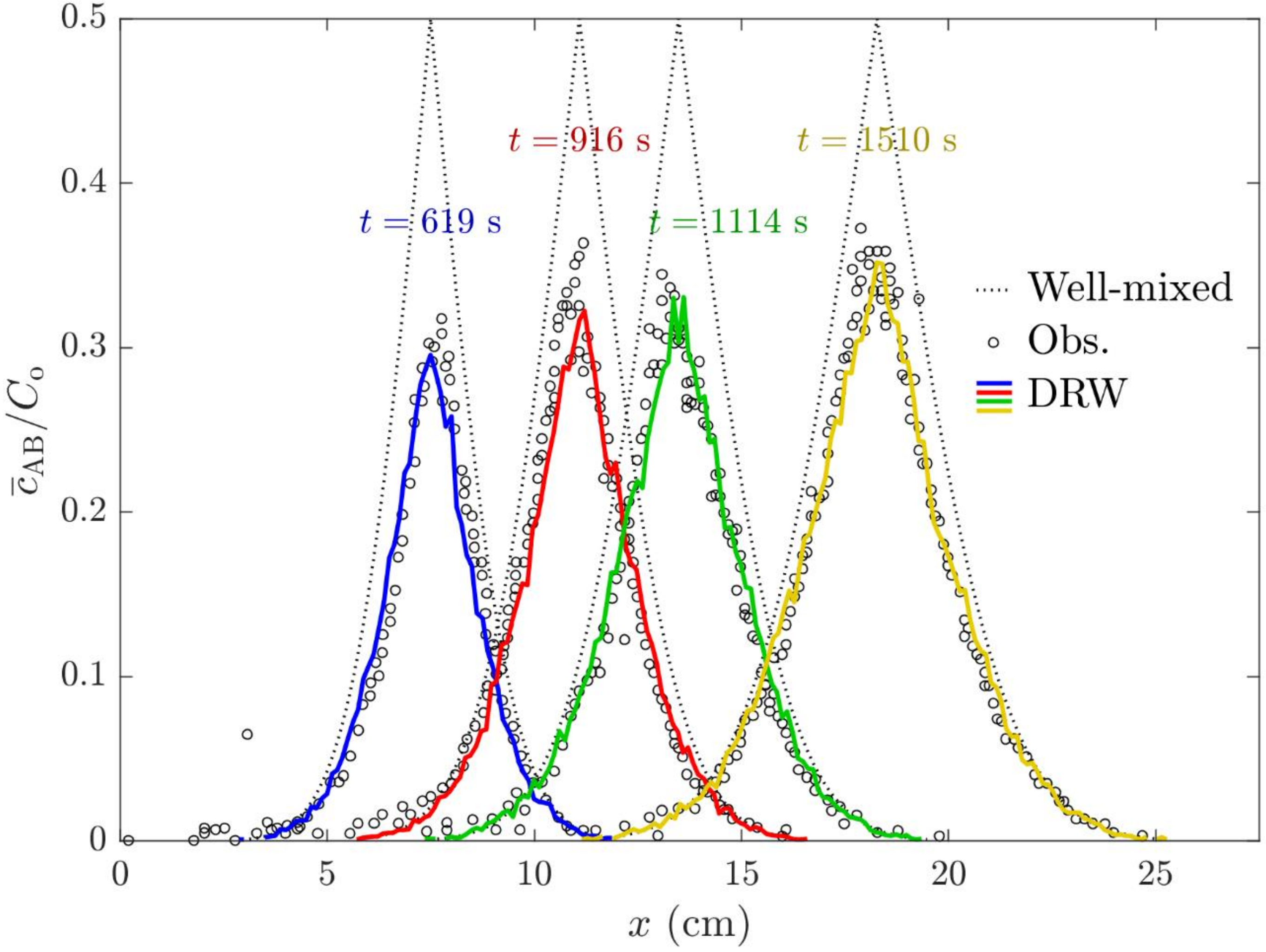
3.2. Product mass formation

PERFECT MIXING

MIXING LIMITATION



3.4. Product concentrations



$$\frac{\mathrm{d}C'_{A,p}}{\mathrm{d}t} = -\eta \frac{\mathrm{d}\bar{c}_{A,p}}{\mathrm{d}t} - \chi C'_{A,p}$$

$\eta \approx 0.45$

$\chi \approx 10^{-3}\ \mathrm{s}^{-1}$

$(D_\mu = 7 \cdot 10^{-7}\ \mathrm{cm^2 s^{-1}};\ \ \chi = D_\mu / s^2)$

$s \approx 0.26\ \mathrm{mm} = 0.2 \cdot \ell$

20% of the grain size

3.5. Main advantages with respect to other "mixing-limitation" models

- Convergence with the **number of numerical particles** / particle support volume.
- Independent of a "time origin" or "unmixed initial condition", hence potentially applicable to **general initial and boundary conditions**.
- The model also reproduces the transport of (local) **concentration variance**

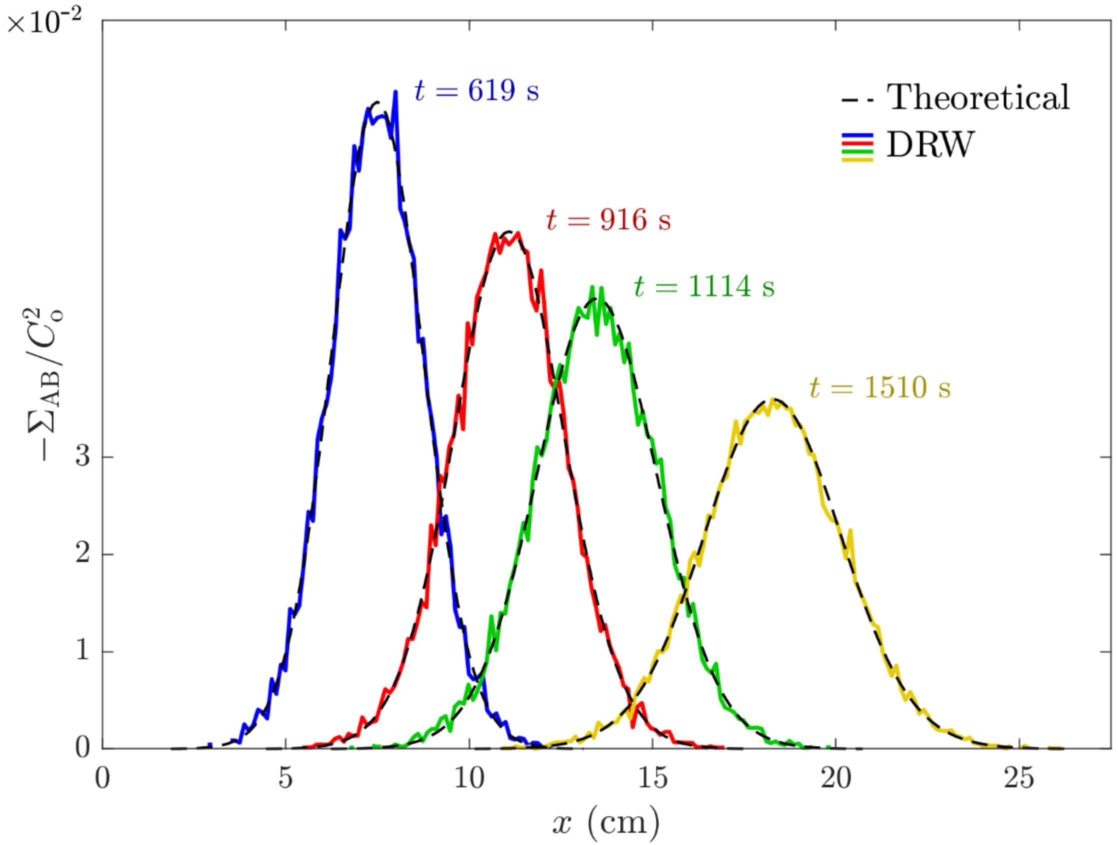
4. CONCENTRATION VARIANCE AND MIXING

4.1. Concentration Covariance

$$\begin{cases} \mathrm{d}X_p = v\mathrm{d}t + \sqrt{2D\mathrm{d}t}\,\xi \\ \dfrac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = -\eta \dfrac{\mathrm{d}\bar{c}_{\mathrm{A},p}}{\mathrm{d}t} - \chi C'_{\mathrm{A},p} \end{cases}$$

$$\Sigma_{\mathrm{AB}} := \overline{C'_{\mathrm{A}} C'_{\mathrm{B}}}$$

$$\boxed{\frac{\partial \Sigma_{\mathrm{AB}}}{\partial t} = \underbrace{2\eta D \frac{\partial \bar{c}_{\mathrm{A}}}{\partial x}\frac{\partial \bar{c}_{\mathrm{B}}}{\partial x}}_{\substack{\text{Covariance}\\ \textbf{Generation}}} \underbrace{- 2\chi \Sigma_{\mathrm{AB}}}_{\substack{\text{Covariance}\\ \textbf{Destruction}}} \underbrace{- v\frac{\partial \Sigma_{\mathrm{AB}}}{\partial x} + D\frac{\partial^2 \Sigma_{\mathrm{AB}}}{\partial x^2}}_{\substack{\text{Covariance}\\ \textbf{Transport}}}}$$



Equivalent to **Kapoor et al. (1994)** concentration variance conservation equation!

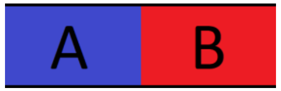
Fundamental difference: For Kapoor et al., $1 - \eta = D_\mu / D$ **(stationarity assumption!)**

$\chi = D_\mu / s^2$

4.2. Mixing State: Gramling

- Mixing state: $$M_{\mathrm{AB}} \coloneqq M_{\mathrm{AB}}^{\bar{\mathrm{c}}} + M_{\mathrm{AB}}^{\Sigma} = \int_{\mathbb{R}} \bar{c}_{\mathrm{A}}\,\bar{c}_{\mathrm{B}}\,\mathrm{d}x + \int_{\mathbb{R}} \Sigma_{\mathrm{AB}}\,\mathrm{d}x \qquad \gamma_{\mathrm{AB}} \coloneqq M_{\mathrm{AB}}^{\Sigma} / M_{\mathrm{AB}}^{\bar{\mathrm{c}}}$$

- Gramling's setup:



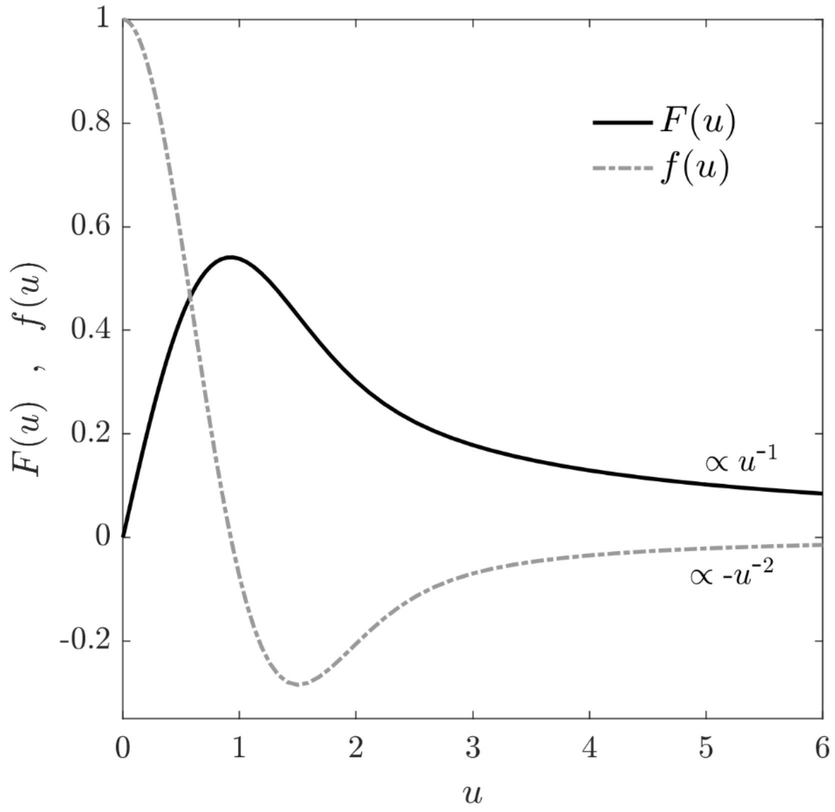
$$M_{\mathrm{AB}}^{\bar{\mathrm{c}}}(t) = C_{\mathrm{o}}^{2}\sqrt{2Dt/\pi}$$

$$M_{\mathrm{AB}}^{\Sigma}(t) = -\frac{\eta C_{\mathrm{o}}^{2}\sqrt{D}}{\pi\chi}\,F\left(\sqrt{2\chi t}\right)$$

$$\gamma_{\mathrm{AB}}(t) = -\frac{1}{\sqrt{2\chi t}}F\left(\sqrt{2\chi t}\right)$$

$$F(u) \coloneqq \mathrm{e}^{-u^{2}}\int_{0}^{u}\mathrm{e}^{r^{2}} \approx$$

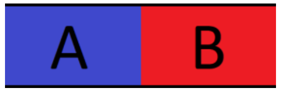
"Dawson's Integral" $$\approx \begin{cases} u, & (u \ll 1) \\ (2u)^{-1}, & (u \gg 1) \end{cases}$$



4.2. Mixing State: Gramling

- Mixing state: $$M_{\mathrm{AB}} := M_{\mathrm{AB}}^{\bar{\mathrm{c}}} + M_{\mathrm{AB}}^{\Sigma} = \int_{\mathbb{R}} \bar{c}_{\mathrm{A}}\, \bar{c}_{\mathrm{B}}\, \mathrm{d}x + \int_{\mathbb{R}} \Sigma_{\mathrm{AB}}\, \mathrm{d}x \qquad \gamma_{\mathrm{AB}} := M_{\mathrm{AB}}^{\Sigma} / M_{\mathrm{AB}}^{\bar{\mathrm{c}}}$$

- Gramling's setup:



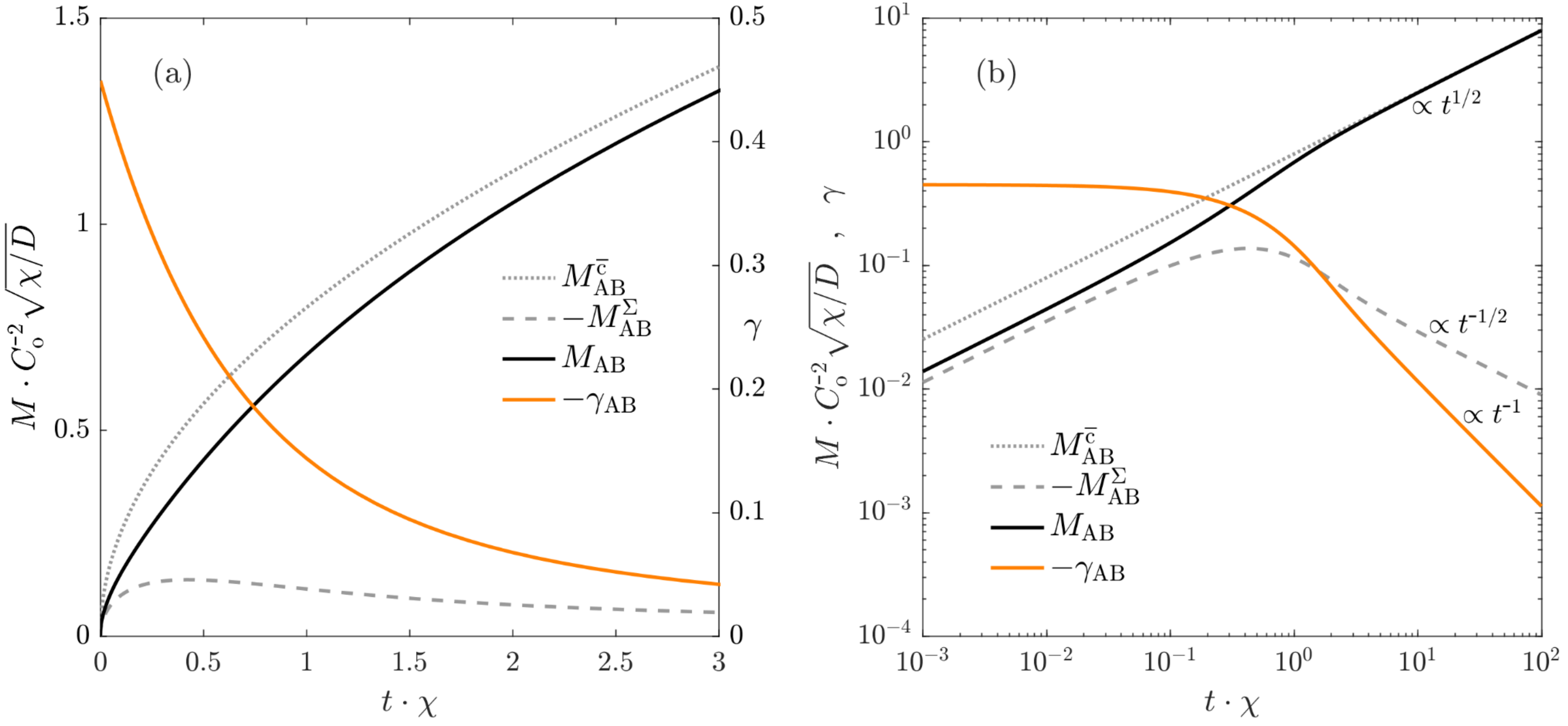
$$M_{\mathrm{AB}}^{\bar{\mathrm{c}}}(t) = C_{\mathrm{o}}^2 \sqrt{2Dt/\pi}$$

$$M_{\mathrm{AB}}^{\Sigma}(t) = -\frac{\eta C_{\mathrm{o}}^2 \sqrt{D}}{\pi \chi} F\left(\sqrt{2\chi t}\right)$$

$$\gamma_{\mathrm{AB}}(t) = -\frac{1}{\sqrt{2\chi t}} F\left(\sqrt{2\chi t}\right)$$

$$F(u) := \mathrm{e}^{-u^2} \int_0^u \mathrm{e}^{r^2} \approx$$

"Dawson's Integral" $$\approx \begin{cases} u, & (u \ll 1) \\ (2u)^{-1}, & (u \gg 1) \end{cases}$$



4.3. Mixing State: “Dirac” Injection

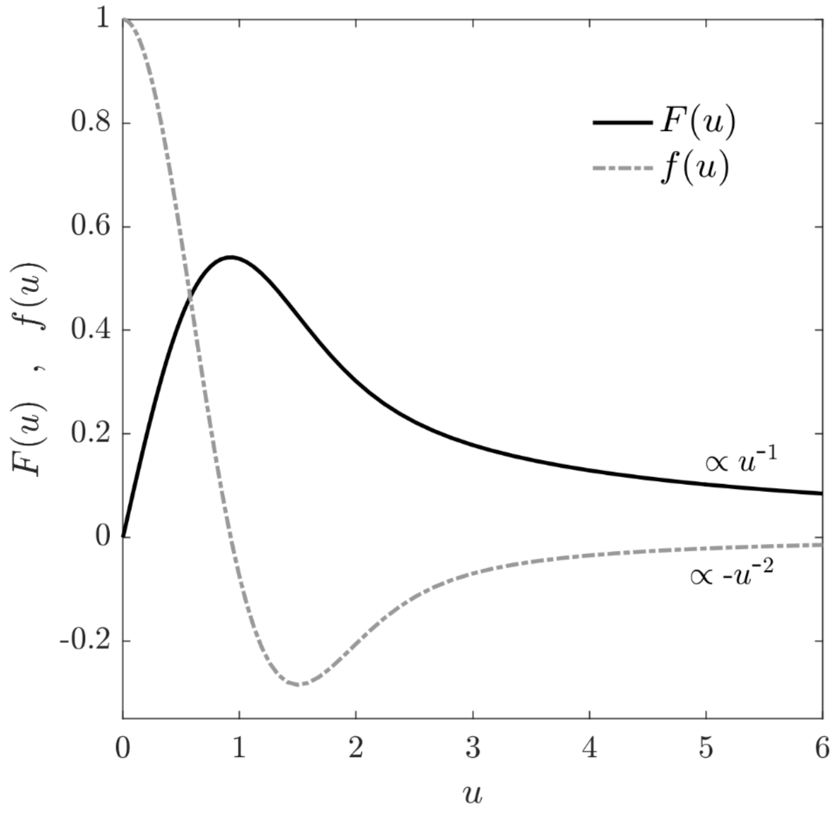
- Mixing state: $$M_{\mathrm{AA}} := M_{\mathrm{AA}}^{\bar{c}} + M_{\mathrm{AA}}^{\Sigma} = \int_{\mathbb{R}} \bar{c}_{\mathrm{A}}^{2}\, \mathrm{d}x + \int_{\mathbb{R}} \Sigma_{\mathrm{AA}}\, \mathrm{d}x \qquad \gamma_{\mathrm{AA}} := M_{\mathrm{AA}}^{\Sigma} / M_{\mathrm{AA}}^{\bar{c}}$$

- “Dirac” injection:

A

$$\gamma_{\mathrm{AA}}(t) = \eta\left[\left(1+\sqrt{\frac{t}{t_{\mathrm{o}}}}\right)\mathrm{e}^{-2\chi t} - f\left(\sqrt{2\chi t}\right)\right]$$

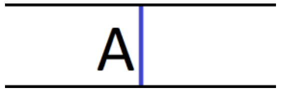
$$f(u) := \partial F/\partial u \approx \begin{cases} 1, & (u \ll 1) \\ -\frac{1}{2}u^{-2}, & (u \gg 1) \end{cases}$$



4.3. Mixing State: "Dirac" Injection

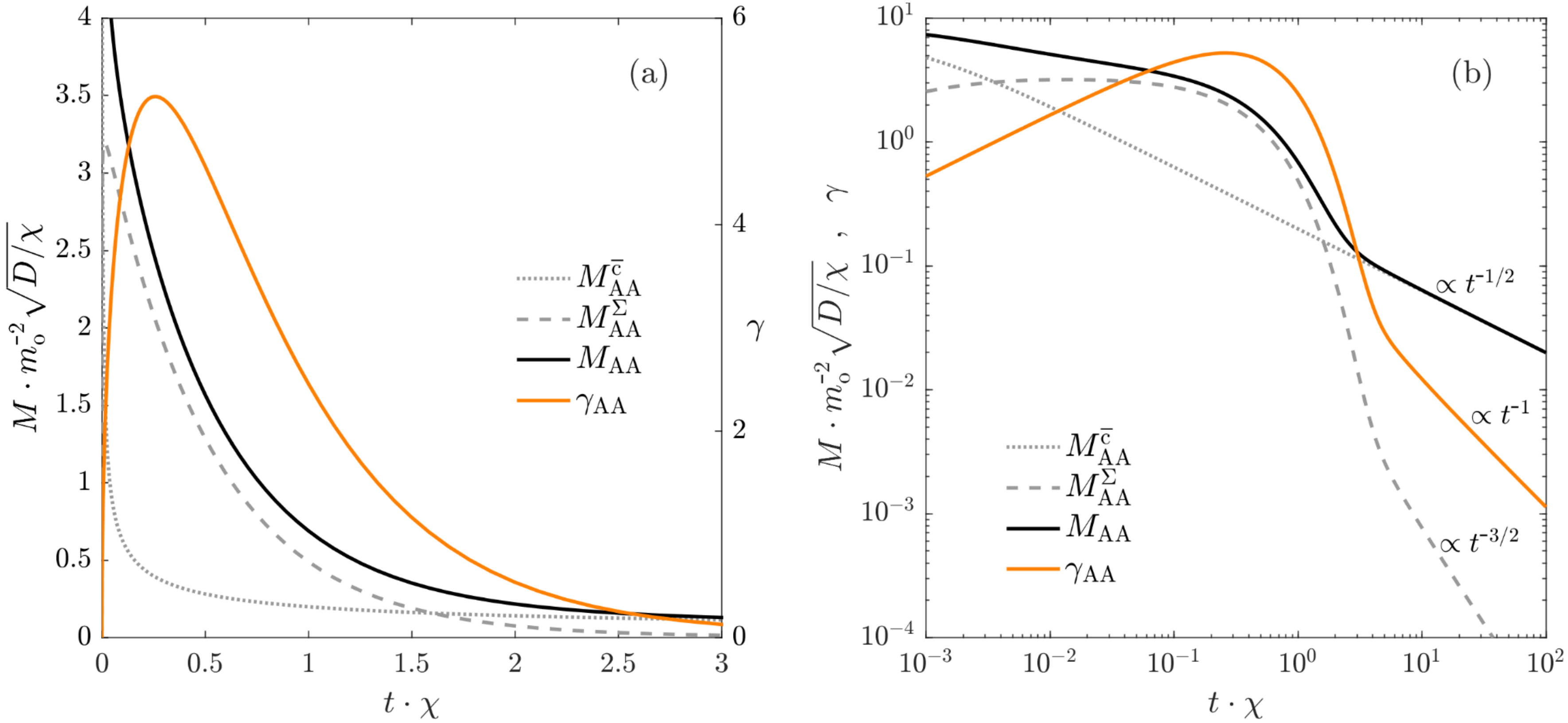
- Mixing state: $M_{\mathrm{AA}} \coloneqq M_{\mathrm{AA}}^{\bar{c}} + M_{\mathrm{AA}}^{\Sigma} = \int_{\mathbb{R}} \bar{c}_{\mathrm{A}}^{2}\,\mathrm{d}x + \int_{\mathbb{R}} \Sigma_{\mathrm{AA}}\,\mathrm{d}x$ $\quad \gamma_{\mathrm{AA}} \coloneqq M_{\mathrm{AA}}^{\Sigma}/M_{\mathrm{AA}}^{\bar{c}}$

- "Dirac" injection:

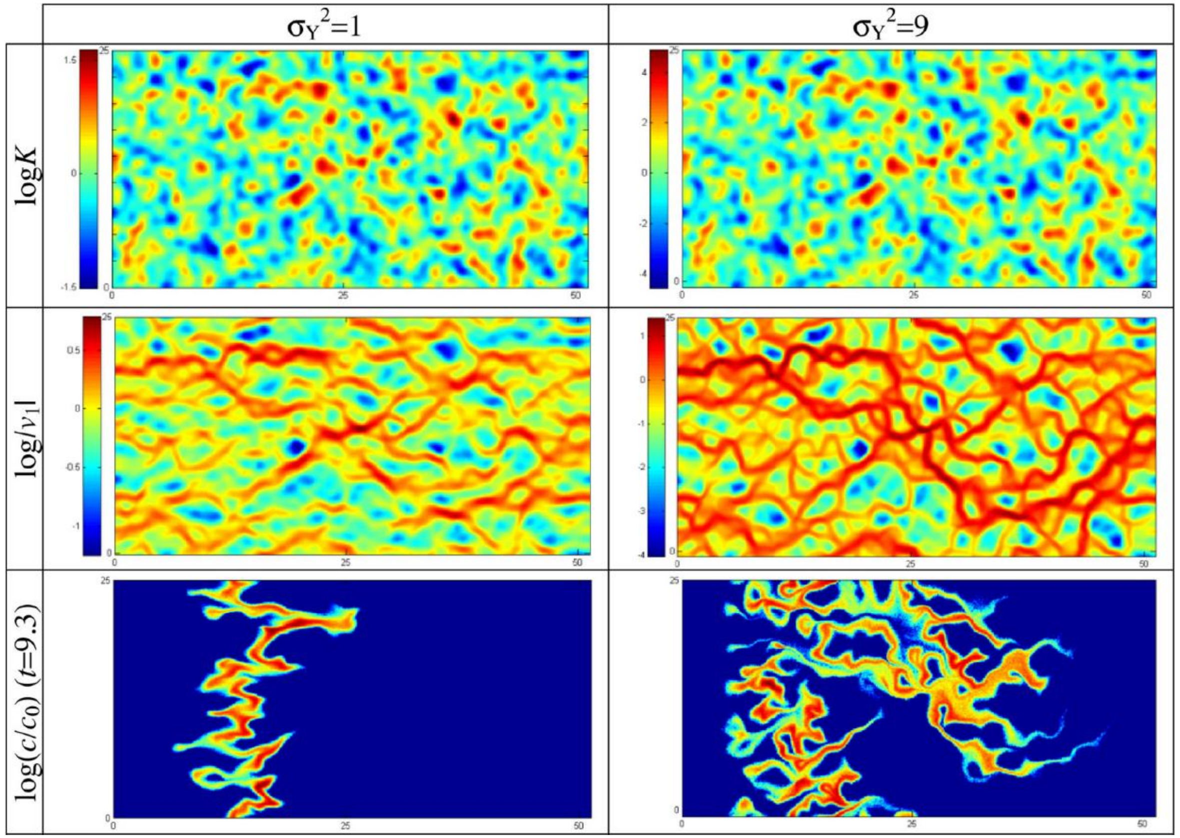


$$\gamma_{\mathrm{AA}}(t) = \eta\left[\left(1+\sqrt{\frac{t}{t_{\mathrm{o}}}}\right)\mathrm{e}^{-2\chi t} - f\left(\sqrt{2\chi t}\right)\right]$$

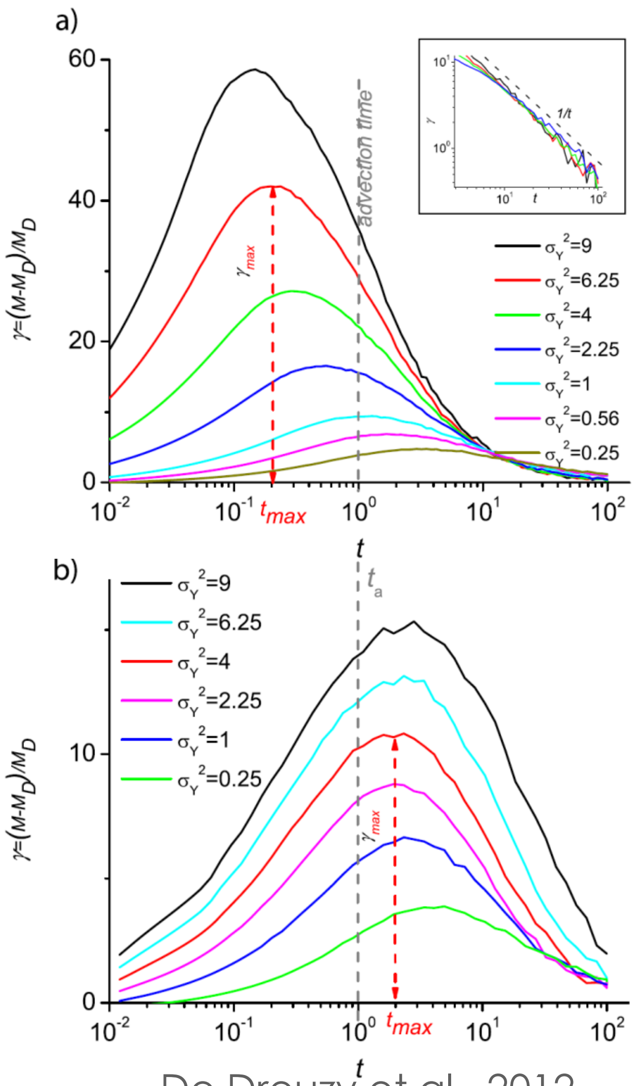
$$f(u) \coloneqq \partial F/\partial u \approx \begin{cases} 1, & (u \ll 1) \\ -\frac{1}{2}u^{-2}, & (u \gg 1) \end{cases}$$



5.1. De Dreuzy et al., 2012 simulations in randomly heterogeneous porous media

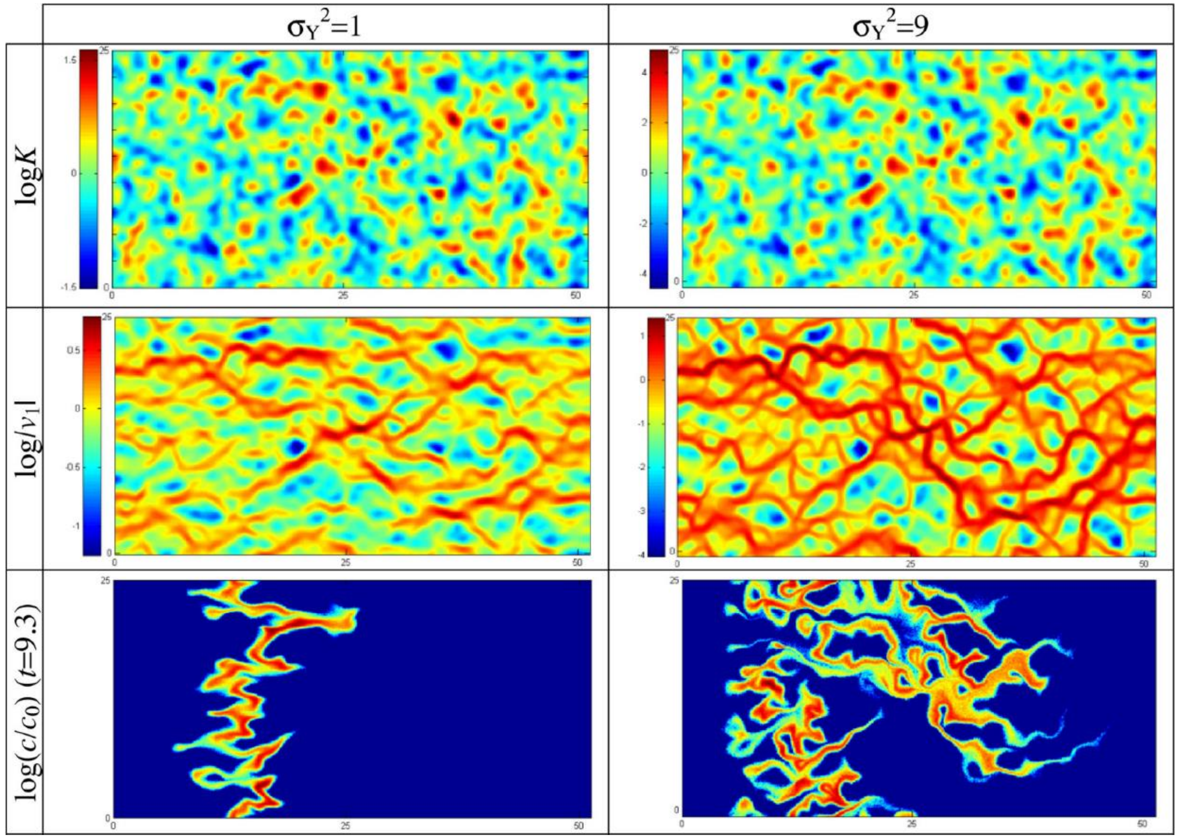


De Dreuzy et al., 2012

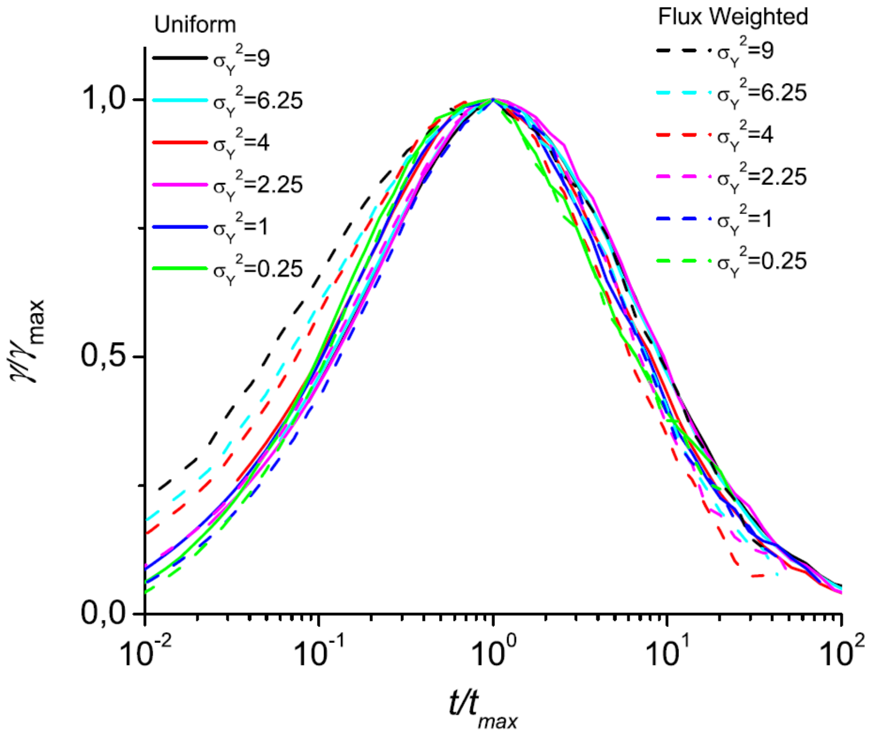


De Dreuzy et al., 2012

5.1. De Dreuzy et al., 2012 simulations in randomly heterogeneous porous media



De Dreuzy et al., 2012



De Dreuzy et al., 2012

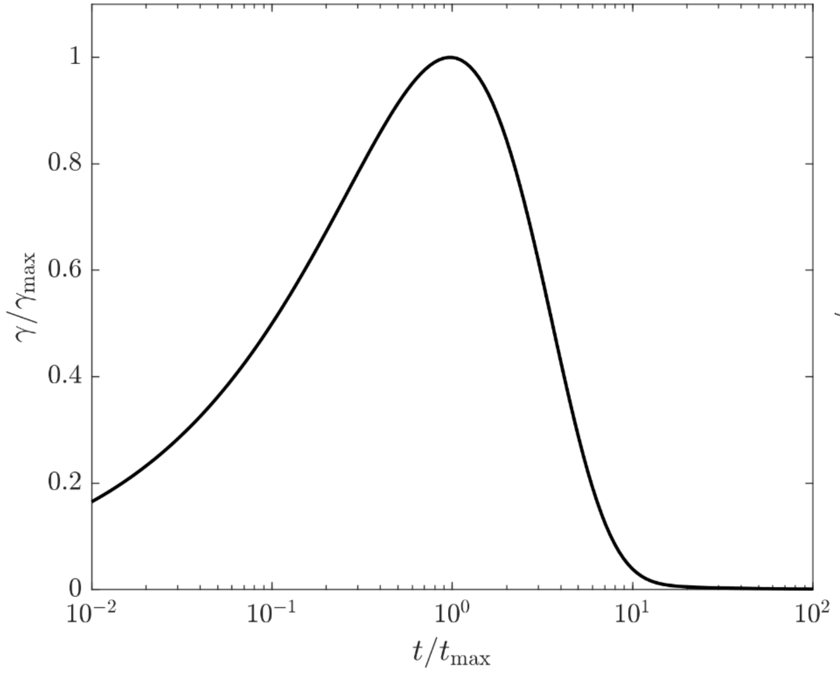
5.2. Multi-rate model generalization

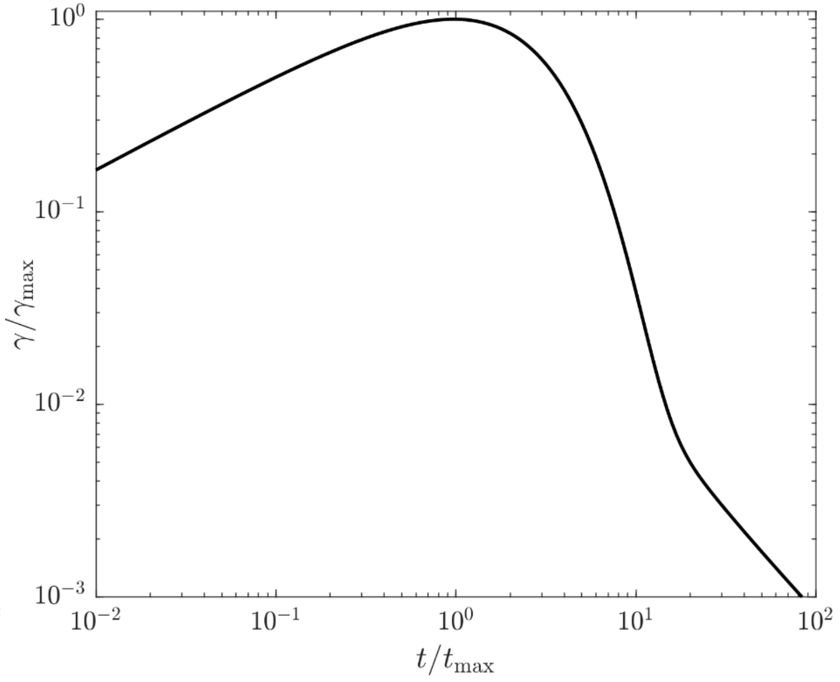
$$\gamma^*_{\mathrm{AA}}(t;\chi) = \left(1+\sqrt{t/t_{\mathrm{o}}}\right)\mathrm{e}^{-2\chi t} - f\left(\sqrt{2\chi t}\right)$$

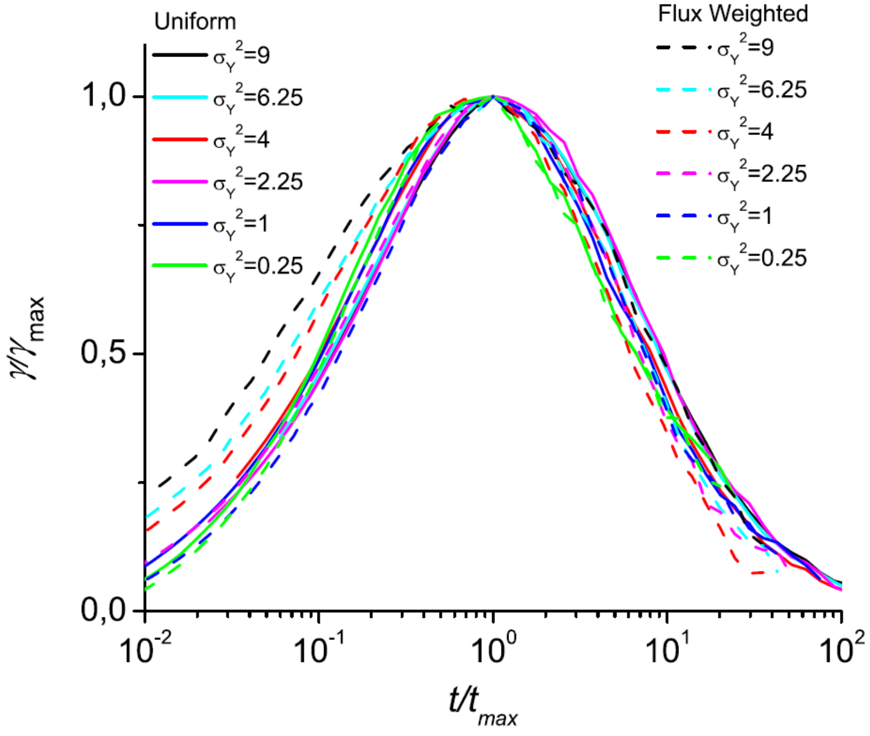
$$\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = -\eta\frac{\mathrm{d}\bar{c}_{\mathrm{A},p}}{\mathrm{d}t} - \chi C'_{\mathrm{A},p}$$

η, χ

$$\gamma^{\mathrm{s.r.}}_{\mathrm{AA}}(t) = \eta\,\gamma^*_{\mathrm{AA}}(t;\chi)$$







De Dreuzy et al., 2012

5.2. Multi-rate model generalization

$$\gamma^*_{\mathrm{AA}}(t;\chi) = \left(1+\sqrt{t/t_o}\right)\mathrm{e}^{-2\chi t} - f\left(\sqrt{2\chi t}\right)$$

From a **single rate**…

$$\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = -\eta\frac{\mathrm{d}\bar{c}_{\mathrm{A},p}}{\mathrm{d}t} - \chi C'_{\mathrm{A},p}$$

η, χ

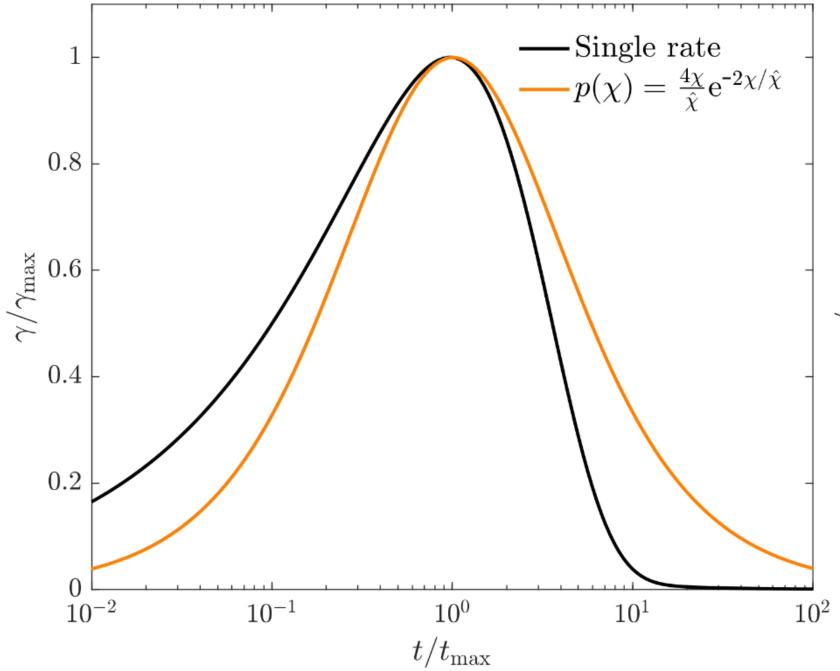
$$\gamma^{\mathrm{s.r.}}_{\mathrm{AA}}(t) = \eta\,\gamma^*_{\mathrm{AA}}(t;\chi)$$

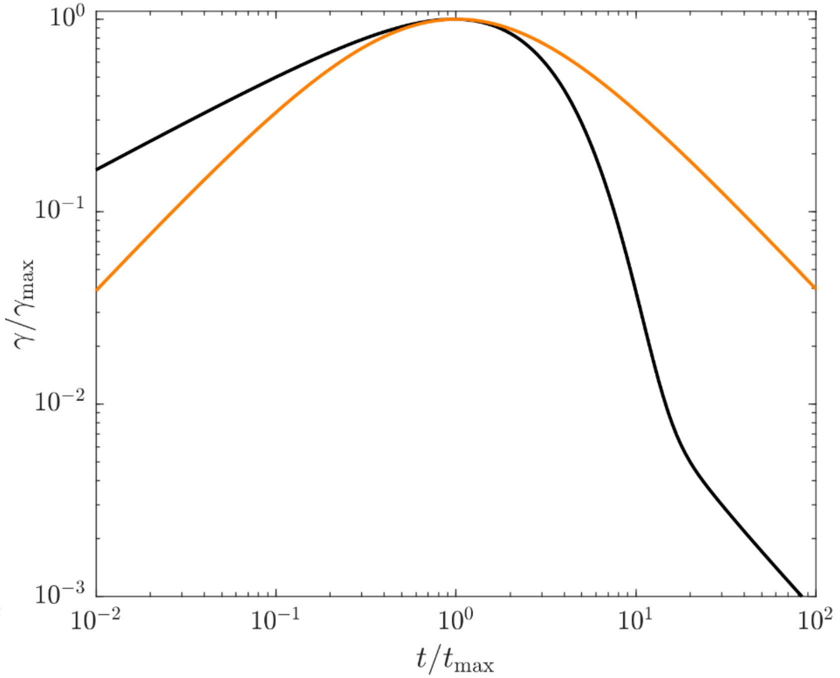
… to a **multi-rate**

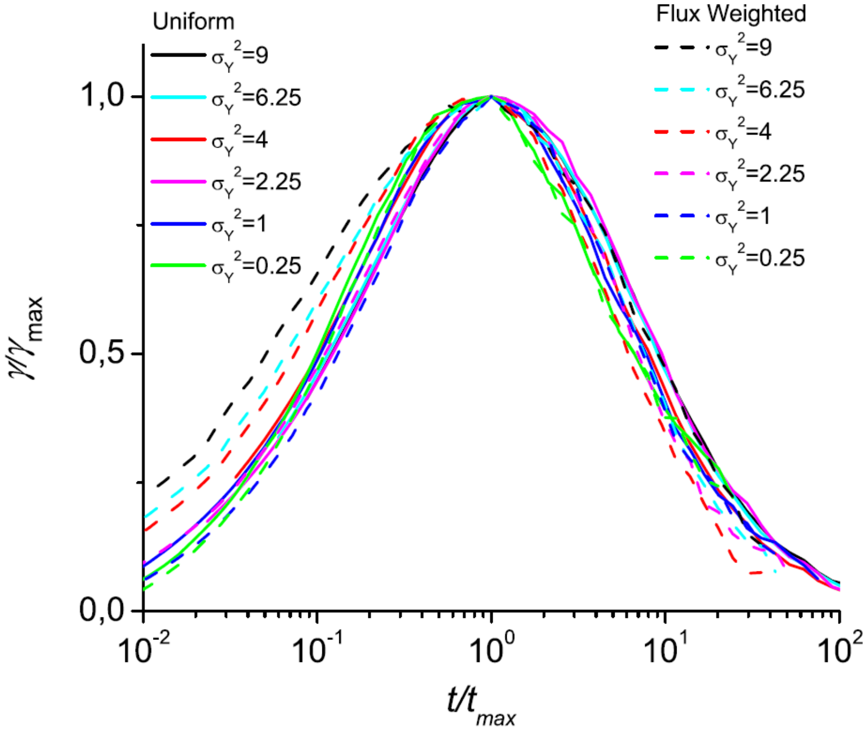
$$\frac{\mathrm{d}C'_{\mathrm{A},p}}{\mathrm{d}t} = -\frac{\mathrm{d}\bar{c}_{\mathrm{A},p}}{\mathrm{d}t} - \chi_p C'_{\mathrm{A},p}$$

$p(\chi)$

$$\gamma^{\mathrm{m.r.}}_{\mathrm{AA}}(t) = \int_0^\infty p(\chi)\gamma^*_{\mathrm{AA}}(t;\chi)\mathrm{d}\chi$$







De Dreuzy et al., 2012

6. SUMMARY AND CONCLUSIONS

- We have proposed a particle-based **random walk** formulation to simulate advection-dispersion-reaction with a **sub-scale mixing limitation**.
- Core idea: **coexistence** of a **Eulerian** ("averaged") and a **Lagrangian** ("local") concentration, with a simplistic parametrization of the **local mixing process**.
- Gramling's **experimental results** were accurately reproduced. The adjusted mixing rate parameter (χ) appears to be capturing the **pore-scale diffusion**.
- The PDE governing the **concentration variance** in a REV is mathematically equivalent to **Kapoor et al.'s (1994) equation**, with a different **parameter interpretation**.
- The incomplete mixing $-M_{\mathrm{AB}}^{\Sigma}$ in Gramling's setup follows the **Dawson function** of $\sqrt{t}$.
- The proposed model, or a **multi-rate** version of it, may be also capable of reproducing a randomly heterogeneous **Darcy sub-scale**.

7. TO-DO LIST

- Towards actual **predictability**:
  - Reach an accurate understanding of the **link** between the **model parameters** (η,χ) and the **physics** of the sub-scale Stokes flow and diffusion (e.g. Peclet number).
  - Explore the apparent ability of the **multi-rate** extension to account for a heterogeneous **Darcy flow sub-scale** (and link to hydraulic conductivity variance, etc).

- Explore model **implications**:
  - Incomplete mixing effect on **different types of reactions** (e.g. biochemical)
  - Coupling with **other processes** (e.g. Sorption, heterogeneous reaction…)