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

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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 $\rightarrow$ 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$_2$O). The natural sequence is:

  - $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$  \hspace{1cm} $\Delta G=120$ kcal/mol C
  - $\text{CH}_2\text{O} + 0.8\text{NO}_3^- + 0.8\text{H}^+ \rightarrow \text{CO}_2 + 0.4\text{N}_2 + 1.4\text{H}_2\text{O}$  \hspace{1cm} $\Delta G=114$
  - $\text{CH}_2\text{O} + 2\text{MnO}_2 + 4\text{H}^+ \rightarrow \text{CO}_2 + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$  \hspace{1cm} $\Delta G=81$
  - $\text{CH}_2\text{O} + 4\text{Fe(OH)}_3 + 8\text{H}^+ \rightarrow \text{CO}_2 + 4\text{Fe}^{2+} + 11\text{H}_2\text{O}$  \hspace{1cm} $\Delta G=28$
  - $\text{CH}_2\text{O} + 0.5\text{SO}_4^{2-} + \text{H}^+ \rightarrow \text{CO}_2 + 0.5\text{H}_2\text{S} + \text{H}_2\text{O}$  \hspace{1cm} $\Delta G=25$
  - $\text{CH}_2\text{O} (0.5\ \text{CH}_2\text{O} + 0.5\ \text{CH}_2\text{O}) \rightarrow 0.5\text{CO}_2 + 0.5\text{CH}_4$  \hspace{1cm} $\Delta G=22$

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**

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Eulerian numerical modeling

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

\[ E \, c + F \, \frac{dc}{dt} = G \]

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

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Lagrangian numerical modeling

Position at time $t$

Position at time $t + \Delta t$

Reaction

Species B

Advection

Dispersion

Movement

Reactions

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An example
**Advantages and disadvantages**

<table>
<thead>
<tr>
<th>Eulerian (mesh-based)</th>
<th>Lagrangian (meshless)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
<td><strong>Advantages</strong></td>
</tr>
<tr>
<td>• Well established and documented</td>
<td>• Absence of numerical dispersion</td>
</tr>
<tr>
<td>• Can be used with a wide range of chemical reactions and conditions</td>
<td>• Easy to incorporate anomalous transport and multiple porosity systems</td>
</tr>
<tr>
<td>• Comercial codes and softwares available</td>
<td>• Absence of artificial mixing</td>
</tr>
<tr>
<td><strong>Limitations</strong></td>
<td>• Computationally efficient</td>
</tr>
<tr>
<td>• Susceptible to numerical dispersion and oscillations</td>
<td>• Not yet well established and documented</td>
</tr>
<tr>
<td>• Overestimation of reaction rates and mixing</td>
<td>• Limited number of chemical reactions available</td>
</tr>
<tr>
<td>• Computationally demanding</td>
<td>• Statistical fluctuations from the reconstruction of concentrations based on limited number of particles</td>
</tr>
</tbody>
</table>
Can we really simulate chemical reactions with an Eulerian?

A simple example  

\[ A + B \rightarrow M \]  

\[ \frac{\partial A}{\partial t} = -q\nabla A + \nabla \cdot (\phi D \nabla A) + \phi r \]  

Species A  

\[ \frac{\partial B}{\partial t} = -q\nabla B + \nabla \cdot (\phi D \nabla B) + \phi r \]  

Species B  

\[ A \cdot B = K_{sp} \]  

Equilibrium

De Simoni et al. (2005)  

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

where  

\[ u = A - B \]

Three coupled equations 2 of them PDE (non-linear system)
Implications to Eulerian Approaches

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

- Affected by numerical dispersion
- Affected by truncation errors
- The role of heterogeneity

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An experimental example

$A + B \rightarrow M$

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Lagrangian techniques are attractive then:

- Absence 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:

\[
c \approx \sum_p \frac{m_p I\{x \in B_j\}}{\phi \Delta V_j}
\]

Plume at $t = 0$

Plume at $t = 1000$ días

\[
\begin{align*}
\alpha_T &= 10 \text{ m} \\
\alpha_L &= 100 \text{ m} \\
\nu &= 1 \text{ m/dia} \\
\phi &= 0.17 \\
N_p &= 1000
\end{align*}
\]
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Fluctuations + Smoothing

- **Undersmoothing** → fluctuations
- **Oversmoothing** → bias
Fundamentals

Traditional PDF estimation

Kernel PDF estimation

Normalized concentrations

\[ u \approx \hat{u} = \frac{1}{M_t} \sum_p m_p \frac{I(X_p \in B_j)}{\Delta V_j} \]

Count particle mass in bins

\[ u \approx \hat{u} = \frac{1}{M_t} \sum_p m_p K_H(x - X_p) \]

Area of influence

\( K_H \) is the weight assigned to a particle

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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 estimate 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 $h$.

whereas an increase in the support tends to over smooth the estimated concentration distribution $h$.

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,...

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.

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What about tailing...


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

Locally adaptive h

\[
c(t) \approx \frac{1}{Q} \sum_{i=1}^{n} m_i K \left( \frac{t - t_i}{h_i} \right)
\]
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\[ r = \phi H \nabla u^t D_d \nabla u \]

What about reaction rates...
What happens in heterogeneous media??

\[ A + B \rightarrow M \]
Heterogeneous media

Concentrations, $u(x,y)$ \quad $u = A - B$

Reaction rate, $r(x,y)$

Reaction rate:

$$r = \phi \nabla u^t D_d \nabla u$$

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Use of state transition probabilities (kinetic)

Let us consider network reactions, for instance

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].

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

Application of state transition probabilities

- Particle is associated to a given species \( j \)
- At each time step perform a Bernoulli trial on the corresponding state transition probability
- Particle stays in the same species
- Particle changes species
- Move according to species properties at that location
- Find the new species after a time \( dt \) by generating a random number \( R \)

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

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Interactions between nearby particles

Non-linear reactions

\[ \text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3^{(s)} \]
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**.

\[
\text{Risk} = 1 - e^{\text{CPF}_{\text{metal},i} \times \text{ADD}_{\text{metal},i}}
\]

**Toxicity Value:** Cancer Potency Factor (CPF)

**Exposure Time:** Average Daily Dose (ADD)

\[
\text{ADD}_{\text{metal},i} = \left( \frac{\text{IN}_i}{\text{BW}} \right) \frac{\text{ED} \times \text{EF}}{\text{AT}}
\]

**Environmental Concentration:** \( \langle C \rangle \)

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

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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)*
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Subsurface properties largely unknown (K)

Uncertainty & Lagrangian methods

Determine preferential pathways, travel times and concentrations

Lagrangian methods are well suited for Monte Carlo Simulations

MADE site

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)

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

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

Performance

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.

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

$$D_R = \frac{d}{d_c} = \frac{d}{\nu_a t_c}$$

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

Derived analytically

Can preferential channels be beneficial? **YES**

**Beneficial impact of connectivity**

Sensitive location at $d < d_c$ or $D_R < 1$

**Detrimental impact of connectivity**

Sensitive location at $d > d_c$ or $D_R > 1$

\[ d_c = v_a t_c \]
\[ t_c = F(k_i, R_i, toxicology) \]

Affected by heterogeneity and preferential channels → Uncertain


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Thank you