Uncertainty Quantification for Reactive Transport of Contaminants

Gowri Srinivasan
Theoretical Division
Los Alamos National Lab, Los Alamos, NM, USA

September 22, 2011

Abstract

Predictions of reactive transport in the subsurface are routinely compromised by both model (structural) and parametric uncertainties. In the first part of this talk, I will present a set of computational tools for quantifying these two types of uncertainties. The model uncertainty is resolved at the molecular scale where epistemic uncertainty incorporates aleatory uncertainty. The parametric uncertainty is resolved at both molecular and continuum (Darcy) scales. The second part of the talk will deal with the combined effects of uncertainty in reactions and heterogeneity of the medium on the transport of reactive contaminants. Quantification of uncertainty in multi-component reactive transport using a stochastic Lagrangian framework and a Continuous Time Random Walk formulation will be discussed in detail.

Outline

- Uncertainties in Geochemical Reactions
- Lagrangian Model for Reactive Transport
- Continuous Time Random Walk Formulation
- Conclusions

Part I

Quantification of Uncertainties in Geochemical Reactions

Collaborators :

Daniel Tartakovsky, UC San Diego
Bruce Robinson, Los Alamos National Lab
Alejandro Aceves, Southern Methodist University

A Simple Chemical Reaction

Consider an irreversible chemical reaction involving three reacting species, two reactants A_1 and A_2 forming a species A_3, such that

$$A_1 + A_2 \to A_3.$$

The reaction rate equations for the concentrations C_i of each species can be written as

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = -kC_1C_2, \quad i = 1, 2, \qquad \frac{\mathrm{d}C_3}{\mathrm{d}t} = kC_1C_2,$$

where the reaction rate constant k, initial conditions are specified

$$C_1(0) = C, \qquad C_2(0) = C, \qquad C_3(0) = 0,$$

C and k have precisely determined values.

Deterministic Model

The system of reaction equations described in the previous slide can be solved exactly by introducing new variables

$$u_1 = C_1 - C_2, \quad u_2 = C_1 + C_3, \quad u_3 = C_1 + C_2 + 2C_3$$

which yields a set of decoupled equations

$$\frac{\mathrm{d}u_i}{\mathrm{d}t} = 0, \qquad i = 1, \ldots, 3.$$

Due to the Initial Conditions, $C_1(t) = C_2(t)$, which leads to

$$C_1(t) = C_2(t) = \frac{C}{Ckt + 1}, \qquad C_3(t) = \frac{Ckt}{Ckt + 1}.$$

Uncertainties in Chemical Reactions

- Parametric uncertainty : Refers to the imperfect knowledge about the coefficients entering the functions F_i $(i = 1, \ldots, n)$ and/or initial concentrations.
- Parametric uncertainties relating to reaction rate constant are studied here.
- Model uncertainty : Refers to the imperfect knowledge about the functional forms of F_i $(i = 1, \ldots, n)$.
- Model Uncertainty relating to imperfect molecular collisions and imperfect mixing are considered.
- The solution in the determinsitic case is compared with those that consider each or both types of uncertainty.

Quantification of Parametric Uncertainty

This uncertainty can be quantified by treating the reaction rate constant k as a random process $k(t)$ with a mean $\bar{k}$, variance σ_k^2.

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = -\bar{k}C_1C_2 - \delta k C_1 C_2, \quad i = 1, 2, \qquad \frac{\mathrm{d}C_3}{\mathrm{d}t} = \bar{k}C_1C_2 + \delta k C_1 C_2,$$

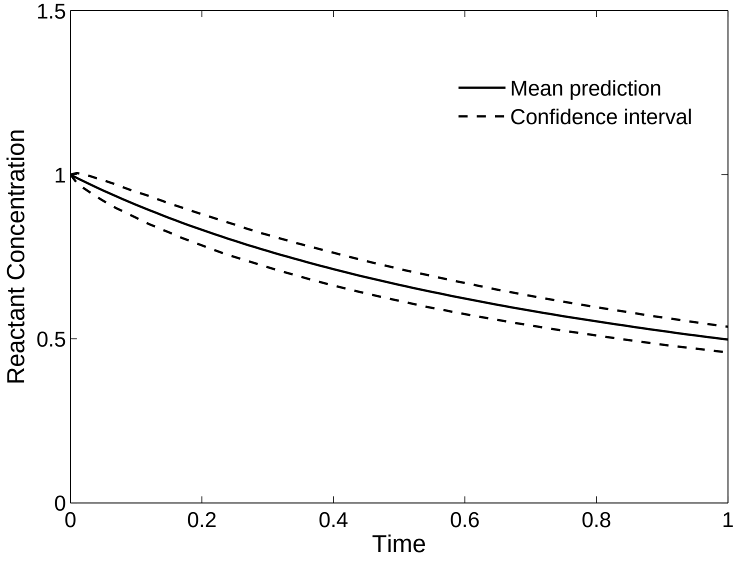
The numerical solution is given (Kloeden and Platen,)by

$$C_1(t + \Delta t) = C_1(t) - \bar{k}C_1(t)C_2(t)\left[\Delta t + \Delta W\right],$$

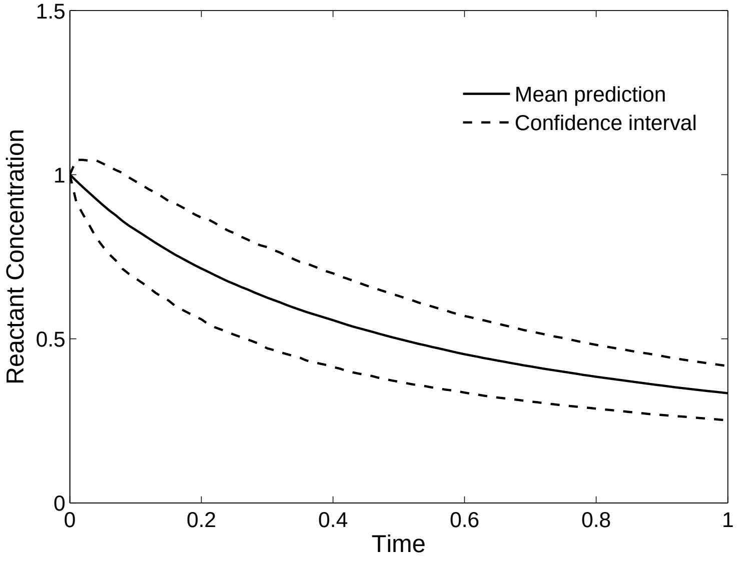
where Δt is a time step and ΔW is a Gaussian variable with zero mean and the variance proportional to the variance of k.

Results : Error Bars

99.7% Confidence Interval



Normal distribution



Log-Normal Distribution

Quantification of Model Uncertainty

Modified Gillespie algorithm: Reaction PDF $P(\tau, \mu)$ for reaction μ to occur in the infinitesimal time interval $[t + \tau, t + \tau + \Delta\tau]$ given a certain state at time t.

Residence time τ, during which no reactions occur, depends upon the total molecular population of all reacting species and reflects the randomness of collisions.

A constant deterministic value τ corresponds to standard reaction rate equations

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = F_i(C_1, C_2, ...C_n), \qquad i = 1, \ldots, n$$

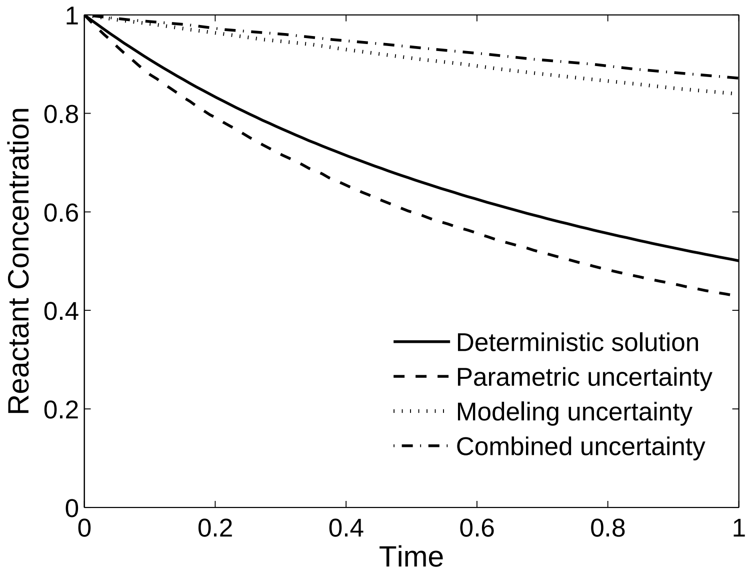
Quantification of Model Uncertainty (cntd.)

Modified SSA:

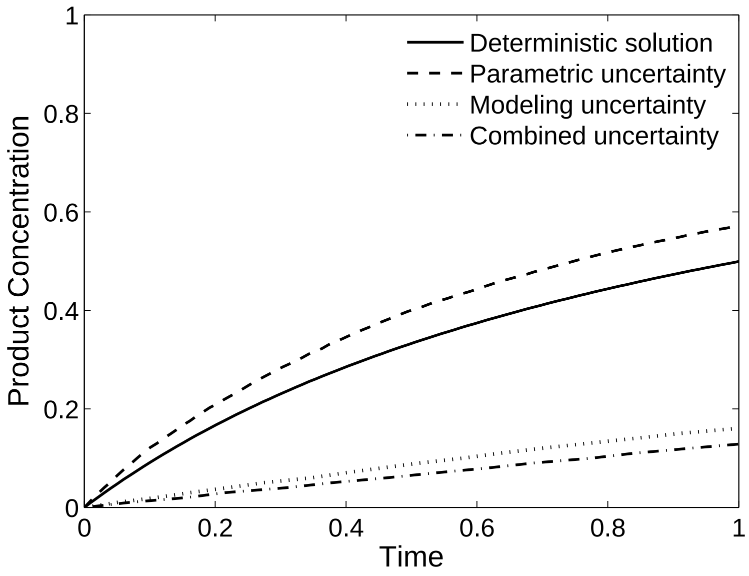
1. Compute the total number of reacting pairs of molecules available for each reaction a_i, and compute their sum $a_0 = \sum a_i$
2. Generate random numbers r_1 and r_2 on the uniform unit interval and m uniformly random on the interval $[1, 10]$
3. Compute $\tau = -m a_0^{-1} \ln r_1$
4. Determine which reaction μ occurs by taking μ to be that integer for which $\sum_{j=1}^{\mu-1} a_j < r_2 a_0 \leq \sum_{j=1}^{\mu} a_j$
5. Update time by τ and molecular levels for reaction μ (decrease reactants by 1 and increase products by 1)
6. Repeat steps 1-5 until either of the reactant population goes to zero or steady state is reached

Quantification of Joint Uncertainty

To account for both sources of uncertainty, we modify the first step of the algorithm by replacing the constant value k with its random counterpart whose mean and variance are $\bar{k}$ and σ_k^2, respectively.



Reactant Concentration



Product Concentration

Example: Neptunium Ion Exchange

Reacting system:

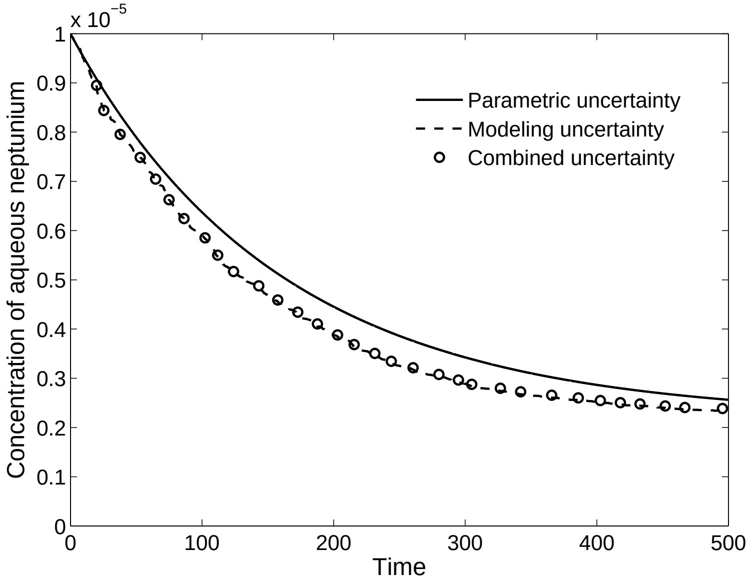
$$NpO_2^+ + \{tAl - Na\} \rightleftharpoons \{tAl - NpO_2\} + Na^+$$
$$Ca^{2+} + 2\{tAl - Na\} \rightleftharpoons \{2tAl - Ca\} + 2Na^+.$$

Standard deterministic model:

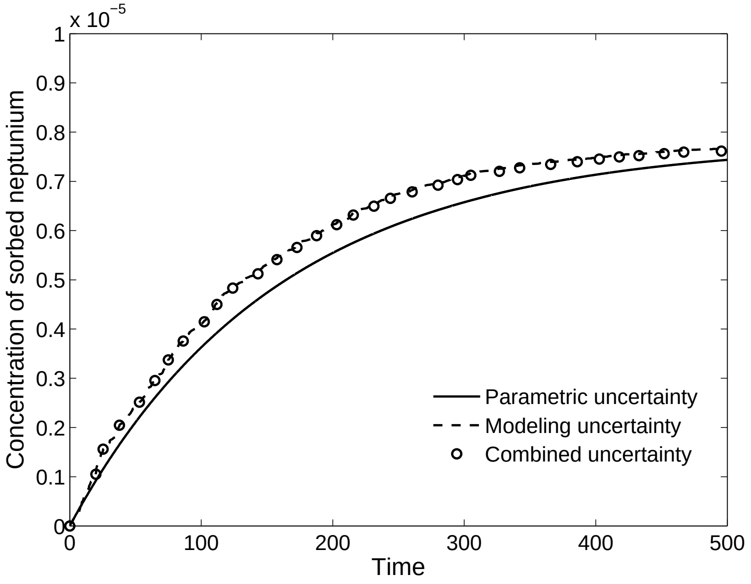
$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = -k_1C_1C_4 + k_2C_2C_3 - 2k_3C_1^2C_6 + 2k_4C_2^2C_5,$$
$$\frac{\mathrm{d}C_2}{\mathrm{d}t} = k_1C_1C_4 - k_2C_2C_3 + 2k_3C_1^2C_6 - 2k_4C_2^2C_5,$$
$$\frac{\mathrm{d}C_3}{\mathrm{d}t} = k_1C_1C_4 - k_2C_2C_3, \qquad \frac{\mathrm{d}C_4}{\mathrm{d}t} = -k_1C_1C_4 + k_2C_2C_3,$$
$$\frac{\mathrm{d}C_5}{\mathrm{d}t} = k_3{C_1}^2C_6 - k_4C_2^2C_5, \qquad \frac{\mathrm{d}C_6}{\mathrm{d}t} = -k_3{C_1}^2C_6 + k_4C_2^2C_5$$

Neptunium Ion Exchange : Results

To account for uncertainty in the reaction rate constants k_1, k_2, k_3, and k_4, we treat them as normal white noise, whose mean values were determined from experimental data (Viswanathan et al, 1998).



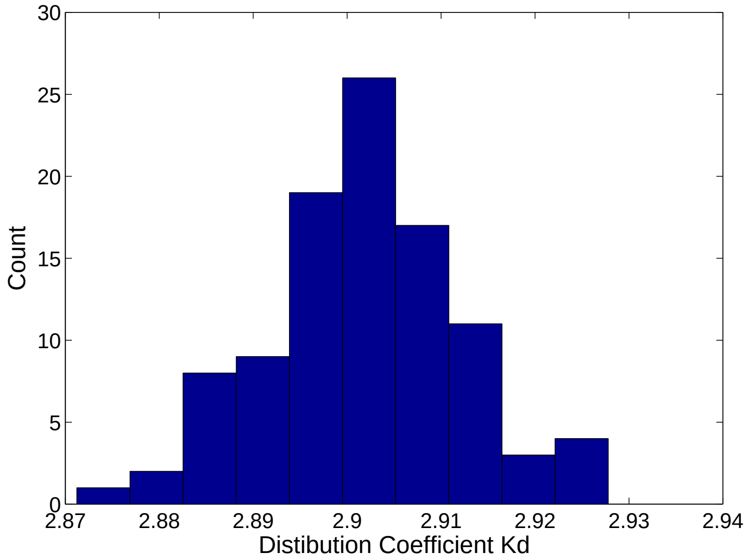
Aqueous Neptunium



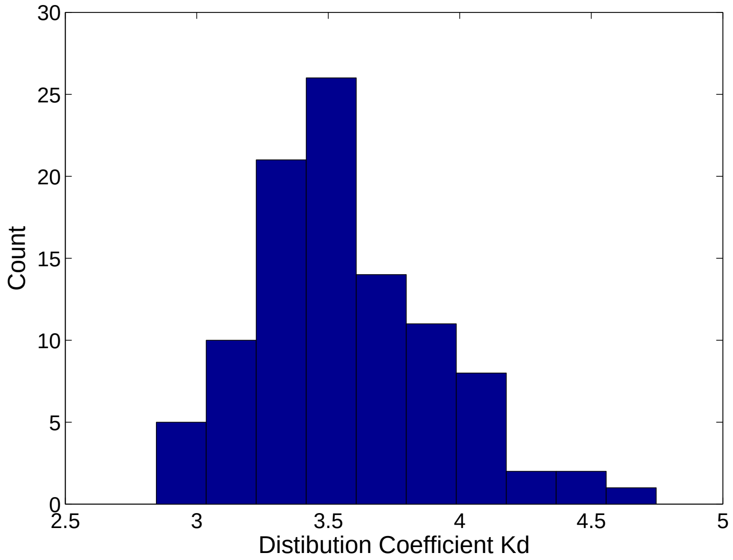
Sorbed Neptunium

Neptunium Ion Exchange: Results

Distribution coefficient $K_d = C_3/C_4$:



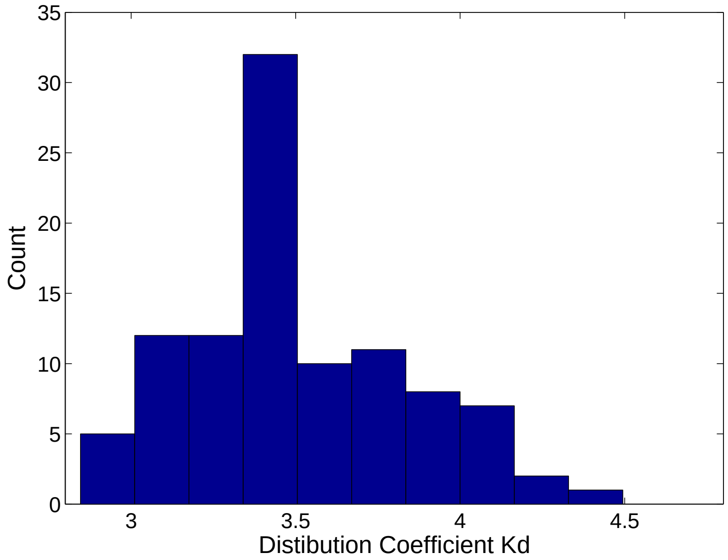
Parametric Uncertainty



Model Uncertainty

Neptunium Ion Exchange: Results

Distribution coefficient $K_d = C_3/C_4$:



Joint Uncertainty

Summary of Results

1. The rate at which a reaction occurs varies greatly due to the inclusion of various sources of uncertainty.

2. The range of distribution coefficients obtained for the neptunium competitive ion exchange process considered underscores the need for uncertainty quantification. It is expected that the same behavior will be present in more complex, multicomponent systems involving more chemical species.

3. The proposed approach yields a complete probabilistic description of the reaction rates and distribution coefficient, key parameters affecting the fate and migration of neptunium in the subsurface. This is important, since these distributions are highly skewed.

Summary of Results

4. The uncertainty quantification tools employed in this study are fully scalable and can be used to investigate any number of coupled reversible or irreversible geochemical reactions.

5. Transport of radionuclides such as neptunium could be greatly affected by the reactions that take place in the subsurface and hence quantification of modeling and parametric uncertainties is crucial in describing the overall transport.

6. Srinivasan et al, 2007, Quantification of Uncertainty in Geochemical Reactions, Water Resources research, 43, W12415.

Part II

Lagrangian Model of Reactive Transport in Heterogeneous Porous Media with Uncertain Properties

Collaborators :

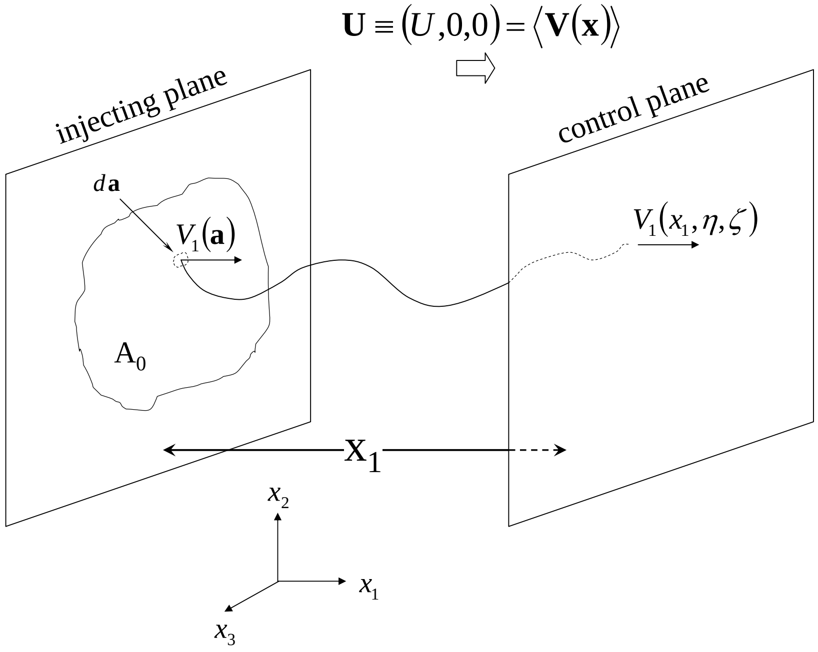
Gerardo Severino, UC San Diego
Daniel Tartakovsky, UC San Diego
Hari Viswanathan, Los Alamos National Lab

Lagrangian Formulation : Motivation

- Transport of reactive contaminants is affected by heterogeneities in the medium as well as uncertainties in the geochemical reactions.
- Heterogeneity in porous media : Hydraulic conductivity K varies spatially and can be considered as a random space function.
- The reaction rate is treated as an unknown, reflecting parametric uncerties in non-linear reactions.
- We employ a Lagrangian approach to study the combined effects of both.
- Transport of 3 species with a bi-molecular reaction is considered here as an example, but the analysis can be extended to general multi-component non-linear reactive systems.

Lagrangian Formulation : Introduction

Consider a mixture of N dissolved species entering the system at $t \geq 0$ through an injection area A_0 located in the plane $x_1 = 0$. The flow path for any one realization, arriving at a control plane $x_1 > 0$ at time $t = \tau$ is as shown



Lagrangian Formulation : Introduction

For a particle located at $\mathbf{a} \in A_0$ at $t = 0$, let $\mathbf{X}(t; \mathbf{a}) = (X_1, X_2, X_3)^T$ denote its trajectory. Since the flow velocity $\mathbf{V}$ is random, the particle trajectory $\mathbf{X}(t; \mathbf{a})$ satisfies a stochastic ordinary-differential equation

$$\frac{\mathrm{d}\mathbf{X}}{\mathrm{d}t} = \mathbf{V}(\mathbf{X}), \qquad \mathbf{X}(0; \mathbf{a}) = \mathbf{a}. \tag{1}$$

We derive a Lagrangian alternative (Cvetkovic and Dagan, 1994) by replacing the Eulerian coordinates $\mathbf{x} = (x_1, x_2, x_3)^T$ with their Lagrangian counterparts $\boldsymbol{\xi} = (\xi_1, \xi_2, \xi_3)^T$ defined as

$$\xi_1 = \tau(x_1; \mathbf{a}), \qquad \xi_2 = x_2 - \eta(x_1; \mathbf{a}), \qquad \xi_3 = x_3 - \zeta(x_1; \mathbf{a}). \tag{2}$$

where $\tau(x_1; \mathbf{a})$ denotes the travel time from the injection plane $(x_1 = 0)$ to the control plane $(x_1 > 0)$, η and ζ are defined as

Lagrangian Formulation : Introduction

$\eta(x_1; \mathbf{a}) = X_2(\tau; \mathbf{a})$ and $\zeta(x_1; \mathbf{a}) = X_3(\tau; \mathbf{a})$, such that a streamline originating at the point $\mathbf{a}$ is described by equations $x_2 = \eta(x_1; \mathbf{a})$ and $x_3 = \zeta(x_1; \mathbf{a})$.

Neglecting dispersion, a fluid particle stays on the same streamline, so that $\xi_2 = \xi_3 = 0$. The transport equation in the Lagrangian coordinate system is now one-dimensional, given by

$$\mathcal{L}\,\mathbf{C} = \mathbf{\Psi}\Big(\mathbf{C}, \frac{\partial \mathbf{C}}{\partial t}\Big), \qquad \mathcal{L} \equiv \frac{\partial}{\partial t} + \frac{\partial}{\partial \tau}, \tag{3}$$

which applies to any stream-tube originating from $\mathbf{a} \in A_0$. The concentrations $\mathbf{C} = (C_1, \ldots, C_N)$ are now functions of the Lagrangian variables τ and t.

Lagrangian Formulation : Introduction

- The goal is to express the ensemble statistics of travel time τ and corresponding breakthrough curves (BTCs) in terms of the statistics of the input parameters, i.e. log-conductivity $Y(\mathbf{x})$ and reaction rates.

- We derive expressions for the BTCs and their temporal moments for N reacting contaminants.

- The example used here for the purpose of illustratation involves reactants A, B and product C participating in the following irreversible reaction with reaction rate κ

$$A + B \rightarrow C. \tag{4}$$

Lagrangian Formulation : Assumptions

- Porous media are assumed to be mildly heterogeneous. The assumption of mild heterogeneity refers to the requirement that the variance of log-conductivity be small, $\sigma_Y^2 < 1$.

- Local-scale molecular diffusion and hydrodynamic dispersion are neglected.

- Uncertain reaction rate constants are treated as random variables.

- Fluid flow is unaffected by chemical reactions.

- Flow is uniform in the mean.

Lagrangian Formulation : Derivations

The ensemble mean of the flux-averaged concentration for species i is given by

$$\overline{C}_i^f(t; x_1) \simeq \frac{\displaystyle\int_{A_0} V_1(\mathbf{x}) C_i(\mathbf{x}, t) \mathrm{d}\mathbf{a}}{\displaystyle\int_{A_0} V_1(\mathbf{x}) \mathrm{d}\mathbf{a}}. \tag{5}$$

where V_1 is the flow along the streamline.

Suppose that the set of chemical reactions is controlled by a set of M random reaction constants $\boldsymbol{\kappa} = (\kappa_1, \ldots, \kappa_M)$ with a joint probability density function (`PDF`) $g_{\boldsymbol{\kappa}}(\boldsymbol{\mathcal{K}})$.

Let $g_\tau(\mathcal{T}; x_1)$ denote a `PDF` of the travel time τ that is related to the statistics of g_Y, the `PDF` of log-conductivity Y. Then $\overline{C}_i(t; x_1)$, the ensemble mean of the concentration $\overline{C}_i^f(t; x_1)$ averaged over all

Lagrangian Formulation : Derivations

possible realizations of $\boldsymbol{\kappa}$, is given by

$$\begin{aligned}\overline{C}_i(t;x_1) &\equiv \int\int C_i(x_1,t;\mathcal{Y},\boldsymbol{\mathcal{K}})g_Y(\mathcal{Y})g_{\boldsymbol{\kappa}}(\boldsymbol{\mathcal{K}})\mathrm{d}\mathcal{Y}\mathrm{d}\boldsymbol{\mathcal{K}} \\ &= \int\int C_i(x_1,t;\mathcal{T},\boldsymbol{\mathcal{K}})g_\tau(\mathcal{T};x_1)g_{\boldsymbol{\kappa}}(\boldsymbol{\mathcal{K}})\mathrm{d}\mathcal{T}\mathrm{d}\boldsymbol{\mathcal{K}}. \qquad (6)\end{aligned}$$

Irreversible Bi-Molecular Reaction

For the reaction (4), we will denote the concentrations of the species as γ ($\gamma = A, B, C$), and κ as the rate coefficient. The Lagrangian equations for the 3 species are

$$\mathcal{L}\, C_\gamma = -\kappa\, C_A C_B \quad (\gamma = A, B), \qquad \mathcal{L}\, C_C = \kappa\, C_A C_B. \tag{7}$$

The Lagrangian equations (7) are defined on the semi-infinite domain $x_1 > 0$, and are subject to the initial and boundary conditions

$$C_\gamma(\tau, 0) = C_\gamma^{\rm in}(\tau) \quad \text{and} \quad C_\gamma(0, t) = C_\gamma^0(t) \qquad (\gamma = A, B, C), \tag{8}$$

where $C_\gamma^{\rm in}$ and C_γ^0 are the initial and boundary concentration of the species γ, respectively.

Irreversible Bi-Molecular Reaction

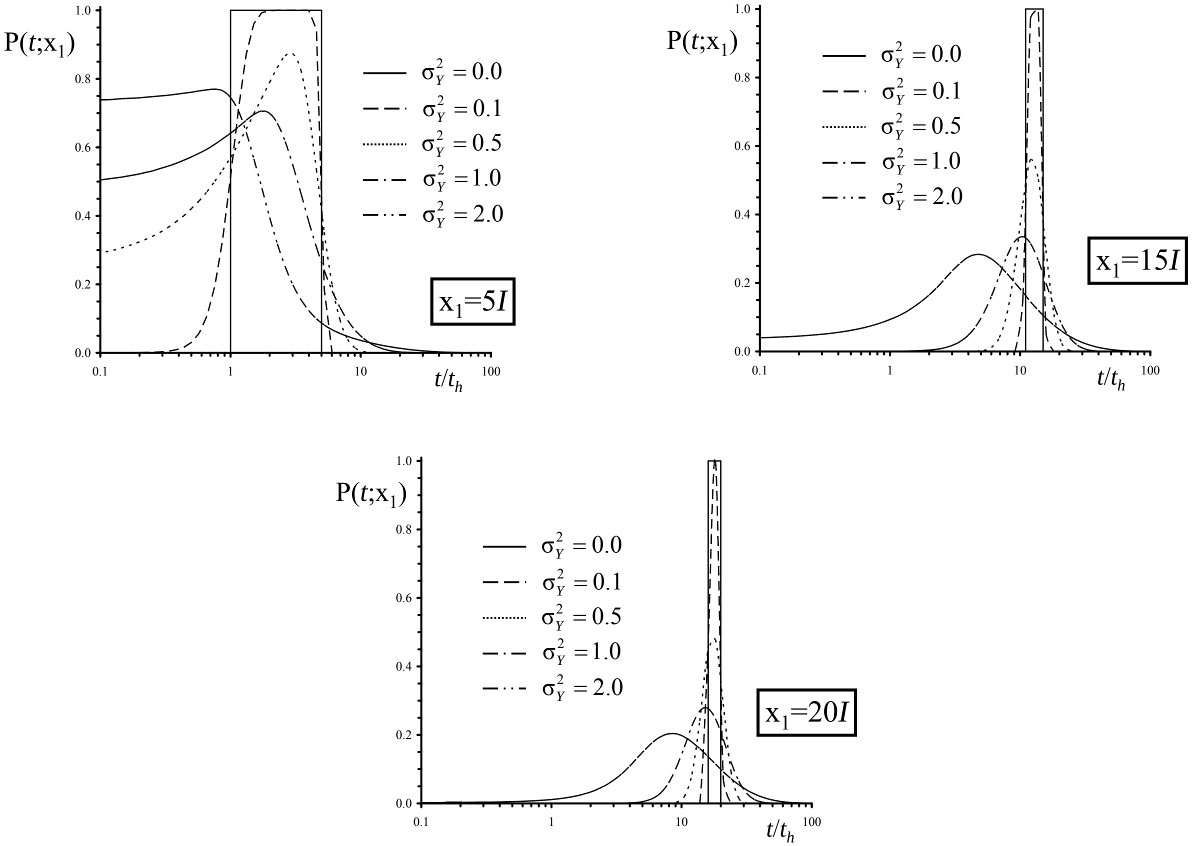
Initial concentrations of the two reactants are set to

$$C_\gamma^{\text{in}}(x) = c_\gamma^{\text{in}} \begin{cases} 1 & U\tau_a < x < U\tau_b \\ 0 & \text{otherwise,} \end{cases} \tag{9}$$

The initial concentration of the reactant product is set to $C_C^{\text{in}} = 0$.

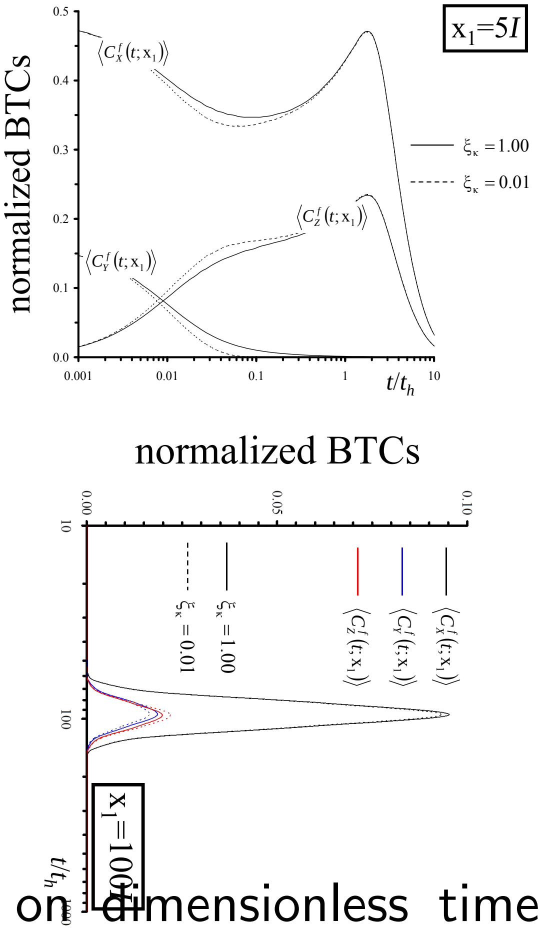
The reaction rate κ is distributed uniformly on the interval $[\overline{\kappa} - \Delta, \overline{\kappa} + \Delta]$ with mean $\overline{\kappa}$ and half-band Δ, i.e. $g_\kappa(\mathcal{K}) = 1/(2\Delta)$. We also set $c_\gamma^0 = 0$, $\lambda = 0.1$ and $\sigma_Y^2 = 1$.

Results : Temporal behavior



Temporal behavior of $\mathtt{P}(t;x_1)$ at control planes (a) $x_1 = 5I_h$, (b) $x_1 = 15I_h$ and (c) $x_1 = 20I_h$ for $\lambda = 0.1$, $\tau_a = 0$, $\tau_b = 4t_h$, and several values of σ_Y^2. The time t is scaled with the characteristic time $t_h = I_h/U$.

Results : Breakthrough Curves



Dependence of the BTCs on dimensionless time $t_d = t/t_h$ ($t_h \equiv I_h/U$) at control plane $x_1 = 5I_h$ and $x_1 = 100I_h$, for $\mathrm{Da} = 10^2$ and two values of ξ_κ. Other parameter values: $\lambda = 0.1$, $\sigma_Y^2 = 1$, $\tau_a = 0$ and $\tau_b = 4t_h$, and $\alpha_{\mathrm{in}} = 1/3$.

Summary of Results

1. The concentrations of reactants and their product are simultaneously influenced by the distribution of the travel time τ and a geochemical irreversible reaction.

2. The variance of the time it takes particles to travel from the injecting plane to the control plane quantifies uncertainty in the advective component of the solute transport.

3. The Damköhler number Da, a dimensionless parameter defined as the ratio of the advection and reaction time scales, determines the relative importance of various sources of parametric uncertainty. For large Da, i.e. when reactions are much faster than advection, uncertainty in the reaction rate constants dominates predictive uncertainty. For small Da, this source of parametric uncertainty is

Summary of Results

negligible.

4. Our analysis of the breakthrough curves of the reactants and their product concentrations reveals that for given Da the control plane should be located at $x_1 = I_h/\mathrm{Da}$ (where I_h is the integral scale of log-conductivity) in order to detect the reaction regime.

5. Severino et al, 2011, Lagrangian Model of Reactive Transport in Heterogeneous Porous Media with Uncertain Properties, to appear in Procedings of the Royal Society A.

Part III

Random Walk Particle Tracking Simulations of Non-Fickian Transport in Heterogeneous Media

Collaborators :

Daniel Tartakovsky, UC San Diego
Marco Dentz, Institute of Environmental Assessment and Water Research, Barcelona
Hari Viswanathan, Los Alamos National Lab
Bruce Robinson, Los Alamos National Lab

CTRW Formulation for Transport

- Traditional ways to model transport include analytical approaches, finite difference, finite element or particle tracking methods.

- Particle tracking aproach eliminates numerical dispersion and allows for stochastic time steps.

- Particle tracking methods are mainly concerned with the breakthrough of concentration across a control plane, rather than with the resolution of the plume over the entire field of study which is possible with the Convolution Based Particle Tracking (CBPT) method described here.

- Most particle tracking techniques use the ADE as the basis for modeling transport.

CTRW Formulation for Transport

- The ADE is only capable of simulating Fickian transport, a phenomenon not always observed at the lab or field scales.

- The Continuous Time Random Walk (CTRW) theory provides a convincing description of non-Fickian transport.

- We combine the advantages of both these methods CBPT and CTRW in our particle tracking algorithm.

Convolution Based Particle Tracking (CBPT)

The mass density function $\hat{c}(\xi, x, t)$ is defined as the probability of locating mass from source location ξ at a control volume centered at location x at time t. In addition, consider a time-varying input mass flux $\dot{m}(\xi, t)$ at ξ. Applying the principle of superposition in time, the concentration $c(\xi, x, \tau)$ at time τ can be computed using the following numerical convolution equation:

$$c(\xi, x, \tau) = \int\limits_0^\tau \dot{m}(\xi, \tau - t)\hat{c}(\xi, x, t)dt$$

The total concentration $C(x, \tau)$ is determined by the superposition of the individual concentrations obtained from each source term.

$$C(x, \tau) = \Sigma_i c(\xi_i, x, \tau)$$

Convolution Based Particle Tracking (CBPT)

The equation for particle displacements is given by

$$X_{N+1} = X_N + A[X_N]\Delta t + B[X_N].\xi_N \sqrt{\Delta t}$$
$$t_{N+1} = t_N + \Delta t$$

where X_N is the particle location at step N, ξ_N is a random 3-dimensional vector and A and B are related to the flow and transport properties of the medium as follows:

$$A = v + \nabla.D$$

$$B.B^T = 2D$$

A is referred to as the background drift.

CTRW theory

We define transition rates of particles from position x from x' as $w(x, x')$. The Master Equation or the transport equation can be written as follows:

$$\frac{\partial C(x,t)}{\partial t} = -\Sigma_{x'} w(x', x) C(x,t) + \Sigma_{x'} w(x, x') C(x', t)$$

where $C(x,t)$ is the particle concentration at position x and time t.

A form of the equations similar to the ADE can be derived (Berkowitz et al, 2002) from a Taylor expansion of transition rates $w(x, x')$ substituted into the Master Equation to yield the following

CTRW theory

CTRW equation for transport

$$\frac{\partial C(x,t)}{\partial t} = -v(x).\nabla C(x,t) + \nabla.\nabla\left[D(x)C(x,t)\right]$$

where $v(x)$ is the velocity field and $D(x)$ is the dispersion tensor, both defined in terms of spatial moments of the transition rate.

The CTRW equations in this implementation are

$$X_{N+1} = X_N + A[X_N]\Delta t + B[X_N].\xi_N\sqrt{\Delta t}$$
$$t_{N+1} = t_N + \tau_N \Delta t$$

where A, B and ξ are as described above. The random processes ξ_N and τ_N are each uncorrelated.

CTRW theory

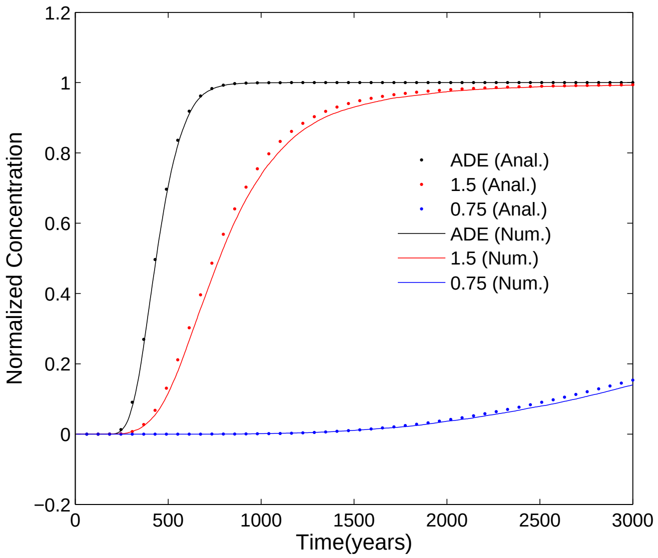
The transition time distribution is given by a truncated power-law distribution (see Dentz and Berkowitz, 2004 for details)

$$\psi(t) = \left(t_1 \tau_2^{\beta} exp(\tau_2^{-1}) \Gamma(-\beta, \tau_2^{1})\right)^{-1} \frac{exp(-t/t_2)}{(1 + t/t_1)^{1+\beta}}$$

where $\tau_2 = t_2/t_1$ and $\Gamma(a, x)$ is the incomplete Gamma function.

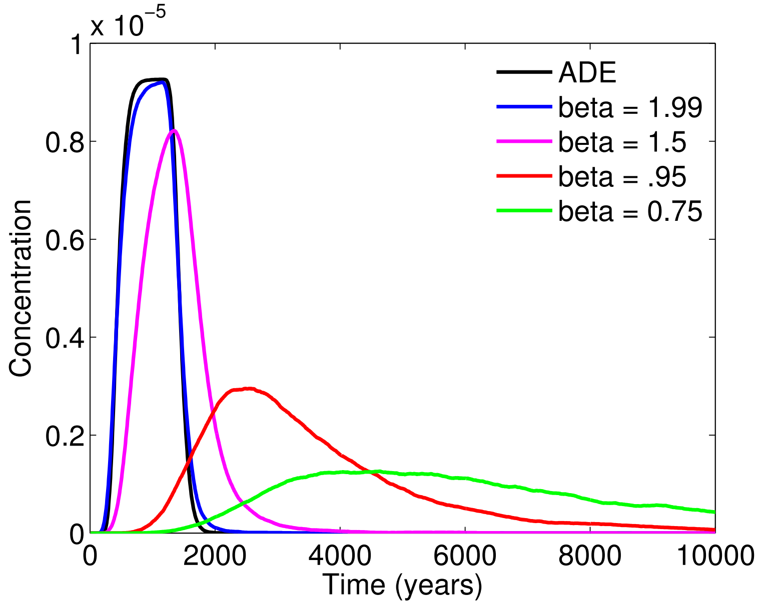
Results : Comparison with Analytical Solution

The test case chosen here uses continuous injection of solute at the inlet. The breakthrough is computed at a distance of $x = 15.2$ km over a total time of 3000 years. The results from both analytical (CTRW toolbox, dots) and numerical (hybrid CBPT- CTRW model, solid lines) are plotted.

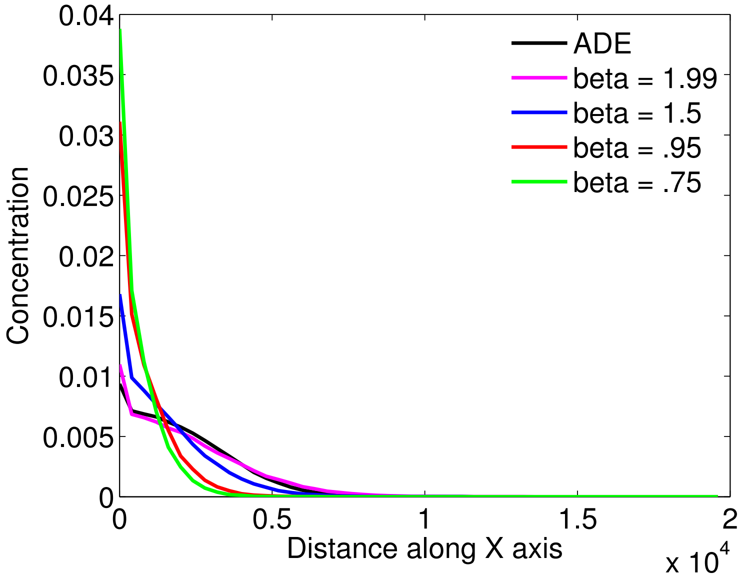


Breakthrough Curve

Results : Hybrid CBPT-CTRW model

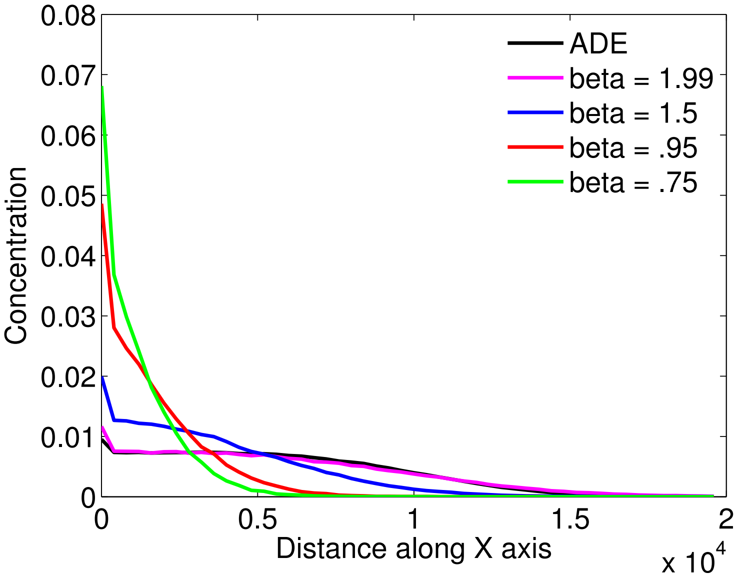


Breakthrough Curve

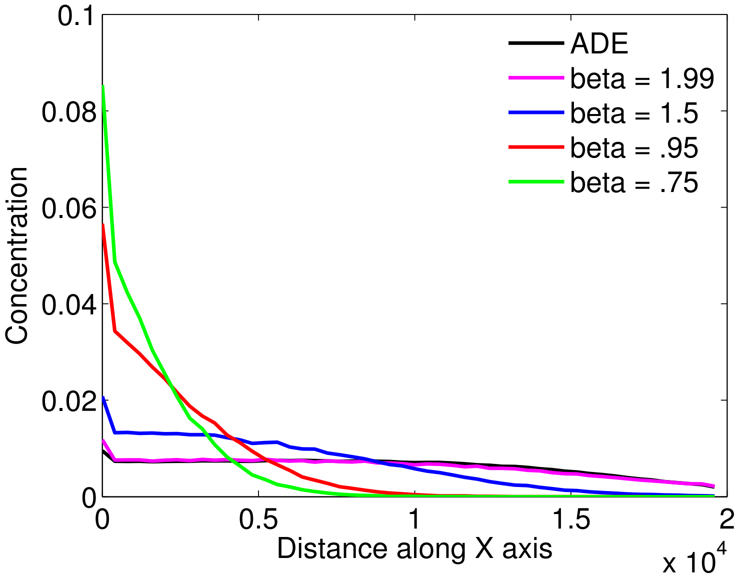


Plume at 100 years

Results : Hybrid CBPT-CTRW model

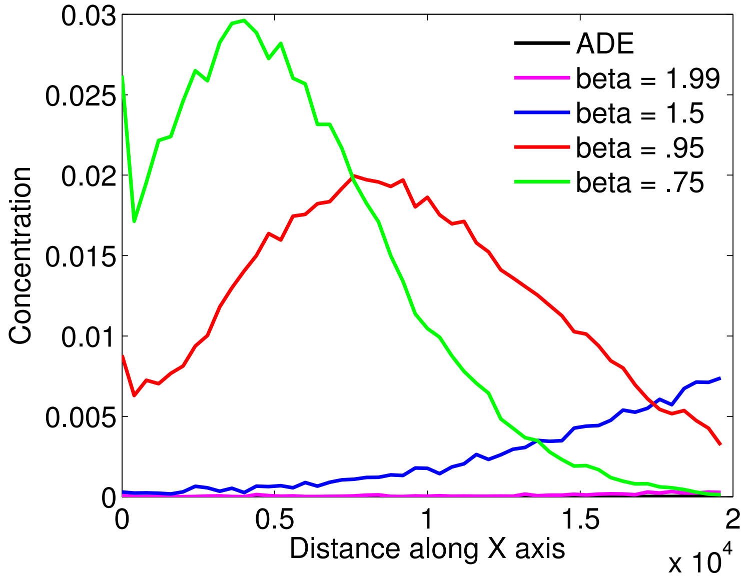


Plume at 300 years

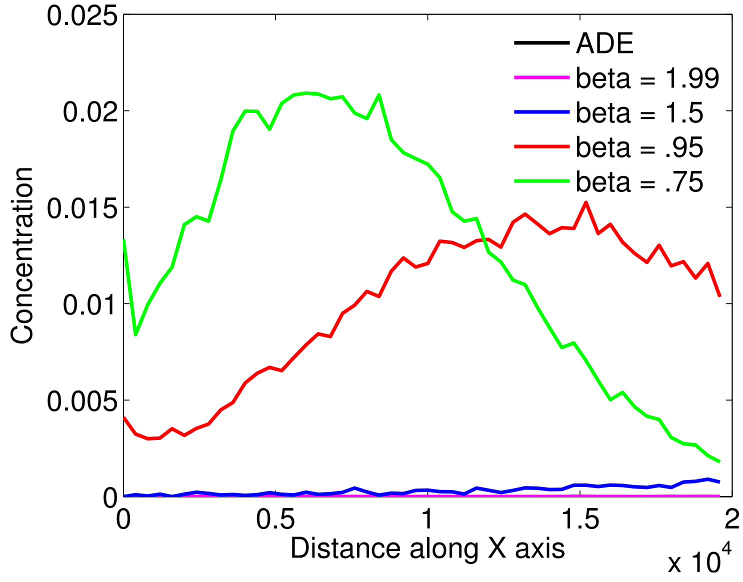


500 years

Results : Hybrid CBPT-CTRW model



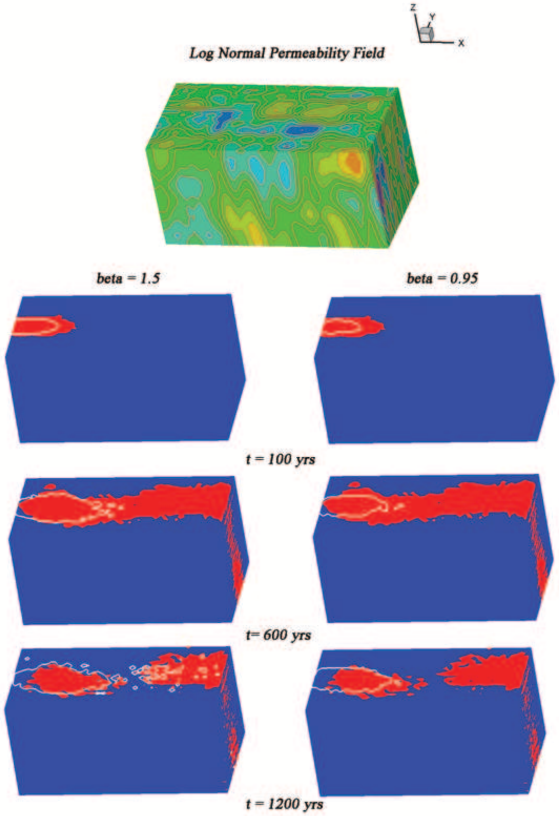
Plume at 2000 years



3000 years

Results : Heterogeneous Medium

The next test case is for a heterogeneous porous medium, with a log-normal permeability distribution $k(\mathbf{x})$.



Plume for the ADE and different values of β

Summary of Results

1. In this research, we have successfully incorporated the CTRW theory into a particle tracking algorithm (CBPT) and verified against the analytical solution.
2. The CTRW theory succesfully provides an alternate approach to transport that accounts for these subgrid scale heterogeneities.
3. Combining these two approaches, CTRW and CBPT now allows the modeling of non-Fickian transport at large scale sites with non-uniform properties.
4. Srinivasan et al, 2010, Random Walk Particle Tracking Simulations of Non-Fickian Transport in Heterogeneous Media, Journal of Computational Physics, 229 (11),4304-4314 .

Key Results

- The modified Stochastic Simulation Algorithm was developed to account for parametric and model uncertainties in complex reacting systems. This yielded a complete probabilistic description of the reaction rates and distribution coefficient which is crucial, since these distributions were highly skewed. This algorithm can be used to quantify parametric and model uncertainty in multi-component complex reacting systems.

- The problem of anomalous or non-Fickian transport was succesfully modeled by incorporating a time random walk formulation into a particle tracking technique (hybrid CBPT-CTRW model). Since this is a fully scalable method, it can be implemented at field scale sites with non-uniform properties.

Key Results

- The concentrations of reactants and their product are simultaneously influenced by the distribution of the travel time τ and a geochemical irreversible reaction. The variance of the time it takes particles to travel from the injecting plane to the control plane quantifies uncertainty in the advective component of the solute transport. The Damköhler number Da determines the relative importance of various sources of parametric uncertainty.

Ongoing and Future Work

- Study the transport behavior of Neptunium ions undergoing competitive sorption in a heterogeneous field using the Lagrangian stochastic approach.

- Incorporate reactions and the uncertainties therein, into the CBPT-CTRW model.

- Verify the conclusions of the different theoretical models studied here using experimental data.

Questions?

Thank you!