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4. TITLE AND SUBTITLE

Final Report: Reactive Random Walks - Embracing Complexity, Incomplete Mixing, and Heterogeneity to Predict Reactions in Environmentally Relevant Porous Media Systems

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W911NF-18-1-0338

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University of Notre Dame
ND Research
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13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Diogo Bolster
UU	UU	UU	UU		19b. TELEPHONE NUMBER: 574-631-0965

RPPR Final Report
as of 05-Jul-2022

Agency Code: 21XD

Proposal Number: 73063CH **Agreement Number: W911NF-18-1-0338**
INVESTIGATOR(S):

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DUNS Number: 824910376 EIN: 350868188
Report Date: 09-Mar-2022 Date Received: 28-Jun-2022
Final Report for Period Beginning 10-Aug-2018 and Ending 09-Dec-2021
Title: Reactive Random Walks - Embracing Complexity, Incomplete Mixing, and Heterogeneity to Predict Reactions in Environmentally Relevant Porous Media Systems
Begin Performance Period: 10-Aug-2018 **End Performance Period:** 09-Dec-2021
Report Term: 0-Other
Submitted By: Diogo Bolster Email: Diogo.Bolster.5@nd.edu
Phone: (574) 631-0965
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: **STEM Participants:** 4

Major Goals: We propose to extend state of the art Lagrangian random walk methods for reactive transport. In particular our goal is to develop methods that can handle large and realistic complex reaction chains, including kinetic, equilibrium and multiphase reactions. Additionally, our goal is to design our methods to be able to handle realistic multi-scale heterogeneity that is ubiquitous in environmental systems, but not accounted for in classical formulations. These approaches will be developed by deriving and testing accurate, physically-based model equations and simulation techniques for transport and chemical reactions in complex environmental systems, particularly in relation to redox reactions and mobility of metals in subsurface waters. In the original proposal we listed four objectives or goals/objectives, which were:

• G1: Formalize the theory for Lagrangian random walks for arbitrarily complex reactions

• G2: Implement Lagrangian reactive random walk framework in a general and flexible coding environment (Github)

• G3: Couple with existing geochemical libraries

• G4: Apply to complex reactive systems of environmental relevance (metal cycling in soils, NOM induced metal remobilization)

And we propose to test the following hypotheses:

Hypothesis 1: Due to the nonlinear nature of chemical reactions, sub-scale fluctuations in highly coupled systems have cascading effects, driving behaviors away from equilibria predicted under the assumption of perfect mixing.

Hypothesis 2: In real geologic systems sediment characteristics, flow and geochemical environments can vary rapidly over small spatial distances and/or evolve quickly in time. Models that do not account for these sub-scale variations will fail to predict metal mobility in real soils.

Hypothesis 3: Particle-based Lagrangian methods, deeply rooted in stochastic theory, are naturally suited to capturing sub-scale fluctuations in concentrations and Eh/pH as well as representing subsurface transport complexity. As such they can faithfully represent real systems without empirical tweaking of parameters and make accurate predictions at the field-scale.

Hypothesis 4: Real hydrologic systems have velocities that can vary over orders of magnitude. Conventional Eulerian models will only treat this as an increase in mean velocities, but not adequately account for the fact that subscale velocity fluctuations will change dramatically also. This has strong implications for speciation. Lagrangian particle methods can naturally account for the change in subscale fluctuations thus resulting in models that scale more naturally over a full range of anticipated velocities.

Accomplishments: See attached file.

Training Opportunities: One graduate student at Colorado School of Mines and one postdoctoral researcher at Notre Dame have been very directly and actively involved in this project. The graduate student is in the the middle of his PhD studies and will continue to work in this area over coming years. The postdoctoral scholar at Notre Dame is half way through their second year and will continue to work with us here. Two new PhD students have also been working on the numerical data sets generated as part of this effort. Two former students continued to be involved in this work, having now moved on to postdoctoral positions at Sandia and Lawrence Berkeley National labs.

Results Dissemination: We have published several papers in high profile academic journals and with the return of travel to conferences and the likes have also presented relevant work at the AGU Fall Meeting and several seminars that PIs were invited to give. We will also be presenting it at an upcoming Gordon Conference that will be well attended by the most expert people in the field of porous media.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Diogo Bolster
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Co PD/PI
Participant: David Benson
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Lucas Schauer
Person Months Worked: 7.00 **Funding Support:**
Project Contribution:
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Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Leonardo Bertassello
Person Months Worked: 3.00 **Funding Support:**
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ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Advances in Water Resources
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Volume: 126 Issue: First Page #: 108
Date Submitted: 8/1/19 12:00AM Date Published: 4/1/19 4:00AM
Publication Location:
Article Title: Numerical equivalence between SPH and probabilistic mass transfer methods for Lagrangian simulation of dispersion
Authors: Guillem Sole-Mari, Michael J. Schmidt, Stephen D. Pankavich, David A. Benson
Keywords: Smoothed Particle Hydrodynamics, Mass Transfer
Abstract: Several Lagrangian methodologies have been proposed in recent years to simulate advection-dispersion of so- lutes in fluids as a mass exchange between numerical particles carrying the fluid. In this paper, we unify these methodologies, showing that mass transfer particle tracking (MTPT) algorithms can be framed within the context of smoothed particle hydrodynamics (SPH), provided the choice of a Gaussian smoothing kernel whose band- width depends on the dispersion and the time discretization. Numerical simulations are performed for a simple dispersion problem, and they are compared to an analytical solution. Based on the results, we advocate for the use of a kernel bandwidth of the size of the characteristic dispersion length ?? = ?2 ????? , at least given a “dense enough ”distribution of particles, for in this case the mass transfer operation is not just an approximation, but in fact the exact solution, of the solute’s displacement by dispersion in a time step.
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Journal: Journal of Contaminant Hydrology
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Date Submitted: 8/1/19 12:00AM Date Published: 4/1/19 8:00AM
Publication Location:
Article Title: A spatial Markov model for upscaling transport of adsorbing-desorbing solutes
Authors: Thomas Sherman, Amir Paster, Giovanni Porta, Diogo Bolster
Keywords: Upscaling, Reactions, Spatial Markov
Abstract: The Spatial Markov Model (SMM) is an upscaled model with a strong track record in predicting upscaled behavior of conservative solute transport across hydrologic systems. Here we propose an SMM that can account for reactive linear adsorption and desorption processes and test it on a simple benchmark problem: flow and transport through an idealized periodic wavy channel. The methodology is built using trajectories that are obtained from a single high resolution random walk simulation of conservative transport across one periodic element. Our approach encodes information about where a particle starts at the inlet, where it leaves at the outlet, how long it takes to cross the domain and one additional piece of information, the number of times a particle strikes the boundary, with the objective of predicting large scale transport with arbitrary linear adsorption and desorption rates. Our benchmark problem demonstrates that predictions made with our proposed SMM agree favorably with results
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Volume: 11 Issue: 1 First Page #: 53
Date Submitted: 8/1/19 12:00AM Date Published: 12/1/18 10:00AM
Publication Location:
Article Title: Upscaling Mixing in Highly Heterogeneous Porous Media via a Spatial Markov Model
Authors: Elise Wright, Nicole Sund, David Richter, Giovanni Porta, Diogo Bolster
Keywords: heterogeneous porous media; upscaling; mixing; dilution
Abstract: In this work, we develop a novel Lagrangian model able to predict solute mixing in heterogeneous porous media. The Spatial Markov model has previously been used to predict effective mean conservative transport in flows through heterogeneous porous media. In predicting effective measures of mixing on larger scales, knowledge of only the mean transport is insufficient. Mixing is a small scale process driven by diffusion and the deformation of a plume by a non-uniform flow. In order to capture these small scale processes that are associated with mixing, the upscaled Spatial Markov model must be extended in such a way that it can adequately represent fluctuations in concentration. To address this problem, we develop downscaling procedures within the upscaled model to predict measures of mixing and dilution of a solute moving through an idealized heterogeneous porous medium. The upscaled model results are compared to measurements from a fully resolved simulation and found to be in good agre
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Volume: 55 Issue: 4 First Page #: 3556
Date Submitted: 8/1/19 12:00AM Date Published: 4/1/19 8:00AM
Publication Location:
Article Title: Accelerating and Parallelizing Lagrangian Simulations of Mixing?Limited Reactive Transport
Authors: Nicholas B. Engdahl, Michael J. Schmidt, David A. Benson
Keywords: Parallel Computing, Reactions
Abstract: Recent advances in random walk particle tracking have enabled direct simulation of mixing and reactions by allowing the particles to interact with each other using a multipoint mass transfer scheme. The mass transfer scheme allows separation of mixing and spreading processes, among other advantages, but it is computationally expensive because its speed depends on the number of interacting particle pairs. This note explores methods for relieving the computational bottleneck caused by the mass transfer step, and we use these algorithms to develop a new parallel, interacting particle model. The new model is a combination of a sparse search algorithm and a novel domain decomposition scheme, both of which offer significant speedup relative to the reference case—even when they are executed serially. We combine the strengths of these methods to create a parallel particle scheme that is highly accurate and efficient with run times that scale as 1/P for a fixed number of particles, where P is t
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Volume: 123 Issue: First Page #: 40
Date Submitted: 8/1/19 12:00AM Date Published: 1/1/19 5:00AM
Publication Location:
Article Title: On the separate treatment of mixing and spreading by the reactive-particle-tracking algorithm: An example of accurate upscaling of reactive Poiseuille flow
Authors: David A. Benson, Stephen Pankavich, Diogo Bolster
Keywords: Upscaling, Mixing, Reactions
Abstract: The Eulerian advection-dispersion-reaction equation (ADRE) suffers the well-known scale-effect of reduced apparent reaction rates between chemically dissimilar fluids at larger scales (or dimensional averaging). The dispersion tensor in the ADRE must equally and simultaneously account for both solute mixing and spreading. Recent reactive-particle-tracking (RPT) algorithms can, by separate mechanisms, simulate 1) smaller-scale mixing by inter-particle mass transfer, and 2) mass spreading by traditional random walks. To test the supposition that the RPT can accurately track these separate mechanisms, we upscale reactive transport in Hagen-Poiseuille flow between two plates. The simple upscaled 1-D RPT model with one velocity value, an upscaled Taylor macro-dispersivity, and the local molecular diffusion coefficient matches the results obtained from a detailed 2-D model with fully described velocity and diffusion. Both models use the same thermodynamic reaction rate....
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Volume: 137 Issue: First Page #: 103509
Date Submitted: 8/28/20 12:00AM Date Published: 3/9/20 8:00AM
Publication Location:
Article Title: Entropy; The former trouble with particles;including a new numerical model computational penalty for the Akaike information criterion)
Authors: Benson,David A., Pankavich, Stephen, Schmidt, Michael, Sole-Mari, Guillem
Keywords: Entropy, Particles and Reactions
Abstract: Traditional random-walk particle-tracking (PT) models of advection and dispersion do not track entropy, because particle masses remain constant. Newer mass-transfer particle tracking (MTPT) models have the ability to do so because masses of all compounds may change along trajectories. Additionally, the probability mass functions (PMF) of these MTPT models may be compared to continuous solutions with probability density functions, when a consistent definition of entropy (or similarly, the dilution index) is constructed. This definition reveals that every numerical model incurs a computational entropy. Similar to Akaike's entropic penalty for larger numbers of adjustable parameters, the computational complexity of a model (e.g., number of nodes) adds to the entropy and, as such, must be penalized. The MTPT method can use a particle-collision based kernel or an SPH-derived adaptive kernel. The latter is more representative of a locally well-mixed system
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Volume: 132 Issue: First Page #: 103386
Date Submitted: 8/27/21 12:00AM Date Published: 10/1/19 4:00PM
Publication Location:
Article Title: Aging and mixing as pseudo-chemical-reactions between, and on, particles;#x23;x3a#x3b; Perspectives on particle interaction and multi-modal ages in hillslopes and streams
Authors: Benson, D. A., M. J. Schmidt, D. Bolster, C. Harman, and N. B. Engdahl
Keywords: Grounwater Age, Reactions, Particles
Abstract: The particle-tracking method was recently extended to allow inter-particle mass transfer and arbitrarily complex reactions by allowing each particle to repre- sent any number of distinct chemical compounds. This methodology allows the tracking (and broadening due to mixing) of the age probability density function (PDF) on each particle. Aquifer heterogeneity leads to channeling and multi- modal age PDFs in stream samples. This observation supports the concept of age classes but clearly shows the more complicated interplay of dispersion, mixing, and travel times on the age distributions.
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Journal: Journal of Contaminant Hydrology
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Volume: 234 Issue: First Page #: 103642
Date Submitted: 8/28/20 12:00AM Date Published: 10/1/20 8:00AM
Publication Location:
Article Title: Reactive particle-tracking solutions to a benchmark problem on heavy metal cycling in lake sediments
Authors: Michael J. Schmidt, Stephen D. Pankavich, Alexis Navarre-Sitchler, Nicholas B. Engdahl, Diogo Bolster,
Keywords: Lagrangian modelingParticle methods; Imperfect mixing; Diffusion-reaction equation; Heavy metal cycling
Abstract: Geochemical systems are known to exhibit highly variable spatiotemporal behavior. This may be observed both in non-smooth concentration curves in space for a single sampling time and also in variability between samples taken from the same location at different times. However, most models that are designed to simulate these systems provide only single-solution smooth curves and fail to capture the noise and variability seen in the data. We apply a recently developed reactive particle-tracking method to a system that displays highly complex geochemical behavior. When the method is made to most closely resemble a corresponding Eulerian method, in its unperturbed form, we see near-exact match between solutions of the two models. More importantly, we consider two approaches for perturbing the model and find that the spatially-perturbed condition is able to capture a greater degree of the variability present in the data. This method of perturbation is a task to which particle methods are un
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Volume: 132 Issue: First Page #: 103386
Date Submitted: 8/28/20 12:00AM Date Published: 10/1/19 8:00AM
Publication Location:
Article Title: Aging and mixing as pseudo-chemical-reactions between, and on, particles#x3a; Perspectives on particle interaction and multi-modal ages in hillslopes and streams
Authors: David A. Benson, Michael J. Schmidt, Diogo Bolster, Ciaran Harman, Nicholas B. Engdahl
Keywords: Particle methods; MixingAging; Age distribution
Abstract: Geochemical systems are known to exhibit highly variable spatiotemporal behavior. This may be observed both in non-smooth concentration curves in space for a single sampling time and also in variability between samples taken from the same location at different times. However, most models that are designed to simulate these systems provide only single-solution smooth curves and fail to capture the noise and variability seen in the data. We apply a recently developed reactive particle-tracking method to a system that displays highly complex geochemical behavior. When the method is made to most closely resemble a corresponding Eulerian method, in its unperturbed form, we see near-exact match between solutions of the two models. More importantly, we consider two approaches for perturbing the model and find that the spatially-perturbed condition is able to capture a greater degree of the variability present in the data. This method of perturbation is a task to which particle methods are un
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Publication Location:
Article Title: A mass-transfer particle-tracking method for simulating transport with discontinuous diffusion coefficients
Authors: Michael J. Schmidt, Nicholas B. Engdahl, Stephen D. Pankavich, Diogo Bolster
Keywords: Lagrangian Modeling; Particle tracking; Discontinuous Diffusion
Abstract: Geochemical systems are known to exhibit highly variable spatiotemporal behavior. This may be observed both in non-smooth concentration curves in space for a single sampling time and also in variability between samples taken from the same location at different times. However, most models that are designed to simulate these systems provide only single-solution smooth curves and fail to capture the noise and variability seen in the data. We apply a recently developed reactive particle-tracking method to a system that displays highly complex geochemical behavior. When the method is made to most closely resemble a corresponding Eulerian method, in its unperturbed form, we see near-exact match between solutions of the two models. More importantly, we consider two approaches for perturbing the model and find that the spatially-perturbed condition is able to capture a greater degree of the variability present in the data. This method of perturbation is a task to which particle methods are un
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Publication Location:
Article Title: Lagrangian Modeling of Mixing?Limited Reactive Transport in Porous Media: Multirate Interaction by Exchange With the Mean
Authors: Guillem Sole-Mari, Daniel Fernandez-Garcia, Xavier Sanchez-Vila, Diogo Bolster
Keywords: Lagrangian Mixing Reactions
Abstract: Geochemical systems are known to exhibit highly variable spatiotemporal behavior. This may be observed both in non-smooth concentration curves in space for a single sampling time and also in variability between samples taken from the same location at different times. However, most models that are designed to simulate these systems provide only single-solution smooth curves and fail to capture the noise and variability seen in the data. We apply a recently developed reactive particle-tracking method to a system that displays highly complex geochemical behavior. When the method is made to most closely resemble a corresponding Eulerian method, in its unperturbed form, we see near-exact match between solutions of the two models. More importantly, we consider two approaches for perturbing the model and find that the spatially-perturbed condition is able to capture a greater degree of the variability present in the data. This method of perturbation is a task to which particle methods are un
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Volume: 125 Issue: 1 First Page #:
Date Submitted: 8/28/20 12:00AM Date Published: 1/1/20 5:00AM
Publication Location:
Article Title: Characterizing the Influence of Fracture Density on Network Scale Transport
Authors: Thomas Sherman, Jeffrey Hyman, Marco Dentz, Diogo Bolster
Keywords: Lagrangian; Fractures
Abstract: Geochemical systems are known to exhibit highly variable spatiotemporal behavior. This may be observed both in non-smooth concentration curves in space for a single sampling time and also in variability between samples taken from the same location at different times. However, most models that are designed to simulate these systems provide only single-solution smooth curves and fail to capture the noise and variability seen in the data. We apply a recently developed reactive particle-tracking method to a system that displays highly complex geochemical behavior. When the method is made to most closely resemble a corresponding Eulerian method, in its unperturbed form, we see near-exact match between solutions of the two models. More importantly, we consider two approaches for perturbing the model and find that the spatially-perturbed condition is able to capture a greater degree of the variability present in the data. This method of perturbation is a task to which particle methods are un
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Date Submitted: 8/28/20 12:00AM Date Published: 5/1/20 4:00AM
Publication Location:
Article Title: Upscaling transport of a sorbing solute in disordered non periodic porous domains
Authors: Thomas Sherman, Emanuela Bianchi Janetti, Gaël Raymond Guédon, Giovanni Porta, Dic
Keywords: Reactive Transport; Upscaled Model; Statistical Sampling
Abstract: Geochemical systems are known to exhibit highly variable spatiotemporal behavior. This may be observed both in non-smooth concentration curves in space for a single sampling time and also in variability between samples taken from the same location at different times. However, most models that are designed to simulate these systems provide only single-solution smooth curves and fail to capture the noise and variability seen in the data. We apply a recently developed reactive particle-tracking method to a system that displays highly complex geochemical behavior. When the method is made to most closely resemble a corresponding Eulerian method, in its unperturbed form, we see near-exact match between solutions of the two models. More importantly, we consider two approaches for perturbing the model and find that the spatially-perturbed condition is able to capture a greater degree of the variability present in the data. This method of perturbation is a task to which particle methods are un
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Volume: 35 Issue: 8 First Page #: 1529
Date Submitted: 8/20/21 12:00AM Date Published: 4/1/21 8:00AM
Publication Location:
Article Title: Upscaling bimolecular reactive transport in highly heterogeneous porous media with the LAgrangian Transport Eulerian Reaction Spatial (LATERS) Markov model
Authors: Elise E. Wright, Nicole L. Sund, David H. Richter, Giovanni M. Porta, Diogo Bolster
Keywords: reactions, heterogeneous
Abstract: The LAgrangian Transport Eulerian Reaction Spatial (LATERS) Markov model was developed to predict upscaled bimolecular reactive transport in a flow around an array of solid cylinders. This method combines the stochastic Lagrangian Spatial Markov model (SMM) to predict transport and a volume averaged reaction rate equation to predict reactions of the form ??+???? A+B??. Here, we extend the LATERS Markov model to upscale bimolecular reactive transport in a Darcy flow through an idealized heterogeneous porous medium. In agreement with previous literature, the accuracy of the prediction is a function of the Damköhler (Da) numbers, i.e., high Da are more challenging because of incomplete mixing. It was found that a key component which must be incorporated into the upscaled model in these high Da systems is the idea that nearby A and B particles should be more likely to react than those that are farther apart. This is here achieved by appropriately reducing the resolution of the spatial g
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Date Submitted: 8/20/21 12:00AM Date Published: 4/1/21 4:00AM
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Article Title: Random Walk Modeling of Reactive Transport in Porous Media With a Reduced?Order Chemical Basis of Conservative Components
Authors: Guillem Sole?Mari, Michael J. Schmidt, Diogo Bolster, Daniel Fernàndez?Garcia
Keywords: random walk, reactions
Abstract: The LAgrangian Transport Eulerian Reaction Spatial (LATERS) Markov model was developed to predict upscaled bimolecular reactive transport in a flow around an array of solid cylinders. This method combines the stochastic Lagrangian Spatial Markov model (SMM) to predict transport and a volume averaged reaction rate equation to predict reactions of the form ??+???? A+B??. Here, we extend the LATERS Markov model to upscale bimolecular reactive transport in a Darcy flow through an idealized heterogeneous porous medium. In agreement with previous literature, the accuracy of the prediction is a function of the Damköhler (Da) numbers, i.e., high Da are more challenging because of incomplete mixing. It was found that a key component which must be incorporated into the upscaled model in these high Da systems is the idea that nearby A and B particles should be more likely to react than those that are farther apart. This is here achieved by appropriately reducing the resolution of the spatial g
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Journal: Transport in Porous Media
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Volume: Issue: First Page #:
Date Submitted: 8/20/21 12:00AM Date Published: 3/1/21 5:00AM
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Article Title: Characterizing Reactive Transport Behavior in a Three-Dimensional Discrete Fracture Network
Authors: Thomas Sherman, Guillem Sole-Mari, Jeffrey Hyman, Matthew R. Sweeney, Daniel Vassallo, Diogo Bol
Keywords: Fractures Reactions Network
Abstract: While several studies have linked network and in-fracture scale properties to conservative transport behavior in subsurface fractured media, studies on reactive transport cases remain relatively underdeveloped. In this study, we explore the behavior of an irreversible kinetic reaction during the interaction of two solute plumes, one consisting of species A and the other species B. When the plumes converge, these species react kinetically to form a new species C via ??+???????? A+B?C. This reactive system is studied using a three-dimensional discrete fracture network (DFN) model coupled with reactive Lagrangian particle tracking. We find that the interplay of network topology and chemical properties of the reactive solutes controls reactive transport processes. The network topology drives species A and B together, and the chemical properties dictate whether and how quickly a reaction occurs. Results demonstrate that reactions are most likely to occur in high-velocity fractures that m
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Article Title: Nonparametric, data-based kernel interpolation for particle-tracking simulations and kernel density estimation
Authors: David A. Benson, Diogo Bolster, Stephen Pankavich, Michael J. Schmidt
Keywords: kernel, smoothing
Abstract: Traditional interpolation techniques for particle tracking include binning and convolutional formulas that use pre-determined (i.e., closed-form, parameteric) kernels. In many instances, the particles are introduced as point sources in time and space, so the cloud of particles (either in space or time) is a discrete representation of the Green's function of an underlying PDE. As such, each particle is a sample from the Green's function; therefore, each particle should be distributed according to the Green's function. In short, the kernel of a convolutional interpolation of the particle sample "cloud" should be a replica of the cloud itself. This idea gives rise to an iterative method by which the form of the kernel may be discerned in the process of interpolating the Green's function. When the Green's function is a density, this method is broadly applicable to interpolating a kernel density estimate based on random data drawn from a single distribution. We formulate and construct the a
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Article Title: A Closer Look: High-Resolution Pore-Scale Simulations of Solute Transport and Mixing Through Porous Media Columns
Authors: Guillem Sole-Mari, Diogo Bolster, Daniel Fernàndez-Garcia
Keywords: High Resolution Numerical Simulations; Mixing, Reactions
Abstract: Mixing is pivotal to conservative and reactive transport behaviors in porous media. Methods for investigating mixing processes include mathematical models, laboratory experiments and numerical simulations. The latter have been historically limited by the extreme computational resources needed for solving flow and transport at the microscopic scale within the complex pore structure of a three-dimensional porous medium, while dealing with a sufficiently large domain in order to generate meaningful emergent continuum-scale observables. We present the results of such a set of virtual column experiments, which have been conducted by taking advantage of modern high-performance computing infrastructure and Computational Fluid Dynamics software capable of massively parallel simulations. The computational approach has important advantages such as full control over the experimental conditions as well as high spatial and temporal resolution of measurements. Hydrodynamic dispersion results agree w
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Article Title: Optimal Time Step Length for Lagrangian Interacting-Particle Simulations of Diffusive Mixing
Authors: Michael J. Schmidt, Nicholas B. Engdahl, David A. Benson, Diogo Bolster
Keywords: Numerical Simulations; Lagrangian
Abstract: To date, Lagrangian mass-transfer-based interacting particle methods have been shown to be rigorous and capable of modeling a diverse range of sophisticated problems but have lacked formal criteria for choosing an optimal time step length.In Eulerian (grid-based) methods, a user can typically reduce ??? to an arbitrary level and expect to see corresponding gains in accuracy. The particle methods that we consider behave similarly, but only up to a point: for a fixed number of particles, ??? can become so small that the magnitude of diffusion restricts particles from communicating via mass-transfer, and at this point, solution accuracy begins to degrade. In this work, we formalize criteria for determining when this transition takes place, based on the properties of a particular system, and we use this criteria to choose the optimal time step. We test these results with numerical experiments that demonstrate accurate prediction of the optimal time step for a variety of conditions.
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I certify that the information in the report is complete and accurate:
Signature: Diogo Bolster
Signature Date: 6/28/22 12:37PM

During the last phase of this project (since our last interim report) we have primarily worked on two things: (1) Analyzing the data obtained from the high performance computing simulations of reactive transport in a numerically simulated pore-scale column experiment and (2) Developing massively parallel implementation of our novel Lagrangian reactive particle methods.

(1) Pore Scale Simulations

(i) Tracking the interfacial area along which reactions happen

Figure 1 below shows a snapshot at a given time of the interfacial area between two reactants being displaced in our numerical column. We have developed novel algorithms with which to track how this interface grows over time. By doing this we are developing the information required with which to build rigorous upscaled models that can predict reactions at larger Darcy scales. In particular note the highly filamentous and complex structure that emerges. This is very different from the smooth interface predicted by classical models. By painting a better picture of this we will be able to account for incomplete mixing at pore scales much more accurately than before.

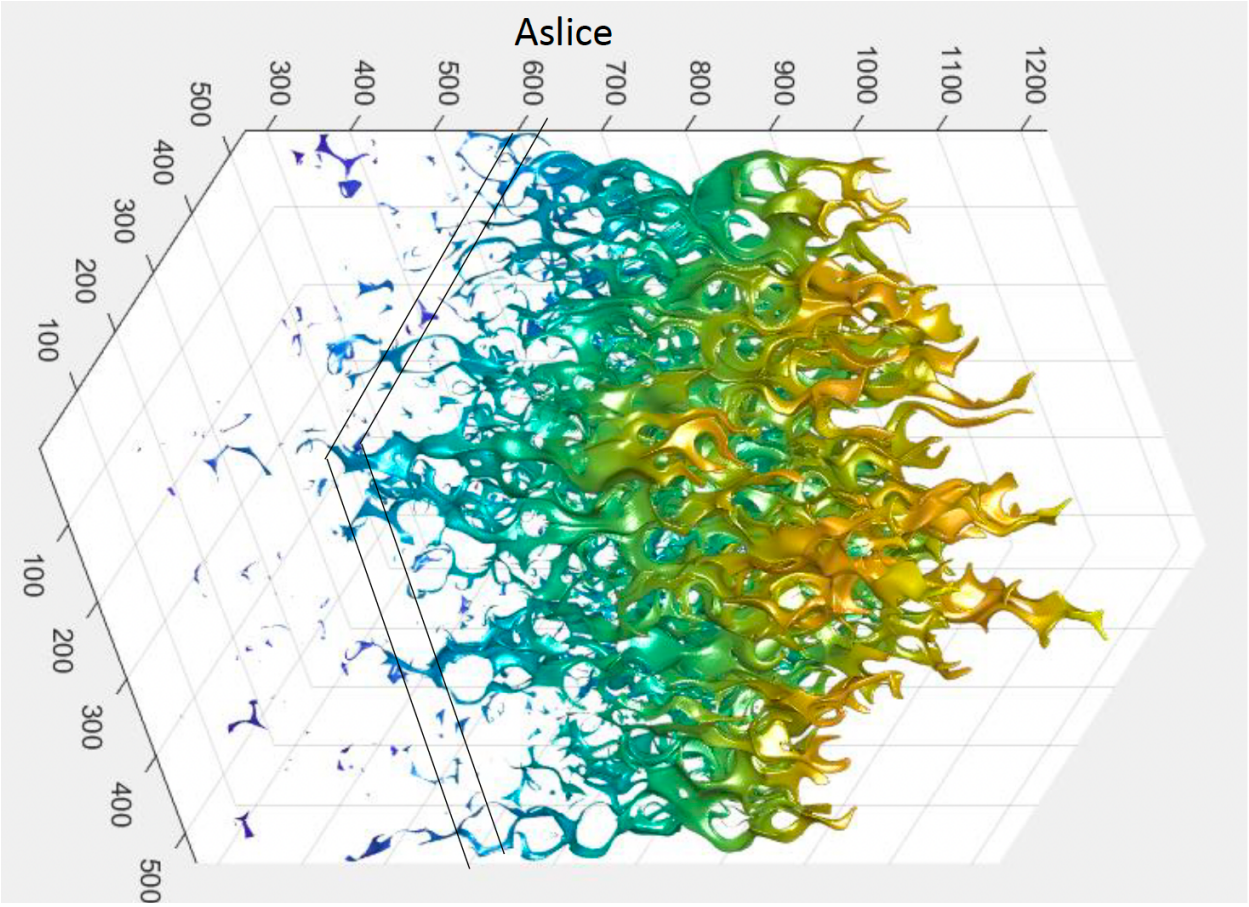

Figure 1: A pore scale snapshot in time of the three-dimensional interface between two reactants in a porous column from high performance computing simulations.

(ii) Probability Density Functions (PDFs) of Concentrations

One of the biggest mismatches that occurs between classical theories and observations of reactive transport is that observations is that experimental observations typically display a much broader distribution of concentrations than classical theories would predict, which is in line with the observations of the complex interface noted above. We have developed a novel technique for measuring the distribution of concentrations. We have then compared this distribution to classical as well as newer state of the art models for the evolution of concentration pdfs. We have found that even state of the art model miss many of the essential details and have added new corrections to these models that sill significantly improve predictions at larger scales.

(2) Massively Parallel Lagrangian Models

In order for the Lagrangian models that we have developed and that show significant advantages over many current approaches to compete with their Eulerian counterparts it will be essential to implement them in high performance computing environments. Eulerian codes have decades worth of investment in this, but Lagrangian models do not. We have, for the first time, implemented a fully three-dimensional version of our Lagrangian models. In particular we have implemented it on both shared and distributed memory machines and shown excellent scaling of simulations using up to 512 cores, meaning that our approaches can now be competitive with current Eulerian methods. We have also coupled these approaches to multiple geochemical libraries meaning that extremely complex reactions can be readily implemented. We are in the process of publishing the work and once vetted will share this openly with the whole scientific community.

Outcomes of Goals and Hypotheses

In terms of the original objectives set forth in this project, we have fully completed goals G1-G4 listed in the Major Goals section that were set out in the original proposal.

With regard to the hypotheses we have the following conclusions:

Hypothesis 1: Due to the nonlinear nature of chemical reactions, sub-scale fluctuations in highly coupled systems have cascading effects, driving behaviors away from equilibria predicted under the assumption of perfect mixing.

We have shown that this hypothesis is in general true across a broad range of environmental settings including at pore and Darcy scales.

Hypothesis 2: In real geologic systems sediment characteristics, flow and geochemical environments can vary rapidly over small spatial distances and/or evolve quickly in time. Models that do not account for these sub-scale variations will fail to predict metal mobility in real soils.

We have shown that this is also in general true as well as demonstrated that models that do accurately account for these subscale heterogeneities and fluctuations in an upscaled environment can much more accurately predict metal mobility in real soils.

Hypothesis 3: Particle-based Lagrangian methods, deeply rooted in stochastic theory, are naturally suited to capturing sub-scale fluctuations in concentrations and Eh/pH as well as representing subsurface transport complexity. As such they can faithfully represent real systems without empirical tweaking of parameters and make accurate predictions at the field-scale.

We have demonstrated that Lagrangian models can indeed achieve this, but to state that this is absolutely true would be an exaggeration. Lagrangian models are able to capture certain types of subscale variations very well, but there are certain complexities that give rise to fluctuations that they cannot capture without further modification. While we maintain that Lagrangian models have certain benefits in terms of capturing incomplete mixing, further work is needed to completely generalize this to highly complex environments, particularly those with multiscale heterogeneity of multiple properties (e.g. porosity, permeability, surface charge, multiphase characteristics). We believe that this is doable, but further theoretical and numerical developments are still needed.

Hypothesis 4: Real hydrologic systems have velocities that can vary over orders of magnitude. Conventional Eulerian models will only treat this as an increase in mean velocities, but not adequately account for the fact that subscale velocity fluctuations will change dramatically also. This has strong implications for speciation. Lagrangian particle methods can naturally account for the change in subscale fluctuations thus resulting in models that scale more naturally over a full range of anticipated velocities.

Similar to hypothesis 3 we find this to be true for certain types of heterogeneities that give rise to variable velocity fields, but cannot confidently assert this as true in general. Lagragian methods certainly appear to have benefits that can naturally capture these effects, but as with all models they also have their limits. In velocity heterogeneities that are induced by physical heterogeneity this seems to work very well, but systems with chemical and multiphase heterogeneities certainly require further investigation.