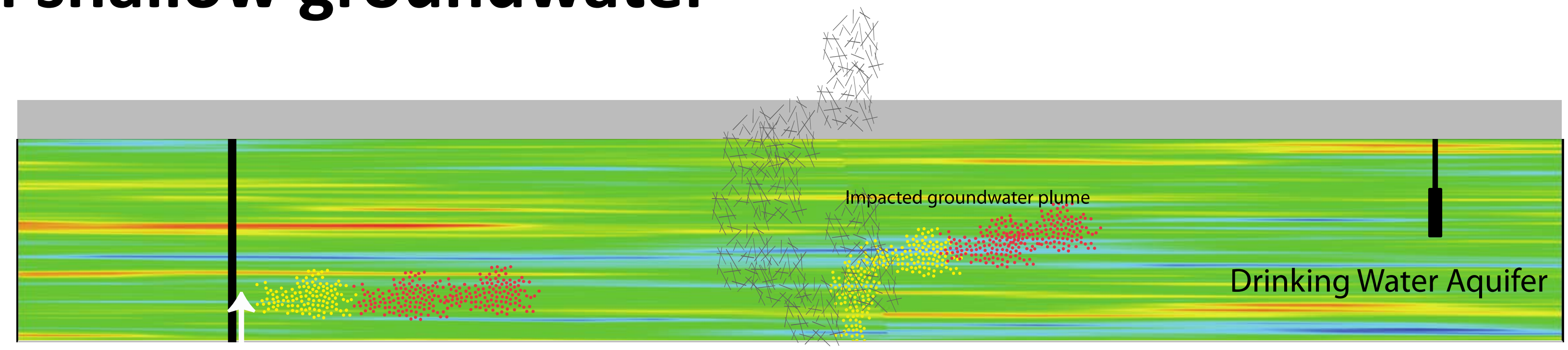
Towards an understanding of uncertainty, heterogeneity and reactive transport in a human health risk framework for CO2 sequestration impacts on shallow groundwater



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This is a large, collaborative project…

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GOLDEN ENERGY COMPUTING ORGANIZATION

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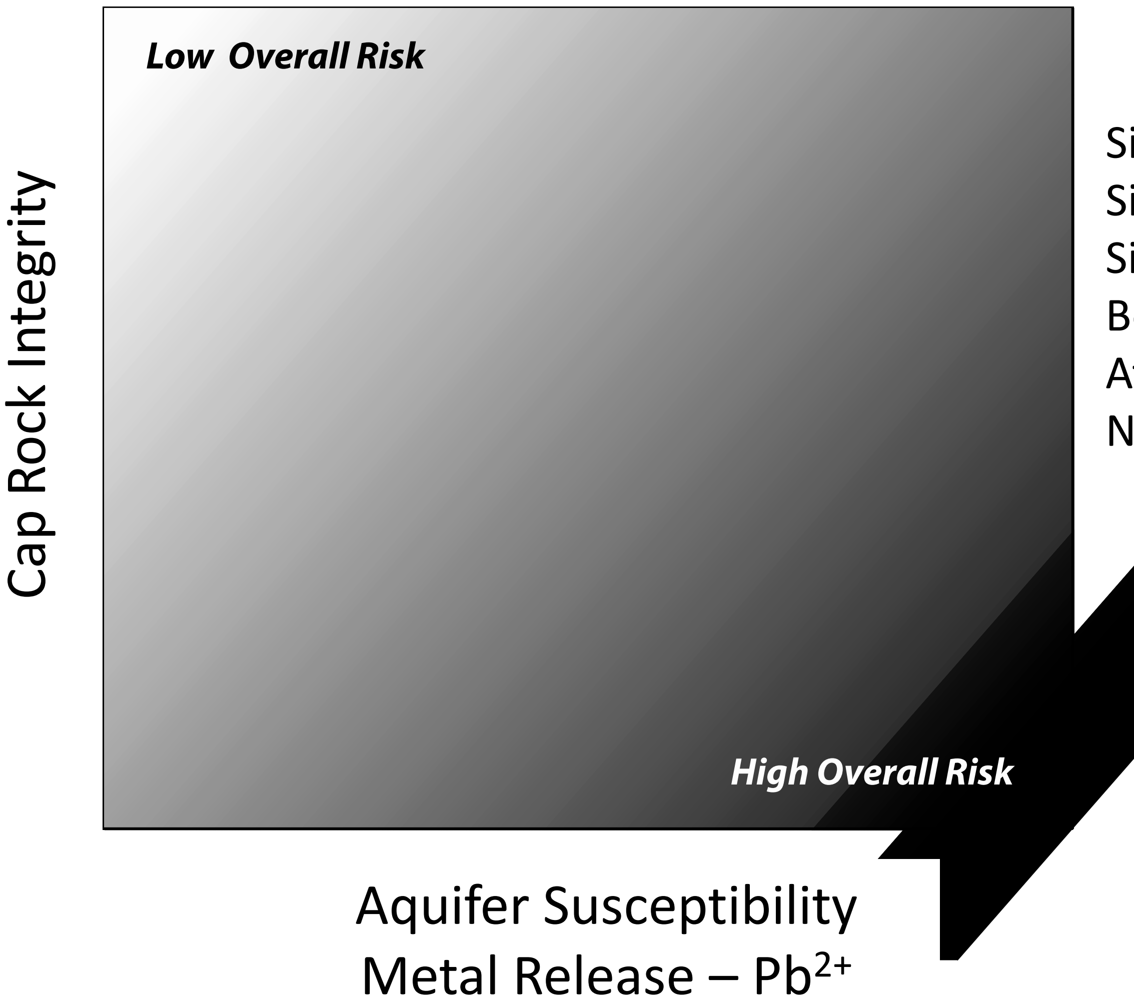
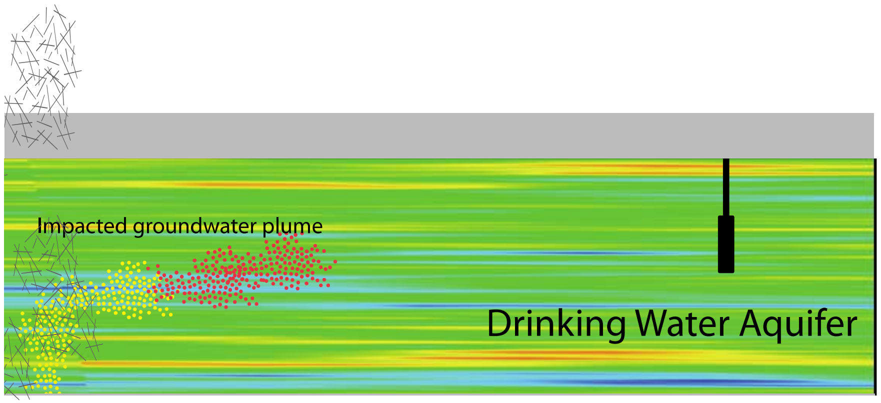
Simulations are required for risk assessment of CO_2 leakage



Siirila, et al. 2012 AWR
Siirila and Maxwell 2012 WRR
Siirila and Maxwell 2012 STOTEN
Bearup, et al., 2012 ES&T
Atchley, et al. 2013 AWR
Navarre-Sitchler et al., AWR 2013

And we incorporate uncertainty and variability into the approach



•Primarily ***variable*** parameters

-Imprecision due to actual differences among members of a population

-Cannot be reduced (only more accurately characterized)

•Primarily ***uncertain*** parameters

-Imprecision based on limitations in thoroughness and or measurements

-Can be reduced

-Use stochastic methods

Modeling fully kinetic reactive transport is computationally expensive

Hammond et al. 2007, Hammond et al. 2010.

Because…

Reactive transport includes complex hydrological and chemical processes.

e.g. Cirpka and Kitanidis, 2000; McLaughlin and Ruan, 2001; Green et al. 2010; Le Borgne et al. 2010.

Specific to CO_2 leakage, reactive transport may occur over a large area, necessitating large model domains.

e.g. Carroll et al., 2009; Zeng et al., 2009; Apps et al., 2010; Wilken et al., 2011; Siirila et al., 2012

Simplifications necessary to reduce computational needs

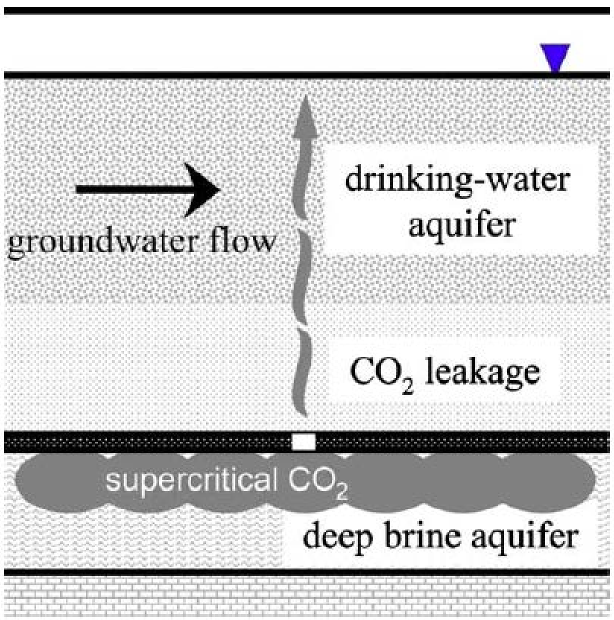
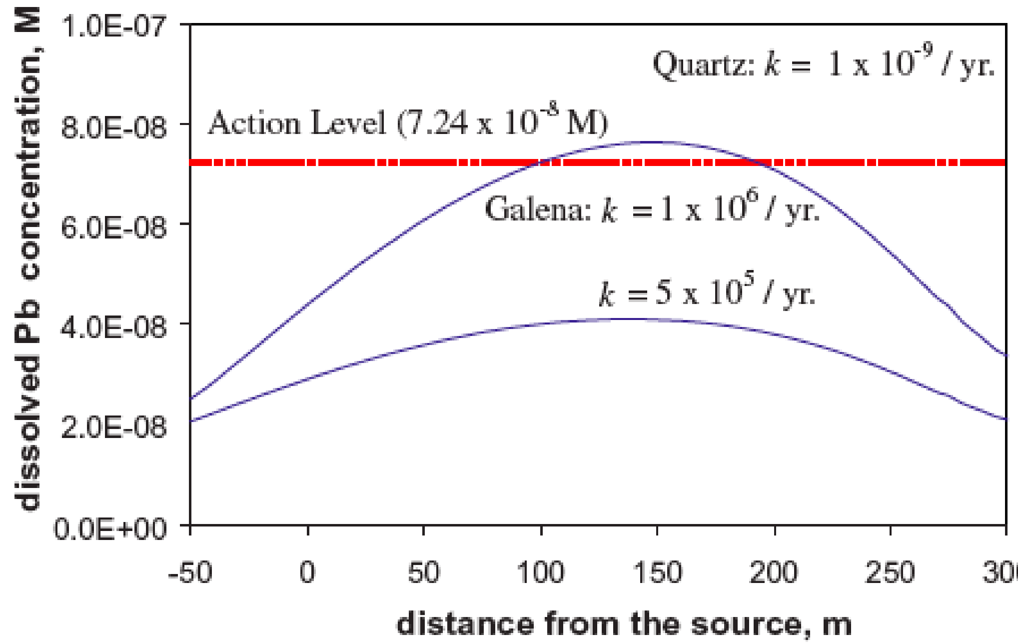


Fig. 2. Schematic diagram for the model simulations.

Wang and Jaffe, 2004



Geochemically simple

Constant velocity

Galena as only source of Pb

First steps of this work were to develop a CCS CO_2 leakage framework

Risk assessment is well established: (Bogen and Spear, 1987; McKone 1987; Massmann, and Freeze, 1987; Freeze, et al., 1990; Mckone, and Bogen, 1991; Mckone, and Bogen, 1992; Andričević et al., 1994; Pelmulder et al., 1996; Andričević, Cvetković, 1996; Bogen, and Gold, 1997; Maxwell et al., 1998; Maxwell, and Kastenberg, 1999; Maxwell, and Kastenberg, 1999; Maxwell, et al., 1999; Uricchio, et al., 2004; Ozbek, M. and Pinder, 2006; Li et al., 2007; Maxwell et al., 2008; Bolster and Tartakovsky, 2008; de Barros and Rubin, 2008; de Barros et al., 2009, Siirila et al., 2012, Siirila and Maxwell, 2012, Siirila and Maxwell, 2012b)

Risk *in CCS* has been studied in terms of:

- CO_2 storage failure (Price and Oldenburg, 2009)
- Probability and degree to which a leak occurs (Kopp et al., 2010; et al., 2010; LeNeveu, 2008; Vivalda et al., 2009)

A framework which quantifies the risk to human health in CCS has yet to be developed

- Needed as a decision-making tool in the large scale implementation of CCS
- Needed to protect drinking water resources (and therefore the general public of consumers)

Publication:

Siirila, E.R., Navarre-Sitchler, A.K., Maxwell, R.M., and McCray, J.M. A quantitative methodology to assess the risks to human health from CO_2 leakage into groundwater, Advances in Water Resources 2012.

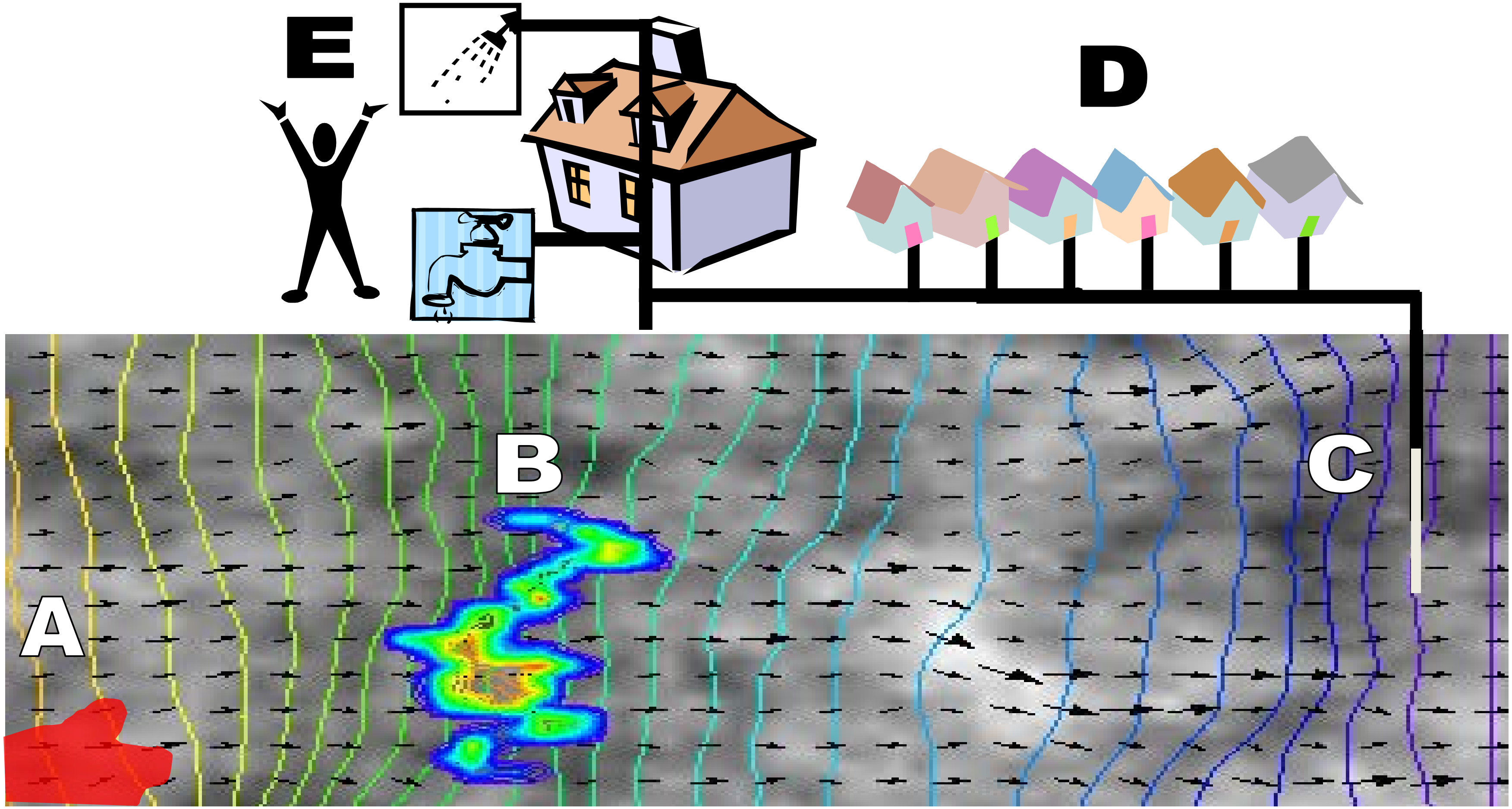
A: Contamination source

B: Heterogeneous subsurface flow and contaminant transport

C: Possible capture in one or more down-gradient wells

D: Water delivery system to many different households

E: Exposure and health risk via multiple pathways to varying individuals



After: Maxwell et al 1998, 1999, 2008; Maxwell and Kastenberg 1999; Siirila et al., 2012

mepage: www.elsevier.com/locate/advwatres

A quantitative methodology to assess the risks to human health from CO_2 leakage into groundwater

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Metal mobilization
Carbon dioxide leakage
Monte Carlo
Human health risk
Joint Uncertainty and Variability

A B S T R A C T

Leakage of CO_2 and associated gases into overlying aquifers as a result of geologic carbon capture and sequestration may have adverse impacts on aquifer drinking-water quality. Gas or aqueous-phase leakage may occur due to transport via faults and fractures, through faulty well bores, or through leaky confining materials. Contaminants of concern include aqueous salts and dissolved solids, gaseous or aqueous-phase organic contaminants, and acidic gas or aqueous-phase fluids that can liberate metals from aquifer minerals. Here we present a quantitative risk assessment framework to predict potential human health risk from CO_2 leakage into drinking water aquifers. This framework incorporates the potential release of CO_2 into the drinking water aquifer; mobilization of metals due to a decrease in pH; transport of these metals down gradient to municipal receptors; distributions of contaminated groundwater to multiple households; and exposure and health risk to individuals using this water for household purposes. Additionally, this framework is stochastic, incorporates detailed variations in geological and geostatistical parameters and discriminates between uncertain and variable parameters using a two-stage, or nested, Monte Carlo approach. This approach is demonstrated using example simulations with hypothetical, yet realistic, aquifer characteristics and leakage scenarios. These example simulations show a greater risk for arsenic than for lead for both cancer and non-cancer endpoints, an unexpected finding. Higher background groundwater gradients also yield higher risk. The overall risk and the associated uncertainty are sensitive to the extent of aquifer stratification and the degree of local-scale dispersion. These results all highlight the importance of hydrologic modeling in risk assessment. A linear relationship between carcinogenic and noncarcinogenic risk was found for arsenic and suggests action levels for carcinogenic risk will be exceeded in exposure situations before noncarcinogenic action levels, a reflection of the ratio of cancer and non-cancer toxicity values. Finally, implications for ranking aquifer vulnerability due to geologic configuration, aquifer mineralogy, and leakage scenarios are discussed.

1. Introduction

Although geologic Carbon Capture and Storage (CCS) has recently become a viable option to reduce atmospheric CO_2 emissions, a quantitative methodology to assess the risks to human health from CO_2 leakage has yet to be developed. One of the ben- pathways include, but are not limited to (1) direct leaks such as abandoned wellbores, faults or fractures and (2) diffuse leaks such as permeable caprock material and micro-fractures in the caprock, e.g. [4–7]. If CO_2 leakage was to occur, one of the primary concerns is the contamination of potable water via the mobilization of toxic metals from aquifer material induced through a drop in groundwa-

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

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

Toxicity Value:

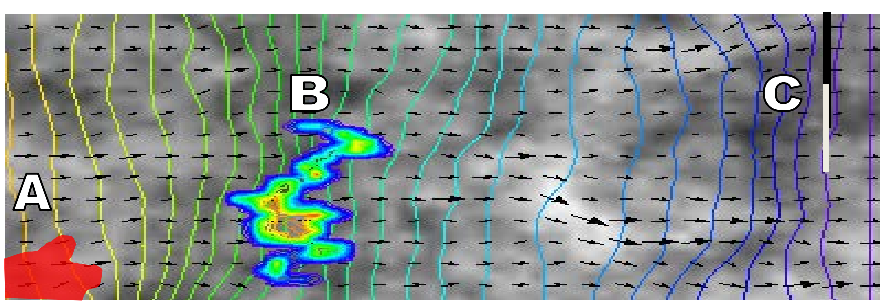
Cancer Potency Factor *(CPF)*

Exposure Time :

Average Daily Dose (*ADD*)

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

Environmental concentration: $\langle C \rangle$



Siirila et al., AWR, 2012

There is *considerable uncertainty and variability* in each of these categories

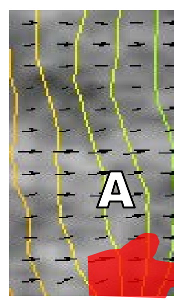
Toxicity Value:

- 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:

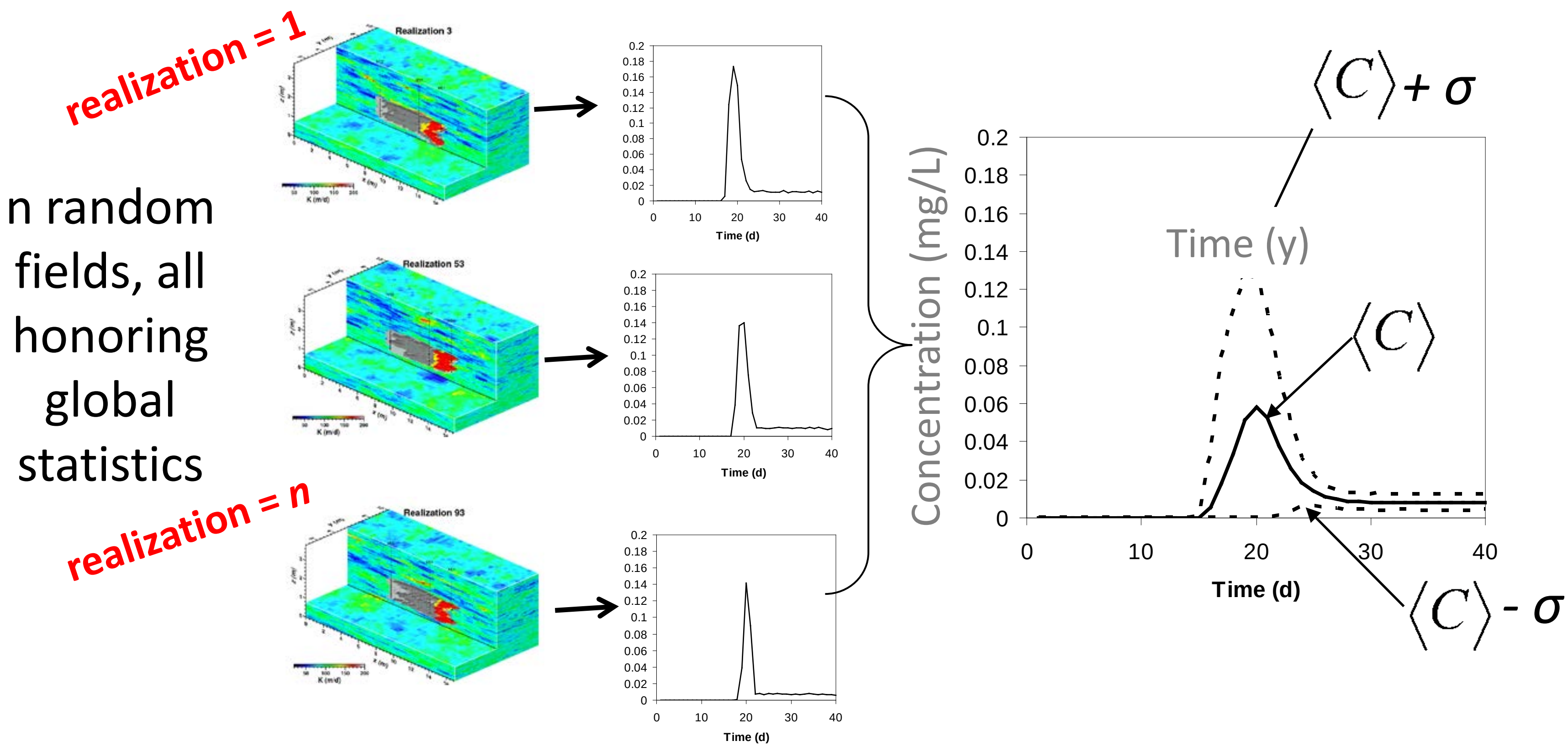


- Lack of knowledge in hydraulic properties and their spatial persistence
  - Effect mixing and therefore concentration dilution
- Uncertainty in geochemical processes, well capture, etc.

Monte Carlo Technique: Uncertainty in *K*

- Uncertainty in subsurface properties is substantial (mainly hydraulic conductivity, ***K***) and determines flow pathways, arrival times, concentrations, etc.

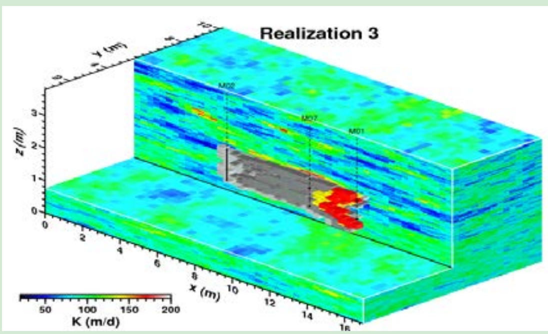
- Identified as a driver of uncertainty in groundwater risk assessment *(Maxwell et al., 1999; Maxwell et al., 2008; de Barros et al., 2009, Siirila et al., 2012, Siirila and Maxwell, 2012)*

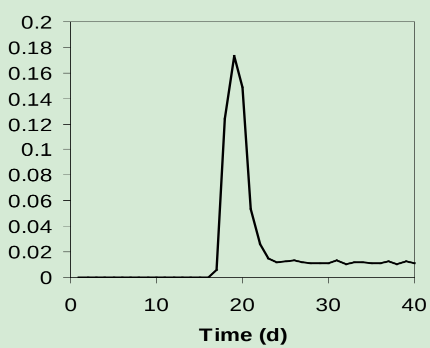


We use a nested Monte Carlo approach

Outer, Uncertainty Loop

MC simulation for environmental concentration





Inner, Variability Loop

MC simulations for differences in a population

Which results in a surface of risk

EPA Remediation Action Levels (RALs)

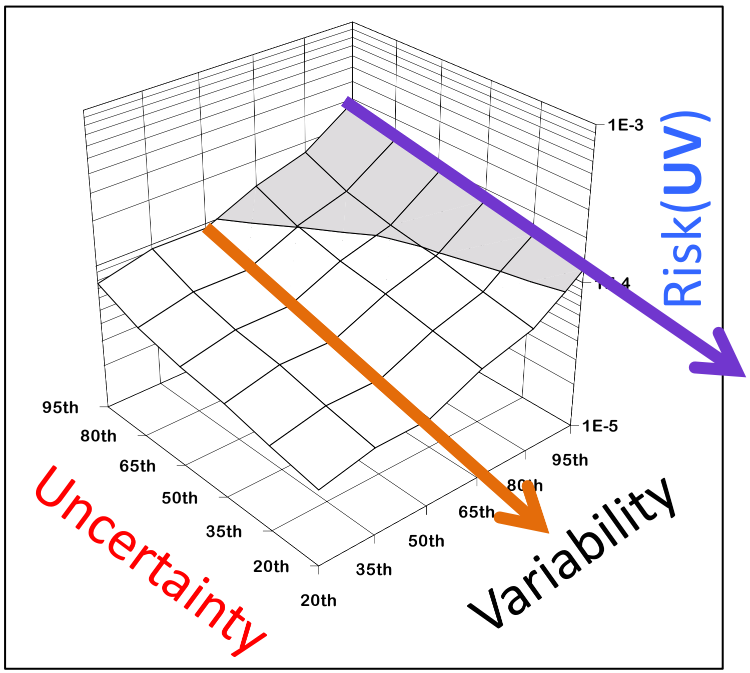
"de minimis", or negligible risk that is too small to be of societal concern; "virtually safe"

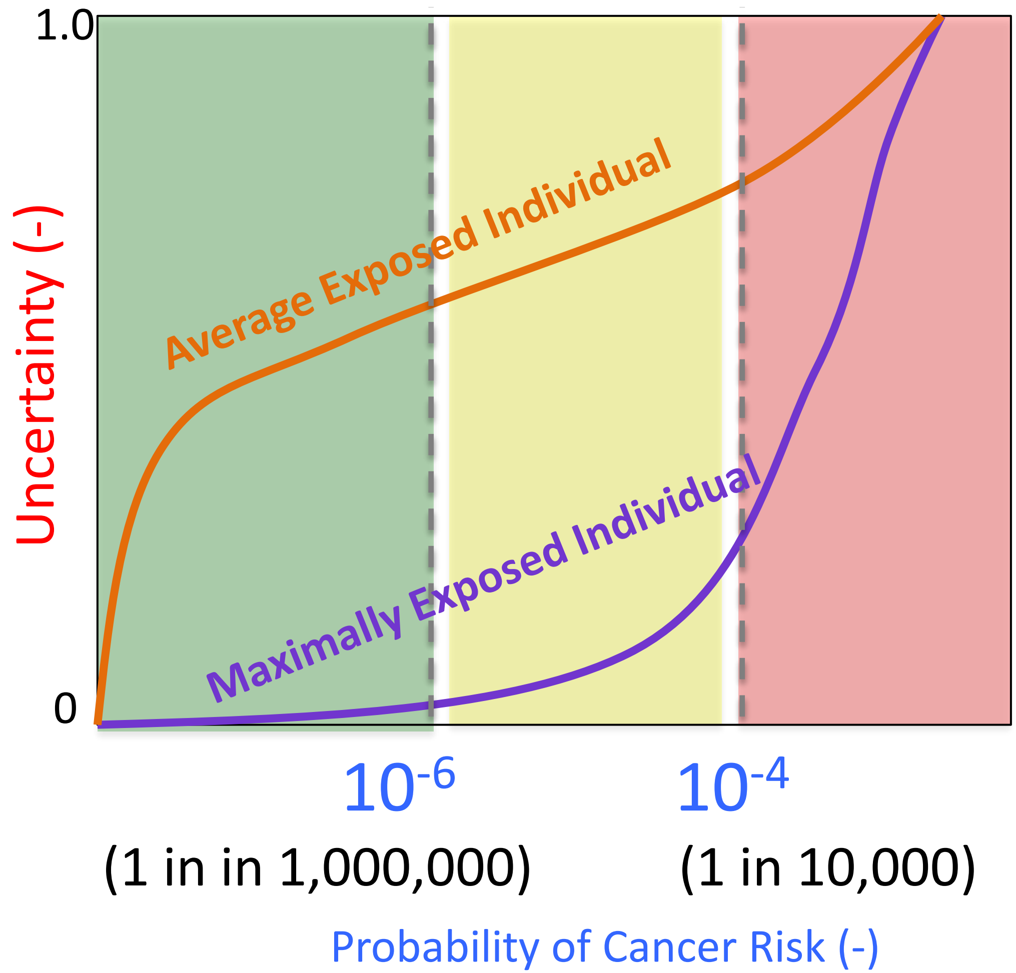
?

Remediation is warranted

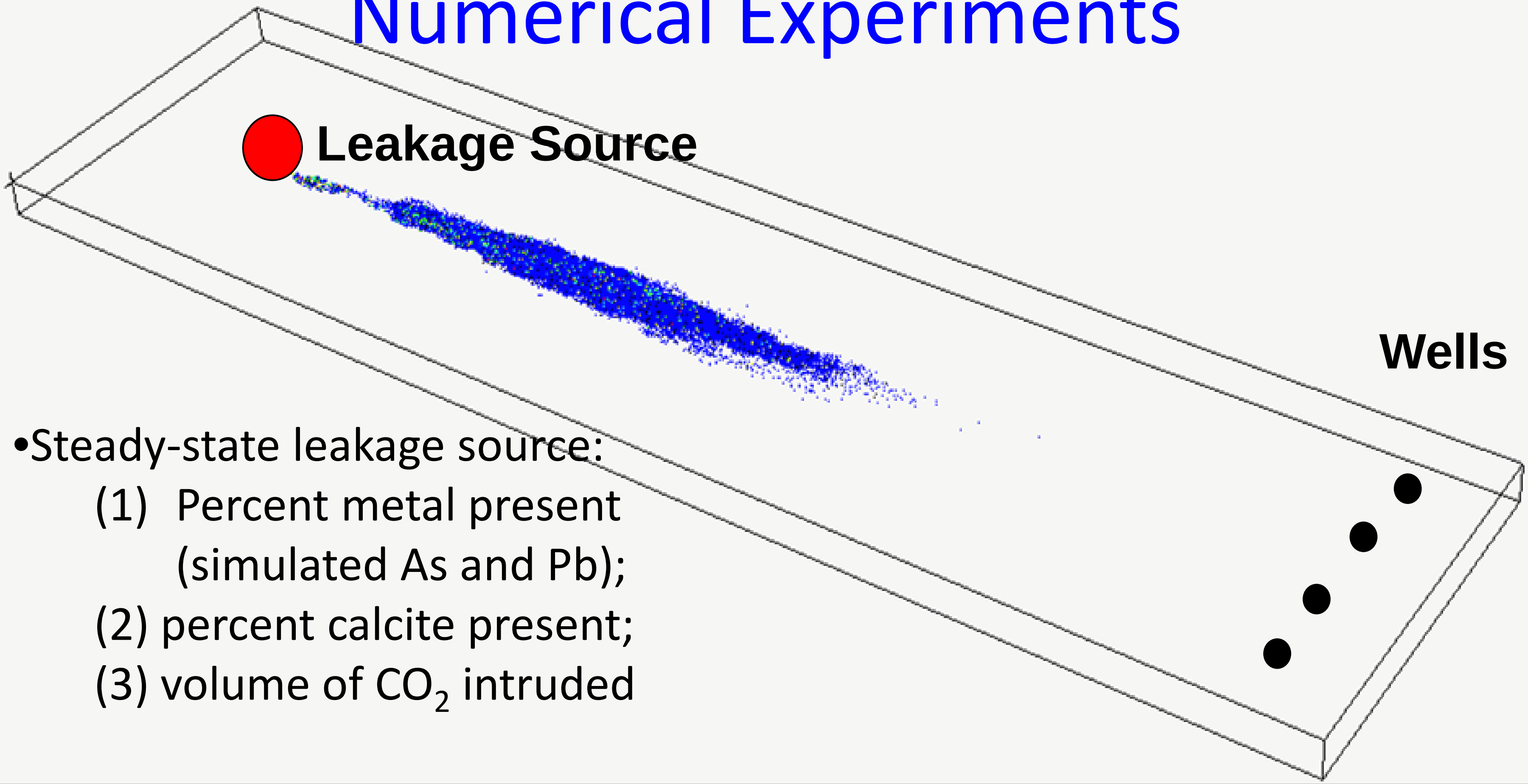
Average Exposed Individual (50th)

Maximally Exposed Individual (99th)





Numerical Experiments



- Steady-state leakage source:
  - (1) Percent metal present (simulated As and Pb);
  - (2) percent calcite present;
  - (3) volume of CO_2 intruded
- Far-field:
  - Large aquifer size (4 x 1 x 0.1) [km]
  - Fine cell discretization (3.0 x 3.0 x 0.3) [m]
  - Two ensembles of *differing stratification*

$\left.\begin{array}{l}\text{Large aquifer size} \\ \text{Fine cell discretization}\end{array}\right\}$ ~150,000,000 cells for 200 realizations

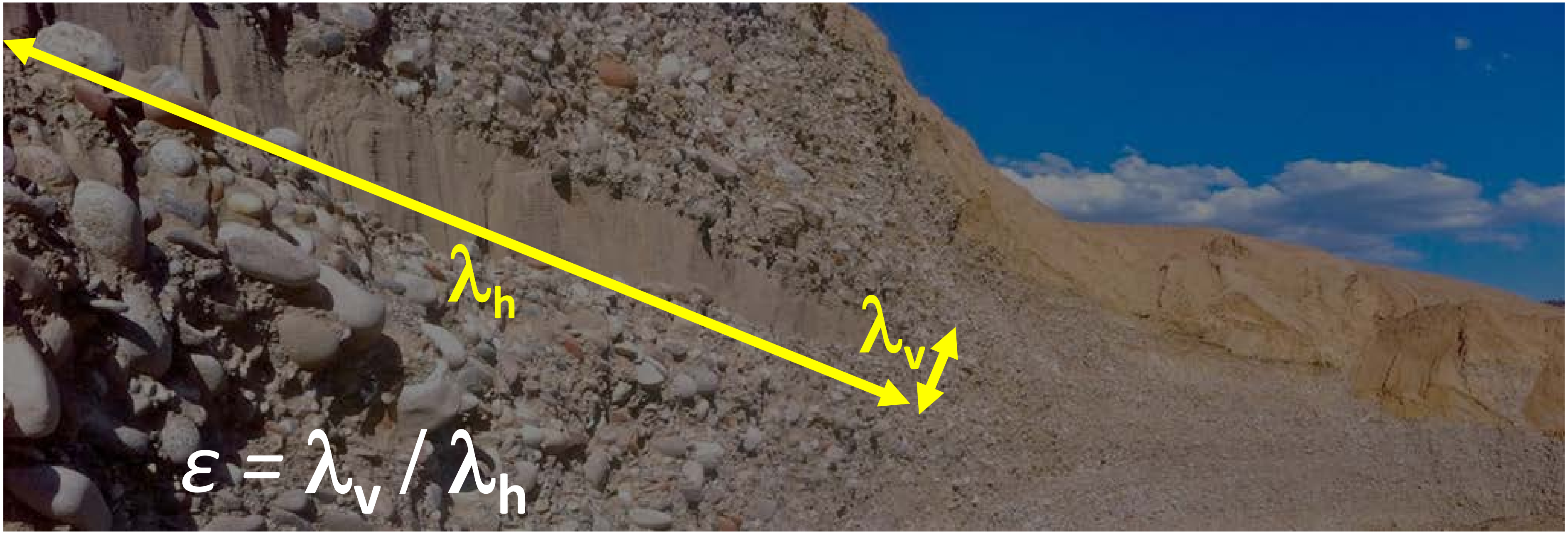
Siirila et al., AWR, 2012

We quantifying *uncertainty* and spatial persistence in subsurface properties

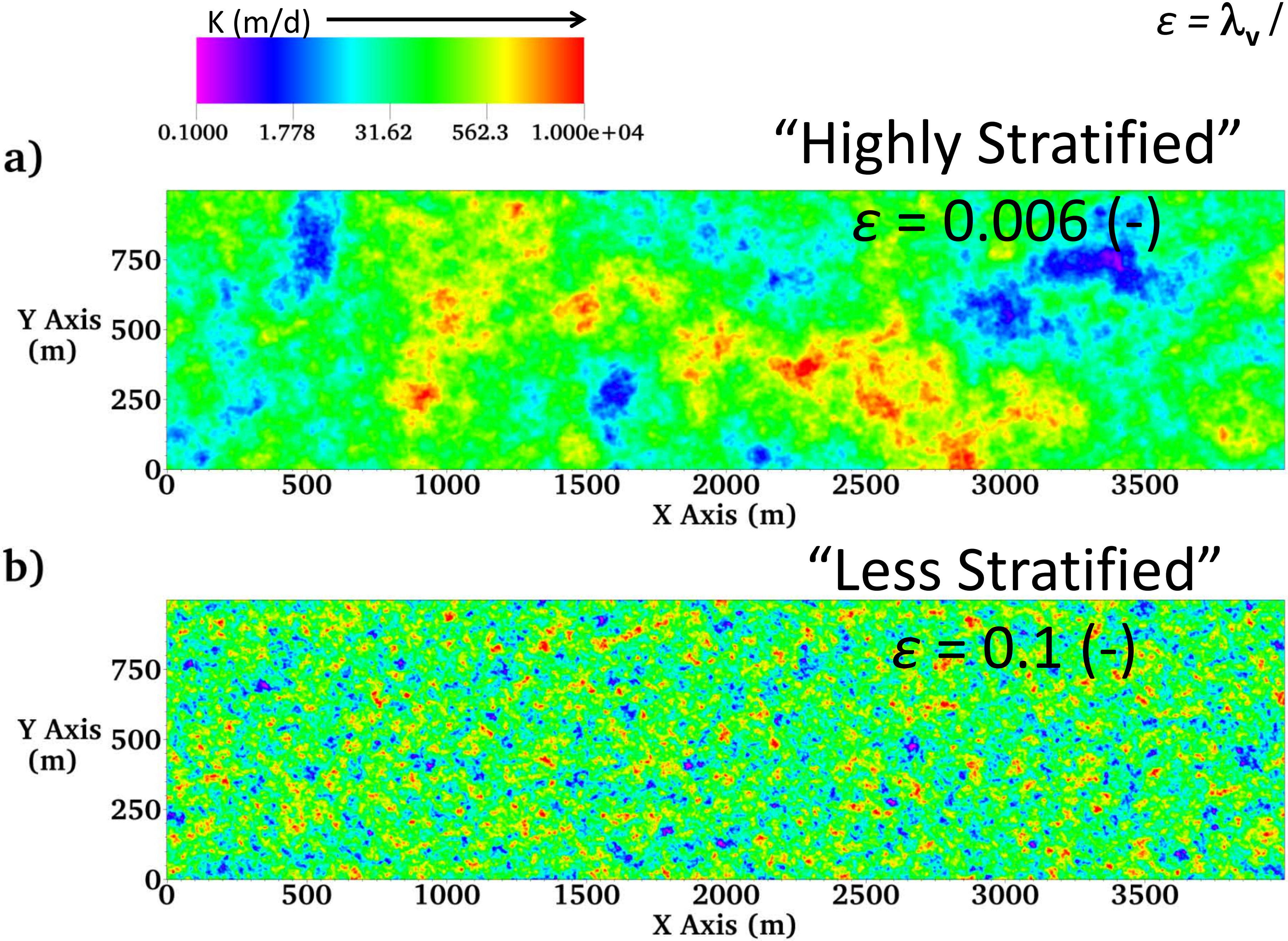
Correlations of heterogeneity can be described using relationships such as:

$$R(lag) = \sigma^2 \exp^{-lag/\lambda}$$

Where '*lag*' is the separation distance (m), and λ is the correlation length in the horizontal or vertical flow direction (m)

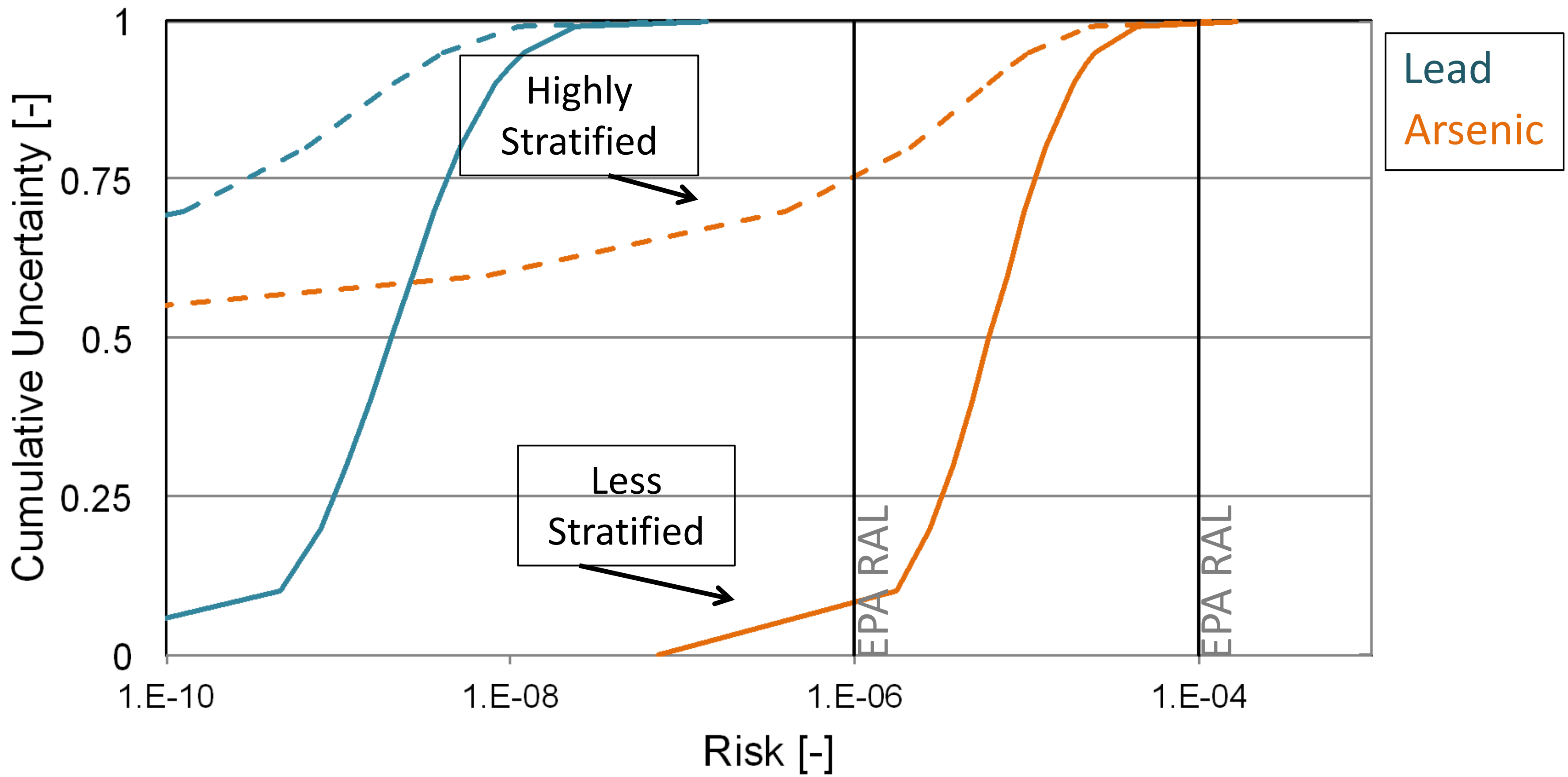


$\varepsilon = \lambda_v / \lambda_h$



Siirila et al., AWR, 2012

Stratification affects flow and transport parameters and *risk*



*** A stratified aquifer experiences less plume mixing, and $\langle C \rangle$ values are more uncertain; this propagates as uncertainty of risk

Siirila et al., AWR, 2012

What about geochemistry and reactive transport?

- Focus on how simplified geochemical and transport processes up-scale and affect far-field mixing patterns.
  1. Local (sub-grid) dispersion
  2. Kinetic (rate-dependent) sorption

- Are there feedbacks between local and macro-scale processes?

- What is the impact on *risk*?

Bearup et al 2012; Atchley et al 2013; Navarre-Sitchler et al 2013; Siirila and Maxwell, 2012

Science & Technology

Kinetic Metal Release from Competing Processes in Aquifers

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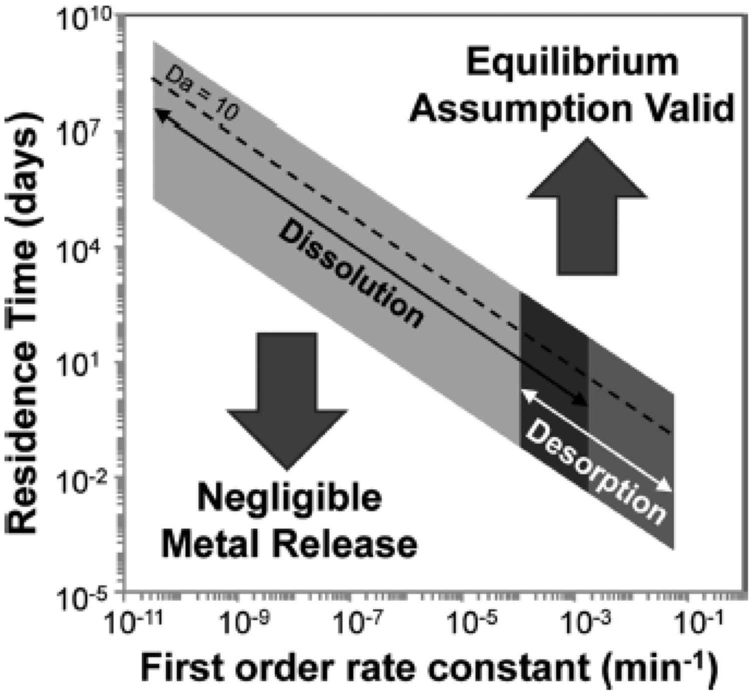
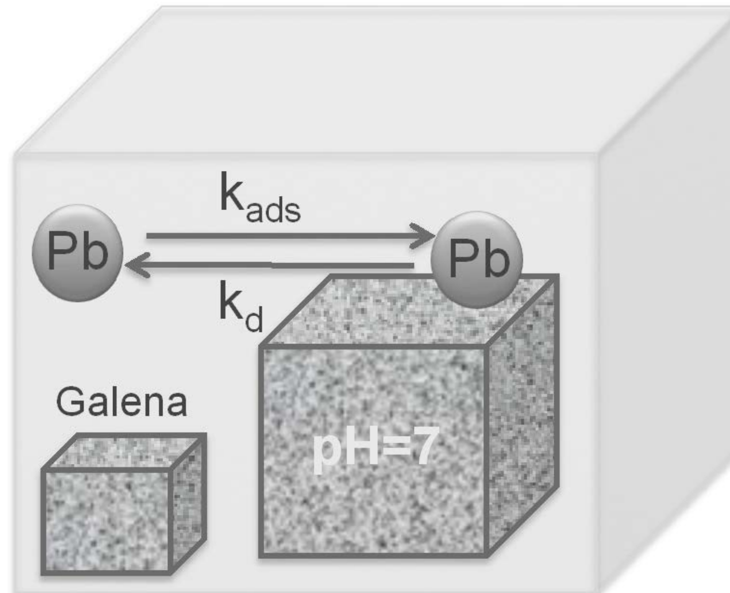
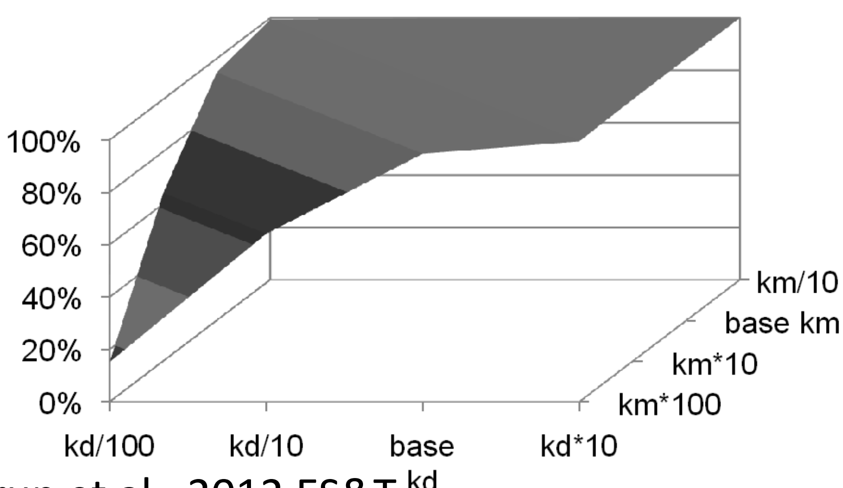
Supporting Information

We can use geochemical simulations to understand role of kinetics

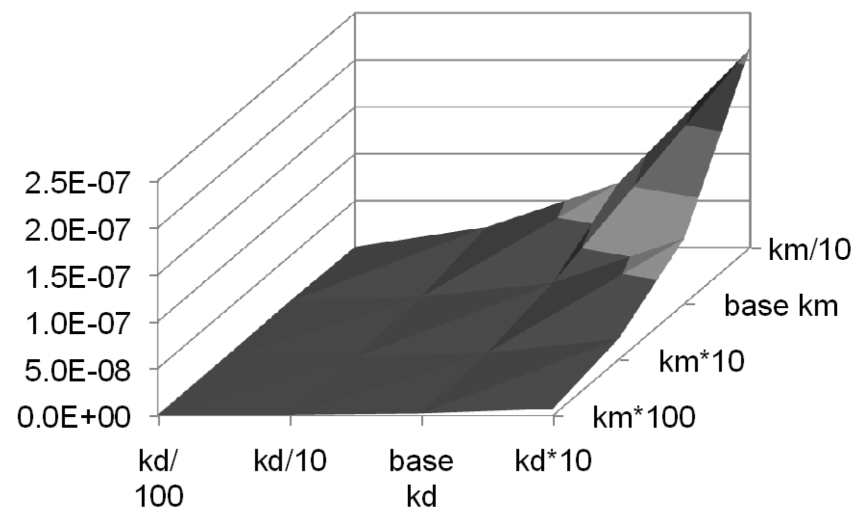




a) Percent Lead from Desorption



b) Total Lead



Bearup et al., 2012 ES&T

We can compare a range of approaches, each with their own simplifications

- Simplified transport (streamline approach)
- Simplified uncertainty (3D geochemical reactive transport)
- Simplified geochemistry (particle tracking)

Atchley et al 2013; Navarre-Sitchler et al 2013; Siirila and Maxwell, 2012

urnal homepage: www.elsevier.com/locate/advwatres

Using streamlines to simulate stochastic reactive transport in heterogeneous aquifers: Kinetic metal release and transport in CO_2 impacted drinking water aquifers

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Streamlines
Stochastic hydrology
Groundwater
Subsurface heterogeneity
CO_2 sequestration

A B S T R A C T

A Lagrangian streamline approach that stochastically represents uncertainty in spatial hydraulic conductivity distribution is coupled to kinetic reactive transport in a heterogeneous 3-D domain. This methodology is designed to efficiently account for uncertainties inherent in subsurface reactive transport while maintaining hydro-geochemical processes. A hypothetical CO_2 leak from a geological carbon storage site into an overlying aquifer is used to simulate reactive transport where contamination may occur. Uncertainty in subsurface hydraulic conductivity is accounted for using correlated, Gaussian random fields in a Monte Carlo approach. In this approach 100 realizations of each ensemble were simulated with variances of the natural log of hydraulic conductivity ($\sigma^2_{\ln K}$) of 1, 3.61, and 16. Peak ensemble lead concentrations were found at $\sigma^2_{\ln K}$ of 3.61, the middle of the variances simulated. $\sigma^2_{\ln K}$ within an aquifer was found to influence chemical residence time, which in turn determined the equilibrium state of the plume along the flow path and at the pumping well thus driving geochemical conditions. However, macrodispersion due to heterogeneous flow paths caused lower contaminant concentrations at the pumping well due to dilution with uncontaminated water. Furthermore, a strong link between $\sigma^2_{\ln K}$ and the probability of well-capture was found, suggesting that proper characterization of the $\sigma^2_{\ln K}$ within an aquifer will help to quantify the impact of uncertainty on risks of groundwater contamination.

1. Introduction

Groundwater constitutes a reliable source of clean drinking water worldwide and provides a substantial portion of drinking water in the Unities States [1]. Carbon capture and storage projects (CCS), a technique under consideration to offset anthropogenic causes of climate change, may adversely affect groundwater quality if the CO_2 injected into deep formations were to leak into overlying

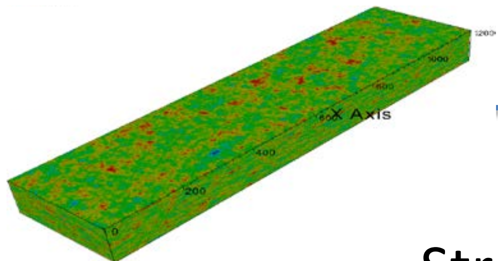
Still, proper quantification of potential impacts of CCS on aquifers suitable for drinking water requires an approach that maintains both geochemical and hydrological complexity found in natural systems and accounts for subsurface uncertainty.

Reduced pH and increased alkalinity resulting from CO_2 leakage have been shown to drive kinetic mineral dissolution and precipitation reactions and metal sorption and desorption from mineral surfaces [2–7,17]. Aquifer properties such as buffering capacity (for

In this approach, transport can be modeled independently on many deconvolved 1D streamlines and as function of time ( ).

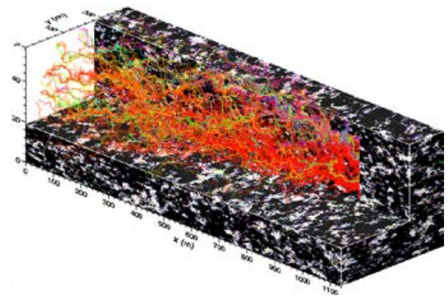
ParFlow

Solve groundwater Flow for
Specific boundary conditions



SLIM-FAST

Trace Streamline paths
from Capture Zone.

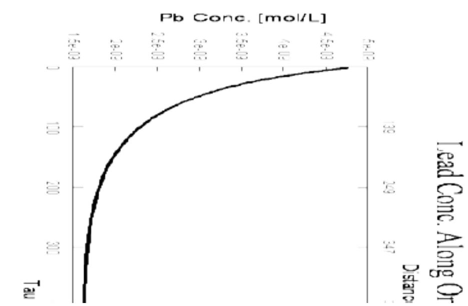


Streamline Transform

$$\frac{\partial c}{\partial t} + v\frac{\partial c}{\partial s} = 0$$

$$\tau = \int_0^s \frac{1}{V(\zeta)}d\zeta$$

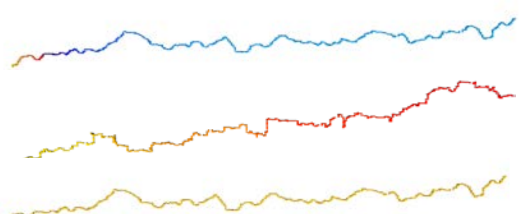
$$\frac{\partial c}{\partial t} + \frac{\partial c}{\partial \tau} = 0$$



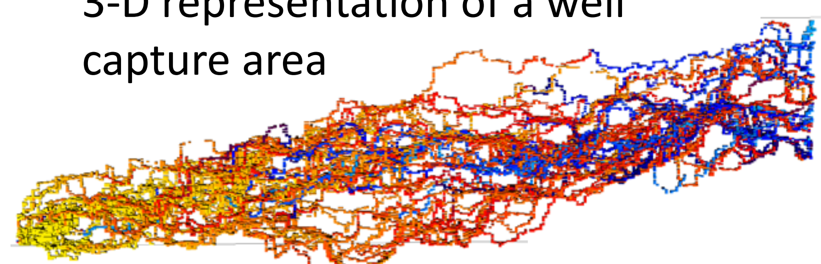
CrunchFlow

Solves Reactive Transport along streamlines

Many 1-D Streamlines



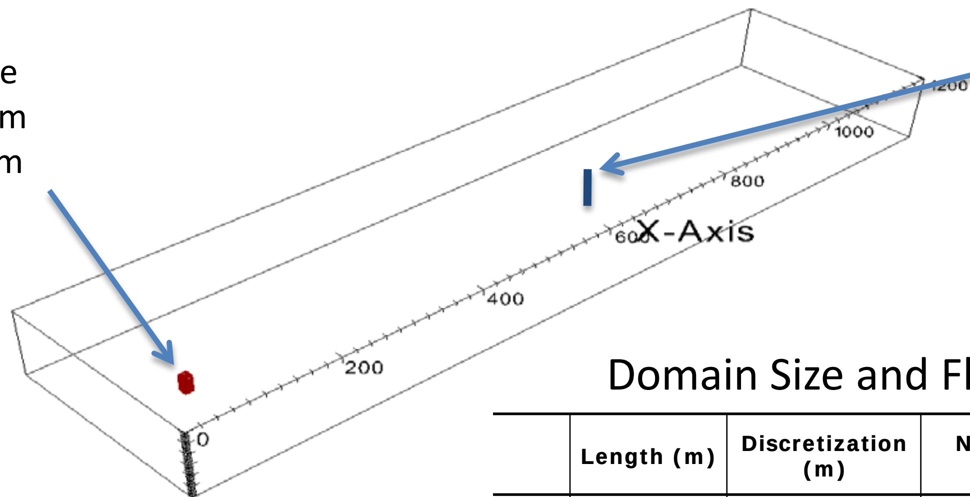
3-D representation of a well
capture area



- All computations were performed on an 8 core linux machine.

A hypothetical continuous CO_2 leak is introduced to an aquifer up gradient from a pumping well used for domestic purposes

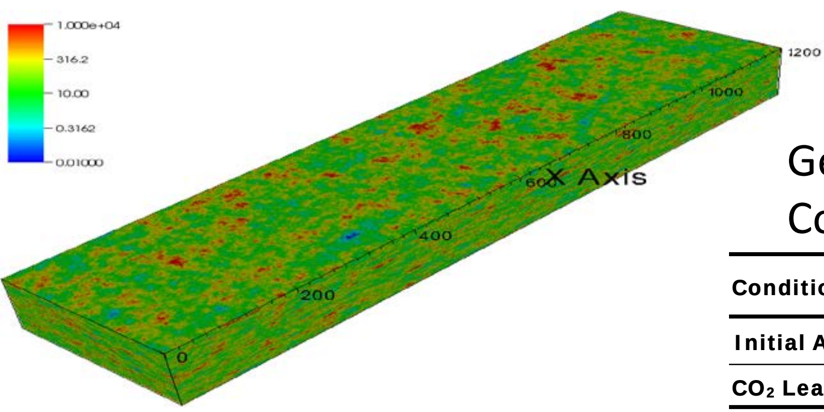
Source zone
X: 100-105m
Y: 145-155m
Z: 2-15m



Well Location:
X: 1000m, Y: 150m,
Z: 25-55m
Pumping Rate: 300 [m^3/d]

Domain Size and Flow Conditions

	Length (m)	Discretization (m)	Number of Cells	Corr. Length (m)	Total Number of Cells	8,000,000
X	1200	3	400	10	$K_{(mean)}$ [m/d]	52
Y	300	3	100	10	Porosity	0.33
Z	60	0.3	200	1	Average Gradient	0.00443



Geochemical Conditions for Initial Aquifer Conditions and CO_2 leak.

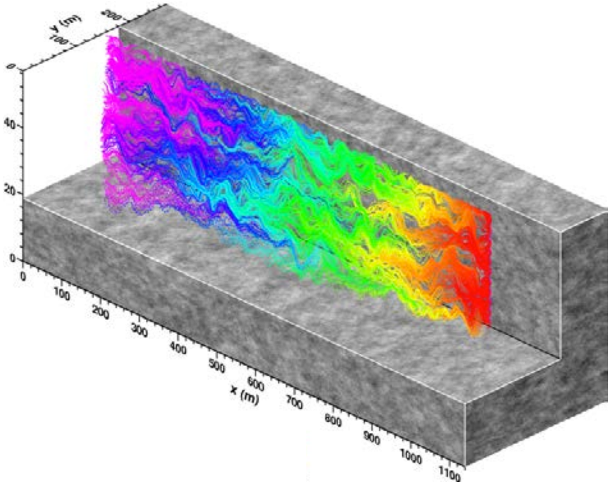
Condition	pH	$PCO_2(g)$ [bar]	$PO_2(g)$ [bar]	Quartz [% vol]	Galena [% vol]	Calcite [% vol]	Charge Balace
Initial Aquifer	7	0.01	1×10^{-70}	64	0.1	3	Cl-
CO_2 Leak	4.5	30	1×10^{-70}	64	0.1	3	Na+

Atchley *et al* AWR 2013

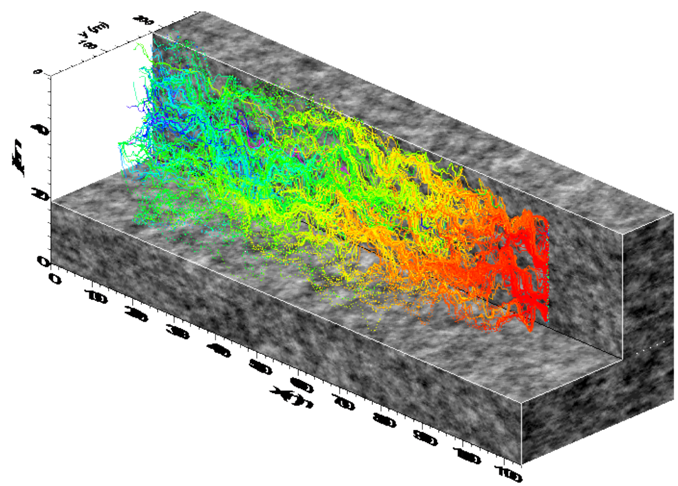
We change the variance ($\sigma^2_{\ln K}$) in a parametric sensitivity study

The affect that hydraulic conductivity variance ($\sigma^2_{\ln K}$) has on geochemical processes and chemical conditions at a pumping well are investigated by simulating 100 realizations with $\sigma^2_{\ln K}$ of 1, 3.6, and 16.

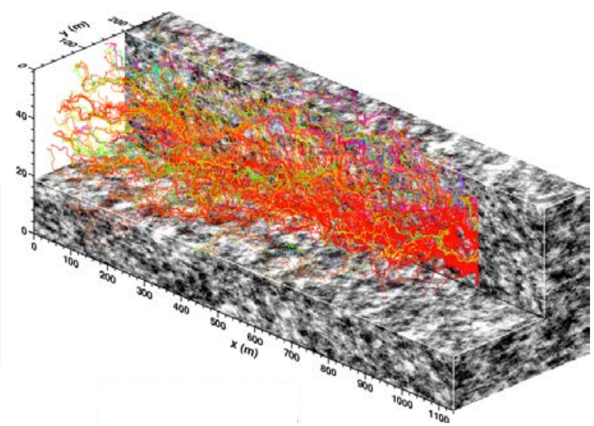
$\sigma^2_{\ln K} = 1$

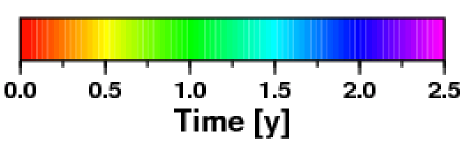


$\sigma^2_{\ln K} = 3.61$



$\sigma^2_{\ln K} = 16$





~ streamline travel time color coded in years.

In addition $\sigma^2_{\ln K} = 8.5$ was also simulated without geochemistry.

Atchley *et al* AWR 2013

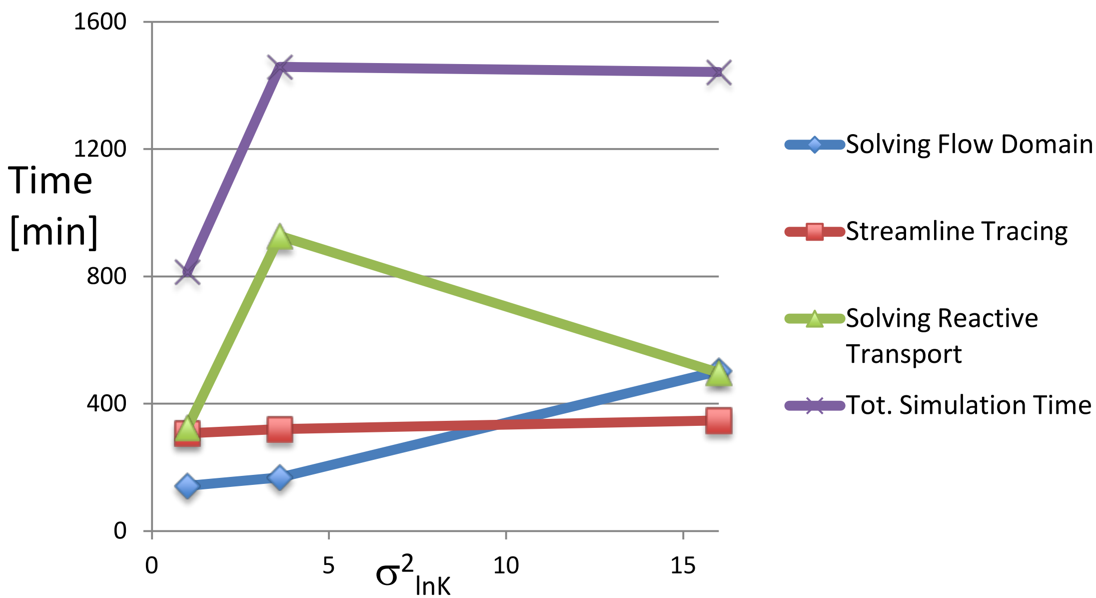
Streamline efficiency enables makes these simulations feasible

- Efficient computation times for the streamline approach are achieved by simulating reactive transport in parallel on streamlines that connect the source zone to the pumping well.

Key to achieving this domain simplification are the assumptions:

1. Transverse mixing between streamlines has a negligible affect on the chemical conditions of each streamline.

1. Hydrological system can be accurately represented in a steady state condition.



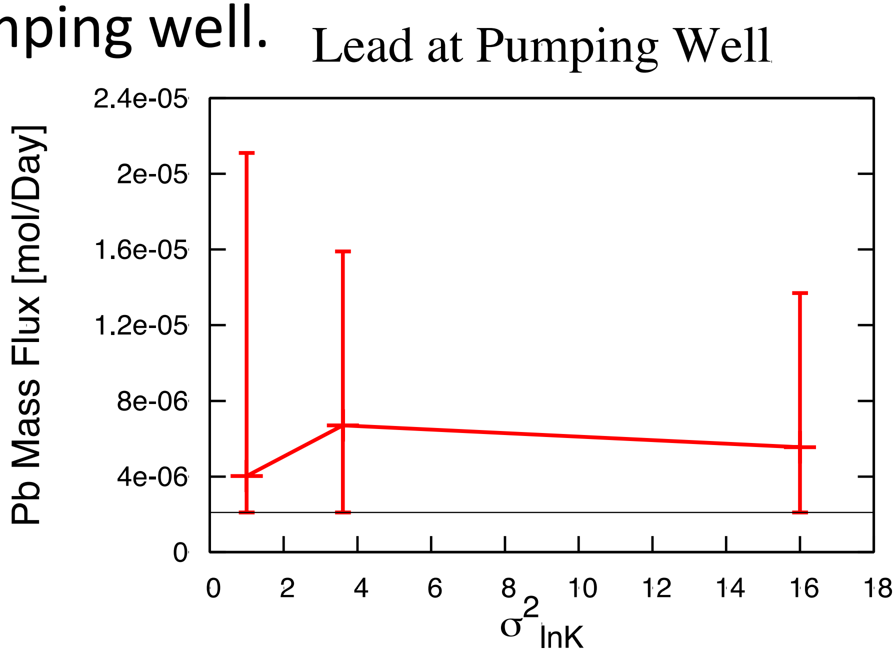
Simulated on an 8 core linux machine

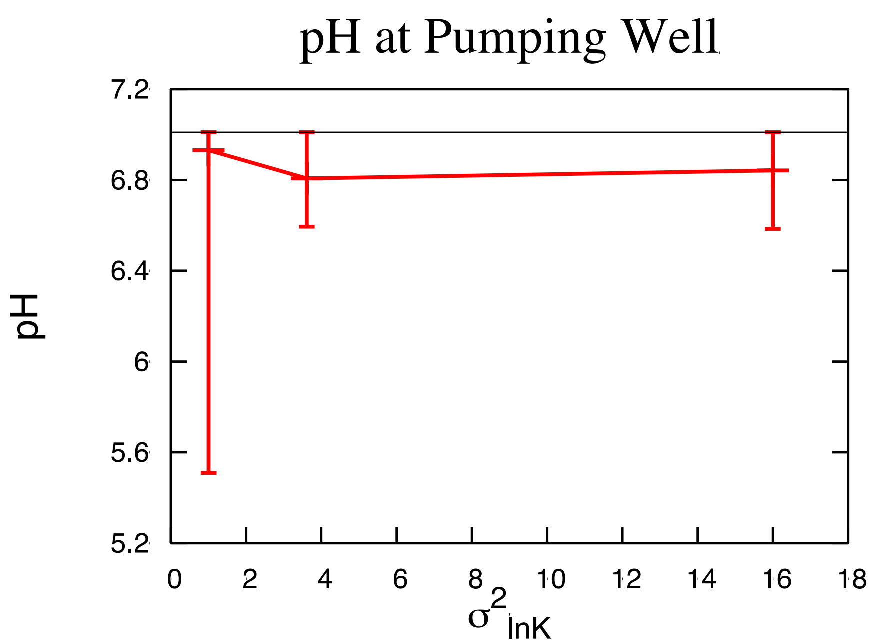
lnK var	Tot. Simulation Time (hr)	Tot. Streamlines Modeled
1	13.6	1234
3.61	24.3	2874
16	24.0	1456

- Time to solving reactive transport along streamlines is proportional to the number of streamlines simulated.

Atchley *et al* AWR 2013

Ensemble results show pH and Lead concentration changes at the pumping well.



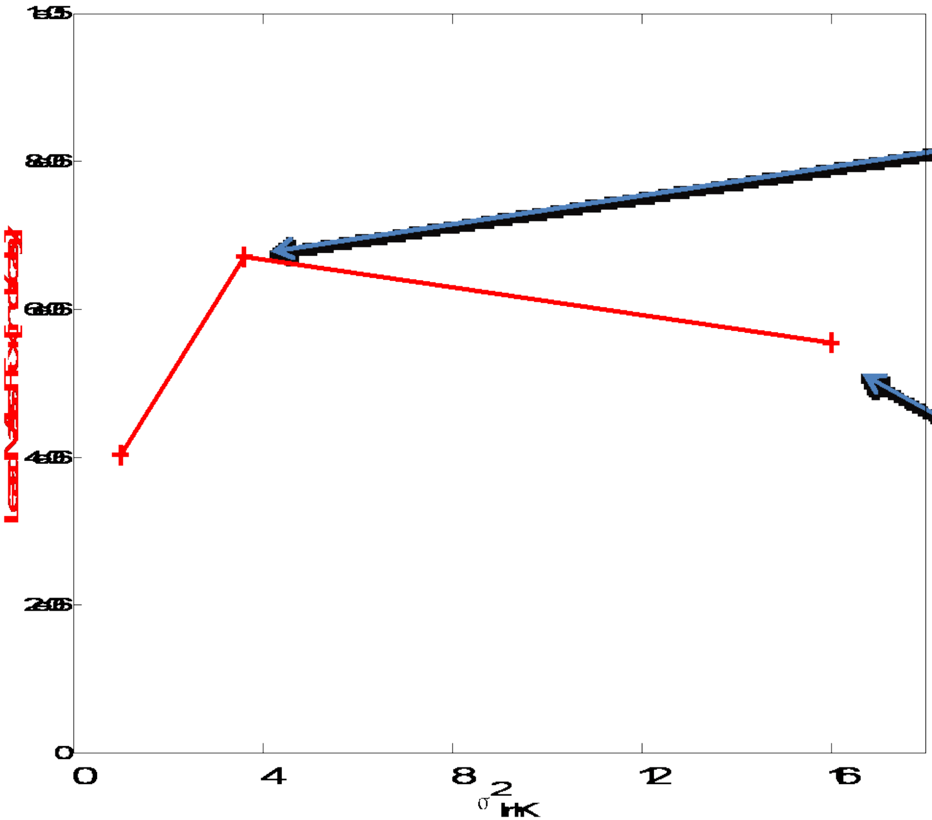


nsemble average
steady state chemistry at the well.

Atchley *et al* AWR 2013

Why is the peak lead concentration at a $\sigma^2_{\ln K}$ of 3.61?

Lead Mass Flux at Pumping Well



Peak lead mass flux of 6.71E-06 [mol/day] at a $\sigma^2_{\ln K}$ of 3.61.

Lead mass flux decreases by 17.3% at a $\sigma^2_{\ln K}$ of 16 compared to a a $\sigma^2_{\ln K}$ of 3.61.

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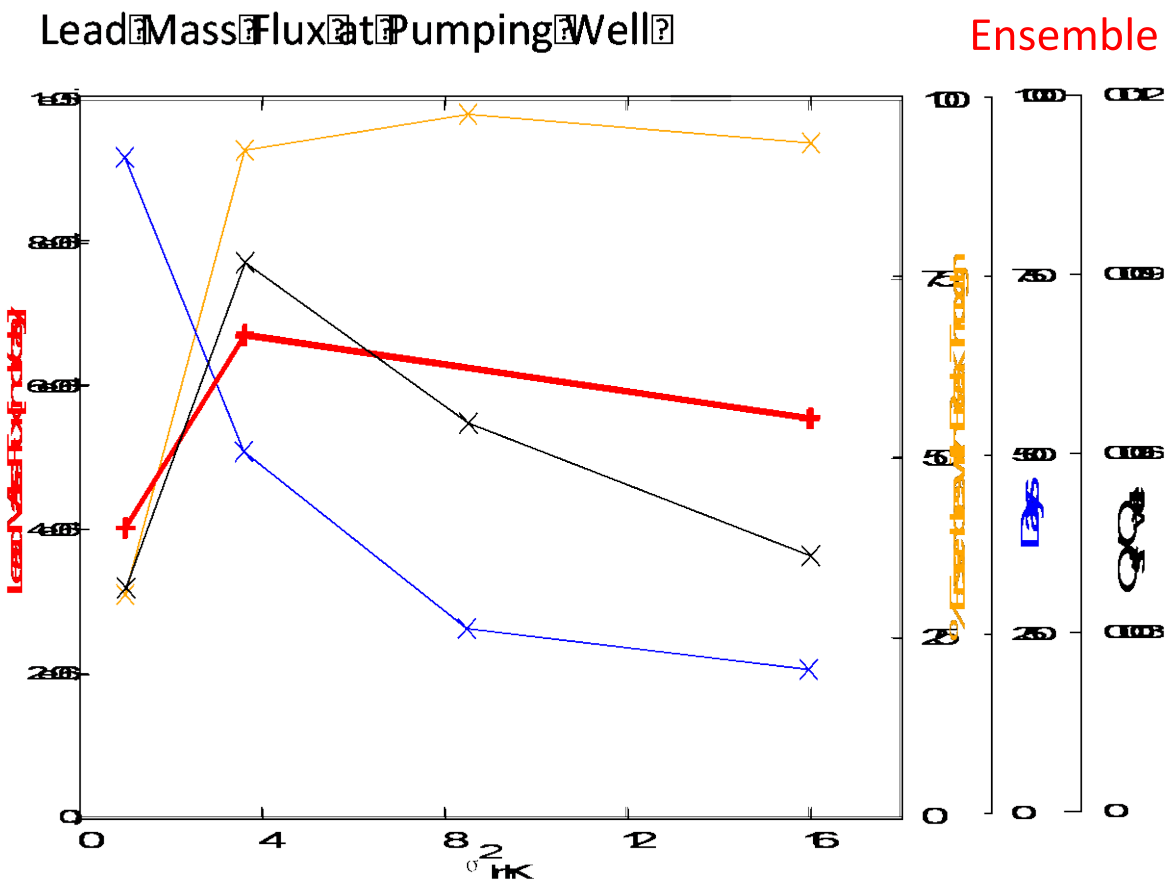
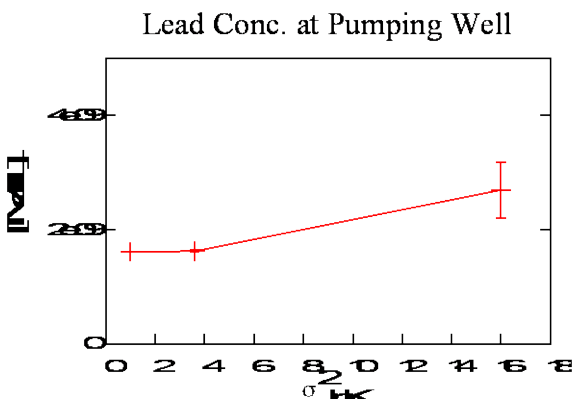
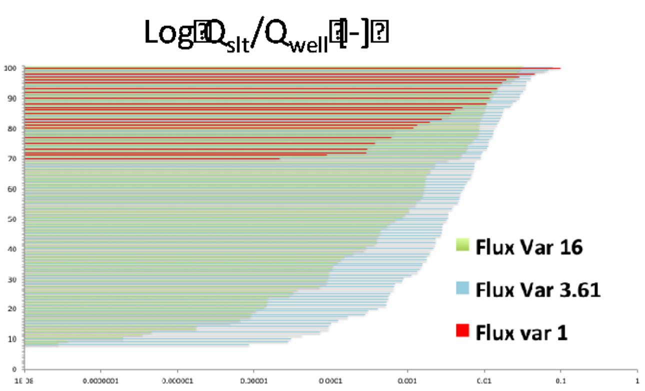
Peak concentration a combination physical and geochemical factors



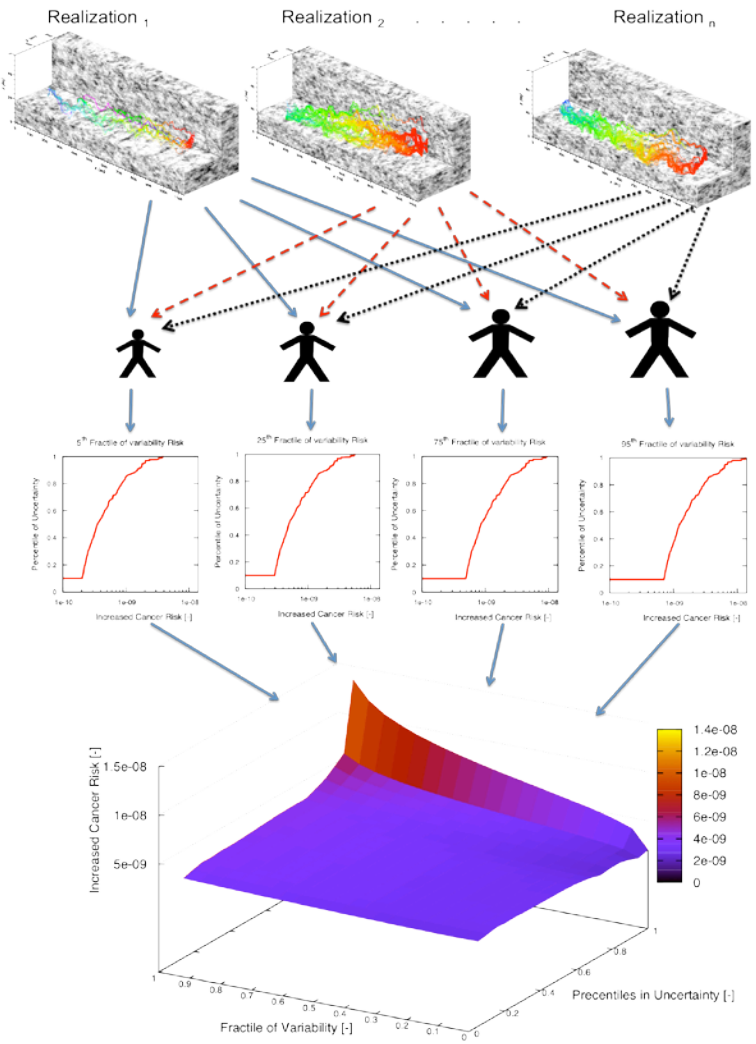


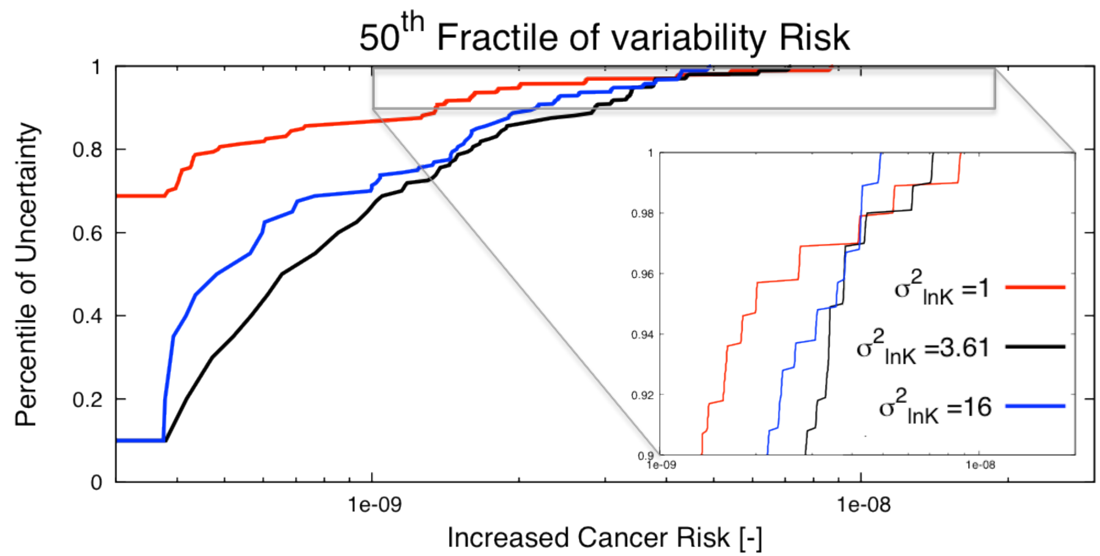


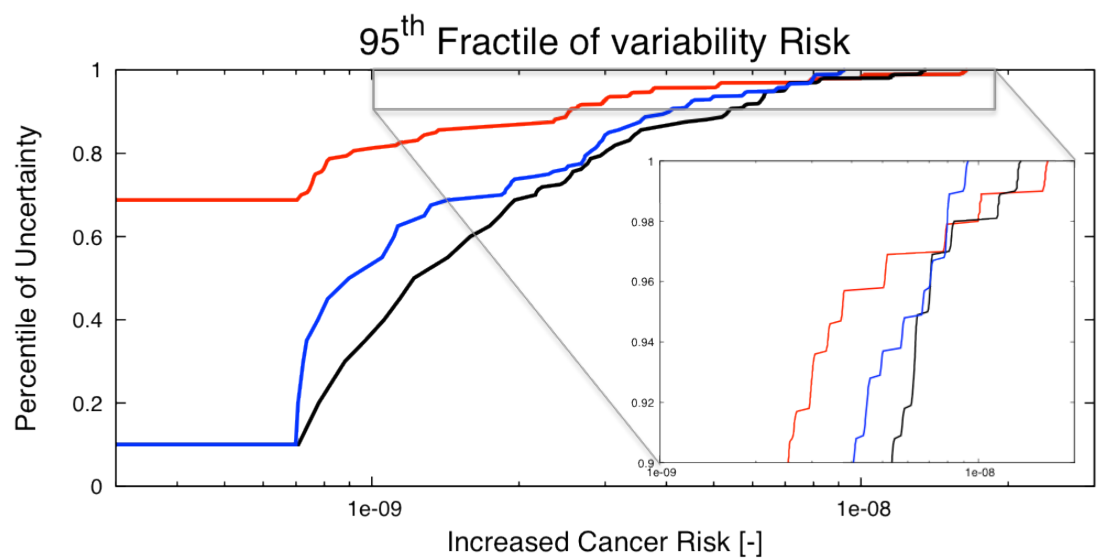
Ensemble Results are a product of:

1. Probability of a given realization having streamlines connecting the source zone to the well.
   - Increasing number of realizations with streamlines crossing the source zone results in increasing ensemble concentration.
2. Solute residence time between the source zone and the well.
   - As σ^2_{lnK} increases solute travel time decreases.
   - Shorter residence time results in higher lead concentration and low pH at the well
3. Ensemble flux from the source zone to the well.
   - Increases of flux from the source zone results increases in concentration per realization.
   - As σ^2_{lnK} increases the average percentage of flux from the source zone decreases after a peak at σ^2_{lnK} 3.61 .

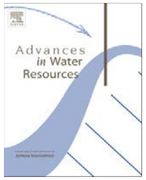
Streamline simulations integrate easily into our risk assessment framework







Atchley et al *EST* in review



urnal homepage: www.elsevier.com/locate/advwatres

Elucidating geochemical response of shallow heterogeneous aquifers to CO_2 leakage using high-performance computing: Implications for monitoring of CO_2 sequestration

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Lead
Leakage

A B S T R A C T

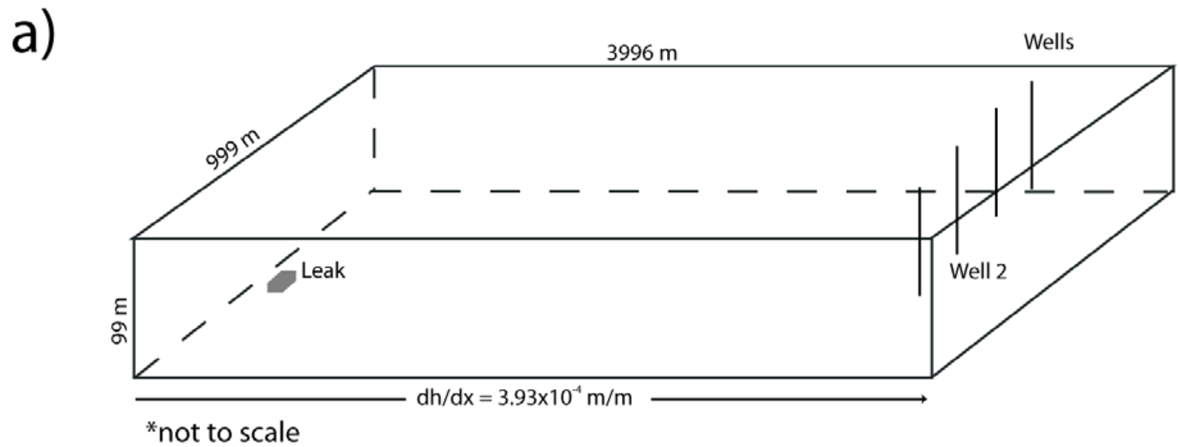
Predicting and quantifying impacts of potential carbon dioxide (CO_2) leakage into shallow aquifers that overlie geologic CO_2 storage formations is an important part of developing reliable carbon storage techniques. Leakage of CO_2 through fractures, faults or faulty wellbores can reduce groundwater pH, inducing geochemical reactions that release solutes into the groundwater and pose a risk of degrading groundwater quality. In order to help quantify this risk, predictions of metal concentrations are needed during geologic storage of CO_2. Here, we present regional-scale reactive transport simulations, at relatively fine-scale, of CO_2 leakage into shallow aquifers run on the PFLOTRAN platform using high-performance computing. Multiple realizations of heterogeneous permeability distributions were generated using standard geostatistical methods. Increased statistical anisotropy of the permeability field resulted in more lateral and vertical spreading of the plume of impacted water, leading to increased Pb^{2+} (lead) concentrations and lower pH at a well down gradient of the CO_2 leak. Pb^{2+} concentrations were higher in simulations where calcite was the source of Pb^{2+} compared to galena. The low solubility of galena effectively buffered the Pb^{2+} concentrations as galena reached saturation under reducing conditions along the flow path. In all cases, Pb^{2+} concentrations remained below the maximum contaminant level set by the EPA. Results from this study, compared to natural variability observed in aquifers, suggest that bicarbonate (HCO_3^-) concentrations may be a better geochemical indicator of a CO_2 leak under the conditions simulated here.

1. Introduction

Injection of carbon dioxide (CO_2) into subsurface geological formations is a promising technology for the reduction of anthropogenic CO_2 emissions [1,2]. However, previous work has discussed risk of leakage of injected CO_2 [3] either through fault or fracture pathways [4], inadequately installed or abandoned wells [5–7]

groundwater quality including potential impacts on the environment [11,12], human health [13], economics, and regulations [14,15]. Methods for leakage detection include remote sensing, soil gas monitoring [16], geophysical techniques [17], pressure monitoring [18], vegetation stress [19] and eddy covariance measurements [20]. Vegetation stress, soil gas monitoring and eddy covariance require the CO_2 leak to reach or come close to the

For this work we use 3D geochemical reactive transport



Grid discretization:
9 m x 9 m x 0.9 m

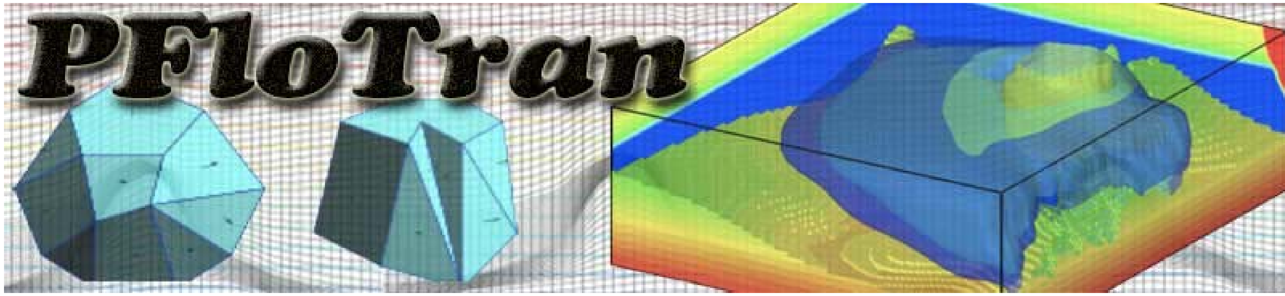
5.4 M Grid Cells
54 M dof

80 simulations

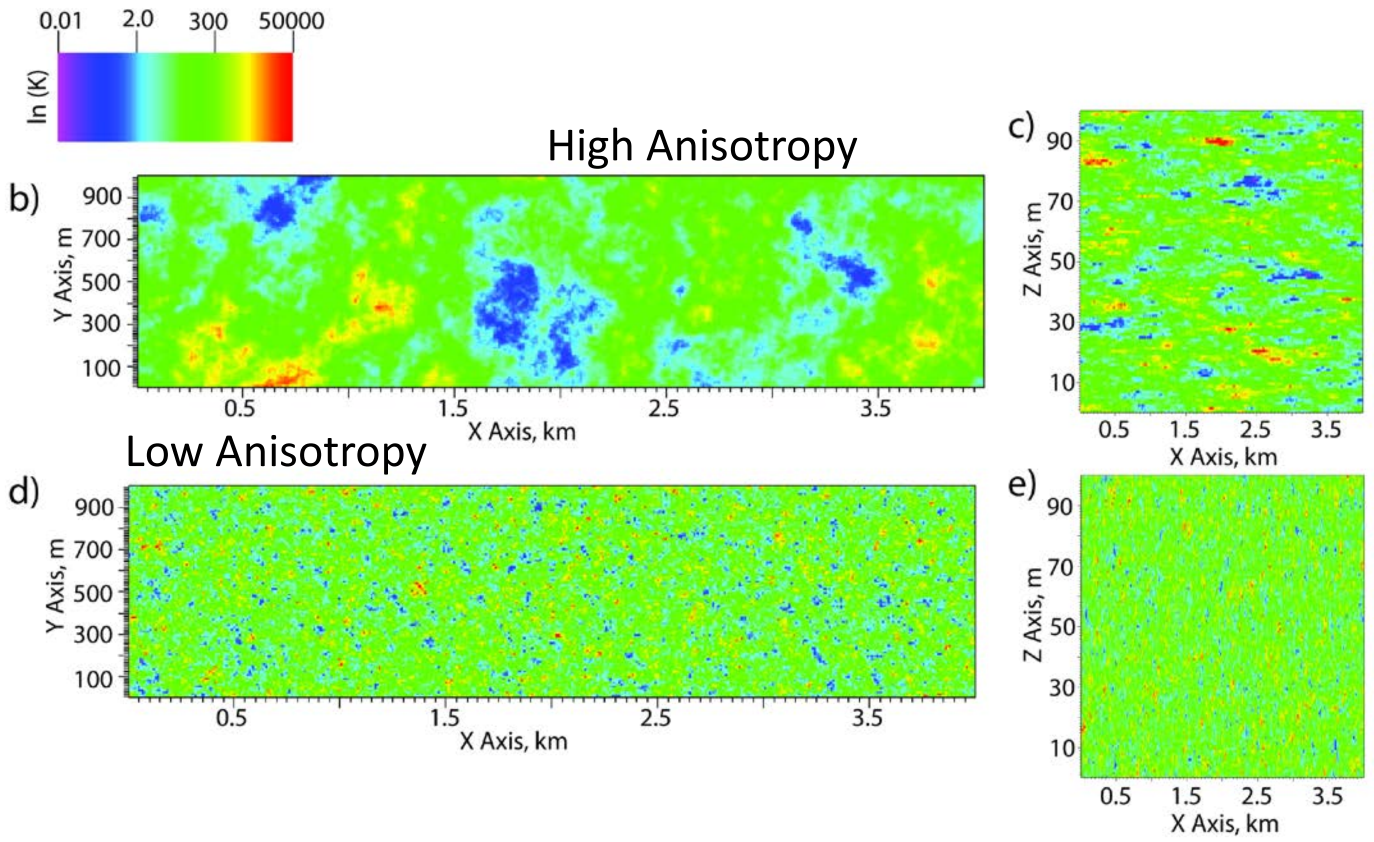
2048 processors
0.6 hours wall clock
> 1200 hrs / simulation

> 11 years total processor time on Jaguar

Navarre-Sitchler *et al* AWR 2013



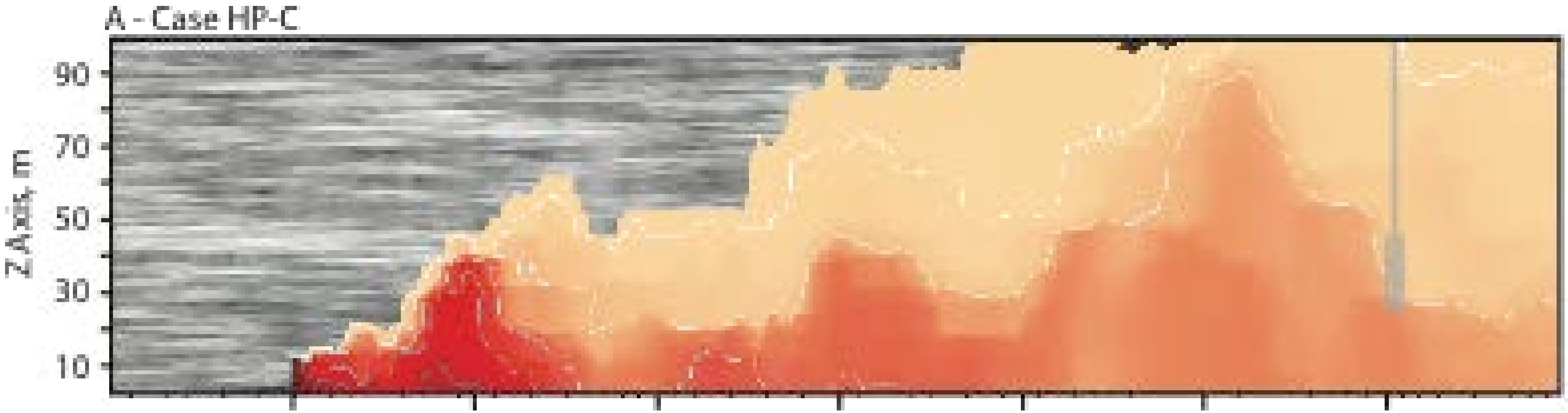
Geostatistically distributed permeability – 10 realizations each are based upon Siirila *et al* (2012)



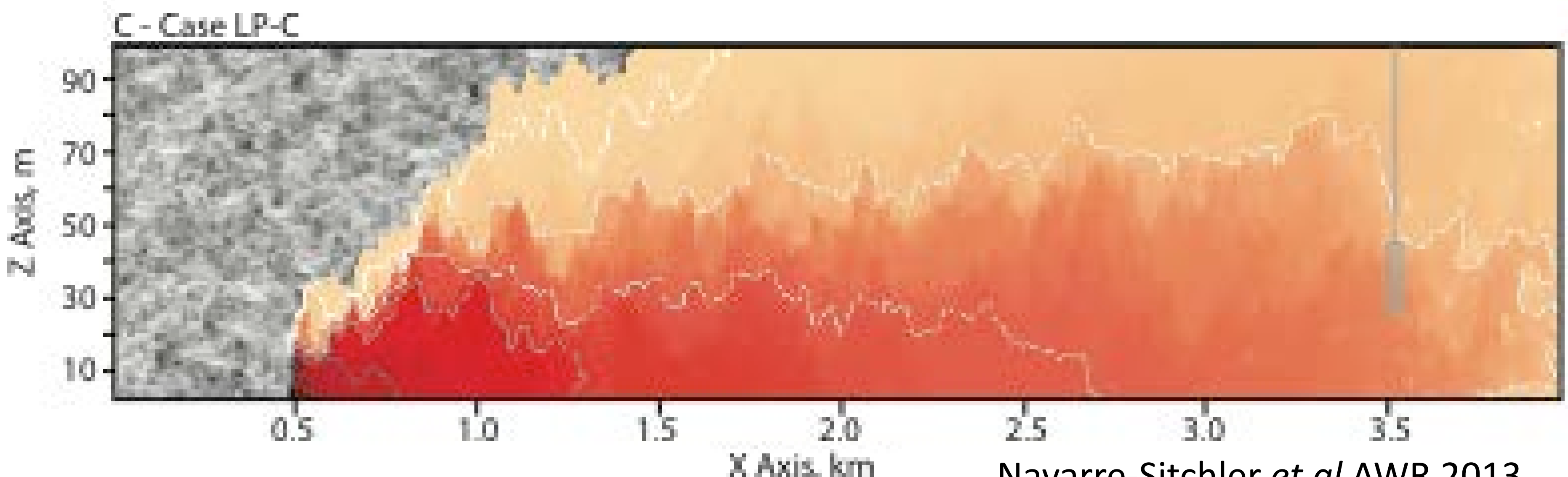
Properties typical of fluvial or glacial outwash sand and gravel aquifers

Navarre-Sitchler *et al* AWR 2013

High Anisotropy



Low Anisotropy



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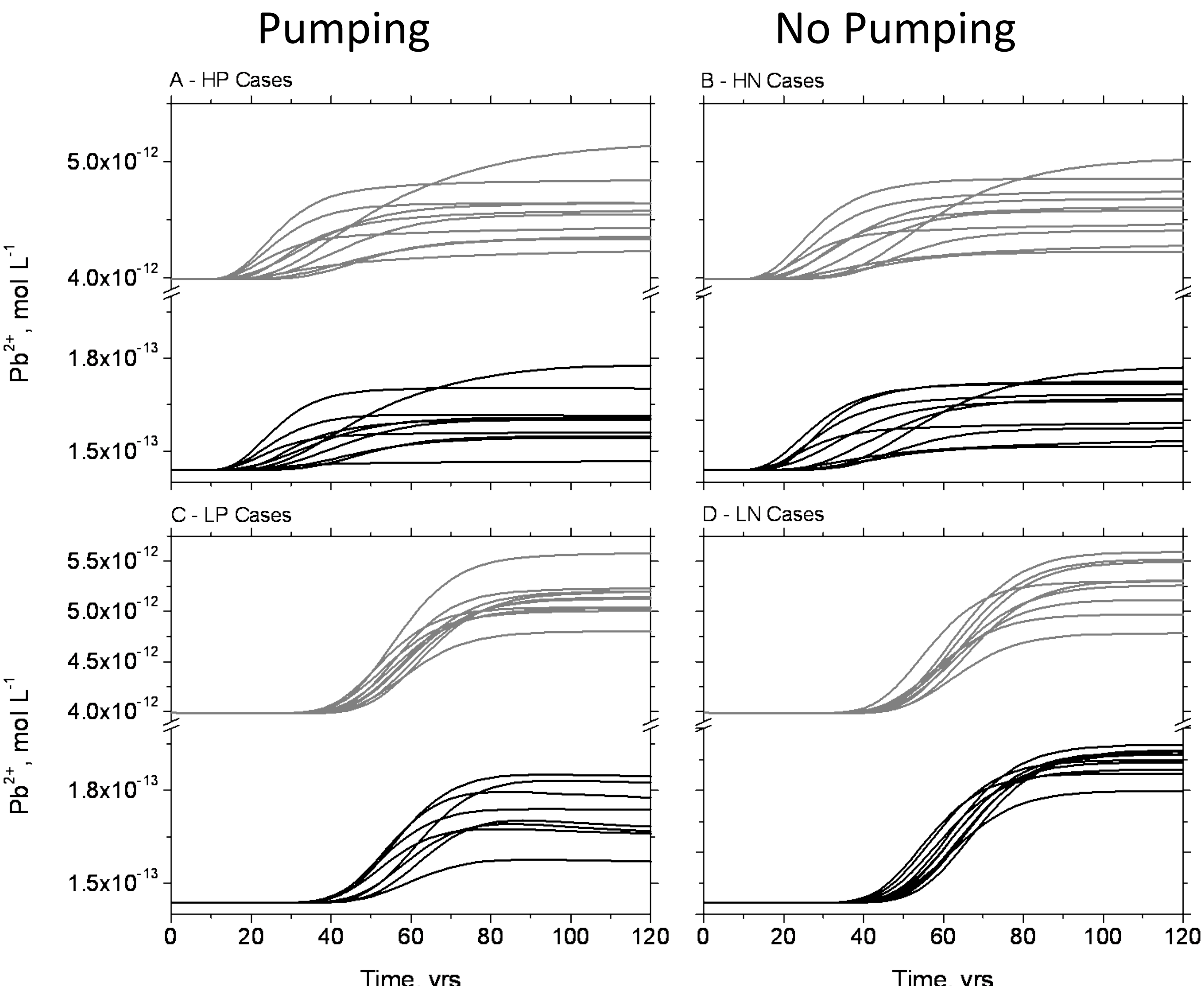
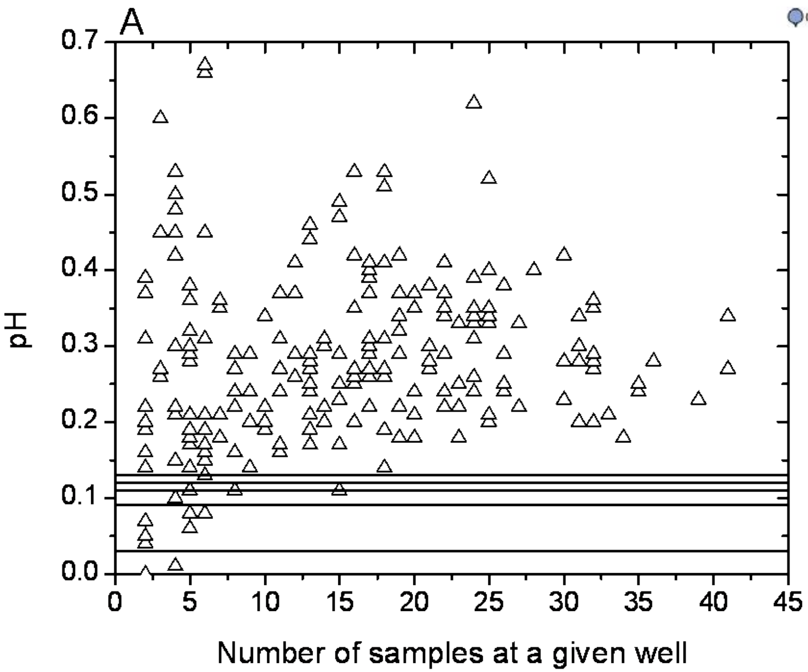
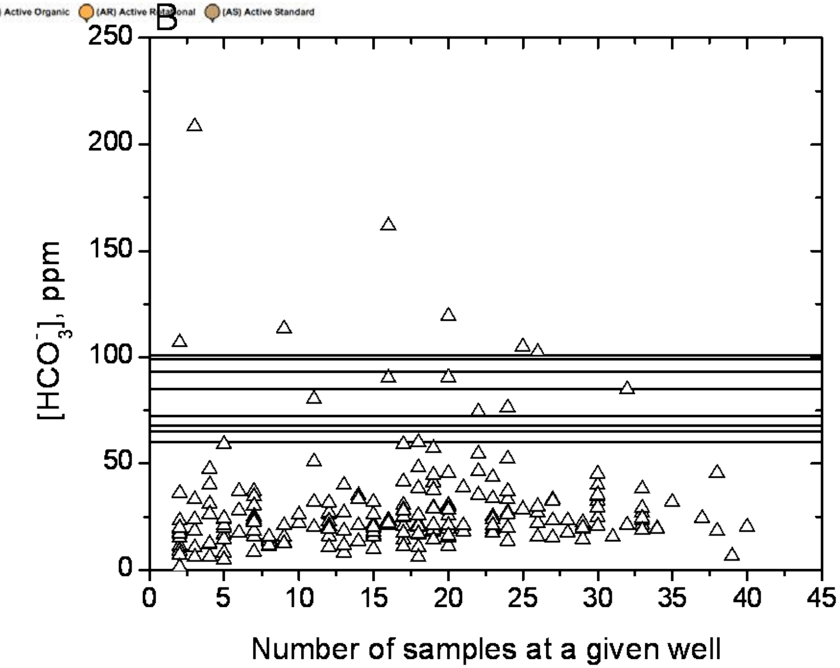
Maximum Pb^{2+} concentration predicted is < 1 μm L^{-1}



Navarre-Sitchler *et al* AWR 2013

Long-term water quality monitoring data shows that bicarbonate is a better indicator of leakage in simulated cases





Are these realistic predictions?

Navarre-Sitchler *et al* AWR 2013

WATER RESOURCES RESEARCH, VOL. 48, W04527, doi:10.1029/2011WR011516, 2012

Evaluating effective reaction rates of kinetically driven solutes in large-scale, statistically anisotropic media: Human health risk implications

Erica R. Siirila[1,2] and Reed M. Maxwell[1,2,3]

Received 17 October 2011; revised 20 January 2012; accepted 7 March 2012; published 25 April 2012.

[1] The interplay between regions of high and low hydraulic conductivity, degree of aquifer stratification, and rate-dependent geochemical reactions in heterogeneous flow fields is investigated, focusing on impacts of kinetic sorption and local dispersion on plume retardation and channeling. Human health risk is used as an endpoint for comparison via a nested Monte Carlo scheme, explicitly considering joint uncertainty and variability. Kinetic sorption is simulated with finely resolved, large-scale domains to identify hydrogeologic conditions where reactions are either rate limited (nonreactive), in equilibrium (linear equilibrium assumption is appropriate), or are sensitive to time-dependent kinetic reactions. By utilizing stochastic ensembles, effective equilibrium conditions are examined, in addition to parameter interplay. In particular, the effects of preferential flow pathways and solute mixing at the field-scale (marcrodispersion) and subgrid (local dispersion, LD) are examined for varying degrees of stratification and regional groundwater velocities (v). Results show effective reaction rates of kinetic ensembles with the inclusion of LD yield disequilibrium transport, even for averaged (or global) Damköholer numbers associated with equilibrium transport. Solute behavior includes an additive tailing effect, a retarded peak time, and results in an increased cancer risk. The inclusion of LD for nonreactive solutes in highly anisotropic media results in either induced solute retardation or acceleration, a new finding given that LD has previously been shown to affect only the concentration variance. The distribution, magnitude, and associated uncertainty of cancer risk are controlled by the up scaling of these small-scale processes, but are strongly dependent on v and the source term.

Citation: Siirila, E. R., and R. M. Maxwell (2012), Evaluating effective reaction rates of kinetically driven solutes in large-scale, statistically anisotropic media: Human health risk implications, *Water Resour. Res.*, *48*, W04527, doi:10.1029/2011WR011516.

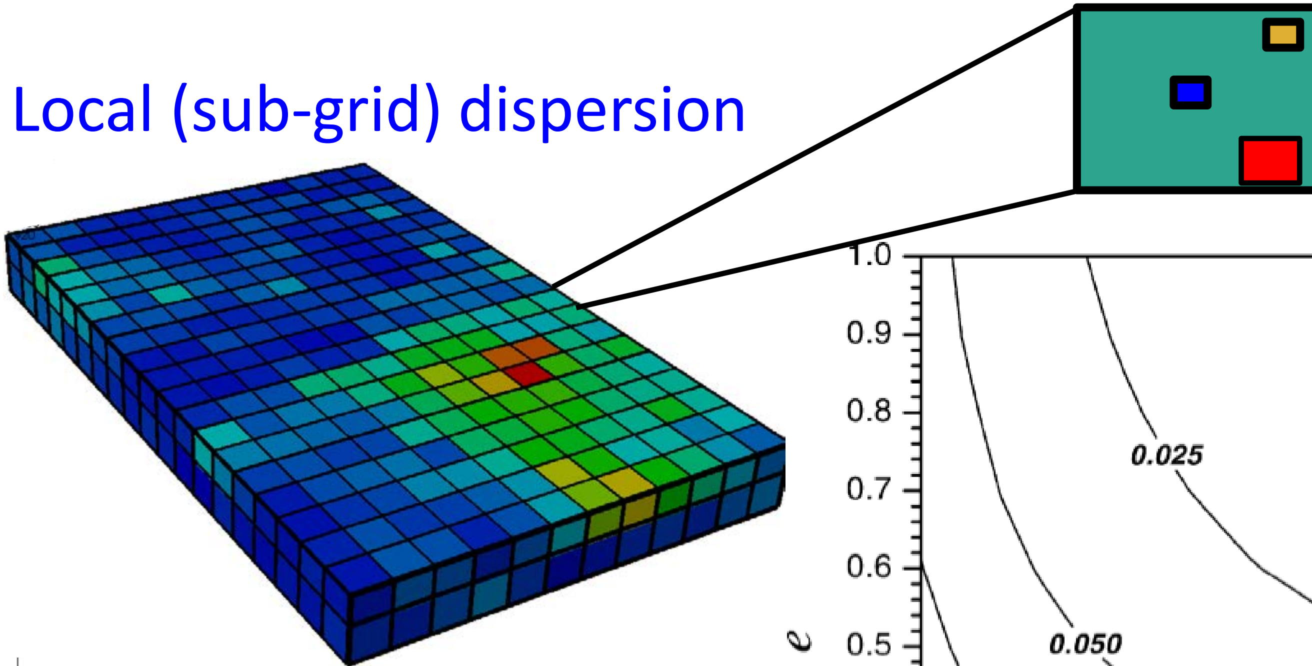
1. Introduction

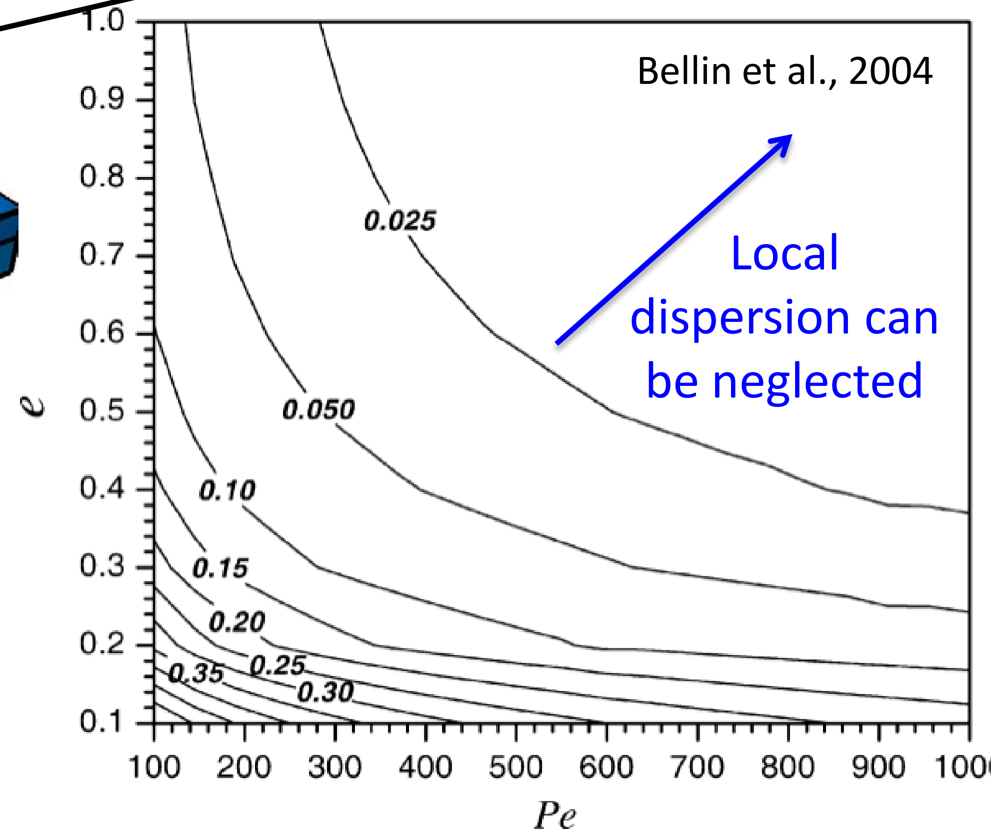
[2] Correctly identifying point values of a contaminant plume (i.e., at a well) is critical to accurately calculate human health risk because groundwater concentrations are often directly used as exposure values to assess risk. The importance of fundamental groundwater flow and transport processes in risk assessment has been demonstrated in multiple studies, but with varying methods. For example, risk

system failure [e.g., *Bolster et al.*, 2009; *Fernandez-Garcia et al.*, 2012]. Probabilistic approaches have also been used [e.g., *Andričević*, 1996; *de Barros and Rubin*, 2008], including a subset of probabilistic approaches which utilize a rigorous treatment of risk via uncertainty and variability methods [e.g., *Maxwell et al.*, 1999; *Smalley et al.*, 2000; *Benekos et al.*, 2007; *Maxwell et al.*, 2008; *de Barros et al.*, 2009; *Siirila et al.*, 2012]. *Maxwell and Kastenberg* [1999] found sorption mechanisms' influence on human

Focusing on two small scale processes:

1. Local (sub-grid) dispersion





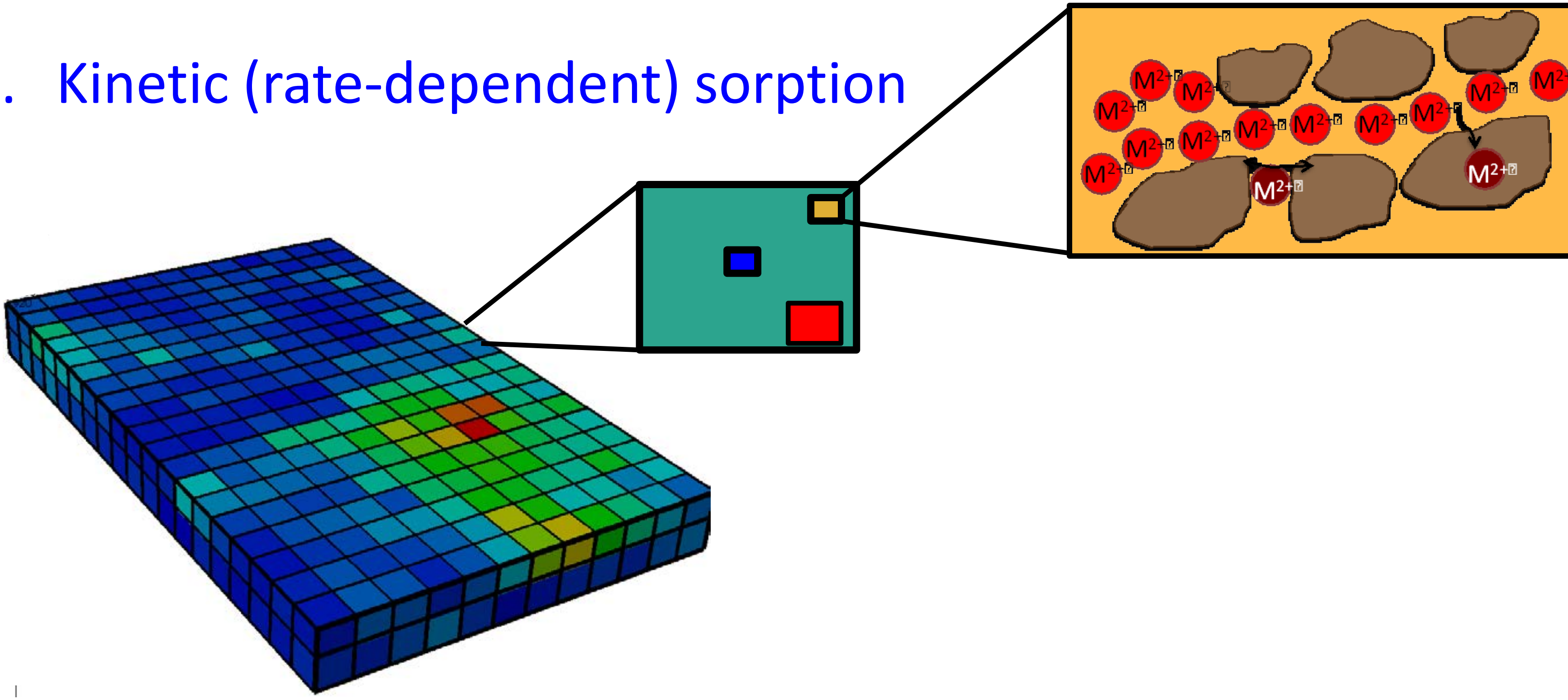
$$Pe = \frac{v_x \lambda_{x=y}}{D_L} = \frac{\lambda_{x=y}}{\alpha_L}$$

mm-scale imposed mixing

Siirila and Maxwell, WRR, 2012

Focusing on two small scale processes:

2. Kinetic (rate-dependent) sorption



<u>*Local Equilibrium Assumption*</u>

<u>*Kinetic*</u>

$$R_{LEA} = 1 + \frac{\rho_b K_d}{\theta} \longrightarrow K_d = \left[\frac{k_f}{k_r} \right] \longrightarrow R_{kin} = 1 + \frac{\rho_b}{\theta} \left[\frac{k_f}{k_r} \right]$$

Siirila and Maxwell, WRR, 2012

Sensitivity analysis

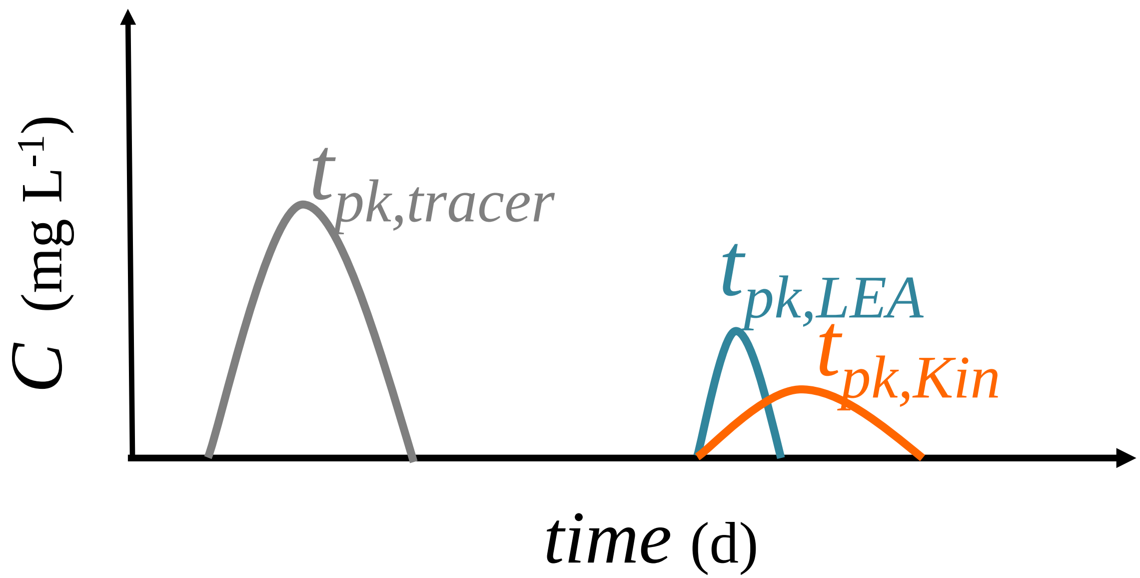
1. Sorption:
   - LEA
   - Kinetic “slow”
   - Kinetic “fast”
   - Tracer
2. Local dispersion
   - $Pe = \infty$
   - $Pe \neq \infty$
3. Anisotropy
   - $\varepsilon = 0.1$
   - $\varepsilon = 0.006$
4. Mean groundwater velocity
   - $v = 0.001$ m/d
   - $v = 0.01$ m/d
   - $v = 0.1$ m/d
5. Continuous and pulse sources

96 ensembles

Per ensemble:

- 200 realizations
- 4 wells

76,800 BTCs to statistically compare

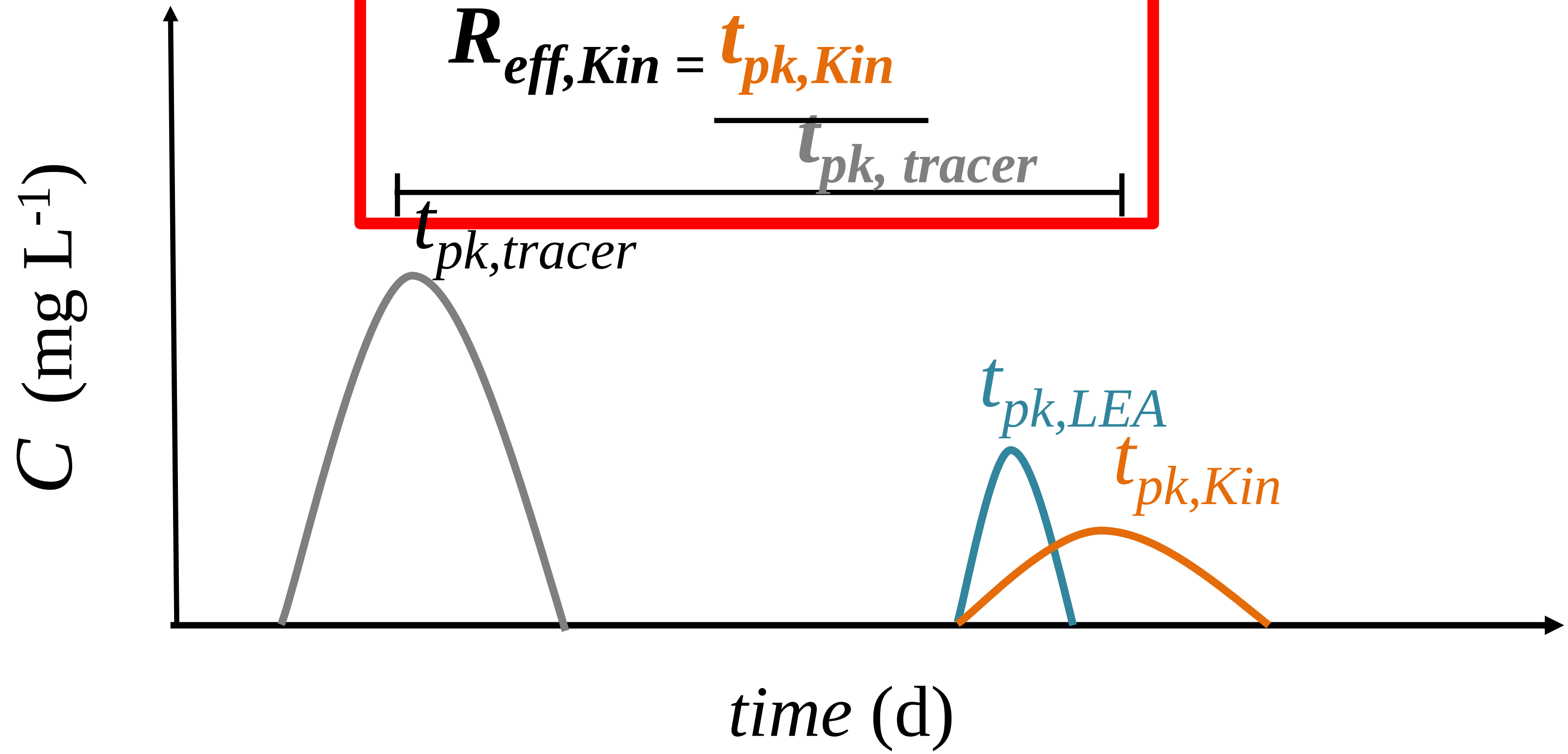


Siirila and Maxwell, WRR, 2012

Effective Retardation as seen in far field conditions

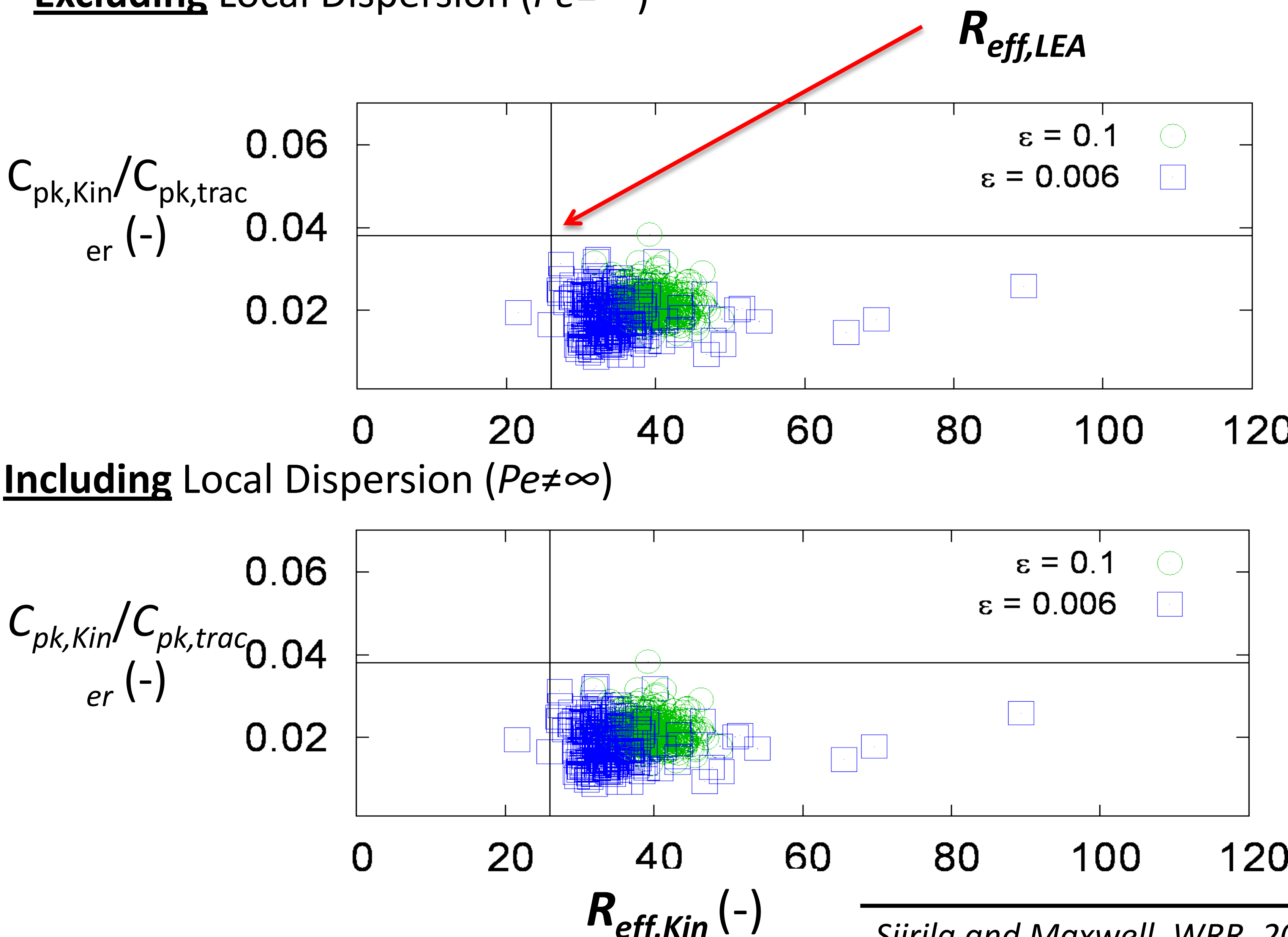
$$R_{eff,LEA} = \frac{t_{pk,LEA}}{t_{pk,\ tracer}}$$

$$\boxed{R_{eff,Kin} = \frac{t_{pk,Kin}}{t_{pk,\ tracer}}}$$



Macroscale effective retardation demonstrates **out of equilibrium**

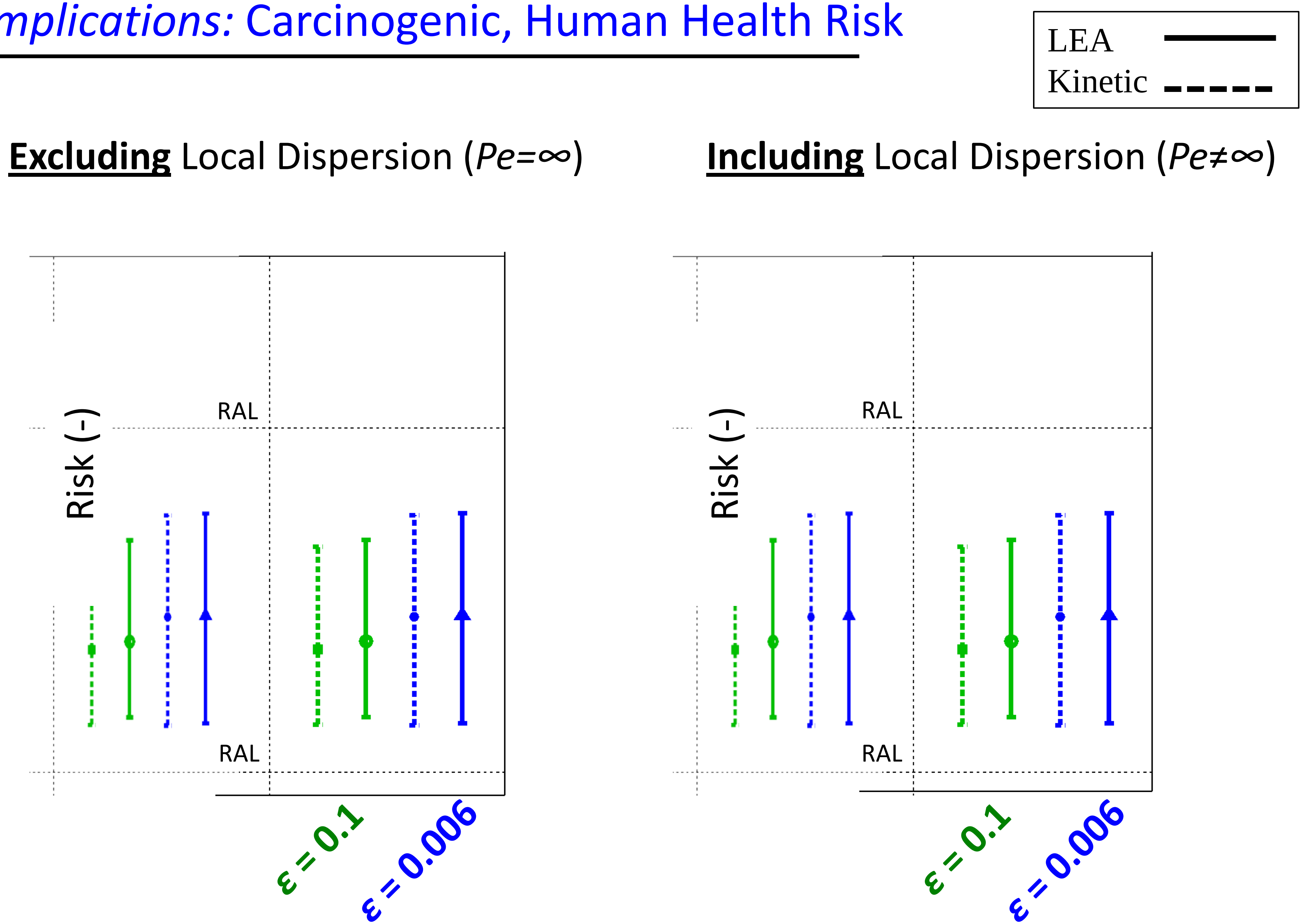
Excluding Local Dispersion (*Pe=∞*)



Including Local Dispersion (*Pe≠∞*)

Siirila and Maxwell, WRR, 2012

Implications: Carcinogenic, Human Health Risk



Siirila and Maxwell, WRR, 2012

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journal homepage: www.elsevier.com/locate/scitotenv

A new perspective on human health risk assessment: Development of a time dependent methodology and the effect of varying exposure durations

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ABSTRACT

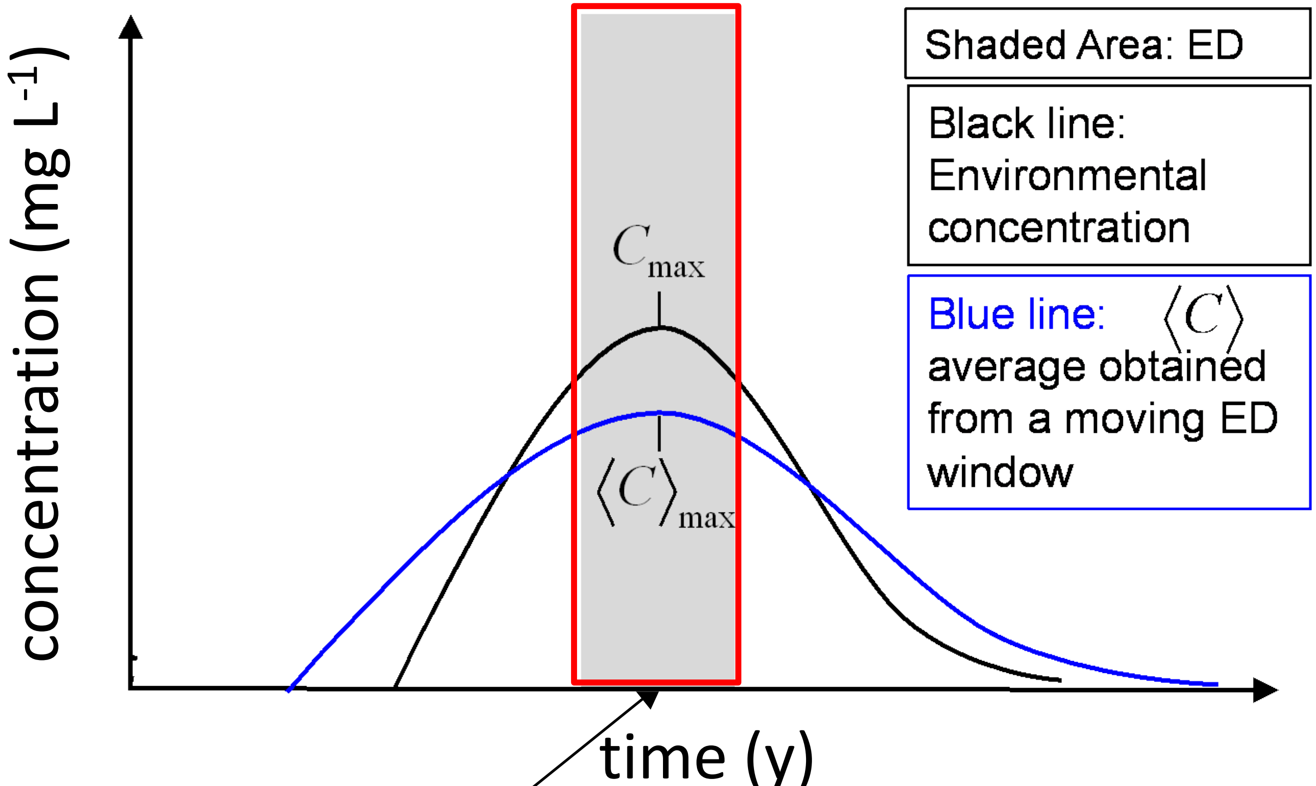
We present a new Time Dependent Risk Assessment (TDRA) that stochastically considers how joint uncertainty and inter-individual variability (JUV) associated with human health risk change as a function of time. In contrast to traditional, time independent assessments of risk, this new formulation relays information on when the risk occurs, how long the duration of risk is, and how risk changes with time. Because the true exposure duration (*ED*) is often uncertain in a risk assessment, we also investigate how varying the magnitude of fixed size durations (ranging between 5 and 70 years) of this parameter affects the distribution of risk in both the time independent and dependent methodologies. To illustrate this new formulation and to investigate these mechanisms for sensitivity, an example of arsenic contaminated groundwater is used in conjunction with two scenarios of different environmental concentration signals resulting from rate dependencies in geochemical reactions. Cancer risk is computed and compared using environmental concentration ensembles modeled with sorption as 1) a linear equilibrium assumption (LEA) and 2) first order kinetics (Kin). Results show that the information attained in the new time dependent methodology reveals how the uncertainty in other time-dependent processes in the risk assessment may influence the uncertainty in risk. We also show that individual susceptibility also affects how risk changes in time, information that would otherwise be lost in the traditional, time independent methodology. These results are especially pertinent for forecasting risk in time, and for risk managers who are assessing the uncertainty of risk.

1. Introduction

Traditionally, risk is calculated using the point of maximum environmental concentration, independent of when that concentration is in time. We present a new formulation that relaxes this assumption to investigate how other time-dependent variables in human health risk may affect the overall assessment. Examples of such time dependent

(U.S.EPA, 1989, 2001) and other regulatory documents (e.g. E.C. and E. C., 1996), the exposure concentration is defined as "the arithmetic average of the concentration that is contacted over the exposure period". Point estimate risk assessments typically use an "upper confidence limit" such as the 95th percentile as a reasonable estimate of the concentration (U.S.EPA, 1989). When conducting probabilistic risk assessments, the US EPA suggests considering either the highest

Traditional, Time *Independent* Framework does not consider plume arrival

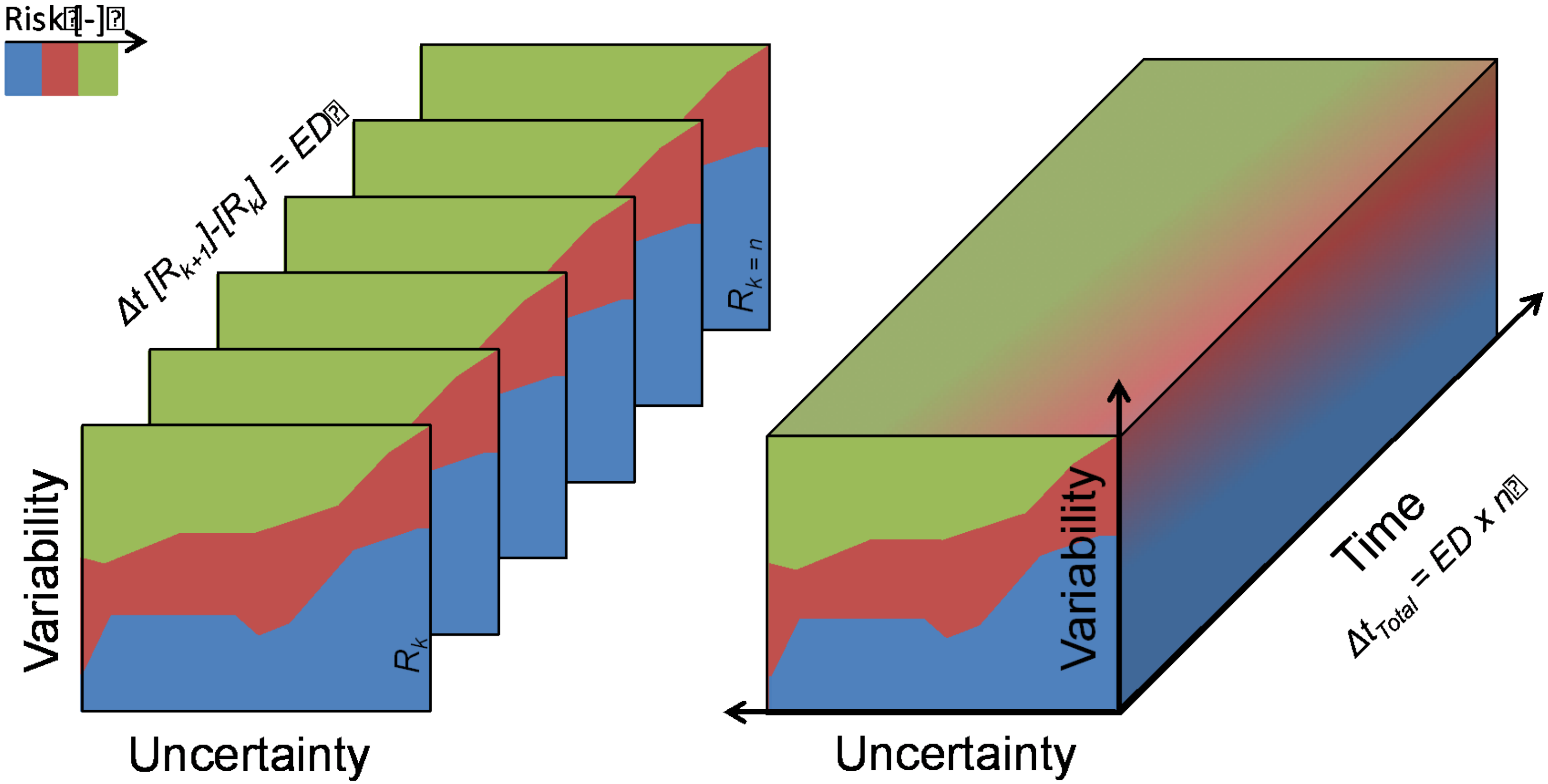


Risk is only calculated during this period of contamination

$$ADD_i = \boxed{< C >_{max}} \left[\frac{IN_i}{BW} \right] \frac{\boxed{ED} \times EF}{AT}$$

$$\sum_{i=1}^{i=p} Risk = 1 - \exp^{-(CPF_z \times ADD_i)}$$

So we developed a Time-Dependent Risk Assessment (TDRA)

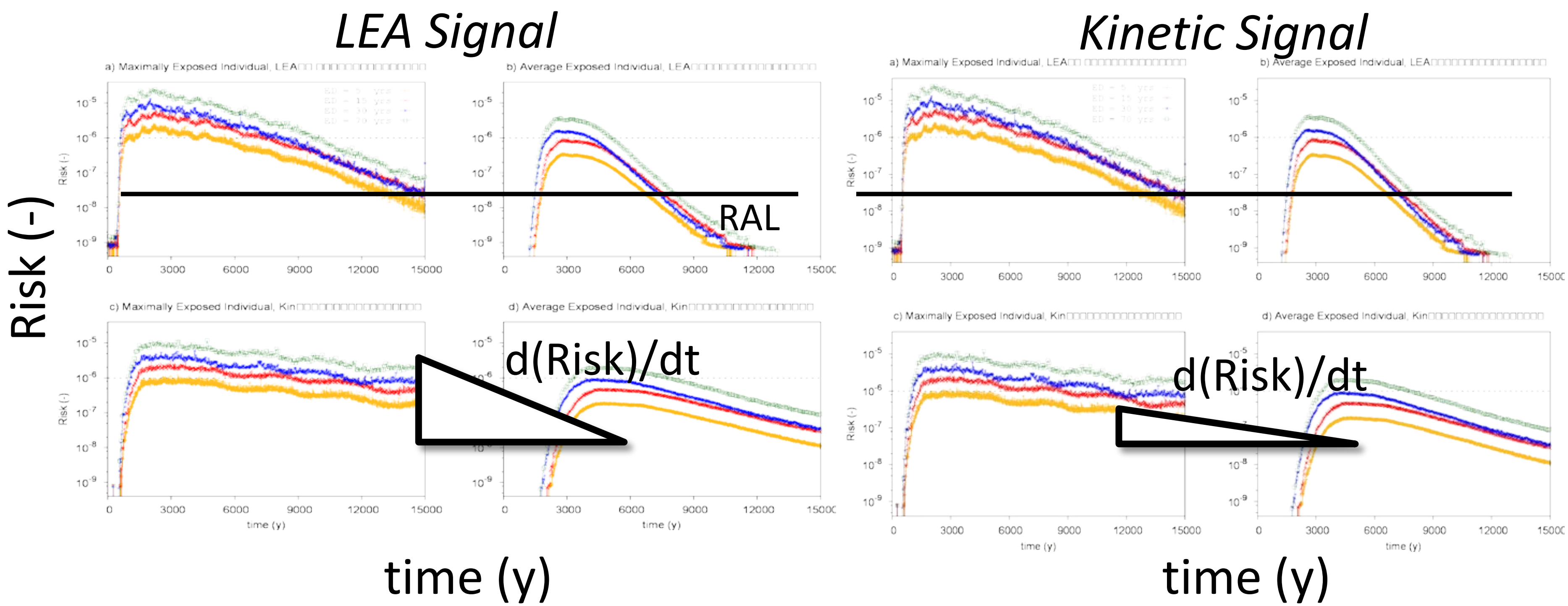


Multiple computations of Time Independent (TI) risk (*left*) are used to compose the risk cube used in Time Dependent (TD) risk (*right*)

***Unlike in TI risk, using TDRA discerns information on how Uncertainty, Variability, and Risk change as a function of time**

Siirila and Maxwell, STOTEN, 2012

TDRA provides information on *when* and for *how long* risk occurs



In this example, the percent of time over the RAL for an of *ED* = 70 (y):

- **LEA: 62%**
- **Kin: 94%**

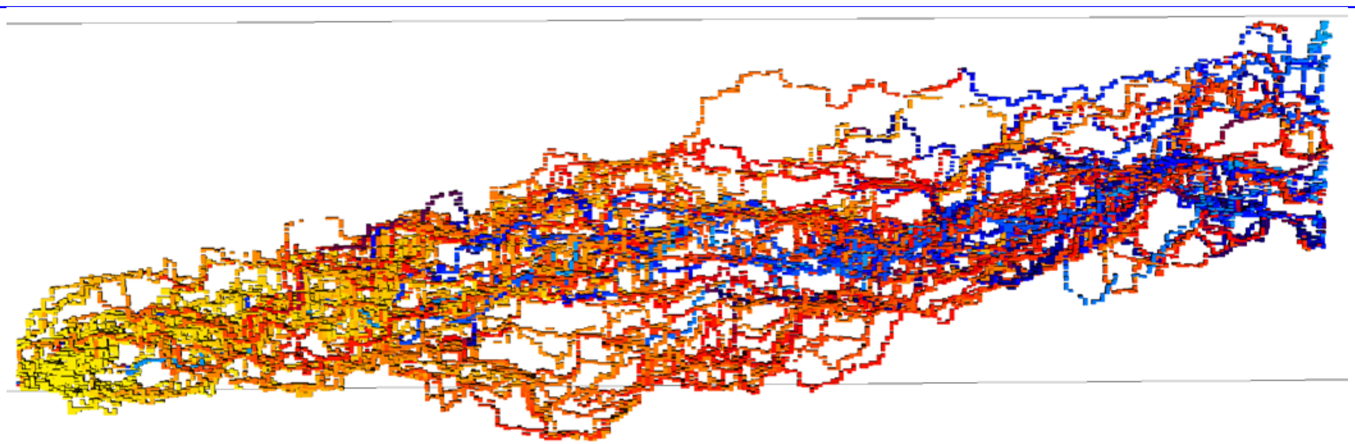
Siirila and Maxwell, STOTEN, 2012

Conclusions: Tools Developed

A framework to quantify human health risks from CO_2 leakage due to metal mobilization

A streamline geochemical reactive transport model that can address heterogeneity, uncertainty very efficiently

A time dependent risk assessment (TDRA) framework to quantify human health risk as a function of time.



Conclusions:

Aquifer stratification controls solute behavior:

- A low degree of stratification increases plume mixing
- Results in varying magnitudes and U/V of risk
- **Subsurface uncertainty greatly affects risk assessment**

Variance of hydrological conductivity influences uncertainty and risk of groundwater contamination.

Hydrological heterogeneity governs the flux from a possible contamination zone to a pumping well, contributing to solute dilution.

Cancer risk is not only sensitive to large-scale hydrologic parameters (such as anisotropy) but also *mm*-scale processes

Conclusions:

Streamlines efficiently solve coupled geochemical and hydrological transport problems allowing for stochastic methods to account for subsurface uncertainty in a human health risk framework.

Regional scale equilibrium was not generally seen even when indicators (e.g. Damköler number) suggest local equilibrium

The time-dependent methodology reveals information otherwise lost in a time independent methodology, such as when risk will occur and how long it will persist

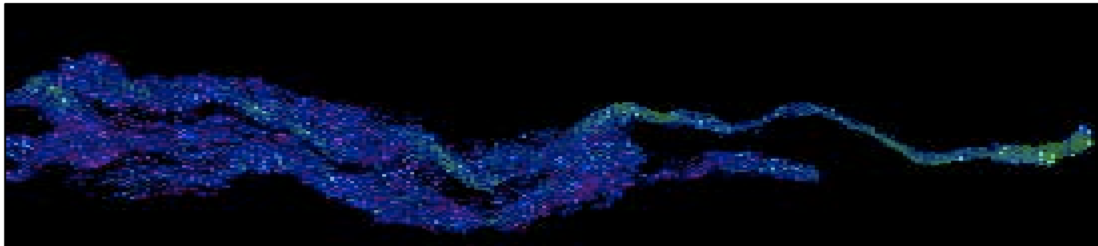
Though we saw evidence of complex, far-field geochemical reactive transport (e.g. pH breakthrough at the well) in general, for our hypothetical scenarios human health risk from CCS leakage was low

Recommendations:

Risk is sensitive to hydrologic flow parameters and warrants further examination in CCS risk assessment

pH may not be a good indicator of CO2 leakage, other indicators with lower natural variability (bicarbonate) might be more robust

While nondimensional variables (e.g. Damköler number) provide insight into contaminate equilibrium, care must be used when scaling from local (< m) to regional (km) scales



Thank you!

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GECO
GOLDEN ENERGY COMPUTING ORGANIZATION

NETL

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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References

1. Siirila, E.R., Navarre-Sitchler, A.K., Maxwell, R.M. and McCray, J.E. A quantitative methodology to assess the risks to human health from CO2 leakage into groundwater. *Advances in Water Resources*, 36(2), 146-164, doi:10.1016/j.advwatres.2010.11.005, 2012.
2. Siirila, E.R. and Maxwell, R.M. Evaluating effective reaction rates of kinetically driven solutes in large-scale, statistically anisotropic media: Human health risk implications. *Water Resources Research* 48, W04527, 23pp, doi:10.1029/2011WR011516, 2012.
3. Siirila, E.R. and Maxwell, R.M. A new perspective on human health risk assessment: Development of a time dependent methodology and the effect of varying exposure durations. *Science of the Total Environment* 431, 221-232, doi:10.1016/j.scitotenv.2012.05.030, 2012.
4. Bearup, L.A., Navarre-Sitchler, A.K., Maxwell, R.M. and McCray, J.E. Kinetic metal release from competing processes in aquifers. *Environmental Science and Technology* 46(12), 6539-6547, doi: 10.1021/es203586y, 2012.
5. Atchley, A.L., Maxwell, R.M. and Navarre-Sitchler, A.K. Using streamlines to simulate stochastic reactive transport in heterogeneous aquifers: Kinetic metal release and transport in CO2 impacted drinking water aquifers. *Advances in Water Resources*, 52:93-106, doi:10.1016/j.advwatres.2012.09.005, 2013.
6. Navarre-Sitchler, A.K., Maxwell, R.M., Siirila, E.R., Hammond, G.E. and Lichtner, P.R. Elucidating geochemical response of shallow heterogeneous aquifers to CO2 leakage using high-performance computing: implications for monitoring of CO2 sequestration. *Advances in Water Resources*, 53:45-55, doi:10.1016/j.advwatres.2012.10.005, 2013.