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141

# Using streamlines for highly-resolved, reactive transport for CO$_2$ leakage contamination in groundwater

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**Abstract** We present a Lagrangian streamline approach where a large, heterogeneous 3D flow field is reduced to a number of 1D transport simulations. The streamline approach allows the mapping of these 1D reactive transport simulations back onto a 3D flow field, thus accounting for spatial heterogeneity within the aquifer and complex aqueous geochemical processes. A CO$_2$ leakage scenario from a hypothetical CCS site is used where a resulting plume of CO$_2$ lowers the groundwater pH and mobilizes metals from an existing mineral host-rock distribution. The plume migration and related metal dissolution and precipitation within the aquifer were simulated using this streamline-geochemical modelling approach under varying hydrological heterogeneity variances ($\sigma^2_{lnK}$). Results showed that heterogeneity significantly influences well contamination and geochemical processes.

**Key words** reactive transport; uncertainty analysis; carbon capture and storage

## BACKGROUND

Modelling reactive transport (involving geochemical processes) over large, finely resolved domains in three-dimensional space has been computationally demanding. Subsurface physical heterogeneity, complex chemistry, and the need to accurately resolve macrodispersion all contribute to computational expense (Hammond *et al.*, 2010). However, the ability to accurately model large-scale reactive transport within heterogeneous domains has become increasingly necessary in order to evaluate potential groundwater contamination scenarios, such as those associated with leakage from Carbon Capture and Storage (CCS) (Apps *et al.*, 2010; Wilkin *et al.*, 2010; Siirilla *et al.*, 2011). Preserving both reactive transport processes and finely resolved heterogeneities within the subsurface will provide a better understanding of the driving processes in reactive plume migration.

Small-scale physical heterogeneities inherent in the subsurface are often difficult to fully characterize spatially. Maintaining and stochastically accounting for physical heterogeneities in the system will provide insight into advection dominated transport and the probabilistic outcomes of transport in a heterogeneous aquifer. It has been shown that spreading of solute due to heterogeneities in permeability results in an assortment of plume fingering which then controls solute mixing (Le Borgne *et al.*, 2010). The dilution of solute, caused by plume spreading and mixing can have important repercussions with regards to the chemistry involved in reactive transport (Herrera *et al.*, 2010). Furthermore, recent work has shown that hydrological complexity can considerably control reactive transport processes (Green *et al.*, 2010). Therefore, modelling finely resolved domains that account for heterogeneous permeability distribution will maintain dynamics of plume spreading and associated reactive transport processes.

Chemical complexities in reactive transport must also be preserved in order to accurately assess outcomes of a chemically dynamic plume, especially when outcomes are dependent on the aquifer geochemistry. The presence of metal containing mineralogy or buffering material could have a large affect on the spatial extent of reactive processes and amount of metals released from the aquifer (Apps *et al.*, 2010; Wilken *et al.*, 2010). The kinetic rate of dissolution/precipitation and sorption/desorption processes can also dictate the plume extent (Apps *et al.*, 2010; Dentz *et al.*, 2011). Chemical reaction rates that control reaction times are then affected both by aquifer characteristics and the chemistry of the plume. Past studies have focused on a characteristic solute flushing rate or residence time for an aquifer to determine chemical weathering rates (Clow &

Drever, 1996; Maher, 2010). Often, groundwater flow can be heavily influenced by preferential flow paths and complex heterogeneities (Green *et al*., 2010). These dynamic features of subsurface flow could potentially affect geochemical outcomes for a reactive transport scenario. Therefore, a coupled relationship between hydrological properties and chemical processes should be accounted for in reactive transport modelling.

A stochastic representation of uncertain aquifer parameters is necessary to evaluate reactive transport within a given aquifer. Given that a large amount of variability exists in hydrological parameters and that there is uncertainty in the spatial extent of the subsurface parameters, a systematic approach should be employed to account for the different combinations of aquifer variability. One such approach is a stochastic Monte Carlo risk assessment framework, where multiple realizations of aquifer heterogeneity representing uncertain aquifer characteristics, are used in concert with population variability to exposure of contaminated water (Maxwell *et al*., 1999; Siirila *et al*., 2011). In this method an end point of health risk is used to measure outcomes between combinations of hydrological and geochemical processes while maintaining the uncertainty inherent in both hydrological and geochemical characteristics.

## Motivaton

In this paper we show that the streamline method can be used to evaluate coupled hydrological and geochemical problems where uncertainty in subsurface conditions necessitate ensemble evaluation. The streamline method is used to investigate how hydrological conditions affect geochemical processes and how coupled hydrological and geochemical processes at a streamline level propagate through ensemble statistical outcomes. With this tool, investigators are able to discern how these coupled processes: (1) control individual outcomes of known conditions, and (2) affect ensemble outcomes that capture uncertainty.

## STREAMLINE MODEL

Streamlines are 1D paths that are traced within a 3- or 2D flow field. In order to maintain 3D, multiple streamlines are needed to capture all the various flow paths that occur in a 3D heterogeneous flow domain. Multiple deconvolved 1D reactive transport problems can easily be solved in parallel, especially when transverse dispersion between streamlines is assumed to be negligible. While multiple streamlines are needed to solve a transport problem in 3D space, tracing streamlines from a capture zone to a source zone can reduce the reactive transport simulation to areas that represent connections between source and well capture (source-well streamlines). Previous work by Batycky *et al*., 1997, Crane & Blunt 1999, and Maxwell *et al*., 2003 has found that streamline simulations can be 10–1000 faster than finite difference models and reduce numerical dispersion. Alternatively, the streamline approach losses efficiency and accuracy in transient flow domains where transverse dispersion has a large affect on plume dynamics and solute spreading.

## Basic structure and methodology

Here the methodology using the streamline approach for coupling hydrological and geochemical processes consists of four steps: (1) mapping a flow domain, (2) tracing streamlines via advective transport within the flow domain, (3) transform streamline spatial coordinates to time of flight, and (4) simulate geochemical reactions along each deconvolved streamline path. In the first step, PARFLOW (Ashby & Falgout, 1996; Jones & Woodward, 2001; Kollet & Maxwell, 2006) which is a parallel, 3D groundwater flow model, was used to map the flow field domain. Then SLIM-FAST (Maxwell, 2010), a numerical model using a Lagrangian method to solve advective transport along a velocity field, was used to trace streamline paths within the flow field domain. Particles are seeded around a hypothetical well or capture zone and are tracked backwards in a reverse flow condition. Tracked particles in an advection only regime represent paths along streamlines, which contain

spatial and temporal data in the form of time of flight ($\tau$). Instead of cell dimensions of length, the streamlines now alternatively have dimensions of residence time, $\tau$, or time needed to advect particles a given distance. $\tau$ can be long or short depending on the permeability of a given cell and the path a streamline takes across the cell, thus creating an assortment of cell lengths along a streamline. The velocity along a streamline is normalized to one, ensuring that a particle travels through $\tau$ space evenly so that transport along a streamline from source zone to capture zone is a reflection of the travel time between the two points and not distance. CrunchFlow (Steefel, 1994, 2001), a multicomponent reactive flow and transport code, is then used to solve 1D transport and chemical reactions in a globally implicit approach along each streamline.

**CCS leak**

The streamline methodology used to couple complex hydrological and reactive transport is applied to evaluate a hypothetical CCS leak scenario, where the $CO_2$ leak occurs in an overlying aquifer above a deep $CO_2$ storage site. Downgradient from the leak a pumping well with a flux of 300 $m^3$/day is used for domestic purposes and the effect of $CO_2$ leakage on water quality and probability of capture is investigated. The aim is to present the usefulness of the streamline methodology in evaluating relevant study areas containing uncertain hydrological and geochemical conditions. Hydrological heterogeneity, a highly variable and uncertain parameter governs plume migration and therefore the probability of solute capture at a pumping well. Furthermore, few studies have attempted to characterize the influence of hydrological heterogeneity on geochemical processes.

The effect that changing the log hydraulic conductivity variance ($\sigma^2_{lnK}$) characteristic for a flow domain would have on pumping well solute breakthrough curves and probability of source zone to well connectivity was tested. A log hydraulic conductivity variance [$\sigma^2$] of 1, 3.61, and 16 were examined with reactive transport along connected streamlines. For a given $\sigma^2_{lnK}$ flow condition, a set of 100 equally probable permeability fields was simulated with geochemical processes along streamlines connecting the source zone to the pumping well as an ensemble set. Using ensembles of 100 realizations allowed for the capture of uncertainty while providing an ensemble average to describe overall trends. All ensembles of 100 realizations were simulated on an 8 core Linux machine, with an ensemble run time of approximately 24 h.

**Flow domain**

A finely resolved grid is used to map the 3D flow field with cell sizes of $3 \times 3$ m in the X and Y direction and 0.3 m in the Z direction. There were 400 grid cells in the X direction, 100 in the Y, and 200 in the Z directions, totalling 8 million grid cells in the domain. Flow is along the X direction with a mean hydraulic conductivity of 52 m/day and an average gradient of 0.00443 across the flow field, thus representing a permeable aquifer that may be used as a domestic water source. Aquifer properties are summarized in Table 1.

Figure 1 shows a schematic of the leak location and the pumping well location within a possible heterogeneous permeability field. It is important to note that the pumping well screen has a Z location in the domain between 25 and 55 m, and the $CO_2$ leak source has a Z location between 2 and 15 m of the bottom of the aquifer. This domain configuration places the source zone below the direct path of flow to the well, which in turn will affects the connectivity of the source to the well for any given $\sigma^2_{lnK}$ description of the aquifer.

**Table 1** Domain discretization and hydrological conditions.

|  | Length (m) | Discretization (m) | Number of cells | Corr. length (m) |
|---|---|---|---|---|
| X | 1200 | 3 | 400 | 10 |
| Y | 300 | 3 | 100 | 10 |
| X | 60 | 0.3 | 200 | 1 |
| $K_{(mean)}$ [m/d] | 52 | Total number of cells | 8 000 000 |  |
| Porosity | 0.33 | Average gradient | 0.00443 |  |
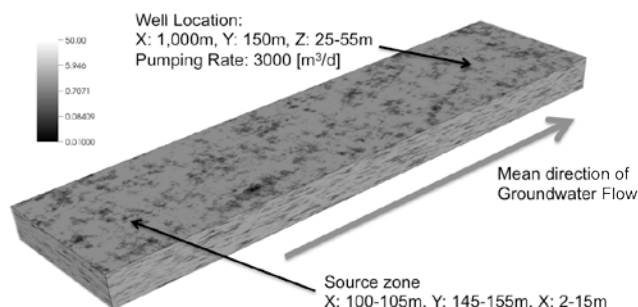
**Fig. 1** A possible permeability field is shown along side the source and pumping well location.

## Geochemical set-up

The hypothetical aquifer model had a porosity of 33% and volume fractions of 64% quartz, 3% calcite and 0.1% galena. Galena serves as the source of lead. It is assumed to be under anoxic conditions to provide a basic but relevant reactive transport scenario. Reactive transport was only simulated along 1D streamlines that had a connection between the source zone and the pumping well in order to reduce the computational resources needed to simulate breakthrough curves (BTC) at the well. The initial condition had a pH of 7 and a partial pressure for $CO_2$ gas of 0.01 bar, and was applied to all cells along a streamline in $\tau$ space. The $CO_2$ leak condition was applied to the boundary of $\tau$ cell 1 at a ghost node, and had a pH of 4.5 and a $PCO_2$ gas of 30 bar. $CO_2$ from the leak was assumed to be in the form of gas or dissolved $CO_2$ in the groundwater, as determined by Henry's law. CrunchFlow allows for simulation of full kinetic chemistry, dissolution/precipitation of mineral species and kinetic modelling sorption/desorption processes. Here only kinetic dissolution and precipitation is simulated. Kinetic rates are a function of thermodynamic properties, solute concentration, and pH, as well as a function of mineral surface area. In this work rate constants are assumed to be log –15, –11.5, and –11 (mol/m$^2$ s) for quartz, galena, and calcite, respectively. The surface areas are assumed to be 0.3, 0.6 and 0.9 (m$^2$) for quartz, galena and calcite, respectively. Carbonate chemistry and pH buffering within the streamlines and all dissolution/precipitation processes were simulated allowing for geochemical processes to determine the outcome.

Streamline reactive transport simulated 3000 days in order to capture all breakthrough curves for a given realization. Streamline chemistry profiles for each realization were taken at 0.01 days for an initial condition profile and at 3000 days for a file condition and at intermittent intervals to observe how the chemical conditions evolved during the simulation. BTC's of a non-reactive tracer, pH, and aqueous lead concentration were taken from each streamline, and averaged for each realization and ensemble to produce mass flux per day for the tracer and lead. pH was calculated for all streamlines with a source to well connection at the pumping well, thereby excluding water dilution from streamlines that are not connected with the source zone. Total well water pH was also analysed to include dilution from clean sources. Average BTC were then evaluated using only the realizations within an ensemble that had a connection between the source zone and the pumping well (source-well average). BTC's were then compared to ensemble results that included all realizations incorporating realizations with no source to well connection to provide a probabilistic outcome based on the hydrological characteristics.

## RESULTS

All three ensembles, each with 100 equally probable realizations that simulated coupled hydrological and geochemistry streamlines finished near 24 h or below. The accuracy of our methodology was compared against the analytical solutions derived from the cumulative travel time for each streamline. The analytical solutions were then averaged for each ensemble in order to evaluate the effect of numerical error propagating from the streamline level to the ensemble level.
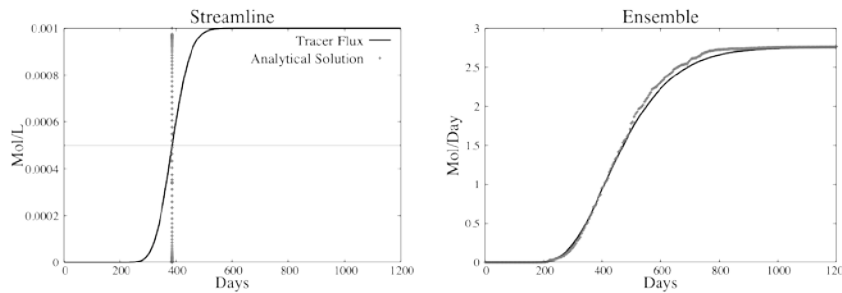
**Fig. 2** Numerical BTC solutions are compared to the analytical solution BTC for a single streamline and an entire ensemble.

Figure 2 shows the numerical BTC compared to the analytical solution BTC for a single streamline and an entire ensemble. While numerical dispersion is apparent when comparing the tracer from a single streamline to the analytical solution, it is evenly distributed around the analytical solute arrival time. Overall, error appears to be insignificant especially when realizations are averaged over an ensemble of 100 realizations. Considering the BTC accuracy attained, especially at the ensemble level, and the simulation solve time, the streamline methodology maybe a good option for evaluating reactive transport problems that necessitate uncertainty analysis or ensemble characterizations.

**Table 2** Streamline flux statistics from source-zone to pumping well.

| | | $\sigma^2_{lnK} = 1$ | $\sigma^2_{lnK} = 3.61$ | $\sigma^2_{lnK} = 16$ |
|---|---|---|---|---|
| Total ensemble statistics | Tot. num. of connected rel/ensemble | 31 | 93 | 94 |
| | Ave. source-well/rel | 10 | 26 | 14 |
| | Ave. flux/rel | 1.15 | 2.77 | 1.31 |
| Source-well connection statistics | Ave. source-well/rel | 34.16 | 28.87 | 15.3 |
| | Ave. flux/rel | 3.7 | 2.97 | 1.39 |

The ensemble flux from the source zone to the well is a product of the model domain heterogeneity. Given that the source zone and the pumping well are offset, a certain amount of heterogeneity must be present for a source-well connection to occur for any giving realization. Therefore, it is expected that heterogeneous domains have a high probability of containing a source-well streamline within any realization. The total number of connected realizations per ensemble listed in Table 2 indeed increases as $\sigma^2_{lnK}$ increases from 1 to 16. In a homogeneous domain, if a contaminant source is not directly upgradient from a pumping well there is greater chance of a plume entirely missing the capture zone of the well. However, homogeneous domains can in effect draw directly from a source zone with little mixing from uncontaminated areas if the source is directly upgradient. If only realizations where a source-well connection occurs are considered, then the trend reverses, as shown in Table 2. Both the average number of source-well streamlines increase and most importantly the average mass flux from a contaminant source zone increases, for low $\sigma^2_{lnK}$ aquifer characterizations. Therefore, for the case presented here where CO₂ leakage into a potable aquifer is offset from the direct line upgradient of a pumping well, there is a high likelihood of contamination within highly heterogeneous aquifers, but the contamination will typically be small. However, in a more homogenous aquifer there is a low probability of well contamination, but if contamination does occur, the well could potentially be highly contaminated. This explains that for low $\sigma^2_{lnK}$ cases the ensemble average change in pH, and lead concentration is small, but when only considering the source-well connected realizations, the pH change and lead concentration are high.

## Break Through Curves (BTC)
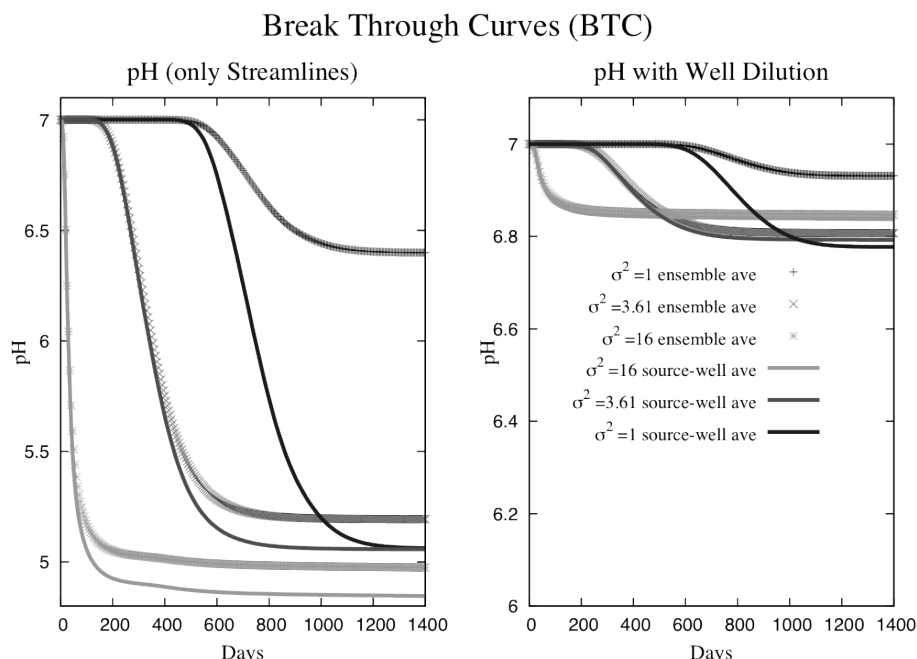


**Fig. 3** Ensemble average and source-well average pH BTC without well dilution in left plot, ensemble average and source-well average pH BTC with well dilution in right plot.

Likewise, pumping wells in heterogeneous aquifers could potentially draw water from an assortment of aquifer areas. This in turn increases the pumping well dilution. Whereas homogenous aquifers tend to draw water from specific areas, and therefore will not have the added well dilution occurring. For this model set up it is apparent that well dilution could mask pH BTCs for all levels of heterogeneity tested. However, the least amount of pumping well dilution occurs in the least heterogeneous domains, suggesting that heterogeneity increases the amount of well dilution and therefore could mask well contamination.

### Fast path *vs* slow path geochemistry

Geochemical outcomes were found to differ as a result of physical heterogeneity. Streamlines within low $\sigma^2_{lnK}$ domains typically had lower changes in pH and lead concentrations at the pumping well than streamlines in high $\sigma^2_{lnK}$ domains. Driving the differences in geochemical processes was the time of flight each streamline had associated with transporting a solute along its path. Figure 3 shows ensemble concentration differences along with different BTC time for the three $\sigma^2_{lnK}$ characterizations tested. It is apparent that increased $\sigma^2_{lnK}$ had earlier BTC arrival times compared to low $\sigma^2_{lnK}$. This is because flow moving through the flow domain found preferential paths to the well, which in turn decreased $\tau$ for the majority of streamlines in the high $\sigma^2_{lnK}$ domains. Kinetically controlled reactions are dependent on the amount of time each chemical constituent has in contact with reactive components. Therefore, a concentration profile along a streamline is a reflection of the residence time for each streamline. In the case of a $CO_2$ leak, where pH drops due to carbonation of the water from metals that are dissolved from the host mineralogy, a dis-equilibrium occurs and a certain amount of time is needed before the new geochemical regime can come back to equilibrium. For the simple case presented here, the pH drops due to an increase in $CO_2$ at a hypothetical source. The drop in pH, even though buffered from calcite dissolution, also results in the dissolution of lead from galena. However, the lead almost immediately becomes saturated and slowly precipitates back out of solution and reforms galena along the streamline path. The role that hydrological properties have is in determining the time needed for lead to precipitate back. When a domain is defined by slower solute travel times,

as is the case with low $\sigma^2_{lnK}$ domains, the majority of lead has time to precipitate out of solution before reaching the pumping well. Conversely, for domains that are defined by fast solute travel times, as is the case with the high $\sigma^2_{lnK}$ domains, the lead does not have enough time to precipitate out of solution, and the lead concentration remains high along the entire length of the streamline. Given that increased hydraulic heterogeneity of a flow domain is characterized by faster flow paths, even when slower paths with long residence times coexist, chemical conditions at the pumping well will have more source-well connected streamline discharges that represent source or near source contamination. However, as mentioned above, the same hydraulic heterogeneous properties can also contribute to increased well dilution, thereby masking the changes observed in faster flow reactive transport.
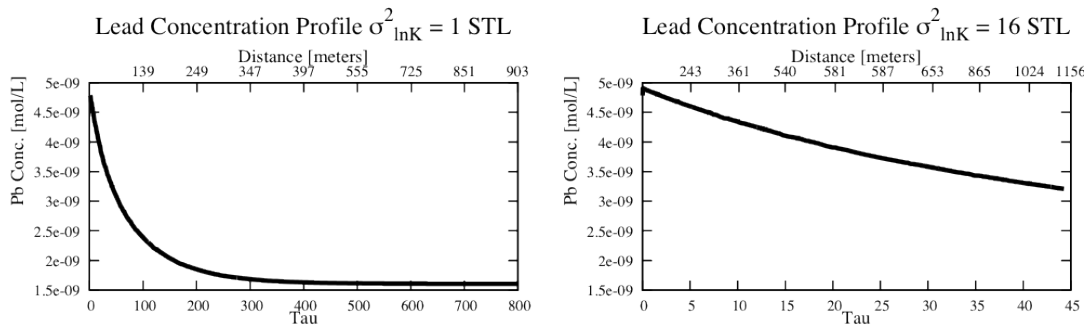


**Fig. 4** Lead concentration profiles for all streamlines within a realization are shown above a plot of a representative streamline from the realization for a $\sigma^2_{lnK}=1$ (left) and a $\sigma^2_{lnK}=16$ (right).

## CONCLUSIONS

The use of a streamline methodology allowed for an efficient and acceptably accurate examination of linked hydrological and geochemical processes with uncertain domain configurations. The ability to solve 100 unique realizations within 24 h allows for probabilistic ensemble characterization of uncertain conditions. For a given hydrological characteristic a probabilistic outcome can be determined, and a dominant geochemical process can be described.

Aquifer characterization of the variation of hydraulic conductivity played a large role in both the probability of a contamination from a hypothetical $CO_2$ leak reaching a pumping well and what a contamination might look like. If a leak is off-set from the direct upgradient path from a pumping well, heterogeneity will increase the likelihood that well contamination will occur. However, heterogeneity also increases the spread of the well capture area that may have no contamination, thus diluting any contamination from the $CO_2$ leak source area. Conversely, if an aquifer displays small variations in inflow paths, the likelihood of well contamination is low, but if a contamination occurs, it could be substantial. This suggests that there is a middle $\sigma^2_{lnK}$ range that both has enough heterogeneity to establish source-well flow paths and enough homogeneity that the source-well paths capture a substantial portion the source contamination.

By coupling geochemistry and hydrological processes a link between residence time and $\sigma^2_{lnK}$ was established and shown to greatly influence the geochemical process. While dilution was found to mask geochemical outcomes at the ensemble level, important geochemical phenomenon were found as a result of $\sigma^2_{lnK}$ at both the realization and single streamlines level. Residence time or solute flushing has been recognized as a controlling agent in geochemical interactions (Clow & Drever, 1996; Green *et al*., 2010; Maher, 2010). Where this work differs is that specific paths of varying residence times are shown within detailed aquifer characterizations, and the level of hydrological heterogeneity can greatly influence geochemical interactions. Here we see similar residence time behaviour with regards to chemical reactions in long or short residence time systems by applying constant hydrological boundary conditions across the domain, specifically the

groundwater head, hydrological gradient, and average hydrological conductivity. Hydrological heterogeneity is then the only physical governing agent for chemical reactions determined by time. The importance of residence time in determining chemical reactions then points to the need for accurate kinetic rate representation and hydrological complexity.

Uncertainties are inherent in subsurface characterizations and therefore contaminant hydrology. The ability to capture uncertainty via Monte Carlo methods will enable a better quantification of the risk involved in a possible $CO_2$ leak from a CCS site and better guide characterizations of hydrological and geochemical conditions needed to understand possible outcomes. While simplified assumptions were made in this modelling exercise, the ability to couple complex hydrology and kinetic geochemistry over multiple realizations allowed for a probabilistic evaluation of a given scenario. The streamline method proved to be a useful tool in evaluating uncertainty conditions along with identifying important geochemical and hydrological linkages.

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