Assessment of Predictive Uncertainty in Coupled Groundwater Reactive Transport Modeling

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Abstract

Groundwater reactive transport modeling provides a systematic framework for integrating hydrologic and biogeochemical conceptual process models into a quantitative description of subsurface behaviors. However, subsurface environments are open and complex and subject to multiple interpretations and conceptualizations given available data and information. The model uncertainty is quantified using the Bayesian Model Averaging method (BMA), in which multiple plausible reactive transport models are postulated and calibrated against observations. Instead of making predictions based on a single model, predictions of reactive transport are made using the calibrated model ensemble, and BMA jointly assesses parametric uncertainty and model uncertainty. The BMA methodology is applied to seven surface complexation models of varying complexity developed for simulating U(VI) transport in columns. Model probabilities, measures of plausibility of the models, are calculated using the Maximum Likelihood version of BMA (MLBMA) based on model calibration results, and used as model averaging weights. Model uncertainty exceeds parametric uncertainty even in these well-controlled laboratory experiments and model averaging gives superior predictions relative to any single model.

Bayesian Model Averaging

A practical method for evaluating prediction uncertainty in hydrogeologic modeling with joint consideration of ***model*** and ***parameter*** uncertainty is Maximum Likelihood version of Bayesian Model Averaging (MLBMA) (Neuman, 2003; Ye et al., 2004). In MLBMA, the posterior distribution of the quantity of interest, Δ, given a set of data $\mathbf{D}$ is:

$$p(\Delta \mid \mathbf{D}) = \sum_{k=1}^{K} p(\Delta \mid \mathbf{D}, M_k)\, p(M_k \mid \boldsymbol{D})$$

- Model uncertainty is represented using a set of alternative models, M_k, each model being consistent with the available site information.
- Parameter uncertainty enters through $p(\Delta \mid M_k, \mathbf{D})$ as a component of the posterior distribution of $\mathbf{D}$ for a given model, M_k, estimated from the results of a maximum likelihood model calibration.

The posterior mean and variance of Δ are

$$E[\Delta \mid \boldsymbol{D}] = \sum_{k=1}^{K} E[\Delta \mid \boldsymbol{D}, M_k]\, p(M_k \mid \boldsymbol{D})$$

$$Var[\Delta \mid \boldsymbol{D}] = \underbrace{\sum_{k=1}^{K} Var[\Delta \mid \boldsymbol{D}, M_k]\, p(M_k \mid \boldsymbol{D})}_{\text{within-model variance}} + \underbrace{\sum_{k=1}^{K} \left(E[\Delta \mid \boldsymbol{D}, M_k] - E[\Delta \mid \boldsymbol{D}, M_k]\right)^2 p(M_k \mid \boldsymbol{D})}_{\text{between-model variance}}$$

The posterior probability, $p(M_k \mid \mathbf{D})$, of model M_k is given by Bayes' rule

$$p(M_k \mid \mathbf{D}) = \frac{p(\mathbf{D} \mid M_k)\, p(M_k)}{\sum_{l=1}^{K} p(\mathbf{D} \mid M_l)\, p(M_l)} = \frac{\exp\left(-\frac{1}{2} KIC_k\right) p(M_k)}{\sum_{l=1}^{K} \exp\left(-\frac{1}{2} KIC_l\right) p(M_l)}$$

which is a function of the model likelihood and the subjective prior model probability. *KIC* is a model discrimination criterion computed from the results of a maximum likelihood model calibration as (Ye et al., 2008)

$$KIC_k = -2\ln[L(\hat{\boldsymbol{\theta}}_k \mid \mathbf{D})] - 2\ln p(\hat{\boldsymbol{\theta}}_k) - N_k \ln(2\pi) + \ln|\mathbf{F}_k|$$

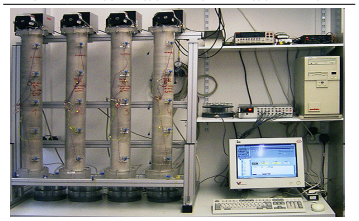
where L is the likelihood function estimated at the calibrated model parameters, $\hat{\boldsymbol{\theta}}_k$, N_k is the number of calibrated parameters, $p(\hat{\boldsymbol{\theta}}_k)$ is the prior parameter distribution, and $\mathbf{F}$ is the observed Fisher information matrix.

Surface Complexation Models

Model	Reactions
C1	$S_1OH+UO_2^{2+}+H_2O=S_1OUO_2OH+2H^+$
C2	$S_1OH+UO_2^{2+}+H_2O=S_1OUO_2OH+2H^+$
	$S_2OH+UO_2^{2+}+H_2O=S_2OUO_2OH+2H^+$
C3	$S_1OH+UO_2^{2+}+H_2O=S_1OUO_2OH+2H^+$
	$S_2OH+UO_2^{2+}=S_2OUO_2^{+}+H^+$
C4	$S_1OH+UO_2^{2+}+H_2O=S_1OUO_2OH+2H^+$
	$S_2OH+UO_2^{2+}+H_2O=S_2OUO_2OH+2H^+$
	$S_2OH+UO_2^{2+}=S_2OUO_2^{+}+H^+$
C5	$S_1OH+UO_2^{2+}+H_2O=S_1OUO_2OH+2H^+$
	$S_2OH+UO_2^{2+}+H_2O=S_2OUO_2OH+2H^+$
	$S_1OH+UO_2^{2+}=S_1OUO_2^{+}+H^+$
	$S_1OH+UO_2^{2+}+H_2O=S_1OUO_2OH+2H^+$
C6	$S_1OH+UO_2^{2+}+H_2O=S_1OUO_2OH+2H^+$
	$S_2OH+UO_2^{2+}+H_2O=S_2OUO_2OH+2H^+$
	$S_2OH+UO_2^{2+}=S_2OUO_2^{+}+H^+$
	$S_1OH+UO_2^{2+}=S_1OUO_2^{+}+H^+$
C7	$S_1OH+UO_2^{2+}+H_2O=S_1OUO_2OH+2H^+$
	$S_2OH+UO_2^{2+}+H_2O=S_2OUO_2OH+2H^+$
	$S_3OH+UO_2^{2+}+H_2O=S_3OUO_2OH+2H^+$

Conditions of the Column Experiments

Experiment	pH	[U(VI)] [μM]	[F] [μM]	U(VI), % Recovered	Retardation Factor
1	4.26 ± 0.02	1.0	0	96.9	8.9
2	3.90 ± 0.02	1.0	0	98.6	3.2
3	4.79 ± 0.02	1.0	100	94.8	8.7
4	4.39 ± 0.02	1.0	100	97.1	2.5
5	3.89 ± 0.02	1.0	0	96.0	2.9
6	5.6 ± 0.1	0	1000	N/A	N/A
7	4.26 ± 0.02	50.0	0	99.4	6.5
8	4.22 ± 0.02	50.0	0	99.5	3.7



Column experiments assembly

Model Calibration

Procedure of Uncertainty analysis

(1) Calibrate experiments 1, 2, and 8 to estimate model parameters (i.e., surface complexation formation constant and fraction of the total surface site density strong site).
(2) Calculate model probabilities based on the calibration results.
(3) Simulate experiments 3, 4, 5, and 7 for validation.
   - Assess parametric uncertainty of each model.
   - Jointly assess parametric and model uncertainty.

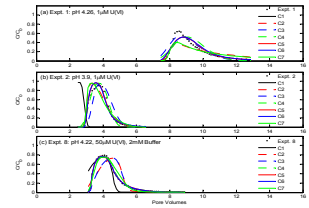


Figure 1: Comparison of observed breakthrough curves and fitted transport simulations for surface complexation model formaulations of increasing complexity.

Parameter Sensitivity and Uncertainty

Parametric uncertainty describes the confidence in the selection of a parameter to be used in a model. Parameters 'K1, K2, K3' are unknown reaction rates for 3 reactions chosen to represent the reaction network in a model. Parameter 'Sites' describes nature of the adsorption sites of the media To investigate the observed sensitivity of K1 (Fig 2), a numerical Monte Carlo experiment was conducted. Holding 'K2, K3, Sites' constant to calibrated values for model 'C4', K1 was varied for 1000 realizations using a uniform distribution from provided feasible minimum and maximum values. Future study will involve using the Morris Method to investigate global sensitivity.

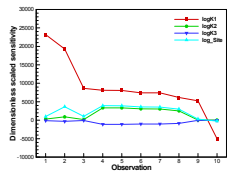


Figure 2: Sensitivity of model parameters

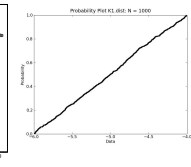


Figure 3: Parameter distribution, N=1000 realizations

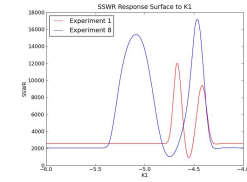


Figure 4: Optimal parameter values for one experiment subject to the same model does not necessarily produce a feasible parameter value for another experiment.

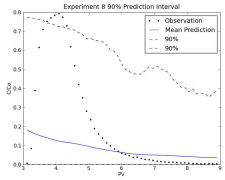


Figure 5: Prediction interval subject to distribution in Figure 3. The mean does a poor job of predicting the peak concentration of uranium. The prediction interval does not cover the observed peak.

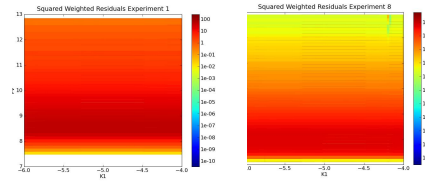


Figure 6: Error is highly subject to the model's ability to simulate the concentration of uranium over time, rather than a selection of K1 as a parameter.

Prediction Uncertainty

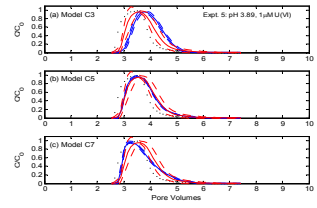


Figure 7: Comparison of observed breakthrough curves and predicted transport simulations for single model and model averaging; Black dots represent measured U(VI) concentration, blue lines are for mean predictions and uncertainty bounds of individual models, and red lines are for posterior mean and variance of model averaging.

Table 1: Model probability (%) based on all the calibration data

	C1	C2	C3	C4	C5	C6	C7
$p(M_k \mid \mathbf{D})$(%)	0	0.59	5.97	18.28	40.46	34.67	0.03

Table 2: Predictive logscore and predictive coverage (%) of single model and MLBMA (based on all data) for simulating Experiment 5.

	C1	C2	C3	C4	C5	C6	C7	MLBMA
Predictive logscore	2825	76	194	103	172	174	104	31
Predictive coverage	27	46	37	32	39	29	37	68