Stochastic capture zone analysis of an arsenic-contaminated well using the generalized likelihood uncertainty estimator (GLUE) methodology

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[1] In 1992, Mexican researchers discovered concentrations of arsenic in excess of World Heath Organization (WHO) standards in several municipal wells in the Zimapan Valley of Mexico. This study describes a method to delineate a capture zone for one of the most highly contaminated wells to aid in future well siting. A stochastic approach was used to model the capture zone because of the high level of uncertainty in several input parameters. Two stochastic techniques were performed and compared: "standard" Monte Carlo analysis and the generalized likelihood uncertainty estimator (GLUE) methodology. The GLUE procedure differs from standard Monte Carlo analysis in that it incorporates a goodness of fit (termed a likelihood measure) in evaluating the model. This allows for more information (in this case, head data) to be used in the uncertainty analysis, resulting in smaller prediction uncertainty. Two likelihood measures are tested in this study to determine which are in better agreement with the observed heads. While the standard Monte Carlo approach does not aid in parameter estimation, the GLUE methodology indicates best fit models when hydraulic conductivity is approximately $10^{-6.5}$ m/s, with vertically isotropic conditions and large quantities of interbasin flow entering the basin. Probabilistic isochrones (capture zone boundaries) are then presented, and as predicted, the GLUE-derived capture zones are significantly smaller in area than those from the standard Monte Carlo approach. *INDEX TERMS:* 1829 Hydrology: Groundwater hydrology; 1832 Hydrology: Groundwater transport; 1869 Hydrology: Stochastic processes; *KEYWORDS:* Bayesian, capture zone, GLUE, Zimapan

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1. Introduction

[2] Uncertainty analysis is often undertaken when the model parameters are not well known. This is increasingly becoming the case with new models that attempt to describe interactions between multiple systems (atmospheric, biologic, surface water, vadose zone, and groundwater) that inherently require numerous parameters to be specified. One form of uncertainty analysis treats modeling parameters as random variables within a Monte Carlo framework. A traditional Monte Carlo analysis calculates the uncertainty in the model output based solely on the uncertainty in the input parameters. Each output realization is equally weighted without consideration to its ability to represent observed system behavior. In contrast, the generalized likelihood uncertainty estimator (GLUE) procedure [*Beven and Binley*, 1992] incorporates both parameter uncertainty and weights realizations based on their relative goodness of fit. The inclusion of this additional information (in this case, observed hydraulic heads) into the uncertainty analysis provides a common sense methodology to apply less weight to those realizations that do not honor the field observations.

[3] The majority of applications of the GLUE methodology in the earth sciences have been in catchment models and land surface-atmosphere models that require multiple input parameters [*Beven and Binley*, 1992; *Franks and Beven*, 1997; *Freer et al.*, 1996; *Kuczera and Parent*, 1998]. However, GLUE has been applied to groundwater studies by *Buckley et al.* [1994] in contaminant transport and by *Feyen et al.* [2001] in capture zone delineation. *Feyen et al.* [2001] assessed the uncertainty of hydraulic

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Figure 1. Location of the Zimapan Valley in the Mexican state of Hidalgo.

conductivity in the capture zone of a hypothetical flow field originally presented by *Bear and Jacobs* [1965]. Capture zones using different measures of goodness of fit were compared with numerical solutions to determine which measure of goodness of fit produced the capture zone closest to the ''true'' solution [*Feyen et al.*, 2001]. Several other studies have performed uncertainty analysis in capture zone modeling but mainly with hypothetical model regimes [*Varljen and Shafer*, 1991; *Bair et al.*, 1991; *Franzetti and Guadagnini*, 1996; *van Leeuwen et al.*, 1998; *Guadagnini and Franzetti*, 1999].

[4] This study focuses on defining the capture zone for an arsenic-contaminated well in rural Mexico. In 1992, researchers discovered concentrations of arsenic in excess of 0.05 mg/L (the WHO and Mexican recommended drinking water limit) in several municipal wells in the Zimapan Valley in the Mexican state of Hidalgo (Figure 1) [*Armienta et al.*, 2001]. These wells served as the primary water source for approximately 9000 people [*Armienta et al.*, 2001]. It is hypothesized that the arsenic contamination in the deep (~180 m) municipal wells is derived from reductive desorption of arsenic from the host carbonate rock [*Morse*, 2001]. One of the municipal wells in particular, El Muhi, had an arsenic concentration of 1.00 mg/L (Figure 2) [*Armienta et al.*, 2001]. Because of the rural location, very little hydraulic data exists for the Zimapan Valley.

[5] The purpose of this study is to define the capture zone for the El Muhi well and uncertainty associated with prediction due to uncertainties in the input parameters. Standard Monte Carlo analysis will be compared with the GLUE methodology [*Beven and Binley*, 1992]. Because the GLUE technique incorporates the goodness of fit of the model and the associated parameter set, it is hypothesized that the GLUE procedure will result in a more tightly constrained capture zone for El Muhi well. In addition, this study will attempt to define the best manner of implementing the GLUE procedure in capture zone analysis for this model.

2. GLUE Procedure

[6] The GLUE procedure is an extension of Monte Carlo random sampling to incorporate the goodness of fit of each simulation. In the framework of the GLUE methodology the goodness of fit is called a likelihood measure. The likelihood measure can be evaluated in both a quantitative and qualitative manner. In this study, the likelihood measure is a subjective evaluation of the quantitative goodness of fit:

$$L\left(\vec{H}|\vec{\theta}_i\right) = \left[\frac{1}{E_i}\right]^N \quad (1)$$

where $L(\vec{H}|\vec{\theta}_i)$ is the likelihood of the vector of observed hydraulic heads, $\vec{H}$, knowing the parameter set, $\vec{\theta}$; E_i is an objective function; and N is a likelihood shape factor. If one assumes that the head errors are weakly correlated, then E_i can be expressed as the weighted sum of squared errors:

$$E_i = \sum_{k=1}^{N_{obs}} w_k \left[h^i_{sim,k} - h_{obs,k}\right]^2 \quad (2)$$

where $h^i_{sim,k}$ is the simulated head in observation well k for realization i, $h_{obs,k}$ is the observed head in observation well k; w_k is a measure to weight the observation wells, and N_{obs} is the number of observation wells. The N factor and the choice of the sum of squares as the error model are the subjective portions of choosing the likelihood measure.

[7] As N approaches 0, the likelihood function yields equal weights for all realizations, which is analogous to the traditional Monte Carlo analysis. As N approaches infinity, the best fitting realizations receive essentially all of the weight as is the case in inverse solution. This is conceptually

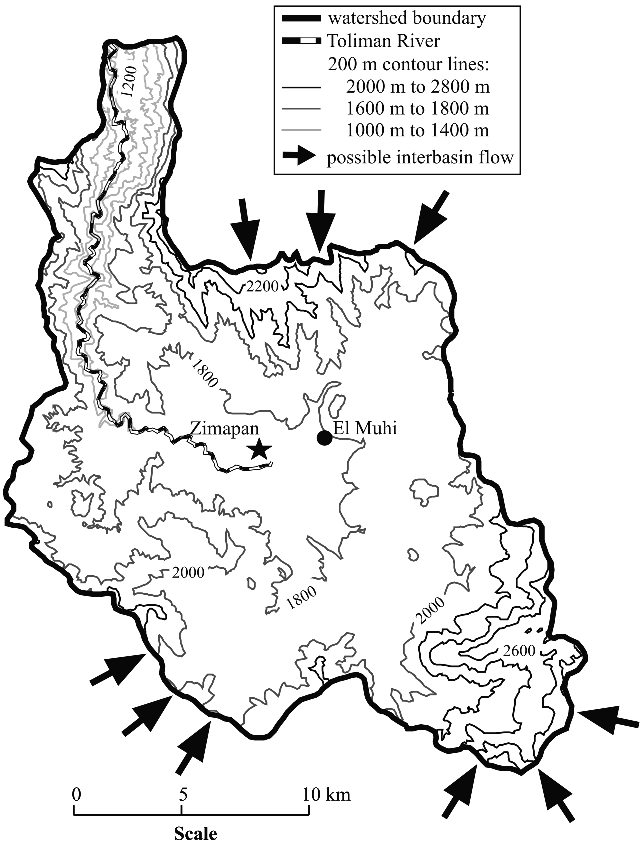

Figure 2. Map of the Zimapan Basin showing topography, the Toliman River, the city of Zimapan, possible locations of interbasin flow, and the arsenic-contaminated well El Muhi.

Table 1. MODFLOW and MODPATH Stochastic Parameters Showing Range and Distribution of Each Parameter (GLUE Prior Probabilities)

Parameter	Units	Minimum	Maximum	Distribution
Hydraulic conductivity	m/s	10^{-8}	10^{-5}	$\log_{10}$uniform
Vertical anisotropy ratio		10^{-1}	1	$\log_{10}$uniform
Total interbasin flow	m^3/s	0.00	0.425	$\log_{10}$uniform
Porosity	%	10^{-1}	10	$\log_{10}$uniform

similar to using a maximum likelihood estimator. In this study, a value of 1 is used for N as a starting point. A sensitivity analysis is performed on N in section 7, and a method to estimate N is proposed in section 8.

[8] Likelihood measures can also incorporate qualitative information, such as knowledge about the conditions that are being modeled. For example, if it was known that a group of wells upgradient of El Muhi had minor arsenic concentrations, then a simulation that showed arsenic coming from the region of this noncontaminated well could be given a likelihood of zero. Two wells to the southeast of El Muhi contain very low concentrations of arsenic, but it is difficult to implement this qualitative information. For example, the two wells could lie within the capture zone of El Muhi well and still have low arsenic concentrations, because the arsenic could be derived from a different portion of the capture zone, and mixing with the noncontaminated groundwater. Due to difficulty of resolving this issue, the qualitative information provided by these two wells was not included in this study.

3. Stochastic Modeling Approach

[9] The groundwater flow modeling was performed using the US Geological Survey's MODFLOW and the particle tracking using MODPATH [*McDonald and Harbaugh*, 1988; *Pollock*, 1994]. A simple 4-layer conceptual model was created based on geologic maps and cross-sections. Boundary conditions were specified as no-flow occurring at a topographically defined watershed boundary (Figure 2). However, because of the region's mountainous terrain, deep interbasin flow was simulated at model boundaries near areas of high topographic relief. This was accomplished using injection wells in the lower three layers of the model at locations marked in Figure 2. The Zimapan River flows through and out of the basin, and, with the exception of evapotranspiration losses, is the only outflow from the basin (Figure 2).

[10] Extremely little hydraulic information is known in the study area, therefore certain input parameters are treated as random variables (Table 1). For simplicity, the model is assumed to be homogeneous, and the hydraulic conductivity is assumed to span the range of 10^{-8} to 10^{-5} m/s. The flow in the basin consists entirely of fracture flow, so the vertical anisotropy ratio was also assumed to be a random variable that spans from 0.1 to 1. The interbasin flow is assumed to range from 0.0 to 0.425 m^3/s over 147 injection wells. Lastly, the porosity is assumed to span from 0.1% to 10%. All of the random variable parameters were assumed to be uniformly distributed based on a $\log_{10}$ transformation.

[11] An analysis of output statistics for various numbers of realizations showed that a total of 10,000 realizations were required to ensure stability of capture zone statistics. The input parameters were randomly selected from the $\log_{10}$-uniform distributions (Table 1). Forward particle tracking from all cells in the top layer of the model was performed for a total of 5000 years. Particles that intersected the El Muhi well within a 5000-year time frame were considered to fall within the capture zone for a particular realization. A total of 16 hydraulic head observation points were used to calculate the likelihood for the GLUE procedure, and wells located within 2 km of the El Muhi well were given twice the weight as those further away.

4. Capture Zone Uncertainty

[12] Traditional Monte Carlo methods and the GLUE procedure were used to assess the uncertainty in the predicted capture zones. The Monte Carlo method utilizes the uncertainty in the input parameters to calculate the uncertainty of the simulated capture zones such that each realization is equiprobable. The GLUE procedure uses the prior distribution of the input parameters and then weights individual realizations based on an application of Bayes equation in the form:

$$L\left(\vec{\theta}_i|\vec{H}\right) = \frac{L\left(\vec{H}|\vec{\theta}_i\right)L_o\left(\vec{\theta}_i\right)}{C} \tag{3}$$

where $L(\vec{\theta}_i)$ is the prior likelihood for realization, i; $L(\vec{H}|\vec{\theta}_i)$ is the likelihood measure from equation (1); $L(\vec{\theta}_i|\vec{H})$ is the posterior likelihood; and C is a normalization constant calculated as:

$$C = \sum_{i=1}^{n} L\left(\vec{H}|\vec{\theta}_i\right)L_o\left(\vec{\theta}_i\right) \tag{4}$$

to ensure that the cumulative posterior likelihood is unity.

[13] MODPATH is used to calculate the forward particle paths within the prescribed flow field. For each realization, an isochrone is defined as the boundary of the capture zone that envelops all starting locations whose particles intersect the El Muhi well within the 5000-year time frame. The probability that a particle starting from location (x', y') is captured by the well is determined numerically as:

$$P(x', y') = \sum_{i=1}^{n} L\left(\vec{\theta}_i|\vec{H}\right) \tag{5}$$

where $L(\vec{\theta}_i|\vec{H})$ is the posterior probability of all realizations that fall within the capture zone, and $P(x', y')$ is the probability that a starting location (x', y') falls within the capture zone. The calculation of the capture zone probability for the traditional Monte Carlo method is similar to that of the GLUE procedure, but the posterior likelihoods are equiprobable.

[14] The capture zone likelihood distributions are plotted using equation (5) for the GLUE and Monte Carlo cases. Given a confidence level, α, one can plot the uncertainty bounds as:

$$\alpha < P(x', y') < 1 - \alpha \tag{6}$$

Because $L(\vec{\theta}_i|\vec{H})$ is the joint probability of four parameters, the marginals of $L(\vec{\theta}_i|\vec{H})$ must be taken to obtain the

Table 2. A Comparison of GLUE (when $N = 1$) and Monte Carlo (MC) Statistics of the Posterior Distributions of the Three MODFLOW Random Parameters: Log Hydraulic Conductivity (K), the Vertical Anisotropy Ratio, and the Interbasin Flow[a]

	Log_{10} K, m/s		Vertical Anisotropy Ratio		Interbasin Flow, m^3/s	
	GLUE Result	MC Result	GLUE Result	MC Result	GLUE Result	MC Result
Mean	−6.59	−7.22	0.535	0.536	0.221	0.209
Δ95% C.I.	0.64	1.49	0.855	0.856	0.400	0.405

[a]The 95% confidence interval is denoted Δ95% C.I.

probability of each parameter. The marginal likelihood of the *j*th parameter is calculated by integrating out the density of the other three parameters (*l*, *m*, *n*):

$$L\left(\theta_{i,j}|\vec{H}\right) = \int_{l,m,n} L\left(\vec{\theta}_i|\vec{H}\right) d\Theta \tag{7}$$

5. Analysis of Input Parameters

[15] The Monte Carlo probabilities of the parameters are calculated from the GLUE prior probabilities. Therefore the traditional Monte Carlo approach does not aid in parameter estimation. The GLUE procedure utilizes the likelihood measure to determine which parameter sets achieve the best model fits. The GLUE mean of the *j*th input parameter is:

$$\bar{\theta}_j = \sum_{i=1}^{10,000} L\left(\theta_{i,j}|\vec{H}\right)\theta_{i,j}; \qquad j = 1, 2, \cdots 4 \tag{8}$$

where, $\theta_{i,j}$ is the value of the *j*th input parameter for the *i*th realization, and $L\left(\theta_{i,j}|\vec{H}\right)$ is the marginal posterior likelihood of the *j*th parameter for the *i*th realization. The GLUE confidence intervals of each parameter are derived from the cumulative distribution functions of the marginal posterior likelihoods of each individual parameter.

[16] Table 2 shows a quantitative comparison of the mean and Δ95% confidence intervals of the parameters for the Monte Carlo (prior) and GLUE (posterior) procedures. The hydraulic conductivity parameter shows the largest difference between standard Monte Carlo and GLUE results. This will be elaborated on in section 7.

[17] Dot plots of each MODFLOW parameter versus GLUE likelihood show the sensitivity of individual parameters to the goodness of fit of the model (in terms of hydraulic heads) (Figure 3). Note that porosity is not one of the parameters shown because the goodness of fit of the head field is not a function of porosity. Figure 3a shows that the hydraulic conductivity parameter is highly sensitive, and simulations in the range of $10^{-6.5}$ m/s result in "good" models (high likelihoods correspond to a low head objective function). Simulations with hydraulic conductivities greater than approximately $10^{-6.3}$ m/s result in model cells going dry, and MODPATH not being able to converge on a solution. Both the vertical anisotropy ratio parameter (Figure 3b) and interbasin flow parameter (Figure 3c) are relatively insensitive input parameters (in comparison with the hydraulic conductivity). High likelihoods (better fitting models) are seen toward more isotropic conditions, and with high values of interbasin flow. Figure 3 also shows the prior probabilities, which are equivalent to the Monte Carlo result, in relation to the likelihoods.

[18] While dot plots show the sensitivity of individual parameters toward the model fit, we are more likely to be interested in how combinations of parameters affect the model. Figure 4 presents two joint probability density functions that show the effect of two of the three input parameters on likelihood. Figures 4a and 4b corroborate

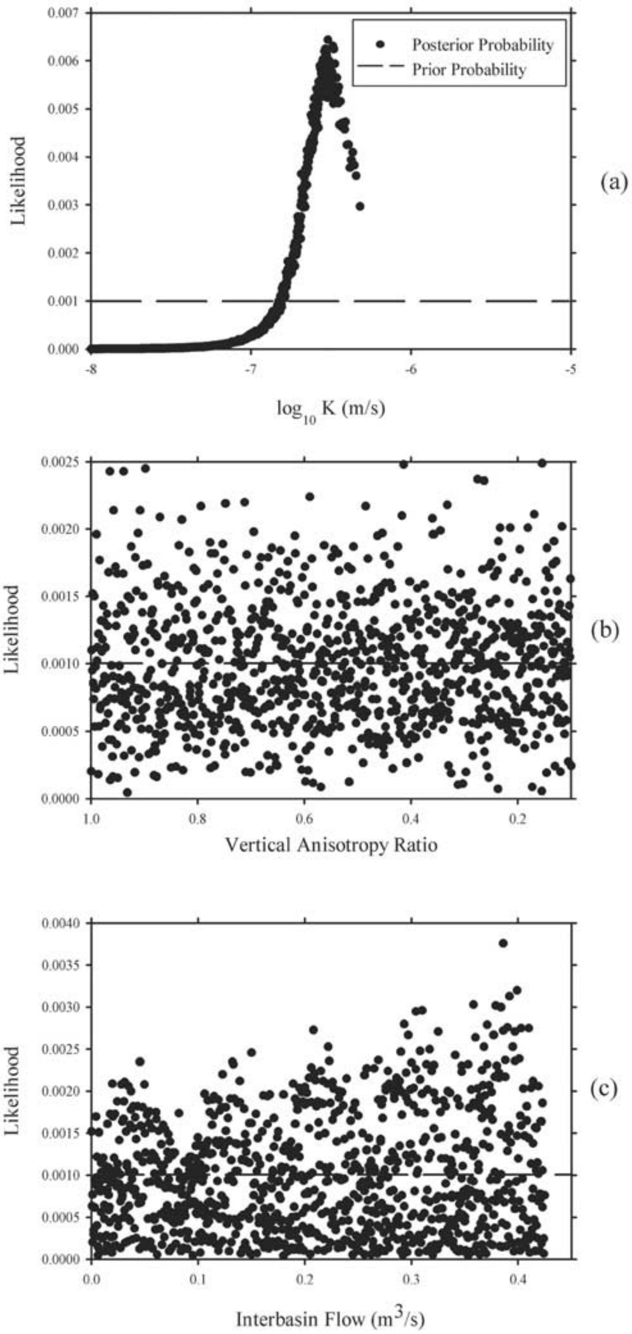

Figure 3. Dot plots of three MODFLOW input parameters versus likelihood (when $N = 1$). Higher likelihoods indicate better model fits. Prior probabilities of each parameter are shown as dashed lines at 0.001.

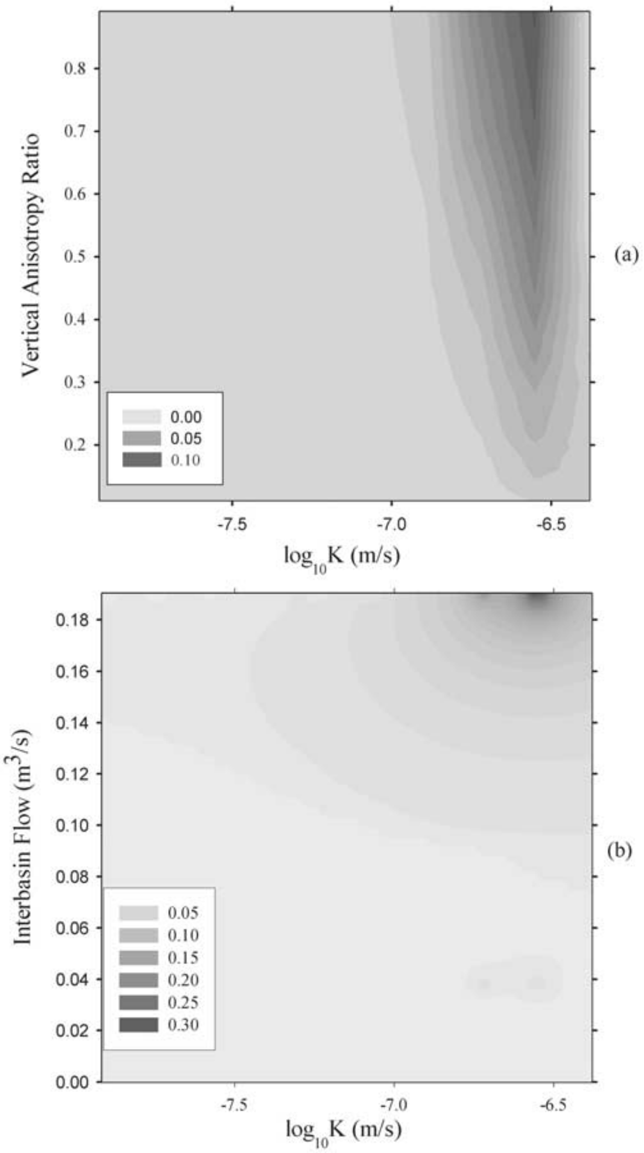

Figure 4. Joint probability density functions of three input parameters versus normalized likelihood. Best fit regions (high likelihoods) are shown in darker colors. Hydraulic conductivity shows a best fit region around $10^{-6.5}$ m/s. Higher likelihoods are also seen toward (a) larger vertical anistropy ratio values (more isotropic conditions) and (b) with very large quantities of interbasin flow.

what is seen in the dot plots (Figure 3), high likelihoods when hydraulic conductivity is in the range of $10^{-6.5}$ m/s, and toward vertically isotropic conditions, with large quantities of interbasin flow.

6. Analysis of Model Output

[19] The model output was assessed in terms of the hydraulic heads and the arsenic capture zone for El Muhi well. Unlike the hypothetical study area of *Feyen et al.* [2001], this study had access to only head data to compare and check model output. Observed head values were compared with 95% uncertainty quantiles calculated from the simulated heads of 16 observation points. Monte Carlo and GLUE 95% confidence intervals are presented along with observed heads in Figure 5. Observed head values lie close to the lower 95% uncertainty boundary for both the Monte Carlo and GLUE results (Figure 5). The upper Monte Carlo 95% uncertainty bound is several thousand meters above observed head values, because the Monte Carlo methodology does not take into account that many of the realizations (particular parameter sets) do not result in head fields close to the observed heads (Figure 5). Because the GLUE methodology conditions its response on the head measurements, the GLUE uncertainty quantiles fit the observed head values significantly better than the standard Monte Carlo methodology (Figure 5).

[20] Monte Carlo and GLUE 95% confidence regions ($0.025 < P < 0.975$) of the isochrones of El Muhi are presented in Figure 6. The difference in the size of the confidence regions is better seen quantitatively (Table 3). Application of the GLUE procedure results in a capture zone 1.6 km^2 smaller than what standard Monte Carlo analysis produces (Table 3). As indicated with the input parameters, the GLUE result is significantly more constrained due to the conditioning on head observations.

7. Sensitivity of the GLUE Parameter, *N*

[21] Part of the difficulty inherent in using the GLUE methodology is the subjectivity inherent in choosing a value for the parameter, *N* [*Gupta et al.*, 1998; *Thiemann et al.*, 2001; *Beven and Freer*, 2001]. The *N* parameter is often referred to as a likelihood shape factor, which, according to *Beven and Freer* [2001], "can be used to control the shape of the distribution of simulated variables and resulting prediction quantiles." Increasing the value of *N* decreases the prediction uncertainty, while decreasing *N* places a more uniform weight on each realization, similar to standard Monte Carlo analysis. This is illustrated in Figure 7, which shows changes in the 95% confidence interval for the three different input parameters as the value of *N* is changed. The Monte Carlo result (dotted line) is independent of the *N* parameter, and thus stays constant. The prediction uncertainty in each parameter tend toward zero as *N* increases and more weight is placed on the "best" realization(s). Table 2 shows that when $N = 1$ the GLUE 95% confidence interval of the vertical anisotropy ratio and interbasin flow parameters are essentially equivalent to the Monte Carlo 95% confidence intervals. The reason for this is well illustrated in Figures 7b and 7c. When $N = 1$, the GLUE result has already converged to the Monte Carlo solution where all realizations are equally weighted. However, at higher values of N the vertical anisotropy ratio and interbasin flow parameters place more weight on the best fit parameter sets (Figures 7b and 7c).

[22] The next section presents a derivation for an alternative estimator for the GLUE parameter, *N*. This is

Table 3. Comparison of the Monte Carlo and GLUE (when $N = 1$) Areas of the Capture Zone Between the 0.025 and 0.975 Probabilities[a]

	0.025 < Area < 0.975
Monte Carlo	36,413,989
GLUE $N = 1$	34,777,957

[a]Area is in m^2.

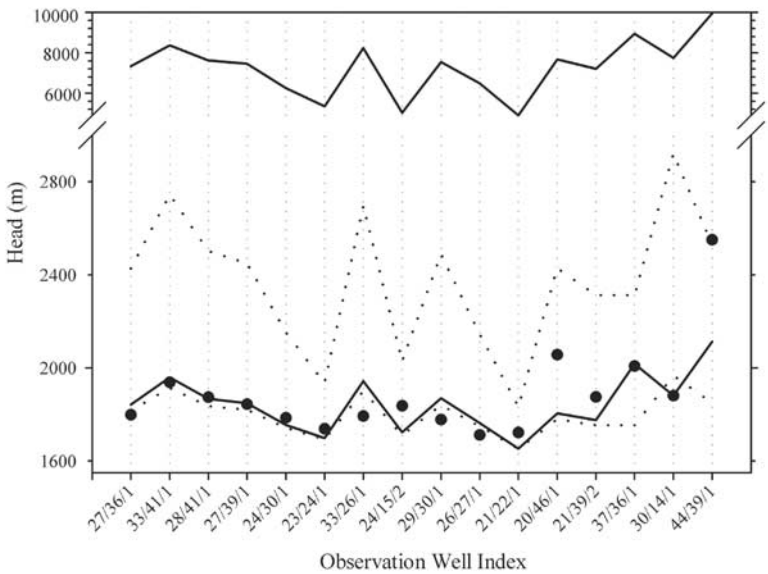

Figure 5. Monte Carlo (solid line) and GLUE (dotted line) (when $N = 1$) 95% uncertainty bounds around 16 head observations (circles). Note that the upper Monte Carlo uncertainty bounds are incredibly high.

followed by a discussion and method for choosing the "best" value of N by using field observations (section 9).

8. An Alternative Likelihood Measure

[23] In their study of Bayesian statistics, *Box and Tiao* [1973] assume a more general exponential density of the errors, rather than a sum of squares error as used in this study:

$$P(\varepsilon) = \omega(\beta)\sigma^{-1} \exp\left[-c(\beta)\left|\frac{\varepsilon}{\sigma}\right|^{2/(1+\beta)}\right] \qquad (9)$$

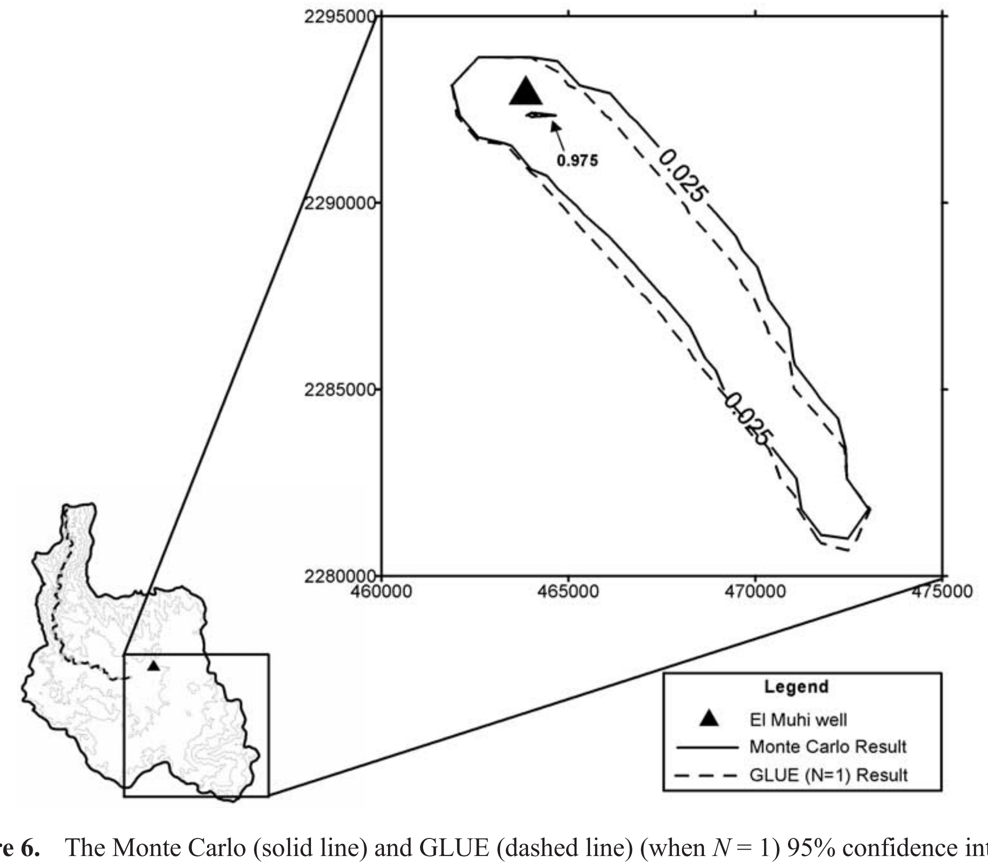

Figure 6. The Monte Carlo (solid line) and GLUE (dashed line) (when $N = 1$) 95% confidence intervals ($0.025 < P < 0.975$) for the capture zone of El Muhi (triangle). The GLUE procedure produces a smaller capture zone than the standard Monte Carlo approach.

where:

$$c(\beta) = \left(\frac{\Gamma[3/2(1+\beta)]}{\Gamma[1/2(1+\beta)]}\right)^{1/(1+\beta)} \qquad \omega(\beta) = \frac{\{\Gamma[3/2(1+\beta)]\}^{1/2}}{(1+\beta)\{\Gamma[1/2(1+\beta)]\}} \tag{10}$$

ε is the error, σ is the standard deviation of error distribution, and β is a shape parameter indicative of the kurtosis of the error density.

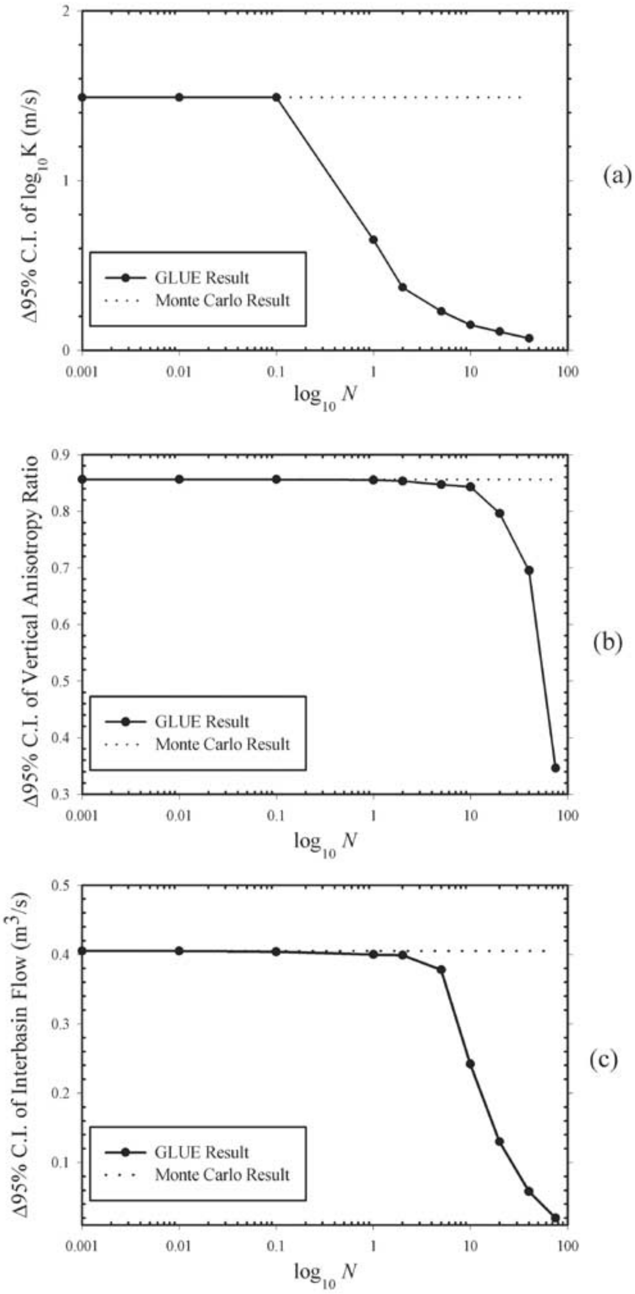

Figure 7. The sensitivity of the GLUE parameter N for three input parameters: (a) hydraulic conductivity, (b) vertical anistropy ratio, and (c) interbasin flow. As N decreases, the GLUE result approaches the Monte Carlo result because realizations are more equally weighted. As N increases, the Δ95% confidence interval (C.I.) becomes smaller as more weight is placed upon the better fitting parameter sets.

Table 4. Comparison of the Monte Carlo and GLUE (When $N = 1$ and When $N = 8$ ($N = 0.5N_{obs}$)) Areas of the Capture Zone Between the 0.025 and 0.975 Probabilities[a]

	0.025 < Area < 0.975
Monte Carlo	36,413,989
GLUE $N = 1$	34,777,957
GLUE $N = 8$	28,742,813

[a]Area is in m^2.

[24] As in section 3.4 of *Box and Tiao* [1973], manipulating the error density (equation 9) and Bayes theorem (equation 3) results in the following form of the posterior density of θ

$$L\left(\vec{\theta}|\beta,\vec{H}\right) = \frac{[M(\theta)]^{-0.5n(1+\beta)}}{C} \tag{11}$$

where

$$M(\theta) = |\varepsilon|^{2(1+\beta)} \tag{12}$$

C is a normalization constant, and n is the number of observations, $i = 1,2,\ldots n$. Note that when β equals 0, $M(\theta)$ reduces to the sum of squares error (equation 2). The parameter, β, varies between -1, where $P(\varepsilon)$ tends toward a uniform density; to 0, where the density is normal; to 1, where the density is double exponential.

[25] With some assumptions, the more generalized *Box and Tiao* [1973] methodology can be compared to the likelihood defined in this study (equations 1 and 2). Assuming $\beta = 0$ (and therefore the errors are assumed to be normally distributed) and the prior distributions are uniformly distributed, the *Box and Tiao* [1973] formulated posterior likelihood of $\vec{\theta}_i$ is

$$L\left(\vec{\theta}_i|\beta,\vec{H}\right) = \frac{1}{C}\left[\frac{1}{E_i}\right]^{0.5N_{obs}} = \frac{1}{C}\left[\frac{1}{E_i}\right]^{-8.0} \tag{13}$$

since $N_{obs} = 16$ head observation points in this study. Therefore the GLUE result is equivalent if the likelihood shape factor, N equals 0.5 N_{obs}. Unfortunately, weighting the inverse of the error by half of the number of observations (equation 13) could lead to overconditioning of the optimum parameter set(s) if a large number of observations exist. Applying $N = 0.5N_{obs}$ to the capture zone modeling of El Muhi well results in a 95% confidence region of the capture zone that is 7.7 km^2 smaller than the Monte Carlo result, and 6.0 km^2 smaller than the $N = 1$ GLUE result (Table 4).

[26] *Feyen et al.* [2001] found that using $N = 0.5\ N_{obs}$ as a likelihood measure in combination with a sum of squares error model (analogous to equation 13) resulted in solutions not converging. In contrast, representative locations from this study were found to converge both when $N = 1$ (Figure 8a), and when $N = 0.5\ N_{obs}$ (Figure 8b).

9. Choice of an Appropriate Likelihood

[27] As indicated by the sensitivity of both the parameter estimation and capture zone prediction, the choice of a likelihood function is critical. *Beven and Freer* [2001]

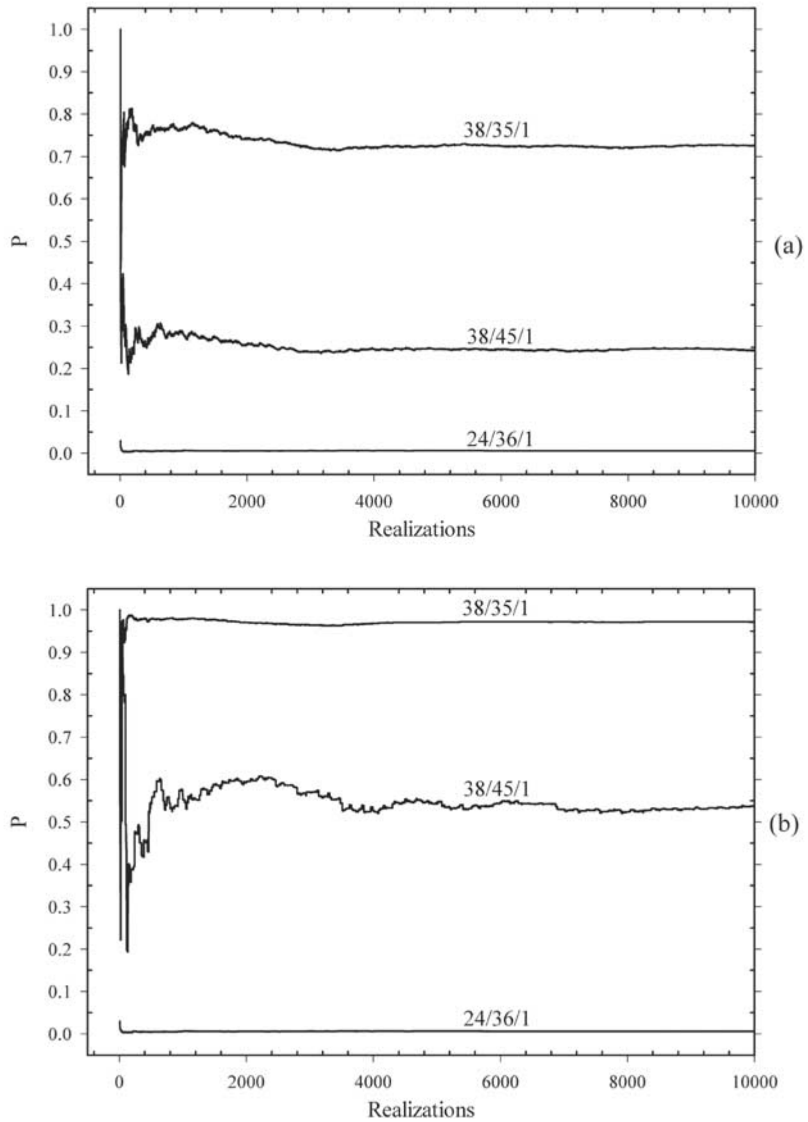

Figure 8. Plots showing stabilization of the probability P of a particle being captured by three starting locations (in cell inidices format $J/I/K$) (a) when $N = 1$ and (b) when $N = 8$. When $N = 1$ (Figure 8a) the probabilities converge to a solution after approximately 3000 realizations. When $N = 8$ (Figure 8b) the probability of starting location 38/45/1 does not converge for approximately 7,000 realizations.

present several options for different likelihood measures. Yet it is still a subjective choice in deciding which to use in the GLUE procedure. A study by *Franks et al.* [1999] attempts to slightly reduce this problem by changing the likelihood shape parameter, N, until the 90% uncertainty quantile encompasses 90% of the observations. This method still requires an assumption of which error model to be used, and requires observations to be compared against.

[28] This study performs a similar methodology to that of *Beven and Freer* [2001] to determine the most appropriate value for N. This is accomplished by changing N in order to maximize the number of head observations that fall within the GLUE 95% confidence interval of simulated head values. A weighted sum of squares error function is still assumed to be the objective function (equation 2). Interestingly, the head observations are best encompassed by the 95% confidence interval of the observed heads when $0.176 < N < 1.692$. Therefore for this study, it appears that the more conservative $N = 1$ is more appropriate than using the measure derived in section 8, where $N = 0.5N_{obs}$.

10. Conclusions

[29] The primary goal of this study was to determine the capture zone of the arsenic-contaminated well, El Muhi, in rural Mexico. Because of the large uncertainty in the input parameters to model such a situation, a stochastic methodology was used. Two stochastic techniques were performed and then compared, standard Monte Carlo analysis and the GLUE methodology. The GLUE methodology is implemented in the same manner as standard Monte Carlo analysis (uniform random sampling), but incorporates the goodness of fit of realizations. The goodness of fit is evaluated using the Bayesian concept of a likelihood function. For this groundwater flow and particle-tracking model, the goodness of fit (the likelihood) is a function of

how well each parameter set (each realization) fits the observed heads. Incorporating this extra information reduces the uncertainty in parameter estimation and in prediction of the capture zone location and size.

[30] Four model input parameters are treated as random variables: hydraulic conductivity, vertical anisotropy, interbasin flow, and porosity. Hydraulic conductivity is significantly more sensitive than the other parameters with a GLUE mean of $10^{-6.59}$ m/s. Better model fits are also seen toward vertically isotropic conditions, and with the principal component of inflow to the basin from interbasin flow (as opposed to recharge). The sensitivity of porosity is not able to be assessed because the simulated heads are not a function of porosity.

[31] Confidence intervals of the capture zones for El Muhi well are presented based on standard Monte Carlo analysis and the GLUE methodology. As expected with the inclusion of the head observations in the GLUE methodology, the GLUE-derived capture zone is significantly smaller than what a standard Monte Carlo approach would predict.

[32] Using the GLUE methodology entails making some assumptions, but those assumptions can be constrained through matching model-simulated output with observations. The choice of a likelihood function in this study was calculated by how well the confidence regions of simulated heads encompassed the 16 observed heads. By conditioning the fit of each parameter set on the observation data, the GLUE methodology combines the ability to take into account parameter uncertainty (standard Monte Carlo analysis) with the value of information. This enables modelers to make predictions not just based on parameter uncertainty, but also on the ''realism'' of the model. Further field examples will illustrate the power of this technique in capture zone prediction and many other disciplines.

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References

Armienta, M. A., R. Rodriquez, A. Aguayo, N. Ceniceros, G. Villasenor, and O. Cruz, Arsenic contamination of groundwater at Zimapan Mexico, *Hydrogeol. J.*, *5*, 39–46, 1997.

Armienta, M. A., G. Villasenor, R. Rodriguez, L. K. Ongley, and H. Mango, The role of arsenic-bearing rocks in the groundwater pollution at Zimapan Valley, Mexico, *Environ. Geol.*, *40*, 571–581, 2001.

Bair, E. S., C. M. Safreed, and E. A. Stasny, A Monte Carlo-based approach for determining traveltime-related capture zones of wells using convex hulls as confidence regions, *Ground Water*, *29*(6), 849–855, 1991.

Bear, J., and M. Jacobs, On the movement of water bodies injected into aquifers, *J. Hydrol.*, *3*, 37–57, 1965.

Beven, K. J., and A. M. Binley, The future of distributed models: Model calibration and uncertainty prediction, *Hydrol. Processes*, *6*, 279–298, 1992.

Beven, K. J., and J. Freer, Equifinality, data assimilation, and uncertainty estimation in mechanistic modeling of complex environmental systems using the GLUE methodology, *J. Hydrol.*, *249*, 11–29, 2001.

Box, G., and G. Tiao, *Bayesian Inference in Statistical Analysis*, John Wiley, New York, 1973.

Buckley, K. M., A. M. Binley, and K. J. Beven, Calibration and predictive uncertainty estimation of groundwater quality models: Application to the Twin Lake Tracer Test, in *Groundwater Quality Management: Proceedings of the GQM 3 Conference Held in Tallinn, September 1993*, *IAHS Publ.*, *220*, 205–214, 1994.

Feyen, L., K. J. Beven, F. De Smedt, and J. Freer, Stochastic capture zone delineation within the generalized likelihood uncertainty estimation methodology: Conditioning on head observations, *Water Resour. Res.*, *37*(3), 625–638, 2001.

Franks, S. W., and K. J. Beven, Bayesian estimation of uncertainty in land-atmosphere flux predictions, *J. Geophys. Res.*, *102*, 23,991–23,999, 1997.

Franks, S. W., K. J. Beven, and J. H. C. Gash, Multi-objective conditioning of a simple SVAT model, *Hydrol. Earth Syst. Sci.*, *3*(4), 477–489, 1999.

Franzetti, S., and A. Guadagnini, Probabilistic estimation of well catchments in heterogeneous aquifers, *J. Hydrol.*, *174*, 149–171, 1996.

Freer, J., K. J. Beven, and B. Ambroise, Bayesian estimation of uncertainty in runoff prediction and the value of data: An application of the GLUE approach, *Water Resour. Res.*, *32*, 2161–2173, 1996.

Guadagnini, A., and S. Franzetti, Time-related capture zones for contaminants in randomly heterogeneous formations, *Ground Water*, *37*(2), 253–260, 1999.

Gupta, H. V., S. Sorooshian, and P. Yapo, Toward improved calibration of hydrologic models: Multiple and noncommensurable measures of information, *Water Resour. Res.*, *34*, 751–763, 1998.

Kuczera, G., and E. Parent, Monte Carlo assessment of parameter uncertainty in conceptual catchment models: The Metropolis algorithim, *J. Hydrol.*, *211*, 69–85, 1998.

McDonald, M., and A. Harbaugh, A modular three-dimensional finite-difference ground-water flow model, *U. S. Geol. Surv. Techniques Water Resour. Invest.*, 1988.

Morse, B. S., Comment on ''The role of arsenic-bearing rocks in groundwater pollution at Zimapan Valley, Mexico'' by Armienta and others [*Environmental Geology 40*(4/5)], *Environ. Geology*, *41*, 241–243, 2001.

Pollock, D. W., Users guide for MODPATH/MODPATH-PLOT, version 3: A particle tracking post-processing package for MODFLOW, the US Geological Survey finite-difference ground-water flow model, *U. S. Geol. Surv. Open File Rep., 94-464*, 1994.

Thiemann, M., M. Trosset, H. Gupta, and S. Sorooshian, Bayesian recursive parameter estimation for hydrologic models, *Water Resour. Res.*, *37*(10), 2521–2535, 2001.

van Leeuwen, M., C. B. M. te Stroet, A. P. Butler, and J. A. Tompkins, Stochastic determination of well capture zones, *Water Resour. Res.*, *34*(9), 2215–2223, 1998.

Varljen, M. D., and J. M. Shafer, Assessment of uncertainty in time-related capture zones using conditional simulation of hydraulic conductivity, *Ground Water*, *29*, 737–748, 1991.

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