

1 **Predicting the Tails of Breakthrough Curves in Regional-scale Alluvial**

2 **Systems**

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7 **Abstract** The late tail of the breakthrough curve (BTC) of a conservative tracer in a regional-  
8 scale alluvial system is explored using Monte Carlo simulations. The ensemble numerical BTC,  
9 for an instantaneous point source injected into the mobile domain, has a heavy late tail  
10 transforming from power law to exponential due to a maximum thickness of clayey material.  
11 Haggerty et al.'s (2000) multiple-rate mass transfer (MRMT) method is used to predict the  
12 numerical late-time BTCs for solutes in the mobile phase. We use a simple analysis of the  
13 thicknesses of fine-grained units noted in boring logs to construct the memory function that  
14 describes the slow decline of concentrations at very late time. The good fit between the  
15 predictions and the numerical results indicate that the late-time BTC can be approximated by a  
16 summation of a small number of exponential functions, and its shape depends primarily on the  
17 thicknesses and the associated volume fractions of immobile water in “blocks” of fine-grained  
18 material. The prediction of the late-time BTC using the MRMT method relies on an estimate of  
19 the average advective residence time,  $t_{ad}$ . The predictions are not sensitive to estimation errors in  
20  $t_{ad}$ , which can be approximated by  $L/\bar{v}$ , where  $\bar{v}$  is the arithmetic mean groundwater velocity  
21 and  $L$  is the transport distance. This is the first example of deriving an analytical MRMT model  
22 from measured hydrofacies properties to predict the late-time BTC. The parsimonious model  
23 directly and quantitatively relates the observable subsurface heterogeneity to nonlocal transport  
24 parameters.

25 **Key words:** Solute transport (Physical processes), Stochastic modeling (Monte Carlo methods),  
26 Analytical modeling (Solute transport), Anomalous dispersion, Multi-rate mass transfer,  
27 Breakthrough curve

## 28 **Introduction**

29 The dispersion of conservative solutes in natural porous media is often observed to be  
30 “anomalous,” which typically denotes non-Gaussian plume shapes and/or non-Fickian growth  
31 rates. Either phenomenon may lead to earlier and later arrival of solute at a control plane (i.e.,  
32 the breakthrough curves (BTCs)), than those predicted for a homogeneous medium. Recent  
33 discussions of anomalous laboratory-scale and measured BTCs are given by Benson et al.  
34 (2001), Levy and Berkowitz (2003), Bromly and Hinz (2004), and Klise et al. (2004), among  
35 many others. Anomalous dispersion can be attributed to the long-range dependence (Dagan  
36 1989) and high variance (Fogg 2004) of the permeability field. Because these two conditions are  
37 intrinsic characteristics of typical alluvial systems, a number of detailed studies of anomalous  
38 dispersion have been conducted in alluvial aquifers. Generally speaking, the networks of ancient  
39 stream channels can form preferential flow paths and cause early arrivals in BTCs, while the  
40 surrounding fine-grained aquitard materials sequester the movement of plumes and result in late  
41 tails in BTCs (Fogg et al. 2000; LaBolle and Fogg 2001).

42 Although transport coefficients have been shown numerically to be time-dependent in  
43 alluvial systems by LaBolle and Fogg (2001), the quantitative analyses of tailing behaviors of  
44 BTCs in regional-scale alluvial systems are still needed, especially for practical problems  
45 involving a long time-scale (decades to centuries) and a large space-scale (hundreds to thousands  
46 of meters), such as ground water age dating (Weissmann et al. 2002), vulnerability assessment of  
47 regional aquifers (Fogg et al. 1998), and evaluation of aquifer remediation by pump and treat  
48 techniques (LaBolle and Fogg 2001). Two methods have evolved to simulate the anomalous  
49 transport in highly heterogeneous porous media, using either numerical or analytical approaches.

50 Numerical methods directly simulate aquifer/aquitard structures that might be encountered by  
51 a plume. The transport times depend on the architecture of the modeled subsurface  
52 heterogeneity, which is commonly built according to various statistical models of observed  
53 heterogeneity. In this case, one typically uses the Monte Carlo method to consider a range of  
54 equally probable realizations of the heterogeneity. Thus the numerical approach requires the  
55 generations of many models, and the repeated computation of water flow and solute transport  
56 within these models. Despite of its computational intensity, the Monte Carlo simulation can be  
57 the only applicable tool in capturing solute transport for cases where the available, detailed  
58 subsurface heterogeneity is critical to solute transport and can not be characterized by any  
59 analytical or empirical model. Analytical techniques have been developed to overcome the  
60 computational burdens of the numerical approach, but a simple method of developing and  
61 parameterizing these equations in a predictive mode (in the absence of tracer tests and/or the  
62 Monte Carlo simulations) is lacking.

63 Several closely related analytical methods have been developed to simulate anomalous  
64 dispersion in porous media, especially to capture the heavy tails. Benson et al. (2000) and  
65 Schumer et al. (2003) have applied the analytical solutions of non-local, fractional-order  
66 advection-dispersion equations (fADE) to predict or fit the skewed and power law early- and/or  
67 late-time tails in BTCs. The orders of fractional derivatives characterize the local properties of  
68 heterogeneous media. Dentz et al. (2004) have extended the continuous time random walk  
69 (CTRW) to reproduce late-time BTCs by assigning a transition density to individual particle  
70 motions. The transition densities are due to subsurface heterogeneity, which is analogous to the  
71 fADE method. Because they also attempt to capture the transition of later tails from power law  
72 to exponential, the transition times used in the CTRW are more general, but require additional

73 fitting parameters. These methods have been applied to fitting the BTCs measured in field or  
74 laboratory experiments, in most cases in an empirical manner with limited knowledge of the  
75 heterogeneity of the porous medium. The predictive capability of these methods is limited by the  
76 unclear quantitative relationship between subsurface heterogeneity and main fitting parameters,  
77 which is one of the motivations of this study. Another method proposed by Haggerty and  
78 Gorelick (1995) and Haggerty et al. (2000) attempts to capture the later tail of BTCs in mobile  
79 domains by accounting for multiple rates of mass transfer between mobile and relatively  
80 immobile water. This method has been used for idealized geometries of immobile water, or by  
81 fitting BTCs, but it has not been tested in a predictive mode by examining a realistic,  
82 complicated hydraulic conductivity ( $K$ ) distribution. Wang et al. (2005) extended the multirate  
83 mass transfer (MRMT) approach of Haggerty et al. (2000) to more general, transient flow fields.  
84 They also emphasized the need of tests of the method under realistic field conditions.

85 The purposes of this study are to 1) explore the tailing behaviors of BTCs for anomalous  
86 transport in detailed representations of regional-scale alluvial aquifers; 2) develop applicable  
87 analytical or empirical methods to predict the BTCs given the knowledge of heterogeneities; and,  
88 3) explore the influences of geological properties on BTC tails. Based on these analyses, the  
89 predictability of the BTC tails can be evaluated systematically, which is important for real-world  
90 predictions.

91 The rest of the paper is organized as follows. First, the Monte Carlo method is used to  
92 simulate flow and transport of conservative tracers through an alluvial system based on the data  
93 from the Lawrence Livermore National Laboratory site. The numerical BTCs are used as the  
94 “real” data for the following prediction and fitting. Second, we extend Haggerty et al.'s (2000)  
95 MRMT method to predict the late-time BTC of solutes in the mobile domain, based on the

96 measured thicknesses of low- $K$  zones. To our knowledge, this is the first study that attempts to  
97 systematically parameterize an analytical MRMT model from measured hydrofacies properties  
98 (thicknesses and volume fractions from boring logs) in order to predict the late-time BTCs.  
99 Third, the characteristics of the simulated and predicted BTC are discussed in the context of the  
100 measured subsurface heterogeneity. Finally, in supplementary material (available as part of the  
101 on-line article at <http://www.blackwell-synergy.com>), we develop a multi-channel transport  
102 solution based on the distribution of high- $K$  materials to fit/predict the early tail of the BTCs.  
103 We also discuss the special difficulties associated with these predictions.

#### 104 **Monte Carlo Calculation of Breakthrough**

105 The transition probability geostatistical approach of Carle and Fogg (1996, 1997) is used to  
106 model the spatial variability of aquifer and aquitard units. Their method is based on facies  
107 concepts and reduces the reliance on empirical curve-fitting of hydraulic conductivity  
108 autocorrelation functions. Readily observable geologic attributes in alluvial settings, including  
109 volumetric proportions, mean facies length (e.g., thickness and width), and juxtapositional  
110 tendencies (e.g., fining-upward or -downward), can be incorporated directly into development of  
111 a three-dimensional transition probability/Markov chain model. The Markov chain model, in  
112 turn, is used in a cokriging procedure during conditional sequential indicator simulation and  
113 simulated quenching to generate “realizations” of subsurface facies distribution. The  
114 mathematical details were given by Carle and Fogg (1996, 1997) and the simulation steps were  
115 given by Carle and Fogg (1998). Several interesting applications of this approach are given by  
116 Carle et al. (1998). Note that the transition probability/Markov chain model is calculated by the  
117 matrix exponential

118 
$$T(h_\phi) = \mathbf{exp}(R_\phi h_\phi), \tag{1}$$

119 where  $T$  denotes a matrix of interfaces transition probabilities,  $h_\phi$  is a separation vector along  
120 direction  $\phi$ , and  $R$  is a matrix of transition rates. An eigenvalue analysis showed that the  
121 Markov chain model for each entry in  $T(h_\phi)$  consists of a linear combination of exponential  
122 structures (Weissmann et al. 1999), some of which may have complex rate coefficients  
123 indicating cyclicity. Thus the Markov chain potentially may model structures with non-  
124 exponentially decaying autocorrelation (Carle and Fogg 1997).

125 Four hydrofacies: debris flow, floodplain, levee, and channel (Table 1), were identified from  
126 detailed interpretations of 5,500m of core taken from an alluvial system at the Lawrence  
127 Livermore National Laboratory (LLNL) site (also see LaBolle and Fogg, 2001). The LLNL  
128 aquifer system is dominated by fine-grained sediments. The geologic details and the Markov  
129 chain model building procedures were discussed by Carle (1996). This Markov chain model has  
130 been applied to regional-scale transport models by Fogg et al. (1998) and LaBolle and Fogg  
131 (2001). LaBolle et al. (2006) used a similar approach to analyze  $^3\text{H}/^3\text{He}$  fractionation by  
132 diffusion and the effect on ground water age dating. In this study, we made two modifications to  
133 this model. First, we did not use any of the original conditioning data when generating the facies  
134 model, because we wanted to capture the full range of possible spatial variability. Second, we  
135 set up a high- $K$  zone within each heterogeneity model by assigning “hard” conditioning data  
136 consisting of a cluster of high- $K$  channel facies in the source area. This high- $K$  source area is  
137 retained in every aquifer realization and is used as the injection location of contaminants in  
138 solute transport modeling. This is done to emphasize the influence of aquifer/aquitard  
139 interaction as a plume travels, rather than the influence of the injection facies. To obtain  
140 ensemble results, we generated a set of 100 equally probable realizations (one example is shown

141 in Figure 1). Each finite-difference block is  $5 \times 10 \times 0.5$  m in the depositional strike ( $x$ -axis),  
142 depositional dip ( $y$ -axis), and vertical ( $z$ -axis) directions. The overall dimensions of the  
143 simulated region are  $405 \times 970 \times 40.5$  m in each direction, with approximately 640,000 cells in the  
144 model domain. The same grid and domain sizes were used in the ground water flow and solute  
145 transport simulations described immediately.

146 The steady-state head and discharge vectors were calculated using MODFLOW (Harbaugh  
147 and McDonald 1996). Each cell was given one of four hydraulic conductivity values based on  
148 the four simulated hydrofacies determined by the geostatistical realization. The value of each  $K$   
149 is equal to the measured average  $K$  for each facies. General head boundary conditions were used  
150 in the modeling to simulate inflow and outflow through the two lateral boundaries of the model,  
151 to minimize the boundary effects on solute transport. Hydraulic head values were defined for the  
152 two lateral boundaries using a general gradient of 0.004 parallel to the stratigraphic dip direction  
153 ( $y$ -axis in Figures 1 and 2). The other boundaries are specified as no-flow conditions (Figure 2).

154 Solute transport is assumed to follow the classical advection-dispersion equation at the small  
155 (local) scale. Transport simulations employed a random walk particle tracking (RWPT) method,  
156 described by LaBolle et al. (1996, 1998, 2000, and 2006) and LaBolle (2006). Particles follow  
157 analytical streamlines for the advective portion of each motion, and we use an isotropic and  
158 constant local-scale dispersivity of 0.01 m and an effective molecular diffusivity of  $5.2 \times 10^{-5}$   
159  $\text{m}^2/\text{day}$ , which are the same values used by LaBolle and Fogg (2001) in a similar study. The  
160 small longitudinal dispersivity was used because previous simulations showed that solute  
161 migration is sensitive to the transverse dispersivity, but insensitive to the longitudinal  
162 dispersivity, due to the dominant effects of geologic variability as represented in the  
163 geostatistical simulations (LaBolle and Fogg 2001). The isotropic dispersivity also optimizes

164 performance of the RWPT algorithm (LaBolle and Fogg 2001; Weissmann et al. 2002). In each  
 165 Monte Carlo realization, 1,000,000 particles were released at a point at  $x = 202.5\text{m}$ ,  $y = 855.0\text{m}$ ,  
 166 and  $z = 19.1\text{m}$  to simulate an instantaneous point source. The injection point is located in the  
 167 middle of the high- $K$  conditioning cluster (Figure 2). Connectivity analysis (Fogg et al. 2000)  
 168 indicates that the high- $K$  cluster is always spatially interconnected and fully percolates in the  
 169 three coordinate directions. Velocity analysis (shown later) demonstrates that the solute  
 170 transport in the high- $K$  cluster is advection dominated, and thus the source is always placed in a  
 171 relatively mobile phase within  $5 \times 10 \times 2.5$  m (the  $x \times y \times z$  size of the high- $K$  cluster) around the  
 172 injection point. The total modeling time is 10,000 yrs, with a 1-yr interval of output. The  
 173 control plane extends through the entire domain perpendicular to the main flow direction (Figure  
 174 2), and in the following analyses we use  $L$  [L] to denote the distance between the point source  
 175 and the control plane. The simulated BTCs were used as “real” data to test the predictions using  
 176 the analytical methods described in the next section.

## 177 **The Analytical MRMT Method to Predict the Late Tail of BTCs**

178 The linear, multiple-rate solute transport equation can be written as follows (Haggerty and  
 179 Gorelick 1995):

$$180 \quad \frac{\partial C_m}{\partial t} + \sum_{j=1}^n \beta_j \frac{\partial C_{im,j}}{\partial t} = S(C_m), \quad (2)$$

181 where  $C_m$  and  $C_{im,j}$  [ $ML^{-3}$ ] represent the solute concentrations in the mobile zone and the  $j$ th  
 182 immobile zone, respectively,  $\beta_j$  [dimensionless] is the capacity coefficient and is the ratio of  
 183 contaminant mass in the  $j$ th immobile zone to the total mass in the mobile zone at equilibrium,  
 184 and  $S()$  is the linear operator in space representing the advection, dispersion and fluid

185 sources/sinks in the mobile domain. This equation assumes that 1) the contamination is initially  
 186 placed in the mobile phase (Schumer et al. 2003; Wang et al. 2005), and 2) the porosity does not  
 187 change with space. Chemical sorption is not modeled in this study. Also note that the  
 188 classification of immobile zone capacity coefficients in this study depends on the volumes of  
 189 “blocks” of material with relatively immobile ground water. The rate of mass transfer between  
 190  $C_m$  and each  $C_{im,j}$  can be described by a first-order rate mass transfer model:

$$191 \quad \frac{\partial C_{im,j}}{\partial t} = \alpha_j (C_m - C_{im,j}), \quad (3)$$

192 which has a solution of exponential decay, at rate  $\alpha_j [T^{-1}]$ , of  $C_{im,j}$  for some spike of  
 193 concentration that is placed in an immobile phase surrounded by clean mobile water.

194 The summation term in the left-hand side of (2) denotes the change of concentration in  
 195 immobile zones due to the divergence of advective and dispersive flux of a mobile phase, and it  
 196 can be expressed as a convolution of the form (Haggerty et al. 2000; Schumer et al. 2003)

$$197 \quad \sum_{j=1}^n \beta_j \frac{\partial C_{im,j}}{\partial t} = g(t) * \frac{\partial C_m}{\partial t}, \quad (4)$$

198 where the symbol  $*$  denotes convolution, and  $g(t) [T^{-1}]$  is a “memory function” defined  
 199 (subsequently) by the proportion of immobile porosity represented by each rate coefficient. By  
 200 placing (4) into (2), the mobile solute concentration can often be solved when  $g(t)$  is known. An  
 201 approximation of the mobile zone breakthrough at some distance  $L$  that is valid for large time is  
 202 given by Haggerty et al. (2000):

$$203 \quad C_m(L, t_{late}) \approx t_{ad} \left( C_0 g - m_0 \frac{\partial g}{\partial t_{late}} \right), \quad (5)$$

204 where  $t_{ad} [T]$  is the average advective residence time of conservative solute in porous media,  $C_0$   
 205  $[ML^{-3}]$  is the initial concentration in the mobile phase, and  $m_0 [MTL^{-3}]$  is the zeroth temporal

206 moment of the breakthrough curve. For equation (5) to be valid, the observation time  $t_{late}$  must  
 207 be much larger than the sum of the mean advection time across the control plane  $L$  and the  
 208 standard deviation of that advection time (Haggerty et al. 2000). The memory function is a  
 209 weighted sum of the exponential decay from individual immobile zones (Haggerty et al. 2000):

$$210 \quad g(t) = \int_0^\infty \alpha b(\alpha) \exp(-\alpha t) d\alpha = \sum_{j=1}^n \beta_j \alpha_j \exp(-\alpha_j t), \quad (6)$$

211 where  $b(\alpha) = \sum \beta_j \delta(\alpha - \alpha_j)$  is a density function of first-order rate coefficients  $[T]$ . After  
 212 inserting (6) into (5), we get the mobile solute concentration at later time after a pulse injection  
 213 into the mobile zone with zero initial concentration

$$214 \quad C_m(L, t_{late}) \approx t_{ad} m_0 \sum_{j=1}^n \beta_j \alpha_j^2 \exp(-\alpha_j t_{late}). \quad (7)$$

215 Thus the mobile solute BTC at a control plane at later time is largely dictated by the sum of  
 216 diffusion times out of all immobile domains between the point of injection and the control plane  
 217 (see also the discussion in Haggerty et al. 2000).

218 We will apply equation (7) to predicting the “real” resident concentration of the mobile  
 219 solute at the later time simulated by the Monte Carlo method. To do this, we first need to define  
 220 the parameters  $\alpha_j$  and  $\beta_j$  in (7). The  $\alpha_j$  and  $\beta_j$  were defined to characterize the  $j$ th class of  
 221 immobile zone. Exact expressions for the multirate series of  $\alpha$  and  $\beta$  have been proposed and  
 222 tested by Haggerty and Gorelick (1995) and Haggerty et al. (2000) for various idealized  
 223 immobile zone geometries including spheres, cylinders and layers. Although their series cannot  
 224 be used directly in this study due to the irregular geometry and the mixed scales of real-world  
 225 immobile zones, the general principals can be followed here. Haggerty and Gorelick (1995)  
 226 defined  $\alpha_j$  to be proportional to  $D^*/R^2$ , where  $R [L]$  is the distance from the center to the edge of

227 the immobile zone. Here we approximate each rate  $\alpha_j$  by the inverse of the mean residence  
 228 time of a particle, which is primarily controlled by the shortest dimension of an immobile block,  
 229 taken here to be the vertical thickness:

$$230 \quad \alpha_j = D^* / z_j^2, \quad (8)$$

231 where  $z_j$  [L] is the thickness of the  $j$ th class (defined below) of fine-grained sediment. In this  
 232 study, the immobile block is defined as a cluster composed of floodplain facies in the uniform  
 233 hydrofacies model. This definition is consistent to the conclusion of LaBolle and Fogg (2001),  
 234 who find that the diffusion tends to dominate transport in low-permeability floodplain deposits in  
 235 a similar hydrofacies model. Flow models discussed above also show that the simulated  
 236 velocities within floodplains are significantly small (with an upper limit around  $1 \times 10^{-5}$  m/day).

237 The capacity coefficient should be proportional to the ratio of contaminant mass in the  
 238 immobile zone to the total mass in the mobile zone at equilibrium:

$$239 \quad \beta_j = \frac{(R_{im})_j (\theta_{im})_j}{R_m \theta_m}, \quad (9)$$

240 where  $(R_{im})_j$  and  $R_m$  [dimensionless] are the retardation factors for the immobile zones and the  
 241 mobile zone, respectively. Here the porosities refer to the ratio of the volume of water in each  
 242 phase to the total volume of the porous media. In this study, only conservative solutes were  
 243 considered, and the porosity within each phase is assumed to be constant. Therefore, the  
 244 porosities in (9) can be converted to the volume fractions of any phase in the aquifer. This  
 245 simplified  $\beta_j$ , which is proportional to the volume fraction of the immobile block, was then  
 246 used:

$$247 \quad \beta_j = f_j \beta_{tot} = \frac{(V_{im})_j}{V_{im}} \beta_{tot}, \quad (10)$$

248 where  $f_j = (V_{im})_j / V_{im}$  [dimensionless] denotes the volume fraction (relative to the volume of the  
249 immobile facies) of the  $j$ th immobile zone, and  $(V_{im})_j$  and  $V_{im}$  [ $L^3$ ] are the volumes of each class  
250 of immobile zone and the total immobile facies, respectively. Any number of classification  
251 schemes could be used to divide the fine-grained units. Here we define 28 classes up to 14 m  
252 thick, in 1/2 m intervals (Figure 3), so that  $z_j$  in (8) varies from 0.5 m to 14 m with  $j$  from 1 to  
253 28. The immobile zones are classified by their thicknesses, because the immobile blocks with  
254 the same thickness have roughly the same mass transfer rate, and the capacity coefficient  $\beta_j$  can  
255 be regarded as the weighting function assigned to each associated rate coefficient  $\alpha_j$  (Haggerty  
256 and Gorelick 1995). The sum of  $\beta_j$  is not 1, but  $\beta_{tot}$ , although in this study,  $\beta_{tot} = V_{im} / V_m \approx 1$ .  
257 This definition is different from Wang et al. (2005), in which  $\sum \beta_j = 1$ . Note that the parameters  
258 for the memory function may be estimated by looking at the geometrical characteristics of the  
259 diffusion-limited (low- $K$ ) zones. In particular, we use information that may come from the  
260 boring logs, because the thicknesses of individual fine-grained units define both the volume  
261 proportions and effective rate coefficients. The only unknown parameter in the BTC prediction  
262 (7) is the mean advection time  $t_{ad}$ . We address this after the next section.

263 The numerical BTC and the analytical MRMT model developed in this study are limited to  
264 conservative tracers. For a reactive tracer with a linear sorption or first-order decay (such as  
265 radioactive decay, first-order biodegradation or hydrolysis), the formula (7) with simple  
266 modification of transport parameters (as shown by equations (1) and (6) in Haggerty et al.  
267 (2000)) or linear decay of mass may still be used to approximate the late-time BTC. Variable  
268 retardation and/or porosity in different fine-grained facies can also be easily incorporated into the  
269 calculation of  $\beta_j$  in (9). For complex reactions, however, the chemical action term should be

270 added into the governing equation (1) and then transferred into the late-time concentration  
271 approximation (7). A non-conservative tracer is beyond the scope of this study, and we leave it  
272 for a future study.

## 273 **Numerical Results**

274 The ensemble BTC from the Monte Carlo simulations are characterized by three primary  
275 features:

276 1) Due to the exponential decay of the transition probabilities, the pdfs of the simulated  
277 immobile zone thicknesses are approximately exponential, with a greater number of thin blocks  
278 than thick ones (Figure 3). A similar trend is observed in the drillers' logs, although there is  
279 more noise in the measured pdf (small rectangles in Figure 3) and higher probability of thicker  
280 aquitard layers. The similarity of the simulated and measured pdfs indicates that the aquifer  
281 realizations capture most of the statistical properties of the observed heterogeneity (i.e., thickness  
282 of clayey materials). Most importantly, it implies the possibility of predicting the late-time  
283 solute transport directly from the measured heterogeneity without the burden of explicitly  
284 modeling the aquifer heterogeneity, ground water flow, and solute transport.

285 2) The ensemble numerical BTCs are positively skewed with a steep, Gaussian-like early tail  
286 and a heavy late tail (Figure 4). The late-time tail transforms gradually from power-law to  
287 exponential at approximately 1,000 years. In our simulations, the slope of the log-log power-law  
288 late-time BTC of  $C_m$  is always around  $-2$ , no matter how distant the control plane is (Figure 4).  
289 However, the length of the power law section in BTCs decreases when the control plane distance  
290 increases.

291 3) At later time, the immobile solute BTCs are very close to the total solute BTCs (not shown  
292 here), while the mobile solute BTCs have a power law slope 1 steeper than the immobile and  
293 total solute BTCs. This differential slope is expected (Schumer et al. 2003) when the memory  
294 function has a power law tail.

295 In all 100 realizations, the velocity at the source cell is  $3.6 \times 10^{-2} \pm 1.7 \times 10^{-2}$  m/day, which is  
296 advection-dominated. Also note that 100 Monte Carlo simulations required 120 hours using SGI  
297 Altix 3000 superclusters, with 18 1.3Ghz Itanium2 CPUs and 72 Gigabytes RAM  
298 (<http://www.aces.dri.edu:8888/sgi-altix.jsp>). The same simulations would require months on a  
299 personal computer with single CPU. This computational burden motivates our search for simple  
300 analytical predictions of ensemble BTC, based on simple measures of the random thicknesses of  
301 the relatively mobile and immobile hydrofacies.

### 302 **Late Tails of Breakthrough Curves**

303 Because we use a control plane at distance  $L$  to construct the BTC, we have the ability to  
304 calculate several different concentrations at any time. First, we can count the number of random  
305 walkers (particles) in the very near vicinity of the plane, regardless of the facies containing the  
306 particles. This is denoted  $C_{R,total}$ : the total resident concentration. We can also distinguish  
307 between the mobile facies and immobile facies particles, and we are particularly interested in the  
308 mobile resident concentration, denoted  $C_{R,m}$ . We can further distinguish between particles that  
309 have crossed the plane irrevocably, as opposed to particles that have diffused back across the  
310 plane, primarily from molecular diffusion but also from the Brownian motion approximation of  
311 macrodispersion. Particles that move irrevocably across the plane are counted as the flux, rather  
312 than the resident, concentration. The flux concentration may also be present in mobile or

313 immobile facies. The distinction between resident and flux concentration is very important,  
314 because the two may differ by orders-of-magnitude, and different field measurement methods  
315 will tend toward one or another. For example, a lightly purged monitoring well will measure the  
316 resident concentration (also primarily the mobile phase), while a production well measures a flux  
317 concentration, because solute particles are removed from the well and cannot move back into the  
318 formation. Excellent discussions of the relationship between flux and resident concentrations for  
319 classical dispersion are given by Kreft and Zuber (1978) and Toride et al. (1995). Zhang et al.  
320 (2006) extended these analyses to some anomalous cases.

### 321 ***Prediction of Late Tails***

322 As discussed above, the only unknown parameter in the BTC late tail prediction (7) is the  
323 mean advection time  $t_{ad}$ . In a typical alluvial aquifer system, the mean velocity of solutes may  
324 be closer to the arithmetic mean velocity (denoted as  $\bar{v}$ ) than other, smaller, mean velocities  
325 (such as the geometric or harmonic mean), due to the preferential transport of solutes within  
326 paths composed of interconnected high- $K$  materials. Solute also may move much faster than the  
327 upscaled (average) pore-water velocity in a heterogeneous porous medium, especially when the  
328 medium is dominated by low-permeable sediments. The upscaling of velocity is actually a  
329 process of assigning unevenly distributed water fluxes evenly along a cross-section  
330 perpendicular to the main flow direction. The solutes, however, usually move preferentially  
331 within along sparse but spatially interconnected channels in alluvial systems. Therefore, as a  
332 first approximation, the largest mean (arithmetic) of the thickness-weighted average  $K$  values can  
333 be used to estimate  $\bar{v}$  and  $t_{ad}$ .

334 To test this hypothesis, we estimated  $t_{ad}$  by calculating  $\bar{t} = L/\bar{v}$  based on the simulated  
335 distributions of hydrofacies. Using this value of  $\bar{t}$ , along with the memory function  $g(t)$  built by

336 equation (6), the prediction is remarkably close to the “real” BTC (Figure 5(b)). Another  
337 estimated velocity, the “peak velocity” denoting the local water velocity (which can be measured  
338 in the field) at the injection point, is also tested here (Figure 5(a)). Although the *a priori*  
339 estimated  $t_{ad}$  based on this velocity is about  $\sim 3$  times smaller than  $\bar{t}$ , the analytical model still  
340 provides a reasonable prediction of late-time BTC (Figure 5(b)). This is because the general  
341 trend of the BTCs is not sensitive to the exact value of  $t_{ad}$ . Even when the estimation error is  
342 one order-of-magnitude higher or lower than the best-fit one (discussed below), the predicted  
343 late-time BTC can still capture the general behavior of the “real” late tail of the ensemble BTC.

344 In the field, we can estimate the upper and lower limits of  $t_{ad}$ . Wells in the source area, if  
345 present in high- $K$  material, can be used as the upper limit of tracer velocities (see the “Peak  
346 velocity” in Figure 5(a)). Fluxes at downstream monitoring wells can be calculated too, and the  
347 average flux can be used as the approximate value of  $\bar{v}$ . If one also measures the distribution of  
348 the thicknesses of the low- $K$  material, then the MRMT method provides a good predictive model  
349 of the late-time BTC.

350 The fitted mean advective residence time,  $t_{ad}$ , increases with the increase of distance and  
351 asymptotically reaches the time corresponding to  $\bar{v}$ , the arithmetic mean of ground water  
352 velocities in the whole model domain (Figure 5(a)), supporting the use of the simple analytical  
353 model. If the control plane distance,  $L$ , is more than approximately four times longer than the  
354 mean length of the channels, then a quick approximation of the mean advection time is  
355  $t_{ad} = \bar{t} = L / \bar{v}$ .

356 ***Influence of Immobile Zone Thicknesses on Late Tails***

357 The best-fit BTCs using the multiple-rate mass transfer method match the numerical late-  
358 time BTCs of solutes in mobile domain extremely well (Figure 5(c)). The analytical models  
359 capture the transition time of the BTC from power law to exponential, if one is allowed to  
360 empirically fit the advection time  $t_{ad}$ . The immobile blocks with different thicknesses and  
361 volume proportions (i.e., pdfs) have different contributions to the ensemble average of BTCs  
362 (Figure 5(c)).

363 The thicknesses and the associated volume fraction density of immobile blocks control the  
364 slope and the transition period of the late-time BTCs. Equation (7) and the fitting results (Figure  
365 5(c)) indicate that solute concentrations can be very closely approximated by a summation of  
366 exponential functions (i.e.,  $\exp(-\alpha_j t_{late})$ ) with specific weights. The exponential functions  
367 themselves depend on the size (thickness) of immobile blocks, and the specific weight of each  
368 function depends on the probability (or in the case of a single or real-world realization) volume  
369 fraction of layers of a certain thickness.

370 When tracers originating from mobile zones diffuse into a thin immobile layer, they can exit  
371 and diffuse back into the mobile zones relatively quickly. Then these tracers may reach the  
372 control plane relatively early and form the early part of late-time BTCs. On the contrary, it takes  
373 much longer for the tracers to hit the control plane if they enter a much thicker immobile zone.  
374 The thick immobile blocks dominate the latest section of the BTCs, especially the period that the  
375 tail transfers gradually from power law to exponential. Note that as shown by Figure 5(c), the  
376 exponential-part of late tail is not due to the single, thickest immobile block, but a mixture of  
377 several thickest immobile blocks. The lateral boundaries of the numerical model reflected  
378 particles back into the domain, simulating an infinite, mirrored system. An alternative model  
379 might be one where these boundaries are thick aquitards, or porous bedrock so that mass diffuses

380 into and out of these structures. Very often, in numerical studies, these boundaries are aquitards  
 381 with large vertical extent, so the boundaries may greatly influence the latest BTC. In fact, the  
 382 transition from power law to exponential is guaranteed by the finite numerical domain size.  
 383 Thus a typical field site may have an effectively (with respect to the duration of interest) infinite  
 384 reservoir into which solute may be sequestered, so that the power law always persists.

385 The volume fractions of immobile blocks classified by thickness control the slope of the  
 386 power law late-time BTCs. As mentioned before, we get exponential pdfs of immobile block  
 387 thickness and the associated volume fraction by using an exponential-form Markov chain  
 388 transition probability, although the exponential-form transition probability is reported to  
 389 potentially generate nonexponential-looking structures. The constant slope of power law late-  
 390 tails is the result of the summation of exponential functions with an exponential pdf. However,  
 391 the slopes of log-log BTCs observed in field and laboratory tests are not limited to  $-2$ . A reliable  
 392 method, whether Monte Carlo or analytic, should be able to capture a wide range of slopes. To  
 393 address this, we further tested the MRMT method by assuming different pdfs of volume fractions  
 394 of immobile blocks classified by thickness. It is difficult to accurately judge the functional form  
 395 of the pdf of immobile block volumes, especially for the largest blocks. However, a power law  
 396 pdf of immobile block volumes is possible in some systems (and could be used for the histogram  
 397 in Figure 3), so we explore the BTC that would result. If the immobile block volume fraction for  
 398 larger blocks is a power law function of its thickness, i.e.,  $f_j \propto z_j^{-m}$ , then the late-time BTCs  
 399 contain a power law tail of the form (see Appendix in supplementary material):

$$400 \quad C_m(L, t_{late}) \propto t_{late}^{(-m-3)/2} \quad (11)$$

401 for  $t_{late} \ll z_n^2 / D^*$  where  $z_n$  is the size of the largest class (for example, in this study we have  
402  $t_{late} \ll z_n^2 / D^* \approx 10^4$  yr). Thus the summation of exponential functions with power law weights is  
403 itself a power law function for the time  $t \ll z_n^2 / D^*$ . The (power-law part) late tail slope  $C_{R,m}$   
404 calculated by the MRMT method should not be limited to  $-2$ .

405 Becker and Shapiro (2003) observe a slope of  $-2$  in their tests in fractured granite, and  
406 explain it by the presence of a multitude of slow advection channels. In the present case,  
407 however, our low- $K$  zones are clearly diffusion-dominated, with  $K = 4.32 \times 10^{-5}$  m/day (Table 1),  
408 so we conclude that the slope is coincidental.

409 Special caution is needed when using the MRMT method for some cases. For example,  
410 when the immobile blocks have variable thickness but a constant volume fraction pdf (e.g.,  $m = 0$   
411 in (11)), then the mobile power law BTC has a slope of  $-3/2$ . When immobile blocks are  
412 infinite, the  $-3/2$  slope will last forever. When the immobile blocks have similar thickness and  
413 the thickness is small enough, then the late tail of BTC for solutes in all domains remains  
414 exponential (i.e., the solution reverts to the single rate mobile/immobile equation, see Toride et  
415 al. 1995).

416 We envision two further studies concerning the features of late-time BTCs that would be  
417 valuable. First, using different power-law forms of transition probability, we could generate  
418 hydrofacies models with power law distributed thicknesses (and the associated volume fractions)  
419 to investigate the veracity of the analytical equation (11). Second, the alluvial system in this  
420 study is dominated by fine-grained material. It would be instructive to explore the BTCs in a  
421 coarse-grain dominated system (e.g., Weissmann et al. 2002).

422 We note here that the MRMT method has been shown to be functionally equivalent to the  
423 CTRW method (Dentz et al. 2004; Schumer et al. 2003). However, all parameters required by  
424 the MRMT method have obvious geologic meanings, and thus they are easily calculated, fitted,  
425 or even predicted, given the knowledge of subsurface heterogeneity.

#### 426 *Predictability of the Ensemble Average Versus Individual Realizations*

427 Two control planes were selected to illustrate the variability between realizations and the  
428 predictability of the ensemble average BTC with the transport distance. The first plane is 20 m  
429 from the source (Figure 6(a)). The second is 600 m away from the source, almost 10 times larger  
430 than the mean length of all hydrofacies (Figure 6(b)).

431 The predictability of the ensemble average BTC at later time becomes better with an increase  
432 of transport distance (Figure 6). Poor predictability at short distances might be due to the local  
433 spatial variations of hydrofacies between realizations. The hydrofacies distributions generated  
434 by stationary transition probabilities can be non-stationary at a small scale close to the mean  
435 length of hydrofacies. The non-stationarity results in variations of thickness(es) for the thickest  
436 immobile block(s) among realizations. The late-time BTC, therefore, may transform from power  
437 law to exponential at different periods among realizations (Figure 6(a)). The non-stationary  
438 distributions also let different realizations have a different thickness of the thickest channel(s).  
439 The slope of early tail and the peak of BTC, therefore, vary among realizations. On the contrary,  
440 a relatively good predictability at long distances is due to the stationary distributions of  
441 hydrofacies at a scale much larger than the mean length of hydrofacies (Figure 6(b)).

442 We did further tests to check whether a single realization with non-point source could be  
443 used to assess the ensemble BTC without the computational burden. Realization 5 with a point  
444 source produces a BTC significantly different from the ensemble BTC, compared to the other

445 four realizations shown in Figure 6. Hence we selected realization 5 as an example to check  
446 whether it can assess the ensemble BTC. Ten million particles (containing the same mass) were  
447 released on the upstream plane, and the number of particles within each cell in this plane was  
448 scaled by the cell's flux. The particles were almost all in high-permeable cells representing the  
449 mobile phase, because the flux through floodplain cell is significantly small compared to the flux  
450 in mobile cells. The resultant BTC is similar to the ensemble one (see Figure 7), although the  
451 BTC from a single realization has a larger mean advective travel time. Therefore, a single  
452 realization with non-point source may assess the main behavior of ensemble BTC. The larger  
453 mean advective time is probably due to the lack of the conditioning high- $K$  cluster for the cells  
454 located in the upstream plane. Further simulations with more realizations are needed to validate  
455 the above conclusion.

#### 456 ***Transformation between the Late-time Flux and Resident Concentrations***

457 The concentration described by (7) is the resident concentration in the mobile phase. In  
458 applications where the detection/injection mode(s) is different, the distinction between the  
459 resident versus flux concentrations is necessary (c.f., Kim and Feyen 2000). Furthermore, the  
460 determination of risk-based cleanup levels might be most interested in the mobile flux  
461 concentration, which could be many orders of magnitude less than the resident concentration  
462 (Zhang et al. 2006). Because the main focus of this study is to predict the BTC of  $C_{R,m}$ , we only  
463 discuss the transformation briefly.

464 For a mobile/immobile model with a power-law memory function  $g(t) = t^{-\gamma} / \Gamma(1 - \gamma)$   
465 (Schumer et al. 2003), the flux concentration can be transformed directly from its resident  
466 counterpart (Zhang et al. 2006):

467 
$$C_F(x,t) \approx \frac{x\gamma}{vt - x(1-\gamma)} C_R(x,t) \quad . \quad (12)$$

468 However, when the memory function is a summation of exponentials like (6), the transformation  
 469 cannot be derived analytically, except for the single rate transfer model (for example, see the  
 470 transformation given by Toride et al. 1993; 1995). Thus we explore the transformation  
 471 numerically here.

472 Fitting results (represented by the light lines in Figure 4) suggest the following transform  
 473 formula

474 
$$C_{F,m}(x,t_{late}) = b \frac{x}{t_{late}} C_{R,m}(x,t_{late}) \quad , \quad (13)$$

475 where  $C_{F,m}$  denotes the flux concentration in the mobile phase, and the fitting parameter  $b$  [ $TL^{-1}$ ]  
 476 is 0.2 yr/m for all control planes. The transformation (13) may be physically interpreted as the  
 477 actual travel process: it takes a time of  $t$  for the solute with mass  $C_{R,m}(x,t)$  to reach (actually  
 478 cross) location  $x$ . The magnitude of  $b$  may be related to the velocity  $v$  and the memory function  
 479  $g(t)$ , and the best-fit parameter  $b$  may imply the similarity of the transformation (13) to (12).  
 480 Because the slope of the log-log power-law late-time BTC of  $C_{R,m}$  is approximately  $-2$  (see  
 481 Figure 4), the index  $\gamma$  in (12) should be approximately 1 (for details, see Zhang et al. 2006; or  
 482 Schumer et al. 2003). The best-fit value of  $b$ , 0.2 yr/m, is actually very close to the ratio of  $\gamma/v$ .  
 483 So the formula (13) can be regarded as a special case of (12). Future study is needed to test this  
 484 hypothesis and explore the geological meaning of the parameter  $b$ .

485 **Conclusions**

486 1) Monte Carlo simulations show that the transport of conservative tracers in regional-scale  
 487 alluvial aquifer/aquitard systems is non-Fickian (or anomalous), because the ensemble BTC

488 contains a heavy late tail and thus deviates significantly from Gaussian plume. The majority of  
489 the late tail decays according to a power law with a final transition to exponential decay. The  
490 power law decay of the mobile domain BTC is faster than the immobile domain (and the total  
491 domain), with a difference of unity between the slopes on a log-log plot. Furthermore, the BTC  
492 based on the flux concentration also decays faster than the resident concentration, and the  
493 difference in slopes on a log-log plot is also unity.

494 2) The late-time concentration for solutes in the mobile domain can be approximated by a  
495 weighted sum of exponential functions. The shape of the late tail of BTCs depends on the  
496 thicknesses and the associated volume proportions of diffusion-limited layers. This information  
497 can be gleaned from boring logs.

498 3) The late tail of BTCs can be predicted quite accurately using the MRMT method, if we  
499 can estimate the mean advective residence time  $t_{ad}$ , which can be approximated by  $L/\bar{v}$ , where  
500  $\bar{v}$  is the arithmetic mean of ground water velocities. Accurate prediction of the late-time BTC is  
501 relatively insensitive to errors in the estimation of  $t_{ad}$ .

502 4) The difference in breakthrough for each realization, signifying the lack of predictability of  
503 a single particular field setting, is greatest for the early BTC at close distances (see also the  
504 discussion in supplementary material). When the control plane is located a number of mean  
505 facies lengths away from the source, all realizations have similar late-time BTC tails.

506 5) The application of the MRMT method should not be limited to the fine-grain dominated  
507 alluvial system discussed by this study. The MRMT method is appropriate for different pdfs of  
508 immobile block volumes and can simulate different late tails.

509 6) This is the first example of parameterizing an analytical MRMT model from measured  
510 hydrofacies properties (volume fractions of fine-grained layers from boring logs) to predict the  
511 late time BTCs. We anticipate that the extremely parsimonious model developed in this study  
512 may also be used to quantitatively relating the subsurface heterogeneity to nonlocal transport  
513 parameters, such as the empirical waiting time density used in the CTRW formalism.

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613 Figure 1. A three-dimensional view of the heterogeneous model for Monte Carlo realization 1.

614 Figure 2. Schematic of flow system. “GHB” denotes the general head boundary. “NFB” denotes  
615 the no-flow boundary.  $L$  denotes the distance between the point source and the control plane.  
616 The main direction of flow is in the depositional dip direction.

617 Figure 3. Volume fractions of immobile blocks based on their thicknesses: the simulated versus  
618 the measured results from the drillers’ logs. The dashed line denotes the best-fit power-law  
619 trend, with a slope  $-2.3$ .

620 Figure 4. The simulated (symbols) versus the fitted (lines) flux- and resident-concentration based  
621 BTCs in the mobile phase (denoted as  $C_{R, m}$  and  $C_{F, m}$ , respectively) for a control plane located at  
622  $L = 20\text{m}$  (a),  $100\text{m}$  (b),  $200\text{m}$  (c), and  $400\text{m}$  (d). The dark line denotes the fitted  $C_{R, m}$  using the  
623 MRMT formula (7), and the light line denotes the  $C_{F, m}$  transformed from  $C_{R, m}$  using the  
624 transformation (13).

625 Figure 5. (a) The velocity corresponding to the best-fit advective residence time (circles) and  
626 some related velocities. “Peak velocity” denotes the local water velocity at the injection point;  
627 and “Arithmetic mean velocity” denotes the velocity corresponding to the arithmetic mean of  
628 conductivity. (b) The predicted late tails of BTCs using the estimations of  $t_{ad}$  for a control plane  
629 located at  $L=100\text{m}$  on a log-log plot. The 21 yr is the (best) predicted  $t_{ad}$  based on the arithmetic  
630 mean of conductivities. The 8.2 yr represents a prediction based on the “Peak velocity” shown in  
631 (a). The 1.8 yr and 180 yr represents an estimation error as high as one order of magnitude of the  
632 best-fit  $t_{ad}$ . (c) The best-fit late tail of resident concentration based BTC in the mobile phase by

633 the MRMT method for a control plane located at  $L = 100\text{m}$ . In the legends,  $\alpha_1 \sim \alpha_{28}$  represent the  
634 breakthrough associated with each thickness class. The thickness for each  $\alpha_j$  is  $j/2$  meter.

635 Figure 6. The ensemble average of the solute BTCs (dashed line) versus the BTCs of single  
636 Monte Carlo realizations (solid lines) for a control plane located at  $L=20\text{m}$  (a) and  $L=600\text{m}$  (b),  
637 for realizations 1~5 (denoted as R1~R5 in the legend).

638 Figure 7. The simulated BTC of realization 5 using the single point source (solid gray line) or the  
639 multiple source (solid dark line) versus the ensemble average of BTC (dashed line), for the  
640 control planes located at  $L=20$  (a) and  $100$  m (b), respectively. The symbols represent the best-  
641 fit concentrations using the MRMT approach (with different mean advective travel times).

642 Table 1. Hydrofacies properties, including hydrofacies conductivity (m/day), mean length (m),  
 643 and volumetric proportion.

Hydrofacies	Direction and mean length			Proportion	$K$ (m/day)
	Strike (m)	Dip (m)	Vertical (m)		
Debris Flow	8	24	1.1	7%	0.432
Floodplain	27	67	2.1	56%	0.0000432
Levee	6	20	0.8	19%	0.173
Channel	10	50	1.3	18%	5.184

644













