ground water

Review Paper/

Lessons Learned from 25 Years of Research at the MADE Site

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Abstract

Field studies at well-instrumented research sites have provided extensive data sets and important insights essential for development and testing of transport theories and mathematical models. This paper provides an overview of over 25 years of research and lessons learned at one of such field research sites on the Columbus Air Force Base in Mississippi, commonly known as the Macrodispersion Experiment (MADE) site. Since the mid-1980s, field data from the MADE site have been used extensively by researchers around the world to explore complex contaminant transport phenomena in highly heterogeneous porous media. Results from field investigations and modeling analyses suggested that connected networks of small-scale preferential flow paths and relative flow barriers exert dominant control on solute transport processes. The classical advection-dispersion model was shown to inadequately represent plume-scale transport, while the dual-domain mass transfer model was found to reproduce the primary observed plume characteristics. The MADE site has served as a valuable natural observatory for contaminant transport studies where new observations have led to better understanding and improved models have sprung out analysis of new data.

Introduction

Field studies at intensively instrumented research sites have played a preeminent role in the development of contaminant hydrogeology. In particular, tracer experiments conducted at several well-known field sites have provided critical insights and extensive data sets for development and testing of transport theories and mathematical models. These include the sites in Borden, Canada (MacKay et al. 1986); Mobile, Alabama (Molz et al. 1986); Twin Lake, Minnesota (Killey and Moltyaner 1988); Cape Cod, Massachusetts (LeBlanc et al. 1991); Mirror Lake, New Hampshire (Shapiro and Hsieh 1991); and Columbus, Mississippi (Boggs et al. 1992).

Of the sites mentioned in the preceding text, the one that is continuing to perplex and inspire the groundwater transport community is the site located on the Columbus Air Force Base in Columbus, Mississippi, commonly known as the Macrodispersion Experiment (MADE) site. Since the mid-1980s, the data collected at the MADE site have been used extensively by numerous researchers around the world to gain new insights into transport processes in highly heterogeneous aquifers. It has also served as a catalyst for theoretical and computational model development toward more accurate descriptions and predictions of contaminant transport and remediation. Several research projects are currently ongoing at the MADE site to achieve more fundamental understanding of nonideal transport processes and develop new high-resolution site characterization approaches.

This paper is intended to provide an overview of a long line of research work at the MADE site since the mid-1980s and to discuss the most important lessons learned

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over the past 25 years. After this introductory section, Section "A Brief History of the MADE Site" describes the site history and hydrogeological conditions, including all major experiments conducted at the site. Section "Inadequacy of Classical Advection-Dispersion Model" discusses the difficulties encountered in applying the classical advection-dispersion (ADM) model to interpret the tracer test results. Section "Need for Dual-Domain Mass Transfer Model" presents the rationale and simulation results for the dual-domain mass transfer model. Section "A Matter of Connectivity: Role of Small-Scale Preferential Flow Paths" discusses the important role of connected small-scale preferential flow paths and relative flow barriers in controlling solute transport at the site. The final two sections provide a summary and some concluding remarks.

A Brief History of the MADE Site

Figure 1 shows the location of the MADE site located on the Columbus Air Force Base in Mississippi in the southeastern United States. Field work at the MADE site started in 1983, after it was selected by the researchers from the Massachusetts Institute of Technology and Tennessee Valley Authority, to serve as a test location for evaluating macrodispersion theory in a heterogeneous aquifer (Boggs et al. 1990). Field research at the MADE site has continued since then.

The shallow unconfined aquifer which immediately underlies the MADE site consists of alluvial terrace deposits with an average thickness of approximately 10 m. The highly heterogeneous aquifer is composed of poorly sorted to well-sorted sandy gravel and gravely sand with significant amounts of silt and clay. The shallow unconsolidated aquifer is underlain by a continuous clay layer. Figure 2 shows a geological facies model for the MADE site based on geophysical and sedimentological investigations (Bowling et al. 2005). A more detailed description of site conditions is provided in Boggs et al. (1990, 1992) and Zheng (2007).

The spatial distribution of horizontal hydraulic conductivity (K) at the MADE site was first determined on

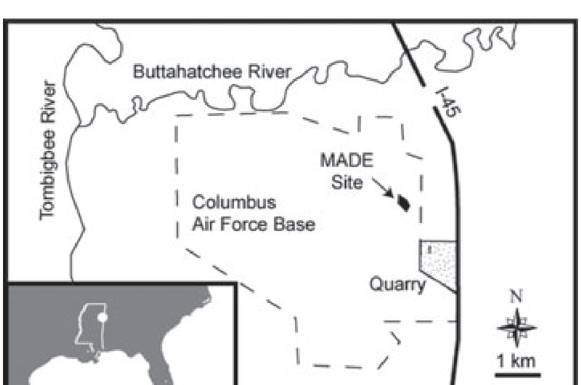

Figure 1. Location of the MADE site in Columbus, Mississippi.

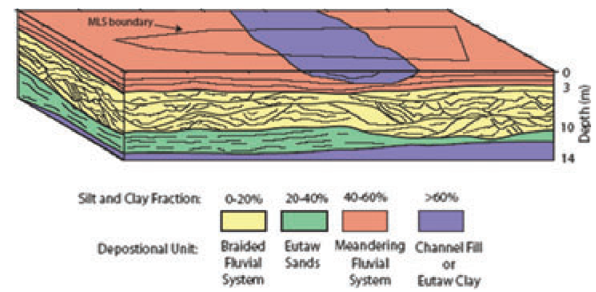

Figure 2. Geological facies model of the MADE site based on geophysical and sedimentological data (Bowling et al. 2005).

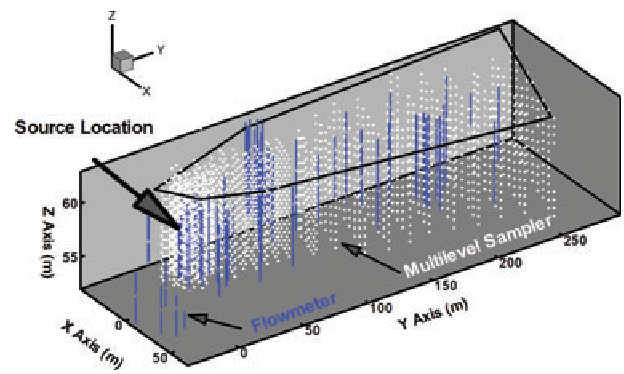

Figure 3. Three-dimensional view of the monitoring network at the MADE site (Zheng and Gorelick 2003). Vertical lines of closely spaced dots indicate the locations of flowmeter wells. Circles indicate the locations of MLS. The direction of groundwater flow is generally parallel to the y axis.

the basis of 2187 measurements obtained from borehole flowmeter tests conducted in 58 fully penetrating wells by Rehfeldt et al. (1992). The locations of these flowmeter test wells are shown in Figure 3. The vertical spacing of K measurements within each flowmeter well was approximately 15 cm. Details of the borehole flowmeter tests are described in Rehfeldt et al. (1992). More flowmeter test wells were added in subsequent studies, resulting in a cumulative total of 3925 measurements from 86 test wells (Boggs et al. 1995; Julian et al. 2001). The geometric mean of the measured horizontal K data is approximately 5×10^{-3} cm/s, but the variations in these data typically range from two to four orders of magnitude at each test well site. The overall variance of the natural logarithm of horizontal K data (LnK) is 4.5 (Rehfeldt et al. 1992), which is significantly greater than that at any previously reported major tracer test sites. For example, the reported variance of LnK is 0.29 for the Borden site (Sudicky 1986), 0.26 for the Cape Cod site (LeBlanc et al. 1991), and 0.031 for the Twin Lake site (Killey and Moltyaner 1988).

Figure 4 shows a three-dimensional (3D) distribution of LnK interpolated through an ordinary kriging (OK) procedure (Deutsch and Journel 1998) from all available flowmeter data. The horizontal hydraulic conductivity varies greatly both within each flowmeter borehole and spatially over the entire tracer experiment site. An overall

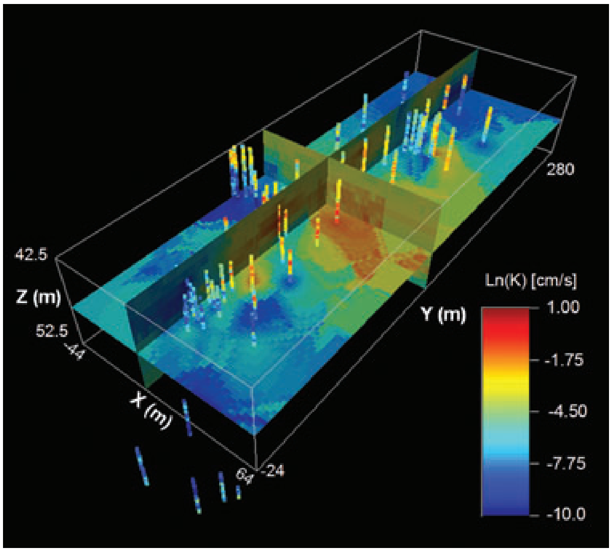

Figure 4. Three-dimensional visualization of the horizontal hydraulic conductivity distribution based on ordinary kriging of the flowmeter data for the MADE site.

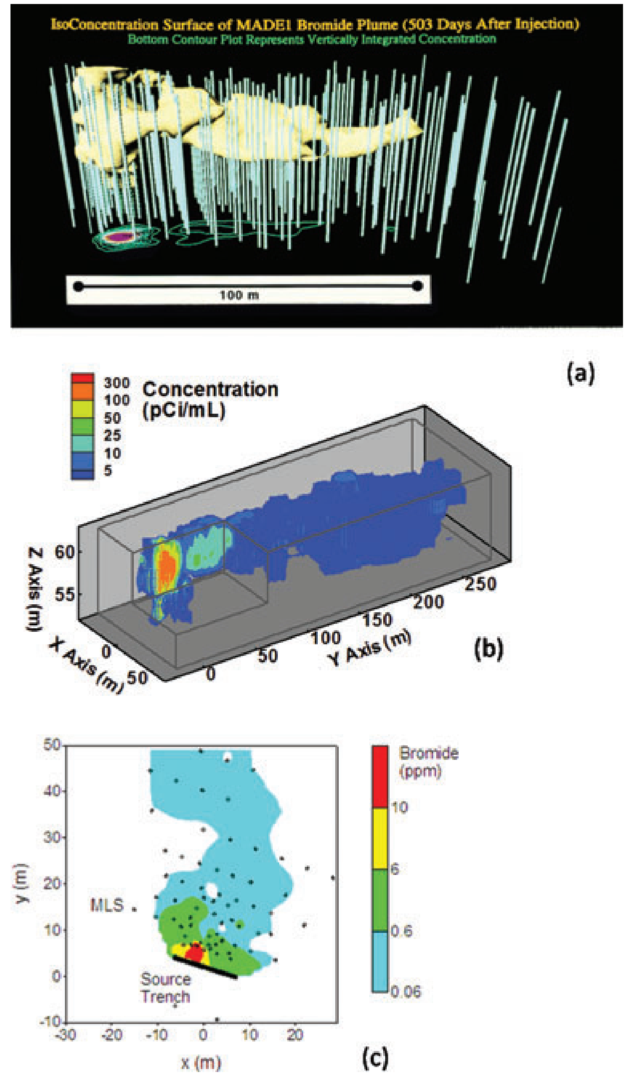

Figure 5. Observed conservative tracer plumes at the MADE site: (a) MADE-1 bromide plume at 503 days after injection (Harvey and Gorelick 2000; Harvey 1996); (b) observed MADE-2 tritium plume at 328 days after injection (Zheng and Gorelick 2003); (c) observed MADE-3 bromide plume at 152 days after trench source release (the 2D contour map is constructed from the peak concentrations at each MLS location [Julian et al. 2001]).

trend is visually apparent from Figure 4. The horizontal hydraulic conductivity is lower near the injection source zone (to the left side of Figure 4), increasing toward the middle of the site, and decreasing again at the downstream end (to the right side of Figure 4).

Three natural-gradient tracer tests were conducted in this aquifer. In the first test (MADE-1, October 1986 to June 1988), conservative tracers including bromide were injected into a linear array of wells over 48 h (Boggs et al. 1990, 1992). The migration of the plume was then monitored through a network of multilevel samplers. Eight sampling events, designed to provide "snapshots" of the plume, were conducted over the test period. One such snapshot (503 days) is shown in Figure 5a. Additional information on the first experiment was provided by Adams and Gelhar (1992) and Boggs and Adams (1992). In the second test (MADE-2, June 1990 to September 1991), tritium was injected into the same array, also over 48 h (Boggs et al. 1993; MacIntyre et al. 1993) and sampled in monitoring wells on five occasions. One of the five snapshots (328 days) is shown in Figure 5b. In the third test (MADE-3, also referred to as the Natural Attenuation Study, December 1995 to September 1997), hydrocarbon- and bromide-coated sand was placed in a trench near the previous injection array (Boggs et al. 1995; Libelo et al. 1997; Stapleton et al. 2000; Brauner and Widdowson 2001; Julian et al. 2001), and sampled six times over 20 months. The snapshot at 152 days is shown in Figure 5c.

A notable characteristic of the bromide and tritium plumes was their highly asymmetric nature (Figures 5a to 5c). In all three natural-gradient tests, the highest concentrations remained close to the source, while portions of the plume spread far beyond the source in diluted concentrations. Methods to model these highly asymmetrical plumes have been the focus of significant discussions and debates within the groundwater research community, as described in the subsequent text.

More recently, the emphasis in MADE site field research has shifted to smaller scale forced-gradient tracer tests to focus more on the examination of the role of preferential flow pathways in controlling solute transport. During a field project in 2004 (referred to hereafter as MADE-4), a new well was drilled and a large amount of water mixed with the dye-tracer brilliant blue FCF was injected into the well (Liu et al. 2010). After a resting period, 20 soil cores were collected from a region within 1.5 m of the injection well (Figure 6a). To preserve the solute and fluid distribution relative to the stratigraphic position within each core, the cores contained in transparent plastic tubing were placed in an onsite freezer filled with dry ice immediately after they were removed

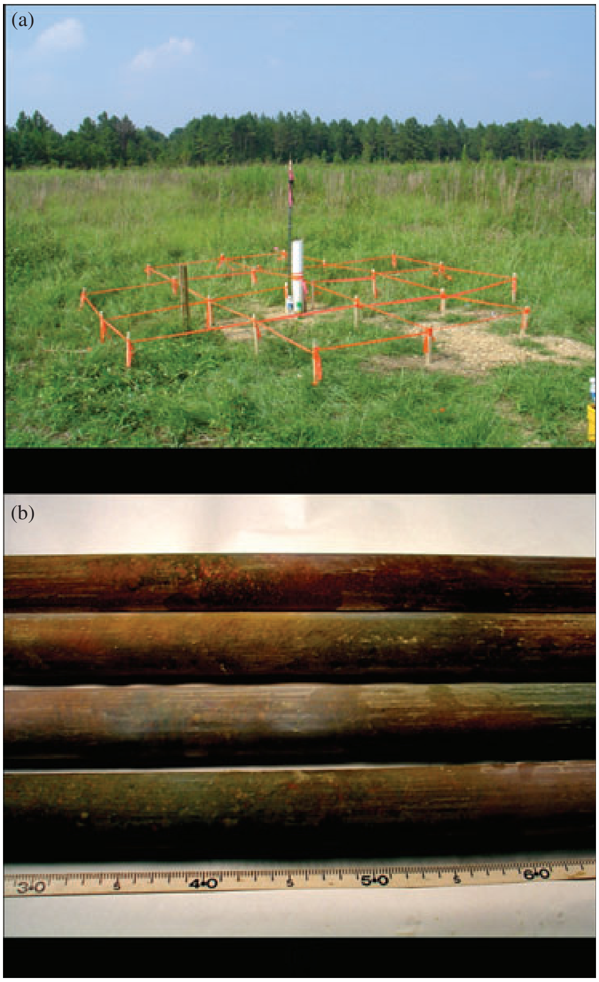

Figure 6. A grid of 20 soil cores collected at the MADE site with a grid spacing of approximately 0.5 m (a); images of selected frozen cores showing stripes of dye-tracer brilliant blue FCF (b).

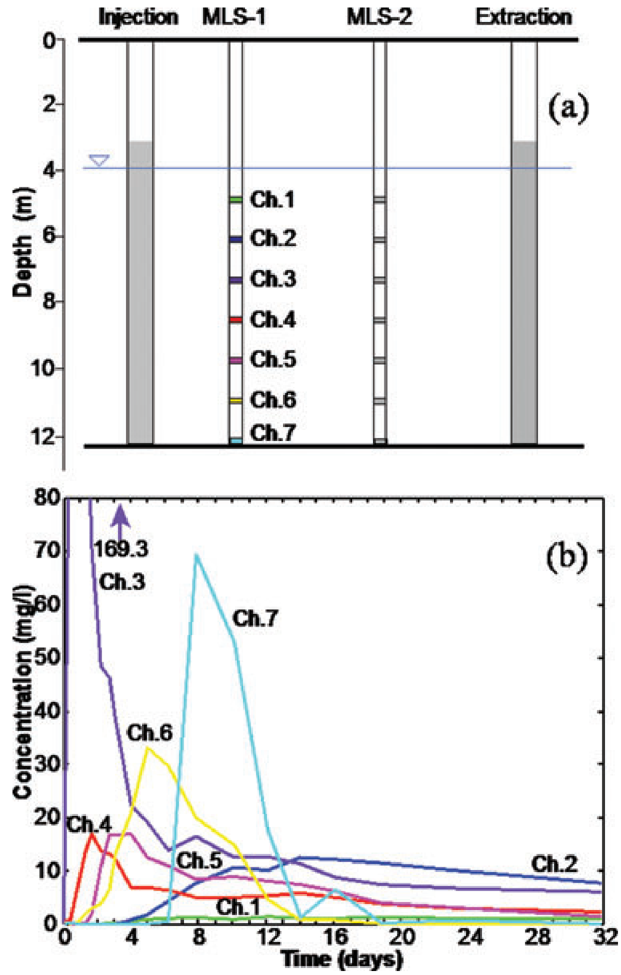

Figure 7. Configuration of a new dipole test (a) and breakthrough curves observed at seven sampling ports (each is referred to as a channel or Ch.) of the first multilevel sampler (MSL-1) well (b) (modified from Bianchi et al. 2010a).

from the core sampler. These cores stayed in the freezer for digital imaging and further analysis in the laboratory. Digital photos of several frozen cores are shown in Figure 6b. Some stripes of the dye tracer, ranging from centimeter to decimeter in width, are visible on the cores. This provides visual evidence for the existence of small-scale preferential flow channels as the dye tracer filled the high-K channels preferentially before it diffused into the relatively immobile low-K matrix.

Another forced-gradient tracer test was conducted in 2007 (referred to hereafter as MADE-5) employing a dipole (injection-extraction) configuration (Figure 7a). Between the fully mixed injection and extraction wells, two multilevel sampler (MLS) wells were installed to measure the concentration breakthrough curves at different elevations. Figure 7b shows seven concentration breakthrough curves from the MLS well closest to the injection well (Bianchi et al. 2010a). The considerable variation exhibited by these breakthrough curves, in terms of peak concentration, peak arrival time, and degree of tailing, suggests the presence of a complex network of preferential flow pathways between the injection and extraction wells.

In addition to the tracer experiments discussed in the preceding text, a number of geophysical surveys have been conducted at the MADE site to improve site characterization. These include ground penetrating radar (GPR), seismic, and resistivity surveys (Bowling et al. 2005, 2006, 2007). The seismic method was considered to be of limited utility because of the low resolution relative to the small site scale, while GPR was shown to be very useful in delineating hydrofacies boundaries (Bowling et al. 2005, 2007). Bowling et al. (2006) found a good log-log correlation between the electric resistivity (Figure 8) and hydraulic conductivity at the MADE site.

The wealth of field data accumulated over the past 25 years has provided unprecedented opportunities to obtain insights into the critical role of aquifer heterogeneities in controlling solute transport processes and to improve our ability to parameterize and predict plume-scale transport. In the subsequent sections, we discuss several key lessons learned from trying to understand the data sets and field observations.

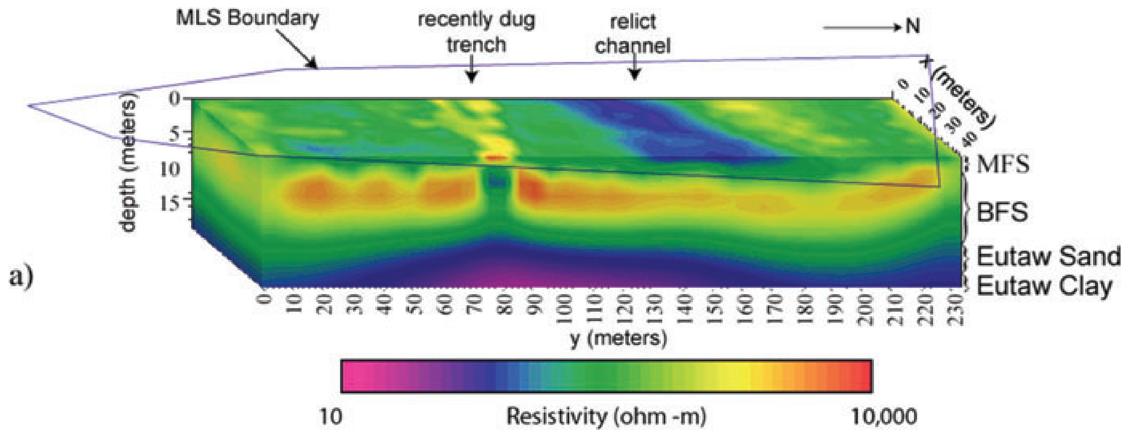

Figure 8. Distribution of resistivity values inverted from field survey data at the MADE site. The image shows moderate resistivities associated with sandy-clay facies of the meandering fluvial system (MFS), high resistivities associated with gravely sands of the braided fluvial system (BFS), moderate resistivities associated with fine-grained sands just below the BFS, and low resistivities associated with the high clay content of the underlying aquitard (Bowling et al. 2005).

Lesson 1: Inadequacy of Classical ADM

The classical advection-dispersion equation describing the fate and transport of conservative solutes in 3D groundwater flow systems can be written as follows (Zheng and Bennett 2002):

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(q_i C) + q_s C_s \quad (1)$$

where C is the solute concentration; θ the porosity of the medium; t the time; x_i the distance along the respective Cartesian coordinate axes; D_{ij} the hydrodynamic dispersion coefficient tensor (including both mechanical dispersion and molecular diffusion); q_i the specific discharge or Darcy flux; q_s the volumetric flow rate per unit volume of aquifer representing fluid sinks/sources; and C_s the solute concentration in the fluid sources/sinks.

The fundamental assumption embedded in Equation 1 is that the mechanical dispersion, caused by variations in seepage velocity due to aquifer heterogeneity, is analogous to molecular diffusion governed by Fick's law so that the dispersive flux is given by (Anderson 1979)

$$F_i = -D_{ij}\frac{\partial C}{\partial x_j} \quad (2)$$

Under this assumption, the macrodispersivities that account for the effect of mechanical dispersion can be estimated from the geostatistical properties of the hydraulic conductivity field (Gelhar and Axness 1983; Sudicky 1986; Dagan 1989).

From early on, it was clear that the tracer experimental data collected from the MADE site did not fit the classical ADM (Boggs et al. 1992; Harvey 1996; Eggleston and Rojstaczer 1998; Zheng and Jiao 1998; Feehley et al. 2000; Harvey and Gorelick 2000). The work by Harvey and Gorelick (2000) and Feehley et al. (2000) presented a clear illustration of the mismatch between the field-measured and model-calculated plumes for the first two natural-gradient tracer tests.

Harvey and Gorelick (2000) represented the flow field at the MADE site using a 2D analytical model that captured the key features of the observed hydraulic head and gradient distributions. They further simplified the 3D MADE-1 bromide tracer plume into a 1D profile by integrating mass over the planes perpendicular to the flow direction (Figure 9). As evident from Figure 9, after 503 days following the source injection, the integrated mass distribution along the flow direction (shown in orange) is highly asymmetric with the high-concentration peak near the source and extensive spreading downstream in low concentrations. The mass profile calculated by the classical ADM (shown in blue) does not fit the data at all. The parameters used to fit the ADM are described in detail in Harvey and Gorelick (2000).

Feehley et al. (2000) developed a 3D flow and transport model to interpret the MADE-2 tritium tracer

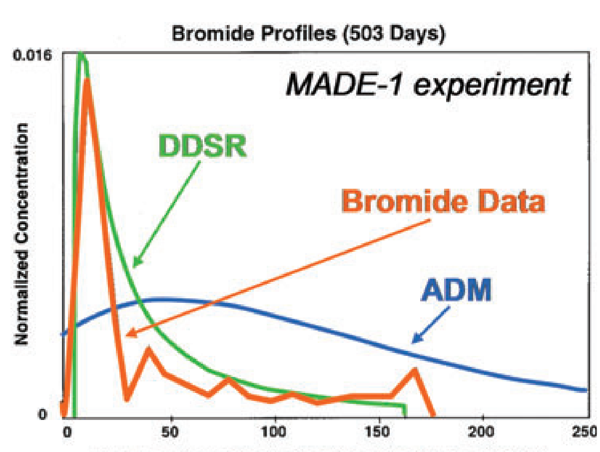

Figure 9. Comparison of model-calculated mass distributions with the field-measured bromide plume for the MADE-1 test at 503 days after the source injection. ADM is the acronym for the classical advection-dispersion model, while DDSR stands for the dual-domain mass transfer model with a single uniform mass transfer rate coefficient.

test using the MODFLOW (McDonald and Harbaugh 1988) and MT3DMS (Zheng and Wang 1999) codes. The flow and transport model has a grid spacing of 2 m in the horizontal direction and 0.5 m vertically. The model directly incorporated the 3D hydraulic conductivity distribution based on the flowmeter data through either a kriging procedure or multifractal-based geostatistical simulation. Figure 10b shows the simulated concentration distribution at 328 days based on the kriged K field. It can be seen that the classical ADM failed to reproduce the observed tritium tracer plume at 328 days after source injection (Figure 10a). This is also true in terms of integrated mass distributions along the flow direction (Figure 10d). Although the ADM solution matched the high-concentration zone reasonably well, it missed the extensive spreading to the far field at diluted concentrations. It is noteworthy that the effect of the low-K source zone and higher-K middle zone had been fully accounted for as the detailed 3D K distribution was directly incorporated into the numerical model. The ADM solution was based on a single "effective" porosity of 0.35 and longitudinal, horizontal transverse, and vertical transverse dispersivities of 5, 0.05, and 0.005 m, respectively.

Barlebo et al. (2004) and Hill et al. (2006) argued that with the ADM solution it would be possible to improve the fit to the downstream spreading in diluted concentrations by calibrating the hydraulic conductivity values substantially beyond those obtained from the flowmeter and pumping tests. Molz et al. (2006) pointed out, however, that in so doing the calibrated K values were too high while the simulated high-concentration peak was too low (by a factor of 8 compared to the measured value). Salamon et al. (2007) used a new geostatistical interpretation of the flowmeter data and a smaller support scale to implement multiple ADMs for simulating the longitudinal integrated mass profile of the MADE-2 experiment. Each ADM simulation was based on a realization of the random K field conditioned to the flowmeter data. Salamon et al. (2007) showed that six realizations (out of 40) generated using one of the three predefined variogram models could reproduce the strong anomalous tracer spreading reasonably well.

The work at the MADE site has provided clear, compelling evidence that the classical advection-dispersion theory is inadequate for characterizing plume-scale solute transport in highly heterogeneous media. The representation of mechanical dispersion by Fick's law is appropriate when heterogeneity and mixing serve as randomizing processes during solute advection in which case the classical ADM works quite well, as at the Borden and Cape Cod sites, among others. However, when the effect of connected heterogeneity, such as channels or layers (Dagan

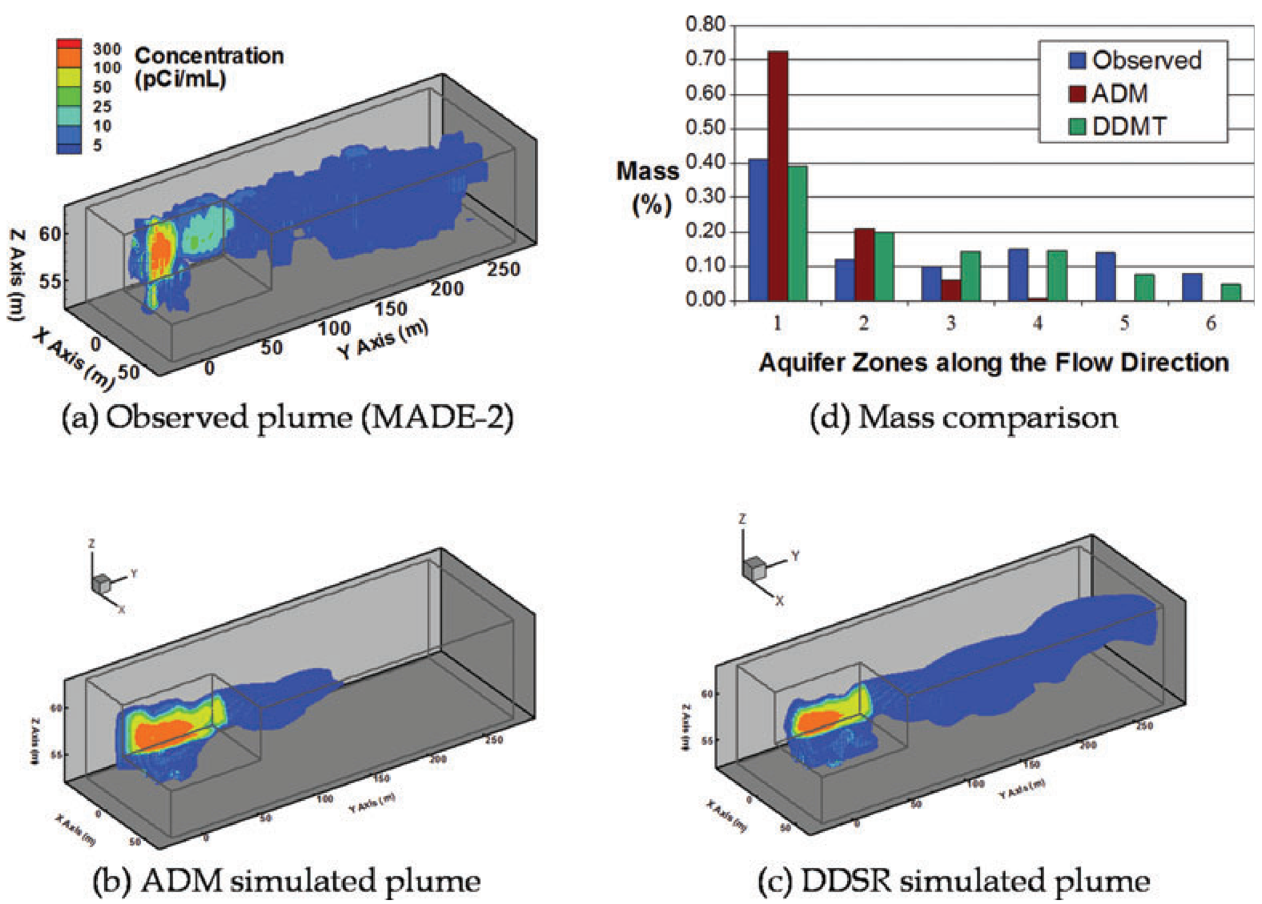

Figure 10. Comparison of model-calculated tritium plumes with the field-measured for the MADE-2 test at 328 days after the source injection (Feehley et al. 2000).

1989), enhances advection, the classical ADM fails, as at the MADE site where the hydraulic conductivity is more than one order of magnitude more variable than at the Borden and Cape Cod sites. Carrera (1993) lists several observed anomalies that are not satisfactorily described by the Fickian advection-dispersion theory, and concludes that each of these anomalies is directly or indirectly the result of aquifer heterogeneity. Indeed, as pointed out by Carrera and shown in a number of studies (Thompson and Gelhar 1990; Güven et al. 1992; Zheng and Gorelick 2003; Liu et al. 2004), if microscale variations of water flux due to aquifer heterogeneity could be precisely described, the natural model would be based solely on a combination of advection and molecular diffusion; macrodispersion would not be a dominant process. However, the scale needed to achieve a sufficiently precise description of aquifer heterogeneity may be so small that the resulting data collection effort and model of groundwater flow and solute transport become impractical in field-scale studies. Thus a practical alternative to the classical ADM would be needed for solute transport in some highly heterogeneous aquifers.

Lesson 2: Need for Dual-Domain Mass Transfer Model

Earlier frustration with the inability of the classical ADM to reproduce the observed tracer plumes was followed by the realization that a dual-domain mass-transfer model may be more appropriate than the classical ADM to represent the observed behavior of the tracer experiments at the MADE site. The dual-domain mass transfer model is not new and has been developed and applied successfully to laboratory and field studies since the 1960s (Coats and Smith 1964; van Genuchten and Wierenga 1977; Nkedi-Kizza et al. 1983; Haggerty and Gorelick 1995; Griffioen et al. 1998; Flach et al. 2004; Culkin et al. 2008). With this model, the aquifer is conceptualized as consisting of two disseminated zones: a mobile fluid zone (mobile domain) in which transport is predominately by advection, and an immobile fluid zone (immobile domain) in which transport is controlled by molecular diffusion to and from the mobile fluid zone. As a simple approximation of diffusional mass transfer, the effective exchange between the two domains is characterized by a kinetic mass transfer term. The governing equations for the dual-domain mass transfer model of a conservative tracer can be expressed as follows (Zheng and Bennett 2002):

$$\theta_\mathrm{m}\frac{\partial C_\mathrm{m}}{\partial t} + \theta_\mathrm{im}\frac{\partial C_\mathrm{im}}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta_\mathrm{m} D_{ij}\frac{\partial C_\mathrm{m}}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(q_i C_\mathrm{m}) + q_\mathrm{s} C_\mathrm{s} \tag{3}$$

$$\theta_\mathrm{im}\frac{\partial C_\mathrm{im}}{\partial t} = \beta(C_\mathrm{m} - C_\mathrm{im}) \tag{4}$$

where C_m and C_im are the concentrations in the mobile and immobile domains, respectively; θ_m and θ_im are the porosities of mobile and immobile domains, respectively; and β is the first-order mass transfer rate coefficient between the mobile and immobile domains.

For the dual-domain conceptual model, mechanical dispersion occurs only in the mobile domain and its role is secondary because actual hydrodynamic mixing caused by aquifer heterogeneity is accounted for to a large extent by mass transfer between the mobile and immobile domains. As the mass transfer rate coefficient β is increased, that is, the exchange between the mobile and immobile domains becomes increasingly fast, the dual-domain model functions more and more like the single-domain classical ADM with its porosity approaching the total porosity of the porous medium. At the other end of the spectrum, as β approaches zero, the dual-domain model also becomes equivalent to the single-domain model, but with its porosity equal to the porosity of the mobile zone.

Harvey and Gorelick (2000), Feehley et al. (2000), and Julian et al. (2001) presented simulations of MADE-1, MADE-2, and MADE-3 tracer tests using the dual-domain mass transfer model. The work of Harvey and Gorelick (2000) for the MADE-1 test is shown in Figure 9. Again, as in the case of the ADM, the solution by the dual-domain mass transfer model (shown in green) is in the form of an integrated 1D mass profile along the flow direction. It is clear that the match with the bromide data is much improved using the dual-domain model over the classical ADM. The dual-domain mass transfer model solution captures both the high-concentration peak and low-concentration spreading downstream. The dual-domain model parameters used in the simulation are presented in Harvey and Gorelick (2000).

The simulation result using the dual-domain mass transfer model for the MADE-2 test by Feehley et al. (2000) is shown in Figure 10. The spatial and temporal discretization of the dual-domain mass transfer model is identical to that of the ADM as described in preceding discussions. Again, the 3D hydraulic conductivity distribution based on the flowmeter data had been incorporated directly as the same flow solution was used for both the advection-dispersion and dual-domain mass transfer models. The simulated tritium plume based on the dual-domain mass transfer model (Figure 10c) reproduced the observed key features of spreading and migration (Figure 10a), while that based on the ADM (Figure 10b) did not. In terms of the integrated mass distribution (Figure 10d), the dual-domain solution agrees well with the observed pattern while the advection-dispersion solution overestimates the mass near the source zone and underestimates the mass downstream. The result of the dual-domain model simulation shown in Figure 10 is based on the value of 1 to 8 for the ratio of mobile to total porosities and the value of 1.0×10^{-3} per day for the mass transfer rate coefficient (Feehley et al. 2000). The values of these parameters are very similar to those used in Harvey and Gorelick (2000). Guan et al. (2008) provided additional analysis and insight on the behavior of the mass transfer rate coefficient during the MADE-2 experiment.

Julian et al. (2001) applied the dual-domain mass transfer model to simulate the MADE-3 bromide plume. Although the flow and transport models were 3D, the comparison between the observed and calculated concentrations was done in two dimensions using the highest concentration measured at all elevations of each MLS location. With the MADE-3 test, a trench was dug into the aquifer to approximately the midpoint of the total saturated thickness with temporary sheet piles used to maintain trench stability and prevent seepage. Then the bromide tracer was mixed with sands and placed inside the source trench to mimic an instantaneous source once the sheet pile was removed. As shown in Figure 11, the simulated bromide distributions agreed reasonably well with the observed peak concentrations at two different snapshots (112 and 152 days). The key features of the observed plume, that is, a high-concentration zone near the source and extensive spreading to the far field, are captured by the simulation results. The model parameters used in the MADE-3 simulation were similar to those used for MADE-2 simulation with minimal adjustment. Thus, in some sense, the MADE-3 simulation can be considered a verification of the dual-domain mass transfer model for the MADE site.

More recently, Llopis-Albert and Capilla (2009) presented a stochastic inverse model that was able to reproduce the heavy tailing of the MADE-2 tracer plume by using a dual-domain mass transfer approach and conditioning to the flowmeter K data, transient hydraulic head and solute concentration measurements. Results confirmed the necessity of using a dual-domain mass transfer approach when modeling plume-scale transport regardless of which random function is used to generate the K distribution from the flowmdeter data. Another study is by Liu et al. (2008) who applied a data assimilation approach based on the ensemble Kalman filter to improve the match between observed and simulated MADE-2 tritium plumes. The dual-domain mass transfer model was found to be necessary to achieve a reasonably close match.

There is ample experimental and observational evidence suggesting the mobile-immobile mass transfer process as the key to understanding the anomalous plume behavior at the MADE site. As Harvey and Gorelick (2000) pointed out, unlike the classical ADM, the dual-domain mass transfer model explains the facts that the observed mass of the plume was greater than the injected mass in early snapshots of the plume and less than the injected mass at late times. They suggested that, at early times, the relatively clean water in the immobile domain was not sampled and thus the observed mass was overestimated if the same high concentration was assumed to occur in both mobile and immobile domains (Figure 12a). Conversely, at late times, the mass was underestimated because the solute trapped in the immobile domain was not sampled and thus ignored (Figure 12b).

Boggs and Adams (1992) found that nearly 2 years after the first MADE tracer injection (seven months after the last snapshot), a substantial amount of bromide mass (~80%) remained in the core samples they took from the field. In a series of post-tracer-test experiments, they conducted vacuum extractions at 0.5-bar and 5-bar vacuums on portions of initially saturated core samples collected in the vicinity of selected MLSs. The 0.5-bar extraction drained the larger, high conductivity voids, which released about 12% of the total pore water; the following 5-bar extraction removed an additional 20% of the pore water. Bromide concentration measurements showed on average that the 5-bar extracts contained about three times the bromide concentration of the 0.5-bar extracts (Figure 13), which provided at least a partial explanation for the observed mass balance discrepancy, as discussed in detail by Boggs and Adams (1992).

The success of the dual-domain mass transfer model to interpret the tracer test results at the MADE site is most likely because the approach represents the key

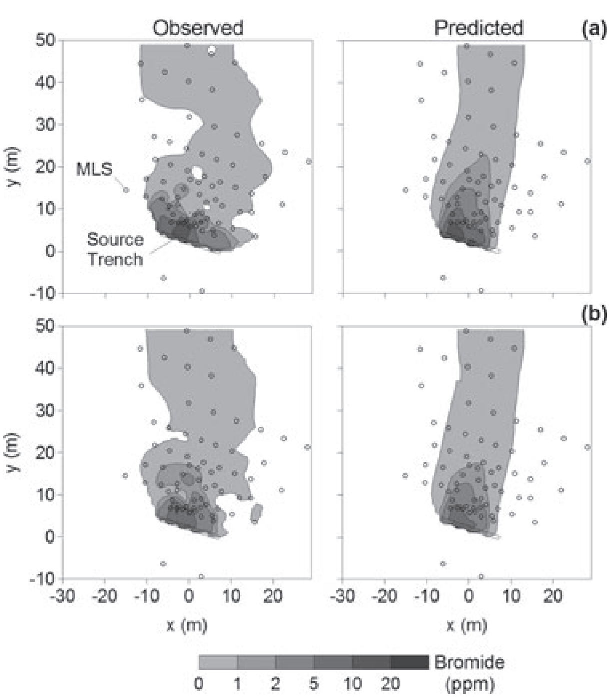

Figure 11. Comparison of the field-measured bromide plumes with those simulated by the dual-domain mass transfer model for the MADE-3 test at snapshots of 112 and 132 days after the source release (Julian et al. 2001).

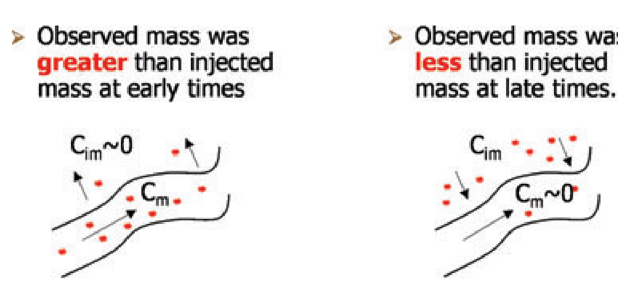

Figure 12. Schematic illustration of mass discrepancy if the dual-domain behavior is ignored in interpreting the mass balance during the tracer test.

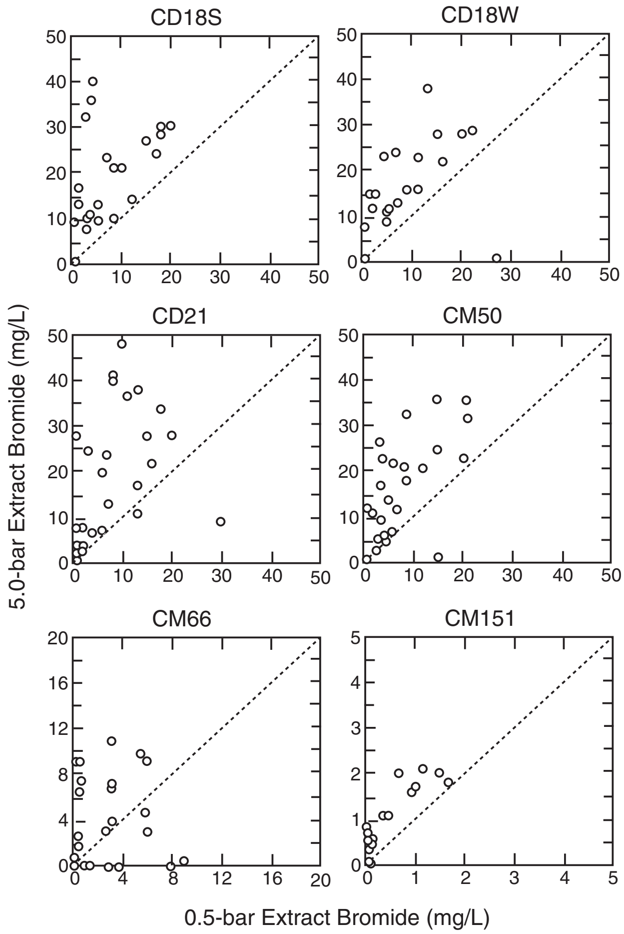

Figure 13. Bromide measurements for 0.5-bar and 5.0-bar vacuum extracts from soil cores (Boggs and Adams 1992).

Figure 14. An outcrop image from a rock quarry in close proximity to the MADE site (Zheng and Gorelick 2003).

transport mechanisms: transport along small-scale relative preferential flow paths and mass transfer into and out of immobile zones. The dual-domain model is needed because detailed geometry of the flow paths and "side pockets" was not reflected in the hydraulic conductivity distribution based on the flowmeter data. Moreover, even if all small-scale heterogeneities had been captured in the hydraulic conductivity distribution, their effects might still not be fully accounted for unless the detailed heterogeneity can be completely represented by a highly resolved spatial discretization beyond that used in the simulation models discussed in the preceding text.

Lesson 3: A Matter of Connectivity: Role of Small-Scale Preferential Flow Paths

The ability of the dual-domain mass transfer model to match the three site-scale natural-gradient tracer test results suggests that transport at the MADE site is controlled by a network of connected preferential flow paths embedded between low-conductivity sediments. Presumably, if the preferential flow paths operate at a scale greater than the grid spacing, they could be explicitly accounted for in an ADM by incorporating the detailed spatial distribution of hydraulic conductivity.

The empirical evidence for the existence of preferential flow paths at decimeter or smaller scales is provided by aquifer outcrops exposed in several rock quarries in close proximity to the MADE site. Figure 14 is an image from one of such outcrops which shows a well-sorted coarse sand lenses sandwiched between a clay layer and poorly sorted cemented mixture of gravel, sand and silt (Zheng and Gorelick 2003). The coarse sand lenses form an excellent decimeter-scale preferential flow path, contained between relative flow barriers.

Young (1995) carried out a large number of borehole flowmeter tests at 37 wells in a small plot about 50 m from the MADE site. The fraction of the total pumped flow from each 20 cm interval along the borehole was delineated for each test well. As seen in Figure 15, the distribution of flow exhibits strong variations. As much as 50% of the total flow may come from a single interval. This suggests that the vertical distribution of the horizontal flow into a borehole is highly fragmented due to the presence of small preferential flow networks.

Additional evidence for existence of small-scale preferential flow paths is provided by the soil cores from the MADE site as discussed in an earlier section (Figure 6). Wilson (2008) conducted an extensive grain-size analysis of these soil cores. Each soil core was cut into a series of 5 cm long segments and the hydraulic conductivity value for each segment was estimated from the grain-size distribution through an empirical petrophysical relation, resulting in 1741 hydraulic conductivity estimates within a block of 4 m × 4 m × 6 m (Wilson 2008). Although the absolute values of hydraulic conductivity estimated this way are approximate in nature, the primary use of these data was the relative ranking based on their magnitudes. Bianchi et al. (2010b) present a detailed geostatistical analysis of the soil core hydraulic conductivity data. One conditional realization of the hydraulic conductivity field based on transitional probability geostatistical simulation (T-PROGS) (Carle and Fogg 1996) is shown in Figure 16. It is noteworthy that the unconsolidated deposits within

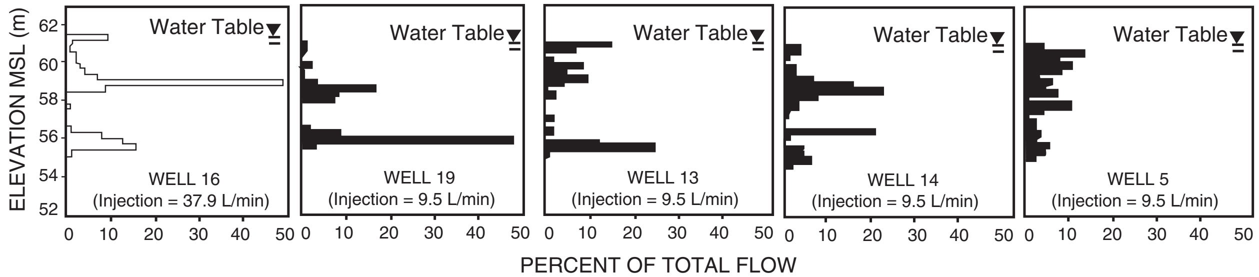

Figure 15. Profiles of the steady-state horizontal flow as measured by the electromagnetic borehole flowmeter at one injection well and four withdrawal wells (Young 1995).

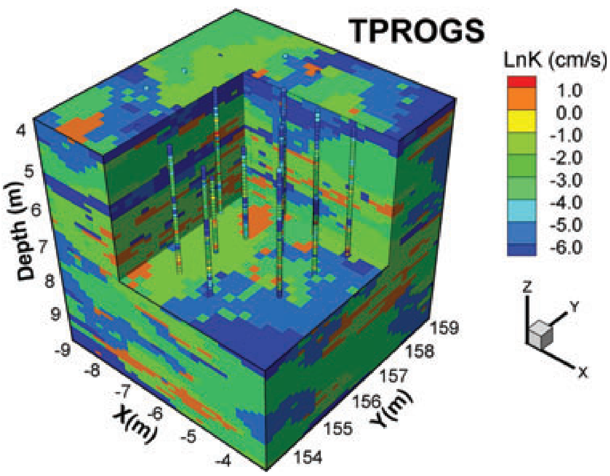

Figure 16. A realization of the hydraulic conductivity field for the soil core grid shown in Figure 6. The K field is generated using T-PROGS conditioned to the measured 1741 K data points (modified from Bianchi et al. 2010b).

the block form numerous interconnected high-K as well as low-K lenses or layers at the submeter scale. More detailed information on additional analysis and implications of these soil core K data is provided in Bianchi et al. (2010b).

A number of recent studies have examined the role of connectivity in controlling solute transport in heterogeneous aquifers where heterogeneity is characterized by connected high-conductivity structures (Fogg et al. 2000; LaBolle and Fogg 2001; Zheng and Gorelick 2003; Zinn and Harvey 2003; Liu et al. 2004; Tiedeman and Hsieh 2004; Knudby and Carrera 2005; Ronayne et al. 2008). It is most likely that the presence of decimeter-scale and smaller well-connected preferential flow paths at the MADE site makes the classical macrodispersion theory inadequate and incapable of reproducing the observed tracer plumes. The classical macrodispersion theory using constant dispersivity values is based on the premise that groundwater velocity variations are due to heterogeneity in hydraulic conductivity, which is assumed to be correlated but otherwise random. However, from a geologic perspective, this premise is often unjustified because connectedness and significant continuity rather than randomness is expected in heterogeneous aquifers. The dual-domain mass transfer model is in fact the simplest alternative to the classical ADM that aims to accommodate connected preferential flow paths and flow barriers at the subgrid scale.

Fogg et al. (2000) and LaBolle and Fogg (2001) were among the first to simulate "anomalous" transport behavior from a geologic perspective and a "connected-network" paradigm. Their 3D hydrofacies model of the Lawrence Livermore National Laboratory (LLNL) site represented connected high-K channel deposits at the meter scale. Using flow simulation, Fogg et al. (2000) demonstrated the influence of connected heterogeneity on pump test response. Using the same hydrofacies model, LaBolle and Fogg (2001) showed that solute migration depended on connected hydrostratigraphic features and molecular diffusional exchange. Zinn and Harvey (2003) found substantially different flow and transport behaviors in the K fields with different degrees of connectivity despite the fact that each K field had nearly identical log-normal univariate conductivity distributions, and nearly identical spatial covariances. Most recently, Knudby and Carrera (2005) evaluated to what extent geostatistical indicators can be used to predict flow and transport connectivity, and Ronayne et al. (2008) showed that geologically realistic aquifer heterogeneity must include connected high-K channels to explain significant difference in pump-test responses at neighboring observation wells at the LLNL site.

Inspired by the findings from the MADE site, Zheng and Gorelick (2003) used percolation theory to generate a 2D network of decimeter-scale preferential flow paths embedded in an otherwise homogeneous low-K matrix as a surrogate for a hydraulic conductivity field dominated by connected preferential flow paths and flow barriers. Solute transport in the networked K field was simulated using a fine-resolution numerical model so that it attains an explicit and complete representation of the connected pathways. Because the prescribed heterogeneity was fully represented, only advection and diffusion were needed in the numerical model. Zheng and Gorelick (2003) concluded that the simulation results captured the key characteristics of the tracer plumes observed at the MADE site, namely the high concentration peak remains close to the instantaneous source, while some solutes spread to the far field at diluted concentrations.

Liu et al. (2004) extended the approach of Zheng and Gorelick (2003) to 3D and reached similar conclusions. They demonstrated numerically that the classical ADM is of limited utility in representing solute transport in a hydraulic conductivity field characterized by connected decimeter-scale dendritic preferential flow paths. On the other hand, Liu et al. (2007) showed that the dual-domain mass transfer model can provide an adequate approximation to solute transport in the same type of K field. Gorelick et al. (2005) presented a general expression for predicting the mass transfer rate coefficient based on the general geometric characteristics of a dendritically distributed preferential flow path network. Ronayne et al. (2010) developed a hybrid heterogeneity model for a portion of the MADE site that explicitly combines submeter connected channels with a matrix represented by a correlated multivariate Gaussian hydraulic conductivity field. The resulting heterogeneity model successfully reproduced the single-well push-pull tracer test of Liu et al. (2010). These studies have provided motivations for development of a new class of high-resolution field characterization and modeling approaches that will give special consideration to the connectivity of aquifer heterogeneity.

Summary and Discussion

The MADE site has played an important role in the brief history of contaminant hydrogeology. This site was first chosen over 25 years ago for the purpose of evaluating the applicability of macrodispersion theory to represent solute transport in highly heterogeneous porous media. The repeated tracer tests and modeling analyses since then have illuminated the limitation of the classical ADM. The failure of the classical model to reproduce the observed tracer behavior was attributed to the existence of connected small-scale preferential flow paths. Empirical and observational data as well as theoretical work have suggested that these small-scale preferential flow paths along with relative flow barriers exert crucial control on solute transport at the MADE site. The presence of connected preferential flow paths invalidates the premise of the classical macrodispersion theory based on second-order stationary random K fields with constant dispersivity values. Unless the preferential flow paths are fully delineated and explicitly represented in the ADM, there is no mechanism to capture the preferential transport along high-K channels and mass into or out of the low-K zones. Clearly it is not feasible to fully delineate and represent the preferential flow paths because they may be too small and numerous. Furthermore, in predictive numerical models, the grid spacing needed to accommodate the small-scale preferential flow paths may be so small that the model size required for a field-scale model would be computationally prohibitive.

Work at the MADE site has demonstrated that the dual-domain mass transfer model can significantly improve the match with field observed tracer plumes at the 0.5- to 2-m grid scale used in the simulations. The dual-domain mass transfer model captures the key characteristics of plume-scale transport at the MADE site, namely, 1) advection-dominated rapid transport along connected high-K channels at decimeter or smaller scale, and 2) mass exchange between the high-K channels and low-K matrix, which functions as relative flow barriers and solute storage reservoirs. The dual-domain mass transfer model becomes necessary when 1) the scale of the preferential flow paths is below the grid spacing, and 2) the measured spatial distribution of hydraulic conductivity does not have sufficiently high resolution to discriminate discrete preferential flow networks.

The MADE site has highlighted the need for the "connectedness" paradigm in site characterization (Fogg et al. 2000). As pointed out by a number of previous studies (LaBolle and Fogg 2001; Western et al. 2001; Zinn and Harvey 2003; Knudby and Carrera 2005), the spatial connectivity of heterogeneous sediments is more crucial to understanding and modeling solute transport than the variation of hydraulic conductivity alone. However, the connectivity of aquifer heterogeneity is very difficult to characterize and quantify. A new generation of novel and cost-effective techniques must be developed for field characterization and interpretation of connected preferential flow networks (Butler et al. 2002, 2009; Hyndman and Tronicke 2005; Hyndman 2007; Dietrich et al. 2008; Liu et al. 2009).

The MADE site has provided key impetus for further development of more recent transport theories and models, including the dual-domain mass transfer model with multiple rate coefficients (Haggerty and Gorelick 1995; Haggerty et al. 2004; Wang et al. 2005), the fractional-order ADM (Benson et al. 2001; Lu et al. 2002; Schumer et al. 2003; Zhang et al. 2007; Zhang and Benson 2008), the subordinated ADM (Baeumer et al. 2001), and the continuous-time random walk model (Berkowitz and Scher 1998; Dentz and Berkowitz 2003; Berkowitz et al. 2008). Other alternative approaches include modern stochastic models that allow scale dependencies and capture plume asymmetry via nonlocal terms (Guadagnini and Neuman 2001). These next-generation models are all intended to provide additional mechanisms that account for "nonideal" or "non-Fickian" transport behavior that could not be explained by the classical macrodispersion theory. However, parameterization of these models, such as the mass transfer rate coefficient and mobile/immobile porosity ratio, for plume-scale transport remains a major challenge.

Concluding Remarks

In spite of tremendous effort and progress over the past three decades, our ability to predict solute transport processes in highly heterogeneous media remains very limited. However, recent advances in theoretical understanding and breakthroughs in measurement technology have provided us with an unprecedented opportunity to break the impasse by collecting and analyzing a massive amount of field data from a comprehensive suite of carefully designed and tightly integrated field experiments. With the rich data and valuable insights accumulated over the past 25 years, the MADE site has become a natural observatory for addressing important questions of general relevance for solute transport and contaminant remediation in aquifers.

Future work should focus on characterization and mapping of the hydraulic conductivity distribution and the resulting preferential flow pathways at a vertical and horizontal resolution far beyond the capability of the current generation of field measurement techniques. The spatial connectivity of aquifer heterogeneity should be explicitly considered. The new data will in turn allow us to test and evaluate various theoretical models and parameterization methods that are purported to accommodate complex transport behavior controlled by the presence of extremely variable and highly connected features.

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References

Adams, E.E., and L.W. Gelhar. 1992. Field study of dispersion in a heterogeneous aquifer, 2, Spatial moments analysis. *Water Resources Research* 28, no. 12: 3293–3307.

Anderson, M.P. 1979. Using models to simulate the movement of contaminants through ground water flow systems. *Critical Reviews in Environmental Control* 9, no. 2: 97–156.

Baeumer, B., D.A. Benson, M.M. Meerschaert, and S.W. Wheatcraft. 2001. Subordinated advection-dispersion equation for contaminant transport. *Water Resources Research* 39, no. 10: 1296. DOI:10.1029/2003WR002141.

Barlebo, H.C., M.C. Hill, and D. Rosbjerg. 2004. Investigating the Macrodispersion Experiment (MADE) site in Columbus, Mississippi, using a three-dimensional inverse flow and transport model. *Water Resources Research* 40: W04211. DOI:10.1029/2002WR001935.

Benson, D.A., R. Schumer, M.M. Meerschaert, and S.W. Wheatcraft. 2001. Fractional dispersion, Levy motion, and the MADE tracer tests. *Transport in Porous Media* 42: 211.

Berkowitz, B., S. Emmanuel, and H. Scher. 2008. Non-Fickian transport and multiple-rate mass transfer in porous media. *Water Resources Research* 44: W03402. DOI:10.1029/2007 WR005906.

Berkowitz, and B., and H. Scher. 1998. Theory of anomalous chemical transport in random fracture network. *Physical Review E* 57, no. 5: 5858–5869.

Bianchi, M., C. Zheng, G.R. Tick, and S.M. Gorelick. 2010a. A new forced gradient tracer test to assess the importance of preferential flow paths on solute transport at the Macrodispersion Experiment (MADE) site. *Ground Water.* DOI:10.1111/j.1745-6584.2010.00746.x.

Bianchi, M., C. Zheng, C. Wilson, G.R. Tick, G. Liu, and S.M. Gorelick. 2010b. A field investigation of spatial connectivity in a highly heterogeneous aquifer. *Water Resources Research.* In press.

Boggs, J.M., J.A. Schroeder, and S.C. Young. 1995. Data to support model development for natural attenuation study. Report No. WR28-2-520-197. TVA Engineering Laboratory, Tennessee Valley Authority, Norris, Tennessee.

Boggs, J.M., L.M. Beard, S.E. Long, M.P. McGee, W.G. MacIntyre, C.P. Antworth, and T.B. Stauffer. 1993. Database for the Second Macrodispersion Experiment (MADE-2). Technical Report TR-102072, Electric Power Research Institute, Palo Alto, California.

Boggs, J.M., and E.E. Adams. 1992. Field study of dispersion in a heterogeneous aquifer, 4, Investigation of adsorption and sampling bias. *Water Resources Research* 28, no. 12: 3325–3336.

Boggs, J.M., S.C. Young, and L.M. Beard. 1992. Field study of dispersion in a heterogeneous aquifer, 1, Overview and site description. *Water Resources Research* 28, no. 12: 3281–3291.

Boggs, J.M., S.C. Young, D.J. Benton, and Y.C. Chung. 1990. Hydrogeologic Characterization of the MADE Site. Interim Report EN-6915, Electric Power Research Institute, Palo Alto. California.

Bowling, J.C., D.L. Harry, A.B. Rodriguez, and C. Zheng. 2007. Integrated geophysical and geological investigation of a heterogeneous fluvial aquifer in Columbus Mississippi. *Journal of Applied Geophysics* 62: 58–73.

Bowling, J.C., C. Zheng, A.B. Rodriguez, and D.L. Harry. 2006. Geophysical constraints on contaminant transport modeling in a heterogeneous fluvial aquifer. *Journal of Contaminant Hydrology* 85: 72–88. DOI:10.1016/j.jconhyd.2006.01.006.

Bowling, J.C., A.B. Rodriguez, D.L. Harry, and C. Zheng. 2005. Delineating alluvial aquifer heterogeneity using resistivity and GPR data. *Ground Water* 43, no. 6: 890–903.

Brauner, J.S., and M.A. Widdowson. 2001. Numerical simulation of a natural attenuation experiment with a petroleum hydrocarbon NAPL source. *Ground Water* 39, no. 6: 939–952.

Butler, J.J. Jr., P. Dietrich, V. Wittig, and T. Christy. 2009. Characterizing hydraulic conductivity with the direct-push permeameter. *Ground Water* 45, no. 4: 409–419.

Butler, J.J. Jr., J.M. Healey, G.W. McCall, E.J. Garnett, and S.P. Loheide II. 2002. Hydraulic tests with direct-push equipment. *Ground Water* 40, no. 1: 25–36.

Carle, S.F., and G.E. Fogg. 1996. Transition probability-based indicator geostatistics. *Mathematical Geology* 28, no. 4: 453–476.

Carrera, J. 1993. An overview of uncertainties in modeling groundwater solute transport. *Journal of Contaminant Hydrology* 13: 23–48.

Coats, K.H., and B.D. Smith. 1964. Dead-end pore volume and dispersion in porous media. *Society of Petroleum Engineers Journal* 4: 73–84.

Culkin, S.L., K. Singha, and F.D. Day-Lewis. 2008. Implications of rate-limited mass transfer for aquifer storage and recovery. *Ground Water* 46, no. 4: 591–605.

Dagan, G. 1989. *Flow and Transport in Porous Formation.* New York: Springer-Verlag.

Dentz, M., and B. Berkowitz. 2003. Transport behavior of a passive solute in continuous time random walks and multirate mass transfer. *Water Resources Research* 39, no. 5: 1111. DOI:10.1029/2001WR001163.

Deutsch, C.V., and A.G. Journel. 1998. *GSLIB: Geostatistical Software Library and User's Guide*, 2nd ed. New York: Oxford University Press.

Dietrich, P., J.J. Butler Jr., and K. Faiß. 2008. A rapid method for hydraulic profiling in unconsolidated formations. *Ground Water* 46, no. 2: 323.

Eggleston, J., and S. Rojstaczer. 1998. Identification of large-scale hydraulic conductivity trends and the influence of trends on contaminant transport. *Water Resources Research* 34, no. 9: 2155–2168.

Feehley, C.E., C. Zheng, and F.J. Molz. 2000. A dual-domain mass transfer approach for modeling solute transport in heterogeneous porous media, application to the MADE site. *Water Resources Research* 36, no. 9: 2501–2515.

Fogg, G.E., S.F. Carle, and C. Green. 2000. Connected network paradigm for the alluvial aquifer system. In *Theory, Modeling, and Field Investigation in Hydrogeology: A Special Volume in Honor of Shlomo P. Neuman's 60th Birthday*, ed. D. Zhang and C.L. Winter, 25–42. Boulder, Colorado: Geological Society of America Special Paper 348.

Flach, G.P., S. Orisman, and F.J. Molz. 2004. Comparison of single-domain and dual-domain subsurface transport models. *Ground Water* 42, no. 6: 815–828.

Gelhar, L.W., C. Welty, and K. Rehfeldt. 1992. A critical review of data on field-scale dispersion in aquifers. *Water Resources Research* 28, no. 7: 1955–1974.

Gelhar, L.W., and C.L. Axness. 1983. Three-dimensional stochastic analysis of macrodispersion in aquifers. *Water Resources Research* 19, no. 1: 161–189.

Gorelick, S.M., G. Liu, and C. Zheng. 2005. Quantifying mass transfer in permeable media containing conductive dendritic networks. *Geophysical Research Letters* 32, L18402. DOI:10.1029/2005GL023512.

Griffioen, J.W., D.A. Barry, and J.Y. Parlange. 1998. Interpretation of two-region model parameters. *Water Resources Research* 34, no. 3: 373–384.

Guadagnini, A., and S.P. Neuman. 2001. Recursive conditional moment equations for advective transport in randomly heterogeneous velocity fields. *Transport in Porous Media* 42: 37–67.

Guan, J., F.J. Molz, Q. Zhou, H.H. Liu, and C. Zheng. 2008. Behavior of the mass transfer coefficient during the MADE-2 experiment: New insights. *Water Resources Research* 44: W02423. DOI:10.1029/2007WR006120.

Güven, O., F.J. Molz, J.G. Melville, S. El Didy, and G.K. Boman. 1992. Three-dimensional modeling of a two-well tracer test. *Ground Water* 30, no. 6: 945–957.

Haggerty, R., C.F. Harvey, C.F. von Schwerin, and L.C. Meigs. 2004. What controls the apparent timescale of solute mass transfer in aquifers and soils? A comparison of diverse experimental results. *Water Resources Research* 40: W01510. DOI:10.1029/2002WR001716.

Haggerty, R., and S.M. Gorelick. 1995. Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. *Water Resources Research* 31, no. 10: 2383–2400.

Harvey, C.F., and S.M. Gorelick. 2000. Rate-limited mass transfer or macrodispersion: which dominates plume evolution at the Macrodispersion Experiment (MADE) site?. *Water Resources Research* 36, no. 3: 637–650.

Harvey, C.F. 1996. Solute transport in spatially heterogeneous aquifers: Mapping large-scale structures and modeling small-scale effects. Ph.D. diss., Stanford University, Stanford, California.

Hill, M.C., H.C. Barlebo, and D. Rosbjerg. 2006. Reply to comment by F. Molz et al. on "Investigating the Macrodispersion Experiment (MADE) site in Columbus, Mississippi, using a three-dimensional inverse flow and transport model." *Water Resources Research* 42: W06604. DOI:10.1029/2005WR004624.

Hyndman, D.W. 2007. Geophysical and tracer characterization methods: Chapter 11. In *Handbook of Groundwater Engineering*, 2nd ed., ed. J.W. Delleur. Boca Raton, Florida: CRC Press.

Hyndman, D.W., and J. Tronicke. 2005. Hydrogeophysical case studies at the local scale: the saturated zone, Chapter 13. In *Hydrogeophysics*, ed. Y. Rubin and S. Hubbard. The Netherlands: Springer.

Julian, H.E., J.M. Boggs, C. Zheng, and C.E. Feehley. 2001. Numerical simulation of a natural gradient tracer experiment for the Natural Attenuation Study: flow and physical transport. *Ground Water* 39, no. 4: 534–545.

Killey, R.W.D., and G.L. Moltyaner. 1988. Twin Lake tracer tests: methods and permeabilities. *Water Resources Research* 24, no. 10: 1585–1613.

Knudby, C., and J. Carrera. 2005. On the relationship between indicators of geostatistical, flow and transport connectivity. *Advances in Water Resources* 28, no. 4: 405–421.

LaBolle, E.M., and G.E. Fogg. 2001. Role of molecular diffusion in contaminant migration and recovery in an alluvial aquifer system. *Transport in Porous Media* 42: 155–179.

LeBlanc, D.R., S.P. Garabedian, K.M. Hess, L.W. Gelhar, R.D. Quadri, K.G. Stollenwerk, and W.W. Wood. 1991. Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts, 1: experimental design and observed tracer movement. *Water Resources Research* 27, no. 5: 895–910.

Libelo, E.L., T.B. Stauffer, M.A. Geer, W.G. MacIntyre, and J.M. Boggs. 1997. A field study to elucidate processes involved in natural attenuation, In *4th International In Situ and On-Site Bioremediation Symposium*. New Orleans, Louisiana.

Liu, G., C. Zheng, G.R. Tick, and J.J. Butler Jr., and S.M. Gorelick. 2010. Relative importance of dispersion and rate-limited mass transfer in highly heterogeneous porous media: analysis of a new tracer test at the Macrodispersion Experiment (MADE) site. *Water Resources Research* 46: W03524. DOI:10.1029/2009WR008430.

Liu, G., and J.J. Butler Jr., G.C. Bohling, E. Reboulet, S. Knobbe, and D.W. Hyndman. 2009. A new method for high-resolution characterization of hydraulic conductivity. *Water Resources Research* 45: W08202. DOI:10.1029/2009 WR008319.

Liu, G., Y. Chen, and D. Zhang. 2008. Investigation of flow and transport processes at the MADE site using ensemble Kalman filter. *Advances in Water Resources* 31, no. 7: 975–986.

Liu, G., C. Zheng, and S.M. Gorelick. 2007. Evaluation of the applicability of the dual-domain mass transfer model in porous media containing connected high-conductivity channels. *Water Resources Research* 43: W12407. DOI:10.1029/2 007WR005965.

Liu, G., C. Zheng, and S.M. Gorelick. 2004. Limits of applicability of the advection-dispersion model in aquifers containing high-conductivity channels. *Water Resources Research* 40: W08308. DOI:10.1029/2003WR002735.

Llopis-Albert, C., and J.E. Capilla. 2009. Gradual conditioning of non-Gaussian transmissivity fields to flow and mass transport data: 3. Application to the Macrodispersion Experiment (MADE-2) site, on Columbus Air Force Base in Mississippi (USA). *Journal of Hydrology* 371, no. 1–4: 75–84. DOI:10.1016/j.jhydrol.2009.03.016.

Lu, S., F.J. Molz, and G.J. Fix. 2002. Possible problems of scale dependency in applications of the three-dimensional fractional advection-dispersion equation to natural porous media. *Water Resources Research* 38, no. 9: 1165–1171. DOI:10.1029/2001WR000624.

MacIntyre, W.G., J.M. Boggs, C.P. Antworth, and T.B. Stauffer. 1993. Degradation kinetics of aromatic organic solutes introduced into a heterogeneous aquifer. *Water Resources Research* 29, no. 12: 4045–4051.

MacKay, D.M., D.L. Freyberg, P.V. Roberts, and J.A. Cherry. 1986. A natural gradient experiment on solute transport in a sand aquifer, 1, Approach and overview of plume movement. *Water Resources Research* 22, no. 13: 2017–2029.

McDonald, M.G., and A.W. Harbaugh. 1988. A modular three-dimensional finite-difference ground-water flow model, *U.S. Geological Survey Techniques of Water Resources Investigations.* Book 6. Reston, Virginia.

Molz, F.J., C. Zheng, S.M. Gorelick, and C.F. Harvey. 2006. Comment on "Investigating the Macrodispersion Experiment (MADE) site in Columbus, Mississippi, using a three-dimensional inverse flow and transport model" by H. C. Barlebo, Mary C. Hill, and D. Rosbjerg. *Water Resources Research* 42: W06603. DOI:10.1029/2005WR004265.

Molz, F.J., O. Güven, J.G. Melville, R.D. Crocker, and K.T. Matteson. 1986. Performance, analysis, and simulation of a two-well tracer test at the Mobile site, an examination of scale-dependent dispersion coefficients. *Water Resources Research* 22, no. 7: 1031–1037.

Nkedi-Kizza, P., J.W. Biggar, H.M. Selim, M.T. van Genuchten, P.J. Wierenga, J.M. Davison, and D.R. Nielsen. 1983. Modeling tritium and chloride 36 transport through an aggregated oxisol. *Water Resources Research* 19, no. 3: 691–700.

Rehfeldt, K.R., J.M. Boggs, and L.W. Gelhar. 1992. Field study of dispersion in a heterogeneous aquifer, 3, Geostatistical analysis of hydraulic conductivity. *Water Resources Research* 28, no. 12: 3309–3324.

Ronayne, M.J., S.M. Gorelick, and C. Zheng. 2010. Geological modeling of sub-meter scale heterogeneity and its influence on tracer transport in a fluvial aquifer. *Water Resources Research*. DOI:10.1029/2010WR009348.

Ronayne, M.J., S.M. Gorelick, and J. Caers. 2008. Identifying discrete geologic structures that produce anomalous hydraulic response: an inverse modeling approach. *Water Resources Research* 44. DOI:10.1029/2007WR006635.

Salamon, P., D. Fernàndez-Garcia, and J.J. Gómez-Hernàndez. 2007. Modeling tracer transport at the MADE site: the importance of heterogeneity. *Water Resources Research* 43: W08404. DOI:10.1029/2006WR005522.

Schumer, R., D.A. Benson, M.M. Meerschaert, and B. Baeumer. 2003. Fractal mobile/immobile solute transport. *Water Resources Research* 39, no. 10: 1296. DOI:10.1029/2003WR002141.

Shapiro, A.M., and P.A. Hsieh. 1991. In Research in fractured-rock hydrogeology: characterizing fluid movement and chemical transport in fractured rock at the Mirror Lake drainage basin, New Hampshire, in U. S. Geological Survey Toxic Substances Hydrology Program. In *Proceedings of the Technical Meeting*, ed. G.E. Mallard and D.A. Aronson 155–161. Washington, DC, Monterey, California: USGS.

Stapleton, R.D., G.S. Sayler, and J.M. Boggs. 2000. Changes in subsurface catabolic gene frequencies during natural attenuation of petroleum hydrocarbons. *Environmental Science and Technology* 34, no. 10: 1991–1999.

Sudicky, E.A. 1986. A natural gradient experiment of solute transport in a sand aquifer: spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resources Research* 22, no. 13: 2069–2082.

Thompson, A.F.B., and L.W. Gelhar. 1990. Numerical simulation of solute transport in three-dimensional randomly heterogeneous porous media. *Water Resources Research* 26, 2541–2562.

Tiedeman, C.R., and P.A. Hsieh. 2004. Evaluation of longitudinal dispersivity estimates from simulated forced- and natural-gradient tracer tests in heterogeneous aquifers. *Water Resources Research* 40: W01512. DOI:10.1029/2003WR002401.

van Genutchen, M.Th., and P.J. Wierenga. 1977. Mass transport studies in sorbing porous media, 2, Experimental evaluation with tritium (^3H_2O). *Soil Science Society of America Journal* 41: 272–278.

Wang, P.P., C. Zheng, and S.M. Gorelick. 2005. A general solution approach to advective-dispersive transport with multirate mass transfer. *Advances in Water Resources* 28: 33–42.

Western, A.W., G. Bloschl, and R.B. Grayson. 2001. Toward capturing hydrologically significant connectivity in spatial patterns. *Water Resources Research* 37, no. 1: 83–97.

Wilson, C.S. 2008. Characterization of small-scale preferential flow paths through aquifer core analysis. M.S. thesis, Department of Geological Sciences, University of Alabama, Tuscaloosa, Alabama.

Young, S.C. 1995. Characterization of high-K pathways by borehole flowmeter and tracer test. *Ground Water* 33, no. 2: 311–318.

Zhang, Y., and D.A. Benson. 2008. Lagrangian simulation of multidimensional anomalous transport at the MADE site. *Geophysical Research Letters* 35: L07403. DOI:10.1029/2008.

Zhang, Y., D.A. Benson, M.M. Meerschaert, and E.M. LaBolle. 2007. Space-fractional advection-dispersion equations with variable parameters: Diverse formulas, numerical solutions, and application to the Macrodispersion Experiment site data. *Water Resources Research* 43, no. 5. W05439. DOI:10.1029/2006WR004912.

Zheng, C., and G.D. Bennett. 2002. *Applied Contaminant Transport Modeling*, 2nd ed. New York: Wiley.

Zheng, C., and P.P. Wang. 1999. *MT3DMS: A Modular Three-Dimensional Multispecies Model for Simulation of Advection, Dispersion and Chemical Reactions of Contaminants in Groundwater Systems; Documentation and User's Guide.* Contract Report SERDP-99-1, U.S. Vicksburg, Mississippi: Army Engineer Research and Development Center.

Zheng, C., and J.J. Jiao. 1998. Numerical simulation of tracer tests in a heterogeneous aquifer. *Journal of Environmental Engineering* 124, no. 6: 510–516.

Zheng C. 2007. Accounting for aquifer heterogeneity in solute transport modeling: a case study from the Macrodispersion Experiment (MADE) site in Columbus, Mississippi. In *Handbook of Groundwater Engineering*, 2nd ed., ed. J.W. Delleur. Boca Raton, Florida: CRC Press.

Zheng, C., and S.M. Gorelick. 2003. Analysis of the effect of decimeter-scale preferential flow paths on solute transport. *Ground Water* 41, no. 2: 142–155.

Zinn, B., and C.F. Harvey. 2003. When good statistical models of aquifer heterogeneity go bad: a comparison of flow, dispersion, and mass transfer in connected and multivariate Gaussian hydraulic conductivity fields. *Water Resources Research* 39, no. 3: 1051–1069. DOI:10.1029/2001WR001146.