Geoelectrical evidence of bicontinuum transport in groundwater

Kamini Singha,[1] F. D. Day-Lewis,[2] and J. W. Lane Jr.[2]

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[1] Bicontinuum models and rate-limited mass transfer (RLMT) explain complex transport behavior (e.g., long tailing and rebound) in heterogeneous geologic media, but experimental verification is problematic because geochemical samples represent the mobile component of the pore space. Here, we present geophysical evidence of RLMT at the field scale during an aquifer-storage and recovery experiment in a fractured limestone aquifer in Charleston, South Carolina. We observe a hysteretic relation between measurements of pore-fluid conductivity and bulk electrical conductivity; this hysteresis contradicts advective-dispersive transport and the standard petrophysical model relating pore-fluid and bulk conductivity, but can be explained by considering bicontinuum transport models that include first-order RLMT. Using a simple numerical model, we demonstrate that geoelectrical measurements are sensitive to bicontinuum transport and RLMT parameters, which are otherwise difficult to infer from direct, hydrologic measurements. **Citation:** Singha, K., F. D. Day-Lewis, and J. W. Lane Jr. (2007), Geoelectrical evidence of bicontinuum transport in groundwater, *Geophys. Res. Lett.*, *34*, L12401, doi:10.1029/2007GL030019.

1. Introduction

[2] Concentration breakthrough curves from tracer experiments and pump-and-treat contaminant remediation in fractured and heterogeneous porous media commonly show tailing—the progressively slower recovery of concentration through time—and concentration rebound that is not described by advective-dispersive transport [e.g., *Adams and Gelhar*, 1992; *LaBolle and Fogg*, 2001; *Meigs and Beauheim*, 2001; *Gorelick et al.*, 2005]. Observations of such anomalous transport behavior have prompted some to consider bicontinuum mass transfer as a controlling process [e.g., *Goltz and Roberts*, 1986; *Haggerty and Gorelick*, 1994, 1995; *Harvey et al.*, 1994; *Benson et al.*, 2000; *Feehley et al.*, 2000; *Harvey and Gorelick*, 2000; *Dentz and Berkowitz*, 2003; *Zinn and Harvey*, 2003]. In bicontinuum models of geologic media, a representative elementary volume is conceptualized as consisting of (1) a well-connected pore space and/or connected fracture porosity (the mobile domain), and (2) a poorly connected pore space and/or dead-end fractures (the immobile domain). Advection and dispersion processes occur in the mobile domain, with local rate-limited mass transfer (RLMT) of solute mass between the mobile and immobile domains. Understanding the processes controlling anomalous tailing and rebound is critical to addressing problems ranging from the design of cost-effective pump-and-treat remediation for ground water, to the implementation of aquifer-storage recovery (ASR) systems, to the selection of nuclear waste disposal sites.

[3] Although bicontinuum models have successfully matched field-experimental concentration data [e.g., *Feehley et al.*, 2000; *Harvey and Gorelick*, 2000; *Köhne et al.*, 2004], their validity is debated in the literature [*Hill et al.*, 2006; *Molz et al.*, 2006], and other mechanisms, such as heterogeneity in hydraulic properties, have been suggested as alternative explanations for tailing behavior [*Hill et al.*, 2006]. Experimental verification of RLMT in field settings is difficult because conventional geochemical measurements preferentially sample pore fluid from the mobile domain and provide only indirect information about the volume of immobile pore space; hence only circumstantial evidence is available to verify the existence of a bicontinuum or identify values of controlling parameters.

[4] To investigate the hypothesis that bicontinuum RLMT is a fundamental transport process in heterogeneous geologic media, we conducted direct-current electrical-resistivity surveys to monitor a push-pull tracer test in fractured rock. Geophysical techniques have been used to guide and constrain groundwater and solute-transport models, but have not yet been applied to RLMT. In a single continuum where solute transport is governed by advection and dispersion, petrophysical theory [*Keller and Frischknecht*, 1966] predicts a linear relation between the bulk electrical conductivity and the fluid conductivity that would be measured in direct, geochemical sampling. In the presence of a bicontinuum, however, fluid samples would be drawn from the mobile domain, whereas electrical current would flow through both mobile and immobile pore space; hence the combination of geochemical and geoelectrical measurements provides a potential means of verifying the occurrence of bicontinuum transport and, perhaps, measuring RLMT.

2. Methods

[5] The field experiment was conducted at a pilot-scale ASR project site, in Charleston, South Carolina. The target zones for ASR and resistivity monitoring comprise two transmissive, fractured intervals over depths ranging from about 115 to 135 m below land surface; these zones are located within the Tertiary limestone and sand sections of the Santee Limestone and Black Mingo Group [*Campbell et al.*, 1997; *Petkewich et al.*, 2004]. The field site consists of four wells, including three observation wells arranged around a central injection/extraction well at radial distances between 8 and 10 m. The wells are 140-155 m deep. During

[1]Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania, USA.
[2]Office of Ground Water, Branch of Geophysics, U.S. Geological Survey, Storrs, Connecticut, USA.

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Table 1. Input Parameters for the Base-Case Flow and Transport Model

	Fracture Zone	Outer Zone
Mass-transfer coefficient, d^{-1}	0.05	1×10^{-4}
Hydraulic conductivity, m/d	10	10
Mobile porosity	0.05	0.05
Immobile porosity	0.10	0.10
Specific Storage, m^{-1}	1.5×10^{-5}	1.5×10^{-5}
Injection rate, m^3/day	170	170
Pumping rate, m^3/day	480	480
Background fluid conductivity, S/m	0.49	0.49
Freshwater fluid conductivity, S/m	0.016	0.016

the experiment, freshwater was injected into the brackish, confined aquifer, stored, and extracted by pumping.

2.1. Aquifer-Storage and Recovery Test

[6] From 27 August to 7 September 2005, a volume of 870 m^3 of freshwater with a fluid electrical conductivity of approximately 0.016 S/m was injected into the aquifer, which contained high salinity fluids (up to 0.7 S/m), at 170 m^3/day over 5 days, stored for 2 days, and then pumped at 480 m^3/day over 4 days. Open-hole hydraulic heads were recorded using pressure transducers, and fluid electrical conductivity were measured at depths adjacent to the lower fracture zone in the three sampling wells (well 733, 9.2 m southwest of the injection-extraction well; well 844, 8.2 m southeast of the injection-extraction well; and well 843, 8.7 m north of the injection-extraction well). Small-volume porewater samples were extracted from the three observation wells at intervals ranging from 40 minutes to about 6 hours, for 12 consecutive days. A conductivity probe was used to measure fluid electrical conductivity of each groundwater sample. Measured heads and concentrations at well 843 indicated that this well was poorly connected to the injection-extraction well, as compared to wells 733 and 844.

2.2. Geoelectrical Measurements

[7] During the ASR experiment, geoelectrical data were collected using 4-electrode arrays given 24 electrodes, spaced 1.25-m apart, in each of the three sampling wells. To collect bulk electrical conductivity data, electrical current was injected between two electrodes in a single well, and the resultant potential difference was measured between two neighboring electrodes in the same well. Data were collected using a Wenner configuration with 1.25-m spacing, where the current electrodes surround the two potential electrodes, and all four electrodes are evenly spaced. The electrodes were below the water table at depths of 110 to 139 m below land surface. Apparent bulk conductivities were measured prior to and during the push-pull experiment. The current and potential electrodes were swapped for each measurement to estimate data quality—errors were generally less than 1%. Bulk apparent conductivity data shown here correspond to measurements that straddle one fracture zone, which was previously identified in borehole logs.

2.3. Numerical Simulations of Fluid Flow, Transport, and Electrical Conduction

[8] We used MODFLOW-2000 [*Harbaugh et al.*, 2000], a finite-difference model, to simulate radial transient flow; particle-tracking in MT3DMS [*Zheng and Wang*, 1999] to simulate radial advective transport with first-order, dual-domain RLMT; and a finite-volume model written in Matlab to simulate three-dimensional electrical conduction [*Pidlisecky et al.*, 2007]. The model domain for flow and transport consists of a single layer, which extends approximately 4,800 m radially from the central well. Injection was simulated for 5 days, storage for 2 days, and recovery for 4 days to mimic the field experiment. The aquifer was discretized in true radial coordinates as a single 2-m layer with no fluid or concentration flux out the top and bottom.

[9] In the radial numerical model, the fracture zone extends about 10 m away from the ASR well and is embedded within an outer zone, which is conceptualized as a region of lower density and poorly connected fractures. The mass-transfer coefficient depends on the molecular diffusion of ions in water and the length scale over which the diffusion occurs; the assumed mass-transfer coefficient in the fracture zone corresponds to a length-scale on the order of a centimeter, consistent with diffusion between small fractures and carbonate dissolution features present in rocks at the Charleston site. Within the outer zone bounding the known fracture zone, a lower mass-transfer coefficient is assumed, consistent with larger diffusion lengths (Table 1). A homogeneous specific storage of 1.5×10^{-5} m^{-1} is assumed throughout the model domain. For simplicity, hydraulic conductivity is also assumed to be homogeneous. Because our model is radial, consists of a single layer, and has a specified pumping rate boundary condition, contrasts in hydraulic conductivity between the inner and outer zones would change only the hydraulic gradient and would not affect groundwater velocity or transport.

[10] The transport model produced concentrations (as fluid conductivity) that were converted to bulk conductivity, σ_b:

$$\sigma_b = (n_{mob} + n_{immob})^{m-1} \cdot (n_{mob}\sigma_{f,mob} + n_{immob}\sigma_{f,immob}), \qquad (1)$$

where $\sigma_{f,mob}$ is the mobile fluid conductivity at a given location [S/m], $\sigma_{f,immob}$ is the immobile fluid conductivity [S/m], n_{mob} is the mobile domain porosity [-], n_{immob} is the immobile porosity [-], and m is the empirical cementation factor in Archie's Law [*Archie*, 1942], assumed to equal 1.3, a standard value [*Keller and Frischknecht*, 1966].

[11] Experimenta bulk conductivity data are volume averages rather than point measurements. We used a numerical electrical-conduction model to confirm the accuracy of using Equation 1 to convert simulated, point fluid conductivity to predicted measurements of apparent bulk conductivity. The apparent bulk conductivities from the conduction simulation fit the co-located, point values estimated from Equation 1 with an $R^2 = 0.99$ and a slope of 0.986; thus the transport simulation results can be transformed to bulk conductivity and directly compared to field-measured apparent conductivity for the synthetic models considered here. Although numerical modeling suggests that apparent bulk resistivity measurements approximate point values for the survey geometry and system considered, more rigorous

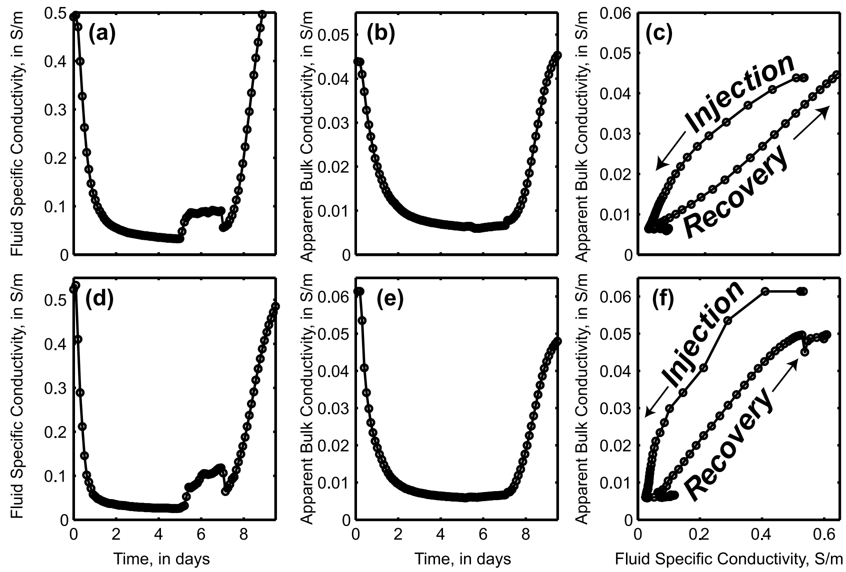

Figure 1. Data from the Charleston, South Carolina site, including (a) fluid conductivity history (b) bulk conductivity history, and (c) the hysteresis in the bulk versus fluid conductivity curves at observation well 844 (8.2 m from the injection-extraction well); and (d) fluid conductivity history, (e) bulk conductivity history, and (f) the hysteresis in the bulk versus fluid conductivity curves at observation well 733 (9.2 m from the injection-extraction well). Injection was from 0–5 days, storage from 5–7 days, and recovery from 7–10 days.

electrical-conduction modeling may be required to account for support volume discrepancies in other situations.

3. Results

[12] The experimental data show a nonlinear, hysteretic relation between bulk and fluid electrical conductivity, in contradiction to standard advective-dispersive transport and Archie's Law [*Keller and Frischknecht*, 1966]. During the storage period, we observe a rebound of salinity (as fluid electrical conductivity) (Figure 1a, d); concurrently, the bulk conductivity data from electrical measurements at the same locations show little change (Figure 1b, e). The relation between the bulk electrical conductivity measured by the geophysics and the fluid conductivity measured by the chemical sampling thus appears hysteretic (Figure 1c, f).

[13] We postulate a bicontinuum conceptual model to explain the experimental results. During the injection cycle (days 0–5), freshwater rapidly fills the mobile domain and the mobile fluid conductivity decreases, while the bulk conductivity lags behind because the immobile domain remains comparatively brackish. During the storage cycle (days 5–7), local rate-limited mass transfer of salt from the immobile domain to the mobile domain causes an increase in mobile fluid electrical conductivity (a rebound in salinity), but does not impact the bulk electrical conductivity. During the recovery cycle (days 7–10), water is drawn back toward the extraction well. Injected water that reached the outer zone, where mass transfer is slower, may remain relatively fresh; this could produce the observed short-term decrease in fluid electrical conductivity (a downdip in salinity) at observation wells. Over time, however, increasingly brackish water is drawn through the mobile domain toward the extraction well, and fluid electrical conductivity increases, while bulk electrical conductivity lags behind because the water in the immobile domain is now comparatively fresh.

[14] Based on the field conditions and the injection-extraction scheme, we constructed a numerical model of flow and transport to simulate the field experiment, described above, where RLMT was used to qualitatively explain the mobile-domain concentrations (Figure 2a) and the bulk electrical conductivity (Figure 2b). The relation between simulated fluid and bulk conductivity is hysteretic (Figure 2c) and similar to that observed experimentally (Figure 1c, f). Consistent with the experimental data and conceptual model, the numerical simulations show (1) saline, immobile pore fluids and, thus, high bulk conductivity during injection, and (2) fresher, immobile pore fluids and, thus, a low bulk conductivity during extraction. Substantial changes are neither predicted nor observed in the bulk electrical conductivity during the storage period; however, minor changes were observed in the field data which may be indicative of other second-order processes, such as dispersion or advection under ambient head gradients.

[15] Although hysteresis between fluid and bulk conductivity occurs even in homogeneous models with RLMT, heterogeneity in the mass transfer coefficient was used to mimic the decrease in fluid conductivity observed at the start of the extraction. During the injection, freshwater was pushed into the surrounding outer zone, where mass transfer is slower; this water remained relatively fresh during storage and was quickly extracted after the start of pumping. Although radial heterogeneity in mass-transfer coefficient is considered here, the observed data also could be explained by vertical variability (i.e., a semi-confined aquifer) or internal variability in the target aquifer (i.e., lateral variations in fracture aperture or connectivity).

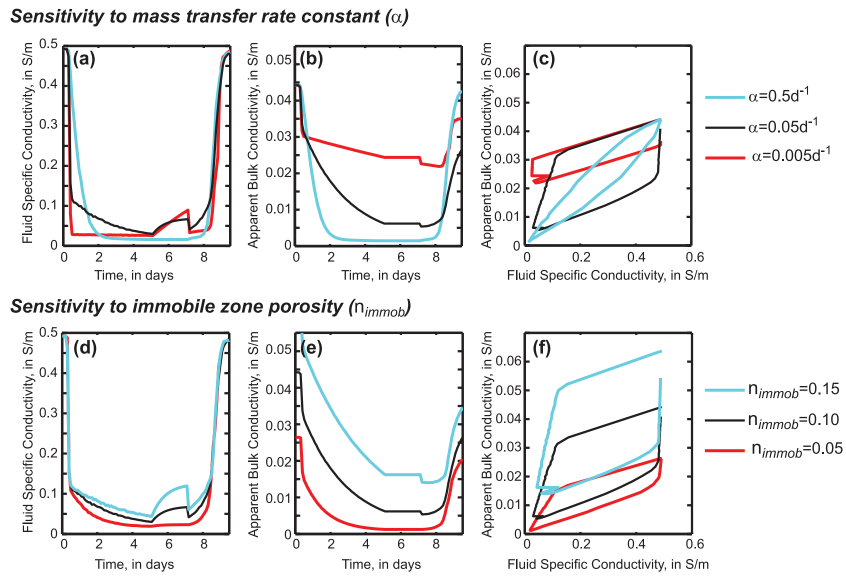

Figure 2. Sensitivity analysis from numerical modeling of RLMT processes for an aquifer-storage and recovery experiment: (a) mobile-domain fluid conductivity history, (b) bulk conductivity history, and (c) hysteresis assuming variation in the mass-transfer coefficient of the fracture zone; (d) mobile-domain fluid conductivity history, (e) bulk conductivity history, and (f) hysteresis assuming variation in the immobile porosity of the fracture zone.

[16] Numerical modeling results suggest that (1) RLMT can explain the observed hysteresis between bulk and fluid electrical conductivity, and (2) electrical methods may be used in conjunction with traditional fluid sampling to verify and perhaps measure mass transfer between mobile and immobile domains. Fluid conductivity, bulk conductivity, and the hysteretic relation between them, are highly sensitive to order-of-magnitude variations in mass transfer coefficient (Figures 2a–2c). With lower mass transfer rates, the saline concentration in the immobile domain changes less with time, and the system retains high fluid conductivity in the pore space throughout the experiment. With higher mass transfer rates, the concentrations in the mobile and immobile domains are closer to equilibrium, and the two domains behave more like a single continuum with classical advective-dispersive behavior.

[17] The immobile porosity also affects the degree, and form, of the hysteretic relation between bulk and fluid conductivity. For lower immobile porosity, the system behaves more like a single continuum because less storage is available in the immobile pore space (Figures 2d–2f). Conversely, greater immobile porosity provides more storage and results in increased overall bulk electrical conductivity according to Archie's Law [*Archie*, 1942], which predicts a linear relation between bulk conductivity and porosity [*Keller and Frischknecht*, 1966]. The electrical conductivity results are comparatively insensitive to changes in the outer zone mass-transfer coefficient (not shown). For faster mass transfer in the outer zone, the decrease in electrical conductivity as extraction begins disappears because communication between the mobile and immobile domains increases, and no freshwater is pulled back toward the extraction well from the outer zone because it has already had the opportunity to diffuse between domains. For greater mobile porosity, the injected freshwater progresses more slowly through the fracture zone, and returns sooner during extraction; the opposite occurs for lower mobile porosity.

4. Discussion and Conclusions

[18] The anomalous transport behavior and electrical hysteresis observed during an ASR experiment are consistent with transport through a bicontinuum and first-order rate-limited mass transfer between mobile and immobile domains. Diffusive, local exchange of solute between mobile and immobile components of the pore space results in measurements of pore-fluid conductivity that are out of equilibrium with bulk electrical conductivity. Our experimental results suggest that bicontinuum transport is a fundamental process with an observable geoelectrical signature; furthermore, results of numerical modeling suggest that the combination of geoelectrical measurements and conventional geochemical sampling can provide insight into parameters controlling field-scale mass transfer.

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J. W. Lane Jr. and F. D. Day-Lewis, Office of Ground Water, Branch of Geophysics, U.S. Geological Survey, 11 Sherman Place, Unit 5015, Storrs, CT 06269, USA.
K. Singha, Department of Geosciences, Pennsylvania State University, 311 Deike Building, University Park, PA 16802, USA. (ksingha@psu.edu)