

## Electrical characterization of non-Fickian transport in groundwater and hyporheic systems

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[1] Recent work indicates that processes controlling solute mass transfer between mobile and less mobile domains in porous media may be quantified by combining electrical geophysical methods and electrically conductive tracers. Whereas direct geochemical measurements of solute preferentially sample the mobile domain, electrical geophysical methods are sensitive to changes in bulk electrical conductivity (bulk EC) and therefore sample EC in both the mobile and immobile domains. Consequently, the conductivity difference between direct geochemical samples and remotely sensed electrical geophysical measurements may provide an indication of mass transfer rates and mobile and immobile porosities in situ. Here we present (1) an overview of a theoretical framework for determining parameters controlling mass transfer with electrical resistivity in situ; (2) a review of a case study estimating mass transfer processes in a pilot-scale aquifer storage recovery test; and (3) an example application of this method for estimating mass transfer in watershed settings between streams and the hyporheic corridor. We demonstrate that numerical simulations of electrical resistivity studies of the stream/hyporheic boundary can help constrain volumes and rates of mobile-immobile mass transfer. We conclude with directions for future research applying electrical geophysics to understand field-scale transport in aquifer and fluvial systems subject to rate-limited mass transfer.

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### 1. Introduction

[2] The fate and transport of chemicals in hydrologic systems is commonly described by advection and diffusion processes, and advective-dispersive transport models have been developed to predict movement of contaminants in diverse settings [e.g., Zheng and Bennett, 2002]. In both model development and applied studies of solute transport, the transport equations describe temporal solute concentration dynamics observed at a particular location—often the “outlet” or end of a region of interest. In many heterogeneous settings, however, transport behavior during tracer experiments or contaminant remediation does not fit standard advective-dispersive behavior. For example, long tailing behavior may be apparent in concentration histories, or contaminant concentration may rebound after pump-and-treat remediation has ceased. These phenomena have prompted many to hypothesize that other processes may control contaminant or solute transport in hydrologic systems. Anomalous solute transport tailing behavior has been observed in countless hydrologic settings and is commonly

explained by diffusion and mass transfer between a mobile and immobile domain or velocity variations based on heterogeneity [e.g., Goltz and Roberts, 1986; Haggerty and Gorelick, 1994; Harvey et al., 1994; Haggerty and Gorelick, 1995; Benson et al., 2000; Feehley et al., 2000; Harvey and Gorelick, 2000; Haggerty et al., 2002; Dentz and Berkowitz, 2003; Zinn and Harvey, 2003]. Many of these experimentally observed breakthrough curves have been observed to be skewed toward late times, resulting in “heavy-tailed” behavior.

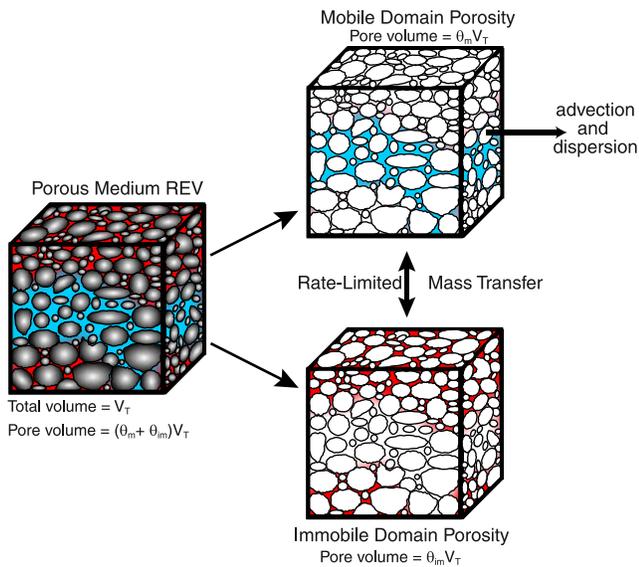
[3] Anomalous tailing behavior, which may be controlled by diffusion into low-permeability materials or by sorption, severely impedes aquifer remediation [*National Research Council*, 1994]. In this context, mass transfer can impose limitations on the efficiency of pump-and-treat remediation schemes, because contamination can diffuse slowly out of less mobile pore space into the mobile pore space (Figure 1), maintaining high concentrations for long time spans. Such limitations can result in longer-than-anticipated cleanup times [Haggerty and Gorelick, 1995]. Similar transport behavior has been observed in watershed settings, where solute exchanges between the stream channel and near-stream aquifer or stagnant side pools [e.g., Bencala, 1984; Wallis et al., 1989], where contaminant fate is controlled by biogeochemical gradients. Quantification of processes occurring at this interface impacts water quality and ecosystem services [Findlay, 1995; Brunke and Gonser, 1997]. The region near the stream that contains stream exchange flows is defined as the hyporheic zone. How the hyporheic zone buffers stream chemistry remains a critical area of

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**Figure 1.** Conceptual model of mass transfer. The representative elementary volume (REV) consists of two domains, one mobile, one immobile. Advection and dispersion occur in the mobile domain, which consists of open, connected pore space and/or fractures. Exchange between the mobile domain and immobile domain, which consists of poorly connected pores or dead-end fractures, is modeled as a diffusive process. The rate(s) of diffusion are controlled by the distribution of length scales—possibly from the grain to facies scales.

science as human impacts and climate change continue to affect aquatic and riparian habitats.

[4] Processes that affect solute transport are usually inferred from an “end of the pipe” concentration breakthrough curve. These concentration histories are used to quantify advection and dispersion, as well as exchange between the active domain and storage zones [Choi *et al.*, 2000]. Parameters estimated from tracer experiments such as dispersion coefficient, porosity, mass transfer rate, or flow direction may be unreliable for several reasons, especially in complex watershed and stream systems: (1) tracer experiments are sensitive to more than just storage processes [Harvey *et al.*, 1996]; (2) storage parameters are difficult to estimate precisely [Wagner and Harvey, 1997]; and (3) concentrations measured at one location in space give an integrated measure of what occurs upgradient and no information about variability along the transport pathway. Identifying heterogeneous characteristics that control exchange is critical to improving quantification of water quality in down-gradient systems [e.g., Triska *et al.*, 1993; Wondzell and Swanson, 1999; Cardenas and Zlotnik, 2003; Gooseff *et al.*, 2006]. Temporal scales are also important: seasonal variations in flows may control transport behavior [Wroblicky *et al.*, 1998], yet few methods are available to collect data at the appropriate spatial and temporal scales. The presence of both mobile and immobile domains, as opposed to heterogeneity within a single domain, is not clear, nor is the operation of controlling parameters under varying conditions.

[5] There is a critical need for new field-experimental approaches to verify and characterize the processes that

control mass transfer. Currently, we have a limited understanding of transfer rates and scales, and we lack experimental means to cost-effectively estimate spatially variable parameters controlling mass transfer for input to predict models of fate and transport. Recent advances in hydrogeophysical technology and data analysis are enabling characterization and monitoring of hydrologic processes at spatial and temporal resolution heretofore impossible (for reviews, see Rubin and Hubbard [2005] and Vereecken *et al.* [2006]). Time-lapse geophysical imaging has provided high-resolution (in space and time) information about transport of fluids and solutes in diverse geologic settings. Geoelectrical and radar methods have been used extensively to monitor transport of conductive tracers in the field [e.g., Kemna *et al.*, 2002; Day-Lewis *et al.*, 2003, 2006a; Singha and Gorelick, 2006a; Johnson *et al.*, 2007; Oldenborger *et al.*, 2007], as well as movement of water through the unsaturated zone [Daily *et al.*, 1992; Park, 1998; Binley *et al.*, 2002; Yeh *et al.*, 2002]. Preliminary pilot-scale experiments suggest the potential of using these data for monitoring mass transfer processes in situ; furthermore, preliminary numerical modeling suggests the approach is highly sensitive to controlling parameters (e.g., immobile domain porosity and rate constant) both at the field and column scales [Singha *et al.*, 2007; Day-Lewis and Singha, 2008]. Whereas traditional geochemical sampling only provides information on mobile fluids and solutes, electrical resistivity (ER) methods are sensitive to total concentration of electrically conductive solute and, hence, both mobile and immobile fluids. Consequently, ER data can help to identify salient mass transfer processes and infer values of controlling parameters.

[6] Here, we outline the theoretical framework for determining parameters controlling mass transfer with electrical resistivity data, review a case study where mass transfer processes were observed in a pilot-scale aquifer storage recovery test, and develop a technique for discerning processes controlling mass transfer on the basis of total (mobile and immobile) bulk and fluid EC dynamics within the hyporheic zone of a synthetic stream system. The presented example is for a simplified stream system, but demonstrates the plausibility of using ER techniques to characterize mass transfer governed by a single exchange timescale.

## 2. Background

[7] Electrical characterization of mass transfer is based on the combination of electrical-resistivity imaging of hydrologic processes and the physics underlying solute transport in the presence of mass transfer. In this section, we briefly review (1) the relevant principles of solute transport, in groundwater and hyporheic systems; (2) approaches for geophysical monitoring of transport; (3) a new approach to infer mass transfer parameters from collocated geophysical and geochemical time series; and (4) a recent, pilot-scale field example to demonstrate our approach.

### 2.1. Advective-Dispersive Exchange Processes

[8] To account for heavy-tailed behavior, modified models of the advection-dispersion equation (ADE), with additional terms that account for longer timescales of transport, have been developed [e.g., Haley *et al.*, 1991; Berkowitz,

2002]. The primary conceptual models for these additional transport processes are (1) the inclusion of additional diffusion processes in the mobile domain as a function of heterogeneity within the experimental media [e.g., Berkowitz *et al.*, 2006; Dentz and Tartakovsky, 2006; Hill *et al.*, 2006], or (2) kinetic exchange between mobile and immobile zones within porous media (e.g., first-order, spherical, or multimodal) [Lapidus and Amundson, 1952; Oddson *et al.*, 1970; van Genuchten *et al.*, 1974]. Haggerty *et al.* [2000] note that the representation of the exchange process can take many forms, each of which will result in different simulated residence time distributions of tracer in the system. Residence time distributions are generally estimated from the first temporal moment of the concentrations measured from the outlet of a system [Harvey and Gorelick, 1995].

[9] For example, one-dimensional (1-D) advective-dispersive transport with generic mass transfer between the mobile and immobile zones is described by:

$$\frac{\partial C_m}{\partial t} = -v \frac{\partial C_m}{\partial x} + D \frac{\partial^2 C_m}{\partial x^2} + \beta \frac{\partial C_{im}}{\partial t} \quad (1)$$

where  $C$  is the concentration of pore fluids [ $M/L^3$ ], subscript  $m$  indicates mobile zone, subscript  $im$  indicates the immobile zone,  $t$  is time [T],  $x$  is the spatial dimension along which transport occurs [L],  $v$  is the pore-scale velocity of the mobile fluid [ $L/T$ ],  $D$  is the dispersion coefficient [ $L^2/T$ ], and  $\beta$  is the ratio of the size of the immobile zone to the mobile zone [–]. Generally, exchange processes are determined by characterizing the mobile concentration breakthrough curves ( $C_m(t)$ ) at some “end point” of a mobile-immobile system (Figure 1).

[10] One commonly used 1-D solute transport model to investigate mobile-immobile hyporheic interactions characterizes the  $\beta(\partial C_{im}/\partial t)$  term in equation (1) as a linear mass transfer process,  $\alpha(C_{im} - C_m)$ , where  $\alpha$  is the first-order exchange coefficient [ $T^{-1}$ ] between the mobile zone (i.e., a stream, fractures, or connected pore space) and a lumped representation of transient storage (i.e., eddies, side pools, hyporheic exchange, dead-end fractures, or less connected pore space) into a single immobile zone. Commonly, this formulation employs the following additional differential equation to track transient solute storage in the bulk immobile zone:

$$\frac{\partial C_{im}}{\partial t} = \frac{\alpha}{\beta}(C_m - C_{im}). \quad (2)$$

[11] Often unknown when using transient storage models are  $\alpha$  and  $\beta$  [Wagner and Harvey, 1997], which are parameterized as aquifer- or reach-representative values when simulating data collected from tracer experiments. While transient storage models with single storage zones have been found to fit field experiments [e.g., Choi *et al.*, 2000], averaging along the stream reach or flow pathway makes it difficult to estimate more parameters in the field; that is, data from one or several locations provide limited information about heterogeneity or the existence of multiple zones or exchange rates within a given area. Several recent studies have employed multiple storage zone models because a single storage zone with transient storage did not

adequately represent processes observed during stream tracer experiments [Gooseff *et al.*, 2004; Harvey *et al.*, 2005]. Additionally, numerous authors have suggested that a single rate coefficient  $\alpha$  (or even a few) may be inappropriate in a complex subsurface environment where, among other issues, heterogeneity occurs over all scales and variability exists in pore geometries, specific surface area, and organic carbon content [Karickhoff and Morris, 1985; Coates and Elzerman, 1986; Ball *et al.*, 1990; Weber *et al.*, 1992; Haggerty and Gorelick, 1995; Hollenbeck *et al.*, 1999]. However, determining  $\alpha$  in situ traditionally has been based solely on limited data sets of mobile domain breakthrough curves. Although useful for matching concentration data at numerous groundwater sites [e.g., Boggs and Adams, 1992; Feehley *et al.*, 2000; Harvey and Gorelick, 2000], application of mass transfer models for predictive purposes, such as water resource management and optimization of remediation designs, is limited by (1) lack of experimental methods to directly identify heterogeneous model parameters—specifically the mass transfer rate and mobile and immobile porosity independently—in situ, and (2) the definition of the mechanism responsible for non-equilibrium solute concentration gradients [Nkedi-Kizza *et al.*, 1984; Cunningham *et al.*, 1997].

## 2.2. Geophysical Imaging of Transport

[12] New experimental approaches are required to directly verify parameters controlling mass transfer in situ. Recent work has presented direct evidence of mass transfer in situ using geophysical methods [Singha *et al.*, 2007; Day-Lewis and Singha, 2008]. Geophysical data can provide spatially localized information on transport conditions that is complementary to the spatially integrated response obtained during tracer tests. Indeed, both ER and radar methods increasingly are used to monitor tracer tests [Slater *et al.*, 2000; Day-Lewis *et al.*, 2003, 2006a; Singha and Gorelick, 2006b]. ER imaging methods, in particular, are useful for monitoring time-lapse processes. The multidimensionality of ER methods and their capability for long-term continuous monitoring given semipermanently emplaced electrodes can be highly advantageous for transport studies compared to traditional point-based methods that require more time-consuming data collection.

[13] ER methods are used to estimate the distribution of electrical resistivity (or its reciprocal, EC) of a medium by establishing an electrical potential gradient between two source electrodes and measuring the resultant potential distribution at two or more receiver electrodes. The measured resistances are averages of the electrical properties of the porous media and conductive fluid in the system [Keller and Frischknecht, 1966]. Because ER methods are sensitive to changes in the EC of the subsurface, ER has been used to monitor spatial and temporal hydrologic changes in water content and pore fluid chemistry [e.g., Kemna *et al.*, 2002; Yeh *et al.*, 2002; Singha and Gorelick, 2005; Vanderborght *et al.*, 2005]. In the field, this method has been found to resolve targets from the submeter to tens-of-meters scale depending on the support volume of measurements or tomographic resolutions, which are complicated functions of the EC distribution of the subsurface, the data acquisition geometry, heterogeneity, and data noise [Daily and Ramirez, 1995; Day-Lewis *et al.*, 2005]. We stress that mass transfer may occur at scales much smaller than the geophysical

resolution. We do not seek or require millimeter-scale characterization; rather, we use the ER measurements (or tomographic estimates) to understand bulk concentration and thus understand the upscaled, effective transport behavior. ER methods show promise for testing the operation of mass transfer parameters on effective-scale mass transport in situ, because they are sensitive to the total concentration of ionic tracers, rather than that of the mobile water alone.

[14] Assuming that electrolytic conduction occurs in both mobile and immobile domains, which are overlapping in an aquifer setting, the bulk EC ( $\sigma_b$ , [S/m]) of the bicontinuum is given by [after *Day-Lewis et al.*, 2006a; *Singha et al.*, 2007]:

$$\sigma_b = a(\theta_m + \theta_{im})^{q-1}(\theta_m \sigma_{f,m} + \theta_{im} \sigma_{f,im}), \quad (3)$$

where  $\sigma_{f,m}$  is the mobile domain fluid EC at a given location [S/m];  $\sigma_{f,im}$  is the immobile domain fluid EC [S/m];  $\theta_m$  is the mobile domain porosity [–];  $\theta_{im}$  is the immobile domain porosity [–];  $q$  is the cementation exponent [–], and  $a$  is an effective tortuosity for the bicontinuum [–]. The derivation of equation (3) assumes that bulk EC varies linearly with total concentration [e.g., *Keller and Frischknecht*, 1966], and thus the EC of mobile and immobile porosities average arithmetically, as for resistors in parallel. Despite the assumption of arithmetic averaging, we will show later that the estimation approach we describe requires only the relative timing of breakthrough, which will not be impacted greatly by the choice of averaging.

[15] Another caveat is that while we account for porosity in our assumption of an effective formation factor for a representative elementary volume, we implicitly assume identical tortuosity for the two domains. The Archie formation factor,  $F$ , defined most simply by

$$\sigma_f = F \sigma_b \quad (4)$$

where  $\sigma_f$  is fluid conductivity and  $\sigma_b$  is bulk conductivity, depends on the pore volume and how that pore volume is connected in the direction of electrical current flow. Tortuosity estimates are hard to determine experimentally [*Boudreau*, 1996; *Mota et al.*, 1999], and this difficulty is particularly acute for the immobile domain. We assume, therefore, equal tortuosities due to lack of other available data. Consequently, changes in mobile and immobile fluid EC have similar effects on bulk EC. Pore connections in the immobile domain may be more tortuous, however, in which case a change in immobile fluid EC would translate into a smaller change in bulk EC than that assumed. Mass transfer may therefore cause the apparent formation factor to appear to vary in time [e.g., *Singha and Gorelick*, 2006a]. Equation (3) could be modified to account for variability in tortuosity if such data were available. Here, we ignore this potential complication and capitalize on the value of bulk EC as a surrogate for total concentration and show that ER data may be used to help constrain values of  $\alpha$  and  $\beta$  in situ.

### 2.3. Theoretical Framework for Estimating Mass Transfer From ER Methods

[16] *Day-Lewis and Singha* [2008] developed a framework to directly estimate heterogeneous  $\alpha$  and  $\beta$  values

from time-lapse ER and conventional sampling of mobile domain concentration. Here, we provide a brief review of this framework, which is based on a bicontinuum formulation of Archie's Law and temporal moment-generating equations for mass transfer [*Harvey and Gorelick*, 1995].

[17] Temporal moments are commonly used to describe breakthrough curves. The  $n^{\text{th}}$  temporal moment,  $m_n$ , is defined as

$$m_n = \int_0^\infty t^n C(t) dt \quad (5)$$

where  $t$  is time [e.g., *Goltz and Roberts*, 1986]. The zero-through second-order moments are related to total mass, mean arrival time, and concentration spread, respectively. Under linear mass transfer (equations (1) and (2)) and for certain boundary conditions, *Harvey and Gorelick* [1995] showed that the  $n^{\text{th}}$  moment of immobile concentration,  $m_n^{im}$ , is linearly related to the moments of mobile concentration,  $m_n^m$  up to order  $n$ :

$$m_n^{im} = n! \sum_{i=0}^n \frac{m_i^m}{i!} \frac{1}{\alpha^{n-i}} + n! \frac{C_0^{im}}{\alpha^n} \quad (6)$$

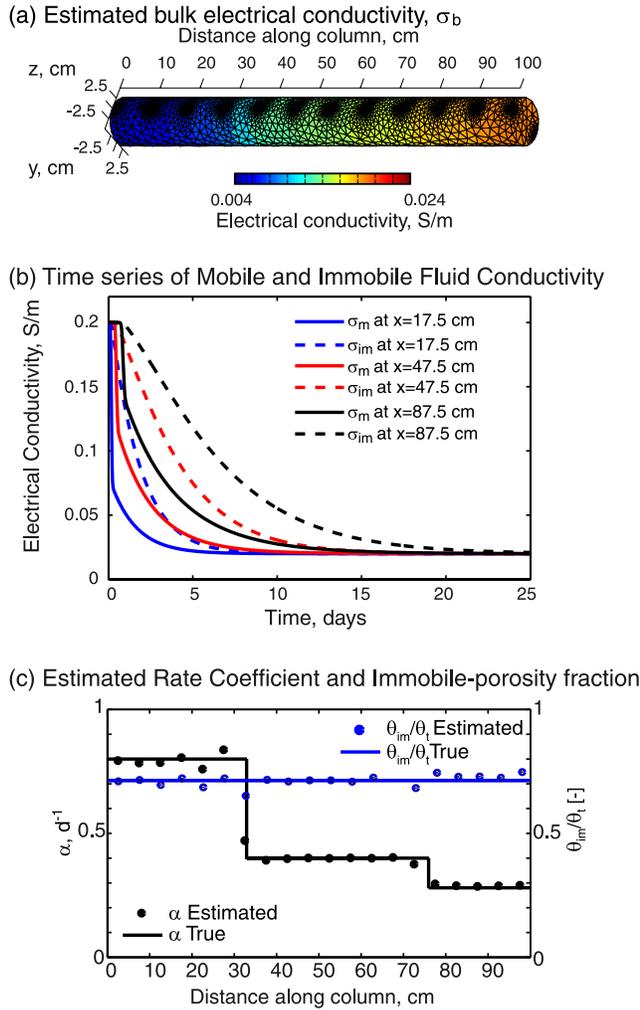
where  $C_0^{im}$  is the initial immobile concentration. On the basis of equation (6), the relation between  $m_n^m$  and  $m_n^{im}$  is independent of velocity variations, heterogeneity of  $\alpha$ , and heterogeneity of hydraulic conductivity. Consequently, given estimates of  $m_n^m$  and  $m_n^{im}$  from laboratory or field data, it would be possible to estimate the parameters controlling mass transfer. Immobile domain concentration is, however, difficult to measure. Combining equations (6) and (3) and a relation between fluid conductivity and solute concentration, *Day-Lewis and Singha* [2008] developed an approach based on temporal moments of bulk conductivity (from ER) and mobile domain conductivity (from fluid sampling). For a purge experiment—where the immobile and mobile concentration are initially in equilibrium and a solute is added to flush the original concentration out—consideration of moments up to order one produces sufficient nonredundant equations to solve for mass transfer parameters:

$$\alpha = \frac{m_0^T - m_0^m}{m_1^T - m_1^m - m_0^m(m_0^T - m_0^m)/C_0^{im}}, \quad (7)$$

and

$$\beta = \frac{C_0^{im}(m_1^T - m_1^m) - m_0^m(m_0^T - m_0^m) - (m_0^T - m_0^m)^2}{C_0^{im}(m_1^T - m_1^m) - m_0^m(m_0^T - m_0^m)}, \quad (8)$$

where  $m_n^T$  is the  $n^{\text{th}}$  moment of total concentration. Note that the estimation approach only requires relative mass and timing of breakthrough (zeroth and first temporal moments). Results from a synthetic column experiment, considering a purge injection, are shown in Figure 2. Given  $m_0^T$ ,  $m_1^T$ ,  $m_0^m$  and  $m_1^m$  along the column, equations (7)–(8) are used to estimate spatially variable  $\alpha$  and immobile porosity fraction with reasonable accuracy (Figure 2c).



**Figure 2.** Representative results from synthetic column experiments of a step injection. (a) Simulated bulk electrical conductivity in the column at 1 day; (b) scaled time series of measured mobile electrical conductivity and inverted bulk conductivity at  $x = 0.725$  m; and (c) estimated and true mass transfer rate constant,  $\alpha$ , along column (after *Day-Lewis and Singha* [2008]).

[18] The results of synthetic experiments demonstrate the utility of the approach as well as its limitations. In practice, the range of  $\alpha$  that can be estimated reliably—with ER methods and conventional approaches alike—likely depends on flow velocity, length of tracer transit, and the duration of the experiment. If the timescale of mass transfer is small relative to the timescale of advection, exchange between domains is so rapid that the breakthrough curves for  $c_m$  and  $c_{im}$  are near equilibrium. For such cases, the calculated first moments may be unreliable. Conversely, for large timescales of mass transfer, the exchange between domains is so slow that breakthrough curves may be truncated prematurely depending on the experimental design, also leading to spurious estimates of moments. It is, therefore, recommended to design monitoring experiments to achieve a equivalent rates of advection and mass transfer, i.e., an experimental Damkohler number,  $Dal$ , of approxi-

mately 1.0 [*Wagner and Harvey, 1997; Day-Lewis and Singha, 2008*]:

$$Dal = \frac{\alpha \left(1 + \frac{1}{\beta}\right) L}{v}, \quad (9)$$

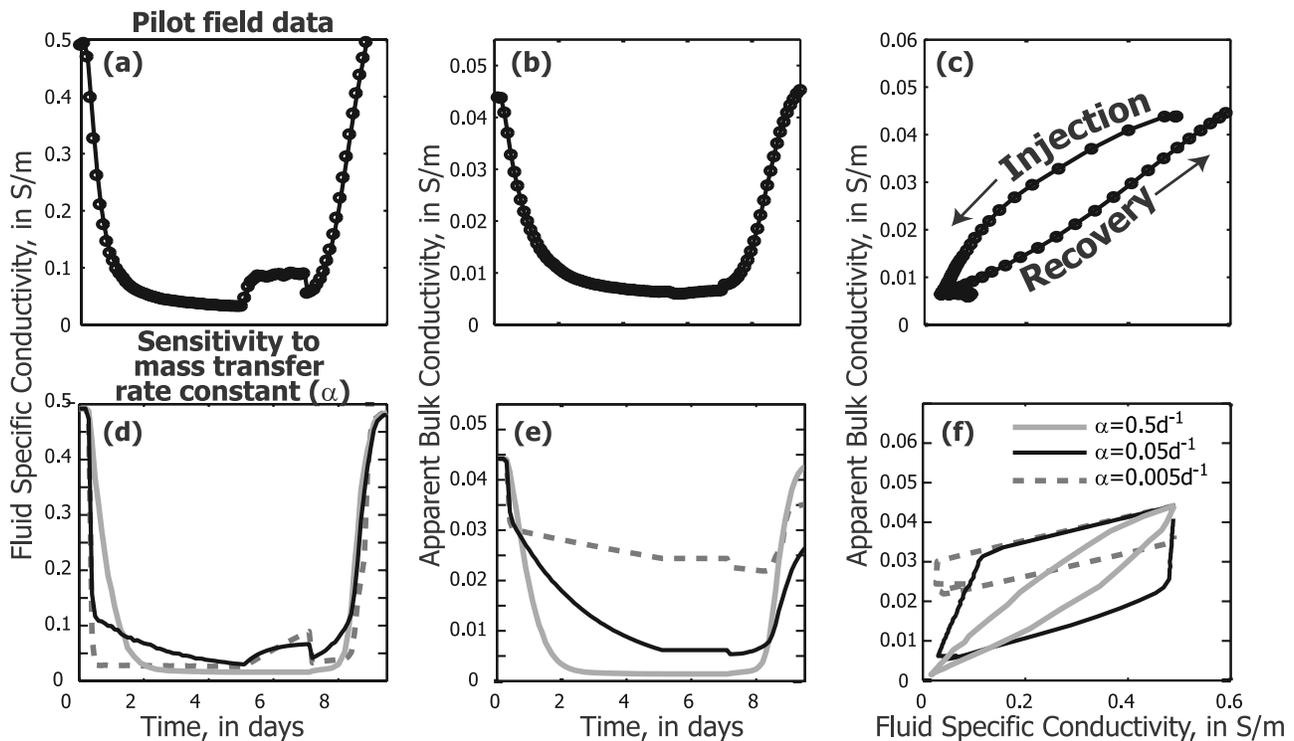
where  $L$  is the length of the stream reach over which the experiment is conducted [L], and  $v$  is the average advective transport velocity [L/T] [e.g., *Bahr and Rubin, 1987*].

[19] A second issue for ER monitoring of mass transfer is that of geophysical support volume. The length scale of mobile/immobile domains must be smaller than that of our geophysical resolution. Consequently, we cannot look at scales of mass transfer corresponding to sizes larger than our geophysical support volume; that is, if a length scale (corresponding to a rate constant) operates on a scale larger than the support volume of the tomographic estimate, that length scale will not be resolved using our approach.

#### 2.4. Review of a Pilot-Scale Experiment

[20] A recent experiment confirms the potential of using geophysical measurements for identifying the occurrence of mass transfer in situ. We briefly review field-experimental and modeling results from an aquifer storage and recovery (ASR) experiment [*Singha et al., 2007*]. In ASR, fresh water is injected into an aquifer during times of surplus and stored for later use during water deficits or natural disaster. The ASR injection displaces the native aquifer fluid, which may be brackish, creating a reservoir of potable water [*Eastwood and Stanfield, 2001*]. The impact of mixing between mobile and less mobile domains was shown to affect ASR efficiency, as potable water may be degraded within the freshwater bubble as well as at the edges where mixing may occur [*Culkin et al., 2008*].

[21] In the work of *Singha et al.* [2007], measurements of the bulk EC were collected during an ASR experiment conducted in a brackish aquifer in Charleston, South Carolina. During the storage period, a rebound in directly measured fluid EC was observed; concurrently, the bulk EC from ER measurements at the same locations showed little change (Figures 3a and 3b). The data show a hysteretic relation between measurements (Figure 3c), suggesting the local transfer of salts from the immobile to the mobile pore space rather than advective migration from elsewhere. The authors hypothesized that first-order mass transfer could explain the experimental results. They developed an axisymmetric flow and transport model, assuming a single first-order mass transfer rate (equations (1) and (2)) and the bicontinuum formulation of Archie's Law (equation (3)). Considering only simple, layered heterogeneity, the field-experimental data were reproduced. The modeling results indicated that the combination of bulk and fluid EC data is highly sensitive to controlling parameters such as rate coefficient  $\alpha$  and immobile domain porosity (Figures 3d–3f). These results point to the potential of ER methods to provide insight into field-scale mass transfer processes; however, as noted in regard to synthetic column experiments (section 2.3), the electrical signature of mass transfer depends on the relative timescales for advection and mass transfer, as described by  $Dal$ . The manifestations of mass transfer observed by *Singha et al.* [2007] might have been



**Figure 3.** Fluid electrical and ER data from Charleston, South Carolina and sensitivity analysis from numerical modeling of mass transfer processes for an aquifer storage and recovery experiment in groundwater. Field data: (a) mobile domain fluid conductivity history, (b) bulk conductivity history, and (c) the hysteresis in the bulk versus fluid conductivity curves at an observation well 8.2 m from the injection-extraction well. Modeling: (d) mobile domain fluid conductivity history, (e) bulk conductivity history, and (f) hysteresis assuming different values for the mass transfer coefficient,  $\alpha$ , of the fracture zone. Injection was from 0 to 5 days, storage from 5 to 7 days, and recovery from 7 to 10 days. These results provide evidence that geophysical methods can be used to estimate parameters controlling mass transfer in situ [after Singha *et al.*, 2007].

impossible to observe under higher or lower injection or extraction rates.

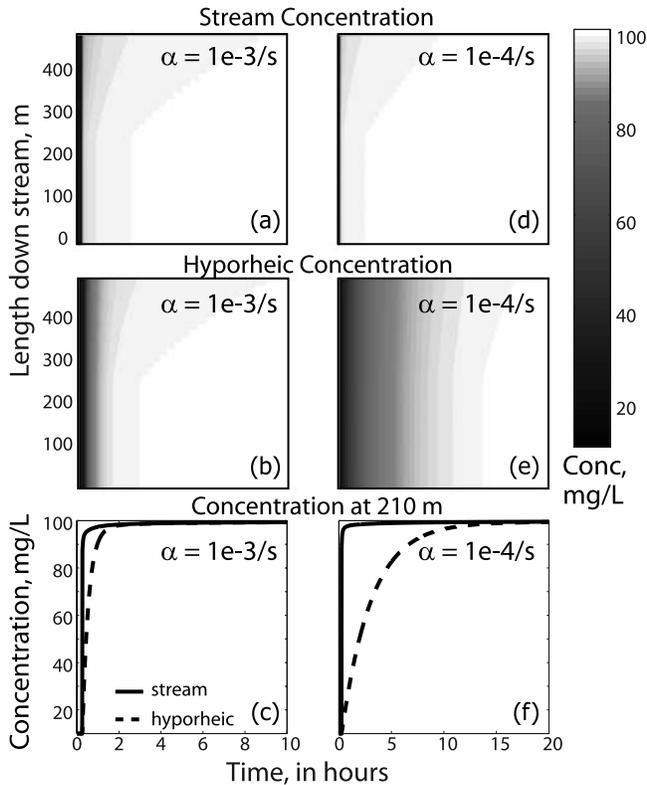
### 3. Development of a New Way to Image Hyporheic Mass Transfer in Streams

[22] ER methods have not been frequently used in streams. Acworth and Dasey [2003] used electrical imaging to determine the shape of a hyporheic zone beneath a tidal creek in a sand aquifer, where the EC of the hyporheic zone varied greatly with the tide. The inverted images show a clear distinction between the creek, a high-salinity hyporheic zone surrounding the creek, and the low-salinity area outside of the hyporheic zone. ER methods additionally have been used in streams as a method to detect the onset of streamflow [Blasch *et al.*, 2002], in marine settings to estimate submarine groundwater discharge [Day-Lewis *et al.*, 2006b; Swarzenski *et al.*, 2007], and in streams to explore groundwater discharge into streams [Nyquist *et al.*, 2008]; however, they have not been used, to the best of our knowledge, to quantify solute transfer between the stream and the hyporheic zone.

[23] Here, we present a series of synthetic examples that demonstrate the utility of ER methods to characterize hyporheic mass transfer. We use a simple transport code to simulate mass transfer between a mobile stream and less

mobile hyporheic domain, estimate the changes in bulk and fluid EC that would occur during the transport of a saline tracer, and assess the utility of ER methods to identify the mass transfer rate in situ. We note that this proof-of-concept experiment considers the simplest type of mass transfer—first order, single-rate mass transfer that does not vary in space—between a stream and a less mobile hyporheic zone. Unlike the column and aquifer experiments described earlier, where the mobile and less mobile domains overlap, here the domains are physically separate from one another, adding a level of complexity to our interpretation. Here, raw, uninverted resistance data, as used in the aquifer example, are not informative of the system, as these apparent measurements are a function of the stream above and the sediment below the electrodes. Inversion is required to determine the spatial significance of the ER data, and allow us to determine (1) the location (in distance and depth) where solute transport occurs, which cannot be estimated from the raw resistance data; and (2) temporal moments of the total EC, as described above.

[24] We use OTIS, a U.S. Geological Survey (USGS) finite difference code developed to simulate one-dimensional transport with transient storage [Runkel, 1998] and a 2.5-D finite volume forward and inverse code for modeling of ER data [Pidlisecky and Knight, 2008]. We consider a simple 500-m-long stream flowing at 1 m<sup>3</sup>/s with no



**Figure 4.** Concentration simulations, in mg/L from OTIS models for two mass transfer rates: (a) stream concentrations for  $\alpha = 1e - 3/s$ ; (b) hyporheic concentrations for  $\alpha = 1e - 3/s$ ; (c) a comparison of the two at  $x = 210$  m; (d) stream concentrations for  $\alpha = 1e - 4/s$ ; (e) hyporheic concentrations for  $\alpha = 1e - 4/s$ ; and (f) a comparison of the two at  $x = 210$  m. With high mass transfer rates, the concentrations in the stream and less mobile hyporheic domain are close to equilibrium, and the two domains behave more like a single continuum. For low mass transfer rates, the saline concentration in the immobile domain changes slowly, and the domains are more clearly separated.

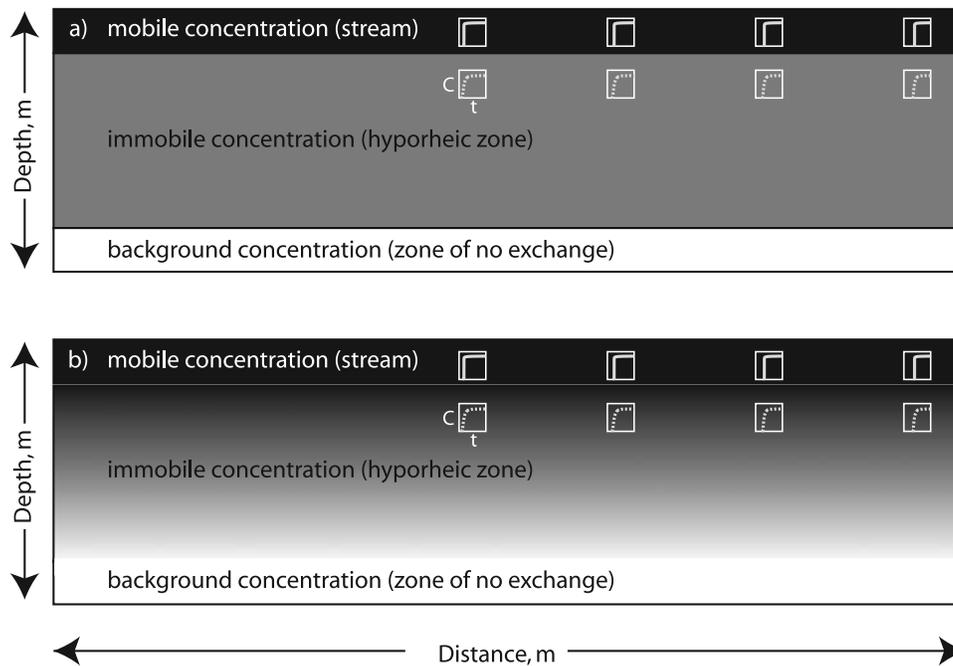
additional inflow or outflows. This synthetic stream has a depth of 1 m and a hyporheic (immobile) volume area equal to the stream (mobile) volume ( $\beta = 1.0$ ). A continuous solute source (with respect to concentration and rate) is introduced to the stream and monitored over 20 h, in analogy to the purge experiments conducted in the column example described above. A concentration of total dissolved solids of 100 mg/L, given an initial stream concentration of 10 mg/L, is introduced. In these models,  $DaI$  between approximately 0.001 and 100 are considered by varying  $\alpha$  from  $10^{-2}/s$  to  $10^{-5}/s$ .  $DaI$  is approximately equal to 1.0 for  $\alpha$  equal to  $10^{-3}/s$ . In all cases, the solute front moves quickly through the stream (Figure 4), making capture of the rising limb of the mobile concentration curve difficult given any reasonable sampling scheme, regardless of mass transfer. We assume that fluid EC samples are collected every transport time step, ranging from 35 s at the beginning of the tracer test, expanding out to every 42 min near the end of the test.

[25] For our synthetic examples, OTIS-based concentrations must be converted to cross sections of EC for input to

the electrical forward model. To do so, we first interpolate the OTIS concentrations, calculated every 15 m, to a finer mesh in the  $x$  direction as needed for modeling electrical conduction. The stream concentration/EC is considered to correspond to the mobile domain concentration in OTIS, and the hyporheic zone concentration (which must vary vertically) is calculated on the basis of the immobile domain concentrations in OTIS. To distribute immobile zone concentration vertically below the streambed and maintain mass balance, we consider the hyporheic zone to have a porosity of 0.25 and assign a depth to the hyporheic zone equal to 4 times the 1-m stream depth, based on the assumed porosity and  $\beta = 1$ . This procedure results in a 2-D cross-sectional model of concentration with the same mass as simulated in OTIS.

[26] The conversion from concentration to EC is not straightforward and underscores an important assumption in OTIS and other models of solute transport and mass transfer in streams—that the storage zone is well-mixed. In OTIS, exchange processes are one-dimensional [Runkel, 1998], and the zone of transient storage has no vertical extent. Clearly these assumptions provide for only a gross approximation of processes occurring substream. For example, in the synthetic experiments here, the stream becomes electrically conductive with the introduction of tracer, and the hyporheic zone below becomes increasingly conductive with time from exchange with the stream from above. In reality, concentration may not be well-mixed within the storage zone, and may instead vary vertically. We consider two sets of models to evaluate the assumption of a well-mixed storage zone and produce realistic examples of ER monitoring of hyporheic exchange. In the first set of models, concentration within the hyporheic zone is vertically homogeneous, and the OTIS-simulated mobile concentration is simply stacked above the immobile concentration, which represents a well-mixed storage zone (Figure 5a). However, this representation of the subsurface is unlikely to occur in field settings, where it is more likely that there is a gradient in the hyporheic zone from the stream to some depth beneath the stream outside the zone of exchange. In the second set of models, we distribute solute mass such that a linear vertical gradient is established from the streambed to a depth of 4 m, while conserving mass in the immobile domain (Figure 5b). The gradient in the immobile zone is more realistic with respect to processes we would expect to see in the field and predicted by groundwater flow models [Elliott and Brooks, 1997]. In contrast to the well-mixed models, these models result in more realistic and more challenging tests of the capabilities of electrical geophysics to characterize mass transfer. Both sets of models preserve mass balance.

[27] Regardless of how the storage zone is represented, the 2-D cross sections of concentration are converted to cross sections of electrical conductivity at each time step. The concentrations are converted first to fluid electrical conductivities assuming 1 mg/L equates to  $2 \mu S/cm$  as approximated by Keller and Frischknecht [1966]. In the hyporheic zone, we then convert from fluid EC to bulk EC, assuming an Archie cementation exponent of 2, as commonly used in the literature [Knight and Endres, 2005]. These EC fields are then used in a 2.5-D ER finite volume forward model of electrical conduction lengthwise down the



**Figure 5.** Schematic of how the concentration results from OTIS are converted to a 2-D section of electrical conductivity used for ER forward modeling. The hyporheic zone is  $4\times$  the depth of the stream to conserve mass, accounting for the porosity of the sediment beneath the stream. The bottom of the model is padded with a block of constant concentration through time, where mass is not exchanging. To calculate temporal moments, we consider the change in electrical conductivity at a series of pixels in the stream (as demonstrated by the white boxes) to those just beneath the stream.

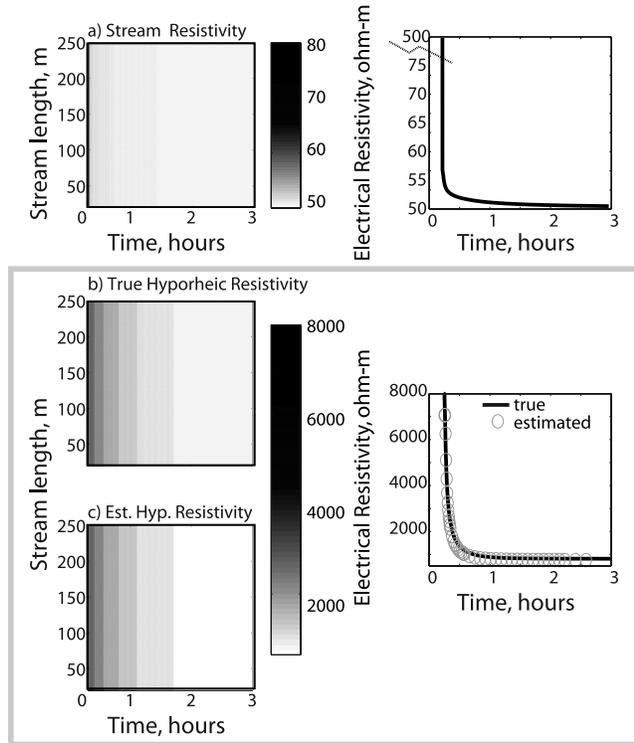
stream where 100 electrodes with 5-m spacing are emplaced along the base of the water column, to produce a series of 840 resistance observations per time step. With a fast multichannel ER acquisition system, it would take a few minutes to collect this data set. Faster technologies are also currently being developed in the laboratory that may later make field acquisition more rapid [Mitchell *et al.*, 2007]. The forward model mesh is set up with a pixel size of 0.25 m on a side.

[28] For the ER inversions, a uniform grid of pixels was used with cells regularly spaced at 1 m in length and 0.5 m in depth. Because these models are synthetic, the mesh need not be padded to deal with errors in the boundary conditions. The inversion was parameterized on a coarser grid than the original forward model grid. Inverting on a coarser grid is more consistent with the information content in the ER data, requires less regularization and consequently will yield better estimates of mass, albeit averaged over a larger volume. The 840 resistance measurements are inverted without added noise, although by inverting on a coarser grid, inherent numerical noise is introduced to the data.

[29] We note that, in general, a number of issues complicate interpreting images from ER inversion: there is not enough information to uniquely determine all the local bulk EC parameter values because there is finite spatial sampling and a limited number of resistance measurements that can be collected; data errors create ill-conditioning; and calculating the true distribution of EC in the subsurface is a highly nonlinear problem because the current paths through the medium are dependent on the EC structure [Day-Lewis *et al.*, 2005; Singha and Moysey, 2006]. Most tomographic problems in geophysics are solved with an excess number

of model parameters and use regularization to create a mathematically stable solution [e.g., Constable *et al.*, 1987]. While this approach is useful for imaging large-scale (low spatial frequency) structures, it yields poor results when attempting to infer quantitative values from the recovered images [e.g., Binley *et al.*, 2002; Singha and Gorelick, 2005; Day-Lewis *et al.*, 2007]. This effect is often caused by overregularization of the solution during inversion, as well as by overparameterization of the inverse problem. However, if one reduces the model space size, the need for regularization can be greatly reduced, and we can obtain inversion results that are less smooth. By minimizing the parameter space, we are not necessarily giving up resolution; rather, if the data were sufficient to resolve fine-scale features, regularization would be minimal and the inverse problem would be well determined. By solving a less overparameterized inverse problem, we are being consistent with the information content of the data and thus acquire more robust, interpretable results.

[30] In addition to the challenges outlined above, recovering quantitative ER information in the hyporheic zone presents unique challenges. Most significant is that the stream is substantially more conductive than the underlying hyporheic zone (in the cases presented here, as much as 16 times more conductive). This contrast causes the inversion to have a much higher sensitivity to changes in the stream water column than the hyporheic zone. To circumvent this, the inversion pixels in the stream were fixed at known concentration values (which in the field would be obtained from stream-based fluid EC probes), the base of the stream was considered known (which could be determined approximately in the field), and the inversion was performed only



**Figure 6.** Map of (a) OTIS-estimated stream resistivity and (b) hyporheic zone resistivity (converted from Figures 4a and 4c), and the ER-estimated (c) hyporheic resistivities given a mass transfer rate of  $1e - 3/s$ . Data are shown for the first 3 h, where most of the changes occur, and the first 250 m of the stream. The hyporheic resistivity was inverted for at each time step. Line plots are from 210 m.

in the hyporheic zone, essentially treating the stream as a boundary condition. We note that these are strong assumptions, and that they require field data to substantiate; previous work in marine resistivity has indicated that errors in the depth of the water column, for instance, can propagate throughout an inversion, making quantitative analysis of images difficult [Day-Lewis *et al.*, 2006b]. For the models presented here, we reduce the number of model parameters by treating the area beneath the stream as a single layer that varies only in the  $x$  direction; furthermore, we coarsen the inversion grid in the  $x$  direction. As mentioned earlier, inverting on a coarser grid is more consistent with the information content in the ER data and results in a better determined inverse problem.

[31] The outcome of these choices is that we are able to eliminate regularization in the  $z$  direction, and reduce the need for regularization in the  $x$  direction. The net effect is that the inversion yields a better estimate of concentration. One implication of this choice is that we have assumed that the inverted conductivity should vary in space. We do not explicitly regularize in time, but create a starting model for each time step on the basis of the average value of the solution from the previous time step. Representative results from the inversions for  $\alpha = 10^{-3}/s$  are shown in Figure 6 for the simulation with the blocked concentration model. These plots are the “true” EC of the subsurface (from Figure 4) and the estimated values. The relation between the true and estimated EC in the stream is linear and 1:1 because the conductivity is assumed known in the stream for the inversion. The estimated bulk EC in the hyporheic zone is not exactly equal to the true conductivity because of the inversion regularization and the spatially variable sensitivity of the geophysics. Despite this, we find that these inversion results map the temporal changes in solute content in the immobile zone.

[32] We calculate the temporal moments on the basis of the mobile and total concentrations for the two sets of models. Temporal moments can be calculated wherever we can collect concentration (or EC) data, and can consequently be determined at many locations along the stream reach. We calculate the temporal moments of the mobile and immobile concentration from OTIS considering the first 250 m of the stream system (Tables 1 and 2). Because solute transfers downstream quickly, the first three temporal moments (mass, mean arrival time, and concentration spread) calculated along the stream reach, from the transport simulations alone, do not vary greatly in the downstream direction. Consequently, we present only an average value over the entire stream reach. In field scenarios where the mass transfer rate may vary greatly in space, these moments could be considered with respect to location along the stream.

[33] As expected, the moments between the OTIS-simulated mobile and immobile concentration differ with the mass transfer rate. An important point to note is that the temporal moments for the mobile domain do not vary substantially in this environment for the range of mass transfer rate coefficients considered, whereas the immobile domain moments vary strongly with mass transfer rate. Consequently, geochemical data alone would provide limited information to understand mass transfer for these examples. Plots of collocated bulk EC from the streambed, reconstructed by inversion, versus “sampled” mobile fluid

**Table 1.** Temporal Moments for a Series of Mass Transfer Rates for the OTIS-Simulated Mobile and Immobile Concentrations and ER-Estimated Immobile Concentrations Assuming the Streambed Porosity<sup>a</sup>

	$\alpha = 1e - 2/s$			$1e - 3/s$			$1e - 4/s$			$1e - 5/s$		
	Mob	Im	Est Im	Mob	Im	Est Im	Mob	Im	Est Im	Mob	Im	Est Im
$m_0$	9.22	11.7	11.5	9.16	32.5	32.3	8.53	235	235	6.59	365	226
$\mu$	2.25	1.85	1.84	2.30	1.08	1.08	2.60	2.85	2.84	2.02	5.99	4.86
$\sigma^2$	7.57	6.63	6.65	7.58	2.93	2.90	8.68	5.89	5.84	7.09	15.8	11.2
Est. $\alpha$		$1.1e - 2/s$			$1.1e - 3/s$			$1.1e - 4/s$			$1.1e - 4/s$	

<sup>a</sup>Values are the average for the first 250 m of the stream, given the “block” conductivity models. Variables are as follows:  $m_0$  is the mass in  $mg L^{-1}d$ ,  $\mu$  is the mean arrival time in  $mg L^{-1}d^2$ , and  $\sigma^2$  is the concentration spread in  $mg L^{-1}d^3$ . Mob is mobile, Im is immobile, Est Im is estimated immobile. Mobile values are considered known.

**Table 2.** Temporal Moments for a Series of Mass Transfer Rates for the OTIS-Simulated Mobile and Immobile Concentrations and ER-Estimated Immobile Concentrations Assuming the Streambed Porosity<sup>a</sup>

	$\alpha = 1e - 2/s$			$1e - 3/s$			$1e - 4/s$			$1e - 5/s$		
	Mob	Im	Est Im	Mob	Im	Est Im	Mob	Im	Est Im	Mob	Im	Est Im
$m_0$	9.22	11.1	24.5	9.16	32.6	32.2	8.53	250	136	6.59	365	935
$\mu$	2.25	1.82	4.87	2.30	1.06	3.79	2.60	3.59	2.50	2.02	5.99	6.15
$\sigma^2$	7.57	6.55	20.0	7.58	2.64	19.0	8.68	10.5	12.9	7.09	15.8	15.8
Est. $\alpha$	$1.7e - 2/s$			$1.1e - 3/s$			$1.9e - 4/s$			$2.7e - 5/s$		

<sup>a</sup>Values are the average for the first 250 m of the stream, given the models using the imposed concentration gradient in the hyporheic zone.  $m_0$  is the mass in  $mg L^{-1}d$ ,  $\mu$  is the mean arrival time in  $mg L^{-1}d^2$ , and  $\sigma^2$  is the concentration spread in  $mg L^{-1}d^3$ . Mob is mobile. Im is immobile. Est Im is estimated immobile. Mobile values are considered known.

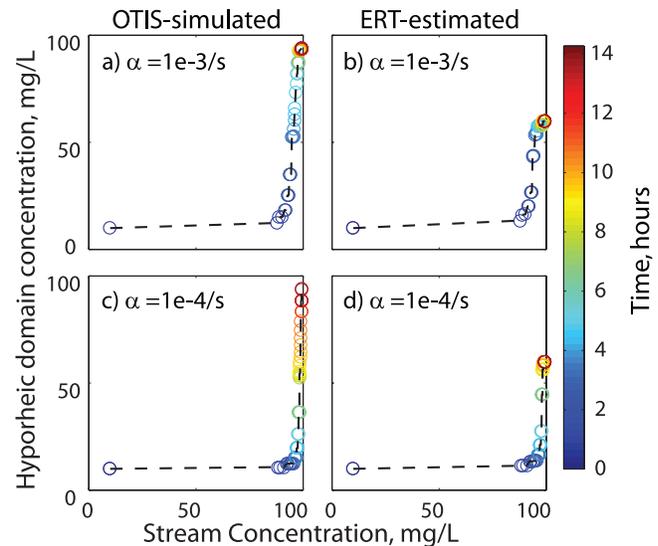
EC in the stream show that while the shape of the curve does not vary greatly with the mass transfer rate, the curves are quite different with respect to timing (Figure 7). This supports our hypothesis that the temporal moments of the mobile and immobile domain concentrations—or mobile and total conductivity—may be instructive with regards to identifying parameters controlling mass transfer when used together.

[34] We estimate the moments of the immobile concentration on the basis of the ER data. The moments for the concentration in the mobile domain, on the basis of the ER inversion, are the same as in the OTIS simulation, since, again, the fluid EC is assumed to be known; however, the immobile domain moments differ from the true case as a function of spatially variable sensitivity of the ER methods. On the basis of equation (5), we can estimate  $\alpha$ , the mass transfer rate between the mobile and immobile domain, on the basis of the zeroth moments of the mobile and immobile concentration and starting concentration for the tracer test.

[35] For the blocked models with a vertically homogeneous hyporheic zone (Table 1), we use the pixels at the stream base for our mobile concentration measurements, and compare them to the pixels just beneath the stream. By greatly simplifying the inversion to minimize the number of inversion blocks considered, we find that we generally do an excellent job of matching the temporal moments for the given scenarios, and consequently can accurately and easily estimate the mass transfer rate with these data, at least for models with  $DaI$  between 0.1 and 10. For the models with an imposed gradient, we calculate the moments similarly to the block model above, although we take an average of the pixels beneath the stream to calculate the “true” immobile moments. We note that even with the gradient models, we are generally able to map the mass transfer rate, as estimated from the zeroth moment, within an order of magnitude (Table 2). The disparity between estimated and “true” moments in the immobile zone is likely a consequence of the “well mixed” assumption inherent in the gradient solute transport model, and the inability of the ER methods to capture that gradation. We note here that the results of the model with the concentration gradient highlight a critical issue when using ER, and other geophysical methods, for hydrologic inference. The issue is the need to parameterize the ER inversion model in a manner that is not only consistent with the information content in the ER data, but is also consistent with the underlying physics of the hydrologic problem under consideration. The results for the blocked conductivity model are in excellent agreement with

the true model. This is due in large part to the fact that our chosen geophysical model is physically consistent with the conductivity distribution. In the gradient model, the block model assumption used in the geophysical solution is less representative of the process we are trying to map; there is an EC gradient that we are approximating with a single parameter, which for large gradients can be a poor approximation.

[36] These results show promise for using remotely sensed data to directly estimate hydrologic parameters controlling mass transfer in situ, including scales of mass transfer rates (or diffusion lengths), immobile zone size, and flow velocities. The results of our synthetic example indicate that ER techniques may greatly enhance our ability to study mobile-immobile exchange processes, particularly in



**Figure 7.** Change in hyporheic zone versus stream concentration at a point 100 m alongstream the system for (a) simulated concentration and (b) ER-estimated concentration for a mass transfer rate of  $1e - 3/s$ ; and (c) simulated concentration and (d) ER-estimated concentration for a mass transfer rate of  $1e - 4/s$ . The colors indicate timing during the experiment, from dark blue prior to injection to red near the end of the 20-h experiment. Initial time steps are 6 min, stretching to 42 min at the end of the experiment. Although the ER data underestimate the concentrations seen in the hyporheic zone and the shapes of the curves are similar regardless of mass transfer rate, the timing of the transport varies distinctly with mass transfer rate.

stream-hyporheic studies. Estimates of mass transfer parameters are applicable for the particular conditions incurred during the investigation (e.g., flow conditions). One great advantage of time-lapse ER data acquisition will be the ability to discern changes in mass transfer processes under varying conditions.

#### 4. Discussion and Future Directions for Research

[37] Hydrogeophysical methods increasingly are used to provide insight into hydrologic processes ranging from natural phenomena to engineered remediation to aquifer storage and recovery. For watershed characterization, tools are needed that can image processes occurring over long spatial and temporal scales, and ER methods may be useful for this, particularly in stream settings. Mass transfer is a principal control on the efficiency of aquifer remediation and stream water management, yet the occurrence and rates of mass transfer remain poorly understood. Conventional experimental approaches focus on measurement of mobile domain concentration, and provide only indirect information about the immobile or less mobile domains. We contend that, in combination with conventional tracer tests, geophysical methods can provide valuable insight into mass transfer. By coupling electrical geophysical methods with geochemical sampling and numerical modeling, we can explore the properties and parameters controlling transport and mass transfer between mobile and less mobile domains. Underlying our approach is the premise that electrical geophysical data quantify total concentration, rather than the mobile concentration available from direct geochemical sampling.

[38] Although ER methods show promise for determining mass transfer parameters in situ, a number of complications and unsolved problems remain that were not explored fully in the simplified synthetic model presented here, and additional research is needed to understand issues associated with (1) geophysical support volume (volume of material that influences a measurement), survey geometries and alternative electrical or electromagnetic measurements for characterizing mass transfer; (2) the effect of gaining and losing stream sections; (3) inversion choices; and (4) coupled inversion. We consider these issues independently here. For example, differences between the support volumes of direct sampling and geophysical imaging could produce discrepancies between the temporal moments of concentration and ER response in the absence of mass transfer. In the work presented here, support volume discrepancy cannot explain the difference in timing between bulk and fluid EC shown in the mobile-immobile concentration curves; however, in cases where small-scale heterogeneity controls transport, the behavior between fluid and bulk EC may be different. Other electrical or electromagnetic methods that measure EC over a smaller support volume (e.g., time domain reflectometry) may also be appropriate for characterizing solute mass transfer in stream settings.

[39] Related to issues of scale, careful laboratory work is also required to better understand the controls on mass transfer. This would include column-scale studies for consideration of aquifer processes, and flume-scale work for hyporheic zone transfer where control of flow velocities and diffusion lengths could be investigated. Additionally, imaging of smaller features at scales beneath the geophysical

support volume, specifically quantifying the mobile and immobile domain tortuosities and relative volumes, may clarify some of the issues seen in both laboratory and field settings regarding what appear to be time-varying formation factors [e.g., *Singha and Gorelick, 2006a*].

[40] We note that our synthetic case of hyporheic exchange is simplified for the sake of demonstration. True hyporheic dynamics in streams are likely to be heterogeneous in space, with variable locations of upwelling and downwelling. Further real world complexity will come from the hydrologic setting of the hyporheic zone, whether the stream is generally gaining or losing. For example, in streams in desert landscapes, which may be generally losing and yet also accommodate hyporheic exchange, the application of ER methods may result in a very different observed distribution of tracer in the subsurface with a relatively shallow exchange zone and a deeper penetration of salt tracer. For gaining streams, it is likely that the observed tracer distribution would be confined to a shallow exchange depth. Similar findings have been suggested by hydrodynamic simulations [*Woessner, 2000*] and coupled hydrodynamic and heat transport simulations [*Cardenas and Wilson, 2007*]. Moreover, side pools contribute to transient storage in some settings, yet the use of ER measurements assumes transient storage occurs below the stream.

[41] We note that this experiment could take many forms. We consider purge tests here, which require a significant mass of tracer to be added to the stream; pulse tests could also be considered, as described by *Day-Lewis and Singha [2008]*. A complication with pulse injections, however, is that moments up to order 2 are required, and calculation of higher-order moments is more prone to error than that of lower-order moments. Regardless of the injection strategy, data acquisition should continue beyond the end of the experiment to image postinjection hyporheic zone interactions.

[42] Another area of critical importance is developing problem-specific solutions to geophysical inverse problems. As shown here, choices were made in framing the inverse problem so that we would obtain quantitative information to answer the question of interest. By designing a problem-specific inverse parameterization and appropriate regularization, we can maximize the utility of the geophysical data for answering the hydrologic question under investigation. Using “black box” inversion algorithms can lead to ER tomograms that yield, at best, qualitative estimates. Obtaining quantitative information from geophysical data is a challenging problem that can best be addressed by recognizing the importance of taking a multidisciplinary approach, between hydrologists and geophysicists, to framing the inverse problem.

[43] The methodology outlined here is based on temporal moments, and has been demonstrated for a number of synthetic experiments. Application in field settings is necessary to substantiate the theory presented here, and additional work is required to investigate the possible advantages of alternative survey geometries (e.g., cross-stream) and alternative measurement techniques (e.g., time domain reflectometry). Our general methodology could be extended through inverse modeling to consider more complicated, multirate models of mass transfer or transport in nonuniform flow fields. In cases where inferred moments are poor

because of limited resolution or measurement error, joint inversion of geophysical and hydrologic data sets may provide a better characterization of mass transfer behavior. Furthermore, ER techniques to characterize bulk tracer distribution will be valuable for developing a new understanding of solute transport in porous media, and informing the numerical models that would follow such breakthroughs. Many of the currently available models of mobile-immobile exchange assume well mixed conditions in immobile zones at some level. This underlying assumption is a simplification that currently cannot easily be informed, and is inaccurate at scales beyond a single pore. Clarifying immobile zone dynamics is critical to advancing our understanding of contaminant transport in a host of environments. As mentioned above, future applications of ER methods to solute transport should include solute tracer experiments in the laboratory and at both simple and complex field sites. Such experiments will result in additional information to constrain novel solute transport models, thereby advancing our ability to more accurately simulate contaminant fate and transport. Furthermore, such advances will be the fruit of multiple investigator groups that can leverage off of individual expertise.

[44] In this paper we (1) reviewed the theoretical framework for studying mass transfer using electrical geophysics; (2) outlined field-experimental data and modeling for an aquifer storage and recovery experiment; and (3) presented an emerging method for quantifying mass transfer processes for hyporheic applications. Our findings underscore the potential of electrical geophysical methods for understanding mass transfer at different scales and in different hydrologic settings. This work represents the initial steps toward developing novel field-scale methods of determining mass transfer behavior in hyporheic systems, and provides a basic framework for estimating parameters controlling mass transfer in simple systems.

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