Published in final edited form as:

J Contam Hydrol. 2011 April 25; 123(3-4): 104–113. doi:10.1016/j.jconhyd.2010.12.011.

ASSESSMENT OF A SIMPLE FUNCTION TO EVALUATE THE RELATIONSHIP BETWEEN MASS FLUX REDUCTION AND MASS REMOVAL FOR ORGANIC-LIQUID CONTAMINATED SOURCE ZONES

Erica L. DiFilippo¹ and Mark L. Brusseau^{1,2}

¹ Hydrology and Water Resources, School of Earth and Environmental Sciences, University of Arizona, 429 Shantz Building, Tucson, Arizona 85721

² Soil, Water, and Environmental Science, School of Earth and Environmental Sciences, University of Arizona, 429 Shantz Building, Tucson, Arizona 85721

Abstract

The efficacy of a simple mass-removal function for characterizing mass-flux-reduction/mass-removal behavior for organic-liquid contaminated source zones was evaluated using data obtained from a series of flow-cell experiments. The standard function, which employs a constant exponent, could not adequately reproduce the non-singular (multi-step) behavior exhibited by the measured data. Allowing the exponent to change as a function of mass removal (as the organic-liquid distribution and relative permeability change) produced non-singular relationships similar to those exhibited by the measured data. Four methods were developed to characterize the variability of the exponent through correlation to measurable system parameters. Key factors that mediate the magnitude of mass flux (dilution and source accessibility) were accounted for using measures of source zone cross-sectional area, ganglia-to-pool (GTP) ratio, and relative permeability. The two methods that incorporated only the ganglia-to-pool ratio produced adequate simulations of the observed behavior for early stages of mass removal, but not for later stages. The method that incorporated parameters accounting for the source zone cross-sectional area (i.e., measure of system dilution) and source accessibility (GTP ratio and relative permeability) provided the most representative simulations of the observed data.

Keywords

DNAPL; Source zone; Mass transfer

1. Introduction

The contaminant mass flux or mass discharge emanating from a source zone is recognized as a primary determinant of the risk associated with a contaminated site (e.g., EPA, 2003, NRC, 2005). Concomitantly, the reduction in mass flux achieved with a specific level of

Correspondence to: Mark L. Brusseau.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

source-zone mass removal (or mass depletion) is a key metric for evaluating the effectiveness of a source-zone remediation effort. Several approaches, based on “source-depletion” models or simple “mass-removal” functions, have been employed for characterizing the relationship between mass flux reduction and mass removal (e.g., Enfield et al., 2002; Rao et al., 2002; Parker and Park, 2004; Falta et al., 2005; Jawitz et al., 2005; Basu et al., 2008a; Brusseau et al., 2008; DiFilippo and Brusseau, 2008; Maji and Sudicky, 2008; Zhang et al., 2008).

One simple approach for simulating mass-flux-reduction/mass-removal behavior is based on treating changes in mass flux as a direct function of the change in contaminant mass:

$$1 - \frac{J_f}{J_i} = \left(1 - \frac{M_f}{M_i}\right)^n \quad (1)$$

where J is mass flux [M/t], M is source zone mass [M], n is a fitting parameter, and the subscripts i and f represent initial and final, respectively. This approach has been applied in several studies during the past decade (e.g., Rao et al., 2002; Brooks et al., 2004; Zhu and Sykes, 2004; Falta et al., 2005; Basu et al., 2008a, 2008b; Brusseau et al., 2008; DiFilippo and Brusseau, 2008; Kaye et al., 2008; Maji and Sudicky, 2008; Parker et al., 2008; Chen and Jawitz, 2009; DiFilippo et al., 2010; Marble et al., 2010). The parameter n defines the specific mass-flux-reduction/mass-removal relationship, and is a lumped-process term that incorporates the impact of organic-liquid distribution, flow-field dynamics (e.g., changes in relative permeability), and mass-transfer processes.

Concurrent with investigation of simple models and functions for characterizing organic-liquid dissolution and associated mass flux, interest has developed in the use of system-indicator parameters for forecasting the type of mass-flux-reduction/mass-removal behavior expected for a given set of conditions. One example is using the ganglia-to-pool (GTP) ratio to define organic-liquid distribution (e.g., Lemke et al., 2004; Christ et al., 2006; Lemke and Abriola, 2006; Suchomel and Pennell, 2006; Basu et al., 2008a, Brusseau et al., 2008, Christ et al., 2009). The GTP is the ratio of the volume of organic liquid present at or below residual saturation divided by the volume present at saturations greater than residual saturation. In addition to organic-liquid distribution, mass-flux-reduction/mass-removal behavior may also be influenced by the magnitude and time scale of contact between the flowing water and the source zone (dilution effects, flow rate, system dimensions), and the overall amount of organic liquid present, especially under conditions wherein one or more mass-transfer processes are rate limited. Thus, other potential system-indicator parameters include global organic-liquid saturation, source-length/system-length ratio, and source-area/system-area ratio (cross-sectional areas). Statistical measures of organic-liquid saturation and permeability distributions have also been employed as system-indicator parameters (e.g., Mayer and Miller, 1996; Jawitz et al., 2005; Saenton and Illangasekare, 2007; Basu et al., 2008a, 2008b, DiFilippo et al., 2010).

The robustness of simple mass-removal functions and system indicator parameters for predicting mass-flux behavior is anticipated to be generally limited, particularly for complex systems (e.g., Christ et al., 2006; Basu et al., 2008a; Brusseau et al., 2008, DiFilippo and Brusseau, 2008; Marble et al., 2008; DiFilippo et al., 2010). However, such approaches may have use for example in providing a “first-order” approximation of mass-flux behavior. The purpose of this study is to evaluate the use of a simple mass-removal function to simulate mass-flux-reduction/mass-removal behavior, the potential mass-removal dependency of this function, and means of estimating mass-flux-reduction/mass-removal behavior using measurable system-indicator parameters.

2. Materials and Methods

2.1 Systems Investigated

Data obtained from a series of flow-cell experiments were used to evaluate performance of the simple mass removal function. The flow-cell systems were designed to reflect a variety of organic-liquid distributions and flow-field heterogeneities. The methods employed for, as well as the results obtained from, these experiments are presented in detail by DiFilippo et al. (2010); therefore, only a brief description is presented below.

Rectangular and cylindrical flow cells were used for the four experiments from which the data used for this study were obtained (Table 1). The Control and Homogeneous experiments each consisted of a homogeneous pack of 40/50 mesh sand. A residual saturation of trichloroethene (TCE) was emplaced within these two flow cells, the only difference being that TCE was uniformly distributed within the entire system for the former experiment whereas it resided in a subsection of the system for the latter. For the Control experiment, a residual saturation of TCE was established throughout by injecting organic liquid into the influent end of the cylindrical flow cell. Mobile organic liquid was removed prior to the initiation of water flooding by pumping several pore volumes of TCE-saturated solution through the column. This method developed a source zone wherein organic liquid was assumed to be present at residual saturation ($S_n = 0.18$) throughout the entirety of the flow field. The source zone for the Homogeneous experiment was developed in the middle of the flow cell by manually mixing and packing the source zone with organic liquid using standard procedures (e.g., Brusseau et al., 2000; Brusseau et al., 2002; Brusseau et al., 2008). This method developed a source zone wherein organic liquid was present at residual saturation in a small portion (10%) of the total flow field.

The rectangular flow cell (40 cm long by 20 cm high by 2.6 cm wide) was used to conduct the Mixed Source and Heterogeneous experiments (see Figure 1). The Mixed-Source experiment consisted of a homogeneous pack of 40/50 mesh sand with a 2-cm thick capillary barrier of 70/100 mesh sand along the bottom boundary. The Heterogeneous experiment consisted of a matrix of 40/50 mesh sand with lenticular lenses of 20/30 mesh and 70/100 mesh sands. The source zones for both the Mixed-Source and Heterogeneous experiments were developed by injecting TCE through injection ports at the top of the flow cell using a gas-tight syringe and needle. Organic liquid, dyed with Sudan IV (Aldrich) at a concentration of 100 mg/L, was injected at a rate of 1 ml/min and allowed to naturally distribute within the porous media for a period of 48 hours prior to the initiation of water flushing. For the Mixed-Source experiment, all of the organic liquid (~12 ml) was injected through the central injection port. For the Heterogeneous experiment, injection of the organic liquid (~15 ml) was partitioned between two ports: 66% was injected in the far left port and 33% was injected through the center port. Once a flow cell was prepared, deionized, de-aired water was injected at a constant rate, equivalent to an average pore-water velocity of approximately 9 cm/h (an equivalent hydraulic gradient of ~0.01). The total flow was evenly distributed among the four influent ports. For all experiments, mass flux was calculated using the total system discharge, often referred to as mass discharge.

For the Mixed-Source and Heterogeneous experiments, the distribution of organic liquid was characterized using a Light Reflection Visualization (LRV) method, similar to that described by Kechavarzi et al. (2000). The LRV method was tested using two independent measures of organic-liquid volumes: (1) known injection volumes and moment analysis of effluent concentration, and (2) a partitioning tracer test (DiFilippo et al., 2010). The results demonstrated that the method provided reasonably robust measures of organic-liquid saturation over a relatively wide range of S_n values, with greater uncertainty at the lowest values as would be expected.

2.2 Simple Mass-Removal Function

The performance of the simple mass-removal function was evaluated using two approaches. In the first set of analyses, the efficacy of the function for characterizing mass-flux-reduction/mass-removal behavior was evaluated by examining its ability to match the data obtained from the flow-cell experiments (i.e., curve-fitting). In the second set of analyses, the ability of the function to independently simulate observed behavior was investigated. Using the function in the latter mode requires a means by which to determine a priori values for the n parameter.

The Initial GTP (IGTP) method (Table 2) was developed to provide estimates of n based on a parameter used to account for source accessibility, the measured initial GTP. The IGTP method is based on establishing a relationship between n and GTP, similar to the approach used by Christ et al., 2006, who presented a relationship between the exponent of the first-order concentration/mass-depletion function and GTP. In the current study, data reported by Lemke and Abriola (2006), who used a numerical model to simulate organic-liquid distribution and dissolution in heterogeneous porous media, were used as the source data to characterize a relationship between n (exponent for the mass-flux-reduction/mass-removal function) and GTP. Specifically, the concentration/mass-removal data reported by Lemke and Abriola (2006) were first converted to mass-flux-reduction/mass-removal curves, after which the simple mass-removal function was fit to each curve using a least-squares-regression routine to determine a value for the n parameter. The n values were then regressed against the GTP values reported for each simulation. A positive correlation was obtained between n and GTP, which was best expressed by a power-law model (Figure 2). This regression, which is in terms of the mass-flux-reduction function, spans a reasonably large range of GTP ratios ($0.17 < \text{GTP} < 65.6$, $R^2 = 0.93$), and provides an alternative to the regression presented by Christ et al. (2006), which is in terms of the concentration/mass-depletion function. As will be discussed below, additional functions were developed and evaluated to characterize n as a function of changing system conditions.

3. Results and Discussion

3.1 Mass-Flux-Reduction/Mass-Removal Behavior

The reductions in mass flux associated with mass removal for the experiments are presented in Figure 3. The initial GTP ratios for all four experiments are presented in Table 1. The mass-flux-reduction/mass-removal behavior for these systems is discussed in detail elsewhere (DiFilippo et al., 2010), therefore, only a brief description is provided below.

Minimal reduction in mass flux occurred until a large fraction of mass was removed for the systems wherein organic liquid was present solely as residual saturation in regions that were hydraulically accessible. Conversely, significant reductions in mass flux occurred with relatively minimal mass removal for systems wherein organic liquid was present at both residual and higher saturations. Of particular note, the latter systems exhibited non-singular or “multi-step” mass-flux-reduction/mass-removal behavior.

3.2 Application of the Simple Mass-Removal Function

The simple mass-removal function was applied to the data sets reported herein (Figure 3). The best-fit values for n were determined using a least-squares-regression routine and are reported in Table 1. For the Control and Homogeneous experiments, the measured data were well simulated by the simple mass-removal function. The initial behavior for the Mixed Source and Heterogeneous experiments was also well simulated by the function. However, the non-singular behavior observed at larger mass removals was poorly simulated.

The relationship between n and GTP reported in Figure 2 was used to determine an initial value for the n parameter used in the simple mass-removal function. Using the initial GTP ratio from the image analysis, n values of 0.86 and 0.72 were calculated for the Mixed Source and Heterogeneous experiments, respectively. These values are similar in magnitude to the best fit n values determined using least squares regression (Table 1). The predicted curves reasonably match the measured data for approximately the first 40% of the total mass removed (Figure 4). These results support the robustness of the n -GTP correlation, and suggest that the IGTP method may be useful for providing first-order characterization of initial mass-flux-reduction/mass-removal behavior.

While the IGTP method provided reasonable predictions for initial mass removal, the predicted curves were unable to capture the later, nonsingular mass-flux-reduction/mass-removal behavior. In addition, whereas the initial GTP ratios for the Control and Homogeneous experiments were the same, the mass-flux-reduction/mass-removal behavior for these two experiments was different due to different source zone areas and lengths (DiFilippo et al., 2010). These results illustrate that the initial GTP ratio alone is not sufficient for characterizing the complete mass-flux-reduction/mass-removal relationship. This conclusion is consistent with results presented in previous studies (Christ et al., 2006; Basu et al., 2008b; Brusseau et al., 2008; DiFilippo and Brusseau, 2008).

Organic-liquid distribution and flow-field conditions change as organic liquid is depleted from the source zone. Therefore, it can be anticipated that describing mass-flux-reduction/mass-removal behavior with a simple function parameterized solely on initial source-zone characteristics would be limited. For the specific case of the simple function used herein (equation 1), singular mass-flux-reduction/mass-removal curves are produced when n is a constant (a function only of initial conditions). However, non-singular or multi-step mass-flux-reduction/mass-removal behavior has been observed in prior flow-cell experiments (e.g., Brusseau et al., 2008; Kaye et al., 2008; DiFilippo et al., 2010; Marble et al., 2010), mathematical-modeling studies (e.g., Lemke et al., 2004; Phelan et al., 2004; Soga et al., 2004; Lemke and Abriola, 2006; Basu et al., 2008b; Maji and Sudicky, 2008; Christ et al., 2009), and for measured field data (Brusseau et al., 2007; DiFilippo and Brusseau, 2008). This non-singular behavior is a result of changes in organic-liquid distribution and relative permeability during the course of mass removal. For the simple mass-removal function to adequately simulate the non-singular behavior, the parameter n would need to change as a function of mass removal to reflect changes in organic-liquid distribution and flow-field conditions. For example, by changing n from 0.63 to 0.25 once 66% of the total mass has been removed, the mass-removal function provides a better representation of the measured data for the Mixed Source experiment. Similarly, the mass-removal function is able to capture the behavior observed for the Heterogeneous experiment if n is allowed to gradually increase from 0.56 to 2.5 once 80% of the total mass is removed from the system. These results show that, as would be expected, the performance of the simple mass-removal function can be improved significantly by allowing n to vary with mass removal.

3.3 System-Indicator Parameters and Mass-Removal Dependent Functions

The simple mass-removal function can simulate the non-singular behavior observed for the measured data by allowing n to change as a function of mass removal. However, to use the mass-removal function in a predictive manner, the mass-removal dependency of n needs to be characterized. One possible approach is to relate n to system-indicator parameters that change during the course of mass removal. The following analysis evaluates system parameters that may be considered as surrogates representing major factors that influence organic-liquid dissolution and associated mass flux (Table 2). Specifically, the magnitude and rate of contact (dilution effects, contact time) will be represented through use of source

zone cross-sectional area and length. Organic-liquid accessibility will be represented through the GTP ratio and relative permeability.

3.3.1 Variable GTP (VGTP) Method—Changes in organic-liquid distribution can be characterized by determining the GTP ratio at multiple times throughout mass removal. The GTP ratio for both the Mixed Source and Heterogeneous experiments varied significantly as organic-liquid mass was removed through dissolution (Figure 1; DiFilippo et al., 2010). The Variable GTP (VGTP) method attempts to account for changes in organic-liquid distribution by allowing n to change as a function of the changing GTP ratio (Table 2). For this method, n was updated at each imaging timestep by use of the measured GTP ratio and the regression equation presented in Figure 2. The simulated mass-flux-reduction/mass-removal relationships obtained using the VGTP method are presented in Figure 5a. This method was able to capture the initial behavior observed for the Heterogeneous experiment; however, it was unable to capture the increase in mass flux associated with mass removal from the pool zone. This method was also unable to simulate the observed behavior for the Mixed Source experiment. These results are consistent with those above regarding the limitation of the GTP ratio.

3.3.2 Variable Source Size (VS) Method—The Variable Source Size (VS) method accounts for changes in mass flux by allowing n to change as a function of changes in dilution and residence time (cross-sectional area and length of the source zone) (Table 2). Changes in the organic-liquid distribution were defined by the ratios of the source-zone cross-sectional area and length to the total cross-sectional area and length of the system, respectively. This method uses the initial GTP ratio to calculate an initial value for n , which provides a measure of the initial organic-liquid distribution and hence relative accessibility.

The mass-flux-reduction/mass-removal relationships simulated using the VS method are presented in Figure 5b. Changes in source-zone cross-sectional area and length are presented in Figure 6. This method provided a reasonable simulation of the multi-step behavior exhibited for the Mixed Source experiment. However, the VS method over-calculated the amount of mass flux reduction observed for the Heterogeneous experiment at high mass removals and was unable to simulate the increased mass flux observed when only the pool source remained.

3.3.3 Multi-Domain (MD) Method—The Multi-Domain (MD) method is a modification of the VS method, wherein the source-zone is sub-divided into regions based on intrinsic permeability (Table 2). This method accounts for the presence of multiple sub-regions of differing properties within the source zone, and is similar in concept to the two-region/multi-region models widely used in contaminant hydrology. The relative importance of each region to the overall mass flux behavior is a function of the relative fractions of organic liquid present in each region. Only one region was required for the Mixed Source experiment since all of the organic liquid was present in a single porous medium. The source zone for the Heterogeneous experiment was divided into two regions, the matrix and the higher intrinsic-permeability zone located in the upper right-hand corner of the flow cell (Figure 1). The dimensions employed for the two regions were based on the physical dimensions of the permeability units. Additional simulations produced for the Heterogeneous experiment employing more than two regions did not improve the performance of this method. As for the prior method, the initial GTP ratio is used to calculate an initial value for n .

The mass-flux-reduction/mass-removal relationships simulated using the MD method are presented in Figure 5c. Changes in source-zone cross-sectional area and length (in the flow direction) for each permeability zone in the Heterogeneous experiment are presented in

Figure 7. This method captured the early behavior exhibited by the Heterogeneous experiment; however, it was unable to simulate the multi-step behavior observed at later stages of mass removal. In addition, the MD method over-calculated the amount of mass flux reduction observed at early stages of mass removal for the Mixed Source experiment. Evaluation of both the VS and MD methods shows that accounting for the initial organic-liquid distribution and dilution effects was not sufficient to fully simulate the measured mass-flux-reduction/mass-removal behavior.

3.3.4 Multi-Domain Relative Permeability (MDRP) Method—The Multi-Domain Relative Permeability (MDRP) method accounts for changes in source-zone accessibility through changes in relative permeability, in addition to accounting for initial organic-liquid distribution and dilution effects (Table 2). With this method, the source zone was subdivided into regions based on the intrinsic permeability of the porous medium, and the impact of changes in dilution and residence time (cross-sectional area and length of the source zone) was accounted for (as done for the MD method). In addition, the impact of relative permeability on organic-liquid accessibility was accounted for using a simple relative permeability function. Changes in permeability were defined by the ratio of the hydraulic conductivity at a given time to the initial hydraulic conductivity of the region. The zones were weighted based on the fraction of organic liquid present in each zone. For the Mixed Source experiment, the MDRP method reduced to the VS method (assuming negligible reductions in relative permeability), given all of the organic liquid was present in one permeability zone.

The mass-flux-reduction/mass-removal relationships simulated using the MDRP method are presented in Figure 5d. Changes in the hydraulic conductivity for each permeability zone in the Heterogeneous experiment are presented in Figure 7. This method provided the most representative simulations of the behavior exhibited by both the Mixed Source and Heterogeneous experiments. Of particular note, this method was able to simulate the increase in mass flux (decrease in mass flux reduction) observed for the Heterogeneous experiment at approximately 75% mass removal.

3.3.5 Method Comparison—The relative differences between the model simulations and the measured data were quantified using the root-mean-square error (RMSE):

$$RMSE = \sqrt{\frac{1}{k} \sum_{i=1}^n (S_i - O_i)^2} \quad (4)$$

where k is the total number of samples [–], S is the method simulated reduction in mass flux [–], and O is the observed reduction in mass flux [–]. The computed RMSE value for each method is presented in Table 3. The MDRP method best represented the observed behavior for both the Mixed Source and Heterogeneous experiments. This was expected since this method is the most inclusive in accounting for changes in both organic-liquid distribution and the flow field.

4.0 Summary

Significant effort has been directed at developing models for simulating dissolution of organic liquids and associated source-zone mass-removal and mass-flux behavior. It has been clearly demonstrated through comparison of simulations to measured data that complex dissolution models can be used successfully to simulate organic-liquid dissolution in heterogeneous systems when sufficient information is available regarding the spatial

distribution of permeability and organic-liquid mass (e.g., Powers et al., 1998; Frind et al., 1999; Zhang and Brusseau, 1999; Detwiler et al., 2001; Brusseau et al., 2002; Brusseau et al., 2007; Marble et al., 2008). However, the application of complex mathematical models requires detailed characterization of the system, which is often not possible for field sites. This leads to the alternative of employing simplified models, and the host of issues associated with such an approach.

One major issue associated with the simplified approaches such as the function presented in equation one, as well as streamtube-based source-depletion models (e.g., Soerens et al., 1998; Jawitz et al., 2005) and deterministic dissolution models employing continuous-distribution dissolution functions (e.g., Garg and Rixey, 1999; Zhang and Brusseau, 2004) is that they typically produce singular mass-flux-reduction/mass-removal curves, whereas as noted above, non-singular behavior is often observed for more complex systems. While simulations produced by the simplified models may be deemed to adequately represent measured non-singular behavior in some cases, the error associated with the simulated curves may be quite significant, particularly at the field scale where deviations may translate to many years of system operation and attendant costs. Modifying these approaches to represent the existence of distinct regions of differing conditions within the system (e.g., through the use of multi-region approaches) may in some cases improve performance. However, their effectiveness remains constrained by the use of only initial-condition information. One potential approach to improving the performance of simplified models for simulating mass-flux-reduction/mass-removal behavior, and in particular non-singular behavior, is to dynamically inform (update) the model via system indicator parameters throughout the course of mass removal.

Several methods were developed herein to describe the mass-flux-reduction/mass-removal relationship using a dynamic mass-removal function and measurable system indicator parameters. The methods incorporated measures of source zone architecture (GTP ratio, source zone cross-sectional area and length) and flow field dynamics (changes in relative permeability). Methods that incorporated only the GTP ratio were adequate for obtaining a first-order approximation of initial mass-flux-reduction/mass-removal behavior. However, these methods were unable to describe the later-stage, non-singular behavior observed in the data sets. A method that incorporated parameters accounting for the source zone cross-sectional area and length as well as changes in relative permeability provided the most representative simulations of the observed data. This is consistent with the results of prior work wherein inclusion of relative-permeability dynamics has been shown to improve model performance (e.g., Powers et al., 1998; Brusseau et al., 2002; Zhang et al., 2008).

As has been discussed, approaches based solely on an initial characterization of the system often have difficulty in providing adequate simulations of observed mass-flux-reduction/mass-removal behavior for complex systems (e.g., Christ et al., 2006; Brusseau et al., 2008; DiFilippo and Brusseau, 2008; Zhang et al., 2008). The approach presented herein represents an attempt to mediate this constraint, and based on the results presented herein, has the potential to improve characterization of mass-flux-reduction/mass-removal behavior. However, this approach requires determination of system indicator parameters multiple times during the course of a mass-removal event. As is widely acknowledged, such measurements may be difficult to obtain for many field applications, and multiple measurements will increase costs. More work is needed to investigate readily measurable system parameters useful as indicators of mass-removal and mass-flux behavior.

Acknowledgments

This research was supported by the Department of Defense's Strategic Environmental Research and Development Program (SERDP) (Grant Number ER 1614), with additional support from the National Institute of Environmental Health Sciences Superfund Basic Research Program (Grant Number ES04940). We also thank the reviewers for their constructive comments.

References

- Basu NB, Fure AD, Jawitz JW. Simplified contaminant source depletion models as analogs of multiphase simulators. *J Contam Hydrol*. 2008a; 97(3–4):87–99. [PubMed: 18343529]
- Basu NB, Fure AD, Jawitz JW. Predicting dense nonaqueous phase liquid dissolution using a simplified source depletion model parameterized with partitioning tracers. *Water Resour Res*. 2008b; 44(7):W07414.
- Brooks MC, Annable MD, Rao PSC, Hatfield K, Jawitz JW, Wise WR, Wood AL, Enfield CG. Controlled release, blind test of DNAPL remediation by ethanol flushing. *J Contam Hydrol*. 2004; 69(3–4):281–297. [PubMed: 15028395]
- Brusseau ML, Nelson NT, Oostrom M, Zhang Z, Johnson GR, Wietsma TW. Influence of Heterogeneity and Sampling Method on Aqueous Concentrations Associated with NAPL Dissolution. *Environ Sci Technol*. 2000; 34 (17):3657–3664.
- Brusseau ML, Zhang Z, Nelson NT, Cain RB, Tick G, Oostrom M. Dissolution of Non-Uniformly Distributed Immiscible-liquid: Simulating Intermediate-Scale Experiments Using Local-Scale Mass-Transfer Coefficients. *Environ Sci Technol*. 2002; 36 (5):1033–1041. [PubMed: 11917988]
- Brusseau ML, Nelson NT, Zhang Z, Blue JE, Rohrer J, Allen T. Source-zone characterization of a chlorinated-solvent contaminated Superfund site in Tucson, AZ. *J Contam Hydrol*. 2007; 90 (1–2): 21–40. [PubMed: 17049404]
- Brusseau ML, DiFilippo EL, Marble JC, Oostrom M. Mass-removal and mass-flux-reduction behavior for idealized source zones with hydraulically-poorly-accessible immiscible liquid. *Chemosphere*. 2008; 71(8):1511–1521. [PubMed: 18279910]
- Chen X, Jawitz JW. Convergence of DNAPL strength functions with site age. *Environ Sci Technol*. 2009; 43(24):9374–9379. [PubMed: 19928794]
- Christ JA, Ramsburg CA, Pennell KD, Abriola LM. Estimating mass discharge from dense nonaqueous phase liquid source zones using upscaled mass transfer coefficients: An evaluation using multiphase numerical simulations. *Water Resour Res*. 2006; 42(11):W11420.
- Christ JA, Lemke LD, Abriola LM. The influence of dimensionality on simulations of mass recovery from nonuniform dense non-aqueous phase liquid (DNAPL) source zones. *Adv Water Resour*. 2009; 32 (3):401–412.
- Detwiler RL, Rajaram H, Glass RJ. Nonaqueous-phase-liquid dissolution in variable-aperture fracture: Development of a depth-averaged computational model with comparison to a physical experiment. *Water Resour Res*. 2001; 37(12):3115–3130.
- DiFilippo EL, Brusseau ML. Relationship between mass-flux reduction and source-zone mass removal: Analysis of field data. *J Contam Hydrol*. 2008; 98 (1–2):22–35. [PubMed: 18407371]
- DiFilippo EL, Carroll KC, Brusseau ML. Impact of organic-liquid distribution and flow-field heterogeneity on reductions in mass flux. *J Contam Hydrol*. 2010; 115(1–4):14–25. [PubMed: 20434229]
- Dobson R, Schroth MH, Oostrom M, Zeyer J. Determination of NAPL-water interfacial areas in well-characterized porous media. *Environ Sci Technol*. 2006; 40 (3):815–822. [PubMed: 16509323]
- Enfield, CG.; Wood, AL.; Brooks, MC.; Annable, MD. Interpreting tracer data to forecast remedial performance. In: Thorton, S.; Oswald, S., editors. *Groundwater Quality 2001: Natural and enhanced restoration of groundwater pollution; Proceedigs of the Groundwater Quality 2001 Conference*; Sheffield, UK. 2002. p. 11-16.
- EPA (U.S. Environmental Protection Agency). Expert panel on DNAPL remediation. 2003. The DNAPL remediation challenge: Is there a case for source depletion?. EPA/600/R-03/143

- Falta RW, Rao PS, Basu N. Assessing the impacts of partial mass depletion on DNAPL source zones I. Analytical modeling of source strength functions and plume response. *J Contam Hydrol.* 2005; 78(4):259–308. [PubMed: 16019108]
- Frind EO, Molson JW, Schirmer M, Guiguer N. Dissolution and mass-transfer of multiple organics under field conditions: The Borden emplaced source. *Water Resour Res.* 1999; 35:683–694.
- Garg S, Rixey WG. The dissolution of benzene, toluene, m-xylene and naphthalene from a residually trapped non-aqueous phase liquid under mass-transfer limited conditions. *J Contam Hydrol.* 1999; 36(3–4):313–331.
- Jawitz JW, Fure AD, Demmy GG, Berglund S, Rao PSC. Groundwater contaminant flux reduction resulting from nonaqueous phase liquid mass reduction. *Water Resour Res.* 2005; 41(10):10408–10423.
- Kaye AJ, Cho J, Basu NB, Chen XS, Annable MD, Jawitz JW. Laboratory investigation of flux reduction from dense non-aqueous phase liquid (DNAPL) partial source zone remediation by enhanced dissolution. *J Contam Hydrol.* 2008; 102(1–2):17–28. [PubMed: 18420303]
- Kechavarzi C, Soga K, Wiart P. Multispectral image analysis method to determine dynamic fluid saturation distribution in two-dimensional three-fluid phase flow laboratory experiments. *J Contam Hydrol.* 2000; 46(3–4):265–293.
- Lemke LD, Abriola LM. Modeling dense nonaqueous phase liquid mass removal in nonuniform formations: Linking source zone architecture and system response. *Geosphere.* 2006; 2(2):74–82.
- Lemke LD, Abriola LM, Lang JR. Influence of hydraulic property correlation on predicted dense nonaqueous phase liquid source zone architecture, mass recovery and contaminant flux. *Water Resour Res.* 2004; 40(W12417)10.1029/2004WR003061
- Maji R, Sudicky EA. Influence of mass transfer characteristics for DNAPL source depletion and contaminant flux in a highly characterized glaciofluvial aquifer. *J Contam Hydrol.* 2008; 102(1–2):105–119. [PubMed: 18929427]
- Marble JC, DiFilippo EL, Zhang Z, Tick GR, Brusseau ML. Application of a Lumped-process Mathematical Model to Dissolution of Nonuniformly Distributed Immiscible Liquid in Heterogeneous Porous Media. *J Contamin Hydrol.* 2008; 100:1–10.
- Marble JC, Carroll KC, Janousek H, Brusseau ML. In situ oxidation and associated mass-flux-reduction/mass-removal behavior for systems with organic liquid located in lower-permeability sediments. *J Contam Hydrol.* 2010; 117(1–4):82–93. [PubMed: 20685008]
- Mayer AS, Miller CT. The influence of mass transfer characteristics and porous media heterogeneity on nonaqueous phase dissolution. *Water Resour Res.* 1996; 32(6):1551–1567.
- NRC (National Research Council). Contaminants in the Subsurface: Source Zone Assessment and Remediation. National Academy Press; Washington, D.C: 2005.
- Parker JC, Park E. Modeling field-scale dense nonaqueous phase liquid dissolution kinetics in heterogeneous aquifers. *Water Resour Res.* 2004; 40(5):W05109.
- Parker JC, Park E, Tang GP. Dissolved plume attenuation with DNAPL source remediation, aqueous decay and volatilization - Analytical solution, model calibration and prediction uncertainty. *J Contam Hydrol.* 2008; 102(1–2):61–71. [PubMed: 18502537]
- Phelan TJ, Lemke LD, Bradford SA, O'Carroll DM, Abriola LM. Influence of textural and wettability variations on predictions of DNAPL persistence and plume development in saturated porous media. *Adv Water Resour.* 2004; 27(4):411–427.
- Powers SE, Nambi IM, Curry GW Jr. Non-aqueous phase liquid dissolution in heterogeneous systems: Mechanisms and a local equilibrium modeling approach. *Water Resour Res.* 1998; 34(12):3293–3302.
- Rao, PSC.; Jawitz, JW.; Enfield, CG.; Falta, RW.; Annable, MD.; Wood, AL. Groundwater Quality - Natural and Enhanced Restoration of Groundwater Pollution. Sheffield, UK: 2002. Technology integration for contaminated site remediation: clean-up goals and performance criteria; p. 571-578.
- Saenton S, Illangasekare TH. Up-scaling of mass transfer rate coefficient for the numerical simulation of DNAPL dissolution in heterogeneous aquifers. *Water Resour Res.* 2007; 43:W02428.
- Soerens T, Sabatini D, Harwell J. Effects of flow bypassing and nonuniform NAPL distribution on the mass transfer characteristics of NAPL dissolution. *Water Resour Res.* 1998; 34(7)10.1029/98WR00554

- Soga K, Page JWE, Illangasekare TH. A review of NAPL source zone remediation efficiency and the mass flux approach. *J Haz Mat.* 2004; 110(1–3):13–27.
- Suchomel EJ, Pennell KD. Reductions in contaminant mass discharge following partial mass removal from DNAPL source zones. *Environ Sci Technol.* 2006; 40(19):6110–6116. [PubMed: 17051808]
- Zhang CY, Yoon H, Werth CJ, Valocchi AJ, Basu NB, Jawitz JW. Evaluation of simplified mass transfer models to simulate the impacts of source zone architecture on nonaqueous phase liquid dissolution in heterogeneous porous media. *J Contam Hydrol.* 2008; 102(1–2):49–60. [PubMed: 18579257]
- Zhang Z, Brusseau ML. Nonideal transport of reactive solute in heterogeneous porous media 5. Simulating regional-scale behavior of a trichloroethene plume during pump-and-treat remediation. *Water Resour Res.* 1999; 35 (10):2921–2935.
- Zhang Z, Brusseau ML. Nonideal transport of reactive contaminants in heterogeneous porous media: 7. distributed-domain model incorporating immiscible-liquid dissolution and rate-limited sorption/desorption. *Journal of Contaminant Hydrology.* 2004; 74:83–103. [PubMed: 15358488]
- Zhu J, Sykes JF. Simple screening models of NAPL dissolution in the subsurface. *J Contam Hydrol.* 2004; 72(1–4):245–258. [PubMed: 15240175]

Figure 1.

Organic-liquid distribution at four different times for the Mixed Source and Heterogeneous experiments. Organic-liquid saturation was determined using imaging as described in the text. The matrix of the Mixed Source experiment was composed of 40/50 sand and the gray zone was composed of 70/100 sand. The matrix of the Heterogeneous experiment was composed of 40/50 sand. The black-outlined zones were composed of 20/30 sand and gray zones were composed of 70/100 sand. The organic-liquid saturation is defined using the color scale, where warm colors indicate high organic-liquid saturation and cool colors represent low saturation. The ganglia-to-pool (GTP) ratio was calculated using the image data with a residual-saturation threshold of 0.20 for the 40/50 sand and 0.16 for the 20/30 sand (Dobson et al., 2006). The percent mass removal was calculated based on moment analysis of the elution data. The spatial resolution for each image is 0.02 mm^2 . This figure is reproduced from DiFilippo et al., (2010).

Figure 2. Relationship between n (parameter from equation 1) and ganglia-to-pool (GTP) ratio. See text for description of data source and analysis methods.

Figure 3.

Mass flux reduction versus mass removal behavior for the experiments. Also shown are best-fit mass-flux-reduction/mass-removal curves produced with the simple mass-removal function (equation 1). This figure is reproduced from DiFilippo et al., (2010).

Figure 4. Measured and predicted mass-flux-reduction versus mass-removal behavior for the Mixed Source and Heterogeneous experiments. The solid (Mixed-source) and dashed (Heterogeneous) lines were obtained with the simple mass-flux-reduction/mass-removal function wherein the values for the n parameter were obtained independently using the initial GTP ratio (IGTP method).

Figure 5.

Mass flux reduction versus mass removal behavior for the Mixed Source and Heterogeneous experiments, and application of the various methods for characterizing mass-flux-reduction/mass-removal behavior. (a) Variable GTP method (VGTP), (b) Variable Size method (VS), (c) Multi-Domain method (MD), and (d) Multi-Domain Relative Permeability method (MDRP). The model simulations for the Mixed Source and Heterogeneous experiments are represented by the solid and dashed lines, respectively.

Figure 6.

(a) Ratio of the source-zone cross-sectional area to the total system cross-sectional area as a function of mass removal for the Mixed Source and Heterogeneous experiments. (b) Ratio of the source-zone length to the total system length as a function of mass removal for the Mixed Source and Heterogeneous experiments.

Figure 7.

Measure of the source zone parameters as a function of mass removal for each permeability zone in the Heterogeneous experiment. The matrix refers to portion of the organic liquid present in the 40/50 matrix and the pool refers to the portion of the organic liquid that is present initially at high saturation in the 20/30 zone (c.f. Figure 1). (a) Fraction of organic liquid, (b) GTP ratio, (c) normalized source-zone cross-sectional area, (d) normalized source zone length, (e) normalized hydraulic conductivity.

System indicator parameters for the experiments

Table 1

Experiment	PV (ml)	Q (ml/min)	v (cm/hr)	L ¹ (cm)	A ¹ (cm ²)	S _{n, global} ²	GTP _{initial} ³	n ⁴
Control	8.8	0.6	30.1	7	3.5	0.18	Inf	13.1
Homogeneous	185.4	2.7	9.4	10	48.5	0.01	Inf	4.3
Mixed Source	913.3	3.3	9.1	40	61.8	0.01	1.7	0.63
Heterogeneous	812.9	3.3	9.7	40	59.5	0.02	1.2	0.59

¹The source zone length and area were determined using image analysis (DiFilippo et al., 2010). The source zone length was determined parallel to the flow direction and the cross-sectional area was determined perpendicular to the flow direction.

²S_{n, global} is defined as the volume of organic liquid divided by the pore volume of the entire system (source zones plus matrix).

³Ganglia-to-pool ratio, defined as the volume of organic liquid occurring as "ganglia" (S_n < residual saturation) divided by the volume of organic liquid residing in pools (S_n > residual saturation). Residual saturation thresholds for the 40/50 and 20/30 sand were 0.2 and 0.16, respectively (Dobson et al., 2006).

⁴The parameter *n* was obtained by fitting the simple mass-removal function to the observed data using a least squares regression routine.

Table 2

Summary of methods developed to predict the mass-flux-reduction/mass-removal relationship

Method	Equation *	Figure
Initial GTP (IGTP)	$n = 0.65(GTP_i)_{0.52}$	4
Variable GTP (VGTP)	$n = f(GTP_t)$	5a
Variable Source Size (VS)	$n = n_0 \left(\frac{A_{sz,t}}{A_{tot}} \right) \left(\frac{L_{sz,t}}{L_{tot}} \right)$ where $n_0 = 0.65(GTP_i)_{0.52}$	5b
Multi-Domain (MD)	$n = n_0 \left(\sum_{i=1}^k A_{norm,i} L_{norm,i} f_i \right)$	5c
Multi-Domain Relative Permeability (MDRP)	$n = n_0 \left(\sum_{i=1}^k A_{norm,i} L_{norm,i} K_{norm,i} f_i \right)$	5d

$$* A_{norm} = \frac{A_{sz,t}}{A_{sz,0}}, L_{norm} = \frac{L_{sz,t}}{L_{sz,0}}, K_{norm} = \left(\frac{K_t}{K_0} \right)^3, K = k_r K_{sat}$$

GTP_i is the initial GTP ratio for the experiment [–], A_{sz} is the source zone area [L^2], L_{sz} is the source-zone length [L], A_{tot} is the total cross-sectional area of the flow cell [L^2], L_{tot} is the total length of the flow cell [L], K is hydraulic conductivity [L/t], k_r is the relative permeability [–], K_{sat} is the water saturated hydraulic conductivity [L/t], f_i is the fraction of organic-liquid mass in each zone, k is the total number of zones, and the subscripts 0 and t represent initial time and later time t , respectively. The threshold values for residual saturation for each sand mesh sizes used in our experiments are provided by Dobson et al., (2006). The relative permeability for each system was obtained from image analysis (DiFilippo et al., 2010).

Table 3

Root-mean-square error (RMSE) values for each method*

	IGTP	VGTP	VS	MD	MDRP
Mixed Source	0.10	0.52	0.05	0.08	0.05
Heterogeneous	0.08	0.08	0.11	0.08	0.07

* High values represent poorer predictions and vice versa.