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MATHEMATICAL MODELING OF ORGANIC LIQUID DISSOLUTION IN HETEROGENEOUS SOURCE ZONES

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Abstract

A simple one-dimensional heterogeneous-source model was used to simulate dissolution of organic liquid that was non-uniformly distributed in physically heterogeneous porous media. The permeability field was depicted as a pseudo-homogeneous medium. The source zone was discretized into multiple domains representing different organic-liquid configurations and hydraulic accessibilities, each with a different representative upscaled mass transfer rate coefficient that is temporally variable. This simplified approach represents a system where minimal information is available regarding system heterogeneities. All factors that influence dissolution were incorporated into the calibrated mass transfer terms. The mass transfer terms were calibrated for each zone separately. The one-dimensional, heterogeneous-source model adequately simulated the multi-stage dissolution behavior observed for column-scale systems that were packed with different natural soils, as well as for flow-cell systems wherein the source zone consisted of both a residual zone and pool. The results indicate that the model adequately simulated the presence of multiple organic-liquid zones in porous media with different configurations and hydraulic accessibilities, which accounts for the non-ideal dissolution behavior observed. The calibrated mass transfer terms for each source type were consistent with those obtained for systems that contained only one of either source type.

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Conflict of Interest

The authors declare no competing financial interest.

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Keywords

NAPL dissolution; Multi-stage mass discharge; Upscaled models; Heterogeneous-source model

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1. Introduction

One of the most critical issues associated with hazardous waste sites is the presence of non-aqueous phase liquids (NAPL), such as fuels, creosote, coal tars and chlorinated solvents, in the subsurface (NRC, 1994; 2000; 2005; 2013). Once released, these organic liquids can migrate downward into the aquifer and serve as long-term sources of contamination. A great amount of research has been conducted on NAPL source-zone behavior over the past several decades. It is now well established that the mass discharge associated with such source zones depends upon the distribution and configuration of the organic liquid (e.g., pool or ganglia), as well as the structure of the flow field.

Numerous mathematical models and functions have been developed to simulate NAPL dissolution and mass discharge from NAPL source zones. Most simplified models produce singular mass discharge (dissolution) profiles comprising monotonic decreases in concentration. However, so-called multi-stage mass discharge, due to the variability of NAPL distribution and configuration in the source zone, has been observed in field measurements (e.g., Brusseau et al., 2007; DiFilippo and Brusseau, 2008; Brusseau et al., 2013; Brusseau and Guo, 2014; Teramoto and Chang, 2017), laboratory experiments (e.g., Zhang et al., 2008; Russo et al., 2009; DiFilippo et al., 2010; Mateas et al., 2017; Karaoglu et al., 2019), and numerical simulations (e.g., Lemke et al., 2004; Soga et al., 2004; Christ et al., 2010; Yang et al., 2018). This multi-stage behavior typically exhibits alternating periods of pseudo steady-state dissolution and relatively rapid declines in concentration, as shown in Figure 1. The abrupt change in concentration is typically caused by a transition of the particular source-zone domain or configuration predominantly contributing to mass discharge, i.e., between regions of NAPL contamination that have significantly different hydraulic accessibilities. A simple extreme example would be the transition from a ganglia-dominated system to a pool-dominated system (e.g., Lemke et al., 2004; Parker and Park, 2004; Christ et al., 2010; Rivett et al., 2014; DiFilippo et al., 2010; DiFilippo and Brusseau, 2011a).

A number of approaches have been used for simulating multi-stage dissolution of organic liquid and mass discharge from source zones. Multi-process mathematical models can be applied to represent dissolution in complex, heterogeneous systems (e.g., Zhang and Brusseau, 1999; Christ et al., 2006; Karaoglu et al., 2019). However, these models require detailed characterization of system heterogeneities and source-zone architecture and the information is often unavailable. In addition, the complexity and cost of computing remains high even with current computational capacity. Consequently, there is great interest in using simpler, upscaled models to simulate source dissolution.

In the past two decades, several different types of simple, upscaled models have been developed and tested, such as equilibrium streamtube methods, power law relationships between concentration and mass, dual-domain models, and other methods with upscaled

effective mass transfer rate coefficients (Parker and Park, 2004; Jawitz et al., 2005; Basu et al., 2008; Marble et al., 2008; Christ et al., 2010; DiFilippo and Brusseau, 2011a; Boroumand and Abriola, 2015). However, most of these models (e.g., Parker and Park, 2004; Jawitz et al. 2005; Basu et al., 2008; Marble et al., 2008; Luciano et al., 2018) produce smooth singular dissolution profiles and thus are not able to capture non-singular dissolution behavior caused by the complexity of the source zone architectures.

Two general approaches have been taken to attempt to simulate multi-stage dissolution behavior. One is based on the dual-domain conceptualization. Such models have been used successfully to simulate solute transport in heterogeneous NAPL-contaminated systems (e.g., Brusseau, 1992; Powers et al., 1998; Falta, 2003; Konikow, 2011; Vasudevan et al. 2016; Guo et al., 2019). Christ et al. (2010) presented an upscaled two-domain mass-transfer model to reproduce dissolution behavior in pool-dominated scenarios, which divided the source zone into two domains, ganglia- and pool-dominated regions. The dissolution process was described by simple mass-removal functions. The model successfully simulated the two-stage NAPL dissolution process. However, it requires prior knowledge of the source structures, i.e. the fractions of NAPL mass located in ganglia and pools, which is not always available for field systems. Moreover, the model cannot capture the complex dissolution behavior evident when more than two effective domains exist.

The second approach is based on using macroscopic system-indicator parameters that are allowed to change with time to account for the temporal evolution of the source zone (e.g., DiFilippo and Brusseau, 2011a; Kokkinaki et al., 2014). DiFilippo and Brusseau developed a model that incorporated macroscopic parameters accounting for the source zone cross-sectional area and length as well as changes in relative permeability. These parameters varied as a function of mass removal with time (as the organic-liquid distribution and relative permeability change). The model was successful in simulating multi-stage dissolution behavior observed for flow-cell experiments. Kokkinaki et al. (2014) used an approach similar to that of DiFilippo and Brusseau, explicitly considering the temporal evolution of parameters representing the local DNAPL saturation, the source zone projected area, and the relative permeability. The model was evaluated by simulating data obtained from both real and hypothetical source zones and demonstrated the capability to describe the multi-stage dissolution behavior. These two studies demonstrated the effectiveness of the temporally variable system-indicator approach for simulating multi-stage dissolution behavior. However, measurements of these indicator parameters multiple times during mass-removal is likely to be difficult and expensive for many field applications. Therefore, a method that can be readily applied to complex NAPL source zones to reproduce the multi-stage dissolution process is still a focus of research.

The purpose of this study is to investigate the use of a one-dimensional, heterogeneous-source model to simulate organic-liquid dissolution from a source zone consisting of multiple NAPL configurations and hydraulic accessibilities. The model assumes uniform flow and transport but treats the organic-liquid source zone as comprising multiple domains with different upscaled mass transfer rate coefficients. The dissolution process was explicitly described, and incorporates the impact of temporal evolution of the source zone on mass transfer rate coefficients. The model is applied to data sets generated from column

experiments comprising different soils and flow cell experiments with different domain configurations.

2. Materials and Methods

2.1 Systems investigated

As noted above, the objective of this study was to evaluate the use of a one-dimensional, heterogeneous-source model for simulating organic-liquid dissolution from systems with complex source types (i.e., containing organic liquid in both residual zones and pools). Data obtained from a series of column experiments and flow-cell experiments were used to evaluate the model. The systems were designed to reflect a variety of organic-liquid distributions and flow-field heterogeneities.

2.1.1 Column experiments—Data were generated in previously published studies (Russo et al., 2009a; Mahal et al., 2010). A brief overview is discussed herein. Experiments were conducted with 7-cm long and 2.1-cm ID stainless steel columns (Alltech). Trichloroethene (TCE) (Aldrich Chemical Co., Inc, Milwaukee, WI) was used as the model organic liquid. Pentafluorobenzoic Acid (PFBA) (Aldrich Chemical Co., Inc.) was used as a conservative tracer to determine the hydrodynamic properties of the packed column. The porous media used were Eustis soil, Borden soil, Hayhook soil and Mt. Lemmon soil as well as a mixed sand. The media encompass a wide range of particle size distributions (reflected in the uniformity coefficients) (Table 1).

Dissolution began by flushing the column with CaCl_2 solution and collecting aqueous samples at a flowrate of 0.7 ml/min. Electrolyte solution was pumped into the column from the bottom (the same direction as injection) using a HPLC pump. Samples were collected in 2 ml or 5 ml glass syringes (Popper & Sons, Inc, New Hyde Park, N.Y.), and were diluted as needed. PFBA samples were analyzed using a UV-vis spectrophotometer (SPD-10A Shimadzu) at a wavelength of 262 nm. Aqueous TCE samples, ranging in concentrations from saturation (1200-1500 mg/L) to approximately 10 mg/L were analyzed using a UV-vis at a wavelength of 232 nm. A GC-ECD (Electron Capture Detector) was used to analyze samples below 10 mg/L. The detection limit on this instrument is approximately 0.2 $\mu\text{g/L}$.

2.1.2 Flow cell experiments—The flow cell data were published in DiFilippo et al. (2010); a brief description is presented below. Three natural sand media with different median particle diameters were used in these experiments, 713 μm (20/30 mesh), 359 μm (40/50 mesh), and 172 μm (70/100 mesh) (Unimin Corp.). Representative hydraulic conductivities for the three media are 15, 4, and 0.1 cm/min, respectively (Schroth et al., 1996). Trichloroethene (TCE), ACS grade (Aldrich), was used as the organic liquid. The organic liquid was dyed with Sudan IV (Aldrich) at a concentration of 100 mg/L, which has been shown to have minimal impact on fluid properties and behavior (Schwille, 1988; Kennedy and Lennox, 1997).

A total of three experiments were conducted for the study (Table 2). The Control experiment consisted of a homogeneous pack of 40/50 sand. A residual saturation of TCE was emplaced in the middle of the flow cell by manually mixing and packing the source zone with organic

liquid using standard procedures (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 Mixed-Source experiment consisted of a uniform pack of 40/50 sand with a 2 cm thick capillary barrier (70/100 sand) located along the bottom. The Heterogeneous experiment consisted of a matrix of 40/50 sand with lenticular zones of coarser (20/30) and finer (70/100) sand. Organic liquid distribution was spatially nonuniform for both of these experiments and encompassed a range of saturations (Figure 1). For the Mixed-Source and Heterogeneous experiments, the distribution of organic liquid was characterized using a Light Reflection Visualization (LRV) method (Kechavarzi et al., 2000; DiFilippo and Brusseau, 2011b).

2.2 Conceptualization

In this work, a simple one-dimensional dissolution and solute transport model is used to simulate dissolution from a non-uniformly distributed source zone. The porous medium and water flow were assumed to be uniform. Two sets of simulations were used to predict dissolution from these systems. The first set of simulations (one-dimensional, one-domain) treated the organic-liquid as one source, uniformly distributed across the entire length and cross-section of the system. The second set of simulations (one-dimensional, heterogeneous-source) divided the organic liquid source into multiple sources representing the residual portions and pool portions with different mass transfer rate coefficients in the source zone. Mass-transfer coefficients were calibrated for each domain separately.

2.3 One-Dimensional, Heterogeneous-Source Model

The governing equation for solute transport in the flow cells with dissolution of organic liquid is described by:

$$\theta_a \frac{\partial C}{\partial t} + \rho_N \frac{\partial \theta_N}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta_a D_{ij} \frac{\partial C}{\partial x_j} \right) - q_i \frac{\partial C}{\partial x_i} \quad (1)$$

where C is the aqueous concentration of solute; θ_a is the fractional volumetric water content; θ_N is the fractional volumetric content of the organic liquid; ρ_N is density of the organic liquid; q_i is Darcy velocity; D_{ij} is the dispersion coefficient tensor; x_i is cartesian coordinates; $i, j = 1, 2, 3$ and conforms to the summation convention; and t is time. Sorption of the organic compounds by the media used in these experiments is minimal, and is therefore ignored.

The model allowed for discretization of organic liquid into multiple domains. Organic liquid in each domain was assumed to be uniformly distributed across the entire length and cross-sectional area of the system. With this approach, larger scale factors influencing dissolution and transport are not explicitly represented in the model. Their impacts are incorporated into calibrated dissolution rate coefficients. The importance of each domain to the overall dissolution behaviour was controlled by the ratio of the cross-sectional area of each source type to the cross-sectional area of the entire source zone. Organic-liquid dissolution in each domain is described with the widely used first-order mass transfer equation:

$$\rho_N \frac{\partial \theta_N}{\partial t} = k_{La}(C - C_s) \quad (2)$$

where k_{La} is a lumped mass transfer coefficient for dissolution, and C_s is the aqueous solubility of the organic liquid. The time dependency of k_{La} is represented by:

$$k_{La}(t) = k_{La}^0 \left[\frac{Re(t)}{Re^0} \right]^{\beta_1} \left[\frac{\theta_N(t)}{\theta_N^0} \right]^{\beta_4} \quad (3)$$

where k_{La}^0 and Re^0 are the initial local (nodal) values; Re is the Reynolds number; β_1 and β_4 are coefficients. The organic dissolution can be described as:

$$\rho_N \frac{\partial \theta_{N_i}}{\partial t} = k_{La_i}^0 \left[\frac{Re_i(t)}{Re_i^0} \right]^{\beta_1} \left[\frac{\theta_{N_i}(t)}{\theta_{N_i}^0} \right]^{\beta_4} (C - C_s)$$

where $i=1,2,\dots,m$; and m is the total number of discrete dissolution domains. As described in Zhang and Brusseau (2004), values of β_1 were provided by Powers et al. (1994) based on analysis of dissolution data. β_4 is solely associated with the temporal variability of k_{La} . Therefore, two parameters were calibrated, k_{La} and β_4 in this study. The simulations were very sensitive to the magnitude of the calibrated terms, with coefficient of variations of less than approximately 5%. A single region approach was also used to model the observed data. It assumes that the dissolution of the organic liquid in the system is controlled by a single rate coefficient and one effective organic liquid configuration or interfacial area.

3. Results and Discussion

3.1 Experiments results

3.1.1 Column experiments—As discussed previously, column experiments were conducted with various natural porous media (Borden, Eustis, Hayhook and Mt. Lemmon soils) as well as a mixed sand. Borden and Eustis dissolution experiments had a residual saturation of 11.4 and 14.7%, respectively. Mt. Lemmon soil and the mixed sand had residual saturations of 8.1 and 8.2%, respectively. Hayhook soil experiments had higher residual saturations of approximately 20% saturation. Observed dissolution behavior was characterized by an initial steady state stage followed by a transient region. In addition, a secondary step in the dissolution process was observed at approximately one log below solubility (Figure 2), in which concentrations decreased gradually for a significant number of pore volumes.

The secondary region extends for approximately 50 pore volumes for both Eustis and Borden dissolution experiments. For Hayhook soil, the secondary region begins at less than one log below solubility and extends for approximately 100-150 pore volumes (Figure 3). Similar behavior was also observed for the mixed sand experiments, where secondary stages are observed at less than one log below solubility and extend for approximately 100-200 pore volumes (Figure 4). For Mt. Lemmon soil dissolution, the secondary region is observed

at approximately three logs below solubility and extends for approximately 700 pore volumes. The high organic carbon content associated with Mt. Lemmon soil may have an impact on TCE configuration and thus the observed dissolution behavior.

3.1.2 Flow cell experiments—The contaminant elution curves for the control and flow-cell experiments are presented in Figure 6. The effluent concentrations for the control experiment initially remained steady and after 40% of the total organic-liquid mass was removed, the concentration dropped quickly to three orders of magnitude lower. The elution curves for the Mixed Source and Heterogeneous experiments exhibited relatively extensively asymptotic periods after the concentrations gradually decreased approximately one order of magnitude, and then declined rapidly to lower concentration. The multi-stage behaviors are due to the source distributions, which also reflects the impacts of mass-removal constraints. And the steady state period represents the transition of dissolution of pool source to ganglia source.

3.2 Mathematical Modeling

3.2.1 Single region model—Mathematical modeling was conducted to simulate the observed organic immiscible liquid dissolution behavior. Initially, attempts were made to describe observed dissolution behavior with a single-region model. The single-region model was not able to reproduce the multi-stage dissolution behavior observed in the column experiments (results not shown).

For the flow cell experiments, the one-dimensional, one-source simulations of the measured data are presented in Figure 6. The calibrated values for k_{La} and β_4 are presented in Table 2. Inspection of Figure 6 shows that the predicted simulations provide a good match to the Control experiment, as well as the early elution behavior for both the Mixed Source and Heterogeneous experiments. The early stage elution behavior for the Mixed Source and Heterogeneous experiments is controlled by dissolution of organic-liquid mass from the residual saturation regions of the source zone, which had initial saturations of 0.11 and 0.14 for the Mixed Source and Heterogeneous experiments, respectively (DiFilippo et al., 2010). The calibrated k_{La} and β_4 values for the Mixed Source and Heterogeneous experiments are consistent with simulations of systems with a similar initial residual saturation source zone ($S_n = 0.06$) that is hydraulically accessible (Marble et al., 2008). The one-source model, however, does not adequately simulate the late stage elution behavior for either the Mixed Source or Heterogeneous experiments. The late stage elution behavior for these experiments is controlled by dissolution from the hydraulically-poorly accessible organic-liquid pools, which had initial saturations of 0.18 and 0.20 for the Mixed Source and Heterogeneous experiments, respectively (DiFilippo et al., 2010).

3.2.2 Heterogeneous-source model—For the column experiment results, a multiple region model with three zones was used for the majority of the experiments, although in some cases, two zones were sufficient to describe the behavior. The multi-region model is based on the assumption that more than one organic liquid configuration is present in the column, with one organic liquid configuration contributing to the steady state region and another organic liquid configuration contributing to the observed dissolution behavior for the

secondary region. Results of the mathematical modeling are shown in Table 3. Zone fractions are shown in the table, representing the different fractions of organic liquid volumes in each section of the model required to support the observed dissolution behavior.

The majority of the organic liquid is observed in the first and second zone with only a very small amount of organic liquid present in the last zone. This distribution intuitively makes sense, because in the third zone, the accessible residual organic liquid in the system has been removed, leaving a small amount of organic liquid wherein mass removal is transitioning to the sorption/desorption phase of the removal process. Although the sorption/desorption tail can exist for a long time, the mass that is being removed during this time is relatively small, with approximately 99% of the mass being previously removed during the dissolution process (Johnson et al., 2003).

The lumped mass transfer coefficient (k_{La}), which includes the organic-liquid/water interfacial area, is also compared in Table 3. The interfacial area decreases during dissolution, which in turn decreases the mass transfer rate which is reflected in the lumped mass transfer rate coefficient. The lumped mass transfer rate coefficient is larger for the Hayhook experiments in the first zone than for the Eustis and Borden experiments. However, the mass transfer coefficient for the 2nd zone in all the experiments remains similar. From these results we can see that different rates of mass transfer are present during the dissolution process. This is further evidence that several effective organic liquid configurations could be present in the system, leading to the observed non-ideal behavior.

In a previous study (Russo et al., 2009b), X-ray Synchrotron microtomography imaging was conducted to observed dissolution behavior of TCE in Hayhook soil at the pore scale. Dissolution was observed to be non-ideal, in which TCE mass was removed from the entire length of the column during each step of dissolution. This is in contrast to the expected dissolution behavior, in which removal of organic liquid first occurs nearest the inlet end of the column. The dissolution front would then migrate downgradient through the column once all of the organic liquid nearest the inlet has been removed. This stepwise organic liquid removal was not observed in imaging.

The type of pore-scale behavior observed from imaging can be related to the column scale behavior observed in which secondary regions were present before large decreases in concentration occurred. We can hypothesize that the initial steady-state region is supported by dissolution of a particular set of organic liquid blobs and ganglia, while the second observed region is supported by a different set with a different distribution or configuration at the pore scale. The modeling results (Figure 3 and 4) presented in this study further support this hypothesis. The lumped mass transfer coefficient, k_{La} , includes the organic-liquid/water interfacial area which decreases during dissolution, which in turn should decrease the k_{La} . From Table 3, we observe that lumped mass transfer coefficient values for the first and second zones in most experiments are relatively similar. This indicates that small changes have occurred to alter the organic-liquid/water interfacial areas, which would occur if only a small portion of the immiscible liquid present in the system was being affected by the initial dissolution process.

For the flow cell experiments, a one-dimensional, two-source model was used to simulate the measured data. The calibrated k_{La} and β_4 values for each zone are presented in Table 4. The organic-liquid dissolution area (A) for each zone was calculated as the ratio of the cross-sectional area of each zone to the total cross-sectional area of the source zone (Table 4). Inspection of Figure 7 shows that predicted simulations using the two-source model provide a good overall fit to both the early and late stage observed elution behavior. The late stage increases in concentration observed in the heterogeneous experiment is not captured by the model. This increase in concentration is due to changes in the relative permeability of this zone as organic-liquid was removed through dissolution (DiFilippo et al., 2010) which was not explicitly defined in the model. The model does, however, capture the general elution behavior in this region. The calibrated k_{La} and β_4 values for zone 2 are consistent with simulations for systems with organic liquid pools with a similar initial saturation ($S_n = 0.2$) (Marble et al., 2008).

4. Summary and Conclusions

A simple one-dimensional, heterogeneous-source model was used to simulate the multistage dissolution behavior observed for column experiments comprising different natural soils, as well as for flow-cell systems wherein the source zone consisted of both a residual zone and pool. This highly simplified approach represents a system where minimal information is available regarding system heterogeneities. All factors that influence dissolution were incorporated into the calibrated mass transfer coefficients. The mass transfer coefficients are different for each zone with different source type, which is also varied temporally with evolution of source zone.

Mathematical modeling of dissolution experiments supports the hypothesis that different organic-liquid configurations are present that have different hydraulic accessibilities and therefore different rates of dissolution. The different organic-liquid configurations contribute to the occurrence and magnitude of the secondary regions. The one-source model was not able to simulate the multi-stage dissolution behavior observed in both column and flow cell experiments. Conversely, the heterogeneous-source model (three sources used for column experimental results and two sources used for flow-cell experimental results) successfully reproduced the observed data. The mass transfer rate terms were calibrated for each zone separately. The calibrated mass transfer rate terms for each source type (residual or pool) were consistent with similar systems which contained only one source type. Based on this, it provides a possibility of applying the method to a system without calibrating the parameters, where the initial saturation for each zone, pool or residual, is acquired by some independent means. The mass transfer rate coefficients determined for prior sites with similar saturation for each source type can be applied. In contrast to other methods that require prior knowledge of the source structures (Christ et al., 2010) or parameters such as source zone projected area, the averages of local DNAPL saturations and water relative permeabilities (Kokkinaki et al., 2014) or permeability indicator (DiFilippo and Brusseau, 2011a), the method developed in this study offers a relatively simple and feasible way to model the multi-stage behavior. However, when applying the parameter values that are calibrated from small scale, such as column experiments, to field scale, the dilution effect needs to be considered as illustrated in Mable et al. (2008).

In addition, Boroumand and Abriola (2015) showed the correlation between mass transfer and source zone and indicated that the mass transfer rates are changing with source depletion during the mass removal, and also the potential flow field change (Guo et al., 2020). However, while most previous studies have focused on reproducing changing mass flux due to properties associated with site or source conditions, studies on the temporal change in mass transfer are rare. Therefore, incorporating the temporal change in mass transfer due to evolution of source zone or flow field is important for accurately modeling the dissolution during site remediation. Exploring a robust method that can predict the multi-stage dissolution behaviors remains challenge and very important for sites with complex source structure and high heterogeneity during the remediation. By combining the heterogeneous-source system with temporally varied mass transfer rate coefficients for each zone, this work provides insight on development of a more cost-effectively and robust way modeling the dissolution process in large complex systems.

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Highlights:

- NAPL dissolution in heterogeneous media was simulated by a 1D heterogeneous-source model.
- The model simulated the presence of multiple organic-liquid domains in porous media.
- The model adequately simulated the multi-stage dissolution behavior.
- Incorporating the temporal change in mass transfer is important to simulate dissolution.

Figure 1.

Conceptual NAPL dissolution behavior during a mass removal process. The solid line represents multi-stage dissolution behavior, and the dash line represents singular behavior. The conceptualization is based on laboratory and field experiment observations in prior research (e.g., DiFilippo and Brusseau, 2008; Russo et al., 2009; DiFilippo et al., 2010; Brusseau et al., 2013; Brusseau and Guo, 2014).

Figure 2.

Organic-liquid distribution for the (a) Mixed Source and (b) 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 spatial resolution for each image was 0.02 mm^2 .

Figure 3. Mathematical simulations and experiment data for dissolution experiments with Eustis and Borden soil in column experiments.

4a

4b

Figure 4.

Elution curve for dissolution experiments with Hayhook soil (a) and Mt. Lemmon soil (b) in column experiments.

Figure 5.
Elution curve for dissolution experiments with Mixed sand in the column experiment.

Figure 6. Measured effluent concentrations and model simulations using the one-dimensional, one-source model for the control and flow-cell experiments.

Figure 7. Measured effluent concentrations and model simulations using the one-dimensional, dual-source model for the flow-cell experiments.

Table 1

Properties of Porous Media in Column Experiments

Porous Media	Sand %	Silt %	Clay %	Bulk Density (g/cm ³)	Porosity	Median Grain Diameter d ₅₀ (mm)	Organic Content (OC)	Uniformity Coefficient (UC)	R
Borden soil	96.2	2	1.8	1.74	0.34	0.21	0.03	1.92	1.54
Eustis soil	95.9	1	4.4	1.69	0.36	0.27	0.38	2.3	2.43
Hayhook soil	85.5	4.3	10.2	1.64	0.38	0.26	0.08	16	1.34
Mixed sand *				1.87	0.29	0.34		3.45	1.58

* mixed sand – accusand and granusil Michele mahal, bulk density avg of organic liquid exps

Table 2.

Summary of system parameters and modeling calibrated parameters for the one-dimensional, one-source model

Experiment	Q (ml/min)	PV (ml)	q (cm/hr)	v (cm/hr)	k_{La}	β_4
Control	2.65	185.4	3.28	9.42	0.4	0.5
Mixed Source	3.27	913.3	3.18	9.13	0.16	1.2
Heterogeneous	3.33	812.9	3.36	9.66	0.05	0.8

Table 3

Dissolution Experiments and Modeling Parameters for Column Experiments

Porous Media	Initial Saturation %	Zone fractions*	Kla (h ⁻¹)
Borden soil Exp 1	11.4	0.7, 0.27, 0.08	25.7, 23.7, 4.5
Eustis soil Exp 2	14.7	0.67, 0.31, 0.08	30.4, 24.9, 4.3
Hayhook soil Exp 1	24.5	0.52, 0.24, 0.24	51.5, 21.3, 2.9
Hayhook soil Exp 2	21.1	0.54, 0.25, 0.26	49.2, 21.4, 3.2
Mixed sand Exp 1	23.7	0.77, 0.22	32.3, 5.0
Mixed sand Exp 2	21.9	0.5, 0.4995, 0.005	7.0, 5.0, 9.0
Mt. Lemmon soil Exp 1	8.14	1.05, 0.29	21.0, 0.07

* Zone fractions refer to number of zones used for simulation

Table 4.

Summary of system parameters and modeling calibrated parameters for the one-dimensional, dual-source model

Experiment	Zone 1			Zone 2		
	k_{La}	β_4	A	k_{La}	β_4	A
Control	0.4	0.5	1.0	-	-	-
Mixed Source	0.16	1.2	0.9	0.03	0.09	0.2
Heterogeneous	0.05	0.8	1.0	0.03	0.06	0.2