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IMPACT OF ORGANIC-LIQUID DISTRIBUTION AND FLOW-FIELD HETEROGENEITY ON REDUCTIONS IN MASS FLUX

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Abstract

A series of flow-cell experiments was conducted to investigate the impact of organic-liquid distribution and flow-field heterogeneity on the relationship between source-zone mass removal and reductions in contaminant mass flux from the source zone. Changes in source-zone architecture were quantified using image analysis, allowing explicit examination of their impact on the mass-flux-reduction/mass-removal behavior. The results showed that there was minimal reduction in mass flux until a large fraction of mass was removed for 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. The latter systems exhibited multi-step mass-flux-reduction/mass-removal behavior, and characterization of the organic-liquid saturation distribution throughout flushing allowed identification of the cause of the nonideal behavior. The age of the source zone (time from initial emplacement to time of initial characterization) significantly influenced the observed mass-flux-reduction/mass-removal behavior. The results of this study illustrate the impact of both organic-liquid distribution and flow-field heterogeneity on mass-removal and mass-flux processes.

1. Introduction

The contamination of groundwater by hazardous organic chemicals and the associated risks to human health and the environment are issues of great importance. One of the most critical issues associated with hazardous waste sites is the potential presence of organic-liquid source zones in the subsurface. Organic liquids, such as chlorinated solvents, creosote, coal tars, and fuels, once introduced into the subsurface become entrapped, and serve as long-term sources of contamination. The contaminant mass flux or mass discharge emanating from a source zone, also referred to as the source strength or source function, is recognized as a primary determinant of the risk associated with a contaminated site. Concomitantly, the reduction in mass flux achieved with a specific level of source-zone mass removal (or mass depletion) is a key metric for evaluating the effectiveness of a source-zone remediation effort. Thus, there is great interest

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in characterizing, estimating, and predicting relationships between mass flux reduction and mass removal.

The fundamental concept of contaminant mass flux, its relationship to mass-removal processes and source-zone properties, and its impact on risk has long been established (e.g., Fried et al., 1979; Pfannkuch, 1984). An early effort to quantify the relationship between contaminant mass flux reduction and mass removal, and the resultant reduction in risk, was presented by Freeze and McWhorter (1997). Conceptual mass-flux-reduction/mass-removal relationships and their associated elution and mass-removal curves, are presented elsewhere (e.g., Freeze and McWhorter, 1997; Enfield et al., 2002; Rao et al., 2002; Rao and Jawitz, 2002; Stroo et al., 2003; Brooks et al., 2004; Jawitz et al., 2005; Brusseau et al., 2008; DiFilippo and Brusseau, 2008). Several studies based on mathematical modeling and a small number of studies employing flow cells have been conducted to examine the influence of source-zone architecture on mass removal and mass flux reduction (e.g., Sale and McWhorter, 2001; Jayanti and Pope, 2004; Lemke et al., 2004; Parker and Park, 2004; Phelan et al., 2004; Soga et al., 2004; Falta et al., 2005; Jawitz et al., 2005; Fure et al., 2006; Lemke and Abriola, 2006; Saenton and Illasakengare, 2007; Suchomel and Pennell, 2007; Basu et al., 2008; Brusseau et al., 2008; DiFilippo and Brusseau, 2008; Kaye et al., 2008; Zhang et al., 2008). The results indicate generally that significant reductions in mass flux are induced by relatively small fractions of mass removal for systems with greater source-zone heterogeneity, wherein some portion of the organic liquid is hydraulically poorly accessible (e.g., organic liquid distributed as a mix of lower and higher saturations, or organic liquid trapped in lower-permeability zones). Conversely, larger fractions of mass removal are required to induce significant mass flux reductions for more homogeneous systems. These prior studies have focused primarily on characterizing the initial conditions of the source zone and monitoring effluent concentration data. The temporal dynamics of a system undergoing mass removal are also of interest, such as the impact of source-zone evolution on mass flux reduction. Examination of such behavior would be enhanced through use of in-situ imaging of saturation distributions.

The purpose of the study reported herein was to investigate the impact of source zone architecture on the mass-flux-reduction/mass-removal relationship under continuous water-flushing conditions. The impact of organic-liquid distribution was evaluated by varying organic-liquid saturation distribution in a homogeneous flow field (Control, Homogeneous and Mixed-Source experiments as described below). The impact of flow field heterogeneity was evaluated by varying porous media distributions (Mixed-Source and Heterogeneous experiments as described below). Changes in source-zone architecture were characterized using image analysis, allowing explicit examination of their impact on the mass-flux-reduction/mass-removal behavior.

2. Materials and Methods

A total of six experiments were conducted for this study (Table 1). The Control and Homogeneous experiments both consisted of a homogeneous pack of 40/50 sand. A residual saturation of 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. The Homogeneous-EF experiment was identical in setup to the Homogeneous experiment. 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. This distribution promoted the formation of a zone of higher organic-liquid saturation (e.g., pool) at the material boundary. The Heterogeneous and Heterogeneous-EF experiments consisted of a matrix of 40/50 mesh sand with lenticular lenses of 20/30 mesh and 70/100 mesh sands.

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; Brusseau et al., 2000). 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 (e.g., Schuille, 1988; Kennedy and Lennox, 1997).

Both rectangular and cylindrical flow cells were used for the four experiments reported in this study (Table 1). The rectangular flow cell (used for the Mixed-Source and Heterogeneous experiments as referenced below) was constructed of stainless steel and tempered glass, with dimensions of 40 cm long by 20 cm high by 2.6 cm wide. This flow cell was equipped with multiple, evenly spaced injection/extraction ports on each end. In addition, three ports were evenly spaced at the top of the flow cell to allow injection of organic liquid. Water tight seals were made with Teflon and silicon sealant. The cylindrical flow cell (used for the Homogeneous and Homogeneous-EF experiments as referenced below) was constructed of stainless steel and was 7.6-cm diameter and 10-cm long. Finally, the Control experiment was conducted with a 2-cm diameter and 7-cm long stainless steel column.

For the Control experiment, a residual saturation of TCE was established throughout the column by injecting organic liquid into the influent end of the column. Mobile organic liquid was removed prior to the initiation of water flooding by flushing 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 ($S_n = 0.18$, (Dobson et al., 2006)) throughout the entirety of the flow field. The source zones for the Homogenous and Homogeneous-EF experiments were 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 (Figure 1). The organic-liquid saturation within the zone was 0.10 and the global saturation (volume of organic liquid divided by total pore volume of the flow cell) was 0.01 (Table 1).

The source zones for the Mixed-Source, Heterogeneous, and Heterogeneous-EF experiments were developed by injecting TCE through the top injection ports using a gas-tight syringe and needle. The injection needle was driven to a depth of approximately 7 cm from the top of the flow cell, creating a point injection source. Organic liquid 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. Previous studies have reported that stable organic-liquid distributions were attained after 24 hours (e.g., Fure et al., 2006; Suchomel and Pennell, 2007; Kaye et al., 2008). 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. Sampling and analytical methods were similar to previous studies (e.g., Brusseau et al., 2008).

Two enhanced flushing (EF) experiments were conducted with the surfactant Tween-80 (experiments Homogeneous-EF and Heterogeneous-EF). The flow field and organic-liquid source zone for the Homogeneous-EF experiment were developed using the same methods as those previously described for the Homogeneous experiment. The Heterogeneous-EF

experiment was conducted with the same porous media configuration as the previously described Heterogeneous experiment. The source zone was created by injecting TCE into the top injection ports, with 75% injected in the far left port and 25% injected through the center injection port (total volume of 20 ml). Once the flow cell was prepared, a solution of 2% (wt.) Tween-80 was injected at a constant rate, equivalent to an average pore-water velocity of 9 cm/h. The total flow was evenly distributed among the influent ports and sampling and analytical methods were similar to previous studies (Brusseau et al., 2008).

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 used is discussed in detail elsewhere (DiFilippo 2008); therefore, only a brief description is provided below. At any given time, a series of three photographs of the flow cell was taken using a high resolution digital camera (Nikon D70 with an AF-S Nikkor 18-70 mm lens). Each photograph contained an optical density photographic card (Kodak) to correct for lighting differences between images and to convert pixel intensity to optical density. An average pixel-by-pixel optical density value for a given time was determined by averaging the optical density of the three images. Very little variability was observed among the three images. Any background anomalies caused by changes in lighting across the front of the flow cell were corrected by subtracting an organic-liquid free image set (taken prior to injection) from the image set of interest. Organic-liquid saturation was calculated based on a pre-determined organic-liquid saturation versus optical density calibration curve. 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, 2008). 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 (Table SI-1).

Mass-flux-reduction/mass-removal behavior was simulated based on treating changes in mass flux as a direct function of the change in contaminant mass (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., 2008, Brusseau et al., 2008, DiFilippo and Brusseau, 2008, Maji and Sudicky, 2008):

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

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. The parameter n defines the specific mass-flux-reduction/mass-removal relationship, and thus is a lumped-process term that incorporates the impact of organic-liquid distribution, flow-field dynamics, and mass-transfer and displacement processes.

3. Results and Discussion

3.1 Initial Organic Liquid Distribution

The initial distributions of organic liquid for the Mixed-Source and Heterogeneous experiments are shown in Figures 1, SI-1 and SI-2. For the Mixed-Source experiment, organic liquid migrated downward through the matrix and spread laterally along the top of the capillary barrier, forming a region of high saturation. The average initial organic-liquid saturation was 0.11 within the entire contaminated portion of the matrix. The residual-saturation threshold for the 40/50 matrix is 0.20 (Dobson et al., 2006). The organic-liquid saturation for the region at the capillary barrier interface ranged from 0.05 to 0.45, with a mean value of 0.18.

For the Heterogeneous experiment, organic liquid migrated downward and pooled along the top boundary of the 70/100 zone on the left side of the flow cell (Figure 2). In the center of the flow cell, organic liquid migrated downward to the 70/100 zone. The organic liquid moved laterally along this boundary, spilled over the edge, and then wicked into the adjacent 20/30 zone and pooled. The initial organic-liquid saturation ranged from 0.05 to 0.35 (mean of 0.14) for the 40/50 matrix and from 0.05 to 0.40 (mean of 0.20) for the 20/30 zone. Inspection of the image data shows that the system attained stable organic-liquid distributions prior to the start of dissolution (see Figure SI-2).

3.2 Contaminant Elution Behavior

The contaminant elution curves obtained from the flow-cell and control experiments are presented in Figure 3. As expected, the initial effluent concentration for the control experiment was equal to the aqueous solubility of TCE and the concentration remained high until almost all of the organic-liquid mass was removed (Figure 3). The effluent concentrations for the other flow-cell experiments were less than aqueous solubility values, as expected, due to dilution effects associated with the system configuration. The effluent concentrations for the Homogeneous experiment initially remained steady and gradually decreased after 14 pore volumes of water flushing. The elution curves for the Mixed-Source and Heterogeneous experiments exhibited relatively extensive periods wherein the concentrations decreased gradually (the first 25 pore volumes for the Mixed-Source experiment and 70 pore volumes for the Heterogeneous experiment), reflecting the impacts of mass-removal constraints associated with system configuration.

For the Mixed-Source experiment, organic-liquid mass associated with the hydraulically-accessible region (i.e., the residual zone within the matrix) was completely removed after approximately 25 pore volumes of water flushing (Figure 2). The mass associated with the less hydraulically-accessible, higher-saturation region above the capillary barrier was the last to be removed (Figure 2). Removal of mass from this region occurred along a dissolution front moving progressively down gradient (Figure 2), similar to results reported in previous studies (e.g. Brusseau et al., 2000; Brusseau et al., 2002; Imhoff et al., 1994). This resulted in steady effluent concentrations for an extended period of flushing from approximately 30 to 100 pore volumes (Figure 3). Additional images of organic-liquid distribution during the experiment are presented in the Supporting Information materials (Figure SI-1).

The elution curve for the Heterogeneous experiment also displayed an initial period wherein effluent concentration gradually decreased with flushing (Figure 3). The initial decrease in concentration reflects the preferential removal of organic-liquid mass from the 40/50 matrix (Figure 2). During flushing, the organic-liquid mass in the 20/30 zone remained relatively constant with time until all of the organic-liquid mass was removed from the matrix (Figure 2). The delay in removal of organic liquid from the 20/30 zone was primarily due to the presence of organic-liquid sources located directly upgradient. This behavior is similar to that observed in prior modeling studies (Sale and McWhorter, 2001). After approximately 60 pore volumes of flushing, the organic liquid associated with the 20/30 zone mobilized within this zone (Figure SI-2). After approximately 94 pore volumes, the concentration eluting from the flow cell increased from 66 mg/L to 95 mg/L and remained constant until only a small portion of the pool remained. This increase resulted from changes in the relative permeability (k_r) associated with flushing of the 20/30 pool zone, and is similar to behavior observed in prior work (Powers et al., 1998; Nambi and Powers, 2000) (see Supporting Information for further discussion of this issue). Additional images of organic-liquid distribution during the experiment are presented in the Supporting Information materials (Figure SI-2).

3.3 Mass-Flux-Reduction/Mass-Removal Behavior

For both the Control and Homogeneous experiments, significant reductions in mass flux did not occur until relatively large fractions of mass (>50%) were removed (Figure 4). Such mass-removal behavior is evident from the contaminant elution curves obtained for the two experiments (Figure 3), wherein concentrations are maintained at or near maximal levels for the majority of flushing. The mass-flux-reduction/mass-removal behavior observed for the Homogeneous experiment was generally similar to that of the Control experiment even though the organic liquid was not uniformly distributed throughout the flow field as it was for the Control. For the control experiment, minimal mass flux reduction occurred until approximately 75% of the mass was removed. For the Homogeneous experiment, reduction in mass flux occurred after removing approximately 50% of the mass, with the earlier reduction due to the shorter length of the source zone in the direction of flow and associated mass-transfer constraints. The general behavior observed for both experiments is expected for systems wherein organic liquid is distributed relatively homogeneously (e.g., occurs only as residual) and is accessible to water flow, illustrating the impact of relatively ideal mass-transfer and displacement on mass flux and mass removal, as observed in prior studies (Fure et al., 2006; Brusseau et al., 2008).

The mass-flux-reduction/mass-removal relationships for both the Mixed-Source and Heterogeneous experiments exhibited nonsingular or multi-step behavior. Such multi-step mass-flux-reduction/mass-removal behavior has been observed in prior flow-cell experiments (Brusseau et al., 2008), selected individual realizations in recent mathematical-modeling studies (Lemke et al., 2004; Phelan et al., 2004; Soga et al., 2004; Lemke and Abriola, 2006), and in measured field data (Brusseau et al., 2007; DiFilippo and Brusseau, 2008). Measurement of the temporal evolution of organic-liquid saturation distribution for the present study allows an analysis of this behavior, which has not been characterized or discussed to a significant extent in prior work. The multi-step behavior comprised two distinct stages. In the first stage, reductions in mass flux were observed after removing less than 2% of the total mass in the flow cell. These early reductions in mass flux reflect the preferential removal of organic liquid residing at lower saturations in hydraulically-accessible regions of the flow cell (Figure 2). The mass flux from the flow cell continued to decrease until all of the highly-accessible organic liquid mass was removed. The final stage of the mass-flux-reduction/mass-removal relationship reflects the removal of the higher saturation, more poorly-accessible organic-liquid mass.

For the Mixed Source experiment, the removal of organic-liquid mass from the region of high saturation resulted in steady effluent concentrations for many pore volumes of flushing. The steady effluent concentrations resulted in minimal reductions in mass flux until almost all of the organic-liquid mass was removed from the system, which produced the change in slope in the mass-flux-reduction/mass-removal relationship observed after greater than 60% mass removal. For the Heterogeneous experiment, changes in the relative permeability of the 20/30 zone during dissolution (see Supporting Information) resulted in an increase in effluent concentrations and, consequently, an increase in the mass flux from the flow cell. This increase produced the change in slope observed in the mass-flux-reduction/mass-removal relationship. Following this, there was an extended period during which mass flux remained constant due to steady state effluent concentrations associated with the dissolution of mass within the region of high saturation.

The simple mass-removal function was applied to the data sets reported herein (Figure 4B). In the case of the Control and Homogeneous experiments, the simple mass-removal function provided good matches to the measured data. The function also provided good matches to the early time behavior for the Mixed Source and Heterogeneous experiments. However, the late time, multi-step behavior was poorly simulated.

3.4 Impact of Source-Zone Age

Sites where organic-liquid contamination has existed for many years will likely have had a portion of the highly accessible source-zone mass removed prior to the initiation of source-zone characterization and remediation. Behavior observed for such systems may differ from that observed for newly contaminated systems such as represented by the flow-cell experiments discussed above. The impact of source-zone age was investigated for the Mixed-Source and Heterogeneous experiments by re-assessing the mass-flux-reduction/mass-removal behavior after the most highly accessible mass was removed. For the Mixed-Source experiment, a new initial condition was established after 29 pore volumes of flushing. This coincides with the complete removal of the highly accessible organic liquid within the center of the flow cell, leaving only the more poorly accessible higher-saturation organic liquid located along the top of the capillary barrier. The new initial condition for the Heterogeneous experiment was established after 106 pore volumes of flushing, corresponding to the complete removal of organic liquid from the 40/50 matrix. The mass-flux-reduction/mass-removal relationships were then recalculated based on these new initial conditions (Figure 5).

The mass-flux-reduction/mass-removal behavior for these high-saturation-dominated systems is significantly different from the initial relationships derived for these experiments. The modified Mixed-Source data set (hereafter referred to as Mixed-Source-2) exhibited multi-step behavior, marked by three distinct stages. Although the original Mixed-Source data set also displayed multi-step behavior, the three stages for the Mixed-Source-2 data set occurred significantly earlier in relation to relative mass removal. In the initial stage, reductions in mass flux were observed after removing less than 10% of the mass. This initial reduction in mass flux reflects the preferential removal of the accessible mass along the top boundary of the source zone. Next, there was a period of minimal reduction in mass flux associated with the downgradient progression of the dissolution front through the source zone. In the final stage, there were again large reductions in mass flux associated with the complete removal of the remaining organic-liquid mass from the source zone.

The modified Heterogeneous data set (hereafter referred to as Heterogeneous-2) exhibited minimal reductions in mass flux until nearly all of the source-zone mass was removed. This behavior is in great contrast to that observed for the original data set, and is similar to that observed in a modeling-based study for source zones consisting of only pooled organic liquid (Sale and McWhorter, 2001). Although the mass flux emanating from the systems are significantly different, the mass-flux-reduction/mass-removal behavior exhibited by the Heterogeneous-2 data set is similar to that of the Control experiment (Figure 4). This is related to the fact that both systems have relatively unimodal distributions of organic liquid.

3.5 Impact of Organic-Liquid Distribution

Changes in organic-liquid distribution and their impact on observed mass-flux-reduction/mass-removal behavior can be examined by evaluating the ganglia-to-pool (GTP) ratio (the ratio of the volume of residual to pooled organic liquid, (e.g., Lemke et al., 2004; Parker and Park, 2004; Lemke et al., 2006; Suchomel and Pennell, 2007) at various flushing times (Figure 6). The Mixed-Source experiment had an initial GTP of 1.7. During flushing, the GTP ratio increased until all of the organic-liquid mass was present at or below residual saturation ($GTP = \infty$). Therefore, the system became more residual dominated with time as would be expected. The initial GTP ratio for the Heterogeneous experiment was 1.2 and the GTP ratio remained relatively constant until approximately 30% of the total mass was removed from the system. After this, the GTP ratio decreased at a gradually increasing rate until 85% mass removal, indicating that the system became more pool dominated as the hydraulically-accessible organic liquid present at lower saturations was removed. The final portion of the decrease in the GTP ratio corresponded to the late-stage increase in effluent concentration observed in Figure 3,

indicating that organic liquid present at lower (residual) saturations in the 20/30 higher-saturation zone was preferentially removed during this time. Eventually, the GTP ratio for this zone increased, indicating a more residual dominated system, as mass removal proceeded to completion.

In prior studies, larger fractions of mass removal were required to induce mass flux reductions for systems with higher GTP ratios, whereas smaller fractions of mass removal were required for systems with moderate to low ratios (Lemke et al., 2004; Phelan et al. 2004; Lemke and Abriola, 2006; Suchomel and Pennell, 2007; Brusseau et al., 2008). The initial GTP ratios for all four experiments are presented in Table 1. In general, our results agree with the prior studies, in that larger fractions of mass removal were required to induce mass flux reductions for experiments with higher initial GTP ratios (Control and Homogeneous) and smaller fractions of mass removal were required for experiments with lower initial GTP ratios (Mixed-Source and Heterogeneous). In contrast, the Heterogeneous-2 data set had a low initial GTP ratio (0.3) but displayed minimal reduction in mass flux until nearly all of the source-zone mass was removed. This disparity illustrates a limitation associated with use of the GTP ratio for source zones comprising a single-source type in physically heterogeneous systems. The present case of organic liquid occurring at only high saturation (pool dominated system) is one such example. Another case for which use of the GTP ratio is limited is that wherein organic liquid at low saturation resides within lower-permeability zones (residual dominated system), as discussed by Brusseau et al. (2008).

Source-zone architecture can also be described using statistical measures of saturation distribution (e.g., Saenton and Illangsasekare, 2007; Basu et al., 2008). The initial mean (μ) and variance (σ^2) for the spatial distribution of organic-liquid saturation for the entire flow field is presented in Table 1 for each experiment. Reductions in mass flux were observed at earlier stages of mass removal for the systems with larger saturation variance.

Changes in organic-liquid distribution through time were characterized by determining the mean and variance for only the regions with organic-liquid present (i.e., organic-liquid free regions of the flow field were not included) (Figure 7). For the Mixed-Source experiment, the mean organic-liquid saturation decreased once the mass associated with the residual-dominated matrix was removed and remained constant until almost all of the remaining mass was removed from the system. This further illustrates the sequential down-gradient progression of the dissolution front in the region just above the capillary barrier. The variance in saturation remained relatively constant until the majority of mass was removed. For the Heterogeneous experiment, the mean remained relatively constant until only the mass associated with the pool remained, at which time there was a sharp increase in the mean saturation. The variance in saturation distribution displayed similar behavior, indicating that organic-liquid distribution was more uniform in the 40/50 matrix than in the 20/30 zone. The observed results with respect to saturation variance are similar to those obtained from model simulations reported by Basu et al. (2008).

3.6 Impact of Flow-Field Heterogeneity

Changes in flow-field heterogeneity and its associated impact on mass-flux-reduction/mass-removal behavior were examined by evaluating the spatial variance in organic-liquid distribution and hydraulic conductivity at various times during flushing (Figure 8). The variances presented in Figure 8 were calculated for the entire system in order to evaluate the impact of the entire flow field on reductions in mass flux. The calculated hydraulic conductivity for each image set incorporates the impact of organic liquid on relative permeability. Further examination and discussion of relative permeability effects is presented in the SI.

For the Mixed-Source experiment, the variance in hydraulic conductivity decreased linearly as organic liquid was removed from the system (i.e., decrease in the variance in S_n). This is consistent with flow occurring in a physically homogeneous domain and continued removal of the organic liquid resulting in a lessening impact of relative-permeability effects. For the Heterogeneous experiment, the variance in hydraulic conductivity increased non-linearly as mass was removed from the system. This is due to the fact that the presence of regions of high organic-liquid saturation in the 20/30 zone reduced the relative permeability of this zone, and therefore reduced the initial hydraulic-conductivity disparity of the system. However, removal of organic liquid from the 20/30 zone reduced the relative-permeability effect, resulting in an increase in the hydraulic-conductivity disparity (towards the maximum value associated with the intrinsic-permeability differences).

3.7 Impact of Flushing Agent

Two experiments were conducted to determine if the multi-step mass-removal/mass-flux-reduction behavior observed under water-flooding conditions may also be observed for enhanced-solubilization conditions. A solution of 2% (wt.) Tween-80 was chosen because it has been shown to significantly enhance TCE dissolution without mobilization (e.g., Suchomel and Pennell, 2006). The mass-removal/mass-flux-reduction behavior for the two enhanced flushing experiments is presented in Figure 4. The observed behavior for the Homogeneous-EF experiment is similar to that observed for the Homogeneous experiment, indicating that mobilization did not occur during the surfactant flushing. The mass-removal/mass-flux-reduction behavior for the Heterogeneous-EF experiment displays similar nonsingular behavior compared to the Heterogeneous experiment, indicating that increased rates of mass removal may not be sufficient to overcome the hydraulic accessibility constraints of the source zone.

4. Conclusions

A series of flow-cell experiments was conducted to investigate the impact of source-zone architecture and flow-field heterogeneity on the mass-removal/mass-flux-reduction relationship. Our results illustrate the impact of organic-liquid distribution and hydraulic accessibility on mass-flux-reduction/mass-removal behavior. Large fractions of mass removal may be required to induce significant reductions in mass flux for systems with uniform distributions of organic liquid (i.e., all residual or all pool) residing in hydraulically-accessible flow domains. Conversely, significant reductions in mass flux may be induced with relatively minimal mass removal for systems wherein organic liquid is present at both residual and higher saturations. Multi-step behavior was observed for the heterogeneous source-zone systems, and characterization of the organic-liquid saturation distribution throughout flushing allowed identification of the cause of the nonideal behavior. Such behavior will complicate estimation and prediction efforts based on simplified approaches.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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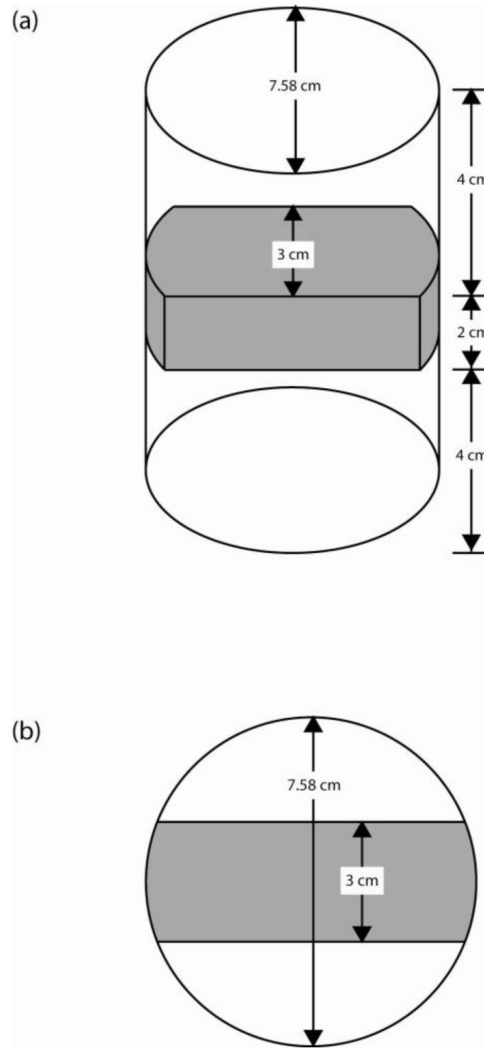


Figure 1. Schematic diagram for the source zone of the Homogeneous experiment. The gray zone in the center represents the zone containing organic liquid. (a) Longitudinal view. (b) Plan view.

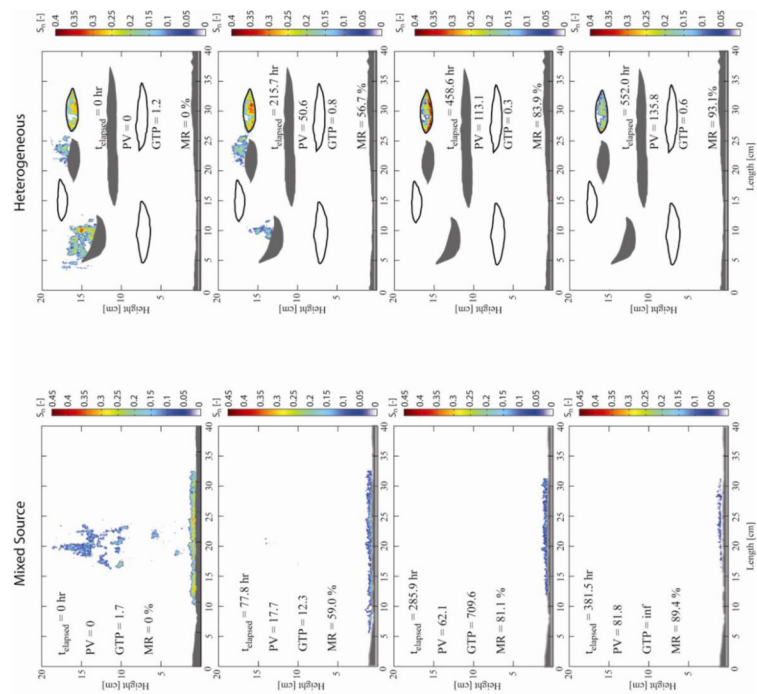


Figure 2.

Organic-liquid distribution at four different flushing 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. The percent mass removed (MR) was calculated based on moment analysis of the elution data. PV is pore volumes of water flushed. The spatial resolution for each image was 0.02 mm^2 .

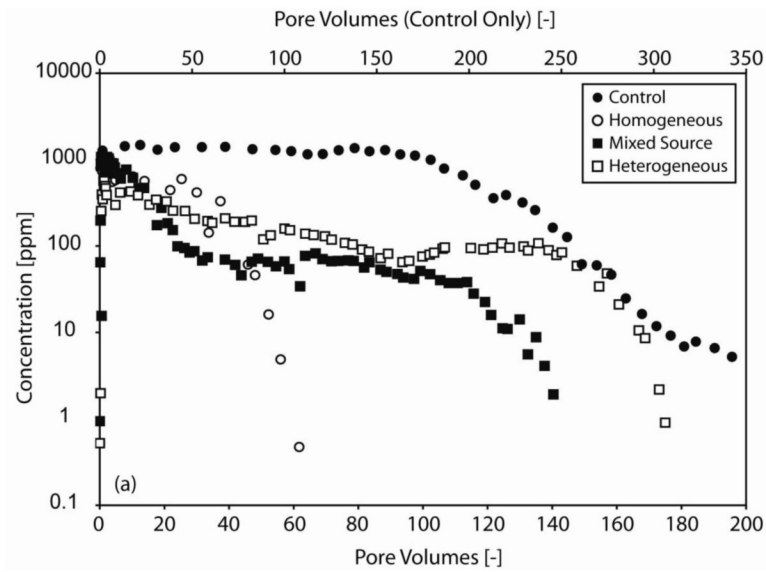


Figure 3.

Effluent concentration as a function of the number of pore volumes flushed for the four aqueous flushing experiments. The pore volumes for the Control, Homogeneous, Mixed-Source and Heterogeneous experiments are 9, 185, 913, and 813 ml, respectively. The Homogeneous, Mixed-Source and Heterogeneous experiments are plotted using the bottom axis and the Control experiment is plotted using the top axis.

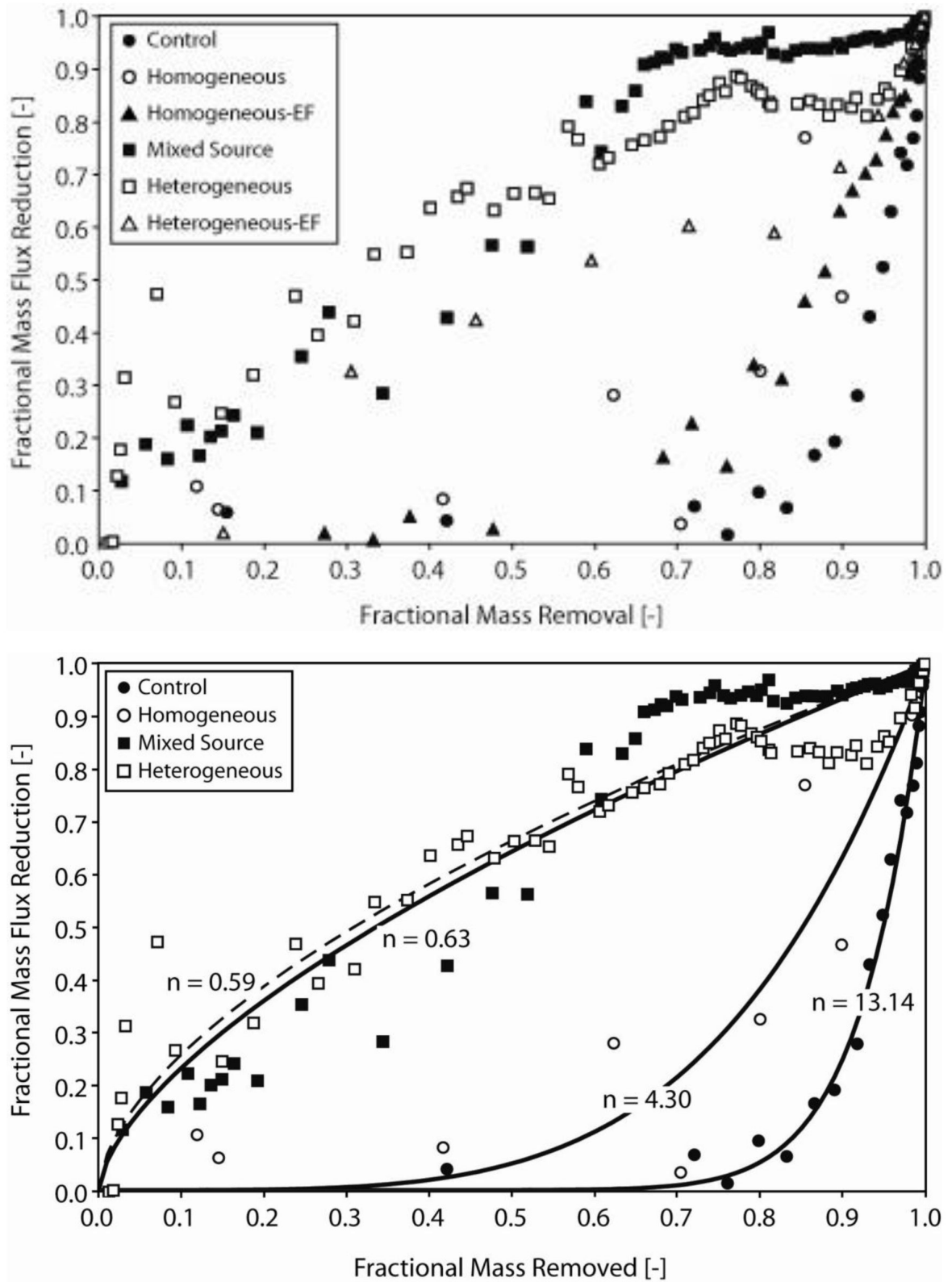


Figure 4.

Mass flux reduction versus mass removal behavior for the aqueous flushing and enhanced flushing experiments. A. Measured Data; B. Simulations produced with simple model.

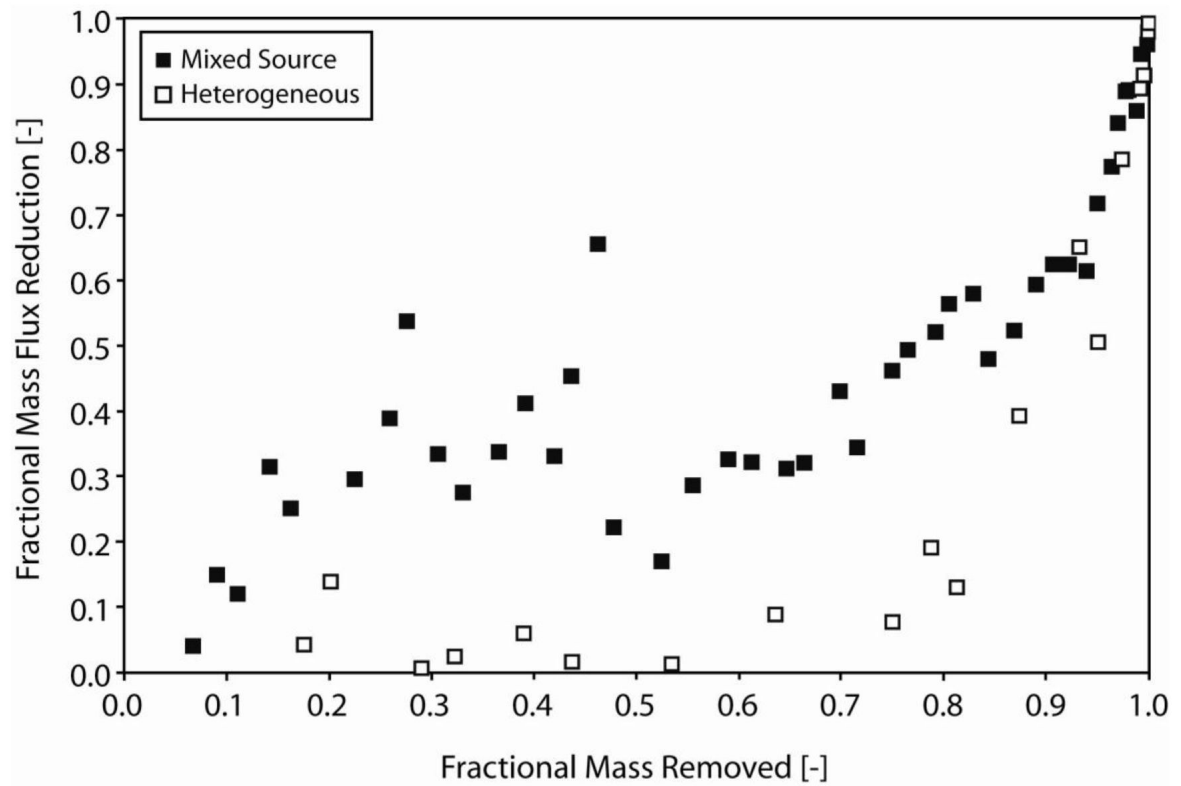


Figure 5.

Impact of Source-zone aging on mass flux reduction versus mass removal behavior for the modified Mixed-Source and Heterogeneous experiments (Mixed-Source-2 and Heterogeneous-2, respectively). For the Mixed-Source experiment, a new initial condition was established after 29 pore volumes of flushing. This coincides with the complete removal of the highly accessible residual organic liquid, leaving only the more poorly accessible organic liquid pool located along the top of the capillary barrier. The new initial condition for the Heterogeneous experiment was established after 106 pore volumes of flushing, corresponding to the complete removal of organic liquid mass from the 40/50 matrix.

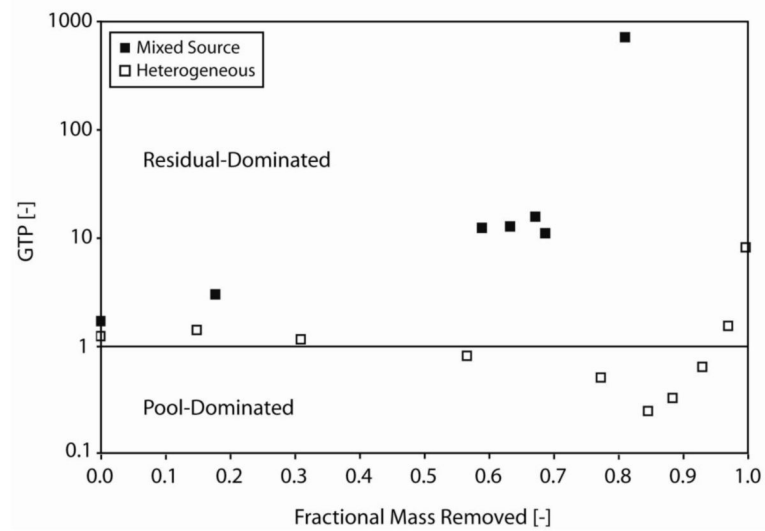


Figure 6. Ganglia-to-pool (GTP) ratio as a function of mass removal for the Mixed-Source and Heterogeneous experiments. The GTP ratio is the ratio of the volume of organic liquid \leq residual (ganglia) to volume $>$ residual (pool).

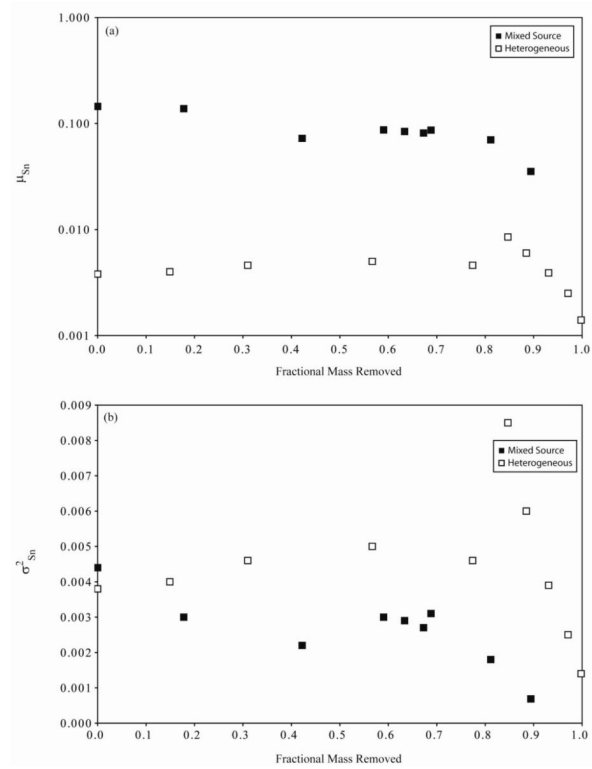


Figure 7. Mean (μ_{S_n}) and variance ($\sigma^2_{S_n}$) of organic-liquid saturation distribution for the Mixed-Source and Heterogeneous experiments as a function of mass removal. The mean and variance were calculated for only the regions of the flow cell where organic-liquid was present. (a) Mean (b) Variance.

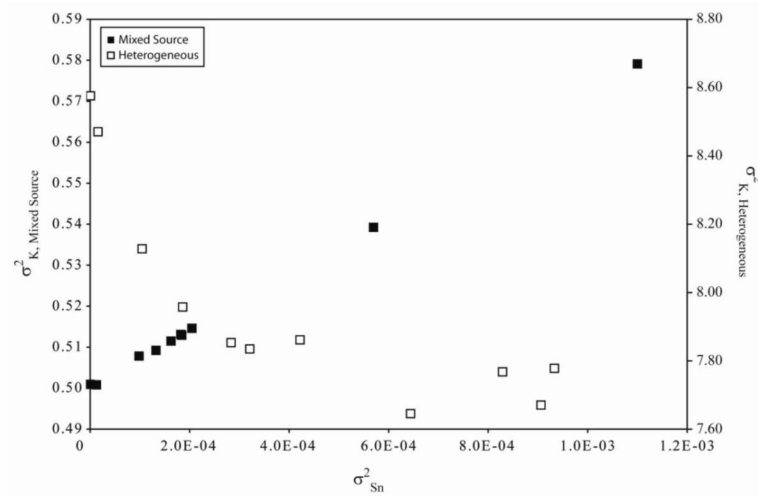


Figure 8. Hydraulic conductivity variance (σ^2_K) for the Mixed-Source and Heterogeneous experiments as a function of the variance in organic-liquid saturation distribution (σ^2_{Sn}). The variance in hydraulic conductivity and organic-liquid saturation were calculated for the entire flow cell, including organic-liquid free regions.

Table 1

Parameters for the aqueous flushing experiments.

Experiment	Q (ml/min)	v (cm/hr)	L (cm)	A (cm ²)	S _{n,global} ^a	GTP _{initial} ^b	μSn, initial ^c	σ ² Sn, initial ^c
Control	0.6	30.1	7	3.5	0.18	Inf	0.18	0
Homogeneous	2.7	9.4	10	48.5	0.01	Inf	6.7 × 10 ⁻³	1.9 × 10 ⁻⁴
Mixed-Source	3.3	9.1	40	61.8	0.01	1.7	6.6 × 10 ⁻³	1.1 × 10 ⁻³
Heterogeneous	3.3	9.7	40	59.5	0.02	1.2	5.3 × 10 ⁻³	9.3 × 10 ⁻⁴
Homogeneous- EF	2.7	9.4	10	48.5	0.01	Inf	0.18	0
Heterogeneous- EF	3.3	9.7	40	58	0.02	1.2	5 × 10 ⁻³	1 × 10 ⁻³

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

^b Ganglia-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).

^c The mean and variance in organic-liquid distribution was calculated for the entire system.