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Characterizing Long-term Contaminant Mass Discharge and the Relationship Between Reductions in Discharge and Reductions in Mass for DNAPL Source Areas

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Abstract

The objective of this study was to characterize the temporal behavior of contaminant mass discharge, and the relationship between reductions in contaminant mass discharge and reductions in contaminant mass, for a very heterogeneous, highly contaminated source-zone field site. Trichloroethene is the primary contaminant of concern, and several lines of evidence indicate the presence of organic liquid in the subsurface. The site is undergoing groundwater extraction for source control, and contaminant mass discharge has been monitored since system startup. The results show a significant reduction in contaminant mass discharge with time, decreasing from approximately 1 to 0.15 kg/d. Two methods were used to estimate the mass of contaminant present in the source area at the initiation of the remediation project. One was based on a comparison of two sets of core data, collected 3.5 years apart, which suggests that a significant (~80%) reduction in aggregate sediment-phase TCE concentrations occurred between sampling events. The second method was based on fitting the temporal contaminant mass discharge data with a simple exponential source-depletion function. Relatively similar estimates, 784 and 993 kg, respectively, were obtained with the two methods. These data were used to characterize the relationship between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR). The observed curvilinear relationship exhibits a reduction in contaminant mass discharge essentially immediately upon initiation of mass reduction. This behavior is consistent with a system wherein significant quantities of mass are present in hydraulically poorly accessible domains for which mass removal is influenced by rate-limited mass transfer. The results obtained from the present study are compared to those obtained from other field studies to evaluate the impact of system properties and conditions on mass-discharge and mass-removal behavior. The results indicated that factors such as domain scale, hydraulic-gradient status (induced or natural), and flushing-solution composition had insignificant impact on the CMDR-MR profiles and thus on underlying mass-removal behavior. Conversely, source-zone age, through its impact on

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contaminant distribution and accessibility, was implicated as a critical factor influencing the nature of the CMDR-MR relationship.

Keywords

DNAPL remediation; Source zone; Mass flux; source containment

INTRODUCTION

The use of contaminant-mass-discharge or mass-flux measurements to characterize site conditions and assess remediation performance is becoming more widespread (Rosenbloom et al., 1993; Butcher and Gauthier, 1994; Freeze and McWhorter, 1997; DiGiulio et al., 1999; Einarson and Mackay, 2001; Rao et al., 2002; Newell et al., 2003; Bockelmann et al., 2003; Stroo et al., 2003; Brooks et al., 2004; Soga et al., 2004; NRC, 2005; SERDP, 2006; Brusseau et al., 2007; Basu et al., 2009; ITRC, 2010; Brusseau et al., 2011a, 2011b). Almost all applications to date have been based on obtaining one or two discrete measurements of contaminant mass discharge (e.g., collected before and after a remedial action), using multi-point transects or short-term pumping tests that are often applied within the contaminant plume. While this approach provides useful information, additional information and insight can be gained by measuring time-continuous profiles of contaminant mass discharge (Brusseau et al., 1999, 2007, DiFilippo and Brusseau, 2008; Brusseau et al., 2011a, 2011b). Such data can be used to characterize mass-transfer processes, assess mass-removal magnitudes and conditions, estimate contaminant distributions and quantities, as well as measure mass discharge.

An effective means by which to measure time-continuous profiles of contaminant mass discharge is to conduct a long-term contaminant mass discharge test, wherein one or more extraction wells are pumped for an extended time (e.g., months) and contaminant concentrations and flow rates are monitored (Brusseau et al., 1999, 2007, 2011a). For example, these authors conducted several contaminant mass discharge tests within the source area of a chlorinated-solvent contaminated site to characterize source conditions with respect to resident contaminant mass, mass removal, and operative mass-transfer processes. In cases wherein extraction-based remedies (e.g., pump and treat, soil vapor extraction) are in place, operational data can be used to obtain time-continuous measures of contaminant mass discharge (Brusseau et al., 2007, 2010, 2011a, 2011b).

Temporal profiles of contaminant mass discharge, combined with knowledge of initial contaminant mass, can be used to evaluate the relationship between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR). The CMDR-MR relationship is a defining characteristic of system behavior, and is mediated by system properties and conditions such as permeability distribution, contaminant distribution, and mass-transfer processes. These relationships have been characterized in several laboratory and mathematical-modeling studies (Rao et al., 2002; Jayanti and Pope, 2004; Phelan et al., 2004; Jawitz et al., 2005; Fure et al., 2006; Brusseau et al., 2008; DiFilippo and Brusseau, 2008; Kaye et al., 2008; Maji and Sudicky, 2008; Carroll and Brusseau, 2009; Christ et al., 2009, 2010; Tick and Rincon, 2009; DiFilippo et al., 2010; Marble et al., 2010). However, very few measurements of CMDR-MR relationships have been reported to date for field systems (Brusseau et al., 2007; DiFilippo and Brusseau, 2008). Collecting additional field-scale data sets would be very useful for an improved understanding of contaminant mass discharge behavior, and for the testing of mathematical models and estimation functions.

A project was implemented to characterize the temporal nature of contaminant mass discharge for a very heterogeneous, highly contaminated source-zone field site. The study site is located in Tucson, AZ, and is contaminated by trichloroethene, most likely including an organic-liquid (DNAPL) phase. Hydraulic source control was initiated at the site in the fall of 2007 to limit contaminant discharge from the source area. The operation has been monitored since startup to measure the contaminant mass discharge and the mass of contaminant removed via groundwater extraction from the source-control wells. These data constitute in essence the results of an extended source-zone contaminant mass discharge test.

The objective of the study is to characterize the temporal nature of contaminant mass discharge for the field site, and to use this information to determine the relationship between reductions in contaminant mass discharge and reductions in contaminant mass. Analysis of these data provides a means by which to assess the impact of groundwater flow on mass transfer and mass removal within the source area. A major limitation to characterizing the CMDR-MR relationship for field systems is the lack of known values for initial contaminant mass. Two methods were used herein to estimate the mass of contaminant present in the source area at the initiation of source control. One was based on collecting sediment-core data at two times, while the second method was based on fitting the temporal contaminant mass discharge data with a simple exponential source-depletion function.

MATERIALS AND METHODS

Study Site

The site that was the focus of the study is part of the Tucson International Airport Area (TIAA) federal Superfund site in southern Arizona (Leake and Hanson, 1987). The TIAA site was placed on the National Priorities List in 1983 in response to the detection of trichloroethene (TCE) in groundwater from several potable water supply wells. A large, multiple-source plume of TCE exists in the upper portion of the regional aquifer, which is the primary source of potable water for the Tucson metropolitan area. Contaminants are believed to have entered the subsurface by seepage from unlined pits and other features used during the 1940’s to mid-1970’s for disposal of organic solvents. Administratively, the TIAA site is separated into three major zones, the North, Central, and South sections. The site for the current study is located within the Central section.

The study site comprises a local saturated zone, referred to as the shallow groundwater zone, which exists as a persistent feature above the regional aquifer. The site consists of a small source area (approximately 8400 m^2) and a groundwater contaminant plume extending approximately 600 m to the west (Figure 1). Trichloroethene is the primary groundwater contaminant, and aqueous concentrations upwards of 100 mg/L (~10% of solubility) and greater have been reported for samples collected from groundwater monitoring wells within the source area. The source area corresponds to a facility that was used in the past to clean aircraft parts and the external surfaces of military aircraft. TCE vapor degreasers, decarbonizers, and parts-cleaning tanks were located in several small buildings at the site. The activities at the site in conjunction with the high observed aqueous concentrations suggest that liquid TCE is likely present in the subsurface. A technical impracticability waiver was granted by the U.S. EPA for the source area based on the degree of contamination and extensive lower-permeability materials present. Such waivers are granted when it is deemed that attaining remediation to standard regulatory objectives (e.g., maximum contaminant level) is likely to be technically impracticable, and allows the establishment of alternative, protective remedies (EPA, 2012).

The TIAA Superfund site is located in the Tucson Basin, which is underlain by many hundreds of meters of alluvial sediments interbedded locally with volcanic flows, agglomerates, and tuffaceous sediments. A simplified schematic of the stratigraphy for the shallow groundwater zone is presented in Figure 2. The subsurface consists of clay and silty clay units with localized and discontinuous intervals/lenses of silt, sand, and gravel. The clay is typically highly plastic, and is comprised primarily of muscovite, illite, and montmorillonite (Matthieu et al., 2012). A prominent feature is a sand and/or gravel unit, termed the gravel sub-unit, of significant areal extent present between approximately 34 and 38 m below land surface (bls). The clay layer below the gravel sub-unit separates the shallow groundwater zone from the regional aquifer. The potentiometric surface for the shallow groundwater zone is approximately 28-29 m bls in the vicinity of the source area, resulting in a saturated zone spanning the interval between approximately 29-37 m bls. The shallow groundwater zone merges with the regional aquifer at the western edge of the site, and thus the leading edge of the shallow-groundwater-zone contaminant plume is indeterminate as it merges into the regional aquifer at this transition zone (CRA, 2010).

Several aquifer pumping tests have been conducted within the source area (CRA, 2004). Hydraulic conductivities ranging from 4×10^{-5} to 3×10^{-4} m/s were measured for the gravel sub-unit, and values from 1×10^{-6} to 5×10^{-6} m/s were measured for the primary clay unit above the gravel sub-unit. Transmissivities of 2.4×10^{-4} and 3.1×10^{-4} m^2/s were obtained from tests conducted for the source-area extraction wells CRA-5 and DP-1, respectively. Based on the results of the pumping tests, the shallow groundwater zone is considered to act as a leaky confined aquifer system of limited areal extent. Natural hydraulic gradients for the gravel sub-unit have ranged historically between 5×10^{-3} and 1×10^{-2}. The principal source of recharge to the zone is flow from the regional aquifer originating upgradient of the site (CRA, 2010).

Site Remediation and Contaminant Mass Discharge Measurement

A multi-element remediation project was initiated at the shallow groundwater zone site in the fall of 2007. The effort consists of three components: soil vapor extraction for the vadose-zone section of the source area, hydraulic containment for the saturated-zone section of the source area, and pump and treat for the groundwater-contaminant plume. Two extraction wells are used for source control (Figure 2), and currently four extraction wells are operated within the plume. The extraction wells are screened at depth intervals of 35 – 38 m bls, corresponding to the gravel sub-unit. The total extraction rate for the two source-control wells (CRA-5 and DP-1) is currently approximately 75 m^3/d, while the total for the plume wells is approximately 300 m^3/d. Four extraction wells are used for the soil vapor extraction system, which has a total discharge of approximately 20,000 m^3/d. The vapor extraction wells are screened at two depth intervals, approximately 9 - 15 and 18 - 23 m bls. The source-zone groundwater extraction and soil vapor extraction systems have to date removed approximately 690 and >3000 kg of TCE, respectively.

The contaminant mass discharge (CMD) associated with operation of the source-control wells has been monitored since system startup. Samples of extracted groundwater are collected approximately once per month for both wells. The contaminant concentrations for these samples represent composite values for the zone of influence associated with each well. The groundwater samples were analyzed using either GC/MS or GC-ECD, with detection limits of approximately 1 ug/L. Total extraction flow rates were monitored continuously and summed for each month. Contaminant mass discharge was calculated as the product of flow rate and TCE concentration. These data provide a measure of the integrated contaminant mass discharge for the source area from startup in Fall 2007 to the end of the research project in Spring 2012.

Sediment Coring and Analyses

Two sets of six boreholes were drilled within the source area to collect complete sets of sediment cores from each borehole (see Figure 1). One set of cores (set-1) was collected in the fall of 2008, approximately one year after the start of the remediation effort. The second set of cores (set-2) was collected in the spring of 2012. The cores were obtained using roto-sonic drilling, which is a useful method for collecting continuous cores. The drilling was terminated in each borehole at the base of the gravel sub-unit (37-38 m bls) to avoid penetrating the clay aquitard that overlies the regional aquifer. The cores were analyzed with high spatial resolution (~6-cm intervals in saturated and confining units; lesser resolution for the vadose zone) wherein 10-mL subsamples were collected from the internal central axis of the core with disposable open-tip plastic syringes. The subsamples were placed in 40-mL glass vials containing 20 mL of methanol (>99.9% pure), placed in a chilled container, and transported to the laboratory. The subsamples were placed on a shaker for 24 h, after which they were centrifuged for 10 minutes. A 2-mL subsample of the eluent was removed from the vial with a glass syringe and injected into a 2-mL autosampler vial with no headspace. The samples were analyzed by GC/MS/MS (gas chromatography tandem mass spectrometry). After extraction, the sediment samples were dried and weighed. The detection limit for sediment-phase concentrations of TCE was approximately 0.03 mg/kg-dry sediment.

A detailed lithologic description of the borehole core materials was completed using standard sediment identification procedures (ASTM, 2009). Approximately 250-mL samples of sediment were collected periodically and placed in mason jars. These samples were used for characterization of physical and chemical properties. Particle size distribution was determined using standard sieve analysis combined with a hydrometer. Hydraulic conductivities were measured using a laboratory falling-head permeameter apparatus. Sediment organic carbon was measured as follows. A small subsample of sediment was ball milled and then mixed with a 10% phosphoric acid solution to remove inorganic carbon (carbonates). The samples were then dried at 60 °C, and analyzed with a carbon analyzer at 1000 °C.

Estimation of Initial Contaminant Mass in Source Area

As noted above, the total contaminant mass initially present in the source area is a critical variable that is often unknown for most field sites. Furthermore, this value is very difficult to measure, especially for sites with DNAPL present. Two methods were used herein to estimate this quantity for the saturated zone of the source area. The first method is a slight variation of the standard approach employing sediment-core data. With the standard approach, sediment-phase concentrations of the contaminant obtained for example by solvent extraction of core data are used in conjunction with values for the bulk density and volume of contaminated media to calculate absolute values of contaminant mass. However, uncertainty in bulk densities and especially domain volumes can add to overall method uncertainty. This source of uncertainty can be minimized by using core data collected at two times to determine the relative change in concentrations and mass. This information, combined with the mass-removed quantity determined from integration of the extraction-well CMD data, can be used to estimate an initial mass (M_0) using the relation:

$$\mathrm{M_0 = M_{\Delta t} / \Delta M_f + M_{t-1}} \quad (1)$$

where $M_{\Delta t}$ is the quantity of contaminant mass removed in the period between collection of the two sets of cores determined from integration of the CMD data (442 kg), ΔM_f is the fractional mass reduction for the period between collection of the two sets of cores, which was obtained from the core data (0.82), and M_{t-1} is the mass removed prior to collection of the first core set (245 kg), also determined from integration of the CMD data. This latter term accounts for the fact that the first set of cores was obtained a year after the start of the source-control operation. The ΔM_f term was calculated as $1-\overline{C}_2/\overline{C}_1$, where $\bar{C}_1$ and $\bar{C}_2$ are the mean, aggregate sediment-phase contaminant concentrations obtained from the core data for sets 1 and 2, respectively.

The second method used to estimate the initial contaminant mass present in the saturated zone of the source area is based on fitting a mass-depletion function to the temporal CMD data. In general, a mechanistic-based reactive transport model can be cablibrated to historical concentration data to solve the inverse problem for M_0. However, the use of advanced transport models for field sites is typically constrained by a lack of information needed to parameterize the model. In lieu of this approach, simplified mass-depletion functions can be fit to measured data to estimate M_0. For example, simplified functions have been fit to temporal concentration data collected from monitoring wells located within contaminant plumes to provide estimates of source mass (Butcher and Gauthier, 1994; Basu et al., 2009). It is anticipated that CMD data measured directly for the source area via a contaminant mass discharge test will provide a more robust data set for estimation of source mass.

The method is based on a conservation of mass argument for a system undergoing fluid extraction:

$$\mathrm{dM/dt}=\mathrm{Q_t C_t} \quad (2)$$

where M is contaminant mass (M), Q is fluid discharge (L^3/T), C (M/L^3) is the concentration of the contaminant in the extracted fluid, and it is assumed that there are no other sources of mass reduction, and that mass discharge into the system is 0. A selected source-depletion function can now be specified to relate changes in concentrations and mass discharge to changes in mass. The power function is one such, widely used, function (e.g., Zhu and Sykes, 2004; Falta et al., 2005):

$$\mathrm{C_t/C_0}=(\mathrm{M_t/M_0})^{\Gamma} \quad (3)$$

where C_0 is initial contaminant concentration and Γ is the power index term, representing the impact of a host of conditions and processes on mass-removal behavior. Substituting equation 3 into 2 yields:

$$\mathrm{dM/dt}=(\mathrm{Q_0C_0/M_0^{\Gamma}})\mathrm{M}^{\Gamma} \quad (4)$$

Given that the terms in parentheses are constants, one can define $k = Q_0C_0/M_0^{\Gamma}$ as a source depletion rate coefficient, as noted in prior applications (e.g., Zhu and Sykes, 2004; Falta et al., 2005). For the special case wherein $\Gamma = 1$, the equation reduces to a first-order, exponential function, with a solution for CMD given as $QC_t = QC_0\exp(-kt)$. The function was fit to the measured CMD data, optimizing for k. M_o was then calculated with the optimized k and the known value for initial CMD (Q_0C_0).

RESULTS AND DISCUSSION

Sediment Data

Textural evaluation of the core material collected from the source area confirmed the stratigraphic model presented in Figure 2. The results of the laboratory hydraulic-conductivity measurements were consistent with the results of the field tests, wherein values for subsamples of the gravel-sub-unit were 2-3 orders-of-magnitude greater than those measured for the clay subsamples. The organic-carbon contents for the subsamples ranged from 0.02 to 0.08%.

The concentrations of TCE were measured for sediment samples collected from the boreholes drilled in 2008 (set 1) and 2012 (set 2). Approximately 1400 total samples were collected for each set. Illustrative results are presented in Figure 3 for the two most contaminated and two least contaminated cores for each set.

The highest concentrations for the set-1 cores were obtained for core CRA-26 (Figure 3a), ranging up to almost 20 mg/kg and with a mean of 2 mg/kg for the interval 28-38 m bls. These concentrations may be somewhat low for samples associated with suspected DNAPL presence (e.g., Feenstra et al., 1991). However, it must be noted that this first set of samples was collected more than a year after startup of groundwater extraction, and that 245 kg of TCE was extracted from the source area prior to core collection. For all 6 set-1 cores, the highest concentrations were associated with the interval between 25 to 30 m bls. This interval corresponds to the lower-permeability silty clay layer in which the interface between the vadose zone and saturated zone resides (Figure 1). Some of the cores had another smaller peak at the interval 33-35 bls, which corresponds to the bottom of the clay layer above the gravel sub-unit.

The mean concentration for all 6 set-1 cores was approximately 0.9 mg/kg for the interval 28-38 m bls. The TCE concentrations for the set-2 cores were significantly lower, with a mean of 0.14 mg/kg for the interval 28-38 m bls. The set-2 cores had approximately 4 times as many non-detects as did set 1 (45% vs. 12%). Comparison of the two sets of data suggests that a significant, ~80%, reduction in aggregate TCE concentrations occurred between sediment-sampling events for the 28-38 m interval. This value was calculated using the 0.03 mg/kg detection limit as a conservative estimate to quantify values for samples for which non-detects were reported. This apparent reduction would be the result of mass removal via water flushing, with a possible contribution from soil vapor extraction for the uppermost section of the interval.

Contaminant Concentrations and Mass Discharge

The concentrations of TCE in the groundwater pumped from the two source-area extraction wells are presented in Figure 4. After an initial peak, the concentrations declined relatively rapidly for some time, and currently exhibit asymptotic tailing. The peak and asymptotic concentrations are 30 and 2 mg/L, respectively, for well CRA-5 and 8 and 1 mg/L, respectively, for well DP-1. These concentrations are quite high considering that they are associated with extraction wells as opposed to monitoring wells. As noted above, concentrations of 100 mg/L and higher have been observed for samples collected from monitoring wells in the source area. These high concentrations, and the quantity of TCE removed with soil vapor extraction, are consistent with the presence of liquid TCE (DNAPL) in the subsurface.

The flow rates for the source extraction wells are also presented in Figure 4. The extraction rate has remained relatively constant for DP-1, with a factor-of-two decrease in later years, and has increased over time for CRA-5. Operation of the source-control wells has established containment of the source area, which has resulted in its isolation from the contaminant plume. This, in combination with the operation of the plume extraction wells, is expected to minimize the impact of the plume on mass discharge measured with the source-control wells. A hydraulic residence time of approximately 1 year is estimated for the source area based on the extraction rates and the estimated domain volume and porosity. Thus, it is estimated that the total groundwater extraction to date equates to approximately 4 pore volumes of flushing.

The contaminant mass discharge associated with operation of the source-control wells is presented in Figure 5. The initial peak values averaged approximately 1 kg/d. These are at the very high end of the range of values reported in a recent survey of mass-discharge field data (ITRC, 2010). More than 90% of the total mass discharge is associated with well CRA-5, which is expected given that it is located near the center of the source, whereas well DP-1 is located near the downgradient edge. The total contaminant mass discharge has declined asymptotically to a current value of approximately 0.15 kg/d. The total mass of TCE removed from the source area via groundwater extraction as of spring 2012 is 687 kg based on integration of the data presented in Figure 4.

The total contaminant mass discharge has decreased significantly, approximately 85%, since the initiation of groundwater extraction. This decrease is a direct function of the reduction in TCE concentrations observed for the extraction wells (Figure 4), given that the total extraction flow rate has actually increased over the course of operations (Figure 4). The decrease in TCE concentrations may be a result of reductions in contaminant mass, changes in hydraulic conditions, or some combination thereof. As noted above, a significant reduction in aggregate sediment-phase concentration of TCE was observed for the core data. This observation, in conjunction with the large quantity of TCE removed via groundwater extraction indicates that there was a significant reduction in contaminant mass for the system. Regarding potential hydraulic effects, the extraction wells have been operated consistently since startup, with no individual well cycling, etc. However, the extraction rate for CRA-5 has increased with time, and it is possible that effects associated with the increased flow rate (dilution due to expanded zone of influence, increased mass-transfer constraints) may have contributed to the decrease in TCE concentration.

Inspection of Figure 4 shows that after initial startup there were three periods wherein extraction rates for CRA-5 were essentially uniform, the first from months 8-23, the second from months 24-40, and the third from month 40 to current. Inspection of Figures 4 and 5 shows that TCE concentration and contaminant mass discharge decreased during each of these many-month-long periods of steady state extraction. The decreases in TCE concentrations observed during these periods would be primarily induced by reductions in contaminant mass. In addition, the contaminant mass discharge has decreased by approximately 90% for DP-1, whereas the extraction rate for DP-1 has decreased by a factor of two (as opposed to the increase registered for CRA-5). In summary, the results indicate that the observed reduction in contaminant mass discharge is associated primarily with a reduction in contaminant mass.

Estimation of Initial Contaminant Mass

The contaminant mass discharge for the source-area hydraulic-control system is known with a relatively high degree of certainty, based on the resolution of data collection. The total quantity of contaminant mass removed via groundwater extraction for the two source-area control wells is also known with relatively high certainty as it reflects the same data set. What is not known is the mass of contaminant present in the saturated zone of the source area at the start of remediation operations, which is typical for most sites. Two methods were used to estimate this initial source mass.

Based on the core data and the mass-removed quantity determined from the extraction-well CMD data, the initial TCE mass was estimated to be 784 kg using method 1. The total fraction of mass reduction to date based on this estimated initial mass is ~86%. The estimated initial mass is recognized to have potential significant uncertainty, the degree of which depends on the representativeness of the core data for the entire source area. For example, it is possible that the coring missed zones of higher contaminant concentrations; the impact of this is likely to be more significant for the initial coring given the higher aggregate concentrations present. Another potential source of uncertainty is the possibility that the soil vapor extraction system may have contributed to removal of mass for the interval of interest. Thus, it is anticipated that the estimation method is more likely to produce an under-estimate rather than over-estimate of initial mass. Assuming an arbitrary 25% error for illustrative purposes produces an estimate of approximately 1000 kg for the initial mass, which translates to a total to-date fractional mass reduction of ~70%.

Inspection of Figure 5 shows that the exponential depletion function provides a good fit to the CMD data. An optimized value of 0.47 yr^{-1} was obtained for k. Using this value, and an initial CMD of 1.28 kg/d, produces an estimate of 993 kg for M_0. The total fraction of mass reduction to date based on this estimated initial mass is 69%. Uncertainty in the estimated value would depend upon the representativeness of the CMD data for the entire target zone, and the robustness with which the fitted function describes the measured data throughout the mass-depletion history. The zones of influence of the extraction wells span the entire source area, and thus the measured CMD data is considered to be representative. Considering this and the fact that the function provides a good fit to approximately 4 years of CMD data, it is likely that the estimated M_0 is relatively robust. Interestingly, the value obtained based upon the core data is approximately 20% lower than the value obtained by fitting the CMD data. This is consistent with the discussion above regarding potential underestimation using the core data.

The methods discussed above were used to estimate the mass of TCE present in the saturated zone of the source area at the start of remediation. Also of interest is the mass of TCE initially present in the saturated zone of the source prior to development of the groundwater contaminant plume, i.e., the mass of TCE that initially entered the saturated zone. Determining this quantity requires estimates of the mass associated with the plume in addition to the source. The plume-associated mass was estimated in part as the sum of the mass of TCE present in the plume at the end of the project and the mass of TCE that has been removed from the plume via groundwater extraction during the project, which totals approximately 170 kg. In addition, the mass of TCE lost to the regional aquifer at the western, leading edge of the plume was estimated using an average hydraulic gradient of 0.0075, a mean hydraulic conductivity (K) of ~8.6 m/d, a mean C of 0.1 mg/L, and the estimated cross-sectional area, producing a CMD of ~0.02 kg/d. Applying this natural-gradient CMD for an elapsed time of 60 years results in a mass of ~390 kg.

Adding the two plume-associated masses to the initial source mass (M_0) estimated above produces 1342 and 1539 kg for methods 1 and 2, respectively. Based on these values, it is estimated that approximately one-third of the TCE mass that initially entered the saturated zone of the source area had been removed (generating the observed contaminant plume) prior to the start of the source-control effort. Using the K and gradient values noted above, and the dimensions of the source area, it is estimated that the equivalent of approximately 40 pore volumes of water had been flushed through the source area prior to the start of remediation. A removal of one-third of the initial mass is reasonable given this estimated magnitude of flushing. The total initial spill masses estimated for the saturated-zone source area are less than one-half of the contaminant mass (>3000 kg) that has been removed to date from the vadose zone via soil vapor extraction. This is reasonable given the surface-application mode of disposal of the waste materials.

Relationship Between Reductions in Contaminant Mass Discharge and Contaminant Mass

The relationship between the measured reduction in contaminant mass discharge and the estimated reduction in contaminant mass for the source area was determined using the CMD data and M_0 values discussed above, where CMDR = $1\text{-}CMD_t/CMD_0$ and MR = $1\text{-}M_t/M_0$. The data associated with the initial few months of operation were not used in the calculations given that the system had not attained quasi-steady-state, as reflected in the initial rise in CMD (Figure 5). The contaminant mass removed during this initial stage (~95 kg) was subtracted from the tabulation of initial mass and mass reduction. Two curves are presented in Figure 6, one for each of the two M_0 estimates reported above. A line representing one-to-one correspondence is included for reference.

The mass discharge is observed to decrease essentially immediately upon initiation of mass reduction. The data exhibit a curvilinear convex-upward profile that resides above the one-to-one reference line. A few prior CMDR-MR profiles have been reported based on laboratory experiments and mathematical modeling (e.g., Rao et al., 2002; Jayanti and Pope, 2004; Phelan et al., 2004; Jawitz et al., 2005; Fure et al., 2006; Brusseau et al., 2008; Kaye et al., 2008; Maji and Sudicky, 2008; Carroll and Brusseau, 2009; Christ et al., 2009, 2010; Tick and Rincon, 2009; DiFilippo et al., 2010; Marble et al., 2010). The results span a wide range of behavior, from convex-downward curves residing below the reference line (for which there is relatively small reduction in CMD during the early stages of mass reduction), to approximately one-to-one profiles, to convex-upward profiles similar to those observed herein.

The convex-upward profile is generally associated with systems wherein significant quantities of mass are present in hydraulically poorly accessible domains, for which mass removal is influenced by mass-transfer constraints. It is reasonable to expect that a large fraction of the contaminant mass present at the study site at the start of the project would be poorly accessible, given the presence of extensive silt and clay layers and the fact that ~60 years of natural-gradient groundwater flushing most likely removed a major portion of the more accessible mass. The data obtained from the sediment cores, which showed that the highest TCE concentrations were associated with lower-permeability units, supports this contention.

The CMDR-MR relationship is often simulated using a simple power function, wherein CMDR = MR^n (e.g., Rao et al., 2002). The parameter n defines the specific CMDR-MR relationship, and is a lumped-process term that incorporates the impact of contaminant distribution, flow-field dynamics, and mass-transfer processes. Note that this relationship is related, but not identical, to the relationship presented in equation 3. The curves obtained with this function, with $n = 0.55$ and 0.4, match the measured data relatively well (Figure 6).

Comparison to Other Field Data

Very few measurements of time-continuous profiles of contaminant mass discharge have been reported to date for field systems. The lack of such measurements, in combination with the typical uncertainty regarding initial contaminant mass for most sites, limits the opportunities for time-continuous-based characterization of the CMDR-MR relationship for field systems. Initial time-continuous-based characterizations of CMDR-MR relationships for field sites were reported by Brusseau et al. (2007) and DiFilippo and Brusseau (2008). Brusseau et al. (2007) determined the integrated CMDR-MR relationship associated with combined pump and treat of the sources and groundwater contaminant plume for the south section of the TIAA complex. DiFilippo and Brusseau (2008) determined the CMDR-MR relationships for emplaced-source experiments conducted at the Borden site in Canada, using raw concentration and flow-rate data reported by Broholm et al. (1999) and Rivett and

Feenstra (2005). For these experiments, known quantities of three-component chlorinated-solvent liquids were introduced into the subsurface, after which mass removal under natural-gradient groundwater (Rivett and Feenstra (2005) or sequential groundwater and cosolvent (Broholm et al., 1999) floods was monitored in detail. In addition, DiFilippo and Brusseau (2008) compared the behavior observed for the Borden data to that of the south-TIAA site, including the integrated source and plume data as well as data for a single source area.

The data obtained for the current study are compared to the data reported for the single source area of the south-TIAA site (Site 3) and the Borden experiments in Figure 7. Distinctly different CMDR-MR relationships are observed for the various sites. For example, relatively small reductions in contaminant mass discharge are observed up to approximately 40% mass reduction for the Borden data, in contrast to the essentially immediate reduction observed for the present study. The profile for the south-TIAA site is intermediate to the other two. Differences in the nature of the MDR-MR relationships observed for the different sites are most likely manifestations of differences in system properties and conditions, such as permeability distribution, contaminant distribution, and mass-transfer processes. It is possible that differences in experiment conditions, such as spatial scale, hydraulic gradient, and the use of three-component DNAPL for the Borden experiments, may also have had some influence. The issue of the three-component DNAPL was addressed in part by determining the aggregate CMD and mass removal based on mole fractions (DiFilippo and Brusseau, 2008). The issues of scale and hydraulic-gradient conditions are addressed in a following paragraph.

Regarding differences in system properties and conditions, the Borden site has a comparatively small degree of permeability variability, with the target subsurface zone comprised of medium- to fine-grained lacustrine sand with occasional beds of coarse sand/gravel and silt (Broholm et al., 1999). Conversely, the TIAA sites are very heterogeneous, with extensive sequences of clay alternating with laterally discontinuous lenses of silts, sands, and gravels. Furthermore, the Borden sites were freshly-contaminated systems, with monitoring of mass discharge commencing soon after emplacement of the contamination. In contrast, the TIAA sites are mature sites, with characterization commencing many years after contamination emplacement (approximately 60 and 35 years for the central-TIAA and south-TIAA sites, respectively). Mass transfer and mass removal processes occurring during the intervening decades, as documented by the extensive groundwater contaminant plumes present at the TIAA sites, would be expected to have significantly altered the contaminant distribution within the source areas, with much of the mass preferentially removed from the more accessible domains. For example, for the current study site, it was estimated above that approximately one-third of the initial contaminant mass in the saturated-zone source area was removed via natural-gradient flushing prior to the start of characterization and remediation activities. In total, it is likely that a larger fraction of contaminant mass was accessible for mass removal via advective and diffusive transport for the Borden experiments compared to the TIAA sites. The CMDR-MR relationships observed for the Borden versus the TIAA sites are consistent with this supposition that site age through its impact on contaminant distribution and accessibility is a significant discriminatory factor. In addition, it is possible that the difference observed between the two TIAA sites may be related in part to the significant difference in source-zone age associated with the two sites.

Additional illustration of the impact of contaminant accessibility is presented by the Borden-1 data. Interestingly, a significant reduction in CMD is observed to begin at ~40% mass reduction for this data set. The marked change in the profile indicates a significant change in mass-removal conditions, transitioning from a system controlled by more-accessible mass to one controlled by less-accessible mass (Brusseau et al., 2008; DiFilippo et al., 2010; Christ et al., 2010). Excavation and characterization of the source after experiment completion indicated that the majority (~85%) of the remaining contaminant mass was associated with a single 0.5-cm thick, areally extensive pool of DNAPL (Broholm et al., 1999). This mass would be expected to be poorly accessible to water flushing. These results support the conclusion that mass removal at the latter stage of the experiment was controlled by poorly accessible mass. Furthermore, based on the characterization results, 50% or more of the initial contaminant mass was present as pools (i.e., was relatively poorly accessible). This is consistent with the observed CMDR transition point, which occurred at approximately 40% mass reduction (with that fraction likely representing the more accessible mass). Characterization of CMD and mass removal for the Borden-1 source area after the more accessible mass has been removed (i.e., an aged source) produces a CMDR-MR profile that is shifted leftward and is more similar to that observed for the TIAA-site 3 site (data not shown).

As noted, another major difference between the Borden and TIAA sites is spatial scale, wherein the Borden experiment systems are small (~4 × 5 m) and the TIAA source areas are much larger (~100 × 100 m). The potential impact of scale was investigated by examining two additional characterizations of field-scale CMDR-MR relationships that were determined herein using raw concentration and flow-rate data reported in the literature. These experiments were conducted at the Dover AFB test site, using a sheet-pile enclosed cell (3 × 4.6 m) emplaced in the subsurface, into which tetrachloroethene was injected under controlled conditions. The experiment zone is a shallow, unconfined aquifer that consists of medium to fine sands with interbedded gravels, silts, and clay lenses (Tick et al., 2003). After initial contamination, an alcohol flood was conducted (Brooks et al., 2004), followed by a surfactant flood (Childs et al., 2006) and a complexing-sugar flush (Tick et al., 2003). The three experiments were conducted sequentially in the same cell, with the primary difference being that the surfactant flood employed vertical-circulation extraction wells for a majority of the flood whereas the complexing-sugar flush (CSF) employed a standard horizontal line-drive system. Additional tetrachloroethene was injected into the cell prior to both the surfactant and CSF experiments.

The CMDR-MR relationships determined for the surfactant and CSF experiments are presented in Figure 8. The curves are similar wherein there is minimal reduction in CMD for the initial stage of mass reduction, followed by a sharp, significant reduction in CMD that starts at approximately 15-25% mass reduction. The similarity of the two profiles suggests that the fluid-control configuration (vertical versus horizontal floods) did not have a significant impact on observed behavior. Each of the three treatments removed only a portion of the total tetrachloroethene mass present, and this mass was therefore present for the subsequent experiments. Thus, the system can be considered to have been under partially aged conditions for the surfactant and CSF experiments, with a combination of more-accessible mass (a portion of the newly added mass) and poorly accessible mass (a portion of the newly added mass and the mass remaining from the prior test). The observed CMDR-MR profiles are consistent with these conditions.

The CMDR-MR profiles observed for the two Dover experiments are generally similar to those observed for the TIAA-Site 3 and Borden-1 data sets (Figure 7). The scale of the Dover experiment site is very similar to that of the Borden experiment sites, and much smaller than that of the TIAA sites. Given this, it appears that the difference in scale did not contribute significantly to the differences in behavior observed between the Borden and TIAA sites. In addition, the Dover experiments, as well as the TIAA studies, were conducted under induced-gradient conditions. Conversely, the Borden experiments were conducted under natural-gradient conditions. For example, the mean pore-water velocity for the Dover CSF experiment was 1 m/d (Tick et al., 2003) compared to 0.1 m/d for the Borden-1 experiment (Broholm et al., 1999). The fact that similar CMDR-MR profiles were obtained for the Borden-1, Dover, and TIAA-site 3 systems indicates that hydraulic-gradient status did not have a significant impact on the underlying mass-removal behavior. It should be noted that the two Dover experiments involved enhanced-solubility floods, while the Borden-1 experiment comprised a sequential water and cosolvent flood and the TIAA studies involved strictly water flushing. The similarity of the CMDR-MR profiles among the different systems indicates that the composition of the flooding solution also did not have a significant impact on the underlying mass-removal behavior. This is consistent with results obtained from laboratory experiments (Carroll and Brusseau, 2009; Tick and Rincon, 2009; DiFilippo et al., 2010). It should also be noted that the Dover data sets as well as the Site 3 and Borden-1 data exhibit non-singular (“S-shaped”) profiles that cannot be simulated with the simple CMDR-MR function, which has also been observed in prior studies (Brusseau et al., 2008; DiFilippo and Brusseau, 2008; Christ et al., 2010; DiFilippo et al., 2010).

SUMMARY

The use of contaminant-mass-discharge measurements to characterize site conditions and evaluate remediation performance is becoming a critical component of site assessment. Time-continuous measurements of contaminant mass discharge, obtained by conducting extended contaminant mass discharge tests or by capturing operational fluid-extraction data, can provide useful information to characterize mass-transfer processes, assess mass-removal magnitudes and conditions, and estimate contaminant distributions and quantities. In the present study, the temporal behavior of contaminant mass discharge was characterized for a very heterogeneous source-zone field site contaminated by TCE DNAPL. The results showed that contaminant mass discharge decreased asymptotically with time, from approximately 1 to 0.15 kg/d. Comparison of two sets of core data, collected 3.5 years apart, suggests that aggregate sediment-phase TCE concentrations decreased by ~80% between sampling events. The results reported herein provide insight to the impact of hydraulic-based remedial efforts on contaminant mass discharge for heterogeneous, DNAPL-contaminated source zones.

Two methods were used to estimate the mass of contaminant initially present in the source area, and they produced reasonably similar results. Each method has associated sources of uncertainty, as well as requirements that can limit their use. Limitations associated with method 1, sediment coring, are well known. Regarding the second method, it is based on fitting a mass-depletion function to temporal CMD data, and obviously requires availability of such data. Prior similar efforts of estimating source mass have been implemented by fitting simplified functions to temporal concentration data collected from monitoring wells located within contaminant plumes (Butcher and Gauthier, 1994; Basu et al., 2009). This approach has broad potential applicability given the general widespread availability of monitoring-well data for many sites. However, it is anticipated that CMD data (rather than solely concentration data) measured directly for the source area via an extended contaminant mass discharge test as done herein will provide a more robust data set for estimation of source mass. The second method is a useful alternative to standard coring, particularly for cases wherein coring is technically or economically impractical. The method is also useful for cases wherein temporal CMD data can be captured from analysis of operational data for fluid-extraction systems such as pump and treat or soil vapor extraction. Such analysis of historic-operations data provides a simple means by which to estimate initial contaminant mass for the treatment domain.

Contaminant mass discharge data can be integrated with measurements of initial mass to characterize the relationship between reductions in contaminant mass discharge and reductions in contaminant mass. The CMDR-MR relationship is a defining characteristic of system behavior, reflecting system properties and conditions. These relationships are typically characterized using time-continuous CMD data, which provides the means to assess the temporal dynamics of mass removal as influenced by changes in contaminant distribution and configuration, and resultant impacts on flow and mass-transfer processes. However, CMDR-MR relationships can also be obtained for specific snapshots of time by collecting spatially discrete data. For example, Brooks et al. (2004) reported CMDR-MR data obtained from two sets of measurements (before and after a remedial action) collected at six monitoring locations, and used these spatial data to represent a CMDR-MR profile for the alcohol-flood pilot test conducted at Dover AFB that was discussed above.

As noted, very few time-continuous measurements of CMDR-MR relationships have been reported to date for field systems (Brusseau et al., 2007; DiFilippo and Brusseau, 2008). The data collected during the study were used develop such a relationship for the source area of the site. The profile exhibited by the data is consistent with a system wherein significant quantities of mass were present in hydraulically poorly accessible domains, for which mass removal is influenced by mass-transfer constraints. This contention is supported by the sediment-core data, which showed that the highest concentrations of TCE are associated with lower-permeability units, and by the estimates of the amount of groundwater flushing and associated contaminant mass removal experienced by the source area in the ~60 years prior to project startup. The results obtained from the present study were compared to those obtained from other field studies to evaluate the impact of system properties and conditions on behavior. The results indicated that factors such as domain scale, hydraulic-gradient status (induced or natural), and flushing-solution composition had insignificant impact on the CMDR-MR profiles and thus on underlying mass-removal behavior. Conversely, source-zone age, through its impact on contaminant distribution and accessibility, was implicated as a critical factor influencing the nature of the CMDR-MR relationship. This is consistent with the results of mathematical modeling studies and laboratory experiments (Jawitz et al., 2005; Brusseau et al., 2008; DiFilippo et al., 2010).

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References

ASTM. Standard Practice for Description and Identification of Soils. ASTM D2488 - 09a. 2009

Basu NB, Rao PSC, Poyer IC, Nandy S, Mallavarapu M, Naidu R, Davis GB, Patterson BM, Annable MD, Hatfield K. Integration of traditional and innovative characterization techniques for flux-based assessment of Dense Non-aqueous Phase Liquid (DNAPL) sites. J Contam Hydrol. 2009; 105:161–172. [PubMed: 19211169]

Bockelmann A, Zamfirescu D, Ptak T, Grathwohl P, Teutsch G. Quantification of mass fluxes and natural attenuation rates at an industrial site with a limited monitoring network: a case study. J Contam Hydrol. 2003; 60:97–121. [PubMed: 12498576]

Broholm K, Feenstra S, Cherry JA. Solvent release into a sandy aquifer. 1. Overview of source distribution and dissolution behavior. Environ Sci Technol. 1999; 33:681–690.

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; 69:281–297. [PubMed: 15028395]

Brusseau, ML.; Rohrer, JW.; Decker, TM.; Nelson, NT.; Linderfelt, WR. Contaminant transport and fate in a source zone of a chlorinated-solvent contaminated superfund site: Overview and initial results of an advanced site characterization project. Chapter 19. In: Brusseau, ML.; Sabatini, DA.; Gierke, JS.; Annable, MD., editors. Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies. American Chemical Society; Washington DC: 1999.

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; 90:21–40. [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 organic liquid. Chemosphere. 2008; 71:1511–1521. [PubMed: 18279910]

Brusseau ML, Rohay V, Truex MJ. Analysis of Soil Vapor Extraction Data to Evaluate Mass-Transfer Constraints and Estimate Source-Zone Mass Flux. Ground Water Monitor Remed. 2010; 30:57–64.

Brusseau ML, Carroll KC, Allen T, Baker J, DiGuiseppi W, Hatton J, Morrison C, Russo A, Berkompas J. The Impact of in-situ chemical oxidation on contaminant mass discharge: Linking source-zone and plume-scale characterizations of remediation performance. Environ Sci Technol. 2011a; 45:5352–5358. [PubMed: 21615133]

Brusseau ML, Hatton J, DiGuiseppi W. Assessing the impact of source-zone remediation efforts at the contaminant-plume scale: application to a chlorinated-solvent site. J Contam Hydrol. 2011b; 126:130–139. [PubMed: 22115080]

Butcher JB, Gauthier TD. Estimation of residual dense NAPL mass by inverse modeling. Ground Water. 1994; 32:71–78.

Carroll KC, Brusseau ML. Dissolution, cyclodextrin-enhanced solubilization, and mass removal of an ideal multicomponent organic liquid. J Contam Hydrol. 2009; 106:62–72. [PubMed: 19233508]

Childs J, Acosta E, Annable MD, Brooks MC, Enfield CG, Harwell JH, Hasegawa M, Knox RC, Rao PSC, Sabatini DA, Shiau B, Szekers E, Wood AL. Field demonstration of surfactant-enhanced solubilization of DNAPL at Dover Air Force Base, Delaware. J Contam Hydrol. 2006; 82:1–22. [PubMed: 16233935]

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 Res. 2009; 32:401–412.

Christ JA, Ramsburg CA, Pennell KD, Abriola LM. Predicting DNAPL mass discharge from pool-dominated source zones. J Contam Hydrol. 2010; 114:18–34. [PubMed: 20227132]

CRA (CONESTOGA-ROVERS & ASSOCIATES). Shallow Groundwater Zone (SGZ) Subsurface Investigation, Extraction Well Installation and Aquifer Testing. 2004 Jul.13711(19) Ref. No.

CRA (CONESTOGA-ROVERS & ASSOCIATES). Performance Evaluation Report, Airport Property. Tucson International Airport Area Superfund Site. 2010 May.13711(54) Ref. No.

DiFilippo EL, Brusseau ML. Relationship between mass flux reduction and source-zone mass removal: Analysis of field data. J Contam Hydrol. 2008; 98:22–35. [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; 115:14–25. [PubMed: 20434229]

DiGiulio DC, Ravi V, Brusseau ML. Evaluation of mass flux to and from ground water using a vertical flux model (VFLUX): Application to the soil vacuum extraction closure problem. Ground Water Monitoring and Remediation. 1999; 19:96–104.

Einarson MD, Mackay DM. Predicting impacts of groundwater contamination. Environ Sci Technol. 2001; 35:66A–73A.

Environmental Protection Agency. Guidance for Evaluating Technical Impracticability of Ground-Water Restoration. 2012. http://www.epa.gov/superfund/health/conmedia/gwdocs/techimp.htm

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]

Feenstra S, MacKay DM, Cherry JA. A Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples. Groundwater Monitoring Review. 1991; 11(No. 2)

Freeze RA, McWhorter DB. A framework for assessing risk reduction due to DNAPL mass removal from low-permeability soils. Ground Water. 1997; 35:111–123.

Fure AD, Jawitz JW, Annable MD. DNAPL source zone depletion: Linking architecture and response. J Contam Hydrol. 2006; 85:118–140. [PubMed: 16527371]

Interstate Technology and Regulatory Council (ITRC). Use and Measurement of Mass Flux and Mass Discharge. 2010. www.itrcweb.org

Jawitz JW, Fure AD, Demy GG, Berglund S, Rao PSC. Groundwater contaminant flux reduction resulting from nonaqueous phase liquid mass reduction. Water Resour Res. 2005; 41:10408–10423.

Jayanti, S.; Pope, GA. Remediation of Chlorinated and Recalcitrant Compounds. Battelle Press; Columbus, OH: 2004. Modeling the benefits of partial mass reduction in DNAPL source zones. Paper 2C-04

Kaye AJ, Cho J, Basu NB, Chen X, 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; 102:17–28. [PubMed: 18420303]

Leake, SA.; Hanson, RT. U S Geol Survey, Water-Resources Investigation Report. 1987 Jan. Distribution and movement of trichloroethylene in ground water in the Tucson area, Arizona; p. 86-4313.

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; 102:105–119. [PubMed: 18929427]

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; 117:82–93. [PubMed: 20685008]

Matthieu DE, Brusseau ML, Johnson GR, Artiola JL, Bowden ML, Curry JE. Intercalation of trichloroethene by sediment-associated clay minerals. Chemo. 2012 in press.

Newell, CJ.; Conner, JA.; Rowen, DL. Groundwater Remediation Strategies Tool. American Petroleum Institute; 2003. Publ. No. 4730

NRC (National Research Council). Contaminants in the Subsurface: Source Zone Assessment and Remediation. National Academy Press; Washington, D.C: 2005.

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; 27:411–427.

Rao, PSC.; Jawitz, JW.; Enfield, CG.; Falta, RW.; Annable, MD.; Wood, AL. Groundwater Quality-Natural and Enhanced Restoration of Groundwater Pollution. Vol. 275. IAHS Publ; 2002. Technology integration for contaminated site remediation: clean-up goals and performance criteria; p. 571-578.

Rivett MO, Feenstra S. Dissolution of an emplaced source of DNAPL in a natural aquifer setting. Environ Sci Technol. 2005; 39:447–455. [PubMed: 15707043]

Rosenbloom J, Mock P, Lawson P, Brown J, Turin HJ. Application of VLEACH to an Arizona superfund site. Ground Water Monitor, Remed. 1993 Summer;:159–169.

Soga K, Page JWE, Illangasekare TH. A review of NAPL source zone remediation efficiency and the mass flux approach. J Hazard Mater. 2004; 110:13–27. [PubMed: 15177723]

Strategic Environmental Research and Development Program (SERDP). Final report: SERDP/ESTCP expert panel on reducing the uncertainty of DNAPL source-zone remediation. 2006. http://docs.serdp-estcp.org/viewfile.cfm?Doc=DNAPLWorkshopReport.pdf

Stroo HF, Unger M, Ward CH, Kavanaugh MC, Vogel C, Leeson A, Marqusee JA, Smith BP. Remediating chlorinated solvent source zones. Environ Sci Technol. 2003:224A–230A.

Tick GR, Lourenso F, Wood AL, Brusseau ML. Pilot-Scale Demonstration of Cyclodextrin as a Solubility-Enhancement Agent for Remediation of a Tetrachloroethene-Contaminated Aquifer. Environ Sci Technol. 2003; 37:5829–5834. [PubMed: 14717202]

Tick GR, Rincon EA. Effect of enhanced-solubilization agents on dissolution and mass flux from uniformly distributed immiscible liquid trichloroethene (TCE) in homogeneous porous media. Water Air Soil Poll. 2009; 204:315–332.

Zhu J, Sykes JF. Simple screening models of NAPL dissolution in the subsurface. J Contam Hydrol. 2004; 72(1-4):245–258. [PubMed: 15240175]

Highlights

Temporal contaminant mass discharge (CMD) was measured for a DNAPL source zone

The relationship between reductions in CMD and reductions in mass was characterized

The results were compared to data processed for other field sites

Source-zone age was indicated as a significant mediator of observed behavior

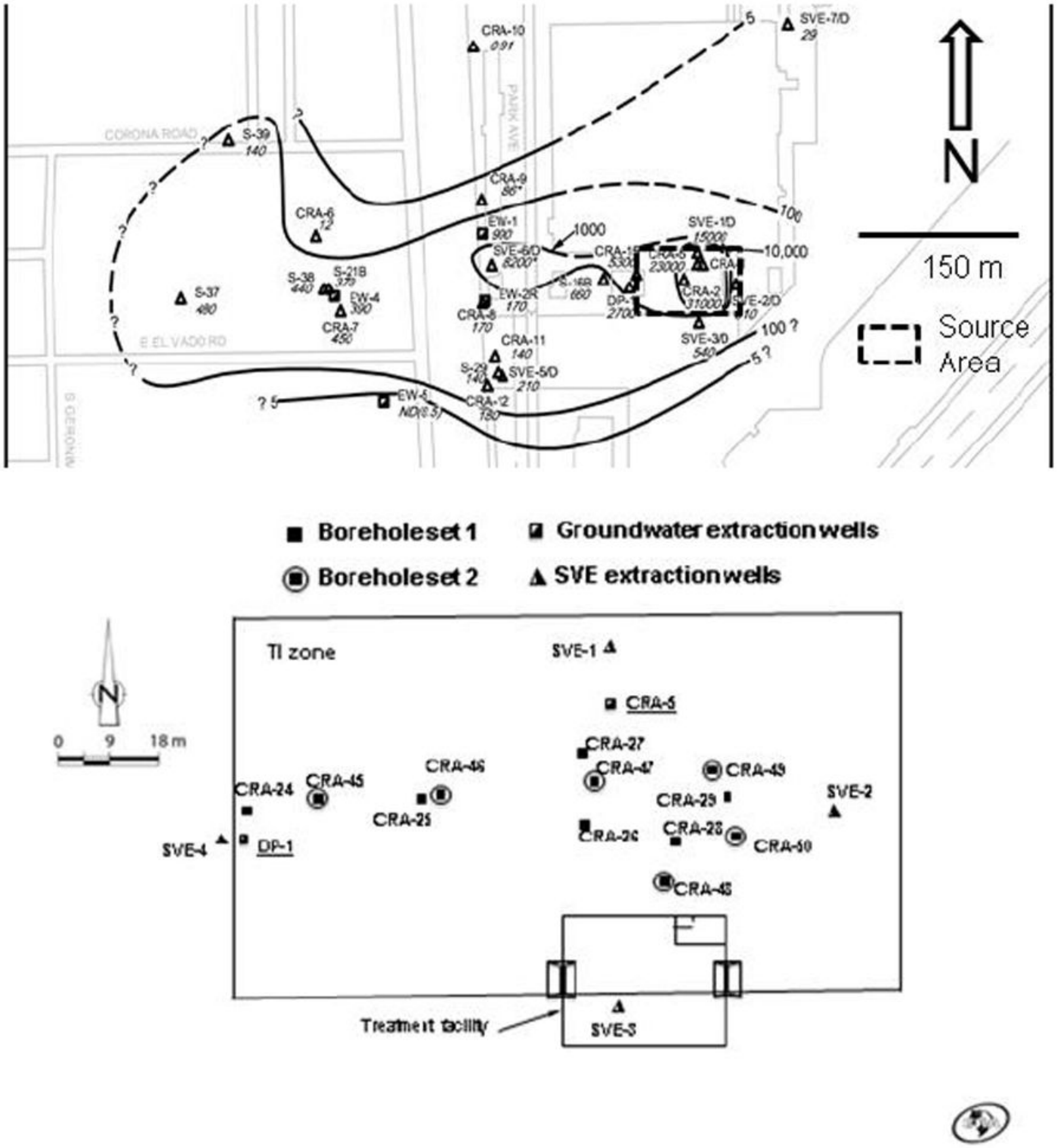


Figure 1.

Maps of the field site. The upper figure presents contours of TCE concentrations (μg/L) in the gravel sub-unit for 2007 prior to the start of groundwater extraction; the lower figure is a schematic of well and borehole locations in the source area.

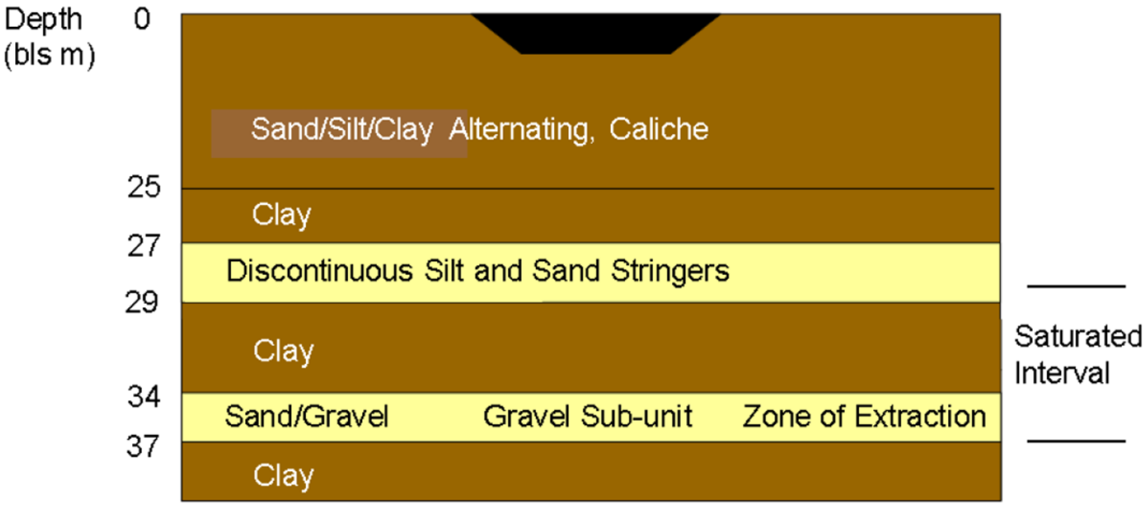
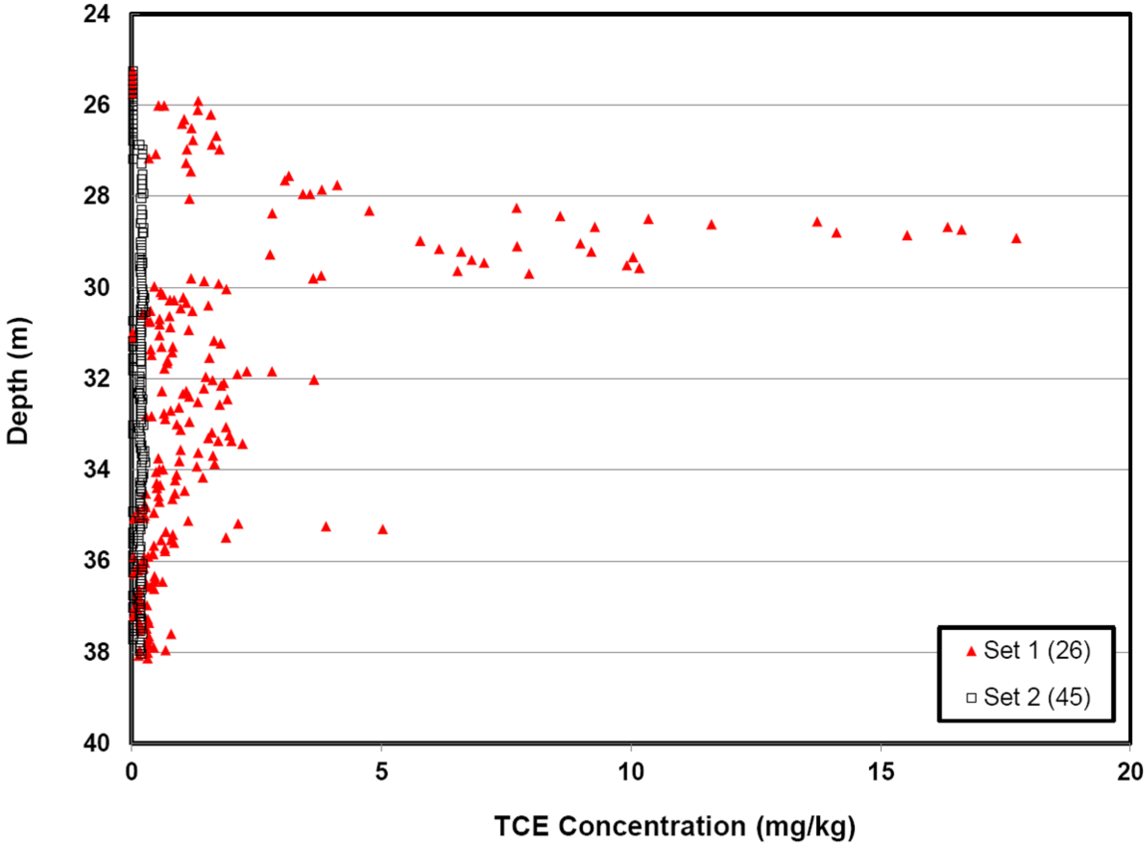
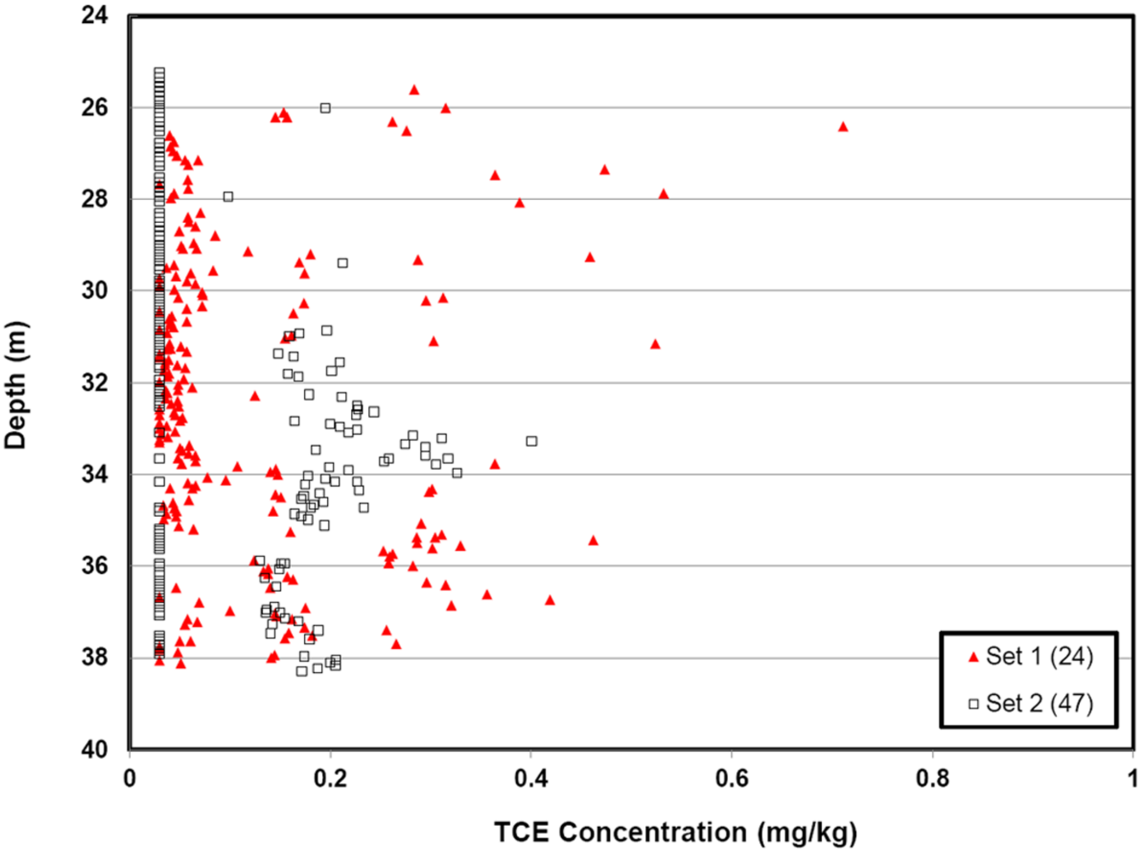


Figure 2.
Schematic of local stratigraphy for the site.


Depth (m)
24
26
28
30
32
34
36
38
40
0
5
10
15
20
TCE Concentration (mg/kg)
▲ Set 1 (26)
□ Set 2 (45)

a



b

Figure 3.
Sediment-phase trichloroethene (TCE) concentrations for core samples collected in 2008 (set 1) and 2012 (set 2); see Figure 2 for key to locations: a) the most contaminated cores for each set, b) the least contaminated cores for each set. Specific borehole numbers (minus CRA prefix) are noted in parentheses. Note that the paired cores are not co-located.

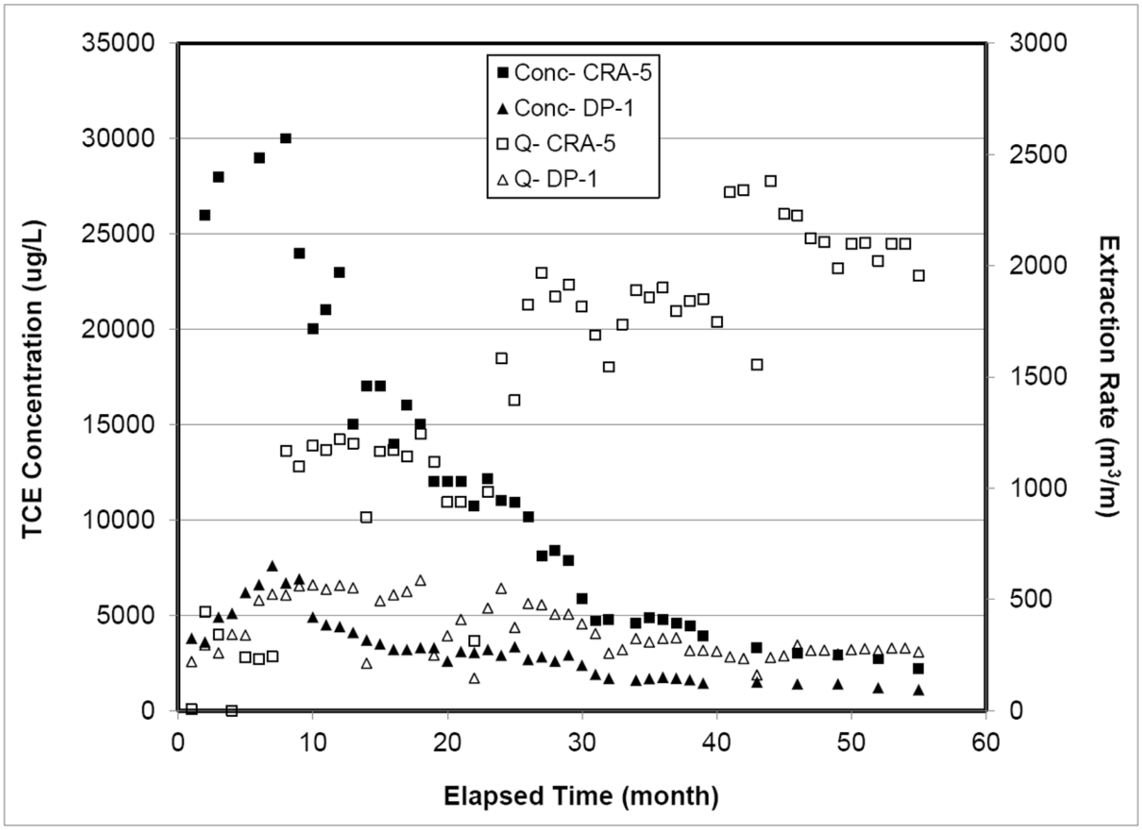


Figure 4.
Concentrations of trichloroethene (TCE) in groundwater extracted with the two source-area extraction wells and associated flow rates. Zero time corresponds to system startup in fall 2007.

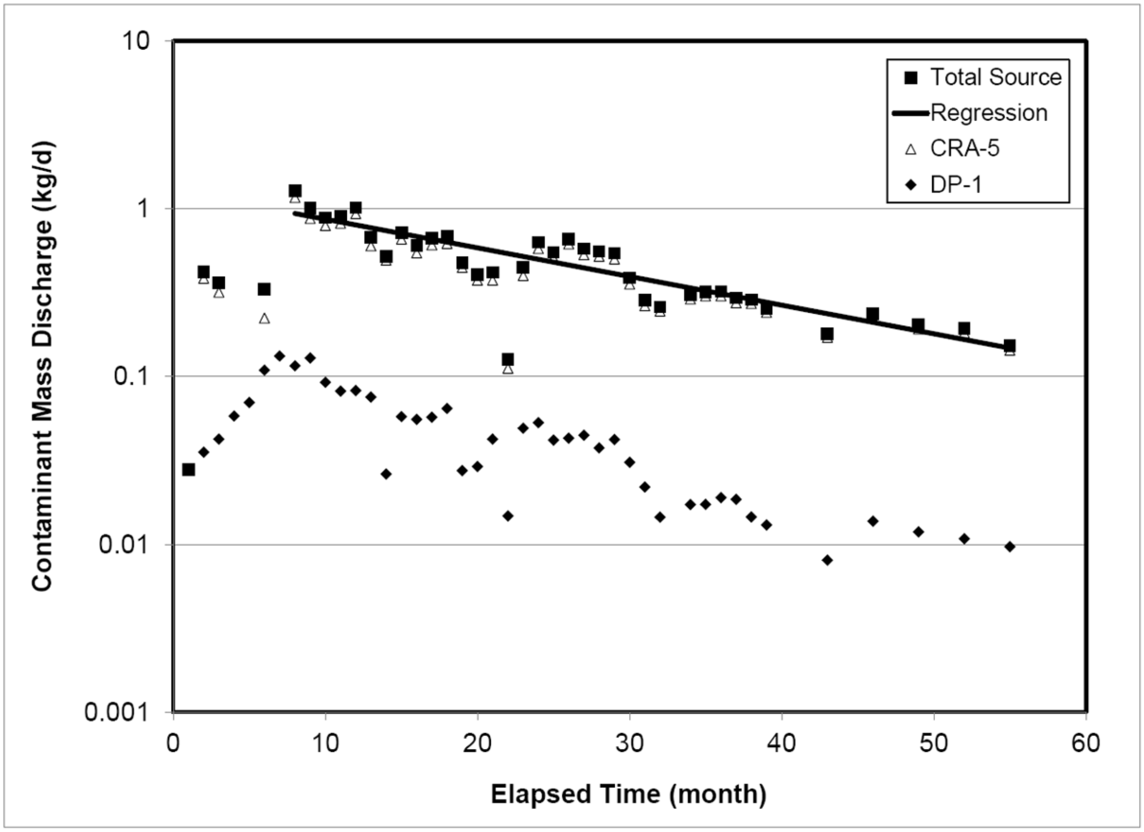


Figure 5.

Contaminant mass discharge for the source area. Zero time corresponds to system startup in fall 2007. The regression represents a fit of the exponential-depletion function to total CMD ($r^2 = 0.86$).

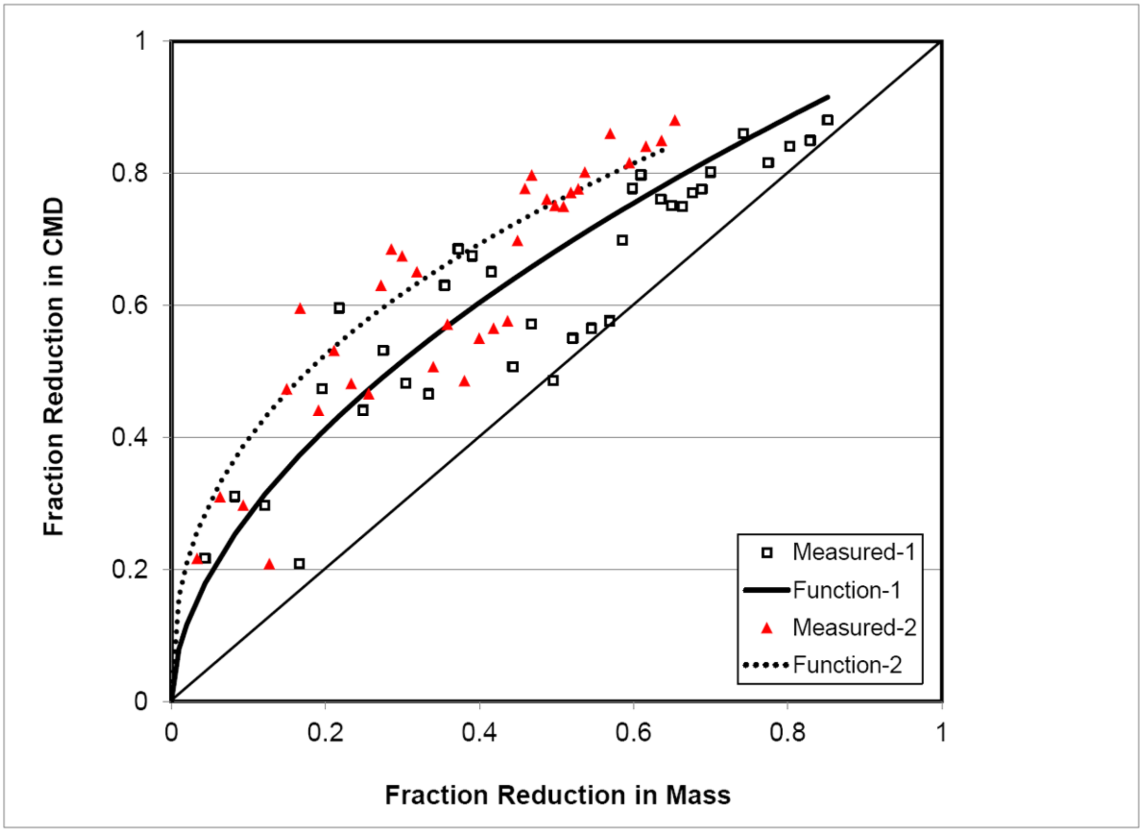


Figure 6.
Relationship between the reduction in contaminant mass discharge (CMD) and the reduction in contaminant mass for the source area. Methods 1 and 2 refer to the two methods used to estimate initial contaminant mass (see text). Also shown are fitted simulations produced with a simple function CMDR = MR^n.

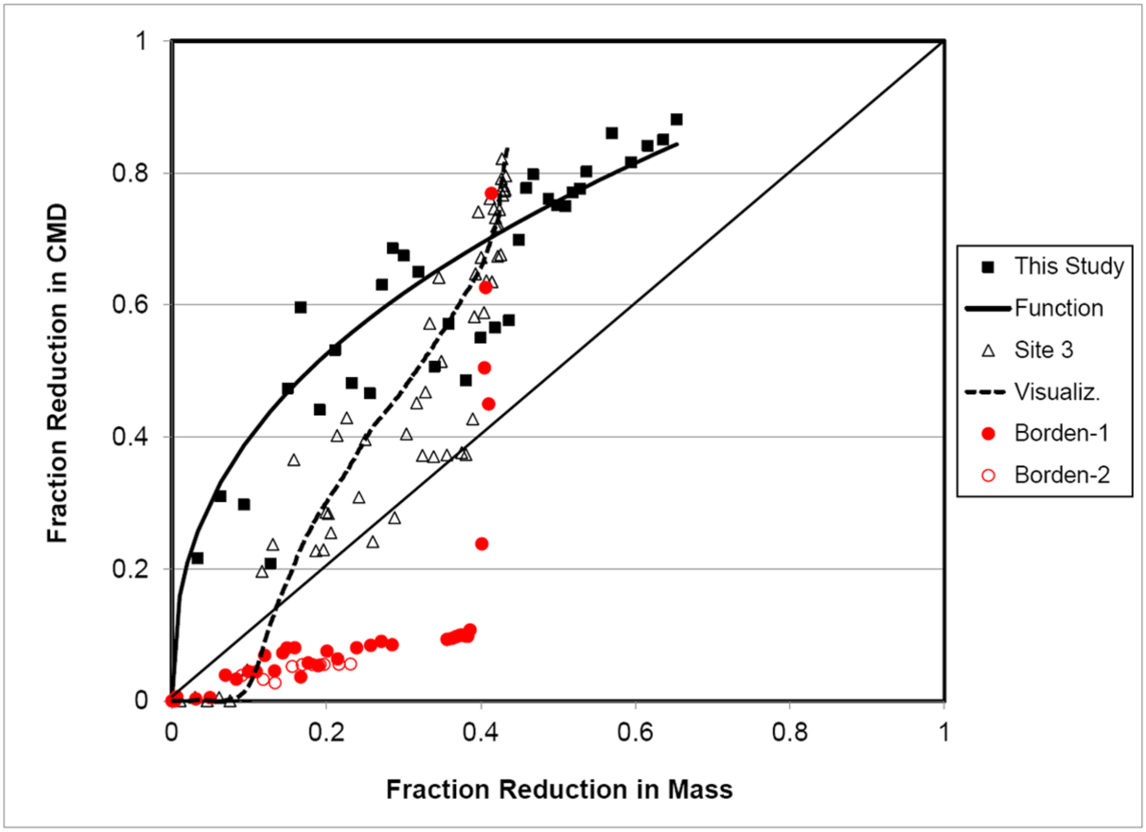


Figure 7.

Relationship between the reduction in contaminant mass discharge (CMD) and the reduction in contaminant mass: comparison of measured field data. The relationships for Site 3 and Borden were calculated and reported originally by DiFilippo and Brusseau (2008), using raw concentration and flowrate data reported by Brusseau et al. (2007) for Site 3, Broholm et al. (1999) for Borden-1, and Rivett and Feenstra (2005) for Borden-2. The line for the Site 3 data is for visualization purposes and is not produced with a mathematical function. The data for this study are based on the M_0 obtained with method 2.

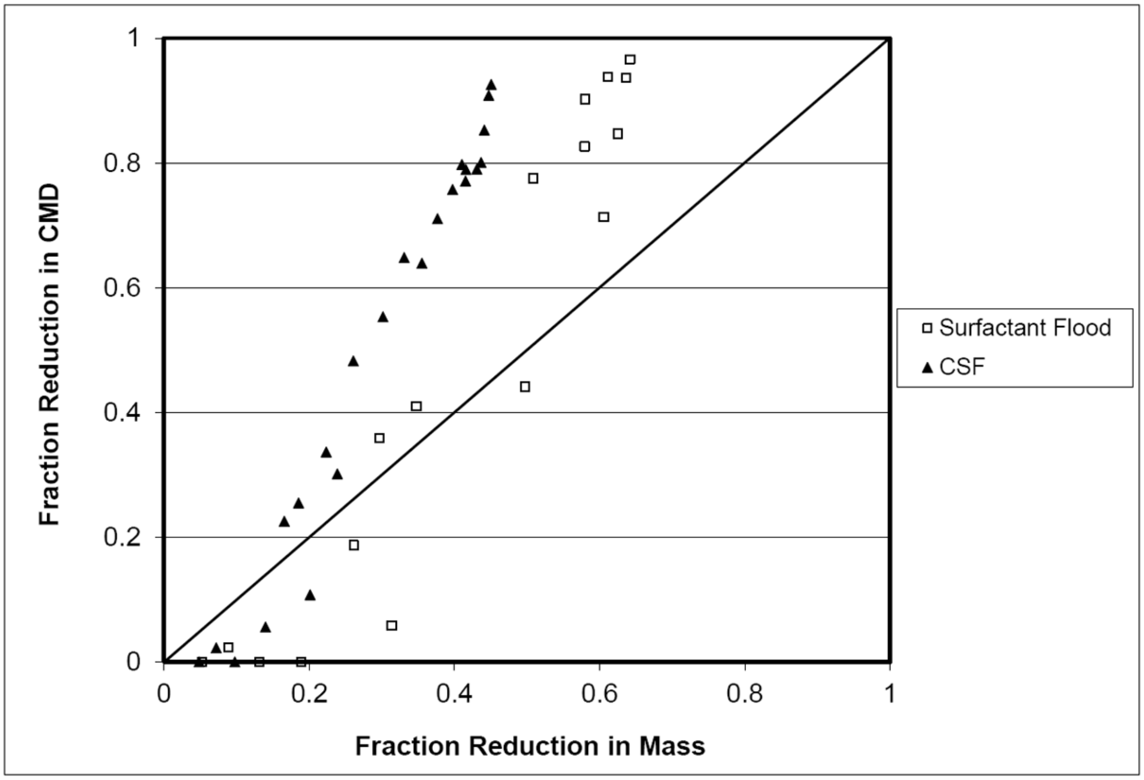


Figure 8.
Relationship between the reduction in contaminant mass discharge (CMD) and the reduction in contaminant mass: comparison of measured field data from Dover test site. Relationships calculated using raw concentration and flowrate data reported by Childs et al. (2006) for the surfactant flood and Tick et al. (2003) for the CSF (complexing sugar flush).