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RELATIONSHIP BETWEEN MASS FLUX REDUCTION AND SOURCE-ZONE MASS REMOVAL: ANALYSIS OF FIELD DATA

Erica L. DiFilippo[1] and **Mark L. Brusseau**[1,2]

[1]Department of Hydrology and Water Resources, University of Arizona Tucson, AZ 85721

[2]Department of Soil, Water and Environmental Science, University of Arizona Tucson, AZ 85721

Abstract

The magnitude of contaminant mass flux reduction associated with a specific amount of contaminant mass removed is a key consideration for evaluating the effectiveness of a source-zone remediation effort. Thus, there is great interest in characterizing, estimating, and predicting relationships between mass flux reduction and mass removal. Published data collected for several field studies were examined to evaluate relationships between mass flux reduction and source-zone mass removal. The studies analyzed herein represent a variety of source-zone architectures, immiscible-liquid compositions, and implemented remediation technologies. There are two general approaches to characterizing the mass-flux-reduction/mass-removal relationship, end-point analysis and time-continuous analysis. End-point analysis, based on comparing masses and mass fluxes measured before and after a source-zone remediation effort, was conducted for 21 remediation projects. Mass removals were greater than 60% for all but three of the studies. Mass flux reductions ranging from slightly less than to slightly greater than one-to-one were observed for the majority of the sites. However, these single-snapshot characterizations are limited in that the antecedent behavior is indeterminate. Time-continuous analysis, based on continuous monitoring of mass removal and mass flux, was performed for two sites, both for which data were obtained under water-flushing conditions. The reductions in mass flux were significantly different for the two sites (90% vs. ~8%) for similar mass removals (~40%). These results illustrate the dependence of the mass-flux-reduction/mass-removal relationship on source-zone architecture and associated mass-transfer processes. Minimal mass flux reduction was observed for a system wherein mass removal was relatively efficient (ideal mass transfer and displacement). Conversely, a significant degree of mass flux reduction was observed for a site wherein mass removal was inefficient (nonideal mass transfer and displacement). The mass-flux-reduction/mass-removal relationship for the latter site exhibited a multi-step behavior, which cannot be predicted using some of the available simple estimation functions.

Keywords

Mass Flux; DNAPL; Source Zone; Remediation

1.0 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 immiscible-liquid contamination in the subsurface. Immiscible liquids, such as chlorinated solvents, creosote,

Correspondence to: Mark L. Brusseau.

coal tars, and fuels, once introduced into the subsurface become entrapped, and serve as long-term sources of contamination. The presence of immiscible-liquid contamination at a site can greatly impact the costs and time required for site remediation. It is widely acknowledged that cleaning up sites contaminated with denser-than-water immiscible liquids is one of the greatest challenges in the field of environmental remediation (NRC 1994,1997,1999,2000,2005).

Significant effort has been directed over the past decade to developing methods to remediate immiscible-liquid contaminated source zones. These methods include thermal-based technologies (e.g., electrical resistance heating, steam injection), in-situ flushing using solubilization/mobilization reagents (e.g., surfactants, cosolvents), and in-situ chemical treatment (e.g., chemical oxidation). Unfortunately, because of the complexities associated with the transport, retention, and mass-transfer of immiscible liquids, as well as the heterogeneity of subsurface environments, it is generally not possible to remove all immiscible-liquid mass from the source zone (e.g., DOD, 2001; ITRC, 2002; EPA, 2003; NRC, 2005). As a result, application of a source-zone remediation technology will typically result in only partial mass removal. The magnitude of the reduction in contaminant mass flux obtained for a partial depletion of source-zone mass is a key consideration for evaluating the effectiveness of a source-zone remediation effort. Thus, there is great interest in characterizing, estimating, and predicting relationships between mass flux reduction and mass removal.

Contaminant mass flux, also referred to as mass discharge, source strength, and mass-flow rate, is defined as the rate at which dissolved contaminant mass moves across a control plane. 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). The impact of subsurface heterogeneity, immiscible-liquid distribution, and mass-transfer dynamics on mass-removal behavior and aqueous concentration profiles (mass flux) has been examined for some time through laboratory, modeling, and field studies (e.g., Schwille, 1988; Dorgarten, 1989; Guiguer, 1991; Anderson et al., 1992; Brusseau, 1992; Guarnaccia and Pinder, 1992; Mayer and Miller, 1996; Berglund, 1997; Nelson and Brusseau, 1997; Powers et al., 1998; Unger et al., 1998; Broholm et al., 1999; Brusseau et al., 1999a; Frind et al., 1999; Zhang and Brusseau, 1999; Nambi and Powers, 2000; Zhu and Sykes, 2000; Brusseau et al., 2000, [2002]; Saba and Illangasekare, 2000; Sale and McWhorter, 2001; Rivett et al., 2001; Enfield et al., 2002; Rao et al., 2002; Rao and Jawitz, 2003; Jayanti and Pope, 2004; Lemke et al., 2004; Parker and Park, 2004; Phelan et al., 2004; Soga et al., 2004; Falta et al., 2005a,[b]; Jawitz et al., 2005; Rivett and Feenstra, 2005, Fure et al., 2006; Lemke and Abriola, 2006; Suchomel and Pennell, 2006; Brusseau et al., 2007, 2008). 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). The specific relationship between mass flux reduction and mass removal has since been examined and discussed in a number of studies (Enfield et al., 2002, Rao et al., 2002, Rao and Jawitz, 2003; Stroo et al., 2003; Brooks et al., 2004; Jayanti and Pope, 2004; Lemke et al., 2004; Parker and Park, 2004; Phelan et al., 2004; Soga et al., 2004; Jawitz et al., 2005; NRC, 2005; Fure et al., 2006; Lemke and Abriola, 2006; Brusseau et al., 2007, 2008).

Three simplified, prototypical relationships between mass flux reduction and mass removal, representative of systems for which the source zone is undergoing continuous water flushing, which are useful for comparative discussion are presented in Figure 1a. These relationships can be readily developed by employing a simple limiting-case analysis of the temporal contaminant-elution/mass-removal function for immiscible-liquid systems (as shown in Figure 1b), from which the mass-flux-reduction/mass-removal relationship can be obtained directly. The curve in the lower right-hand section of Figure 1a represents the relationship for a system for which the flushing process (mass-transfer and displacement) is relatively ideal, wherein immiscible-liquid dissolution and other mass-transfer processes are under equilibrium conditions and all contaminant mass is accessible to flowing groundwater. Removal of mass from the source zone will be relatively efficient for such conditions (i.e., maximum amount of mass removed per unit volume of water displaced), as illustrated by the corresponding contaminant-elution and mass-removal curves (Figure 1b and 1c). Because contaminant mass-transfer and displacement is relatively ideal, the aqueous-phase contaminant concentrations are maintained at maximal or near-maximal levels, and thus there is minimal reduction in mass flux until almost all of the mass has been removed. The curve in the upper left of Figure 1a represents the relationship for a system governed by non-ideal mass-transfer and displacement behavior (e.g., rate-limited dissolution, by-pass flow phenomena), wherein mass removal is relatively inefficient (Figure 1b and 1c), and there is a significant reduction in mass flux with minimal mass removed. The third curve represents the special case wherein there is a one-to-one relationship between mass flux reduction and mass removal (e.g., first-order mass removal).

Knowing the mass-flux-reduction/mass-removal relationship for a given system would be of great assistance in evaluating the potential benefits and cost-effectiveness of a proposed remediation effort. Unfortunately, determining the precise relationship for a given site is difficult and time consuming. Characterizing mass-flux-reduction/mass-removal relationships for field applications representing a range of conditions would improve our understanding of the impact of system properties and conditions on the relationship between mass flux reduction and mass removal. This, in turn, would enhance the development of predictive tools.

An expert-panel workshop was recently convened to discuss the research needs for characterization and remediation of immiscible-liquid source zones (SERDP, 2006). The panel noted that significant uncertainty remains with respect to our understanding of the long-term behavior of immiscible-liquid source zones and the benefits of source-zone remediation. Improved understanding of the relationship between mass flux reduction and mass removal was deemed a high priority research need. The objective of this research was to investigate mass-flux-reduction/mass-removal behavior using data sets collected from several field studies.

2.0 METHODS

2.1 Source Zone Mass and Mass Flux Calculations

There are two general approaches to characterizing relationships between mass flux reduction and mass removal, end-point analysis and time-continuous analysis. End-point analysis is based on determining mass flux before and after a source-zone remediation effort. Several field-scale source-zone remediation projects were examined and a total of 21 studies, representing 12 different sites, are included in this analysis (Figure 2). Time-continuous analysis is based on continual monitoring of aqueous-phase contaminant concentration (mass flux) and mass removal, from the initial stages of mass removal to a given end point. Time-continuous analyses for three studies (representing two sites), all conducted under water-flushing conditions, are included herein.

For most of the studies, measurements of source-zone contaminant mass were obtained using either sediment-core or partitioning tracer test data. In a few cases, the initial mass was known a priori via a controlled release. For two studies, mathematical modeling was used to assist in the calculation of initial source-zone mass. In addition, for some cases, contaminant mass removed (and thus final masses) could be calculated using continuous measurements of effluent concentrations. Fractional mass removal (MR) is defined as the ratio of the final mass to the initial mass present in the source zone. Therefore, a reduction of 1.0 indicates that all of the contaminant mass was removed from the source zone during remediation.

Mass flux measurements were obtained using aqueous concentration data. The groundwater samples were collected primarily with multilevel sampling devices. The nature of the sampling network varied from study to study. In some cases, the network comprised several monitoring wells spread throughout the source-zone proper. In other cases, one or more monitoring wells were located downgradient of the source-zone. In a few cases, samples were collected from extraction wells. Fractional mass flux reduction (MFR) is defined as:

$$MFR=1-\frac{J_f}{J_i}=1-\frac{Q_f C_f}{Q_i C_i} \tag{1}$$

where J is the mass flux (M/t), Q is the volumetric flow rate (L^3/t), C is concentration (M/L^3), and the subscripts i and f represent initial and final, respectively. If the volumetric flow rate is the same during measurement of initial and final groundwater concentrations, then equation (1) reduces to:

$$MFR=1-\frac{C_f}{C_i} \tag{2}$$

A few of the studies involved multiple-component immiscible-liquid contamination. For these cases, composite mass flux reductions and mass removals were calculated by weighting the values for each component by their initial mass fraction of the total contaminant mass. This allowed for direct comparison with the data sets comprising single-component contamination.

2.2 Uncertainty Analysis

There are a number of uncertainties associated with the mass flux and mass removal calculations presented in this study (Table 1). It is not possible to conduct a fully quantitative assessment of uncertainty due to the lack of required information. Thus, a qualitative uncertainty analysis was developed based on the methods by which the underlying data were obtained. The most reliable measures of initial contaminant mass are presumed to be those obtained from controlled release studies. Contaminant mass measurements obtained via analysis of sediment-core data and partitioning tracer tests are considered to have generally similar levels of uncertainty given that the two methods have provided similar results for field applications (e.g., Cain et al., 2000;Rao et al., 2000;Meinardus et al., 2002;Brusseau et al., 2003). Measurements obtained with these two methods are expected to have higher degrees of uncertainty compared to measurements associated with a controlled release.

The post-remediation source zone mass was obtained via continual measurement of extracted mass (e.g., effluent concentrations) or analysis of sediment-cores and partitioning tracer tests. The highest certainty in contaminant mass removed is assumed to be obtained from studies with a continual measure of the extracted mass via sampling of extraction-well effluent. Similar to the measurement of initial mass, sediment-core and partitioning tracer test analysis are expected to have higher degrees of uncertainty compared to continual measurement of extracted effluent.

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Similarly, there is uncertainty associated with the calculated values of mass flux, which are based primarily on analysis of aqueous contaminant concentrations collected from monitoring or extraction wells. The robustness of the mass flux measurements are expected to be dependent on the method of sample collection, the design of the sampling network, and the resultant representativeness of the collected data. Extraction wells that collect all of the water flowing through the source zone are considered to provide the most reliable data. Down-gradient control planes comprised of a series of multilevel sampling devices are considered to have a higher degree of uncertainty compared to extraction wells. Finally, mass flux estimates obtained using data collected from monitoring wells placed within the source zone are considered to have the highest uncertainty.

Based on the preceding rationale, a grouping scheme was developed to qualitatively characterize the uncertainty for the field data discussed in this study (Table 1). Group A comprises controlled release studies with continual monitoring of total mass removal via extraction-well sampling. In addition, extraction well data were used to calculate mass flux for all of these studies. Group B includes studies wherein (1) initial and final source-zone masses were determined through controlled release with continual monitoring of total mass removal, and mass flux was calculated using data collected at a down-gradient control plane, or (2) initial and final source-zone masses were determined with sediment cores or PTTs or in combination with mathematical modeling, and mass flux was calculated using extraction well data. Finally, studies classified into Group C are those for which sediment cores or PTTs were used to determine initial and final source-zone mass, and data collected with monitoring wells placed within the source zone were used to calculate mass flux.

2.3 Simple Mass-Removal Function

Several approaches, based on “source-depletion” models or simple “mass-removal” functions, have recently been proposed for estimating the relationship between mass flux reduction and mass removal (e.g., Enfield et al., 2002; Rao et al., 2002; Parker and Park, 2004; Zhu and Sykes, 2004; Falta et al., 2005a; Jawitz et al., 2005). One simple approach is based on treating changes in mass flux as a direct function of the change in contaminant mass:

$$1-\frac{J_f}{J_i}=\left(1-\frac{M_f}{M_i}\right)^{1/n} \tag{3}$$

where M is source zone mass [M], and n is a fitting parameter. The parameter n defines the specific mass-flux-reduction/mass-removal relationship, and thus incorporates the impact of source-zone architecture, flow-field dynamics, and mass-transfer and displacement processes. Lesser degrees of mass flux reduction are observed for n values increasingly less than 1. Applications of this approach are discussed in several recent publications (e.g., Rao et al., 2002, Zhu and Sykes, 2004; Falta et al., 2005a).

3.0 SITES INVESTIGATED

Each study included in the analysis is summarized in Table 2. In some cases, mass flux reductions and mass removals were reported directly in the associated publications. In other cases, the values were calculated using reported data, as noted in the Supplemental Materials. For sites where reductions in mass flux were calculated from observed data, it was assumed that the groundwater flow rate did not vary significantly throughout the course of the study. A brief description of each field study is provided in the Supplemental Materials.

4.0 RESULTS

4.1 End-Point Analysis

The end-point based analysis of mass flux reduction as a function of source-zone mass removal is presented in Figure 3 for the tabulated field data. Note that the uncertainties associated with the measurements of mass and mass flux are incorporated in Figure 3 as discussed in the Methods section. It is observed that mass removals of greater than 60% were obtained for all but three of the studies. Furthermore, mass removals of 90% or greater were attained for several of the studies. The three studies for which smaller mass removals were attained represent those studies for which water flushing (pump and treat) was used for contaminant removal.

Inspection of Figure 3 reveals that appreciable reductions in mass flux were obtained for most of the studies. There is significant disparity in the reported mass-flux-reduction values. For example, mass flux reductions range from approximately 30% to 85% for the three studies for which mass removals were approximately 90%. In addition, these single-snapshot characterizations are limited in that the antecedent behavior is indeterminate.

The data in Figure 3 can be evaluated with respect to the prototypical mass-flux-reduction/mass-removal curves presented in Figure 1a, as well as the simple mass-removal function (Equation 3). Significant reductions in mass flux were attained for relatively small fractions of mass removal for sites that plot in the upper left-hand section of Figure 3. The data point for the Tucson International Airport Area (TIAA) Superfund site, which will be discussed later, falls within this section. A curve produced using the simple mass-removal function with n = 10 is representative of this behavior. Conversely, large fractions of mass removal produced minimal reductions in mass flux for sites that plot in the lower right-hand section (n values of approximately 0.05). The data points for two sites are located within this section: Paducah Gaseous Diffusion Plant and the Former Recycling Facility. Measurements of mass flux at both of these sites were conducted with a single monitoring well located down-gradient of the source zone; therefore, the mass flux reductions for these two sites are likely to have the highest degree of uncertainty of all the studies. The majority of the data fall within the central section, exhibiting mass flux reductions ranging from slightly less than to slightly greater than one-to-one (n values between 0.5 and 2). However, without additional mass-flux-reduction data at lower ranges of mass removal, it is not possible to fully characterize the mass-flux-reduction/mass-removal behavior for these sites.

Some of the site variables most likely to influence mass-flux-reduction/mass-removal behavior are presented in Table 3. The majority of these site variables may in some way affect the accessibility of the immiscible liquid to the groundwater flow regime. Sites with large fractions of highly accessible source zone mass would generally be expected to experience more efficient mass removal, leading to lesser initial magnitudes of mass flux reductions. The ganglia-to-pool ratio (GTP) has been proposed as an indicator of source zone immiscible-liquid configuration (e.g. Lemke at al., 2004), under the assumption that sites dominated by residual zones will likely have more efficient mass removal than pool-dominated sites. Information needed to estimate GTP values was not available for most of the sites. A global immiscible liquid saturation (S_n) value was estimated based on the initial source zone mass, source zone size, and porosity. In addition, the age of the contamination is included in Table 3. Sites where contamination has existed for 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 sites may differ from that observed for newly contaminated sites.

The effect of source-zone architecture on mass-flux-reduction/mass-removal may be reflected in the comparative results obtained from the three studies conducted at the Dover site. The single-snapshot measurements obtained for both cosolvent studies exhibit a one-to-one to slightly lesser mass-flux-reduction/mass-removal relationship. Conversely, the mass flux reduction was greater for a similar mass removal for the surfactant-flood study. The initial source-zone mass for the surfactant demonstration (Dover study 3), which was conducted immediately after the ethanol flood (Dover study 1) in the same cell, comprised a portion of immiscible liquid mass remaining from the prior study. A large fraction of this mass may have been present in the more hydraulically inaccessible regions of the test cell (Brooks et al., 2002). Consequently, the surfactant demonstration may have had a larger fraction of source-zone mass present in hydraulically inaccessible regions compared to the ethanol demonstration, resulting in more inefficient mass removal and concomitantly greater reduction in mass flux. The data point for the TIAA site falls on the same curve (n = 10) as the data point for the SEAR demonstration at Dover (Dover study 3). The TIAA site, which will be discussed in further detail below, also contains a large fraction of source-zone mass present in hydraulically inaccessible regions. Conversely, the four studies conducted at the Borden site, for which the immiscible liquid is relatively hydraulically accessible, exhibit lesser than one-to-one reductions in mass flux (n = 0.5).

4.2 Time-Continuous Analysis

It is important to note that the results obtained with the end-point analysis represent a single snapshot of the mass-flux-reduction/mass-removal behavior for a site. This type of analysis does not provide insight into the pathway (greater than, lesser than, one-to-one) that each site followed to achieve this end point. Uncertainty in the calculation of mass removed and mass flux reduction further complicates the characterization of the end-point based relationships. Therefore, it is important to recognize the limitations of such an analysis.

In contrast to end-point analysis, time-continuous analysis provides “complete” characterization of the mass-flux-reduction/mass-removal relationship. This approach is a considerably more time consuming and arduous analysis compared to end-point analysis since it requires continual monitoring of effluent concentration and mass removal. Direct, experiment-based investigations of time-continuous mass flux-reduction/mass-removal behavior are just now being reported. For example, Fure et al. (2006) and Brusseau et al. (2008) conducted flow-cell experiments under continuous water-flushing conditions to examine the impact of source-zone architecture on mass-flux-reduction/mass-removal behavior. Brusseau et al. (2007) reported a time-continuous analysis of the mass-flux-reduction/mass-removal behavior for the Tucson International Airport Area (TIAA) Superfund site, which is currently undergoing pump-and-treat remediation (for detailed site information see Supplemental Material).

Time-continuous analysis was performed using data collected from the two water flushing experiments conducted at the CFB Borden site. Mass removal for both studies appeared to be fairly ideal, as illustrated by the relatively high, steady-state effluent concentrations of the dissolved components observed after arrival of the plume front at the monitoring location (Figure 4). TCM was the only component in either Borden study that experienced measurable reduction in concentration and, consequently, mass flux (Figure 5a). The mass-flux-reduction/mass-removal behavior for the TCM component is similar for both studies (Figure 5a), indicating similar mass-removal conditions. Composite elution and mass-flux-reduction/mass-removal curves were calculated for both studies by weighting the values for each component by their initial mass fraction of the total contaminant mass (Figures 5b). The composite mass-flux-reduction/mass-removal relationships for both sites display slight reductions in mass flux at earlier stages of mass removal compared to the single-component curves, reflecting the preferential removal of TCM (which comprised the smallest fraction of the mixture). The simple mass-removal function was used to evaluate the time-continuous data reported for the Borden studies (Figures 5a & 5b). For these studies, it is evident that the curve (n = 0.5) that matches the TCM-component data also matches reasonably the composite data for both water flushing studies. Furthermore, this same curve also encompasses the end-point analysis data for all four studies conducted at the site (Figure 5b).

Brusseau et al. (2007) reported a time-continuous analysis of the mass-flux-reduction/mass-removal behavior for the Tucson International Airport Area (TIAA) Superfund site, which is currently undergoing pump-and-treat remediation (for detailed site information see Supplemental Material). The mass-flux-reduction/mass-removal relationship obtained for the TIAA site shows an initial decrease in mass flux that begins before 10% of the initial mass is removed and continues until approximately 25% of the initial mass is removed (Figure 6a). The behavior displayed during this period reflects primarily the removal of the aqueous-phase mass associated with the contaminant plume. The initial mass flux reduction is followed by a steady-state period (for mass removals between 25 to 40%), where minimal reductions in mass flux are observed, after which the mass flux begins to sharply decrease once again.

The contaminant mass removals for the other studies included in this analysis do not encompass large fractions of sorbed and aqueous-phase mass associated with a large contaminant plume. Therefore, it is advantageous to exclude the portion of the mass-flux-reduction/mass-removal curve that is associated with the removal of the contaminant plume in order to compare the behavior observed for the TIAA site with that observed for the other studies. This was done by excluding the mass (~6900 kg) associated with the first pore volume of groundwater extraction. It is noteworthy that this mass is very similar to the aqueous-phase mass that was estimated to be initially present in the plume (~6600 kg). The modified mass-flux-reduction/mass-removal relationship, which reflects only the impact of the source zones, shows an initial steady-state period where there is minimal reduction in mass flux (Figure 6b). The initial steady-state period is followed by a period of significant mass flux reduction (> 90%) with moderate reduction in source-zone mass (< 40%).

As previously mentioned, the immiscible-liquid mass at the TIAA site is located in several discrete source zones. The mass-flux-reduction/mass-removal behavior for a single source zone at the site was examined to evaluate the efficacy of the approach used to exclude the impact of plume removal, as well as to assess the effect of uncertainties associated with the estimate of the initial source-zone mass for the entire TIAA site. The selected source zone is located on the edge of the large contaminant plume. Partitioning tracer tests were employed at this source zone and, based on their results, it was determined that 5600 kg of immiscible-liquid mass was present at this site (Nelson and Brusseau, 1996; Zhang and Brusseau, 1999). The total amount of sorbed and aqueous-phase contaminant mass was estimated to be approximately 100 kg, less than 2% of the total mass present in the source zone. Because sorbed and aqueous-phase mass comprised only a small portion of the total mass for this source zone, no correction for the contaminant plume was performed. The effluent concentration, and hence mass flux, was determined from one extraction well that draws water from the entire span of the source zone.

The mass-flux-reduction/mass-removal behavior exhibited for the single source zone is similar to that observed for the entire TIAA site (contaminant plume mass excluded) (Figure 6b). This similarity provides added confidence in the mass-flux-reduction/mass-removal relationship obtained for the entire site. This site exhibits a large reduction in mass flux for a moderate fraction of mass removal. As previously mentioned, such behavior is expected for a system controlled by non-ideal mass transfer and displacement, leading to inefficient source-zone mass removal. This is consistent with observations at the site, in particular the presence of high TCE concentrations within lower-permeability units, concentration rebound when the pump-and-treat system is offline, and the asymptotic decrease of the pump-and-treat system effluent concentrations, as well as the results of modeling-based analyses (Brusseau et al., 1999a; Zhang and Brusseau, 1999; Brusseau et al., 2007).

Inspection of Figure 7 shows that the Borden and TIAA studies have similar fractions of mass removal. However, the mass flux reductions are significantly different. The different mass-removal behaviors are evident when comparing the contaminant elution curves obtained for the two studies (Figure 4). A steady state concentration profile wherein concentrations are maintained at near maximal levels is observed for the composite elution data from the Borden-Forest Site study. Conversely, after peaking, the effluent concentrations exhibit a continual, gradual decline for the TIAA study. The contrasting behavior likely results from differences in source-zone architecture and mass-transfer dynamics for the two sites, illustrating the impact of relatively ideal mass-transfer and displacement for the Borden site (Frind et al., 1999) and the non-ideal mass-transfer and displacement for the TIAA site. In contrast to the composite Borden data, the TCM single-component elution curve for the Borden study displays a minimal steady state period followed by a gradual decrease in concentration. This elution curve is generally similar in shape to the elution curve for the TIAA study. However, the decrease in TCM concentration is due to near complete removal of mass from the source zone under ideal mass-transfer and displacement conditions. Conversely, the decrease in TCE concentration at the TIAA site is due to the aforementioned nonideal behavior within the source zones.

Inspection of Figure 6b reveals that the mass-removal function ($n = 10$) matched to the end-point data is not capable of predicting the early stage of the time-continuous mass-flux-reduction/mass-removal behavior for the TIAA site. Conversely, a curve ($n = 0.5$) matched to the early mass-flux-reduction/mass-removal behavior cannot reproduce the later behavior. It is evident from Figure 6b that the simple mass-removal function, which produces singular curves, is not capable of capturing the complex, multi-step mass-flux-reduction/mass-removal relationship observed at the TIAA site.

5.0 CONCLUSION

The studies examined in this paper represent a variety of source-zone architectures, immiscible-liquid compositions, and implemented remediation technologies. Mass removals of greater than 60% were obtained for all but three of the studies. The three studies for which smaller mass removals were attained represent those studies for which water flushing (pump and treat) was used for contaminant removal. Appreciable reductions in mass flux were observed for most of the studies. The significance of these reductions in terms of the effectiveness and beneficial impacts of the remedial actions is of course dependent upon site-specific defined goals and objectives, the analysis of which is beyond the scope of this study.

As noted above, a significant degree of disparity was observed in the reported mass-flux-reduction values. Some of this disparity may be due to the uncertainty associated with the mass flux and mass removal measurements. However, it is likely that the observed disparity to some degree reflects the dependency of mass flux reduction and mass removal on source-zone architecture and mass-transfer dynamics, factors whose manifestation and resultant impacts are site specific. This is illustrated by the contrasting mass-flux-reduction/mass-removal relationships observed between the Borden and TIAA sites. The observed disparity suggests that the use of simple tools, especially those not tuned to site-specific conditions, to predict mass-flux-reduction/mass-removal relationships may be fraught with a high degree

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of uncertainty. Based on these results, it is clear that additional, well-controlled field studies are required to further characterize the relationship between mass flux reduction and mass removal for a variety of conditions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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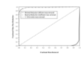

Figure 1a.

Three simplified, prototypical relationships between mass flux reduction and mass removal (from Brusseau et al., 2008). The mass-flux-reduction/mass-removal functions were produced from the contaminant elution curves presented in Figure 1b. Integration of the elution curve provides cumulative mass removed and total mass, from which fractional mass removed is obtained; fractional mass flux reduction is obtained from 1-C/C_0, assuming constant Q (Equation 1).

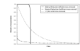

Figure 1b.
Contaminant elution curves corresponding to the two limiting cases of mass removal (efficient and inefficient), and that of first-order mass removal (from Brusseau et al., 2008). The contaminant elution curves representing the two limiting cases reflect a simple conceptual limiting-case analysis ("ideal" vs. "nonideal" or "efficient vs inefficient") of flushing-based mass removal for immiscible-liquid systems, the typical behavior for which is widely reported in the literature.

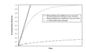

Figure 1c.
Contaminant mass-removal with time for the two limiting cases of mass-removal (efficient and inefficient), and that of first-order mass removal.

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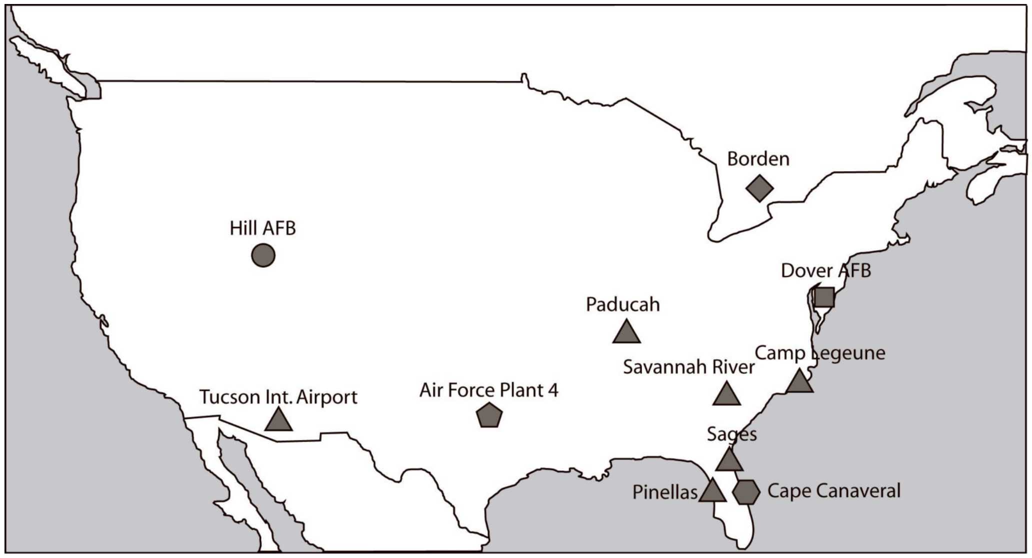

Figure 2.
Geographical location of the 12 sites presented in this study. The symbols represent the field studies presented in Table 1.

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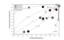

Figure 3.

Mass flux reductions as a function of source-zone mass removal for several field studies. The symbols represent the field studies presented in Table 1. Qualitative uncertainty analysis is represented through shading and symbol size (Table 2). Group A (largest symbols with darkest background) comprises the studies with the lowest uncertainty and Group C (smallest symbols with the white background) are those with the highest uncertainty based on the methods used to determine initial mass, mass flux, and mass removal. The dashed lines represent curves generated using the simple mass-removal function (Equation 3).

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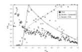

Figure 4.
Comparison of the contaminant elution behavior observed at the Borden–Forest and TIAA sites. For both studies, mass removal was effected via continuous water flushing. The y-axis is aqueous concentration normalized by the maximum observed concentration (Borden-Forest Site: PCE = 7 mg/L, TCE = 20 mg/L, TCM = 24 mg/L, TIAA: TCE = 330 ug/L). The x-axis is the time normalized by the total time of observation at each site (Borden = 204 days, TIAA = 19 years). The composite elution curve for the Borden study was calculated by weighting the values for each component by their initial mass fraction of the total contaminant mass. Note that the overall fractional mass removed is similar for both studies. Solid lines are included to assist visualization.

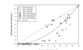

Figure 5a.
Mass-flux-reduction/mass-removal behavior for the individual components used in the Borden – Emplaced Source (ES) and Forest studies. The solid line represents the mass-flux-reduction/mass-removal relationship produced with the simple mass removal function. The mass removal values were calculated based on the individual component masses.

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Figure 5b.
Comparison of the composite mass-flux-reduction/mass-removal behavior for the ES and Forest studies and the end point analysis for the ISCO and SEAR studies. The solid line represents the mass-flux-reduction/mass-removal relationship produced with the simple mass-removal function. The mass removal values were calculated based on the total contaminant mass.

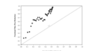

Figure 6.a.

Mass-flux-reduction/mass-removal relationship for the entire TIAA site.

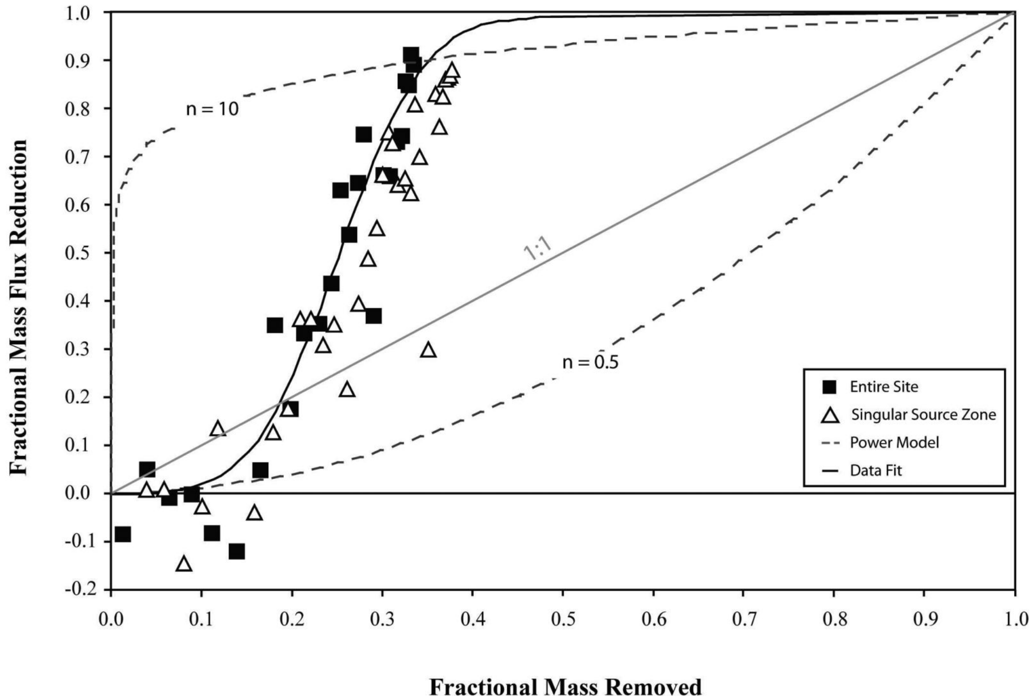

Figure 6b.

Mass-flux-reduction/mass-removal relationship for the entire TIAA site excluding the initial aqueous-phase mass associated with the plume; and comparison to the mass-flux-reduction/ mass-removal relationship for one specific source zone. The dashed lines represent curve simulated using the simple mass-removal function (Equation3). The solid line was fit to the data using a cumulative distribution function.

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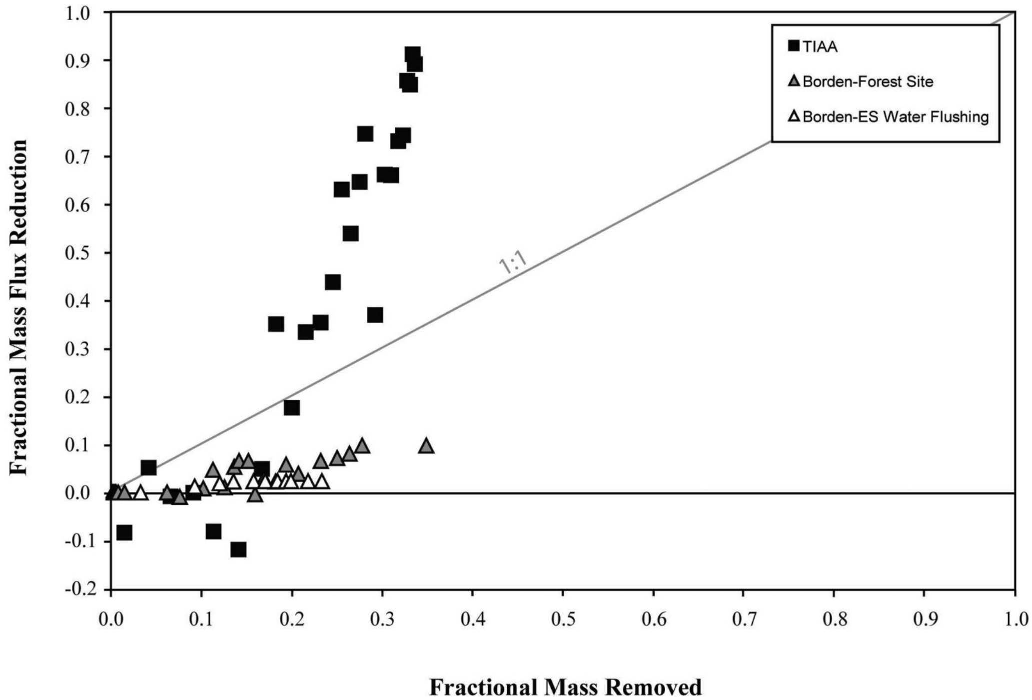


Figure 7.
Comparison of the mass-flux-reduction/mass-removal relationships for three aqueous flushing field studies.

Table 1

Qualitative uncertainty for end-point analysis

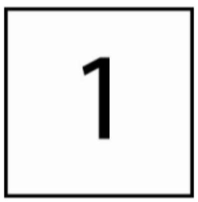
Group*	Calculation of Initial Mass	Calculation of the Mass Removed/Final Mass	Mass Flux Measurement	Studies
A	Controlled Release	Continuous Measure of Total Mass Removal	Integrated Extraction	CFB Borden: Forest Site CFB Borden: SEAR Dover AFB: Ethanol Flush Dover AFB: *n*-propanol Flush Dover AFB: SEAR
B	Controlled Release or Cores, PTTs and/or Modeling	Continuous Measure of Total Mass Removal or Cores, PTTs	Downgradient Control Plane or Integrated Extraction	CFB Borden: Emplaced Source CFB Borden: ISCO Tucson Int. Airport Area Cape Canaveral: EZVI Camp Legeune
C	Cores, PTTs	Cores, PTTs	In-situ Monitoring Well	Hill AFB: Cosolvent Hill AFB: Cyclodextrin Hill AFB: SEAR Cape Canaveral: ISCO Air Force Plant 4: SPH Air Force Plant 4: ERH Sages Dry Cleaners Paducah Gaseous Diff. Plant Former Recycling Facility Savannah River Site Pinellas Site

*Group A is considered to have the least uncertainty and Group C is considered to have the highest uncertainty.

Table 2

Summary of Remediation Technologies

Symbol	Name of Study	Remediation Technology	Source Zone Mass Measurement	Location of Mass Flux Measurement	Natural or Induced Gradient*	Reference
	*CFB Borden Site* Emplaced Source	Water Flush	Controlled Release, Continuous Effluent Monitoring, and Soil Cores	MLS fence 1-m downgradient of source zone	Natural Gradient	Rivett et al., 1994 Rivett et al., 2001 Rivett and Feenstra, 2005
	ISCO	$KMnO_4$	Modeling and Soil Cores	MLS fence 1-m downgradient of source zone	Induced Gradient	Frind et al., 1999 Thomson et al., 2000
	Forest Site	Water Flush	Controlled Release, Continuous Effluent Monitoring, and Soil Cores	Extraction well located within test zone	Natural Gradient	Broholm et al., 1999
	SEAR	2% nonylphenol ethoxylate phosphate	Controlled Release, Continuous Effluent Monitoring, and Soil Cores	Extraction well located within test zone	Induced Gradient	Fountain et al., 1996
	*Hill Air Force Base* Cosolvent	72% ethanol, 28% water and 70% ethanol, 12% *n*-propanol, 18% water	Soil Cores	MLS located within test zone	Static Ground-water	Rao et al., 1997

Symbol	Name of Study	Remediation Technology	Source Zone Mass Measurement	Location of Mass Flux Measurement	Natural or Induced Gradient*	Reference
	Cyclodextrin	10% HPCD	Soil Cores	MLS located within test zone	Static Ground-water	McCray and Brusseau, 1998 Brusseau et al., 1999b
	*Hill Air Force Base (cont.)* SEAR	7.55 % wt. sodium dihexyl sulfosuccinate, 4.47% wt. isopropanol, 7000 mg/L NaCl	PTT	Monitoring well within test area	Induced Gradient	Brown et al., 1999 Londergan et a., 2001
	*Dover National Test Site* Ethanol Flush	70% ethanol 30% water	Controlled Release, Continuous Effluent Monitoring, and PTT	Extraction wells within test area	Induced Gradient	Brooks et al., 2004
	*n*-Propanol Flush	70% n-propanol 30% $CaCl_2$	Controlled Release, Continuous Effluent Monitoring, and PTT	Extraction wells within test area	Induced Gradient	Falta et al., 2005a Wood and Enfield, in press
	SEAR	3.3% wt. sodium dihexyl sulfosuccinate 3.3% wt. isopropanol 0.4% wt. $CaCl_2$	Controlled Release, Continuous Effluent Monitoring, and PTT	Extraction wells within test area	Induced Gradient	Childs et al., 2006

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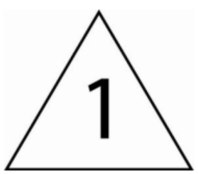
Symbol	Name of Study	Remediation Technology	Source Zone Mass Measurement	Location of Mass Flux Measurement	Natural or Induced Gradient*	Reference
	*NASA Launch Complex 34* ISCO	$KMnO_4$	Soil Cores	Monitoring wells within test area	Induced Gradient	IT Corporation, 2000
	EZVI	Emulsified zero-valent iron	Soil Cores	MLS transect downgradient of test area	Natural Gradient	Quinn et al., 2005
	*Air Force Plant 4* Six Phase Heating (SPH)	SPH	Soil Cores	Monitoring wells within test area	Natural Gradient	Fain et al., 2002
	Electrical Resistive Heating (ERH)	ERH	Soil Cores	Monitoring wells within test area	Natural Gradient	Fleming, 2006
	Sages Dry Cleaners	95% ethanol 5% water	Continuous Effluent Monitoring, Soil Cores and PTT	Monitoring well within test area	Natural Gradient	Jawitz et al., 2000 EPA, 2003
	Tucson International Airport	Pump and Treat	Modeling, PTTs, and Continuous Effluent Monitoring	Extraction wells surrounding source zones	Induced Gradient	Nelson and Brusseau, 1996 Brusseau et al., 1999a Zhang and Brusseau, 1999 Brusseau et al., 2007

Symbol	Name of Study	Remediation Technology	Source Zone Mass Measurement	Location of Mass Flux Measurement	Natural or Induced Gradient*	Reference
3	Paducah Gaseous Diffusion Plant	SPH	Soil Cores	One monitoring well located downgradient of test area	Natural Gradient	Smart, 2005
4	Camp Legeune	4% wt. Alfoterra, 16% wt. isopropanol, 0.17% wt. $CaCl_2$	Soil Cores and PTT	Extraction wells within test area	Induced Gradient	Yeh and Landman, 1999 ESTCP, 2001
5	Former Recycling Facility	20% hydrogen peroxide 10% sulfuric acid	Soil Cores	monitoring well downgradient of test area	Natural Gradient	DeHghi et al., 2002
6	Savannah River Site	GeoCleanse®	Soil Cores	Monitoring wells within test area	Induced Gradient	Jerome et al., 1996 Jerome et al., 1998
7	Pinellas Site	Rotary Steam Stripping	Soil Cores	Monitoring wells within test area	Natural Gradient	Rice, 1998

* Natural/induced gradient conditions refer to circumstances under which the mass flux was determined.

Table 3

Comparison of Site Variables

Name of Study	NAPL (single or multicomponent)	Mean K (m/d)	K Range (m/d)	Time Since Initial Release (yr)	Pre-Remediation S_n
Borden – ES and ISCO	Multicomponent	5.48	0.02 – 26.96	0	0.07
Borden - Forest	Multicomponent	5.48	0.02 – 26.96	0	0.003
Borden - SEAR	Single	5.48	0.02 – 26.96	0	0.01
Hill AFB	Multicomponent	17	12.96 – 35.42	40-50	0.126
Dover	Single	2.50	0.69 – 43.20	0	0.08
Cape Canaveral	Single	2.42	0.12 – 9.11	~40	0.02
Fort Worth	Single	NA	3.97 – 40.61	Unknown	0.0001
Sages	Single	6.00	NA	Unknown	0.004
TIAA	Single	24.00	0.10 – 82.00	~30	0.0006 – 0.05
Paducah	Multicomponent	NA	328 – 3280	~20	0.001
Camp Legeune	Single	0.43	NA	Unknown	0.003 – 0.045
Former Recycling Facility	Multicomponent	NA	NA	Unknown	0.004
Savannah River	Multicomponent	NA	NA	~40	0.0007
Pinellas Site	Multicomponent	NA	0.01 – 0.86	~40	0.0001