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# Relationship between mass-flux reduction and source-zone mass removal: Analysis of field data

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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 (non-ideal 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.



## 1. Introduction

The contamination of groundwater by hazardous organic chemicals and the associated risks to human health and the environment are issues of great importance. One of the most critical issues associated with hazardous waste sites is the potential presence of immiscible-liquid contamination in the subsurface. Immiscible liquids, such as chlorinated solvents, creosote, coal tars, and fuels, once introduced into the subsurface become entrapped, and serve as long-term sources of contamination. The 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).

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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; Busseau, 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 Illangasakare, 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 Fig. 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 Fig. 1b), from which the mass-flux-reduction/mass-removal relationship can be obtained directly. The curve in the lower right-hand section of Fig. 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 (Fig. 1b and c). 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 Fig. 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 (Fig. 1b and c), 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. 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