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Mass-removal and mass-flux-reduction behavior for idealized source zones with hydraulically poorly-accessible immiscible liquid

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Abstract

A series of flow-cell experiments was conducted to investigate aqueous dissolution and mass-removal behavior for systems wherein immiscible liquid was non-uniformly distributed in physically heterogeneous source zones. The study focused specifically on characterizing the relationship between mass flux reduction and mass removal for systems for which immiscible liquid is poorly accessible to flowing water. Two idealized scenarios were examined, one wherein immiscible liquid at residual saturation exists within a lower-permeability unit residing in a higher-permeability matrix, and one wherein immiscible liquid at higher saturation (a pool) exists within a higher-permeability unit adjacent to a lower-permeability unit. The results showed that significant reductions in mass flux occurred at relatively moderate mass-removal fractions for all systems. Conversely, minimal mass flux reduction occurred until a relatively large fraction of mass (>80%) was removed for the control experiment, which was designed to exhibit ideal mass removal. In general, mass flux reduction was observed to follow an approximately one-to-one relationship with mass removal. Two methods for estimating mass-flux-reduction/mass-removal behavior, one based on system-indicator parameters (ganglia-to-pool ratio) and the other a simple mass-removal function, were used to evaluate the measured data. The results of this study illustrate the impact of poorly accessible immiscible liquid on mass-removal and mass-flux processes, and the difficulties posed for estimating mass-flux-reduction/mass-removal behavior.

Keywords: Transport; DNAPL; Contamination; Groundwater

1. Introduction

One of the most critical issues associated with hazardous waste sites is the potential presence of immiscible-liquid source zones in the subsurface. Immiscible liquids serve as long-term sources of subsurface contamination, and their presence can greatly impact the costs and time required for site remediation. In fact, the presence of dense nonaqueous-phase liquids (DNAPLs) is usually considered the single most important factor constraining the risk assessment, characterization, and cleanup of organic-contaminated sites (NRC 1994, 1997, 1999, 2000, 2005; ITRC, 2002; EPA, 2003). The contaminant mass flux or mass discharge emanating from a source zone, also referred to as the source strength or source function, is recognized as a primary determinant of the risk associated with a contaminated site. Concomitantly, the reduction in mass flux achieved with a specific level of source-zone mass removal (or mass depletion) is a key metric for evaluating the effectiveness of a source-zone remediation effort. Thus, there is great interest in characterizing, estimating, and predicting relationships between mass flux reduction and mass removal.

The fundamental concept of contaminant mass flux, its relationship to mass-removal processes and source-zone

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properties, and its impact on risk has long been established (e.g., Fried et al., 1979; Pfannkuch, 1984). The impact of subsurface heterogeneity and non-uniform immiscible-liquid distribution on mass-removal behavior and associated aqueous-phase concentrations (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; Blue et al., 1998; Powers et al., 1998; Unger et al. 1998; Broholm et al., 1999; Brusseau et al., 1999, 2000, 2002, 2007; Frind et al., 1999; Oostrom et al., 1999; Zhang and Brusseau, 1999; Nambi and Powers, 2000; Saba and Illangasekare, 2000; Zhu and Sykes, 2000; Rivett et al., 2001; Sale and McWhorter, 2001; Jayanti and Pope, 2004; Lemke et al., 2004; Parker and Park, 2004; Phelan et al., 2004; Soga et al., 2004; Falta et al., 2005; Jawitz et al., 2005; Rivett and Feenstra, 2005; Fure et al., 2006; Lemke and Abriola, 2006). 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 (e.g., 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; Falta et al., 2005; Jawitz et al., 2005; NRC, 2005; Fure et al., 2006; Lemke and Abriola, 2006; Brusseau et al., 2007).

Three simplified, prototypical relationships between mass flux reduction and mass removal useful for comparative discussion are illustrated in Fig. 1A. Such 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 of Fig. 1A represents the relationship for a system governed by relatively ideal mass-transfer behavior, wherein mass removal is relatively efficient, as illustrated by the corresponding contaminant elution curve presented in Fig. 1B. Because mass removal is relatively efficient, 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 behavior (e.g., rate-limited dissolution, by-pass flow phenomena), wherein mass removal is relatively inefficient (Fig. 1B), 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).

There are two general approaches to characterizing the relationship between mass flux reduction and mass removal, end-point analysis and time-continuous analysis. End-point analysis is based on comparing mass fluxes measured before and after a source-zone remediation effort. For example, Suchomel and Pennell (2006) conducted flow-cell experiments to examine the impact of surfactant-enhanced solubilization on mass-flux-reduction/mass-removal behavior. Several examples of end-point analyses based on field studies have recently been reported (Brooks et al., 2004; Childs et al., 2006; McGuire et al., 2006; Brusseau et al., 2007). The end-point analysis approach provides critical information for evaluating the impact of a source-zone remediation effort on mass flux. However, the single-snapshot characterization of mass-flux-reduction/mass-removal behavior obtained with this approach is constrained in that the antecedent behavior remains indeterminate. Conversely, as the name implies, time-continuous analysis incorporates a "complete" characterization of the relationship between mass flux reduction and mass removal, from the initial stages of mass removal to a given end point. This approach provides a more robust characterization of mass-flux behavior as a function of mass removal. Direct, experiment-based investigations of time-continuous mass-flux-reduction/mass-removal behavior are just now beginning to be reported. For example, Fure et al. (2006) 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) report a time-continuous mass-flux-reduction/mass-removal relationship for a large chlorinated-solvent contaminated Superfund site in Tucson, AZ.

An expert-panel workshop was convened recently to discuss the research needs for characterization and remediation of DNAPL source zones (SERDP, 2006). The panel noted that significant uncertainty remains with respect to the impact of source-zone architecture and mass-transfer dynamics on mass-removal and mass-flux-reduction behavior. One issue that was particularly emphasized was the behavior of systems in which immiscible liquid is associated with regions of the subsurface that are poorly accessible to flowing groundwater (i.e., that are "flow limited"). For example, the majority of the chlorinated-solvent contaminated sites in the US are several to many decades old. For such sites, it would generally be expected that a large fraction of the more hydraulically accessible immiscible-liquid mass has been removed in the intervening time (thus producing the associated aqueous contaminant plumes). For another example, source-zone remediation efforts are generally considered to be able to remove or deplete only a portion of the total contaminant mass, and it is likely that the majority of mass removed is primarily that which is more accessible. Thus, for both examples (i.e., both unremediated and remediated source zones), a "residual" mass of immiscible liquid will typically remain in the source zones, and this mass will most likely be associated with