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Characterization and Remediation of Chlorinated Volatile Organic Contaminants in the Vadose Zone: An Overview of Issues and Approaches

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Abstract

Contamination of vadose-zone systems by chlorinated solvents is widespread, and poses significant potential risk to human health through impacts on groundwater quality and vapor intrusion. Soil vapor extraction (SVE) is the presumptive remedy for such contamination, and has been used successfully for innumerable sites. However, SVE operations typically exhibit reduced mass-removal effectiveness at some point due to the impact of poorly accessible contaminant mass and associated mass-transfer limitations. Assessment of SVE performance and closure is currently based on characterizing contaminant mass discharge associated with the vadose-zone source, and its impact on groundwater or vapor intrusion. These issues are addressed in this overview, with a focus on summarizing recent advances in our understanding of the transport, characterization, and remediation of chlorinated solvents in the vadose zone. The evolution of contaminant distribution over time and the associated impacts on remediation efficiency will be discussed, as will the potential impact of persistent sources on groundwater quality and vapor intrusion. In addition, alternative methods for site characterization and remediation will be addressed.

INTRODUCTION

Chlorinated volatile organic compounds (e.g., trichloroethene, tetrachloroethene, carbon tetrachloride), or CVOCs, are ubiquitous subsurface contaminants. Characterization and remediation of sites contaminated by these organic immiscible liquids is complicated by a host of issues (e.g., NRC, 1994, 1999, 2004). One issue of increasing prominence is CVOC contamination of vadose zones. This is particularly relevant for regions such as the Southwest US wherein deep (~30–300 m) vadose-zone systems are present.

CVOC contamination located in the vadose zone (below the direct soil contact zone) does not have a direct human-health exposure risk. However, there are two primary human-health-related concerns associated with sites that contain vadose-zone CVOC sources, i.e., wherein the solvent itself is (or was) present in the vadose zone (Figure 1). First, discharge

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of contaminant vapor from the vadose-zone source may impact the underlying groundwater. This process is illustrated by the results of numerical simulations presented in Figure 2, wherein is shown the groundwater contaminant plume generated solely by vapor discharge from a CVOC source in the vadose zone (Carroll et al., 2012). Such contamination can contribute to overall risk posed by the site, and delay attainment of groundwater cleanup goals. Second, contaminant vapor from the vadose-zone source may migrate to the land surface and transfer into buildings, thereby causing vapor intrusion and creating another source of exposure risk. Vapor intrusion into buildings is of particular importance for CVOCs. The current version of EPA’s Subsurface Vapor Intrusion Guidance (EPA, 2002) provides technical and policy recommendations on determining if the vapor intrusion pathway poses an unacceptable risk to human health at waste sites.

Quantification of potential risks must include evaluation of all exposure pathways, as mediated by transport and contaminant attenuation processes. A conceptual illustration of the potential migration pathways from a persistent vadose-zone source to both groundwater and the land surface (and indoor air) is presented in Figure 1. There are several contaminant storage and attenuation processes that may impact the transport and fate of CVOCs in both the vadose zone and groundwater. In addition, note that the exposure pathway from the vadose zone to groundwater requires mass transfer across the capillary fringe and water table. Similarly, the vapor-intrusion pathway requires mass transfer across the interface between the land surface and the building foundation. Figure 1 also illustrates that groundwater contaminant plumes can serve as a source of contamination to the vadose-zone, which may impact the land surface and cause vapor intrusion.

Volatile contaminants are typically present in the vadose zone because they were disposed as solutes in aqueous waste or as a non-aqueous-phase-liquid (NAPL) waste at or near the land surface. The amount of contamination present in the vadose zones of sites contaminated by CVOCs can be quite large, approaching many thousands to tens of thousands of kg (see Table 1). Thus, the vadose zone can serve as a long-term source of CVOC contamination to groundwater and the land surface.

Currently, the decision to remediate a vadose-zone source is typically based on assessing the current impact of the vadose-zone source on groundwater or vapor intrusion. Concomitantly, setting appropriate vadose-zone remediation goals once the decision is made, as well as evaluating attainment of these remediation goals, requires evaluating the longer-term impact of the vadose-zone source on groundwater or vapor intrusion. Characterizing the impacts of vadose-zone contaminant sources requires an understanding of source-zone dynamics and vapor-phase contaminant transport.

A significant body of research has been developed over the past two decades concerning the behavior, characterization, and remediation of organic-liquid source zones. This research has established that the configuration and distribution of contamination, in concert with the physical and biogeochemical properties of the subsurface, exert a significant control on mass-transfer, transport, and mass-removal processes. In addition, the contaminant configuration and distribution change with time, and the rate and magnitude of change can be enhanced by remedial actions.

The impact of source-zone dynamics on remedial actions is such that, typically, rates of mass removal or reduction slow with time, eventually reaching a point at which the operation becomes ineffective. This phenomenon is generally associated with the presence of contaminant that is poorly accessible to the remedial vector (e.g., advecting soil-gas for soil vapor extraction). Standard practices for assessing performance of remedial operations do not effectively account for source-zone dynamics and the associated impacts on system conditions.

These issues are of particular relevance for soil vapor extraction (SVE), which is the most widely used remedy for vadose-zone systems contaminated by CVOCs. SVE has been the presumptive remedy for CVOCs in the vadose zone for approximately 20 years (EPA, 1993), and has been applied successfully at many sites. However, SVE operations typically experience reduced effectiveness at some point, at which time issues of remediation-performance assessment and evaluation of closure and alternative-action selection become prominent. Addressing these issues is critical to successful long-term management of sites with vadose-zone CVOC contamination.

The purpose of this paper is to provide an overview of the issues associated with CVOCs in the vadose zone, and to summarize recent advances in our understanding of the transport, characterization, and remediation of CVOCs in the vadose zone. The evolution of CVOC contaminant distribution over time and the associated impacts on remediation efficiency will be discussed, as will the potential impact of persistent sources on groundwater quality and vapor intrusion. In addition, alternative methods for site characterization and remediation will be addressed. While this overview is focused on CVOCs, much of the material presented is also pertinent to other volatile and semi-volatile contaminants such as hydrocarbons.

SVE OPERATIONS AND MASS-REMOVAL EFFECTIVENESS

SVE Operations

The application of soil vapor extraction, or alternatively soil venting, to remove volatile organic contamination from water-unsaturated (vadose-zone) systems began in the early 1980’s (e.g., Thornton and Wootan, 1982; Marley and Hoag, 1984). SVE was adapted quickly, and within a decade had become the default remedy for CVOCs in the vadose zone. Several guidance documents have been developed covering the design, operation, and performance assessment of SVE systems (e.g., EPA, 1991; EPA, 1995a; EPA, 1998a; AFCEE, 2001; EPA, 2001, USACE, 2002).

Data from several SVE operations were collected as part of this review, and are tabulated in Table 1. The sites were selected based on data accessibility, with four data sets reported in EPA case-study reports, one representing a small-scale controlled field study conducted at the Borden research site, and the others available through the authors’ contacts. The sites represent a wide range of system conditions, including size of treatment domain, extent of contamination, porous-medium properties, operation time, and pore-volume throughput. Inspection of the data (see Figures 3 and 4) reveals that mass-removal rates decreased by approximately 1.5 to 3 orders of magnitude during the operation period. The initial rates of mass removal exhibit significant variation, ranging from approximately 10 to 1500 kg/d.

The size of the treatment domain, number of wells used, and the SVE extraction rate vary widely among the sites (Table 1), making it difficult to directly compare mass-removal behavior. The data presented in Figure 3 were re-plotted as described in the figure caption as relative contaminant mass discharge and relative pore-volume discharge (see Figure 5). It is observed that contaminant mass discharge starts to decrease soon after startup for most, but not all, of the sites. In addition, there is a large range in the rates of decrease.

As illustrated by the example data sets, SVE tends to be highly effective for extraction of CVOC mass during the early stages of operation, but exhibits reduced effectiveness at later times. Factors contributing to reduced effectiveness are discussed in the following section. The reductions in treatment efficiency typically observed for SVE operations necessitate consideration of changes in system operation or closure. Thus, effective long-term management of SVE operations requires that data be obtained periodically during the remediation life cycle to update the conceptual site model, including characterization of the location and distribution of the persistent sources of contamination and the dominant transport processes.

Factors Affecting SVE Operations and Mass Removal

Vapor-phase advection is the predominant transport and mass-removal mechanism for SVE. However, CVOCs not only reside in the gas-filled pore space of the vadose zone, but are also present in the aqueous phase (dissolved in pore-water), are sorbed to sediment grains, and are often present as immiscible-liquid phases. Hence, mass removal via SVE is mediated significantly by inter-phase mass transfer processes, including evaporation of the NAPL into the soil atmosphere, dissolution of the NAPL into pore-water, volatilization, and sorption-desorption. In addition, SVE-effected mass removal is also influenced by the material-property heterogeneity inherent to subsurface environments. For example, the permeability-distribution field will mediate the gas-flow field as well as influence the initial distribution of contamination. Furthermore, physical and biogeochemical heterogeneity can impart spatial variability to the magnitudes and rates of mass-transfer and transformation processes. In total, the configuration of the source with respect to permeability and contaminant distributions (source-zone architecture) in combination with the various mass-transfer and transformation processes and their potential spatial and temporal variability (source-zone dynamics) mediate the operational behavior of SVE systems. In turn, operation of the SVE system influences the conditions of the source zone.

The relationship between source-zone status in the vadose zone and SVE operation is illustrated in Figure 6, which depicts the typical three main stages of the life-cycle of a contaminated site undergoing SVE remediation. A similar conceptualization was presented recently for groundwater systems (Stroo et al., 2012). The evolving contamination distribution within the vadose-zone source is coupled with a generalized time-series plot of SVE-effluent concentrations and cumulative CVOC mass removal. The figure illustrates the behavior typically observed for SVE systems, wherein effluent concentrations are relatively high and constant during the early stage of operation, and concomitantly mass-discharge and mass-removal rates are relatively large. At some point, effluent concentrations and mass-removal rates start to decline, at first relatively rapidly and ultimately asymptotically, to significantly lower values. These transitions are related to changes in the configuration and distribution of contaminant in the source zone, which mediate the accessibility of the contaminant to remediation. Generally, hydraulic- and pneumatic-based remedies preferentially remove contaminant mass from the more accessible (e.g., higher permeability) regions. Thus the contamination remaining after a period of remediation typically comprises a greater fraction of poorly accessible mass relative to initial conditions. Such mass, for example, may be located within or adjacent to low-permeability regions, or may be associated with leaking waste containers (e.g., buried drums). The time frames associated with each of the stages can vary greatly among sites, and will depend upon site-specific conditions. For example, stage-1 behavior (high, steady-state effluent concentrations) was exhibited for just a few months for most of the sites for which data are presented in Figure 3. Conversely, stage-1 behavior was observed for several years for the sites represented by the data sets presented in Figure 4a–c.

The reduction in mass-removal effectiveness typical to SVE, and its association with the development of mass-transfer limitations, was recognized soon after wide-scale application (e.g., Johnson et al., 1990; Brusseau, 1991; Kearl et al., 1991; Rathfelder et al., 1991; Silka et al., 1991; Crotwell et al., 1992; DiGiulio, 1992; Gierke et al., 1992; Ho and Udell, 1992; Benson et al., 1993; Armstrong et al., 1994). Mass-transfer limitations can be produced by a number of factors, including rate-limited evaporation of organic liquid, compositional effects of multi-component organic liquids, rate-limited and/or nonlinear desorption, rate-limited volatilization (gas/water partitioning), diffusion between lower and higher permeability media, nonuniform contaminant distributions and associated dilution effects, and other source conditions (e.g., leaking waste containers). All of these factors in some way limit the accessibility of the contamination to the advecting gas phase, thereby reducing the amount of contaminant removed per volume of gas extracted compared to ideal conditions.

A significant amount of research was conducted in the 1990’s examining the kinetics of interphase mass transfer and associated impacts on vapor transport (e.g., Brusseau, 1991; Rathfelder et al., 1991; Gierke et al., 1992; Ho and Udell, 1992; Cho et al., 1993; Armstrong et al., 1994; Conklin et al., 1995; Wilkins et al., 1995; Fischer et al., 1996; Lingineni and Dhir, 1996; Poulsen et al., 1996; Nadim et al., 1997; Popovicova and Brusseau, 1998; Yoon et al., 2002). For example, several researchers have reported kinetic limitations during evaporation, the transfer of compounds from the organic immiscible liquid phase to air. Additionally, several researchers have suggested similar kinetic limitations during mass transfer between the air and water phases (i.e., dissolution into water and volatilization into air). These mass-transfer limitations are generally believed to be caused by boundary-layer diffusion from an essentially immobile phase (e.g., water or organic liquid) into a mobile phase (e.g., air). An enormous body of research exists concerning the sorption of organic compounds by soils and sediments (see Brusseau and Rao, 1989 and Luthy et al., 2003 for comprehensive reviews). This research has shown that desorption of organic compounds from geomedia is rate limited and nonlinear for many cases. The significance of potential rate-limited interphase mass transfer depends on the characteristic time of mass transfer (which depends on the configuration of the phases and the associated interface) and the residence time associated with the advective gas flow. The results of several investigations indicate that factors related to the composition of multiple-component organic liquids may also play a role in the development of mass-transfer-limited conditions (e.g., Johnson et al., 1990; Benson et al., 1993; Liang and Udell, 1999; Harper et al., 2003; Wang et al., 2003; Abriola et al., 2004; McColl et al., 2008; Carroll et al., 2009).

The results of multiple investigations have demonstrated the impact of material-property heterogeneity (e.g., spatially variable permeability), nonuniform contaminant distributions, and associated diffusion-limited mass transfer on vapor-phase mass removal (e.g., Johnson et al., 1990; Brusseau, 1991; Kearl et al., 1991; Silka et al., 1991; DiGiulio, 1992; Benson et al., 1993; Johnson and Ettinger, 1994; Rodriguez-Maroto et al., 1994; Poulsen et al., 1996; Popovicova and Brusseau, 1997; DiGiulio et al., 1998; Kaleris and Croise, 1999; Massmann et al., 2000; Switzer et al., 2004; Stauffer et al., 2007; Switzer and Kosson, 2007). Gas will flow preferentially through zones of higher air permeability, effectively bypassing lower-permeability regions. Thus, removal of contamination present within lower-permeability regions often occurs predominantly by diffusion. Nonuniform distributions of water and organic liquid can exacerbate nonuniform flow behavior and enhance diffusive mass-transfer constraints. For example, water contents may often be higher for lower-permeability media compared to adjacent higher-permeability zones. This differential in water contents would further enhance by-pass flow via relative-permeability effects. In addition, diffusion limitations would increase greatly as diffusion in the aqueous phase, which is orders-of-magnitude slower than gas-phase diffusion, becomes more prominent. Given the large contrasts in permeability and water content typical to most field sites, diffusion-limited mass transfer from lower to higher permeability regions is likely to be a prevalent and dominant factor for CVOCs in the vadose zone. Furthermore, its impact is likely to increase as SVE proceeds and contaminant mass is removed primarily from higher-permeability media.

The impacts of system conditions on SVE-operation effectiveness are illustrated by the results of a small-scale field study conducted at the Borden test site (Thomson and Flynn, 2000). A block (9×9×3.3 m) of subsurface was isolated with sheet piling, and tetrachloroethene was injected to create a NAPL source of known volume. An SVE system was installed and operated for approximately one year. The effluent tetrachloroethene concentration and extraction rate were monitored with relatively high density. The mass removal rate versus time profile is shown in Figure 3A. It would be anticipated that conditions for mass removal by SVE would be closer to optimal at the Borden site compared to most other sites given the site properties (low degree of permeability variability, freshly contaminated). However, significant mass-removal constraints were observed, as discussed by the authors.

CHARACTERIZATION OF CONTAMINANT DISTRIBUTIONS AND CONTAMINANT MASS DISCHARGE

Characterization of CVOC Contaminant Mass and Distribution

The characterization of CVOC contaminant mass and distribution in the vadose zone may include sampling and analysis of one or all phases (i.e., bulk sediment, soil-water, soil-gas, organic liquid) in which CVOCs can reside. Sampling of pore water for CVOCs can be challenging due to low water contents of soils and the impact of suction for extraction on volatilization of CVOCs (e.g., Fares et al., 2009). Sampling of the organic-liquid phase has similar challenges, and is also limited by the general difficulty in locating such phases.

Sediment sampling, accomplished by a number of methods, in conjunction with solvent-based extraction is a standard method for characterizing CVOC contamination. The EPA *Soil Screening Guidance* (EPA, 1996) describes the process for collecting and processing samples, calculating soil screening levels, and assessing the results. A major advantage of this method is that it provides a relatively accurate, direct measurement of total contamination associated with the sediment (sorbed by sediment grains and/or organic liquid). A primary disadvantage is the point-specific nature of the method and the uncertainty associated with spatial variability (e.g., Rossabi et al., 2003; Feenstra, 2005). As a result, it is typically cost prohibitive to use this method for quantitative source-zone characterization.

Because the vapor phase provides an effective medium for sample collection in the vadose zone, and soil-gas concentrations can be related to contaminant concentrations in other phases, characterization of CVOC sources in the vadose zone has focused on monitoring of soil gas (vapor-phase contaminant concentrations) as in traditional soil-gas surveys. While this method can provide useful information, it has obvious limitations (e.g., Marrin, 1988; Marrin and Kerfoot, 1988; DeGroot and Lutenegger, 1998; McAlary et al., 2009). For example, due to practical and cost limitations on the number of sampling points, the soil-gas survey method often does not provide data of sufficient resolution to accurately characterize the spatial distribution of the contaminant, particularly in the vertical dimension. Second, some portion of contaminant mass in the vadose zone is usually associated with regions that are poorly accessible (e.g., low-permeability zones). Characterizing mass associated with these regions may often be problematic with the soil-gas survey method. Third, the soil-gas survey method is typically not able to characterize the temporal variability of mass-transfer processes. As a result of these and other issues, the soil-gas survey method is typically influenced by a large degree of uncertainty with respect to characterizing source location and strength. Thus, its utility for supporting risk assessment and evaluation of SVE performance can be limited in some cases.

Some of the limitations noted above were illustrated in the study conducted by Thomson and Flynn (2000). As part of their project, they directly compared bulk-soil sampling and soil-gas sampling for characterization of a persistent CVOC source after cessation of SVE operations. They observed limitations of soil-gas surveys for this application. In some cases, soil-gas concentrations were persistent in areas where soil sampling indicated that significant mass removal occurred. Additionally, in areas where contaminant mass was inaccessible to SVE removal and thus remained present in the vadose zone (i.e. in low permeability/high moisture zones), the observed soil-gas concentrations decreased, which incorrectly indicated removal of mass.

Partitioning tracer tests (PTT), wherein the magnitude of retardation observed for tracers that reversibly partition to organic liquid is used to estimate organic-liquid volume, are an alternative method for source-zone characterization. Gas-phase PTTs are used specifically in the vadose zone to characterize the quantities and distributions of organic liquid and water (Brusseau et al., 1997a; Deeds et al., 1999a, 1999b; Mariner et al., 1999; Nelson et al., 1999; Whitley et al., 1999; Brusseau et al., 2003a,b; Carlson et al., 2003; Keller and Brusseau, 2003; Peng et al., 2005; Simon and Brusseau, 2007). The PTT method provides measurements at a scale that is much larger than that associated with point-measurement methods. This is an advantage for economical characterization of relatively large areas. In addition, the scale of measurement can be tailored to the sampling objectives by modifying the tracer sampling network (e.g., distances between wells). Potential constraints and limitations associated with the tracer methods have been documented, such as difficulty in measuring all organic liquid or water in poorly-accessible domains. In addition, the PTT method does not characterize contaminant in the dissolved and sorbed phases. These factors are especially significant for the later stages of SVE operation. Also, this method provides estimates of contaminant mass, the application of which as a cleanup metric has been shown to be problematic (as noted below).

The two standard methods for characterizing CVOCs in the vadose zone are based on the collection of soil-gas and soil (sediment) samples to determine contaminant concentrations. As discussed, there are several factors that can limit the effectiveness of these methods. In addition, as will be discussed further below, cleanup objectives based on contaminant concentrations have been shown to be problematic. Hence, developing improved methods to characterize sources in the vadose zone was noted as a critical need during a recent review of research needs for reducing the uncertainty of DNAPL source-zone remediation (SERDP, 2006).

The Use of Contaminant Mass Discharge for Characterization, Risk Assessment, and Remediation Evaluation

Measurement of contaminant mass flux, or mass discharge (also referred to as the source strength or source function), has recently gained significant interest for source-zone characterization, risk assessment, and remediation-performance evaluation. As discussed above, characterizing the impact of vadose-zone contaminant sources on groundwater or vapor intrusion (e.g., risk assessment) requires determination of the contaminant mass discharge from the source. In addition, contaminant mass discharge is also now recognized as a key metric for assessing remediation performance. Contaminant mass discharge is a measure of both mass removal from the source zone (illustrative of source longevity) and mass delivery from the source zone to the vadose zone (potential impact to soil gas and groundwater). As such, mass discharge inter-relates source-zone dynamics and contaminant disposition in the vadose zone.

The fundamental concept of contaminant mass discharge, its relationship to mass-removal processes and source-zone properties, and its impact on risk have long been established (e.g., Fried et al., 1979; Pfannkuch, 1984). Practical application of contaminant mass discharge for site characterization and assessment began primarily in the 1990’s (e.g., Rosenbloom et al., 1993; Freeze and McWhorter, 1997; Schwarz et al., 1998; DiGiulio et al., 1999). Interest in its measurement and application has since grown during the past decade from these initial applications (e.g., Einarson and Mackay, 2001; ITRC, 2002; Rao et al., 2002; Bockelmann et al., 2003; EPA, 2003a; Newell et al., 2003; Brooks et al., 2004; Soga et al., 2004; SERDP, 2006; Brusseau et al., 2007, 2011a,b; DiFilippo and Brusseau, 2008; ITRC, 2010). To date, research has focused on evaluating mass discharge for groundwater sources, and only a few studies have directly evaluated mass-discharge behavior associated with sources in the vadose zone (e.g., Rosenbloom et al., 1993; Poulsen et al., 1996; DiGiulio et al., 1999; Jellali et al., 2003; Truex et al., 2009; Brusseau et al., 2010; Oostrom et al., 2010; Stauffer et al., 2011; Carroll et al., 2012, 2013).

One approach to characterizing contaminant mass discharge is based on the use of mathematical models. Employing advanced, distributed-process, three-dimensional numerical models to simulate fluid flow and transport and fate of contaminants is a powerful method that can support robust decision-making regarding risk assessment and implementation, optimization, and closure of remediation systems (e.g., Abreu and Johnson, 2005; Stauffer et al., 2007, 2011; Bozkurt et al., 2009; Yu et al., 2009; Oostrom et al., 2010). However, the use of such models involves significant data requirements and user expertise, such that their application may be impractical for many hazardous waste sites. In lieu of advanced models, methods employing simpler models, often termed screening models, can be used to estimate contaminant concentrations or contaminant mass discharge. For example, the mass discharge from a vadose-zone source to groundwater has been estimated using such modeling, with the results used as the basis for assessing the need for vadoze-zone remediation (e.g., Rosenbloom et al., 1993; DiGiulio et al., 1999; Truex et al., 2009). Similarly, assessing potential risk for vapor-intrusion issues is routinely based on using screening models to estimate the impact of contaminant sources in the vadose zone (and groundwater) on resultant concentrations in indoor air (e.g., Johnson and Ettinger, 1991; EPA, 2002; Hers et al., 2002; Johnston and Gibson, 2011). Screening models can be useful for first-order analysis, but can be subject to significant uncertainty. The degree of uncertainty is mediated primarily by the quality of the input data, which is typically obtained from sediment or soil-vapor sampling (which have their own uncertainties as discussed), and the relevance of the factors and processes considered and ignored.

The mass removed during operation of an SVE system is a measure of vapor-phase contaminant mass discharge for the source. Similarly, contaminant mass discharge (CMD) tests, which involve measuring flow rates and effluent contaminant concentrations during extended pumping of one or more extraction wells (Brusseau et al., 1999, 2007; Brusseau et al., 2011a), provide a measure of contaminant mass discharge. However, the rates of mass removal produced under the induced-gradient conditions associated with these methods are likely to be greater than, and thus not representative of, values associated with natural conditions. The concentration or mass-discharge data collected during such operation can however be used to ground-truth a mathematical model, which can then be used to produce simulations for natural conditions (Brusseau et al., 2007; Stauffer et al., 2011). The data can also be used to evaluate mass-transfer processes and mass-removal behavior, as will be discussed in a following section. In addition, mass-depletion functions can be fit to such data to produce estimates of initial contaminant mass present in the treatment domain (Butcher and Gauthier, 1994; Basu et al., 2009; Brusseau et al., 2013).

A field-based method, the vapor-phase cyclic contaminant mass discharge (CCMD) test, was recently developed that uses vapor-phase contaminant concentration data collected during cyclic operation of one or more vapor-extraction wells to characterize mass discharge associated with both induced-gradient and natural-gradient conditions (Brusseau et al., 2010). The CCMD test consists of three phases, an extended initial extraction phase (which is identical to a standard CMD test), a rebound phase, and a second, shorter extraction phase. In brief, an initial extraction phase is implemented wherein concentrations of contaminant in the effluent gas are monitored. The extraction continues until quasi steady state is attained with respect to effluent concentrations. At this point, the extraction is stopped, and the system is monitored to characterize potential rebound of vapor-phase concentrations. A second, shorter-term, extraction phase is then implemented once concentrations have stabilized. Data collected during the initial stage of vapor extraction are used to quantify the maximum mass discharge obtained under induced-gradient conditions. Data collected at the end of the extraction phase (during the steady state condition) are used to quantify the minimum induced-gradient mass discharge. These data can be used to help evaluate SVE performance for sites that have active SVE operations, or to provide data for design and implementation of a new SVE system. The contaminant mass discharge associated with the source under natural-gradient conditions (i.e., during the rebound period) is determined from the total mass of contaminant removed for the first gas-pore-volume extracted during the second extraction phase (i.e., after the rebound period). This mass is presumed to represent primarily mass that transferred from the source domains during the preceding non-extraction period. This mass is divided by the time required to attain stable concentrations during the non-extraction phase to determine mass discharge (mass per time). SVE operational data collected at the Department of Energy’s Hanford site were used by Brusseau et al. (2010) to illustrate the approach.

The CCMD test has several advantages, including providing direct measures of contaminant mass discharge that span a large domain. One disadvantage is the lack of spatially discrete information provided under standard operation. The location and spatial distribution of contaminant sources can be characterized to an extent by conducting a series of shorter-term standard CMD tests in different sections of the site. For example, the concentration-time signal observed for a specific extraction well will be mediated by the location of that well with respect to the source (see Figure 7). Thus, the signals obtained for the tests can be interpreted to locate the source (taking into account initial conditions and other relevant factors). This approach was applied recently by Carroll et al. (2013) at the DOE Hanford site. The results of the multi-location CMD tests confirmed a heterogeneous distribution of permeability and contaminant mass discharge throughout the vadose zone. The trends in mass discharge were analyzed to determine the location and extent of the primary source zone, which coincided with an extensive lower-permeability unit at the site.

The tests discussed above can be further modified by collecting depth-specific data at multiple monitoring wells during the extraction and/or rebound phases of the test (Brusseau et al., 2011c). This vapor-flux tomography method allows determination of discrete contaminant mass discharge distributions in three dimensions. This approach is analogous to the hydraulic and pneumatic tomography tests that have been developed to characterize permeability distributions (e.g., Gottlieb and Dietrich 1995; Paillet and Morin 1997; Yeh and Liu 2000). The vapor-flux tomography method is currently being tested at the laboratory and field scale. The information provided by these tests is useful for evaluating the performance of SVE operations, and to support decisions concerning system alteration or closure based on risk assessments of the impact of vadose-zone sources on groundwater contamination or vapor intrusion.

Characterizing Mass-Transfer Constraints

As discussed above, mass-transfer limitations can significantly reduce the effectiveness of SVE operations. Hence, it is valuable to understand if the target system will be or is influenced by such processes. One direct means by which to evaluate the potential for the development of mass-transfer limitations is to conduct a SVE pilot study in a manner that would enhance potential limitations (DiGiulio, 1992). The CMD test discussed above can also be used to assess mass-transfer constraints. With this approach, the resultant contaminant-elution curve obtained during the extraction and non-extraction phases can be examined for the appearance of specific landmarks, such as length of the steady-state stage, occurrence of an asymptote, and occurrence of a rebound. Concentration and mass-removal data collected during CMD tests and SVE operations can be analyzed with appropriate mathematical models to further evaluate mass-transfer constraints. The impact of vertical variability in permeability and contaminant concentrations on potential SVE mass-extraction rates can be evaluated by conducting pilot-scale SVE tests that incorporate depth-specific sampling (e.g., Widdowson et al., 1997; USACE, 2002; EPA, 2003b).

Vapor-extraction rebound testing, characterizing the response (rebound or lack thereof) in concentrations after a cessation of extraction, can serve as an alternate or additional source of information to help characterize mass-transfer constraints. Cyclic operation (flow interruption or pulsed pumping) of a fluid-extraction system, such as pump and treat or SVE, has been used for some time to evaluate the occurrence of rate-limited mass transfer processes (e.g. Brusseau et al. 1989, 1997b; Harvey et al. 1994; USACE 2002; Switzer et al. 2004). In addition, rebound data have been analyzed to provide information on contaminant source location (e.g., Switzer et al. 2004; Switzer and Kosson 2007). For example, observation of rapid, large rebound is likely indicative that the monitoring location is near an area that has significant contaminant mass discharge that is under mass-transfer-limited conditions.

Clearly, mass transfer at the system boundaries, the water table or land surface, is central to the impact of vadose-zone sources. Mass transfer at the land surface or into buildings can be characterized by collecting vapor samples adjacent to the land surface or within structures to evaluate the potential for vapor intrusion or other land-surface impacts. There are a host of issues that complicate such methods (e.g., EPA, 2002; ITRC, 2007). Similarly, groundwater and vapor samples can be collected near the water table to characterize mass transfer across (in either direction) the capillary fringe (e.g., Ronen et al., 2005). A comparison is often made between the observed soil-gas concentrations just above the water table and calculated vapor concentrations at equilibrium (based on Henry’s Law) with the adjacent groundwater concentrations. Mass transfer from the water table to the vadose zone may be indicated if measured soil-gas concentrations are lower than the predicted equilibrium concentrations.

Conversely, mass transfer from the vadose zone to groundwater may be indicated if the reverse is true. At sites with thick capillary fringes (i.e., in fine-grained materials), groundwater concentrations may be somewhat isolated from the vadose zone due to the relatively slow diffusion rate through this zone, particularly if there is significant downward moisture infiltration. If it is suspected that contaminant vapors are emanating from the capillary fringe and water table, the use of flow and concentration profiling may be conducted to confirm this conclusion.

Characterizing the Relationship between Reductions in Contaminant Mass Discharge and Reductions in Mass

As previously discussed, concentrations and mass discharge of contaminants will decline throughout operation of an SVE system or other remedial action as contaminant mass is removed. The degree and rate of decrease are central to remediation effectiveness and risk reduction, and are controlled by site conditions. Examination of mass-removal behavior is facilitated by evaluating changes in contaminant mass discharge directly as a function of the associated reduction in contaminant mass (e.g., Rao et al., 2002; Jayanti and Pope, 2004; Phelan et al., 2004; Brusseau et al., 2007).

The reduction in contaminant mass discharge (CMDR) as a function of the mass reduction (MR) is a reflection of source conditions and of mass-transfer processes occurring within the system. Thus, this relationship serves as a defining characteristic for a given system, and is useful for analysis and interpretation of mass-removal behavior and assessment of remediation performance. CMDR-MR relationships have been developed based on mathematical modeling and laboratory experiments that determine time-continuous profiles of CMD and mass reduction. However, the typical lack of robust measures of initial contaminant mass unfortunately precludes its development for many field sites. Thus, only a very few time-continuous CMDR-MR relationships have been reported to date for field systems (Brusseau et al., 2007; DiFilippo and Brusseau, 2008; Brusseau et al., 2013).

One situation wherein the CMDR-MR relationship may be determined with relatively lower uncertainty is for cases wherein SVE operations have been completed or are near completion, and post-closure characterization indicates minimal remaining contaminant mass. Such was the case for a few of the sites included in Table 1. An illustration of a CMDR-MR relationship is presented in Figure 8 for the Verona site, with the values normalized relative to initial contaminant mass discharge (CMD) and initial contaminant mass. CMDR-MR relationships have been reported for groundwater systems, but to our knowledge not previously for vapor-phase discharge in vadose-zone systems.

The specific behavior observed for a given SVE system will be mediated by the relative accessibility (and ranges of accessibility) of the contamination to gas flow, which in turn is mediated by site conditions (permeability distribution, contaminant distribution). It is important to note that the distribution and configuration of contamination can change with time as contaminant mass is removed due to natural (e.g., diffusion, barometric pumping) and anthropogenic (remedial actions) processes. Thus the “age” of the site, as characterized for example with respect to the contamination remaining versus that present initially, is an important factor influencing CMDR-MR behavior (e.g., Jawitz et al., 2005; Brusseau et al., 2008; DiFilippo et al., 2010; Brusseau et al., 2013).

REMEDIATION PERFORMANCE, ALTERNATIVE ACTIONS, AND CLOSURE

Operational Performance Evaluation and Optimization

Direct characterization of SVE performance is typically accomplished by monitoring concentrations of CVOCs in SVE effluent, or equivalently monitoring contaminant mass discharge and mass removed. The onset of asymptotic, low-concentration conditions and other changes in these parameters may denote progression through the life cycle depicted in Figure 6. SVE system performance monitoring may change to evaluate this shift, which may also support operational changes in an attempt to optimize mass extraction from the existing system. When assessing performance, it is important to note that other factors, such as inefficient well-field design or operation (e.g., incomplete coverage of contaminated zone, development of stagnation zones, mismatch between well location or screened interval and contamination location) can cause or contribute to reduced effectiveness. These factors need to be considered and addressed if present.

The measurement of operational parameters from the SVE system provides important information on both the subsurface conditions and the magnitude and location of remaining contamination sources that was not necessarily available during initial site characterization. Compilation and interpretation of these measurements contributes to improving the site conceptual model and supports decisions on appropriate future actions. For example, extraction flow rates for individual wells, in conjunction with the corresponding applied vacuum, provide at least qualitative information on the spatial (horizontally and possibly vertically) distribution of relative air permeabilities (e.g., Farhan et al., 2001). In particular, the vacuum data/airflow paths should be considered in the context of understanding the contaminant mass distribution at the site. Several guidance documents exist for conducting performance assessments of SVE (e.g., AFCEE, 2001; EPA, 2001, USACE, 2002).

Optimization approaches to improve the effectiveness of SVE systems have been outlined by AFCEE (2001) and USACE (2002). Existing SVE systems can be tailored to enhance removal of remaining mass by focusing extraction on existing wells that are still moving air through or past the source(s) and shutting down superfluous wells. In some cases, air throughput is inadequate at specific locations and depths and new wells with depth-specific screened intervals are appropriate. Coupling air injection with active extraction may better focus air flow through zones with remaining mass and can address “stagnation zones” between active extraction wells. The use of air injection can reduce the vacuum required for the extraction wells, and can help limit water-table upwelling at sites where contamination is concentrated near the water table. Air injection can be done passively by allowing some wells to be open to the atmosphere, or actively through the use of separate piping and blowers. Passive air injection is usually limited by the low vacuum experienced by venting wells. Active air injection, which can deliver more air, should be limited to a rate that can be captured by the vapor extraction wells. As such, active injection is usually limited to some fraction of the total extraction rate (USACE, 2002). Directional wells and vertical circulation wells may be useful for enhancing flow through low-permeability zones. If the remaining mass resides in relatively thick low-permeability material, hydraulic or pneumatic fracturing of the soil may enhance flow through the lower permeability zones (e.g., Frank and Barkley, 1995; EPA, 1997). Modeling of air flow can assist in the analysis of such modifications (USACE, 2002). Construction of a surface barrier (capping) to reduce water infiltration and gas influx may enhance SVE efficiency by reducing water content (and vertical VOC migration with infiltration) and by reducing gas inflow from the surface, which decreases SVE vacuum and radial extraction distance.

As the remaining mass becomes more mass-transfer-limited, SVE operation can be transitioned to a periodic or cyclic operation such that active extraction occurs in intervals separated by periods of no extraction during which diffusion allows mass to re-enter advective pathways. Pulsing can be done on a rotating basis at a large site such that active extraction is occurring at a subset of wells while other wells at the site are inactive. The period of non-pumping depends on the rate of diffusion and can be determined based on monitoring of the rebound of concentrations following cessation of extraction. The length of the inactive period may represent the time to a rebound to some percentage (e.g., 60%) of a baseline concentration (USACE, 2002). The effectiveness of cyclic versus steady SVE operation will depend upon specific site conditions (e.g., Armstrong et al., 1994; Kaleris and Croise, 1997; Kirtland and Aelion, 2000).

Closure or Transition Criteria and Evaluation

There is a characteristic decline in mass-removal effectiveness observed for most SVE systems, as previously discussed. Thus, SVE systems typically reach a point of diminishing returns, and managing this type of response has been a continuing area of effort due to the large number of systems operating and the need to have an effective basis for decision making. For most SVE systems, a decision point eventually develops regarding whether to continue under the reduced-efficiency conditions, to modify the extraction protocol and/or system, to switch to other remediation methods, or to cease remediation.

Several criteria or remediation objectives can and have been used to evaluate SVE closure. For example, closure can be based on attaining a specific (e.g., 90 or 99%) reduction in effluent CVOC concentrations or mass-removal rates measured for the SVE system. However, such data do not provide direct indication of the impact of the remedial effort on risk posed by the source to groundwater or the land surface. Another possible criterion is attainment of a specific reduction in sediment-phase contaminant mass. This is difficult to implement given that the initial mass present at the site is rarely known for most sites. In addition, this approach does not account for the fact that reductions in CMD (which mediates risk) can vary for a given reduction in mass, as illustrated in Figure 8. The constraints associated with these approaches limit their effective and robust implementation.

An alternative approach was developed based on evaluating the impact of the vadose-zone source on groundwater remediation goals or vapor-intrusion concerns, employed though determination of the contaminant mass discharge (e.g., Johnson and Ettinger, 1991; Rosenbloom et al., 1993; DiGiulio et al., 1999). This approach is considered to be optimal for most cases as it explicitly accounts for the primary potential human-health risks of the vadose-zone source. The U.S. Environmental Protection Agency (EPA, 2001, 2002) and the

U.S. Army Corps of Engineers (USACE, 2002) provide guidance for assessing transition and closure of SVE systems based upon consideration of vadose-zone contaminant mass discharge. The approaches for closure/transition decisions can be summarized with the following elements using an organization based on the four steps outlined by the EPA:

1. Define a conceptual model of the site that is appropriate for use as a context to support SVE data analysis relative to closure/transition decisions (e.g., how is the contaminant distributed in the vadose zone and how does this relate to SVE effectiveness and closure analysis)
2. Provide design information that shows how SVE was configured and operated to appropriately address the contamination.
3. Provide SVE performance monitoring to demonstrate mass extraction and decreases in the subsurface contamination.
4. Quantify the mass discharge to groundwater or land surface to define the impact of remaining vadose zone contamination on remediation goals and thereby set a quantitatively determined remediation endpoint for the vadose-zone contamination.

A recently published guidance document (Truex et al., 2012) builds upon the prior work to clarify and focus on the specific actions and decisions related to SVE optimization, transition, and/or closure. The process of gathering information and performing evaluations to support SVE remedy decisions is presented in this guidance document in a stepwise approach. Steps start with revisiting the conceptual site model after SVE has been operated for a period of time. The guidance also describes information that needs to be considered in terms of the environmental impact and compliance context for optimization, transition, and closure decisions. Quantitative approaches are provided to evaluate the impact or remaining vadose zone contaminant sources on groundwater in support of optimization, transition, and closure decisions. The material in these initial steps is then synthesized using a decision-logic approach to optimize transition and closure decisions.

An illustration of establishing closure criteria for SVE systems in terms of future impact to groundwater was recently presented by Carroll et al. (2012). They used numerical modeling of vapor-phase contaminant transport to investigate the correlation between measured vapor-phase mass discharge (as characterized for example by the method of Brusseau et al. 2010) from a persistent, vadose-zone contaminant source and the resulting groundwater-contaminant concentrations. This relationship was shown to be linear for the study site, and was used to directly assess SVE remediation progress over time and to determine the level of remediation in the vadose zone necessary to protect groundwater (Figure 9). Although site properties and source characteristics must be specified to establish a unique relationship between mass discharge and the groundwater contaminant concentration, this correlation provides insight into SVE performance and support for decisions to optimize or terminate the SVE operation or to transition to another type of treatment.

Alternatives to SVE or Coupled Remedies with SVE

Various alternatives or enhancements have been developed to support the removal or management of low-accessibility persistent sources that cause SVE to become inefficient during later stages of operation. Given that the primary concerns associated with vadose-zone sources are typically the impacts to groundwater or the land surface, methods that control vapor migration (flux control) may be useful. Such methods may be more cost-effective, particularly for cases wherein the remaining contaminant mass is highly recalcitrant. One option is passive SVE, the use of which would reduce operations costs. Passive extraction may be an option at sites where there is a significant lag in subsurface pressure response to atmospheric pressure changes, such that there are large differential pressures between the subsurface and the atmosphere (e.g., Rossabi et al., 1998; Ellerd et al., 1999; Christensen et al., 2000; Kamath et al., 2009). Another option is the periodic operation of SVE. This is similar to the cyclic SVE method noted above, except that the objective is to control vapor migration rather than effect mass removal. The frequency of operation would be based on changes in contaminant concentrations, which would be tracked via a monitoring program. Another option is to emplace a barrier between the source and the sensitive zone. For example, air can be injected between the source and the land surface to prevent vapor migration to sensitive surface areas. For another example, the placement of a layer of non-toxic oil near the water table was recently demonstrated to impede mass transfer across the groundwater-vadose-zone interface. The oil is expected to slowly dissolve and may need to be replenished. Dissolved oil may act as an electron donor to promote reductive dechlorination in ground water (Riha et al., 2012). In some cases, surface remedies, as are commonly applied for vapor intrusion, may be the most cost-effective approach (EPA, 2008).

If site closure requires additional reduction of contaminant mass in the vadose zone beyond what was attained with SVE, more aggressive remedies may be needed beyond flux control. These approaches include multi-phase extraction or air sparging (if the mass is primarily concentrated in high-moisture soils near the water table), enhanced bioremediation, and in-situ thermal remediation. In some cases, vapor extraction via SVE is part of the technology, but other mechanisms of mass removal are also involved. Examples of available methods are introduced below. Detailed discussion of the application and potential limitations of the methods is beyond the scope of this effort.

Multiphase extraction involves the simultaneous extraction of vapors and liquids using the same well, employing either a single vacuum pump or separate pumps for the separate phases. The liquid extraction may enhance the removal of CVOC mass from the location of the smear zone/capillary fringe by lowering both the water table and levels of water saturation. The application of vacuum can also enhance the removal of liquids from soils with modest permeabilities (e.g., 10^{-3} to 10^{-5} cm/sec) for simultaneous recovery of dissolved mass or NAPL from the source areas (USACE, 1999).

Contaminant mass in the vicinity of the water table and capillary fringe is not readily accessible to SVE. Air sparging is an option for treatment of such contamination, and involves the injection of air into wells with screened intervals below the water table (e.g., Johnson et al., 1993; USACE, 2008). The injected air moves through pore-space channels outwards and upwards from the well based on buoyancy and air-entry pressures of the sediment. The injected air induces CVOC volatilization from groundwater, and the contaminants travel with the gas to the vadose zone before subsequent extraction to the surface by SVE. Air sparging is an alternative for cases wherein dewatering the upper portion of the aquifer (to allow SVE access) is impractical.

At sites where the contaminants are primarily aerobically biodegradable (or cometabolically degradable), replacing active extraction with air injection (i.e., bioventing) would provide oxygen to the native bacteria and stimulate additional contaminant removal without the cost of off-gas treatment. Air injection can be pulsed, with the pulse frequency and duration based on observed oxygen uptake rates. Air can be supplemented by a co-metabolite, such as methane, propane, or toluene vapors to promote the expression of enzymes by aerobic bacteria that fortuitously degrade recalcitrant chlorinated compounds. Existing SVE wells, piping, and blowers can often be used. The addition of gaseous nutrients (e.g., nitrous oxide, triethyl phosphate) may be needed to maximize the degradation rates, although many sites have been addressed without nutrient addition. Bioventing is addressed in several design manuals (e.g., EPA, 1995c; USACE, 1999, 2002).

Heat may be introduced through electrical-resistivity heating (passing currents between electrodes placed into the soils to be treated), thermal-conduction heating (heat propagates through conduction from heaters placed in wells), hot-air injection, or steam injection (e.g., USACE, 2009; Kingston et al. 2010). The vapors generated by the process are typically collected via vapor extraction wells. The application of heat results in higher vapor pressures for most organic contaminants and is accompanied by changes in the solubility, viscosity, surface tension, and density of non-aqueous phase liquids. In addition, rates of bioremediation (and hydrolysis for chlorinated ethanes) may be significantly enhanced at elevated temperatures.

The injection of a dry gas to reduce the water content of the vadose zone is termed desiccation. This approach has been shown to enhance SVE effectiveness (e.g., Garciagerruzo et al., 1994, Oostrom et al., 2005). The reduction in water content has the potential to increase the accessibility of areas of the vadose zone that were inaccessible due to high water content and low relative gas permeability, thereby reducing bypass flow. In addition, a reduction in water content may also reduce mass-transfer limitations by reducing the significance of aqueous-phase diffusion.

SUMMARY AND REMAINING CHALLENGES

Contamination of subsurface environments by chlorinated-solvent compounds remains a significant human-health issue in the U.S.A. and many other countries. Contaminant sources in the vadose zone pose specific potential risks though their impact on groundwater quality and vapor intrusion. Currently, these impacts constitute the primary risk drivers for decision making concerning remediation of vadose-zone sources.

As discussed above, assessing the impact of vadose-zone sources requires measurement or estimation of the contaminant mass discharge associated with the source. Accurate measurement of contaminant mass discharge for vadose-zone sources remains a significant challenge, and necessitates development of robust methods that consider the unique factors associated with the multi-phase, highly dynamic properties inherent to chlorinated-solvent-contaminated vadose zones. Inroads to this issue are being made with the development of field-based measurement methods as noted.

SVE remains the most widely used remedy for CVOC-contaminated vadose zones. It has been used successfully at innumerable sites. However, SVE operations typically exhibit reduced mass-removal effectiveness at some point due to the impact of poorly accessible contaminant mass and associated mass-transfer limitations. Addressing the reduced performance of SVE, and decisions on alternative remedies and SVE closure, is a pressing issue. Alternative remedies, such as flux control, air sparging, and multi-phase extraction are often used in conjunction with or after closure of SVE.

Developing robust methods for collecting, analyzing, and employing information in support of remedy selection, alteration, and closure is critical for successful long-term management of sites contaminated by chlorinated solvents. An approach that incorporates analysis of SVE operations data, implementation of contaminant mass discharge tests, and mathematical modeling provides a flexible means to produce such information, as illustrated by recent efforts conducted at two DOE sites (Truex et al., 2009; Brusseau et al., 2010; Stauffer et al., 2011; Carroll et al., 2012, 2013). This integrated approach is anticipated to be able to better address issues such as the changes in source-zone architecture and dynamics likely to occur during remediation, and the inherent uncertainty associated with characterizing site properties and conditions.

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REFERENCES

Abreu LDV, Johnson PC. Effect of vapor source—building separation and building construction on soil vapor intrusion as studied with a three-dimensional numerical model. Environ. Sci. Technol. 2005; 39:4550–4561. [PubMed: 16047792]

Abriola LM, Bradford SA, Lang J, Gaither CL. Volatilization of binary nonaqueous phase liquid mixtures in unsaturated porous media. Vadose Zone Journal. 2004; 3:645–655.

Air Force Center for Environmental Excellence (AFCEE). Guidance on Soil Vapor Extraction Optimization. Books AFB, TX: U.S. Air Force Environmental Restoration Program; 2001.

Armstrong JE, Frind EO, McClellan RD. Nonequilibrium mass transfer between the vapor, aqueous, and solid phases in unsaturated soils during vapor extraction. Water Resources Research. 1994; 30:355–368.

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]

Benson DA, Huntley D, Johnson PC. Modeling vapor extraction and general transport in the presence of NAPL mixtures and nonideal conditions. Ground Water. 1993; 31:437–445.

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]

Bozkurt O, Pennell KG, Suuberg EM. Simulation of the Vapor Intrusion Process for Nonhomogeneous Soils Using a Three-Dimensional Numerical Model. Ground Water Monitoring & Remediation. 2009; 29:92–104. [PubMed: 20664816]

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. Transport of organic chemicals by gas advection in structured or heterogeneous porous media: development of a model and applications to column experiments. Water Resources Research. 1991; 27:3189–3199.

Brusseau ML, Rao PSC. Sorption nonideality during organic contaminant transport in porous media. Crit. Rev. Environ. Control. 1989; 19:33–99.

Brusseau ML, Rao PSC, Jessup RE, Davidson JM. Flow interruption: a method for investigating sorption nonequilibrium. Journal of Contaminant Hydrology. 1989; 4(3):223–240.

Brusseau ML, Popovicova J, Silva JAK. Characterizing gas-water-interfacial and bulk-water partitioning for gas-phase transport of organic contaminants in unsaturated porous media. Environmental Science and Technology. 1997a; 31:1645–1649.

Brusseau ML, Hu Q, Srivastava R. Using flow interruption to identify factors causing nonideal contaminant transport. Journal of Contaminant Hydrology. 1997b; 24:205–219.

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. In: Brusseau, ML.; Sabatini, DA.; Gierke, JS.; Annable, MD., editors. Chapter 19 in: Innovative Subsurface Remediation: Field Testing of Physical, Chemical, and Characterization Technologies. Washington DC: American Chemical Society; 1999.

Brusseau ML, Nelson NT, Costanza-Robinson MS. Partitioning tracer tests for characterizing immiscible-fluid saturations and interfacial areas in the vadose zone. Vadose Zone Journal. 2003a; 2(2):138–147.

Brusseau ML, Bronson KM, Ross S, Nelson NT, Carlson TD. Application of gas-phase partitioning tracer tests to characterize immiscible-liquid contamination in the vadose zone beneath a fuel depot. Vadose Zone Journal. 2003b; 2(2):148–153.

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. Journal of Contaminant Hydrology. 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]

Brusseau, ML.; Carroll, KC.; Truex, MJ. Use of Mass-Flux Measurement and Vapor-Phase Tomography to Quantify Vadose-Zone Source Strength and Distribution, ER-201125. U.S. Department of Defense Environmental Security Technology Certification Program; 2011c. http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-201125/ER-201125/%28language%29/eng-US.

Brusseau ML, Matthieu DE III, Carroll KC, Mainhagu J, Morrison C, McMillan A, Russo A, Plaschke M. Characterizing Long-term Contaminant Mass Discharge and the Relationship Between Reductions in Discharge and Reductions in Mass for DNAPL Source Areas. J. Contam. Hydrol. 2013 (in review).

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

Carlson TD, Costanza-Robinson MS, Keller J, Wierenga PJ, Brusseau ML. Intermediate-scale tests of the gas-phase partitioning tracer method for measuring soil-water content. Soil Science Society of America Journal. 2003; 67(2):483–486.

Carroll KC, Taylor R, Gray E, Brusseau ML. The Impact of Composition on the Physical Properties and Evaporative Mass Transfer of a PCE-diesel Immiscible Liquid. Journal of Hazardous Materials. 2009; 164:1074–1081. [PubMed: 18926630]

Carroll KC, Oostrom M, Truex MJ, Rohay VJ, Brusseau ML. Assessing performance and closure for soil vapor extraction: integrating vapor discharge and impact to groundwater quality. Journal of Contaminant Hydrology. 2012; 128:71–82. [PubMed: 22192346]

Carroll KC, Truex MJ, Brusseau ML, Parker KR, Mackley RD, Rohay VJ. Characterization of Persistent Volatile Contaminant Sources in the Vadose Zone. Submitted to Ground Water Monitoring and Remediation. 2013 (In Review).

Cho JH, Jaffe PR, Smith JA. Simulating the volatilization of solvents in unsaturated soils during laboratory and field infiltration experiments. Water Resources Research. 1993; 29(10):3329–3342.

Christensen AG, Fischer EV, Nielsen HH, Nygaard T, Ostergaard H, Lenschow SR, et al. Passive soil vapor extraction of chlorinated solvents using boreholes. Groundwater. 2000; 2000:409–410.

Conklin MH, Corley TL, Roberts PA, Davis JH, van de Water JG. Nonequilibrium processes affecting forced ventilation of benzene and xylene in a desert soil. Water Resources Research. 1995; 31(5): 1355–1365.

Costanza-Robinson MS, Brusseau ML. Air-water interfacial areas in unsaturated soils: evaluation of interfacial domains. Water Resources Research. 2002; 38(10):1195–1211.

Crotwell, AT.; Waehner, MJ.; Lyon, BF.; MacInnis, JM.; Travis, CC. Oak Ridge National Laboratory. Oak Ridge, TN: U.S. Department of Energy; 1992. An evaluation of vapor extraction of vadose zone contamination. ORNL/TM-12117.

Deeds NE, McKinney DC, Pope GA, Whitley GA Jr. Difluoromethane as partitioning tracer to estimate vadose water saturations. Journal of Environmental Engineering. 1999a Jul.:630–633.

Deeds NE, Pope GA, McKinney DC. Vadose zone characterization at a contaminated field site using partitioning interwell tracer technology. Environmental Science and Technology. 1999b; 33:2745–2751.

DeGroot DJ, Lutenegger AJ. Reliability of soil gas sampling and characterization techniques. Geotechnical Site Characterization. 1998; Vols 1 and 2:629–634.

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]

DiGiulio, DC. Evaluation of Soil Venting Application. EPA/540/S-92/004. 1992.

DiGiulio, DC.; Brusseau, ML.; Ravi, V. Use of diffusion modeling to aid assessment of rate-limited vapor transport for SVE closure. In: Wickramanayake, GB.; Hinchee, RE., editors. Physical, Chemical, and Thermal Technologies: Remediation of Chlorinated and Recalcitrant Compounds (C1–5); Proceedings of the first international conference on remediation of chlorinated and recalcitrant compounds; May 18–21, 1998; Monterey, CA. Battelle, Columbus, OH: 1998.

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(2):96–104.

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

Ellerd MG, Massmann JW, Schwaegler DP, Rohay VJ. Enhancements for passive vapor extraction: The Hanford study. Ground Water. 1999; 37:427–437.

Environmental Protection Agency (EPA). Soil Vapor Extraction Technology Handbook. EPA/540/2-91/003. 1991.

Environmental Protection Agency (EPA). Presumptive Remedies: Site Characterization and Technology Selection for CERCLA Sites with Volatile Organic Compounds in Soils. EPA 540-F-93-048. 1993.

Environmental Protection Agency (EPA). Innovative Site Remediation Technology: Vacuum Vapor Extraction. EPA 542-B-94-002. 1995a.

Environmental Protection Agency (EPA). Remediation Case Studies: Soil Vapor Extraction. 542-R-95-004. 1995b.

Environmental Protection Agency (EPA). Manual: Bioventing Principles and Practice. EPA/540/R-95/534a. 1995c.

Environmental Protection Agency (EPA). Soil Screening Guidance: User's Guide. Second Ed. 1996. EPA/540/R-96/018.

Environmental Protection Agency (EPA). Analysis of Selected Enhancements for Soil Vapor Extraction. EPA/542/R-97/007. 1997.

Environmental Protection Agency (EPA). Innovative Site Remediation Technology: Vacuum Extraction and Air Sparging. EPA 542-B-97-010. 1998a.

Environmental Protection Agency (EPA). Remediation Case Studies: In Situ Soil Treatment Technologies. 542-R-98-012. 1998b.

Environmental Protection Agency (EPA). Development of Recommendations and Methods to Support Assessment of Soil Venting Performance and Closure. EPA/600/R-01/070. 2001.

Environmental Protection Agency (EPA). OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance). EPA/530/D-02/004. 2002.

Environmental Protection Agency (EPA). Expert Panel on DNAPL Remediation. EPA/600/R-03/143. 2003a. The DNAPL Remediation Challenge: Is There a Case for Source Depletion?.

Environmental Protection Agency (EPA). Site Characterization and Monitoring Case Study: Vertical Profiling at Nellis Air Force Base, Site 46. Las Vegas, NV: Office of Solid Waste and Emergency Response, Technology Innovation Office; 2003b Jun.

Environmental Protection Agency (EPA). Engineering Issue Paper, Indoor Air Vapor Intrusion Mitigation Approaches. EPA/600/R-08/115. 2008.

Fares A, Deb SK, Fares S. Review of vadose zone soil solution sampling techniques. Environmental Reviews. 2009; 17:215–234.

Farhan S, Holsen TM, Budiman J. Interaction of soil air permeability and soil vapor extraction. Journal of Environmental Engineering-ASCE. 2001; 127:32–37.

Feenstra S. Soil sampling in NAPL source zones: Challenges to representativeness. Environmental Forensics. 2005; 6:57–63.

Fischer U, Schulin R, Keller M. Experimental and numerical investigation of soil vapor extraction. Water Resources Research. 1996; 32(12):3413–3427.

Frank U, Barkley N. Remediation of Low Permeability Subsurface Formations by Fracturing Enhancement of Soil Vapor Extraction. Journal of Hazardous Materials. 1995; 40:191–201.

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.

Garciagerruzo F, Gomezlahoz C, Rodriguezjimenez JJ, Wilson DJ, Garciadelgado RA, Rodriguezmaroto JM. Influence of Water Evaporation on Soil Vapor Extraction (SVE). Water Science and Technology. 1994; 30:115–118.

Gierke JS, Hutzler NJ, McKenzie DB. Vapor transport in unsaturated soil columns: implications for vapor extraction. Water Resources Research. 1992; 28:323–335.

Gottlieb J, Dietrich P. Identification of the Permeability Distribution in Soil by Hydraulic Tomography. Inverse Problems 11 no. 1995; 2:353–360.

Harper BM, Stiver WH, Zytner RG. Nonequilibrium nonaqueous phase liquid mass transfer model for soil vapor extraction systems. Journal of Environmental Engineering - ASCE. 2003; 129:745–754.

Harvey CF, Haggerty R, Gorelick SM. Aquifer remediation: a method for estimating mass transfer rate coefficients and an evaluation of pulsed pumping. Water Resources Research. 1994; 30:1979–1991.

Hers I, Zapf-Gilje R, Evans. D, Li L. Comparison, Validation, and Use of Models for Predicting Indoor Air Quality from Soil and Groundwater Contamination. Soil Sed. Contamination: An International Journal. 2002; 11(4):491–527.

Ho CK, Udell KS. An experimental investigation of air venting of volatile liquid hydrocarbon mixtures from homogeneous and heterogeneous porous media. Journal of Contaminant Hydrology. 1992; 11:291–316.

Interstate Technology and Regulatory Council (ITRC). Regulatory Overview: DNAPL Source Reduction: Facing the Challenge. 2002.

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. Columbus, OH: Battelle Press; 2004. Modeling the benefits of partial mass reduction in DNAPL source zones. Paper 2C-04.

Jellali S, Benremita H, Muntzer P, Razakarisoa O, Schafer G. A large-scale experiment on mass transfer of trichloroethylene from the unsaturated zone of a sandy aquifer to its interfaces. Journal of Contaminant Hydrology. 2003; 60:31–53. [PubMed: 12498573]

Johnson PC, Stanley CC, Kemblowski MW, Byers DL, Colthart JD. A practical approach to the design, operation, and monitoring of in-situ soil venting systems. Ground Water Monitoring & Remediation. 1990; 10(2):159–178.

Johnson PC, Ettinger RA. Heuristic Model for Predicting the Intrusion Rate of Contaminant Vapors into Buildings. Environmental Science and Technology. 1991; 25:1445–1452.

Johnson RL, Johnson PC, Mcwhorter DB, Hinchee RE, Goodman I. An Overview of in-Situ Air Sparging. Ground Water Monitoring and Remediation. 1993; 13:127–135.

Johnson PC, Ettinger RA. Considerations for the design of in situ vapor extraction systems: radius of influence vs. zone of remediation. Ground Water Monitoring Remediation. 1994; 14(3):123–128.

Johnston JE, Gibson JM. Probabilistic approach to estimating indoor air concentrations of chlorinated volatile organic compounds from contaminated groundwater: a case study in San Antonio, Texas. Environmental Science and Technology. 2011; 45:1007–1013. [PubMed: 21162557]

Kaleris V, Croise J. Estimation of Cleanup Time for Continuous and Pulsed Soil Vapor Extraction. Journal of Hydrology. 1997; 194:330–356.

Kaleris V, Croise J. Estimation of cleanup time in layered soils by vapor extraction. Journal of Contaminant Hydrology. 1999; 36:105–129.

Kamath, R.; Adamson, DT.; Newell, CJ. Enhanced Attenuation Technologies: Passive Soil Vapor Extraction. SRNL-STI-2009-00571. Aiken, South Carolina: Savannah River National Laboratory; 2009.

Kearl PM, Korte NE, Gleason TA, Beale JS. Vapor extraction experiments with laboratory soil columns: implications for field programs. Waste Management. 1991; 11:231–239.

Keller JM, Brusseau ML. In-situ characterization of soil-water content using gas-phase partitioning tracer tests: field-scale evaluation. Environmental Science and Technology. 2003; 37(14):3141–3144. [PubMed: 12901662]

Kingston JLT, Dahlen PR, Johnson PC. State-of-the-Practice Review of In Situ Thermal Technologies. Ground Water Monitoring and Remediation. 2010; 30:64–72.

Kirtland BC, Aelion CM. Petroleum mass removal from low permeability sediment using air sparging/soil vapor extraction: impact of continuous or pulsed operation. Journal of Contaminant Hydrology. 2000; 41:367–383.

Liang HC, Udell KS. Experimental and theoretical investigation of vaporization of liquid hydrocarbon mixtures in water-wetted porous media. Water Resources Research. 1999; 35:635–649.

Lingineni S, Dhir VK. Controlling transport processes during NAPL removal by soil venting. Advances Water Resources. 1996; 20:157–169.

Luthy RG, Aiken GR, Brusseau ML, Cunningham SD, Gschwend PM, Pignatello JJ, Reinhard M, Traina SJ, Weber WJ Jr, Westall JC. Sequestration of hydrophobic organic contaminants by geosorbents. Environ. Sci. Technol. 1997; 31:3341–3347.

Marrin DL. Soil-Gas Sampling and Misinterpretation. Ground Water Monitoring Review Spring. 1988:51–57.

Marrin DL, Kerfoot HB. Soil-gas surveying techniques. Environ. Sci. Technol. 1988; 22:740–745. [PubMed: 22195653]

Mariner PE, Jin M, Studer JE, Pope GA. The first vadose zone partitioning interwell tracer test for nonaqueous phase liquid and water residual. Environmental Science and Technology. 1999; 33(16):2825–2828.

Marley, ME.; Hoag, GE. proceedings of NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Houston, Texas. Dublin, OH: National Ground Water Association; 1984. Induced soil venting for the recovery/restoration of gasoline hydrocarbons in the vadose zone.

Massmann J, Shock S, Johannesen L. Uncertainties in cleanup times for soil vapor extraction. Water Resources Research. 2000; 36:679–692.

McAlary TA, Nicholson P, Groenevelt H, Bertrand D. A Case Study of Soil-Gas Sampling in Silt and Clay-Rich (Low-Permeability) Soils. Ground Water Monitoring and Remediation. 2009; 29:144–152.

McColl CM, Johnson GR, Brusseau ML. Evaporative mass transfer behavior of a complex immiscible liquid. Chemosphere. 2008; 73:607–613. [PubMed: 18614196]

Marrin DL. Soil-Gas Sampling and Misinterpretation. Ground Water Monitoring Review Spring. 1988:51–57.

Marrin DL, Kerfoot HB. Soil-gas surveying techniques. Environ. Sci. Technol. 1988; 22:740–745. [PubMed: 22195653]

Nadim F, Nadim A, Haog GE, Dahmani AM. Desorption rate limitation in the extraction of organic molecules from unsaturated soils during soil venting operations. Journal of Contaminant Hydrology. 1997; 25:21–37.

NRC. Alternatives for Ground Water Cleanup. Washington, DC: National Research Council (NRC); 1994.

NRC. Groundwater and Soil Cleanup: Improving Management of Persistent Contaminants. Washington D.C.: National Research Council (NRC); 1999.

NRC. Contaminants in the Subsurface: Source-zone Assessment and Remediation. Washington, DC: National Research Council (NRC); 2004.

Nelson NT, Brusseau ML, Carlson TD, Costanza MS, Young MH, Johnson GR, Wierenga PJ. A gas-phase partitioning tracer method for the in situ measurement of soil-water content. Water Resources Research. 1999; 35(12):3699–3707.

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

Oostrom M, Dane JH, Wietsma TW. Removal of Carbon Tetrachloride from a Layered Porous Medium by Means of Soil Vapor Extraction Enhanced by Desiccation and Water Table Reduction. Vadose Zone J. 2005; 4(4):1170–1182.

Oostrom M, Truex MJ, Tartakovsky GD, Wietsma TW. Three-dimensional simulation of volatile organic compound mass flux from the vadose zone to groundwater. Groundwater Monitoring and Remediation. 2010; 30(3):45–56.

Paillet FL, Morin RH. Hydraulic tomography in fractured bedrock aquifers using high-resolution borehole flowmeter measurements. Modern Geophysics in Engineering Geology no. 1997; 12:267–272.

Peng S, Brusseau ML. Gas-phase partitioning tracer test method for water content measurement: evaluating efficacy for a range of porous-medium textures. Vadose Zone Journal. 2005a; 4(3): 881–884.

Peng S, Brusseau ML. The impact of soil texture on air-water interfacial areas in unsaturated sandy porous media. Water Resources Research. 2005b; 41(3):W03021.

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.

Popovicova J, Brusseau ML. Dispersion and Transport of Gas-Phase Contaminants in Dry Porous Media: Effect of Heterogeneity and Gas Velocity. Journal of Contaminant Hydrology. 1997; 28:157–169.

Popovicova J, Brusseau ML. Contaminant Mass Transfer During Gas-Phase Transport in Unsaturated Porous Media. Water Resources Research. 1998; 34:83–92.

Poulsen TG, Massmann JW, Moldrup P. Effects of vapor extraction on contaminant flux to atmosphere and ground water. Journal of Environmental Engineering. 1996; 122:700–706.

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.

Rathfelder KW, Yeh W-G, Mackay D. Mathematical simulation of soil vapor extraction systems: model development and numerical examples. Journal of Contaminant Hydrology. 1991; 8(3/4): 263–297.

Riha, B.; Looney, B.; Noonkester, J.; Hyde, K.; Walker, R. SRNL-STI-2012-00290. Aiken, South Carolina: Savannah River National Laboratory; 2012. Treatability Study for Edible Oil Deployment for Enhanced cVOC Attenuation for T-Area, Savannah River Site.

Rodriguez-Maroto JM, Gomez-Lahoz C, Wilson DJ. Soil cleanup by in situ aeration: XVIII. Field scale models with diffusion from clay structures. Separation Science & Technology. 1994; 29:1367–1399.

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

Rossabi J, Riha BD, Vanpelt RS, Kmetz T, Pemberton BE. Passive soil vapor extraction for interim remediation at the Savannah River Site. First International Conference on Remediation of Chlorinated and Recalcitrant Compounds. 1998; Vol. 5:161–167.

Rossabi J, Riha BD, Eddy-Dilek CA, Looney BB, Hyde WK. Recent advances in characterization of vadose zone dense non-aqueous phase liquids (DNAPL) in heterogeneous media. Environmental & Engineering Geoscience. 2003; 9:25–36.

Ronen D, Graber ER, Laor Y. Volatile organic compounds in the saturated-unsaturated interface region of a contaminated phreatic aquifer. Vadose Zone Journal. 2005; 4:337–344.

Schwarz, RTPtak; Holder, T.; Teutsch, G. Groundwater risk assessment at contaminated sites: a new investigation approach. Groundwater Quality: Remediation and Protection; Proceedings of the GQ'98 Conference held at Tubingen; September 1998; Germany. IAHS Pub. no. 250.

Silka, LR.; Cirpili, HD.; Jordan, DL. App G. in Soil Vapor Extraction Technology Reference Handbook. EPA/540/2-91/003. 1991. Modeling applications to vapor extraction systems.

Simon MA, Brusseau ML. Analysis of a gas-phase partitioning tracer test conducted in an unsaturated fractured-clay formation. Journal of Contaminant Hydrology. 2007; 90(3-4):146–158. [PubMed: 17157956]

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]

Stauffer, PH.; Hopkins, JK.; Anderson, T. A soil vapor extraction pilot study in a deep arid vadose zone part 2: Simulations in support of decision making processes; Presented at the Annual Waste Management Conference; Feb. 25 – March 1, 2007; Tucson, AZ. 2007.

Stauffer, PH.; Birdsell, KH.; Rice, WJ. 3-D Model Validation in Support of Site Closure. Material Disposal Area L, Los Alamos, NM; Presented at the Annual Waste Management Conference; March 7–11, 2011; Phoenix, AZ. 2011.

Strategic Environmental Research and Development Program (SERDP). Final report: SERDP/ESTCP expert panel workshop on reducing the uncertainty of DNAPL source zone remediation. 2006.

Stroo HF, Leeson A, Marqusee JA, Johnson PC, Ward CH, Kavanaugh MC, et al. Chlorinated Ethene Source Remediation: Lessons Learned. Environmental Science & Technology. 2012; 46:6438–6447. [PubMed: 22558915]

Switzer C, Kosson DS. Soil vapor extraction performance in layered vadose zone materials. Vadose Zone Journal. 2007; 6:397–405.

Switzer C, Slagle T, Hunter D, Kosson DS. Use of rebound testing for evaluation of soil vapor extraction performance at the Savannah River Site. Ground Water Monitoring & Remediation. 2004; 24:106–118.

Thomson NR, Flynn DJ. Soil vapor extraction of perchloroethylene from the Borden aquifer. Ground Water. 2000; 38:673–688.

Thornton JS, Wootan WL Jr. Venting for the removal of hydrocarbon vapors from gasoline contaminated soil. Environmental Science and Health. 1982; A17(1):31–40.

Truex MJ, Oostrom M, Brusseau ML. Estimating persistent mass flux of volatile contaminants from the vadose zone to ground water. Ground Water Monitoring & Remediation. 2009; 29:63–72.

Truex, MJ.; Becker, DJ.; Simon, MA.; Oostrom, M.; Rice, AK.; Johnson, CD. Soil Vapor Extraction System Optimization, Transition, and Closure Guidance. Richland, WA: PNNL-XXX, Pacific Northwest National Laboratory; 2012.

U.S. Army Corps of Engineers (USACE). Engineering and Design: Multi-Phase Extraction. EM 1110-1-4010. 1999.

U.S. Army Corps of Engineers (USACE). Engineering and Design: Soil Vapor Extraction and Bioventing Manual. EM 1110-1-4001. 2002.

U.S. Army Corps of Engineers (USACE). Engineering and Design: In-Situ Air Sparging. EM 1110-1-4005. 2008.

U.S. Army Corps of Engineers (USACE). Engineering and Design: Design: In Situ Thermal Remediation. EM 1110-1-4015. 2009.

Wang G, Reckhorn SBF, Grathwohl P. Volatile organic compounds volatilization from multicomponent organic liquids and diffusion in unsaturated porous media. Vadose Zone Journal. 2003; 2:692–701.

Whitley GAJ, McKinney DC, Pope GA, Rouse BA, Deeds NE. Contaminated vadose zone characterization using partitioning gas tracers. Journal of Environmental Engineering. 1999 Jun.: 574–582.

Wilkins MD, Abriola LM, Pennell KD. An experimental investigation of rate-limited nonaqueous phase liquid volatilization in unsaturated porous media: steady state mass transfer. Water Resources Research. 1995; 31:2159–2172.

Yeh TCJ, Liu SY. Hydraulic tomography: Development of a new aquifer test method. Water Resources Research 36 no. 2000; 8:2095–2105.

Yoon H, Kim JH, Liljestrand HM, Khim J. Effect of water content on transient nonequilibrium NAPL-gas mass-transfer during soil vapor extraction. Journal of Contaminant Hydrology. 2002; 54:1–18. [PubMed: 11848263]

Yu S, Unger AJA, Parker B. Simulating the fate and transport of TCE from groundwater to indoor air. J. Contamin. Hydrol. 2009; 107:140–161.

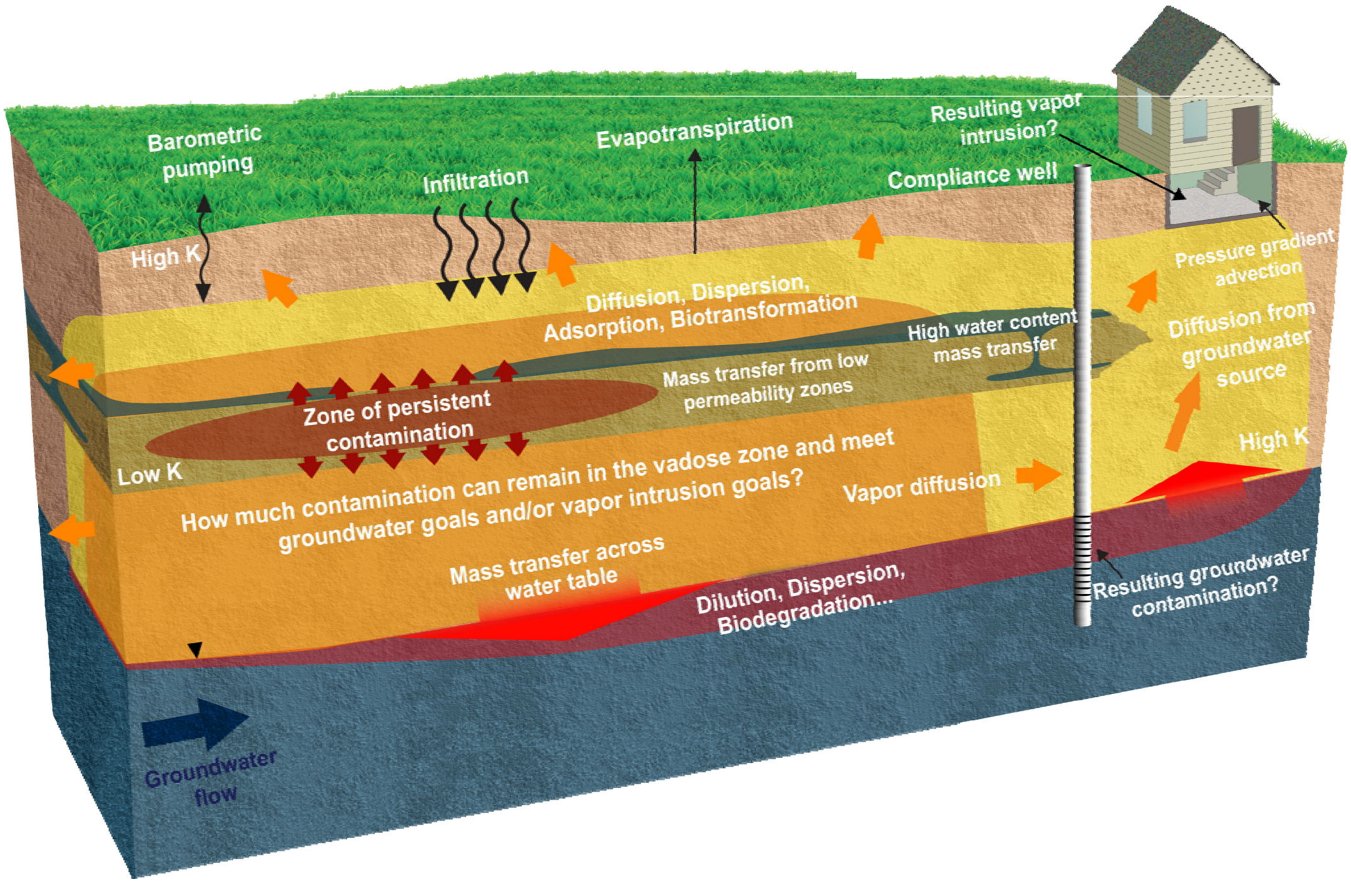


Figure 1.

The results of numerical simulations showing concentrations of a CVOC in groundwater caused by vapor discharge from an overlying vadose-zone source. The source is located 30 m from the water table, and the initial vapor-phase concentration of CVOC is 1 mg/L. From Carroll et al. (2012).

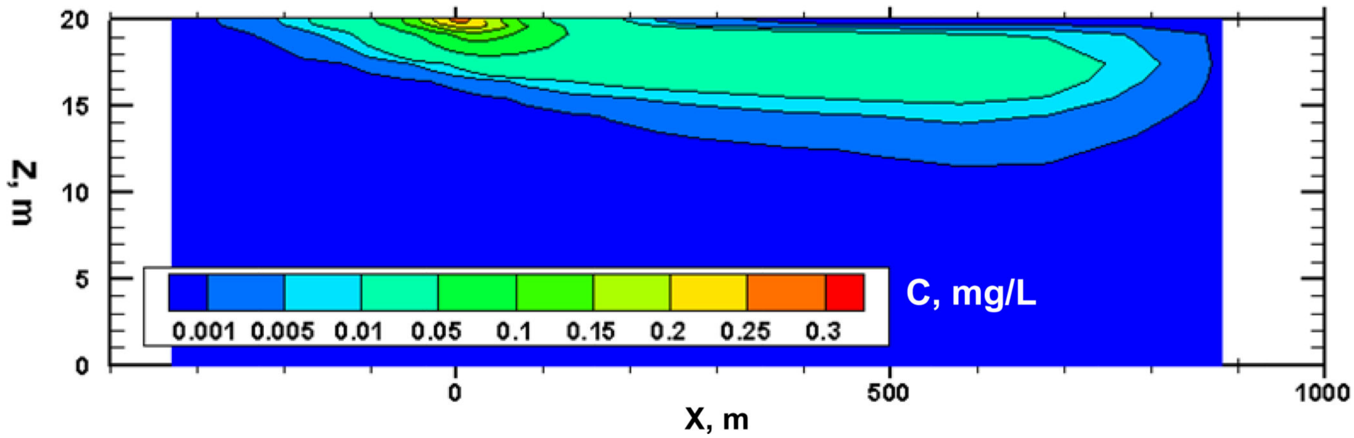
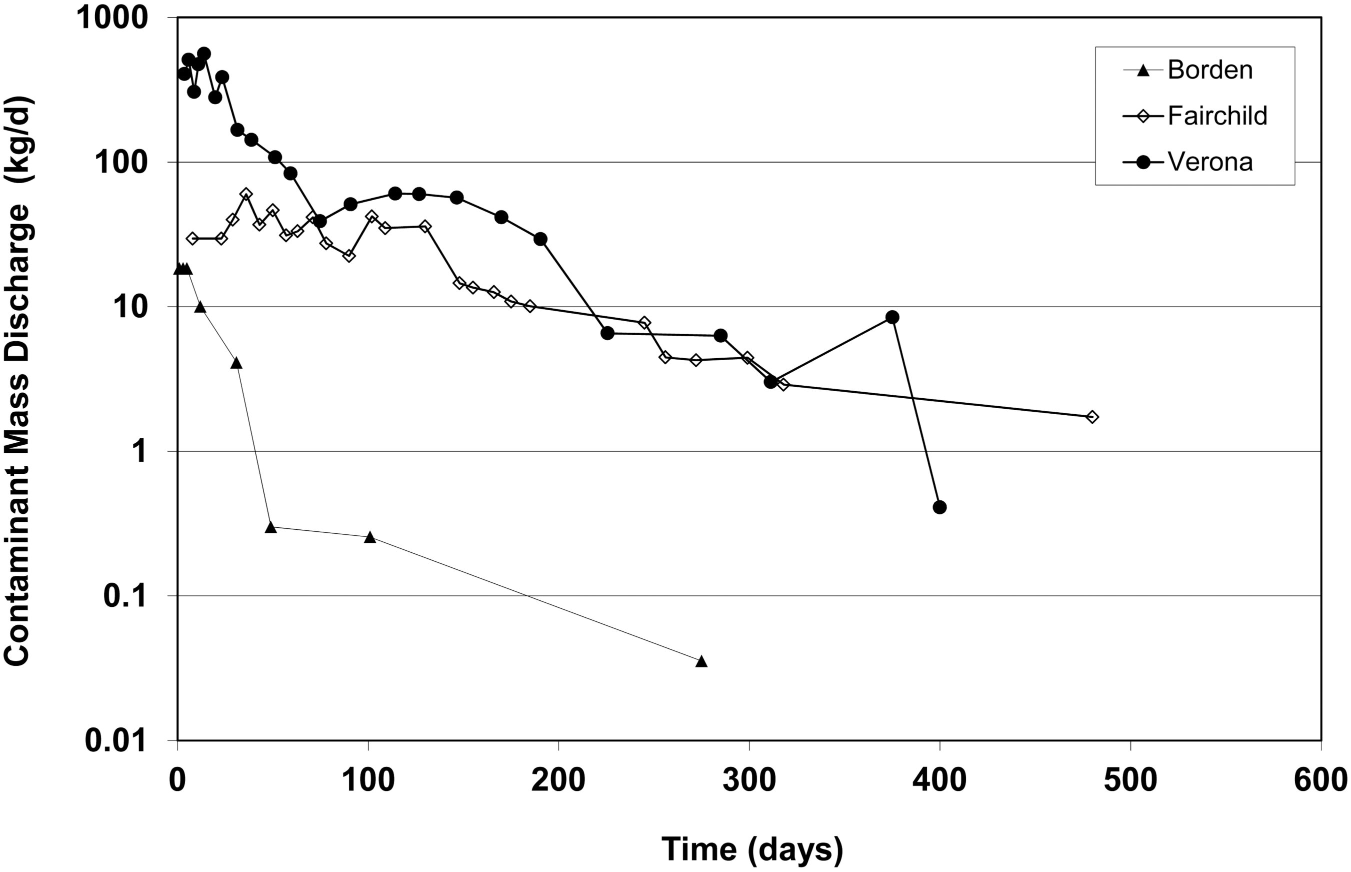


Figure 2.

Conceptual diagram illustrating the transport and mass-transfer processes relevant to the impact of vadose-zone sources on groundwater and vapor intrusion. Adapted from Carroll et al. (2012).

A


Contaminant Mass Discharge (kg/d)
1000
100
10
1
0.1
0.01
0
100
200
300
400
500
600
Time (days)
Borden
Fairchild
Verona

B

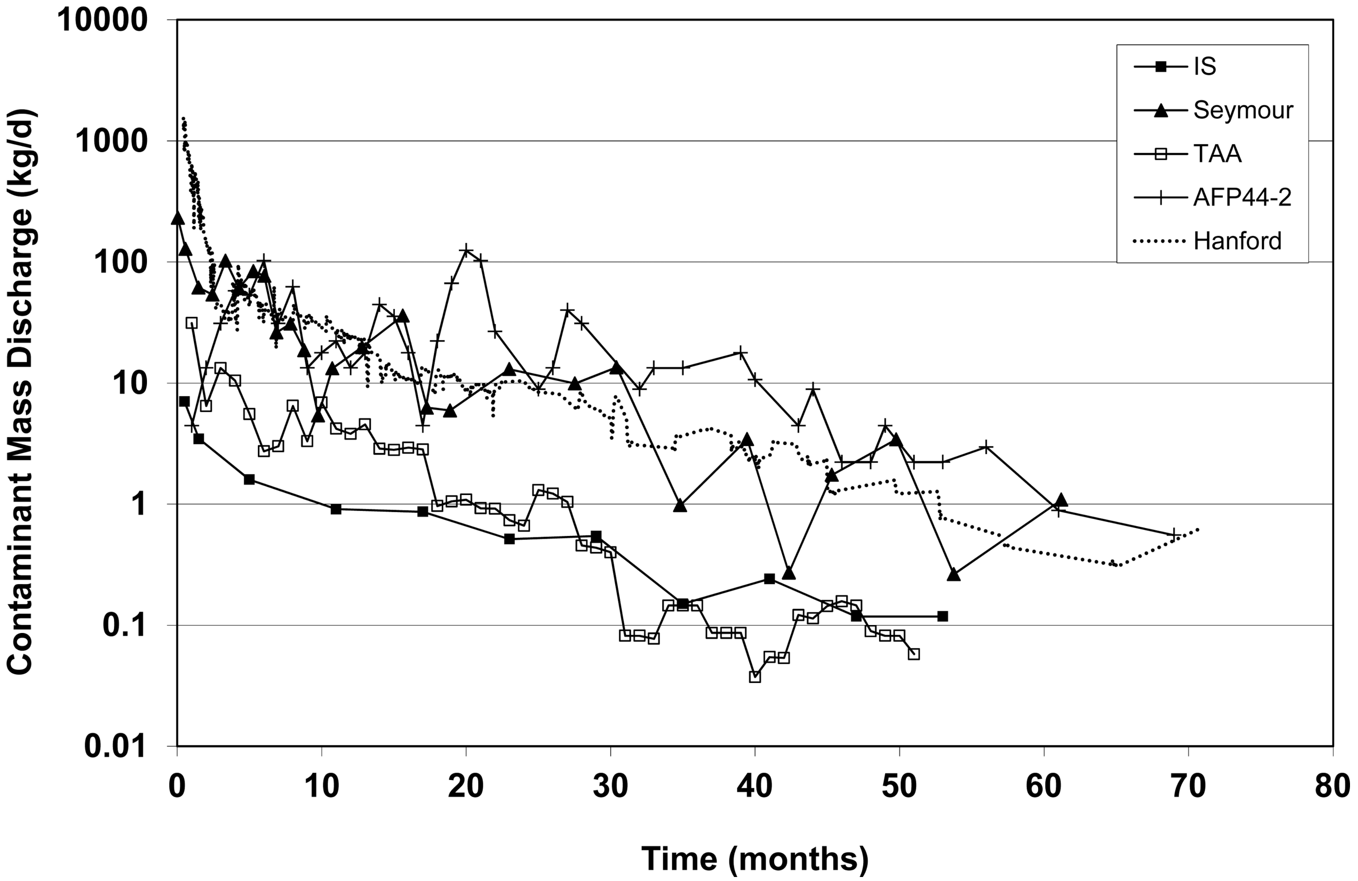
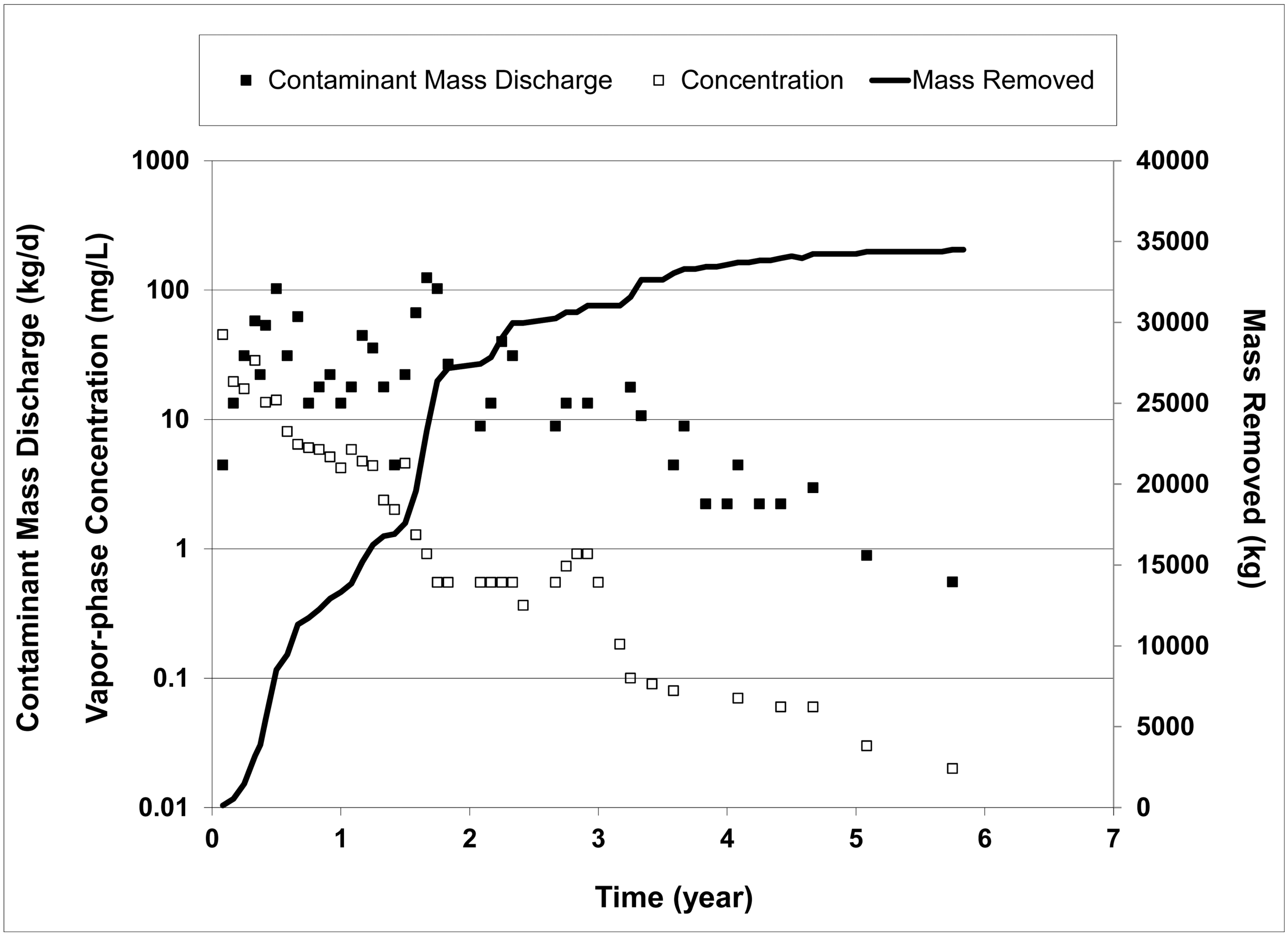


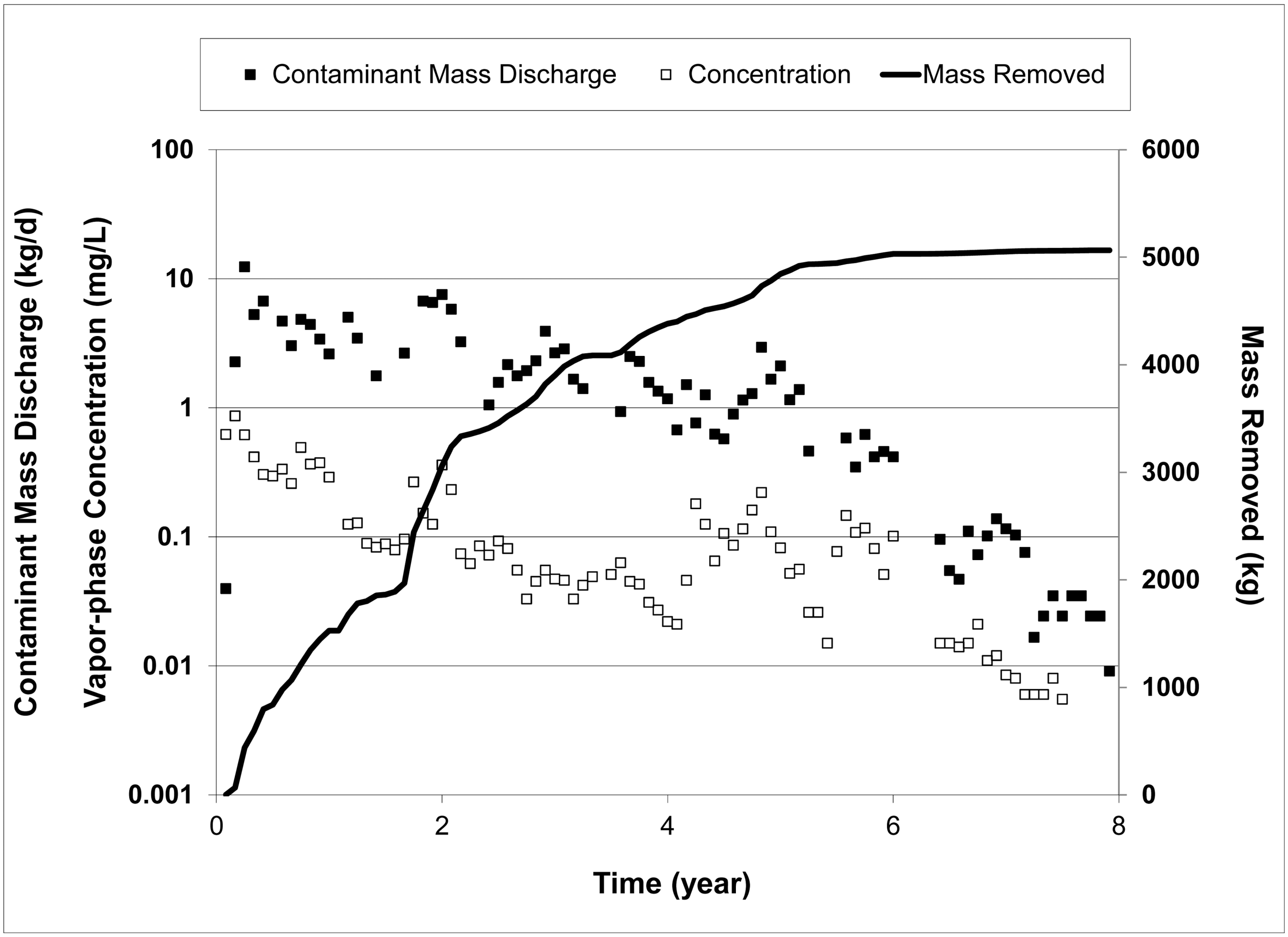
Figure 3.

Data collected for several SVE operations (see Table 1 for key): A) One-year operations; B) Multi-year operations. Time represents operational time (periods of non-operation removed).

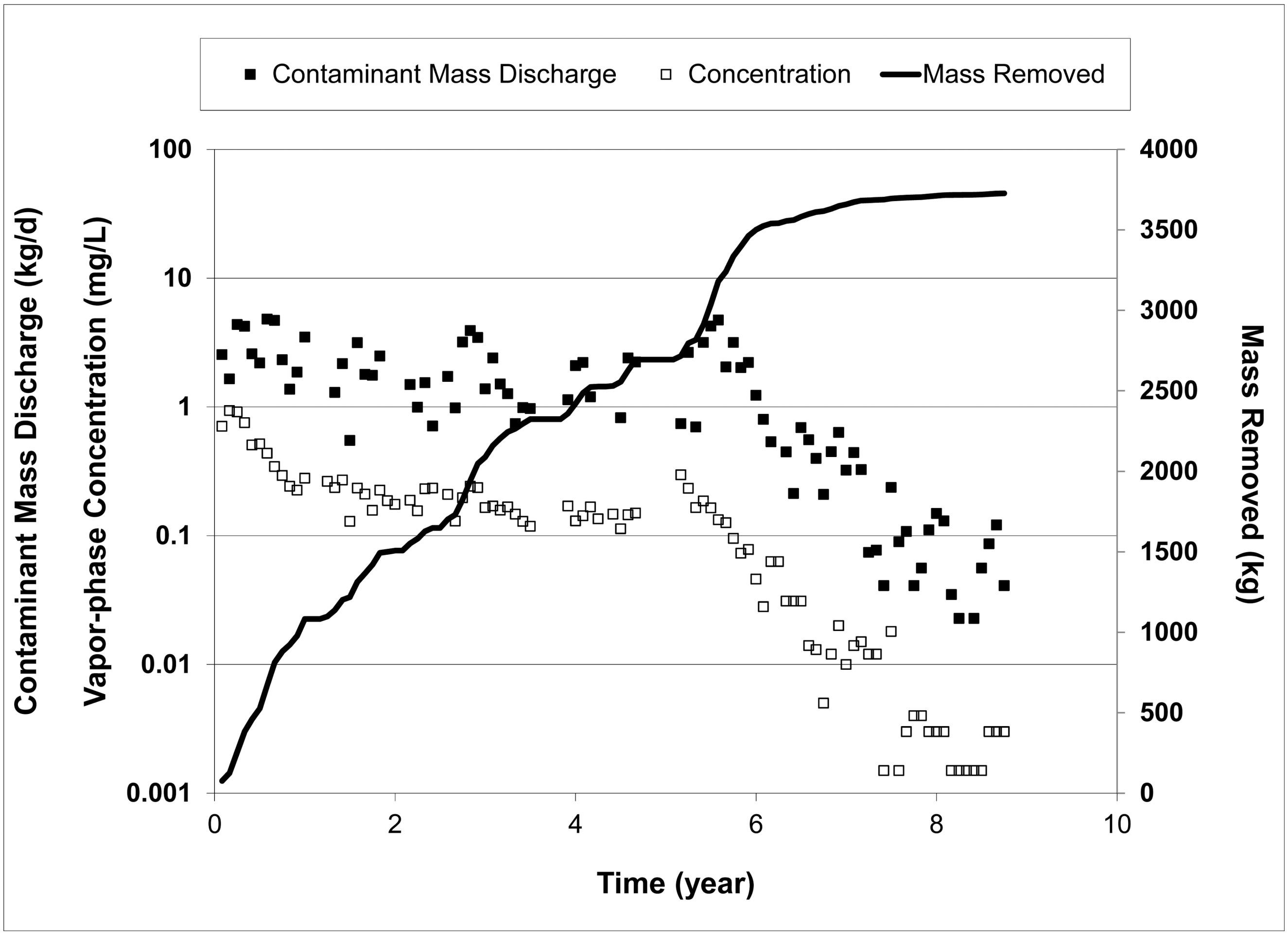
A


■ Contaminant Mass Discharge
□ Concentration
Mass Removed
Contaminant Mass Discharge (kg/d)
Vapor-phase Concentration (mg/L)
Mass Removed (kg)
Time (year)
1000
100
10
1
0.1
0.01
40000
35000
30000
25000
20000
15000
10000
5000
0
0
1
2
3
4
5
6
7

B


■ Contaminant Mass Discharge
□ Concentration
Mass Removed
Contaminant Mass Discharge (kg/d)
Vapor-phase Concentration (mg/L)
100
10
1
0.1
0.01
0.001
6000
5000
4000
3000
2000
1000
0
Mass Removed (kg)
0
2
4
6
8
Time (year)

C


■ Contaminant Mass Discharge
□ Concentration
Mass Removed
Contaminant Mass Discharge (kg/d)
Vapor-phase Concentration (mg/L)
100
10
1
0.1
0.01
0.001
Mass Removed (kg)
4000
3500
3000
2500
2000
1500
1000
500
0
0
2
4
6
8
10
Time (year)

D

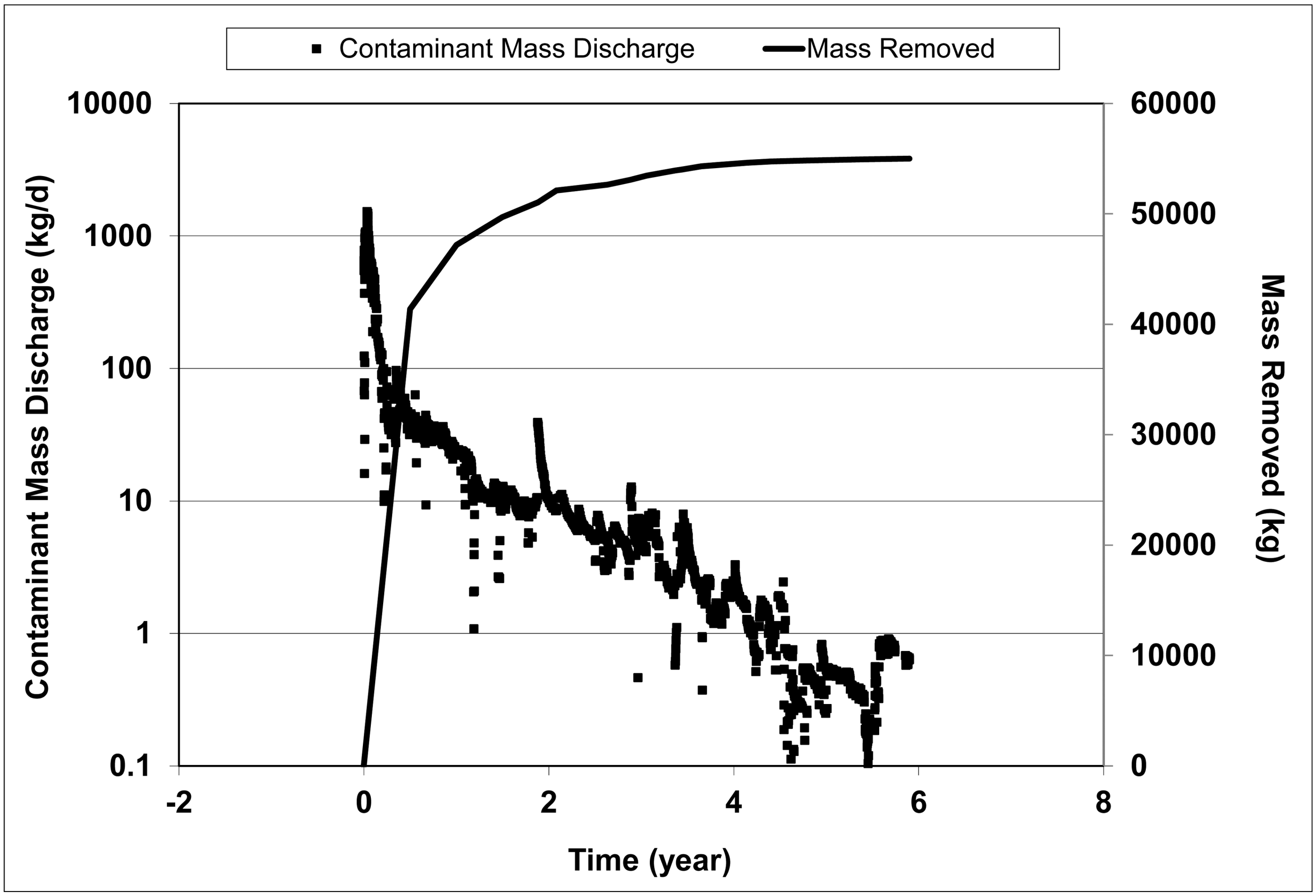


Figure 4.

High-resolution data collected for SVE operations: A) AFP44 site 2, Tucson International Airport Area Superfund site in Tucson, AZ; B) AFP44 site 3, Tucson International Airport Area Superfund site in Tucson, AZ; C) AFP44 site 5, Tucson International Airport Area Superfund site in Tucson, AZ; D) Hanford Z-9 Trench site, U.S. Department of Energy, Hanford, WA. Time represents operational time (periods of non-operation removed).

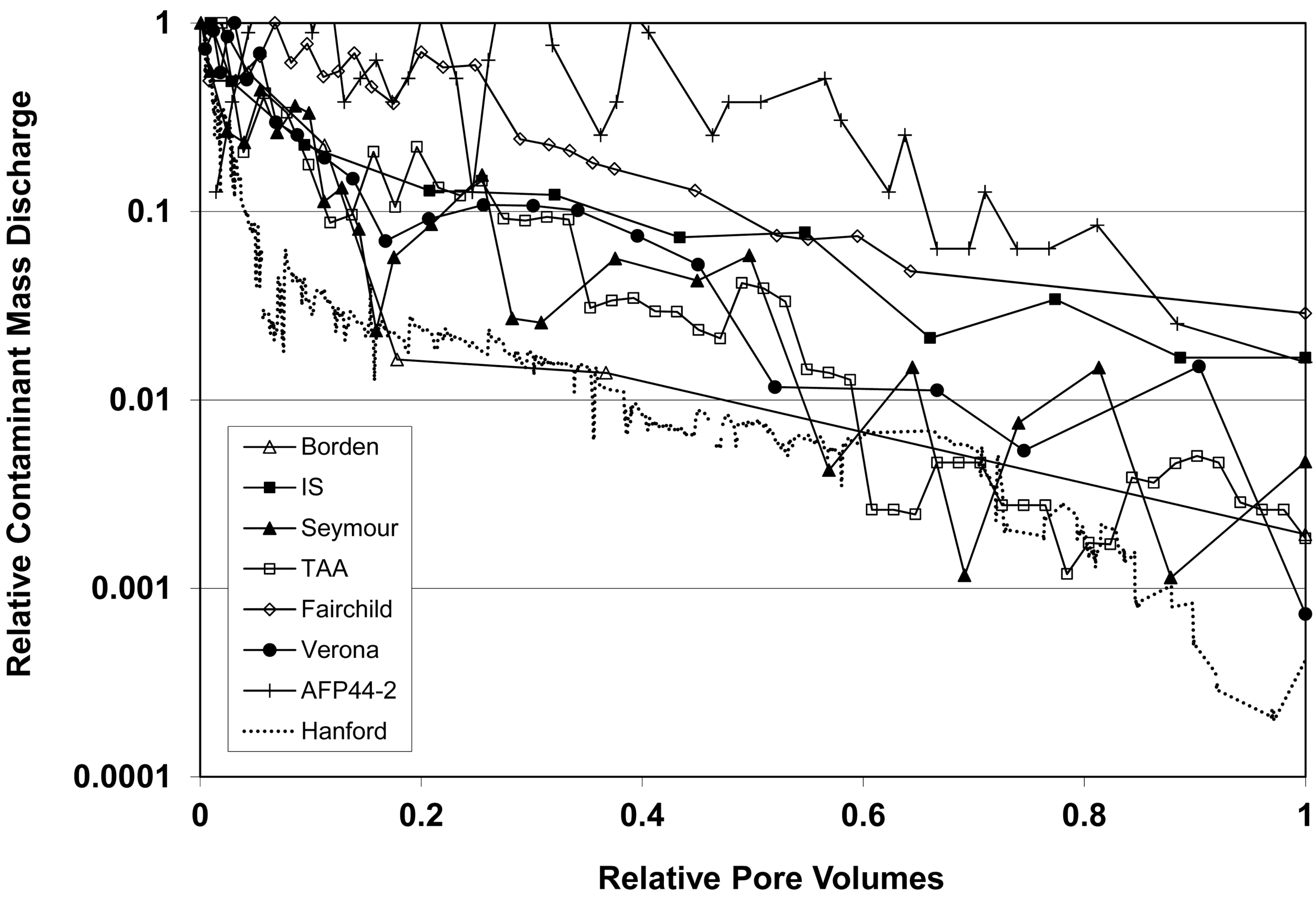
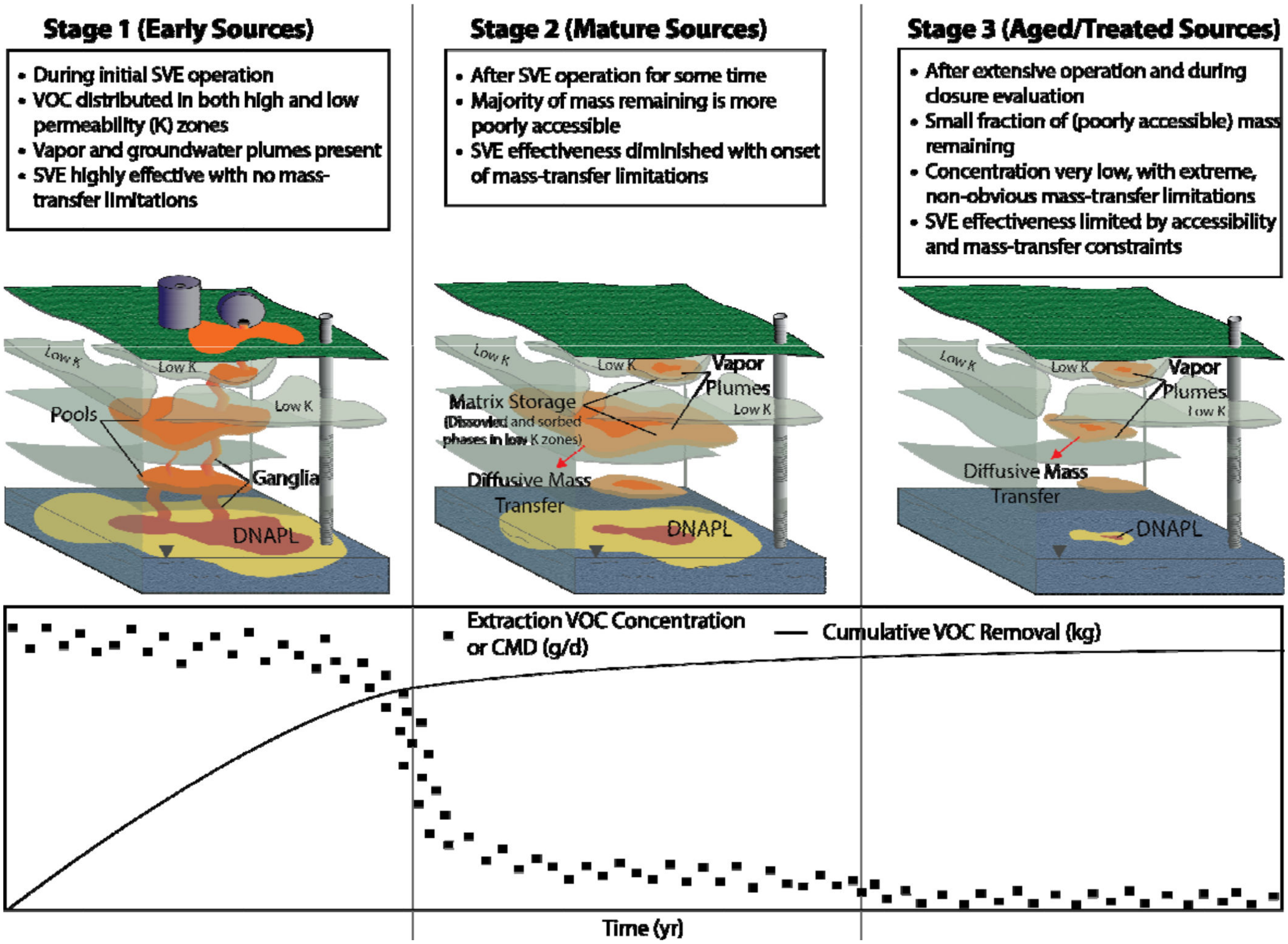


Figure 5.

Data presented in Figure 3, normalized in terms of relative CMD and relative pore-volume discharge as follows. Elapsed operational time was multiplied by the SVE extraction rate to determine cumulative vapor discharge. This was normalized by the estimated pore volume of the treatment domain to determine pore-volume discharge. This value was scaled for each site by the maximum pore-volume discharge of the site. The contaminant mass discharge was normalized by the maximum value.



Stage 1 (Early Sources)

- During initial SVE operation
- VOC distributed in both high and low permeability (K) zones
- Vapor and groundwater plumes present
- SVE highly effective with no mass-transfer limitations

Stage 2 (Mature Sources)

- After SVE operation for some time
- Majority of mass remaining is more poorly accessible
- SVE effectiveness diminished with onset of mass-transfer limitations

Stage 3 (Aged/Treated Sources)

- After extensive operation and during closure evaluation
- Small fraction of (poorly accessible) mass remaining
- Concentration very low, with extreme, non-obvious mass-transfer limitations
- SVE effectiveness limited by accessibility and mass-transfer constraints

Figure 6.

Conceptual diagram illustrating remediation issues and concentration-time and mass-removal-time profiles for the three stages typical to SVE remediation of sites contaminated by CVOCs. Subsurface block schematics modified from Stroo et al. (2012).

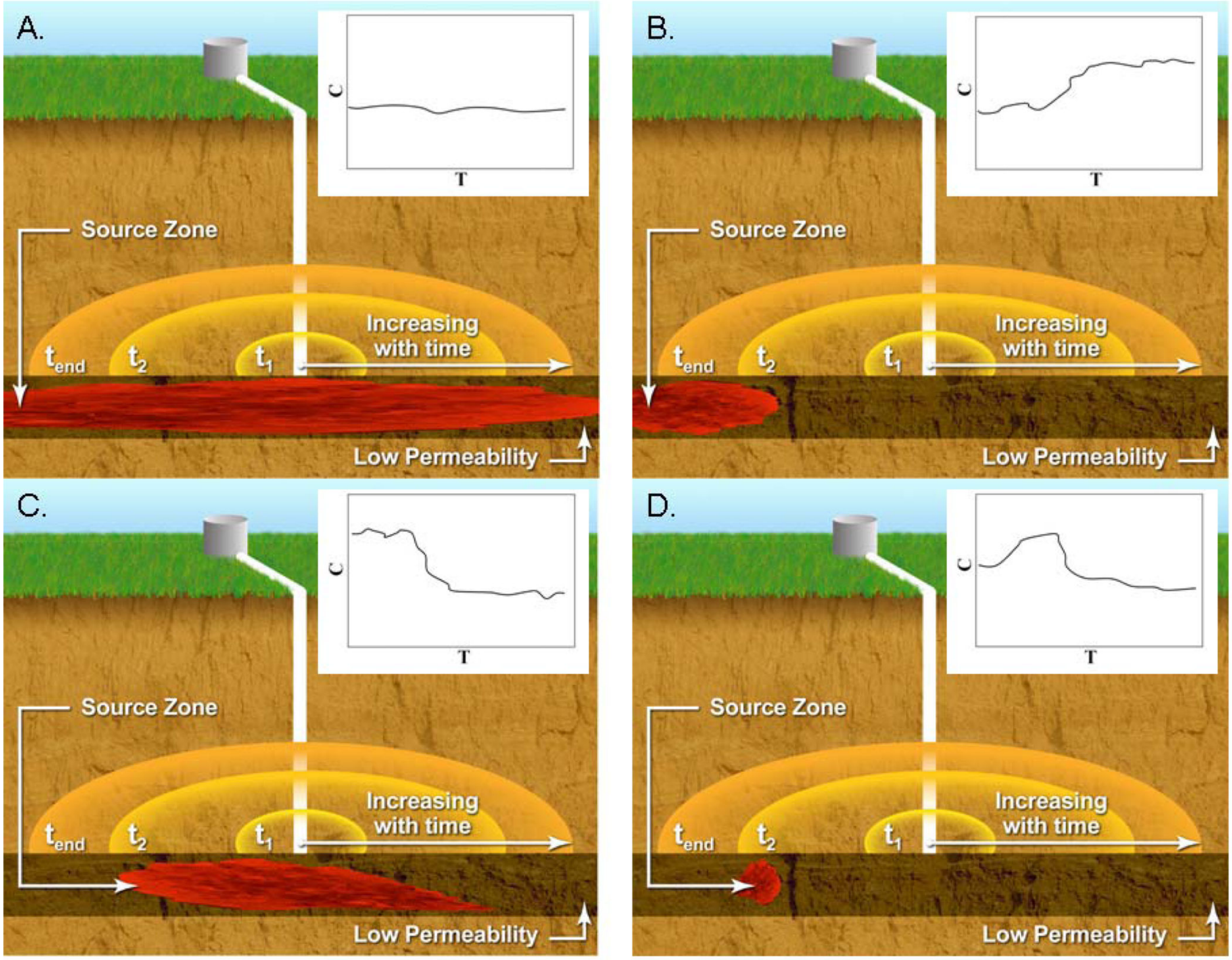


Figure 7.

Illustrative cross-sectional diagrams of a hypothetical well’s swept volume, as radial distance from the extraction well, at a few elapsed times (t_{end} equals end of test) in relation to the location of a source. Inset plots contain concentration (C) versus time (T) responses for each associated scenario. From Carroll et al. (2013).

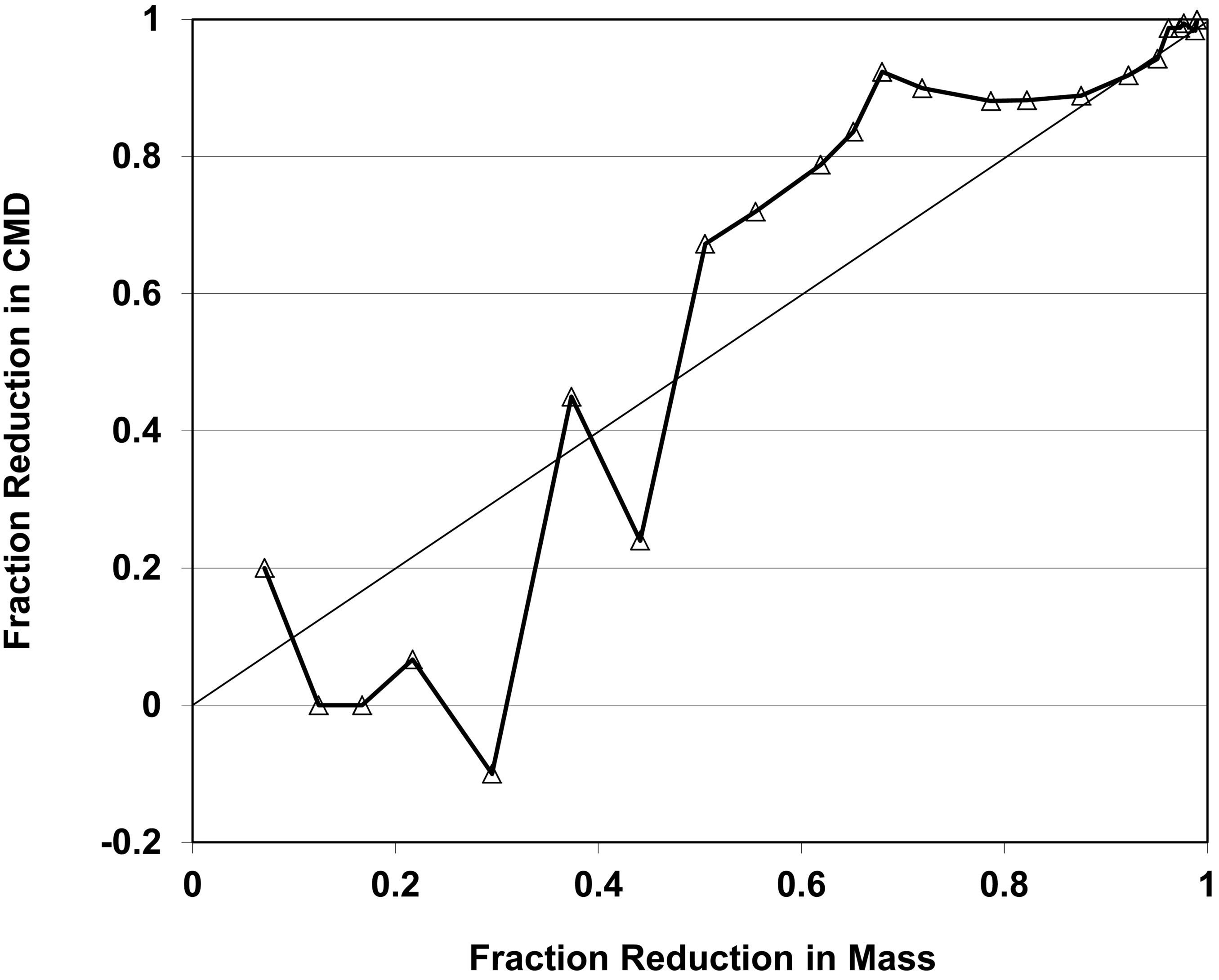


Figure 8.

Relationship between reduction in contaminant mass discharge (CMD) and reduction in contaminant mass for the Verona SVE operation. The one-to-one line is shown for reference.

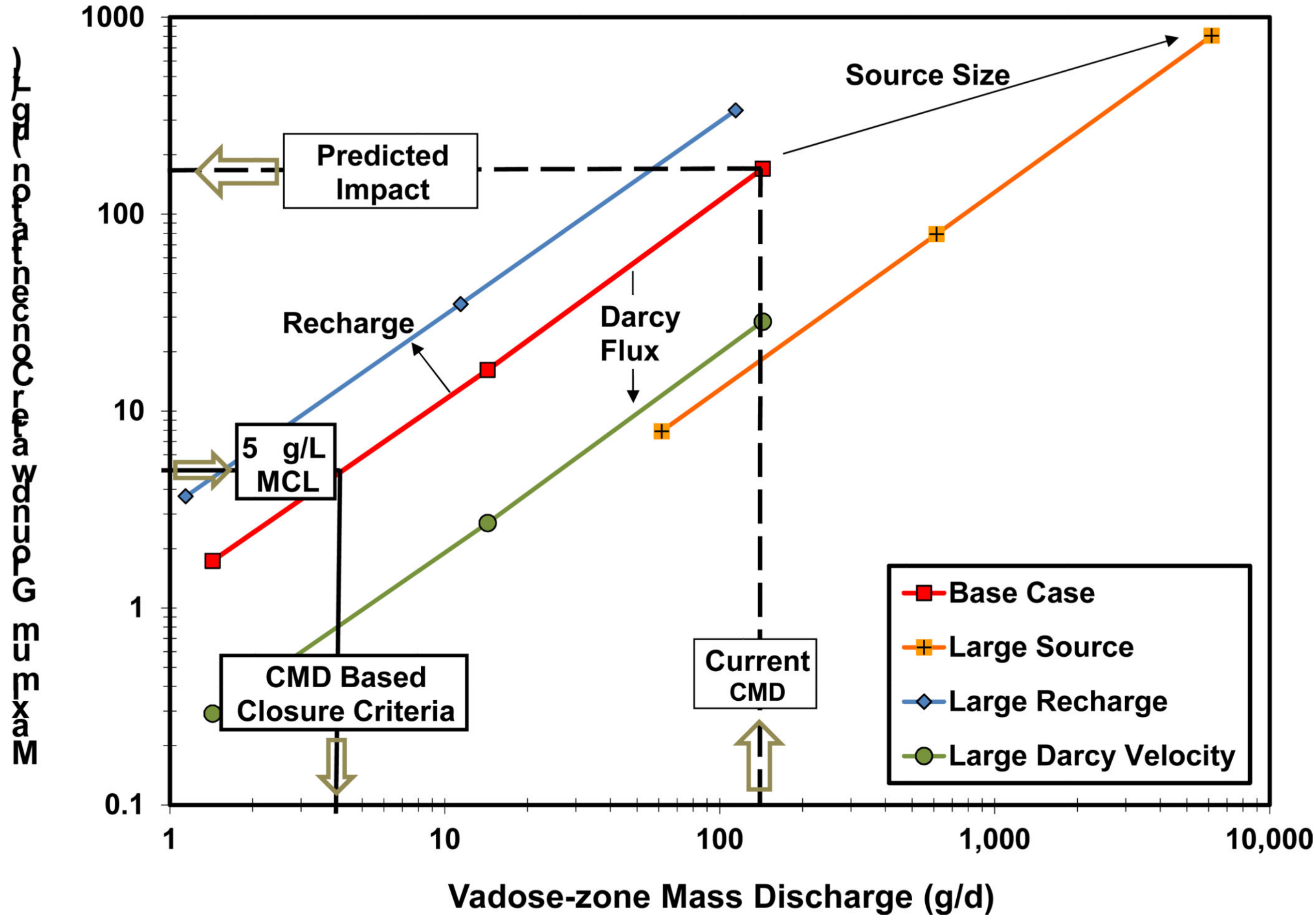


Figure 9.

Correlations of simulated vadose-zone contaminant mass discharge (CMD) versus the predicted long-term maximum concentrations of CVOC in groundwater. Note that groundwater concentration is calculated by assuming mixing through a vertical depth of 10 meters (screened monitoring well). The nomograph is used by inserting the measured or estimated contaminant mass discharge at the x-axis, drawing a vertical line upward to the type-curve that best represents the site conditions, and then drawing a horizontal line to intersect the y-axis to determine the associated groundwater concentration. The two examples are keyed to the “Base Case” type-curve. Adapted from Carroll et al. (2012).

Table 1

Information collected for several soil vapor extraction applications.

Site Key	Extraction Wells	Total Extraction Rate (m^3/d)	Treatment Zone (m^3)	PVT[a] (pv/day)	Mass of Contaminant Removed (kg)	Data Source
AFP44-2	75	44,900	2,000,000	0.07	35,000	Personal communication
AFP44-3	16	36,700	N.A.	N.A.	5,100	Personal communication
AFP44-5	12	30,000	N.A.	N.A.	3,800	Personal communication
Borden	6	950	100	10	376	Thomson and Flynn, 2000
Fairchild	25	9,700	32,000	0.9	7,300	EPA, 1995b
Hanford	3–24	8100–61000	2,900,000	0.04–0.08	55,000	Personal communication
Intersil/Siemens (IS)	7	1800–5200	214,000	0.05	1,360	EPA, 1998b
Seymour	Horizontal wells	2100–5000	39,000	0.3	13,600	EPA, 1998b
TAA	4	20,000	180,000	0.3	3,500	Personal communication
Verona	14	61,000	20,000	9	20,000	EPA, 1995b

[a] PVT = pore-volume throughput (discharge rate normalized by pore-volume equivalent of treated zone)