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Assessing the Impact of Source-Zone Remediation Efforts at the Contaminant-Plume Scale Through Analysis of Contaminant Mass Discharge

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Abstract

The long-term impact of source-zone remediation efforts was assessed for a large site contaminated by trichloroethene. The impact of the remediation efforts (soil vapor extraction and in-situ chemical oxidation) was assessed through analysis of plume-scale contaminant mass discharge, which was measured using a high-resolution data set obtained from 23 years of operation of a large pump-and-treat system. The initial contaminant mass discharge peaked at approximately 7 kg/d, and then declined to approximately 2 kg/d. This latter value was sustained for several years prior to the initiation of source-zone remediation efforts. The contaminant mass discharge in 2010, measured several years after completion of the two source-zone remediation actions, was approximately 0.2 kg/d, which is ten times lower than the value prior to source-zone remediation. The time-continuous contaminant mass discharge data can be used to evaluate the impact of the source-zone remediation efforts on reducing the time required to operate the pump-and-treat system, and to estimate the cost savings associated with the decreased operational period. While significant reductions have been achieved, it is evident that the remediation efforts have not completely eliminated contaminant mass discharge and associated risk. Remaining contaminant mass contributing to the current mass discharge is hypothesized to comprise poorly-accessible mass in the source zones, as well as aqueous (and sorbed) mass present in the extensive lower-permeability units located within and adjacent to the contaminant plume. The fate of these sources is an issue of critical import to the remediation of chlorinated-solvent contaminated sites, and development of methods to address these sources will be required to achieve successful long-term management of such sites and to ultimately transition them to closure.

Keywords

mass flux; mass discharge; DNAPL; chlorinated solvent; pump and treat

INTRODUCTION

Chlorinated organic solvent compounds such as tetrachloroethene, trichloroethene, carbon tetrachloride, and vinyl chloride are among the most common groundwater contaminants

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due to their prior widespread use for numerous industrial and commercial applications. Large groundwater contaminant plumes often form at chlorinated-solvent contaminated sites because chlorinated solvents have relatively high aqueous solubilities in comparison to regulatory standards, typically have relatively low retardation, and often are minimally influenced by transformation reactions. In many cases, the plumes are hundreds of meters to several kilometers long. This extensive groundwater contamination can pose significant risks to human health, and may also significantly impact regional water resources sustainability.

Pump and treat has been the primary method for containing and treating groundwater contaminant plumes at chlorinated-solvent sites. Concomitantly, enormous effort has been expended over the past three decades to develop methods to enhance the remediation of these sites. A primary approach has been the implementation of source-zone remediation efforts such as enhanced solubilization/mobilization, in-situ chemical oxidation, and thermal-based methods. An issue of prime import is the relative costs and benefits associated with such efforts (e.g., ITRC, 2002; EPA, 2003; NRC, 2005; SERDP, 2006).

The standard method for assessing remediation performance is based on analysis of changes in contaminant concentrations for groundwater samples collected from one or more monitoring wells located within the treatment zone. Recently, interest has grown in the use of contaminant mass flux or discharge, which is recognized as a primary determinant of the risk associated with a contaminated site, as a more integrative measure of the performance and effectiveness of remediation efforts (e.g., Freeze and McWhorter, 1997; Schwarz et al., 1998; DiGiulio et al., 1999; Einarson and Mackay, 2001; ITRC, 2002; Rao et al., 2002; EPA, 2003; Stroo et al., 2003; Brooks et al., 2004; Soga et al., 2004; NRC, 2005; SERDP, 2006). While its use is expanding, it has been applied to a relatively few sites (see DiFilippo and Brusseau, 2008 and ITRC, 2010 for recent reviews).

Characterization of contaminant mass discharge for purposes of evaluating the performance of source-zone remediation efforts is typically conducted at the source-zone scale. However, it can also be useful to evaluate the impact on plume-scale mass discharge. This is relatively straightforward for sites consisting of a single source zone and a relatively small associated plume. However, it becomes a more complex endeavor for sites with multiple source zones and large plumes. Assessments for such sites can be implemented or enhanced through the use of historical data collected during operation of a plume-scale pump-and-treat system.

The purpose of the research presented herein is to assess the long-term impact of full-scale source-zone remediation efforts for a site that is representative of the many large, complex chlorinated-solvent contaminated sites present in the USA and elsewhere. The impact of remediation efforts was assessed through analysis of contaminant mass discharge. The standard approach of characterizing discharge at the source-zone scale is expanded to provide additional characterization at the plume scale, thereby linking source-zone remediation to impacts on site-wide risk. A high-resolution data set comprising 23 years of operation of a large pump-and-treat system and two major source-zone treatment actions was used for the analysis.

METHODS

Study Site

The site that was the focus of the study is part of the Tucson International Airport Area (TIAA) federal Superfund site in southern Arizona (Leake and Hanson, 1987; Graham et al., 2001). The TIAA site was placed on the U.S. National Priorities List in August 1983 in response to the detection of trichloroethene in groundwater from several potable water

supply wells. A large, multiple-source plume of trichloroethene and 1,1-dichloroethene exists in the upper portion of the regional aquifer (Figure 1), which is the primary source of potable water for the Tucson metropolitan area. The regional aquifer is overlain by a clay layer, ranging from 1.5 to 7.5 m in thickness, which appears to act as a confining unit. There is uncertainty regarding the areal extent and integrity of this unit. The results of laboratory tests indicate that sorption of the contaminants by the aquifer sediments is low, with retardation factors less than 1.2 (Johnson et al., 2003a, 2009). The potentiometric surface of the regional aquifer is located 30 to 40 m below ground surface, and the general direction of groundwater flow under natural conditions is north-northwest. Administratively, the TIAA site is separated into three major zones, the North, Central, and South sections. The study site is located within the South section (see Figures 1 and 2).

A large pump-and-treat groundwater remediation project was initiated in the South section of the site in 1987. Air stripping was used as the primary treatment process from startup to 2009. Treatment was then changed to an advanced oxidation process comprising a combination of hydrogen peroxide and ozone. The treated water is reinjected as part of the pump-and-treat operations. The number of extraction wells in operation at a given time has varied, as has the total extraction rate. The locations of the extraction wells are shown in Figure 2. The TIAA site has had a significant impact on regional water resources, with total groundwater pumping associated with remediation efforts representing approximately 15% of total annual groundwater withdrawal for Tucson.

Three major source zones wherein solvents were disposed in unlined pits and ponds during the late 1950's to mid 1970's have been identified for the South section of the TIAA complex- Sites 2, 3, and 5 (see Figure 2). Pilot-scale soil vapor extraction tests were conducted in 1993 and 1994. Full-scale soil vapor extraction systems were operated from February 1995 to November 2000 for Site 2, September 1996 to July 2004 for Site 3, and September 1995 to June 2004 for Site 5. Pilot-scale tests of in-situ chemical oxidation using permanganate were conducted at source-zone Sites 2 and 3 in 2000. Full-scale implementation started in December 2002 and ended in December 2005 for Site 2, and started in October 2004 and ended in August 2006 for Site 3. The permanganate solutions were injected within the saturated zone and within the vadose-zone/saturated-zone interface. Note that soil vapor extraction had ended at both sites prior to full-scale implementation of in-situ chemical oxidation.

Contaminant Mass Discharge Calculations

Samples of extracted groundwater have been collected once or twice a week throughout the 23 years of operation of the pump-and-treat system, which is designed and operated to capture the entire plume. The data used for the mass-discharge analysis comprise concentrations for samples collected from a point just prior to the treatment system. As such, the concentrations represent composite values for all groundwater inflow into the pump-and-treat system. Extraction flow rates are monitored continuously. These data provide an unprecedented resolution of contaminant mass discharge for a very large, long-term remediation operation.

The samples are collected using standard EPA-approved protocols, and are analyzed by gas chromatography and/or GC-mass spectrometry using standard EPA methods. To calculate mass discharge, groundwater extraction volumes were composited monthly, and mean TCE and DCE concentrations were calculated for each month using the 4 to 8 data points available for each month. Monthly totals of contaminant mass removed were then calculated, from which mass discharge values were obtained.

RESULTS AND DISCUSSION

Contaminant Mass Removal

The pump-and-treat system has been in operation for approximately 23 years. Approximately 12,000 kg of solvent mass have been removed with the system to date. This quantity is approximately twice the amount of mass that was estimated to be initially present in the dissolved and sorbed phases prior to startup of pump and treat. In addition, it is approximately half of the total mass, including organic liquid, estimated to have been initially present in the water-saturated portion of the subsurface (i.e., excluding vadose-zone mass) based on the results of partitioning tracer tests and mathematical modeling (Nelson and Brusseau, 1996; Zhang and Brusseau, 1999; Brusseau et al., 2007).

The concentration of trichloroethene in the extracted groundwater is shown as a function of time in Figure 3. After an initial increase with system startup, the concentrations declined rapidly for the first three years of operation. At that point, asymptotic behavior began, with concomitant reductions in the rate of mass removal. Concentrations have declined from approximately 100 µg/L at the start of the asymptotic stage to 15 µg/L at present. The results of prior characterization efforts conducted at the site, using several methods of analysis, provided strong evidence that organic liquid was present in both the unsaturated and saturated portions of the primary source zones (Nelson and Brusseau, 1996; Brusseau et al., 1999, 2007; Zhang and Brusseau, 1999; Simon and Brusseau, 2007). The results of field tests, laboratory experiments, and mathematical modeling indicated that the asymptotic behavior observed in Figure 3 was caused primarily by constrained mass removal of poorly-accessible organic liquid present in the source zones, with additional contributions from diffusive mass transfer of aqueous mass between zones of lower and higher permeability within and adjacent to the contaminant plume (i.e., “back diffusion”) and nonideal (nonlinear, rate-limited) sorption/desorption (Nelson and Brusseau, 1997; Blue et al., 1998; Brusseau et al., 1999, 2007; Zhang and Brusseau, 1999; Johnson et al., 2003a,b,2009; Nelson et al., 2003).

Contaminant Mass Discharge Prior to Source-zone Remediation

The contaminant mass discharge as a function of time is presented in Figure 4. Inspection of the data reveals several stages of distinct behavior. After an initial increase, the mass discharge attained a peak value of approximately 7 kg/d. The mass discharge then decreased relatively rapidly over the next three years to a value of approximately 2 kg/d. This reduction reflects the removal of high-concentration aqueous-phase contamination during initial operation of the pump-and-treat system. After year 3, the contaminant mass discharge began to exhibit quasi steady-state behavior wherein the values decreased relatively minimally over the next approximately six years. As noted above, this behavior reflects the impact of mass-removal constraints.

Contaminant concentration and groundwater extraction data are collected for each extraction well, which allows an assessment of the relative contributions of the source zones and of the plume to total contaminant mass discharge (see Figure 5). Inspection of Figure 5 reveals significantly different behavior for the plume and source zones, wherein the discharge for the plume decreases relatively steadily through year 10 while that for the source zones remains essentially constant. Thus, the gradual net decrease in total contaminant mass discharge observed during this period is due primarily to reductions associated with the plume contribution. It is estimated that the three source zones contributed approximately two thirds of the total discharge during this period, with Site 3 contributing approximately half (contaminant mass discharge of ~1 kg/d).

A compilation of contaminant mass discharge measurements was reported recently by the ITRC (2010). Data were collected for approximately 40 sites, which comprised a variety of contaminants and site types. The reported values for conditions prior to source-zone remediation efforts, and excluding natural-attenuation effects if applicable, ranged primarily from 0.001 to 1 kg/d. The quasi steady-state contaminant mass discharge measured for the site reported herein, prior to source-zone remediation, is larger than all of the values obtained from the survey, and one or more orders-of-magnitude larger than the vast majority of the values. In addition, the value measured for the Site 3 source zone is similar to the largest values reported in the survey.

The contaminant mass discharge of approximately 2 kg/d observed during the quasi steady-state period represents the inherent long-term rate for the pump-and-treat system under the extant mass-transfer limited conditions. It is likely that this behavior would have persisted for a significant time without the advent of the source-zone remediation efforts. This potential was examined by Brusseau et al. (2007), who conducted predictive simulations to evaluate the impact of source-zone management on plume-scale remediation. The predictions were obtained using the model presented by Zhang and Brusseau (1999), employing the same conditions and parameters that they used to successfully simulate the observed plume-scale contaminant transport behavior over the course of the first 10-plus years of the pump-and-treat operation. For the modeling conducted by Zhang and Brusseau (1999), a three-dimensional heterogeneous hydraulic-conductivity field was generated using information obtained from borehole logs and pumping tests. Sorption and local-scale mass transfer parameters were obtained from laboratory experiments conducted with aquifer material collected from the site. Initial organic-liquid saturations were based on the results of partitioning tracer tests conducted at the site. For the predictive simulations presented in Brusseau et al. (2007), it was assumed for the case of source-zone remediation that all organic-liquid mass in the saturated portion of the source zones was removed prior to the start of the simulation period (the impact of vadose-zone mass was not evaluated). This assumption represents a limiting case to the actual conditions expected for partial mass removal. A single, constant set of flow rates was used for the injection and extraction wells. Thus, the influence of flow-rate variations associated with changes in the pump-and-treat operation was not reflected in the predictions.

The predicted composite trichloroethene concentrations reported by Brusseau et al. (2007) were combined herein with the average measured extraction rate for the pump-and-treat system to calculate predicted values for contaminant mass discharge. The predicted values for the cases with and without source-zone remediation are presented with the measured values for the period after the start of ISCO in Figure 6. The results for the simulation without source-zone remediation illustrate that contaminant mass discharge is predicted to decrease at a small rate in the absence of source-zone remediation (i.e., under the influence of only pump and treat). For example, it is estimated that it would take approximately 75 years from the start of the simulation period for the pump-and-treat system to attain the current mass discharge (~ 0.2 kg/d).

The prediction obtained for the case with source-zone remediation provides a reasonably good representation of the measured data, considering the assumptions employed. No organic-liquid contaminant mass was present in the system for this simulation. Hence, the simulation represents the condition wherein the mass removed is that associated solely with the aqueous and sorbed phases. Inspection of the contaminant elution curve (see Brusseau et al., 2007) and of Figure 6 reveals asymptotic behavior, which indicates that mass removal is constrained. For example, under the simulation conditions, it is estimated that it would require approximately 63 years of pump and treat to reach an influent concentration of 5 ug/L (equivalent to a reduction in contaminant mass discharge of roughly 99%) after source-

zone remediation. This is approximately 7-times longer than would be expected under ideal mass-removal conditions, given an approximate hydraulic residence time of six years (Brusseau et al., 2007) and assuming essentially complete removal within 1.5 pore volumes for ideal conditions. The extended time required for removal of the aqueous and sorbed mass (i.e., plume-associated mass) illustrates the impact of back diffusion and nonideal sorption/desorption on plume persistence.

Contaminant Mass Discharge After Source-zone Remediation

Full-scale soil vapor extraction was initiated at the source zones in years 8 to 9. The SVE operations removed approximately 49,000 kg of solvent mass, which is more than four times the amount removed via pump and treat to date. The mass-removal rates for the SVE systems were relatively constant for the first few years of operation, averaging approximately 38, 3, and 2 kg/d for Sites 2, 3, and 5, respectively (see Figure 7). Interestingly, these values are significantly larger than the respective source-zone aqueous-phase mass discharges associated with pump and treat.

The vapor-phase contaminant mass discharges began to decline relatively rapidly after the first few years of operation for all three sites. The discharges decreased to values approximately 100-times smaller than the initial values (~99% reduction) within three years after the start of the decline, at which point the SVE systems were shut down. The extracted vapor concentrations at this point were very low (~3 µg/L). Sampling of vapor monitoring wells a year after SVE closure showed minimal rebound of contaminant concentrations. In addition, contaminant concentrations for almost all of the sediment samples collected from several boreholes drilled within the source zones after SVE completion were below regulatory screening levels. These results suggest that most of the contaminant mass initially present in the vadose zone portion of the source zones was removed by the SVE operations.

After startup of the SVE operations, the site-wide aqueous-phase contaminant mass discharge began to decrease at a significantly greater rate (Figure 4), declining from approximately 1.8 to approximately 0.7 kg/d over the first four years after startup. Inspection of Figure 5 shows that the plume-associated mass discharge remained relatively constant for this period, whereas the discharge for the source zones decreased. The decrease in source-zone discharge corresponds to significant (factor of ~4) decreases in trichloroethene concentrations for groundwater pumped from the primary source-zone extraction wells. As noted above, a low-permeability layer exists above the saturated zone. However, the integrity and areal extent of this layer is uncertain, and windows wherein the layer is not present appear to exist (Zhang and Brusseau, 1998). In addition, measurements from pressure transducers and of water levels indicate the likely existence of a hydraulic connection between the vadose zone and the saturated zone. While these results suggest that SVE implementation may have contributed to the observed reduction in discharge, it is difficult to definitively and quantitatively address this issue given the uncertainties associated with the site regarding the impact of vadose-zone contaminant mass on groundwater. However, removal of the very large quantity of solvent from the vadose zone is likely to have ameliorated a long-term source of contamination to groundwater.

In-situ chemical oxidation was initiated at two of the two primary source zones (Sites 2 and 3) in year 16. Almost immediately, the aqueous-phase contaminant mass discharge began to decrease at a significantly greater rate (Figure 4). The mass discharge decreased from approximately 0.7 to 0.1 kg/d after implementation of in-situ chemical oxidation. This reduction was due to a combination of reductions in trichloroethene concentrations and reductions in flow rates for source-zone extraction wells (Brusseau et al., 2011). More than 37,000 kg of permanganate was injected into the two primary source zones over a three and a half year period. While it is not possible to quantify the mass depletion associated with this

effort, evaluation of system conditions, including the mass of contaminant present and natural oxidant demand, indicated that the amount of permanganate injected was sufficient to cause a significant depletion in contaminant mass (Brusseau et al., 2011). This is consistent with the significant reduction in contaminant mass discharge observed after the implementation of in-situ chemical oxidation. The contaminant mass discharge rebounds to a value of approximately 0.2 after year 20, which corresponds to completion of the in-situ chemical oxidation effort. The increase in mass discharge was due primarily to an increase in trichloroethene concentrations (Brusseau et al., 2011). The ISCO project and its impact on contaminant mass discharge are discussed in detail by Brusseau et al. (2011).

Contaminant mass discharge has stabilized once again (Figure 4), with minimal change observed for the past three years (2008–2010). The current quasi steady-state mass discharge reflects mass-removal behavior associated with the remaining contamination. This remaining contaminant mass is hypothesized to comprise poorly-accessible mass in the source zones, as well as aqueous (and sorbed) mass present in the extensive lower-permeability units located within and adjacent to the contaminant plume.

Assessing the Benefits of Remediation

The initial quasi steady-state period observed during years 4 to 9 in Figure 4 represents the inherent long-term mass-removal behavior for the pump-and-treat system under the extant mass-transfer limited conditions, as discussed above. As noted, it is likely that this behavior would have persisted for a significant time without the advent of the source-zone remediation efforts. The rate of decline in mass discharge over this period can be used to estimate mass discharge values for future times under conditions wherein pump and treat was the sole remediation action. This allows an assessment of the benefit of employing the source-zone remediation efforts in terms of the additional reduction in mass discharge attained compared to the projected decrease that would have occurred solely from pump and treat. Treating the decrease in mass discharge as a first-order function, the estimated mass discharge with no source-zone remediation is projected to be approximately 1.1 kg/d for the current year. This corresponds to a projected reduction in contaminant mass discharge of approximately 40% achieved from the pump-and-treat operation alone. The measured contaminant mass discharge was reduced from approximately 1.85 kg/d at the end of the initial quasi steady-state period to approximately 0.2 kg/d currently, a total reduction of approximately 89%. These results suggest that the source-zone remediation efforts significantly enhanced the reduction in mass discharge beyond the projected reduction that would have been achieved solely with the pump-and-treat operation.

The rate of decline in mass discharge for the initial quasi steady-state period can also be used to estimate the time required for mass-discharge values to reach a specified target via only the pump-and-treat operation (no source zone remediation). For example, it is estimated that it would take approximately 65 years from year 9 for the pump-and-treat system to attain the current mass discharge (~0.2 kg/d). This estimated value is within the range of the estimated time of approximately 75 years obtained from the predictive modeling noted above. The implementation of the source-zone remediation efforts is thus projected to have in effect eliminated approximately 50 years of pump-and-treat operations (accounting for the time elapsed during source-zone remediation). The operations and maintenance costs for pump-and-treat (roughly \$1 million per year) associated with this reduction can be compared to the costs associated with implementation of the source-zone remediation efforts (roughly \$15 M and \$1 M for SVE and ISCO, respectively) to evaluate relative cost effectiveness. A complete cost assessment would require an accounting of several factors and is beyond the scope of this research.

CONCLUSIONS

The data collected during 23 years of remediation operations at the TIAA site represent a valuable data set that can be used to assess the impact of remediation efforts on plume-scale contaminant mass discharge and associated risk at an unprecedented resolution and scale. The results indicate that these efforts resulted in significant reductions in mass discharge. Use of the data to evaluate the reduced length of pump and treat operations afforded by the source-zone remediation efforts, which can be used to estimate the cost savings associated with the decreased operational period, was illustrated. While it is recognized that such extrapolation-based analyses are fraught with uncertainty, they can provide useful information for purposes of site assessment and remediation-performance evaluation.

The analysis presented herein was based on employing contaminant mass discharge as an integrative measure of the performance and effectiveness of remediation efforts. The standard approach of characterizing discharge at the source-zone scale was expanded to provide characterization at the plume scale, which was evaluated by examining the change in contaminant mass discharge associated with the site-wide pump-and-treat system. This approach allows linking the impacts of source-zone remediation to effects on site-wide risk. There are several potential sources of uncertainty associated with this analysis, including the impact of natural-attenuation processes, the influence of temporal variability of the pump-and-treat operations, and uncertainty regarding the impact of vadose-zone sources on groundwater quality (this latter factor was discussed above).

As discussed by Brusseau et al. (2011), there appears to be minimal impact from natural-attenuation processes at the site. Regarding the second factor, overall extraction and injection flow rates for the pump-and-treat system have varied temporally, as have the specific sets of wells employed at a given time. Quantifying the impact of this flow-field variability on contaminant mass discharge would be a complex endeavor for a site such as this, with multiple source zones and multiple extraction wells, and wherein mass-transfer constraints are operative. For example, the impact of changes in flow rate is not straightforward (e.g., a reduction in flow will not necessarily result in a lower mass discharge), as the change in flow rate may impact contaminant concentrations due to factors such as mass-transfer constraints and spatially variable contaminant distributions. Similarly, turning off a given extraction well does not necessarily eliminate the associated mass discharge, as it may be captured by another extraction well.

While significant reductions were attained, it is evident that implementation of the source-zone remediation efforts has not completely eliminated contaminant mass discharge. Remaining contaminant mass contributing to the current mass discharge is hypothesized to comprise poorly-accessible mass in the source zones, as well as aqueous (and sorbed) mass present in the extensive lower-permeability units located within and adjacent to the contaminant plume. The results of mathematical modeling illustrated the impact of back diffusion and nonideal sorption/desorption on the time required for removal of the plume-associated mass, and the implications for plume persistence. The fate of these sources is an issue that is likely to be of critical import for many chlorinated-solvent contaminated sites. Development of methods to address these sources will be required to achieve successful long-term management of such sites and to ultimately transition them to closure.

Highlights

The long-term impact of source-zone remediation was assessed for a TCE-contaminated site

The impact of remediation was assessed through analysis of plume-scale contaminant mass discharge

The two source-zone remediation actions reduced contaminant mass discharge by approximately 90%

The approach allows linking source-zone remediation to their impacts on site-wide risk

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Figure 1.
Map of the Tucson International Airport Area (TIAA) Superfund site.

Figure 2.
Diagram of the study area, comprising the South section of the TIAA site presented in Figure 1, with locations of extraction wells used for the pump-and-treat system.

Figure 3.
Concentration of trichloroethene in groundwater extracted with the pump-and-treat system.
Also shown is cumulative solvent mass removed.

Figure 4. Contaminant mass discharge as a function of time; time zero corresponds to the start of the pump-and-treat operation (April 1987).

Figure 5.
Contaminant mass discharge for the first 13 years as a function of source; time zero corresponds to the start of the pump-and-treat operation (April 1987).

Figure 6.
Predicted contaminant mass discharge for cases with and without source-zone remediation; time zero corresponds to the start of the ISCO remediation effort.

Figure 7.
Vapor-phase contaminant mass discharge and cumulative mass removed for soil vapor extraction operations: A. Site 2 source zone; B. Site 3 source zone; C. Site 5 source zone.