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Assessing Contaminant-Removal Conditions and Plume Persistence through Analysis of Data from Long-term Pump-and-Treat Operations

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Abstract

Historical groundwater-withdrawal and contaminant-concentration data collected from long-term pump-and-treat operations were analyzed and used to examine contaminant mass discharge (CMD) and mass-removal behavior for multiple sites. Differences in behavior were observed, and these differences were consistent with the nature of contaminant distributions and subsurface properties of the sites. For example, while CMD exhibited a relatively rapid decline during the initial stage of operation for all three sites, the rate of decline varied. The greatest rate was observed for the PGN site, whereas the lowest rate was observed for the MOT site. In addition, the MOT site exhibited the lowest relative reduction in CMD. These results are consistent with the actuality that the MOT site likely contains the greatest proportion of poorly accessible contaminant mass, given that it comprises a combined alluvium and fractured-bedrock system in which solvent and dissolved mass are present directly in the bedrock. The relative contributions of the source zones versus the plumes to total CMD were determined. Constrained contaminant mass removal was observed to influence the plumes for all three sites, and was attributed to a combination of uncontrolled (or imperfectly controlled) sources, back diffusion, and well-field hydraulics. The results presented herein illustrate that detailed analysis of operational pump-and-treat data can be a cost-effective method for providing value-added characterization of contaminated sites.

Keywords

DNAPL; mass flux; source depletion

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Introduction

Contamination of groundwater by chemicals used in industrial, commercial, and other applications continues to pose significant threats to human health and the environment. Examples of compounds of concern include chlorinated solvents (e.g., trichloroethene, tetrachloroethene, carbon tetrachloride), 1,4-dioxane, methyl tertiary-butyl ether (MTBE), and perchlorate. Extensive dissolved-phase groundwater contaminant plumes typically form at sites contaminated by these compounds because of their relatively high aqueous solubilities (in comparison to regulatory standards), limited retardation, and generally low (or very site dependent) transformation potential. In many cases, the plumes are hundreds of meters to several kilometers long. These large plumes are very expensive to contain and remediate, and present difficult challenges to long-term management of contaminated sites.

It is now recognized that most complex sites with large groundwater plumes comprising these contaminants will require many decades before cleanup will be achieved under current methods and standards (e.g., NRC, 2013). The primary factors contributing to constrained contaminant removal and plume persistence have been noted long ago (e.g., Keely, 1989; Mackay and Cherry, 1989), and include source-zone mass discharge (primarily organic-liquid dissolution), diffusive mass transfer (back diffusion) of dissolved contaminant associated with lower-permeability zones, nonideal (rate-limited, nonlinear) desorption of contaminant from the sediment phase, and well-field hydraulics (inter-well stagnation zones, dilution effects). The central importance of source-zone discharge on the creation and maintenance of plumes is well recognized. Prior research conducted at sites for which the source zone has been remediated or contained indicates that the contaminant plumes have continued to persist beyond the timeframe expected based upon ideal contaminant-removal conditions (e.g., Zhang and Brusseau, 1999; Chapman and Parker, 2005; Rivett et al., 2006; Brusseau et al., 2007; Parker et al., 2008; Brusseau et al., 2011; Rasa et al., 2011), indicating the potential importance of diffusive mass transfer, desorption, and well-field hydraulics. Understanding the specific contributions of these factors to plume persistence, and their potential temporal variability, is critical to effective design, and implementation, and management of remediation efforts.

One of the primary constraints to delineating the specific factors influencing plume persistence for a given site is uncertainty in site properties (e.g., geologic, hydrologic) and conditions (e.g., nature and distribution of contamination). Recent reviews have identified the need to develop improved methods and approaches for site characterization that will enhance understanding of the factors and processes that influence contaminant removal and persistence (e.g., DOD, 2011; NRC, 2013). Pump and treat is currently a primary method used to contain and treat contaminated groundwater at sites with large groundwater contaminant plumes. Groundwater-withdrawal and contaminant-concentration data are routinely collected under regulatory requirement for the pump-and-treat operations. However, these data are rarely used for purposes other than to monitor the mass of contaminant removed. These data sets constitute a source that can be mined to provide additional information to enhance site characterization activities and remediation-performance assessments (Brusseau et al., 2007, 2011a,b, 2013). The information obtained from mining of the data can be used to update the site conceptual model, to revise the design

and operation of the remediation systems, and to support decision-making concerning remedy modification and closure.

The objective of this paper is to investigate plume persistence and the associated contributory factors for sites contaminated by chlorinated solvents, including the presence of organic liquids in source zones. Historical operations data were collected from long-term pump-and-treat systems for multiple sites. The data were analyzed to evaluate mass-removal constraints and to delineate the relative impact of source discharge versus other factors on plume persistence.

Materials and Methods

Data collected from five federal Superfund sites (i.e., listed on the Environmental Protection Agency, EPA, National Priorities List) are used herein. The sites are Air Force Plant 44 (AFP44), which is part of the Tucson International Airport Area (TIAA) site in Tucson AZ; Tucson airport remediation project (TARP), also part of the TIAA site; Motorola/52nd St OU1 (MOT) in Phoenix AZ; Phoenix/Goodyear North (PGN) in Phoenix AZ; and Chem-dyne (CD) in Hamilton OH. Maps for all of the sites are provided in the supplementary material. All of the sites are contaminated by chlorinated-solvent compounds and have large groundwater contaminant plumes (see Table 1). Pump-and-treat systems have been in operation at the sites for approximately 20 years or longer. The data, generally reported in official site-related documents, were graciously provided by EPA project managers and/or subcontractors working with the EPA or responsible parties.

All of the sites can be considered to be aged sites with respect to contaminant removal. Specifically, a fraction of the initial mass of contamination that entered the subsurface in the source areas has since been removed by natural groundwater flushing, as evidenced by the extensive groundwater contaminant plumes present. It should be noted that the data for each of the sites, with the exception of the TARP and PGN sites, represents the contributions of extraction wells located within identified source zones (areas with organic liquid present in the subsurface) as well as within the plume. The pump-and-treat systems represent the sole source of mass removal for the saturated zone for these sites, as no source remediation efforts have been implemented. The exception is AFP44, at which in-situ chemical oxidation was used for source remediation starting in year 16 (Brusseau et al., 2011b). Note that soil vapor extraction systems have been operated at all of the sites at some point to remediate vadose-zone contamination in the source areas.

There are some relevant differences in properties and conditions for the five sites. The aquifer at the AFP44 site comprises sand and gravel alluvium, and is bounded at the top and bottom by silty clay units that represent more than half of the total treatment-zone thickness. Prior site-characterization activities have shown that dissolved/sorbed contaminant is present in these units, serving as a source of back diffusion to the aquifer (Brusseau et al., 2007). Solvent disposal occurred via surface pits. Multiple lines of evidence indicate that solvent fluid is present in the source zones at the site (Nelson and Brusseau, 1996; Brusseau et al., 2007). The contaminated groundwater, comprising primarily trichloroethene (and 1,1-dichloroethene at much lower concentration), extends to ~60 m below ground surface. The

AFP44 site comprises the south section of the primary contaminant plume at the TIAA site. The well field for the pump-and-treat system (started in 1987) is designed such that several extraction wells are located within each of the three primary source zones, which are located at different regions within the plume. Several other extraction wells are distributed within the plume, for a combined (source and plume) total of ~20 wells. Treated groundwater is reinjected into 16 wells located primarily along the perimeter of the plume.

The TARP site comprises the north section of the primary contaminant plume at the TIAA site. The geologic and hydrologic conditions for the TARP site are similar to those for AFP44. In contrast to the AFP44 site, however, no source areas are located within or adjacent to the plume. Groundwater contamination comprising the TARP plume is thought to have originated by migration from the AFP44 and other source areas upgradient (south) of TARP. The well field for the pump-and-treat system (started in 1994) is designed such that five wells are located in a line, normal to the mean gradient, in the center of the plume, and four other wells are located at the downgradient perimeter of the plume. Treated groundwater is not reinjected.

The contaminated zone at the MOT site encompasses a sand and gravel alluvium unit residing above a fractured bedrock unit. Solvent disposal occurred primarily via fluid injection into a dry well, the total volume of which was approximately 350,000 liters. Notably, solvent fluid has been directly observed to exist in the fractured bedrock of the source zone, and ~60 liters have been recovered from a well screened solely in the bedrock. The contaminated groundwater, comprising primarily trichloroethene (and several other chlorinated aliphatics at much lower concentrations), extends to ~60 m below ground surface. The well field for the pump-and-treat system (started in 1992) is designed such that five extraction wells are located within the source zone, and nine other extraction wells are distributed along a single line (normal to direction of natural hydraulic gradient) located midway within the plume approximately 800 m downgradient of the source. Treated groundwater is not reinjected at this site.

The aquifer at the PGN site comprises sand and gravel alluvium, with a ~20-m thick silty clay unit (unit B) bisecting the coarse zone in to upper (unit A) and lower (unit C) sections. The lower permeability unit represents roughly less than one-quarter of the total treatment-zone thickness. Solvent disposal occurred via gravity injection into shallow (~4 m deep) dry wells. The contaminated groundwater, comprising essentially solely trichloroethene, extends to ~85 m below ground surface. The well field for the pump-and-treat system (started in 1994) is designed such that there are no extraction wells located directly within the source area. Two extraction wells, one screened in unit A and one in unit B, are located approximately 100 m downgradient from the source zone, with all other extraction wells distributed further within the plume. These wells are grouped in two sets. One set of six wells is located approximately 330 m downgradient of the plume and serves as a hydraulic interception barrier. The other set of six wells is arranged along the perimeter of the plume. Treated groundwater extracted from the nearer-source wells is reinjected into wells located approximately 600 m upgradient of the source zone. Treated water extracted from the wells located on the east and northeast perimeter is reinjected into wells located approximately 800 m further east. Treated water extracted from the wells located on the west and northwest

perimeter is discharged to a distant canal. The wells located on the eastern and northern perimeter have come online only recently, and thus have been in operation for two to five years.

The aquifer at the CD site consists of glaciofluvial deposits comprising primarily sand and gravel, overlain by a shallow unit of silts, clayey silts, and silty and fine sands. Contamination is associated with the prior storage of more than 100,000 liquid waste drums. The contaminated groundwater, comprising a mix of volatile organic compounds including several chlorinated aliphatics, extends to ~15 m below ground surface. The pump-and-treat system (started in 1987) consists of several extraction wells distributed within and at the perimeter of the plume. A portion of the treated water is reinjected on site.

Contaminant concentrations measured for samples collected from the extraction-well systems and groundwater withdrawal totals were used to determine the contaminant mass removed per year, which we will refer to as contaminant mass discharge (CMD). This value represents an integrated measure of contaminant mass being removed from the treatment zones via operation of the pump-and-treat systems. The contributions of the source areas and of the plumes to total CMD were delineated when feasible by separate tabulation of data obtained from extraction wells located within source areas and those within the plume proper, respectively. Note that total measured volatile organic compound mass is used for all sites for which multiple contaminants are present in groundwater. The total annual pumpage rates for the pump-and-treat systems have varied somewhat at all of the sites. The well-field configurations have not been changed significantly, except for the PGN site (as noted above). To enhance data comparison, the data were re-plotted in terms of relative CMD (measured CMD normalized by the peak CMD) and pore volumes (relative time) for the sites for which this was feasible. The resident pore volume for the site was estimated using the reported dimensions of the treatment domain and the porosity. Pore volumes pumped were then calculated as the quotient of groundwater withdrawal and the resident pore volume.

The initial masses of contaminant present at the start of pump-and-treat operations, which will be designated “initial pre-remediation mass”, were estimated for each site. This was determined for the AFP44 site using the results of partitioning tracer tests conducted at the primary source zone, supplemented with mathematical modeling analysis (Nelson and Brusseau, 1996; Zhang and Brusseau, 1999). The initial pre-remediation mass was estimated using the reported inventory of solvent disposal for the MOT site. For the PGN and CD sites, the initial pre-remediation mass was estimated based on fitting a mass-depletion function to the temporal contaminant mass discharge data (Butcher and Gauthier, 1994; Basu et al., 2009; Brusseau et al., 2013). The power function is one such, widely used, function (e.g., Zhu and Sykes, 2004; Falta et al., 2005):

$$dM/dt = - (Q_0 C_0 / M_0^\Gamma) M^\Gamma \quad (1)$$

where C_0 is initial contaminant concentration, M_0 is initial contaminant mass, M is contaminant mass at time t , Q_0 is initial discharge, Q is discharge at time t , and Γ is the power index term, representing the impact of a host of conditions and processes on mass-

removal behavior. Given that the terms in parentheses are constants, one can define $k = Q_0 C_0 / M_0^\Gamma$ as a source depletion rate coefficient, as noted in prior applications (e.g., Zhu and Sykes, 2004; Falta et al., 2005). For the special case wherein $\Gamma = 1$, the equation reduces to a first-order, exponential function, with a solution for contaminant mass discharge given as $QC_t = QC_0 \exp(-kt)$. The function was fit to the measured CMD data, optimizing for k . M_0 was then calculated with the optimized k and the known value for initial CMD (the initial measurement after the start of pump and treat, $Q_0 C_0$). This method was also used to estimate the initial pre-remediation contaminant mass associated with the plume for the plume-based analyses for the MOT site. The initial pre-remediation plume-associated mass for the AFP44 site was reported by Zhang and Brusseau (1999).

Results and Discussion

Mass Removal and Contaminant Mass Discharge

The mass of contaminant removed with time, the data typically reported for pump-and-treat systems, is presented in Figure 1. The plots exhibit reduced rates of mass removal as the operations continue. This behavior is consistent with what is typically observed for pump-and-treat systems. The total mass removed for the TARP site is much less than the totals for the other sites, reflecting the fact that this site has no on-site source areas and thus involves primarily plume-only mass removal.

The historical CMD for the sites, determined from analysis of the pump-and-treat data, is presented in Figure 2. The initial CMD is observed to range between approximately 0.6 and 10 kg/d. These values are quite large in comparison to the range of values reported in a recent summary (ITRC, 2010). This is reflective of the significant impact of the highly contaminated source zones owing to the large quantities of solvent disposed of therein in combination with the induced-gradient conditions associated with the pump-and-treat systems.

Some degree of asymptotic behavior is observed for the later stage of operation for all of the sites. As noted above, all of the sites are considered to be aged sites with respect to contaminant removal and distribution. First, it is anticipated that the mass that was removed from the source areas prior to the start of the remediation efforts (i.e., during plume formation) comprised primarily the mass that was more readily accessible to flowing groundwater. Concomitantly, it is expected that the mass remaining in the sources at the start of pump and treat comprised a significant fraction that is more poorly accessible to groundwater flushing. Second, the contaminant plumes have been present at the site for several decades, and it is expected that significant quantities of dissolved and sorbed mass are present within the extensive lower-permeability units that are present at the sites. The observed asymptotic behavior is attributed to the impact of this poorly accessible contaminant mass on mass transfer and mass removal. Other factors, such as the impact of well-field hydraulics, may also influence the observed behavior.

The significant increase in CMD that began within the last five years for the PGN site is related primarily to the introduction of additional extraction wells located along the eastern and northern perimeter of the plume. The asymptotic phase for the AFP44 site was truncated

by the advent of the source remediation efforts that were started in year 16 (Brusseau et al., 2011b). Essentially steady state behavior was observed for the TARP site from year 4 through year 16, with an apparent decline since then (note pumpage rates have remained essentially constant). This site has no on-site source areas, and the plume is considered to have been generated by contaminant migration from source areas located upgradient, as noted above. Thus, this site represents primarily plume-only mass removal. However, the continued contribution of upgradient sources is indicated by the observation that the mass of contaminant removed to date is roughly four times larger than the mass estimated to have been present in the plume prior to the start of pump and treat. The contributions from AFP44, a primary potential source, should have been minimized with the advent of the AFP44 pump-and-treat system that started in 1987 (which predates that start of TARP operations). The contributions from another potential source, the Three Hangers facility, should have been minimized with the startup of pump-and-treat at that site in late 2007. Interestingly, the decline in CMD observed for the TARP site coincides with the startup at Three Hangers.

Comparative analysis of the CMD data is complicated by the fact that the design and operation of the well fields varies among the sites. To enhance data comparison, the data were re-plotted in terms of relative CMD (measured CMD normalized by the peak CMD) and pore volumes (relative time). The normalized CMD data are presented in Figure 3 for the three sites for which the calculations could be conducted. It is noted for all three sites that the equivalent of only approximately two pore volumes of groundwater have been pumped during the ~20 years of operation. This illustrates the very low rates of flushing inherent to pump-and-treat systems associated with large groundwater plumes. As a result, long cleanup times should be expected even under the most ideal conditions (e.g., minimal mass-removal constraints).

Inspection of the figure shows that differences are revealed in the temporal CMD profiles among the three sites. For example, while CMD exhibits a relatively rapid decline during the initial stage of operation for all three sites, the rate of decline varies. The greatest rate is observed for the PGN site, whereas the lowest rate is observed for the MOT site. In addition, the MOT site exhibits the lowest relative reduction in CMD. These results are consistent with the conditions of the sites, wherein the MOT site likely contains the greatest proportion of poorly accessible contaminant mass given that it comprises a combined alluvium and fractured-bedrock system in which solvent and dissolved mass are present directly in the bedrock. The greater rate of decline observed for the PGN site compared to the AFP44 site is also consistent with site conditions. First, the relative portion of poorly accessible contaminant mass associated with lower-permeability domains is likely to be greater for the AFP44 site based on the differences in the relative fractions of lower-permeability units comprising the two sites, which is larger for the AFP44 site. Second, the CMD data for the AFP44 site includes the contribution of extraction wells that are located directly within the source zones (which are distributed within the plume). Conversely, there are no extraction wells located directly within the source zone for the PGN site, and thus contaminant discharge from the source is closer to natural-gradient conditions, thereby muting the source contributions.

The CMD and initial-mass data can be used to determine the relationship between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR). The CMDR-MR relationship is a defining characteristic of system behavior, and is mediated by system properties and conditions such as permeability distribution, contaminant distribution, and mass-transfer processes. The CMDR-MR profiles provide a more robust assessment of contaminant-removal conditions compared to analysis of temporal CMD data alone, and also facilitate comparison among different sites.

The CMDR-MR profiles determined for the five sites are presented in Figure 4. It is observed that the profiles reside primarily above the one-to-one line. The nature of the profiles are indicative that substantial amounts of contaminant mass exist at the sites that is poorly accessible to groundwater flushing associated with the pump-and-treat system. The MOT site in particular shows a very sharp decrease in CMD associated with a very small fraction of mass reduction. This is most likely a function primarily of the presence of liquid solvent as well as dissolved mass in the fractured bedrock. The profiles exhibit multi-step behavior, particularly those for AFP44, TARP, and CD. These profiles are considerably more complex than the smooth singular curves predicted by the simplified source-depletion functions often used, as has been discussed previously (Brusseau et al., 2008; DiFilippo and Brusseau, 2008; Christ et al., 2010; DiFilippo et al., 2010).

Potential uncertainties associated with the CMDR-MR profiles, primarily related to uncertainty in the initial-mass estimates (pre-remediation mass in this case), should be considered in the analysis. For example, estimates of initial mass may often be lower than actual values. In such cases, using the larger initial-mass value will result in a leftward shift of the CMDR-MR profile. A very large estimated initial mass was used for the MOT site, based on waste-disposal inventories. The use of a smaller value would result in a rightward shift of the curve. While the positions of the profiles along the abscissa may have a larger degree of uncertainty, the general shapes of the profiles are expected to have significantly less given the typically more robust nature of the CMD measurements.

Plume Persistence

The data presented in the previous section included the contributions of the source zones to total contaminant mass discharge and recovery. The persistence of the contaminant plumes in the absence of source-zone effects can be investigated by examining data specifically associated with only those extraction wells located within the plumes. For the AFP44 and MOT sites, the pump-and-treat systems are designed and operated such that extraction wells located in the source zones in effect serve to minimize mass discharge from the sources to the plumes. Collection of well-specific data allows determination of aggregate contaminant mass discharge and recovery for plume-associated versus source-associated extraction wells for these two sites. For the PGN site, the contributions of EA-01, the extraction well located closest to the source area, the hydraulic interceptor wells (MTS), and the wells located at the plume perimeter (non-MTS) are delineated.

A comparison of the separate contributions of the source zones and the plumes to total CMD is shown in Figure 5 for the AFP44, MOT, and PGN sites. It is observed that the plume provided a greater contribution than the source zones during the initial system startup for the

AFP44 and MOT sites. The near-source extraction well (EA-01) provided a greater contribution than the plume during the early operation for PGN. During the course of operation, the CMD values declined for the plumes, whereas they remained relatively stable (MOT) or declined at a lower rate (AFP44) for the source zones. Hence, the relative contribution of the plumes to total CMD decreased during the course of operation for both sites. While extraction rates have varied for the sites, a decrease in contaminant concentrations is the primary cause of the decrease in CMD observed for the plumes. These results illustrate the continued importance of the source zones to overall site remediation.

Essentially steady state CMD behavior was observed during years 9–14 for the near-source extraction well EA-01 at the PGN site, likely reflecting the impact of the uncontrolled source area. A significant decrease in CMD has been observed for the past four years. This is hypothesized to result from site-wide changes in the direction of the hydraulic gradient, induced in part by the startup of the new eastern plume-extraction wells, such that the near-source well may not be capturing the source discharge to the same degree. This example illustrates the potential significance of well-field hydraulics on mass removal behavior.

The relative CMD profiles for the plume systems in absence of source-zone contributions are presented in Figure 6. The data reinforce that asymptotic mass-removal conditions are present for the plumes. The impact of mass-transfer constraints is also illustrated by the CMDR-MR profiles for the plume-only data, wherein they reside above the one-to-one line (Figure 7). Dissolved contaminant associated with lower-permeability zones is prominent for all of the sites and, hence, back diffusion is anticipated to be a significant common factor contributing to the observed plume persistence. This is supported by the results of prior investigations conducted at the AFP44 site to examine source-zone remediation efforts and associated plume behavior (Nelson and Brusseau, 1996; Blue et al., 1998; Brusseau et al., 1999; Zhang and Brusseau, 1999; Nelson and Brusseau, 2003; Brusseau et al., 2007, 2011a,b). Multiple methods, including forced-gradient contaminant elution tests, multiple-solute tracer tests, sediment coring, analysis of historic pump-and-treat operations data, laboratory experiments, and mathematical modeling, were used to characterize the relative impacts of plume-scale back diffusion, plume-scale sorption/desorption, and dissolution of organic liquid trapped in the source zones on contaminant removal and plume persistence. The results indicated that organic-liquid dissolution was the primary factor influencing contaminant removal and plume persistence. Back diffusion was delineated as a moderate factor, whereas the impact of nonideal sorption was minor in comparison to the other two (consistent with the very low magnitude of sorption measured for the contaminant). Assessment of the historic integrated plume-scale contaminant mass discharge, along with the results of mathematical modeling, indicated that the plume would persist for many decades even with the isolation or removal of the source zones, primarily due to back diffusion of contaminant associated with the lower-permeability units and hydraulic effects.

Based on the prior analyses conducted for AFP44 and the extant conditions for the other two sites, it is hypothesized that back diffusion and well-field hydraulics, in addition to the impact of uncontrolled (or imperfectly controlled) sources, are the primary factors contributing to plume persistence for the sites. Delineating the relative significance of the factors for the sites would require additional analyses that are beyond the scope of this

presentation. While the potential effects of uncontrolled sources and back-diffusion processes have been well documented, the impacts of well-field hydraulics on contaminant-removal behavior have been less so. The results for the PGN site discussed above, specifically the significant recent decline in CMD observed for the near-source extraction well that is suspected to be related to changes in hydraulic conditions, is one such illustration. Another are the results presented by Rivett et al. (2006) for a study conducted at the Borden site in Canada.

Summary

Groundwater-withdrawal and contaminant-concentration data collected from long-term pump-and-treat operations were analyzed and used to examine contaminant-removal behavior for five sites, all of which are considered to be relatively aged with respect to contaminant removal and distribution. Differences in behavior were observed, and these differences were consistent with the nature of contaminant distributions and subsurface properties of the sites. For example, while CMD exhibited a relatively rapid decline during the initial stage of operation for all sites, the rate of decline varied. The greatest rate was observed for the PGN site, whereas the lowest rate was observed for the MOT site. In addition, the MOT site exhibited the lowest relative reduction in CMD. These results are consistent with the actuality that the MOT site likely contains the greatest proportion of poorly accessible contaminant mass, given that it comprises a combined alluvium and fractured-bedrock system in which solvent and dissolved mass are present directly in the bedrock.

The relative contributions of the source zones versus the plumes to total CMD were determined for the AFP44, MOT, and PGN sites. The plume contributions were observed to decrease with time, whereas that of the source zones remained relatively constant for the first two sites. Conversely, CMD was observed to decrease significantly in the last few years for the PGN site, which was attributed to the impact of changes in well-field hydraulics. The data were also used to investigate the relationship between reductions in contaminant mass discharge and reductions in contaminant mass. Constrained contaminant mass removal was observed to influence the plumes for all the sites, and was attributed to a combination of back diffusion, uncontrolled (or imperfectly controlled) sources, and well-field hydraulics. The data sets exemplified the recalcitrance typically associated with chlorinated-solvent contaminated sites, and the impact on plume persistence and associated implications for site cleanup.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

Long-term pump-and-treat data were used to examine mass-removal behavior for five sites

Asymptotic behavior was observed to some degree for all sites

Differences in observed behavior correlated to specific site conditions

Observed plume persistence was attributed to back diffusion, potential uncontrolled sources, and well-field hydraulics

Figure 1.
Cumulative mass of contaminant removed with pump and treat of groundwater for five Superfund sites contaminated by chlorinated-solvent compounds.

Figure 2.

Contaminant mass discharge profiles obtained from analysis of pump-and-treat data for the five sites. Note that data beyond year 16 are not presented for AFP44 due to the impact of source remediation efforts. Time zero corresponds to the start of pump-and-treat operations.

Figure 3. Relative contaminant mass discharge (CMD) as a function of pore volumes of groundwater pumped for three sites; includes contributions from source zones and plumes.

Figure 4. Relationships between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR) for three sites; includes contributions from source zones and plumes.

A

B

C

Figure 5.

Contaminant mass discharge (CMD) profiles obtained from analysis of pump-and-treat data for three sites, comparing the contributions of source zones and plumes to total contaminant mass discharge: (A) AFP44 site (Figure reproduced from Brusseau et al. (2011)); (B) MOT site; (C) PGN site. Note for the PGN site, EA-01 is the extraction well located nearest to the source area, MTS comprises EA-01 and the other wells serving as the downgradient hydraulic interception barrier, non-MTS represent all other extraction wells (which are all located on the downgradient perimeter of the plume), and “plume” represents the contributions of all wells except EA-01.

Figure 6.

Relative contaminant mass discharge (CMD) as a function of pore volumes of groundwater pumped for three sites; includes contributions from only the groundwater contaminant plumes (see discussion in text for PGN site caveat). Note that source remediation via in-situ chemical oxidation started at approximately two pore volumes for the AFP44 site.

Figure 7.

Relationships between reductions in contaminant mass discharge (CMDR) and reductions in contaminant mass (MR) for three sites; includes contributions from only the groundwater contaminant plumes.

Table 1

Selected Properties of Sites Evaluated

Site ^a	Plume Area ^b (km ²)	Annual Pumpage ^c (M m ³)	Mass Recovered ^d to Dated (kg)	Estimated Initial Mass ^e (kg)
AFP44	4	5.0	13,000	24,000
MOT	2	0.6	10,000	570,000
PGN	4	2.4	20,000	29,000
TARP	4	8.7	2,100	7,000
CD	0.2	1.5	16,000	20,000

^a Site names are presented in the Materials and Methods section^b Approximate^c Mean value^d For pump-and-treat systems only, as of last data available^e Total mass (in sources and plume) estimated to be present at the start of pump and treat operations. Methods used to obtain estimates are detailed in the text.