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The Impact of In-situ Chemical Oxidation on Contaminant Mass Discharge: Linking Source-Zone and Plume-Scale Characterizations of Remediation Performance

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Abstract

A large-scale permanganate-based in-situ chemical oxidation (ISCO) effort has been conducted over the past ten years at a federal Superfund site in Tucson, AZ, for which trichloroethene (TCE) is the primary contaminant of concern. Remediation performance was assessed by examining the impact of treatment on contaminant mass discharge, an approach that has been used for only a very few prior ISCO projects. Contaminant mass discharge tests were conducted before and after permanganate injection to measure the impact at the source-zone scale. The results indicate that ISCO caused a significant reduction in mass discharge (approximately 75%). The standard approach of characterizing discharge at the source-zone scale was supplemented with additional characterization at the plume scale, which was evaluated by examining the change in contaminant mass discharge associated with the pump-and-treat system. The integrated contaminant mass discharge decreased by approximately 70%, consistent with the source-zone-scale measurements. The integrated mass discharge rebounded from 0.1 to 0.2 Kg/d within one year after cessation of permanganate injections, after which it has been stable for several years. Collection of the integrated contaminant mass discharge data throughout the ISCO treatment period provided a high-resolution, real-time analysis of the site-wide impact of ISCO, thereby linking source-zone remediation to impacts on overall risk. The results indicate that ISCO was successful in reducing contaminant mass discharge at this site, which comprises a highly heterogeneous subsurface environment. Analysis of TCE sediment concentration data for core material collected before and after ISCO supports the hypothesis that the remaining mass discharge is associated in part with poorly-accessible contaminant mass residing within lower-permeability zones.

Introduction

Contamination of groundwater by chlorinated solvents continues to pose significant risks to human health, and can also significantly impact regional water resources sustainability. A primary approach to remediation of chlorinated-solvent-contaminated sites has been the implementation of aggressive source-zone remediation efforts employing methods such as enhanced solubilization/mobilization, in-situ chemical oxidation (ISCO), and thermal-based

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Supporting Information **Available:** Supplemental expanded-view figures are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

technologies. In particular, in-situ chemical oxidation, wherein solutions containing chemical oxidants such as permanganate are injected into contaminated subsurface zones to promote transformation of target contaminants to benign end products, has recently become a popular remediation method. A large number of ISCO field applications have been conducted over the past decade, and an extensive review was recently published (1).

A key issue for implementing ISCO and other source-zone remediation methods at a given site is their relative costs and benefits in comparison with existing (typically pump and treat) and other potential remediation efforts (2-5). Assessing the quantitative performance of a source-zone remediation effort is central to evaluating associated costs and benefits. The performances of a variety of source-zone remediation efforts have been evaluated in a number of studies (see 6-7 for recent reviews). To date, remediation performance assessment has typically been based on analysis of changes in groundwater contaminant concentrations within the treatment zone, wherein samples are collected from one or more monitoring wells. As is widely recognized, the effectiveness of this point-sampling-based method is often limited for large, complex sites characterized by high degrees of heterogeneity. Interest has increased recently in the use of contaminant mass flux or discharge as a more integrative measure of the performance of source-zone remediation efforts (e.g., 2-5, 8-13). This method has been used successfully in a number of projects, as summarized by (7,13).

In their extensive review of 242 ISCO projects conducted over the past decade, Krembs et al. (1) found that only four of the projects were assessed using estimates or measurements of contaminant mass discharge. Discounting the two that used estimates rather than actual measurements, and including an additional non-tabulated project, results in a total of three ISCO projects for which performance has been assessed based on measurements of contaminant mass discharge. Furthermore, these very few comprise relatively small-scale pilot tests, with two of them having been conducted at the Borden test site (14,15). As noted by the authors of these latter studies, relatively ideal subsurface conditions at the Borden site produced optimal performance results for ISCO that are unlikely to be representative for many sites (14). Thus, there is great interest in assessing the performance of a large-scale ISCO project based on contaminant mass discharge measurements for a site with highly heterogeneous subsurface conditions.

There are two objectives to the research reported herein. The first is to assess the performance of a full-scale remediation effort employing ISCO for a site that is representative of the many large, complex chlorinated-solvent contaminated sites present in the USA and elsewhere wherein multiple source zones have contributed to the creation of a large (~10's km^2) contaminant plume. The second is to illustrate an enhanced approach for performance assessment of source-zone remediation efforts. The performance of the ISCO project is assessed through analysis of changes in contaminant mass discharge. We first employ the standard approach, which involves measuring source-zone discharge once before and once after ISCO implementation. We then employ an additional approach based on a high-resolution, real-time characterization of contaminant mass discharge at the plume scale. This latter approach provides a more robust analysis of discharge perturbations, including potential rebound effects, and provides a means by which to link source-zone remediation to impacts on site-wide risk. The performance assessment covers a period of approximately 10 years, including several years of pre and post monitoring.

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 (16). The TIAA site was placed on the National Priorities List in August 1983 in response to the detection of TCE in groundwater from several potable water supply wells. A large, multiple-source plume of TCE exists in the upper portion of the regional aquifer (Figure 1), which is the primary source of potable water for the Tucson metropolitan area. Contaminants are believed to have entered the subsurface by seepage from unlined pits and ponds used during the late 1950's to mid 1970's for disposal of organic solvents. 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 (Figure S1). Three chlorinated-solvent source zones have been identified for the South section- Sites 2, 3, and 5.

The TIAA Superfund site is located in the Tucson Basin, which is underlain by several thousand feet of alluvial sediments interbedded locally with volcanic flows, agglomerates, and tuffaceous sediments. The major hydrogeologic units in the area of the site have been designated as (in descending order with depth): the Unsaturated Zone, the Upper Aquifer, the Aquitard Unit, and the Lower Aquifer. The Unsaturated Zone extends from the land surface to the regional groundwater surface, which is located 30 to 40 m below ground surface (BGS). The Upper Aquifer extends from the regional groundwater surface to a depth of approximately 54 to 66 m BGS, where it is underlain by the Aquitard Unit. In the vicinity of the study site, the Upper 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. The Lower Aquifer unit extends to varying depths below the Aquitard unit. Contamination is associated primarily with the upper three units.

Remedial Operations and Site Characterization Activities

A large pump-and-treat groundwater remediation project was initiated in the South section of the Superfund site in 1987. The number of extraction and recharge wells in operation at a given time has varied, ranging from 30-40 to approximately 20 currently. Concomitantly, the total extraction rate has ranged from approximately 20,000 to 10,000 m^3/d. 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. The concentration of TCE in the extracted groundwater is shown as a function of time in Figure S2. 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 associated reductions in the rate of mass removal.

An extensive site-characterization project was initiated in 1993 for the primary source zones. The project consisted of several components, including traditional site-characterization activities, tracer tests, contaminant mass discharge tests, laboratory experiments conducted with core material collected from the site, and mathematical modeling (summarized in 17,18). The results of several methods of analysis provided conclusive evidence that organic immiscible liquid (i.e., solvent) was present in both the unsaturated and saturated portions of the primary source zones (17-21). Based on the results of partitioning tracer tests and two scales of mathematical modeling, it is estimated that approximately 4500 kg and 7000 kg of solvent mass were present in the Site 3 and Site 2 source zones, respectively, prior to the start of ISCO. The mass of TCE in aqueous and sorbed phases was estimated to comprise a few percent of the total mass. The source zones are characterized by a large degree of heterogeneity with respect to spatial distributions of hydraulic conductivity and contaminant concentrations, and it appears that the majority of source-zone contaminant mass prior to ISCO was associated with lower-permeability zones and hence poorly accessible to flowing groundwater (17,18,21). This source-zone configuration produces significant constraints to mass transfer and mass removal (17,18,21,22).

In-situ Chemical Oxidation

Potassium permanganate was selected as the oxidant for the in-situ chemical oxidation project. Laboratory tests were conducted prior to the pilot tests to characterize the natural oxidant demand associated with the site sediment. The results indicated minimal natural oxidant demand.

Pilot-scale tests of in-situ chemical oxidation were conducted at two of the source zones (Sites 2 and 3) in 2000 (23). Approximately 1000 kg of potassium permanganate in solution at a concentration of approximately 2.5% was injected at each source zone. Prior to injection, permanganate powder and water from the groundwater treatment system was added to a 800 L polyester tank at the wellhead. The solution was mixed with an electric mixer, and then allowed to gravity feed into the well. The water level in the injection well was monitored during injection and inflow was adjusted accordingly to prevent the well from overfilling. Once the injection was completed, the mixing tank, drum lifter, and other equipment were moved to the next well and the process was repeated.

The solution was injected into wells with screens spanning the bottom portion of the unsaturated zone and the upper portion of the Upper Aquifer. This was done to target the lower-permeability units located in this interval, wherein it was postulated that a significant accumulation of contaminant mass was present. The results of the pilot tests indicated that the permanganate injections significantly reduced aqueous-phase concentrations of TCE. Rebounds in TCE concentrations were observed several months after completion of injections for a majority of monitoring wells. Based on the results, full-scale application was implemented at both source zones.

Full-scale implementation started in December 2002 at Site 2 and October 2004 at Site 3. For each source zone, the injections were conducted in increments and involved 22-24 injection wells. A schematic showing the majority of the injection wells for Site 3 is presented in Figure S3. Injections were conducted for three to five wells at a time, with an interval of approximately one month between each set of injections. A second round of injections was conducted approximately 1.5 years after the first round at each site, employing a subset of the initial injection locations. The final injections occurred in December 2005 and August 2006 for Sites 2 and 3, respectively. The permanganate concentration for the injection solutions ranged from approximately 0.2 to 2%. A total of approximately 25,000 and 12,500 Kg of potassium permanganate was injected for Sites 2 and 3, respectively.

Contaminant Mass Discharge

Contaminant mass discharge tests were conducted at the Site 3 source zone before and after the permanganate injections to characterize the impact of ISCO treatment at the source-zone scale. Two tests were conducted before ISCO implementation, a short-term test of approximately one month duration and a longer-term test of 21 months duration. The longer-term test was completed the year prior to ISCO startup. The post-injection test was conducted four years after the last injection of permanganate to minimize the impact of potential rebound effects. Prior to each test, all injection and extraction wells in the vicinity of the well were turned off for at least several months to allow quasi-equilibrium conditions to develop with respect to contaminant concentrations. Tests were not conducted at Site 2 due to site restrictions.

The same extraction well (E-14), located in the center of the permanganate injection zone, was used for all the tests (see Figure S3). For the short-term pre-ISCO test and the post-ISCO test, the extraction well was pumped continuously for several weeks at a flow rate of approximately 200 L/min. For the longer-term pre-ISCO test, the extraction well was pumped continuously for 21 months at a flow rate of approximately 400 L/min. This latter value is an approximate average of historical pumping rates for this well. Groundwater levels were monitored before, during, and after the tests for multiple wells across the test area. The results indicated that the effective zone of influence of the extraction well encompassed the approximate extent of the source zone. Samples of groundwater were collected periodically from the extraction-well effluent. The samples were analyzed for TCE, Mn, dissolved oxygen, dissolved solids, oxidation-reduction potential, and color. The samples were collected using standard EPA-approved protocols, and were analyzed by gas chromatography and/or GC-mass spectrometry (TCE) and inductively-coupled plasma-MS (Mn) using standard EPA methods.

The impact of ISCO treatment at the plume scale was assessed by measuring contaminant mass discharge associated with the aqueous-phase contaminant plume. This was accomplished by analyzing time-series data collected for the pump-and-treat system, which is designed and operated to capture the entire plume Samples of extracted groundwater were collected at a minimum of once per week from a point just prior to the treatment facility used for the pump-and-treat system. The contaminant concentrations associated with these samples represent composite values for all groundwater inflow into the pump-and-treat system. Thus, analysis of these data provides a means by which to assess the impact of ISCO conducted at the two source zones on the integrated contaminant mass discharge for the entire site. Collection of the data throughout the ISCO treatment period allowed for a continuous, real-time analysis of the site-wide impact of ISCO. The samples were collected and analyzed as noted above. Total extraction flow rates were monitored continuously.

Sediment Coring and Groundwater Sampling

The use of sediment coring to evaluate changes in contaminant mass was problematic for this project given the large size of the site and the high degree of heterogeneity. However, a single set of boreholes was drilled to provide an illustrative evaluation of the impact of permanganate injection on sediment-phase contaminant concentrations. One borehole was drilled prior to the start of ISCO, and one 3.5 years after the final permanganate injections. The two boreholes are approximately 5 m apart, with the post-ISCO borehole located approximately 5 m from a well used for permanganate injection. The boreholes were drilled using roto-sonic drilling, providing continuous 15-cm diameter cores. The cores were analyzed with high spatial resolution (~6-cm intervals for the water-saturated units). Two sets of subsamples (~10 ml) were collected from the internal central axis of the cores. One set of samples were placed in 40-mL glass vials that contained premeasured volumes of solvent (>99.9% methanol) for solvent-extraction analysis of TCE. A second set was used for analysis of Mn concentrations. The subsamples were collected from the internal central axis of the cores to minimize the impact of drilling effects.

The subsamples for solvent-extraction analysis were placed on a shaker for 24 h, followed by refrigeration for 24 h. The samples were centrifuged for 10 minutes with a Beckman GP Centrifuge. A 2-mL subsample of the eluent was extracted from the vial and placed in a 2-mL autosampler vial with no headspace. The samples were analyzed by GC/MS/MS (gas chromatography tandem mass spectrometry). The mean detection limit for sediment-phase concentrations of TCE was less than 0.1 ug/g-dry sediment.

The samples for Mn analysis were prepared using standard EPA method 3051. For this method, the sediment samples were finely ground, mixed with nitric acid, and heated in a microwave. Aliquots of the digestion solution were then analyzed using ICP-MS. The mean detection limit for sediment-phase concentrations of Mn was less than 0.1 ug/g-dry sediment.

Groundwater samples were collected from several monitoring wells within the source zones before the start of ISCO and three years after the final permanganate injections. The samples were analyzed for TCE and Mn as described above.

Results and Discussion

Contaminant Mass Discharge

The results of the contaminant mass discharge tests conducted at the Site 3 source zone before and after permanganate injection are presented in Figure 1. The initial contaminant mass discharge for the short-term test conducted prior to ISCO was approximately 0.6 kg/d. The values decreased over the course of the test to an asymptotic value of 0.1 kg/d. The results obtained for the longer-term test, which was 21 months in duration, are similar to those for the one-month test. These results suggest that the short-term test provided a representative characterization of contaminant mass discharge for the source zone.

The initial contaminant mass discharge for the test conducted after ISCO was approximately 0.04 kg/d (Figure 1). The values decreased over the course of the test to an asymptotic value of approximately 0.025 kg/d. Thus, both the peak and asymptotic contaminant mass discharge values were lower after permanganate injection, by factors of 15 and 4, respectively. The reduction in contaminant mass discharge is approximately 75% based on comparison of the respective asymptotic values. The magnitude of observed reduction is consistent with reductions reported for several pilot-scale source-zone remediation efforts employing a variety of methods (e.g., 7).

The impact of ISCO at the plume scale was evaluated by examining the change in contaminant mass discharge associated with the pump-and-treat system. The integrated contaminant mass discharge for the entire pump-and-treat system as a function of time is shown in Figure 2. The composite contaminant mass discharge was essentially constant for several years prior to implementation of ISCO, with a value of approximately 0.7 kg/d. This behavior indicates that mass removal via pump and treat had stabilized to a quasi steady-state under the extant conditions. Contaminant mass discharge began to decrease almost immediately upon ISCO startup, and declined to a final value of 0.1 kg/d at the completion of injections. After year 4, the contaminant mass discharge began to increase, before stabilizing at the current value of approximately 0.2 kg/d. Based on these data, implementation of in-situ chemical oxidation resulted in a reduction in plume-scale contaminant mass discharge of approximately 70%.

As noted above, the contaminant mass discharge exhibited a rebound after the completion of permanganate injections. The rebound period lasted for approximately one year before the discharge stabilized. The observation of rebound effects is consistent with results observed for prior ISCO applications wherein rebound is often observed in monitoring-well concentrations (1, 6). The collection of the high-resolution integrated discharge data provided a means to monitor for rebound to ensure that the source-zone tests were conducted after the rebound period. According to the review of Krembs et al., (1), there have been no prior studies evaluating post-ISCO rebound based on continuous measurements of contaminant mass discharge.

In the prior discussions, the reductions in contaminant mass discharge were attributed solely to ISCO. However, the potential impact of other activities and conditions at the site should be evaluated. There is no evidence of natural attenuation of TCE via biotic or abiotic transformation reactions at this site. Hence, aside from the oxidation associated with the ISCO applications, there are no other transformation processes present to contribute to TCE concentration reductions. Full-scale soil vapor extraction operations were implemented at the source zones starting in mid-1996, and were completed in July 2004. Hence, the ISCO implementation at Site 3 occurred after completion of SVE operations. These conditions, in conjunction with the steady-state behavior observed for the integrated (plume-scale) contaminant mass discharge before and after ISCO, indicate that the observed changes in contaminant mass discharge can be attributed to the impact of ISCO.

Groundwater and Sediment Concentrations

The concentration of Mn in groundwater samples collected from the extraction well used for the contaminant mass discharge tests ranged from approximately 2-10 ug/L throughout the post-injection test. These values are consistent with background Mn concentrations measured for multiple wells located in the injection zone, which ranged from approximately 1 to 20 ug/L. The results obtained for dissolved oxygen, oxidation-reduction potential, dissolved solids, and color were also all consistent with background values measured prior to permanganate injection. These results indicate that the injected permanganate had dissipated significantly prior to the post-ISCO characterization efforts. Concentrations of Mn in the influent to the treatment plant have remained below the detection limit throughout operation of the pump-and-treat system, including during and after the permanganate injections.

The concentrations of TCE in groundwater samples collected before and after ISCO from a number of monitoring wells within Site 3 are presented in Figure S3. The TCE concentrations prior to ISCO ranged from 33 to 1000 ug/L. A wide range in concentration reductions was observed, with a mean reduction of 68%. The mean concentration reduction is similar to the reductions in contaminant mass discharge determined from both the source-zone and plume-scale analyses. A mean reduction in TCE concentrations of 87% was observed for Site 2. The greater reduction observed for Site 2 may be related in part to the greater amount of permanganate used at that site.

Concentrations of Mn determined for the sediment samples are presented in Figure 3. The results show that the sediments contain high and somewhat spatially variable background levels of Mn. In addition, while the natural oxidant demand associated with the sediment is low, there could be some impact of permanganate reaction with sediment organic matter. These conditions limit the use of manganese-oxide presence as an indicator of TCE oxidation. However, as noted above, the borehole used to collect the sediment was located approximately 5 m from a well used for permanganate injections. Given such close proximity, it is likely that permanganate solution contacted the sediment. In addition, the significant reductions in sediment-phase TCE concentrations discussed below serve as an indirect indictor of permanganate contact. The similar range of Mn concentrations for before and after ISCO suggests that the use of permanganate and the associated formation of oxides would have minimal impact on hydraulic conductivity. The potential for much higher concentrations of oxide (e.g., rinds) to form in localized association with pockets of organic liquid can not be discounted. Such formation could potentially impact local-scale mass transfer and mass flux, as observed in prior laboratory experiments (e.g., 24-26).

The concentrations of TCE for sediment samples collected from boreholes drilled before and after ISCO are presented in Figure 4. The highest concentrations prior to ISCO are associated with the lower-permeability layer that adjoins the top of the Upper Aquifer. The measurable TCE concentrations remaining after ISCO are associated with the bottom portion of that lower-permeability layer. Remediation of this unit via a hydraulic-based method such as ISCO is expected to be less effective than for the adjacent higher-permeability units. Comparison of the two sets of data indicates that a significant reduction (aggregate ~90%) in TCE concentrations occurred between sampling events. This reduction is the combined result of mass reduction via ISCO and mass removal via water flushing (pump and treat). The impact of pump and treat on mass removal was examined in prior simulations of contaminant transport for the site, which produced an estimated reduction in total source-zone mass of ~15% over an 11-year period of pump and treat (21). While local mass-reduction rates are expected to exhibit significant spatial variability, the modeling results provide an indication that mass reduction via water flushing would in general be expected to be relatively low for the 10-year ISCO project. This suggests that the significant reduction observed for the sediment data was caused primarily by ISCO.

Impact of Source-zone Architecture and Mass-transfer Phenomena on Reductions in Contaminant Mass and Mass Discharge

Maximum discharge rates were observed at the beginning of each contaminant mass discharge test, followed by asymptotic conditions (Figure 1), as noted above. The extraction well was not pumped for at least several months prior to the start of each test, which allowed quasi-equilibrium conditions to form with respect to contaminant distribution between the advective and poorly-accessible domains. The peak discharge at the beginning of the test thus represents removal of a “maximum” loading of mass from the advective domain that was generated during the preceding non-pumping period. Conversely, the asymptotic discharge represents primarily mass removal associated with transfer from the poorly-accessible domains. The rebound of integrated contaminant mass discharge observed after completion of ISCO (Figure 2) is attributed to mass transfer of TCE from the poorly-accessible domains, with additional contribution from displacement by upgradient groundwater. The approximate one year of rebound incorporates the time for permanganate to dissipate once injections ceased, in addition to the inherent characteristic times of contaminant mass transfer and transport.

Measurements of flow and contaminant concentration for each extraction well of the pump-and-treat system allow calculation of the relative contributions of each source zone and the plume to the total integrated contaminant mass discharge. For the three years prior to the start of ISCO, Sites 2 and 3 contributed approximately 47% to total contaminant mass discharge. This was reduced significantly after ISCO. Interestingly, the aggregate mass discharge associated with the plume also decreased after ISCO. This decrease is due primarily to reductions observed for four extraction wells that are all located downgradient of the Site 3 source zone, with distances ranging from approximately 200 to 1100 meters. Significant decreases in TCE concentrations occurred for these wells at varying times after the start of ISCO. For example, distinct decreases in TCE concentrations are observed seven months and three years after the start of ISCO for wells EL02 and E23, respectively (Figure S4), which are located approximately 180 and 675 meters from the perimeter of Site 3. A mean pore-water velocity of approximately 0.7 m/d is estimated based on the elapsed times and distances; this value is similar to the estimated upper range of mean pore-water velocities (~1 m/d) in that area based on measured hydraulic gradients and conductivities (18). Given this, it is possible that the concentration reductions observed for these plume extraction wells reflect the impact of ISCO implementation at the Site 3 source zone.

The significant reduction in contaminant mass discharge observed for the ISCO project suggests that the permanganate injections produced an appreciable reduction in contaminant mass. Direct analysis of mass reductions was not feasible for the project, which is typically the case. Permanganate consumption associated with aqueous-phase TCE and natural sediment demand is estimated to have comprised roughly 10% of the total injected. Hence, given the estimated contaminant mass present and the amount of permanganate injected, it is projected that there was sufficient permanganate to cause a significant reduction in contaminant mass.

While the reduction in mass discharge obtained for this study was significant, it is lower than the weighted-average reduction of approximately 92% observed for a small-scale permanganate-ISCO test conducted at the Borden research site in Canada (14). The reduction in contaminant mass discharge produced by a reagent-injection-based method such as ISCO will be controlled by reagent-contaminant contact, which in turn is a function of several factors including reagent-injection conditions, mass-transfer processes, and source-zone architecture. Thus, contaminant mass discharge results should be interpreted in light of site-specific conditions. One factor likely contributing to the disparity in observed reductions is the degree of heterogeneity associated with the two sites, and the resultant expected differences in mass-removal behavior. The test domain at the Borden site is comprised primarily of a sand unit with a relatively small degree of heterogeneity. Given this and the method by which organic liquid was introduced to the test domain, it would be anticipated that the organic liquid would be relatively accessible to flowing groundwater (and permanganate solution) and thus that mass removal would be minimally influenced by mass-transfer limitations. That such is the case is supported by the results of prior research (7,14,27). In contrast, a large fraction of the contaminant mass at the TIAA site appears to be poorly accessible to flowing groundwater, which significantly constrains mass removal and associated mass discharge.

Different reagent-injection approaches were used for the two sites. The permanganate was introduced via an induced-gradient recirculation approach for the Borden project, which would be anticipated to maximize reagent-contaminant contact for the Borden site conditions (14). Conversely, the use of such an induced-gradient approach for the source-zone architecture present at the TIAA site would be anticipated to exacerbate mass-transfer constraints and thus further limit reagent-contaminant contact. Hence, permanganate was introduced via an injection/natural-dissipation mode for the TIAA site.

Implications—The performance of a large-scale permanganate-based ISCO project was assessed by examining the impact of treatment on contaminant mass discharge. While the effectiveness of ISCO may have been influenced by the high degree of heterogeneity present at the site, a significant reduction in contaminant mass discharge was achieved. One anticipated benefit of this reduction is a decrease in the length of time required to operate the pump-and-treat system. The implementation of ISCO reduced, but did not eliminate, contaminant mass discharge from the source zones. Based on these results, continued management of contaminant mass discharge from the source zones will need to be considered as part of the long-term management of the site. This scenario is likely to be manifest at many of the large chlorinated-solvent contaminated sites in the USA.

The use of contaminant mass discharge, rather than contaminant mass, as a performance metric has several advantages, including greater accessibility, less uncertainty, and greater relevance for risk-based assessment. An enhanced approach for characterizing contaminant mass discharge was illustrated that extends the standard source-zone scale measurements to incorporate additional characterization at the plume scale. Collection of integrated plume-scale contaminant mass discharge data before, during, and after the ISCO treatment period provided a high-resolution, real-time analysis of discharge perturbations, including rebound effects. This approach provides a robust means by which to link source-zone remediation to impacts on site-wide risk, and is anticipated to have broad utility for assessing remediation effectiveness.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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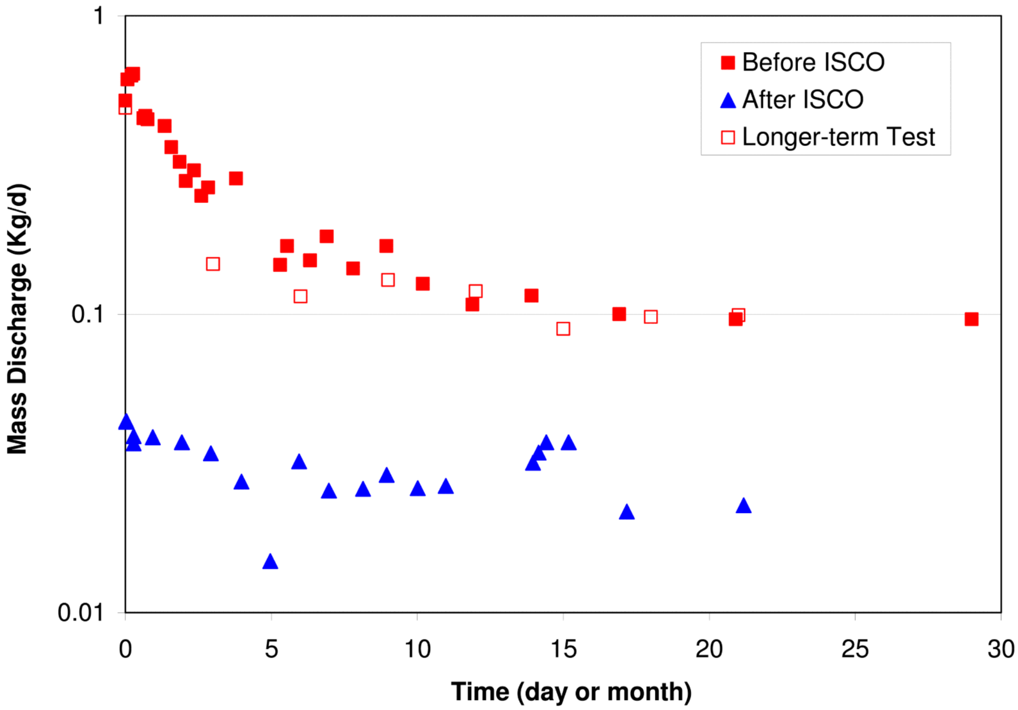

Figure 1.

Results of contaminant mass discharge tests conducted at the Site 3 source zone before and after ISCO. The tests labeled “Before ISCO” and “After ISCO” have a time scale of days; the longer-term test (conducted before ISCO, and at a higher flow rate) has a time scale of months.

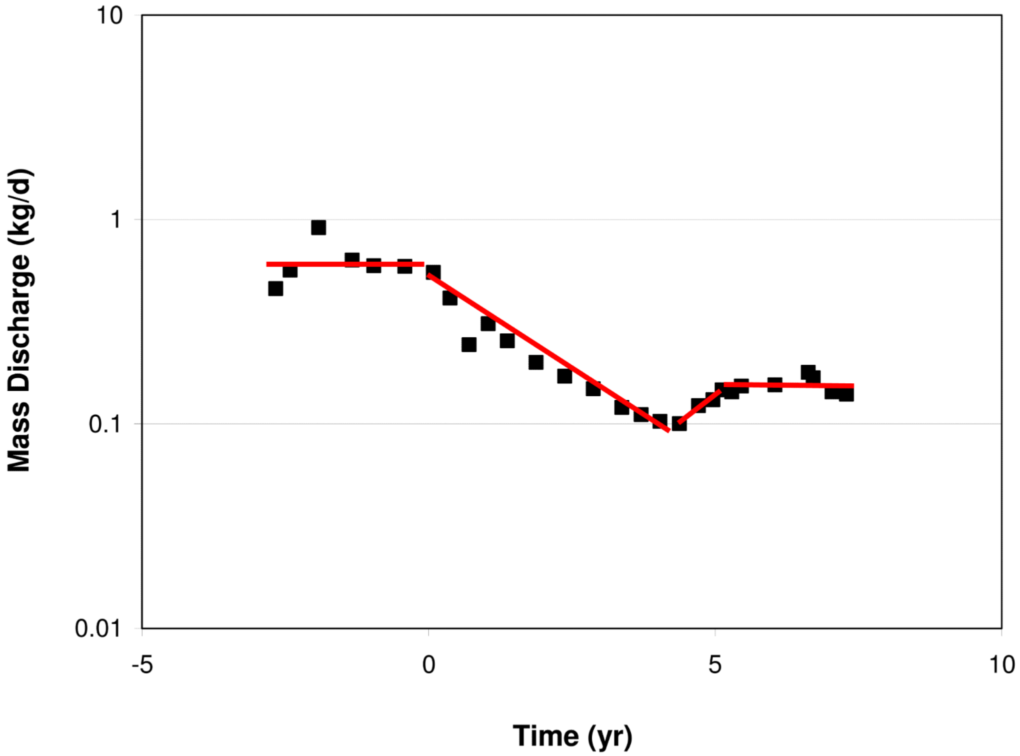

Figure 2.

Integrated contaminant mass discharge for the entire site, including contributions from the source zones and the aqueous-phase contaminant plume. Time zero denotes the start of ISCO. The lines are included for visualization purposes and do not represent any type of quantitative analysis.

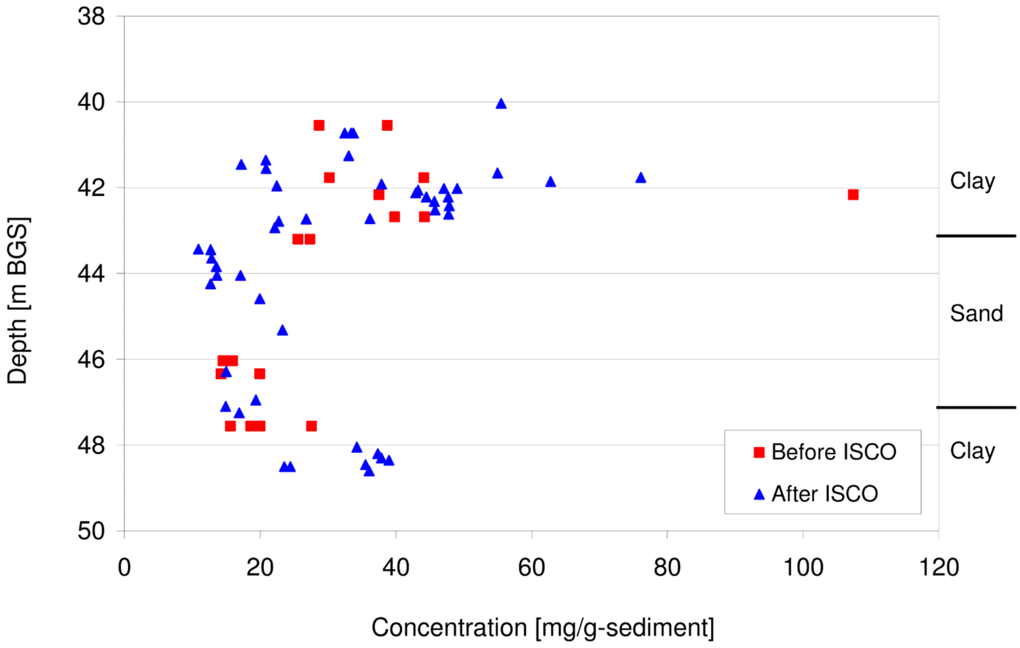

Figure 3.
Sediment concentrations of Mn for core samples collected from a single borehole drilled before ISCO and a single borehole drilled after ISCO for Site 3.

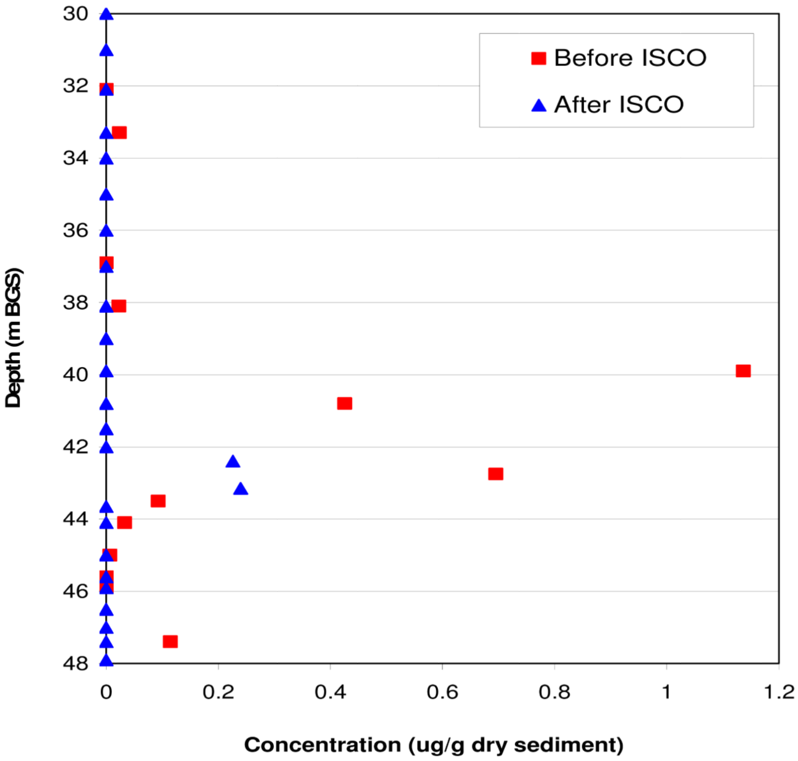

Figure 4.

Sediment concentrations of trichloroethene for core samples collected from a single borehole drilled before ISCO and a single borehole drilled after ISCO for Site 3. For the post-ISCO core, approximately 100 samples were analyzed; only 25% of that total is presented in the figure (concentrations for all samples except the two shown in the figure were below the detection limit).