



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.

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1. Introduction

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

ically 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

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relative costs and benefits associated with such efforts (e.g., EPA, 2003; ITRC, 2002; 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., Brooks et al., 2004; DiGiulio et al., 1999; Einarsen and Mackay, 2001; EPA, 2003; Freeze and McWhorter, 1997; ITRC, 2002; NRC, 2005; Rao et al., 2002; Schwarz et al., 1998; SERDP, 2006; Soga et al., 2004; Stroo et al., 2003). 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 analysis 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.

2. Methods

2.1. 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 (Graham et al., 2001; Leake and Hanson, 1987). 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 (Fig. 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 Figs. 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 Fig. 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 1950s to mid 1970s have been identified for the South section of the TIAA complex—Sites 2, 3, and 5 (see Fig. 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 potassium 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.

2.2. 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.

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