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The Vapor-phase Multi-stage CMD Test for Characterizing Contaminant Mass Discharge Associated with VOC Sources in the Vadose Zone: Application to Three Sites in Different Lifecycle Stages of SVE Operations

M.L. Brusseau^{1,2,*}, J. Mainhagu¹, C. Morrison¹, and K.C. Carroll³

¹Soil, Water and Environmental Science Department, School of Earth and Environmental Sciences, University of Arizona, Tucson, AZ 85721

²Hydrology and Water Resources Department, School of Earth and Environmental Sciences, University of Arizona, Tucson, AZ 85721

³Plant and Environmental Sciences Department, New Mexico State University

Abstract

Vapor-phase multi-stage contaminant mass discharge (CMD) tests were conducted at three field sites to measure mass discharge associated with contaminant sources located in the vadose zone. The three sites represent the three primary stages along the soil vapor extraction (SVE) operations lifecycle- pre/initial-SVE, mid-lifecycle, and near-closure. A CMD of 32 g/d was obtained for a site at which soil vapor SVE has been in operation for approximately 6 years, and for which mass removal is currently in the asymptotic stage. The contaminant removal behavior exhibited for the vapor extractions conducted at this site suggests that there is unlikely to be a significant mass of non-vapor-phase contaminant (e.g., DNAPL, sorbed phase) remaining in the advective domains, and that most remaining mass is likely located in poorly accessible domains. Given the conditions for this site, this remaining mass is hypothesized to be associated with the low-permeability (and higher water saturation) region in the vicinity of the saturated zone and capillary fringe. A CMD of 25 g/d was obtained for a site wherein SVE has been in operation for several years but concentrations and mass-removal rates are still relatively high. A CMD of 270 g/d was obtained for a site for which there were no prior SVE operations. The behavior exhibited for the vapor extractions conducted at this site suggest that non-vapor-phase contaminant mass (e.g., DNAPL) may be present in the advective domains. Hence, the asymptotic conditions observed for this site most likely derive from a combination of rate-limited mass transfer from DNAPL (and sorbed) phases present in the advective domain as well as mass residing in lower-permeability (“non-advective”) regions. The CMD values obtained from the tests were used in conjunction with a recently developed vapor-discharge tool to evaluate the impact of the measured CMDs on groundwater quality.

*Corresponding author, brusseau@email.arizona.edu.

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Keywords

SVE; vapor; mass flux; VOC; groundwater; remediation

1.0 Introduction

The presence of contaminant sources comprised of volatile organic compounds (VOC) in the vadose zone poses two primary risks to human health. First, discharge of contaminant vapor from the vadose-zone source may impact the quality of the underlying groundwater. Such contamination can contribute to overall risk posed by the site, and delay attainment of groundwater cleanup goals. Second, contaminant vapor from the vadose-zone source may migrate to the land surface and transfer into buildings. Such vapor intrusion is of particular importance for chlorinated VOCs, and has received increased focus for exposure risk assessments at many Superfund sites in the US. These two issues are typically the primary risk drivers for decisions regarding remediation of vadose-zone systems. Hence, the development and assessment of cleanup objectives for vadose-zone sources is typically based on evaluating the impact of vapor discharge from the vadose zone on groundwater quality or vapor intrusion (e.g., Rosenbloom et al., 1993; DiGiulio et al., 1999; EPA, 2001; USACE, 2002; Carroll et al., 2012; Brusseau et al., 2013a).

Assessing the potential impact of vadose-zone sources on groundwater or the land surface can be enhanced by determining the contaminant mass discharge (CMD) associated with the source. The standard approach for characterizing vapor-phase mass discharge is to measure static vapor and/or sediment concentrations, and to use them as input for a mathematical screening model to estimate contaminant mass discharge (e.g., Johnson and Ettinger, 1991; Rosenbloom et al., 1993; DiGiulio et al., 1999; Hers et al., 2002). This approach has become widely used to evaluate the impact of vadose-zone sources on groundwater or vapor intrusion. However, this approach can be subject to considerable uncertainty in the estimates obtained, depending upon the robustness of the input data as well as the simplifications employed in the development and application of the screening model. For example, the uncertainty associated with sediment coring due to the typical low density of sampling is well known (e.g., Rossabi et al., 2003; Feenstra, 2005). In addition, it has been shown that soil gas surveys may provide poor results for systems with mass-transfer constraints (e.g., DeGroot and Luttenegger, 1998; Thomson and Flynn, 2000; McAlary et al., 2009). The potential limitations associated with typical screening models for VOC transport are well documented. Hence methods are needed to provide direct measurements of vapor-phase mass discharge.

The vapor-phase cyclic or multi-stage contaminant mass discharge (MS-CMD) test was recently developed to measure mass discharge for vadose-zone sources under both forced-gradient and pseudo natural-gradient conditions (Brusseau et al., 2010). The vapor-phase MS-CMD test consists of three stages, an extended initial extraction stage (which is identical to a standard CMD test), a rebound stage, and a second extraction stage (Figure 1). In brief, an initial extraction stage is implemented and concentrations of contaminant in the effluent gas are monitored. The extraction continues until quasi steady state is attained with respect

to effluent concentrations. The purpose of the initial extraction stage is to sweep vapor-phase contaminant from the advective (pneumatically accessible) domains within the treatment zone. At this point, the extraction is stopped, and the system is monitored to characterize potential rebound of vapor-phase concentrations. A second extraction stage is then implemented once concentrations have stabilized. Contaminant mass removed during the second extraction stage is tabulated to determine the mass that transferred from the poorly accessible domains to the advective domain during the rebound stage.

Data collected during the early portion of the initial (and/or second) vapor-extraction stage can be used to quantify the maximum mass discharge obtained under forced-gradient conditions. Conversely, data collected at the end of the initial extraction stage (during the steady state condition) can be used to quantify the asymptotic forced-gradient mass discharge. This approach, essentially identical to that employed for analysis of data collected from operating soil vapor extraction (SVE) systems (e.g., USACE, 2002), can be used to help evaluate SVE performance for sites that have active SVE operations, or to provide data for design and implementation of a new SVE system. The standard (i.e., single-stage) vapor-phase CMD test can be conducted discretely at several locations within a site to characterize the spatial distribution of sources in the vadose zone (Carroll et al., 2013). Samples can also be collected from multiple monitoring points surrounding each extraction point to further characterize spatial distributions (Mainhagu et al., 2014), leading to the concept of a vapor-phase tomography test (Brusseau et al., 2013a).

The CMD values produced under the forced-gradient conditions associated with vapor extraction may not be directly representative of values associated with natural-gradient conditions, which is the information desired for assessing risk. The innovative component of the vapor-phase MS-CMD test is the ability to measure the CMD associated with the source under pseudo natural-gradient conditions (CMD_{ng}), with the rebound period serving as a limiting-case representation of mass transfer. This entity is determined from information collected during the second and third stages of the test. First, the mass of contaminant removed is tabulated for typically the first one to two equivalent gas-pore-volumes extracted during the second extraction stage (i.e., after the rebound period). The specific number of pore volumes would depend upon the contributions of dispersion and retardation to VOC transport in the advective domain. The mass so tabulated is presumed to primarily represent mass that transferred during the preceding rebound phase from contaminant sources for which mass transfer is constrained. These sources could represent, for example, organic liquid (DNAPL) or sorbed mass in either or both advective and lower-permeability domains, or vapor-phase mass retained in lower-permeability zones. Second, the mass removed is divided by the time required to attain stable concentrations during the rebound stage to determine CMD_{ng} (M/T). The CMD value determined in this manner is a measure of CMD at the specific time of characterization, which can be used to evaluate impacts of the VOC source on groundwater quality and vapor intrusion.

The vapor-phase MS-CMD test has been evaluated in one prior study, conducted by Brusseau et al. (2010) at the Hanford site, a research site for which there exists a wealth of high-resolution data. The objective of the study presented herein is to investigate the use of the MS-CMD test under conditions that are more relevant for application at typical

hazardous waste sites. Data are presented for three field sites, each of which is at a different distinct stage along the SVE operations lifecycle. The SVE system at the first site had been in operation for approximately 6 years prior to the MS-CMD test. Concentrations of TCE in the SVE effluent are low (in the few $\mu\text{g/L}$ range), and contaminant mass discharge appears to have reached asymptotic values. Thus, this site represents a scenario wherein the mass of contaminant remaining in the vadose zone is likely to be relatively small, and conditions are supportive of SVE closure assessment. The SVE system at the second site had been in operation for approximately 9 years prior to the MS-CMD test. However, concentrations and mass-removal rates remain relatively high, representing a scenario wherein SVE operations appear to be midway through the operation lifecycle. Conversely, the conditions at the third site are representative of those for a site that has undergone no prior SVE or other remedial operations for the vadose zone. These three sites thus provide the opportunity to evaluate performance of the MS-CMD test under the three primary extant stages for SVE operations—pre/initial-SVE, mid-lifecycle, and near-closure. In addition, a recently developed vapor-discharge tool is employed to evaluate the impact of the measured CMDs on groundwater quality. Data obtained from ancillary characterization efforts are used to help evaluate the test results and associated interpretations.

2.0 Materials and Methods

2.1 Study Sites

The first site is part of the Tucson International Airport Area (TIAA) federal Superfund site in Tucson, Arizona. A large, multiple-source plume of trichloroethene (TCE) exists in the upper portion of the regional aquifer, which is a source of potable water for the Tucson metropolitan area. The study site comprises a local saturated zone, referred to as the shallow groundwater zone, which exists as a persistent feature above the regional aquifer. The site consists of a small source area and a groundwater contaminant plume extending approximately 600 m to the west (Figure S1 in Supporting Information). Trichloroethene is the primary groundwater contaminant, and aqueous concentrations upwards of 100 mg/L and greater have been reported for samples collected from groundwater monitoring wells within the source area.

The source area corresponds to a facility that was used in the past to clean aircraft parts and the external surfaces of military aircraft. DNAPL contamination was determined to be present at the site based on multiple lines of evidence (Brusseau et al., 2013b). The subsurface consists of clay and silty clay units with localized intervals/lenses of silt, sand, and gravel. The potentiometric surface for the shallow groundwater zone is approximately 28–29 m below land surface (bls) in the vicinity of the source area.

A multi-element remediation project was initiated at the shallow groundwater zone site in the fall of 2007. The effort consists of three components: SVE for the vadose-zone section of the source area, hydraulic containment for the saturated-zone section of the source area, and pump and treat for the groundwater-contaminant plume. Four extraction wells are used for the soil vapor extraction system, which has a total discharge of approximately 20,000 m^3/d . The vapor extraction wells are screened at two depth intervals, approximately 9–15 and 18–23 m bls. The soil vapor extraction system has to date removed approximately 3000 kg of

TCE. Currently, concentrations of TCE in the SVE effluent are low (in the few $\mu\text{g/L}$ range), and contaminant mass discharge appears to have reached asymptotic values (Figure 2).

The second site is the Hassayampa landfill (HASS) federal Superfund site, located 46 miles west of Phoenix, Arizona. The 10-acre landfill was in operation for 18 months, until October 1980. The CMD test conducted for the study was performed in the Special Pits Area. Organic solvents were disposed in the Special Pits area (Figure S2 in Supporting Information). Primary contaminants of concern are 1,1-dichloroethene, 1,1,1-trichloroethane, tetrachloroethene, and trichloroethene, present in the groundwater and in the vadose zone. The subsurface consists of an upper coarse-grained zone (CGZ), from the surface to approximately 9 m bls and a lower fine-grained zone (FGZ) approximately 9–18 m bls. Below the FGZ is a basaltic lava flow unit, approximately 6 m thick tapering out to the north of the site. Between the basalt unit and groundwater lies a deeper unsaturated zone, approximately 3-m thick. The upper saturated zone starts at approximately 27 m bls in a silt and fine sand unit approximately 6 m thick. The second groundwater unit is composed of coarser material, starting at 33 m bls and approximately 30 m in thickness. The results of prior characterization efforts have indicated that the great majority of contaminant mass is restricted to the vadose zone, with the distribution influenced by the presence of the FGZ and basalt, as discussed in the current Conceptual Site Model.

A groundwater pump and treat system was implemented in March 1994 and remains in operation. A total of approximately 170 kg of VOC mass has been removed to date via the pump-and-treat system. An SVE system was in operation between 1996 and 1998. A redesigned SVE system was subsequently implemented in 2006, with a total discharge of approximately 6,600 m^3/d . A single extraction well is screened in the CGZ, thirteen extraction wells are screened in the FGZ, and two are screened in the sub-basalt zone. Since inception, the SVE system has extracted a total of approximately 86,000 kg of VOC. Note that concentrations and mass-removal rates remain relatively high (Figure 3). The two wells used for this study, SP1-F and SP2-F, are screened in the FGZ (above the basalt unit) and are considered to be separated from Unit A groundwater, the surface of which is approximately 3 m below the bottom of the basalt.

The third site is operable unit (OU) 2 at Hill AFB in Utah. The data for this site were obtained from tests conducted at the site by contractors working for the US Air Force (CH2MHILL, 2009, 2010). The OU2 site, located along the northeastern boundary of Hill AFB overlooking the Weber River Valley, is one of 13 OUs at Hill AFB in various stages of the Comprehensive Environmental Response, Compensation, and Liability Act process (CH2MHill, 2010). A groundwater contaminant plume comprising TCE and several other chlorinated compounds resides in the shallow aquifer, extending approximately 500 m downgradient from the source. This shallow aquifer is composed of silts, sands, and gravel that fill a paleochannel incised into the eroded surface of the underlying clay aquitard. Concentrations of TCE in groundwater within the source area are currently in the range of 100 mg/L and lower.

The OU2 source zone includes two unlined disposal trenches, collectively known as Chemical Disposal Pit 3, that were formerly used for disposal of organic and inorganic

wastes. Disposal of spent chlorinated solvents resulted in DNAPL contamination of the underlying shallow aquifer, with two ~2-m thick pools of DNAPL discovered beneath the former trench locations. The recovered DNAPL consists primarily of several chlorinated solvents, approximately 70 percent TCE. Further site characterization activities determined that the DNAPL pools were trapped in “troughs” or depressions in the surface of the thick clay aquitard underlying the shallow aquifer. Existing soil and soil-gas data indicate that soils in the vadose zone contain low to moderate concentrations of VOCs, with the exception of the subsurface beneath the former chemical disposal trenches. Significantly higher VOC concentrations are present beneath the former disposal area, and characterization results indicate the presence of residual DNAPL at depths of approximately 10 m bls (CH2MHill, 2009, 2010).

Numerous remediation activities have been conducted to treat the saturated zone of the source, including DNAPL recovery, groundwater extraction, and enhanced source remediation efforts (CH2MHILL, 2010). A pilot SVE test was conducted at OU2 in 2008 to evaluate the use of SVE for remediation of the vadose zone (CH2MHILL, 2009). A full scale SVE operation was conducted in 2009 (CH2MHILL, 2010). Three extraction wells were used (see Figure S3 in Supporting Information), U2–634, U2–1001, and U2–1003, with extraction conducted using a single well in sequence (starting with U2–1003). Vapor samples were collected from the SVE effluent during operation to measure contaminant concentrations. These data can be used in effect as a vapor-phase MS-CMD test.

2.2 CMD Tests

The MS-CMD test at the TIAA site was conducted in the summer and fall of 2013. Well CRA-28 was used for vapor extraction (Figure S1). This well is located in the center of the source area, in the region with the highest sediment and vapor contaminant concentrations, and is screened continuously from 8.5 to 26 m bls. Note that this interval spans the entire portion of interest of the unsaturated zone, encompasses both screened intervals of the SVE wells, and closely approaches the top of the saturated zone. The SVE system was shut down for 14 days prior to the CMD test to allow TCE concentrations to stabilize to natural-gradient conditions. Vapor samples were collected from all available wells prior to the start of the CMD test to characterize background conditions.

The initial vapor-extraction stage was conducted for 16 days, using a mean flow rate of 5664 L/m. Extraction was implemented using a Tuthill blower, operated under a vacuum of approximately 280 mm Hg. The extraction was stopped after 16 days to initiate stage two, the rebound stage, which lasted for 32 days. Note that this is the time for which there was no extraction, which is not the same as the time actually required to attain steady state concentrations. The second extraction stage was then initiated, and lasted for 8 days with a mean flow rate of 4340 L/m.

Vapor samples were collected from CRA-28 during both extraction stages. Samples were collected using an air sampling pump (SP 402 SA-R-V, Schwarzer Precision) to which was attached a two-chamber cartridge containing coconut charcoal sorbent (Large Orbo-32 tube, Supelco). The cartridges were stored on ice for shipment to the laboratory. Upon receipt in the laboratory, both chambers of each cartridge were extracted with 5 mL of

dichloromethane and then sub-sampled with a 2 mL aliquot placed into a 2 mL headspace free auto-sampler vial for analysis by gas chromatography/mass spectrometry. The quantitative detection limit for TCE was approximately 0.2 µg/L-vapor. A small number of samples were collected using standard Summa canisters and analyzed at a commercial lab for comparison, and produced comparable results.

As described in the Introduction, the CMD under pseudo natural-gradient conditions is determined from information obtained from stage 2 and 3 of the MS-CMD test. The mass of TCE recovered during the second extraction stage was determined by integration of the TCE elution curve obtained for CRA-28. Data collected for the first 2 pore volumes were used to account for dispersion and retardation effects on transport. Two pore volumes was deemed sufficient based on prior empirical and mathematical modeling analysis of transport at the site (Brusseau et al., 2013b) and the fact that sorption of TCE by the site sediment is very low (retardation factor < 1.2, Johnson et al., 2009). The time required for TCE concentrations to equilibrate during the rebound stage was determined using data collected from surrounding monitoring wells CRA-47,48,49,50 (Figure S1) during the rebound stage.

The MS-CMD test at the Hassayampa landfill site was conducted in October of 2014. The test was conducted in one isolated section of the SVE-affected zone. The SVE system was in operation for 180 days, with a mean flow rate of 571 L/min and a vacuum of approximately 130 mm of Hg, prior to shutdown. This operation phase equates to the first extraction stage for purposes of the MS-CMD test. Site access constraints prevented sample collection during this stage. The extraction was stopped for 8 days to implement the rebound stage. Site access constraints limited sample collection during this stage to one day prior to planned extraction restart. The second extraction stage was then initiated, at a mean flow rate of 529 L/min. Vapor samples were collected using summa canisters. The samples were analyzed using method TO-15 by a commercial laboratory (Eurofins air toxics in Folsom, CA). The reported practical quantitation limit for TCE was approximately 3 µg/L-vapor.

For the Hill AFB site, the pilot SVE test is used as the initial extraction stage of a MS-CMD test. The extraction was conducted for several days, using a flow rate of 2400 L/m under a vacuum of ~19 mm Hg. The full-scale SVE operation was started 11 months later, providing an intervening rebound stage. The extraction for the full-scale SVE was conducted for two months, using a flow rate of 1760 L/m under a vacuum of ~17 mm Hg. The full-scale SVE extraction is used as the second extraction stage of a MS-CMD test. Vapor samples were collected using Summa canisters. Sample analysis was conducted with GC/MS using EPA Method TO-15 (CH2MHILL, 2009, 2010). The reported practical quantitation limit for TCE was approximately 3 µg/L-vapor.

Data reported for well U2–1003 are used for the analysis. This well is located in the center of the chemical disposal pit area, in the region with the highest sediment and vapor contaminant concentrations. This well is screened between 9 and 12 m bls, encompassing the interval in which DNAPL is suspected to be present. Groundwater extraction continued during the SVE operations, such that the water table was maintained at or below 12 m bls.

3.0 Results and Discussion

3.1 TIAA Site

The results obtained for the first and second extraction stages of the vapor-phase MS-CMD test conducted at the TIAA site are presented in Figure 4. It is observed that TCE concentrations decrease within approximately two days to a value of $\sim 4 \mu\text{g/L}$, with the elution curves exhibiting asymptotic behavior thereafter. These results are consistent with the SVE operations data, wherein TCE concentrations in the effluent are displaying asymptotic conditions at very low values of approximately 2 to 3 $\mu\text{g/L}$. Furthermore, the rate of mass removal has declined significantly since SVE inception, and the cumulative mass removed has plateaued at approximately 3000 kg (Figure 2). The slightly higher concentrations obtained for the MS-CMD test compared to the SVE operations data is consistent with the fact that the MS-CMD test was conducted in the center of the source zone, which is thought to comprise the most contaminated section of the site.

The pore volume of the zone influenced by operation of well CRA-28, the extraction well used for the MS-CMD test, is estimated to be roughly 13,000 m^3 based on the radius of influence estimated for the well (from pneumatic tests), the screened depth interval, and porosity. The estimated throughput rate is ~ 0.5 pore volume per day for the flow rates used for the MS-CMD test. Thus, the equivalent of approximately 8 and 4 pore volumes of pore gas was discharged for the first and second extraction stages, respectively. These values are anticipated to be more than sufficient to sweep the vapor-phase contaminant mass residing in the advective (pneumatically accessible) regions and to establish mass-transfer limited conditions. The asymptotic conditions observed for vapor extraction support this conclusion.

The mass removed during the first two pore volumes of the second extraction stage was approximately 144 g. TCE concentrations in the monitoring wells surrounding CRA-28 were observed to attain maximum values within approximately 4.5 days during the rebound stage (Figure 4). A CMD_{ng} value of 32 g/d is produced with these data. Recall that this value represents the estimated CMD for the vadose-zone source under pseudo natural-gradient conditions.

Note that asymptotic behavior was observed to begin after 1–2 days for the effluent TCE concentrations (Figure 4). This is consistent with roughly one pore volume of total throughput based on the estimated pore-volume throughput rate. The establishment of asymptotic conditions after a single pore volume of discharge indicates that there is unlikely to be a significant amount of readily accessible non-vapor-phase contaminant (e.g., DNAPL, sorbed phase) present in the advective domains, and that most remaining mass is likely present in mass-transfer limited domains. Given the conditions for this site, this remaining mass is hypothesized to be primarily associated with the low-permeability (and higher water saturation) region in the vicinity of the saturated zone and capillary fringe.

A high-resolution sediment coring effort was conducted at the test site prior to the MS-CMD test (Brusseau et al., 2013b). Six cores were collected using rotosonic drilling, with each core subsequently subsampled every ~ 50 cm for the unsaturated-zone interval for solvent-extraction analysis. The results showed that the mean sediment-phase TCE concentration

was below detection for samples collected in the interval between 0–25 m bls. Conversely, the mean concentration was approximately 200 µg/Kg for the interval between 25–28 bls, which corresponds to the zone between the bottom of the lower screened intervals of the SVE wells and the water table. Removal of the contaminant mass within this region via SVE is expected to be constrained by flow and mass-transfer limitations. The sediment-core data support the interpretation of the MS-CMD test results.

3.2 HASS Site

The results obtained for the second extraction stage of the vapor-phase MS-CMD test conducted at the HASS site are presented in Figure 5. The mean initial TCE concentration is approximately 530 µg/L. This concentration is very similar to the mean concentrations measured for the two wells prior to the start of SVE. In addition, the mean concentration (627 µg/L) for samples collected from SP2-F one day prior to the start of stage 3 were very similar to the initial concentrations obtained for that well upon restart of extraction (620 µg/L). These results indicate that the length of the rebound stage was sufficient for establishing equilibrium conditions. The TCE concentrations decrease within approximately 4–8 hours to values of approximately 250 and 50 µg/L for SP2-F and SP1-F, respectively. The elution curves exhibit apparent steady-state behavior for the remainder of the test. These results are consistent with the SVE operations data for the entire site, wherein TCE and other VOC concentrations in the effluent, and attendant CMD, remain relatively high (Figure 3).

The pore volume of the zone influenced by operation of the two extraction wells used for the MS-CMD test is estimated to be roughly 2,500 m³. The estimated throughput rate is ~0.6 pore volume per day for the flow rates used for the MS-CMD test. Thus, the equivalent of approximately 1.2 pore volumes of pore gas was discharged for the second extraction stage of the test. The TCE masses removed during this stage were approximately 87 and 312 g for SP1-F and SP2-F, respectively. A rebound time of 8 days is used for the CMD calculation, corresponding to the length of the rebound stage. A mean CMD_{ng} value of 25 g/d is produced with these data.

Apparent steady-state conditions were attained after roughly 0.2 pore volume of extraction for the test. This behavior is typically associated with the presence of a poorly accessible (low-advection) domain that comprises a large fraction of the treatment zone. This is consistent with the site conditions, wherein the 9-m thick FGZ comprises the primary treatment zone for the SVE system.

3.3 Hill AFB Site

The results obtained for the pilot and full-scale SVE operations conducted at the Hill AFB OU2 site are presented in Figure 6. The two sets of data are comparable, exhibiting similar overall behavior. It is observed that the initial TCE concentrations are several hundred mg/L, which decline to ~10 mg/L within the first day of operation. Concentrations decline more slowly thereafter, to values less than 1 mg/L. Significant rebound in concentration was observed after extraction ceased (Figure 6).

The pore volume of the zone influenced by operation of well U2–1003, the extraction well for the SVE operations, is estimated to be roughly 1,500 m³ based on the radius of influence estimated for the well (from pneumatic tests), the screened depth interval, and porosity. The estimated throughput rate is 2 pore volumes per day for the flow rates used for the extractions. Thus, the equivalent of approximately 10 and 100 pore volumes of pore gas was discharged for the first and second extraction stages, respectively. These values were sufficient to sweep the vapor-phase contaminant mass residing in the advective (pneumatically accessible) regions and to establish mass-transfer limited conditions.

The mass removed during the first two pore volumes of the second extraction was approximately 48 kg. A rebound time of 178 days was determined based on the extrapolated time required to attain maximum concentrations during the shutdown stage conducted after the full-scale SVE operation. These two values produce a CMD_{ng} value of 270 g/d. This value is roughly an order of magnitude greater than the values determined for the TIAA and HASS sites.

Asymptotic conditions appear to start after approximately 5 days of vapor extraction (Figure 6), which is equivalent to roughly 10 pore volumes of throughput. Asymptotic conditions are typically expected to be attained within 1 to 2 pore volumes of extraction for conditions wherein only vapor-phase mass is present in the advective domain (as was observed for the TIAA site). Hence, the observation that asymptotic conditions did not start until after ~10 pore volumes of extraction suggests that non-vapor-phase contaminant mass (e.g., DNAPL, sorbed) may be present in the advective domains. This is consistent with the observed vapor-phase concentrations, which remained at ~1 mg/L during sustained extraction. It is also consistent with the results of prior characterization activities conducted at the site, which indicate the presence of DNAPL in the region approximately 10 m bls near well U2–1003 (CH2MHILL, 2010). Hence, the asymptotic conditions observed for this site most likely derive from a combination of mass transfer from more accessible DNAPL (and sorbed) phases present in the advective domain as well as mass residing in lower-permeability (“non-advective”) regions.

3.4 Comparison of Forced-gradient and Natural-gradient CMD Values

The relative magnitudes of the CMD_{ng} values determined above, representing pseudo natural-gradient conditions, can be compared to CMD values determined for the steady-state stage of vapor extraction (forced-gradient conditions) as an additional means to evaluate SVE performance (Brusseau et al., 2010). Analysis of 10 years of cyclic SVE operations data reported for the Handford site demonstrated that the difference between forced-gradient and natural-gradient CMD values decreased steadily from a factor of ~7 to a factor of ~2 during the 10 years. This reduction reflects the impact of continued mass removal associated with the SVE operations. For the TIAA site, the forced-gradient CMD determined for the asymptotic phase of both extraction stages of the MS-CMD test is approximately 25 g/d. This value is similar to the natural-gradient value (32 g/d), which indicates that the SVE system is operating primarily in a “containment”, rather than mass-removal, mode. The forced-gradient CMD values determined for the asymptotic phases of the second extraction stages for the HASS and Hill AFB sites are approximately 117 g/d and 1 kg/d, respectively.

These values are approximately 4–5 times larger than the respective natural-gradient values, in contrast to the TIAA site, indicating that the SVE systems are operating in a sustained mass-removal mode.

3.5 Application of Measured CMD Values

A primary reason to conduct a vapor-phase MS-CMD test is to obtain a measured value of CMD under equivalent natural-gradient conditions that can be used in assessing the impact of vadose-zone contamination on groundwater quality or vapor-intrusion potential. This application is illustrated using a recently developed vapor-discharge tool (Carroll et al., 2012; Oostrom et al., 2014). The tool is based on a data base relating long-term, maximum contaminant concentrations in groundwater to short-term vapor-phase mass discharges associated with vadose-zone VOC sources. The data base was generated by conducting more than 1000 sets of simulations of multiphase flow and transport for a wide variety of source conditions. The numerical simulations were conducted using the three-dimensional (3D) water–oil–air operational mode of the STOMP simulator (White and Oostrom, 2006).

A nomograph developed to simplify use of the discharge tool was presented by Carroll et al. (2012), and is adapted for use herein (Figure 7). The CMD_{ng} value of 32 g/d obtained for the TIAA site is used as input. This magnitude of vapor discharge from the vadose-zone source is forecast to produce an estimated maximum TCE concentration of 40 $\mu\text{g/L}$ in groundwater sampled from a monitoring well with a 10 m screened interval. The results obtained from application of the nomograph may have a significant degree of uncertainty because the nomograph is not tuned specifically to the TIAA site. Hence, the full-scale vapor-discharge tool (Oostrom et al., 2014) was used to obtain a site-specific estimate.

Values for several site-specific parameters are required to conduct a site-specific assessment; those used are presented in Table 1 for the TIAA site. The estimated TCE concentration in groundwater depends in part upon the length of the monitoring well's screened interval. The value obtained with the full-scale tool was 52 $\mu\text{g/L}$ for the 10-m well screen used for generating the nomograph in Figure 6. This concentration compares well to the value obtained with the nomograph. An estimated groundwater TCE concentration of $\sim 170 \mu\text{g/L}$ was obtained with the full-scale tool using a well-screen interval of 3 m, representative of the TIAA site monitoring wells. It should be noted that there is uncertainty associated with the estimates produced with the full-scale discharge tool, particularly related to parameters representing source dimensions.

The current mean concentration of TCE in groundwater within and adjacent to the source area is $\sim 1 \text{ mg/L}$, based on analysis of groundwater samples collected from several wells. The estimated maximum groundwater TCE concentrations obtained with application of the nomograph and the full-scale discharge tool are both several times lower than the measured value. This suggests that the vadose-zone VOC source currently has a relatively small impact on groundwater quality compared to contaminant present in the saturated zone.

The CMD_{ng} value of 270 g/d obtained for the Hill AFB site is used as input to the nomograph presented in Figure 7. This magnitude of vapor discharge from the vadose-zone source is forecast to produce an estimated maximum TCE concentration of 300 $\mu\text{g/L}$ in the

underlying groundwater. This value is more than 100 times lower than the current groundwater TCE concentration of ~100 mg/L. This suggests that the current impact of the vadose-zone VOC source on groundwater quality is relatively insignificant compared to the current groundwater TCE concentrations, similar to the results obtained for the TIAA site.

The CMD_{ng} value of 25 g/d obtained for the HASS site is also used as input to the nomograph presented in Figure 7. This magnitude of vapor discharge from the vadose-zone source is forecast to produce an estimated maximum TCE concentration of 30 $\mu\text{g/L}$ in the underlying groundwater. This value is similar to the current groundwater TCE concentration of ~40 $\mu\text{g/L}$. Note that this comparison represents a conceptual assessment of theoretical behavior and is not meant to imply that there is a direct connection between the wells used for the test (which are screened above the basalt unit) and the sub-basalt Unit A groundwater. This suggests that the impact of the vadose-zone VOC source on groundwater quality is significant, perhaps predominant, in contrast to the results obtained for the TIAA and Hill sites. This assessment is consistent with the current Conceptual Site Model.

3.6 Method Uncertainty

There are several sources of uncertainty that may impact the CMD_{ng} values obtained from the MS-CMD test. One source comprises standard “instrument” uncertainty inherent to measurements of concentration and flow rate. These are considered to be relatively small compared to other potential sources. Another potential source is the resolution of the test in terms of the degree to which it captures concentration perturbations, which is relevant for accurate tabulation of mass removed as well as assessment of mass-removal behavior. Based on inspection of the test results (Figures 4–6), we conclude that the data density is of sufficient resolution to adequately characterize the temporal concentration profiles.

A third potential source of uncertainty relates to the estimation of pore volumes and determination of the number of extracted pore volumes to use for tabulation of the mass removed during the second extraction stage of the test. For the TIAA site, the observed point at which the concentration curve exhibited asymptotic behavior was consistent with the pore-volume throughput that was calculated based on the estimated pore volume. This indicates that the method used to estimate pore volume produced reasonable results. The impact of potential uncertainty in determination of the number of extracted pore volumes to use for the mass-removed tabulation was assessed by recalculating the CMD_{ng} value, using 1 rather than 2 pore volumes. This change results in a CMD_{ng} of 19 g/d, compared to the original value of 32 g/d. The significance of this difference can be evaluated by comparing the groundwater concentrations estimated with the nomograph for the two CMD_{ng} values—~20 vs ~40 $\mu\text{g/L}$. This slight difference in estimated values has no impact on the overall conclusion that the vadosezone source has minimal impact on current groundwater quality. Similar analyses for the other two sites produced similar results.

A fourth potential source of uncertainty relates to the determination of rebound time. This was assessed by recalculating the CMD_{ng} value, using 2.25 days than 4.5 days for the TIAA site. The recalculated value is twice the original value. The new value results in a larger estimated groundwater concentration that is still several times smaller than the measured concentration. Similarly, using 4 rather than 8 days for the rebound time for the HASS site

produces a larger CMD_{ng} and a larger estimated groundwater concentration. For the Hill site, inspection of Figure 6 indicates that the 178 day estimate used for the rebound time is unlikely to be significantly longer than the actual value. Use of a time greater than 178 would result in a smaller CMD_{ng} and a lower estimated groundwater concentration, which would further diminish the apparent minimal impact of the vadose-zone source on groundwater quality.

There are also sources of uncertainty associated with the use of the vapor-discharge tool, such as those relating to system representativeness and determination of parameters for site-specific conditions. It is important to recognize that this uncertainty is separate from, and has no import for, the MS-CMD test itself. The performance of the combined MS-CMD test and vapor-discharge tool can be evaluated to some degree by comparing the results to site conditions. For example, the concentration and mass-removal behavior observed for the historic SVE operations data as well as the results of the high-resolution sediment coring effort both indicate that a relatively small quantity of TCE remains in the vadose zone at the TIAA site. Thus, it would be expected that the vadose-zone VOC source would have small impact on groundwater quality, consistent with the test results and associated interpretation.

For the HASS site, it is interesting to note that a total of approximately 86,000 kg of VOC has been removed with the entire SVE system to date. This quantity is orders of magnitude larger than the 187 kg removed to date from the saturated zone with the pump-and-treat system. This disparity in mass removal is consistent with the specific conditions at this site, which produced a scenario in which a great majority of VOC mass resides in the vadose zone. This condition would logically result in contaminant discharge from the vadose-zone VOC source being a predominant mediator of groundwater quality. The theoretical assessment obtained from the MS-CMD test and application of the nomograph is consistent with this scenario.

4.0 Summary

The development and assessment of cleanup objectives for vadose-zone sources, such as for SVE operations, is typically based on evaluating the impact of vapor discharge from the vadose zone on groundwater quality or vapor intrusion. Standard approaches based on measuring soil or vapor concentrations and application of screening models may for some cases have relatively high degrees of associated uncertainty. The vapor-phase MS-CMD test was developed to measure mass discharge associated with contaminant sources located in the vadose zone. The innovative component of this test is the ability to measure the CMD associated with the source under pseudo natural-gradient conditions, which is the entity desired for conducting risk assessments. Vapor-phase MS-CMD tests were implemented successfully at three sites, which span the three primary general stages of SVE operations and which represent a variety of site properties and conditions.

The behavior exhibited for the test conducted at the TIAA site suggests that there is unlikely to be a significant mass of non-vapor-phase contaminant (e.g., DNAPL, sorbed phase) present in the advective domains, and that most remaining mass is likely located in poorly accessible domains. Given the conditions for this site, this remaining mass is hypothesized

to be associated with the low-permeability (and higher water saturation) region in the vicinity of the saturated zone and capillary fringe. This is supported by the results of a sediment-coring effort conducted prior to the MS-CMD test, as well as the data obtained from the historic SVE operations. The results of the test conducted at the Hill AFB site conducted at this site suggest that non-vapor-phase contaminant mass (e.g., DNAPL) may be present in the advective domains. This is consistent with the results of prior characterization activities conducted at the site. Hence, the asymptotic conditions observed for this site most likely derive from a combination of mass transfer from more accessible DNAPL (and sorbed) phases present in the advective domain as well as mass residing in lower-permeability (“non-advective”) regions. The test results for the HASS site are consistent with historic SVE operations data, and with the current Site Conceptual Model.

The CMD values obtained from the tests were used in conjunction with a recently developed vapor-discharge tool to evaluate the impact of the vadose-zone source on groundwater quality. The estimated groundwater TCE concentrations obtained from the assessment were in two cases much lower than the current measured groundwater TCE concentrations. This suggests that for both these sites, the current impact of the vadose-zone VOC source on groundwater quality is relatively small compared to the impact of contamination present in the saturated zone. This implication supports consideration of remedy modification or closure for both sites. These results illustrate the utility of the MS-CMD test for enhancing characterization and assessment efforts at sites containing vadose-zone VOC sources.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

Vapor-phase multi-stage contaminant mass discharge tests are conducted at 3 field sites

The test measures natural-gradient vapor discharge for VOC sources located in the vadose zone

The data were used to interpret mass-removal conditions influencing vapor extraction

The impact of the measured vapor discharge on groundwater quality was evaluated

Figure 1.

Conceptual diagram illustrating the 3 stages of the vapor-phase multi-stage contaminant mass discharge test; CMD_{ng} = pseudo natural-gradient contaminant mass discharge, M = mass, T = time.

Figure 2.
Historic SVE operational data for the TIAA site; time in months (m).

Figure 3.
Historic SVE operational data for the HASS site; time in months (m).

Figure 4.

TCE concentration in vapor effluent for first and second extraction stages of the vapor-phase CMD test conducted at the TIAA site. Also included are the TCE concentrations measured for monitoring well CRA-47 during the intervening rebound stage; note the data point shown at 10 days in actuality represents a sample collected at 32 days (the end of the rebound stage).

Figure 5.
TCE concentrations in vapor effluent for the two extraction wells used for the second extraction stage of the vapor-phase CMD test conducted at the Hassayampa landfill site.

Figure 6. TCE concentration in vapor effluent for SVE tests conducted at the Hill AFB site. Also included are the TCE concentrations measured the intervening rebound stage.

Figure 7.

TCE concentration in groundwater sampled from a downgradient monitoring well (10-m screened interval) for the three sites estimated from input of measured vapor-phase CMD into a nomograph adapted from Carroll et al. (2012).

Table 1

Input parameter values used in the vapor-discharge tool for the TIAA site.

Parameter (Unit)	Value
Temperature (°C)	23
Avg. Moisture Content (wt %)	2
Avg. Recharge (cm/yr)	0.4
Vadose Zone Thickness (m)	28
Depth to Top of Source (m)	20
Source Thickness (m)	5
Source Width (m)	35
GW Darcy Velocity (m/day)	0.175
Distance to Monitoring Well (m)	30
Well Screen Length (m)	3
Source Mass Discharge (g/day)	32