

## **7. TCE CONTAMINATION**

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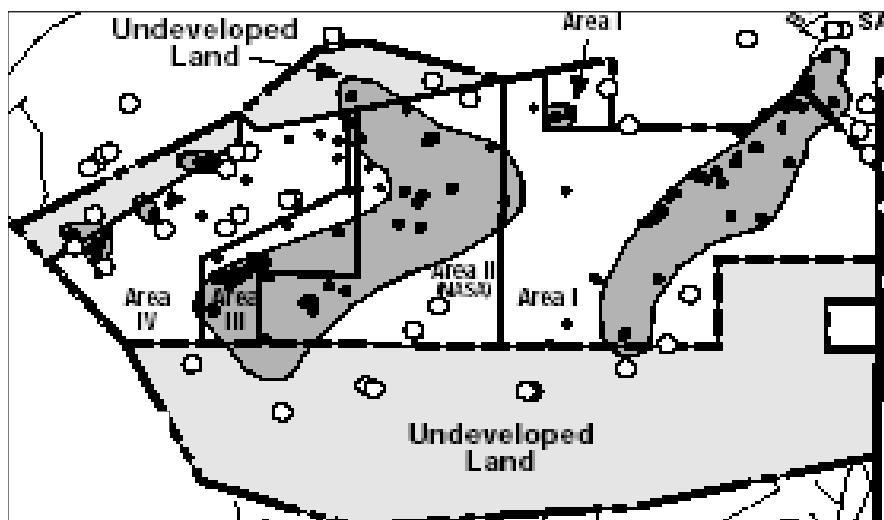
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## 7.0 TCE CONTAMINATION

### 7.1 Overview

Significant groundwater contamination by TCE has been detected at SSFL as early as March 1984 (Rocketdyne, 1988). A TCE plume was found to underlie much of the site's 2,700 acres in Areas I, II, and III (Rocketdyne, 1988; Figure 7-1). The major source of TCE contamination was associated with cleaning of rocket engines in the rocket testing areas (Sections 3.2.2 and 5.3). TCE was detected in groundwater wells at the facility in concentrations of up to 5,200 µg/L (RD-4 near Bravo test area, Area II; see GRC, 1987). The presumed source for most of the groundwater TCE contamination was downward flow from a series of surface water impoundments that drained the rocket engine test areas (GRC, 1987).<sup>7.1</sup> Offsite groundwater contamination by TCE and its degradation products, trans-1,1-DCE and 1,2-DCE, has also been reported (see Appendix H).

**Figure 7-1.** TCE Plumes On Site



**Source:** ATSDR, 1999.

**Note:** Black dots represent groundwater detections; white dots represent groundwater non-detections.

The total amount of TCE that infiltrated groundwater has been estimated at 313,000 gallons (3,660,000 pounds) by CH2M Hill (1993). It is also possible to estimate the total amount of TCE that infiltrated the subsurface using a study by Hurley et al. (2003) and estimates of the superficial areas of different plumes at SSFL. Hurley et al. estimated the amount of TCE per unit area in the contaminated subsurface, based on measurements in seven boreholes drilled on SSFL at locations where TCE infiltration was suspected. The average amount of TCE per unit of area in these seven boreholes is 617 g/m<sup>2</sup> and the surface area of the TCE plumes is on the order of 1,160,000 m<sup>2</sup> (see Section 5.1.4). Therefore, the total amount of TCE in the contaminated zone (i.e., the product of the TCE surface density and the contaminated area) is estimated at about 716

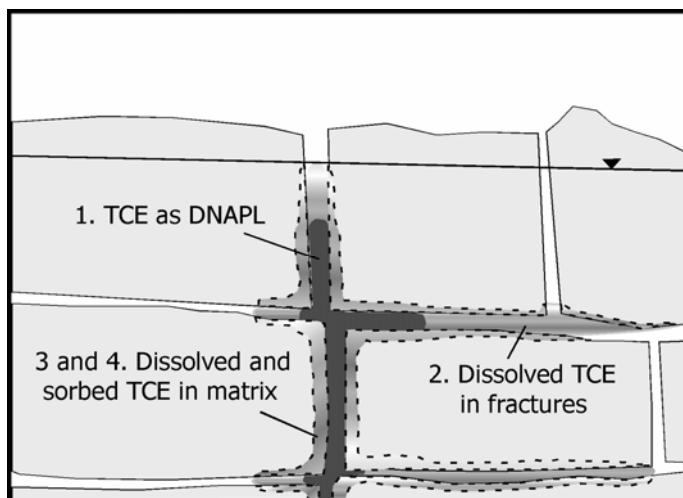
<sup>7.1</sup> Historically, TCE was used to wash the rocket engines between tests (CH2M Hill, 1993). Other chemicals were carried along with the TCE wash and also infiltrated the subsurface soil.

metric tons (1,600,000 pounds). This estimate differs with the estimate by CH2M Hill (1993) by about a factor of 2. The two estimates are, however, within the same order of magnitude (1,600 and 3,660 thousand pounds, respectively). Both indicate that a significant amount of TCE has contaminated the subsurface zone. Sections 7.2 and 7.3 discuss the distribution and extent of TCE contamination of groundwater below SSFL and the potential migration of TCE.

## 7.2 A Simplified Conceptual Model of TCE Distribution in SSFL Groundwater

Groundwater contamination by TCE is extensive relative to contamination by other organic compounds identified at SSFL, and has been the subject of intense investigation (Montgomery Watson, 2000a, b). The past, current, and future status of subsurface TCE in SSFL can be summarized with a conceptual model of the site, depicted in Figure 7-2.

**Figure 7-2.** Conceptual Model of TCE Distribution in a Fractured Sandstone Groundwater Environment



**Note:** The horizontal line with pointer represents the water table in this conceptual model. Adapted from information presented in Montgomery Watson, 2000 a,b.

TCE is categorized as a denser-than-water organic solvent, or a dense nonaqueous-phase liquid (DNAPL). This means that the infiltrating TCE penetrated to depths below the water table and continued to sink until the resistances posed by friction against the fracture walls and buoyancy forces halted its progress. The time period encompassing the release of TCE and its infiltration into the subsurface soil is relatively short (hours to days or weeks after each release episode). While residing in the fractures, the TCE DNAPL (TCE fraction 1) dissolves into slowly passing groundwater (TCE fraction 2). Due to its low aqueous solubility (about 1.1 g/L), TCE can be present as a saturated (pure) DNAPL phase that is extremely persistent in groundwater. Dissolved TCE also diffuses from the DNAPL and from regions of high dissolved TCE concentrations into stagnant water of the fracture network and within the relatively tight porosity of the sandstone matrix (TCE fraction 3). Because TCE is hydrophobic, a significant portion of

the aqueous-phase chemical can partition (or sorb) to the sandstone solids (TCE fraction 4). These latter three processes occur over years—a much larger timescale than infiltration.

*TCE fraction 1: DNAPL entrapped in fractures.* Dissolved TCE has been found in groundwater associated with alluvial sediments as well as in the Chatsworth Formation groundwater. TCE concentrations ranging from a few parts per billion (ppb) to 10–15 parts per million (ppm) have been reported (Montgomery Watson, 2000a; Hurley et al., 2003). Concentrations at the high end of this range may be indicative of the presence of DNAPL TCE in the vicinity of the measurements. The exact location of the DNAPL is difficult to estimate, particularly in a fractured flow system like the one at SSFL, and is related to such issues as the amount and timing of TCE release, the depth to groundwater, and the geometry of the fractures. The depth and distribution of the DNAPL can fluctuate with changing groundwater conditions, such as those caused by pumping, wet periods, or dry periods.

The total amount of subsurface DNAPL is difficult to quantify, as the released amounts and volatilization fractions are highly uncertain. At SSFL, where fractured flow dominates, DNAPL dissolution is expected to be slow and most of the DNAPL that reaches groundwater may still be harbored in the fractures. This issue is pursued further below, in the sections on the aqueous and sorbed TCE mass in the SSFL sandstone.

*TCE fraction 2: aqueous TCE in fractures.* It is this dissolved- (or aqueous-) phase TCE that is detected in monitoring wells throughout SSFL and, in a few cases, just off site. Plume maps, drawn to integrate the observation well data, are presented by Montgomery Watson (2000). Montgomery Watson prepared these maps by interpolating between observations, a generally accepted procedure for alluvial groundwater systems. This approach creates an approximation for fractured flow systems, in which the dissolved contaminant patterns are more closely linked to the fractures. When using such a map for SSFL's fractured flow system, one must realize that the subsurface plume depictions are representations of the contaminated fracture planes and do not necessarily reflect the actual sandstone matrix contamination within the same areas. The extent to which these maps do reflect the overall subsurface contaminant levels depends on the rate of transport of TCE from the fractures into the matrix (TCE fraction 3). Thus, if the rate of transport into the matrix is slow, these plumes may represent a relatively small amount of the TCE that initially infiltrated the fracture network.

*TCE fractions 3 and 4: aqueous and sorbed TCE in the sandstone matrix.* The rate and extent of penetration of TCE into the SSFL sandstone matrix depends on the geometry or “tightness” of the matrix porosity, the strength of the TCE sorption to the sand material making up the matrix, and the contact time between the TCE and the matrix. The penetration process is diffusion-driven: that is, the dissolved TCE is driven from a region of high concentration (the fracture) into a region of low concentration (the sandstone matrix). The diffusion process is hindered by the tortuous path that the TCE molecules must follow through the matrix. TCE progress is further retarded when TCE sorbs onto the sandstone matrix while passing through the matrix pores.

### **7.2.1 A Conceptual Model of TCE in SSFL Groundwater**

A conceptual model posed for TCE (Montgomery Watson, 2000a), and later for perchlorate (Montgomery Watson Harza, 2003a, 2003b, 2003c), proposes that the contaminant sources are stationary and that contamination is transported away from the source by groundwater moving through the fractures and by diffusion into the porous, but stagnant, sandstone matrix. Model simulations were used to demonstrate the slowness of the propagation of contaminants through the fractured sandstone due to the retarding effect of the diffusion process. The models (hereafter collectively termed the Montgomery Watson or MW model) suggest that the TCE and perchlorate have accumulated in the sandstone matrix.

The simulations were two-dimensional and carried out using the numerical model Fractran, developed at the University of Waterloo (Sudicky and McLaren, 1992). Fractran is well-documented, commercially available code (Waterloo Hydrogeologic Software). The two-dimensional model domain employed was a vertical cross-section of fractured media 500 meters long and 100 meters deep. Physical parameters for the model were taken from SSFL site characterization data. The sandstone matrix hydraulic conductivity value and porosity values used were  $1 \times 10^{-6}$  centimeters per second and 0.12, respectively. A fracture network was generated randomly using statistics from the field data on horizontal and vertical fracture lengths, and assigning fracture densities of 0.05 and 0.075 fractures/m<sup>2</sup> in the vertical and horizontal directions, respectively. Horizontal and vertical fracture lengths ranged from 10 to 20 meters and 5 to 10 meters, respectively. Fracture aperture thicknesses were also randomly generated and spatially distributed in the model using a statistical data from SSFL fractures and ranged from 20 to 1000 microns.

The first step of the model simulation was to generate a steady state-flow regime through the fractured sandstone. The modelers accomplished this by specifying a hydraulic head along all four sides of the model domain so as to create 0.5 percent (horizontal) and 0.2 percent (vertical downward) hydraulic gradients, which are estimated from site conditions. The average linear groundwater velocities for these gradients and the matrix and fracture properties outlined above were reported to be 925 meters per year, or m/yr (horizontal) and 105 m/yr (vertical). The model-calculated velocity distribution values used to determine these averages ranged from -2,850 m/yr to 11,500 m/yr (horizontal) and -12,300 m/yr to 9160 m/yr. The negative horizontal velocity is in the direction opposite to the assigned hydraulic gradient, and the negative vertical velocity is downward. A comparison of these model-calculated groundwater velocities with those observed in the field or estimated more directly from field observations was not found in these reports.

Perchlorate and TCE solute transport was then modeled in the context of the steady-state flow regime. A 25-meter-long vertical source of TCE was attributed to the upper edge of the up gradient end of the simulation domain and left constant for 20 years. This was intended to simulate a DNAPL source area that had penetrated vertically into the subsurface via surface fissures. In contrast, perchlorate was admitted to the flow system as a 50-meter-long horizontal source along the top boundary of the up gradient end of the simulation domain and left constant for 10 years. This configuration was intended to simulate a release of solid phase perchlorate at the ground surface followed by infiltration into the subsurface as a solute via recharge water. Site characterization data support the TCE DNAPL source configuration in a general sense; however, the specific geometry and dissolution characteristics of the TCE source zones at SSFL remain

largely unknown. The perchlorate source configuration appears to be more speculative in nature due to limited plume data at SSFL.

Simulations of diffusive transport of dissolved TCE and perchlorate were undertaken to determine the potential impact of matrix diffusion on the transport process. These simulations are based on Fick's Second Law of diffusion (Crank, 1975), modified to account for the presence of a porous medium:

$$\frac{\partial C}{\partial t} = \frac{D/\tau}{R} \frac{\partial^2 C}{\partial x^2} \quad (7.1)$$

where  $C$  is the solute concentration in the soil matrix,  $t$  is time,  $x$  is the coordinate perpendicular to the matrix face (cm),  $D$  is the aqueous diffusion coefficient of the solute ( $\text{cm}^2/\text{s}$ ),  $\tau$  is the dimensionless matrix tortuosity factor ( $\geq 1.0$ ), and  $R$  is the dimensionless retardation factor.<sup>7.2</sup> It is noted that the chemical concentration in soil air phase,  $C_a$ , is related to matrix concentration as  $C_a = C/\phi$ , where  $\phi$  is the soil porosity. Equation 7.1 signifies that the rate of diffusion of a solute is related to the concentration gradient (the steeper the gradient, the faster the diffusion rate) and the diffusion properties of the system—specifically the diffusion coefficient, porosity, tortuosity factor, and retardation factor. For porous systems with sorption, the net effect of these parameters is a retarded diffusion process.

The selection of diffusion and sorption model parameters is critical to assessing the relevance of the MW conceptual model. For TCE, the values applied for  $D$ ,  $\tau$ , and  $R$  were  $1 \times 10^{-5} \text{ cm}^2/\text{s}$ , 10, and 2.0, respectively, resulting in an apparent diffusion coefficient value ( $D_a = D/(\tau R)$ ) of  $5 \times 10^{-7} \text{ cm}^2/\text{s}$ . For perchlorate, the values applied for  $D$ ,  $\tau$ , and  $R$  were  $1.8 \times 10^{-5} \text{ cm}^2/\text{s}$ , 10, and 1.0, respectively, resulting in an apparent diffusion coefficient value of  $1.8 \times 10^{-6} \text{ cm}^2/\text{s}$ . For a non-diffusing solute, the values applied for  $D$ ,  $\phi$ ,  $\tau$ , and  $R$  were adjusted so that the resulting apparent diffusion coefficient was more than six orders of magnitude lower (i.e., negligible) than in the preceding cases. It is worthwhile to note that the tortuosity factor can be applied mathematically in two ways. In Montgomery Watson (2002), it is used as a fractional multiplier to lower the net diffusion rate. In equation 7.1, it is used in the denominator, in which case it must be greater than 1 to show the desired tortuosity effect.

In the MW simulations, the simulated TCE and perchlorate plumes remain within the simulation domain (100 meters vertical distance, 500 meters horizontal distance) even after 100 years, whereas the non-diffusing plume encounters the down gradient boundary in only 3.5 years. Additional two-dimensional simulations were undertaken that examined the sensitivity of this result to the randomly generated fracture network and associated groundwater velocities generated by the model. No sensitivity analysis associated with the diffusion parameters was presented.

The simulations performed in support of the MW conceptual model were useful for illustrative purposes. The general dynamics of the SSFL system are likely to be similar to what the simulations describe. However, specific conclusions as to the current state of TCE and

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<sup>7.2</sup>  $R = 1 + \rho_b K_d / \phi$ , where  $\rho_b$  is the bulk density of the sandstone and  $K_d$  is the sorption distribution coefficient: (mg chemical/g sorbent)/(mg chemical/mL water).

perchlorate, and their containment in the subsurface at SSFL, cannot be drawn from these simulations. There are several reasons for this.

First, the source configurations selected for the simulations are highly idealized and not necessarily characteristic of those at SSFL. While the general locations of the sources (DNAPL) at SSFL are known from site characterization efforts to date (Montgomery Watson, 2002; Hurley et al., 2003), the sources' specific locations and configurations have not been clearly delineated. Actual sources at SSFL are distributed in space; often, more than one source contributes to plume migration. This is evidenced by the existing TCE plumes, which have clearly propagated to lengths exceeding 500 meters in less than 100 years (Montgomery Watson, 2000a).

A second issue has to do with flow parameters used in the model. The flow model has not been calibrated to actual site conditions, and thus is more appropriate as a conceptualization of the general characteristics of the SSFL site. Actual groundwater flow at SSFL is driven by a range of vertical and horizontal hydraulic gradients that fluctuate with recharge and pumping conditions on site. Creating a more realistic, calibrated version of the flow model at SSFL would constitute a major effort, but may be necessary for portions of the site where contaminant plume containment is critical.

A third issue pertains to the estimated diffusion rates into the sandstone, which are defined too narrowly in the simulations. In particular, the retardation and tortuosity effects employed could be greater than the simulations depict. An independent estimate of the TCE diffusion rate in a sample of SSFL sandstone were made for comparison with the abovementioned rate (see Appendix U for method details). The TCE sorption capacity of the sandstone was measured, producing a retardation factor value of about 20. Diffusion estimates for the same sandstone yielded a tortuosity estimate of about 48. This value points to the feasibility of an apparent diffusion coefficient value that is roughly 50 times lower than the values employed in the MW model for TCE. If this is the case, the majority of the mass may not be harbored in the SSFL sandstone matrix and hydraulic containment of the mobile (fracture-driven) groundwater is a key issue in preventing further offsite migration and surface manifestations of contaminant plumes (e.g., at springs).

### 7.3 Extent of Existing TCE in SSFL Groundwater

Extensive past site characterization and monitoring efforts have been reviewed in various previous reports on SSFL. The most recent characterization efforts for groundwater have focused on TCE and perchlorate (Montgomery Watson, 2000a, b, 2002; Montgomery Watson Harza, 2003a, 2003b, 2003c). A large number of contaminants, including other chlorinated solvents and their transformation products, have been identified in SSFL groundwater and remain chemicals of concern. However, the discussion here focuses primarily on the more recent TCE characterization efforts, which provide the most definitive data on potential exposure pathways.

*Horizontal extent of chlorinated solvent plumes.* A network of shallow and deep monitoring wells has identified chlorinated solvent plumes (primarily TCE, along with other solvents and their transformation products) in SSFL groundwater. The plume sources are generally located at

the centers of solvent handling and disposal activities, such as the rocket test areas and former sodium disposal facility. An assessment of SSFL periphery monitoring well data over time (GRC, 1999, 2000) was undertaken to confirm Montgomery Watson's (2000a, b) rendering of the extent of these plumes. The assessment determined that the general configuration of the published plume configurations and boundaries is reasonable. Historical TCE monitoring well data throughout SSFL (GRC, 1999–2002) were examined as time series in order to determine whether the plumes continued to grow longitudinally. Continued plume growth would suggest that the plumes were not being contained by natural attenuation processes and/or groundwater extraction operations at SSFL. This could also mean that the plumes pose a significant risk to water resources and humans using those resources down gradient from the existing plume boundaries.

The time series data were found to be complicated by large variations in groundwater levels over time, caused by onsite pumping and normal seasonal variation at SSFL. Examination of individual wells within plumes at SSFL suggested that most of the plumes had achieved approximately steady-state conditions. This does not mean that contaminants are no longer being dispersed off site. Instead, stationary plumes are receiving mass from their sources as quickly as they lose mass at the plume front (via transport and mixing in water or transformation of the contaminants). The plume size appears to be constant, in part, because of the detection limits of the methods used to measure the concentrations. Note that the stationary state of a plume depends on the existence of a steady hydraulic regime; changes in this regime, such as may be caused by changes in pumping activity or recharge, can change the plume geometry.

Based on historical monitoring data for wells situated at or near approximate plume boundaries, areas of concern were defined qualitatively at the locations of wells where elevated concentrations appeared to persist or where concentrations appeared to be increasing (i.e., where the plumes were not at steady state). One area of concern was in the northeast portion of SSFL, where concentrations at wells RD-38A and OS-24 appeared to increase from 1998 through 2001 (GRC, 1998, 1999, 2000). It is known that TCE is dispersing via the groundwater pathway over SSFL site boundaries in this part of Area I, and substantial additional characterization efforts have focused on this area (Montgomery Watson Harza, 2003a). A second area of concern is located along the northern SSFL boundary, where elevated TCE concentrations in well RD-56A have been observed (GRC, 1998, 1999, 2000). This is the same region where significant levels of transformation products, such as vinyl chloride, have been observed. Note that wells along the western and southwestern boundaries do not indicate current contaminant levels comparable to those in the abovementioned wells. However, these areas are also of some concern due to past detection of chlorinated solvents at RD-59 and OS-5, as well as RD-59's proximity to the former radioactive waste handling facilities and OS-5's proximity to the sodium disposal pond. Note also that TCE was detected on site in a number of Area IV wells at elevated concentrations (see Appendix H, Table H-3) and that this area drains to the southwest via the outfalls.

*Vertical extent of chlorinated solvent plumes and source zones.* Recently a substantial core hole sampling and analysis effort was undertaken to characterize the subsurface source zones for chlorinated solvents (DNAPL) at SSFL (Hurley et al., 2003). The extensive data set described in Hurley et al.'s report delineates the vertical distribution of chlorinated solvents in core holes C-1 through C-7. In core hole C-1, several TCE concentrations as high as 0.5 mg/L were observed at depths greater than 400 feet, while more concentrations above 1 mg/L occur at depths greater

than 300 feet and a still greater frequency of concentrations above 1 to 10 mg/L appears at depths ranging from about 70 to 200 feet. While the connectivity between the source and this aqueous distribution is complex in a fractured flow system, the aqueous distribution here likely corresponds to the vertical DNAPL distribution. This would imply that (in the vicinity of C-1) a large portion of the DNAPL is harbored in the subsurface between 70 and 200 feet, a smaller (but still significant) portion resides between 200 and 300 feet, and a lesser portion resides around 300 to 400 feet. Overall, the plots of chlorinated solvent pore water concentration as a function of depth provide conclusive evidence of DNAPL penetration to a depth of 400 or 450 feet in some instances.

Hurley et al. (2003) employed the core hole data to reach the conclusion that “all or nearly all of the DNAPL has been converted to dissolved and sorbed mass existing in the rock matrix.” This conclusion is suspect for three reasons. First, there is an abundance of elevated TCE concentrations (in the ppm range) persisting near the source zones. Concentrations of this magnitude are difficult to conceive in the absence of nearby DNAPL material. Second, although the core hole investigations represent an appreciable effort, the horizontal extent of the source zones is not delineated by these core holes; many more core holes of this type would be needed to fully delineate the zones’ horizontal extent. Third, mass transfer rates associated with DNAPL dissolution in fractured media are not well understood. These three points suggest that, given the current state of knowledge, there is no basis for dismissing the possibility that there may be appreciable DNAPL mass remaining in the vicinity of the core holes, and that this DNAPL is responsible for the elevated concentrations observed in the core holes.

Crude estimates of the total dissolved and sorbed TCE mass (i.e., the non-DNAPL mass) were made using the Montgomery Watson (2000a) plume maps of the entire SSFL site and the sorption capacity measured for a sample of SSFL sandstone (see Section 7.3.2). These estimates suggest that roughly 3,000 to 56,000 gallons of TCE (depending on the specific diffusion penetration depth and fracture spacing assumed) now reside in an aqueous or dissolved state throughout the SSFL site. The difference between what was released into the ground (and not volatilized) and this aqueous/sorbed portion is the remaining DNAPL phase. Thus, these results suggest that if large volumes ( $\geq$  100,000 gallons) of DNAPL entered the subsurface, then a substantial portion continues to reside as DNAPL in the SSFL subsurface.

Samples from core holes C-1 through C-7 also revealed vertical distributions of DCE isomers (cis-DCE, trans-DCE, and 1,1-DCE) and perchloroethene. The latter is another well-known solvent that was used at SSFL, though to a lesser extent than TCE. As Hurley et al. (2003) discuss, the cis- and trans-DCE levels are consistent with generally observed TCE biotransformation pathways. The 1,1-DCE levels are more difficult to explain: some of the levels are quite elevated (i.e., in the mg/L range), suggesting that this DCE isomer was also used as a solvent at SSFL or was present as an impurity at relatively high levels in the TCE. Vinyl chloride, a well-known transformation product, did not appear in many of the field samples; if transformation of TCE is occurring at the site—as it appears to be in some areas—then vinyl chloride would be expected to be present. Vinyl chloride is a gas at ambient temperatures, and it is therefore difficult to measure accurately in groundwater samples. Investigations into anaerobic oxidation pathways of TCE degradation at the SSFL may help clarify this issue.

### 7.3.1 Interaction Between Sandstone Matrix and Dissolved TCE

The study team used experiments to measure TCE diffusion rates, and thus estimate the rate at which dissolved and sorbed TCE could penetrate into the SSFL sandstone. (It is known that the characteristics of the sandstone vary significantly at SSFL; the study team's measurements were intended to be more representative of site behavior than literature values, but they did not account for spatial variability in the sandstone.) The experiments were carried out on one of two core samples (1 foot long, 3 inches wide) provided by Boeing at the team's request. Both these samples were collected during the drilling of hole C-5. Core 1, the one used for the sorption and diffusion measurements, was a sandstone sample taken roughly 215 feet below ground level. Core 2 was a shale sample taken from 97 to 100 feet below ground surface.

The study team pulverized a portion of Core 1 and split it into sample vials for the sorption study, following accepted methods for sorption measurements (Harmon and Roberts, 1994; see Appendix U for details). Triplicate vials containing the solids were filled with clean water, spiked with varying amounts of TCE, and analyzed after reaching equilibrium. The sandstone-TCE sorption coefficient was measured as roughly 1.1 mL/g, which is not uncharacteristic of sand with low organic carbon content. Using the above value for  $K_d$ , a bulk density value of 2.3 g/cm<sup>3</sup>, and a porosity value of 0.13 (Montgomery Watson Harza, 2003a, b, c), the team obtained a retardation factor ( $R = 1 + \rho_b K_d / \phi$ ) of about 20. This means that the TCE will appear to diffuse roughly 20 times more slowly than it would in the absence of sorption.

The diffusion of TCE into the sandstone was assessed experimentally using a diaphragm-cell (a single unit containing two compartments separated by a porous barrier). Measurements using tritiated water were undertaken because small changes in concentration were more easily measured with this radioactive species. The experimentally derived pore diffusion coefficient value was about  $1.05 \times 10^{-6}$  cm<sup>2</sup>/s (see Appendix U for details). Given that the self-diffusion coefficient for water is about  $2.2 \times 10^{-5}$  cm<sup>2</sup>/s, this implies that the sandstone tortuosity reduces the tritiated water's effective diffusivity by a factor of about 18 for this core sample. Scaling this up to account for the relatively large TCE molecule (see Schwarzenbach et al., 1993) results in a TCE tortuosity factor 2.7 times larger than that for tritiated water—a value of about 48. Also, TCE will be retarded relative to tritiated water (by a factor of roughly 20, as estimated above). Therefore, based on the estimated free aqueous diffusion coefficient for TCE of  $8.6 \times 10^{-6}$  cm<sup>2</sup>/s (Hayduk and Laudie, 1974), the value of the apparent TCE diffusion coefficient in the sandstone sample tested is about  $(\text{MW}_{\text{water}}/\text{MW}_{\text{TCE}}) \times (8.6 \times 10^{-6})(20 \times 48) = 1.15 \times 10^{-9}$  cm<sup>2</sup>/s. This low diffusion coefficient suggests that TCE propagates into the SSFL sandstone extremely slowly. Note that computer simulations by Montgomery Watson (2003) addressing the matrix diffusion issue assume that TCE's free aqueous diffusion coefficient value is  $1 \times 10^{-5}$  cm<sup>2</sup>/s, the tortuosity factor is 0.1 (or a factor of 10 reduction of diffusivity), and the retardation factor is 2; this produces an apparent diffusion coefficient value ( $6.5 \times 10^{-8}$  cm<sup>2</sup>/s) about 56 times greater than the one estimated in the study team's analysis. Thus, the MW model's estimates for diffusive penetration into sandstone are much higher than would be suggested by the team's estimate of the diffusion coefficient of TCE.

### 7.3.2 Estimates of Current TCE Mass in SSFL Groundwater and Sandstone Matrix

The study team used the information on sorption and diffusion described in the previous sections, together with TCE plume maps (Figure 7-3), to estimate the total mass of sorbed and dissolved TCE presently in the SSFL subsurface. This estimate was made under the assumption that the plume maps for the site actually represent flat or “pancake”-type plumes that exist in the fracture network and propagate to some extent into the adjacent sandstone.

The conceptual model used to estimate the amount of dissolved TCE in the fractured sandstone formation is depicted in Figure 7-4. It suggests structured fractures separated by a given fracture spacing. From the edges of these fractures, dissolved TCE diffuses into the sandstone matrix. The penetration depth of the invaded matrix increases as a result of the diffusion progress. Of course, the number of fractures per unit depth (or fracture spacing) and the degree to which the plumes diffuse into the sandstone will greatly affect the estimates generated by this conceptual model. To obtain a rough estimate of the amount of TCE in the subsurface, the study team made a series of assumptions about key parameters. First, the overall plume thickness was assumed to be 50 or 100 meters, based roughly on the core hole data (Hurley et al., 2003). Next, the fracture spacing was assumed to be 2, 5, or 10 meters, based roughly on the fracture density cited in the MW model simulations (Montgomery Watson Harza, 2003a). The matrix porosity was assumed to be 0.1 and the penetration depth of TCE was approximated to be in the range of 50 centimeters to 100 centimeters, based on transient diffusion calculations. The aqueous mass in the fracture as well as in the matrix was then calculated for each plume thickness, with varying penetration depth and fracture spacing. Similarly, the team calculated the sorbed mass in the matrix for each penetration depth, with varying fracture spacing and a value of 1.1 mL/g for the sorption distribution coefficient  $K_d$ .

The TCE plumes at the SSFL site occupy large areas and were estimated using the map reproduced here as Figure 7-3 (Montgomery Watson, 2000a). These areas are specified according to the concentration ranges given in Table 7-1. Using the assumptions listed in the previous paragraph, the team summed the estimated aqueous and adsorbed mass in the plume “layers” with the results plotted in Figure 7-5 (see Appendix U for additional details). This graph depicts the equivalent volume of spilled TCE that is dissolved or adsorbed to the sandstone matrix. These calculations do *not* account for non-dissolved (DNAPL) TCE remaining in the subsurface: an estimated DNAPL volume remaining in the subsurface would be the difference between the estimated net amount that infiltrated the soil (and did not volatilize) and the volumes plotted in Figure 7-5.

**Table 7-1.** Size of TCE-Contaminated Areas

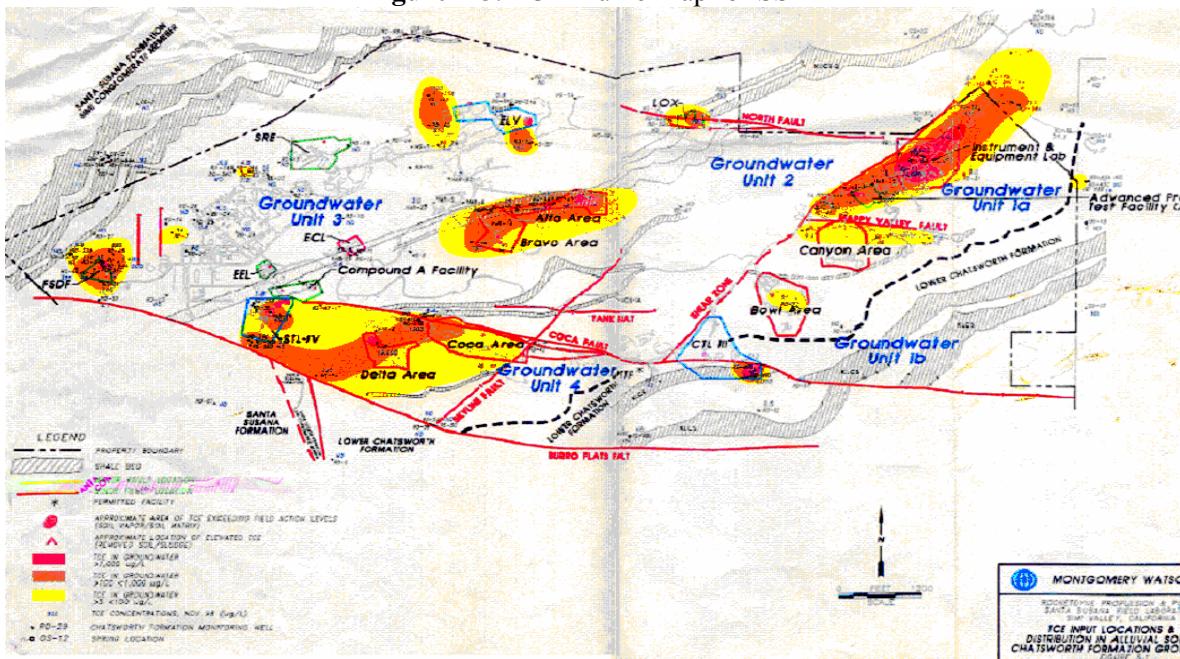
TCE Concentration Range (ppb)	Contaminated Area ( $m^2$ )
5–100	695,000
100–1,000	399,000
1,000–10,000	66,000

The results in Figure 7-5 demonstrate that the estimates of total sorbed and dissolved TCE are strongly related to the fracture spacing and diffusive penetration depth into the sandstone matrix. Given an overall plume thickness estimate of 100 meters, the curves suggest an upper limit of the dissolved and sorbed TCE equivalent to about 56,000 gallons of TCE when all the sandstone is invaded by dissolved TCE (for instance, when the fracture spacing is 2 meters and the penetration depth is 1 meter). These calculations suggest that roughly 3,000 to 56,000 gallons of TCE (depending on the diffusion penetration depth and fracture spacing assumed) now reside in an aqueous or dissolved state, and the remainder is DNAPL.

The above calculations suggest that a relatively large fraction of the TCE that originally infiltrated the SSFL subsurface remains, as DNAPL. However, the study team would need data demonstrating (a) direct evidence of the DNAPL volume remaining in the fractures and (b) penetration depth due to TCE diffusion to conclusively estimate the distribution of TCE in the sandstone groundwater environment. The presence of dissolved TCE (aqueous) concentrations in excess of 10 mg/L in the vicinity of the core holes (Hurley et al., 2003) lends support to the hypothesis that significant DNAPL may indeed persist in the SSFL sandstone.

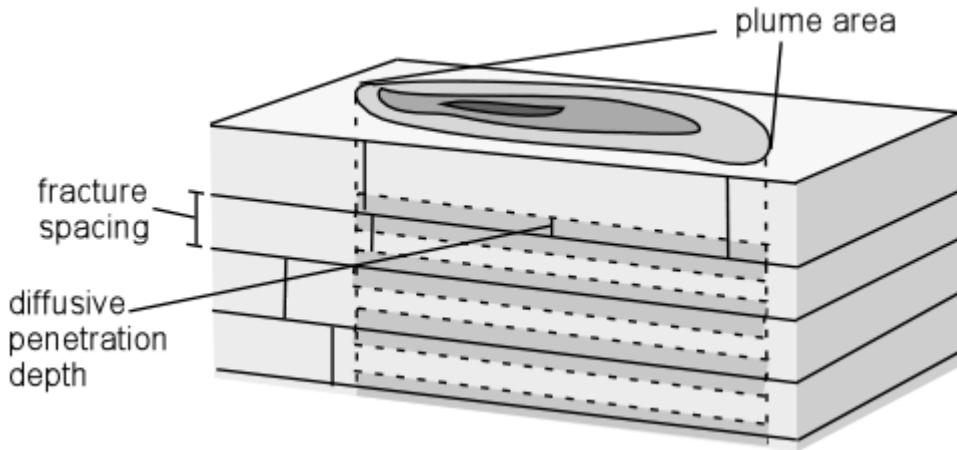
Removal of the large amount of TCE that is estimated to reside in the soil subsurface and groundwater at SSFL is beyond the capabilities of current remediation technologies. Therefore, there is potential for long-term exposure to TCE if contaminated groundwater will come into contact with human and ecological receptors. There is also potential for continuing volatilization of TCE from the soil subsurface. The above concerns are consistent with the conclusions of the 1990 U.S. Army Corps of Engineers-sponsored baseline public health risk assessment for the SSFL property. That assessment concluded that there may be a public health risk associated with residential use of the property. It was stated that “Exposure of site residents to TCE via multiple pathways could lead to cancer risks exceeding the  $1 \times 10^{-6}$  level” (Techlaw, 1990).

**Figure 7-3. TCE Plume Map for SSFL**

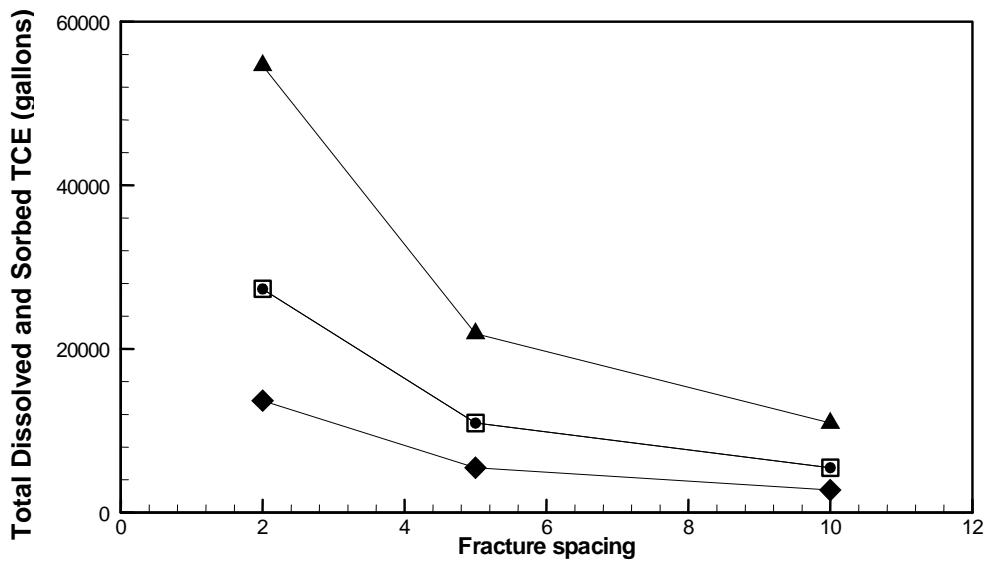


**Source:** Montgomery Watson, 2000a, b.

**Figure 7-4.** Schematic Representation of TCE Distribution in Fractured Sandstone



**Figure 7-5.** Estimated Total Dissolved and Sorbed TCE in SSFL Groundwater  
(Using the Simplified Conceptual Model)



Calculated total dissolved and sorbed TCE volume (in gallons) as a function of sandstone matrix fracture spacing for:

- ▲ 100-meter plume thickness and 1-meter diffusive penetration depth.
- 100-meter thickness and 0.5-meter penetration depth.
- 50-meter thickness and 1-meter penetration depth.
- ◆ 50-meter thickness and 0.5-meter penetration depth.