5. CONTAMINANT FATE AND TRANSPORT

In this chapter, the integration of geologic, hydrologic, and geochemical data lead to development of a Conceptual Site Model (CSM) for the Hematite Site. By its very nature, evaluation of empirical data is a look backward in time, and the CSM is an attempt to explain the distribution of contaminants and the apparent direction and rates of their migration (and degradation) in soil and groundwater based on the physical and chemical forces acting on a complex hydrogeologic system over some period of time (e.g., 50 years for the Hematite Facility corresponding to the years of operation). The goal of the CSM is to provide the basis for explaining the current situation at the Hematite Site and a firm technical rationale for projecting the fate of contaminants in the vicinity of the Site into the future through numerical modeling (i.e., a deterministic approach). The complete modeling assessment appears in Appendix A and SAIC (2005) and is summarized in Sect. 5.6.

The approach to developing the CSM used in this Report includes a detailed examination of the distribution of the principal contaminants in soil and groundwater (from Chapter 4), followed by integration of this information with Site geology and hydrology (Chapter 3). The most important contaminants at the Site include PCE; TCE; cis-1,2-DCE; trans-1,2-DCE; and vinyl chloride, and the following sections will focus on them. However, some soil and groundwater samples contain a limited number of additional contaminants such as uranium, $^{99}$Tc, and nitrate. In addition, other geochemical parameters such as pH and the concentrations of several major dissolved species (e.g., chloride, calcium, etc.) will be incorporated into the analysis, as appropriate.

Chapter 5 begins with an evaluation of the inorganic and radionuclide contamination in terms of their fate and potential for transport (Sect. 5.1). Section 5.2 continues with an in-depth analysis of the distribution of the chlorinated VOC contaminants (PCE and TCE) in soil and an analogous discussion for groundwater is presented in Sect. 5.3. The potential for the presence of a dense, nonaqueous-phase liquid (DNAPL) in the subsurface that might represent a long-term source for plume loading is discussed in Sect. 5.4. Section 5.5 develops the CSM for the Hematite Site and the results of numerical modeling based on the CSM are summarized in Sect. 5.6. Finally, in Sect. 5.7, the fate of PCE, TCE, and their degradation products is discussed within the context of natural attenuation processes.

5.1 EVALUATION OF INORGANIC AND RADIONUCLIDE CONTAMINATION

The fate and transport of inorganics and radionuclides are discussed together because of the commonality of the Hematite Site characteristics upon which their mobility depends. Furthermore, at the Hematite Site, contaminants in this group, with the exception of nitrate, do not migrate as easily as volatile organics. It is also important to recognize that the extent of contamination with inorganics and radionuclides was typically limited and localized near the plant and known disposal locations (Chapter 4).

The factors governing transport of inorganics and radionuclides are primarily the pH and redox conditions of the soil and groundwater system and the soil texture. For example, elements that typically migrate as divalent cations, such as lead and copper, are not readily mobile except at extremes of pH such as might be encountered with acid mine drainage. Many of these elements tend to precipitate as hydroxides or oxyhydroxides when the pH is near neutral.

In contrast, at or near neutral pH, $^{99}$Tc and uranium are very mobile if redox conditions are sufficiently oxidizing. On the other hand, fine-grained soil texture inhibits mobility both by slowing groundwater flow and by providing a high surface area substrate for sorption of the contaminant. The following is a
discussion of specific Site geochemical characteristics that may influence the F&T of inorganics and radionuclides at the Hematite Site.

5.1.1 pH

Available data for the Hematite Site demonstrate that pH is within the range usually considered “normal” for natural waters, that is, within the range of approximately 5 to 9 (Sect. 4.1.3 and Fig. 4.3). Most water samples lie within the pH range that will inhibit migration of metals such as lead. However, eight groundwater samples from overburden have pH values less than 5 and one sample from the Jefferson City-Cotter HSU has a pH of 9.3. The locations of these samples are discussed in Sect. 4.1.3. These nine samples constitute approximately 7% of the samples analyzed.

5.1.2 Redox Conditions

As discussed in Sects. 4.1.5 through 4.1.8, redox conditions at the Hematite Site can be assessed by multiple means. Field data for ORP and DO suggest moderately reducing to mildly oxidizing conditions (Sect. 4.1.5, Figs. 4.4 and 4.5, respectively). In contrast, the high iron and manganese concentrations reported for groundwater samples (especially from overburden) suggests conditions are more reducing (Fig. 4.6 illustrates results for iron). A comparison of iron and manganese in a number of unfiltered and filtered groundwater samples from all formations suggests that these metals are dissolved rather than in particulate form, supporting the observation of reducing conditions in the groundwater. Other indicators of redox conditions are the soil texture and the appearance of degradation byproducts indicating reduction of TCE and PCE (e.g., cis-1,2-DCE). Soils at the Hematite Site, particularly in the area dominated by terrace deposits (Chapter 3), are typically fine-grained, and organic degradation byproducts are definitely present (Sect. 5.3); hence, the overall conditions of the Hematite Site are concluded to be at least mildly reducing.

Consideration of the distribution of nitrate provides additional evidence that conditions are reducing. Because it is an anion, nitrate is repelled by the negative charge on the soil surface. In addition, nitrate is a large ion that does not readily diffuse in and out of soil pores. Thus, nitrate is typically considered a conservative ion, or one that flows at the same rate as groundwater. An exception to this concept is when soil microbes, under reducing conditions, consume nitrate. Nitrate is found in significant concentrations in wells BD-01 and BD-02 in the middle of the plant area (presumably near where it was discharged) and has not migrated much farther. Volatile organics, which exhibit lower rates of microbial degradation than nitrate, have migrated a much greater distance. Therefore, it is concluded that reductive processes occurring in the subsurface have operated as an effective removal mechanism for nitrate.

Under the mildly reducing conditions believed present at the Hematite Site, the mobility of $^{99}$Tc and uranium is expected to be limited. Indeed, a review of the data shows that the bulk of the mass of these contaminants is found principally near the surface and near the Facility, the presumed source(s) of these constituents (Sect. 4.3).

5.1.3 Soil Texture

As discussed in Chapter 3, near-surface soil texture within the terrace deposits underlying the Hematite Facility is generally fine-grained, a fact that will inhibit infiltration and lateral migration. The fine-grained nature of the soil samples was confirmed during the $K_d$ study performed in December 2003 (SAIC 2003c) in which particle size distribution measurements showed the soils to consist of >96% silt- and clay-sized fractions and ~30% clay. That study yielded $K_d$ values for uranium and $^{99}$Tc of 175 and 106 mL/g, respectively; values that indicate strong sorption on soil surfaces. Once again, the distribution of inorganics and radionuclides near known source areas supports this observation.
5.2 EVALUATION OF CHLORINATED VOLATILE ORGANIC COMPOUND CONTAMINANTS IN SUBSURFACE SOILS

For the purposes of this discussion, all subsurface unconsolidated sedimentary material is referred to as subsurface soil. This includes surficial soil, as well as the terrace and alluvial materials (i.e., overburden) that were discussed in Chapter 3.

Subsurface soil samples were taken at the locations identified in Figs. 2.5a and 2.5b. Normally, three samples were selected based on a scan of core material for volatile organic constituents by using a hand-held PID (refer to Sect. 2.3 for details regarding subsurface soil sampling). The vertical location of soil samples varied per sampling location, but typically included samples from the top of the water table and the overburden-bedrock contact. In general, one sample was taken from each 10-ft depth interval. For that reason, it is convenient to examine the subsurface soil results in three increments: surface to 10 ft BGS, 10 to 20 ft BGS, and greater than 20 ft BGS.

An evaluation of soil organic data (Sect. 4.4) indicates that the principal contaminants in subsurface soil at the Hematite Site are PCE and TCE. These two constituents represent the most significant contaminants in terms of concentrations, frequency of detection, and lateral and vertical distribution at the site. Three isomers of DCE (1,1-DCE; cis 1,2-DCE; and trans-1,2-DCE) and vinyl chloride were detected in some soil samples and probably originate through biologically mediated reductive dechlorination reactions (discussed in Sect. 5.5). This is a plausible mechanism for their formation and there is no evidence that any of these constituents was used at the Hematite Facility during its operational period. They occur at relatively low concentrations. Consequently, this section will focus on the distribution of PCE and TCE in soil samples.

Figures 5.1, 5.2, and 5.3 present the results for PCE and Figs. 5.4, 5.5, and 5.6 provide complementary data for TCE for subsurface soil samples from across the Hematite Site. There are several assumptions used in presenting the data in these figures:

- The contours are meant to encompass samples with a range of concentrations (e.g., ND to 10 µg/L; >100 µg/L), but may include samples with non-detect values. The apparent heterogeneity in contaminant distribution is not surprising, given the geologic complexity of the subsurface.

- Contamination is assumed to have entered the subsurface at the Hematite Facility location (i.e., there are no other known disposal areas).

- Soil contamination beyond the Hematite Facility occurred through transport in groundwater or a vapor phase, and subsequent sorption onto natural soil organic matter. Soil contamination will occur only where sufficient soil organic matter exists that can adsorb detectable amounts of the contaminants.

- Soil samples were not collected south of Joachim Creek because the amount of overburden is extremely limited in this area. The steep slope rising to the highlands to the south essentially forms the southern bank of Joachim Creek. Therefore, there is no opportunity for contaminated groundwater in overburden to migrate south of the creek (Sect. 5.3.1).

The general observations from these six figures are:

- The patterns of contaminant distribution in subsurface soil at all depth intervals for both PCE and TCE tend to suggest a close association with the Hematite Facility location as the source area.
• Even for the fine-grain, shallower soils (i.e., 0 to 10 ft depth), it is apparent that PCE and TCE contamination is relatively widely distributed.

• The configuration of the contaminated soil zones appears to correspond to the location of the contaminated groundwater (Sect. 5.3).

• Dashed lines that bound the extent of soil contamination are well constrained by sample data.

Based on information about the Hematite Facility, history and process knowledge obtained during the RI, potential source locations beyond the immediate vicinity of the Hematite Facility have not been identified. Several soil samples in Figs. 5.5 and 5.6 appear to have anomalously high concentrations of TCE in comparison to their location southeast of the presumed source region. However, they occur in an area where groundwater also is highly contaminated with TCE, which could have led to increased partitioning of TCE to soil organic matter.

Shallow, fine-grain soils might not be thought of as a favorable medium for groundwater flow. However, the relatively wide distribution of contaminants in these soils suggests that significant transport has occurred in this unit. For example, vapor migration might be a factor contributing to this observation. Nevertheless, the opportunity for contamination of these soils is significant because their organic content is expected to be relatively high. Indeed, values of organic carbon in excess of 1% are observed in some of these soils. The deepest soil samples (Figs. 5.3 and 5.6) generally include the coarse-grain lithologies where the amount of soil organic matter and the potential for sorption are expected to be lower.

The third observation can be evaluated by comparing the contaminant distribution in soils to the analogous distribution in groundwater as shown in Figs. 5.7 through 5.14 that are introduced in the following section.

5.3 EVALUATION OF THE DISTRIBUTION OF PCE AND TCE IN GROUNDWATER

As discussed in Sect. 4.4.5.6, the most common occurrences of chlorinated VOCs in groundwater at the Hematite Site above their reference concentrations include PCE and TCE and their presumed degradation products: 1,1-DCE; cis-1,2-DCE; trans-1,2-DCE; and vinyl chloride. A variety of other VOCs were detected in groundwater, but most are only found in a few samples and almost always in association with these six primary contaminants. Furthermore, most of these other VOCs are chlorinated compounds and their chemistry and behavior in groundwater are similar to that of the major chlorinated VOC contaminants. None of these ancillary constituents warrants a separate discussion. Consequently, PCE, TCE and their four principal degradation products will be the focus of the following discussion.

Figures 5.7 through 5.10 illustrate the distribution of PCE in the major hydrogeologic units at the site. These units were described in Chapter 3 and include: (1) the shallow overburden HSU (wells completed at 10 to 15 ft BGS in fine-grain soils), (2) deep overburden HSU (wells completed in the lower part of the overburden to the depth of DPT probe refusal, presumed to correspond to bedrock), (3) the Jefferson City-Cotter HSU, and (4) the Jefferson City-Roubidoux Contact Zone HSU. Wells associated with the Roubidoux HSU are all uncontaminated and no figures for this HSU will be presented. Figures 5.11 to 5.14 represent an equivalent set of illustrations showing the distribution of TCE in these units.
5.3.1 PCE and TCE Distribution in Overburden Groundwater

Figures 5.7, 5.8, 5.11, and 5.12 illustrate the distribution of PCE and TCE in groundwater at two levels within the overburden. In general, shallow overburden groundwater has low to moderate levels of contamination for both of these constituents and the location of affected wells is closely associated with the Burial Pits.

As noted in Figs. 5.7 and 5.11, there are no sample locations northeast of Northeast Site Creek. In fact, several Geoprobe™ holes were placed in this region, but no shallow (i.e., perched) groundwater was encountered. Therefore, it appears that Northeast Site Creek marks the approximate extent of shallow groundwater. Shallow groundwater also appears to be absent in the region southeast of wells WS-17B and BP-22B.

The distribution of PCE and TCE in deep overburden groundwater (Fig. 5.8 and 5.12) is sufficient to define plumes, which suggest generally southeastward migration from source regions underlying the Hematite Facility, a direction compatible with the potentiometric surface for this zone of the overburden (Fig. 3.18). There appears to be an association of the zones of highest concentration of PCE and TCE with the location of the Burial Pits and the Evaporation Ponds (including areas underlying Bldgs. 230 and 240 for PCE). In addition, high concentrations of PCE and TCE (>1000 ug/L) define narrow, elongate plumes that appear to have their sources in the vicinity of the Facility. These latter zones of high concentration probably reflect preferential pathways that originate in the source zones underlying the Hematite Facility and allow groundwater to migrate away from the sources with limited opportunity for dilution. The heterogeneous nature of sedimentation in the terrace/alluvium system could yield such pathways.

A sample from well OB-01 (southwest of Site Pond next to Highway P; Fig. 5.8) had a detectable concentration of PCE (10 µg/L) during the December 2004 round of samples. This result is difficult to understand as there is no indication of contamination in other nearby wells. Information provided by Westinghouse indicates that during 2004, elevated concentrations of PCE were observed at Outfall No. 1 (immediately downstream of Site Pond) due to a damaged vitreous clay pipe and this might be a source of contamination, although no credible pathway from Site Creek to OB-01 has been identified. The damaged pipe is being replaced.

As groundwater in the overburden advances toward Joachim Creek, it must either discharge directly into the stream or migrate in a down-stream direction in the coarse alluvial sediments that overlie bedrock next to the stream and discharge to it more gradually. The configuration of the plume contours in Figs. 5.8 and 5.12 suggests that flow pathways turn toward the east (i.e., in a down-stream direction) as they enter the alluvial material and approach Joachim Creek. Although the flux of groundwater and contaminants discharging to Joachim Creek in the reach of the stream illustrated in these figures is unknown, it has not resulted in significantly elevated concentrations in stream water or sediment. Data presented in Table 4.34 illustrate that PCE and TCE concentrations in Joachim Creek water are less than 1 µg/L.

As noted above, the distribution of PCE and TCE illustrated in Figs. 5.8 and 5.12, respectively, appears to suggest the presence of two potential source zones: one located in the northeastern part of the Hematite Facility (near the Burial Pits) and a second near the Evaporation Ponds and adjacent buildings. Figure 5.15 is an attempt to further resolve information about these different inferred source zones. This figure presents a map of the distribution of molar ratio values of PCE:TCE, defined as follows:
Groundwater samples with molar ratio values greater than one are said to be PCE-dominant and samples for which the ratio is less than one are TCE-dominant. Figure 5.15 illustrates that the deep overburden groundwater is clearly divisible into two separate populations, one that is PCE-dominant and the other TCE-dominant. The source of PCE-dominant groundwater appears to be associated with the southwestern part of the Hematite Facility. Indeed, one soil sample collected from location BD-02 under Building 240 had a concentration of PCE of 6600 mg/kg. The apparent source for TCE-dominant groundwater is in the northeastern area of the Hematite Facility (Burial Pits). Consequently, it appears that two major source areas and the principal groundwater plumes related to them in overburden have been identified. These presumed source areas are consistent with the patterns of PCE and TCE soil contamination discussed in Sect. 5.2.

The molar ratio of contaminants may be a useful tool for mapping the pathway(s) by which contamination migrates into bedrock where the connection to a specific source is less certain – a hypothesis that is testable. However, both PCE and TCE will degrade microbially under appropriate conditions and the ratio may change with increasing time, dependant on the relative rates of breakdown of these two contaminants.

5.3.2 PCE and TCE Distribution in Bedrock

Figures 5.9, 5.10, 5.13, and 5.14, respectively, illustrate the distribution of PCE and TCE in the Jefferson City-Cotter, Jefferson City-Roubidoux Contact Zone and Roubidoux HSUs. The principal observation from Figs. 5.9 and 5.13 is that the distribution of both PCE and TCE concentrations in groundwater from the Jefferson City-Cotter HSU define a plume that appears to have its source at the Hematite Facility. There are two components of contaminant migration, as shown by the arrows on Figs 5.9 and 5.13. One element of the plume migrates toward the southeast (toward PW-19); a second migrates toward the northeast (toward BR-04 and BR-09). Comparison of these plumes with the associated potentiometric map in Fig. 3.19 shows a direct correspondence between the hydrologic and contaminant data for this HSU. The only region of PCE and TCE contamination in the Jefferson City-Roubidoux contact zone and Roubidoux HSUs is in private wells PW-16 and/or PW-19 located southeast of the Hematite Facility.

A detailed discussion of the distribution of contaminants in these formations is presented in Sect. 5.4 in which the CSM for contaminant transport is developed.

5.4 EVALUATION OF THE POTENTIAL FOR THE OCCURRENCE OF DNAPL AT THE HEMATITE SITE

If PCE and TCE entered the subsurface under, and in the immediate vicinity of, the Hematite Facility due to spills and leaks in process and waste transfer pipelines, releases from the Evaporation Ponds or burial at waste disposal sites (e.g., Burial Pits), then it is appropriate to examine the potential that this contamination currently exists in the form of a DNAPL. It is important to make this assessment because the limited solubility of PCE or TCE from their respective liquid phases can result in a source that persists for decades before it is completely exhausted. Furthermore, the specific gravity of separate phase TCE or PCE is much greater than that of water. Consequently, if sufficient DNAPL was discharged to the subsurface, it has the potential to migrate downward under the influence of gravity (and independent of groundwater flow), thus leaving a trail of residual DNAPL saturation in overburden pore spaces; it may collect in pools on impermeable layers; and it may enter bedrock through pores (if the pore throat
dimensions are sufficiently large) or fractures (if the apertures are wide enough). In addition, DNAPL in bedrock fractures may diffuse into the rock matrix and become an important, long-term, secondary source of TCE or PCE to groundwater plumes.

The potential for the presence of DNAPL at the Hematite Site can be evaluated by estimating if the amount of PCE or TCE soil contamination is sufficient to suggest the presence of residual DNAPL saturation. The concentration of PCE or TCE in soil that is indicative of the presence of DNAPL ($C_{\text{sat}}$) is determined by accounting for the amount associated with pore water (groundwater at the solubility limit fully saturating the pore volume) and with a sorbed component by the following equation:

$$C_{\text{sat}} \geq \text{Contaminant in pore water} + \text{contaminant sorbed on soil organic matter}$$

It is assumed that soil concentration values in excess of $C_{\text{sat}}$ indicate the presence of DNAPL. This approach and specific approaches for evaluating $C_{\text{sat}}$ are discussed in ITRC (2004). Calculated values of $C_{\text{sat}}$ for TCE range from 230 to 1650 mg/kg and for PCE range from 100 to 750 mg/kg. Soil from boring BD-02 has a PCE concentration of 6600 mg/kg, a clear indication of the presence of DNAPL (see the location in Fig. 5.16). Based on available data, no other soil samples fall within these ranges for either PCE or TCE. Consequently, evidence indicates that DNAPL underlies the Hematite Facility in this location.

It is also possible to infer the presence of DNAPL from the amount of TCE or PCE dissolved in groundwater. A concentration in groundwater greater than 1% of the solubility of the target contaminant frequently is considered to be suggestive of the presence of DNAPL in the vicinity of the sample. However, this method is not a definitive indicator for DNAPL, nor does it yield an estimate of the amount or specific location of DNAPL. Figure 5.16 is a map showing all groundwater data that meet the following criteria:

- TCE concentration greater than 11 mg/L (i.e., 1% of TCE solubility in water = 1100 mg/L) or,
- PCE concentration greater than 2 mg/L (i.e., 1% of PCE solubility in water = 200 mg/L).

Thirteen wells yielded groundwater samples in December 2004 that satisfied one of these criteria. All of these samples are from the overburden and most are underlying or closely associated with the Hematite Facility. The evidence from both soils and groundwater support the likely presence of DNAPL in this area.

The unusually high dissolved concentration of PCE at wells NB-34 and NB-74 and TCE at well NB-72 southeast of the Hematite Facility are not closely associated with the most likely source areas and suggest several alternative explanations. First, these wells may be at locations along particularly transmissive flow paths that convey highly contaminated groundwater rapidly from the source zone and with little dilution. Alternatively, the possibility of DNAPL being in the vicinity of these wells cannot be ruled out. In the absence of information pointing to disposal of waste solvents in these areas in the past, the possibility must be considered that DNAPL was discharged to the subsurface under the Hematite Facility in sufficient quantity that it could have migrated as a mobile, separate phase, possibly along the bedrock interface in the permeable, coarse-grain lithology.

In Chapter 3 it was shown that the bedrock surface underlying the terrace deposits on which the Hematite Facility is located slopes gently toward Joachim Creek (Fig. 3.4). However, this surface has a prominent depression located in the vicinity of BR-04 to the northeast of the Facility that is illustrated in a cross section (Fig. 3.9) and an overburden isopach map (Fig. 3.7). With evidence discussed in this section pointing to the likelihood that organic solvents (i.e. TCE and PCE) exist as free product in soils underlying the Facility, if a sufficient quantity of DNAPL was released to the soil the possibility exists.
that it might have been able to migrate down gradient on the overburden-bedrock surface toward the depression. However, there is no evidence from the TCE and PCE concentrations measured in deep overburden soils that such a migration pathway has been active along this projected trajectory (Figs. 5.3 and 5.6). Similarly, groundwater samples obtained from the overburden in the same vicinity do not support this direction for DNAPL transport (Figs. 5.8 and 5.12). Furthermore, groundwater samples that were collected from the overburden and shallow bedrock in association with the construction of BR-04 during the Interim Hydrogeologic Investigation (LBG, 2002b) show no evidence of detectable VOC concentrations. Collectively, these lines of evidence do not support down gradient migration of DNAPL on the overburden-bedrock surface toward the depression near BR-04. Although the conclusion of this analysis is convincing, it does not rule out the possibility of lateral migration of DNAPL in other directions from the source area (as noted above) or vertical migration through overburden and into fractures within the underlying bedrock.

5.5 CONCEPTUAL SITE MODEL

The contoured data for PCE and TCE shown in Figs. 5.9 and 5.13 for the Jefferson City-Cotter HSU define plumes trending east-southeast that appear to have their origin in the northeastern part of the Hematite Facility. Furthermore, these plumes extend eastward across Joachim Creek. It is significant to note that the molar ratios of PCE:TCE for these groundwater samples are all less than one (i.e., TCE-dominant), which supports an inferred source region under the northeastern part of the Hematite Facility. Available data do not support the PCE-dominant region underlying the southwest part of the Facility as a major source of contamination to bedrock.

Figure 5.17 is a cross-section that is oriented to follow the axis of the PCE plume shown in Fig. 5.9. The cross-section focuses on the Jefferson City-Cotter HSU and is oriented approximately parallel to the regional strike of bedrock in this area. Each well and their respective screened intervals are shown, along with the concentrations of PCE from the December 2004 sampling period for both Jefferson City-Cotter and Roubidoux screened intervals. It is possible to contour these data in the vertical plane to complement the contours in the horizontal plane in Fig. 5.9 and emphasize the three-dimensional nature of the plumes. Figure 5.18 is the same cross-section in which TCE data are plotted and referenced to the plume in Fig. 5.13. These cross-sections emphasize that there are plumes for both TCE and PCE that appear to be migrating in the upper 50 ft of the Jefferson City-Cotter Dolomite underlying the area. It is also apparent that this plume extends south of Joachim Creek within the same interval of elevation.

The vertical gradients between the deep overburden (coarse-grain layer) and the Jefferson City-Cotter HSU, as illustrated in Fig. 3.18, indicate downward flow associated with the groundwater mound underlying the Hematite Facility and an upward flow potential closer to Joachim Creek. Therefore, in addition to the dominant lateral flow to the southeast in this HSU (Figs. 5.17 and 5.18), some upward migration of contaminated groundwater into the deep overburden may be occurring near the stream.

South of Joachim Creek, groundwater contamination abruptly appears to spread vertically downward. Packer testing conducted in private well location PW-19 during this investigation (methods described in Sect. 2.4) yielded depth-discrete groundwater samples obtained in 20-ft increments from a depth of 65 ft to the bottom of the well (250 ft), and reveals that VOC contamination extends throughout this entire depth interval (see Figs. 5.17 and 5.18 for results). It is also important to note that the molar ratio of PCE:TCE for groundwater samples from all depths and all wells in this area are TCE-dominant, which establishes the connection between the plume coming from the Hematite Facility in the Jefferson City-Cotter HSU and the contamination observed to the south of Joachim Creek.
Related sampling occurred in PW-16 in which diffusion bag samples were collected along the length of the open borehole. These data show similar information as for the packer testing in PW-19, but this mode of sampling does not yield samples from isolated zones. Vertical flow of groundwater may have occurred in the well bore during the time the diffusion bags were deployed. If true, the observed vertical distribution of contaminants may not reflect the actual vertical distribution within the bedrock as some vertical mixing may have occurred in the well bore. However, if in-well mixing were significant, greater homogenization of TCE and PCE concentrations would be expected. Consequently, PW-19 results (and probably those from PW-16 as well) establish that significant vertical migration of both PCE and TCE occurred in the vicinity of these wells throughout the bedrock to a depth at least as great as the well depths for PW-19 and PW-16. However, little contamination is observed in BR-07 even though it is located nearby. The bedrock is extremely low permeability in this borehole and may have prevented much local migration of PCE and TCE in this area. However, other factors also may be relevant and are discussed in the following paragraphs.

Drawing upon the empirical geologic, hydrologic, and geochemical data obtained during this investigation and discussed in this report, it is possible to develop a CSM for the Hematite Site. First, it has been shown that contamination from the source zone(s) identified under the Hematite Facility has dissolved in groundwater and migrated vertically downward into at least the top 50 ft of the Jefferson City-Cotter Dolomite. Then it appears that lateral flow and transport away from the source towards the southeast occurs in both the deep overburden and the shallow Jefferson City-Cotter HSU. This interpretation is consistent with both the geochemical (soil and groundwater) and hydrologic results for the Hematite Site that establish the source area, potentiometric gradients, and the configuration of resultant contaminant plumes. Furthermore, the northeasterly component to transport in the Jefferson City-Cotter HSU appears to follow bedding planes and is addressed below in more detail.

While the direction of flow and transport within the overburden is driven by a hydraulic gradient influenced by the water level in Joachim Creek (and mounding underlying the Hematite Facility), contaminant migration in the shallow Jefferson City-Cotter HSU was subject to other influences. Figure 3.18 establishes that groundwater mounding in the source area also impacted the shallow Jefferson City-Cotter HSU near the Hematite Facility. Furthermore, evidence suggests that the southeastward migration of contamination in this unit was driven by hydraulic stresses originating near the city of Festus, Missouri.

Section 3.3.3.4 presents a discussion about changes to the water supply system for the city of Festus that occurred in August 2003. Until that time, the city operated five deep production wells that derived water from the Roubidoux Formation in the lower part of the Ozark Aquifer. These wells are located on the west side of Festus approximately 4 miles from the Hematite Site. The average water consumption in the city of Festus water supply system is approximately 1 million gpd (http://www.cityoffestus.org/cityprofile.asp#utilities). In August 2003, a new water production facility was brought on-line to supply water needs for the area. This “collector well” is located near the Mississippi River and draws water from a very shallow depth (~100 ft) from the alluvial sediments of the floodplain, rather than from the Ozark Aquifer system. Once the collector well became operational, the other production wells went on standby and are only expected to be used during periods of peak demand (e.g., July and August) to supplement the output of the collector well or when the collector well is shut down for repairs.

Before August 2003, the extraction of groundwater by Festus was sufficient to cause significant drawdown in the aquifer that threatened to impact neighboring communities that also relied upon deep wells. Drawdown effects were observed in Pevely, Missouri (~5 miles to the north), and the Hematite Site (~4 miles to the southwest). Consequently, the cone of depression and associated hydraulic stress imposed on the Roubidoux Aquifer was significant and of regional extent. Following the August shutdown of the
deep wells, water levels within the Roubidoux Formation have been observed to rise dramatically (20 to 50 ft near the Hematite Facility), as illustrated in Fig. 3.27.

In addition to the impact of the Festus production wells, the residential community that includes homes associated with wells PW-19, PW-16, and others in the area also were pumping until they were shut down over the time period from early November, 2003 through mid-March, 2004. However, the magnitude of the combined pumping by these residences was insignificant relative to the pumping rate in the Festus wells.

Information presented in Sect. 3.3.3.4 and associated figures indicate that little hydraulic interconnection exists between the Jefferson City-Cotter and the Roubidoux HSUs. This observation also is consistent with the presence of the low transmissivity zone (inferred on the basis of a variety of hydraulic test results) that was described also in Sect. 3.3.3.4.

Indirect evidence for hydraulic isolation between the Jefferson City-Cotter and the Jefferson City-Roubidoux Contact Zone HSUs comes from closer examination of Figs. 5.17 and 5.18. If a hydraulic connection exists between these two HSUs, then TCE and PCE contamination in the shallow screened intervals intercepted by wells BR-08 and BR-10 should have been able to migrate downward under the influence of the hydraulic stress on the Roubidoux Formation caused by pumping in the Festus wells. However, the fact that groundwater samples from the deep zones in both BR-08 and BR-10 are uncontaminated suggests that no significant connection exists between these two zones. Packer testing results for these boreholes also confirm this conclusion (Appendix I).

If the bedrock HSUs are not interconnected hydraulically, then the vertical distribution of contamination along the entire length of wells PW-19 and BR-16 requires a different explanation. The answer appears to be related to the open hole construction of these wells and the fact that they previously provided a direct connection among strata of both the Jefferson City Dolomite and Roubidoux Formation.

It is interpreted that hydraulic stresses generated by the Festus wells, while they were operating continuously, created a significant, regionally extensive, downward head gradient from the Jefferson City Dolomite to the Roubidoux Formation. Because of the existence of a non-transmissive interval between them, these two zones are essentially isolated from each other except where open boreholes exist. The private wells in the vicinity of PW-19 created a direct linkage between the Roubidoux Formation and the Jefferson City-Cotter Dolomite that was able to transmit the hydraulic stress in the Roubidoux Formation into the Jefferson City-Cotter. As a result, groundwater at higher heads in the shallower zones (i.e., Jefferson City-Cotter HSU) could move down these well bores and flow into deeper zones (at lower hydraulic head values) intersected by the open borehole. In principle, with sufficient cumulative vertical flow down the well bores within the residential community, lowered hydraulic heads in the Jefferson City-Cotter HSU would be able to establish a potentiometric low that would result in groundwater flow and contaminant transport from the Hematite Site beneath Joachim Creek toward the open boreholes located south of Joachim Creek.

For such a mechanism to be realistic for the Hematite Site, not only must the private wells interconnect the hydraulically isolated zones, but the potential rate of downward flow must be sufficient to significantly impact flow within the Jefferson City-Cotter HSU. Metz and Brendle (1996) investigated vertical flow rates in open boreholes in Florida and measured rates as high as 100 gpm in some wells. Clearly, the magnitude of vertical flow by this mechanism is dependent on the hydraulic properties of the aquifers and the hydraulic head differences involved as well as details about the wells (e.g., diameter). Only some of this information is known for this site. However, the Metz and Brendle (1996) investigation indicates that significant interaquifer flow is possible under favorable conditions.
With multiple wells potentially participating in vertical flow in the residential community near the Hematite Site, the integrated flux of water and its impact on lateral flow in the Jefferson City-Cotter HSU could be very large even if flow rates for individual wells were much lower than those observed by Metz and Brendle (1996). Head differences and transmissivities of the source and receiving zones are important in defining flow rates by this mechanism and would need to be incorporated into a model if a quantitative assessment of the process is required. However, in the modeling component of this RI, the viability of the process is explored by assigning vertical flow rates and observing the resultant impact on the potentiometric surface and contaminant transport (Sect. 5.6 and SAIC 2005).

This mechanism not only helps explain the configuration of the potentiometric surface for the Jefferson City-Cotter HSU (Fig. 3.19), but also accounts for the formation of the well-defined plumes of PCE and TCE migrating toward the southeast from the Hematite Facility (Figs. 5.17 and 5.18). In addition, it provides a credible explanation for how contaminated groundwater has been able to migrate into the Roubidoux Formation in the vicinity of the private wells, but not elsewhere across the Hematite Site where a nontransmissive zone prevents such communication. Contaminated groundwater from the Jefferson City-Cotter HSU enters the open boreholes of the private wells and is then redistributed into any receiving transmissive zones for which the hydraulic heads are lower, thereby spreading contamination throughout the length of these boreholes. Many years of aquifer stress caused by pumping on the wells operated by the city of Festus would have resulted in transfer of an unknown quantity of contaminated groundwater into deeper, transmissive intervals. In effect, these wells became sources of contamination to these deeper intervals that would have been active as long as the hydraulic conditions imposed by pumping of the Festus production wells continued.

During the time when both the private wells and those operated by the city of Festus were in use, the overall flow of contaminated groundwater down the boreholes would be partially offset by periodic pumping on the private wells to meet domestic needs. However, the rate of downward flow would have greatly exceeded the domestic pumping rate so that downward vertical redistribution of contaminants would have been a dominant process. Once the Festus wells were shut down in August 2003, the potential for downward borehole flow and contaminant transport began to dissipate rapidly.

It is possible to explore this model further by examining the concentration of TCE (the most abundant contaminant) observed in groundwater obtained from PW-16 and PW-19 over a nearly 3-year period. Figures 5.19a and 5.19b present the data that include both historical (bulk samples obtained while the private wells were active, open holes) and more recent results from packer tests, diffusion bags, and samples from screened intervals once these wells were reconfigured. Also noted are the dates of shutdown of both the Festus production wells and the private wells.

The most important feature of these figures is that data obtained following shutdown of the Festus production and private wells reveal consistently low concentrations of TCE relative to what had been seen earlier. Even allowing for the time variability of the earlier results, the trend is remarkable. As noted, during the 6 to 7 months following shutdown of the city of Festus wells, water levels in wells completed in the Roubidoux Formation in the general vicinity of the Hematite Site recovered significantly (Fig. 3.27). Therefore, the driving force for continued vertical spreading of contaminants in the private wells greatly declined during this period of time. However, the ultimate fate of contamination that had spread downward through the boreholes over many years prior to this time should be considered. It is probable that this contamination spread laterally in a direction that was dominated by the influence of the regionally extensive head gradient imposed by pumping on the Festus production wells. Following recovery of water levels in the Roubidoux Formation, the northeasterly regional potentiometric gradient was reestablished and flow directions would have shifted accordingly. The influx of uncontaminated groundwater from the southwest would now have the opportunity to greatly dilute and flush
contamination from the area and would lead to reduction in contaminant levels obtained from these wells in a manner consistent to what is observed in Figs. 5.19a and 5.19b.

A better understanding of the changes in flow occurring over time in the vicinity of well PW-19 and others in the residential community can be obtained by examining changes in the potentiometric relationships associated with shutdown of the Festus production wells. In Sect. 3.3.3.2, the potentiometric map for the Roubidoux HSU, based on water level data collected in December 2004, was presented (Fig. 3.21). This map represents conditions after a significant period of recovery of water levels (16 months) and indicates a northeasterly trending head gradient consistent with the known regional gradient. The shape of the recovery curves for wells BR-01 through BR-04 (Fig. 3.27) suggests that recovery is essentially complete. It is possible to examine the potentiometric map for the Roubidoux HSU at a time when continuous pumping of the Festus wells was still occurring. LBG (2003) prepared such a map and Fig. 5.20 illustrates the results for August 13, 2002, the earliest date for which water levels are available for the wells. Although water level data from only four wells are available, they suggest that the Festus wells had the impact of shifting the head gradient to an easterly direction. This is the potentiometric gradient that would have driven the lateral migration of contaminants transported downward in the open boreholes in the years prior to August 2003. Currently, however, the gradient direction has shifted to the northeast and a commensurate change in plume migration in the Roubidoux HSU in this area is anticipated.

Figures 5.17 and 5.18 indicate that borehole BR-07 is located in close proximity to PW-19 and other private wells. The results of groundwater sampling in this well from the discrete intervals shown in the figures and from packer testing (Appendix I) indicate that only very low levels of chlorinated VOC contamination are observed and only in a few depth intervals. Given its location, it is surprising that more extensive contamination is not observed. It has already been noted that most intervals in this borehole appear to have low transmissivity and this may be a contributing factor to what is observed. It is more likely, however, that the explanation is related to the details of how the contaminant plume in the Jefferson City-Cotter HSU responded to the various open hole wells in which vertical flow was occurring. The approaching plume would tend to split apart with different segments migrating preferentially to those wells having vertical flow. In this way, it is possible that BR-07 may be located in a region bypassed by the different plume segments and not be subject to the influx of significant contamination. However, this is an unresolved issue that cannot be answered with available data because it requires more information on the depths of the open holes, when they were constructed, and the vertical distribution of hydraulic properties in them.

This CSM suggests that private wells in the vicinity of PW-19 have had an important role in moving contaminants southeastward from the Hematite Facility in the shallow Jefferson City-Cotter Dolomite. Private wells also exist on the next ridge to the southwest and it is legitimate to question whether they could impact the distribution of contaminants in a similar fashion, as observed in Figs. 5.17 and 5.18. Monitoring well BR-03-JC lies directly between the Hematite Facility and these private wells, and is screened in the same depth interval that exists at WS-30, WS-31, BR-08, and BR-10. In contrast to these wells, however, BR-03-JC is uncontaminated, as are all of the private wells further to the southeast that have been sampled. It must be concluded that the region between these private wells and the Hematite Facility (including BR-03-JC) behaves differently than what is observed in Figs. 5.17 and 5.18. Apparently, contaminant sources at the Hematite Facility do not create a plume in the shallow Jefferson City-Cotter Dolomite that migrates toward BR-03. Additional information on the hydraulic properties of the shallow bedrock in this area coupled with modeling may help to better understand this observation.

There is a second component to this CSM that incorporates data for wells BR-04, BR-09, and PW-03 into an overall understanding for the Hematite Site. Fig. 5.21 is a cross-section similar to Fig. 3.9 that is
oriented approximately parallel to the dip of bedrock in this area. The cross-section includes wells BR-01, PZ-04, BR-04, PW-03, and BR-05. The following information has been incorporated on this cross-section:

- Stratigraphic correlation based on the sandstone layer near the Jefferson City-Roubidoux contact,
- Screened intervals for each well,
- Concentrations for PCE and TCE for isolated zones, and
- Concentration data from packer testing in PW-03.

The principal observations made from this cross-section are:

- The screened intervals in the Jefferson City-Cotter Dolomite in wells PZ-04 and BR-04 align well with the bedding plane dip based on the deeper sandstone layer (i.e., they sample a common stratigraphic level – the Jefferson City-Cotter HSU).
- This stratigraphic level projects upward to the shallow contaminated part of the Jefferson City-Cotter in the vicinity of PZ-04 and the Hematite Facility.
- The Jefferson City-Cotter wells are contaminated as far east as PW-03, but no contamination is observed in BR-05.
- Contamination in PZ-04 and PW-03 is TCE-dominant whereas BR-04 is strongly PCE-dominant.
- Groundwater samples obtained during packer testing at PW-03 show that contamination has spread vertically across the length of this borehole.

It is possible to project BR-09 into the plane of this cross-section. Had this been done, the only zone of contamination in BR-09 would correlate with the contaminated stratigraphic zones in PZ-04 and BR-04. However, contamination in BR-09 is TCE-dominant.

Available evidence appears to suggest that contaminated groundwater has migrated down dip along transmissive bedding plane fractures or a transmissive lithologic unit in the Jefferson City-Cotter Dolomite at least as far as PW-03, but has not yet reached the location of BR-05. The projection of this interval into the zone of contamination underlying the Hematite Facility (e.g., PZ-04) suggests this region as the source zone. However, the distinctive differences in contamination at BR-04 (PCE-dominant) and PZ-04, BR-09, and PW-03 (TCE-dominant) indicate that the specific sources for contamination are different for these two groups of wells. The detailed locations of sources or specific migration pathways that would yield these results cannot be resolved with available data. However, the proposed mechanism for contaminant migration is sound. The hydraulic driver for bedding plane flow and transport is partially associated with groundwater mounding under the northeastern area of the Hematite Facility.

The mechanism for vertical distribution of contaminants observed in PW-03 packer test samples is consistent with what is interpreted to have occurred at PW-16 and PW-19. The impact of the open borehole at PW-03 as a conduit for transferring contamination vertically downward into deeper horizons in the well appears to be of key importance at the Hematite Site. The hydraulic stress imposed on the Roubidoux Formation (and lower Jefferson City-Cotter Dolomite) from pumping in Festus likely contributed significantly to this overall process.

As noted in Chapter 3, hydraulic heads in the Jefferson City-Cotter wells located between the region of BR-09 and Joachim Creek. (i.e., BR-11 and BR-02) are similar to that for BR-05. Based upon the data, it appears that no potential currently exists for down dip flow to these wells and none of them have any contamination. The lack of a driving force, as provided by the groundwater mounding underlying the
northeast part of the Hematite Facility, for wells represented in Figs. 5.19a and 5.19b may account for this observation.

5.6 SUMMARY OF GROUNDWATER AND CONTAMINANT TRANSPORT MODELING

Groundwater flow and contaminant transport modeling was conducted as part of this RI. Specific activities included (1) pre-modeling calculations of hydraulic gradients, groundwater velocities, and sorption coefficients; (2) developing and calibrating a groundwater flow model using historical and more recent RI water level data; (3) particle tracking simulations to infer source zones; (4) simulating chlorinated solvent transport; and (5) simulating radionuclide transport. Details regarding the modeling effort are described in (SAIC 2007) and Appendix A, while highlights of the modeling results are presented here.

The model domain (Fig. 5.22) encompasses a larger region than the Hematite Site so that assumptions at the model boundaries would not significantly impact flow simulations within the area of interest. The HSUs described in Sect. 3.3.3.1 are generally represented in the MODFLOW layer model (Fig. 5.23). BR Zones 1 and 2 in Fig. 5.23 correspond to the Jefferson City-Cotter HSU and BR Zone 3 corresponds to the Jefferson City-Cotter-Roubidoux Contact Zone, while BR Zone 4 corresponds to the Roubidoux HSU. Use of MODFLOW for groundwater modeling implicitly assumes the bedrock formations are suitably modeled as porous media. Geologic features parallel to bedding planes appear to be influencing contaminant transport. These features may include fractures and/or sedimentary interbeds that would suggest somewhat different modeling approaches. However, use of a porous medium assumption is appropriate given that this modeling effort is the first attempted for the Hematite Site.

Initial estimates for hydraulic conductivities of the layers were based on historical and RI slug test results (Sect. 3.3.3.1), but were later adjusted during model calibration. Cells within the top model layer that coincided with Joachim Creek (Fig. 5.24) were “specified head cells.” Attempts were made to specify heads at cells in the model that corresponded to the Lake Virginia tributary, Site Creek, and Northeast Site Creek. However, specifying heads to represent these streams was exerting an influence on the simulated hydraulic heads that was not apparent in the monitoring well data. The “river” boundary condition was then used, where the interaction of streams and groundwater is simulated through a streambed with a specified conductance. The streambed conductance had to be set to very low values to match measured water levels. As a result, the influence of these surface streams on the groundwater was ignored in the final calibrated model. The latter assumption is consistent with the fine-grained nature of the shallow soils at the Hematite Site, which probably limits leakage from the surficial (some intermittent) streams to groundwater. With the exception of the bottom two layers of the model (Fig. 5.23), all the boundaries (solid line in Fig. 5.22) were specified as no-flow boundaries. For the bottom two layers of the model (the BR Zone 4 layer and the lower part of BR Zone 3, Fig. 5.23), heads were specified along arc A-D and arc B-C in Fig. 5.24, resulting in a regional northeasterly direction in the deeper layers of the model. This is consistent with the regional flow direction inferred from the water level data after August 2003 (when the city of Festus put the new collector well on-line) in the wells screened within the Roubidoux HSU (Sect. 3.3.3.1).

The model was calibrated using the average of historical water levels from deep overburden wells and the bedrock wells. In the Roubidoux wells where significant water level rebound was observed in 2003 and 2004 (Fig. 3.27), only the water levels from April through December 2004 were included when calculating the average water level for model calibration. Initial attempts at model calibration also included historical data from the pre-RI shallow overburden wells. These initial attempts to simulate the water levels in the shallow overburden wells resulted in unreasonable recharge and high heads in the underlying layers. This might have been due to the perched nature of the groundwater in the shallow
overburden (Sect. 3.3.3.2) trapped over a low-conductivity soil (the “fat clay,” as identified by LBG 2002b), which was not explicitly represented in the layer model (Fig. 5.23). Incorporating this low conductivity unit into the model would have required multiple layers to represent the shallow overburden bedrock, which would have increased the number of model grid cells and numerical resources to solve the larger set of equations. Because flow in the shallow overburden bedrock is predominantly downward (Sect. 3.3.3.2), and off-Site contaminant transport is likely from lateral flow through the deep overburden and bedrock, calibration to the shallow overburden wells was discontinued and only the deep overburden and bedrock wells were considered in the final calibrated model.

A comparison between the modeled and calibrated hydraulic heads is shown in Fig. 5.25, where a perfect match is represented by the 1:1 line. The average residual for the final calibrated model is -0.6 ft, with average residuals of -0.02, -1.8, and 0.6 in the deep overburden bedrock, Jefferson City, and Roubidoux wells, respectively. To capture mounding under PZ-04, a high recharge had to be assigned to the northern area of the Burial Pits (0.05 ft/day, compared to 0.0005 to 0.0002 ft/day throughout the rest of the model domain). A higher recharge value over the Burial Pits is plausible since buried objects and use of limestone gravel in the Burial Pits would have resulted in a more permeable layer that is more conductive to percolation of rainfall water to the subsurface. This high recharge alone could not simulate the high heads in the PZ-04 area. To simulate these heads, an injection well flowing at a rate of 2000 ft³/day (~10.4 gpm) was added as a source in the northeastern end of the plant. This injection well possibly represents a combination of leakage from water distribution pipelines or drainage systems, shallow subsurface groundwater flow from the topographically elevated region northwest of the Facility, or storm runoff from the adjacent Highway P could contribute to this observation.

With the combined high recharge in the Burial Pits and the injection well, the mounding under PZ-04 was reproduced (see potentiometric contour lines in Fig. 5.26). The final hydraulic conductivities of the layers in the calibrated model can be found in SAIC 2005. The relative conductivities of the different layers generally follow what was observed in the slug tests. Furthermore, the hydraulic conductivity for BR Zone 3 representing the Jefferson City-Roubidoux contact zone HSU was set to 0.002 ft/day. This value was achieved through successive simulations where the conductivity for this layer was lowered until changes in hydraulic heads within the bottom layer (BR Zone 4, Fig. 5.23) did not affect hydraulic heads in the Jefferson City layers (BR Zone 1 and 2, Fig. 5.23). This is consistent with the lack of hydraulic interconnectivity between the Jefferson City and Roubidoux Formations inferred from time-series water level data (Sect. 3.3.3.4). The hydraulic conductivity assigned to BR Zone 3 (0.002 ft/day or 7 x 10⁻⁷ cm/second) is within the range of hydraulic conductivities reported for limestone and dolomite (Table 2.2, page 29 of Freeze and Cherry 1979).

MODPATH and the calibrated steady-state flow model were used to gain insight into possible sources of chlorinated solvent contamination detected in bedrock wells BR-08-JC, BR-09-JC, and BR-04-JC (Sect. 4.4). Using the backward tracking capability, MODPATH simulations indicate that particles at these locations all have their sources in the vicinity of the Burial Pit Area (Fig. 5.26). Forward particle tracking indicated that particles at these locations will be advected towards Joachim Creek. Particle pathlines and travel times (Fig. 5.26) vary significantly depending on the release point of the particles within the Hematite Facility. Pathlines originating from source zones towards the southwestern part of the Hematite Facility (e.g., BD-02) are directed towards the southeast, following the hydraulic gradient towards Joachim Creek. Travel time for these particles are three times higher than for some particles that are released within the Burial Pit Area (i.e., ~30 versus ~10 years, respectively, see Fig. 5.26). An elevation view of the pathlines (not shown) reveals that the particles from the Burial Pits Area move down and travel towards Joachim Creek mostly within the transmissive zone in the Jefferson City HSU, resulting in shorter travel times than particles from BD-02, which stay mostly within the layer representing the alluvial/terrace deposits. The hydraulic conductivity for this layer is high near Joachim Creek (e.g., BR-06-OB, Table 3.2), but is an order of magnitude lower near the Hematite Facility.
(e.g., NB-84, Table 3.2 and LBG 1999). The pathlines in Fig. 5.26 show a radial pattern from the Burial Pit area, influenced by mounding of groundwater in the vicinity of PZ-04. The model predicts that pathlines directed towards BR-04 turn towards Joachim Creek, as the influence of the mound diminishes. Note that the boundary conditions for the groundwater model implicitly constrain most of the groundwater within the shallow bedrock (e.g., Jefferson City) to discharge into Joachim Creek, and that the regional northeasterly flow exists in the lower (e.g., Roubidoux) layers. However, it is uncertain that groundwater and dissolved contaminants in BR-04-JC (found at a depth of 95 to 105 ft BGS) actually discharge into Joachim Creek, as required by the model. It is possible that at this depth the regional northeasterly flow direction is dominant.

The flow model used for particle tracking includes a simulation of domestic well pumping by specifying well extraction flows at the wells shown in Fig. 5.26 (labeled PW). The domestic well pumping rate was estimated from 2000 USGS water use data (Hutson et al 2005), which stated that for Jefferson County, Missouri, the total population that used self-supplied water was 51.57 x 10^3, and the total groundwater withdrawal from domestic wells was 3.35 x 10^6 gpd, from which the estimated per capita water usage is 65 gpd or 260 gpd (35 ft^3/day) for a household with four members. Although this flow rate was applied to the domestic wells shown in Fig. 5.26 (labeled PW), the pathlines shown in this figure indicate discharge to Joachim Creek. Thus, the numerical modeling suggests that the impact of pumping in the domestic wells (assumed to be equivalent to a steady extraction rate of 35 ft^3/day) was not enough to draw groundwater from the Hematite Facility side of Joachim Creek into the area where the domestic wells are located. On the other hand, if an extraction rate of 2000 ft^3/day (10.4 gpm) is applied to 13 wells in the vicinity of PW-19 to simulate vertical borehole flow, a significant impact on the potentiometric surface is observed, as well as pathlines from BR-08 and BR-09 that now go under Joachim Creek into PW-19 and PW-16 (Fig. 5.27). Note that 10 gpm is the lowest flow rate observed by Metz and Brendle (1996). Because water levels in the Roubidoux have rebounded (Fig. 3.27) and the driving force for this vertical flow rate is no longer present, it is difficult to estimate the actual flow rates that previously existed in the open-borehole domestic wells in the PW-19 area. Nevertheless, the numerical modeling and simulation shown in Fig. 5.27 supports the CSM and the impact of vertical borehole flow described in Sect. 5.5.

Contaminant transport modeling using RT3D was coupled with the flow model for the site, which includes vertical borehole flow to simulate the migration of contaminants from known and suspected source zones at the Hematite Facility. Matching the measured contaminant concentrations with modeled values was not attempted because of the existence of multiple sources and the uncertainty of when these sources were emplaced (e.g., t = 0 for the simulations). As such, the primary purpose of these simulations is to investigate the influence of potential attenuation mechanisms (e.g., sorption and degradation) on the migration of contaminants from known and suspected source zones at the Hematite Facility.

Figures 5.28, 5.29, and 5.30 show simulated PCE concentration contours in the layer corresponding to the deep overburden (Layer 2, Fig. 5.23). The contours emanate from a constant concentration source of 200 mg/L of PCE located at BD-02. Figures 5.28, 5.29, and 5.30 present model results for t = 3,000 days (~8 years); 9,000 days (~25 years); and 15,000 day (~41 years). The sequential degradation (PCE > TCE > cis-1,2-DCE > vinyl chloride) model in RT3D’s chemical reaction package is used, with degradation parameters taken from the lower range of values reported by Newell and Rifai (2002). Sorption of PCE and its daughter products in the overburden layers was also incorporated, using partition coefficients estimated from natural organic matter measurements (SAIC 2003c, estimation described in SAIC 2005). Two observations can be made from Fig. 5.28 through 5.30: (1) sorption and degradation result in a significant attenuation in PCE levels such that concentrations rapidly drop by one or two orders of magnitude just a short distance from the source (i.e., BD-02), and (2) minimal change between the contour plots at t = 25 years and t = 41 years suggests that a steady-state configuration of the plume is
possible if degradation occurs. The predicted plume also tends to be narrow and is directed towards Joachim Creek.

Figure 5.31 shows another simulation using the same sorption parameters used in Figs. 5.28 through 5.30, but with a 100-mg/L PCE source placed in the northern part of the Burial Pits (see the red square in Fig. 5.31). The degradation parameters were reduced by an order of magnitude to determine whether, even at lower rates, steady-state conditions can be attained within approximately the same time frame as in the previous simulation. Figure 5.31 shows simulated PCE concentrations in the layer corresponding to the transmissive Jefferson City HSU at \( t = 15,000 \) (~41 years). The predicted PCE plume is approaching near-steady-state at \( t = 15,000 \) days, as shown by a plot of simulated PCE and TCE concentrations versus time at the location corresponding to BR-04-JC (see the insert in Fig. 5.31). The simulation also indicates an elongated PCE plume configuration that is directed towards BR-04, but also encompasses WS-30, WS-31, BR-09, and BR-08. Spreading along the lateral axis of the plume may partially be from the radial flow that is induced by groundwater mounding under the Hematite Site. Lateral spreading is also controlled by the horizontal dispersivity, which was set at 1/5th of the longitudinal dispersivity in the simulation. Figure 5.32 shows still another simulation where the source is located in the southern part of the Burial Pits area and consists of specified PCE and TCE concentrations of 50 mg/L.

The same degradation and sorption parameters are used as in the simulation in Fig. 5.31, but the overall shape of the PCE and TCE plume (shown in Fig. 5.32) is elongated towards the southeast in the direction of Joachim Creek. As in particle tracking, this suggests that contaminant pathways vary depending on the location of the source, even in the relatively small area of the Burial Pits. This is another illustration of how mounding under the Hematite Site near the Burial Pits may have an impact on contaminant migration away from sources within the Hematite Facility. Figure 5.32 also illustrates the movement of TCE towards the PW-19 area under the influence of vertical borehole flow in the open boreholes. Note that the model shows contamination spreading to BR-07, which is not consistent with the packer testing (Appendix I), and sampling from this well location showed minimal to no contamination (Sect. 4.4). The transmissivity of the formation around BR-07 may be lower than PW-19, reflecting smaller-scale heterogeneities that cannot be captured in the model. The transport simulations also indicate vertical spreading of contamination (results not shown) in the bedrock even though the vertical dispersivity was only set to 1/5th of the longitudinal dispersivity. This is in contrast to the relatively narrow (20 to 30 ft) zones of contamination observed during packer testing of the newly drilled boreholes (Appendix I). This discrepancy may be due to use of a porous medium model to simulate a situation where transport is through discrete fractures. The porous medium model was useful in exploring hydraulic and contaminant transport mechanisms that would explain the observed distribution of contaminants in the overburden and bedrock.

Radionuclide transport modeling shows very limited movement of uranium from sources (Fig. 5.33) in the overburden using the partition coefficient measured in the site-specific \( K_d \) study (175 mL/g, SAIC 2003c). Sources of uranium (specified concentration of 0.2 mg/L) were placed in Deul's Mountain and the Burial Pits. The \( K_d \) factor for uranium is two orders of magnitude higher than the \( K_d \) factor for PCE. Thus, it is not surprising that PCE is much more widespread at the Hematite Site than uranium.

### 5.7 Fate of PCE and TCE: Evaluation of Evidence Supporting Degradation of PCE and TCE by Natural Processes

The most common chlorinated VOC contaminants in groundwater at the Hematite Site include TCE, PCE, and cis-1,2-DCE, with less frequent occurrences of 1,1-DCE; \( \text{trans} \)-1,2-DCE; and vinyl chloride. Of these, only PCE and TCE were used at the Hematite Facility, although it is possible that some of the
others were contaminants in the primary solvent materials. An alternate, and more likely explanation, is that the various DCE isomers and vinyl chloride are the result of anaerobic biological degradation of TCE and PCE in the subsurface. The degradation pathway for PCE/TCE under anaerobic conditions is presented in Fig. 5.34. At most sites, cis-1,2-DCE is recognized as the principal DCE isomer formed and that is true at the Hematite Site. Only a small number of samples had a quantifiable amount of trans-1,2-DCE. An even smaller number of samples had a measurable quantity of vinyl chloride. 1,1-DCE also is frequently observed, but at only relatively low concentrations.

The mix of these chlorinated VOCs found at the Hematite Site represents strong evidence that biologically mediated natural attenuation processes are active in the subsurface. Furthermore, it appears that, for the most part, degradation has stalled at DCE, which is a common occurrence at many sites.

It is prudent to look further at these data to determine if the anaerobic degradation mechanism can be verified for the site. To do this, an index of anaerobic degradation is defined and computed from the molar amounts of the principal contaminants as follows:

\[
\text{Index of Degradation} = \frac{(\text{PCE}+\text{TCE})}{\text{cis-1,2-DCE}}
\]

In general, as biodegradation proceeds, the relative amounts of the parent constituents (PCE and TCE) will decrease and the product (cis-1,2-DCE) will increase (because further degradation to vinyl chloride does not appear to be important at the Hematite Site). This sequence of events will result in a decline in the index. If biodegradation is a causative factor at the Hematite Site, then it is anticipated that the highest values of the index will occur near the source area, with progressively lower values more distant from the source. Figure 5.35 shows how this ratio varies with location in groundwater from the deep overburden at the Hematite Site. Figure 5.36 presents analogous data for the Jefferson City-Cotter and a few Roubidoux wells.

In Fig. 5.35, it is apparent that the two samples with the highest index values are located beneath the Hematite Facility. This is a reasonable observation as the Hematite Facility is the presumed source of PCE and TCE, and contamination in this area probably was released most recently with less time to undergo degradation. There is a second zone of elevated values of the index that extends outward from the source area toward Joachim Creek, which defines a curved plume. This plume is virtually coincident with the PCE-dominant plume illustrated in Fig. 5.16. Because PCE first degrades to TCE before proceeding to cis-1,2-DCE, groundwater that is PCE-dominant should take longer for the index to decline than for TCE-dominant groundwater, where only a single step is required to produce cis-1,2-DCE. The remaining samples in the area have index values of less than 5, except for several samples located next to Northeast Site Creek.

Relatively few samples are available from the Jefferson City-Cotter Dolomite and Roubidoux Formation (Fig. 5.36). With one exception, these samples have low values of the index suggesting that they are relatively mature in terms of the degree of reductive dechlorination that has occurred. The single exception (index = 22.09) is for groundwater from the Jefferson City-Cotter Dolomite at BR-04. Groundwater at this location has significant PCE contamination (1700 µg/L) and, coupled with the elevated index value, may suggest rather rapid and extensive contaminant migration from the source zone under the Hematite Facility to this site.
As a general rule, the relative rates of dechlorination reactions for the chlorinated ethenes decrease with the decreasing number of chlorine atoms on the molecule. Thus, the rates might be expected to decline in the following order:

\[ \text{PCE} > \text{TCE} > \text{cis-1,2-DCE} > \text{vinyl chloride} \]

This rate sequence also may help explain the limited evidence for production of vinyl chloride in these groundwater samples. However, more likely explanations include either the lack of a consortium of bacteria capable of complete degradation of PCE and TCE to ethene or conditions within the subsurface unfavorable to extensive production of vinyl chloride.

In summary, evidence points to the fact that microbial reductive dechlorination of PCE and TCE is occurring at the Hematite Site. However, there is no information supporting their complete degradation to ethene. In general, it appears that the reductive reactions have essentially stalled following production of DCE, except in a few locations where a detectable amount of vinyl chloride is observed.