5.0 CONTAMINANT FATE AND TRANSPORT

5.1 INTRODUCTION

This chapter describes the potential migration pathways and mechanisms for transport of chemical substances found in surface and subsurface soils and groundwater at Load Line 3. Computer-based contaminant fate and transport analyses were performed to predict the rate of contaminant migration in the identified primary transport media and to project likely future contaminant concentrations at receptor locations through these media. The ultimate objectives of these analyses are to evaluate potential future impacts to human health and the environment and to provide a basis for evaluating the effectiveness of the future remedial alternatives.

Fate and transport modeling was used to simulate vertical transport of contaminants from a principal source area containing maximum observed contaminants in soil to groundwater, as well as horizontal transport within the groundwater system from source areas to receptor locations. A summary of the principles of contaminant fate and transport is presented in this chapter, along with the results of modeling activities. Section 5.2 describes the physical and chemical properties of the SRCs (including metals, organic compounds, and explosives) found at Load Line 3. Section 5.3 presents a conceptual model for contaminant fate and transport at Load Line 3 that considers site topography, hydrogeology, contaminant sources, and release mechanisms through the transport media. Section 5.4 presents a soil leachability analysis to identify CMCOPCs. Sections 5.5 describes the fate and transport modeling. The summary and conclusions of the fate and transport analyses are presented in Section 5.6.

5.2 PHYSICAL AND CHEMICAL PROPERTIES OF SITE-RELATED CONTAMINANTS

Inorganic and organic constituents in soil and groundwater are in continuous chemical and physical interaction with ambient surface and subsurface environments. The observed distributions of chemical concentrations in the environment are the result of these interactions. These interactions also determine the chemical fate of these materials in the transport media. Chemicals released into the environment are susceptible to several degradation pathways including hydrolysis, oxidation, reduction, isomerization, photolysis, photo-oxidation, biotransformation, and biodegradation. Transformation products resulting from these processes will behave distinctively in the environment.

The migration of chemical constituents through the transport media is governed by the physical and chemical properties of the constituents and the surface and subsurface media through which the chemicals are transferred. In a general way, chemical constituents and structures with similar physical and chemical characteristics will show similar patterns of transformation, transport, or attenuation in the environment. Solubility, vapor pressure data, chemical partitioning coefficients, degradation rates, and Henry's Law Constant provide information that can be used to evaluate contaminant mobility in the environment. Partitioning coefficients are used to assess the relative affinities of compounds for solution or solid phase adsorption. However, the synergistic effects of multiple migrating compounds and the complexity of soil/water interactions, including pH and oxidation-reduction potential (Eh), grain size, and clay mineral variability, are typically unknown.

The physical properties of the chemical constituents that were detected in the transport media at Load Line 3 are summarized in Tables L-1, L-2, and L-3 of Appendix L. The properties are used to assess the anticipated behavior of each compound under environmental conditions.

5.2.1 Chemical Factors Affecting Fate and Transport

The water solubility of a compound is a measure of the saturated concentration of the compound in water at a given temperature and pressure. The tendency for a compound to be transported by groundwater is directly related to its solubility and inversely related to both its tendencies to adsorb to soil and to volatilize from water (OGE 1988). Compounds with high water solubilities tend to desorb from soils, are less likely to volatilize from water, and are susceptible to biodegradation. The water solubility of a compound varies with temperature, pH, and the presence of other dissolved constituents (including organic carbon and humic acids).

The octanol-water partition coefficient (K_{ow}) can be used to estimate the tendency for a chemical to partition between environmental phases of different polarity. The K_{ow} is a laboratory-determined ratio of the concentration of a chemical in the n-octanol phase of a two-phase system to the concentration in the water phase. Compounds with log K_{ow} values less than 1 are highly hydrophilic, while compounds with log K_{ow} values greater than 4 will partition to soil particles (Lyman, Reehl, and Rosenblatt 1990).

The water/organic carbon partition coefficient (K_{oc}) is a measure of the tendency of a compound to partition between soil and water. The K_{oc} is defined as the ratio of the absorbed compound per unit weight of organic carbon to the aqueous solute concentration. This coefficient can be used to estimate the degree to which a compound will adsorb to soil and, thus, not migrate with groundwater. The higher the Koc value, the greater the tendency of the compound to partition into soil (OGE 1988). The sorption coefficient (K_d) is calculated by multiplying the K_{oc} value by the fraction of organic carbon in the soil.

Vapor pressure is a measure of the pressure at which a compound and its vapor are in equilibrium. The value can be used to determine the extent to which a compound would travel in air, as well as the rate of volatilization from soils and solution (OGE 1988). In general, compounds with vapor pressures lower than 10^{-7} mm mercury will not be present in the atmosphere or air spaces in soil in significant amounts, while compounds with vapor pressures higher than 10^{-2} mm mercury will exist primarily in the air (Dragun 1988).

The Henry's Law Constant value (K_H) for a compound is a measure of the ratio of the compound's vapor pressure to its aqueous solubility. The K_H value can be used to make general predictions about the compound's tendency to volatilize from water. Substances with K_H values less than 10^{-7} atm-m^3/mol will generally volatilize slowly, while compounds with a K_H greater than 10^{-3} atm-m^3/mol will volatilize rapidly (Lyman, Reehl, and Rosenblatt 1990).

5.2.2 Biodegradation

Organic chemicals with differing chemical structures will biodegrade at different rates. Primary biodegradation consists of any biologically induced structural change in an organic chemical, while complete biodegradation is the biologically mediated degradation of an organic compound into carbon dioxide, water, oxygen, and other metabolic inorganic products (Dragun 1988). The first order biodegradation rate of an organic chemical is proportional to the concentration:

$$-dC/dt = kC, \qquad \textbf{(5-1)}$$

where

C = concentration,
t = time,
k = biodegradation rate constant = $\ln 2 / t_{1/2}$,
$t_{1/2}$ = biodegradation half-life.

The biodegradation half-life is the time necessary for half of the chemical to react. The biodegradation rate of an organic chemical is generally dependent on the presence and population size of soil microorganisms that are capable of degrading the chemical.

5.2.3 Inorganic Compounds

Inorganic constituents detected in soil samples at Load Line 3 are associated with both the aqueous phase and with leachable metal ions on soil particles. The transport of these materials from unsaturated soils to the underlying groundwater is controlled by the physical processes of precipitation, infiltration, chemical interaction with the soil, and downward transport of removed metal ions by continued infiltration. The chemistry of inorganic interaction with percolating precipitation and varying soil conditions is complex and includes numerous chemical transformations that may result in altered oxidation states, ion exchange, adsorption, precipitation, or complexation. The chemical reactions, which are affected by environmental conditions including pH, oxidation/reduction conditions, and the type and amount of organic matter, clay, and the presence of hydrous oxides, may act to enhance or reduce the mobility and toxicity of the metal ions. In general, these reactions are reversible and add to the variability commonly observed in distributions of inorganics in soil.

The chemical form of an inorganic constituent determines its solubility and mobility in the environment; however, chemical speciation is complex and difficult to delineate in routine laboratory analysis. Metals in soil are commonly found in several forms, including dissolved concentrations in soil pore water; metal ions occupying exchange sites on inorganic soil constituents, specifically adsorbed metal ions on inorganic soil constituents; metal ions associated with insoluble organic matter; precipitated inorganic compounds as pure or mixed solids; and metal ions present in the structure of primary or secondary minerals.

The dissolved (aqueous) fraction and its equilibrium fraction are of primary importance when considering the migration potential of metals associated with soil. Of the inorganic compounds that are likely to form, chlorides, nitrates, and nitrites are commonly the most soluble. Sulfate, carbonate, and hydroxides generally have low to moderate solubility. Soluble compounds are transported in aqueous form subject to attenuation; whereas, less soluble compounds remain as a precipitate and limit the overall dissolution of the metal ions. The solubility of the metal ions also is regulated by ambient chemical conditions, including pH and oxidation/reduction.

The attenuation of metal ions in the environment can be estimated numerically using the retardation factor (R_d). The extent to which the velocity of the contaminant is slowed is largely derived from the soil/water partitioning coefficient (K_d) and is expressed by the following relation:

$$R_d = 1 + (K_d \rho_b)/\phi_w, \qquad \textbf{(5-2)}$$

where

ρ_b = the soil bulk dry density, (g/cm^3),
ϕ_w = soil moisture content, (dimensionless).

Metal ion concentrations in the environment do not attenuate by natural or biological degradation because of low volatility and solubility of the ions. Metals concentrations may be biotransformed or bioconcentrated through microbial activity.

5.2.4 Organic Compounds

Organic compounds, such as SVOCs or VOCs, detected in soil, sediment, or water at Load Line 3 may be transformed or degraded in the environment by various processes, including hydrolysis, oxidation/reduction, photolysis, volatilization, biodegradation, or biotransformation. The half-life of organic compounds in the transport media can vary from minutes to years, depending on environmental conditions and the chemical structures of the compounds. Some types of organic compounds, such as PCBs and certain pesticides, however, are very stable, and degradation rates can be very slow. Organic degradation may either enhance (through the production of more toxic byproducts) or reduce (through concentration reduction) the toxicity of a chemical in the environment.

Explosive compounds were detected in soil, sediment, and water media at Load Line 3. With regard to these compounds, microbiological transformation may affect the fate and distribution of this class of constituents in the environment as well. For example, based on the results of culture studies involving the removal of TNT by activated sludge microorganisms, it has been concluded that TNT undergoes biotransformation, but not biodegradation (Burrows et al. 1989). It has been found (Funk et al. 1993) that the anaerobic metabolism occurs in two stages. The first stage is the reductive stage in which TNT is reduced to its amino derivatives. In the second stage, degradation to nonaromatic products begins after the reduction of the third nitro group. The biotransformation pathway for TNT in simulated compositing systems proposed by Kaplan and Kaplan (1990) is shown in Figure 5-1.

Limited information exists regarding biotransformation or biodegradation of RDX. One pilot study being conducted by USACE (USACE 2004) that evaluates treatment of pinkwater wastes using an anaerobic fluidized-bed granular activated carbon bioreactor indicated RDX biodegradation in the presence of ethanol. Such data may be useful for evaluating potential use of enhanced bioremediation as a remedial option.

The biotransformation of 2,4-DNT has been systematically studied in laboratory cell cultures. The pathway proposal for this biotransformation is shown in Figure 5-2. The reduction products include the amino and azoxy derivatives as observed with TNT biotransformation. As with TNT and DNT, the principal mode of microbial transformation of the nitroaromatic compounds TNB and dinitrobenzene (DNB) is reduction of nitro groups to form amino groups.

5.3 CONCEPTUAL MODEL FOR FATE AND TRANSPORT

To effectively represent site-specific conditions in numerical modeling applications, the CSM is relied upon to provide inputs on site conditions that serve as the framework for quantitative modeling. Site conditions described by the CSM, which is outlined in Chapter 2.0 and refined in Chapter 8.0, include contaminant source information, the surrounding geologic and hydrologic conditions, and the magnitude of SRCs and their current spatial distribution. This information is used to identify chemical migration pathways at Load Line 3 for fate and transport analysis. The predictive function of the CSM, which is of primary importance to contaminant fate and transport analysis, relies on known information and informed assumptions about the site. Assumptions contained in the CSM are reiterated throughout this section. The better the information and the greater the accuracy of the assumptions, the more accurately the CSM describes the AOC and; therefore, the more reliable the numerical modeling predictions can be.

A summary of the salient elements of the CSM that apply to fate and transport modeling follows.

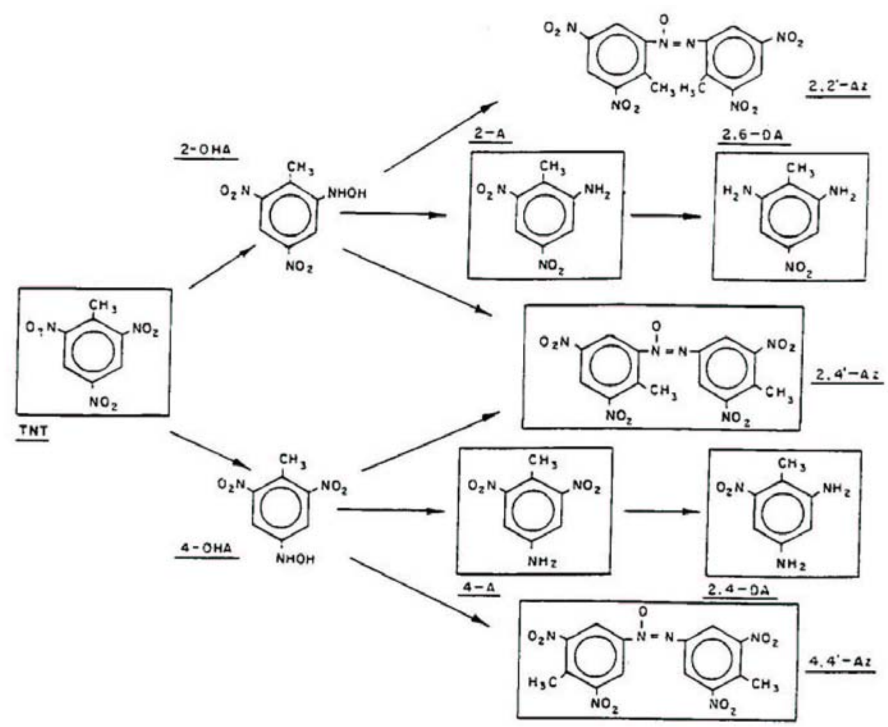

Figure 5-1. 2,4,6-TNT Biotransformation Pathway

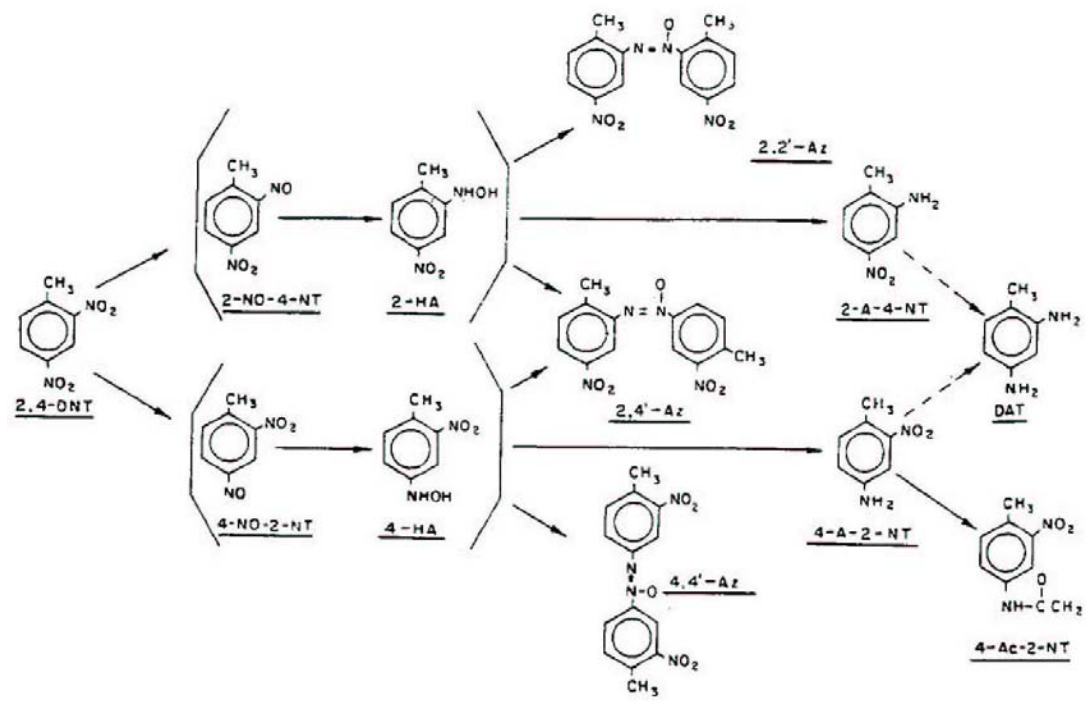

Figure 5-2. 2,4-DNT Biotransformation Pathway

5.3.1 Contaminant Sources

Based on historical records and Phase II RI findings at Load Line 3, the following contaminant sources have been identified.

- Explosive residues and metals are present primarily in the surface soil and shallow subsurface soil adjacent to the footprint of major production buildings, particularly Buildings EA-4, EA-4A, EA-6, and EB-10, and nearby areas (Explosives Handling Areas Aggregate). SVOCs and PCB compounds are found consistently in surface soil. Precipitation may have caused these contaminants to migrate into subsurface soils and into the groundwater.

- The crushed slag that was used throughout RVAAP for roads, railroad beds, and driveways may represent a source of metals contamination to surface soil. Results of analyses of slag and rail ballast at Load Line 3 suggest that leaching effects from these materials quickly diminishes with depth.

- Groundwater at Load Line 3 contains explosive compounds that were identified in the Load Line 3 groundwater with peak concentrations identified in the areas west and downgradient of the Explosives Handling Areas Aggregate. Few metals were identified as SRCs. SVOCs, pesticides, and VOCs were identified as SRCs in groundwater; however, distribution of these constituents is generally limited or concentrations are low.

- Explosives concentrations in sediment in the Cobb's Pond Tributary Aggregate are low, typically less than 1 mg/kg, and distribution is sporadic. Inorganic SRCs were identified throughout the tributary, although values were highest in the furthest upstream locations. SVOCs (primarily PAHs), PCBs, and pesticides are present at sporadic locations at concentrations generally less than 1 mg/kg.

- Water samples from the Cobb's Pond Tributary Aggregate contained no detectable explosives, propellants, SVOCs, PCBs, or VOCs, except trace levels of 2-butanone. Metals SRCs were identified, although the magnitude of background exceedances was generally low.

5.3.2 Hydrogeology

A complete description of the site geology and hydrology is provided in Chapter 2.0 and is summarized as follows.

- Elevations across the AOC vary from approximately 299 to 311 m (980 to 1,020 ft) amsl. In general, the land surface slopes from the east to the west and north towards Cobb's Pond and the tributary entering Cobb's Pond. Along the axis of the AOC, slope is to the west and north towards Cobb's Pond.

- Soil cover thickness varies over Load Line 3. Glacial till and till-derived soil range from 1.1 to 4.6 m (3.5 to 15 ft) thick with an average thickness of about 2.1 m (7 ft) within the load line.

- The groundwater table occurs within the Sharon Conglomerate below the till cover. A groundwater low exists in the southern portion of the Explosive Handling Area Aggregate. The depth to the groundwater table varies from about 3 to 8 m (10 to 28 ft) with an average of approximately 7 m (22 ft). Groundwater flow is directed to the northwest, consistent with regional drainage patterns towards the tributary entering Cobb's Pond, which is presumed to represent the closest shallow groundwater baseflow discharge point. Based on available data, potential groundwater flow off of the AOC appears to occur to the west and northwest.

- Contaminant concentrations are highest within a discrete zone [0 to 0.3 m (0-1 ft)] surface soil interval. Contaminant leaching pathways from soil to the water table are through the thin heterogeneous silt and clay-rich overburden materials and the uppermost portion of the sandstone bedrock interval. The depth to water varies from about 3 to 8 m (10 to 28 ft) with an average of approximately 7 m (22 ft).

5.3.3 Contaminant Release Mechanisms and Migration Pathways

Based on the information presented above, the following contaminant release mechanisms and migration pathways have been identified.

Water infiltrating through contaminated surface and subsurface soils may leach contaminants into the groundwater. The factors that affect the leaching rate include a contaminant's solubility, K_d, and the amount of infiltration. Insoluble compounds will precipitate out of solution in the subsurface or remain in their insoluble forms with little leaching. For the contaminants detected at Load Line 3, sorption processes and the K_d will generally have the greatest effect on leaching. Another factor that affects whether a contaminant will reach the water table through infiltration of rainwater is the contaminant's rate of decay. Most of the organic and explosives compounds decay at characteristic rates that are described by the substance's half-life. For a given percolation rate, those contaminants with long half-lives have a greater potential for contaminating groundwater than those with shorter half-lives. Explosives were detected in groundwater samples; therefore, leaching rates appear to increase faster than chemical decay rates.

Transport of contaminants in either dissolved phase or adsorbed to particulates may occur via surface water (storm) runoff to drainage conveyances and storm drains. These migration pathways were evaluated during the Phase II RI through direct sampling and chemical analysis of sediment and surface water; future evaluation may also be conducted, as needed, through direct monitoring and estimates of mass flux. Therefore, predictive erosion or surface water modeling was not conducted as part of the Phase II RI evaluation of fate and transport.

Release by gaseous emissions and airborne particulates is not significant at Load Line 3. VOCs were not found at significant concentrations in surface soil as they had already volatilized; therefore, there is likely little to no gaseous emission, and contaminant levels in the air pathway are minor to nonexistent.

5.3.4 Water Balance

The potential for contaminant transport begins with precipitation. Infiltration is the driving mechanism for leaching of soil contaminants to groundwater. The actual amount of rainwater available for flow and infiltration to groundwater is highly variable and dependent upon soil type and climatic conditions. A water balance calculation can be used as a tool to quantitatively account for all the components of the hydrologic cycle at Load Line 3. The quantified elements of the water balance are used for inputs to the soil leaching and groundwater transport models discussed later. The components of a simple steady-state water balance model include precipitation (P), evapotranspiration (ET), surface runoff (Sr), and groundwater recharge or percolation (Gr). These terms are defined as follows:

$$P = ET + Sr + Gr, \qquad \textbf{(5-3)}$$

or

$$\text{Rainwater available for flow} \quad = \quad Sr + Gr = P - ET. \qquad \textbf{(5-4)}$$

A relatively moderate amount of runoff occurs from the site. It is expected that loss of runoff occurs in the form of evaporation. The remaining water after runoff is infiltration, which includes loss to the atmosphere by evapotranspiration. The water balance estimations were developed using the Hydrologic Evaluation of Landfill Performance (HELP) model (Schroeder et al. 1994) calculations for Load Line 3 site conditions using precipitation and temperature data for the 100-year period generated synthetically using coefficients for Cleveland, Ohio (Table L-4 of Appendix L).

The annual average water balance estimates for Load Line 3 indicate an evapotranspiration of 65% [0.6 m (24 in.)] of total precipitation [0.9 m (37 in..)]. The remaining 35% [0.3 m (13 in.)] of rainwater is available for surface water runoff and infiltration to groundwater. Of the 0.3 m (13 in.) of rainwater available for runoff or infiltration, groundwater recharge (infiltration) accounts for 16% [0.15 m (6 in.)], and surface runoff accounts for the remaining 19% [0.17 m (7 in.)].

5.3.5 Natural Attenuation of Contaminants in Load Line 3

Natural attenuation accounting for advection, dispersion, sorption, volatilization, and decay effects can effectively reduce contaminant toxicity, mobility, or volume (mass) to levels that are protective of human health and the ecosystem within an acceptable, site-specific time period. Therefore, natural attenuation as a remedial alternative has become a cost-effective approach to site remediation. The overburden materials at Load Line 3 generally have sufficient organic carbon content to cause retardation of organic constituents. In addition, the clay mineralogy results in significant retardation of inorganic constituents by adsorption reactions. Attenuation through adsorption occurs in the vadose zone because of higher organic carbon and clay content in the overburden materials. However, the available data collected to date do not allow quantification of natural attenuation. A focused investigation would be required to quantify natural attenuation at this site and to determine if it would be a viable potential remedial approach.

5.4 SOIL LEACHABILITY ANALYSIS

Soil leachability analysis is a screening analysis performed to define the contaminant migration constituents of potential concern (CMCOPCs). The CMCOPCs are defined as the constituents that may pose the greatest problem if they are migrating from the source.

5.4.1 Soil Screening Analysis

The first step of the soil screening analysis is the development of the SRCs, as discussed in Chapter 4.0. The chemical data in soils were separated into seven area aggregates (Figure 4-1) and screened using frequency-of-detection and RVAAP facility-wide background criteria to identify SRCs:

- Explosives Handling Areas Aggregate,
- Preparation and Receiving Areas Aggregate,
- Packaging and Shipping Areas Aggregate,
- Change Houses Aggregate,
- West Ditches Aggregate,
- DLA Storage Tanks Aggregate, and
- Perimeter Area Aggregate.

The second step of the soil screening analysis is development of the source-specific soil exposure concentrations. The soil exposure concentration of a contaminant in an aggregate represents the 95% upper confidence limit (UCL_{95}) developed using results of all the soil samples within the aggregate, or the maximum value if the UCL_{95} exceeds the maximum.

In the third step of the soil screening analysis, the soil exposure concentrations of all the SRCs are compared with EPA generic soil screening levels (GSSLs). The GSSLs are set for Superfund sites for the migration to groundwater pathway (EPA 1996a). A dilution attenuation factor (DAF) of 1.6 was estimated following EPA (1996a) and applied to the GSSLs. The GSSL is defined as the concentration of a contaminant in soil that represents a level of contamination below which there is no concern under CERCLA, provided conditions associated with GSSLs are met. Generally, if contaminant concentrations in soil fall below the GSSL, and there are no significant ecological receptors of concern, then no further study or action is warranted for that area. However, it should be noted that the purpose of this screen is not to identify the contaminants that may pose risk at downgradient locations, but to target those contaminants that may pose the greatest problem if they are migrating from the site. When the GSSL for an SRC was not available from EPA (1996a), a calculated GSSL was developed using the following equation (EPA 1996a):

$$C_s = C_w \left\{K_d + \frac{\theta_w + \theta_a \ K_H}{\rho_b}\right\} \quad \textbf{(5-5)}$$

where

C_w = target groundwater concentration (mg/L),
C_s = calculated soil screening level (GSSL) (mg/kg),
K_d = soil adsorption coefficient (L/kg),
K_H = Henry's Law Constant (unitless),
ρ_b = dry soil bulk density (kg/L),
θ_w = water-filled soil porosity (volume percent),
θ_a = air-filled soil porosity (volume percent).

Default values, as used by EPA (1996a) to develop the GSSLs, were used in the calculations. Non-zero MCLs or risk-based concentrations (RBCs) for groundwater were used for target groundwater concentrations. Based on this screening, only those constituents that exceeded their published or calculated GSSL multiplied by the DAF were identified as the initial CMCOPCs, based on leaching to groundwater. These initial CMCOPCs, illustrated on Table L-6 in Appendix L, include metals, explosive compounds, pesticides, and VOCs.

In the fourth step, the initial CMCOPCs from Load Line 3 were examined aggregate-by-aggregate to identify the aggregate with maximum contamination. The Explosives Handling Areas Aggregate was observed to have the maximum number of initial CMCOPCs, and it was identified as the aggregate with the maximum contamination. Thereafter, the distribution of the initial CMCOPCs over the aggregate itself was examined. The distribution was observed not to be uniform throughout the aggregate, but to be concentrated in two principal areas. These areas are the vicinities of Buildings EB-4 and EB-4A and they are referred as northwest and southeast source areas, respectively, for clarity. The size of each source area was normalized to 8,365 m^2. Using the procedure described above, the SRCs for the two sources were screened to identify the initial CMCOPCs. A DAF of 1.6 was estimated following EPA 1996a and applied to the GSSLs. The southeast source (Building EB-4A vicinity) was identified as having the largest number of initial CMCOPCs and maximum concentrations; thus, it was selected as the representative source for further screening (Tables L-7 and L-8 of Appendix L). The CMCOPCs from this source were further evaluated using the fate and transport models described in Section 5.5.

5.4.2 Limitations and Assumptions of Soil Screening Analysis

It is important to recognize that acceptable soil concentrations for individual chemicals are highly site-specific. The GSSLs used in this screening are based on a number of default assumptions chosen to be protective of human health for most site conditions (EPA 1996a). These GSSLs are expected to be more conservative than site-specific screening levels based on site geotechnical conditions. The conservative assumptions included in this analysis are (1) no adsorption in the unsaturated zone or in the aquifer, (2) no biological or chemical degradation in the soil or in the aquifer, and (3) contamination is uniformly distributed throughout the source. However, the GSSL does not incorporate the existence of contamination already present in the aquifer. In any case, to evaluate the contaminant migration potential from the source areas, a GSSL screen can be used as an effective tool.

5.5 FATE AND TRANSPORT MODELING

Contaminant fate and transport modeling is based on the conceptual model for Load Line 3 discussed in Section 5.3. Seasonal Soil Compartment (SESOIL) modeling was performed for constituents identified as CMCOPCs from the selected source (see Section 5.5.2). The modeling was performed to predict concentrations of a constituent in the leachate immediately beneath the selected source area just above the water table. If the predicted leachate concentration of a CMCOPC exceeded its MCL or RBC, then lateral migration using the Analytical Transient 1-, 2-, 3-Dimensional (AT123D) model (see Section 5.5.2) was performed to predict the groundwater concentrations at designated receptor locations. The receptor locations identified for the selected source area were (1) the water table immediately below the source, (2) the Cobb's Pond Tributary (and AOC boundary) at its closest point downgradient of the source area, and (3) the RVAAP boundary at its closest point downgradient of the source area. This section discusses applications of these models.

5.5.1 Modeling Approach

Contaminant transport in the vadose zone includes the movement of water and dissolved materials from the source area at Load Line 3 to groundwater. This occurs as rainwater infiltrates from the surface and percolates through the area of contamination, and its surrounding soil, into the saturated zone. The downward movement of water, driven by gravitational potential, capillary pressure, and other components of total fluid potential, mobilizes the contaminants and carries them through the vadose zone. Lateral transport is controlled by the regional groundwater gradient. Vertical transport down through the vadose zone to the water table and the horizontal transport through the glacial deposits to the downgradient locations are illustrated in Figure 5-3.

The output of the contaminant fate and transport modeling is presented as the expected maximum concentration of modeled contaminants at the receptor locations. For SESOIL, the receptor location was the groundwater table beneath the source area. For AT123D modeling, the receptor locations were the Cobb's Pond Tributary and the RVAAP facility boundary. The modeling results allow prediction of the approximate locations of future maximum concentrations resulting from the integration of the contributions from multiple sources and different pathways.

Once the leachate modeling for the source area was completed using the SESOIL model, the predicted maximum groundwater concentrations beneath the source area were determined using the AT123D model, and the concentrations were compared against the existing groundwater concentrations downgradient of the source area. The greater of the predicted and observed concentration in the groundwater was compared against the respective MCLs or RBCs. If the predicted or measured maximum groundwater concentrations were higher than the MCLs or RBCs, groundwater modeling was performed using the higher concentration as the source term concentration. If the predicted and actual concentrations were less than the MCLs or RBCs, the contaminant was eliminated from the list of CMCOPCs, and no further evaluations were performed.

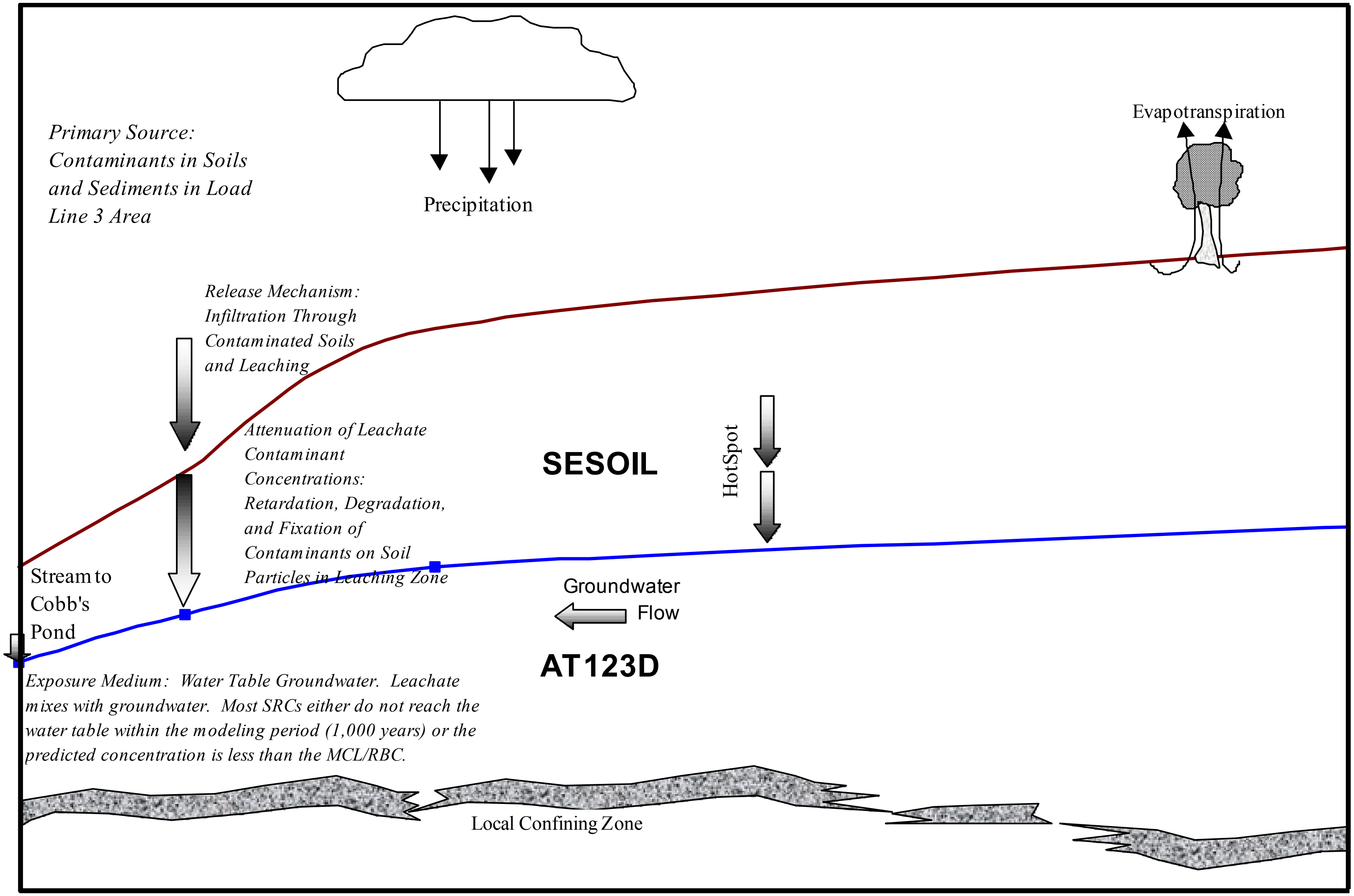

Figure 5-3. Contaminant Migration Conceptual Model

5.5.2 Model Applications

The SESOIL model (GSC 1998) used for leachate modeling, when applicable, estimates pollutant concentrations in the soil profile following introduction via direct application and/or interaction with transport media. The AT123D model (Yeh 1992) is an analytical groundwater pollutant fate and transport model. It computes the spatial-temporal concentration distribution of wastes in the aquifer system and predicts the transient spread of a contaminant plume through a groundwater aquifer. The application of both of these models is discussed in the following subsections.

5.5.2.1 SESOIL modeling

The SESOIL model defines the soil compartment as a soil column extending from the ground surface through the unsaturated zone and to the upper level of the saturated soil zone. Processes simulated in SESOIL are categorized in three cycles-the hydrologic cycle, sediment cycle, and pollutant cycle. Each cycle is a separate submodule in the SESOIL code. The hydrologic cycle includes rainfall, surface runoff, infiltration, soil-water content, evapotranspiration, and groundwater recharge. The pollutant cycle includes convective transport, volatilization, adsorption/desorption, and degradation/decay. A contaminant in SESOIL can partition in up to four phases (liquid, adsorbed, air, and pure). The sediment washload cycle includes erosion and sediment transport. As noted in Section 5.3.3, erosional transport of contaminants was not modeled at Load Line 3; therefore, this module was not used.

Data requirements for SESOIL are not extensive, utilizing a minimum of site-specific soil and chemical parameters and monthly or seasonal meteorological values as input. Output of the SESOIL model includes pollutant concentrations at various soil depths and pollutant loss from the unsaturated soil zone in terms of surface runoff, percolation to groundwater, volatilization, and degradation. The mathematical representations in SESOIL generally consider the rate at which the modeled processes occur, the interaction of different processes with each other, and the initial conditions of both the waste area and the surrounding subsurface matrix material.

SESOIL simulation for a contaminant was performed over a 1,000-year period. The period was selected considering the voluminous output and the lengthy time required to complete a simulation for a longer period of time. Also, EPA suggests a screening value of 1,000 years to be used due to the high uncertainty associated with predicting conditions beyond that timeframe. Therefore, the initial CMCOPCs of the selected source were screened against a travel time of 1,000 years. The travel time is the time required by a contaminant to travel from the base of its contamination to the water table. The estimated travel time for each initial CMCOPC to reach the water table is determined using the following equation:

$$T_t = \frac{T_h \times R_d}{V_p} \qquad \textbf{(5-6)}$$

where

T_t = leachate travel time (year),
T_h = thickness of attenuation zone (ft),
R_d = retardation factor (dimensionless) (Equation 5-2),
V_p = porewater velocity (ft/year).

and

$$Vp = \frac{I}{\theta} \qquad \textbf{(5-7)}$$

where

I = infiltration rate (ft/year),
θ = fraction of total porosity that is filled by water.

If the source depth for a constituent is equal to the thickness of the vadose zone, the constituent is determined to have a travel time equal to zero using the above equations (i.e., no leaching zone). The estimated travel time is then compared to a screening value. If the travel time for a constituent from a source area exceeded 1,000 years, then the constituent was eliminated from the list of CMCOPCs. Initial CMCOPCs with travel times less than 1,000 years are considered to be contaminants of potential concern and are selected for further analysis.

Details of the model layers utilized in this modeling are presented in Tables L-12 and L-13 of Appendix L. The model was calibrated against the percolation rate by varying the intrinsic permeability and by keeping all other site-specific geotechnical parameters fixed. The final site-specific hydrogeologic parameter values used in this modeling are shown in Table 5-1. The intrinsic permeability was derived during calibration of the model to a percolation rate of 0.15 m/year (Table L-4 of Appendix L). The constituents selected for SESOIL modeling are listed in Table 5-2, along with the results of the modeling. The chemical-specific parameters are presented in Appendix L (Table L-3). The distribution coefficients (K_ds) for metals were obtained from EPA's Soil Screening Guidance Document (EPA 1996a) unless stated otherwise. The K_ds for organic compounds were estimated from organic carbon-based water partition coefficients (K_{oc}) using the relationship $K_d = (f_{oc})(K_{oc})$, where f_{oc} = soil organic carbon content as mass fraction obtained from site-specific measurements and K_{oc} values were obtained from EPA's Soil Screening Guidance Document (EPA 1996a), unless stated otherwise. The biodegradation rates presented in Table L-3 are literature based (Howard et al. 1991) and represent the most conservative values. Tables L-10 and L-11 of Appendix L contain additional detail for the modeling output.

5.5.2.2 AT123D modeling in the saturated zone

The fate and transport processes accounted for in AT123D include advection, dispersion, adsorption/retardation, and decay. This model can be used as a tool for estimating the dissolved concentration of a chemical in three dimensions in the groundwater resulting from a mass release over a source area (point, line, area, or volume source). The model can handle instantaneous, as well as continuous, source loadings of chemicals of interest at the site. AT123D is frequently used by the scientific and technical community to perform quick and conservative estimates of groundwater plume movement in space and time. SESOIL and AT123D are linked in a software package (RISKPRO) so that mass loading to the groundwater predicted by SESOIL can be directly transferred to AT123D. Therefore, AT123D was chosen to predict the future receptor concentrations for the contaminants.

The hydrogeologic parameter values used in this modeling are shown in Table 5-1. The chemical-specific parameters are presented in Appendix L (Table L-15). A discussion on model limitations and assumptions is presented in Section 5.5.2.4. The constituents selected for this modeling are listed in Table 5-3, along with the results of the modeling. The CMCOPCs in this table represent all the constituents that were identified as final CMCOPCs from SESOIL modeling plus additional constituents are currently observed in groundwater exceeding their respective MCL or RBC. Constituents for which the predicted maximum groundwater concentration exceeded the MCL or RBC at a receptor location were identified as the contaminant migration contaminants of concern (CMCOCs).

Table 5-1. Unit-Specific Parameters Used in SESOIL and AT123D Modeling for Load Line 3

Parameters	Symbol	Units	Explosive Handling Area	Source for Value
Vadose Zone Data				
Percolation Rate (Recharge Rate)	q	m/yr	1.50E-01	HELP model
Soil Ph	pH	pH	6	Site-specific geotechnical data
Horizontal Area of Aggregate (Source Area Size)	A_p	m^2	8,365	Estimated from soil aggregate
Intrinsic Permeability - clayey sand	p	cm^2	1.9E-10	Calibrated SESOIL model
Disconnectedness Index	c	unitless	9	Calibrated from SESOIL model
Freundlich Equation Exponent	n	unitless	1	SESOIL default
Fraction Organic Carbon	f_{oc}	unitless	2.40E-02	Geotechnical data at Load Line 3
Bulk Density	ρ_b	kg/L	1.8	Geotechnical data at Load Line 4
Porosity - Total	n_T	unitless	0.37	Geotechnical data at Load Line 4
Vadose Zone Thickness	Vz	m	22.5	Based on water level data
Leaching Zone Thickness	Th	m	19.5	Based on soil contamination and water level data
Seepage Velocity	Sv	m/yr	4.0E-01	Calculated
Groundwater Data				
Aquifer Thickness	h	m	30	Conservative assumptions
Hydraulic Conductivity in Saturated Zone	K_S	cm/s	5.4E-05	Site-specific slug test data
Hydraulic Gradient in Saturated Zone	I_S	m/m	1.00E-02	Groundwater surface map in work plan
Effective Porosity	n_e	unitless	0.2	Assumed for sandstone
Distance to the Compliance Point	X	m	343	Shortest downgradient distance to stream boundary
Dispersivity, longitudinal	d_L	m	30.0	0.1 X
Dispersivity, transverse	d_T	m	10	0.3 d_L
Dispersivity, vertical	d_V	m	3	0.1 d_L

NA = Not applicable - parameter not used.

Table 5-2. Summary of Leachate Modeling Results for Load Line 3

Initial CMCOPC	RME 0 to 2 ft (mg/kg)	RME 2 to 3 ft (mg/kg)	Predicted $C_{leachate,max}$ Beneath the Source (mg/L)	Predicted Tmax (years)	Predicted $C_{gw,max}$ At the Source[a] (mg/L)	Observed $C_{gw,max}$ Downgradient of Source (mg/L)	MCL/RBC (mg/L)	Final CMCOPC[b]
Explosive Handling Area								
Metals								
Selenium	1.40E+00	1.40E+00	7.80E-02	2.16E+02	3.18E-02	NA	5.00E-02	No
Explosives								
1,3-Dinitrobenzene	2.00E+00	0.00E+00	1.00E-03	1.10E+01	NA	1.20E-04	3.65E-03	No
2,4-Dinitrotoluene	6.20E-01	0.00E+00	0.00E+00	NA	0.00E+00	NA	7.30E-02	No
2,6-Dinitrotoluene	1.60E+00	0.00E+00	0.00E+00	NA	0.00E+00	NA	3.60E-02	No
4-Nitrotoluene	2.20E+00	0.00E+00	1.08E-01	1.59E+02	4.29E-02	NA	6.10E-02	No
Nitrobenzene	2.30E-01	0.00E+00	0.00E+00	NA	0.00E+00	NA	3.40E-04	No
1,3,5-Trinitrobenzene	1.80E+00	0.00E+00	2.00E+00	8.00E+00	3.24E-01	5.00E-02	1.09E+00	No
2,4,6-Trinitrotoluene	5.50E+03	0.00E+00	0.00E+00	NA	0.00E+00	8.20E-02	2.24E-03	No
RDX	1.10E+01	0.00E+00	8.46E+00	1.20E+01	3.29E+00	7.70E-03	6.10E-04	Yes

[a] The predicted maximum concentration in groundwater (Cgw,max) at the source was calculated using AT123D model based on contaminant loading predicted by SESOIL.
[b] A constituent is a Final CMCOPC if it reaches the water table within 1,000 years and its predicted concentration in groundwater exceeds its MCL/RBC.
NA = Not applicable.
NA = Not analyzed.
AT123D = Analytical Transient 1- ,2-, 3-Dimensional model.
CMCOC = Contaminant migration contaminant of concern.
MCL = Maximum contaminant level.
RBC = Risk-based concentration (EPA Region 9 values).
RDX = Hexahydro-1,3,5-trinitro-1,3,5-triazine.
RME = Reasonable maximum exposure.
SESOIL = Seasonal Soil Compartment model.

Table 5-3. Summary of Groundwater Modeling Results for Load Line 3

CMCOPC	Source Concentration[a] (mg/L)	Receptor Concentration: Cobb's Pond Tributary (mg/L)	Receptor Concentration: RVAAP Boundary (mg/L)	MCL/RBC (mg/L)	CMCOC[b]
Explosives Handling Area					
Metals and Inorganic Compounds					
Manganese[c]	2.20E+00	0.00	0.00	8.76E-01	No
Pesticides and PCBs					
beta-BHC[c]	1.50E-04	0.00	0.00	3.70E-05	No
Heptachlor Epoxide[c]	7.50E-05	0.00	0.00	7.39E-06	No
Explosives					
RDX	3.29E+00	3.75E-01	2.62E-05	6.10E-04	Yes

[a] The predicted maximum concentration in groundwater ($C_{gw,max}$) at the source was calculated using AT123D model based on contaminant loading predicted by SESOIL.
[b] A constituent is a CMCOC if its predicted groundwater concentration at the compliance point/receptor exceeds its MCL/RBC.
[c] The constituent is selected for AT123D modeling because it was detected in groundwater exceeding its MCL or RBC.
AT123D = Analytical Transient 1-, 2-, 3-Dimensional model.
BHC = Benzene hexachloride.
CMCOC = Constituent migration contaminant of concern.
MCL = Maximum contaminant level.
PCB = Polychlorinated biphenyl.
RVAAP = Ravenna Army Ammunition Plant.
RBC = Risk-based concentration (EPA Region 9 values).
RDX = Hexahydro-1,3,5-trinitro-1,3,5-triazine.
SESOIL = Seasonal Soil Compartment model.

5.5.2.3 Modeling results

SESOIL modeling was performed for selenium and eight explosive compounds noted in Table 5-2, which presents the predicted peak leachate and groundwater concentrations beneath the source area and the corresponding time for peak leachate concentrations. In addition, this table presents for comparison the current maximum concentrations in the groundwater downgradient of the source and drinking water MCLs or RBCs (if no MCL is available). Due to the variable groundwater gradient at the site, all wells were considered downgradient from the source so that the highest groundwater concentration measured was taken as the downgradient groundwater concentration. As noted in Table 5-2, selenium was predicted to leach to the water table beneath the source area; however, concentrations were below the groundwater MCL. Of the eight explosives modeled, only RDX was predicted to exceed its MCL or RBC beneath the source area. Based on the SESOIL modeling results, RDX was selected as a final CMCOPC for lateral migration modeling using AT123D.

AT123D modeling was performed for the one constituent exceeding its RBC below the source area based on SESOIL modeling and the additional three chemicals that were observed in groundwater exceeding their MCLs or RBCs. Groundwater source concentrations for AT123D modeling inputs were set equal to the greater of the measured downgradient groundwater concentration or the SESOIL predicted groundwater concentration beneath the source. Predicted leaching values were used for both selenium and RDX, as they exceeded measured concentrations in groundwater. Measured concentrations were used for the remaining CMCOPCs, as they exceeded the predicted leaching concentrations. Table 5-3 presents the predicted groundwater concentrations at the selected downgradient receptor locations. RDX was predicted to reach the Cobb’s Pond Tributary at concentrations exceeding its RBC; therefore, it was identified as a CMCOC. The predicted timeframe to attain peak RDX concentrations at the tributary (0.375 mg/L) was 870 years. This constituent was also predicted to reach the RVAAP boundary within the 1,000-year modeling period, although at a concentration less than the RBC. None of the other CMCOPCs was predicted to reach either the Cobb’s Pond Tributary or the RVAAP boundary within the 1,000-year modeling period.

5.5.2.4 Limitations/assumptions

A conservative modeling approach was used, which may overestimate the contaminant concentration in the leachate for migration from observed soil concentrations. Listed below are important assumptions used in this analysis.

- The use of Kd and Rd to describe the reaction term of the transport equation assumes that an equilibrium relationship exists between the solid- and solution-phase concentrations and that the relationship is linear and reversible.
- The Kd-values used in this analysis for all the CMCOPCs represent literature or calculated values and may not represent the site conditions.
- Flow and transport in the vadose zone is one-dimensional (i.e., only in the vertical direction).
- Initial condition is disregarded in the vadose zone modeling.
- Flow and transport are not affected by density variations.
- A realistic distribution of soil contamination is not considered.

The inherent uncertainties associated with using these assumptions must be recognized. Kd values are highly sensitive to changes in the major chemistry of the solution phase. Therefore, it is important that the values be measured or estimated under conditions that will represent as closely as possible those of the contaminant plume. It is also important to note that the contaminant plume will change over time and will be affected by multiple solutes that are present at the site. Projected organic concentrations in the aquifer are uncertain because of the lack of site-specific data on constituent decay in the vadose zone, as well as in the saturated zone. Use of literature values (particularly partition coefficients) may produce either over- or underestimation of constituent concentrations in the aquifer. In this sense, the modeling may not be conservative. Deviations of actual site-specific parameter values from assumed literature values may significantly affect contaminant fate predictions.

The effects of heterogeneity, anisotropy, and spatial distribution of fractures are not addressed in these simulations. The present modeling study using SESOIL and AT123D does not address the effects of flow and contaminant transport across interfaces in rapidly varying heterogeneous media.

Conceptually, the water table depth was assumed to be 7.5 ft bgs (SESOIL modeling depth). Therefore, the saturated groundwater flow was assumed to occur through the Sharon member (Figure 2-3). Given AT123D limitation, the hydraulic conductivity field for the saturated zone was assumed homogeneous, and its geometric mean value of 6.2E-04 cm/sec based on the slug-test results (Table 2-1) was used in this modeling. Noting the conductivity to range from 3.67E-06 to 2.62E-03 cm/sec, the predicted concentrations appear to represent a mean condition within a range of expected concentrations. The range appears to be orders of magnitude, suggesting the associated uncertainty to be significant.

For AT123D modeling, the key input parameters are hydraulic conductivity (K_s), hydraulic gradient (I_s), effective porosity (n_e), and K_d. The K_s, I_s, and n_e work as a lumped parameter controlling the seepage velocity $V_s = K_s*I_s/n_e$. The impact (sensitivity) of K_d is discussed above. Hydraulic gradient is noted to vary from 0.01 to 0.02 ft/ft near EB-4 and EB-4A (Figure 2-5). Therefore, the impact of the hydraulic gradient is expected to be less than that of K_s. The impact of n_e can be significant given the presence of fractures in the Sharon member (Figure 2-3).

5.6 SUMMARY AND CONCLUSIONS

Based on site characterization and monitoring data, metals and explosives-related compounds exist in the surface and subsurface soils at Load Line 3. Some metals and explosives are also found in the groundwater. Fate and transport modeling using the Building EB-4A vicinity as the selected source indicates that some of these contaminants may leach from contaminated soils into the groundwater beneath the source. Migration of many of the constituents is; however, likely to be attenuated because of moderate to high retardation factors. Conclusions of the leachate and groundwater modeling are as follows.

- Selenium and eight explosive-related compounds were identified as initial CMCOPCs based on soil screening analysis.

- Four constituents, manganese, beta-BHC, heptachlor epoxide, and RDX, were identified as final CMCOPCs based on source loading predicted by the SESOIL modeling or on measured groundwater concentrations downgradient of the source. Maximum groundwater concentrations of these compounds were predicted to exceed their RBCs beneath the source area.

- Only RDX was identified as a CMCOC based on AT123D modeling. The maximum groundwater concentration of this compound was predicted to exceed its RBC at the Cobb's Pond Tributary, which coincides with the AOC boundary. The timeframe to attain the peak RDX concentration of 0.375 mg/L at the tributary was 870 years. This constituent was also predicted to reach the RVAAP boundary within the 1,000-year modeling period, although at a concentration less than the RBC. None of the other CMCOPCs was predicted to reach either the Cobb's Pond Tributary or the RVAAP boundary within the 1,000-year modeling period.

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