5. 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, surface water, and groundwater at LL 1. Computer-based contaminant fate and transport modeling analyses were performed to predict rate of contaminant migration in the identified primary 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 proposed remedial alternative in the FS.

Fate and transport modeling was used to simulate vertical transport of contaminants from source areas to groundwater and horizontal transport within the groundwater system to receptor locations. Air quality modeling was not performed for this RI, as this medium was not identified as a primary pathway of contaminant transport at LL 1. Surface water is a transport pathway for contaminant transport. However, the DQOs for the Phase II RI did not include collection of necessary information for performing flow and transport modeling through this medium.

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 LL 1). Section 5.3 presents a conceptual model for potential contaminant migration pathways at LL 1 that considers site topography, hydrogeology, contaminant sources, distribution in various environmental media, and release mechanisms through transport media. Section 5.4 presents a soil leachability analysis to identify COPCs. Section 5.5 describes the fate and transport modeling. The summary and conclusions of the fate and transport analysis are presented in Section 5.6.

5.2 PHYSICAL AND CHEMICAL PROPERTIES OF SITE-RELATED CONTAMINANTS

The migration of chemical constituents through various media is governed by the physical and chemical properties of the detected chemicals 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 environmental media at LL 1 are summarized in Appendix P, Tables P-1, P-2, and P-3. The properties are used to assess the anticipated behavior of each compound under environmental conditions.

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 and sediments, 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}) 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. The octanol-water partition coefficient can be used to estimate the tendency for a chemical to partition between environmental phases of different polarity. 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 K_{oc} value, the greater the tendency of the compound to partition into soil (OGE 1988). The sorption coefficient (K_d) is calculated from the K_{oc} coefficient 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 soil air 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).

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 biodegradation rate of an organic chemical is proportional to the concentration:

$$-dC/dt = kC^n ,$$

where

C = concentration,
k = biodegradation rate constant = $(1/t')\ln(a/x)$,
t = time,
a = initial concentration at time $t=0$,
n = reaction order,
x = concentration at time $t= t'$.

The half-life ($t_{1/2} = 0.693/k$) is the time necessary for half of the chemical concentration 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.

Inorganic and organic constituents in soil, sediment, and groundwater are in continuous chemical and physical interaction with ambient surface and subsurface environmental conditions. The observed distributions of chemical concentrations in the environment are affected by these interactions and determine the chemical fate of these materials in the various media. Chemicals released into the environment are susceptible to several degradation pathways including hydrolysis, oxidation, reduction, isomerization, photolysis, photooxidation, biotransformation, and biodegradation. Transformation products resulting from these processes will behave distinctively in the environment.

5.2.1 Metals

Metals are ubiquitous in LL 1 soils and sediments. The only TAL metals not detected in every sediment sample were antimony, beryllium, cadmium, magnesium, mercury, selenium, sodium, and thallium. Silver was not detected. All TAL metals were detected in each subsurface soil sample except for antimony, beryllium, cadmium, mercury, selenium, silver, and hexavalent chromium. The metals most commonly detected in surface soils above background across LL 1 were cadmium, copper, lead, mercury, and zinc. The metals most frequently detected above background in filtered groundwater were zinc, cobalt, aluminum, and arsenic.

Inorganic constituents detected in soil and sediment samples at LL 1 are associated with both the aqueous phase (unbound pore water) 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 additional physical mechanism of erosive transport is important for surface soil and sediment dispersal. 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 and sediment.

Metals in soil and sediment are commonly found in several forms (Shuman 1991), 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.

In situations where metal ions have been introduced to the environment by human activities, they are attributed to non-mineralogic occurrences. The dissolved (aqueous) fraction and its equilibrium fraction are of primary importance when considering the migration potential of metals associated with soil and sediment. 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 (Rd). The extent to which the velocity of the contaminant is slowed is largely derived from the soil/water partitioning coefficient (Kd), as expressed by the following relation:

$$R_d = 1 + (K_d\rho_b)/\phi_w ,$$

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.

5.2.2 Organic Compounds

The predominant organic chemical compounds, besides explosives and propellants, detected in LL 1 soil and sediment include SVOCs (primarily PAHs). The most common SVOCs were benzo(a)pyrene, benzo(b)fluoranthene, and fluoranthene. The most commonly detected VOC in sediment was acetone, and the most commonly detected PCB was PCB-1254. Organic contamination in surface soil at LL 1 is minimal with only one VOC detected consistently-1,2-DCE-usually at a concentration of less than 1 ppm. PCBs and pesticides were also detected in the surface soils. Three VOCs, two SVOCs, and one pesticide/PCB were detected in groundwater samples, but all at low concentrations.

These compounds may be transformed or degraded in the environment by various processes, including hydrolysis, oxidation/reduction, photolysis, volatilization, biodegradation, or biotransformation. The half-life (time required to naturally reduce chemical concentration by one-half) of organic compounds in various media can vary from minutes to years, depending on environmental conditions and the chemical structures of the compounds. 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. Biodegradation rates for the detected organic compounds at LL 1 are shown in Table P-2 in Appendix P.

5.2.3 Explosives-Related Compounds

Explosives (nitroaromatic) compounds detected in sediments at LL 1 include 2,4,6-TNT, 2,4-DNT, 4-amino-2,6-DNT, and 2-amino-4,6-DNT. The most commonly detected propellant was nitrocellulose. In subsurface soils, the most commonly detected compounds were TNT, RDX, 2,4-DNT, and nitrocellulose. The most commonly detected explosives and propellant-related compounds detected in surface soils were 2,4,6-TNT and nitrocellulose. Twelve explosive and propellant compounds were detected in groundwater, although most were less than 1 μg/L. RDX was detected at 88 μg/L. The source, nature, and extent of the ammunition-related constituents are discussed in detail in Chapter 4.0.

Microbiological transformation may affect the fate and distribution of munitions-related constituents in the environment. 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).

TNT is readily biotransformed in the environment to amino, diamino, and azoxy compounds (Walsh 1990). 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 composting systems proposed by Kaplan and Kaplan (1982) is shown in Figure 5-1.

The biotransformation of 2,4-DNT has been systematically studied in laboratory cell cultures. The reduction products include the amino and azoxy derivatives as observed with TNT biotransformation. The biotransformation pathway of 2,4-DNT proposed by McCormick et al. (1978) is shown in Figure 5-2. As with TNT and DNT, the principal mode of microbial transformation of the nitroaromatic compounds TNB and DNB is reduction of nitro groups to form amino groups.

5.3 CONCEPTUAL SITE MODEL

The CSM is a statement of known site conditions that serves as the framework for quantitative modeling. Site conditions described by the CSM include waste source information, the surrounding geologic and hydrologic conditions, and the SRCs and their current spatial distribution. This information is combined to identify chemical migration pathways at LL 1. 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 will be clearly stated 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 predictions can be.

The basic framework of the CSM has been presented in Chapter 2.0. A summary of the salient model elements follows.

5.3.1 Contaminant Sources

Based on historical records and the findings of sampling and analysis at LL 1, the following contaminant sources have been identified:

- Individual buildings within the production areas (specifically CB-4, CB-4A, CA-6, CA-6A, CB-10, CA-17, CB-13, and CB-14) and the former settling tanks located north of Building CB-3 and northwest of Building CA-6.

- Explosive residues are present in the soils surrounding these buildings. Precipitation or recent demolition activities 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 also be a source of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, magnesium, and zinc contamination. Only cadmium and zinc occur above background levels in slag samples from LL 1.

5.3.2 Hydrogeology

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

- Topography at LL 1 is moderately subdued, with elevations ranging from 297.2 to 309.6 m (975 to 1,016 ft) amsl in the production area. The topography is the result of the reworking of the original glaciated bedrock surface to accommodate the buildings and other infrastructure of LL 1.

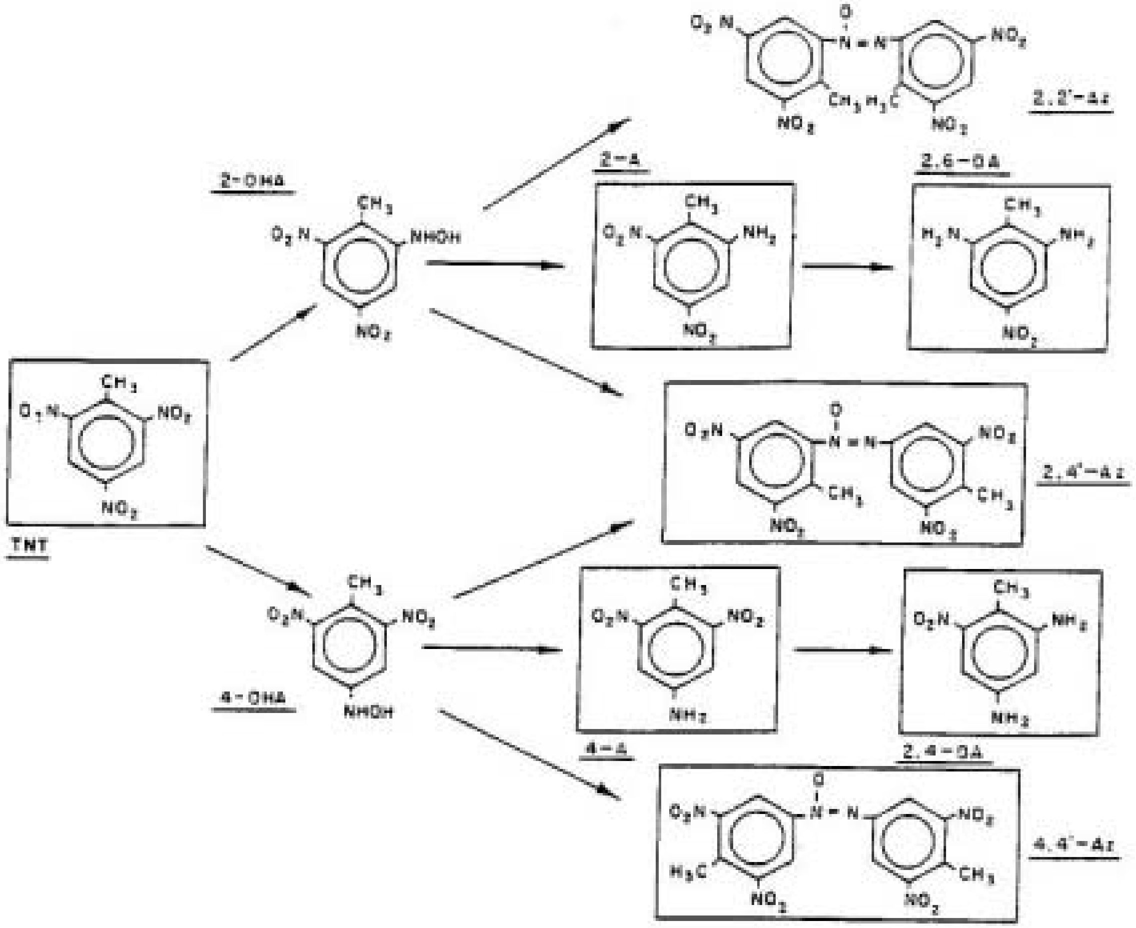

Figure 5-1. 2,4,6-TNT Biotransformation Pathway

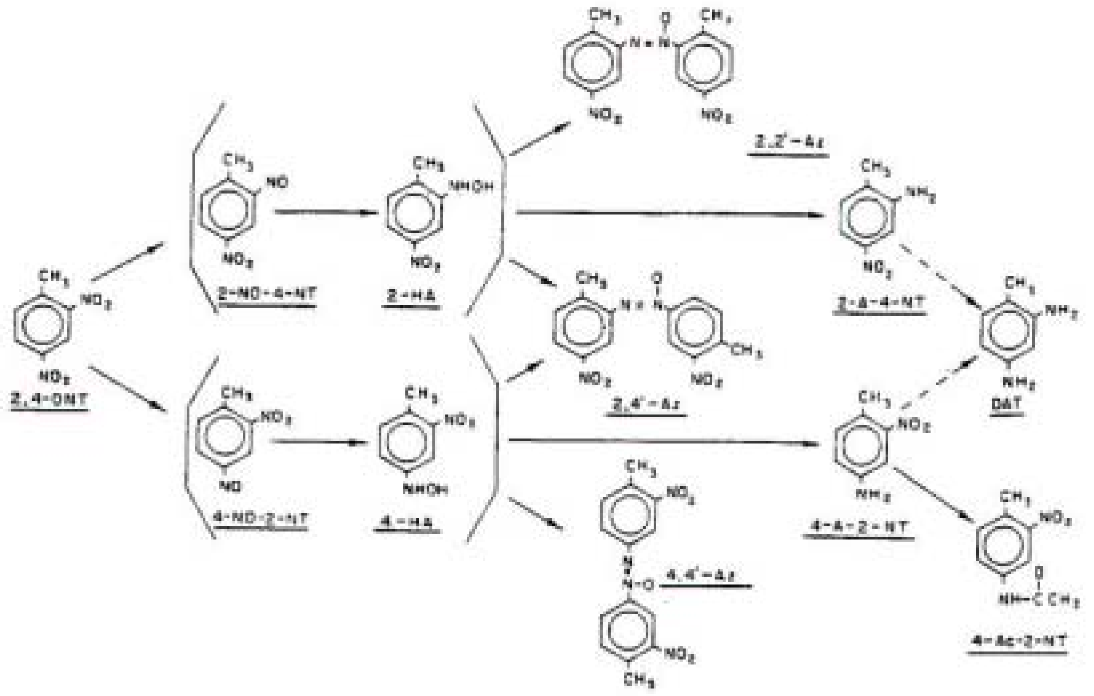

Figure 5-2. 2,4-DNT Biotransformation Pathway

- Soil cover is thin to nonexistent at many locations inside the main production area at LL 1, except where non-native material was brought in during construction of RVAAP or was redistributed during the demolition of buildings at the load line. Bedrock is exposed at locations throughout the production area. Consequently, contaminant leaching pathways from soil to bedrock are short or nonexistent in many areas. Surface soils contain contaminants in the highest concentrations at the melt-pour buildings (CB-4 and CB-4A), Building CB-10, the former settling tanks, and near Building CA-6.

- Groundwater is present in the sandy interbeds found in glacial materials that occur south of the load line proper, at depths from about 4.26 to 4.57 m (14 to 15 ft) below the ground surface. This glacial material exceeds 10.6 m (35 ft) in thickness in some locations. The water-bearing sand units may be laterally discontinuous. Groundwater in the production area of LL 1 occurs in the highly porous, permeable, and fractured Sharon Sandstone. Groundwater is presumed to flow generally from the west to the east across the load line, based on the site's topography and potentiometric surface data from the two previous and eight newly installed monitoring wells within the production area. Northwesterly and southeasterly flow components exist related to a potentiometric high in the central portion of the load line. The water-bearing sandstone behaves as an unconfined system.

- Surface water flow influences surface contaminant distribution and mobility at LL 1. Surface water from precipitation collects in storm water catch basins and unlined ditches throughout the production area. Such runoff is discharged through two exit pathways: (1) Outlets A and B, Outlet C and Charlie's Pond, and Outlets D, E, and F and Criggy's Pond, which all drain into the unnamed tributary that exits the plant at State Route 534 northeast of the AOC; and (2) the North Area Channel that flows into Sand Creek.

- The extensive system of storm and sanitary sewers in the subsurface represents a possible preferred migration pathway for water-borne contaminants. All of these conduits are situated in trenches cut into sandstone bedrock. Leaks from the sewer pipes may have rapidly introduced contaminants from the surface soil source areas to groundwater.

5.3.3 Water Balance

The potential for contaminant transport begins with precipitation. The actual amount of rainwater available for flow 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 LL 1. The components of a simple steady-state water balance model include precipitation (P), evapotranspiration (ET), surface runoff (Sr), and groundwater recharge or percolation (Gr) and are defined as follows:

$$P = ET + Sr + Gr\ ,$$

or

$$\text{Rainwater available for flow} \quad = \quad Sr + Gr = P - ET\ .$$

A relatively moderate amount of runoff occurs from the site. It is expected that there will be loss of runoff water in the form of evaporation. The remaining water after runoff is infiltration, which includes loss to the atmosphere by evapotranspiration. The annual average water balance estimates for LL 1 indicate an evapotranspiration of 65% (24 in.) of total precipitation (37 in.) as compared to 35% (13 in.) for rainwater available for flow. Of this 35% (13 in.), groundwater recharge (percolation) accounts for 16% (6 in.), and surface runoff accounts for the remaining 19% (7 in.). The water balance estimations were developed based on Hydrologic Evaluation of Landfill Performance (HELP) model (Schroeder et al. 1994) calculations for LL 1 site conditions using precipitation and temperature data for the 100-year period generated synthetically using coefficients for Cleveland, Ohio.

5.3.4 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 LL 1, sorption processes and the K_d generally will have the greatest effect on leaching. Metals detected at LL 1 have high K_ds and are not expected to leach into the groundwater at any significant rate. This point is supported by the fact that metals concentrations above background are found in groundwater only in the main process areas and not in the perimeter locations sampled. 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 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. However, at LL 1 the chemicals with longer half-lives (PAHs) have high K_ds, thereby limiting their migration potential to groundwater. Low actual concentrations of explosives, SVOCs, VOCs, and PCBs/pesticides in groundwater indicate that migration of these constituents from sediments and soil to groundwater is minimized by high Kds and other attenuation mechanisms.

Release by gaseous emissions and airborne particulates is not significant at LL 1. VOCs at significant concentrations were not found in surface soils as they have already volatilized; therefore, there is likely little to no gaseous emissions. Thus, contaminant levels in the air pathway are minor to nonexistent. Particulate matter from contaminated surface soil can become airborne as a result of wind erosion. At LL 1, this process is moderated by the presence of vegetative cover throughout a large portion of the AOC.

5.3.5 Natural Attenuation of Contaminants in Load Line 1 Areas of Concern

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 layers found within the shallow overburden material generally have sufficient organic carbon content to cause retardation of organic constituents. In addition, the clay mineralogy results in significant cation 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. Based on site characterization (Chapter 4.0) and the discussion presented above, it may be concluded that LL 1 may be a candidate for natural attenuation remediation approach. However, the data available to this RI do not allow quantification of natural attenuation. A focussed investigation to quantify natural attenuation would be required in order to consider natural attenuation as a viable option for remediation.

5.4 SOIL LEACHABILITY ANALYSIS

Contaminant fate and transport analyses at this site involve a series of screening steps to define the contaminant migration constituents of potential concern (CMCOPCs) at LL 1. The CMCOPCs are defined as the constituents that may pose the greatest problem if they are migrating from the site sources. Once initial CMCOPCs were developed through the screening process, they were further evaluated using a vadose zone contaminant transport model, SESOIL, for vertical migration, and a saturated zone contaminant transport model, Analytical Transient 1-, 2-, 3-Dimensional Model (AT123D), for lateral migration to the receptor locations. The screening steps are discussed in this section, and the modeling procedures are discussed in the following section.

5.4.1 Comparison of Unit-Specific Conceptual Site Model to Soil Screening Level

The first step of the screening process represents the development of the SRCs as discussed in Chapter 4.0. The chemical data in soils were summarized into eight area aggregates according to the source units

- Buildings CB-3/CB-801;
- Buildings CB-4/4A and CA-6/6A;
- Buildings CB-13/CB-10;
- Buildings CB-14, CB-17, and CA-15;
- Area around the base of the former Water Tower;
- Former Change Houses (CB-12, CB-23, CB-8, and CB-22);
- Railroad track bed; and
- Perimeter area.

After completion of the first screening, the conceptual site model was re-examined to check the consistency of the SRCs with respect to the knowledge of contamination at the site. Essential nutrients, calcium, chloride, iron, magnesium, potassium, and sodium were eliminated from the list of SRCs for further evaluations.

The third step of the screening process involves developing the source area-specific soil exposure concentrations. The soil exposure concentration of a contaminant in a source area represents the 95% upper confidence limit (UCL) developed using results of all the soil samples within the source unit, or the maximum value if the UCL exceeds the maximum.

The fourth step of the screening process involves comparing the soil exposure concentrations of all the SRCs with EPA generic soil screening levels (GSSLs). The GSSLs are set for Superfund Sites for the migration to the groundwater pathway (EPA 1996a). A default dilution attenuation factor (DAF) of 20 was applied to the GSSLs. A DAF of 20 is considered protective for sources of 0.5 acre in size (EPA 1996a). However, a DAF of 20 can be protective of larger source areas as well, especially for biodegradable organics and for metals with high adsorption coefficients. The adsorption factor for metals is a function of pH. Usually, adsorption of metals in soils is lower for a lower pH. For this site, the average pH is quite high (7.5 units); therefore, a DAF of 20 is conservative. 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 SSLs 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 here 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 (1996), a calculated GSSL was developed using the following equation (EPA 1996):

$$C_s \; = \; C_w \left[K_d \; + \; \frac{\theta_w + \; \theta_a \;\; K_H}{\rho_b} \right] ,$$

where

C_w = target soil leachate 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 (1996) to develop the GSSLs, were used in the calculations. Non-zero MCLs or risk-based concentrations for groundwater were used for target groundwater concentrations. Based on this screening, only those constituents that exceeded the appropriate GSSL (or calculated GSSL if generic SSLs were not available) multiplied by the default DAF were identified as the initial CMCOPCs, based on leaching to groundwater, and were selected for SESOIL modeling.

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 1996). These GSSLs are expected to be more conservative than site-specific SSLs. 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 evenly 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 SSL screen can be used as an effective tool.

5.5 CONTAMINANT TRANSPORT MODELING

Contaminant fate and transport modeling is based on the conceptual model for LL 1 discussed in Section 5.3. Air is not considered an important pathway for contaminant transport from LL 1. Only groundwater modeling was performed.

5.5.1 Modeling Approach

As discussed earlier, contaminant transport in the vadose zone includes the movement of water and dissolved materials from source areas at LL 1 to groundwater in the Sharon Sandstone. This occurs as rainwater infiltrates from the surface and percolates through the source of contamination, and its surrounding soil and bedrock, 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 Sharon Sandstone to the downgradient locations are illustrated in Figure 5-3.

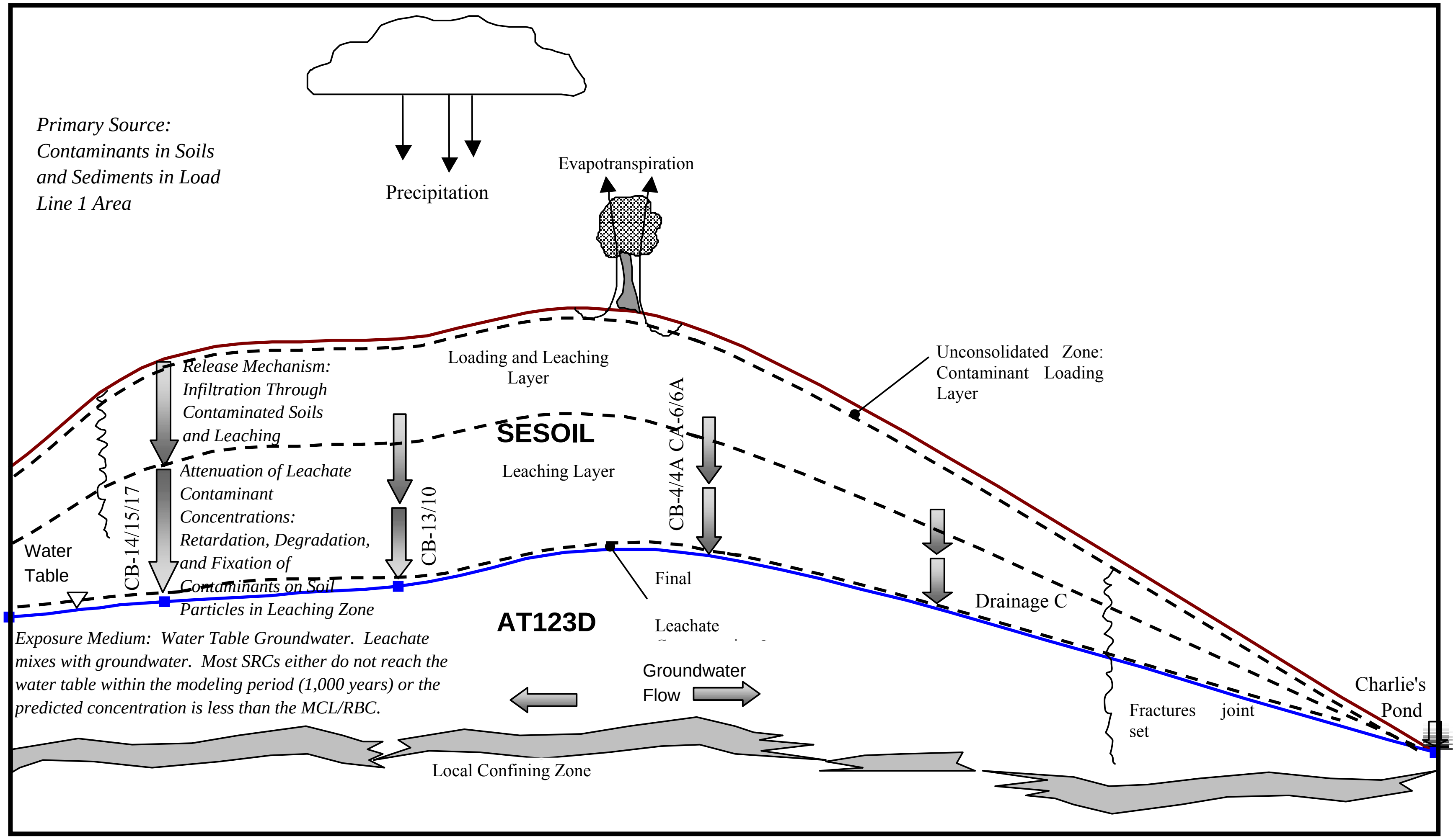

Figure 5-3. Contaminant Migration Conceptual Model

A combination of small-scale analytical groundwater transport models and simple estimates of contaminant attenuation/dilution along specific pathways are combined in the framework of the conceptual model for fate and transport analysis. The combination of methods is site-specific and is discussed in detail later in this section.

The output of the contaminant fate and transport modeling is presented as the expected maximum concentration of modeled contaminants at the receptor locations. These data will allow prediction of the approximate locations of future maximum concentrations resulting from the integration of the contributions from multiple sources and different pathways. For the purpose of this analysis, LL 1 was divided into eight source areas as described in Section 5.4.1. Figure 5-1 shows the conceptual approach for fate and transport analysis. The quantitative modeling accounted for the following:

- contents of the source area;
- identifiable geologic strata beneath the source area;
- contaminated soil layer;
- thickness of each layer in the vadose zone;
- vertical permeability of the unsaturated soils;
- density, width, and depth of cracks which extend from the surface downward;
- water table fluctuations; and
- receptor locations.

The final CMCOPC to be used for SESOIL modeling involves determining an estimated travel time to the water table for each initial CMCOPC. The estimated travel time for each initial CMCOPC to reach the water table is determined using the following equation:

$$T_t = \frac{T_h \times R_f}{V_p} ,$$

where

T_t = leachate travel time (year),
T_h = thickness of attenuation zone (ft),
R_f = retardation factor (dimensionless) (Equation 6-1),
V_p = porewater velocity (ft/year).

and

$$V_p = \frac{I}{\theta} ,$$

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 (i.e., no leaching zone). The estimated travel time is then compared to a screening value. EPA suggests a screening value of 1,000 years to be used due to the high uncertainty associated with predicting conditions beyond that time frame.

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. As shown in Appendix P (Table P-8), all the metals, PAHs, and PCBs were eliminated from the list of initial CMCOPCs based on this time screen. Leachate modeling on all the remaining CMCOPCs from each source area was performed. Once the leachate modeling for all the source areas was completed, the predicted maximum groundwater concentrations beneath the source areas were determined using the model AT123D, and the concentrations were compared against the existing groundwater concentrations in the groundwater downgradient of the source area. If the predicted groundwater concentration exceeded the measured concentration in the groundwater, then the predicted concentration was compared against the respective MCLs or groundwater risk-based concentrations (RBCs) that were derived using a cancer risk of 10^{-6} or hazard index of 1.0. If the predicted and measured maximum groundwater concentrations were below the MCLs or groundwater RBC, the contaminant was eliminated from the list of CM COPCs, and no further evaluations were performed.

5.5.2 Model Applications

As discussed in the previous section, modeling of contaminant migration from the sources to Sharon Sandstone groundwater was accomplished for each of the eight separate soil aggregates.

5.5.2.1 SESOIL modeling

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 other media. The model defines the vadose zone as a column extending from the ground surface through the unsaturated zone and to the upper level of the saturated 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).

Data requirements for SESOIL are not extensive, utilizing a minimum of soil and chemical parameters and monthly or seasonal meteorological values as input. Output of the SESOIL model includes pollutant concentrations at various depths and pollutant loss from the unsaturated zone in terms of surface runoff, percolation to groundwater, volatilization, and degradation.

The mathematical representations used 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 geohydrologic formations.

The source areas used in SESOIL modeling represent the soil aggregates/EUs. The soil concentrations in these EUs were summarized by their respective sapling depth intervals, and SESOIL input source terms were developed. The source terms represent the RME of soil for each interval within the source area (i.e., EU). The RME soil concentration for each source area is defined as the lesser of the 95% upper confidence limit of the mean (95% UCL) concentration or the maximum detected concentration within each source unit. The value used for the RME screening is usually determined with respect to a constituent's distribution across the entire EU and through the entire thickness of the vadose zone.

The simulations using SESOIL were continued until the maximum concentration in leachate beneath the source was attained. However, due to the voluminous amount of output per run and to the large computing time it takes to complete a long-term simulation, the model was run to simulate a maximum time period of 1,000 years. The time of arrival ($T_{arrival}$) for all the initial CMCOPCs from the eight source areas to the groundwater table was estimated using simple analytical equations (see Appendix Table P-8). These estimated arrival times were utilized to select the compounds ($T_{arrival}$ <1,000 years) for SESOIL modeling.

The constituents from each source area selected for SESOIL modeling are listed in Table 5-1 along with the results of the modeling. The maximum predicted leachate concentrations were input into the AT123D model to predict the maximum groundwater concentration beneath the source. Constituents for which the predicted groundwater concentration or the downgradient measured groundwater concentration exceeded the MCL or RBC were selected as final CMCOPCs for lateral migration modeling using AT123D.

The SESOIL model was calibrated against the percolation rate by varying the hydraulic conductivity and the disconnectedness index and by keeping all other site-specific geotechnical parameters fixed. The final parameter values used in this modeling are shown in Table 5-2. The disconnectedness index and the intrinsic permeability were derived during calibration of the model to a percolation rate of 0.15 m/year. The percolation rate was derived by performing water balance simulation for the site using the HELP model.

The SESOIL model may be configured using different layers and even sublayers to represent intervals of the vadose zone having different hydraulic properties or where different leaching processes may apply (e.g., contaminant loading versus attenuation zones). The range of overburden thickness used for LL 1 SESOIL modeling was 1.1 to 10.7 m. The SESOIL model was set up using four layers extending from the ground surface to the average water table surface except for the Drainage C and Ponds sources, where three layers were used. In general, soil contamination at LL 1 is limited to 0 to 3 m, of which 0 to 1 m is most common. Therefore, contaminant-loading layers in SESOIL are comprised of Layer 1 (0 to 1 m) and Layer 2 (1 to 3 m). Whereas, the leaching zone in the model represents the uncontaminated vadose zone through which contaminant leachate is expected to migrate in the future. The leaching zone at LL 1 varied from 9.6-m-thick overburden to approximately 0.8-m-with little or no remaining overburden. Details of the model layers are presented in Appendix P (Table P-4).

5.5.2.2 AT123D modeling in the Sharon Sandstone

The AT123D (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 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. In RISKPRO, SESOIL and AT123D are linked so that mass loading to the groundwater predicted by SESOIL can be directly transferred to AT123D. SESOIL creates an ATX file containing contaminant flux versus time with monthly intervals for the duration of the model that can be imported to create the input file for the AT123D model run. Therefore, AT123D was chosen to predict the future receptor concentrations for the contaminants.

Six explosives compounds were selected for AT123D modeling in the Sharon Sandstone based on source loading predicted by SESOIL or on measured groundwater concentrations downgradient of the sources. Maximum concentrations at the facility boundary were simulated for these constituents. Model input parameters are summarized in Table 5-2.

Table 5-1. Summary of Leachate Modeling Results for Load Line 1

CMCOPCs[a]	**RME**	**Predicted $C_{leachate,max}$ Beneath the Source**	**Predicted T_{max} (years)**	**Predicted $C_{gw,max}$ at the Source**[b]	**Observed $C_{gw,max}$ Downgradient of Source**	**MCL/RBC**	**Final CMCOPC**[c]
CB-13 and CB-10							
2,4-Dinitrotoluene	1.39E+00	411	27	89.0	7.9	73	Yes
2,6-Dinitrotoluene	6.00E-01	181	22	38.5	3.8	37	Yes
RDX	3.44E+00	1.82E+04	10	5550.0	88	0.61	Yes
CB-14 , CB-17, and CA-15							
2,4-Dinitrotoluene	4.40E-01	337	15	71.0	7.9	73	No
RDX	2.14E+01	39680	6	4980.0	88	0.61	Yes
CB-3 and CB-801							
2,4-Dinitrotoluene	1.20E-01	36.8	27	0.5	7.9	73	No
Nitrobenzene	1.50E-01	31.3	31	0.4		3.5	No
RDX	2.60E-01	1.94E+02	10	5.2	88	0.61	Yes
Carbazole,	2.64E+00	0.00E+00	305	0.0		3.3	No
Pentachlorphenol	8.00E-02	4.25E+00	120	0.0		0.56	No
CB-4/4A and CA-6/6A							
1,3,5-Trinitrobenzene	6.35E+00	24847	8	1550.0	12	1100	Yes
1,3-Dinitrobenzene	6.37E+00	4439	9	333.0	1.3	3.7	Yes
2,4-Dinitrotoluene	2.30E-01	81	19	3.9	7.9	73	Yes
2,6-Dinitrotoluene	8.60E-01	493	15	25.6	3.8	37	No
Nitrobenzene	5.90E-01	1.79E+02	22	7.7		3.5	Yes
RDX	8.91E+01	6.00E+01	8	6240.0	88	0.61	Yes
Outlets A and B Drainages							
1,3,5-Trinitrobenzene	1.80E-01	60	25		12	1100	No
2,4-Dinitrotoluene	2.00E+00	9.50E+01	140		7.9	37	No
Outlet C Drainage and Charlie's Ponds							
2,6-Dinitrotoluene	1.30E-01	1.40E+02	15	3.7	3.8	37	No
Outlets D, E, and F Drainages and Criggy's Ponds							
2,4-Dinitrotoluene	7.00E-02	1.70E+00	280		7.9	73	No
Nitrobenzene	1.40E-01	2.50E+00	350			3.5	No

[a] Concentrations are either in µg/g or µg/L.

[b] The predicted maximum concentration in groundwater ($C_{gw,max}$) at the source was calculated using the AT123D model based on contaminant loading predicted by SESOIL.

[c] A constituent is a final CMCOPC if it reaches the water table within 1,000 years and if its predicted concentration in groundwater exceeds its MCL/RBC.

CMCOPC = contaminant migration constituent of potential concern.

MCL = maximum containment level.

RBC = risk-based concentration.

Table 5-2. Unit-Specific Parameters Used in SESOIL and AT123D Modeling for Load Line 1

Parameters	Symbol	Units	Value							Source for LDG Value
			CB-13 and CB-10	CB-14, -17, and CA-15	CB-4/4A and CA-6/6A	CB-3 and CB-801	Outlets A and B Drainage	Outlet C Drainage and Charlie's Ponds	Outlets D, E, and F Drainage and Criggy's Ponds	
Percolation Rate (Recharge Rate)	q	m/yr	1.50E-01	1.50E-01	1.50E-01	1.50E-01	1.50E-01	1.50E-01	1.50E-01	HELP model
Soil pH	pH	pH	6	6	6.0	6.0	6.0	6.0	6	Site-specific geotechnical data
Horizontal Area of Aggregate	A_p	sq. m	32,400	28,700	73,650	19,000	0.0	0.0		Estimated from soil aggregate
Intrinsic Permeability – clayey sand	p	cm^2	1.3E-10	1.3E-10	1.3E-10	1.3E-10	1.3E-10	1.3E-10	1.3E-10	Calibrated from SESOIL model
Disconnectedness Index	c	unitless	9	9	9	9	9	9	9	Calibrated from SESOIL model
Freundlich Equation Exponent	n	unitless	1	1	1	1	1	1	1	SESOIL default
Fraction Organic Carbon[a]	f_{oc}	unitless	2.60E-03	2.60E-03	2.60E-03	2.60E-03	3.39E-02	1.97E-02	3.87E-02	Geotech data at Load Line 1
Bulk Density	ρ_b	kg/L	1.8	1.8	1.8	1.8	1.8	1.8	1.8	Geotech data at Load Line 2
Porosity – total	n_T	unitless	0.32	0.32	0.32	0.32	0.32	0.32	0.32	Geotech data at Load Line 6
Vadose Zone Thickness	Vz	m	10.5	6.4	7.3	10.7	6.1	1.1	10.7	Based on water level data
Leaching Zone Thickness	Th	m	9.6	5.5	6.4	9.8	5.8	0.8	10.4	Based on soil contamination and water level data
Seepage Velocity	Sv	m/yr	6.6E-01	6.6E-01	6.6E-01	6.6E-01	6.6E-01	6.6E-01	6.6E-01	Calculated
Groundwater Data										
Aquifer Thickness	h	m (ft)	6	6	6	6	6	6	6	Conservative assumptions
Hydraulic Conductivity in Saturated Zone	K_S	cm/s	9.8E-05	3.5E-05	3.4E-04	7.0E-04	3.5E-05	1.7E-03	7.0E-04	Site-specific slug test data from Load Line 1 wells (Chap. 2)
Hydraulic Gradient in Saturated Zone	I_S	m/m	1.70E-03	4.00E-03	2.00E-02	4.00E-02				Groundwater potentiometric map
Effective porosity	n_e	unitless	0.2	0.2	0.2	0.2				Assumed for silty clay
Distance to the compliance point	X	m	274	76	145	610				Shortest downgradient distance to site boundary
Dispersivities[b]	d_L, d_Y, d_V	M	5, 1.6, 0.5	5, 1.6, 0.5	5, 1.6, 0.5	5, 1.6, 0.5	5, 1.6, 0.5	5, 1.6, 0.5	5, 1.6, 0.5	Calibrated

[a] Fraction organic carbon (FOC) = Total organic carbon × 10^{-6}. Total organic carbon is derived from geotechnical analyses.

[b] Longitudinal, transverse, and vertical dispersivities.

NA = Not applicable - parameter not used.

5.5.2.3 Modeling results

The results of the contaminant fate and transport analysis for individual source areas are summarized in Tables 5-1 and 5-3. A formal modeling validation process was beyond the scope of the Phase II RI; however, as part of routine QA protocols, an engineering calculation package was prepared. This package, which documents the input parameters and set up of the model, was subject to an independent technical review. This package is maintained as part of the project file.

Presented in Table 5-1 are the predicted peak leachate and groundwater concentrations beneath the source and the corresponding time for peak concentrations using SESOIL. 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). As can be seen from this table, 2,4-dinitrotoluene, 2,6-dinitrotoluene, RDX, 1,3,5-trinitrobenzene, 1,3-dinitrobenzene, and nitrobenzene were predicted to reach concentrations exceeding groundwater RBCs beneath the source areas.

Table 5-3 presents the results of the AT123D modeling of the constituents identified above. None of the six modeled constituents are predicted to reach the LL 1 site boundary at a measurable concentration. Qualitatively, the predicted results of the model are consistent with expected results based on known chemical characteristics and comparatively low mobility of the explosive compounds that were evaluated. Additionally, in the two existing AOC boundary wells east of the site (LL1mw-064 and LL1mw-065), explosive compounds were not detected.

Table 5-3. Summary of Groundwater Modeling Results for Load Line 1

CMCOPC	Source Concentration[a] (µg/L)	Receptor Concentration (µg/L)	MCL/RBC	CM COC[b]
CB-13 and CB-10				
2,4-Dinitrotoluene	89.0	0	73	No
2,6-Dinitrotoluene	38.5	0	37	No
RDX	5550.0	0	0.61	No
CB-14 , CB-17, and CA-15				
RDX	4980.0	0	0.61	No
CB-3 and CB-801				
RDX	5.2	0	0.61	No
CB-4/4A and CA-6/6A				
1,3,5-Trinitrobenzene	1550.0	0	1100	No
1,3-Dinitrobenzene	333.0	0	3.7	No
Nitrobenzene	7.7		3.5	No
RDX	6240.0	0	0.61	No

[a] The predicted maximum concentration in groundwater ($C_{gw,max}$) at the source was calculated using the AT123D model based on contaminant loading predicted by SESOIL.

[b] A constituent is a CMCOPC if its predicted groundwater concentration at the compliance point/receptor exceeds its MCL/RBC.

CMCOC = contaminant migration constituent of concern.

CMCOPC = contaminant migration constituent of potential concern.

MCL = maximum containment level.

RBC = risk-based concentration.

5.5.2.4 Limitations/assumptions

Based upon the data available, a conservative approach was used, which may overestimate the contaminant concentration in the leachate for migration from observed or back-calculated soil concentrations. Listed below are important assumptions used in this analysis.

- The use of K_d and R_d 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 K_d-values used in this analysis for all the CM COPCs 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).
- No biodegradation in the vadose zone (i.e., SESOIL modeling assumes no decay).
- Initial condition is disregarded in the vadose zone modeling.
- Flow and transport are not affected by density variations.
- Horizontal distribution of soil contamination within a source unit is not considered.
- The aquifer is assumed homogenous and isotropic.

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 Sharon Sandstone. Use of literature values may produce either over- or underestimation of constituents' concentrations in the aquifer. Deviations from assumed literature values may significantly affect contaminant fate predictions. In general, conservative values were used, which produced conservative results.

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 a sharply varying heterogeneous media.

5.6 SUMMARY AND CONCLUSIONS

Based on site characterization and monitoring data, metals, organic compounds, and explosives-related compounds exist in the surface and subsurface soils at LL 1. Fate and transport modeling indicates that some of these contaminants may have been leaching from contaminated soils into the groundwater beneath the source areas. Migration of most of the constituents, however, has been attenuated because of moderate to high retardation factors.

Based on the leachability analysis, seven explosives-related compounds, six metals, four pesticides and PCBs, and six PAHs were identified as initial CMCOPCs for all the aggregates combined. However, based on time screen, most of these constituents were eliminated from further analysis as they are expected to take more than 1,000 years before migrating to the water table. The remaining CMCOPCs included 2,4-DNT, 2,6-DNT, 1,3,5-TNB, 1,3-DNB, nitrobenzene, RDX, carbazole, and pentachlorphenol. None of these constituents remained CMCOPCs at the soil aggregates that included the area around the base of the former Water Tower, former Change Houses (CB-12, CB-23, CB-8, and CB-22), the railroad track bed, and the Perimeter Area.

SESOIL modeling results indicated that 2,4-DNT, 2,6-DNT, and RDX from Buildings CB-13/CB-10; RDX from Buildings CB-3/CB-801 and Buildings CB-14, CB-17, and CA-15; and 1,3,5-TNB, 1,3-DNB, 2,4-DNT, nitrobenzene, and RDX from Buildings CB-4/4A and CA-6/6A are expected to leach to groundwater with concentration exceeding the groundwater MCLs or RBCs just beneath the source areas. However, AT123D modeling results indicated that potential off-site migration of these contaminants via groundwater pathways at LL 1 is not expected to be a problem.