

## 7. FATE AND TRANSPORT

This section evaluates the fate and transport of soil and groundwater COPCs at the Site. Primary fate and transport mechanisms occurring at the Site are discussed, as well as a more detailed analysis of groundwater conditions. No COPCs were identified for Ennis Creek sediments. The objective of the fate and transport analysis is to identify the primary mechanisms affecting the distribution and migration of COPCs and the ultimate fate of the COPCs.

### 7.1 Primary Fate and Transport Mechanisms

Primary fate and transport mechanisms for contaminants potentially present in the Uplands Environment of the Site include the following:

- Volatilization of chemicals from soil
- Degradation of chemicals in soil and groundwater
- Erosion of particulate-bound chemicals from soil
- Leaching from soil with infiltrating water
- Transport of chemicals with groundwater flow.

#### 7.1.1 Volatilization

Volatilization can significantly affect the distribution of a chemical in the environment. In soils, the result is a decrease in the amount of a chemical in soil as the chemical volatilizes to soil gas and ultimately discharges to the atmosphere. The end result is a reduction in chemical concentration in soil over time. Volatilization reactions are most significant in surface soils that are in direct (or near-direct) contact with the atmosphere.

Chemical volatility is typically quantified by a chemical's Henry's constant. Henry's constant may be calculated from the chemical's vapor pressure, molecular weight, and solubility. The lower the Henry's constant, the less volatile the chemical. Values of Henry's constant for soil COPCs are summarized in Table 7-1.

The majority of the Site COPCs are characterized by low Henry's constants (i.e.,  $< 0.01$ ), and thus volatilization is not anticipated to substantially influence the fate of these compounds at the Site. Table 7.1 includes several alkanes that frequently comprise the diesel- and residual-range petroleum fractions detected locally in soils at the Site. Although these compounds are less volatile than lighter-weight petroleum fractions (e.g., gasoline-range organics), they are fairly volatile, and volatilization is likely to result in some depletion of petroleum hydrocarbon mass at the Site, particularly that fraction associated with surface soils.

### 7.1.2 Degradation

Numerous chemicals in the environment are subject to naturally occurring biotic (biologically based) and abiotic (non-biologically based) transformation reactions that result in the degradation of the chemical. Many organic compounds are subject to biodegradation reactions under aerobic (in the presence of oxygen) and anaerobic (in the absence of oxygen) conditions. During biodegradation, naturally occurring microorganisms in the subsurface transform a chemical to another state as a direct or indirect consequence of their metabolic processes. Biodegradation reactions often break down organic chemicals to less toxic forms.

Several naturally occurring abiotic reactions can significantly affect the fate of chemicals in the environment. Common abiotic reactions include photodegradation and hydrolysis. Photodegradation is the process of decomposition of a chemical upon exposure to radiant energy such as the action of light, and is most significant to chemicals in surface soil that are in direct contact with sunlight. Hydrolysis is the degradation reaction of the chemical with components of water (e.g., hydroxyl and hydronium ions) and is thus most important in saturated environments.

Degradative processes are unlikely to substantially influence the concentrations of the majority of the COPCs identified in soils at the Site. PCDD/Fs are highly stable under most environmental conditions, and the predominant degradation mechanism affecting their fate is photodegradation. However, this process is limited to PCDD/Fs in the uppermost surface soils and is unlikely to substantially influence the overall occurrence of these compounds at the Site. Similarly, the pesticides, PCBs, and SVOCs identified as COPCs have some potential to degrade in response to abiotic and/or biotic processes; however, the effects of degradation on the fate of these compounds are unlikely to be significant over the near-term. None of the metals at the Site will be influenced by degradation processes.

Petroleum hydrocarbons are known to be biodegraded, particularly under aerobic conditions. It is probable that biodegradation processes have been acting to reduce petroleum concentrations in Site soils, and it is anticipated that these processes will continue to further reduce the concentration of petroleum-related constituents at the Site into the future.

### 7.1.3 Erosion Processes

Erosion processes can substantially affect the distribution of soil-bound particulates in the environment and thus influence the distribution of soil contaminants. High winds can scour fine particles from the soil surface and redistribute these particles downwind. Similarly, runoff resulting from heavy precipitation events can scour fine soil particles from surface soils, eventually depositing the particles during sedimentation downstream. These physical processes often represent the primary mechanism for transport of otherwise immobile chemicals such as metals or PCDD/Fs.

Wind erosion has the potential to affect the distribution of chemicals in surface soils at the Site. The wind direction at the Site is predominantly from the south and southeast, and

(less frequently) from the west-northwest. Under high-wind conditions, there is a potential for fine-sized particles (dust) to be eroded from the immediate soil surface and eventually redeposited in downwind areas. Under the predominant wind direction at the Site, there is a potential for dust particles to be deposited in the Port Angeles Harbor and the Strait of Juan de Fuca—ultimately settling onto surface sediments. However, wind erosion is not anticipated to significantly mobilize COPCs from soils, as much of the Site is either covered with asphalt, concrete, or concrete debris.

Water erosion can also significantly influence the distribution of COPCs in surface soils. Stormwater is currently managed under the Site stormwater management plan (Rayonier 2003), which calls for engineered drainage controls to minimize erosion and capture the majority of stormwater runoff for treatment (if necessary) prior to discharge to Port Angeles Harbor. As a result, water erosion has some potential to redistribute contaminants in surface soils on a localized basis, but offsite migration of these contaminants would be minimal.

#### **7.1.4 Leaching**

Chemicals in soils have the potential to migrate to greater depths with infiltrating water. As rainwater infiltrates, chemicals may be leached from the soil and carried to greater depths and potentially to groundwater. The degree to which a chemical is leached is strongly influenced by the chemical's tendency to partition to the solid or aqueous phases, which is largely a function of the chemical's solubility and particle affinity.

##### **7.1.4.1 Solubility**

Water solubility describes the amount of a chemical that will dissolve in a given quantity of water, and thus is a primary determinant in the transport of a chemical in the environment. Highly soluble chemicals can often readily dissolve in water and are thus susceptible to being mobilized from the soil matrix with infiltrating water and migrate to groundwater.

The solubility of organic chemicals is typically a function of the hydrophobic nature of the chemical. Many organic chemicals are non-polar and thus do not dissolve readily into water—a polar solution. Strongly non-polar compounds, such as PCDD/Fs, have low water solubility and therefore are rarely present in water. Table 7.1 summarizes the water solubility of the organic COPCs identified for soils at the Site. In general, the soil COPCs have low to extremely low water solubility, indicating that these compounds are unlikely to dissolve at high concentrations into Site groundwater or surface water. This conclusion is consistent with the general absence of these chemicals in Site groundwater.

The solubility of inorganic chemicals is typically a function of the tendency of the chemical to form mineral phases and the relative abundance of the chemical ingredients required to form the mineral phase. The solubility is not explicitly provided in Table 7-1 for the inorganic COPCs, as the solubility of these compounds is highly dependent on solution conditions at the Site. Arsenic and chromium will change oxidation state,

depending on reduction-oxidation (redox) conditions in groundwater<sup>15</sup>. Arsenic is most commonly present in aqueous environments as  $\text{As}^{3+}$  or  $\text{As}^{5+}$ . Both arsenic species are soluble (relative to risk-based levels of concern) under most environmental conditions, and the aqueous concentration of arsenic is unlikely to be controlled by a specific mineral phase. Chromium is most frequently present as  $\text{Cr}^{3+}$  or  $\text{Cr}^{6+}$  in the environment.  $\text{Cr}^{6+}$  is substantially more soluble and mobile than  $\text{Cr}^{3+}$ , which will readily precipitate as the mineral  $\text{Cr}_2\text{O}_3$ . As a result, chromium is typically immobile in reducing (i.e., anoxic) environments.

#### 7.1.4.2 Adsorption

The aqueous concentration of chemicals in soil systems can also be substantially influenced by adsorption reactions to the soil matrix. Adsorption is the ability of a substance to bind to the surface of soil particles as a result of reactions that occur between the chemical and the soil particle surface. The tendency for a chemical to be adsorbed is a function of the nature of the chemical and the site-specific soil properties, and is typically quantified by a distribution coefficient ( $K_d$ ). A  $K_d$  is a measure of the ratio of chemical mass that partitions to the solid and liquid phases under equilibrium conditions.

Inorganic compounds are commonly bound to soil particles as a result of electrostatic interactions. The mineral hydrous ferric oxide ( $\text{FeOOH}$ ) is a dominant sorbent for many inorganic compounds in natural systems, owing to its common presence on soil particle surfaces, high surface area, and amphoteric<sup>16</sup> character. As a result, the site-specific  $K_d$  for inorganic compounds is often correlated to the concentration of hydrous ferric oxide in the soil matrix.

Organic compounds are frequently non-polar and thus tend to interact with organic matter commonly associated with the soil matrix. The general tendency of an organic chemical to be adsorbed by soils may be assessed by the chemical's organic carbon partition coefficient ( $K_{oc}$ ), which describes the tendency of the chemical to partition from water to organic carbon. The site-specific  $K_d$  for organic chemicals can be estimated as the product of the fraction of organic carbon ( $f_{oc}$ ) in the soil matrix and the chemical's  $K_{oc}$ .

Table 7-1 summarizes the  $K_d$  values for Site COPCs. Where available, the  $K_d$  values are the default values provided by MTCA to allow for a conservative estimation of the tendency of chemicals to migrate with infiltrating water from soil to groundwater (Ecology 2003). The  $K_d$  values for organic chemicals are estimated based on the  $K_{oc}$  values provided by MTCA (where available) and MTCA's default  $f_{oc}$  of 0.001.

The majority of the COPCs are expected to be strongly adsorbed by Site soils. PCDD/Fs have a very high  $K_d$ —consistent with their immobile character in environmental systems. Similarly, the  $K_d$  values for the SVOCs and Aroclor 1260 (the primary PCB congener detected in onsite soils) are high (>300 L/kg), suggesting that adsorption is likely to highly

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<sup>15</sup> When oxygen is absent, the redox potential is low and when it is present the redox potential is high.

<sup>16</sup> Hydrous ferric oxide is capable of acting as both an acid and a base, and can have both positive and negatively charged functional groups at its surface. This allows the mineral to be capable of binding both cationic and anionic compounds.

limit the migration of these compounds. The migration of arsenic, chromium (VI), and the lighter-weight petroleum fractions (e.g., undecane) are expected to be moderately attenuated by adsorption.

### **7.1.5 Site Conditions**

The majority of chemicals present in Site soils have likely been present for many years. With the exception of environmental improvements made between the 1960s and 1990s, Site operations were generally similar between the 1940s and cessation of operations in 1997. Groundwater samples collected in 2003 were collected six years after operations ceased, and, as discussed in the following section, there have not been significant increases in COPC concentrations in groundwater since monitoring began in 1997. Monitoring generally shows decreasing or stable COPC concentrations over the last six years. Given these trends and the shallow depth of the underlying aquifer system, it is anticipated that sufficient time has passed to allow for migration from soils to groundwater and that significant additional leaching, if any, is unlikely.

A number of geochemical conditions that can influence chemical behavior in groundwater are highly variable throughout the Site, and may help to explain the patchy distribution of elevated chemical concentrations (discussed in the following sections). Although the pH of groundwater is generally neutral (between 6 and 8 pH units, there are a few locations with unusually high pH (11.4 at MW-29 and 12.0 at MW-56) or unusually low pH (4.5 at PZ-04). Station MW-59 had usually high concentrations of organic carbon (1,070 ppm) and tannins/lignins (786 ppm), which are known to complex with metals and organic compounds, and may enhance metal solubility. Oxygen concentrations are low at many locations, typically below 2 ppm and sometimes below 1 ppm. These sub-oxic conditions may become locally anoxic, enhancing the reductive dissolution of iron and manganese oxyhydroxide and any associated trace metals (e.g., arsenic, copper). Not surprisingly, wells next to the shoreline (e.g., MW-51, MW-54, MW-55, MW-56, MW-59), have elevated conductivity and total dissolved solids, probably due to the influence of seawater infiltration at the nearshore. It is likely that these groundwater-seawater mixing zones are locations of active flocculation, sorption, and redox processes.

## **7.2 Fate And Transport of COPCs in Groundwater**

The assessment of chemical fate and transport in groundwater focuses on the distribution, historical trends, and subsurface migration of COPCs. COPCs in groundwater may be transported to saltwater in Port Angeles Harbor or, to a lesser extent, to freshwater in Ennis Creek.

The rate of migration of COPCs in groundwater is largely dictated by the groundwater flow rate, interstitial velocity, and the chemical-specific attenuation.

As discussed in Section 6, the groundwater flow rate (Q) to the harbor is estimated as a product of the hydraulic conductivity, the hydraulic gradient, the average thickness of the saturated shallow aquifer, and the width of the interface between groundwater and the sea

(the shoreline). As shown below, the relative thinness and low hydraulic gradient of the aquifer limit the flux of groundwater to the harbor:

$$Q \text{ (average)} = 8 \text{ ft/day} \times 0.006 \times 10 \text{ ft} \times 2,700 \text{ ft} = 1,500 \text{ ft}^3/\text{day} \text{ or } 6.5 \text{ gpm.}$$

The average interstitial velocity ( $v$ ) at which groundwater flows beneath the lower, northern portion of the Site is estimated as the product of the hydraulic conductivity and the hydraulic gradient divided by the effective porosity:

$$v \text{ (average)} = 8 \text{ ft/day} \times 0.006/0.3 = 0.15 \text{ ft/day}$$

Thus, groundwater flowing across the lower, northern portion of the Site (i.e., between PZ-4 and the shoreline), will take approximately 4,000 days (or 11 years) to cross the 600 ft to the shoreline.

Chemical migration rates are often slowed relative to groundwater flow due to attenuation reactions that occur in the subsurface. As discussed earlier in this section, two common attenuation mechanisms are adsorption and degradation reactions—both of which are highly dependent on subsurface conditions. The effect of adsorption reactions on chemical migration rates is typically quantified through the use of a retardation factor ( $R$ ), which may be estimated from the chemical-specific partition coefficient ( $K_d$ ) and soil bulk density ( $\rho_b$ ) and porosity ( $n$ ) per the following equation:

$$R = 1 + (\rho_b/n) \times K_d.$$

The velocity of contaminant migration ( $v_c$ ) can then be estimated from the interstitial velocity ( $v$ ) as:

$$v_c = v/R.$$

Table 7-1 includes calculated retardation factors for Site COPCs based on conservative  $K_d$  values provided by MTCA. The effects of retardation can be significant, particularly for compounds characterized by high  $C$  values. For example, the above calculations indicate that chrysene, an SVOC, would migrate at a rate of nearly 2,000 times slower than groundwater flow.

### 7.2.1 Semivolatile Organic Compounds

The RI and historic detections of SVOC and PAH COPCs are dispersed spatially, with the exception of chrysene, which was widely detected at low concentrations during the 2003 sampling event. Detections of these COPCs have only marginally exceeded screening criteria (typically less than a factor of 2). The single exception is the MW-23 detection of pentachlorophenol of 83 ppb in December 2002. The concentration at MW-23 in 2003 was 5.4 ppb, near the screening criteria.

In general, the high number of aromatic rings and molecular weight of SVOCs and PAHs results in low water solubility and high  $K_{oc}$  (Table 7-1). The high  $K_{oc}$  values (and thus

high  $K_d$  values) indicate a strong tendency for the compound to partition in the organic matter in soil, resulting in lower mobility. Calculated retardation factors (Table 7-1) indicate that migration of COPC SVOCs will be several orders of magnitude slower than advective groundwater flow.

With  $K_d$  values ranging from 350 to 3,500, even the most water-soluble COPCs would not be readily mobile in the dissolved phase. This observation is consistent with the lack of 2,4,6-trichlorophenol and pentachlorophenol detections in wells downgradient of MW-23, where the highest detections of both compounds occurred in 2003. There are no wells downgradient of MW-51 and MW-56 (shoreline wells), where the higher detections of benzo(a)anthracene and chrysene occurred in 2003. However, migration rates of these compounds are expected to be extremely slow.

The lack of mobility is further illustrated by the number and distribution of SVOCs in soil exceeding screening criteria compared to the sporadic, low number of occurrences of screening exceedences in groundwater. For example, chrysene was detected above the Method B unrestricted soil criterion in 13 samples and was the most frequently detected PAH in the main process area. Chrysene was detected in only one well above groundwater screening criteria in the main process area (MW-51). The Method B unrestricted soil criterion was exceeded for seven PAHs at nine of the 31 RI sampling locations. Groundwater COPCs were limited to two PAHs at two of the 20 sampling locations.

Pilings treated with creosote were used in construction of the mill. The primary chemicals of concern in creosote are PAHs. Previous discussions in this section indicate that PAHs have a low potential to migrate in groundwater. In addition, of the 304 PAH analyses conducted on groundwater samples collected from the site during the RI, only three had detected concentrations above the minimum screening criteria (see Table 6-5). The former east roll storage warehouse was supported by numerous creosoted pilings. Two subsurface soil samples were collected from within the building footprint during the RI and no PAHs were detected in either sample. This information suggests that the creosote treated pilings are not a concern as a source of PAHs.

The key conclusions regarding the fate and transport of the SVOC and PAH COPCs in groundwater are as follows:

- Detections have been widely spaced, spatially and temporally.
- Detections have typically been within a factor of 2 or less of the screening criteria.
- The  $K_{oc}$  and solubility of the COPCs are not conducive to mobility.
- The types of chemicals and concentration distributions observed in soil are not consistent with the types of chemicals and concentration distribution observed in groundwater.

## 7.2.2 Metals

Metals, which are naturally occurring, were detected in virtually all groundwater samples. Background or reference concentrations have not been established for chemicals in Site groundwater. Table 6-4 of EPA's ESI (E&E 1998) shows that data from PZ-12 were used as background for evaluating groundwater samples collected during EPA's ESI. EPA's rationale for selecting PZ-12 as the background well appears on page 6-3 of the ESI - "Groundwater sample results are compared to sample PZ-12, collected from a piezometer located south of the secondary wastewater treatment plant. This sample was selected as the background groundwater sample; because it was collected from the same shallow aquifer as the other groundwater samples, it is located in an area upgradient of the site and the remainder of the groundwater samples and concentrations in this sample were sufficiently low to meet background sample objectives."

Using well PZ-12 as a reference (except arsenic, which uses the state of Washington natural background value), the number of locations with detected values elevated above reference (EAR) by ratios greater than 2, 5, and 10 are summarized below.

**Number of Metals Samples (2003) Exceeding  
EAR at the Ratio Shown**

| COPC     | Ratio >2 | Ratio >5 | Ratio >10 |
|----------|----------|----------|-----------|
| Arsenic  | 2        | 1        | 1         |
| Chromium | 9        | 6        | 4         |
| Copper   | 8        | 3        | 1         |
| Nickel   | 3        | 0        | 0         |
| Mercury  | 6        | 2        | 0         |

The relative proportion of metals between the dissolved and particulate phases is controlled by a complex combination of precipitation and sorption reactions. In addition, metals in solution may exist as "free" ions or complexed with other dissolved inorganic or organic compounds. Water solubility is a primary determinant in the transport of a chemical in the environment. As noted in Section 7.1, the solubility of metals is highly dependent on geochemical conditions at the Site.

Solubility of metals will be controlled by precipitation and adsorption reactions, which are likely to be the most significant factors affecting metals migration.  $K_d$  factors published by Ecology (Table 7.1) for metals COPCs indicate a large range in the migration rates and retardation. The magnitude of these mechanisms on metals migration and retardation will be a function of solution chemistry, including pH, oxygen concentration, and the concentrations of other chemicals in groundwater—all of which vary widely across the Site. Further, as discussed in Section 7.1, hydrous ferric oxide is a dominant sorbent in most environmental systems. The effects of iron adsorption can be dynamic. Variations in the oxidation conditions in the aquifer can lead to the precipitation or dissolution of hydrous ferric oxide from the aquifer matrix. Generally, dissolved iron will precipitate as hydrous ferric oxide in the presence of oxygen in the aquifer, resulting in depletion of dissolved metal mass from groundwater as the metal adsorbs to the oxide surface.

Conversely, if reduced conditions are established in the aquifer (e.g., as the result of the release of an organic-rich solution), hydrous ferric oxide may be dissolved and adsorbed metals released to groundwater. Both oxidized and reduced conditions are present at the Site and are expected to evolve as organic-rich materials are depleted due to naturally occurring degradation reactions. As a result, the effect of adsorption on metals migration is likely to vary across the Site, both temporally and spatially.

The fate and transport of metals COPCs in groundwater are summarized in the following sections.

### 7.2.2.1 Arsenic

Arsenic is typically present in groundwater as its trivalent state (as the anion  $\text{H}_2\text{AsO}_3^-$  or as  $\text{H}_3\text{AsO}_3$ ) under reduced conditions and its pentavalent state (as the anions  $\text{H}_2\text{AsO}_4^-$  or  $\text{HAsO}_4^{2-}$ ) under oxidized conditions. The trivalent forms are generally more poorly sorbed, and thus more mobile than the pentavalent forms. Overall, arsenic is moderately soluble and is readily transported in groundwater.

Four samples collected in 2003 exceeded screening criteria. The highest arsenic concentrations were observed at MW-59 and PZ-9, both of which displayed unusually high concentrations of TOC and lignin/tannins. Both are located near the former SSL lagoon.

Current and historic arsenic concentrations above screening criteria are summarized on Figure 7-1. As shown, arsenic has been detected in four wells at concentrations above screening criteria. The two wells described above (PZ-9 and MW-56), have had higher concentrations of arsenic in the past. MW-59 concentrations decreased over the two events in which it was analyzed. Arsenic concentration in RI soil samples from the PZ-9 and MW59 area (SSL20, SSL21, SSL22) did not have high arsenic concentrations (2.7 to 3 ppm). Reductive dissolution of aquifer arsenic (due to historical SSL releases) is a potential source for the arsenic concentrations observed in this area.

Arsenic has exceeded criteria at two wells downgradient of the main process area. MW-51 just exceeded criteria for the first time in 2003. Concentrations at MW-56 have been decreasing with an exceedence of less than two times criteria in 2003.

The ratio (EAR) of 2003 concentrations to that of natural background is greater than 2 for two wells and greater than 10 for one well (MW-59).

### 7.2.2.2 Chromium

Chromium typically exists in groundwater in its trivalent or hexavalent oxidation state. As discussed in above,  $\text{Cr}^{3+}$  is much less soluble in groundwater than  $\text{Cr}^{6+}$ . Two groundwater samples collected in 2003 exceeded screening criteria—both by a factor of 3 or less. Historical detections of chromium above screening criteria have been limited to wells PZ-9, MW-59, MW-51 and MW-56 (Figure 7-2). The 12 historical detections above screening criteria ranged up to 1.15 ppm. As was the case for arsenic, PZ-9 and MW-59 have the highest chromium concentrations, although concentrations have been decreasing or stable since 1997. MW-56 had only one historical exceedence of screening criteria.

The ratios of 2003 concentrations to that of PZ-12, the upgradient well, are typically between 2 and 5, indicating that most concentrations observed at the Site are near reference levels.

### **7.2.2.3 Copper**

Copper is strongly bound to inorganic and organic materials in soil and groundwater. Eleven groundwater samples collected in 2003 had detected concentrations above screening criteria. Over the entire monitoring period, copper has been detected in 14 wells at concentrations above screening criteria (Figure 7-3). The highest copper concentrations have been at the wells near the former SSL lagoon, MW-56 and PZ-9. There is no discernable increasing or decreasing trends for these wells. The highest copper concentration measured in 2003 was found at MW-56, which also had an unusually high pH (12.0).

### **7.2.2.4 Nickel**

Nickel was detected at three wells in 2003 at concentrations above screening criteria. Historically, concentrations at MW-54 and MW-55 were above screening criteria; however, concentrations were less than screening criteria in 2003. The most recent two monitoring events show decreasing concentrations at MW-56 and MW-59 (Figure 7-4).

### **7.2.2.5 Mercury**

Mercury is typically present as a free cation ( $\text{Hg}^{2+}$ ) in most natural water systems. Mercury has only been sampled during the 2003 RI investigation. Dissolved mercury exceeded screening criteria at MW-56 and MW-57, both by a factor of less than 2.

### **7.2.2.6 Metals Summary**

The key conclusions regarding the fate and transport of metals COPCs in groundwater are as follows:

- Based on the configuration of the wells and the detected concentrations, the metals COPCs in groundwater do not appear to have identifiable downgradient migration patterns or concentration plumes that would be expected if a localized source was present.
- Metals distribution patterns can be partially explained by some of the unusual chemical conditions that are present in Site groundwater. Locations with elevated TOC and lignin/tannin also have elevated concentrations of arsenic, chromium, copper, and nickel. Wells with unusually high pH (i.e., MW-56 and MW-29) also tended to have elevated metals concentrations.
- Patchy concentration distributions may be due to the highly variable geochemical conditions (pH, dissolved oxygen, conductivity, TOC content) in Site groundwater.

### 7.2.3 Pesticides and PCBs

In general, sorption to organic matter and dissolution rates are important factors limiting the mobility and transport of pesticides and PCBs in groundwater. Solubility and volatility tends to be low for these chemicals (Table 6-1), indicating that they are not readily dissolved in groundwater. Furthermore, the high retardation factors that characterize these chemicals highlight the tendency for the migration of these chemicals to be greatly slowed by sorption reactions. Estimated retardation factors indicate the chemical migration rates for dissolved pesticides and PCBs are 50 to 3,500 times slower than the rate of groundwater movement.

Detections of pesticides are limited to the 2003 sampling event. The low detection limits achieved with the 2003 sampling event resulted in a total of 23 pesticide detections above screening criteria. The distribution of detected pesticides in groundwater is sporadic and does not appear to be related to locations where other pesticides are detected or to specific areas of the Site (Figures 6-38 through 6-46). For example, four COPC pesticides were detected (both above and below screening criteria) at one location (PZ-10) and three pesticides were detected at five locations (PZ-3, MW-52, MW-53, MW-57, and MW-59), each with a different suite of COPCs. Pesticide COPCs were not detected at seven locations.

No reference values for pesticides in groundwater have been established for the Site. 4,4-DDD was detected in the upgradient well (PZ-12), and alpha chlordane exceeded the screening criteria. These values and the lowest non-detected values of the other analytes are used in the table below to evaluate EARs.

**Number of Pesticide Samples (2003) Greater Than Screening Criteria Exceeding EAR at the Ratio Shown**

| COPC            | Ratio | Ratio >2 | Ratio >5 | Ratio >10 |
|-----------------|-------|----------|----------|-----------|
| 4,4-DDD         | 7     | 0        | 0        | 0         |
| 4,4-DDE         | 2     | 2        | 2        | 2         |
| 4,4-DDT         | 5     | 5        | 1        | 1         |
| alpha Chlordane | 3     | 1        | 0        | 0         |
| Dieldrin        | 2     | 2        | 1        | 1         |
| Endrin          | 1     | 1        | 1        | 1         |
| Heptachlor      | 3     | 3        | 2        | 2         |

Fourteen of the 23 detected concentrations of pesticide COPCs exceeded the EAR by a factor of 2 or more. Seven of the detected concentrations exceed the EAR by a factor of 10 or more.

### 7.2.4 Ammonia

Ammonia is very soluble and readily transported in groundwater. It is also readily oxidized, and will transform to more oxidized forms of nitrogen in the presence of oxygen. There is an inverse correlation between dissolved oxygen and ammonia among wells at the

Site. Wells with low dissolved oxygen (e.g., <1 ppm O<sub>2</sub>) tend to have high ammonia concentrations. The most likely source of ammonia is organic matter, which is present in material used as fill on the Site.

Seven samples collected in 2003 had ammonia (as NH<sub>3</sub>) concentrations above screening criteria. The locations of wells with high ammonia concentrations in 2003 are consistent with historical data. MW-56 and MW-57 have had the highest concentrations, followed by MW-29, PZ-2 (not sampled in 2003), PZ-3, and PZ-9. Generally, there do not appear to be increasing or decreasing trends in ammonia concentrations with time.

A spatial trend may be present downgradient of MW-57, where the highest 2003 concentration was detected at 4.64 ppm. Downgradient wells (PZ-4, MW-54 and MW-55) had concentrations of 0.11 ppm or lower.

## 7.3 Loading Evaluation

### 7.3.1 Ennis Creek

Potential loading of Site COPCs to sediments in Ennis Creek has been directly measured by collection of sediment samples during the RI and previous studies. None of the sediment samples contained COPCs at concentrations exceeding the sediment quality benchmarks used in Washington State as guidance values or upgradient background. Therefore, Ennis Creek sediments are no longer considered a media of concern at the Site.

### 7.3.2 Port Angeles Harbor

Loading of dissolved metals and organic compounds to Port Angeles Harbor can be estimated from the groundwater flow and the average water quality data from wells located near the shoreline. The mass of COPCs discharging daily along the shoreline can be estimated as the product of the underflow and the average concentrations as shown below:

$$\text{Mass} = Q (\text{mean}) \times C (\text{mean})$$

Where:

- Q (mean) = the mean groundwater discharge based on mean hydraulic conductivity and mean hydraulic gradients (see Section 7.1.5)
- C (mean) = the mean COPC concentrations of shoreline wells (PZ-3, PZ-9, MW-53, MW-54, MW-55, MW-56, and MW-59) for the 2003 monitoring event

These calculations are order-of-magnitude estimates because of the simplifying assumptions used. The primary assumptions affecting the values include:

- The gradients assumed for the shallow aquifer represent an average over several years during different seasons and tides.
- The thickness of the aquifer is variable and undefined in some areas of the Site. An average saturated thickness of 10 ft was used in the calculations.

- The flow front length includes the entire Site. COPC concentrations vary spatially at shoreline wells, and local loading will vary.
- The calculations are conservative in that no attenuation or retardation of chemical migration is considered.

Metals loading is estimated to be 1/1000th of a pound or less per day. Organic compound loading is estimated to be two to four orders of magnitude less.

The average discharge of groundwater underflow into the harbor is estimated to be 6.5 gallons per minute across the 2,700-ft shoreline. COPCs in groundwater will mix with seawater at the interface in response to tidal fluctuations and currents. The concentrations of COPCs in seawater, therefore, are expected to be several orders of magnitude less than concentrations in the groundwater.

Groundwater flow to Ennis Creek was not quantified in the calculations above. Groundwater elevation measurements made in previous investigations indicate a predominantly northerly groundwater flow direction towards Port Angeles Harbor with a locally variable lateral component towards Ennis Creek (HLA, 1993). The extent of contamination from this lateral movement is considered minor, and has not resulted in elevated chemical levels in the creek as noted by the sediment samples collected by EPA and discussed in Section 5.3.

## 7.4 Fate and Transport Summary

The fate and transport of COPCs in soil and groundwater are governed by physical and chemical properties, including volatilization, degradation, erosion, leaching, and transport with groundwater flow. Volatilization is not expected to be an important fate and transport parameter with Site chemicals. Degradation via photodegradation, hydrolysis, abiotic, and biotic process is also not expected to be an important process for most Site COPCs; however, ammonia is very susceptible to redox transformations and is likely to oxidize at the shoreline mixing zone between seawater and groundwater and upon discharge to the oxygen-rich marine waters. Erosion may have some capacity to distribute Site COPCs in sloped areas not covered with asphalt, concrete, or concrete debris, although these exposed areas do not currently exist. Leaching of Site soil COPCs to groundwater is not expected to be a significant future transport mechanism. The majority of Site soil COPCs have been present for many years and monitoring following Site closure in 1997 has generally shown 1) a general lack identifiable soil sources for observed groundwater detections, and 2) decreasing or stable concentrations in groundwater COPCs.

In general, historical groundwater data indicate that metals concentrations are decreasing or stable. Spatial distributions and comparison to soil data indicate no identifiable source in soil and no downgradient migration patterns or migration plumes. Metals distribution patterns can be partially explained by some of the unusual chemical conditions that are present in Site groundwater. Locations with elevated TOC and lignin/tannin also have elevated concentrations of arsenic, chromium, copper, and nickel. Wells with unusually

high pH (i.e., MW-56 and MW-29) also tended to have elevated metals concentrations. In general, patchy concentration distributions of groundwater COPCs may be due to the highly variable geochemical conditions (pH, dissolved oxygen, conductivity, TOC content) in Site groundwater.

A loading evaluation of groundwater transport was conducted for Ennis Creek and Port Angeles Harbor. Direct measurement of Ennis Creek sediments indicates that no Site COPCs are detected above screening criteria. Loading of dissolved COPCs to the harbor was calculated based on estimates of groundwater flow from the Site to the harbor and average concentrations of COPCs at shoreline wells. This evaluation estimated metals loading at less than 1/1000<sup>th</sup> of a pound per day and 2 to 4 orders of magnitude less for organic compounds. The loading calculations are conservative in that geochemical processes or mixing with seawater were not included in the evaluation.