***TECHNICAL MEMORANDUM***

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Date: June 20, 2007

Subject: Cadmium, Copper, and Lead Partition Coefficients for Berm Materials in T4 CDF Groundwater Transport Models

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This memorandum summarizes the technical information and rationale used to recommend appropriate site-specific cadmium, copper, and lead partition coefficients for characterizing berm materials in the “long-term” and “short-term” groundwater transport models being developed for the T4 confined disposal facility (CDF).

## 1. Background

Following filling of the CDF with dredged sediment, water is expected to migrate through CDF berm materials to the adjacent river and that water has the potential to transport constituents leached from the dredged sediment to the river. Groundwater transport models are being developed to predict concentrations of metals in groundwater flows to the river over time. A “short-term” transport model will predict transport of sediment-derived constituents through the berm during filling of the CDF with ponded river water and dredged material elutriate. A “long-term” transport model will predict potential for transport of sediment-derived constituents by groundwater migration through the CDF and berm after the CDF is fully constructed to an upland grade. Both models will take into account chemical attenuation resulting from metals partitioning to berm materials, and the modeled attenuation will be defined by partition coefficients (i.e., solid-solution distribution coefficient, $K_d$) selected to describe metals partitioning to the solids in berm construction materials.

This memo identifies data relied on to develop recommended mean and minimum $K_d$ values for these groundwater transport models. The recommended $K_d$ values are appropriate for the expected pH and ionic strength conditions during the filling of the CDF (i.e., short term) and after completion of the CDF (i.e., long term). The $K_d$ values recommended for use in both the short-term and long-term models are based on experimentally determined, pH-dependent values presented by Hassan et al. (1996). The effects of solution ionic strength were also considered in recommending minimum $K_d$ values for the long-term model.

## 2. Site-Specific Conditions

The berm material characteristics and the anticipated pH and ionic strength characteristics of water migrating through the berm are based on the following assumptions, as supported by site data to the extent possible.

### 2.1 Berm Chacteristics

The following assumptions regarding the characteristics of berm materials have been adopted:

- The berm materials will likely be locally-quarried sand and gravel. Local quarries provide materials that reflect the local geology, which is generally dominated by iron- and magnesium-rich, basaltic-andesitic volcanic rocks and volcanic sediments.

- Quarried materials are expected to contain low organic matter content and some iron-oxyhydroxide and clay minerals due to weathering of volcanic parent rock. They may also contain natural zeolite minerals. Iron oxyhydroxide and clay minerals are expected to provide metals sorption potential; the presence of zeolites would substantially increase the metals sorption potential of the berm materials.

### 2.2 Short-term Ponded-water Transport Conditions

The following assumptions regarding the characteristics of water migrating through the berm have been adopted for the short-term ponded-water transport scenario:

- River water pH = 7.0 to 7.6 ($10^{th}$ to $90^{th}$ percentile values from USGS monitoring data for Willamette River Portland gage); average pH = 7.2;

- Elutriate water generated from dredged sediment slurry will have conductivity slightly higher than river water, as indicated by modified-elutriate test (MET) results for sediment and water at 1:4 ratio (BBL, 2005);

- Average conductivity of river water = 76.5 μmho (USGS monitoring data for Willamette River Portland gage) and average conductivity of water from dredged sediment elutriate = 103 μmho.

Using equation (5) from Hassan et al. (1996) to convert conductivity in mS to ionic strength in moles/Liter (M), the ionic strength of the CDF ponded water migrating through the berm is expected to remain less than approximately 0.0015 M.

## 2.3 Long-term Groundwater Transport Conditions

Site Groundwater

The following assumptions regarding the characteristics of site groundwater have been adopted for the long-term groundwater transport scenario:

- Local groundwater has near-neutral pH typically ranging from 6.1 to 7.3 ($10^{th}$ to $90^{th}$ percentiles) and averaging 6.7.

- Local groundwater has electrical conductivity typically ranging from 0.18 milliSiemens (mS) to 0.76 mS ($10^{th}$ and $90^{th}$ percentiles), and averaging 0.42 mS.

Using equation (5) from Hassan et al. (1996) to convert conductivity in mS to ionic strength in moles/Liter (M), the ionic strength of groundwater typically ranges from 0.002 M to 0.010 M.

Dredged Sediment Leachate

The leachate generated by dredged sediments behind the berm is expected to have the following characteristics:

- Leachate has an average pH of 6.46.

- The average conductivity of leachate from sediment is 112 mS, and the calculated average ionic strength of leachate is approximately 1.46 M.

Leachate characteristics were determined from pancake column leaching test (PCLT) results, as presented in BBL (2005, Appendix F). Groundwater flow analysis indicates pore-volume turnover times in the CDF are likely to range from about 30 to 100 years. Therefore, only the first ten pore volumes were utilized in the PCLT test to estimate leachate pH and ionic strength. This is a conservative assumption because ionic strength of the leachate tends to decrease over time in the PCLT; therefore, preferential use of earlier leachate cycles will tend to reduce solids partitioning and reduce attenuation of constituents in the berm.

Groundwater-Leachate Mixing

The groundwater leachate mixture will comprise approximately 10 parts groundwater and 1 part leachate, based on Terminal 4 groundwater flow modeling. Based on simplistic two-component mixing assumptions, the pH of the 10:1 groundwater:leachate mixture will range from approximately 6.1 to 7.1, and the ionic strength will range from approximately 0.135 M to 0.141 M.

| Ionic Strength of Solution (GW:Leachate) | | | | |
|---|---|---|---|---|
| Groundwater conductivity and ionic strength | | | Leachate ionic strength | **GW:Leachate 10:1 Mix** |
| percentile of distribution | EC (mS) | IS (mM) | IS (mM) | **IS (mM)** |
| 90th | 0.76 | 9.88 | 1456 | **141.3** |
| 75th | 0.54 | 7.02 | 1456 | **138.7** |
| mean | 0.42 | 5.46 | 1456 | **137.3** |
| 25th | 0.22 | 2.86 | 1456 | **135.0** |
| 10th | 0.18 | 2.34 | 1456 | **134.5** |

### 3. Mean $K_d$ Values for Short-Term and Long-Term Models

Hassan et al. (1996) provide empirical data for clean sandy sediments, which are physically similar to berm construction materials. One of their sample sites – Ona Beach in Newport, Oregon – provides partitioning data for sandy sediments that are expected to be chemically similar to berm construction materials. Sand at Ona beach is derived from volcanic parent rocks in the Pacific Northwest. Also, the solution pH associated with Ona Beach sand (pH = 6.8) is neutral and consistent with both local site groundwater at Terminal 4 (mean pH = 6.7) and also Willamette River water (mean pH = 7.2). The Ona Beach data provide the basis for recommended mean $K_d$ values, which were previously approved in a memo from EPA's consultants dated April 27, 2007:

| **Approved Mean $K_d$s for Groundwater Transport Models** | **Cu** | **Cd** | **Pb** |
|---|---|---|---|
| Mean $K_d$ | 165 | 79 | 179 |

The mean $K_d$ values are applicable to both short-term and long-term groundwater models. These values are appropriate for the neutral pH of the CDF ponded water (comprised predominantly of Willamette River water) that migrates through the berm during the short-term model scenario and for near-neutral groundwater migrating through the berm during the long-term model scenario. However, if more acidic pH and/or higher ionic strength waters are present, for example when groundwater mixes with leachate from dredged material disposed in the CDF (refer to Section 2.3 above), metals partitioning to solids may be more limited. For this reason, minimum $K_d$ values, which account for the effects of possible pH and ionic strength variability, were developed for use in sensitivity analyses of the groundwater models, as discussed below.

### 4. Minimum $K_d$ Values for Short-Term Model

As noted above in Section 2.2, the minimum expected pH of ponded CDF water remains neutral (pH = 7) and the maximum expected ionic strength remains low (<0.0015 M). Therefore, variations in pH and/or ionic strength would have minimal effects on metals

partitioning in the short-term scenario. The lower end of the range of $K_d$ values reported for Ona Beach sand (Hassan et al., 1996) are recommended for use as minimum $K_d$ values for sensitivity analysis in the short-term model. These values are provided below:

| **Recommended Minimum $K_d$s for Short-Term Groundwater Model** | **Cu** | **Cd** | **Pb** |
|---|---|---|---|
| Minimum $K_d$ | 133 | 59 | 109 |

## 5. Consideration of pH for Minimum $K_d$ Values in Long-Term Model

The solution pH has a strong influence on metals partitioning to solids. Hassan et al. (1996) provide empirical data that can be used to compute pH-dependent partition coefficients for cadmium, copper, and lead partitioning to relatively clean river and beach sands. Hassan et al. (1996) describe these computed partition coefficients as "minimum $K_d$ values" for the purpose of screening sediments for potential to release metals to pore waters.

Regression equations from Hassan et al. (1996) were used to compute pH-specific $K_d$ values for cadmium, copper, and lead and to develop recommended minimum $K_d$ values for the long-term transport model. The 10$^{th}$ percentile pH value for the groundwater:leachate mixture (pH = 6.1) and the regression equations from Hassan et al. (1996) were used to compute the following minimum, pH-dependent, $K_d$ values:

| **Groundwater:Leachate at 10:1** | | **Calculated $K_d$ (pH adjusted)** | | |
|---|---|---|---|---|
| | pH | Cu | Cd | Pb |
| Minimum $K_d$ | 6.1 | 100 | 38 | 144 |

## 6. Consideration of Ionic Strength for Minimum $K_d$ Values in Long-Term Model

The ionic strength of the solution also has influence on metals partitioning to solids. Empirical data presented by Hassan et al. (1996) are based on results from batch tests performed with low ionic strength solutions (<0.005 M), whereas groundwater:leachate mixtures in the long-term scenario may have ionic strengths greater than approximately 0.135 M due to mixing with 1.46 M leachate from the CDF (refer to Section 2.3). Therefore, effects of ionic strength should also be considered for the minimum $K_d$ values that will be used in the long-term model.

Effects of ionic strength on metals partitioning behavior have been described in a number of relevant publications. These effects are summarized below, and the referenced scientific literature serves as the basis for the methods used to adjust metals $K_d$ values to account for higher ionic strength solutions migrating through the berm materials. Those adjustment methods are also described below.

## 6.1 Effect of ionic strength on metals partitioning

Hassan et al. (1996) conducted batch sorption tests using a range of ionic strength solutions and clean, chromatographic sand. They demonstrated that sorption behaviors of cadmium and lead, in particular, are sensitive to ionic strength effects (copper, nickel, and zinc sorption was not as sensitive to increases in ionic strength). Although Hassan et al. (1996) demonstrate that ionic strength is important for predicting metals partitioning, the results of their batch tests on chromatographic sand are not specifically applicable to the groundwater-berm interactions at the Terminal 4 CDF. Chromatographic sand has particularly low sorption potential and is not comparable, geochemically, to the local quarry materials that will ultimately be used to construct the CDF berm.

Other laboratory studies have been conducted on natural materials, primarily surface soils, to evaluate the effects of ionic strength on metals partitioning behavior. A number of metals sorption studies utilizing solutions of various ionic strengths were reviewed to identify a technical basis for adjusting cadmium and lead partition coefficients and address effects of the 0.136 M ionic strength of the groundwater solution.

For cadmium, Naidu et al. (1994) present a series of batch sorption tests conducted using soils with a range of metals sorption capacities and solutions with pH ranging from approximately 2 to 8 and ionic strengths ranging from 0.003 M to 1.5 M ($NaNO_3$). Test results from series run at varying ionic strength values are presented in Figures 4 and 6 of Naidu et al. (1994). Figure 4 presents results from tests run without adjusting pH as ionic strength was increased, and Figure 6 presents results from tests run holding pH constant while ionic strength increased. For soils with relatively low sorption capacities, the mass of cadmium sorbed decreased by approximately 70 percent (Figure 4c) to 20 percent (Figure 4d). However, during the course of the experiment, pH also decreased 0.4 to 1 pH unit, and the authors were not able to unequivocally separate the effects of pH and ionic strength on adsorption. When the solution pH was held constant at 6.5 and 6.0, the mass of cadmium sorbed to a soil with low sorption potential decreased when ionic strength was increased to 0.150 M, but the decreases observed were less than 5 percent at pH of 6.5 and approximately 10 to 15 percent at pH 6.0 (Figure 6a). The same tests were conducted on a soil with relatively higher sorption potential, and in those tests increasing ionic strength to 0.150 M reduced cadmium sorption by approximately 15 percent at solution pH of 6 and less than 5 percent at a solution pH of 7. The conclusion by Naidu et al. (1994) was that ionic strength had little effect on cadmium sorption above pH 6.

A similar soil-sorption study has not been performed for lead, to our knowledge based on recent literature review. However, previous studies have demonstrated that lead partitioning to solids may also be sensitive to solution ionic strength (e.g., refer to Harter and Naidu, 2001; Hassan et al., 1996; Puhls et al., 1991; DiToro and Mahony, 1984).

Puhls et al. (1991) tested lead sorption to kaolinite clay at varying pH and ionic strength conditions. At pH of 5 (refer to Figure 5 of Puhls et al. 1991), lead sorption decreased by 50 to 60 percent when ionic strength was increased from 0.010 M to 0.10 M ($NaClO_4$). The authors do not report whether pH also varied during the test series where ionic strength was varied.

Kooner (1993) tested lead sorption to synthetic goethite, in a system where goethite was abundant, and found no significant change in sorption from solutions with ionic strengths of 0.010 M and 0.100 M ($NaNO_3$).

Based on these and other studies, lead sorption by clays appears more strongly influenced by ionic strength than sorption to iron oxyhydroxide. Therefore, the extent to which ionic strength influences lead partitioning to solids depends to some extent on the solids that are present and their relative abundance. Both clays and iron-oxyhydroxide-type minerals are expected to be present in the quarried materials used for berm construction; however, their relative abundance in those materials is not known at this time.

## 6.2 Procedure for ionic strength adjustment of long-term model minimum $K_d$s

Based on available information about the berm materials and relevant published data in the scientific literature, the following adjustments appear warranted to provide the most conservative, or minimum, $K_d$ values for cadmium and lead. Assuming that the groundwater:leachate solution has an ionic strength of approximately 0.14 M and an average pH of approximately 6.7, the minimum $K_d$ values for cadmium and lead should be estimated as follows:

- 15 percent reduction in the mean $K_d$ value for cadmium. This reduction is consistent with the results reported in Naidu et al. (1994) for a range of soil sorption capacities.

- 30 percent reduction in the mean $K_d$ value lead. This is consistent with results indicating up to 60 percent reduction in lead sorption to clay and less than 5 percent reduction in lead sorption to goethite. Both clays and iron hydroxides are expected to be present in the berm materials.

The minimum $K_d$ value recommended for use in the long-term groundwater transport model is the smaller of two conservatively estimated $K_d$ values: either the pH-dependent $K_d$ computed for the minimum expected pH (pH = 6.1) or the ionic strength adjusted mean $K_d$ value. These values are summarized in the table below.

| **Recommended Minimum $K_d$s for Long-term Groundwater Transport Model** | **Cu** | **Cd** | **Pb** |
|---|---|---|---|
| Mean $K_d$ (previously recommended and accepted) | 165 | 79 | 179 |
| Mean $K_d$ adjusted (reduced) to address ionic strength effects | --- | 67 | 125 |
| Minimum $K_d$ calculated for 10:1 groundwater:leachate mixture with minimum pH = 6.1 | 100 | 38 | 144 |
| Recommended minimum $K_d$: smaller of either pH-dependent $K_d$ calculated for minimum pH or ionic strength adjusted mean $K_d$) | **100** | **38** | **125** |

Both the mean and recommended minimum $K_d$ values for each metal are considered conservative because they are based on conservative assumptions regarding the nature of the berm materials.

These $K_d$ values also appear conservative in light of the range of $K_d$ values that have been reported for soils and sediment under a range of geochemical conditions.

- Much higher cadmium $K_d$s (i.e., >500) have been measured for near-neutral, loamy/sandy soils (e.g., EPA, 1999). Lower cadmium $K_d$s have also been measured, but those correspond to more acidic pH conditions (i.e., <6) (e.g., EPA, 1999; Gomes et al., 2001).

- Published compilations of lead $K_d$s observed for a wide range of soils and sediments (e.g., EPA, 1999) with solution pH conditions as low as 4 do not include values as low as the proposed minimum $K_d$ value of 125.

## 7. Summary of Recommended $K_d$ Values

| **Recommended $K_d$s for Groundwater Transport Models** | **Cu** | **Cd** | **Pb** |
|---|---|---|---|
| **Short-Term Model** | | | |
| Mean $K_d$ | 165 | 79 | 179 |
| Minimum $K_d$ | 133 | 59 | 109 |
| **Long-Term Model** | | | |
| Mean $K_d$ | 165 | 79 | 179 |
| Minimum $K_d$ | 100 | 38 | 109* |

Note that the recommended minimum $K_d$ value for lead in the long-term model (previously calculated at 125) was further reduced to be consistent with the minimum $K_d$ value for lead in the short-term model (109; see asterisk). The difference between the two values is caused by two different analytical approaches – i.e., an empirically determined value was used for the short-term model (based on Ona Beach sand) whereas a more theoretically determined value was used for the long-term model (based on pH and ionic strength considerations). This small difference in $K_d$ values is likely within the uncertainty of the analysis. Therefore, for consistency, the smaller and more conservative short-term $K_d$ value was also assigned to the long-term scenario.

## 8. References


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