6.0 LOADING, FATE, AND TRANSPORT FOR SELECT CONTAMINANTS

This section presents an assessment of contaminant loading mechanisms to the Study Area from external sources as well as in-river processes affecting the concentration, transport, and fate of select contaminants within the Study Area. The evaluation provided in this section is presented in two main parts. First, Section 6.1 assesses current and historical contaminant inputs (i.e., external loading) to the Study Area. The loading terms/pathways discussed include upstream loading via surface water and sediment bedload, stormwater runoff, permitted point-source and non-stormwater discharges, upland groundwater plume transport to river, atmospheric deposition to the river surface, direct upland soil and riverbank erosion, groundwater advection through subsurface sediments (chemical partitioning from subsurface sediment to pore water and advection to the surface sediment interval), and overwater releases. Loading from surface sediment to the surface water via sediment erosion and resuspension is not quantitatively evaluated in this RI report. Second, Section 6.2 describes fate and transport processes that act on contaminants in abiotic and biotic media within the Study Area. The discussion of fate and transport processes is grouped into sediment and pore water processes, surface water processes, and biotic processes.

The primary purpose of this loading assessment and discussion of relevant fate and transport processes is to support development of the CSM, which is presented in Section 10. –The loading assessment will also support the fate and transport modeling effort, which is being conducted in parallel with development of the RI to support the FS and will be documented in separate project deliverables.

The information presented in this section is organized by individual loading, fate, and transport mechanism. A comparative, contaminant-by-contaminant assessment of these processes is presented in the CSM, along with the other informational components considered in development of the CSM, including the observed cross-media contaminant distribution patterns, the potential for human and ecological exposure, and the understanding of current and historical sources.

The contaminant lists for this assessment are presented in Table 6.0-1. This table includes separate lists for surface water, stormwater, upland groundwater plumes, atmospheric deposition, and equilibrium partitioning (advective loading from subsurface sediment to surface sediment and from surface sediment to surface water). These lists were generated from the overall list of contaminants for loading, fate, and transport developed in consultation with USEPA, and reflect data availability by media and relevance of the contaminant to the loading mechanism. For example, equilibrium partitioning contaminants primarily focus on hydrophobic ~~chemicals~~ contaminants and metals, stormwater and atmospheric deposition contaminants reflect the limited available data sets, and upland plume loading contaminants reflect individual upland plumes, etc. Development of the loading contaminants lists considered the contaminant

lists for in-river ~~nature and extent~~distribution presented in Section 5, as well as the lists for CSM presentation ~~-~~and fate and transport modeling for the FS.

6.1 EXTERNAL LOADING

This section evaluates current and historical contaminant loading to the surface sediment and surface water of the Study Area by external loading mechanisms. The boundaries of the Study Area includes the upstream and downstream river mile designations (RM 1.9 and 11.8), the surface of the river, the river bank sediment/riparian soil boundary at an elevation of +13 ft NAVD88, and the surface sediment/subsurface sediment boundary at 30 cm bml. Contaminant masses passing through these boundaries into the Study Area are external loads.

These loading mechanisms are differentiated from the sources described in Section 4 in that they represent the combined estimated load from all Study Area sources for the corresponding pathway. A simplified conceptualization of the external loading pathways (loading terms) to the Study Area and internal transport processes within the Study Area is presented in Figure 6.1-1. The loading terms presented on that figure were determined in consultation with USEPA (Integral et al. 2006, pers. comm.)~~,~~ and include the following:

- Upstream loading via surface water, including suspended sediment load and sediment bedload
- Stormwater runoff
- Permitted non-stormwater point source discharges
- Upland groundwater plume transport to the river
- Atmospheric deposition to the river surface
- Upland riverbank erosion
- Groundwater advection through sediments (partitioning from deep sediment, advecting to shallow sediments)
- Overwater releases.

Numerical loading estimates were generated for all of the above terms except for upland riverbank erosion, sediment bedload, and overwater releases. Contaminant releases from current and/or historical overwater activities~~-~~, such as sandblasting, painting, material transfer, maintenance, repair, and operations at riverside docks, wharfs, or piers~~,~~; discharges from vessels~~,~~; fuel releases~~,~~; and spills, are not considered quantifiable and are not addressed in this section. Releases of this nature are expected to have been more significant historically, prior to improved BMPs. While improved BMPs are likely to have reduced the occurrence of overwater releases significantly, it is acknowledged that current and future releases could occur. Due to insufficient

available information, no attempt is made in this report to predict and quantify such releases as a current loading term.

This section also presents loading estimates for groundwater advection through surface sediments (partitioning from surface sediment to surface water), which is an internal loading process within the Study Area. Internal transfer mechanisms are those that involve the transport of chemical mass from one media to another within the Study Area, but which do not add new ~~chemical~~ contaminant mass to the Study Area. Internal fate and transport mechanisms include sediment resuspension/transport/ deposition, solid/aqueous-phase portioning, abiotic/biotic transformation and degradation, biological uptake, and groundwater advection through surface sediments (partitioning from surface sediment to surface water). Groundwater advection is the only internal process that is quantified here. The other internal processes may be very significant in the transfer of ~~chemicals~~ contaminants from abiotic media and to biota, and many of these terms will be quantified as part of the FS fate and transport modeling effort.

For all loading terms for which numerical estimates were generated, a range of estimates (central estimate and upper- and lower-bounds) is provided to give perspective on the uncertainty associated with a given pathway and ~~chemical~~contaminant. The estimation approach for each term varies in nature and approach depending on the degree to which loading associated with a given transport pathway could be evaluated using available information. Most, if not all, of the attributes utilized in the loading estimations are based on site-specific measurements and monitoring results. If attributes were either not measurable or site-specific data are not available, literature data or empirical data collected outside of the Study Area are used. Some assumptions and modeling or calculation techniques may be used in these assessments. The assessments of external loading terms in Section 6.1 are intended to illustrate the estimated magnitude and variability in contaminant loads to the Study Area under typical conditions, i.e., in an average water year.[1] Assessment of year-to-year temporal variability was not the intent of this analysis.[2] The target scale of assessment of current loading rates is mass per year to the entire Study Area; however, in many cases, the data set supports (and calls for) calculation of loading estimates at higher temporal and/or spatial resolution. Where possible and relevant to understanding the system for the purposes of the RI, these more refined loading estimates were generated and are presented and discussed.

Table 6.1-1 summarizes the load estimate quantification level and calculation approach for the estimated loading terms, including the approach for generating the range of

[1] Because every water year is slightly different from the theoretical "average water year," the analyses include data collected during a range of environmental conditions. This variability is taken into account in the analyses to the extent possible. The approach to assessment of each term is discussed in detail in Appendix E.

[2] Extreme events are discussed for bedload in Section 6.1.1.2 to present additional information from the numerical modeling work used to generate the estimates for a typical water year. Such numerical modeling information is not available at this time to estimate extreme event loading for other loading terms.

estimates. Because of data limitations for some mechanisms and ~~chemicals~~contaminants, the range of estimates does not always represent the full understanding of uncertainty in the estimate. Thus, additional discussion of variability and uncertainty in the estimates is provided after discussion of approach for each loading mechanism in the following subsections.

The loading rates presented in this section are estimates, and subject to varying degrees of uncertainty that necessarily influence their utility as lines of evidence for the CSM. In Section 10, this information will be considered along with nature and extent information for all media, understanding of the physical system, understanding of contaminant behavior, risk information from the baseline ~~RAs~~risk assessments, and the understanding of current and historical sources. As such, the present section focuses on simple presentation of the loading analyses and general, mechanism-specific findings and patterns.

Subsections 6.1.1 through 6.1.7 define each current external loading term, identify and discuss the term's target contaminant list, describe the approach to assessment of the term's current loading rates, discuss the understanding of uncertainty in the estimates, and summarize and discuss any numerical estimates. Additional details of data sources, calculation approaches, and numerical results are presented in Appendix E. Each loading term has a historical component that may be responsible for much of the observed sediment conditions in the Study Area, particularly in the subsurface. Very limited quantitative data are available to support estimates of these historical terms. Therefore, historical loading is discussed qualitatively in Section 6.1.8.

6.1.1 Upstream Loading

Upstream loading is defined as the mass rate of transport of a given contaminant into the Study Area at RM 11.8 via dissolved and particulate transport mechanisms. Upstream loading is subdivided into loading via the surface water column (dissolved and suspended solids fractions) and sediment bedload (rolling, sliding, and saltating of sediment grains). Per discussions with USEPA during scoping of the fate and transport model for the FS, quantification of sediment bedloads into the Study Area and associated contaminant transport was deemed unnecessary because the sediment bed of the lower Willamette River is mainly cohesive. Hence, bedload transport processes are not significant components of upstream loading. Surface water loading is assessed in this section for typical flow conditions, as well as extreme observed and modeled high~~-~~-flow conditions.

While upstream loading terms are presented here simply as dissolved surface water and suspended particulate loads, it is important to recognize that these loads represent the combined input to the Study Area from a variety of loading processes in the upstream watershed. These inputs include upstream point sources, upstream stormwater runoff, upstream CSOs, upstream atmospheric deposition, and upstream in-river sources. Distinguishing these individual contributions to the combined upstream load is beyond the scope of this document.

6.1.1.1 Empirical Surface Water Loading Estimates

Empirical concentration and flow rate data from the site were used to generate a range of estimates of annual upstream surface water loading rates. Estimates for dissolved, particulate, and total loading rates are presented. The surface water loading contaminants listed in Table 6.0-1 were the focus of the calculations. This list is based on contaminants to be assessed in the ~~F~~fate and ~~T~~transport ~~M~~model for the FS and the CSM~~. Chemicals from~~. From this combined set of contaminants, those that were not analyzed in the RI surface water sampling program were removed from the final surface water list.

Upstream surface water loading at RM 11.8 was estimated based on the combined analytical data collected from the two nearest sampling transects: RM 16 and 11. In addition to upstream surface water loading at RM 11.8, loading rates were generated at the other RI surface water sample transect locations in the lower Willamette River: RM 16, 11, 6.3, 4, and 2. Estimated loads are also presented for the transect located in Multnomah Channel near its upstream connection with the Willamette River at RM 3. These loading estimates are not representative of upstream loading, but were generated to provide additional insight into the nature of the contaminant load transported by surface water as it moves through and out of the Study Area. The sum of the estimated loads at Multnomah Channel and RM 2 represents the estimated load of contaminants leaving the Study Area.[3]

The following subsections provide a summary of the data sets and approach used in the calculations, as well as a presentation and discussion of the findings. Detailed presentations of the data sets, data treatment, calculations, assumptions, and results can be found in the supporting Appendix E, Section 2.0.

6.1.1.1.1 Data Sets and Approach

Surface water loading rates were estimated based on Round 2A and 3A surface water ~~chemical~~ contaminant concentration data from transect sampling locations and USGS flow information from RM 12.8 (Morrison Bridge Station 14211720). To differentiate surface water loads associated with high-flow and low-flow conditions during a typical flow year, the first step in the analysis was to determine the fraction of a typical water year that is described by each flow regime. Three surface water sampling events from the Round 2A sampling effort and four surface water sampling events from the Round 3A sampling effort provided the analytical data for the surface water loading calculations. Of these seven sampling events, four occurred during low-flow conditions (<50,000 cfs), two were during high-flow conditions (>50,000 cfs), and one was during a low-flow stormwater event (active runoff to the Study Area with river flow rate <50,000 cfs). Average discharge rates (recorded as cfs) for each event are based on 30-

[3] Due to the complicating influence of water from the Columbia River on Willamette River flow volume and direction at the RM 2 and Multnomah Channel transect locations (described in Section 5.~~3~~4), modeled flow data were used to estimate loads for these two transects. The load calculation approach is discussed in detail in Appendix E, Section 2.

minute measurements collected by the USGS at the stream flow station located upstream of the Morrison Bridge at RM 12.8 (Station 14211720).[4] Total flow volumes and high-flow: low-flow volume fractions for the individual years and the 28-year average are presented in Table E2-1. Because the data sets compared well, the 28-year hydrograph was considered adequately representative for use as the basis for defining the high-flow: low-flow volume ratio for a typical year. Fifty-two percent of the total annual volume occurred during high-flow conditions and 48 percent during low-flow conditions, for a volume ratio of 1.07. The average annual duration of the low-flow period is 268 days, while high flows occur for a much shorter period of 98 days. Accordingly, a ratio of 52:48 was used to apportion the fractions of the typical annual hydrograph assigned as high flow to that assigned as low flow. This step is described in detail in Appendix E, Section 2.2.1. The Round 2A and 3A surface water sampling events and daily hydrograph data for the years characterized by those events (2004 through 2007) are presented in Figures 5.~~3~~4-2 through 5.~~3~~4-5. Surface water sampling events superimposed on the 36-year average annual hydrograph are presented in Figure 5.~~3~~4-1.

The distribution of Willamette River flows between Multnomah Channel and RM 2 ~~were~~was based on the results from the EFDC physical transport modeling effort (WEST 2006~~a~~). The results of this model provided the average daily flow rates at Multnomah Channel, RM 2, and upstream transects (modeled upstream transect flows were used for comparison purposes only). A detailed description of the use of these model flow results is presented in Appendix E, Section 2.2.1. The surface water data include particulate and dissolved ~~chemical~~ contaminant concentrations.[5] Loading estimates for these fractions were combined to generate the total surface water loading estimates.

Next, the surface water analytical data set was used to estimate representative concentration ranges for high-flow and low-flow conditions for each transect. This calculation step, described in detail in Appendix E, Section 2.2.2, involved averaging individual data points associated with a transect (e.g., NB, NS, east, middle, west, etc.) to resolve the data set to one concentration estimate per transect per sampling event. Using these results, a set of minimum, mean, and maximum measured concentrations at each transect was generated for both high-flow and low-flow conditions.

Loading rates at each transect were then estimated as the product of the ~~chemical~~ contaminant concentrations and the flow volumes associated with the high-flow and

[4] Note: The flow rate values presented here are daily mean stream flow measurements from the USGS National Water Information System, www.waterdata.usgs.gov. These values were taken from the USGS Web site on June 16, 2008, and are considered to be draft and subject to change by USGS, which may refine ratings and calculations as needed.

[5] A comparison of surface water particulate concentrations and physical characteristics of suspended sediment to sediment trap results was conducted to assess the adequacy of the surface water information for describing an entire water year. This assessment is presented in Appendix E, Section 2. The assessment indicated that the ranges in surface water suspended sediment concentration generally capture the range observed in the sediment trap data set.

low-flow portions of the hydrograph. For each transect, lower, central, and upper estimates of high-flow loading were estimated by multiplying the minimum, mean, and maximum concentrations, respectively, by the total annual flow volume estimated for high-flow conditions. Likewise, a range of low-flow rate loading estimates for each transect was estimated using the minimum, mean, and maximum of ~~sub~~averaged concentrations and the estimated flow volume for low-flow conditions. The range of annual mass loading rate estimates were, in turn, generated by summing the fractional loading contributions estimated for high-flow and low-flow conditions at the given transect (i.e., the total annual central flow estimate was calculated as the sum of the central high-flow estimate and the central-low flow estimate).

There are no surface water sample results available from RM 11.8, which defines the upstream boundary of the Study Area. Therefore, high-flow and low-flow concentrations at RM 11.8 were estimated by combining data from RM 16 with selected data from RM 11. Because some of the surface water samples collected at RM 11 appear to have been influenced by one or more source areas of contaminants between RM 11.8 and ~~RM~~ 11, some of the RM 11 results are not representative of water quality at RM 11.8. Prior to combining the data, the RM 11 data set was assessed for each selected contaminant to determine whether the data represented the same population of upstream data as that sampled at RM 16. This approach assumes that the surface water concentrations at RM 11.8 would be more similar to those at RM 16 than those at RM 11, recognizing that although there are additional sources between RM 11.8 and 16, the proximity of likely sources to the RM 11 transect are expected to have the larger effect. A comprehensive graphical and statistical comparison of the ~~chemical~~ contaminant data from RM 16 and 11 was conducted for each selected contaminant.[6] This involved plotting and evaluating data, running Mann-Whitney U statistical tests, and removing RM 11 sample results from the combined set where the evidence indicated the potential influence of a local source area. This analysis and all figures and statistical results are presented in detail in Appendix E, Section 2.2.2.1.

6.1.1.1.2 Uncertainty

Uncertainty associated with the surface water loading estimates is related primarily to the adequacy and representativeness of the analytical data set. The data sets are derived from grab samples, not time-weighted composites. Further, a limited number of samples were collected under a limited number of flow conditions. This prohibits a thorough understanding of temporal and flow variability in surface water quality and is an important source of uncertainty. The magnitude and direction of bias on loading estimates is unknown. Finally, additional uncertainty is associated with the RM 2 and Multnomah Channel loading results stemming from the use of modeled flow rates and the variable influence of the Columbia River in the lower reaches of the Study Area.

[6] Data were available for RM 11 and RM 16 for all selected contaminants except BEHP, which was only sampled at RM 11. For this chemical, upstream loads were calculated based on the RM 11 sampling results.

Sediment trap data provide some additional perspective regarding uncertainty in the suspended solids component of the surface water loading estimates because they reflect longer sampling periods (four quarterly samples). However, for direct comparison, these samples are spatially (not representative of an entire transect) and mechanism-limited (not necessarily likely to equally capture particles of all sizes). The sediment trap results are discussed in comparison to surface water TSS in Appendix E, Section 2.4.1. This comparison suggests that the surface water TSS data reasonably approximate the longer-term sediment concentrations provided by the sediment traps, in spite of the snapshot nature of the surface water samples, lending some confidence to the use of the TSS data in the loading estimates.

6.1.1.1.3 Findings

Upstream (RM 11.8) surface water loading estimates are presented on an annualized basis for all surface water loading contaminants and are further differentiated for high-flow and low-flow periods of the annual hydrograph, as well as for the particulate and dissolved fractions. Surface water loading estimates at RM 16, 11, 6.3, 4, Multnomah Channel (RM 3), and RM 2 are also presented for select indicator contaminants—PCBs, PCDD/Fs, total DDx, and PAHs—to provide insight into patterns of mass transport of these ~~chemicals~~ contaminants in surface water. Loading estimates for all transects for the surface water contaminants are presented in Appendix E, Section 2.3.

Annual Upstream Loading

Table 6.1-2 presents the range of total (dissolved plus particulate) annual upstream loading estimates (RM 11.8) for each surface water loading contaminant selected. The following paragraphs discuss the findings for each contaminant (or contaminant group) regarding patterns in total loading rate estimates, loads as a function of surface water flow regime (high flow versus low flow), and particulate-dissolved components of the loads.

Figure 6.1-2 presents total surface water loading estimates for total PCB congeners, selected individual PCB congeners, and PCB TEQ. Both the total PCBs and PCB TEQ loading estimates show higher aggregate loads during the low-flow period of the year as compared to the high-flow period. On a daily basis, total PCB loads are higher during the high-flow period than during the low-flow period. Total PCBs and PCB TEQ show significant contributions of particulate-associated concentrations to the total surface water PCB loads for most flow conditions (Figure 6.1-3), which is expected given the highly hydrophobic nature of PCBs.[7] These patterns in flow conditions and particulate/dissolved ratios are also generally apparent in the individual congener data sets. PCBs 81, 126, and 169 exhibited low detection frequency in the upstream surface water loading data set (19 percent, 40 percent, and 14 percent, respectively; see Table

[7] In surface water, partitioning theory (often discussed in the context of groundwater or pore water) still holds; however, the total chemical mass in the dissolved state in surface water can be comparable to or greater than the total chemical mass in the sorbed state, even for very hydrophobic chemicals. This is because the mass ratio of water to solids (suspended) in surface water is much higher than in groundwater or sediment.

E2-5 in Appendix E); therefore, the loading estimates presented for these analytes are considered more uncertain than those for other contaminants with higher detection frequency.

Total PCDD/Fs and TCDD TEQ (Figures 6.1-4 and 6.1-5) are primarily associated with particulate matter, which is also expected given the highly hydrophobic nature of these ~~chemicals~~contaminants. Neither the aggregate low-flow nor the high-flow load estimates dominate the total annual loading for both total PCDD/Fs and TCDD TEQ. Instead, the relative contributions to the annual load from high-flow and low-flow periods are comparable (Figure 6.1-4). On a daily basis, total PCDD/Fs and TCDD TEQ loads are higher during the high-flow period than during the low-flow period.

The results for DDx compounds (Figures 6.1-6 and 6.1-7) indicate a different pattern than those noted for PCBs and PCDD/Fs. While the loads are generally higher in the particulate fraction, as typically seen for the other strongly hydrophobic contaminants, the patterns with surface water flow regime differ. For DDx compounds, the annual aggregate upstream load associated with the high-flow period is consistently higher than that associated with the low-flow period of the year. On a daily basis, total DDx loads are higher during the high-flow period than during the low-flow period. Further, the 4,4'-isomers of the DDx components compose the majority of the total DDx upstream load, with DDT isomers being the greatest fraction, and DDD isomers being the smallest fraction of the total DDx.

Upstream surface water loads of total PAHs are significantly higher (approximately an order of magnitude) than total cPAHs (Figure 6.1-8). This indicates that PAHs in the water column are dominated by LPAHs rather than HPAHs, as the total cPAHs sum includes the majority of HPAH compounds. This pattern is also reflected in loads for naphthalene (an LPAH) as compared to BaP (an HPAH). For both LPAHs and HPAHs, the annual aggregate load associated with the high-flow period is higher than that associated with the low-flow period of the year. On a daily basis, total PAHs loads are higher during the high-flow period than during the low-flow period. The LPAHs (naphthalene), which have higher solubility than HPAHs, show higher fractions of dissolved as compared to particulate load (Figure 6.1-9). In contrast, the HPAHs (cPAHs~~,~~ and BaP), which are more hydrophobic, show higher fractions of particulate as compared to dissolved load. It is important to note that total naphthalene exhibited low detection frequency in the upstream surface water loading data set (10 percent; see Table E2-5 in Appendix E). Therefore, the loading estimates presented for naphthalene are considered more uncertain than those for other contaminants with higher detection frequency.

Upstream loading rate ranges for BEHP and hexachlorobenzene are presented on Figures 6.1-10 and 6.1-11. The total annual BEHP load is almost exclusively associated with high-flow periods of the hydrograph, with three high-flow samples measured above detection limits and one detected low-flow sample. Total BEHP exhibited low detection frequency in the upstream surface water loading data set (19 percent; see

Table E2-5 in Appendix E). Therefore, the loading estimates presented for BEHP are considered more uncertain than those for other contaminants with higher detection frequency. The high-flow contribution for hexachlorobenzene is also higher than the low-flow contribution, but only by approximately 15 percent for the central estimate. Hexachlorobenzene shows consistent fractions of particulate and dissolved contributions to the total load under all flow conditions, with the particulate fraction making up roughly 15 to 20 percent of the total load.

Upstream surface water loading rate estimates for the indicator non-DDx pesticides are presented on Figures 6.1-12 and 6.1-13. These figures show that, dieldrin exhibits the highest annual upstream loads, whereas aldrin loads are comparatively very low. This difference may reflect the fact that aldrin degrades relatively rapidly in surface water by photochemical or microbial processes (discussed further in Section 6.2). Similar to the DDx pesticides discussed previously, most non-DDx pesticides exhibit higher loads during high-flow conditions, with the exception of gamma-hexachlorocyclohexane (Lindane) (gamma-HCH), which exhibits approximately 60 percent of the annual load during low-flow conditions. In contrast to the DDx pesticides, the total surface water loads for the non-DDx pesticides are dominated by the dissolved fraction (Figure 6.1-13).

Figures 6.1-14 and 6.1-15 present the upstream surface water loading rate estimates for the indicator metals. The highest overall loading rates are observed for zinc and copper, two common elements. Nickel and chromium loads are the next highest and exhibit similar loading rate estimates. Lead and arsenic exhibit the next highest loading estimates, with mercury loads being the lowest and the result of only a few detections. Total mercury exhibited low detection frequency (23 percent; see Table E2-5 in Appendix E). Therefore, the loading estimates presented for this analyte are considered more uncertain than those for other contaminants with higher detection frequency. Loading rates during high-flow conditions for all of these metals are greater than loading rates during low-flow conditions. Further, the particulate fraction contributes more than the dissolved fraction to the total loading estimates for the majority of the metals, especially under high-flow conditions (Figure 6.1-15).

Estimated upstream total surface water loads for TBT are presented on Figure 6.1-16. There is no presentation of dissolved versus particulate fractions for TBT because the surface water data set includes measurements of total concentrations only. TBT in upstream surface water was detected only once, and that was during a low-flow sampling event (high-flow results were below detection limits). Therefore, no meaningful comparisons could be made regarding the relative loading of TBT with regard to low-flow versus high-flow conditions.

In summary, with the exception of PCBs and gamma-HCH, surface water contaminants exhibit higher upstream loading rates during high-flow conditions than during low-flow conditions. Loads for all of the contaminants are generally higher on a daily basis during high flows than during low flows. The particulate fraction represents the larger

component for PCBs, PCDD/Fs, DDx pesticides, and metals. The dissolved fraction is the larger component for LPAHs, non-DDx pesticides, and hexachlorobenzene. In general, the ratios of particulate to dissolved mass loading for all surface water loading contaminants do not show large or consistent variations under different flow conditions, indicating possible conditions of equilibrium or near equilibrium, as discussed further in Section 6.2.2.

Surface Water Mass Transport within the Study Area

To evaluate spatial trends in surface water loading estimates moving downstream through the Study Area, loading estimates were plotted for each available transect for total PCBs, total PCDD/Fs, TCDD TEQ, total DDx, and total PAHs. These plots are presented in Figures 6.1-17 through 6.1-19. As mentioned above in the approach discussion, upstream loads at the RM 11.8 Study Area boundary were estimated based on combining RM 11 and RM 16 data. Further, the fraction of the Willamette River load leaving the Study Area at RM 2 and Multnomah Channel was estimated based on measured concentrations and modeled river flows, due to the hydrologically complex influence of water from the Columbia River on flows in the lower Willamette River. These transect estimates are distinguished with blue (RM 11.8) and orange (RM 2 and Multnomah Channel) symbols on Figures 6.1-17 through 6.1-19. The sum of the estimated loads at Multnomah Channel and RM 2 represents the estimated load of ~~chemicals~~ contaminants leaving the Study Area.

The total PCB plots (Figure 6.1-17) show that central estimates of surface water loading increase continually from RM 16 to 4. The upper and lower estimates show the same increasing trend. Comparison of the central estimate results from the upstream estimate (RM 11.8) and the from the Multnomah Channel and RM 2 transects indicate that the total PCB load leaving the Study Area is estimated to be greater than the upstream end of the Study Area. This observation of a loading increase from upstream to downstream is supported by the observed concentration increase between RM 11 and RM 4 in six of seven surface water sampling events, as discussed in Section 5.4.

Total PCDD/Fs and TCDD TEQ loads show patterns similar to PCBs (Figure 6.1-18), with increasing loads moving downstream through the Study Area; however the increase is not as steady, with comparable central loading estimates at RM 11 and 6.3. Comparison of the central estimate results from for RM 11.8 with the Multnomah Channel and RM 2 transects indicates that the total PCDD/F and TCDD TEQ loads leaving the Study Area are estimated to be greater than the upstream end of the Study Area. However, the RM 11 transect loads are comparable to the summed RM 2 and Multnomah Channel loads, suggesting that much of this loading increase occurs between RM 11.8 and 11. Consistent with the loading observations, total PCDD/F concentrations in surface water do not display consistent trends from upstream to downstream within the Study Area, as discussed in Section 5.4.5.

Total DDx pesticides (Figure 6.1-19, top plot) show fairly consistent loads between RM 16 and 11, with loads increasing in the Study Area between RM 11 and 4. Finally,

total PAHs (Figure 6.1-19, bottom plot) show a continually increasing load between RM 16 and 4. As with PCBs and PCDD/Fs, the central estimates of DDx and PAH loads leaving the Study Area at Multnomah Channel and RM 2 are somewhat higher than the loads estimated at the upstream end of the Study Area (RM 11.8). For both DDx and PAHs, this observation of a loading increase from upstream to downstream is supported by the observed concentration increase between RM 11 and 4 in six of seven surface water sampling events, as discussed in Section 5.4.6 (DDx) and 5.4.7 (PAHs).

A graphical summary comparison of loading terms is presented in Section 10.2 for the 13 CSM ~~chemicals~~contaminants.

6.1.1.2 Modeled Sediment Fluxes

The 2009 HST model was used to evaluate the relative scale of the sediment fluxes to the Study Area over a range of flow conditions. As discussed previously, bedload is not quantified in the HST model because the physical CSM for the ~~L~~lower Willamette River assumes that bedload represents a relatively small fraction of the total sediment load entering the Study Area at RM 11.8. This is because of the ~~L~~lower Willamette River's morphology and the fact that its flows are regulated by upstream control structures. As noted in Section 3, the Study Area occupies the lower portion of the ~~L~~lower Willamette River where the river widens and has been deepened by dredging. The reach upstream of the Study Area, from Willamette Falls through downtown Portland, is generally narrower and faster moving, so suspended loads tend to be transported into the Study Area before settling out. In addition, dams at Willamette Falls (RM 26) and further upstream trap bedload moving downstream from the middle Willamette River to the ~~L~~lower Willamette River. The only significant tributary to the ~~L~~lower Willamette River below RM 26, the Clackamas River at RM 24.7, is a gravel-bed stream. Much of the bedload from the Clackamas River is likely deposited in the Willamette River well upstream of the Study Area; the main stem of the ~~L~~lower Willamette River just upstream and at Ross Island has several large depressions in the channel (see Map 3.1-~~6~~13) that trap bedload materials moving downstream.[8] From a contaminant loading perspective, the significance of bedload is further reduced because this process transports relatively coarse-grained, non-cohesive, clastic sediments, which have a generally low organic carbon content and low surface-to-volume ratio. Therefore, associated contaminant concentrations are presumably much lower than concentrations associated with finer grained suspended sediment.

6.1.1.2.1 Modeled Sediment Flux

The 2009 HST model was used to predict sediment loads entering the Study Area from upstream at RM 11.8 under five different flow regimes. The flow regimes range from the 5th to 95th percentiles of flow conditions based on the ~~L~~lower Willamette River flow data recorded since 1972. The specific flow years modeled (starting on October 1 and

[8] As discussed in Section ~~5.6~~6.2.1, there are also several man-made borrow pits spread across the channel in the upper Study Area between RM 10 and 11, which also likely entrain bedload entering the Study Area.

running through September 30 of the year indicated) and the mean annual flows for those years are listed below:

- 5th Percentile Flow Year 2001 – mean flow 454 m^3/sec
- 25th Percentile Flow Year 1981 – mean flow 787 m^3/sec
- 50th Percentile Flow Year 1986 – mean flow 878 m^3/sec
- 75th Percentile Flow Year 1995 – mean flow 1,078 m^3/sec
- 95th Percentile Flow Year 1997 – mean flow 1,522 m^3/sec.

These flow year percentiles were developed for use in the fate and transport modeling effort to support evaluations of contaminant fate, transport, and loading for the RI and FS. As noted above, the fate and transport modeling effort is ongoing and the results will be evaluated and reported separately.

The HST model estimates the daily-averaged flux of water and suspended sediment (cohesive and non-cohesive). Table 6.1-3 and Figure 6.1-20 (Petroni 2011, pers. comm.) summarize the modeled suspended sediment fluxes for each flow regime entering the Study Area at RM 11.8 and exiting the Study Area in the main stem of the ~~L~~lower Willamette River at RM 1.2[9] and in ~~the~~ Multnomah Channel. Negative values in Table 6.1-3 indicate material leaving the Study Area. The averaged annual modeled flow estimates illustrate the relative percent increase is discharge out ~~the~~ Multnomah Channel at lower flow levels in the l~~L~~ower Willamette River ~~flow levels~~. The lower portion of Table 6.1-3 shows the combined sediment fluxes exiting the harbor at RM 1.2 and in the Multnomah Channel and then tallies the modeled suspended and total sediment loads entering and leaving Portland Harbor for each flow regime.

The net flux of suspended sediment for all flow regimes modeled is positive, indicating that the harbor is generally a trap for material entering from upstream. Across all flow regimes, an average of 82 percent of the total modeled sediment flux entering the harbor at RM 11.8 passes through and exits at RM 1.2 and ~~the~~ Multnomah Channel. The 18 percent retained within the Study Area represents an estimated average annual net sediment accumulation of 277 million kg/year and reflects the overall net depositional character of the Study Area. However, as detailed in Section 3.1.5.2.6, various areas within the Study Area may be largely depositional, erosional, or subject to both processes.

6.1.2 Stormwater Runoff

This section presents the results of the calculated stormwater loading to the Study Area using stormwater and outfall sediment trap data collected as part of the RI/FS. The

[9] The Study Area boundary is RM 1.9 but the HST model grid extends downstream to RM 1.2. This model boundary, as well as the downstream end of the Multnomah Channel model cell, were used as the downstream boundaries for these calculations.

contaminants listed in Table 6.0-1 as stormwater loading contaminants were the focus of the calculations described in this section. This list was derived from the sediment, biota, and surface water contaminants designated for fate and transport evaluation ~~using~~ and for discussion in the RI CSM, and was further reduced based on availability in the stormwater data set.

Estimated stormwater loads were generated for each contaminant and fate and transport model cell and for the entire Study Area. The following subsections present a summary of the data sets and approach used in the calculations, as well as a presentation and discussion of the findings.

Appendix E, Section 3.0 describes the detailed steps taken to calculate stormwater loading estimates, from data sources/data treatment to calculation approach, results, and a brief discussion of the associated uncertainty. The results are also discussed in Section 10.

6.1.2.1 Data Sources and Calculation Approach

The stormwater composite water and sediment trap data were collected in accordance with the Round 3A Stormwater FSP and Addendum (Anchor and Integral 2007~~a,b~~b,c) and its companion document, the Round 3A Stormwater Sampling Rationale (Anchor and Integral 2007~~c~~d) and analyzed in accordance with the QAPP Addendum 8 (Integral 2007~~b~~m).

The stormwater sampling location rationale was developed in accordance with a commonly used approach of applying representative estimates of stormwater ~~chemical~~ contaminant concentrations for various land use types (Scheuler 1987). A land-use-based ~~chemical~~ contaminant load modeling approach was used to estimate loads across the entire Study Area. ~~Chemical~~ Contaminantl loading models use site characteristics (e.g., land use and percent impervious area) and land-use-specific loading rates to estimate overall loading into the receiving waters. This approach has been modified to better fit the data needs and land use characteristics of the Study Area, as well as the practical constraints for this sampling effort.

Loads to the Study Area are calculated based on composite water and sediment trap data collected from heavy industrial, light industrial, residential, parks/open space, major transportation, and non-representative locations. Non-representative sites are those sites with non-representative ~~chemical~~ contaminant sources that cannot be easily extrapolated from generalized land use measurements. Twenty-seven stormwater outfalls were sampled within the Study Area to estimate stormwater loads. In general, three to five composite water samples and one sediment trap sample were collected at each stormwater sample site. As discussed in Appendix E, Section 3.5.1, pesticides were analyzed at a small subset of locations (8 stations) in composite water samples, but they were analyzed at nearly all locations (22 stations) in sediment trap samples. Due to the lack of representative composite water samples for pesticides, sediment trap data and the resulting statistics (e.g., central tendencies) used in loading estimates were

substituted for composite water statistics for light industrial, parks/open space, residential, and transportation land uses, as well as for 1 of 3 non-representative locations that did not have composite water data (WR-147). Additionally, composite water data and the resulting statistics used in loading estimates were substituted for sediment trap statistics for 2 of 3 non-representative locations that did not have sediment trap data (OF-22B and WR-96). For most non-pesticide ~~chemicals~~contaminants, load estimates to water are based on roughly 100 stormwater samples across all land uses and sites. For these non-pesticide ~~chemicals~~contaminants, the ranges of numbers of composite water samples available for loading estimates were 27 to 72 for heavy industrial, 10 to 16 for light industrial, 9 to 10 for residential, 2 to 3 for parks/open space, 7 to 9 for major transportation, and 3 to 5 for each non-representative location. For pesticides, load estimates are based on approximately 26 composite water samples (from 8 stations) and about 19 sediment trap samples (from 19 stations) across all land uses and sites. For the pesticides, the ranges of numbers of composite water samples available for loading estimates were 12 for heavy industrial, 4 for light industrial (from one station), 3 for residential (from 1 station), zero for parks/open space, zero for major transportation, and 3 to 4 for each non-representative location. (Note that composite sample water data were only used for loading estimates for the heavy industrial and non-representative locations.) The numbers of sediment trap samples available for pesticide loading estimates were 11 for heavy industrial, 3 for light industrial, 2 for residential, 1 for parks/open space, and 1 for major transportation, and 1 for non-representative locations.

As detailed in Section 4.4.1.2 and Appendix E, Section 3.0, representative samples from five general categories of land use (heavy industrial, light industrial, residential, major transportation, and parks/open space), as well as samples from non-representative locations, were included to obtain a practicable and sufficient data set to estimate stormwater loading to the Study Area. Samples were collected from a subset of drainage basins/outfalls within each land use category in the Study Area. These locations were sampled by the LWG and Port of Portland (Terminal 4) during two sampling efforts in the spring/summer of 2007 (Round 3A) and the fall/winter of 2007-2008 (Round 3B). One additional site (GE Decommissioning) was sampled by GE during the same time frame. Results from the GE investigation are also included in the overall LWG stormwater data set. In early 2008, the City of Portland collected three additional samples to supplement the residential data set, and these samples are included as well.

As a first step, the stormwater analytical data set was used to generate concentration ranges for each land use and non-representative site. Both stormwater composite water samples and sediment trap chemistry data were used to provide two independent means of estimating stormwater contaminant loads.

Next, the stormwater runoff volumes draining to each ~~F~~fate and ~~T~~transport ~~M~~model cell were calculated for each land use and non-representative location using the City of Portland's GRID model as summarized in Appendix E~~3~~, Section 3.5.3. It was not

possible to develop runoff volumes and stormwater load estimates for individual outfalls due to uncertainty of stormwater basin boundaries for many outfalls.

As explained in Appendix E, Sections 3.5.1 and 3.5.2, loads were then estimated as a product of the calculated concentration estimates and the flow rate from the 50th percentile flow year to represent the central tendency (CT) of flow conditions. The annual mass loads were generated by adding the loading contributions from each land use and non-representative site for each ~~F~~fate and ~~T~~transport ~~M~~model segment.

The process for estimating stormwater loads, as well as all figures, maps, and statistical results, is presented in detail in Appendix E, Section 3.0.

6.1.2.2 Uncertainty

The primary sources of uncertainty in the stormwater loading estimates are the sample size and sampling period extrapolated to represent the composite conditions of a typical water year over the entire ~~L~~lower Willamette River runoff area. Specifically, data used to estimate the stormwater loads were collected during a total of 15 storm events, with each outfall sampled an average of three times. Sediment traps were left in place for ~~three~~3 to ~~seven~~7 months during two separate sampling periods. Due to the limited time span of sampling and the known variability of stormwater, these data should be considered to represent a "snapshot" of stormwater entering the Study Area during the sampling period. Additionally, particular records were peremptorily excluded from the working database due to various factors that have been identified by the Stormwater Technical Team. These specific exclusions and associated uncertainty are discussed in Appendix E, Section 3.0.

The methodology for calculating stormwater loading assumes that concentrations measured in individual sampled outfalls at non-representative sites are indicative of concentrations for all stormwater discharging from the site. This methodology has inherent uncertainty associated with it, as concentrations can vary significantly based on the physical characteristics of the drainage basins associated with the stormwater discharges. For example, if a drainage basin that was sampled drains a known upland source area, the concentrations measured in this discharge may be significantly higher than stormwater discharges at the remainder of the site. Thus, this example could overestimate stormwater loading for this site. Overall, however, the direction of any bias in the estimates created by these uncertainties is unknown.

Additionally, other more specific factors within this particular study's methods that may contribute to the uncertainty of the stormwater loading estimates are discussed in Appendix E, Section 3.0.

6.1.2.3 Summary of Findings

This section presents the findings of the stormwater loading analysis. Stormwater loading to the Study Area is presented and discussed for stormwater contaminants using

both the stormwater composite water and sediment trap data sets, where available, as two independent ways of estimating loads.

In addition to Study Area stormwater loads, loading estimates by ~~F~~fate and ~~T~~transport ~~M~~model cell are presented for PCBs, PAHs, and total DDx to provide insight into patterns of loading throughout the Study Area. Loading estimates for each of the selected contaminants and ~~F~~fate and ~~T~~transport ~~M~~model cell for the entire Study Area are presented in both graphic and tabular format in Appendix E, Section 3.6.

Table 6.1-4 presents the range of annual stormwater loads to the Study Area for each stormwater ~~IC~~contaminant for both composite water and sediment trap data. These ranges are also presented graphically on Figures 6.1-21 through 6.1-35 for each ~~chemical~~ contaminant group, including ranges of the annual load estimated using both composite water and sediment trap data. The findings regarding patterns of total loads estimates are discussed for each ~~chemical~~ contaminant group in the following paragraphs. Refer to the maps in Appendix E, Section 3.6 (Maps E3-1a–b through E3-32a–b) for a graphical representation of loads for each of the selected contaminants throughout the Study Area. Tables 6.1-5a–b present a percentage comparison of loads to the Study Area by land use and non-representative location for both composite~~d~~ water and sediment trap data.

Loads for total PCBs estimated using composite~~d~~ water data are slightly higher than the sediment trap estimated loads (Figure 6.1-21). The estimated loading rate for total PCBs is highest for the heavy industrial land use category as compared to other land uses, although one non-representative location contributes the highest estimated load. A comparison of loads of individual PCB congeners and total PCB TEQ ~~are~~is shown in Figures 6.1-22 and 6.1-23. Generally, composite~~d~~ water estimated loads for the various PCB components are slightly higher than the sediment trap estimated loads.

Stormwater loads for DDx pesticides are presented in Figure 6.1-24. The results for these compounds show that the composite~~d~~ water estimated loads are generally within the range of loads calculated from the sediment trap data. The estimated annual loads for total DDx is highest for the heavy industrial land use category as compared to other land uses; however, the highest estimated loading rates are from non-representative sites in Basin 20 (RM 6.8 to 7.4W). Loading rates from non-representative sites are based on the results from a single outfall (from the former DDT process area) that was included in summations of all land use types to represent stormwater runoff from the entire site. The estimated loads for non-DDx pesticides are highest for the heavy industrial land use category. Stormwater loads for non-DDx pesticides are presented on Figure 6.1-28. Generally, composite~~d~~ water estimated loads for non-DDx pesticides are typically higher than the sediment trap estimated loads.

Annual load estimates for total PAHs using composite~~d~~ water data compared well with estimates using sediment trap data (Figure 6.1-25). The estimated load for total PAHs is highest for the heavy industrial land use as compared to other land uses, with four

Commented [A1]: Integral: Throughout this section, the RI, and Appendix E, we have using the term "composite water" without the "d" (including on many map captions), therefore we did not accept this insertion to maintain consistency.

non-representative locations contributing a substantial portion to the total stormwater load.

Stormwater loads for BEHP are presented on Figure 6.1-26. BEHP annual loads estimated using composite~~d~~ water data are higher than those generated using sediment trap data. The highest estimated loading rates for BEHP are from the heavy industrial land use areas.

Stormwater loads for hexachlorobenzene are presented on Figure 6.1-27. The results for hexachlorobenzene indicate that the sediment trap estimates are within the range of the composite~~d~~ water estimates. The highest estimated annual loads for hexachlorobenzene are from the heavy industrial land use areas.

Stormwater loads for non-DDx pesticides (aldrin, dieldrin, gamma-HCH, and total chlordanes) are presented on Figure 6.1-28. For each of these ~~chemicals~~contaminants, the composite~~d~~ water annual load estimates were higher than estimates developed using sediment trap data.

Stormwater loads for metals are presented on Figure 6.1-29. Typically, for metals, the composite~~d~~ water load estimates were slightly higher than estimates developed using sediment trap data. The highest overall estimated loads are observed for zinc, copper, and lead. Chromium, arsenic, and nickel have the next highest loads, and of the metals evaluated, mercury has the lowest. The highest estimated annual loads for metals are from the heavy industrial land use areas.

Stormwater loads to the Study Area are presented by river mile for total PCBs, total PAHs, and total DDx pesticides in Figures 6.1-30 through 6.1-35.

A graphical summary comparison of stormwater discharges to other loading terms is presented in Section 10.2 for the 13 CSM ~~chemicals~~contaminants.

6.1.3 Permitted Point Source Discharges

Point source permitted non-stormwater discharges to the Study Area include NPDES-permitted discharges from commercial, industrial, private, and municipal outfalls or operations. This section presents the results of estimation of the current annual mass load of ~~chemicals~~ contaminants from these outfalls to the Study Area. The details of data compilation and loading estimation are presented in Appendix E, Section 4.0.

Both Oregon DEQ general and individual NPDES permits were considered in this evaluation. Active NPDES permits inside the Study Area were located using Oregon DEQ's Facility Profiler 2.0[10], and the DEQ Wastewater Permits Database[11] was used to query the permit file numbers. ~~As of this writing, t~~There are 14 NPDES wastewater

[10] Oregon DEQ's Facility Profiler 2.0: http://deq12.deq.state.or.us/fp20/
[11] DEQ Wastewater Permits Database: http://www.deq.state.or.us/wq/sisdata/sisdata.asp

permitted discharges in the Study Area listed as either Individual or GEN 15A Permits. Map 6.1-1 shows the facility locations for these 14 permits. Note that this analysis is specifically limited to permitted wastewater discharges to the Study Area and does not represent stormwater discharges (included in stormwater loading term analysis; see Section 6.1.2) or other types of point sources.

Permitted direct discharge loading analyses were based on water ~~chemical~~ contaminant concentration data and discharge/flow data in discharge monitoring reports (DMRs), where available. These data were available for the following 10 of the 14 NPDES wastewater permitted discharges:

- EOSM
- Kinder Morgan/Portland Bulk Terminal 4
- Koppers Inc.
- Starlink Logistics, Inc.
- Siltronic Corporation
- ARCO Products Company
- Kinder Morgan Liquid Terminals
- Equilon Enterprises
- Pinnacle Condominium Complex
- Univar USA.

The remaining four NPDES wastewater permitted discharges listed below were not included in the loading calculations due to insufficient data for calculations and are shaded orange on Map 6.1-1:

The facilities and the reasons they were not included are:

- Ash Grove – No flow or ~~chemical~~ contaminant data reported
- Columbia River Sand and Gravel – No flow data reported and no ~~chemical~~ contaminant analysis required (only TSS and turbidity monitored)
- Vigor (Cascade General) – No flow data reported on DMRs
- Hoyt Street Properties – No flow or concentration data reported.

The discharge information from these sites would be expected to increase the upper and lower end estimates of total loading to the Study Area for the ~~chemicals~~ contaminants included in their permits. The lack of data for these facilities is not expected to represent a significant loading data gap for any parameters.

Ranges of loading estimates were generated by considering the DMR discharge flow rates and ~~chemical~~ contaminant concentration data for all the selected contaminants. Because of limited analyte lists in the DMRs and the permits, data for some ~~IC list~~ parameters were not available for all facilities. Additionally, several of the selected contaminants were never monitored at any of the facilities. The results are summarized in Table 6.1-6 for the subset of selected contaminants for which data were available.

While there is uncertainty associated with the annual estimates for this loading term, the findings are expected to be reasonably representative of the relative significance of this pathway (as defined above) for current loading of contaminants to the Study Area. The primary source of uncertainty in these estimates is the limited monitoring records available for many sites. There are four sites that could not be included in this assessment due to lack of information. If there is flow related to these permits, then discharge information from these sites would be expected to increase the upper and lower end estimates of total loading to the Study Area for the contaminant~~chemicals~~ included in their permits. This analysis is specifically limited to permitted wastewater discharges to the Study Area and does not represent stormwater discharges (included in stormwater loading term analysis; Section 6.1.2) or other types of point sources.

Review of these results indicates that only a few of the analytes on the combined loading contaminant list are presented in the DMRs (for one or more permit, results are presented for DDT, select PAHs, TPH, select metals, select VOCs, and cyanide). For all of the parameters analyzed, the estimated range of results is narrow—ranging over a factor of 5. While flow volumes are relatively large for some dischargers (total permitted discharge volume is estimated to be only slightly less than stormwater runoff), the concentrations ranges are low, and the resulting loads are generally low. Because of limited volume and low contaminant~~chemical~~ concentrations, permitted point source discharges were not found to be a primary source of contaminants to the Study Area for those facilities and parameters for which data was available. Overall, it is expected that this loading term, as defined and assessed here, is not currently a primary source of contaminants to the Study Area since permitted discharges are regulated and monitored. A graphical summary comparison of permitted point source discharges to other external loading terms is presented in Section 10.2 for the 13 CSM contaminant~~chemicals~~.

6.1.4 Atmospheric Deposition

Contaminant~~Chemicals~~ present in the atmosphere as a result of emissions from stationary sources (e.g., industrial smokestacks), mobile sources (e.g., vehicle emissions), and non-point sources (e.g., fugitive dust) produce a load to the Study Area through the processes of dry and wet deposition. Further, persistent contaminant~~chemicals~~ can travel long distances through the atmosphere from other parts of the world. Dry deposition refers to the deposition of air pollutants from atmospheric suspension in the absence of precipitation. Wet deposition refers to deposition of air pollutants from atmospheric suspension via rain or snow.

The following subsections present the approach and data sources applied to generate estimates of the annual loading of selected analytes to the Study Area via dry and wet atmospheric deposition. Air deposition loading estimates presented here focus on dry and wet deposition directly onto the water surface of the lower Willamette River within the Study Area. Atmospheric deposition to land in the Study Area watershed, which could subsequently be transported to the Study Area via stormwater runoff, is captured, though not distinguishable from other sources, in the stormwater loading assessment (Section 6.1.2). A qualitative discussion of atmospheric deposition to land in the Study Area watershed is provided in ~~subsection~~Section 6.1.4.3.2.

The selected contaminants list for atmospheric deposition loading is presented in Table 6.0-1. This list was limited to those contaminant~~chemical~~s on the combined ~~IC~~contaminant loading list for which data were available to support the atmospheric loading estimates. The detailed data sets, methodologies, and results for dry and wet deposition loading to the Study Area water surface are presented in Appendix E, Section 5.0. As with other loading term estimates, the atmospheric deposition estimates are presented as a range representing the relative uncertainty, as discussed further below.

6.1.4.1 Data Sets and Approach

Atmospheric deposition is the sum of both dry and wet deposition loads. Under conditions of no precipitation, gases and particles are deposited to the ground or river surface in a process known as dry deposition. Dry deposition is driven by the gravitational force on the particulate matter and the gas aerosol. Numerous studies have been performed to characterize the dry deposition of various contaminant~~chemical~~s onto a variety of ground surfaces. USEPA has conducted a review of many of these studies and concluded that dry depositions of both particulate matter and gases will contribute to the contaminant~~chemical~~ concentrations in soils and surface water bodies (USEPA 2005~~a~~b). Wet deposition occurs when gases and particles are scavenged by rain droplets, freezing rain, snow, or fog droplets and are ultimately deposited to the surface. The following subsections briefly describe the data sets and approach applied to assess dry and wet deposition loading to the Study Area.~~,~~ ~~a~~Additional detail on the calculations and data sources is provided in Appendix E, Section 5.0.

6.1.4.1.1 Dry Deposition to the River Surface

Atmospheric dry deposition to the Study Area was estimated based on an assumed deposition velocity, Study Area-specific and non-local air concentration monitoring data, and the Study Area surface water extent. For a given analyte, dry deposition loading (kg/yr) to the Study Area can be calculated as the product of the air concentration (mass/volume), the deposition velocity (length/time), and the surface area of the Study Area (length^2). The rate of contaminant~~chemical~~ deposition to a surface (deposition velocity) is a function of atmospheric turbulence, properties of the contaminant~~chemical~~ species, and the relative reactivity of the species with the receiving surface (Seinfeld and Pandis 1998). Where available, Study Area-specific or local ambient air concentration data were used. For those contaminant~~chemical~~s for

which local sampling data were not available, concentration values from publicly available data sources, including DEQ and USEPA, were used. The assumptions and data sources applied to determine these factors are presented in detail in Appendix E, Section 5.0. In summary, local information[12] was used in dry deposition calculations for all the metals, BaP, naphthalene, TPH (diesel), total PCBs, hexachlorobenzene, total PAHs, and total cPAHs; exclusively external data sources were used for dry deposition estimates for the rest of the atmospheric deposition contaminants. A range of estimates was generated for the dry deposition loading fraction of the total atmospheric load. This range was based on the range of ambient air concentration results compiled.[13] Specific effort was made to analyze the local monitoring and modeling data for BaP and naphthalene to ensure the representativeness of the data values for dry deposition loading over the river surface (see Appendix E for details).

6.1.4.1.2 Wet Deposition to the River Surface

Although wet deposition flux can be modeled, the most reliable estimation method is to collect precipitation in suitable samplers, measure the contaminant~~chemical~~ concentrations, and calculate the deposition flux corresponding to the sampling period (Reinfelder et al. 2004). Subsequently, the total annual wet deposition loading is calculated by multiplying the deposition flux by the total area of the Study Area. Unfortunately, such data are limited. From the contaminant list, Study Area-specific wet deposition monitoring results were only found for total PCBs (MWH 2008) and mercury. In the MWH (2008) study, wet deposition data were collected from three monitoring stations within the Study Area for a ~~two~~2-month sampling period spanning May through June of 2007. The MWH (2008) study reported wet deposition loading rates calculated from the monitoring concentration data (taking into consideration the field blank values). Mercury findings from Hope (2005) were considered for comparison with estimates based on the New Jersey Atmospheric Deposition Network (NJADN) data (Reinfelder et al. 2004). Briefly, the Hope study used precipitation monitoring data from Oregon Mercury Deposition Network sites (one site near Beaverton and one site near the southern end of the basin), and found wet deposition estimates comparable to those generated here by the NJADN ratio approach.[14] In summary, local information was used for mercury and total PCBs, and non-local/modeling data sources were used for all other contaminant~~chemical~~s.

[12] Local is defined here as monitoring data or modeling results for Portland, Oregon or Multnomah County, Oregon.

[13] The maximum value of 0.32 µg/m^3 BaP was determined to be an outlying value among the values from the LASAR data based on statistical analysis and was excluded from the calculation; an average value of 0.19 µg/m^3 was also excluded for the same reason. The following values for naphthalene were excluded from calculations based on statistical analysis: 2.16 µg/m^3 as one of the maximum values, 1.87 µg/m^3 as an average value, and 1.55 µg/m^3 as a minimum value. Please see Appendix E for more details.

[14] Hope (2005) calculated dry, wet, and total mercury loading rates to surface water for the entire Willamette River basin (398,000,000 m^2). When scaled down to the sub-area of the basin represented by the Study Area (8,791,735 m^2, 2 percent of the open water area estimated by Hope), Hope estimates a total atmospheric mercury load of 0.08 kg/yr. This result is slight lower than, but comparable to, the lower mercury load (0.11 kg/yr) presented here.

With the exception of PCBs and mercury, for which Study Area-specific precipitation monitoring results were available, the monitoring results from NJADN (Reinfelder et al. 2004) were used, corrected by the ratios of 1) total atmospheric concentrations between Portland, Oregon, and Jersey City, New Jersey (where available in both), and 2) total annual precipitation between Portland and Jersey City. This approach of scaling NJADN data sets to develop wet deposition loading estimates generated only a single point estimate rather than a range because only average values were reported from the NJADN study. The detailed methodology, data sources, loading results, and associated uncertainties are presented in Appendix E, Section 5.0. Uncertainty and results are also discussed in Section 6.1.4.2 and 6.1.4.3, respectively.

6.1.4.1.3 Total Deposition to the River Surface

The total deposition loading to the Study Area for each selected contaminant was estimated simply by summing the dry deposition and wet deposition loading estimates. Since only central estimates could be generated for wet deposition loading, the ratio of the central estimate for wet deposition to the central estimate for dry deposition was assumed to be representative of the ratios across the range of wet deposition loading estimates. From this, upper and lower range estimates were generated for wet deposition for use in estimating the total deposition range. Where wet deposition data were inadequate to allow for estimation of even a central estimate, total loads were assigned based on the dry deposition estimates. Wet deposition estimates were unavailable for PCB TEQ, TCDD TEQ, 4,4'-DDE, 4,4'-DDT, naphthalene, total PAHs, TPH (diesel), hexachlorobenzene, aldrin, and dieldrin. The estimates are still considered to be useful, however, based on the relatively low contribution of wet deposition to the total estimates for similar contaminant~~chemical~~s: total DDx (<2 percent), BaP (~10 percent), ~~and~~ total cPAHs (~21 percent), and total chlordanes (~16 percent). This source of uncertainty is noted in the following subsection.

6.1.4.2 Uncertainty

The lack of the Study Area-specific, analyte-specific, and temporally proximal data inputs for many of the contaminants places significant uncertainty on the estimates for the atmospheric deposition loading term. Specifically, local data were available only for metals, BaP, naphthalene, cPAHs (modeled), total PAHs (modeled; based on 16 individual PAHs), hexachlorobenzene, TPH (diesel), and total PCBs (modeled) for dry deposition calculations; for wet deposition calculations, local data were available only for mercury and total PCBs (limited sampling period). In the case of the atmospheric deposition loading estimates, the presented range of estimates (lower, central, upper) is not expected to fully capture or represent the uncertainty associated with this term, due to significantly limited local empirical data.

The major uncertainties associated with dry deposition loading estimates are as follows:

- The limited available local atmospheric concentration data
- The necessarily simplified calculation methodology

- The uncertainty associated with selection and uniform application of a deposition velocity.

The major uncertainties associated with wet deposition loading estimates, are as follows:

- The limited local wet deposition monitoring data. Empirical data were available only for mercury and PCBs.
- The uncertainty associated with application of precipitation correction factors to allow for use of NJADN data.

In summary, atmospheric deposition to the river surface is one of the most uncertain loading terms, primarily due to the limited availability of local atmospheric concentration and precipitation concentration monitoring data. The direction of any bias in the estimates created by these uncertainties is unknown. Fortunately, deposition to the watershed and subsequent runoff to the river is captured in the empirical stormwater runoff data set and stormwater loading estimates (discussed in Section 6.1.2).

6.1.4.3 Findings

This section presents the findings of the estimation of atmospheric deposition to the river surface described above. A qualitative discussion of atmospheric deposition to the watershed is also provided.

6.1.4.3.1 Atmospheric Deposition to the River Surface

Table 6.1-7 presents the estimated ranges of annual total atmospheric deposition to the river surface for the entire Study Area. Figures 6.1-36 through 6.1-40 graphically present the estimated ranges of annual loads for dry deposition, wet deposition, and total atmospheric deposition to the Study Area for each contaminant group.

PCBs and TCDD TEQ – The estimated ranges of dry, wet, and total deposition for total PCBs and TCDD TEQ are presented on Figure 6.1-36. The dry deposition fraction of the annual load represents the majority of the total annual loading estimate for total PCBs, with only less than 0.5 percent of the load attributed to wet deposition. No wet deposition data were available for PCB TEQ or TCDD TEQ estimates.

Pesticides – The estimated ranges of dry, wet, and total deposition for pesticides are presented in Figure 6.1-37. The total annual loads for pesticides are dominated by the dry deposition load estimates. However, wet deposition estimates were only available for DDx and total chlordanes, and wet deposition composed 2 and 16 percent of the total, respectively (see Appendix E, Table E5-2). Further, total DDx estimates based on NJADN estimates are lower than the 4,4'-DDE and 4,4'-DDT estimates based on ATSDR ambient concentration estimates. This difference reflects the range of uncertainty in the various data sources. In light of this uncertainty, total DDx estimates

to be used in the CSM discussion in Section 10 will reflect the combined ranges of the estimates.

PAHs – The estimated ranges of dry, wet, and total deposition for PAHs are presented on Figure 6.1-38. The total annual loading estimates are significantly higher for naphthalene than BaP (10 times for upper value, 3 times for central, and about the same for lower value), suggesting dominance of the LPAH fraction. Further, for all PAHs, the dry deposition fraction of the annual load represents the majority of the total annual loading estimate, with only a very small fraction attributed to wet deposition.[15] (Total PAH atmospheric loads are based on 16 PAHs from Oregon USEPA National Air Toxics Assessment data [USEPA 1996], which includes all of the Study Area PAHs except for 2-methylnaphthalene.) The PAH loading estimates are considered to be highly uncertain based on comparison with other loading term estimates. Furthermore, statistical analysis USEPA LASAR data for BaP and naphthalene indicated some data values are out of the statistical ranges that are suitable for atmospheric loading calculations, and therefore, the total PAHs values could be affected by the outliers.

Total Petroleum Hydrocarbons (~~d~~Diesel) and Hexachlorobenzene – The estimated ranges of dry and total deposition for ~~DRH~~TPH (diesel) and hexachlorobenzene are presented on Figure 6.1-39. No wet deposition data were available for these contaminant~~chemical~~s. Furthermore, as discussed in Appendix E, no data to support estimates of dry, wet, or total atmospheric deposition rates were available for other TPH fractions (i.e., gasoline-range and residual-range hydrocarbons).

Metals – The estimated ranges of dry, wet, and total deposition for metals are presented on Figure 6.1-40. Lead, zinc, and copper exhibited the greatest total annual loading estimates by atmospheric deposition. Dry deposition loading contribution to total annual deposition was greater than the wet deposition contribution with the exception of mercury, which exhibited ~~seven~~7 times greater annual deposition by wet deposition. While dry deposition estimates were greater than wet deposition for the other metals, dry deposition estimates were all within a factor of 10 of the wet deposition estimates, suggesting both mechanisms are important to the overall load.

6.1.4.3.2 Atmospheric Deposition to the Watershed

Contaminant~~Chemical~~s that are deposited via atmospheric deposition to soils and impervious surfaces in the Study Area watershed may subsequently be transported to the Study Area via stormwater runoff. In general, for surface water bodies with

[15] Wet deposition data were not available for total PAHs based on Oregon USEPA NATA data (USEPA 1996) for direct calculation of wet loading estimates; however, a closer look at the NJADN data set suggests that wet deposition is not expected to be a significant fraction of the total deposition for this chemical set. Wet deposition data were available from the NJADN study for a total based on 36 PAHs. Analysis of that New Jersey data shows that wet deposition loads are 3 orders of magnitude lower than dry deposition loads. Similarly, analysis of the 13 Study Area PAHs included in the New Jersey data set of 36 also shows that wet deposition loads are 3 orders of magnitude lower than dry deposition loads.

relatively smaller watershed areas compared to water surface area, the total atmospheric deposition loading to the surface water is greater than the deposition loading to the watershed (Steuer 1995). But for a riverine system such as the ~~L~~lower Willamette River, with small surface water areas relative to the contributing watershed, atmospheric deposition to the watershed plays a greater role.

A review of available literature indicates that the relative importance of the atmospheric deposition loading term, relative to other loading terms, varies by site and by contaminant~~chemical~~. Some studies found atmospheric deposition to the watershed to be a significant source to the surface water bodies. For instance, atmospheric deposition was found to be the dominant source term for total PCBs to the North and Baltic Seas (Struyf and Van Grieken 1993; Wania et al. 2001) and for HCH to the North Sea (Struyf and Van Grieken 1993). A recent study performed by Sun et al. (2007) in the Great Lakes region correlates average gas-phase atmospheric PCB concentrations with local population size, suggesting a strong urban source of atmospheric PCBs. Likewise, Motelay et al. (2006) found atmospheric deposition to impervious surfaces to be the most important source of PAHs to the urbanized Seine River basin near Le Havre, France. Further, one of the most recent systematic monitoring studies (the NJADN) found that direct (dry, wet, and gaseous air-water exchange) and indirect (runoff) atmospheric deposition are of major importance to the accumulation of certain elements (e.g., mercury) and major nutrients in surface water ecosystems (Reinfelder et al. 2004). Findings from a separate, locally relevant study led by Hope (2005) of Oregon DEQ produced loading rate estimates for mercury comparable to those from the NJADN study.

Other studies found atmospheric deposition to the watershed to be less significant as a source of contaminant~~chemical~~s to surface water. A study of numerous urban U.S. streams (not including the Willamette River) evaluated the relative importance of different non-point sources of VOCs to total loading, finding that atmospheric deposition was of secondary importance for VOCs compared to the loading from urban land sources (Lopes and Bender 1998).

Because of the complexity of the fate and transport of contaminant~~chemical~~s via stormwater runoff, a simple application of the flux rate estimated for deposition to the water surface is not appropriate for estimating loads to the Study Area from atmospheric deposition to the watershed. Contaminant~~Chemical~~s deposited in the watershed surfaces are subject to a number of loss mechanisms outside of runoff transport, including leaching, degradation (biotic and abiotic), and volatilization (USEPA 2005~~a~~b). Further, it is difficult to appropriately estimate the amount of deposited contaminant~~chemical~~ mass that would be transported by runoff, and even more difficult to determine how much of that entrained contaminant~~chemical~~ mass would be transported to the Study Area surface water given the complexity of routing and settling, etc. along the pathway. Other studies (Deletic et al. 1997; Grottker 1987) highlight the complexity of quantitatively estimating the relative contribution of atmospheric deposition to surface water bodies. These studies note that such estimates

require a detailed understanding of the geochemical process and transport fluxes specific to the urban watersheds.

The only empirical information available to assess the atmospheric contribution to the stormwater load is present in the stormwater data set. While many areas sampled as part of the LWG stormwater program have contaminant sources other than atmospheric sources, it could be assumed that samples collected from open space areas (and possibly residential areas, depending on the contaminant) represent primarily atmospheric deposition sources. Target contaminants for stormwater loading were detected in stormwater runoff in water and/or sediment trap samples in all sampled open space land-use type locations, except for 4,4'-DDD, total DDD, aldrin, dieldrin, gamma-HCH, hexachlorobenzene, naphthalene, PCB 081, PCB 126, PCB 169, and total chlordanes. PCDD/Fs and TPH were not sampled in stormwater runoff for any land-use type. Given the complexities/variables of runoff routing, adsorption of contaminant~~chemical~~s to varying surfaces, stormwater controls, etc., a more rigorous assessment of the stormwater data set is not warranted. These variables confound the utility of a direct comparison of open-space runoff to other land-use type runoff for the purposes of assessing atmospheric deposition contributions. A discussion of stormwater data by land use type is presented in Section 4, and the stormwater annual load estimates by land use type were presented in Section 6.1.2.

6.1.5 Upland Groundwater Plumes

Upland groundwater plumes flowing toward the river are a potential source of contaminant~~chemical~~s to the in-river sediments, TZW, and surface water in the Study Area. This section presents the approach, data sources, and findings of an estimation of the loading of contaminants to the Study Area from upland groundwater plumes. Empirical seepage rate and TZW concentration data information from the nine GWPA study sites (a detailed discussion of site selection and GWPA data interpretation is presented in Appendix C ~~Section~~ 2) were applied to generate an estimated range of annual loads for the individual study sites.[16] There may be additional sites that lack upland groundwater data but have complete groundwater pathways; however, such sites have not been identified or assessed.

The contaminants listed in Table 6.0-1 are the focus of this loading assessment.

In order to generate estimates for this loading term, a simplifying assumption was applied that is not reflective of actual conditions in all areas/for all contaminants. Specifically, these estimates assume that observed TZW concentrations are entirely attributable to upland groundwater. In areas where there are both upland groundwater

[16] Study Area loading estimates are based on empirical information from only nine study sites, and it is possible that other sites will be identified that have a complete pathway for upland groundwater plumes to the Study Area. The groundwater pathway site selection process was designed to identify all sites with a reasonable likelihood of exhibiting a complete transport pathway for upland groundwater plumes to the Study Area. Detailed discussion of the groundwater pathway site selection process is presented Appendix C ~~Section~~ 2.

plume and sediment sources, contaminants detected in TZW samples may be partly or wholly attributable to contamination originating in sediment solids (partitioning into pore water). For certain contaminants (e.g., redox-sensitive metals, petroleum-related hydrocarbons, etc.), as discussed in Appendix C~~ Section~~ 2, differentiation of the origin of contaminants present in the pore water in areas with groundwater discharge and upland groundwater plumes was often not possible with the available information. In such instances, the estimates of groundwater plume loading are expected to be redundant with advective loading estimates in the specific TZW study areas. Advective loading estimates based on equilibrium partitioning assumptions and sediment concentrations are presented in Section 6.1.6. This redundancy was recognized and accepted in this analysis to allow for assessment/approximation of each of the terms and comparison of the relative, Study Area-wide effects. Loading estimates for the fate and transport model will address loading from upland groundwater plumes and advective loading from groundwater discharge through sediments somewhat differently. The model simulates the transport of ~~chemical~~contaminants within and out of the sediment bed via processes such as advection due to movement of groundwater, diffusion, and dispersion this transport includes partitioning. In the specific areas where there are contributions from upland plumes, an upland plume loading term is specified based on available TZW concentrations and flux estimates from filtered trident and peeper data; this additional mass is subject to the same transport processes and partitioning within the bed.)

The following subsections present a summary of the data sets and approach used in the upland groundwater plume loading calculations, as well as a presentation and discussion of the findings. Detailed presentations of the data sets, data treatment, calculations, assumptions, and results are presented in the supporting Appendix E, Section E6.1.

6.1.5.1 Data Sets and Approach

Estimates of groundwater plume contaminant loading to the Study Area are based on site-specific identification of potential plume discharge zones offshore of the nine TZW study sites, measured concentrations of contaminants in TZW, and measured groundwater discharge rates in potential plume discharge zones. The following data sources were used to determine these terms:

- Twenty-eight flow zone areas identified offshore of the nine TZW study sites were used to group data sets for the calculations. These flow zones are presented with discussions supporting the interpretations in Appendix C~~ Section~~ 2. The zones are also presented in Appendix E in support of the detailed approach discussion presented in Appendix E, Section 6.1.
- Measured shallow TZW contaminant concentrations from 150 sample locations at the nine study sites were applied to the calculations. These samples represent the complete TZW data set for the sample depth interval from 0 to 38 cm bml (see Maps 2.~~2-6~~1-20a-~~e~~l). The sampling methods used to produce this data set include small-volume peeper, Trident, and Geoprobe samplers. Both unfiltered

and filtered (where available) results were included in the evaluation. These TZW analytical results were presented in detail and discussed in Section 5.~~4~~5.

- Seventy-seven seepage meter measurements from the 28 flow zone areas were used to estimate groundwater flux for each zone. This seepage rate data is presented in Appendix C~~ Section~~ 2.

As a first step, Thiessen polygons based on the TZW sampling locations were generated within each flow zone based on the TZW sampling locations to assign an area to each sample. This step was necessary to support area-weighting of each TZW analytical result. Loading estimates were prepared for each flow zone area by summing the estimated loads for each of the sample polygons within the flow zone, using the following general equation:

$$Load_{flowzone} = \Sigma(C_{sample} \times A_{sample} \times UnitFluxRate)$$

Where,

$Load_{flowzone}$	=	the estimated annual mass load to surface water, µg/yr
C_{sample}	=	the contaminant~~chemical~~ concentration in the TZW, µg/L
A_{sample}	=	the area of the Thiessen polygon associated with the given sample, ft^2
UnitFluxRate	=	groundwater seepage flux rate for the given flow zone, $L/ft^2/yr$.

A range of load estimates for each flow zone was determined by applying both the filtered and unfiltered concentrations to the calculations, as well as the average and the maximum measured seepage flux for the given flow zone. From the resulting four estimates, the highest and lowest values were assigned to designate the range. The estimate based on the average measured flux and the unfiltered concentrations was assigned as the central estimate.

The range of estimated annual loads for a given study site was determined by summing the estimated ranges for each Thiessen polygon. The ranges of load estimates for the Study Area were, in turn, generated by summing the estimates for each of the nine study sites. Detailed presentation of the steps in this approach and complete tabulated results are provided in Appendix E, Section 6.1.

6.1.5.2 Uncertainty

The upland groundwater plume loading estimates are based on empirical, Study Area-specific TZW chemistry and groundwater flux data collected offshore from the nine upland sites included in the GWPA sampling program conducted as part of the RI. The range of results presented for this term is expected to be a reasonable approximation of

the uncertainty in the loading estimates, though there are additional potential sources of uncertainty that may not be reflected in these ranges. Specifically, the following sources of uncertainty are acknowledged in the upland groundwater plume loading estimates:

- This assessment does not include loading from sites other than the nine study sites where empirical TZW data were collected. As described in the site selection process (Section 4.4.3.1 and Appendix C~~ Section~~ 2), these nine sites represent those with a confirmed or reasonable likelihood for discharge of upland groundwater COIs to Portland Harbor. Eighty-three other upland sites reviewed during the site selection process lacked sufficient data to determine the completeness of the groundwater pathway. To the extent that a complete groundwater transport pathway to the ~~L~~lower Willamette River could be identified in the future at one or more of these 83 sites or other currently unidentified sites, total groundwater plume loading to the Study Area may be underestimated.
- The spatial resolution of the analysis is limited to the resolution of the sampling data sets, as reflected in the Thiessen polygon approach.
- There is no attempt made in these estimates to distinguish the origin of the contaminants in the TZW, and it is expected that the empirical TZW data set includes contaminants originating from sediment (as assessed in the advective loading analysis in Section 6.1.6 and Appendix E, Section 6.2).
- The GWPA study design specifically targeted areas of higher seepage and higher TZW concentrations for sampling in the areas offshore of the study sites.
- The TZW concentration estimates do not account for any additional attenuation to sediments that may occur in the upper 38 cm bml.
- Sampling was conducted during the hydrologic season of highest expected groundwater flow rates to maximize the observed groundwater signal (plume concentration and flow rate). Consequently, the lower end of the groundwater signal in the discharge areas is not captured in the empirical data set.

6.1.5.3 Findings

The estimated ranges of upland groundwater plume annual loads are presented in Table 6.1-8 at the Study Area scale (sum of all nine study sites) and in Table 6.1-9 for the individual study sites. Groundwater plume loads at the Study Area scale are also presented graphically by contaminant group in Figures 6.1-41 through 6.1-45. These group plots show the estimated loads based on filtered and unfiltered estimates to allow for comparison of these data sets. Load estimates for the individual study sites are presented graphically in Figures 6.1-46 and 6.1-47 for total DDx and total PAHs only~~,~~; PCBs and dioxin/furans were not sampled in TZW.

Figure 6.1-41 presents load estimates based on filtered and unfiltered TZW sampling data for DDx components. The unfiltered results are consistently higher than the filtered results for this group of hydrophobic contaminant~~chemical~~s. As discussed in ~~Section 5.4~~5Appendix D4.4, unfiltered results are likely biased high due to entrainment of sediments in the TZW samples. Further, the DDD components compose the largest fraction of the total DDx load estimates for both filtered and unfiltered samples, while the DDE components make up the smallest fraction. Figure 6.1-46 presents the total DDx loading estimates for the two study sites where this contaminant was sampled in TZW.

Figure 6.1-42 presents the upland groundwater plume loading estimates for PAHs. The majority of the total PAHs load from upland groundwater plumes is from LPAHs ~~-~~as opposed to HPAHs. This result follows behavior expectations that the LPAHs are more soluble than the HPAHs. Both HPAHs and LPAHs show a pattern of higher unfiltered concentrations and lower filtered concentrations. This pattern is expected of hydrophobic molecules such as PAHs.

Estimates for upland groundwater plume loading of metals at the Study Area scale (sum of all nine study sites) are presented on Figure 6.1-43. These estimates cover a large range of values, from a central estimate of approximately 0.02 kg/yr for mercury to a central estimate of 8,500 kg/yr for manganese. It is interesting to note that the unfiltered/filtered loading ratios vary for different metals. The ratios for arsenic and manganese show little difference; barium, cadmium, nickel, and mercury unfiltered loading estimates are moderately greater than filtered estimates. Zinc, copper, and lead exhibit large disparities between unfiltered and filtered loading estimates. Estimated metals loads associated with groundwater discharges at individual study sites are provided in Table 6.1-9.

Figures 6.1-44 and 6.1-45 present the upland groundwater VOC and SVOC loading estimates at the Study Area scale (sum of all nine study sites). These plots are broken into two groups of VOCs: Group 1 includes chlorinated, non-aromatic VOCs, Group 2 contains aromatic VOCs and carbon disulfide. Among the Group 1 VOCs (Figure 6.1-44), chloroform and methylene chloride dominate the loading scale~~,~~. *cis*-1,2-~~DCEd~~Dichloroethene exhibits the highest loads among ~~TCE~~trichloroethene and its daughter products.[17] Chloroethane exhibits the highest loads among ~~TCA~~trichloroethane and its daughter products. Among Group 2 (Figure 6.1-45), benzene loads dominate the BTEX contaminant~~chemical~~s, and chlorobenzene loads are higher than 1,2-~~DCB.~~dichlorobenzene. Estimated VOC and SVOC annual loading are provided in Table 6.1-9.

[17] Loading estimates for ~~TCE~~trichloroethene, *cis*-1,2-~~DCE~~dichloroethene, and vinyl chloride are dominated by results from a single TZW sample offshore of the Siltronic site. The groundwater pathway for ~~TCE~~trichloroethene is discussed in detail in Appendix C ~~Section~~ 2.

Upland groundwater loading estimates are compared to other loading rate estimates as part of the CSM presentation in Section 10.

6.1.6 Advective Loading

Advection of groundwater through contaminated sediments can transport contaminant~~chemicals~~ that desorb from sediment solids into the aqueous phase and then migrate with the flowing groundwater, a process defined as advective loading. Two types of advective loading were evaluated for this RI ~~R~~report:

- Subsurface advective loading is migration of contaminants associated with subsurface sediments (deeper than 30 cm bml) to surface sediments via desorption and groundwater advection and sorption to surface sediments. This is considered to be an external loading term to the Study Area.
- Surface advective loading is migration of ~~chemicals~~contaminants associated with surface sediment (0 to 30 cm bml) to surface water via desorption and groundwater advection. This is considered to be an internal fate and transport process in this RI, as it involves contaminant~~chemical~~ mass transfer between media within the Study Area.

Section 6.1 generally focuses on external loading mechanisms, such as subsurface advective loading, which transport mass into the Study Area. However, although considered strictly an internal fate and transport process, surface advective loading is also described in this section to allow for parallel description of the common calculation approach and for comparison of results for both surface and subsurface sediment advective loading. This section describes the approach and results of the analyses to generate estimates of subsurface and surface advective loads.

The surface and subsurface advective loading terms were assessed for the advective loading list presented in Table 6.0-1. These contaminants were selected because they are likely to sorb to sediment solids and are subject to the chemical partitioning processes relevant to this loading mechanism. Both terms were assessed on the scale of the relevant available sediment data set. Loading estimates for each term were generated in units of mass loading per year and presented for the entire Study Area and by river mile.

These advective loading estimates differ from the upland groundwater plume loading estimates presented in Section 6.1.5 in that in-river sediment contamination, as opposed to upland groundwater contamination, is considered to be the contaminant~~chemical~~ source for the advective loading analysis. In areas where concentrations in pore water are attributable to both upland groundwater plumes and in-river sediment sources, the plume loading and advective loading assessments may overlap, resulting in some double-counting of loads. The extent of this overlap depends on the relative magnitude of the groundwater plume concentrations versus the sediment-derived pore water concentrations based on equilibrium partitioning. (The TZW plume study areas account for less than 5 percent of the Study Area). As described in Section 6.1.5, loading

estimates for the fate and transport model address loading from upland groundwater plumes and advective loading from groundwater discharge through sediments somewhat differently than the empirical estimates developed for the RI.

6.1.6.1 Data Sets and Approach

The following subsections briefly describe the data sets and approaches applied to generate estimates of surface and subsurface advective annual loads, as well as accumulation rates of contaminants in surface sediment. Detailed presentation of data sources and approaches is provided in Appendix E, Section 6.2.

6.1.6.1.1 Loading Estimates

The first step in the analysis was to derive Thiessen polygon sets for each contaminant for surface and subsurface sediment. Uniform sediment concentration, bulk density, and organic carbon are assigned to each polygon.

Advective loading rates were developed for each polygon by first estimating pore water concentrations under an assumption of equilibrium, then applying an estimated advection rate to generate a mass annual load. This approach required two major assumptions. First, partitioning between sediment and pore water is assumed to be at equilibrium at all times. Second, the groundwater advection rate is assumed to be constant throughout the system. While these assumptions do not directly reflect the heterogeneity of conditions throughout the Study Area (limited assessment of proximal pairs of pore water and sediment concentration data are provided in Sections 6.2.1.1.1 for organic contaminants and 6.2.1.1.2 for inorganic contaminant~~chemical~~s). However, both of these assumptions are considered necessary to allow for development of loading estimates for the entire Study Area.

Pore water concentrations in surface and subsurface sediment were estimated for each sediment sample. For each sediment sample, pore water concentrations were calculated for a range of equilibrium partitioning values (K_{oc} or K_d), applying the sediment sample percent solids value and organic carbon content (for non-metals). The formulas used and the steps to compile ranges of K_{oc} and K_d values, as well as the full compilation, are presented in Appendix E, Section 6.2.

The groundwater discharge rate was estimated using upland hydrogeologic data gathered under Round 2, applying Darcy's Law to generate an estimated total discharge rate to the river, and converting that discharge to a unit flux through the river sediment surface. The complete data sets and the calculations are presented in detail in Appendix E, Section 6.2. This approach generated estimates of total groundwater discharge rates to the Study Area of 4.6 cfs (lower estimate) to 11 cfs (upper estimate), with a central estimate of 7.3 cfs. Dividing by the surface area of sediment in the Study Area, this corresponds to a range of unit groundwater flux rates of 1.5 to 3.6 ft/yr, with a central estimate of 2.4 ft/yr.

The estimated groundwater discharge rate used in the advective loading calculations was compared with the flow rates observed by seepage meter measurements as part of the groundwater plume loading estimates. The Darcy's Law estimate range is roughly 15 percent of the unit discharge rate observed with seepage meters in the nearshore groundwater plume discharge areas. The selective placement of these seepage meters[18] and the measurement exclusively during hydrogeologic times of higher groundwater discharge (by sampling design) explains the disparity between the two ranges. Overall, the order-of-magnitude agreement between the unit flux rates developed using these two information sources offers confidence in the utility of the Darcy's Law-estimated rates.

From the ranges of estimated pore water concentrations, the range of groundwater advection rates, and the areas associated with each sediment sample,[19] ranges of advective loads were estimated for each sediment polygon by the following equation:

$$Load_{polygon} = C_{TZW} \times A_{polygon} \times Q$$

Where,

C_{TZW} = the estimated contaminant~~chemical~~ concentration in the pore water

$A_{polygon}$ = the area of the polygon

Q = the estimated annual groundwater flux rate.

Annual loading estimates for surface advection to surface water were arrived at by summing the loading assessed for all surface sediment polygons in the Study Area (or within a river mile). Subsurface advective loading (to the surface sediment interval), estimates were only generated for areas where organic carbon-normalized (OC-normalized) subsurface sediment concentrations for the given analyte were greater than the corresponding OC-normalized concentration for the surface sediment.[20] This approach is described in greater detail in Appendix E, including graphical presentation

[18] In the design of the TZW study, seepage meters were purposefully placed at locations where there was an indication (based on pore water temperature measurements, sediment texture, or screening results) of higher flow rates. As such, the seepage meter measurements are expected to be biased high relative to an average unit discharge for the entire Study Area.

[19] Each sediment sample was assigned an area, based on Thiessen polygon sets generated for the surface and subsurface sediment data sets. This step is described in detail in Appendix E, Section 6.2.1.

[20] Upward flux of chemicals from subsurface sediments due to desorption and advection can increase chemical concentrations in surface sediments if surface bulk sediment concentrations (OC-normalized) are initially lower than the underlying subsurface interval. If surface concentrations are greater than or equal to subsurface concentrations, mass flux from the subsurface will not accumulate in surface sediments but will instead discharge to overlying surface water. Existing estimates of advective flux from surface sediments to surface water are assumed to be inclusive of the latter phenomenon. Therefore, the scope of this analysis is restricted to locations in the Study Area where "cleaner over dirtier" conditions exist.

of the spatial breakdown of this approach for PCBs, PAHs, DDx, and dioxin/furans, and a table of the spatial breakdown for all other advective loading analytes. In general, the percent of the Study Area with subsurface loading assessed to surface sediment ranges widely, from 6 percent for aldrin to 94 percent for total PAHs (these percentages reflect the percent areas where OC-normalized subsurface sediment concentrations exceed OC-normalized surface sediment concentrations, and are discussed further in the historical loading section below, Section 6.1.8). Table E6-4 in Appendix E summarizes the percent of the Study Area over which subsurface advective loading was assessed for the entire suite of contaminant~~chemical~~s assessed.

Mass loading estimates to surface sediment (by subsurface advective loading) and to surface water (by surface advective loading) were generated for the advective loading contaminants following the approach described above. The range in each estimate reflects the range of equilibrium partitioning values and the central groundwater discharge rate in ~~to~~ the calculations. Specifically, the upper and lower advective mass loading estimates were calculated with the maximum and minimum equilibrium partitioning values, respectively. The primary equilibrium partitioning values (described in Appendix E, Section ~~E~~6.2.2.2.1) were used to calculate the central advection loading estimate. These results are presented and discussed below in Section 6.1.6.3.

6.1.6.2 Uncertainty

There is significant uncertainty associated with the advective annual load estimates related to applied assumptions (including equilibrium behavior of all contaminants and uniform groundwater discharge rates), as well as the data sets used in the calculations (literature equilibrium partitioning coefficients, and roughly estimated groundwater discharge rates).

The primary uncertainty related to equilibrium is the assumption of equilibrium in all parts of the complex sediment/pore water environment at all times. This calculation fails to capture reaction kinetics and the sorption-desorption-resorption dynamics that occur in advective transport through sediment. For example, to the extent that non-equilibrium conditions may exist in the pore water environment as a result of kinetic limitations on desorption from contaminated sediments, the assumption of equilibrium will overstate pore water concentrations and advective loading rates. Beyond the assumption of equilibrium, the Study Area organic carbon associated with sediments may differ in character from that defined by the range of literature K_{oc} values. Likewise, the location-specific chemical and geochemical conditions (redox, pH, ionic strength and composition, sediment matrix composition, etc.) likely differ in character from those associated with the applied specific literature values. Further, this assessment ignores any chemical or biological transformation processes that may occur in the migration process.

There are a number of significant uncertainties related to the groundwater flux rate estimates. First, they are based on the limited available upland data and not on

groundwater modeling of the area or direct measurement of seepage rates representative of the entire Study Area. Second, the groundwater advection rate estimates rely on a simple and conservatively high cross-sectional area. Third, the advection rate estimates apply a projection of the sediment surface area to represent the actual sediment surface area (thereby increasing the unit discharge estimate). Finally, the assumption of a uniform groundwater discharge rate for the entire Study Area does not capture the spatial variability that is inherent in groundwater discharges to rivers. The discharge rates are assumed to be constant in time and do not account for variability caused by seasonal recharge patterns, changes in river flow rates and stages, and tidal fluctuations ("tidal pumping"). Among all seepage meter locations where net positive average advective groundwater fluxes were measured, the largest net negative recharge rate ~~measured in a seepage meter~~ during a rising tide was offshore of the Siltronic site (Appendix C~~ Section~~ 2). At this location, the negative recharge period covered roughly 9.5 hours, with an average seepage rate of –6.7 cm/day. This corresponds to a net negative seepage flux of 2.65 cm into the sediment bed over the 9.5~~-~~-hour tidal recharge period. Assuming sediment porosity of 25 percent, the maximum depth of influence for this period of negative seepage would be approximately 10.6 cm before the direction reversed to positive discharge with the tidal change. Although tidal pumping may in some instances lead to increased loading of contaminant~~chemical~~s from the sediment bed to the water column by introducing relatively clean surface water into the uppermost several centimeters of the sediment bed with each tidal cycle, uncertainty in the loading estimates due to this effect is expected to be minor compared to the other sources of uncertainty inherent in these calculations.

The large range in most of the estimates presented in the following subsection reflects the range in literature equilibrium partitioning coefficients. These large-scale estimates of advective annual loads are considered to be highly uncertain, but useful for general comparison to other loading terms for each contaminant~~chemical~~. Any local recontamination concerns identified by the FS may require consideration of specific contaminant~~chemical~~ and localized physical conditions, including collection of additional information and/or more complex assessments of advective loading.

6.1.6.3 Findings

This section discusses the results of the analysis and considers the results for surface sediment and subsurface sediment advective loading estimation for the entire Study Area for all advective loading contaminants, as well as results by river mile for PCBs, PCDD/Fs, DDx, and PAHs.

6.1.6.3.1 Study Area Annual Loading Estimates

Study Area-wide loading estimates for the subsurface and surface sediment advective loading terms are presented in Table 6.1-10. These results are also presented graphically on Figures 6.1-48 through 6.1-60, showing both surface and subsurface annual loading estimate ranges. Patterns and other observations for each of the contaminants groups are discussed in the following paragraphs.

The central estimated ranges of annual loads for total PCBs (Figure 6.1-48) are slightly higher for surface sediment to surface water ~~relative~~ than for subsurface to surface sediment. However, the difference for total PCBs (subsurface sediment advection versus surface sediment advection) is only a factor of 1.5 for the central estimates. This observation is expected due to the Study Area-wide higher average PCB concentrations in subsurface as compared to surface sediments. For the individual congeners, estimated load ranges were generally higher for subsurface sediment loading to surface sediments when compared to advective loading from surface sediment to surface water (Figure 6.1-49). Of the individual congeners analyzed, PCB 118 and PCB 105 exhibit the highest annual loads, whereas PCB 169 is the smallest contributor.

Advective loading estimates for PCDD/Fs (Figure 6.1-50) show a slightly greater loading from surface sediment to surface water compared to subsurface- to surface sediments. Estimates of advective loading from surface sediment to surface water are higher by a factor of 2.5 for PCDD/Fs compared to rates of subsurface partitioning to surface sediments. The OC-normalized PCDD/Fs concentrations used in the load calculations are generally similar in surface sediment and subsurface sediment, with 54 percent of the subsurface concentrations being greater than concentrations in surface sediment (Table E6-4). However, the Study Area-wide loading estimates are dominated by individual high surface sediment concentration values, resulting in the greater Study Area-wide total PCDD/Fs advective loading from surface sediment as compared to subsurface sediment.

Commented [A2]: Integral: Retain the word "partitioning" for clarity.

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DDD isomers comprise the largest share of the central estimate total DDx advection load estimates for both surface and subsurface sediment, followed by DDT, and then DDE (Figure 6.1-51). The Study Area-wide subsurface loading to surface sediment is slightly greater than the loading to surface water for each of the DDx compounds (by a factor of 1.8 for total DDx). Approximately 35 percent of the Study Area is not expected to exhibit advective loading of DDx from the subsurface to the surface sediment due to higher OC-normalized sediment concentrations in the surface.

Total PAHs annual load from both the surface and subsurface sediments ~~are~~is dominated by LPAHs (Figure 6.1-52). HPAHs exhibit slightly higher surface sediment loading to surface water relative to subsurface loading to surface sediments. In contrast, naphthalene and total PAHs loading from subsurface to surface sediment is greater than to surface water. The estimated PAH loading from subsurface to surface sediment is greater than loading to surface water by a factor of 3 for the central estimate. OC-normalized subsurface sediment concentrations of ~~LPAHs and HPAHs~~PAHs are higher over 60 to 65 percent of the Study Area (Table E6-4).

The range of advective load estimates for BEHP are presented on Figure 6.1-53. The 5 orders of magnitude range in the estimated loads is a direct reflection of the large range in the literature K_{ow} (octanol-water partitioning coefficient) values. These estimates show slightly more surface sediment loading (by a factor of approximately 2 for the central estimates).

Non-DDx pesticide advective loading estimates are presented on Figure 6.1-54. Among these, gamma-HCH exhibits the highest mass loading, while aldrin the least (possibly due to a tendency for aldrin to degrade to dieldrin in environmental systems). The subsurface to surface advective loading ratios are 0.9 and 1.15 for aldrin and dieldrin, respectively. This ratio is lower for gamma-HCH (0.6) and higher for total chlordanes (~2.5). Non-DDx pesticides exhibit lower OC-normalized subsurface sediment concentrations relative to surface sediment in over 85 percent of the Study Area, except for total chlordanes at approximately 60 percent (Table E6-4).

Advective loading rate estimates for arsenic, copper, lead, and mercury are presented on Figure 6.1-55. Arsenic and copper show the highest Study Area-wide loading, followed by lead. Mercury exhibits the lowest loading estimates, with central estimates 4 orders of magnitude below the corresponding estimates for arsenic and copper. Copper, mercury, and lead surface and subsurface loadings were essentially equal (ratios of 0.8 to 1.1), and representative of the fairly even distribution of surface and subsurface sediment concentrations[21] over approximately 60 to 70 percent of the Study Area (Table E6-4). The arsenic surface sediment to surface water loading estimate is 2.2 times greater than the subsurface loading to surface sediment estimated loading, and only 40 percent of the Study Area exhibits subsurface concentrations greater than in surface sediment (Table E6-4).

Estimated TBT advective loads (Figure 6.1-56) vary over 3 orders of magnitude from the lower to upper estimates. The subsurface-to-surface sediment loading estimate is 3.7 times higher than the surface sediment loading to surface water for the central estimates. Approximately 40 percent of the Study Area was not considered to be loading to the surface sediment, due to higher OC-normalized surface to subsurface sediment concentrations ~~as~~ (Table E6-4).

Commented [A4]: Integral: The central estimates are not simple averages. Retain "central", do not replace with "mean".

Commented [A5]: EPA: OK

In summary, Study Area-wide advective annual loads from subsurface sediment to surface sediment were higher than advective loading from surface sediment to surface water for PCBs, DDx pesticides, LPAHs (and total PAHs, which are dominated by LPAHs), BEHP, arsenic, total chlordanes, and TBT. The opposite was true for PCDD/Fs, gamma-HCH, and HPAHs. There was little difference between the surface and subsurface advective loading estimates for aldrin, dieldrin, copper, mercury, and lead. These differences are a direct reflection of the patterns of relative OC-normalized concentration of each contaminant~~chemical~~ in surface as compared to subsurface sediment. This pattern is addressed further in the historical loading discussion (Section 6.1.8).

6.1.6.3.2 Annual Loading by River Mile

Figures 6.1-57 through 6.1-60 present annual surface sediment and subsurface sediment advective loading for each river mile in the Study Area for total PCBs, total PCDD/Fs,

[21] Surface and subsurface sediment concentrations comparisons to support the calculations for metals were not OC-normalized, reflecting the use of K_d values as opposed to K_{oc} values.

total DDx, and total PAHs. Given the nature of the analysis (Thiessen-polygon-based scale of assessment), variations in river-mile-scale annual load estimates are indicative of variations in sediment contaminant~~chemical~~ concentrations and organic carbon content. Groundwater flux rates and assumptions of equilibrium behavior were held constant over the entire Study Area in advective loading calculations.

The sediment advective loading pattern for total PCBs is fairly complex. As shown on Figure 6.1-57, the highest central estimates of advective loading from subsurface sediment to surface sediment are observed at RM 8 to 9. The highest annual surface sediment loading estimates to surface water are observed at RM 9 to 9.9.

Subsurface sediment advective annual loading to surface sediment, and surface sediment advection to surface water for total PCDD/Fs (Figure 6.1-58) are fairly consistent across the Study Area, with the exception of higher annual loading estimates to surface water from RM 7 to 7.9.

The highest surface and subsurface sediment advective loads for DDx are predicted at RM 7 to 7.9 (Figure 6.1-59). Subsurface-to-surface sediment advective loading annual estimates are comparable or greater than the estimates of surface sediment advection to surface water in all river miles except RM 9 to 10 and RM 11 to 12, where the load from advection to surface water is somewhat greater.

The highest subsurface advective loading to surface sediment for PAHs (Figure 6.1-60~~),~~) is observed at RM 6 to 6.9.[22] The maximum load estimates for surface sediment advection to surface water ~~load estimates~~ are observed at RM 5 to 5.9. Subsurface-to-surface sediment advective loading estimates are comparable to or greater than the load estimates for surface sediment advection to surface water in all river miles except RM 5 to 6 and RM~~-~~ 9 to 10, where the load from advection to surface water is somewhat greater.

6.1.7 Riverbank Erosion

This section assesses the susceptibility of riverbanks within the Study Area to erosion, and presents the limited data set available for characterizing riverbank materials. No quantitative estimation of the loading of contaminants to the in-water portion of the Study Area from bank erosion is presented.

For the purposes of this analysis, riverbank materials are defined as soil and sediment that are between the mean high water mark (MHWM)[23] and the ordinary high water

[22] This peak comprises the majority of the Study Area total load assessed for this term, and is attributed largely to LPAHs (see Table E6-7 and E6-8 in Appendix E).

[23] The MHWM is the elevation defining the shoreline boundary of the Portland Harbor Superfund Site, which is +13.3 ft (NAVD88). This elevation is based on a DEQ memorandum dated July 9, 2003 to USEPA regarding the upland/in-water boundary for the Superfund ~~S~~site (DEQ 2003~~b~~).

mark (OHWM).[24] This includes gently sloped upper beach areas as well as steeper bank areas. While erosion of bank materials containing contaminants from above the OHWM, including materials much farther upland, is also possible, upland erosion is primarily caused by overland transport (stormwater runoff), which is discussed in Section 6.1.2, and by flood events.

The primary mechanisms for riverbank erosion are river water moving over bank materials, direct overland transport across these materials, and sporadic mass wasting or slumping events when bank slopes become over-steepened or otherwise unstable. Wind erosion, shoreline construction and other human activities, and activities of animals~~,~~ are also possible erosion mechanisms. However, these can reasonably be considered to be minor in comparison to river and stormwater flows (construction is considered minor because such projects are regulated and permitted to minimize erosion of bank materials into surface waters).

River water can cause erosion when river levels rise and come into contact with the bank. The MHWM (elevation +13.3 ft NAVD88) is based on the monthly average water level for the 16-year period from 1987 to 2002. During certain periods, particularly during winter months, riverbanks above this elevation can become inundated by river water. Erosive mechanisms during these periods include the direct and shear stress forces of currents with sufficient nearshore velocity to suspend soil and sediment particles. Nearshore velocities can be affected by a number of factors, including the following:

- Bends in the river, where outer bends tend to be subject to greater velocities
- Other shoreline features that may create eddies
- The presence of nearshore structures, which tend to slow nearshore currents unless localized focusing effects or strong eddies are generated
- The general "roughness" and physical complexity of the bank surface.

Wind-generated wave action or vessel wakes can also cause bank erosion as these waves break on the shoreline and dislodge riverbank materials. Wave action can be diminished or augmented in particular areas due to concentration of reflected waves and/or the length of wind fetch to which the shoreline is exposed.

Erosion of relatively exposed bank material can occur in localized areas where stormwater sheet flow, particularly from nearshore impervious surfaces, flows to small low spots and becomes concentrated into rivulets or small streams. These flows can

[24] The OHWM refers to the upper edge of the riverbank and is defined as approximately +20 ft (NAVD88; DEQ 2003~~b~~). The OHWM defines the elevation beyond which inundation by the river is limited to extreme flow events, which occur approximately every ~~five~~5 years.

also cause saturation of bank soil and sediment, which may make them more unstable and susceptible to mass wasting.

For riverbank materials to represent a potential loading term to a river, two conditions must be met: 1) the materials must be in a form that is potentially available for erosion into the river; and 2) contaminants must be present at elevated levels within bank soils and sediment. Because most banks in the Study Area are longstanding, vegetated, and in equilibrium with common currents, boat wakes, and overland transport or runoff, mass wasting during extreme events may be the only significant loading process. For typical years, there is likely no significant load from riverbanks, as discussed below.

6.1.7.1 Bank Materials Available for Erosion

Regardless of the force exerted on the bank, the degree of erosion generated is highly dependent on the physical conditions of the bank itself, the type of materials present, and how directly exposed the materials are to these forces. Primary factors affecting the susceptibility of banks to erosion include the following:

- Presence of protective and stabilizing vegetation (natural or planted)
- Presence of stabilizing structures such as bulkheads
- Presence of riprap, concrete, or other materials intended to protect the bank
- Steepness and overall profile of the bank
- Type of soils and sediment (e.g., consolidated, loose, gravel, sand, silt, cohesive clay, fill, or natural materials)
- Degree of saturation
- Presence of debris or artificial bank structures placed for purposes other than bank protection (e.g., boat ramps)
- Presence of docks, piers, dolphins, pilings, breakwaters, groins, and shoreline structures
- Presence of bench or beach areas below the bank, which can act to dissipate wave forces higher on the bank.

Where protective vegetation, structures, or materials are present, the type and condition of the materials underneath are often less important to erosion rates. An ODFW study (Vile and Friesen 2004) reviewed and inventoried the shoreline features from Willamette Falls (RM 26.5) to the confluence with the Columbia River (RM 0) and broke them into twelve general classifications based on nearshore habitat types. Using ~~this~~these data and several other sources of information, the City of Portland updated its natural resource inventory from the Broadway Bridge (RM 11.6) to the Columbia River, and reported (City of Portland 2008~~d~~a) the most common bank types within this area are vegetated riprap, sandy and rocky beach, and unclassified fill. Percentages of shoreline bank classification are as follows:

- Vegetated riprap—25 percent
- Beach—23 percent
- Unclassified fill—21 percent
- Pilings limiting light—13 percent
- Non-vegetated riprap—12 percent
- Bio-technically engineered banks (artificial materials with vegetation aimed at bank stabilization)—3 percent
- Sea wall—2 percent
- Rock—1 percent
- Pilings allowing light—0 percent.

Map 3.1-17 ~~maps~~depicts these bank classifications, adapted from the 2004 ODFW study. Only beach and unclassified fill, which together represent approximately 44 percent of the shoreline, are likely to be at all susceptible to erosion. Unclassified fill occurs in areas that were filled over time with a variety of unconsolidated materials and debris. No engineered riprap covers the surface, and banks can become unstable from erosive river forces and slump into the river. River beach areas are less steep, are in equilibrium with in-river physical processes, and can often act as a buffer. Thus, unclassified fill is likely to be the most susceptible to erosion during extreme events. However, this classification represents a diverse range of physical conditions, and some of these areas have surfaces composed of various-sized rocks, sporadic vegetation, artificial debris of various types, and natural debris such as logs and wood, all of which may protect some of these areas to some extent.

For purposes of loading estimation, approximately 15 to 25 percent of the shoreline is assumed to be potentially susceptible to erosion of bank materials. The low end of the range accounts for the presence of vegetation and natural and artificial debris that can reduce the potential for erosion. The high end of the range overestimates the amount of unclassified fill that is susceptible to erosion, but it allows for the fact that some portions of the other categories may include small areas that are relatively susceptible to erosion.

6.1.7.2 Bank Material Chemistry

The LWG has searched documents available from DEQ through December 2007 for bank soil and sediment chemistry results associated with upland sites. Very little bank soil and sediment chemistry data are available for Portland Harbor. Nearshore soil and sediment chemistry data from other parties were compiled from DEQ documents and uploaded to the LWG's SCRA database. The bank data contained in the SCRA database are summarized in Table E7-1, Appendix E, and are provided in full in the SCRA data file provided on CD in Appendix E, Section 7.0 (Attachment E-3). The selection process for summarizing the bank data included the following:

- Data collected between RM 1.9 and 11.8
- Data collected since May 1997
- Surface sediment or soil data (0–40 cm)
- Samples collected between 11 and 20 ft NAVD88
- Category 1 and 2 data.

The locations of the riverbank data points relative to the bank categories described above are shown in Map E7-1, Appendix E. As noted above, the table and map include samples that were taken near but not necessarily within the zone from +13 to +20 ft NAVD to capture as much bank data as possible. Riverbank soil and sediment data are available upstream of the Study Area in the downtown reach (Zidell South Waterfront property and Ross Island) and upriver (Oaks Bottom Landfill area and Willamette Falls). These data are not summarized in Table E7-1, but they are provided with the complete bank SCRA data file provided on CD in Appendix E, Section 7.0.

A considerable portion of the harbor riverbank materials that may be generally susceptible to erosion have no existing bank chemistry data. In these cases, it is impossible to quantify the concentrations and extent of contaminants that may be present and available for transport to the river via bank erosion. Among the sites with available bank chemistry data, contaminants on the loading lists were detected in bank soils and sediment that are potentially susceptible to erosion (Table E7-1).

6.1.7.3 Riverbank Erosion Loading

Due to the paucity of existing bank condition and chemistry information at multiple shoreline sites, it is not possible at this time to estimate loading from this source to the river. Although it is estimated that approximately 15 to 25 percent of the banks within the Study Area are potentially susceptible to erosion, it is not possible to estimate typical erosion rates or a range of rates that might apply to these areas given the wide range of conditions present. However, it is unnecessary to develop such loading estimates for the purposes of the RI/FS. Because bank erosion is an area-specific condition dependent on both the erodibility and contaminant concentrations at any given bank area, the potential role of bank erosion may need to be evaluated as a part of the future remedial design process for each sediment management area ~~(SMA)~~.

6.1.8 Historical Loading

The previous sections focused on current loading to the Study Area. However, historical loading is an important element of the CSM because it affects the current contaminant distribution. Historical loading is defined as any loading of selected contaminants to the Study Area that occurred prior to collection of the data sets used to assess the current loading terms. Historical loading is reasonably expected to have occurred by all of the loading mechanisms assessed above: upstream surface water, bedload, stormwater, non-stormwater direct permitted discharges (as defined in Section 6.1.3), groundwater plume discharge, atmospheric deposition, riverbank erosion, and

advective loading. For each mechanism, the historical load may be significantly greater than current load due to changes in regulations and reduction or elimination of contaminant~~chemical~~ use in the Study Area and Willamette Basin. Additionally, historical records indicate that releases from overwater activities[25] were significant in the Study Area, though they are not specifically quantifiable with available records.

This section presents a qualitative discussion of historical loading to the Study Area, focusing on the expected relative load from historical versus current sources. This discussion complements the presentation of historical sources in Section 4. Information from both of these sections and from the subsurface sediment record are presented together in Section 10 and evaluated to assess the current traces of existing contamination to historical sources.

Upstream Surface Water Loading – Historical surface water loading to the Study Area is relevant to the extent that associated suspended solids were deposited and remain within the Study Area. It is likely that historical loading via upstream surface water was significantly greater than current loading for many contaminant~~chemical~~s due to widespread historical use of pesticides and herbicides~~,~~; historical wastewater, and sanitary and stormwater management practices~~,~~; and generally more limited regulatory controls on many ~~ICs~~contaminants.

Upstream Bedload – The relative contribution of historical compared to current upstream sediment loading is uncertain. Various factors, including historical dredging, sediment transport during flood events, complex sediment deposition patterns, and the lack of information regarding historical versus current upstream bedded sediment concentrations make it difficult to predict or generalize about the duration and long-term impact of upstream sediment migration and loading.

Stormwater Loading – Stormwater loading to the Study Area is expected to have been higher historically, prior to implementation of upland stormwater runoff controls in some areas, control of CSOs, changes in chemical use/production/incidental production (PCBs, dioxins), and control of industrial discharges to storm drains and CSOs.

Non-Stormwater Direct Discharge Loading – Historical loading to the Study Area from industrial discharges is likely to have been significantly higher than current loading prior to the adoption and regulation of discharge permits and controls.

Upland Groundwater Plume Loading – Upland groundwater plumes are generally the result of historical releases. Groundwater plume loading to the Study Area was more significant historically, prior to institution of groundwater controls. However, the

[25] While improved BMPs are likely to reduce the occurrence of overwater releases significantly, it is acknowledged that current and future releases could occur. No attempt is made in this report to predict and quantify such releases as a current loading term, and no additional analysis of this term is planned for the RI/FS.

transport time for contaminants in upland groundwater to reach the river makes it difficult to predict or generalize about the timing of the peak historical loads.

Atmospheric Deposition – It is likely that overall atmospheric loading to the Study Area has decreased from historical levels due to widespread adoption by many countries of controls on chemical production, use, and air emissions. As a result, atmospheric concentrations have decreased, but have not been eliminated entirely.

Riverbank Erosion – The historical composition and chemistry of bank materials—and thus the overall impact of historical bank erosion—is unknown. Nevertheless, contaminant loading to the Study Area due to bank erosion was likely more significant historically, prior to upland soil cleanups and installation of erosion controls in many areas, including riprap and sea walls.

Overwater Releases – Historical loading from overwater releases is expected to have been more significant historically, prior to improved BMPs. While available records do not support quantification of these historical releases, the current sediment record provides some information in known release areas (see further discussions in Section 10.2).

Advective Loading – The relative historical advective loading rate from subsurface sediments to surface sediments is unknown. ~~h~~However, assuming that subsurface sediment (as defined for this analysis) generally reflects historical rather than recent releases to the Study Area, a comparison of surface and subsurface advective loading estimates (discussed in detail in Section 6.1.6.3) offers initial insight into the combined effects of historical loading to sediment from all sources. Subsurface advective loading for PCBs, PCDD/Fs, DDx, and PAHs exceeds surface advective loading at the scale of the entire Study Area. This suggests that loading of these contaminant~~chemical~~s to the sediment bed, as indicated by the subsurface interval, was historically higher. The total PAH loading rate estimate is dominated by LPAHs, which are much more mobile in groundwater than HPAHs. Thus, it is possible that the subsurface advective loading of PAHs is influenced by ongoing (current) upland groundwater plume loading, in addition to historical PAH contamination of subsurface sediments

6.1.9 External Loading Summary

The project data sets and relevant literature were evaluated to assess current and historical external contaminant~~chemical~~ loading terms to the Study Area. The following external loading terms were considered in this evaluation—upstream loading via surface water (including suspended sediment load and sediment bedload), stormwater runoff, non-stormwater permitted discharges, upland groundwater plume transport to the Study Area, atmospheric deposition to the river surface, upland soil and riverbank erosion, groundwater advection through sediments, and overwater releases. A range of current annual loads to the Study Area were estimated. Historical loading is expected to have occurred by all of these loading mechanisms, but insufficient data are

available to support quantitative estimates. Therefore, historical loading was only qualitatively assessed.

Table 6.1-11 provides a summary of the central estimates of external current loading to the Study Area for upstream surface water, stormwater runoff, non-stormwater permitted discharge, atmospheric deposition, upland groundwater plumes, and advection through subsurface sediments. The estimated annual loads for the internal transport mechanism of advection through surface sediments to surface water is also shown in Table 6.1-11 for comparison.

6.2 FATE AND TRANSPORT

This section describes the physical, chemical, and biological processes that influence the fate and transport of contaminants within the in-water portion of the Study Area. This discussion of fate and transport processes is organized in three main subsections, corresponding to the major environmental compartments of the Study Area: 1) surface mixed sediment layer and associated pore water, 2) surface water, and 3) biota. Figure 6.1-1 presents a conceptual drawing of these major environmental compartments.

For each of these three compartments, the relevant fate and transport processes are discussed for each of the contaminant~~chemical~~ groups in the combined list of loading contaminants (Table 6.0-1). These include PCBs, PCDD/Fs, pesticides (DDx and non-DDx), PAHs, petroleum hydrocarbons, SVOCs, metals, TBT, and VOCs. Insights into fate and transport processes gained from assessment of empirical information and the sediment physical transport modeling (HST modeling) are also discussed. Due to project timing, results from the ongoing fate and transport modeling effort will be presented in the FS.

6.2.1 Sediment and Pore Water Fate and Transport Processes

The following subsections discuss fate and transport processes relevant to select contaminants in the sediment and pore water[26] environment. General discussion of organic and inorganic contaminant~~chemical~~ behavior in sediment and pore water is presented, followed by discussion of physical transport processes for these media. Insights from empirical data and from HST model results, where applicable, are also presented to help assess the relative importance of the various processes for the contaminant~~chemical~~s on the combined loading contaminant list.

6.2.1.1 Contaminant Distribution between Sediment and Pore Water

In the sediment and pore water environment, the distribution of a contaminant~~chemical~~ between the solid and aqueous phases is among the most important physiochemical processes affecting its migration, bioavailability, and half-life. The equilibrium distribution of a contaminant~~chemical~~ between water (dissolved aqueous phase) and

[26] The general term "pore water" is used here instead of TZW to acknowledge that the discussion also includes interstitial water in the sediment, which does not contain upland groundwater.

solid (sorbed to sediment or associated organic matter) is generally described by a solid/water distribution coefficient (K_d).

Major processes and environmental factors that control this distribution (which varies in response to environmental conditions such as pH, temperature, and salinity) are discussed below in general terms for organic and inorganic analytes. Observed partitioning ratios in the LWG-collected TZW and paired sediment data sets are compared to published literature values for relevant analyte groups for additional perspective. Finally, degradation and transformation mechanisms for contaminant~~chemical~~s in the sediment/pore water environment are also discussed.

6.2.1.1.1 Organic Contaminants

For organic analytes, the K_d term describes the combined effect of all possible equilibrium partitioning mechanisms affecting distribution between sediment and pore water, including hydrophobic sorption onto organic matter associated with the sediment, electrostatic attractions of oppositely charged ionic functional groups, and covalent bonding or complexation of ionic organic molecules with reactive surface groups. For nonionic organic contaminant~~chemical~~s (PCBs, pesticides including DDx, PCDD/Fs, PAHs, SVOCs, and VOCs), the primary mechanism defining the K_d term is hydrophobic sorption onto organic matter. Therefore, for nonionic organic contaminant~~chemical~~s, K_d describes two-phase partitioning to the organic matter on the solid surfaces and is a function of the tendency of the contaminant~~chemical~~ to sorb to organic carbon (K_{oc}) and the fractional organic matter content of the solids (f_{oc}).

In addition to temperature, several factors can affect equilibrium partitioning behavior for nonionic organic contaminant~~chemical~~s:

- **Salinity** – High-salinity environments can cause increased adsorption (decreased solubility and higher observed K_d than predicted at lower salinity). This may be relevant in the highly saline sediment and pore water environment local to offshore areas on the west side of the river, between roughly RM 7 and 7.5, where pore-water salinities in excess of typical seawater have been observed. It is unlikely to be a significant factor elsewhere in the river.
- **Cosolvents** – The presence of miscible organic liquids in solution with hydrophobic contaminant~~chemical~~s can result in increased solubility (and therefore decreased K_d) of the hydrophobic contaminant~~chemical~~. This effect, however, requires significant amounts of cosolvent contaminant~~chemical~~s in solution (more than 10 percent by volume [Yalkowsky et al. 1976]).
- **Colloids** – Colloids are organic and/or inorganic particles in the system defined by their behavior (tendency to remain dispersed in water, not settle rapidly, and not filter easily) and size (usually 1 nm to 1 µm in diameter [Lyklema 1991]). Colloids represent a portion of the surface area available for sorption of organic contaminant~~chemical~~s. Because colloids can be mobile in water within a sediment matrix, they can increase the "apparent" concentration of the

hydrophobic contaminant~~chemical~~ in the aqueous phase. Because colloids are <1 µm in diameter, they would be included in both filtered and unfiltered water samples.

- **Characteristics of natural organic matter** – The nature of the organic matter present in the sediment can also affect the extent of partitioning, making partitioning behavior variable across different environments.

TPH, as analyzed for the RI, is the measure of all hydrocarbons that can be quantified in the carbon range from C_6 to C_{40}. Further, the components~~ (~~ TPH~~-~~ (diesel~~,~~), TPH~~-~~ (residual~~,~~), and TPH~~-~~ (gasoline~~))~~ are simply descriptive terms for the fractions of TPH and do not represent source assignments or indications of toxicity. TPH represents a vast mixture of hydrocarbon contaminant~~chemical~~s, of both natural and anthropogenic origin, with an equally vast range of partitioning behaviors. As such, its behavior as a contaminant~~chemical~~ group cannot be accurately characterized by a K_{oc} value. Because the components of TPH are unknown for all sampling results, the subcomponents also cannot be accurately characterized by K_{oc} values.

The only definitively ionic organic compound on the combined ~~IC~~contaminant loading list is TBT. The partitioning behavior of TBT is strongly affected by pH and the identity of anions in solution that pair with the TBT ion (Arnold et al. 1997). Measured log K_{oc} values are on the order of 4 at pH 10 to 7, and approximately 2 at pH 7 to ~~pH~~ 3, corresponding to a substantial behavioral variability as pH varies. The mean surface water pH is 7.38 (10th percentile is 6.98 and 90th percentile is 7.76). The observed pore water pH values measured in the GWPA ranged from 5.6 to 8.1.

Ranges of literature equilibrium partitioning values for organic contaminant~~chemical~~s on the advective loading contaminant list for which equilibrium partitioning assessment is relevant were compiled for the advective loading analysis (discussed in Section 6.1.6) and are presented in Appendix E, Table E6-5. The average range in the K_{oc} values for organic analytes is 1 order of magnitude, with PCDD/Fs, TBT, and BEHP exhibiting a range of more than 2 orders of magnitude, representing substantial variability in partitioning behavior.

Site-specific empirical information to assess sediment pore~~-~~ water partitioning of organic contaminant~~chemical~~s is limited to the filtered TZW data set with paired surface sediment samples. This data set is limited as it focuses only on the offshore area of the TZW study sites, and not all ~~contaminants of interest~~COIs in sediment were analyzed in TZW samples (for example, PCBs were not analyzed in any TZW samples, and DDx and PCDD/Fs were analyzed in only a small fraction of the samples). However, because ~~it is~~they are the only available empirical data, observed partitioning values were plotted against corresponding literature partitioning values. Observed partitioning for PAHs and DDx pesticides between filtered TZW and sediment are shown in Figures 6.2-1 and 6.2-2, respectively. These figures also show the literature values compiled for use in the advective loading assessment (Section 6.1.6). Results for DDx exhibit a wide range of partitioning coefficients cited in the literature.

Comparisons of the literature-derived partitioning values for DDx pesticides with observed partitioning behavior are limited by the small number of sample pairs (*n*=4) for which a given isomer was detected in both TZW and sediment. This limited set of observed partitioning values also spans a broad range. In contrast, the range of partitioning coefficients obtained from literature sources for individual PAHs (Figure 6.2-1) ~~exhibits a~~is relatively narrow~~ range, while~~, whereas the observed partitioning shows much wider ranges, especially for the LPAH constituents. The wide variability in observed partitioning may reflect multiple factors, including non-equilibrium conditions between TZW and sediment, small-scale spatial variability (sediment and TZW sample pairs were not always co~~-~~located), and/or filtered samples not reflecting truly dissolved concentrations.

6.2.1.1.2 Inorganic Contaminants

The fate and transport of inorganic species in pore water is defined by the distribution between the aqueous and solid phases. A wide range of mechanisms control the distribution of metals between these phases, most commonly precipitation/dissolution reactions and sorption/ion-exchange processes. Precipitation and dissolution are controlled by the concentration of species present both in solution and as mineral phases. Sorption and ion exchange are controlled by a variety of factors, including electrostatic attraction, covalent bonding, and weak intermolecular attractions such as van der Waals forces.

The distribution of inorganic species between the aqueous and solid phases is controlled by a number of mechanisms that are a function of the physical, chemical, and biological characteristics of the solid-aqueous system. The characteristics most important for the aqueous solution phase include the following:

- pH
- Oxidation-reduction potential (Eh)
- Presence of competing ions
- Aqueous complexation reactions
- Ionic strength and the specific ions in solution.

The solid phase characteristics of importance include the following:

- Grain size
- Composition/mineralogy
- Sorbed organic carbon content and type
- Surface characteristics such as charge, coatings, and area.

In addition, there is a range of factors that cannot easily be assigned to one phase, such as temperature and the fugacity of gases such as oxygen and carbon dioxide.

The aqueous-solid chemistry of the sediment and pore water environment can be strongly influenced by microbial processes. Microbial oxidation of labile organic carbon frequently depletes dissolved oxygen in pore water, resulting in chemically reduced conditions and the production of alkalinity. Further, under anaerobic conditions, microbial processes can induce numerous environmentally relevant changes to the chemical environment, such as dissolution of iron and manganese oxide minerals and production of sulfides.

Sorption and ion-exchange mechanisms for metals can empirically be described by the solubility constant K_d~~-~~. Unlike organic contaminant~~chemical~~s, the appropriate K_d term is not a function of f_{oc} (although organic matter can also sequester inorganic contaminant~~chemical~~s, thereby affecting the K_d value). Literature K_d values were compiled for the metal advective loading ~~ICs~~contaminants: arsenic, copper, lead, and mercury. These values were used in the calculation of pore water concentrations for estimation of loading to surface water from surface sediment via groundwater advection. This analysis and the significant uncertainty associated with the inherent assumptions are presented in Section 6.1.6, and the range of literature K_d values is presented in Appendix E, Table E6-6. These values show ranges of 1 to 3 orders of magnitude. The wide range in literature K_d values for metals reflects the strong, highly variable geochemical factors described above that influence partitioning behavior in environmental systems. Considering this, literature K_d values should be considered site-specific estimates resulting from the geochemical conditions particular to individual studies. Limited site-specific empirical information, consisting of the filtered TZW data set with paired surface sediment samples for arsenic, copper, lead, and mercury, is presented for general comparison purposes on Figure 6.2-3.

6.2.1.2 Degradation/Transformation Processes

A variety of abiotic degradation/transformation reactions, including hydrolysis, dehalogenation, oxidation, and reduction, can occur in aqueous systems. Hydrolysis is a reaction by which alkyl halides, esters, or ester analogs are converted to alcohols or organic acids. Dehalogenation ~~are~~ is a reaction~~s~~ in which halogen atoms (such as chlorine) are removed from halogenated hydrocarbons. Oxidation and reduction are complementary reactions that involve the loss of one or more electrons (oxidation) by one chemical and the gain of one or more electrons (reduction) by another. Metals in environmental systems are subject to both oxidation and reduction reactions, depending on the particular metal, its speciation in the environment, and other geochemical conditions. Organic contaminants on the combined contaminant loading list are subject to degradation/transformation by abiotic processes in the sediment/pore water environment, though the degradation rates are relatively slow for PCBs, BEHP, hexachlorobenzene, 1,2-~~DCB~~dichlorobenzene, chlordanes, dieldrin, and dioxins. Photo-oxidation of contaminants present in surface water is discussed in Section 6.2.2.3.

Biodegradation can be a significant process for various organic contaminants found in sediments and pore water in the Study Area. It involves the metabolic oxidation or

reduction of organic compounds and is carried out predominantly by bacteria in aqueous environments, but yeasts and fungi may also contribute to biodegradation. In general, oxidation of organic compounds occurs under aerobic conditions and reduction under anaerobic conditions, although both processes can occur under both conditions. Microbes may either gain chemical energy directly as a result of biodegradation of an organic compound~~,~~ or during the process of co-metabolism, the concurrent degradation of another substrate with the organic compound. Microbially~~-~~ mediated transformation of metals is only significant for mercury[27] and lead[28] organocompounds.

Biodegradation rates depend on chemical structure and concentration, the concentration of bacteria responsible for the biodegradation, the availability of organic matter to serve as food and energy sources for bacterial growth, and physical and chemical conditions at the site, such as temperature and oxygen level. The extent to which the organic compound is bound to particles may also affect the biodegradation rate as the bound organic compounds may be biologically less available for microbial uptake.

A wide variety of microbial species that utilize different biochemical pathways to metabolize anthropogenic contaminants have been identified. Biodegradation can proceed to full mineralization with end products of carbon dioxide and water, or an intermediate compound may be formed that is not easily further biodegraded. For example, DDT is relatively readily biodegraded to DDE, but DDE is more persistent. The susceptibility of organic compounds to biodegradation depends on several factors, such as the presence and type of functional groups (oxygen- and nitrogen-containing groups increase biodegradation rates), the size and chemical structure of the organic compound (small molecules biodegrade more readily than large molecules), and solubility (more soluble organic compounds biodegrade more readily). A literature review has been completed to find appropriate biodegradation rate constants for use in the ~~F~~fate and ~~T~~transport ~~M~~model.

[27] Mobilization of sorbed mercury can be caused by bioreduction to elemental mercury and bioconversion to more volatile and soluble forms, such as methylmercury. Methylmercury is the most hazardous mercury species due to its high stability, its lipid solubility, and its possession of ionic properties that allow it to readily pass through cellular membranes (Eisler 1987). Mercury discharged into rivers, bays, or estuaries can be converted into methylmercury compounds by natural biological (bacterial microorganisms) or chemical processes (Eisler 1987). The mercury methylation process depends on mercury loadings, microbial activity, nutrient content, pH and redox condition, suspended sediment load, sedimentation rates, and other variables; anaerobic conditions favor methylmercury formation more than aerobic conditions (Eisler 1987). Bacterial microbes are also responsible for methylmercury decomposition (demethylation).

[28] Tetraethyllead and tetramethyllead are the most stable organoleads, and the most important because of their widespread use as antiknock fuel additives. Both are clear, colorless, volatile liquids and highly soluble in many organic solvents. Solubility in water is only 0.18 mg/L for tetraethyllead~~,~~ and 18.0 mg/L for tetramethyllead. Both undergo photochemical degradation in the atmosphere to elemental Pb and free organic radicals, although the fate of automotive organoleads has yet to be fully evaluated (Eisler 1988). In general, organolead compounds are more toxic than inorganic Pb compounds, food chain biomagnification of Pb is negligible, and younger organisms are most susceptible (Eisler 1988).

6.2.1.3 Sediment Physical Transport Processes

Hydrophobic ~~chemicals~~contaminants are strongly associated with sediment particles, in particular cohesive or fine-grained particles (silts and clays). As a result, the physical transport of sediments, especially silts and clays, will affect the distribution and fate of hydrophobic ~~ICs~~contaminants within the Study Area. Hydrophobic contaminants found in Portland Harbor include PCBs, PCDD/Fs, organochlorine pesticides, and PAHs.

Sediment movement into, within, and through the Study Area occurs as suspended load in the water column and as bedload along the riverbed. Cohesive or fine-grained sediments generally move as suspended load, which is defined as transport in the water column. Noncohesive sediments (sands and coarser) typically move as bedload transport, which refers to sediment transported along or very close to the riverbed. However, a variable fraction of noncohesive sediments moves as suspended load as a function of the flow regime (i.e., as flows increase, a larger fraction of noncohesive sediment will move in suspension).

The movement of sediments in the ~~L~~lower Willamette River is controlled by both natural and anthropogenic forces that affect water movement and bottom shear stresses. As discussed in Section 3, natural flow regimes exhibit a wide range between the dry summers and rainy winters in Portland Harbor. Based on empirical, site-specific erosion velocities measured with Sedflume and modeled bottom shear stress, significant natural resuspension and movement of sediments does not generally occur at river flows below approximately 40–50,000 cfs (Section 3.1.5~~4~~.2.3). Late spring through fall ~~L~~lower Willamette River flows are typically well below this level (see Figure 3.1-~~4~~8), whereas late fall and winter flows exceed this threshold for variable lengths of time, depending on the intensity of winter precipitation events in the Willamette Basin. This strong seasonal pattern applies to the deep channel environment in the ~~L~~lower Willamette River which, on an areal basis, makes up much of the riverbed. Flows in nearshore, off-channel areas are severely dampened by nearshore structures, bottom drag, and shoreline configuration (e.g., sheltered embayments and slips). As shown on Map 3.1-11, modeled bottom shear in many off-channel areas remains relatively low even during a river flow event of 160,000 cfs. This pattern is important because most of the areas of relatively high sediment contaminant concentrations in Portland Harbor are located in off-channel areas (Section 5.~~1~~2).

Commented [A6]: Integral: Revised numbering in Final Section 3, this is now Section 3.1.5.2.3

In contrast to the channel environment, sediment disturbance/resuspension/scour in nearshore areas, particularly around working piers, berths, marine terminals, and others areas with significant boat traffic, may be largely a function of anthropogenic factors, such a prop wash, rather than natural factors alone. This effect may be accentuated during low flow portions of the year (late summer/fall) when river stage is also low (Figure 3.1-~~3~~7) reducing vessel drafts. This anthropogenic influence is suggested by the time-series bathymetric measurements (Map 3.1-~~7~~6), which reveal scour patterns in sheltered areas, such as Swan Island Lagoon and the International Slip, as well as very close to shore in portions of the main stem that do not experience high bottom shear forces even during high river flows.

As described in Section 3.1 and summarized in Table 3.1-11, the physical character of the ~~L~~lower Willamette River transitions rather abruptly near the upstream end of the Study Area (about RM 10) from a relatively narrow, high velocity river characterized by coarse-grained riverbed channel sediments upstream to a broader, slower river dominated by fine-grained sediments downstream. This relatively wide, fine-grained character extends to the lower end of the RI Study Area at RM 1.9, with the exceptions of a distinct, narrow, higher energy reach between RM 5 and 7 and a small area at the head of the Multnomah Channel; both of these areas are dominated by sands (Map 3.1-~~2~~3). Measured areas of sediment scour and deposition from 2002 to 2009 (time-series bathymetry) and modeled predicted bed change during a major flood events are shown on Map 3.1-12, and depict consistent areas of erosion and deposition in the ~~L~~lower Willamette River during both typical (observed) and extreme (modeled) flow conditions. These areas correspond to sand-dominated (erosion) and silt-dominated (deposition) reaches. Again, this pattern applies to the deeper, in-channel portions of the river and appears to reflect the influences of natural forces. Nearshore areas are subject to a more complex mix of natural forces and smaller-scale, anthropogenic factors, such as vessel traffic, river stage variations, and in-water construction/dredging and fill activities that affect localized sediment texture and resuspension/transport patterns.

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Within the general framework of Study Area sediment transport regimes summarized above and detailed in Section 3.1, the major transport and fate processes relevant to sediment-bound contaminant~~chemical~~s are sediment transport into the Study Area from upstream, downstream sediment migration out of the Study Area (either in the main stem or Multnomah Channel), and the fate and transport of sediments within the Study Area, such as surface sediment mixing and resuspension, permanent burial at depth in the sediment column, and biological uptake. These processes are addressed below.

6.2.1.3.1 Sediment Flux into/out of the Study Area

Sediment enters Portland Harbor as suspended and bedload. Suspended and bedload sediment fluxes are discussed separately below.

Suspended Sediments

Suspended sediment data ~~has~~have been collected in the ~~L~~lower Willamette River across a range of hydrologic conditions both by the LWG, as part of the surface water sampling program and as an HST model need, and by other entities (e.g., the City of Portland), as part of long-term monitoring programs. These data are described in Section 3.1.5.2.4 and show that suspended loads are strongly correlated with flow and vary from approximately 5 to 50 mg/L seasonally and annually (see Figures 3.1-26 and 3.1-25a–h). Higher suspended loads are observed on the rising limbs of the hydrographic events than on the falling limbs. Finally, a series of *in-situ* suspended particle size measurements conducted for the hydrodynamic modeling data collection effort indicate that suspended sediment particles sizes are comparable throughout the Study Area, with a median percentile particle diameter between 15 and 30 µm (silt). In contrast, the median grain-size diameter at an upriver location (RM 18) was 78 µm (fine

Commented [A8]: Integral: Changes to figure numbering and content from Final Section 3

sand), reflecting the higher energy environment in the upper portion of the ~~L~~lower Willamette River (Figure 3.1-29).

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The modeled HST suspended load fluxes into and out of the Study Area are included in Table 6.1.3. Across the modeled flow years (5th, 25th, 50th, 75th, and 95th percentiles), average total suspended sediment flux into the Study Area from upstream equals about 1.53 billion kg/yr, and the average total suspended sediment flux out of the Study Area equals about 1.26 billion kg/yr, indicating a net accumulation of about 0.28 billion kg/yr in the Study Area. Averaged over time, about 18 percent of the suspended material entering the harbor accumulates somewhere between RM 11.8 and 1.2. The average annual net sediment accumulation rate calculated from empirical bathymetric survey data collected between 2003 and 2009 was 0.20 billion kg/year, which is in very good agreement with the model estimates, especially the 50th percentile model estimates, which correspond to a net accumulation of 0.19 billion kg/year. Net sediment accumulation represents a combination of new material entering the Study Area from upstream and some percentage of bedded sediment that is resuspended from the riverbed within the Study Area and then redeposited further downstream, but before exiting the Study Area.

Bedload Sediments

Noncohesive bedload sediments move downstream along (rolling, sliding) or just above the riverbed (saltation) whenever near-bottom shear stresses exceed the threshold for sediment movement. Unlike suspended load, no direct measurements of bedload have been made as part of the RI/FS, as it is extremely difficult to measure in the field. Additionally, bedload is assumed to be a minor sediment transport mechanism due to the generally cohesive character of the sediment bed of the ~~L~~lower Willamette River. Consequently, bedload processes are not quantified in the RI/FS fate and transport evaluation.

6.2.1.3.2 Sediment Fate and Transport in the Study Area

The spatial pattern and extent of deposition and erosion in the Study Area was measured directly with the time-series of precision bathymetric surveys conducted from 2002 to 2004 (described in Section 3.1.5.2.~~-~~2). The bathymetric change data show distinct zones of deposition and erosion that reflect the cross-sectional area and resultant hydrodynamics of specific portions of the Study Area (see Maps 3.1-10 and 3.1-9). These hydrodynamic reaches, described in Section 3.1.5.2.6, share attributes such as sediment texture and general sediment stability.

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Based on surface and subsurface grain-size (percent fines) distribution (Maps 3.1-3 and 3.1-5) and bathymetric features (Map 3.1-9), areas of fine-grained sediment accretion appear to be dominant from RM 8 to 10, along the channel edge from RM 4 to 5, and from RM 1.5 to 3. The downstream and upstream areas noted here are known to be long-term sediment accumulation areas based on historical dredging needs. Upstream depressions (borrow pits) between RM 9.5 and 11, that in combination span the navigation channel, likely capture some suspended and much of the bedload

(noncohesive) sediments that are entering the system. The Study Area reaches between RM 5 and 7 and RM 10 and 11.8, where the river is relatively narrow, are dominated by areas of small-scale net erosion, as is the western off-channel area from RM 0 to 3 (outside bend of the lower Willamette River as it turns toward the Columbia).

Analysis of the time-series bathymetric change data presented in Section 3.1.5.2.2 indicates that during typical flow conditions only about 10 percent of the riverbed exhibited net bathymetric changes (erosion or accretion) greater than 30 cm, but that relatively "small-scale" scour or accretion from about 8 cm (the limit of bathymetric resolution) to 30 cm in extent was widespread, possibly indicating that the top 30 cm of the sediment column is relatively unconsolidated and more susceptible to resuspension/erosion than deeper sediments.

As described ~~in~~further in Section 6.3 ~~Appendix E.#.#,~~ radioisotope cores were collected in upstream borrow pits at RM 10.5 and 10.9 in an attempt to quantify sedimentation rates in known depositional locations. A detailed evaluation of the radioisotope data from these cores is provided in ~~Appendix E####.~~Anchor (2007e). However, generation of a timeline with depth was precluded as these depressions appear to be collecting a complex mix of suspended and bedload sediments with heterogeneous origins. The history of the borrow pits (the estimated original depths of the borrow pits when excavated in 1988 compared to the observed mudline elevations at the time of sampling in 2007) points to long-term average sedimentation rates in these low-lying portions of the channel of approximately 45 cm/yr (1.5 ft/yr) at RM 10.9 and 30 cm/yr (1 ft/yr) at RM 10.5 (see ~~Appendix E###).~~Section 6.3). Additional empirical evidence on relatively long-term net sedimentation rates is provided by the harbor-wide measured riverbed elevation changes over the ~~seven~~7-year period from 2002 to 2009 (see Map 3.1-6). The net sediment accumulation rates in these upstream borrow pits at RM 10.9 and 10.5, based on these data, are estimated to be approximately 41 and 31~~-~~ cm/yr at RM 10.9 and 10.5, respectively, over this time~~-~~ frame, consistent with the 19-year estimates noted previously. The borrow pits themselves, spanning the channel in this reach and presenting a relatively larger channel cross-sectional area (because of their greater depth) than in reaches immediately upstream, provide conditions that promote sedimentation. However, based on the bathymetric survey data, sedimentation rates in this portion of the lower Willamette River outside the borrow pits, such as the large shoal that occupies the western portion of the navigation channel from RM 8 to 10, are comparable in scale (31 cm/yr at the maximum shoaling point at RM 9.6, see Map 3.1-10~~.~~). This shoal area has historically required regular maintenance dredging (see Section 3.2.3.1.13).

The long-term sedimentation rate observations noted above apply to the Study Area channel environment. Based on bathymetric change, SPI data, and limited radioisotope sampling for ~~monitored natural recovery (~~MNR~~)~~ assessment (Anchor 2005b), nearshore and off-channel areas do not appear to accumulate sediment at these rates. Short-term active sediment deposition and resuspension are indicated by these data sets, likely due in many areas to anthropogenic activity. Seasonal (rainy season) inputs of fine-grained

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Commented [A13]: EPA: This information is not discussed in Section 5 since it is not discussing nature and extent of contamination. The 3 pages of text in Appendix H can be added to Appendix E.

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sediments in areas adjacent to the channel are also evident. However, seasonal comparison of surface sediment textures at similar locations in the spring versus the fall suggests that some nearshore deposits can be remobilized over time and dispersed (WEST and Tetra Tech 2009), minimizing net accumulation rates. These observations are supported by the radioisotope data from four nearshore areas in 2004 (Anchor 2005b), which show well-mixed surface sediment layers and calculated net sedimentation rates of approximately 1 cm/yr.

The HST model prediction of bed elevation change for the high-flow flood scenario depicted on Figure 3.1-~~19~~30 indicates that the spatial pattern of erosion predicted by the model for the extreme event is generally consistent with measured bathymetric change from 2002 to 2009 under more typical hydrologic conditions. However, in some areas, the magnitude of bed changes during the extreme event is dramatically greater, with erosion or deposition predicted to occur to one or more meters over observed changes (Map 3.1-12).

6.2.1.3.3 Surface Sediment Dynamics

Particles that settle out or move along the bottom are subjected to a wide range of physical, biological, and chemical processes:

- **Sediment mixed-layer turbation** – Biogenic mixing by benthic infauna or bottom-foraging fish can preclude or slow consolidation of surface sediments, as can natural (e.g., wind waves) and anthropogenic (e.g., prop wash) forces. These factors can greatly complicate the spatial and temporal degree of bed erodibility. The SPI survey conducted throughout the ~~L~~lower Willamette River in the late fall of 2001 revealed a complex mosaic of surface sediment processes in the top 22 cm of the sediment column (the maximum depth of the SPI images) across the Study Area (SEA 2002b). Areas of fine-grained, low-shear sediments contrasted with coarse-grained, more compacted bottom areas. In the channel environment, these large-scale gradients in gross characteristics coincided with and helped first define the hydrodynamic reaches described in Section 3. In some fine-grained areas, infaunal feeding pockets and worm tubes indicated that biogenic activity approached 20 cm depth. In other areas, minimal biogenic mixing activity was apparent. A well-mixed, biologically active zone appears to be on the order of 5 cm in many images, although this varied widely across the Study Area. Many nearshore areas showed steep onshore-offshore gradients in physical and biological conditions as a function of water depth, riverbed slope, and/or the degree of shoreline protection (e.g., embayments, structures). In some areas, layers of freshly deposited sediments exceeding 10 to 15 cm in extent were apparent. This survey was conducted during the onset of the rainy season in late November. Overall, the SPI survey in combination with the bathymetric change data point to a dynamic surface sediment bed in much of Portland Harbor that is subjected to physical disturbance in the form of deposition or scour (on a multi-centimeter scale) due to natural and anthropogenic forces, biogenic mixing, and geochemical

disturbance factors, such a methane bubble ebullition. Under typical (non-flood event) flow conditions, these disturbance factors appear to be limited to a maximum extent of the top 30 cm harbor-wide. Thus, frequent widespread physical and biological surface sediment mixing is likely restricted to much shallower depths over much of the Study Area.

- **Long-term sediment burial beneath the mixed layer** – Particles and associated contaminants that are advectively transported or buried below the mixed layer are permanently removed from the active transport system throughout most of the Study Area. In portions of the navigation channel upstream of RM 10.5 and between RM 5 to 7, erosion of bedded sediments to about 2 m is predicted to occur during 100-yr flood events, but this deep erosion is limited in areal extent (see Map 3.1-8b). Consequently, absent anthropogenic disturbance, bedded sediment below 30 cm in most of the Study Area is stable under the long-term hydrologic conditions anticipated for Portland Harbor.
- **Sediment ingestion/uptake by biota** – Filter and deposit feeder organisms may actively or passively ingest particles in suspension or on the sediment bed. High densities of filter feeders can biologically enhance transfer of suspended particles to the sediment bed. Also, contaminants associated with ingested particles can enter the food web.

6.2.1.4 Pore Water Physical Transport Processes

Contaminants in pore water are subject to diffusive and advective physical transport processes. These mechanisms are discussed in the following subsections.

6.2.1.4.1 Diffusive Transport

Diffusion is the movement of particles or dissolved contaminants from higher to lower potential energy (as represented by a difference in concentration in the case of diffusion from the pore water to the overlying water column). This is a spontaneous physical process that requires no additional energy inputs or expenditure. It is distinguished from advective transport in that it only requires a concentration gradient. Diffusive transport acts on any contaminants in solution and is therefore potentially relevant to all of the combined loading list contaminants.

Diffusive transport of contaminants is being assessed for the Study Area as part of the fate and transport model for the FS.

6.2.1.4.2 Advective Transport

Advective transport of contaminants in the sediment/pore water environment refers to the aggregate movement of contaminants by flow of pore water through the sediments to the water column in the form of groundwater discharge. It represents a transport pathway for contaminants in surface sediment/pore water to migrate to the water column, and is distinguished from the upland groundwater plume loading term described in Section 6.1.5. In certain parts of the Study Area, both mechanisms are likely occurring simultaneously for contaminants present in upland plumes and in

sediments from other sources. A detailed estimation of Study Area-wide loading to surface water via groundwater advective transport is presented in Section 6.1.6 along with an analysis of the external loading of surface sediment via advective transport from subsurface sediment.

6.2.2 Surface Water Fate and Transport Processes

Fate and transport processes for contaminants present in the dissolved phase and sorbed to suspended solids include partitioning between surface water, air, and suspended sediment, physical transport of surface water and suspended solids, and physiochemical and biological processes as described below in Sections 6.2.2.1 through 6.2.2.3.

6.2.2.1 Contaminant~~Chemical~~ Distribution between Surface Water and Suspended Sediment

As described in Section 6.2.1.1, the tendency of a contaminant to be associated with suspended solids or dissolved in the water column is described by its K_d.

The observed partitioning between surface water (filtered) and suspended sediment for surface water samples for PAHs, DDx pesticides, PCDD/Fs, PCB homologs, and non-DDx pesticides is presented on Figures 6.2-4 though 6.2-8. Limited site-specific empirical information for arsenic, copper, lead, and mercury is presented for general comparison purposes on Figure 6.2-9. These figures also show the literature K_{oc} and K_d values compiled for use in the advective loading assessment (Section 6.1.6). For most contaminants (PCBs, pesticides, PAHs), the observed partitioning between suspended sediment and filtered surface water spans a wider range than the literature K_{oc} values. The source of this variability is unknown, but may be attributable to nonequilibrium conditions between surface water and suspended sediment, errors introduced by the estimation method for the f_{oc} content of suspended sediment (see Appendix E, Section 2.~~2.1~~4), filtered surface water samples not reflecting truly dissolved concentrations, or a combination of these factors. Based on visual inspection of the information presented on Figures 6.2-4 through 6.2-9, the central part of the range of observed partitioning values corresponds with the CT in the literature values for PCB homologs, PCDD/Fs, and non-DDx pesticides. In contrast, the observed partitioning in the RI data set generally appears to be biased high relative to literature K_{oc}/K_d for PAHs and, to a lesser degree, DDx pesticides and metals. McGroddy et al. (1995, 1996) noted that only a small fraction of PAHs present in bulk sediment from Boston Harbor appeared available for equilibrium partitioning~~,~~; empirically~~-~~ derived log K_{oc} values were significantly greater than literature values, specifically for phenanthrene and pyrene. They concluded that PAH compounds associated with soot particles typical in many coastal and estuarine areas may be less available to exchange with the pore water than suggested by the literature, and that equilibrium partitioning models overestimated the pore water and desorption aqueous-phase PAH concentrations by as much as a factor of 100. Thus, modeled PAHs concentrations may be overestimated when based on literature values for K_{oc} and an assumption of equilibrium partitioning.

6.2.2.2 Physical Transport of Contaminants in Surface Water

Advection is the flow of river water in response to gravitational forces, and is the primary mechanism for transport of surface water and its load of dissolved and particle-bound contaminants. River flow is quantified using water velocity and discharge. Water velocity is dependent on the slope, shape, and physical characteristics of the riverbed and has the dimensional units of length/time (e.g., ft/s). Discharge represents the quantity of water passing a specific location within a specific time interval. It is calculated as the average velocity times the cross-sectional area of the river, and has the dimensional units volume/time (e.g., cfs or L/yr). The surface water mass flux of a contaminant is the product of the concentration and the volumetric flow rate of the river, producing dimensional units of mass/time (e.g., kg/yr), as calculated in Section 6.1.1.1 for surface water load estimates.

The dominant direction of water flow in the ~~L~~lower Willamette River is downstream along the hydraulic gradient. However, the flow direction reverses on flood tides during low-flow periods (see Section 3.1.4.3~~.2~~). Upstream flow has been identified as far upstream as RM 12.8 during low-flow conditions (Figures 3.1-~~13a~~22a–h; Caldwell and Doyle 1995).

Lateral and vertical movement of contaminants in surface water occurs primarily as a result of turbulent (eddy) dispersion (mechanical mixing), and to a lesser extent as a result of mixing/diffusion resulting from concentration, thermal, and density gradients. The velocity of river water is greatest near the center of the river and decreases toward the sides and bottom. These differences in velocity result in velocity shear, which gives rise to eddies. Eddies may also be caused by channel irregularities, including structures in the water. These processes serve to mix the water and dilute contaminant concentrations as they move away from the source. The suspended load of particle-sorbed contaminants can also decrease due to settling of particles to the riverbed sediment surface.

Sources of contaminants to surface water~~-~~, such as industrial point discharges or groundwater plume discharge areas, can result in plume formation as the contaminants mix with~~-~~ and diffuse into river water flowing downstream. Mixing patterns and plume sizes depend on differences in density between the effluent and river water; the depth, velocity, and turbulence of the river~~,~~; and any density stratification of the river itself. Density is a function of the temperature and salinity of the water.

Suspended particles provide an important vehicle for exchange of contaminants between the sediment bed and surface water. Suspended particles can be derived from mineral sources, including eroded and weathered rock, or from organic sources, such as decaying plant material or plankton. The density of mineral particles is generally 2 to 3 g/cm^3, whereas the density of organic particles is close to the density of water (1 g/cm^3). The entrainment and settling of suspended particles are functions of river flow rate, particle size, particle shape, and particle density, as described in Section 6.2.1.3. The sediment-carrying capacity of river water increases with increasing stream flow and

turbulence, which vary spatially as well as temporally. Stream flow, turbulence, and TSS loads are greater in areas where the river is narrower (e.g., upstream of RM 10), and throughout the river during high-flow events. Within the water column, suspended particle concentrations generally decrease from the riverbed to the water surface. TSS in surface water across the Study Area increases with increasing flow rate. The range of TSS as a function of flow rates~~,~~ decreases~~ing~~ by RM 2, where ~~the~~ river turbulence decreases. ~~(Figure 5.3-13).).~~

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Sediment entrained from the river bottom as bedload may be redeposited on the river bottom downstream, which may disperse contaminants in the sediment as they are transported downstream with the bedload. However, as discussed in Sections 6.1.1.2 and 6.2.1.3, bedload is not considered a major contributor to contaminant transport in Portland Harbor relative to the suspended solids load.

6.2.2.3 Physiochemical and Biological Attenuation Processes in Surface Water

In addition to equilibrium partitioning, several physical, chemical, and biological processes can result in transfer of contaminants found in surface water between abiotic media, or in degradation/transformation reactions. These include chemical precipitation, volatilization, abiotic degradation (chemical reaction or photolysis), and biodegradation. With the exception of volatilization and photolysis, these processes also generally pertain to pore water and sediment interactions, and were previously discussed in Section 6.2.1.2.

Volatilization is the transfer of contaminants dissolved in surface water to the atmosphere, and is most important for small organic molecules such as VOCs. It is dependent on water and air temperature, dissolved concentration, and vapor pressure. Water turbulence and wind velocity at the air/water interface will also affect volatilization rates. Volatilization typically decreases with increasing molecular weight. Additionally, various forms of mercury (elemental mercury [Hg^0] and methylmercury) and organolead compounds may also volatilize from the water column.

Equilibrium partitioning between dissolved volatilized phases is defined by the Henry's law constant (H)~~,~~ and is temperature-specific.

Photolysis degradation or transformation reactions occur in response to absorption of solar energy, and can occur either directly or indirectly. Direct photolysis is the breaking of molecular bonds by electromagnetic radiation, particularly high-energy ultraviolet radiation. Indirect photolysis involves formation of a reactive species such as a hydroxyl radical or oxygen singlet, which subsequently reacts with an organic molecule. Examples of indirect photolysis include cleavage of aromatic rings, hydrolysis, hydroxylation, or dechlorination reactions. The degree to which photolysis occurs is affected by the depth and turbidity of the water, and by the intensity and angle of incidence of light. It can be significant for aldrin, PAHs (especially LPAHs), PCP, TBT, and organolead compounds. Additionally, contaminants sorbed to labile organic

carbon can be released to the water column through degradation of the dissolved/suspended organic matter. PCBs and PCDD/Fs are also subject to photolysis in surface water, though the process is considered to be minor for PCBs and is only relevant to PCDD/Fs near the water surface (USEPA 1994).

6.2.3 Biota-Related Fate and Transport Processes

A number of processes govern how organisms living in the ~~L~~lower Willamette River are exposed to contaminants and how contaminants are transformed, excreted, or stored in tissue. Organisms living in the ~~L~~lower Willamette River take up contaminants through physical (e.g., diffusion), chemically, and biologically mediated processes, including transfer of waterborne contaminant~~-chemical~~s across gill structures or other tissues, consumption of prey, or ingestion of sediment. Organisms can modify the contaminant~~chemical~~ burden in their tissues through growth, reproduction, excretion, metabolic transformation, or sequestration. Some contaminant~~-chemical~~s are transferred among organisms through trophic interactions, resulting in increases in concentrations of some contaminant~~-chemical~~s at higher trophic levels.

PCBs, pesticides, PCDD/Fs, and PAHs, and similar hydrophobic contaminants, are likely to be associated with organic materials (i.e., lipids in tissues, dissolved or particulate carbon in the surface water, pore water, and sediment). However, some metals (e.g., lead and zinc) also tend to associate with organic and inorganic solids because the geochemical properties (e.g., ionic charge) governing their behavior tend to promote sorption.

Once released to the aquatic environment, contaminant~~-chemical~~s enter the food web in a number of ways~~,~~; the process is not sequential in that all trophic levels can interact with abiotic media. The behavior of contaminant~~-chemical~~s within an aquatic food web is briefly described below.

Primary producers such as phytoplankton and plants take up contaminant~~-chemical~~s primarily through diffusion from water.~~,~~ ~~t~~The lipid content of phytoplankton also serves as a substrate for the partitioning of organic compounds. Metabolic byproducts of phytoplankton contribute to the colloidal material in the water column, which can also serve as a binding substrate for dissolved contaminants. These colloidal materials can be directly utilized by bacteria, other phytoplankton, and zooplankton, serving as an additional uptake and transfer mechanism for recycling contaminants within the water column food chain. Zooplankton prey upon phytoplankton and other zooplankton, further recycling contaminants within the water column. More complex aquatic organisms (invertebrates and fish) can take up dissolved- or colloidally-bound contaminants from surface water and pore water across gill membranes, skin, and other permeable tissues, such as the mantle in clams (shells, exoskeletons, and scales are less permeable). Sediment surfaces may be coated with bacteria and bacterial slimes, natural organic polymers, and other amorphous organic molecules that serve as binding sites. Finer-grained sediments have a greater surface area-to-volume ratio and thus have a greater organic carbon content and contaminant concentrations.

Once sediment or prey is ingested by invertebrates and fish, the rate of contaminant~~chemical~~ absorption across gut membranes is affected by the size of the molecule (larger molecules are more difficult to transfer across membranes), concentration gradients between gut content and surrounding tissues, acidity of the gut, and other physical/chemical conditions in the gut. Absorbed contaminants may undergo various metabolic processes that change the chemical structure and properties.

Once absorbed, metals that are not excreted may be stored in calcium carbonate matrices (invertebrates) or bone (vertebrates), which tend to reduce the reactivity of the metal. Organic contaminants that are not metabolized tend to be stored in organs or fatty tissues, including gametes. These stores can be released within the aquatic and terrestrial food webs when these organisms are ingested by others, upon their death and decomposition, or by transfer to their offspring.

The relative contributions of bedded sediment versus surface water contamination to tissue contamination levels in the Study Area will be addressed in the FS fate and transport modeling effort. Bioaccumulation modeling to predict chemical uptake by invertebrates and fish is presented in Windward ~~2009b.~~(2009~~a~~). A mechanistic model (Arnot and Gobas 2004) that describes the bioaccumulation of hydrophobic organic contaminants is used to evaluate bioaccumulation of selected contaminants (total PCBs, TCDD~~,~~) and pesticides (including DDx) via water, sediments, and prey. Bioaccumulation of other substances, such as PAHs, is evaluated using a statistical approach based on biota-sediment accumulation factors ~~(BSAFs)~~ or biota-sediment accumulation regressions ~~(BSARs)~~. Under current conditions, the bioaccumulation model determined that sediments are an important source of benthic invertebrate and fish tissue concentrations for the bioaccumulative contaminants.

6.3 SELECT INDICATOR CONTAMINANTS IN UPPER STUDY AREA SEDIMENT DEPOSITIONAL AREAS

As an empirical line of evidence for the quality sediments entering and accumulating in the Study Area, this section details contaminant concentration with depth from cores collected in known depositional areas at the upper end of the Study Area. Three cores were collected in Round 3A in three different known depositional areas based on the time-series bathymetric data (Figure 6.3-1). This sampling effort is detailed in the Round 3A FSP (Integral 2006q), and the full data sets are presented in the corresponding data report (Integral 2007g,h).

The objectives of this sampling effort were to analyze both radioisotopes and conventional/contaminant chemistry at uniform and continuous depth intervals in long-term depositional areas expected to act as natural sediment traps. Because of the location of these cores (i.e., in the upper portion of the Study Area), these data allow inferences to be made about deposition rates and the chemical quality of sediments settling out in the upper Study Area. Two of the three stations sampled, RC02-2 at RM 10.9 and RC01-2 at RM 10.5, are situated in formerly excavated borrow pits with mudline depths well below the authorized channel depth of -40 ft CRD. The third

station, RC483-2 at RM 9.6, is located in the main channel on the large shoal that occurs along the western half of the channel in this area.

Detailed evaluation of the radioisotope data from these cores is provided in Anchor (2007e). Because of the heterogeneous origins of the sediments making up the deposits (e.g., a complex mix of suspended and bedload sediments over time from a variety of lateral, upstream, and atmospheric sources), the radiochemical data did not support the assignment of a timeline to the sediment profiles. However, empirical data on the history of the borrow pits (core samples RC02-2 and RC01-2; i.e., the timing and original depths of the excavations compared to the observed mudline elevations at the time of sampling), as well as the shorter-term LWG time-series bathymetric data, support overall sedimentation rates of approximately 1.5 ft/yr (45 cm/yr) at RC02-2 and 1 ft/yr (30 cm/yr) at RC01-2 (Anchor 2007e). It is important to note that these rates represent a long-term average over multiple years. The actual sedimentation in any given year is likely variable and may be higher or lower than this net long-term average.

The remainder of this section focuses on the conventional and contaminant chemical data (PCBs, TCDD TEQ, DDx, and PAHs) measured in these cores with depth. Unlike other RI/FS subsurface sampling, these core samples were subsectioned and sampled in 30-cm segments from the mudline to the bottom of each core. This allows inferences to be made about the quality of material entering and settling in the upper portion of the Study Area over time.

6.3.1 Upper Study Area Depositional Core Sediment Quality

The locations of the three depositional cores in the upper Study Area are presented on Figure 6.3-1. As noted above, RC483 is a shoal area on the western side of the channel at RM 9.6. RC01 and RC02 are located in dredged borrow pits on the western side of the channel at RM 10.5 and RM 10.9, respectively. Summary statistics for all core segments for all three cores combined are provided in Table 6.3-1 and for each core individually in Tables 6.3-2 through 6.3-4. A range of contaminants plus grain size and percent TOC are included in these tables. The upper Study Area depositional core data evaluation that follows focuses on the physical nature of the cores and the measured concentrations of the four specific indicator contaminants, total PCBs (Aroclors)[29], TCDD TEQ, total DDx, and total PAHs.

6.3.1.1.1 Physical Texture

Figure 6.3-2 shows the core log physical description for each core. Core recovery ranged about 260 cm at RC01 to 330 cm at RC02. All three cores show a general pattern of an upper silt layer (30 to 40 cm in thickness) deposited over a distinct sand interval, which is approximately 40 cm thick at RC01 and approximately 15 cm at RC483 and RC02. This subsurface sand layer may represent coarse-grained material

[29] PCB congeners were not analyzed in these core samples, so total PCBs concentrations are based on Aroclor data only.

deposited during the most significant, recent high-flow event on the lower Willamette River (approaching 200,000 cfs; see Figure 3.1-8) that occurred in December 2005/January 2006. The overlying 30 to 40 cm of silt would be consistent with an approximate 1-year time frame (cores collected in February 2007) and both the estimated long-term sedimentation rate of 30 to 45 cm/yr based on the borrow pit in-filling data noted above and the measured 2002 bathymetric change at stations RC01 and RC02, which averaged 38 cm/yr and 34 cm/yr, respectively, over the 7-year period from 2002 to 2009. Below this sand layer in each core, there is a thick silt layer that varies somewhat in character between the three cores. The silt layer is interbedded with fine sand lenses in RC483, the shoal location at RM 9.6, and RC02, the borrow pit at RM 10.9. In RC02, the texture becomes increasingly sandy below 240 cm down to another distinct sand layer at 315 cm. It is very possible that this deep sand layer reflects the high-flow event (approaching 250,000 cfs; see Figure 3.1-8) that occurred in the lower Willamette River during the winter of 1998/1999. The 315 cm of accumulation over the 8-year period from this horizon to 2007 equals an average sedimentation rate of 39 cm/yr. This is consistent with the long-term sedimentation rates estimated for this area. At RC01, the subsurface silt layer exhibits thick organic beds below 90 cm, suggesting some heterogeneity in the quality of material settling out within this portion of the river.

Figure 6.3-3 shows the 30-cm composite interval results for grain size and TOC with depth for each core. Grain size with depth is consistent with visual core log information at RC483 and RC02, with fine-grained sediments (60 to 80 percent fines) dominant throughout the core except for where distinct sand layers are evident. RC01 is more variable in texture with depth but does show the distinct shallow subsurface sand lenses. Reflecting the organic debris observed at depth in RC01, TOC values are somewhat higher in this core below 90 cm (exceeding 3 percent in most intervals) than in the other cores.

6.3.1.1.2 Contaminant Vertical Profiles

Figures 6.3-4 through 6.3-7 present vertical profiles of the bulk sediment chemistry concentrations on both a dry-weight and TOC-normalized basis for total PCBs, TCDD TEQ, total DDx, and total PAHs in each core. Non-detects are plotted at the full detection limit with an open symbol. Selected summary statistics (using detected values only) for the data from all three depositional cores combined, as well as each individual core, are provided in Table 6.3-5.

The vertical profile data across the four analytes show some general trends. First, as expected, it is evident from dry-weight data that contaminant concentrations in all three cores vary with sediment grain size and TOC, with lower concentrations for all contaminants measured in the sand layers. Another noteworthy trend is the generally low measured values for all of these analytes across all cores and the corresponding minimal vertical gradients within and between cores. Some exceptions to these general trends include an isolated dioxin and PCB spike in the 180-to-210 cm interval in RC01, which may correlate with organic-rich beds in the silt layer. Assuming average

sedimentation rates, this horizon -may correspond to the atypically low-flow water year in 2001 (Figure -3.1-8). Another exception is the notably higher total PCBs levels at RC02 (RM -10.9) compared with RC01 (RM 10.5) and RC483 (RM 9.6). While the levels in RC02 average less than 20 µg/kg, this compares with mostly undetected values in the cores farther downstream. This difference appears to reflect the influence of the proximal source or sources of PCBs on the east side of the river at RM 11.5 (see Section -5.2). Finally, slight vertical trends with concentrations increasing with depth are evident in the TOC-normalized PCB and possibly the TOC-normalized PAH data at RC02.

The vertical profiles of the four indicator contaminants measured in three cores from known depositional areas in the upper portion of the Study Area show relatively low concentrations for all contaminants and minimal gradients with depth within each core and between cores. The farthest upriver core at RM 10.9 exhibits slightly elevated PCB levels (compared with the other cores), and this may reflect the influence of the elevated PCBs detected just upstream at RM 11.5E. Otherwise, the relatively low contaminant concentrations measured in these known depositional area cores appear to reflect the quality of sediments entering and settling out in the upstream portion of the Study Area over approximately the last 10 years. Perhaps this is not unexpected given that periods of significant sediment deposition and accumulation in the lower Willamette River are likely associated with conditions (higher flows, precipitation) that bring large volumes of sediment to the river, and this would act to dilute the relatively localized sources of contamination in bulk sediment deposits.