Preliminary Sediment Cleanup Objectives for Port Angeles Harbor Port Angeles, WA

FINAL REPORT

Prepared for

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1.0 Introduction

The Washington State Department of Ecology's (Ecology) intent is to facilitate a framework for setting sediment cleanup levels (SCL) for cleanups in Port Angeles Harbor. As established by the new Sediment Management Standards (SMS) rule revisions in section 173-204-560 of the Washington Administrative Code (WAC), the SCL is the concentration or level of biological effects of a contaminant in sediment determined by Ecology to be protective of human health and the environment.

The SCL is initially established at the sediment cleanup objective (SCO), and subsequently adjusted upward based on site-specific factors (Table 1). An SCL may not be set above the cleanup screening level (CSL). The purpose of this report was to begin the SCL selection process by setting preliminary SCOs. Existing site data and laboratory capabilities were evaluated to determine risk based concentrations (RBCs), natural background, and practical quantitation limits (PQLs) applicable to Port Angeles Harbor.

All potentially liable parties (PLPs) would be expected to either (a) incorporate the preliminary SCOs, as appropriate, when proposing preliminary SCLs for use in Port Angeles Harbor cleanups, or (b) demonstrate to Ecology why a different number should be used for a particular action. Preliminary SCOs developed for any particular site remain preliminary and draft until they are set by Ecology in the future during the finalization of cleanup action plan(s) for site(s) involving any portion of Port Angeles Harbor.

The existing data used to develop the preliminary SCOs in Port Angeles Harbor were based on the results of the Port Angeles Harbor Sediment Investigation Report (SIR) (E&E 2012), which included site-specific Human Health and Ecological Risk Assessments (HHRA and ERA). The development of the preliminary SCOs followed the process presented in Figures 1 and 2, based on guidance from the Washington State Model Toxics Control Act (MTCA) and the revised SMS.

The process began with determining the indicator hazardous substances (IHS) for the harbor that met the criteria outlined in Figure 1, based on WAC 173-340-703(2). Tissue and sediment RBCs were then developed for each of the substances. Biota sediment accumulation factors (BSAFs) were calculated for each substance and then used to convert tissue RBCs to sediment RBCs. As outlined in Figure 2, the preliminary SCO for each IHS was the highest value from the comparison of the RBCs, natural background, and the PQL (WAC 173-204-560(3)).

Though not calculated in this report, the next step in the process is to determine the CSL. RBCs calculated at a risk of 10^{-5} or hazard quotient (HQ) of 1, PQLs, and regional background sediment concentrations are considered when establishing the site CSLs for the IHS (Table 1). The CSL is the maximum allowed concentration of any contaminant and level of biological effects permissible at the site or sediment cleanup unit after completion of a cleanup action and is represented by the highest value from the comparison of RBCs, PQLs, and regional background sediment concentrations (WAC 173-204-560(4)). Regional background sediment concentrations for Port Angeles Harbor are expected in fall 2013.

At the request of Ecology, NewFields used the data reported in the SIR and the results of the associated risk assessments to identify the chemicals of potential concern (COPCs) and calculate the corresponding preliminary SCOs based on the methodology described above. This report provides a summary of the SIR findings, including a determination of the human IHS for Port Angeles Harbor (Section 2); development of ecological and benthic IHSs for the harbor (Section 3); development of tissue RBCs for each of the IHS and the derivation of sediment RBCs based on the tissue RBCs (Section 4); development of sediment RBCs based on direct contact and ingestion of sediment (Section 5); a summary of natural background concentrations developed for the Port Angeles and environs (Section 6); the derivation of the PQLs (Section 7); the selection of preliminary SCOs based on a comparison of the RBCs, the natural background concentrations, and the PQL (Section 8). A discussion of uncertainties and their potential effect on the selected preliminary SCOs is also included in Section 8.

2.0 Human Health Risk Drivers

The IHS are the COPCs that represent the majority of risk to human health or environmental receptors. Human health IHS were identified following the step-wise process developed by Ecology and described in Section 1.0. The IHS included the COPCs that represented greater than 1 percent of the overall risk, chemicals for which there was a known source or gradient, and those chemicals that are collocated with other IHS (Figure 1). The following section describes the process for determining the human health IHS for Port Angeles Harbor and lists the COPCs that are IHS for human health. Potential IHS associated with ecological receptors are evaluated following a different process and are discussed in Section 3.0.

As indicated in Figure 1, the first step was to determine whether any of the COPCs exceeded the risk threshold for any of the human health exposure routes. Risk thresholds were defined as excess cancer risk above 10^{-6} or a non-cancer HQ greater than or equal to 1.0. Exposure routes for cancer risks included ingestion of tissue or shellfish, ingestion of sediment, and dermal exposure to sediment. Exposure routes for non-cancer risks included ingestion of tissue or shellfish.

Since subsistence fishers are likely to be the most highly exposed receptor group, exposure scenarios were based on input provided by the Lower Elwha Klallam Tribe (LEKT). Cancer risks were calculated using the combined adult/child exposure scenario, while non-cancer risks were calculated using the child exposure scenario. Table 2 includes all of the COPCs that exceeded the risk thresholds for these exposure routes calculated using the reasonable maximum exposure (RME) scenario. RME is defined in MTCA as the highest exposure that can be reasonably expected to occur for humans or other living organisms at a site under current and potential future site use (WAC 173-340-200).

The list of COPCs that exceeded the risk threshold of 10^{-6} or an HQ of 1.0 was refined by identifying IHS with a relative percent total risk greater than or equal to 1 percent. These COPCs are highlighted in Table 2.

Arsenic, cadmium, cobalt, copper, iron, selenium, methylmercury, alpha-benzene hexachloride (BHC), carcinogenic polycyclic aromatic hydrocarbons (cPAH), polychlorinated biphenyl (PCB) Aroclors, and dioxin/furan toxicity equivalent (TEQ) were selected as the primary IHS based on the 1 percent exceedance criteria. Arsenic and dioxin/furan TEQ exceeded the risk threshold for all exposure routes, and exceeded the 1 percent relative risk for cancer and non-cancer risks based on tissue ingestion. Like most metals, arsenic is naturally occurring. In Port Angeles Harbor, arsenic concentrations may potentially result from industrial processes in the inner harbor (NewFields 2013a). Therefore, arsenic is considered an IHS.

PCB Aroclors exceeded the risk threshold and 1 percent relative risk for cancer and non-cancer risks based on tissue ingestion. The remaining COPCs represented greater than 1 percent relative risk for either the cancer or non-cancer tissue ingestion exposure route.

Following the step-wise approach outlined in Figure 2, additional IHS were identified as possibly having known or potential sources, being collocated with other risk drivers, or showing a strong gradient. With a relative percent risk of 0.68, zinc did not qualify as an IHS based on exceedance of the risk threshold. However, there are known or potential sources of zinc within Port Angeles

Harbor and measured concentrations exceeded SMS criteria (NewFields 2013a). As a result, zinc has been identified as an IHS in Table 2.

Additional organic COPCs were also observed to exceed SMS benthic criteria, but the spatial distribution did not indicate potential sources. These compounds were not identified as human health IHS. However, these COPCs are evaluated relative to ecological risk in Section 3.2.

Though cobalt and iron were considered COPCs, there was no further evaluation of the preliminary SCOs for these metals as they were considered naturally occurring and not cause for concern. In addition, there is limited iron and cobalt data available relative to other metals, and no potential industrial sources have been identified. Iron and cobalt were not analyzed for in sediment samples from any of the data sets used in the Port Angeles Harbor Supplemental Data Evaluation (SDE) (NewFields 2012). The SDE was the source of data used in this report. As a result, it was not possible to calculate biota accumulation factor (BAF) values or determine natural background concentrations for these metals. PQLs for cobalt and iron were not included in the list of sediment method detection limits (MDLs) and PQLs compiled by Hart Crowser (McGinnis 2011, personal communication). In addition, these metals are not part of the analyte list for the proposed regional background sediment characterization. Methylmercury exceeded 1 percent non-cancer relative risk for the tissue ingestion pathway. When calculating tissue ingestion risks, E&E conservatively assumed 100 percent of mercury consumed from fish and shellfish was methylmercury (E&E 2012). Methylmercury was not analyzed in sediment samples, which may constitute a data gap relative to potential risk from mercury. As a result, the preliminary cleanup levels in this report are determined using total mercury.

The relative risks due to the presence of PCB Aroclors in sediment and tissue were determined because Aroclors were analyzed in the majority of sediment samples. However, a subset of samples was analyzed solely for PCB congeners. While they were analyzed as part of the Rayonier Phase 2 Addendum Remedial Investigation (RI) (Malcolm Pirnie 2007b), congeners were not analyzed in the samples collected during the initial phase of the RI (Malcolm Pirnie 2007a) or the SIR (E&E 2012).

Since the Aroclors and PCB congener data were collected for separate studies in different areas of the harbor, preliminary SCOs were determined for both PCB Aroclors and congeners. The Aroclor preliminary SCO is included for reference purposes only. Congener analysis is recommended for any further investigation in Port Angeles for two reasons: (1) PCB congeners better represent the bioaccumulation of PCBs, and (2) CSLs will be calculated only for PCB congeners as Aroclors are not being analyzed for the regional background sediment characterization.

Following MTCA rules, the preliminary SCO for Aroclors was calculated as the sum of the Aroclor mixture, while the preliminary SCO for congeners was calculated as the PCB congener TEQ based on toxicity equivalency factors (TEF) from Ecology 2007 (WAC 173-340-708(8ii)).

Lead was specifically evaluated as a potential IHS. The Adult Lead Model (ALM) equation was used with the parameters from the HHRA to evaluate the potential risk of lead concentrations in Port Angeles Harbor. The combined sediment exposure and tissue ingestion pathways of lead contributed less than two percent to the baseline adult lead level. Given the limited potential input, lead was not selected as an IHS. No other metals were evaluated as potential human health IHS.

3.0 Ecological and Benthic Risk Drivers

The intent of the preliminary SCOs developed in this report is that they will be protective of both human health and the environment. Preliminary SCOs based on human health are generally protective of ecological receptors. However, there may be some COPCs that were not considered human health risks, but pose risk to ecological receptors or benthic organisms. The ERA evaluated the existing risks for four receptor groups including marine plants, benthic invertebrates, fish, and wildlife (E&E 2012). The results of the ERA findings are summarized in this section. Any COPCs that represent a risk based on the current conditions will be evaluated relative to the preliminary SCOs derived from the HHRA or included as additional IHS.

3.1 Marine Plants

Marine plants include species such as eelgrass (*Zostera sp*.) and macroalgae such as bull kelp (*Nereocystis luetkana*). Marine plants provide valuable habitat and food resources for marine invertebrates, fish, and birds. As indicated in the ERA, there are no established sediment quality criteria for plants, nor are there established critical tissue burdens for COPCs (based on the U.S. Army Corps of Engineers [USACE] Environmental Residue Effects Database). The ERA based its evaluation of marine plant risk on a qualitative evaluation of habitat quality, with wood debris identified as the primary impact.

Wood debris can be characterized by a variety of natural or anthropogenic woody material including large woody debris, wood chips, wood pulp, and fibers. Significant amounts of wood debris in sediment can alter the physicochemical properties, including creating a physical barrier at the sediment surface or creating anoxic conditions in surface sediments, and can produce concentrations of potentially toxic ammonia and sulfides through degradation. The potential adverse impacts of wood debris on marine habitats are dependent on the source and form of the wood debris and are evaluated by Ecology on a case-by-case basis.

The last sediment profile imaging (SPI) survey in Port Angeles Harbor was conducted in 1999 (SAIC 1999). Analysis of images found that wood waste covered approximately 25 percent, or 500 acres, of the bottom of Port Angeles Harbor. The majority of this wood debris was found in the nearshore log booming areas. Wood debris is considered as an "other deleterious substance" (ODS) and is evaluated separately from other COPCs. Due to a lack of quantitative wood debris measurements in Port Angeles Harbor, it is difficult to evaluate the extent of impacted areas. Issues related to wood debris as a potential risk driver are discussed further in Sections 3.2. No COPCs were identified as IHS for marine plants (E&E 2012).

3.2 Benthic Invertebrates

Ecological risks to marine benthic invertebrates were evaluated by comparing sediment concentrations to sediment benchmarks, interpretation of toxicity testing results, and habitat quality. Sediment benchmarks and bioassay results were evaluated under SMS (E&E 2012).

The SMS evaluation for marine sediments is a tiered process. Sediments exceeding the sediment quality standards (SQS) or lowest apparent effects threshold $(LAET¹)$, criteria may be subsequently evaluated for benthic toxicity using a suite of confirmatory bioassays. The toxicity testing endpoints include amphipod survival, juvenile polychaete growth, and larval development (normal survival). Chemical and/or toxicity results exceeding the SQS criteria result in preliminary SCOs being set at the SQS. Sediments exceeding the CSL or second lowest apparent effects threshold $(2LAET^1)$ also have preliminary SCOs set at the SQS.

A total of 35 surface sediment locations (Table 3) and 14 subsurface locations or depth intervals (Table 4) sampled in Port Angeles Harbor exceeded either the SQS/LAET or CSL/2LAET criteria for one or more COPCs. Four of these COPCs (arsenic, cadmium, mercury, and PCB Aroclors) were already identified as human health IHS. Total PCB congeners (not converted to TEQ) are also included in Table 3 evaluated against the SMS/LAET criteria for Aroclors. This comparison is made for reference purposes only. As noted previously, PCB congeners will be evaluated as human health IHS. However, in the remainder of this report PCB congeners will be discussed on a TEQ basis. The additional COPCs listed in Tables 3 and 4 are considered risk drivers for benthic invertebrates.

Surface sediment COPCs included zinc, bis-2-ethylhexylphthalate, butylbenzylphthalate, fluoranthene, 2,4-dimethylphenol, 4-methyl phenol, and phenol (Table 3). All of these COPCs except butylbenzylphthalate exceeded either a CSL/2LAET sediment criteria or exceeded the SQS sediment criteria and had a bioassay failure. Butylbenzylphthalate exceeded the SQS sediment criteria in two samples, neither of which were tested for sediment toxicity. Subsurface sediment COPCs included 2-methyl naphthalene, acenaphthene, fluorene, naphthalene, phenanthrene, total low molecular weight PAH (LPAH), 4,4'-DDD and 4,4'-DDE. Bioassay testing was not conducted with subsurface sediment samples.

To be protective of benthic receptors, the preliminary SCOs for the benthic risk COPCs are set at the sediment SQS/LAET. The spatial patterns for these COPCs are evaluated with the preliminary SCOs in Section 8.2.

The SIR also identified wood debris as a potential risk to benthic invertebrates for the same reasons presented in Section 3.1. There are no SMS criterion for wood debris in sediment. An Ecology SMS Clarification Paper (Kendall and Michelsen 1997) presents an approach using sediment total organic carbon (TOC) and total volatile solids (TVS) concentrations to address the impacts of wood debris accumulations in sediments. Surface sediment TOC concentration less than 10 percent (dry weight basis) and TVS levels less than 25 percent (dry weight basis) are not likely to pose a risk to aquatic life.

Data collected for the SIR did not include TVS measurements. TOC concentrations were evaluated in sediments and their spatial distribution is summarized in Figure 3. Those areas with TOC concentrations exceeding 10 percent were located in the western harbor and in the vicinity of the former Rayonier dock. TVS was measured in sediments near the former Rayonier dock and log pond during the Rayonier Mill Site Phase 2 Addendum RI (Malcolm Pirnie 2007b).

 \overline{a} ¹ When total organic carbon is less than 0.5 or greater than 3.5 percent for the organic chemicals that are organic carbon normalized under the SQS/CSL criteria, the concentrations are compared to the LAET/2LAET criteria. This TOC range was established in the SIR and recommended by Ecology. See Figure 3 for a list of sediment locations outside this range.

Concentrations exceeded 25 percent at Stations MD-22, LP-03, LP-04, LP-07, and LP-08. An additional station in the western harbor, WP-11 also exceeded the recommended value of 25 percent. These locations overlap areas where TOC was greater than 10 percent. Further evaluation of TVS in harbor sediments, or more quantitative measures of woody debris, is required to refine the sediment quality impacts associated with wood debris.

3.3 Fish

Estimates of ecological risk to fish were based on a comparison of fish tissue residues in lingcod and rock sole to background concentrations and to RBCs from the literature (E&E 2012). With the exception of arsenic, none of the tissue residues measured in fish from Port Angeles Harbor were likely to cause adverse effects. The mean arsenic residue in rock sole tissues was 2.77 mg/kg (E&E 2012), exceeding the human health tissue RBC of 1.7 mg/kg. A sediment RBC that would be protective of rock sole was calculated using the BAF values determined in Section 4.0. The calculated rock sole RBC was four orders of magnitude higher than the sediment RBC selected to be protective of human health. Therefore, the arsenic sediment RBC determined for human health is presumed protective of fish in Port Angeles Harbor.

3.4 Wildlife

Risks to wildlife were evaluated for Brandt's cormorant, double-crested cormorant, greater scaup, harbor seal, raccoon, and bald eagle (E&E 2012). The raccoon was the only wildlife receptor that had a HQ-no observable adverse effects level (HQ-NOAEL) that exceeded 1, for exposure to arsenic. The raccoon total chemical exposure for arsenic was 1.3 mg/kg/d. This value is above the NOAEL of 1.04 $mg/kg/d$, but below the lowest observable adverse effects level (LOAEL) of 1.66 mg/kg/d. An HQ-NOAEL greater than 1 does not necessarily mean adverse effects are occurring. The sediment RBC selected for arsenic from the human health risk assessment is lower than the sediment concentration used to calculate the daily arsenic exposure for raccoons and therefore would also be protective of raccoons.

4.0 Tissue RBCs and Tissue-Derived Sediment RBCs

Risk-based concentrations are those COPC concentrations below which risk to human or ecological receptors is acceptable. This section presents the derivation of RBCs in sediments from tissue RBCs derived from the HHRA (E&E 2012).

4.1 Derivation of Tissue RBCs

Site-specific tissue RBCs for finfish and shellfish were calculated using the equations and input parameters summarized in Appendix A. For the tissue ingestion RBCs, the risks associated with the consumption of finfish and shellfish from the site were based on a tribal exposure scenario provided by the LEKT. The exposure scenario in the HHRA includes ingestion rate for adult subsistence fishers of 1.27 pounds of fish and shellfish from the site per day for 70 years. For child subsistence fishers, consumption rates were 0.6 pound per day for 6 years. In the HHRA, risks were calculated using RME and central tendency (CT) scenarios (E&E 2012). All RBCs in this report were calculated using the more conservative RME scenario.

Tissue RBCs for the cancer risk scenario were calculated for arsenic, alpha-BHC, cPAH TEQ, PCB Aroclors, PCB congener TEQ, and dioxin/furan TEQ (Table 5). Tissue RBCs were calculated separately for lingcod, rock sole, geoduck, horse clam, coonstripe shrimp, and Dungeness crab using the adult/child combined exposure scenario. The risk was set to 10^{-6} for each species and the equation was solved for the RBC using species-specific consumption rates (Equation 3 and Tables A-1 and A-2, Appendix A).

Non-cancer tissue RBCs were calculated for arsenic, cadmium, copper, selenium, zinc, mercury (as a substitute for methylmercury), alpha-BHC, PCB Aroclors, PCB congener TEQs, and dioxin/furan TEQ for tissue ingestion by child subsistence fishers (Table 5). RBCs were determined separately for each species. The HQ for each equation was set to 1 for each species and solved for the RBC using species specific consumption rates (Equation 10 and Tables A-5 and A-6, Appendix A).

RBC values were determined separately for each tissue type for the cancer and non-cancer ingestion risks. Calculating the RBCs in this manner resulted in cumulative risks from tissue ingestion that were greater than 10^{-6} or a HQ of 1. The implications of considering the risks separately are discussed in the uncertainties section (Section 8.3.2).

4.2 Determining Sediment RBCs from Tissue RBCs

This section summarizes the calculation of sediment RBC values from the tissue RBC values using the BSAF. The biota-sediment accumulation factor is a simple tool used to predict the bioaccumulation of certain COPCs in aquatic biota from measured concentrations in sediment. The BSAF was used to derive a sediment RBC from a known tissue RBC. Site-specific BSAF values were calculated for each of the COPCs using tissue and sediment data collected from Port Angeles Harbor (E&E 2012). BSAF values were also obtained from literature sources for comparison and possible use when there was insufficient site-specific data.

4.2.1 Port Angeles Harbor Tissue and Sediment Data

BSAFs were generated from tissue and sediment data collected in Port Angeles Harbor. Depending upon the completeness and representativeness of these data sets, they represent the best estimators of site-specific uptake, as they take into account site-specific factors that control availability. BSAFs were generated from paired data sets of tissue and sediments data from three different survey efforts:

- Port Angeles Harbor Sediment Investigation Report (E&E 2012),
- Remedial Investigation for the Marine Environment Near the Former Rayonier Mill Site (Malcolm Pirnie 2007a), and
- Phase 2 Addendum Remedial Investigation for the Marine Environment Near the Former Rayonier Mill Site (Malcolm Pirnie 2007b).

All tissue data from these studies were incorporated into the BSAF calculations. Tissue and sediment location pairings are presented in Table 6.

Tissue data were paired with sediment data based on sampling date, proximity, and the home range of the target species. Ideally, sediment samples were collected concurrent to the tissue samples. Whenever possible, sediment data were only paired with tissues from within the same sampling program. In three instances, tissue samples from one sample program were paired with sediment from another.

In the first instance, tissue samples collected for the SIR were analyzed for PCB congeners, while the sediment data were analyzed for PCB Aroclors. Tissue samples from the SIR (E&E 2012) were paired with sediments from the Rayonier Phase 2 Addendum RI for PCB congeners (Malcolm Pirnie 2007b). In the second instance, tissue samples, but no sediment samples, were collected from Freshwater and Dungeness Bays as part of the Rayonier RI (Malcolm Pirnie 2007a). These tissue samples were paired with sediment samples collected during the Rayonier Phase 2 Addendum RI (Malcolm Pirnie 2007b). In the third instance, tissue samples collected from Dungeness Bay as part of the Rayonier Phase 2 Addendum RI (Malcolm Pirnie 2007b) were paired with the Dungeness Bay references sediment samples from the SIR (E&E 2012).

For species with extremely limited home ranges, the selected sediment sampling locations were in the immediate vicinity of the tissue sampling location. For example, clams are generally filter feeders, consuming floating algae or detritus at the sediment-water interface or sediment surface. Clams also have high site affinity and are closely tied to local sediment quality conditions. As a result, clam tissue data and sediment data were often collocated.

When data from collocated sediment locations were not available, the closest sampling location was selected provided that the physical environments for the two locations were similar (for example a nearshore sediment sampling location would not have been paired with tissues collected from a depositional location). An exception to this was made for clams from Freshwater and Dungeness Bays. In these bays, sediments and clam tissues were not collocated or even from the same study. Since COPC concentrations were similar throughout each respective bay, sediment data from all locations were averaged and used with the clam tissue data to calculate the BSAFs.

Crab and shrimp are larger invertebrate detritivores that may feed higher on the food web. It is important to consider this group differently when evaluating uptake. Because crabs can have large home ranges, the link between tissue and sediment concentrations becomes more tenuous. The scenario is similar for fish. Evaluating uptake of contaminants from sediments into fish tissues is challenging due to the large home range of most fish species and the limited interaction that many fish species have with sediments. Lingcod were assumed to have a narrow home range, while flatfish were further reaching.

For shrimp and lingcod, the mean sediment concentrations were used from locations within a reasonably sized home-range. For crabs and flatfish, with a home range that included the entire harbor, mean sediment concentrations of all sediment sampling locations were used from their respective collection areas in Port Angeles Harbor, Freshwater Bay, or Dungeness Bay. The tissue locations and associated sediment locations are listed in Table 6.

4.2.2 BSAF/BAF Calculations

The BSAF value is the lipid normalized tissue concentration divided by the TOC normalized sediment concentration. BSAF values were calculated for mercury, alpha-BHC, cPAH TEQ, total PCB Aroclors, PCB congener TEQ, and dioxin/furan TEQ. A BAF is not normalized for lipid content or organic carbon and was calculated for arsenic, cadmium, copper, selenium, and zinc. BAFs are typically used for lipophobic COPCs. A BAF represents the tissue concentration divided by the sediment concentration. Equations for calculating BSAF and BAF values are presented as Equations 11 and 12 in Appendix A, respectively.

Tissue concentrations were paired to the nearest sediment location or locations as listed in Table 6 and described above. Sediment concentrations were averaged if multiple sediment locations were representative of one tissue location, and tissue concentrations were averaged if replicates were taken at a given location. BSAF and BAF were determined for all tissue types (whole body, fillet, etc.) for each of the target species. For Dungeness crab, a whole body tissue concentration was calculated by using the consumption rates of 25 percent hepatopancreas and 75 percent muscle, which were presented in the SIR (E&E 2012). If either the tissue or sediment concentration was flagged non-detect for any of the COPCs, the BSAF/BAF was not calculated.

Dioxin/furan TEQs, cPAH TEQs, PCB congener TEQs, and PCB Aroclor totals used in the BSAF calculations followed Ecology's guidelines for congener, compound, and Aroclor summation (Ecology 2007). Total PCB Aroclors were the sum of all detected Aroclors. If all Aroclors were undetected, the highest detection limit was used. Dioxin/furan and PCB congener TEQs were calculated using a one-half detection limit substitution for non-detected congeners. TEQs for cPAHs were also calculated using a one-half detection limit substitution for nondetected compounds.

BSAF values calculated from Port Angeles Harbor data are presented in Table 7. The average BSAF/BAF, standard deviation, and sample size are summarized for each species and tissue type.

4.2.3 BSAF Literature Review

Ecology requested that NewFields evaluate the scientific literature for BSAF values for the Port Angeles Harbor IHS. Literature BSAF values were used to either confirm the site-specific

BSAFs, or used in place of the site-specific values if there were insufficient local data. If the literature BSAFs were similar to the Port Angeles specific values, the site-specific BSAF was used to calculate the sediment RBC.

Two on-line databases are separately maintained by the USACE and U.S. Environmental Protection Agency (USEPA). The USACE Engineer Research and Development Center (ERDC) maintains a BSAF database that includes qualified data sets from a number of peer-reviewed and grey literature sources (http://el.erdc.usace.army.mil/bsafnew/BSAF.html). The Mid-Continent Division of the EPA also maintains a database that includes BSAF values generated for EPArelated sites (http://www.epa.gov/med/Prods_Pubs/bsaf.htm). Both the ERDC and EPA databases are limited to BSAFs calculated from nonionic organic chemicals. Other sources of data reviewed include the following references:

- E&E 2009. Control of Toxic Chemicals in Puget Sound. Phase 2: Sediment Flux/Puget Sound Sediments Bioaccumulation Model.
- EPA 2003. Technical Summary of Information Available on the Bioaccumulation of Arsenic in Aquatic Organisms.
- EPA 1999. Screening Level Ecological Risk Assessment Protocol. Appendix C: Media to Receptor Bioconcentration Factors (BCFs).
- EPA 1997. Mercury Study Report to Congress.
- Sanborn and Brodberg 2006. Evaluation of Bioaccumulation Factors and Translators for Methylmercury.
- SAIC 2008. Sediment Characterization Study Budd Inlet, Olympia, WA.

Data were considered for inclusion based on completeness and relevance. BSAFs developed for freshwater species were not included in this compilation. Chemical availability can be dramatically altered by salinity, so freshwater BSAFs are generally not applicable in marine systems.

Data from literature sources was grouped by trophic level (TL) and major taxa. The Port Angeles Harbor RA evaluated six different species representing fish (TL 4), shrimp (TL 2/3), crab (TL 2/3), and clams (TL 2). Data extracted from the literature were sorted into these major groups.

Literature resources for BSAFs include limited data on bottom-oriented marine or estuarine fish species. Depending upon the contaminant, the EPA and ERDC databases included BSAFs for several finfish species, including several bottom-oriented fish species. Several other sources provided additional data for flatfish and general TL 4 consumers.

Data were included only for marine and estuarine species that are considered to be bottomoriented, living near the bottom and feeding on benthic epifauna. Midwater and pelagic species were not included, as their link to sediments are typically through several trophic levels and they generally have larger home ranges, making it difficult to link tissue burdens to sediment concentrations.

BSAF data from all literature sources are presented with the calculated values from Port Angeles in Table 7. The calculated or site-specific values are presented in bold text, while literature values are in normal text. A species and COPC specific summary related to the BSAF literature

search is presented in the following paragraphs. A full list of references for the literature BSAF values can be found in Table 7.

Fish: There are no values for dioxin/furan TEQs for fish in the ERDC or EPA databases. Instead, only an incomplete list of congener data is available. One of the most complete data sets for dioxins in fish tissues is the sediment characterization of Budd Inlet conducted by Science Applications International Corporation (SAIC) for Ecology (SAIC 2008). Starry flounder and English sole were collected from three areas of Budd Inlet and were paired with weighted-mean sediment concentrations. BSAFs were calculated for whole body samples and ranged from 0.01 to 0.18 for starry flounder and 0.11 to 0.15 for English sole. These values are similar to those for lingcod in Port Angeles Harbor and slightly higher than for rock sole.

Similarly, data for cPAH TEQs are not available for fish in the ERDC or EPA databases. Tissue concentration for individual cPAH compounds is available for a limited number of samples.

The EPA database for PCB Aroclors in fish includes a number of estuarine species such as winter flounder and as several bottom-oriented roundfish (sand seatrout and croaker). Additional BSAFs are provided by the Condon model (as summarized in E&E 2009), which determined total PCB Aroclor uptake for several Puget Sound fish species or groups, including English sole and two groups of demersal fish. The EPA BSAF values and those modeled by Condon ranged from 0.22 to 6.04 and were similar to those derived from Port Angeles lingcod and rock sole.

None of the literature sources that were reviewed included BSAF values for PCB congener TEQ or BSAF values for the individual dioxin-like PCB congeners. When BSAF values were provided for congeners, only a subset of dioxin-like PCBs was included. Therefore, literature values were not used to evaluate PCB-like congeners in fish.

EPA and the California EPA Office of Environmental Health Hazard Assessment provide mercury BSAFs for TL 4 consumers. It is important to note that the BSAFs provided by these agencies are for methylmercury in tissues and waters or porewaters. Thus, they may be used to generate a sediment-porewater RBC for methylmercury but should not be used to generate a total mercury sediment RBC.

Invertebrates: Literature dioxin/furan BSAF values were available for some invertebrates. The sediment characterization of Budd Inlet included calculation of BSAF for ghost shrimp (SAIC 2008). The BSAF generated from this data set was 0.48, similar to crustacean values from Port Angeles Harbor. The Budd Inlet survey also generated a BSAF for *Macoma nasuta* of 0.35, slightly higher than the value of 0.13 for geoduck in Port Angeles Harbor. The EPA database included congener data for the fiddler crab, with a BSAF of 0.25.

BSAF values for total PCB Aroclors are provided by EPA for whole body blue crab and penaeid shrimp at 3.35 and 1.99, respectively. This is similar to the range of values calculated for Dungeness crab from Port Angeles Harbor (1.86 and 2.45). The literature includes a variety of bivalve species with various feeding strategies. BSAF values ranged from 0.14 to 9.73.

EPA provides data for 10 of the 12 dioxin-like PCB congeners in the electronic database. PCBs 123 and 169 are not reported, possibly because concentrations were below detection limits. Based on the 10 congeners, the BSAFs for PCB congener TEQ were 0.5 and 0.63 for blue crab and penaeid shrimp, respectively. These are lower than the values derived from shrimp and crab collected in Port Angeles Harbor.

The ERDC database contains a limited number of BSAF values for the pesticide alpha-BHC (alpha-BHC) in estuarine waters on the Atlantic coast. For whole-body tissues, the BSAF value for the hard clam was 0.74, while the values for the burrowing crab ranged from 0.1 to 1. The BSAF for the hard clam was much lower than that from geoduck and horse clams at Port Angeles, while the BSAF values for the burrowing crab were more comparable.

Values are reported for arsenic by EPA for TL 2 consumers (EPA 2003). BSAFs are based on uptake by mussels and oysters, with a mean BSAF of 5,270. As with mercury, these data are based on uptake from waters to tissues and should be applied to interstitial water.

4.3 Sediment RBCs from BSAF

Tissue-derived sediment RBCs were estimated for each of the COPCs and tissue types from the BSAF/BAF values and the tissue RBCs presented in Table 7. Sediment RBCs were calculated using Equations 13 and 14 in Appendix A and are also presented in Table 7.

Whenever possible, sediment RBCs calculated from Port Angeles specific BSAF/BAF values were selected. An exception was using the literature BSAF value for PCB Aroclors in bivalves. Of the site-specific values, the lowest sediment RBC value was chosen for each COPC and tissue type for comparison with the natural background and PQL in determining the preliminary SCO. Selected values are highlighted in Table 7.

Sediment RBCs from each tissue type were compared for a given COPC. The lowest reasonable sediment RBC for each COPC for both cancer and non-cancer risks is presented in Table 8. The lowest reasonable RBCs were selected using the following criteria. If an RBC for a specific tissue type was dramatically lower than all other tissue types and species, but was unlikely to comprise a high proportion of daily intake, a slightly higher value was selected.

The sediment RBC values for alpha-BHC and cPAH were based on whole body geoduck clams. The remainder of the sediment RBCs were based on the modified whole body Dungeness crab (assumed 25 percent hepatopancreas, 75 percent muscle). As mentioned in Section 4.2.1, the link between sediment and tissue concentrations for a wide-ranging species such as crab was tenuous. It is possible a better pairing of sediment and tissue data would change the resultant sediment RBC values.

5.0 Sediment RBC for Sediment Ingestion and Direct Contact

The HHRA identified two direct pathways for exposure to sediments: sediment ingestion and direct contact. The exposure scenario for sediment ingestion from the site is based on 0.1 gram of sediment per day, for 104 days over the course of 70 years. For children, the exposure scenario is 0.2 gram per day for 104 days over the course of 16 years. For direct contact, the exposure scenario assumes that clammers' heads, hands, arms, legs, and feet will contact sediment over that same time period (E&E 2012).

Based on the exposure scenarios in the HHRA, sediment RBCs for arsenic, alpha-BHC, cPAH, PCB Aroclors, PCB congener TEQs, and dioxin/furan TEQ were calculated for sediment ingestion and dermal exposure using the combined adult/child cancer risk scenario. As with the tissues, the risk for each equation was set to 10^{-6} and was solved for the exposure point concentration (EPC) parameter. The EPC is equivalent to the RBC. Equation 3 and Tables A-1 and A-2 in Appendix A show the equation and input parameters for calculating the sediment ingestion RBC. The dermal exposure sediment RBC is calculated from Equation 7 using the input parameters from Tables A-3 and A-4 in Appendix A. Sediment ingestion and dermal exposure were calculated separately. The possible cumulative risks from tissue ingestion, sediment ingestion, and dermal exposure are discussed in Section 8.3.2.

The Sediment RBCs for dermal exposure and sediment ingestion are presented in Table 8. The lowest reasonable tissue-derived sediment RBCs are also presented in Table 8. The lowest of the RBC values is presented in the far right column and was used in the preliminary SCO determination.

6.0 Determining Natural Background Concentrations

Natural background is the concentration of hazardous substance consistently present in the environment that has not been influenced by localized human activities. Surface sediment data from the 2008 OSV Bold Sediment Survey (DMMP 2009), Dungeness Bay investigations, and Freshwater Bay investigations were used to compile three natural background data sets for Port Angeles Harbor.

Each of the three natural background data sets differed both in spatial scale and in the type of samples included. The Puget Sound-wide background consisted of all sampling locations from the 2008 OSV Bold Sediment Survey. The Puget Sound Reference background consisted only of samples collected from reference areas as part of the 2008 Bold Survey. The Port Angeles Proximal Area background consisted of samples collected near the Strait of Juan de Fuca and around the San Juan Islands as part of the 2008 Bold Survey as well as the locations sampled in Freshwater and Dungeness Bays.

Advantages and disadvantages of each of these background data sets are described in detail in the Port Angeles Harbor Supplemental Data Evaluation (NewFields 2012). Based on the available data, the Port Angeles Proximal Area background was recommended for determining background concentrations. This data set encompasses similar natural and anthropogenic sources to those found in Port Angeles Harbor, and use of this data set will result in the most conservative natural background.

As described in NewFields 2012, upper percentiles were chosen to represent natural background rather than upper confidence limits (UCL). Briefly, MTCA methods (as described in WAC 173- 340-709) were applied to calculate the upper percentiles. For log normally distributed data sets, MTCA defines background as the true upper 90th percentile or four times the true 50th percentile, whichever is lower. MTCA requires a minimal sample size of ten to define natural background for soil, but does not specify a minimum number for sediments.

COPC data for all of the background data sets were log normally distributed, but natural background was calculated without log transformation. Table 9 displays the calculated 90th percentile natural background for each of the IHS.

An important criterion for the selection of a background data set is matching the grain size characteristics to the site. Although the grain size range present in the Port Angeles Proximal Area background samples is comparable to that determined in the Port Angeles Sediment Investigation, median values suggest that the Proximal Area data set is predominantly coarsergrained than the study area. Use of this data set for calculating Port Angeles Harbor natural background will likely result in grain size effects that will underestimate natural background concentrations. Additional discussion about a potential grain size bias is presented in the uncertainties Section 8.3.3.

7.0 Practical Quantitation Limits

The SMS rule revisions contain no guidance for the selection of practical quantitation limits. MTCA requirements dictate that when a PQL is used as a cleanup level, it must meet the more stringent of either: (1) the PQL being no greater than ten times the MDL, or (2) the PQL is no greater than that established by the USEPA and used to establish requirements in 40 Code of Federal Regulations (CFR) 136, 40 CFR 141-143, or 40 CFR 260-270.

Given that natural and regional background concentration can define the SCL, an additional recommendation is that the PQL must meet the data quality objectives necessary for determining a background characterization. Specifically, the PQL should be low enough to minimize the number of non-detects and maximize the number of unqualified results.

The PQLs selected for this study are within a factor of ten of the MDLs and were specifically selected as appropriate for a background characterization. Using PQLs appropriate for a background study to potentially define the preliminary SCO has another benefit in that the PQL for the SCO and the CSL are the same value, potentially avoiding a scenario where the SCO is higher than the CSL (Table 10).

The PQLs for the bioaccumulative COPCs chosen in this study (arsenic, cadmium, mercury, cPAHs, dioxin/furan, and PCB congeners) are the same as the PQLs chosen for use in the North Olympic Peninsula Regional Background Sediment Characterization sampling and analysis plan (NewFields 2013b). These values and the associated methods are presented in Table 10. Arsenic and cadmium PQLs are reported for EPA Method 200.8, and mercury for EPA Method 7471A. For cPAH, the laboratory prescreens all samples for low concentrations. Low concentration samples are analyzed by a low level variant of EPA 8270 SIM with a PQL of 0.5 for each compound.

The cPAH PQL is not a true PQL, but was modified by the TEF. A TEQ was calculated for cPAH using TEF values from the Ecology guidelines for determining TEQs (Ecology 2007). PQL values from the low level variant of EPA 8270 were multiplied by the compound specific TEF values listed in Table 10. The resulting PQL is 0.76 µg TEQ/kg.

The dioxin/furan and PCB congener PQLs were calculated in the same manner as cPAH. A TEQ was calculated for dioxin/furan and PCB congeners from the TEFs listed in Table 10. For dioxin/furan congeners, the resulting PQL is 2.3 ng TEQ/kg with EPA Method 1613B. For PCB congeners, the PQL is 0.052 ng TEQ/kg using EPA Method 1668. A low end calibration point was used for all congener analyses to obtain the lowest PQLs.

The PQLs for several IHS, including copper, selenium, zinc, and PCB Aroclors, came from the laboratory survey conducted by Hart Crowser, Inc. (McGinnis 2011, personal communication). Several laboratories were contacted for their currently achievable PQLs. The sample size, minimum, maximum, average, and median values were determined for each method. PQLs from multiple methods are included in Table 11 for metals.

Listed methods for the metals include EPA 6010 and EPA 6020. EPA 6020 is a common analytical method that was used in the Port Angeles sediment investigation (E&E 2012). Median PQLs from EPA 6020 were selected for copper, selenium, and zinc.

The PQLs for PCB Aroclors were taken from the low level variant of EPA Method 8082. The maximum median PQL among the Aroclors is 5.5 µg/kg. This value was used as the PQL for total PCB Aroclors. This is consistent with Ecology methods for calculating total PCB Aroclors.

The Hart Crowser laboratory survey did not include any PQL data for alpha-BHC. PQLs for the isomer, gamma-BHC, ranged from 0.55 to 2.5 for methods EPA 8081LL and EPA 8081, respectively. EPA 8081A was used for the analysis of alpha-BHC during the Port Angeles sediment investigation. The median PQL from the reported data was 1.3 μ g/kg. This value was used to represent the PQL in the preliminary SCO determination. However, it should be noted that PQL values did vary by sample and no sample results exceeded the PQL for alpha-BHC.

8.0 Identifying Preliminary Cleanup Goals

The final preliminary SCOs are identified in this section along with a discussion about uncertainties relating to determination of the sediment RBCs, natural background, and PQLs.

8.1 Preliminary Cleanup Goals for Human Health Risk Drivers

The human health preliminary cleanup goals were determined from a comparison of the selected sediment RBCs (Table 8), Port Angeles Proximal natural background (Table 9), and the PQL (Tables 10 and 11). Based on the decision framework developed by Ecology (Figure 2), the highest of these three values was identified as the preliminary SCO. All three values are presented in Table 12 for each IHS. The preliminary SCO is presented in the second to last column. For reference, the number of samples and the number of samples exceeding the preliminary SCO are listed in the final column.

Figures 4 through 13 present locations of the harbor that exceed the preliminary SCOs for the various COPCs. Depending on the spatial extent of the COPC data, these figures either display harbor-wide interpolations of COPC concentrations evaluated relative to the preliminary SCOs, or discrete sample locations that exceeded the preliminary SCOs. All figures include data from the three studies listed in Section 4.2.1, as well as data from the Environmental Baseline Investigation (Exponent 2008). No figure was created for alpha-BHC. Even though 20 samples exceeded the median PQL from the Port Angeles sediment investigation, no sample exceeded its sample-specific PQL for alpha-BHC.

In the interpolated figures, areas that exceeded the human health preliminary SCO values are marked by cross-hatching. The color gradient and cross-hatching were completed as separate interpolations to account for non-detects. Non-detect values were included in the color gradient interpolation at the detection limit, as that represents the maximum concentration that could be at a given location. Non-detects were included in the cross-hatched interpolation at a value of zero, so that a non-detected result would not be considered to exceed the preliminary SCO. All undetected concentrations in the figures are marked with a red X.

When relevant, the preliminary SCO, SQS/LAET, and CSL/2LAET are included in each figure as interpolation boundaries to show areas likely to pose benthic risks. Selenium and PCB congener TEQ data were not spatially interpolated as there were too few locations sampled.

The selected preliminary SCO of 7.0 mg/kg for arsenic was defined by natural background. The PQL for arsenic was 14 times lower than natural background, and the sediment RBC was five orders of magnitude lower. The area within this preliminary SCO boundary includes a small section of the former Rayonier log pond and all but the nearshore areas of the southern-most western harbor (Figure 4). One location in the western harbor (IH02A) exceeded the SQS criteria.

The preliminary SCOs for cadmium and copper were also defined by natural background (Figures 5 and 6, respectively). The natural background for cadmium was 0.49 mg/kg, four times higher than the PQL, and nearly five times higher than the sediment RBC. The natural background for copper was 30 mg/kg (Figure 6), with a PQL of 0.35 mg/kg and sediment RBC of 5.6 mg/kg. Both of these metals had similar spatial patterns for preliminary SCO exceedances, encompassing the former Rayonier log pond and dock area, and the majority of the western harbor.

Selenium was not detected in any of the natural background samples. As a result, the preliminary SCO for selenium was defined by the PQL at 0.60 mg/kg. The spatial extent of data for selenium was mainly limited to the vicinity of the former Rayonier Mill property (Figure 7). Due to the limited data, no interpolation could be performed. Fifteen of 54 selenium samples exceeded the PQL.

The initial tissue-derived sediment RBC for zinc was 104 mg/kg and was based on the consumption of Dungeness crab (Table 8). 104 mg/kg exceeded both the PQL and natural background. Following Figure 2, the cumulative RBC was recalculated to include all tissue types. The revised cumulative value was 55 mg/kg, higher than the PQL, but lower than the natural background of 70 mg/kg. Following this process, the preliminary SCO for zinc was set at the natural background concentration (Table 9). Zinc exceedances of the preliminary SCO encompassed the western half of Port Angeles Harbor, including areas of the western harbor with CSL and SQS exceedances (Figure 8). Fifty-seven out of 180 samples exceeded the preliminary SCO for zinc.

Like arsenic, cadmium, and copper, mercury was also defined by natural background. The preliminary SCO for mercury was determined to be 0.079 mg/kg. Both the PQL and sediment RBC were within the same order of magnitude (Table 12). Concentrations exceeding the preliminary SCO surround the former Rayonier Mill site, but the highest concentrations were measured in the western harbor. One location in the former Rayonier log pond and three in the lagoon exceeded SQS. An additional four western harbor locations exceeded the CSL criteria. Collectively, the locations exceeding CSL criteria result in a stronger concentration gradient for mercury than arsenic. In addition, the spatial area of Port Angeles Harbor that exceeds the preliminary SCO for mercury is larger than that of arsenic (Figure 9).

The preliminary SCO for cPAH TEQ was defined by a natural background concentration of 9.2 µg TEQ/kg. The preliminary SCO was exceeded in 149 of 157 samples, the highest proportion for any of the COPCs. Both the sediment RBC and PQL had similar concentrations at 0.748 and 0.76 µg TEQ/kg, respectively. The spatial area exceeding natural background included all of Port Angeles Harbor and extended out of the harbor to the east. However, many of the PAH concentrations at the nearshore locations east of Rayonier were composed of non-detects. Nearly all of the nearshore areas in the harbor had cPAH TEQ concentrations five times greater than natural background, and three locations had cPAH concentrations 50 times greater than natural background (Figure 10).

The area exceeding the preliminary SCO for PCB Aroclors included the vicinity of the former Rayonier Mill property, the southern harbor in proximity to active combined sewer overflows, and the western-most harbor. These same areas also include several non-detect data points due to the high detection limits used in many of the studies (Figure 11). The preliminary SCO was determined by a PQL of 5.5 µg/kg (Table 10). A typical MDL used during the analysis of the sediment samples in Port Angeles Harbor was closer to 20 µg/kg. As a result, there were many non-detects located throughout the harbor that exceed the preliminary SCO (Figure 11). The only area with a large number of detected concentrations of PCB Aroclors that exceeds the preliminary SCO is in the vicinity of the former Rayonier Mill property. Additional sampling

may be warranted to achieve a lower MDL, preferably using congener analysis, to better delineate the area relative to PCB contamination.

There was insufficient PCB congener data collected to perform spatial interpolation. Figure 12 shows the PCB congener TEQ concentrations by sampling location. Forty nine of 50 locations exceeded the natural background based preliminary SCO of 0.077 ng TEQ/kg (Table 12).

The preliminary SCO for dioxin/furan congeners was determined from the PQL of 2.3 ng TEQ/kg. The potentially impacted area for dioxin/furan congeners is similar to that of arsenic and mercury. There was a small area exceeding the preliminary SCO around the former Rayonier Mill property and a much larger area emanating from the western harbor and including the lagoon (Figure 13). The PQL was six times the natural background and over 300 times the sediment RBC.

8.2 Preliminary Cleanup Goals for Benthic Receptors

Table 13 shows the SQS/LAET and CSL/2LAET criteria for the COPCs identified as posing risks to benthic receptors in Section 3.2. The preliminary SCO for each of these COPCs is set at the SQS or LAET criteria. Figures 14 through 19 show the sediment locations that exceed the benthic risk COPCs for the surface sediment COPCs. Concentrations for the organic benthic risk COPCs were frequently undetected, making spatial interpolations impractical. Organic contaminant concentrations at specific locations are highlighted if they exceed relevant criteria. Undetected organic contaminant concentrations in sediments are marked with a red X.

Sediment sampling locations that exceeded the SQS criteria for bis(2-ethylhexyl)phthalate, butylbenzyl phthalate, and fluoranthene are presented in Figures 14, 15, and 16, respectively. Each of these COPCs was carbon normalized before comparing to SQS/CSL criteria for locations between 0.5 and 3.5 percent $TOC²$ Approximately 60 percent of the locations sampled in Port Angeles Harbor were within this TOC range. Locations outside this TOC range were not normalized and were compared to LAET/2LAET criteria.

Bis(2-ethylhexyl)phthalate exceeded the SQS or CSL criteria at five locations in the marina and western harbor and exceeded the 2LAET criteria at one location in the log pond (Figure 14). Butylbenzyl phthalate exceeded the SQS criteria at one location in the lagoon and one location near the marina (Figure 15). Fluoranthene exceeded the 2LAET criteria at one location in the log pond (Figure 16).

The phenols are presented in Figures 17 through 20. 2,4-dimethyphenol and 2-methylphenol both exceeded the CSL at one location in the log pond (R05LP-06). 4-methylphenol exceeded the CSL at eight locations around the Rayonier log pond and mill dock. Phenol exceeded the SQS at two locations near the marina and two in the vicinity of the Rayonier log pond and mill dock. Elevated detection limits are common with the phenolic compounds. 2,4-dimethyphenol, 2 methylphenol, and phenol all had locations with undetected concentrations that exceeded the SQS or CSL criteria. All samples that exceeded criteria for phenolic compounds from the marina and Rayonier log pond were in areas with greater than 5 percent TOC, implying wood debris as a

 \overline{a} ² When total organic carbon is less than 0.5 or greater than 3.5 percent for the organic chemicals that are organic carbon normalized under the SQS/CSL criteria, the concentrations are compared to the LAET/2LAET criteria. This TOC range was established in the SIR and recommended by Ecology.

possible source. Some of the locations near the Rayonier mill dock had lower TOC but were close enough to the log pond that wood debris may be a contributing factor.

8.3 Uncertainties

The determination of the preliminary SCOs followed a stepwise decision framework developed by Ecology, using RBCs, natural background, and PQLs. There are several uncertainties associated with each of these potential criteria. This section discusses the major source of uncertainties associated with each of these potential criteria and how they may affect the preliminary SCO values presented in Table 12.

8.3.1 Risk-Based Criteria

Site-specific risk-based criteria are often used for cleanup objectives because they take into account local sediment properties, ecological conditions, and exposure scenarios. For Port Angeles Harbor, the tissue RBCs and tissue-derived sediment RBCs are well below natural background and PQLs. There are three important sources of uncertainty associated with these RBCs: the number of tissue samples for some of the target species; the interaction of the target species with impacted sediments; and the exposure scenarios used in the HHRA.

The development of RBCs was based on data collected from Port Angeles Harbor. For some species and certain analytes, there were limited data available for evaluation. For geoduck and rock sole, one tissue sample was available for some analytes. One individual does not represent exposure to all of the contaminants present in the harbor, nor is one individual representative of the uptake characteristics of that target species. This source of uncertainty could either overestimate or underestimate contaminant uptake, thereby decreasing or increasing the calculated sediment RBC.

The BSAF relationship used to derive sediment RBCs assumes that the tissues are at equilibrium with the surrounding sediments. However, if sediment samples are not collocated with tissue samples or if the target species are mobile and far-ranging, the tissue residues are unlikely to be closely related to the sediment concentrations. In the Port Angeles data set this is particularly true for Dungeness crab and rock sole tissue residues, which were paired with harbor-wide mean sediment concentrations. This source of uncertainty could either overestimate or underestimate contaminant uptake, thereby decreasing or increasing the sediment RBC.

The exposure scenario used in the HHRA includes a number of conservative estimates associated with seafood consumption, particularly for the exposure scenario for tribal subsistence fishers. The scenario assumes a diet of 1.27 pounds of shellfish and finfish from the site consumed daily over 70 years. Ten percent of this diet is pelagic fish, excluding salmon, and 5 percent is composed of bottom fish. Horse clam, geoduck, and crab each comprise 25.5 percent of the total diet, and shrimp encompasses the remaining 8.5 percent of the tribal subsistence diet. Throughout the HHRA, this and other estimators of exposure have compounded, resulting in highly conservative RBCs.

The RBCs were calculated assuming 100 percent of the finfish and shellfish diet was collected from the harbor, as opposed to other locations in the Strait of Juan de Fuca (E&E 2012). While the daily consumption rates are not likely to change, it can be argued that not all of the fish and shellfish consumed by subsistence fishers would come solely from Port Angeles Harbor. The

fractional intake (FI) parameter of the RBC equations (Appendix A, Table A-2) can be adjusted to show the impact of consuming some fish and shellfish from outside the harbor. Changes in the FI result in linear changes to the sediment RBC. For example, if the FI were reduced from 1 to 0.5, the RBC values in Table 12 would double.

The ingestion and direct-contact sediment RBCs are also based on conservative estimates of exposure (E&E 2012). However, the impact of this bias on the selection of preliminary SCOs is minimal as the risks associated with sediment ingestion or dermal contact are far lower than those associated with seafood ingestion.

One additional source of potential error in the RBC calculations for mercury is the role of methylmercury. The IHS identified in the human health risk assessment was methylmercury, the organic form of mercury, which is the sole form of mercury in human tissues. The sediment RBC was determined for total mercury, which includes both the inorganic and organic form. Since the BSAFs used in the sediment RBC calculations are site specific, the BSAFs incorporate the relative contribution of inorganic and organic mercury to the tissue burdens. However, if the sediment-tissue pairings that were used to develop the BSAF are not representative of the methylmercury content of sediments throughout the harbor, uptake may be under or overestimated. Further evaluation of methylmercury distribution within the harbor may be required if mercury is identified as a primary driver of a cleanup action.

Like mercury, arsenic has an organic and inorganic form which differs in toxicity and bioavailability for uptake into tissues. Inorganic arsenic is considered to be the primary toxic form to aquatic life and humans. However, organic arsenic is also thought to exhibit some toxicity. While the inorganic form of arsenic is generally more common in sediments, 85 to 90 percent of arsenic found in edible portions of marine fish and shellfish is present in the organic form (EPA 2003). For the purposes of generating the preliminary SCOs, site-specific sediment and tissue data were used to generate a site-specific BAF. If the sediment-tissue pairings that were used to develop the BAF are not representative of the relationship of inorganic and organic arsenic in sediment and tissue, uptake may be under or overestimated.

8.3.2 Cumulative Risks

For the cancer exposure scenarios, RBC values from sediment ingestion, dermal exposure, and tissue ingestion from each individual tissue type were calculated separately with the risk set to 10^{-6} . For the non-cancer scenarios, RBCs from each of the individual tissue types were calculated separately with a HQ of 1. As a result, cumulative risks for the cancer scenarios may exceed 10^{-6} and HQ for the non-cancer scenarios may exceed 1.0.

Attempts were made to calculate the total risks from the sediment RBCs in Table 12 and the BSAF values from Table 7. Solving for each individual RBC with a risk of 10^{-6} or HQ of 1 resulted in cumulative risks up to three times higher. Therefore, the RBCs selected for comparison against natural background and PQLs are overestimates. The impact of this bias is minimal as all the RBCs except zinc were lower than their respective natural background and PQLs in the determination of site-specific preliminary SCOs. Following Figure 2, cumulative RBCs were only calculated when the initial species-specific RBC was greater than the PQL or natural background.

8.3.3 Natural Background Concentrations

The natural background concentrations that were selected for inclusion in the preliminary SCOs were based on Port Angeles area data sets and should be representative of the local study area. However, as discussed in NewFields (2012), the natural background data were generally collected in areas with coarser sand, whereas the nearshore areas in Port Angeles Harbor are typically finer sands and silts or clays. Finer silts and clays are typically associated with higher concentrations of COPCs due to increased surface areas and higher TOC content. The utilized data set may underestimate the actual natural background concentrations of COPCs, particularly contaminants that are likely to adsorb onto sediment surfaces. Therefore, the preliminary SCOs based on natural background concentrations may be overly conservative. Collection of a more robust and representative natural background data set may be warranted.

8.3.4 Practical Quantitation Limits

The PQLs presented were selected with the data quality objectives needed to determine a sediment background concentration. Low PQLs reduce the number of non-detects and increase the amount of unqualified data. Using low PQLs increases the likelihood that natural background will represent the preliminary SCO. The PQLs chosen for bioaccumulative COPCs in this study are the same as those chosen for use in the North Olympic Peninsula Regional Background Characterization SAP (NewFields 2013b).

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Tables
Table 1. Selection of the Sediment Cleanup Level under the SMS Rule Revision

Cleanup Screening Level (CSL) is highest of :

- \bullet Lowest sediment RBC at risk of 10⁻⁵ or hazard quotient of 1
- Practical Quantitation Limit (PQL)

• Regional Background

Sediment Cleanup Level

 Established between the CSL and SCO as determined by Ecology to be protective of human health and the environment.

Sediment Cleanup Objective (SCO) is highest of:

- Lowest sediment RBC at risk of 10^{-6} or hazard quotient of 1
- Practical Quantitation Limit (PQL)
- Natural Background

Source: E&E 2012

Notes:

Indicator Hazardous Substances are highlighted.

1 – RBCs for PCB congeners are evaluated concurrent with Aroclors in this document.

BHC – benzene hexa chloride

cPAH – carcinogenic polycyclic aromatic hydrocarbons

DDE – dichlorodiphenyldichloroethylene

DDT – dichlorodiphenyltrichloroethane

PCB – polychlorinated biphenyl

TEQ – Toxicity Equivalent

Table 3. List of COPCs and Locations and that Exceed SQS and CSL Criteria and Associated Toxicity Testing Results

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Table 3. List of COPCs and Locations and that Exceed SQS and CSL Criteria and Associated Toxicity Testing Results (continued)

Exceeds SQS/LAET criteria for sediment chemistry or SQS for toxicity Exceeds CSL/2LAET criteria for sediment chemistry or CSL for toxicity

1 – Evaluated at the LAET/2LAET

2 – For reference purposes only, the sum of detected PCB congeners are compared to the LAET/2LAET criteria for total Aroclors. For the remainder of this report,

PCB congeners are treated as a total TEQ.

− Concentration below SMS criteria

na – Not analyzed for sediment toxicity

Exceeds SQS/LAET criteria for sediment chemistry or SQS for toxicity

Exceeds CSL/2LAET criteria for sediment chemistry or CSL for toxicity

1 – Evaluated at the LAET/2LAET

− Concentration below SMS criteria

Table 5. Tissue Ingestion Risk-based Concentration (RBC) Values for Cancer and Non-cancer Risk Scenarios

Source: Values calculated from equations and input parameters in the human health risk assessment (E&E 2012)

Notes:

PCB – polychlorinated biphenyl

RBC – risk-based concentration

TEQ – toxicity equivalent

Table 6. Tissue Samples and Paired Sediment Samples for Port Angeles Data Sets

Table 6. Tissue Samples and Paired Sediment Samples for Port Angeles Data Sets (continued)

Table 6. Tissue Samples and Paired Sediment Samples for Port Angeles Data Sets (continued)

Geoduck are sessile filter feeders; potential route of exposure is through ingestion of re-suspended sediments at the sediment water interface or direct contact with sediments; potential integration of sediment-bound COCs from "upcurrent" sources. Selected locations that are in the immediate vicinity or upcurrent.

Horse clams are sessile filter feeders; potential route of exposure is through ingestion of re-suspended sediments at the sediment-water interface or direct contact with sediments; potential integration of sediment-bound COCs from "upcurrent" sources. Select locations that are in the immediate vicinity or locations that are predominantly upcurrent. **Dungeness crab** are carnivores and detritavores. Adult Dungeness crab can range substantially, within and outside the harbor, and were paired with a mean sediment concentration for Port Angeles Harbor.

Coonstripe shrimp are generally oriented to structure, such as rock piles, logs, or dock pilings. While they have some site affinity, they are less in direct contact with sediments. **Lingcod** are carnivores, with high site affinity as adults. **Rock sole** are carnivores feeding primarily on benthic infauna and epifauna and can move between shallow and deeper waters throughout the year. **Starry flounder** are oriented to finer sediments and may have more site affinity, particularly when young.

T2: Trophic level 2 consumer

T3: Trophic level 3 consumer

FB: Freshwater Bay

PA: Port Angeles Harbor

DB: Dungeness Bay

Sources: EPA 1997; EPA 2003; E&E 2009; SAIC 2008

Notes:

With some exceptions, highlighted cells represent the most conservative RBC for the particular animal class. **Boldface** RBC results are those calculated from Port Angeles site-specific data. Literature values are in normal text.

1 – Sample size inclusive of replicates.

2 – Dungeness whole body represents 25% hepatopancreas and 75% muscle concentrations.

3 – TOC and lipid values represent PA averages.

BSAF – biota sediment accumulation factor example of the PA Data – Port Angeles data from this report EPA db – EPA BSAF database RBC – risk-based concentration ERDC – USACE BDAF database SD – standard deviation OEHHA – CA EPA Office of Environmental Health Hazard Assessment TOC – total organic carbon

Analyte	Units	Tissue-Derived Sediment RBC			Sediment Ingestion	Dermal Exposure	Selected RBC
		Driver ¹	Cancer	Non-cancer			
Arsenic	(mg/kg)	Dungeness Crab	7.07E-05	0.0174	1.05	0.847	7.07E-05
Cadmium	(mg/kg)	Dungeness Crab		0.0982			0.0982
Copper	(mg/kg)	Dungeness Crab		5.6			5.6
Selenium	(mg/kg)	Dungeness Crab		0.226			0.226
Zinc	(mg/kg)	Dungeness Crab		104			104
Total Mercury	(mg/kg)	Dungeness Crab		0.0552			0.0552
alpha-BHC	$(\mu g/kg)$	Geoduck	0.00679	187	250	60.5	0.00679
cPAH	$(\mu g/kg)$	Geoduck	0.748		216	40.2	0.748
PCB Aroclors	$(\mu g/kg)$	Dungeness Crab	0.164	3.57	790	140	0.164
PCB Congeners	(ng/kg)	Dungeness Crab	0.000762	0.0626	10.5	8.47	0.000762
Dioxin TEQ	(ng/kg)	Dungeness Crab	0.00585	0.481	10.5	8.47	0.00585

Table 8. Sediment Risk-Based Concentrations (RBCs)

Source: Sediment ingestion and dermal exposure RBCs are calculated from the equations and input parameters in the human health risk assessment (E&E 2009). Tissue-derived sediment RBCs are calculated from the tissue RBCs in Table 2 and BSAF values in Table 4.

Notes:

1 – BSAF/BAF values from whole body concentrations were used for geoduck and Dungeness crab.

PCB – polychlorinated biphenyl

RBC – risk-based concentration

TEQ – toxicity equivalent

Table 9. Natural Background for the Port Angeles Proximal Area

Notes:

1 – Includes PCB Aroclors 1026, 1221, 1232, 1242, 1248, and 1260.

2 – The natural background for this COC was calculated for this report and was not included in NewFields 2012.

3 – alpha-BHC was not detected in 12 of the 13 samples.

– No background concentration was determined because there were no detections.

Table 10. Practical Quantitation Limits (PQL) from the North Olympic Regional Background Characterization

Notes:

1 – All 209 congeners/congener pairs will be analyzed for the regional background characterization. The PQL for each of the congeners not listed in this table is 0.4 ng/kg.

2 – Regional background PAH samples will undergo a prescreening process at the analytical laboratory and low concentration samples will be analyzed at 8270 SIM LL with a reporting limit of 0.5, while higher concentration samples will be analyzed at a PQL of 5.0. The effective PQL is 0.5 µg/kg.

3 – The PCB and dioxin/furan congener values are not a true PQL; rather, they are PQL-based. A TEQ is calculated from the PQL using TEF values from Ecology 2007.

DW – dry weight

LL – low level modification of analytical method

Table 11. Summary Statistics for Practical Quantitation Limits (PQL) Compiled from a Survey of Analytical Laboratories

Source: McGinnis 2011, personal communication.

Notes:

Highlighted PQL values are used for the comparison between the RBC and background in determining a preliminary **SCO**

1 – PQL for alpha-BHC was not compiled by Hart Crowser. Listed value represents median PQL from E&E 2012 data set.

Min – minimum

Max – maximum

DW – dry weight

LL – low level modification of analytical method

N – number of laboratories providing information

Table 12. Preliminary Sediment Cleanup Objectives (SCOs) for the Human Health Risk Indicator Hazardous Substances

Notes:

***** 104 mg/kg represents the sediment RBC for consumption of Dungeness crab. This RBC was the higher than the BTV and PQL. Following Figure 2, a cumulative RBC which included all tissue types was calculated for zinc. The cumulative RBC of 55 mg/kg was lower than the BTV, resulting in the selection of the BTV as the PCG.

1 – Sediment RBCs calculated using exposure scenarios for subsistence fishers. All exposure parameters were taken from E&E 2012.

2 – Background values were calculated from data collected in Freshwater and Dungeness Bays and from samples collected in the Strait of Juan de Fuca and around the San Juan Islands as part of the 2008 Bold Survey. 3 – PQLs for various methods and analytes were taken from the North Olympic Peninsula Regional Background Characterization SAP (NewFields 2013), while additional PQLs were from a survey of laboratory capabilities conducted by Hart Crowser, Inc. (McGinnis 2011, personal communication).

4 – Following Ecology guidance, the preliminary SCO is the highest of the sediment RBC, natural background, or PQL.

5 – The cPAH, PCB, and dioxin/furan congener values are not a true PQL; rather, they are PQL-based. A TEQ is calculated from the PQL using TEF values from Ecology 2007.

6 – All 20 samples were qualified as being lower than the sample specific PQL.

ND – not detected in any of the background samples

PQL – practical quantitation limit

RBC – risk-based concentration

Table 13. SQS/CSL and LAET/2LAET Criteria for Protection of Benthic Receptors

Notes:

Preliminary sediment cleanup objectives are set at the SQS/LAET.

– SQS/CSL and LAET/2LAET for these COPCs are functionally equivalent.

1 – When total organic carbon is less than 0.5 or greater than 3.5 percent for the organic chemicals that are organic carbon normalized under the SQS/CSL criteria, the concentrations are compared to the LAET/2LAET criteria. This TOC range was established in the SIR and recommended by Ecology.

2 – Ecological COPC for surface sediment.

CSL – cleanup screening level

LAET – lowest apparent effects threshold

2LAET – second lowest apparent effects threshold

SQS – sediment quality standard

Figures

Figure 1. Identification of Indicator Hazardous Substances (IHS)

Figure 2. Determination of Preliminary Sediment Cleanup Objectives (SCOs)

Figure 5. Interpolated Cadmium Concentrations in Port Angeles Harbor Delineated by the Preliminary Sediment Cleanup Objective

 \overline{N}

 0 0.25 0.5 1 0.25 Miles

 \overline{N}

Figure 7. Selenium Concentrations in Port Angeles Harbor Marked with the Preliminary Sediment Cleanup Objective

Figure 8. Interpolated Zinc Concentrations in Port Angeles Harbor Delineated by the Preliminary Sediment Cleanup Objective

Figure 11. Interpolated PCB Aroclor concentrations in Port Angeles Harbor Delineated by the Preliminary Sediment Cleanup Objective

Figure 13. Interpolated Dioxin/Furan TEQ Concentration in Port Angeles Harbor Delineated by the Preliminary Sediment Cleanup Objective

Figure 14. Bis(2-ethylhexyl)phthalate Concentrations in Port Angeles Harbor Marked with SQS/LAET Exceedances

 $\mathsf N$

Figure 15. Butylbenzyl Phthalate Concentrations in Port Angeles Harbor Marked with SQS/LAET Exceedances

Figure 16. Fluoranthene Concentrations in Port Angeles Harbor Marked with SQS/LAET Exceedances

Figure 19. 4-methylphenol Concentrations in Port Angeles Harbor Marked with SQS Exceedances

 $\mathsf N$

Appendix A Equations for the Calculation of Human Health Risks and Risk-Based Concentrations

Appendix A

Equations for the Calculation of Human Health Risks and Risk-Based Concentrations

This appendix presents the equations used to calculate the exposure risks for adult/child dermal exposure for carcinogens, adult/child tissue and sediment ingestion for carcinogens, and child tissue ingestion for non-carcinogens as reported in the HHRA (E&E 2012). The risk-based concentrations (RBC) in the report were calculated by rearranging the equations for each exposure pathway to solve for the exposure point concentration (EPC).

The equations for calculating risk and the RBC values are listed by exposure pathway. Definitions and numerical values for all of the input parameters necessary to calculate the RBCs are included with each set of equations. All input parameters are based off subsistence fisher exposure scenarios. Port Angeles specific EPC values for calculation of exposure risks can be found in the HHRA (E&E 2012).

Tissue and Sediment Ingestion – Carcinogen

Carcinogen sediment and tissue ingestion risks were calculated using Equations 1 and 2. Exposure risks for sediment and tissue were calculated separately. Exposure risks are additive, meaning the total exposure risk from tissue is equal to the sum of the individual chronic daily intakes (CDI) from consumption of pelagic fish, bottom fish, geoduck, horse clam, crab, and coonstripe shrimp multiplied by the slope factor (SF).

Equation 3 shows the calculation of the sediment and tissue RBC values. For each chemical of potential concern (COPC), the appropriate slope factor was used (Table A-1) along with the adult and child input parameters from Table A-2. RBCs were calculated for sediment and each of the six tissue types separately. The Risk parameter in Equation 3 was set to 10^{-6} for each of the RBC calculations. The cumulative risks that result from using a 10^{-6} input for each exposure pathway are discussed in Section 8.3.2 of the report.

$$
\text{Equation 1} \qquad CDI_o = \frac{EPC_{sed/tissue} \times FI \times CF}{AT} \left(\frac{ED_c \times EF_c \times IR_c}{BW_c} + \frac{(ED_a \times ED_c) \times EF_a \times IR_a}{BW_a} \right)
$$

Equation 2 **Equation** 2

$$
Risk = CDI_o \times SF
$$

 $Dist_{\Omega}U \times AT$

Equation 3

$$
RBC_{sed/tissue} = \frac{RISK \times AI}{SF \times FI \times CF \left(\frac{ED_c \times EF_c \times IR_c}{BW_c} + \left(\frac{(ED_a - ED_c) \times EF_a \times IR_a}{BW_a}\right)\right)}
$$

Values in Table A-2 represent the reasonable maximum exposure (RME) scenario.

Dermal Exposure – Carcinogen

Dermal sediment exposure risks were calculated using Equations 4, 5, and 6. Equation 5 solves for the absorbed dose per event (DA*event*), while Equation 4 represents the dermally absorbed dose (DAD).

The dermal exposure RBC is calculated from Equation 7 using the COPC specific dermal absorption fraction (ABS*dermal*) and SF from Table A-3. Table A-4 presents the adult and child input parameters. When solving for the dermal RBC, *Risk* was set to 10^{-6} .

Equation 4
$$
DAD = \frac{DA_{event} \times EV \times ED_{c} \times EF_{c} \times SA_{c}}{BW_{c} \times AT} + \frac{DA_{event} \times EV \times (ED_{a} - ED_{c}) \times EF_{a} \times SA_{a}}{BW_{a} \times AT}
$$

Equation 5
$$
DA_{event} = EPC_{sed} \times CF \times AF \times ABS_{dermal}
$$

Equation 6
$$
Risk = DAD \times SF
$$

$$
Risk \times AT
$$

$$
FQuation 7
$$

Table A-3. Carcinogen Dermal Absorption Fractions and Slope Factors for COPCs

1 – Oral cancer and adjusted dermal cancer slope factors are equal.

Values in Table A-4 represent the reasonable maximum exposure (RME) scenario.

RBC Tissue Ingestion – Noncarcinogen

Noncarcinogen tissue ingestion hazard quotients (HQ) were calculated using Equations 8 and 9. Like the risks for carcinogens, noncarcinogen HQ are additive. The sum of the CDI values from each tissue type divided by the reference dose (RfD) equals the hazard quotient.

Equation 10 shows the calculation of the tissue RBC values. Specific RfD for each COPC from Table A-5 were used with the child exposure input parameters from Table A-6. RBCs were calculated separately for each of the tissue types using an HQ of 1. This results in a cumulative HQ of greater than 1 for some COPCs. These cumulative HQs are discussed in Section 8.3.2 of the report.

Equation 8
$$
CDI_0
$$

$$
CDI_o = \frac{EF \times ED \times FI \times CF}{BW \times AT} \times EPC_i \times IR_i
$$

Equation 9 ࡵࡰ **RfD** Equation 10

$$
RBC_{tissue} = \frac{HQ \times BW \times AT \times R_fD}{EF \times ED \times FI \times CF \times IR}
$$

Table A-6. Input Parameters for Calculation of Child Tissue Ingestion RBC Values

BSAF/BAF Calculation

The BSAF value is the lipid normalized tissue concentration divided by the total organic carbon (TOC) normalized sediment concentration (Equation 11). A biota accumulation factor (BAF) is not normalized for lipid content or organic carbon and is simply the tissue concentration divided by the sediment concentration (Equation 12). BSAF values are calculated for lipophilic compounds, and BAF values are calculated for lipophobic compounds.

Equation 11

\n
$$
BSAF = \frac{C_{tissue}}{C_{sediment}} \times \frac{\%TOC}{\%Lipid}
$$

$$
BAF = \frac{C_{tissue}}{C_{sediment}}
$$

Equation 12

Tissue-derived sediment RBCs were estimated for each of the COPCs and tissue types from the BSAF values and the tissue RBCs and are presented in Table 5 of the report. Sediment RBCs were calculated using the following equations for BSAF and BAF values, respectively:

Equation 13
\n
$$
RBC_{sediment} = \frac{RBC_{tissue}}{BSAF} \times \frac{\%TOC}{\%Lipid}
$$
\nEquation 14
\n
$$
RBC_{sediment} = \frac{RBC_{tissue}}{BAF}
$$

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