

North Olympic Peninsula Regional Background Sediment Characterization

Port Angeles-Port Townsend, WA

Sampling and Analysis Plan

FINAL

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Sampling and Analysis Plan

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List of Acronyms

AOI area of interest

ARI Analytical Resources, Inc.

COC chain of custody

COPC chemicals of potential concern

cPAH carcinogenic polycyclic aromatic hydrocarbon

CSL contaminant screening level

DGPS differential global positioning system
Ecology Washington State Department of Ecology
EIM Environmental Information Management
EPA U.S. Environmental Protection Agency

FM Field Manager

GPM Government Project Manager
HDPE high density polyethylene
HSP Health and Safety Plan

ICP-MS inductively coupled plasma-mass spectrometry

LMCL lower method calibration limit

LCS/LCSD laboratory control sample/laboratory control sample duplicates

MLLW mean lower low water

MS/MSD matrix spike/matrix spike duplicate

MTCA Model Toxics Control Act NAD83 1983 North American Datum

NOAA National Oceanic and Atmospheric Association

PAH polycyclic aromatic hydrocarbon

PCB polychlorinated biphenyl
PPE personal protective clothing
PQL practical quantitation limit

PSAMP Puget Sound Ambient Monitoring Program

PSEP Puget Sound Estuary Program

QA Quality Assurance QC Quality Control

RI/FS Remedial Investigation/Feasibility Study

RPD relative percent difference

RRQRR Reverse Randomized Quadrant-Recursive Raster

R/V Research Vessel

SAP Sampling and Analysis Plan

SIM select ion monitoring

SMARM Sediment Management Annual Review Meetings

SMS Sediment Management Standards

SQS Sediment Quality Standard

TCDD 2,3,7,8-Tetrachlorodibenzodioxin

TEF toxic equivalent factor
TEQ toxic equivalent quotient
TOC total organic carbon
TVS total volatile solids
UCL upper confidence level
UTL upper tolerance limit

WAC Washington Administrative Code

WHO World Health Organization

Introduction

The scope of work described in this Sampling and Analysis Plan (SAP) is designed to aid in the establishment of regional background sediment concentrations to support implementation of the 2013 Sediment Management Standards (SMS) rule revisions. The regional background concentrations established as part of this characterization will be used for comparison with contaminated sediment sites in the North Olympic Peninsula ranging from Port Townsend in the east to Port Angeles in the west.

During the advisory group process for the SMS rule revisions, conducted from 2010 through 2011, Ecology was informed that it should be Ecology's responsibility to establish regional background sediment concentrations for the state. The purpose of this SAP is to present a data collection effort designed for establishing regional background sediment concentrations for selected bioaccumulative chemicals of concern representative of the North Olympic Peninsula (Figure 1). In the process of establishing regional background, it is recognized that some of the data to be collected will be representative of natural background. The subsequent data evaluation will attempt to discern the difference between natural and regional background sediment concentrations. Port Angeles Harbor is one of several embayments currently identified for focused sediment investigation, cleanup, and source control under the Washington State Department of Ecology (Ecology) Toxics Cleanup Program's Puget Sound Initiative. As a result, this SAP includes a discussion regarding Port Angeles Harbor as it is the first embayment in the North Olympic Peninsula region where these regional background concentrations will be applied.

Background

For a number of bioaccumulative chemicals, risk-based cleanup levels based on protecting human health fall below natural background, as defined in WAC 173-204-505. Sediments are a sink for typically hundreds of contamination sources, including a mix of permitted and unpermitted stormwater, atmospheric deposition, and historical releases from industrial activities. In urban embayments with developed shorelines, sediment concentrations are frequently higher than natural background. Consequently, an entire embayment could be considered a cleanup site for exceeding natural background concentrations due to numerous sources and potentially liable parties.

The previous SMS rule included numeric criteria for the protection of benthic invertebrates from the toxic effects of contaminants but did not address background concentrations nor provide detail for assessing human health risk. The 2013 SMS rule revisions retained the two-tiered structure used to establish the sediment cleanup level (SCL), but now incorporates human health risk for bioaccumulative contaminants as well as MTCA natural background (as the Sediment Cleanup Objective) and a new term and concept, regional background (as the Cleanup Screening

Level). Table 1 presents the two-tiered structure of the 2013 SMS rule revision. Under the new rule, the determination of a regional background concentration is a critical part of providing some flexibility in determining the SCL. If a regional background concentration cannot be obtained, or is equal to natural background, than the SCL will defer to the higher of the PQL or natural background.

The SMS rule revisions provided a definition for regional background (WAC 173-204-505 (16); Ecology 2013) and parameters to establish regional background (WAC 173-204-560(5)):

"Regional Background" means the concentration of a contaminant within a departmentdefined geographic area that is primarily attributable to diffuse sources, such as atmospheric deposition or storm water, not attributable to a specific source or release.

However, the SMS revisions are intended to provide flexibility to establish regional background on a case by case basis and do not prescribe specifically how regional background shall be established. In particular, there is no guidance for how to differentiate regional background concentrations from either natural background sediments or sediment contaminated from point sources. This will be an exploratory process, particularly where limited regional information is available. The reporting of the data evaluation process will be detailed and transparent, clearly describing what decisions are made regarding data, why those decisions are made, and how they affect the resulting background statistics.

The requirements for establishing regional background include several key items that are particular relevant for the establishment of Regional Background sediment concentrations for the North Olympic Peninsula:

WAC 173-204-560 (5)(c): The department expects that regional background will usually be greater than natural background. If the department determines, based on sampling data, that regional background is not greater than natural background, the department will establish regional background at natural background.

WAC 173-204-560 (5)(d): Calculation of Regional Background for a contaminant must excludes samples from areas with an elevated level of contamination due to the direct impact of known or suspected contaminant sources, including areas within a sediment cleanup unit or depositional zone of discharge.

WAC 173-204-560 (5)(f): If a water body is not beyond the direct influence of a significant contaminant source, the department may use alternative geographic approaches to determine regional background for a contaminant. Several factors must be evaluated when determining an alternate geographic approach including:

- (i) Proximity of sampling to the site;
- (ii) Similar geologic origins as the site sediment
- (iii) Similar fate and transport and biological activities as the site; and
- (iv) Chemical similarity with the site.

The approach and methods contained in this SAP serve as an example of how regional background concentrations for selected bioaccumulative hazardous substances (arsenic, cadmium, mercury, carcinogenic polycyclic aromatic hydrocarbons [cPAHs], dioxins/furans, and polychlorinated biphenyls [PCBs]) can be established in a particular Ecology-defined geographic area. This SAP describes how the selected geographic area representative of regional background was created to avoid known point sources, and also provides potential statistical methods that can be used to differentiate regional and natural background concentrations from within this area.

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

Cleanup Screening Level (CSL) is highest of:

- 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 by Ecology by adjusting upwards from the SCO based on technical possibility and net adverse environmental impacts.

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

Port Angeles Harbor

As mentioned, Port Angeles Harbor is the first embayment where the new North Olympic Peninsula regional background sediment concentrations will be applied, making its site history particularly relevant. The North Olympic Peninsula regional background sediment concentrations resulting from this characterization are intended to be applicable to other marine embayments. Port Angeles Harbor is located along the northern coast of Washington's Olympic Peninsula on the Strait of Juan de Fuca (Figure 1). Port Angeles contains 26 miles of marine shoreline and is considered a deepwater port with depths exceeding 90 feet near the eastern end. A defining feature of the harbor is the 2.5-mile-long Ediz Hook that extends to the east from the harbor's west end. The Ediz Hook protects the harbor from Pacific Ocean storms and offers sheltered moorage for commercial ships, fishing vessels, and pleasure boats. In addition, the city of Port Angeles has maintained 11 combined sewer overflows (CSOs) that at one time discharged into the harbor. Of these 11 CSOs, 7 have been removed from service. The city is working to eliminate the remaining CSO discharges by directing the flow to the city's

wastewater treatment plant. This will largely eliminate the potential for recontamination from the CSOs.

For the past 100 years Port Angeles Harbor has been home to a number of industries including saw mills, plywood manufacturing, pulp and paper production, marine shipping and transport, boat building, bulk fuel facilities, marinas, fish pens, and commercial fishing. The largest of these facilities was the former Rayonier Mill pulp and paper mill at the east end of the harbor.

Numerous aquatic investigations conducted in the harbor have identified areas potentially affected by industrial activity that may require remedial action. These studies found chemicals of potential concern (COPCs) exceeding the SMS Sediment Quality Standards (SQS) and the Cleanup Screening Level (CSL) in the marine sediments. As a result of these studies, the harbor was identified by the Washington State Department of Ecology (Ecology) as a priority cleanup and restoration site under the Puget Sound Initiative. Ecology's Toxic Cleanup Program is responsible for overseeing source control, cleanup, and restoration of the harbor area (Ecology 2008a).

The regional background concentrations determined from the sampling proposed in this SAP will be used in the determination of the CSL for Port Angeles Harbor (Table 1). However, no sampling locations are proposed in Port Angeles Harbor for the following reasons, ranked by importance:

- 1. Numerous sediment investigations and chemometric (chemical fingerprinting) analysis for dioxin/furan congeners have demonstrated that sediment contamination in the Harbor is from two source areas in both the eastern and western Harbor (Figure 2; Ecology 2012a, NewFields 2012, NewFields 2013a). The boundaries drawn in Figure 2 are study areas being investigated by PLPs from each source area. The combined study areas approximate the area of the harbor impacted by point sources. The PLPs for these two potential source areas are currently under agreed orders with Ecology to delineate the sites. As the combined boundaries of the study areas approximate the outer extent of contamination from known potential sources, it is not currently possible to delineate an area representative of regional background within Port Angeles Harbor without violating Ecology's definition of regional background. Therefore, an alternative geographic approach is proposed as per WAC 173-204-560 (5) (d) and (f).
- 2. The geographic area of Port Angeles Harbor that could potentially be considered regional background is too limited in spatial area for adequate characterization (Figure 2). Based on the approximate boundaries of impacted areas in Figure 2, and given the recommended distance of 500 meters between background sampling locations, it would not be possible to fit the requisite number of sampling locations within the Harbor. A minimum of 25 locations were recommended for determination of regional background. Contiguous aquatic areas immediately outside of Port Angeles Harbor (i.e., the Strait of Juan de Fuca) were not considered as potential sampling locations as they are

- geomorphologically too different for characterizing regional background sediments (WAC 173-204-560 (5) (f) (ii) & (iii)).
- 3. The portion of Port Angeles Harbor that could possibly be considered regional background at this time (outer harbor near Ediz Hook) has a coarser grain size distribution than much of the nearshore and Western Harbor locations. Sediments outside the approximated site boundaries are typically less than 50 percent fines. Grain size affects the absorption of most contaminants, to the extent that finer sediments typically have higher concentrations. Collection of samples solely from an area with coarse grain size would result in non-representative regional background sediment concentrations.
- 4. The CSOs in Port Angeles likely carried particulate material containing dioxins/furans from hog fuel boilers that had aerially deposited in upland areas into the harbor. Because these dioxins/furans were from point sources, not urban diffuse sources, this contribution should not be included as part of regional background.

The nearby embayments of Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay are proposed as an alternate geographic approach for the collection of regional background sediments for the following reasons:

- These bays are geomorphologically similar and proximal to Port Angeles Harbor, and have a wide range of grain size necessary for calculating a representative regional background (WAC 173-204-560 (5) (f) (i), (ii), & (iii)).
- Collectively, these four bays are potentially impacted by many of the same non-point sources as Port Angeles Harbor (WAC 173-204-560 (5) (f) (iv)).
- Combined, the bays represent a large enough geographical area to allow for the collection of 40 baseline samples, and compare sediment contaminant concentrations from each of the bays.

Results from this sampling effort will be evaluated separately for each bay and as a combined data set. This tiered analysis is intended to investigate whether there are any individual outliers (on a contaminant by contaminant basis) within a bay, and whether the distributions of sediment contaminant concentrations from each bay are comparable to each other, or if multivariate pattern differences exist between embayments for the major analyte groups (i.e., PCBs, cPAHs, and dioxins/furans).

It is expected that some of the results from these four bays will be representative of natural background, rather than regional background. If this is a case, results deemed natural will be used to supplement the existing natural background dataset for the selection of the SCO in Port Angeles Harbor. Results representative of regional background sediment concentrations from the four bays will likely serve as the CSL and facilitate the remedial decision-making process in Port Angeles Harbor. It should be noted that if the regional background

concentrations are not greater than natural background, then natural background (or PQL—whichever is higher) would be the CSL (WAC 173-204-560 (5) (C).

Project Scope

The purpose of this SAP is to describe the manner and methods by which data collection efforts and analyses will be performed. If necessary, the results of this sampling effort will be used in conjunction with previously collected data to aid in the determination of regional background sediment concentrations for the North Olympic Peninsula. The bioaccumulative contaminants of concern for this investigation include:

- metals (arsenic, cadmium, and mercury)
- carcinogenic polycyclic aromatic hydrocarbons (cPAHs),
- dioxins/furans congeners, and
- polychlorinated biphenyls congeners (PCBs).

The SAP for this study was prepared in accordance with the SMS requirements. Sediment sampling procedures correspond to those presented in the Sediment Sampling and Analysis Plan Appendix (Ecology 2008b). Analytical procedures and methods are also identified in the SAP in accordance with WAC 173-340-830 and WAC 173-204 (Ecology 2008b).

Project Team and Responsibilities

NewFields and associated subcontractors will implement the SAP under the direction of Ecology. The following sections describe the key roles and responsibilities of the project team.

Project Planning and Coordination

Pete Striplin of Ecology will serve as the Government Project Manager (GPM) who will oversee the overall project coordination, supply government-furnished data and services, review reports, and coordinate with contractors. Tim Hammermeister will serve as the NewFields project manager and be responsible for executing the approved SAP, overseeing the collection and analysis of field samples, and reporting analytical results.

Ecology

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NewFields

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Phone: (425) 967-5285 x101 thammermeister@newfields.com

Sample Collection

Dr. Will Hafner of NewFields will serve as field manager (FM) responsible for collecting and processing samples in accordance with the SAP, and transporting samples to the analytical laboratory for analysis. The FM will ensure accurate station positioning and reporting.

Laboratory Coordinator and QA/QC Management

Dr. Will Hafner of NewFields will serve as laboratory coordinator responsible for subcontracting state-certified laboratories, delivering samples to the analytical laboratories, and ensuring observation of established protocols for decontamination, sample preservation, holding times, chain-of-custody documentation, and laboratory reporting. Dr. Hafner will also serve as the NewFields quality assurance/quality control (QA/QC) manager providing quality assurance oversight for the laboratory programs ensuring that the laboratory analytical and QA/QC data are considered valid, and that procedures meet the required analytical quality control limits.

Health and Safety Manager

Jasper Boas will serve as the designated NewFields Health and Safety Manager. Mr. Boas is responsible for ensuring that all personnel are properly trained, fully aware of potential site hazards, conduct all work in a safe manner, wear appropriate personal protective clothing (PPE), and abide by the conditions set forth in the site-specific Health and Safety Plan (HSP).

Subcontractor Support

The NewFields project team will consist of the following subcontractors and external support to assist in the data collection activities and provide analytical laboratory services:

• Sampling Vessel (*R/V Kittiwake*)

Bio-Marine Enterprise

Charles Eaton 2717 3rd Ave. N Seattle, WA 98109 Phone: (206) 714-1055

cmeaton@msn.com

• Analytical Chemistry (metals, cPAHs, sediment conventionals)

Analytical Resources, Incorporated

Cheronne Oreiro

4611 South 134th Place

Tukwila, WA 98166

Phone: (206) 695-6214

cheronneo@arilabs.com

• Dioxin/Furan and PCB Congener Analysis

Axys Analytical Services, Ltd.

Candice Navaroli

2045 Mills Road

Sidney, BC V8L 3S8 CANADA

Phone: (250) 655-5839 cnavaroli@axys.com

• Statistical Guidance

TerraStat Consulting Group

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323 Union Avenue

Snohomish, WA 98290

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Data Validation

EcoChem

Christine Ransom

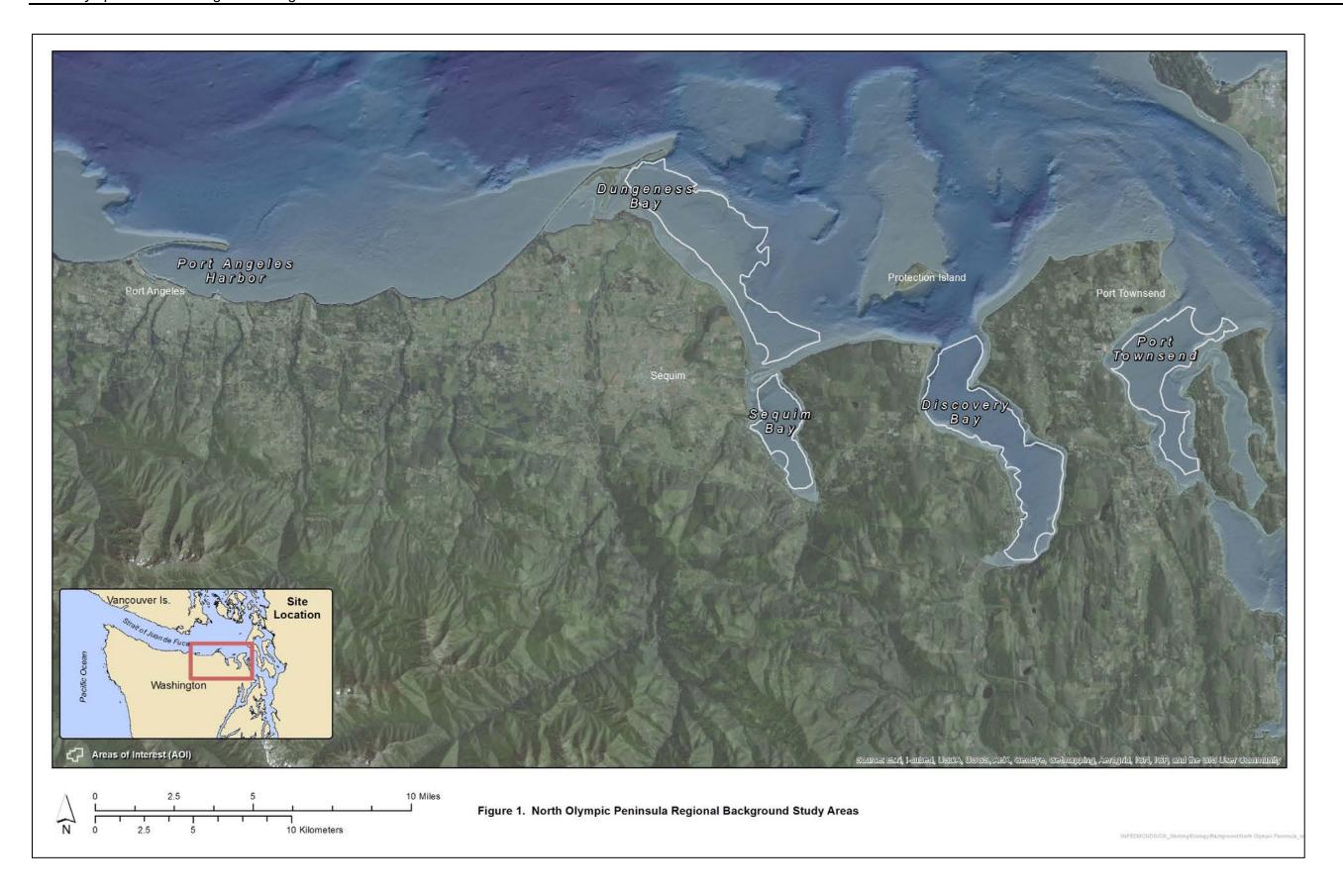
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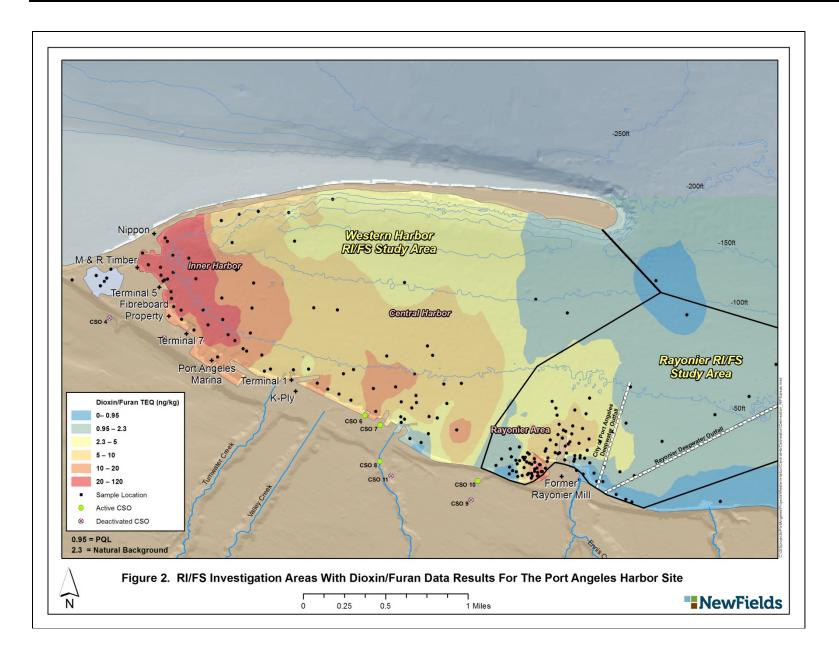
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Schedule

The proposed schedule for field activities is the seven business days between May 6 and May 14, 2013.





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Study Design

This section describes the study design for the data collection effort for the North Olympic Peninsula regional background characterization. Several key study objectives were taken into consideration in the development of the study design:

- Define an area representative of regional background conditions.
- Produce a baseline dataset with temporal consistency.
- Determine the minimum number of baseline samples needed to calculate regional background.
- Define the minimum distance between sampling locations to ensure independent results.
- Assess the quality and usability of existing data for supplementing the baseline dataset.
- Randomly select sediment sampling locations to meet collective study objectives.

The following sections discuss the development and the details of the study design.

Determination of Area Representative of Regional Background

As mentioned above, the entirety of Port Angeles Harbor is currently under evaluation for potentially impacted sediments, so no samples will be collected within the Harbor for calculation of regional background. Nearby embayments and coastal features with similar geomorphology and land use types were selected as representative of regional background for the North Olympic Peninsula, including portions of Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay. The combination of these bays encompass similar geomorphologic, depositional, and water circulation patterns to what is observed in Port Angeles Harbor. Given the potential importance of nonpoint runoff in influencing regional background sediment concentrations, land use types were also considered for determining bays that could be representative of the North Olympic Peninsula.

Land cover type from the National Oceanographic Atmospheric Administration's Coastal Services Center (NOAA 2008) was used to compare Port Angeles Harbor alongside the four proposed for regional background sediment sampling (Figure 3). The area is primarily characterized by forest, developed areas, pasture, cultivated grassland, scrub, and wetland areas. To simplify the analysis a combined set of land cover types were used to compare each embayment's associated watershed (Figure 4). Combined land cover types included high, medium, and low intensity development; cultivated and pasture; forest types; and all wetland types > than 1 percent cover. In addition, the land cover summary for the Lower Dungeness

River, Sequim Bay, Discovery Bay, and Port Townsend Bay drainage areas was combined for comparison to the Port Angeles Harbor.

The drainage areas are primarily characterized by forest ranging from 44 percent of the drainage area for Dungeness Bay to over 70 percent of the drainage area for Discovery Bay. Dungeness Bay also has significant percentages of both pasture-cultivated (21percent) and developed areas (16 percent). Port Angeles Harbor has a highest percentage of developed area (21%) and Discovery Bay has the lowest percentage (2%). Developed area for Port Townsend is 10 percent. In additional to forest (60 percent), the Combined Regional Background Embayments has significant contributions of pasture-cultivated (10 percent) and scrub (11 percent). While none of the four bays contain the same percentage of developed land as Port Angeles, they were the closest match available in the mostly rural northern Olympic Peninsula (Figure 4).

Freshwater Bay to the west of Port Angeles Harbor was also considered as a candidate regional background area, but was excluded because of dissimilar geomorphology and its direct exposure to the currents of the Strait of Juan de Fuca.

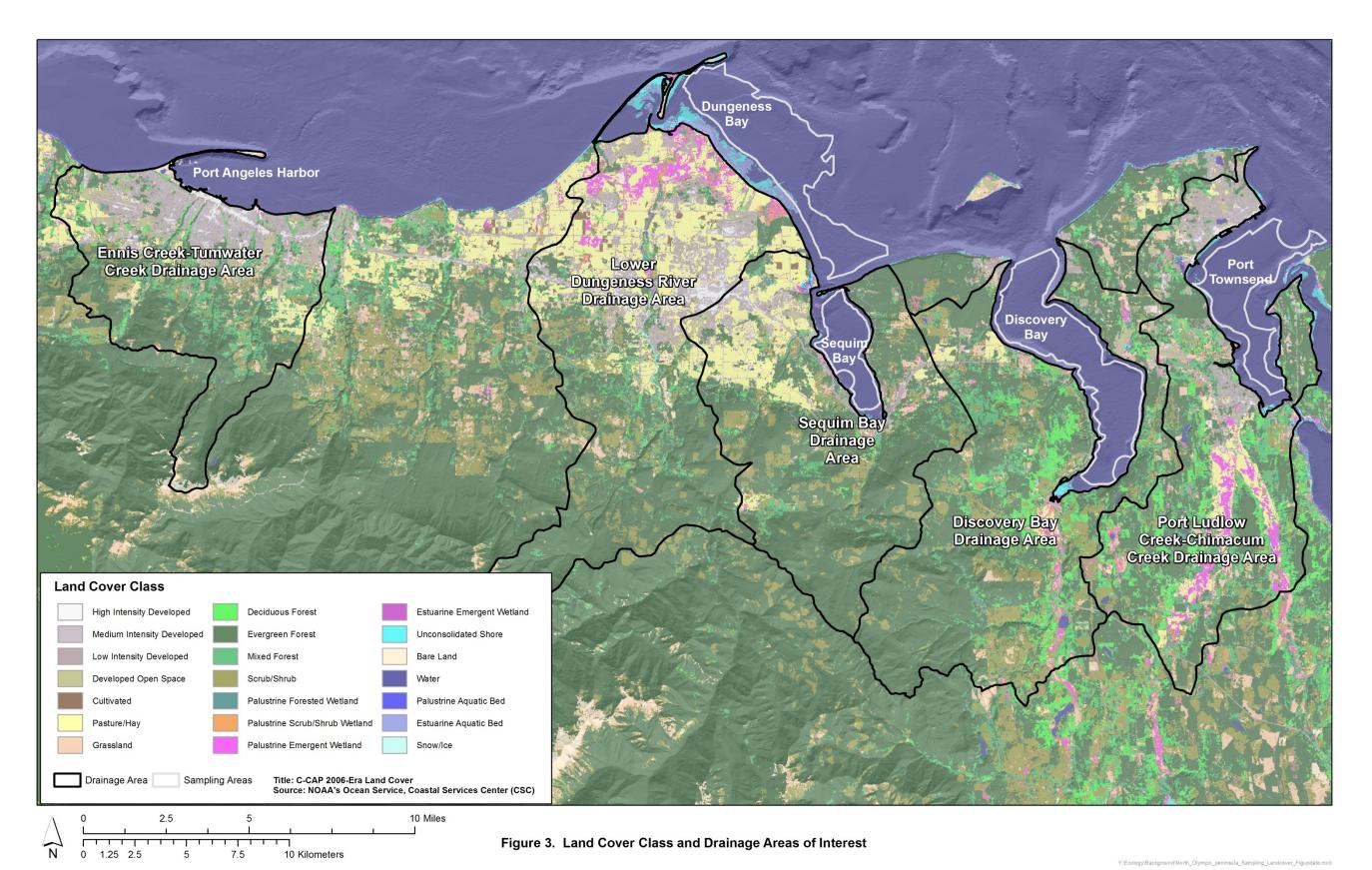
Once the target bays were selected, Environmental Systems Research Institute's Geographic Information System ArcGIS was used to allow for the study design to be viewed and developed in context of various geographic layers. Area of interest (AOI) polygons within Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay were determined to encompass a range of conditions bounded by known or suspected source areas, and transitioning through regional background to natural background areas (Figure 1).

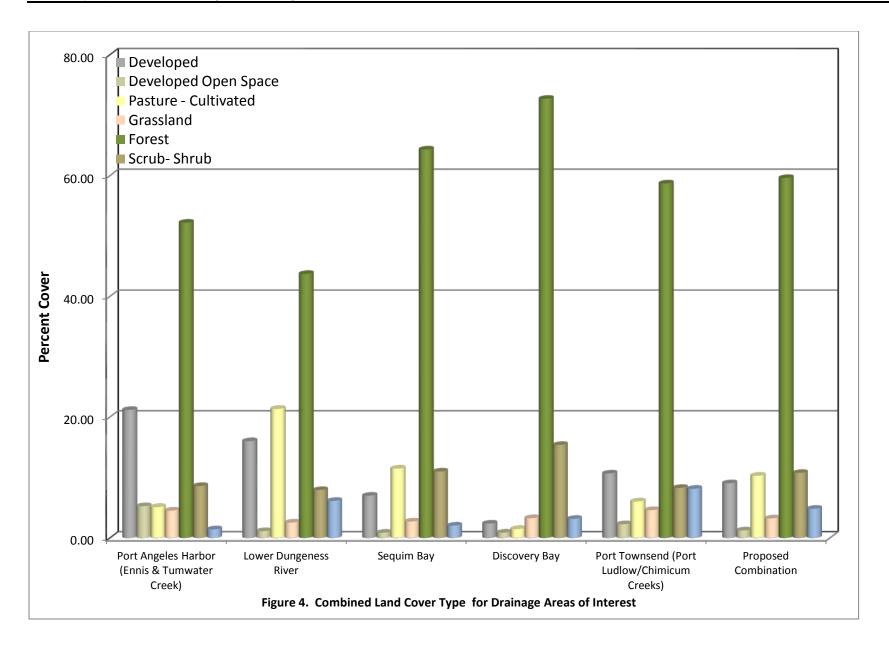
The AOI defines the extent of the bays where proposed sampling locations for this investigation could be placed. The AOI was defined as a marine environment that excluded areas near potential sources (i.e. active or historical outfalls), developed shoreline, marinas, fish pens, shallow areas above -6ft MLLW as well as areas that could be more representative of natural background sediments (as defined in WAC 173-340-200 and proposed in WAC 173-204-505) such as those near the Strait of Juan de Fuca. It should be noted, that due to the lower developed land use in the North Olympic Peninsula relative to more urban embayments, such as Elliott Bay or Bellingham Bay, the regional sediment background concentrations may not differ much, if at all, from natural background sediment concentrations. The specific criteria for defining the AOI in each targeted bay were:

- In Dungeness Bay, a 500 meter (m) distance was used to buffer the AOI from a known outfall (potential point source) and to avoid the shallow region along the western boundary where large kelp beds were observed. The AOI bounds the shelf on the eastern boundary at approximately -120 feet avoiding the steepest bathymetric slope in this area.
- In Sequim Bay, a 500m buffer was used around potential point sources including the outfall and the marina. The steepest bathymetric slope along the shoreline and the shallow region (less than -6 ft MLLW) in the southern bay were avoided. The southern boundary was drawn seaward of steepest slope.

- In Discovery Bay, the northern boundary was drawn to avoid the cable area crossing at the mouth of the bay. A 500m buffer was used around the fish pens at the southern end of the bay. The AOI was defined avoiding the steepest bathymetric slope along the shoreline.
- In Port Townsend Bay, the northern boundary was drawn from Port Townsend to Marrowstone Island. A 500m buffer was drawn around the restricted anchorage on the northern boundary. A 500m buffer was applied to the developed shoreline of Port Townsend, including the pulp mill outfall. A 500m buffer was drawn around the more developed southwestern shore of the bay that includes the Irondale cleanup site. A 500 meter buffer was also applied to the restricted area surrounding the Indian Island Naval Facility. The City of Port Townsend outfall is not part of the AOI, as it discharges into the Strait of Juan de Fuca.

Based on previous analysis conducted during the creation of regional background sampling and analysis plans for Bellingham Bay and Port Gardner Bay (Appendix D), a distance of 500m was used as the independent interval between potential sampling locations. This spacing was sufficient to achieve an independent dataset, yet small enough to allow for a large number of samples to be located within the study AOI.





Sample Number and Density

The regional background data set will be used to characterize the concentration distributions of target analytes within the four embayments encompassing the AOI. The North Olympic Peninsula regional background AOI is more complex than other contiguous areas used for developing regional sediment background concentrations (i.e., Bellingham Bay or Port Gardner Bay). Consequently, a larger sample size was needed to adequately characterize the entire AOI and a stratified sampling approach was used to account for possible differences between the four embayments.

In a traditional stratified design, the distribution of samples would be allocated based on standard deviation of the existing data, with more samples in the stratum with more variability. The historical data from Ecology's EIM database was evaluated for each of the four bays. Samples within each bay's AOI were considered usable if they met the criteria outlined in the bullet points of Appendix A. Existing site data are presented in Figure 5.

Due to the small amount of existing data, it was difficult to compare variability between bays. In Dungeness Bay, dioxin/furan and PCB congener data was limited to four and five locations, respectively. As a result, no comparisons could be made for these contaminants. With one exception, existing data for cPAH and metals were only available from samples collected as part of PSAMP. One PSAMP sample was located in the Dungeness Bay AOI, while at least four samples were located in the other three bays (Figure 5). PSAMP protocols differ from other Ecology sampling procedures in that they involve sampling the top 0 to 2 cm of sediment, rather than the top 0 to 10 (i.e. biologically active zone) as prescribed in this SAP. Therefore, the concentration ranges measured in the PSAMP data may not be representative of the biologically active zone as required by WAC 173-204-560 (5) (6) as the point of compliance.

The ratios of the standard deviations between Discovery, Sequim, and Port Townsend Bays varied depending on the chemical constituent. These differences in variance, the lack of dioxin/furan and PCB congener data in three of the bays, and the shallow depth interval used with the PSAMP data made it difficult to draw any conclusions from the existing data that would be relevant to the current study design. Rather than employing a traditional stratified approach based on variance, the distribution of sampling locations selected for this SAP were spatially stratified based on the relative areas of each embayment's AOI.

An initial sample size of 40 was considered sufficient to provide an indication of the shape of the concentration distributions for each bay, and preliminary estimates for the mean and variance of each analyte. The relative area of each bay to the total area is 11 percent for Sequim Bay, 21 percent for Port Townsend Bay, 33 percent for Discovery Bay, and 35 percent for Dungeness Bay. The baseline sampling locations were distributed between the bays in rough approximation

to their relative size as follows: 5 locations in Sequim Bay, 10 locations in Port Townsend Bay, 12 locations in Discovery Bay, and 13 locations in Dungeness Bay.

In addition to the 40 baseline locations, 25 random secondary sampling locations will be sampled during this investigation to archive sufficient sediment for further analysis as needed. Due to the short holding times, all 25 of the secondary samples will be submitted for mercury and total sulfides analysis. All secondary samples will also be submitted for the analysis of grain size to better characterize percent fines in each of the bays. Following the same stratified spatial design resulted in the placement of 3, 8, 9, and 5 secondary sample locations in Sequim Bay, Discovery Bay, Dungeness Bay, and Port Townsend Bay, respectively.

Following the initial data analysis, the baseline dataset may be supplemented with existing data from Sequim, Discovery, Dungeness and Port Townsend Bays to determine data sufficiency. Data sufficiency will be determined based on the precision of the mean for this combined data set. A target for these data is to achieve a 95 UCL on the mean that is within 25% of the stratified mean.

The initial 40 samples analyzed from the four embayments will be combined with any existing data deemed acceptable. From this combined data set, the regional background mean (i.e., 95 UCL on the mean) will be estimated from the distribution after excluding any outlier(s), utilizing the most appropriate parametric or non-parametric methods. Graphs depicting the relationship between the 95 UCL on the mean and sample size will be constructed for each analyte. From these graphs, the optimal sample size to achieve the desired precision in the mean will be estimated. For any analyte where the desired precision of the mean has not been met, additional samples may be randomly selected from the set of archived samples for analysis. Additional analyses will only be performed where they are deemed to be most appropriate for reducing uncertainty in the dataset.

The minimum spacing of 500m between samples for an independent data set was used as the default distance based on results from other regional background areas in Puget Sound (Appendix D). Once the boundaries for the AOI and the minimum spacing between samples were defined, a spatially-balanced random sampling design was developed using a Reverse Randomized Quadrant-Recursive Raster (RRQRR) algorithm (Theobald et al, 2007). This method requires the use of a probability raster grid specifying the probability (0 to 1) that a given raster cell will be selected relative to other cells. To account for the minimum sampling interval, a site sampling grid with a 500m resolution inclusion probability raster was created from the AOI polygon. This raster effectively acts as a uniformly spaced sampling grid ensuring the minimum distance between any two randomly placed sampling locations is at least 500 meters. For this case, all cells were assigned a value of 1, which allows for an equal probability of an individual cell being selected. This allowed for the spatial distribution of proposed sampling locations to be placed throughout the AOI while maintaining sample independence.

Through this spatially balanced selection process, the 40 baseline sample locations were randomly placed within the AOI, without regard for existing data as to better maintain a completely random distribution for a baseline of data. To preserve spatial independence, the sample placement for the 5, 12, 13, and 10 samples for each respective bay were determined separately. If any of the 40 baseline locations were within 500m of a location with existing data (Figure 5), the new sample results will take precedence (Figure 6).

The 25 secondary locations were added separately and randomly placed by the same method described above. To maximize sample size and spatial coverage a 500m buffer was maintained between the 40 baseline sample locations (Figure 7). This allows for the use of secondary locations to be used for further analysis, as needed, to supplement the combined baseline and existing dataset. In cases where existing data for a given analyte are within 500m of a selected secondary location, the existing data may be used and the next randomly selected secondary location will be submitted for analysis.

Summary of Existing Data

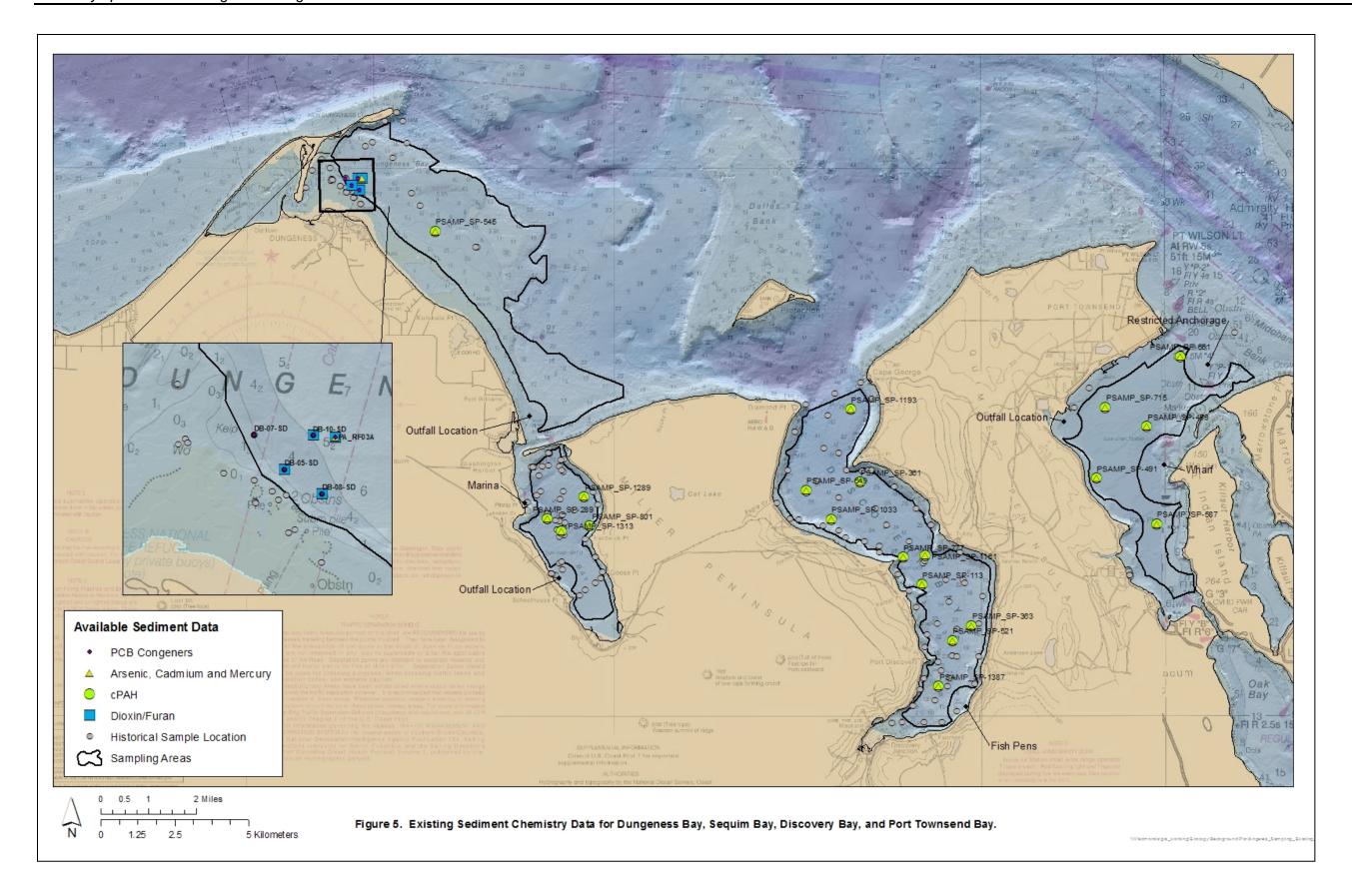
The chemistry results from three previous studies were reviewed and determined to have existing data that may be usable, in part, to supplement the regional background data set. The description of the data screening process and the existing data results are provided in Appendix A. The locations of the existing data results are provided in Figure 5. A brief description of each study, including the study name and Study_ID as identified in EIM, are provided herein.

The Puget Sound Assessment and Monitoring Program's Spatial/Temporal Monitoring 2002-Present (EIM Study_ID: PSAMP_SP) – The objectives of the Puget Sound Ambient Monitoring Program (PSAMP) spatial and temporal monitoring were similar in scope to the long term monitoring. Chiefly, the goals of this monitoring that were relevant to the current background study were to determine the incidence and severity of toxicity and chemical contamination of sediments, identify spatial patterns, and estimate the spatial extent of contamination. All data were validated at EPA Level 4.

Port Angeles Harbor Sediment Characterization Study Port Angeles, Washington (EIM Study_ID: PASED08) – Sampling efforts for this sediment characterization included the collection of surface sediment, subsurface cores, and tissue samples from Port Angeles Harbor. The only samples that could be used as existing data for the determination of regional background were three surface sediment reference samples collected from Dungeness Bay (E&E 2012).

Phase 2 Addendum Remedial Investigation for the Marine Environment near the Former Rayonier Mill Site (EIM Study_ID: PAMILLRI) – This report is an addendum to the Marine Remedial Investigation report that was issued in April 2005. The samples collected as a part Phase 2 were intended to further characterize PCB and dioxin/furan congener concentrations in

surface sediment in Port Angeles Harbor, Freshwater Bay, and Dungeness Bay (Malcolm Pirnie 2007b). Only samples from Dungeness Bay are included as existing data for this SAP.



Sediment Sampling Locations

A total of 65 sediment sampling locations, including 40 baseline locations and 25 secondary locations will be occupied sequentially as part of this investigation (Tables 2 and 3).

Baseline Sediment Sample Locations

The purpose of baseline sediment sample locations is to provide a minimum number of randomly placed sampling locations, at least 500 m apart, and to provide reasonable spatial coverage for an area pre-determined to be representative of regional background conditions. The following data collection activities have been identified and are summarized in Table 2:

- Collect 40 surface sediment (0-10 cm) grab samples using a spatially-balanced random design placed within the perimeter of an area designated as representing regional background conditions. The 40 sample locations include 13 in Dungeness Bay, 12 in Discovery Bay, 10 in Port Townsend Bay, and 5 in Sequim Bay.
- Submit sediment samples for analysis of the following bioaccumulative contaminants:
 - o Metals (arsenic, cadmium, and mercury)
 - o Dioxin/furan congeners
 - o PCB congeners
 - o cPAHs
- Submit sediment samples for analysis of sediment conventionals (grain size distribution, total solids, total volatile solids, total sulfides, and total organic carbon).
- Archive sediment from each location for additional analysis or re-analysis as needed.

The proposed baseline sediment sample locations are presented in Figure 6. Target coordinates are provided in Table 4.

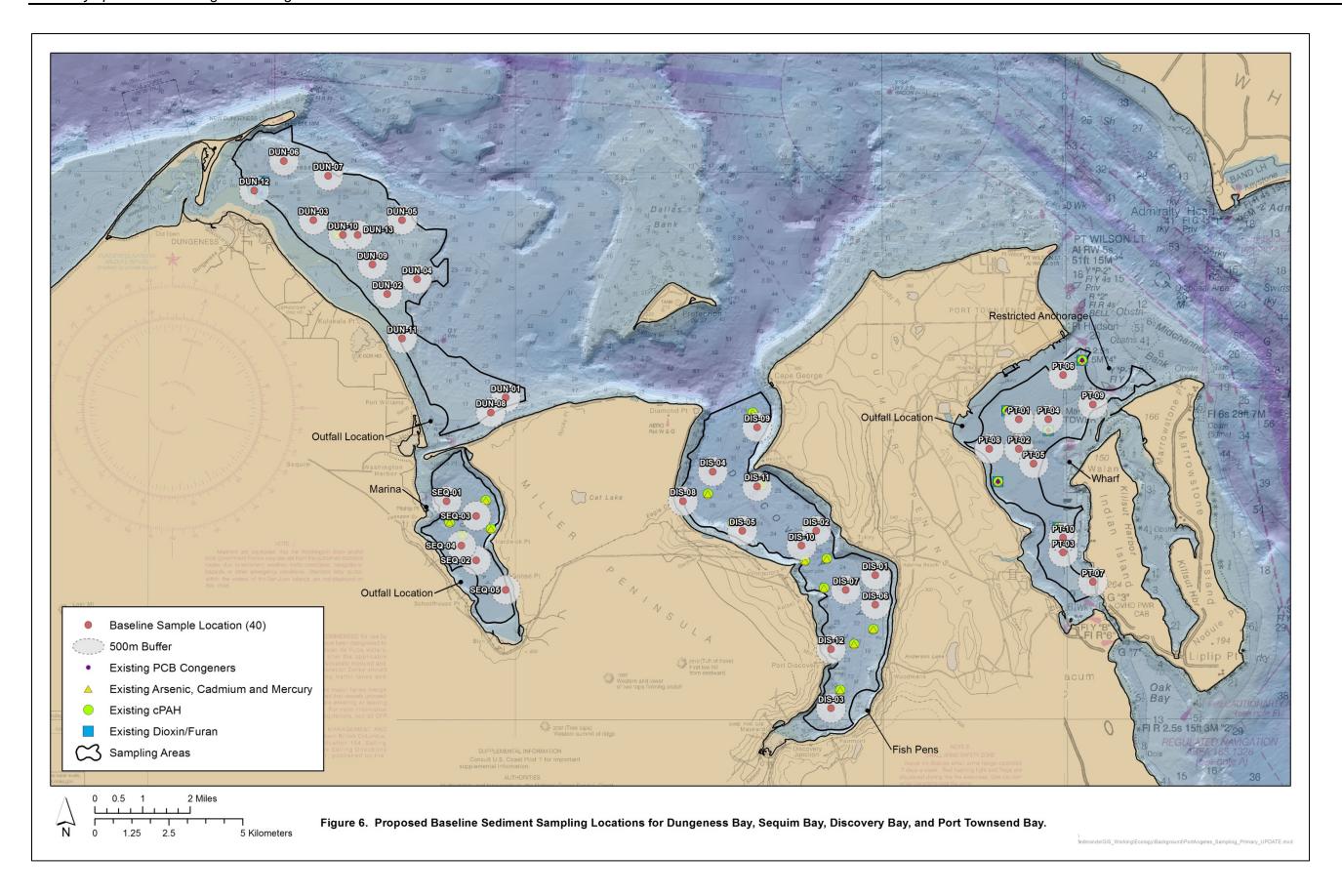
Table 2. Baseline Sediment Sample Locations and Analyses

Sampling	Sediment	2		Dioxin/Furan	Furan PCB 3		
Location	Conventionals ¹	Metals ²	cPAH	Congeners	Congeners	Archive ³	
Sequim Bay				Congeners	Congeners		
SEQ-01	X	X	X	X	X	A	
SEQ-01	X	X	X	X	X	A	
SEQ-02 SEQ-03	X	X	X	X	X	A	
SEQ-03 SEQ-04	X	X	X	X	X	A	
SEQ-04 SEQ-05	X	X	X	X	X	A	
		Λ	Λ	Λ	Λ	A	
Discovery B DIS-01	X	X	X	X	X	Ι Δ	
DIS-01 DIS-02	X	X	X	X	X	A	
	X	X	X	X	X	A	
DIS-03						A	
DIS-04	X	X	X	X	X	A	
DIS-05	X	X	X	X	X	A	
DIS-06	X	X	X	X	X	A	
DIS-07	X	X	X	X	X	A	
DIS-08	X	X	X	X	X	A	
DIS-09	X	X	X	X	X	A	
DIS-10	X	X	X	X	X	A	
DIS-11	X	X	X	X	X	A	
DIS-12	X	X	X	X	X	A	
Dungeness 1							
DUN-01	X	X	X	X	X	A	
DUN-02	X	X	X	X	X	A	
DUN-03	X	X	X	X	X	A	
DUN-04	X	X	X	X	X	A	
DUN-05	X	X	X	X	X	A	
DUN-06	X	X	X	X	X	A	
DUN-07	X	X	X	X	X	A	
DUN-08	X	X	X	X	X	A	
DUN-09	X	X	X	X	X	A	
DUN-10	X	X	X	X	X	A	
DUN-11	X	X	X	X	X	A	
DUN-12	X	X	X	X	X	A	
DUN-13	X	X	X	X	X	A	
Port Towns	end Bav					L	
PT-01	X	X	X	X	X	A	
PT-02	X	X	X	X	X	A	
PT-03	X	X	X	X	X	A	
PT-04	X	X	X	X	X	A	
PT-05	X	X	X	X	X	A	
PT-06	X	X	X	X	X	A	
PT-07	X	X	X	X	X	A	
PT-08	X	X	X	X	X	A	
PT-09	X	X	X	X	X	A	
PT-109	X	X	X	X	X	A	
	A arcinogenic polycyclic a						

Notes: cPAH-carcinogenic polycyclic aromatic hydrocarbons SMS-Washington State Sediment Management Standards PCB-polychlorinated biphenyls

 $\boldsymbol{X}-submitted \ for \ analysis \qquad \boldsymbol{A}\text{-archived sediment}$

1-sediment conventionals include total organic carbon (TOC), total volatile solids (TVS), total solids, total sulfides, and grain size distribution 2-metals include arsenic, cadmium, and mercury 3-sediment archived for potential analysis or reanalysis



Secondary Sediment Sample Locations

The purpose of the secondary sediment sample locations is to archive additional samples from randomly placed sampling locations that meet the minimum of 500m apart from the nearest baseline location, and provide probability-based spatial balance for an area pre-determined to be representative of regional background conditions. These archived samples would then be available, as needed, for chemical analysis to ensure a sufficient number of usable data are available for calculation of regional background concentrations. If a randomly selected secondary location is within 500m of an existing data location for the needed analyte, then the next randomly selected archived sample not within 500m of an existing data location would be analyzed for that analyte. The following data collection activities have been identified and are summarized in Table 3:

The secondary sediment data collection activities include:

- Collect 25 surface sediment (0-10 cm) grab samples using a spatially-balanced random design placed within the perimeter of the area designated as representing regional background conditions. The 25 sampling locations for archival include 9 from Dungeness Bay, 8 from Discovery Bay, 5 from Port Townsend Bay, and 3 from Sequim Bay.
 - o Analyze all 25 samples for mercury due to short holding time.
 - o Analyze all 25 samples for sulfides due to the short holding time.
 - Archive sediment for all other analyses.

The proposed secondary sediment sample locations are presented in Figure 7. Target coordinates are provided in Table 5.

Table 3. Secondary Sediment Sample Locations and Analyses.

Sampling	Sediment	23		Dioxin/Furan	PCB		
Location	Conventionals ¹	Metals ^{2,3}	сРАН	Congeners	Congeners	Archive ⁴	
Sequim Bay							
SEQ-06	X^5	X^3	A	A	A	A	
SEQ-07	X^5	X^3	A	A	A	A	
SEQ-08	X^5	X^3	A	A	A	A	
Discovery B	Bay						
DIS-13	X^5	X^3	A	A	A	A	
DIS-14	X^5	X^3	A	A	A	A	
DIS-15	X^5	X^3	A	A	A	A	
DIS-16	X^5	X^3	A	A	A	A	
DIS-17	X^5	X^3	A	A	A	A	
DIS-18	X^5	X^3	A	A	A	A	
DIS-19	X^5	X^3	A	A	A	A	
DIS-20	X^5	X^3	A	A	A	A	
Dungeness 1							
DUN-14	X^5	X^3	A	A	A	A	
DUN-15	X^5	X^3	A	A	A	A	
DUN-16	X^5	X^3	A	A	A	A	
DUN-17	X^5	X^3	A	A	A	A	
DUN-18	X^5	X^3	A	A	A	A	
DUN-19	X^5	X^3	A	A	A	A	
DUN-20	X^5	X^3	A	A	A	A	
DUN-21	X^5	X^3	A	A	A	A	
DUN-22	X^5	X^3	A	A	A	A	
Port Townsend Bay							
PT-11	X^5	X^3	A	A	A	A	
PT-12	X^5	X^3	A	A	A	A	
PT-13	X^5	X^3	A	A	A	A	
PT-14	X^5	X^3	A	A	A	A	
PT-15	X^5	X^3	A	A	A	A	
Notes:							

Notes:

cPAH-carcinogenic polycyclic aromatic hydrocarbons

SMS-Washington State Sediment Management Standards

PCB-polychlorinated biphenyls

X- submitted for analysis A-archive sediments

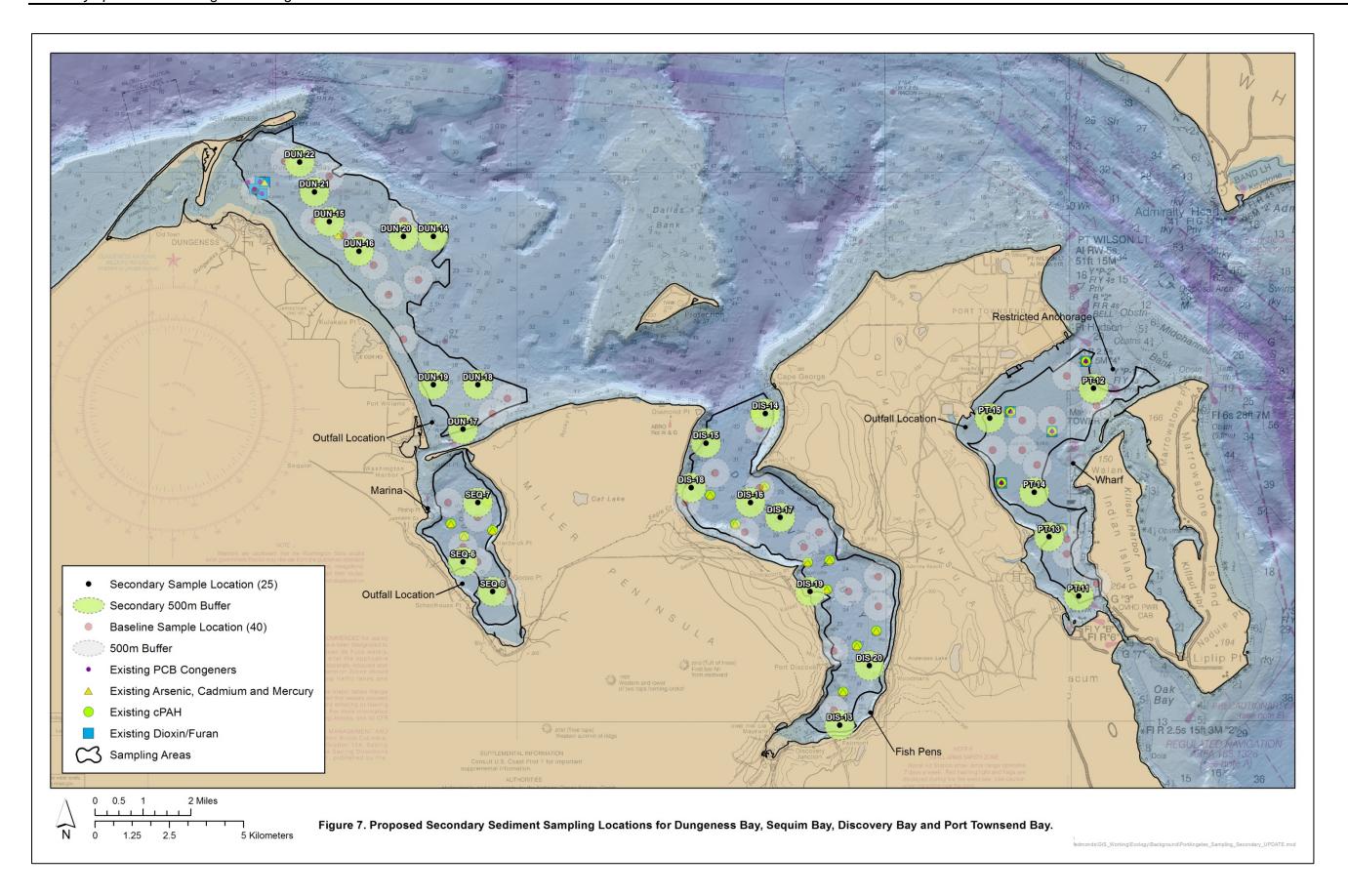
1-sediment conventionals include total organic carbon (TOC), total volatile solids (TVS), total solids, and grain size distribution

2-metals include arsenic, cadmium, and mercury

3-only mercury to be analyzed, remaining sediment will be archived

4-sediment archived for potential analysis or reanalysis

5-only grain size and total sulfides to be analyzed, remaining sediment jars will be archived



Sample Collection and Handling Methods

This section describes the methodology for positioning, sample collection, processing, identification, documentation, equipment decontamination, and waste handling for the proposed field investigation. The following section presents the laboratory methods for chemical analysis.

Sampling Platforms

The R/V *Kittiwake*, owned and operated by Mr. Charles Eaton of Bio-Marine Enterprises will be used for the surface sediment grabs in Discovery Bay, Dungeness Bay, and Sequim Bay.

Station Positioning and Navigation

NewFields will ensure that vessel navigation provides accurate station positioning, and that sample locations and water depths are recorded. A differential global positioning system (DGPS) will be used aboard the R/V *Kittiwake* for station positioning. A U.S. Coast Guard differential correction signal will be utilized to obtain a minimum accuracy of \pm 3 meters. The DGPS receiver will be placed above the block on the sampling device deployment boom to accurately record the position of the sampling device.

Sampling location target coordinates will be provided in advance and programmed into the R/V *Kittiwake*'s navigation system. Upon sampling device deployment, the actual position will be recorded once the device reaches the seafloor and the deployment cable is in a vertical position. Latitude and longitude station coordinates will be recorded in degrees decimal minutes using the 1983 North American Datum (NAD83). Water depths will be measured using the winch meter wheel and verified by the ship's fathometer. In the event a successful grab cannot be obtained at the target location, additional attempts will be made within a 50-m radius of the target location. If a proposed target location cannot be sampled due to unforeseen conditions (i.e., shoaling, rocky substrate, etc.), a new location that meets the same criteria as the baseline locations will be occupied. Tables 4 and 5 provide the target coordinates for the baseline and secondary sample locations, respectively.

Table 4. Target Coordinates for Baseline Sampling Locations.

	Easting	Northing	Latitude	Longitude
Station ID	(SPN NAD83)	(SPN NAD83)	(NAD83)	(NAD83)
Sequim Bay				
SEQ-01	1103084.88	396706.84	-123.031268	48.066516
SEQ-02	1106180.75	390053.14	-123.017839	48.048524
SEQ-03	1106319.34	394974.13	-123.017844	48.062020
SEQ-04	1104586.62	391739.66	-123.024550	48.053022
SEQ-05	1109369.02	386680.09	-123.004420	48.039529
Discovery B	ay			
DIS-01	1150423.43	387165.60	-122.836708	48.043911
DIS-02	1144000.69	392271.35	-122.863506	48.057442
DIS-03	1145086.74	372541.22	-122.856945	48.003451
DIS-04	1132703.17	399156.01	-122.910447	48.075482
DIS-05	1135799.06	392502.31	-122.897057	48.057477
DIS-06	1150331.05	383884.95	-122.836736	48.034914
DIS-07	1147096.58	385617.66	-122.850138	48.039431
DIS-08	1129330.13	395967.74	-122.923885	48.066495
DIS-09	1137762.74	403938.41	-122.890280	48.088960
DIS-10	1142314.18	390677.21	-122.870228	48.052951
DIS-11	1137577.96	397377.10	-122.890318	48.070966
DIS-12	1145271.49	379102.54	-122.856895	48.021445
Dungeness E	Bay			
DUN-01	1109969.55	408004.36	-123.004425	48.098010
DUN-02	1097170.29	419856.22	-123.058185	48.129484
DUN-03	1089199.62	428288.82	-123.091823	48.151955
DUN-04	1100497.14	421404.15	-123.044750	48.133989
DUN-05	1099041.59	428011.66	-123.051488	48.151980
DUN-06	1086103.74	434942.52	-123.105305	48.169937
DUN-07	1090978.53	433163.61	-123.085123	48.165456
DUN-08	1108283.03	406410.23	-123.011140	48.093511
DUN-09	1095622.35	423183.06	-123.064916	48.138478
DUN-10	1092434.09	426556.11	-123.078371	48.147466
DUN-11	1098672.04	414889.04	-123.051452	48.115992
DUN-12	1082730.70	431754.25	-123.118734	48.160927
DUN-13	1094074.41	426509.91	-123.071649	48.147471
Port Townse	end Bay			
PT-01	1166833.84	404006.16	-122.771375	48.091214
PT-02	1166741.46	400725.51	-122.771415	48.082217
PT-03	1171339.09	389104.69	-122.751426	48.050686
PT-04	1170114.49	403913.77	-122.757946	48.091187
PT-05	1168335.59	399039.00	-122.764722	48.077705
PT-06	1171893.39	408788.55	-122.751166	48.104668
PT-07	1174527.36	385731.67	-122.738053	48.041659
PT-08	1163460.81	400817.90	-122.784842	48.082243
PT-09	1175081.64	405415.52	-122.737779	48.095641
PT-10	1171385.28	390745.01	-122.751405	48.055184
PT-09	1175081.64	405415.52	-122.737779	48.09564

Notes:

SPN NAD83: Washington State Plane North, North American Datum 1983

NAD83: North American Datum 1983

Table 5. Target Coordinates for Secondary Sampling Locations.

	Easting	Northing	Latitude	Longitude
StationID	(SPN NAD83)	(SPN NAD83)	(NAD83)	(NAD83)
Sequim Bay				
SEQ-6	1104540.42	390099.33	-123.024548	48.048523
SEQ-7	1106365.53	396614.45	-123.017845	48.066519
SEQ-8	1107728.69	386726.29	-123.011128	48.039528
Discovery B	ay			
DIS-13	1145672.15	370883.11	-122.854377	47.998949
DIS-14	1138440.53	405560.95	-122.887685	48.093456
DIS-15	1131786.84	402465.07	-122.914560	48.084482
DIS-16	1136523.05	395765.18	-122.894455	48.066472
DIS-17	1139757.51	394032.47	-122.881043	48.061960
DIS-18	1130007.93	397590.28	-122.921294	48.070992
DIS-19	1142807.21	385738.44	-122.867679	48.039452
DIS-20	1149137.57	377352.04	-122.840916	48.016926
Dungeness E	Bay			
DUN-14	1102273.10	426173.95	-123.038039	48.147199
DUN-15	1090837.00	428137.64	-123.085100	48.151672
DUN-16	1094025.26	424764.59	-123.071643	48.142684
DUN-17	1104953.22	404757.30	-123.024567	48.088722
DUN-18	1106732.13	409632.09	-123.017858	48.102219
DUN-19	1101811.15	409770.67	-123.038006	48.102214
DUN-20	1098992.44	426266.34	-123.051483	48.147194
DUN-21	1089289.06	431464.48	-123.091839	48.160664
DUN-22	1087741.11	434791.33	-123.098580	48.169655
Port Townse	end Bay			
PT-11	1172505.75	384400.26	-122.746180	48.037873
PT-12	1174792.73	407318.57	-122.739154	48.100837
PT-13	1169409.86	391053.93	-122.759511	48.055896
PT-14	1167908.10	396021.09	-122.766160	48.069405
PT-15	1163218.09	404361.28	-122.786202	48.091937

Notes:

SPN NAD83: Washington State Plane North, North American Datum 1983

NAD83: North American Datum 1983

Sediment Sample Collection

Surface sediment samples will be collected at 65 locations for the North Olympic Peninsula Regional Background Sediment Characterization. Table 6 lists the sediment samples to be collected, chemical analyses, the number and type of QA/QC samples, sample containers, sample volumes, preservation requirements, and samples to be archived.

Table 6. Sediment Sample Collection, Analysis, Containers, and Holding Times

Analyses	Grain Size	Total Solids, TOC, TVS	Total Sulfides	SIM cPAH	Dioxin/Furan &/or PCB Congeners	Metals	Mercury	Archive
Container(s)	16 oz. HDPE	8 oz. glass	2 oz. glass	8 oz. glass	8 oz. amber glass	4 oz.	glass	16 oz. glass ^{4,5} ;
Preservative	4°C	4°C/-18°C	4°C; zinc acetate	4°C/-18°C	4°C/-18°C	4°C/-18°C	-18°C	-18°C
Holding Time	6 months	14 days/ 6 months	7 days	14 days/ 1year	14 days/ 1 year	14 days/ 1year	28 days	1year
Baseline	40X	40X	40X	40X	40X	40X	40X	$40A^4$
Secondary	25X ⁵	25A	25X ⁵	25A	25A	-	25X ⁵	$25A^4$
QA/QC Samples								
Duplicates ¹	4X	3X	4X	3X	3X	3X	4X	-
Triplicates ^{1,2}	4X	3X	4X	-	-	-	-	-
Equipment Rinsate ³	-	-	-	3X	-	3X	4X	-
CRM	-	-	-	-	1X	-	-	-
Rinsate Blank ³	-	-	-	X	-	X	X	-
Rinsate Totals	-	-	-	4	-	4	5	-
Sample Totals	73	71	73	68	68	6	9	65

Notes

X: sample to be collected and submitted for analysis/testing;

 ${f A}$: sample to be archived -: no sample will be collected at this location;

HDPE: high density polyethylene

- **1.** Frequency of analysis is one per 20 samples (5%).
- 2. Triplicate analysis for sediment conventional parameters only.
- ${\bf 3.}$ Equipment rinsate and rinsate blanks conducted for organics and metals only.
- **4.** One 16-oz glass jar to be collected for archive at all sampling locations.
- 5. Grain size, total sulfides and mercury will be analyzed from the secondary samples. Remaining sediment will be archived.

Surface Sediment Grabs

Surface sediment grabs will be collected for chemical analysis from the R/V *Kittiwake* using a stainless steel 0.2 m² dual van Veen (0.1m² per bucket) or similar sampling device.

Established deployment and recovery procedures for the grab sampling gear, described in PSEP, will be followed to ensure recovery of the best possible samples and minimize risks to personnel and equipment (PSEP 1997a). Once a grab sample is retrieved, the overlying water will be carefully siphoned off one side of the sampler. If the sample is judged to be acceptable according to PSEP specifications, the penetration depth will be measured with a decontaminated stainless steel ruler, and sample quality, color, odor, and texture will be described in the sample log (Appendix B).

If needed, multiple grab samples will be collected and composited for each sampling location to provide sufficient volume for chemical analysis. The general procedure for collecting sediment using a grab sampler is as follows:

- 1. Make logbook and field form entries as necessary throughout the sampling process to ensure accurate and thorough record-keeping.
- 2. Position the sampling vessel at the targeted sampling location.
- 3. Set the sampler jaws in the open position, place the sampler over the edge of the boat, and lower the sampler to the bottom.
- 4. Record the location using the DGPS; measure and record the water depth.
- 5. Retrieve the sampler and place it securely in the sampling vessel.
- 6. Examine the sample for the following sample acceptance criteria:
 - a. The sampler is not overfilled with sample so that the sediment surface is pressing against the top of the sampler.
 - b. The sample does not contain large foreign objects (i.e., trash or debris). A sample that is rock/gravel fill will be rejected in favor of depositional material (i.e., sand/silt/clay).
 - c. Overlying water is present indicating minimal leakage.
 - d. Overlying water is not excessively turbid indicating minimal sample disturbance.
 - e. Sediment surface is relatively flat and/or intact without any indications of disturbance or winnowing.
 - f. A penetration depth has been achieved that allows the collection of the upper 10 cm of sediment, whenever feasible. In instances where 10 cm penetration is not possible due to sandy sediments, the maximum penetration depth will be recorded.
 - g. If sample acceptance criteria are not achieved, the sample will be rejected and another sample collection attempt will be made.
 - h. If multiple attempts within 50 m of a given target location do not produce an

acceptable sample, the sampling location will be relocated.

- 7. Siphon off any overlying surface water.
- 8. Collect samples for total sulfides analysis directly from the grab sampler and place the sediment aliquots in appropriate, pre-cleaned, labeled sample containers (Table 6). Add approximately 2 mL of zinc acetate preservative to the jar, fasten the lid and shake until mixed.
- 9. Measure and collect the top 10 cm with a stainless steel spoon, avoiding any sediment that is in contact with the inside surface of the grab sampler, then place the sediment into a stainless steel bowl and cover with aluminum foil.
- 10. Record the following observations of sediment sample characteristics on the field form (Appendix B); repeat steps 4 through 11 if more sample volume is required.
 - a. Texture
 - b. Color
 - c. Biological organisms or structures (i.e., shells)
 - d. Presence of debris (i.e., natural or anthropogenic objects)
 - i. Estimate percentage of wood debris
 - e. Presence of oily sheen or obvious contamination
 - f. Odor (e.g., hydrogen sulfide, petroleum)
- 11. Wash excess sediment back into the water away from any areas remaining to be sampled.
- 12. Percent fines will be determined by rinsing 100 ml of sediment through a 63.5 micron sieve until the water is clear. Percent fines are equal to 100 minus the volume of remaining sediment.
- 13. Once sufficient sediment volume has been collected and homogenized to a consistent texture, samples should be placed in the appropriate, pre-cleaned, labeled sample containers, placed in a cooler maintained at 4°C, and prepared for shipment to the analytical laboratory.
- 14. Confirm all relevant documentation has been completed, entries are accurate, and paperwork has been signed.
- 15. Decontaminate all sampling equipment before proceeding to the next sampling location.

A single replicate sample will be collected from each target sampling location, with the exception of field duplicates and QA/QC samples to be collected randomly at the field supervisor's discretion.

Sample Identification, Containers, and Labels

Samples will be identified based on the project, sampling area, location, and sample type. All samples collected during will be labeled clearly and legibly. Each sample will be labeled with a unique alphanumeric sample identification number that identifies characteristics of the sample as follows:

Project	Study Area	Location Number	Sample Type
RB13-	DIS-	01-	S

Project consists of four characters describing the project (RB13 = Regional Background 2013).

Study Area consists of three characters describing the sampling area representative of North Olympic Peninsula Regional Background (DIS=Discovery Bay, DUN=Dungeness Bay, SEQ=Sequim Bay, PT=Port Townsend)

Location Number consists of two characters identifying the station location number

Sample Type consists of one to two characters indicating the sample type. S denotes a sediment sample. Sediment QA/QC samples are further identified with D = duplicate, T = triplicate, ER = equipment rinsate, RB = rinsate blank.

Sample labels will be self-adhering, waterproof material. An indelible pen will be used to fill out each label. Each sample label will contain the project name (North Olympic Peninsula Harbor Regional Background Sediment Characterization), sample identification, date and time of collection, analyses, preservative (as applicable), and the initials of the person preparing the sample. In addition, a unique, sequentially numbered jar tag will be present on each sample container for tracking purposes. Jar tag numbers will be recorded in a Sample Container Logbook (Appendix B). Sample labels will be protected by packaging tape wrapped around the entire jar to prevent loss or damage of the labels during handling and storage.

Sample Storage and Delivery

All samples will be stored in insulated coolers and preserved by cooling to a temperature of 4°C or as required by analytical methods. Maximum sample holding and extraction times will be strictly adhered to by field personnel and the analytical and testing laboratories.

Preparation of jars for shipment will be performed in the following manner:

- 1. Wipe or decontaminate the outside of filled, capped sample bottles to ensure there is no sample residual on the outside of the container. Secure sample lid jars with electrical tape to prevent leakage.
- 2. Label jars with prepared labels. Each set of samples will have a unique sample ID and jar tag number.
- 3. Secure labels with clear packaging tape.
- 4. Record the samples in Sample Container Logbook (see Appendix B) and the Chain of Custody forms.
- 5. Place sample containers in plastic zip-loc bubble-pack bags, or wrap in bubble pack and secure with packaging tape.
- 6. Prepare an empty insulated cooler by placing three to four ice packs in a garbage bag at the bottom of the cooler. Place sample containers in a garbage bag and fill with the

- sample bottles. Add additional bags of ice as needed to surround the bag containing the samples.
- 7. Seal the cooler with strapping tape and a custody seal. Samples for chemical analyses will be shipped via overnight courier to the analytical laboratory once per day or whenever a cooler is filled, and accompanied by the chain-of-custody record, which identifies the shipment contents. The chain-of-custody will be signed by the individual relinquishing samples to the onsite laboratory representative. The field personnel will be responsible for:
 - a. Packaging the samples;
 - b. Signing the chain-of-custody before placing inside the cooler to be sealed;
 - c. Applying a shipping label, an air bill, a custody seal, and strapping tape to the cooler; and
 - d. Shipping the samples in accordance with the maximum holding time allowed for the analyses to be performed.

A separate chain-of-custody form will be filled out for each analytical laboratory. The chain-of-custody will be signed by the individuals relinquishing the samples and will be placed inside the cooler before it is sealed.

All sediment samples will be retained for a minimum of 6 months from the time they were received using standard laboratory handling procedures. They may be removed from the laboratory prior to the end of the 6-month period only at the direction of the contractor project manager in consultation with Ecology.

Field Documentation

A complete record of field activities will be maintained. Documentation necessary to meet QA objectives for this project include field notes and field forms (Appendix B), sample container labels, and chain-of-custody forms. The field documentation will provide descriptions of all sampling activities, sampling personnel, and weather conditions, and will record all modifications, decisions, and/or corrective actions to the study design and procedures identified in this work plan.

Field Logbooks

All handwritten documentation must be legible and completed in permanent waterproof ink. Corrections must be marked with a single line, dated, and initialed. All documentation, including voided entries, must be maintained within project files.

The Field Manager will keep the field logbook(s) on site during field operations. Daily activities will be recorded in a bound field logbook of water-resistant paper. Separate logbooks consisting of bound, paginated field forms will be kept for surface sediment grab descriptions, and an inventory of sample containers (separate from chain of custody [COC] documentation).

Examples of the various field forms to be used are presented in Appendix B. All entries will be made legibly, in indelible ink, and will be signed and dated. Information recorded will include the following:

- Date, time, place, and location of sampling;
- Onsite personnel and visitors;
- Daily safety discussion and any safety issues;
- Quality control samples (e.g., duplicate samples, field blanks, etc.);
- Calibration of field equipment (including make and model of equipment);
- Field measurements and their units:
- Observations about site, location, and samples (i.e., weather, current, odors, appearance); and
- Equipment decontamination verification.

Field logbooks are intended to provide sufficient data and observations to enable participants to reconstruct events that occur during project field activities. Entries should be factual, detailed, and objective. Unless restricted by weather conditions, all original data recorded in field logbooks and on sample identification tags, COC records, and field forms will be written in waterproof ink. If an error is made, the individual responsible may make corrections simply by crossing out the error and entering the correct information. The erroneous information should not be obliterated. All corrections must be initialed and dated.

Chain-of-Custody Procedures

The field crew will retain samples at all times until contractor personnel deliver samples to the appropriate laboratory. All samples will be held and transported in coolers with ice or frozen gelpacks at approximately 4°C.

COC forms will be initiated at the time of sample collection to ensure that all collected samples are properly documented and traceable through storage, transport, and analysis. When all line items on the form are completed or when the samples are relinquished, the sample collection custodian will sign and date the form, list the time, and confirm the completeness of all descriptive information contained on the form. Each individual who subsequently assumes responsibility for the sample will sign the COC form and provide the reason for assuming custody. The field COC terminates when the laboratory receives the samples. The FM should retain a copy of the completed, signed COC form(s) for project files.

Equipment Decontamination

Sample processing equipment (i.e., spoons, bowls, and reusable containers from which samples are transferred to sample jars) will be washed with a laboratory-grade detergent (e.g., Liquinox) and water solution, rinsed with site or tap water, and will undergo a final distilled water rinse

prior to field operations. Decontaminated equipment will be wrapped or covered with aluminum foil. Sub-sampling and processing equipment will be decontaminated before use at each station in order to prevent cross-contamination of samples. Any deviations from these procedures will be documented in the field notebook.

Personal non-disposable field equipment (i.e., boots, waterproof gloves, and garments) will be rinsed with water and brushed clean prior to leaving the immediate vicinity of the sample collection area. Special attention will be given to removing mud that may adhere to boot treads.

Waste Disposal

During the field investigation, field personnel will be responsible for securing appropriate waste containers, and placing wastes in labeled storage containers, performing appropriate testing, preparing wastes for disposal, and proper disposition of wastes.

Excess sediment sample not submitted to the laboratories, and disposable protective clothing, sampling equipment, and packaging are the two types of waste the activities described in this work plan will generate.

Sediment Samples

Small quantities of excess sediment and rinsate water generated during sample processing will be returned to the site. Care will be taken to not dispose of sediment and/or rinsate at locations targeted for subsequent sampling.

Disposable Protective Clothing and Sampling Equipment

Used PPE, such as protective Tyvek suits or gloves, and sampling equipment, such as aluminum foil and paper towels, and any packaging material that cannot be recycled, will be placed in plastic storage bags and disposed of as municipal waste.

Laboratory Analytical Methods

All of the analytical methods used in this program will be performed in accordance with the PSEP guidelines. The laboratory analysis will be consistent with PSEP guidelines (PSEP 1997a, b), any recent modifications proposed during the Sediment Management Annual Review Meeting (SMARM), and/or the most current laboratory recommendations. Each laboratory participating in this program will institute internal QA/QC plans. Analyses will be required to conform to accepted standard methods and internal QA/QC checks prior to final approval.

Chemical Analyses

Analytical Resources, Inc. (ARI), and AXYS Analytical Services (AXYS) will conduct the chemical analysis. Table 7 presents the sample preparation methods, analytical methods, and practical quantitation limits (PQL) for the target conventionals, metals, cPAH compounds, and dioxin/furan congeners. Each sample will also be analyzed for the full list of PCB congeners. The congeners and congener pairs obtainable by EPA method 1668A are presented in Table 8.

The analytical results from this supplemental investigation will be used for the determination of regional background concentrations. Accordingly, the data quality objectives are greater than those required under most sediment characterizations as the intent of any background study is to obtain as few non-detects and as many unqualified results as possible. The PQLs required for analysis in this study are lower than most standard methods provide. Efforts were made for many of the analytes to find methods that provide lower PQLs.

Few requirements exist for the selection of PQLs. MTCA guidance does stipulate that where the PQL is used as a cleanup level, it must meet the more stringent of the following conditions (WAC 173-340-707(2)(a) and (b)):

- The PQL is no greater than ten times the method detection limit (MDL).
- The PQL is no greater than that established by the U.S. EPA and used to establish requirements in 40 CFR 136, 40 CFS 141-143, or 40 CFR 260-270.

For all target analytes, the PQL is within a factor of ten of the MDL.

cPAH will be analyzed in select ion monitoring (SIM) mode. Metals will be analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) for sediment samples to achieve lower PQLs for arsenic and cadmium. An additional low end point will be added to the calibration standard for dioxin/furan and PCB congener analysis to provide for lower reporting limits. The PQL values listed for dioxin/furan and PCB congeners in Tables 7 and 8 are lower method calibration limits (LMCL), which is defined by the lower limit of the calibration curve. The LMCL is equivalent to the PQL in that it meets the definition provided in WAC 173-204-505:

"PQL means the lowest concentration that can be reliably measured within specified limits of precision, accuracy, representativeness, completeness, and comparability during routine laboratory operating conditions, using department approved methods".

The PQLs listed may be subject to modification due to elevated sample concentrations, heterogeneous samples (sediment), and potential matrix interferences that may preclude obtaining the desired quantification limit. Specifically:

- Two possible ions are used for the quantification of arsenic. The specific ion used is dependent upon the matrix and interferences. As a result, two reporting limits are listed for arsenic in Table 7.
- The standard reporting limit for cPAH compounds is 5.0 μg/kg using EPA method 8270 SIM. If necessary, ARI can achieve a PQL as low as 0.5 μg/kg using a low level version of 8270 SIM, but only in samples where the concentration is below the standard reporting limit. ARI will prescreen a solvent shake-out of the sample for potential high concentrations and analyze using the appropriate method.
- Matrix interferences for PCB congeners were noted with samples collected for the Port Gardner Regional Background Characterization. To minimize these interferences with the NOP Characterization, Axys will conduct an additional alumina column cleanup prior to analysis.

In the event either laboratory is unable to meet the PQLs additional clean-up measures may be used. If the PQLs still cannot be met, the reasons for the deviation will also be reported.

Table 7. Target Analytes, Methods, and Practical Quantitation Limits.

Conventional Parameters Grain size PSEP Total Solids (%) PSEP 0.1 Total Solidides PSEP 0.10 Total Volatile Solids (%) PSEP 0.1 Metals (mg/kg DW) Arsenic EPA 3050B/3051 EPA 200.8 0.2/0.5† Cadmium EPA 3050B/3051 EPA 200.8 0.1 Mercury EPA 7471A EPA 7471A 0.025 cPAHs (µg/kg DW) Benzo(a)pyrene EPA 3546 8270-SIM PAH* 5.0 Benz(a)pyrene EPA 3546 8270-SIM PAH* 5.0 Benz(b)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Benzo(k)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Chrysene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Dioxin/Furan Congeners (ng/kg DW)* EPA 1613B (CS-0.2) 1.2 1,2,3,7,8-PCDD <	Analyte	Preparation Method	Analytical Method	PQL
Grain size PSEP Total Solids (%) PSEP 0.1 Total Sulfides PSEP 1.0 Total organic carbon (%) PSEP 0.10 Total Volatile Solids (%) PSEP 0.1 Metals (mg/kg DW) Arsenic EPA 3050B/3051 EPA 200.8 0.2/0.5† Cadmium EPA 3050B/3051 EPA 200.8 0.1 Mercury EPA 7471A EPA 7471A 0.025 CPAHS (µg/kg DW) EPA 3546 8270-SIM PAH* 5.0 Benzo(a)pyrene EPA 3546 8270-SIM PAH* 5.0 Benzo(b)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Benzo(k)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Chrysene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Dioxin/Furan Congeners (ng/kg DW)‡ 2.3,7,8-T				
Total Sulfides PSEP 1.0 Total organic carbon (%) PSEP 0.10 Total Volatile Solids (%) PSEP 0.1 Metals (mg/kg DW) PSEP 0.1 Arsenic EPA 3050B/3051 EPA 200.8 0.2/0.5† Cadmium EPA 3050B/3051 EPA 200.8 0.2/0.5† Mercury EPA 4711A EPA 7471A 0.025 CPAHS (µg/kg DW) Benzo(a)pyrene EPA 3546 8270-SIM PAH* 5.0 Benzo(b)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Benzo(b)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Chrysene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene <td>Grain size</td> <td></td> <td>PSEP</td> <td></td>	Grain size		PSEP	
Total Sulfides PSEP 1.0 Total organic carbon (%) PSEP 0.10 Total Volatile Solids (%) PSEP 0.1 Metals (mg/kg DW) PSEP 0.1 Arsenic EPA 3050B/3051 EPA 200.8 0.2/0.5† Cadmium EPA 3050B/3051 EPA 200.8 0.2/0.5† Mercury EPA 4711A EPA 7471A 0.025 CPAHS (µg/kg DW) Benzo(a)pyrene EPA 3546 8270-SIM PAH* 5.0 Benzo(b)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Benzo(b)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Chrysene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene <td>Total Solids (%)</td> <td></td> <td>PSEP</td> <td>0.1</td>	Total Solids (%)		PSEP	0.1
Total Volatile Solids (%) PSEP 0.1 Metals (mg/kg DW) Arsenic EPA 3050B/3051 EPA 200.8 0.2/0.5† Cadmium EPA 3050B/3051 EPA 200.8 0.1 Mercury EPA 7471A EPA 7471A 0.025 CPAHS (µg/kg DW) EPA 3546 8270-SIM PAH* 5.0 Benzo(a)pyrene EPA 3546 8270-SIM PAH* 5.0 Benzo(b)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Benzo(k)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Chrysene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Diboxin/Furan Congeners (ng/kg DW)‡ 2,3,7,8-PCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 1,2,3,7,8-PeCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,8-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8-PeCDD EPA 1613B/3540C			PSEP	1.0
Metals (mg/kg DW) Arsenic EPA 3050B/3051 EPA 200.8 0.2/0.5† Cadmium EPA 3050B/3051 EPA 200.8 0.1 Mercury EPA 7471A EPA 7471A 0.025 cPAHs (µg/kg DW) Benzo(a)pyrene EPA 3546 8270-SIM PAH* 5.0 Benzo(a)unthracene EPA 3546 8270-SIM PAH* 5.0 Benzo(b)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Benzo(k)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Chrysene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Dioxin/Furan Congeners (ng/kg DW)‡ 2,3,7,8-PeCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 1,2,3,7,8-PeCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8-PacDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8,9-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0	Total organic carbon (%)		PSEP	0.10
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Benzo(k)fluoranthene EPA 3546 8270-SIM PAH* 5.0 Chrysene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Dioxin/Furan Congeners (ng/kg DW)‡ 5.0 2,37,8-TCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 1,2,3,7,8-PeCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,47,8-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 0CDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 0CDD EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 2,3,7,8-TCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 2,3,4,7,8-PeCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,8-PxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,6,	Benz(a)anthracene	EPA 3546	8270-SIM PAH*	5.0
Chrysene EPA 3546 8270-SIM PAH* 5.0 Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Dioxin/Furan Congeners (ng/kg DW);* *** *** 2,3,7,8-TCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 1,2,3,7,8-PeCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,7,8-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8,9-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,6,7,8-HpCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 0CDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 0CDD EPA 1613B/3540C EPA 1613B (CS-0.2) 2.0 2,3,7,8-PeCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 2,3,7,8-PeCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,7,8-PeCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,6,7,8-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0	Benzo(b)fluoranthene	EPA 3546	8270-SIM PAH*	5.0
Dibenz(a,h)anthracene EPA 3546 8270-SIM PAH* 5.0 Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Dioxin/Furan Congeners (ng/kg DW)‡ 5.0 EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 1,2,3,7,8-TCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8-PeCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,6,7,8-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8-PeCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,6,7,8-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 0CDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 0CDD EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 1,2,3,7,8-PeCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 2,3,4,7,8-PeCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,7,8-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,6,7,8-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8,9-HxCDF </td <td>Benzo(k)fluoranthene</td> <td>EPA 3546</td> <td>8270-SIM PAH*</td> <td>5.0</td>	Benzo(k)fluoranthene	EPA 3546	8270-SIM PAH*	5.0
Indeno(1,2,3-cd)pyrene EPA 3546 8270-SIM PAH* 5.0 Dioxin/Furan Congeners (ng/kg DW)‡ EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 1,2,3,7,8-TCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8-PeCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,7,8-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8,9-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,6,7,8-HpCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 OCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 2.0 2,3,7,8-TCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 1,2,3,7,8-PeCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 2,3,4,7,8-PeCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,7,8-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8,9-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8,9-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8,	Chrysene	EPA 3546	8270-SIM PAH*	5.0
Dioxin/Furan Congeners (ng/kg DW)‡ 2,3,7,8-TCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 1,2,3,7,8-PeCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,7,8-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,6,7,8-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8,9-HxCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,6,7,8-HpCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 OCDD EPA 1613B/3540C EPA 1613B (CS-0.2) 2.0 2,3,7,8-TCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 0.2 1,2,3,7,8-PeCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 2,3,4,7,8-PeCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,7,8-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8,9-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,7,8,9-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,6,7,8-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1	Dibenz(a,h)anthracene	EPA 3546	8270-SIM PAH*	5.0
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2,3,4,6,7,8-HxCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,6,7,8-HpCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,7,8,9-HpCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0	1,2,3,6,7,8-HxCDF	EPA 1613B/3540C	EPA 1613B (CS-0.2)	1.0
1,2,3,4,6,7,8-HpCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0 1,2,3,4,7,8,9-HpCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0	1,2,3,7,8,9-HxCDF	EPA 1613B/3540C	EPA 1613B (CS-0.2)	1.0
1,2,3,4,7,8,9-HpCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 1.0		EPA 1613B/3540C	EPA 1613B (CS-0.2)	1.0
	1,2,3,4,6,7,8-HpCDF	EPA 1613B/3540C	EPA 1613B (CS-0.2)	1.0
OCDF EPA 1613B/3540C EPA 1613B (CS-0.2) 2.0	_	EPA 1613B/3540C		1.0
	OCDF	EPA 1613B/3540C	EPA 1613B (CS-0.2)	2.0

Notes

SIM-select ion monitoring PQL-practical quantitation limit DW-dry weight

CS-0.2-additional low level calibration point cPAH-carcinogenic polycyclic aromatic hydrocarbons

[†] PQL for arsenic dependent on the quantified ion, which is in turn dependent on the matrix and interferences

^{*} Samples will undergo a prescreening process at ARI and low concentration samples will be analyzed by a low level variant of 8270-SIM with a reporting limit of 0.5 μ g/kg.

[‡] Values listed for dioxin/furan congeners are the lower method calibration limits (LMCL) defined by the lowest concentration on the calibration curve. The LMCL is functionally equivalent to the PQL.

Table 8. PCB Congener Methods and Practical Quantitation Limits.

Analyte	Preparation Method	Analytical Method	PQL
*PCB-156/157	EPA 1668A	EPA 1668A (CS-0.2)	0.8
see below	EPA 1668A	EPA 1668A (CS-0.2)	0.4
	and Congener Pairs (ng/kg DW	` ′	
of 0.4		, , 101 110 p	001 1 111111 1 Q 22
PCB-1	PCB-48	PCB-110/115	PCB-164
PCB-2	PCB-50/53	PCB-111	PCB-165
PCB-3	PCB-52	PCB-112	PCB-167
PCB-4	PCB-54	PCB-113/90/101	PCB-169
PCB-5	PCB-55	PCB-114	PCB-170
PCB-6	PCB-56	PCB-117/116/85	PCB-171/173
PCB-7	PCB-57	PCB-118	PCB-172
PCB-8	PCB-58	PCB-120	PCB-174
PCB-9	PCB-59/62/75	PCB-121	PCB-175
PCB-10	PCB-60	PCB-122	PCB-176
PCB-11	PCB-61/70/74/76	PCB-123	PCB-177
PCB-12/13	PCB-63	PCB-126	PCB-178
PCB-14	PCB-64	PCB-127	PCB-179
PCB-15	PCB-66	PCB-128/166	PCB-180/193
PCB-16	PCB-67	PCB-130	PCB-181
PCB-17	PCB-68	PCB-131	PCB-182
PCB-19	PCB-69/49	PCB-132	PCB-183/185
PCB-21/33	PCB-72	PCB-133	PCB-184
PCB-22	PCB-73	PCB-134/143	PCB-186
PCB-23	PCB-77	PCB-136	PCB-187
PCB-24	PCB-78	PCB-137	PCB-188
PCB-25	PCB-79	PCB-138/163/129/160	PCB-189
PCB-26/29	PCB-80	PCB-139/140	PCB-190
PCB-27	PCB-81	PCB-141	PCB-191
PCB-28/20	PCB-82	PCB-142	PCB-192
PCB-30/18	PCB-83/99	PCB-144	PCB-194
PCB-31	PCB-84	PCB-145	PCB-195
PCB-32	PCB-88/91	PCB-146	PCB-196
PCB-34	PCB-89	PCB-147/149	PCB-197/200
PCB-35	PCB-92	PCB-148	PCB-198/199
PCB-36	PCB-94	PCB-150	PCB-201
PCB-37	PCB-95/100/93/102/98	PCB-151/135/154	PCB-202
PCB-38	PCB-96	PCB-152	PCB-203
PCB-39	PCB-103	PCB-153/168	PCB-204
PCB-41/40/71	PCB-104	PCB-155	PCB-205
PCB-42	PCB-105	PCB-156/157*	PCB-206
PCB-43	PCB-106	PCB-158	PCB-207
PCB-44/47/65	PCB-107/124	PCB-159	PCB-208
PCB-45/51	PCB-108/119/86/97/125/87	PCB-161	PCB-209
PCB-46	PCB-109	PCB-162	

Notes

PQL-practical quantitation limit DW-dry weight CS-0.2-additional low level calibration point

Analytical Laboratory Reporting

Analytical laboratory reports will be accompanied by sufficient backup data and QC results to enable independent reviewers to evaluate the quality of the data results. Analytical data will be reported in the units specified by the PQLs listed in Tables 7 and 8.

All PQLs will be met. If matrix interferences exist that prevent meeting the listed PQL, the reason will be listed in the laboratory narrative. All non-detect sample results for cPAH will be reported to the method detection limit and detected results less than the target PQL will be qualified. All non-detect results for metals will be reported at the PQL. Metals data are not qualified below the PQL.

Non-detect results for dioxin/furan and PCB congeners will be reported at the sample specific detection limit. All detected congener results less than the LMCL/PQL will be qualified.

The analytical laboratory deliverables will include the following:

- Case narrative (including any problems encountered, protocol modifications, and/or corrective actions taken);
- Sample analytical and QA/QC results with units;
- All protocols used during analyses;
- Any protocol deviations from the approved sampling plan;
- Surrogate recovery results;
- MS/MSD results;
- Laboratory duplicate/triplicate results;
- Blank results:
- Sample custody records (including original chain-of-custody forms); and
- Electronic analytical results in Ecology's Environmental Information Management (EIM) format.

Quality Assurance Project Plan

The purpose of the project QA/QC is to provide confidence in the project data results through a system of quality control performance checks with respect to data collection methods, laboratory analysis, data reporting, and appropriate corrective actions to achieve compliance with established performance and data quality criteria. This section presents the QA/QC procedures to ensure that the investigation data results are defensible and usable for their intended purpose.

Measurements of Data Quality

The tolerable limits for the data reported by the laboratory will be measured with regard to precision, accuracy, representativeness, completeness, and comparability.

Precision is a measure of mutual agreement among individual measurements of the same property under prescribed conditions. Precision will be assessed by the analysis of matrix spike/matrix spike duplicates (MS/MSDs), field duplicate and triplicates, and laboratory control sample/laboratory control sample duplicates (LCS/LCSD). The calculated relative percent differences (RPDs) for field duplicates and triplicates and MS/MSD pairs will provide information on the precision of sampling and analytical procedures, and the RPDs for LCS/LCSD pairs will provide information on precision of the analytical procedures.

Accuracy is the degree to which an observed measurement agrees with an accepted reference or true value. Accuracy is a measure of the bias in the system and is expressed as the percent recoveries of spiked analytes in MS/MSD and LCS/LCSD samples. Accuracy will also be evaluated through the surrogate spikes in each sample. The laboratory control limits for surrogates will be used for the project.

Representativeness expresses the degree to which data accurately and precisely represent an actual condition or characteristic at a particular sampling point. Representativeness is achieved by collecting samples representative of the matrix at the time of collection. Representativeness can be evaluated using replicate samples, additional sampling locations, and blanks.

Completeness refers to the amount of measurement data collected relative to that needed to assess the project's technical objectives. It is calculated as the number of valid data points achieved divided by the total number of data points requested by virtue of the study design. For this project, completeness objectives have been established at 95 percent.

Comparability is based on the use of established USEPA-approved methods for the analysis of the selected parameters. The quantification of the analytical parameters is based on published methods, supplemented with well-documented procedures used in the laboratory to ensure reproducibility of the data.

Quality Assurance and Quality Control for Chemistry Sediment Samples

Field and laboratory QA/QC samples will be used to evaluate the data precision, accuracy, representativeness, and comparability of the analytical results.

Field QA/QC for Sediment Chemistry

Field QC samples will be collected during sampling to quantitatively measure and ensure the quality of the sampling effort and the analytical data. Field QC samples include field duplicates, equipment rinsate, and rinsate blanks. QC samples are to be handled in the same manner as the environmental samples collected. Brief descriptions of the field QC samples are provided below.

Field Duplicates and Triplicates

Field duplicates and triplicates are collected at the same time as the original sample using identical sampling techniques. Field duplicate sample results (triplicates for sediment conventional parameters) are used to assess the precision of the sample collection process and to help determine the representativeness of the sample. Field duplicates/triplicates will be collected at a five percent frequency. The duplicates/triplicates will be designated for the same analysis as the original samples. The field duplicates/triplicates will be collected from the same homogenate as the original sample.

Equipment Rinsate and Rinsate Blanks

The equipment rinsate blank and decontamination water (rinsate) blank provide a quality control check on the potential for cross contamination by measuring the effectiveness of the sampling and processing decontamination procedures. The equipment rinsate sample consists of deionized water rinsed across sample collection and processing equipment after they have been used to collect a sample and have been decontaminated for use at the next sampling location. Equipment rinsate will be collected at a five percent frequency. The decontamination water blank is an unadulterated sample of the de-ionized water used to create the rinsate blank, analyzed to ensure no contaminants were present in the rinse water. A single rinsate blank will be collected for this sediment characterization.

Laboratory QA/QC for Sediment Chemistry

One laboratory matrix spike (MS) and matrix spike duplicate (MSD) will be analyzed for every 20 samples submitted or for each analytical batch of samples (if less than 20 submitted) for the analysis of cPAHs, metals, and TOC. The combination of these spiked samples will provide information on the accuracy and precision of the chemical analysis, and to verify that the extraction and measured concentrations are acceptable. The MS/MSDs will be analyzed in accordance with USEPA methods for each respective analyte.

One laboratory replicate will be analyzed for all constituents (except grain size, TOC, and total solids) for every 20 samples submitted or for each analytical batch of samples (if less than 20 submitted). Laboratory triplicates will be analyzed for grain size, TOC, and total solids. These QA/QC samples will be analyzed in accordance with the respective USEPA method and will be used to evaluate the precision of the analytical method.

One laboratory method blank and laboratory control sample (LCS) will be analyzed for all constituents (except grain size and total solids) for each analytical batch of 20 samples to assess potential laboratory contamination and accuracy. An laboratory control sample duplicate (LCSD) will be analyzed if required by the method, or if the laboratory does not have enough sample volume to prepare an MS/MSD.

Laboratory control samples, ongoing precision and recovery samples, and surrogate spikes will be used as defined by the analytical methods and equipment calibration requirements. One certified reference material sample will be analyzed for dioxin/furan congeners.

Data Validation

The data generated as part of this investigation will undergo an independent quality assurance review and data validation. A QA2 (USEPA Stage 4) chemistry data review will be conducted that examines the complete analytical process from calculation of instrument and method detection limits, practical quantification limits, final dilution volumes, sample size, and wet-to-dry ratios to quantification of calibration compounds and all analytes detected in blanks and environmental samples (PTI 1989a; USEPA 2009).

The independent data validation will be conducted by EcoChem, Inc. of Seattle, WA.

Data Analysis and Reporting

This section describes the data analysis and reporting requirements for the data collection activities described in this SAP.

Analysis of Sediment Chemistry Data

The sediment chemistry data will be summarized and presented in tables indicating sediment locations, detected contaminants, detection limits that exceed target PQLs, and data qualifiers assigned by the laboratory or during the data validation efforts. Concentrations of relevant COCs may be mapped to better demonstrate the spatial distributions.

For reporting, dioxin/furan and PCB congeners will be normalized to the toxicity of 2,3,7,8-TCDD (Tetrachlorodibenzo-p-Dioxin) using toxic equivalent factors (TEFs) updated by the WHO in 2005 (Van den Berg et al. 2006). TEQs for dioxin/furan congeners and PCB congeners will be reported separately. The toxic equivalent quotient (TEQ) is equivalent to the sum of the concentrations of individual congeners multiplied by their TEF (potency relative to 2, 3,7,8-TCDD). Non-detected values will be assessed as zero, half of the sample specific detection limit, and at the sample specific detection limit for data reporting purposes. The sample specific detection limit is essentially a method detection limit that is unique to the sample and matrix being analyzed.

TEQ values will also be calculated using Kaplan-Meier analysis to estimate concentrations for non-detected congeners (Helsel 2010). The final TEQ sums will be qualified to indicate the level of censoring within each sample.

PCB congeners will also be reported as total PCBs. Total PCBs is the sum of all detected congeners. In a rare case where all PCB congeners are not detected, the highest detection limit will be used to represent the total PCB concentration.

The concentrations for cPAH will be determined by normalizing individual cPAH to the toxicity of benzo(a)pyrene using TEFs present in Ecology's guidance document *Evaluating the Toxicity* and Assessing the Carcinogenic Risk of Environmental Mixtures Using Toxicity Equivalency Factors (Ecology 2007). Non-detected values will be reported and assessed as zero, half of the method detection limit, and at the method detection limit for data reporting purposes.

TEQ values will also be calculated using Kaplan-Meier analysis to estimate concentrations for non-detected PAH compounds (Helsel 2010). The final TEQ sums will be qualified to indicate the level of censoring within each sample.

Calculation of the Regional Background Concentration

The background statistics of interest are the 95 UCL on the mean for risk-based exposure estimates, and an upper tolerance limit (UTL) as a cleanup screening level. These summary statistics should be calculated on a single data distribution, excluding outliers, for samples assumed to be representative of either natural or regional background.

The North Olympic Peninsula regional background AOI is complex and may potentially be comprised of four distinct populations. The stratified sampling approach allows the assumption of a single population to be investigated, and the data dealt with appropriately depending on the result of those investigations.

The distribution of the data will be evaluated within each bay separately. The five samples collected from Sequim Bay may be insufficient to fully describe that distribution, so if Discovery, Dungeness, and Port Townsend Bays appear to be consistent, Sequim Bay may be assumed to follow the same distributional form. Distributional comparisons among the four embayments will use graphical evaluations (e.g., empirical cumulative distribution curves) and a goodness-of-fit test [i.e., Kolmogorov-Smirnov]) for each chemical endpoint. Results for all chemical endpoints will be evaluated, and a weight-of-evidence approach will be used to support whether one or more populations are present. In addition, multivariate evaluation (e.g., principal components analysis or multidimensional scaling) of the complete dataset will be used to explore whether the chemistry results group samples either by embayment or by regional vs. natural signal. These analyses will be used in part to help differentiate natural and regional background concentrations throughout the study area. If multiple populations are present, then the summary statistics will be computed using appropriate methods for a stratified population. If a single population appears appropriate, and the population appears representative of regional background, then the combined data will be treated as a simple random sample from a single population (since the sample size allocation between bays was proportional to relative AOI in each bay).

The shape of the distribution and the presence of potential outliers, or mixtures of distinct populations will be assessed using graphical tools (e.g., boxplots and Q-Q plots) in conjunction with formal outlier tests (e.g., Dixon's or Rosner's test) for identifying samples with extreme concentrations for a single analyte or TEQ. Some samples may not have extreme concentrations for individual analytes, but may still exhibit very different patterns within the suite of PCBs, cPAHs, or dioxin/furan congeners. The presence of samples with very different congener patterns may signify unique contaminant sources or signify the difference between natural and regional background. Once identified, these samples, along with their surrounding areas, may be excluded from the regional background distribution dataset.

Multivariate outlier investigations will be screened using the Mahalanobis distances. Mahalanobis distance is a metric very similar to Euclidean distance (i.e., the familiar metric used to calculate the distance between two points on a line). To identify multivariate outliers, the Mahalanobis distance is calculated as the distance between each observation and the center of mass for the remaining observations, scaled to the covariance among congeners in the direction of that observation. A large distance in a direction of high covariance is more likely than a moderate distance in a direction of very low covariance. An observation that doesn't fall within the "cloud" of other data points is identified as a potential multivariate outlier.

Outliers will contaminate the distribution, producing higher variance estimates and subsequently greater uncertainty in the tolerance limit. Any identified outliers will be discussed with the project team, and the regional background will be calculated both with and without the outliers to determine their impact. Any concentrations deemed to be outside the range of regional background will be excluded from the calculations of the cleanup standards. Excluded concentrations that are more representative of natural background may be used to supplement the existing natural background dataset currently used as the Port Angeles SCO (NewFields 2013b).

After the removal of any outliers, goodness-of-fit tests and graphical displays (e.g., Q-Q plots) will be used to identify the best-fit distributional form for the data. For the calculation of the 95UCL on the mean and UTLs, if the assumption of a particular parametric distribution is not deemed appropriate for the data, non-parametric methods such as the bootstrap or order statistics will be used. In all cases where concentrations are present below detection limits, methods appropriate for left-censored data will be used. All of the statistical tools required for this analysis are available in ProUCL 4.1.00 (USEPA 2010), with the exception of the multivariate pattern analysis. The multivariate analysis tools are available in Scout version 1.00.01 (USEPA 2008, runs only up to Windows 98), and R (R Development Core Team 2011); as well as in other commercially available statistical software.

Ecology will be kept informed of all aspects of data analysis including the determination of the data distribution, presence of outliers, and the possible inclusion of existing data or analysis of archived secondary sediment samples. Statistical findings will be presented to the stakeholders prior to the finalization of the report.

Reporting Procedures

A written data report documenting all activities associated with collection, transportation, and chemical analyses of sediment samples will be prepared. The chemical and QA/QC reports will be included as appendices. At minimum, the Final Report will include:

- A summary of the purpose of the investigation;
- Description of sampling and analysis activities;
- Protocols used during sampling and testing, and an explanation of any deviations from the

- sampling plan protocols or the approved work plan;
- Methods used for station positioning, sample collection locations reported in latitude and longitude to the nearest tenth of a second (NAD83);
- Maps showing actual locations of sampling stations;
- Maps and data tables of sediment chemistry (results in mg/kg organic carbon, and dry weight);
- Chain-of-custody records;
- Analytical laboratory reports;
- Copies of field and sampling logs as appendices;
- QA/QC summary;
- Data validation reports;
- Data analysis and interpretation for determination of background concentrations; and
- Summary statistics, outliers, and uncertainties associated with calculation of regional background.

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Appendices

Appendix A. Existing Chemistry Data

A1: Screening of Existing Data

NewFields queried the EIM database to find all data present in Dungeness Bay, Discovery Bay, Sequim Bay, and Port Townsend Bay that could be relevant to the determination of regional background concentrations for the North Olympic Peninsula. There were some caveats to the data available from EIM. The level of QAQC on the studies was variable, though most were thought to be above a level QA1 data validation. There was no consistent reporting for non-detect results. Some results were reported at the MDL, while some were at the PQL.

Several steps were taken to filter the existing data so as to match the sampling methodologies and data quality objectives of the current study. The following steps were not analyte specific:

- **Sample Date.** Samples collected within the last decade (2002 through 2012) were extracted from EIM.
- Sample Depth. Only samples from within the top 0 to 10 cm were retained. A sample was excluded if the Field_Activity_Lower_Depth and Field_Activity_Upper_Depth were either both zero or both left blank. This interval includes PSAMP samples which were collected at an interval of 0 to 2 or 3 cm. A final determination for the inclusion of the PSAMP data will be made after evaluation of the baseline results.
- **Field Replicates.** Field replicates were marked in the Sample_Field_Replicate_ID, Sample_Replicate_Flag, and occasionally in the Sample_Sub_ID columns. Use of these columns to mark field replicates was not always consistent. If any of these columns indicated a replicate, and the same parameter was analyzed multiple times at a location, the samples marked as replicates were excluded.
- **Laboratory Replicates.** All laboratory replicates marked in the Result_Lab_Replicate_ID column were excluded.
- Composite Samples. If the Sample_Composite_Flag was marked with "Y" the sample was excluded.

Results for specific analytes were further reduced after the preliminary data screening. The full suite of PCB congeners were only available in Dungeness Bay from the Former Rayonier Mill Phase 2 Addendum RI. Only three of these samples remained after the spatial screening process summarized below (Table A-3).

Metals were first filtered by method. If the Result_Method column was marked UNKNOWN or left blank, the result was excluded. The remaining analytical methods were consistent with those presented in the Sediment Sampling and Analysis Plan Appendix (Ecology 2008) or those used in the current study. Screening of metals concentrations based on non-detects was unnecessary as all concentrations for the AOI were detected.

cPAH and dioxin/furan congener samples were also screened by method. Samples with methods marked UNKNOWN were excluded. For cPAH, only samples analyzed by derivations of EPA method 8270 were retained. For dioxin/furan congeners, only samples analyzed by EPA method 1613 were retained.

TEQ values were calculated for cPAH compounds and dioxin/furan congeners using Ecology guidance (Ecology 2007). A concentration of one half the reported MDL/PQL was used for non-detected results. A separate TEQ was calculated using the same process, but only incorporated the non-detected results. If the non-detect TEQ made up ≥50 percent of the total TEQ, the sample was excluded. Three cPAH samples were excluded where all seven compounds were non-detects. At least six out of the seven cPAH compounds were detected in each of the remaining samples. All but five dioxin/furan samples were excluded.

The final criteria for excluding data were based on the spatial distribution of existing data and the random placement of the baseline and secondary sampling locations. Existing data within 500 meters of a new baseline location were excluded. Although these samples are not presented in Tables A-1, A-2, and A-3, they may be incorporated at a later date for evaluating uncertainty in regional background concentrations in light of small-scale (<500m) field variability. Existing data within 500 meters of a secondary location were included. If necessary, archived sediment from the secondary location may be submitted for analysis of analytes not present at the nearby existing data location. Existing data greater than 500 meters from baseline and secondary locations were also included.

Table A-1 presents the available existing data for arsenic, cadmium, mercury, and cPAH. Table A-2 presents the existing data for dioxin/furan congeners. Table A-3 presents the existing PCB congener data.

Table A-1. Screened existing data for arsenic, cadmium, mercury, cPAH, and dioxin/furan congeners.

			PSAMP_SP-			·	
LocationID	PSAMP_SP-545	PSAMP_SP-289	1289	PSAMP_SP-801	PSAMP_SP-777	PSAMP_SP-113	PSAMP_SP-649
Date	6/17/2003 Q	6/11/2002 Q	6/18/2003 Q	6/18/2003 Q	6/20/2003 Q	6/12/2002 Q	6/17/2003 Q
Metals (mg/kg DW)							
Arsenic	2.34	4.29	9.14	8.82	10.1	3.43	5.21
Cadmium	0.36	0.53	1.83	1.62	0.74	0.19	0.81
Mercury	0.016	0.0246	0.079	0.074	0.089	0.0159	0.072
Carcinogenic Polycyclic Aroma	tic Hydrocarbons (μ	g/kg DW)					
Benzo(a)pyrene	1.1	8.1	32	20	25	4.4	21
Benzo(a)anthracene	1.4	7.6	27	17	45	4.4	18
Benzo(b)fluoranthene	2.9 J	9.8	49 J	34 J	34 J 36 J		27 J
Benzo(k)fluoranthene	2.5 J	9.9	42 J	26 J	25 J	3.5	27 J
Dibenzo(a,h)anthracene	0.49 U	2.4	7.5	0.56 U	6.7	1.4	5.5
Indeno(1,2,3-cd)pyrene	1.4	5.8	26	21	24	2.8	18
Chrysene	2.1	13	28	17	23	7	20
cPAH TEQ (1/2 DL)	2.15	13.0	50.0	31.5	41.0	6.84	32.6

Q – data qualifier U- the analyte was analyzed for but not detected TEQ – toxicity equivalency

J or JT – the analyte was positively identified, the associated numerical value is the approximate concentration of the analyte in the sample

Table A-1. Screened existing data for arsenic, cadmium, mercury, cPAH, and dioxin/furan congeners.

LocationID	PSAMP_SP-1193	PSAMP_SP-363	PSAMP_SP-521	PSAMP_SP-1387	PSAMP_SP-1161	PSAMP_SP-491	PSAMP_SP-651
Date	6/17/2003 Q	6/19/2003 Q	6/19/2003 Q	6/19/2003 Q	6/19/2003 Q	6/5/2003	6/6/2003
Metals (mg/kg DW)							
Arsenic	4.72	16.2	15.3	4.11	11.9	5.85	2.97
Cadmium	0.72	1.72	1.55	0.18	0.94	0.42	0.21
Mercury	0.054	0.1	0.11	0.026	0.09	0.075	0.022
Carcinogenic Polycyclic Aroma	tic Hydrocarbons (μg,	/kg DW)					
Benzo(a)pyrene	13	37	31	5.9	32	30	3.7
Benzo(a)anthracene	12	28	20	4.1	27	34	3.7
Benzo(b)fluoranthene	17 J	42 J	43 J	8.6 J	43 J	43 J	4.5 J
Benzo(k)fluoranthene	18 J	35 J	31 J	7.4 J	29 J	34 J	4.8 J
Dibenzo(a,h)anthracene	3.3	9.3	7	1.7	8.2	8	1.3
Indeno(1,2,3-cd)pyrene	11	31	28	5.7	31	23	3
Chrysene	14	24	24	5.1	28	28	3.7
cPAH TEQ (1/2 DL)	20.53	53.9	46.3	9.2	48.6	44.48	5.5

Q – data qualifier U- the analyte was analyzed for but not detected TEQ – toxicity equivalency

J or JT – the analyte was positively identified, the associated numerical value is the approximate concentration of the analyte in the sample

Table A-2. Screened existing data for dioxin/furan congeners.

LocationID	DB-05-SD		DB-08-SD					
Date	10/2/2006	Q	10/2/2006	Q				
Dioxin/Furan Congeners (ng/kg DW)								
2,3,7,8-TCDD	0.079	U	0.0837	U				
1,2,3,7,8-PeCDD	0.175	U	0.292	Τ				
1,2,3,4,7,8-HxCDD	0.179	U	0.263	Т				
1,2,3,6,7,8-HxCDD	0.727	Т	1.06	Т				
1,2,3,7,8,9-HxCDD	0.422	Т	0.703	Т				
1,2,3,4,6,7,8-HpCDD	7.05		8.02					
OCDD	33.3		46.4					
2,3,7,8-TCDF	0.409	Т	0.547					
1,2,3,7,8-PeCDF	0.162	U	0.248	U				
2,3,4,7,8-PeCDF	0.131	U	0.248	U				
1,2,3,4,7,8-HxCDF	0.24	U	0.248	U				
1,2,3,6,7,8-HxCDF	0.0696	U	0.248	U				
1,2,3,7,8,9-HxCDF	0.0841	U	0.0452	U				
2,3,4,6,7,8-HxCDF	0.24	U	0.248	U				
1,2,3,4,6,7,8-HpCDF	1.35	Т	1.94	Τ				
1,2,3,4,7,8,9-HpCDF	0.153	U	0.128	U				
OCDF	2.35	Т	2.94	Т				
Dioxin/Furan TEQ (1/2 DL)	0.441		0.787					

Q – data qualifier U- the analyte was analyzed for but not detected TEQ – toxicity equivalency T – the analyte was detected, but below the PQL. J or JT – the analyte was positively identified, the associated numerical value is the approximate concentration of the analyte in the sample

Table A-3. Screened existing data for PCB congeners.

LocationID	DB-05-SD		DB-07-SD		DB-08-SD	
Date	10/2/2006	Q	10/2/2006	Q	10/2/2006	Q
PCB-001	0.00218	L	0.0068		0.00224	1
PCB-002	0.0101		0.0103		0.0136	
PCB-003	0.00271	L	0.00415		0.00252	
PCB-004	0.00363		0.00895		0.00392	
PCB-005	0.000428	U	0.00206	U	0.000912	U
PCB-006	0.00143		0.00526		0.00196	
PCB-007	0.000447	U	0.00349		0.000871	C
PCB-008	0.00852		0.0222		0.0122	
PCB-009	0.000502	U	0.00276		0.000945	U
PCB-010	0.000434	U	0.00112	U	0.000529	C
PCB-011	0.0111		0.0213		0.0221	
PCB-012/013	0.00171		0.00518		0.00247	
PCB-014	0.000454	U	0.00188	U	0.000832	C
PCB-015	0.0166		0.0123		0.0139	
PCB-016	0.0074		0.00791		0.00475	
PCB-017	0.00277		0.00799		0.00526	
PCB-018/030	0.0181		0.0154		0.0113	
PCB-019	0.00159	L	0.00158		0.000989	
PCB-020/028	0.03		0.038		0.0396	
PCB-021/033	0.00915		0.0185		0.0106	
PCB-022	0.0079		0.0111		0.0101	
PCB-023	0.000628	U	0.00193	U	0.000665	U
PCB-024	0.00134		0.000772	U	0.000338	U
PCB-025	0.00209		0.00293		0.00265	
PCB-026/029	0.00417		0.0066		0.00472	
PCB-027	0.000559	U	0.00126	L	0.0012	
PCB-031	0.0196		0.0237		0.0229	
PCB-032	0.00435		0.00425		0.00429	
PCB-034	0.000658	U	0.002	U	0.000678	U
PCB-035	0.00142		0.00212	U	0.00174	
PCB-036	0.000637	U	0.00184	U	0.00118	
PCB-037	0.0154		0.0115		0.0146	
PCB-038	0.000602	U	0.0019	U	0.000634	U
PCB-039	0.000668	U	0.00185	U	0.00062	U
PCB-040/041/071	0.01		0.0122		0.0118	
PCB-041	0.00212		0.00619		0.00198	
PCB-042	0.000529	U	0.00942		0.0083	
PCB-043	0.000953		0.00194	U	0.000885	L
PCB-044/047/065	0.0215		0.031		0.028	
PCB-045	0.00216		0.00502	L	0.00232	
PCB-046	0.000793		0.00154	U	0.00101	
PCB-048	0.00356		0.00938		0.00411	
PCB-049/069	0.0137		0.0188		0.0182	
PCB-050/053	0.00217		0.00384		0.00282	
PCB-051	0.000653		0.00128	U	0.000782	
PCB-052	0.0263		0.0386		0.0338	
PCB-054	0.000356	U	0.000518	U	0.000429	U
. 55 55 1	0.000000		0.000310		3.000723	

Table A-3. Screened existing data for PCB congeners.

rabie A-3. Screened existir						
LocationID	DB-05-SD		DB-07-SD		DB-08-SD	
Date	10/2/2006	Q	10/2/2006	Q	10/2/2006	Q
PCB-055	0.00059	U	0.00253	U	0.000755	U
PCB-056	0.0133		0.0149		0.0168	
PCB-057	0.000484	U	0.00207	U	0.000622	U
PCB-058	0.000537	U	0.00243	U	0.000735	U
PCB-059/062/075	0.000312	U	0.00262	L	0.00267	
PCB-060	0.00778		0.00702	L	0.00901	
PCB-061/070/074/076	0.0531		0.0588		0.0642	
PCB-063	0.00119		0.00179	U	0.00137	
PCB-064	0.0105		0.0112		0.0102	
PCB-066	0.0323		0.034		0.0412	
PCB-067	0.00117		0.00206	U	0.00136	
PCB-068	0.000472	U	0.00209	U	0.000635	U
PCB-072	0.000473	U	0.00207	U	0.000622	U
PCB-073	0.000314	U	0.00107	U	0.000355	U
PCB-077	0.0068		0.00545		0.00717	
PCB-078	0.000617	U	0.00238	U	0.000702	U
PCB-079	0.000676		0.002	U	0.000594	U
PCB-080	0.000516	U	0.00204	U	0.000615	U
PCB-081	0.000664	U	0.0023	U	0.000698	U
PCB-082	0.0058		0.00607	L	0.005	
PCB-083	0.00223		0.00168	U	0.00205	
PCB-084	0.00822		0.00923		0.00731	
PCB-085/116/117	0.00878		0.00935		0.00868	
PCB-086/087/097/108/119/125	0.0306		0.0311		0.0269	
PCB-088	0.000626	U	0.00194	U	0.000577	U
PCB-089	0.000568	U	0.00171	U	0.000501	U
PCB-090/101/113	0.0554	_	0.0487		0.0463	
PCB-091	0.00444		0.00468		0.00356	L
PCB-092	0.00951		0.01		0.00922	
PCB-093/098/100/102	0.000568	U	0.00162	U	0.000475	U
PCB-094	0.0006	U	0.0017	U	0.000506	U
PCB-095	0.0299		0.0291		0.0231	
PCB-096	0.000543	U	0.000564	U	0.0004	L
PCB-098	0.0011	L	0.00171	U	0.00049	U
PCB-099	0.0297		0.0301		0.0274	
PCB-102	0.000932		0.00129	U	0.00119	
PCB-103	0.000464	U	0.00128	U	0.000561	
PCB-104	0.000549	U	0.000496	U	0.000294	U
PCB-105	0.0264		0.0186		0.0243	
PCB-106	0.000471	U	0.00125	U	0.000372	U
PCB-107/124	0.00249		0.00125	U	0.00205	<u> </u>
PCB-109	0.00453		0.00323		0.00203	
PCB-110	0.0509		0.0487		0.0452	
PCB-111	0.000466	U	0.00116	U	0.000336	U
PCB-112	0.00049	U	0.00110	U	0.000395	U
. 55 112	0.00043	J	0.00123		0.000333	

Table A-3. Screened existing data for PCB congeners.

Table A-3. Screened existin		1 00		J.		
LocationID	DB-05-SD		DB-07-SD		DB-08-SD	
Date	10/2/2006	Q	10/2/2006	Q	10/2/2006	Q
PCB-114	0.00154		0.00111	U	0.00112	
PCB-115	0.000802		0.001	U	0.000303	U
PCB-117	0.00111		0.00135	U	0.00129	
PCB-118	0.0546		0.039		0.051	
PCB-120	0.000494	U	0.00126	U	0.000517	L
PCB-121	0.000434	U	0.00117	U	0.000344	U
PCB-122	0.000736	L	0.00125	U	0.000661	
PCB-123	0.00128		0.0012	U	0.00103	
PCB-126	0.000472	U	0.00135	U	0.000558	U
PCB-127	0.000529	U	0.00121	U	0.000349	U
PCB-128/166	0.0105		0.00992		0.0106	
PCB-130	0.00544		0.0032		0.00461	
PCB-131	0.000656	U	0.00114	U	0.000537	L
PCB-132	0.0191		0.0104		0.0114	
PCB-133	0.00102	L	0.0011	U	0.0011	L
PCB-134	0.00378	_	0.00226	L	0.00224	
PCB-135/151	0.03		0.0132		0.0142	
PCB-136	0.0104		0.00456		0.00539	
PCB-137	0.00146	L	0.00436		0.00359	
PCB-139/140	0.000855		0.00120	U	0.000921	
PCB-141	0.0138		0.00104		0.00487	
PCB-141	0.000719	U	0.00400	U	0.000487	U
PCB-143	0.000713	U	0.00128	U	0.000337	U
PCB-144	0.00048	0	0.00113	L		
PCB-144 PCB-145	0.00451	U	0.00149	U	0.00196 0.000278	U
		U		U		U
PCB-146	0.0148		0.00855		0.0115	
PCB-147/149	0.0652		0.0287		0.0341	
PCB-148	0.000642	U	0.00112		0.000323	
PCB-150	0.000374	U	0.000695	<u>U</u>	0.00029	<u>U</u>
PCB-152	0.000359	U	0.000672	U	0.000281	U
PCB-153/168	0.088		0.0432		0.0596	
PCB-154	0.00114	L	0.000999	U	0.00096	
PCB-155	0.000384	U	0.000638	U	0.000279	U
PCB-156/157	0.00866		0.00487		0.00641	
PCB-158	0.00752		0.00325		0.0045	
PCB-159	0.00131	L	0.00135	U	0.00053	U
PCB-160	0.00054	U	0.000948	U	0.000281	U
PCB-161	0.000496	U	0.000796	U	0.00025	U
PCB-162	0.000492	U	0.00124	U	0.000486	U
PCB-163/164	0.0914		0.0458		0.0668	
PCB-164	0.0047		0.0025		0.00256	
PCB-165	0.000575	U	0.000959	U	0.000303	U
PCB-167	0.0034		0.0018		0.0025	
PCB-169	0.00066	U	0.00155	U	0.000586	U
PCB-170	0.0225		0.00863		0.0122	

Table A-3. Screened existing data for PCB congeners.

LocationID	ationID DB-05-SD DB-07-SD DB-08-SD					
			DB-07-SD			_
Date PCB-171/173	10/2/2006 0.0075	Q	10/2/2006 0.0033	Q	10/2/2006 0.00411	Q
PCB-172	0.00441		0.0012	U	0.00241	
PCB-174	0.0259		0.0102		0.0118	
PCB-175	0.00177		0.00121	U	0.000876	
PCB-176	0.0028		0.00102	L	0.00149	
PCB-177	0.0172		0.00913		0.011	
PCB-178	0.00712		0.00291		0.00362	L
PCB-179	0.0143		0.00486		0.00657	
PCB-180/193	0.0558		0.0175		0.0224	
PCB-181	0.000894	U	0.00113	U	0.000524	U
PCB-182	0.000913	U	0.00116	U	0.000535	U
PCB-183	0.0154		0.00695		0.00816	
PCB-184	0.000597	U	0.000758	U	0.000419	U
PCB-185	0.00248		0.00112	U	0.000453	U
PCB-186	0.000571	U	0.000799	U	0.000435	U
PCB-187	0.0408		0.0209		0.0238	
PCB-188	0.000496	U	0.000622	U	0.000343	U
PCB-189	0.00109		0.00216	U	0.000731	U
PCB-190	0.00581		0.00163	L	0.00244	
PCB-191	0.00113		0.00102	U	0.000503	L
PCB-192	0.000965	U	0.00109	U	0.000527	U
PCB-194	0.0154		0.00678		0.00865	
PCB-195	0.00568		0.00235	U	0.00302	L
PCB-196	0.00828		0.00162	L	0.00383	
PCB-197	0.000667	U	0.000876	U	0.000481	U
PCB-198/199	0.0267		0.00772		0.0139	
PCB-199	0.00285		0.00153		0.00163	
PCB-201	0.00181		0.000946	U	0.000644	U
PCB-202	0.00409		0.00161	L	0.00302	
PCB-203	0.0117		0.00309		0.00657	
PCB-204	0.000776	U	0.000995	U	0.000601	U
PCB-205	0.000999		0.00166	U	0.000926	U
PCB-206	0.00812		0.00532		0.00774	
PCB-207	0.00123	U	0.00201	U	0.0014	L
PCB-208	0.00297		0.00203	U	0.00299	
PCB-209	0.0058		0.00524		0.00861	

U- the analyte was analyzed for but not detected

Appendix B. Field Forms

Appendix C. Health and Safety Plan

North Olympic Peninsula Regional Background Sediment Characterization Port Angeles, WA

Health and Safety Plan

Prepared for:



Toxics Cleanup Program 300 Desmond Drive Lacey, Washington 98504

Prepared by:



March 1, 2013

1.0 Introduction

This Site-Specific Health & Safety Plan (HASP) has been developed as part of the North Olympic Peninsula Regional Background sediment chemistry characterization. This plan is intended to incorporate sampling activities in support of the sediment collection, and must be reevaluated should project conditions change.

The procedures and protocols in this plan have been established to ensure that a mechanism is in place to address project personnel in the event that hazards from field work or site contamination are encountered during the project. This plan addresses typical on-site activities such as collection of contaminated sediment samples and marine vessel use. This HASP is not designed to replace existing procedures or to address all health and safety procedures that could be required during typical emergency response activities.

Compliance with this HASP is required from all authorized NewFields project personnel, project support personnel, and visitors who enter the work areas of this project. No field work will be conducted without meeting the requirements of this HASP.

The content of this HASP may change or undergo revision based upon unexpected field conditions, modifications to the technical scope of work or additional information made available to health and safety (H&S) personnel. Any proposed changes must also be reviewed and approved by designated NewFields personnel.

1.1 Project Location

The intent of the project is to characterize regional background sediment concentrations for the North Olympic Peninsula. The entirety of Port Angeles Harbor is currently under investigation for potentially impacted sediment quality. As a result, sediment collection efforts will be conducted in nearby Dungeness Bay, Sequim Bay, and Discovery Bay. In-water work will be conducted from the R/V *Kittiwake*.

1.2 Personnel and Emergency Contact Information

Table 1 lists relevant project personnel and local emergency contact information. Additional detailed emergency information is found in Section 6.0 along with written hospital directions and accompanying maps.

All project personnel, project support personnel, and visitors present during field work must sign in the space provided in Table 1 prior to initiating project work. A signature below indicates commitment to implement this plan and to ensure that project fieldwork is conducted safely. A signature below also indicates review and approval of the plan and agreement that the anticipated hazards are correct and that planned hazard controls are sufficient.

Table 1. Project Personnel and Local Emergency Contact Information

Project Manager, Tim Hammermeister (206) 890-8667 Field Manager, Will Hafner (425) 318-0420 Health and Safety Officer, Jasper Boas (425) 314-0977 WDOE, Connie Groven (360) 407-6254 Emergency Contact Information Sequim Police Department 911 or 360-683-	7227
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Emergency Contact Information Sequim Police Department 911 or 360-683-	7227
Sequim Police Department 911 or 360-683-	7227
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Fire Department 911 or 360-683-	1212
Sequim Fire and Rescue	4242
Ambulance 911	
Hospital:	
Olympic Medical Center (360) 417-7000	
939 Caroline Street	
Port Angeles, WA 98362	
Jefferson Healthcare (360) 385-2200	
834 Sheridan Avenue	
Port Townsend, WA 98368	
U.S. Coast Guard (360) 417-5800	
National Response Center (NRC) for Oil/Chemical Spills (800) 424-8802	
Poison Control Center (800) 222-1222	
Name Signature Date	

2.0 Health and Safety Personnel

The following section briefly describes the health and safety designations and general responsibilities for this project.

2.1 Project Manager – NewFields

The Project Manager or designee has overall executive responsibility for all activities and personnel on the site during all project activities described in this HASP.

2.2 On-Site Health and Safety Officer

The HSO is responsible for the development of safety protocols and procedures, pursuant to the all hazardous aspects of this project, implementation and enforcement of this HASP. The HSO has the authority to modify this HASP based on actual site working conditions and procedures. The HSO will also be responsible for the resolution of any outstanding health and safety issues which arise during the conduct of site work.

Health and safety-related duties and responsibilities will be assigned only to qualified individuals by the HSO. The HSO has stop-work authorization, which will be executed upon determination of an imminent safety hazard, emergency situation, or other potentially dangerous situation, such as extreme weather conditions. An Authorization to Proceed with work will be issued by the HSO after such action. The HSO or designee will initiate and execute contact with support facilities and personnel when this action is appropriate. The HSO may periodically conduct QA/QC surveys of the health and safety procedures implemented onsite.

3.0 Site and Project Description

Dungeness Bay, Discovery Bay, and Sequim Bay are located on the northern edge of the Olympic Peninsula along the shore of the Strait of Juan de Fuca in Clallam and Jefferson Counties, WA. The current investigation will involve sediment chemistry collection throughout these three bays to determine regional background concentrations of the analytes of concern.

3.1 Scope of Work

Under direction of the Washington Department of Ecology (Ecology), NewFields will conduct a sediment chemistry evaluation at locations throughout the Dungeness Bay, Discovery Bay, and Sequim Bay. The objective of the study is to determine regional background concentrations for selected contaminants that are representative Port Angeles Harbor. Sediment sampling is proposed at 60 locations spread throughout these three bays. A more detailed description of the scope of work and maps of the sample locations can be found in the Sampling and Analysis Plan (SAP).

Surface sediment samples will be collected for chemical analyses using a dual van Veen grab sampler deployed from the R/V *Kittiwake*, operated by Charles Eaton of Bio-marine enterprises. Hazards associated with grab sampling are primarily physical in nature. Slipping/tripping hazards are present on the sampling vessel when the deck is wet. There are numerous pinch points on the sampling equipment as well as the vessel itself. All personnel will be trained in the operation and deployment of the field gear, and will receive a vessel-specific safety briefing from Charles Eaton, owner and operator of the R/V *Kittiwake*. All members of the sampling crew will wear slip-resistant boots, safety glasses, nitrile gloves, personal flotation devices (PFDs).

Sediment samples will be processed on deck. Equipment decontamination includes potential contact with decontamination chemicals (Liquinox) and will be mediated by the use of nitrile gloves.

4.0 Hazard Assessment

This section summarizes hazards that may exist during project related tasks.

4.1 Task Specific Hazard Assessment

For the field sampling tasks described in Section 3, the overall hazard level is low. Hazards encountered during this sampling program are due to physical safety hazards associated with the field operations. Types of potential hazards associated with the field sampling effort are summarized in Tables 2. Potential hazards while working at the site include, but are not limited to, the following:

- Physical hazards from use of sampling equipment and operations on a vessel
- Physical hazards from working conditions (e.g., slips/trips/falls, drowning, hypothermia).
- Physical hazards from operating a motor vehicle to transit to and from the work site.

As described below, protective equipment and safe working procedures will help prevent accidents caused by these hazards. Exposure to harmful microbial organisms or other organisms in the sediments is not expected during this program.

Table 2. Sediment Sampling – Types of Potential Hazards

Physical Hazards				
Name of Physical Hazard		Source	Exposure Level/ Potential	Exposure Limit
Boating Operation	S	boat deck	Likely	N/A
Heat (ambient)		sun	Likely	N/A
Cold Weather Ope	erations	boat deck area	Likely	N/A
Heavy Manual Lif	ting/Moving	van Veen grab	Likely	N/A
Slips/Trips/Falls		boat deck area	Likely	N/A
Inclement Weather		boat deck area	Likely	N/A
Material Handling		sediment	Likely	N/A
Vehicular Travel		van shuttle	Likely	N/A
Working Over Wa	ter	boat deck area	Likely	N/A
Biological Hazards	S			
Name of Biological Hazard		Source	Exposure Level/ Potential	Exposure Limit
Insect bites and st	ings	boat area	Likely	N/A
Control Measures	Used			
Engineering Cont	rols:			
Level of PPE: D				
Location: on boat deck, stream/intertidal PPE Equipment: Chemical-resistant steel toe boots or waders, PVC Bib-style overalls (and jacket with hood as necessary), splash-proof safety goggles, nitrile gloves, PFD Type III. Long sleeve protective clothing and insect repellant is recommended during dusk and dawn to mitigate the risk of insect bites.				
-Frequent changes of disposable nitrile gloves -Wash hands and face with soap and water after each sampling event -Take shower at end of workday -Check extension cords are intact and connections are not in contact with wet surfaces.				

NA = Not applicable.

4.2 Physical Hazards

The following is a general discussion of the hazards that may be encountered on site. Information on any contaminants encountered during this project may be found in standard health and safety references, such as the NIOSH "Pocket Guide to Chemical Hazards." Internet site: http://www.cdc.gov/niosh/npg/npg.html

4.2.1 Sampling Vessel Operations

The physical hazards associated with the deployment and retrieval of sampling equipment result from their weight and the method of deployment. Only appropriate personnel whose presence is

required will be deploying and retrieving sampling gear. Under circumstances of potentially dangerous waves or winds, the field manager or boat operator will employ best professional judgment to ensure safe field operations.

To avoid injuries from slipping on wet surfaces, rubber boots or waders with appropriate tread will be worn when working on the work deck or loading/unloading heavy equipment from the vessel. No overhead gear will be deployed, however, hard hats will be worn if overhead hazards exist. Sample handling equipment, containers, deck lines, not in immediate use will be kept clear of walkways and work areas until needed. Each time operations at a given location have been completed, excess sediment on the deck will be washed overboard to prevent slipping, minimize personnel exposure to potentially contaminated sediment, and limit cross-contamination between sample locations.

Life vests will be provided for and worn by all personnel working on the deck, or as directed by the Site Safety Officer or vessel operator.

If someone falls overboard, maneuver the boat's stern away from him. Shift into neutral immediately (kill the motor if you do not have a gearshift) and throw a buoyant cushion or life jacket near the victim (try to get it close, but do not aim directly at the victim). Make sure you are well clear of the person in the water before shifting into gear again. Circle around quickly, selecting a course that will allow you to approach the person with the boat headed into the wind. Approach him slowly, taking care to come alongside and not over him. Stop the motor before attempting to get the victim aboard. When alongside, extend a paddle or boathook to him, or one end of a line. With the motor stopped, lead him around to the stern, where the freeboard is the lowest, if there is enough space at the transom for him to get aboard without contacting the motor. If this is not feasible, help the victim aboard over the side as far aft as possible. To avoid capsizing while the victim is coming aboard, other passengers should shift their weight to the opposite side to maintain trim as much as possible. When helping a person aboard, hold him under the armpits and lift gently.

4.2.2 Motor Vehicle Operation

Motor vehicles will be used to transport field personnel, equipment, and supplies to the sampling sites or laboratories. Only sampling team personnel with valid driver's licenses and liability insurance (per local state laws) will operate motor vehicles required for work activities. All field staff will use best professional judgment at all times to ensure safe operation of motor vehicles, including:

- Operators are to practice defensive driving and drive in a courteous manner
- Be aware of pedestrians and give them the right-of-way
- All vehicles are to be operated in a safe manner and in compliance with statutory traffic regulations and ordinances
- Verifying safety seat belts are in proper operating order
- Seat belts are to be worn by the driver and all passengers whenever the vehicle is in motion
- No persons are allowed to ride in the back of any vehicles, unless equipped with seatbelts
- Vehicles are to be driven in conformance with local speed limits
- Avoid excessively long driving periods

- Personnel who are impaired by fatigue, illness, alcohol, illegal or prescription drugs, or who are otherwise physically unfit, are not allowed to drive
- Personnel are to avoid using cellular phones or engaging in other distractions while driving
- Motor vehicle accidents are to be reported to the responsible law enforcement agency, the NewFields manager, and the NewFields HSO.

4.2.3 Weather

If severe weather occurs that may affect the safety of site workers, the NewFields PM or their designee shall stop affected field operations. The PM or their designee will resume operations when weather conditions improve to acceptable levels.

4.2.4 Heat and Cold Stress

Depending on the time of year and weather conditions, cold or heat stress may be a potential problem. The PM will ensure that the heat and cold stress programs are implemented and that adequate rest breaks and liquid (i.e., water, Gatorade) consumption occur.

Proposed work/rest schedules will be dependent upon the weather conditions encountered and the level of personal protective equipment being utilized by on-site personnel. The PM or designee will establish work/rest schedules prior to the commencement of the project tasks and will adjust as needed. Table 3 provides the suggested frequency for heat stress monitoring.

Table 3. Suggested Frequency of Physiological Monitoring for Fit and Acclimatized Workers

Adjusted Temperature	Normal Work Ensemble	Impermeable Ensemble
90° F (32.2°C) or >	After each 45 min of work	After each 15 min of work
87.5-90°F (30.8-32.2°C)	After each 60 min of work	After each 30 min of work
82.5-87.5°F (28.1 -30.8°C)	After each 90 min of work	After each 60 min of work
77.5-82.5°F (25.3-28.1°C)	After each 120 min of work	After each 90 min of work

4.2.5 Illumination

If work activities occur before sunrise and/or after sunset, lighting will be provided at each work area to meet the requirements of 29 CFR 1910.120(m). The Standard states that while any work is in progress, the general site areas shall be lighted to not less than 5 foot-candles; excavation, waste areas, access ways, active storage areas, loading platforms, and field maintenance areas shall be lighted to not less than 3 foot-candles; and first aid stations not less than 30 foot-candle.

4.2.6 Slip, Trip and Fall Hazards

As in any work area, it is expected that the ground may be uneven, the surface may be unreliable due to surface evenness, debris may be present, work is being performed on poly sheeting, and wet or muddy areas may exist. Therefore, the potential for slipping, tripping, and falling is present, especially considering that encapsulating suits and respiratory protection will which can impede vision. Severe trip hazards will be identified prior to commencement of project activities and demarcated by flags or caution tape.

4.2.7 Manual Lifting

Manual lifting of heavy objects such as coolers with samples may be required. Failure to follow proper lifting technique can result in back injuries and strains. Site workers will be instructed to use power equipment to lift heavy loads whenever possible and to evaluate loads before trying to lift them (i.e. they should be able to easily tip the load and then return it to its original position). Carrying heavy loads with a buddy and proper lifting techniques, 1) make sure footing is solid, 2) make back straight with no curving or slouching, 3) center body over feet, 4) grasp the object firmly and as close to your body as possible, 5) lift with legs, and 6) turn with your feet, don't twist, will be stressed. Back injuries are a serious concern as they are the most common workplace injury, often resulting in lost or restricted work time, and long treatment and recovery periods. In addition, hand digging for pipes may present lifting/ergonomic hazards.

4.2.8 Other Physical Hazards

Incorporating the following basic safety procedures can prevent many of the most common causes of injury or accident during field sampling:

- Implement good housekeeping practices, including immediate cleanup of spills and safe storage of all materials. All equipment or materials not in immediate use will be removed from the immediate work area.
- Use proper lifting and moving techniques to prevent back or muscle strain or injury. Any heavy equipment, boxes, coolers etc. should be tested before lifting and if it is too heavy, the equipment should be broken into smaller components or assistance requested. Lifting should be done with the legs, not the back.
- Use extra caution when handling sharp tools or sampling devices and when possible, wear protective gloves.

4.2.9 Biological Hazards

The project location is such that risks from biological hazards are low.

5.0 Work Clothing and Levels of Personnel Protection

5.1 Work Clothing and Personal Protective Equipment

The PM or designee will recommend appropriate levels of protective clothing to be worn in the event that hazardous materials are encountered. The sediment and water field sampling activities described in this site-specific HASP will be performed in Level D or modified Level D PPE, as specified in **Tables 2, 3, and 4**. If site conditions include hazards that exceed the protection of Level D or modified Level D PPE, work will be halted and personnel will immediately exit the area while site conditions and PPE levels are re-evaluated by the Site Supervisor and HSO.

Definition of Levels of Protection:

Level D: Work coveralls

Gloves

Appropriate work boots

Hardhat (if overhead gear is present)

Safety glasses with side shields or splash goggles as needed

A respirator is not required.

Level C: Chemical-resistant disposable coveralls

Chemical-resistant outer gloves Chemical-resistant inner gloves

Appropriate leather work boots with chemically resistant outer boots or

chemically resistant rubber boots

Hardhat

Full or Half face, Air Purifying Respirator (APR) with combination HEPA - P,O,N 100 (dusts, fumes, aerosols) and chemical cartridge as appropriate for

hazard.

Level B: Chemical-resistant disposable coveralls

Chemical-resistant outer gloves Chemical-resistant inner gloves

Appropriate leather work boots with chemically resistant outer boots or

chemically resistant rubber boots

Hardhat

Supplied air - air line or self-contained breathing apparatus (SCBA).

Level A: Fully encapsulating chemical-resistant/gas tight suit

Attached chemical-resistant outer gloves

Chemical-resistant inner gloves Attached chemical-resistant boots. Self-contained breathing apparatus.

5.2 Donning and Doffing

Manufacturers procedures for donning and removing PPE ensembles will be followed in order to prevent damage to PPE, reduce and eliminate migration from the work area and a transfer of contaminants to the wearer's body or others.

5.3 Storage and Inspection

Protective equipment will be stored and maintained in the company vehicles on site or in the work trailer. Items such as gloves, protective suits, and hearing protection will be kept within a suitable storage area. Table 4 lists PPE storage and cleaning procedures.

Employees are responsible for inspecting personal protective equipment prior to donning, during use and at the end of the shift. Defective equipment shall be removed from service and reported to the PM. All reusable equipment will be maintained in a sanitary condition, in accordance with the manufacturer's recommendations.

Table 4. Level D Storage and Cleaning Procedures.

Level D Storage Procedures:

In the Field laboratory, decontamination solutions such as nitric acid, methanol and acetone will be stored in dedicated cabinets and the outside doors labeled with flammable and acid labels respectively. Alconox soap powder does not require special storage and will be placed on a shelf. Any plastic containers containing Alconox will be labeled as such.

Level D Cleaning Procedures:

Cleaning procedures for PPE require that hard hats, nitrile gloves, rain gear, boots, and personal floatation devices be brushed thoroughly with a solution of Alconox and rinsed with tap water after each sampling event.

6.0 Emergency Plan

Emergency situations can be characterized as an accident or injury to the field personnel. Emergency phone numbers are listed in Section 1 of this Health and Safety Plan. In case of emergency, it is important that the following Incident Reporting Procedure be observed:

It is important to assure the rapid and accurate transfer of information appropriate personnel in the event of an emergency situation. To simplify the procedure, emergency situations can be reported by dialing 911. This includes incidents requiring police assistance, fire department, or medical emergencies.

Be sure to provide the following information to the dispatcher:

- 1. Caller full name
- 2. The nature of the incident (i.e. "Fire")
- 3. The location of the incident (i.e., "Street location and nearest intersection") The more specific the better.
- 4. What you need (i.e. "Fire Department and First Aid")
- 5. If you are able, where you will meet emergency responders (i.e. At end of West Street, near train tracks)
- 6. If applicable, a call back number or your cell phone number (e.g., "I'll be at the scene; my cell phone number is 123-4567").
- 7. Status of the situation. (e.g., is the situation stabilized or "I have the fire under control")
- 8. If anyone is injured or in need of emergency assistance (e.g., "A mechanic working on a pump was burned.")

6.1 Site Emergency Coordinator

Site Emergency Coordinator: Jasper Boas (HSO)

6.2 Personnel Injury

In the event of an emergency situation, the local emergency response group will be called. In case of a life-threatening situation, emergency first aid may be applied on-site as deemed necessary. The individual should be cleaned up and/or decontaminated and then transported to the nearest medical facility if needed.

The local rescue squad shall be contacted for transport as necessary in an emergency. Since some situations may require transport of an injured party by other means, transportation by automobile may be required.

6.3 Personnel Exposure Treatment

SKIN CONTACT: Use copious amounts of soap and water. Wash and/or rinse affected area thoroughly, then provide appropriate medical attention. Eyes should be thoroughly rinsed with water for at least 15 minutes.

INHALATION: Move to fresh air and, if necessary, decon/transport to hospital.

INGESTION: Decontaminate and transport to emergency medical facility.

PUNCTURE WOUND OR LACERATION: Decontaminate, if possible, and transport to emergency medical facility.

6.4 Hospital

The nearest hospitals are located in Port Angeles and Port Townsend. Olympic Medical Center in Pt. Angeles is the nearest hospital to Dungeness and Sequim Bays. Jefferson Healthcare in Pt. Townsend is the nearest hospital to Discovery Bay.

Port Angeles Hospital:

Olympic Medical Center

939 Caroline Street Port Angeles, WA 98362 (360) 417-7000

Port Townsend Hospital:

Jefferson Healthcare

834 Sheridan Avenue Port Townsend, WA 98368

Note: For non-emergency treatment, an urgent care clinic is located en route to the

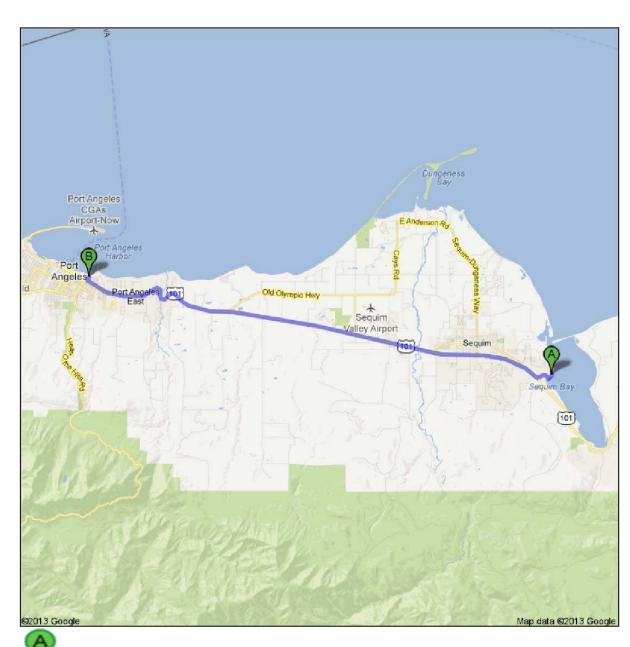
Port Angeles hospital:

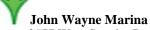
ClinicCare

621 E Front Street Port Angeles, WA 98362 (360) 452-5000

Directions to 939 Caroline St, Port Angeles, WA 98362

18.9 mi – about 26 mins





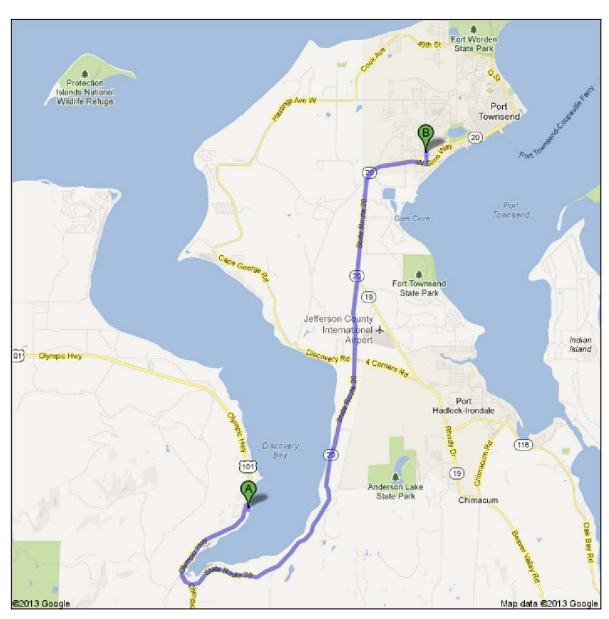
2577 West Sequim Bay Road, Sequim, WA 98382

1. Head south on W Sequim Bay Rd toward Whitefeather Way	go 0.2 mi
2. Take the 1 st right onto Whitefeather Way	go 0.5 mi
3. Turn right onto US-101 W	go 18.0 mi
4. Turn right onto N. Washington St.	go 0.1 mi

5. Turn left onto Caroline St. Destination on the left. 939 Caroline St, Port Angeles, WA 98362

Directions to 834 Sheridan St, Port Townsend, WA 98368

13.6 mi – about 22 mins





WorldMark Discovery Bay

141 Orcas Drive, Port Townsend, WA 98368

1. Turn left onto US-101 E/Olympic Hwy

go 2.2 mi

2. Turn left onto **WA-20 E** (signs for Port Townsend)

go 10.3 mi

3. At the traffic circles continue straight onto W. Sims Way/State Route 20 $\scriptstyle\rm E$

go 3.0 mi

4. Turn left onto Sheridan St., Destination on the right, 834 Sheridan St., Port Townsend, WA 98368

Appendix D. Background Memorandum

Characterizing Natural or Regional Background Populations for Washington Department of Ecology – Final Draft – February 18, 2013

1.0 Introduction

Washington Department of Ecology (Ecology) contracted with TerraStat Consulting Group to help identify statistical tools that could be used to distinguish between populations of Natural Background and Regional Background, as well as how to best summarize available data for background for the different objectives required under Sediment Cleanup programs. Statistical tools that can be used to separate a dataset into distinct populations with overlapping concentrations generally rely on either *a priori* description of the underlying characteristics for one of the populations so that separation of a mixture distribution can be accomplished; or data sets with sufficient spatial coverage such that the concentration surfaces can be modeled and locations where changes in the concentrations occur can be identified. Neither of these scenarios is met by the data that are generally available for Puget Sound background sites, so this work product ultimately became the description of a process for describing and generating appropriate summary statistics from existing Regional Background and/or Local Natural Background data sets.

TerraStat reviewed existing approaches to the description of Background that have been used by various agencies; these definitions and approaches are briefly touched on in **Section 2**. Knowledge from Ecology staff, from other agency approaches, and about the statistical tools appropriate for the type of data available for Puget Sound Background areas was integrated to describe a process for identifying and characterizing Background. A description of the process and important considerations to this process are included in **Section 3**; applications to three Puget Sound case studies are included in **Section 4**. Final recommendations regarding the description of Background are provided in **Section 5**.

2.0 Approaches to Background

TerraStat reviewed approaches to Background as described in USEPA guidance (US EPA 1995, US EPA 2002), and as used by WDOE for several local sites (summarized by NewFields 2011), by OR DEQ for the lower Willamette River, and by the ACOE for DMMP sites (DMMP 2011). These approaches all started with the *a priori* selection of the geographic boundaries that constitute background and then proceeded to summarize the background data set in different ways for different purposes.

Some working definitions of background in use by EPA in the CERCLA (Superfund) program (US EPA 2002) are "substances or locations that are not influenced by the releases from a site, and are usually described as naturally occurring or anthropogenic:

- 1) <u>Naturally occurring</u> substances present in the environment in forms that have not been influenced by human activity [matches Ecology's definition for 'Natural Background']; and,
- 2) <u>Anthropogenic</u> natural and human-made substances present in the environment as a result of human activities (but not specifically related to the CERCLA site in question)" [matches Ecology's definition of 'Regional Background'].

In the EPA documents reviewed, the background data set is not extracted and statistically separated from a larger dataset, but rather it is acquired via appropriate sampling within the

boundaries of the area expected to meet the background definition. EPA emphasizes that background sampling is a strategic, biased sampling event with sampling to occur "in areas expected to be outside the area influenced by the site." So information about the fate and transport of contamination from the site, as well as best professional judgment (BPJ) must be used to identify the background areas. It is also recommended that possible concentration outliers should be identified and decisions regarding these outliers be made by the project team (US EPA 2010).

The reviewed approaches used by Washington DOE, Oregon DEQ, and Puget Sound DMMP all define the geographic boundaries for the background population using BPJ and knowledge about the site, which is consistent with EPA's recommendations. Once the background population has been identified, the summary statistics suited to the intended application may be calculated (e.g., central tendency value such as 95UCL on the mean for exposure related questions, or an upper threshold of the distribution such as 90/90 UTL for a not-to-exceed value for station-by-station comparisons).

3.0 Background Considerations and Recommendations

As with any sampling or analysis plan, it is important to clearly state the objective up front. Sampling Objective: To characterize a "Background" population in order to set clean-up goals for a site, and to delineate site clean-up boundaries.

Caveats:

- Current DOE guidance utilizes several definitions of "Background", including Puget Sound-wide Natural Background, Local Natural Background, and Regional Background. The method(s) proposed herein will not separate the available data into these separate populations; but they will allow the proper estimation of summary statistics from whatever boundaries are considered to constitute the relevant background population.
- We provide no statistical recommendations for how to separate Local Natural from Regional Background –pattern matching requires knowledge of the source pattern; and existing sampling locations may be insufficient to adequately describe the spatial patterns needed to statistically identify boundaries of the different types of background.
- Identifying the site-influenced areas needs to be done first with site knowledge combined with spatial contouring. Areas near known point sources, or areas adjacent to those point sources with elevated concentrations, are excluded *a priori* from the possible background population. If there are obvious trends away from the site, then a boundary can be determined with the help of contour mapping.
- Methods to identify univariate and multivariate outliers should be used, and samples that are clearly different from the others should probably be excluded from the background population.

3.1 Designing a Sampling Plan to Characterize Background

The ideal situation where a new survey is designed specifically to characterize background involves first determining an appropriate boundary for the Local Natural or Regional Background area, and then taking a spatially-balanced random sample that uniformly covers the area using a systematic random sample (e.g., random samples within a grid). Other

methods for achieving a spatially-balanced random sample can also be used (e.g., generalized random tessellation stratified [GRTS] sampling used by US EPA [2011], and implemented via the RRQRR algorithm in GIS), but are not generally necessary for this situation. If there are areas that are found to have elevated concentrations and are suspected to be due to a point source, the boundary of the regional background area can be adjusted after sampling (i.e., the areas with high concentrations and their corresponding data can be excluded). If the gridded samples are found to be spatially autocorrelated, the gridded data points can be subsampled or methods that account for autocorrelation can be used to generate summary statistics. Otherwise, the set of samples taken on the grid can be assumed to be an independent random sample, and the appropriate summary statistics can be easily generated in ProUCL (for example).

3.2 Working With Existing Data to Characterize Background

The following recommendations address situations when compilations of existing data sets are being used to characterize background. In these cases, the "ideal" design may not have been used to generate the background data set, and the background area may have been sampled non-uniformly and non-randomly.

For the case studies examined in this report, sampling points were located unevenly through space and time, and collected for different purposes. In these case studies, the boundary of the characterized area is delineated by the locations of the existing samples and these existing sampling locations may be insufficient to fully characterize the background population. Within the compilation of data available to use for background, there may be non-randomness, non-independence, and more than one population represented. The simplest statistics (e.g., 95th UCL on the mean) assume an independently and identically distributed (i.i.d.) random sample. If the dataset violates these basic assumptions, then the simple statistics may be biased, and the variance poorly estimated. These basic assumptions are relevant to a number of available methods for summarizing data (i.e., bootstrapping, generating a trend surface via interpolation, kriging, etc.).

Given a data set consisting of multiple studies, there are three main steps to be followed to define a background concentration distribution and produce unbiased estimates of summary statistics. These are:

- <u>Step 1</u>. Delineate Background by excluding areas near known point sources, and areas suspected to be of a different population based on proximity to local influences (e.g., developed shorelines). Initial evaluation of the compiled data should include identification of possible outliers.
- <u>Step 2</u>. Determine the extent of autocorrelation and/or trend in samples from the background area.
- <u>Step 3</u>. Generate upper bound estimates for the regional background concentration distribution using an independent subset of the data based on the results from Steps 1 and 2.

3.2.1 <u>Step 1. Drawing Background Boundaries</u>

Unless new data are collected, the background population will be defined by the area that has been sampled. However, the sample locations should be examined to ensure that areas

near known point sources are excluded. In this stage it is also important to identify possible outliers indicative of an unsuspected source signal, potential mixture distributions due to the presence and blending of two or more strong and different local signals (e.g., Bellingham Bay), and to determine spatial gaps in the background data set. For example are there internal areas which have not been sampled, but which should be included in the background population? Is the existing boundary too limited, and more sampling is required? Or, is the existing boundary too broad, and should some areas with unusual contamination patterns be excluded until more information is available? If the samples were not all collected using a random or systematic random design within the total area (e.g., some samples were targeted to address questions regarding local sources), then adjustments to the data set are needed to reduce the risk of bias in the summary statistics from over-sampling sub-regions of the population. We recommend two possibilities for this adjustment: 1) adjust the boundary of the background population to be a union of circles surrounding each sampled point. If the circles do not overlap, the samples then comprise a systematic sample of the population thus defined. Or, 2) use a spatial interpolation method (e.g., kriging, or area weighted averaging) to estimate a concentration surface for a larger background boundary. There may not be enough data to accomplish the latter alternative, and the boundary for the former alternative may not be acceptable. In that case, more data must be collected. These two alternatives are discussed in more detail in Section 3.2.3.

3.2.2 <u>Step 2. Examine Trend Characteristics and Autocorrelation of Samples within the Background Data Set</u>

The presence of trends, differences in mean concentrations, and spatial autocorrelation within a data set require special attention. Ignoring trends or autocorrelation can result in biased estimates of population parameters and summary statistics that are not representative of the entire background population.

Spatial autocorrelation is important to identify so that only the independent samples may be used. Clusters of samples that targeted a particular sub-region of the background area should not be allowed to overly emphasize conditions of that sub-region in the description of the entire background area.

If there are concentration trends, or areas with clearly different concentrations (i.e., separate strata), these should be removed prior to estimating autocorrelation (i.e., autocorrelation is estimated from data that exhibit no trend and have a zero mean). In this report, a relatively simplistic approach to evaluating trends is used; an in-depth evaluation and description of a trend surface is beyond the scope of this report. For each case study in Section 4.0, several surface concentration models were used to evaluate potential trends in concentrations. Least squares polynomial surface models of orders 0 to 4 (i.e., from no trend up to a 4th order polynomial) were considered. (The total number of samples for the case studies is 26 to 27, which is probably too few for adequate fitting of the 4th order polynomial model. However, it is considered for illustration purposes.) The five polynomial regression models were compared using Aikake Information Criterion corrected for sample size (AIC_c, Burnham and Anderson, 2002). Note that the AIC_c is based on the maximum likelihood, which is a function of the residuals, and this metric may be somewhat compromised if autocorrelation is present in the residuals. For final trend models, the process is iterative – trend should be re-evaluated after autocorrelation is

removed. Autocorrelation is not expected to have a large effect on the trend evaluation in this context of these case studies, mainly due to limitations of the spatial distribution of the small data sets.

There are many methods for evaluating spatial autocorrelation (e.g., using GIS or other spatial statistics packages). The simple method used here could be done manually in MS Excel, or in R (R Development Core Team, 2011). The case studies do not have a regularly spaced grid of samples, so the boundary of autocorrelation is estimated by evaluating correlation among pairs of points within a certain distance of each other. An autocorrelation boundary can be estimated if there are a reasonable number of points that are close enough together to be autocorrelated. Pairs of sample points are grouped into bins of similar distances. For example, if there are at least six pairs of points within 200m of each other, the distance bins could be 0-200m, then 200-400m, etc. Theoretically, any existing positive autocorrelation would be highest in the first bin. The autocorrelation is estimated by Pearson's linear correlation coefficient between concentrations for all possible station pairs within a distance bin.

The presence of autocorrelation should be tested on the residuals from the best-fit trend model (i.e., the detrended data). The closest distance that could tested for autocorrelation was the smallest distance yielding at least six pairs. In spatial statistics literature, six is a small number of pairs on which to test the autocorrelation (e.g., Journel and Huijbregts, 1978), and is considered to be a bare minimum for a correlation test. For this small sample size, a significance test of the autocorrelation within each distance bin used $\alpha = 0.20$ in order to limit Type II errors (i.e., failing to reject the null hypothesis when autocorrelation is present). This binned hypothesis testing approach is useful given the data limitations (i.e., insufficient pairs of samples at sequentially increasing distances) and the objective of estimating the minimum distance between independent samples. If the data were to be used to estimate a kriged trend surface, then a smoothed autocorrelation function is required, where autocorrelation is described as a continuous function of distance.

3.2.3 Step 3. Calculate Summary Statistics

In the preceding two steps, the valid background samples and the background population boundary have been identified, along with potential trends and autocorrelations within the data set. At this point, we consider two methods for generating appropriate summary statistics in the presence of autocorrelation and/or trends:

Method 1. Adjust the background boundary to be simply the union of the set of independent circles (radius > autocorrelation range) surrounding the existing sampling locations, and treat samples from these independent circles as an independent data set; or

Method 2. Generate a concentration surface for the defined background boundary and use the surface for generating upper bound estimates (e.g., 95 UCL on the mean and 90/90 UTL).

For *Method 1*, the boundary of the background population is redefined to be exactly the area that has been independently and systematically sampled. This is simply a union of circles around each sampled point, with the radius of the circles greater than or equal to the autocorrelation range. Only one observation within each circle can be used, so that the data set is a uniform independent sample from the defined population. The radius can be larger than the autocorrelation range in order to make the background boundary larger, but

this may cause overlapping circles and require subsampling to maintain a uniform and independent systematic sample of the defined population. It also increases the uncertainty, because now a single observation is representative of a larger (unsampled) area, where the concentrations are unknown. If there are unsampled gaps among the sampled locations, these areas are not actually part of the background population as defined. Without information about whether the concentrations in the unsampled gap areas are homogeneous or trending, it is perhaps an overstatement of the available information to assert that the concentrations remain constant within these unsampled areas. Consequently, the background population as defined may not be contiguous.

Method 1 is a fairly simple and reasonable choice if the area that has been sampled reflects an adequate boundary for background. This method requires minimal assumptions, and does not extrapolate beyond, or interpolate between points.

Method 2 may be desirable if the area described by the union of circles around each sampled point is not acceptable, and more samples cannot be collected. For this method, a concentration surface is generated by kriging or another surface contouring method to estimate concentrations for the areas between the sampled points. Method 2 can be complex and requires more assumptions about the behavior of the data, but it is the only way to estimate concentrations across a broader boundary area. For example, if a large unsampled area is located between two areas of high concentrations, then the surface model would predict concentrations in that area to be similar to neighboring concentrations, rather than simply excluding that area from the described population. Uncertainty in the estimate of the concentrations in interpolated areas reflects prediction error from the model, so the upper bound on the mean for the total background area will quickly increase as you spatially interpolate or extrapolate beyond your data. This approach is not advisable when the data are sparse. Note that the simplest trend surface model would use Thiessen polygons to divide the area into polygons represented by one sampled point. This is a model that assumes constant concentrations within each polygon, and estimates of uncertainty are not readily available (although bootstrapping could be used).

3.2.3.1 Process for Estimating Summary Statistics from Existing Data Using Method 1

The autocorrelation distance *d* is defined to be the smallest distance between data points for which independence can be assumed. This distance may be derived from site-specific data, results from similar data sets in other areas, or best professional judgment (BPJ). To estimate background summary statistics using *Method 1*:

- a. Establish a sample boundary radius $r \ge d$. The larger the radius, the larger the boundary of the background area, but the smaller the overall sample size may be (only one sample per circle is permitted). There is a tradeoff between a large background area with high uncertainty and a smaller, perhaps non-contiguous background area with lower uncertainty.
- b. Identify all samples greater than *r* away from all other samples. These samples are assumed to be independent, random observations given our estimated autocorrelation range. If this captures all of the samples (i.e., only one sample per circle), then the existing data are i.i.d. random samples from the background

- population and summary statistics can be generated on this dataset, with no need to subset the data. Otherwise:
- c. Identify clusters that have two or more samples within r of each other. Permute all possible ways of selecting one or more independent samples (>r apart) from each cluster.
- d. Combine the samples from b) and c) to form all the possible combinations of samples from the data set that are > r apart from every other sample. For each of these permutations, generate summary statistics (mean, variance, 95 UCL on the mean, 90^{th} percentile, and 90/90 UTL).
- e. Use the distribution of each statistic (e.g., 95 UCL on the mean) to find the best summary statistic for the population (e.g., the maximum 95UCL on the mean will be most likely to capture the true background population mean). Each of the individual UCLs represents a slightly different background boundary, but each is a possible representation of the regional background. The permutation distributions of these summary statistics reflect part of the uncertainty in the background boundary. A highly variable distribution of background 95 UCLs indicates that different background boundaries can produce widely different results, an indicator of small-scale changes in concentration and the need, perhaps, for a re-evaluation of the first steps of the background boundary definitions (i.e., Steps a and b).

3.3 Sampling to Augment Existing Background Data

For existing background data sets, there are likely to be four features that could be improved by additional sampling: 1) temporal consistency; 2) spatial extent; 3) sampling density; and 4) sample size adequacy.

<u>Temporal consistency:</u> Placing new samples in the areas with outdated sample results may be a priority.

<u>Spatial extent</u>: For the spatial extent (boundaries) of the background population, BPJ is required to decide whether the outer boundaries are sufficient to fully capture the target background conditions. Addressing the boundary question uses BPJ and possibly geophysical modeling information about the mechanisms distributing the sediments throughout the area from anthropogenic contributions (e.g., what are the boundaries of influence from non-point source runoff) or natural sources (e.g., what are the boundaries of influence from river sediments).

Sampling density: If the sampling locations are sparsely distributed, then the union of overlapping circles for the point locations sampled may not result in a contiguous background area. Large unsampled or under-sampled areas within the background area should be sampled to reduce uncertainty. Existing data may indicate that trends are present, so sampling at fairly regular intervals along that trend is recommended. Bathymetry and hydrologic flow patterns provide information about sedimentation or disturbance patterns. This information can be used to identify areas within the background population that have potentially different contamination levels, and where additional sampling is recommended.

Overall Sample Size: If more data are needed to satisfy one or more of the three features described above, grid sampling is recommended. The minimum grid size should be d (the autocorrelation range). The actual grid size will be determined by budget in most cases, but sample sizes needed for a desired estimate of precision can be estimated using existing data. These calculations, however, assume that additional samples will have the same mean and variance as the existing data, which may not be a valid assumption when sampling from a patchy distribution or a trending surface. At best it provides an informed guess regarding the change in precision of the mean estimate (i.e., width of the 95UCL on the mean) with additional samples.

4.0 Case Study Examples

Ecology provided dioxin/furan TEQ concentrations (ng/kg, dry weight) for three case study sites: Fidalgo Bay, Port Gardner, and Bellingham Bay. For each of these case studies, we illustrate the process of defining the regional background boundaries, evaluating concentration trends in the data, estimating the autocorrelation distance, and using Method 1 (Section 3.2.3.1) to estimate upper bound summary statistics.

4.1 Fidalgo Bay Case Study

Ecology staff used BPJ to identify samples that were too near to point sources, or were from a different area-of-influence and therefore considered to be inappropriate for comparison to Fidalgo Bay Site concentrations. The sampling locations are shown in Figure 1; the grid overlaid on the map is a 0.5 km square grid used simply to illustrate the scale of the distance between samples. The latitude and longitude for the sampling locations and their associated TEQ concentrations (ng/kg, dry weight) are provided in Appendix Table A-1.

4.1.1 Trends and Autocorrelation in Fidalgo Bay

The first step in estimating the autocorrelation range is to remove any existing trends that may be present in the samples. For the Fidalgo Bay data set the first-order polynomial (i.e., a linear trend) fits the trend surface best (indicated by the lowest AICc for all trend surface models considered). There appears to be a linear increasing trend to the northwest (Figure 2).

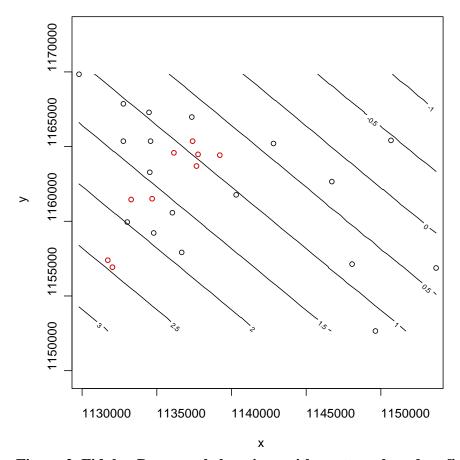


Figure 2. Fidalgo Bay sample locations with contours based on first-order polynomial fit. Samples that are <460m from other samples are highlighted in red.

The maximum distance between the six closest pairs of points in Fidalgo Bay is approximately 460m apart, so bin sizes are set to multiples of 460m. The data points within the first distance bin are highlighted with a different color in Figures 1 and 2. A distance of 460 m is the smallest autocorrelation range that we can test with these data. There may be autocorrelation present at smaller distances, but we cannot test whether the correlation is significant because of insufficient numbers of data pairs available for that distance. The correlation results after removing the linear trend from the data are shown in Table 1.

Table 1. Autocorrelation Results for Fidalgo Bay.

			one-tailed
		Pearson's	p-value for
		Correlation	parametric
Bin Endpoints (m)	N	Coefficient	test
0-460	6	0.338	0.512
460 – 920	33	0.246	0.168
920-1380	42	0.0894	0.573
1380 – 1840	59	-0.00570	n/a

The autocorrelation coefficient decreases with distance (Table 1). The autocorrelation in the first bin is not significantly different from zero (α =0.20). Sample sizes after the first bin increase dramatically, so it is appropriate to use a lower α -level to assess significance in the second bin (e.g., α =0.10 or 0.05), from which we would conclude that the autocorrelation is not significantly different from zero in this distance range (460 – 920 m). We varied the size of the first bin, and the autocorrelation was evaluated for pairwise distances from zero to increasingly larger maximum distances, up to 914m, but no strong correlations were seen at any of these distances. There are insufficient samples close to each other to estimate autocorrelation less than 460m. There may be autocorrelation at smaller ranges, but it is not a testable hypothesis on this dataset, so we could assume that the data set is roughly uncorrelated at the distances that were sampled. However, we don't want to underestimate autocorrelation, so we also compare the estimation results by subsampling the data (*Method 1*, Section 3.2.3.1) based on a minimum separation distance of approximately 460m (for convenience we round up to 500m).

4.1.2 Method 1 Applied to Fidalgo Bay

Subsets of independent samples were generated from the full data set, as described above. The autocorrelation range used in this approximation was 500m.

There were 27 samples from acceptable non-site affected stations in Fidalgo Bay. Of these 27 samples, 15 were more than 500m away from any other samples. The remaining 12 samples were grouped into three clusters of two or more samples each. All permutations were constructed of independent samples within each of these clusters and combined with the other 15 samples (24 possible permutations). For each of the permutations, summary statistics for TEQ values were generated (i.e., mean, variance, bootstrapped 95 UCL on the mean, and 90/90 UTL for the best fit gamma distribution). The distributions of these TEQ summary statistics are shown in Figure 3. The red lines indicate the values calculated by assuming that the data are uncorrelated at the distances that were sampled (i.e., we have an independent data set). We can see that the full data set (n=27) produced a 95 UCL on the mean (1.55 ng/kg TEQ) that was lower than some of the permutations. For the permutations, 95UCL values range from 1.4 to 1.8 ng/kg TEQ. For the 90/90 UTL, permutation values ranged from 2.5 to 3.6 ng/kg, and the observed data had a TEQ value of 3.1 ng/kg.

4.1.3 Fidalgo Bay Conclusions and Recommendations

The trend surface regression models indicate a linear trend in Fidalgo Bay background concentrations. For this case study, the observed data can be used to estimate background population characteristics as is, or, to ensure independence, after the data have been subsampled to generate a set of independent observations using the autocorrelation range (at 500 m). From the permutation distribution of UCLs, we could choose the maximum value (1.9 ng/kg) as this is the value most likely to capture the true mean, even though the coverage will likely exceed 95%.

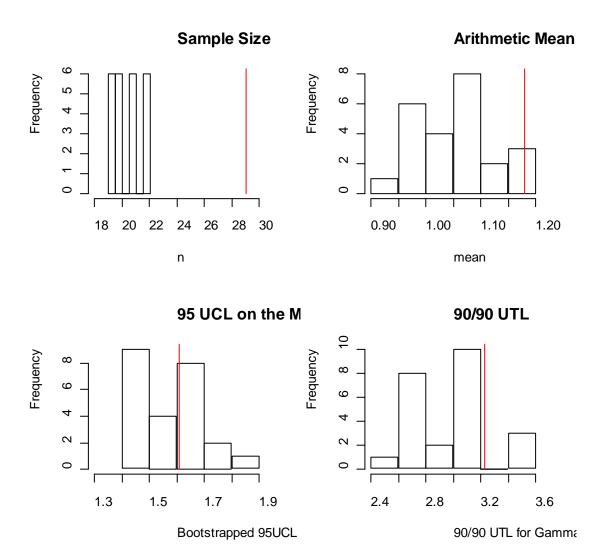


Figure 3. Distribution of summary statistics on TEQ values (ng/kg, dry wt) for the permutations of independent samples (>500m) at Fidalgo Bay. The red lines indicate the values for the observed data set.

For sample adequacy, we consider the following:

Temporal consistency: The data within background areas are collected from 2007 and 2010, so time period is probably not an issue and all these data are useable.

Number of samples: The existing data are not significantly different from a gamma distribution (ProUCL, alpha=0.05). We plot the number of samples vs. the width of the gamma confidence interval on the mean (Figure 4). The figure shows that our sample size of 27 provides a UCL width that is 37% of the mean; we're not on the steepest part of the curve but are on a part of the curve where it's starting to flatten out for our sampled population. Doubling the sample size is expected to decrease the UCL halfwidth to 24%, assuming that the mean and the variance stay the same. This assumption may not be realistic given that there is a trend in these data – samples collected from a different area will affect both the mean and the variance, so this graph provides simply a ballpark estimate of expected sample size adequacy.

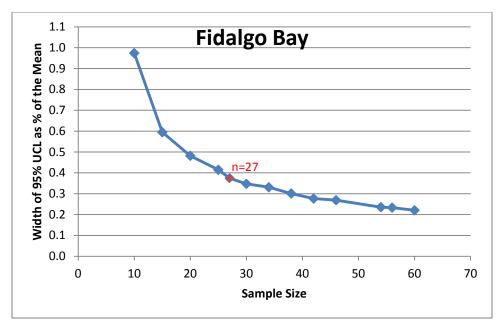


Figure 4. Sample size vs. precision of the mean using Fidalgo Bay data, fit using a gamma distribution.

<u>Spatial Extent</u>: The best trend surface was a 1st order polynomial, decreasing to the northwest away from the Anacortes shoreline. Currently, most of the samples are closer to Anacortes in Fidalgo Bay, so these might describe Regional Background, whereas samples in Padilla Bay describe Local Natural Background, for example. There are rather few samples in Padilla Bay, so if this area is included as part of Regional or Local Natural Background, it would be wise to place more samples on that side of the Bay. <u>Sampling Density</u>: Based on the autocorrelation range test, we recommend samples no closer than 500m apart (rounding up from 460m). This minimum spacing is expected to achieve independent samples. Any new samples would be placed as evenly as possible within the desired boundaries for the background population, and at least 500m away from any other new or existing samples.

- Option #1: Spatial extent for regional background is a line drawn from Anacortes west to Hat Island and south to March Point (?). Take 5-10 more samples within any of the available grid squares, trying to achieve uniform distribution of samples throughout the area and minimum separation between samples of 500m. Pros: this provides a good spatial coverage within the delineated regional background of Fidalgo Bay. Cons: none, assuming that the boundary for background is sufficient.
- Option #2: Include Padilla bay in the Background characterization. Pursue Option #1, plus additional 5-10 samples from Padilla Bay. Use a grid approach to try to achieve a uniform distribution throughout the area with minimum separation of 500m. Pros: larger background area; provides data to test if Padilla Bay is a separate population. Cons: The higher cost over Option #1 may not be necessary; the shallower depths and the large Intertidal areas in Padilla Bay may make this an inappropriate background data set for the subtidal sites in Fidalgo Bay.

Option #3: Include Padilla Bay in the Background characterization, and fill as many squares as possible in both Fidalgo and Padilla Bay, increasing the grid size to 1km (we exchange small scale accuracy for broad scale information). Pros:
 More information about both areas and a dataset that may be sufficient for drawing a surface contour map. Cons: Cost and potentially sampling overkill.

4.2 Port Gardner Case Study

Ecology staff used BPJ to identify samples that were too near to point sources, or were from a different area-of-influence and therefore considered to be inappropriate for comparison to Port Gardner site concentrations. The sampling locations are shown in Figure 5; the grid overlaid on the map is a 0.5 km square grid used simply to illustrate the scale of the distance between samples. The latitude and longitude for the sampling locations and their associated TEQ concentrations (ng/kg, dry weight) are provided in Appendix Table A-2.

4.2.1 Trend and Autocorrelation in Port Gardner

For the Port Gardner data set, the trend surface is best fit by the third order polynomial (the model with the lowest AICc; Figure 6).

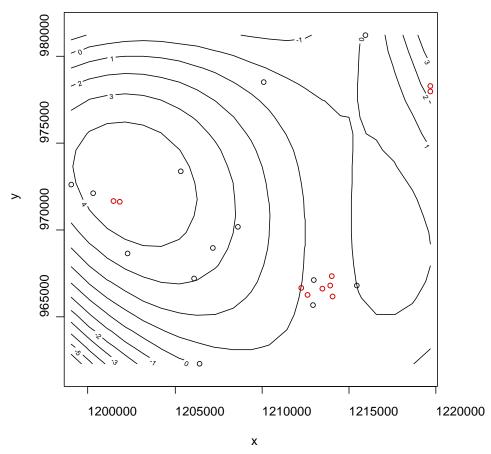


Figure 6. Port Gardner sample locations with contours based on third-order polynomial fit. Samples that are <200 m from other samples are highlighted in red.

The maximum distance between the six closest pairs of points is 200m, so the bin sizes were set to multiples of 200 m. The autocorrelation results are shown in Table 2.

Table 2. Autocorrelation Results for Port Gardner data.

			one-tailed
		Pearson's	p-value for
		Correlation	parametric
Bin Endpoints (m)	N	Coefficient	test
0-200	6	0.735	0.048
200-400	15	-0.261	n/a
400-600	15	-0.0598	n/a
600-800	5	-0.300	n/a

With the polynomial trend removed, there is evidence that samples within 200m of each other are still correlated. We are limited by the number of samples and the distances among them in our estimation process of the autocorrelation range. The data indicate that samples within 200m of one another should not be treated as independent samples. The minimum distance for independence is at least 200m. Samples between 200m and 400m apart were not correlated, though this appears to be strongly influenced by a single elevated sample in the cluster of stations near Weyerhaeuser (the cluster of stations close to shore in Figure 5). 4.2.2 Method 1 applied to Port Gardner

4.2.2 <u>Memoa i appuea to i ori Garaner</u>

Subsets of independent samples were generated from the full data set, as described above. The autocorrelation range used in this approximation was 200m. There were 26 samples from acceptable non-site affected stations in Port Gardner. Of these 26 samples, 17 were more than 200m away from any other samples. The remaining nine samples were grouped into four clusters of two or more samples each. All permutations were constructed of independent samples within each of these clusters and combined with the other 17 samples (24 possible permutations).

There were a few samples that were just beyond 200m apart, so we also calculated results for autocorrelation range of 305m. For this range, there were 14 samples more than 305m away from any other samples. The remaining 12 samples were grouped into four clusters of two or more samples each, and all permutations were constructed of independent samples within each of these clusters and combined with the other 14 samples (28 possible permutations).

Sample sizes ranged from 18 to 20 for the permutations at 305m distance; and were always 21 for the permutations at 200m distance. Arithmetic mean values were higher for the 305m distance: ranging from 1.86 to 2.01ng/kg TEQ compared to a range of 1.77 to 1.84 ng/kg TEQ for the 200m distance. The distributions of the 95UCL and the 90/90 UTL values for the TEQ of these two sets of permutations are shown in Figure 7. The larger values for the 305m distance partially reflects the smaller sample size (even for an identical distribution, a smaller n generates a larger UCL and UTL because of the greater uncertainty). But the larger values in the 305m distance permutations also indicate the presence of some small scale spatial variability, as observed in the tight cluster of samples near Weyerhaeuser (the cluster of stations close to shore in Figure 5).

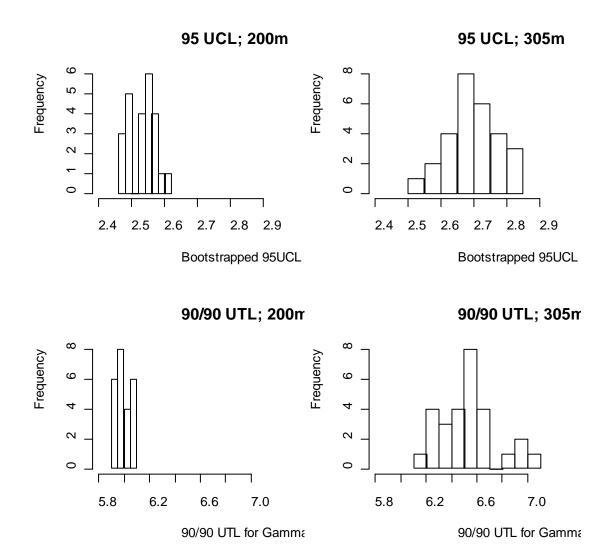


Figure 7. Distribution of 95UCL and 90/90 UTL for TEQ values (ng/kg, dry wt) for the permutations of independent samples in Port Gardner using 200m autocorrelation range (left side), or 305m autocorrelation range (right side).

4.2.3 Port Gardner Conclusions and Recommendations

The autocorrelation investigation and the trend surface regression models indicate that there is trend and/or patchiness in Port Gardner background concentrations of TEQ values (ng/kg, dry weight). Using an independent subset of the existing data will describe the area sampled (the union of the circles around our points sampled), but there are large areas un-sampled with uncertainty about what concentrations might be found there. The differences in the results for the autocorrelation range of 200m vs. 305m indicate the patchy nature of TEQ concentrations in at least some of the areas (although this could only be tested for the dense sample cluster near Weyerhaeuser). This means that interpolation could lead to erroneous conclusions about area averages.

For sample adequacy, we consider the following:

<u>Temporal consistency:</u> The data within background areas are collected from 2004 to 2010. The data from 2004 are all from the Weyerhaeuser sampling, which were also found to be highly influential in the subsetting exercise. Additional sampling in this area may be desirable to describe more current conditions in the area.

<u>Number of samples:</u> The existing data are bimodal, and are not well fit by any parametric distribution (ProUCL). For this data set we can't generate any assumptions about sample size adequacy.

Spatial Extent: The best trend surface was a 3rd order polynomial, indicating patchiness with low concentrations near Weyerhaeuser; higher concentrations near the DMMP disposal site. This site would benefit from additional samples placed out beyond the DMMP disposal site (to see how far out those concentrations extend), and the area between Jetty Island and the disposal site. It may also be desirable to sample the area north and northwest of the current northern boundary of the existing data in order to capture what influence the Snohomish River may have on the bay concentrations.

Sampling Density: Based on the autocorrelation tests, we recommend samples at least 400m – 500m apart. This sampling interval will miss some of the small scale spatial variability that is present, but would allow efficient description of a larger area. In addition, a grid spacing of 500m is expected to achieve independent samples. Any new samples would be placed as evenly as possible within the desired boundaries for the defined background population, and at least 500m away from any other new or existing samples.

- Option #1: Modify the spatial boundary for <u>regional background</u> to exclude everything north to northwest of the line drawn from the southern point of Jetty Island out into Possession Sound. Take at least 10 more samples within any of the available grid squares (500m grid), trying to achieve uniform distribution of samples throughout the area and minimum separation between samples of 500m.
 <u>Pros:</u> A smaller boundary allows a greater sampling density within the area considered representative of regional background. Excluding the areas on the Snohomish River delta may be justified if the project locations are not heavily influenced by the river. <u>Cons:</u> the spatial boundary may be too limited.
- Option #2: Modify the spatial boundary to exclude the deeper subtidal areas, and include only the areas strongly influenced by the Snohomish River. Pros: A smaller boundary allows a greater sampling density within the area considered representative of local background. Excluding the areas outside of the Snohomish River influence may be justified if the project locations are primarily influenced by the river. Cons: the spatial boundary may be too limited.
- Option #3: Combine Options 1 and 2 to describe a larger background area. Sample in as many grid squares as is affordable, increasing the grid size to 1km (exchange small scale accuracy for broad scale information). Try to achieve a uniform distribution throughout the area and minimum separation between all new and existing data of 0.5-1km. Pros: A broader area is defined that allows the description of an overall background average; if separate populations are present

near the mouth of the Snohomish River vs. subtidal Possession Sound, it may be apparent by these data. Cons: Cost.

4.3 Bellingham Bay Case Study

Ecology staff used BPJ to identify samples that were too near to point sources, or were from a different area-of-influence and therefore considered to be inappropriate for comparison to Bellingham Bay site concentrations. The sampling locations are shown in Figure 8; the grid overlaid on the map is a 0.5 km square grid used simply to illustrate the scale of the distance between samples. The latitude and longitude for the sampling locations and their associated TEQ concentrations (ng/kg, dry weight) are provided in Appendix Table A-3.

4.3.1 <u>Trend and Autocorrelation in Bellingham Bay</u>

For the Bellingham Bay data set, the second-order polynomial provides the best fit (the model with the lowest AICc) for the trend surface model (Figure 9).

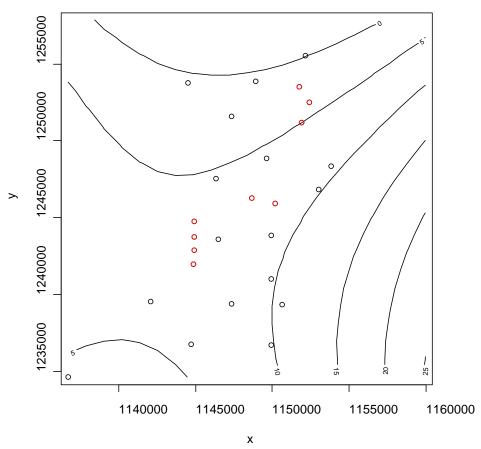


Figure 9. Bellingham Bay sample locations with contours based on second-order polynomial fit. Samples that are <472 m from other samples are highlighted in red

The maximum distance between the six closest pairs of points is 472m, so the bin sizes are set to multiples of 472m. This is the smallest autocorrelation range that we can test with these data. There may be autocorrelation present at smaller distances, but we cannot test

whether the correlation is significant because of insufficient numbers of data pairs available for that distance. The correlation results after removing the trend from the data are shown in Table 3.

Table 3. Autocorrelation results for Bellingham Bay data.

			one-tailed
		Pearson's	p-value for
Bin Endpoints		Correlation	parametric
(m)	N	Coefficient	test
0 - 472	6	0.315	0.543
472 - 945	23	-0.118	n/a
945 - 1416	41	-0.0704	n/a
1416 - 1890	42	-0.218	n/a

There is no evidence of autocorrelation in the 0-472m range. There may be autocorrelation at smaller ranges, but it is not a testable hypothesis on this dataset, so we could assume that the data set is roughly uncorrelated at the distances that were sampled. However, we don't want to underestimate autocorrelation, so we also test the estimation results by subsampling the data based on a minimum separation distance of 472m (round up to 500m).

4.3.2 Method 1 applied to Bellingham Bay

Subsets of independent samples were generated from the full data set, as described above, using an autocorrelation range of 500m, slightly larger than the smallest autocorrelation range that could be tested.

There were 26 samples from acceptable non-site affected stations in Bellingham Bay. Of these 26 samples, 16 were more than 500m away from any other samples. The remaining ten samples were grouped into three clusters of two or more samples each. All permutations were constructed of independent samples within each of these clusters and combined with the other 16 samples (12 possible permutations). The distributions of summary statistics for these permutations are shown in Figure 10. The red lines indicate the values calculated by assuming that the data are roughly uncorrelated at the distances that were sampled. We can see that the full data set (n=26) produced a lower 95 UCL on the mean (7.3 ng/kg TEQ, dry weight) than some of the random permutations. For the permutations, 95UCL values range from 7.0 to 7.7 ng/kg TEQ. For the 90/90 UTL, permutation values ranged from 14.5 to 15.9, and the observed data had a value of 14.6 ng/kg TEQ.

One of the clusters of samples had substantial variability in the reported TEQ values: 1.5, 1.6, and 6.3 ng/kg. The first two concentrations were reported for samples from the 0-12cm horizon; the last for a sample from the 0-55cm horizon. This was the only sample included in this background data set that was collected beyond the 0-12cm depth horizon. Permutation results excluding this deeper horizon sample had 95 UCL values ranging from 7.0 to 7.4 ng/kg, and 90/90 UTL values ranging from 14.5 to 15.3 ng/kg. So, this sample definitely had an effect on the upper range of the estimates, but it's unknown whether it reflects greater contamination at depth or overall small scale spatial variability in surface concentrations.

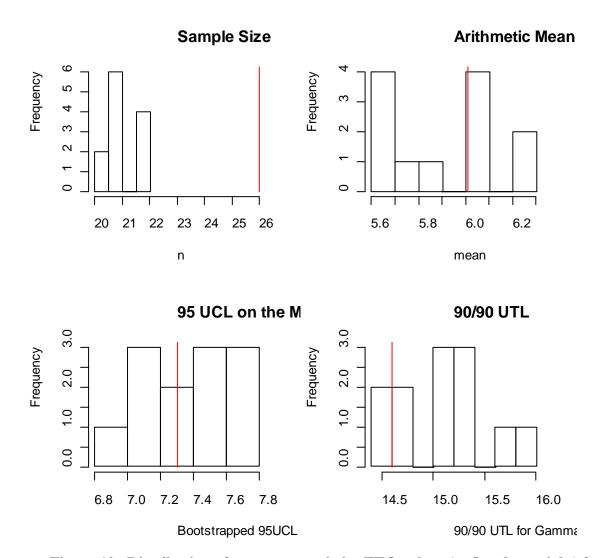


Figure 10. Distribution of summary statistics TEQ values (ng/kg, dry weight) for the permutations of independent samples (>500m) at Bellingham Bay. Red lines indicate the values for the observed data set.

4.3.3 Bellingham Bay Conclusions and Recommendations

The trend surface regression models indicate that there is significant trend in Bellingham Bay background concentrations. The autocorrelation investigation indicated that the data could be considered independent as sampled, but there are large areas un-sampled with uncertainty about what concentrations might be found there.

Given the strong appearance of trends, and potentially two competing trends (one from the southern shoreline of Bellingham Bay, and another from the Nooksak River in the north), this site would benefit from additional samples. Where the boundary is drawn depends on BPJ regarding the relevance of the Nooksak River influence on the Regional Background concentrations. An independent sampling interval would be 500m, but the large area that needs to be sampled justifies using a larger sampling interval (e.g., 1000m) if needed.

For sample adequacy, we consider the following:

Temporal consistency: The data within the background area are collected from 2007 to 2010, so time period is probably not an issue and all these data are useable. Number of Samples: The existing data are not significantly different from either the normal or the gamma distributions (ProUCL, alpha=0.05). For this sample size calculation, we use the gamma distribution because it allows for more potential skewness in the distribution and a more conservative sample size calculation. We plot the number of samples vs. the width of the gamma confidence interval on the mean (Figure 11). The figure shows that our sample size of 26 provides a UCL width that is 32% of the mean for the area sampled; we're close to the part of the curve where it's starting to flatten out for our sampled population indicating incrementally smaller advantage from each additional sample. Doubling the sample size is expected to decrease the UCL half-width to about 20%, assuming that the mean and the variance stay the same. This assumption may not be realistic given that there is a trend in these data – samples collected from a different area will affect both the mean and the variance, so this graph provides simply a ballpark estimate of expected sample size adequacy.

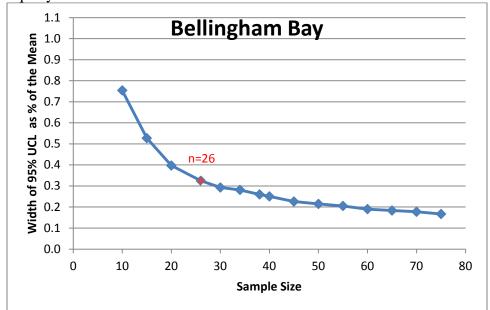


Figure 11. Sample size vs. precision of the mean using Bellingham Bay data, fit with a gamma distribution.

<u>Spatial Extent</u>: The best trend surface was a 2nd order polynomial, showing a strong trend decreasing away from the Bellingham shoreline along the SE portion of the Bay, and a weaker trend that decreases approaching the northern portion of the Bay and the Nooksak River delta. Where the boundary for background is drawn depends on BPJ regarding the relevance of the Nooksak River influence on the Regional Background concentrations.

<u>Sampling Density</u>: Based on the autocorrelation tests, we recommend samples no closer than 0.5km apart to get a data set of independent samples.

• Option #1: Draw the spatial boundary to be just outside of the existing sampling locations, and take an additional 10 samples within any of the available 500m grid

squares within that boundary. As much as possible try to achieve spatial evenness, and a minimum separation of 500m. <u>Pros:</u> Maximizes the use of the existing data and fills some data gaps for this background boundary. <u>Cons:</u> If the northern area influenced by the Nooksak River is more of a local natural background, this data set will be a combination of two blending populations.

- Option #2: Draw the spatial boundary to exclude some of the existing locations in the northern portion of the bay where the Nooksak River may be influencing concentrations. Take an additional 10 samples within any of the available 500m grid squares within this area, trying to achieve spatial evenness and a minimum separation of 500m. Pros: Same cost as Option 1, but a smaller boundary allows a greater sampling density within the area considered representative of regional background. Excluding the areas of the bay with strong Nooksak River influence may be justified if the project locations are more strongly regionally influenced similar to what's found in the southern portion of the Bay. Cons: the spatial boundary may be too limited (encompasses an area generally within 3km of the shoreline) and therefore may be focused too much on the upper concentration end of the trend.
- Option #3: Draw the spatial boundary further out into the Bay to try to identify where the two trends meet. The grid size could be increased to 1km (exchange small scale accuracy for broad scale information). Try to achieve a uniform distribution throughout the area and minimum separation of 0.5-1km. Pros: A broader area is defined that allows better understanding of the two local influences (i.e., the river and the urban area), and therefore a better description of an overall background average. Cons: Cost, and sampling overkill if the regional background is what's needed for project comparison.

5.0 General Recommendations

The approach used by agencies (US EPA, OR DEQ, WA DOE, and ACOE) for describing background involves the initial definition of the population. Given a narrative description of Regional Background, or Local Natural Background, the spatial boundaries for the appropriate background are a site-specific question and must be drawn using existing data from the area, information about fate and transport of contamination from the site, regional influences, as well as best professional judgment.

Once the data within the presumed background area have been compiled, it is fairly simple to fit a selection of modeled trend surfaces, and look for autocorrelation in the residuals. The trend surface provides some information about spatial variability and local patchiness in the concentrations, which can assist in helping determine the best locations for additional sampling. The presence of observable trends also indicates that a random sample (or even a random subset of the existing data) may inadequately describe background areas that have <u>not</u>

been uniformly sampled. Treating a non-uniform sample from a trending population as if it were i.i.d. can result in biased estimates of the mean and the 95UCL on the mean. Existing data may be insufficient to detect the presence of a trend (i.e., just because we don't detect a trend doesn't mean it's not there). The optimal sampling design in the presence of trends is one that achieves spatial evenness. Since there is no harm in assuming that trends are present, the optimal design should always attempt to achieve uniform spatial coverage using systematic random samples, or more complex designs such as GRTS sampling (US EPA 2011).

The autocorrelation investigation helps uncover the magnitude of spatial autocorrelation in existing background data sets. Using the autocorrelation range estimate, we can assume that samples outside of this distance range can be considered effectively independent. The sampling density of the existing data set may be insufficient to measure the true autocorrelation range, but it should be sufficient to provide an approximate minimum separation distance to define the grid size for future sampling. If the existing data set does contain dense clusters of samples, then the autocorrelation investigation allows those data to be treated appropriately for the calculation of background summary statistics by selecting independent subsets of the data (i.e., *Method 1*).

Finally, we emphasize that *Method 1* described herein only allows description of the areas that are directly sampled (the union of circles around the sampled data points). Any extrapolation beyond, or interpolation between the sampled locations is avoided. Spatial modeling (*Method 2*) can provide estimates for interpolated concentrations across a broader area but has the disadvantages that it can be complex, requires more assumptions about the behavior of the data, and cannot be done adequately when the data are sparse.

6.0 References

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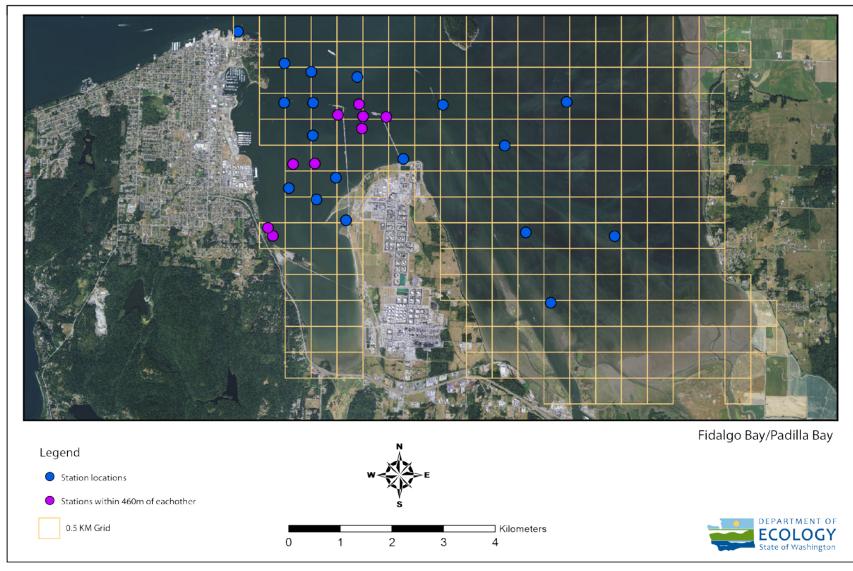


Figure 1. Map of Fidalgo Bay case study site, showing locations of existing data.

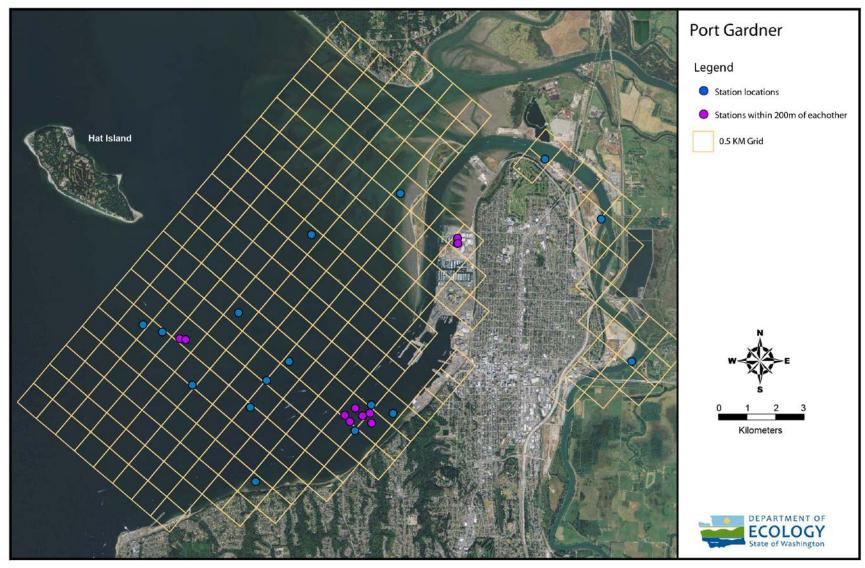


Figure 5. Map of Port Gardner case study site, showing locations of existing data.

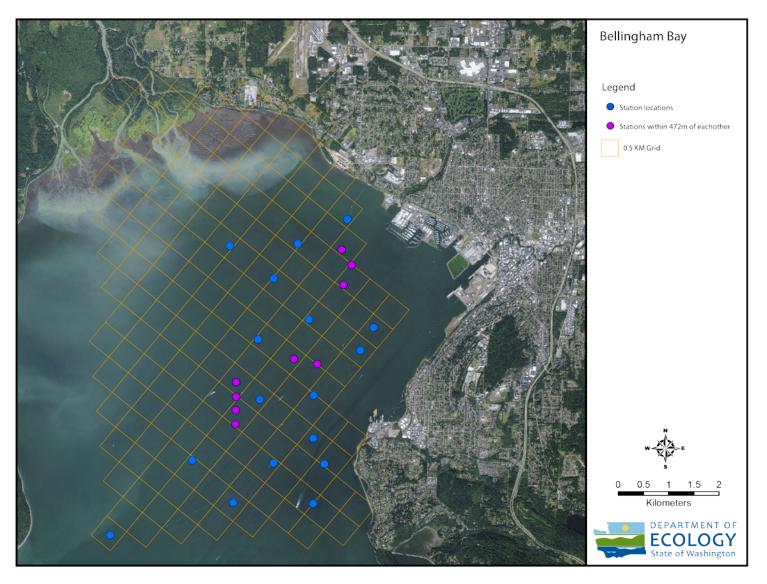


Figure 8. Map of Bellingham Bay case study site, showing locations of existing data.

Table A-1. Fidalgo Bay Case Study TEQ Data for Marine Sediments used as Regional Background

			FieldActivity						TEQ Conc
StudyID	LocationID	Study Location Name	StartDate	SampleID	Latitude	Longitude	Study_Type	Location_Setting	(pptr)
FBCPDX48	FSID6858-PB-10	PADILLABAY-10	6/8/2010	SDS-PB-10	48.476283	-122.5225	SiteInvestigation	Intertidal	0.56
FBCPDX48	FSID6858-CT-05	CLAMCOLLECTIONSITE-05	6/14/2010	SDS-CT-05	48.488004	-122.5969	SiteInvestigation	Intertidal	1.3
FIDALG08	FB-A3-42	FB-A3-42	9/4/2007	FB-A3-42	48.486639	-122.5956	InitialInvestigation	Estuary	3.4
FBCPDX48	FSID6858-PB-08	PADILLABAY-08	6/8/2010	SDS-PB-08	48.488383	-122.5295	SiteInvestigation	Intertidal	0.24
FBCPDX48	FSID6858-PB-09	PADILLABAY-09	6/8/2010	SDS-PB-09	48.48815	-122.5063	SiteInvestigation	Intertidal	0.13
FBCPDX48	FSID6858-FB-10	FIDALGOBAY-10	6/8/2010	SDS-FB-10	48.493153	-122.5844	SiteInvestigation	Intertidal	2
FIDALG08	FB-A3-41	FB-A3-41	9/4/2007	FB-A3-41	48.4897	-122.5766	InitialInvestigation	Intertidal	3.8
FBCPDX48	FSID6858-CPD-12	CUSTOMPLYWOODMILL-12	6/10/2010	SDS-CPD-12	48.495	-122.5918	SiteInvestigation	Intertidal	1.7
FIDALG08	FB-A2-38	FB-A2-38	8/30/2007	FB-A2-38	48.497	-122.5795	InitialInvestigation	Subtidal	1.9
FIDALG08	FB-A3-25	FB-A3-25	9/5/2007	FB-A3-25	48.4992	-122.5908	InitialInvestigation	Subtidal	1.9
FBCPDX48	FSID6858-FB-09	FIDALGOBAY-09	6/8/2010	SDS-FB-09	48.4994	-122.5851	SiteInvestigation	Intertidal	1.3
FIDALG08	FB-A2-35	FB-A2-35	8/30/2007	FB-A2-35	48.5006	-122.562	InitialInvestigation	Intertidal	0.72
FBCPDX48	FSID6858-PB-07	PADILLABAY-07	6/7/2010	SDS-PB-07	48.503367	-122.5356	SiteInvestigation	Intertidal	0.22
FBCPDX48	FSID6858-FB-07	FIDALGOBAY-07	6/8/2010	SDS-FB-07	48.504233	-122.5859	SiteInvestigation	Intertidal	0.79
FBCPDX48	FSID6858-FB-08	FIDALGOBAY-08	6/8/2010	SDS-FB-08	48.50565	-122.573	SiteInvestigation	Intertidal	0.67
FBCPDX48	FSID6858-FB-04	FIDALGOBAY-04	6/8/2010	SDS-FB-04	48.509783	-122.5935	SiteInvestigation	Intertidal	1.1
FBCPDX48	FSID6858-FB-05	FIDALGOBAY-05	6/8/2010	SDS-FB-05	48.509917	-122.586	SiteInvestigation	Intertidal	0.41
FBCPDX48	FSID6858-FB-06	FIDALGOBAY-06	6/8/2010	SDS-FB-06	48.510183	-122.5742	SiteInvestigation	Intertidal	0.33
FIDALG08	FB-A2-03	FB-A2-03	8/30/2007	FB-A2-03	48.5079	-122.5794	InitialInvestigation	Subtidal	1.8
FIDALG08	FB-A2-06	FB-A2-06	8/30/2007	FB-A2-06	48.5078	-122.5668	InitialInvestigation	Subtidal	1.4
FIDALG08	FB-A2-05	FB-A2-05	8/31/2007	FB-A2-05	48.5078	-122.5728	InitialInvestigation	Subtidal	2.7
FBCPDX48	FSID6858-PB-05	PADILLABAY-05	6/7/2010	SDS-PB-05	48.510167	-122.552	SiteInvestigation	Intertidal	0.57
FBCPDX48	FSID6858-PB-06	PADILLABAY-06	6/7/2010	SDS-PB-06	48.5112	-122.5197	SiteInvestigation	Intertidal	0.13
FBCPDX48	FSID6858-FB-02	FIDALGOBAY-02	6/8/2010	SDS-FB-02	48.515283	-122.5866	SiteInvestigation	Intertidal	0.51
FBCPDX48	FSID6858-FB-03	FIDALGOBAY-03	6/8/2010	SDS-FB-03	48.514567	-122.5746	SiteInvestigation	Intertidal	0.46
FBCPDX48	FSID6858-FB-01	FIDALGOBAY-01	6/8/2010	SDS-FB-01	48.516633	-122.5937	SiteInvestigation	Intertidal	0.31
FIDALG08	FB-A4-20	FB-A4-20	9/5/2007	FB-A4-20	48.5219	-122.6061	InitialInvestigation	Subtidal	1.4

Dioxin data downloaded from EIM. TEQs were calculated using TEFs from WAC Tables, found at: http://apps.leg.wa.gov/wac/default.aspx?cite=173-340-900. TEQs were calculated using substitution of non-detects at one-half the detection limit.

Table A-2. Port Gardner Case Study TEQ Data for Marine Sediments used as Regional Background

		Study Location	FieldActivity					TEQ Conc
StudyID	LocationID	Name	StartDate	SampleID	Latitude	Longitude	Location_Setting	(pptr)
DMMP_Dioxin_2005-07	DMMP-PGT15	PGT15	6/29/2006	PGT15-A	47.98630	-122.3020	SUBTIDAL	4.30
DMMP_Dioxin_2005-07	DMMP-PGT13	PGT13	6/29/2006	PGT13-A	47.98505	-122.2968	SUBTIDAL	4.20
DMMP_Dioxin_2005-07	DMMP-PGT11	PGT11	6/29/2006	PGT11-A	47.98392	-122.2921	SUBTIDAL	4.40
DMMP_Dioxin_2005-07	DMMP-PGP08_1	PGP08_1	6/29/2006	PGP08_10cm	47.98380	-122.2905	SUBTIDAL	3.90
DMMP_Dioxin_2005-07	DMMP-PGP07_1	PGP07_1	6/30/2006	PGP07_10cm	47.97562	-122.2885	SUBTIDAL	3.80
DMMP_Dioxin_2005-07	DMMP-PGP01_1	PGP01_1	6/30/2006	PGP01_10cm	47.98880	-122.2765	SUBTIDAL	5.00
DMMP_Dioxin_2005-07	DMMP-PGB01	PGB01	6/29/2006	PGB01_10cm	47.97192	-122.2728	SUBTIDAL	3.40
PortGardner_08	A1-46B	A1-46B	9/4/2008	8 A1-46B-S	47.95856	-122.2710	ESTUARY	0.18
DMMP_Dioxin_2005-07	DMMP-PGP09_1	PGP09_1	6/29/2006	PGP09_10cm	47.97679	-122.2686	SUBTIDAL	3.20
DMMP_Dioxin_2005-07	DMMP-PGB09_1	PGB09_1	6/30/2006	PGB09_10cm	47.98029	-122.2627	SUBTIDAL	3.00
PortGardner_08	A2-02	A2-02	9/4/2008	3 A2-02-S	48.00314	-122.2575	ESTUARY	0.18
KIMCLK04	KIMCLK04AKC-7	AKC-7	2/26/2004	AKC-7SD	47.97088	-122.2476	Subtidal	0.66
KIMCLK04	KIMCLK04AKC-3	AKC-3	2/26/2004	AKC-3SD	47.96972	-122.2461	Subtidal	0.28
KIMCLK04	KIMCLK04AKC-5	AKC-5	2/26/2004	AKC-5SD	47.97218	-122.2447	Subtidal	0.51
KIMCLK04	KIMCLK04AKC-6	AKC-6	2/26/2004	AKC-6SD	47.96814	-122.2447	Subtidal	1.20
KIMCLK04	KIMCLK04AKC-2	AKC-2	2/26/2004	AKC-2SD	47.97086	-122.2427	Subtidal	0.61
KIMCLK04	KIMCLK04AKC-1	AKC-1	2/26/2004	AKC-1SD	47.97131	-122.2408	Subtidal	0.42
KIMCLK04	KIMCLK04AKC-8	AKC-8	2/26/2004	AKC-8SD	47.97282	-122.2405	Subtidal	0.72
KIMCLK04	KIMCLK04AKC-4	AKC-4	2/26/2004	AKC-4SD	47.96955	-122.2403	Subtidal	0.21
PortGardner_08	A1-31B	A1-31B	9/4/2008	8 A1-31B-S	47.97136	-122.2346	ESTUARY	0.18
PortGardner_08	A2-08	A2-08	9/4/2008	3 A2-08-S	48.01088	-122.2340	ESTUARY	0.26
AODE6677	AO6677-462.1	A/H-SED-1	12/10/2010	SED-1	48.00310	-122.2184	Subtidal	2.55
AODE6677	AO6677-465	A/H-SED-4	12/10/2010	SED-4	48.00217	-122.2183	SUBTIDAL	2.10
PortGardner_08	A2-30	A2-30	9/12/2008	8 A2-30-S	48.01762	-122.1954	ESTUARY	0.42
PortGardner_08	A2-32	A2-32	9/4/2008	8 A2-32-S	48.00702	-122.1800	ESTUARY	0.16
PortGardner_08	A2-37B	A2-37B	9/4/2008	A2-37B-S	47.98164	-122.1710	ESTUARY	0.18

Dioxin data downloaded from EIM. TEQs were calculated using TEFs from WAC Tables, found at: http://apps.leg.wa.gov/wac/default.aspx?cite=173-340-900. TEQs were calculated using substitution of non-detects at one-half the detection limit.

Table A-3. Bellingham Bay Case Study TEQ Data for Marine Sediments used as Regional Background

Upper Lower **FieldActivity** Depth Depth **TEQ Conc Study Location Name** StartDate SampleID StudyID LocationID (cm) (cm) Latitude Longitude Setting (pptr) DMMP Dioxin 2005-07 **BBB04** 7/19/2007 BBB04 0 48.6998 -122.5846 Subtidal 4.3 J DMMP-BBB04 DMMP Dioxin 2005-07 DMMP-BBP04 **BBP04** 7/19/2007 BBP04 0 10 48.7137 -122.5631 Subtidal 5.2 J DMMP Dioxin 2005-07 DMMP-BBP01 BBP01 7/19/2007 BBP01 0 10 48.7062 -122.5517 Subtidal 5.5 J DMMP Dioxin 2005-07 BBP02 0 48.7136 -122.5411 Subtidal 8.5 J DMMP-BBP02 7/19/2007 BBP02 **BELSEDDF** BBDIOX-10 BBDIOX-10 6/9/2010 BBDIOX-10 0 12 48.7064 -122.5303 Subtidal 11 J **BBT05** 0 7.2 J DMMP Dioxin 2005-07 DMMP-BBT05 7/20/2007 BBT05 10 48.7254 -122.5517 Subtidal BBP03 7 J DMMP Dioxin 2005-07 DMMP-BBP03 7/19/2007 BBP03 0 48.7204 -122.5517 Subtidal 7 J **BBT04** 0 48.7230 -122.5517 Subtidal DMMP Dioxin 2005-07 DMMP-BBT04 7/19/2007 BBT04 10 **BBT06** 0 6.8 J DMMP_Dioxin_2005-07 DMMP-BBT06 7/20/2007 BBT06 10 48.7281 -122.5518 Subtidal **BELSEDDF UWI 32 UWI 32** 6/10/2010 UWI 32 0 12 48.7250 -122.5453 Subtidal 2.6 J **BELSEDDF** BBDIOX-11 BBDIOX-11 6/9/2010 BBDIOX-11 0 12 48.7182 -122.5307 Subtidal 6.7 J DMMP-BBB02 BBB02 7/20/2007 BBB02 0 48.7136 -122.5275 Subtidal 10 J DMMP Dioxin 2005-07 10 0 **BELSEDDF** BBDIOX-9 BBDIOX-9 6/10/2010 BBDIOX-9 12 48.7260 -122.5309 Subtidal 10 J **BELSEDDF UWI 277 UWI 277** 6/9/2010 UWI 277 0 12 48.7359 -122.5462 Subtidal 5.7 J **Bellingham Bay** Bellinghambay08 HART17 BBDXSS05 Dioxin BBDx-SS-05 9/18/2008 BBDX-SS-05 0 12 48.7326 -122.5365 Subtidal 12 **BELSEDDF** BBDIOX-1A BBDIOX-1A 6/15/2010 BBDIOX-1A 0 12 48.7317 -122.5302 Subtidal 11 J **BELSEDDF** BBDIOX-3A BBDIOX-3A 6/15/2010 BBDIOX-3A 0 12 48.7527 -122.5545 Subtidal 0.57 J **BELSEDDF** BBDIOX-4 **BBDIOX-4** 6/11/2010 BBDIOX-4 12 48.7470 -122.5425 Subtidal 1.7 J **BELSEDDF** BBDIOX-6 **BBDIOX-6** 6/11/2010 BBDIOX-6 0 12 48.7397 -122.5327 Subtidal 3 J Bellingham Bay Bellinghambay08 HART17 BBDXSS04 Dioxin BBDx-SS-04 9/19/2008 BBDX-SS-04 0 48.7344 -122.5186 Subtidal 13 J 12 **BELSEDDF** UWI 29 **UWI 29** 0 6 J 6/9/2010 UWI 29 11 48.7386 -122.5153 Subtidal **BELSEDDF UWI 35** 48.7534 -122.5363 Subtidal 1.4 J UWI 35 6/11/2010 UWI 35 **BELSEDDF** BBDIOX-5 **BBDIOX-5** 6/15/2010 BBDIOX-5 0 48.7462 -122.5236 Subtidal 1.6 J 12 48.7498 -122.5216 6.29 J DMMP O&M Squalicum Sq-15 Sq-15 9/7/2010 Sq-15 0 55 Bellingham Bay HART17_BBDXSS01 Bellinghambay08 Dioxin BBDx-SS-01 9/19/2008 BBDX-SS-01 0 48.7526 -122.5244 Subtidal 1.5 12 **BELSEDDF** BBDIOX-2 BBDIOX-2 6/10/2010 BBDIOX-2 0 48.7581 -122.5231 Intertidal 0.7 J

Dioxin data downloaded from EIM. TEQs were calculated using TEFs from WAC Tables, found at: http://apps.leg.wa.gov/wac/default.aspx?cite=173-340-900. TEQs were calculated using substitution of non-detects at one-half the detection limit.