DEPARTMENT OF
ECOLOGY
State of Washington

North Olympic Peninsula Regional Background Sediment Characterization

Port Angeles – Port Townsend, Washington

Data and Evaluation Report

February 2016
Publication no. 16-09-142

Publication and Contact Information

This report is available on the Department of Ecology's website at:
www.ecy.wa.gov/biblio/1609142.html

For more information contact:

Toxics Cleanup Program
P.O. Box 47600
Olympia, WA 98504-7600

Phone: 800-826-7716

Washington State Department of Ecology - www.ecy.wa.gov

o Headquarters, Olympia	360-407-6000
o Northwest Regional Office, Bellevue	425-649-7000
o Southwest Regional Office, Olympia	360-407-6300
o Central Regional Office, Yakima	509-575-2490
o Eastern Regional Office, Spokane	509-329-3400

If you need this document in a format for the visually impaired, call the Toxics Cleanup Program at 800-826-7716. Persons with hearing loss can call 711 for Washington Relay Service. Persons with a speech disability can call 877-833-6341.

North Olympic Peninsula Regional Background Sediment Characterization

Data and Evaluation Report

Prepared by

NewFields

NewFields
115 2nd Ave N
Suite 100
Edmonds, WA 98020

Toxics Cleanup Program
Washington State Department of Ecology
Olympia, Washington

This page purposely left blank for duplicate printing

Table of Contents

Appendices

Figures

Tables

Acronyms and Abbreviations

AOI	area of interest
ARI	Analytical Resources Inc.
Axys	Axys Analytical
Bold	2008 OSV Bold Survey
Bold plus	Bold plus select data sets
cfs	cubic feet per second
COC	contaminant of concern
cPAH	carcinogenic polycyclic aromatic hydrocarbon
CSL	cleanup screening level
CSO	combined sewer overflow
DQO	data quality objective
EcoChem	EcoChem, Inc.
Ecology	Washington State Department of Ecology
EMPC	estimated maximum possible concentration
KM	Kaplan-Meier
MCD	minimum covariance determinant
MDL	method detection limit
mg/kg	milligrams per kilogram
µg TEQ/kg	micrograms TEQ per kilogram
ng/kg	nanograms per kilogram
ng TEQ/kg	nanograms TEQ per kilogram
NOP	North Olympic Peninsula
PA Proximal	Port Angeles Proximal Area
PAH	polycyclic aromatic hydrocarbon
PCA	principal components analysis
PCB	polychlorinated biphenyl
PQL	practical quantitation limit
PSAMP	Puget Sound Assessment and Monitoring Program
PSEP	Puget Sound Estuary Program
QA	quality assurance
QC	quality control
RPD	relative percent difference
RSD	relative standard deviation
SAP	Sampling and Analysis Plan
SCUM II	Sediment Cleanup User’s Manual II
SCO	sediment cleanup objective
SDE	supplemental data evaluation
SMS	Sediment Management Standards

SRM	standard reference material
TEF	toxicity equivalency factor
TEQ	toxicity equivalent
TOC	total organic carbon
TVS	total volatile solids
UCL	upper confidence limit
USEPA	U.S. Environmental Protection Agency
UTL	upper tolerance limit
WAC	Washington Administrative Code

1.0 Introduction

In early 2013, the Washington State Department of Ecology (Ecology) revised the Sediment Management Standards (SMS) to establish a new framework for the determination and delineation of contaminated sediment sites. A key component of this framework was the concept of regional background sediment concentrations, which could potentially serve as the cleanup screening level (CSL) for these sites. The *North Olympic Peninsula Regional Background Sediment Characterization, Port Angeles-Port Townsend, Washington, Sampling and Analysis Plan* (SAP; Ecology 2013a) included an approach for determining a regional area of interest (AOI) for the North Olympic Peninsula (NOP) that would be applicable to contaminated sediment sites ranging from Port Townsend in the east to Port Angeles in the west (Figure 1).

A discussion of the process used to determine the randomized target sample locations within this AOI, as well as suggestions for statistical methodologies that could be used to determine representative regional background sediment concentrations from the sample results, is provided in the SAP. The sample results and statistical methodologies are presented in this data report to:

- Provide summary statistics for the sediment chemistry results and provide the spatial distributions of these data within the AOI.
- Document a logical and statistically rigorous process for evaluating a regional background data set and calculating representative sediment concentrations.
- Calculate the regional background sediment concentrations for the NOP using this process.

Section 1.0 puts the concept of regional background into context by discussing the SMS rule revisions and describing the AOI for the NOP. Section 2.0 summarizes the sampling efforts and describes any modifications from the SAP that were made in the field. It also includes the practical quantitation limits (PQLs) used for the chemical analysis as part of this project. Section 3.0 includes the chemical and physical results of the sample analysis presented as summary statistics and spatial distributions. Quality assurance/quality control (QA/QC) measures taken to ensure a useable data set are described in Section 4.0. Section 5.0 presents the process developed to calculate regional background concentrations and the resultant concentrations. A discussion of a Port Angeles Harbor-specific regional background concentration for carcinogenic polycyclic aromatic hydrocarbons (cPAHs) is presented in Section 6.0. References are provided in Section 7.0.

1.1. Regional background definition

For a number of bioaccumulative chemicals, risk-based values protective of human health and upper trophic levels fall below natural background concentrations, as defined in the SMS

(Washington Administrative Code [WAC] 173-204-505). Sediments are a sink for chemicals from potentially hundreds of sources, including a mixture of permitted and unpermitted stormwater, atmospheric deposition, and historical releases from industrial activities. In urban embayments with developed shorelines, chemical concentrations in sediment are frequently higher than natural background concentrations.

The 2013 SMS rule revisions retained the two-tiered framework used to establish sediment cleanup levels, but now incorporates natural background (as the potential sediment cleanup objective [SCO]) and a new term and concept, regional background, as the potential CSL. The SMS rule includes a definition for regional background (WAC 173-204-505[16]) and parameters for establishing regional background (WAC 173-204-560[5]):

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

The SMS is intended to provide flexibility in establishing regional background on a case-by-case basis and does not prescribe, specifically, how regional background should be established. The approach and methods contained in the SAP (Ecology 2013a) were developed by Ecology to establish regional background concentrations for the following analytes: arsenic, cadmium, mercury, cPAHs, dioxins/furans, and polychlorinated biphenyls (PCBs). This study serves as one example of how regional background concentrations can be established in a particular Ecology-defined geographic area.

Ecology's approach to establishing regional background has evolved over time through working on initial bays and after receiving comments from stakeholders and tribes. The concept and flexibility of regional background was expanded on in Chapter 10.3 of the *Sediment Cleanup User's Manual II: Guidance for Implementing the Cleanup Provisions of the Sediment Management Standards* (SCUM II; Ecology 2015a). The initial rationale for the NOP study design is described below, followed by (1) a description of some of the changes to the regional background approach that have been instituted since the collection of NOP field samples, and (2) how these changes were applied to this report.

1.2. Defining the North Olympic Peninsula region

The regional background sediment concentrations resulting from this characterization are intended to be applicable to marine embayments throughout the NOP ranging from Port Townsend to Port Angeles. Although the regional background concentrations calculated for this study can be used, in part, to develop a new CSL at Port Angeles, a preliminary decision was made that no samples would be collected from Port Angeles Harbor for this characterization.

Numerous aquatic investigations conducted in Port Angeles Harbor identified areas potentially affected by industrial activity that may require remedial action. These studies found various contaminants, including mercury and PCBs, exceeding the SMS benthic criteria. In addition, dioxin/furan congeners were present throughout Port Angeles Harbor at concentrations exceeding natural background and risk-based concentrations. As a result of these studies, Port Angeles Harbor was identified by Ecology as a priority cleanup and restoration site under the Puget Sound Initiative.

It was this complexity of sediment issues within Port Angeles Harbor that made it difficult to decide which, if any, locations could be sampled to represent regional background. Ultimately, it was decided that no samples would be collected from Port Angeles Harbor. The full reasoning behind this decision is presented in the SAP (Ecology 2013a), with a summary provided below:

- Numerous sediment investigations and chemometric (chemical fingerprinting) analyses for dioxin/furan congeners demonstrated that sediment dioxin/furan contamination in Port Angeles Harbor was from two potential source areas in both the Eastern and Western Harbor (Ecology 2012a, 2012b, 2013c). Delineation of these source areas was beyond the scope of a regional background investigation. Therefore, the entire Harbor was considered an active dioxin/furan site, precluding sampling of other contaminants of concern (COCs). An alternative geographic approach was proposed, as per WAC 173-204-560(5)(d)(f).
- As part of the study design, the minimum distance between regional background sample locations was set at a conservative 500 meters. Because the distribution of dioxins/furans was so large, the geographic area of Port Angeles Harbor that could potentially be considered regional background was too limited in spatial area for adequate characterization given the large buffer distance.
- The limited portion of Port Angeles Harbor that could possibly have been considered for use in calculating regional background concentrations (the outer Harbor near Ediz Hook) had a coarser grain size distribution than much of the nearshore and Western Harbor locations. Regional background may not have been representative of potential site sediments had this limited area been sampled.
- The combined sewer overflows (CSOs) in Port Angeles likely carried particulate material containing dioxin/furan congeners from hog fuel boilers that had aerially deposited in upland areas into Port Angeles Harbor sediments.

The nearby embayments of Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay were selected as alternate areas for the collection of regional background sediments for the following reasons:

- These bays are geomorphologically similar and proximal to Port Angeles Harbor, and together include the 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 to compare sediment contaminant concentrations from each of the bays separately.

1.3. Stakeholder discussions

Based on comments and discussions with stakeholders during the regional background sediment characterization process, Ecology incorporated changes into the final regional background characterization reports for Port Gardner and Bellingham Bay (Ecology 2014, 2015b, respectively). Some of the key changes that had implications for the NOP regional background characterization included:

- **Differentiating from Natural Background.** Existing data could be examined to identify areas within the range of natural background concentrations (as defined in SCUM II; Ecology 2015a). These areas could be excluded from sampling and from calculating regional background; in addition, areas that were sampled as part of a regional background characterization could be excluded from the data set if the resulting concentrations were considered more appropriate to natural background. For example, select samples from Bellingham Bay (Ecology 2015b) and all Phase I Port Gardner samples collected from the Snohomish River Delta (Ecology 2014) were removed from the regional background data set due to similarity to natural background.
- **Determining Areas of Primary Influence.** The area in which sediment samples could be collected was modified, but remained consistent with the SMS definition of regional background (WAC 173-204-505[16]). Modifications entailed sampling closer to the shoreline, sources, and sites, but outside areas of known direct influence. This was particularly relevant with regard to CSOs. King County modeling presented at the September 2013 Elliott Bay Regional Background Workshop demonstrated that CSO contaminants generally deposit in the near field, as close as 100 to 300 feet (30 to 91 meters) from the outfall (Fujisaki et al. 2013). Because of this finding, the sampling exclusion distance around outfalls was reduced to 75 meters for Bellingham Bay (Ecology 2015b). In a similar manner, the distance between sample locations was reduced from 500 to 250 meters.
- **Differing AOIs for Different Analytes.** In the study design phase for Bellingham Bay, different analytes were found to be elevated above natural background in different areas of the bay. cPAHs were determined to be elevated over a larger area than other chemicals. Therefore, a larger AOI was used for sampling regional background concentrations of cPAHs. Defining separate AOIs also means that the presence of one COC from a point source in an embayment does not preclude sampling for other COCs. For example, multiple

COCs were targeted for sampling and analysis in Bellingham Bay, even though much of the Bay was impacted by mercury from a well-defined point source.

Sample results in this report were evaluated as prescribed in the SAP (Ecology 2013a), but also in accordance with the above modifications. These changes have impacted the report in two primary ways.

The first impact was in the evaluation of data from Dungeness Bay. Pre-existing samples from Dungeness Bay were already included as part of the natural background data set for Port Angeles Harbor. New samples also were collected from Dungeness Bay as part of this study. Separate portions of a single bay can represent both natural and regional background, but only if the data belong to separate populations. In Section 5.3.2, samples from Dungeness Bay are evaluated relative to the existing natural background data set and data from the other three embayments. Based on this evaluation, the decision was made to remove Dungeness Bay from the regional background data set.

The second impact was a reevaluation of cPAHs in Port Angeles Harbor. Ecology determined the final NOP regional background value for cPAHs was not representative of the more industrial conditions and higher population in Port Angeles Harbor. As a result, the NOP data set was supplemented with existing data from Port Angeles Harbor to create a more realistic regional background value for cPAHs (Section 6.0).

This page purposely left blank for duplicate printing

2.0 Sampling and Analysis

Sediment sampling was conducted May 6 through 10, 2013. Sample collection was confined to the AOI shown in Figure 1. The AOI encompassed four embayments and was designed so that no samples would be collected within 500 meters of each other, or of known point sources, such as outfalls.

Sediment collection within the AOI consisted of two types of samples, baseline and secondary. The same volume of sediment was collected for both sample types following the same collection methodologies. The difference between the sample types was that baseline samples were submitted for a full suite of chemical analysis, while secondary samples were initially analyzed for only mercury and total sulfides due to short holding times. Secondary samples also were analyzed for grain size to better characterize the physical characteristics of the AOI and to aid in the selection of secondary samples for potential analysis. The remainder of the sediment from the secondary samples was archived for potential future analysis.

A total of 40 baseline samples and 25 secondary samples were collected. The target sampling locations were randomly placed throughout the AOI at a minimum distance of 500 meters between locations.

2.1. Station positioning and navigation

The R/V *Kittiwake* was used for the surface sediment grab sampling throughout the AOI. A differential Global Positioning System was used aboard the R/V *Kittiwake* for station positioning. The baseline and secondary sampling location target coordinates were provided in advance and programmed into the R/V *Kittiwake's* navigation system. Upon sampling device deployment, the actual position was recorded once the device reached the seafloor and the winch cable was in a vertical position. Latitude and longitude station coordinates were recorded in degrees decimal minutes using the 1983 North American Datum. Water depths were measured using the winch meter wheel and verified by the ship's fathometer. Tables 1 and 2 provide the actual coordinates, water depths, and distances between the target and actual locations for the baseline and secondary sample locations, respectively. Figures 2 and 3 show the target and actual locations for the baseline and secondary samples, respectively. In both figures, a 500-meter buffer was drawn around the actual coordinates.

There was one instance where a grab sample could not be collected at the target location. The first grab sample at location DIS-08-S was mostly washed out and contained rocks and shell hash. A successful grab sample was collected on the second attempt, approximately 99 meters southeast of the target location (Table 1; Figure 2).

2.2. Surface sediment grab samples

Surface sediment grab samples were collected at 65 locations: 8 in Sequim Bay, 15 in Port Townsend Bay, 20 in Discovery Bay, and 22 in Dungeness Bay. All samples were collected using a stainless steel van Veen grab sampler deployed as either a dual or single bucket (0.1 square meter per bucket). Sampling followed the stepwise procedure outlined in the SAP (Ecology 2013a). Notes related to sampling activities are presented in Appendix A. A brief summary of field sampling methods is provided below.

Established deployment and recovery procedures for the grab sampling gear, described by the Puget Sound Estuary Program (PSEP), were followed to ensure recovery of the best possible samples and to minimize risks to personnel and equipment (PSEP 1997). Once a grab sample was retrieved, the overlying water was carefully siphoned off one side of the sampler. If the sample was judged to be acceptable according to PSEP specifications, the penetration depth was measured with a decontaminated stainless steel ruler, and sample quality, color, odor, and texture were described in the sample log. Scanned copies of the surface sediment grab logbook are presented in Appendix B.

The target depth for surface sediment collection was 10 centimeters. Four samples from Dungeness Bay (DUN-10, DUN-13, DUN-14, and DUN-16), with penetration depths of 7, 7, 9, and 9.5 centimeters, respectively, did not meet the target depth. With the exception of sample DUN-16, multiple attempts were made at each location to improve penetration. Over-penetration was an issue in the softer sediments of Discovery Bay. To minimize over-penetration, the lead weights on the van Veen grab sampler were removed. In an attempt to further reduce the weight of the grab, only one weightless bucket of the van Veen grab sampler was used. Despite these efforts, slight over-penetration occurred at five locations in Discovery Bay (DIS-01, DIS-02, DIS-06, DIS-07, and DIS-10); however, very little surface sediment was disturbed, and the grab samples were deemed acceptable.

Percent fines were determined at each location by rinsing 40 milliliters of sediment through a 63.5-micron sieve until the water was clear. Percent fines are equal to 40 minus the volume of remaining sediment divided by 40. The amount of sediment retained on the sieve was recorded in the surface sediment grab logbook (Appendix B).

2.3. Sample storage, delivery, and chain of custody

After filling the jars with homogenized aliquots of sediment, all samples were labeled, and the lids were wrapped with electrical tape to seal the jars and prevent leakage. Each label was marked with a jar tag number for tracking purposes. Sample identification and jar tag numbers were recorded in the sample container logbook (Appendix C).

After labeling, all samples were stored in insulated coolers and preserved by cooling to a temperature of 4 degrees Celsius.

Samples were picked up by or delivered to Analytical Resources Inc. (ARI) on May 9, 10, and 13, 2013. Samples were shipped to Axys Analytical (Axys) on May 14, and received on May 15, 2013. All of the archived sediment from the remaining baseline locations and all secondary locations was delivered to the NewFields biological laboratory in Port Gamble by May 16, 2013. All archive samples were frozen at -18 degrees Celsius. The chain of custody forms for all samples are presented in Appendix D.

2.4. Laboratory analysis

Samples were submitted to laboratories subcontracted by NewFields to conduct the chemical analysis. Axys analyzed the samples for dioxin/furan and PCB congeners. ARI analyzed samples for the sediment conventionals (total organic carbon [TOC], total solids, total volatile solids [TVS], grain size, and total sulfides), arsenic, cadmium, mercury, and cPAHs. Archived sediment was stored at the NewFields Port Gamble biological laboratory. Table 3 lists all samples collected as part of the NOP regional background sediment characterization and includes the analytical method. Further details relating to chemical analysis can be found in the SAP (Ecology 2013a).

Additional samples collected for QA/QC purposes are listed in Table 3. Full duplicates and triplicates were collected at locations SEQ-03-S, DUN-05-S, and DIS-09-S, while duplicate and triplicate samples for mercury and total sulfides were collected at location PT-13-S. Rinsate blanks and equipment rinsate samples also were collected as part of field sampling.

Because of expected low concentrations, the data quality objectives (DQOs) used in this study were greater than those required under most sediment characterizations. As a result, the target PQLs for analysis were lower than most standard methods could provide. The PQLs for the analytes are listed in Table 4. This table includes the PQLs for the dioxin-like PCB congeners. The PQLs for the non-listed PCB congeners were all 0.4 nanograms per kilogram (ng/kg). The PQLs for the conventional parameters and the full list of PCB congeners can be found in the SAP (Ecology 2013a).

All non-detect sample results for cPAHs were reported to the method detection limit (MDL), and detected results less than the target PQL were “J” qualified. All non-detect results for metals were reported at the PQL. Metals data are not qualified below the PQL. Non-detect results for dioxin/furan and PCB congeners were reported at the sample-specific detection limit. All detected congener results less than the PQL were “J” qualified.

Laboratories do not provide PQL values for toxicity equivalent (TEQ) concentrations. Instead, these values were calculated for cPAHs, dioxin/furan congeners, and PCB congeners using the toxicity equivalency factors (TEFs) from Ecology’s guidelines for determining TEQ values

(Ecology 2007) and the individual compound- or congener-specific PQLs in Table 4. The Ecology guide for determining TEQs includes the dioxin/furan TEF values updated by the World Health Organization in 2005 (Van den Berg et al. 2006). The resultant PQL for cPAHs was 0.76 micrograms TEQ per kilogram (µg TEQ/kg). The PQLs for dioxin/furan and PCB congeners were 2.3 and 0.052 nanograms TEQ per kilogram (ng TEQ/kg), respectively.

Cadmium was analyzed by U.S. Environmental Protection Agency (USEPA) Method 200.8, which dictates results be reported at two significant figures for concentrations under 10 milligrams per kilogram (mg/kg). To meet this criterion, ARI reported cadmium concentrations below 10 mg/kg to one decimal place. However, this reporting system means concentrations less than 1 mg/kg contain only one significant figure. Many of the cadmium concentrations reported for this background study were below 1 mg/kg, meaning results are listed at one significant figure in the laboratory data packages. ARI was able to provide the metals analysis sheets that contain additional decimal places for cadmium. Cadmium concentrations measured to two decimal places were taken from these sheets and used in the final data tables (Appendix E) and the reporting and statistical analysis discussions. The laboratory data packages are provided as Appendix F.

3.0 Data Validation

A QA2[1] (USEPA Stage 3/4) chemistry data review was conducted by EcoChem, Inc. (EcoChem). The review examined the complete analytical process from calculation of instrument detection limits, MDLs, PQLs, final dilution volumes, sample size, and wet-to-dry ratios to quantification of calibration compounds and all analytes detected in blanks and environmental samples. The intent of the independent data validation was to ensure that the investigation data results are defensible and usable for their intended purpose. This section briefly summarizes the data validation reports for the baseline and secondary sample analyses. The full validation reports are provided in Appendix G.

When necessary, EcoChem applied the following data qualifiers to the chemical results:

- U – The analyte was analyzed for, but was not detected above, the reported sample quantitation limit.
- UJ – The analyte was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
- J – The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample. “J” qualifiers were assigned by the laboratories for results less than the PQL and greater than the MDL, or by EcoChem for results that failed to meet study-specific QA/QC criteria.
- DNR – Do not report; a more appropriate result is reported from another analysis or dilution.

The use of the “DNR” qualifier was limited to selecting the appropriate results for 2,3,7,8-tetrachlorodibenzofuran, as results were reported for analysis on two separate columns. The remainder of the data was usable. Reason codes for applying the “U,” “UJ,” and “J” qualifiers, and the definition for these codes, are given in the validation reports (Appendix G).

Several qualifiers given by Axys were reclassified by EcoChem. Axys assigned a “B” qualifier to all results where the analyte was detected in the method blank. EcoChem established an action level of five times the blank concentration. If a sample result was above that, the “B” qualifier was removed. If the result was below the action level, the result was qualified as not detected (“U”).

The laboratory assigned “K” qualifiers to dioxin/furan and PCB congener data. This qualifier implied that a peak was detected, but did not meet identification criteria. These data were considered estimated maximum possible concentrations (EMPCs). All EMPC results were given

---

[1] A QA2 data review is described in detail in the *Data Validation Manual for Selected Sediment Variables* (PTI 1989).

a “U” qualifier by EcoChem, but remained at the reported concentration, which represented an elevated PQL for that congener.

Project-specific QA/QC measures were employed during sample collection and analysis to ensure the precision, accuracy, and reproducibility of the results. This included field QA/QC samples, such as equipment rinsates, rinsate blanks, and field duplicates and triplicates. Laboratory measures included the analysis of specific certified reference material or standard reference material (SRM).

The equipment rinsate blank and decontamination water rinsate provided a QC check on the potential for cross-contamination by measuring the effectiveness of the sampling and processing decontamination procedures. Rinsate samples were collected for metals and PAHs (Table 3). None of these analytes were detected in the rinsate samples.

Field duplicates and triplicates were collected at the same time as the original samples using identical sampling techniques. Duplicates and triplicates were used to determine the precision of the sample collection process and the representativeness of the sample. Table 4 lists the specific duplicates and triplicates collected for this study.

The relative percent difference (RPD) was used to evaluate duplicate samples, while the relative standard deviation (RSD) was used to evaluate triplicates. In general, if the RPD or RSD was greater than 50 percent, the affected results of the duplicate and/or triplicate sample were “J” qualified. For duplicate sample DIS-09-S/D, the RPDs for total tetra dioxins and PCB-156 were greater than the control limit, and these results were qualified. The RSD for sulfides was greater than the control limit for triplicate samples DIS-09-S/D/T and PT-13-S/D/T.

Overall, the high precision of the field duplicates indicates that the study results were representative of the sediment from which they were collected, which is important for reducing variability in the data set.

The recently developed Puget Sound SRM was submitted for analysis for dioxin/furan and PCB congeners. The published acceptance criterion for this SRM was ±50 percent of the average value (http://www.nws.usace.army.mil/Missions/CivilWorks/Dredging/SRM.aspx). The result for 1,2,3,7,8,9-hexachlorodibenzofuran was less than the lower control limit, and the result for octachlorodibenzofuran was greater than the upper control limit. For PCBs, the results for congeners 3, 4, and 56 were less than the lower control limit. The recoveries for congeners 129/138/160/163 and 134/143 were greater than the upper control limits. No results were qualified based on these outliers, as the reference material is still undergoing evaluation and is not yet certified.

4.0 Data Results

This section summarizes the laboratory analysis results. Results are presented in terms of general usability by listing the number of non-detected and qualified results for each analyte (Figure 4). The results of the conventionals analyses (grain size distribution and TOC) are presented in Figures 5 and 6. The spatial distributions of the measured analytical results throughout the AOI are presented in Figures 7 through 13. Complete data results are presented in Appendix E. Laboratory data packages are available electronically as Appendix F.

4.1. Calculation of toxicity equivalents

The calculation of the TEQ, when many of the congener concentrations within a sample are reported below the detection limits, can be problematic. A common approach is to substitute zero, one-half, or one times the detection limit in place of a non-detected concentration. Substitution methods were used for the multivariate analyses where individual congener data were required. A more-rigorous method for calculating total TEQs when non-detect values are present is the Kaplan-Meier (KM) approach, which is a statistical method for estimating a sum or mean when part of the population is censored (Helsel 2010, 2012). The methods for addressing non-detects, including KM, are discussed in greater detail in SCUM II (Ecology 2015a).

Traditional substitution of non-detects at zero, one-half, or one times the detection limit introduces uncertainty and produces variable bias in estimates of the mean and the standard deviation, which increases with the frequency of non-detects in a data set (Hewett and Ganser 2007). The KM method for estimating a mean (or sum) is useful in that it (1) is completely distribution-free; (2) is appropriate for summing the individual congeners/compounds within a sample that are neither independent nor identically distributed; (3) is based purely on observed percentiles; and (4) consistently introduces a positive bias (Hewett and Ganser 2007), thus allowing the KM estimate of a TEQ to be considered an upper bound.

KM TEQs were calculated separately for the PCB congeners, dioxin/furan congeners, and cPAH compounds from each sample. The KM means reported for the TEQ data in this report were calculated using R version 3.0.0 (R Core Team 2013) using the ‘cenfit’ function from the ‘NADA’ package (Lee 2012). The KM sum was calculated, and the number and distribution of censored values were evaluated. The following rules were applied to the final KM TEQs:

- If the percentage of non-detect congeners within a sample exceeded 50 percent, the KM TEQ value was qualified as a less-than value (L qualified), followed by the number of censored congeners (see data in Appendix E). For example, if 12 of the 17 dioxin/furan congeners were not detected, the detection frequency is 29 percent and the KM TEQ would be calculated and qualified with L12.

- If the lowest detection limit for a non-detect was lower than all of the detected values (as is often the case), the positive bias in the KM estimate was adjusted downward by using Efron’s bias correction (Klein and Moeschberger 2003). This method simply treated the lowest-ranked value as detected even if it was reported as a non-detected data point.
- If the highest detection limit was greater than the highest detected value, the highest non-detected value provides no meaningful information, and this high non-detect value is typically ignored in the KM estimation of the mean. For risk calculations, it may not be acceptable to omit this high censored data point, as this may underestimate the true TEQ. The highest toxicity equivalent concentration value is always treated as uncensored in the KM TEQ calculation, and the TEQ is qualified with an “L” if the original value had been censored. All “L”-qualified TEQ values were treated as non-detects in the distributional assessments and when calculating summary statistics across samples.

Calculated KM TEQs are presented in the data tables in Appendix E along with the traditional zero, one-half, and one detection limit substitutions. A brief comparison was made of the results from these four estimates of total TEQ. The mean and 90th percentiles were calculated for each method. For cPAHs, the mean and 90th percentiles were the same regardless of the method used. The same was true for the mean of the dioxin/furan TEQ, while there were minor differences in the 90th percentile depending on the method (between 3.75 and 3.76 ng TEQ/kg). Larger differences were noted for PCB TEQ due to the greater frequency of non-detects, but even these differences were small. PCB TEQ means ranged from 0.0844 ng TEQ/kg for the zero detection limit substitution to 0.0914 ng TEQ/kg for the one detection limit substitution. The 90th percentiles ranged from 0.178 to 0.190 ng TEQ/kg. Given the small differences between the methods, the more statistically robust KM TEQ values are used in statistical summaries and analysis for the remainder of this report when discussing total TEQ concentrations.

4.2. Summary of qualified results

As mentioned in the previous section, the DQOs of this study necessitated PQLs that were lower than those typically used in Puget Sound sediment investigations, as the intent of any background study is to obtain as few non-detects and as many unqualified results as possible. Too many non-detects could create a skewed distribution that would not meet the project requirements for precision (Section 5.2), while too much data qualified as estimated for a given analyte could result in an unreliable regional background concentration or one that is below the project-specific PQLs summarized in Table 4.

The number of qualified (both non-detect and estimated) results for each chemical analyte is shown in Figure 4. Non-detect results are represented by dark blue and included all data given a qualifier flag of “U” or “UJ.” Estimated values were given a qualifier flag of “J” and are represented by a medium blue color. A “J” qualifier indicates the result was considered an estimate either because the value was less than the PQL and greater than the MDL, or the data validation indicated QA/QC issues. The lightest blue color indicates sample results that were not qualified. The total sample counts in Figure 4 include the field duplicates.

None of the arsenic results were qualified. Fourteen results were qualified for cadmium as non-detect concentrations. A total of 50 samples and 3 duplicates were analyzed for mercury. Seventeen of these results were non-detects, and an additional 10 samples were qualified as estimates.

Most of the cPAH compounds were detected. Dibenz(a,h)anthracene had the most qualified results with 13 non-detects and 3 estimated results. The remainder of the PAH compounds all had less than four non-detects. Benzo(a)pyrene is the most influential PAH in terms of calculating the TEQ, as it has a TEF of 1. Benzo(a)pyrene concentrations were qualified in eight samples, with two of these results being non-detects. Overall, the total cPAH TEQ concentrations from eight samples were below the PQL of 0.76 µg TEQ/kg (Figure 4).

Non-detects were more common with the dioxin/furan congeners. 2,3,7,8-Tetrachlorodibenzo-p-dioxin and 1,2,3,7,8-pentachlorodibenzo-p-dioxin have the greatest impact on total TEQ (TEF of 1). These 2 congeners alone comprised nearly 43 percent of the total TEQ on average and were not detected in 18 and 8 samples, respectively. The hepta- and octa-chlorinated congeners were detected with the greatest frequency. These congeners had some of the highest concentrations, but also the lowest TEF values. Twenty-eight samples had a total TEQ less than the PQL of 2.3 ng TEQ/kg (Figure 4).

Except for PCB-81 and PCB-169, the dioxin-like PCB congeners were typically detected in more than 75 percent of samples. PCB-105 and PCB-118 were not qualified in any of the samples. PCB-123 contributes the most to the total TEQ with a TEF of 0.1. It was not detected in three samples. The total PCB TEQ was less than the PQL of 0.052 ng TEQ/kg in 15 samples (Figure 4).

A similar summary of qualified results was not determined for the remaining PCB congeners due to the large numbers of congeners present, and because the measure of total PCB congeners for this study was calculated as a sum of all detected congeners, meaning non-detects have no contribution to the total.

Overall, most of the analytes were detected without qualifiers in more than half of the samples analyzed. Dioxin/furan congeners were an exception, with 28 samples under the PQL of 2.3 ng TEQ/kg.

4.3. Summary and spatial distribution of results

This section provides an initial evaluation of the sample results prior to the more in-depth statistical evaluations of Section 5.0. Therefore, no potential outliers have been removed from the summary statistics or spatial distribution figures. It also means that any discussion of the data is limited to simply describing the concentration range and spatial distribution of analytes measured in each bay.

Summary statistics, including the minimum, median, average, and maximum concentrations for each contaminant, are presented in Table 5. Summary results are presented for each individual embayment and for the combined data set. Table 5 also includes the Pearson correlation coefficient squared (r-square) and its significance level (p-value) for the correlation of each contaminant to percent fines for the combined data set (i.e., all four embayments). A more in-depth evaluation of the grain size relationship is discussed in Appendix H for the individual bays and in Section 5.3.2 for the combined data set.

Field duplicates and triplicates were averaged prior to mapping the spatial distributions and calculating the summary statistics in Table 5. The concentrations were averaged using the following rules. Only detected concentrations were averaged for a given location. If all concentrations were non-detects, the maximum detection limit was used.

Non-detect concentrations were included in the summary statistics using a PQL substitution for the metals. The TEQ values presented in this section were calculated using the KM method described in Section 4.1.

4.3.1. Conventional parameters

Conventional parameters analyzed for this study included grain size, TOC, total solids, sulfides, and TVS. Samples from all 40 baseline and 25 secondary locations were analyzed for grain size and sulfides. Sediment from the 40 baseline locations was analyzed for the remaining conventionals. Figure 5 presents combined results for the grain size distribution and percent TOC for the baseline locations. The segments of the pie charts represent the gravel, sand, silt, and clay fractions. The size of the pie charts is scaled to represent the percent TOC.

The percent fines (combined silt and clay fraction) distribution across the AOI varied by embayment. Sediments in the Dungeness Bay portion of the AOI were the most exposed to the higher energies of waves and currents of the Strait of Juan de Fuca. Fines throughout Dungeness Bay averaged just 25 percent. By contrast, percent fines from sediments in the more-protected embayment of Sequim Bay averaged nearly 87 percent. Discovery Bay and Port Townsend Bay had some locations with sandy sediments, but the central portions of both bays were depositional and dominated by fines (Figure 5). This information is presented as a histogram in Figure 6. In this figure, the bars are color coded by embayment. The respective coarse and fine distributions of Dungeness and Sequim Bays are apparent. It also is clear that most of the sediments were either coarse or fine, with only 7 of the 40 samples between 30 and 70 percent fines.

As evidenced by Figure 5, the distribution of percent fines and the TOC were similar in that the smaller circles representing low-percent TOC contain higher percentages of sand. This correlation was evaluated statistically. Although not shown in Table 5, the r-square value for the correlation between fines and TOC was 0.376 ($r = 0.613$). While statistically significant ($p<0.001$; evaluated using Excel data analysis), the r-square value is lower than expected due to two high TOC concentrations in Discovery Bay that skewed the correlation. Locations DIS-07 and DIS-10 had the highest percent TOC of the study at 8.29 and 5.79 percent, respectively. Only one location, DUN-11, had a TOC concentration below 0.5 percent.

TVS was strongly correlated to percent fines. Except for two samples, concentrations in Dungeness Bay were less than 3 percent. Sequim Bay had the highest average TVS concentration at 7.8 percent. Sulfides analysis was conducted on all 65 locations due to its short holding time. Fourteen locations had concentrations greater than 100 mg/kg, while six locations had concentrations greater than 1,000 mg/kg. All six of these locations were in Discovery Bay.

4.3.2. Metals

Arsenic concentrations ranged between 1.9 and 14 mg/kg, with a median of 5.1 mg/kg across the entire AOI. The median concentrations between all four bays varied by less than a factor of three (Table 5). The highest concentrations (above 10 mg/kg) were measured in Discovery Bay at DIS-01, DIS-02, DIS-06, and DIS-07 (Figure 7). Arsenic was correlated to percent fines with an r-square of 0.645 and statistically significant p-value (<0.001).

Cadmium concentrations exhibited substantial variability between embayments. The overall median concentration was 0.24 mg/kg, but the maximum was a factor of 15 higher (Table 5). Dungeness Bay had the lowest concentrations, with cadmium being non-detect in 10 of 13 samples (Figure 8). Port Townsend Bay had similarly low concentrations, with none exceeding 0.5 mg/kg. The same four locations in Discovery Bay that had elevated arsenic concentrations displayed elevated cadmium concentrations. These four locations, plus all five locations from Sequim Bay, had concentrations above 1.0 mg/kg. Due to these elevated concentrations, the correlation between cadmium and fines was skewed, resulting in the lowest r-square value of any analyte from the study at 0.315 ($p<0.001$; Table 6).

All 65 samples were analyzed for mercury. Concentrations ranged from non-detect up to 0.35 mg/kg at location DIS-04 in Discovery Bay. This sample is evaluated as an outlier in Section 5.3.2.2. Aside from location DIS-04, the next highest concentration was 0.14 mg/kg. The overall median concentration was 0.070 mg/kg (Table 5), with most of the elevated concentrations of mercury present in Discovery Bay (Figure 9). The r-square value for this correlation was 0.496 ($p<0.001$; Table 5). As expected from this correlation, the lowest concentrations of mercury were in the sandy areas of Dungeness Bay, where non-detects were common.

4.3.3. Organics

The measured cPAH concentrations ranged from 0.166 to 32.6 µg TEQ/kg, with a median of 14.0 µg TEQ/kg (Table 5). The spatial distribution of cPAH concentrations is shown in

Figure 10. The cPAH concentrations demonstrated the highest correlation to fines of the analytes in this study (r-square = 0.859; $p<0.001$).

Location DIS-06 had the maximum dioxin/furan concentration of 5.29 ng TEQ/kg. Two other locations, PT-05 and PT-08, had concentrations greater than 4.0 ng TEQ/kg. The overall median concentration was 1.67 ng TEQ/kg. Dioxin/furan congeners were strongly correlated to fines (r-square = 0.746; $p<0.001$). Because of this correlation, dioxin/furan congeners exhibited a similar spatial distribution as cPAHs (Figure 11).

The PCB congener TEQ is based on the toxicity of dioxin/furan congeners. However, the TEFs for PCBs are lower than those of dioxin/furan congeners, resulting in lower TEQs. PCB congener TEQs had a median concentration of 0.0809 ng TEQ/kg, and a maximum concentration of 0.44 ng TEQ/kg (Table 5). The maximum concentration was present at location DIS-06 (Figure 12), which is evaluated as an outlier in Section 5.3.2.2. Concentration differences between bays were attributable to the correlation to fines (r-square = 0.586; $p<0.001$). As such, the median concentration in Dungeness Bay was 0.0189 ng TEQ/kg, compared to 0.149 ng TEQ/kg in Discovery Bay.

Total PCB concentrations ranged from 137 to 11,100 ng/kg, with a median of 2,340 ng/kg (Table 5). Like the PCB TEQ, the maximum concentration was observed at location DIS-06. The spatial distribution of total PCBs was similar to the PCB congener TEQ (Figure 13), and the r-square value for the correlation to fines was also similar at 0.598 ($p<0.001$).

5.0 Data Analysis

This section describes the approach used to evaluate results from the four separate embayments with the objective of calculating a regional background sediment concentration for each analyte. Factors that contributed to the overall complexity of this analysis also are discussed in this section. These factors included:

- The difficulties associated with combining results from four separate embayments into a single regional background sediment concentration.
- The likelihood that some of the data, particularly results from Dungeness Bay, may be more consistent with existing natural background sediment concentrations.

The evaluation of the different embayments as regional background was accomplished using a variety of statistical methods. Descriptions of these methods and discussion of the resultant background concentrations are described in this section.

This section begins with a discussion of the natural background data set specific to Port Angeles and provides some context from the SMS rule revision to explain any potential overlap with the NOP regional background sediment concentrations.

5.1. Natural background for the North Olympic Peninsula

According to SCUM II, data from the OSV Bold Summer 2008 Survey (Bold) plus select data sets (Bold plus) are appropriate for use as natural background for sites throughout Puget Sound (DMMP 2009). However, it may be appropriate to use a subset of local Bold data as background for specific locations (Ecology 2015a).

In the process of developing the supplemental data evaluation (SDE) and preliminary SCO reports, there was some concern as to whether the complete Bold plus data set was representative of Port Angeles Harbor (Ecology 2012b, 2013b). As a result, a unique local natural background data set was assembled from previously collected samples in Freshwater Bay and Dungeness Bay and local Bold samples from the Strait of Juan de Fuca and San Juan Islands. This local natural background was called the Port Angeles Proximal Area (PA Proximal) natural background.

The natural background values for Port Angeles were calculated as the 90/90 upper tolerance limit (UTL) from the PA Proximal data set. There were concerns about the robustness of the PA Proximal data set, and both the SDE and preliminary SCO reports included recommendations for the collection of additional sediment samples to supplement PA Proximal natural background (Ecology 2012b, 2013b). It was recommended in the SDE that a more-ideal proximal data set may consist of samples from Dungeness Bay. One of the assumptions in collecting samples from

Dungeness Bay for this investigation was that if they could not be used for regional background, that they could supplement PA Proximal natural background. Section 5.3.2.1 investigates whether Dungeness Bay is more representative of a regional or natural background sampling location.

5.2. Potential analysis of secondary samples

Sediment sampling was divided into baseline and secondary locations. Sediment from the secondary locations was archived after sample collection. Analysis of these samples would be conducted if a larger sample size was needed to supplement the baseline results. The flow chart in Figure 14 outlines the process followed for determining whether or not to analyze the secondary samples.

The first step was to evaluate the precision of the mean expressed as the width of the 95 percent upper confidence limit (UCL) of the mean, divided by the mean:

$$\text{Precision} = \frac{t_{0.05(1),df} S/\sqrt{n}}{\bar{X}}$$

where

$\bar{X}$ = the arithmetic mean of the n baseline samples;

$t_{0.05(1),df}$ = the one-tailed critical value from the t-distribution, for df degrees of freedom and $\alpha = 0.05$;

df = the degrees of freedom associated with the sample standard deviation (S). This is n-1, where n is the number of observations used to estimate the variance;

S = standard deviation of the sample = $\sqrt{\frac{\sum_{i=1}^{n}(X_i - \bar{X})^2}{(n-1)}}$.

Precision of the mean expressed in this way is a common frame of reference for quantifying uncertainty in the population estimates that are necessary for the calculation of the background threshold value.

A precision value of 25 percent was selected as a guideline. If this target was met, no additional analysis was needed. Table 6 shows the precision of the mean for each analyte for each embayment and for the combined four-bay data set. For the combined data set, it was assumed there were four distinct strata, and the stratified mean and its associated precision were calculated. The precision for the individual embayments was variable and often above 25 percent. Factors, such as small sample size and inconsistent grain size distribution, were responsible for the high values. As a result, only the precision of the combined data sets was evaluated using Figure 14. In all cases, the precision was at or below the 25-percent precision target, meaning additional analysis was unnecessary.

Had the precision exceeded the target, the baseline data would have been evaluated against the established natural background and the study PQLs. If the regional background value for an analyte was less than the PA Proximal natural background, the CSL would default to natural background. In such a situation, the analysis of additional samples for regional background would not be beneficial. The same principle was used to compare regional background to the study PQLs from Table 4. If the regional background value was already below the PQL, additional analysis was not required. The final step in Figure 14 was to estimate whether a larger sample size would improve confidence in the upper tail of the distribution.

5.3. Determination of regional background

It was acknowledged in the SAP that the results derived from the NOP regional background AOI would be complex, and may potentially comprise up to four distinct or overlapping populations (Ecology 2013a). As a result, appropriate methods for mixture populations were used to describe the characteristics of this stratified population. Samples identified as outliers or as more representative of natural background (e.g., Dungeness Bay samples) were identified and excluded from the final calculation of regional background.

As part of the preliminary analysis, each bay and analyte combination was evaluated separately. Section 5.3.1 briefly summarizes this evaluation, with more detail provided in Appendix H. From this preliminary evaluation, Dungeness Bay appeared to have a somewhat different contaminant signal than the other bays. Principal components analysis (PCA) was used (Section 5.3.2.1) to investigate how the chemical patterns in Dungeness Bay compared to the other three regional background data sets, as well as to PA Proximal natural background, with the intent of determining whether Dungeness Bay was more likely to represent natural or regional background.

5.3.1. Bay-specific investigations

Each analyte and bay combination was evaluated to describe the best-fit distribution of the data, identify extreme values that may be unduly influential or represent outliers, describe the relative range of concentrations by bay, and identify any correlation between sediment concentration and grain size. A full description of these investigations is presented in Appendix H. The key findings that influenced the direction of this report were:

- In absolute terms, Dungeness Bay had the lowest average concentrations for each bay (Table 6). These low concentrations may be due, in part, to the influence of grain size (with Dungeness Bay having primarily coarse-grained sediments). The flatter slopes of the regressions of sediment concentration on percent fines, particularly for organics, suggest that the low concentrations at Dungeness Bay may be indicative of different chemical loading in this bay.

- Several samples were identified as extreme values (Appendix H), a term defined in SCUM II to indicate values that may represent outliers (Ecology 2015a). Subsequently, a more-comprehensive analysis of the complete multivariate data set was needed to identify and remove influential outliers that could unduly affect the calculated regional background values.

5.3.2. Multivariate evaluation of regional and natural background

Multivariate analyses were used to determine whether Dungeness Bay was more similar to natural or regional background (Section 5.3.2.1) and whether any outlier samples were present in the data set (Section 5.3.2.2).

5.3.2.1. Principal components analysis

Dungeness Bay was previously included in the PA Proximal natural background data set (Ecology 2012b, 2013b). The inclusion of Dungeness Bay in this regional background sampling effort provided a broader chemical description of the sediments in Dungeness Bay, which was used to determine whether Dungeness Bay was more similar to regional or natural background. The patterns observed with the analyte correlations with grain size suggest that Dungeness Bay may be a better fit with natural background, but a more-comprehensive evaluation was needed to make this determination.

PCA is a statistical method for reducing the complexity of a compound, multivariate data set. In reducing the complexity, PCA groups samples with shared components and reveals underlying patterns in the data that would otherwise go unnoticed based on simple evaluations of individual chemical endpoints.

Data from PA Proximal natural background and the NOP regional background bays were all used in the PCA. The available data are summarized in Table 7, based on the following three groups:

- <u>Dungeness Bay</u> included the 13 locations from this regional background sampling that contained all analytes, and the 11 locations from the PA Proximal data set that contained a subset of analytes.
- <u>Regional Background</u> included the 6 locations from Sequim Bay, the 10 locations from Port Townsend Bay, and the 12 locations from Discovery Bay from this regional background sampling.
- <u>Natural Background</u> included all samples from the PA Proximal data set, excluding Dungeness Bay; this group includes the samples from Freshwater Bay and the subset of Bold samples.

These sample groups were used simply as a way of highlighting the results of the PCA for identifying any separation between regional and natural background, and where Dungeness Bay samples fall in that continuum.

The application of PCA is limited by the following: it does not accommodate missing values; therefore, any samples included in a PCA run must have observations for every chemical endpoint included in that analysis, and the number of variables cannot exceed the number of observations. Therefore, the PCA analyses were run for the chemical groups that were most commonly measured, most frequently detected, and with the greatest association to local urban influences, thereby providing information to distinguish between natural and regional backgrounds. Consequently, the decision was made to run two PCA scenarios: dioxin/furan congener data for 75 samples (Table 7), and a combined scenario with both dioxin/furan congener and cPAH data for 53 samples (Table 7). Both scenarios were run twice, substituting non-detected values with zero or the detection limit to determine the influence of non-detects on the PCA outcomes. All PCA analyses were run on the correlation matrices of the data to remove the influence of differences in magnitude of the concentration scales.

Figures 15a and b show the PCA model outputs for the combined scenario and the dioxin/furan congener data only, using substitution at the detection limit for non-detected values. The points are color-coded according to their group: regional background (blue), PA Proximal natural background (green), and Dungeness Bay (red) (Table 7). For both scenarios, the majority of the variability was explained by the first two principal components. The first principal component in each PCA was an overall average of all the variables used in that PCA, representing 74 and 86 percent of the total variance in the two scenarios, respectively. These high percentages indicate that there was substantial covariance among the individual congeners.

In Figures 15a and 15b, concentrations increase from right to left on component 1. In Figure 15a, PA Proximal natural background and Dungeness Bay samples cluster on the right side of the plot indicative of their lower concentrations, and regional background samples are on the left half of the plot indicating higher concentrations. The exceptions to this pattern are six regional background locations (three from Port Townsend and three from Discovery Bay) with low concentrations and coarse grain size. These six sample anomalies and the corresponding grain size influence are discussed below.

In Figure 15a, component 2 was primarily an average of three PAH compounds: indeno(1,2,3-cd)pyrene, benzo(k)fluoranthene, and dibenz(a,h)anthracene. This component captured the unusually high detection limits for these compounds reported in three samples collected from Dungeness Bay (PA_RF01, PA_RF02, and PA_RF03) with non-detected cPAH concentrations.

In Figure 15b, component 1 was an overall average of the dioxin/furan congener concentrations (86 percent of the total variability), with concentrations increasing from right to left along component 1. Component 2 was predominately driven by 1,2,3,7,8,9-hexachlorodibenzofuran, a congener that was rarely detected. The variability expressed by this component was driven by detection limits. The exception was regional background sample PT-05, one of five samples in the data set where this congener was detected.

Figure 16a presents the PCA output of the combined scenario using substitution at zero for non-detected values. The observed pattern is similar to those shown in Figures 15a and 15b, but with less variability on component 2 due to consistent detection limits for non-detects (set to zero). Component 1 is an overall average of all dioxin/furan congeners and cPAH compounds (capturing 87 percent of the total variance), with concentrations increasing from right to left. Like the PCA model based on substitution at the detection limit (Figure 15b), component 2 in Figure 16a also was driven by 1,2,3,7,8,9-hexachlorodibenzofuran.

Figure 16b shows the same PCA output, but with point size scaled to percent fines (larger dots indicate higher fines). The samples with higher concentrations (on the left side of Figure 16b) include the regional background samples with high percent fines, ranging from 66 to 96 percent. The six regional background samples located on the lower-concentration, right side of the PCA plots (i.e., from +1 to +5 on the x-axis for Figures 16a and 16b), were coarser-grained samples with percent fines ranging from 1 to 40 percent, and an average of 14 percent.

An important observation is that there were PA Proximal and Dungeness Bay samples with relatively high fines of up to 84 percent for PA Proximal samples and up to 62 percent for Dungeness Bay samples (i.e., the larger green and red dots on Figure 16b). Despite the higher fines, the concentrations for these samples were low and confined to the right side of the PCA plots.

Overall, the multivariate analysis of the dioxin/furan congener and cPAH concentration patterns for the PA Proximal and Dungeness Bay samples revealed:

- The majority of samples from Discovery, Port Townsend, and Sequim Bays contained high percent fines and clustered on the left, or high-concentration, side of component 1.
- Six samples from Discovery Bay and Port Townsend Bay with low concentrations and low percent fines clustered along the right side of component 1.
- Regardless of percent fines, which ranged up to 64 percent, all samples from Dungeness Bay clustered on the right, or low-concentration, side of component 1.
- Regardless of percent fines, which ranged up to 84 percent, all samples from PA Proximal clustered on the right, or low-concentration, side of component 1.

The analysis suggests that Dungeness Bay contaminant patterns are more similar to PA Proximal natural background samples than to samples from the other three bays included in this regional background survey. Therefore, Dungeness Bay samples will not be included in the calculation of regional background values for the NOP (Section 5.3.3).

5.3.2.2. Outlier analysis

SCUM II includes an approach for evaluating outliers within a regional background data set (Ecology 2015a). The approach contains several steps:

1. Compare the bay-specific distribution to natural background, which, in this case, represents the PA Proximal natural background. Further evaluation is warranted if the potential outlier(s) exceeds natural background.
2. Conduct the appropriate statistical analysis to identify potential outliers.
3. Determine whether the potential outlier may have been directly impacted by a current or historical source.
4. If so, exclude the sample, and calculate the 90/90 UTL of the data set with and without the potential outlier. If the calculated results are substantially different, exclude the outlier.

Bay-specific data for each analyte are compared to each other, PA Proximal natural background, and Bold natural background in Figures H-8 and H-9 of Appendix H. Several samples appear elevated relative to these other data sets, including one cadmium sample from Sequim Bay, one mercury sample from Discovery Bay, and one PCB sample from Discovery Bay.

A more-detailed multivariate outlier investigation was conducted using robust Mahalanobis distances. Mahalanobis distance is a metric very similar to Euclidean distance, which is 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 the chemical variables. Simply stated, this is a multivariate extension of the idea of expressing distance from the mean by the number of standard deviations.

A large difference in a direction in which the data covary (i.e., are correlated) is less alarming than a smaller difference in a direction that lacks correlation. For example, Figure 17 shows the relationship between arsenic and mercury, two metals that are highly correlated, with the exception of one unusual sample. The blue dot represents the centroid and is located at the means for the two metals. The Euclidean distances between the centroid and samples DIS-04 and DIS-06 are 0.3 and 8.7, respectively. The distance from the centroid to sample DIS-04 is of a much-smaller magnitude than the distance from the centroid to sample DIS-06. Yet, it is clear that, sample DIS-04 is much more unusual because it is outside the direction of correlation. An observation that falls outside the multi-dimensional cloud of other data points (e.g., sample DIS-04 for two dimensions in Figure 17) could be identified as a multivariate outlier.

The Mahalanobis distance represents this same comparison of distance from the mean, but is calculated using multiple variables, or dimensions.

More specifically, the Mahalanobis distance is a sum of the individual distances for the chemical variables considered, and weights the individual distances by an element from the inverse of the covariance matrix, so that a difference in a direction of high correlation (e.g., sample DIS-06 in Figure 17) has a lower weight than a difference in a direction that lacks correlation (e.g., sample

DIS-04 in Figure 17). In short, the smaller the Mahalanobis distance, the more closely the sample is related to the remainder of the data.

The Mahalanobis distances were calculated using robust estimates of location (center of mass) and scale (covariance), thus avoiding skewing the estimates of the centroid by the presence of any extreme values that this method intends to detect. Robust estimates of location and scale utilized the fast minimum covariance determinant (MCD) algorithm, which estimates the location and scale from a central subset (e.g., 50 to 75 percent) of the data whose covariance matrix has the smallest determinant. The *covMcd* function of the *robustbase* package (Rousseeuw et al. 2014) in R was used to estimate robust location and scale, and the Mahalanobis distances were calculated using the *mahalanobis* function in R.

The (squared) Mahalanobis distances were calculated for six analyte variables using robust MCD estimators of location and scale based on 75 percent of the data. Total PCBs were not included due to statistical similarities to the PCB congener TEQ. The squared distances are reported because these are expected to follow a chi-square distribution. A quantile-quantile plot for these distances is shown in Figure 18a, and the sorted Mahalanobis distances are presented in Table 8. The long tail for this distribution indicates diversity in the chemical patterns. The dominance of Sequim samples in Figure 18a and Table 8 is driven by the relatively high cadmium concentrations in these samples. These Sequim Bay samples were not associated with elevated concentrations for any of the other analytes.

Sample DIS-04 was identified as an outlier due to an unusually high mercury concentration, and sample DIS-01 was identified as a potential multivariate outlier due to high cadmium (Table 8). Because of the influence of cadmium in identifying so many Sequim Bay samples, a second evaluation of the robust Mahalanobis distances was done for five analyte variables, excluding cadmium. These results (Table 8 and Figure 18b) show sample DIS-04 as the only real outlier due to mercury. The sample with the next highest Mahalanobis distance was DIS-06, which had high values for PCB TEQ. The distance value for sample DIS-01 dropped substantially when cadmium was excluded from the analysis (Table 8). There is no indication that any of these samples was impacted by a current or historical source.

Outliers will contaminate a distribution by producing biased estimates of the mean, higher-variance estimates, and subsequently greater uncertainty in the UCL of the mean and the UTL. These impacts were evaluated by calculating the 90/90 UTLs with and without the potential outliers. Excluding outliers, UTLs differed 9.5 percent for cadmium, 15 percent for PCBs, and 27 percent for mercury. Even given the magnitude of these differences, it is possible that some of the discussed elevated values represent the upper bounds of a regional background signature that has not been fully characterized. Because of this possibility, a conservative approach was used in removing data as outliers.

Ultimately, three data points were excluded from the statistical determination of the 90/90 UTL. Several samples from Sequim Bay and one sample from Discovery Bay had elevated concentrations of cadmium. The highest of these concentrations, SEQ-05, was removed from the data set due to its large Mahalanobis distance (Table 9). The remaining samples with slightly elevated cadmium concentrations were retained in the data set, and the data were reevaluated for outliers excluding cadmium. Sample DIS-04 was removed as an outlier for mercury, and sample DIS-06 was excluded for PCB congener TEQ and total PCBs.

5.3.3. Calculation of regional background using a mixture population

The NOP regional background AOI is best described as a mixture, or stratified population, meaning the data set consists of a combination of sometimes distinct substrata represented by the different bays. As discussed in Section 5.3.2.1, Dungeness Bay was excluded from the regional background data set due to its greater similarity to PA Proximal natural background data than to the other regional background data sets.

Samples from the remaining three bays represent regional background conditions for the NOP. The estimate of the 90/90 UTL for the NOP regional background was calculated following the guidance presented in SCUM II (Ecology 2015a) using methods appropriate for a stratified, or mixture, population.

The 90/90 UTL is the 90 percent upper confidence bound on the 90th percentile. A bootstrap-based procedure was used to estimate the 90/90 UTL of the NOP AOI, which was represented by a mixture distribution of the three embayments. Bootstrapping assumes only that the observed sample data are independent and representative of the underlying population; therefore, random sampling is a prerequisite for an appropriate application of this method. The NOP regional background data set consisted of a mixture population comprised of three different embayments. Random sampling was used within each embayment, and sample sizes were proportional to the area that each bay represented of the total area of the NOP AOI, such that each bay was stratified by area. A stratified bootstrap with proportional and independent resampling within each embayment was used to effectively simulate the mixture population.

The bootstrap-*t* procedure is quite versatile and can be applied to construct confidence limits for any pivotal statistic, including tolerance limits of a mixture distribution (Rebafka et al. 2007, Fernholz and Gillespie 2001, Smith 2002). The tolerance limit of the NOP mixture distribution used a double bootstrap procedure. Each bootstrap sample mimics the same proportion of mixing of the four embayments, with each bay contributing to the whole NOP population in direct proportion to its area. A detailed description of the bootstrap approach and the bootstrap results, including a sensitivity analysis, are presented in Appendix I.

From the sensitivity analysis results, the bootstrap-based tolerance limits generated from this data set were concluded to be robust and representative of the mixture population present in the NOP AOI. Thus, it is estimated that there is a 90-percent confidence that at least 90 percent of the samples that may be collected from the NOP AOI will not exceed the estimated UTLs. As such, the UTLs are appropriate as regional background sediment concentrations.

5.4. Regional background values

Table 9 presents the 90/90 UTL values with the select outliers removed and the PA Proximal natural background concentrations calculated as the 90/90 UTL. All values are presented to two significant figures. All regional background 90/90 UTL values were calculated without Dungeness Bay. The PA Proximal natural background values in Table 9 do not currently include the 13 samples from Dungeness Bay.

All of the regional background 90/90 UTL values were higher than PA Proximal natural background for all analytes. The 90/90 UTL for arsenic was 14 mg/kg. The 90/90 UTL for cadmium was 2.4 mg/kg. This cadmium value was driven by the elevated concentrations from Sequim Bay, even with outlier SEQ-05 removed. Mercury also had an outlier removed (sample DIS-04). The 90/90 UTL for mercury was 0.13 mg/kg.

The 90/90 UTL for cPAH was 31 µg TEQ/kg. The 90/90 UTL for dioxin/furan congeners was 5.0 ng TEQ/kg. The 90/90 UTL for PCB congeners was 0.21 ng TEQ/kg. The 90/90 UTL for total PCBs was 5,300 ng/kg. Sample DIS-06 was excluded as an outlier for the calculation of PCB regional background.

6.0 Carcinogenic Polycyclic Aromatic Hydrocarbon Regional Background Value for Port Angeles Harbor

Polycyclic aromatic hydrocarbons (PAHs) are unique among the target analytes in that they have both current and historical sources and are typically correlated to industry and population density. Port Angeles is the largest city on the NOP, with a long history of industry. As such, PAH concentrations in Port Angeles Harbor are expected to be higher than surrounding bays. As mentioned in Section 1.2, the primary rationale for not collecting regional background samples from within Port Angeles Harbor was that the distribution of elevated dioxins/furans was not defined within the Harbor, leaving only a small portion near the tip of Ediz Hook available for sampling.

To account for excluding Port Angeles Harbor from regional background sampling, efforts were made while writing the SAP (Ecology 2013a) to ensure that the land use surrounding the four NOP embayments was similar to that of Port Angeles. However, land use is not necessarily a good surrogate for industrialization and population. The cPAH regional background value of 31 µg TEQ/kg derived from the less-industrialized and populated embayments is likely biased low relative to Port Angeles Harbor.

Incorporating lessons learned during the development of regional background concentrations for Port Gardner and Bellingham Bays (Section 1.3) and clarifications in the SCUM II guidance (Ecology 2015a), calculation of regional background values using samples from Port Angeles Harbor is permissible for analytes not directly associated with a point source. This section describes the rationale for developing a site-specific cPAH regional background value solely for use within Port Angeles Harbor.

6.1. Applicability of North Olympic Peninsula carcinogenic polycyclic aromatic hydrocarbon regional background to Port Angeles Harbor

Published scientific literature shows a positive correlation between PAH sediment concentrations and population density and industrial activity partially attributable to surface water runoff, creosote pilings, vessel traffic, and aerial deposition (Van Metre et al. 2000, Stout 2003, Kannan et al. 2005, Mitsova et al. 2011, Hong et al. 2011, Kumar et al. 2014). Although a large amount of variability was noted, most studies found surface water runoff to be the largest contributor because of the buildup of PAH in road dust, followed by a storm water pulse to the receiving water body following rain events. Much of the variability in loadings was attributed to seasonal rainfall differences.

PAH sources and pathways to sediment from urban areas are similar throughout Puget Sound. Both the Port Gardner Bay and Bellingham Bay regional background characterizations resulted in regional background values for cPAH, which were consistent with the influence of these diffuse urban sources.

Based on this information, Ecology determined that the NOP regional background cPAH value did not adequately represent diffuse sources of cPAH to Port Angeles Harbor, because all three bays used in the NOP regional background calculation had lower populations and less anthropogenic influence. To address this issue, Ecology decided to incorporate existing cPAH data collected from within Port Angeles Harbor to supplement the data collected from the three NOP bays. The cPAH spatial pattern in surface sediments of Port Angeles Harbor indicates a significant contribution from diffuse urban sources.

Ecology also considered whether similar arguments could be made for PCBs and dioxins/furans in Port Angeles Harbor. For both analytes, Ecology found that the data did not indicate a significant contribution from diffuse sources. Multiple studies have been conducted in Port Angeles Harbor, which showed the highest levels of PCB aroclors and congeners in sediment are localized in proximity to their presumed sources. These historical sources include the Rayonier Mill facility at the east end of the Harbor (Windward 2014), and the combined properties in the Western Harbor. Although sediment transport processes are likely to have dispersed PCBs beyond the source areas, they were not detected in the majority of Port Angeles Harbor-wide samples.

Ecology's *Port Angeles Harbor Dioxin Source Study, Port Angeles, Washington* (Ecology 2013c) found four distinct dioxin/furan congener source signatures. Spatial patterns for three of the dioxin/furan sources indicated the contamination was confined to specific areas adjacent to the Rayonier Mill and the Western Harbor. The spatial pattern for the fourth, and most widespread and abundant, source was related to combustion from four historical hog fuel burners that operated along the shoreline of Port Angeles Harbor. Because the concentrations of dioxins/furans are attributed to the direct impact of identifiable sources, sediment samples within the harbor cannot be used to establish regional background for dioxins/furans.

6.2. Regional background concentrations in other bays

In concert with the NOP, regional background characterizations also have been completed for both Port Gardner and Bellingham Bays (Ecology 2014, 2015b). As with the NOP, the AOI for each of these characterizations had their own unique set of issues, which included the distribution of cPAHs.

6.2.1. Port Gardner Bay

A conservative approach was taken in delineating the Phase I AOI for Port Gardner. A buffer distance of at least 500 meters was used along the developed southern shore, and much of the

AOI included the relatively coarse-grained sediment on the Snohomish River delta (Ecology 2014).

The Snohomish River has a watershed area of 1,800 square miles; a discharge rate of 10,000 cubic feet per second (cfs); and a suspended sediment load of over 490,000 tons per year (USGS 2011). The coarse fraction of this large sediment load settles on the river delta, with the finer fraction being carried offshore and to the south. This continual influx of low-concentration sediment from the river resulted in the northern half of the Phase I AOI being considered representative of natural background.

Phase II sampling included areas closer to the southern shoreline and associated sources. Rather than using a default buffer distance to determine the Phase II AOI, bay-specific information was used to exclude depositional areas of outfalls or areas directly affected by identifiable sources. The northern and western boundaries of the Phase II AOI were defined by excluding areas within the concentration ranges of natural background, which generally included depositional areas influenced by the Snohomish River and deeper areas that were part of Puget Sound proper.

A transposition of the Phase I and adjusted Phase II AOIs is presented in the *Port Gardner Bay Regional Background Sediment Characterization Report: Final Data Evaluation and Summary Report, Everett, Washington* (Ecology 2014).

For Port Gardner, regional background for cPAHs was established at 56 µg TEQ/kg and calculated using a pooled 90/90 UTL statistical metric.

6.2.2. Bellingham Bay

In Bellingham Bay, different AOIs were established for different analytes. Most of the bay was directly influenced by a single source for mercury and subsequently identified as a cleanup site for mercury. Therefore, mercury was not included as an analyte for regional background. However, Ecology determined that the bay could be sampled for other analytes unrelated to the mercury cleanup site. Extensive data were available to establish the AOIs. Using remedial investigation data, the general boundaries of cleanup sites were identified. An additional 75-meter buffer was established beyond these boundaries, as well as any other potential sources, to ensure the AOI was outside their direct influence.

Areas that had previously been contaminated with mercury, cPAHs, and dioxins/furans were recovering rapidly in the top 10 centimeters of sediment due primarily to the sediment load from the Nooksack River. Similar to Phase II of Port Gardner Bay (Section 6.2.1), areas in the depositional zone of the Nooksack River were predetermined to be representative of natural background. The river drains 840 square miles of watershed, with a flow of 3,200 cfs, and has a sediment load of over 1,400,000 tons per year (USGS 2011). This sediment load was deposited in the nearshore areas east and south of the river mouth, effectively recovering areas to natural background levels.

In Bellingham Bay, regional background for cPAHs was established as 86 µg TEQ/kg and calculated using a pooled 90/90 UTL statistical metric (Ecology 2015b).

6.3. Establishing a carcinogenic polycyclic aromatic hydrocarbon regional background value applicable to Port Angeles Harbor

The use of existing analyte data to inform and supplement regional background data has been a key part of the study design process. Based on experience gained during the Port Gardner and Bellingham Bay regional background efforts, Ecology decided to incorporate existing data from locations within Port Angeles Harbor when establishing regional background for cPAHs.

Using the Bellingham Bay regional background model as a guide, Ecology assumed no relationship between the distributions of dioxins/furans and cPAHs within Port Angeles Harbor. Unlike Port Gardner and Bellingham Bays, natural recovery is very limited in Port Angeles Harbor, as there are no significant inputs of clean sediment. The three creeks (Tumwater, Valley, and Peabody) that empty into the harbor have a combined watershed area of 12.8 square miles, a discharge of approximately 12 cfs, and a loading of approximately 33 tons of sediment per year. As a result of the low sedimentation, existing surface sediment contamination from direct sources demonstrates little or no natural recovery from historical inputs.

Several steps were taken to filter the existing data present in Port Angeles Harbor. All available cPAH data from within the top 0 to 10 centimeters were extracted from Ecology’s Environmental Information Management database. The majority of these samples were collected within the last 10 years. In addition, all results must have undergone data validation at a level sufficient for use as regional background. All samples identified in the data review are presented in Figure 19.

Ecology decided to maintain the original 500-meter buffer along the southern and western Harbor shorelines, as well as Ediz Hook, used in the NOP SAP (Ecology 2013a). This buffer excluded sediments that could have been impacted by potential sources of cPAHs, including the City CSOs 6 and 7, several large cleanup sites, deteriorating creosote pilings, and the immediate depositional zones of storm water outfalls. This buffer excluded the majority of samples in Port Angeles Harbor. An additional buffer was drawn within 500 meters of the Rayonier Mill dock, excluding two more samples (Figure 19 cross-hatched area).

This approach identified 14 samples in Port Angeles Harbor outside of direct influence of potential sources (Figure 19). The total cPAH TEQ concentrations for these samples are presented in Table 10. Complete sample results, including individual PAH compounds, are presented in Table E-4 of Appendix E.

Eight of these samples were surface grabs collected by Ecology as part of the 2008 Port Angeles Harbor sediment investigation (Ecology 2012a). The remaining six samples were data from the Puget Sound Assessment and Monitoring Program (PSAMP) (Table 10). The PSAMP collected and analyzed sediment samples for the standard SMS chemicals but not for dioxins/furans.

The data from the NOP regional background study and the eight samples from within Port Angeles Harbor were from the top 10 centimeters of surface sediment, while the PSAMP samples were collected from the top 3 centimeters of surface sediment. Evaluations of radioisotope dating cores and sediment profile imaging within the harbor have led to an estimated sediment deposition rate of 0.17 centimeters per year. At this rate, it would take approximately 59 years to accumulate 10 centimeters of surface sediment; therefore, the top 3 centimeters would represent approximately 17 years of sediment deposition.

Ecology determined that the samples listed in Table 10 include a mixture of historic and recent sediment deposition and represent the current concentrations of cPAHs in Port Angeles Harbor from diffuse sources. These samples have a cPAH concentration range between 10.2 and 172 µg TEQ/kg, with an average of 49.7 µg TEQ/kg (Table 11). By comparison, the average concentrations from Discovery Bay, Sequim Bay, and Port Townsend Bay ranged between 16.1 and 19.7 µg TEQ/kg (Table 5).

Sample PSAMP_SP-1537 was evaluated as an outlier using the same stepwise criteria presented in Section 5.3.2.2 as follows:

- This sample was well above the distribution of results from the PA Proximal natural background data set.
- This sample was identified as a formal outlier using Dixon’s outlier test.
- This sample may have been impacted by a direct source given its location near the 500-meter buffer in the south/southwest portion of Port Angeles Harbor.

For the above reasons, sample PSAMP_SP-1537 was excluded as an outlier for the calculation of regional background in Section 6.4. Table 11 shows the population summary statistics of Port Angeles Harbor and the combined data set with and without this outlier. The average of the combined data set decreases by 3.5 µg TEQ/kg with PSAMP_SP-1537 removed. The precision of the mean also was calculated for each iteration (Table 11). The precision of the combined data set without the outlier was 20 percent, below the 25-percent guideline established in Section 5.2.

6.4. Port Angeles-specific carcinogenic polycyclic aromatic hydrocarbon regional background

The decision of how to determine an appropriate regional background value for cPAH applicable to Port Angeles Harbor is based on Ecology’s interpretation of the SMS rule, lessons learned from previous regional background studies, extensive bay-specific data from Port Angeles

Harbor, and recent literature linking population density and industrialization to cPAH concentrations in sediment.

Based on the information presented in this section, a Port Angeles Harbor-specific regional background value for cPAH was calculated by pooling the cPAH data from Discovery Bay, Sequim Bay, and Port Townsend Bay with 13 samples from central Port Angeles Harbor. The total sample size for the combined data set was 40 samples. Such an approach effectively maintains stratified populations for Discovery Bay, Port Townsend Bay, and Sequim Bay, as the sample counts in these bays were based on their area. This approach also gives more weight to the Port Angeles Harbor samples than would be warranted based on area alone, which is suitable for a Port Angeles Harbor-specific value. Using this pooled 90/90 UTL statistical metric, the cPAH regional background value for Port Angeles Harbor is established as 64 µg TEQ/kg (Table 12). All other NOP regional background values for the remaining analytes from Table 9 apply to Port Angeles Harbor.

7.0 References

DMMP (Dredged Material Management Program). 2009. OSV Bold Summer 2008 Survey: Data Report. Prepared by DMMP. June 25.

Ecology (Washington State Department of Ecology). 2007. Evaluating the Toxicity and Assessing the Carcinogenic Risk of Environmental Mixtures Using Toxicity Equivalency Factors.

Ecology. 2012a. Port Angeles Harbor Sediment Characterization Study, Port Angeles, Washington. Sediment Investigation Report. Prepared by NewFields, Edmonds, WA. December.

Ecology. 2012b. Port Angeles Harbor Supplemental Data Evaluation to the Sediment Data Evaluation Report, Port Angeles, Washington. Prepared by NewFields, Edmonds, WA. December.

Ecology. 2013a. North Olympic Peninsula Regional Background Characterization, Port Angeles-Port Townsend, Washington, Sampling and Analysis Plan. Prepared by NewFields, Edmonds, WA. Publication No. 13-09-107. May.

Ecology. 2013b. Preliminary Sediment Cleanup Objectives for Port Angeles Harbor, Port Angeles, Washington. Prepared by NewFields, Edmonds, WA. May.

Ecology. 2013c. Port Angeles Harbor Dioxin Source Study, Port Angeles, Washington. Prepared by NewFields, Edmonds, WA, with support from Infometrix, Bothell, WA, and Greg Glass, Seattle, WA, February.

Ecology. 2014. Port Gardner Bay Regional Background Sediment Characterization: Final Data Evaluation and Summary Report, Everett, Washington. December.

Ecology. 2015a. Sediment Cleanup User's Manual II: Guidance for Implementing the Cleanup Provisions of the Sediment Management Standards, Chapter 173-204 Washington Administrative Code. Draft Report. Publication No. 12-09-057. March.

Ecology. 2015b. Bellingham Bay Regional Background Sediment Characterization: Final Data Evaluation and Summary Report. Publication No. 15-09-044. February.

Fernholz, Luisa T. and John A. Gillespie. 2001. "Content-Corrected Tolerance Limits Based on the Bootstrap." *Technometrics*, 43(2):147-155. May.

Fujisaki, A., K. Schock, J. Stern, and B. Nairm. 2013. Analysis of sedimentation and accumulation of PCBs from CSO discharges into a dynamic receiving environment in Duwamish River. Prepared by King County Department of Natural Resources and Parks, Seattle, WA.

Helsel, Dennis R. 2010. "Summing Nondetects: Incorporating Low-Level Contaminants in Risk Assessment." *Integrated Environmental Assessment and Management*, 6(3):361-366.

Helsel, Dennis R. 2012. Statistics for Censored Environmental Data Using Minitab and R, Second Edition. Wiley-Interscience, John Wiley & Sons, New Jersey. 324 pp.

Hewett, Paul and Gary H. Ganser. 2007. "A Comparison of Several Methods for Analyzing Censored Data." *Ann. Occup. Hyg.*, 51(7):611-632.

Hong, Y., Y. Shen, G. Yu, Y. Liu, G. Li, and M. Wand. 2011. "Impacts of urbanization on surface sediment quality: evidence for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) contaminations in the Grand Canal of China." *Environ. Sci. Pollut. Res.* 19:1352-1363.

Kannan, K., B. Johnson-Restrepo, S.S. Yohn, J.P. Glesy, and D.T. Long. 2005. "Spatial and temporal distribution of polycyclic aromatic hydrocarbons in sediment from Michigan inland lakes." *Environ. Sci. Technol*, 39:4700-4706.

Klein, J.P. and M.L. Moeschberger. 2003. Survival Analysis: Techniques for Censored and Truncated Data, Second Edition. Springer, New York. 536 pp.

Kumar, R., B. Gupta, H. Gupta, and M. Rani. 2014. "Distribution of persistent organic pollutants in urban aquatic systems." *Int. Jour. of Sci. Res. In Envir. Sci*., 2(7):233-243.

Lee, Lopaka. 2012. NADA: Nondetects and Data Analysis for Environmental Data. R package version 1.5-4. Available online at: <http://CRAN.R-project.org/package=NADA>.

Mitsova, D., V. Jaap, P. Gardenali, and I. Stafeychuk. 2011. "Variability in road runoff pollution by polycyclic aromatic hydrocarbons (PAHs) in the urbanized area adjacent to Biscayne Bay, Florida." *Journal of Environmental Protection*, 2:1317-1330.

PSEP (Puget Sound Estuary Program). 1997. Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound. U.S. Environmental Protection Agency, Region 10, Seattle, WA. April.

PTI (PTI Environmental Services). 1989. Data Validation Guidance Manual for Selected Sediment Variables. Draft Report. Prepared for Washington State Department of Ecology, Olympia, WA. June.

R Core Team. 2013. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0. Available online at: <http://www.R-project.org/>.

Rebafka, Tabea, Stephan Clemencon, and Max Feinberg. 2007. "Bootstrap-based tolerance intervals for application to method validation." *Chemometrics and Intelligent Laboratory Systems*, 89:69-81.

Rousseeuw, Peter, Christophe Croux, Valentin Todorov, Andreas Ruckstuhl, Matias Salibian-Barrera, Tobias Verbeke, Manuel Koller, and Martin Maechler . 2014. robustbase: Basic Robust Statistics. R package version 0.91-1. Available online at: <http://CRAN.R-project.org/package=robustbase>.

Smith, Robert W. 2002. "The Use of Random-Model Tolerance Intervals in Environmental Monitoring and Regulation." *Journal of Agricultural, Biological, and Environmental Statistics*, 7(1):74-94.

Stout, S.A. 2003. Chemical Fingerprinting of PAHs in Sediment – Recognizing the Contribution of Urban Background. Guidance for Environmental Background Analysis – Naval Facilities Engineering Command, Washington, D.C. User's Guide UG-2054-ENV, Pages 153-179. April.

USGS (U.S. Geological Survey). 2011. Sediment Load from Major Rivers into Puget Sound and its Adjacent Waters. U.S. Department of the Interior, U.S. Geological Survey. Fact Sheet 2011–3083. August.

Van Metre, P.C., B.J. Hahler, and E.T. Furlong. 2000. "Urban Sprawl Leaves Its PAH Signature." *Environ. Sci. Technol.* 34:4064-4070.

Van den Berg, M., L.S. Bimbaum, M. Denison, M. De Vito, W. Farland, M. Feeley, H. Fiedler, H. Hakansson, A. Hanberg, L. Haws, M. Rose, S. Safe, D. Schrenk, C. Tohyama, A. Tritscher, J. Tuomisto, M. Tysklind, N. Walker, and R. Peterson. 2006. The 2005 World Health Organization Re-Evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds. Prepared for the World Health Organization. ToxSci Advance Access published July 7, 2006. Published by Oxford University Press on behalf of the Society of Toxicology.

Windward (Windward Environmental LLC). 2014. Former Rayonier Mill in Port Angeles, Interim Action Report Volume II: Marine Data Summary Report. Final. Prepared for Rayonier, Inc. Seattle, WA.

This page purposely left blank for duplicate printing

Figures

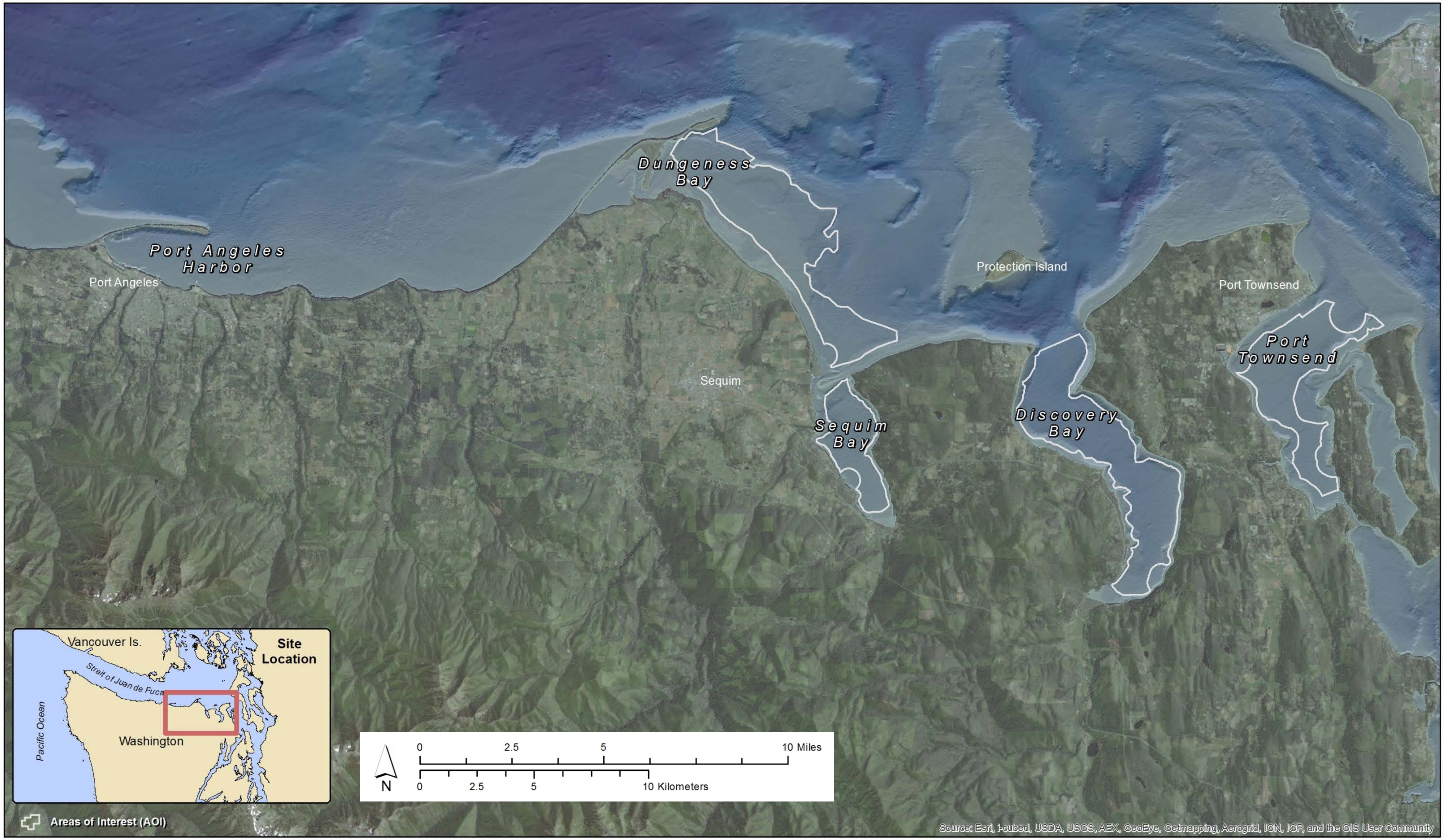

Figure 1. North Olympic Peninsula background study areas

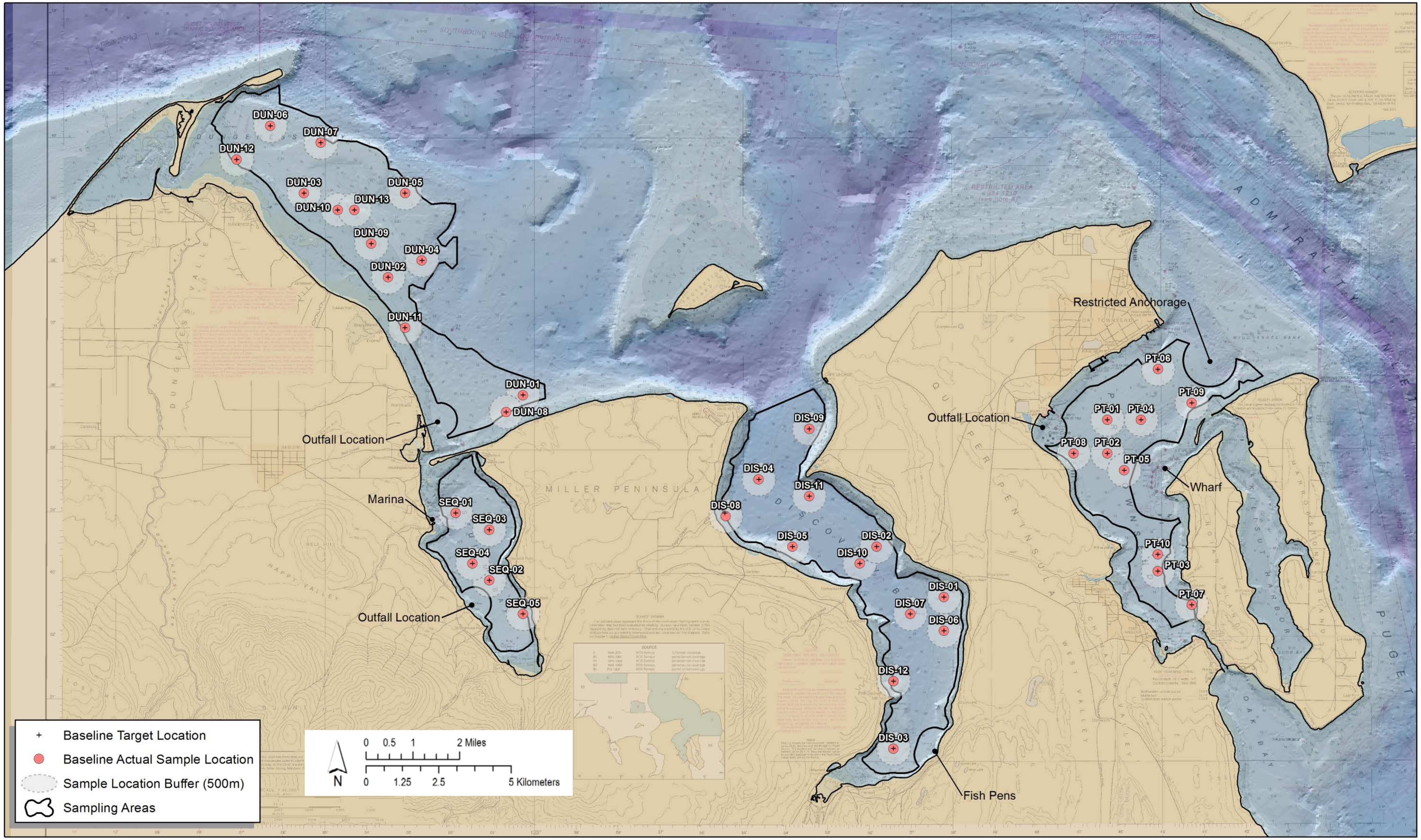

Figure 2. Baseline sediment sampling locations for Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay

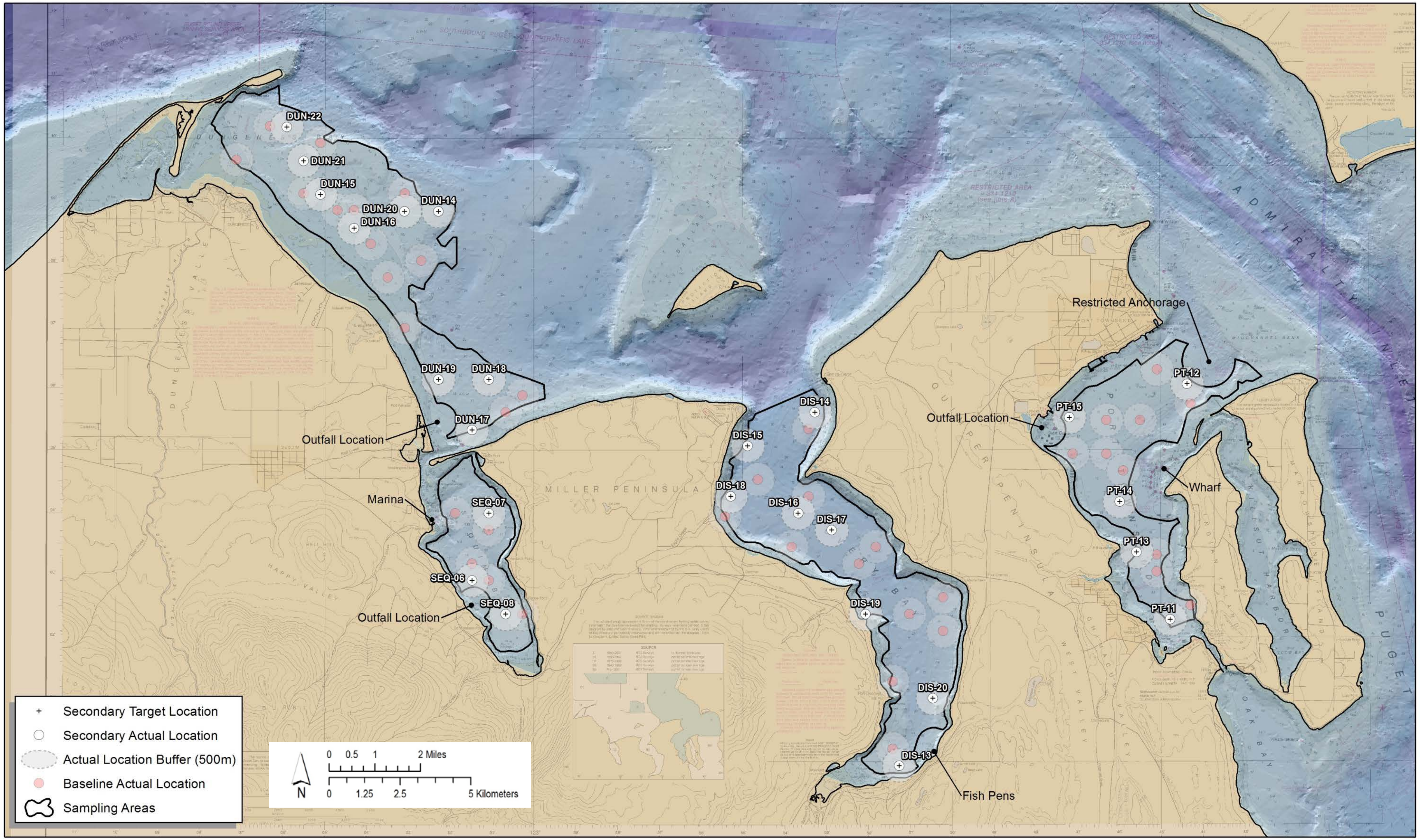

Figure 3. Secondary sediment sampling locations for Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay

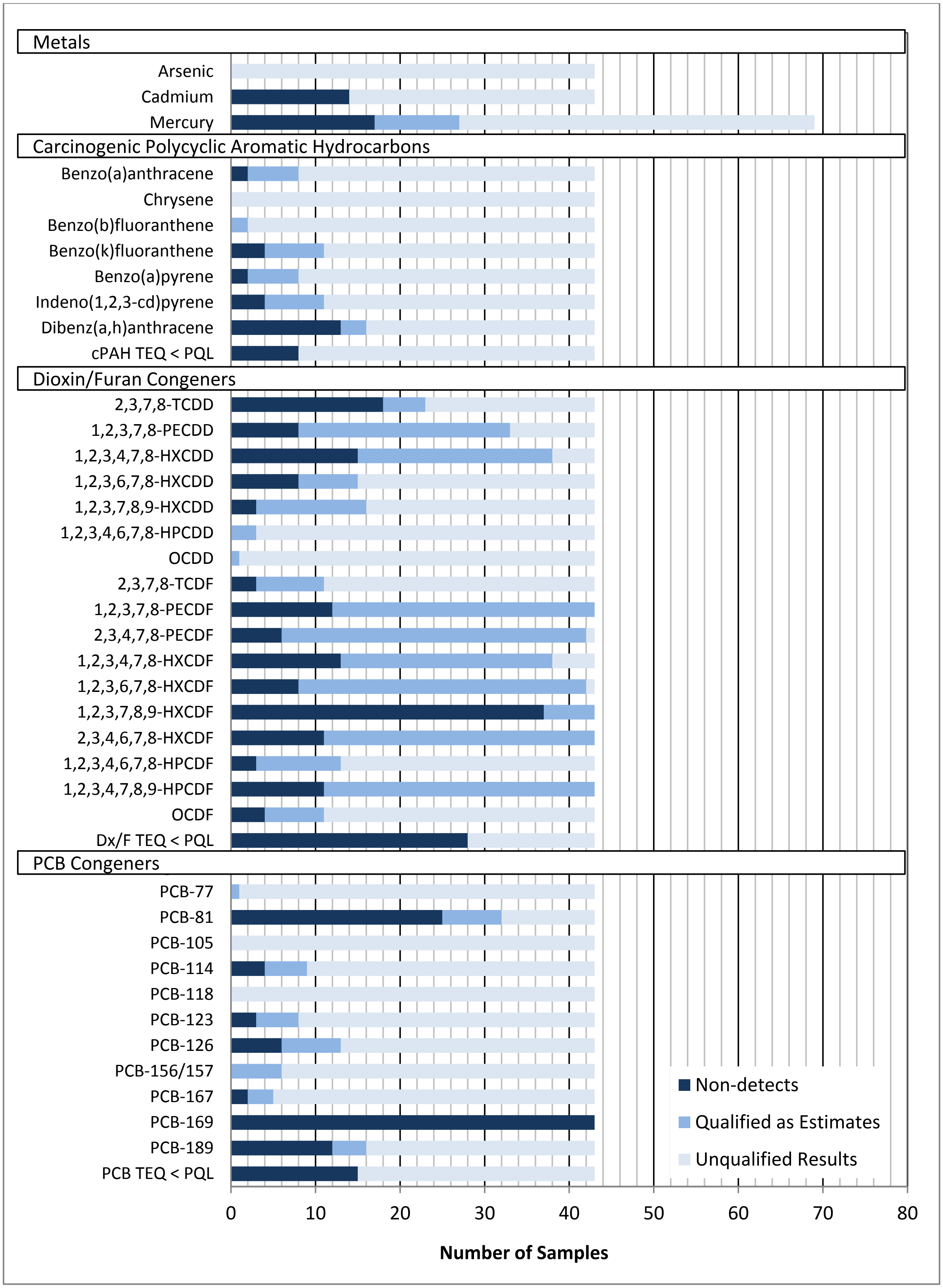

Figure 4. Summary of non-detect and estimated results

This page purposely left blank for duplicate printing

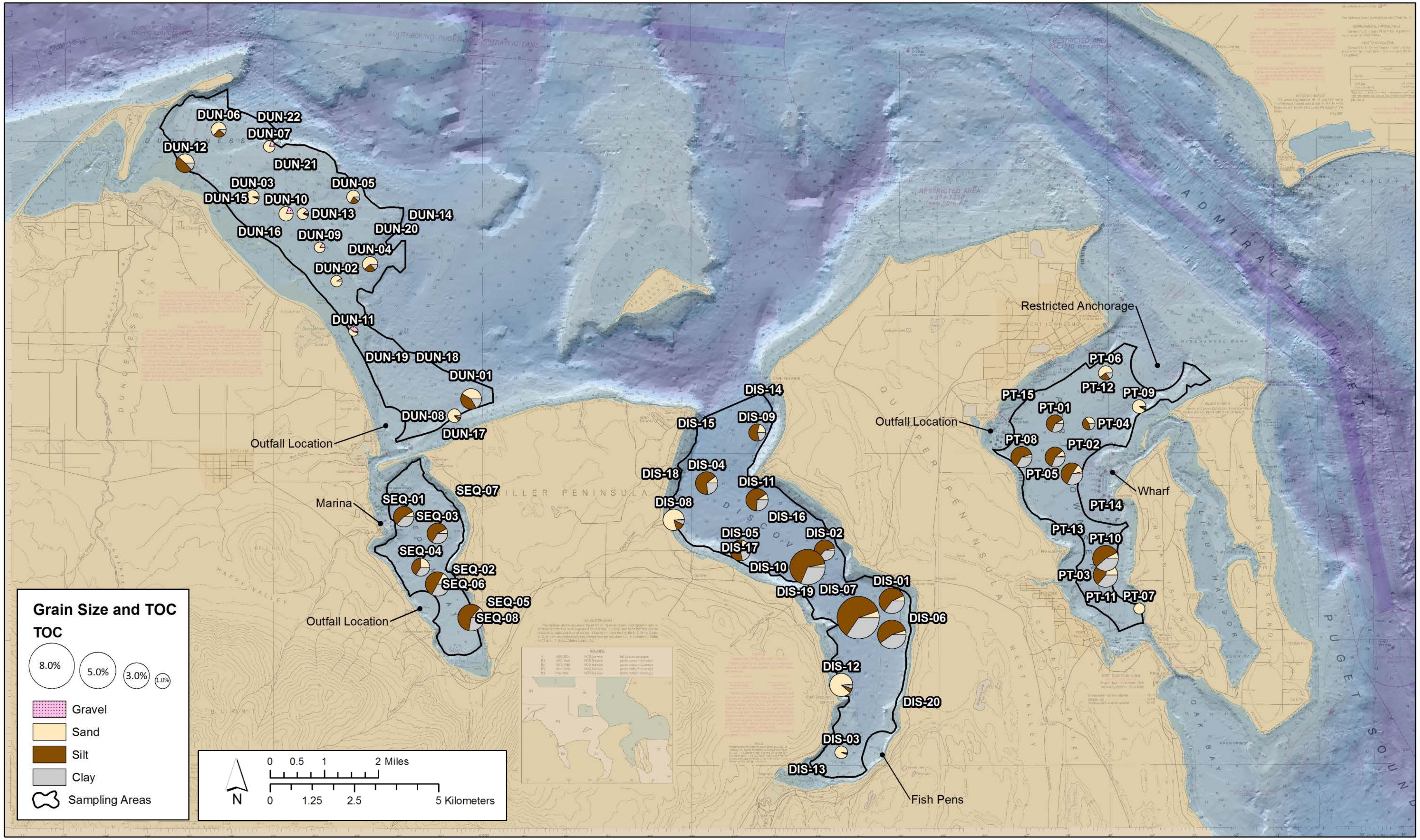

Figure 5. Grain size and total organic carbon distribution for the baseline samples collected at locations from Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay

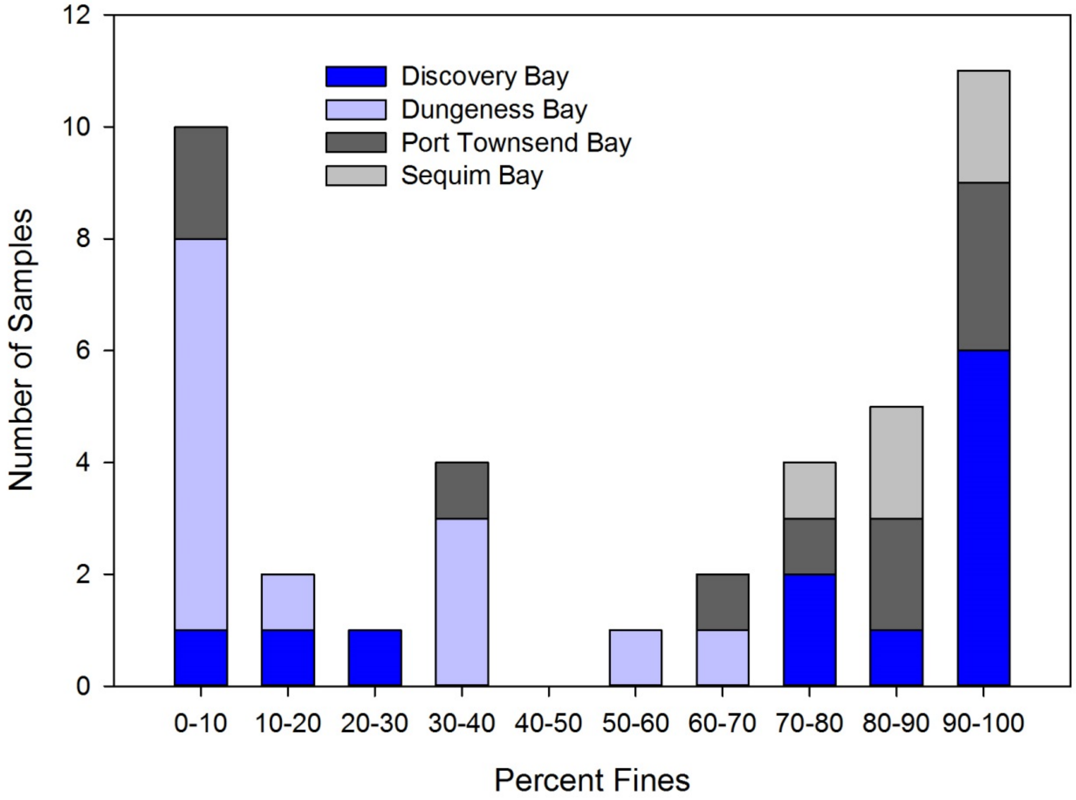

Figure 6. Histogram of the grain size distribution for all baseline samples

This page purposely left blank for duplicate printing

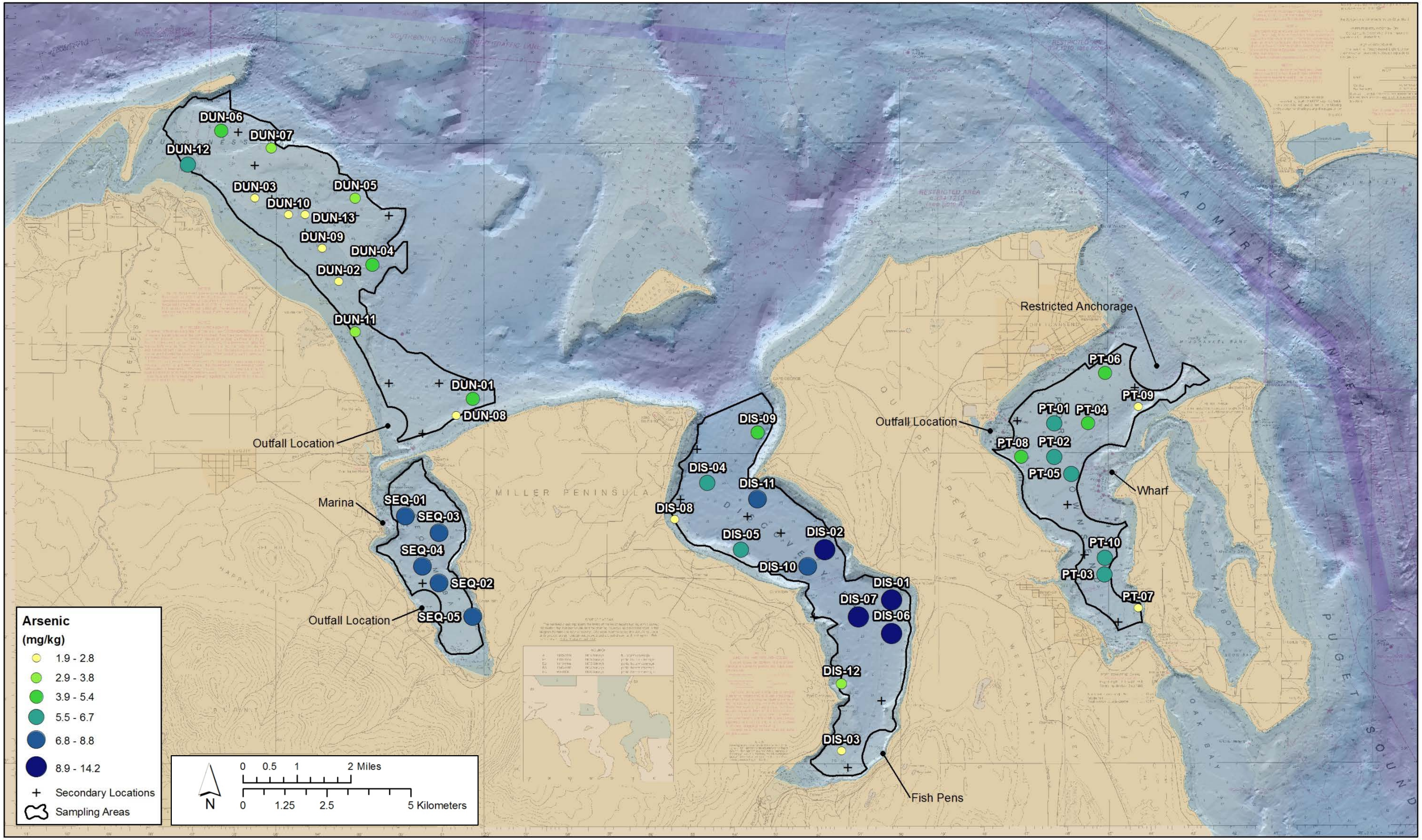

Figure 7. Arsenic distribution for samples collected at the baseline locations from Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay

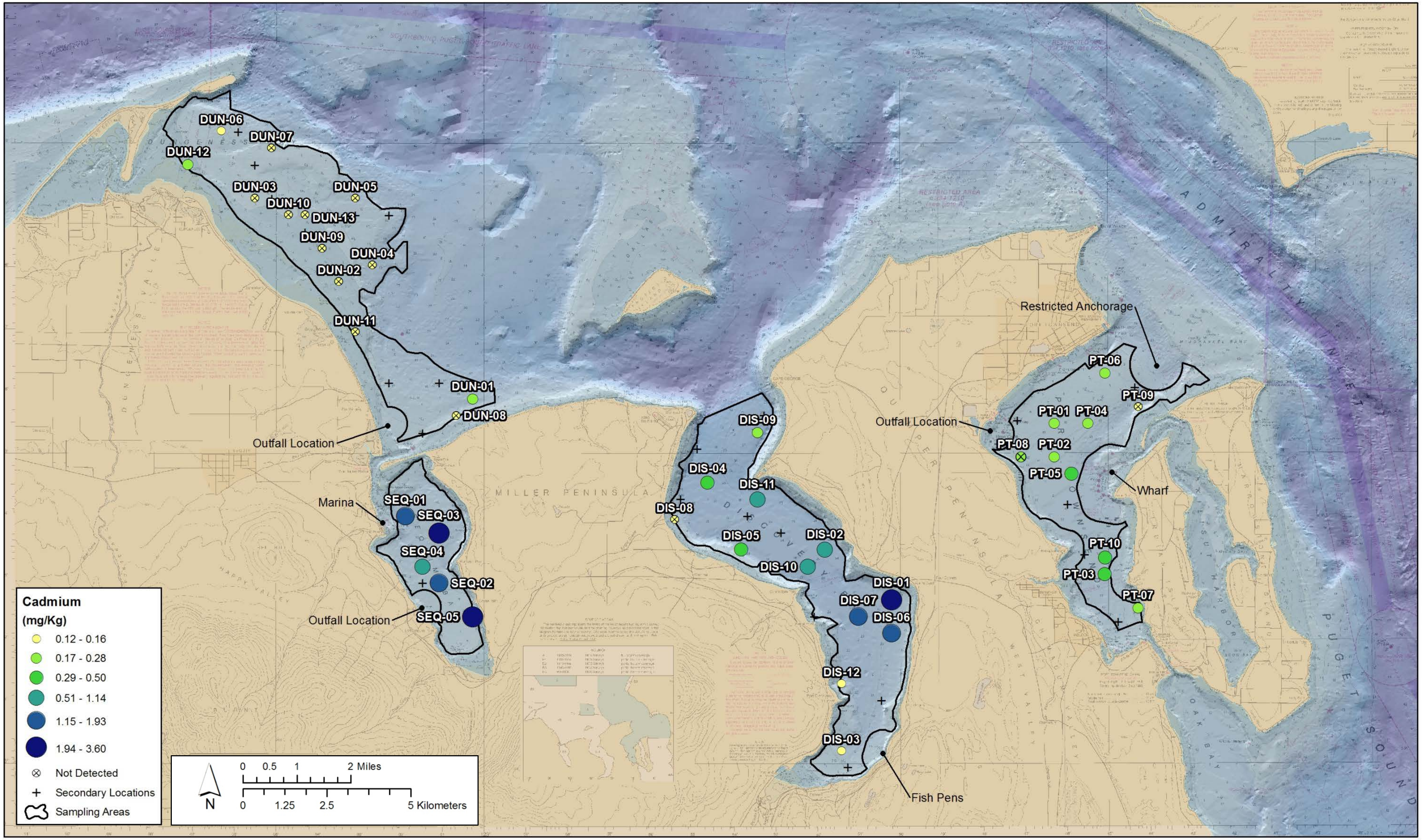

Figure 8. Cadmium distribution for samples collected at the baseline locations from Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay

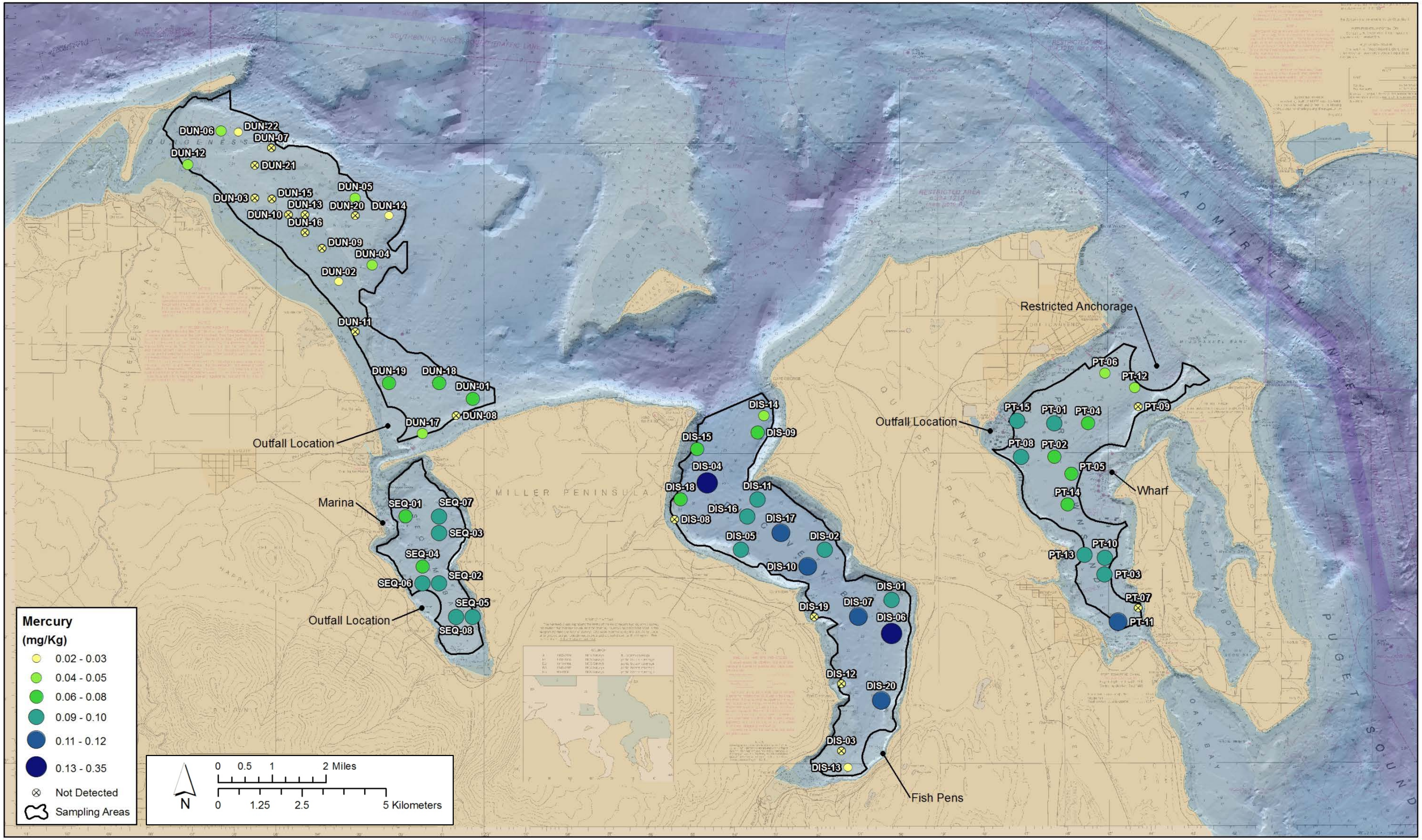

Figure 9. Mercury distribution for samples collected at the baseline and secondary locations from Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay

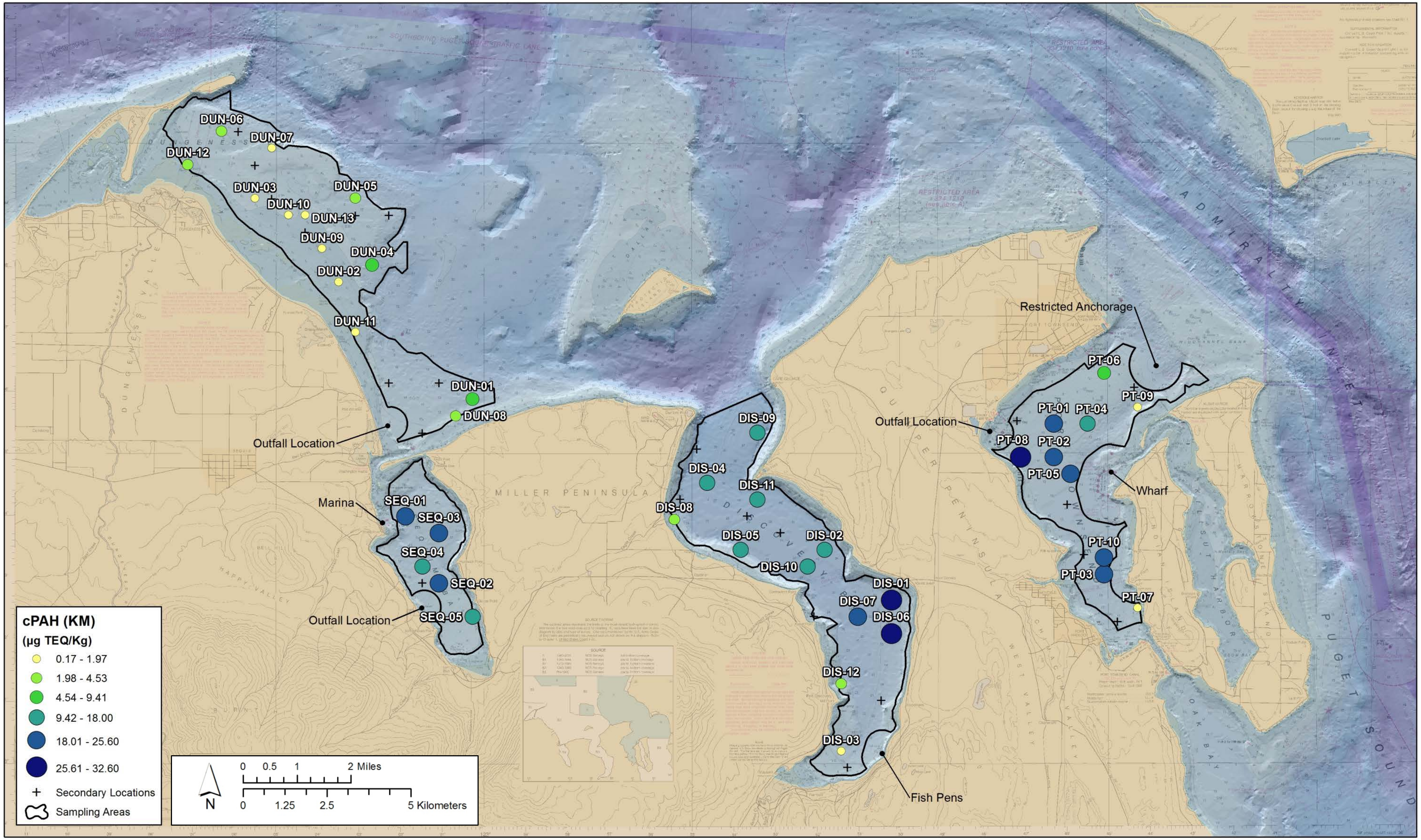

Figure 10. Carcinogenic polycyclic aromatic hydrocarbon distribution for samples collected at the baseline locations from Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay

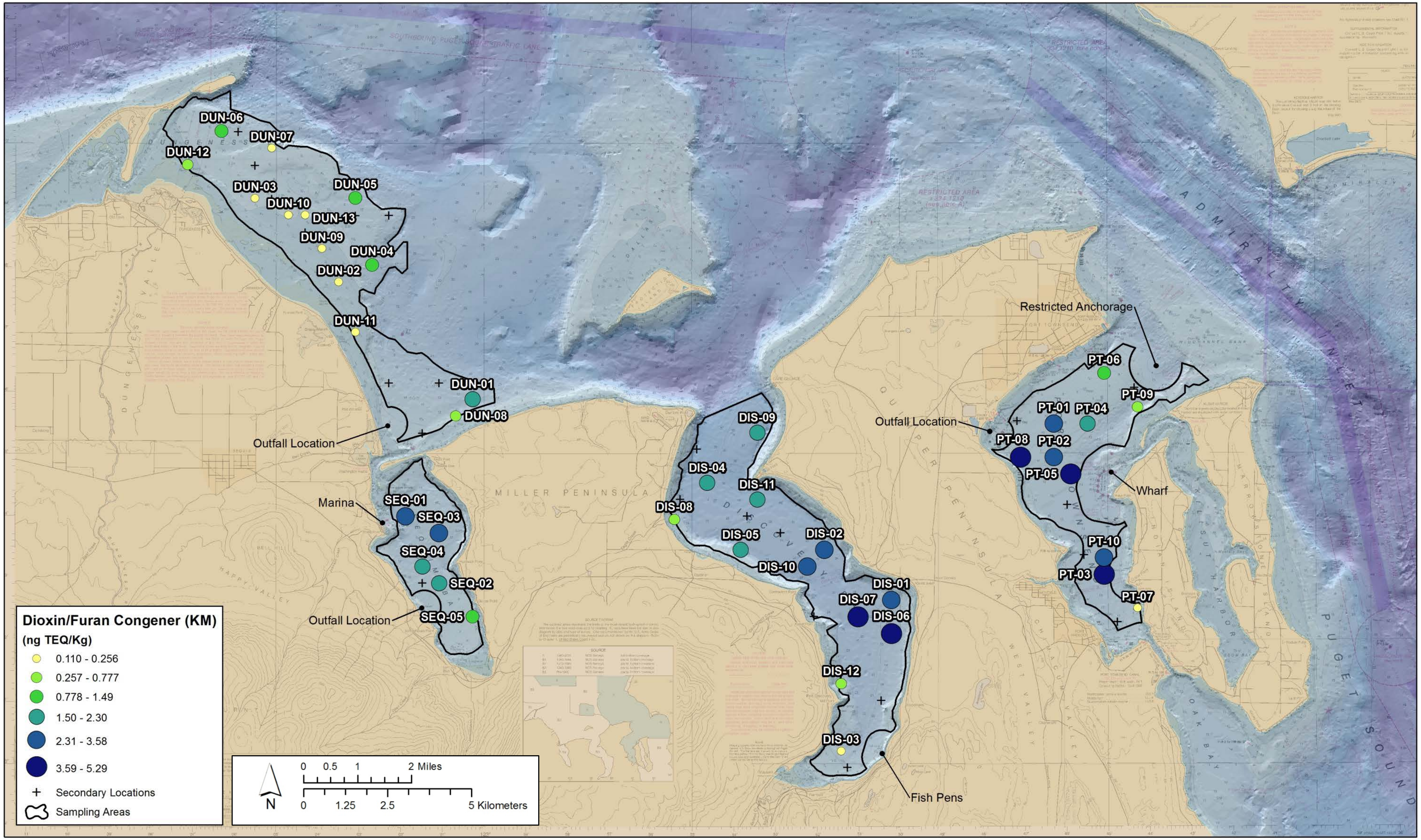

Figure 11. Dioxin/furan congener toxicity equivalent distribution for samples collected at the baseline locations from Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay

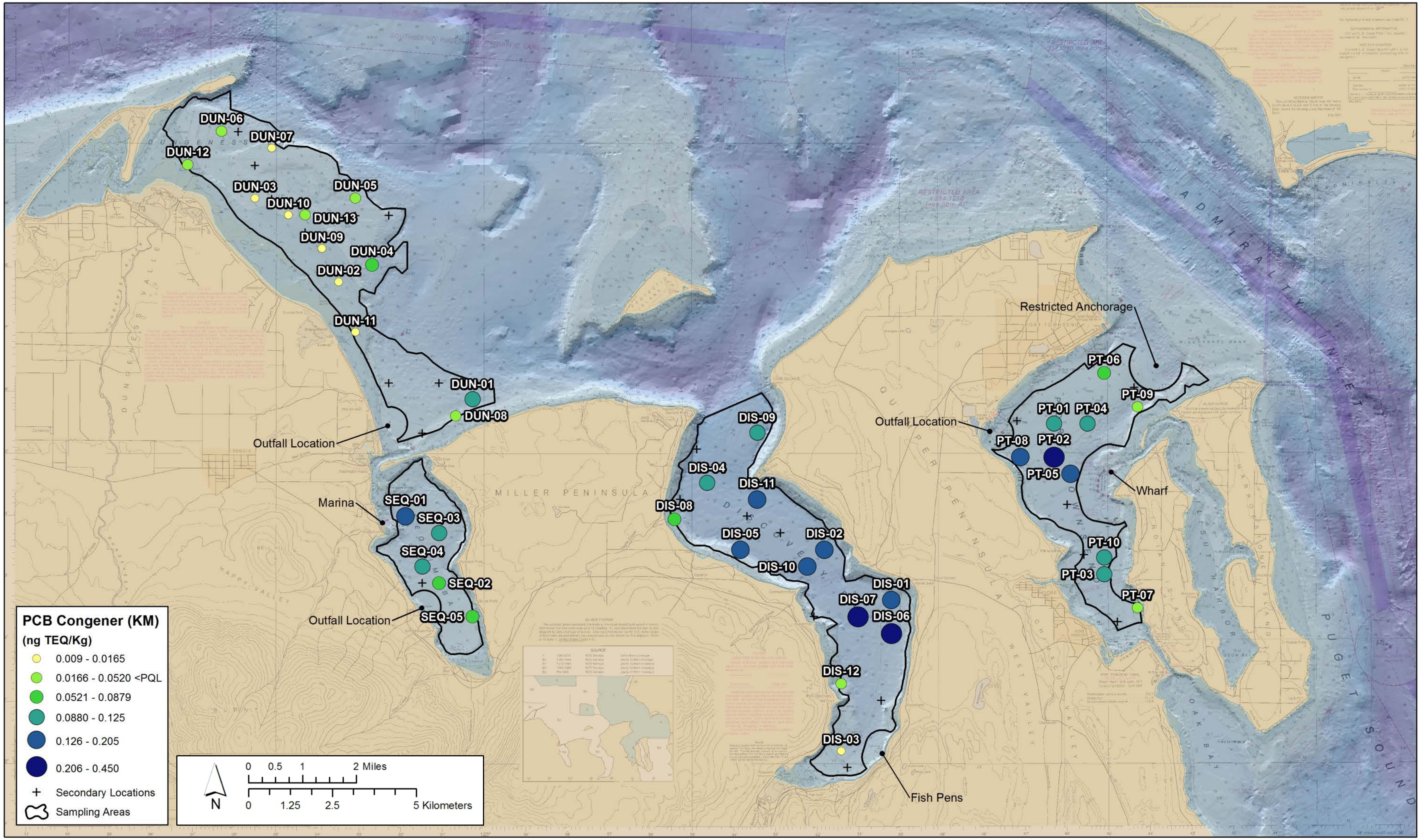

Figure 12. Polychlorinated biphenyl toxicity equivalent distribution for samples collected at the baseline locations from Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay

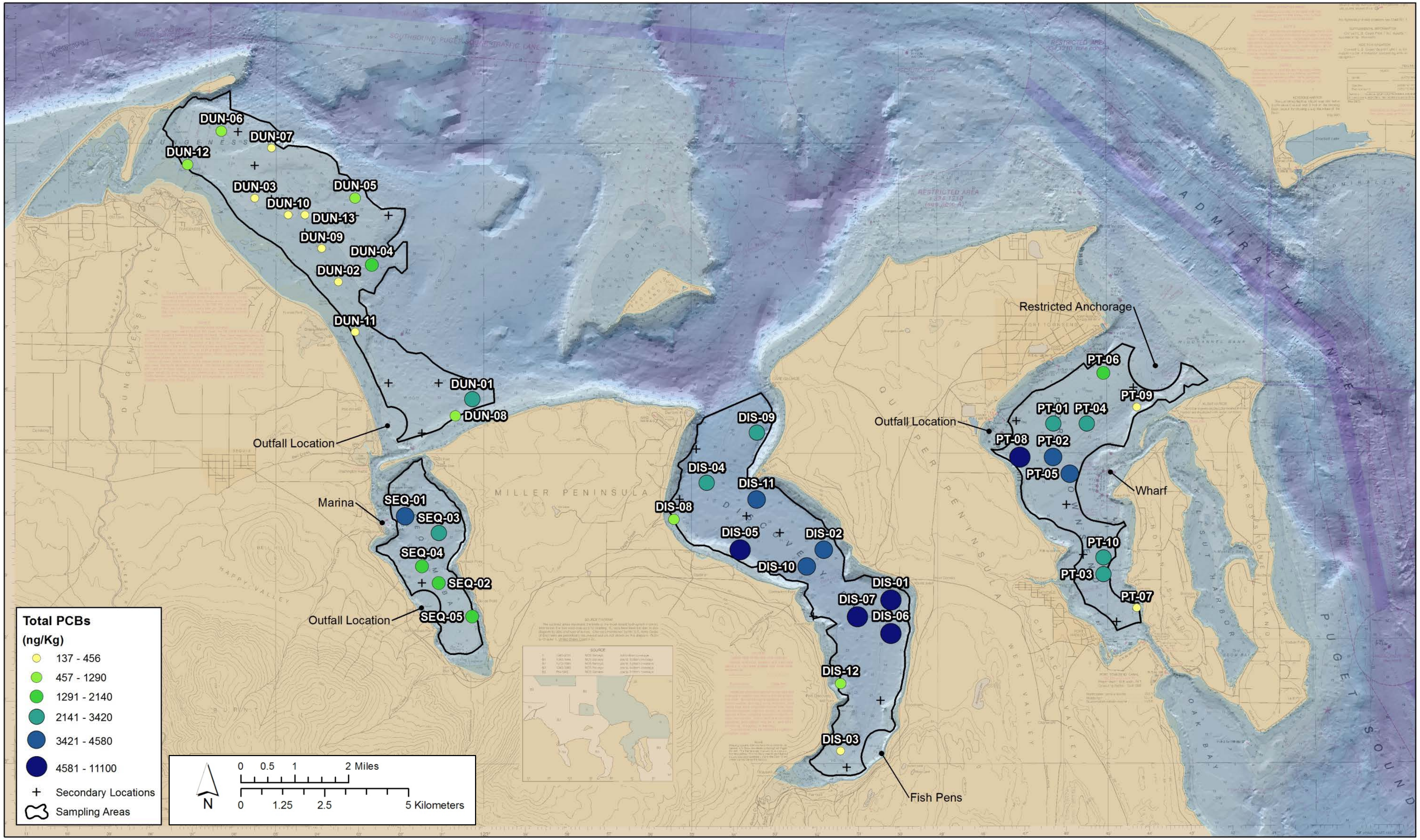

Figure 13. Total polychlorinated biphenyl distribution for samples collected at the baseline locations from Dungeness Bay, Sequim Bay, Discovery Bay, and Port Townsend Bay

This page purposely left blank for duplicate printing

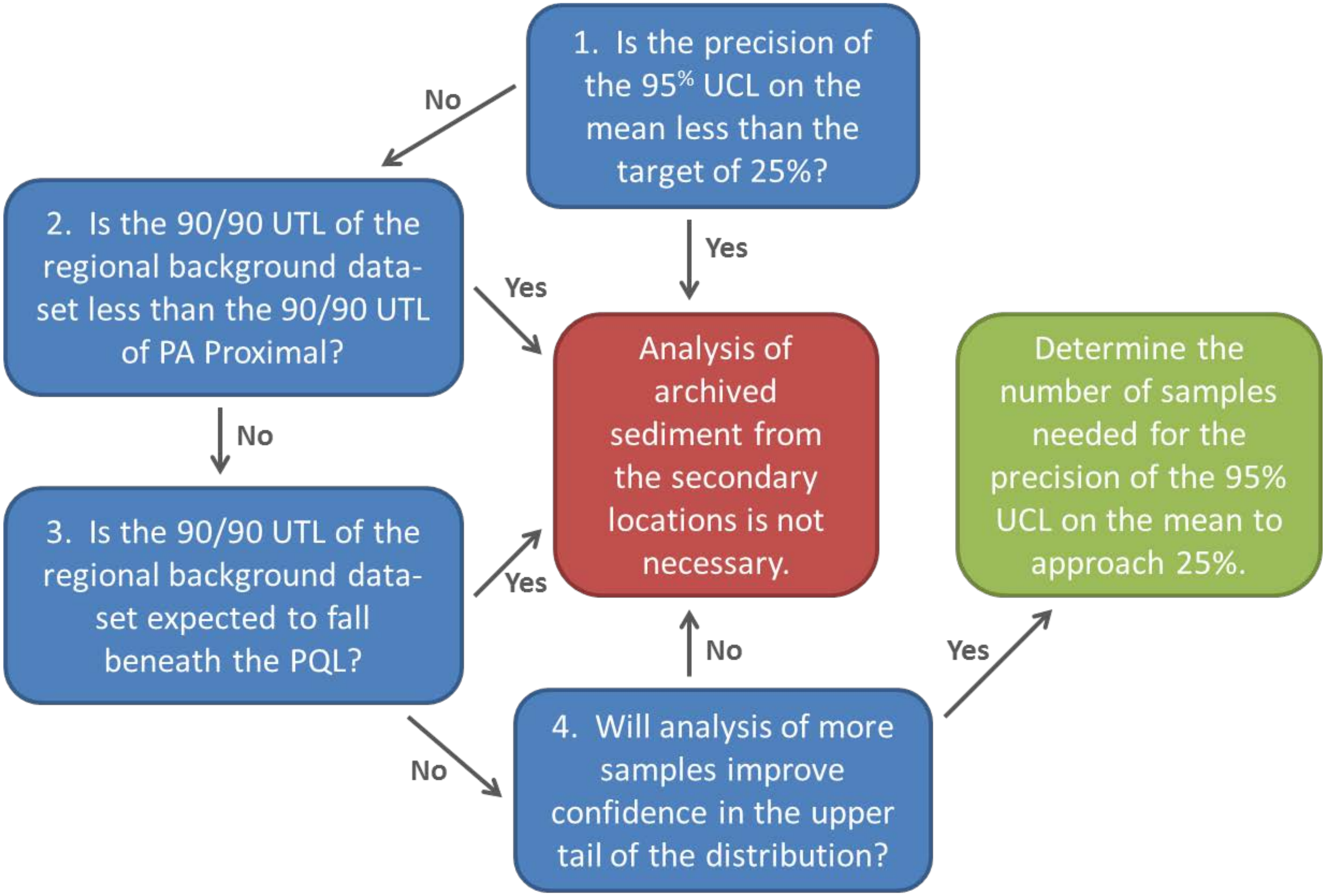

Figure 14. Decision process for the evaluation of secondary samples

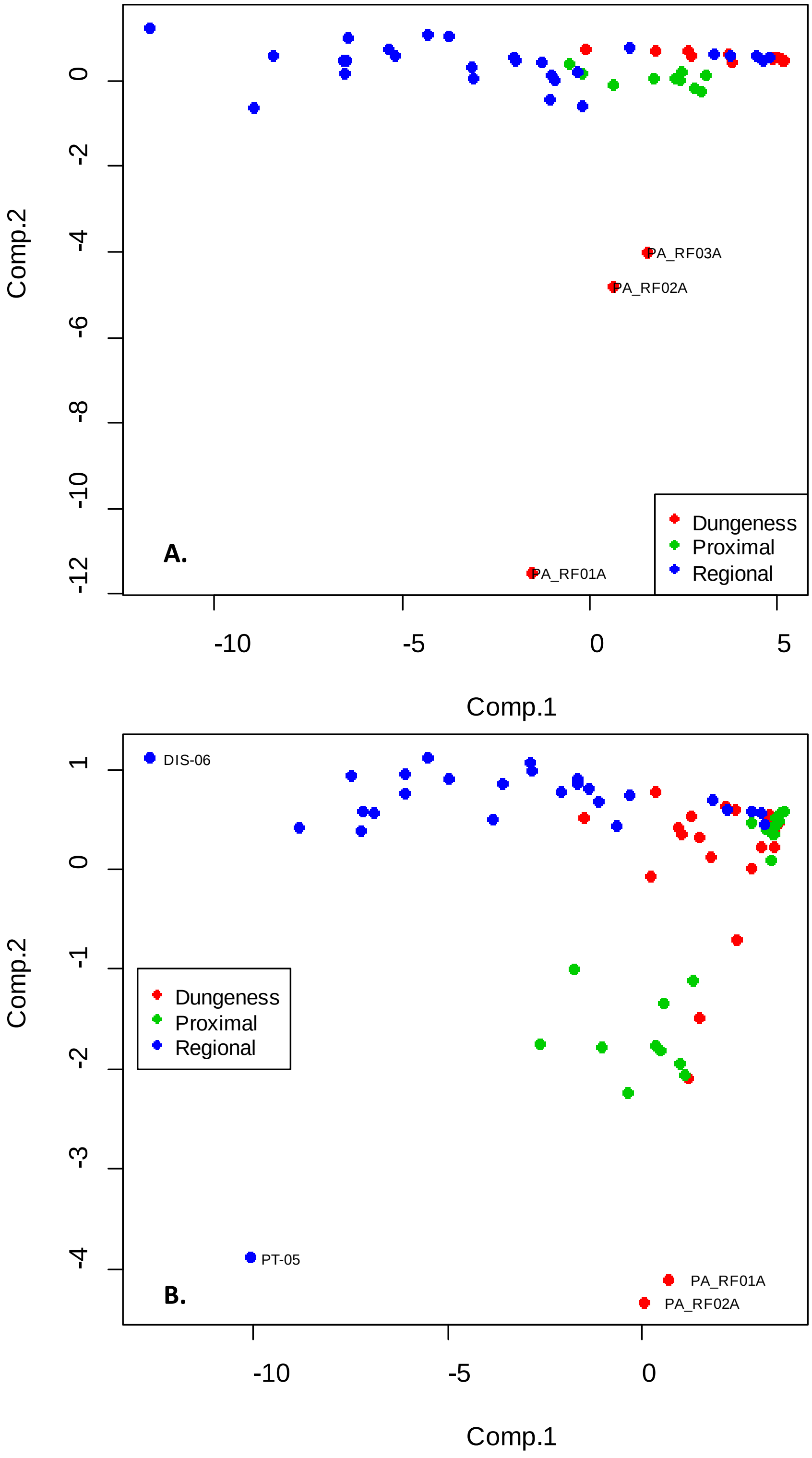

Figure 15. Principal components analysis results with non-detect values substituted with the detection limit for (a) the combined scenario of dioxin/furan congeners and carcinogenic polycyclic aromatic hydrocarbon compounds (n = 53 samples), and (b) dioxin/furan congeners only (n = 75 samples)

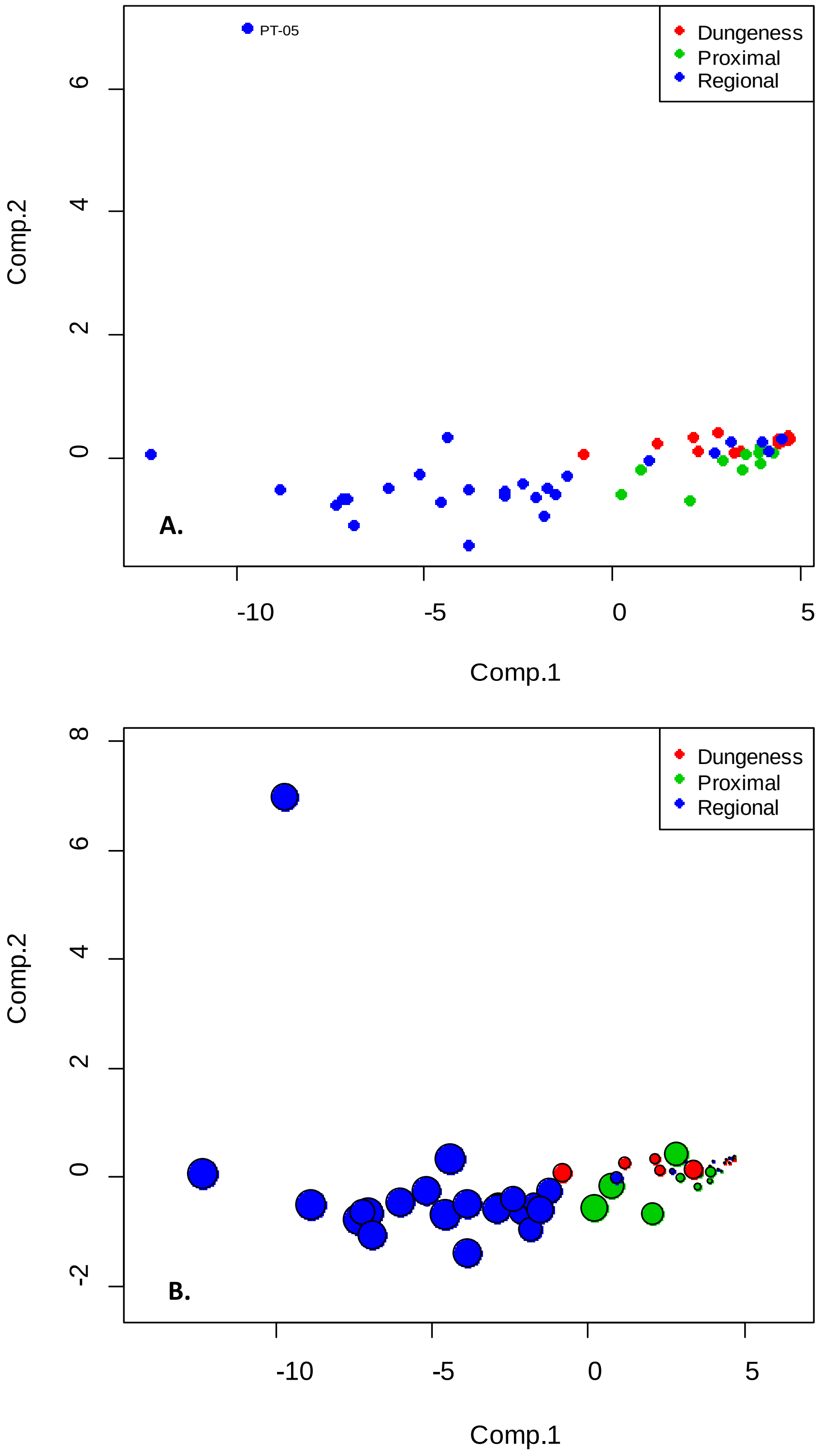

Figure 16. Principal components analysis results with non-detect values substituted with zero for (a) the combined scenario of dioxin/furan congeners and carcinogenic polycyclic aromatic hydrocarbon compounds (n = 53), and (b) the same results with points scaled to percent fines (larger points have larger fines)

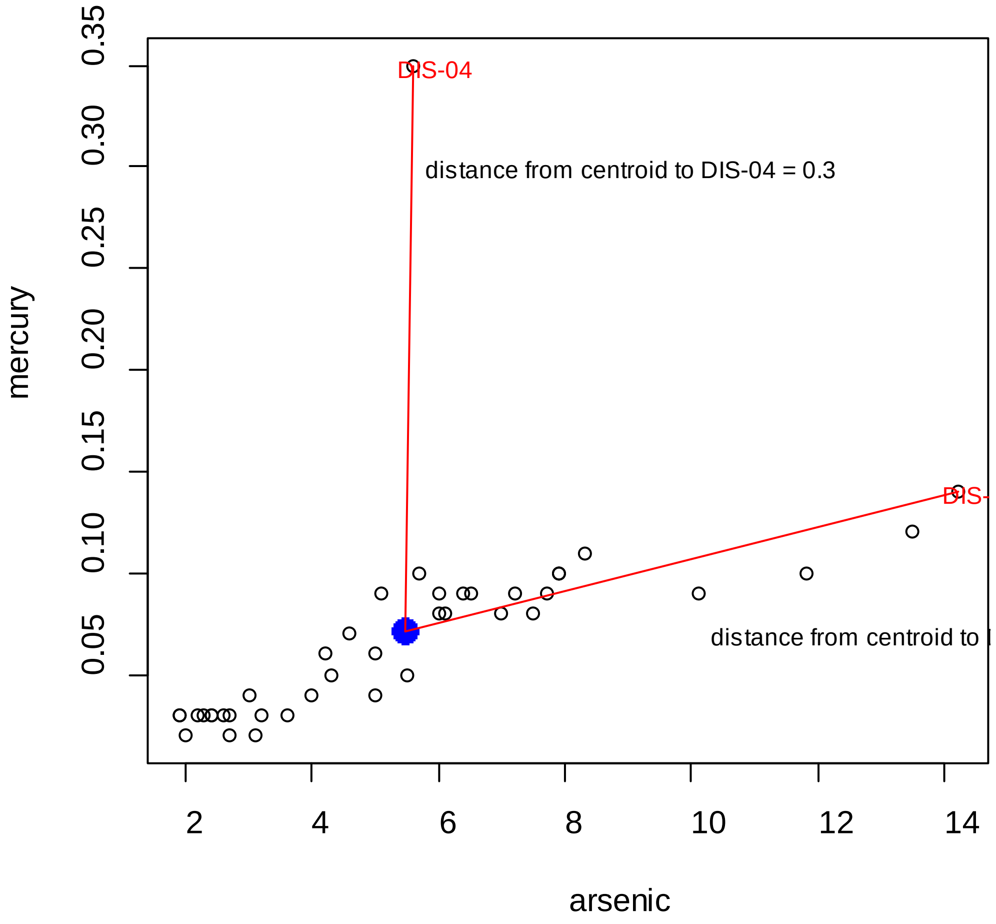

Figure 17. Scatterplot of arsenic versus mercury for the baseline samples from the North Olympic Peninsula area of interest (n = 40). The centroid is shown as the blue dot, located at the mean concentrations for the two metals. The absolute Euclidean distance from the centroid to sample DIS-04 is smaller but much more unusual than the distance from the centroid to sample DIS-06 due to the direction of covariance/correlation

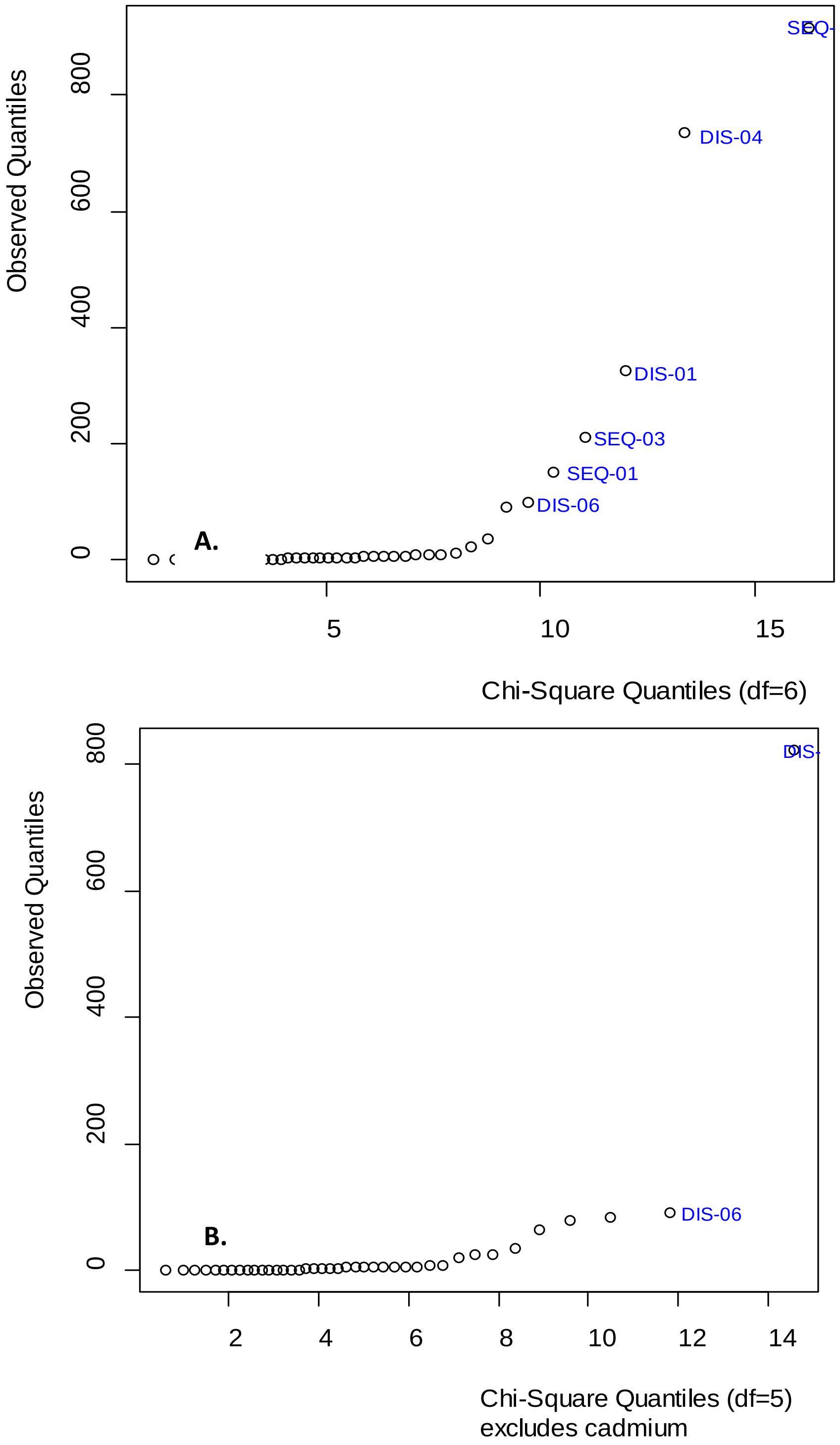

Figure 18. Quantile-quantile plot for the distribution of the squared robust Mahalanobis distances for the baseline samples from the North Olympic Peninsula area of interest (n = 40) for (a) six chemical endpoints (arsenic, cadmium, mercury, carcinogenic polycyclic aromatic hydrocarbon toxicity equivalent [TEQ] [Kaplan-Meier (KM)], dioxin/furan TEQ [KM], and polychlorinated chlorinated TEQ [KM]); and (b) the same chemical list, excluding cadmium

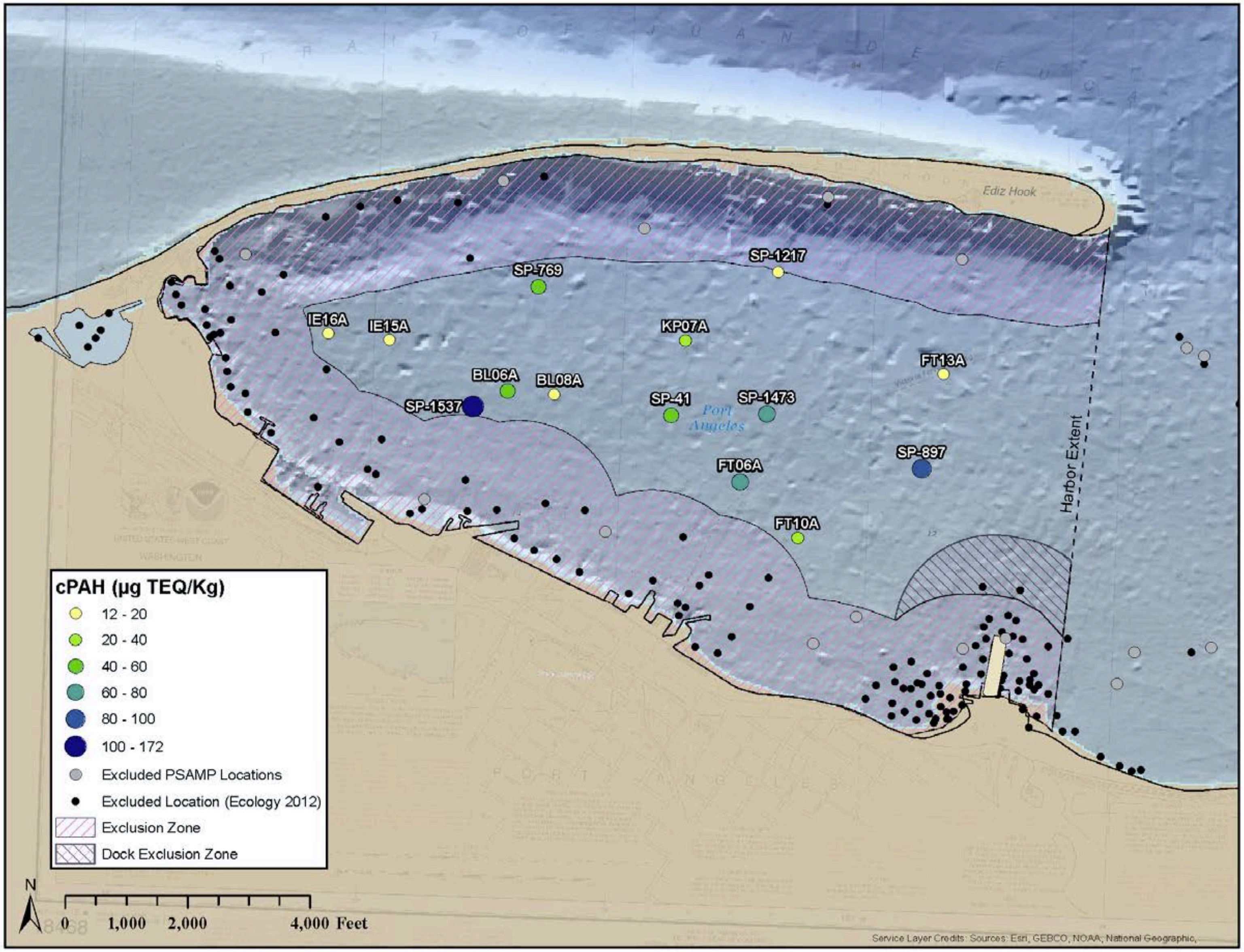

Figure 19. Carcinogenic polycyclic aromatic hydrocarbon distribution of existing samples in Port Angeles Harbor

Tables

This page purposely left blank for duplicate printing

Table 1. Actual coordinates, water depths, and distances from target coordinates for baseline locations

Station Identifier	Mudline Depth (meter) (MLLW)	Easting (SPN NAD83)	Northing (SPN NAD83)	Latitude (NAD83)	Longitude (NAD83)	Distance from Target (meter)
Sequim Bay						
SEQ-01	-30.1	1103082.8	396705.4	48.06651	-123.03128	0.7
SEQ-02	-21.0	1106182.2	390053.3	48.04853	-123.01783	0.5
SEQ-03	-22.0	1106318.7	394975.3	48.06202	-123.01785	0.4
SEQ-04	-24.5	1104586.7	391738.4	48.05302	-123.02455	0.4
SEQ-05	-12.0	1109368.3	386681.8	48.03953	-123.00442	0.6
Dungeness Bay						
DUN-01	-28.1	1109967.9	408003.3	48.09801	-123.00443	0.6
DUN-02	-3.6	1097169.1	419856.4	48.12949	-123.05819	0.4
DUN-03	-10.8	1089199.6	428287.6	48.15195	-123.09182	0.4
DUN-04	-32.6	1100495.4	421402.7	48.13399	-123.04476	0.6
DUN-05	-23.8	1099042.6	428008.6	48.15197	-123.05148	1.0
DUN-06	-18.4	1086103.8	434940.5	48.16993	-123.10531	0.6
DUN-07	-15.1	1090976.3	433158.6	48.16544	-123.08513	1.6
DUN-08	-19.2	1108283.8	406410.6	48.09351	-123.01114	0.3
DUN-09	-6.3	1095621.0	423182.7	48.13848	-123.06492	0.4
DUN-10	-10.6	1092443.4	426555.9	48.14747	-123.07833	2.9
DUN-11	-3.4	1098675.0	414891.8	48.11600	-123.05144	1.3
DUN-12	-6.8	1082729.7	431754.1	48.16093	-123.11874	0.2
DUN-13	-11.9	1094075.5	426509.6	48.14747	-123.07165	0.4
Discovery Bay						
DIS-01	-31.7	1150426.9	387165.1	48.04391	-122.83669	1.1
DIS-02	-46.5	1144005.1	392274.2	48.05745	-122.86349	1.7
DIS-03	-24.9	1145086.4	372539.7	48.00345	-122.85695	0.6
DIS-04	-53.7	1132701.9	399152.8	48.07547	-122.91045	1.0
DIS-05	-46.0	1135798.0	392501.7	48.05748	-122.89706	0.4
DIS-06	-33.5	1150340.0	383888.1	48.03492	-122.83670	3.0
DIS-07	-44.8	1147100.6	385619.0	48.03944	-122.85012	1.3
DIS-08	-11.9	1129396.9	395649.1	48.06563	-122.92358	99.2
DIS-09	-51.2	1137763.2	403940.1	48.08897	-122.89028	0.6
DIS-10	-48.2	1142311.6	390678.7	48.05296	-122.87024	0.8
DIS-11	-52.2	1137577.5	397373.6	48.07096	-122.89032	1.1
DIS-12	-26.2	1145272.9	379104.8	48.02145	-122.85689	0.8

Table 1. Actual coordinates, water depths, and distances from target coordinates for baseline locations (continued)

Station Identifier	Mudline Depth (meter) (MLLW)	Easting (SPN NAD83)	Northing (SPN NAD83)	Latitude (NAD83)	Longitude (NAD83)	Distance from Target (meter)
Port Townsend Bay						
PT-01	-19.2	1166832.2	404007.1	48.09122	-122.77138	0.5
PT-02	-22.1	1166736.6	400729.1	48.08223	-122.77144	1.9
PT-03	-27.6	1171339.0	389103.7	48.05068	-122.75143	0.4
PT-04	-21.8	1170117.5	403913.7	48.09119	-122.75793	0.9
PT-05	-24.9	1168335.7	399039.5	48.07771	-122.76472	0.2
PT-06	-16.0	1171900.2	408790.4	48.10467	-122.75114	2.2
PT-07	-12.8	1174529.7	385730.7	48.04166	-122.73804	0.8
PT-08	-20.6	1163462.9	400818.5	48.08225	-122.78483	0.6
PT-09	-26.3	1175082.7	405415.7	48.09564	-122.73778	0.2
PT-10	-28.1	1171386.7	390740.3	48.05517	-122.7514	1.6

Notes:
MLLW = mean lower low water
SPN NAD83 = Washington State Plane North, North American Datum 1983

Table 2. Actual coordinates, water depths, and distances from target coordinates for secondary locations

Station Identifier	Mudline Depth (meter) (MLLW)	Easting (SPN NAD83)	Northing (SPN NAD83)	Latitude (NAD83)	Longitude (NAD83)	Distance from Target (meter)
Sequim Bay						
SEQ-06	-21.2	1104538.5	390103.7	48.04854	-123.02456	1.4
SEQ-07	-20.3	1106367.2	396612.5	48.06651	-123.01784	0.7
SEQ-08	-13.8	1107727.0	386725.8	48.03953	-123.01114	0.5
Dungeness Bay						
DUN-14	-31.2	1102277.1	426179.1	48.14721	-123.03802	2.1
DUN-15	-11.0	1090841.9	428135.5	48.15167	-123.08508	1.6
DUN-16	-6.7	1094025.1	424762.4	48.14268	-123.07164	0.7
DUN-17	-17.1	1104954.6	404754.7	48.08872	-123.02456	0.8
DUN-18	-30.9	1106734.3	409628.8	48.10221	-123.01785	1.2
DUN-19	-22.8	1101810.6	409772.9	48.10222	-123.03801	0.8
DUN-20	-22.7	1098993.2	426265.0	48.14719	-123.05148	0.4
DUN-21	-13.0	1089289.5	431461.8	48.16066	-123.09184	0.8
DUN-22	-21.9	1087742.8	434794.8	48.16967	-123.09857	1.2
Discovery Bay						
DIS-13	-20.7	1145670.1	370882.2	47.99895	-122.85439	0.7
DIS-14	-55.2	1138442.2	405561.0	48.09346	-122.88768	0.5
DIS-15	-65.8	1131791.7	402466.5	48.08449	-122.91454	1.6
DIS-16	-48.6	1136527.4	395759.0	48.06646	-122.89444	2.3
DIS-17	-46.7	1139758.6	394033.7	48.06196	-122.88104	0.5
DIS-18	-52.6	1130008.5	397590.3	48.07099	-122.92129	0.1
DIS-19	-16.0	1142807.3	385737.5	48.03945	-122.86768	0.2
DIS-20	-36.0	1149141.1	377350.5	48.01692	-122.84090	1.2
Port Townsend Bay						
PT-11	-21.7	1172503.2	384401.7	48.03788	-122.74619	0.8
PT-12	-21.8	1174794.4	407316.0	48.10083	-122.73915	0.9
PT-13	-28.5	1169408.6	391056.7	48.05590	-122.75952	0.8
PT-14	-24.5	1167906.5	396019.8	48.06940	-122.76617	0.6
PT-15	-16.9	1163218.3	404364.2	48.09195	-122.78620	0.9

Notes:
MLLW = mean lower low water
SPN NAD83: Washington State Plane North, North American Datum 1983

Table 3. Collected sediment samples, target analytes, and analytical methods

Sampling Location	Sediment Conventionals[a]	Metals[b]	cPAHs	Dioxin/Furan Congeners	PCB Congeners	Archive
Method	**PSEP**	**See Notes[b]**	**LL SIM 8270**	**USEPA 1613B**	**USEPA 1668A**	**--**
Sequim Bay						
SEQ-01-S	X	X	X	X	X	A
SEQ-02-S	X	X	X	X	X	A
SEQ-03-S	X	X	X	X	X	A
SEQ-03-D	X	X	X	X	X	-
SEQ-03-T	X	-	-	-	-	-
SEQ-04-S	X	X	X	X	X	A
SEQ-05-S	X	X	X	X	X	A
SEQ-06-S	A,X[c]	A,X[d]	A	A	A	A
SEQ-07-S	A,X[c]	A,X[d]	A	A	A	A
SEQ-08-S	A,X[c]	A,X[d]	A	A	A	A
Dungeness Bay						
DUN-01-S	X	X	X	X	X	A
DUN-02-S	X	X	X	X	X	A
DUN-03-S	X	X	X	X	X	A
DUN-04-S	X	X	X	X	X	A
DUN-05-S	X	X	X	X	X	A
DUN-05-D	X	X	X	X	X	-
DUN-05-T	X	-	-	-	-	-
DUN-06-S	X	X	X	X	X	A
DUN-07-S	X	X	X	X	X	A
DUN-08-S	X	X	X	X	X	A
DUN-09-S	X	X	X	X	X	A
DUN-10-S	X	X	X	X	X	A
DUN-11-S	X	X	X	X	X	A
DUN-12-S	X	X	X	X	X	A
DUN-13-S	X	X	X	X	X	A
DUN-14-S	A,X[c]	A,X[d]	A	A	A	A
DUN-15-S	A,X[c]	A,X[d]	A	A	A	A
DUN-16-S	A,X[c]	A,X[d]	A	A	A	A
DUN-17-S	A,X[c]	A,X[d]	A	A	A	A
DUN-18-S	A,X[c]	A,X[d]	A	A	A	A
DUN-19-S	A,X[c]	A,X[d]	A	A	A	A
DUN-20-S	A,X[c]	A,X[d]	A	A	A	A
DUN-21-S	A,X[c]	A,X[d]	A	A	A	A
DUN-22-S	A,X[c]	A,X[d]	A	A	A	A
Discovery Bay						
DIS-01-S	X	X	X	X	X	A
DIS-02-S	X	X	X	X	X	A
DIS-03-S	X	X	X	X	X	A
DIS-04-S	X	X	X	X	X	A
DIS-05-S	X	X	X	X	X	A
DIS-06-S	X	X	X	X	X	A
DIS-07-S	X	X	X	X	X	A
DIS-08-S	X	X	X	X	X	A
DIS-09-S	X	X	X	X	X	A

Table 3. Collected sediment samples, target analytes, and analytical methods (continued)

Sampling Location	Sediment Conventionals[a]	Metals[b]	cPAHs	Dioxin/Furan Congeners	PCB Congeners	Archive
Method	**PSEP**	**See Notes[b]**	**LL SIM 8270**	**USEPA 1613B**	**USEPA 1668A**	**--**
DIS-09-D	X	X	X	X	X	-
DIS-09-T	X	-	-	-	-	-
DIS-10-S	X	X	X	X	X	A
DIS-11-S	X	X	X	X	X	A
DIS-12-S	X	X	X	X	X	A
DIS-13-S	A,X[c]	A,X[d]	A	A	A	A
DIS-14-S	A,X[c]	A,X[d]	A	A	A	A
DIS-15-S	A,X[c]	A,X[d]	A	A	A	A
DIS-16-S	A,X[c]	A,X[d]	A	A	A	A
DIS-17-S	A,X[c]	A,X[d]	A	A	A	A
DIS-18-S	A,X[c]	A,X[d]	A	A	A	A
DIS-19-S	A,X[c]	A,X[d]	A	A	A	A
DIS-20-S	A,X[c]	A,X[d]	A	A	A	A
Port Townsend Bay						
PT-01-S	X	X	X	X	X	A
PT-02-S	X	X	X	X	X	A
PT-03-S	X	X	X	X	X	A
PT-04-S	X	X	X	X	X	A
PT-05-S	X	X	X	X	X	A
PT-06-S	X	X	X	X	X	A
PT-07-S	X	X	X	X	X	A
PT-08-S	X	X	X	X	X	A
PT-09-S	X	X	X	X	X	A
PT-10-S	X	X	X	X	X	A
PT-11-S	A,X[c]	A,X[d]	A	A	A	A
PT-12-S	A,X[c]	A,X[d]	A	A	A	A
PT-13-S	A,X[c]	A,X[d]	A	A	A	A
PT-13-D	A,X[c]	A,X[d]	-	-	-	-
PT-13-T	A,X[c]	A,X[d]	-	-	-	-
PT-14-S	A,X[c]	A,X[d]	A	A	A	A
PT-15-S	A,X[3]	A,X[d]	A	A	A	A
Rinsate Samples						
NOP-RB	-	X	X	-	-	-
NOP-ER-1	-	X	X	-	-	-
NOP-ER-2	-	X	X	-	-	-
NOP-ER-3	-	X	X	-	-	-
NOP-ER-4	-	X[d]	-	-	-	-

Notes:

[a] Sediment conventionals include total organic carbon, total volatile solids, total solids, total sulfides, and grain size distribution

[b] Metals include arsenic (USEPA 200.8), cadmium (USEPA 200.8), and mercury (USEPA 7471A)

[c] Only total sulfides and grain size were analyzed from the secondary locations; the remaining sediment was archived

[d] Only mercury was analyzed from the secondary locations; the remaining sediment was archived

A = archive
cPAH = carcinogenic polycyclic aromatic hydrocarbon
LL = low level
PCB = polychlorinated biphenyl
PSEP = Puget Sound Estuary Program
SIM = select ion monitoring
USEPA = U.S. Environmental Protection Agency

Table 4. Target analytes, methods, and PQLs

Analyte	Preparation Method	Analytical Method	PQL
Metals (mg/kg DW)			
Arsenic	USEPA 3050B/3051	USEPA 200.8	0.5[a]
Cadmium	USEPA 3050B/3051	USEPA 200.8	0.1
Mercury	USEPA 7471A	USEPA 7471A	0.025
cPAHs (µg/kg DW)			
Benzo(a)pyrene	USEPA 3546	USEPA 8270 SIM LL	0.5
Benz(a)anthracene	USEPA 3546	USEPA 8270 SIM LL	0.5
Benzo(b)fluoranthene	USEPA 3546	USEPA 8270 SIM LL	0.5
Benzo(k)fluoranthene	USEPA 3546	USEPA 8270 SIM LL	0.5
Chrysene	USEPA 3546	USEPA 8270 SIM LL	0.5
Indeno(1,2,3-cd)pyrene	USEPA 3546	USEPA 8270 SIM LL	0.5
Dibenz(a,h)anthracene	USEPA 3546	USEPA 8270 SIM LL	0.5
cPAH TEQ[b]	--	--	0.76
PCB Congeners (ng/kg DW)			
PCB-77	USEPA 1668A	USEPA 1668	0.4
PCB-81	USEPA 1668A	USEPA 1668	0.4
PCB-105	USEPA 1668A	USEPA 1668	0.4
PCB-114	USEPA 1668A	USEPA 1668	0.4
PCB-118	USEPA 1668A	USEPA 1668	0.4
PCB-123	USEPA 1668A	USEPA 1668	0.4
PCB-126	USEPA 1668A	USEPA 1668	0.4
PCB-156	USEPA 1668A	USEPA 1668	0.8
PCB-157	USEPA 1668A	USEPA 1668	
PCB-167	USEPA 1668A	USEPA 1668	0.4
PCB-169	USEPA 1668A	USEPA 1668	0.4
PCB-189	USEPA 1668A	USEPA 1668	0.4
PCB Congener TEQ[b]	--	--	0.052
Dioxin/Furan Congeners (ng/kg DW)			
2,3,7,8-TCDD	USEPA 1613B/3540C	USEPA 1613B	0.2
1,2,3,7,8-PeCDD	USEPA 1613B/3540C	USEPA 1613B	1
1,2,3,4,7,8-HxCDD	USEPA 1613B/3540C	USEPA 1613B	1
1,2,3,6,7,8-HxCDD	USEPA 1613B/3540C	USEPA 1613B	1
1,2,3,7,8,9-HxCDD	USEPA 1613B/3540C	USEPA 1613B	1
1,2,3,4,6,7,8-HpCDD	USEPA 1613B/3540C	USEPA 1613B	1
OCDD	USEPA 1613B/3540C	USEPA 1613B	2
2,3,7,8-TCDF	USEPA 1613B/3540C	USEPA 1613B	0.2
1,2,3,7,8-PeCDF	USEPA 1613B/3540C	USEPA 1613B	1
2,3,4,7,8-PeCDF	USEPA 1613B/3540C	USEPA 1613B	1
1,2,3,4,7,8-HxCDF	USEPA 1613B/3540C	USEPA 1613B	1
1,2,3,6,7,8-HxCDF	USEPA 1613B/3540C	USEPA 1613B	1
1,2,3,7,8,9-HxCDF	USEPA 1613B/3540C	USEPA 1613B	1

Table 4. Target analytes, methods, and PQLs (continued)

Analyte	Preparation Method	Analytical Method	PQL
2,3,4,6,7,8-HxCDF	USEPA 1613B/3540C	USEPA 1613B	1
1,2,3,4,6,7,8-HpCDF	USEPA 1613B/3540C	USEPA 1613B	1
1,2,3,4,7,8,9-HpCDF	USEPA 1613B/3540C	USEPA 1613B	1
OCDF	USEPA 1613B/3540C	USEPA 1613B	2
Dioxin/Furan TEQ[b]	--	--	2.3

Notes:

[a] Two possible ions are used for the quantification of arsenic, both with separate PQLs (0.2 and 0.5 mg/kg). The ion is dependent upon matrix and interferences. The higher PQL is listed

[b] TEQ values were calculated by multiplying the PQL by the appropriate toxicity equivalency factor

Yellow highlighting indicates the project-specific PQL

cPAH = carcinogenic polycyclic aromatic hydrocarbon
DW = dry weight
LL = low level
µg/kg = micrograms per kilogram
mg/kg = milligrams per kilogram
ng/kg = nanograms per kilogram
PCB = polychlorinated biphenyl
PQL = practical quantitation limit
SIM = select ion monitoring
TEQ = toxicity equivalent
USEPA = U.S. Environmental Protection Agency

Table 5. Summary statistics and correlation to percent fines for target contaminants

Location Identifier	Arsenic	Cadmium	Mercury	cPAH TEQ[a]	Dioxin/Furan TEQ[a]	PCB TEQ[a]	Total PCBs
Units	**mg/kg**	**mg/kg**	**mg/kg**	**µg TEQ/kg**	**ng TEQ/kg**	**ng TEQ/kg**	**ng/kg**
Discovery Bay							
Sample Size	12	12	20	12	12	12	12
Minimum	2.2	0.13	0.02	1.97	0.214	0.016	386
Average	7.5	0.8	0.093	16.1	2.35	0.156	3,820
Median	6.5	0.45	0.09	16.9	2.3	0.149	3,870
Maximum	14.2	2.6	0.35	32.6	5.29	0.44	11,100
Dungeness Bay							
Sample Size	13	13	22	13	13	13	13
Minimum	1.9	0.12	0.02	0.166	0.11	0.009	137
Average	3.3	0.17	0.038	2.69	0.571	0.0336	687
Median	3	0.13	0.03	0.663	0.207	0.0189	281
Maximum	5.5	0.28	0.07	9.41	1.87	0.104	2,270
Port Townsend Bay							
Sample Size	10	10	15	10	10	10	10
Minimum	1.9	0.13	0.02	0.562	0.207	0.0205	235
Average	4.9	0.28	0.075	17.2	2.65	0.108	2,660
Median	5.1	0.24	0.08	20.6	2.69	0.118	2,890
Maximum	6.4	0.46	0.11	28.5	4.55	0.216	4,760
Sequim Bay							
Sample Size	5	5	8	5	5	5	5
Minimum	7	1.1	0.08	16.3	1.49	0.0688	1,680
Average	7.6	2	0.091	19.7	2.13	0.106	2,410
Median	7.7	1.7	0.09	20.2	1.83	0.109	1,940
Maximum	7.9	3.6	0.1	22.1	3.09	0.162	3,790
Combined Data Set Summary Statistics							
Sample Size	40	40	65	40	40	40	40
Minimum	1.9	0.12	0.020	0.166	0.11	0.009	137
Average	5.5	0.6	0.069	12.0	1.76	0.0974	1,920
Median	5.1	0.24	0.070	14.0	1.67	0.0809	2,340
Maximum	14	3.6	0.35	32.6	5.29	0.440	11,100
Pearson's Linear Correlation to Percent Fines							
DF	39	39	64	39	39	39	39
r-square	0.645	0.315	0.496	0.859	0.746	0.586	0.598
p-value	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Notes:

[a] TEQs calculated using Kaplan-Meier

cPAH = carcinogenic polycyclic aromatic hydrocarbon
DF = degrees of freedom
kg = kilogram
µg = micrograms
mg/kg = milligrams per kilogram
ng = nanogram
ng/kg = nanograms per kilogram
PCB = polychlorinated biphenyl
TEQ = toxicity equivalent

Table 6. Evaluation of precision for the specific and combined bay data sets

COC	Sample Size	Percent Detect	Mean	95 UCL on Mean[a]	Precision
Arsenic (mg/kg)					
Discovery Bay	12	100%	7.45	9.62	29%
Dungeness Bay	13	100%	3.28	3.84	17%
Port Townsend Bay	10	100%	4.89	5.77	18%
Sequim Bay	5	100%	7.59	7.94	5%
Combined NOP[b]	40	100%	5.47	6.19	13%
Cadmium (mg/kg)					
Discovery Bay	12	92%	0.80	1.21	50%
Dungeness Bay	13	23%	0.17	0.19	12%
Port Townsend Bay	10	80%	0.28	0.34	21%
Sequim Bay	5	100%	1.96	2.89	48%
Combined NOP	40	68%	0.60	0.75	25%
Mercury (mg/kg)					
Discovery Bay	20	80%	0.09	0.13	42%
Dungeness Bay	22	50%	0.04	0.04	13%
Port Townsend Bay	15	87%	0.08	0.09	14%
Sequim Bay	8	100%	0.09	0.10	6%
Combined NOP[b]	65	74%	0.07	0.08	13%
cPAH* (µg TEQ[c]/kg)					
Discovery Bay	12	100%	16.09	21.08	31%
Dungeness Bay	13	85%	2.69	6.27	133%
Port Townsend Bay	10	100%	17.18	23.10	34%
Sequim Bay	5	100%	19.66	22.08	12%
Combined NOP[b]	40	95%	12.02	14.02	17%
Dioxin/Furan (ng TEQ[c]/kg)					
Discovery Bay	12	92%	2.35	3.10	32%
Dungeness Bay	13	54%	0.57	0.92	61%
Port Townsend Bay	10	90%	2.65	3.59	36%
Sequim Bay	5	100%	2.13	2.78	31%
Combined NOP[b]	40	80%	1.76	2.07	18%
PCB (ng TEQ[c]/kg)					
Discovery Bay	12	92%	0.16	0.22	40%
Dungeness Bay	13	62%	0.03	0.06	66%
Port Townsend Bay	10	100%	0.11	0.15	34%
Sequim Bay	5	100%	0.11	0.15	37%
Combined NOP[b]	40	85%	0.10	0.12	21%

Table 6. Evaluation of precision for the specific and combined bay data sets (continued)

COC	Sample Size	Percent Detect	Mean	95 UCL on Mean[a]	Precision
Total PCBs (ng/kg)					
Discovery Bay	12	--	3.82	5.30	39%
Dungeness Bay	13	--	0.69	1.17	71%
Port Townsend Bay	10	--	2.66	3.51	32%
Sequim Bay	5	--	2.41	3.24	34%
Combined NOP[b]	40	--	2.32	2.83	22%

Notes:

[a] Precision column shows the half-width of the 95% UCL on the mean relative to the mean (t*sd/sqrt[n]/mean); the target value is 25%

[b] For the combined NOP, it was assumed there were four strata, and the stratified mean and its precision are presented

[c] TEQ values were calculated using Kaplan-Meier

-- = not applicable
COC = contaminant of concern
kg = kilogram
µg/kg = micrograms per kilogram
mg/kg = milligrams per kilogram
ng = nanogram
ng/kg = nanograms per kilogram
NOP = North Olympic Peninsula
% = percent
PCB = polychlorinated biphenyl
TEQ = toxicity equivalent
UCL = upper confidence limit

Table 7. Total available data for principal components analysis

Regional Background					Dungeness Bay					Natural Background (PA Proximal)				
	Metals	**cPAH**	**Dx/F**	**PCBs**		**Metals**	**cPAH**	**Dx/F**	**PCBs**		**Metals**	**cPAH**	**Dx/F**	**PCBs**
Sample Size	**27**	**27**	**27**	**27**	**Sample Size**	**16**	**16**	**27**	**27**	**Sample Size**	**12**	**12**	**21**	**21**
DIS-01-S	X	X	X	X	DUN-01-S	X	X	X	X	SJF_10_C	X	X	X	X
DIS-02-S	X	X	X	X	DUN-02-S	X	X	X	X	SJF_12_C_GS	X	X	X	X
DIS-03-S	X	X	X	X	DUN-03-S	X	X	X	X	SJF_2	X	X	X	X
DIS-04-S	X	X	X	X	DUN-04-S	X	X	X	X	SJF_3	X	X	X	X
DIS-05-S	X	X	X	X	DUN-05-S	X	X	X	X	SJF_9_C	X	X	X	X
DIS-06-S	X	X	X	X	DUN-06-S	X	X	X	X	SJI_0	X	X	X	X
DIS-07-S	X	X	X	X	DUN-07-S	X	X	X	X	SJI_1	X	X	X	X
DIS-08-S	X	X	X	X	DUN-08-S	X	X	X	X	SJI_20_C_GS	X	X	X	X
DIS-09-S	X	X	X	X	DUN-09-S	X	X	X	X	SJI_3	X	X	X	X
DIS-10-S	X	X	X	X	DUN-10-S	X	X	X	X	SJI_8_C	X	X	X	X
DIS-11-S	X	X	X	X	DUN-11-S	X	X	X	X	FB-02-SD	--	--	X	X
DIS-12-S	X	X	X	X	DUN-12-S	X	X	X	X	FB-05-SD	--	--	X	X
SEQ-01-S	X	X	X	X	DUN-13-S	X	X	X	X	FB-06-SD	--	--	X	X
SEQ-02-S	X	X	X	X	DB-01-SD	--	--	X	X	FB-07-SD	--	--	X	X
SEQ-03-S	X	X	X	X	DB-02-SD	--	--	X	X	FB-08-SD	--	--	X	X
SEQ-04-S	X	X	X	X	DB-03-SD	--	--	X	X	FB-09-SD	--	--	X	X
SEQ-05-S	X	X	X	X	DB-04-SD	--	--	X	X	FB-10-SD	--	--	X	X
PT-01-S	X	X	X	X	DB-05-SD	--	--	X	X	FB-11-SD	--	--	X	X
PT-02-S	X	X	X	X	DB-06-SD	--	--	X	X	FB-13-SD	--	--	X	X
PT-03-S	X	X	X	X	DB-07-SD	--	--	X	X	FB-14-SD	--	--	X	X
PT-04-S	X	X	X	X	DB-08-SD	--	--	X	X	FB-15-SD	--	--	X	X
PT-05-S	X	X	X	X	DB-09-SD	--	--	X	X	PSAMP_SP-417	X	X	--	--
PT-06-S	X	X	X	X	DB-10-SD	--	--	X	X	PSAMP_SP-545	X	X	--	--
PT-07-S	X	X	X	X	DB-11-SD	--	--	X	X					
PT-08-S	X	X	X	X	PA_RF01A	X	X	X	--					
PT-09-S	X	X	X	X	PA_RF02A	X	X	X	--					
PT-10-S	X	X	X	X	PA_RF03A	X	X	X	--					

Notes:

-- = not analyzed

cPAH = carcinogenic polycyclic aromatic hydrocarbon

Dx/F = dioxin/furan congeners

PA Proximal = Port Angeles Proximal Area

PCB = polychlorinated biphenyl as toxicity equivalent and sum of congeners

Table 8. Sorted robust Mahalanobis distances for the baseline samples

Location Identifier	Squared Distance[a] (p = 6)	Location Identifier	Squared Distance[b] (p = 5)
SEQ-05	919.1	DIS-04	1,073.6
DIS-04	734.4	DIS-06	257.4
DIS-01	327.4	PT-08	188.5
SEQ-03	211.7	PT-05	152.9
SEQ-01	151.5	PT-03	150.1
DIS-06	99.0	PT-10	110.0
SEQ-02	92.0	PT-01	95.1
SEQ-04	37.3	SEQ-02	57.1
DIS-07	23.9	DIS-01	56.2
DIS-02	13.1	SEQ-03	51.1
PT-02	10.0	DIS-07	43.7
PT-01	9.1	SEQ-05	43.7
DIS-10	8.9	PT-02	17.2
PT-05	7.1	DIS-02	15.8
PT-04	6.6	SEQ-01	14.4
PT-08	5.8	DIS-10	6.9
PT-10	5.5	SEQ-04	6.3
DUN-04	5.1	DUN-12	6.2
PT-03	4.7	PT-04	5.0
DUN-12	4.3	DIS-05	4.9
DUN-06	4.0	DUN-04	4.1
DIS-05	3.9	DUN-01	3.8
PT-07	3.4	DIS-09	3.7
DUN-01	3.1	DUN-06	3.5
DIS-11	2.7	DIS-08	3.0
DUN-11	2.7	PT-06	2.5
DIS-09	2.5	DIS-11	1.9
DIS-08	2.1	DUN-11	1.6
DUN-07	2.1	DUN-10	1.6
DUN-10	2.0	DUN-07	1.6
DIS-03	1.6	PT-07	1.4
PT-09	1.4	PT-09	1.3
DUN-09	1.4	DIS-03	1.2
PT-06	1.3	DUN-03	1.0
DUN-03	1.0	DUN-02	0.8
DUN-13	0.9	DUN-13	0.8
DUN-02	0.8	DUN-09	0.7
DUN-08	0.6	DUN-05	0.7
DIS-12	0.6	DUN-08	0.5
DUN-05	0.5	DIS-12	0.4

Notes:

[a] Distances based on six chemical endpoints: arsenic, cadmium, mercury, carcinogenic polycyclic aromatic hydrocarbon (cPAH) toxicity equivalent (TEQ) (Kaplan-Meier [KM]), dioxin/furan TEQ (KM), and polychlorinated biphenyl (PCB) TEQ (KM)

[b] Distances based on five chemical endpoints: arsenic, mercury, cPAH TEQ (KM), dioxin/furan TEQ (KM), and PCB TEQ (KM)

Table 9. Regional background values for the North Olympic Peninsula compared to Port Angeles Proximal natural background

Analyte	Units	Regional Background 90/90 UTL[e]	Port Angeles Proximal Natural Background 90/90 UTL[f]
Arsenic	mg/kg	14	12
Cadmium	mg/kg	2.4[b]	0.82
Mercury	mg/kg	0.13[c]	0.11
cPAH TEQ[a]	µg TEQ/kg	31	16
Dioxin/Furan TEQ[a]	ng TEQ/kg	5.0	1.2
PCB Congener TEQ[a]	ng TEQ/kg	0.21[d]	0.10
Total PCB Congeners	ng/kg	5,300[d]	960

Notes:

[a] TEQ values were calculated using Kaplan-Meier

[b] 90/90 UTL calculated excluding SEQ-05 as an outlier

[c] 90/90 UTL calculated excluding DIS-04 as an outlier

[d] 90/90 UTL calculated excluding DIS-06 as an outlier

[e] Dungeness Bay samples not included in regional background

[f] Port Angeles proximal natural background does not currently include Dungeness Bay samples collected as part of regional background

cPAH = carcinogenic polycyclic aromatic hydrocarbon
kg = kilogram
µg = microgram
mg/kg = milligrams per kilogram
ng = nanogram
ng/kg = nanograms per kilogram
PCB = polychlorinated biphenyl
TEQ = toxicity equivalent
UTL = upper tolerance limit

Table 10. Existing cPAH data from Port Angeles Harbor

Location Identifier	Date Collected	Depth (cm)	cPAH[a,b] (µg TEQ/kg)	Qualifier[b]
PA_BL06A	06/11/08	0 - 10	40.8	
PA_BL08A	06/09/08	0 - 10	17.5	L
PA_FT06A	06/12/08	0 - 10	64.1	
PA_FT10A	06/12/08	0 - 10	37.5	
PA_FT13A	06/11/08	0 - 10	13.1	
PA_IE15A	06/09/08	0 - 10	11.1	L5
PA_IE16A	06/09/08	0 - 10	10.2	L7
PA_KP07A	06/11/08	0 - 10	21.8	
PSAMP_SP-1217	06/19/13	0 - 3	38.7	
PSAMP_SP-1473	06/19/13	0 - 3	66.9	
PSAMP_SP-1537	06/18/13	0 - 3	172	
PSAMP_SP-41	06/10/02	0 - 3	55.6	
PSAMP_SP-769	06/20/13	0 - 3	59.1	
PSAMP_SP-897	06/18/13	0 - 3	87.2	

Notes:

[a] TEQ values were calculated using Kaplan-Meier

[b] Concentrations and qualifiers for the individual polycyclic aromatic hydrocarbon compounds are available in Table E-4 in Appendix E

cm = centimeter

cPAH = carcinogenic polycyclic aromatic hydrocarbon

kg = kilogram

µg = microgram

L = the detection frequency of compounds within a sample was less than 50 percent; the numeric value indicates the number of non-detects

TEQ = toxicity equivalent

Table 11. Summary statistics and evaluation of precision for Port Angeles Harbor and the combined data sets

Summary Statistics	Port Angeles	Combined NOP[a]
Sample Size	14	41
Minimum	10.2	0.562
Average	49.7	28.2
Median	39.8	20.6
Maximum	172	172
Precision	41%	28%
Excluding Outlier(s)		
Sample Size	13	40
Minimum	10.2	0.562
Average	40.3	24.7
Median	38.7	20.4
Maximum	87.2	87.2
Precision	29%	20%

Notes:

[a] Combined data set includes Discovery Bay, Port Townsend Bay, Sequim Bay, and Port Angeles Harbor

NOP = North Olympic Peninsula

% = percent

Table 12. Port Angeles-specific regional background value for cPAH compared to Port Angeles proximal natural background

Chemical of Potential Concern	Units	Port Angeles-Specific Regional Background 90/90 UTL[a]	Port Angeles Proximal Natural Background 90/90 UTL[b]
cPAH TEQ	µg TEQ/kg	64	9.2

Notes:

[a] Dungeness Bay samples not included in regional background

[b] Port Angeles proximal natural background does not currently include Dungeness Bay samples collected as part of regional background

cPAH = carcinogenic polycyclic aromatic hydrocarbon
kg = kilogram
µg = microgram
TEQ = toxicity equivalent
UTL = upper tolerance limit