



Budd Inlet and Oakland Bay Dioxins and Furans

2011 Sediment Results



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Budd Inlet and Oakland Bay Dioxins and Furans

2011 Sediment Results

by

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- 14

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Abstract

During 2011, sediment samples were collected for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) analyses from Budd Inlet (Thurston County) and Oakland Bay (Mason County). Previous sediment surveys for Budd Inlet and Oakland Bay (2007 and 2008 respectively) found moderate-to-high concentrations of PCDD/Fs.

This study was conducted by the Washington State Department of Ecology Toxic Cleanup Program and included in the Marine Sediment Monitoring Team's annual Puget Sound Ecosystem Monitoring Program (PSEMP) and Ecology's Urban Water's Initiative (UWI) Monitoring Program.

In Budd Inlet, sampling was performed largely to increase the area previously sampled and to generate a data set which could be used to estimate background levels for PCDD/Fs in sediments. In Oakland Bay, sampling was conducted at different depths to determine whether recently deposited sediment might be cleaner.

Most samples indicated elevated PCDD/Fs levels (>4.0 ng/kg TEQ¹) and ranged from 0.692 to 53.7 ng/kg TEQ for Budd Inlet and 2.09 to 55.2 ng/kg TEQ for Oakland Bay. No clear pattern was found when comparing the upper portion (0-2 cm) of the samples to the lower portions (up to 10 cm) in either bay. Background levels were not clearly defined, although Budd Inlet was found to exhibit a strong decreasing trend from south to north and a less clear trend increasing from west to east.

Levels of PCDD/F in Oakland Bay upper 0-2 cm samples appear to remain elevated. This could possibly be due to natural or local disturbances or potentially a continuing source of PCDD/F. It has been found that sediment deposited within Oakland Bay generally stays confined within the bay.

PCDD/F congener profiles for both bays match previous studies and also the U.S. Environmental Protection Agency's profiles for Technical Grade Pentachlorophenol (PCP) and black liquor recovery boiler emissions, which have been linked to activities within these bays.

Recommendations include additional research to understand the important roles of hydraulic energy, sediment deposition and resuspension, natural and local disturbances, and potential ongoing sources in the distribution and fate of PCDD/F in these bays.

¹ Toxic equivalency

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- Pete Striplin
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Introduction

In 2007 and 2008, the Washington State Department of Ecology's (Ecology's) Toxic Cleanup Program conducted studies to characterize sediments in Budd Inlet and Oakland Bay, respectively, as part of the Puget Sound Initiative, an effort to restore Puget Sound by the year 2020 (PSP, 2008). Both bays are located in the southern portion of Puget Sound and are tidally influenced with a range of around 20 feet. Budd Inlet is located near the city of Olympia, and Oakland Bay is located near the city of Shelton (Figure 1). This study was requested by the Toxics Cleanup Program to augment data from the 2007 and 2008 characterization studies.

Budd Inlet is approximately 1.5 miles wide by 7 miles long and ranges in depth from <35 feet to 100 feet at high tide, south to north respectively. The large Deschutes River tributary flows through man-made Capitol Lake before reaching the West Bay of the inlet, and the small Moxlie Creek tributary is diverted through a mile-long pipe underneath the city before entering the southern end of the East Bay (SAIC, 2008). The water circulates in a counter-clockwise pattern with a flushing time of approximately 10 days (SAIC, 2008).

The east and west bays of Budd Inlet historically and currently support wood product industries, recreational marinas, and boat construction/repair facilities. The Port of Olympia marine terminal resides along the shoreline of West Bay. The North Inlet consists primarily of residential properties. Additional information for Budd Inlet can be found on Ecology's website at www.ecy.wa.gov/programs/tcp/sites_brochure/psi/buddInlet/psi_buddInlet.html.

Oakland Bay is approximately three-quarter miles wide by 4 miles long and ranges generally from 10 to 45 feet deep at high tide in a somewhat northerly to southerly direction, where Hammersley Inlet, a long narrow waterway, links the bay to Puget Sound Basin. There are nine major tributary creeks: Deer, Cranberry, Campbell, Johns, Uncle John, Malaney, Shelton, Mill, and Goldsborough. Due to the restrictive nature of Hammersley Inlet, Oakland Bay has low flushing, high retention, and high refluxing rates, which means the bay retains and re-circulates water back and forth while gradually flushing it out: around 5 days for only one-half to disperse out of the bay (Herrera and E&E, 2010; Albertson, 2004).

Current and historical land use around Oakland Bay includes rural residential, commercial forest, commercial shellfish, small farms, and some industrial and commercial development, primarily along the west and south sides of the bay. Several timber and wood product manufacturing industries reside on the city of Shelton's waterfront and harbor. A pulp mill operated in Shelton Harbor from the mid-1920s to late 1950s. Additional information for Oakland Bay can be found on Ecology's website at www.ecy.wa.gov/programs/tcp/sites_brochure/oaklandBay/oaklandBay_hp.htm.

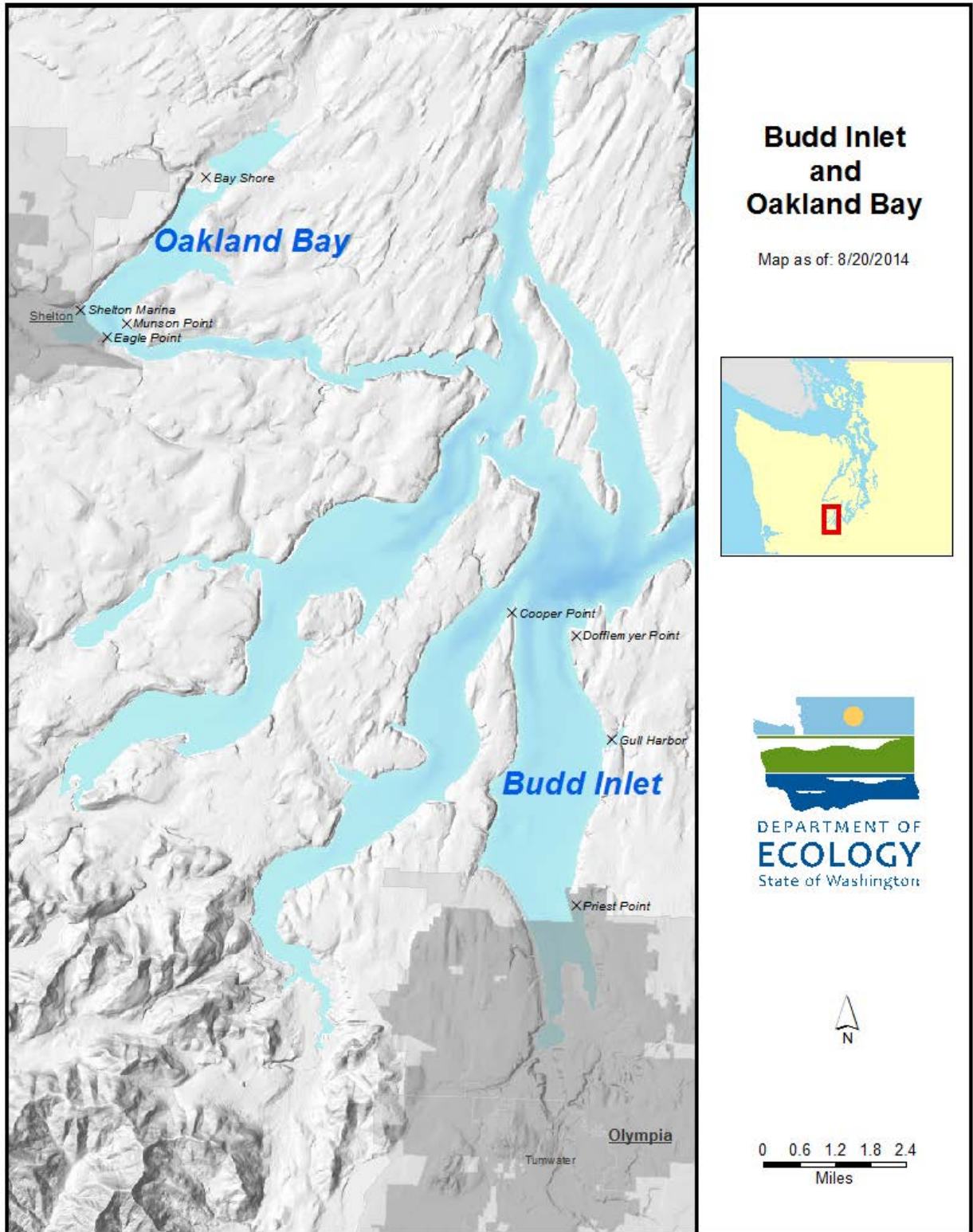


Figure 1. Map of Budd Inlet and Oakland Bay.

Surveys conducted in Budd Inlet (SAIC, 2008) and Oakland Bay (Herrera and E&E, 2010) indicated that sediments contain moderate-to-high concentrations of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). This study provided additional sampling in both water bodies during 2011 to gain further information about PCDD/Fs. In Budd Inlet, the sampling was performed largely to increase the area previously sampled for PCDD/Fs in sediments. In Oakland Bay, the sampling was conducted at different depths to determine whether recently deposited sediment might be cleaner.

This document reports on the methods and results of the 2011 sampling.

Goals and Objectives

Ecology's Marine Sediment Monitoring Team (MSMT) conducted sediment sampling in Budd Inlet and Oakland Bay as part of their annual Puget Sound Ecosystem Monitoring Program (PSEMP) and Ecology's Urban Water's Initiative (UWI) Monitoring Program. The goal of these programs is to characterize sediment quality in various regions and urban bays throughout Puget Sound.

During 2011, Ecology collected additional samples for measuring the concentrations of 17 chlorinated dioxin and furan congeners in surface sediments from selected stations in Budd Inlet and Oakland Bay as a special project for Ecology's Toxic Cleanup Program. The objectives of this special study are as follows:

Budd Inlet

- Increase spatial coverage and reduce data gaps within Budd Inlet, particularly in the outer bay area, and provide a data set to estimate PCDD/F concentrations that might represent background conditions for Budd Inlet. Using these results will help determine if and where surface sediment PCDD/F concentrations in Budd Inlet decline to "background"² conditions in order to aid future cleanup decisions.
- Evaluate potential natural recovery from historical levels of PCDD/F contamination through the collection of a few surface samples in the top two centimeters of the sediment.

Oakland Bay

- Assess recovery potential for contaminated sediments in Oakland Bay and help evaluate whether natural recovery is occurring by way of the addition of clean sediments from freshwater sources or bluff erosion.

² PCDD/F background concentrations are currently being developed for several bays in Puget Sound but have not been finalized at the writing of this report. Specific rules are being developed regarding what samples are eligible to be counted toward background calculations, but this is beyond the scope of this report.

Methods

Study Design

Table 1 summarizes the samples collected.

Table 1. Number of Sampling Sites, Samples Collected, and Analyses.

Sample Origin/Type	Number of Stations	Number of Samples / Surface Layer Depth			Number of Analyses by Parameter		
		0-2 cm	0-10 cm	2-10 cm	GS	TOC	17 PCDD/F Congeners
Budd Inlet, Central & Outer	24	2	24	--	26	26	26
Budd Inlet, Inner	6	4	6	--	10	10	10
Oakland Bay / Shelton Harbor	5	5	--	5	10	10	10
Total Stations	35	11	30	5	46	46	46
Quality Control Samples							
Method Blanks					--	√	√
Lab Replicates					√	√	√
Matrix Spikes					--	--	√
Standard Reference Material (SRM)					--	√	√

GS: Grain Size

TOC: Total Organic Carbon

Site Selection

This study selected 35 stations for sediment sampling: thirty in Budd Inlet and five in Oakland Bay. Most stations were chosen from the PSEMP Spatial/Temporal and UWI stations. Stations for this program were selected using a stratified-random sampling design (Ecology, 2012). Six stations were not chosen from the PSEMP and UWI stations but were selected for specific reasons such as areas with historically high levels of contamination.

Sample site coordinates are listed in Appendix A. Coordinates listed in Ecology's Environmental Information Management (EIM) database may differ within a few feet in order to co-locate samples (www.ecy.wa.gov/eim/index.htm listed under Study ID "BuddOakDioxins").

Budd Inlet

Figure 2 shows Budd Inlet sampling locations. For this study's purposes:

- Inner Budd Inlet is defined as the area south of latitude 47.0666 (decimal degrees (DD)) or approximately below Priest Point Park.
- Outer and central Budd Inlet is defined as the area north of latitude 47.0666 (DD) or approximately north of Priest Point Park to south of a line between Dofflemyer Point on the east bank and Cooper Point on the west bank.

Demarcation between outer and central Budd Inlet is roughly drawn across the bay at Gull Harbor (Figure 1). These areas reflect the variation within the inlet as designated in the Budd Inlet Scientific Study Final Report (LOTT, 1998).

Two stations for inner Budd Inlet were specifically chosen to confirm past results showing high PCDD/F concentrations (BI-S30 and BI-S7-0-10cm). Other stations in the inner area were selected for sampling within the east and west bays of the Port of Olympia and just outside of these bays. Stations in the central and outer areas were primarily chosen to fill spatial data gaps for PCDD/F concentrations and to better understand concentration gradients in the inlet.

Oakland Bay

Figure 3 shows the five stations sampled for Oakland Bay, of which three were chosen from PSEMP and UWI stations. This study includes Shelton Harbor, which is defined from Eagle Point to the Port of Shelton Marina (Figure 1).

Two new stations were added in upper Oakland Bay. One of the new stations (OB-10-SC, which is the second most northerly station) was at the same coordinates as one of the 2008 samples. No other sites were co-located with prior locations. The most northerly station (OB-12.5S) is in-between two of the samples from the 2008 study.

All the Oakland Bay station locations were chosen to determine whether more recently deposited (overlying) material is cleaner than older (deeper) sediments. Therefore, these stations were selected within areas of known elevated PCDD/F concentrations based on the 2008 sampling.

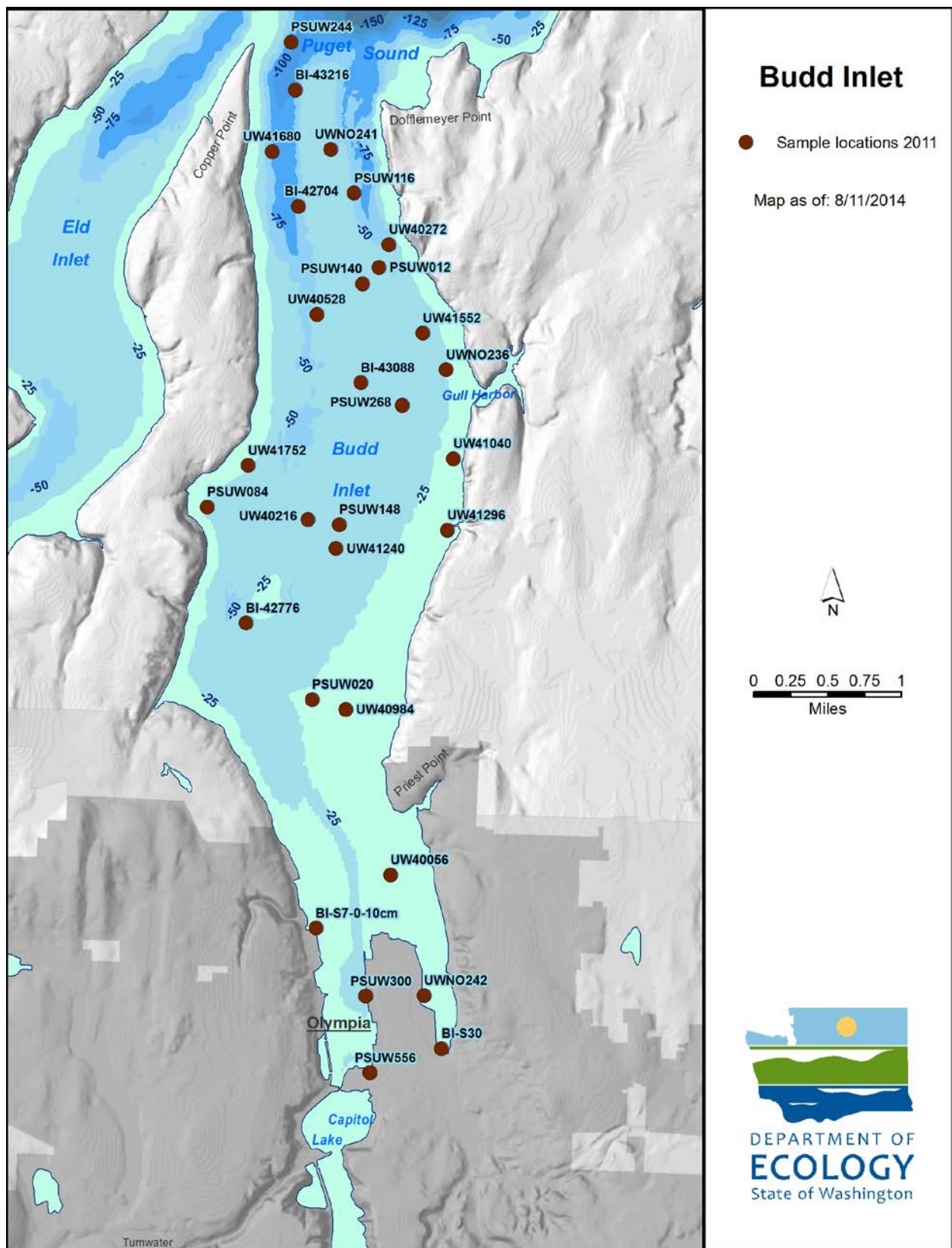


Figure 2. Surface Sediment Sampling Locations in Budd Inlet, 2011.

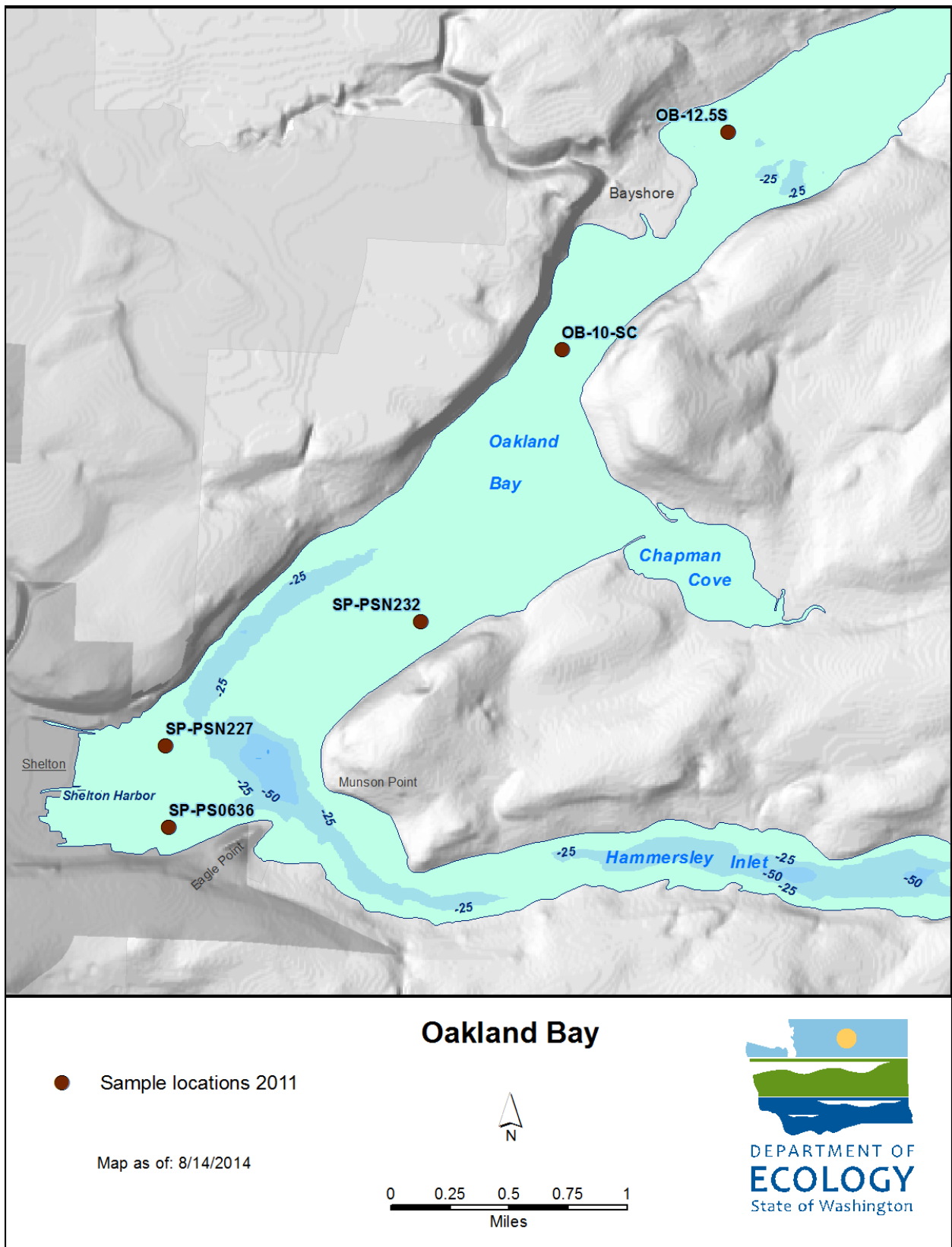


Figure 3. Surface Sediment Sampling Locations in Oakland Bay, 2011.

Sample Collection

Surface sediment samples were collected from a single grab collected with a 0.1 m² double vanVeen from each station from the *R/V Kittiwake*. Sampling was conducted as described in the 2009 QA Project Plan for the PSEMP Spatial/Temporal and UWI Monitoring Programs (Dutch et al., 2009). Most samples collected in Budd Inlet were taken from the top 0-10 centimeters (cm) of sediment horizon. A small subset of Budd Inlet samples were collected from the top 0-2 cm. In Oakland Bay, sediments were collected from the top 0-2 cm and the 2-10 cm horizons at each of the stations surveyed.

Once collected, the sediment sample was visually inspected. Any grab sample lacking fine-grained particles in the sediment (*i.e.*, composed of all cobble, shell hash, or wood) or for which the jaws of the grab did not close completely, was rejected. Any grab sample that had either a less-than-adequate penetration depth or over-penetration was discarded.

Laboratory Analysis

Sample handling, storage, holding times, and chain-of-custody procedures are described by Ecology (2012). Analytical Resources Incorporated (ARI), Ecology's Manchester Environmental Laboratory (MEL), and Cape Fear Analytical (CFA) used standard methods to measure the grain size distribution (PSEP, 1986), total organic carbon (PSEP, 1986), and PCDD/Fs (EPA, Method 1613B), respectively. Although there were no deviations from these methods noted, nearly all (about 84%) of the PCDD/F results were below the estimated quantitation limit (EQL), lowering confidence in those results. Additional quality control (QC) and analyses were conducted and described below. The samples were re-analyzed for PCDD/F, which are reported here.

Data Quality

Data quality was assessed by reviewers at CFA and by MEL's QA Coordinator, Karin Feddersen. The PCDD/F data were reviewed for "qualitative and quantitative accuracy following the National Functional Guidelines for Organic Data Review adapted for high resolution dioxin analysis and using the EPA Region 10 Standard Operating Procedures (SOP) for the Validation of PCDD/PCDF" (EPA, 1996).

The authors of this data report reviewed:

- All chain-of-custody forms to assess whether sampling handling, storage conditions, and holding times required by the QA Project Plan and standard methods were met.
- All data deliverables (print and electronic) received from the various laboratories to assess whether results met the Data Quality Objectives (DQOs) listed in the QA Project Plan.
- Overall quality and usability of the data.

Furthermore, additional extensive review of the data was conducted by the analyzing laboratories, the authors of this report, and an independent contractor.

Dioxin Results

In the initial analysis of PCDD/Fs, the majority (about 84%) of the results were below the EQL. For these results, the EQL is defined as lowest calibration standard. Furthermore, the initial results were extremely low compared to results from the same or nearby locations from the 2007 and 2008 studies. Not only was the confidence lowered in those results, the large difference between studies indicated that there may have been a problem with the analysis.

Additional analyses for PCDD/F were conducted on certain samples collected in 2011, which showed different results than the original analysis, revealing a likely systematic error in the previous results. Therefore, the analyzing laboratory (CFA) re-analyzed the sample aliquots for PCDD/Fs in 2013. All samples were stored and shipped frozen. The re-analyzed results are reported here. A more complete discussion of the PCDD/Fs analysis is included in Appendix B.

PCDD/F Re-analysis

All results met DQOs and were deemed usable for the stated purposes. Over 80% of these results were reported as detected. No results were rejected, but the following QA issues were noted:

- All re-analyzed results were assigned an estimated value and qualified with a “J”: the results were considered estimates because they were re-analyzed outside the holding time required by the QA Project Plan (>1 year). All samples were verified to be at proper holding temperature (<4°C) throughout storage and transport since they were kept frozen. According to EPA Method 1613B (EPA, 1994), there are no demonstrated maximum holding times associated with PCDD/Fs. Therefore, the length of holding (about 24 months) should not impair the result usability.
- Some samples were flagged as estimates (“J” qualified) because their concentration was below the EQL and because of interferences.
- Congeners detected but not meeting the isotopic abundance ratio, and retention time criteria for positive identification were qualified as not detected (nondetects) and flagged “UJ,” which means the analyte was not detected at or above the reported estimate.
- Certain compounds were detected in the laboratory blanks. When these same congeners were detected in the samples, the sample results <5 times the method blank are qualified as nondetects at the EQL level. The blank contamination is considered insignificant if the sample result is >5 times the method blank and no qualifications are necessary.
- Deviations in the matrix spike and duplicates were most likely due to inhomogeneity of the samples.
- Two of the three samples and subsamples (laboratory duplicates) were outside of the measurement quality objectives (MQOs) acceptable range of <50 relative percent difference (RPD) (samples 1106045-12 and 1106045-30). This variation is not uncommon among subsamples (e.g., laboratory duplicates) with varying proportions of particle sizes. Larger particles tend to carry lower contaminant loadings, versus smaller particles with higher loadings, causing the subsamples to have different concentration results (ITRC, 2012). Both samples contained varying sizes of particles (approximately 60% fines and 40% sand and

gravel) and visible organic matter (woody debris). Also, TOC was higher (>4%) in these two samples and their duplicates than most of the other samples in the data set, which confirms the presence of the organic matter and the different particle sizes observed. Results from the samples – not the subsamples (i.e., duplicates) – were used in this report.

Ancillary Analyses

All TOC and grain size results were within laboratory QC limits as required in the QA Project Plan. These parameters were not re-analyzed, as was the PCDD/Fs.

TOC and grain size results reported here are from the 2011 analysis, which should be fairly comparable to the archived aliquots used for PCDD/F re-analysis. The assumption was that the results would be similar because all samples were homogenized in the field and then kept frozen. Organic debris (i.e., wood particles) and shell fragments were found in a few of the samples analyzed for grain size. These were noted in the laboratory notes.

Data Handling

Total toxic equivalency (TEQ) concentrations were calculated as the sum of 17 congener TEQs based on World Health Organization (WHO) 2005 mammalian toxic equivalent factors (TEFs) (Van den Berg et al., 2006). Congeners that were not detected were assigned concentrations using two methods, as described in Gries (2011):

- Substitution: Nondetect (ND) concentrations were set equal to one-half the estimated detection limit (EDL)³ ($ND=EDL/2$) and reported in the remainder of this report. For comparison, nondetects set to zero are listed in Appendix C.
- Kaplan-Meier (KM): Nondetect congeners were assigned concentrations using the KMstats.xls model (version 1.5) (Helsel, 2005).

When comparing the Substitution and KM methods, this study concluded there were no differences in the results since most results in this data set were detected. For samples with nondetects, the KM results were generally >90% of the substituted result, with one exception of >75%, which still compared relatively well. Differences are greatest when the concentrations are low and the number of nondetects is high within a sample.

This study used the substitution method ($1/2$ EDL for nondetects) for calculating and reporting results below detection limits. This is consistent with the 2007 Budd Inlet Sediment Characterization and 2008 Oakland Bay Studies (SAIC, 2008; and Herrera and E&E, 2010, respectively).

³ Estimated detection limit (EDL) values reflect levels that are approximately 2.5 times the signal-to-noise ratio, which is the same criterion used for the method detection limit (MDL) described by 40CFR. Nondetect results are reported to the EDL and are estimated "UJ." Results derived from responses outside the calibration range are considered estimates.

Dioxin/furan concentrations have not been TOC normalized in this report. Weak positive correlations exist between TOC and surface sediment TEQ for Budd Inlet and Oakland Bay samples ($r^2=0.25$ and $r^2=0.11$ respectively). The absolute toxicity, or TEQ, of sediment is more important for purposes of comparison and regulation than a TOC adjusted value.

Mapping and geostatistical analyses were done using ArcMap Version 10.1 (ESRI, 2010). SPSS Release 11 (SPSS, 2001/2005), ProUCL software (EPA, 2013), and Microsoft Excel (2007) were used to conduct statistical analyses.

Results

A total of 46 samples were collected at 30 stations in Budd Inlet and five stations in Oakland Bay/Shelton Harbor. The *R/V Kittiwake* crew found six of the Budd Inlet target stations to be inaccessible or to have sediments with sand, gravel, or cobble content that prevented the vanVeen sampler from adequate penetration. For these six stations, the pilot repositioned the vessel to a nearby alternate station where the crew collected surface sediment from appropriate depth intervals. All Oakland Bay target stations were accessible. Figures 2 and 3 show final locations.

Results are reported below for Budd Inlet and Oakland Bay separately and are listed in Appendix C.

Budd Inlet

Conventional Parameters

Silt and clay particles (fines) dominated most surface sediment samples collected from Budd Inlet. The fines content of the 36 samples analyzed for Budd Inlet averaged 73% (Table 2). These results match Ecology's Marine Monitoring Unit's 2011 focus study for Budd Inlet which found the sediments were predominately mixed (40 to 80% silt-clay) and fine-grained (>80% silt-clay) (Partridge et al., 2014a). In characterizing Budd Inlet, the SAIC study (2008) noted very fine-grained surface sediments (silts and clays) in most sub-tidal areas of Budd Inlet.

Table 2. Budd Inlet Grain Size and TOC (N=36).

Percent (%)	Minimum	Mean	Maximum
Gravel	0.1 U	6.4	34
Sands	5.2	21	84
Silts	8.6	47	63
Clays	6.1	25	36
Fines	15	73	91
TOC	1.1	3.0	7.4

U= Not detected at detection limit shown

The sediment samples collected from deep waters of the central and outer inlet contained the highest percent fines (Figure 4). Samples collected from the head of East Bay and along the western shoreline of outer Budd Inlet contained >40% sand. Some stations in lower Budd Inlet (UWNO242, PSUW300, PSUW556) and the eastern half of central Budd Inlet (UW40984, -41040, -41240, -41296) contained substantial amounts of gravel (>10%).

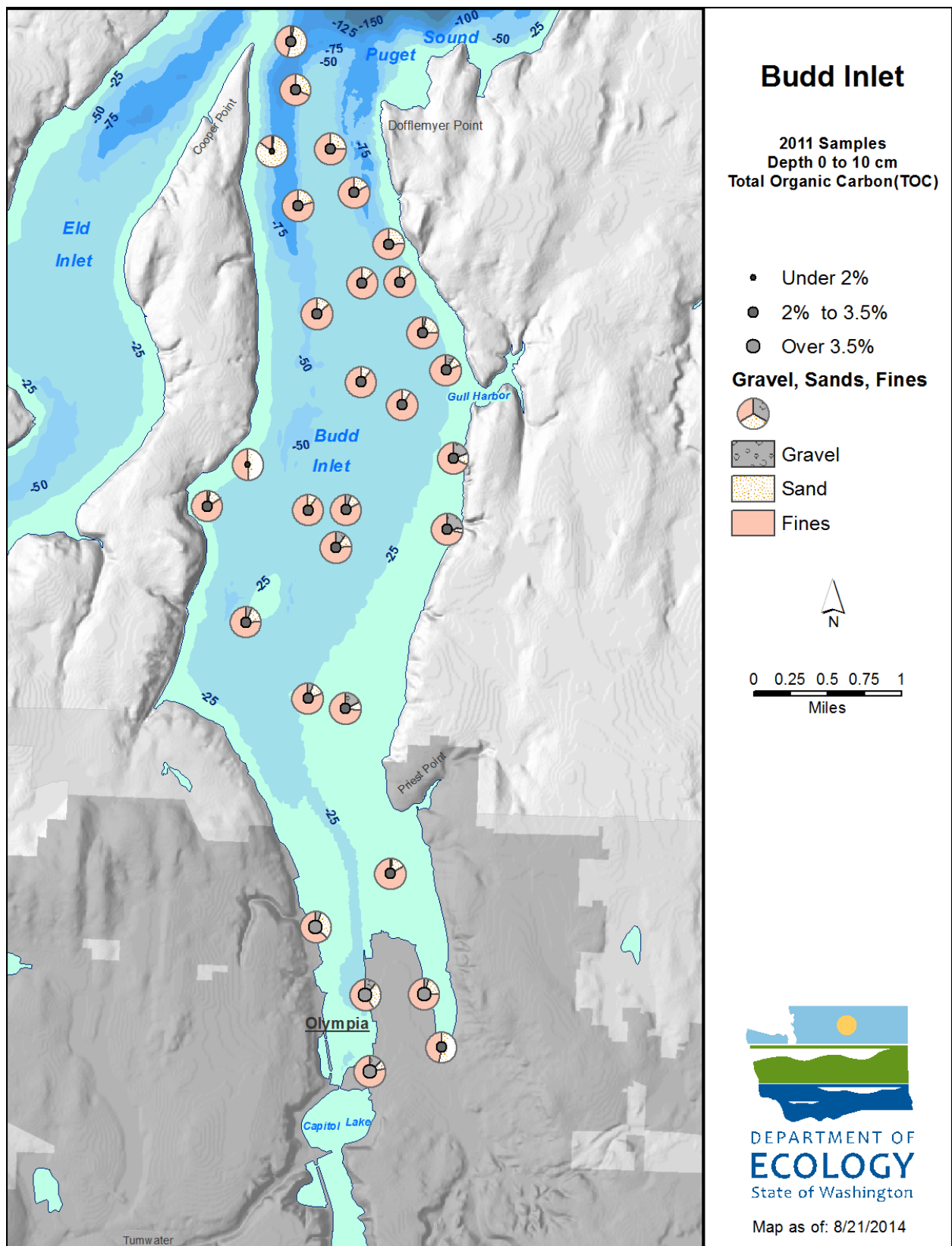


Figure 4. Percent Grain Size and TOC in Surface Sediments of Budd Inlet, 2011.

The top two centimeters (0-2 cm) of six stations were sampled for comparing to the deeper portion (0-10 cm) depth (Figure 5). All but one sample contained over 50% fines. The one exception was station PSUW300 located along the eastern side of West Bay with 46% fines near the surface which, as mentioned above, contained substantial amounts of gravel in the lower portion (0-10 cm). Although >10% gravel was also found in other stations in Budd Inlet, most samples compared contained predominately fine grained sediments.

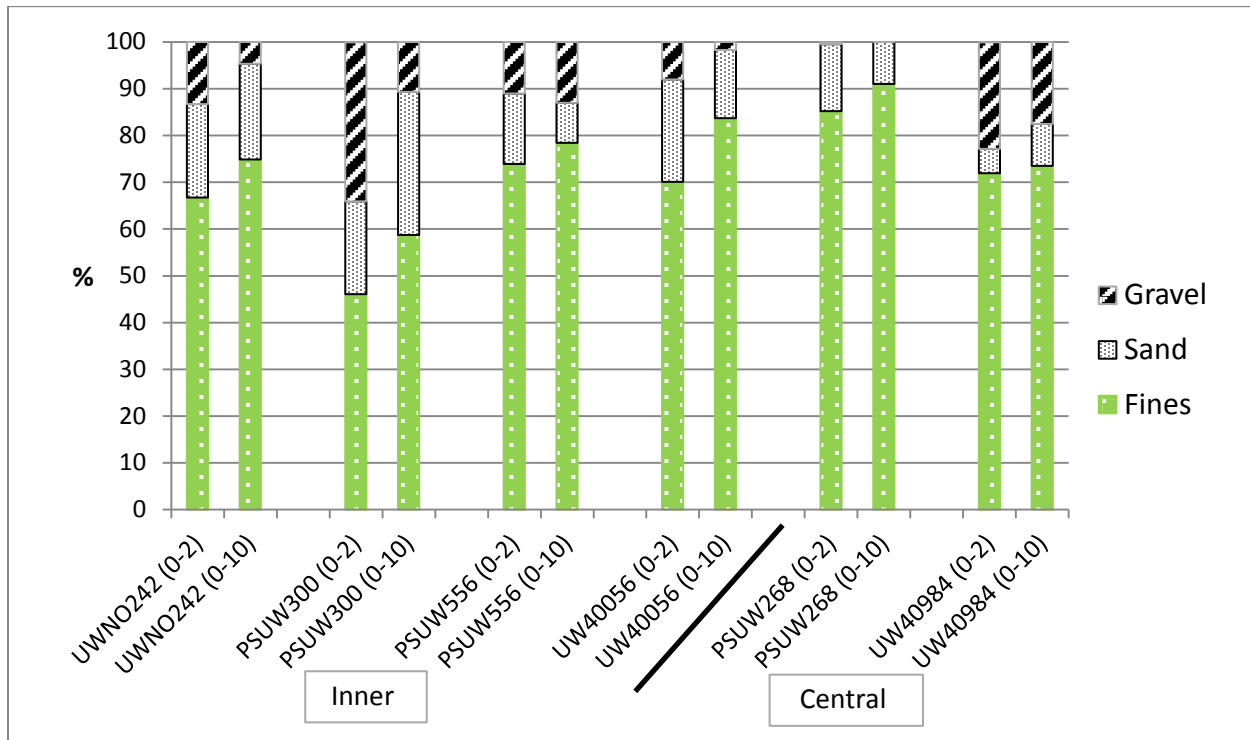


Figure 5. Budd Inlet Grain Size Compared at Different Depths.

The TOC content of samples ranged from 1.1% to 7.4%, and averaged 3.0% (Figure 4). The highest percent TOC tended to be in lower Budd Inlet. These results matched Ecology's Marine Monitoring Unit's 2011 focus study for Budd Inlet (Partridge et al., 2014a), with 3% TOC average and increasing from the outer to the inner bay. Likewise, the 2007 Budd Inlet study reported TOC averaging 3.2% and ranging from 0.6 to 9.3% (SAIC, 2008). The percent TOC appears to be elevated in areas with organic debris such as wood waste rather than with fines.

TOC percentage was similar when compared at different depths; 0-2 cm and 0-10 cm (Figure 6). TOC averaged 3.6% for the top two centimeters compared to 3.5% for the 0-10 cm. These averages were on the upper level overall for Budd Inlet and match the above findings with highest percent TOC found in lower Budd Inlet or where organic debris may be located.

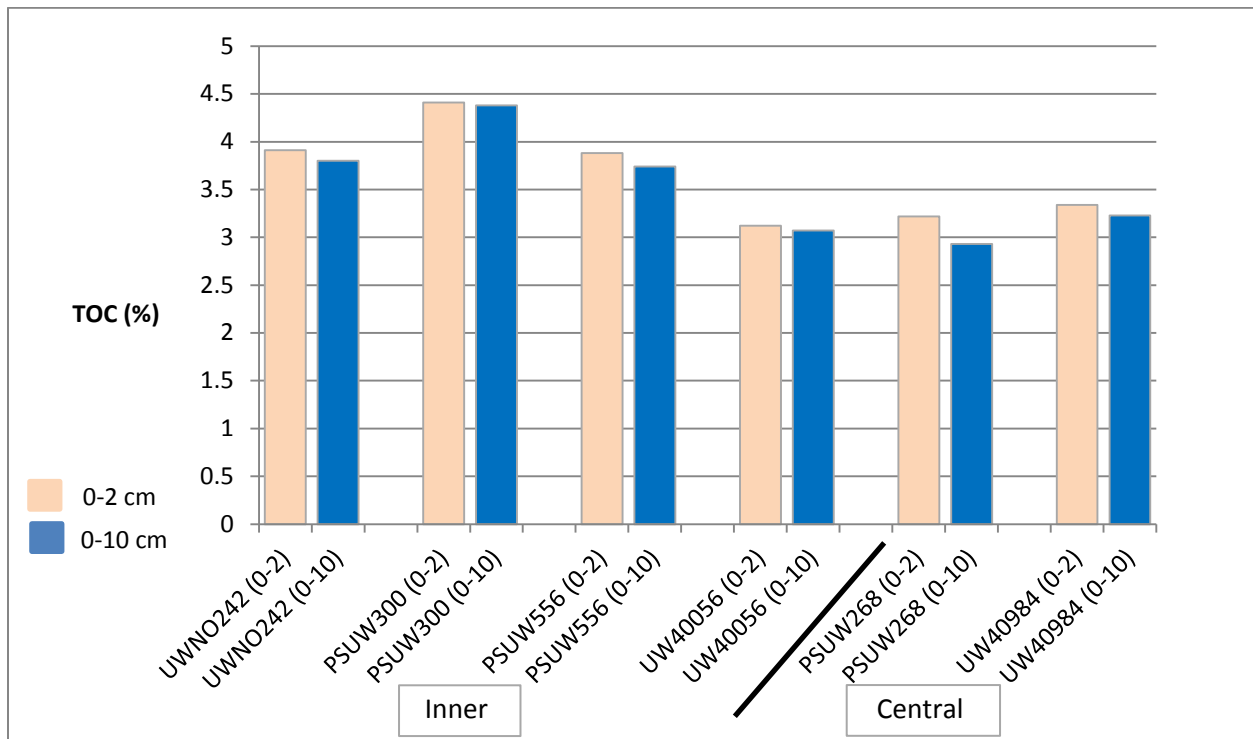


Figure 6. Budd Inlet TOC Compared at Different Depths.

PCDD/Fs

PCDD/Fs were detected in all 36 sediment samples (Table 3). Congener 2,3,7,8-TCDD was detected in 78% of the samples for Budd Inlet and ranged from 0.307 to 1.52 ng/kg. Of the detected results, the average 2,3,7,8-TCDD concentration was 0.627 ng/kg.

Table 3. Budd Inlet PCDD/Fs TEQs (N=36).

	Budd Inlet	
	Central/Outer	Inner
Number of Samples	26	10
Mean (ng/kg)	14.4	24.7
Median (ng/kg)	13.4	22.4
Minimum (ng/kg)	0.692	6.85
Maximum (ng/kg)	35.5	53.7
Maximum Location	UW40984 (1106045-18)	UWNO242 (1106045-41 aka 1106046-45)

TEQs for all Budd Inlet sediment samples ranged from 0.692 to 53.7 ng/kg, with a mean TEQ of 17.3 ng/kg and a median TEQ of 14.2 ng/kg. The highest TEQs were found in inner Budd Inlet, with an overall average of 24.7 ng/kg, which included the highest values: East Bay (53.7 ng/kg) and West Bay (41.9 ng/kg) (Figure 7). PCDD/F results for each sample are listed in Appendix C.

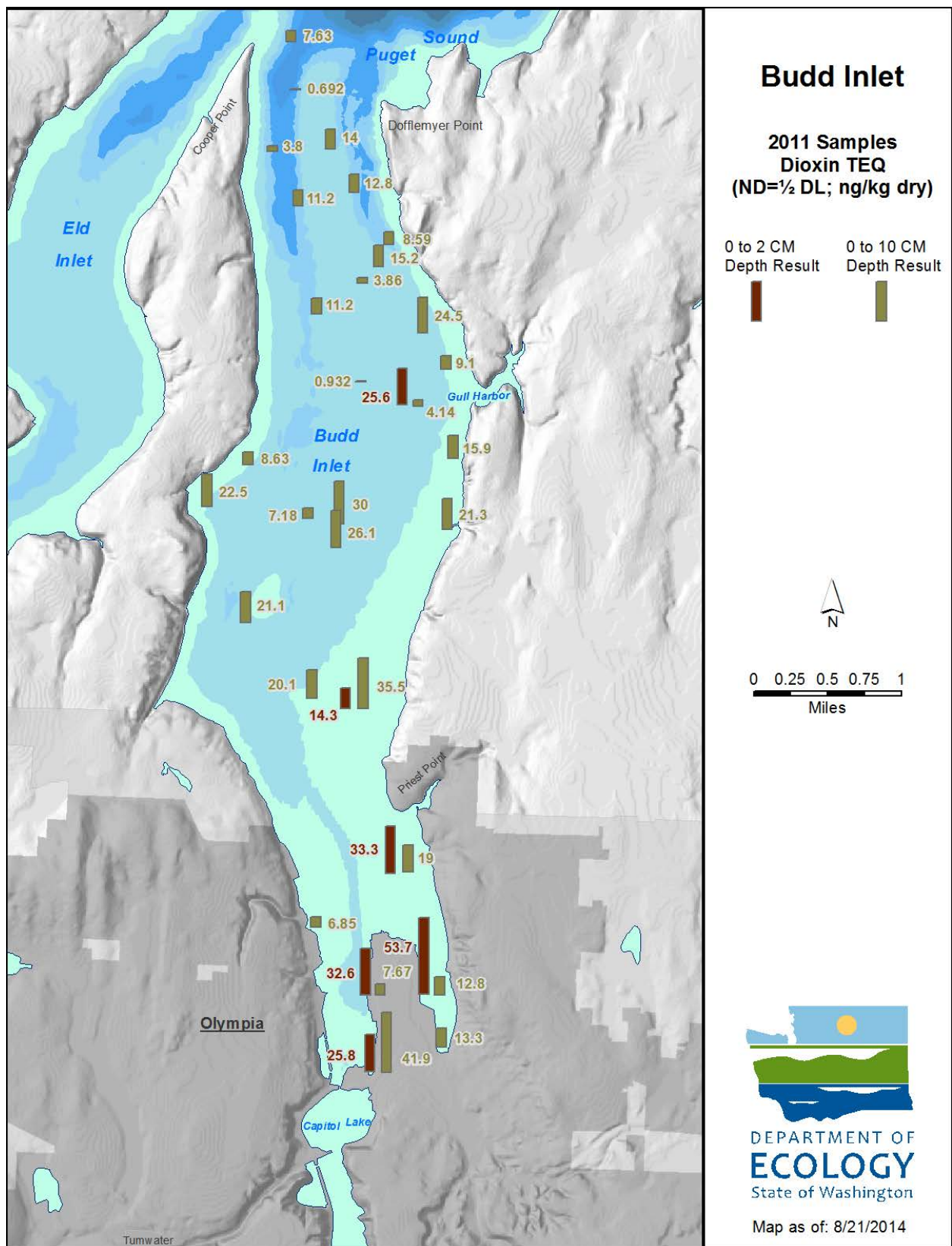


Figure 7. Distribution of PCDD/Fs Expressed as Total TEQ in Surface Sediments of Budd Inlet, 2011.

Six sediment samples from Budd Inlet included a 0-2 cm depth analysis along with the 0-10 cm and showed varying results for PCDD/Fs (Figure 8). Four of these samples were located within inner Budd Inlet, and two were located in central Budd Inlet south of Gull Harbor.

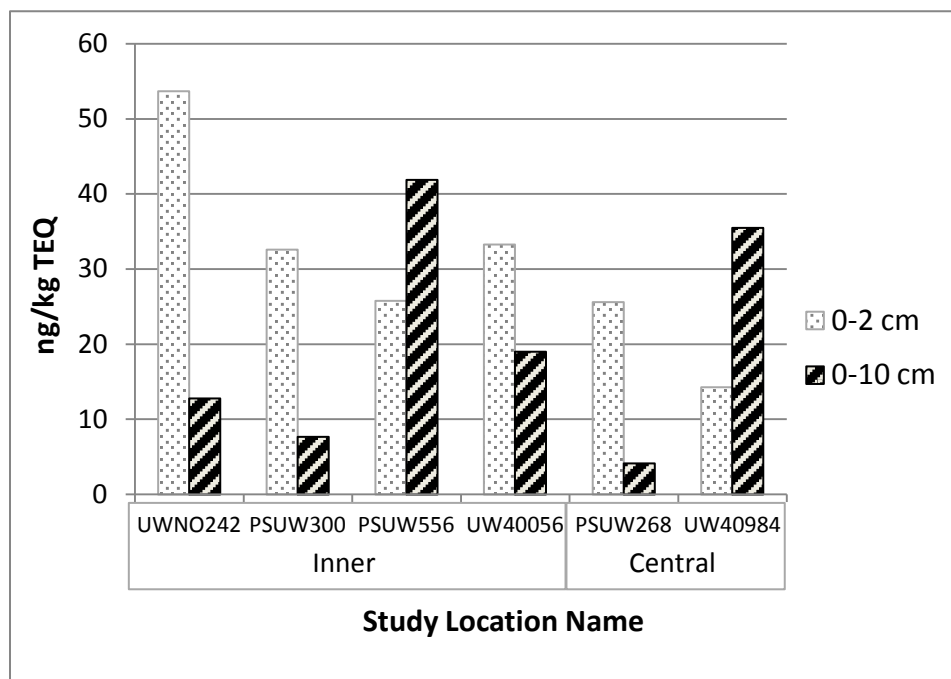


Figure 8. Budd Inlet PCDD/Fs TEQs Compared at Different Depths.

Four locations had higher PCDD/F concentrations in the upper portions of the samples, and two locations had lower concentrations, although no difference was found in comparison (no difference using t-test and nonparametric Wilcoxon-Whitney-Mann test, $p < 0.05$). The two highest results were from two sites having the maximum concentrations found in the bay for this study. These areas (within East and West Bays) are known to have some of the highest in the bay (SAIC, 2008), and considerations should be taken for indicating a possible ongoing source.

When comparing PCDD/F with TOC or fines, no relationship was found ($r^2 = 0.06$ and $r^2 = 0.003$ respectively). Likewise, no trends were observed when analyzing TOC and grain size with PCDD/Fs ($r^2 < 0.05$ and $r^2 < 0.2$ respectively) in the Ocean Survey Vessel (OSV) Bold Survey for PCDD/F background levels in Puget Sound (USACE, 2009).

In comparison, SAIC (2008) found somewhat weak positive correlation with TOC and percent fines, and a negative correlation with percent sand, for the majority of Budd Inlet surface samples (r^2 values of 0.384, 0.123, and 0.095 respectively). Two exceptions were noted in the SAIC study which had higher PCDD/F concentrations than expected by their respective amounts of TOC and fines. One (BI-S30) was sampled near the discharge of Moxlie Creek near the south end of East Bay, and the other (BI-S7-0-10cm) was sampled near Hardel Mutual Plywood at the north end of West Bay. Removing those in the analysis improved the correlation (r^2 values were 0.411, 0.423, and 0.297 for TOC, percent fines, and percent sand, respectively). Although this

2011 study sampled these locations, the PCDD/F results did not show the same relationship between these analyses.

Discussion

Thirty surface samples taken in Budd Inlet during 2011 showed a wide variation of PCDD/F concentrations (0.692 to 53.7 ng/kg TEQ) throughout the bay, making it difficult to determine a background⁴ concentration using these results. Above median concentrations (>14.2 ng/kg TEQ) found in the top portions (0-2 cm) of six samples hint to recent or ongoing contamination, or mixing/redistribution of deeper sediments. Accessing these results in light of current and historical land uses and examining the inlet's circulatory system may help decipher whether the PCDD/Fs could be from a current source, dispersal patterns within the bay, or simply sample variation.

PCDD/F Results and Bay Hydraulics

Extensive investigation has shown that water in Budd Inlet follows a counter-clockwise pattern (LOTT, 1998; SAIC, 2008). Cold, dense marine water flows into the bay near the bottom along the western shore while warmer, less saline water flows out of the bay near the surface along the eastern shore. The central inlet contains a weak counter-clockwise gyre (Figure 9).

The net flow circulation was shown to be atypical of other Puget Sound estuaries; i.e., an upper layer of water flowing out of the inlet above a deeper inflowing layer (LOTT, 1998). Instead, Budd Inlet appears to be separated horizontally with southward (landward) net flow at all depths in the western half of the central and outer portions, and northward (seaward) net flow at all depths in the eastern half (LOTT, 1998). The inner inlet acts as a pump to this tidal circulation due to the tides and freshwater addition from East and West Bays (LOTT, 1998). This agrees with the bathymetry of the inlet: a north-south oriented trough along the western side forming an upwelling channel for flooding currents, a large underwater hill (Olympia Shoal) in the center, and shallower depths on the eastern side, indicating sediment deposition.

The LOTT study (1998) found the patterns below prevalent year-round, although varied with season and tidal cycle—increased activity in the winter versus the summer. The circulation pattern was predominantly driven by tidal dynamics and less so by freshwater inputs, although West Bay experiences some unique circulatory dynamics as a result of Capital Lake intermittently discharging Deschutes River water. For a short time each day, discharges to West Bay resemble an estuary of a major river, but then receives minimal freshwater input when the gates are closed. Overall, freshwater inputs increase the net transport and circulation somewhat but do not change the hydraulic patterns.

⁴ PCDD/F background concentrations are currently being developed for several bays in Puget Sound but have not been finalized at the writing of this report. Specific rules are being developed regarding what samples are eligible to be counted toward background calculations, which are beyond the scope of this report.

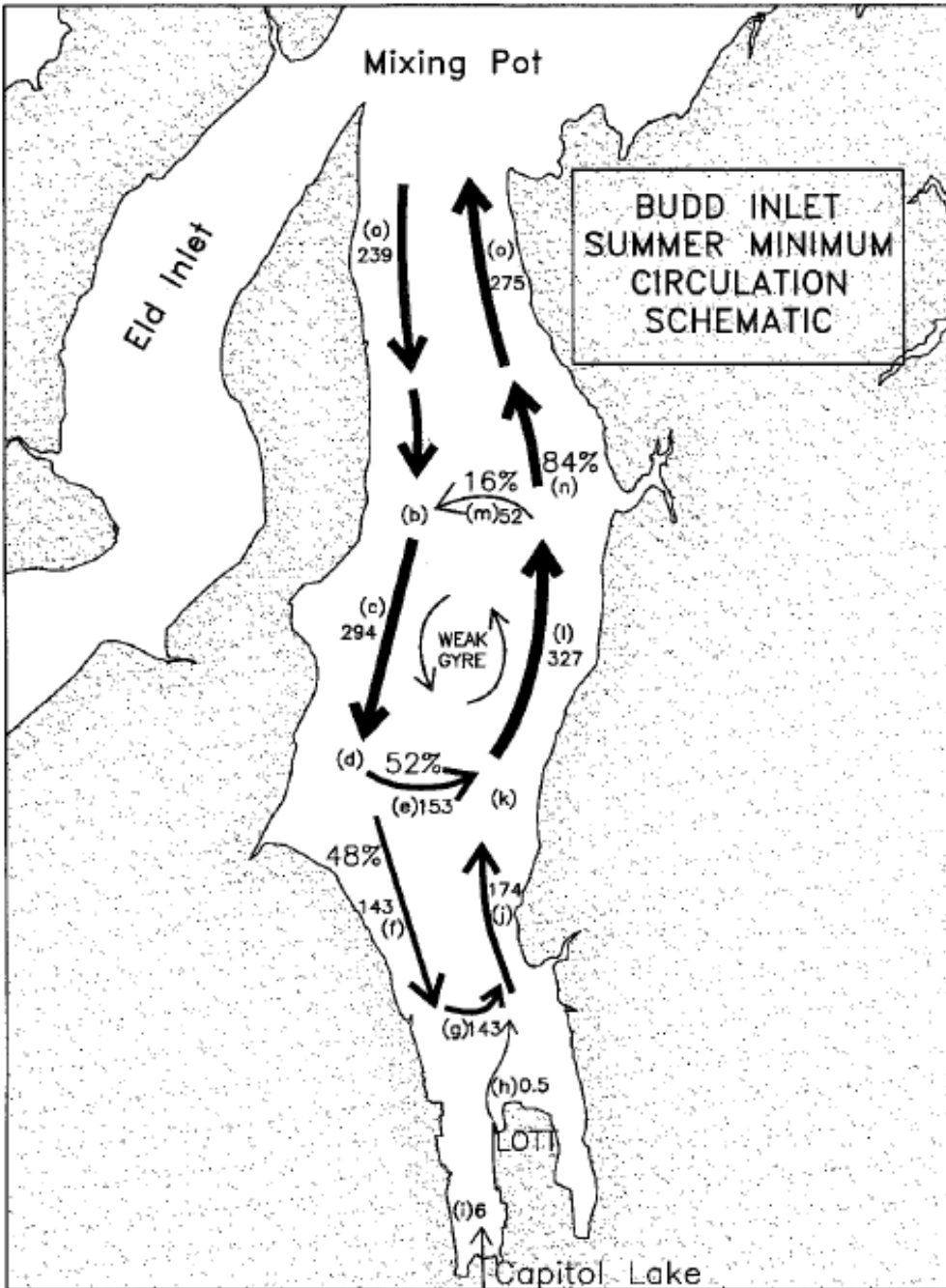


Figure 9. Budd Inlet Water Circulation.

Taken from LOTT (1998) showing Schematic Plan View during August 1997.

Notes for Figure 9:

Arrows indicate water flow scaled with thickness approximately proportionate to net volume transport (m^3/s). Refluxing is shown by the percentages of the main flows diverted east and west across the inlet forming the weak gyre in the Central Inlet.

Letter codes (a-o) following the water flow counterclockwise around the inlet denote the following:
 (a) From the mixing pot, the Outer Inlet main inflow transports southward $239 m^3/s$ as a submerged jet-like current hugging the western shore of the Outer Inlet.

- (b) Outer Inlet main inflow merges with water refluxed from the outflow in the Central Inlet.
- (c) Main inflow in the Central Inlet equals 294 m³/s comprised of 82% water from the Outer Inlet (239 m³/s) and 18% water refluxed from the Central Inlet main outflow (52 m³/s).
- (d, e) Central Inlet main inflow diverges with approximately half (48%; 143 m³/s) flowing into the Inner Inlet, and half refluxing (e; 52%; 153 m³/s) around the Central Inlet gyre.
- (f) Inner Inlet main inflow (143 m³/s) moves southward to the vicinity of the LOTT outfall.
- (g, h, i) Inner Inlet main inflow merges with discharges from LOTT (h) and Capitol Lake (i).
- (j) Inner Inlet main outflow (174 m³/s) exits primarily as a thin layer a few meters thick.
- (k) Inner Inlet main outflow merges with water refluxed from the Central Inlet main flow.
- (l) Central Inlet main outflow in a thin layer a few meters thick (327 m³/s) flows around the east side of the gyre.
- (m, n) Central Inlet main outflow diverges (n) with a secondary fraction (m: 16%; 52 m³/s) refluxing westward into the Central Inlet main inflow (b, c).
- (o) Outer Inlet main outflow (275 m³/s) exits northward to the mixing pot.

Figure 10 shows a bathymetric map for Budd Inlet and PCDD/F (total TEQ ng/kg) concentrations plotted in Budd Inlet. Besides areas of known elevated concentrations near the more urbanized portions of Budd Inlet, areas of higher PCDD/F concentrations also tend to be in the areas with less tidal energy and higher chance of deposition (shallow water or reduced circulation, continuing as far north as the mouth of the inlet) or around deltas from freshwater inputs. Further investigation in previous work may further substantiate this observation, which is discussed briefly below.

To explore spatial relationships and the possible effects of circulation throughout the bay, a geostatistical analysis was applied to the PCDD/F results from this study and then reran to include all results from previous studies as mentioned above. When spatial autocorrelation exists (i.e., sample values taken close to one another are more alike than samples taken far away from each other), traditional statistical methods, which rely on the independence among observations, cannot be used reliably.

Initial geostatistical analyses determined that all results taken together were somewhat normally distributed but somewhat weighted (right tailed) by elevated concentrations from samples in the Inner bay areas. Normality was not as certain when testing just this study's results because of the smaller sample size and reduced spatial locations. Furthermore, both data sets showed trends decreasing from south to north and somewhat from east to west (see below). Cross validations on the statistical test showed a fairly good fit to the model. Data explorations and QA results are discussed further in Appendix D.

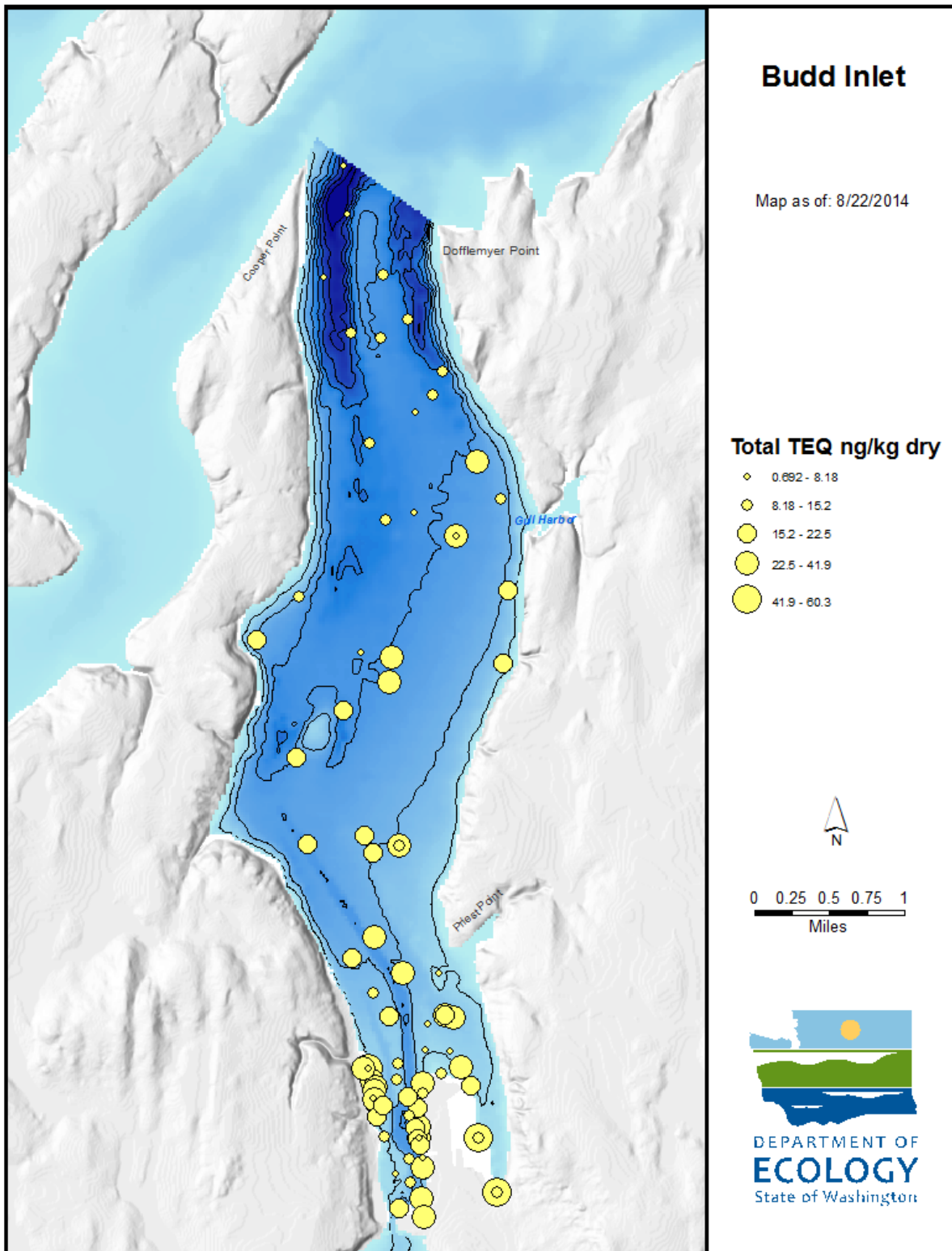


Figure 10. PCDD/F Concentrations (total TEQ ng/kg) (SAIC, 2008; Ecology, 2007).
Plotted Using Natural Breaks (Jenks) on a Bathymetric Map for Budd Inlet.

Figure 11 shows a surface layer with interpolated values across most of Budd Inlet resulting from the geostatistical analysis using this study's (2011) PCDD/F TEQ concentrations. A color gradient was applied to show where lower to higher levels of PCDD/F concentrations could be found under this model (green = lower value; red = higher values).

A fairly strong south-to-north decreasing trend is visible from the 2011 PCDD/F surface map. Mixed PCDD/F values in Central Budd Inlet appear to mask other trend possibilities such as hydraulic energy effect discussed above.

In comparison, a surface map created using all results from this study and previous studies shows some of the variability prevalent within the bay (Figure 12). The south-to-north decreasing trend is observed in both surface maps, but a clearer picture between the east and west sides—lower and higher hydraulic energies—emerges, even though certain elevated concentration areas still strongly influenced the analysis. Lower values at the head of the basin and following the outgoing hydraulic scheme described above may reflect input from spring runoff or rain events. The historical 2007 samples were collected in April, whereas the 2011 samples were collected in June.

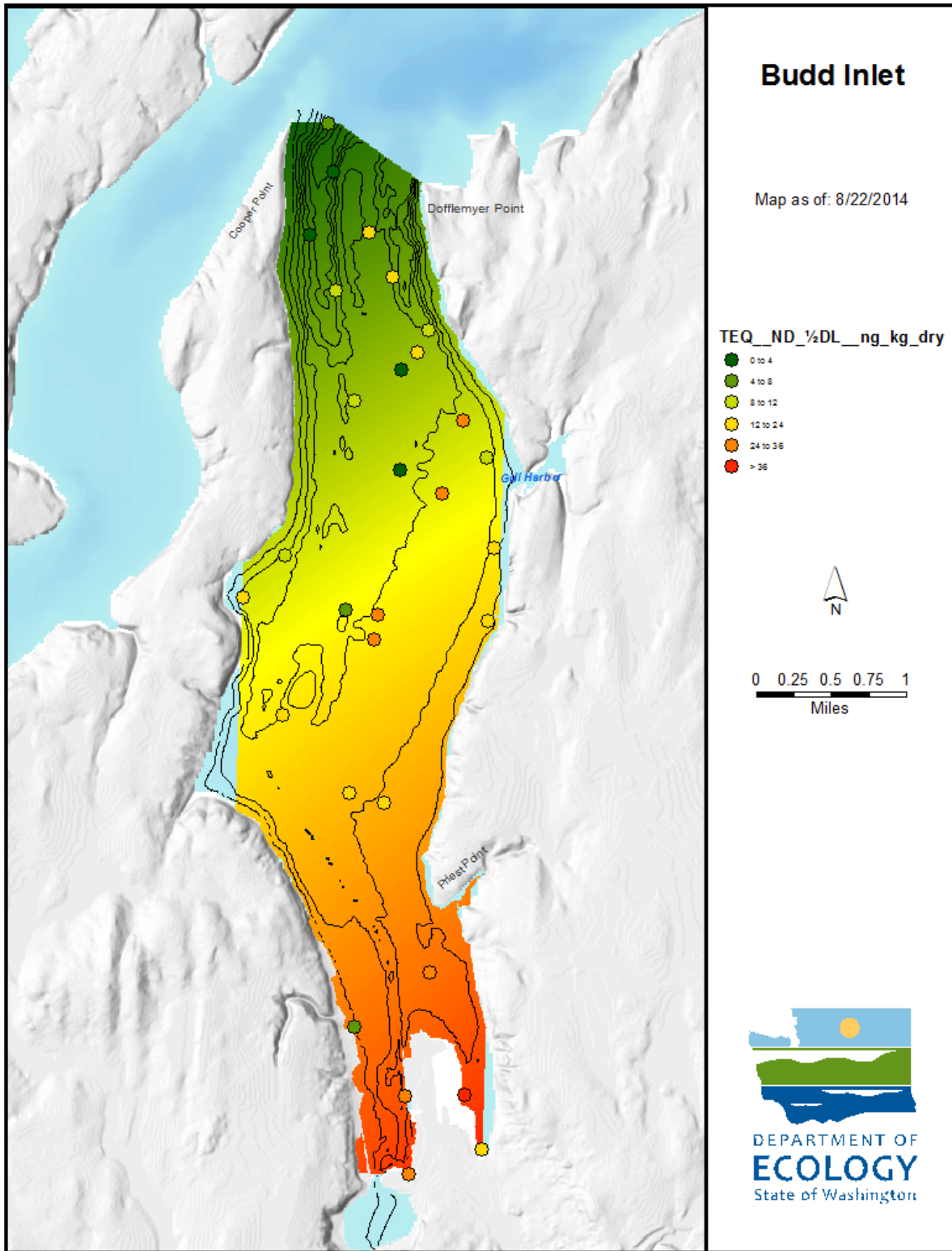


Figure 11. Surface Map of PCDD/F Concentrations Interpolated within Budd Inlet, 2011.

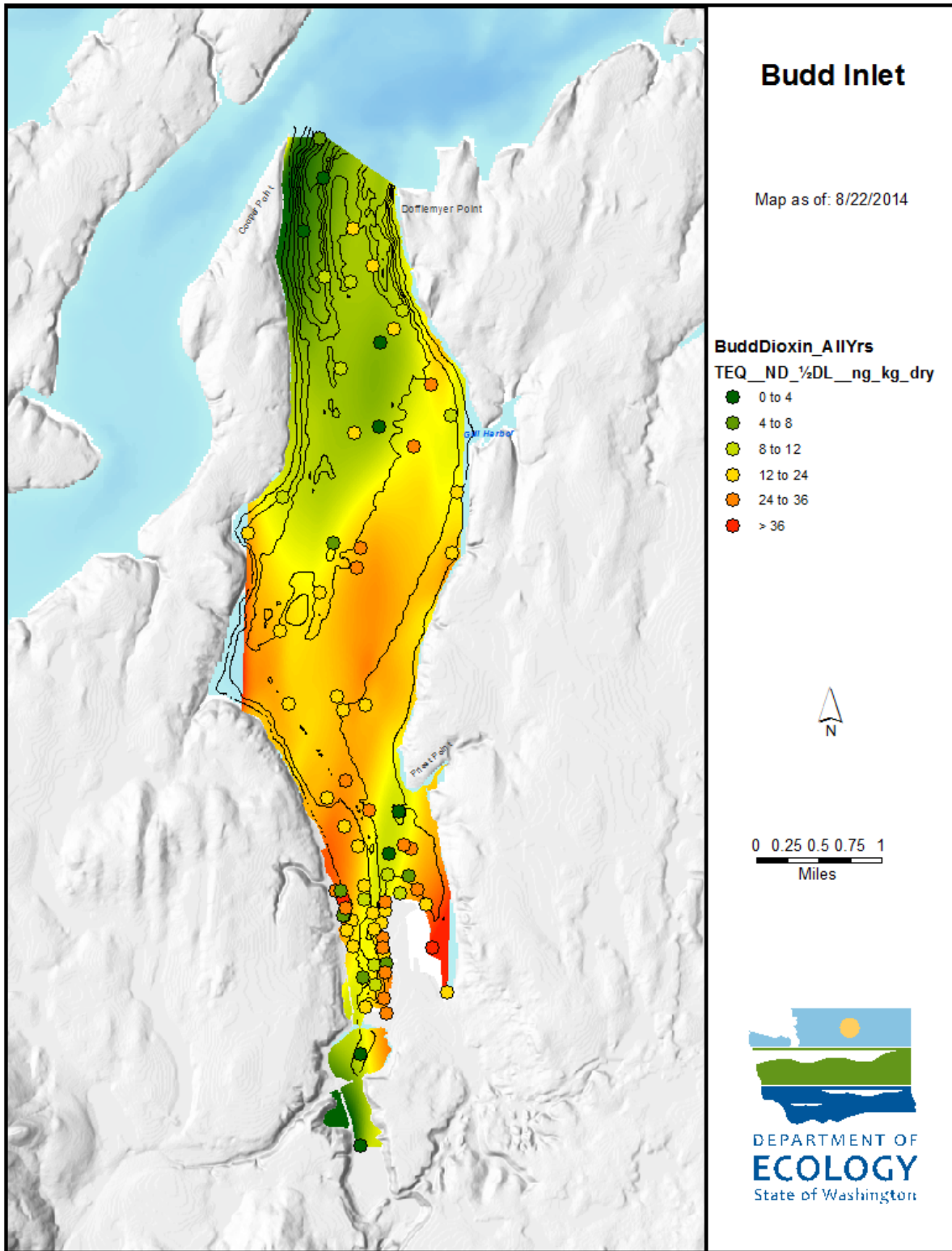


Figure 12. Surface Map of PCDD/F Results for Multiple Studies Interpolated within Budd Inlet.

Sedimentation and resuspension may need to be evaluated for their added affects on PCDD/F concentrations. Ecology (Norton, 2009) determined gross sedimentation rates for Budd Inlet using sediment traps in one location (deepest part of the bay) as 0.7-1.6 g/cm²/yr. Similarly, sedimentation rates estimated from the change in ²¹⁰Pb radionuclide with depth within four core samples collected for the LOTT study (1998) ranged from 0.26 to 2.0 cm/yr. The highest rate was from a core located near the head of Budd Inlet in West Bay, whereas the lowest rate was found in the core taken in an area of higher tidal activity, where the inner inlet main outflow merges with water refluxed from the inflow from the central inlet near Ellis Cove (Figure 9(k)). The two other cores showed intermediate sedimentation rates but was higher in the core near Priest Point (0.84 cm/yr) compared to the core near Gull Harbor (0.64 cm/yr).

PCDD/F concentrations appear to somewhat coincide with levels of sediment accumulation near the head of West Bay and also in East Bay, as higher levels of PCDD/Fs have been found in these locations. Varied PCDD/F concentrations remain unclear for the area of reflux north of the bays, probably due to variations in the circulation pattern.

Concentrations within the top sediments generally are indicative of recent PCDD/F sources unless there are local disturbances to the sediment within the area. Local disturbances could include the circulatory fluxes described above or anthropogenic influences such as vessel or dredging activities. Although determining the role of local disturbances is beyond the scope of this report, resuspension can be discussed briefly.

Sediment traps were used in the LOTT study to measure the flux of material through the water column to the sediments, which includes both fresh material settling for the first time and remixed material that has been resuspended by waves and currents and is resettling. LOTT estimated more than half of the material caught in the sediment traps was derived from resuspension of bottom sediments at all times of the year. Resuspension values ranged from 47% during winter to 88% during summer (LOTT, 1998).

Resuspension from circulation characteristics or local disturbances in Budd Inlet may play a greater role in understanding spatial PCDD/F concentration levels than previously considered. Additionally, the fluxes described here show that establishing a PCDD/F background concentration for Budd Inlet may be more complicated than originally thought.

Results and Puget Sound Background Levels

Currently, Ecology's Toxics Cleanup Program has no numeric Sediment Quality Standard (SQS) or Cleanup Screening Level (CSL) criteria for PCDD/Fs. The OSV Bold Survey (USACE, 2009) identified a TEQ of 4.0 ng/kg for a PCDD/F background level in Puget Sound sediments.

Most results from this 2011 study and previous studies combined, as discussed above, were above this level in both Inner and Outer Budd Inlet (Figures 13 and 14).

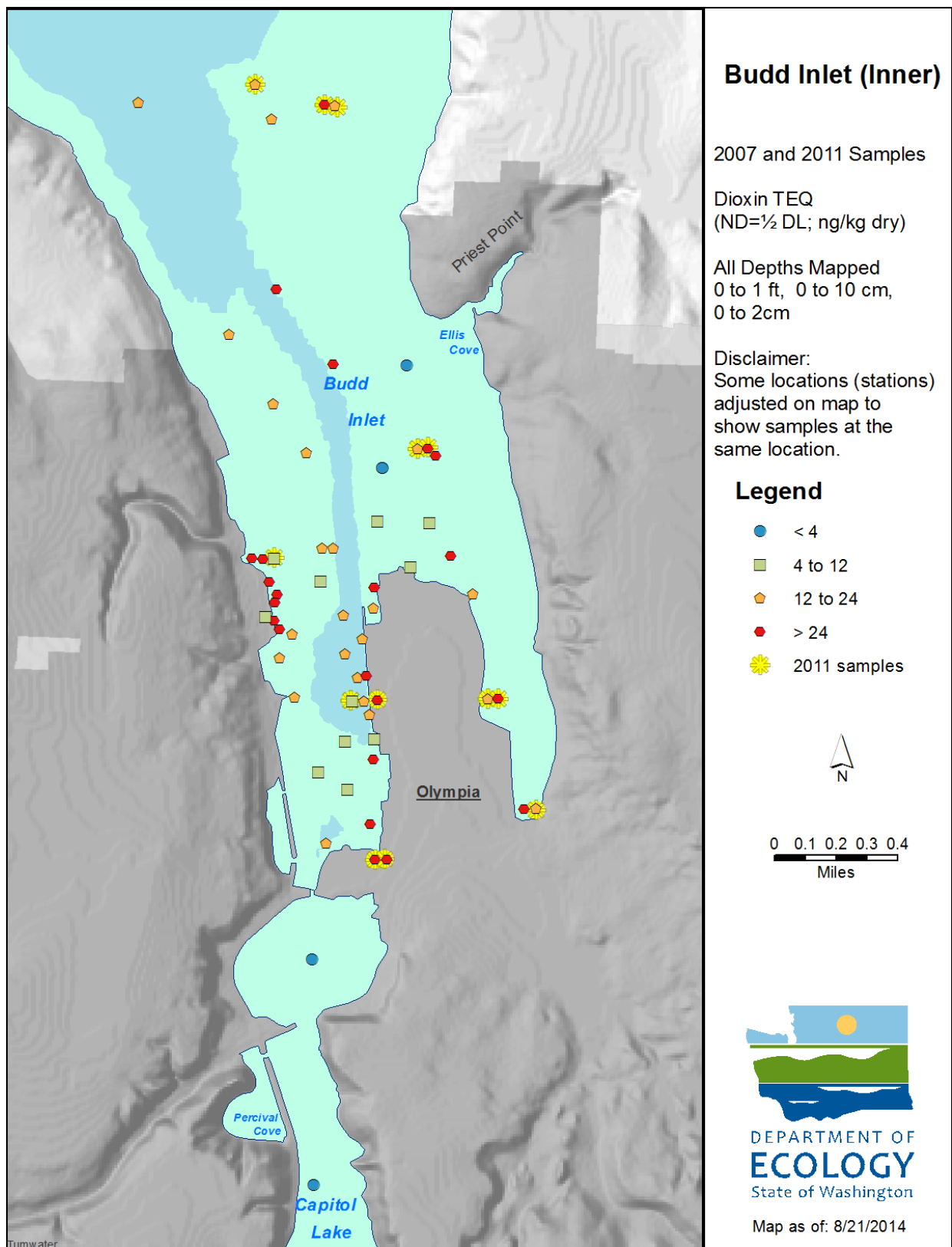


Figure 13. Total TEQ PCDD/F Concentrations from This 2011 Study and Previous Studies (SAIC, 2008 and Ecology, 2007) in Inner Budd Inlet.

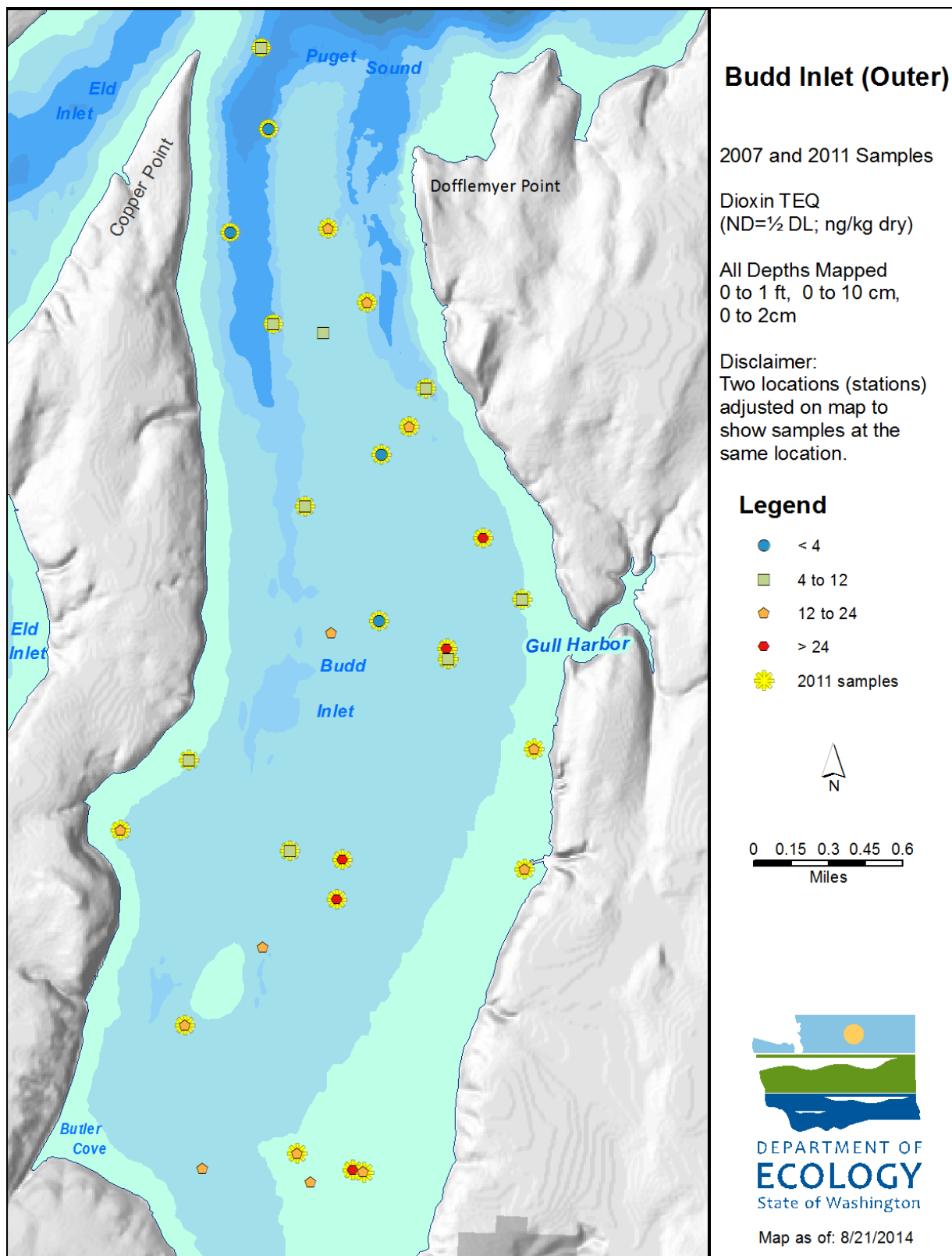


Figure 14. Total TEQ PCDD/F Concentrations from This 2011 Study and Previous Studies (SAIC, 2008 and Ecology, 2007) in Outer Budd Inlet.

Results below 4.0 ng/kg TEQ from this study were located in outer Budd Inlet from Gull Harbor and further north (stations PSUW140, UW41680, BI-43088, and BI-43216). Other results below this level from previous studies were located in Central Budd Inlet or collected within West Bay in areas that were dredged. All lower level results were from samples interspersed among higher level results or from the same sample that contained both lower and higher PCDD/F concentrations varying between the depths analyzed (results below one foot not shown).

Two samples showed lower concentrations compared to the 2007 samples at the same targeted location; BI-S7-0-10 cm at 6.85 ng/kg versus 59.83 ng/kg TEQ, and BI-S30 at 13.3 ng/kg versus 60.29 ng/kg TEQ, for 2011 and 2007, respectively. Although lower, these concentrations were still above 4.0 ng/kg. The difference between the concentrations may be due to several variables. The BI-S7-0-10 cm sample was collected 55 meters east of the target location (mouth of West Bay along the western shore near Hardel) due to rocks prohibiting collection. The BI-S30 sample was collected near the mouth of Moxlie Creek (head of East Bay), where one could expect variability from natural eroding shores and accumulations of sediments in that area. Furthermore, reduced concentrations may be the result of several cleanup efforts since 2007 (PTC, 2010; Beard et al., 2011; Berlin, 2011) and Capitol Lake draw downs, which occurred between December 9, 2009, and March 5, 2010, in an attempt to control invasive New Zealand mudsnails.

Congener Profiles

Congener profiles were used to screen for source identification and to compare the fingerprint of this 2011 study results to the 2007 characterization study by SAIC. The concentration of each individual congener (not adjusted to TEQ) was divided by the sum of the total PCDD/F concentration in a given sample. The resulting profile illustrates the relative amount of each congener observed in each sample.

Figures 15 and 16 show the PCDD/F congener profiles for Budd Inlet sediment analysis at two depths (0-10 cm and 0-2 cm). Mean values are indicated by a line bar within the sample data points for each congener.

The PCDD/F profiles from both depths are nearly identical. The OCDD congener dominated the profile at a much higher percent concentration (around 75%-90%). In the absence of OCDD, 1,2,3,4,6,7,8,-HpCDD dominates the congener profile ranging between <40% to >60%.

These profiles match fairly closely to EPA's profile for pentachlorophenol (PCP) used in treating wood (Cleverly et al., 1997) (Figure 17). PCP contains dioxin/furan congeners as impurities.

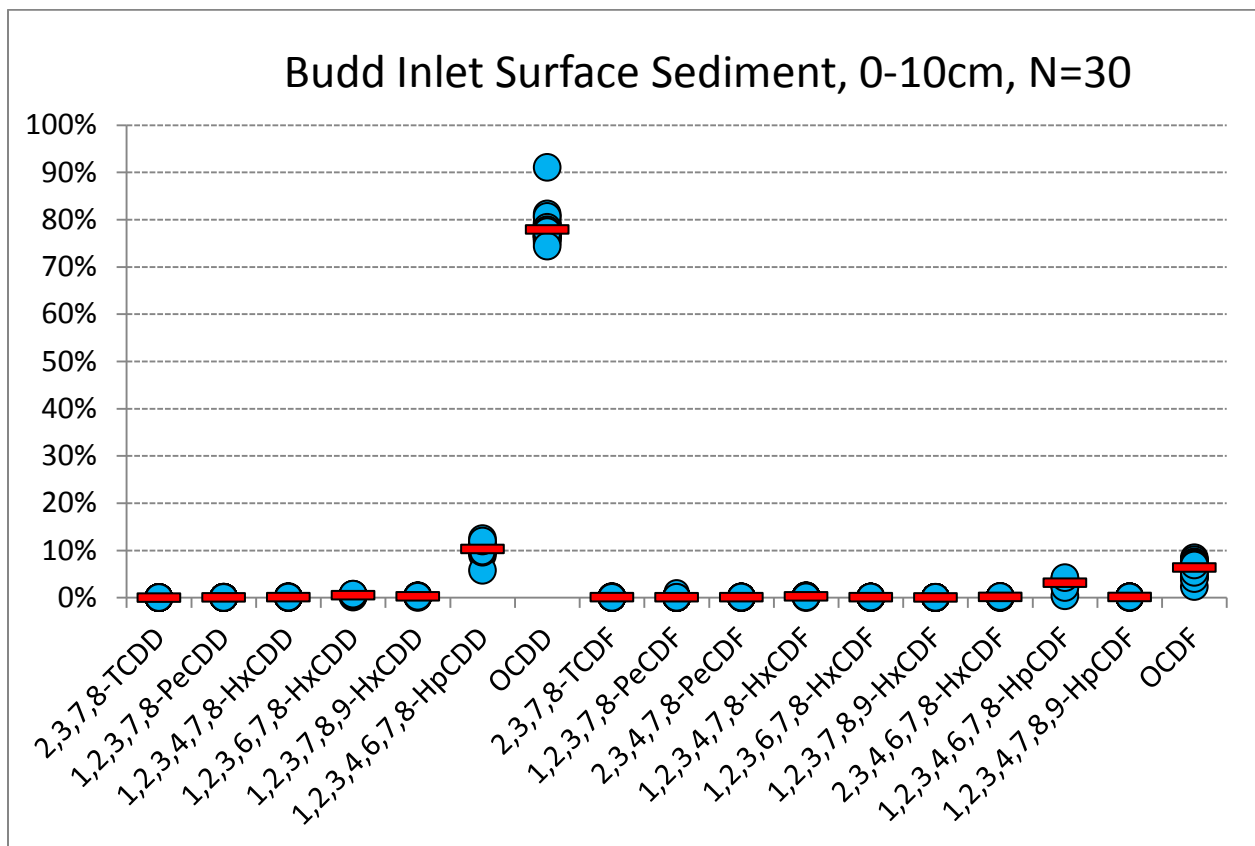


Figure 15. Budd Inlet Surface Sediment Profile, 0-10 cm. (N=30).

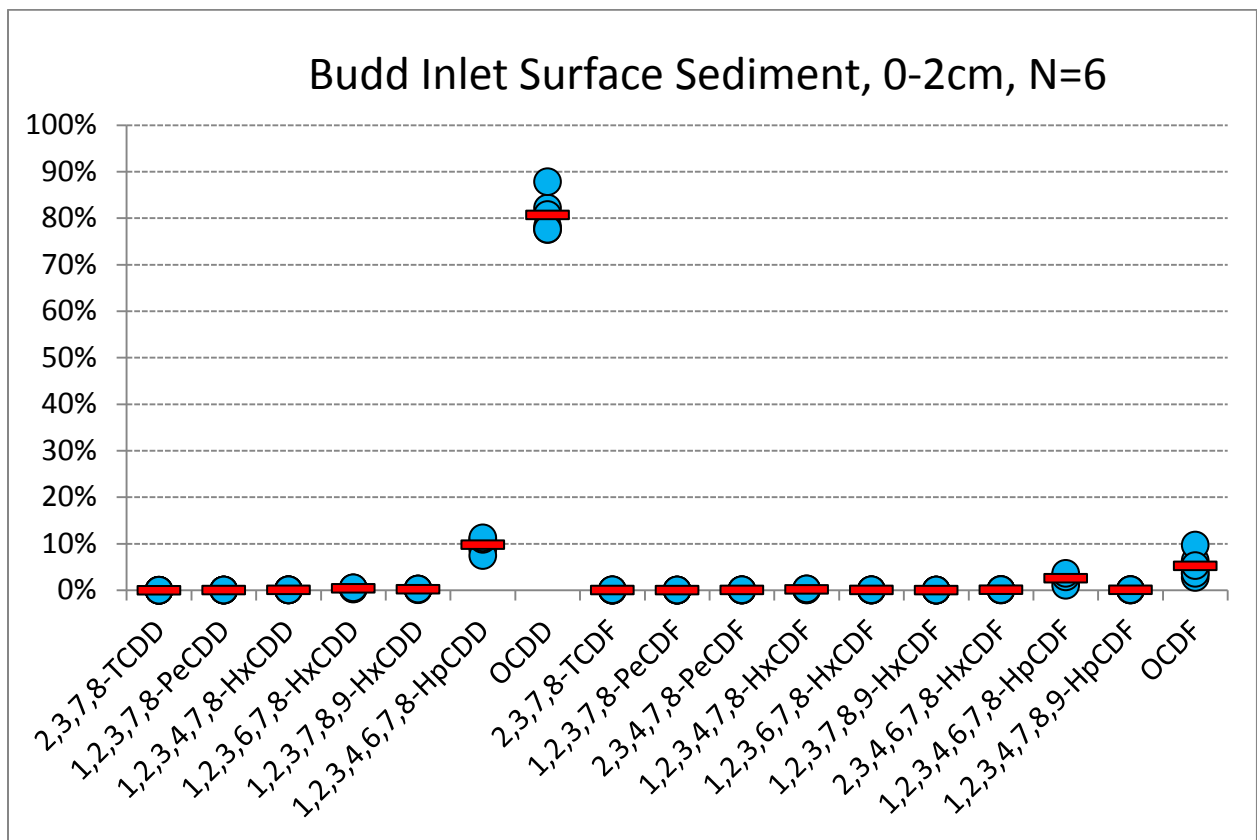


Figure 16. Budd Inlet Surface Sediment Profile, 0-2 cm. (N=6).

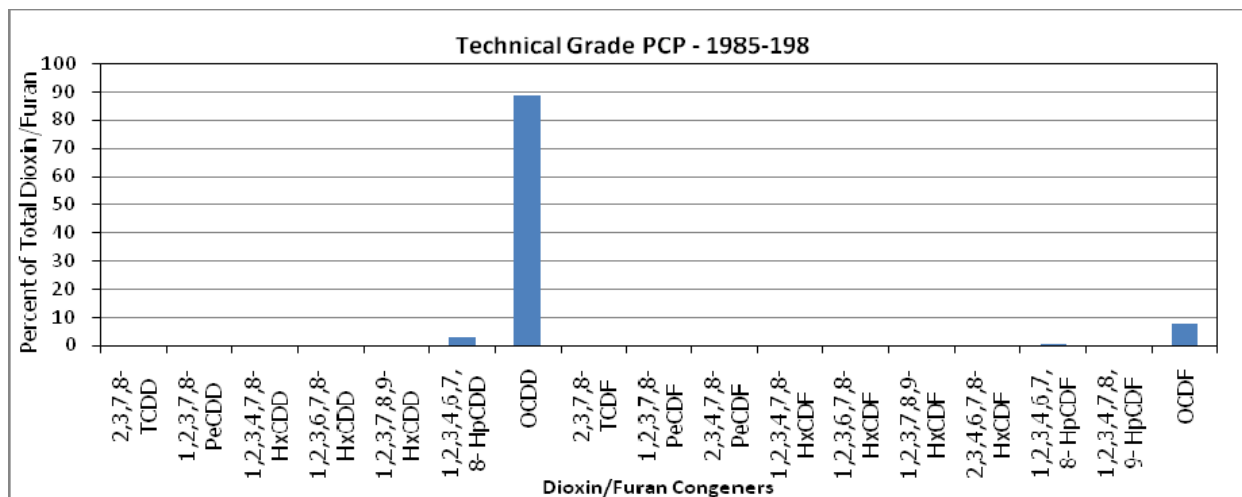


Figure 17. Technical Grade Pentachlorophenol Profile (taken from Herrera, 2010).

The same profile was seen in results from the 2007 characterization study of Budd Inlet. SAIC (2008) points to the Cascade Pole wood treatment site as the source of contamination, but notes that all wood treatment facilities present could contribute to contamination, and to narrow down the source to a single facility would be difficult.

This PCDD/F profile has been found throughout Puget Sound (Herrera, 2010). (See discussion for congener profiles for Oakland Bay below which includes congener comparison to black liquor recovery boiler emissions as well as for PCP.) Because this profile appears to be a dominant trend throughout Puget Sound, it may be advantageous to plot the TEQ-adjusted profiles from future, more extensive data sets to help identify potential PCDD/F sources.

Conclusions

Budd Inlet exhibits a variety of dynamic variables that influence PCDD/F concentrations within sediment samples. Grain size was predominantly fines, and the highest TOC (>3.5%) was found in lower Budd Inlet or where organic debris may be located. The highest PCDD/F TEQs were found also in Inner Budd Inlet, with an overall average of 24.7 ng/kg. Mixed PCDD/F results were found in the few (six) locations where the upper portion (0-2 cm) of the sample was compared to the 0-10 cm results, although the highest concentration for this study was found in the upper 2 cm portion (inner and central areas). This variability makes it unclear whether there has been change over time, but two 2011 results taken from the same general location as in 2007 had lower concentrations, which may reflect cleaner sediment because of several cleanup projects or Capital Lake drawdown events previous to 2011.

Background PCDD/F concentrations were difficult to determine because of high variability found in the samples throughout the bay. Budd Inlet's counterclockwise circulation, with over half the water refluxing in a weak gyre, distributes sediments to the lowest energy areas of the bay. It is unknown the role local disturbances may play in sediment resuspension. Since it was found that more than half of the sediment is resuspended at all times of the year (LOTT, 1998), the possibilities of elevated PCDD/F concentrations from known areas of contamination could be a function of hydraulic circulation and energy. This could be, in part, why the upper portion (0-2 cm) of samples continues to have elevated PCDD/F concentrations.

A decreasing PCDD/F concentration south-to-north trend was observed through spatial analysis. A less clear trend was noted increasing from west to east. Results from samples with high levels of PCDD/Fs from areas known for contamination masked the findings by weighting the model towards those areas.

Further investigating and characterizing sediment deposition and resuspension would help define areas where fresh versus older sediment is deposited. Low levels of PCDD/F concentrations would likely be found in areas where resuspended sediment is low, assuming no current source of contamination exists. These areas appear to be favoring the northwest portion of the bay.

Four samples in this study were below the TEQ concentration of 4.0 ng/kg as identified by the OSV Bold Survey (USACE, 2009). These samples were located in northern Outer Budd Inlet.

Profiles of PCDD/F congeners in this 2011 study matched previous investigations identifying Technical Grade Pentachlorophenol used in treating wood. Although Cascade Pole has been identified as one source of PCDD/F contamination, it is known that there were other historic sources to Budd Inlet, such as hog fuel boilers found previously along the shoreline at the Hardel lumber yard site.

Oakland Bay

Conventional Parameters

Ten sediment samples collected (each at 0-2 cm and 2-10 cm depths at five stations) from Oakland Bay contained a mix of sand (ranging from 9.5% - 68%) and fines (ranging from 31% - 90%) (Table 4). These results are consistent with the Oakland Bay Sediment Characterization Study (Herrera, 2010) which collected over 30 cores and grain size samples within the bay and Hammersley Inlet and found the distribution of sediment varies from coarse to fine along the direction of transport. Coarser material was found at the creek deltas, with finer material moving to the deeper and less hydraulic energetic portions of the bay.

Table 4. Oakland Bay Grain Size and TOC (N=10).

Percent (%)	Minimum	Mean	Maximum
Gravel	0.1	0.9	2.5
Sands	9.5	41	68
Silts	24	38	52
Clays	7.3	21	38
Fines	31	59	90
TOC	2.5	3.0	3.3

Samples in this study that contained coarser material (i.e., sand) were collected in Shelton Harbor and north of Bayshore Point (Figures 18 and 19). Goldsborough and Shelton Creeks, located in the middle and north areas of Shelton Harbor respectively, provide hydraulic energetic transport, distributing the more fine-grain sediments into the middle of the harbor and possibly further out in the bay, with Goldsborough Creek transporting the majority of the sediment input (Herrera, 2010).

Near Bayshore Point there is a deep hole maintained by intermittent intense flow, which deposits coarse materials including shells transported via bedload (transport that occurs near the bed) (Herrera, 2010). Heavy material is trapped, but fine grains are not deposited because the currents in the areas are too strong.

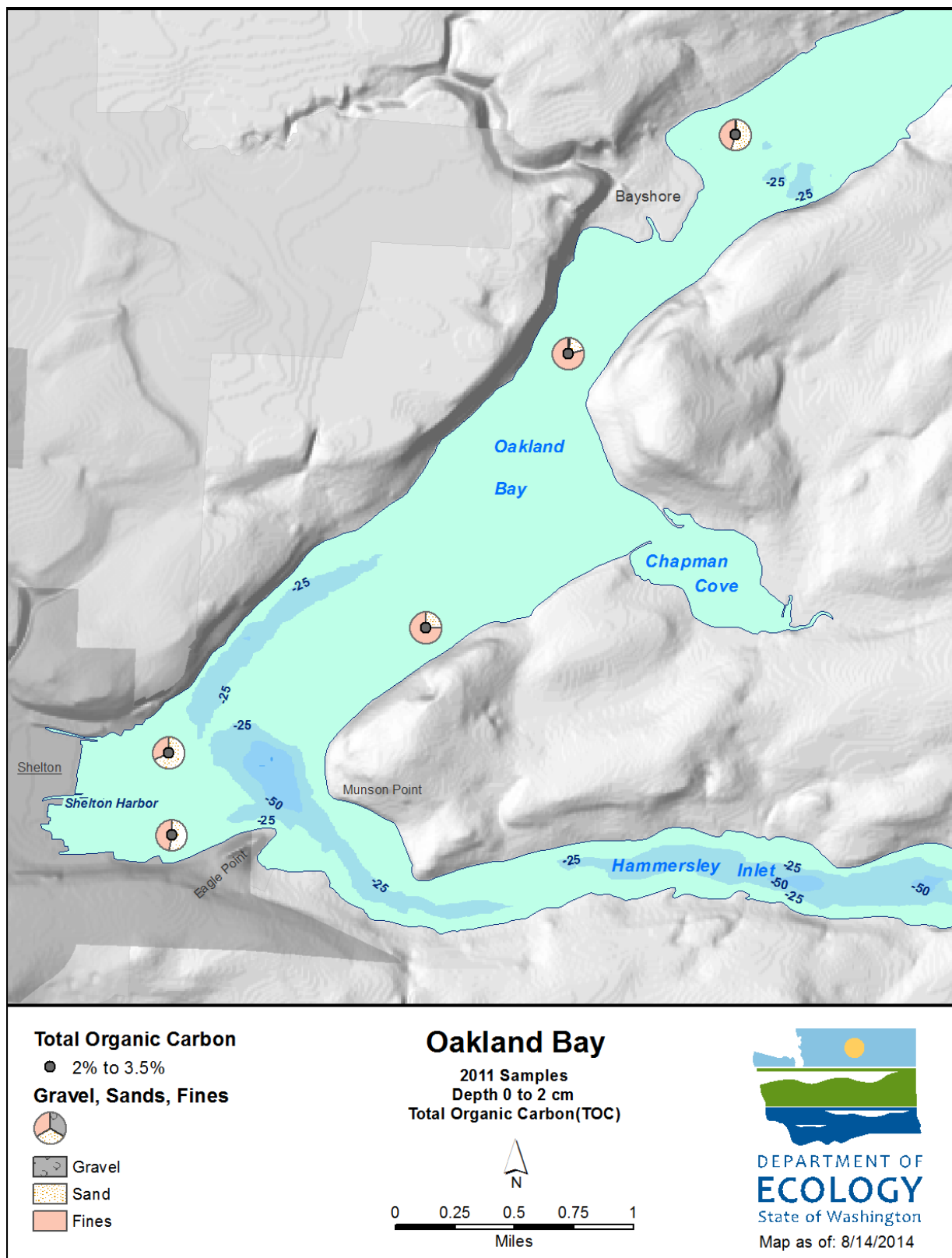


Figure 18. Percent Grain Size and TOC in Surface Sediments (0-2 cm) of Oakland Bay, 2011.

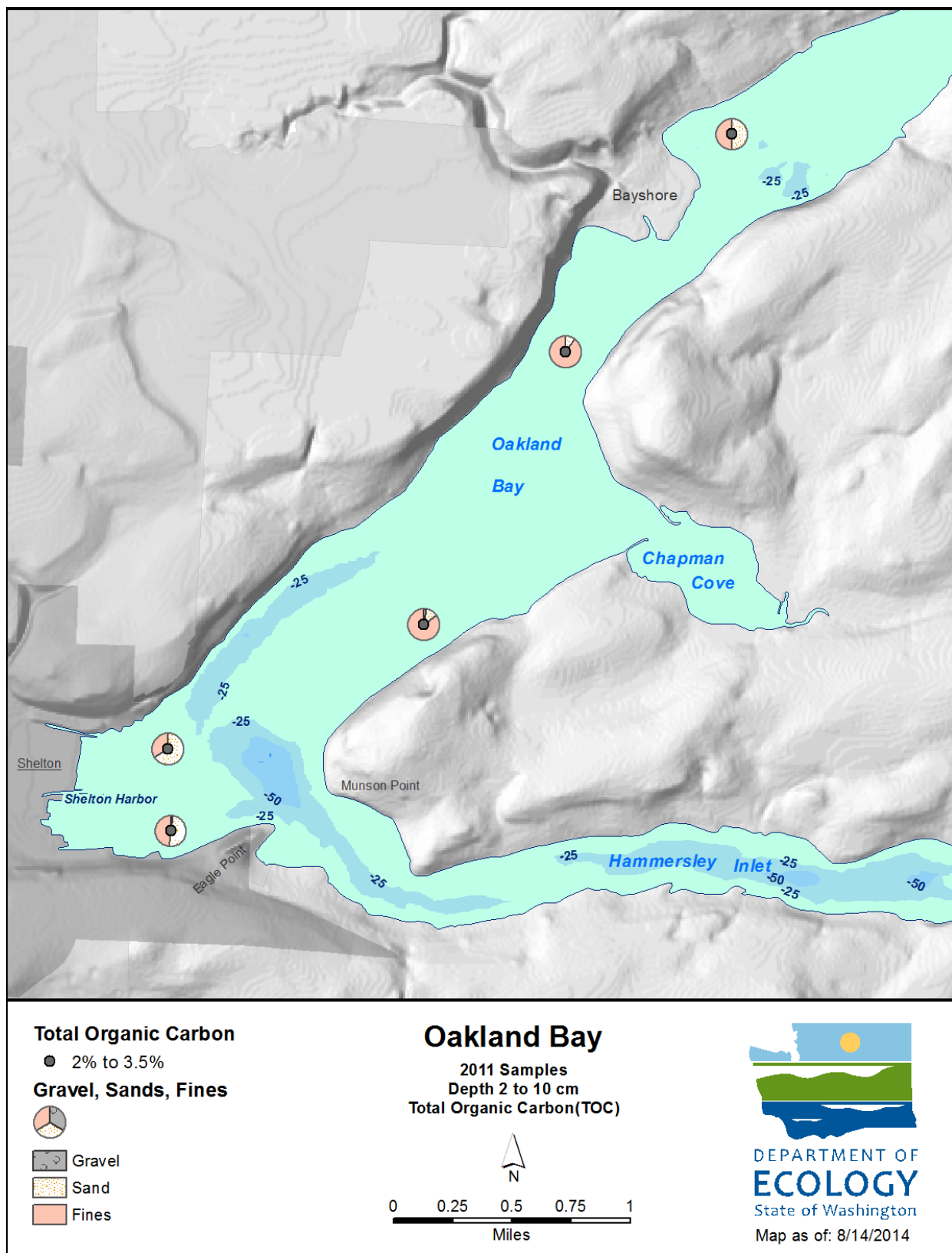


Figure 19. Percent Grain Size and TOC in Surface Sediments (2-10 cm) of Oakland Bay, 2011.

Figure 20 illustrates the difference between the upper portion (0-2 cm) and a lower portion (2-10 cm) of the Oakland Bay sediment samples collected for this study.

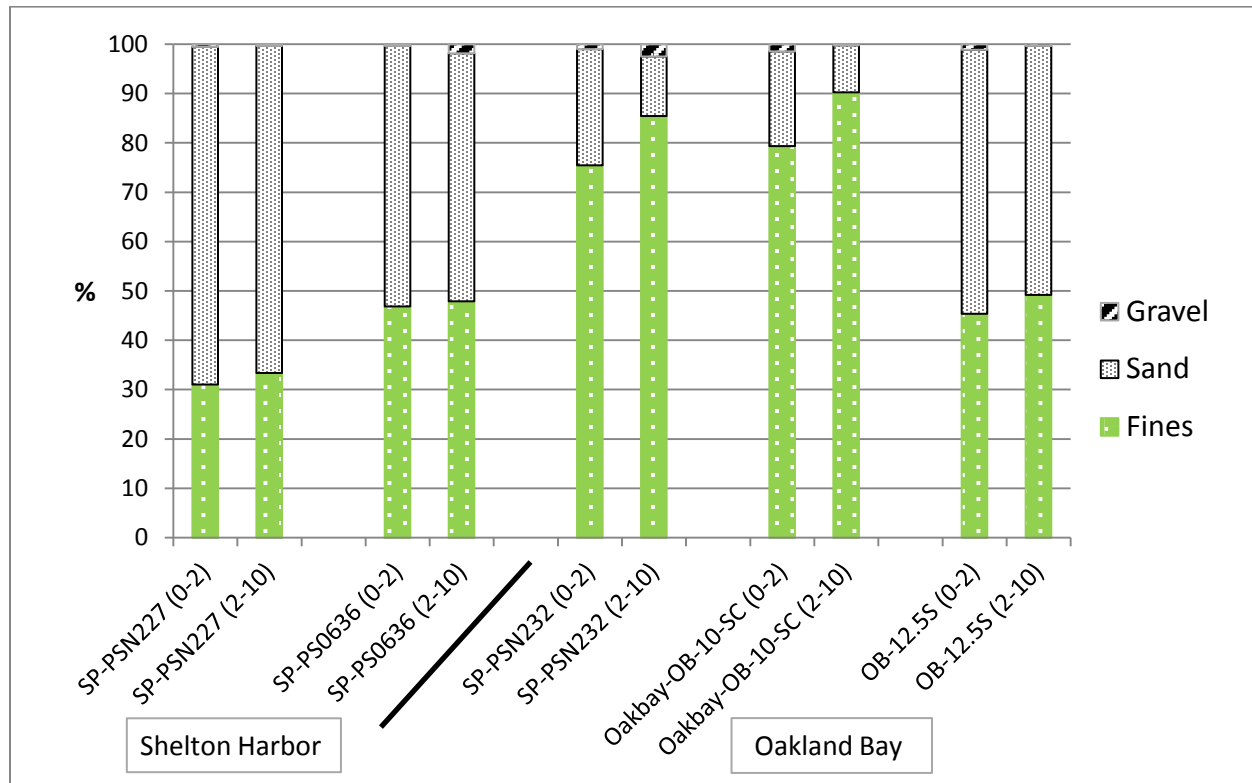


Figure 20. Oakland Bay Grain Size Compared at Different Depths, 2011.

Two of the five samples (SP-PSN232 and Oakbay-OB-10-SC) contained predominantly fines (>70%). These samples were collected within the middle portion of the bay and represent most of the bay where hydraulic energy transport is low. The other three samples (SP-PSN227, PS-PS0636, and OB-12.5S) had over 50% sand and were collected in more energetic areas such as within Shelton Harbor and near Bayshore Point as described above. Very little gravel was found within the top 10 centimeters of this study's samples, but Herrera (2010) found alluvial deposits of sand and gravel overlying fine-grain marine deposits, generally within areas of high hydraulic energy as described above.

Overall, Oakland Bay has a broad distribution of fine material. Nearly all the sediment deposited within Oakland Bay stays confined within the bay and reasonably close to where it first enters the marine waters (Herrera, 2010; Albertson, 2004).

TOC content in these samples was all within the narrow range of 2.5% to 3.3% and averaged 3.0% (Figures 18 and 19). The highest TOC content was found in the harbor area. The 2008 characterization study found that, in general, TOC values above 4% were found along the shoreline in the former pond saw area throughout the southwest portion of Shelton Harbor, which also corresponded to locations with total fines greater than 45% (Herrera, 2010). In this

2011 study, no TOC results were above 4% in the five samples analyzed, and the sample (SP-PSN227) with the highest TOC had the lowest percent fines (<35%).

TOC percentage was similar when compared at different depths, 0-2 cm and 2-10 cm (Figure 21). TOC averaged 3.1% for the top 2 cm compared to 2.8% for the 2-10 cm.

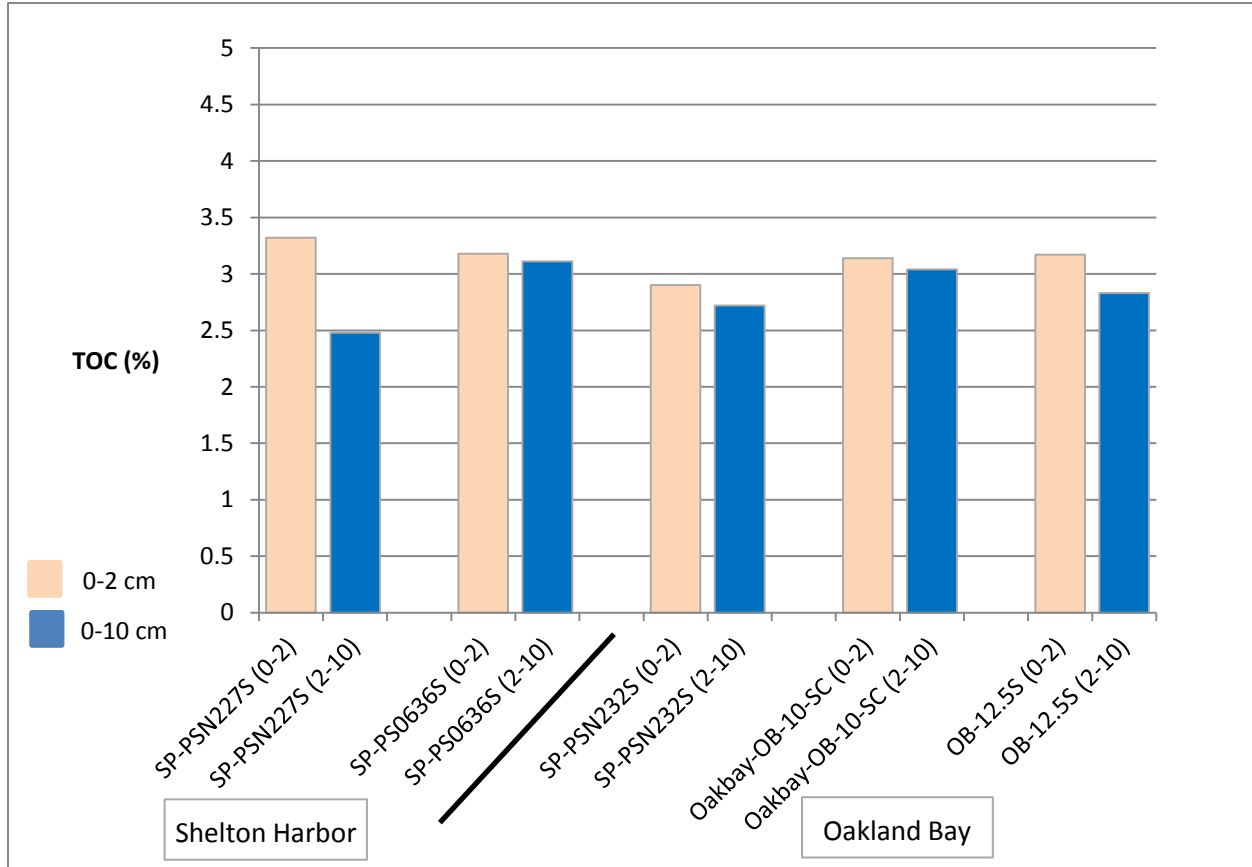


Figure 21. Oakland Bay TOC Compared at Different Depths, 2011.

TOC and fines were not much different among samples in this study, probably because of the small sample size. Herrera (2010) found TOC was generally <4% in Oakland Bay and suggests that TOC may be elevated in areas with organic debris such as wood waste. Also in agreement, Ecology’s South Puget Sound study reported fine-grained sediments and highest TOC contents located in the terminal inlets (Partridge et al., 2014b).

PCDD/Fs

PCDD/Fs were detected in all Oakland Bay sediment samples (Table 5). Congener 2,3,7,8-TCDD was detected in 7 out of the 10 samples and ranged from 0.269 ng/kg to 1.61 ng/kg. Of the detected results, the average 2,3,7,8-TCDD concentration was 1.41 ng/kg.

Table 5. Oakland Bay PCDD/Fs TEQs (N=10).

	Oakland Bay	
	Shelton Harbor	Central/Outer
Number of Samples	4	6
Mean (ng/kg)	18.8	31.7
Median (ng/kg)	17.7	36.2
Minimum (ng/kg)	4.39	2.09
Maximum (ng/kg)	35.5	55.2
Maximum Location	SP-PS0636 (1106045-36)	Oakbay-OB-10-SC (1106045-37)

TEQs for these samples ranged from 2.09 to 55.2 ng/kg, with a mean TEQ of 26.5 ng/kg and a median TEQ of 29.6 ng/kg for all samples. The highest TEQs were found in the middle portion of the bay, in the two samples that contained predominantly fines and where hydraulic energy is low (Oakbay-OB-10-SC and SP-PSN232) (Figure 22). PCDD/F results for each sample are listed in Appendix C.

No pattern was evident in PCDD/Fs concentrations when comparing 0-2 cm (recent) sediments with 2-10 cm (historic) sediments. Testing was performed using a t-test and nonparametric Wilcoxon-Whitney-Mann test, $p < 0.05$. Two samples had higher concentrations, and three samples had lower concentrations in the upper portions of the samples. Most samples were relatively close in PCDD/F TEQ concentration between the upper and lower portions. The small sample size limited the statistical power of the comparison tests.

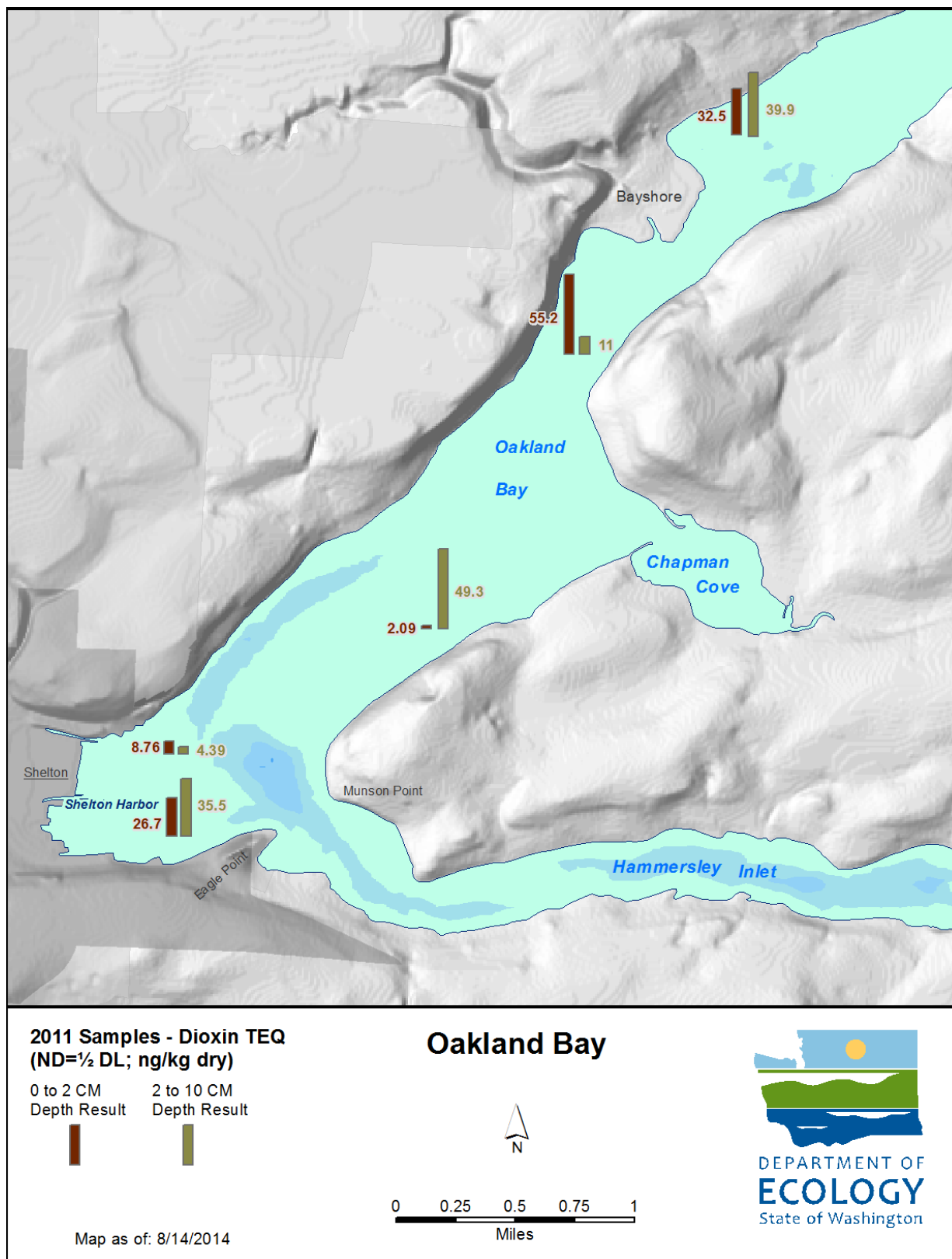


Figure 22. Distribution of PCDD/Fs Expressed as Total TEQ in Surface Sediments of Oakland Bay, 2011.

Discussion

Samples taken in Oakland Bay during 2011 showed mixed results for deciphering whether there has been a change in surface sediment concentrations for PCDD/F. The small sample size (five locations) limited the probability of seeing an effective difference between the upper (0-2 cm) and lower (2-10 cm) portions of each sample unless the differences had been large and uniform. Understanding the bay's hydraulic energy system in light of current and historical land uses may help decipher these results.

PCDD/F Results and Bay Hydraulics

Although uncertain, the different results between sample locations may be explained, in part, by the location dynamics. Hydraulics can affect the transport of sediments around the bay, and local events may explain vertical differences.

Dense seawater comes into Oakland Bay in local, high-velocity tides, flowing along a deep channel bottom from Hammersley Inlet then turning north along the western edge of lower Oakland Bay. Less dense freshwater from creeks enter the bay transporting sediment. Although some mixing occurs, the less dense freshwater tends not to mix deeply with the marine water. An effect of this is that the heavier grained sediment settles out closer to the mouths of the creeks, forming large deltas, whereas the fine-grain sediments travel further out in the bay. Some of the fine grain and colloidal fractions, but a small fraction of the total sediment load, will move out of the bay near the surface (Albertson, 2004; Herrera, 2010).

Herrera (2010) found substantial creek sediment input to Shelton Harbor. The creek sediment source could be a cleaner source, but only if confirmed within the creek itself. A recent study found PCDD/Fs measured in sediment from three streams – Shelton, Goldsborough, and Johns Creeks located in north Shelton Harbor, middle Shelton Harbor, and Bay Shore area, respectively – were very low (generally below 4.0 ng/kg TEQ) (Coots, 2013). However, two soil samples taken from a large ash mound on the bank of Shelton Creek had TEQ concentrations comparable to those reported here (21.3 and 41.1 ng/kg). Downstream of the ash mound, Shelton Creek had somewhat elevated PCDD/Fs in sediments (although well below the highest levels found throughout the bay). Based on this information, it is possible that the mound could be a potential source of PCDD/Fs, particularly during run-off periods and higher flow.

In light of the above information, one should not rule out the possibility of deposition of fines moving further out in the bay due to higher hydraulic energy found near the creeks. Core samples indicated high rates of accumulation within central Oakland Bay, implying that sediment does migrate from Shelton Harbor (Herrera, 2010). This could help explain the elevated levels found further out in the bay.

Local events near some of the sampling locations for this study may give some explanation of the mixed differences found between samples in the vertical deposition of PCDD/Fs concentrations. Two of the samples outside of Shelton Harbor may have possibly undergone local disturbances. Herrera found Bayshore Point an area of transition between disturbed and undisturbed sedimentation when analyzing core samples. Sample OB-12.5S for this study was

collected in this area. PCDD/Fs concentration results between the upper and lower portion of the sample may be within the variability possible for this area.

Current seepage and landslide activity (in 2002) (Herrera, 2010; Ecology, 2014) in the area near sample SP-PSN232 may mask the results by overlaying sediment with cleaner soil from the disturbed bank. This sample had the largest difference between the upper and lower portions of the sediment (2.09 and 49.3 ng/kg TEQ, respectively).

Only sample Oakbay-OB-10-SC appeared to be located in an area without local disturbances or high hydraulic energy (below Bay Shore in the central portion of the bay), which coincides with high fines and elevated PCDD/F in the upper portion of the sample (55.2 ng/kg TEQ). Furthermore, the concentration of 55.2 ng/kg in the upper portion (0-2 cm) of this sample was similar to the result of 53.6 ng/kg TEQ collected in the same location (0-10 cm) in 2008. The concentration in the lower portion (2-10 cm) of the 2011 sample was much lower (11.0 ng/kg TEQ).

The two samples from the inner harbor area showed lower results. Goldsborough Creek draining into the harbor area contributes substantially to the sediment deposition found in the bay and may explain these lower levels of PCDD/F.

Results and Puget Sound Background Levels

Currently Ecology's Toxic's Cleanup Program has no numeric Sediment Quality Standard (SQS) or Cleanup Screening Level (CSL) criteria for PCDD/Fs. The OSV Bold Survey (USACE, 2009) identified a TEQ of 4.0 ng/kg for a suggested PCDD/F background level in Puget Sound sediments. As reported above, all results in this 2011 study for Oakland Bay were above this level except for SP-PSN232 in the upper portion (0-2 cm) of the sample, which was at 2.09 ng/kg TEQ. This may indicate cleaner deposition, which is possible since this site is near a bank that is failing between Munson Point and Chapman Cove. The sloughing bank could be distributing cleaner soil into the bay system.

One sample (OB-10-SC) had higher concentrations at 55.2 ng/kg TEQ in the top two centimeters compared to the lower depth (11.0 ng/kg TEQ).

Overall, PCDD/Fs continue to be present in Oakland Bay sediments above acceptable levels. Figure 23 shows all dioxin results from this study, along with results from the Herrera study.

Herrera (2010) reported PCDD/Fs ranging from 1 to 175 ng/kg TEQ, with the mean highest in Shelton Harbor (42.8 ng/kg TEQ) and the mean for Oakland Bay of 32.1 ng/kg TEQ. Both this study and the Herrera study show that the continued presence of dioxin in surface sediments indicates that there is either a continuing source of dioxin or that mixing of deeper with shallower sediments has occurred through human or natural processes.

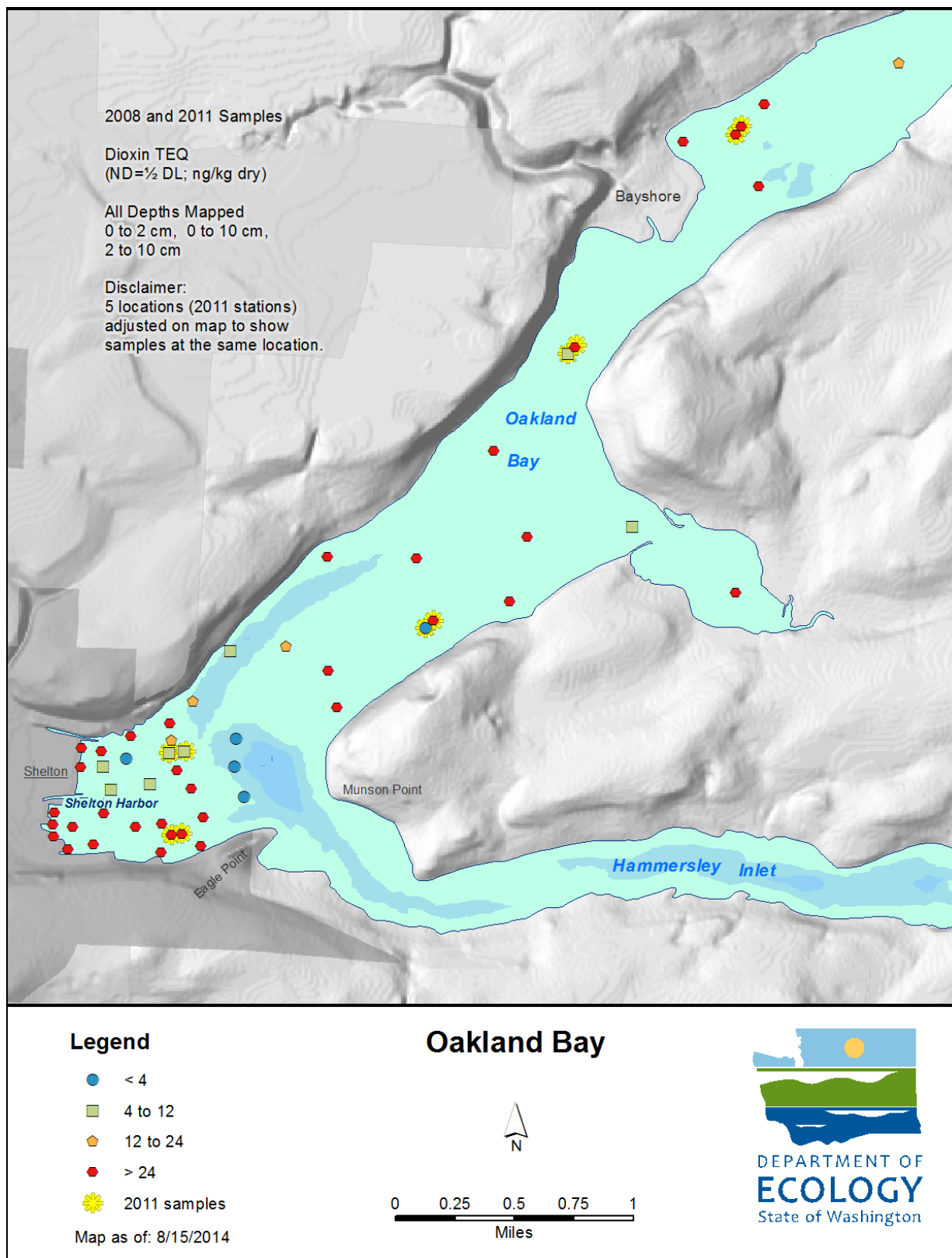


Figure 23. TEQ PCDD/F Concentrations from This 2011 Study and the Herrera Study (Herrera, 2010) in Oakland Bay.

Congener profiles

Congener profiles were used to screen for source identification and to compare the fingerprint of this 2011 study results to the 2008 characterization study by Herrera. The concentration of each individual congener (not adjusted to TEQ) was divided by the sum of the total PCDD/F concentration in a given sample. The resulting profile illustrates the relative amount of each congener observed in the each sample. TEQ-adjusted profiles were not compared in this study but may be advantageous to plot from future, more extensive data sets to help identify potential sources.

Figures 24 and 25 show the PCDD/F congener profiles for Oakland Bay sediment analysis at two depths (0-2 and 2-10 cm). Mean values are indicated by a line bar within the sample data points for each congener.

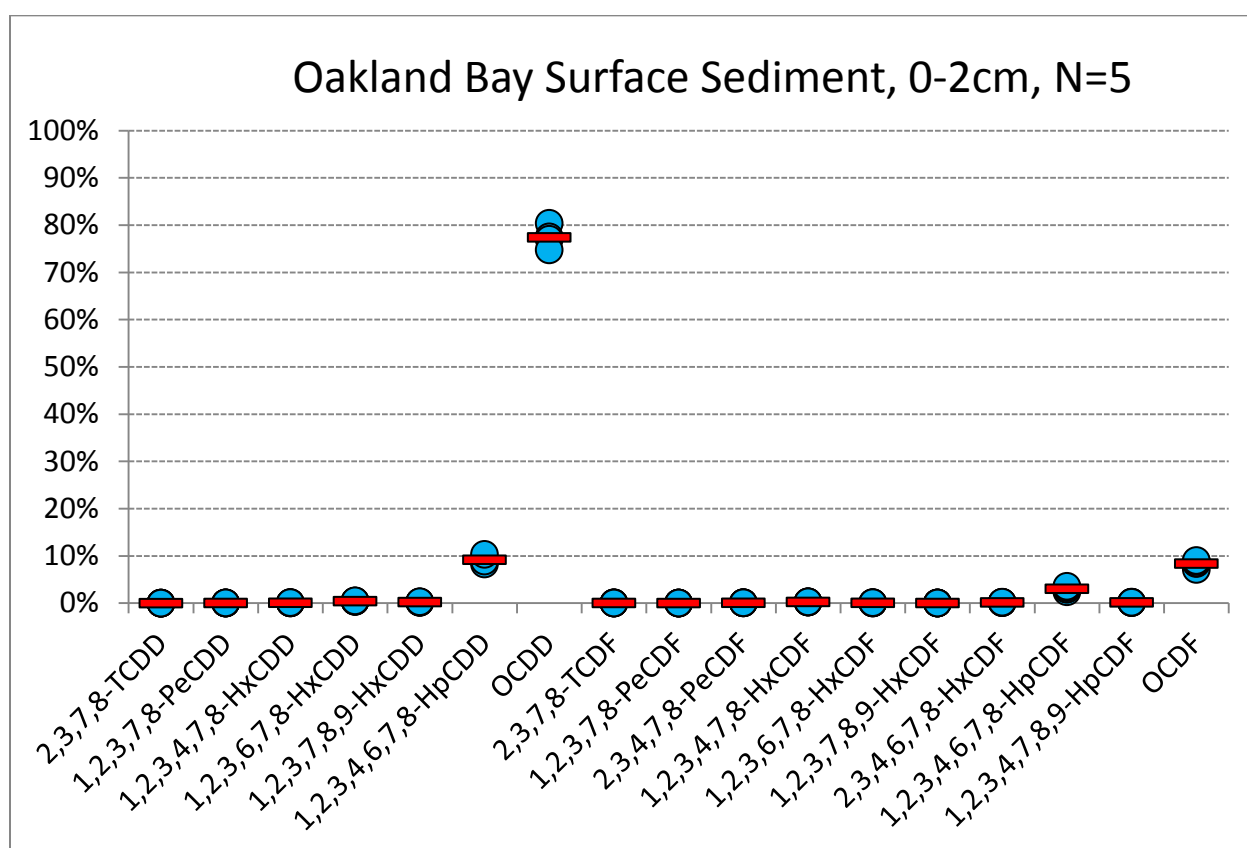


Figure 24. Oakland Bay Surface Sediment Profile, 0-2 cm. (N=5).

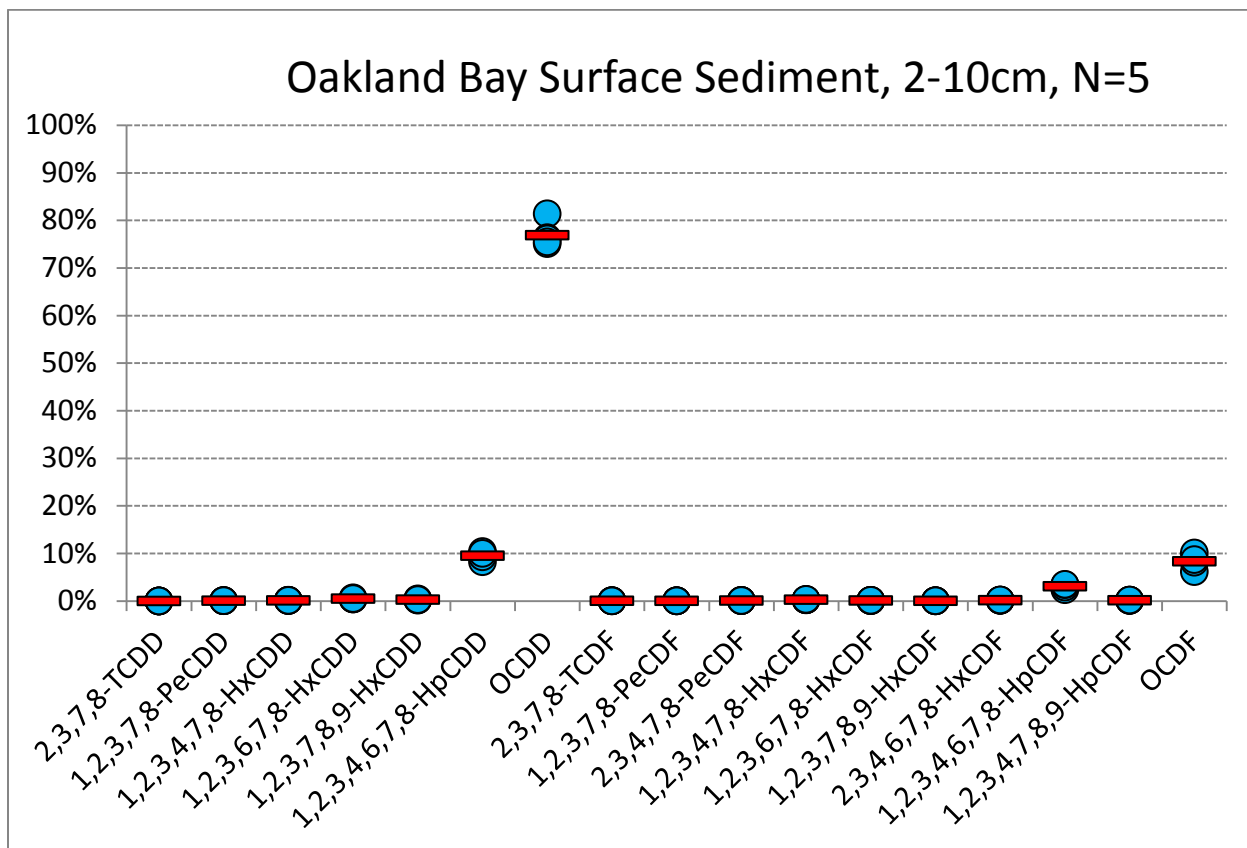


Figure 25. Oakland Bay Surface Sediment Profile, 2-10 cm. (N=5).

The PCDD/F profiles from both depths appear identical. The OCDD congener dominated the profile at a much higher percent concentration (around 75%-80%). In the absence of OCDD, 1,2,3,4,6,7,8,-HpCDD dominates the congener profile, ranging from <40% to >60%.

These profiles match profiles found in the characterization study of Oakland Bay (Figure 26). Herrera (2010) compared four sub-areas within Oakland Bay (central and outer portion of Oakland Bay, Shelton Harbor, Hammersley Inlet, and reference stations). The results of the visual profile indicated that the source of PCDD/Fs were consistent throughout Oakland Bay, including the reference areas, although concentrations in the reference samples were significantly lower than in Oakland Bay.

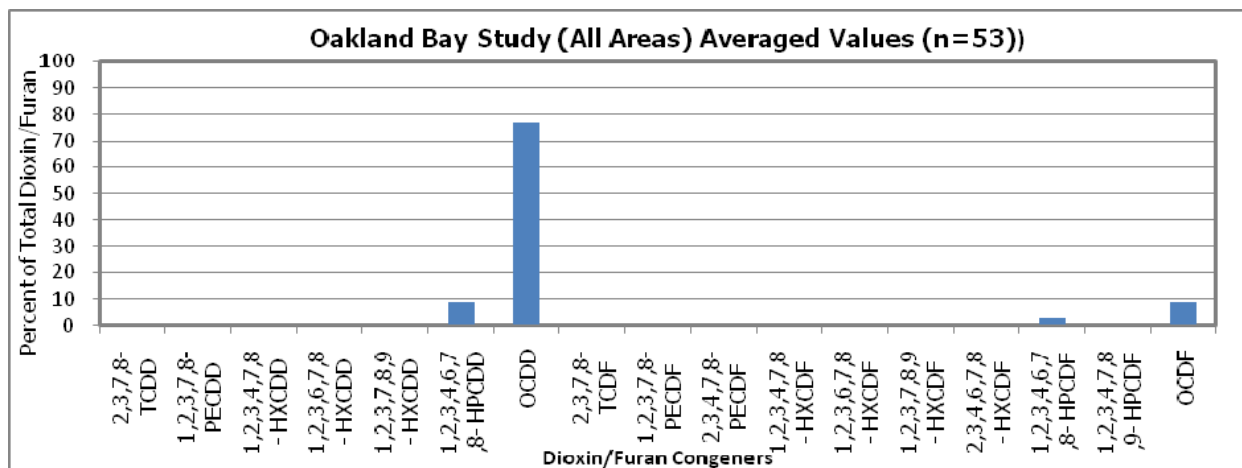


Figure 26. Oakland Bay Study Sediment PCDD/F Profile (taken from Herrera, 2010).

Data from Goose Lake and the OSV Bold Survey (USACE, 2009) background study were also compared by Herrera. The Goose Lake congener profile was similar, but did indicate greater variability than profiles of Oakland Bay (Herrera, 2010). Likewise, the congener profile for the Puget Sound background study (OSV Bold Survey) was very similar, with OCDD contributing the greatest amount to the sum total of PCDD/Fs (70% to 80%) and 1,2,3,4,6,7,8-HpCDD (around 10%).

Although these results match EPA’s profile for technical grade PCP (Figure 19), there are other similar profiles. Citing information from the extensive screening by Herrera, five EPA congener profiles were similar. These included technical grade PCP, black liquor recovery boiler stack emissions, forest fires, combustion of Bleach-Kraft mill sludge in wood residue boilers, and unleaded fueled automobiles with catalytic converters (Herrera, 2010). The PCP and black liquor recovery boiler emissions appeared to match the closest, which have been linked to activities within the Oakland Bay area.

Conclusions

This 2011 study found that the limited number of samples (five locations; two sample depths) were generally in agreement with the Oakland Bay Sediment Characterization Study (Herrera, 2010). Oakland Bay has a broad distribution of fine material, and the TOC averaged 3.0%. The highest TOC was found in the harbor area, which is known for organic wood waste from former saw mills.

The highest TEQs were found in the middle portion of the bay, in the two samples that contained predominantly fines and where hydraulic energy is low. Two samples had higher PCDD/F concentrations and three samples had lower concentrations in the upper portions of the samples.

Location dynamics were examined briefly to determine the effect of recent deposition because, unless the PCDD/F concentration differences in the samples were large and uniform, the small sample size limits statistical power.

Several studies (mentioned above) determined that nearly all the sediment deposited within Oakland Bay stays confined within the bay and close to where it first enters the marine waters. However, deposition further out in the bay should not be ruled out since Oakland Bay has some of the more energetic hydraulics in Puget Sound (large tidal swings).

For this study, only sample Oakbay-OB-10-SC appears to be located from an area without local disturbances or high hydraulic energy, which coincides with high fines and elevated PCDD/F in the upper portion of the sample. That said, data gaps exist for certain areas that may have contamination sources, such as the ash mound described in a recent Ecology study (Coots, 2013).

As reported above, all results in this study for Oakland Bay were above the level of 4.0 ng/kg TEQ (OSV Bold Survey) except one, which may indicate cleaner deposition possibly due to bank erosion. Overall, PCDD/Fs continue to be present in Oakland Bay sediments above acceptable levels.

This study found the PCDD/F congener profiles in Oakland Bay matched the profiles found in the characterization study of Oakland Bay (Herrera, 2010). Although these results match EPA's profile for technical grade PCP, there are other similar profiles as described above. The PCP and black liquor recovery boiler emissions appeared to match the closest, which have been linked to activities within the Oakland Bay area. It would be difficult to determine an exact source without further sampling and analyses to match specific sources.

Summary

Results of this 2011 study support the following conclusions:

- Total TEQ concentrations of PCDD/Fs in Budd Inlet ranged from 0.692 to 53.7 ng/kg.
- The highest PCDD/F concentrations were present in inner Budd Inlet.
- A strong decreasing gradient from south to north was evident in Budd Inlet. There was also evidence of a weaker increasing gradient from west to east.
- Total TEQ concentrations of PCDD/Fs in Oakland Bay ranged from 2.09 to 55.2 ng/kg.
- There is evidence to suggest the distribution of PCDD/Fs in both bays is affected by hydraulic circulation and local events (e.g. vessel and dredging activities or seepage and landslides).
- Greater than 89% of the samples in both bays exceed the level of 4.0 ng/kg TEQ (OSV Bold Survey).
- There was no clear evidence of changes in PCDD/Fs concentrations over time in either bay, based on comparison between higher (0-2 cm) and deeper (10 cm) samples.
- Both bays exhibited a congener pattern that is similar to those of technical grade PCP and, to a lesser extent, black liquor recovery boiler emissions.

Recommendations

Results of this 2011 study support the following recommendations:

- To evaluate trends, analyze PCDD/Fs in sediment samples as part of Ecology's Marine Monitoring survey for long-term monitoring, which includes samples from Budd Inlet and Oakland Bay during the South Puget Sound rotation every 5 years.
- Develop a model to predict the length of time sediments will take for recovery in each bay.
- Investigate the impact of natural and anthropogenic local disturbances on sediment deposition and resuspension for each bay. Include not only natural processes (freshwater inputs and bank seepage and sloughing), but also marine vessel and other anthropogenic disturbances.
- Determine if PCDD/F pollutants are entering Budd Inlet from current upland sources.
- Conduct additional research for Oakland Bay to determine if PCDD/Fs contamination is coming from current sources (e.g., ash mound on Shelton Creek, industrial stormwater discharges). Samples should be collected from industrial and municipal stormwater discharges and upland soils/ash mound area. Sediment traps may be considered to better understand the dynamics of sediment deposition and transport in the bay.
- Compare PCDD/F congener profiles for potential sources by plotting both TEQ-adjusted and non-TEQ-adjusted congeners.

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Appendices

Appendix A. Identification and Location for Budd Inlet and Oakland Bay Sample Sites, 2011

Table A - 1. Identification and location for Budd Inlet and Oakland Bay sediment sample sites.

Manchester Environmental Lab (MEL) Sample ID	Sample Date	Target Latitude	Target Longitude	Final Latitude	Final Longitude	Depth (meters)
		(NAD 1983)				(MLLW)
1106045-01	6/7/2011	47.12407	-122.90705	47.12408	-122.90706	-13.1
-2	6/1/2011	47.08154	-122.91473	47.08154	-122.9147	-5.8
-3	6/7/2011	47.10008	-122.93065	47.10008	-122.93064	-8.1
-4	6/1/2011	47.13127	-122.91092	47.13127	-122.91092	-16.1
-5	6/21/2011	47.12242	-122.90933	47.12242	-122.90934	-11.9
-6	6/3/2011	47.09875	-122.91161	47.09875	-122.91162	-10.2
-7	6/1/2011	47.11424	-122.89695	47.11423	-122.89695	-7.3
-8	6/7/2011	47.13547	-122.9145	47.13547	-122.91451	-11.6
-9	6/6/2011	47.05286	-122.89736	47.05286	-122.89734	-3.1
-10	6/2/2011	47.14588	-122.92064	47.14483	-122.91849	-30.1
-11	6/6/2011	47.1106	-122.90308	47.11059	-122.90308	-9.7
-12	6/1/2011	47.05261	-122.90552	47.05262	-122.90576	-12.7
-13	6/6/2011	47.04513	-122.90357	47.04513	-122.90479	-3
-14	6/3/2011	47.06458	-122.9027	47.06458	-122.9027	-2.9
-15	6/6/2011	47.09917	-122.91611	47.09917	-122.9161	-11
-16	6/3/2011	47.12633	-122.90571	47.12634	-122.9057	-19.1
-17	6/1/2011	47.11928	-122.91573	47.11928	-122.91573	-14.1
-18	6/6/2011	47.08067	-122.90988	47.08068	-122.90986	-4.9
-19	6/6/2011	47.10551	-122.8942	47.10553	-122.89552	-3.7
-20	6/6/2011	47.0964	-122.91197	47.0964	-122.91197	-10.2
-21	6/2/2011	47.09853	-122.89604	47.09852	-122.89628	-4
-22	6/3/2011	47.11775	-122.90043	47.11774	-122.90042	-9.9
-23	6/6/2011	47.13508	-122.92285	47.13534	-122.92159	-27.7
-24	6/1/2011	47.10428	-122.92496	47.10429	-122.92496	-6.1
-25	6/2/2011	47.12982	-122.91889	47.1298	-122.91991	-27.4
-26	6/15/2011	47.08882	-122.92458	47.08879	-122.92458	-10.2
-27	6/15/2011	47.11271	-122.90905	47.11269	-122.9091	-11.7
-28	6/15/2011	47.1412	-122.91984	47.1412	-122.91981	-27.4
-29	6/15/2011	47.04772	-122.89463	47.0477	-122.89463	1.3
-30	6/16/2011	47.05915	-122.91318	47.05908	-122.91248	0
-31	6/16/2011	47.21257	-123.08407	47.21257	-123.08407	-3.4
-32	6/15/2011	47.21257	-123.08407	47.21257	-123.08407	-3.4
-33	6/15/2011	47.22068	-123.06149	47.22065	-123.06148	-2.4
-34	6/15/2011	47.22068	-123.06149	47.22065	-123.06148	-2.4

Manchester Environmental Lab (MEL) Sample ID	Sample Date	Target Latitude	Target Longitude	Final Latitude	Final Longitude	Depth (meters)
		(NAD 1983)				(MLLW)
-35	6/15/2011	47.20758	-123.08358	47.20758	-123.08358	-2.4
-36	6/1/2011	47.20758	-123.08358	47.20758	-123.08358	-2.4
-37	6/3/2011	47.2376	-123.0496	47.23761	-123.04961	-3.3
-38	6/1/2011	47.2376	-123.0496	47.23761	-123.04961	-3.3
-39	6/7/2011	47.25125	-123.03525	47.25123	-123.03525	1.1
-40	6/6/2011	47.25125	-123.03525	47.25123	-123.03525	1.1
-41 (1106046-45)	6/6/2011	47.05286	-122.89736	47.05202	-122.89736	-3.2
-42 (1106046-53)	6/7/2011	47.1106	-122.90308	47.1106	-122.9031	-9.9
-43 (1106046-55)	6/1/2011	47.05261	-122.90552	47.05261	-122.90574	-12.2
-44 (1106046-60)	6/7/2011	47.04513	-122.90357	47.04512	-122.90478	-3.2
-45 (1106046-62)	6/1/2011	47.06458	-122.9027	47.06458	-122.9027	-3.1
-46 (1106046-67)	6/21/2011	47.08067	-122.90988	47.08067	-122.90988	-5

MLLW: mean lower low water height of each tidal day observed over the National Tidal Datum Epoch.

Table A - 2. Identification and location of sample sites requiring repositioning of vessel.

Station ID	Target Lat/Lon	Position Adjustment	Final Lat / Lon (mean)
BI-300	47.0526 / -122.9055	Under dock, moved 18 m west	47.0526 / -122.9057
BI-556	47.0451 / -122.9036	On land, moved 93 m west	47.0451 / -122.9048
BI-41040	47.1056 / -122.8942	Intertidal, moved 100 m west	47.1055 / -122.8955
BI-41296	47.0985 / -122.8960	Buoy present, moved 18 m west	47.0985 / -122.8963
BI-41680	47.1351 / -122.9228	Rocky, moved 100 m WNW	47.1353 / -122.9216
BI-S7	47.0592 / - 122.9132	Rocky, moved 55 m east	47.0591 / -122.9125

Appendix B. Data Quality Discussion for Dioxin

In 2011, samples were collected from Budd Inlet and Oakland Bay for dioxin and furan (PCDD/F) analysis to compare with results from samples previously collected in 2007 and 2008, respectively. PCDD/Fs were detected at elevated concentrations in both areas in the earlier samples, but were dramatically lower in the 2011 samples. After an extensive review of the data, data quality, laboratory calculations, and laboratory procedures, and also conducting additional tests on some samples, Ecology decided to re-analyze all of the 2011 samples. Below is a brief discussion on the findings that initiated the decision to reanalyze the samples. Additional information is available upon request.

Low PCDD/F Results in Original Analysis

The original analysis reporting 2011 PCDD/F dioxin results were all dramatically lower than what had been found in the previous studies in Budd Inlet and Oakland Bay in 2007 and 2008, respectively. For example, the co-located sample in Oakland Bay (OB-10) contained 53.63 ng/kg TEQ of PCDD/F in 2008 versus 0.43 ng/kg TEQ in 2011. Environmental conditions such as natural recovery do not account for this size of reductions in concentrations in just three years. Furthermore, most concentrations in the 2011 data set were lower than values from non-urban (“background”) areas detected in a 2008 study of Puget Sound known as the OSV Bold Survey (USACE, 2009).

The OSV Bold Survey collected 70 samples from reference sites and locations distant from known sources of dioxin contamination for the Dredged Material Management Program (DMMP) to evaluate guidelines for sediment concentrations found within Puget Sound (DMMP, 2009). Results ranged from 0.05 to 11.6 ng/kg and had a median value of 0.862 ng/kg TEQ in the OSV Bold Survey. Similarly, the 2011 results ranged from 0.02 to 12.7 ng/kg TEQ, with a median value of 0.8216 ng/kg TEQ.

Furthermore, nearly all (about 84%) of the PCDD/F results were below the estimated quantitation limit (EQL), lowering confidence in those results. The EQL is set to increase the confidence level in quantifying results. Laboratories aim to quantify the environmental sample concentrations with a degree of certainty. The degree is decided by the quality of the instrument and the nature of the sample objectives. For these results, the EQL is defined as lowest calibration standard. Based on what was known about the sediment concentrations from previous studies, the low concentrations did not make sense. This inconsistency with the previous data sets led to reanalysis of the 2011 samples, though no fatal flaw in the sampling and analysis performed was detected.

Additional Testing

Additional analyses for PCDD/Fs were conducted on certain samples collected in 2011. Archived aliquots from two of the 2011 samples were provided blind (not marked or identified as being part of this study) to the analytical laboratory. Results from those reanalyzed samples showed much higher concentrations than the original analysis, confirming suspicions that the

2011 data were incorrect and revealing a possible systematic error in the previous results. TEQs were 19.86 versus 0.42 ng/kg for Oakland Bay, and 40.82 versus 0.94 ng/Kg for Budd Inlet (sample identified as OB-10 and BI-S7, respectively). Although these results were still somewhat different than the previous results (2007 and 2008), they were within the same order of magnitude.

Review and Re-analysis

Data quality was assessed by reviewers at the analyzing laboratory and MEL's QA Coordinator. The PCDD/F data were reviewed for "qualitative and quantitative accuracy following the National Functional Guidelines for Organic Data Review adapted for high resolution dioxin analysis and using the EPA Region 10 SOP for the Validation of PCDD/PCDF." (EPA, 1996)

The authors of this data report reviewed:

- All chain-of-custody forms to assess whether sample handling, storage conditions, and holding times required by the QA Project Plan (Ecology, 2012) and standard methods were met.
- All data deliverables (print and electronic) received from the various laboratories to assess whether results met the DQOs listed in the QA Project Plan.
- Overall quality and usability of the data.

In addition, Ecology hired a consultant to conduct a formal data validation on one of the lab data packages and to review the lab methods. Results from the additional blind analysis mentioned above were also compared.

Although, results from this review showed that the lab validation checked out and QC criteria were generally met, one difference was noted in the procedures during the pre-extraction sample drying step. If the sample is not dried to "finely divided" solids as described in Method 1613B, then the extraction may not be efficient, resulting in low recoveries.

To further investigate the bias and accuracy of the method using the improved drying techniques, Ecology initiated a round robin test (i.e., an inter-laboratory test performed independently several times) between four laboratories, including the laboratory that performed the original analyses. Two archived samples (sample ID 1106045-33 and 1106045-34) were homogenized together then divided among each laboratory. Laboratories were to follow similar methods, including the techniques for drying the sample referred to above.

Results were similar among laboratories, and total dioxin congener values ranged from roughly 3400 to 5700 ng/kg. Duplicate results for each laboratory ranged from 12.1% to 34.7% RPD. TEQs were calculated to evaluate the results in the context of previous results. These showed good agreement and ranged from 22.4 to 43.3 ng/kg TEQ for eight samples: four laboratories original and duplicate results. Furthermore, these values were within the range of sediment results in the same vicinity reported in a previous study from 2008, ranging from 27.6 to 45.5 ng/kg TEQ.

Ecology decided to have all of the original samples collected for the 2011 sediment project reanalyzed by the original laboratory, using the same procedures used for this round robin sample. Recommendations included improving lab prep methods such as in mixing and drying techniques and following the improved techniques.

Archived aliquots of the samples kept frozen in Ecology's sample freezers were retrieved and sent for reanalysis.

Appendix C. Results for Budd Inlet and Oakland Bay, 2011

Table C - 1. Budd Inlet and Oakland Bay sampling results.

Water Body	Station ID	Sample ID (1106045-XX)	PCDD/F Conc. ¹ (ng/kg)	PCDD/F TEQ (ND=EDL/2) (ng/kg)	PCDD/F TEQ (ND=0) (ng/kg)	TOC (%)	Gravel (%)	Sand (%)	Fines (%)	Sample Portion (cm)
Budd Inlet	PSUW012	1106045-01	3070	15.2	15.2	2.49	0.10*	12.9	87.1	0-10
Budd Inlet	PSUW020	-2	4170	20.1	20.1	3.19	6	13.4	80.7	0-10
Budd Inlet	PSUW084	-3	4570	22.5	22.5	2.68	3	13.4	83.7	0-10
Budd Inlet	PSUW116	-4	2560	12.8	12.8	2.12	0.2	16.7	83.1	0-10
Budd Inlet	PSUW140	-5	734	3.86	3.08	2.52	0.7	12.2	87	0-10
Budd Inlet	PSUW148	-6	7010	30.0	30	2.92	5.1	12.3	82.6	0-10
Budd Inlet	UWNO236	-7	2180	9.10	8.05	2.95	8.5	10.2	81.4	0-10
Budd Inlet	UWNO241	-8	2850	14.0	14	2.31	0.10*	24.2	75.8	0-10
Budd Inlet	UWNO242	-9	3240	12.8	12.8	3.8	4.7	20.4	74.9	0-10
Budd Inlet	PSUW244	-10	1720	7.63	6.86	2.78	2.4	52.1	45.5	0-10
Budd Inlet	PSUW268	-11	930	4.14	3.1	2.93	0.10*	9	91	0-10
Budd Inlet	PSUW300	-12	2310	7.67	7.51	4.38	10.7	30.6	58.7	0-10
Budd Inlet	PSUW556	-13	31400	41.9	41.8	3.74	13	8.6	78.4	0-10
Budd Inlet	UW40056	-14	4400	19.0	19	3.07	1.7	14.6	83.7	0-10
Budd Inlet	UW40216	-15	1190	7.18	6.7	2.85	0.5	8.8	90.8	0-10
Budd Inlet	UW40272	-16	1830	8.59	8.59	2.05	0.5	23.9	75.6	0-10
Budd Inlet	UW40528	-17	2470	11.2	11.2	2.34	0.10*	13.5	86.5	0-10
Budd Inlet	UW40984	-18	8600	35.5	35.5	3.23	17.5	9	73.5	0-10
Budd Inlet	UW41040	-19	3310	15.9	15.9	2.97	19.7	12.2	68.1	0-10
Budd Inlet	UW41240	-20	6130	26.1	26.1	2.97	10.2	12.8	77	0-10
Budd Inlet	UW41296	-21	5340	21.3	21.3	3.27	23.2	5.4	71.4	0-10
Budd Inlet	UW41552	-22	5390	24.5	24.5	2.69	3.4	20.7	76	0-10
Budd Inlet	UW41680	-23	846	3.80	3.76	1.12	1.6	83.7	14.7	0-10
Budd Inlet	UW41752	-24	1990	8.63	8.52	1.62	0.7	49.6	49.7	0-10
Budd Inlet	BI-42704	-25	2350	11.2	11.2	2.24	0.3	20.6	79.2	0-10
Budd Inlet	BI-42776	-26	4700	21.1	21.1	2.87	6.3	17.2	76.5	0-10
Budd Inlet	BI-43088	-27	184	0.932	0.556	2.83	0.1	10.8	89.1	0-10
Budd Inlet	BI-43216	-28	106	0.692	0.569	2.3	0.4	30.5	69.2	0-10
Budd Inlet	BI-S30	-29	2480	13.3	13.3	2.97	0.1	52.8	47.2	0-10
Budd Inlet	BI-S7-0-10cm	-30	1330	6.85	6.07	7.38	5.2	32	62.8	0-10
Shelton Harbor	SP-PSN227	-31	2260	8.76	8.76	3.32	0.5	68.4	31.1	0-2
Shelton Harbor	SP-PSN227	-32	1000	4.39	4.17	2.48	0.3	66.3	33.4	0-10
Oakland Bay	SP-PSN232	-33	538	2.09	1.68	2.9	1	23.5	75.5	0-2

Water Body	Station ID	Sample ID (1106045-XX)	PCDD/F Conc. ¹ (ng/kg)	PCDD/F TEQ (ND=EDL/2) (ng/kg)	PCDD/F TEQ (ND=0) (ng/kg)	TOC (%)	Gravel (%)	Sand (%)	Fines (%)	Sample Portion (cm)
Oakland Bay	SP-PSN232	-34	11400	49.3	49.3	2.72	2.5	12	85.5	0-10
Shelton Harbor	SP-PS0636	-35	6790	26.7	26.7	3.18	0.3	52.8	46.9	0-2
Shelton Harbor	SP-PS0636	-36	7340	35.5	35.5	3.11	1.8	50.3	47.9	0-10
Oakland Bay	Oakbay- OB-10-SC	-37	13900	55.2	55.2	3.14	1.4	19.2	79.4	0-2
Oakland Bay	Oakbay- OB-10-SC	-38	2580	11.0	10.8	3.04	0.1	9.5	90.3	0-10
Oakland Bay	OB-12.5S	-39	6820	32.5	32.5	3.17	1.1	53.5	45.4	0-2
Oakland Bay	OB-12.5S	-40	8420	39.9	39.9	2.83	0.4	50.5	49.2	0-10
Inner Budd Inlet	UWNO242	-41	14800	53.7	54.7	3.91	13.3	20	66.7	0-2
		(1106046-45)								
Inner Budd Inlet	PSUW268	-42	5800	25.6	26.6	3.22	0.4	14.3	85.2	0-2
		(1106046-53)								
Inner Budd Inlet	PSUW300	-43	9650	32.6	33.6	4.41	34	19.8	46.1	0-2
		(1106046-55)								
Inner Budd Inlet	PSUW556	-44	11700	25.8	26.6	3.88	11	15.1	73.9	0-2
		(1106046-60)								
Inner Budd Inlet	UW40056	-45	8240	33.3	34.3	3.12	8	21.9	70.1	0-2
		(1106046-62)								
Central Budd Inlet	UW40984	-46	3060	14.3	15.3	3.34	22.8	5.2	71.9	0-2
		(1106046-67)								

¹ Total concentration: nondetects=1/2 detection limit (ND=EDL/2).

*not detected.

Appendix D. Geostatistical Analysis

Results from the 2011 Budd Inlet dioxin and furan (PCDD/F) study were analyzed using ESRI Geographical Information System (GIS) (ESRI, Inc., 2010). PCDD/F results from previous studies were included in some analyses (SAIC, 2008; Ecology, 2007). The Geostatistical Analysis extension was used to generate results for spatial relationships among the PCDD/F results and to help describe spatial patterns and interpolate possible values (outcomes) for locations where samples were not taken.

Assumptions underlying geostatistics is that values in the study area are of a random process with dependence (autocorrelation); things that are close to one another are more alike than those farther away from one another. Brief explanations of the process and interpretation are based on ESRI resources found at <http://resources.arcgis.com>. General discussion of the findings and quality assurance (QA) are presented below.

Exploring the Data Sets

Distribution of the 2011 PCDD/F results showed a tail to the right of the center, which resulted from elevated PCDD/F concentrations found in three samples in Inner Budd Inlet (Figure D - 1). When including results from all studies, a more normal distribution was observed, but still showed the same areas within the right tail of the distribution curve (Figure D - 2). As these samples were measured from areas known for PCDD/F contamination, they were not considered outliers.

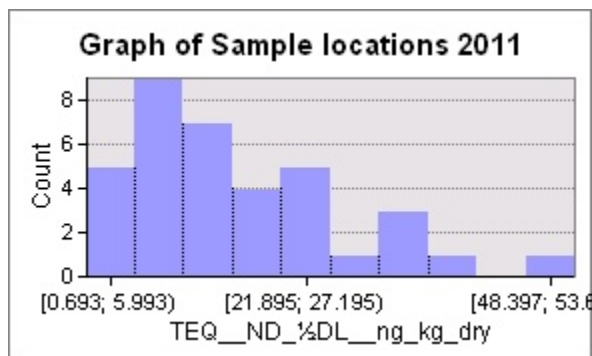


Figure D - 1. Histogram of the 2011 PCDD/F results.

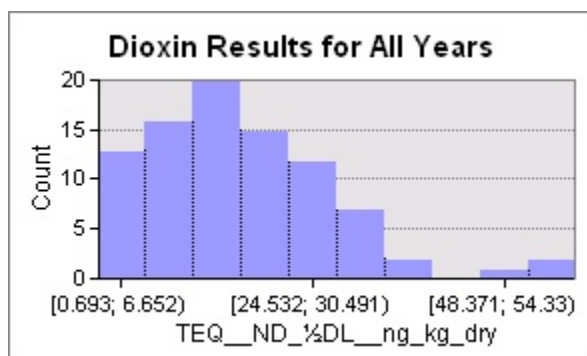


Figure D - 2. Histogram of all PCDD/F results from 2011 and including previous results.

Trend analysis for each data set (2011 and all years) was performed plotting the data on a 3D-grid with an X axis for east to west, a Y axis for south to north, and a Z axis for result values. Results from all samples (all depths) were included for a more inclusive data set.

Figure D - 3 shows a south-to-north (Inner to Outer Budd Inlet) trend (blue line) increasing along the Y axis for both data sets (a). The east-to-west relationship (green line) (a and b) was less clear along the X axis in both data sets, probably because Budd Inlet has somewhat of an “S” shape: first west then east rather than oriented along the latitude and longitudinal coordinates, which would add weight to the trend towards the west from the elevated results within Inner Budd Inlet. However, upon rotation of the graph (c), an east-to-west trend can be seen decreasing to the west. Since this trend shows a curved line, a first order polynomial was applied when modeling.

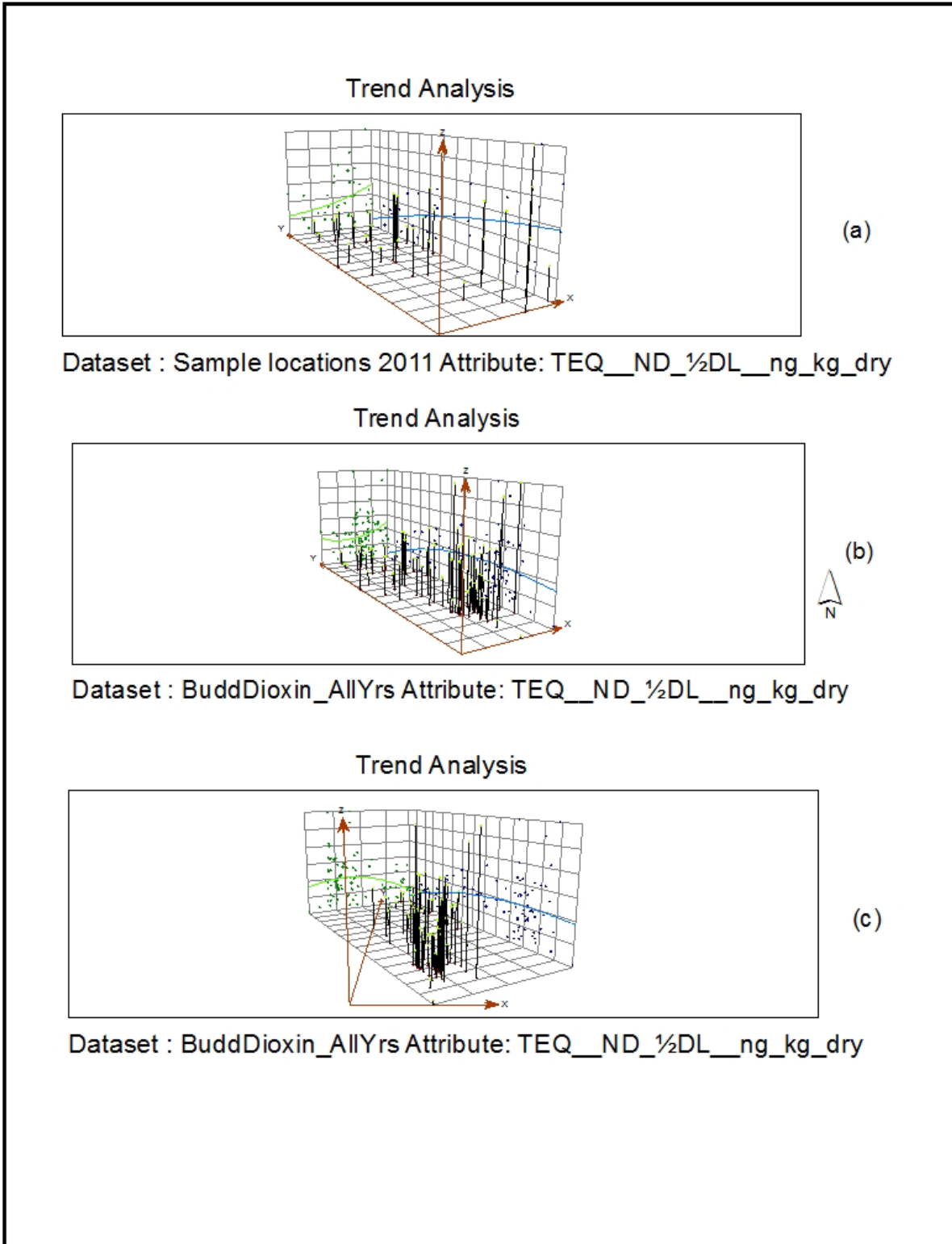


Figure D - 3. Trend Analysis for 2011 PCDD/F results and previous results. (a) 2011 PCDD/F results; (b) all years' results included; (c) all years' graph rotated counterclockwise 30 degrees.

Modeling

To create an interpolated surface, a Universal Kriging model was employed. This model was selected because it is used for trends that vary and where regression coefficients are unknown. This model can assess the uncertainty associated with a predicted value at the unmeasured locations. Measures of uncertainty are given to provide information on the possible values for each location, rather than just one interpolated value. Measurement error occurs when it is possible to have several differing observations at the same location.

As with other geostatistical models, this model uses sample points taken at different locations in a landscape and creates (interpolates) a continuous surface. Universal Kriging is basically a regression model that uses coordinates as the explanatory variables. However, instead of assuming the errors $\epsilon(s)$ are independent, errors are modeled to be autocorrelated (a function of distance). This becomes important for making decisions based on the results.

Model Methods

Parameters set in the Universal Kriging model included:

- Source data set included each of 2011 PCDD/F and all years' results.
- Data field included all results for TEQ (1/2 nondetect values).
- Prediction surface type.
- No transformations.
- First order of trend removal.
- Zero for exploratory trend.
- Exponential Kernel function.
- Semivariogram used.
- Nugget enabled and calculated.
- Measurement variation is set to 100% so the default predictions at measured locations will be based on the spatial correlation of the data and the measured values at nearby locations.
- Model type is stable.
- Use of anisotropy so the semivariogram will change with direction as well as with distance. This seemed reasonable based on the trends observed in the data sets.
- Partial sill calculated.
- Size and number of lags set to default (0.002 and 12 respectively).
- Smooth neighborhood type to adjust sampling weights using a smoothing sigmoidal function defined by a smoothing factor (default 0.2).
- Use of variogram copy.

Model Results

Kriging results for 2011 results included:

- Predicted regression function: $0.261032232894314 * x + 11.9862459355113$.
- Error regression function: $-0.738967767105687 * x + 11.9862459355113$.
- Standardized error regression function: $-0.0724315955829904 * x + 1.17680863234947$.

- Sampled 36 out of 36.
- Mean = -0.01178643.
- Root-Mean-Square = 11.05053.
- Mean Standardized = -0.0007077074.
- Root-Mean Square Standardized = 1.080491.
- Average Standard Error = 10.2312.

Kriging results for all years included:

- Predicted regression function: $0.110716556107422 * x + 16.2433931912203$.
- Error regression function: $-0.889283443892579 * x + 16.2433931912203$.
- Standardized error regression function: $-0.0724424540874318 * x + 1.28827775344962$.
- Sampled 87 out of 88. One result did not have enough neighbors for evaluation.
- Mean = 0.3792549.
- Root-Mean-Square = 12.78964.
- Mean Standardized = 0.01939288.
- Root-Mean Square Standardized = 1.050881.
- Average Standard Error = 12.48171.

Model Cross-validation and Interpretation

To determine the quality of the model, cross-validation was performed. This process was incorporated into the Geostatistical Wizard, and the results are discussed here. Cross-validation uses all the data to estimate the trend and autocorrelation models. The goal is to have average error and standardized mean prediction errors near 0, small root-mean-squared prediction errors, average standard error near root-mean-squared prediction errors, and standardized root-mean-squared prediction errors near 1.

For the above analyses, both data sets (the 2011 and all the years' results) showed fairly good fit of the model. The Mean and Mean Standardized were near zero (< 0.02), Root-Mean Square Standardized close to one (< 1.08), and the average standard error near the root-mean-squared prediction error (10.2312 near 11.05053 for 2011 data set and 12.48171 near 12.78964 for all years' data sets).

Although both data sets show probable variation in predicted values throughout the area with root-mean-square ranging from 10.2 to 12.7, these seemed reasonable in light of the notable trends associated with these results. Overall, this model appears to be a good fit for accessing PCDD/F concentrations throughout Budd Inlet. Caution is advised not to use these results for applying predictive values, but rather for an overall assessment of Budd Inlet condition possibilities.

Appendix E. Glossary, Acronyms, and Abbreviations

Glossary

Anthropogenic: Human-caused.

Bathymetry: Sea floor topography.

Congener: In chemistry, congeners are related chemicals. For example, polychlorinated biphenyls (PCBs) are a group of 209 related chemicals that are called congeners.

Flushing time: Time required to fully replace the volume of water in a water body.

Flux: Rate of flow of a substance.

Gyre: Circular movement of water usually formed between two adjacent currents flowing counter to each other; larger than an eddy.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

Reflux: A back flowing of water.

Salinity: Amount of dissolved salts in sea water.

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Acronyms and Abbreviations

DL	Detection limit
DQO	Data quality objective
Ecology	Washington State Department of Ecology
EDL	Estimated detection limit
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
EQL	Estimated quantitation limit
GIS	Geographic Information System software
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
N	Number
ND	Non Detect
OCDD	Octachlorodibenzodioxin
OSV	Ocean Survey Vessel

PCDD/F	Polychlorinated dibenzo- <i>p</i> -dioxins and polychlorinated dibenzofurans
PCP	Pentachlorophenol
PSEMP	Puget Sound Ecosystem Monitoring Program
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
SOP	Standard operating procedures
TEF	Toxic equivalent factor
TEQ	Toxic equivalency
TOC	Total organic carbon
USGS	U.S. Geological Survey
UWI	Urban Water Initiative
WHO	World Health Organization
WRIA	Water Resource Inventory Area

Units of Measurement

cm/yr	centimeters per year
dw	dry weight
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
m	meter
ng/kg	nanograms per kilogram (parts per trillion)